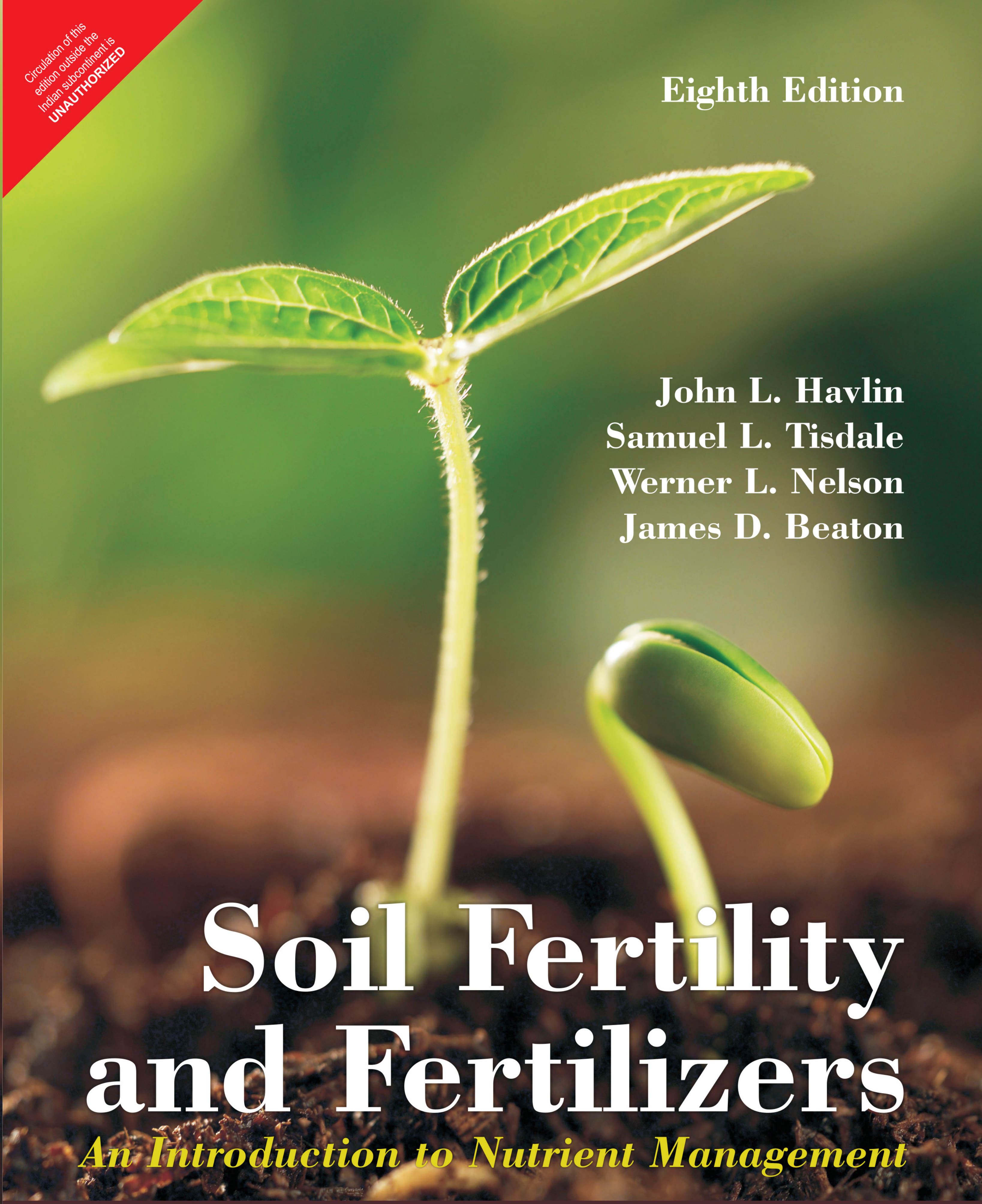

Eighth Edition

John L. Havlin
Samuel L. Tisdale
Werner L. Nelson
James D. Beaton

Soil Fertility and Fertilizers

An Introduction to Nutrient Management

ALWAYS LEARNING

PEARSON

SOIL FERTILITY AND FERTILIZERS

AN INTRODUCTION TO NUTRIENT MANAGEMENT

EIGHTH EDITION

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Preface

Soil Fertility and Fertilizers was first published in 1956. Although this edition has been substantially revised to reflect rapidly advancing knowledge and technologies in plant nutrition and nutrient management, the outstanding contributions of Samuel L. Tisdale (1918–1989) and Werner L. Nelson (1914–1992) will always be remembered and appreciated.

The importance of soil fertility and plant nutrition to the health of all life cannot be overstated. As human populations continue to increase, human disturbance of the Earth's ecosystems to produce food and fiber will place greater demand on soils to supply plant nutrients. As the soils' native supply of nutrients decreases with increasing cropping intensity, it is essential that we enhance our understanding of nutrient behavior in soil and to efficiently utilize every available nutrient source to optimize nutrient availability. One of the greatest challenges of future generations will be to develop and implement soil, crop, and nutrient management technologies that enhance plant productivity, while protecting the quality of the soil, water, and air. If we do not improve and/or sustain the productive capacity of our fragile soils, we cannot continue to support the food and fiber demand of our growing population.

ABOUT THE NEW EDITION:

- This textbook is designed for use in an undergraduate classroom or distance education course. Other books on the market are less functional for use in an undergraduate course.
- This text includes a wide diversity in crop systems (agriculture, horticulture, turf, etc.) that will appeal to students from diverse geographic regions, backgrounds, and interests.
- This edition greatly expands description of tools and technologies essential to increase nutrient use efficiency, with a substantially enhanced focus on environmental impacts of nutrient use.
- This text illustrates critical quantitative skills essential to professional success in nutrient management and related disciplines. It also provides many examples and the Instructor's Manual includes answers to all quantitative questions at the end of each chapter.
- It covers topics and issues from the soil sample to the field scale and to a global perspective.
- This textbook provides an unbiased approach to the use of inorganic and organic nutrient sources and expands emphasis on organic nutrient sources as alternatives to common fertilizers.
- Materials are presented in the most logical order, allowing a student to first learn principles of basic nutrient behavior in soil and then to apply the knowledge to practical field scale problems.
- Increased number of photographs, diagrams, and other visuals of nutrient response in crops, soil management effects on crop growth, nutrient application equipment, and others.

TO THE STUDENT

The goal of this book is to provide a thorough understanding of plant nutrition, soil fertility, and nutrient management so that you can (1) describe the influence of soil biological, physical, and chemical properties and interactions on nutrient availability to crops; (2) identify plant nutrition–soil fertility problems and recommend proper corrective action; and (3) identify soil and nutrient management practices that maximize productivity and profitability while maintaining or enhancing the productive capacity of the soil and quality of the environment. The *quantitative* approach is essential to accurately assess nutrient status in soils and plants, and to quantify nutrients needed for optimum plant health and productivity.

The specific objectives are to (1) describe how plants take up or absorb plant nutrients and how the soil system supplies these nutrients; (2) identify and describe plant nutrient-deficiency symptoms and methods used to quantify nutrient problems; (3) describe how soil organic matter, cation exchange capacity, soil pH, parent material, climate, and human activities affect nutrient availability; (4) evaluate nutrient and soil amendment materials on the basis of content, use, and effects on the soil and the crop; (5) quantify, using basic chemical principles, application rates of nutrients and amendments needed to correct plant nutrition problems in the field; (6) describe nutrient response patterns, nutrient use efficiency, and the economics involved in nutrient use; and (7) describe and evaluate soil and nutrient management practices that either impair or sustain soil productivity and environmental quality.

TO THE TEACHER

Motivate your students to learn by showing them how the knowledge and skills gained through the study of soil fertility will be essential for success in their careers. Use teaching methodologies that enhance their critical thinking and problem-solving skills. In addition to understanding qualitative soil fertility and plant nutrition relationships, students must know how to quantitatively evaluate nutrient availability and nutrient management. Environmental protection demands that nutrients be added in quantities and by methods that maximize crop productivity and recovery of the added nutrients.

Since some of the examples used in this text may not be representative of your specific region, frequently integrate additional field examples from your region to illustrate the qualitative and quantitative principles. Strongly reinforce the reality that production agriculture, sustainability, and environmental quality are compatible provided soil, crop, and nutrient management technologies are used properly. Develop in your students the desire and discipline to expand beyond this text through reading and self-learning. Demand of your students what will be demanded of them after they graduate—to think, communicate, cooperate, and solve problems from an interdisciplinary perspective.

An Instructor's Manual is available from the publisher and provides qualitative and quantitative information pertinent to each chapter. Instructors should utilize the questions at the end of each chapter as learning aids to help students gain confidence with the material and to prepare for exams. Answers to each question and complete solutions to quantitative calculations are provided in the Instructor's Manual. To access supplementary materials online, instructors need to request an instructor access code. Go to www.pearsoned.co.in/JohnLHavlin, where you can register for an instructor access code. After registering, you will receive a confirmation email, including your instructor access code. Once you have received your code, go to the site and log on for full instructions on downloading the materials you wish to use.

Thank you to the professors who helped review the manuscript: Jorge D. Hernandez, Southern Illinois University; Nels Hansen, The Ohio State University; Thomas L. Thompson, Texas Tech University; Joan Davenport, Washington State University; Larry J. Cihacek, North Dakota State University.

We hope your students find the text a valuable resource throughout their careers. Please feel free to provide suggestions for enhancing the effectiveness of the text as a teaching and learning aid.

John L. Havlin

We would like to thank D. Sangeetha, Department of Mechanical Engineering, College of Engineering, Anna University, Chennai, for contributing insightful content to the book and making it more relevant and contextual for Indian students.

1

Introduction

Essential nutrients to support healthy human life are acquired through diverse food sources, ultimately supplied from soil. While plants are a major direct human food source, animals used as human food also obtain nutrients from a variety of plants (forage and grains) in their diets. Even fresh and salt water food sources contain nutrients that ultimately originate from soluble and sediment-bound nutrients deposited in surface waters from surface and subsurface runoff. Therefore, management of nutrients in the soil is essential to ensure adequate nutrient supply to plants. The following sections describe how the demand for food, fiber, and other products from agricultural systems will increase over the next four to five decades, and assess our ability to meet this demand. Obviously, any increase in agricultural output requires additional nutrient supply. While native soil nutrient supply must be enhanced with inorganic fertilizers and recycling of organic waste materials, it is essential to understand nutrient reactions and processes in soils to optimize nutrient availability to crops and minimize environmental risk of nutrient use.

For students in non-food-related programs such as urban lands, environmental science, forestry, and many others, nutrient cycling and management principles are just as important to understand. While you may never engage in a food and fiber production-related profession, meeting future demands for these resources will challenge all societies to enhance agroecosystem output, while maintaining or enhancing the diversity and health of all ecosystems.

> *When we perceive that civilization rests on the food giving capacities of the soil, when we perceive that all of the future advances of our kind depends upon the preservation and enhancement of its fertility, we are in a position to consider the duty which we owe to it.*
>
> (Shaler, 1891)

GLOBAL POPULATION GROWTH

As human populations have grown, organized agricultural systems were developed to ensure food security (Table 1-1). Despite advances in agricultural production technologies, a significant proportion of the current world population is undernourished, primarily in undeveloped nations (e.g., sub-Saharan Africa and Asia) that exhibit high population growth rates and often rely on unproductive farming methods. In contrast, developed

TABLE 1-1
CAPABILITY OF AGRICULTURAL SYSTEMS TO PRODUCE FOOD AND SUPPORT POPULATION

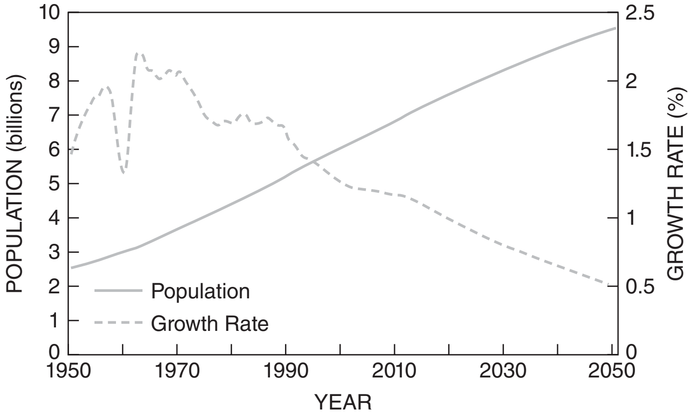
Agricultural System	Cultural Stage or Time	Cereal Yield (t/ac)	World Population (millions)	Acres/ Person[1]
Hunting and gathering	Paleolithic (>10,000 years ago)	0.30	2–7	
Shifting agriculture (early cultivation)	Neolithic (10,000 years ago)	0.33	10–100	76.8
Medieval rotation	A.D. 500–1450	0.37	100–400	12.8
Livestock farming	Late 1700s	0.42	1,000	3.8
Modern agriculture	1900	0.48	1,650	2.3
	1950	0.92	2,527	1.5
	2000	3.00	6,113	0.6
	2050	5.20	9,181	0.4

[1] Assumes 1.55 billion ha of arable and permanent cropland.
Source: Adapted from McCloud, 1975, *Agron. J.*, 67:1; FAO, 2008, http://www.un.org/esa/population/publications/sixbillion/sixbilpart1.pdf.

countries utilizing modern agricultural technologies are generally self-sufficient in food production and provide the majority of food exports to undeveloped and developing nations.

Currently about 15–20 million people (<0.3% of world population) are affected by famine or risk of death due to food shortage; however, malnutrition affects nearly 1 billion people or 15% of world population. Although many political, economic, climate, and other factors influence food insecurity, increasing world population pressure, availability of suitable cropland, and degradation of soil productivity will challenge our agricultural production systems to meet future food, fiber, fuel, and water needs. The importance of increasing agricultural productivity to secure sufficient food for a growing population is obvious (Table 1-1). World population has doubled over the last 40 years to over 7 billion people, and will increase by 50% over the next 40 years to over 9 billion in 2050 (Fig. 1-1). Most of the projected population increase will occur in developing countries, primarily in Asia and Africa. World population is expected to stabilize at about 12 billion by 2100, as the annual growth rate continues to decline (Fig. 1-1). Despite decreasing population growth rates, providing food and other agricultural resources for 9 billion by 2050 will require substantial increases in production.

Figure 1-1
Actual and projected world population growth from 1950 to 2050
(United Nations, 2007).



FOOD CONSUMPTION, PRODUCTION, AND AGRICULTURAL LAND USE

Increasing population over the next four decades will drive food consumption (Fig. 1-2). These data illustrate that cereal consumption for food will increase about 50%, while meat consumption will double. Most of these projected increases will occur in developing nations, particularly in China and India, whose economies are experiencing rapid growth in disposable income. As percentage of animal products in the diet increases, cereal use for feed will increase.

Currently, world food production is meeting food demand (Fig. 1-2). In 2008, total cereal consumption was about 2,350 million tonnes (Mt) compared to nearly 2,400 Mt of total cereal production. In 2050, total cereal consumption is estimated at nearly 3,200 Mt compared to nearly 3,600 Mt of total cereal production. Of course this assumes that over the next 40 years current growth in cereal production continues (Fig. 1-2). These data show that average total cereal yield was 3,400 kg/ha in 2008 and projected to be 5,200 kg/ha in 2050, where the annual increase in yield is nearly 44 kg/ha/yr (slope of the linear best fit in Fig. 1-2).

Rapid human population growth in the last century has extensively impacted land use more than in any comparable time in human history. Approximately 12% of total world land area (13 billion ha) and about 32% of agricultural land (4.93 billion ha) are current croplands (1.55 billion ha) (Table 1-2). The remaining 3.38 billion ha of agricultural land, primarily (90%) in Latin America and sub-Saharan Africa, is forests, permanent pasture, and other non-crop uses. Most estimate these remaining agricultural lands represent only 20% of yield potential of the most productive cropland; thus, cropland expansion in these areas occurs at a large economic cost (poor

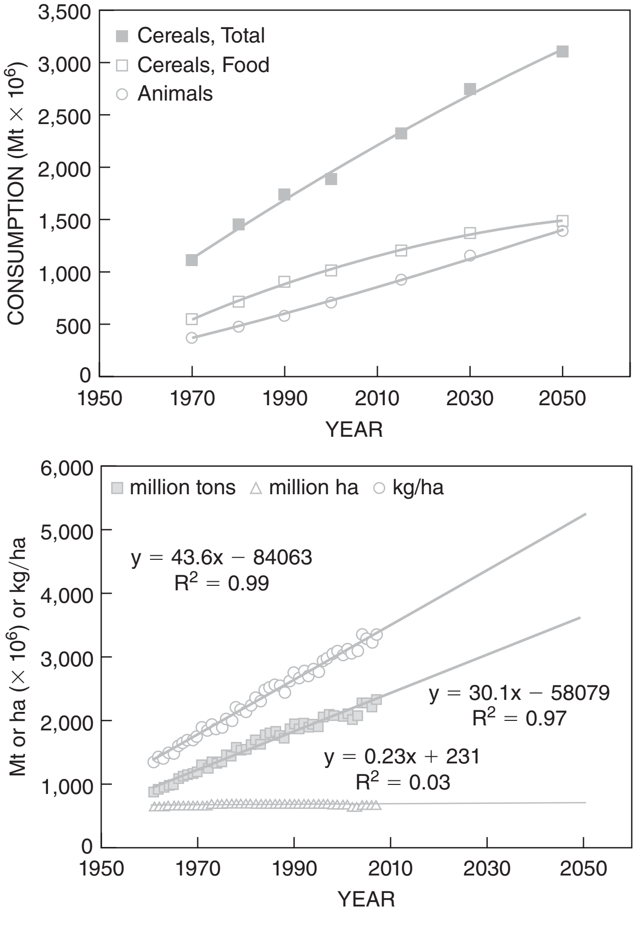


Figure 1-2
Actual and projected cereal and animal product consumption from 1970 to 2050 (top), and actual and projected world cereal production (million tonnes, Mt), cereal yield (kg/ha), and cereal production area (million ha) from 1960 to 2050 (bottom) (FAO, 2008).

TABLE 1-2
APPROXIMATE WORLD LAND AREA USED FOR FOOD PRODUCTION (FAO, 2007)

	Million ha
World land area	13,009
Agricultural area	4,932
Cropland	1,554
Pulses	73
Cereals	700
Roots and tubers	55
Vegetables and melons	52
Tree nuts	8
Oil crops	251
Fruit	47
Fiber crops	36

soil fertility, shallow soil depth, low rainfall, etc.) and causes a great risk to biodiversity, soil erosion, and other factors impacting ecosystem health.

Total agricultural land has been relatively constant since 1990, whereas cropland has increased slightly (+0.22%/yr), likely into these less productive land areas (Fig. 1-3). Per capita cropland use decreased nearly 50% from 0.44 in 1960 to 0.23 ha/person in 2007 (Fig. 1-3). By 2050, world cropland use further decreases by about 30%

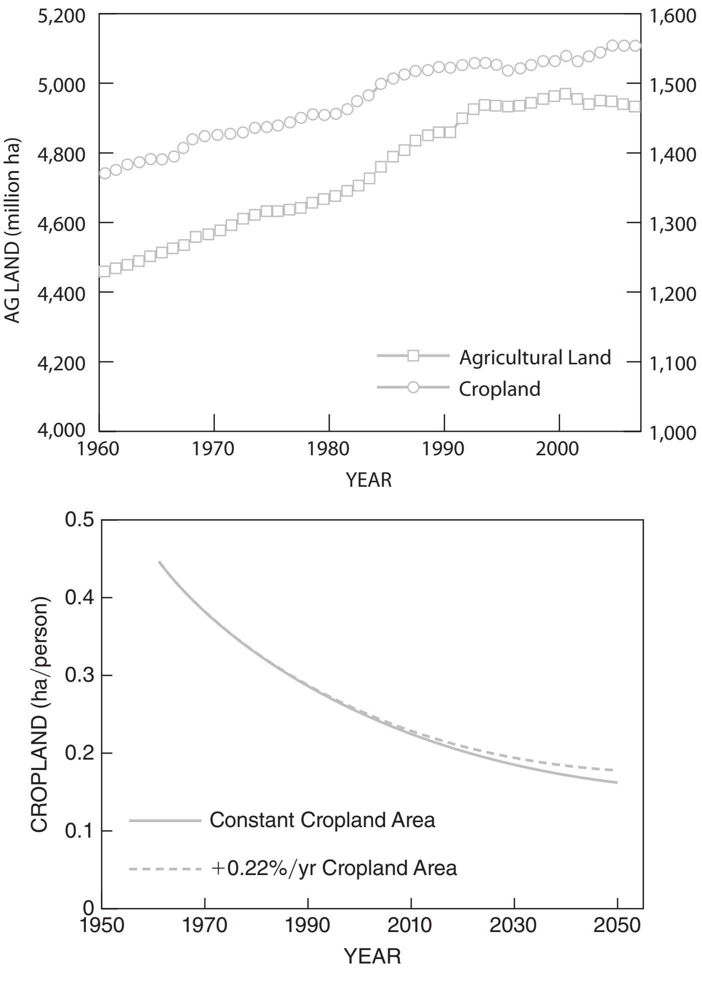


Figure 1-3
Change in world agricultural land and cropland since 1960 (top), *where cropland represents arable and permanent cropland, and historical and projected per capita world cropland use* (bottom). *Projections are based on no expansion of current cropland area of 1.55 billion ha (solid line) or the 1996–2007 annual rate of cropland increase of ~3.38 million ha/yr or 0.22%/yr* (FAO, 2008).

TABLE 1-3
CROPLAND AREA DEGRADED TO LEVELS THAT REDUCE CROP PRODUCTIVITY

Continent	Cropland Area	Degraded Area	
	million ha	million ha	%
Africa	187	121	65
Asia	536	204	38
Australia/Pacific	49	12	25
Europe	287	73	25
North America	236	60	25
Latin America	180	92	51
Total	1,475	562	38

Source: Oldeman et al., 1991, UN Environment Program.

to 0.16 ha/person, assuming constant cropland area. If the small annual increase in cropland area continues (~3.38 million ha/yr or 0.22%/yr), then per capita cropland use only slightly increases to 0.18 ha/person. It is important to recognize that per capita cropland assessments are misleading because of the changing distribution of human populations in rural and urban areas. Similar to population growth rate, the rate of urbanization has been decreasing, but the absolute urban population is increasing. For the first time in history, >50% of world population (3.6 billion) lived in urban areas in 2010. By 2050 >60% or nearly 6 billion people will live in urban areas. Therefore, the impact of increasing population on conversion of cropland to urban uses is lessened by the disproportionate expansion of urban areas. However, urban population growth commonly occurs on highly productive lands, where urban expansion in developing countries decreases cropland by 0.5 million ha/yr.

Expanding cropland into remaining agricultural lands that are substantially less productive will limit global crop production growth. Current estimates suggest that 90% of future crop production increases will come from intensification compared to expansion of cropland. Unfortunately, the poorest cropland occurs in regions with the greatest need to expand production. In developing countries (sub-Saharan Africa, Latin America, etc.), projected croplands will increase only 0.3%/yr or 120 million ha/yr over the next several decades, which is less than in previous decades. Little or no increases are expected in developed countries.

Since cropland expansion will have minimal impact on crop production, production (yield per area) on existing cropland must increase; however, continued degradation of world soil productivity threatens our ability to meet future global food and fiber demand. Although soil degradation varies widely between regions, approximately 38% of the world's cropland has degraded (Table 1-3). The primary causes of soil degradation are water and wind erosion. About 2 million ha of rainfed and irrigated agricultural lands are lost to production every year due to severe land degradation, which increases the productivity demand on remaining croplands, while increasing pressure on converting less productive land into cropland. The relationships between soil productivity and agricultural sustainability are discussed in Chapter 12.

IMPACT ON U.S. AGRICULTURE

Since future population growth will occur primarily in undeveloped and developing nations, and the majority of agricultural land in these regions that could be converted to cropland is substantially less productive than current croplands, these

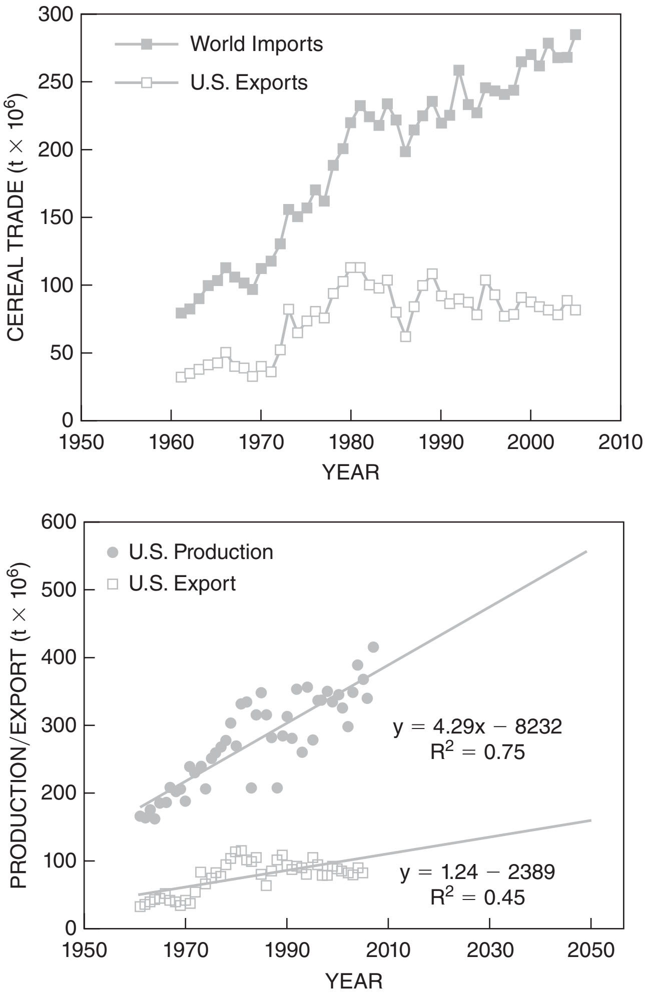


Figure 1-4
Total world cereal imports and U.S. cereal exports (top), *and historical and projected U.S. cereal production and exports* (bottom) (FAO, 2008; USDA-ERS, 2008).

nations will continue to depend on agricultural imports. Historically, North America and the European Union have been the major suppliers of grain to many food-poor nations, whereas the United States provides about 60% of world food aid and is meeting nearly 30% of cereal imports (Fig. 1-4). Current U.S. exports are approximately 100 Mt, which represents 25% of total U.S. cereal production (Fig. 1-4). Of total world cereal production of 2,350 Mt in 2008 (Fig. 1-2), 100 Mt of U.S. cereal exports represents about 4.3%. Assuming that global cereal grain consumption and production will increase nearly 50% by 2050, U.S. cereal export will need to increase to about 150 Mt (Fig. 1-4). At this level of cereal export, U.S. cereal production will need to increase from current cereal production of about 400 Mt to 580 Mt in 2050 (Fig. 1-4).

Currently, about 60 million ha in the United States are harvested for cereal production at an average yield of 6,500 kg/ha (Fig. 1-5). Assuming 580 Mt of cereal production are needed in 2050, and maintaining current land area (60 million ha) in cereal production, cereal yield will need to increase to about 9,600 kg/ha by 2050, an increase of 45%. Linear extrapolation of current growth in U.S. cereal production shows that cereal yield will be approximately 9,700 kg/ha by 2050; thus, current growth rate in cereal yields should meet 2050 cereal demand.

Unfortunately, agricultural land area is decreasing at an annual rate of 0.15 million ha (Fig. 1-5). This trend is somewhat misleading, as the annual decrease from 1990 is about 0.54 million ha. This is likely an overestimate as cereal cropland loss at this rate would result in about 35 million ha of cereal cropland in 2050 (Fig. 1-5).

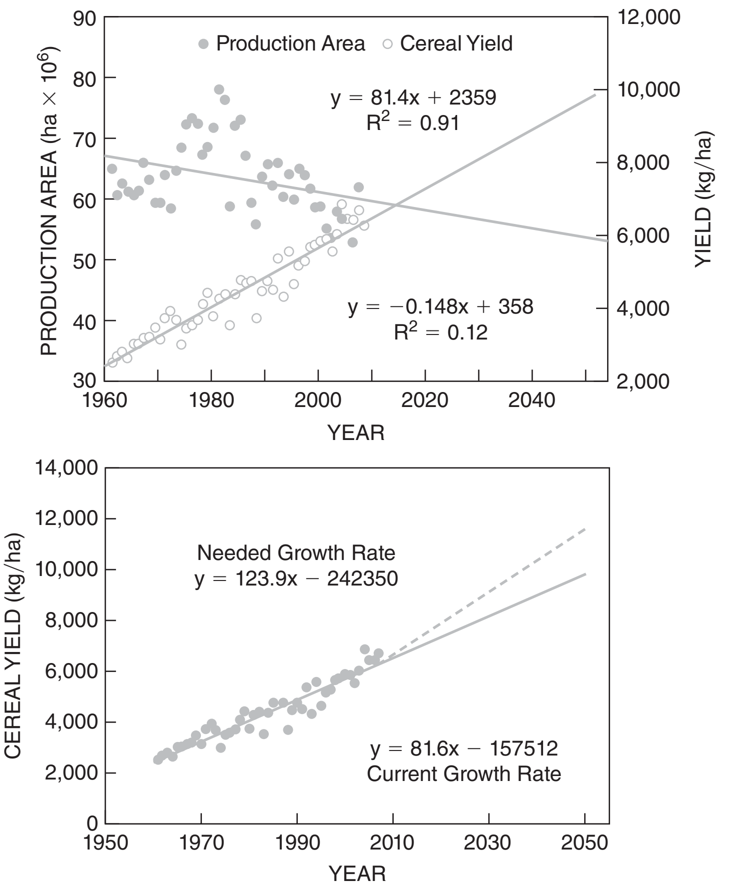


Figure 1-5
Historical and projected cereal yield and production area in the United States (top), *and current growth in U.S. cereal yields (solid line) and cereal yield growth rate needed to meet world cereal demand (dashed line) in 2050* (bottom). *Current growth rate assumes constant cereal cropland area (~60 million ha) and needed growth rate assumes 10 million ha fewer cereal cropland in the United States* (FAO, 2008).

Recent estimates suggest approximately 0.40 million ha/yr of total U.S. cropland loss to predominately rural residential uses. With about 70% of total U.S. cropland in cereals, annual cereal cropland loss would be 0.25–0.30 million ha. If the conservative estimate of 0.25 million ha/yr is used, then 10 million fewer ha of cereal cropland will be available in 2050. With approximately 50 million ha of cereal production, cereal yields need to increase to over 11,600 kg/ha compared to 9,700 kg/ha under current cereal yield increases on 60 million ha (Fig. 1-5). To achieve an additional 2,000 kg/ha cereal yield by 2050, annual growth rate in cereal yield must be increased from 82 kg/ha/yr to about 124 kg/ha/yr, a 50% increase in annual yield growth rate. To achieve this, substantial advances in genetics and soil/crop management technologies will be needed. Greater cereal yields per unit land area will also require substantial increases in fertilizer nutrient use.

UTILIZING FOOD CROPS FOR NON-FOOD USES

Increased consumption and cost of energy have driven technology development and policy decisions in food-secure nations to utilize grain crops to produce ethanol, biodiesel, and other energy sources. In the last decade, U.S. ethanol production has increased over four fold (Fig. 1-6). The United States and Brazil annually produce 90% (~15 billion gal/yr) of world ethanol used for fuel. Current ethanol production capacity is approximately 10 billion gallons, requiring over 3.5 billion bushels of corn, at 2.8 gal ethanol/bu. This level of ethanol production utilizes 30% of total U.S. corn production (Fig. 1-6). If current U.S. energy goals of 35 billion gallons of ethanol are realized by 2017, over 12 billion bushels of corn would be needed, which consume the entire current U.S. corn crop. Despite increases in grain yield and acreage planted to fuel-dedicated grain crops, if proposed ethanol production

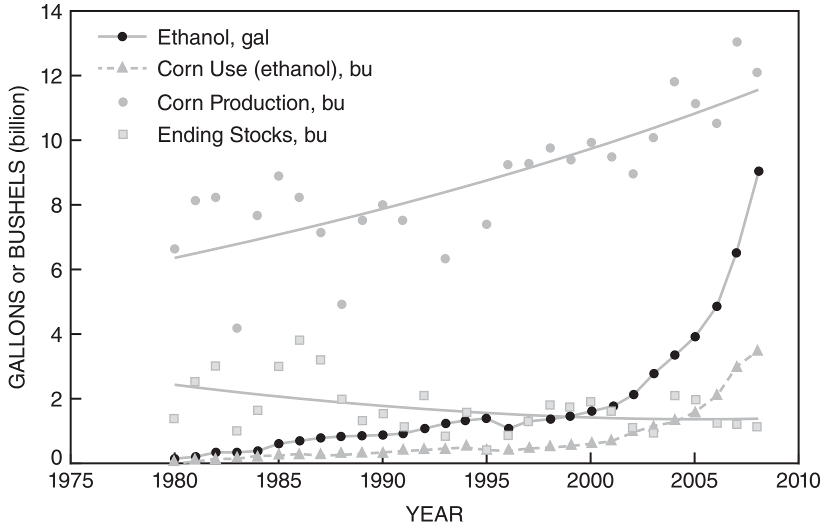


Figure 1-6
Total ethanol, corn, corn used for ethanol, and ending corn stocks in the United States (USDA-ERS, 2008).

goals are attained (35 billion gal), corn grain available for export will be between 30 and 50% of current levels. The rapid increase in corn-based ethanol has reduced ending corn stocks by 50% over the last several decades (Fig. 1-6). This reduces our ability to support global food security goals, placing additional stress on undeveloped and developing countries to meet basic food needs. Thus, using corn for ethanol is not sustainable, especially since cropland area in the United States is decreasing (Fig. 1-5). Using ethanol as a major fuel source in the future will require use of lignocellulose feedstocks (crop residue, forest products, etc.). However, there are limits to utilizing field crop residues for ethanol as organic residues returned to soils are critical to sustaining soil and crop productivity (Chapter 12).

CROP YIELDS AND NUTRIENT USE

While we expect limited expansion of cropland into less productive agricultural lands, expansion of non-agricultural land uses (wildlife habitat, forests, municipal, industrial, etc.) will also reduce available land area for cultivation. Maintaining and enhancing natural land areas is critical to sustaining ecosystem diversity and health. Therefore, meeting future food and fiber demand, while protecting environmental health, will require agricultural intensification. Advances in agricultural production technologies must occur to enhance productivity per unit of cropland to ensure world food security.

In the United States, crop yields have increased greatly over the last half-century (Fig. 1-7). This remarkable achievement is directly related to the development and adoption of agricultural technologies over the last 50 years (Fig. 1-8). The principal factors contributing to higher crop yields include development of improved varieties and hybrids, nutrient and pest management, soil and water conservation, and cultural practices. Development and use of fertilizer is partially related to increased crop productivity in the United States (Fig. 1-9); however, since 1980 growth in fertilizer use has been much lower. In contrast, world fertilizer use continues to increase (Fig. 1-9). In the last decade, growth in world use of nitrogen (N) fertilizers was nearly 60 times greater than in the United States. Continued growth in world fertilizer demand will increase demand for fossil fuel, since natural gas (CH_4) is a primary ingredient in the manufacture of N fertilizers (Chapter 4).

Since 1970, concerns for environmental quality have resulted in the development and adoption of improved management technologies that have stabilized nutrient use and provided important environmental protection in the United States. Nutrient use

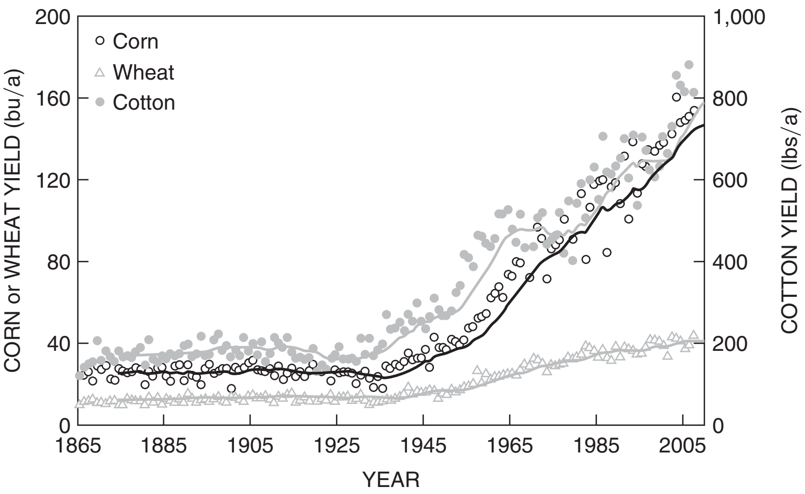


Figure 1-7
Historical yields of major food and fiber crops in the United States. Solid line represents a 10-year moving average (USDA-NASS, 2008).

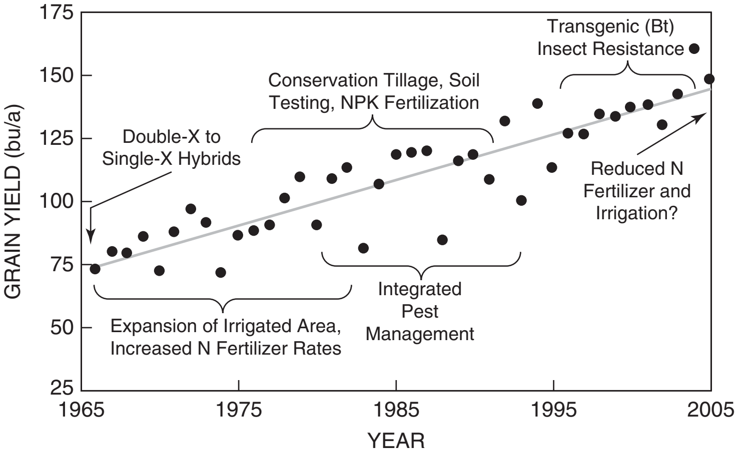


Figure 1-8
Growth in U.S. corn yield (1966–2005) and the technological innovations that contributed to yield increases (CAST Commentary, QTA2006-3, Nov. 2006).

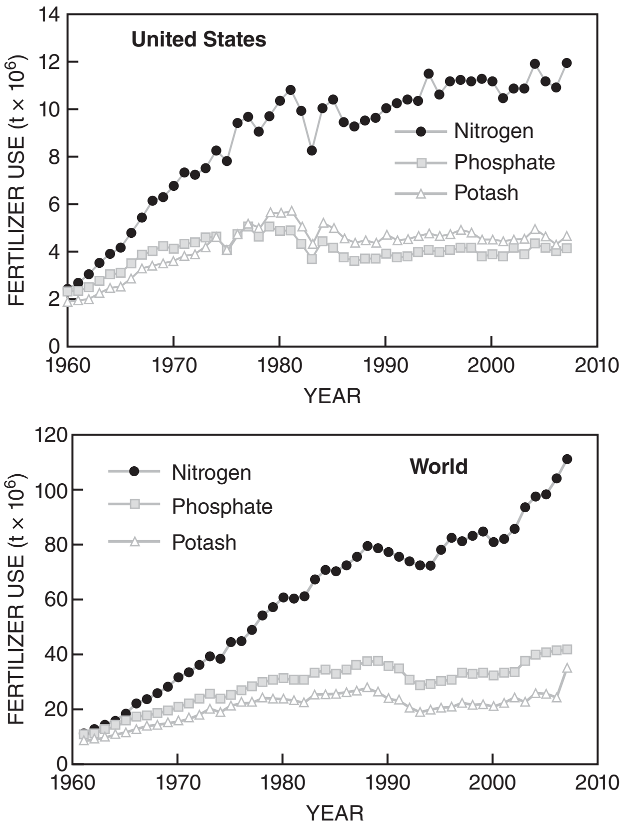


Figure 1-9
Fertilizer use in the United States and the world (FAO, 2008; USDA-ERS, 2008).

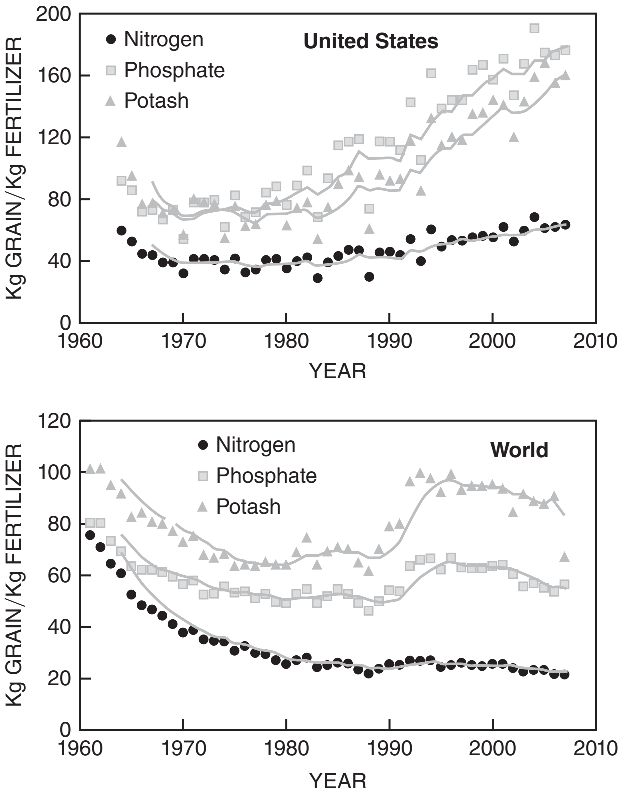


Figure 1-10
Nutrient use efficiency in U.S. corn production (top) *and world cereal production* (bottom). *Solid lines represent 4-year moving average* (FAO, 2008; USDA-ERS, USDA-NASS, 2008).

efficiency or quantity of crop production per unit nutrient applied has increased over the last several decades in the United States (Fig. 1-10). Nutrient use efficiency in world cereals has decreased, which means fertilizer use is increasing faster than cereal yields (Fig. 1-10). Despite the improvement in nutrient use efficiency in many crops in the United States, improved nutrient management technologies are still needed to reduce the impact of nutrient use on environmental quality and ecosystem health (Chapter 12). One important nutrient management principle discussed throughout the textbook is the importance of maximizing crop productivity to increase the quantity of applied nutrient recovered by the crop. This reduces the quantity of applied nutrient in the soil after harvest and, thus, reduces the impact of nutrient use on the environment.

CROP YIELD LIMITING FACTORS

Obtaining the maximum production potential of a particular crop depends on growing season environment and the skill of the producer to identify and eliminate or minimize factors that reduce yield potential. Many factors affect crop growth and yield potential (Table 1-4). Although the producer cannot control many of the climate factors, most of the soil and crop factors can and must be managed to maximize productivity.

For maximum yield potential, plants must utilize a high percentage of available solar energy. Based on available solar energy, the maximum potential yield for most crops exceeds current yield levels. For example, maximum potential yields are nearly 600, 250, and 300 bushels per acre (bu/a) of corn, soybean, and wheat, respectively. Worldwide, the dominant stresses reducing crop yield potential are related to plant available water, temperature, and nutrient availability (Table 1-5). Environment and nutrient-related stresses occur on about 55 and 20% of the land area, respectively.

Most factors influencing yield potential interact with each other to increase or decrease plant growth and yield (Chapter 11). The challenge is to accurately

TABLE 1-4
FACTORS AFFECTING CROP YIELD POTENTIAL

Climate Factors	Soil Factors	Crop Factors
Precipitation	Organic matter	Crop species/variety
Quantity	Texture	Planting date
Distribution	Structure	Seeding rate and geometry
Air temperature	Cation exchange capacity	Row spacing
Relative humidity	pH and base saturation	Seed quality
Light	Slope and topography	Evapotranspiration
Quantity	Soil temperature	Water availability
Intensity	Soil management factors	Nutrition
Duration	Tillage	Pests
Altitude/latitude	Drainage	Insects
Wind	Others	Diseases
Velocity	Depth (root zone)	Weeds
Distribution	Nutrient supply (soil test)	Harvest efficiency
CO_2 concentration	Element toxicity	Crop sequence or rotation

TABLE 1-5
PRIMARY CLIMATE AND SOIL STRESSES THAT REDUCE CROP YIELD POTENTIAL

	Global Land Area	
Dominant Soil Stress	*Million acres*	*% of total*
Low moisture stress	9,015	27.95
Low temperatures	5,385	16.69
Seasonal moisture stress	2,544	7.89
Soil salinity, alkalinity	2,235	6.93
Low nutrient-holding capacity	1,927	5.97
Shallow soils	1,828	5.67
Excessive nutrient leaching	1,111	3.44
Excessive soil acidity	1,013	3.14
Low moisture and nutrient stress	864	2.68
Low water-holding capacity	840	2.60
Other	4,483	13.90
Few constraints	1,013	3.14
Total	32,258	100

Source: Wiebe, 2003, USDA-ERS, Agric. Econ. Rep. No. 823.

identify all yield-limiting factors and eliminate or minimize the influence of those that can be managed. The importance of this principle was identified by the 19th-century-scientists Carl Sprengel and Justus von Liebig. The *Law of the Minimum* states that crop yield is proportional to the amount of the most limiting nutrient. Once this nutrient deficiency is corrected, yield will increase to a level limited by some other nutrient and so on. While the Law of the Minimum was originally based on nutrient limits, the principle can be applied to other factors influencing crop yield. For example, a producer may have planted the correct variety at the optimum time and population and may have applied all of the optimum nutrients using the most efficient methods, but still might not attain maximum yield potential because plant available water was the most limiting

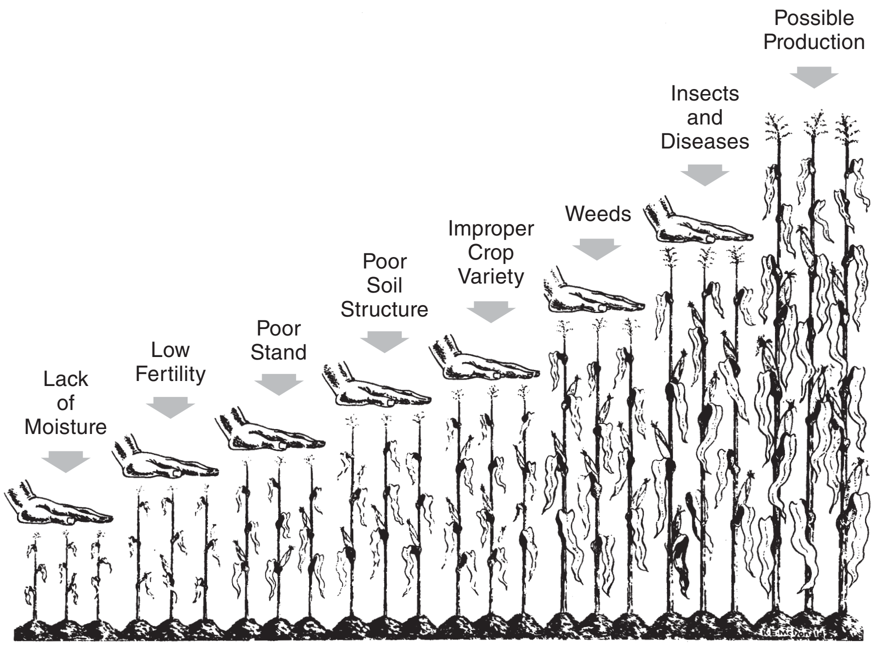


Figure 1-11
Law of the Minimum *states that the most limiting factor determines yield potential. Producers should minimize or eliminate the most limiting factor first, then the second most limiting factor, and so forth. Only in this manner can maximum yield potential be achieved.*

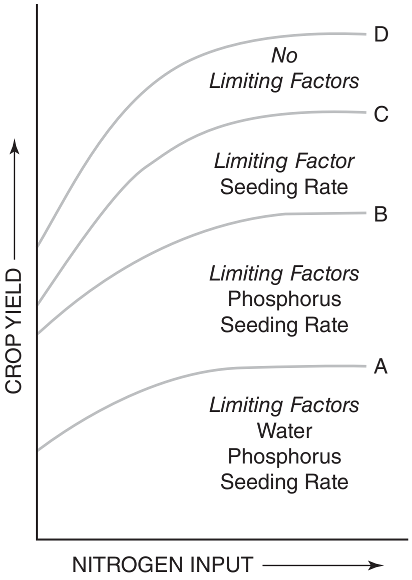


Figure 1-12
Yield response to increasing N inputs with water, phosphorus, and seeding rate limiting yield potential (A); with only phosphorus and seeding rate limiting yield potential (B); with only seeding rate limiting yield potential (C); and with no manageable factors limiting yield potential (D).

factor (Fig. 1-11). Thus, until the producer minimizes water as a limiting factor to yield potential, yield response to management of any other factor(s) will be substantially less than if plant available water were non-limiting (Fig. 1-12).

Sufficient nutrient availability in soil is required to realize maximum yield potential. Before thoroughly discussing the complex soil chemical, biological, and physical factors influencing nutrient supply to plants, as well as nutrient management strategies to optimize crop productivity, a brief review of the nutrients required for plant growth is necessary.

ELEMENTS IN PLANT NUTRITION

An element is considered essential to plant growth and development if

- the element is directly involved in the nutrition of the plant,
- a deficiency makes it impossible for the plant to complete its life cycle, and
- a deficiency is specific to the element and can only be prevented or corrected by supplying the element.

Usually, the plant exhibits a visual symptom indicating a deficiency in a specific nutrient, which normally can be corrected or prevented by supplying that nutrient. Visual nutrient deficiency symptoms can be caused by many other plant stresses; therefore, caution should be exercised when diagnosing deficiency symptoms (Chapter 9). The following terms are commonly used to describe nutrient levels in plants:

> *Deficient:* when the concentration of an essential element is low enough to severely limit yield and distinct deficiency symptoms are visible. Extreme deficiencies can result in plant death. With moderate or slight deficiencies, symptoms may not be visible, but yields will still be reduced.
>
> *Critical range:* the nutrient concentration in the plant below which a yield response to added nutrient occurs. Critical levels or ranges vary among plants and nutrients but occur somewhere in the transition between nutrient deficiency and sufficiency.
>
> *Sufficient:* the nutrient concentration range in which added nutrient will not increase yield but can increase nutrient concentration. The term *luxury consumption* is often used to describe nutrient absorption by the plant that does not influence yield.
>
> *Excessive or toxic:* when the concentration of essential or other elements is high enough to reduce plant growth and yield. Excessive nutrient concentration can cause an imbalance in other essential nutrients, which can also reduce yield.

Figure 1-13 shows that yield is severely affected when a nutrient is deficient, and when the nutrient deficiency is corrected, growth increases more rapidly than nutrient concentration. Under severe deficiency, rapid increases in yield with added nutrient can cause a small decrease in nutrient concentration. This is called the *Steenberg effect* (Fig. 1-13) and results from dilution of the nutrient in the plant by rapid plant growth. When the concentration reaches the *critical range*, plant yield is generally maximized. Nutrient sufficiency occurs over a wide concentration range, where yield is unaffected. Increases in nutrient concentration above the critical range indicate that the plant is absorbing nutrients above that needed for maximum yield, commonly called *luxury consumption*. Elements absorbed in excessive quantities can reduce plant yield directly through toxicity or indirectly by reducing concentrations of other nutrients below their critical ranges.

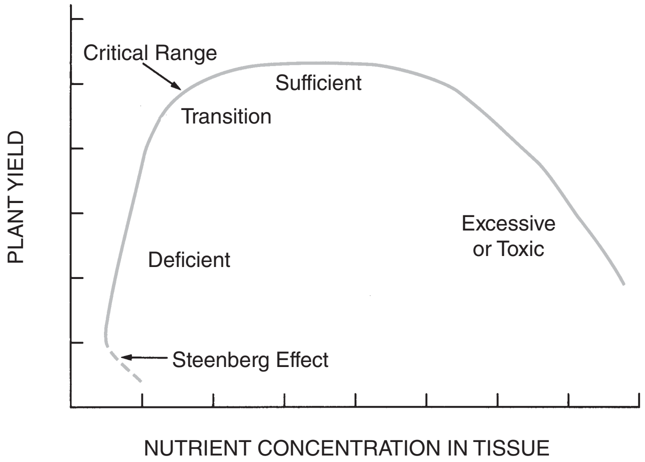


Figure 1-13

Relationship between essential plant nutrient concentration and plant growth or yield. As nutrient concentration increases toward the critical range, *plant yield increases. Above the critical range, the plant contains sufficient levels for normal growth and can continue to absorb nutrients without increasing yield* (luxury consumption). *Excessive absorption of a nutrient or element can be* toxic *to the plant and reduce yield or cause plant death.*

TABLE 1-6
RELATIVE AND AVERAGE PLANT NUTRIENT CONCENTRATIONS

	Nutrient		Concentration in Plants[1]	
Classification	*Name*	*Symbol*	*Relative*	*Average*
Macronutrients	Hydrogen	H	60,000,000	6%
	Carbon	C	40,000,000	45%
	Oxygen	O	30,000,000	45%
	Nitrogen	N	1,000,000	1.5%
	Potassium	K	250,000	1.0%
	Calcium	Ca	125,000	0.5%
	Magnesium	Mg	80,000	0.2%
	Phosphorus	P	60,000	0.2%
	Sulfur	S	30,000	0.2%
Micronutrients	Chloride	Cl	3,000	100 ppm (0.01%)
	Iron	Fe	2,000	100 ppm
	Boron	B	2,000	20 ppm
	Manganese	Mn	1,000	50 ppm
	Zinc	Zn	300	20 ppm
	Copper	Cu	100	6 ppm
	Nickel	Ni	2	0.1 ppm
	Molybdenum	Mo	1	0.1 ppm

[1] Concentration expressed on a dry matter weight basis.

Seventeen elements are considered essential to plant growth (Table 1-6). Carbon (C), hydrogen (H), and oxygen (O) are not considered mineral nutrients but are the most abundant elements in plants. The photosynthetic process in green leaves converts CO_2 and H_2O into simple carbohydrates from which amino acids, sugars, proteins, nucleic acids, and other organic compounds are synthesized. The supply of CO_2 has increased from 310 to 390 ppm since 1960. The supply of H_2O rarely limits photosynthesis directly but does so indirectly through various effects resulting from moisture stress.

The remaining 14 essential elements are classified as macronutrients and micronutrients, and the classification is based on their relative abundance in plants (Table 1-6). The macronutrients are nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg). Compared with the macronutrients, the concentrations of the eight micronutrients—iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), chloride (Cl), molybdenum (Mo), and nickel (Ni)—are very small. Four additional elements—sodium (Na), cobalt (Co), vanadium (V), and silicon (Si)—have been established as beneficial micronutrients in some plants. Micronutrients are often referred to as minor elements, but this label does not mean that they are less important than macronutrients. Micronutrient deficiency or toxicity can reduce plant yield just as macronutrient deficiency or toxicity does.

Although aluminum (Al) is not an essential plant nutrient, Al in plants can be high when soils contain relatively large amounts of Al (Chapter 3). In fact, plants absorb many nonessential elements, where more than 60 elements have been identified in plant materials. When plant dry matter is burned, the remaining plant ash contains all of the essential and nonessential mineral elements except C, H, O, N, and S, which are volatilized as gases.

Plant nutrient content is affected by many factors, including soil, climate, crop variety, and management. Because many biological and chemical reactions occur with nutrients in soils, plants do not absorb all of the nutrients applied, regardless of nutrient source. Proper management can maximize the proportion of applied nutrient absorbed by the plant (Chapter 10). As plants absorb nutrients from the soil, complete their life cycle, and die, the nutrients in the plant residue are returned to the soil. These plant nutrients are subject to the same biological and chemical reactions as nutrients applied as fertilizer and waste materials. Although this cycle varies considerably among nutrients, understanding nutrient dynamics in the soil-plant-atmosphere system is essential to efficient nutrient management.

The remaining chapters will detail our current knowledge of soil fertility and nutrient management. Use of this knowledge to identify nutrient availability problems and provide economically and environmentally sound nutrient management recommendations will be essential to a world with a secure supply of safe nutritious food, fiber, and other agricultural commodities.

STUDY QUESTIONS

1. What factors might be influencing the decreasing population growth rate shown in Figure 1-1?
2. Using Figures 1-1 and 1-2, estimate current (2010) and future (2050) cereal consumption and production per capita (per person).
3. If population in 2050 will be 10 billion, how much yield and total production would be required, by assuming a constant 750 million ha of cropland in cereal production. Also determine the additional production needed when the cereal cropland is reduced to 650 million ha in 2050.
4. How much additional production (kg/ha and Mt) is needed if cereal cropland is reduced to 600 million ha?
5. In Table 1-4, identify which climate, soil, and crop factors limiting crop yield potential can be practically managed?
6. Define the Law of the Minimum and provide an example.
7. Identify two criteria for establishing whether an element is an essential nutrient required in plants.
8. Crop yields have been increasing with time because of advances in tillage, varieties, pest control, fertilization, and so on. What factor(s) will *ultimately* limit further yield increases?
9. Among the environmental factors limiting crop response to nutrients, which is probably the most easily and inexpensively changed?
10. Crop yields have increased more in the last 50 years than in the 200 years before 1950. What factors are related to the increased yields since 1950?
11. List down and classify the essential elements required for the plant growth.
12. What factors affect the plant's nutrient content? Explain.
13. What is Steenberg effect?
14. What is meant by luxury consumption?
15. Using Figure 1-13, explain the relationship between plant growth and essential plant nutrient concentration.
16. What is the impact of rapid human population growth in the last century?

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2

Basic Soil–Plant Relationships

The interaction of numerous physical, chemical, and biological properties in soils controls plant nutrient availability. Understanding these processes and how they are influenced by environmental conditions enables us to optimize nutrient availability and plant productivity. The purpose of this chapter is to review basic chemical principles and reactions in soils that are important to understanding the soils' ability to provide plant nutrients. This knowledge is essential for decisions regarding management of nutrients to optimize plant growth and health, and to minimize nutrient application impacts on the environment. We also build the foundation of quantitative skills essential to nutrient management.

Nutrient supply to plant roots is a very dynamic process (Fig. 2-1). Plant nutrients (cations and anions) are *absorbed* from the soil solution by plant roots, which also release small quantities of ions (H^+, OH^-, and HCO_3^-) back to the soil solution (reactions 1, 2). All aqueous solutions (soil water or plant cell water) must remain electrically neutral where an equal number of ions with positive (cations) and negative (anions) charges are present. Thus, if there is an imbalance in cation–anion uptake in plant root cells, these cells release cations or anions depending on the imbalance (Fig. 2-2). This process can influence soil solution pH (Chapter 3).

As plant roots absorb nutrients, the nutrient concentration in the soil solution decreases (Fig. 2-1). As a result, several chemical and biological reactions occur to *buffer* or resupply these nutrients to the soil solution. The specific reaction that occurs depends on the cation or anion. Ions *adsorbed* to the surface of clay minerals *desorb* from these surfaces to resupply the soil solution (reaction 3). Ion exchange (*adsorption* and *desorption*) in soil is an important chemical reaction to plant nutrient availability. Soils also contain minerals that can *dissolve* to resupply the soil solution (reaction 6). Addition of nutrients or ions through fertilization or other inputs increases ion concentration in the soil solution. Although some of the added ions remain in solution, some are *adsorbed* to mineral surfaces (reaction 4) or *precipitated* as solid minerals (reaction 5). As soil microorganisms degrade plant residues, they can absorb ions from the soil solution into their tissues (reaction 7). When microbes or other organisms die, they release nutrients back to the soil solution (reaction 8). Microbial reactions are important to plant nutrient availability as well as other properties related to soil productivity.

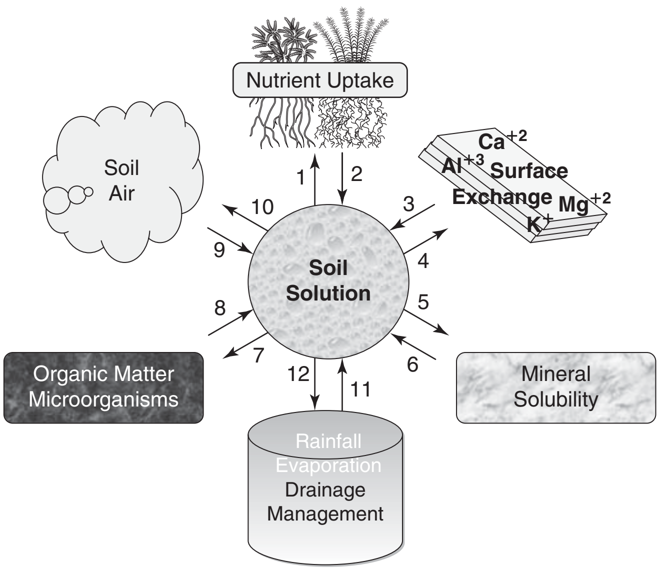


Figure 2-1
Diagram of the various soil components that influence plant nutrient concentration in the soil solution.

Microbial activity is dependent on adequate energy supply from organic C (i.e., crop residues), inorganic ion availability, and numerous environmental conditions. Plant roots and soil organisms utilize O_2 and respire CO_2 through metabolic activity (reactions 9, 10). As a result, CO_2 concentration in the soil air is greater than in the atmosphere. Numerous environmental factors and human activities can influence ion concentration in soil solution, which interacts with the mineral and biological processes in soils (reactions 11, 12). For example, adding P fertilizer to soil initially increases $H_2PO_4^-$ concentration in soil solution. With time, $H_2PO_4^-$ concentration will decrease with plant uptake (reaction 1), $H_2PO_4^-$ adsorption on mineral surfaces (reaction 4), and P mineral precipitation (reaction 5).

All of these processes and reactions are important to plant nutrient availability; however, depending on the specific nutrient, some processes are more important than others. For example, microbial processes are more important to N and S availability than mineral surface exchange reactions, whereas the opposite is true for K, Ca, and Mg.

ION EXCHANGE IN SOILS

Cation and anion exchange in soils occurs on surfaces of clay and other minerals, organic matter (OM), and roots (Fig. 2-2). Ion exchange is a reversible process by which a cation or anion adsorbed on the surface is exchanged with another cation or anion in the soil solution. Cation exchange is generally considered to be more important, since the *cation exchange capacity* (CEC) is much larger than the *anion exchange capacity* (AEC) of most agricultural soils. Ion exchange reactions in soils are very important to plant nutrient availability and retention in soil. Thus, it is essential that we understand the origin of the surface charge on soil minerals and OM.

Cation Exchange of Clay Minerals in Soil

Solid materials in soils comprise about 50% of the soil volume, with the remaining volume occupied by water and air. The solid portion comprises both inorganic minerals and OM in various stages of decay. The inorganic fraction consists of sand, silt, and clay particles. The clay fraction primarily consists of aluminosilicate minerals composed of sheets of layers of silica (Si) tetrahedra and aluminum (Al) octahedra

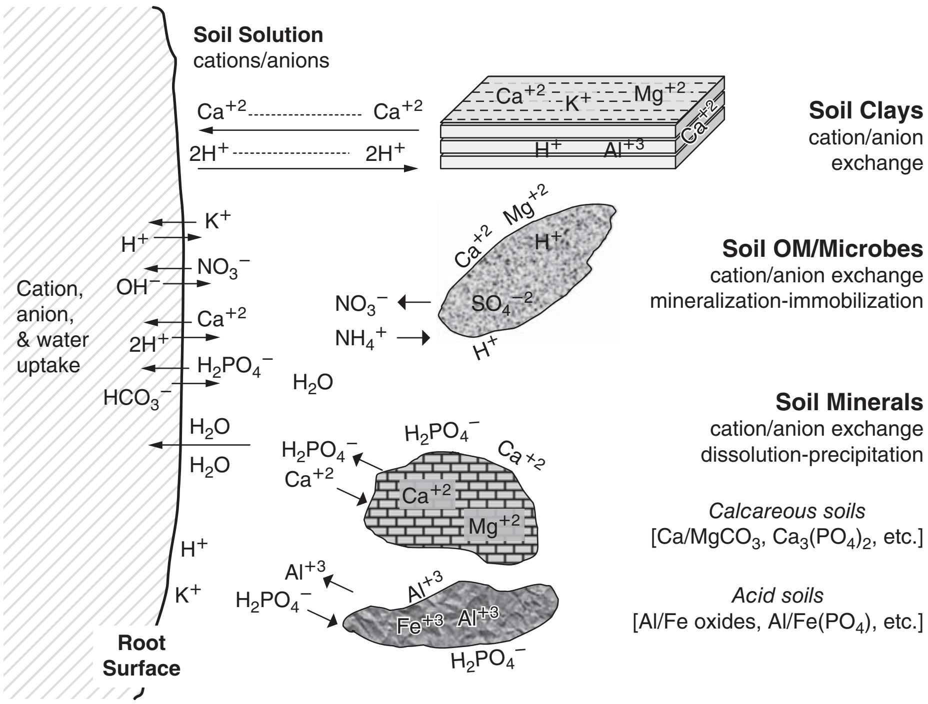


Figure 2-2
Mineral, organic matter, and root exchange surfaces in soils. Also shown is the ion absorption by roots and root exudation of ions to maintain electrical neutrality of the soil solution.

(Fig. 2-3). The structure of a Si tetrahedra is one Si^{+4} cation bonded to four O^{-2} anions, whereas the Al octahedra is one Al^{+3} cation bonded to six OH^- anions. The long sheets or layers of tetrahedra and octahedra are bonded together to form the aluminosilicate or clay minerals.

The clay minerals exist in 1:1, 2:1, and 2:1:1 forms. Kaolinite is the most common 1:1 clay and is composed of one Si sheet and one Al sheet (Fig. 2-4). The 2:1 clays are composed of an Al octahedral layer between two Si tetrahedral layers, where mica, smectite, and vermiculite are the most common 2:1 clays (Fig. 2-5).

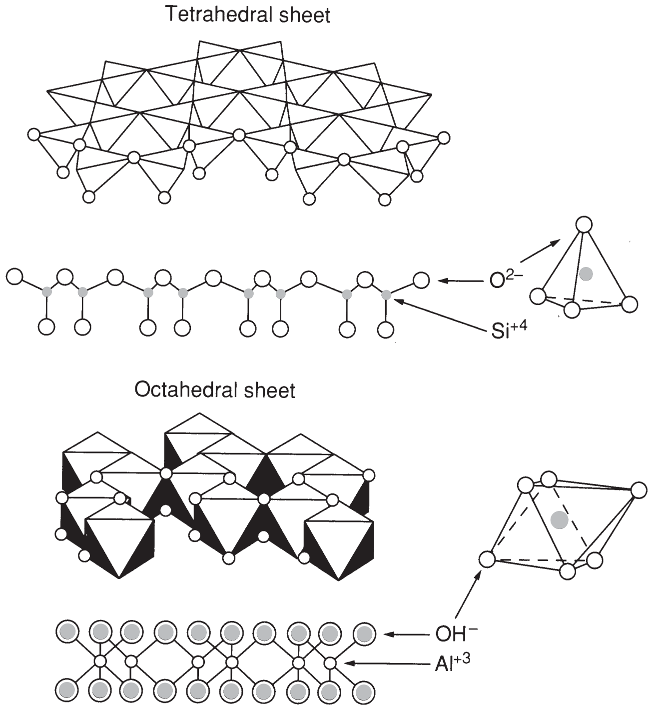


Figure 2-3
Chemical structure of Si tetrahedra, Al octahedra, and the tetrahedral and octahedral sheets.

(Adapted from Sposito, 1989, The Chemistry of Soils, *Oxford University Press.)*

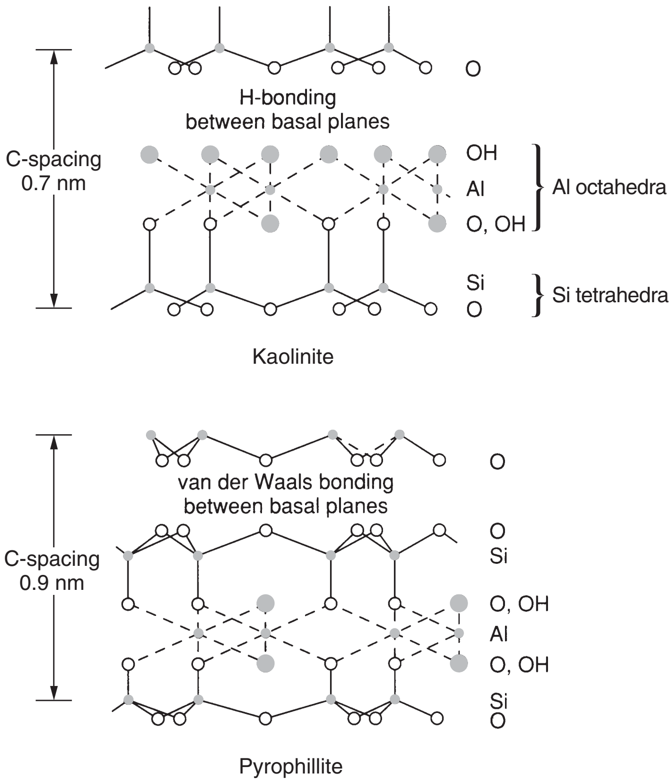


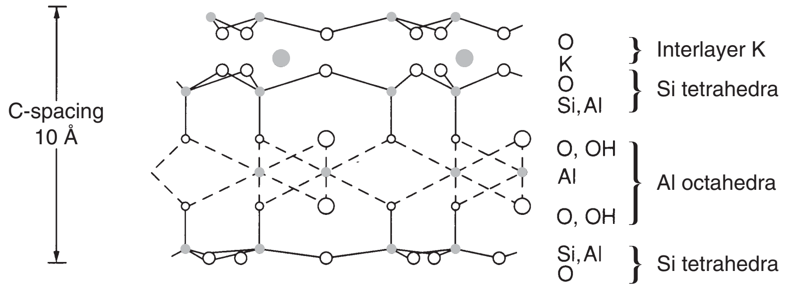
Figure 2-4
Structures of a 1:1 mineral, kaolinite, and a 2:1 mineral, pyrophyllite. No isomorphic substitution occurs in the tetrahedral or octahedral layers. A nanometer (nm) is 1×10^{-9} m. C-spacing is the distance between each unit cell (tetrahedral-octahedral layer including the space between layers).
(Adapted from Bear [Ed.], 1964, Chemistry of the Soil, *ASC Monograph Series No. 160.)*

Pyrophyllite 2:1 minerals (Fig. 2-4) are not common in soils, but illustrate 2:1 clays with no isomorphic substitution (defined in the next paragraph). Chlorites are 2:1:1 aluminosilicates that consist of an interlayer Al (acid soils) or Mg (basic soils) hydroxide sheet in addition to the 2:1 structure referred to previously (Fig. 2-6).

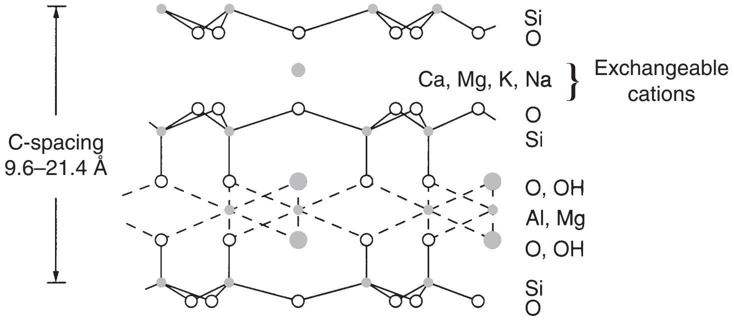
Clay minerals exhibit negative (CEC) and positive (AEC) surface charge. The major source of negative charge arises from replacement of either the tetrahedral Si^{+4} or octahedral Al^{+3} cations with cations of lower charge. Cation replacement in minerals is called *isomorphic substitution* and occurs predominately in 2:1 minerals, with very little substitution in 1:1 minerals. Isomorphic substitution occurs during the formation of these minerals and is largely unaffected by present environmental conditions.

Muscovite mica has a similar structure to pyrophyllite (Fig. 2-4) except for the substitution of one Al^{+3} for every fourth Si^{+4} in the tetrahedral layer, resulting in an increase of one negative $(-)$ charge for each substitution. The high $(-)$ surface charge combined with the unique geometry of the tetrahedral layer allows K^+ cations to neutralize the $(-)$ charge between two 2:1 layers (Fig. 2-5). The resulting mica mineral exhibits a lower C-spacing, and the mineral is considered "collapsed," with little of the $(-)$ surface charge available to attract cations. Thus, muscovite mica has a lower CEC than other 2:1 minerals because the interlayer surfaces are not accessible to cation exchange (Table 2-1). Other micas exist in soil depending on the source parent materials; however, most differ from muscovite with additional isomorphic substitution of Mg^{+2} and/or Fe^{+2} for Al^{+3} in the octahedral layer. *Illite* is a term often used for mica, but it is more weathered with a structure between muscovite mica and smectite, with isomorphic substitution in both tetra- and octahedral layers and some of the interlayer K^+ has been replaced with other cations (Ca^{+2}, Mg^{+2}).

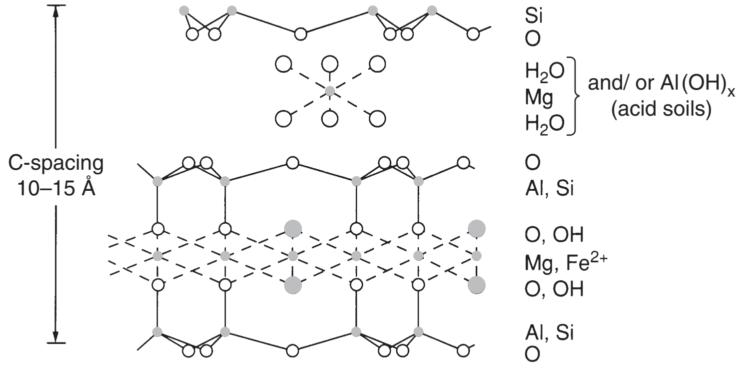
In smectites, Mg^{+2} or Fe^{+2} replaces some of the octahedral Al^{+3}, again resulting in an increase of one $(-)$ charge for each substitution. Compare the unsubstituted 2:1 pyrophyllite (Fig. 2-4) with the isomorphic substitution in the 2:1 mica (muscovite) and 2:1 smectite (montmorillonite) (Fig. 2-5). With montmorillonite,



Mica (Illite)



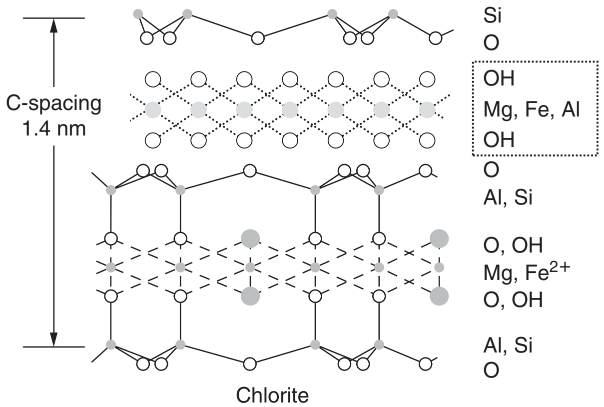
Smectite (Montmorillonite)



Vermiculite

Figure 2-5
Structures of mica, montmorillonite, and vermiculite, all 2:1 minerals. Isomorphic substitution occurs in the tetrahedral and octahedral layers.

(Adapted from Bear [Ed.], 1964, Chemistry of the Soil, ACS Monograph Series No. 160.)



Chlorite

Figure 2-6
Structure of chlorite, a 2:1:1 mineral. Isomorphic substitution occurs in the tetrahedral and octahedral layers. The interlayer is occupied with $Mg(OH)_x$ or $Al(OH)_x$ layer.

(Adapted from Bear [Ed.], 1964, Chemistry of the Soil, ACS Monograph Series No. 160.)

TABLE 2-1
SELECTED PROPERTIES OF THE COMMON LAYERED ALUMINUM-SILICATE CLAY MINERALS IN SOILS

Clay Mineral[1]	Chemical Formula[2]	Clay Type	IS[3]	Layer Charge[4]	Interlayer Cations[5]	C-spacing[6] (nm)	Degree of Expansion[7]	CEC[8] (meq/100 g)
Kaolinite	$Al_4Si_4O_{10}(OH)_8$	1:1	none	0	H	0.7	None	2–15
Mica	$Al_2(Si_3Al_1)O_{10}(OH)_2$	2:1	T (O)	1	K	1.0	None	10–40
Smectite	$(Al, Fe, Mg)_4Si_8O_{20}(OH)_4$	2:1	O (T)	0.2–0.6	Ca, Mg, K	1.0–2.1	High	80–150
Vermiculite	$(Al, Fe, Mg)_4(Si, Al)_8O_{20}(OH)_4$	2:1	T (O)	0.6–0.9	Mg, Al	1.0–1.5	Low	100–180
Chlorite	$(Al, Mg)_4(Si, Al)_8O_{20}(OH_4)$	2:1:1	T, O	1	Mg, $Al(OH)_6$	1.4	None	10–40

[1] Represents a type of common mineral, where several variations of each can exist in soils depending on source parent material and weathering environment.

[2] General representation as several variations exist under each mineral type.

[3] Dominant isomorphic substitution (some variations exist); T = tetrahedral layer; O = octahedral layer; thus, T (O) means dominant substitution in tetrahedral, where some mineral types also have substitution in octahedra.

[4] Net negative charge in a half unit of the mineral due to the isomorphic substitution.

[5] Dominant interlayer cation or compound; in chlorite and vermiculite, the presence of Mg or Al depends on pH (more Al in acid soil, more Mg in alkaline soils).

[6] Distance of tetrahedral + octahedral + interlayer (see Figs. 2-4, 2-5, and 2-6); nm is nanometer (1×10^{-9} m).

[7] Shrink-swell potential.

[8] CEC of the pure mineral.

isomorphic substitution occurs only in the octahedral layer $(Mg^{+2}$ and $Fe^{+2})$, where interlayer attraction forces are less than in clay minerals with tetrahedral substitution. Thus, montmorillonite has a much higher CEC and readily expands and contracts with wetting and drying conditions.

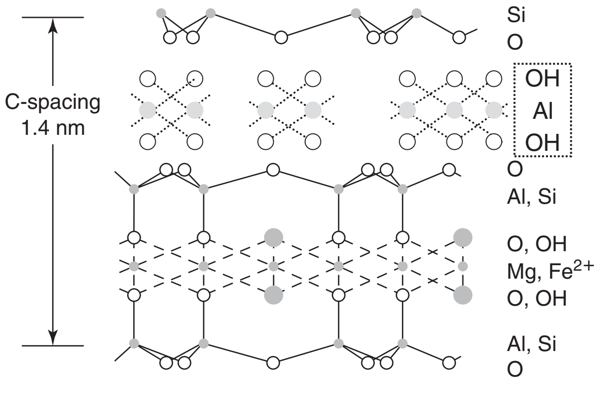
The 2:1 vermiculite is commonly weathered from micas; thus, isomorphic substitution occurs in both the octahedral and tetrahedral layers. Although isomorphic substitution $(Al^{+3}$ for $Si^{+4})$ in the tetrahedral layer is less than in mica, the tetrahedral charge attracts hydrated cations (Ca^{+2}, Mg^{+2}), which limits expansion of the interlayer compared to smectites. Therefore, vermiculite has a higher CEC, but lower interlayer expansion when wet compared to smectites (Table 2-1).

Chlorites are similar to other substituted 2:1 minerals except that the interlayer space is occupied by a layer of $Mg(OH)_x$ called *brucite* or $Al(OH)_x$ called *gibbsite* (Fig. 2-6). The surface of these layers is $(+)$ charged and is attracted to the $(-)$ charged tetrahedral surface. As a result, adsorption of H_2O or other cations in the interlayer is limited, thus chlorites are non-expansive and exhibit a low CEC (Table 2-1).

The location of the isomorphic substitution (tetrahedral, octahedral, or both) imparts specific properties to the clay minerals that affect the quantity of $(-)$ surface charge or CEC (Table 2-1). For example, isomorphic substitution $(Al^{+3}$ for $Si^{+4})$ in the tetrahedral layer locates the $(-)$ charge closer to the mineral surface compared with octahedral substitution. Compared to mica, smectite is an expanding mineral (wide variable C-spacing); however, expansion in vermiculite is more restricted because total layer charge (isomorphic substitution) is greater and also partially located in the tetrahedra, which collapses the interlayer more in the smectites minerals like montmorillonite (Fig. 2-5).

Intergrade 2:1 minerals are similar to smectites and vermiculites except the interlayer area contains discontinuous "islands" of brucite in alkaline soils or gibbsite in acid soils (Fig. 2-7). The latter hydroxyl-Al interlayered vermiculites are common in ultisols and other highly weathered acid soils typical of the southeastern United States. As with chlorites, the intergrade minerals are non-expansive and exhibit a much lower CEC compared to vermiculites and smectites.

Many other non-layered minerals exist in soils that exhibit surface exchange properties (Table 2-2). The clay-sized crystalline or amorphous compounds impart both CEC and AEC, and occur as distinct minerals or as coatings on layered silicates and other minerals.



Hydroxy-Al Vermiculite

Figure 2-7
Structure of hydroxy-Al vermiculite. The interlayer is occupied with "islands" of $Al(OH)_x$. While isomorphic substitution occurs in both tetrahedral and octahedral layers, the net $(+)$ charge of the $Al(OH)_x$ neutralizes $(-)$ surface charge, reducing CEC. Mineral exhibits high pH-dependent charge as some of the H^+ on the Al-OH are neutralized exposing $(-)$ charge from $Al-O^-$.
(Adapted from Bear [Ed.], 1964, Chemistry of the Soil, ACS Monograph Series No. 160.)

TABLE 2-2
PRIMARY AND SECONDARY MINERALS IN SOILS

Increasing weathering intensity

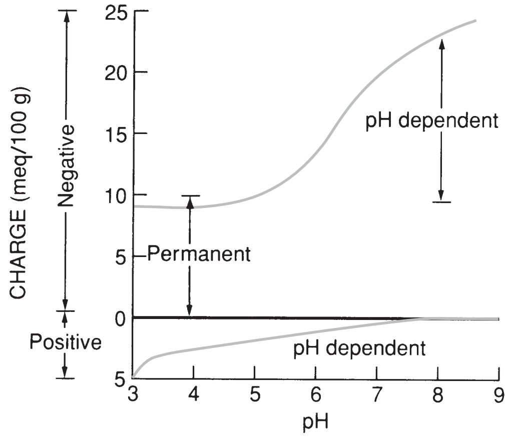
Mineral	Classification[1]	Chemical Formula
Gypsum	Primary	$CaSO_4 \cdot 2H_2O$
Calcium Carbonate	Primary	$CaCO_3$
Amphiboles	Primary	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Hornblend	Primary	$NaCa_2(Mg, Fe, Al)_5(SiAl)_8O_{22}(OH)_2$
Olivine	Primary	$(Mg, Fe)_2SiO_4$
Mica (biotite)	Primary	$K(Mg, Fe)_3(Si_3Al)O_{10}(OH)_2$
Feldspar	Primary	$(Ca, K, Na)Al_2Si_2O_8$
Quartz	Primary	SiO_2
Mica (muscovite)	Primary	$KAl_2(Si_3Al)O_{10}(OH)_2$
Chlorite	Secondary	$[Mg, Al(OH)_6](Al, Mg)_4(Si, Al)_8O_{20}(OH)_4$
Vermiculite	Secondary	$(Al, Mg, Fe)_4(Si, Al)_8O_{20}(OH)_4$
Smectite	Secondary	$(Al, Fe, Mg)_4Si_8O_{20}(OH)_4$
Kaolinite	Secondary	$Al_4Si_4O_{10}(OH)_8$
Allophane, Imogolite	Secondary	$Al_2O_3 \cdot SiO_2$
Gibbsite	Secondary	$Al(OH)_3$
Hematite	Secondary	Fe_2O_3
Goethite	Secondary	$FeOOH$

[1] Secondary minerals are weathered from primary minerals

Note: The phyllosilicates (layered clay minerals) are in bold. Minerals are listed in order of increasing weathering intensity, where gypsum occurs in relatively unweathered soils and gibbsite commonly occurs in highly weathered soils. Notice how the proportion of basic cation (Ca, Mg, K, Na) content decreases as weathering intensity increases.

The $(-)$ charge associated with isomorphic substitution is uniformly distributed over the surface of the clay minerals and is considered a *permanent charge* and unaffected by solution pH (Fig. 2-8). Another source of charge is associated with the *edge surface* of clay minerals. The quantity of $(-)$ or $(+)$ charge on the edges depends on soil solution pH (Fig. 2-8). The edge charge is called a *pH-dependent charge*. Under low pH, the edge is $(+)$ charged because of the excess H^+ ions associated with the exposed Si-OH and Al-OH groups (Fig. 2-9). As soil solution pH increases, some of the H^+ is neutralized, and the edge charge becomes more negative. Increasing the pH above 7.0 results in a nearly complete removal of H^+ ions on the Si-OH and Al-OH groups, which maximizes the $(-)$ edge charge. Only about 5–10% of the $(-)$ charge on 2:1 clays is pH dependent, whereas 50% or more of the charge developed on 1:1 clay minerals is pH dependent.

Figure 2-8
Permanent and pH-dependent charge associated with clay minerals.



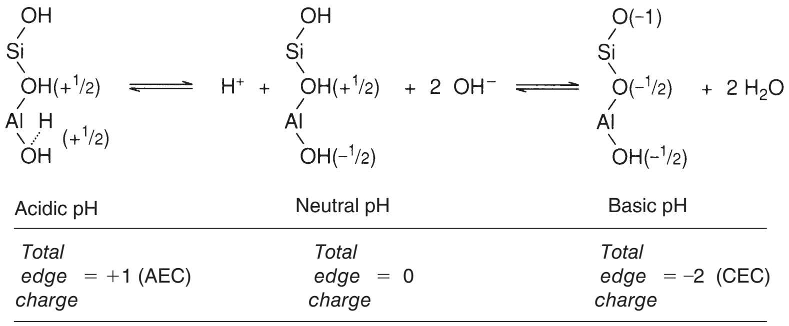


Figure 2-9
The pH-dependent charge associated with broken edges of kaolinite.

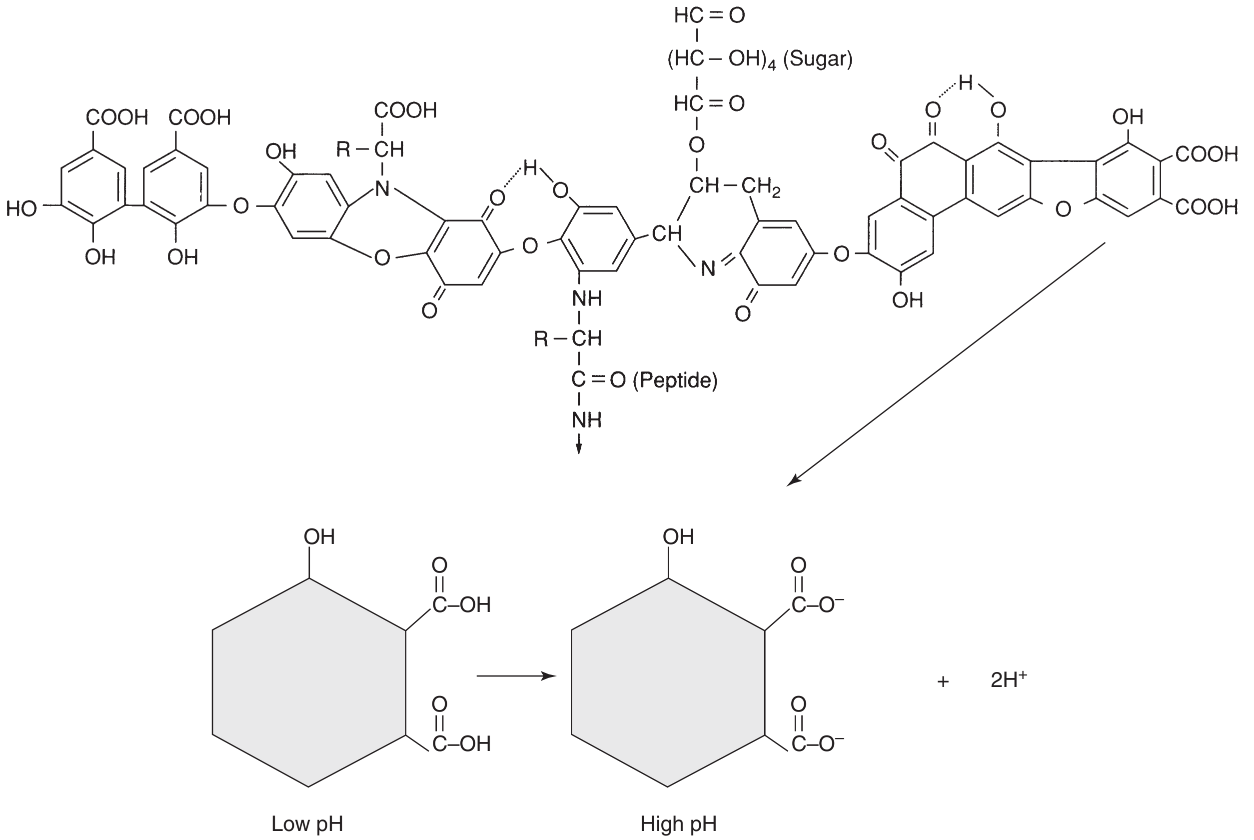


Figure 2-10
Suggested structure for humic acid in soil. The COOH groups are the pH-dependent sites, where increasing pH increases (−) sites or CEC and decreasing pH increases (+) sites or AEC.

Another source of pH-dependent charge is associated with soil OM (Fig. 2-10). Most of the (−) charge originates from the dissociation of H^+ from carboxylic acid and, to a lesser extent, phenolic acid groups. As pH increases, some of these H^+ ions are neutralized, increasing the (−) surface charge. Although the CEC is highly variable depending on soil pH, soil OM contributes greatly to total soil CEC. Pure soil OM is estimated to have a CEC of 100–300 meq/100 g soil.

CEC of Whole Soil

The CEC of a soil is strongly affected by the nature and quantity of clay minerals and OM in the soil (Table 2-1). Soils with predominately 2:1 minerals have higher CEC than soils with predominately 1:1 minerals or higher weathered soils containing

TABLE 2-3
TYPICAL RANGE IN CEC FOR MOLLISOLS AND ULTISOLS OF THE MIDWEST AND SOUTHEASTERN UNITED STATES

Soil Textural Class	Mollisol	Ultisol
	meq/100 g	
Sands (light colored)	3–5	~1
Sands (dark colored)	10–20	1–3
Loams	10–15	1.5–5
Silt loams	15–25	2–6
Clay and clay loams	20–50	3–5
Organic soils	50–100	20–40

hydroxyl-Al vermiculite. Soils with high clay and OM contents have a higher CEC than sandy, low OM soils (Table 2-3).

The CEC of southeastern U.S. soils (ultisols) is mostly pH dependent, whereas that of Midwest soils (mollisols) is mostly permanent charge (Table 2-3). The pH-dependent CEC originates from three reactions:

- Soil clays with sesquioxide $[\mathrm{Al, Fe(OH)_x}]$ coatings develop a $(-)$ charge as surface H^+ on Al, $\mathrm{Fe(OH)_x}$ are neutralized with liming and increasing surface $(-)$ charge.
- Hydroxyl-Al vermiculite (2:1:1) is a dominant clay mineral in southeastern U.S., where $\mathrm{Al(OH)_x}$ is present in the interlayer. As pH increases with liming, the H^+ associated with the interlayer $\mathrm{Al(OH)_x}$ are neutralized, resulting in additional $(-)$ charge.
- The $(-)$ charge of the carboxyl group in soil OM (Fig. 2-10) is neutralized by Al^{+3} and $\mathrm{Al(OH)_x}^{+n}$, which are tightly adsorbed by COO^- groups and are not exchangeable. As pH increases with liming, Al^{+3} and $\mathrm{Al(OH)_x}^{+n}$ are neutralized, increasing surface $(-)$ charge.

The differences in mineralogy cause the CEC of Midwest soils to be four to five times higher than southeastern soils at similar clay and OM contents.

The following example shows the importance of content and type of clay mineral and OM on soil CEC.

EXAMPLE

A soil has 27% clay (1/3 each of kaolinite, montmorillonite, vermiculite) and 4% OM. Calculate the CEC in meq/100 g of this soil.

$$
\begin{array}{llrl}
\text{kaolinite} & \rightarrow & 10\ \text{meq/100 g} \times 9\% = & 0.9 \\
\text{montmorillonite} & \rightarrow & 100\ \text{meq/100 g} \times 9\% = & 9.0 \\
\text{vermiculite} & \rightarrow & 140\ \text{meq/100 g} \times 9\% = & 12.6 \\
\underline{\text{soil OM}} & \rightarrow & 200\ \text{meq/100 g} \times 4\% = & \underline{8.0} \\
\text{soil CEC} & & = & 30.5\ \text{meq/100 g}
\end{array}
$$

This example is for illustration purposes only, because in practice, substantial technical expertise is required to quantify specific clay mineral content in soils and, thus, these analyses are not routinely performed.

Cations and Anions on Soil Exchange Surface

Except for Al^{+3} and Na^{+}, most of the exchangeable cations are plant nutrients (Table 2-4). In acidic soils, the principal cations are Al^{+3}, H^{+}, Ca^{+2}, Mg^{+2}, and K^{+}, whereas in neutral and basic soils, the predominant cations are Ca^{+2}, Mg^{+2}, K^{+}, and Na^{+}. Cations are adsorbed to the CEC with different adsorption strengths, influencing the ease with which cations can be replaced or exchanged with other cations. For most minerals, the strength of cation adsorption, or *lyotropic series*, is generally represented by:

$$Al^{+3} > H^{+} > Ca^{+2} > Mg^{+2} > K^{+} = NH_4^{+} > Na^{+}$$

The properties of the cations determine the strength of adsorption or ease of desorption. First, the strength of adsorption is directly proportional to the charge on the cations (> charge > adsorption strength). The H^{+} ion is unique because of its very small size and high charge density; thus, its adsorption strength is between Al^{+3} and Ca^{+2}. Second, the adsorption strength for cations with similar charge is determined by the size or radii of the hydrated cation (Table 2-4). As the size of the hydrated cation increases, the distance between the cation and the clay surface increases. Larger hydrated cations cannot get as close to the exchange surface as smaller cations, resulting in decreased strength of adsorption.

Strict interpretation of the lyotropic series is difficult as many factors influence the potential of a charged mineral surface to preferentially adsorb one cation over another. These include mineral type (kaolinite vs. vermiculite vs. montmorillonite), solution pH, dominant anions present, electrical potential of the charged surface, and other factors beyond the scope of this text. For example, vermiculite can adsorb K^{+} and NH_4^{+} preferentially over Ca^{+2}, where the reverse is true for montmorillonite. At neutral or higher soil pH, kaolinite shows higher preference for divalent than monovalent cations, where the opposite occurs in acid solutions. Compared to solution

TABLE 2-4
CATIONS AND ANIONS ASSOCIATED WITH SURFACE EXCHANGE IN SOILS

Ion	Atomic Weight	Equivalent Weight	Ionic Radii	
			Nonhydrated	*Hydrated*
	g/mole	*g/eq or mg/meq*	*nm*	
Cations				
Al^{+3}	27	9	0.051	
H^{+}	1	1		
Ca^{+2}	40	20	0.099	0.96
Mg^{+2}	24	12	0.065	1.08
K^{+}	39	39	0.133	0.53
NH_4^{+}	18	18	0.143	0.54
Na^{+}	23	23	0.095	0.79
Anions				
$H_2PO_4^{-}$	97	97		
SO_4^{-2}	96	48		
NO_3^{-}	62	62		
Cl^{-}	35	35		
OH^{-}	17	17		

SO_4^{-2}, Ca^{+2} is held stronger in the presence of Cl^-. Despite these differences, the general lyotropic series depicted earlier can be used; however, the order of adsorption strength does not mean that adding Ca^{+2} when liming an acid soil would replace all of the exchangeable Al^{+3}. If the solution cation concentration increases sufficiently (lime, fertilizers, other amendments), then any cation can be exchanged through mass action, similar to NH_4^+ replacing all exchangeable cations in the example on page 31. There are situations where knowledge of the lyotropic series can explain cation exchange behavior in soils and we will highlight these in subsequent chapters.

Quantifying CEC and AEC

CEC is one of the most important soil chemical properties influencing nutrient availability and retention in soil. Soil CEC represents the total quantity of $(-)$ surface charge on minerals and OM available to attract cations in solution. CEC is expressed as milliequivalents of $(-)$ charge per 100 g of oven-dried soil (meq/100 g).[1] The meq unit is used instead of mass because CEC represents both the meq/100 g of $(-)$ charge and the total meq/100 g of cations adsorbed to the CEC. Since the specific cations associated with CEC will vary, it is more meaningful to simply quantify the total charges involved.

EXAMPLE

Converting CEC units from meq/100 g soil to cmol/kg soil
A soil has a CEC of 15 meq/100 g soil.

$$\frac{15\text{ meq CEC}}{100\text{ g soil}} \times \frac{1\text{ mole }(-)}{\text{eq}} \times \frac{1\text{ eq}}{10^3\text{ meq}} \times \frac{10^2\text{ cmole}}{\text{mole}} \times \frac{10^3\text{ g}}{\text{kg}}$$
$$= \frac{15\text{ cmole CEC}}{\text{kg soil}}$$

Before we quantify CEC and related properties in soils, it is important to review the basic quantitative chemistry needed to perform these calculations.

The definitions of equivalents and *equivalent weight* are developed from the following:

- Atomic weight: mass (g) of 6×10^{23} atoms of the substance. One *mole* (m) of a substance is 6×10^{23} atoms, molecules, ions, compounds, and so on; therefore, units of atomic weight are *grams per mole* (g/mole). A mole exactly represents 6×10^{23} atoms, ions, compounds, and so on, similar to the word *dozen* exactly represents 12!
- Equivalent weight: mass (g) of a substance (e.g., cation, anion, or compound) that will react with (equivalent to) 1 g of H^+ or 1 mole (6×10^{23}) of charges; therefore, units of equivalent weight are *grams per equivalent* (g/eq).

---

[1] The International System of Units or SI unit system is used by the scientific community. Thus, meq/100 g becomes cmol/kg in SI units, representing the centimole (cmol) of charge per kilogram of soil. The conversion is 1 meq/100 g soil = 1 cmol/kg. We use meq/100 g in this text because all soil testing laboratories in the United States report CEC in meq/100 g units. When encountering soil test data from international laboratories, you may see cmol/kg unit for CEC. The conversion is simple as shown in the example on this page.

The definitions of atomic weight and equivalent weight are very similar:

atomic weight $= \text{g}/6 \times 10^{23}$ ions or molecules
equivalent weight $= \text{g}/6 \times 10^{23}\ (-)$ or $(+)$ charges $=$ g/mole charge $=$ g/eq

Let's practice these principles with several exchangeable cations. For example, consider a soil that contains 1 mole of K^+ cations:

1 mole K^+ ions $= 6 \times 10^{23}\ K^+$ ions
$= 1\ (+)$ charge/ion $\times\ (6 \times 10^{23})$ ion/mole
$= 6 \times 10^{23}$ charges/mole
$= 1$ mole $(+)$ charges
From the periodic table, the atomic weight of $K^+ = 39$ g/mole K^+ ions
Therefore, the equivalent weight of $K^+ = 39$ g/mole $(+)$ charge or
since 1 mole $(+)$/equivalent, then $= 39$ g/eq

Since the number of ions and charges are equal for K^+, the atomic weight $=$ equivalent weight.

For a *divalent* ion:

1 mole Ca^{+2} ions $= 6 \times 10^{23}\ Ca^{+2}$ ions
$= 2\ (+)$ charges/ion $\times\ (6 \times 10^{23})$ ions/mole
$= 12 \times 10^{23}\ (+)$ charges/mole
$= 2$ mole $(+)$ charges
From the periodic table, the atomic weight of $Ca^{+2} = 40$ g/mole Ca^{+2} ions
Therefore, the equivalent weight of $Ca^{+2} = 40$ g/2 moles $(+)$ charge
$= 20$ g/1 mole $(+)$ charge or
since 1 mole $(+)$/equivalent, then $= 20$ g/eq

For a *trivalent* ion:

1 mole Al^{+3} ions $= 6 \times 10^{23}\ Al^{+3}$ ions
$= 3\ (+)$ charges/ion $\times\ (6 \times 10^{23})$ ions/mole
$= 18 \times 10^{23}\ (+)$ charges/mole Al^{+3}
$= 3$ moles $(+)$ charges
From the periodic table the atomic weight of $Al^{+3} = 27$ g/mole Al^{+3} ions
Therefore, the equivalent weight of $Al^{+3} = 27$ g/3 moles $(+)$ charge
$= 9$ g/1 mole $(+)$ charge or
since 1 mole $(+)$/equivalent, then $= 9$ g/eq

The use of equivalent weight in soil fertility is a convenient way to quantify cations and anions involved in exchange reactions (Fig. 2-2). If K^+ replaces Ca^{+2} on the exchange surface, then it will take 2 moles of K^+ to replace or exchange 1 mole of Ca^{+2} [2 $(+)$ charges exchanges with 2 $(+)$ charges]. If Ca^{+2} replaces Al^{+3}, then 3 moles of Ca^{+2} replaces 2 moles of Al^{+3} [6$(+)$ charges exchanges with 6 $(+)$ charges]. Therefore, 1 mole of $(+)$ charge replaces 1 mole of $(+)$ charge regardless of which ions are involved or:

$$1 \text{ equivalent of A} = 1 \text{ equivalent of B}$$

where A and B are ions or compounds involved in the reaction.

The equivalent weight of a compound is determined by knowing the reaction involved. For example:

$$CaCO_3 + 2H^+ \rightleftarrows Ca^{+2} + CO_2 + H_2O$$

The equivalent weight of calcium carbonate $(CaCO_3)$ is determined from the periodic table by:

1 molecular weight of $CaCO_3$ $(100\ g/m)$ neutralizes or reacts with 2 moles of H^+ (see reaction).

Now, remember 1 mole H^+ = 1 equivalent H^+ (1 mole ions = 1 mole charge for univalent ions); thus,

$$\frac{100\ g\ CaCO_3}{2\ moles\ H^+} = \frac{50\ g\ CaCO_3}{1\ mole\ H^+} = \frac{50\ g\ CaCO_3}{eq}$$

Expressing concentration

$$\begin{aligned} ppm = \text{part per million} &\rightarrow 1\ g\ \text{per}\ 10^6\ g \\ &\ 1\ \text{pound per}\ 10^6\ \text{pounds} \end{aligned}$$

Convert 10 ppm Ca^{+2} in soil to mg Ca^{+2}/kg soil

$$10\ ppm\ Ca^{+2}\ \text{in soil} = \frac{10\ g\ Ca^{+2}}{10^6\ g\ soil} \times \frac{10^3\ g\ soil}{kg\ soil} \times \frac{10^3\ mg\ Ca^{+2}}{g\ Ca^{+2}} = \frac{10\ mg\ Ca^{+2}}{kg\ soil}$$

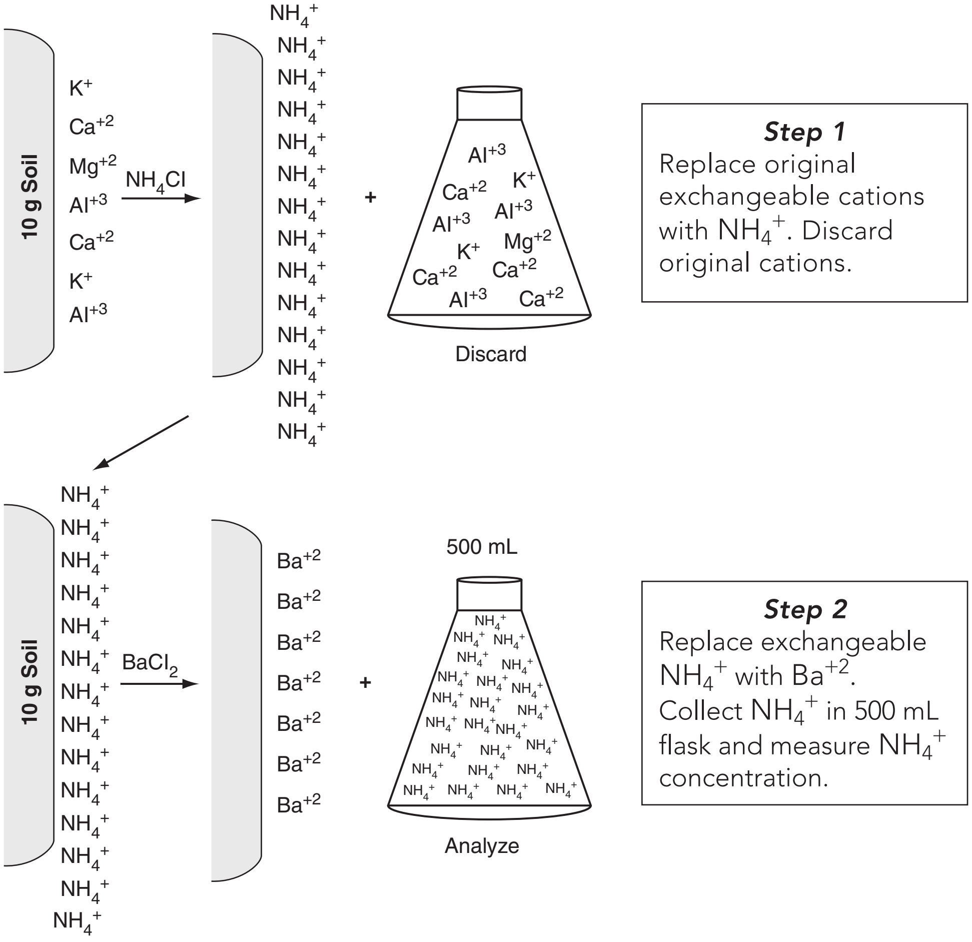
Convert 10 ppm Ca^{+2} in soil solution to mg Ca^{+2}/L solution

$$\begin{aligned} 10\ ppm\ Ca^{+2}\ \text{in solution} &= \frac{10\ g\ Ca^{+2}}{10^6\ g\ H_2O} \times \frac{1\ g\ H_2O}{1\ mL\ H_2O} \times \frac{10^3\ mL\ H_2O}{L\ H_2O} \\ &\times \frac{10^3\ mg\ Ca^{+2}}{g\ Ca^{+2}} = \frac{10\ mg\ Ca^{+2}}{L\ H_2O} \end{aligned}$$

Determination of CEC

While descriptions of detailed laboratory methods for soil analysis are not provided in this text, visualizing cation exchange in this manner is helpful in quantifying CEC and the proportion of cations on the CEC. A conventional method of CEC measurement is to extract a soil sample with neutral 1 N ammonium acetate (NH_4OAc). Sufficient NH_4^+ is added so that all of the exchangeable cations are replaced by NH_4^+, and the CEC becomes saturated with NH_4^+ (see Step 1). If this NH_4^+ saturated soil is extracted with a solution of a different salt, such as $BaCl_2$, the Ba^{+2} will replace all the NH_4^+ (see Step 2). If the soil-$BaCl_2$ suspension is filtered, the filtrate will contain NH_4^+ that was previously adsorbed to the CEC. The quantity of NH_4^+ in the filtrate is a measure of the CEC. Recall that

1 equivalent of A = 1 equivalent of B
so, # equivalents NH_4^+ = # equivalents of CEC



Step 1
Replace original exchangeable cations with NH_4^+. Discard original cations.

Step 2
Replace exchangeable NH_4^+ with Ba^{+2}. Collect NH_4^+ in 500 mL flask and measure NH_4^+ concentration.

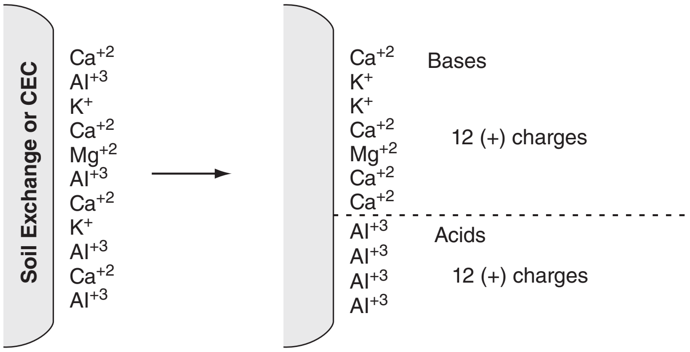
For example, suppose that the concentration of NH_4^+ in the 500 mL flask was 72 ppm (10 g of soil; 500 mL final solution volume). The CEC is calculated as follows:

$$
\begin{aligned}
&72\text{ ppm }NH_4^+ &&= 72\text{ mg }NH_4^+/\text{L}\\
&(72\text{ mg }NH_4^+/\text{L}) \times (0.5\text{ L}/10\text{ g soil}) &&= 3.6\text{ mg }NH_4^+/\text{g soil}\\
&(3.6\text{ mg }NH_4^+/\text{g soil}) \div (18\text{ mg }NH_4^+/\text{meq}) &&= 0.2\text{ meq }NH_4^+/\text{g soil}\\
&(0.2\text{ meq }NH_4^+/\text{g soil}) \times 100/100 &&= 20\text{ meq }NH_4^+/100\text{ g soil}\\
& &&= 20\text{ meq CEC}/100\text{ g soil}
\end{aligned}
$$

The 20 meq NH_4^+/100 g soil represents the CEC because the NH_4^+ replaced the original cations on the CEC. Thus, meq cations = meq CEC. The equivalent weight of NH_4^+ is given in Table 2-4.

Base Saturation

One of the important properties of a soil is its base saturation (BS), which is defined as the percentage of total CEC occupied by Ca^{+2}, Mg^{+2}, K^+, and Na^+. In the following diagram, cations on the exchange are both acids (Al^{+3}) and bases (Ca^{+2}, Mg^{+2}, K^+). In this example, Na^+ is not included because most soils with appreciable exchangeable acidity (Chapter 3) contain negligible exchangeable Na^+. There are 12(+) charges as bases and 12(+) charges as acids, or 50% BS ($12/24 \times 100 = 50\%$).



To further illustrate, suppose that the following ion concentrations were measured in the 500 mL NH_4Cl extract of the 10 g soil in the *previous CEC example*, where CEC = 20 meq/100 g soil.

$$\begin{aligned} Ca^{+2} &= 48 \text{ ppm} \\ Mg^{+2} &= 4.8 \text{ ppm} \\ K^{+} &= 7.8 \text{ ppm} \end{aligned}$$

The equivalent weights of the cations are found in Table 2-4. The following calculations are used to express the cation concentrations in CEC units and determine BS.

$$\begin{aligned} Ca^{+2} = 48 \text{ ppm} \quad &= 48 \text{ mg/L} \times (0.5 \text{ L}/10 \text{ g soil})/(20 \text{ mg/meq}) \times 100/100 \\ &= 12 \text{ meq } Ca^{+2}/100 \text{ g soil} \\ Mg^{+2} = 4.8 \text{ ppm} \quad &= 4.8 \text{ mg/L} \times (0.5 \text{ L}/10 \text{ g soil})/(12 \text{ mg/meq}) \times 100/100 \\ &= 2 \text{ meq } Mg^{+2}/100 \text{ g soil} \\ K^{+} = 7.8 \text{ ppm} \quad &= 7.8 \text{ mg/L} \times (0.5 \text{ L}/10 \text{ g soil})/(39 \text{ mg/meq}) \times 100/100 \\ &= 1 \text{ meq } K^{+}/100 \text{ g} \\ \text{Total } (Ca^{+2} + Mg^{+2} + K^{+}) \quad &= 15 \text{ meq bases}/100 \text{ g} \\ \text{Base saturation \%} \quad &= (\text{total bases/CEC}) \times 100 \\ &= [(15 \text{ meq}/100 \text{ g})/(20 \text{ meq}/100 \text{ g})] \times 100 \\ &= 75\% \text{ BS} \end{aligned}$$

The saturation with any cation may be calculated in a similar fashion. For example, from the preceding data, %Mg saturation = (2 meq Mg^{+2}/20 meq CEC) × 100 = 10% Mg.

Generally, BS of uncultivated soils is higher for arid- than for humid-region soils. The BS of soils formed from limestone or basic igneous rock is greater than that of soils formed from sandstone or acidic igneous rock.

The availability of Ca^{+2}, Mg^{+2}, and K^{+} to plants increases with increasing BS. For example, a soil with 80% BS would provide cations to growing plants far more easily than a similar soil with 40% BS. The relation between BS and cation availability is modified by the nature of the soil colloids. As a rule, soils with large amounts of OM or 1:1 clays can supply nutrient cations to plants at a much lower BS than soils high in 2:1 clays.

Soil pH–BS relationship Base saturation increases with increasing soil pH (Fig. 2-11). In this example, pH 5.5 equals about 50% BS and pH 6.5 equals 75% BS. If the CEC of this soil was 20 meq/100 g, then:

$$\begin{aligned} 50\% \text{ BS} \times 20 \text{ meq CEC}/100 \text{ g soil} &= 10 \text{ meq bases}/100 \text{ g soil} \quad @ \text{ pH } 5.5 \\ 75\% \text{ BS} \times 20 \text{ meq CEC}/100 \text{ g soil} &= 15 \text{ meq bases}/100 \text{ g soil} \quad @ \text{ pH } 6.5 \end{aligned}$$

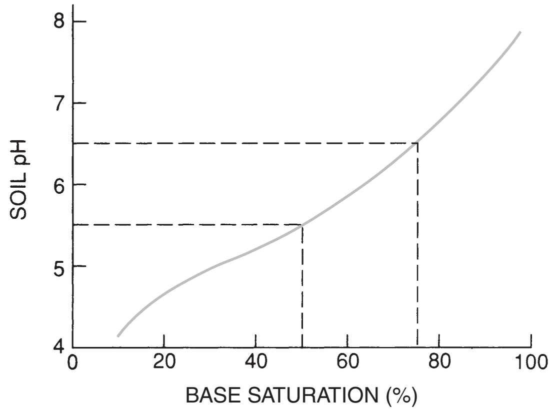


Figure 2-11
General relationship between soil pH and base saturation.

The soil pH–BS relationship varies slightly among different soils (Fig. 2-12). In ultisols, BS is ~50% at pH 5, 80% at pH 6, and ~100% at pH 7. Despite the variation between soils, pH–BS relationships can be helpful in evaluating lime requirements for acidic soils (see Chapter 3). Increasing pH has a greater effect on increasing CEC in the OM fraction in soil compared to montmorillonite, which exhibits little pH-dependent charge (Fig. 2-13). Thus, the influence of pH on CEC is greatest in soils high in OM. Weathered, acidic soils containing hydroxyl-Al vermiculites (ultisols) also exhibit strong pH-dependent CEC, due to the large quantity of $Al(OH)_x$ in the interlayer space of these clays (Fig. 2-7).

Anion Exchange

Anions in soil solution are adsorbed to $(+)$ charged sites on clay mineral edges and OM. Anion exchange may also occur with OH groups on the hydroxyl surface of kaolinite. Displacement of OH from hydrous Fe and Al oxides is also an important mechanism for anion exchange, particularly in highly weathered soils of the tropics and subtropics.

AEC increases as soil pH decreases (Fig. 2-8). Further, AEC is much greater in acid soils high in 1:1 clays and those containing Fe and Al oxides than in soils with predominately 2:1 clays. The exception is soils that contain hydroxyl-Al vermiculites common to the southeastern United States. Montmorillonitic minerals usually have

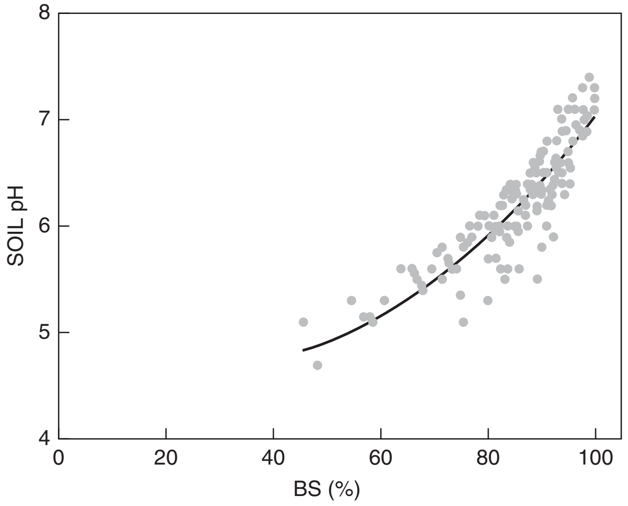
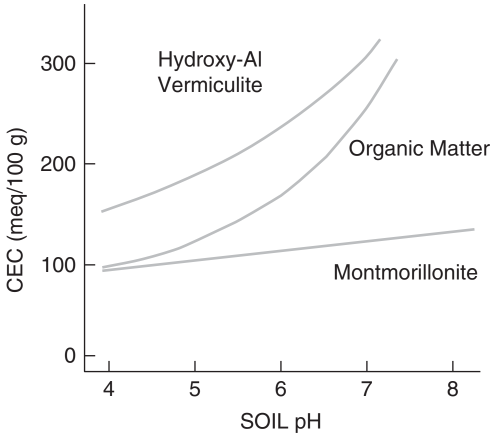


Figure 2-12
Relationship between soil pH and BS for ultisols in the southeastern United States.

Figure 2-13
Influence of pH on CEC in pure OM, montmorillonite, and hydroxyl-Al vermiculite clay minerals.



an AEC of less than 5 meq/100 g, whereas kaolinites can have an AEC as high as 40 meq/100 g at pH 4.7. Anions such as Cl^- and NO_3^- may be adsorbed, although not to the extent of $H_2PO_4^-$ and SO_4^{-2}. The order of adsorption strength is

$$H_2PO_4^- > SO_4^{-2} > NO_3^- > Cl^-$$

In most soils, $H_2PO_4^-$ is the primary anion adsorbed, although some acidic soils also adsorb significant quantities of SO_4^{-2}. The mechanisms for $H_2PO_4^-$ adsorption in soils are much more complex than the simple electrostatic attraction, as with SO_4^{-2}, NO_3^-, and Cl^-. $H_2PO_4^-$ can be adsorbed by Al and Fe oxide minerals through reactions that result in chemical bonds that are non-electrostatic (Fig. 2-14).

Root Cation Exchange Capacity

Plant roots exhibit a CEC ranging from 10 to 30 meq/100 g in monocotyledons (grasses) and 40 to 100 meq/100 g in dicotyledons (broadleaves, legumes) (Table 2-5). The exchange properties of roots are attributable mainly to carboxyl groups (COOH), similar to the exchange sites on humus (Fig. 2-10), and account for 70–90% of root CEC. Legumes and other plant species with high root CEC tend to absorb divalent cations preferentially over monovalent cations, whereas the reverse occurs with grasses. These root CEC properties help to explain why, in grass-legume pastures on soils containing less than adequate K^+, the grass survives but the legume disappears. The grasses absorb K^+ more effectively than legumes.

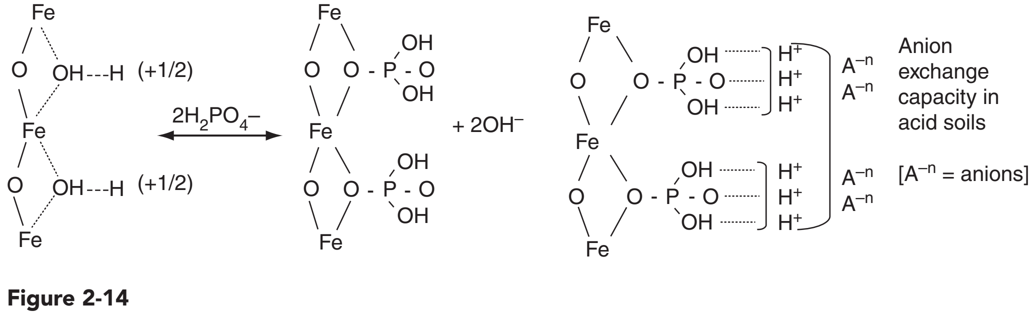


Figure 2-14
Chemical adsorption of phosphate ($H_2PO_4^-$) to iron hydroxide [$Fe(OH)_3$] minerals in soils and how anion exchange may be exhibited in acid soils.

TABLE 2-5
CEC OF SELECTED ROOTS

Species	CEC meq/100 g Dry Root
Wheat	23
Corn	29
Bean	54
Tomato	62

BUFFERING CAPACITY

One of the most important chemical principles in soil chemistry and nutrient management is the soil *buffer capacity* (BC). Plant nutrient availability depends on the concentration of nutrients in solution but, more importantly, on the capacity of the soil to *maintain* the concentration in solution. The BC represents the ability or capacity of the soil to resupply an ion to the soil solution.

The BC involves all of the solid components in the soil system. Therefore, cations and anions must exist in soils as solid compounds, adsorbed to exchange sites, and in soil OM (Fig. 2-2). For example, when Al^{+3} in solution is neutralized by liming, Al^{+3} will desorb from the mineral or OM exchange sites. The solution pH is then buffered by exchangeable Al^{+3} and will not increase until significant quantities of exchangeable Al^{+3} (*buffer capacity*) have been neutralized. Similarly, as plant roots absorb nutrients such as K^+, exchangeable K^+ is desorbed to resupply solution K^+. If the quantity of exchangeable K^+ (%K saturation) is low, then the soil's capacity to meet crop K^+ requirement is low and K^+ must be applied to sustain normal plant growth. With some nutrients, such as $H_2PO_4^-$, solid P minerals dissolve to resupply or buffer the solution $H_2PO_4^-$ concentration.

Soil BC can be described by the ratio of the concentrations of adsorbed (ΔQ) and solution (ΔI) ions. Fig. 2-15 illustrates the quantity (Q) and intensity (I) relationships between two soils. Soil A has a higher BC than soil B, as indicated by the steeper slope $(\Delta Q/\Delta I)$. Thus, increasing the concentration of adsorbed ions increases the solution concentration in soil B much more than that in soil A,

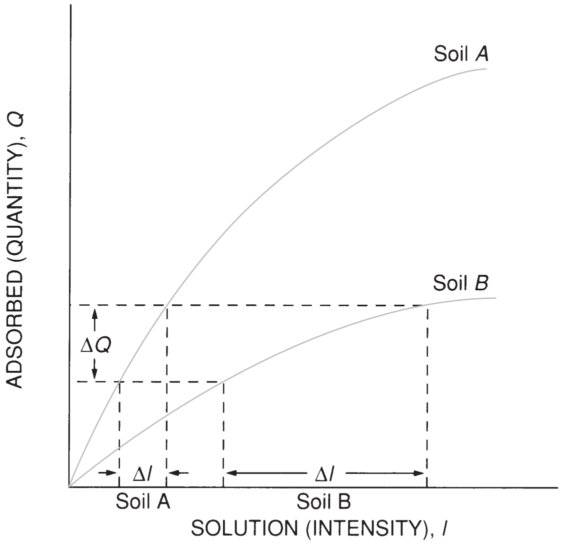


Figure 2-15
Relationship between quantity of adsorbed nutrient and concentration of the nutrient in solution (intensity). BC $(\Delta Q/\Delta I)$ of soil A is greater than that of soil B.

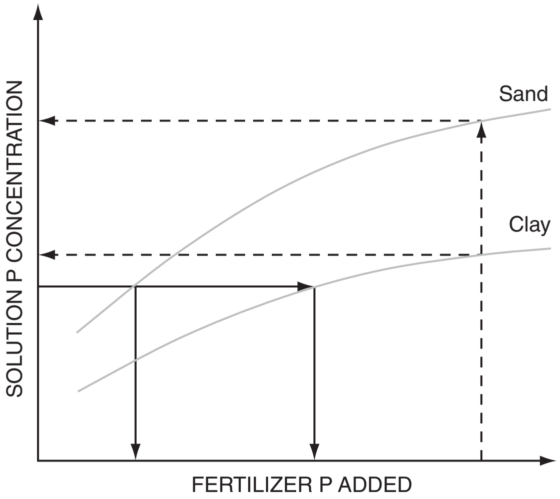


Figure 2-16
Graphical representation of the influence of BC on changes in solution P concentration with addition of fertilizer P. To maintain the same solution P concentration in both soils, fertilizer P rate would be greater for the clay soil than the sandy soil (——). If the same rate of fertilizer P is added to both soils (----), the resulting solution $H_2PO_4^-$ concentration will be greater in the sandy soil than in the clay soil because the $BC_{clay} > BC_{sand}$.

indicating that $BC_A > BC_B$. Alternatively, decreasing the solution concentration by plant uptake decreases the quantity of ion in solution much less in soil A than in soil B.

The BC in soil increases with increasing CEC, OM, and other solid constituents in the soil. For example, the BC of montmorillonitic, high OM soils is greater than that of kaolinitic, low OM soils. Since CEC increases with increasing clay content, fine-textured soils will exhibit higher BC than coarse-textured soils. If exchangeable K^+ decreases (e.g., as a result of plant uptake or leaching), the capacity of the soil to buffer solution K^+ is lower in a sandy soil. The nutrient may become deficient, and K^+ fertilizer will be needed to increase exchangeable K^+ and correct the K^+ deficiency. Addition of P fertilizer will increase adsorbed $H_2PO_4^-$, while some $H_2PO_4^-$ may also precipitate as solid P compounds both of which contribute to the P BC in soils.

Thus, it is apparent that BC is a very important soil property that strongly influences nutrient availability. Fig. 2-16 further illustrates the BC relationships in soils. If the same rate of fertilizer P is added to both soils, the resulting solution $H_2PO_4^-$ concentration will be greater in the sandy soil than in the clay soil because $BC_{clay} > BC_{sand}$. Alternatively, if we wanted to establish the same solution P concentration in both soils, then more fertilizer P would be needed in the clay soil compared to the sandy soil, again because $BC_{clay} > BC_{sand}$.

MINERAL SOLUBILITY IN SOILS

As nutrient concentrations in the soil solution decrease by plant uptake, nutrients in soil solution are replenished from exchange surfaces, soil OM, or dissolution of soil minerals (Fig. 2-2). The solubility of a soil mineral refers to the concentration of the elements or ions in solution supported or maintained by the specific mineral. For example, when $CaSO_4 \cdot 2H_2O$ (gypsum) is added to water, it dissolves.

$$CaSO_4 \cdot 2H_2O \rightleftarrows Ca^{+2} + SO_4^{-2} + 2H_2O$$

The product of the two ion (Ca^{+2} and SO_4^{-2}) concentrations is called the solubility product, or Ksp, where

$$Ksp = (Ca^{+2})(SO_4^{-2})$$

The Ksp is a constant, such that when the product of the ion concentrations is <Ksp, then the mineral will dissolve, and when the product of the ion concentrations is >Ksp, then the mineral will precipitate. When $CaSO_4 \cdot 2H_2O$ is added to water, it begins to dissolve, and the reaction initially proceeds only to the right as the concentration of Ca^{+2} and SO_4^{-2} increases. Eventually, as more $CaSO_4 \cdot 2H_2O$ dissolves, the backward reaction will start to occur, and an *equilibrium* between the forward (*dissolution*) and backward (*precipitation*) reactions is established. When this occurs, the solution is *saturated*. If more water is added, Ca^{+2} and SO_4^{-2} in solution are diluted or their concentration decreases. When this occurs, the product of the concentrations is $<$Ksp, causing more $CaSO_4 \cdot 2H_2O$ to dissolve. If enough water is added to dissolve *all* of the solid, then the solution is *unsaturated*. Similarly, if water is removed (i.e., evaporation), then more $CaSO_4 \cdot 2H_2O$ will precipitate because the product of the concentrations is $>$Ksp. Likewise in this example, if $MgSO_4 \cdot 7H_2O$ were added, the resulting SO_4^{-2} concentration would increase, *causing* more $CaSO_4 \cdot 2H_2O$ to precipitate because the product of the concentrations $(Ca^{+2})(SO_4^{-2})$ is $>$Ksp.

There are many minerals in soils that influence the concentrations of ions and plant nutrients in soil solution. For example, in acid soils, $FePO_4 \cdot 2H_2O$ is a common mineral that influences P availability.

$$FePO_4 \cdot 2H_2O + 2H^+ \rightleftarrows Fe^{+3} + H_2PO_4^- + 2H_2O$$

The Ksp for this reaction is

$$\text{Ksp} = \frac{(Fe^{+3})(H_2PO_4^-)}{(H^+)^2}$$

As the soil solution concentration of $H_2PO_4^-$ decreases with plant uptake, the product of the ion concentrations is now $<$Ksp, so the $FePO_4 \cdot 2H_2O$ mineral dissolves to resupply or buffer solution $H_2PO_4^-$. Alternatively, if $H_2PO_4^-$ is added through fertilizers or manures, the $H_2PO_4^-$ concentration in solution increases, causing $FePO_4 \cdot 2H_2O$ to precipitate (product of the concentrations is $>$Ksp). The reaction also shows that the solubility is dependent on pH, which was not the case with $CaSO_4 \cdot 2H_2O$. With $FePO_4 \cdot 2H_2O$, increasing pH (decreasing H^+ concentration) causes Fe^{+3} and $H_2PO_4^-$ to decrease as $FePO_4 \cdot 2H_2O$ precipitates. Recall that Ksp is a constant, so if the denominator decreases, the numerator must also decrease. Solubility relationships are particularly important for plant availability of P and many of the micronutrients. Solubility reactions (Fig. 2-2) are essential in buffering the solution concentration of many plant nutrients.

SUPPLY OF NUTRIENTS FROM OM

Microbial activity and nutrient cycling through soil OM substantially impacts plant nutrient availability. Soil solution concentration of N, S, P, and several micronutrients is intimately related to the microbial (organic) fraction in soils.

In virgin (uncultivated) soil, the OM content is determined by soil texture, topography, and climatic conditions that predominately influence the quantity of CO_2 fixed by plants (total plant biomass) and recycled to the soil. Generally, OM content is higher in cooler than in warmer climates and, with similar annual temperature and vegetation, increases with effective precipitation. These differences are related to reduced potential for OM oxidation with cooler temperatures and increased biomass production with increased rainfall. Soil OM content is greater in fine-textured than in coarse-textured soils and is related to increased biomass production in fine-textured soils because of improved soil water and nutrient storage and reduced OM oxidation potential. Soil OM contents are higher under grassland vegetation than under forest cover. These relations are generally true for well-drained soil conditions. Under poor drainage, aerobic decomposition is impeded and organic residues build

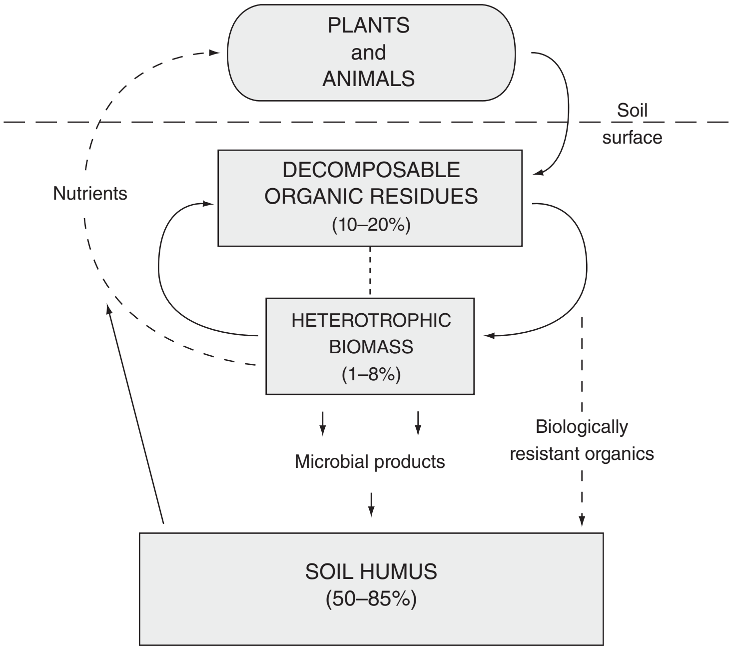


Figure 2-17
Conceptual model of the degradation of plant residues to stable soil humus. Relative sizes of the microbial and organic biomass components are shown.
(*Doran and Smith, 1987,* SSSA Spec. Publ. 19, *p. 55.*)

up to high levels, regardless of temperature or soil texture. In general, soils with higher OM content will be more productive. The influence of soil and crop management on soil OM and its relationship to soil and crop productivity is discussed in Chapter 12.

Soil OM comprises organic materials in all stages of decomposition. Crop residues degrade through autotrophic and heterotrophic microbial processes that ultimately form relatively stable soil humus (Fig. 2-17). The size of these components depends on climate, soil type, and soil and crop management, all of which influence the quantity of crop residues produced and returned to the soil. Fresh plant or other organic residues are subject to fairly rapid decomposition. The relatively small heterotrophic biomass (1–8% of total soil OM) represents soil microorganisms and fauna responsible for the majority of organic–inorganic transformations that influence nutrient availability. Soil humus, the largest component of soil OM, is relatively resistant to microbial degradation; however, it is essential for maintaining optimum soil physical conditions important for plant growth, water-holding capacity, nutrient availability, and many other properties important to soil productivity (Chapter 12). The primary microbial processes involved in fresh residue and humus turnover or cycling in soils are *mineralization* and *immobilization*.

$$\begin{array}{l}\text{Organic}\\\text{Complexed}\\\text{Nutrients}\end{array}\ \underset{\textit{immobilization}}{\overset{\textit{mineralization}}{\rightleftarrows}}\ \begin{array}{l}\text{Inorganic}\\\text{Nutrients in}\\\text{Solution}\end{array}$$

These reactions, combined with other physical, chemical, and environmental factors, are important in OM stability and in plant nutrient availability (Fig. 2-1). As plant and other organic residues are returned to the soil, many different types of soil microorganisms degrade these residues to a family of relatively stable organic compounds called *humus* (Fig. 2-10). In the degradation process, organically complexed ions in the residue can be *mineralized* or converted from organic to inorganic forms of the particular nutrient (i.e., N, S, P). If there are insufficient nutrients in the residue to meet the microbial demand, then inorganic ions in the soil solution will be *immobilized* into the microbial tissues. The microbial cycle of *mineralization* and *immobilization* occurs over a wide range of environmental conditions, but activity is maximized at about the same relative moisture and temperature conditions optimum for plant growth. Microbial transformations important to nutrient availability will be detailed in Chapter 4.

MOVEMENT OF IONS FROM SOILS TO ROOTS

Ion absorption by plant roots requires contact between the ion and the root surface. There are generally three ways in which nutrients reach the root surface: (1) root interception, (2) mass flow, and (3) diffusion. The relative importance of these mechanisms in supplying nutrients to plant roots is shown in Table 2-6.

Root Interception

Root interception represents exchange of ions through physical contact between the root and mineral surfaces (Fig. 2-18). Ion absorption by root interception is enhanced by increasing the quantity of absorbing roots in a given volume of soil. As roots develop and exploit more soil, soil solution and soil surfaces retaining adsorbed ions are exposed to the increasing root mass. Ions such as H^+ adsorbed to the surface of root hairs may exchange with ions held on the surface of clays and OM because of the intimate contact between roots and soil particles. The ions held by electrostatic forces at these sites oscillate within a certain volume (Fig. 2-18). When the oscillation volumes of two ions (H^+ and K^+) overlap, ion exchange occurs. In this way, Ca^{+2} on a clay surface could then presumably be absorbed by the root and utilized by the plant.

The quantity of nutrients that can come in direct contact with plant roots is the amount in a volume of soil equal to the volume of roots. Roots usually occupy 1–3% of the soil volume.

Root interception of nutrients can be enhanced by *mycorrhiza*, a symbiotic association between fungi and plant roots. The beneficial effect of mycorrhiza is greatest when plants are growing in infertile soils. The extent of mycorrhizal colonization is also enhanced under conditions of slightly acidic soil pH, low P, adequate N, and

TABLE 2-6
SIGNIFICANCE OF ROOT INTERCEPTION, MASS FLOW, AND DIFFUSION IN ION TRANSPORT TO CORN ROOTS

		Percentage Supplied by		
Nutrient	**Nutrients Required for 200 bu/a of Corn**	*Root Interception*	*Mass Flow*	*Diffusion*
N	225	1	99	0
P	45	2	4	94
K	200	2	20	78
Ca	50	120	440	0
Mg	55	27	280	0
S	25	4	94	2
Cu	0.12	8	400	0
Zn	0.40	25	30	45
B	0.25	8	350	0
Fe	2.5	8	40	52
Mn	10.40	25	130	0
Mo	0.012	8	200	0

Note: The contribution of diffusion was estimated by the difference between total nutrient needs and the amounts supplied by interception and mass flow. If root interception + mass flow ≥ 100%, then diffusion = 0.

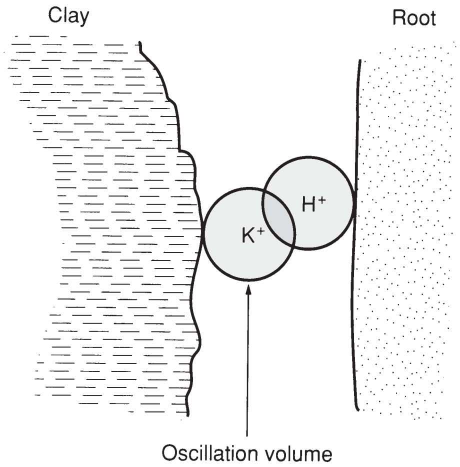


Figure 2-18
Conceptual model for root interception or contact exchange of nutrients between ions on soil and root exchange sites. Overlapping oscillation volumes cause exchange of H^+ *on the root with* K^+ *on the clay mineral surface.*

low soil temperatures. The hyphal threads of mycorrhizal fungi act as extensions of plant root systems, resulting in greater soil contact. (See Fig. 5-6 for a diagrammatic representation of a mycorrhizal infected root.) The two major groups of mycorrhizas are ectomycorrhizas and endomycorrhizas. The ectomycorrhizas occur mainly in the tree species of the temperate zones but can also be found in semiarid zones. The endomycorrhizas are more widespread. The roots of most agronomic crops have vesicular arbuscular mycorrhiza. The fungus grows into the cortex. Inside the plant cells, small structures known as arbuscules, considered to be the site of transfer of nutrients from fungi to host plants, are formed. Increased nutrient absorption is due to the larger nutrient-absorbing surface provided by the fungi, which can be up to 10 times that of uninfected roots. Fungal hyphae can extend up to 8 cm into the soil surrounding the roots, thus increasing absorption of nutrients. Enhanced P uptake is the primary cause of improved plant growth from mycorrhiza, which results in improved uptake of other elements (Table 2-7).

Mass Flow

Mass flow occurs when ions in soil solution are transported to the root as a result of water uptake (transpiration) by the plant, water evaporation at the soil surface, and percolation of water in the soil profile. Transport of ions in the soil solution to

TABLE 2-7
EFFECT OF INOCULATION OF ENDOMYCORRHIZA AND P ON NUTRIENT CONTENT IN CORN SHOOTS

	Content in Shoots (μg)			
	No P		*25 ppm P Added*	
Nutrient	*No Mycorrhiza*	*Mycorrhiza*	*No Mycorrhiza*	*Mycorrhiza*
P	750	1,340	2,970	5,910
K	6,000	9,700	17,500	19,900
Ca	1,200	1,600	2,700	3,500
Mg	430	630	990	1,750
Zn	28	95	48	169
Cu	7	14	12	30
Mn	72	101	159	238
Fe	80	147	161	277

Source: Adapted from Lambert et al., 1979, *SSSAJ*, 43:976.

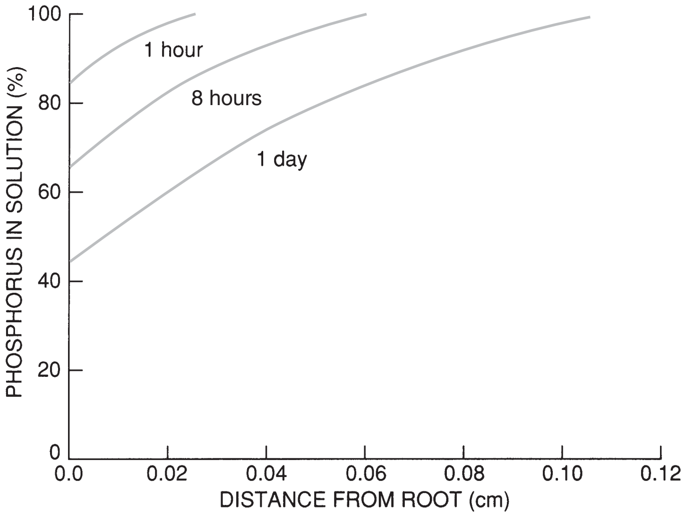


Figure 2-19
The influence of P uptake on the distribution of P in the soil solution as a function of distance from the root surface.

root surfaces by mass flow is an important factor in supplying nutrients to plants (Table 2-6).

The quantity of nutrients reaching roots by mass flow is determined by the rate of water flow or the water consumption of plants and the average nutrient concentrations in the soil water. Mass flow can supply an excess of Ca^{+2}, Mg^{+2}, several micronutrients, and most of the soluble nutrients, such as NO_3^-, Cl^-, and SO_4^{-2} (Table 2-6). As soil moisture is reduced (increased soil moisture tension), water transport to the root surface decreases. Mass flow is also reduced at low temperatures because transpiration demand by plants and water evaporation at the soil surface decreases at low soil temperature.

Diffusion

Diffusion occurs when an ion moves from an area of high concentration to one of low concentration. As roots absorb nutrients from the surrounding soil solution, the nutrient concentration at the root surface decreases compared with the "bulk" soil solution concentration (Fig. 2-19).

Therefore, a nutrient concentration gradient is established that causes ions to diffuse toward the root. A high plant requirement for a nutrient results in a large concentration gradient, favoring a high rate of ion diffusion from the soil solution to the root surface. Most of the P and K move to the root by diffusion (Table 2-6). Ion diffusion in soils can be quantified by the following equation (Fick's law) that helps us understand the factors that influence diffusion in soil:

$$\frac{dC}{dt} = De \bullet A \bullet \frac{dC}{dX}$$

where dC/dt = rate of diffusion (change in concentration C with time)
dC/dX = concentration gradient (change in concentration with distance)
De = effective diffusion coefficient
A = cross-sectional area through which the ions diffuse

The diffusion equation shows that the rate of nutrient diffusion (dC/dt) is directly proportional to the concentration gradient (dC/dX). As the difference in nutrient concentration between the root surface and the bulk solution increases, the rate of nutrient diffusion increases. Also, increasing the cross-sectional area for diffusion increases dC/dt, which means diffusion should be greater in a clay compared to a sand because of greater water-filled pore space. The diffusion rate is also proportional to the diffusion coefficient, De, which partially controls nutrient diffusion to the root. For a given spacing between roots, D*e* determines the fraction of nutrients in the soil that can reach the roots during a specific period of plant growth. D*e* is described as follows:

$$\mathrm{D}e = \mathrm{D}w \bullet \theta \bullet \frac{1}{\mathrm{T}} \bullet \frac{1}{b}$$

where $\mathrm{D}w$ = diffusion coefficient in water
θ = volumetric soil water content
T = tortuosity factor
b = soil BC

This relationship shows the diffusion coefficient in soil (D*e*) is directly related to the diffusion coefficient for the same nutrient in water (D*w*). Inherent in the D*w* term is a temperature factor such that increasing temperature increases D*w*, which increases D*e*, and then $d\mathrm{C}/d\mathrm{t}$. Also, as soil moisture content (θ) increases, D*e* increases, which results in an increase in diffusion rate, $d\mathrm{C}/d\mathrm{t}$. As moisture content decreases, moisture films around soil particles become thinner and ion diffusion through these films becomes more *tortuous*. Transport of nutrients to the root surface is most effective at field capacity soil moisture content. Therefore, raising θ reduces tortuosity, or the diffusion path length, which in turn increases $d\mathrm{C}/d\mathrm{t}$. Tortuosity (T) is also related to soil texture. Nutrients diffusing in coarse-textured soils experience a more tortuous path to the root surface (less water-filled pore space). As T increases with increasing sand content, 1/T decreases, which reduces the D*e* and thus $d\mathrm{C}/dt$. While tortuosity is less in clay soils (increasing diffusion rate $d\mathrm{C}/d\mathrm{t}$), clay soils also have a greater buffer capacity (b) than sandy soils, which would decrease $d\mathrm{C}/d\mathrm{t}$. Thus, D*e* is inversely related to *b*. Increasing BC of the soil decreases D*e*, which decreases $d\mathrm{C}/d\mathrm{t}$. Compared to a soil with a high BC, a low BC soil would likely have higher nutrient concentration in solution resulting in a higher D*e*, and higher potential $d\mathrm{C}/d\mathrm{t}$. Increasing the solution ion concentration also increases the diffusion gradient, $d\mathrm{C}/d\mathrm{X}$, which contributes to increased $d\mathrm{C}/d\mathrm{t}$.

Ion uptake by roots, which is responsible for creating and maintaining the diffusion gradient, is strongly influenced by temperature. Within the range of about 10–30°C, an increase of 10°C usually causes the rate of ion absorption to go up by a factor of two or more. Nutrient diffusion is slow under most soil conditions and occurs over very short distances in the vicinity of the root surface. Typical diffusion distances are 1 cm for N, 0.2 cm for K, and 0.02 cm for P. The mean distance between corn roots in the top 15 cm of soil is about 0.7 cm, indicating that some nutrients would need to diffuse half of this distance, or 0.35 cm, before they would be in a position to be absorbed by the plant root.

Roots do not absorb all nutrients at the same rate, causing certain ions to accumulate at the root surface, especially during periods of rapid absorption of water. This situation results in back diffusion, where the concentration gradient is away from the root surface and back toward the "bulk" soil solution. Nutrient diffusion away from the root is much less common than diffusion toward the root; however, higher concentrations of some nutrients in the rhizosphere can affect the uptake of other nutrients.

The importance of diffusion and mass flow in supplying ions to the root surface depends on the ability of the solid phase of the soil to replenish or buffer the soil solution (Fig. 2-2). Ion concentrations are influenced by the types of clay minerals in the soil and the distribution of cation and anions on the CEC or AEC. For example, the ease of replacement of Ca^{+2} from colloids varies in this order: peat > kaolinite > illite > montmorillonite. An 80% Ca-saturated 2:1 clay provides the same percentage of Ca^{+2} release as a 35% Ca-saturated kaolinite or a 25% Ca-saturated peat.

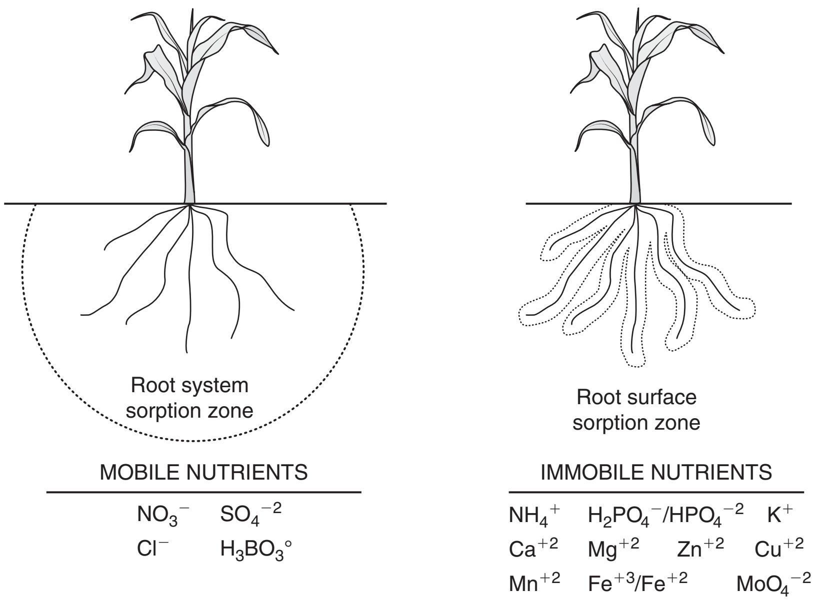


Figure 2-20
Relationship between nutrient mobility and nutrient extraction zones. Plants obtain mobile nutrients from the whole soil volume occupied by plant roots. In contrast, plants obtain immobile nutrients from the small soil volume immediately surrounding the plant root.

(Courtesy B. Raun and G. Johnson, Oklahoma State University.)

Mass flow and diffusion processes are also important in nutrient management. Soils that exhibit low diffusion rates because of high BC, low soil moisture, or high clay content may require application of immobile nutrients near the roots to maximize nutrient availability and plant uptake.

Nutrient Mobility in Soil

Inherent in any discussion of ion transport to plant roots is the principle of nutrient mobility in soil. Nutrient mobility varies between ions, where NO_3^-, SO_4^{-2}, Cl^- and $H_3BO_3^\circ$ are not strongly attracted to exchange sites and are soluble in soils so they can readily move through the root zone with water. As a result, mobile nutrients within the whole soil volume occupied by the plant root system are available for transport to the root in percolating and transpirational water (Fig. 2-20). The relative mobility of each nutrient will depend on soil pH, temperature, moisture, soil texture, type of clay, and OM content.

Immobile nutrients interact with mineral and OM surfaces, are less soluble, and do not readily move throughout the root zone (Fig. 2-20). While classified as immobile nutrients in soil, some are more mobile than others. Generally, NH_4^+, K^+, Ca^{+2}, and Mg^{+2} are more soluble and mobile than the micronutrient cations, and much more mobile than $H_2PO_4^-/HPO_4^{-2}$ and MoO_4^{-2}. Since these nutrients are relatively immobile in soil, plant roots access these nutrients from a small volume of soil surrounding individual roots. Plants create a small zone around the root that has very low concentration of these immobile nutrients due to plant uptake. The concentration gradient allows diffusion to transport nutrients that are further away from the root surface toward the root. If the soil has a high BC for an immobile nutrient, then the solution can be replenished and diffusion continues. With a low BC, solution concentration (and diffusion) ultimately decreases, causing a nutrient deficiency.

Understanding nutrient mobility in soils is essential to managing nutrient applications to maximize plant growth and recovery of applied nutrients by the plant (Chapter 10). For example, N can be broadcast or band applied with fairly similar results because of its mobility in soil. However, P is generally placed in concentrated bands because it is generally immobile in soil.

ION ABSORPTION BY PLANTS

Once nutrients are at the root surface, they enter the outermost root cells where they are transported through the plant. Ion transport out of the root also occurs and can influence rhizoshere pH. Thus, it is important to understand how ions and water move into plant roots. While only a basic description is presented in this text, selected references provide a thorough treatment of ion absorption processes.

Plant uptake of ions from the soil solution can be described by *passive* and *active* processes, where ions passively move to a "boundary" through which ions are actively transported to organs in plant cells that metabolize the nutrient ions. Solution composition or ion concentrations outside and inside of the boundary are controlled by different processes, each essential to plant nutrition and growth.

Water and Ion Uptake by Roots

A considerable fraction of the total volume of the root is accessible for the passive absorption of ions. Water and ion uptake occurs at the root hairs and the rest of the root epidermis (Fig. 2-21). The apparent free space or *apoplast* is the intercellular spaces of the epidermal and cortical cells. The apoplast allows transport of water and ions in root tissue regions that do not require transport across an impermeable membrane. Water uptake from the soil into the apoplast occurs through *capillary action* and *osmosis*. Capillary action results when the intercellular space is smaller than the water-filled space in the soil, thus the matrix potential in the cortex is more negative than in the surrounding soil, and water will move to areas of lower water potential. Osmosis is the transport of water from an area of low to high solute concentration.

The *casparian bands* in the endodermis function as an impermeable barrier, which allows the endodermis to select and regulate ion absorption. Water transport through the apoplastic pathway into the xylem vessels occurs primarily in young tissues where casparian bands are not fully developed (Fig. 2-21). In older tissues, the casparian band prevents water and ion transport directly into the xylem. Thus, water and ions entering the cell or cytoplasm must be transported across the plasma membrane (Fig. 2-22). Once inside the cell, water and ion transport can occur through the symplastic pathway through cellular connections or plasmodesma (Fig. 2-22).

The concentration of ions in the apparent free space is normally less than the bulk solution concentration; therefore, diffusion occurs in response to the resulting high to low concentration gradient. Interior surfaces of cells in the cortex are negatively charged, attracting cations. Cation exchange readily occurs along the extracellular surfaces and

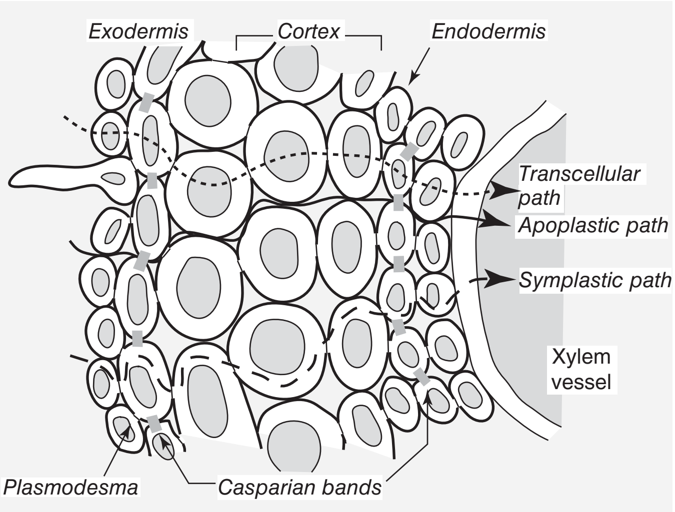
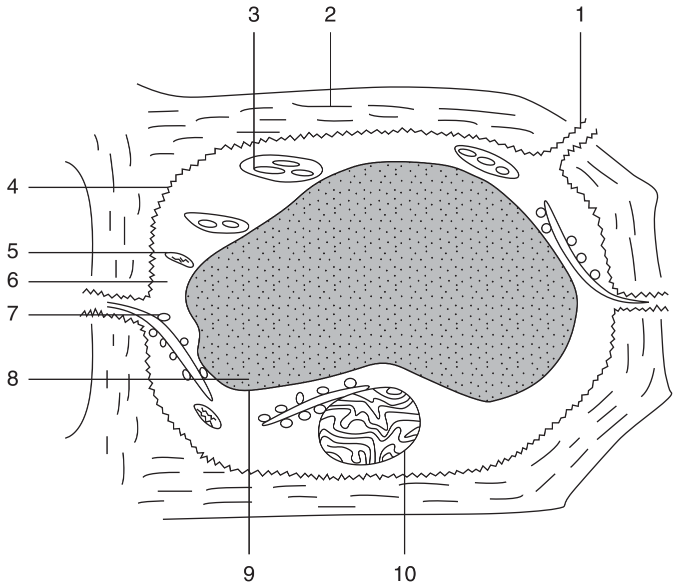


Figure 2-21
Cross-section of a plant root. Site of passive uptake is the apparent free space, which is outside of the casparian strip in the cortex.



1. Plasmodesma
2. Cell wall
3. Chloroplast
4. Plasmalemma
5. Mitochondrion
6. Cytoplasm
7. Endoplasmic reticulum with ribosomes
8. Vacuole
9. Nucleus
10. Tonoplast

Figure 2-22
Diagram of a plant cell. Active ion uptake occurs at the plasmalemma.
(Mengel and Kirkby, 1987, Principles of Plant Nutrition, *IPI.)*

explains why cation uptake usually exceeds anion uptake. To maintain electrical neutrality, the root cells release H^+, decreasing soil solution pH near the root surface. Diffusion and ion exchange are passive processes because uptake into the apoplast is controlled by ion concentration (diffusion) and electrical (ion exchange) gradients.

These processes are nonselective and do not require energy produced from metabolic reactions within the cell.

Passive and Active Ion Uptake by Cells

In a plant cell, the plasma membrane (plasmalemma) and tonoplast are selectively permeable barriers consisting primarily of phospholipids and proteins that regulate transport of water, ions, and metabolites into the cell and vacuole, respectively (Fig. 2-22). Plasma membranes are permeable to O_2, CO_2, and some neutral compounds; are slightly permeable to water; and are nearly impermeable to inorganic ions and small-molecular-weight organic compounds (i.e., sucrose, amino acids). Proteins are required to transport H^+, inorganic ions, and organic solutes across the plasma membrane and the tonoplast at rates sufficient to meet the needs of the cell. To maintain a relatively constant internal environment, membrane permeability properties ensure that ions and molecules such as glucose, amino acids, and lipids readily enter the cell, metabolic intermediates remain in the cell, and unneeded compounds leave the cell.

Whether a molecule or ion is transported actively or passively across a membrane (casparian band, plasma membrane, or tonoplast) depends on the concentration and charge of the ion or molecule, which in combination represent the electrochemical driving force. Ions and molecules diffuse from areas of high to low concentrations. Thus, diffusion does not require the plant to expend energy. In contrast, for ions diffusing against the concentration gradient, energy is required. Thus, passive transport across the plasma membrane occurs with the electrochemical potential and active transport occurs against the electrochemical potential, a process that requires the cell to expend energy.

As a result, ion concentration on either side of the plasma membrane and tonoplast is different. The H^+ concentration can be a 1,000-fold higher (lower pH) in the apoplast and vacuole than in the cytoplasm (~pH 7), but Ca^{+2} concentration gradients can vary over an even wider range (Ca^{+2} concentration is ~100 nM in the cytoplasm). At ~pH 7 proteins in the cytoplasm are negatively charged. These and other charge imbalances result in the establishment of an electrical potential gradient at the plasma membrane. This potential creates a strong electric field that provides the energy for ion transport against concentration gradients, and the opening and closing of channels through the selectively permeable membranes (voltage-gated channels).

Passive transport *Simple diffusion* through membranes occurs with small, nonpolar molecules (i.e., O_2, CO_2). For small, polar species (i.e., H_2O, ions, amino acids), specific proteins in the membrane facilitate the diffusion down the electrochemical gradient. This mechanism is referred to as *facilitated diffusion*. These proteins form channels, which can open and close, and through which ions or H_2O molecules pass in single file at very rapid rates (Fig. 2-23). For example, water movement across the tonoplast and plasma membrane is determined by osmotic pressure gradients and by passive transport through channel proteins called *aquaporins* that act as "water channels" to facilitate water transport across membranes. Aquaporins account for 5–10% of the total protein in a membrane. A K^+ and NH_4^+ transport channel has been suggested that is lined with (−) charges, where K^+ moves across the membrane because of the net negative charge inside the cell. In addition, Na^+ can also enter the cell by facilitated diffusion since the concentration inside is less than that outside the cell; however, Na^+ transport outside the cell requires an active transport mechanism, since it is against the electrochemical gradient.

Another mechanism involves *transporters* or *cotransporters* responsible for the transport of ions and molecules across membranes (Fig. 2-23). Transporter proteins, in contrast to channel proteins, bind only one or a few substrate molecules at a time. After binding a molecule or ion, the transporter undergoes a structural change specific to a specific ion or molecule. As a result, the transport rate across a membrane is slower than that associated with channel proteins. Three types of transporters have been identified. *Uniporters* transport one molecule (i.e., glucose, amino acids) at a time down a concentration gradient. In contrast, *antiporters* and *symporters* catalyze movement of one type of ion or molecule against its concentration gradient coupled to movement of a different ion or molecule down its concentration gradient (Fig. 2-23). Therefore, the energy for *antiporter* and *symporter* transport originates from the electric potential and/or chemical gradient of a secondary ion or molecule, which is often H^+. The high H^+ concentration in the apoplast provides the energy for symporter

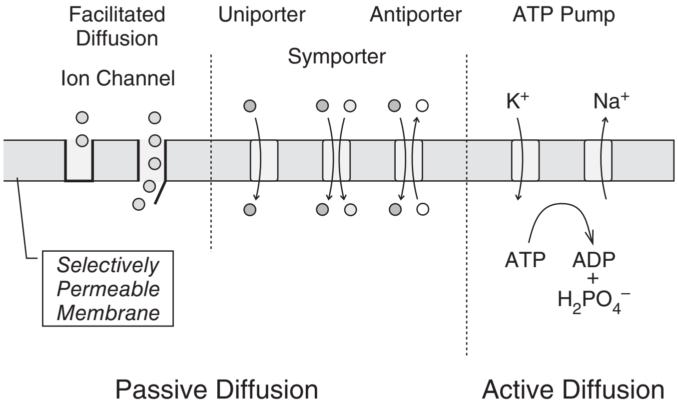


Figure 2-23
Generalized diagram of passive and active transport processes that include protein channels and other facilitated diffusion transport mechanisms, as well as ATP pump mechanism to transport ions and molecules against a concentration gradient.

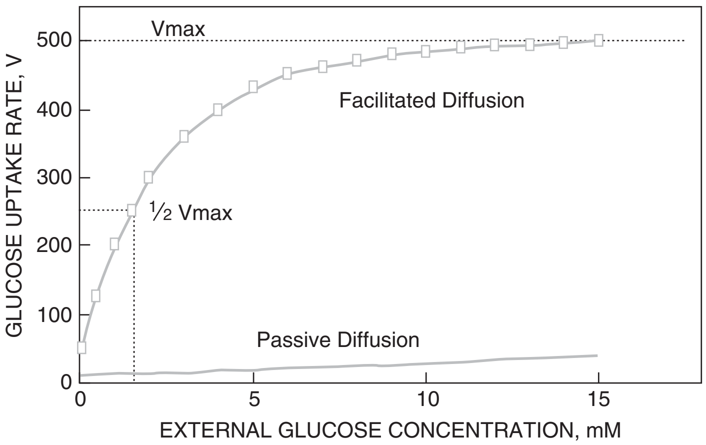


Figure 2-24
Comparison between simple diffusion and facilitated transport on the rate of glucose transport across a membrane.

transport of NO_3^- and other anions. Examples of antiporter transport are H^+-Na^+ and H^+-Ca^{+2} transport into the vacuole. Evidence of facilitated transport is shown in Fig. 2-24, where the rate of glucose uptake is substantially greater than that observed with simple diffusion along a concentration gradient.

Active transport Larger, more-charged molecules have greater difficulty in moving across a membrane, requiring active transport mechanisms (i.e., sugars, amino acids, DNA, ATP, ions, phosphate, proteins). Active transport across a selectively permeable membrane occurs through ATP-powered pumps that transport ions against their concentration gradients (Fig. 2-23). This mechanism utilizes energy released by hydrolysis of ATP. In plant cells, H^+-ATP pumps transfer H^+ across the plasma membrane or tonoplast to acidify the cytoplasm or vacuole, respectively. The Na^+-K^+ ATP pump transports K^+ into the cell and Na^+ out of the cell, which maintains a high cytoplasm K^+ concentration essential for maintaining the electrical potential gradient across the plasma membrane. The Ca^{+2} ATP pump transports Ca^{+2} out of the cytoplasm, which maintains Ca^{+2} concentration lower than in extracellular areas, which is essential for establishing a high concentration gradient that provides the energy for facilitated Ca^{+2} diffusion into the cell.

STUDY QUESTIONS

1. Define *cation exchange capacity* (CEC). What units are commonly used to express CEC?
2. A soil test shows CEC = 14.3 meq/100 g soil. Calculate the CEC in cmol/kg soil.
3. Identify the origin of CEC in mineral soil colloids and factors that influence CEC.
4. Explain the influence of the following on CEC in soils:
   a. increasing pH from 6.0 to 7.5
   b. increasing weathering intensity (over the long term)
   c. adding bases such as Ca^{+2} or Mg^{+2}
5. Which clay minerals would likely be present in a weathered acid soil?
6. Why are 2:1 clay minerals more common in soils of the Midwest or Great Plains regions of North America?
7. As soils age from thousands of years of weathering, some soil properties change. List two of these properties and how these changes might affect soil productivity.
8. What are the two sources of negative charge in clay minerals?
9. Explain how isomorphic substitution in the tetrahedral or the octahedral layer influences shrink-swell potential in soils.
10. What is meant by *buffer capacity* (BC)? What soil properties influence the soil BC?

11. Thirty pounds of P/a is added to two soils. The resulting solution P concentration in soil A is four times lower than that in soil B, although plant uptake in soil A is greater than that in soil B. What is causing the differences in these soil and plant P observations?

12. What is the basis for the lyotropic series for cations?

13. In addition to clay minerals, what other soil constituents contribute to total CEC?

14. Why are AECs of ultisols usually greater than those of mollisols?

15. What are active and passive absorption of elements by root cells? How are the inner and outer space of cells involved? What is the proposed mechanism that describes active absorption?

16. You are addressing a group of farmers and business managers who understand crop production but are not familiar with the technical aspects of plant nutrition and soil fertility. You have to explain the nature of cation exchange and why it is important to crop production. How would you proceed? Someone asks why Cl^- and NO_3^- will leach from soils but $H_2PO_4^-$, which also has a negative charge, will not. What is your answer?

17. Mass flow can potentially move enough Ca and Mg to the plant root to meet the nutritional needs. Which anions would most likely move with them and why?

18. Describe the relative importance of root interception, diffusion, and mass flow in nutrient transport to plant roots. What is the effect of soil texture on these mechanisms?

19. Briefly describe the influence of the following on ion diffusion in soils:

a. temperature
b. soil moisture
c. soil texture
d. buffer capacity
e. specific ion (i.e., one ion vs. another)

20. What soil factors influence diffusion of nutrient ions to roots? Describe and explain why diffusion rate is greater in a clay soil than in a sand.

21. A *solution* contains 20 ppm Ca^{+2}. Express the Ca^{+2} concentration in the following terms:

a. g Ca^{+2} in 1,000,000 mL water ($mL = 0.001$ L)
b. g Ca^{+2} in 100 mL water
c. % Ca^{+2} in the 100 mL water
d. mg Ca^{+2}/kg water ($mg = 0.001\ g = 0.000001$ kg)
e. molarity (M or moles Ca^{+2}/L)

22. Express the Ca^{+2} concentration of 1500 ppm in

a. % Ca^{+2}
b. mg Ca^{+2}/kg soil
c. mg Ca^{+2}/100 g soil
d. lbs Ca^{+2}/afs

23. A soil sample was analyzed and found to contain the following cations: $Ca^{+2} = 450$ ppm, $Mg^{+2} = 90$ ppm, $K^+ = 230$ ppm and $Na^+ = 40$ ppm. Calculate the

a. mg/kg of each nutrient
b. % content of each nutrient

24. A *solution* contains the following:
$Ca^{+2} = 1000$ ppm; $Mg^{+2} = 480$ ppm;
$K^+ = 400$ ppm; $Na^+ = 460$ ppm.

a. Calculate the M (mole/L) for each nutrient.
b. Calculate the % concentration for each nutrient.
c. Calculate the mg/kg for each nutrient.

25. A soil contains 800 ppm Ca^{+2}. Calculate lbs Ca^{+2}/afs, lbs Ca^{+2}/1,000 ft^2, and meq Ca^{+2}/100 g soil.

26. A soil sample contains 1% Ca^{+2}. Calculate

a. lbs Ca^{+2}/afs
b. lbs Ca^{+2}/1000 ft^2
c. meq Ca^{+2}/g soil

27. A soil is 40% acid saturated. Ten grams of soil are titrated with 25 mL 0.05 N base. Calculate the CEC.

28. Twenty grams of soil was extracted with NH_4OAc and the extract diluted to 1 L. The solution was analyzed for cation content and contained: 38 ppm Ca^{+2}; 9 ppm Mg^{+2}; 7 ppm K^+; 4 ppm Na^+. Estimate the CEC. If the measured CEC were 20 meq/100 g, calculate the BS.

29. A soil contains 30% clay (1/3 each of montmorillonite, kaolinite, vermiculite) and 5% OM. Calculate the CEC in meq/g of soil.

30. The NH_4^+ concentration in 1000 ml solution of 5 g of soil was 50 ppm. Calculate the CEC in meq/100g soil.

31. Diagrammatically explain the influence of the soil components on the soil's nutrient concentration.

32. Name the process that is important for the availability of the following elements in the soil.

a. Ca
b. N
c. Mg
d. K
e. S

33. Explain the importance of ion exchange processes in soil.

34. Represent the structures of
  a. Kaolinite
  b. Chlorite
  c. Pyrophyllite
  d. Vermiculite

35. What factors strongly affect the CEC of a soil.

36. A soil has 10% kaolinite, 10% illite, 10% chlorite along with 5% OM. Determine the CEC in meq/100g of the soil.

37. What is lyotropic series? What is it's use?

38. Mathematically express the Fick's law of diffusion.

39. Distinguish between active and passive transports.

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3

Soil Acidity and Alkalinity

Throughout the world, soil acidity and alkalinity problems increasingly influence plant health and yield. Therefore, it is essential to understand the chemistry of these processes to effect proper management for optimum plant productivity. Acid topsoils occur on approximately 30% of the ice-free land area in the world, whereas 75% of these acid soils also overlay acid subsoils (Table 3-1). The majority of the world's acid soils occur in Asia, Africa, and the Americas (Fig. 3-1). As we discuss the primary sources of soil acidity in the next sections, you will recognize that as soil nutrient removal increases by higher crop yields and increased use of fertilizers, soil acidity–related production problems will also increase.

ACIDITY IN WATER

Pure water undergoes slight dissociation:

$$H_2O \rightleftarrows H^+ + OH^-$$

The H^+ actually attaches to another H_2O molecule to give:

$$H_2O + H^+ \rightleftarrows H_3O^+$$

Since both H^+ and OH^- are produced, H_2O is a weak acid and weak base. The H^+ (or H_3O^+) and OH^- concentrations in pure H_2O, not in equilibrium with atmospheric CO_2, are 10^{-7} M (M = molarity, moles/liter or m/L). The product of H^+ and OH^- concentration, shown in the following equation, is the dissociation constant for water, or K_w.

$$\begin{aligned}[H^+] \times [OH^-] &= [10^{-7}\,M] \times [10^{-7}\,M] \\ &= 10^{-14} = K_w\end{aligned}$$

In equilibrium with atmospheric CO_2, the pH of H_2O is 5.5–5.7 because of the following reaction:

$$H_2O + CO_2 \rightleftarrows H^+ + HCO_3^-$$

Therefore, rainfall is a natural source of soil acidity and important in chemical weathering of parent materials. Adding an acid to H_2O will increase $[H^+]$, but $[OH^-]$ would decrease because K_w is a constant 10^{-14}. For example, in a 0.1 M HCl solution, the $[H^+]$ is 10^{-1} M; thus, the $[OH^-] = 10^{-13}$ M by:

$$\begin{aligned}K_w = [H^+] \times [OH^-] &= 10^{-14} \\ [10^{-1}\,M] \times [OH^-] &= 10^{-14} \\ [OH^-] &= 10^{-13}\end{aligned}$$

TABLE 3-1
GLOBAL DISTRIBUTION OF ACID SOILS

	Land Area			
Region	*Total*[1]	*Cultivated*	*Acidic*[2]	
	million ha			%
World	13,100	1,500	3,950	30
America				
North	1,867	216	662	35
Central	245	31	36	15
South	1,760	113	916	52
Asia	3,094	505	1,038	34
Europe	2,207	277	391	18
Africa	2,964	219	659	22
Oceania	849	46	245	29

[1] Ice-free land area.
[2] Percentage of acid topsoils of the total land area.
Source: Adapted from Sumner and Noble. 2003. Soil Acidification: The World Story. In Rengel (ed.), *Handbook of Soil Acidity*. New York: Marcel Dekker.

The H^+ concentration in solution can be conveniently expressed using pH and is defined as follows:

$$\mathrm{pH} = \log\frac{1}{(\mathrm{H}^+)} = -\log(\mathrm{H}^+)$$

Thus, a solution with $H^+ = 10^{-5}$ M has a pH of 5.0.

$$10^{-5}\ \mathrm{M} \rightarrow -\log[10^{-5}] = -[-5] = 5$$

Each unit increase in pH represents a 10-fold decrease in H^+ or increase in OH^- (Table 3-2). Solutions with $\mathrm{pH} < 7$ are acidic, those with $\mathrm{pH} > 7$ are basic, and those with $\mathrm{pH} = 7$ are neutral. The pH represents the H^+ concentration in solution and does not measure the undissociated or *potential* acidity. Soil solution pH is classified according to:

<4.5	extremely acidic	6.6–7.3	neutral
4.5–5.0	very strongly acidic	7.4–7.8	mildly alkaline
5.1–5.5	strongly acidic	7.9–8.4	moderately alkaline
5.6–6.0	medium acidic	8.5–9.0	strongly alkaline
6.1–6.5	slightly acidic		

SOURCES OF SOIL ACIDITY

Precipitation

As discussed earlier, H_2O in equilibrium with atmospheric CO_2 has a pH of about 5.6, resulting from:

$$\mathrm{H_2O} + \mathrm{CO_2} \rightleftarrows \mathrm{H_2CO_3} \rightleftarrows \mathrm{H^+} + \mathrm{HCO_3^-}$$

Rainfall containing no acid-forming contaminants will continually add acid to soil, contributing to weathering of soil minerals and soil acidity. The quantity of acid added is small, and with near neutral or greater soil pH, most of this acid will be

Figure 3-1
Major acid soil regions in the world. (*SAGE, 2002, http://www.sage.wisc.edu/atlas/maps.php.*) (No data for Greenland.)

TABLE 3-2
RELATIONSHIP BETWEEN pH, pOH, AND H^+ AND OH^- CONCENTRATION (M)

pH	H^+	OH^-	pOH
	m/L		
0	10^{0}	10^{-14}	14
1	10^{-1}	10^{-13}	13
2	10^{-2}	10^{-12}	12
3	10^{-3}	10^{-11}	11
4	10^{-4}	10^{-10}	10
5	10^{-5}	10^{-9}	9
6	10^{-6}	10^{-8}	8
7	10^{-7}	10^{-7}	7
8	10^{-8}	10^{-6}	6
9	10^{-9}	10^{-5}	5
10	10^{-10}	10^{-4}	4
11	10^{-11}	10^{-3}	3
12	10^{-12}	10^{-2}	2
13	10^{-13}	10^{-1}	1
14	10^{-14}	10^{0}	0

Note: The shaded area represents the commonly observed range in soil pH.

neutralized. However, as the quantity of precipitation increases, more acid is added. Acid soils in the United States (Fig. 3-2) generally occur in regions where annual precipitation exceeds 25–30 in. (Fig. 3-3).

Precipitation pH varies with region, with lower pH in eastern U.S. regions as a result of greater pollutant loading into the atmosphere (Fig. 3-4). Primary pollutants are SO_2, NH_3, and various NO_x gases that include *nitric oxide* (NO), *nitrogen dioxide* (NO_2), and *nitrous oxide* (N_2O). The global sources of NO_x gases include fossil fuel combustion (40%), biomass combustion (22%), lightning (15%), soil microbial activity (15%), and chemical oxidation of NH_3 (8%). About 50% of the global SO_2 emission is anthropogenic, primarily related to burning coal to produce electricity and other industrial emissions (steel manufacturing, etc.). The remaining 50% of SO_2 emission is due to natural processes including ocean biogenic production (20%), volcanoes (10%), soil, plant, animal emissions (10%), wind-raised dust (6%), coastal zone and wetland biogenic sources (2%), and biomass burning (2%). The emission of NH_3 varies depending on region. In North America and Europe, 65–75% is due to livestock production systems (including manure application to soils), 10–15% from fertilizer application, and the remainder from industrial sources.

Ultimately, the oxidation and hydrolysis reactions of these gases in the atmosphere (reactions with O_2 and H_2O) produce NH_4^+ and H^+. The emission of NH_3 is not acid forming since it combines with H_2O by:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

The base (OH^-) produced neutralizes some of the acids produced from NO_x and SO_2 emission. However, once in the soil, microorganisms convert NH_4^+ to NO_3^- producing H^+ by:

$$NH_4^+ + 2O_2 \rightleftarrows NO_3^- + H_2O + 2H^+$$

When SO_2 enters the atmosphere, the acid producing reaction is:

$$SO_2 + {}^1/_2O_2 + H_2O \rightleftarrows SO_4^{-2} + 2H^+$$

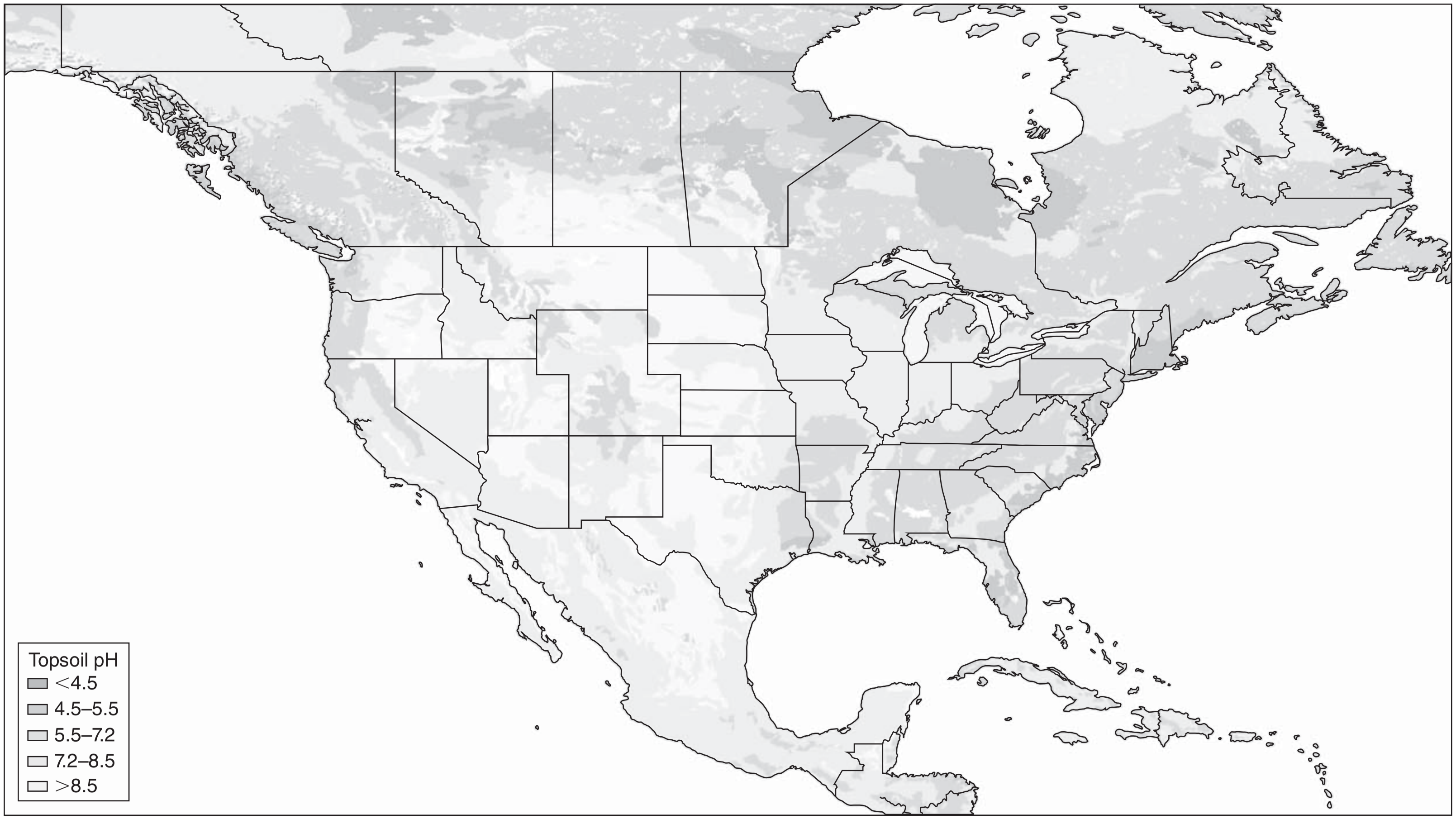


Figure 3-2
Predominate acid soil regions in the United States. *(SAGE, 2002, http://www.sage.wisc.edu/atlas/maps.php.)*

Figure 3-3
Average annual precipitation in the United States.

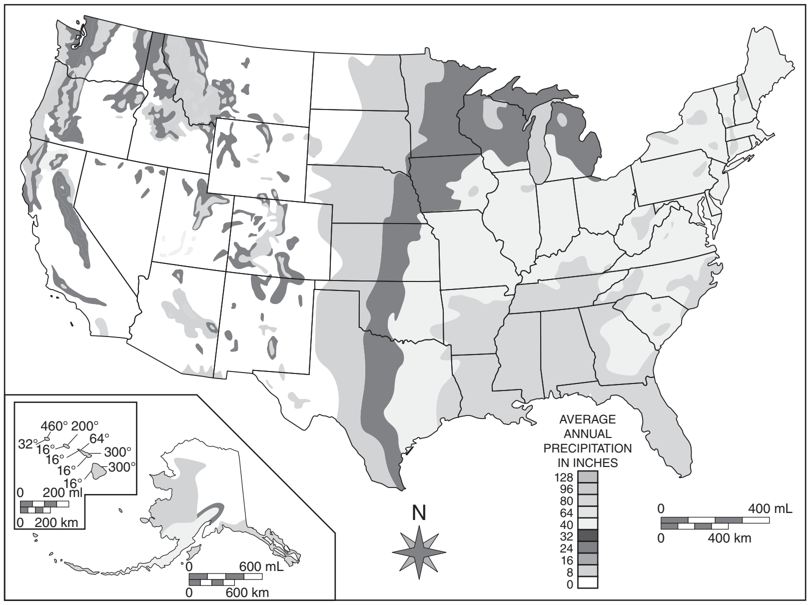
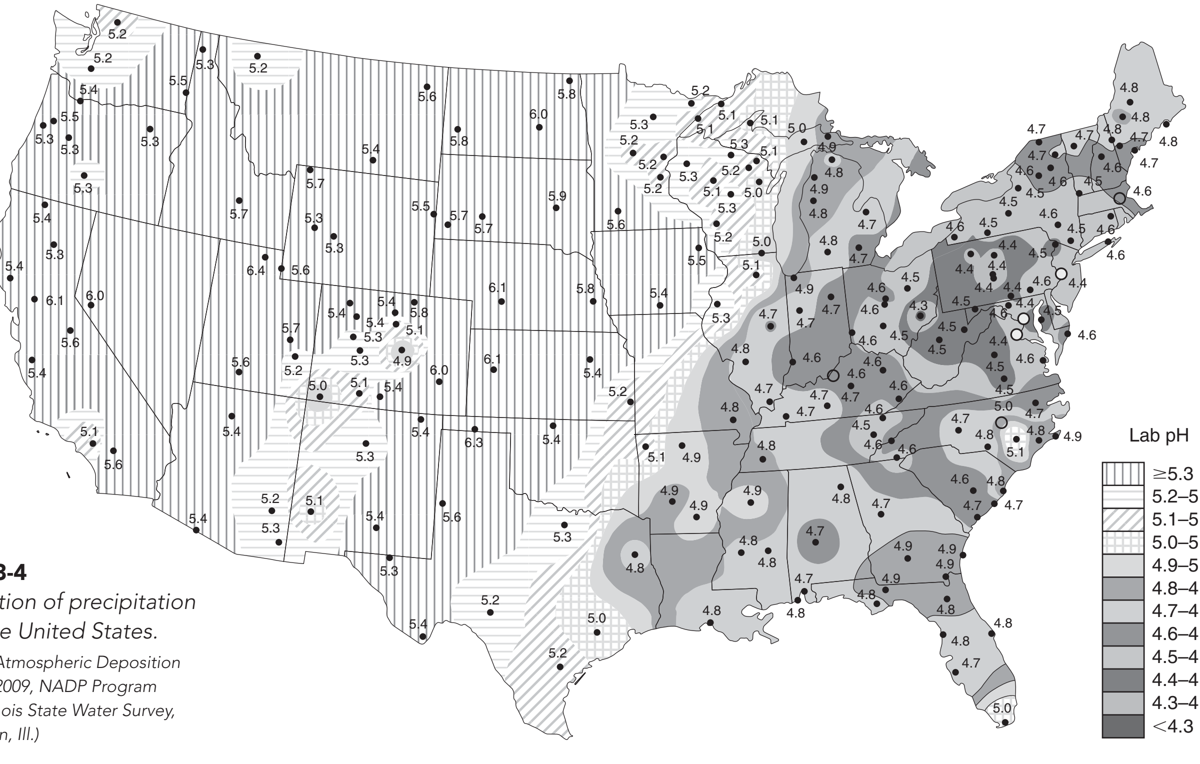


Figure 3-4
Distribution of precipitation pH in the United States.
(National Atmospheric Deposition Program, 2009, NADP Program Office, Illinois State Water Survey, Champaign, Ill.)



Leaching

One of the largest effects on acid formation in soils is the transport of water below the root zone, carrying dissolved or soluble ions. The most soluble anions are NO_3^-, Cl^-, and HCO_3^-, while the most soluble cations are Na^+, Ca^{+2}, Mg^{+2}, and K^+. Electrical neutrality of the soil solution must be maintained; thus, as anions leach, basic cations also leach reducing base saturation (BS) and pH. The environment exhibiting greater leaching potential will be more acidifying (Fig. 3-5). Leaching potential increases with increasing rainfall (Fig. 3-6). As NO_3^- is produced from nitrification of NH_4^+ from plant residues, manures, soil OM, or N fertilizers, no net H^+ would be produced if all the NO_3^- were absorbed by plants (Table 3-3). Unfortunately, crop

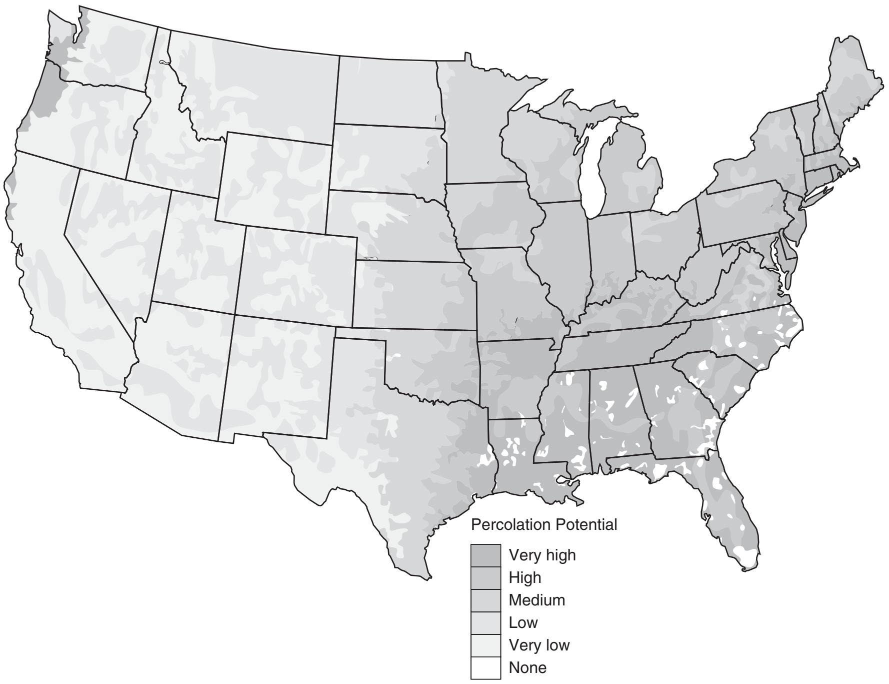


Figure 3-5
Potential water percolation below the root zone in the United States. Potential established from USDA-NRCS percolation factor that includes precipitation adjusted for crop water use and hydrologic soil group, which vary with surface and subsurface water transport properties.
(Adapted from Kellogg, 2000; USDA-NRCS.)

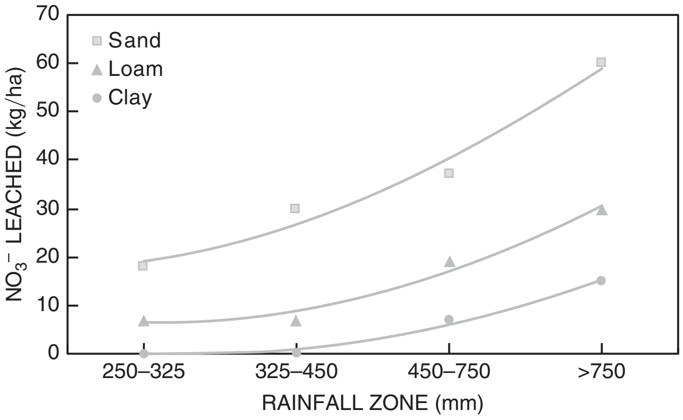


Figure 3-6
Influence of rainfall and soil texture on NO_3^- leaching in wheat.
(*Adapted from Anderson et al., 1998,* Aust. J. Agric. Res., 49:345–361.)

recovery of NO_3^- is not complete and some NO_3^- leaching occurs in nearly every cropping situation, if sufficient water is present for transport below the root zone. Net soil profile acidification occurs only when leaching water containing NO_3^- (and an *equivalent* quantity of bases) is transported below the root zone. Movement of NO_3^- within the root zone results in no net acidification as roots exude organic anions when NO_3^- uptake occurs lower in the root zone. Although wide variations exist between cropping systems, non-legume systems where fertilizer or waste N is used exhibit greater NO_3^- leaching than legume-based rotations. Also, NO_3^- leaching and soil acidity can be greater in unfertilized legume pastures compared to unfertilized grass pastures. Similar differences in soil acidity have been observed between deciduous and leguminous forest systems.

Crop Nutrient Uptake and Other Transformations

Nutrient requirements of crops vary greatly (Chapter 9). Crop removal of basic cations will reduce base saturation and increase soil acidity. Plants alter the soil pH through imbalances in cation/anion uptake. As cations are absorbed by plant roots, electrical neutrality is maintained through uptake of an anion or extrusion of H^+ and/or organic acids. When anions are absorbed, uptake of cations or extrusion of

TABLE 3-3
NUTRIENT UPTAKE AND SELECTED NUTRIENT TRANSFORMATIONS IN SOILS THAT INFLUENCE SOIL pH

Process	Reaction	pH Effect[1]
		mole H^+/mole N or S
	Nitrogen	
NO_3^- uptake	$NO_3^- + 8H^+ + 8e^- \rightleftarrows NH_2 + 2H_2O + OH^-$	−1
Mineralization	$R\text{-}NH_2 + H^+ + H_2O \rightleftarrows R\text{-}OH + NH_4^+$	−1
Denitrification	$2NO_3^- + 2H^+ \rightleftarrows N_2 + 2\frac{1}{2}O_2 + H_2O$	−1
Urea hydrolysis	$(NH_2)_2CO + 3H_2O \rightleftarrows 2NH_4^+ + 2OH^- + CO_2$	−1
NH_4^+ uptake	$NH_4^+ + R\text{-}OH \rightleftarrows R\text{-}NH_2 + H^+ + H_2O$	+1
Immobilization	$NH_4^+ + R\text{-}OH \rightleftarrows R\text{-}NH_2 + H^+ + H_2O$	+1
Volatilization	$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$	+1
Nitrification	$NH_4^+ + 2O_2 \rightleftarrows NO_3^- + H_2O + 2H^+$	+2
	Sulfur	
SO_4^{-2} uptake	$SO_4^{-2} + 8H^+ + 8e^- \rightleftarrows SH_2 + 2H_2O + 2OH^-$	−2
Mineralization	$R\text{-}S + 1\frac{1}{2}O_2 + H_2O \rightleftarrows SO_4^{-2} + 2H^+$	+2

[1] Negative number represents increase in pH; positive number represents decrease in pH.

OH^- or HCO_3^- occurs to maintain electrical neutrality. When cation exceeds anion uptake, excess H^+ is released into the rhizosphere, while OH^-/HCO_3^- is released when anion exceeds cation uptake. Generally, most plants take up more cations than anions, resulting in soil acidification (Table 3-4). For example in legumes, cation uptake is greater than anion uptake because legumes provide a majority of N through N_2 fixation. Alternatively, rhizosphere pH will increase slightly with plants relying entirely on NO_3^-, which does not commonly occur (Fig. 3-7). The net effect of crop growth on soil acidity depends on plant species, the proportion of NH_4^+ and NO_3^- uptake, total biomass production (or yield), quantity of plant material harvested, and quantity of NO_3^- leached. Higher legume or non-legume (fertilized with NH_4^+) biomass production results in greater soil acidity. Soil acidity would be lower with grain harvest compared to grain plus residues. Increasing the quantity of biomass left in the field increases acidity produced through microbial degradation.

Transformations of nutrients in soil can be both acid-producing and acid-consuming (Table 3-3). Inspection of N and S transformations shows little net effect on soil pH, except as NO_3^- and SO_4^{-2} leach, along with an equivalent quantity of cations, decreasing soil pH.

Soil OM

As microorganisms decompose soil OM, they release CO_2 that quickly reacts with H_2O to produce H^+ and HCO_3^-. Decomposition of organic residues and root respiration increases CO_2 in soil air to about ten times the atmospheric CO_2; thus, acidity produced from CO_2 in soil air is greater than that produced in the atmosphere. In addition, microorganisms produce organic acids by:

$$\text{Organic C} \rightarrow R\text{-}COOH \rightarrow R\text{-}COO^- + H^+$$

The type of residue added influences the quantity of acid produced. For example, residue in a coniferous forest produces more acid than in soils under deciduous forest or grasslands. Also, soil OM contains reactive carboxylic and phenolic groups that behave as weak acids releasing H^+ (Fig. 2-10). Soil OM content varies with the environment, vegetation, and soil; thus, its contribution to soil acidity varies accordingly.

TABLE 3-4
VARIATION IN EXCESS CATION UPTAKE IN LEGUME AND NON-LEGUME CROPS

Species	H^+ Production	Excess Cations
	cmol/kg shoot[1]	*cmol/kg plant*
	Grain Legumes	
Chickpea	58–220	108–177
Soybean	72–117	85–142
Narrow-leafed lupin	55–178	93–142
Grasspea	144	122
Yellow lupin	31–145	82–119
Field pea	78–132	110–116
Faba bean	32–68	60–122
Common vetch	149	126
	Forage Legumes	
Sweet clover	96–184	118–173
Lucerne	120–187	101–173
Red clover	128–180	129–180
White clover	120–190	165–185
Subterranean clover	28–100	88–175
	Cereal Grains	
Oats	—	48–76
Barley	—	26–49
Sorghum	—	29–44
Wheat	—	25–73
Corn	—	38–75

[1] cmol/kg shoot = meq/100g shoot

Source: Tang and Rengel. 2003. In Rengel (ed.), *Handbook of Soil Acidity* (pp. 57–81). New York: Marcel Decker.

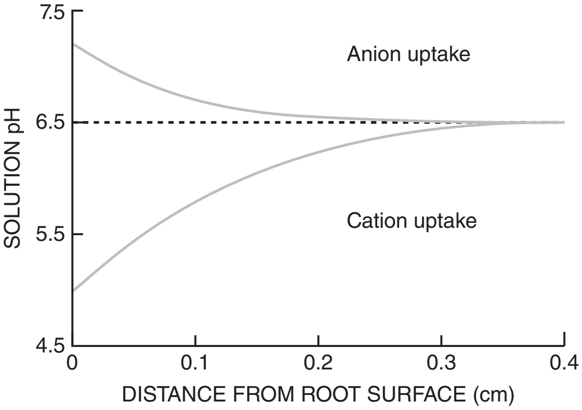


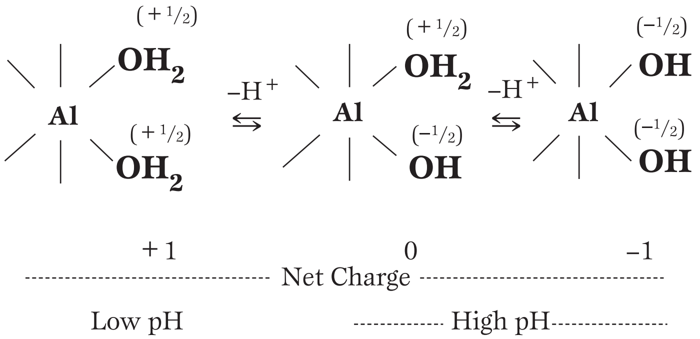
Figure 3-7
Relative influence of anion and cation uptake on rhizosphere pH.

In peat and muck soils and in mineral soils containing large amounts of OM, organic acids contribute significantly to soil acidity.

Soil Mineral Exchange and Hydrolysis Reactions

The dissociation of H^+ from edges of clay minerals, Al and Fe oxides, and soil OM surfaces contributes to soil acidity and pH buffering. The edges of clay minerals such as kaolinite (1:1) and montmorillonite (2:1) can buffer soil pH (Fig. 2-9).

The pH buffering capacity associated with Al and Fe oxides behaves similarly, as follows:



As pH decreases, adsorbed H^+ increases, which increases the surface (+) charge or AEC. Soils with high clay, Al/Fe oxide, and/or soil OM contents exhibit greater pH buffer capacity than sandy and/or low OM soils.

In acid soils containing $Al(OH)_3$, changes in soil pH affect Al^{+3} concentration in soil solution according to:

$$Al(OH)_3 + 3H^+ \rightleftarrows Al^{+3} + 3H_2O$$

The equilibrium reaction shows that as pH decreases (increasing H^+), the equilibrium shifts to the right where $Al(OH)_3$ dissolves to produce Al^{+3}, which can then be adsorbed to the CEC. Depending on pH, Al^{+3} will hydrolyze according to:

$$Al^{+3} + H_2O \rightleftarrows Al(OH)^{+2} + H^+$$
$$Al(OH)^{+2} + H_2O \rightleftarrows Al(OH)_2{}^+ + H^+$$
$$Al(OH)_2{}^+ + H_2O \rightleftarrows Al(OH)_3{}^0 + H^+$$
$$Al(OH)_3{}^0 + H_2O \rightleftarrows Al(OH)_4{}^- + H^+$$

Each successive step occurs at a higher pH (Fig. 3-8). At low pH, more of the Al hydrolysis species are (+) charged (Al^{+3}, $Al(OH)_2{}^+$), which enables greater Al adsorption to CEC. Hydrolysis of Al^{+3} generates H^+ and lowers pH, unless there is a source of OH^- to neutralize H^+.

If a base is added (i.e., $CaCO_3$), H^+ will be neutralized first. With continued addition of base, Al^{+3} hydrolyzes, with the production of H^+. In this way, Al^{+3} hydrolysis buffers the increase in solution pH. Soil pH will not increase until sufficient base is added to decrease soluble Al^{+3}. It should be noted that $Al(OH)_3$ will precipitate at pH 6.5, decreasing Al^{+3} in solution and increasing pH.

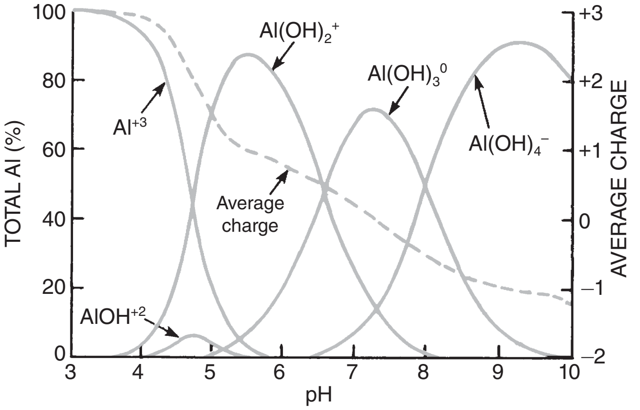


Figure 3-8
Relationship between pH and the distribution and average charge of soluble Al species. As pH decreases below 5, Al^{+3} concentration in solution greatly increases.

Hydrolysis of Fe^{+3} is similar to Al^{+3}. Although Fe is more acidic than Al, the acidity is buffered by Al hydrolysis reactions. Thus, Fe hydrolysis has little effect on soil pH until most of the soil Al has reacted. Al and Fe hydroxides occur as amorphous or crystalline colloids, coating clay and other mineral surfaces. They are also held between the lattices of expanding clay minerals, preventing collapse of these lattices as water is removed during drying.

Soluble Salts

Acidic, neutral, or basic salts in the soil solution originate from mineral weathering, OM decomposition, or addition of fertilizers and manures. The cations of these salts will displace adsorbed Al^{+3} in acidic soils and thus decrease soil solution pH as the Al^{+3} hydrolyzes. Divalent cations have a greater effect on lowering soil pH than monovalent metal cations (see the *lyotropic series* in Chapter 2).

Band-applied fertilizer will result in a high soluble-salt concentration in the affected soil zone, which will decrease pH through Al^{+3} hydrolysis. With high rates of band-applied fertilizer in soils with pH 5.0–5.5, the increased soluble Al^{+3} can be detrimental to plant growth.

Fertilizers

Fertilizer materials vary in their soil reaction pH. Nitrate sources carrying a basic cation are less acid-forming than NH_4^+ sources. Compared with P fertilizers, NH_4^+ containing or forming sources exhibit greater effect on soil pH (Table 3-5). The acidity produced is greater when S and P sources are combined with NH_4^+ than with N-only sources. Phosphoric acid released from dissolving P fertilizers can temporarily acidify small, localized zones at the site of application. With triple superphosphate, reaction zone pH is 1.5, and with monoammonium phosphate reaction zone pH is 3.5; however, the quantity of H^+ produced is very small and has little long-term effect on bulk soil pH. Diammonium phosphate will initially raise soil pH to about 8, unless the initial soil pH is greater than the pH of the fertilizer (see Table 5-10). Acidity produced by the nitrification of the NH_4^+ will offset this initial pH increase.

Table 3-5 shows the theoretical quantity of $CaCO_3$ needed to neutralize the acidity produced per unit of N or S fertilizer applied. For example, with

TABLE 3-5
SOIL ACIDITY PRODUCED BY N AND S FERTILIZERS

Fertilizer Source	*Soil Reaction*	*mole H^+/mole N or S*	*$CaCO_3$ Equiv.*[1]
Anhydrous ammonia	$NH_3 + 2O_2 \rightarrow H^+ + NO_3^- + H_2O$	1	3.6
Urea	$(NH_2)_2CO + 4O_2 \rightarrow 2NO_3^- + 2H^+ + CO_2 + H_2O$	1	3.6
Ammonium nitrate	$NH_4NO_3 + 2O_2 \rightarrow 2NO_3^- + 2H^+ + H_2O$	1	3.6
Ammonium sulfate	$(NH_4)_2SO_4 + 4O_2 \rightarrow 2NO_3^- + 4H^+ + SO_4^{-2} + H_2O$	2	7.2
Monoammonium phosphate	$NH_4H_2PO_4 + O_2 \rightarrow 2NO_3^- + 2H^+ + H_2PO_4^- + H_2O$	2	7.2
Diammonium phosphate	$(NH_4)_2HPO_4 + O_2 \rightarrow 2NO_3^- + 3H^+ + H_2PO_4^- + H_2O$	1.5	5.4
Elemental S	$S + 1\frac{1}{2}O_2 + H_2O \rightarrow SO_4^{-2} + 2H^+$	2	7.2
Ammonium thiosulfate	$(NH_4)_2S_2O_3 + 6O_2 \rightarrow 2SO_4^{-2} + 2NO_3^- + 6H^+ + H_2O$	1.5	5.4

[1] The $CaCO_3$ equivalent represents the lb $CaCO_3$/lb N or S applied to neutralize acidity in the fertilizer.
Source: Adams, 1984, *Soil Acidity and Liming, No. 12*, p. 234, ASA.

$(NH_4)_2SO_4$, 7.2 lb $CaCO_3$ are needed to neutralize the H^+ produced per lb of N applied. The method used to determine $CaCO_3$ equivalent for $(NH_4)_2SO_4$ is:

$$4 \text{ moles of } H^+ \text{ produced/2 moles N applied}$$

or,

$$4 \text{ equivalent weights of } H^+ \text{ produced/2 equivalent weights of N applied}$$

thus,

$$4 \text{ equivalent weights of } CaCO_3 \rightarrow \text{neutralize 4 equivalent weights of } H^+ \text{ produced/2 equivalent weights of N applied}$$

$$\frac{4 \times 50 \text{ g } CaCO_3/\text{eq}}{2 \times 14 \text{ g N/eq}} = \frac{7.2 \text{ g } CaCO_3}{\text{g N}} = \frac{7.2 \text{ lb } CaCO_3}{\text{lb N}}$$

The theoretical $CaCO_3$ equivalents are usually an overestimate of the $CaCO_3$ required to neutralize the acidity produced from application of fertilizers. As previously discussed, root absorption of fertilizer anions (NO_3^-, SO_4^{-2}, or $H_2PO_4^-$) would neutralize some of the acidity produced from nitrification of NH_4^+ or oxidation of S (Table 3-3). When anion uptake effects are considered, the $CaCO_3$ equivalent is often reduced by ~50%, which may be too extreme considering the acidity produced with NH_4^+ uptake.

The extent and rate of soil pH decline with fertilization varies among soils and management. Plant growth problems due to high soil acidity might develop in 5 years on a sandy soil or 10 years on a silt loam, but might take 15 years or more on a clay loam. For example, after 20 years of 200 lb N/a as NH_4NO_3 applied annually to bromegrass, surface soil pH decreased 1 pH unit (6.5–5.5 pH) (Fig. 3-9). After 40 years, surface soil pH decreased more than 2 pH units (6.5–4.1 pH).

Estimating the effect of N fertilizer use on soil pH Using Table 3-5 and Figure 2-11, we can predict the decrease in soil pH caused by applying N fertilizers. This valuable tool can be used to estimate future lime requirements to maintain optimum soil pH (see Table 3-8, pg. 70).

For example, assume you are managing a field of tall fescue (optimum pH 5.5–6.5). Your soil test report shows:

soil pH	6.5
CEC	10 meq/100g
OM	3%
BS	75%

You make four applications of 40 lb N/a as $(NH_4)_2SO_4$ each year. Estimate the decrease in soil pH after 5 years of N management on this turf (see NOTE, pg. 62).

1. *Determine total N application.*

   $$40 \text{ lb N/a} \times 4 \text{ applications/yr} = 160 \text{ lb N/a/yr} \times 5 \text{ yr} = 800 \text{ lb N/a}$$

2. *Estimate quantity of lime needed to neutralize acidity produced with this N source. In Table 3-5, use 7.2 lb $CaCO_3$/lb N as $(NH_4)_2SO_4$.*

   $$800 \text{ lb N/a} \times 7.2 \text{ lb } CaCO_3/\text{lb N} = 5{,}760 \text{ lb } CaCO_3/\text{a}$$

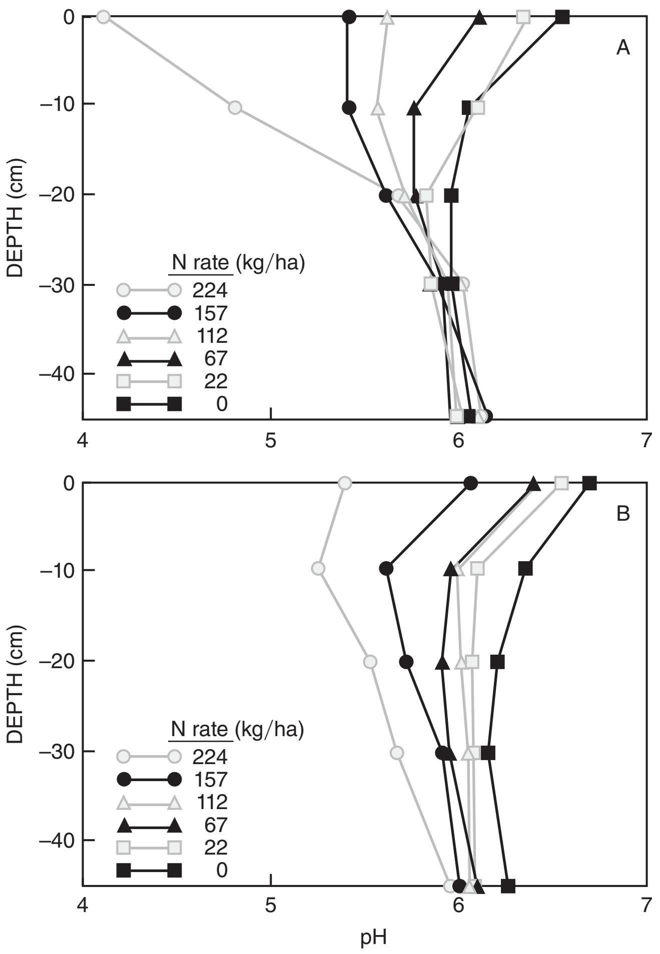


Figure 3-9
Soil pH decreases dramatically with increasing N rate and years of application. Soil fertilized annually since 1946 (A) and fertilized annually from 1946 to 1965 (no N applied since 1965). Soils were sampled in 1985.
(Schwab et al., 1990, SSSAJ, 53:1412–1417.)

3. *Determine quantity of acid (meq/100 g) added* (assume 6″ soil depth or afs; see Chapter 2).

$$\frac{5{,}760\text{ lb CaCO}_3}{\text{afs}} = \frac{5{,}760\text{ lb CaCO}_3}{2 \times 10^6\text{ lb soil}}$$

$$\frac{5{,}760\text{ lb CaCO}_3}{2 \times 10^6\text{ lb soil}} \times \frac{0.5 \times 10^{-4}}{0.5 \times 10^{-4}} = \frac{0.288\text{ lb CaCO}_3}{100\text{ lb soil}}$$

$$= \frac{0.288\text{ g CaCO}_3}{100\text{ g soil}} \times \frac{10^3\text{ mg}}{\text{g}}$$

$$= \frac{288\text{ mg CaCO}_3}{100\text{ g soil}}$$

$$\frac{288\text{ mg CaCO}_3}{100\text{ g soil}} \times \frac{1\text{ meq}}{50\text{ mg CaCO}_3} = \frac{5.76\text{ meq CaCO}_3}{100\text{ g soil}}$$

$$\frac{5.76\text{ meq CaCO}_3}{100\text{ g soil}} = \frac{5.76\text{ meq acid added}}{100\text{ g soil}}$$

$$\frac{5.76\text{ meq acid added}}{100\text{ g soil}} = \frac{5.76\text{ meq bases removed from CEC}}{100\text{ g soil}}$$

4. *Convert meq acid/100 g soil added to decrease in BS (initial BS = 75%).*

$$75\%\ \text{BS} \times \frac{10\ \text{meq CEC}}{100\ \text{g soil}} = \frac{7.5\ \text{meq bases}}{100\ \text{g soil}} \quad [\text{initial bases on CEC}]$$

$$\frac{7.5\ \text{meq base}}{100\ \text{g soil}} - \frac{5.76\ \text{meq bases removed from CEC}}{100\ \text{g soil}} = \frac{1.74\ \text{meq base}}{100\ \text{g soil}} \quad [\text{bases left on CEC}]$$

$$\frac{1.74\ \text{meq base}}{100\ \text{g soil}} \div \frac{10\ \text{meq CEC}}{100\ \text{g soil}} \times 100 = 17.4\%\ \text{BS} \quad [\text{new BS after 5 yr N addition}]$$

5. *Estimate new soil pH (Fig. 2-11).*

$$17.4\ \%\text{BS is} \sim 4.5\ \text{pH} \quad [\text{from Fig. 2-11}]$$

Therefore, applying 800 lb N/a over 5 years would decrease soil pH by 2 units (6.5 → 4.5 pH). The reason soil pH would likely decrease this amount is because the coarse-textured soil (10 meq CEC/100 g soil) has little buffer capacity for the added acid. If this soil had a CEC = 20 meq/100 g soil, the change in %BS would have been (assuming initial 75% BS):

$$15\ \text{meq}/100\ \text{g soil} - 5.76\ \text{meq acid}/100\ \text{g soil} = 9.24\ \text{meq base left}/100\ \text{g soil}$$

$$9.24\ \text{meq}/100\ \text{g soil} \div 20\ \text{meq CEC}/100\ \text{g soil} \times 100 = 46.2\%\ \text{BS}$$

Therefore, with this clay or clay loam soil, BS decreases from 75 to 46.2%. Using Figure 2-11, pH would decrease from 6.5 to 5.3.

SOIL pH BUFFERING

Soil behaves like a weak acid that will buffer pH. In acid soils, adsorbed Al^{+3} will be in equilibrium with Al^{+3} in soil solution, which hydrolyzes to produce H^+, depending on solution pH. If H^+ is neutralized by a base (i.e., $CaCO_3$), solution Al^{+3} precipitates as $Al(OH)_3$, causing exchangeable Al^{+3} to desorb to resupply solution Al^{+3}. Thus, soil pH remains the same or is buffered. As more base is added, the reaction continues, with more adsorbed Al^{+3} neutralized and replaced on the CEC with the cation of the added base. As a result, soil pH gradually increases (Fig. 3-10). Thus, soil is a pH buffer, where the buffer capacity (BC) increases with increasing clay and OM content and decreasing pH or quantity of exchangeable acid. The H-saturated clay (Fig. 3-10) was prepared in a laboratory to demonstrate how increasing the amount and form of the exchangeable acid can increase the pH buffering properties. In this case, significantly more base is needed to change pH in the H-saturated clay than in the Al-saturated clay.

NOTE:

Application of nutrients and other inputs in the turf industry is commonly based on 1,000 ft^2 instead of an acre (43,560 ft^2). The conversion is simple:

$$1{,}000\ ft^2 = 1/43.56\ \text{acre}$$

Using the previous example

$$160\ \text{lb N/a} \div 43.56 = 3.67\ \text{lb N}/1{,}000\ ft^2$$

$$5{,}760\ \text{lb}\ CaCO_3/\text{a} \div 43.56 = 132\ \text{lb}\ CaCO_3/1{,}000\ ft^2$$

While the $CaCO_3$ rate was determined on the afs basis (1 acre and 6″ deep), products are applied on an area basis, allowing lb/afs/43.56 conversion to lb/1,000 ft^2.

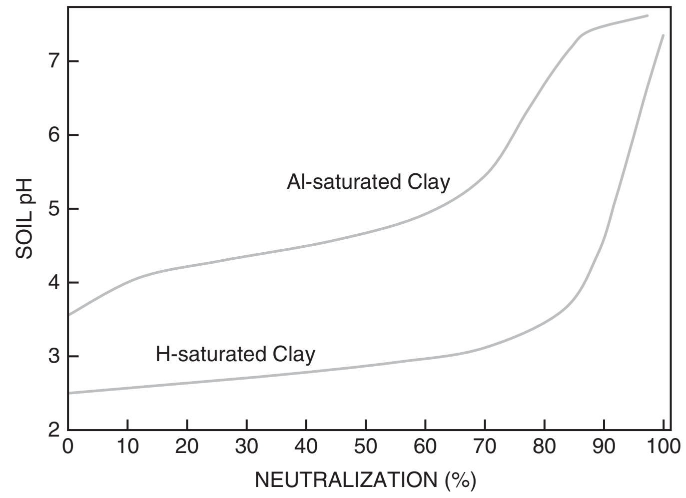


Figure 3-10
Titration of Al-saturated and H-saturated montmorillonite clays. The buffer behavior of the Al-saturated clay is typical of many acid soils. The H-saturated clay was prepared in a laboratory as they rarely occur naturally.
(*Adapted from Chesworth, 2008,* Encyclopedia of Soil Science, Springer, N.Y.)

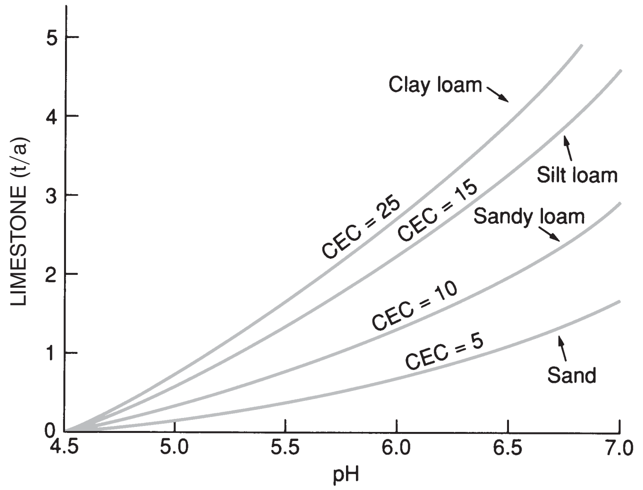


Figure 3-11
Approximate limestone (t/a) required to raise surface soil pH (7-in. depth) of four textural classes with typical CEC (meq/100 g soil).

The reverse reaction also occurs. As acid is continually added, OH^- in the soil solution is neutralized. Gradually, the $Al(OH)_3$ dissolves, to resupply OH^-, which increases Al^{+3} in solution and subsequently on the CEC. As the reaction continues, soil pH continuously but slowly decreases as the Al^{+3} replaces adsorbed basic cations.

The quantity of clay minerals and OM in a soil determines the extent of buffering in soils (see Buffering Capacity, pg. 35). Soils containing large amounts of clay and OM are highly buffered and require larger amounts of lime to increase pH than soils with a lower BC. Sandy soils with small amounts of clay and OM are poorly buffered and require only small amounts of lime to effect a given change in pH. Soils containing mostly 1:1 clay minerals (ultisols and oxisols) are generally less buffered than soils with principally 2:1 clay minerals (alfisols and mollisols). For example, the lime requirement increases with increasing clay content and CEC (Fig. 3-11).

DETERMINATION OF ACTIVE AND POTENTIAL ACIDITY IN SOILS

Active Acidity

Active acidity represents the H^+ and Al^{+3} concentrations in the soil solution. The most accurate and widely used method involves measuring pH in a saturated paste or a more diluted soil-water mixture with a pH meter and a glass electrode. On a soil test report, *soil pH* represents the acidity in a soil solution. However, soil pH is a useful indicator of the presence of exchangeable Al^{+3} and H^+. Exchangeable H^+ is present at $pH < 4$, while exchangeable Al^{+3} occurs predominantly at $pH < 5.5$. Increasing the dilution of the soil from saturation to 1:1 to 1:10 soil : water ratio increases the measured pH compared with the pH of a saturated paste. To minimize differences in solution ion concentration between soils, some laboratories dilute the soil with 0.01 M $CaCl_2$ instead of water. Adding Ca^{+2} decreases the pH compared with soil diluted with water. Changes in measured pH with dilution and added salt are generally small, ranging between 0.1 and 0.5 pH unit.

Potential Acidity

Soil pH measurements are excellent indicators of soil acidity, but do not measure potential acidity. Potential acidity represents the H^+ and Al^{+3} on the CEC (Fig. 3-12). Quantifying potential soil acidity requires titrating the soil with a base, which can be used to determine the lime requirement or quantity of $CaCO_3$ needed to increase pH to a desired level. Thus, the lime requirement of a soil is related not only to soil pH, but also to its BC or CEC (Fig. 3-11). High clay and/or high OM soils have higher BCs and lime requirements, whereas coarse-textured soils low in clay and OM have lower BCs and lime requirements.

To demonstrate how BC influences the quantity of base needed to neutralize potential acidity (exchangeable Al^{+3}), we use two soils with CEC = 20 meq/100 g and 10 meq/100 g. Both have 50% exchangeable Al^{+3}, or 50% acid saturation (AS), or alternatively 50% BS.

$$\text{Soil 1} \rightarrow 50\%\ \text{AS} \times 20\ \text{meq CEC}/100\ \text{g soil} = 10\ \text{meq acids}/100\ \text{g soil}$$

$$\text{Soil 2} \rightarrow 50\%\ \text{AS} \times 10\ \text{meq CEC}/100\ \text{g soil} = 5\ \text{meq acids}/100\ \text{g soil}$$

If we wanted to neutralize all of the exchangeable acid (Al^{+3}), then we would need to add an equivalent quantity of base ($CaCO_3$):

$$\text{Soil 1} \rightarrow 10\ \text{meq acids}/100\ \text{g soil} = 10\ \text{meq CaCO}_3/100\ \text{g soil}$$

$$\text{Soil 2} \rightarrow 5\ \text{meq acids}/100\ \text{g soil} = 5\ \text{meq CaCO}_3/100\ \text{g soil}$$

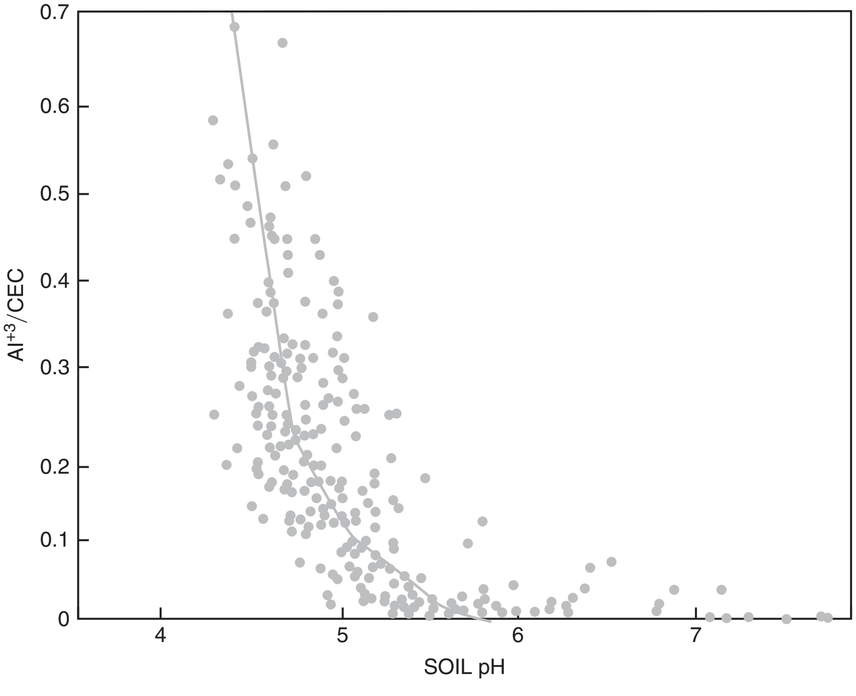


Figure 3-12
As soil pH increases, Al^{+3} saturation decreases. In most soils, little or no effect of Al^{+3} toxicity on plant growth is observed above pH 5.0–5.5.

(*Adapted from Thomas and Hargrove, 1984, in Adams (ed.),* Soil Acidity and Liming, *ASA, CSSA, SSSA, Madison, Wis.*)

Now convert the charge units (meq $CaCO_3$/100 g soil) to mass units (lb $CaCO_3$/afs).

For Soil 1:

$$\frac{10 \text{ meq } CaCO_3}{100 \text{ g soil}} \times \frac{50 \text{ mg } CaCO_3}{\text{meq}} = \frac{500 \text{ mg } CaCO_3}{100 \text{ g soil}}$$
$$= \frac{0.5 \text{ g } CaCO_3}{100 \text{ g soil}}$$
$$= \frac{0.5 \text{ lb } CaCO_3}{100 \text{ lb soil}}$$
$$\frac{0.5 \text{ lb } CaCO_3}{100 \text{ lb soil}} \times \frac{2 \times 10^6 \text{ lb soil}}{\text{afs}} = \frac{10{,}000 \text{ lb } CaCO_3}{\text{afs}}$$

For Soil 2, the quantity of base needed would only be 5,000 lb $CaCO_3$/afs. On a practical basis, both rates are higher than needed because all the exchangeable acids do not need to be neutralized to increase pH. Figure 3-12 shows that decreasing Al^{+3} saturation to 5% would increase pH to about 5.5.

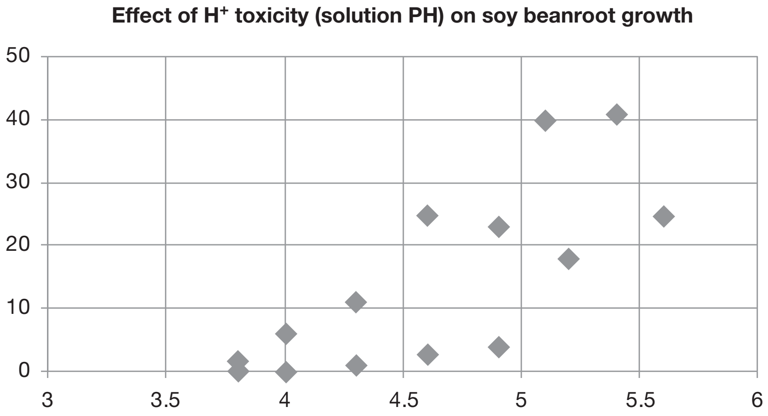
PLANT GROWTH PROBLEMS IN ACID SOILS

High soil acid content can severely restrict plant growth, an increasing problem throughout the world. The primary effects of soil acids on plant health are related to acid toxicity effects on root growth and reduced nutrient availability (Table 3-6). Recognizing acid soil problems is essential to effective management of horticultural and agricultural plants.

TABLE 3-6
POTENTIAL PLANT NUTRIENT PROBLEMS RELATED TO EXCESSIVE SOIL ACIDITY

Nutrient Problem	Soil pH and Other Conditions	Effect of Liming
Al and Mn toxicity	Usually pH $<$ 5.0–5.5, depends on crop and variety	Exchangeable Al, solution Al/Mn decrease with increasing pH
H^+ toxicity	pH $<$ 4.0, Al/Mn toxicity commonly occurs first; observed mostly in solution culture	Decrease solution and adsorbed H^+
Ca deficiency	Low CEC, pH $<$ 4.5–4.8, tropical, highly weathered soils	Increase exchangeable Ca
Mg deficiency	pH $<$ 5.5, low CEC or BS	Increase Mg saturation
Mo deficiency	pH $<$ 5.5	Liming to increase solution Mo
N deficiency	pH $<$ 5.0–5.5, decreased nitrification and mineralization; low OM	Increase microbial activity; add residues as OM decomposition increases pH
P deficiency	pH $<$ 5.0; highly weathered soils dominant in Al/Fe oxides	Decrease exchangeable Al and AEC; increase BS and CEC; increase solubility of Fe/Al-P minerals
K deficiency	pH $<$ 5.0, low CEC, low BS, highly leached soils, high exchangeable Al	Decrease exchangeable Al, increase BS

Figure 3-13
Effect of H^+ *toxicity (solution pH) on soybean root growth.*
(*Adapted from Sanzonowicz et al., 1998.* J. Plant Nutr., *21:387–403.*)



Al^{+3}, Mn^2, and H^+ Toxicity

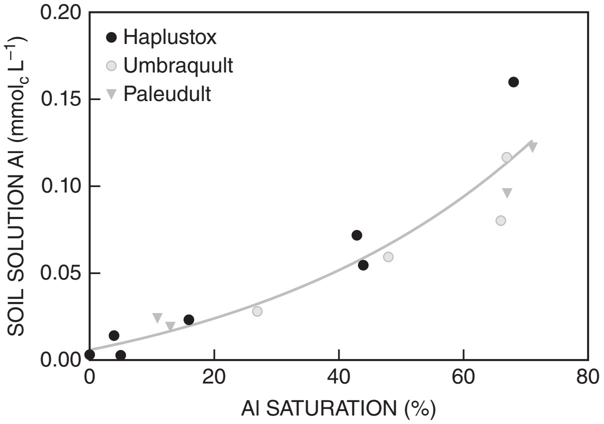
In soil, increased Al^{+3} and Mn^{+2} solubility at low pH confounds the direct assessment of H^+ toxicity in plants. Although exchangeable H^+ increases relative to exchangeable Al^{+3} at soil pH < 4, it is difficult to separate the toxicity effects of these elements. Using hydroponic growth techniques, where Al^{+3} and Mn^{+2} concentrations can be eliminated or controlled, true H^+ toxicity can be observed. With low solution pH, visual H^+ toxicity symptoms include stunted top growth, reduced lateral root growth, and brownish discoloration of roots (very similar to Al^{+3} toxicity). Excess H^+ deteriorates root membrane structure and function, increasing root permeability and loss of organic substrates, and reducing nutrient uptake. Root growth decreases substantially below pH 5 (Fig. 3-13).

Al^{+3} toxicity limits plant growth, depending on solution and exchangeable Al^{+3} concentration, the crop, and in many cases the cultivar or variety. The toxic effects of Al^{+3} in plants are due to increased soluble Al^{+3}, which substantially increases below pH 5 (Fig. 3-8), or exchangeable Al^{3+} increases above about 10–30% of the CEC (Fig. 3-12). Increasing exchangeable Al^{+3} increases Al^{+3} in solution (Fig. 3-14).

The initial symptom of Al^{3+} toxicity is a rapid inhibition of root growth that occurs before any visual effects are observed on the above-ground plant tissues (Fig. 3-15). Despite increasing soil pH, maintaining high solution Al^{+3} concentration severely restricts root growth. These data suggest that normal root growth occurs when solution Al^{+3} is very low, which requires low exchangeable Al^{+3}.

The site of Al toxicity is localized in the root apex. Initially, roots appear discolored, which indicates a deterioration of cells in the root cap, root apex, and vascular

Figure 3-14
Influence of exchangeable Al^{+3} *on* Al^{+3} *concentration in solution in oxisols and ultisols.*
(*Gonzalez et al., 1979,* SSSAJ, *43:1155–1158; Jallah and Smyth, 1998,* Comm. Soil Sci. Plant Anal., *29:37–50.*)



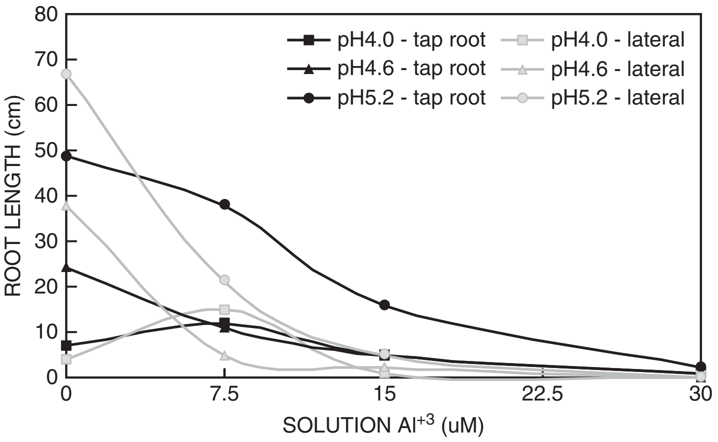


Figure 3-15
Influence of soil solution pH and Al^{+3} on soybean root growth.
(Sanzonowicz et al., 1998, Agron. J., *21:387–403.)*

elements (Fig. 3-16). Root cell division is inhibited or ceases, resulting in a reduction and/or cessation in tap and lateral root growth, with subsequent failure of the whole root system to elongate. Ultimately, the deterioration of root cells decreases the root membrane permeability to water and nutrients, which reduces both root and top growth.

Crops differ widely in their susceptibility to Al^{+3} toxicity; thus, Al^{+3} tolerance is genetically controlled (Table 3-7). Different crop varieties also vary widely in their tolerance to Al^{+3}, where some grasses are quite Al^{+3} tolerant.

Manganese is an essential plant nutrient, but at high concentrations can be toxic to plants. The dominant Mn specie in solution is Mn^{+2} in equilibrium with MnO$_2$:

$$\mathrm{MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{+2} + 2H_2O}$$

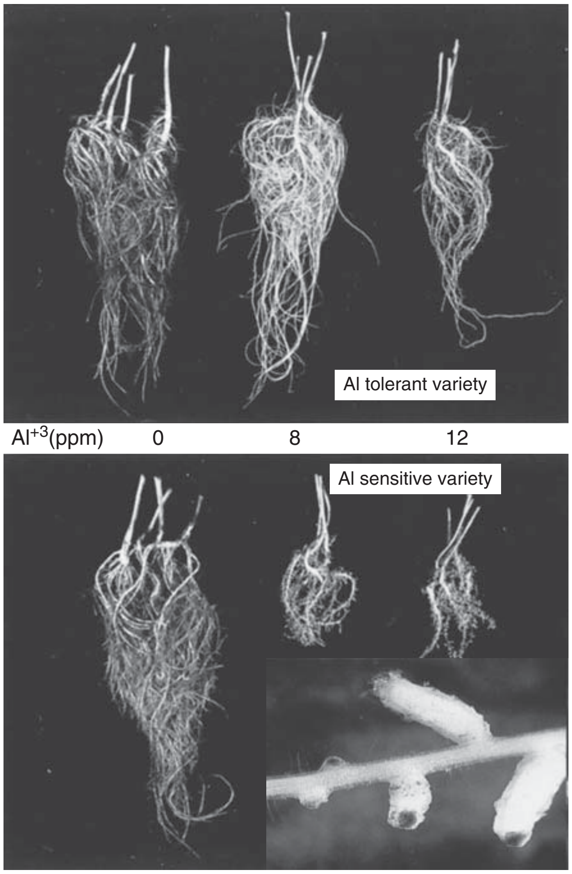


Figure 3-16
Differential effects of Al^{+3} on root growth of Perry (top) and Chief (bottom) soybean varieties grown in solution containing 2 ppm Ca. Left to right: 0, 8, 12 ppm Al^{+3} added. Inset photo shows an example of root tip damage by Al^{+3}.
(Foy et al.,1969, Agron. J., 61:505., with permission, copyright American Society of Agronomy.)

TABLE 3-7
ALUMINUM TOLERANCE OF SELECTED CROPS

Highly Sensitive	Sensitive	Tolerant	Highly Tolerant
Alfalfa	Canola	Ryegrass	Orchard grass[1]
Annual medics	Barley[1]	Tall fescue	Rhodes grass
Red clover	Wheat[1]	White clover	Lovegrass
	Buffel grass	Orchard grass[1]	Paspalum
	Lesedeza	Wheat[1]	Oats
	Cotton	Subterranean clover	Triticale
	Soybean	Lupins	Yellow serradella
	Sorghum	Dallsigrass	Cereal rye
	Peanuts	Corn	Bermuda grass
	Rice[1]	Rice[1]	Bahia grass
		Barley[1]	

[1] Some crops are listed twice because Al tolerance depends on variety.

As soil pH decreases, Mn^{+2} in solution increases at soil pH < 5 (Fig. 3-17). Since solution Al^{+3} also increases greatly below pH 5, Mn and Al toxicity can occur together. Since Mn^{+2} is readily absorbed and translocated from roots to shoots, the initial toxicity symptoms appear in the shoots. In many grain crops, yellow-brown spots appear between leaf veins, often appearing like interveinal chlorosis similar to Fe deficiency (see color plates). In legume and broadleaf crops, necrosis of leaf edges occurs and leaves appear crinkled.

Iron toxicity can also occur; however, Al toxicity dominates in most strongly acid soils. When tidal marshlands in coastal areas are drained, the underlying FeS_2 oxidizes generating substantial acidity and soluble Fe^{+2}/Fe^{+3} (Chapter 7). Once oxidized, soil pH drops from near neutral to <4 pH. These soils are difficult to manage for plant growth and require large rates of lime to raise soil pH.

Ca^{+2}, Mg^{+2}, and P Deficiency

Soils with high levels of soluble or exchangeable Al^{+3}, especially low CEC soils, generally contain low exchangeable Ca^{+2} and Mg^{+2}, resulting in potential Ca and Mg deficiency (Fig. 3-18). As soluble and exchangeable Al^{+3} increases, nutrient uptake and transport to shoots decrease (Fig. 3-19). In acid soils, the detrimental effects of Al toxicity can be reduced or prevented by increasing solution Ca^{+2}. Magnesium deficiencies caused by inhibition of Mg^{+2} uptake by Al^{+3} and H^+ commonly occur

Figure 3-17
Relationship between soil pH and solution Mn in oxisols.
(Hue et al., 2001, SSSAJ, 65:153–160.)

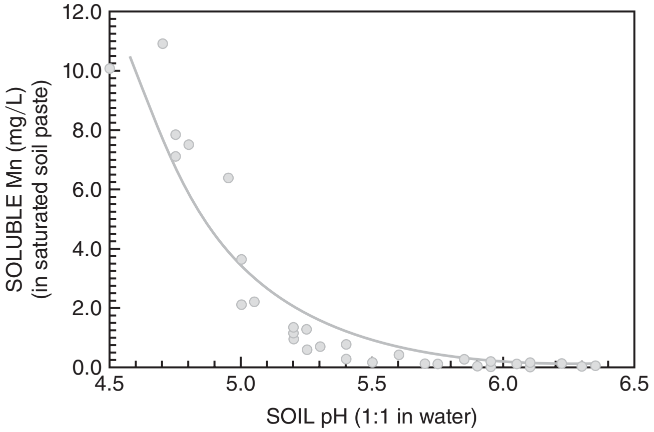


Figure 3-18
Influence of added Ca on remediating Al toxicity.
(Dr. Eugene J. Kamprath)

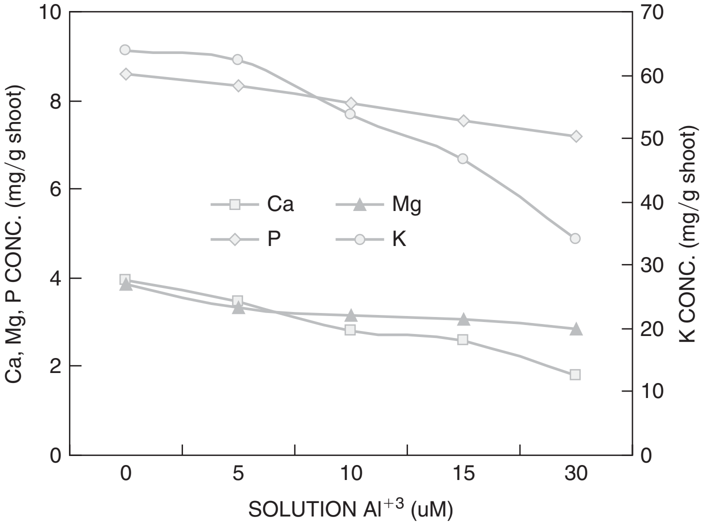


Figure 3-19
Effect of increasing soluble Al^{+3} on nutrient accumulation in corn.
(Adapted from Pintro et al., 1996, J. Plant Nutr., 19:729–741.)

on acid ($pH < 5$), sandy soils. As with Ca^{2+}, Mg^{2+} availability is more a function of the level of Mg saturation than the quantity of exchangeable Mg^{+2}. Generally, optimum plant growth occurs at 5–10% Mg saturation. Liming soils to greatly reduce Al saturation will generally increase Mg availability. In soils with low Mg saturation, application of dolomitic lime is required.

Phosphorus deficiency is common in highly weathered acid soils (e.g., oxisols and ultisols). In these soils, low P solubility exists due to P reactions with Fe and Al oxides. Phosphorus availability decreases as pH decreases below 6.5 due to P precipitation as $Al/FePO_4 \cdot 2H_2O$ and adsorption on Al and Fe oxide surfaces (Chapter 5). Therefore, increasing soil pH by liming can increase P solubility and availability to crops. Elevated Al^{+3} levels at the root surface also enhance formation of insoluble $AlPO_4 \cdot 2H_2O$ that limits $H_2PO_4^-$ uptake. In addition, as root growth is reduced by Al toxicity, P uptake is reduced because the soil volume explored by roots is reduced. Correction of P deficiency in these acid soils can require substantial P application rates; however, the Al toxicity still must be remediated for optimum production.

In weathered-, acid-, course-textured soils, K^+ deficiencies also are common. Reducing exchangeable Al^{+3} by liming will generally increase CEC; however, since these soils are also low in K-bearing minerals, K fertilization is required for optimum plant growth (Chapter 6).

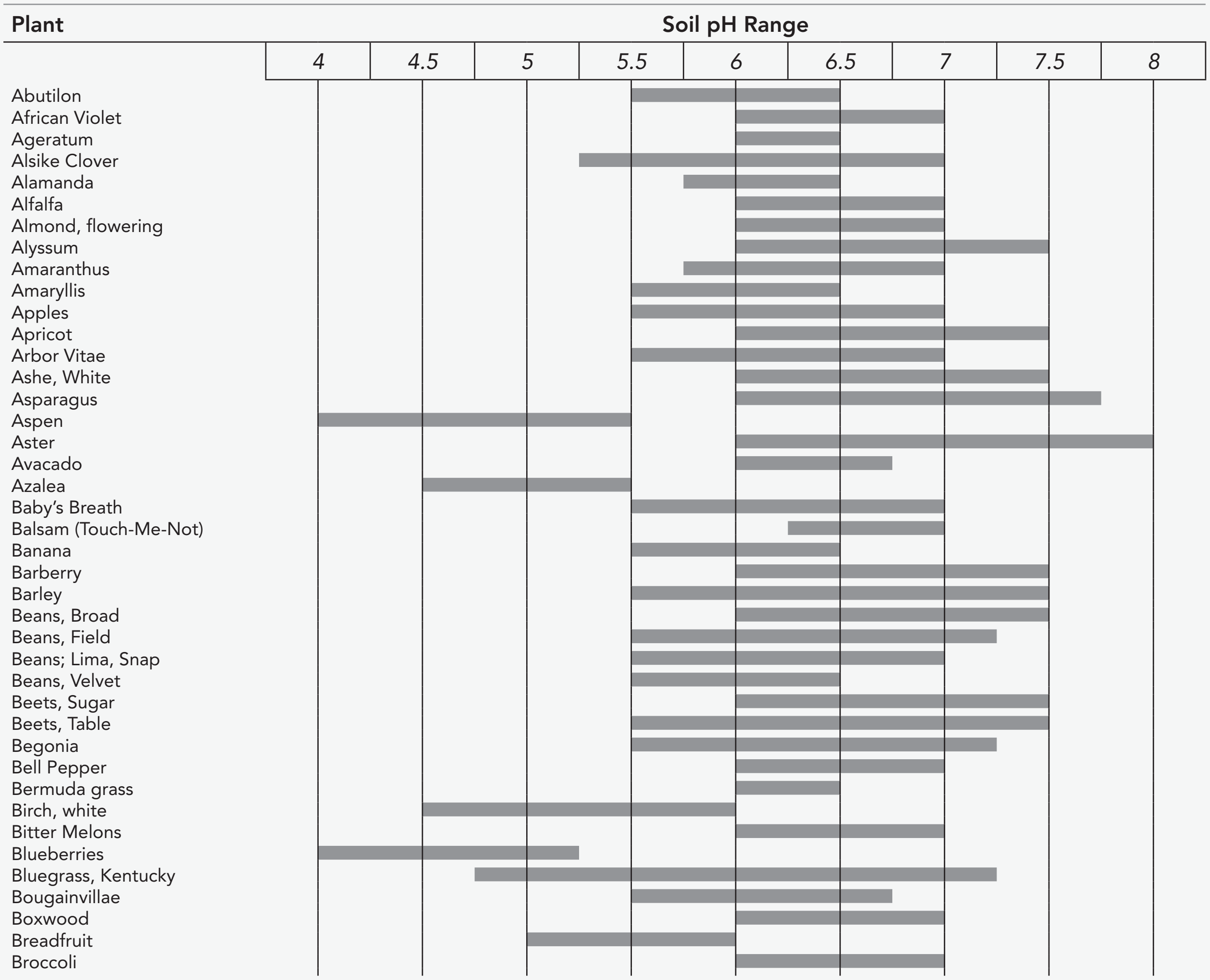
Molybdenum availability in soils decreases with decreasing soil pH; thus, in acid soils crop response to applied Mo or liming can be observed. In acid soils, MoO_4^{-2} is adsorbed by Al and Fe oxides, which is exchanged with OH^- as pH is increased by liming. This is particularly important with legume crops, since Mo is essential to rhyzobia in their function in converting N_2 to NH_4^+. Many legumes often respond to liming acid soils above pH 6. Increasing pH to 6.0–6.2 increases Mo availability to bacteria involved in N_2 fixation. Therefore, higher pH levels for optimum legume productivity are related to increased solubility of soil Mo and subsequent enhancement of N_2 fixation by bacteria.

REDUCING SOIL ACIDITY EFFECTS ON PLANTS

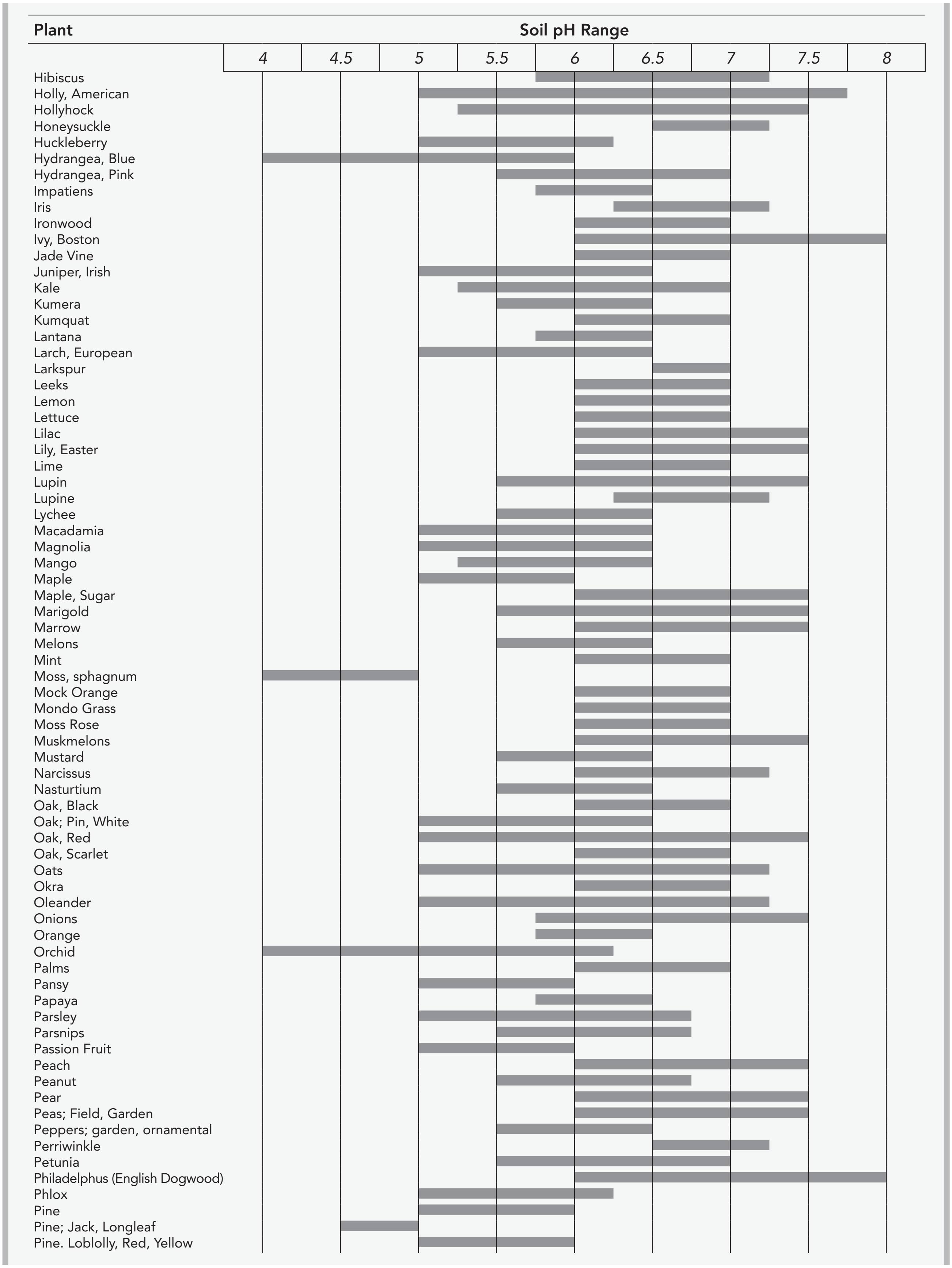
Plant Tolerance to Al

Crop species and genotypes within a specie can vary greatly in their ability to tolerate toxic levels of Al^{+3}. Therefore, careful selection of crops and cultivars can help reduce Al toxicity effects and enhance productivity (Table 3-8).

TABLE 3-8
SOIL pH RANGE FOR OPTIMUM GROWTH OF SELECTED CROPS




Plant
Soil pH Range
4
4.5
5
5.5
6
6.5
7
7.5
8
Broom
Buckwheat
Butterfly Bush
Burning bush
Cabbage
Caladium
Camellia
Candytuft
Carnation
Carrots
Cauliflower
Cedar, White
Celery
Centipede grass
Cherry
Chrysanthemum
Clematis
Clover, Kaimi
Clover, Red
Clover, Sweet
Clover, White
Club moss
Cockscomb (Celosia)
Coconut
Coffee
Coleus
Corn, Field
Corn, Sweet
Cornflower
Cotton
Cowpeas
Crab apple
Cranberries
Crapemyrtle
Crimson Clover
Croton
Cucumber
Dahlia
Date
Daylilly
Dianthus
Dichondra
Dogwood
Duranta
Eggplant
Elm
Erica
Eucalyptus
Euonymus
Fescue, Tall
Ficus
Fig
Fir, balsam
Fir, Douglas
Flax
Forsythia
Four-O-Clock
Foxglove
Gardenia
Garlic
Geranium
Geranium, Ivy
Gerbera
Ginger
Gladiolus
Gloxinia
Gobo
Gourde
Grapefruit
Grapes
Grass; Flame, Kikuyu, Pangola
Guava
Hazelnut
Heather
Hemlock


Plant
Soil pH Range
4
4.5
5
5.5
6
6.5
7
7.5
8
Hibiscus
Holly, American
Hollyhock
Honeysuckle
Huckleberry
Hydrangea, Blue
Hydrangea, Pink
Impatiens
Iris
Ironwood
Ivy, Boston
Jade Vine
Juniper, Irish
Kale
Kumera
Kumquat
Lantana
Larch, European
Larkspur
Leeks
Lemon
Lettuce
Lilac
Lily, Easter
Lime
Lupin
Lupine
Lychee
Macadamia
Magnolia
Mango
Maple
Maple, Sugar
Marigold
Marrow
Melons
Mint
Moss, sphagnum
Mock Orange
Mondo Grass
Moss Rose
Muskmelons
Mustard
Narcissus
Nasturtium
Oak, Black
Oak; Pin, White
Oak, Red
Oak, Scarlet
Oats
Okra
Oleander
Onions
Orange
Orchid
Palms
Pansy
Papaya
Parsley
Parsnips
Passion Fruit
Peach
Peanut
Pear
Peas; Field, Garden
Peppers; garden, ornamental
Perriwinkle
Petunia
Philadelphus (English Dogwood)
Phlox
Pine
Pine; Jack, Longleaf
Pine. Loblolly, Red, Yellow


Plant
Soil pH Range
4
4.5
5
5.5
6
6.5
7
7.5
8
Pine, White
Pineapple
Poinsettia
Pomegranate
Poppy
Potatoes
Potatoes, Sweet
Potatoes, White
Primula
Pummelo
Pumpkin
Radishes
Raspberries
Raspberry, Red
Red Clover
Redbud
Rhododendron
Rhubarb
Rice
Roses
Rye
Ryegrass
Salvia
Shasta Daisy
Snapdragon
Snowball
Sorghum
Soybeans
Spinach
Spiraea.
Spruce, Black
Spruce, Colorado
Spruce, White
Squash
St. Augustine
Strawberreis
Sudangrass
Sugarcane
Sunflower
Sweet William
Sweetpea
Sycamore
Tamarack
Tangerine
Taro
Timothy
Tobacco
Tomatoes
Trefoil, Birdsfoot
Turnips
Tulips
Verbena
Vetch
Viburnum
Vinca
Viola
Vitex
Walnut, Black
Watercress
Weeping Willow
Wheat
Whiteclover
Yew, Japanese
Zinnia
Zoysia

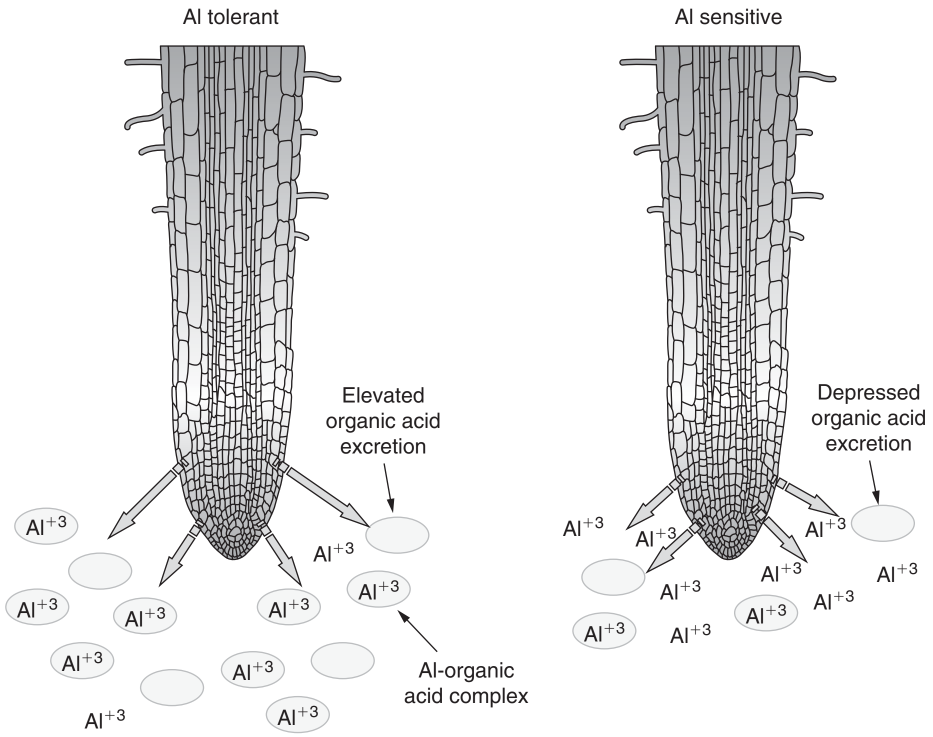


Figure 3-20
Mechanism of Al tolerance in selected species and varieties within species.
(Adapted from Delhaize et al., 2004. Proc. Natl. Acad. Sci., *101:15249–15254.)*

The mechanisms of Al tolerance include both internal and external processes. The internal mechanism is based on observations that some plants tolerate high Al levels through accumulation of Al in the shoot where internal Al detoxification can occur. For example, *Hydrangea* (an ornamental plant) flowers turn from red to blue when transplanted to an acid soil, which is due to Al accumulation in the sepals. *Hydrangea* can accumulate about 3,000 ppm Al, while buckwheat accumulates as high as 15,000 ppm Al in leaves when grown on acid soils. These plants complex Al^{+3} with oxalate and citrate in the roots and leaves.

The external mechanism is based on a correlation between Al tolerance and Al-activated organic acid release (Fig. 3-20). Certain plant genotypes tolerate Al^{+3} because they exude organic acids (malate, citrate, or oxalate) from the root tips. These organic acids chelate or complex soluble Al^{+3} at the root surface and effectively limit Al^{+3} uptake. Genotypes within several species (Table 3-9) release more organic acid than Al-sensitive genotypes.

Recent research has identified the specific gene in Al tolerant wheat that controls organic acid exudation and Al tolerance. Wheat breeding programs are currently developing varieties with enhanced Al tolerance. The Al tolerance gene has also been

TABLE 3-9
PLANT SPECIES WHERE SPECIFIC ORGANIC ACID EXUDATION BY ROOTS IS CORRELATED WITH AL TOLERANCE

Barley
Buckwheat
Corn
Oat
Radish
Rapeseed
Rye
Snapbeans
Sorghum
Soybean
Sunflower
Taro
Tobacco
Triticale
Wheat

Figure 3-21
Genetically modified barley with the wheat Al tolerance gene (left) and the unmodified barley plant (right) grown on acid soil.
(Photo by Carl Davies; permission provided Manny Delhaize and Peter Ryan, CSIRO Plant Industry, PO Box 1600, Canberra, ACT 2601, Australia.)

successfully inserted into barley (Fig. 3-21). Improving Al tolerance through genetic modification of many important food crops will be invaluable to optimizing plant growth in acid soils.

One short-term management strategy for reducing Al^{+3} toxicity in seedlings is band application of fertilizer P (Table 3-10). These data show that band-applied P at planting reduces Al^{+3} toxicity and increased wheat and sorghum yield on low pH, high P soils.

TABLE 3-10
LIME AND P EFFECTS ON WHEAT AND SORGHUM GROWN ON LOW pH SOILS

	Lime Rate	P Rate & Application Method		
			Broadcast	*Band*[1]
Crop (*lb P_2O_5/a*)	*lb ECCE/a*	*0*	*40*	*40/35*
		—— bu/a ——		
	0	38	42	54
Wheat (40)	3,750	51	51	57
	7,500	49	49	55
	0	55	—	76
Sorghum (35)	5,000	63	—	83
	10,000	73	—	83

[1] Initial soil pH 4.5; high soil test P.
Source: Adapted from Lamond et al., 1997, *Better Crops*, 81:10–11.

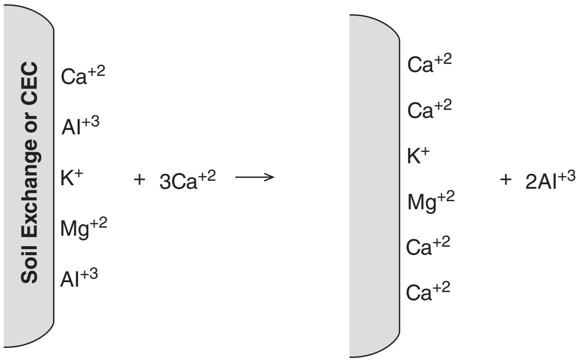
Neutralizing Soil Acidity with Lime

Liming reactions in soil Liming reactions begin with the neutralization of H^+ in the soil solution by adding a base (usually OH^- or CO_3^{-2}) originating from the lime material. For example, $CaCO_3$ behaves as:

$$CaCO_3 + 2H^+ \rightleftarrows Ca^{+2} + CO_2 + H_2O$$

The fast reaction of $2H^+ + CO_3^{-2} \rightarrow CO_2 + H_2O$ neutralizes H^+ in soil solution. Exchangeable Al^{+3} desorbs from the CEC as solution Ca^{+2} increases from the dissolving $CaCO_3$. Two Al^{+3} on the CEC are replaced by three Ca^{+2} [6(+) charges of Al replaced by 6(+) charges of Ca]. Once in solution the Al^{+3} hydrolyzes to produce more H^+, which is neutralized by CO_3^{-2}. In this way, both soil pH and BS increase (Fig. 2-11). Since the majority of exchangeable acidity occurs as exchangeable Al^{+3}, the neutralization reaction can be represented by:

Step 1: Exchange $2Al^{+3}$ on the CEC with $3Ca^{+2}$ from the $CaCO_3$.



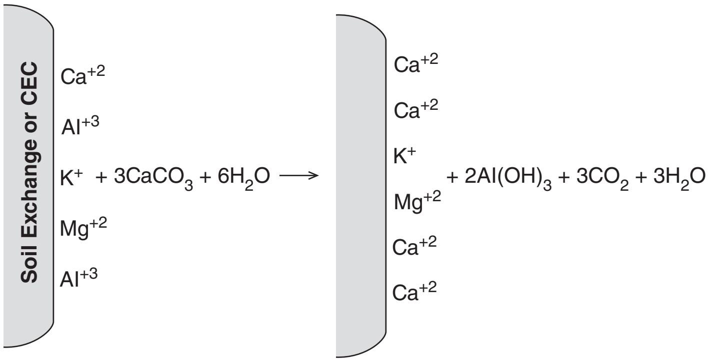
Step 2: Al^{+3} in solution hydrolyzes (reacts with water) to produce $6H^+$; the $Al(OH)_3$ precipitates out of solution.

$$2Al^{+3} + 6H_2O \rightleftarrows 2Al(OH)_3 + 6H^+$$

Step 3: CO_3^{-2} (from $CaCO_3$) neutralizes the H^+ produced from Step 2.

$$3CO_3^{-2} + 6H^+ \rightleftarrows 3CO_2 + 3H_2O$$

Overall Reaction



The rate of the reaction is directly related to the rate at which the H^+ ions are neutralized in solution. As long as sufficient $CaCO_3$ is available, H^+ will be converted to H_2O. The continued removal of H^+ from the soil solution will ultimately result in the precipitation of Al^{+3} as $Al(OH)_3$ and replacement on the CEC with Ca^{+2}. Thus, as soil pH increases, BS also increases (Fig. 2-11).

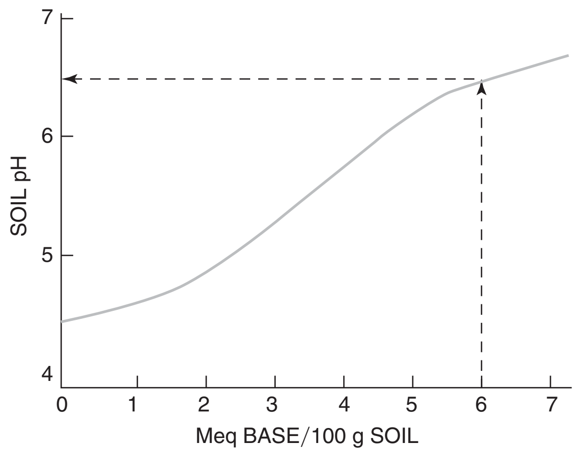


Figure 3-22
Example titration to determine lime requirement of an acid sandy loam soil. Initial soil pH is 4.5. Increasing addition of base (meq/100 g soil) increases soil pH.

Determining lime requirement The lime requirement of a soil can be determined by several different methods. Titrating a soil with a base [i.e., $Ca(OH)_2$] will increase soil pH (Fig. 3-22). After equilibration, pH is determined and the pH values are plotted against the quantity (meq) of base added. From these data it is simple to determine the amount of lime to be added. For example, increasing pH from 4.5 to 6.5 requires adding 6.0 meq base/100 g soil (Fig. 3-22). Thus, the quantity of $CaCO_3$ needed to increase pH to 6.5 would be:

$$\frac{6 \text{ meq base}}{100 \text{ g soil}} = \frac{6 \text{ meq CaCO}_3}{100 \text{ g soil}}$$

$$\frac{6 \text{ meq CaCO}_3}{100 \text{ g soil}} \times \frac{50 \text{ mg CaCO}_3}{\text{meq}} = \frac{300 \text{ mg CaCO}_3}{100 \text{ g soil}}$$

$$= \frac{0.3 \text{ g CaCO}_3}{100 \text{ g soil}}$$

$$= \frac{0.3 \text{ lb CaCO}_3}{100 \text{ lb soil}}$$

$$\frac{0.3 \text{ lb CaCO}_3}{100 \text{ lb soil}} \times \frac{2 \times 10^6 \text{ lb soil}}{\text{afs}} = \frac{6{,}000 \text{ lb CaCO}_3}{\text{afs}}$$

Soil titration with a base is not generally used in routine soil testing for lime requirements because titrations are usually time consuming. However, reliable titration methods have been recently developed that can be practically used in determining lime requirements (Fig. 3-23).

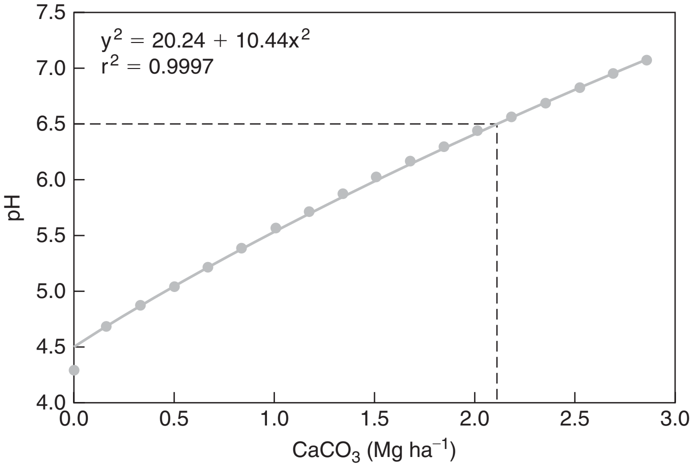


Figure 3-23
Titration curve for a loam soil using a 30-minute time interval between additions of $Ca(OH)_2$. Volume of base added is converted to equivalent $CaCO_3$ (Mg/ha).
(Liu et al., 2004, SSSAJ, 68:1228–1233.)

TABLE 3-11
COMMON BUFFER METHODS USED TO DETERMINE LIME REQUIREMENT

Buffer Method	Buffer pH	Target pH	Intended Use	$CaCO_3$ Required/0.1 Decrease in Buffer pH
				t/a
SMP	6.8	6.8	Exchangeable Al-alfisols	0.27
		6.4		0.22
		6.0		0.18
Woodruff	7.0	6.5–7.0	Mollisols	0.22
Adams-Evans	8.0	6.5	Low CEC-ultisols	0.04
Mehlich	6.6	6.0	Exchangeable Al-ultisols	0.07

Source: van Lierop. 1990. Soil pH and Lime Requirement Determinations. In R. L.Westerman (ed.), *Soil Testing and Plant Analysis* (3rd ed., pp. 73–126). Soil Sci. Soc. Am., Madison, Wis.

The most common method used to estimate lime requirement is based on the change in pH of a buffered solution (the base) added to a soil (the acid). When a buffer solution of known base concentration is added to an acid soil, the buffer pH is depressed in proportion to the original soil pH and its BC. A large drop in buffer pH would indicate a low pH soil with a large reserve or potential acidity, and a high lime requirement. A specific volume of the buffer solution is added to a given weight or volume of soil, and the decrease in pH of the buffer solution is related to the amount of soil acidity and ultimately the lime requirement.

Four buffer methods are commonly used to determine the lime requirement (Table 3-11). The Shoemaker, McLean, and Pratt (SMP) buffer is used with soils containing 2:1 and 2:1:1clays, especially high OM alfisols. The SMP and Woodruff buffers are commonly used in regions dominated with mollisols. The Adams-Evans buffer was developed for low CEC and kaolinitic soils. The Mehlich buffer was initially developed for use on moderate to highly weathered ultisols, although it is increasingly used in other regions. Recently, Mehlich and SMP buffer methods were compared on nearly 100 mollisol and alfisol soils, and both methods accurately estimated lime requirements (Fig. 3-24).

Liming materials The most common lime sources are calcitic and dolomitic limestone (Table 3-12). The accompanying anion must neutralize H^+ in solution and hence Al^{+3} on the CEC. Common anions associated with liming materials are CO_3^{-2}, OH^-, and O^{-2}. Gypsum ($CaSO_4 \cdot 2H_2O$) and other neutral salts cannot neutralize H^+, as shown by:

$$CaSO_4 \cdot 2H_2O + 2H^+ \rightleftarrows Ca^{+2} + 2H^+ + SO_4^{-2} + 2H_2O$$

In fact, neutral salts lower soil pH. In the previous example, Ca^{+2} replaces adsorbed Al^{+3} that increases solution Al^{+3}, which hydrolyzes to generate H^+ and decreases pH. This is especially true with band-applied salts where the fertilized zone pH is depressed. Although gypsum will not neutralize soil pH, increasing Ca^{+2} in solution may enhance growth if Ca^{+2} is marginally deficient. Also, formation of $AlSO_4^0$ reduces Al^{+3} in solution and subsequent potential Al toxicity. Other neutral salts that are not liming materials include $MgSO_4 \cdot 7H_2O$, KCl, $CaCl_2$, and $MgCl_2$. NaOH could be considered a liming material but addition of Na on the CEC is not recommended (see Saline, Sodic, and Saline-Sodic Soils).

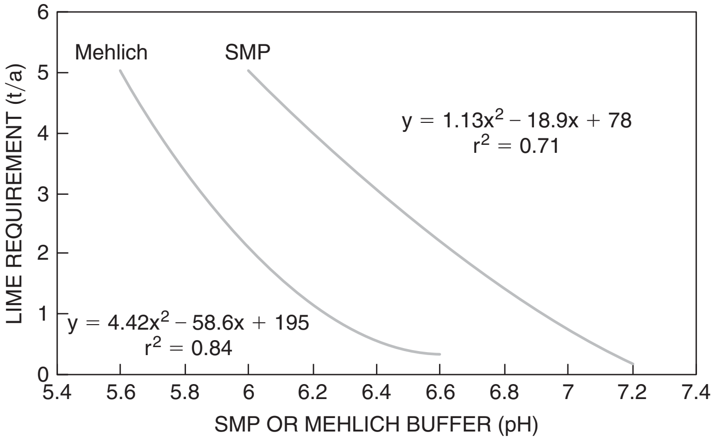


Figure 3-24
Comparison of SMP and Mehlich buffer methods for estimated lime requirement. For a lime requirement of 2 t/a, the Mehlich and SMP buffer pH would be about 6 and 6.6, respectively.
(Godsey et al., 2007, SSSAJ, 71:843–850.)

Calcium Carbonate Equivalent

The value of a liming material depends on the quantity of acid that a unit weight of lime will neutralize, which is related to its composition and purity. Pure $CaCO_3$ is the standard against which other liming materials are measured, and its neutralizing value is 100%. The *calcium carbonate equivalent* (CCE) is defined as the acid-neutralizing capacity of a liming material expressed as a weight percentage of $CaCO_3$. Consider the following reactions:

$$CaCO_3 + 2H^+ \rightleftarrows Ca^{+2} + CO_2 + H_2O$$
$$Ca(OH)_2 + 2H^+ \rightleftarrows Ca^{+2} + H_2O$$

In each reaction, 1 mole of either material will neutralize 2 moles of H^+. The molecular weight of $CaCO_3$ is 100 g/mole, whereas that of $Ca(OH)_2$ is only 74 g/mole; thus, 74 g of $Ca(OH)_2$ will neutralize the same amount of acid as 100 g of $CaCO_3$. Therefore, the neutralizing value, or CCE, of equal weights of the two materials is calculated by:

$$\frac{100\text{g } CaCO_3/\text{mole}}{74\text{g } Ca(OH)_2/\text{mole}} \times 100 = 135\% \text{ CCE}$$

Therefore, $Ca(OH)_2$ will neutralize 1.35 times as much acid as the same weight of $CaCO_3$ (CCE = 135%).

The same procedure is used to calculate the neutralizing value of other liming materials (Table 3-12). Dolomite is unique in that there are $2CO_3^{-2}$ in each $CaMg(CO_3)_2$, so half the molecular weight is used to determined CCE.

$$CaMg(CO_3)_2 + 4H^+ \rightleftarrows Ca^{2+} + Mg^{+2} + 2CO_2 + 2H_2O$$

$$\frac{100 \text{ g } CaCO_3/\text{mole}}{0.5 \times 184 \text{ g } CaMg(CO_3)_2/\text{mole}} \times 100 = 109\% \text{ CCE}$$

Lime material composition can also be expressed by its Ca and/or Mg content. For example, pure $CaCO_3$ contains 40% Ca calculated by the ratio of molecular weights:

$$\frac{40 \text{ g Ca/mole}}{100 \text{ g } CaCO_3/\text{mole}} \times 100 = 40\% \text{ Ca}$$

Calcium and Calcium-Magnesium Carbonates. Calcium carbonate ($CaCO_3$), or calcite, and calcium-magnesium carbonate [$CaMg(CO_3)_2$], or dolomite, are the most common liming materials and generally referred to as Ag-lime. The CCE of *pure* $CaCO_3$ is 100%, while the CCE of pure dolomite is 109%; however, these

TABLE 3-12
COMMON LIME MATERIALS

Lime Material	Chemical Composition	Properties	CCE (%)[1]
Calcium carbonate	$CaCO_3$ (pure)	Reference material	100
Calcitic limestone (Ag-lime)	$CaCO_3$	Variable fineness	80–100
Suspension or fluid lime	$CaCO_3$	Very fine particles	95–100
Dolomitic limestone	$CaMg(CO_3)_2$	$<50\%$ Mg	95–100
Dolomite	$CaMg(CO_3)_2$	$>50\%$ Mg	100–120
Marl	$CaCO_3$	Clay contamination	70–90
Burned lime	CaO	Hard to handle	150–175
Hydrated or slaked lime	$Ca(OH)_2$	Fast acting	120–135
Slag	$CaSiO_3$	Variable composition	60–90
Wood ash	Ca, Mg, K oxides	Depends on type of burn	30–70
Power plant ash	Ca, Mg, K oxides	Highly variable	25–50
Ground oyster shells	$CaCO_3$	Localized use	Up to 95
Cement kiln dusts	Ca oxides	Localized use	40–100
Biosolids and by-products	CaO, $Ca(OH)_2$,	Variable composition	Variable

[1] CCE → calcium carbonate equivalent represents the neutralizing value of the material compared to pure $CaCO_3$. For example, pure $Ca(OH)_2$ neutralizes 35% more acid than the same weight of pure $CaCO_3$.

open-pit–mined materials contain impurities. Calcitic limestone contains $\geq 85\%$ $CaCO_3$ and small amounts of $MgCO_3$ and other minerals, where the CCE $< 100\%$ (Table 3-12). Dolomite contains both $MgCO_3$ and $CaCO_3$ with at least 15% $MgCO_3$. Consequently, the CCE of dolomite is higher than calcitic lime as calculated earlier. Although dolomite has a slightly higher CCE than calcite, dolomite has a lower solubility and thus will dissolve more slowly; however, the difference is generally too small to observe in field crop response. The primary factors in determining which carbonate source to apply are if soil Mg supply is low and the difference in material cost. Dolomite should be used on acid soils testing low or very low in Mg. If Mg is not needed, then either source can be used, depending on cost.

Pelletized lime is made from finely ground (100–200 mesh) dolomitic or calcitic lime. The fine particles are formed into round pellets (~0.1–0.2-in. diameter) using a lignosulfonate or other water-soluble binding agent. The primary advantage is easier handling, more uniform application, and reduced dust compared to Ag-lime. Pelletized lime products are commonly used in the turf and landscape industry, although its use in agriculture is increasing.

Fluid or suspension lime is commonly a 50/50 mixture of very finely ground (~200 mesh) Ag-lime and water. Suspending agents (0.5% clay, tetrasodium pyrophosphate) are added to maintain dispersion. Liquid urea-ammonium nitrate may be used as the suspending agent adding a small amount of N to the suspension. Fluid lime products can also come from lime materials used in municipal water treatment plants. Fluid lime can be applied uniformly with standard fluid application equipment; however, single pass application rates are ≤ 500 lb/a.

Pelletized and fluid limes are excellent materials that generally react faster in soil than Ag-lime; however, the finer particle size of these materials does not increase their neutralizing value. Increasing soil pH to a target level will require an equivalent (neutralizing value) quantity of lime, regardless of the source. Recall that neutralizing 2 meq acid/100 g soil requires application of 2 meq base/100 g soil (see pg. 29). In addition, the cost of pelletized lime is considerably higher than Ag-lime.

Calcium Oxide and Hyroxide. Calcium oxide (CaO) is the only material to which the term *lime* may be correctly applied. Also known as unslaked lime, burnt lime, or quicklime, CaO is a white powder, shipped in paper bags because of its caustic properties. It is manufactured by heating $CaCO_3$ in a furnace, driving off CO_2. CaO is the most effective of all liming materials (Table 3-12). When unusually rapid results are required, either CaO or $Ca(OH)_2$ should be used. Because of its high reactivity with water, avoid contact with skin, eyes, and lungs.

Calcium hydroxide $[Ca(OH)_2]$, or slaked lime, hydrated lime, or builders' lime, is a white powder and difficult to handle. Neutralization of acid occurs rapidly. Slaked lime is prepared by hydrating CaO and has a high CCE (Table 3-12).

Marl. Marls are soft, unconsolidated deposits of $CaCO_3$ frequently mixed with earthen impurities and usually quite moist. Marl deposits are generally thin, recovered by dragline or power shovel after the overburden has been removed. The fresh material is stockpiled and allowed to dry before being applied to the land. Marl is almost always low in Mg, and its CCE ranges from 70 to 90%, depending on clay content.

Calcium Silicates. Calcium silicate is surface mined from natural deposits frequently near coastal regions and has a CCE of 60–90%. A more common source of $CaSiO_3$ is slag by-products of iron manufacturing. In the blast-furnace reduction of Fe ore, $CaCO_3$ loses CO_2 and forms CaO, which combines with molten Si to produce a slag that is either air or water cooled. Slags usually contain appreciable amounts of Ca, Mg and P, depending on the source of Fe ore and manufacturing process (Table 3-13). Availability of these materials is often limited to Fe manufacturing regions.

Wood and Other Ash Products. Burning plant and waste residues (wood, crop residue, animal waste) produces ash-containing Ca, Mg, K, Na, and other metal oxides and hydroxides. While these ash by-products neutralize acidity, their CCE is highly variable and must be determined before correct application rates can be established. Coal or fly ash from coal-burning power plants also has a variable CCE; however, these materials should also be analyzed for heavy metal content before use.

Biosolids, By-Products, and Other Materials. Other materials used as liming agents in areas close to their source are biosolids from waste treatment plants, lime or flue dust from cement manufacturing, pulp mill lime, carbide lime, acetylene lime, packing house lime, and so on. These by-products contain variable CCE that should be determined to ensure effective application and soil pH management.

TABLE 3-13
CHEMICAL AND LIME CHARACTERISTICS OF SLAG MATERIALS COMPARED TO AG-LIME

Property	Slag Source		Agricultural Lime
	Steel Furnace	*Blast Furnace*	
pH	12.5	10.3	8.2
CCE	79.8	81.1	97
ECCE	22	27	77
Ca, %	22.2	25.2	21.1
Mg, %	5.5	5.1	12.6
Fe, %	15.9	0.9	0.2
Al, %	1.6	3.8	0
P, ppm	23	59	34

Source: Adapted from D. Munn, 2003, *Turfgrass Trends.*

Fineness Factor of Limestone or Particle Size Distribution

The effectiveness of liming materials also depends on their particle size distribution or *fineness*, because the reaction rate depends on the surface area in contact with the soil. CaO and $Ca(OH)_2$ are powders with the smallest particle size, but limestone needs to be crushed to reduce particle size. Sieve size or *mesh* is the number of openings per inch (Fig. 3-25). A 60-mesh sieve has 60 openings per inch. A particle passing 60-mesh sieve would have a diameter <0.0098 in. (<0.25 mm) (Fig. 3-26).

When crushed limestone is thoroughly incorporated into the soil, the reaction rate will increase with deceasing particle size (increasing fineness) (Fig. 3-27). Decreasing the particle size fraction of a liming material decreases the lime rate required to raise soil

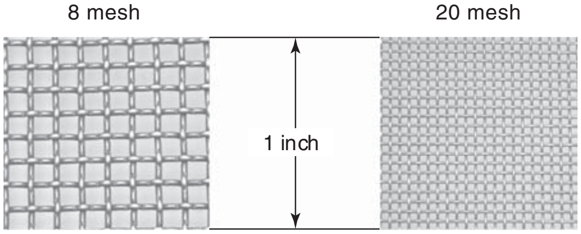


Figure 3-25
Sieve size or mesh represents the number of openings per inch of screen.

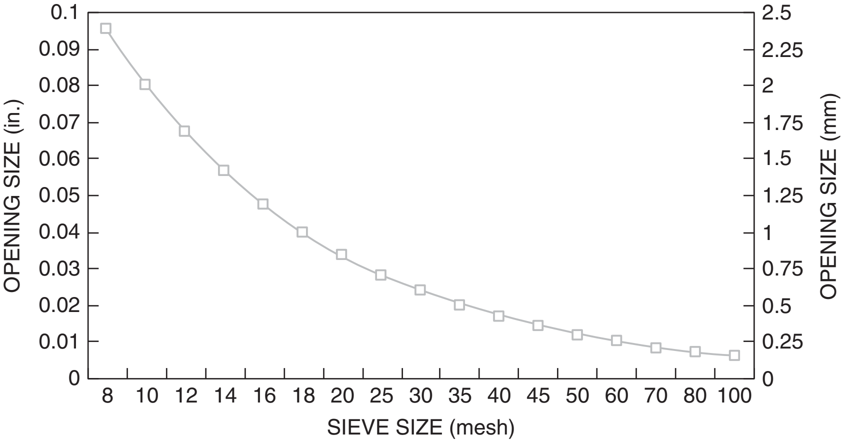


Figure 3-26
Relationship between sieve mesh size (# opening/inch) and individual opening distance in in. and mm.

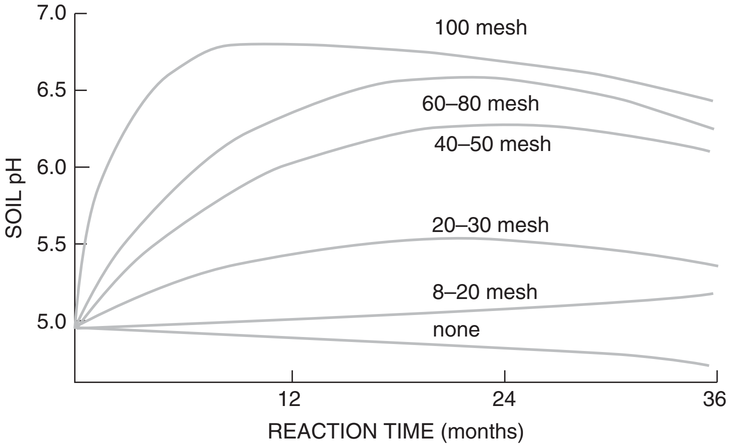


Figure 3-27
Typical effect of lime particle size on soil pH over 3 years.
(Meyer and Volk, 1952, Soil Sci., *73:37–52.)*

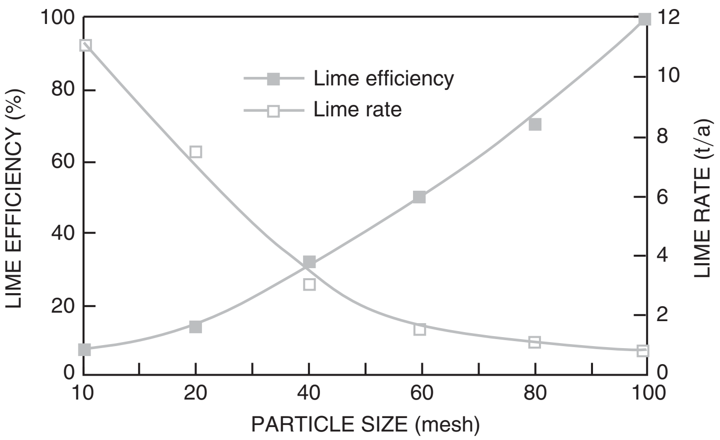


Figure 3-28
Relative lime efficiency of different size fractions of limestone in raising soil pH to 7.0. Greater lime rates are needed for coarser lime material (low mesh) to raise soil pH to the same level as a finer material (high mesh).

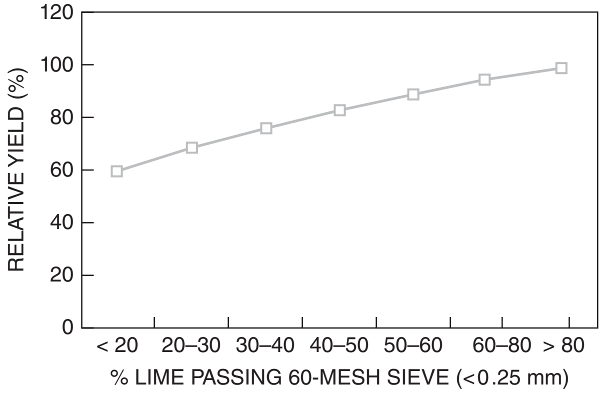


Figure 3-29
Effect of increasing proportion of finer particles on relative crop yield. Data are averages of lime responses on six different crops over 6–8 years.

(Adapted from Barber, 1984, Soil Acidity and Liming, *Agron No. 12, ASA, Madison, Wis.)*

pH, or increases the effectiveness of a given lime material (Fig. 3-28). In this example, a 100-mesh lime material (100% efficient) requires only 1 t/a to increase soil pH to 7.0, whereas a 50-mesh lime material (40% efficient) requires 2 t/a. When applied at the same lime rate, increasing the proportion of finer particles improves crop productivity because of increased neutralization of soil acids (Fig. 3-29), but also increases the cost of the material. Because limestone cost increases with fineness, materials that require minimum grinding, yet contain enough fine material to change pH rapidly and maintain desired pH for 4–5 years, are preferred.

Agricultural limestones contain both coarse and fine materials. Fineness is quantified by measuring the distribution of particle sizes in a given limestone sample. Particle size distribution or fineness represents the particles passing through or retained on a specific sieve size. Most agricultural lime contains a range of particle sizes from very fine, dust-size particles to coarse, sand-size particles. The standards for particle size distribution vary between regions (Table 3-14). The fineness factor is the sum of the percentages of each size fraction multiplied by the appropriate efficiency factor (Table 3-15).

Overall Lime Quality

The effective calcium carbonate equivalent (ECCE) rating of a limestone is the product of the CCE and fineness factor (Table 3-15). Manufacturers guarantee the CCE and fineness of any lime product sold. Thus, if 4,000 lb $CaCO_3$/a were recommended, it would take 4,000 lb/a ÷ 0.68 = 5,882 lb/a of material “A” and 4,000 lb/a ÷ 0.81 = 4,938 lb/a of material “B” to increase soil pH to the same

TABLE 3-14
FINENESS FACTORS FOR AGRICULTURAL LIMESTONE IN THE UNITED STATES AND CANADA

Region	Particle Size (*mesh*)	Fineness Factor
Indiana, Kansas, Michigan, (Nebraska), North Carolina	>8	0
	8–60	0.5 (0.4)
	<60	1.0
Alabama, Idaho, (Kentucky), Mississippi, [Ontario]	>10	0
	10–60 (50)	0.5 [0.4]
	<60 (50)	1.0
Iowa	>4	0.1
	4–8	0.3
	<60	0.6
Minnesota, Ohio, Texas, Wisconsin	>8	0
	8–20	0.2
	20–60	0.6
	<60	1.0
Missouri (Illinois)	>8	0
	8–40 (30)	0.25
	40–60 (30)	0.6
	<60	1.0
Virginia	>20	0
	20–60	0.4
	60–100	0.8
	<100	1.0
Oregon	>10	0
	10–20	0.3
	20–40	0.6
	<40	1.0
Alberta	>10	0.05
	10–30	0.2
	30–60	0.5
	<60	1.0

TABLE 3-15
FINENESS EFFECTS ON EFFECTIVE CALCIUM CARBONATE EQUIVALENT OF TWO LIME SOURCES

	Lime Material "A"	Lime Material "B"
Calcium Carbonate Equivalent (CCE)	80	90
Fineness (% passing through sieve)		
>8 mesh	3	2
8–60 mesh	24	36
<60 mesh	73	62
Fineness Factor Calculation (Table 3-14; Indiana)		
>8 mesh × 0	3 × 0 = 0	2 × 0 = 0
8–60 mesh × 0.5	24 × 0.5 = 12	36 × 0.5 = 18
<60 mesh × 1.0	73 × 1.0 = 73	62 × 1.0 = 62
Fineness Factor (*FF*) FF = sum of 3 individual factors	73 + 12 = 85	62 + 18 = 90
Effective Calcium Carbonate Equivalent (ECCE) ECCE = CCE × FF	0.80 × 85 = 68	0.90 × 90 = 81

level. For the same degree of fineness, the material that costs the least per unit of CCE should be used.

$$\text{Lime “A”} \rightarrow \$25/\text{t} \qquad \frac{5{,}882\text{ lb lime A}}{\text{a}} \times \frac{1\text{ t}}{2{,}000\text{ lb}} \times \frac{\$25}{\text{t}} = \frac{\$73.53}{\text{a}}$$

$$\text{Lime “B”} \rightarrow \$34/\text{t} \qquad \frac{4{,}938\text{ lb lime B}}{\text{a}} \times \frac{1\text{ t}}{2{,}000\text{ lb}} \times \frac{\$34}{\text{t}} = \frac{\$83.95}{\text{a}}$$

The ECCE of lime “B” is greater than “A”; however, the cost per acre of lime “A” is lower and should be selected. This also assumes that the moisture content in both materials is the same.

Lime “A” → 5% moisture

$$\frac{5{,}882\text{ lb lime A}}{\text{a}} - (0.05)\frac{5{,}882\text{ lb lime A}}{\text{a}} = \frac{5{,}588\text{ lb lime A (dry)}}{\text{a}}$$

Lime “B” → 15% moisture

$$\frac{4{,}938\text{ lb lime B}}{\text{a}} - (0.15)\frac{4{,}938\text{ lb lime B}}{\text{a}} = \frac{4{,}197\text{ lb lime B (dry)}}{\text{a}}$$

Now recalculate the lime cost ($/a) based on equal moisture contents.

$$\text{Lime “A”} \rightarrow \qquad \frac{5{,}588\text{ lb lime A}}{\text{a}} \times \frac{1\text{ t}}{2{,}000\text{ lb}} \times \frac{\$25}{\text{t}} = \frac{\$69.85}{\text{a}}$$

$$\text{Lime “B”} \rightarrow \qquad \frac{4{,}197\text{ lb lime B}}{\text{a}} \times \frac{1\text{ t}}{2{,}000\text{ lb}} \times \frac{\$34}{\text{t}} = \frac{\$71.35}{\text{a}}$$

Adjusting for moisture content shows the two lime sources are similarly priced.

Application of liming materials

Tillage Systems

For high lime rates, broadcasting one-half the lime, followed by disking and/or plowing, and then broadcasting the other half and disking, is effective in mixing lime throughout the 0–6-in. depth. Lime recommendations are generally made on the basis of a 6–8-in. soil depth. With deeper tillage, lime recommendations should be increased (Table 3-16).

Neutralization of subsoil acidity through deep incorporation of surface-applied lime is possible with large tillage equipment. The effect of incorporation depth on cotton growth showed that the amount and depth of cotton rooting were

TABLE 3-16
ADJUSTMENT FACTORS FOR DEPTH OF LIME INCORPORATION

Incorporation Depth (in.)	Adjustment Factor	
	Ohio	*Kansas*
3	0.38	0.43
5	0.62	0.71
7	0.88	1.00
9	1.13	1.29
11	1.38	1.57

Sources: Adapted from Mullen et al., 2005, Ohio State Univ. 14th ed., Bull. 472-05; adapted from Witney and Lamond, 1993, Kansas State Univ. MF-1065.

Figure 3-30
Amount and depth of cotton rooting as affected by depth of lime incorporation. From left to right: unlimed; limed 0–6 in.; limed 0–18 in.
(Doss et al., 1979, Agron. J., *71:541, with permission, copyright American Society of Agronomy).*

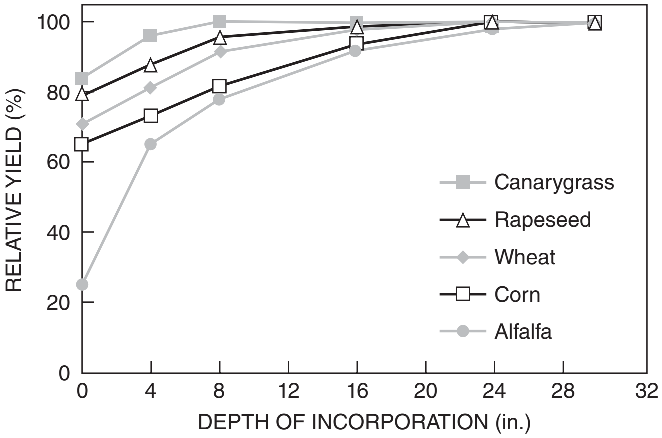


Figure 3-31
Effect of depth of lime incorporation on relative crop yield.
(Adapted from Bouldin, 1979, Cornell Int. Agr. Bull. *74, Cornell Univ.; and Pinkerton and Simpson,1986,* Aust. J. Exper. Agric.*, 26:107–113.)*

increased by mixing lime to a depth of 18 in. (Fig. 3-30). Depth of lime incorporation will increase with increasing rooting depth characteristics of different crops (Fig. 3-31). Surface lime applications without some mixing in the soil are not immediately effective in increasing soil pH below the surface 0–2-in. depth. In several studies it was observed that 10 or more years were required for surface-applied lime without incorporation to raise soil pH at a depth of 6 in. Keeping surface soils at a higher pH over time is one option to increase subsoil pH (Table 3-17).

No-Tillage Systems

With no-till cropping systems, surface soil pH can decrease substantially in a few years because of the acidity produced by surface-applied N fertilizers and decomposition of crop residues (Table 3-18). If the increased acidity is concentrated in the soil surface, surface liming applications are effective. With low pH subsoil, limestone

TABLE 3-17
EFFECT OF SURFACE SOIL pH LEVELS ON SUBSOIL pH

Soil Depth (in.)	pH at Various Depths with Increasing Surface Soil pH			
0–7	4.9	5.5	6.0	6.5
7–14	4.9	5.2	5.9	6.7
14–21	4.7	4.8	5.2	5.4

Source: Ohio Agronomy Guide, 1985, Cooperative Extension Service, Ohio State Univ.

TABLE 3-18
SOIL pH AFTER 7 YEARS OF CONTINUOUS CORN UNDER CONVENTIONAL AND NO-TILLAGE SYSTEM

N Rate	Soil Depth	Conventional Tillage		No Tillage	
lbs/a	*in.*	*Limed*	*Unlimed*	*Limed*	*Unlimed*
150	0–2	5.9	5.2	5.9	4.8
	2–6	6.3	5.6	5.9	5.5
	6–12	6.2	5.7	6.0	5.9
300	0–2	5.3	4.9	5.5	4.3
	2–6	5.9	5.1	5.3	4.8
	6–12	6.0	5.5	5.8	5.5

Source: Blevins et al., 1978, *Agron. J.*, 70:322.

should be incorporated to the desired depth before initiating a no-tillage system. If subsoil pH is adequate, maintenance of both surface and subsoil pH can be accomplished with surface lime applications. In no-tillage systems, surface-applied lime every 3 years can be as effective in maintaining surface and subsoil pH as annual lime applications; however, higher lime rates may be needed to effect vertical lime movement. Where incorporation is not possible, surface application of limestone to acid soils is effective even though the immediate effect occurs only near the soil surface. Compared to conventional tillage systems where lime incorporation is feasible, more frequent applications are necessary in no-till systems to maintain soil pH with depth. If subsoil pH is low, surface unincorporated lime applications may have little effect on subsoil pH (Fig. 3-32).

Time and Frequency of Liming Applications

For rotations with legumes and other crops with higher optimum pH ranges (Table 3-8), lime should be applied 3–6 months before seeding. Sufficient time for acid neutralization is particularly important on low pH soils. Applied too close to planting, lime may not have adequate time to react, unless finer particle size lime products are used (pelletized or fluid lime). In cereal-legume rotations, lime is best applied prior to cereal planting to allow more time for the lime to react and increase soil pH. However, lime applications before wheat planting should also accompany control of take-all disease. Caustic forms of lime [CaO and $Ca(OH)_2$] should be spread well before planting to prevent injury to germinating seeds.

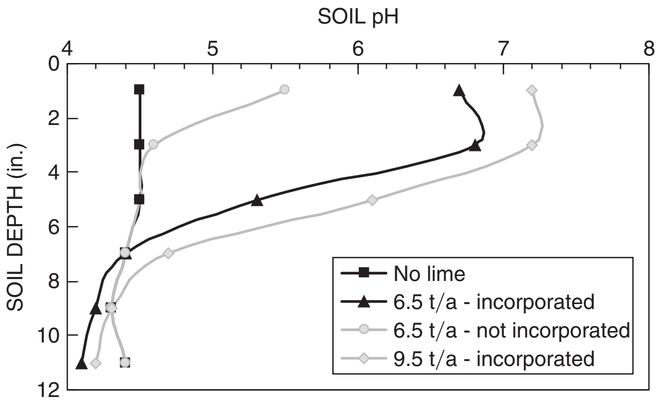


Figure 3-32
Comparison of Ag-lime incorporation on surface soil pH in no-till crop production. Lime applied in 1985, soil sampled in 1992.
(Sawyer and Peck, 1991, Ill. Fert. Conf. Proc., pp. 95–100.)

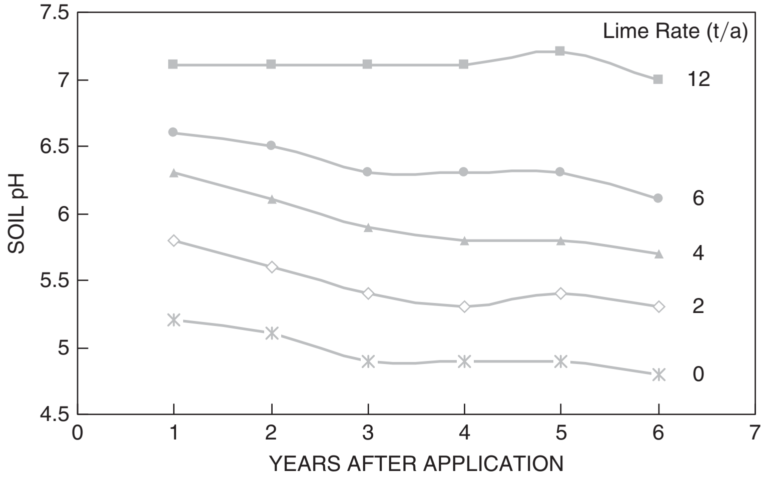


Figure 3-33

Influence of lime rate and time after application on soil pH. Target pH was 6.2, where re-application of 4 t/a every 4–5 years is recommended.

(Patrick et al., 1995, SSSAJ, *95:248–254.)*

Lime application frequency generally depends on soil texture, tillage system, N source and rate, crop removal, precipitation patterns, and lime rate. On sandy soils, more frequent applications are preferable, whereas on fine-textured soils, larger amounts may be applied less often. Finely divided lime (high ECCE) reacts more quickly, but its effect is maintained over a shorter period than coarse materials. The only reliable method to determine re-liming needs is through soil testing (Chapter 9). Samples should be taken at least every 3 years, unless production problems potentially related to soil acidity persist (Fig. 3-33). These data show that liming is required about every 4–5 years to maintain optimum soil pH at 6.2. Regular soil testing is the best way to identify frequency and rate of lime to maintain optimum soil pH.

Equipment

Dry lime applied by the supplier or the producer is the most common method. The spinner truck spreader that distributes lime in a semicircle from the rear of the truck is common in agricultural and turf crops (Fig. 3-34). Smaller equipment in turf, landscape, and other horticultural systems is commonly used. Regardless of the method employed, care should be taken to ensure uniform application. When high lime rates are needed, applying no more than 2 t/a per application will help ensure uniform distribution of lime material. Non-uniform distribution can result in excesses and deficiencies in different parts of the same field and corresponding non-uniform crop growth.

Plant and soil response to liming Adding lime to neutralize exchangeable acids will change pertinent soil test properties (Table 3-19). Maintaining a regular soil testing program where soils are sampled and analyzed every 2–3 years is essential to removing soil acidity as a limiting factor to optimum plant growth. In most mineral soils, liming to pH 5.5–6.5, depending on the plant (Table 3-8), substantially reduces exchangeable Al^{+3} (Fig. 3-12). When lime is added to acid soils, exchangeable and solution Al^{+3} is reduced by precipitation as $Al(OH)_3$, which increases yield potential (Table 3-20). As a result of reduced adsorbed and solution Al^{+3}, Al toxicity potential is greatly reduced. Many studies have demonstrated an increase in crop productivity with an increase in soil pH (Table 3-21, Fig. 3-35).

Figure 3-34
Common field scale lime application equipment. Top photo shows a spinner spreader, whereas the photo below it is a close-up of the spinner device. The third photo shows a forced-air applicator, and the bottom photo shows a liquid applicator for fluid lime.

(First Photo: Stahly. Second Photo: Adams Fertilizer Equipment Manufacture.)

TABLE 3-19
EFFECT OF INCREASING LIME RATE ON SOIL TEST PROPERTIES

Lime Rate[1]	Soil pH	P	K	Ca	Mg	K	Na	H	CEC
t/a		ppm		meq/100 g Soil					
0	5.25	19.1	112	7.6	1.6	0.2	0.8	5.4	15.5
0.5	5.38	18.1	126	8.1	1.7	0.2	0.8	5.4	16.2
1	5.48	15.7	119	8.5	1.8	0.2	0.8	3.3	14.6
2	5.71	21.7	145	9.7	2.2	0.2	0.9	2.1	15.2
3	6.28	16.2	114	10.3	2.4	0.2	0.9	0	13.8
4	6.49	22.2	121	10.9	2.6	0.2	0.7	0	14.4
6	6.84	29.2	126	11.5	2.8	0.2	0.8	0	15.3
8	7.18	31.5	123	12.3	3.0	0.2	0.8	0	16.2

[1] ECCE; broadcast incorporated May 1999; soil samples collected Oct 2003 (0–6-in. depth).

Note: Shaded columns represent significant responses to lime rate.

Source: S. Henning, 2004, Iowa State Univ., ISRF04-13.

TABLE 3-20
LIME EFFECTS ON WHEAT YIELDS, SOIL pH, AND EXTRACTABLE Al^{+3}

Lime Rate	Wheat Yield	Soil pH	Al^{+3}
lb ECC/a	bu/a		ppm
0	14	4.6	102
3,000	37	5.1	26
6,000	38	5.9	0
12,000	37	6.4	0

Note: 1986–89 average yield data; soil pH and KCl extractable Al^{+3} measured in 1989.

Source: Whitney and Lamond, 1993, *Liming Acid Soils*, Kansas State Univ. Coop. Ext. MF-1065.

TABLE 3-21
AVERAGE CROP RESPONSES TO LIME FROM 1992 TO 2003

Crop	Unlimed	Limed	Lime Response	
	t/ha			%
Wheat	1.45	3.10	1.64	113
Oat	1.96	2.48	0.52	26
Triticale	1.88	2.77	0.89	47
Canola	0.83	1.66	0.85	101
Pea	0.36	1.21	0.85	241
Lupin	1.39	1.41	0.02	1

Note: Crops grown in rotation.

Source: Adapted from Li and Conyers, 2006, *Crop Responses to Lime*, NSW Dept Primary Ind., Prinefact 33.

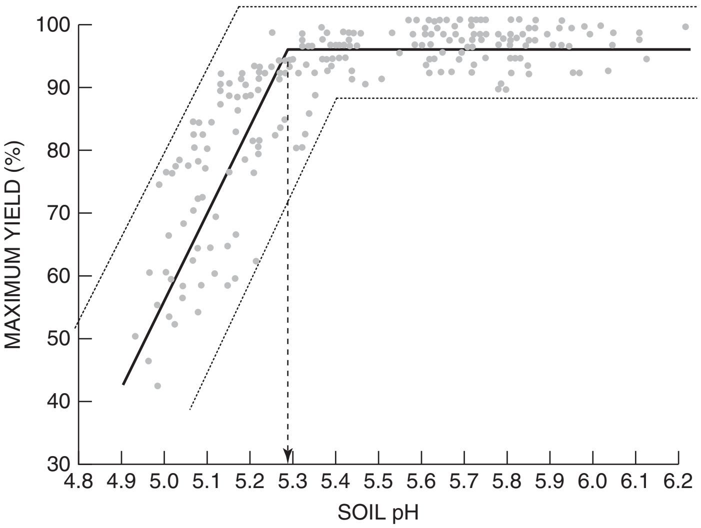


Figure 3-35
Effect of increasing soil pH on relative wheat yield.
(Mahler and McDole, 1987.)

On alfisols and mollisols, liming to pH 6.4–6.6 is optimum for most crops except forage legumes (alfalfa, sweet clover), whereas liming to pH 6.7–6.9 is recommended. Liming ultisols and oxisols to pH 5.5–6.0 is suitable for most plants; overliming these soils can reduce micronutrient availability. Liming highly weathered soils is essential for production of most legume crops (Table 3-22). Symbiotic N_2 fixation is favored by adequate liming (Chapter 4). Activity of rhizobium is restricted by soil pH < 6.0; thus, liming will increase legume growth because of increased N_2 fixation. Adequate liming is also essential for plants to utilize residual or applied N (Fig. 3-36).

In soils with high OM content, exchangeable Al^{+3} is strongly adsorbed to R-COO^- sites (Fig. 2-10) reducing soluble Al^{+3}, and potential Al toxicity, compared to mineral soils. As a result, the critical pH below which plant yield is reduced (pH ~5) is lower than that for mineral soils. Thus, liming high OM soils to pH 5 provides adequate Ca to reduce Al^{+3}/H^+ toxicity effects on plant growth (Table 3-22).

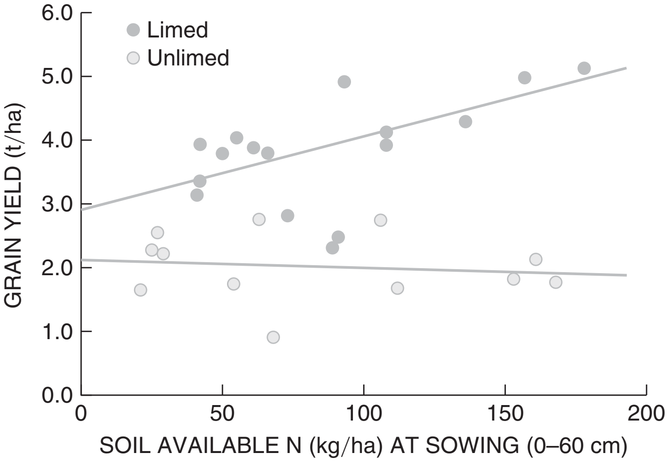
In low pH, high Al and Fe oxide soils, P precipitates as insoluble Fe/Al-P compounds (Chapter 5). Liming these acidic soils will precipitate Al^{+3} as $Al(OH)_3$, thus

TABLE 3-22
EFFECT OF LIMING ON SOIL pH AND NODULATION IN SOYBEAN

Soil	pH	Shoot Dry Weight	Nodules
		g/pot	*number/pot*
Ultisol	4.6	2.4	21
	5.2	3.2	64
	5.9	3.6	77
Histosol	4.3	1.4	0
	4.5	2.3	64
	4.7	3.5	165
	5.1	2.9	113
	5.3	2.7	91

Source: Sartain and Kamprath, 1975, *Agron. J.*, 67:507–510; Mengel and Kamprath, 1978, *Agron. J.*, 70:959–963.

Figure 3-36
Liming effect on wheat response to plant available N in the soil.
(Li and Conyers, 2006, Crop responses to lime, NSW Dept Primary Ind., *Prinefact 33.)*



increasing plant available P. Alternatively, liming soils to >pH 6.8–7.0 can reduce P availability because of the precipitation of Ca or Mg phosphates. A liming program should be planned so that the pH can be kept between 5.5 and 6.8, depending on crop, if maximum benefit is to be derived from applied P. With the exception of Mo, micronutrient availability decreases with increasing pH (Chapter 8). Lime addition reduces solution concentration of many micronutrients, although soil pH values of 5.5–6.0 are usually sufficient to maintain adequate micronutrient availability. Overliming will reduce micronutrient availability below needed levels. A regular soil testing program will help identify potential nutrient problems.

Liming has a significant role in the control of certain plant pathogens. Clubroot is a disease of cole crops that reduces yields and causes infected roots to enlarge and become distorted. Lime does not directly affect the clubroot organism, but at soil pH > 7 germination of clubroot spores is inhibited (Table 3-23). Alternatively, liming increases the incidence of diseases such as scab in root crops. Severity of take-all infection in wheat, with resultant yield reductions, is increased by liming soils to near neutral pH. Lime applications before wheat planting are not advised unless take-all disease has been controlled.

Structure of fine-textured soils may be improved by liming, as a result of enhanced flocculation of Ca-saturated clays. Favorable effects of lime on soil structure include reduced soil crusting, better emergence of small-seeded crops, and lower power requirements for tillage operations. However, the overliming of oxisols and ultisols can result in the deterioration of soil structure, with a decrease in water percolation.

TABLE 3-23
EFFECT OF LIMING ON CLUBROOT DISEASE IN CAULIFLOWER

Lime Rate	Marketable Yield	Clubroot Rating[1]	Soil pH at Harvest
t/a	%		
0	38	3.5	5.6
2.5	56	2.7	6.5
5.0	77	2.2	6.8
10.0	80	1.5	7.2

[1] Clubroot rating = Σ [# roots at a rating × rating]/total # roots.
Rating: 0, no visible clubroot; 1, fewer than 10 galls on the lateral roots; 2, more than 10 galls on the lateral roots, taproot free of clubroot; 3, galls on taproot; 4, severe clubbing on all roots.
Source: Waring, 1980, Proc. 22nd Lower Mainland Hort. Assoc. Short Course, pp. 95–96.

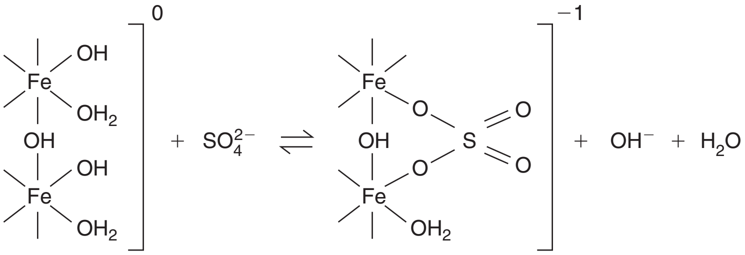


Figure 3-37
Potential mechanism for increasing subsoil pH through SO_4^{-2} adsorption following application of $CaSO_4 \cdot 2H_2O$ (gypsum).

Even at high application rates, lime may have only minimal effects on acidity below the depth of incorporation. Gypsum can improve the rooting environment to about 0.75-m depth depending on the soil. As discussed earlier, gypsum is not a liming material; however, application of gypsum has been shown to ameliorate subsoil acidity in highly weathered soils. The increase in pH may be related to adsorption of SO_4^{-2} on Al/Fe oxides with subsequent release of OH^- and the precipitation or polymerization of Al due to the reaction with OH^- (Fig. 3-37). The negative charge developed by this reaction results in Ca^{+2} being held on the exchange site. In general, acid subsoil amelioration in soils with Al-hydroxy interlayer minerals requires greater quantities of gypsum than soils that are dominantly kaolinitic. To determine which soils are responsive to gypsum applications, pH measurements are made of acid subsoils with solutions of KCl and K_2SO_4. Responsive soils will have a higher pH in K_2SO_4 than in KCl due to the replacement of OH^- from the hydrated oxides of Al and Fe by SO_4^{-2}. Unless acid subsoils contain appreciable amounts of hydrated Al and Fe oxides, application of gypsum will not be effective in alleviating subsoil acidity.

CALCAREOUS SOILS

General Description

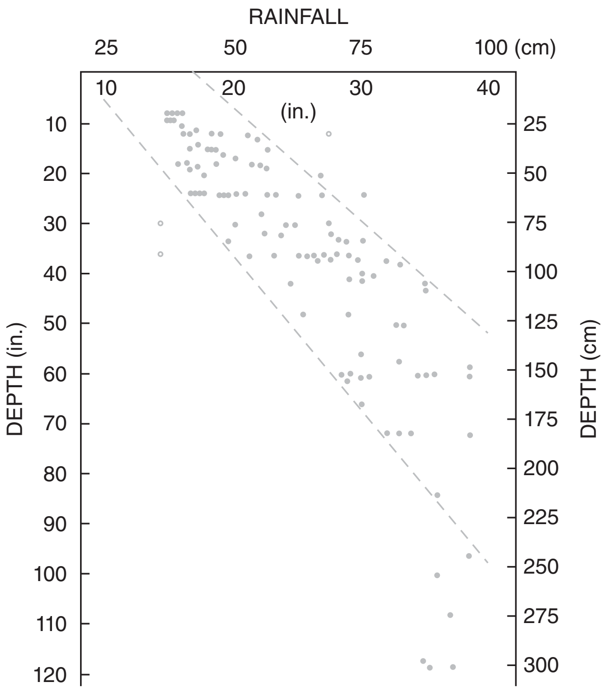
Calcareous soils contain measurable quantities of native $CaCO_3$ mineral. These soils commonly occur in semiarid and arid regions where annual precipitation is <20 in. and will have soil pH values > 7.2 (Figs 3-1 and 3-2). Globally, about 6% of total ice-free land area soils are classified as calcareous (Table 3-24). As precipitation increases from semiarid to humid regions, depth to $CaCO_3$ increases

TABLE 3-24
GLOBAL DISTRIBUTION OF CALCAREOUS, SALINE, AND SODIC SOILS

	Land Area							
Region	Total[1]	Cultivated	Calcareous[2]		Saline[2]		Sodic[2]	
	ha × 10^6	ha × 10^6	ha × 10^6	%	ha × 10^6	%	ha × 10^6	%
World	13,100	1,500	796.2	6.1	187.3	1.4	135.3	1.0
America								
North	1,867	216	114.7	6.1	0.1	0.0	10.7	0.6
South/Central	2,005	144	24.3	1.2	24.3	1.2	34.7	1.7
Asia	3,094	505	315.4	10.2	95.4	3.1	30	1.0
Europe	2,207	277	56.7	2.6	2.3	0.1	7.9	0.4
Africa	2,964	219	171.2	5.8	48.6	1.6	13.8	0.5
Oceania	849	46	113.9	13.4	16.6	2.0	38.1	4.5

[1] Ice-free land area.
[2] Percenatge of acid topsoils of the total land area.

Figure 3-38
As rainfall increases from one region to another, the depth to measurable $CaCO_3$ content increases. Thus, in arid and semiarid regions, $CaCO_3$ is present in the surface soil.



(Fig. 3-38). Generally, when annual precipitation exceeds 30–40 in., no free lime is present in the rooting zone. The pH of a soil containing $CaCO_3$ in equilibrium with atmospheric CO_2 is 8.5; however, the 10-fold higher CO_2 content in soil air decreases pH to 7.2–7.5. Calcareous soils with pH > 7.6 are influenced by high salt and/or Na.

The presence of $CaCO_3$ will generally not reduce plant productivity; however, common production problems observed in calcareous soils include low P (Chapter 5) and micronutrient availability (Chapter 8), especially with plants less tolerant of low levels of these nutrients.

Acidifying Calcareous Soil

Calcareous soils can be very productive, although water is frequently the most limiting plant growth factor. Plants favoring acid soils will not be productive on calcareous soils; this is especially true for plants with low optimum soil pH (Table 3-8). For example, blueberry and azalea production is not possible in calcareous soils. Micronutrient deficiencies commonly affect many turfgrass species grown on calcareous surface soils (Chapter 8).

In regions where the surface soil is slightly acidic, land leveling to facilitate surface irrigation can expose calcareous subsoils that are less favorable for plant growth. Problems of high soil pH are not confined to arid and semiarid areas. Acidifying paddy soil has increased rice yields, which is often related to increased availability of micronutrients. In humid regions, overliming or dust from limestone-graveled roads may blow onto field borders, increasing soil pH. In other areas, moderately acidic soils may need further acidification for optimum production of blueberries, cranberries, azaleas, rhododendrons, camellias, potatoes, and conifer seedlings.

Acidifying calcareous soils can be difficult and expensive. To decrease soil pH, $CaCO_3$ in the soil must be dissolved or neutralized by adding acid or acid-forming materials. In most field crop situations, reducing soil pH by neutralizing $CaCO_3$ is not practical. For example, the quantity of elemental S° needed to neutralize a soil with only 2% $CaCO_3$ (0–6-in. depth) is estimated by:

2% $CaCO_3$ content in 6-in. surface soil depth ($\sim 2 \times 10^6$ lb soil/afs)

$$2\%\ \mathrm{CaCO_3} = \frac{2\ \mathrm{g\ CaCO_3}}{100\ \mathrm{g\ soil}} = \frac{2{,}000\ \mathrm{mg\ CaCO_3}}{100\ \mathrm{g\ soil}}$$

$$\frac{2{,}000\ \mathrm{mg\ CaCO_3}}{100\ \mathrm{g\ soil}} \div \frac{50\ \mathrm{mg\ CaCO_3}}{\mathrm{meq}} = \frac{40\ \mathrm{meq\ CaCO_3}}{100\ \mathrm{g\ soil}}$$

Thus, if there are 40 meq $CaCO_3$, then 40 meq of acid is required to neutralize the $CaCO_3$ (remember meq A = meq B), thus:

$$\frac{40\ \mathrm{meq\ CaCO_3}}{100\ \mathrm{g\ soil}} = \frac{40\ \mathrm{meq\ S^\circ}}{100\ \mathrm{g\ soil}}$$

$$\frac{40\ \mathrm{meq\ S^\circ}}{100\ \mathrm{g\ soil}} \times \frac{16\ \mathrm{mg\ S^\circ}}{\mathrm{meq}} = \frac{640\ \mathrm{mg\ S^\circ}}{100\ \mathrm{g\ soil}} = \frac{0.64\ \mathrm{g\ S^\circ}}{100\ \mathrm{g\ soil}} = \frac{0.64\ \mathrm{lb\ S^\circ}}{100\ \mathrm{lb\ soil}}$$

$$\frac{0.64\ \mathrm{lb\ S^\circ}}{100\ \mathrm{lb\ soil}} \times \frac{2 \times 10^4}{2 \times 10^4} = \frac{12{,}800\ \mathrm{lb\ S^\circ}}{2 \times 10^6\ \mathrm{lb\ soil}} \times \frac{1\ \mathrm{t}}{2{,}000\ \mathrm{lb}} = \frac{6.4\ \mathrm{t\ S^\circ}}{\mathrm{afs}}$$

Once neutralized, soil pH would likely be about the same as before neutralization because the CEC would still be nearly 100% saturated with basic cations (100% BS). To ultimately lower soil pH below 7, additional S° would be needed to produce H^+ and Al^{+3}, which would in turn reduce the BS necessary to lower soil pH. The additional quantity of S° can be estimated similarly to the pH-BS calculations shown earlier. More importantly, 6.4 t S/a would be very expensive and thus impractical. On calcareous soils, it is more logical to plant crops tolerant of higher soil pH (Table 3-8). However, it is practical to lower calcareous soil pH if a small volume (or mass) of soil is used, typical of horticultural landscape or potted plants.

If the soil is not calcareous and needs to be acidified, then the chemistry of soil acidification is the reverse of liming acid soils. For example, assume a soil at pH 6.5 is acidified to pH 5.5 (CEC = 20 meq/100 g soil). Using Figure 2-11, the estimated quantity of S° needed is:

at soil pH 6.5 →	~75% BS
at soil pH 5.5 →	~50% BS
	~25% decrease in %BS

$$0.25 \times \frac{20\ \mathrm{meq\ CEC}}{100\ \mathrm{g\ soil}} = \frac{5\ \mathrm{meq\ base\ reduction}}{100\ \mathrm{g\ soil}} = \frac{5\ \mathrm{meq\ acid\ needed}}{100\ \mathrm{g\ soil}}$$

$$\frac{5\ \mathrm{meq\ S^\circ}}{100\ \mathrm{g\ soil}} \times \frac{16\ \mathrm{mg\ S^\circ}}{\mathrm{meq}} = \frac{80\ \mathrm{mg\ S^\circ}}{100\ \mathrm{g\ soil}} = \frac{0.08\ \mathrm{g\ S^\circ}}{100\ \mathrm{g\ soil}} = \frac{0.08\ \mathrm{lb\ S^\circ}}{100\ \mathrm{lb\ soil}}$$

$$\frac{0.08\ \mathrm{lb\ S^\circ}}{100\ \mathrm{lb\ soil}} \times \frac{2 \times 10^4}{2 \times 10^4} = \frac{1{,}600\ \mathrm{lb\ S^\circ}}{2 \times 10^6\ \mathrm{lb\ soil}} = \frac{1{,}600\ \mathrm{lb\ S^\circ}}{\mathrm{afs}}$$

TABLE 3-25
QUANTITY OF ELEMENTAL S° REQUIRED TO REDUCE SOIL pH (7-IN. DEPTH)

Desired pH Change	Sands	Loamy Sands	Sandy Loams	Loams	Clay Loams	Organic
			lb S/a			
7.0–6.0	300	400	500	700	1,100	1,750
6.0–5.0	800	1,000	1,200	1,400	1,400	2,750
5.0–4.0	800	1,000	1,200	1,400	1,400	4,500
			lb S/1,000 ft^2			
7.0–6.0	7	10	12	16	25	39
6.0–5.0	18	23	28	32	32	63
5.0–4.0	18	23	28	32	41	103

Note: The conversion from lb/a to lb/1,000 ft^2 is lb/43,560 ft^2 (or 1 acre) ÷ 43.56 = lb/1,000 ft^2.
Source: USDA Handbook #60, Diagnosis and improvement of saline and alkaline soils.

This S° application rate is similar to that needed to acidify the loam/clay loam soil from pH 6 to pH 5 (Table 3-25). Any differences would be related to differences in the CEC used in the above calculation and that assumed for the textural classes in Table 3-25. In addition, the pH-BS relationship in Figure 2-11 is a general representation, which would vary between soil types.

These calculations are illustrated for elemental S°; however, several acidic or acid-forming materials can be used. The calculations are conducted in the same manner with the other materials, although the equivalent weight of each compound is different (see pg. 30).

Sources of Acids

Elemental S°

Elemental S° is an effective soil acidulent. When S° is applied, the soil reaction is:

$$S + 1.5O_2 + H_2O \rightleftarrows SO_4^{-2} + 2H^+$$

For every mole of S° applied and oxidized, 2 moles of H^+ are produced, which decreases soil pH. S° oxidation is a microbial mediated process that may be slow, particularly in cold and dry alkaline soils with no history of S° application. Finely ground S° should be broadcast and incorporated several weeks or months before planting to assure complete reaction.

Under some conditions, it may be advisable to acidulate a zone near plant roots to increase micronutrient and/or P availability. Both of these conditions frequently need to be corrected on saline-alkaline soils. Elemental S° can be applied in bands as either granular S° or S° suspensions. When S° is band applied, lower rates are required than broadcast S° (Chapter 7).

Sulfuric Acid

Sulfuric acid (H_2SO_4) has been used for reclaiming Na- or B-affected soils, increasing availability of P and micronutrients, reducing NH_3 volatilization potential, increasing water penetration, controlling certain weeds and soilborne pathogens, and enhancing the establishment of range grasses. The favorable influence of H_2SO_4 and other acidifying treatments on sorghum (Fig. 3-39) and rice yield (Table 3-26) is partially related to increased nutrient availability.

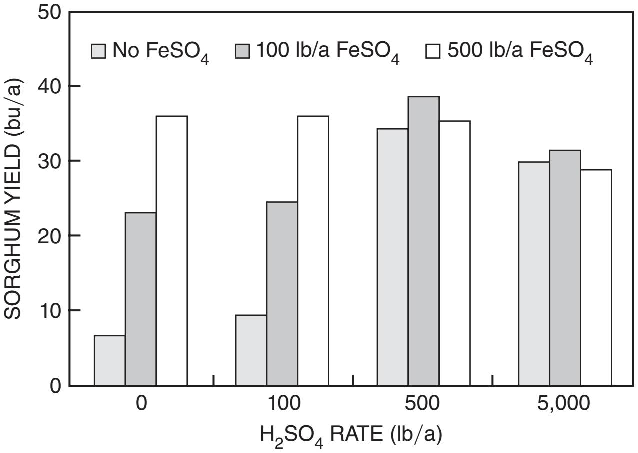


Figure 3-39
Effects of H_2SO_4 and $FeSO_4$ on grain sorghum yields on a calcareous soil. Reducing soil pH with H_2SO_4 increases Fe availability to similar levels as adding $FeSO_4$.
(Mather, 1985, Fertilizer Technology and Use, *Soil Sci. Soc. Am.)*

TABLE 3-26
EFFECT OF SOIL ACIDIFIERS ON THE YIELD OF TWO VARIETIES OF RICE

Soil Amendment	Bluebonnet 50	IR661
	bu/a	
Control	40	87
Gypsum	43	96
S	48	100
H_2SO_4	55	104

Source: Chapman, 1980, *Aust. J. Exp. Agric. Animal Husb.*, 20:725–730.

H_2SO_4 can be added directly to the soil, but it requires the use of special acid-resistant equipment and clothing. It can be dribbled on the surface or applied with a knife applicator (Chapter 10). It can also be applied in high pH or HCO_3^- containing irrigation water. H_2SO_4 has the advantage of reacting instantaneously with the soil.

Aluminum Sulfate

Aluminum sulfate $[Al_2(SO_4)_3]$ is used by floriculturists for acidulating soil for production of azaleas, camellias, and similar acid-tolerant ornamentals, although it is not commonly used in agriculture. When $Al_2(SO_4)_3$ is added to water, it hydrolyzes to produce an acid solution:

$$Al_2(SO_4)_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 6H^+ + 3SO_4^{-2}$$

Iron sulfate $(FeSO_4)$ is applied to soils for acidification and as an Fe source will behave similarly to $Al_2(SO_4)_3$. Use this product with caution as increasing Al^{+3} in solution may promote Al toxicity problems.

Ammonium Polysulfide

Liquid ammonium polysulfide (NH_4S_x) is used to lower soil pH and to increase water penetration in irrigated saline-alkaline soils. It can be applied in a band 3–4 in. to the side of the seed or metered into furrow irrigation systems. Band application is more effective in correcting micronutrient deficiencies than application through irrigation water. The polysulfide decomposes into ammonium sulfide and colloidal S° when applied. The S° and S^{-2} are oxidized to H_2SO_4. Potassium polysulfide can also be used.

Organic Sources

Any organic material incorporated into the surface soil will ultimately reduce soil pH, except in calcareous soils. Examples of such materials are yard waste, pine straw, sawdust, and peat. Generally, the higher the N content (lower C:N ratio) of the residue, the more acid will be generated through mineralization of organic N to NH_4^+ and its subsequent nitrification to NO_3^- (Table 3-3; Chapter 4). Use of high C:N ratio materials (sawdust, pine straw, etc.) will produce acids, but also will immobilize plant available N, thus additional N may be needed to meet plant N requirement (Chapter 4). For maximum benefit, organic materials should be incorporated into the surface 3–4 in. of soil. The decrease in soil pH will depend on the material source and quantity incorporated. Heavy application rates are generally needed.

Acidification in Fertilizer Bands

Because of the high BC for pH in calcareous soils, it is usually too expensive to use enough acidifying material for complete neutralization of $CaCO_3$. It is unnecessary to neutralize the entire soil mass because soil zones more favorable for root growth and nutrient uptake can be created by confining the acid-forming materials to bands and other localized placement. Band-applied ammonium thiosulfate and ammonium polyphosphate fertilizers can acidify soil in and near the band, which can increase micronutrient availability.

SALINE, SODIC, AND SALINE-SODIC SOILS

Soluble salts occur in all natural waters. Sea water contains 2.2 lb salt/ft^3, while fresh water contains 0.01 lb salt/ft^3. Thus, sea water is 220 times saltier than fresh water. Soil water also contains soluble salts, where the quantity of salt in the root zone can vary widely. When the salt concentration increases, soils can become *salt-affected*, restricting plant growth depending on the salt concentration and the salt tolerance of the plant. Soil salinity can increase to excessive levels either naturally or by poor irrigation water management. Salt-affected soils commonly occur in arid regions and semiarid regions, where generally soil $pH > 7.2$ (Figs 3-1 and 3-2). Only 2.5% of the world's land area is saline or sodic (Table 3-24). However, current estimates suggest that 6–8% of cropland is salt affected. Development of salt-affected irrigated soils is the most common form of chemical degradation of soil and increasingly affects crop productivity. The primary processes involved in salt accumulation in soils are:

- weathering of rocks and parent materials
- high water table with high evaporative demand
- exposure to salt water spray or flooding near the ocean; sea water intrusion into groundwater
- poor quality (high salt) irrigation water; irrigation mismanagement, with poor internal soil drainage
- excessive application of salts in fertilizer, animal manure, or compost

Rapid extension of irrigated lands over the last four decades has increased salinity of cultivated soils. Large areas of the Indian subcontinent have been rendered unproductive by salt accumulation. Salinity is a major problem in paddy rice production.

Under low rainfall, high evaporative conditions in arid regions, H_2O moves upward from shallow water tables and evaporates, leaving salts at the soil surface to form saline, sodic, or saline-sodic soils (Fig. 3-40). Runoff water containing additional salts is collected in landscape depressions, increasing salt accumulation. These soils are widespread in semiarid and arid regions, where rainfall is not sufficient for adequate leaching, usually <20 in./yr (Figs 3-3 and 3-41).

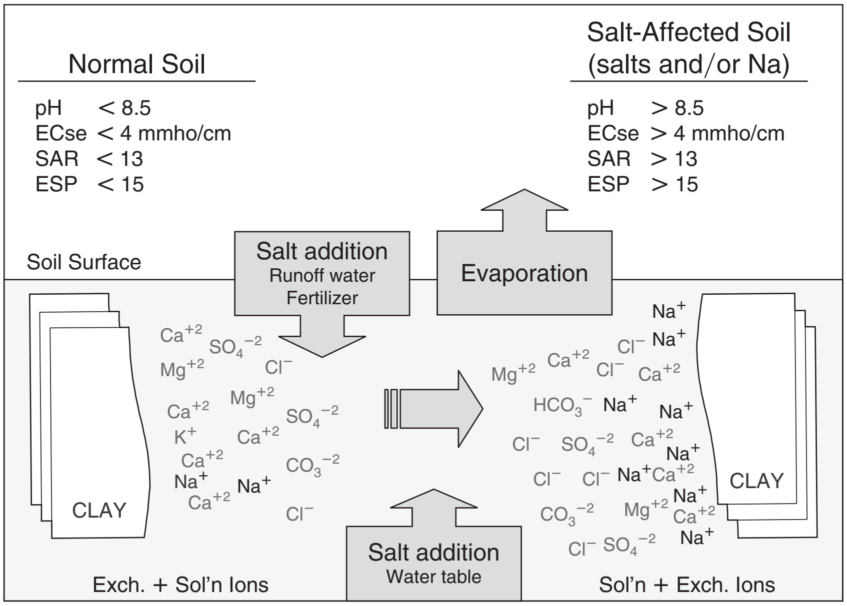


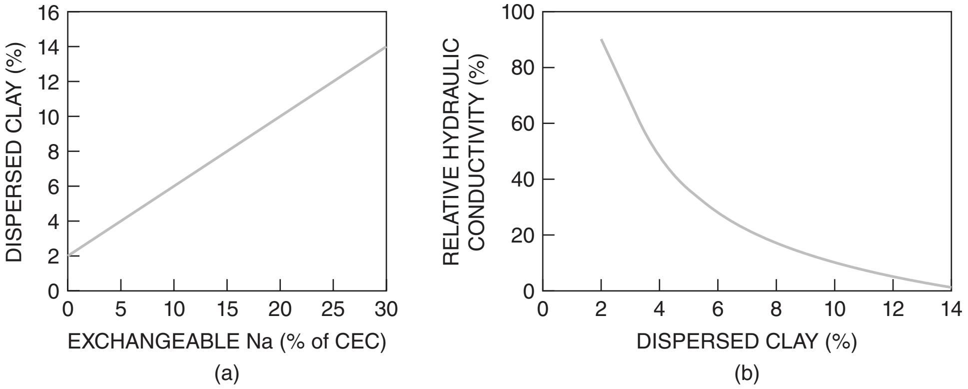
Figure 3-40
Processes involved in development of saline, sodic, or saline-sodic soils.

Figure 3-41
Areas in the United States where soil salinity limits yield potential.
(USDA-NRCS, 1992.)

Accumulated salts contain the cations Na^+, K^+, Ca^{+2}, and Mg^{+2}, and the anions Cl^-, SO_4^{-2}, HCO_3^-, and CO_3^{-2}. They can be weathered from minerals and accumulate in areas where the precipitation is too low to provide leaching. Na is particularly detrimental, because of its both toxic effect on plants and effect on soil structure. When a high percentage of the CEC is occupied by Na^+, soil aggregates disperse, reducing natural aggregation and soil structure. These soils become impermeable to water, develop hard surface crusts, and may keep a water layer, or "slick spot," on the surface longer than low Na^+ soils. As exchangeable Na^+ increases, the percentage of dispersed clay increases (Fig. 3-42), resulting in substantial decreases in hydraulic conductivity (or less permeability to water).

Dispersion problems occur at different exchangeable Na^+ contents. Fine-textured soils with montmorillonitic clays disperse when approximately 15%

Figure 3-42
Increasing exchangeable Na content increases the amount of clay dispersed (a) and decreases the hydraulic conductivity (b).



of the CEC is Na^+ saturated. On tropical soils high in Fe and Al oxides and on some kaolinitic soils, 40% Na^+ saturation is required before dispersion is serious. Soils with low clay content are also less prone to problems because they are more permeable.

Definitions

Saline soils Saline soils have an *electrical conductivity of the saturated extract* (ECse) > 4 mmho/cm, pH < 8.5, and *exchangeable sodium percentage* (ESP) $< 15\%$ (Table 3-27; Fig. 3-43). Saline soils were formerly called *white alkali* because of the deposits of salts on the surface following evaporation. The excess salts can be leached out, with no appreciable rise in pH. The concentration of soluble salts is sufficient to interfere with plant growth, although salt tolerance varies with plant species.

Sodic soils Sodic soils occur when ESP $> 15\%$, ECse < 4 mmho/cm, and pH > 8.5 (Table 3-27). They were formerly called *black alkali* because of the dissolved OM deposited on the surface along with the salts. In sodic soils, excess Na^+ disperses soil colloids and creates nutritional disorders in most plants.

Saline-sodic soils Saline-sodic soils have both ECse > 4 mmho/cm to qualify as saline and high exchangeable Na^+ ($>15\%$ ESP) to qualify as sodic; however, soil pH is usually <8.5. In contrast to saline soils, when the salts are leached

TABLE 3-27
CLASSIFICATION AND PROPERTIES OF SALT-AFFECTED SOILS

Classification	ECse (mmho/cm)[1]	Soil pH	ESP %	Physical Condition
Saline	>4	<8.5	<15	Normal
Sodic	<4	>8.5	>15	Poor
Saline-sodic	>4	<8.5	>15	Normal

[1] ECse represents the electrical conductivity of the saturated extract. Distilled H_2O is added to a soil sample to exactly fill the pore space. After equilibration, the soil water is removed through vacuum filtration. An electrode is inserted into the saturated soil extract and the electrical conductivity is measured. A high ECse means a high salt concentration (more ions in solution conduct more current). Low salt concentration would result in a low ECse reading. The unit mmho/cm comes from the unit of electrical resistance (ohm), such that conductivity, or the opposite of resistance, is given the unit "mho." An "mmho" is 0.001 × mho. The "cm" unit in mmho/cm comes from the separation distance between the $(-)$ and $(+)$ charged surfaces of the electrode that senses ECse.

Also, mmho/cm = ds/m in SI units; where ds = decisiemen.

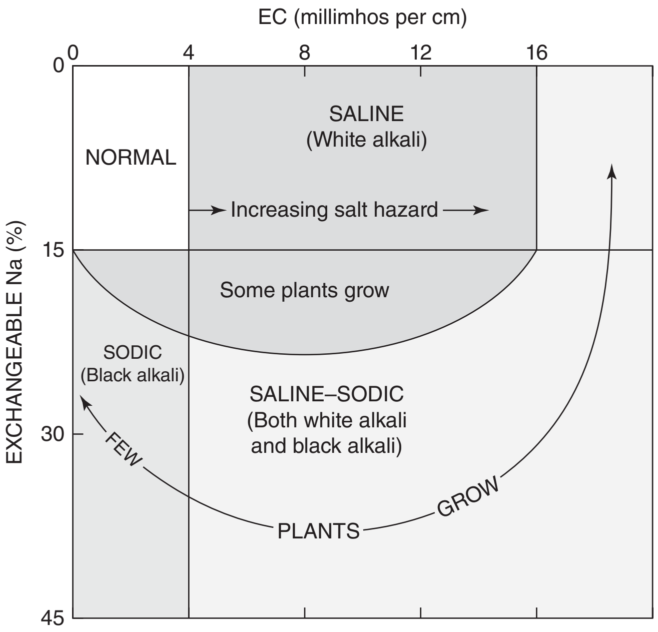


Figure 3-43 *Classification system or saline, sodic, and saline-sodic soils.* (*U.S. Salinity Lab*, Handbook 60, 1954.)

out, the exchangeable Na^+ hydrolyzes and the pH increases, which results in a sodic soil (Table 3-27).

Relationships

Several interrelated parameters are commonly used to quantify salt- and Na^+-affected soils. By measuring ECse of a soil, the total quantity of salts in the soil solution can be estimated by:

$$\text{ECse} \times 10 = \text{total soluble cations (meq/L)}$$

Also,

$$\text{Total dissolved salts (ppm or mg/L)} = 640 \times \text{ECse (mmho/cm)}$$

If the soluble cations are measured in the saturated extract, the *sodium adsorption ratio* (SAR) can be calculated by:

$$\text{SAR} = \frac{Na^+}{\sqrt{\dfrac{(Ca^{+2} + Mg^{+2})}{2}}} \quad [\text{all units in meq/L soil water}]$$

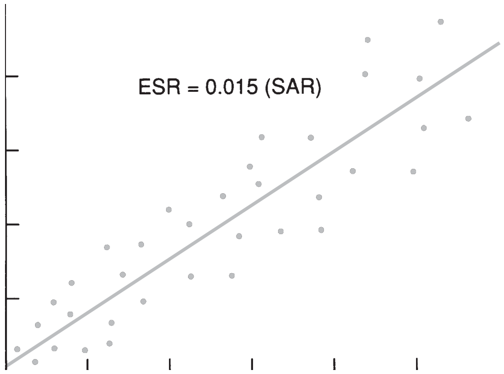
Although SAR represents the ratio of cations in solution, values ≥13 usually indicate high exchangeable Na^+. Because of the equilibrium relationships between solution and exchangeable cations in soils, the SAR should be related to the quantity of Na^+ on the CEC, which is expressed as the *exchangeable sodium ratio* (ESR). The ESR is defined by:

$$\text{ESR} = \frac{\text{Exchangeable } Na^+}{\text{Exchangeable } (Ca^{+2} + Mg^{+2})} \quad [\text{all units in meq/100 g soil}]$$

The relationship between solution and exchangeable cations in salt-affected soils can be used to estimate the ESR from the SAR if the quantity of exchangeable cations has not been measured (Fig. 3-44). The following equation represents the linear relationship:

$$\text{ESR} = 0.015\ (\text{SAR})$$

Figure 3-44
Relationship between ESR and SAR in salt-affected soils.



Again, ESR (cations on CEC) is being estimated from the concentration of Ca^{+2}, Mg^{+2}, and Na^{+} in soil solution. Subsequently, ESR is related to ESP previously used to classify Na^{+}-affected soils (Table 3-27) and is given by:

$$\text{ESP} = \frac{\text{Exchangeable Na}^{+}}{\text{CEC}} \times 100 \quad [\text{all units in meq/100 g soil}]$$

Thus, if a laboratory provides the concentration of exchangeable cations (meq/100 g soil), the ESP can be directly calculated. If the laboratory only measured cation concentration in the soil solution, then the ESP can be estimated from the SAR. First, estimate the ESR from the SAR (see above), then estimate the ESP from the ESR by:

$$\text{ESP} = \frac{100\ \text{ESR}}{1 + \text{ESR}}$$

These parameters and interrelationships are valuable in characterizing the solution and exchange chemistry of salt- and Na^{+}-affected soils. The following example illustrates how these relationships can be used. Additional examples are provided in the *Instructors Manual.*

A soil analysis revealed that the saturated extract contained:

$$20\ \text{meq}\ Ca^{+2}/L$$
$$10\ \text{meq}\ Mg^{+2}/L$$
$$100\ \text{meq}\ Na^{+}/L$$

The ECse = 2.2 mmho/cm, soil pH = 8.6, and CEC = 25 meq/100 g soil. Evaluate this soil for potential salinity or sodicity problems. Since the laboratory only provided cation concentrations in the soil solution, first calculate the SAR:

$$\text{SAR} = \frac{100}{\sqrt{\frac{(20 + 10)}{2}}} = 25.8 \quad [\text{all units in meq/L soil water}]$$

then estimate the ESR:

$$\text{ESR} = 0.015\ (25.8) = 0.39$$

then estimate the ESP:

$$\text{ESP} = \frac{100\ (0.39)}{1 + (0.39)} = 28\%$$

Since the ECse < 4 mmho/cm and the ESP $> 15\%$, this soil would be classified as sodic. Gypsum application would likely be recommended to reduce the ESP (see pg. 111 for example calculation).

Effects on Plant Growth

Soil salinity limits plant growth by (1) a water imbalance in the plant (physiological drought), (2) ion imbalances that result in increased energy consumption (carbohydrate respiration) to maintain metabolic processes, and (3) toxicity from Na^+ and Cl^-. Decreasing the osmotic potential of soil water due to elevated salt concentration reduces water movement into plant root cells, causing the cell to collapse (plasmolysis). The plant may show signs of drought stress. Early signs of salt stress are chlorosis (leaf yellowing) or darker bluish-green leaf color depending on the plant species. In each case plants are stunted with shortened internodes. Symptoms show up first in older needles and leaves, where salts accumulate. In conifers, needles are yellow and turn brown from the tips downward. Broadleaf plants and woody species show the greatest symptoms at leaf tips and margins, which eventually turn necrotic. Saline irrigation water can also result in leaf burn, depending on the crop (Table 3-28). As soil salinity increases above threshold levels (Table 3-29), plant growth rate decreases. Top growth is usually affected more than root growth.

High Na^+ is toxic to plants roots, especially during drought conditions when Na^+ concentration in the soil solution increases and enhances dehydration of root tissue. Under sodic conditions, Na^+ can replace Ca^{+2} in cell membranes, increasing membrane permeability and transport of ions. Many plants, especially grasses, accumulate Na^+ in leaves, resulting in necrosis of leaf tips and edges.

Although Cl^- is an essential micronutrient, excess Cl^- in soil solution or in irrigation water can reduce productivity in sensitive crops. Woody plants are more sensitive to Cl^- than non-woody species. For most crops, the salinity tolerance provides an approximate guideline for Na^+ and Cl^- toxicity (Table 3-29).

Toxicity to excessive B occurs in some arid region soils. B accumulates in leaf tissues causing necrosis. Removing grass clippings can help remove some B from the system. Most turf grasses are B tolerant, whereas many fruit and vegetable crops are sensitive (Chapter 8).

Although in most situations yield decrease is related to total salt concentration in the soil solution, excess soil salinity may induce nutrient imbalances (deficiencies or toxicities). For example, excessive SO_4^{-2} and low Ca^{+2} and/or Mg^{+2} can occur in saline soils, causing internal browning in lettuce, blossom-end rot in tomato and pepper, and blackheart in celery.

Plants differ greatly in their tolerance to soil salinity (Table 3-29). For example, old alfalfa is more tolerant than young alfalfa. Barley and cotton have considerable

TABLE 3-28
SENSITIVITY OF SEVERAL CROPS TO LEAF BURN CAUSED BY Cl^- IN SPRINKLER IRRIGATION WATER

Tolerant	Semi-Tolerant	Sensitive	Very Sensitive
Cotton	Barley	Alfalfa	Potato
Sugar beet	Corn	Sesame	Tomato
Sunflower	Safflower	Soybeans	Fruit crops
	Sorghum		Citrus fruits

TABLE 3-29
SALT TOLERANCE OF SELECTED CROPS

Crop	Threshold ECse (mmho/cm)	% Yield Decrease/ Unit ECse Increase	ECse @ 50% Yield Loss	Salt Tolerance Rating[1]
Alfalfa	2.0	7.3	8.8	MS
Almond	1.5	19	4.3	S
Apple	1.0	15	4.3	S
Apricot	1.6	24	3.8	S
Avocado	1.0	24	3.1	S
Barley (forage)	6.0	7.1	13.1	MT
Barley (grain)	8.0	5.0	18.0	T
Bean	1.0	19	3.6	S
Beet (garden)	4.0	9.0	9.6	MT
Bentgrass	2.5	7.0	8.3	MS
Bermudagrass	6.9	6.4	14.7	T
Blackberry	1.5	22	3.8	S
Boysenberry	1.5	22	3.8	S
Broad bean	1.6	9.6	6.8	MS
Broccoli	2.8	9.2	8.3	MT
Bromegrass	2.5	7.2	8.7	MT
Cabbage	1.8	9.7	7.0	MS
Canarygrass (reed)	2.0	6.4	7.0	MS
Carrot	1.0	14	4.6	S
Clover (berseem)	1.5	5.8	10.1	MT
Clover (red, ladino, alsike)	1.5	12	5.7	MS
Corn (forage)	1.8	7.4	8.6	MS
Corn (grain, sweet)	1.7	12	5.9	MS
Cotton	7.7	5.2	17.3	T
Cowpea	1.3	14	4.9	MS
Cucumber	2.5	13	6.3	MS
Date	4.0	3.6	17.9	T
Fescue (tall)	3.9	5.3	13.3	MT
Flax	1.7	12	5.9	MS
Grape	1.5	9.5	6.8	MS
Grapefruit	1.8	16	4.9	S
Hardinggrass	4.6	7.6	11.2	MT
Lemon	1.0	14	6.8	S
Lettuce	1.3	13	5.1	MS
Lovegrass	2.0	8.5	7.9	MS
Meadow foxtail	1.5	9.7	6.7	MS
Onion	1.2	16	4.3	S
Orange	1.7	16	4.8	S
Orchardgrass	1.5	6.2	9.6	MT
Peach	3.2	19	5.8	S
Peanut	3.2	29	4.9	MS
Pepper	1.5	14	5.1	MS
Plum	1.5	18	4.3	S
Potato (sweet)	1.5	11	6.0	MS
Potato (white)	1.7	12	5.9	MS
Radish	1.2	13	5.0	MS
Rice (paddy)	3.0	12	7.2	MS
Ryegrass (perennial)	5.6	7.6	12.2	MT
Sorghum	4.8	8.0	11.1	MT
Soybean	5.0	20	7.5	MT
Spinach	2.0	7.6	8.6	MS
Strawberry	1.0	33	2.5	S
Sudangrass	2.8	4.3	14.4	MT
Sugar Beet	7.0	5.9	15.5	T

Crop	Threshold ECse (mmho/cm)	% Yield Decrease/ Unit ECse Increase	ECse @ 50% Yield Loss	Salt Tolerance Rating[1]
Sugarcane	1.7	5.9	10.2	MS
Tomato	2.5	9.9	7.6	MS
Trefoil (big)	2.3	19	4.9	MS
Trefoil (birdsfoot)	5.0	10	10.0	MT
Vetch (common)	3.0	11	7.5	MS
Wheat	6.0	7.1	13.0	MT
Wheatgrass (crested)	3.5	4.0	16.0	MT
Wheatgrass (fairway)	7.5	6.9	14.7	T
Wheatgrass (tall)	7.5	4.2	19.4	T
Wild rye (beardless)	2.7	6.0	11.0	MT

[1] S, sensitive; MS, moderately sensitive; MT, moderately tolerant; T, tolerant.

salt tolerance, but high salt will affect vegetative more than reproductive growth. Cultivar or variety differences also exist. For example, soybean varieties differ in Cl^- exclusion (Table 3-30). Effective excluders of Na^+ and Cl^- may still exhibit low yield because of salt-related water stress. Tolerant crops that do not exclude Na^+ have a capacity to maintain a high K^+/Na^+ ratio in the growing tissue. Conventional breeding and genetic engineering methods are being used to improve adaptation and tolerance to saline and sodic soil environments.

Quantifying salt tolerance Plant tolerance to soil salinity is expressed as the yield decrease with a given amount of soluble salts compared with yield under non-saline conditions. Threshold salinity levels have been established for most crops and represent the minimum salinity level (ECse) above which salinity limits plant growth (Table 3-29). These values represent general guidelines, since many interactions among plant, soil, water, and environmental factors influence salt tolerance. Above the threshold ECse level, plant growth generally decreases linearly with increasing salinity (Fig. 3-45).

Relative yield loss (Y) at any given ECse level can be calculated for any crop from the values in Table 3-29 for threshold levels (A) and the % yield decrease per unit increase in ECse (b) above the threshold by the following:

$$Y = 100 - b\,(\mathrm{ECse} - A)$$

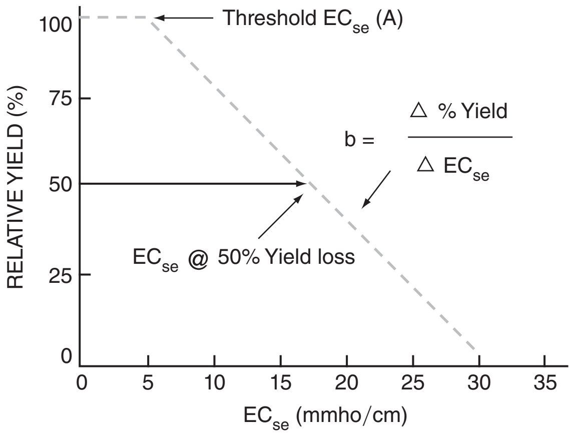
TABLE 3-30
LEAF-SCORCH RATINGS, YIELD, AND Cl^- CONCENTRATION IN LEAVES AND SEEDS OF FIVE SUSCEPTIBLE AND TEN TOLERANT SOYBEAN CULTURES

Soybean Type	Leaf Scorch Rating[1]	Yield	Cl^- concentration: Leaves	Cl^- concentration: Seed
		bu/a	*%*	*ppm*
Cl susceptible	3.4	15	1.67	682
Cl tolerant	1.0	24	0.09	111

[1] 1 = none, 5 = severe.

Source: Parker et al., 1986.

Figure 3-45
Graphical representation of salt tolerance threshold (A) and yield loss associated with increasing ECse. The slope "b" represents the % yield loss per unit increase in ECse.



For example, alfalfa yield decreases about 7.3% per unit increase in ECse above the 2.0 mmho/cm ECse threshold (Table 3-29). Thus, if a soil analysis showed 4.0 mmho/cm ECse, then the estimated relative alfalfa yield would be:

$$Y = 100 - 7.3\,(4.0 - 2.0) = 85.4\%$$

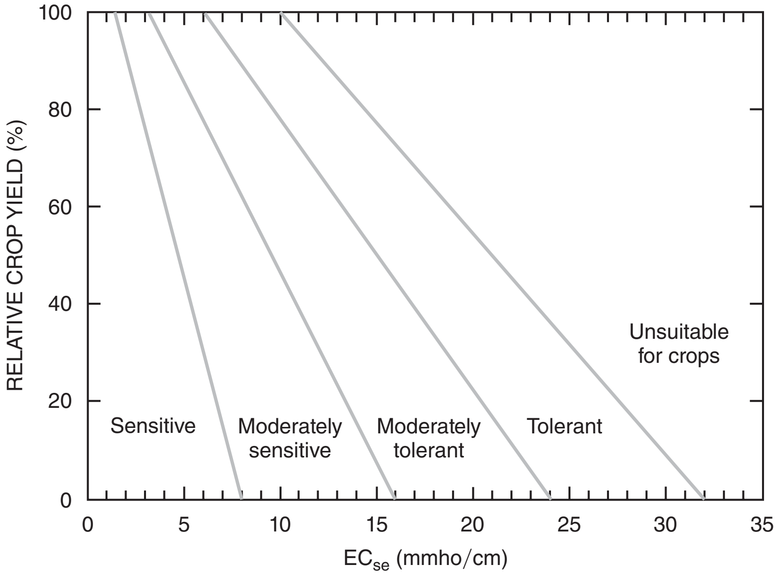
Using these linear relationships, plants can be categorized into groups based on sensitivity or tolerance to soil salinity (Fig. 3-46). These ratings are only relative but can be used to estimate yield depression at specific soil salinity levels for many crops (Fig. 3-47). Salt tolerance ratings for other crops are provided in the *Instructors Manual*.

Factors affecting salt tolerance

Plant Factors

For some plants soil salinity influences growth at all growth stages, but for many crops sensitivity varies with the growth stage. For example, several grain crops (e.g., rice, wheat, corn, and barley) are relatively salt tolerant at germination and maturity but are very sensitive during early seedling and, in some cases, vegetative growth stages. In contrast, sugarbeet, safflower, soybean, and many bean crops (including soybean) are sensitive during germination. The growth reduction often depends on

Figure 3-46
Divisions for classifying crop tolerance to salinity.



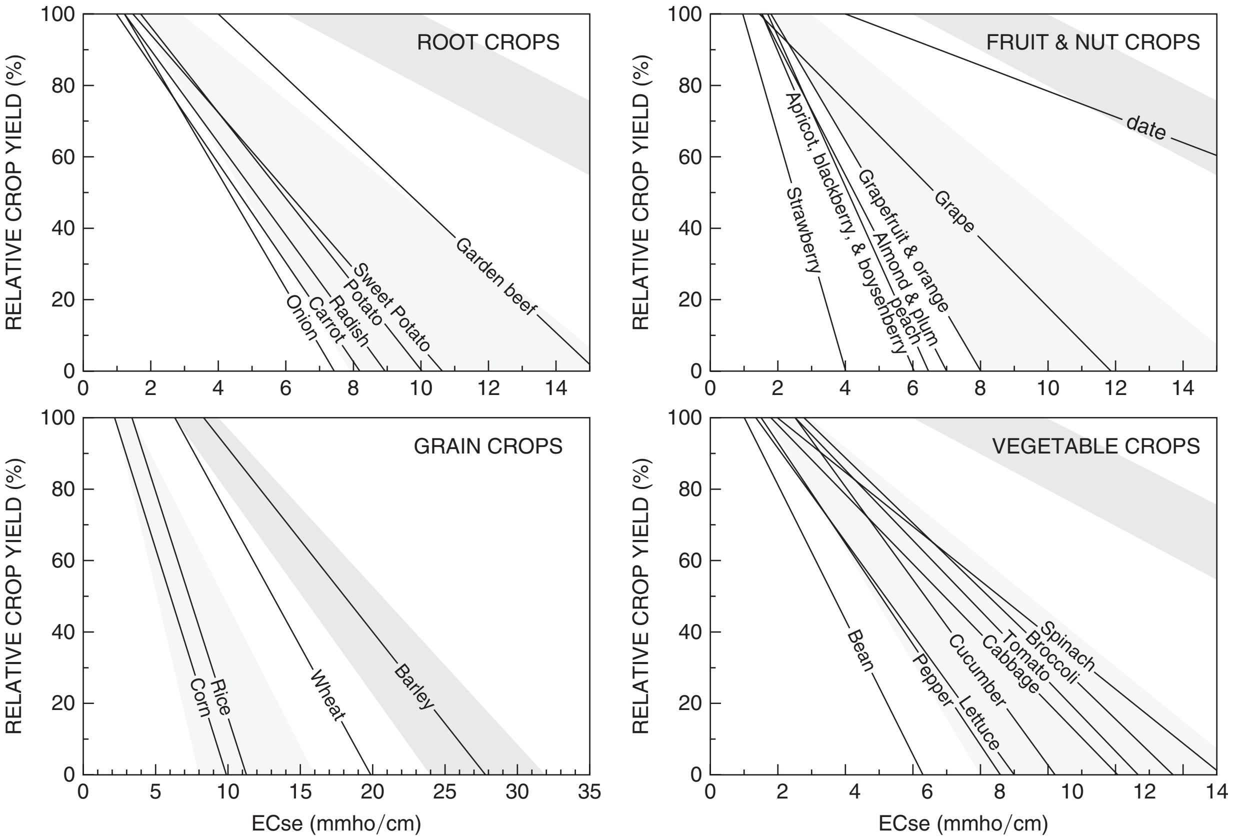


Figure 3-47

Relationship between salinity level (ECse) and relative crop yield (%) for selected crops. The light and dark shaded zones correspond to salt tolerance classified as moderately tolerant *and* tolerant, *respectively (Fig. 3-46). The ECse scales are not the same. For example, barley is much more salt tolerant than corn, whereas corn is much more tolerant than strawberry.*

(El-Swaify, 2000, in Silva and Uchida (eds.), Plant Nutrient Mgmt. Hawaii's *Soils, pp. 151–158, Univ. of Hawaii-Manoa.)*

the variety, particularly with many grasses and some legume crops. Differences in salt tolerance have also been observed between different vine and fruit tree rootstocks. Fruit tree and some vine crops are particularly sensitive to Cl^- toxicity; however, salt-tolerant varieties exhibit reduced Cl^- accumulation in the roots and/or Cl translocation from roots to above-ground tissues. Most grasses used in the turf industry are relatively salt tolerant.

Soil Factors

In general, crops grown on nutrient-deficient soils are more salt tolerant than the same crops grown in soils with sufficient nutrients. Lower growth rates and lower water demand are likely causes for the increased tolerance to soil salinity. In these cases, nutrient deficiency is the most limiting factor to maximum yield potential; thus, nutrient additions would increase plant growth and subsequently decrease salt tolerance.

Because saline and sodic soils have $pH > 7.0$, micronutrient deficiencies can be more common (Chapter 8). Overfertilization with N can decrease salt tolerance in some crops because of increased vegetative growth and water demand. At recommended rates, little or no effect on soil salinity or salt tolerance is observed with either inorganic or organic nutrient addition. Continued overapplication of manure, as well as N and K fertilizers, can increase soil salinity, especially in poorly drained, irrigated soils. Overapplication with band-applied fertilizers containing relatively high concentrations of N and K can cause salt damage to germinating seeds and seedlings (Chapter 10).

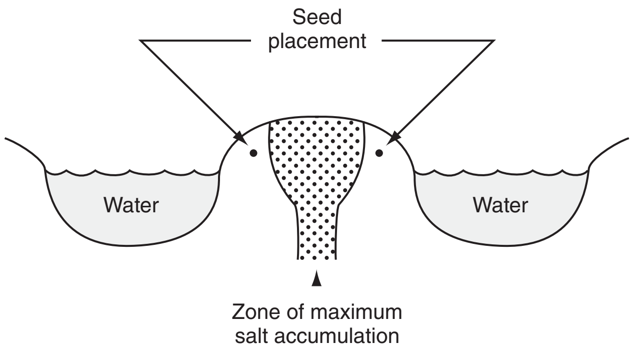


Figure 3-48
In furrow-irrigated cropping systems, salts accumulate near the center of the bed. Seeds should be planted on the side of the beds to avoid salinity problems.
(Ludwick et al., 1978, Colorado State Univ. Coop. Ext. No. 504.)

Proper irrigation management is essential to reducing soil salinity effects on plant growth and yield. Total salt concentration in the soil solution is the highest when the water content has been reduced by evapotranspiration. With irrigation, soil solution salts are diluted and ECse decreases. If soil salinity increases above threshold levels (Fig. 3-47) during dry periods, more frequent irrigation will be required to prevent water and salinity stress and, thus, negative effects on plant growth and yield. Also, the percentage of plant available water decreases with increasing salinity (higher osmotic potential), requiring more frequent irrigation. Excessive irrigation reduces aeration, especially in poorly drained soils, and can reduce salt tolerance in some plants. Under furrow irrigation conditions, excess water leaches into the furrow area; however, soil water movement from the bottom of the furrow to the midrow area deposits salts as water evaporates from the soil surface. Salt-sensitive crops must be planted to the side of the midrow to minimize salt injury to germinating seeds and seedlings (Fig. 3-48). Much lower water rates are used in trickle irrigation compared with furrow irrigation, resulting in greater salt accumulation and potential for yield losses.

Environmental Factors

Under hot, dry conditions, most crops are less salt tolerant than under cool, humid conditions because of greatly increased evapotranspiration demand. These climatic effects of temperature and humidity on salt tolerance are particularly important with the most salt-sensitive crops.

Reducing Salts and/or Na in Soils

Critical soil test information is required before a management strategy is implemented to remediate salt- and/or Na^+-affected soils. These include:

- soil pH
- ECse
- solution and exchangeable cations and anions (Ca^{+2}, Mg^{+2}, Na^+, Cl^-, SO_4^{-2}, CO_3^{-2}, HCO_3^-)
- CEC, soil texture
- $CaCO_3$ content, or qualitative determination of its presence
- analysis of available irrigation water quality (pH, EC, Na^+ content)

From these soil test data, the following parameters are calculated or estimated:

- total dissolved solids
- SAR
- ESP
- gypsum ($CaSO_4 \cdot 2H_2O$) requirement (if a sodic or saline-sodic soil)

From these results, the soil is classified as saline, sodic, or saline-sodic. The following general management should be considered.

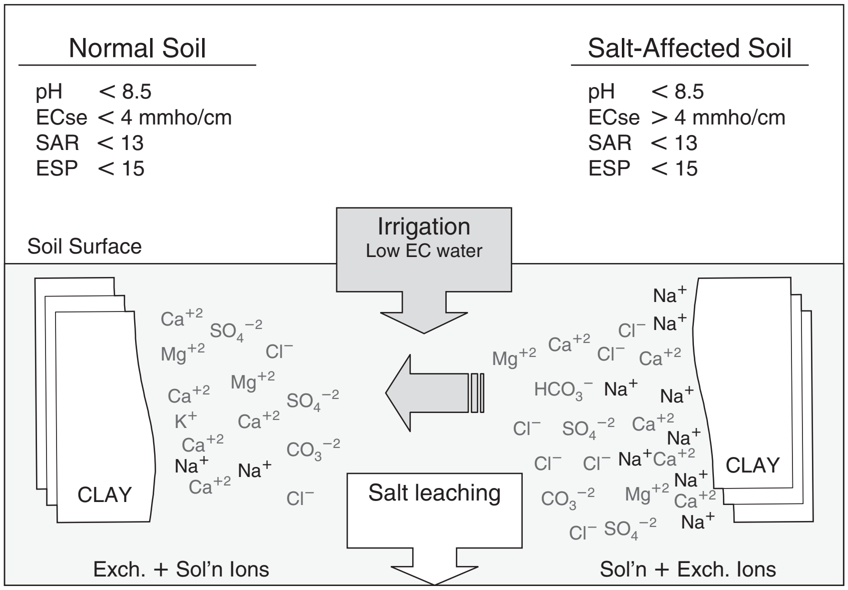


Figure 3-49
Reclaiming a saline soil by adding low salt and/or Na irrigation water and leaching soluble salts in the soil solution below the root zone.

Saline soils Saline soils are relatively easy to reclaim if adequate amounts of low-salt irrigation waters are available and internal and surface drainage are feasible. Salts must be leached below the root zone and out of contact with subsequent irrigation water (Fig. 3-49).

The quantity of irrigation water needed to leach the salts out of the root zone, or the leaching requirement (LR), can be estimated by the following relationship:

$$LR = \frac{ECiw}{5(ECse) - ECiw}$$

where LR = leaching requirement

ECse = threshold ECse for a given crop
ECiw = EC of irrigation water

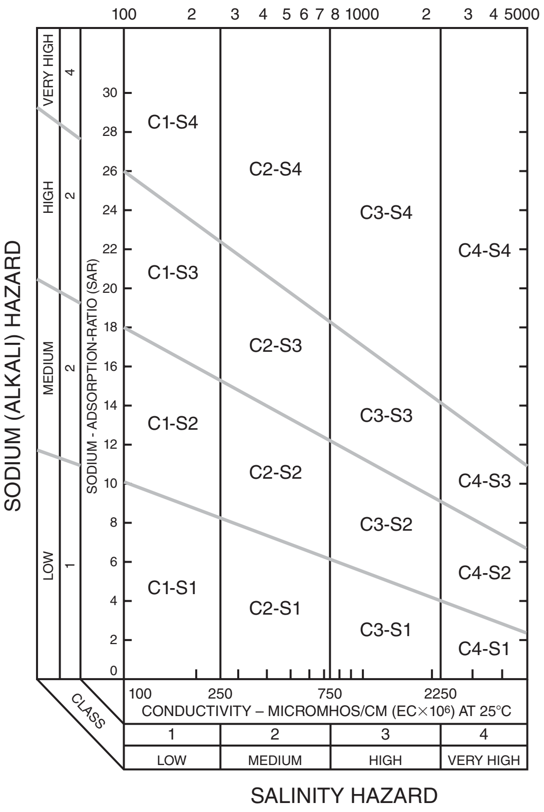
For example, Kentucky bluegrass's threshold ECse = 3.0. If the ECiw = 1.5, then the LR is:

$$LR = \frac{1.5}{5(3) - 1.5} = 0.111$$

LR represents the additional water (LR = 11.1%) needed to leach out salts over that needed to saturate the profile. Although this relationship provides an estimate of the water volume needed to reduce salts in the soil, more sophisticated calculations are generally used to precisely estimate the amount of leaching water needed. The amount of leaching water required depends on (1) the desired ECse, which depends on the salt tolerance of the intended crop; (2) irrigation water quality (ECiw); (3) rooting or leaching depth; and (4) soil water-holding capacity.

As seen in the LR calculation, the quality of irrigation water used to leach salts below the root zone is an important factor in managing soil salinity. The EC and SAR of the available water must be determined before application. Based on these values, water quality can be evaluated (Fig. 3-50). As the EC and SAR of the irrigation water increase, greater precautions should be taken in using it to leach salts below the root zone.

In soils with a high water table, drain installation may be required before leaching. If there is a dense calcareous or gypsiferous layer or the soil is impervious, deep chiseling



1. Salinity classification	2. Sodium classification
C1 - Low-salinity water can be used for irrigation with most crops on most soils, with little likelihood that a salinity problem will develop. Some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability.	S1 - Low-sodium water can be used for irrigation on almost all soils with little danger of the development of a sodium problem. However, sodium-sensitive crops, such as stone-fruit trees and avocados, may accumulate injurious amounts of sodium in the leaves.
C2 - Medium-salinity water can be used if a moderate amount of leaching occurs. Plants with moderate salt tolerance can be grown in most instances without special practices for salinity control.	S2 - Medium-sodium water may present a moderate sodium problem in fine-textured (clay) soils unless there is gypsum in the soil. This water can be used on coarse-textured (sandy) or organic soils that take water well.
C3 - High-salinity water cannot be used on soil with restricted drainage. Even with adequate drainage, special management for salinity control may be required, and plants with good salt tolerance should be selected.	S3 - High-sodium water may produce troublesome sodium problems in most soils and will require special management, good drainage, high leaching, and additions of organic matter. If there is plenty of gypsum in the soil, a serious problem may not develop for some time. If gypsum is not present, it or some similar material may have to be added.
C4 - Very-high-salinity water is not suitable for irrigation under ordinary conditions but may be used occasionally under very special circumstances. The soil must be permeable, drainage must be adequate, irrigation water must be applied in excess to provide considerable leaching, and very-salt-tolerant crops should be selected.	S4 - Very-high-sodium water is generally unsatisfactory for irrigation except at low- or medium-salinity levels, where the use of gypsum or some other amendment makes it possible to use such water.

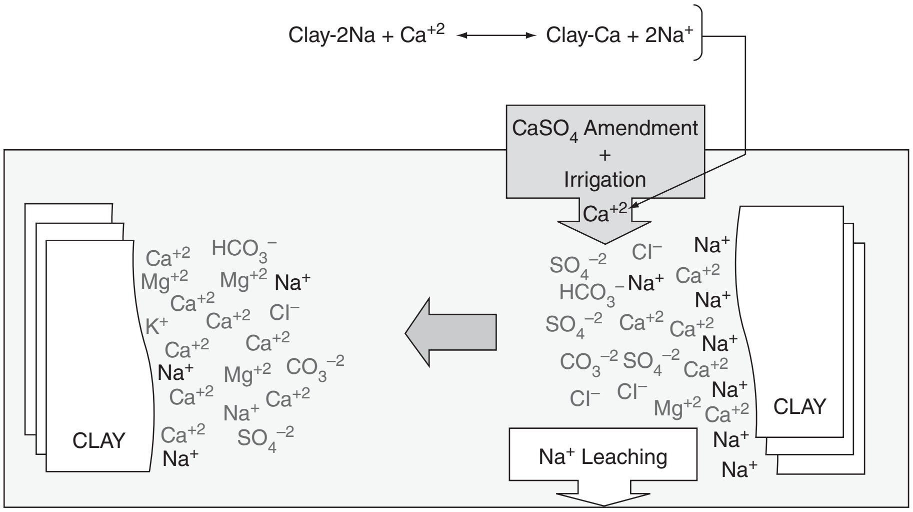
Figure 3-50
Classification of irrigation waters. (U.S. Salinity Laboratory, Handbook 60, *1954.)*

or plowing may be needed to improve infiltration. When only rainfall or limited irrigation is available, surface organic mulches will reduce evaporation and increase drainage.

Managing the soil to minimize salt accumulation is essential, especially in semiarid and arid regions. Maintaining the soil near field capacity with frequent watering dilutes salts. Light leaching before planting or light irrigation after planting moves salts below the planting and early rooting zone. If water is available, periodic leaching when crops are not growing will move salts out of the root zone. Much of the salt may precipitate as $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ or $MgCO_3$ during dry periods and will not react as soluble salt, although precipitation of Ca and Mg will increase the proportion of Na^+ present in solution (see SAR definition).

Managing soils for improved drainage is essential for controlling soil salinity. When ridge-tillage systems are used, the salt moves upward with capillary H_2O and is deposited on the center of the ridges where the water evaporates. Planting on the shoulders or edge of the ridges helps to avoid problems associated with excess salts (Fig. 3-48).

Sodic or saline-sodic soils (no $CaCO_3$ present) In sodic and saline-sodic soils, exchangeable Na^+ and/or ECse must be reduced, which can be difficult because the soil clay may be dispersed, preventing infiltration. Reducing exchangeable Na^+ is accomplished by replacement with Ca^{+2} by adding appropriate rate of gypsum ($CaSO_4 \cdot 2H_2O$). The reaction is:



Estimating the quantity of $CaSO_4 \cdot 2H_2O$ required is similar to the calculation for estimating the $CaCO_3$ required to increase pH. For example, a soil with CEC = 24 meq/100 g soil contains 15% ESP, and we need to reduce the ESP to 5%; thus, 15% − 5% = 10% reduction in ESP.

Reduce ESP from 15 to 5% of the CEC, or 10% of CEC occupied by Na^+ must be removed and is calculated by:

$$0.10 \times \frac{24 \text{ meq CEC}}{100 \text{ g soil}} = \frac{2.4 \text{ meq Na}^+}{100 \text{ g soil}} \quad [\text{Na}^+ \text{ removal}]$$

Thus,

$$\frac{2.4 \text{ meq Na}^+ \text{ removed}}{100 \text{ g soil}} = \frac{2.4 \text{ meq Ca}^{+2} \text{ added}}{100 \text{ g soil}}$$

$$= \frac{2.4 \text{ meq CaSO}_4 \cdot 2\text{H}_2\text{O added}}{100 \text{ g soil}}$$

NOTE:

The *equivalent weight* of $CaSO_4 \cdot 2H_2O$ is determined exactly as we did for $CaCO_3$ on page 30:

$$CaSO_4 \cdot 2H_2O \rightleftarrows Ca^{+2} + SO_4^{-2} + 2H_2O$$

$$\text{Clay-2Na}^+ + Ca^{+2} \rightleftarrows \text{Clay-Ca}^{+2} + 2Na^+$$

Thus, 1 mole or molecular weight of $CaSO_4 \cdot 2H_2O$ (172 g/m) exchanges or reacts with 2 moles Na^+.

Now, remember 1 mole Ca^{+2} = 2 moles (+) or 2 equivalents; thus:

$$\frac{172\text{ g } CaSO_4 \cdot 2H_2O}{2\text{ moles } Na^+} = \frac{86\text{ g } CaSO_4 \cdot 2H_2O}{1\text{ mole } Na^+}$$

$$= \frac{86\text{ g } CaSO_4 \cdot 2H_2O}{\text{eq}} = \frac{86\text{ mg } CaSO_4 \cdot 2H_2O}{\text{meq}}$$

Now convert the charge units (meq/100 g soil) to mass units (lb/afs):

$$\frac{2.4\text{ meq } CaSO_4 \cdot 2H_2O\text{ added}}{100\text{ g soil}} \times \frac{86\text{ mg } CaSO_4 \cdot 2H_2O}{\text{meq}} = \frac{206\text{ mg } CaSO_4 \cdot 2H_2O}{100\text{ g soil}}$$

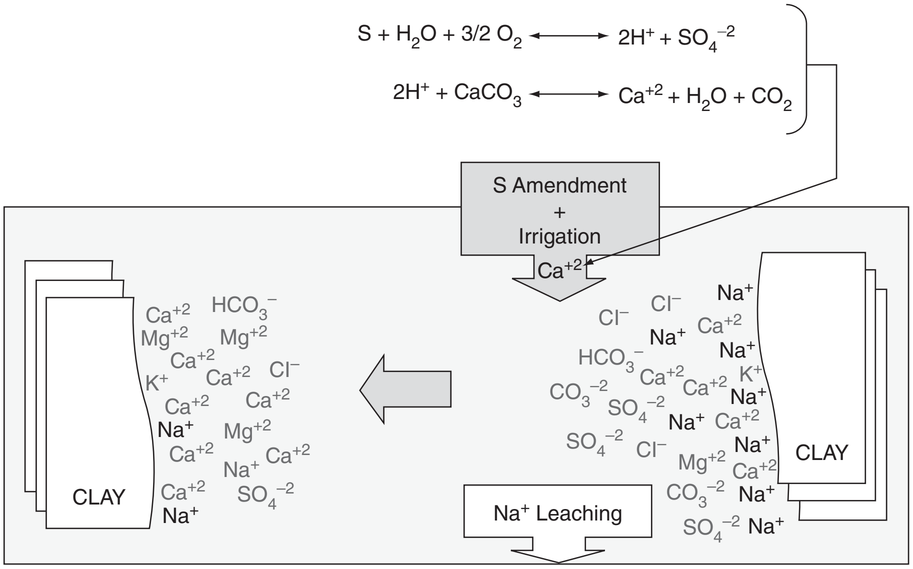
$$= \frac{0.206\text{ g } CaSO_4 \cdot 2H_2O}{100\text{ g soil}}$$

$$= \frac{0.206\text{ lb } CaSO_4 \cdot 2H_2O}{100\text{ lb soil}}$$

$$\frac{0.206\text{ lb } CaSO_4 \cdot 2H_2O}{100\text{ lb soil}} \times \frac{2 \times 10^4}{2 \times 10^4} = \frac{4{,}120\text{ lb } CaSO_4 \cdot 2H_2O}{\text{afs}}$$

If it were desired to reduce exchangeable Na^+ in 0–12-in. depth instead of 0–6-in. depth (afs), then the $CaSO_4 \cdot 2H_2O$ rate would be doubled (8,240 lb/a-ft). The recommended gypsum would be broadcast applied followed by slow irrigation to dissolve the $CaSO_4 \cdot 2H_2O$ and move the Ca^{+2} into the target soil depth. The Na-Ca exchange and leaching process can take several months.

Sodic or saline-sodic soils ($CaCO_3$ present) In calcareous soils, the soil already has an available Ca^{+2} source in $CaCO_3$. Thus, the amendment could be an acid or acid-forming material to dissolve the $CaCO_3$ to produce Ca^{+2} that would then replace exchangeable Na^+ according to:



NOTE:

The *equivalent weight* of S is determined by:

$$S + 1.5O_2 + H_2O \rightleftarrows SO_4^{-2} + 2H^+$$

Thus, 1 mole or molecular weight of S (32 g/m) oxidizes to form 2 moles H^+.

$$CaCO_3 + 2H^+ \rightleftarrows Ca^{+2} + CO_2 + H_2O$$

2 moles H^+ dissolves 1 mole $CaCO_3$ to produced 1 mole Ca^{+2}.

$$\text{Clay-}2Na^+ + Ca^{+2} \rightleftarrows \text{Clay-}Ca^{+2} + 2Na^+$$

Thus, 1 mole S resulted in the exchange of 2 moles Na^+, so the equivalent weight of S is:

$$\frac{32\text{ g S}}{2\text{ moles Na}^+} = \frac{16\text{ g S}}{1\text{ mole Na}^+} = \frac{16\text{ g S}}{\text{eq}} = \frac{16\text{ mg S}}{\text{meq}}$$

In the previous example, assume the soil also contained 2% $CaCO_3$. Thus, a reduction of 2.4 meq exchangeable Na^+/100 g soil is still required; however, elemental S is added that will oxidize to produce $2H^+$, which will dissolve exactly 2.4 meq $CaCO_3$/100 g soil to produce 2.4 meq Ca^{+2}/100 g soil:

$$\begin{aligned}\frac{2.4\text{ meq Na}^+\text{ removed}}{100\text{ g soil}} &= \frac{2.4\text{ meq Ca}^{+2}\text{ added}}{100\text{ g soil}}\\ &= \frac{2.4\text{ meq CaCO}_3\text{ in soil}}{100\text{ g soil}}\\ &= \frac{2.4\text{ meq S added}}{100\text{ g soil}} \quad [\text{to dissolve CaCO}_3]\end{aligned}$$

The calculation for S rate is:

$$\begin{aligned}\frac{2\ .4\text{ meq S added}}{100\text{ g soil}} \times \frac{16\text{ mg S}}{\text{meq}} &= \frac{38\text{ mg S}}{100\text{ g soil}}\\ &= \frac{0.038\text{ g S}}{100\text{ g soil}}\\ &= \frac{0.038\text{ lb S}}{100\text{ lb soil}}\end{aligned}$$

$$\frac{0.038\text{ lb S}}{100\text{ lb soil}} \times \frac{2 \times 10^4}{2 \times 10^4} = \frac{760\text{ lb S}}{\text{afs}}$$

Since the oxidation of S is a microbially mediated reaction, additional time is required for the amendment process to be completed. In some situations, the remediation of sodic soils can take several months, often taking the field out of production until the remediation process is completed.

To use S as an amendment to reduce exchangeable Na^+ (ESP), the soil must be calcareous or contain sufficient $CaCO_3$. In the previous example, the minimum $\%CaCO_3$ content is estimated by:

$$\begin{aligned}\frac{2\ .4\text{ meq Na}^+\text{ removed}}{100\text{ g soil}} &= \frac{2.4\text{ meq Ca}^{+2}\text{ added}}{100\text{ g soil}}\\ &= \frac{2.4\text{ meq CaCO}_3\text{ in soil}}{100\text{ g soil}}\end{aligned}$$

$$\frac{2.4 \text{ meq CaCO}_3 \text{ added}}{100 \text{ g soil}} \times \frac{50 \text{ mg CaCO}_3}{\text{meq}} = \frac{120 \text{ mg CaCO}_3}{100 \text{ g soil}}$$
$$= \frac{0.120 \text{ g CaCO}_3}{100 \text{ g soil}}$$
$$= 0.12\ \%\ \text{CaCO}_3$$

Estimating amendment rates for sodic or saline-sodic soils is relatively easy once the reduction in exchangeable Na^+ is determined:

$$\frac{\text{X meq Na}^+ \text{ removed}}{100 \text{ g soil}}$$
$$= \frac{\text{X meq Ca}^{+2} \text{ needed}}{100 \text{ g soil}}$$
$$= \frac{\text{X meq CaSO}_4 \cdot 2\text{H}_2\text{O added}}{100 \text{ g soil}}$$
$$= \frac{\text{X meq S added}}{100 \text{ g soil}} \quad [\text{if CaCO}_3 \text{ present in soil}]$$
$$= \frac{\text{X meq CaCO}_3 \text{ in soil}}{100 \text{ g soil}} \quad [\text{minimum CaCO}_3 \text{ needed in soil}]$$

Gypsum (or S) should be broadcast and thoroughly incorporated into the surface 3–4 in. of soil. Once uniform application is accomplished, high quality irrigation water is applied at rates to ensure water is transported below the root zone or to depths ($>2 - 3$ ft) where exchangeable Na^+ will have minimal impact on plant growth. Fields with little or no slope can be flooded to ensure adequate percolation of water and salts. In some cases, high ESP will initially limit infiltration; however, eventually sufficient Ca will improve aggregation and water transport. Following reclamation, ESP will again increase as evaporative waters transport salts to the surface soil. Regular soil testing will identify when subsequent amendment is needed.

STUDY QUESTIONS

1. A solution has $10^{-5.2}$ M H^+ concentration. What is the solution pH?
2. Identify the principal sources of soil acidity?
3. Distinguish between active and potential acidity. Which of these two forms is measured when soil pH is determined?
4. Solution A has a pH of 3.0. Solution B has a pH of 6.0. The active acidity of solution A is how many times greater than that of solution B?
5. How is soil pH affected by fertilizer applications? Provide several example reactions.
6. Define lime requirement. The term *Ag-lime* usually refers to what materials?
7. How does soil BC influence the lime requirement?
8. How is the lime requirement of a soil determined?
9. Write the chemical reactions that occur when lime is added to an acid soil.
10. Can $CaSO_4 \cdot 2H_2O$ be used as a liming agent? Write the neutralization reaction.
11. Define *neutralizing value* or *calcium carbonate equivalent* (CCE). What is the CCE of Na_2CO_3?
12. You analyze limestone and find that it has a neutralizing value of 85%. How many tons of this limestone would be equivalent to 3 t of pure $CaCO_3$?
13. In addition to purity and neutralizing value, what other property of limestone is important as a liming material?
14. Using the following reactions, indicate if the material can be used as a suitable liming material.

a. $\text{clay-2H}^+ + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftarrows \text{clay-Ca}^{+2} + 2\text{H}^+ + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$
b. $\text{clay-2H}^+ + 2\text{KOH} \rightleftarrows \text{clay-2K}^+ + 2\text{H}_2\text{O}$
c. $\text{clay-2H}^+ + \text{Mg(HCO}_3)_2 \rightleftarrows \text{clay-Mg}^{+2} + 2\text{CO}_2 + 2\text{H}_2\text{O}$
d. $\text{clay-2H}^+ + 2\text{KCl} \rightleftarrows \text{clay-2K}^+ + 2\text{H}^+ + \text{Cl}^-$
e. $\text{clay-2H}^+ + \text{Na}_2\text{CO}_3 \rightleftarrows \text{clay-2Na}^+ + \text{CO}_2 + \text{H}_2\text{O}$

15. Adding lime will increase BS of an acid soil. A grower indicates that adding gypsum will do the same thing at half the cost. What would you advise this grower?

16. A soil sample has a pH of 6.0 and CEC of 25 meq/100g. 50 g of soil was titrated with 50 ml of 0.1 N kOH to pH 7.0. Calculate the lime recommendation in lb/afs.

17. Calculate the lb/afs of CaCO_3 (using Figure 2-11), to raise the soil pH from 5.0 to 6.5. The CEC is 30 meq/100 g.

18. A grower received a lime recommendation of 8 t/afs of 80% ECC lime material. His soil test results showed pH = 5.5 and CEC = 26 meq/100 g. The grower thought that this recommendation was too high. How much would the soil pH increase if the grower only applied 4 t/afs of the lime material? (Use Fig. 2-11 and assume all the lime reacted.)

19. A golf course superintendent wants to plant fescue in two fairways that have drastically different soil properties.

Fairway 1—silt loam texture; soil
pH = 5.7; BS = 58%; CEC = 15 meq/100 g
Fairway 2—clay loam texture; soil
pH = 6.0; BS = 60%; CEC = 40 meq/100 g

a. Calculate the CaCO_3 (lb/afs) required to neutralize soil acidity in Fairway 1 to pH 6.8 and BS of 90%.
b. Calculate the CaCO_3 (lb/afs) required to neutralize soil acidity in Fairway 2 to pH 6.8 and BS of 90%.

20. A soil had an initial pH of 5.5 and a CEC = 25 meq/100 g. After the producer applied the lime, the pH increased to 6.5. How much lime did she apply? (Use Fig. 2-11 and assume all the lime reacted.)

21. A soil has the following properties: clay content = 50%; CEC = 40 meq/100 g; pH = 5.2; %Ca saturation = 40; %Mg saturation = 6; %K saturation = 8; %Na saturation = 0. The lab recommended 3 t/afs of CaCO_3. Is this a good recommendation? If not, what would you recommend? Show all calculations.

22. A grower received a lime recommendation of 4 t/afs of CaCO_3. The only material available is dolomite or $\text{CaMg(CO}_3)_2$. The dolomite has a CCE of 90% and 54% passes a 60-mesh screen, 25% passes an 8-mesh screen, while the remainder will not pass the 8-mesh screen (use Indiana in Table 3-14).
a. Calculate the ECC of this dolomite.
b. How many lb dolomite/afs does he need to apply?

23. Titration of a 50 g soil sample with 10 mL of 0.25 N NaOH raises soil pH from 5.3 to 6.5. How many lb/afs of the following materials would be required?
a. Pure CaCO_3
b. Pure $\text{CaMg(CO}_3)_2$
c. Lime material with CCE of 85% and the following screen analysis (use Indiana in Table 3-14).

Mesh Size	% of Material
<60	50
8–60	25
>8	25

24. Are benefits derived from deep mixing of lime in soil? Can long-term liming of surface soil influence subsoil acidity?

25. You have lost the liming recommendations sent to you by the soil laboratory, but you do recall that 3 t/a were recommended for field B. Because the pH is the same in both fields, you apply 3 t to field A as well. Have you acted wisely? Why or why not?

26. 30 ml of 1 N H_2SO_4 was added to completely neutralize the line content of 10 g of calcareous soil. Excess acid was titrated with 10 ml 0.5 N NaOH. What is the percentage of lime content?

27. Answer the following questions for the soil data listed below.

	Exchangeable Cations (ppm Soil)	**Cations in Saturated Extract (ppm Solution)**
Ca	1,600	180
Mg	600	20
Na	1,000	900
K	600	5

CEC (meq/100 g) = 17 pH (sat'd paste) = 8.6
CaCO_3 (%) = 2 ECse (mmho/cm) = 4.5

  - **a.** Calculate CEC and compare with measured CEC. Suggest a reason why the two values may be different.
  - **b.** Calculate SAR and estimate SAR from the exchangeable cation data.
  - **c.** Calculate and estimate ESR and ESP.

28. Explain how S acidulates a soil.

29. What are the main cations in saline, sodic, and saline-sodic soils? Explain how sodic soils become impermeable.

30. Write the chemical reactions when S is added as an amendment to reduce exchangeable Na.

31. Explain why $CaSO_4$ is effective in reclaiming saline soils.

32. A soil has the following properties: $pH = 8.6$; $ESP = 18\%$; $CEC = 25$ me/100 g; $CaCO_3 = 2\%$.
  - **a.** Calculate the SAR.
  - **b.** A lab recommended adding 4,300 lb gypsum/afs. Calculate the final ESP if the grower followed the recommendation.
  - **c.** If the grower added S instead of gypsum, calculate the final $CaCO_3$ content.

33. A laboratory analysis showed the following results:

$$\begin{aligned} \text{CEC} &= 28 \text{ meq/100 g} \\ \text{solution Ca} &= 6 \text{ meq/L} \\ \text{solution Mg} &= 2 \text{ meq/L} \\ \text{solution Na} &= 36 \text{ meq/L} \\ \text{EC} &= 5.2 \text{ mmhos/cm} \\ CaCO_3 &= 0.2\% \\ \text{soil pH} &= 8.6 \end{aligned}$$

  - **a.** Calculate SAR, ESR, and ESP.
  - **b.** Calculate the S (lb/afs) required to neutralize all the lime.
  - **c.** Calculate the gypsum (lb/afs) required to reduce ESP to 5%.

34. A golf course manager complained that when he irrigated the fairways the water would not infiltrate very readily. Soil samples were collected and the soil solution (saturated extract) contained:

$$\begin{gathered} 1{,}600 \text{ ppm } Ca^{+2} \\ 960 \text{ ppm } Mg^{+2} \\ 2{,}760 \text{ ppm } Na^{+} \end{gathered}$$

The CEC was 35 meq/100 g soil and the lab recommended lowering the ESP to 5% to improve infiltration.
  - **a.** Calculate the gypsum required to lower ESP to 5% (lb/a-ft).
  - **b.** How much S (lb/a-ft) would be required to lower the ESP to 5%?
  - **c.** The soil contained 0.2% lime. Was there enough lime present to supply enough Ca^{+2} to lower ESP to 5%?

35. Using Figure 3.1, identify the major acid soil regions in the world.

36. Mention the sources of soil acidity.

37. How do you classify irrigation waters based on
  - **a.** Salinity
  - **b.** Sodium content.

38. On the basis of soil test data, how do you classify soil?

39. Proper irrigation management is essential to reduce soil salinity effects on plant growth and development. Justify.

40. Define
  - **a.** Saline soil,
  - **b.** Sodic soil and
  - **c.** Saline-sodic soil.

41. Describe the processes involved in the salt accumulation of soil in detail.

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4

Nitrogen

Nitrogen (N) is the most frequently deficient nutrient in nonlegume plants, while quantities of N_2 fixed by legumes can be sufficient for their growth. Because most soils cannot supply sufficient amounts of plant available N, inorganic and/or organic N sources must be applied to meet plant N requirements (Fig. 4-1). Globally, agricultural N use has substantially increased over the last 50 years, contributing to our ability to feed a growing planet (Chapter 1). However, global N use has also increased N loading in the environment (Chapter 12). Understanding the biology and chemistry of N in the soil-plant-atmosphere continuum is essential for maximizing plant growth and productivity, while reducing the impacts of N inputs on the environment.

THE N CYCLE

The ultimate source of all N used by plants is N_2, which constitutes 78% of the earth's atmosphere. Unfortunately, higher plants cannot metabolize N_2 directly into protein. N_2 must first be converted to plant available N by:

- microorganisms that live symbiotically on legume roots,
- free-living or nonsymbiotic soil microorganisms,
- atmospheric electrical discharges forming N oxides, or
- the manufacture of synthetic N fertilizers.

The large reservoir of atmospheric N_2 is in equilibrium with all fixed forms of N in soil, seawater, and living and nonliving organisms (Table 4-1). Cycling of N in the soil-plant-atmosphere system involves many transformations between inorganic and organic forms (Fig. 4-2). The N cycle can be divided into N inputs or gains, N outputs or losses, and N cycling within the soil, where N is neither gained nor lost (Table 4-2). Except for industrial fixation and combustion, all of these N transformations occur naturally; however, humans influence many of these N processes. This chapter describes the chemical and microbial cycling of N and how humans influence or manage these transformations to optimize N availability to plants.

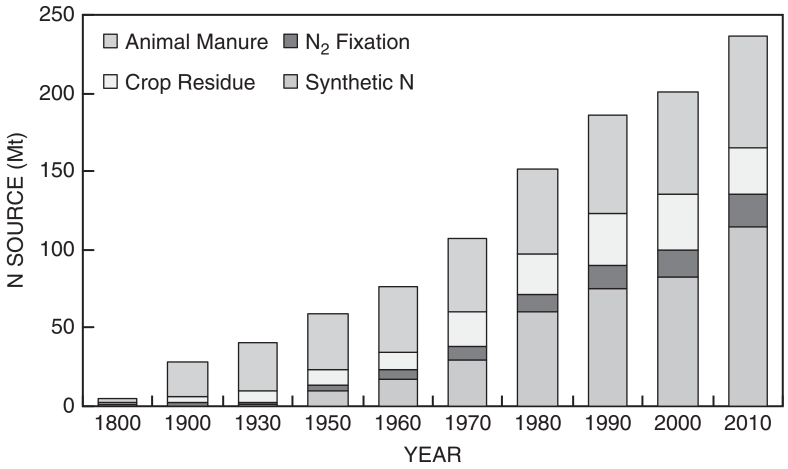


Figure 4-1
Global agricultural N sources from 1800 to 2010. Synthetic N use is increasing relative to other N sources.
(*Adapted from Mosier, 2001,* Plant and Soil, *228:17–27.*)

TABLE 4-1
APPROXIMATE DISTRIBUTION OF N THROUGHOUT THE SOIL-PLANT/ANIMAL-ATMOSPHERE SYSTEM[1]

N Source	Metric Tons	% of Total
Atmosphere	3.9×10^{15}	99.3840
Sea	2.4×10^{13}	0.6116
Soil	4.5×10^{11}	0.0038
Plants	1.5×10^{10}	0.00038
Microbes in soil	6×10^{9}	0.00015
Animals (land)	2×10^{8}	0.000005
People	1×10^{7}	0.00000025

[1] Not included in the above is ~180 × 10^{15} t of N contained in rocks and other materials unavailable to soil-plant-atmosphere system.

FUNCTIONS AND FORMS OF N IN PLANTS

Forms

Plants contain 1–6% N by weight and absorb N as both nitrate (NO_3^-) and ammonium (NH_4^+) (Fig. 4-2). In moist, warm, well-aerated soils, soil solution NO_3^- is generally greater than NH_4^+. Both move to plant roots by mass flow and diffusion.

The rate of NO_3^- uptake is usually high, causing an increase in rhizosphere pH. When plants absorb high levels of NO_3^-, there is an increase in anion (HCO_3^-, OH^-, organic anions) transport out of cells. Plants metabolize NO_3^- to NH_4^+ to amino acids and to proteins. NO_3^- reduction to NH_4^+ is an energy requiring process that uses two nitrate reductase (NADH) molecules for each NO_3^- reduced in protein synthesis. Thus, NH_4^+ is the preferred N source since energy is conserved compared to NO_3^- (one less step in the reduction process). Plants supplied with NH_4^+ may have increased carbohydrate and protein levels compared with NO_3^-.

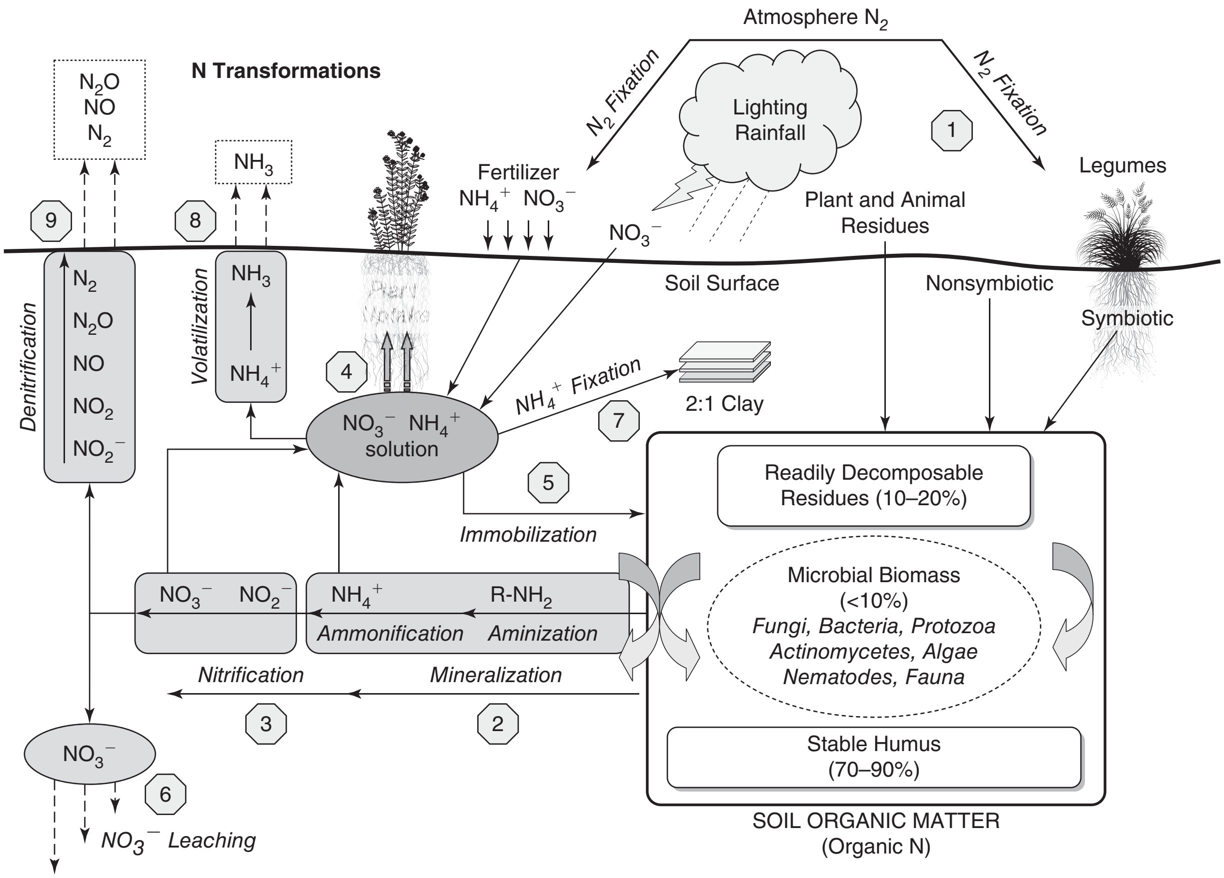


Figure 4-2
The N cycle. Most of the **N transformations** (italics) *are facilitated by the microbial biomass and cycle through the organic fraction in soil. In step 1, N in plant and animal residues and N derived from the atmosphere through electrical discharges, legumes, and industrial processes (N_2 is combined with H_2 or O_2) are added to the soil. In step 2, organic N is* **mineralized** *to NH_4^+ by soil organisms. Much of the NH_4^+ is converted to NO_3^- by bacteria through* **nitrification** (step 3). *In step 4, NO_3^- and NH_4^+ in soil solution are taken up by plant roots. In step 5, some solution NH_4^+ and NO_3^- are converted back to organic N through* **immobilization**. *Solution NO_3^- can be lost by* **leaching** *to groundwater or drainage systems as a result of downward movement below the root zone in percolating water* (step 6). *In step 7, NH_4^+* **fixation** *by 2:1 clay minerals can occur. In step 8, NH_4^+ can be* **volatilized** *to gaseous NH_3. NO_3^- derived from nitrification, fertilization, or rainfall can be converted by denitrifying bacteria to N_2, N_2O, NO that escape into the atmosphere* (**denitrification**; step 9), *completing the cycle.*

TABLE 4-2
N INPUTS, OUTPUTS, AND CYCLING IN THE SOIL-PLANT-ATMOSPHERE SYSTEM[1]

N Inputs (Gains)	N Outputs (Losses)	No Net N Gain or Loss (Cycling)
Fixation	Plant uptake	Mineralization
Biological (bacteria)	Denitrification	Immobilization
Industrial (Haber-Bosch)	Volatilization	Nitrification
Electrical (lightning)	Leaching	
Combustion (fossil fuel)	NH_4^+ fixation[2]	
Animal manure		
Crop residue		

[1] Some N inputs, outputs, and cycling components can be influenced by management but generally are not managed.

[2] Some fixed NH_4^+ can be released (input).

Plant uptake of NH_4^+ reduces Ca^{+2}, Mg^{+2}, and K^+ uptake while decreasing rhizosphere pH, caused by H^+ exuded by the root to maintain electroneutrality or charge balance inside the plant. Differences in two pH units near the root surface have been observed for NH_4^+ versus NO_3^- uptake, which can affect nutrient availability and biological activity in the vicinity of roots (Fig. 3-7).

While preference for NH_4^+ or NO_3^- differs between plants, plants have evolved with a preference for NO_3^- as a primary N source because NH_4^+ rapidly converts to NO_3^- in moist, well-aerated soils. Although energy within the plant is conserved with NH_4^+ as the primary N source, NH_4^+ tolerance limits are narrow, where high levels of NH_4^+ can retard growth and restrict uptake of other cations. For example, a 75:25 ratio of $NO_3^-:NH_4^+$ is recommended for nutrient solutions used in horticulture, where NH_4^+ toxicity can occur if NH_4^+ exceeds 50%. In contrast, plants can accumulate and tolerate comparatively high NO_3^- levels in tissues.

For most plants, growth is improved when nourished with both NO_3^- and NH_4^+ compared with NO_3^- (or NH_4^+) alone. It is difficult to maintain NH_4^+ in soils; however, split application of NH_4^+ or NH_4^+-forming fertilizers later in the growing season and use of nitrification inhibitors can increase NH_4^+ availability. For example, 50:50 $NH_4^+:NO_3^-$ ratios have been shown to improve yield in cereals and corn. This would be advantageous in calcareous soils where increased NH_4^+ uptake would lower rhizosphere pH and increase the availability of P and micronutrients. In contrast, plants grown under anaerobic soil conditions (e.g., rice) predominantly utilize NH_4^+, as NO_3^- is denitrified under these conditions.

Some plant diseases are more severe when either NH_4^+ or NO_3^- predominate. Two processes may be involved. One is the direct effect of N form on pathogenic activity; the other is the influence of NH_4^+ or NO_3^- on organisms affecting the availability of micronutrient cations. For example, high NO_3^- supply stimulates certain bacteria, which lowers Mn availability in wheat. The effect of N form on rhizosphere soil pH is partially responsible for differences observed in disease incidence and severity.

Functions

Before NO_3^- can be used in the plant, it must be reduced to NH_4^+. Nitrate reduction involves two enzyme-catalyzed reactions that occur in roots and/or leaves, depending on the plant species. Both reactions occur in series so that toxic nitrite (NO_2^-) does not accumulate.

	Reduction Reaction	**Enzyme**	**Reaction Site**
Step 1	$NO_3^- \rightarrow NO_2^-$	Nitrate reductase	Cytoplasm
Step 2	$NO_2^- \rightarrow NH_3$	Nitrate reductase	Chloroplast

The NH_3 produced is assimilated into amino acids that are subsequently combined into proteins and nucleic acids. Proteins provide the framework for chloroplasts, mitochondria, and other structures in which most biochemical reactions occur. The type of protein formed is controlled by a specific genetic code in nucleic acids, which determines the quantity and arrangement of amino acids in each protein. The nucleic acid, deoxyribonucleic acid (DNA), present in the nucleus and mitochondria of the cell (Fig. 2-22), duplicates genetic information in the chromosomes of the parent cell to the daughter cell. Ribonucleic acid (RNA), present in the nucleus and cytoplasm of the cell, executes the instructions coded within DNA molecules. Most enzymes controlling these metabolic processes are also proteins and are continually metabolized and resynthesized.

Figure 4-3
A simplified representation of a chlorophyll molecule.

In addition to the formation of proteins, N is an integral part of chlorophyll, which converts light into chemical energy needed for photosynthesis. The basic chlorophyll structure is the porphyrin ring, composed of four pyrrole rings, each containing one N and four C atoms (Fig. 4-3). A single Mg atom is bonded in the center of each porphyrin ring.

Nitrogen is a component of energy-transfer compounds, such as adenosine diphosphate (ADP) and adenosine triphosphate (ATP), which allows critical cellular use, and transfer, of energy released in metabolism.

An adequate supply of N is associated with high photosynthetic activity, vigorous vegetative growth, and a dark green color. An excess of N in relation to other nutrients, such as P, K, and S, can delay crop maturity. In many plants grown in humid environments, excess N stimulates vegetative growth and increases the incidence of foliar diseases. In semi-arid and arid climates, stimulation of heavy vegetative growth early in the season can reduce soil moisture during the reproductive growth stage, where plants are most sensitive to water stress.

The supply of N influences carbohydrate utilization. Under low N, carbohydrates will be deposited in vegetative cells, causing them to thicken. When N supplies are adequate and conditions are favorable for growth, proteins are formed from the manufactured carbohydrates. With less carbohydrate deposited in the vegetative portion, more protoplasm is formed, and because protoplasm is highly hydrated, a more succulent plant results. Excessive succulence in cotton weakens the fiber, and with grain crops, lodging may occur, particularly with a low K supply or with varieties not adapted to high levels of N. In some cases, excessive succulence enhances susceptibility to diseases or insects. Crops such as wheat and rice have been modified for growth at higher densities and at higher levels of N fertilization. Shorter plant height and improved lodging resistance have been bred into plants, which respond in yield to much higher N rates.

Visual Deficiency Symptoms

When plants are N deficient, leaves or leaf veins appear yellow. The loss of protein N from chloroplasts in older leaves produces the yellowing, or chlorosis, indicative of N deficiency. Chlorosis usually appears first on the lower leaves, the upper leaves remaining green; under severe N deficiency, lower leaves turn brown and die. This necrosis begins at the leaf tip and progresses along the midrib until the entire leaf is dead (see color plates). The tendency of newer growth to remain green as the lower leaves turn yellow or die indicates the mobility of N in the plant. When roots are unable to absorb sufficient N, protein in the older plant parts is converted to soluble N, translocated to the active meristematic tissues, and reused in the synthesis of new protein.

BIOLOGICAL (SYMBIOTIC) N_2 FIXATION

Many organisms have the unique ability to fix atmospheric N_2 (Table 4-3). Estimates of total annual biological N_2 fixation worldwide range from 130 to 180 $\times 10^6$ Mt, with about 50% fixed by *Rhizobia*. In contrast, world fertilizer N use was about 100 $\times 10^6$ Mt in 2008 (Fig. 1-9). In the United States, reliance on biological N_2 fixation for crop production has declined dramatically since the 1950s because of increased production and use of low-cost synthetic N fertilizers (Fig. 4-4). About 20% of N supplied to crops in the United States is from legumes and crop residues (Table 4-4). Under high fertilizer N costs, rotation with forage legumes is generally cost effective, increases soil OM content, and reduces soil erosion potential. Inclusion of grain legumes in the rotation will also reduce fertilizer N costs; however, soil erosion potential may increase.

In addition to forage and grain legumes, N_2 fixation by leguminous trees is important to the ecology of forests and agroforestry systems. Numerous leguminous tree species fix appreciable amounts of N_2. In the United States, mimosa, acacia, and black locust are common. Three woody leguminous species—*Gliricidia sepium*, *Leucaena leucocephala*, and *Sesbania bispinosa*—are used as green manure crops in rice-based cropping systems.

Some widely distributed non-leguminous plants also fix N_2 by a mechanism similar to legume and rhizobial symbiosis. *Frankia*, an actinomycete, is responsible for N_2 fixation by several non-leguminous woody plants including Betulaceae, Elaeagnaceae, Myricaceae, Coriariaceae, Rhamnaceae, and Casuarinaceae (Table 4-3). For example, alder and ceanothus, two species commonly found in the Douglas fir forest region of the Pacific Northwest, contribute substantial N to the ecosystem.

TABLE 4-3
ECONOMICALLY IMPORTANT MICROORGANISMS INVOLVED IN BIOLOGICAL N_2 FIXATION

Organisms	General Properties	Agricultural Importance
Azotobacter	Aerobic; free fixers; live in soil, water, rhizosphere, leaf surfaces	Minor benefit to agriculture; found in vascular tissue of sugarcane, with sucrose as an energy source for N_2 fixation
Azospirillum	Microaerobic; free fixers; or found in association with roots of grasses	Inoculation benefits some non-legume crops, shown to increase root hair development
Rhizobium	Fix N_2 in legume-Rhizobium symbiosis	Legume crops are benefited by inoculation with proper strains
Actinomycetes	Fix N_2 in symbiosis with non-legume wood trees—alder, Myrica, Casuarina	Potentially important in reforestation, wood production
Cyanobacteria (Anabaena)	Contains chlorophyll, mostly aquatic, some terrestrial	Enhance rice in paddy soils; Azolla (a water fern) symbiosis; used as green manure

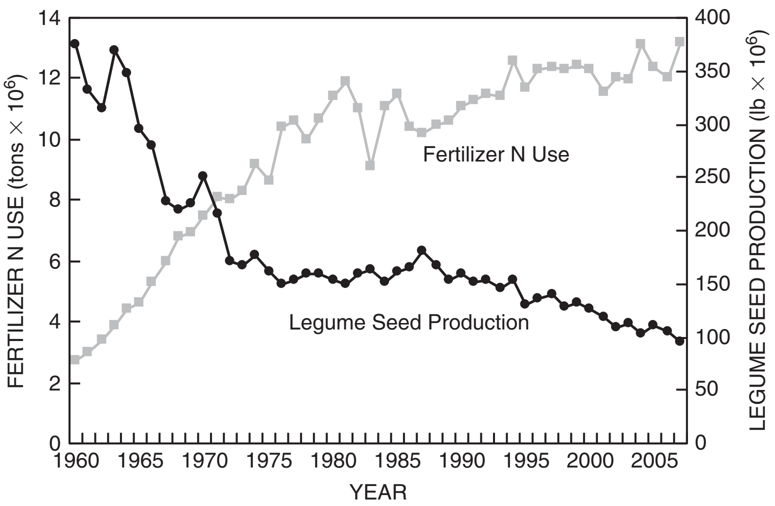


Figure 4-4
Inverse relationship between N fertilizer use and legume seed production in the United States. Part of the decrease in U.S. production is offset by increased production in Canada.

TABLE 4-4
ESTIMATED PERCENTAGE OF TOTAL N ADDED TO U.S. CROPLAND BY VARIOUS SOURCES

N Source	Total (million tons)	% of Total
Commercial N	13.2	57
Legumes, crop residues	5.6	24
Animal manures	3.4	15
Other sources	0.9	4

Source: USDA-ERS, 2008; Howarth et al., 2002, *Ambio*, 31:89–96.

N_2 Fixation by Legumes

When legume root growth begins, N_2-fixing bacteria in soil invade root hairs and multiply. Legume roots respond by forming tumor-like structures called *nodules* on the root surface (Fig. 4-5). The specialized bacteria called rhizobia inside the nodule absorb N_2 from soil air and convert it to NH_4^+ (Fig. 4-6). Rhizobia use

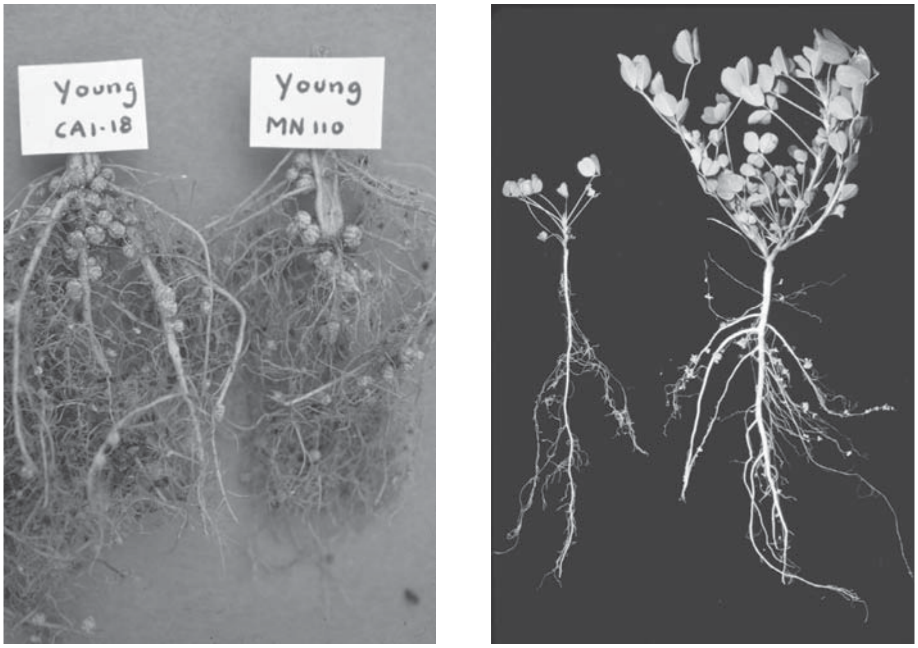
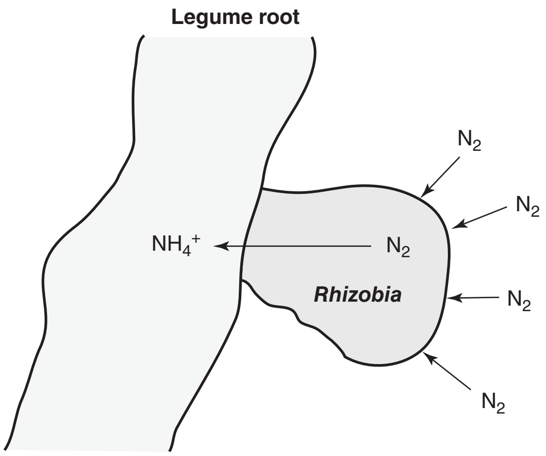


Figure 4-5
Example of nodules on soybean (left) showing differences in nodulation between varieties, and alfalfa (right) showing non-inoculated (left) and inoculated (right) with proper rhizobia bacteria.
(Courtesy D. Israel (soybean) and J. Burns, D. Chamblee, and J. Green (alfalfa), NC State University.)

Figure 4-6
Conversion of N_2 to NH_4^+ by rhizobia inside a legume root nodule.



$$N_2 + 16\text{ ATP} + 2H^+ \xrightarrow{\text{nitrogenase}} 2NH_4^+ + 16\text{ ADP} + H_2$$

the enzyme nitrogenase and energy from the transformation of ATP to ADP to break the strong triple bond ($N{\equiv}N$) in N_2. The *symbiotic* relationship between legume host plant and nodule bacteria is mutually beneficial. Plants provide energy (sugars, carbohydrates, ATP) for rhizobia to fix N_2, and rhizobia in turn provide NH_4^+ for production of proteins by the host plant. Most of the fixed N_2 is utilized by the host plant, although some may be excreted from the nodule into the soil and used by other nearby plants, or released as nodules decompose after the plant dies.

Numerous rhizobium species exist in soil, each requiring a specific host legume plant. For example, symbiotic bacteria specific to soybean will not fix N_2 with alfalfa. Inoculation of the legume seed with the correct inoculum is recommended the first time a field is planted to a new legume species. Carefully matching cultivars with inoculum strains will increase N_2 fixation, which increases plant yield and protein content (Table 4-5). A wide range in yield increases to inoculation has been observed (10–90%), but commonly are 15–25% with 5–20% increases in protein content. Typical legume response to inoculation is shown in Table 4-6.

As the population of the desired rhizobia increase, the effect of inoculation on N_2 fixation decreases. Since laboratory assays for specific rhizobia strains are costly, producers generally inoculate legumes at planting regardless of the presence of native

TABLE 4-5
INFLUENCE OF *RHIZOBIAL* INOCULATION ON LEGUME SEED YIELD AND N CONTENT

Legume Species	No. of Trials Where Inoculation Increased Yield or Seed N Content		Average Seed N (%)	
	Yield	*Seed N*	*Inoculated*	*Uninoculated*
Soybean	83	100	6.2	5.7
Lima bean	60	80	3.2	3.0
Common bean	33	50	3.0	2.8
Cowpea	0	80	4.2	3.9

Source: J. Thies, Ph.D. Dissertation, University of Hawaii, 1990.

TABLE 4-6
INFLUENCE OF *RHIZOBIAL* INOCULATION ON GRAIN YIELD IN COMMON FOOD LEGUME CROPS

Legume	+ Inoculant	− Inoculant	Increase
	kg/ha		%
Soybean	2195	1652	32.9
Common Bean	1825	1363	33.9
Mungbean	651	484	34.5
Groundnut	1079	1031	4.6

Source: Adapted from Singleton et al., 1990, Applied BNF Technology, Univ. of Hawaii.

rhizobia *because* the economic risk of poor production is far greater than the cost of the inoculum. Sufficient native rhizobia occur when legume crops are frequently grown in the same fields or with previous legume inoculations. Inoculation assures the producer an adequate population of rhizobia for the crop.

The presence of nodules on legume roots does not necessarily indicate N_2 fixation by active rhizobia. Mature effective alfalfa nodules tend to be elongated (2–4 by 4–8 mm), clustered on the primary roots, and have pink to red centers. The red color is due to leghemoglobin, which indicates that rhizobia are actively fixing N_2. Ineffective nodules are small (<2 mm in diameter), usually numerous, and scattered over the entire root system. In some cases, they are very large (>8 mm in diameter), few in number, and have white or pale-green centers.

Quantity of N_2 Fixed Generally, nodule bacteria fix 25–90% of the total legume N (Table 4-7). Under optimum conditions, N_2 fixation by most perennial forage legumes exceeds short-season annual legumes. Most of the N_2 fixed is found in the above-ground plant material (Table 4-8). These data also illustrate that N_2 fixation represented 63% of total N uptake, increasing through the season as the contribution from soil N decreased.

The amount of N_2 fixed by rhizobia varies with yield level, effectiveness of inoculation, amount of soil N, and environmental conditions. Soybeans remove about 1.5 lb N/bu from the soil and fix 40% or more of the total N in the plant. However, on sandy, low-OM soils, soybeans may fix 80% or more. In many environments, the quantity of N removed by soybean grain at harvest exceeds the quantity of N_2 fixed.

All legumes recover some soil N, but grain legumes generally remove more soil N than forage legumes since most of the N is transferred to the seed and removed from the field at harvest. Forage legumes generally increase soil N, reducing additional N needed for subsequent crops, because the growth period is usually longer with forage legumes, developing more extensive root systems than grain legumes. Forage legume roots and nodules contain high amounts of N that ultimately increase soil N.

Factors Affecting N_2 Fixation

Soil Nutrient Supply

As with any plant, legumes prefer soil N (NO_3^- and NH_4^+) because it requires less energy for the plant to take up soil N than to fix N_2. As soil N availability decreases, N_2 fixation generally increases. Maximum N_2 fixation occurs only when available soil N is at a minimum. Excess NO_3^- availability reduces nitrogenase activity, which reduces N_2 fixation by competition for photosynthate between NO_3^- reduction and N_2-fixation reactions.

TABLE 4-7
RANGE IN QUANTITY OF N_2 FIXED BY SELECTED LEGUMES

Legume	N fixed (lb/a/yr) Range	N fixed (lb/a/yr) Typical
Alfalfa	50–300	200
Beans	20–80	40
Birdsfoot Trefoil	50–100	70
Black gram	80–140	100
Chickpeas	20–100	50
Clovers (general)	50–300	150
Cluster beans	30–200	60
Common Bean	10–120	40
Cowpeas	60–120	90
Crimson clover	30–180	80
Faba beans	50–240	130
Field peas	50–180	100
Green gram	30–60	40
Groundnut	70–120	90
Hairy vetch	50–200	140
Kudzu	20–150	110
Ladino clover	80–200	150
Lentils	40–130	60
Leucaena	350–480	450
Lespedezas (annual)	30–120	85
Lucerne	180–250	220
Lupin	60–100	80
Mung bean	170–225	200
Peanuts	20–200	60
Pigeon Pea	140–220	200
Red clover	70–160	115
Soybean	20–260	100
Sweet clover	20–80	20
White clover	30–150	100
Winter peas	10–80	50

TABLE 4-8
N BUDGET FOR FIRST-YEAR ALFALFA

N Budget Component	Harvest 1st	Harvest 2nd	Harvest 3rd	Total
	lbs/a			
Forage yield	3,128	2,727	1,032	6,887
Total plant N	105	113	53	271
N from N_2 fixation[1]	51 (49%)	91 (81%)	30 (57%)	172 (63%)
Leaves/stems	46	66	20	132
Roots/crown	4	25	11	40
N from soil	54	22	22	99
Leaves/stems	48	16	14	79
Roots/crown	6	6	8	21

[1] Percent of total plant N.

Source: Heichel and Barnes, 1981, *Crop Sci.*, 21:330–35.

Even under adequate soil N supply, inoculation of the legume seed is still important for optimum yields (Fig. 4-7). Sometimes a small amount of N fertilizer at planting provides young legume seedlings adequate N until rhizobia become established on the roots. Early spring N application can also benefit legume crops where rhizobial activity is restricted by cold, wet conditions. With some legumes, N_2 fixation is low and usually unreliable (e.g., common bean), so N fertilization is recommended.

In acid soils, Ca^{+2} and $H_2PO_4^-$ deficiencies can limit rhizobial growth and reduce host plant productivity (Fig. 4-8). N_2 fixation requires more Mo than the host plant because Mo is a component of nitrogenase; thus, Mo deficiency is the most important micronutrient deficiency affecting N_2 fixation. Initiation and development of nodules can also be affected by B, Fe, and Cu deficiencies. Differences exist in the sensitivity of various rhizobial strains to nutrient stress.

Soil pH

Soil acidity can restrict the survival and growth of rhizobia in soil and severely affect nodulation and N_2-fixation process. Generally at pH < 5.5, rhizobial infection, root growth, and legume productivity can be severely reduced. Significant differences in sensitivity of rhizobia to soil acidity exist. For example, soil pH < 6 drastically reduces *Rhizobium meliloti* population, degree of nodulation, and alfalfa yield, whereas soil pH 5.0–7.0 has little effect on *Rhizobium trifoli* associated with red clover. Liming acid soils increases alfalfa growth dependent on *Rhizobium meliloti*. For locations where lime may not be readily available, high levels of inoculum and coating inoculated seeds with lime can improve inoculation. Another approach is to select and use acid-tolerant rhizobia (Fig. 4-9).

Environment

A high rate of photosynthate production is strongly related to increased N_2 fixation by rhizobia. Factors that reduce the rate of photosynthesis will reduce N_2 fixation, including reduced light intensity, moisture stress, and low temperature.

Legume Management

In general, any management practice that reduces legume stands or yield will reduce the quantity of N_2 fixed by legumes. These factors include water and nutrient stress, excessive weed and insect pressure, and improper harvest management. Harvest

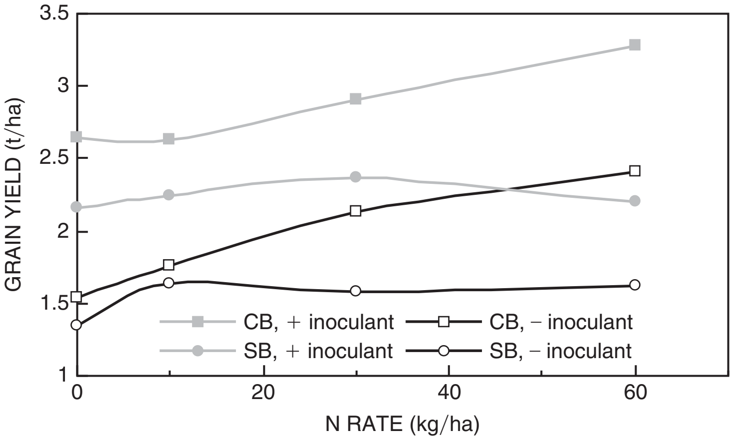


Figure 4-7

Influence of inoculation and N rate on soybean (SB) and common bean (CB) yield.

(Singleton et al., 1990, Applied BNF Technology, Univ. of Hawaii.)

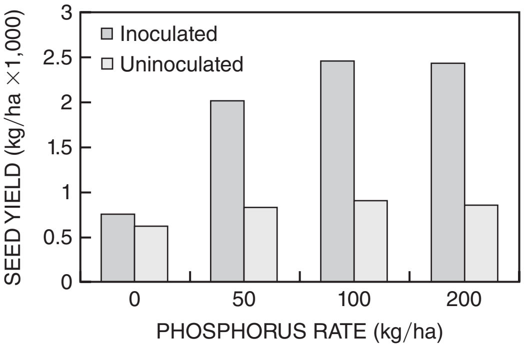


Figure 4-8

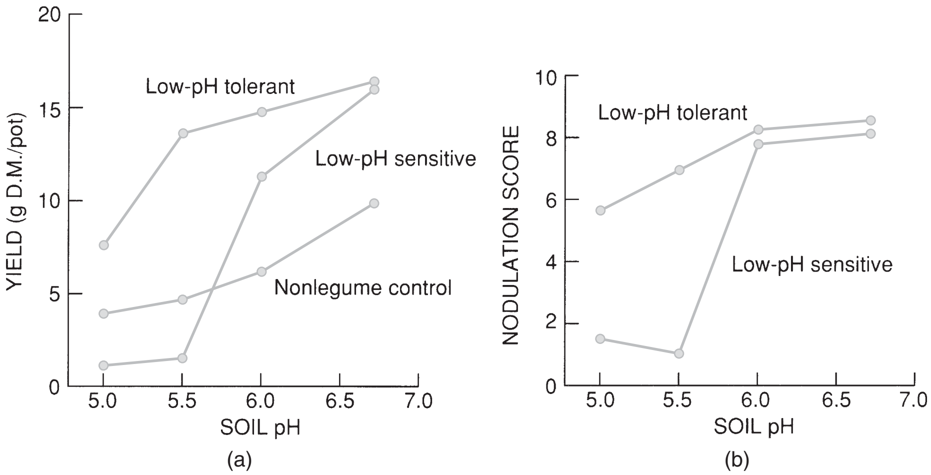
Soybean yield as influenced by P availability and inoculation.

(Singleton et al., 1990, Applied BNF Technology, Univ. of Hawaii.)

Figure 4-9

Forage yields (a) and nodulation scores (b) of alfalfa inoculated with low-pH-tolerant and low-pH-sensitive strains of Rhizobium meliloti. *Barley was the non-legume control.*

(*Rice, 1989,* Can. J. Plant Sci., *62:943.*)



practices vary greatly with location, but excessive cutting frequency, premature harvest, and delayed harvest, especially in the fall, can reduce legume stands and the quantity of N_2 fixed.

Legume N Availability to Non-Legume Crops Yields of non-legume crops are often increased when grown following legumes. For example, when corn follows soybean, the N required for optimum yield is less than that required for corn after corn (Fig. 4-10). Similarly, less N is needed to maximize wheat grain yield following lupins (Fig. 4-11). Reduced N rates with the non-legume crop following a legume, compared to continuous non-legume rotations, are due to:

- decomposition of legume residue providing plant available N
- greater N immobilization in continuous non-legume rotations
- enhanced soil microbial activity resulting in increased N mineralization in legume rotations

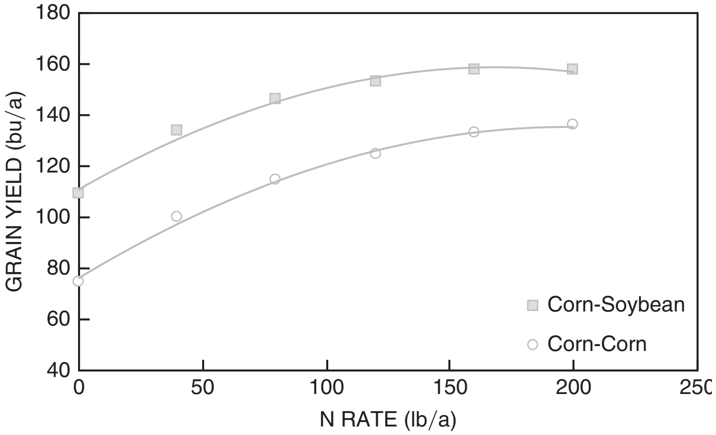
For example, recent studies showed that soil organic N at planting decreased ≈10% by corn harvest but increased ≈10% from soybean planting to harvest (Table 4-9). Rotation benefits can also be related to reduced soilborne diseases and improved soil physical properties (Chapter 12).

When a perennial legume such as alfalfa is used in rotation, the response of the following non-legume crop to applied N varies with time (Fig. 4-12). Little or no response to N fertilization is observed in the first year; however, the amount

Figure 4-10

Typical corn grain yield response to N following corn and soybean.

(O'Leary et al., 2008, Providing Proper N Credit for Legumes, Univ. of Minnesota, WW-03769-GO.)



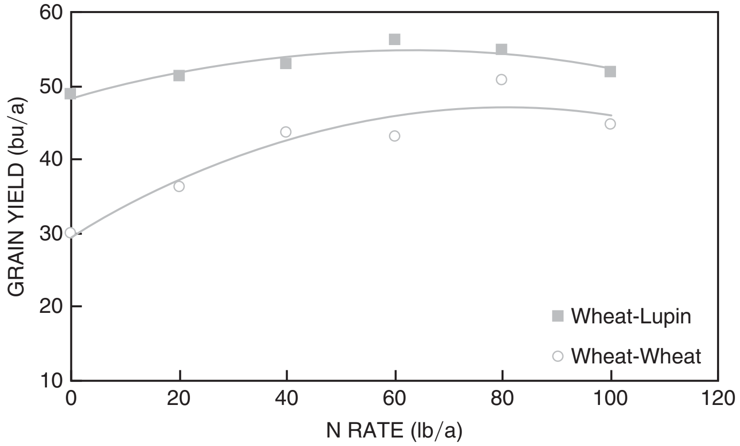


Figure 4-11
Typical wheat grain yield response to N following wheat and lupin.
(*Doyle et al., 1988,* Aust. J. Agric. Res., *39:1029–1037.*)

TABLE 4-9
CHANGE IN SOIL ORGANIC N BETWEEN PLANTING AND HARVEST OF CORN AND SOYBEAN GROWTH (0–6-IN. DEPTH)

	Organic N			
Crop	*Planting*	*Harvest*	**Change**	
	kg/ha			%
Corn	3661	3294	−367	−11
Soybean	3304	3623	+319	+12

Note: Values are averaged over 10 locations.

Source: Martens et al., 2006, *Soil Sci. Soc. Am. J.*, 70:382–392.

of N required for optimum crop production increases with time as the legume N reserves are depleted. N availability in the legume cropping system depends on the quantity of N_2 fixed, the amount and type of legume residue returned, and soil and environmental conditions influencing residue decomposition and N mineralization. Legume N incorporated into the soil from first year alfalfa varies between 35 and 300 kg/ha. Vigorous, high N_2 fixing, alfalfa stands can usually supply all or most of the N to a non-legume crop in the first year. Several studies suggest that the N credit commonly attributed to legumes in rotation is overestimated. These contrasting results can probably be explained by soil, climate, and legume management effects.

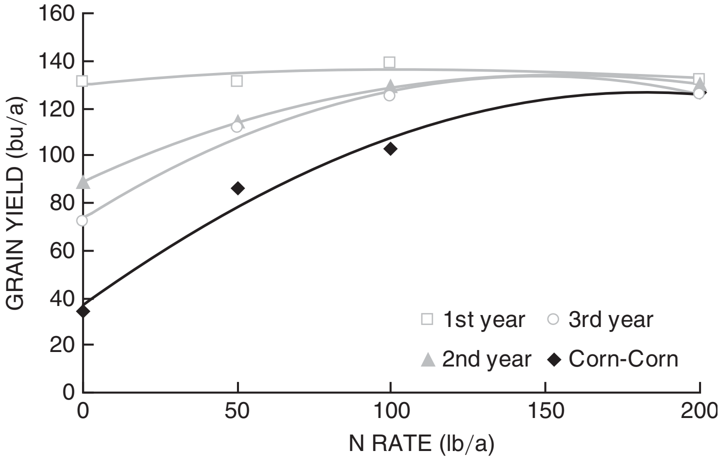
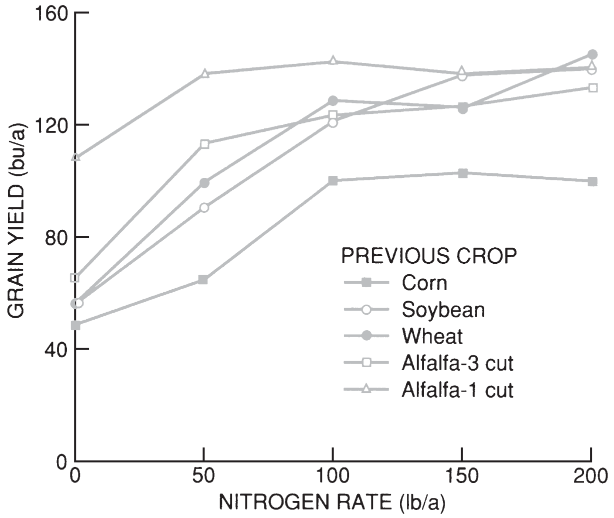


Figure 4-12
Typical corn grain yield response to N following alfalfa. Corn yields were monitored over 3 years following alfalfa and compared to continuous corn response to N.
(O'Leary et al., 2008, Providing Proper N Credit for Legumes, Univ. of Minnesota, WW-03769-GO.)

Figure 4-13

Corn grain yields as influenced by previous crop and fertilizer N.

(Heichel, 1987, Role of Legumes in Conservation Tillage Systems, Soil Cons. Soc. Am., p. 33.)



Forage legumes are used for green manure and animal feed, where all or part of the legume biomass is incorporated into the soil. Since the majority of legume N is in above-ground plant material, the quantity of N returned can be substantial. With forage legumes grown for animal feed, a smaller part of the N_2 fixed is returned to the soil because most of the forage is harvested. For example, legume N availability can be greater in a one-cut system compared with a three-cut system because of the increased amount of N incorporated with less-frequent harvests (Fig. 4-13). Forage legumes generally return more N than grain legumes, because most of the fixed N is in the grain compared to residue N left on the field.

Forage legumes are also used as winter cover crops to protect surface soil from erosion. Depending on the legume and amount of growth (N_2 fixation), winter cover crops will provide some of the N needed by the subsequent non-legume crop (Table 4-10). As a non-legume, using rye as a cover crop will provide protection from erosion, but has little influence on N availability.

The yield benefit of rotations with some legumes may not always be related to the legume N supply. Figure 4-13 illustrates that corn yield response to fertilizer N was similar following soybean or wheat. The rotation response compared

TABLE 4-10
INFLUENCE OF LEGUME AS A WINTER COVER CROP ON SOIL N AND SORGHUM YIELD

	Soil N		Sorghum Yield	
Cover Crop	*Inorganic*	*Organic*	*0 lb N/a*	*100 lb N/a*
	lb/a	%	bu/a	
Fallow[1]	7.1	5.8	43	58
Rye	7.1	6.5	38	58
Crimson clover	12.5	6.5	58	63
Subterranean clover	17.9	8.1	58	57
Hairy vetch	18.8	8.0	59	56
Common vetch	12.5	6.3	54	59

[1] Fallow means field was idled with no crop.

Source: Hargrove, 1986, ***Agron. J.***, 78:70–74.

with continuous corn is commonly referred to as a *rotation effect*. Whether the non-legume yield response following a legume is due to N or to a rotation effect, the benefit can be observed for several years although the majority of the benefit occurs in the first year.

Optimum utilization of legume N by a non-legume crop requires that mineralization of legume N occurs over the same time as crop N uptake. Legume N mineralization by soil microbes is controlled predominately by environment. The quantity of crop N uptake also varies during the season. Thus, for maximum utilization of legume N by the non-legume crop, N uptake must be in *synchrony* with N mineralization. For example, the N uptake period for winter wheat is considerably earlier than for corn (Fig. 4-14). The hypothetical distribution of N mineralization shows that corn N uptake is more synchronous with N mineralization than is winter wheat. Therefore, compared with corn, winter wheat may not utilize much legume N and, when mineralization occurs, the inorganic N is subject to leaching and other losses. Therefore, efficient management of legume N requires careful crop selection.

Legumes grown with forage grasses generally supply N for both crops, where 50–70% of the grass N originates from the legume. Legume N availability to a companion crop is not well understood. Small amounts of amino acids and other organic N compounds may be excreted by the legume roots. Microbial decomposition of the sloughed off root and nodule tissue may also contribute N to the crop growing with legumes. Under some conditions, the quantity of fixed N_2 and/or legume N availability is not sufficient, and N fertilization is required for optimum production of both non-legume and legume crops.

Fertilizer N Value of Legumes Direct measures of the quantity of N fixed by legumes in rotation are difficult; however, the legume value in rotation with non-legume crops can be estimated in fertilizer N units. Crop yield response to N must be determined for the non-legume crop grown in rotation with a legume and grown continuously (Fig. 4-15). In this example, N response was measured with corn grown in rotation with soybean compared to continuous corn. The fertilizer N value of the previous soybean crop is the N rate needed in continuous corn to produce the same yield in rotation with soybean without N fertilizer. Notice in this example corn yields are higher in rotation with soybean than in continuous corn even at high N rates. The additional yield is due to rotation effects other than the N value from the soybean.

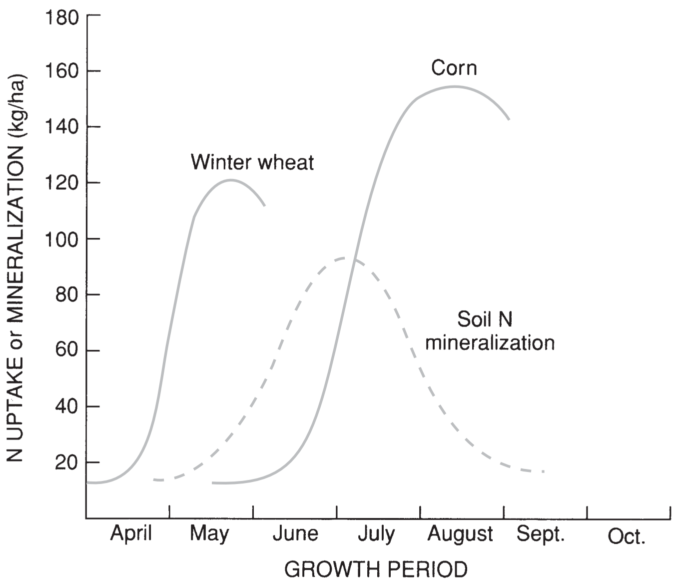


Figure 4-14
Synchrony of soil N mineralization and crop N uptake in corn and winter wheat.

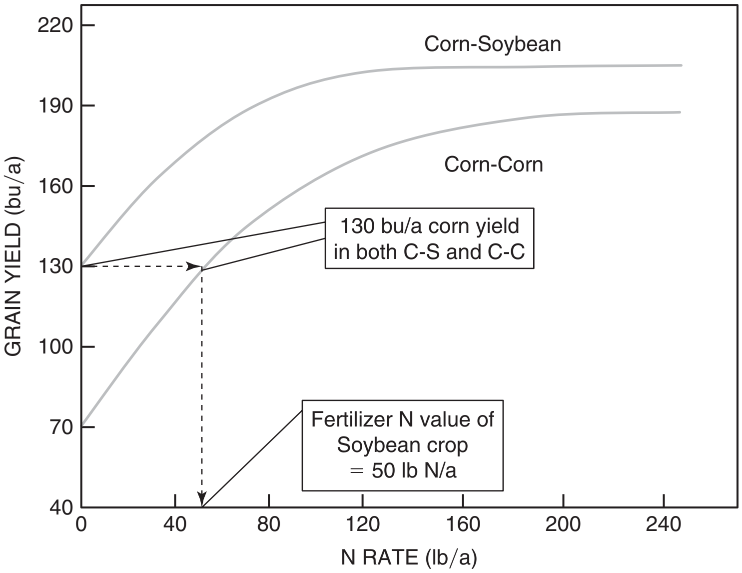


Figure 4-15
Estimating the fertilizer N value of soybean in rotation with corn. With no fertilizer N, corn yield is 130 bu/a in the corn-soybean rotation; however, 50 lb N/a are needed in continuous corn to produce the same yield (130 bu corn/a).

Legume Rotations The primary reason for including legumes in a rotation is to supply N, but with development and availability of relatively inexpensive fertilizer N, most agricultural production does not involve legume N (Fig. 4-4). In a livestock farming system, the main purpose of legumes is to supply large amounts of high-quality forage (hay or pasture). Legumes are generally of superior quality, with higher protein and mineral concentrations compared with N-fertilized grasses.

Management decisions regarding the use of legumes or fertilizer N are based on the highest net return on investment. Fertilizer N costs have increased in recent years because of greater global demand and higher fossil fuel costs. As a consequence, interest in legumes to substitute partially for the fertilizer N requirements of non-legume crops has increased. In some developing countries, commercial N may not be available or is too expensive. Therefore, cropping systems that include legumes are essential to supply some or all of the N needed for non-legumes.

In spite of the advantages of legume rotations, it may not always be economical and thus varies greatly between regions (Table 4-11). For example, producers may not have a use or market for forage legumes. Higher water use and lower drought tolerance in some legumes is a disadvantage in semi-arid areas.

Nonsymbiotic N_2 Fixation

Soil Microorganisms Nonsymbiotic N_2 fixation in soils occurs with certain strains of free-living bacteria (Table 4-3). More common in flooded than in well-drained soils, cyanobacteria are autotrophic, requiring only light, water, N_2, CO_2, and essential nutrients. Because they need light, they contribute only small quantities of N in upland agricultural soils after crop canopy closure. In desert or semi-arid regions, cyanobacteria or lichens containing them become active following occasional rains and fix considerable quantities of N_2 during their short-lived activity. N availability to other organisms provided by cyanobacteria is important to chemical weathering in the early stages of soil formation.

N_2 fixation by cyanobacteria is significant in tropical rice soils. The symbiotic relationship between *Anabaena azolla* (a cyanobacteria) and *Azolla* (a water fern) in temperate and tropical waters is capable of supplying all of the N needs of the host plant. The N_2-fixing bacteria is located in protected leaf cavities of the water fern. In southeast Asia, *Azolla* has been used for centuries as a green

TABLE 4-11
EXAMPLES OF REGIONAL USE OF LEGUMES IN THE UNITED STATES

Region	Legume Species	Cropping or Tillage System
Southeast	Crimson clover, hairy vetch	Winter cover crop—no-till corn
	Bigflower vetch, crown vetch, alfalfa, lupine, arrowleaf clover, red clover	Winter cover crops preceding grain sorghum and cotton
Northeast	Alfalfa, birdsfoot trefoil, red clover	Legumes grown for hay or silage in rotations that include conventional or no-till corn as feed grain or silage; also used as living mulches
North Central	Soybean, pea	Grown in rotation with nonlegume, possibly in conservation tillage; peas may precede soybean in double-crop system
	Alfalfa, red clover, white clover, alsike clover	Grown for 2+ years in 3-5 year rotations with small grains or corn, possibly in conservation tillage
	Birdsfoot trefoil, crown vetch, sweet clover	Used for forage, silage, or pasture
Great Plains	Native legumes	Rangeland for grazing
Pacific Northwest	Dry pea, lentil, chickpea Austrian winter pea	Rotation or double cropped with grains, green manure or alternated with winter wheat
	Alfalfa	Grown in rotation with winter wheat, spring barley, and winter peas
	Fava bean	Grown in rotation for silage
California	Dry bean, lima bean, blackeye pea, chickpea	Grown for grains in various rotations
	Alfalfa	Grown for seed on irrigated land and for erosion control and forage on steeply sloping soils
	Subterranean clover	Rangeland for grazing

Source: Heichal, 1987, Role of Legumes in Conservation Tillage Systems, Soil Cons. Soc. Am.

manure in wetland rice culture, as a fodder for livestock, as a compost for production of other crops, and as a weed suppressor. In California, the *Azolla-Anabaena* N_2-fixing association supplies $\approx$90 lb N/a, or 75% of the N requirements of rice. When used as a green manure, it provides $\approx$50 lb N/a and substantially increases yields over unfertilized rice.

Certain N_2-fixing bacteria can grow on root surfaces and to some extent within root tissues of corn, millet, rice, sorghum, wheat, sugarcane, and many other grasses. *Azospirillum brasilense* is the dominant N_2-fixing bacterium that has been identified. Inoculation of cereal crops with azospirillum can improve growth and N nutrition, although the response to inoculation is variable. In most of the studies in which inoculation was beneficial, the response was related to factors other than increased N_2 fixation. Some of the possibilities are increased root hair growth that enhances water and nutrient uptake and improved root permeability. Azotobacter- and clostridium-inoculated seed may provide $\approx$5 lb N/a; therefore, these nonsymbiotic organisms are of little value to N availability in intensive agriculture.

Atmospheric N N compounds in the atmosphere are deposited with rain and snow as NH_4^+, NO_3^-, NO_2^-, and organic N. Because of the small amount of NO_2^- present in the atmosphere, NO_3^- and NO_2^- are combined and reported as NO_3^-. About 10–20% of the NO_3^- is formed during atmospheric electrical discharges, with the remainder from industrial waste gases or denitrification from soil. NH_4^+ comes largely from industrial sites where NH_3 is used or manufactured. Soil has a high capacity for adsorbing NH_3 gas from the atmosphere. NH_3 also escapes (volatilization) from the soil surface (Fig. 4-2). Finely divided organic residues swept into the atmosphere from the earth's surface are deposited in rainfall.

Total N deposition as $NH_4^+ + NO_3^-$ in rainfall is usually <8 lb N/a/yr, depending on the location, where ≈75% is NO_3^- (Fig. 4-16). Total N deposition is higher around areas of intense industrial and agricultural activity and is greater in tropical than in polar or temperate zones. Localized NH_4^+ deposition can depress soil pH (Fig. 4-17). NH_3 emissions from confined poultry facilities are greater than with other confined animal production systems.

Greenhouse Gases

Nitrous oxide (N_2O) is emitted to the atmosphere from numerous sources and is ≈300 times more effective than CO_2 in trapping heat in the atmosphere; however, N_2O contributes only a few percent to overall greenhouse warming. Although N_2O is unreactive and long-lived in the lower atmosphere (troposphere), it slowly rises into the stratosphere reacting with ozone (O_3). Decreasing upper atmospheric O_3 increases ultraviolet radiation reaching the earth's surface. Global atmospheric N_2O has increased ≈18% since 1750 and is ≈4% higher than in 1990. In the United States, agricultural soil management and fertilizer use contributes 67% of atmospheric N_2O with fossil fuel combustion contributing 15% (Chapter 12).

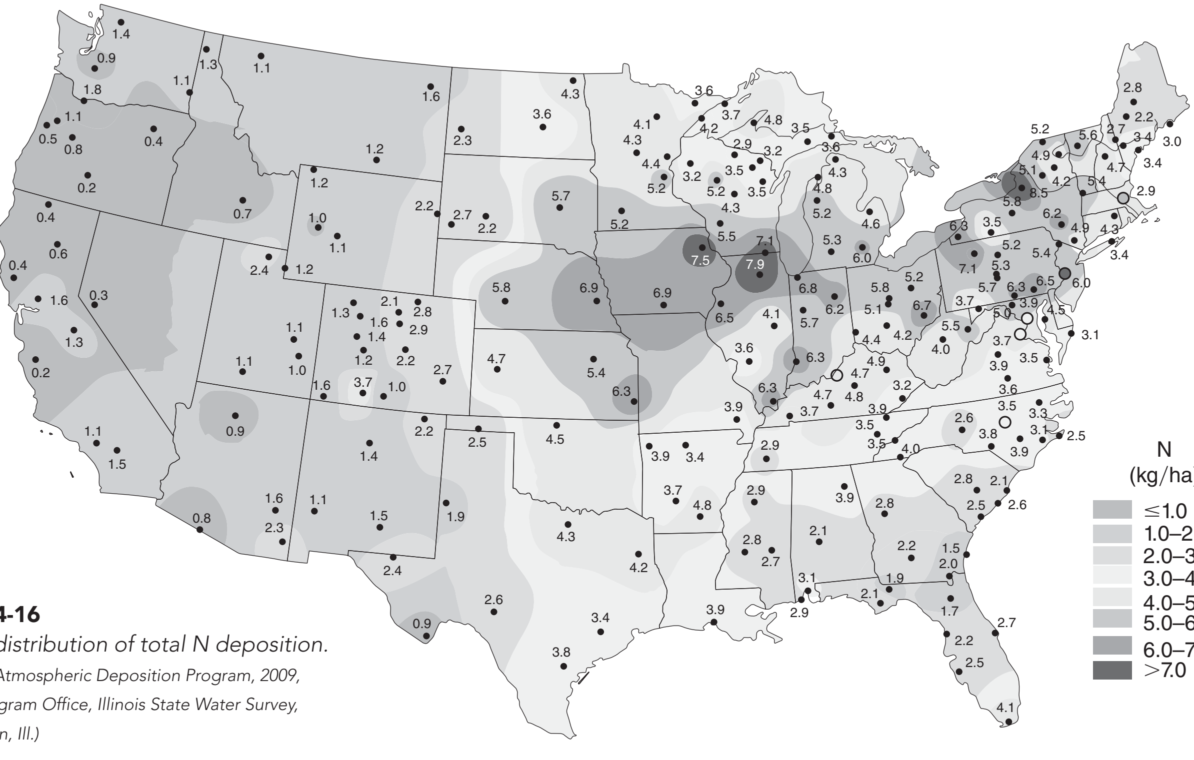


Figure 4-16
Spatial distribution of total N deposition.
(National Atmospheric Deposition Program, 2009, NADP Program Office, Illinois State Water Survey, Champaign, Ill.)

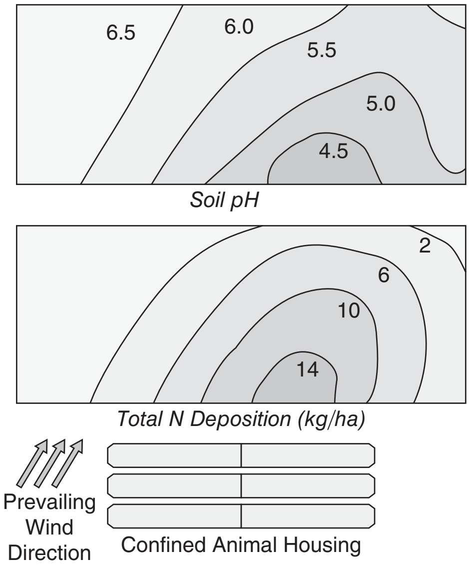


Figure 4-17
NH_3 produced from the poultry houses (20,000 animals) deposits NH_4^+ downwind and reduces soil pH. Field is approximately 20 acres and poultry houses had been operated for 18 years before air and soil sampling in 1986. NH_4^+ deposition data were collected over 1 month.
(*Adapted from Speirs and Frost, 1987,* Research & Development in Agriculture, *4:83–86.*)

Ammonia and NO_x (NO_2 + NO) are highly reactive and short-lived in the troposphere, thus contribute little to atmospheric warming. Nitric oxide (NO) catalyzes the formation of smog. In sunlight, NO and O_2 react with hydrocarbons emitted by automobile exhausts to form ozone, the most dangerous component of smog. Ground-level ozone has serious detrimental effects on human health as well as the health and productivity of crops and forests. NO_x also combines with H_2O and O_2 to form atmospheric HNO_3, a component of acid rain (Fig. 3-4). Combustion (fossil fuel, deforestation, etc.) and denitrification are the dominant sources of NO_x. In contrast, NH_3 neutralizes acids in the atmosphere by:

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

Nearly 70% of global NH_3 emissions are related to NH_3 losses from fertilizer use, storage and application of animal wastes, and forest combustion.

Industrial N Fixation The industrial fixation of N_2 is by far the most important source of N to plants. Industrial N_2 fixation is based on the Haber-Bosch process (Fig. 4-18). The NH_3 produced can be used directly as a fertilizer (anhydrous NH_3), although numerous other fertilizer N products are manufactured from NH_3 (see Fig. 4-49). Development of the NH_3 synthesis process was essential to world food security through increased crop yields with fertilizer N; however, contamination of water and air resources has also increased.

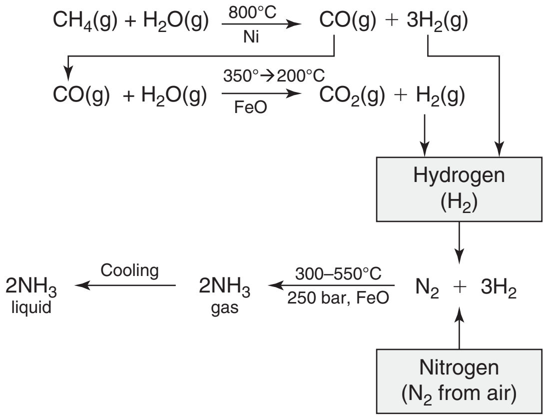


Figure 4-18
Industrial synthesis of NH_3 in the Haber-Bosch process.

FORMS OF SOIL N

Total soil N content ranges from 0.02–0.5% in mineral soils, increasing with soil OM content (Fig. 4-19). In organic soils, total N content can be $>2.5\%$. Total N content decreases with soil depth (Fig. 4-20). Total soil N occurs as inorganic or organic N, where $\approx$95% of total N in surface soils is organic N.

Assuming surface soil (acre-furrow slice or $\approx$6-in. depth) contains an average of 0.4% total N, then:

$$2 \times 10^6 \text{ lb soil/afs} \times 0.4\% \text{ N} = 8{,}000 \text{ lb N/afs}$$

If this entire N were plant available, plants would not need supplemental N as fertilizers or organic amendments. Therefore, it is critical to quantify native plant available N in soils, and potential plant available N mineralized from soil organic N during the growing season to accurately estimate additional N needed.

Organic N Compounds

Organic soil N occurs as proteins, amino acids, amino sugars, and other complex N compounds. The proportion of soil organic N in these various fractions is:

amino acids	30–45%
bound NH_4^+	20–35%
acid insoluble	20–35%
amino sugars	5–10%
unidentified	10–20%

The exact origin of each fraction is not clearly defined. Most are associated with humic and fulvic acids that comprise soil OM and are characterized by their solubility in acids or bases. For example, humic acids are acid insoluble, whereas fulvic acids are both acid and base soluble. Proteins are commonly found in combination with clays, lignin, and other materials resistant to decomposition. While all of these forms contribute to plant available N to some extent, the easily decomposable compounds (amino acids) and organic bound NH_4^+ comprise the majority of mineralizable N during the growing season. Dependence on these reserves to meet non-legume plant N requirements will result in N deficiency and reduce growth and yield.

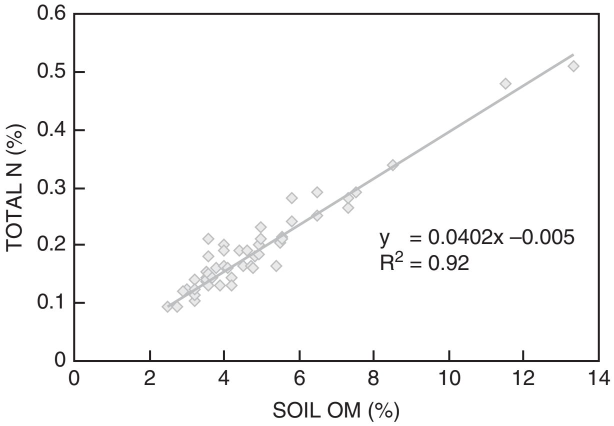


Figure 4-19
Influence of soil OM on total soil N content.
(Zheng, 2008, M.S. Thesis, Dept. *Earth Sci., Indiana Univ.)*

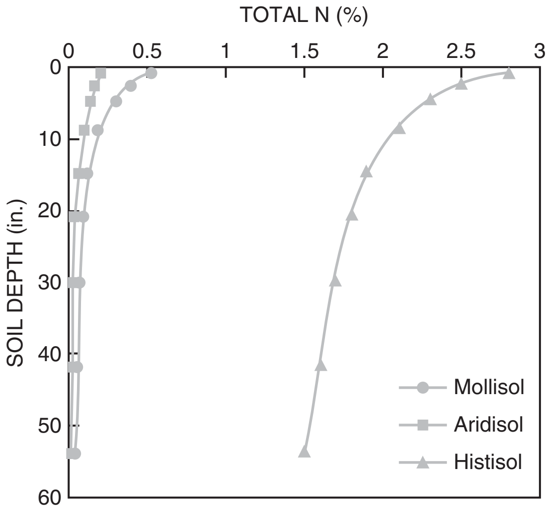


Figure 4-20
Relative distribution of total N content with soil depth in selected soil orders.

Inorganic N Compounds

Inorganic soil N includes ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), and elemental N (N_2) which is inert except for its utilization by rhizobia and other N-fixing microorganisms. For plants, NH_4^+ and NO_3^- are most important and are produced from aerobic decomposition of soil OM or from addition of N fertilizers. These forms represent 2–5% of total soil N. N_2O, NO, and NO_2 are important N forms lost through denitrification.

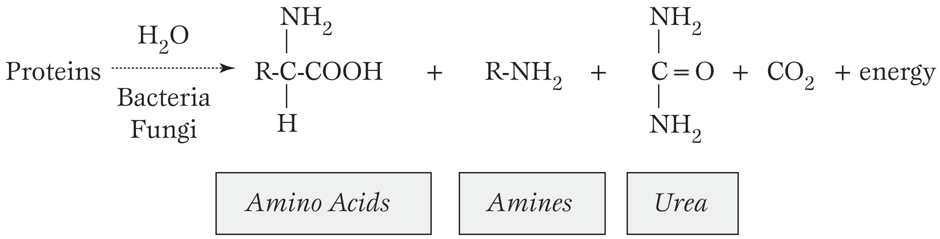
N TRANSFORMATIONS IN SOILS

Supplying sufficient NH_4^+ and NO_3^- to meet plant requirement depends on the quantity of N mineralized from soil organic N with the remainder provided through fertilizer or organic N applications. The amount of plant available N released from organic N depends on many factors affecting N mineralization, immobilization, and losses of NH_4^+ and NO_3^- from the soil.

N Mineralization and Immobilization

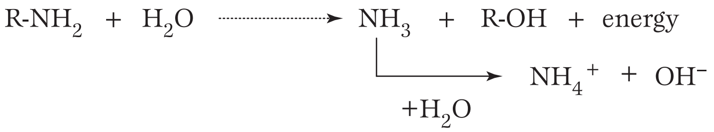
Mineralization N *mineralization* is the conversion of organic N to NH_4^+ through two reactions, *aminization* and *ammonification* (Fig. 4-2). Mineralization occurs through the activity of heterotrophic microorganisms that require organic C for energy. Heterotrophic bacteria dominate the breakdown of proteins in neutral and alkaline environments, with some involvement of fungi, while fungi predominate in acid soils. The end products of the activities of one group furnish the substrate for the next and so on until the material is decomposed. Aminization converts proteins in residues to *amino acids*, *amines*, and *urea* (Step 1). These are organic N compounds that are further converted to inorganic NH_4^+ by ammonification (Step 2). A diverse population of aerobic and anaerobic bacteria, fungi, and actinomycetes is capable of converting the products of aminization to NH_4^+.

Step 1. *Aminization*



$$\text{Proteins} \xrightarrow[\text{Bacteria Fungi}]{H_2O} \underset{H}{\overset{NH_2}{\text{R-C-COOH}}} + \text{R-NH}_2 + \underset{NH_2}{\overset{NH_2}{C=O}} + CO_2 + \text{energy}$$

Step 2. *Ammonification*



$$\text{R-NH}_2 + H_2O \longrightarrow NH_3 + \text{R-OH} + \text{energy}$$

$$NH_3 \xrightarrow{+H_2O} NH_4^+ + OH^-$$

The NH_4^+ produced through ammonification is subject to several fates (Fig. 4-2). NH_4^+ can be:

- converted to NO_2^- and NO_3^- (*nitrification*),
- absorbed directly by higher plants (*N uptake*),
- utilized by heterotrophic bacteria to decompose residues (*immobilization*),

- fixed as biologically unavailable N in the lattice of certain clay minerals (NH_4^+ *fixation*), or
- converted to NH_3 and released back to the atmosphere (*volatilization*).

Soil moisture content regulates the proportions of aerobic and anaerobic microbial activity (Fig. 4-21). Maximum aerobic activity and N mineralization occur between 50 and 70% water-filled pore space. Soil temperature also influences microbial activity and N mineralization (Fig. 4-21). Most biological reactions are influenced by temperature, where optimum soil temperature for microbial activity ranges between 25 and 35°C. The temperature coefficient, Q_{10}, is 2 over the range of 5–35°C. Thus, a twofold change in mineralization is associated with a shift of 10°C (Fig. 4-22). While N mineralization can occur over a wide range in soil moisture and temperature, N mineralization rates generally increase as temperature and moisture increase (Fig. 4-23). However, increasing moisture to saturation and temperature above 50°C will dramatically reduce N mineralization potential due to reduced microbial activity (Fig. 4-21).

Soil OM contains about 5% N and during a growing season 1–3% of organic N is mineralized to inorganic N. As total soil N content increases, the quantity of N mineralized from soil organic N increases (Fig. 4-24). Therefore, soil and crop management strategies that conserve or increase soil OM will result in a greater contribution of mineralizable N to plant N availability.

The quantity of N mineralized during the growing season can be estimated. For example, if a soil contained 2% OM with 2% mineralization rate, then:

$$2\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times (5\%\ \text{N}) \times (2\%\ \text{N mineralized}) = 40\ \text{lb N/a}$$

Thus, each year, 40 lb N/a as NH_4^+ are mineralized, which can be utilized by plants or other soil N processes (Fig. 4-2). Depending on the nature of the previous crop residue being degraded, 50–75% of organic N mineralized can be utilized by the crop.

Figure 4-21
Influence of soil moisture (water-filled pore space) and temperature on relative microbial activity in soil.
(*Doran and Smith, 1987,* SSSA Spec. Publ. 19.)

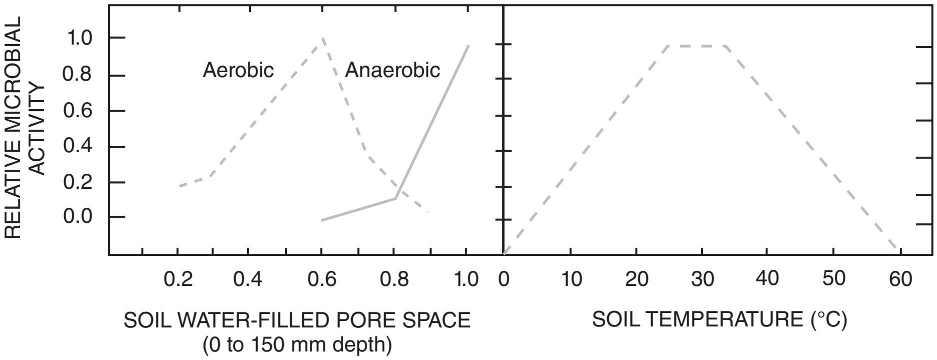
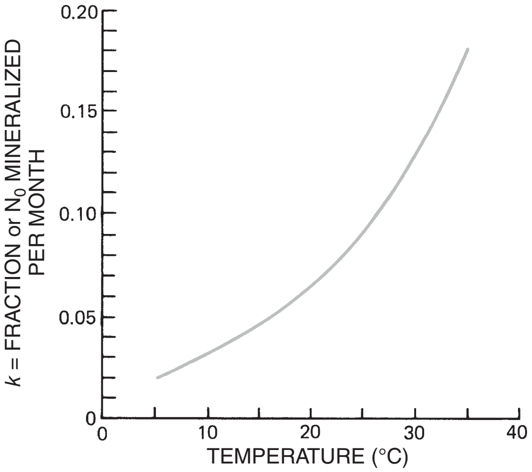


Figure 4-22
Fraction of N mineralized per month, k, in relation to temperature (k was estimated graphically for observed average monthly air temperatures).
(*Stanford et al., 1977,* Agron. J., *69:303.*)



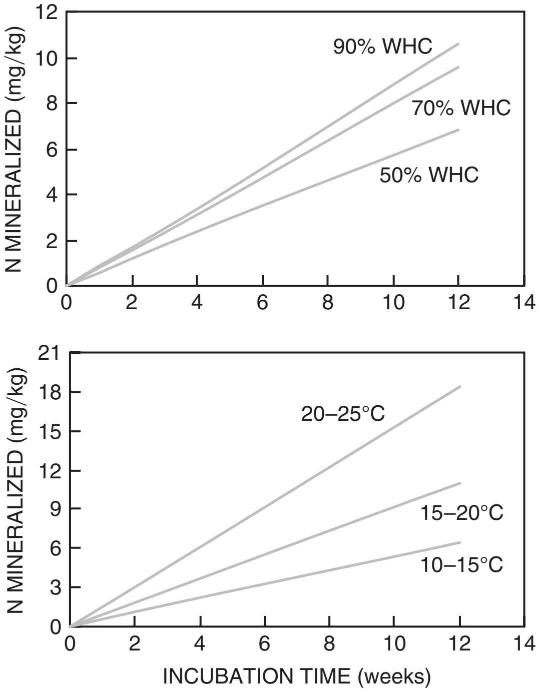


Figure 4-23
Effect of temperature and moisture on cumulative N mineralization (mg N/kg soil). Sandy clay loam soil contained 3.6% OM and 0.44% total N. WHC represents water holding capacity.
(*Agehara and Warncke, 2005,* SSSAJ, *69:1844–1855.*)

Immobilization N immobilization is the conversion of inorganic N (NH_4^+ and NO_3^-) to organic N (Fig. 4-2). If decomposing residues contain low N, microorganisms will immobilize NH_4^+ and NO_3^- in the soil solution. Microbes need N in a C:N ratio of ~8:1; therefore, inorganic soil N is utilized by the rapidly growing population, reducing NH_4^+ and NO_3^- to very low levels. Microorganisms outcompete plants for NH_4^+ and NO_3^- during immobilization, and plants can readily become N deficient. Fortunately, in most cropping systems, sufficient N is applied to compensate for N immobilization by microbes and crop N uptake. If added organic material contains high N, immobilization will not proceed because the residue contains sufficient N to meet microbial demand, and inorganic N will increase from mineralization of organic N in the residue.

C:N Ratio Effects on Mineralization and Immobilization The ratio of %C to %N (C:N ratio) defines the relative quantities of C and N in crop residues and other organic materials, soil OM, and soil microorganisms (Table 4-12). The N content of stable soil OM is ~5%, whereas C ranges from 50 to 58%, giving a C:N ratio ranging

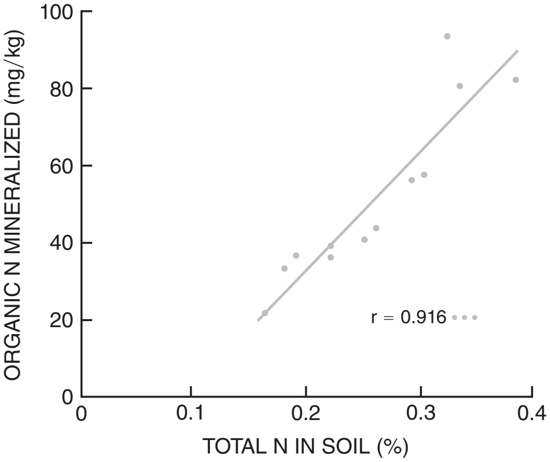


Figure 4-24
Influence of total soil N on quantity of N mineralized.

TABLE 4-12
C:N RATIOS OF SELECTED ORGANIC MATERIALS COMPARED TO SOIL OM AND MICROORGANISMS

Organic Material	C:N Ratio	Organic Material	C/N Ratio
Soil microorganisms	8:1	Bitumens and asphalts	95:1
Soil OM	10:1	Coal liquids and shale oils	125:1
Sweet clover (young)	12:1	Oak	200:1
Barnyard manure (rotted)	20:1	Pine	300:1
Clover residues	23:1	Crude oil	400:1
Green rye	36:1	Sawdust (generally)	400:1
Corn/sorghum residues	60:1	Spruce	1000:1
Grain straw	80:1	Fir	1200:1
Timothy	80:1		

between 10 and 12. Whether N is mineralized or immobilized depends on the C:N ratio of the OM being decomposed by soil microorganisms. For example, a typical soil mineralizes 0.294 mg N, as measured by plant uptake (Table 4-13). When residues of variable C:N ratio are added to soil, N mineralization or immobilization would be indicated if plant uptake was greater or less than 0.294 mg N, respectively. In this study, a C:N ratio of ~20:1 was the dividing line between immobilization and mineralization. The N content of the residue being added to soil also can be used to predict whether N is immobilized or mineralized (Fig. 4-25). Generally, N mineralization occurs with residue N content >2% under aerobic conditions.

The progress of N mineralization and immobilization following residue addition can be estimated (Fig. 4-26). During the initial stages of decomposition of added residue, there is a rapid increase in the number of heterotrophic organisms, indicated by the increased evolution of CO_2. If the C:N ratio of the fresh material is >20:1, N immobilization occurs, as shown in the hatched area under the top curve (Fig. 4-26). As residue decay proceeds, residue C:N ratio decreases, due to decreasing

TABLE 4-13
N MINERALIZED FROM VARIOUS RESIDUES AS MEASURED BY PLANT UPTAKE

Plant Residue*	C:N Ratio	N Uptake (mg)
Check soil	8:1	0.294
Tomato stems	45:1	0.051
Corn roots	48:1	0.007
Corn stalks	33:1	0.038
Corn leaves	32:1	0.020
Tomato roots	27:1	0.029
Collard roots	20:1	0.311
Bean stems	17:1	0.823
Tomato leaves	16:1	0.835
Bean stems	12:1	1.209
Collard stems	11:1	2.254
Collard leaves	10:1	1.781

*Residues above the dashed line have a C:N ratio >20:1 (net immobilization).
Residues below the dashed line have a C:N ratio <20:1 (net mineralization).
Source: Iritani and Arnold, 1960, Soil Sci., *89:74.*

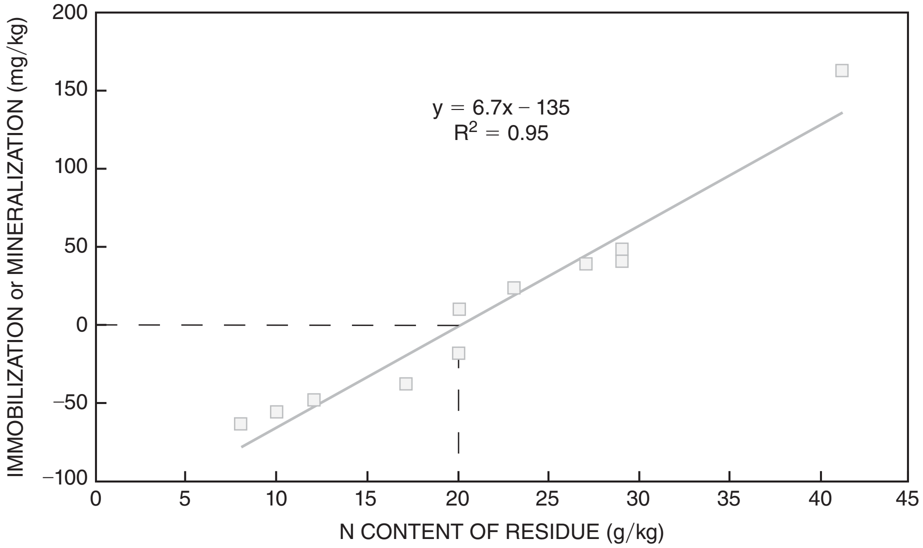


Figure 4-25
Effect of N content of organic materials on apparent N immobilization or mineralization.
(Goos, 1995, J. Nat. Resources Life Sci. Educ., *24:68–70.)*

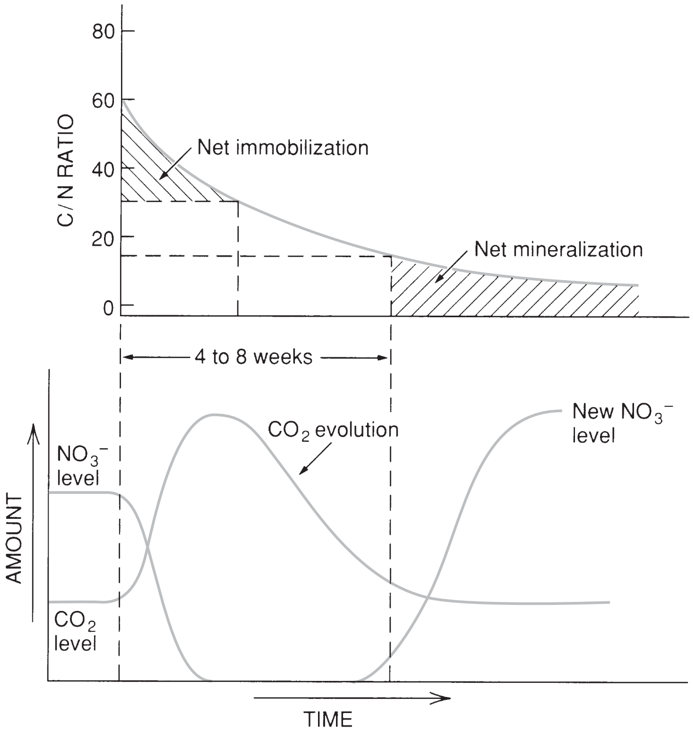


Figure 4-26
General description of N mineralization and immobilization following addition of residue to soil.
(Adapted from B. R. Sabey, Univ. of Illinois.)

C (respiration as CO_2) and increasing N (N immobilized from soil solution). Microbial activity eventually decreases as the residue C supply decreases (decreasing CO_2 evolution). Ultimately a new equilibrium is reached, accompanied by mineralization of N (indicated by the hatched area under the top curve) (Fig. 4-26). The net result is that final soil inorganic N may be higher than the original level, as a result of N added in the residue.

Generally, when residues with C:N $>$ 20:1 are added to soil, soil N is immobilized during the initial decomposition process. For residues with C:N $<$ 20:1, there is a release of mineral N early in the decomposition process. Soil OM may also increase, depending on the quantity and type of residue added and the quantity of OM loss through oxidation (mineralization) or physical soil loss (Chapter 12). The time required for residue decomposition depends on the quantity added, degree of surface residue incorporation, inorganic soil N supply, resistance of the residue to microbial attack (a function of the amount of lignins, waxes, and fats present), and soil temperature and moisture.

Estimating N Immobilization Potential

When high C:N residues are added to soil, N in the residue and inorganic soil N are used by the microorganisms during residue decomposition. The quantity of inorganic soil N immobilized by microbes can be estimated. For example, assume 3,000 lb/a residue (40% C) and C:N = 60.

$$3{,}000 \text{ lb/a residue} \times 40\% \text{ C} = 1{,}200 \text{ lb C/a in residue } (\mathrm{C_{residue}})$$

Microbial activity will utilize ≈35% of the residue C (increasing microbial biomass), while the remaining ≈65% is respired as CO_2 (Fig. 4-27). Thus, the microbes will use 420 lb of residue C.

$$1{,}200 \text{ lbs } \mathrm{C_{residue}} \times 35\% \text{ C} = 420 \text{ lb C used by microbes } (\mathrm{C_{microbe}})$$

The increasing microbe population will require N governed by microbe C:N = 8:1 (Table 4-12):

$$\frac{420 \text{ lb } \mathrm{C_{microbe}}}{x \text{ lb } \mathrm{N_{microbe}}} = \frac{8}{1}$$
$$= 52.5 \text{ lb } \mathrm{N_{microbe}}/\mathrm{a}$$

Thus, the microbes will need 52.5 lb N/a to degrade the 1,200 lb C/a in the residue. As microbes digest the residue, they access residue N during decomposition determined by:

$$\frac{1{,}200 \text{ lb } \mathrm{C_{residue}}}{x \text{ lb } \mathrm{N_{residue}}} = \frac{60}{1}$$
$$= 20 \text{ lb } \mathrm{N_{residue}}/\mathrm{a}$$

If the residue N content were known (assume 0.67%N), the lb N/a would be determined by:

$$3{,}000 \text{ lb residue/a} \times 0.67\% \ \mathrm{N_{residue}} = 20 \text{ lb } \mathrm{N_{residue}}/\mathrm{a}$$

Thus, the quantity of N immobilized is:

$$52.5 \text{ lb N/a needed by microbes} - 20 \text{ lb N/a in residue} = 32.5 \text{ lb N/a immobilized}$$

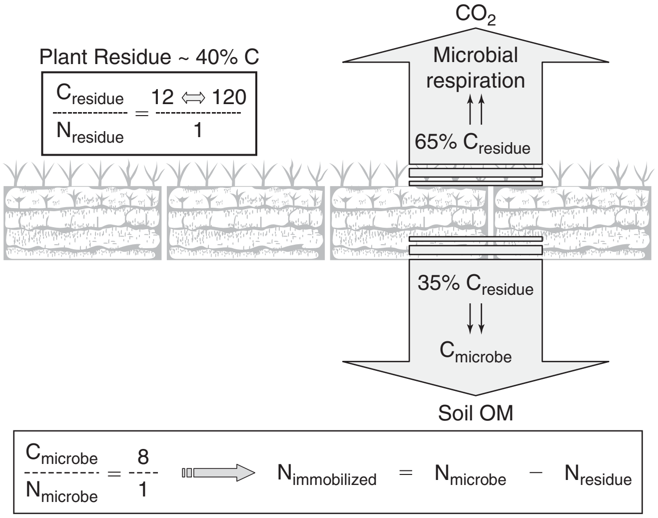


Figure 4-27
Partitioning of residue C added to soil into CO_2, soil microbe C, and soil OM, and its influence in N immobilization/mineralization. Plant residues contain an average of 40% C with variable C:N ratio. As microbes degrade the added residue, 65% of residue C is respired to the atmosphere as CO_2. The remaining 35% is incorporated into the microbes as their population increases because of the residue addition. The increase in microbe C is governed by its C:N ratio (8:1). Therefore, additional N needed by the microbes (N immobilization) is the difference in total N needed by the microbe to degrade the residue and the residue N content (see example calculation on this page).

Therefore, at least 32.5 lb N/a will be needed to compensate for immobilization of inorganic N by the microbes degrading the residue added. Routine N recommendations usually account for N immobilization requirements (Chapter 9).

Large amounts of small grain straw, corn stalks, or other high C:N residues incorporated into soils with low inorganic N content will result in N immobilization by microorganisms as residues are decomposed. If crops are planted immediately after residue incorporation, they may become N deficient. Deficiencies can be prevented by adding sufficient N to supply the needs of the microorganisms and the growing crop.

N Mineralization and Immobilization Effects on Soil OM The C:N ratio of undisturbed topsoil is about 10 or 12. Generally, C:N narrows in the subsoil because of lower C content. An uncultivated soil has a relatively stable soil microbial population, a relatively constant amount of plant residue returned to the soil, and usually a low rate of N mineralization. If the soil is disturbed with tillage, the increased O_2 supply increases N mineralization rate. Continued cultivation without the return of adequate crop residues ultimately leads to a decline in soil OM content. The influence of soil and crop management on soil OM and its relationship to soil and crop productivity is discussed in Chapter 12.

Any change in soil OM content dramatically reduces the quantity of N mineralized, and thus native soil N availability to crops. The differences in N mineralization can be readily calculated. For example, suppose that a virgin soil has a 5% OM content, and as the soil is cultivated (conventional tillage), the rate of OM loss is 3% per year. The quantity of N mineralized in the first year is:

$$5\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times 3\%\ \text{OM loss/yr} \times 5\%\ \text{N in OM}$$
$$= 150\ \text{lb N/a/yr mineralized}$$

Notice that the 150 lb N/a would meet or exceed the quantity of N required by most crops. Now assume that after 50 years of cultivation, the OM declined to 2% or one-half the original level (Fig. 4-28). Assume that 2% of the OM oxidizes per year; thus, the quantity of N mineralized is:

$$2\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times 2\%\ \text{OM loss/yr} \times 5\%\ \text{N in OM}$$
$$= 40\ \text{lb N/a/yr mineralized}$$

Figure 4-28
Decline in total soil N with years of cropping at three locations in Kansas. Each site was in wheat-fallow-wheat, with all residues incorporated with tillage. Total soil N represents soil OM, since 95% of total N is organic N.
(*Haas and Evans, 1957*, USDA Tech. Bull. No. 1164.)

The estimated N mineralized illustrates that cultivation of virgin soils mineralized sufficient N to optimize yields of most crops, especially at lower yield levels experienced 50 years ago. The excess N not utilized by the crop was subject to several losses, which include leaching and denitrification. However, at present yield levels, mineralization of 40 lb N/a is insufficient to meet crop demand and fertilizer or manure N is needed to optimize yields.

The decline in soil OM following cultivation is well documented. Depending on soil type, climate, cropping system, and tillage intensity, initial soil OM content can decline by 50% in 40–70 years. These observations indicate that the loss of soil OM can be extensive resulting in a loss of productivity. Maintaining or increasing soil OM content can dramatically improve soil productivity and crop yield. While soil and crop productivity relationships will be detailed in Chapter 12, we can use the N mineralization–immobilization calculations to estimate time required to increase soil OM.

Estimating Soil OM Production

A soil contains 1.5% OM with an annual decomposition rate of 1%. The producer wants to increase OM to 2%. How many years will it take if he produces 8,000 lb crop residue/yr (residue contains 40% C and C:N is 80:1). Also assume 80% of residue N ultimately ends up as N in soil OM.

Step 1. *Estimate annual soil OM loss.*

$$\mathrm{OM_{lost}} \rightarrow 1.5\%\ \mathrm{OM} \times (2 \times 10^6\ \mathrm{lb\ soil/afs}) \times 1\%\ \mathrm{loss\ rate}$$

$$= 300\ \mathit{lb\ OM_{lost}/afs/yr}$$

Step 2. *Estimate annual soil OM produced.*

$$\mathrm{OM_{made}} \rightarrow 8{,}000\ \mathrm{lb\ residue/a} \times 40\%\ \mathrm{C} = 3{,}200\ \mathrm{lb\ C_{residue}}$$

$$\frac{3,200\ \mathrm{lb\ C_{residue}}}{x\ \mathrm{lb\ N_{residue}}} = \frac{80}{1}$$

$$= 40\ \mathrm{lb\ N_{residue}}$$

About 80% of residue N goes into forming N in OM, thus:

$$40\ \mathrm{lb\ N_{residue}} \times 0.8 = 32\ \mathrm{lb\ N_{OM}} \quad \text{(this is N in soil OM from residue N)}$$

OM has a 10:1 C:N ratio (Table 4-12), so:

$$\frac{10\ \mathrm{lb\ C_{OM}}}{1\ \mathrm{lb\ N_{OM}}} = \frac{x}{32}$$

$$= 320\ \mathrm{lb\ C_{OM}}$$

Since there is about 50% C in OM, then:

$$\frac{320\ \mathrm{lb\ C_{OM}}}{0.5\ \mathrm{lb\ C/lb\ OM}} = 640\ \mathrm{lb\ OM_{made}/afs/yr}$$

Therefore,

$$640\ \mathrm{lb\ OM_{made}} - 300\ \mathrm{lb\ OM_{lost}} = 340\ \mathrm{lb\ OM\ net\ gain/afs/yr}$$

want to increase soil OM from 1.5% OM → 2% OM = 0.5% *OM gain:*

$$0.5\%\ \mathrm{OM\ gain} \times (2 \times 10^6\ \mathrm{lb/afs}) = 10{,}000\ \mathrm{lb\ OM/afs\ needed}$$

$$\frac{10,000\ \mathrm{lb\ OM}}{340\ \mathrm{lb\ OM\ gain/yr}} = 29.4\ \mathrm{years}$$

The important concept is recognizing that soil OM can increase over time if the C added in the residue exceeds soil C lost. Therefore, increasing C inputs and reducing C loses will increase soil OM; however, it takes many decades to effect any measurable change (Chapter 12).

Nitrification

A major portion of the NH_4^+ produced from mineralization is converted to NO_3^- through microbial oxidation or *nitrification* (Fig. 4-2). Nitrification is a two-step process where NH_4^+ is converted to NO_2^- and then to NO_3^-. Oxidation of NH_4^+ to NO_3^- is represented by:

Step 1

$$2NH_4^+ + 3O_2 \xrightarrow{\textit{nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+$$

$$(-3) \xrightarrow[\textit{increasing oxidation of N}]{} (+3)$$

Step 2

$$2NO_2^- + O_2 \xrightarrow{\textit{nitrobactor}} 2NO_3^-$$

$$(+3) \xrightarrow[\textit{increasing oxidation of N}]{} (+5)$$

Net Reaction

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$

Nitrosomonas and *Nitrobacter* are chemoautotrophic bacteria that obtain their energy from the oxidation of N and their C from CO_2. Other autotrophic bacteria (*Nitrosolobus*, *Nitrospira*, and *Nitrosovibrio*), and some heterotrophic bacteria, can oxidize NH_4^+ and other reduced N compounds (i.e., amines). Recently *Crenarchaeota* (*Archaea*) have been established as NH_4^+ oxidizers in soils, and may contribute more to nitrification than bacteria.

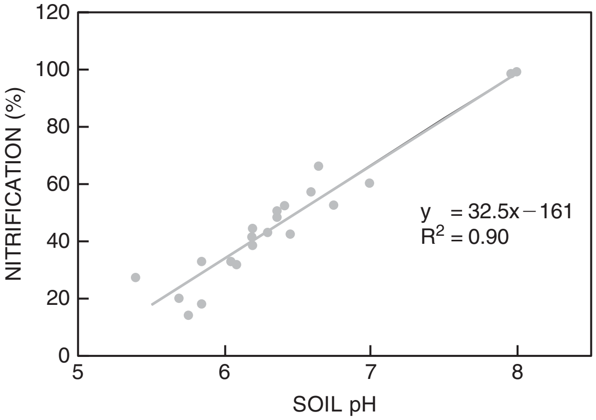
The source of NH_4^+ can be from N mineralization or N fertilizers or manures containing or forming NH_4^+. Nitrification reaction rates in well-drained soils are $NO_2^- \rightarrow NO_3^- \gg NH_4^+ \rightarrow NO_2^-$. As a result, NO_2^- generally does not accumulate in soils, which is fortunate since NO_2^- is toxic to plant roots. Both reactions require molecular O_2; thus, nitrification occurs rapidly in well-aerated soils. The reactions also show that nitrification of one mole of NH_4^+ produces two moles of H^+. Increasing soil acidity with nitrification is a natural process, although soil acidification is accelerated with continued application of NH_4^+-containing or NH_4^+-forming fertilizers (Fig. 3-9). Since NO_3^- is readily produced, it is very mobile and subject to leaching losses. Understanding factors affecting nitrification in soils will improve management practices that minimize NO_3^- leaching.

Factors Affecting Nitrification Because nitrification is a microbial process, soil environmental conditions influence nitrification rate. Generally, the environmental factors favoring the growth of most agricultural plants are those that also favor the activity of nitrifying bacteria.

Supply of NH_4^+

A supply of NH_4^+ is the first requirement for nitrification. If conditions do not favor mineralization, or if NH_4^+-containing or NH_4^+-forming sources are not added to soils, nitrification is minimal.

Figure 4-29
Influence of pH on % nitrification of fertilizer N. Anhydrous NH_3 fall applied, soils sampled after planting in spring.
(*Kyveryga et al., 2004, SSSAJ, 68:545–551.*)



Population of Nitrifying Organisms

Soils differ in their ability to nitrify NH_4^+ even under similar temperature, moisture, and NH_4^+ content. Variation in nitrifier population results in differences in the lag time between addition of NH_4^+ and buildup of NO_3^-. Because of the tendency of microbial populations to multiply rapidly, total nitrification is not affected by the number of organisms initially present, provided that temperature and moisture conditions are favorable for sustained nitrification.

Soil pH

Nitrification takes place over a wide range in pH (5–9), although optimum is ~pH 8 (Fig. 4-29). Nitrifying bacteria need an adequate supply of Ca^{+2}, $H_2PO_4^-$, and micronutrients. The influence of soil pH and Ca^{+2} on activity of nitrifiers supports the importance of liming.

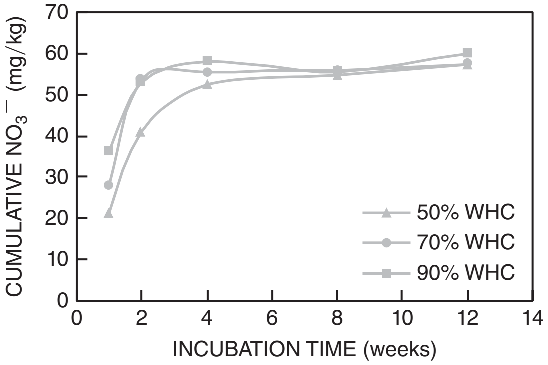
Soil Aeration

Aerobic nitrifying bacteria will not produce NO_3^- in the absence of O_2 (see reactions under "Nitrification"). Soil conditions that permit rapid gas diffusion are important for maintaining optimum soil aeration. Soils that are coarse textured or possess good structure facilitate rapid gas exchange and ensure an adequate supply of O_2 for nitrifying bacteria. Incorporation of crop residues and other organic amendments will help maintain or improve soil aeration.

Soil Moisture

Soil moisture and soil aeration are closely related in their effects on nitrification. Nitrification rates are generally highest at field capacity (Fig. 4-30). These data show that nitrification was initially slowed at the lower soil moisture content (50% WHC). N mineralization and nitrification are reduced when soil moisture exceeds field capacity (0.3 bar) or nears air dryness (>15 bar).

Figure 4-30
Influence of soil water content on cumulative nitrification of urea applied to soil.
(*Agehara and Warncke, 2005, SSSAJ, 69:1844–1855.*)



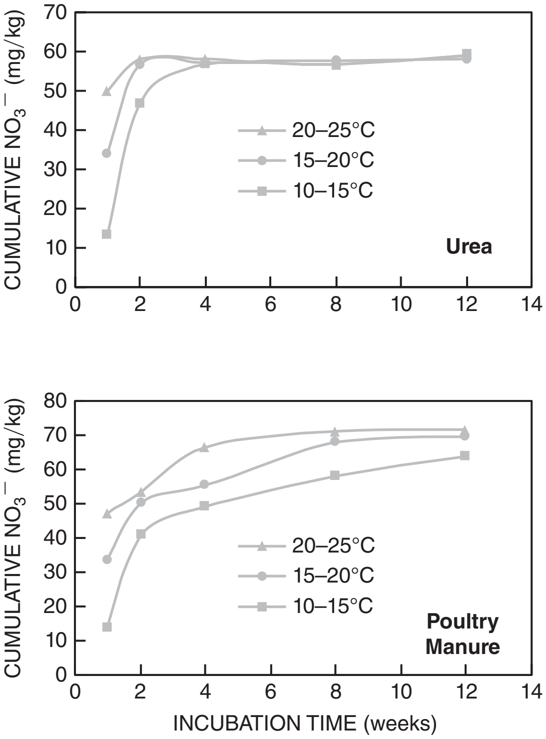


Figure 4-31
Effect of temperature on cumulative nitrification of N added as urea and poultry manure. Temperature range represents 10 h and 14 h at each temperature, respectively.
(*Agehara and Warncke, 2005,* SSSAJ, *69:1844–1855.*)

Soil Temperature

Although nitrification occurs over a wide temperature range, optimum soil temperature is 25–35°C. Observe how nitrification of urea or poultry manure is slowed at the lower soil temperature regime (Fig. 4-31). For off-season application of NH_3 or NH_4^+-containing or NH_4^+-forming fertilizers, winter soil temperatures should be low enough to retard NO_3^- formation, thereby reducing the risk of leaching and denitrification losses. Fall NH_4^+ applications are most efficient when minimum air temperatures are below 40°F (4.4°C) or when soil temperatures are below 50°F (10°C). Application of nitrification inhibitors can help retard nitrification for several months. These are best used in moderately to well-drained soils under conditions optimum for nitrification (>50°F, pH>5.5, well-aerated soil, fall NH_4^+ applications).

Even if temperatures are occasionally high enough to permit nitrification of fall-applied NH_4^+, this is not detrimental if leaching does not occur. In low rainfall areas, moisture movement through the soil profile during the winter months is insufficient to leach NO_3^-. In humid areas, water movement through the soil profile can be excessive, and NO_3^- losses occur. Whether NH_4^+ can be applied in the fall without significant NO_3^- loss depends on local soil and weather conditions.

Nitrate Leaching

NO_3^- is very soluble in water and is not strongly adsorbed to the AEC. Consequently, it is highly mobile and subject to leaching losses when both soil NO_3^- content and water movement are high (Fig. 4-32). N leaching is considered a major pathway of N loss in humid climates (Fig. 3-5) and under irrigated cropping systems. NO_3^- leaching must be carefully controlled because of the serious impact on the environment. High NO_3^- levels in surface runoff and water percolating through soil can pollute drinking water sources and stimulate unwanted plant and algae growth in lakes and reservoirs. Some of the factors

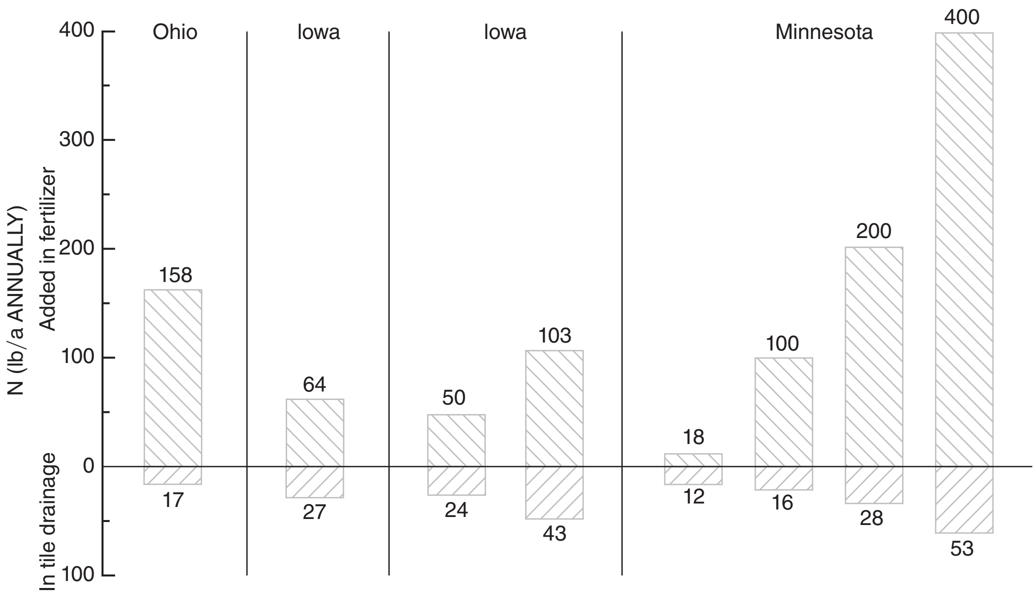


Figure 4-32
N added in fertilizer and lost as NO_3^- in tile drainage water in experiments in Ohio, Iowa, and Minnesota.
(*CAST, 1985,* Agric. and Groundwater Qual., Report No. 103, *Ames, Iowa.*)

that influence the magnitude of NO_3^- leaching losses are (1) rate, time, source, and method of N fertilization; (2) intensity of cropping and crop N uptake; (3) soil profile characteristics that affect percolation; and (4) quantity, pattern, and time of precipitation and/or supplemental irrigation. It is important to match crop N needs with soil and applied N so that leachable NO_3^- is minimized. NO_3^- leaching into water draining from tile lines located several feet below the soil surface occurs in many areas of the Midwest (Fig. 4-32). Generally, NO_3^- leaching losses in tile-drained systems can approach 30–40% of applied fertilizer or manure N, while under natural-drainage systems values between 10 and 30% are common.

In general, increased leaching potential is related to N rates exceeding crop yield potential (Fig. 4-33). Exceeding the optimum N rate increases profile N content and N leaching potential. If other factors reduce yield potential, crop recovery of applied N will be reduced. For example, when corn yield was reduced by P deficiency, correcting the P deficiency increased yield and N uptake, decreasing profile N (Fig. 4-34).

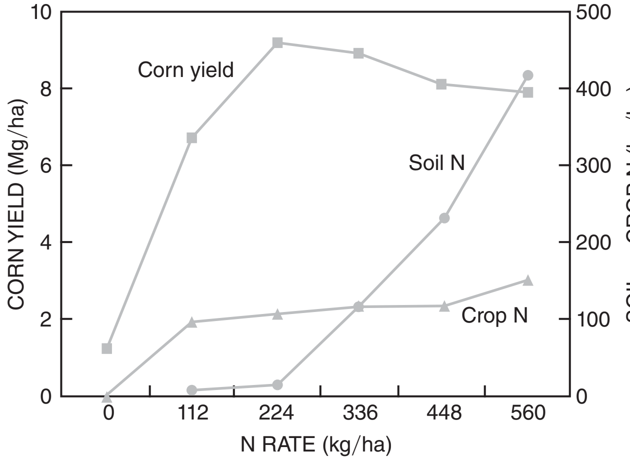


Figure 4-33
Typical relationship between N rate, crop yield, and N accumulation in the soil profile.
(Schepers et al., 1996.)

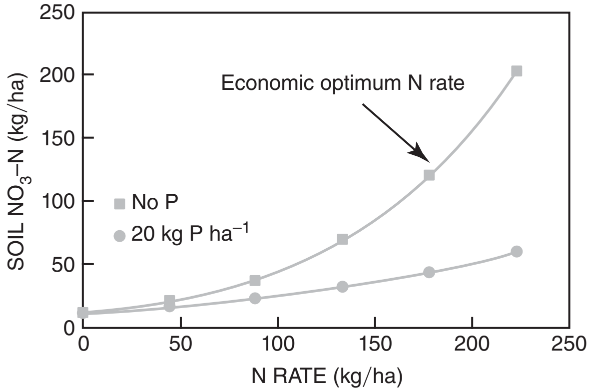


Figure 4-34
Influence of N rate on soil NO_3^- content (0–3 m depth) after 30 years of irrigated corn production. Economic optimum N rate occured at 180 kg N/ha. Addition of P reduced soil NO_3^-.
(*Schlegel et al., 1996,* J. Prod. Agric., *9:114.*)

One of the most important factors that reduces NO_3^- leaching potential is applying N synchronous with periods of high crop N demand. The same principle holds for matching peak N uptake periods with peak N mineralization (Fig. 4-14). In addition, N leaching potential increases when elevated inorganic profile N occurs during periods of low evapotranspiration (low crop water and N demand) that coincides with periods of high precipitation, soil water content, and drainage water (Fig. 4-35). Timing N applications to avoid periods of high water transport through the profile reduces leaching potential. The quantity of residual fertilizer N (N not recovered by the crop) can be substantially reduced with legumes in crop rotations (10–30% reduction) and/or cover crops (20–80% reduction). N management and NO_3^- leaching impacts on environmental quality are discussed in Chapter 12.

Ammonium Fixation

Certain clay minerals, particularly vermiculite and mica, are capable of fixing NH_4^+ by replacement with cations in the expanded lattices of clay minerals (Fig. 4-36). Fixed NH_4^+ can be replaced by cations that expand the lattice (Ca^{+2}, Mg^{+2}, Na^+, H^+) but not by those that contract it (K^+). Coarse clay (0.2–2 mm) and fine silt (2–5 mm) are important fractions in fixing added NH_4^+. In a high NH_4^+-fixing clay soil dominated by mica, substantial amounts of added NH_4^+ were fixed, increasing with soil dryness (Fig. 4-37). Increasing moisture likely increases nitrification of the added NH_4^+. Greater NH_4^+ fixation occurs with broadcast application due to increased soil-fertilizer contact.

Alternate cycles of wetting-drying and freezing-thawing contribute to the stability of recently fixed NH_4^+. The presence of K^+ often restricts NH_4^+ fixation since K^+ can also fill fixation sites (Chapter 6). Consequently, K fertilization before

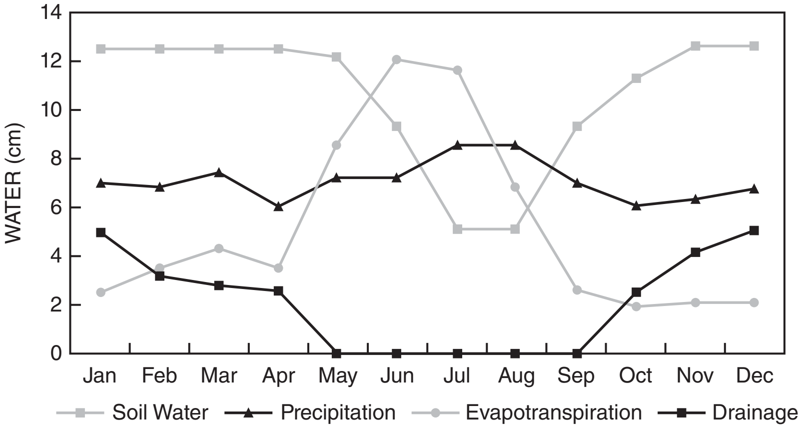


Figure 4-35
Typical soil-plant-water cycle for a humid region, sandy loam soil in the southeast United States. Soil water content in surface 1 m and water drainage below 1 m.

Figure 4-36
Diagram of an expanding clay mineral capable of fixing native or applied NH_4^+.

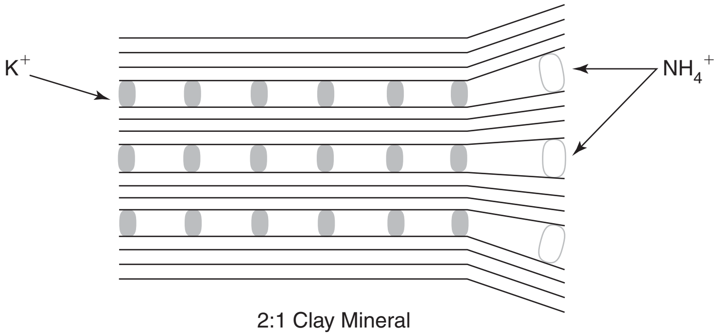
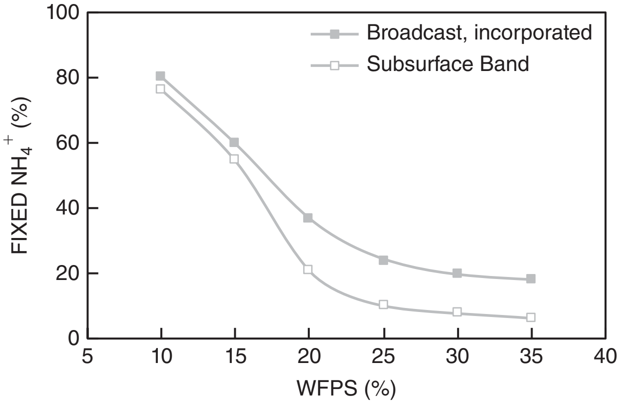


Figure 4-37
Influence of soil moisture content and NH_4^+ application method on relative fixation of NH_4^+ added as NH_4HCO_3 fertilizer.
(*Tong et al., 2004*, Pedoshere, *14:247–252.*)



NH_4^+ application can reduce NH_4^+ fixation. The availability of fixed NH_4^+ ranges from negligible to relatively high. Clay fixation of NH_4^+ provides some degree of protection against volatilization, nitrification, and subsequent leaching. Although the agricultural significance of NH_4^+ fixation is not great, it is important in certain soils. For example, selected soils from Oregon and Washington fixed 1–30% of the applied NH_4^+. In certain soils of eastern Canada, 14–60% of fertilizer NH_4^+ can be fixed. Native-fixed NH_4^+ is significant in many of these soils and can amount to 10–30% of the total fixation capacity. Intensive cropping generally cannot readily remove native-fixed NH_4^+. In contrast, while some added NH_4^+ is fixed in soils, intensive cropping generally recovers recently fixed NH_4^+.

GASEOUS LOSSES OF N

The major losses of N from the soil are due to crop removal and leaching; however, under certain conditions, inorganic N can be converted to gases and lost to the atmosphere (Fig. 4-2). The primary pathways of gaseous N losses are by denitrification and NH_3 volatilization.

Denitrification

When soils become waterlogged, O_2 is excluded and anaerobic conditions occur (Fig. 4-21). Some anaerobic organisms obtain their O_2 from NO_2^- and NO_3^-, with the accompanying release of N_2 and N_2O. Although several possible mechanisms exist (Table 4-14), the most probable biochemical pathway for denitrification is:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\uparrow \rightarrow N_2\uparrow$$

TABLE 4-14
GASEOUS LOSSES OF N FROM SOILS

Form of N Lost	Source of N	General Reaction
N_2 and N_2O	Denitrification of NO_3^-	$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\uparrow \rightarrow N_2\uparrow$
	Nitrification of NH_4^+	$NH_4^+ \rightarrow NH_2OH \rightarrow H_2N_2O_2 \rightarrow NO_2^- \rightarrow NO_3^-$ ↓ N_2O
	Reactions of NO_2^- with:	
	NH_4^+	$NO_2^- + NH_4^+ \rightarrow N_2\uparrow + 2H_2O$
	Amino acids	$NO_2^- + NH_2R \rightarrow N_2\uparrow + R\text{-}OH + OH^-$
	Lignin	$NO_2^- + \text{lignin} \rightarrow N_2\uparrow + N_2O\uparrow + CH_3ONO$
	Decomposition of NO_2^-	
	H^+	$3NO_2^- + 2H^+ \rightarrow 2NO + NO_3^- + H_2O$
	Fe^{+2}	$NO_2^- + Fe^{+2} + 2H^+ \rightarrow Fe^{+3} + NO + H_2O$
	Mn^{+2}	$NO_2^- + Mn^{+2} + 2H^+ \rightarrow Mn^{+3} + NO + H_2O$
NH_3	Fertilizers	
	anhydrous NH_3	NH_3 (liquid) $\rightarrow NH_3$ (gas)
	urea	$(NH_2)_2CO + H_2O \rightarrow 2NH_3\uparrow + CO_2$
	NH_4^+ salts	$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$ (pH > 7)
	Residue decomposition	Organic N $\rightarrow NH_4^+ \rightarrow NH_3\uparrow$

Source: Modified from Kurtz, 1980, ASA Spec. Publ. 38, p. 5.

Conversion of NO_3^- to N_2 under anaerobic conditions can be monitored with time (Fig. 4-38). In this example, NO_3^- decreases as NO_2^- increases, then NO_2^- is replaced by N_2O, which is ultimately converted to N_2.

Large populations of denitrifying microorganisms exist, the most common are the bacteria *Pseudomonas*, *Bacillus*, and *Paracoccus*, and several autotrophs (*Thiobacillus denitrificans* and *Thiobacillus thioparus*). Denitrification potential is high in most field soils, but conditions must arise that cause a shift from aerobic respiration to a denitrifying metabolism involving NO_3^- as an electron acceptor in the absence of O_2. N_2O and N_2 losses are highly variable because of fluctuations in environmental conditions between years, between seasons, and within a given field. N_2 loss predominates, sometimes accounting for about 90% of the total denitrification, while N_2O loss is greater under less-reduced conditions.

Factors Affecting Denitrification When assessing the potential for denitrification and the magnitude of N loss, three major issues must be evaluated: (1) will the surface soil environment be waterlogged or anaerobic, (2) is NO_3^- and to a lesser extent NO_2^- present in the anaerobic zone, and (3) does the surface soil contain an ample supply of decomposable or soluble C. If each of these parameters occurs together, denitrification potential and quantity of N loss are high. While other factors can influence denitrification, these are the most important.

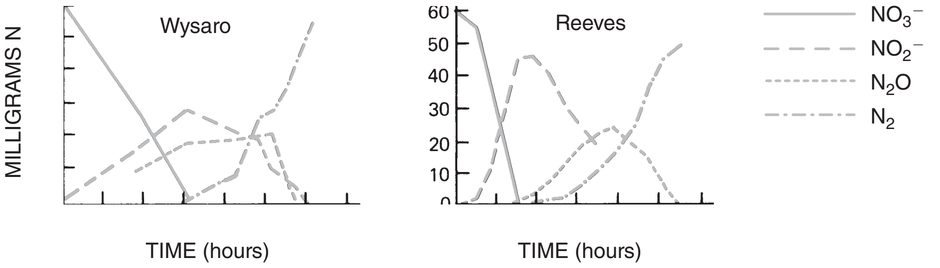


Figure 4-38
Sequence and magnitude of N products formed and utilized during anaerobic denitrification of Wysaro clay (pH 6.1) and Reeves loam (pH 7.8) at 30°C.
(*Cooper and Smith, 1963,* Soil Sci. Soc. Am. J., *27:659.*)

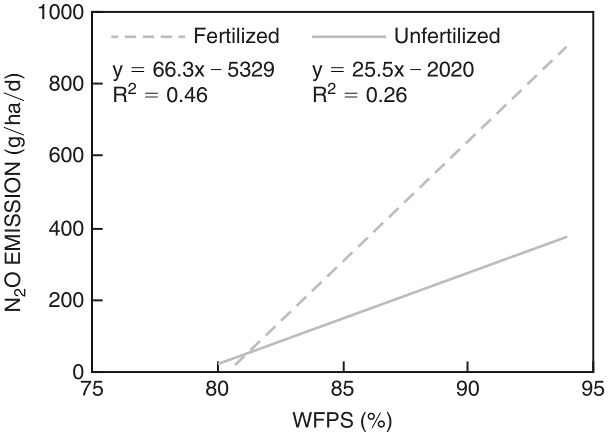


Figure 4-39
Relationship between denitrification rate (N_2O emission) and water-filled pore space (WFPS) in unfertilized soil and fertilized with 210 kg N/ha as urea.
(*Sainz Rozas et al., 2001*, SSSAJ, *65:1314–1323.*)

Soil Drainage (Moisture and Aeration)

Soil moisture content is critical to denitrification because of its effect on aeration. Denitrification proceeds only when the O_2 supply is too low to meet aerobic microbial requirements. Generally, when soil water-filled pore space exceeds 60%, aerobic activity declines, while anaerobic microbial activity increases (Fig. 4-21); however, appreciable N loss generally occurs at $>80\%$ water-filled pore space (Fig. 4-39).

As soil moisture increases, O_2 diffusion through soil is impeded. Denitrification accelerates under low O_2 diffusion in soil and a high microbial respiratory demand (high C source). When O_2 content of well-aerated soil ($\approx$16–18% O_2) declines to 8–10% O_2, denitrification is optimized (Fig. 4-40). Denitrification can also occur in aerated soils, presumably in anaerobic microsites or aggregates, where O_2 diffusion is slow (Fig. 4-41).

Soil NO_3^- and NO_2^-

NO_3^- must be present for denitrification to occur, and high NO_3^- increases denitrification potential. Residual or freshly applied N from fertilizer, manure, or other waste materials in aerated soil will mineralize and/or nitrify to produce NO_3^-, which will be readily denitrified if anaerobic conditions occur after application (Fig. 4-42).

In flooded rice soils, NO_3^- fertilizers are not used because of rapid conversion to N_2 by denitrification. Only NH_4^+ or NH_4^+-forming N sources are used.

Although NO_2^- does not usually accumulate in soil, detectable amounts occur in high pH soils and in localized soil zones containing NH_4^+ or NH_4^+-forming fertilizers. High rates of band-applied urea, anhydrous NH_3, or $(NH_4)_2HPO_4$ fertilizers

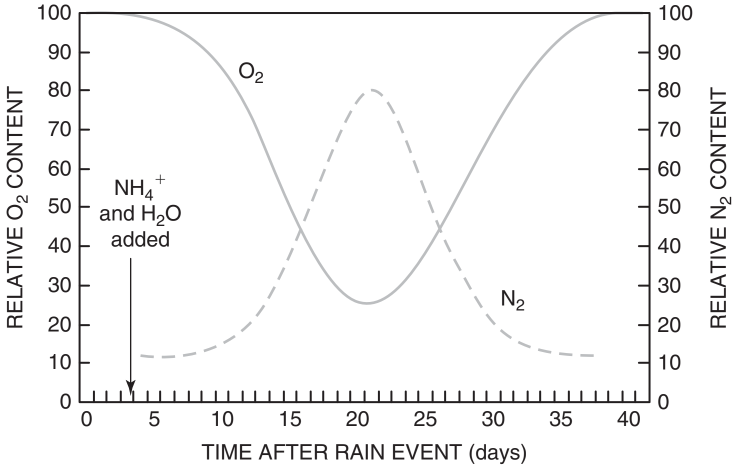


Figure 4-40
General relationship between reducing O_2 content in soil air following a rainfall event and increasing N_2 production. Release of N_2 peaked when soil O_2 decreases to ~25% of that observed at field capacity. Total N loss depends on duration of low O_2 conditions.

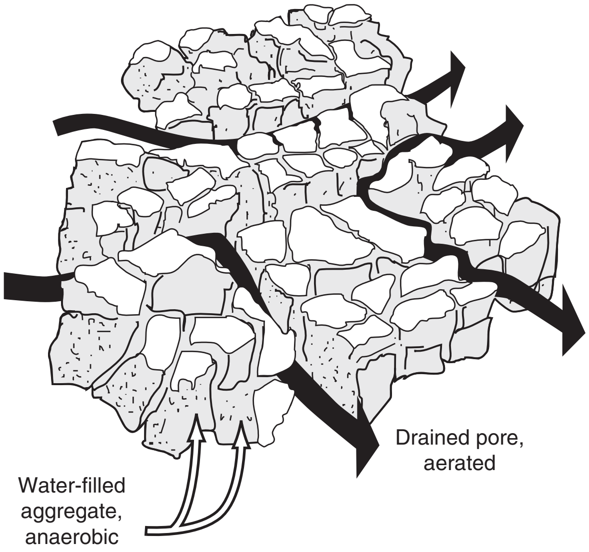


Figure 4-41
Diagram of microsites within an aerated soil that represent anaerobic, water-saturated aggregates in which native or applied N can be denitrified.

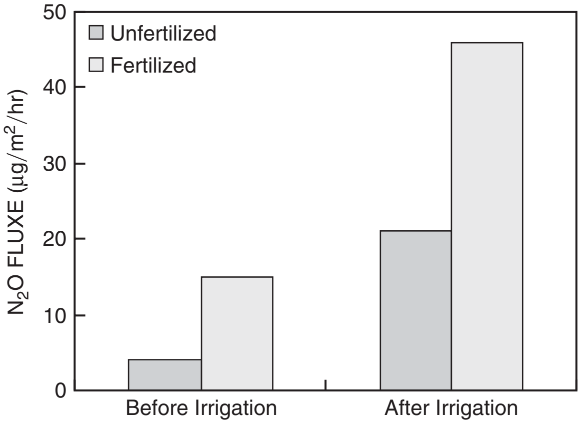


Figure 4-42
Influence of N fertilization and irrigation on rate of N_2O emission from winter wheat. Urea applied a 120 kg N/ha.
(*Su et al., 1995,* Terrestrial, Atmos., and Oceanic Sci., *6:409–417.*)

cause temporary increases in pH, which encourages NO_2^- accumulation in the band, regardless of initial soil pH. Diffusion and/or dilution of NH_4^+ in the fertilizer bands will restore conditions suitable for conversion of NO_2^- to NO_3^-. NO_2^- can diffuse beyond the fertilizer band to a soil environment, where *Nitrobacter* will readily convert it to NO_3^-. If anaerobic conditions occur during the nitrification of applied N, some of the intermediate NO_2^- can be denitrified.

Decomposable OM

Decomposable soil OM or soluble C enhances denitrification potential in soil (Fig. 4-43). The reactions with available C required for microbial reduction of NO_3^- to N_2O or N_2 are:

$$4(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 4CO_2 + 2N_2O + 6H_2O$$

$$5(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$$

Carbonaceous exudates from active roots support denitrifying bacteria growth in the rhizosphere. Under field conditions, freshly added crop residues can stimulate denitrification. Fields where animal wastes are regularly applied provide a high reservoir of soluble C.

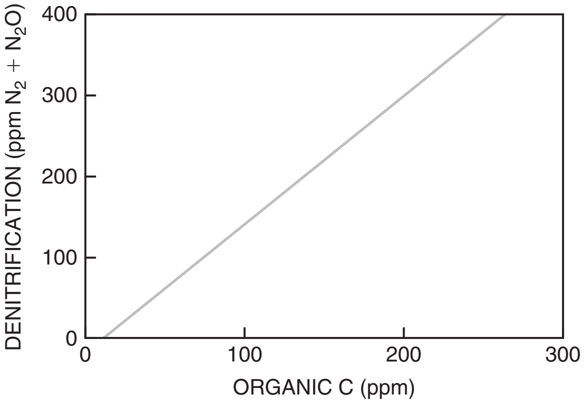


Figure 4-43
Relationship between denitrification capacity and water-soluble organic C.
(*Burford and Bremner, 1975,* Soil Biol. Biochem., *7:389.*)

Soil pH

Denitrifying bacteria are sensitive to low pH; however, denitrification has been observed over a wide range in soil pH. Generally, formation of NO occurs at pH < 5.5, whereas at pH < 6.0–6.5 N_2O represents more than half of the N loss. N_2 is the primary compound observed at near neutral or greater pH.

Temperature

Denitrification increases rapidly in the 2–10°C range. Denitrification will proceed at slightly higher rates when temperature is increased to 25–60°C, but is inhibited by temperatures >60°C. The increase in denitrification at elevated soil temperatures suggests that thermophilic microorganisms play a major role in denitrification.

Rapid conversion of NO_3^- to N_2O or N_2 occurs when rain saturates a warm soil. Denitrification losses of 10–30 lb N/a following saturation have been measured. Saturation during spring snowmelt may cause N losses related to accelerated denitrification rates when soils are quickly warmed from 2 to 12°C or higher.

Agricultural and Environmental Significance of Denitrification Under reducing conditions, NO_3^- is subject to denitrification losses to the atmosphere. Since the earth's atmosphere is largely N_2 and the oceans are virtually NO_3^- free, denitrification is responsible for returning N_2 to the atmosphere (Fig. 4-2).

Two categories of N loss by denitrification exist: (1) rapid and extensive flushes associated with heavy rains, irrigation, and snowmelt; and (2) continuous small losses over extended periods in anaerobic microsites. Generally, as soil water-filled pore space increases >70–80%, loss of NO, N_2O, and N_2 increases (Fig. 4-39). Under conditions of high soil NO_3^-, temperature, and water content (low O_2), denitrification losses can reach 1 lb N/ac/day. While difficult to quantify, denitrification losses generally represent a small percentage of fertilizer N applied, and is usually greater with manure N (Table 4-15). Under high rainfall or irrigated conditions, denitrification loss can be higher ranging 2–25% of soil N in well-drained soils, compared to 6–55% in poorly drained soils (Table 4-16). With fall-applied N, when heavy winter snows persist into late spring, N deficiencies can occur. N fertilizer use efficiency can be reduced 25–50% under these conditions. In systems where NO_3^- enters drainage water, controlled drainage and riparian buffer systems can denitrify relatively large quantities of NO_3^- (Chapter 12). Thus, field measures of denitrification of fertilizer N applied to the soil surface would be relatively low compared to total eventual denitrification in the system.

Worldwide increase in N fertilizer use has increased emissions of N_2O from soils and contributed to deterioration of the ozone layer. Although there is evidence that denitrification of fertilizer-derived NO_3^- is responsible for N_2O emission,

TABLE 4-15
ANNUAL GLOBAL N GAS EMISSIONS FROM N FERTILIZER OR MANURE APPLIED TO CROPS AND GRASSLANDS

N Source	N Applied ($t \times 10^6$)		N Loss		
			N_2O	NO	NH_3
Fertilizer	78	$t \times 10^6$	0.9	0.6	11.2
		% of N applied	1.2	0.8	14.4
Manure	32	$t \times 10^6$	2.5	1.4	7.8
		% of N applied	7.8	4.4	24.4

Source: US EPA, 2007.

Table 4-16
Denitrification Estimates for Various Soils and Recommended Adjustments for Tillage, Manure, Irrigation, and Soils

	Soil Drainage Classification				
Soil OM Content	*Excessively well drained*	*Well drained*	*Moderately well drained*	*Somewhat poorly drained*	*Poorly drained*
%	*% inorganic soil N denitrified (all sources)*[1]				
<2	2–4	3–9	4–14	6–20	10–30
2–5	3–9	4–16	6–20	10–25	15–45
>5	4–12	6–20	10–25	15–35	25–55

[1] Sources are primarily fertilizer, irrigation, precipitation, soil N not due to fertilizer. Site-specific adjustments: No-tillage or compacted layer below tillage depth use one wetter drainage class; manure N double all values; tile-drained soils use one drier drainage class; paddy systems use poorly drained only; irrigation or humid climates use value at upper end of range; semi-arid/arid sites (nonirrigated) use value at lower end of range.

Source: Meisinger and Randall, 1991. In Managing N for Groundwater Quality and Farm Profitability (pp. 85–122). *SSSA, Madison, Wis.*

contributions from natural transformations of soil OM and fresh crop and animal waste residues also contribute to N_2O emission.

Volatilization of NH_3

NH_3 is a natural product of N mineralization of which only small amounts are volatilized compared to NH_3 volatilization from surface-applied N fertilizers and manure (Fig. 4-2). The reversible reaction is:

$$NH_4^+ \leftrightarrows NH_3 + H^+ \ (\mathrm{pKa} = 9.3)$$

Urea and other amines are products of N mineralization (aminization) and ammonification of urea mineralized from soil OM could be subject to NH_3 volatilization. The biological hydrolysis of urea requires the enzyme *urease*, which is abundant in soils. Large numbers of bacteria, fungi, and actinomycetes in soils possess urease. Urease activity increases with the size of the soil microbial population and with OM content. The presence of fresh plant residues often results in abundant supplies of urease (Fig. 4-44).

Urease activity is greatest in the rhizosphere where microbial activity is high. Although temperatures up to 37°C favor urease activity, urea hydrolysis occurs at temperatures of ≤2°C. As a result, a portion of fall-applied or early winter-applied

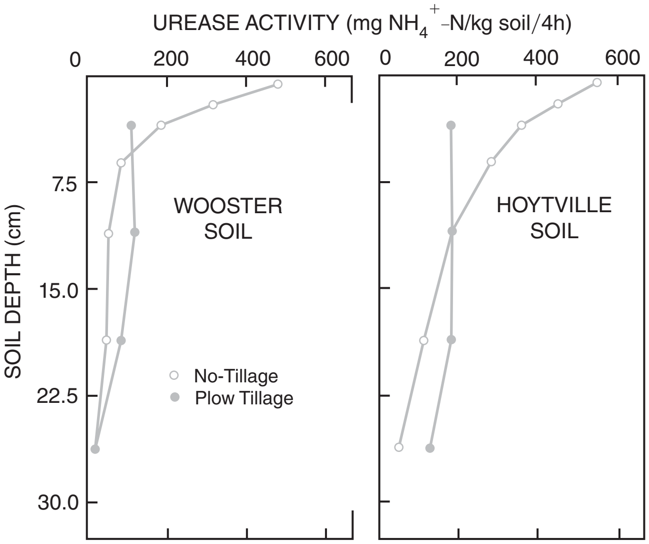


Figure 4-44
Distribution of urease activity in soil profiles as affected by tillage.
(*Dick, 1984, SSSAJ, 48:569.*)

urea may be converted to NH_3 or NH_4^+ before the spring. Urease activity is generally greater at optimum soil moisture content for plant growth.

While NH_3 volatilization is generally low in native unmanaged systems, adding fertilizer or manure N sources to soils can greatly increase N losses by volatilization. Understanding soil, environmental, and N management factors influencing volatilization reactions is essential to minimize NH_3 loss.

Factors Affecting Volatilization

Soil pH

Volatilization of NH_3 depends on the quantity of NH_3 and NH_4^+ in the soil solution, which is dependent on pH (Fig. 4-45). Appreciable quantities of NH_3 loss occur when soil solution pH > 7.5. When NH_4^+ fertilizers are added to acidic or neutral soils, little or no NH_3 volatilization occurs because of low soil solution pH. Recall that soil pH decreases slightly when the NH_4^+ is nitrified to NO_3^-. When NH_4^+-forming fertilizers (e.g., urea) are added to acidic or neutral soils, solution pH around the urea granule increases during hydrolysis:

$$CO(NH_2)_2 + H^+ + 2H_2O \leftrightarrows 2NH_4^+ + HCO_3^-$$

Solution pH increases above 7 because H^+ is consumed in the reaction; thus, the $NH_4^+ \leftrightarrows NH_3$ equilibrium shifts to the right to favor NH_3 loss. Therefore, in neutral and acidic soils, NH_4^+-containing fertilizers are less subject to NH_3 loss than urea and urea-containing fertilizers; however, NH_3 volatilization can occur with an NH_4^+ source depending on soil and environmental conditions (see "N Sources for Crop Production" for more detail).

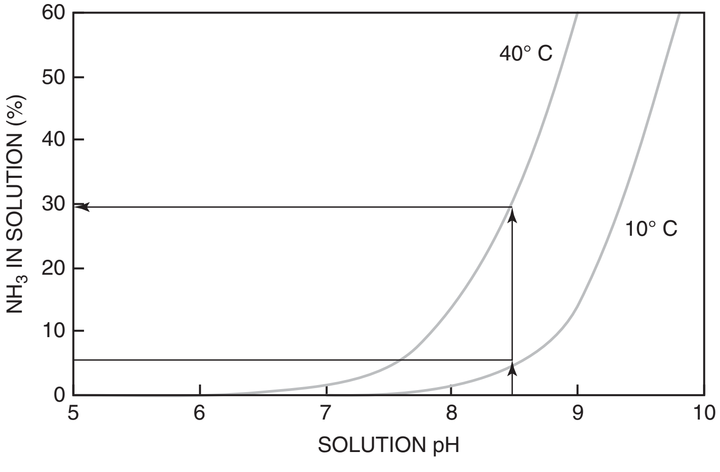
Buffer Capacity (BC)

Soil BC greatly influences NH_3 volatilization loss (Fig. 4-46). Soil pH and subsequent NH_3 loss will be less in a soil with high BC compared with low BC because of increased adsorption of NH_4^+ on the CEC. Soil BC will increase with increasing CEC and OM content.

Environment

NH_3 loss by volatilization increases with increasing temperature up to about 45°C, which is related to higher reaction rates and urease activity (Fig. 4-45). With a dry soil surface, microbial activity and volatilization reaction rates are reduced (Fig. 4-47). Maximum potential NH_3 loss occurs when the soil surface is at or near field-capacity moisture content and when slow drying conditions

Figure 4-45
Influence of pH and temperature on the %NH_3 of total $NH_3 + NH_4^+$ in solution. At pH 8.5, %NH_3 in solution increases from 5 to 30% with increasing temperature.
(Adapted from Cabrera and Kissel, Univ. of Georgia, personal communication.)



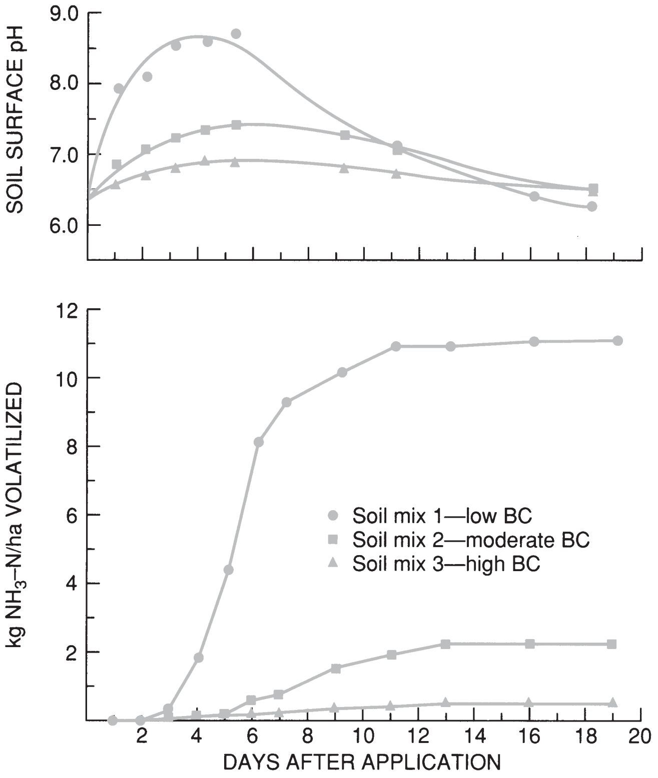


Figure 4-46
Soil BC effects on soil pH and NH_3 volatilization after N fertilizer application.
(*Ferguson et al., 1984*, SSSAJ, *48:578.*)

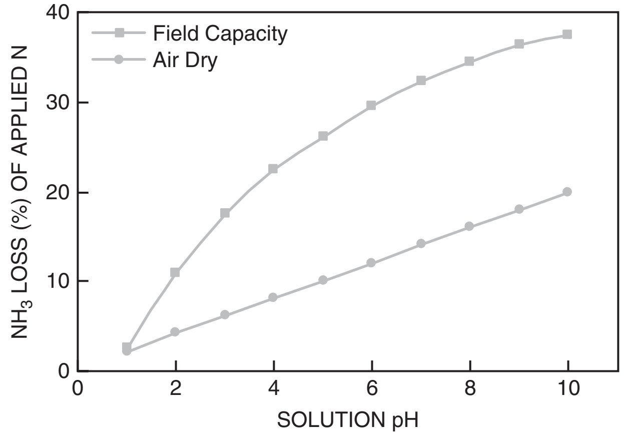


Figure 4-47
Influence of soil moisture on cumulative NH_3 loss from surface applied urea.
(*Al-Kanani et al., 1991*, SSSAJ, *55:1716–1766.*)

exist for several days. Water evaporation from the soil surface encourages NH_3 volatilization.

Surface Crop Residue

Surface crop residues increase potential NH_3 volatilization by maintaining wet, humid conditions at the soil surface and by reducing the quantity of urea diffusing into the soil. Crop residues also have a high urease activity.

N Source (Fertilizer and Manure N)

Volatilization of N applied as fertilizer or animal wastes varies greatly and depends on soil conditions, climate, and method of application. Since soil pH has a large influence on conversion of NH_4^+ to NH_3, potential N volatilization loss is greater in calcareous soils than in acid soils. In calcareous soils, $CaCO_3$ buffers solution pH around 7.5; thus, urea and NH_4^+-containing fertilizers may be subject to volatilization, depending on climate and application method (Table 4-17).

TABLE 4-17
VOLATILIZATION ESTIMATES FOR VARIOUS FERTILIZER N SOURCES, METHOD OF N APPLICATION, SOILS, AND CLIMATE

		Precipitation after N Application		
		Humid climate ≥0.5 in. rain within 2 d	*Subhumid 0–0.25 in. rain within 7 d*	*Dry climate little/no rain within 7 d*
Fertilizer N Source	**N Application Method**	*% fertilizer N loss*[1]		
		Soil pH > 7		
Urea or UAN	Broadcast	0–20	2–30	2–40
	Dribble	0–15	2–20	2–30
	Incorporated	0–10	0–10	0–10
Ammonium sulfate	Broadcast	0–40	2–50	5–60
	Incorporated	0–10	0–20	0–30
Ammonium nitrate	Broadcast	0–20	2–25	5–30
	Incorporated	0–10	0–15	0–20
Anhydrous NH_3	Injected	0–2	0–3	0–5
		Soil pH < 7		
Urea	Broadcast	0–5	5–30	5–40
	Dribble	0–5	2–20	2–30
	Incorporated	0	0–2	0–2
UAN	Broadcast	0–5	2–15	2–20
	Dribble	0–5	2–10	2–15
	Incorporated	0	0–2	0–2
Other N sources	Any method	0	0–2	0–2

[1] Adjust estimates for BC, and surface residue by:

low CEC (<10 meq/100 g): use upper end of range
high CEC (>25 meq/100 g): use lower end of range
>50% surface residue cover: use upper end of range
paddy systems: use values under dry climate & surface broadcast

Source: Meisinger and Randall, 1991. In Managing N for Groundwater Quality and Farm Profitability *(pp. 85–122)*. SSSA, Madison, Wis.

When applied to soil, urea is hydrolyzed by the enzyme urease to NH_4^+, which can be converted to NH_3 at the soil surface by:

$$CO(NH_2)_2 + H^+ + 2H_2O \leftrightarrows 2NH_4^+ + HCO_3^-$$
$$\downarrow$$
$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O$$

Solution pH increases (~8–9 pH) near the dissolving urea granule because of the HCO_3^- produced, increasing volatilization potential.

Urea hydrolysis proceeds rapidly in warm, moist soils, with most of the urea converted to NH_4^+ in several days. Conditions for best performance of surface-applied urea are cold, dry soils at the time of application and/or the occurrence of significant precipitation (0.25–0.5 in.) within the first 3–6 days after application. Movement of soil moisture containing dissolved NH_3 and diffusion of moisture vapor to the soil surface during the drying process contribute to NH_3 volatilization at or near the soil surface.

NH_4^+-containing fertilizers are also subject to volatilization. When $(NH_4)_2SO_4$ is applied to a calcareous soil, the reaction is:

$$(NH_4)_2SO_4 + CaCO_3 + 2H_2O \rightarrow 2NH_4^+ + 2HCO_3^- + 2OH^- + CaSO_4$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

Solution pH increases because of the OH^- and HCO_3^- produced. Since $CaSO_4$ is slightly soluble in calcareous soil, the reaction proceeds to the right and NH_3 volatilization is favored due to increasing pH driven by precipitation of insoluble Ca precipitates. Similar reactions occur with other NH_4^+ fertilizers that produce insoluble Ca precipitates (e.g., NH_4HCO_3, $[NH_4]_2HPO_4$). In comparison, volatilization losses are reduced with NH_4^+ fertilizers that produce soluble Ca reaction products (e.g., NH_4NO_3).

Generally, NH_3 volatilization losses in calcareous soils are greatest with urea fertilizers and the NH_4^+ salts that form insoluble Ca precipitates. However, NH_3 losses also occur when N fertilizers are surface applied to acid soils (Table 4-17), especially in pasture, turf, and no-tillage systems with high surface residue cover. NH_3 losses also increase with increasing fertilizer rate and with liquid compared with dry N sources. Urease inhibitors can be added to urea or UAN (urea ammonium nitrate) to reduce volatilization potential (see "N Sources for Crop Production").

Volatilization of N in animal waste can be as high as 40% depending on waste source, N content, and placement (Table 4-18). Immediate incorporation of broadcast manure will reduce volatilization losses (see Chapter 10 for more detail).

N Placement

NH_3 volatilization is much greater with broadcast compared to subsurface or surface band applications (Tables 4-17 and 4-18). Immediate incorporation of broadcast N greatly reduces NH_3 volatilization potential by increasing the volume of soil to retain NH_4^+. With subsurface placement or incorporation of urea or urea-containing N solutions, NH_3 formed must diffuse over greater distances before reaching the atmosphere. If soil and other environmental conditions are favorable

TABLE 4-18
VOLATILIZATION ESTIMATES FROM MANURE APPLIED TO SOILS

Manure Type	Manure Application Method	Time after Application *Short Term*	 *Long Term*
		% manure N loss	
Solid	Broadcast, no incorporation	15–30	25–45
Liquid		10–25	20–40
Solid	Broadcast, immediate incorporation	1–5	1–5
Liquid		1–5	1–5
Liquid	Broadcast	15–35	20–40
	Knifed	0–2	0–2

Source: Meisinger and Randall, 1991. In Managing N for Groundwater Quality and Farm Profitability *(pp. 85–122). SSSA, Madison, Wis.*

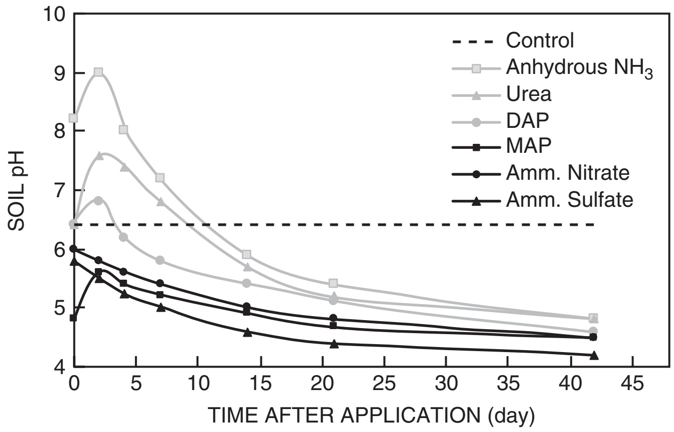


Figure 4-48
Generalized effect of band-applied N fertilizers on soil pH in the band. NH_4^+/NH_3 produced with NH_3, urea, and DAP initially raises soil pH. With time nitrification of added NH_4^+ will decrease pH below the unfertilized soil pH (see nitrification reaction in Table 3-3). Ultimately $(NH_4)_2SO_4$ is more acid forming than any N source (see Table 3-5).
(*Adapted from Mulvaney et al., 1997,* Biol. Fert. of Soils, *24:211–220.*)

for NH_3 volatilization, deep incorporation is preferred over shallow surface tillage. Some of the N losses from broadcast UAN with high surface residue cover are due to N immobilization.

Band placement of urea results in soil changes comparable to those produced by applications of anhydrous NH_3 (Fig. 4-48). Diffusion of urea from banded applications can be 2.5 cm (1 in.) within 2 days, while appreciable NH_4^+ can be observed at distances of 3.8 cm (1.5 in.) from the band. After dilution or dispersion of the band by moisture, hydrolysis begins within a few days under favorable temperature conditions.

Agricultural and Environmental Significance of Volatilization Although substantial losses of NH_3 from various N sources have been measured in laboratory studies, their validity should be closely examined. Experimental systems can impose artificial conditions of air movement, temperature, and relative humidity different from those occurring in the field. For example, NH_3 volatilization losses as high as 70% of fertilizer N have been reported from laboratory studies.

Field studies conducted under a wide range of conditions show that volatilization losses with $(NH_4)_2SO_4$ broadcast on a calcareous soil can be about 50% of the fertilizer N applied, while NH_3 volatilization losses can be as high as 30% with urea in field crop systems, and can be much higher in turf systems. In acid soil, NH_3 losses are greater for urea than for $(NH_4)_2SO_4$. Typical NH_3 losses in arable systems are usually $<25\%$ in low-pH soils and about double this amount in high-pH soils. In flooded rice systems, NH_3 loss has been reported as high as 75% of applied N.

In general, N source effects on NH_3 loss decrease with $NH_4HCO_3 > (NH_4)_2SO_4 \geq CO(NH_2)_2 > NH_4NO_3$. Increasing N rate significantly increases NH_3 volatilization. Volatilization loss is minimal when soil $pH < 5$, but greatly increases up to pH 8.5. Potential NH_3 volatilization increases with temperature. As temperature approaches 35–45°C, nitrification of NH_4^+ is reduced, which increases availability of NH_4^+ for NH_3 volatilization.

Soil and environmental conditions conducive to maximizing NH_3 losses are high soil pH, low BC, broadcast/unincorporated urea-containing fertilizer or manures, and warm/moist surface soil conditions (Table 4-19). When optimum conditions exist for N volatilization, utilizing urease inhibitors with urea-based products can reduce NH_3 volatilization and increase N use efficiency (see "Urease and Nitrification Inhibitors").

NH_3 Exchange by Plants NH_3 absorption and loss occur in plant leaves. The quantity depends on soil-surface wetness and extent of evaporation, which influence the amount of NH_3 released into the air coming into contact with plant canopies.

Table 4-19
Summary of Relative Risk Factors for NH_3 Volatilization

Condition	High Risk	Low Risk
Soil pH	>7	<6
Soil moisture	Moist	Dry
Rainfall, irrigation	Little or none, heavy dew	>0.3 in. after N applied
CEC (meq/100g)	<10	>25
Soil temperature	>20°C (70°F)	<10°C (50°F)
Soil surface	>50% residue cover (turf, pasture, no-till)	Bare
N source[1]	Manure, $(NH_4)_2SO_4$, $CO(NH_2)_2$, UAN, NH_4HCO_3	NH_3, NH_4NO_3 (urea/UAN + inhibitor)[1]
N application	Surface broadcast	Incorporate, subsurface apply

[1] NBPT is a common urease inhibitor (see Table 4-24). If using urea/UAN on high-risk site, consider using a urease inhibitor.

Field crops exposed to air containing normal levels of atmospheric NH_3 may obtain 5–10% of their N requirement by direct absorption of NH_3. Plant seedlings are a natural sink for atmospheric NH_3, absorbing about 40% of the NH_3 from air containing 1 ppm NH_3. NH_3 produced near the ground surface of grass-clover pasture can be completely absorbed by the plant cover. NH_3 volatilization from plant foliage also occurs during ripening and senescence, with values ranging 10–30 lb N/ac/yr.

N SOURCES FOR CROP PRODUCTION

Both organic and inorganic N sources supply the N required for optimum crop growth. Efficient management of N inputs requires understanding N cycling and transformations in soils (Fig. 4-2). Management practices that minimize N losses and maximize the quantity of applied N recovered by the crop will increase production efficiency and reduce potential impacts of N use on the environment. N management technologies are discussed in greater detail in Chapter 10, but the commonly available N sources used in agricultural production systems and their reactions with soil are presented here.

Inorganic N Sources

Manufactured fertilizers are the most important sources of N to plants. Over the last 30 years, world N consumption has increased from 60 to 110 million metric tons (Fig. 4-1).

Anhydrous NH_3 is the basic building block for almost all chemically derived N fertilizer materials (Fig. 4-49). NH_3 is manufactured using the Haber-Bosch reaction with N_2 from the air and H_2 produced from natural gas (CH_4) (Fig. 4-18). Since CH_4 is a limited resource (fossil fuel) and is also used for heating, cooking, and so on, conservation of this vital resource is essential. Increasing demand for CH_4 and decreasing supply increase CH_4 cost, subsequently increasing fertilizer N costs (Chapter 11).

Worldwide about 74% of NH_3 produced is used to manufacture other N fertilizer materials, while 3% is applied directly to soil and the remaining 23% accounts for non-fertilizer uses (Fig. 4-50). In the United States, N solutions, urea, and anhydrous NH_3 account for nearly 90% of total fertilizer N use (Fig. 4-51). The United States

Figure 4-49
Simplified schematic of common N fertilizers manufactured from NH_3.

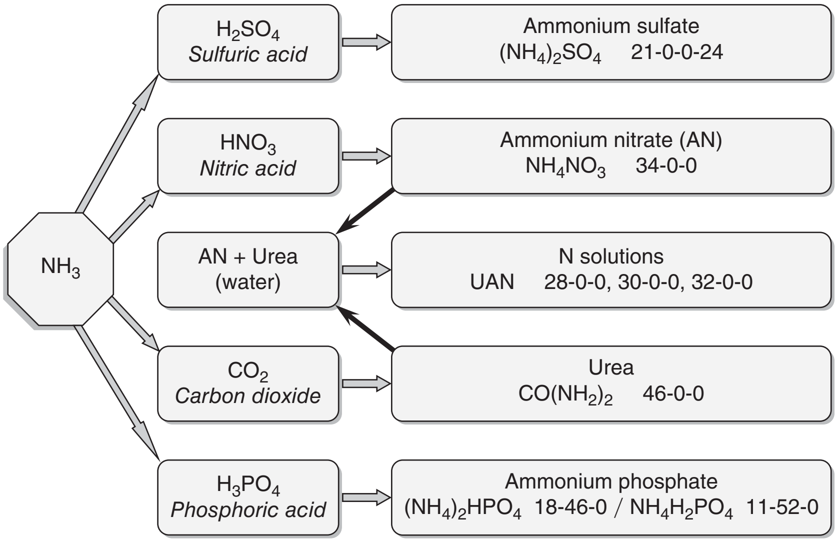


Figure 4-50
Global use of NH_3.

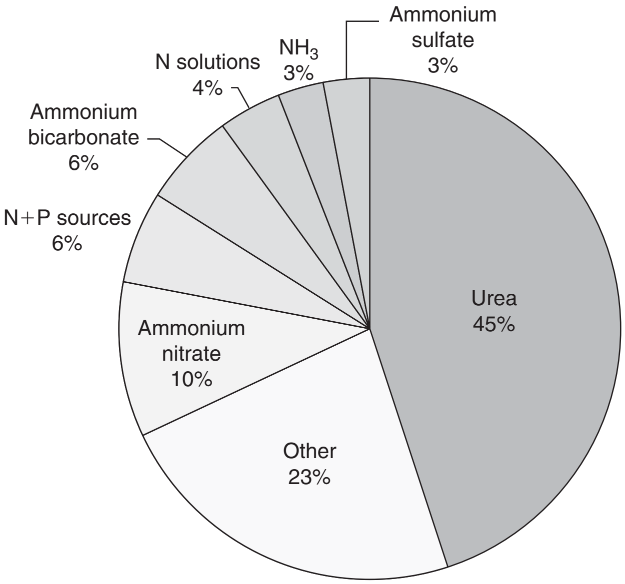
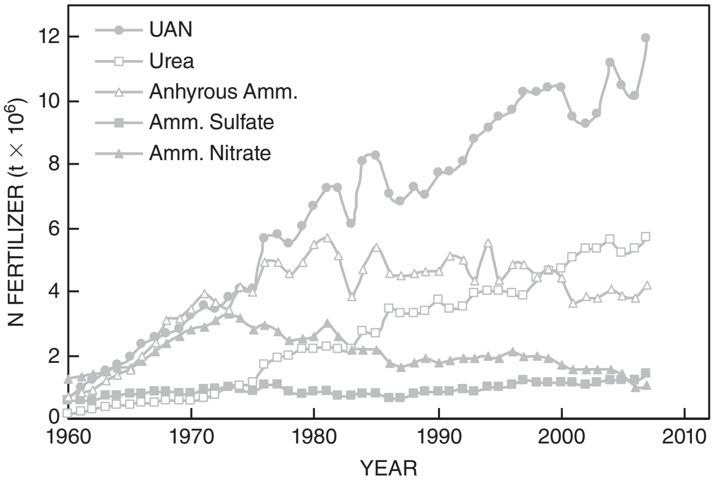


Figure 4-51
Common N sources used in the United States.
(USDA-ERS, 2009.)



and Canada represent nearly all of the direct NH_3 application in agriculture. For convenience, the various N compounds are grouped into three categories: ammoniacal, nitrate, and slowly available (Table 4-20).

NH_4^+ or NH_4^+-Forming Sources

Urea [$CO(NH_2)_2$]

Favorable manufacturing, handling, storage, and transportation economics make urea a competitive N source. It is the most widely used N source in the world. Urea represents ~21% of total fertilizer N use in the United States (Fig. 4-51). Granular urea has noteworthy characteristics, including (1) less tendency to stick and cake than NH_4NO_3, (2) no risk of explosion, and (3) less corrosive to handling and application equipment. Substantial savings in handling, storage, transportation, and application costs are possible because of urea's high N content (Table 4-20).

During manufacturing, biuret (NH_2-CO-NH-CO-NH_2) concentration in urea is kept low due to its phytotoxicity. Biuret levels of 2% can be tolerated in most fertilizers, unless applied to sensitive crops (i.e., citrus, pineapple, and other crops) where $<0.25\%$ is recommended. Solutions made from urea containing $<1.5\%$ biuret are acceptable for foliar application. Urea high in biuret should not be placed near or in the seed row. Biuret is not a problem in most urea products.

As discussed in the previous section (Volatilization of NH_3), careful management of urea and urea-based fertilizers will reduce the potential for NH_3 volatilization losses and increase effectiveness of urea fertilizers. Surface applications of urea are most efficient when they are applied to soils with low volatilization potential. Incorporation with tillage or dissolved into the soil with irrigation or adequate rainfall

TABLE 4-20
COMPOSITION OF SOME COMMON SOLUBLE FERTILIZER N SOURCES

	Nutrient Content (%)							
N Source	*N*	*P_2O_5*	*K_2O*	*Ca*	*Mg*	*S*	*Cl*	**Physical State**
			NH_4^+ or NH_4^+ forming					
Anhydrous ammonia	82	—	—	—	—	—	—	Gas
Aqua ammonia	20–25	—	—	—	—	—	—	Liquid
Ammonium bicarbonate	21–23	—	—	—	—	—	—	Solid
Ammonium chloride	25–26	—	—	—	—	—	66	Solid
Ammonium nitrate	33–34	—	—	—	—	—	—	Solid
Ammonium sulfate	21	—	—	—	—	24	—	Solid
Ammonium thiosulfate	12	—	—	—	—	26	—	Liquid
Calcium ammonium nitrate	15–27			9–19				Solid or Liquid
Ammonium polyphosphate	10–11	34–37	—	—	—	—	—	Liquid
Diammonium phosphate	18–21	46–54	—	—	—	—	—	Solid
Monoammonium phosphate	11	48–55	—	2	0.5	1–3	—	Solid
Urea	45–46	—	—	—	—	—	—	Solid
Urea-ammonium nitrate	28–32	—	—	—	—	—	—	Liquid
Urea-ammonium phosphate	21–38	13–42	—	—	—	—	—	Solid
Urea phosphate	17	43–44	—	—	—	—	—	Solid
Urea-sulfate	30–40	—	—	—	—	6–11	—	Solid
			NO_3^-					
Calcium nitrate	15	—	—	34	—	—	—	Solid
Potassium nitrate	13	—	44	0.5	0.5	0.2	1.2	Solid
Sodium nitrate	16	—	—	—	—	—	0.6	Solid

TABLE 4-21
NO-TILL CORN GRAIN YIELD AS AFFECTED BY UAN RATE AND METHOD OF APPLICATION

		Surface Band	
N Rate	**Broadcast**	*Unincorporated*	*Incorporated*
lb/a		*bu/a*	
80	89	118	125
160	108	133	141
240	114	139	154

Reduced yield with broadcast N is related to both N loss to volatilization and immobilization.

Source: Touchton and Hargrove, 1982, *Agron. J.*, 74:825.

after application will enhance N availability with urea (Table 4-21). Use of coated urea products will also reduce N volatilization losses (see "Controlled and Slow Release Compounds").

Placement of urea with the seed at planting should be carefully controlled because of the toxic effects of free NH_3 on germinating seedlings (see reactions in "Volatilization of NH_3"). The harmful effects of urea placed in the seed row can be eliminated or greatly reduced by banding at least 2.5 cm (1 in.) directly below and/or to the side of the seed row of most crops. Seed-placed urea should not exceed 5–10 lb N/a.

The effect on germination of urea placed near seeds is influenced by available soil moisture. With adequate soil moisture in medium-textured soils, urea at 30 lb N/a can be used without reducing germination and crop emergence. However, in low moisture, coarse-textured soils, urea at 10–20 lb N/a often reduces both germination and crop yields. Seedbed moisture is less critical in fine-textured (clay and clay loam) soils, and urea can usually be drilled in at rates of up to 30 lb N/a.

To summarize, the effectiveness of urea depends on the interaction of many factors, which cause some variability in the crop response to urea. However, if managed properly, urea can be as effective as other N sources (also see "Urease and Nitrification Inhibitors").

N Solutions

Of the liquid N fertilizers used for direct application, N solutions are most common, representing 44% of total N consumption in the United States (Fig. 4-51). Some advantages of N solutions include:

- easier and safer to handle and apply than other N fertilizers (especially NH_3)
- applied more uniformly and accurately than solid N sources
- many pesticides are compatible with N solutions, allowing simultaneous application
- applied through various types of irrigation systems
- excellent source for use in formulation of fluid N, P, K, and S fertilizers

N solutions are usually produced from urea, NH_4NO_3, and water and are referred to as UAN solutions (Fig. 4-49; Table 4-20). Each UAN solution has a specific salting-out temperature, below which dissolved fertilizer salts precipitate. The salting-out temperature determines feasibility of outside winter storage and the time of year for application. Salting-out temperatures vary with N concentration in solution (Table 4-22).

TABLE 4-22
PHYSICAL AND CHEMICAL CHARACTERISTICS OF UAN

Composition and Properties	Fertilizer Grade (% N by weight)		
	28%	*30%*	*32%*
Ammonium nitrate, NH_4NO_3 (%)	40	42	45
Urea, $CO(NH_2)_2$ (%)	30	33	35
Water (%)	30	25	20
Density (lbs/gal) at 15.5°C (60°F)	10.65	10.84	11.06
Salting-out temperature, °C (°F)	−17 (+1)	−10 (+14)	−2 (+28)

Anhydrous NH_3

Anhydrous NH_3 contains 82% N, the highest N content of any fertilizer (Table 4-20). About 16% of all N fertilizer used in the United States is applied as NH_3. Over the last several decades, NH_3 use in the United States has declined as urea and UAN use has increased (Fig. 4-51).

Like H_2O, NH_3 can exist as a solid, liquid, and gas depending on temperature. At room temperature, NH_3 is a colorless, highly irritating gas with a pungent, suffocating odor. NH_3 gas dissolves easily in water to form ammonium hydroxide (NH_4OH), a weak base. NH_3 gas is easily compressed and forms a clear liquid under pressure, which is stored and shipped as a compressed liquid in steel containers. NH_3 is not highly flammable, but can explode when exposed to high heat. When liquid NH_3 is released from a pressurized tank, it expands rapidly, vaporizes, and produces a white cloud of water vapor formed by water condensation in the air surrounding NH_3 as it vaporizes.

Anhydrous NH_3 is hygroscopic and is rapidly absorbed by water. Because NH_3 is very irritating to the eyes, lungs, and skin, safety precautions must be taken with anhydrous NH_3. Safety goggles, rubber gloves, and an NH_3 gas mask are required safety equipment. A large container of water attached to NH_3 application equipment is required for washing skin and eyes exposed to NH_3. Current regulations require certification for anyone applying NH_3.

Because anhydrous NH_3 is a gas at atmospheric pressure, some may be lost to the atmosphere during and after application (Chapter 10). If the soil is hard or full of clods during application, the slit behind the applicator blade will not close or fill, and some NH_3 escapes to the atmosphere.

NH_3 reacts rapidly with soil water and various organic and inorganic soil components through several possible reactions:

- $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
- $NH_3 + H^+ \rightarrow NH_4^+$
- reaction with OH^- groups and tightly bound water of clay minerals
- reaction with water of hydration around exchangeable cations on CEC
- reaction with OM
- NH_4^+ fixation by expanding clay minerals
- adsorption by clay minerals and organic components through H-bonding

Immediately after NH_3 injection, a localized zone high in both NH_3 and NH_4^+ is created (Fig. 4-52). The horizontal, roughly circular- to oval-shaped zone is about 2–5 in. in diameter, depending on several factors influencing NH_3 retention in soil:

Soil moisture content → NH_3 retention increases with soil moisture content, with maximum retention occurring at or near field capacity. As soils become

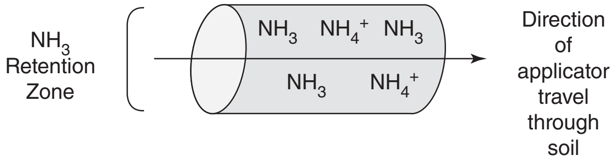


Figure 4-52
Diagram of an NH_3 retention zone.

drier or wetter than field capacity, they lose their ability to hold NH_3. The size of the initial retention zone decreases with increasing soil moisture. Diffusion of NH_3 from the injection zone is impeded by high soil moisture, because of the strong affinity of NH_3 for water.

Clay content → NH_3 retention increases with the clay content. NH_3 diffusion is greater in sandy soils than in clay soils due to larger pores and lower retention capacity of soil colloids.

Injection depth → NH_3 retention increases with increasing depth of injection and varies considerably, depending on soil properties and conditions. Deeper injection depths are required for sandy soils compared to clay soils. In dry soil, NH_3 loss declines with increasing placement depth.

Injection spacing → At a given N rate, NH_3 applied per unit volume of soil decreases with decreasing injection spacing. With the greater retention achieved with narrow spacing, there is less chance of NH_3 loss, especially in sandy soils with limited NH_3 retention capacity.

Soil OM → NH_3 retention increases with increasing soil OM. At least 50% of the NH_3 retention capacity is due to OM.

Temporary changes in soil chemical, biological, and physical conditions occur in the NH_3 retention zone. High NH_3 and NH_4^+ levels ($\approx$1,000–3,000 ppm) produce high soil pH ($\geq$9) and osmotic potential ($\geq$10 bar), resulting in partial and temporary sterilization of soil within the retention zone. NH_3 is toxic to microorganisms, higher plants, and animals. Bacterial activity is probably affected most by free NH_3, while fungi are depressed by the high pH in the retention zone. Partial sterilization in the retention zone can persist for several weeks. As a consequence of reduced microbial activity, nitrification of NH_4^+ will be reduced until conditions return to normal.

The OH^- produced by the reaction of NH_3 with H_2O will dissolve or solubilize soil OM. Most of these effects on OM are only temporary. Solubilization of OM may temporarily increase the availability of nutrients associated with OM.

Contrasting beneficial and harmful effects on soil structure have been reported following use of anhydrous NH_3. Several long-term studies have shown no difference among N sources on soil physical properties. Impairment of soil structure is not expected to be serious or lasting except in situations involving low-OM soils, in which any loss of OM would likely be harmful.

Aqua NH_3

The simplest N solution is aqua NH_3, which is made by forcing compressed NH_3 gas into water, and contains 25–29% NH_3 by weight (Table 4-20). Transportation and delivery costs limit aqua NH_3 production to small, local fluid-fertilizer plants. Aqua NH_3 is used for direct soil applications or to produce other liquid fertilizers. The NH_3 will volatilize quickly at temperatures above 50°F; thus, aqua NH_3 is usually injected into soil to depths of 2–4 in. At temperatures over 50°F, surface applications of aqua NH_3 should be immediately incorporated into the soil.

Ammonium Nitrate (NH_4NO_3)

NH_4NO_3 contains 33–34% N and is manufactured by reacting nitric acid (HNO_3) with NH_3 (Fig. 4-49). Use of NH_4NO_3 in the United States has declined, and for internal security reasons, it is now banned in some countries (Fig. 4-51).

NH_4NO_3 dissolves to NO_3^- and NH_4^+ and is readily available to crops. Several disadvantages of NH_4NO_3 include:

- hygroscopic compound (absorbs water) that results in caking during storage
- high risk of explosion when combined with oxidizable C (oil, diesel fuel, gasoline, etc.)
- less effective for flooded rice than urea or NH_4^+ fertilizers
- more prone to leaching and denitrification than NH_4^+-only products

Ammonium sulfate nitrate (Sulf-N 26) was recently released as an N source that eliminates the explosive properties of NH_4NO_3. The product (26% N, 14% S) is too new in the marketplace to report agronomic responses; however, its behavior in soil would be similar to NH_4NO_3 and $(NH_4)_2SO_4$.

Ammonium Sulfate [$(NH_4)_2SO_4$]

Ammonium sulfate represents only about 5% of total N fertilizer use in the United States (Fig. 4-51). The advantages of $(NH_4)_2SO_4$ include low hygroscopicity and is a source of both N and S. $(NH_4)_2SO_4$ depresses soil pH greater than other N sources (Table 3-5). The main disadvantage of $(NH_4)_2SO_4$ is its relatively low N content (21% N) compared to other sources; however, it can be an economical N source when S is also required.

Ammonium Phosphates

Monoammonium ($NH_4H_2PO_4$) and diammonium [$(NH_4)_2HPO_4$] phosphates are more important P sources than N sources (see Chapter 5).

Ammonium Chloride (NH_4Cl)

NH_4Cl contains 25% N (Table 4-20). The majority of NH_4Cl is used in Japan, China, India, and Southeast Asia. Some of its advantages include higher N concentration than $(NH_4)_2SO_4$ and is superior to $(NH_4)_2SO_4$ for rice. NH_4Cl is an excellent N source for Cl responsive crops (i.e., coconut, oil palm, kiwifruit). NH_4Cl is as acid forming as $(NH_4)_2SO_4$ per unit of N and, thus, is undesirable in acid soils requiring lime. Other shortcomings are its low N content compared to urea or NH_4NO_3, and its high Cl^- content, which limits its use to Cl^- tolerant crops.

Ammonium Bicarbonate (NH_4HCO_3)

This low-analysis N source (19% N) is commonly used in China (25% of total fertilizer N use), but is now being phased out in favor of urea because of its relatively low quality and instability. It is manufactured by passing CO_2 into a concentrated solution saturated with NH_3. At room temperature, NH_4HCO_3 is a white, crystalline powder that dissolves in water to produce a pH ≈ 8. Applied to warm, moist soils NH_4HCO_3, NH_3 volatilization potential is higher than with urea.

Urea-Based Fertilizers

Urea phosphate [$CO(NH_2)_2H_3PO_4$] is a crystalline product formed by the reaction of urea with phosphoric acid. The common grade is 17-44-0, which is primarily used to produce other grades of lower analysis. Urea phosphates with lower purity standards may be adequate for production of suspension fertilizers and for fertigation. Urea has also been combined with $(NH_4)_2HPO_4$ into a solid 28-28-0.

Granular urea sulfate with grades ranging from 40-0-0-4 to 30-0-0-13 has been produced. The N:S ratio may vary from 3:1 to 7:1, providing enough flexibility to correct N and S deficiencies in crops. Although numerous urea-based fertilizers have been produced in pilot plants, they are not commonly used in North America.

NO_3^- Sources In addition to NH_4NO_3, sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), and calcium nitrate $Ca(NO_3)_2$ should be mentioned because of their importance in certain regions (Table 4-20). NO_3^- sources are soluble and mobile in soil, and therefore susceptible to leaching. Unlike NH_4^+ fertilizers, NO_3^- salts are not acid forming. Because NO_3^- is absorbed by crops more rapidly than the accompanying cation, HCO_3^- and organic anions are exuded from roots, resulting in a slightly higher soil solution pH (Chapter 2). Prolonged use of $NaNO_3$, for example, will maintain or even raise the original soil pH; however, this product should not be used in semi-arid and arid climates because of buildup of exchangeable Na (Chapter 3).

At one time, $NaNO_3$ (16% N) was a major source of N in many countries. Most of it originated in large natural deposits in Chile, where $NaNO_3$ production continues to be a major industry.

Potassium nitrate (KNO_3, 13% N) contains two essential plant nutrients and is a common source in vegetable and tree crops. KNO_3 properties that make it attractive include moderate salt index, rapid NO_3^- uptake, favorable N/K ratio, and negligible Cl^- content.

Calcium Ammonium Nitrate (CAN)

Two commercial products are available that contain different amounts of Ca^{+2} and N (Table 4-20). The most common product in the United States contains $Ca(NO_3)_2 + NH_4NO_3$ (17% N, 8.8% Ca) and is available as a solid or liquid. This product is used on vegetable and tree crops in California, Arizona, and the Pacific Northwest. The value of Ca^{+2} in this material is likely through its positive effect on maintaining the integrity of plant cell membranes (Chapter 2) to enhance cation uptake, referred to as the Viets effect.

Another granular CAN product contains $CaCO_3 + NH_4NO_3$ (27% N, 8% Ca; or 15% N, 19% Ca), helps neutralize acid produced through nitrification of NH_4^+ (Table 3-5), and eliminates potential combustion hazards of NH_4NO_3. This product is commonly used in China and Europe.

Controlled and Slow Release Compounds Because the crop recovery of soluble fertilizer N is $\leq$50%, development of N fertilizer products that potentially minimize fertilizer N losses through volatilization, denitrification, and leaching have been developed (Table 4-23). Use of controlled release fertilizer (CRF) or slow release fertilizer (SRF) may improve N use efficiency, while reducing environmental risk of N use. Compared to the major N sources used throughout the world, SRF and CRF use is small, but has nearly doubled in the last decade. North America, Japan, and Europe are the major consumers, primarily in non-agricultural markets (e.g., turf and horticulture) with increasing use in production agriculture.

SRFs represent products where N release is reduced but not well controlled. CRFs are products where the rate and duration of N release is controllable. CRFs or SRFs are classified by:

- organic-N low-solubility compounds → slowly decompose by biological (e.g., urea formaldehyde) or chemical (e.g., isobutylidene diurea) processes
- fertilizer N products with a physical barrier that controls release → fertilizer N coatings include organic polymers, resins, and inorganic materials (e.g., S)
- inorganic low-solubility compounds → fertilizers such as Mg/NH_4 phosphates and partially acidulated phosphates rock (Chapter 5)

TABLE 4-23
CONTROLLED AND SLOW RELEASE N PRODUCTS USED TO REDUCE POTENTIAL N LOSSES BY LEACHING, VOLATILIZATION, AND DENITRIFICATION

			N Content	Inhibition Duration
N Source	**Base Compound**	**Common Name(s)**	**— % —**	**— weeks —**
S-coated urea	urea	SCU	30–42	4–12
		Enspan	39	
Polymer/S-coated urea	urea	PolyPlus Poly-S TriKote	38–42	6–16
		XCU	41–43	
Polymer- or resin-coated urea	urea	Polyon, Osmocote,	38–44	8–14
		Meister	25–46	
		Agriform Multicote		
		Escote		
		Prokote		
		ESN		
		Nutrisphere		
Urea formaldehyde	ureaforms	Nitroform	38	10–30+
		FLUF	18	6–10
		Folocron	29	
		GP-4340	30	
	methylene urea	Nutralene	40	7–12
		Hydrolene		
		Nitamin		
	methylol urea	Resi-Grow	30	6–10
	polymethylene urea	CoRoN	12 or 28	7–9
Isobutylidene diurea	isobutylidine urea	IBDU	31	10–16
Triazone	triazone/urea	N-Sure, Nitamin TriSert, Formolene	28–33	6–10
Crotonylidene diurea	urea/crotonaldehyde	Crotodur, CDU, Triabon	34	6–12
Melamine	2,4,6 triamino-1,3,5-triazine	Nitrazine	50–60	6–12

While there is no official differentiation, generally SRFs are microbial degraded N products such as urea formaldehydes, and CRFs are commonly coated or encapsulated products.

SRF → Organic-N Low-Solubility Compounds

These SRF products reduce the rate of N released to soil solution compared to urea or other inorganic N sources. By slowly dissolving during the growing season, NO_3^- will not exceed crop utilization rate, thereby reducing potential N losses predominately through leaching, but reduced denitrification and volatilization losses are also possible.

Urea formaldehyde (UF) is the most common SRF, containing 35–40% N (Table 4-23). Urea is reacted with formaldehyde producing a mixture of UF, unreacted urea, methylol urea, and methylene urea, which can be separated into SRF products of variable solubility or N release rates. For example, methylol urea and methylene urea are more H_2O soluble than UF and, thus, release N faster. The N release rate from UF products is characterized by their solubility in water by determining the activity index (AI) given by:

- cold water (25°C) soluble N (CWSN) contains mostly unreacted urea and exhibits fast N release rate
- hot water (100°C) soluble N (HWSN) contains methylene urea and UF and is slowly released into the soil

- hot water insoluble N (HWIN) contains long-chain UF and has extremely slow N release rate

Once these values are determined, then cold water insoluble N (CWIN) is calculated by:

$$\text{CWIN} = \text{HWSN} - \text{CWSN}$$

Then AI is determined by: $\text{AI} = (\text{CWIN} - \text{HWIN})/\text{CWIN} \times 100$. AI represents the % of relatively long N release (~6 months). Current UF products have ≈ 50–60% AI values.

Applied to soil, UF products are converted to plant available N through microbial decomposition or hydrolysis. Microbial decomposition is the primary mechanism of N release with the carbon in the methylene urea polymers providing the site for microbial activity. Increasing soil temperature and moisture (up to field capacity) increases the rate of N release.

Another related SRF is *isobutylidene diurea* (IBDU) formed by reacting isobutyraldehyde with urea. IBDU is nearly 90% H_2O soluble and contains 31% N. N release is through chemical decomposition and hydrolysis. Depending on soil moisture and temperature, IBDU can release N for 2–4 months after application (Table 4-23). High soil pH (>7) will reduce N release rate. As a granular material, decreasing particle size will increase exposed surface area and N release rate.

Triazone is a SRF containing 28% N (Table 4-23). Because of the closed-ring structure and strong C-N bonds, N is released slowly. Triazone (N-Sure) is predominately used as a foliar-applied N source, exhibiting excellent absorption properties with no toxicity to plants and commonly used in turf. A new product (Nitamin) is a combination of triazone and methylene urea and contains 22 or 30% N depending on formulation.

Crotonylidene diurea (CDU) contains 32% N, although a commercial product Triabon contains only 16% N.

CRF Coated Fertilizers

These urea-based CRFs are slightly soluble in soil solution, where the N release rate depends on microbial activity and hydrolysis. These products are commonly used in turf, vegetable, and ornamental systems; however, they are increasingly used in cereal grain systems. Like SRF products, CRFs reduce the rate of NH_4^+ and ultimately NO_3^- released to soil solution, thereby reducing leaching, volatilization, and denitrification potential.

Sulfur-coated urea (SCU) is one of the oldest CRFs consisting of a shell of S around each urea granule with 32–38% N and 12–22% S content (Table 4-23). Urea granules are coated with molten S, and then a coating of wax is added to seal cracks in the S coating. An additional layer of conditioner is added to reduce dust and improve handling (Fig. 4-53). Dissolution rate depends on the quality of the S coating. S must be oxidized by soil microorganisms before the urea is exposed and

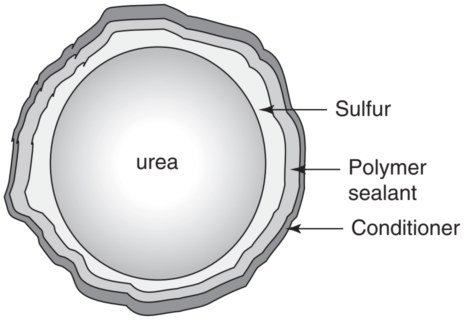


Figure 4-53
Urea coatings used as slow and controlled release N fertilizers. SCU will not contain the polymer coating, whereas PSCU contains all three layers shown. Polymer-coated urea will not contain the S coating.

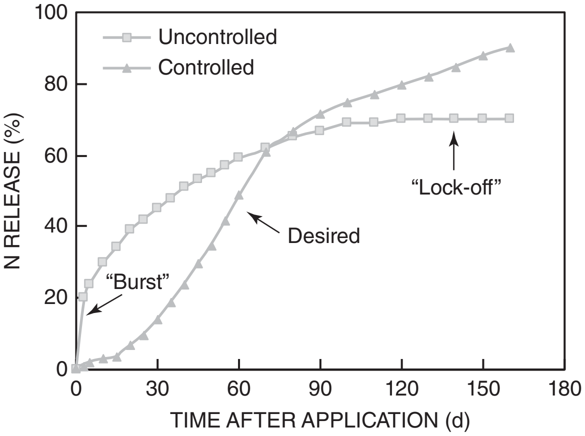


Figure 4-54
Typical N release pattern from selected coated urea products. The controlled N release product releases desired amounts of N at the desired time. The uncontrolled N release product illustrates an initial N "burst" or rapid release, followed by reduced N release or "lock-off" where N release may be insufficient for crop need. Ideally, fertilizer N release occurs just ahead of N uptake demand by the crop (Fig. 4-56).

subsequently hydrolyzed. Only about 30% of SCU granules are perfectly coated, whereas the coating of remaining granules is thin and/or cracked, which accelerates dissolution of the urea granule and N release (Fig. 4-54). If the S coating is too thick, then N release is slowed or "locked-off" (no N release). Therefore, the initial rapid N release could occur too early for recovery by the target plant, and a portion not released or released after the N is needed by the plant. Coating degradation rate will increase with soil temperature and moisture, increasing N release.

Polymer-coated SCU (PSCU) were developed to better control the N release characteristics of SCU (Fig. 4-54). With these products, the SCU is coated with an organic polymer or resin (Fig. 4-53), where the polymer thickness partially controls N release rate. In the soil, H_2O initially diffuses through the polymer layer, into the cracks and defects of the S layer, where urea hydrolysis can begin and NH_4^+ diffuses back through the polymer layer into the soil solution. PSCU products generally provide more uniform N release compared to SCUs.

Polymer-coated CRFs are the most recent technology for controlling N release and reducing N losses by leaching, denitrification, and volatilization (Table 4-23). Similar to PSCUs, N release occurs by the diffusion rate of H_2O (in) and NH_4^+ (out) through the polymer coating (Fig. 4-55). The N release rate is controlled by varying the specific polymer and its thickness. Polymers are alkyd (polyester), polyurethane, or polyolefin coatings. The alkyd-type resin (e.g., Osmocote) is primarily a dicyclopentadiene with a glycerol ester and provides a uniform coating around the fertilizer granule. N release occurs through micropores in the resin. Polyurethane coatings (e.g., Multicote, Polyon) are unique, where the polyurethane reacts with the fertilizer granule and is often referred to

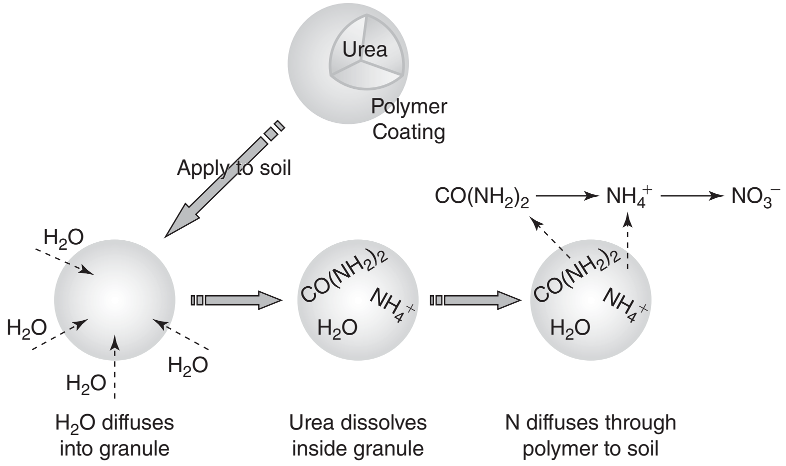


Figure 4-55
Process of controlled N release from a polymer-coated urea granule.

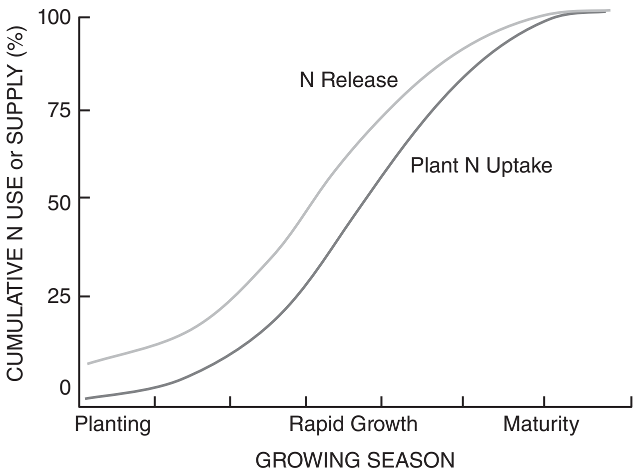


Figure 4-56
Relationship between timing of N released from a CRF or SRF and N demand by the plant.

as a *reacted layer coated fertilizer* (RLCF). RLCF products provide good control of N release, again depending on thickness. Increasing temperature will increase N release, while soil moisture, pH, and microbial activity have little effect. A new product (Nutrisphere) uses a maleic-itaconic polymer that also shows controlled N release characteristics.

Agricultural and Environmental Significance of CRF/SRF The primary purpose of CRF or SRF technology is to provide sufficient N to meet plant requirement, while reducing potential N losses to the environment through leaching, volatilization, and denitrification. In many environments, preplant application of total N needed by the plant will increase N loss potential by any or all of these pathways depending on site-specific conditions. To be classified as a CRF/SRF:

- ≤15% N released in 1 day
- 15–75% N released in 28 days
- at least 75% N released in stated release time

Thus, CRF/SRF technologies are designed to release N throughout the growing season (Fig. 4-56). Ideally, some N must initially release to meet early growth demand; if not, then a low rate of soluble N should be preplant applied. Just ahead of the period of high N demand (maximum vegetative growth rate), sufficient N release must occur. As plant N needs are reduced during maturation, all of the N should have been released. N release without plant N uptake will increase N loss potential.

Generally, CRFs/SRFs cost more than soluble N fertilizers. As a result, their use in production agriculture is much less than in higher value turf, horticultural, and ornamental plant systems. Development of new manufacturing processes is lowering the cost of these products and their use in agriculture is increasing.

It is well documented that use of CRFs/SRFs in turf systems provide sufficient N for optimum turf growth and quality, while reducing N leaching (Fig. 4-57) and volatilization (Fig. 4-58) losses. The extent of their benefit depends on the specific product and the environmental conditions after application. For example with cool-season grasses, IBDU provides better N response than ureaforms and some polymer-coated products because its N release is not temperature dependent. Alternatively with warm-season grasses in high rainfall areas, coated CRFs exhibit longer N release period more synchronous with N requirements of warm-season grasses.

Under irrigated systems, N leaching potential can be enhanced. It is critical to select the CRF/SRF that provides optimum N availability while reducing N transport below the root zone (Fig. 4-59).

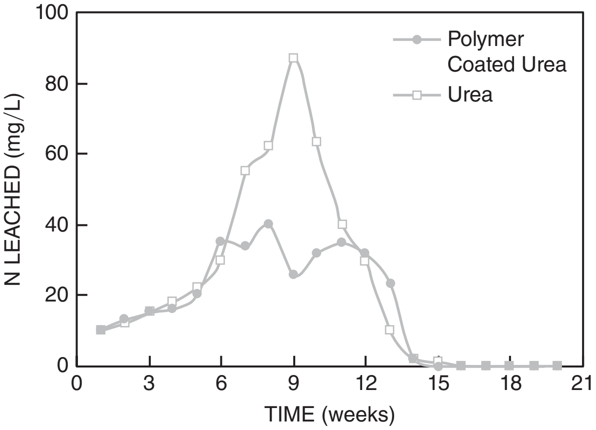


Figure 4-57
Effect of polymer-coated urea on N leached in bermudagrass golf green.
(Shuman, 2001, Proc. Georgia Water Resources Conf. Univ. Georgia, Athens.)

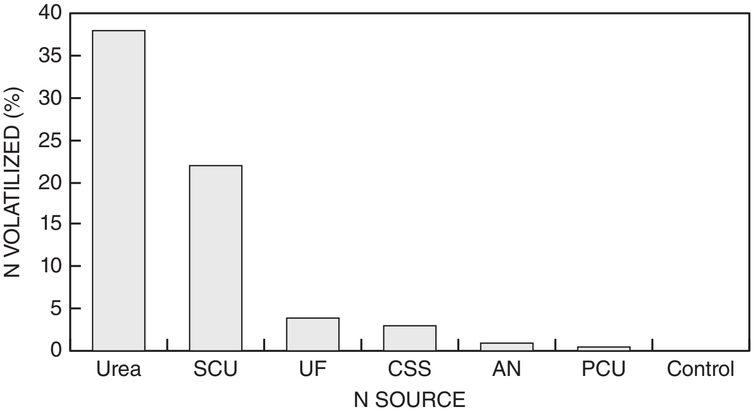


Figure 4-58
Effect of urea products on N volatilization in creeping bentgrass. SCU = sulfur-coated urea; UF = urea formaldehyde; CSS = composted sewage sludge; AN = ammonium nitrate; PCU = polymer-coated urea.
(Knight et al., 2007, Crop Sci., 47:1628–1634.)

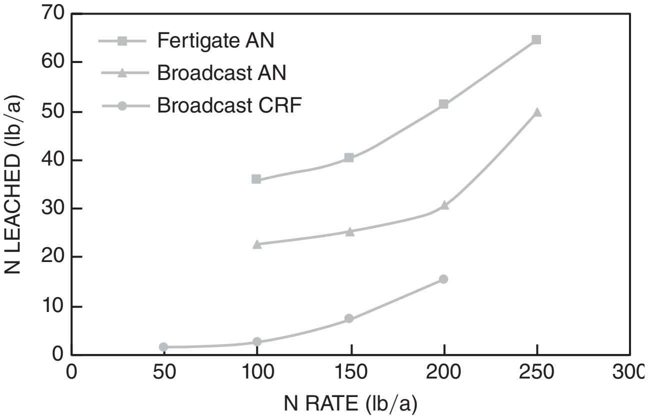


Figure 4-59
Effect of polyolefin resin-coated urea (CRF) compared to ammonium nitrate (AN) on NO_3-N leached in citrus. One application of CRF was compared to same N rate split broadcast (4 split applications) and dissolved in irrigation water (15 applications). Same amount of irrigation water applied to all treatments.
(Paramasivam et al., 2001, SSSAJ, 65:914–921.)

In agricultural systems, similar effects of water and temperature will influence the performance of specific CRFs/SRFs. While studies have shown highly variable responses, when conditions are optimum for N loss, these products can improve N availability and yield (Fig. 4-60). Over this 3-year study, corn yield increased an average of 6 bu/a, while the N rate required to maximize yield was 17 lb N/a less when the polymer-coated CRF was used.

Urease and Nitrification Inhibitors Preserving N applied as fertilizers or manures in plant available forms during plant growth will increase N use efficiency and reduce N losses to the environment. Urea in fertilizers and manures will hydrolyze to NH_4^+ with potential loss of volatile NH_3, depending on soil and environmental conditions (see "Volatilization of NH_3"). Subsequent nitrification of NH_4^+ to NO_3^-, or direct

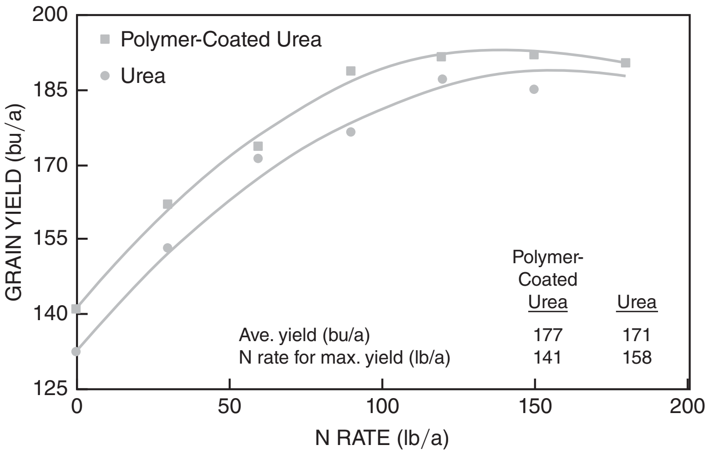


Figure 4-60
Corn yield response to N applied as urea and polymer-coated urea (ESN). Data are averaged over 5 site-years (2003–05). Average yield increase with the CRF was 6 bu/a using 17 lb N/a less N.
(Killorn et al., 2005, Iowa State Univ. ISRF05-29, 31.)

application of NH_4^+ or NO_3^-, presents increased leaching and denitrification potential, also depending on soil and environmental conditions (see "Nitrification" and "Denitrification"). Thus, controlling urea hydrolysis and nitrification processes can improve N recovery by the crop and reduce N losses to the environment.

Urease Inhibitors

Inhibition of urea hydrolysis occurs by reducing the enzymatic activity of urease, reducing the rate of urea conversion to NH_4^+. Ni is important for urease activity and new urease inhibitor products may inhibit urease by adsorbing Ni on the CEC of the polymer coating the urea granule.

NBPT (n-butyl-thiophosphoric triamide) is the most common urease inhibitor and can be used with any N source or method of application (Table 4-24). These products are more effective in reducing N loss under conditions of high volatilization potential, especially where urea or UAN is surface applied in heavy residue environments. *Thiosulfate* also has activity in reducing N volatilization and nitrification.

Nitrification Inhibitors

Nitrification inhibitors (NI) interfere with the nitrification process by direct toxicity to *Nitrosomonas* bacteria (see "Nitrification"). Adding NIs to fertilizer or manure reduces NO_3^- formation, maintaining more of the applied N as NH_4^+, thus, reducing N leaching potential. NIs also reduce potential denitrification of applied N by reducing the amount of NO_3^- available for denitrification.

Nitrapyrin and *dicyandiamide* are the most common NIs that reduce N losses when conditions are suitable for rapid nitrification to NO_3^- (Table 4-24). If soil and environmental conditions are favorable for NO_3^- losses, treatment with an inhibitor often increases the amount of applied N recovered by the plant. A new NI DMPP has been recently developed.

A tropical forage grass (*Brachiaria humidicola*) has the ability to regulate nitrification in soils by releasing exudates from roots that inhibit nitrification. Current research efforts are evaluating genetic transfer of these mechanisms into grain crops (e.g., rice, wheat, maize, and soybean) and forages.

Agricultural and Environmental Significance of Urease and Nitrification Inhibitors Additives to most solid and liquid N fertilizers have been developed to reduce nitrification, volatilization, and denitrification potential. Improving the effectiveness of urea through subsurface band placement and other N management practices can reduce N volatilization potential without use of urease inhibitors; however, broadcast application may be the only option in certain systems (i.e., no-tillage, turf), where urease inhibitors can substantially reduce N loss. For example, a summary of

Table 4-24
Fertilizer Additives Used to Reduce Potential N Losses by Leaching, Volatilization, and Denitrification

Additive	Base Compound	Common Name(s)	N Content	N Process	Inhibition Duration
			— % —		— weeks —
		Nitrification Inhibitors			
Nitrapyrin	2-chloro-6-trichloromethyl pyridine	N-Serve Stay-N 2000	–	Nitrification Denitrification	2–6
DCD	Dicyandiamide	DCD Ensan	1.6		4–8
DMPP	3,4-dimethypyrazole phosphate	DMPP ENTEC	– 12–26		6–8
		Urease Inhibitors			
NBPT	n-butyl-thiophosphoric triamide	Agrotain SuperU	– 46	Volatilization	2–3
Thiosulfate	Ammonium or calcium thiosulfate	ATS CaTS	12	Volatilization nitrification	2–3
		Combination Products			
DCD + NBPT	Dicyandiamide + n-butyl-thiophosphoric triamide	Agrotain Plus HYDREXX	—	Volatilization Nitrification Denitrification	6–8
DCD + NBPT + urea		UMAXX UFLEXX SuperU	47 46		8–12 6–8
Polymer	Maleic-itaconic copolymer	Nutrisphere	—		6–12
Polymer + urea		SSN	46		6–12

78 field trials over 5 years demonstrated a 4.3 and 1.6 bu/a corn yield increase with urease inhibitor (NBPT) included in urea or UAN, respectively (Table 4-25). Use of NBPT also reduces NH_3 volatilization with urea applied in turfgrass (Fig. 4-61). With irrigated turfgrass systems, application of water within a few days of urea application can substantially reduce volatilization; however, it may increase denitrification if excess water is applied. Ammonium thiosulfate (ATS) has been evaluated as a urease inhibitor. Generally, reduction in volatilization and increased N recovery by the crop have not been as consistent as with NBPT.

Table 4-25

Summary of Corn Yield Increases from Application of NBPT with Surface-Applied Urea and UAN

Experimental sites	Number of sites	Yield increase	
		Urea	*UAN*
		bu/a	
All sites	78	4.3	1.6
N responsive	64	5.0	2.8
Significant NH_3 loss	59	6.6	2.7

Source: Hendrickson, 1992, J. Prod. Agric., *5:131–137.*

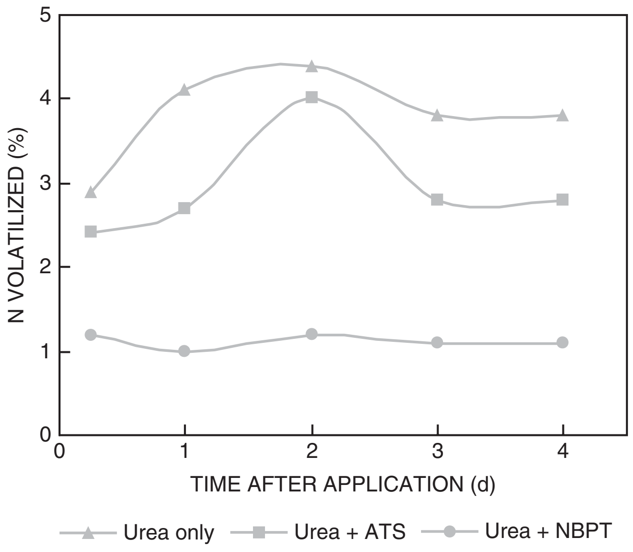


Figure 4-61
Effect of urease inhibitors on N volatilized as a % of urea-N applied (49 kg N/ha) to Kentucky bluegrass.
(Joo et al., 1989, Proc. 6th Inter. Turfgrass Res. Conf.)

The effectiveness of NIs depends on cropping system, climate, soil type, and time of application. NIs can be effective for 2–8 weeks depending on NI and the site-specific conditions. Thus, NIs can help reduce N leaching potential in sandy soils compared to clay soils. In contrast, denitrification in clay soils is generally higher than in coarse-textured soil due to reduced aeration, especially when fertilizer or manure N is applied just prior to irrigation or significant rainfall (Table 4-26). These data illustrate that DCD (dicyandiamide) had a greater effect on reducing N_2O loss as soil H_2O content increased. While ATS also reduced denitrification, it was not as effective as DCD. In contrast, ATS and nitrapyrin were equally effective in increasing fertilizer N availability and N uptake efficiency in spring wheat under wet soil conditions (high winter snowfall) after N application (Table 4-27).

Development of products that contain both urease and nitrification inhibitors has been prompted by studies documenting a positive response when both are included in the fertilizer N (Table 4-28). A summary of field trails throughout the Corn Belt showed 3–30% range in yield increases to NIs included in fertilizer N applied to corn (Table 4-29). For fall-applied N, the primary goal is to maintain applied N as NH_4^+ until soil temperatures decline below 40–50°F; nitrification potential is greatly reduced in cold soils. This is particularly important in cold, wet winter

TABLE 4-26
INFLUENCE OF NITRIFICATION INHIBITORS AND SOIL MOISTURE CONTENT ON TOTAL N_2O-N EMISSION FROM UREA APPLIED (62.5 MG/KG) TO A CLAY SOIL

	Soil H_2O Content	
Treatment	**Field Capacity**	**80% WHC[1]**
	$\mu g\ N_2O - N/kg$ soil	
Control	55	79
Urea	334	744
Urea-DCD	218	416
Urea-ATS	314	655

[1] WHC = water holding capacity.

Source: Kumar et al., 2000, *Current Sci.*, 79:224–228.

TABLE 4-27
INFLUENCE OF NITRIFICATION INHIBITORS ON SPRING WHEAT YIELD, N UPTAKE, AND SOIL N

Fertilizer Treatment	Grain Yield	Grain N Uptake	Total N Uptake	Apparent NUE[1]	N in Fertilizer Band[2]			
					After Application		Before Planting	
					NH_4^+	NO_3^-	NH_4^+	NO_3^-
	bu/a	lb/a		%	ppm			
Control	23.5	25.2	34.6	—	3	1	2	2
Aqua	38.0	40.5	52.9	24	32	21	0	9
Aqua + nitrapyrin	45.4	55.3	72.3	50	65	13	26	11
Aqua + ATS	47.3	58.3	77.0	56	54	17	13	23

[1] NUE = N uptake efficiency.

[2] 75 lb N/a injected 4" deep on Oct 3. Fertilizer bands sampled 3 weeks after application (Oct 24) and 1 day before planting (May 14).

Source: Goos and Johnson, 1999, *Agron. J.*, 91:1046–1049.

TABLE 4-28
COMBINED EFFECT OF DCD AND NBPT ON SPRING WHEAT

Treatment	Yield	Protein	N Recovery
	g/pot	%	
Urea	8.1	16.4	65.2
Urea + NBPT	8.5	16.8	68.2
Urea + DCD	8.4	16.3	69.4
Urea + NBPT + DCD	10.4	18.0	80.9

Source: Hou et al., *Agric. J.*, 1:109–112.

TABLE 4-29
SUMMARY OF CORN YIELD RESPONSES TO NITRIFICATION INHIBITORS APPLIED WITH UREA OR UAN IN THE U.S. CORN BELT

Region in the Corn Belt	N Application Time	Irrigation	Yield Increase with NI[1]	
			% of Sites	*Average %*
Southeast	Fall	No	17	14
GA, MD, NC, SC, TN	Spring		43	15
Eastern	Fall	No	69	9
IL, IN, OH, KY	Spring		51	3
	Spring (no-till)		82	13
Northern	Fall	No	25	5
MI, MN, WI	Spring		17	12
Western (sandy soils) KS, MN, NE	Spring	Yes	52	30
Western (loam & clay soils) KS, NE	Spring	Yes	10	5

[1] Data represent % of sites and average % yield increase to NIs added to fertilizer N.

Source: Nelson and Huber, 1992, *Nat. Corn Handbook*, Iowa State Univ.

climates where denitrification can occur even at soil temperature <40–50°F. For spring preplant applications of N, NIs can retain applied N as NH_4^+ when plant N demand is low and rainfall potential is high. Generally, the highest probability of yield response to NIs is on sandy soils (excessive leaching) and poorly drained fine-textured soils. Under these conditions, potential N loss through leaching and denitrification are the highest, respectively. With any NI, as temperature increases, their effectiveness decreases.

Organic N Forms

Before 1850, virtually all of the N consumed was primarily animal manure and legume N. Presently these materials account for 40% of the total N use in the United States (Table 4-4). Annually, over 1 billion tons of agricultural, municipal and industrial wastes are generated in the United States. When used as a nutrient source, considerable quantities of N and other nutrients are added, depending on the rate of material applied. This section will provide general information regarding N content of selected organic N sources, while Chapter 10 will provide detailed information on organic nutrient management.

Organic nutrients are classified by their source and effects on the soil and target plant. Source generally refers to animal- or plant-based materials, while effects are characterized by:

- materials that have a stable organic base with a low N content and N mineralization potential (e.g., composts, peat)
- materials with short-term nutrient supply, relatively high N content, and/or readily mineralizable organic N content (e.g., manures, biosolids)

In agricultural cropping systems, the average N content in most organic materials utilized is low (1–12% N) relative to crop N need. Using these materials to meet crop N requirement requires high application rates, which often results in an imbalance of other nutrients (Chapters 10 and 11). To avoid nutrient imbalances and risk to environmental quality, lower rates of organic amendments are supplemented with fertilizer N. In ornamental, turf, and other horticultural systems, plant N requirements can usually be met with appropriate rates of organic N sources.

Non-Manure Sources Many organic materials can be utilized in diverse plant or cropping systems to provide nutrients. The majority used in agricultural and horticultural systems are by-products of animal- or plant-processing facilities and municipal waste treatment plants. About 75% of the sewage handled by municipal treatment plants is of human origin, and the remaining 25% is from industrial sources. The end products of all sewage treatment processes are sewage sludge and sewage effluent. Sewage sludge or biosolids are produced during sewage treatment. Sewage effluent is essentially clear water containing low concentrations of plant nutrients and traces of OM, which may be chlorinated and discharged into surface waters. Biosolids are a heterogeneous material, varying in composition between cities and even from one day to the next in the same city. The United States produces nearly 10 million tons (dry weight) of biosolid waste per year, and about 60% is processed for land application. The remainder is incinerated or buried in landfills.

Biosolids contain 1–6% N (Table 4-30). While there are strict regulations regarding their use in agriculture, they are a valuable nutrient source. Management of biosolids and other organic nutrient sources will be discussed in Chapter 10.

Much of the remaining organic materials used to supply nutrients are waste products from either animal- or plant-processing facilities (Table 4-30). With animal-based materials, the N content is relatively high and the C:N ratio is relatively

TABLE 4-30
SELECTED ORGANIC SOURCES OF N AND OTHER NUTRIENTS

Material	C:N	N	P	K	Ca	Mg
		% dry weight				
		Animal Based				
Blood meal	2–3	9–13	0.2–1.0	0.2–1.5	1.5–3	0.3–0.4
Bone meal	4–5	4–6	7–12	0.2–0.3	18–25	0.5–0.6
Carcass meal	3–4	6–11	2–7	0.3–0.5	4–10	0.1–0.2
Guano	3–4	8–16	2–7	1–3	18–20	3–5
		Plant Based				
Fruit pulp	40–50	0.8–1.4	0.2–0.3	1.2–1.4	0.6–0.9	0.1
Brewers grain	10–12	3–5	0.4–0.7	0.5–1.0	0.2–0.3	0.1–0.2
Distillers pulp	8–10	5–6	0.7–1.0	0.8–6.0	0.2–0.3	0.1–0.2
		Compost				
Biogenic waste	15–25	1–2	0.2–0.5	0.5–1.3	1.5–5.0	0.3–1.6
Yard waste	30–50	1–2	0.1–0.3	0.5–0.7	4–6	0.4–0.6
		Municipal Sewage				
Biosolids		1–6	1.5–7.0	0.2–0.5	0–12	0.4–0.7

Source: Adapted from Trenkel, 2007, Fertilizers. In *Ullmans Agrochemicals* 1:3–142. Wile-VCH.

low. As a result, N mineralization potential is high making these materials excellent sources of plant available N. In contrast, most plant-based materials (including manures) have low N content and provide little mineralizable N. As a result, plant-based organic wastes are commonly used in ornamental and horticultural systems, where N requirements are lower compared to agricultural cropping systems.

Before using any organic N source, the material should be analyzed for nutrient content by a soil testing laboratory.

Manure Sources The total quantity of manure produced annually in the United States is nearly 150 million tons (dry weight), with about 60% produced and deposited by grazing animals (Table 4-31). The remaining 40% is produced in confined animal feeding operations (CAFO). Approximately 16 million acres (8%) of cropland were fertilized with manure, with the majority ($\approx 60\%$) applied to corn. Of the total manure produced, 1.3 million tons of N is available for land application (Fig. 4-62). Since the majority of recoverable N is associated with CAFO, many regions in the United States produce more N than can be utilized on-farm. About 60% of recoverable N exceeds that used to meet on-farm crop N requirements, where the majority is related to poultry production (Fig. 4-62). Nutrients in excess of on-farm use must be transported to other areas.

Average annual manure production ranges 6–15 tons per animal unit (Table 4-32). The quantity of N in manure and the availability to plants vary greatly and depend on (1) nutrient content of the animal feed, (2) method of manure handling and storage, (3) quantity of added materials (i.e., bedding, water), (4) method and time of application, and (5) soil properties. Most wastes exiting the animal contain 75–90% water. Storage and handling usually reduce water content in solid-storage systems and increase water content in liquid systems, such as the lagoon storage common with swine production (see Chapter 10).

TABLE 4-31

ANIMAL MANURE PRODUCTION IN THE UNITED STATES, WITH TOTAL N AND P EXCRETED AND RECOVERABLE (USABLE) AS A NUTRIENT SOURCE

Manure source	No. Animals	Dry manure	N Excreted	N Recoverable	N Total	N Organic
	# × 10^6	t × 10^6			%	
Dairy	12.3	27.0	1.00	0.32	2–3	1.0 –1.5
Beef	68.4	91.5	3.87	0.26	1–2	0.7 –1.5
Swine	8.5	9.3	0.60	0.14	3 –5	1.5 –2.5
Poultry	6.1	17.9	0.99	0.58	4–6	2.4 – 3.6
Total	95.3	145.7	6.45	1.29		

Source: USDA-ERS, http://www.ers.usda.gov/Data/manure/default.asp?ERSTab=2.

Figure 4-62
Total manure N available and the proportion in excess for on-farm utilization.
(Gollehon et al., 2001. USDA-ERS. Agric. Information Bull. No. 771).

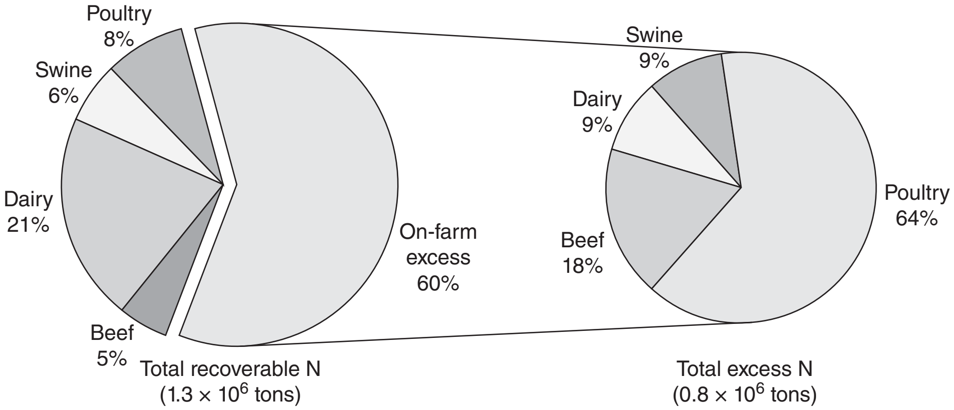


TABLE 4-32

TYPICAL ANNUAL MANURE AND N PRODUCTION PER ANIMAL UNIT (AU) FOR COMMON ANIMAL TYPES

Animal Type	Animals per AU[1]	Manure Production (as excreted)	N (as excreted)	N (after losses[2])
		tons/AU	lb/t	
Beef cows	1	11.5	11.0	3.3
Dairy cows	0.74	15.2	10.7	4.3
Heifers, dairy calves	1.82	12.1	6.1	1.8
Steers, calves, bulls	1.64	10.6	11.0	3.3
Swine, breeders	2.67	6.1	13.3	3.3
Swine, slaughters	9.09	14.7	11.3	2.8
Hens & pullets	250	11.5	26.9	18.5
Broilers	455	15.0	26.8	16.1
Turkeys for slaughter	67	8.2	30.4	16.2
Turkeys hens for breeding	50	9.1	22.4	11.2

[1] AU =1,000 lb animal weight.
[2] Volatilization and denitrification.
Source: Kellogg et al., 2000, USDA-NRCS, ERS, Report No. nps 00-0579.

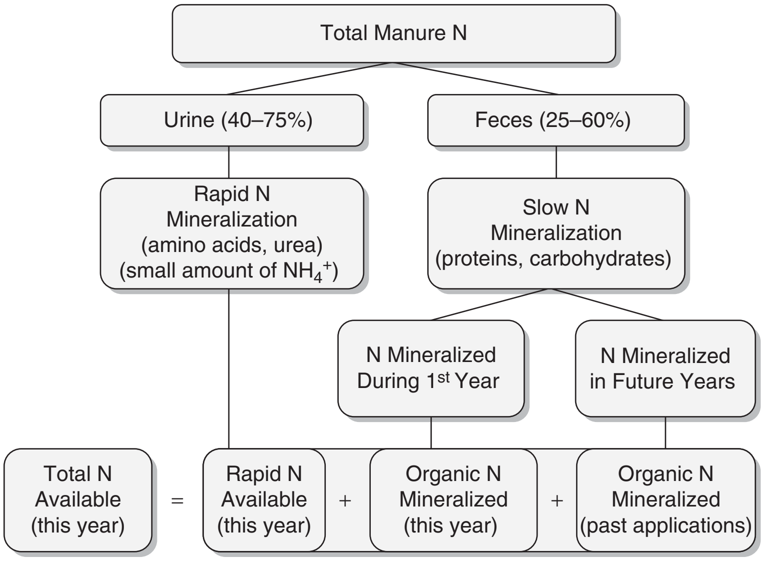


Figure 4-63
Form and relative N availability in land-applied manure.

N Availability with Organic Nutrient Sources With any organic N source, N availability to a plant will depend on the quantity of organic or mineralizable N (Table 4-31). With manure, total N contents range from 1 to 6%, 50 to 75% of the total N is organic N, while the remaining 25 to 50% is NH_4^+. A large proportion of the initial N excreted is volatilized during storage and handling (Table 4-32). Thus, manure N availability to plants depends on mineralization of the organic N. The mineralization process is the same as described previously for soil OM.

Organic N in manure is composed of stable and unstable forms (Fig. 4-63). Depending on the animal, a large proportion of the waste is urine, which contains some NH_4^+ and readily mineralizable organic N compounds (e.g., urea, amino acid, uric acid). If not volatilized during or after application (see Chapter 10), these N sources are immediately plant available.

Since NH_4^+ can be converted to NH_3 under optimum soil and environmental conditions, significant volatilization losses of manure N are possible, ranging from 15 to 40% of total N. In lagoon systems, 60–90% of total manure N can be lost through denitrification and volatilization during storage and land application.

The remaining stable organic N will mineralize in the first and subsequent years after application (Table 4-33). The less-resistant stable organic N will generally mineralize in the year of application. This fraction represents 30–60% of total manure N, depending on manure source. The more-resistant stable organic N mineralizes slowly over the next several years, where about 30, 15, and 5% of the N mineralized in the first year is mineralized in the second, third, and fourth years, respectively. N mineralization rates vary between manure sources (Fig. 4-64). These data show that total N mineralized is much greater with poultry waste compared to beef and swine waste. The initial N mineralization rate is also much higher with poultry waste.

The kinetics of N mineralization from manure, legume, or native soil OM can often be described by a first-order rate equation:

$$N_{min} = N_o\,(1 - e^{-kt})$$

where N_{min} = amount of N mineralized at time, t
N_o = the total mineralizable N pool
k = mineralization rate constant (t^{-1})

This equation indicates that when "k" increases, larger quantities of N mineralize initially, with decreasing N mineralized with time (Fig. 4-65). In this example, increasing

TABLE 4-33

MINERALIZATION FACTORS FOR SELECTED ANIMAL WASTES AND STORAGE/HANDLING METHODS[1]

	Mineralization Factor[2]	
Animal	Solid Storage[3]	Liquid Storage[3]
Swine	0.50–0.60	0.30–0.35
Beef cattle	0.25–0.35	0.25–0.30
Dairy cattle	0.25–0.35	0.25–0.30
Sheep	0.25–0.35	—
Poultry	0.50–0.60	0.50–0.70
Horses	0.20–0.35	—

[1] Factors represent the proportion of organic N mineralized in the first year of application.

[2] Mineralization factors are reduced for surface application compared with subsurface injection.

[3] Higher factors in a storage column represent anaerobic liquid storage and solid manure without bedding or litter added. Lower factors in a storage column represent aerobic liquid storage and solid manure with bedding or litter added.

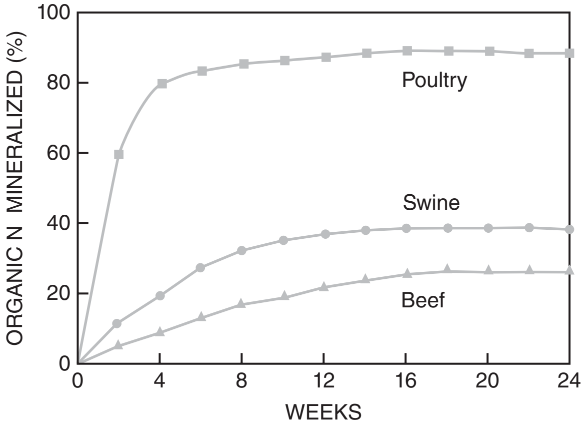


Figure 4-64
N mineralization of organic N in selected liquid animal manures applied to a sandy soil.
(*Van Faassen, 1987, Netherlands. In V. D. Meer [Ed.],* Animal Manure on Grassland and Fodder Crops, *Martinus Nijhoff Publ. Dordrecht, Netherlands.*)

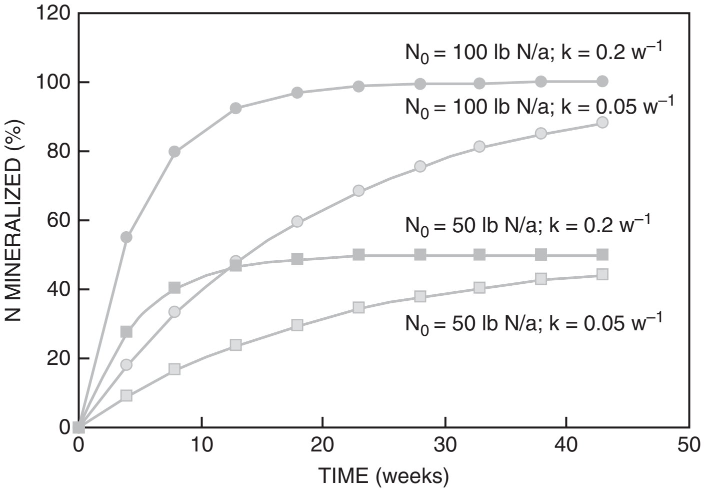


Figure 4-65
General first-order kinetics of N mineralization. Two manure sources with different total mineralizable N (N_o = 100 lb N vs. N_o = 50 lb N). The N mineralization rate constant (k) is varied between 0.05 and 0.2 per week (w^{-1}). Higher "k" represents manures that mineralize N at a faster rate.

"k" from 0.05 to 0.2 per week (w^{-1}) increases rate of N mineralized, where given enough time both materials provide the same total mineralizable N because $N_o = 100$ in both. Decreasing N_o decreases total mineralizable N.

Because of the importance of N to meeting future food and fiber needs, and the growing environmental impacts of fertilizer and manure N use, it is critical to understand N processes in soil and their influence on N availability to plants. Protecting the quality of air and water resources depends on our judicious use of N inputs to optimize plant growth while minimizing off-site N transport. Chapter 10 will provide additional information on N management in diverse plant systems.

STUDY QUESTIONS

1. Describe the major functions of N in plants and how they might relate to distinctive visual deficiency symptoms.
2. Do crops utilize both NH_4^+ and NO_3^-; which is preferred and why? Does the stage of growth influence crop uptake of either NH_4^+ or NO_3^-?
3. Identify an important soil property that can be altered by uptake of NH_4^+ or NO_3^-.
4. How is atmospheric N made usable to higher plants (exclude synthetic N fixation)? What microorganisms are responsible for N fixation?
5. What soil property can exercise considerable influence on the survival and growth of *Rhizobia* in soil? Describe at least two practical ways of improving the effectiveness of *Rhizobia*.
6. Define ammonification and nitrification. What factors affect these reactions in soils?
7. Why does intensive cultivation of land lead to a rapid decomposition of OM? How does this influence N availability in both the short and long term?
8. What is the difference between N fixation and nitrification?
9. Nitrification is a two-step reaction. What are the two steps and what organisms are responsible for each? Why is nitrification important and a mixed blessing?
10. If leaching losses of N are to be minimized after fall application of NH_4-N, soil temperatures during winter months should not rise above what point? As a general rule, is fall application of NO_3-N fertilizers to a spring-planted crop a sound practice? Why or why not?
11. What is NH_4^+ fixation? What are the soil conditions under which it occurs? How important is NH_4^+ fixation to N availability?
12. Barley straw was incorporated a week before planting fall wheat. At planting, you applied 20 lb N/a, 10 lb P/a, and 30 lb K/a fertilizer. The wheat germinates and turns yellow. Tests show low N in the tissue. What is wrong with the wheat? What would you advise?
13. In what forms may N gas be lost from soil? Discuss the conditions under which each form is lost, and write the reactions involved. Can there be large losses of N gases from soil? How would you prevent or minimize the various gaseous losses of N?
14. Classify the various forms of N fertilizers. What are the most important sources of N?
15. What developments have resulted in the great increase in urea use?
16. List changes in soil properties influenced in the injection zone of anhydrous NH_3.
17. What conditions favor NO_2^- accumulation? Describe the harmful effects of NO_2^- on crops.
18. Ammonium volatilization of urea in soils can be an important N loss mechanism. The reaction is $NH_2\text{-}C\text{-}NH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$
    a. Volatilization losses of urea fertilizer applied to the soil can occur if not properly managed. List the factors/conditions that would maximize the potential for NH_3 volatilization.
    b. What urea management recommendations would you make to minimize NH_3 volatilization?
    c. What other source of urea (besides urea in fertilizer or manure) is subject to volatilization?
19. What is urease and why is it important? How do urease inhibitors reduce N loss?
20. What are the important factors governing the selection of fertilizer N source?
21. Why does NH_4-N have an acidifying effect on the soil?
22. Describe the conditions in which nitrification inhibitors have the greatest potential for increasing the efficiency of N fertilizer management.

23. A crop consultant recommends 80 lb N/a to a sorghum crop in a soybean-sorghum rotation. The following data are available:

Previous Soybean Crop	**Sorghum Crop**	**Soil Data**
30 bu/a grain yield	100 bu/a yield goal	2% OM
40 lb residue/bu	56 lb/bu test weight	1% OM degradation rate
40% residue C	75 lb residue/bu	20 lb/a profile N content
30:1 C:N ratio	1.8% grain N	30 lb N/a soybean credit
	0.6% residue N	

Is the recommendation accurate? Show all work.

24. A turf specialist annually applies 100 lb N/a as $(NH_4)_2SO_4$ to turfgrass. Initial soil pH was 6.8 and the CEC = 14 meq/100 g. After 20 years, would the soil pH drop below 6.8 if 1 ton/a $CaCO_3$ were applied every 4 years? If so, by how much (use Table 3-3)?
25. A farmer wants to increase the OM from 1.5% to 2.0%. How many years will he take, if he produces 6000 lb/yr crop residue (60:1 C:N, 40% C, 80% of residue N used to make OM)? The annual decomposition rate of the soil is 1%.
26. For 3000 lb/a residue (40% c) and C:N = 60, calculate the quantity of inorganic soil N immobilized by micro lies.
27. A soil contains 2% OM with an annual decomposition rate of 1%. The producer wants to increase OM to 3%. How many years will it take if he produces 10,000 lb crop residue/yr (residue contains 40% C and C:N is 80:1). Assume 80% of residue N ends up as N in soil OM, ultimately.
28. With a neat diagram, explain the N cycle.
29. How nitrogen supply influences the utilization of carbohydrates? Explain.
30. Mention the economically important microorganisms involved in biological N_2 fixation. What are their general properties and agricultural importance?
31. Discuss the steps involved in the industrial synthesis of NH_3. Write the chemical reactions.
32. What are green house gases?
33. What is C:N ratio? What is it's effect on mineralization?
34. Classify the organic nutrients by their source and effects on soil.

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5

Phosphorus

Total phosphorus (P) in surface soils varies from 0.005 to 0.15%, and decreases with increasing weathering intensity. Thus, total soil P is much lower in humid and tropical region soils compared to semi-arid and arid region soils. Unfortunately, the quantity of total soil P has little or no relationship to P availability to plants. Although semi-arid region soils are often high in total P, many are low in plant available P. In contrast, loading soils with P in excess of plant requirements, which is common in soils where manure is continuously applied, may increase potential for P transport to surface and ground waters. Therefore, understanding the relationships and interactions of P in soils and the factors that influence P availability to plants is essential for efficient P management and protection of water quality.

THE P CYCLE

As with N, the relationships between the various P forms in soils can be illustrated in a P cycle (Fig. 5-1). The decrease in soil solution P with absorption by plant roots is buffered by both inorganic and organic P fractions in soils. Primary and secondary P minerals dissolve to resupply $H_2PO_4^-$ and HPO_4^{-2} in solution. Inorganic P ($H_2PO_4^-$, HPO_4^{-2}) adsorbed on mineral and clay surfaces can also desorb to buffer solution P (Fig. 5-2). Soil microorganisms digest plant residues and other organic amendments (manures, biosolids, etc.) producing organic P compounds that are mineralized through microbial activity to supply solution P.

Water-soluble fertilizer or waste P applied to soil increases P in soil solution. In addition to P uptake by roots, inorganic and organic P fractions buffer the increase in solution P through P adsorption on mineral surfaces, precipitation as secondary P minerals, and immobilization as microbial or organic P. Maintaining solution P concentration (*intensity*) for adequate P nutrition depends on the ability of adsorbed, mineral, and organic P (*quantity*) to replace soil solution P taken up by the plant. The ratio of *quantity* to *intensity* factors defines buffer capacity (BC) or the relative ability of the soil to buffer changes in soil solution P (Fig. 2-15 and 2-16). The larger the BC, the greater the ability to buffer changes in solution P concentration and provide plant available P.

Understanding the dynamics of P transformations in soils will provide the basis for sound management of soil and fertilizer P to ensure adequate P availability to plants (Chapter 10) and to reduce P losses to surface and ground waters (Chapter 12).

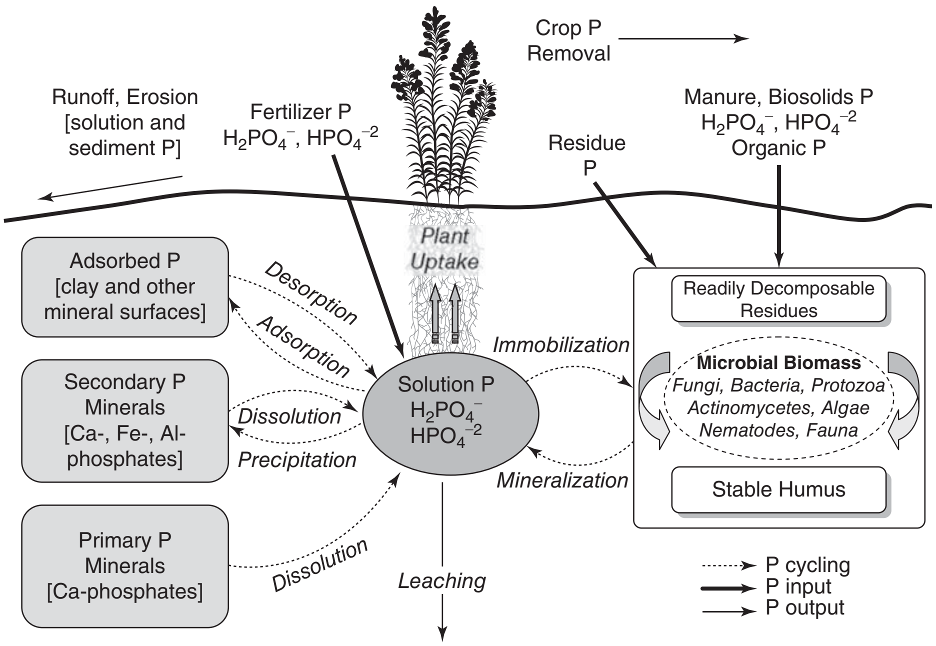
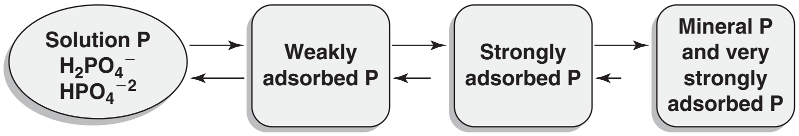


Figure 5-1
P cycling in soil. Internal P cycling (dashed lines) between soil solution P and adsorbed P, solid mineral P, and organic P controls P availability to plants. Removal of P from the system occurs primarily through crop removal; however, P losses occur from soil erosion, runoff, and leaching.



P form or source	Soluble P	P adsorbed to clay and other mineral surfaces		Ca, Fe, Al-P minerals and very strongly adsorbed P
Extractability by soil tests	High	High	Low	Very low
Availability to plants	High	High	Low	Very low

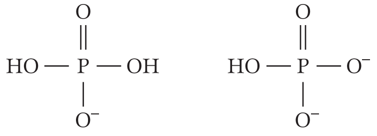
Figure 5-2
Relative plant availability and extractability of inorganic P forms in soil. $H_2PO_4^-$ or HPO_4^{-2} in soil solution or weakly adsorbed to AEC sites on mineral surfaces are the dominant P sources immediately available to plants. The strongly adsorbed and P-containing minerals provide little immediate plant available P. The arrows between P forms indicate that solution P can be converted to any adsorbed or mineral P form. While weakly adsorbed P (labile P) can be readily desorbed to solution (long arrow), strongly adsorbed (non-labile P) and mineral P conversion to soluble P is substantially lower (short arrow).

FORMS AND FUNCTIONS OF P IN PLANTS

Forms

P concentration in plants ranges between 0.1 and 0.5%, considerably lower than N and K. Plants absorb either $H_2PO_4^-$ or HPO_4^{-2} (orthophosphate) depending on soil pH (see p. 191).

Orthophosphate ions



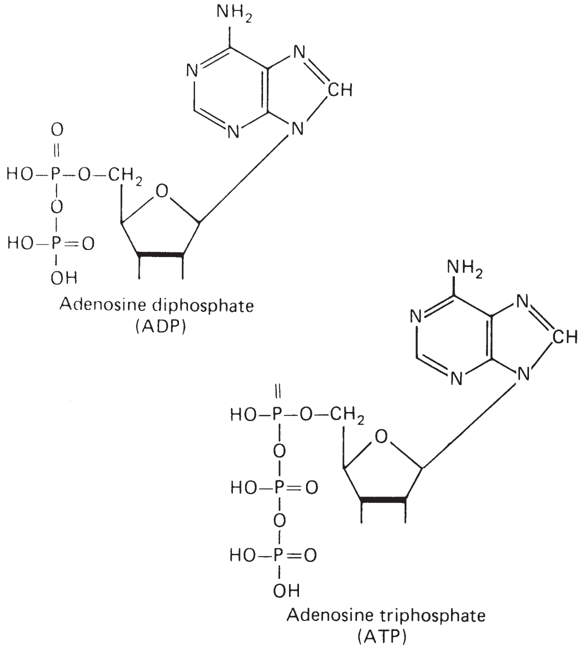
$\mathrm{HO{-}P({=}O)(O^-){-}OH}$ $\quad$ $\mathrm{HO{-}P({=}O)(O^-){-}O^-}$

$H_2PO_4^-$ $\quad$ HPO_4^{-2}

Although it has been suggested that plants also absorb soluble, low-molecular weight organic P compounds (i.e., nucleic acid and phytin), these P compounds are likely converted to $H_2PO_4^-$ in the rhizosphere.

Functions

The most essential function of P in plants is in energy storage and transfer. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP) act as "energy currency" within plants (Fig. 5-3). When the terminal $H_2PO_4^-$ molecule from either ADP or ATP is split off, a large amount of chemical energy (12,000 cal/mole) is liberated. Energy obtained from photosynthesis and metabolism of carbohydrates is stored in phosphate compounds for subsequent use in growth and reproductive processes. Phosphorylation is the transfer of energy-rich $H_2PO_4^-$ molecules from ATP to energy-requiring substances in the plant. In this reaction ATP is converted to ADP. ADP and ATP are formed and regenerated in



Adenosine diphosphate (ADP)

Adenosine triphosphate (ATP)

Figure 5-3
Structure of ADP and ATP.

TABLE 5-1
PROCESSES AND FUNCTIONS OF ADP AND ATP IN PLANTS

Membrane transport	Generation of membrane electrical potentials
Cytoplasmic streaming	Respiration
Photosynthesis	Biosynthesis of cellulose, pectins, hemicellulose, and lignin
Protein biosynthesis	Lipid biosynthesis
Phospholipid biosynthesis	Isoprenoid biosynthesis → steroids and gibberellins
Nucleic acid synthesis	RNA and DNA

the presence of sufficient P. Almost every metabolic reaction of any significance involves $H_2PO_4^-$ derivatives (Table 5-1). As a result, P deficiency is associated with restricted growth and development.

P is an essential element in deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) that contain the genetic code of the plant to produce proteins and other compounds essential for plant structure, seed yield, and genetic transfer. Phospholipids, phosphoproteins, coenzymes, and nucleotides are important structural components of membrane chemistry and related functions. Thus, P is essential for vigorous growth and development of reproductive parts (fruits, seeds, etc.).

Adequate P is associated with increased root growth. When soluble $H_2PO_4^-$ is applied in a band, plant roots proliferate extensively in P-treated soil. Similar observations are made with both NO_3^- and NH_4^+ applied in a band near roots (Fig. 5-4). The increased root proliferation should encourage extensive exploitation of the treated soil areas for nutrients and water. Adequate P is essential for fruit and seed development. P also enhances crop maturity and reduces the time required for seed and fruit ripening (Fig. 5-5).

Adequate P increases straw strength in cereals and increases N_2-fixation capacity of legumes. The quality of certain fruit, forage, vegetable, and grain crops is improved and disease resistance enhanced under adequate P availability. The effect of P on raising the tolerance of small grains to root-rot diseases is particularly noteworthy. Also, the risk of winter damage to small grains can be decreased with sufficient P, particularly on low P soils and with unfavorable growing conditions.

Visual Deficiency Symptoms

The most common visual symptoms include overall stunting of the plant and a darker green coloration of leaves. With increasing P deficiency, the dark green color changes to a grayish-green to bluish-green metallic luster. In some crops (i.e., sugar beets), dark green leaves appear in the early seedling stage, developing to brown, netted veining in older leaves as the plant matures. Purple leaf coloration is commonly associated with P deficiency. Symptoms appear on lower leaf tips and progress along leaf margins until the entire leaf is purple. Lower leaves are necrotic under severe P deficiency. The purple color is due to accumulation of sugars that enhances synthesis of anthocyanin (a purple pigment) in the leaf (see color plates).

P is mobile in plants, and is translocated from older to newly developing tissues. Consequently, early growth stage responses to P are common. In the reproductive stage, P is translocated to fruit and seeds. Thus, P deficiencies late in the growing season affect both seed development and crop maturity.

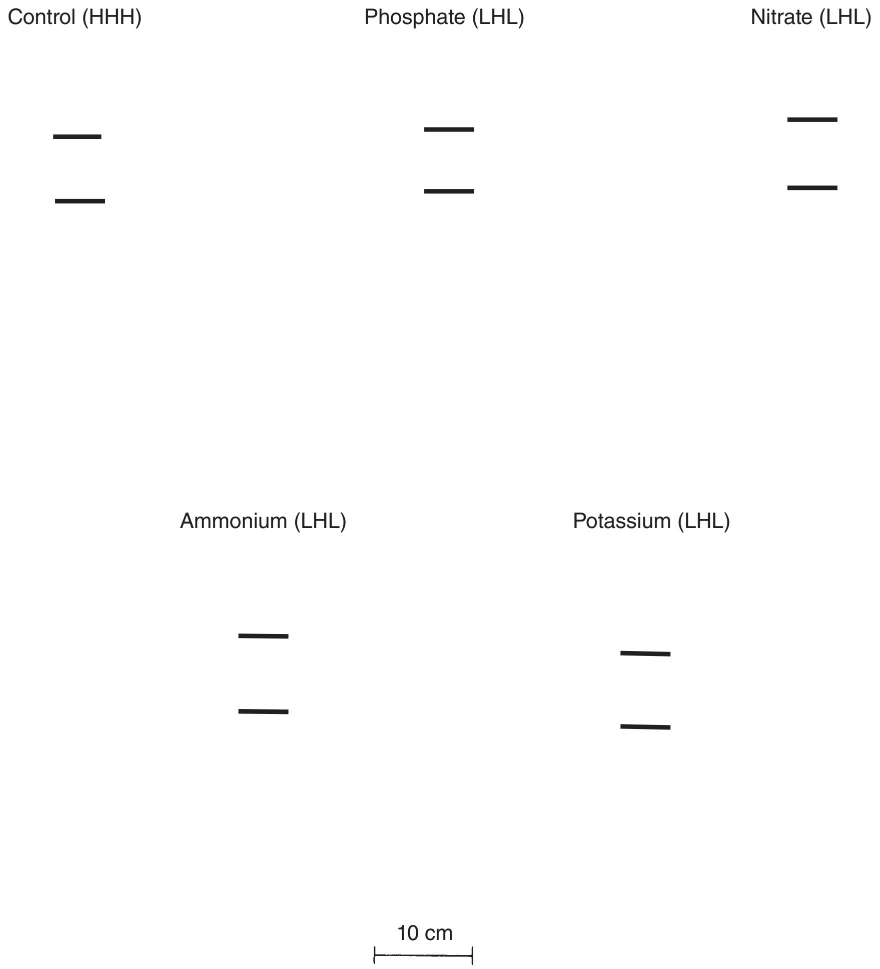


Figure 5-4
Effect of a localized supply of phosphate, nitrate, ammonium, and potassium on root growth. Control plants (HHH) received the complete nutrient solution to all parts of the root system. The other roots (LHL) received the complete nutrient solution only in the middle zone, the top and bottom being supplied with a solution deficient in the specified nutrient.
(*Drew,* 1975, New Phytol., *75:486.*)

P deficiency symptoms can appear in P sensitive crops emerging under cool, wet conditions, even in soils with sufficient plant available P. Reduced P diffusion in cool soils combined with small root systems in young plants causes P deficiency symptoms. Increasing soil temperature and expanding root growth usually corrects the P deficiency. When this condition is anticipated, starter P applications can prevent early season P deficiency (Chapter 10).

P supply to plant roots is greatly enhanced by a symbiotic relationship between plant roots and fungal microorganisms called *mycorrhizae* (Fig. 5-6). Mycorrhizal fungi infect roots of most plants and function primarily by enhancing nutrient uptake (Table 2-7). Ectomycorrhiza predominately infect tree species, while endomycorrhiza (vesicular-arbuscular mycorrhiza [VAM]) infect most other plants, although plants vary in the degree of fungal infection. As new roots develop, mycorrhizal fungi infect or enter the root and develop extensive structures extending into and beyond the rhizosphere influenced by root hairs. Plants with a high dependency on VAM generally exhibit (1) low root surface area due to low root branching, (2) few or short

Figure 5-5
Effect of P fertilization on grain sorghum (top) and winter wheat (bottom) maturity. Notice the advanced maturity of both crops receiving P (left) in contrast to those that received no P (right).

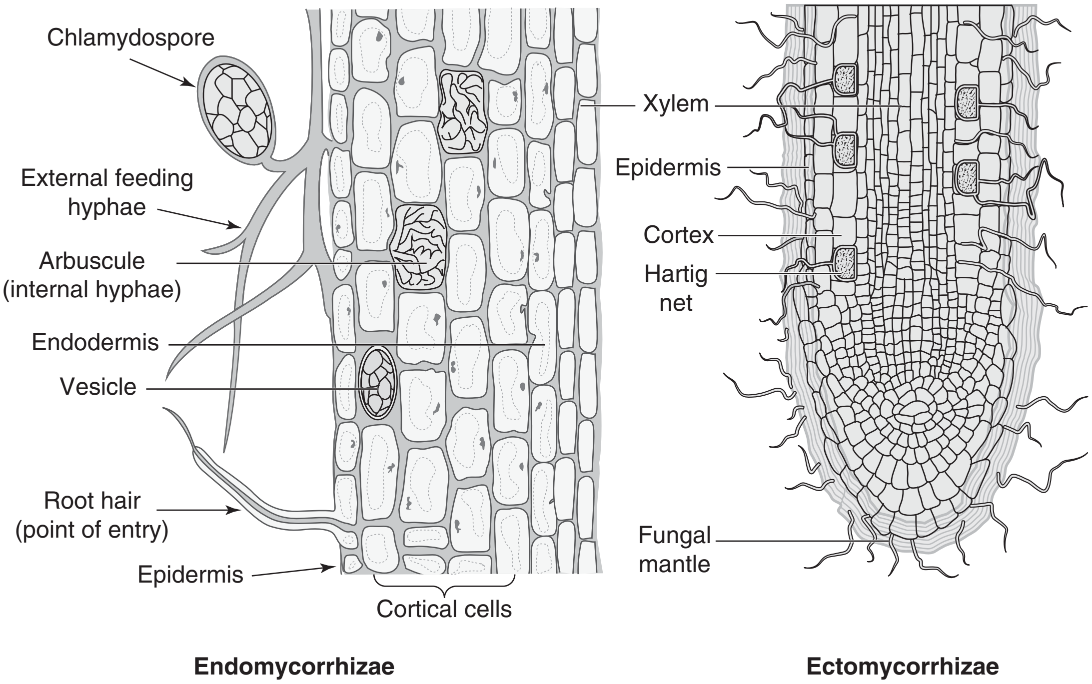


Figure 5-6
Schematic of primary types of symbiotic mycorrhizal infection of plant roots. Endomycorrhizae, commonly associated with many annual and perennial plants, infect the plant through the root hair, occupying intercellular space and cell membranes in the cortex (arbuscules, vesicles), enhancing nutrient supply to the plant. Ectomycorrhizae, common to woody plants, form a sheath or mantle over the root tips and a cover (Hartig net) over cells in the cortex, which enhances nutrient supply to plant cells.

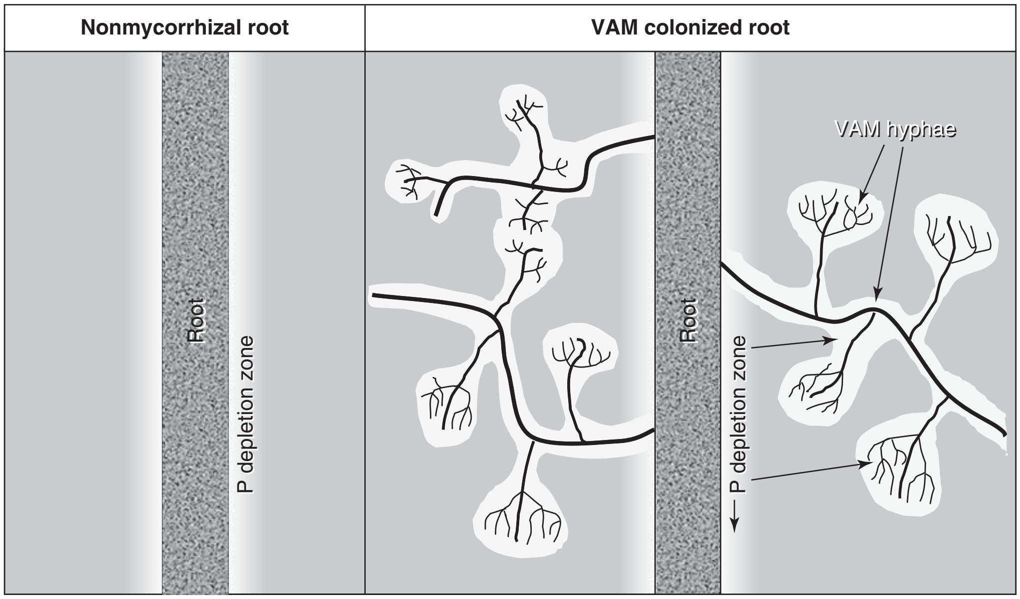


Figure 5-7
Influence of VAM-colonized roots on soil volume accessed for P uptake.

root hairs, (3) slow root growth rate, and (4) reduced root exudation. Under low soil-nutrient availability, VAM-infected roots explore a substantially larger soil volume from which to absorb nutrients. For example, VAM-dependent plants explore greater soil P extraction volume to satisfy P requirement (Fig. 5-7). In many cases, excessive N and/or P fertilization and soil tillage can reduce the contribution of mycorrhiza-related nutrient uptake.

FORMS OF SOIL P

Solution P

The amount of $H_2PO_4^-$ and HPO_4^{-2} present in solution depends on soil pH (Fig. 5-8). At pH 7.2, $H_2PO_4^- \approx HPO_4^{-2}$. Below this pH, $H_2PO_4^- > HPO_4^{-2}$, whereas $HPO_4^{-2} > H_2PO_4^-$ above pH 7.2. Plant uptake of HPO_4^{-2} is much slower than with $H_2PO_4^-$. Soil solution P concentration varies widely among soils from 10^{-7} (very low) to 10^{-4} M (very high), or 0.003–3 ppm P (average ~0.05 ppm).

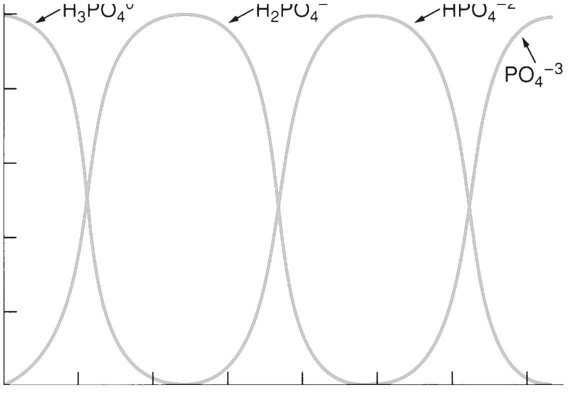


Figure 5-8
Influence of pH on the distribution of orthophosphate species in solution.

TABLE 5-2
ESTIMATED SOIL SOLUTION P CONCENTRATION ASSOCIATED WITH 75 AND 95% OF MAXIMUM YIELD OF SELECTED CROPS

	Approximate Soil Solution P for Two Yield Levels	
Crop	*75% Maximum Yield*	*95% Maximum Yield*
	ppm	
Cassava	0.003	0.005
Peanuts	0.003	0.010
Corn	0.008	0.025
Wheat	0.009	0.028
Cabbage	0.012	0.040
Potatoes	0.020	0.180
Soybeans	0.025	0.200
Tomatoes	0.050	0.200
Head lettuce	0.100	0.300

Source: Fox, 1982, Better Crops Plant Food, *66:24.*

Soil solution P required by plants depends on crop species and level of production (Table 5-2). For example, maximum corn yields may be obtained with 0.01 ppm P if yield potential is low, but ≥0.05 ppm P is needed with high yield potential (Fig. 5-9).

With relatively low solution P concentration (~0.05 ppm P), supplying the quantity of P needed or accumulated by plants (~0.3% P) requires soil solution P to be frequently replenished. The following example illustrates the rate of solution P replenishment needed to meet plant P requirement.

Assume soil solution P concentration = 0.3 ppm P

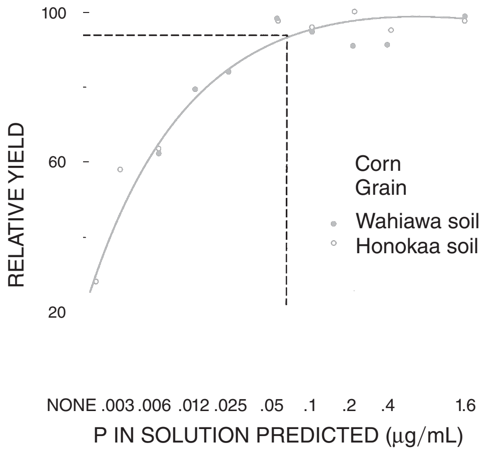
Calculate kg P/ha in the soil solution:

$$0.3 \text{ ppm P} = \frac{0.3 \text{ mg P}}{\text{L solution}} \qquad [\text{see note on pg. } 193]$$

Estimate soil water volume (L):

Assume 1 ha area −30 cm soil depth

Figure 5-9
Influence of inorganic P in soil solution on corn grain yield.
(Fox, 1981, Chemistry in the Soil Environment, p. 232, ASA, Madison, Wis.)



$$\frac{10{,}000\ \text{m}^2}{\text{ha}} \times 0.3\ \text{m} = \frac{3 \times 10^3\ \text{m}^3\ \text{soil}}{\text{ha} - 30\ \text{cm}}$$

$$\frac{3 \times 10^3\ \text{m}^3}{\text{ha} - 30\ \text{cm}} \times \frac{1\ \text{L}}{1 \times 10^{-3}\ \text{m}^3} = \frac{3 \times 10^6\ \text{L soil}}{\text{ha} - 30\ \text{cm}} \qquad [\text{see note below}]$$

Assume volumetric soil water content = 18%

$$\frac{3 \times 10^6\ \text{L soil}}{\text{ha} - 30\ \text{cm}} \times 0.18 = \frac{5.4 \times 10^5\ \text{L solution}}{\text{ha} - 30\ \text{cm}}$$

$$\frac{5.4 \times 10^5\ \text{L solution}}{\text{ha} - 30\ \text{cm}} \times \frac{0.3\ \text{mg P}}{\text{L solution}} = \frac{1.62 \times 10^5\ \text{mg P}}{\text{ha} - 30\ \text{cm}} \times \frac{\text{g}}{10^3\ \text{mg}} \times \frac{\text{kg}}{10^3\ \text{g}}$$

$$= \frac{0.16\ \text{kg P}}{\text{ha} - 30\ \text{cm}}$$

Since we are basing these estimates on the surface 30 cm or 1 ft soil depth, we assume 25% of total rooting depth (120 cm or 4 ft.).

$$\frac{0.16\ \text{kg P}}{\text{ha} - 30\ \text{cm}} \times 0.25 = \frac{0.04\ \text{kg P}}{\text{ha} - 30\ \text{cm}}$$

Thus, 0.3 ppm P in solution represents 0.04 kg P/ha; however, plants generally require 0.3–0.5 kg P/ha/day (Fig. 5-10). Therefore, soil solution P must be resupplied about 10 times each day. Under P deficiency where solution P is tenfold less at 0.03 ppm P (Fig. 5-9), then only 0.004 kg P/ha is available and solution P must be resupplied about 100 times each day.

Note:

Converting ppm to mg/L:

$$0.3\ \text{ppm P} = \frac{0.3\ \text{g P}}{10^6\ \text{g H}_2\text{O}} \times \frac{10^3\ \text{mg}}{\text{g}} \times \frac{1\ \text{g H}_2\text{O}}{\text{mL}} \times \frac{10^3\ \text{mL}}{\text{L}} = \frac{0.3\ \text{mg P}}{\text{L solution}}$$

Converting m^3 to L:

$$\frac{1\ \text{mL}}{\text{cm}^3} \times \frac{\text{L}}{10^3\ \text{mL}} \times \left(\frac{10^2\ \text{cm}}{\text{m}}\right)^3 = \frac{\text{L}}{1 \times 10^{-3}\ \text{m}^3}$$

where,

$$\left(\frac{10^2\ \text{cm}}{\text{m}}\right)^3 = \frac{10^6\ \text{cm}^3}{\text{m}^3}$$

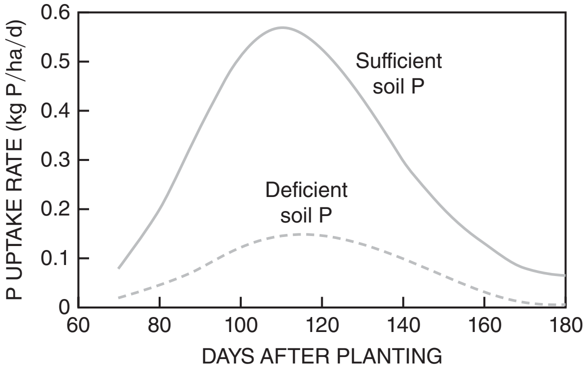


Figure 5-10
Influence of soil P availability on rate of P uptake in spring barley.
(*Adapted from Leigh and Johnston, 1986,* J. Agric. Sci., *107:329–333.*)

TABLE 5-3
DIFFUSION COEFFICIENTS AND DIFFUSION RATE OF SELECTED IONS IN SOIL SOLUTION

	Diffusion Coefficient		
Ion	*Range*	*Average*	Diffusion Rate
	m^2/sec	m^2/sec	*mm/day*
NO_3^-	10^{-10} to 10^{-11}	5×10^{-11}	3.0
K^+	10^{-11} to 10^{-12}	5×10^{-12}	0.9
$H_2PO_4^-$	10^{-12} to 10^{-15}	1×10^{-13}	0.13

The actively absorbing surface of plant roots is the young tissue near the root tips. Rapid replenishment of solution P is important where roots are actively absorbing P. As roots absorb P from soil solution, diffusion and mass flow transport additional P to the root surface (Chapter 2). Mass flow in low P soils provides very little of the P requirement. For example, assume a transpiration ratio[1] of 400 and 0.3% P in the crop. If the average solution concentration is 0.05 ppm P, then the quantity of P moving to the plant by mass flow is:

$$\frac{400 \text{ g } H_2O}{\text{g plant}} \times \frac{100 \text{ g plant}}{0.3 \text{ g P}} \times \frac{0.05 \text{ g P}}{10^6 \text{ g } H_2O} \times 100 = 0.67\%$$

In fertilized soil with a solution concentration of 1 ppm P, mass flow contributes approximately 13% of the total requirement. The very high P concentrations (2–14 ppm) that exist temporarily in and near fertilizer bands are expected to encourage further P uptake by mass flow and diffusion. Since mass flow provides little P to the root surface, P diffusion is the primary mechanism of P transport, especially in low P soils (Chapter 2).

In soil solution, $H_2PO_4^-$ diffusion rate is also low compared to other ions (Table 5-3). Using an average diffusion coefficient of 1×10^{-13} m^2/sec, $H_2PO_4^-$ diffusion would be only 0.13 mm/day, which explains why sufficient supply of readily available P throughout the soil volume explored by roots is essential to meet crop P demand. Low solution P and low P diffusion rate help explain why plants frequently respond to P fertilizer placed in concentrated bands near active roots (Chapter 10).

Inorganic Soil P

As organic P is mineralized to inorganic P or as P is added to soil, inorganic P in solution ($H_2PO_4^-/HPO_4^{-2}$) not absorbed by roots or immobilized by microorganisms can be *adsorbed* to mineral surfaces or *precipitated* as secondary P compounds (Fig. 5-1). Surface adsorption and precipitation reactions are collectively called P *fixation* or retention. The extent of inorganic P fixation depends on many factors, most importantly soil pH (Fig. 5-11). In acid soils, inorganic P precipitates as Fe/Al-P secondary minerals and/or is adsorbed to surfaces of Fe/Al oxide and clay minerals. In neutral and calcareous soils, inorganic P precipitates as secondary minerals of Ca-P (Mg-P in high Mg soils) and/or is adsorbed to surfaces of clay minerals and $CaCO_3$.

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[1] Transpiration ratio = weight of H_2O transpired per unit plant weight.

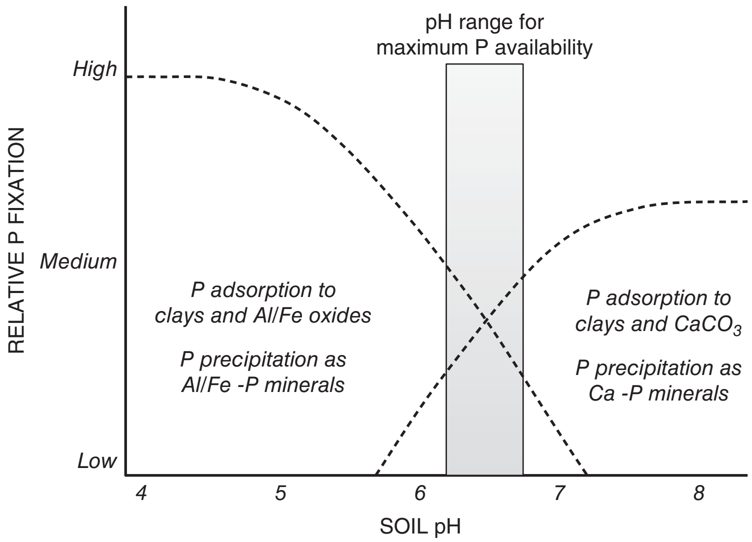


Figure 5-11 *Relative effect of soil pH on P adsorption and precipitation.*

P fixation is a continuous sequence of precipitation and adsorption. With low solution P concentrations, adsorption dominates, while precipitation reactions proceed when solution P exceeds the solubility product (Ksp) of the specific P-containing mineral (Chapter 2). Where water-soluble fertilizers or organic wastes are applied, soil solution P concentration increases greatly depending on P rate and method of application (band vs. broadcast). Both adsorption and precipitation reactions occur, to some extent, immediately following P addition. P precipitation reactions occur as solution P exceeds a specific mineral solubility, while adsorption occurs when adsorption capacity is not saturated with P. Regardless of the contributions of adsorption and precipitation, understanding P fixation processes is important for optimum P nutrition and efficient fertilizer P management.

P Mineral Solubility The P cycle illustrates that solution P levels are buffered by adsorbed P on mineral surfaces, organic P mineralization, and P mineral dissolution (Fig. 5-1). Ultimately, solution P concentration is controlled by P mineral solubility. The most common P minerals found in acid soils are Al-P and Fe-P minerals, while Ca-P minerals predominate in neutral and calcareous soils (Table 5-4).

TABLE 5-4
COMMON P MINERALS FOUND IN ACID, NEUTRAL, AND CALCAREOUS SOILS

	Acid soils
Variscite	$AlPO_4 \cdot 2H_2O$
Strengite	$FePO_4 \cdot 2H_2O$
	Neutral and calcareous soils
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4 \cdot 2H_2O$
Dicalcium phosphate (DCP)	$CaHPO_4$
Octacalcium phosphate (OCP)	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$
β-tricalcium phosphate (β-TCP)	$Ca_3(PO_4)_2$
Hydroxyapatite (HA)	$Ca_5(PO_4)_3OH$
Fluorapatite (FA)	$Ca_5(PO_4)_3F$

Note: Minerals are listed in order of decreasing solubility.

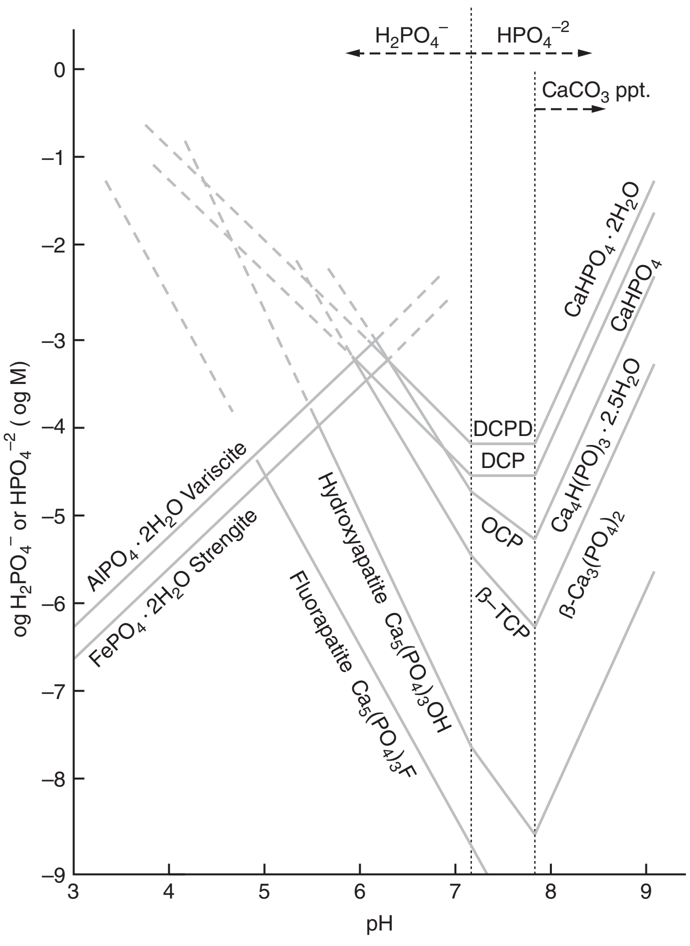
Mineral solubility represents the ion concentration maintained in the soil solution by a specific mineral. Each P mineral supports specific ion concentrations that depend on the solubility product (Ksp) of the mineral. For example, $FePO_4 \cdot 2H_2O$ will dissolve according to:

$$FePO_4 \cdot 2H_2O + H_2O \leftrightarrows H_2PO_4^- + H^+ + Fe(OH)_3 \quad [1]$$

As $H_2PO_4^-$ decreases with P uptake, strengite dissolves to resupply or maintain solution $H_2PO_4^-$ concentration. This reaction also shows that as H^+ increases (decreasing pH), $H_2PO_4^-$ decreases. Therefore, specific P minerals present in soil and the concentration of solution P supported by these minerals are dependent on solution pH.

The relationship between the solubility of the common P minerals and solution pH is shown in Figure 5-12. The y-axis represents $H_2PO_4^-$ or HPO_4^{-2} concentration in soil solution. $H_2PO_4^-$ is the predominant ion at $pH<7.2$, while HPO_4^{-2} dominates at $pH>7.2$ (Fig. 5-8). At pH 4.5, $AlPO_4 \cdot 2H_2O$ and $FePO_4 \cdot 2H_2O$ control $H_2PO_4^-$ concentration in solution. Increasing pH increases $H_2PO_4^-$ concentration because the Al-P and/or Fe-P minerals dissolve according to reaction [1], which is also depicted in the diagram as a positive slope. Increasing P availability is often observed when acid soils are limed. Also, hydroxyapatite or fluorapatite can be used as a fertilizer in low pH soils ($pH<4.5$), as shown by their high solubility at low pH (Fig. 5-12). In contrast, they cannot be used to supply plant available P in neutral or calcareous soils because of their low solubility.

Figure 5-12
Solubility of Ca, Al, and Fe phosphate minerals in soils. See text for discussion.
(*Adapted from Lindsay, 1979,* Chemical Equilibria in Soils, *Wiley Interscience, p. 181.*)



As pH increases, variscite and strengite solubility lines intersect several lines representing the solubility of Ca-P minerals. For example, at pH 4.8, both strengite and fluorapatite can exist in soil, supporting $10^{-4.5}$ M $H_2PO_4^-$ in solution. Between pH 6.0 and 6.5, Al-P and Fe-P minerals can coexist with β-tricalcium phosphate (β–TCP), octacalcium phosphate (OCP), dicalcium phosphate (DCP), and DCP dihydrate (DCPD) at about $10^{-3.2}$ M $H_2PO_4^-$, which is about the highest solution P concentration that can exist in most unfertilized soils.

Ca-P mineral solubility is affected much differently than Al-P and Fe-P minerals, as shown by the negative slopes of the Ca-P lines (Fig. 5-12). As pH increases, $H_2PO_4^-$ concentration decreases as Ca-P precipitates, as described by the following equation for DCPD:

$$CaHPO_4 \cdot 2H_2O + H^+ \leftrightarrows Ca^{+2} + H_2PO_4^- + 2H_2O \quad [2]$$

For example, assume that a soil contains β-TCP at pH 7.0. If pH decreases, $H_2PO_4^-$ increases until pH ≈ 6.0 as β-TCP dissolves. As pH continues to decrease below 6.0, $H_2PO_4^-$ decreases as strengite/variscite precipitate (reaction [1]). The Ca-P lines (Fig. 5-12) change slopes at pH>7.2 because HPO_4^{-2} predominates in solution compared with $H_2PO_4^-$. The solubility lines represent only HPO_4^{-2} at pH>7.2.

Above pH 7.8, Ca-P solubility lines exhibit a positive slope, which means that as pH increases above 7.8, HPO_4^{-2} concentration increases. The change in solubility is due to the competing reaction of $CaCO_3$ solubility given by:

$$\begin{array}{rl}
CaHPO_4 \cdot 2H_2O \leftrightarrows Ca^{+2} + HPO_4^{-2} + 2H_2O & [3] \\
Ca^{+2} + CO_2 + H_2O \leftrightarrows CaCO_3 + 2H^+ & [4] \\
\hline
CaHPO_4 \cdot 2H_2O + CO_2 \leftrightarrows HPO_4^{-2} + 2H^+ + H_2O + CaCO_3 & [5]
\end{array}$$

$CaCO_3$ precipitation occurs at pH 7.8 and above. As solution Ca^{+2} decreases with $CaCO_3$ precipitation (reaction [4]), DCPD will dissolve (reaction [3]) to resupply solution Ca^{+2}. When DCPD dissolves, HPO_4^{-2} increases (reaction [5]), which is the sum of reactions [3] and [4]. All Ca-P minerals (Table 5-4) behave similarly in calcareous soils. Even though these P solubility relationships show solution P concentration increasing above pH 7.8, P availability to plants can decrease by HPO_4^{-2} adsorption to the precipitating $CaCO_3$.

P minerals that support the lowest P concentration (lowest P solubility) are the most stable in soils. For example, apatite minerals (β-TCP and OCP) are more stable than DCPD in slightly acid and neutral soils. Therefore, P mineral-solubility relationships (Fig. 5-12) can be used to understand the fate of inorganic P applied to soils (see "Behavior of P Fertilizers in Soils").

An important fertilizer P source is monocalcium phosphate (MCP) $[Ca(H_2PO_4)_2]$, which is very soluble in soil. When MCP dissolves, $H_2PO_4^-$ concentration is much higher than P concentrations supported by native P minerals (Fig. 5-12). Because soil P minerals have lower solubility, $H_2PO_4^-$ from fertilizer will likely precipitate as these minerals. For example, in an acid soil, fertilizer $H_2PO_4^-$ reacts with solution Al^{+3} and Fe^{+3} to form $AlPO_4$ and $FePO_4$ compounds, respectively. As a result, solution $H_2PO_4^-$ decreases once the precipitation reactions begin. In neutral and calcareous soils, fertilizer $H_2PO_4^-$ initially precipitates as DCDP and DCP within the first few weeks after application. After 3–5 months, OCP begins to precipitate, with β-TCP forming after 8–10 months. After long periods of time, apatite minerals may eventually form. Thus, after MCP is applied to soil, reactions occur that decrease the elevated solution $H_2PO_4^-$ concentration as insoluble P minerals precipitate. These reactions cannot be controlled and explain why plant recovery of applied P is lower than recovery of soluble nutrients such as NO_3^- and SO_4^{-2}.

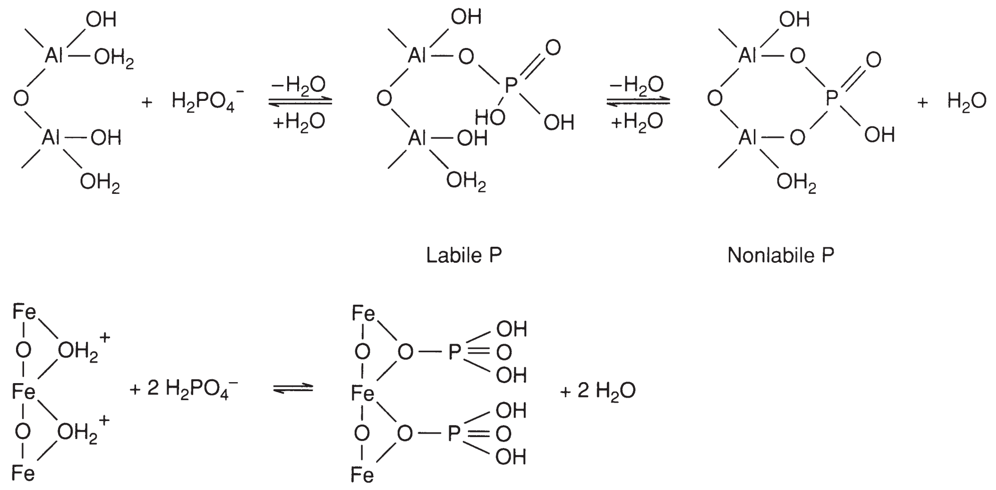


Figure 5-13
Mechanism of P adsorption to Al/Fe oxide surface. Phosphate bonding through one Al-O bond results in readily desorbed (labile) P; however, bonding through two Fe-O or Al-O bonds produces a stable structure that results in very little P desorption.

P Adsorption Reactions $H_2PO_4^-$ and/or HPO_4^{-2} will adsorb to mineral surfaces (Fig. 5-1). In acid soils, Al and Fe oxide and hydroxide minerals are primarily involved in P adsorption. Because of the acidic solution, the mineral edge surface has a net (+) charge, although both (+) and (−) sites exist (Chapter 2). The predominance of (+) charges readily attracts $H_2PO_4^-$ and other anions. P ions adsorb to the Fe/Al oxide surface by interacting with −OH and/or OH_2^+ groups on the mineral surface (Fig. 5-13).

When $H_2PO_4^-$ is bonded through one Al-O-P bond, the $H_2PO_4^-$ can be readily desorbed (labile P) from the mineral surface to soil solution. When $H_2PO_4^-$ bonds with two Al-O, a stable six-member ring is formed (Fig. 5-13). Consequently, desorption is more difficult (non-labile P), reducing plant available P. In acid soils, P adsorption also readily occurs on the broken edges of kaolinite clay minerals (Fig. 2-9). Again, exposed−OH groups can exchange for $H_2PO_4^-$ similarly to surface exchange with Fe/Al oxides. Cations held to the surface of silicate clay minerals also influence P adsorption by developing a small (+) charge near the mineral surface saturated with cations. This small (+) charge attracts small quantities of anions such as $H_2PO_4^-$. As discussed earlier, precipitation of Al-P minerals in acid soils and Ca-P minerals in neutral and calcareous soils occurs at high P concentrations.

In calcareous soils, small quantities of P can be adsorbed through replacement of CO_3^{-2} on $CaCO_3$ surfaces. At low P concentrations, surface adsorption predominates; however, at high P concentrations, Ca-P minerals precipitate on the $CaCO_3$ surfaces. Other minerals, mostly $Al(OH)_3$ and $Fe(OH)_3$, also contribute to adsorption of solution P in calcareous soils.

Adsorption Equations

Many equations can be used to describe the adsorption of ions or compounds on mineral surfaces (Fig. 5-14). Freundlich and Langmuir equations are commonly used and are helpful in understanding the relationship between quantity of P adsorbed per unit soil weight and the concentration of P in solution. The Freundlich equation is represented by:

$$Q = aC^{-x}$$

where Q = quantity of P adsorbed on mineral surface (per unit soil weight)
C = solution P concentration
a, x = coefficients that vary among soils

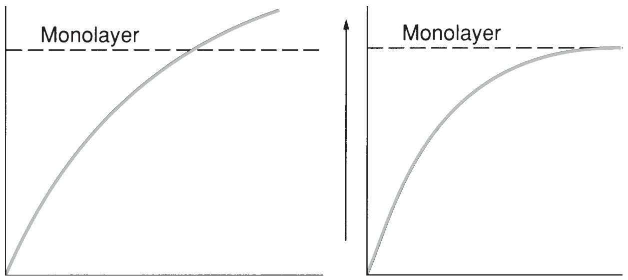


Figure 5-14
Graphical representation of adsorption isotherms of the Freundlich (a) and Langmuir (b) equations used to describe P adsorption in soils.

The Freundlich equation does not include a maximum adsorption capacity and therefore is reliable at low solution P concentrations (Fig. 5-14). Since P adsorption data exhibit a maximum P adsorption capacity at some solution P concentration, another equation is needed to describe situations in which the adsorption sites are saturated with P.

The Langmuir equation includes a term for the maximum P adsorption described by:

$$Q = \frac{abC}{1 + aC}$$

where Q, C, a = defined as before
b = P adsorption maximum

P adsorption maximum "b" implies that a monolayer of P ions is adsorbed on the surface of the mineral, which occurs at relatively higher solution P concentrations than described by the Freundlich equation. The Langmuir equation also shows that further increases in solution P concentration do not increase P adsorption.

Adsorption equations provide no information about adsorption mechanisms or whether Fe/Al oxides, silicate clays, or $CaCO_3$ dominate adsorption reactions. P adsorption is initially rapid, slowing with time, as the adsorption sites become saturated with P. Once maximum P adsorption is attained, if P is continually added to soil, the solution P concentration will rapidly increase with no additional increase in adsorbed P. Under this scenario, potential soluble P transport by surface runoff or leaching enhances risk to water quality (Chapter 12).

In general, adsorbed P is not readily desorbed. *Hysteresis* occurs when the quantity of adsorbed P (or other ion or compound) is greater than can be desorbed (Fig. 5-15). The extent of desorption depends on the nature of the adsorption mechanism at the mineral surface. With P adsorption on Al/Fe oxides, formation of ring structures limits P desorption (Fig. 5-13), and contributes to hysteresis of P in soils.

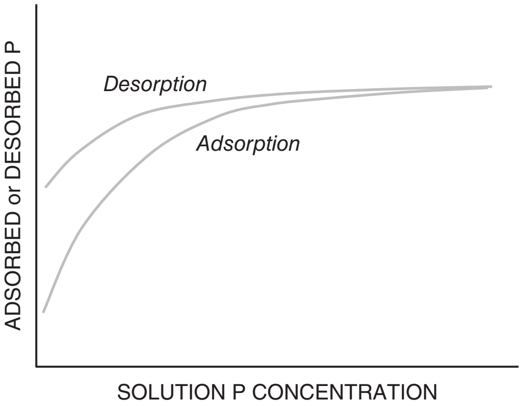


Figure 5-15
General depiction of hysteresis *in soil, where the quantity of P desorbed is less than the quantity of P adsorbed.*

Factors Influencing P Fixation in Soils Many physical and chemical soil properties influence P solubility and adsorption reactions in soils. Consequently, these soil properties also affect solution P concentration, P availability to plants, and fertilizer P recovery by crops. In general, P adsorption is greater in soils with low initial adsorbed P. As fertilizer P is added and the quantity of adsorbed P increases, the potential for additional P adsorption decreases. When all adsorption sites are saturated with $H_2PO_4^-$, further adsorption will not occur.

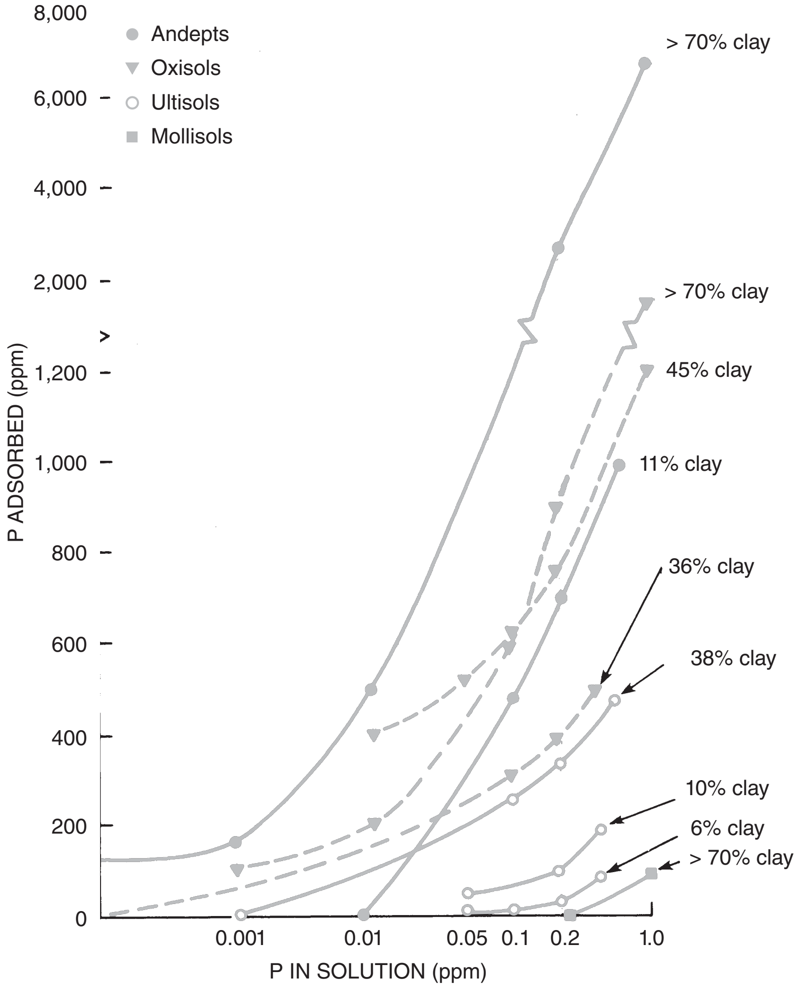
Soil Minerals

Adsorption and desorption reactions are affected by the type of mineral surfaces in contact with solution. Fe/Al oxides are abundant in acid soils and have the capacity to adsorb large amounts of solution P. Fe/Al oxides occur as discrete particles in soils or as coatings or films on other soil particles. They also exist as amorphous Al hydroxy compounds between the layers of expandable Al silicates. In soils with significant Fe/Al oxide content, the less crystalline or more amorphous the oxides, the larger the P-fixation capacity because of greater surface area.

P is adsorbed to a greater extent by 1:1 clays (e.g., kaolinite) than by 2:1 clays (e.g., montmorillonite) because of the higher amounts of Fe/Al oxides associated with kaolinitic clays that predominate in highly weathered soils. Kaolinite has a larger number of exposed OH groups in the Al layer that can exchange with P. In addition, kaolinite develops pH-dependent charges on its edges that can adsorb P (Fig. 2-9).

Figure 5-16 shows the influence of clay mineralogy on P adsorption. First, compare the three soils with >70% clay content. Compared with the oxisol and

Figure 5-16
P adsorption influenced by clay content.
(*Sanchez and Uehara, 1980,* The Role of Phosphorus in Agriculture, *p. 480, ASA, Madison, Wis.*)



andept soils, very little P adsorption occurred in the mollisol, composed mainly of montmorillonite, with only small amounts of kaolinite and Fe/Al oxides. The oxisol soils contained Fe/Al oxides and exhibited considerably more P adsorption capacity compared with mollisols. Greatest P adsorption occurred with the andept soils, composed principally of Fe/Al oxides and other minerals.

Soils containing large quantities of clay will fix more P than soils with low clay content (Fig. 5-16). In other words, the more surface area exposed with a given type of clay, the greater the tendency to adsorb P. For example, compare the three ultisol soils with 6, 10, and 38% clay. A similar relationship is evident in the oxisol soils (36, 45, and 70% clay) and the andept soils (11 and 70% clay).

In calcareous soils, P adsorption to $CaCO_3$ surfaces occurs; however, much of the adsorption is attributed to Fe oxide impurities. The amount and reactivity of $CaCO_3$ will influence P fixation. Impure $CaCO_3$ with large surface area exhibits greater P adsorption and more rapid precipitation of Ca-P minerals. Calcareous soils with highly reactive $CaCO_3$ and high Ca-saturated clay content will exhibit low solution P levels, since P can readily precipitate or adsorb.

In relative terms, acid soils fix twice as much P per unit surface area than neutral or calcareous soils. In addition, adsorbed P is held with five times more bonding energy in acid soils than in calcareous soils. To maintain a given level of solution P in soils with a high fixation capacity, it is necessary to add larger quantities of P fertilizers (Fig. 2-16). Larger additions of P are required to reach a given solution P concentration in fine-textured compared with coarse-textured soils. Consequently, high clay soils often require more fertilizer P than loam soils to optimize yields.

Soil pH

P adsorption by Fe/Al oxides declines with increasing pH. Gibbsite $[Al(OH)_3]$ adsorbs the greatest amount of P at pH 4–5, while P adsorption by goethite (FeOOH) decreases steadily between pH 3 and 12 (Fig. 5-17).

P availability in most soils is at a maximum near pH 6.5 (Fig. 5-11). At low pH, P fixation is largely from reaction with Fe/Al oxides and precipitation as $AlPO_4$ and $FePO_4$ (Fig. 5-12). As pH increases, solution Fe and Al decreases, which reduces P adsorption/precipitation and increases solution P concentration. Above pH 7.0, Ca^{+2} precipitates with P as Ca-P minerals (Fig. 5-12) and P availability decreases. Minimum P adsorption at pH 6.0–6.5 (Fig. 5-11) corresponds with the pH range of maximum P solubility (Fig. 5-12). Liming acidic soils generally increases P in solution. Overliming can depress P solubility due to the formation of insoluble Ca-P minerals.

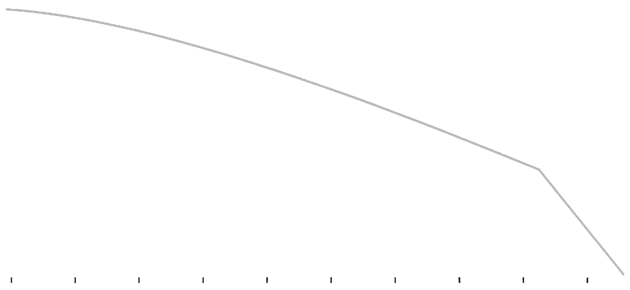


Figure 5-17
The adsorption of P by Fe oxide (goethite) as influenced by soil pH.
(Adapted from Hingston et al., 1968, Trans. 9th Int. Cong. Soil Sci., 1:1459–1461.)

Cation and Anion Effects

Divalent cations on the CEC enhance P adsorption relative to monovalent cations. For example, clays saturated with Ca^{+2} retain greater amounts of P than those saturated with Na^{+} or other monovalent ions. Divalent cations increase the accessibility of (+)-charged edges of clay minerals to P. This occurs at $pH < 6.5$, because at greater soil pH Ca-P minerals would precipitate.

Concentration of exchangeable Al^{+3} is also an important factor in P adsorption in soils since 1 meq of exchangeable Al^{+3}/100 g soil may precipitate up to 100 ppm P in solution. The following illustrates how hydrolyzed Al^{+3} adsorbs soluble P.

Step 1. Cation exchange

$$\text{Clay}\left)\begin{matrix}\text{Al}^{+3}\\ \text{Al}^{+3}\end{matrix}\right. \quad + \quad 3\text{Ca}^{+2} \quad \leftrightarrows \quad \text{Clay}\left)\begin{matrix}\text{Ca}^{+2}\\ \text{Ca}^{+2}\\ \text{Ca}^{+2}\end{matrix}\right. \quad + \quad 2\text{Al}^{+3}$$

Step 2. Hydrolysis

$$\text{Al}^{+3} + 2\text{H}_2\text{O} \leftrightarrows \text{Al(OH)}_2^{\ +} + 2\text{H}^{+}$$

Step 3. Precipitation and/or adsorption

$$\text{Al(OH)}_2^{\ +} + \text{H}_2\text{PO}_4^{\ -} \leftrightarrows \text{Al(OH)}_2\text{H}_2\text{PO}_4$$

Both inorganic and organic anions can compete with P for adsorption sites, resulting in decreased P adsorption. Weakly held inorganic anions such as NO_3^{-} and Cl^{-} are of little consequence, whereas adsorbed OH^{-}, $H_3SiO_4^{-}$, SO_4^{-2}, and MoO_4^{-2} can be competitive. The anion adsorption strength determines the competitive ability. For example, SO_4^{-2} is unable to desorb much $H_2PO_4^{-}$, since $H_2PO_4^{-}$ is capable of forming a stronger bond than is SO_4^{-2}.

Soil OM

Organic compounds in soils increase P availability by (1) formation of organophosphate complexes that are more soluble, (2) organic anion replacement of $H_2PO_4^{-}$ on adsorption sites, (3) coating of Fe/Al oxides by humus to form a protective cover and reduce P adsorption, and (4) increasing the quantity of organic P mineralized to inorganic P.

Organic anions produced from OM decomposition form stable complexes with Fe and Al, preventing reaction with $H_2PO_4^{-}$. These complex ions exchange for P adsorbed on Fe/Al oxides. Anions that are most effective in replacing $H_2PO_4^{-}$ are citrate, oxalate, tartrate, and malate.

Time and Temperature

P adsorption in soils occurs by an initial rapid reaction followed by a much slower reaction. Adsorption reactions involving exchange of P for anions on Fe/Al oxide surface are rapid. The slower reactions involve (1) formation of covalent Fe-P or Al-P bonds on Fe/Al oxide surfaces (Fig. 5-13) and (2) precipitation of P compounds (Fig. 5-12). These slow reactions involve a transition from more loosely bound (labile) to more tightly bound (non-labile) adsorbed P, which is less accessible to plants.

The initial P compounds precipitated during the reaction of fertilizer P in soils are initially unstable and are converted to more stable and less soluble compounds. For example, ≥70% conversion of added DCPD to OCP occurred after 10 months at 10°C and after only 4 months at ≥20°C (Fig. 5-18). P adsorption in soils of warm regions is generally greater than in soils of temperate regions, due to faster reaction

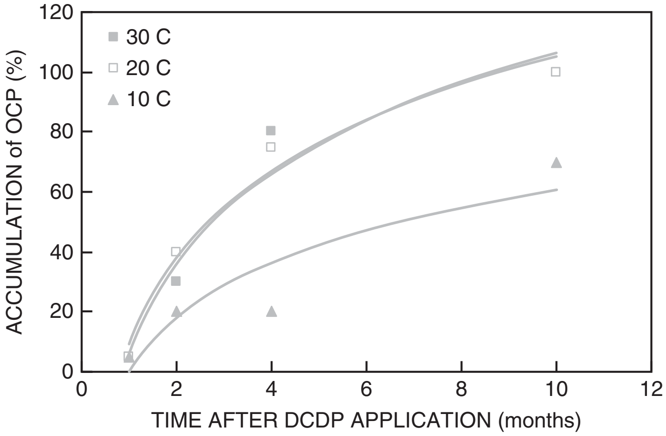


Figure 5-18
Percentage of DCPD converted to OCP as a function of time and temperature.
(*Adapted from Sheppard and Racz, 1980, Western Canada Phosphate Symp., p. 170.*)

rates and higher Fe/Al oxide content associated with a greater mineral weathering environment. Mineralization of P from soil OM or crop residues depends on soil biological activity, which increases with increasing temperature. Usually, mineralization rates double with each 10°C increase in temperature (Fig. 4-22).

Flooding

In most soils plant available P increases after flooding, largely due to a conversion of Fe^{+3}-P minerals to more soluble Fe^{+2}-P minerals. Other mechanisms include increased mineralization of organic P in acid soils and increased solubility of Ca-P in calcareous soils. These changes in P availability explain why response to applied P by irrigated rice is usually less than an upland crop grown on the same soil.

Fertilizer P Management Considerations

An important practical consequence of P adsorption and precipitation reactions is the time after application during which the plant is best able to utilize the added P. On soils with high P-fixation capacity, this period may be short, whereas with other soils it may last for months or even years. The reaction time will determine whether fertilizer P should be applied at one time in the rotation or in smaller, more frequent applications.

Adsorption of fertilizer P is greater in fine-textured soils because the reactive mineral surface area is greater than in coarse-textured soils. Also, if fertilizer P is broadcast applied, P is exposed to a greater amount of soil; hence, more P fixation occurs than if the same amount of P is band applied. Band placement reduces contact between soil and fertilizer, with a subsequent reduction in P adsorption (see Chapter 10). Although this is only one factor to consider in P fertilizer placement, it is very important for crops grown on low P soils with a high P adsorption capacity, where band placement generally increases plant utilization of fertilizer P.

Organic Soil P

Organic P represents about 50% of total soil P and typically varies between 15 and 80% (Table 5-5). Like OM, soil organic P decreases with depth, and the distribution with depth also varies among soils (Fig. 5-19). These data also illustrate the correlation between organic C and organic P in soils. P content in soil OM ranges from 1 to 3%. Although soil organic P increases with increasing organic C and/or N, the C:P and N:P ratios are more variable among soils than C:N ratio. Soils are characterized by C:N:P:S ratio (Table 5-6). Average C:N:P:S ratio in soil is 140:10:1.3:1.3.

Most soil organic P compounds are esters of orthophosphate $(H_2PO_4^-)$ including inositol phosphates (10–50%), phospholipids (1–5%), and nucleic acids (0.2–2.5%). Inositol phosphates represent a series of phosphate esters ranging from monophosphate up to hexaphosphate.

TABLE 5-5
RANGE IN ORGANIC P LEVELS IN VARIOUS SOILS

Location	Organic P	
	mg/kg	*% Total P*
Australia	40–900	5–60
Canada	80–700	10–55
Denmark	150–350	25–80
England, Scotland	200–900	20–80
New Zealand	120–1,400	30–80
Nigeria	160–1,200	10–40
Tanzania	5–1,200	30–90
United States	5–100	5–50

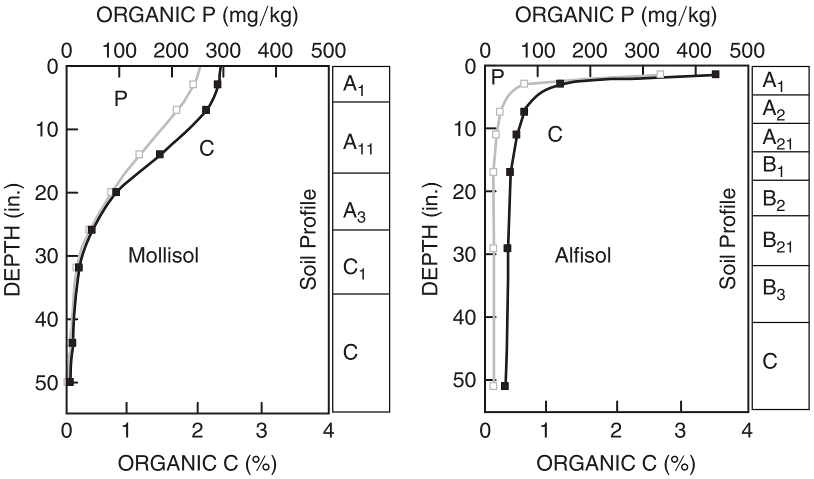


Figure 5-19
Distribution of organic P and C with depth in Iowa mollisol and alfisol soils.
(*Adapted from Stevenson, 1986, Cycles of Soil, p. 261, John Wiley & Sons.*)

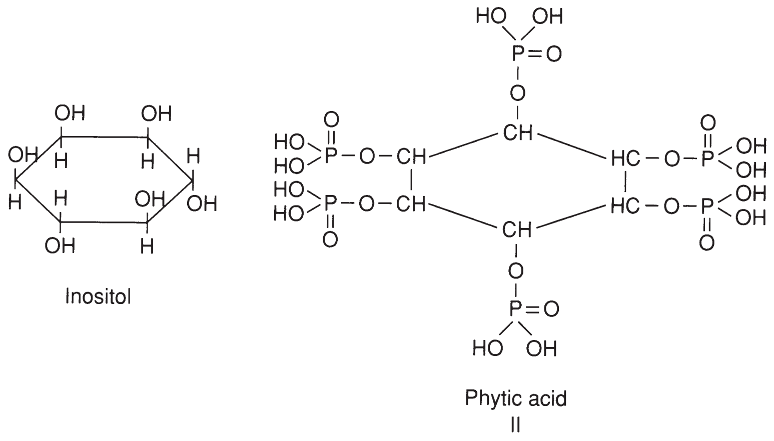
TABLE 5-6
ORGANIC C:N:P:S RATIO IN SELECTED SOILS

Location	Number of Soils	C:N:P:S
Iowa	6	110:10:1.4:1.3
Brazil	6	194:10:1.2:1.6
New Zealand[1]	22	140:10:2.1:2.1
India	9	144:10:1.9:1.8
Scotland[2]		
Calcareous	10	113:10:1.3:1.3
Noncalcareous	40	147:10:2.5:1.4

[1] Values for subsurface layers (35–53 cm) were 105:10:3.5:1.1.

[2] Values for S given as total S.

Source: Stevenson, 1986, *Cycles of Soil*, p. 262, John Wiley & Sons.



Inositol

Phytic acid
II

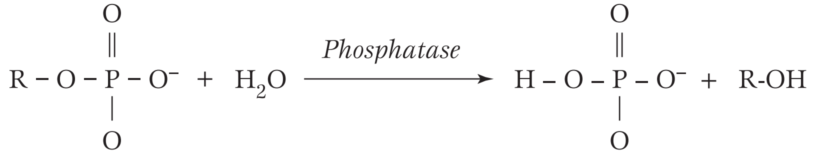
Figure 5-20
Chemical structure of inositol and inositol phosphate (phytic acid).

Phytic acid (myoinositol hexaphosphate) has six $H_2PO_4^-$ groups attached to each C atom in the benzene ring (Fig. 5-20). Successive replacement of $H_2PO_4^-$ with OH^- represents the other five phosphate esters. For example, the pentaphosphate ester has five $H_2PO_4^-$ groups and one OH^-. Inositol hexaphosphate is the most common phosphate ester and comprises ≈50% of total soil organic P. Most inositol phosphates and nucleic acids in soils are products of microbial degradation of plant residues. Two distinct nucleic acids, RNA and DNA, are released into soil in greater quantities than inositol phosphates. Since nucleic acids are rapidly degraded by soil microbes, they represent a small portion of total soil organic P. The common phospholipids are derivatives of glycerol and are insoluble in water, but also readily degraded by soil microbes. Thus, phospholipids also represent a small proportion of total organic P. The remaining soil organic P compounds originate from microbial activity, where, bacterial cell walls contain large amounts of stable P esters.

P Mineralization and Immobilization in Soils In general, P mineralization and immobilization are similar to N in that both processes occur simultaneously in soils and can be depicted as follows:

$$\text{Organic P} \underset{\textit{Immobilization}}{\overset{\textit{Mineralization}}{\rightleftarrows}} \text{Inorganic P } (H_2PO_4^-/HPO_4^{-2})$$

Soil organic P originates from plant and animal residues, which are degraded by microorganisms to produce other organic compounds and release inorganic P (Fig. 5-1). Phosphatase enzymes catalyze the mineralization reaction of organic P by:



$$R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O^- + H_2O \xrightarrow{\textit{Phosphatase}} H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O^- + R\text{-}OH$$

The quantity of P mineralized in soils increases with increasing organic P content (Fig. 5-21). In contrast, the quantity of inorganic P immobilized is inversely related to soil organic P, such that as the ratio of soil organic C:P increases (i.e., decreasing organic P), P immobilization increases (Fig. 5-22). Residue C:P ratio determines the predominance of P mineralization over immobilization, just as residue C:N

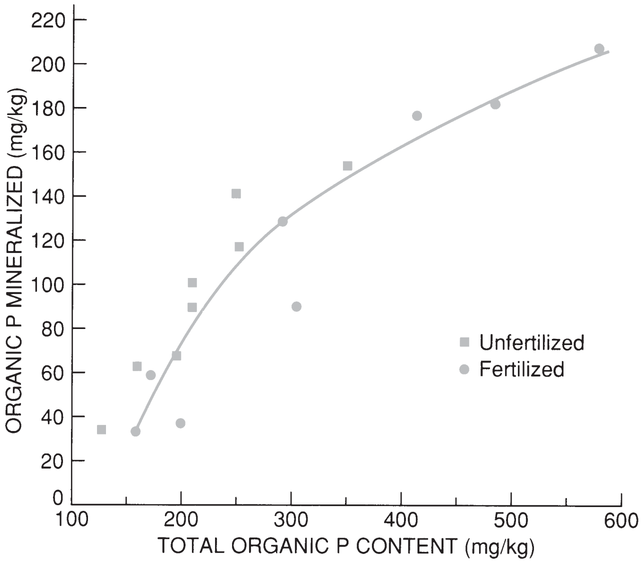


Figure 5-21
Mineralization of organic P in soil as influenced by total organic P.
(*Sharpley, 1985, SSSAJ, 49:907.*)

influenced N mineralization and immobilization. The following guidelines have been suggested:

C:P Ratio	Mineralization/Immobilization
<200	Net mineralization of organic P
200–300	No gain or loss of inorganic P
>300	Net immobilization of inorganic P

Expressed as % residue P, net P immobilization occurs when residue P < 0.2% and net mineralization occurs with >0.3% residue P. When residues are added to soil, net P immobilization occurs during the early stages of decomposition, followed by net P mineralization as the C:P ratio of the residue decreases.

P mineralization-immobilization processes are similar to N (Fig. 4-2). Factors affecting the quantity of P mineralization/immobilization are temperature, moisture, aeration, pH, cultivation intensity, and P fertilization. The environmental effects are similar to those described for N mineralization-immobilization, since both are microbial processes (see Chapter 4).

Inorganic fertilizer P can be immobilized to organic P by microorganisms. The quantity of P immobilized varies widely, with values of 25–100% of applied P reported. Continued fertilizer P applications can increase organic P content and subsequently increase P mineralization. Increases of 3–10 lb/a/yr in organic P mineralization with continued P fertilization are possible. In general, organic P will accumulate with P fertilization when C and N are available in quantities relative to the C:N:P ratio of soil OM. Inorganic P will likely accumulate if C and N are limiting.

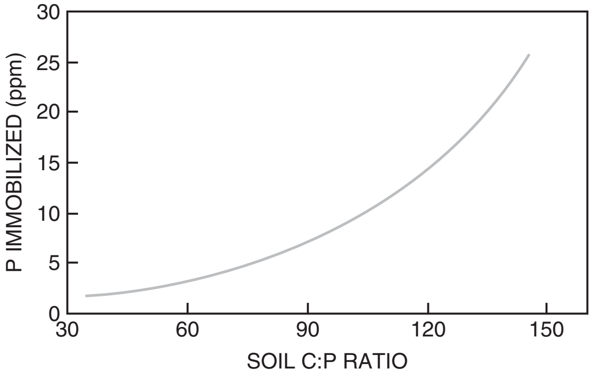


Figure 5-22
Relative effect of C:P ratio in soil on organic P immobilization.

TABLE 5-7
ORGANIC P LOSS WITH CULTIVATION IN THREE CANADIAN PRAIRIE SOILS

Soil Association	Native Prairie	60–70 Years of Cultivation	C or P Loss
	mg/g		— % —
	Blaine Lake		
Organic C	48	33	32
Total P	0.82	0.72	12
Organic P	0.65	0.53	18
Inorganic P	0.18	0.20	
	Sutherland		
Organic C	38	24	37
Total P	0.766	0.66	12
Organic P	0.50	0.41	17
Inorganic P	0.26	0.25	
	Bradwell		
Organic C	32	17	46
Total P	0.75	0.53	29
Organic P	0.45	0.32	29
Inorganic P	0.30	0.21	29

Source: Tiessen et al., 1982, Agron. J., *74:831.*

As with N, continued cultivation increases organic P mineralization decreasing soil organic P. When virgin soils are brought under cultivation, the soil OM decreases (see Chapter 12). As soil OM is oxidized, organic P is mineralized to inorganic P. For example, in the Northern Plains, organic C and P decreased an average of 38 and 21% after 60–70 years of cultivation, respectively (Table 5-7). Studies in the Midwest showed that after 25 years of cultivation, mineralization reduced organic P by 24% in the surface soil, which was less than the loss in organic C and N. In the Southern Plains, organic P losses are greater because of increased soil temperature. In temperate regions, the decline in organic P with cultivation is generally less than that of organic C and N because of fewer loss mechanisms for P, resulting in comparatively greater conservation of organic P. Under higher temperature and moisture regimes, equal losses of organic C, N, and P have been observed.

Measuring organic P cycling in soils is more difficult than for N because inorganic P produced through mineralization can be removed from solution by (1) P adsorption to clay and other mineral surfaces and (2) P precipitation as secondary Al-, Fe-, or Ca-P minerals. Therefore, the quantity of P mineralized during a growing season varies widely among soils (Table 5-8). Large quantities of organic P are mineralized in tropical, high-temperature environments. In the Midwest, organic P mineralization contributes about 4–10 lb/a/yr of plant available P.

Mineralizable organic P can be quantified in the same manner as mineralizable organic N (Chapter 4). For example, assume a soil contains 2% OM in the surface 6 in., 1% OM degradation rate, 5% N in OM, and a 10:1.3 N:P ratio. Organic P mineralized is estimated by:

$$(2 \times 10^6 \text{ lb soil/afs}) \times 4\% \text{ OM} \times 1\% \text{ OM loss} \times 5\% \text{ N in OM}$$
$$\times\ 1.3/10 \text{ P:N ratio} = 5.2 \text{ lb P/afs mineralized}$$

Since P removal with most crops ranges 10–40 lb P/a, mineralizable P generally cannot meet crop P requirement.

TABLE 5-8
ORGANIC P MINERALIZED IN A GROWING SEASON FOR SEVERAL SOILS

Location	Land Use	Soil	Period	Organic P	Mineralized
			yr	*kg/ha/yr*	*%/yr*
		Slightly weathered, temperate soils			
Australia	Grass	—	4	6	4
	Wheat	—	55	0.3	0.3
Canada	Wheat	Silt loam	90	7	0.4
		Sandy loam	65	5	0.3
England	Grassland	Silt and sandy loam	1	7–40	1.3–4.4
	Arable	Silt and sandy loam	1	2–11	0.5–1.7
	Woodland	Silt loam	1	22	2.8
	Cereal crop	—	—	0.5–8.5	—
	Deciduous forest	Brown earth	1	9	1.2
	Grass	Brown earth	1	14	1.0
Iowa	Row crops	Clay loam	80	9	0.7
Maine	Potatoes	Silt loam	50	6	0.9
Minnesota	Alfalfa	Silty clay loam	60	12	1.2
Mississippi	Cotton	Silt loam	60	5	1.0
	Soybean	Silty clay loam	40	8	1.0
New Mexico	Row crops	Loam	30	2	0.4
Texas	Sorghum	Clay	60	7	1.0
		Weathered, tropical soils			
Honduras	Corn	Clay	2	6–27	6–12
Nigeria	Bush	Sandy loam	1	123	24
	Cocoa	Sandy loam	1	91	28
Ghana	Cleared shaded	Fine sandy loam	3	141	6
	Tropical half shaded		3	336	17
	Rainforest exposed		3	396	17

Source: Stewart and Sharpley, 1987, SSSA Spec. Publ. No. 19, *p. 111.*

Immobilization and mineralization processes for P, C, N, and S cycling are similar and related. For example, if adequate amounts of N, P, and S are added to soils to which crop residues are returned, some of the added nutrients may be immobilized. However, continued cropping of soils without the addition of N, P, and S results in their depletion in soils through mineralization and crop removal.

P SOURCES

Inorganic P

P Fertilizer Terminology Terms used to describe P content in fertilizers are *water soluble*, *citrate soluble*, *citrate insoluble*, *available*, and *total* P (as P_2O_5). A fertilizer sample is first extracted with water, and the P contained in the filtrate represents the water-soluble fraction. The remaining water-insoluble material is extracted with 1 N ammonium citrate to determine citrate-soluble P. The sum of water-soluble and citrate-soluble P represents plant available P. The P remaining after the water and citrate extraction is citrate-insoluble P. The sum of available and citrate-insoluble P represents total P.

P Content of Fertilizers Fertilizer P content is expressed as P_2O_5 instead of elemental P. Although attempts have been made to change from $\%P_2O_5$ to %P, the industry still expresses P concentration in fertilizers as $\%P_2O_5$. Similarly, the concentration of

K in fertilizers is expressed as $\%K_2O$ instead of %K. As a matter of interest, N was formerly guaranteed as $\%NH_3$ rather than as %N, as is now done.

The conversion between %P and $\% P_2O_5$ is:

$$\%P = \%P_2O_5 \times 0.43$$
$$\%P_2O_5 = \%P \times 2.29$$

The conversion factors are derived from the ratio of molecular weights of P and P_2O_5:

$$\frac{2 \times P\ (g/mole)}{P_2O_5\ (g/mole)} = \frac{2 \times 31}{142} = 0.43$$

P Fertilizer Sources

Rock Phosphate

Rock phosphate (RP) is the primary raw material used in the manufacture of P fertilizers (Fig. 5-23). The major RP materials are sedimentary deposits found in Morocco, China, the United States, and Russia, representing nearly 72% of total world production. The United States produces about 18% of the world's RP. RP minerals are apatites $[Ca_{10}(PO_4)_6(X)_2]$, where X is F^-, OH^-, or Cl^-. Fluorapatite $[Ca_{10}(PO_4)_6F_2]$ is the most common RP. RP contains numerous impurities of CO_3, Na, and Mg, with some heavy metals, particularly Cd.

None of the P in RP is water soluble, although the citrate solubility varies 3–20% of total P. Finely ground RP can be applied directly to soil and reacts as:

$$Ca_{10}(PO_4)_6F_2 + 12H_2O \rightarrow 10Ca^{+2} + 6H_2PO_4^- + 2F^- + 12OH^-$$

Increasing soil acidity (lower pH) will increase dissolution of RP, since soil acids will neutralize OH^- produced and force the above reaction to the right. The solubility of RP (fluorapatite) increases as soil pH decreases (Fig. 5-12); therefore, use of RP as a P fertilizer is restricted to very acidic soils in warm, moist climates characteristic of tropical regions. Since the % available P in RP is relatively small (Table 5-9), RP rates are two to four times superphosphate rates. However, at these rates several years of residual availability can occur, which is important for permanent crops such

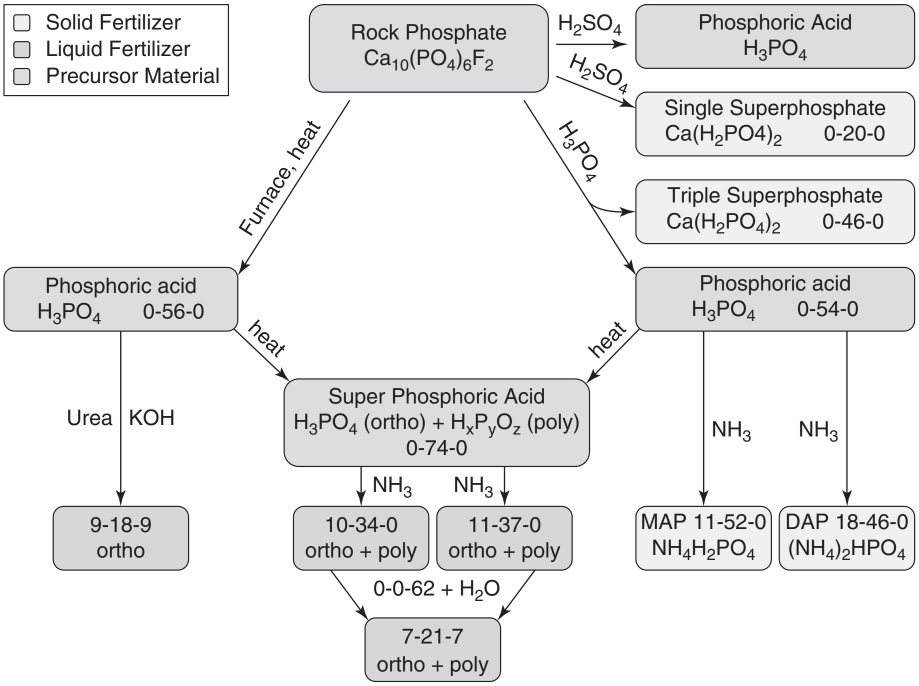


Figure 5-23 *Manufacturing process for common solid and liquid P fertilizers from rock phosphate.*

TABLE 5-9
COMMON ORTHO- AND POLYPHOSPHATE FERTILIZERS

Fertilizer	Commonly Used Abbreviations	Analysis (%)				% Total Available P	P Compound
		N	*P_2O_5*	*K_2O*	*S*		
		Calcium phosphates					
Rock phosphate	RP		25–36			3–20	$Ca_{10}(PO_4)_6 \cdot F_2 \cdot (CaCO_3)_x \cdot (Ca(OH)_2)_x$
Single superphosphate	SSP		16–22		11–12	80–85	$Ca(H_2PO_4)_2$
Triple superphosphate	TSP		44–52		1–2	90–95	$Ca(H_2PO_4)_2$
		Ammonium phosphates					
Monoammonium phosphate	MAP	11–13	48–62		0–2	100	$NH_4H_2PO_4$
Diammonium phosphate	DAP	18–21	46–53		0–2	100	$(NH_4)_2HPO_4$
Ammonium polyphosphate[1]	APP	10–15	35–62			100	$(NH_4)_3HP_2O_7 \cdot NH_4H_2PO_4$
Urea ammonium phosphate[1]	UAP	21–34	16–42			100	$(NH_4)_3HP_2O_7 \cdot NH_4H_2PO_4$
		Potassium phosphates					
Monopotassium phosphate			51	35		100	KH_2PO_4
Dipotassium phosphate			41	41		100	K_2HPO_4

[1] Contains a mixture of ortho- and polyphosphates.

as rubber, oil palm, and cocoa. Ground RP can also be used for restoration of low P soils on abandoned farms and on newly broken lands, usually at rates of 1–3 t/a.

In situations where RP reactivity is inadequate for immediate crop response and P fixation capacity of the soil reduces fertilizer P available to plants, partially acidulated RP can increase the water-soluble P content and improve short-term crop response to RP. Partially acidulated RP is produced by treating RP with 10–20% of the quantity of H_3PO_4 used for the manufacture of triple superphosphate or by reacting it with 40–50% of the amount of H_2SO_4 normally used in the production of single superphosphate (Fig. 5-24).

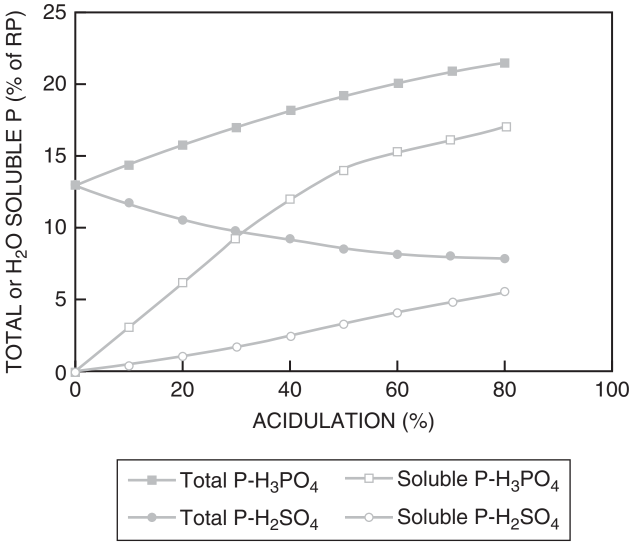


Figure 5-24
Acidulation of North Carolina rock phosphate increases soluble P and ultimately plant available P. Total P increases since P is being added with H_3PO_4.
(Adapted from Schultz, 1986, Inter. Fert. Dev. Center, IFDC-T-31, Muscle Shoals, Ala.)

Reacting RP with H_2SO_4 produces phosphoric acid (H_3PO_4), commonly referred to as green or wet-process acid, containing 17–24% P (39–55% P_2O_5).

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$$

A by-product of green acid production is gypsum ($CaSO_4 \cdot 2H_2O$) that can be used as an S and Ca fertilizer, as an amendment for sodic soils, and for other industrial purposes.

Heating RP in an electric furnace produces elemental P that is reacted with O_2 and H_2O to form H_3PO_4, called white or furnace acid (Fig. 5-23). White acid has a much higher degree of purity than green acid; however, high energy costs involved in manufacturing limits its use in agriculture.

While green acid can be injected in soil or irrigation water, particularly in alkaline and calcareous areas, almost all green acid is used to acidulate RP to make Ca and NH_4 phosphates (Fig. 5-23). Common P fertilizers are produced from either acid- or heat-treated RP to increase water-soluble P (Fig. 5-23; Table 5-9).

Calcium Phosphates

Once the most important P fertilizer, single superphosphate (SSP) and triple superphosphate (TSP) use have decreased relative to NH_4 phosphate sources (Fig. 5-25). Use of SSP in the United States has nearly disappeared (Fig. 5-26).

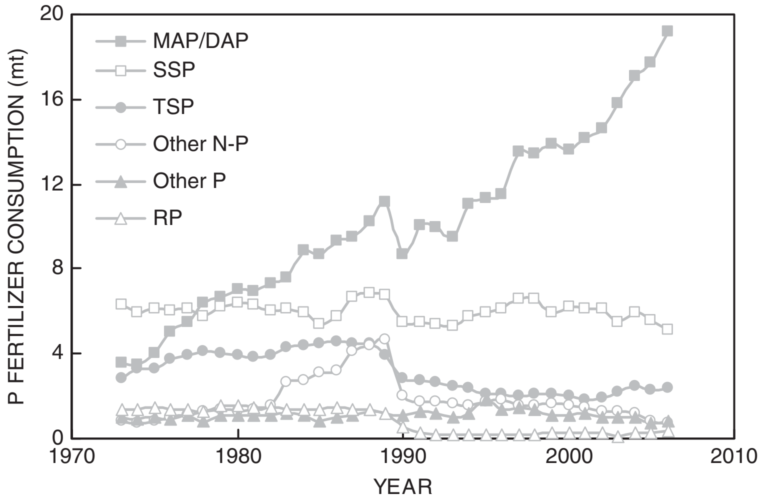


Figure 5-25
World use of common P fertilizers in metric tons of P. MAP/DAP, diammonium phosphate/monoammonium phosphate; SSP, single superphosphate; TSP, triple superphosphate; RP, rock phosphate used for direct application.
(Adapted from International Fertilizer Industry Association, 2009.)

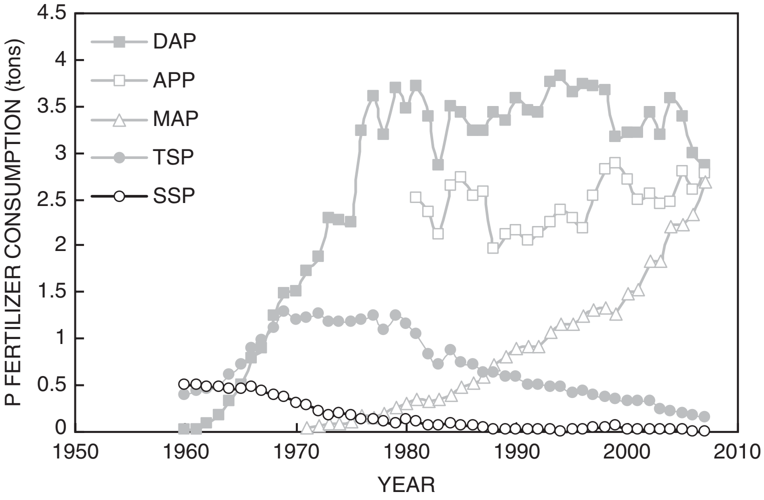


Figure 5-26
Use of common P fertilizers in the United States. DAP, diammonium phosphate; APP, ammonium polyphosphate (also includes other N-P fertilizer); MAP, monoammonium phosphate; TSP, triple superphosphate; SSP, single superphosphate.
(USDA ERS, 2009.)

SSP contains 7–9.5% P (16–22% P_2O_5) and is an excellent source of S (Table 5-9). Similar to production of green acid, SSP is produced by:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 14H_2O \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 \cdot 2H_2O + 2HF$$

The gypsum by-product is utilized as described before.

TSP contains 17–23% P (44–52% P_2O_5) and is produced by treating RP with H_3PO_4:

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$$

TSP was the most common P source used in the United States until the 1970s, when NH_4 phosphates became popular (Fig. 5-26). Its high P content is an advantage because transportation, storage, and handling comprise a large fraction of total fertilizer cost.

Ammonium Phosphates

NH_4 phosphates are produced by reacting wet-process H_3PO_4 with NH_3 (Figs 5-23; 5-27). Monoammonium phosphate (MAP) contains 11–13% N and 21–24% P (48–55% P_2O_5); however, the common grade is 11-22-0 (11-52-0). Diammonium phosphate (DAP) contains 18–21% N and 20–23% P (46–53% P_2O_5); the most common grade is 18-20-0 (18-46-0). Although MAP use has increased significantly, DAP is more widely used than any other P fertilizer in the United States (Fig. 5-26). Increased global use of MAP/DAP results from increased P uptake when NH_4^+ is placed with P fertilizer (see Chapter 10). Both MAP and DAP are granular, water-soluble fertilizers with the advantage of high nutrient content, which reduces shipping, handling, and storage costs. They can be used for formulating solid fertilizers by bulk blending or in manufacturing suspension fertilizers. MAP and DAP are also used for direct application as starter fertilizers.

Soil reaction pH around a dissolving granule of MAP is ≈3.5, compared to pH 8.5 with DAP (Table 5-10). Depending on rate, row or seed placement of DAP can cause seedling injury and inhibit root growth through NH_3 produced according to:

$$(NH_4)_2HPO_4 \rightarrow 2NH_4^+ + HPO_4^{-2} \quad (\text{pH } 8.5)$$
$$2NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

Because of the high dissolution pH (pH 8.5), NH_4^+ will convert to NH_3 (Fig. 4-45), where NH_3 toxicity potential is greater in calcareous or high pH soils. However, adequate separation of DAP from the seed will reduce seedling damage. In most cases, DAP rate should not exceed 15–20 lb N/a applied with the seed (depending on crop, row width, soil pH and texture, and application rate). Seedling injury with MAP is seldom observed except in sensitive crops such as canola, flax, and other salt-sensitive crops (Chapter 3).

Except for differences in reaction pH and seedling injury when applied with the seed, few agronomic differences exist between MAP and DAP. Reports of improved crop response to MAP compared with DAP on high pH or calcareous soils are generally not substantiated. Low-reaction pH with MAP has been claimed to

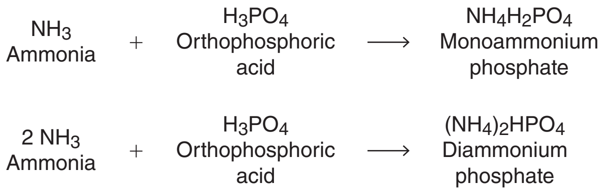


Figure 5-27
Reactions of ammonia with orthophosphate to produce monoammonium phosphate (MAP) and diammonium phosphate (DAP).

TABLE 5-10
FERTILIZER P SOURCES AND THEIR REACTION CHEMISTRY IN SOILS

P Source			Saturated Solution Properties			
Compound	*Formula*	*Symbol*	*pH*	*P (m/L)*	*Primary Cation*	*m/L*
		Highly water soluble				
Monocalcium phosphate	$Ca(H_2PO_4)_2$	TSP	1.5	4.5	Ca	1.3
Monoammonium phosphate	$NH_4H_2PO_4$	MAP	3.5	2.9	NH_4	2.9
Ammonium polyphosphate	$(NH_4)_3HP_2O_7$	APP	6.0	6.8	NH_4	10.2
Diammonium phosphate	$(NH_4)_2HPO_4$	DAP	8.5	3.8	NH_4	7.6
		Sparingly soluble[1]				
Dicalcium phosphate	$CaHPO_4$	DCP	6.5	≈ 0.002	Ca	0.001
Dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	DCPD	6.5	≈ 0.002	Ca	0.001
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	HA	6.5	$\approx 10^{-5}$	Ca	0.001

[1] Compounds not used as fertilizers, included for comparison purposes.

Source: Sample et al., 1980. In F. E. Khasawneh et al. (Eds.), Phosphorus in Agriculture, *p. 275, ASA, Madison, Wis.*

increase micronutrient availability in calcareous soils, but this has not been consistently demonstrated.

Ammonium Polyphosphate

Ammonium polyphosphate (APP) is manufactured by reacting pyrophosphoric acid, $H_4P_2O_7$, with NH_3 (Fig. 5-23). Pyrophosphoric acid is produced from dehydration of wet-process acid. Polyphosphate is a term used to describe two or more orthophosphate ions combined together, with the loss of one H_2O molecule per two $H_2PO_4^-$ (Fig. 5-28). APP is a liquid containing 10–15% N and 15–16% P (34–37% P_2O_5), with about 75 and 25% of the P present as polyphosphate and orthophosphate, respectively. The most common APP grade is 10-15-0 (10-34-0). Liquid APP is a competitive P source and can be directly applied or mixed with other liquid fertilizers. Commonly, UAN and APP are combined and subsurface band applied.

With APP applied to soil, rapid chemical and biological hydrolysis of polyphosphate produces $H_2PO_4^-$. Several factors control hydrolysis rates. Phosphatase associated with plant roots and rhizosphere organisms are responsible for biological

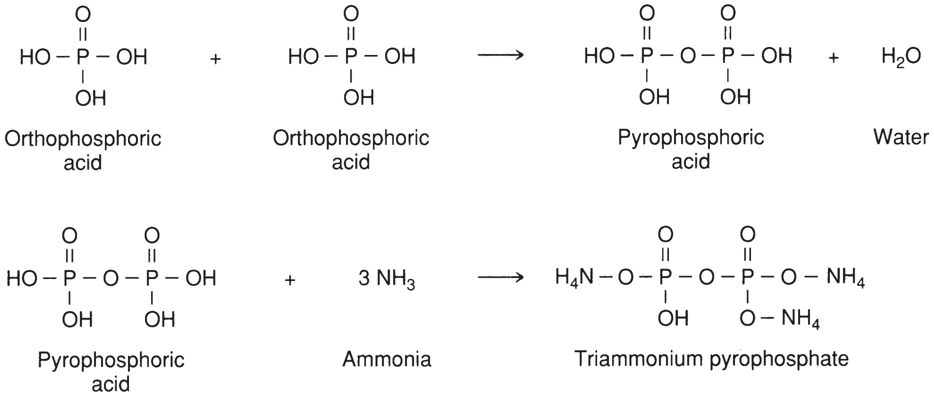
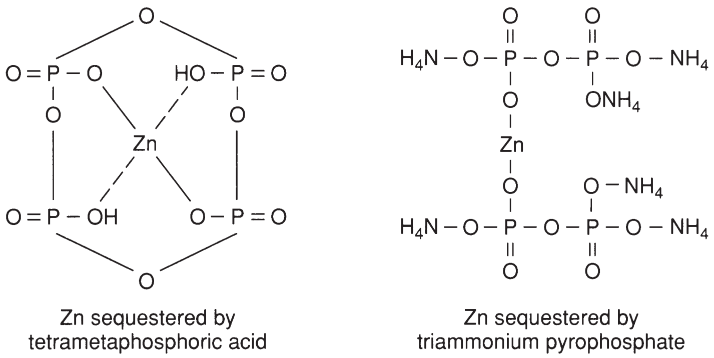


Figure 5-28
Reaction of two H_3PO_4 molecules to produce pyrophosphate. The reaction continues to form longer chains called polyphosphates. Adding NH_3 to pyro- and polyphosphates produces ammonium polyphosphate (APP).

Figure 5-29
Sequestering of Zn by polyphosphate molecules can maintain a greater Zn concentration in solution than Zn added to orthophosphate fertilizers.



hydrolysis of polyphosphates. Temperature, moisture, soil C, pH, and various conditions that encourage microbial and root growth favor phosphatase activity and polyphosphate hydrolysis. Temperature is the most important environmental factor, where hydrolysis of polyphosphate increases substantially as soil temperature increases.

Polyphosphates are as effective as $H_2PO_4^-$ sources for crops. One unique property of APP is chelation or sequestering reaction with micronutrient cations, which maintains higher micronutrient concentration in APP than possible with $H_2PO_4^-$ solutions (Fig. 5-29). APP can maintain 1–3% Zn in solution compared with only 0.05% Zn with $H_2PO_4^-$.

A granular fertilizer, urea ammonium phosphate (UAP), is produced by reacting urea with APP. The fertilizer grade is 28-12-0 (28-28-0), containing 20–40% polyphosphate. UAP can be easily blended with other granular fertilizers. Like DAP, seedling damage may occur when UAP is applied with the seed.

Potassium Phosphate

Potassium phosphate products include KH_2PO_4 and K_2HPO_4 (Table 5-9). They are water soluble and commonly used in the horticulture industry. Their high P and K content makes them ideally suited for solanaceous crops such as potatoes, tomatoes, and many leafy vegetables sensitive to high levels of Cl^- associated with KCl (see Chapter 6). Their low-salt index reduces injury to germinating seeds and to young seedlings when placed close to the seed.

Behavior of P Fertilizers in Soils

Fertilizer P Reactions

Many of the factors affecting native P availability, discussed earlier, also influence fertilizer P reactions and availability in soil. P fertilizer added to soil initially increases solution P, but subsequently solution P decreases through P adsorption to mineral surfaces, precipitation as Al/Fe- or Ca-P minerals, and immobilization by microbes (Fig. 5-1).

Inorganic P fertilizers dissolve rapidly when placed in moist soil. Water sufficient to initiate dissolution moves to the granule or droplet by either capillary or vapor transport. While water is drawn into the fertilizer, the fertilizer solution moves into the surrounding soil. A nearly P-saturated solution forms in and around the fertilizer granule or droplet (Fig. 5-30). Initial P diffusion from the fertilizer seldom exceeds 3–5 cm (Fig. 5-31). Diffusion of P reaction products away from the dissolving granule increases with increasing soil moisture content.

As the saturated P solution moves into the first increments of soil, solution pH ranges from 1.5 to 8.5 depending on fertilizer P source (Table 5-10). Some soil minerals may be dissolved by the concentrated P solution, resulting in the release of cations (Fe^{+3}, Al^{+3}, Mn^{+2}, K^+, Ca^{+2}, and Mg^{+2}) that react with P to form

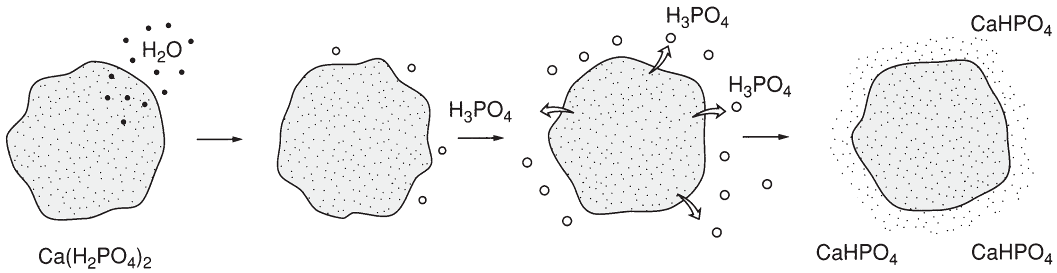


Figure 5-30

Reaction of a monocalcium phosphate (MCP) granule in soil. Water vapor moves toward the granule, which begins to dissolve. Phosphoric acid forms around the granule resulting in a solution pH of 1.5. The acidic solution causes other soil minerals to dissolve, increasing cation (and anion) concentration near the granule. With time the granule dissolves completely and the solution pH increases, with subsequent precipitation of a dicalcium phosphate (DCP) reaction product.

specific compounds, referred to as soil-fertilizer reaction products. For example, as MCP $[Ca(H_2PO_4)_2]$ dissolves, H_3PO_4 forms near the granule and lowers pH to 1.5 (Table 5-10). Other soil minerals in contact with H_3PO_4 may dissolve, increasing solution cation concentration near the granule. Subsequently, the solution pH will increase as H_3PO_4 is neutralized. Within a few days or weeks, DCP and/or DCPD will precipitate as the initial fertilizer reaction product (Fig. 5-12). Depending on the native P minerals initially present in the soil, OCP, TCP, HA, or Fe/$AlPO_4$ may eventually precipitate.

In acid soils, reaction products formed from MCP include DCP and eventually $AlPO_4$ and/or $FePO_4$ precipitates (Fig. 5-12). In calcareous soil, DCP and OCP are the dominant initial reaction products. Because MAP has a reaction pH of 3.5 compared with pH of 8.5 for DAP, P should be more soluble near the dissolving granule (Table 5-10). The acid pH with MAP may temporarily reduce the rate of P reaction product precipitation in calcareous soils.

Although differences in reaction pH among P fertilizers cause differences in reaction products, the overall effect is temporary because the volume of soil influenced by the P granule or droplet is small. Differences in availability of P sources to crops are small compared with differences in other P management factors such as P placement.

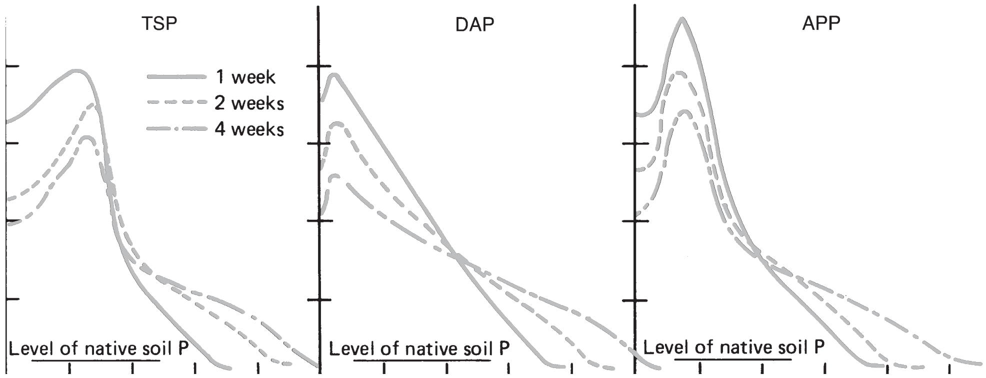


Figure 5-31

P diffusion away from TSP and DAP granules or an APP droplet in soil over 5 weeks.

(*Khasawneh et al., 1974,* Soil Sci. Soc. Am. J., *38:446.*)

Precipitation reactions are favored by high P concentrations that exist near the dissolving P fertilizer. Adsorption reactions are expected to be most important at the periphery of the soil-fertilizer reaction zone, where P concentrations are lower (Fig. 5-31). Although both precipitation and adsorption occur, precipitation accounts for most of the P being retained near the dissolving granule.

Interaction of N with P

N promotes P uptake by plants by (1) increasing top and root growth, (2) altering plant metabolism, and (3) increasing P solubility and availability. Increased root mass is largely responsible for increased crop uptake of P. NH_4^+ fertilizers have a greater stimulating effect on P absorption than NO_3^-. Improved fertilizer P effectiveness can occur with P placed close to NH_4^+ sources (see Chapter 10).

Effect of Granule or Droplet Size

Since water-soluble P is rapidly converted to less-soluble P reaction products, decreasing contact between soil and fertilizer generally improves plant response to P fertilizer. Increasing granule or droplet size and/or band application of the fertilizer decreases soil fertilizer contact and maintains a higher solution P concentration for a longer time compared with broadcast P and/or fine particle size.

Soil Moisture

Soil moisture content influences the effectiveness and availability of applied P. At field capacity, 50–80% of the water-soluble P can diffuse from the fertilizer granule within 24 hours. Even at 2–4% moisture, 20–50% of the water-soluble P moves out of the granule within the same time.

Rate of Application

Even though fertilizer P eventually forms less-soluble P compounds, the P concentration in solution increases with P application rate. With time the P concentration decreases as less-soluble P compounds precipitate. The duration of elevated solution P levels depends on the rate of P fertilizer applied, the method of P placement, the quantity of P removed by the crop, and soil properties that influence P availability.

Modification of Chemistry in Soil Fertilizer Reaction Zone Modification of the chemical environment around fertilizer P particles or bands of fluid P by coatings or additions of a specific family of polymers has been investigated since 1999 on a wide range of crops and soils. The most common polymer is *maleic itaconic copolymer* solution used with solid or liquid P fertilizers (AVAIL®). Nutrisphere® is a similar product used with N fertilizers (Table 4-24).

The suggested mechanism for improving P availability with polymer-enhanced P fertilizers is related to the large negative charge (~1,800 meq CEC/100 g) of the maleic itaconic copolymer. The high CEC attracts cations (Al^{+3}, Fe^{+3}, Ca^{+2}, and Mg^{+2}) in the P fertilizer reaction zone, reducing their interaction with $H_2PO_4^-$ from the applied fertilizer. As discussed in the previous section, high solution cation content enhances formation of less-soluble P fertilizer reaction products, reducing P availability.

Increased crop yield response to polymer-coated P fertilizers occurs, but not consistently or predictably. It is important to recognize that while the polymer has a high CEC, the polymer rate applied is very small compared to the soil CEC.

Residual P Residual fertilizer P availability can persist depending on P rate applied, crop P removal, and soil properties that influence P reaction product chemistry. P-fixation reactions influence residual P availability in acid soils more than in basic soils (Table 5-11). These data show that approximately 45% of fertilizer P was plant

TABLE 5-11
INFLUENCE OF SOIL TYPE ON RESIDUAL FERTILIZER P AVAILABILITY

		% P Available After 6 Months	
Soil Type	**# of Soils**	*Mean*	*Range*
Calcareous	56	45	11–72
Slightly weathered	80	47	7–74
Moderately weathered	27	32	6–51
Highly weathered	40	27	14–54

Note: Resin extractable P measured 6 months after P application.

Source: Sharpley, 1991, Soil Sci. Soc. Am. J., *55:1038.*

available after 6 months over a wide range of soil properties; however, residual P availability was lower in highly weathered, acid soils compared to slightly weathered and calcareous soils.

With increasing P rate, the initial and residual fertilizer P availability increases (Fig. 5-32). After more than 10–12 years, soil test P decreased to its initial level except with the highest P rate. These data demonstrate that relatively high P rates are needed to substantially increase and maintain residual available P over a long time period.

Figure 5-33 illustrates the change in plant available P influenced by P rate and frequency of application. First, plant removal of P in the unfertilized soil caused initial soil test P to decrease substantially over 6 years. Annual application of 100 lb/a P_2O_5 maintained soil test P slightly above the initial soil test level, whereas the intermediate P rate (50 lb/a P_2O_5) resulted in soil test levels between 0 and 100 lb/a P_2O_5 annual rates. Triennial application of 150 lb/a P_2O_5 increased available P in the first year; however, soil test P subsequently decreased below the initial soil test level until the next triennial application. Similarly, 150 lb/a P_2O_5 applied only in the first year maintained soil test P at or above the initial level during the first 3 years, followed by decreasing soil test P in subsequent years. These data illustrate the importance of soil testing for accurately determining when additional fertilizer P is needed for optimum production (Chapter 9).

P placement also influences residual fertilizer P (Fig. 5-34). On this low P soil, broadcast P applied at 45 lb P_2O_5/a did not increase soil test P over the unfertilized treatment, indicating that fertilizer P not taken up by the crop converted to

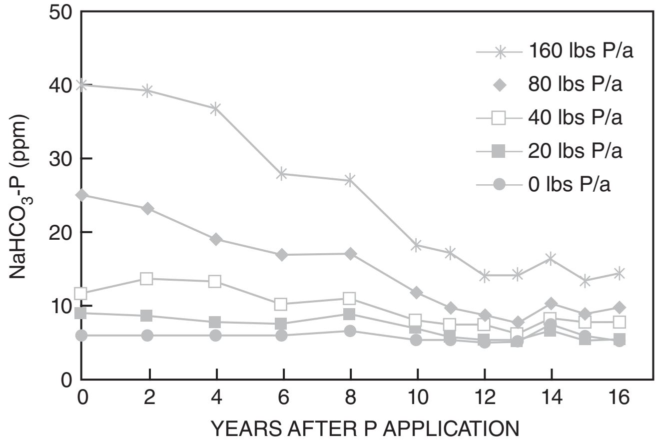


Figure 5-32
Residual effect of single applications of P on $NaHCO_3$ extractable P over 16 years of production.
(*Havlorson, 1989,* Soil Sci Soc. Am. J., *53:839.*)

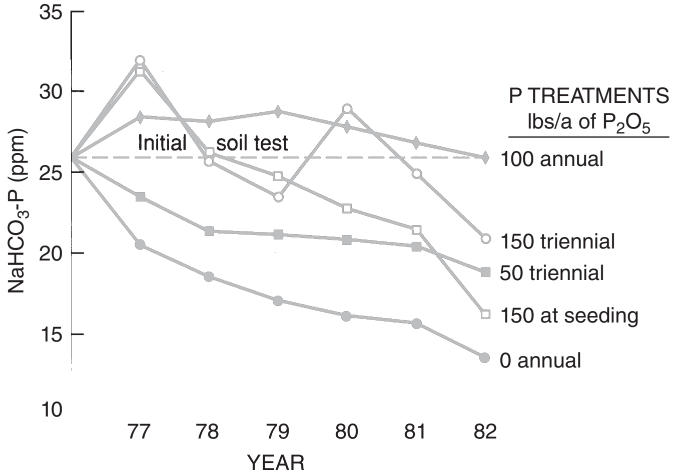


Figure 5-33
Influence of broadcast fertilizer P on buildup or decline in soil test P over 6 years.
(Havlin et al., 1984, SSSAJ, 48:332.)

P compounds with a solubility similar to that of the native P minerals. In contrast, 75 lb P_2O_5/a (broadcast) increased soil test P. Increasing band-applied P from 45 to 75 lb/a P_2O_5 dramatically increased soil test P in the band, indicating that the solubility of the P reaction products is greater than that of the native P minerals and that they persist for several years after application.

There is some question about the need for additional P even when residual P levels are high. Low rates of P in starter fertilizers placed with or near the seed row are potentially beneficial on high P soils when the crop is stressed by cold, wet conditions and diseases such as root rots. Although residual P contributes significantly to crop yields, additional banding of P may be required to maximize crop production (Chapter 10).

Organic P

Organic wastes are excellent sources of plant available P, with manure accounting for 98% of organic P applied to cropland. The form and content of P in fresh organic materials vary widely depending on source and storage/handling prior to application. With animal wastes, inorganic P ranges from 0.3 to 2% of the dry weight, while

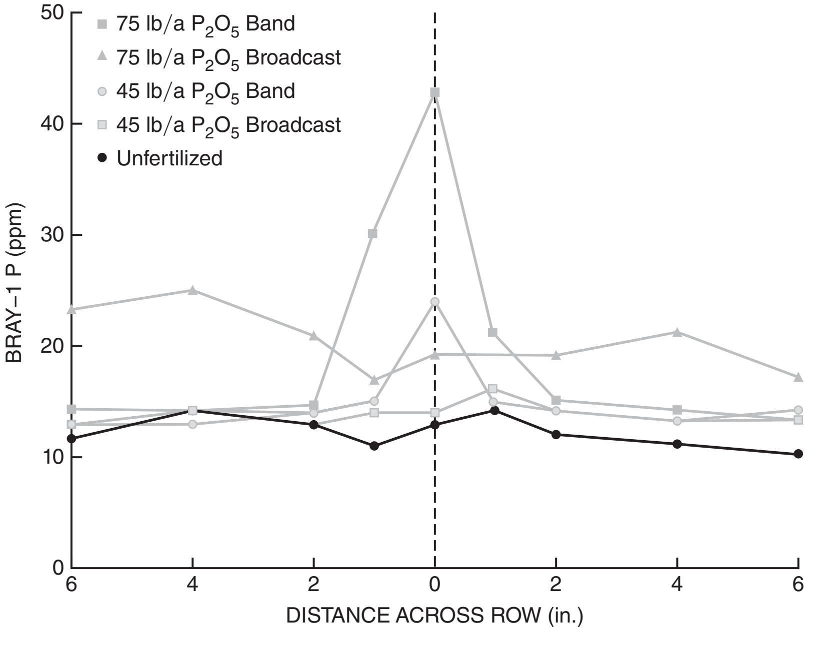


Figure 5-34
Influence of band-applied fertilizer P on soil test P in the band 23 months after application. Band P 1 in. below the seed.
(Havlin et al., 1990, Proc. FFF Symposium, p. 213.)

Table 5-12
P Content of Selected Animal Wastes and Composts

Source	Total P	Inorganic P
	— % of Dry Matter —	
	Animal waste	
Swine	1.5–2.5	0.8–2.0
Beef cattle	0.7–1.2	0.5–0.8
Dairy cattle	0.5–1.2	0.3–1.0
Poultry	0.9–2.2	0.3–1.2
Horses	0.4–1.4	0.2–0.8
	Compost	
Poultry manure	1.1–2.4	0.5–1.2
Lawn clippings, leaves	0.1–0.4	0.05–0.2
Biosolids	1.5–7.0	0.7–4.0

organic P ranges from 0.1 to 1% (Table 5-12; Table 4-30). In fresh manure, organic P represents 30–70% of total P. Composting organic wastes generally increases total P content.

As discussed with N, manure storage and handling can change the nutrient content of manure. Mineralization of organic P during storage usually increases inorganic P content and decreases organic P. For example after 3–4 months of liquid swine waste storage, inorganic P increased from 60–70 to 85% of fresh manure dry weight (Table 5-13).

Table 5-13
Distribution of P Fractions in Liquid Swine Manure After Storage

Animal	Total P (% dry matter)	% of Total P
Total inorganic P	1.5–2.0	85
Total organic P	0.2–0.3	15
Inorganic P in solution	0.01–0.20	5
Organic P in solution	0.01–0.03	<4
Microbial P	0.02–0.04	<2

Source: Van Faassen, 1987. In V. D. Meer (Ed.), Animal Manure on Grassland Crops, *pp. 27–45.*

Table 5-14
Influence of Crop N–Based Waste Application Rates on P Applied in Excess of Crop Need

	Application	Waste Nutrients				Crop Requirement[1]		Excess P
Source	Rate	N		P		N	P	Applied
	lb DM/a	*%*	*PAN*[1]	*%*	*lb/a*	—— *lb/a* ——		*lb/a*
Poultry litter	8,000	2	160	1.7	136	160	25	111
Biosolid	10,000	1.6	160	2.5	250	160	25	225

[1] PAN = plant available N represents the amount of N required by the crop. Waste rate determined by crop N needed. Crop P required based on 200 bu/a corn at ~0.2% P content.

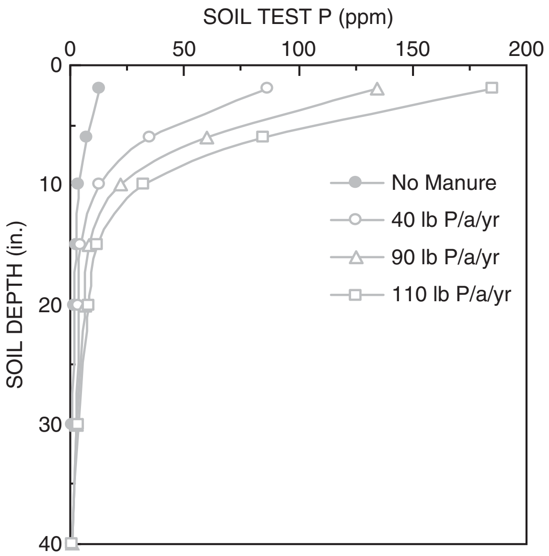


Figure 5-35
Increase in Mehlich P with increasing manure P rates applied annually for 10 years.
(*Adapted from Sharpley et al., 1984,* J. Environ. Qual., *13:211–215.*)

P content in biosolids ranges from 2 to 7%, with most present as inorganic P (Table 5-12). Thus, 40–140 lb P/a would be applied per ton of material. If 80% is inorganic P and plant available during the first year, then 32–175 lb P/a would be applied per ton. Because of relatively high transportation and processing expenses, application rates generally exceed 1 t/a, and therefore the total amount of P applied can greatly exceed typical crop requirements. See Chapter 10 for detailed discussion of manures and manure management.

Animal waste application rates based on the N requirement of the crop also results in P application in excess of crop requirement (Table 5-14). This example illustrates that waste P was applied at rates 4–9 times that needed by the crop. Continued application of wastes based on crop N requirements will substantially increase soil P (Fig. 5-35), and increase risk of P transport to surface and ground waters (Chapter 12).

STUDY QUESTIONS

1. Describe P deficiency symptoms in grasses and broadleaf plants and explain why P-deficient plants exhibit severe stunting.
2. Give brief descriptions of the main pathways of transporting soil P to plant roots. How can P fertilization alter the importance of these pathways?
3. Compare typical soil solution concentrations of P with P content in plants. If a soil contains 0.05 ppm P in solution, calculate the number of times the solution P must be replenished to meet a 0.5 kg P/ha/day demand by the plant.
4. Define P intensity and quantity factors. What is labile soil P?
5. What are the various mechanisms of P retention in acid and calcareous mineral soils?
6. What soil properties influence fixation of fertilizer P and what can be done to reduce the amount of P fixation?
7. Estimate the quantity of P mineralized, if a soil contains 2.5% OM content and the rate of mineralization is 1.5%.
8. How is P availability influenced by soil pH?
9. Refer to Figure 5-12 (P solubility diagram) and answer the following:
   a. A soil contains β-TCP and strengite minerals. The soil pH would be ________ and the soil solution P concentration would be _______ M.
   b. After 20 years of fertilizer N use, the soil pH dropped 2 units. The P mineral present at this pH would be ________ and the solution P concentration would be _______ M.
   c. Assuming the critical P level is 10^{-5} M, the minimum pH for adequate P supply to plants would be _______.

   - **d.** Assume the initial soil pH is 8. Circle one answer in each group. If the pH is slowly decreased, the concentration of P in solution will (increase, decrease, not change) until about pH (7.2, 6.2, 7.8), at which point the solution P level generally (increases, decreases, or stays the same) until pH (7.0, 6.0, 5.0) at which point solution P (increases, decreases, stays the same).
   - **e.** A soil contains octacalcium phosphate and variscite. What is the soil pH range where solution P would be enough for adequate P availability (assume the critical P level is 10^{-5} M)? Soil pH = _____.
   - **f.** Why does P solubility increase above pH 7.8 for the Ca-phosphate minerals?
   - **g.** Fertilizer P is added to a soil at pH 7.2. The P compound in this soil is hydroxyapatite. What is the initial P compound that precipitates in the soil and what is the final P compound to precipitate?

10. What is the original source of most fertilizer P?

11. Under what types of soil and cropping conditions might the use of RP give satisfactory results? Explain.

12. What acids are commonly used to acidify RP? Why does acid treatment of RP render the P more plant-available?

13. Describe the soil and management conditions that you might expect an appreciable downward movement of P through the soil profile.

14. Under what soil conditions would band placement of P result in its greatest utilization by the plant?

15. What advantages or disadvantages exist with high-analysis sources such as DAP, MAP, and TSP?

16. Describe how the presence of N improves plant utilization of P fertilizers. Which of the two forms, NH_4^+ or NO_3^-, is more beneficial?

17. What is residual P? Why is it important agriculturally?

18. What are polyphosphates? Describe the hydrolysis reaction of polyphosphates. Do you expect any difference in crop response to equal rates of APP and MAP?

19. Briefly describe the sequence of events that takes place during the dissolution of P fertilizers.

20. What are typical distances for the initial movement of P from fertilizer application sites? Will P in the reaction zones eventually become more uniformly distributed in the soil? Why or why not?

21. For a crop yield of 3 t/a (0.5% P), estimate the annual excess P applied with 3 t/a swine waste (2% N; 1.52% P).

22. For a transpiration ratio of 500 and 0.4% P in the crop, if the average solution concentration is 0.08 ppm P, calculate the quantity of P in percentage moving to the plant by Mass flow.

23. What is the role of microorganisms in producing P compounds in soil?

24. Discuss the functions of P in plants

25. Why P is considered as an essential element for the growth and development of the reproductive parts of a plant?

26. What are the characteristics of VAM-infected roots?

27. Distinguish between endomycorrhizae and ectomycorrhizae.

28. Using Figure 5.9, briefly explain the influence of inorganic in soil solution on corn grain yield.

29. Explain the mechanism of P adsorption using
   - **a.** Freundlich and
   - **b.** Langmuir equations.

30. Write a note on P mineralization and immobilization in soils.

31. Explain the manufacture of P-fertilizers from Rock phosphate.

32. What is the Mechanism of improving P availability using polymer-enhanced fertilizers?

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6

Potassium

Potassium (K) is the seventh most abundant element (~2.5%) in the earth's crust and is generally absorbed by plants in amounts larger than any other nutrient except N. Total soil K content ranges between 0.05 and 3% and is lower in coarse-textured soils formed from sandstone or quartz and higher in fine-textured soils formed from high K-bearing parent materials. Although total soil K content exceeds crop uptake during a growing season, only a small fraction is plant available.

Highly weathered soils are highly leached and generally have a low K content. In tropical soils, total K content is generally low because of greater weathering by high rainfall and temperatures; thus K deficiency frequently occurs after a few years of cropping a virgin tropical soil. In contrast, moderately weathered soils generally have a high K content because of lower rainfall conditions.

THE K CYCLE

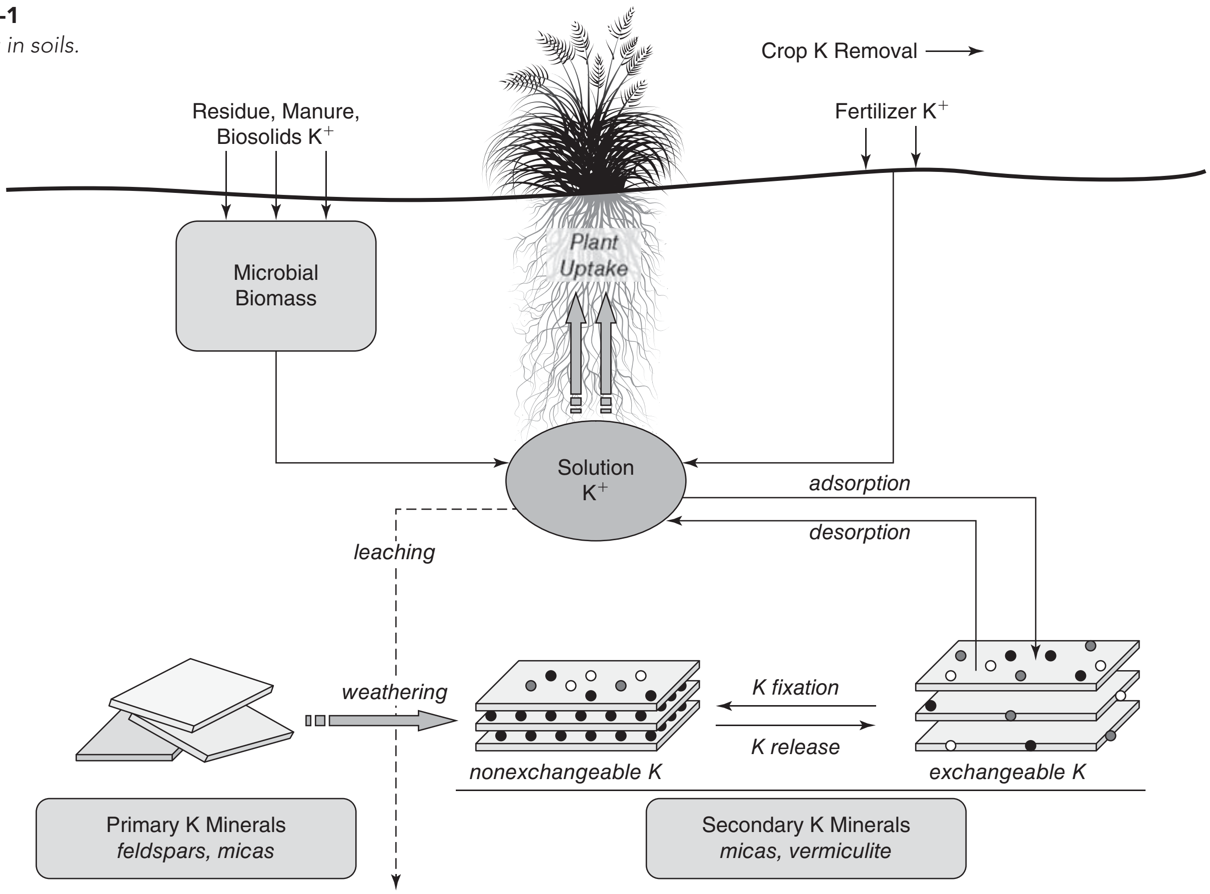
Listed in increasing order of plant availability, soil K exists in four forms:

mineral	5,000–25,000 ppm (0.5–2.5%)
nonexchangeable	50–750 ppm
exchangeable	40–600 ppm
solution	1–10 ppm

Mineral K accounts for 95–98% of total soil K, whereas slowly available (nonexchangeable) and readily available (exchangeable and solution) represents 1–3% and 0.02–2%, respectively. K cycling or transformations among K forms in soils are dynamic (Fig. 6-1). As K is removed by crop uptake and leaching, there is a continuous but slow transfer of K from minerals to exchangeable and slowly available forms. With application of fertilizer K, some reversion to slowly available forms can occur.

Exchangeable and solution K equilibrate rapidly, whereas nonexchangeable K equilibrates very slowly with exchangeable and solution K. Transfer of K from mineral to more available forms is extremely slow in most soils, and this K is essentially unavailable to crops during a single growing season, but slowly available K resupplies solution and exchangeable K.

Figure 6-1
K cycling in soils.



FUNCTIONS AND FORMS OF K IN PLANTS

Forms

K is absorbed by plant roots as K^+ and tissue concentration ranges from 1 to 5% in dry matter.

Functions

Unlike N, P, and most other nutrients, K is not a component of biochemical compounds in the plant. K exists solely in solution or bound to $(-)$ charges on tissue surfaces. As a result, K^+ functions are related to solution ionic strength in plant cells. K is involved in water relations, charge balance, and osmotic pressure in cells and across membranes, which explains its high mobility in the plant.

K is important for many crop quality characteristics due to its involvement in synthesis and transport of photosynthates to plant reproductive and storage organs (grain, fruit, tubers, etc.), and subsequent conversion into carbohydrates, proteins, oils, and other products. For example, in fruits and vegetables (citrus, bananas, tomatoes, potatoes, onions, etc.), adequate K enhances fruit size, color, taste, and peel thickness, which is important for storage quality.

K deficiency influences metabolic processes, primarily related to photosynthesis, and synthesis and translocation of enzymes.

Photosynthesis and Energy Relations K is essential for photosynthesis through several functions including:

- ATP synthesis
- production and activity of specific photosynthetic enzymes (i.e., RuBP carboxylase)
- CO_2 absorption through leaf stomates
- maintenance of electroneutrality during photophosphorylation in chloroplasts

Plants require K for the photosynthetic transfer of radiant energy into chemical energy through production of ATP (photophosphorylation). Energy from ATP is required for metabolic processes in plants that produce carbohydrates, proteins, lipids, oils, vitamins, and other compounds essential for crop productivity and quality. K nutrition for optimum photosynthesis, measured by CO_2 absorption, varies with the crop, where ~2% leaf K is needed in corn (Fig. 6-2) and ~3% K is needed in alfalfa (Fig. 6-3). Increased K supply influences stomatal function to (1) increase CO_2 absorption, (2) increase RuBP carboxylase enzyme activity responsible for combining

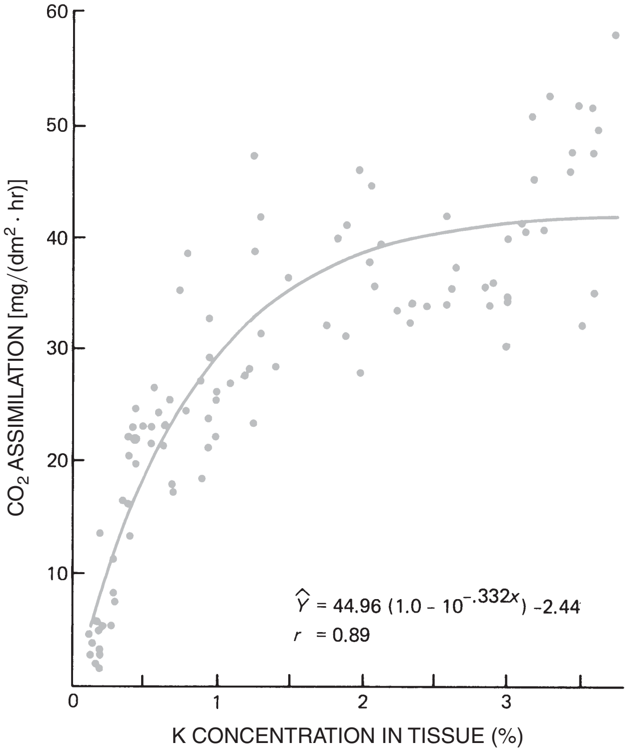


Figure 6-2
Adequate K in corn leaves increases photosynthesis as measured by CO_2 fixation.
(Smid and Peaslee, 1976, Agron. J., 68:907.)

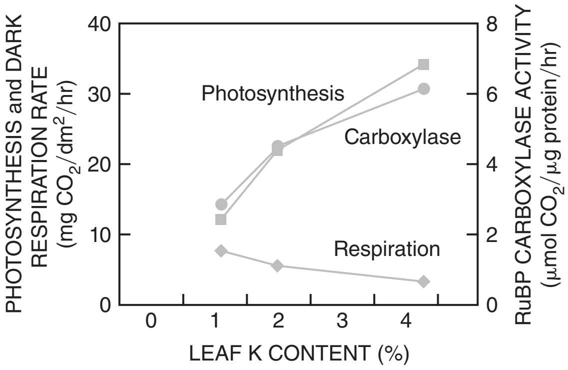


Figure 6-3
Relationship between K nutrition and rate of photosynthesis and dark respiration as measured by CO_2 exchange in alfalfa.
(*Adapted from Marschner, 2002,* Mineral nutrition of higher plants, *2nd ed., Acad. Press, London.*)

ribulose biphosphate and CO_2 to produce 3-phosphoglycerate, the first product of CO_2 fixation in leaves, and (3) decrease dark respiration (Fig. 6-3). The increase in dark respiration under K deficiency reduces plant growth and crop quality.

Enzyme Activation K is involved in activation of enzymes important to energy utilization, starch synthesis, N metabolism, and respiration. These enzymes are abundant in meristematic root and shoot tissues where cell division occurs rapidly (growing points). For example, the starch synthetase enzyme converts sugars into starch, critical for starch accumulation in grains, fruits, and vegetables. Decreased starch conversion causes soluble sugar accumulation that reduces fruit quality. Also, K influences the nitrogenase enzyme required for reduction of N_2 to NH_3 in *rhizobium* (Chapter 4). N_2 reduction depends on carbohydrate supply, where K enhances carbohydrate transport to nodules for amino acid synthesis.

Translocation of Assimilates Once CO_2 is assimilated into sugars during photosynthesis, they are transported from leaves to fruits, roots, tubers, seeds, and grains where they are stored and used for growth. Translocation of sugars uses energy from ATP that requires K for its synthesis. Sugar translocation is greatly reduced in K-deficient plants. For example, normal translocation rate in sugarcane leaves is ~2.5 cm/min, and is reduced to half in K-deficient plants. Under adequate K nutrition, osmotic potential of the phloem sap, water flow rate, and sucrose concentration are higher than in K-deficient plants. K is also important as a counterion (maintaining electrical balance) for NO_3^- transport in the xylem.

Water Relations K provides much of the osmotic "pull" that draws water into plant roots. K-deficient plants are less able to withstand water stress, mostly because of their inability to fully utilize available water. Maintenance of plant turgor is essential for optimum photosynthetic and metabolic function. Stomata open when there is an increase in turgor pressure in the guard cells surrounding each stoma, which occurs by an influx of K. Malfunctioning of stomata with K deficiency is related to lower rates of photosynthesis and less-efficient water use. Transpiration, or water loss through stomata, accounts for most plant water use. K can affect the rate of transpiration and water uptake through regulation of stomata openings (Fig. 6-4).

Visual Deficiency Symptoms

Typical K deficiency symptoms in alfalfa consist of white spots on leaf edges, whereas chlorosis and necrosis of leaf edges are observed with corn and other grasses (see color plates inside book cover). Since K is mobile in the plant, visual deficiency symptoms usually appear first in the lower leaves, progressing toward

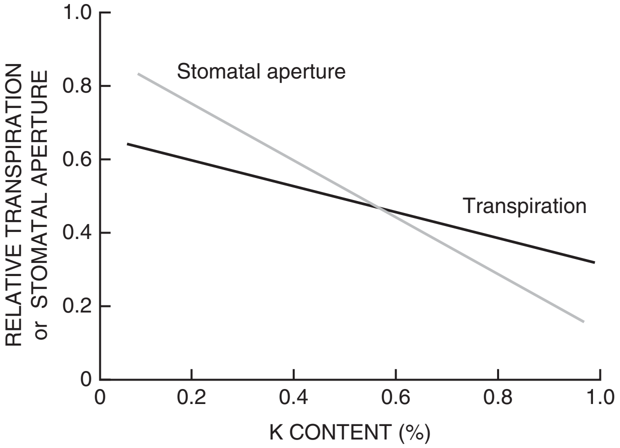


Figure 6-4
Influence of increasing K nutrition on relative stomatal aperture and transpiration rate.

Figure 6-5
Response of corn to K on a low K soil. Note the poor growth and lodged condition of the crop on the right.
(*Courtesy International Plant Nutrition Institute.*)

upper leaves (newer growth). K deficiency can also occur in young leaves of high-yielding, fast-maturing crops such as cotton and wheat.

Another K deficiency symptom is weakening of stalks or stems, which causes lodging in small grains and stalk breakage in corn and sorghum (Fig. 6-5), which can severely reduce harvestable yield (Fig. 6-6).

K stress increases crop damage by bacterial and fungal diseases, insect and mite infestation, and nematode and virus infection (Fig. 6-7). For example, K-deficient soybeans are highly susceptible to pod and stem blight caused by the fungus *Diaporthe sojae L.* Similarly, low K greatly increases the severity of foliar diseases (stem rot, sheath blight, brown leaf spot) in paddy rice. In fruits and vegetables, poor storage and shelf life due to reduced peel or skin thickness and increased skin cracking are related to K deficiency.

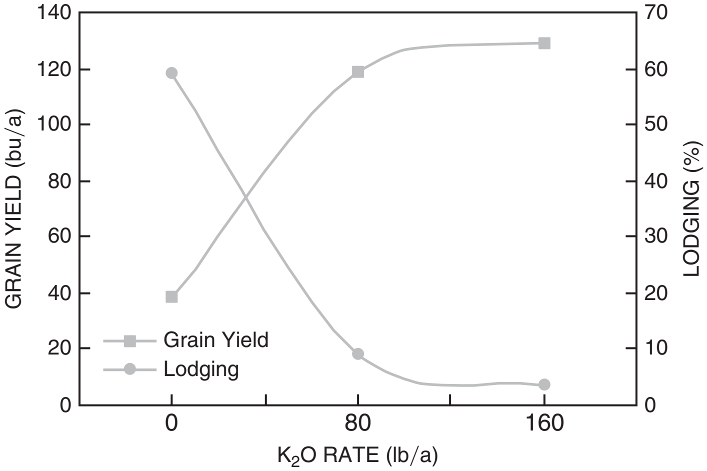


Figure 6-6
Effect of N and K on corn yield and lodging.
(*Schulte, 1975, Proc. Wisconsin Fert. and Aglime Conf., p. 58.*)

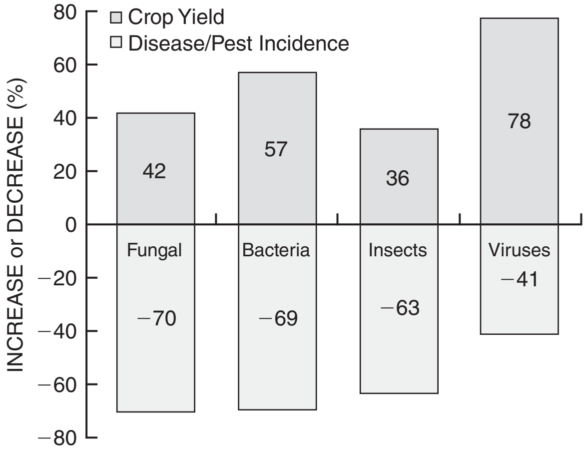


Figure 6-7
Summary of over 2,400 research projects demonstrating the positive effect of adequate K nutrition on crop yield and resistance to diseases and insect infestation.
(*Adapted from Perrenoud, 1990, Potassium and Plant Health, IPI Research Topics No. 3, Switzerland.*)

FORMS OF SOIL K

Soil Solution K

Plant roots absorb K^+ from the soil solution (Fig. 6-1). Solution K^+ concentration for optimum plant growth ranges from 1 to 10 ppm, depending on crop and yield level. The higher values are commonly found in arid or saline soils. K^+ uptake is influenced by the presence of other cations, where increasing Ca^{+2} and Mg^{+2} concentrations can decrease K uptake. In acid and sodic soils, Al^{+3} and Na^+ can reduce K^+ uptake, respectively.

The quantity of K transported to the root surface by diffusion and mass flow is related to K intensity. The relative contribution of mass flow to K absorption can be estimated. For example, if the K content in the crop is 2.5% and the transpiration ratio is 400 g H_2O/g plant, transpirational water should contain >60 ppm K for mass flow to provide sufficient K. Since most soil solutions contain 1–10 ppm K, mass flow contributes ~10% of crop K requirement. Mass flow could supply more K to crops grown in soils naturally high in water-soluble K or where fertilizer K has increased solution K.

K diffusion is a slow process compared with mass flow and is limited to distances of only 1–4 mm (Table 6-1). Diffusion accounts for approximately 90% of K absorption by roots. K diffusion to roots can be seen from autoradiographs made by using ^{86}Rb, which closely resembles K (Fig. 6-8). Since K absorption occurs within only a few millimeters of the root, plant available K that is farther away is not positionally available.

Exchangeable K

Like other exchangeable cations, K^+ is adsorbed to negatively charged soil colloids by electrostatic attraction to three types of exchange sites or binding positions (Fig. 6-9). The planar position (*p*) on the outside surfaces attracts K^+ and other exchangeable cations. The edge (*e*) position is comprised of exchangeable cations held to pH-dependent surface charge (Fig. 2-9) and K^+ held in the interlayer positions, representing the initial K^+ released in the nonexchangeable K release process (see next section). The inner

TABLE 6-1
MECHANISMS AND RATES OF K TRANSPORT IN SOILS

Situation	Mechanism	Rate (cm/day)
In profile	Mainly mass flow	Up to 10
Around fertilizer source	Mass flow and diffusion	<0.1
Around root	Mainly diffusion	0.01–0.1
Out-of-clay interlayers	Diffusion	10^{-7}

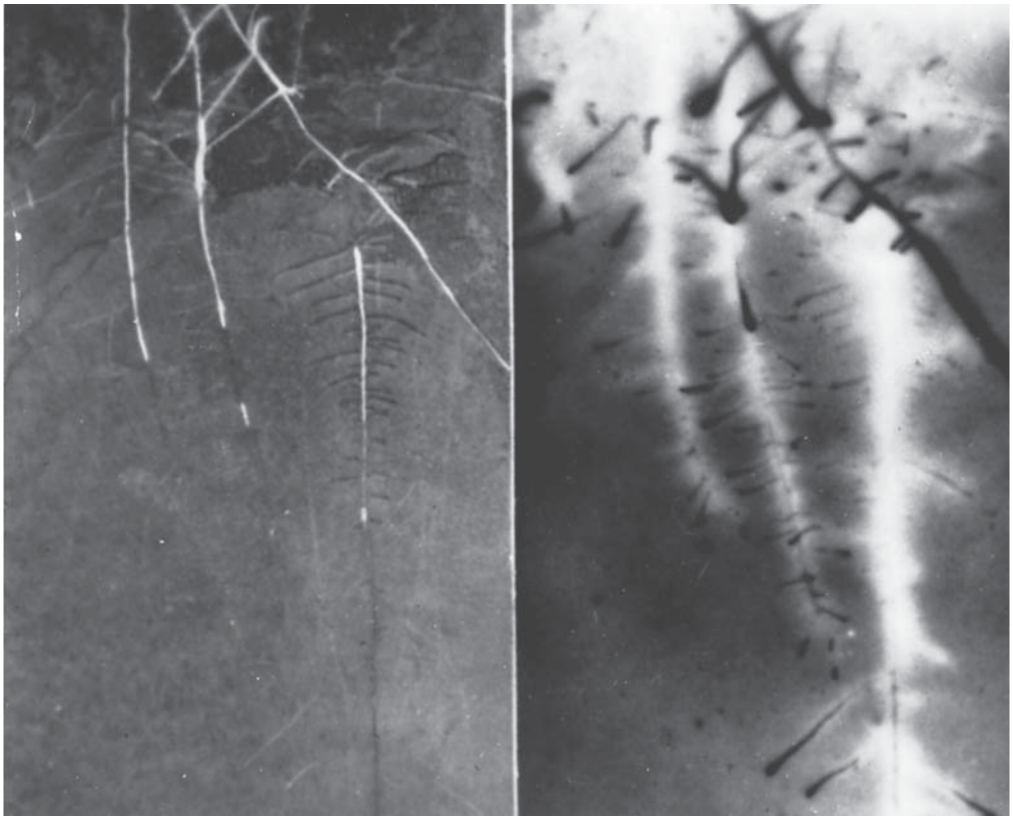


Figure 6-8

Left, corn roots growing through soil. Right, autoradiograph showing the effect of corn roots on ^{86}Rb distribution in the soil. Lighter areas are where ^{86}Rb concentration is reduced by root uptake of ^{86}Rb.

(Barber, 1985. in R. D. Munson (Ed.), Potassium in Agriculture, Reprinted courtesy of American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America).

(*i*) positions have a high specificity for K^+ and represent nonexchangeable K^+ released slowly. During a growing season, solution K^+ concentrations are buffered more readily by exchangeable K^+ held to *p* positions; however, K^+ held on all three positions ultimately buffers solution K^+.

Because of the major role of exchangeable K^+ in buffering changes in solution K^+, the relationship between exchangeable K^+ (quantity, Q) and solution K^+ (intensity, I), or Q:I ratio, is used to quantify K^+ buffering in soils. Q:I measures the ability of the soil to maintain solution K^+ concentration and is proportional to CEC.

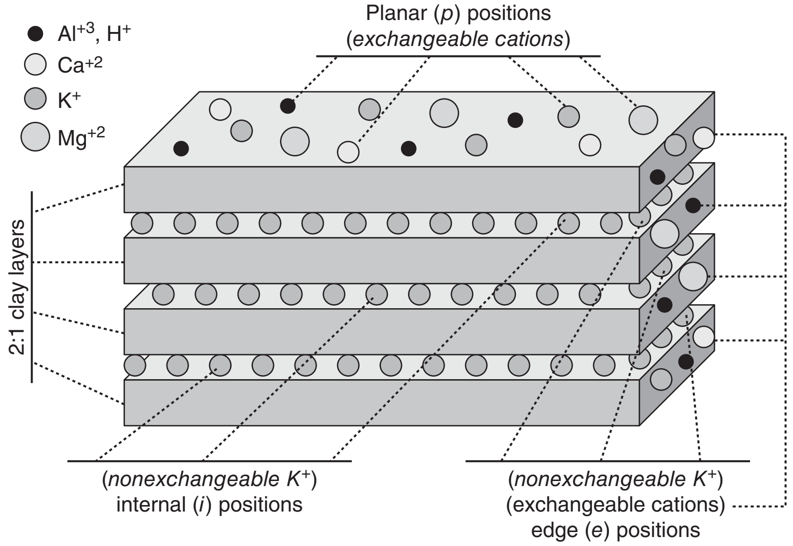


Figure 6-9

Binding sites for K^+ on 2:1 secondary clay minerals such as mica and vermiculite.

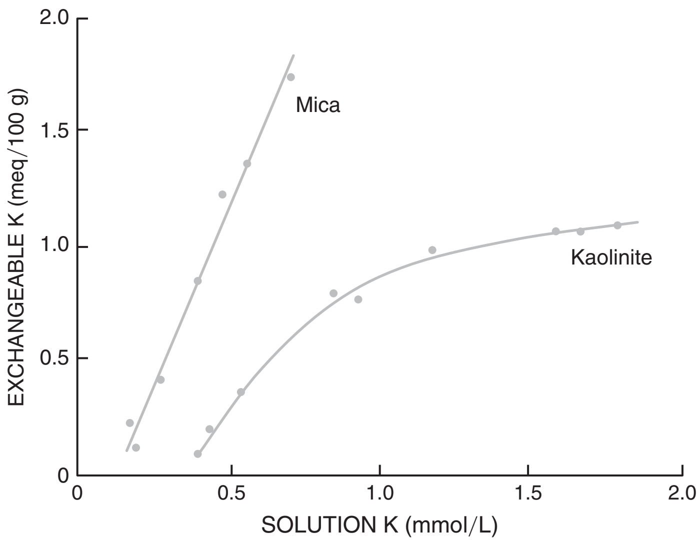


Figure 6-10
Relative difference in BC between two soils with equal clay content (~38%), where the dominant clay is either kaolinite or mica. As exchangeable K is decreased with plant K uptake, solution K is decreased much greater with kaolinite clay compared to mica clay. Thus, the BC for K^+ is greater in a mica-dominated soil.
(*Adapted from Grimme and Nemeth, 1979,* Proc. Congr. Int. Potash Inst., *11:99.*)

A high Q:I signifies good K^+ buffering capacity (BC), whereas a low Q:I suggests a need for K fertilization (Fig. 2-15). Therefore with K^+, soils dominated with kaolinite clay would exhibit a lower K^+ BC than soils with dominantly mica clays (Fig. 6-10). In sandy soils, where BC is small, intense leaching or rapid plant growth can deplete available K (Fig. 6-11). Liming can increase Q:I, presumably as a result of the increase in pH-dependent CEC.

In general, the relation between exchangeable and solution K^+ is a good measure of K availability to plants. Soil-testing laboratories use extractants (e.g., NH_4OAc) to quantify both solution and exchangeable K (Chapter 9). The ability of a soil to maintain solution K against depletion by plant roots and leaching is governed partly by exchangeable K, release of fixed or nonexchangeable K, and factors influencing diffusion and transport of solution K^+ to roots.

Nonexchangeable and Mineral K

The remaining soil K is comprised of *nonexchangeable* and *mineral* K. Although nonexchangeable K reserves are not always immediately available, they contribute significantly to maintenance of exchangeable K. A portion of nonexchangeable K becomes available as exchangeable and solution K^+ are removed by cropping; however, nonexchangeable K release is generally too slow to meet crop demand during the growing season.

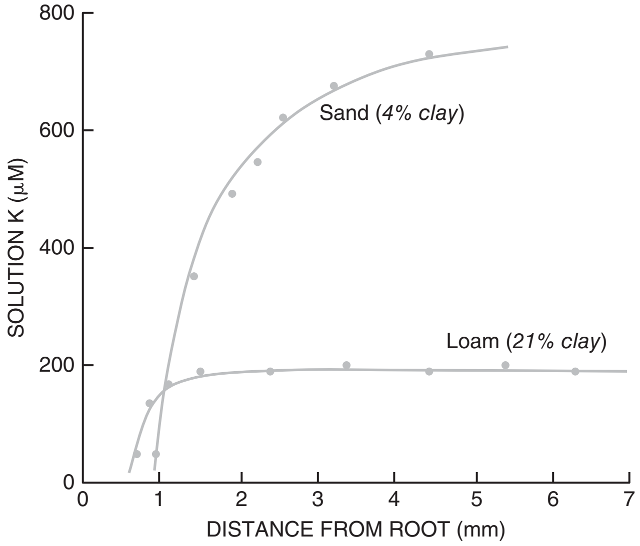


Figure 6-11
Relative effect of clay content on buffering solution K^+. Although initial solution K^+ is much greater in the sand, solution K^+ is depleted much further from the root surface, reflecting a lower BC in the sand compared to the loam soil.
(*Adapted from Claassen and Jungk, 1982,* Z. Pflansenernahr. Bodenk., *147:276.*)

K Release The rate of nonexchangeable K release to solution and exchangeable K is largely governed by weathering of K-bearing micas and feldspars.

feldspars	→	orthoclase, microcline	$KAlSi_3O_8$
micas	→	muscovite	$KAl_3Si_3O_{10}(OH)_2$
		biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$
		phlogopite	$KMg_2Al_2Si_3O_{10}(OH)_2$

Relative K availability from these minerals depends on the ease of weathering and generally is:

$$\text{biotite} > \text{muscovite} > \text{feldspars}$$

Feldspars have a three-dimensional crystal structure, with K located throughout the mineral lattice. K can be released from feldspars only by dissolution of the mineral. K feldspars are the largest natural K reserve in many soils. In moderately weathered soils, there are usually considerable quantities of K feldspars. They often occur in much smaller amounts or may even be absent in strongly weathered soils typical of humid tropical regions.

The micas are 2:1 layer silicates (Chapter 2). K^+ resides mainly between the silicate layers (Figs 6-9 and 6-12). Bonding of interlayer K is stronger in dioctahedral than in trioctahedral micas; therefore, K release generally occurs more readily with biotite than with muscovite. Gradual release of K from positions in the mica lattice results in the formation of hydrous mica and eventually vermiculite, with an increase in CEC (Fig. 6-12). K release from mica is both a cation exchange and a diffusion process, requiring time for the exchanging cation to reach the interlayer site and for the exchanged K^+ to diffuse from the interlayer region. Low solution K^+ favors interlayer K release. Thus, solution K^+ depletion by root absorption or leaching may induce nonexchangeable K release. K release can occur from all interlayer locations, or it may come only from alternate interlayers, leading to formation of interstratified mica-vermiculite.

K Fixation K fixation represents the re-entrapment of K^+ between the layers of 2:1 clays, predominately hydrous mica (Fig. 6-12). The 1:1 minerals (kaolinite) do not fix K^+. K^+ is sufficiently small to enter the interlayer space, where it is firmly held by the negative charge generated by isomorphic substitution (Chapter 2). NH_4^+ has

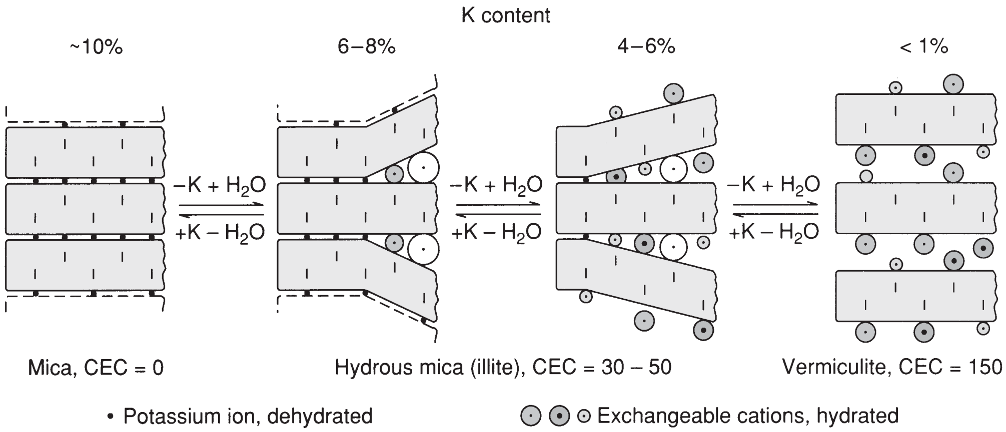


Figure 6-12
Weathering of micas to release fixed K with subsequent transformation into vermiculite clay minerals.

a similar ionic radius as K^+ and can also be fixed (Chapter 4). Cations such as Ca^{+2} and Na^+ have larger ionic radii than K^+ and do not move into the interlayer positions. Because NH_4^+ can be fixed by clays in a manner similar to K^+, its presence will alter both fixation of added K and release of fixed K. Just as the presence of K^+ can block the release of fixed NH_4^+, the presence of NH_4^+ can partially block the release of fixed K^+. NH_4^+ held in the interlayer positions further traps K^+ already present.

K fixation is generally more important in fine-textured soils. Although fixation reactions are not considered a serious factor in limiting crop response to either applied NH_4^+ or K^+, increasing K^+ concentration in soils with a high fixation capacity will obviously encourage greater fixation.

Air drying some soils high in exchangeable K can result in fixation and a decline in exchangeable K. In contrast, drying of field-moist soils low in exchangeable K, particularly subsoils, will frequently increase exchangeable K. The release of K upon drying is thought to be caused by cracking of the clay edges and exposure of interlayer K, which can then be released to exchange sites. Wetting and drying effects on K availability under field conditions are difficult to quantify. They are important, however, in soil testing. Soil test procedures call for air drying samples before analysis. Drying can alter extractable K and subsequent K recommendations. Freezing and thawing of moist soils can also release K in soils containing mica.

As with P, the conversion of K to slowly available or fixed forms reduces its availability for plant uptake. However, it must not be assumed that K fixation is completely unfavorable. K fixation results in conservation of K, which can eventually become available through K release.

FACTORS AFFECTING K AVAILABILITY

Clay Minerals and CEC

The greater the proportion of high K minerals, the greater the potential K availability. Soils containing vermiculite, montmorillonite, or mica have more K than soils containing mainly kaolinitic clays, common in highly weathered soils (Table 2-2). Intensively cropped montmorillonitic soils may be low in K and require K fertilization for optimum crop production. Fine-textured soils usually have a higher CEC and can hold more exchangeable K; however, a higher exchangeable K does not always result in higher solution K. Solution K^+ in fine-textured soils may be considerably lower than in coarse-textured soils at any given level of exchangeable K (Fig. 6-11).

Exchangeable K

Exchangeable K is highly correlated to K availability to plants. As exchangeable K increases, fertilizer K recommendations decrease (Fig. 6-13). In general, the amount of K needed to increase exchangeable K^+ by 1 ppm can vary (5–30 lb K/a), depending on the variation in K-fixation potential among soils. Fortunately, some of the fixed K may be subsequently released to crops, but the release may be too slow to meet plant K demand during a growing season.

Environment

Soil Moisture and Temperature With low soil moisture, water films around soil particles are thinner and discontinuous, resulting in a more tortuous path for K^+ diffusion to roots (Chapter 2). Increasing K levels or soil moisture content will increase K diffusion (Fig. 6-14).

Plants suffering from drought stress exhibit a larger K requirement, which is related to the important role of K in photosynthetic CO_2 fixation. Under drought stress,

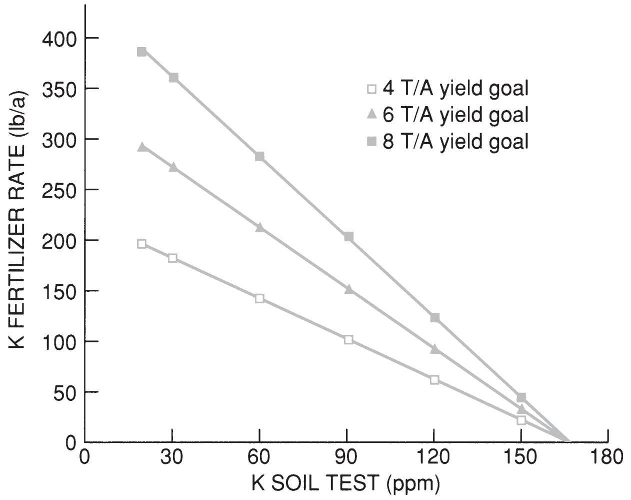


Figure 6-13
Influence of exchangeable K and alfalfa yield level on recommended K rate. Fertilizer K rate decreases with increasing soil test K and decreasing alfalfa yield goal.
(*Adapted from Gerwin and Gelderman, 2005,* South Dakota Fertilizer Rec. Guide, *SDSU, EC750.*)

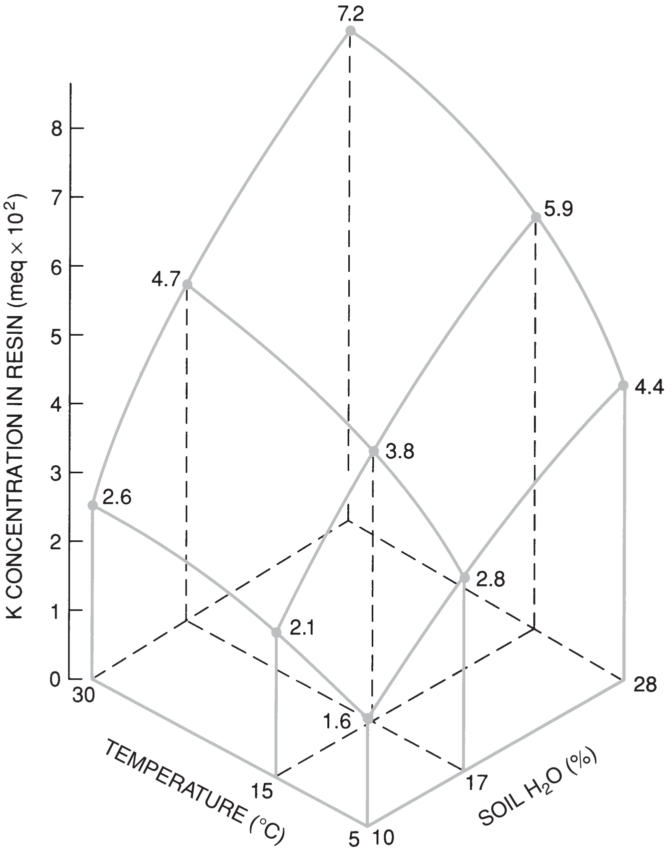
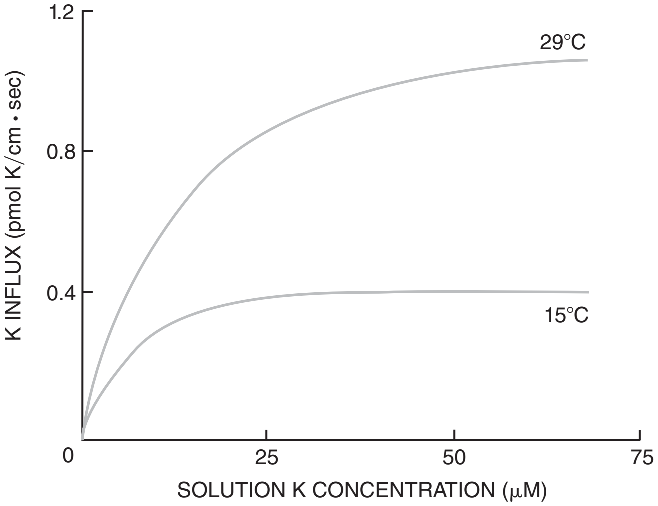


Figure 6-14
Diffusion of K in silt loam as influenced by soil temperature and moisture.
(*Adapted from Skogley, 1981, Proc. 32nd Northwest Fert.Conf., Billings, Mont.*)

stomatal closure decreases CO_2 fixation, which increases formation of reactive oxygen species [e.g., superoxide radical $(O_2\cdot^-)$, hydrogen peroxide (H_2O_2) and hydroxyl radical $(OH\cdot)$]. These compounds damage chloroplasts, reducing photosynthesis and carbohydrate metabolism. As drought severity is enhanced, increased K supply is necessary to maintain photosynthesis and protect chloroplasts from oxidative damage.

The temperature effect on K uptake is due to changes in both K diffusion (Fig. 6-14) and root growth. For example, K influx into corn roots at 15°C was $<50\%$ of that at 29°C (Fig. 6-15). In the same study, root growth was eight times greater at 29°C than at 15°C. K concentration in the shoot was 8% at 29°C and 4% at 15°C. Providing high K levels to increase K uptake at low temperatures

Figure 6-15
Rate of K influx into young corn roots is increased by higher temperature and K concentration in solution.
(*Ching and Barber, 1979,* Agron. J.,71:1040.)



overcomes some of the adverse effect of low temperature on K diffusion. Temperature effects are probably a major reason for crop responses to band-applied K with early planted crops (Fig. 6-16).

Soil Aeration Normal root function is strongly dependent on an adequate O_2 supply. Under high soil moisture or in compacted soils, root growth is restricted, O_2 supply is reduced, and K absorption is slowed. The inhibitory action of poor aeration on nutrient uptake is most pronounced with K.

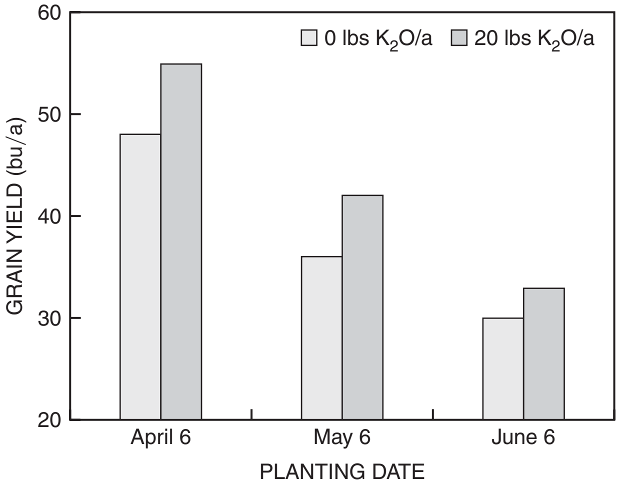
Soil pH In low pH soils, elevated levels of exchangeable Al^{+3} and Mn^{+2} create an unfavorable root environment for nutrient uptake. When acid soils are limed, the reduction in exchangeable Al^{+3} reduces competition with K^+, enabling K^+ to compete with Ca^{+2} for exchange sites. As a consequence, more K^+ can be adsorbed to CEC, reducing potential K leaching losses.

Ca^{+2} and Mg^{+2} compete with K^+ for uptake; thus, soils high in one or both may require K fertilization for optimum K nutrition. Thus, K availability is somewhat dependent on its concentration relative to Ca^{+2} and Mg^{+2}.

K Leaching

In most soils, K leaching losses are small, except in coarse-textured or organic soils in humid regions or under irrigation. In the humid tropics, K leaching is recognized as a major factor in limiting productivity. Under natural vegetation, leaching is low

Figure 6-16
Effect of planting date and band-applied K at planting on barley grain yield.
(*Dubbs, 1981,* Better Crops Plant Food, 65:27.)



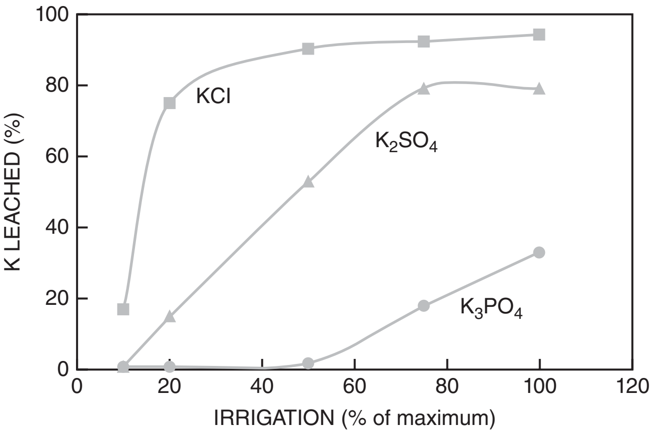
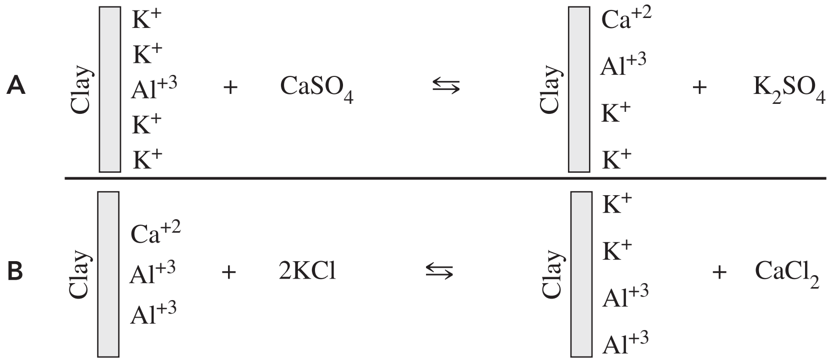


Figure 6-17
Influence of K source on K leaching losses in turfgrass.
(Sartain, 1988, Soil Sci. Fert. Sheet, *SL52, Univ. Florida, Gainesville, Fla.*)

(0–5 lb/a/yr); however, on cleared land after fertilizer application, 30–40% of applied K may be leached with cropping, and much higher losses occur on bare land. In these soils, small annual or split applications should be used rather than higher annual K rates to build up soil K.

K source can influence the amount of K leached (Fig. 6-17). Compared with Cl^-, the SO_4^{-2} and PO_4^{-3} sources exhibit greater anion adsorption to $(+)$ exchange sites. Thus, with fewer anions in solution available for leaching, less K^+ would leach. Recall that solutions must be electrically neutral $[(-)$ charges $= (+)$ charges$]$; therefore, for every $(-)$ charge leached, one $(+)$ charge must also be leached.

Specific cations adsorbed to the CEC also influence K leaching. Consider the following:



In A, the CEC is nearly saturated with K^+ (usually not the case). By adding a neutral salt (e.g., $CaSO_4$), some adsorbed K^+ will be replaced by Ca^{+2}. The amount of replacement will depend on the type and amount of salt added and the quantity of adsorbed K^+. On some soils planted to perennial crops, $CaSO_4$ is applied to encourage K^+ desorption and transport into the subsoil to increase K availability deeper in the profile.

In B, KCl is added to a soil saturated with Ca^{+2} and Al^{+3}. Because Ca^{+2} is easier to displace than Al^{+3}, the added K^+ replaces some of the Ca^{+2}. This reaction illustrates an important point: The greater the degree of Ca^{+2} saturation, the greater the K^+ adsorption. This is consistent with the previous example, where Ca^{+2} from $CaSO_4$ replaces K^+, but less readily replaces Al^{+3} (*lyotropic series* in Chapter 2). In such cases, there will be a net transfer of K^+ to the soil solution. Sandy soils with a high %BS retain more exchangeable K^+ than soils with a low %BS (high exchangeable Al^{+3}), because the added K^+ will exchange with Ca^{+2} easier than in an acid soil with low %BS. Liming increases %BS, thus decreasing exchangeable K^+ loss.

SOURCES OF K

Inorganic K Fertilizers

Deposits of soluble K salts are found well beneath the earth's surface. Many of these deposits have high purity and lend themselves to mining of K salts or potash. The world's largest high grade potash deposit is in Canada, extending 450 miles long by 150 miles wide, with a depth of 3,000–7,000 ft.

Like P, fertilizer K content is presently guaranteed as K oxide (K_2O) equivalent (Table 6-2). Converting between %K and %K_2O is accomplished by:

$$\%K = \%K_2O \times 0.83$$
$$\%K_2O = \%K \times 1.2$$

Potassium Chloride (KCl) Fertilizer-grade KCl contains 50–52% K (60–63% K_2O) and varies in color from pink or red to brown or white, depending on the mining and recovery process. KCl is the most common K fertilizer used for direct application and for manufacture of N-P-K fertilizers (Fig. 6-18). When added to soil, it readily dissolves in water.

Potassium Sulfate (K_2SO_4) K_2SO_4 is a white solid containing 42–44% K (50–53% K_2O) and 17% S. Its global consumption has been increasing and now represents about 7% of total K use. K_2SO_4 is produced in several different ways, including reacting KCl with SO_4-containing salts or H_2SO_4 and recovery from natural brines. It is commonly used on Cl^- sensitive crops such as potatoes and tobacco and for tree fruits and vegetables. Its behavior is similar to KCl in soil but has the advantages of supplying S and having a lower salt index.

TABLE 6-2
PLANT NUTRIENT CONTENT OF COMMON K FERTILIZERS

Source	N	P_2O_5	K_2O	S	Mg
			%		
		Inorganic			
Potassium chloride	—	—	60–62	—	—
Potassium sulfate	—	—	50–52	17	—
Potassium magnesium sulfate	—	—	22	23	11
Potassium nitrate	13	—	44	—	—
Potassium hydroxide	—	—	83	—	—
Potassium carbonate	—	—	68	—	—
Potassium orthophosphates	—	30–60	30–50	—	—
Potassium polyphosphates	—	40–60	22–48	—	—
Potassium thiosulfate	—	—	25	17	—
Potassium polysulfide	—	—	22	23	—
Greensand	—	1	6	—	—
		Organic			
Cottonseed hull ash	1	—	27	—	—
Manure[1]—cattle	1.5	1.5	1.2		0.1
—poultry	1.5–3	1–3	0.5–2	0.2	0.4
—swine	0.5–1.2	0.3-0.7	0.2–0.3	—	—
Wood ashes	—	2	6	—	1
Yard compost	1–2	0.1–0.3	0.5–0.7	0.3–0.5	0.4–0.6

[1] Highly variable nutrient content and waste analysis recommended before application.

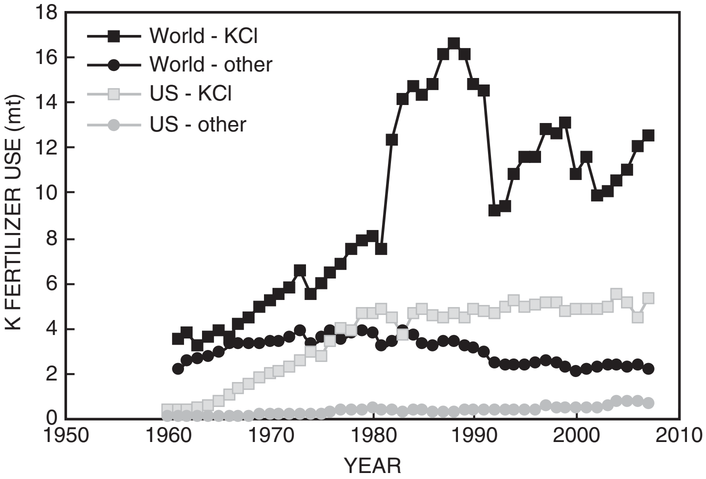


Figure 6-18
World and U.S. consumption of K fertilizers (tonnes × 10^6).
(USDA ERS, 2009; FAO, 2009.)

Potassium Magnesium Sulfate (K_2SO_4, $MgSO_4$) Potassium magnesium sulfate is a double salt containing 18% K (22% K_2O), 11% Mg, and 22% S. It has the advantage of supplying both Mg and S and is frequently included in mixed fertilizers for soils deficient in Mg and S. It reacts as would any other neutral salt when applied to the soil.

Potassium Nitrate (KNO_3) KNO_3 contains 13% N and 37% K (44% K_2O). Agronomically, it is an excellent source of fertilizer N and K. KNO_3 is marketed largely for use on fruit trees and on crops such as cotton and vegetables. If production costs can be lowered, it might compete with other sources of N and K for use on crops of a lower value.

Potassium Phosphates ($K_4P_2O_7$, KH_2PO_4, K_2HPO_4) Several K phosphates have been produced and marketed on a limited basis. Their advantages are (1) high analysis, (2) low salt index, (3) useful for preparation of clear fluid fertilizers high in K_2O, (4) polyphosphate as a P source, and (5) well suited for use on potatoes and other crops sensitive to excessive amounts of Cl^-.

Potassium Carbonate (K_2CO_3), Potassium Bicarbonate ($KHCO_3$), Potassium Hydroxide (KOH) These salts are used primarily for the production of high-purity fertilizers for foliar application or other specialty uses. The high cost of manufacture has precluded their widespread use as commercial fertilizers.

Potassium Thiosulfate ($K_2S_2O_3$) and Potassium Polysulfide (KS_x) Analysis of these liquid fertilizers, $K_2S_2O_3$ and KS_x, is 0-0-25-17 and 0-0-22-23, respectively. $K_2S_2O_3$ is compatible with most liquid fertilizers and is well suited for foliar application and drip irrigation.

Organic K

K in organic wastes (manures and sewage sludge) occurs predominately as soluble inorganic K^+. In animal waste, K content ranges between 0.22% (4–40 lb K/t) of dry matter (Table 6-2). The average K content in biosolids is ~10 lb K/t. Therefore, waste materials can supply sufficient quantities of plant available K, depending on the rate applied. Most waste application rates are governed by the quantity of N or P applied to minimize impacts of land application of waste on surface and groundwater quality. If low waste rates are utilized on K-deficient soils, additional K may be needed.

STUDY QUESTIONS

1. What processes transport K to the plant root surface?
2. Why do K deficiency symptoms commonly appear on old growth first?
3. What factors control the amount of K present in the soil solution?
4. How does exchangeable K buffer solution K?
5. Under what soil conditions is there most likely to be reversion of available or added K to less-available forms?
6. Describe the effect liming an acid soil has on K leaching or retention?
7. Why does the addition of gypsum to an acid soil not result in an increased conservation of K?
8. Describe K fixation in soil. How does fixed K become available to plants?
9. Is K released more readily from feldspar than from the K-bearing micas? Do members of the mica group have similar abilities to supply K? In which soil particle size fractions are feldspar and micas usually found?
10. Describe the changes that occur when mica minerals weather in soils. Why could exchangeable K increase with transformation of mica to montmorillonite or vermiculite?
11. Why might continuous cropping at high yield levels deplete available K over time and increase the probability of a response to K?
12. Under what soil conditions might you prefer to use K_2SO_4-$MgSO_4$ rather than KCl and dolomite or KCl alone? Are there situations where KCl will be more effective than K_2SO_4 or KNO_3?
13. For a soil with CEC = 10 meq/100 g soil and 10% K saturation, calculate the initial and final exchangeable K after one crop. Assume that the alfalfa crop yields 5 t/a/yr at 5% K content.
14. Two soils have CEC = 5 meq/100 g and 25 meg/100 g. Both have 5% exchangeable K. Calculate exchangeable K content for both soils (lb/a). Using the crop data in Question 13, how many years can each soil be cropped before all the exchangeable K is removed? Assume that 1% of the CEC is resupplied by nonexchangeable K release each year after the first year.
15. A soil with CEC = 10 meq/100 g has 10% exchangeable K. Determine the exchangeable K content in lb/a.
16. Why K is essential for photosynthesis? Explain its energy-related functions.
17. Explain the role of K in enzymatic activation.
18. What are the three types of exchanging sites of K^+ ions? Explain their influence on buffering.
19. What is Q : I ratio? What is its significance?
20. What are the important sources of K?

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7

Sulfur, Calcium, and Magnesium

Sulfur (S), calcium (Ca), and magnesium (Mg) are macronutrients required in relatively large amounts by most plants. S and Mg are needed by plants in about the same quantities as P, whereas for many plant species, the Ca requirement is greater than that for P. S reactions in soil are very similar to N reactions, which are dominated by soil organic or microbial transformations (Chapter 4). In contrast, Ca^{+2} and Mg^{+2} are associated with the soil mineral fractions and behave similarly to K^+ (Chapter 6).

SULFUR

The S Cycle

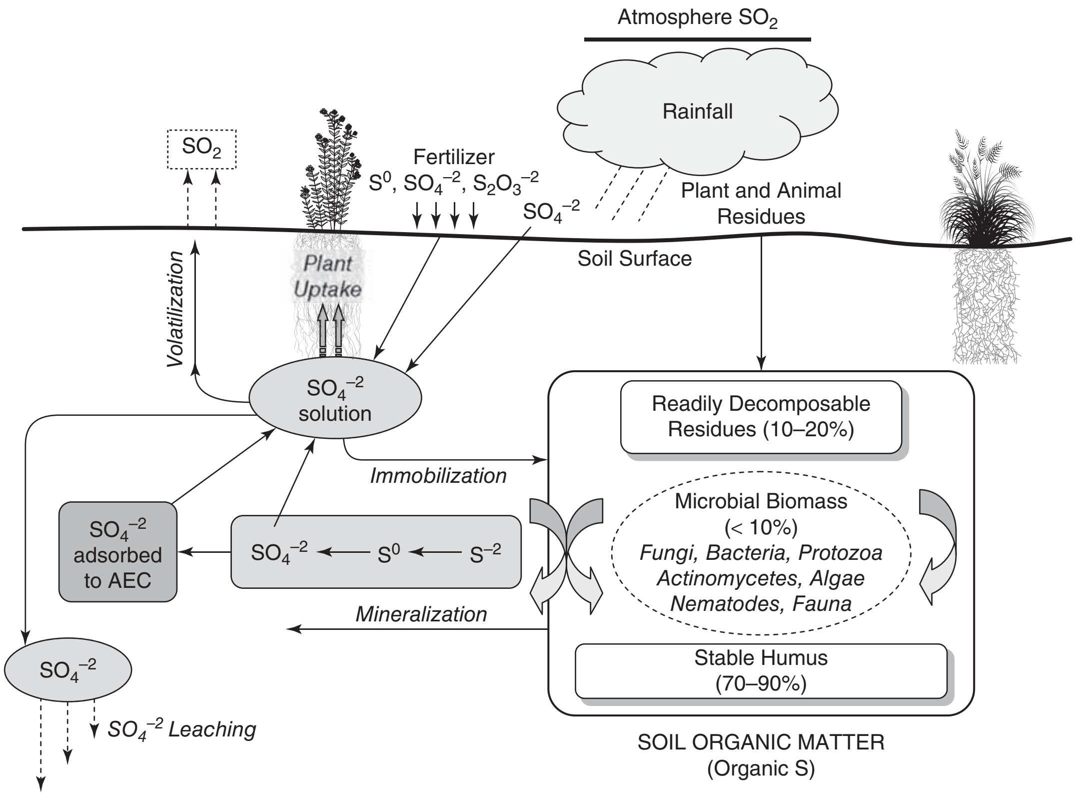
S in the earth's crust averages ≈0.05%, comparable to P. The original source of soil S is metal sulfide minerals that oxidize during weathering from S^{-2} to SO_4^{-2}. The SO_4^{-2} is precipitated as soluble and insoluble SO_4^{-2} salts in arid or semi-arid climates, utilized by living organisms, reduced by microorganisms to S^{-2} or S^0 under anaerobic conditions, and/or transported through runoff to the sea. Oceans contain ~2,700 ppm SO_4^{-2}, whereas natural waters range from 0.5 to 50 ppm SO_4^{-2} but may reach 60,000 ppm (6%) in saline lakes and sediments.

Soil S is present in organic and inorganic forms, although ≈90% of total S in noncalcareous surface soils exists as organic S. Solution and adsorbed SO_4^{-2} represents readily plant available S. S cycling in the soil-plant-atmosphere system is similar to N in that both have gaseous components and their occurrence in soils is mainly associated with OM (Fig. 7-1).

Forms and Functions of S in Plants

Forms S is absorbed by plant roots almost exclusively as sulfate (SO_4^{-2}; Fig. 7-1). Small quantities of SO_2 can be absorbed through plant leaves and utilized within plants, but high concentrations are toxic. Thiosulfate ($S_2O_3^{-2}$) can also be absorbed by roots. When plants absorb thiosulfate ($S_2O_3^{-2}$), less energy may be required by the plant in conversion to S^{-2} and cysteine (Fig. 7-2). SO_4^{-2} uptake is not inhibited by other anions (NO_3^- or $H_2PO_4^-$), but is inhibited by chromate and selenate (Chapter 8).

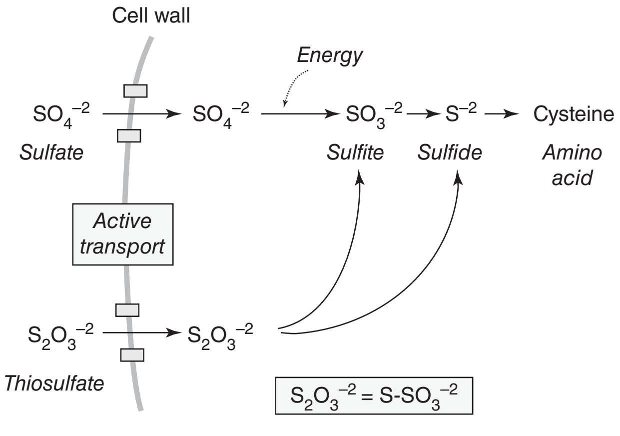
Figure 7-1
S cycling is soil.



Typical S concentrations in plants range from 0.2 to 0.5%. S content increases in the order *Gramineae* < *Leguminosae* < *Cruciferae*, where typical S content of their seeds ranges: 0.17–0.19%, 0.25–0.30%, and 1.0–1.7%, respectively. Most SO_4^{-2} is reduced in the plant to —S—S and —SH forms, although SO_4^{-2} occurs in plant tissues and cell sap. Selected volatile S compounds in the mustard and onion families are responsible for their characteristic taste and smell.

Functions S is required for synthesis of S-containing amino acids (cystine, cysteine, and methionine), which are essential components of plant protein that comprise about 90% of S in plants. Cysteine and methionine content increases with increasing S content in leaves (Fig. 7-3). S-deficient plants accumulate nonprotein N as $-NH_2$ and NO_3^-, while increasing S nutrition decreases plant N:S ratio to the optimum N:S ratio of 9:1–12:1 needed for effective N use by rumen microorganisms (Table 7-1). With S deficiency in vegetables, NO_3^- accumulates in leaves, reducing food quality

Figure 7-2
Proposed model of absorption of thiosulfate that may require less energy to convert to amino acids than absorption of sulfate.



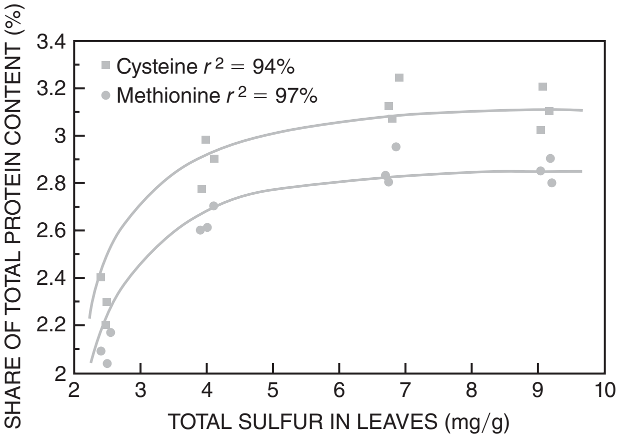


Figure 7-3
Relationship between S status of Kale and concentration of cysteine and methionine in leaf protein.
(Schung,1990, Sulphur in Agric., Washington, D.C.: The SulphurInstitute, 14:2–7.)

TABLE 7-1
EFFECT OF S FERTILIZATION ON YIELD AND QUALITY OF ORCHARD GRASS

S Rate[1]	Yield	Non-protein N	NO_3-N	N:S Ratio
lb/a	*t/a*	%		
0	2.3	1.14	0.14	21.4
20	2.5	0.75	0.11	17.0
40	2.8	0.54	0.10	14.6
80	2.9	0.48	0.09	12.8
100	2.8	0.43	0.07	10.4

[1] S applied with 100 lb N/a.

Source: Baker et al., 1973, *Sulphur Inst. J.*, 9:15.

(Fig. 7-4). In this example, NO_3^- accumulated in lettuce only when plants exhibited visual S-deficiency symptoms.

One of the main functions of S is the formation of disulfide (—S—S—) bonds between polypeptide chains within a protein causing the protein to fold. Disulfide linkages are important in the catalytic or structural properties of proteins. For example, S is needed for synthesis of coenzyme A, which is involved in oxidation and synthesis of fatty acids, synthesis of amino acids, and oxidation of intermediates of the citric acid cycle.

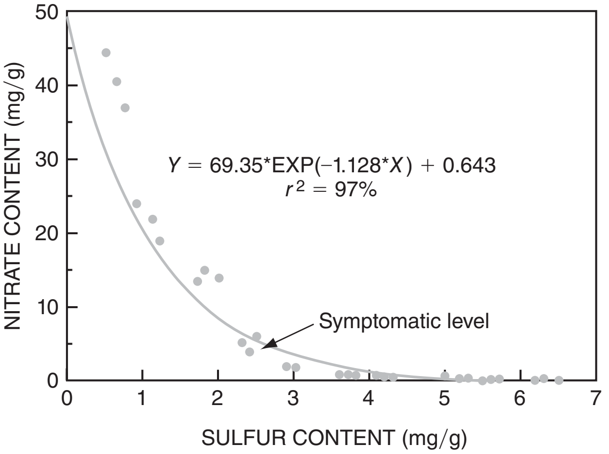


Figure 7-4
Influence of S nutrition on NO_3 concentration in lettuce leaves. S-deficiency symptoms occurred at <2.5 mg S/g leaf (0.25% S).
(Schung, 1990, Sulphur in Agric., Washington, D.C.: The Sulphur Institute,14:2–7.)

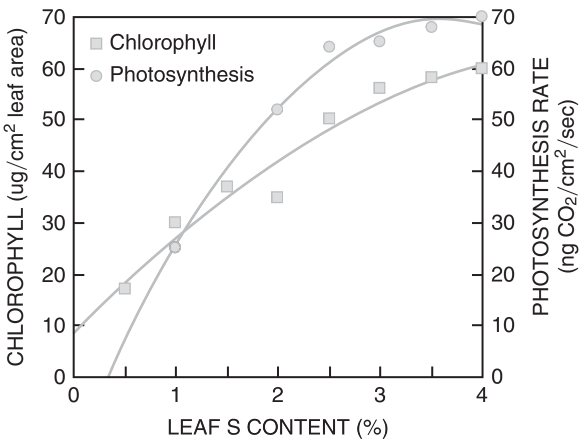


Figure 7-5
Influence of S nutrition on leaf chlorophyll content and photosynthesis rate in sugar beet. Optimum S content is ~2.5% S.
(*Adapted from Terry, 1975,* Plant Physiol., *57:477–479.*)

Although not a constituent, S is required for the synthesis of chlorophyll (Fig. 7-5). S is a vital part of ferredoxin, an Fe-S protein in the chloroplasts, and has a significant role in NO_2^- and SO_4^{-2} reduction, and N assimilation by N_2-fixing soil bacteria.

Visual S-Deficiency Symptoms

S deficiency is characterized by reduced plant growth rate, where plants are stunted, thin-stemmed, and chlorotic (see color plates). Unlike N, however, S is generally less mobile in plants; therefore, deficiency symptoms often occur first in younger leaves. Depending on N status in many plants S is distributed evenly throughout the plant and symptoms may develop in either older (low N) or younger (adequate N) leaves. Initial S deficiency appears as light green leaves, ultimately turning yellow. In many plants, S- and N-deficiency symptoms can be difficult to distinguish. S-deficient cruciferous crops (i.e., cabbage, broccoli, canola/rapeseed) initially develop a reddish color on the undersides of the leaves, where leaves are also cupped inward. As the deficiency progresses, reddening of both upper and lower leaf surfaces occur. Paler-than-normal blossoms and severely impaired seed set also characterize S-deficiency symptoms in rapeseed.

Forms of S in Soil

Solution SO_4^{-2} SO_4^{-2} is transported to roots by mass flow and diffusion. In soils containing $\geq$5 ppm SO_4^{-2}, total S requirement of most crops can be supplied by mass flow. Solution concentrations of 3–5 ppm SO_4^{-2} is sufficient for most crops, although some high S crops (rapeseed/canola, alfalfa, broccoli, etc.) require higher solution S. Sandy, low OM soils often contain <5 ppm SO_4^{-2}. Except for soils in dry areas that may have accumulations of SO_4^{-2} salts, most soils contain <10% of total S as SO_4^{-2}. Large seasonal and year-to-year fluctuations in SO_4^{-2} can occur due to the influence of environmental conditions on organic S mineralization, downward or upward movement of SO_4^{-2} in soil water, and SO_4^{-2} uptake by plants. SO_4^{-2} content of soils is also affected by the application of S-containing fertilizers and wastes, and by SO_4^{-2} deposition in precipitation and irrigation.

Like NO_3^-, SO_4^{-2} can be readily leached through the soil profile. Increasing the quantity of percolation water increases potential SO_4^{-2} leaching. Leaching losses are lower in acid soils with appreciable exchangeable Al^{+3} and AEC to adsorb SO_4^{-2}.

Adsorbed SO_4^{-2} Adsorbed SO_4^{-2} is an important fraction in highly weathered, humid region soils containing large amounts of Al/Fe oxides. Many ultisol (red-yellow podzol) and oxisol (latosol) soils contain up to 100 ppm adsorbed SO_4^{-2} in subsoil and can significantly contribute to S nutrition of plants as root growth progresses. Mechanisms of SO_4^{-2} adsorption include:

- (−) charges on Fe/Al oxides or on clay edges, especially kaolinite, at low pH (Chapter 2)
- adsorption to $Al(OH)_x$ complexes (Chapter 3)
- (−) charges on soil OM at low pH

Reserves of adsorbed SO_4^{-2} in acid subsoil result from SO_4^{-2} leaching from surface soil, accounting for ≈30% total subsoil S compared to ≈10% in surface soil. Although crops utilize subsoil-adsorbed SO_4^{-2}, S deficiency can occur during early growth stages until root development is sufficient to explore the subsoil. Once established, deep-rooted crops (e.g., alfalfa, clover, lespedeza) readily access plant available S in the subsoil.

Factors Affecting SO_4^{-2} Adsorption/Desorption

- *Clay mineral*: SO_4^{-2} adsorption increases with clay content. In general, SO_4^{-2} adsorption in kaolinite is greater than mica, which is greater than montmorillonite. Under low pH and high Al^{+3} saturation, SO_4^{-2} adsorption with kaolinite is ~ equal to mica, which is much greater than montmorillonite.
- *Hydrous oxides*: Fe/Al oxides are responsible for most SO_4^{-2} adsorption in soils.
- *Soil OM*: Increasing soil OM content increases SO_4^{-2} adsorption potential.
- *Soil depth*: SO_4^{-2} adsorption capacity is often greater in subsoils due to higher clay and Fe/Al oxide content.
- *Soil pH*: SO_4^{-2} adsorption potential decreases with increasing pH (<AEC), and is negligible at pH>6.0.
- *Solution* SO_4^{-2}: Adsorbed SO_4^{-2} is in equilibrium with solution SO_4^{-2}; thus increasing solution SO_4^{-2} will increase adsorbed SO_4^{-2}.
- *Competing anion*: SO_4^{-2} is considered to be weakly held, with adsorption strength decreasing in the order $OH^- > H_2PO_4^- > SO_4^{-2} > NO_3^- > Cl^-$. For example, $H_2PO_4^-$ will displace SO_4^{-2}, but SO_4^{-2} has little effect on $H_2PO_4^-$. Cl^- has little effect on SO_4^{-2} adsorption.

Of these factors, the amount and type of clay, pH, soil OM, and presence of other anions exert the greatest influence on SO_4^{-2} adsorption.

SO_4^{-2} Reaction with $CaCO_3$

S occurs as a coprecipitate ($CaCO_3$-$CaSO_4$) impurity in calcareous soils. Availability of SO_4^{-2} coprecipitated with $CaCO_3$ increases with decreasing pH ($CaCO_3$ more soluble), decreasing $CaCO_3$ particle size (more surface area), and increasing soil moisture content. Grinding calcareous soil samples will render SO_4^{-2} accessible to chemical extraction. Consequently, more S will be extracted by a particular soil test procedure than is plant available under field conditions.

Reduced Inorganic S (S^{-2} and S^0) Sulfides do not exist in well-aerated soils. Under waterlogged, anaerobic conditions, H_2S accumulates as OM decays or from added SO_4^{-2}. S^{-2} accumulation is limited primarily to coastal regions dominated by saturated, submerged soils. Characteristic "rotten egg" scent of H_2S is readily detected. Similar reactions also occur under paddy rice culture (Fig. 7-6).

In normal submerged soils well supplied with Fe, H_2S liberated from OM is almost completely removed from solution by reaction with Fe^{+2} to form FeS, which undergoes conversion to pyrite (FeS_2). The dark color observed on the shores of the Black Sea is caused by the accumulation of FeS_2. If H_2S is not subsequently precipitated by Fe and other metals, it escapes to the atmosphere.

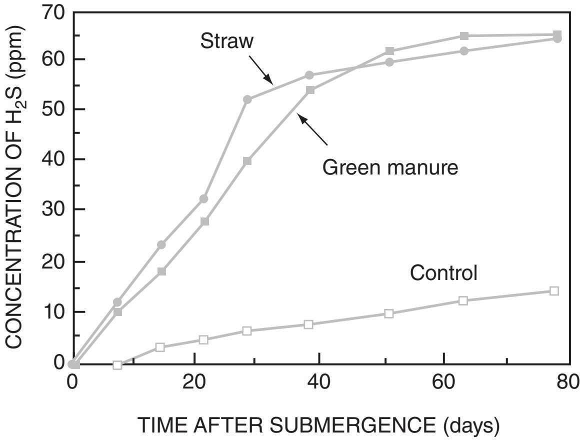


Figure 7-6
Effect of OM on H_2S emission in a saturated paddy rice soil.
(*Adapted from Mandal, 1961,* Soil Sci., *91:121.*)

In some tidal marshlands, large quantities of reduced S compounds accumulate. When these areas are drained, oxidization of S compounds to SO_4^{-2} will reduce pH to <3.5 by:

$$FeS_2 + H_2O + 3\tfrac{1}{2}\,O_2 \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+$$

S^0, S^{-2}, and other reduced S compounds can be chemically oxidized in soil, but these are generally slow reactions. In contrast, microbial oxidation of S^0 is enhanced in well-aerated soils. The rate of microbial S^0 oxidation depends on available S^0 source and soil environmental conditions favorable to aerobic microbial activity.

Factors Affecting S^0 Oxidation

- *Soil microbes*: Heterotrophic fungi and bacteria capable of oxidizing S^0 represent 3–35% of total heterotrophic population in soils. S^0 oxidation is greater in the rhizosphere, where there are large, diverse populations of S^0-oxidizing heterotrophs. The most important group of S-oxidizing bacteria (*Thiobacillus* sp.) are the most active S-oxidizers while other microorganisms including fungi (e.g., *Fusaarium* sp.) and actinomycetes (e.g., *Streptomyces* sp.) are also important. *Thiobacillus* are autotrophic bacteria that obtain their energy from S^0 oxidation and C from CO_2. Photolithotrophic S bacteria oxidize S^{-2} but use light for energy. Addition of S^0 to soil encourages growth of S^0-oxidizing microorganisms. The reaction mediated by *Thiobacilli* is:

$$CO_2 + S^0 + 2\tfrac{1}{2}O_2 + 2H_2O \rightarrow CH_2O + 2SO_4^{-2} + 2H^+$$

- *Soil temperature*: Increasing soil temperature increases S^0 oxidation rate (Fig. 7-7). Optimum temperature is between 25 and 40°C. Microbial activity decreases at temperatures >60°C.
- *Soil moisture and aeration*: S^0-oxidizing bacteria are mostly aerobic, and their activity will decline if O_2 is lacking due to waterlogging. S^0 oxidation is favored by soil moisture levels near field capacity (Fig. 7-8). Also evident is the decline in oxidization when soils are excessively either wet or dry.
- *Soil pH*: Microbial S^0 oxidation occurs over a wide soil pH range.

Organic S There is a close relationship between organic C, total N, and total S in soils. The C:N:S ratio in most well-drained, noncalcareous soils is about 120:10:1.4. Differences in C:N:S between soils are related to variations in soil-forming factors (parent material, climate, vegetation, and topography). The N:S ratio in most soils falls within the narrow range of 6 to 8:1. The organic S fraction governs the production of plant available SO_4^{-2} (Fig. 7-1). Three groups of organic S compounds in soil include *HI-reducible S*, *C-bonded S*, and *residual S*.

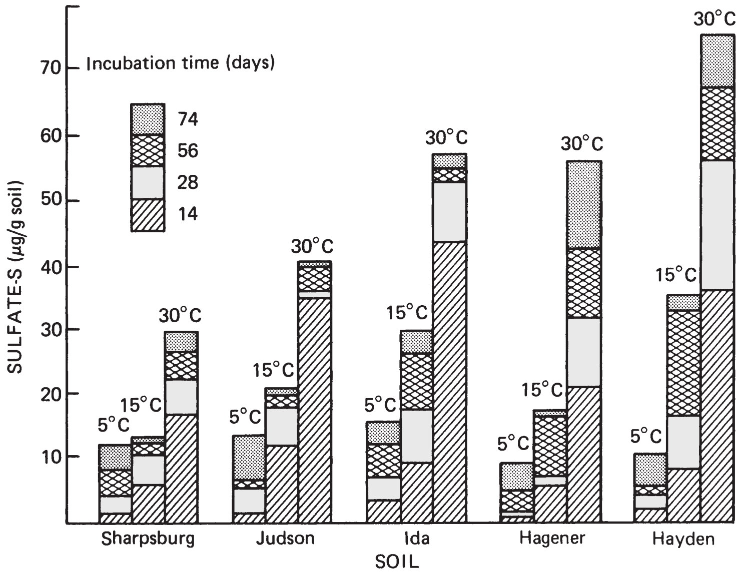


Figure 7-7
Effects of temperature and incubation time on oxidation of S^0 in soils.
(*Nor and Tabatabai, 1979,* Soil Sci. Soc. Am. J., *41:739.*)

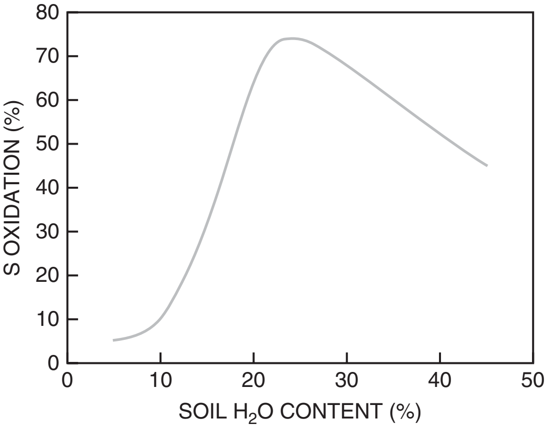


Figure 7-8
Percentage of added S^0 oxidized at various moisture contents with time.
(*Adapted from Kittams and Attoe, 1965,* Agron. J., *57:331.*)

- *HI-reducible S* is soil organic S that is reduced to H_2S by hydriodic acid (HI). The S occurs in ester and ether compounds that have C O S linkages (e.g., arylsulfates, alkylsulfates, phenolic sulfates, sulfated polysaccharides, and sulfated lipids). HI-reducible S represents 40–60% of total organic S.
- *Carbon-bonded S* occurs as S-containing amino acids (cystine and methionine), accounting for ~10–20% of total organic S.
- *Residual S* represents the remaining organic S fraction and generally represents 30–40% of total organic S.

S Mineralization and Immobilization

S mineralization is the conversion of organic S to inorganic SO_4^{-2} and immobilization is the reverse reaction, similar to N mineralization (Chapter 4).

$$\text{amino acid} + 2H_2O \xrightarrow[\text{heterotrophs}]{O_2} S^{-2} + CO_2 + NH_4^{+}$$

$$S^{-2} \rightarrow S^{O} + 1\tfrac{1}{2}O_2 + H_2O \leftrightarrows SO_4^{-2} + 2H^{+}$$

Any factor that affects microbial activity influences S mineralization and immobilization. When plant and animal residues are returned to soil, they are digested by microorganisms, converting some organic S to SO_4^{-2}; however, most S remains as organic S and eventually becomes part of soil humus (Fig. 7-1). S supply to plants depends largely on SO_4^{-2} released from OM and from plant and animal residues. ~2–15 lb/a of S as SO_4^{-2} is mineralized each year from the organic fraction. In calcareous soils, the source of plant available SO_4^{-2} is from dissolution of gypsum ($CaSO_4 \cdot H_2O$).

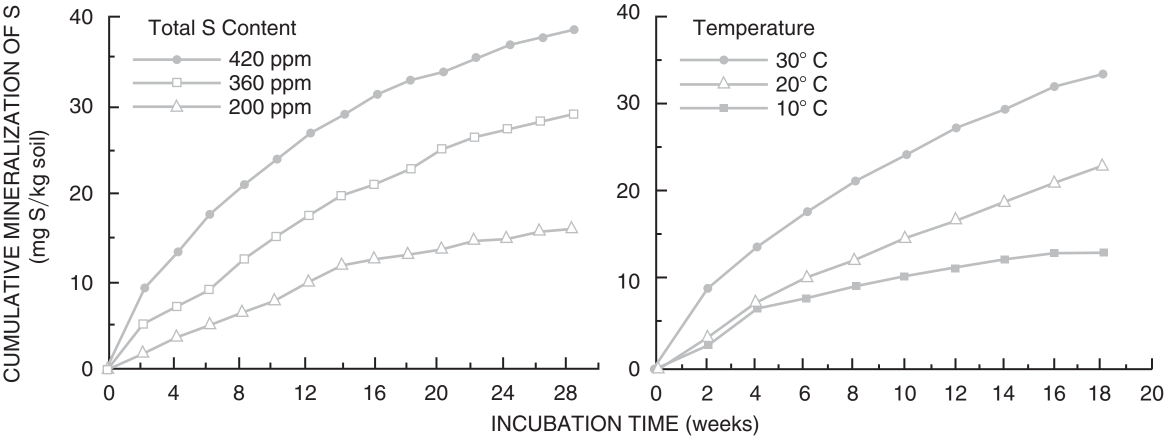
Factors Affecting S Mineralization and Immobilization.

1. *S content of OM.* Like N, S mineralization or immobilization depends on S content of the decomposing material:

C:S ratio in crop residue	Dominant process
<200:1	mineralization
200–400	no change
>400:1	immobilization

Smaller amounts of SO_4^{-2} are liberated from low-S-containing residue. Fresh organic residues commonly have C:S ratios of about 50:1. Where large amounts of straw, stover, or other OM are added to soil, adequate N and S availability is necessary to promote rapid decomposition of the straw. Otherwise, a temporary N or S deficiency may be induced in the subsequent crop. Increasing total soil S content or OM also increases S mineralization (Fig. 7-9).

2. *Soil temperature.* S mineralization is impeded below 10°C, increases with temperatures from 20 to 40°C, and decreases at >40°C (Fig. 7-9). In samples representing 12 major soil series, more S was released during incubation at 35°C than at 20°C (Fig. 7-10). An average Q_{10} of 1.9 occurred in these soils. The temperature effect on S mineralization is consistent with the relatively greater S content of soils in northern climates.
3. *Soil moisture.* S mineralization in soils incubated at low (<15%) and high (>40%) moisture content is reduced compared with the optimum moisture content of 60% water-filled pore space (Fig. 4-21). Gradual moisture changes between field capacity and wilting point have little influence on S mineralization. However, drastic changes in soil moisture can produce a flush of S mineralization in some soils. Increased S availability due to soil wetting and drying may explain increased plant growth after dry periods in S-deficient soils.
4. *Soil pH.* Although in some soils mineralization decreases with increasing soil pH (Fig. 7-10), generally S mineralization is directly proportional to pH up to 7.5. Near-neutral soil pH is normally expected to encourage microbial activity and N, P, and S mineralization.



(a) (b)

Figure 7-9

Increasing total S content (a) or increasing soil temperature (b) increases S mineralization.

(*Ghani, 1994,* Sulphur in Agric., *Washington, D.C.: The Sulphur Institute, 18:13-18.*)

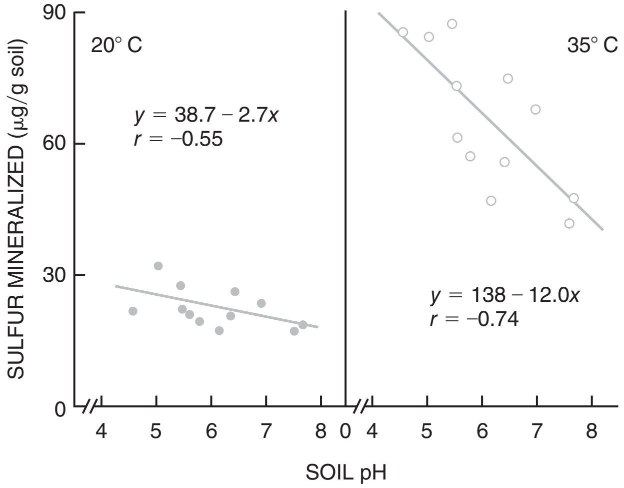


Figure 7-10
Relationship between total S mineralized and pH of soils incubated at 20 or 35°C.
(*Tabatabai and Al-Khafaji, 1980,* Soil Sci. Soc. Am. J., *44:1000.*)

5. *Time and cultivation.* As with N, when soil is first cultivated, its S content declines rapidly. With time, an equilibrium is reached that is characteristic of the climate, cultural practices, and soil type. Before reaching this point, S mineralization gradually diminishes and becomes inadequate to meet plant needs. The C:N:S ratio of virgin soils is larger than those of corresponding cultivated surface soils. Reduction of this ratio with cultivation suggests that S is relatively more resistant to mineralization than C and N or that losses of organic C and N are proportionately greater than S.
6. *Sulfatase activity.* As much as 50% of total S in surface soils may be present as organic S esters. Sulfatase enzymes hydrolyze S esters to release SO_4^{-2} by:

$$\text{R-O-SO}_3^- + H_2O \xrightarrow{\text{sulfatase}} \text{R-OH} + HSO_4^-$$

Ester sulfates are natural substrates for sulfatase enzymes in soil.

S Volatilization

Volatile S compounds are produced through microbial transformations under both aerobic and anaerobic conditions. Where volatilization occurs, the volatile S compounds are dimethyl sulfide (CH_3SCH_3), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), and dimethyl disulfide (CH_3SSCH_3). CH_3SCH_3 accounts for 55–100% of S volatilized. In low OM soils, S volatilization is negligible and generally increases with increasing OM content. The amount of S volatilized represents $<0.05\%$ of total S present in soil and is relatively insignificant under field conditions.

Like NH_3, volatile S (SO_2 and H_2S) evolves from plant leaves. Losses are generally small (0.3–6.0% total plant S), with higher levels observed under high SO_4^{-2} nutrition. Volatile S released by plants may affect the palatability of forage plants to grazing animals. S losses from forages when they are dried in haymaking or pelleting might also influence quality and palatability.

Practical Aspects of S Transformations

Crops grown on coarse-textured soils are generally more susceptible to S deficiency because these soils often have low ($<1.2-1.5\%$) OM contents. S availability generally increases with increasing OM content. Added S can be immobilized in some soils, particularly those that have a high C:S or N:S ratio. In contrast, S mineralization is favored in soils with a low C:S or N:S ratio.

Leaching losses of SO_4^{-2} can be especially high on coarse-textured soils under conditions of high rainfall or irrigation. Under such conditions, SO_4^{-2}-containing fertilizers may have to be applied more frequently than on fine-textured soils or under lower rainfall conditions. In more humid regions, a fertilizer containing both SO_4^{-2} and S^0 may be required to extend the period of S availability to crops.

S Sources

Atmospheric S SO_2 released into the air, oxidizes to SO_4^{-2}, and is deposited in soil through precipitation.

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \leftrightarrows SO_4^{-2} + 2H^+$$

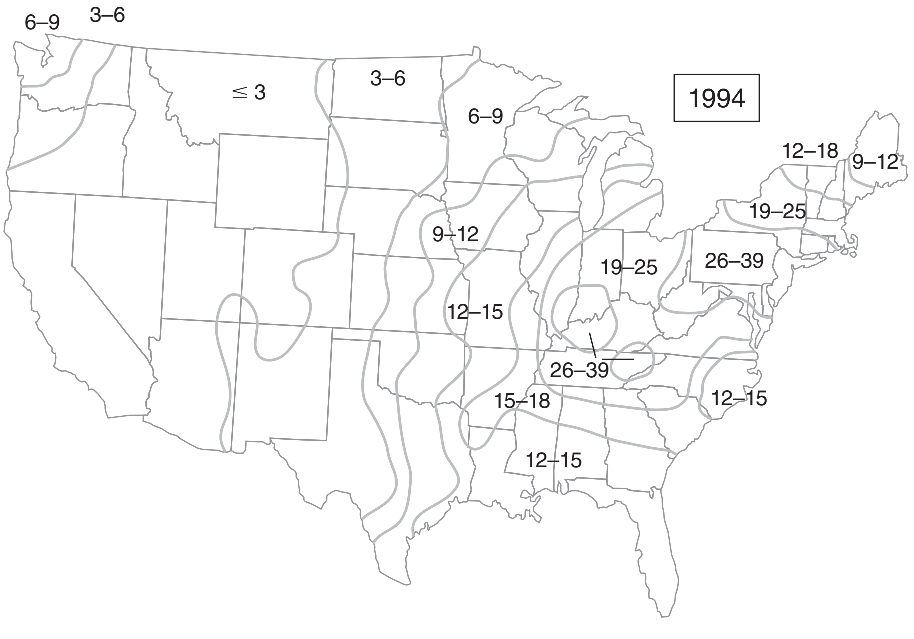
Nearly 70% of the S compounds in the atmosphere are due to natural processes. In localized areas, SO_4^{-2} content of soils can be increased by direct adsorption of SO_2 and the fallout of dry particulates. In addition, plants absorb SO_2 by diffusion into the leaves. However, exposure to ≈ 0.5 ppm SO_2 can cause visible injury to foliage of sensitive vegetation. Volatile S compounds are also released through volcanic activity, tidal marshes, and decaying OM.

Combustion of fossil fuels and other industrial processes (ore smelting, petroleum refining, and others) contributes to atmospheric SO_2. The amount of SO_4^{-2} deposited in precipitation in the United States ranges from 1 lb/a/yr in rural areas to ≈ 20 lb/a/yr near industrial areas. SO_2 emissions are partly responsible for the acid rainfall and snowfall in industrialized regions (Chapter 3). Because of the concern over air pollution, the Clean Air Act was created to substantially reduce SO_2 emissions. As a result, atmospheric deposition of SO_4^{-2} has decreased $\approx 50\%$ since 1994 (Fig. 7-11). As SO_4^{-2} deposition continues to decline, increasing frequency of S deficiency and crop response to S fertilization can be expected. Depending on the crop, the quantity of S removed varies from 5 to 40 lb S/a (see Table 9.1). Annual deposition of 20 kg SO_4^{-2}/ha (18 lb SO_4^{-2}/a) represents ≈ 9 lb S/a, which provides sufficient S for many crops. However, if SO_4^{-2} deposition decreases by 50%, then atmospheric deposition is insufficient for most crops.

S in Irrigation Water Most irrigation water contains SO_4^{-2}. If S deficiency is expected, a water sample should be analyzed for SO_4^{-2} prior to use of S fertilizers. Generally, a response to additional S is possible if the irrigation water contains <5 lb S/a-ft of water or 5 ppm SO_4^{-2}, and is applied to a sandy, low OM soil (see pg. 444).

Organic S Because of the lower S requirement of most crops compared with N, most animal and municipal biosolids contain sufficient quantities of plant available

Figure 7-11
Distribution and decrease in SO_4^{-2} deposition (kg SO_4^{-2}/ha) in the United States between 1994 and 2009.
(National Atmospheric Deposition Program, 2002, Washington, D.C.)



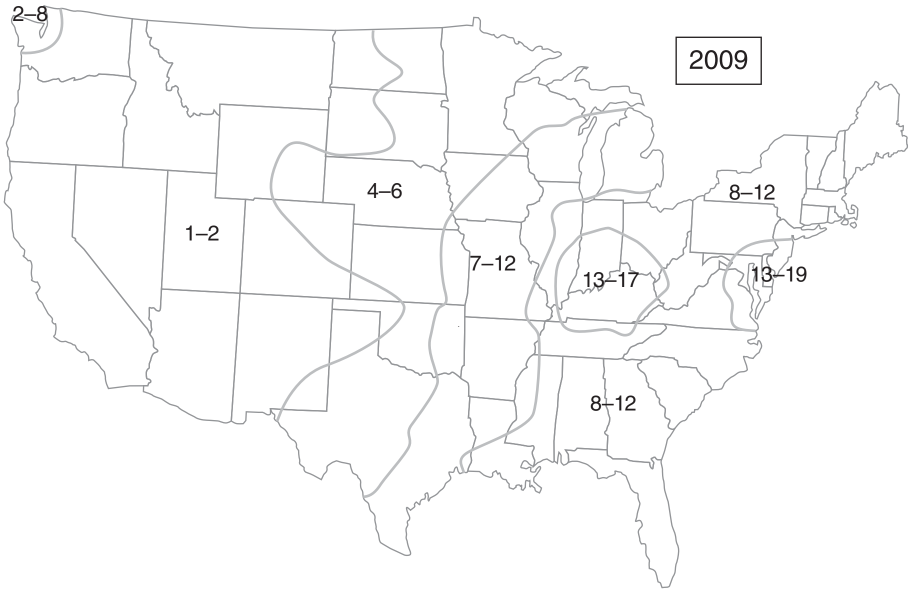


Figure 7-11
(Continued)

S and are excellent S sources. Typical S content in organic wastes ranges from 0.2 to 0.5%, or 5 to 12 lb S/t (dry weight). With typical application rates ranging between 2 and 20 t/a, S applications would range between 10 and 200 lb S/a. Since the majority of S in biosolids products is organic S, mineralization is required to generate plant available SO_4^{-2}.

Inorganic S SO_4^{-2} sources applied to the soil surface and moved into the profile with rainfall or irrigation are immediately plant available unless immobilized by microbes degrading high C:S or N:S residues. Studies comparing the effectiveness of SO_4^{-2} sources (Table 7-2) suggest that one SO_4^{-2} source is generally equal to any other (provided that the accompanying cation is not Zn, Cu, or Mn, which must be applied sparingly) and

Table 7-2
S-Containing Fertilizers

		Plant Nutrient Content (%)				
Material	**Formula**	*N*	*P_2O_5*	*K_2O*	*S*	*Other*
Ammonium polysulfide	NH_4S_x	20	—	—	45	—
Ammonium sulfate	$(NH_4)_2SO_4$	21	—	—	24	—
Ammonium thiosulfate	$(NH_4)_2S_2O_3$	12	—	—	26	—
Calcium polysulfide	CaS_x	—	—	—	22	6 (Ca)
Calcium thiosulfate	CaS_2O_3	—	—	—	10	6 (Ca)
Ferrous sulfate	$FeSO_4 \cdot H_2O$	—	—	—	19	33 (Fe)
Gypsum	$CaSO_4 \cdot 2H_2O$	—	—	—	19	24 (Ca)
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	—	—	—	13	10 (Mg)
Potassium-magnesium sulfate	$K_2SO_4 \cdot MgSO_4$	—	—	22	22	11 (Mg)
Potassium polysulfide	KS_x	—	—	22	23	—
Potassium sulfate	K_2SO_4	—	—	50	18	—
Potassium thiosulfate	$K_2S_2O_3$	—	—	25	17	—
Elemental Sulfur	S^0	—	—	—	100	—
Sulfur (granular w/additives)	S^0	0–7	—	—	60–95	—
Sulfuric acid (100%)	H_2SO_4	—	—	—	33	—
Superphosphate, triple	$Ca(H_2PO_4)_2 \cdot CaSO_4 \cdot 2H_2O$	—	46	—	1.5	—
Urea-sulfur	$CO(NH_2)_2 + S$	38	—	—	10–20	—
Urea-sulfuric acid	$CO(NH_2)_2 + H_2SO_4$	10–28	—	—	9–18	—
Zinc sulfate	$ZnSO_4 \cdot H_2O$	—	—	—	18	36 (Zn)

the factor determining selection should be cost per unit of S applied. General guidelines for proper use of common S-containing fertilizers are summarized in Table 7-3.

Elemental S^0

S^0 is a yellow, water-insoluble solid. When finely ground S^0 is mixed with soil, it is oxidized to SO_4^{-2} by soil microorganisms. The effectiveness of S^0 in supplying S to plants compared with SO_4^{-2} depends on particle size; rate, method, and time of application; and environmental conditions. S^0oxidation rates increase with decreasing particle size (Fig. 7-12). As a general rule, 100% of S^0 must pass through a 16-mesh screen, and 50% of that should pass through a 100-mesh screen. When finely ground S^0 is mixed with soil

TABLE 7-3
GENERAL GUIDELINES FOR S FERTILIZER USE

Materials	Guideline	Remarks
Elemental S^0 Dispersible, granular S^0 Ammonium phosphate–S^0 Urea–S^0	Direct application and bulk blends, apply materials several months before growing season; fall applications are encouraged, allow for dispersion before incorporation of broadcast applications	As starter or preplant, SO_4^{-2} should be included; dispersion of water-degradable granular S at soil surface before incorporation improves effectiveness; incorporate 4–5 months preplant; apply preplant or on severely S-deficient soils, SO_4^{-2} should be included
Ammonium sulfate	Direct application and bulk blends; effective anytime	Segregates in bulk blends unless physical properties are improved by granulation; where leaching losses expected, apply shortly before planting
Ammonium nitrate sulfate Ammonium phosphate sulfate Potassium sulfate Potassium magnesium sulfate	Direct application and bulk blends; effective anytime	Where significant SO_4^{-2} leaching is expected, apply shortly before planting
Calcium sulfate (gypsum)	Direct application; effective anytime	Difficulties encountered in application (dust, caking)
Ammonium thiosulfate Potassium thiosulfate Calcium thiosulfate	Direct application, blending with fluid fertilizers; broadcast preplant or applied in starters; topdress on certain crops (low rate); add through open-ditch and irrigation systems	Blended with neutral fluid P products, all N solutions, most micronutrient solutions
Ammonium polysulfide Potassium polysulfide	Direct application, blending with N solutions; injected into soil; broadcast applications with H_2O dilution; single preplant applications; repeated applications (low rates) through open-ditch irrigation systems	Ammonium polysulfide not suitable for mixing with P-containing fluids
Sulfuric acid	Mixing with ammonium polyphosphate and anhydrous ammonia for clear liquid blends	Applied directly to crops for weed control purposes
Suspensions-containing S^0	Direct application, simultaneous application with other fertilizers, suspensions applied 2–3 months before growing season	Starter or preplant; include SO_4^{-2} (15–20% total S applied)
Suspensions-containing SO_4^{-2}	Effective anytime	Where leaching losses expected, apply preplant or before beginning of growing season

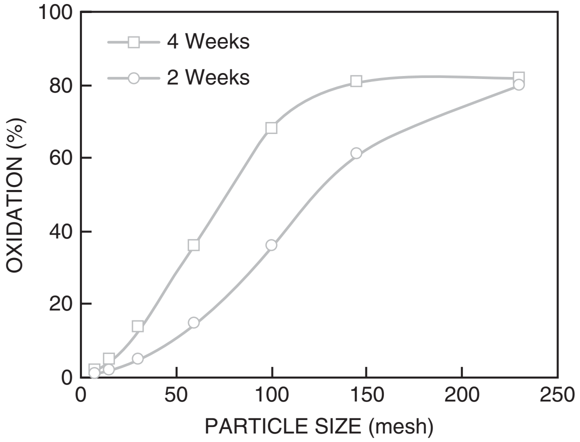


Figure 7-12
Influence of particle size (see Fig. 3-16) of applied S^0 on extent of S^0 oxidation.

possessing a high oxidizing potential, it is usually just as effective as other S sources. However, to assure adequate S availability, S^0 should be incorporated into the soil as far ahead of planting as possible. Application of high S^0 rates will increase surface area exposed to S^0-oxidizing organisms, which should increase plant available S. Uniform distribution of S^0 particles throughout the soil will provide greater exposure to oxidizing microorganisms and minimize any potential problems caused by excessive acidity (Table 3-5).

Dispersible, Granular S^0 Fertilizers

Water-dispersible, granular S^0 fertilizers, such as S-bentonite (~90% S) and micronized granular S (60–95% S), have several important advantages, including high S analysis, lowering costs of transportation and handling; wide distribution of S^0 particle sizes with varying degrees of controlled availability to plants; low susceptibility to leaching losses in areas of high rainfall; and excellent durable physical forms that are well-suited for direct application or blending with most common granular fertilizers except those containing NO_3-N. S-bentonite is manufactured by adding bentonite to molten S^0, whereas micronized granular S^0 consists of 100% $<$ 74-mm ($>$200-mesh) particles bound together with a water-soluble binder.

Dispersion of S^0-bentonite into readily oxidized finely divided S^0 occurs gradually in soil following wetting and swelling of the bentonite. Micronized, granular S^0 disperses rapidly and completely upon wetting in soil. Broadcast applications are usually more dependable than banding because S^0 dispersion is enhanced by exposure to rainfall before soil incorporation. Because of the uncertainty of adequate formation of SO_4^{-2} from S^0-bentonite in the first growing season after application, it should be applied well in advance of planting. When applied just before seeding of high-S-requiring crops grown on S-deficient soils, some SO_4^{-2} should also be provided.

S^0 Suspensions

Addition of finely ground S^0 to water containing 2–3% attapulgite clay results in a suspension containing 40–60% S. These suspensions can be applied directly to soil or combined with suspension fertilizers.

Ammonium Sulfate [$(NH_4)_2SO_4$ or AS]

This solid fertilizer containing 24% S and 21% N was previously described in Chapter 4 (Table 7-2). AS is used predominately when both N and S are required.

Potassium Sulfate (K_2SO_4) and Potassium Magnesium Sulfate (K_2SO_4, $MgSO_4$)

Both materials were discussed in Chapter 6 and are commonly used when both S and K are required.

Ammonium Thiosulfate [$(NH_4)_2S_2O_3$, or ATS]

ATS is a clear liquid containing 12% N and 26% S and is a popular S-containing product (Table 7-2). ATS is compatible with N solutions and complete (N-P-K) liquid mixes, which are neutral to slightly acidic in pH. ATS can be applied directly to soil, in mixtures, or through either sprinkler or open-ditch irrigation systems. When applied to soil, ATS forms colloidal S and $(NH_4)_2SO_4$. SO_4^{-2} is immediately available, whereas the S^0 must be oxidized to SO_4^{-2}, thus extending the availability to the crop. Potassium thiosulfate (KTS) behaves similarly to ATS.

Ammonium Polysulfide (NH_4S_x)

Ammonium polysulfide is a red to brown to black solution having a H_2S odor. It contains ~20% N and 45% S (Table 7-2). In addition to use as a fertilizer, it is used for reclaiming high-pH soils and for treatment of irrigation water to improve water penetration into the soil. Ammonium polysulfide is recommended for mixing with anhydrous NH_3, aqua NH_3, and UAN solutions. Simultaneous application of ammonium polysulfide and anhydrous NH_3 is popular in some areas for providing both N and S. Normally, it is considered incompatible with phosphate-containing liquids. This material has a low vapor pressure, and it should be stored at 0.5 psi to prevent loss of NH_3 and subsequent precipitation of S^0. Potassium polysulfide (0–0–22–23) has been used on a limited basis in sprinkler and flood irrigation systems for salt removal and to supply K.

Calcium Polysulfide (CaS_x) and Calcium Thiosulfate (CaS_2O_3)

Calcium polysulfide (22% S, 6% Ca) and calcium thiosulfate (10% S, 6% Ca) are clear, odorless solutions. They are commonly used in soils to reduce exchangeable Na content and improve water infiltration, while supplying S.

Urea-Sulfuric Acid

Two typical grades used as acidifying amendments, as well as sources of N, contain 10% N and 18% S and 28% N and 9% S, respectively (Table 7-2). They can be applied directly to soil or added through sprinkler systems. Because urea-sulfuric acid formulations have pH values between 0.5 and 1.0, the equipment used must be made from stainless steel and other noncorrosive materials. Workers must wear protective clothing.

CALCIUM

In acid, humid-region soils, Ca^{+2} and Al^{+3} dominate the CEC, while in neutral and calcareous soils Ca^{+2} occupies the majority of exchange sites (Chapters 2 and 3). As with any other cation, exchangeable and solution Ca^{+2} are in equilibrium and provide the majority of plant available Ca^{+2} (Fig. 7-13). If solution Ca^{+2} is decreased by leaching or plant uptake, Ca^{+2} will desorb from the CEC to resupply solution Ca^{+2}. Other soluble cations replace the desorbed Ca^{+2}, or Ca minerals dissolve to provide additional exchangeable and solution Ca^{+2}. Conversely, if solution Ca^{+2} is increased, the equilibrium shifts in the opposite direction, with adsorption of Ca^{+2} on the CEC. The fate of solution Ca^{+2} is less complex than that of K^+, due to K fixation and release reactions (Chapter 6). Ca^{+2} may be (1) adsorbed to CEC, (2) absorbed by plants and microorganisms, (3) leached in drainage water, or (4) reprecipitated as a secondary Ca compound, dominantly in arid climates.

Forms and Functions of Ca in Plants

Plants absorb Ca^{+2} from the soil solution, where mass flow and root interception are the primary mechanisms of Ca transport to the root surface. Ca deficiency is uncommon but can occur in highly leached, unlimed acid soils. Ca^{+2} in plants ranges

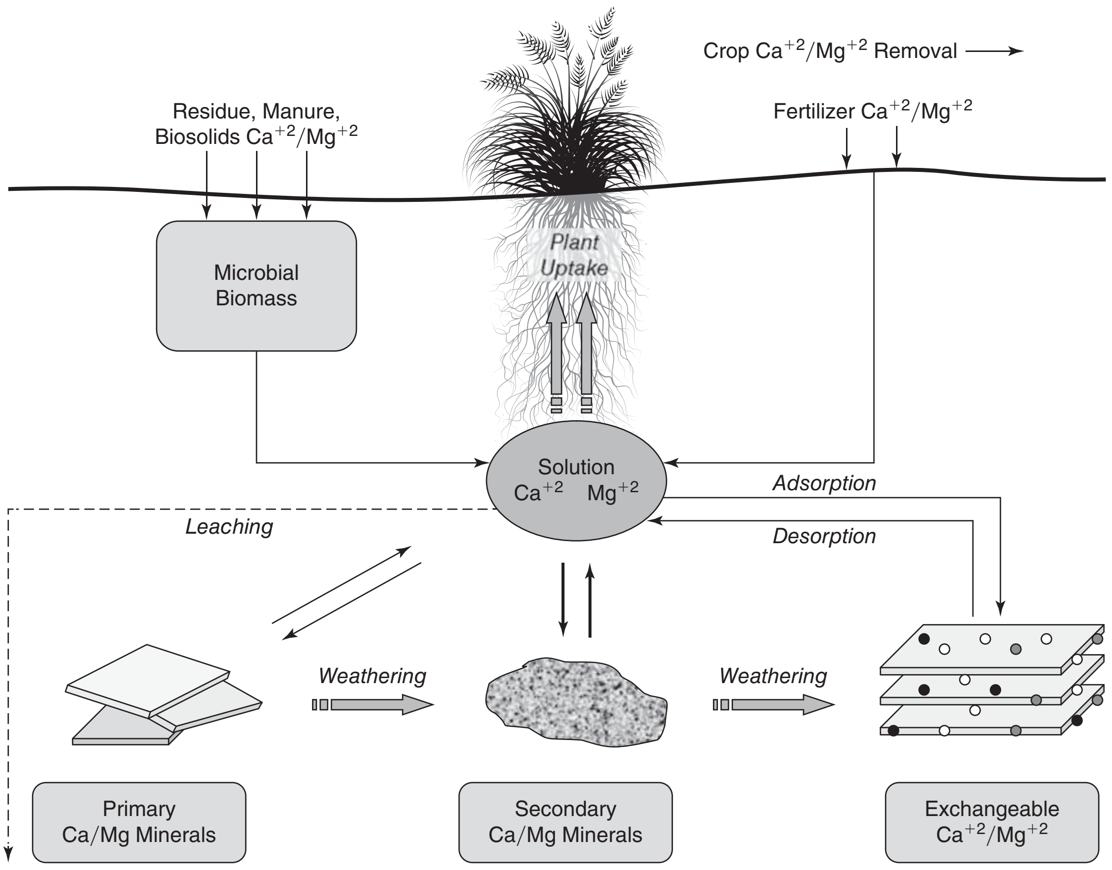


Figure 7-13
Ca and Mg cycling in soil.

between 0.2 and 1.0% and is essential to cell wall membrane structure and permeability. Low Ca^{+2} weakens cell membranes, resulting in increased permeability, loss of cell contents, and failure of nutrient-uptake mechanisms. Ca^{+2} and other cations neutralize organic acids formed during normal cell metabolism. Ca^{+2} is important to N metabolism and protein formation by enhancing NO_3^- uptake. Ca^{+2} also provides some regulation of cation uptake. For example, K^+ and Na^+ uptake are equivalent in absence of Ca^{+2}, but in its presence K^+ uptake greatly exceeds Na^+ uptake.

Ca^{+2} is essential for translocation of carbohydrates and nutrients. Accumulation of carbohydrates in leaves under Ca^{+2} stress decreases carbohydrate content of stems and roots, which impairs normal root function (i.e., water and nutrient absorption) because of low energy supply. As a result, Ca^{+2} deficiency causes malformation of storage tissues in many fruits and vegetable crops.

While Ca^{+2} is important for translocation, Ca^{+2} is generally immobile in the plant. Following absorption, Ca^{+2} moves with transpirational water in the xylem. Once in the leaves, very little Ca^{+2} translocation in the phloem occurs, resulting in poor Ca^{+2} supply to roots and storage organs. Since Ca^{+2} cannot be redistributed within the plant, it is critical that a continuous supply of Ca^{+2} is available for root absorption to support normal growth and fruit development. Soil conditions that reduce root growth (e.g., Al^{+3} toxicity, P deficiency, pests, and diseases) will limit root access to Ca^{+2} and induce deficiency. Problems related to inadequate Ca^{+2} uptake more commonly occur in plants that have small root systems (i.e., tubers) than with plants having more highly developed root systems (fibrous grass roots).

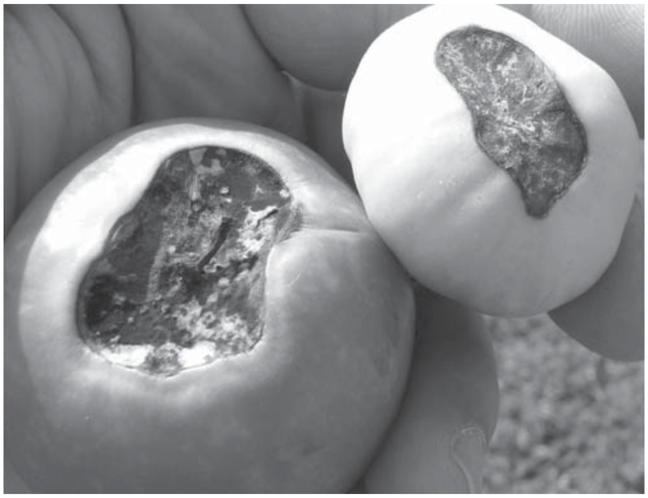


Figure 7-14
Blossom end rot in tomato caused by Ca deficiency.

Ca^{+2} is essential for cell division and elongation; therefore, deficiency symptoms are primarily exhibited in meristematic regions of rapid cell division. Ca^{+2} deficiency inhibits development of shoot terminal buds and apical root tips resulting in deformed tissues and/or death of the growing points (buds, blossoms, root tips). Commonly, leaf tips and margins are chlorotic, colorless, and/or necrotic, a condition referred to as *die back* or *tip burn*. In some crops (i.e., corn), a gelatinous material is secreted causing leaf tips to stick together. Under severe Ca^{+2} deficiency, root development is slow and root tips develop a dark color and die. Ca^{+2} deficiency causes poor nodulation by N_2-fixing bacteria on legume roots, where nodule tissues are white to grayish green compared to the pink/red color found in normal legume nodules.

Low Ca^{+2} uptake combined with limited translocation of carbohydrates causes distinct symptoms in fruits and vegetable crops. Examples are blossom end rot in peppers and tomatoes (Fig. 7-14), deformed watermelons, bitter pit in apples, internal brown spot in potatoes, black heart in peanuts and celery, and cavity spot in carrots. Ca^{+2} deficiency results in discolored and softer fruit with inferior shelf life and marketability. Crop quality in leafy vegetable crops is reduced through burning of leaf tips and margins (e.g., lettuce, cabbage, spinach).

Ca in Soil

The earth's crust contains $\approx$3.5% total Ca. Ca in soils originated from the parent rocks (minerals) from which soil was formed. Anorthite ($CaAl_2Si_2O_3$) is the most important primary source of Ca, although pyroxenes and amphiboles are also common. Small amounts of Ca may also originate from biotite, apatite, and certain borosilicates.

Total Ca in soils varies widely depending on region. Ca normally ranges 0.7–1.5% in noncalcareous soils of humid temperate regions; however, Ca is much lower (0.1–0.3%) in highly weathered, tropical soils (Table 2-2). In contrast, semi-arid and arid region calcareous soils contain 1–30% Ca, predominately as $CaCO_3$ (Chapter 3). Dolomite $[CaMg(CO_3)_2]$ and gypsum $(CaSO_4 \cdot 2H_2O)$ also may be present.

Generally, coarse-textured, humid-region soils formed from low-Ca minerals are low in plant available Ca. Fine-textured soils formed from high-Ca minerals are much higher in both exchangeable and total Ca. However, in humid regions, even soils formed from limestone can be acidic in the surface layers because of removal of Ca and other cations by excessive leaching. As water containing dissolved CO_2 percolates through the soil, the H^+ formed $(CO_2 + H_2O \leftrightarrows H^+ + HCO_3^-)$ displaces

Ca^{+2} and other basic cations on the CEC. If substantial volumes of water percolate through the soil profile, as in humid regions, soils gradually become acidic (Chapter 3). Where leaching occurs, Na^+ is lost more readily than Ca^{+2} (Chapter 2); however, since exchangeable and solution Ca^{+2} are greater than Na^+ in most soils, the quantity of Ca^{+2} lost is also much more. Ca is often the dominant cation in drainage waters with losses ranging 75–200 lb/a per year. Since Ca^{+2} is adsorbed on the CEC, losses by erosion may be considerable in some soils.

In temperate regions, soil solution Ca^{+2} ranges 30–300 ppm. In higher rainfall areas, solution Ca^{+2} ranges 5–50 ppm. About 15 ppm solution Ca^{+2} is adequate for most crops. Solution Ca^{+2} higher than necessary for optimum plant growth has little effect on Ca^{+2} uptake, because uptake is genetically controlled. Although solution Ca^{+2} is about 10 times greater than K^+, its uptake is usually lower than K^+. The limited capacity for Ca^{+2} uptake is due to its absorption being confined to root tips where cell walls of the endodermis are still unsuberized (soft tissue enabling high water and nutrient uptake).

The most important factors in determining Ca^{+2} availability to plants are:

- Total Ca supply
- Soil pH
- CEC
- % Ca^{+2} saturation on CEC
- Type of soil clay
- Ratio of solution Ca^{+2} to other cations

For example, low total Ca in acid, sandy soils can be too low to provide sufficient plant available Ca^{+2}, requiring Ca fertilization or liming. Increasing Ca^{+2} will increase root growth (Fig. 7-15) and Ca (and Mg^{+2}) in above-ground plant tissue (Fig. 7-16). See Chapter 3 for additional examples of plant response to Ca.

In soils not containing $CaCO_3$, $CaMg(CO_3)_2$, or $CaSO_4 \cdot 2H_2O$, solution Ca^{+2} concentration depends on the amount of exchangeable Ca^{+2}. In acid soils, Ca^{+2} is not readily available to plants at low %Ca saturation. For example, a low-CEC soil with 1,000 ppm exchangeable Ca^{+2} but representing a high %Ca saturation can supply plants with more Ca^{+2} compared to a high-CEC soil with 2,000 ppm exchangeable Ca^{+2} and a low %Ca saturation. Thus, as %Ca saturation decreases in proportion to total CEC, the amount of Ca^{+2} absorbed by plants also decreases. High Ca^{+2} saturation indicates a favorable pH for plant growth and microbial activity, and will usually reflect low exchangeable Al^{+3} in acid soils and Na^+ in sodic soils. Many crops respond to Ca applications when Ca saturation is <25% of CEC.

The type of clay influences Ca^{+2} availability; 2:1 clays require higher %Ca saturation than 1:1 clays. Specifically, montmorillonitic clays require ≈50–60%

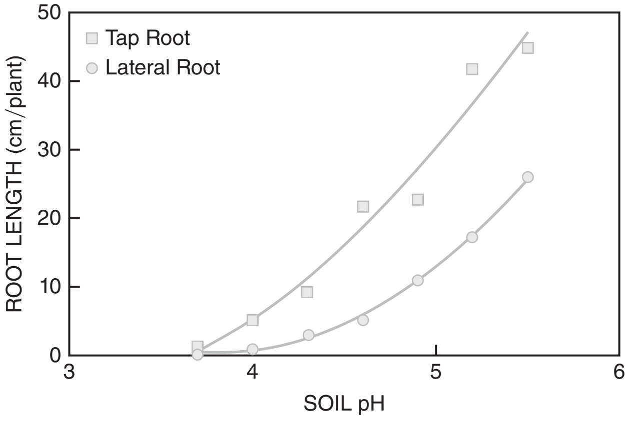


Figure 7-15
Increasing soil pH (and solution Ca^{+2}) increases root growth in soybean.
(*Adapted from Sanzonowicz, et al., 1998,* J. Plant Nutr., *21:785–804.*)

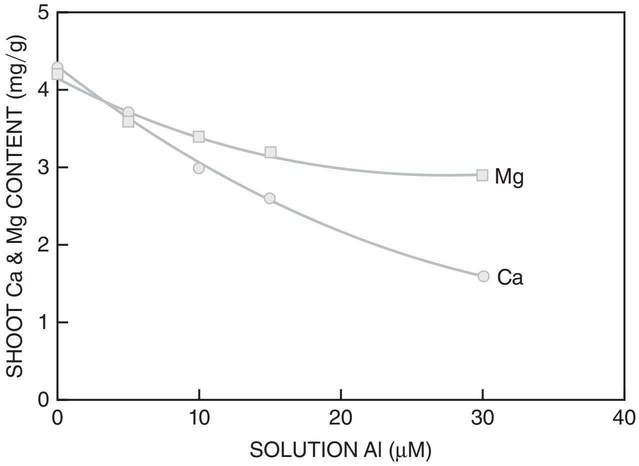


Figure 7-16
Effect of increased soluble Al^{+3} on Ca and Mg accumulation in corn shoots.
(*E. J. Kamprath, 2005, personal communication.*)

Ca saturation for adequate Ca availability, whereas kaolinitic clays are able to supply sufficient Ca^{+2} at 40–50% Ca saturation.

Ca Sources

The primary Ca sources are liming materials such as $CaCO_3$, $CaMg(CO_3)_2$, and others applied to neutralize soil acidity (Chapter 3). In situations where Ca is required without the need for correcting soil acidity, gypsum is used. Gypsum ($CaSO_4 \cdot 2H_2O$) deposits are found at several locations in North America, and large amounts of by-product gypsum are produced in the manufacture of phosphoric acid (Chapter 5). Gypsum has little effect on surface soil pH; however, it has some neutralizing value in acid subsoils (Chapter 3). Gypsum is widely used on sodic soils in arid climates (Chapter 3).

Ca is present in several fertilizer materials including triple superphosphate (12–14% Ca), calcium nitrate (19% Ca), and lime-ammonium nitrate (10% Ca). Synthetic chelates such as CaEDTA contain 3–5% Ca, while some of the natural complexing substances used as micronutrient carriers contain 4–12% Ca. Chelated Ca can also be foliar applied to crops. Rock phosphate contains ≈35% Ca, and when applied at high rates to acid tropical soils, substantial amounts of Ca are supplied. Animal and municipal wastes contain ~2–5% Ca by dry weight and are excellent Ca sources.

MAGNESIUM

Like Ca, Mg occurs predominantly as exchangeable and solution Mg^{+2} (Fig. 7-13). Mg^{+2} absorption by plants depends on the amount of solution Mg^{+2}, soil pH, %Mg saturation on the CEC, quantity of other exchangeable ions, and type of clay. Mg in soil solution may be (1) lost in percolating waters, (2) absorbed by microorganisms, (3) adsorbed on the CEC, or (4) reprecipitated as a secondary mineral, predominantly in arid climates.

Forms and Functions of Mg in Plants

Mg^{+2} is absorbed by plants from the soil solution and, like Ca^{+2}, is supplied to plant roots predominately by mass flow. Root interception contributes much less Mg^{+2} to uptake than Ca^{+2}. The quantity of Mg^{+2} taken up by plants is usually less than Ca^{+2} or K^+.

Plants contain 0.1–0.4% Mg^{+2}. As a primary constituent of chlorophyll, Mg^{+2} is essential for photosynthesis (Fig. 4-3). Chlorophyll accounts for 15–20% of total

Mg^{+2} in plants. Mg also serves as a structural component in ribosomes, stabilizing them in the configuration necessary for protein synthesis. In Mg^{+2}-deficient plants, protein N decreases while nonprotein N increases.

Mg is required for maximum activity of almost every phosphorylating enzyme involved in carbohydrate metabolism. Most reactions involving phosphate transfer from adenosine triphosphate (ATP) require Mg^{+2}. Since the fundamental process of energy transfer occurs in photosynthesis, glycolysis, the Krebs cycle, and respiration, Mg^{+2} is important throughout plant metabolism.

Because of the mobility of plant Mg^{+2} and its ready translocation from older to younger plant parts, deficiency symptoms often appear first on lower leaves. In many plants, Mg^{+2} deficiency causes interveinal chlorosis in leaves, where only leaf veins remain green. Under severe Mg^{+2} deficiency, leaf tissue becomes uniformly chlorotic to necrotic. In other plants (e.g., cotton), lower leaves develop a reddish-purple cast, gradually turning brown and finally necrotic (see color plates).

Grass Tetany Low Mg content in forage crops, particularly grasses, used for animal feed may cause grass tetany (hypomagnesemia), which is an abnormally low level of blood Mg. Low soil Mg, or high rates of NH_4^+ or K^+ fertilizers, may depress Mg^{+2} uptake. For example, Mg content of young corn plants is markedly reduced when NH_4^+ rather than NO_3^- is applied. Because grass tetany often occurs in the spring, NH_4^+ may be greater than NO_3^-, particularly under extended cool-weather conditions. In addition, high protein content of ingested forages (and other feeds) can depress Mg absorption by the animal, especially cattle. Including legumes in the forage program is advised because legumes exhibit higher Mg contents than grasses. The diet can also be supplemented with Mg salts to help prevent grass tetany. Soil Mg may be increased through application of dolomitic limestone, if liming is advisable, or through Mg-containing fertilizers.

Mg in Soil

Mg constitutes ~2% of the earth's crust; however, total soil Mg content ranges from 0.1% in coarse, humid-region soils to 4% in fine-textured, arid, or semi-arid soils formed from high-Mg minerals. Soil Mg originates from weathering of several Mg-bearing minerals including biotite, dolomite, hornblende, olivine, and serpentine. Mg also occurs in clay minerals such as chlorite, illite, montmorillonite, and vermiculite. Substantial amounts of epsomite $(MgSO_4 \cdot 7H_2O)$ and bloedite $(Na_2MgSO_3 \cdot 4H_2O)$ occur in arid or semi-arid soils.

Soil solution Mg^{+2} concentration typically ranges from 5 to 50 ppm in temperate region soils, although Mg^{+2} concentrations between 120 and 2,400 ppm have been observed in arid region soils. Mg^{+2} can be leached (5–60 lb/a/yr), depending on soil Mg content, rate of weathering, leaching intensity, and plant uptake. Mg^{+2} leaching can be a severe problem in sandy soils, particularly following KCl or K_2SO_4 fertilization as K^+ would displace Mg^{+2} on the CEC. As with Ca^{+2}, Mg^{+2} erosion losses can be considerable in some soils.

Mg in clay minerals is slowly depleted by leaching and exhaustive cropping. Vermiculite has a high Mg content, and it can be a significant Mg source in soils. Conditions in which Mg is likely to be deficient include acid, sandy, highly leached soils with low CEC; calcareous soils with inherently low Mg levels; acid soils receiving high rates of liming materials low in Mg; high rates of NH_4^+ or K^+ fertilization; and crops with a high Mg demand. Coarse-textured, humid-region soils exhibit the greatest potential for Mg deficiency. These soils normally contain low total and exchangeable Mg^{+2}, and are likely deficient when they contain $<$25–50 ppm exchangeable Mg^{+2}. In most soils, exchangeable Mg^{+2} is 4–20% of the CEC. Mg saturation for

TABLE 7-4
MG-CONTAINING FERTILIZERS

Material	Formula	Plant Nutrient Content (%)				
		Mg	*P_2O_5*	*K_2O*	*S*	*N*
Epsom salt	$MgSO_4 \cdot 7H_2O$	10	—	—	13	—
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$	11	—	22	22	—
Magnesium Chloride	$MgCl_2$	25	—	—	—	—
Magnesium Nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	9	—	—	—	—
Dolomite	$MgCO_3 \cdot CaCO_3$	12–20	—	—	—	—
Dolomitic limestone	$MgCO_3 \cdot CaCO_3$	4–6	—	—	—	—
Magnesium oxide	MgO	55	—	—	—	—
Kieserite	$MgSO_4 \cdot H_2O$	17	—	—	45	—
Kainite	$MgSO_4 \cdot KCl \cdot 3H_2O$	9	—	18	12	—
Struvite	$MgNH_4PO_4 \cdot 6H_2O$	10	12	—	—	5

optimum plant growth coincides closely with this range, but in most instances, Mg saturation should be $\approx 7–10\%$.

Excess Mg can occur in soils formed from serpentine minerals or influenced by groundwaters high in Mg. Normal Ca nutrition can be disrupted when exchangeable $Mg^{+2} > Ca^{+2}$. Mg deficiencies can also occur in soils with a high Ca:Mg ratio of 10–15:1. In many sandy, humid-region soils, continued use of Ca liming materials may increase Ca:Mg ratio and induce Mg deficiency on certain crops.

Reduced Mg^{+2} uptake also occurs in strongly acid soils with high levels of exchangeable Al^{+3}. Al saturation of 65–70% is often associated with Mg deficiency. High levels of exchangeable K^+ can interfere with Mg uptake by crops. Generally, the recommended K:Mg ratios are <5:1 for field crops, 3:1 for vegetables and sugar beets, and 2:1 for fruit and greenhouse crops.

Competition between NH_4^+ and Mg^{+2} can also reduce Mg uptake. NH_4^+-induced Mg^{+2} stress is greatest with high rates of NH_4^+ fertilizers applied to low exchangeable Mg^{+2} soils. The mechanism of this interaction involves the H^+ released when NH_4^+ is absorbed by roots, as well as the direct effect of NH_4^+.

Mg Sources

Organic biosolids generally contain low Mg, although at rates applied to meet N or other macronutrient needs, sufficient Mg to meet most crop needs is applied. In Mg-deficient acid soils, dolomitic lime applications are recommended to increase soil pH and Mg availability (Table 7-4). Many inorganic Mg fertilizers are available to correct Mg deficiencies if no adjustment in soil pH is required. The most common sources are epsom salt ($MgSO_4 \cdot 7H_2O$), langbeinite ($K_2SO_4 \cdot 2MgSO_4$), and magnesium nitrate $Mg(NO_3)_2$, commonly used in the horticulture industry (Table 7-4). Most Mg fertilizers contain multiple plant nutrients; therefore, only use these when each nutrient in the selected source is needed.

In addition to most inorganic Mg salts, other materials containing synthetic Mg chelates (2–4% Mg) and natural organic complexing substances (4–9% Mg) are well suited for application as foliar sprays. For example, Mg deficiency in citrus trees is frequently corrected by foliar applications of $MgSO_4$ or $Mg(NO_3)_2$.

STUDY QUESTIONS

1. S is an integral part of which amino acids?
2. What mechanism(s) is involved in transport of solution S to plant roots?
3. What is the importance of the C:N:P:S ratio on S availability?
4. What are the soil conditions under which SO_4^{-2} leaching would be expected?
5. Describe soil and climatic conditions where S deficiencies are most likely to occur.
6. Adsorbed SO_4^{-2} is a source of plant available SO_4^{-2}. Why would adsorbed SO_4^{-2} be greater in soils of highly weathered soils compared to slightly weathered soils?
7. Which organic S compound in soil contributes most to mineralizable S?
8. What are the factors affecting the oxidation of S^0 in soils? What soil microorganisms are responsible for S^0 oxidation? When using granular S^0 fertilizer, what conditions will increase rate of oxidation and ultimately plant availability?
9. Identify the important soil and crop factors that influence the type and amount of S fertilizer needed by crops?
10. The soil contains 2% O.M with 2% loss each year (8:1 N:S). A clover crop grown on this soil yields 5 t/a (N:S = 12:1, 3% N content).
    a. How many pounds S/afs are mineralized each year?
    b. Does this crop need S fertilization (assume that all available S comes from the OM)?
    c. How many pounds of gypsum/afs would be required?
11. A farmer irrigates 3 times each season with 3 in. of water (12 ppm S). The total above – ground biomass weighs 4 t/a (3% N, 14:1 N:S). The soil contains 2.5% OM (10:1 N:S), which degrades at a rate of 2% per annum. Calculate the additional S needed by the crop.
12. An irrigation water sample contains 12 ppm S. How many acre-feet of irrigation water would you need to apply 16 lb S/a?
13. Why is a deficiency of Ca sometimes observed under very dry soil conditions?
14. In what ways do Mg- and K-deficiency symptoms resemble each other? In what ways are they dissimilar? What function of Mg in plants is unique?
15. What is the primary transport mechanism of Mg^{+2} and Ca^{+2} to the root surface? Why are they similar or different?
16. What conditions are conducive to Ca and Mg deficiencies?
17. Why is it desirable to have a high degree of Ca saturation on the CEC?
18. Why is soil acidity usually associated with impaired uptake of Ca and Mg?
19. What are some incidental sources of plant-nutrient Ca?
20. A soil sample has a CEC of 5 meq/100g soil. The soil is 50% Ca saturated. Calculate the remaining Ca saturation, if a crop removes 50 lb Ca/afs. Assume that all the Ca uptake is from exchangeable Ca.
21. A soil has a CEC of 15 meq/100 g. The Ca and Mg saturation are 50 and 5% respectively. Estimate the $CaCO_3$ and $MgSO_4$ required to increase the Ca and Mg saturation to 70 and 10% respectively.
22. Discuss the important forms and functions of S in plants.
23. Name the important S-containing amino-acids.
24. Discuss the factors that affect S-mineralization and immobilization.
25. With a neat diagram, Explain the Ca & Mg cycle in soil.
26. Justify with suitable examples.
    a. Increase in solution Ca^{2+} increases roots growth in soybeans.
    b. Increase in soluble Al^{3+} decreases Ca & Mg content in corn shoots.
27. What factors reduces Mg uptake?

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8

Micronutrients

Micronutrients are equally important in plant nutrition as macronutrients; they simply occur in plants and soils in much lower concentrations (Table 1-6). Plants grown in micronutrient deficient soils exhibit similar reductions in productivity as those grown in macronutrient deficient soils. Micronutrients in soil are (1) elements in primary and secondary minerals, (2) adsorbed to mineral and OM surfaces, (3) incorporated in OM and microorganisms, and (4) present in solution. Depending on the micronutrient, some forms are more important than others in buffering micronutrients in soil solution. Understanding the relationships and dynamics among these forms is essential for optimizing plant productivity in micronutrient deficient soils.

IRON (Fe)

Fe Cycle

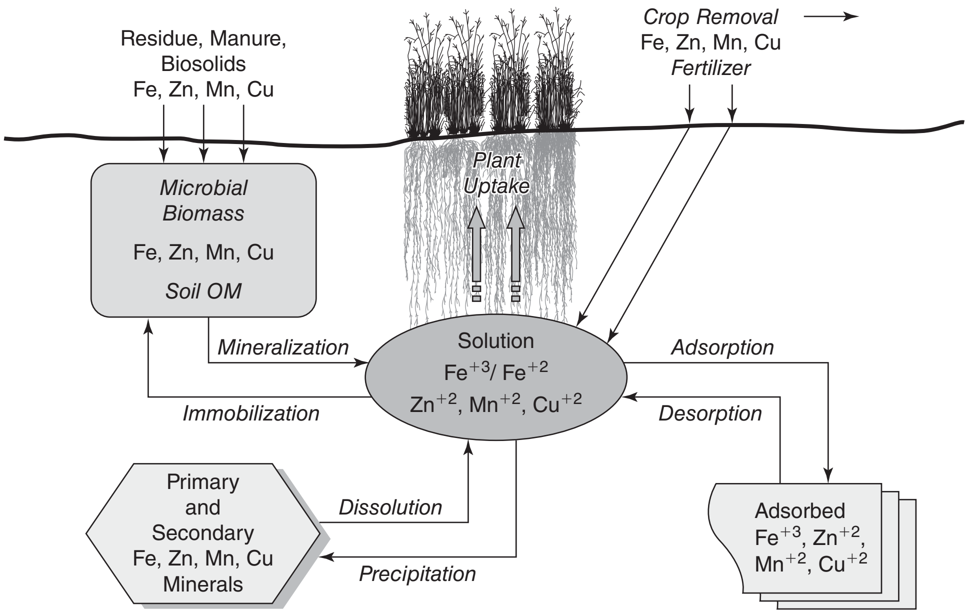
Plant available Fe is governed primarily through mineral and organic fractions in soils (Fig. 8-1). Fe minerals dissolve to buffer reductions in solution Fe caused by plant uptake. Solution Fe can be immobilized by microorganisms and complexed by organic compounds in the soil solution. Because solution Fe concentration is low compared to Ca^{+2}, Mg^{+2}, K^{+}, and Na^{+} (saline/sodic soils) or Al^{+3} (acid soils), only negligible amounts of micronutrient cations like Fe are adsorbed on the CEC. Thus, adsorbed Fe contributes little to plant available Fe.

Fe in Plants

Fe is absorbed by roots as Fe^{+2} and Fe^{+3}. Because Fe can exist in two oxidation states, it accepts or donates an electron ($Fe^{+3} + e^{-} \leftrightarrows Fe^{+2}$), depending on oxidation potential. Transfer of electrons between organic molecules and Fe provides the electrochemical potential for many enzymatic transformations in plants. Several of these enzymes are involved in chlorophyll synthesis, and when Fe is deficient, chlorophyll production is reduced, which results in the characteristic chlorosis symptoms of Fe stress (see color plates).

Fe is a structural component of porphyrin molecules: cytochromes, hemes, hematin, ferrichrome, and leghemoglobin. These substances are involved in oxidation-reduction reactions in respiration and photosynthesis. As much as 75% of cell Fe is associated with chloroplasts, and up to 90% of Fe in leaves occurs with lipoprotein in chloroplast and mitochondria membranes.

Figure 8-1
Fe, Zn, Cu, and Mn cycling in soil.



Fe-containing cytochromes in the chloroplasts function in photosynthetic reduction processes where ferrodoxin, an Fe-S protein, is an electron acceptor. Ferredoxins are the first stable compound of the photosynthetic electron transport chain. Reduction of O_2 to H_2O during respiration is also a common function of Fe compounds. Fe is a constituent of nitrogenase, the enzyme essential for N_2 fixation by rhizobia and other microorganisms. Fe may also be capable of partial substitution for Mo involved in NO_3^- reductase in legumes.

The sufficiency range of Fe in plant tissue is 50–250 ppm, where Fe deficiency occurs at <50 ppm tissue Fe content. Fe deficiency symptoms appear first in young leaves, because Fe is not mobile in the plant. Young leaves develop interveinal chlorosis, which progresses rapidly over the entire leaf. In severe cases, leaves turn entirely white and necrotic.

Fe toxicities commonly occur in plants grown on acid and/or poorly drained soils. Fe toxicity symptoms generally appear as bronzing or bronze colored speckles on leaves and can occur with >300 ppm Fe in leaves.

Fe in Soil

Mineral Fe Fe is the fourth most abundant element, comprising about 5% of the earth's crust. Common primary and secondary Fe minerals are olivine [$(Mg, Fe)_2SiO_4$], siderite ($FeCO_3$), hematite (Fe_2O_3), goethite (FeOOH), and magnetite (Fe_3O_4). Total soil Fe varies widely (1–55%).

Soil Solution Fe Compared with other cations, the solubility of common Fe minerals in soil is very low ($\mathbf{10^{-6}–10^{-20}}$ M Fe^{+3}) depending on pH (Fig. 8-2). In well-drained, oxidized soil, solution $Fe^{+2} < Fe^{+3}$. Soluble Fe^{+2} increases significantly when soils become waterlogged. The pH-dependent relationship for Fe^{+3} in soil solution is:

$$Fe(OH)_3 + 3H^+ \leftrightarrows Fe^{+3} + 3H_2O$$

For each pH unit increase, Fe^{+3} concentration decreases a thousandfold. In contrast, Fe^{+2} decreases hundredfold for each unit increase in pH, which is similar to other divalent cations (Fig. 8-2). Over the normal soil pH range, total solution Fe is not

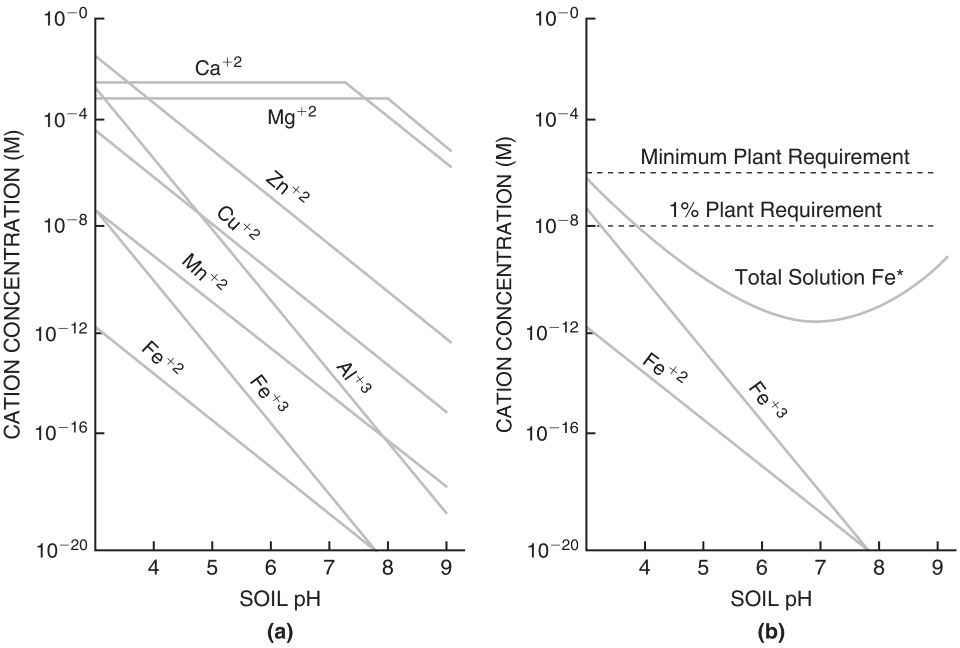


Figure 8-2
(a) Influence of pH on solution Fe^{+3} *concentration relative to other cations. The concentration of* Ca^{+2} *and* Mg^{+2} *decreases above* ~pH 7.2 *due to precipitation of* $CaCO_3$ *and* $MgCO_3$.
*(b) Influence of pH on total solution Fe concentration and its relationship to Fe required by plants. *Includes soluble Fe hydroxide ions* [$FeOH^{+2}$, $Fe(OH)_2^{+}$, $Fe(OH)_3^{o}$, *and* $Fe(OH)_4^{-}$] *not shown on graph b.* (Lindsay, 1981, Chemistry in Soil Environment, Madison, WI: ASA)

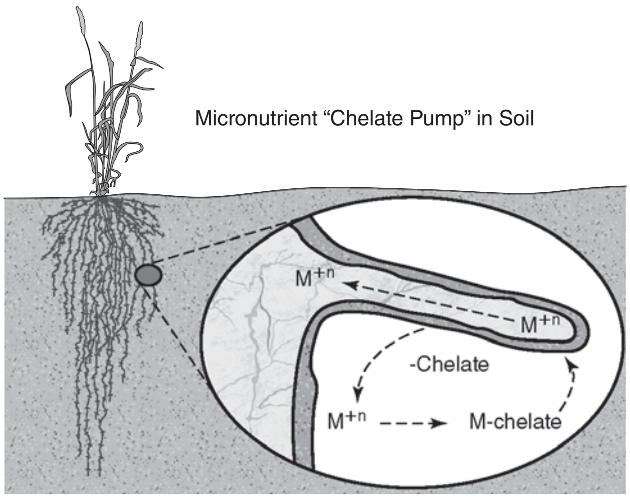
sufficient to meet plant Fe requirements, even in acid soils, where Fe deficiencies occur less frequently than in high-pH and calcareous soils (Fig. 8-2). Obviously, another mechanism that increases Fe availability to plants exists; otherwise, crops grown on almost all soils would be Fe deficient.

Chelate Dynamics Numerous soluble organic compounds in soil are able to complex, or *chelate*, Fe^{+3} and other micronutrients (Table 8-1). *Chelate* is a term derived from a Greek word meaning "claw" (see Fig. 8-6d). The concentration of solution Fe and Fe transported to the root by diffusion can be greatly increased through natural organic chelate–Fe complexes in soil. Natural organic chelates in soils are products of microbial activity and degradation of soil OM and plant residues. Root exudates are also capable of complexing micronutrients. Many natural organic compounds have chelating properties.

TABLE 8-1
COMMON NATURAL AND SYNTHETIC CHELATE COMPOUNDS

Name	Formula	Abbreviation
Natural		
Citric acid	$C_6H_8O_7$	CIT
Oxalic acid	$C_2H_2O_4$	OX
Malonic acid	$C_3H_4O_4$	MAL
Malic acid	$C_4H_6O_4$	MA
Tartaric acid	$C_4H_6O_6$	TAR
Synthetic		
Pyrophosphoric acid	$H_4P_2O_7$	PPA
Ethylenediaminetetraacetic acid	$C_{10}H_{16}O_8N_2$	EDTA
Diethylenetriaminepentaacetic acid	$C_{14}H_{23}O_{10}N_3$	DTPA
Cyclohexanediaminetetraacetic acid	$C_{14}H_{22}O_8N_2$	CDTA
Ethylenediaminedi-o-hydroxyphenylacetic acid	$C_{18}H_{20}O_6N_2$	EDDHA

Figure 8-3
Cycling of chelated micronutrients (M) in soils.



During plant uptake, the concentration of chelated Fe or other micronutrients is greater in the bulk solution than at the root surface; thus, chelated Fe diffuses to the root surface in response to the concentration gradient (Fig. 8-3). At the root surface, Fe^{+3} dissociates from the chelate through interaction between organic cell wall compounds and the chelate. After Fe^{+3} dissociates from the chelate, the "free" chelate will diffuse away from the root back to the "bulk" solution, again in response to a concentration gradient (free chelate concentration near the root is greater than free chelate in bulk solution). The free chelate subsequently complexes another Fe^{+3} from solution. As the *unchelated* Fe^{+3} concentration decreases in solution because of chelation, additional Fe is desorbed from mineral surfaces or Fe minerals dissolve to resupply solution Fe. The chelate-micronutrient "cycling" is an extremely important mechanism in soils that greatly contributes to plant available Fe and other micronutrients.

Factors Affecting Fe Availability

Soil pH and Bicarbonate Fe deficiency is most often observed on high-pH and calcareous soils in arid regions, but it can also occur in acid soils low in total Fe. Irrigation water and soils high in bicarbonate (HCO_3^-) may enhance Fe deficiency, due to high pH associated with HCO_3^- accumulation. Calcareous soil pH ranges from 7.3 to 8.5 (Chapter 3), coinciding with the highest incidence of Fe deficiency and lowest solubility of soil Fe (Fig. 8-2). HCO_3^- forms in calcareous soils by:

$$CaCO_3 + CO_2 + H_2O \leftrightarrows Ca^{+2} + 2HCO_3^-$$

Although the presence of $CaCO_3$ alone does not necessarily induce Fe deficiency, its interaction with certain soil environmental conditions is related to Fe stress.

Excessive Water and Poor Aeration The reaction just noted is promoted by accumulation of CO_2 in excessively wet and poorly drained soils. Consequently, any compact, fine-textured, calcareous soil is potentially Fe deficient. Fe chlorosis is often associated with cool, rainy weather when soil moisture is high and soil aeration is poor. Also, root development and nutrient absorption are reduced under cool, wet conditions, which contribute to Fe stress. High pH or HCO_3^--induced chlorosis often disappears when these soils dry. Flooding and submergence of soils where HCO_3^- formation is of no concern can improve Fe availability by increasing Fe^{+2} concentration.

Soil OM Although lime-induced Fe deficiency occurs in wet soils, low-OM, calcareous soils are often low in plant available Fe. This deficiency occurs especially on eroded portions of the field where the OM-rich topsoil has been removed, exposing calcareous subsoils. Land leveling for irrigation can also expose calcareous, low-OM subsoils. Additions of OM to well-drained soils can improve Fe availability. Organic materials such as manure may increase micronutrient solubility through chelation reactions. Improved soil structure in compacted soils with applications of organic wastes should also increase Fe availability by improved soil aeration.

Interactions with Other Nutrients Metal cations can interact with Fe to induce Fe deficiency. For example, high soil Cu following extended use of $CuSO_4$ as a fertilizer or fungicide can induce Fe stress in sensitive crops. Fe-sensitive crops exhibit Fe chlorosis when grown on soils high in Mn. Fe deficiency in soybeans can occur due to low Fe:(Cu + Mn) ratio in plants. In addition to Fe deficiency caused by excess Cu, Mn, Zn, and Mo, Fe-P interactions have been observed in some plants, probably related to precipitation of Fe-P minerals.

Plants receiving NO_3^- are more likely to develop Fe stress than those receiving NH_4^+. When a strong acid anion (NO_3^-) is absorbed and replaced with a weak acid (HCO_3^-), the pH of the root zone increases, particularly in low-buffered systems, which decreases Fe availability. Thus, Fe solubility and availability are favored by the acidity that develops when NH_4^+ is utilized by plants.

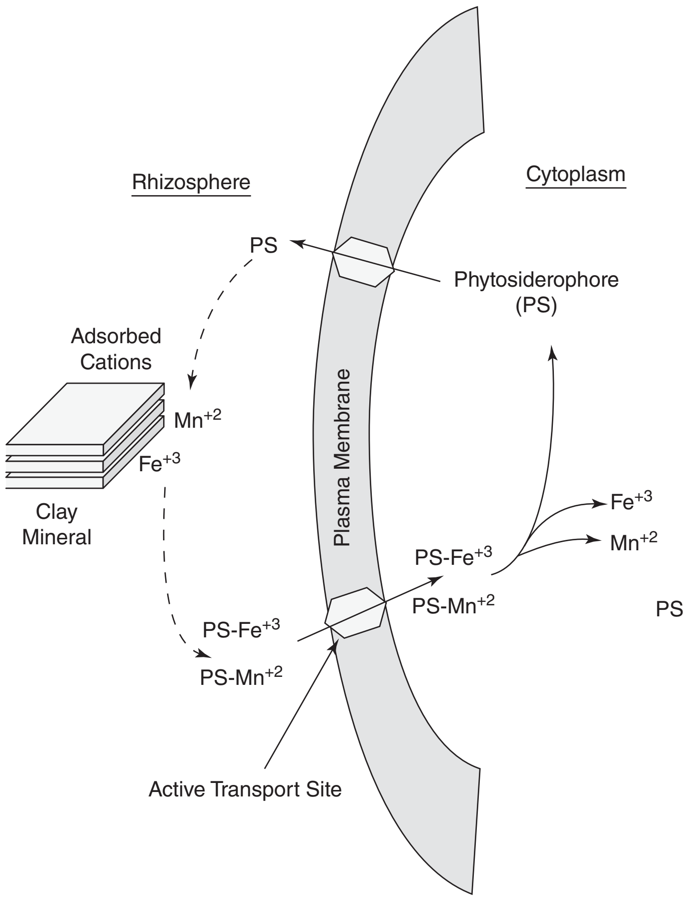
Plant Factors Although diffusion of both Fe^{+3} and Fe^{+2} to the root occurs, Fe^{+3} is reduced to Fe^{+2} before absorption. Plant genotypes differ in their ability to take up Fe and are classified according to their sensitivity or tolerance to low levels of available Fe (Table 8-2). Fe-efficient varieties should be selected where Fe deficiencies are likely to occur.

TABLE 8-2
GENERAL SENSITIVITY OF CROPS TO FE DEFICIENCY*

Sensitive	Moderately Tolerant	Tolerant
Azalea	Alfalfa	Amaranthus
Beans, snap	Asparagus	Barley
Berries	Barley	Flax
Blueberries	Cabbage	Grasses
Broccoli	Corn	Millet
Cauliflower	Cotton	Oat
Citrus	Field peas	Peppermint
Field beans	Flax	Potato
Flax	Forage legumes	Rice
Forage sorghum	Grasses	Sugar beet
Fruit trees	Orchard grass	Sunflower
Grain sorghum	Ornamentals	Wheat
Grapes	Rice	
Maple trees	Sweet corn	
Mint	Tomato	
Ornamentals	Turfgrasses	
Peanuts		
Pin oak		
Raspberries		
Rhododendron		
Soybean		
Spinach		
Strawberries		
Sudan grass		
Vegetables		
Walnut		

*Some crops exhibit variable sensitivity due to differences between varieties of a given crop.

Figure 8-4
Mechanism of enhancing Fe and Mn availability and transport through phytosiderophore (PS) complexes.



The ability of plants to absorb and translocate Fe appears to be a genetically controlled adaptive process that responds to Fe deficiency or stress. Roots of Fe-efficient plants alter their environment to improve Fe availability and uptake by (1) excretion of H^+ and organic acids from roots, (2) excretion of chelating compounds from roots, and (3) enhanced rate of Fe^{+3} to Fe^{+2} reduction at root surface.

Some plants exhibit a unique mechanism to tolerate low Fe availability. For example, grass roots release amino acids called *phytosiderophores* with a high affinity for Fe^{+3}. Phytosiderophore-Fe complexes enhance Fe transport to root surfaces and absorption by root cells (Fig. 8-4).

Fe Sources

Organic Fe Most animal wastes contain small quantities of plant available Fe, typically ranging between 0.02% and 0.1%. Thus, applying 4,000 lb waste/a (0.1% Fe) provides 4 lbs Fe/a. Although sufficient plant available Fe can be provided through manure application at appropriate rates, the major benefit of organic waste application is increased OM and associated chelation effects. Enhanced Fe chelation may supply sufficient plant available Fe, even if the manure contains no Fe. In contrast, municipal waste can contain as much as 5% Fe (Table 8-3).

Inorganic Fe Fe chlorosis is one of the most difficult micronutrient deficiencies to correct in the field. In general, soil applications of inorganic Fe are not effective in correcting Fe deficiency in high-pH soils because of rapid precipitation of insoluble $Fe(OH)_3$. For example, when $FeSO_4 \cdot 7H_2O$ and Fe-EDDHA were applied, only 20% was plant available with $FeSO_4$ after 1 week, compared with 70% and

TABLE 8-3
SOURCES OF FE FERTILIZER

Source	Formula	% Fe
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	19
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 4H_2O$	23
Ferrous oxide	FeO	77
Ferric oxide	Fe_2O_3	69
Ferrous ammonium phosphate	$Fe(NH_4)PO_4 \cdot H_2O$	29
Ferrous ammonium sulfate	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	14
Iron ammonium polyphosphate	$Fe(NH_4)HP_2O_7$	22
Iron chelates	NaFeEDTA	5–14
	NaFeEDDHA	6
	NaFeDTPA	10
Natural organic materials		5–10

25% plant available Fe with FeEDDA after 7 and 14 weeks, respectively (Fig. 8-5). $FeSO_4 \cdot 7H_2O$ applied with or near the seed can reduce Fe stress and increase yield; however, high Fe rates (30–70 lbs Fe/a) are required and Fe responses are greater under irrigated compared to dryland crops. Inorganic Fe applied to Fe-deficient acid soils provides sufficient Fe.

Fe deficiencies are corrected mainly with foliar application of inorganic Fe (Table 8-4). One application of a 2% $FeSO_4$ solution at 15–30 gal/a is usually sufficient to alleviate mild chlorosis. However, several applications at 7–14 days apart may be needed to remedy more severe Fe deficiencies. Fe salts injected directly into trunks and limbs of fruit trees are effective in controlling Fe chlorosis.

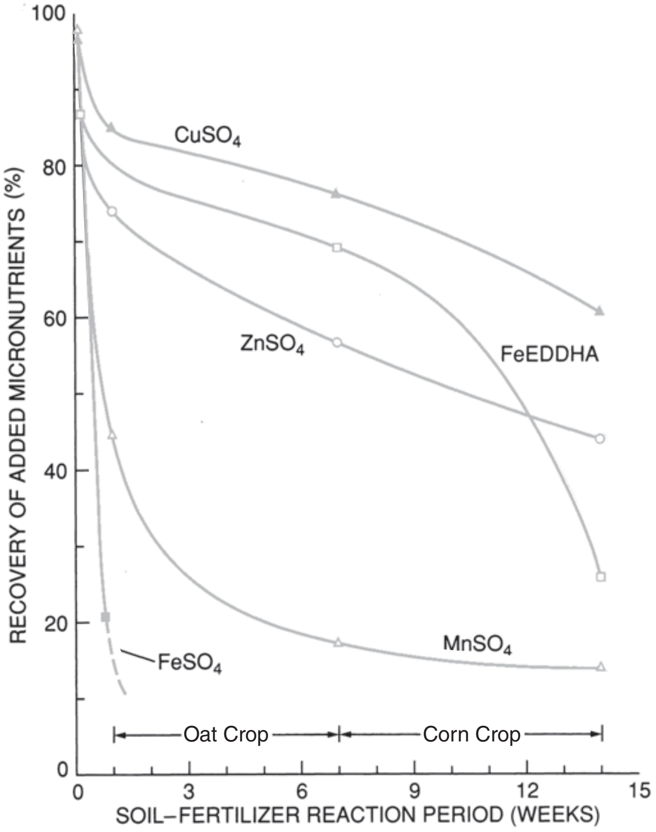


Figure 8-5
Recovery of micronutrients in soils fertilized with various inorganic micronutrient fertilizers.
(*Follett and Lindsay, 1971, SSSAJ, 35:600–602.*)

TABLE 8-4
EXAMPLES OF FE MANAGEMENT FOR SELECTED CROPS

Crop	Fe Source	Fe Rate	Application Method	Remarks
Vegetables	Fe chelates	0.5–1.0 lbs/a	Foliar	Wet leaves, repeat as needed
Citrus	Fe chelates	12–24 g/tree	Foliar	Wet leaves, repeat as needed
Corn, sorghum	$FeSO_4 \cdot 7H_20$	~1 lb/30 gal ~30 gal/a	Foliar	3 applications (2-week intervals)
Field (dry) beans	$FeSO_4 \cdot 7H_20$	~1lb/30 gal 20 gal/a	Foliar	2-week intervals until symptoms disappear
Deciduous fruits	Fe polyflavonoid	0.1–0.2 lb/25 gal	Foliar	Wet leaves, repeat as needed
Soybeans	$FeSO_4 \cdot 7H_20$ Fe chelates	~1 lb/30 gal 0.15 lbs/a Foliar	Foliar	Spray band over row at second trifoliate
Cotton	$FeSO_4 \cdot 7H_20$	1.0 lb Fe/25 gal	Foliar	Wet leaves, repeat as needed
Turfgrass	$FeSO_4 \cdot 7H_20$ Fe chelates	0.5–1.0 lbs/a 0.02 lbs/1,000 ft^2	Foliar	Wet leaves, repeat as needed

With the exception of $FeSO_4$, perhaps the most widely used Fe sources are the synthetic chelates (Table 8-3). Synthetic chelates (Fig. 8-6) are water soluble and can be applied to soil or foliage. Chelated Fe is protected from soil reactions that form insoluble $Fe(OH)_3$. The specific chelate applied depends on the micronutrient and the chelate stability in soil (Fig. 8-7). EDDHA will strongly complex Fe and is stable over the entire pH range. DTPA can be used for soil <pH 7.5, whereas Fe-EDTA is not stable applied to soils >pH 6.5. For example, when Fe-EDTA, Fe-DTPA, and Fe-EDDHA were applied to a high-pH, calcareous soil, EDDHA provided more

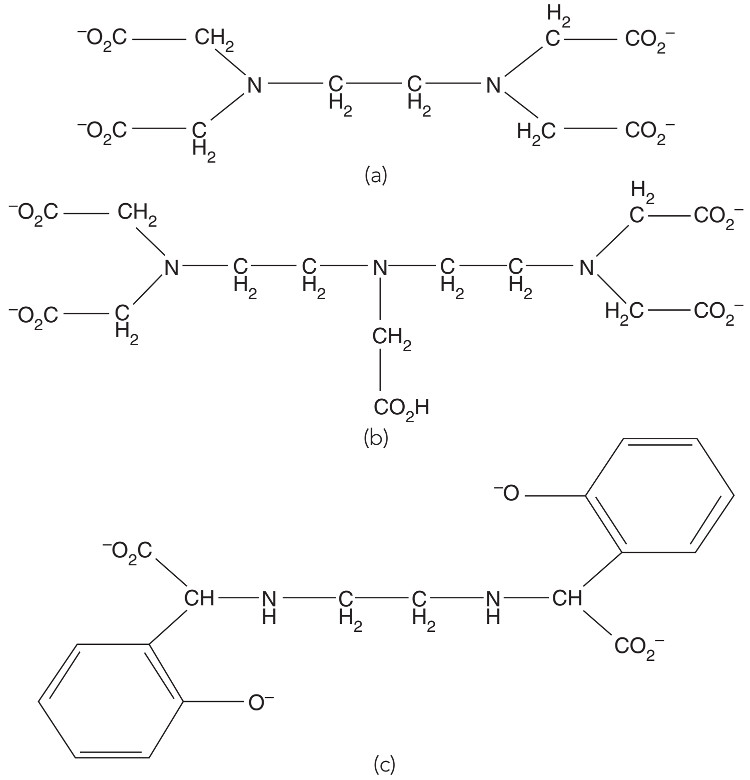


Figure 8-6
The structure of EDTA (a), DTPA (b), EDDHA (c), and Zn-EDTA (d). The COO$^-$ groups surround Zn^{+2} in a "claw" orientation (d)
(*Follett et al., 1981,* Fertilizers and Soil Amendments *Englewood Cliffs, NJ: Prentice-Hall.*)

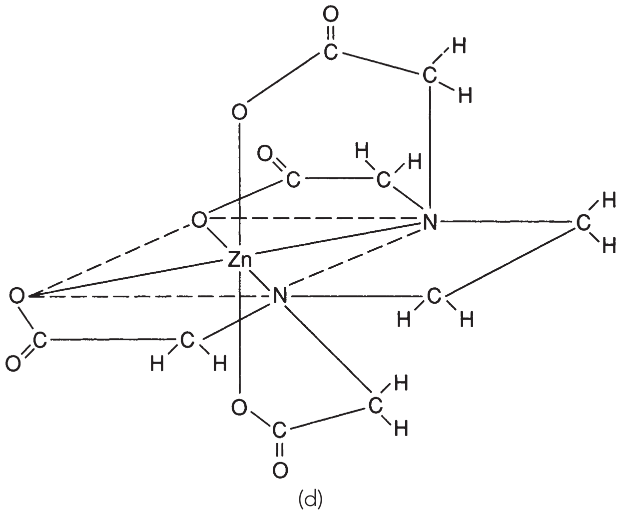


Figure 8-6
(Continued)

plant available Fe than the other chelates (Fig. 8-8). Since Fe-EDDHA is the most stable Fe chelate, it is the preferred chelate fertilizer source, although Fe-DTPA has also been used. Unfortunately, Fe chelates are expensive and their use is usually restricted to high-value horticultural crops.

Local root zone acidification can be effective in correcting Fe deficiencies in calcareous and high-pH soils. Several S products, such as S^0, ammonium thiosulfate, sulfuric acid, and ammonium polysulfide, will lower soil pH and increase solution Fe concentration. Complexing with polyphosphate fertilizers also increases Fe availability, but Fe-EDDHA is more effective than polyphosphate at the same Fe rates.

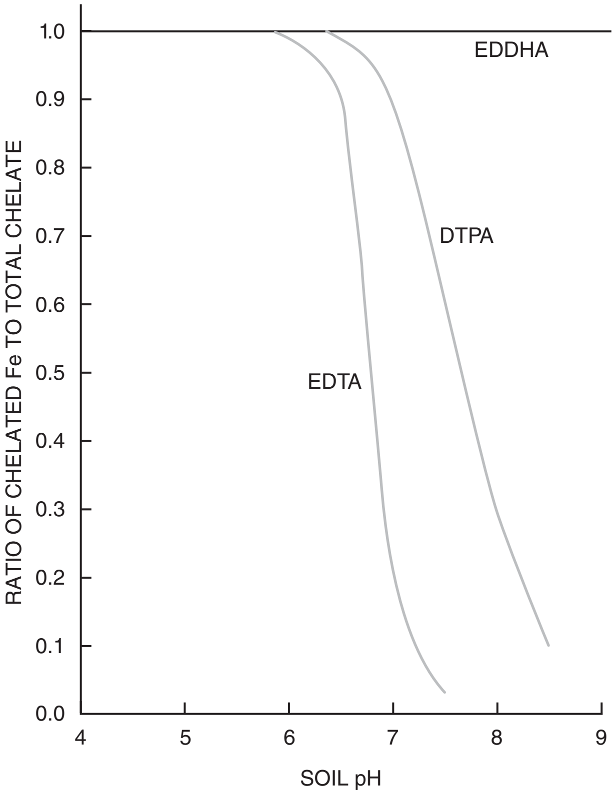


Figure 8-7
Stability of synthetic chelates with Fe in soils.
(*Norvell, 1972,* Micronutrients in Agriculture, *Madison,WI: ASA.*)

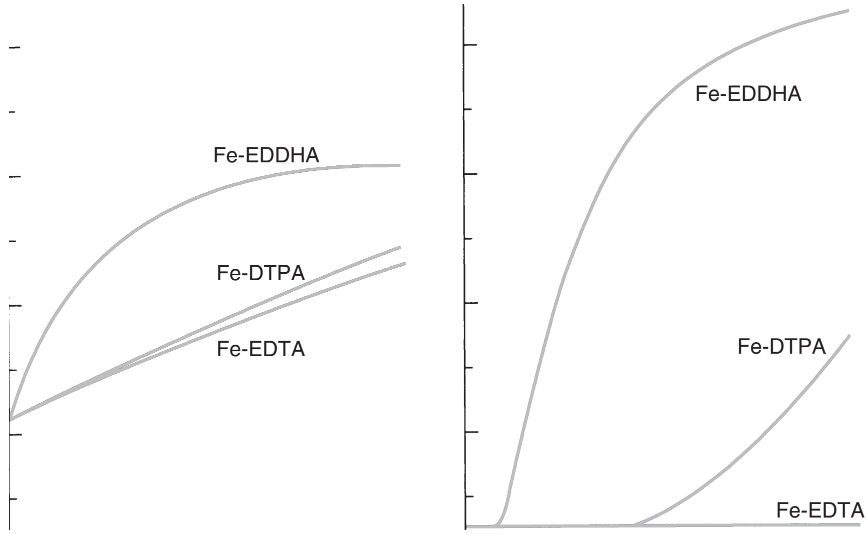


Figure 8-8
Effectiveness of synthetic Fe chelates in supplying Fe to Fe-deficient sorghum.
(*Lindsay and Novell, 1978,* SSSAJ *42:421–428*)

ZINC (Zn)

Zn Cycle

Plant available Zn is governed predominantly by Zn mineral solubility, soil OM, and Zn adsorbed on clay and OM surfaces soils (Fig. 8-1). Primary and secondary minerals dissolve to initially provide solution Zn, which is then adsorbed onto the CEC, incorporated into microbial biomass, or complexed by organic compounds in solution. Like Fe, chelated Zn is important to the transport of Zn to root surfaces for uptake.

Zn in Plants

Plant roots absorb Zn^{+2}, which is involved in many enzymatic activities. For example, Zn is essential for synthesis of tryptophane, a component of some proteins and a compound needed for the production of growth hormones (auxins) such as indoleacetic acid. Reduced growth hormone production in Zn-deficient plants causes shortening of internodes and smaller than normal leaves. Zn is also involved in chlorophyll synthesis, enzyme activation, and cell membrane integrity.

Zn deficiencies are widespread throughout the world, and can be identified by distinctive visual symptoms in leaves, but also can appear in fruit or storage organs, and in overall plant growth (see color plates). Common symptoms include:

- light green, yellow, or white areas between leaf veins, particularly in younger leaves
- eventual tissue necrosis in chlorotic leaf areas
- shortened stem or stalk internodes, resulting in stunted plants or bushy, rosetted leaves
- small, narrow, thickened leaves, often malformed by growth of only part of leaf tissue
- premature foliage loss
- malformation of fruit, often with little or no yield.

Zn deficiency causes characteristic *rosetting* or clustering of small leaves at the top of the plant. Rosetting commonly occurs in fruit and citrus trees. Under severe deficiency in corn, the leaf area between the midrib and leaf edge turns a distinctive white color. In small grains and other grasses, Zn deficiency depresses tillering, and the midrib at the base of young leaves becomes chlorotic. Eventually, older leaves exhibit brown spots or leaf tips turn yellow-orange, eventually progressing to the entire leaf. Under moderate Zn deficiency, symptoms may disappear after several weeks, although plant maturity is sufficiently delayed to limit yield.

Zn concentration in plants ranges between 25 and 150 ppm. Zn deficiencies are usually associated with concentrations of $<$10–20 ppm, depending on the crop, and toxicities occur with leaf Zn concentration $>$400 ppm. Zn toxicity reduces or ceases root growth, resulting in yellowing leaves and eventual plant death. Peanut and soybean are sensitive to high Zn, while most crops are tolerant.

Zn in Soil

Mineral Zn Zn content of the lithosphere is ≈70 ppm, and Zn in soil ranges from 10 to 300 ppm (50 ppm average). Igneous rocks contain ≈70 ppm Zn, while sedimentary rocks (shale) contain more Zn (95 ppm) than limestone (20 ppm) or sandstone (16 ppm). Franklinite ($ZnFe_2O_4$), smithsonite ($ZnCO_3$), and willemite (Zn_2SiO_4) are common Zn-containing minerals.

Soil Solution Zn Soil solution Zn^{+2} is low (2–70 ppb), with more than half complexed by OM. Above pH 7.7, $ZnOH^+$ becomes the most abundant species (Fig. 8-9). Zinc solubility is pH dependent, decreasing with increasing pH, given by:

$$\text{Soil-Zn} + 2H^+ \leftrightarrows Zn^{+2}$$

As a result of Zn^{+2} interactions with OM, thirtyfold reductions in solution Zn^{+2} typically have been observed for every unit pH increase between 5 and 7. Diffusion predominately transports Zn^{+2} to plant roots. Complexing agents or chelates from root exudates or from decomposing organic residues facilitate Zn^{+2} diffusion to roots (Fig. 8-3). Diffusion of chelated Zn^{+2} (and other micronutrients) can be significantly greater than that of unchelated Zn^{+2} (Fig. 8-10).

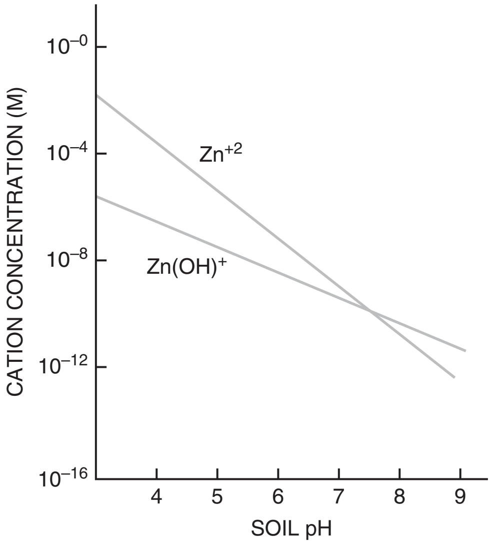
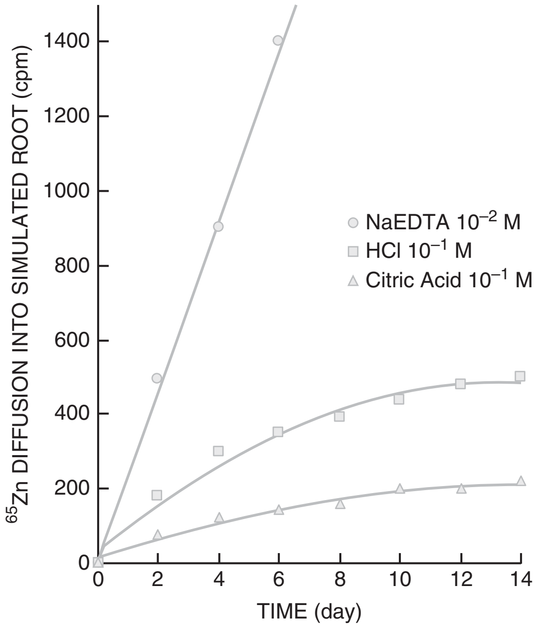


Figure 8-9
Common Zn species in soil solution as influenced by pH.

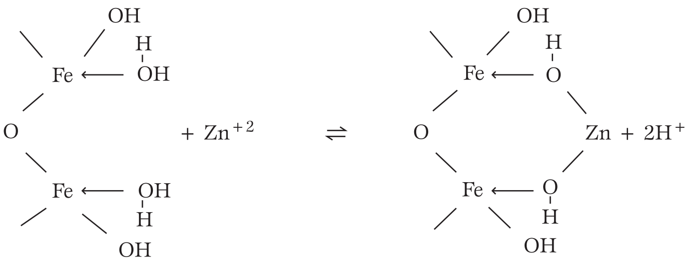
Figure 8-10
Effects of various complexing agents and acids on cumulative Zn diffusion into a simulated root.
(*Elgawhary et al., 1970, SSSAJ, 34:211*)



Factors Affecting Zn Availability

Soil pH Zn^{+2} availability decreases with increasing soil pH (Fig. 8-9). Most pH-induced Zn deficiencies occur in neutral and calcareous soils, although not all of these soils exhibit Zn deficiency because of increased availability from Zn^{+2} chelation (Fig. 8-3). At high pH, Zn precipitates as insoluble amorphous soil Zn, $ZnFe_2O_4$, and/or $ZnSiO_4$, which reduces solution Zn^{+2}. Liming acid soils, especially those low in Zn, will reduce Zn^{+2} uptake, which is related to pH effect on Zn^{+2} solubility. Zn^{+2} adsorption on $CaCO_3$, clay minerals, Al/Fe oxides, and OM surfaces also reduces solution Zn^{+2}, which increases with increasing pH (greater CEC).

Zn Adsorption The mechanism of Zn^{+2} adsorption on oxide surfaces is depicted as:



Zn^{+2} adsorption does not occur to any great extent on the CEC, at least compared to Ca^{+2} and Mg^{+2}. Zn is strongly adsorbed by magnesite ($MgCO_3$), and to a lesser extent by dolomite [$CaMg(CO_3)_2$], where Zn is adsorbed into the crystal surface at sites normally occupied by Mg atoms. Zn adsorption by $CaCO_3$ is partly responsible for reduced Zn^{+2} availability in calcareous soils, where Zn availability decreases with increasing $CaCO_3$ content (Fig. 8-11).

Soil OM Zn^{+2} forms stable complexes with high-molecular-weight organic compounds (i.e., lignin, humic, and fulvic acids) that exist as soluble or insoluble complexes. With insoluble complexes, Zn availability will be reduced as in Zn-deficient peats and humic soils. In mineral soils, formation of soluble chelated Zn complexes enhances availability by keeping Zn^{+2} in solution (Fig. 8-3). Substances present in or derived from freshly applied organic materials also have the capacity to chelate Zn^{+2}.

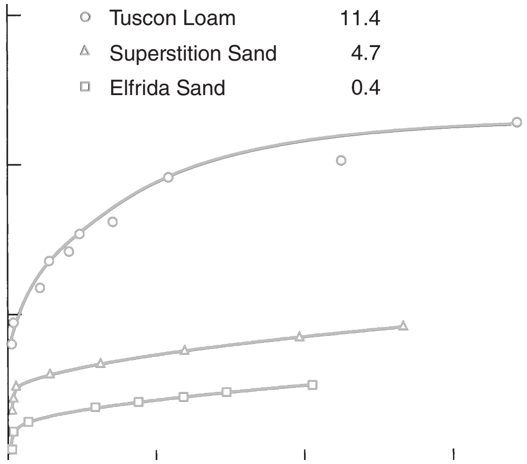


Figure 8-11
Zn adsorption in calcareous soils. (*Udo et al., 1970,* SSSAJ, *34:405*)

Interaction with Other Nutrients Other metal cations inhibit Zn^{+2} uptake, possibly because of competition for the same carrier site in the casparian bands or plasmalemma (Chapter 2). The antagonistic effect is especially prevalent with Cu^{+2} and Fe^{+2}.

High P-availability can induce Zn deficiency, commonly in soils that are marginally Zn deficient. With Zn-deficient plants, cellular regulation of P uptake is impaired, causing absorption of toxic levels of P and translocation to plant tops, creating symptoms resembling Zn deficiency. Mycorrhizae can increase P and micronutrient uptake by many plants; however, P fertilization can suppress mycorrhizal uptake of Zn and induce Zn deficiency.

Flooding When soils are submerged, concentration of many nutrients increases, but not Zn. In acid soils, Zn deficiency may be attributed to increased pH under reducing conditions and subsequent precipitation of franklinite ($ZnFe_2O_4$) or sphalerite (ZnS). Decreasing pH in submerged, calcareous soils would usually increase Zn solubility. However, with high pH and poor aeration, potential Zn deficiency is aggravated.

Climatic Conditions Zn deficiencies are more pronounced during cool, wet seasons and often disappear in warmer weather. Climatic conditions during early spring that can contribute to Zn deficiency are low light intensity, low temperature, and excessive moisture. Increasing soil temperature increases Zn availability by increasing Zn^{+2} solubility and diffusion.

Plant Factors Plant species and varieties differ in their susceptibility to Zn deficiency (Table 8-5). Corn and beans are very susceptible to low Zn. Fruit trees in general, and citrus and peach in particular, are also sensitive. Cultivars differ in their ability to take up Zn, which may be caused by differences in Zn translocation and utilization, different accumulations of nutrients that interact with Zn, and differences in roots and mycorrhizal infection.

Zn Sources

Organic Zn Most animal wastes contain small quantities of plant available Zn, typically ranging from 0.01% to 0.05%. With large manure-application rates, sufficient plant available Zn can be provided. As a result of Zn additions to animal diets,

TABLE 8-5
CROP SENSITIVITY TO ZN DEFICIENCY*

High Sensitivity	Mild Sensitivity	Low Sensitivity
Apples	Alfalfa	Asparagus
Beans, lima beans	Barley	Carrots
Castor bean	Clover	Forage grasses
Citrus	Cotton	Mustard and other crucifers
Corn	Lettuce	Oats
Flax	Potato	Peas
Fruit trees (deciduous)	Sorghum	Peppermint
Grapes	Sugar beet	Rye
Hops	Tomato	Safflower
Onion	Wheat	
Pecan		
Pine		
Rice		
Soybean		
Sudan grass		
Sweet corn		

*Some crops exhibit variable sensitivity due to differences between varieties of a given crop.

combined with annual manure applications, plant available Zn can increase to very high levels. In some cases, extremely high Zn levels have prevented production of sensitive crops (e.g., peanuts). The primary benefit of organic waste application is increased OM and associated natural chelation properties that increase solution Zn concentration and plant availability. Zn content in municipal waste varies greatly depending on the source, with an average Zn content of 0.5%.

Inorganic Zn Zinc sulfate ($ZnSO_4$) is the most common Zn fertilizer source, although use of Zn chelates has increased (Table 8-6). Inorganic Zn sources are satisfactory fertilizers because they are soluble in soils. Fertilizer Zn rates depend on the crop, Zn source, method of application, and severity of Zn deficiency. Rates usually range from 1 to 10 lbs/a with inorganic Zn and from 0.5 to 2.0 lbs/a with chelate or organic Zn sources (Table 8-7). For most field and vegetable crops, 10 lbs/a is recommended in clay and loam soils and 1 to 5 lbs/a in sandy soils. In most cropping situations, applications of 10 lbs/a of Zn can be effective for 2 to 3 years.

TABLE 8-6
SOURCES OF FERTILIZER ZN

Source	Formula	% Zn
Zinc sulfate monohydrate	$ZnSO_4 \cdot H_2O$	35
Zinc oxide	ZnO	78
Zinc carbonate	$ZnCO_3$	52
Zinc phosphate	$Zn_3(PO_4)_2$	51
Zinc chelates	$Na_2ZnEDTA$	9–14
Zinc ligninsulfonate		5–12
Zinc polyflavonoid		7–10

TABLE 8-7

EXAMPLES OF ZN MANAGEMENT FOR SELECTED CROPS

Crop	Zn (lb/a)	Source	Application Method	Comments
Corn	4–10 1–2	$ZnSO_4$, ZnO Zn chelate	Broadcast Banded	Reduce rates for higher soil test Zn levels
Sorghum	3–9 1–2	$ZnSO_4$, ZnO Zn chelate	Broadcast Banded	Reduce rates for higher soil test Zn levels
Soybean	2–3 1–2	$ZnSO_4$, ZnO Zn chelate	Broadcast Banded	Reduce rates for higher soil test values
Rice	7–10 1	$ZnSO_4$, ZnO Zn chelate	Broadcast preplant banded	Reduce rates for higher soil test values
Dry beans	3–4 0.5–3	$ZnSO_4$, ZnO Zn chelate	Broadcast Banded	Reduce rates for higher soil test values
Citrus	0.5 lbs Zn/ 25 gal H_2O	$ZnSO_4$	Foliar	Wet foliage, repeat until symptoms disappear
Pecans	0.05 − 0.1 lb Zn/25 gal H2O; 100 gal/a	$Zn(NO_3)_2$	Foliar	5 applications starting at bud break, repeated weekly
Snap beans, onion, lima beans, potato	0.5–1.0 0.2–0.5 0.1	Zn chelate	Broadcast Banded Foliar	Repeat foliar until symptoms disappear or leaf analysis confirms adequate Zn
Turfgrass	0.44 lbs/a 0.01 lbs/1,000 ft^2	$ZnSO_4$ or chelate	Foliar or broadcast	Annual foliar or every 3–4 years soil appl.

Because of limited Zn mobility in soils, broadcast Zn should be thoroughly incorporated into the soil; however, band application may be more effective, especially in fine-textured and very low-Zn soils. The efficiency of band-applied Zn can be improved by combining with acid-forming N and S fertilizers.

With perennial crops, preplant soil applications of Zn are effective at rates between 20 and 100 lbs/a. Soil applications are of only limited value after these crops have been established. Foliar Zn application is recommended for turfgrass and tree crops. Sprays containing 10 to 15 lbs/a of Zn are usually applied to dormant orchards, whereas 2 to 3 lbs/a can be foliar applied to growing crops. Damage to foliage can be prevented by adding lime to the solution or by using less-soluble materials such as ZnO or $ZnCO_3$. Other methods include seed coatings, root dips, and tree injections. The former treatment may not supply enough Zn for small-seeded crops, but dipping potato seed pieces in a 2% ZnO suspension is satisfactory.

Foliar applications of chelates and natural organics are particularly suitable for rapid recovery of Zn-deficient seedlings. Chelated Zn can be used in high-analysis liquid fertilizers because of their high solubility and compatibility. ZnEDTA or ZnDTPA can be soil applied; however, high cost usually limits their use. In general, Zn chelates are more effective than inorganic Zn at similar rates of application (Table 8-8). Foliar-applied Zn is more effective than soil-applied Zn.

COPPER (Cu)

Cu Cycle

Cu cycling in soils is very similar to that described for Fe and Zn (Fig. 8-1). Soil solution Cu and plant available Cu are governed predominantly by solution pH and Cu adsorbed on clay and OM surfaces. Primary and secondary minerals dissolve to

TABLE 8-8
COMPARISON OF ZN SOURCES AND APPLICATION METHODS ON LEAF ZN CONTENT OF SELECTED CROPS*

		Soil-Applied	Foliar Applied		
		$ZnSO_4$	$ZnSO_4$		ZnEDTA
Crop	Control	(20 kg/ha)	(0.5 kg/ha)	(1.0 kg/ha)	(0.42 kg/ha)
	mg Zn/kg				
Alfalfa	22	37	39	50	43
Ryegrass	18	28	46	61	63
Wheat	17	21	31	41	51
Barley	21	30	43	43	54

*Zn application rates shown in parentheses. *Adapted from* Gupta, 1989, *Can. J. Soil Sci.*, 69: 473.

initially supply solution Cu, which is then adsorbed on mineral and OM surfaces, incorporated into microorganisms, and complexed by soluble organic compounds. A significant "pool" of organically complexed Cu in equilibrium with solution Cu contributes to Cu^{+2} diffusion to plant roots.

Cu in Plants

Plants absorb Cu^{+2}. Normal Cu concentration in plant tissue ranges from 5 to 20 ppm. Deficiencies are probable at <4 ppm Cu. Once absorbed, Cu^{+2} is readily reduced to Cu^{+} and donates an electron to reduce O_2. The ease with which Cu accepts and donates electrons enables it to function in many oxidation-reduction reactions in plants.

Photosynthesis and Respiration Both photosynthesis (reduction of CO_2 to carbohydrates) and respiration (oxidation of carbohydrates to CO_2) involve the transfer of electrons that requires Cu. Fe and Mn are also involved in electron transfer, but they cannot replace Cu. Electron transfer reactions involved in photosynthesis and respiration produce adenosine triphosphate (ATP), which is the primary energy source for synthesis of proteins, lipids, cell wall membranes, and for active nutrient uptake (Chapter 2). Approximately 50% of Cu in the chloroplast is found in *plastocyanin,* a protein involved in energy transfer in photosynthesis reactions. Cu is part of the enzyme *cytochrome oxidase* that catalyzes electron transfer in respiration.

Lignin Formation in Cell Walls Lignin is a constituent in cell walls that imparts strength and rigidity, essential for erect stature of plants. Several enzymes (polyphenol oxidase and diamine oxidase) important to synthesis of lignin contain Cu. Cu deficiency results in deformed leaves and stems, which increases potential for lodging. Lignin also aids natural plant resistance to diseases. Cu-deficient plants are more susceptible to disease.

Carbohydrate and Lipid Metabolism If photosynthesis is impeded by Cu deficiency during the vegetative growth stage, then carbohydrate production and plant growth are reduced. During the reproductive growth stage, carbohydrates accumulate because Cu deficiency impedes pollination and seed set. Reduced seed development, even under reduced photosynthesis, causes carbohydrates to accumulate since carbohydrate storage organs (seeds, fruits, etc.) are not present. Cu deficiency also alters lipid structure in cell membranes that is essential for low-temperature tolerance and resistance to other environmental stresses.

Cu Deficiency and Toxicity Although Cu deficiencies are not as common as other micronutrient deficiencies, they do occur in sensitive crops grown on low-Cu soils. Symptoms of Cu deficiency vary with the crop, but chlorosis in young leaves is a common symptom, because of the Cu-containing enzyme function in the chloroplasts. In corn and small grains, young leaves become yellow and stunted, and as the deficiency progresses, young leaves turn pale and older leaves die back. In advanced stages, necrosis along leaf tips and edges appears similar to K deficiency. Stem melanosis, take-all root rot, and ergot infection can occur in Cu-deficient small grains. In many vegetable crops, leaves lack turgor, develop a bluish-green cast, and become chlorotic, and curl, and flower production fails to take place. Lodging, wilting, and increased incidence of disease is observed due to reduced lignification with low Cu.

Cu toxicity symptoms include reduced shoot vigor, poorly developed and discolored root systems, and leaf chlorosis. The chlorotic condition in shoots superficially resembles Fe deficiency. Toxicities are uncommon, occurring in limited areas of high-Cu availability; after additions of high-Cu materials such as biosolids, swine and poultry manures, and mine wastes; and from repeated use of Cu-containing pesticides. In some plants (e.g., turfgrass), leaf tissue analysis will not identify Cu toxicity because the severe root system damage reduces Cu translocation to leaves. Cu toxicity in most plants occurs at >20 ppm Cu. Cu-containing fungicides (i.e., Bordeaux mixtures) are commonly used on many perennial fruit crops to control fungal diseases on leaves and fruit. Continued use can increase plant available Cu in soil, resulting in increased potential for Cu toxicity.

Cu in Soil

Mineral Cu Cu concentration in the earth's crust averages about 50–70 ppm. Igneous rocks contain 10–100 ppm Cu, while sedimentary rocks contain 4–45 ppm Cu. Total Cu concentration in soils ranges from 1 to 40 ppm and averages about 9 ppm Cu; however, in deficient soils, soil Cu may be 1–2 ppm. Malachite $[Cu_2(OH)_2CO_3]$ and cupric ferrite ($CuFe_2O_4$) are important Cu-containing primary minerals. Secondary Cu minerals include oxides, carbonates, silicates, sulfates, and chlorides, but most are too soluble to persist.

Soil Solution Cu Solution Cu concentration is usually low, ranging between 10^{-6} and 10^{-8} M (Fig. 8-12). The dominant solution species are Cu^{+2} at pH<7 and $Cu(OH)_2^0$ at pH>7. Cu^{+2} solubility is pH dependent, increasing with decreasing pH, as shown by:

$$\text{Soil-Cu} + 2H^+ \Longleftrightarrow Cu^{+2}$$

Cu is supplied to plant roots by diffusion of organically bound, chelated Cu, similar to chelated Fe diffusion (Fig. 8-3). Organic compounds in the soil solution are capable of chelating solution Cu^{+2}, which increases the solution Cu^{+2} concentration above that predicted by Cu mineral solubility.

Adsorbed Cu Cu^{+2} (and $CuOH^+$) is chemically adsorbed to surfaces of clays; OM; and Fe, Al, or Mn oxides. With the exception of Pb^{+2} and Hg^{+2}, Cu^{+2} is the most strongly adsorbed divalent metal to Fe/Al oxides. The adsorption mechanism with oxides is unlike electrostatic attraction of Cu^{+2} on the CEC of clay particles, and involves formation of Cu-O-Al or Cu-O-Fe surface bonds (Fig. 8-13). This

Figure 8-12
Common Cu species in soil solution as influenced by pH.

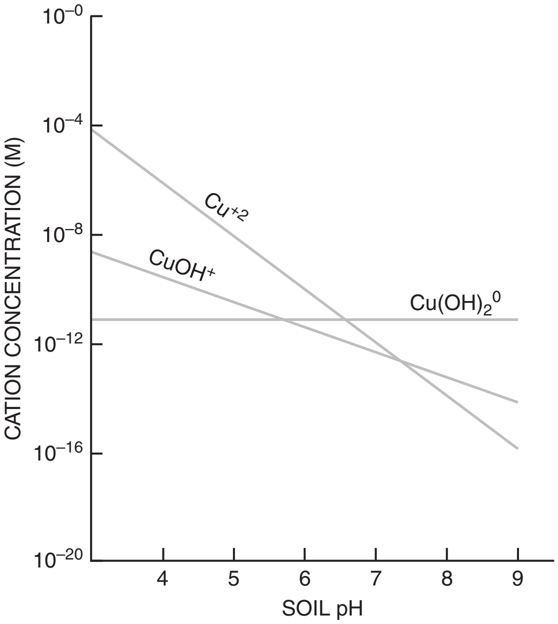
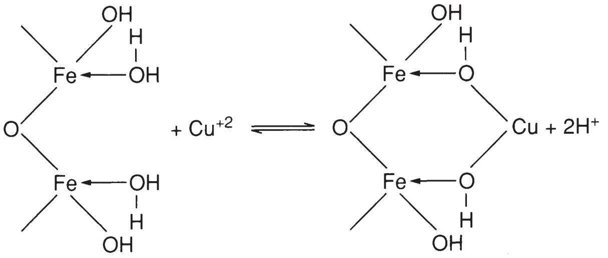


Figure 8-13
Chemisorption of Cu^{+2} *with surface hydroxyls on* $Fe(OH)_3$.



chemisorption process is controlled by the quantity of surface OH-groups. Cu adsorption increases with increasing pH due to (1) increased pH-dependent sites on clay and OM, (2) reduced competition with H^+, and (3) a change in the hydrolysis state of Cu in solution. As pH increases, hydrolysis of Cu^{+2} adsorbed on the CEC decreases exchangeable Cu^{+2} and increases chemisorbed Cu (i.e., decreasing H^+ shifts equilibrium to the right in Fig. 8-13).

Occluded and Coprecipitated Cu A significant fraction of soil Cu is occluded, or buried, in various mineral structures, such as clay minerals and Fe, Al, and Mn oxides. Cu is capable of isomorphic substitution in octahedral positions of silicate clays (Chapter 2). It is present as an impurity within $CaCO_3$ and $MgCO_3$ in arid soils and within $Al(OH)_3$ and $Fe(OH)_3$ in acid soils.

Organic Cu Most of the soluble Cu^{+2} in surface soils is organically complexed and is more strongly bound to OM than any other micronutrient. Cu^{+2} is directly bonded to two or more organic functional groups, chiefly carboxyl or phenol (Fig. 8-14). Humic and fulvic acids contain multiple Cu^{+2} binding sites, primarily carboxyl groups. In most mineral soils, OM is intimately associated with clay, as clay-metal-organic complexes (Fig. 8-15).

At $<8\%$ soil OM, both organic and mineral surfaces are involved in Cu adsorption, while at $>8\%$ OM, binding of Cu takes place mostly on organic surfaces. Thus, Cu deficiency frequently occurs in peat and muck soils. For soils with similar clay and OM contents, the contribution of OM to complexing of Cu is highest with 1:1 versus 2:1 clays.

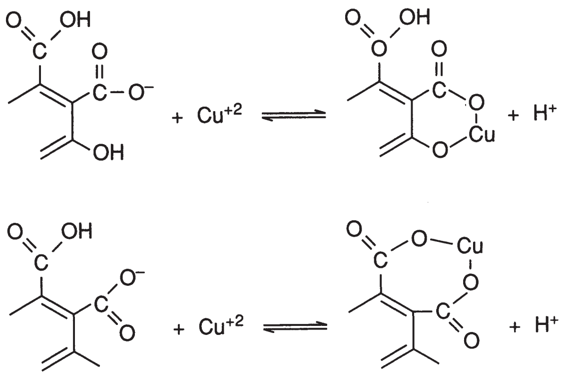


Figure 8-14
Mechanism of Cu complexed by organic matter.
(*Stevenson and Ardakani, 1972, Micronutrients in Agriculture, p. 90, Madison, WI:ASA.*)

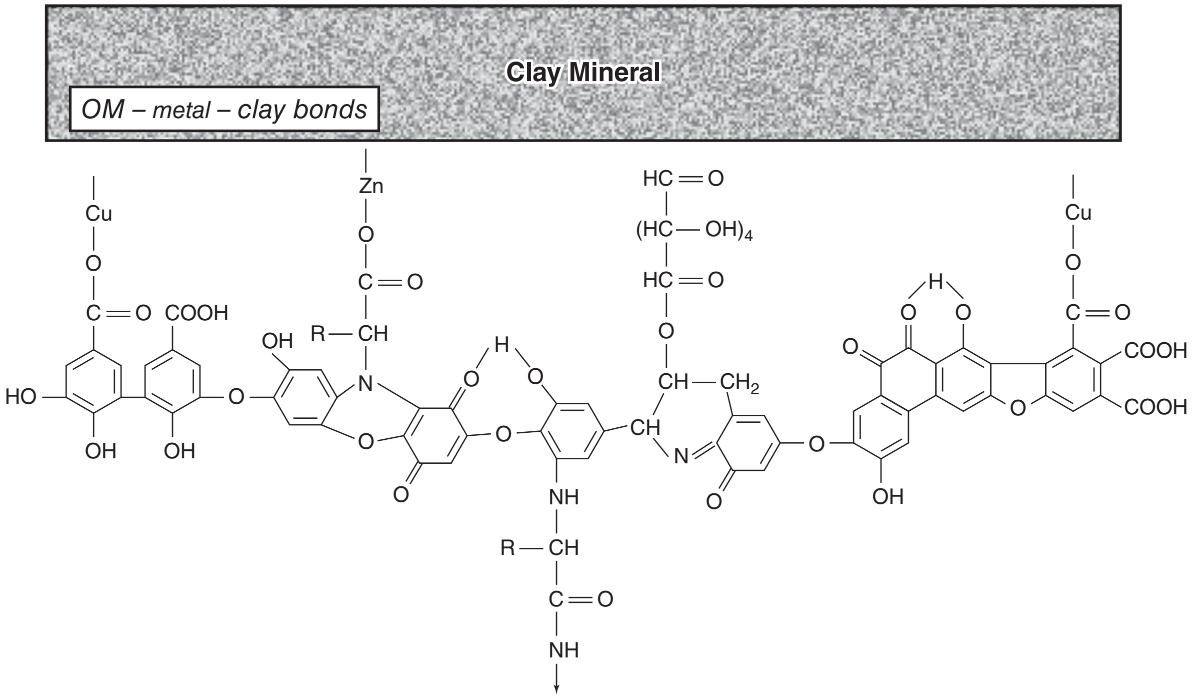


Figure 8-15
Theoretical structure of the clay-micronutrient (metal)-OM complex.

Factors Affecting Cu Availability

Texture The potential for Cu deficiency is greater in excessively leached, coarse-textured soils.

Soil pH Solution Cu decreases with increasing pH due to decreased mineral solubility and increased adsorption.

Interactions with Other Nutrients High Zn, Fe, and P concentrations in soil solution can depress Cu absorption by roots and intensify Cu deficiency. Increased growth response to N or other nutrients may be proportionally greater than Cu uptake, which dilutes Cu concentration in plants. Also, increasing N in plants impedes Cu translocation from older to newer leaves.

TABLE 8-9
CROP SENSITIVITY TO CU DEFICIENCY*

High Sensitivity		*Mild Sensitivity*		*Low Sensitivity*	
Alfalfa	Lettuce	Apples	Cucumber	Beans	Potato
Beets	Onion	Barley	Oats	Beans, snap	Rapeseed
Canary seed	Rice	Blueberries	Parsnips	Canola	Rye
Carrots	Spinach	Broccoli	Radishes	Forage grasses	Soybean
Citrus	Sudan grass	Cabbage	Strawberries		Turfgrasses
Flax	Wheat	Cauliflower	Sweet corn	Grapes	
		Celery	Timothy	Lupine	
		Clover	Tomato	Peas	
		Corn	Turnip		

*Some crops exhibit variable sensitivity due to differences between varieties of a given crop.

Plant Factors Crops vary greatly in their sensitivity to Cu (Table 8-9). Among small grains, rye tolerates low soil-Cu, whereas wheat is highly sensitive. Rye absorbs nearly twice as much Cu as wheat under the same conditions. Varietal differences in tolerance to low Cu can be as large as those among crop species. Genotypic differences are related to (1) differences in Cu absorption rates, (2) greater soil exploration due to greater root mass and/or root hairs, (3) increased Cu solubility due to root exudate influence on soil pH or redox potential, (4) more efficient Cu transport from roots to shoots, and/or (5) lower Cu requirement. Severe Cu deficiency may also occur in crops planted into soils with actively degrading, high C:N residues and is related to (1) Cu complexing with organic compounds originating from decomposing residue, (2) competition for available Cu by a stimulated microbial population, and (3) inhibition of root development and the ability to absorb Cu.

Cu Sources

Organic Cu Although most animal wastes contain small quantities of plant available Cu (0.002%–0.03%), elevated Cu levels occur in swine manure because of Cu added to the feed. Consequently, continued application might create toxic levels of soil Cu, especially with sensitive crops like peanut. With most manures, average application rates provide sufficient plant available Cu. As with Fe and Zn, the primary benefit of organic waste application is increased OM and associated natural chelation properties that increase Cu availability. Cu content in municipal waste is $\approx 0.1\%$, but varies greatly depending on source.

Inorganic Cu The most common Cu source is $CuSO_4 \cdot 5H_2O$, although CuO, mixtures of $CuSO_4$ and $Cu(OH)_2$, and Cu chelates are also used (Table 8-10). $CuSO_4$ is soluble in water and is compatible with most fertilizers. $CuNH_4PO_4.H_2O$ is slightly water soluble, but can be suspended and soil or foliar applied.

Soil and foliar applications are both effective, but soil applications are more common; with Cu rates of 1–20 lbs/a needed to correct deficiencies (Table 8-11). Effectiveness is increased by thoroughly mixing Cu fertilizers into the root zone or by banding near the seed row. Potential root injury exists with high band-applied Cu rates. Additions of Cu can be ineffective when root activity is restricted by excessively wet or dry soil, root pathogens, and toxicities or deficiencies of other nutrients. Residual Cu fertilizer availability can persist for 2 or more years, depending on the soil, crop, and Cu rate.

Table 8-10
Common Cu Fertilizers

Source	Formula	% Cu
Copper sulfate	$CuSO_4 \cdot 5H_2O$	25
Copper sulfate monohydrate	$CuSO_4 \cdot H_{2O}$	35
Copper acetate	$Cu(C_2H_3O_2)_2 \cdot H_2O$	32
Copper ammonium phosphate	$Cu(NH_4)PO_4 \cdot H_2O$	32
Copper chelates	Na_2Cu EDTA	13
Organics	-	<0.5

Table 8-11
Examples of Cu Management for Selected Crops

Crops	Cu Source	Rate (lb Cu/a)	Method
Small grains	$CuSO_4 \cdot 5H_2O$	1–5	Banded
	CuO	3–12	Broadcast
	Cu chelates	0.5–2.0	Banded
	Cu chelates	0.1% solution	Foliar
Corn	$CuSO_4 \cdot 5H_2O$	3–12	Broadcast
	CuO	1–2	Banded
	Cu chelates	0.2–0.4	Banded
Soybeans	$CuSO_4 \cdot 5H_2O$	2–4	Broadcast
		1–2	Banded
Citrus	$CuSO_4 \cdot 5H_2O$	5–20	Broadcast
		0.1% solution	Foliar
Turfgrass	$CuSO_4 \cdot 5H_2O$	0.13	Foliar
	Cu chelates		

Cu application in foliar sprays is confined mainly to emergency treatment of deficiencies identified after planting. In some areas, however, Cu is included in regular foliar spraying programs. Cu chelates (CuEDTA) can be used as a foliar Cu fertilizer; however, soil application is more effective (Table 8-12). These data also show that fall-applied $CuSO_4$ is more effective than spring applications to barley, likely because the material has more time to dissolve and move into the root zone.

Table 8-12
Effect of Cu Fertilizers on Barley Yield

	Application		Cu Rate	Yield
			kg/ha	
$CuSO_4$	Fall	Broadcast/	10	3070
	Spring	Incorporate	10	2370
	Spring		5	1890
CuEDTA	Spring	Broadcast/	2	2960
	Spring	Incorporate	1	2700
	Foliar		1	2100

Source: Manitoba Agric. Agdex No. 541 MG#1853, 1990.

MANGANESE (Mn)

Mn Cycle

The equilibrium among solution, exchangeable, organic, and mineral forms determines Mn availability to plants (Fig. 8-1). The major processes are Mn oxidation-reduction and complexing solution Mn with natural organic chelates. Like Fe, the continuous cycling of OM significantly contributes to soluble Mn. Factors influencing the solubility of soil Mn include pH, redox, and organic complexation. Soil moisture, aeration, and microbial activity influence redox, while complexation is affected by OM and microbial activity.

Mn in Plants

Plants absorb Mn^{+2} and low-molecular-weight organically complexed Mn. Mn concentration in plants typically ranges from 20 to 500 ppm, while Mn-deficient plants contain <15–20 ppm Mn. Mn^{+4} must be reduced to Mn^{+2} for absorption by roots by:

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{+2} + 2H_2O$$

Low-molecular-weight organic compounds are exuded by roots into the rhizosphere. Microbial degradation of these exudates establishes reducing conditions and provides electrons to reduce Mn^{+4} to Mn^{+2} for absorption.

Mn^{+2} enters root cells through the plasmalemma by a specific transporter protein that establishes an electrical gradient where the cell wall is more (+) than the cell interior (Fig. 8-4). Few other cations compete with Mn^{+2} for transport across membranes, which is unique since other cations compete with each other (e.g., Cu^{+2} and Zn^{+2}). However, high concentrations of Ca^{+2} and Mg^{+2} adsorbed to apoplasmic (root) cell walls, especially in high-pH soils, can reduce Mn^{+2} adsorption to cell walls and eventual transport into the cell. Mn is essential to photosynthesis reactions, enzyme activation, and root growth.

O_2 and Photosynthesis Most O_2 in the atmosphere originates from Mn-facilitated electron transfer in photosynthesis. Photosynthetic reduction of CO_2 to carbohydrates $[(CH_2O)_n]$, given by:

$$CO_2 + 2H_2O \xrightarrow{\text{light}} (CH_2O)_n + O_2 + H_2O$$

involves several electron transfer steps. When chlorophyll absorbs light energy, it is oxidized (loses an electron) and provides the energy to reduce CO_2. The oxidized chlorophyll accepts electrons from a Mn-containing protein. When Mn donates electrons to chlorophyll, the oxidized Mn protein will oxidize H_2O to produce O_2:

$$2H_2O + 4Mn^{+3} \longrightarrow 4Mn^{+2} + O_2 + 4H^+$$

The reduced Mn protein again donates electrons to another photo-oxidized chlorophyll molecule. Therefore, Mn is essential to electron transfer through chlorophyll to reduce CO_2 to carbohydrate and produce O_2 from H_2O.

Reducing agents formed in cellular reactions can donate an electron to O_2, forming the superoxide free radical O_2^-. Free radicals are highly reactive and toxic to cellular metabolic reactions (e.g., chlorophyll degradation). Superoxide dismutase (SOD) enzymes are produced to readily convert O_2^- to O_2. Fe-SOD and CuZn-SOD occur in chloroplasts, while Mn-SOD occurs in mitochondria. This protection mechanism is especially important in plants grown under high light intensity where potential free radical production and photo-oxidative damage is the greatest.

Mn and Lignin Synthesis Like Cu, Mn activates several enzymes that synthesize several amino acids and phenols important to lignin production. In addition to lignin, these compounds are used to synthesize phenolic acids and alcohols that provide resistance to infection by pathogens.

Mn Deficiency and Toxicity Because of its essential role in photosynthesis, root and shoot growth rates are substantially reduced in Mn-deficient plants. As a result, N and P accumulate, which increases potential for root and leaf diseases. Mn deficiency also restricts formation of lignin and phenolic acids that also help reduce incidence of diseases. Soil fungi that generally do not infect plant roots can cause disease in Mn-deficient plants. For example, grasses low in Mn are often more susceptible to root-rot diseases.

Mn is immobile in the plant, so younger leaves initially exhibit deficiency symptoms. Mn deficiency produces interveinal chlorosis in most crops. In some crops, low-Mn-related chlorosis of younger leaves can be mistaken for Fe deficiency. Mn deficiency of several crops has been described by such terms as gray speck (oat), marsh spot (pea), and speckled yellows (sugar beet). Mn toxicity occurs in sensitive crops grown on acid soils and poorly drained or waterlogged soils. Mn toxicity occurs at >500-1000 ppm Mn, depending on specie. Crinkle leaf in cotton is commonly observed. Liming will readily correct this problem.

Mn in Soil

Mineral Mn Mn concentration in the earth's crust averages ≈1,000 ppm, and Mn is found in most Fe-Mg rocks. Mn, when released through weathering of primary rocks, will combine with O_2 to form secondary minerals, including pyrolusite (MnO_2), hausmannite (Mn_3O_4), and manganite (MnOOH). Pyrolusite and manganite are the most abundant.

Total Mn in soils generally ranges between 20 and 3,000 ppm and averages about 600 ppm. Mn in soils occurs as various oxides and hydroxides coated on soil particles, deposited in cracks and veins, and mixed with Fe oxides and other soil constituents.

Soil Solution Mn Mn^{+2} is the common form in solution; its concentration decreases hundredfold for each unit increase in pH (Fig. 8-16), similar to the behavior of other divalent metal cations (Fig. 8-2). Mn^{+2} concentration is predominantly controlled by MnO_2, and ranges from 0.01 to 1.0 ppm, with organically complexed Mn^{+2} comprising >90% of solution Mn^{+2}.

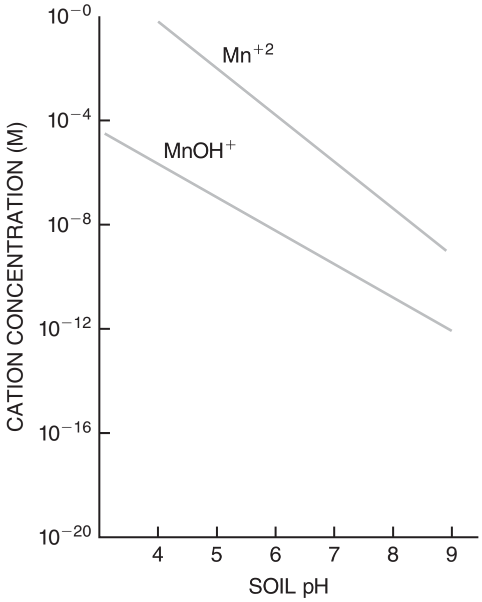


Figure 8-16
Common Mn species in solution as influenced by pH.

Mn^{+2} moves to the root surface by diffusion of chelated Mn^{+2}, similar to Fe (Fig. 8-3). Solution Mn^{+2} is increased under low pH and low O_2 conditions. In extremely acid soils ($pH < 5$), increased Mn^{+2} solubility causes Mn toxicity in sensitive crops. Mn^{+2} can leach from coarse-textured, acid soils. Mn deficiency in organic soils is often attributed to low Mn levels resulting from Mn^{+2} leaching. Sand-based materials used in golf green construction are also commonly low in Mn.

Factors Affecting Mn Availability

Soil pH Management practices that influence soil pH affect Mn^{+2} availability and uptake. Liming acid soils decreases solution and exchangeable Mn^{+2} by precipitation as MnO_2. On the other hand, low Mn availability in high-pH and calcareous soils and in overlimed, poorly buffered, coarse-textured soils can be overcome by acidification through the use of acid-forming N or S materials. High pH also favors the formation of less available organic complexes of Mn. Oats are particularly sensitive to Mn deficiency on $>$pH 6.5 soils.

Excessive Water and Poor Aeration Waterlogged soils exhibit reduced O_2 and lower redox potential, which increases soluble Mn^{+2}, especially in acid soils. Mn availability can be increased by poor aeration in compact soils and by local accumulations of CO_2 around roots and other soil microsites. The resulting low-redox conditions will render Mn more available without appreciably affecting the redox potential or pH of the bulk soil.

Soil OM Low Mn^{+2} availability in high-OM peats and muck soils is attributed to the formation of unavailable chelated Mn^{+2} compounds. In contrast, addition of natural organic materials such as peat moss, compost, and wheat and clover straw will increase solution and exchangeable Mn^{+2} in mineral soils. High rates of green manure crops can cause reducing conditions that increases Mn^{+2} and potential for Mn toxicity.

Weather Effects Under dry soil conditions, Mn availability is generally reduced because of lower diffusion rates. In cold, wet conditions, Mn availability can also be reduced through decreased OM mineralization and reduced root growth. In saturated or waterlogged soils, soluble Mn^{+2} can increase to excessive levels due to chemical reduction of MnO_2 to soluble Mn^{+2}.

Interaction with Other Nutrients High levels of Cu, Fe, or Zn can reduce Mn^{+2} uptake by plants. Addition of acid-forming NH_4^+ fertilizers will enhance Mn uptake by decreasing soil pH.

Plant Factors For satisfactory Mn nutrition, solution and exchangeable Mn should be 2 to 3 ppm and 0.2 to 5 ppm, respectively. Several plant species exhibit differences in sensitivity to Mn deficiency, caused by differences in plant metabolism (Table 8-13). Reductive capacity at the root may be the factor restricting Mn uptake and translocation. There may also be significant differences in the amounts and properties of root exudates generated by plants, which can influence Mn^{+2} availability. Plant characteristics pertinent to Fe-efficient plants may similarly influence plant tolerance to low Mn.

Mn Sources

Organic Mn Mn concentration in most animal wastes is similar to Zn, ranging from 0.01 to 0.05% Mn. Average application rates of most manures will provide sufficient plant available Mn. As with Fe, Zn, and Cu, the primary benefit of organic waste application is increased OM and associated natural chelation properties increasing

TABLE 8-13
CROP SENSITIVITY TO MN DEFICIENCY*

High Sensitivity		*Mild Sensitivity*		*Low Sensitivity*	
Apples	Peas	Alfalfa	Parsnip	Asparagus	Rice
Beans	Potato	Barley	Peppermint	Blueberries	Rye
Cherry	Radish	Broccoli	Potato	Corn	Turfgrass
Citrus	Raspberries	Cabbage	Rice	Cotton	
Cucumber	Sorghum	Carrot	Sweet corn	Field beans	
Fruit trees	Soybean	Cauliflower	Tomato		
Grapes	Spinach	Celery	Turnip		
Lettuce	Strawberries				
Oats	Sugar beet				
Onion	Tomato				
Peaches	Wheat				

*Some crops exhibit variable sensitivity due to differences between varieties of a given crop.

Mn availability. As with the other micronutrients, Mn content in municipal waste varies greatly depending on the source. On the average, Mn content is about half the Cu content (0.05%).

Inorganic Mn Manganese sulfate ($MnSO_4 \cdot 4H_2O$) is the most common Mn source and is soil or foliar applied (Table 8-14). In addition to inorganic Mn fertilizers, natural organic complexes and chelated Mn are available and are usually foliar applied. Manganese oxide is only slightly water soluble and must be finely ground to be effective. Rates of Mn application range from 1 to 40 lbs/a; higher rates are recommended for broadcast application, while lower rates are band and foliar applied (Table 8-15). Band-applied Mn is generally more effective than broadcast Mn, and band treatments are usually one-half broadcast rates. Oxidation to less available forms of Mn is delayed with band-applied Mn. Applications at higher rates are needed on organic soils. Band application of Mn in combination with N-P-K fertilizers is commonly practiced.

Broadcast application of Mn chelates and natural organic complexes is not normally advised because soil Ca or Fe can replace Mn in these chelates, and the freed Mn is usually converted to unavailable forms. Also, the more available chelated Ca or Fe may enhance Mn deficiency. Lime or high-pH-induced Mn deficiencies can be rectified by acidification by use of S or other acid-forming materials.

TABLE 8-14
COMMON MN FERTILIZERS

Source	Formula	% Mn
Manganese sulfate	$MnSO_4 \cdot 4H_2O$	26–28
Manganous oxide	MnO	41–68
Manganese chloride	$MnCl_2$	17
Natural organic	—	<0.2
Manganese chelates	$Na_2MnEDTA$	5–12
Manganese polyflavonoid		5–7
Manganese ligninsulfonate		5

TABLE 8-15
EXAMPLES OF MN MANAGEMENT FOR SELECTED CROPS

Crop	Mn Source	Rate (lb Mn/a)	Method	Comments
Soybean	$MnSO_4 \cdot 4H_2O$	15–40 2–10	Broadcast Banded	Annual application
	$MnSO_4 \cdot 4H_2O$ MnEDTA	0.1–0.3 0.2–0.5	Foliar	Repeat as needed during season
Sugar beet	$MnSO_4 \cdot 4H_2O$	20–80	Broadcast	Annual application
Onion	$MnSO_4 \cdot 4H_2O$ MnO	25–40 10–20	Broadcast Banded	Annual application
Citrus, nuts	$MnSO_4 \cdot 4H_2O$ MnO	0.2–0.4 lbs /25 gal	Foliar	Repeat as needed
Vegetables	$MnSO_4 \cdot 4H_2O$ MnO	2–10	Banded	Annual application
Corn, oats	$MnSO_4 \cdot 4H_2O$ MnO	15–40 2–10	Broadcast Banded	Annual application
Potato	$MnSO_4 \cdot 4H_2O$	2–10	Banded	Annual application
Turfgrass	$MnSO_4 \cdot 4H_2O$ MnEDTA	0.5–1.0 0.01–0.03 lbs/1,000 ft^2	Foliar	Repeat as needed

BORON (B)

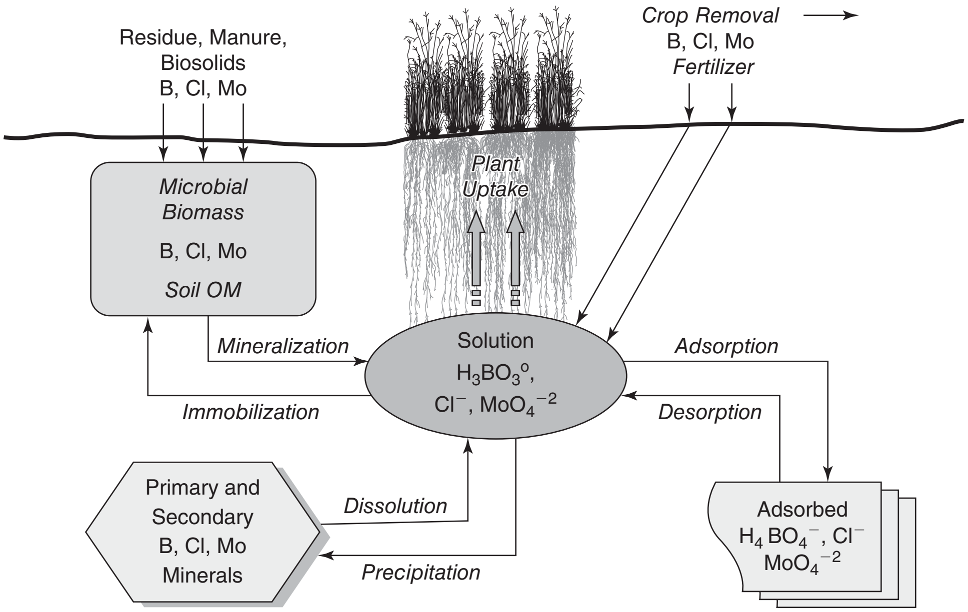
B Cycle

Soil B exists in minerals, adsorbed on clay and Fe/Al oxide surfaces, combined with OM, and in soil solution (Fig. 8-17). Understanding B cycling between solid and solution phases is important because of the narrow range in solution B separating deficiency and toxicity in crops.

B in Plants

B absorbed by plants is predominately undissociated boric acid ($H_3BO_3^o$). The anion forms ($H_2BO_3^-$, HBO_3^{-2}, BO_3^{-3}, and $B_2O_7^{-2}$) exist when soil pH > 7, although

Figure 8-17
B, Cl, and Mo cycling in soil.



plants absorb these less readily than $H_2BO_3^o$. Active B uptake (against a concentration gradient) across the plasma membrane requires co-absorption of H^+. As inside cell pH is greater than outside cell pH, H^+ readily moves across the membrane, sometimes accompanied by $H_2BO_3^o$. This relationship helps explain why B uptake is reduced in alkaline soils where the H^+ gradient is smaller.

Once inside root cells, $H_2BO_3^o$ is readily transported in the xylem to leaves, where much of it occurs in cell walls. B translocation in the phloem from leaves to other plant parts is restricted, thus B accumulates, especially in older leaves. This explains why B toxicity symptoms first appear in older leaf tips. This is consistent with B-deficiency symptoms first appearing in apical meristems and other plant parts receiving water and nutrients through the phloem.

B Functions and Deficiency Symptoms Although required for higher plants and some algae, B is not needed by animals, fungi, or microorganisms. The primary function of B is in plant cell wall structural integrity. B provides cross-links between cell wall polysaccharides that gives a flexible structure to the cell wall—important for cell expansion, regulation of H^+ transport, retention of cellular Ca^{+2}, and control of lignin production following cell expansion. Under B deficiency, normal cell wall expansion is disrupted. These functions are different in dicots and monocots, where grasses are less dependent on B for cell wall structure, although it is still important. Cell wall stability is especially important during pollen tube growth that is essential for seed development. Serious yield reductions in grasses occur due to B deficiency causing male sterility, as exhibited by poorly developed anthers and nonviable pollen grains.

In addition to cell wall structure, B is essential for normal transport of water, nutrients, and photosynthetic sugars to rapidly developing meristematic (growing) tissues, such as root tips, leaves, buds, and storage tissues. Thus, B deficiency commonly appears as a structural deformity in actively growing regions. For example, in legumes, rosetting of new leaves is a common B-deficiency symptom caused by decreased cell division in apical regions. B is also needed for normal development of legume root nodules. B deficiency affects reproductive growth more than vegetative growth. Adequate B increases flower production and retention, and seed and fruit development.

The relative mobility of B in plants varies between species (Table 8-16). In plants where B is immobile, B translocation from older to actively growing tissues is reduced. The first visual deficiency symptom is cessation of terminal bud growth, followed by death of young leaves. In B-deficient plants, the youngest leaves become pale green, losing more color at the base than at the tip. The basal tissues break down, and if growth continues, leaves have a twisted appearance. Plants that exhibit B mobility or phloem transport are those species that also produce higher levels of polyols (i.e., sorbitol, mannitol), including apple, pear, plum, peach, olive, and carrot.

B-deficiency symptoms vary widely with crop species but commonly affect both root and top growth (Fig. 8-18). B-deficiency symptoms often appear in the form of thickened, wilted, or curled leaves; a thickened, cracked, or water-soaked condition of petioles and stems; and a discoloration, cracking, or rotting of fruits, tubers, or roots. Internal cork of apple is caused by B deficiency. Low B in citrus fruits results in uneven thickness of the peel, lumpy fruit, and gummy deposits in the fruit. The breakdown of internal tissues in root crops gives rise to darkened areas referred to as brown heart or black heart. For example, *hollow-heart* in peanut occurs when low B limits Ca translocation that inhibits cell wall development and cell division. Some conifers exhibit striking B-deficiency symptoms including distorted branches and main stems, resin bleeding, and death of major branches.

TABLE 8-16
B MOBILITY IN SELECTED PLANTS

Immobile		Mobile	
Alfalfa	Potato	Almond	Grapes
Bean	Sorghum	Apple	Nectarine
Corn	Strawberry	Apricot	Olive
Cotton	Sugar beet	Asparagus	Onion
Fig	Tobacco	Beans	Pea
Lettuce	Tomato	Broccoli	Peach
Peanut	Walnut	Carrot	Pear
Pecan	Wheat	Cauliflower	Plum
Pistachio		Celery	Pomegranate
		Cherry	Radish
		Coffee	Rutabaga

Figure 8-18
B deficiency on Geranium (USDA) and Cauliflower.
(Courtesy *C. Rosen, Univ. Minnesota*)

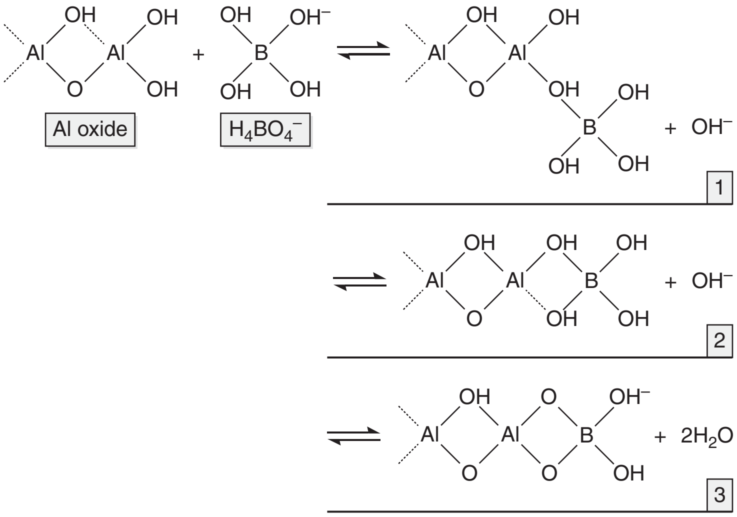
B concentration in monocots and dicots varies between 6 and 18 ppm and 20 and 60 ppm, respectively. B deficiency often occurs with <20 ppm in mature leaf tissue of most crops. B toxicity to plants is uncommon in most arable soils unless it has been added in excessive amounts in fertilizers or urban compost. In arid regions, however, B toxicity may occur naturally or may develop because of a high B content in irrigation waters. B toxicity in most plants occurs at >200 ppm B.

B in Soil

Mineral B B occurs in low concentrations in the earth's crust and in most igneous rocks (<10 ppm). Among sedimentary rocks, shales have the highest B content (<100 ppm). Total B in soils varies between 2 and 200 ppm and frequently is <80 ppm; however, <5% of total soil B is plant available. The main B mineral in soils is *tourmaline*, a relatively insoluble borosilicate. Thus, buffering of solution B is slow, and explains the increasing frequency of B deficiencies, especially under intensive cropping systems. In arid climates, the probability of B deficiency increases due to reduced B mineral solubility with increasing pH, although total B content can be greater because of reduced mineral weathering in arid region soils.

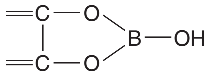
Soil Solution B $H_3BO_3^o$ is the predominant solution species over 5–9 pH. B is transported in soil solution to absorbing plant roots by both diffusion and mass flow. About 0.1 ppm B in solution is considered adequate for most plants.

Adsorbed B B adsorption and desorption can buffer solution B, which reduces B leaching potential. It is a major form of B in alkaline, high-B soils. Primary B adsorption sites are Si-O and Al-O bonds at clay mineral edges and surfaces of Fe/Al oxide and hydroxide compounds given by:

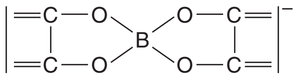


Increasing pH, clay content, OM, and Fe/Al compounds favors $H_2BO_3^-$ adsorption. B-adsorption capacities generally follow the order: mica > montmorillonite > kaolinite.

Organically Complexed B OM represents a large potential source of plant available B in soils, which increases with increasing OM. The B-OM complexes are probably:



or



Factors Affecting B Availability

Soil pH B availability decreases with increasing soil pH, especially at pH > 6.5 (Fig. 8-19). Liming acid soils can cause a temporary B deficiency in susceptible plants

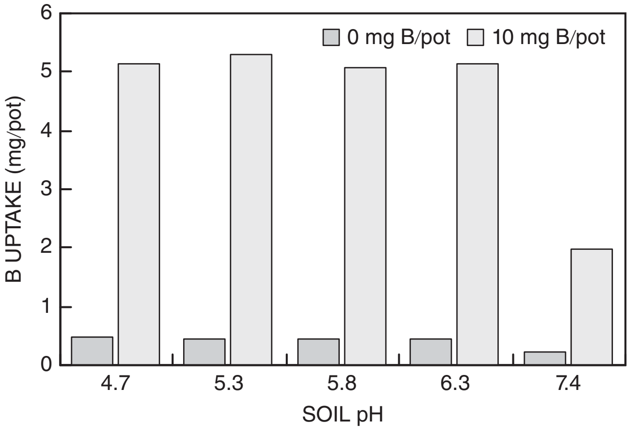


Figure 8-19
Influence of soil pH on B uptake in Tall Fescue.
(Adapted from Peterson and Newman, *1976,* SSSAJ, 40:280).

with the severity depending on crop, soil moisture status, and time elapsed after liming. Lime effect on B availability is caused by B adsorption on freshly precipitated $Al(OH)_3$, with maximum adsorption at pH 7. Moderate liming can be used to depress B availability and plant uptake on high B soils. Heavy liming of soils high in OM may encourage OM decomposition and release of B, increasing B uptake.

Soil OM Higher B availability in surface soils compared with subsurface soils is related to increased soil OM. Applications of OM to soils can increase B in plants and even cause phytotoxicity.

Soil Texture Coarse-textured, well-drained soils can be low in B, and crops with a high requirement respond to B applications of ≥ 3 lbs/a. Sandy soils with fine-textured subsoils generally do not respond to B in the same manner as those with coarse-textured subsoils. B added to soil remains soluble, and up to 80% can be leached in low-OM, sandy soils. Fine-textured soils retain B longer than coarse-textured soils because of greater B adsorption. The fact that clay retains more B than sand does not imply that B uptake in clays is greater than sands. At equal solution B concentration, plants absorb more B from sandy soils than from fine-textured soils, where B uptake can be impeded by higher levels of available Ca.

Interactions with Other Elements When Ca availability is high, plants can tolerate higher B availability. Under low Ca supply, many crops exhibit lower B tolerance. Greater Ca^{+2} supply in alkaline and recently overlimed soils restricts B availability; thus, high solution Ca^{+2} protects crops from excess B. The Ca:B ratio in leaf tissues has been used to assess B status of crops, where B deficiency for most crops is likely when Ca:B ratio is greater than 1,200:1. B deficiency in sensitive crops (e.g., alfalfa) can be aggravated by K fertilization to the extent that B is needed to prevent yield loss, since Ca^{+2} displaced from the CEC by K^{+} can interfere with B absorption.

Soil Moisture B deficiency is often associated with dry weather, where low soil moisture reduces B release from OM and B uptake through reduced B transport (diffusion and mass flow) to absorbing root surfaces.

Plant Factors Because of the narrow range between sufficient and toxic levels of available soil B, the sensitivity of crops to excess B is important (Table 8-17). Genetic variability contributes to differences in B uptake. For example, investigations with tomato varieties and corn hybrids revealed that susceptibility to B deficiency is controlled by a single recessive gene, where one variety is B inefficient, while another is B efficient.

B Sources

Organic B B content in animal wastes ranges between 0.001% and 0.005%, thus, depending on application rates, animal wastes may not provide sufficient plant available B. Similar to other micronutrients, increasing OM and associated chelation properties with waste application will increase B availability. B content in municipal biosolids is also low (~0.01% B).

Inorganic B B is one of the most widely applied micronutrients. Sodium tetraborate ($Na_2B_4O_7 \cdot 5H_2O$) is the most common B source, containing $\approx$15% B (Table 8-18). Solubor is a highly concentrated, soluble B source that can be foliar applied as a liquid or dust. It is also used in liquid and suspension fertilizers.

TABLE 8-17
CROP SENSITIVITY TO B DEFICIENCY

High Sensitivity		*Moderate Sensitivity*		*Low Sensitivity*	
Alfalfa	Cotton	Apple	Peaches	Asparagus	Peppermint
Almond	Olive	Carrot	Pears	Barley	Potato
Apple	Peanut	Clover	Radish	Bean	Rice
Apricot	Pistachio	Grapes	Raspberries	Blueberry	Rye
Broccoli	Plum	Lettuce	Spinach	Citrus	Sorghum
Cabbage	Roses	Parsnip	Tomato	Cucumber	Spearmint
Canola	Rutabaga		Strawberries	Corn	Soybean
Carnation	Sugar beet			Grasses	Sudan grass
Cauliflower	Sunflower			Oat	Wheat
Celery	Table beet			Pea	
Cherry	Turnip				
Conifers	Walnut				

TABLE 8-18
COMMON B FERTILIZERS

Source	Formula	% B
Borax	$Na_2B_4O_7 \cdot 10H_2O$	11
Boric acid	H_3BO_3	17
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	10–16
Sodium pentaborate	$Na_2B_{10}O_{16} \cdot 10H_2O$	18
Sodium tetraborate (Fertibor, Granubor)	$Na_2B_4O_7 \cdot 5H_2O$	14–15
Sodium octaborate (Solubor)	$Na_2B_8O_{13} \cdot 4H_2O$	20–21

Solubor is preferred to borax because it dissolves more readily. The Ca borate mineral colemanite is often used on sandy soils because it is less soluble and less subject to leaching than the sodium borates.

The common B application methods are broadcast, banded, or applied as a foliar spray or dust. In the first two methods, B fertilizer is usually mixed with N-P-K-S products and soil applied. B salts can also be coated on dry fertilizer materials.

B fertilizers should be uniformly soil applied because of the narrow range between deficiency and toxicity. Band applied B should avoid direct seed contact with most crops. Segregation of granular B sources in dry fertilizer blends must be avoided. B application with fluid fertilizers eliminates segregation.

Foliar B application is practiced for perennial tree-fruit crops, often in combination with pesticides other than those formulated in oils and emulsions. B may also be included in sprays of chelates, Mg, Mn, and urea.

B fertilization rates depend on plant species, soil cultural practices, rainfall, liming, soil OM, and other factors (Table 8-19). Soil application rates of 0.5–3 lbs/a are generally recommended, with higher rates used on high B use crops (e.g., legumes, crucifers). B rate also depends on application method. For example, B for vegetable crops is 0.4–2.7 lbs/a broadcast, 0.4–1.0 lbs/a band, and 0.1–0.3 lbs/a foliar applied.

Table 8-19
Examples of B Management for Selected Crops

Crop	B Source	Rate (lb B/a)	Method	Comments
Grapes	Solubor	1–2	Banded	Annual application
		0.1–0.2	Foliar	Pre-bloom, monitor petiole B
Alfalfa	Borax	1.5–2.5	Broadcast	Biennial application
	Solubor	0.1–0.2	Foliar	Annual, monitor leaf B
Cotton	Solubor	0.5–1.5	Band	Preplant or at planting, no seed contact
Broccoli	Solubor	1–3	Broadcast	Perplant
		0.5–1.0	Foliar	Prebloom, 1 lb B/100 gal
Peanut	Solubor	0.3– 0.5	Foliar	Apply with 1st fungicide appl.
Canola	Solubor	0.5–1.0	Broadcast	Preplant
		0.1–0.3	Foliar	Apply with 1st fungicide appl.
Soybean	Solubor	0.1	Foliar	3–5 appl. pre-bloom
	Fertibor	0.5	Band	At planting, no seed contact
		1.0	Broadcast	Preplant, incorporate
Corn	Solubor	0.25	Foliar	Pretassle
		0.5	Band	At planting, no seed contact
		1.0	Broadcast	Preplant, incorporate

CHLORIDE (Cl)

Cl Cycle

Nearly all chloride (Cl^-) in soils exists in soil solution (Fig. 8-17). The mineral, adsorbed, and organic fractions contain negligible quantities of Cl^-. Because of its high solubility and mobility in soils, appreciable Cl^- leaching can occur when rainfall or irrigation exceeds evapotranspiration.

Plant-growth limiting Cl deficiencies are generally rare in areas of significant atmospheric Cl^- deposition (Fig. 8-20). Interaction of wind and sea water ($\approx$4% NaCl) introduces Cl^- into the atmosphere. Compared to annual crop Cl^- requirement ($\approx$4–8 lbs/a), atmospheric deposition supplies adequate Cl^-, although in coastal areas deposition is much greater.

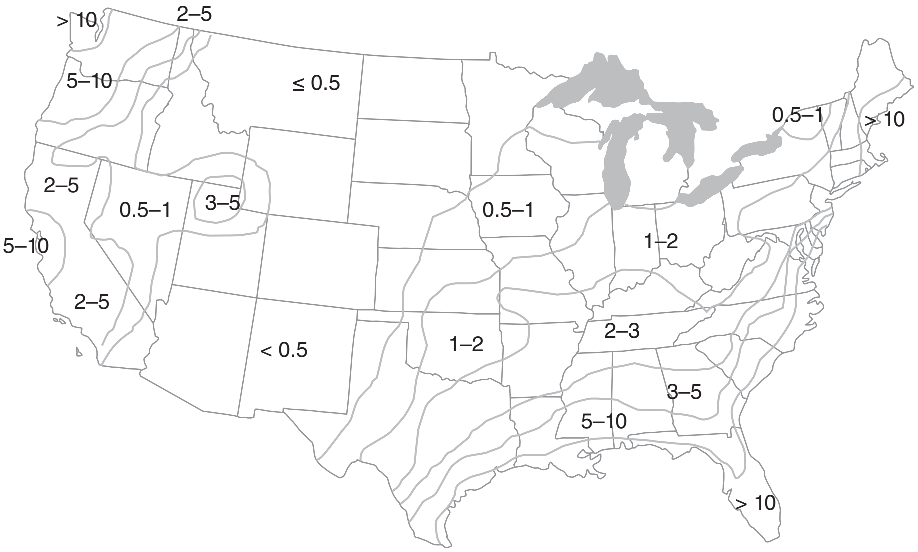


Figure 8-20
Distribution in Cl^- deposition (kg Cl^-/ha) in the U.S.
(National Atmospheric Deposition Program. 2009, Washington, D.C.)

TABLE 8-20
CROP SENSITIVITY TO CL DEFICIENCY

High Sensitivity	Mild Sensitivity	Low Sensitivity
Avocado	Cotton	Barley
Bean	Oats	Corn
Citrus	Potato	Spinach
Legumes	Soybean	Sugar beet
Lettuce	Wheat	Tomato
Peach		
Potato		

Cl in Plants

Cl^- is absorbed by plants through roots and leaves. Active transport of Cl^- across plasma membranes occurs through other anion transporters (i.e., NO_3^-, SO_4^{-2}, $H_2PO_4^-$). Cl^- concentration in plants is about 0.2–2.0%, although levels as high as 10% are possible. All of these values usually exceed the strictly nutritional need of most plants. Although usually considered a micronutrient, its concentration in plants can be similar to S. Tissue concentrations of 0.5% to 2.0% of sensitive crops can be toxic. Similar reductions in yield and quality can occur when $Cl^- \geq 4\%$ in tolerant crops (Table 8-20).

Cl Functions Cl^- primarily is involved in osmotic and ion charge balance, which are important to many biochemical processes in plants. Over 100 Cl^-containing organic compounds are known in plants; however, their functions are not well understood.

O_2 and Photosynthesis Cl^- is important to the function of Mn in photosynthetic production of carbohydrates from CO_2 and evolution of O_2 (see O_2 *and Photosynthesis* under *Mn*). Cl^- will maintain electroneutrality when Mn^{+3} donates an electron during photosynthesis. This function of Cl^- is essential for photosynthesis as evidenced by the $\approx 10\%$ Cl^- in the chloroplasts.

Cell Turgor For rapid gas exchange (CO_2 in and O_2/H_2O out) by leaves during active photosynthesis (daylight), the epidermal guard cells of stomates are turgid, caused by K^+ pumped from neighboring cells into the guard cells. K^+ transport into the guard cells must be balanced by organic anions or Cl^-, depending on plant species. Observation that loss of leaf turgor is a Cl^-deficiency symptom supports the concept that Cl^- is an active osmotic agent. Some of the favorable actions of Cl^- fertilization are attributed to increased water potential and moisture relations. In other cells, inadequate osmotic adjustment reduces cell turgor pressure that inhibits cell enlargement and cell division. Reduction in cell expansion reduces leaf size, a common Cl^-deficiency symptom.

Solute Concentration in Vacuoles For plants to absorb and use nutrients efficiently, nutrients accumulate in vacuoles until transported to growing plant organs. Cl^- is essential for maintaining electrical balance in tonoplasts. Under saline conditions, Cl^- is especially critical in balancing high Na^+ and maintaining proper water status.

Cl^- Deficiency and Toxicity Symptoms Chlorosis in younger leaves and an overall wilting of plants are the two most common Cl^-deficiency symptoms. These observations would support the mobility of Cl^- in plants; however, deficiency symptoms can be observed in younger plant tissues. This discrepancy is likely related to variation in mobility between plant species as is observed with B.

Necrosis in some plant parts, leaf bronzing, and reduction in root and leaf growth may also be observed. Tissue concentrations of 70–700 ppm are usually indicative of Cl^- deficiency. However, higher concentrations may be beneficial for disease suppression and moisture relationships. Cl^- response in small grains in the Great Plains occurs about 50% of the time when plant Cl^- is between 0.1% and 0.4%. Excess Cl^- can be harmful, and crops vary widely in their tolerance to Cl^- toxicity (Table 8-20). Leaves become thickened and tend to roll with excessive Cl^-. Storage quality of tuber crops is reduced by excessive Cl^-. The principal effect of excess Cl^- is an increase in osmotic pressure of soil water that reduces water uptake. Cl toxicity in most plants is exhibited at >3,500 ppm Cl, and commonly occurs in poorly drained coastal region soils and saline soils in arid regions.

Cl in Soil

Mineral Cl Cl concentration is 0.02% to 0.05% in the earth's crust, and occurs primarily in igneous and metamorphic rocks. Soil Cl^- commonly exists as soluble salts such as NaCl, $CaCl_2$, and $MgCl_2$. Cl^- is often the principal anion in saline soil solutions. Solution Cl^- ranges from 0.5 ppm in acid soils to >6,000 ppm in saline/sodic soils.

The majority of Cl^- in soils originates from salts trapped in parent material, from marine aerosols, and from volcanic emissions. Nearly all of soil Cl^- has been in the oceans at least once, being returned to the land by uplift and subsequent leaching of marine sediments or by oceanic salt spray carried in rain or snow. Annual Cl^- depositions of 0.2–5 lbs/a are common and may increase to more than 50 lbs/a in coastal areas (Fig. 8-20). The quantity of Cl^- deposition depends on the amount of sea spray, which is related to temperature; wind strength, frequency, and duration sweeping inland from the sea; topography of the coastal region; and amount, frequency, and intensity of precipitation.

Salty droplets or dry salt dust may be whirled to great heights by strong air currents and carried over long distances. Cl^- concentration in precipitation is decreased in inland areas.

Solution Cl^- Cl^- is highly soluble in soils. Because of Cl^- mobility, it will accumulate where the internal drainage of soils is restricted and in shallow groundwater where Cl^- can be moved by capillarity into the root zone and deposited at or near the soil surface. Problems of excess Cl^- occur in some irrigated areas and are usually the result of interactions of:

- high Cl^- in the irrigation water,
- insufficient water to leach accumulated Cl^-.

Environmental damage in localized areas from high Cl^- concentrations has resulted from road deicing, water softening, saltwater spills associated with the extraction of oil and natural gas deposits, and disposal of feedlot wastes and various industrial brines.

Plant Responses

Depression of Cl^- uptake by high concentrations of NO_3^- and SO_4^{-2} has been observed in a number of plants (Fig. 8-21). Here potato yields increase as Cl^- in petioles increases from 1.1% to 6.9% and NO_3^- decreases. Although beneficial effects of Cl^- on plant growth are not fully understood, improved plant–water relationships and inhibition of plant diseases are two important factors. The negative interaction between Cl^- and NO_3^- has been attributed to competition for carrier sites at root surfaces.

The effect of Cl^- fertilization on root and leaf disease suppression has been observed on a number of crops (Table 8-21). Several mechanisms have been suggested and include (1) increased NH_4^+ uptake through inhibition of nitrification by

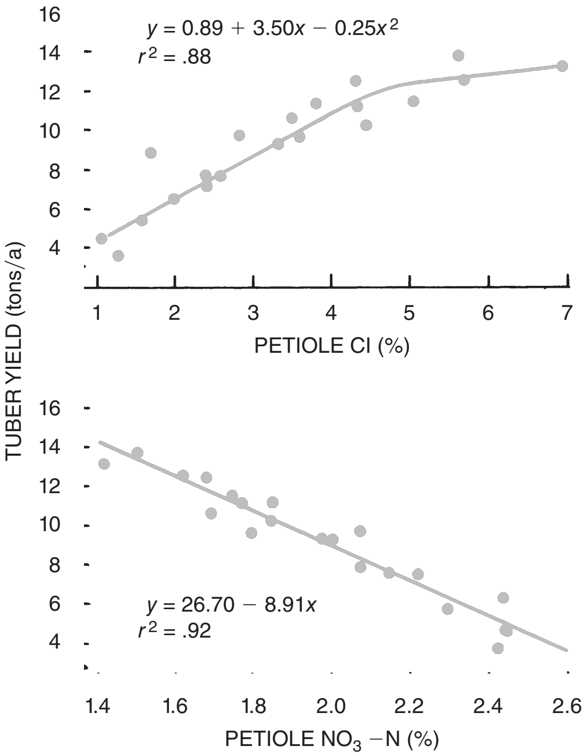


Figure 8-21
Relationship between potato yield and Cl^- and NO_3^- concentration in petioles.
(Jackson et al., 1981, unpublished data, Oregon State Univ.)

Cl^-, which reduces takeall root disease by decreased rhizosphere pH, or (2) competition between Cl^- and NO_3^- for uptake. Plants low in NO_3^- are less susceptible to root-rot diseases. In some regions, Cl^- response in some crops has not been related to disease suppression. For example, in semiarid regions, Cl^- deficiency is caused by low

TABLE 8-21
DISEASES SUPPRESSED BY CL FERTILIZATION

Location	Crop	Suppressed Disease
Oregon	Winter wheat	Take-all, Septoria
	Potato	Hollow heart, Brown center
North Dakota	Winter wheat	Tanspot
	Spring wheat	Common root rot
	Barley	Common root rot, Spot blotch
	Durum wheat	Common root rot
South Dakota	Spring wheat	Leaf rust, Tanspot, Septoria
New York	Corn	Stalk rot
California	Celery	Fusarium yellows
Saskatchewan	Spring wheat	Common root rot
	Barley	Common root rot
Manitoba Take	Spring wheat	Take-all
Alberta	Barley	Common root rot, Net blotch
Germany	Winter wheat	Take-all
Great Britain	Winter wheat	Stripe rust
India	Pearl millet	Downy mildew
Indonesia	Rice	Stem rot, Sheath blight
Philippines	Coconut palm	Gray leaf spot

Source: Fixen, 1987, 2nd National Wheat Res. Conf.

TABLE 8-22
SPRING WHEAT RESPONSE TO CL FERTILIZATION INFLUENCED BY SOIL CL

Category	Soil Cl Content	Yield Response Frequency
	lb/a–2 ft	%
Low	0–30	69
Medium	31–60	31
High	>60	0

Source: Fixen, 1979, *J. Fert. Issues*, 4:95.

soil Cl^-, with the probability of a Cl^- response increasing with decreasing soil Cl^- (Table 8-22).

Cl Sources

Organic Cl Because of the solubility and mobility of Cl^-, most animal and municipal wastes are low in Cl^-.

Inorganic Cl When additional Cl^- is desirable, it can be supplied by the following sources:

• Ammonium chloride (NH_4Cl)	66% Cl
• Calcium chloride ($CaCl_2$)	65% Cl
• Magnesium chloride ($MgCl_2$)	74% Cl
• Potassium chloride (KCl)	47% Cl
• Sodium chloride (NaCl)	60% Cl

Cl^- rates vary, depending on crop, method of application, and purpose of addition (i.e., for correction of nutrient deficiency, disease suppression, or improved plant water status). Where take-all root rot of winter wheat is suspected, banding ≈40 lbs/a of Cl^- with or near the seed at planting is recommended. Broadcasting 75–125 lbs/a of Cl^- has effectively reduced crop stress from take-all and leaf and head diseases (e.g., stripe rust and septoria). Plant nutrient Cl^- requirements for high yields of most temperate-region crops are usually satisfied by only 4–10 lbs/a.

MOLYBDENUM (Mo)

Mo Cycle

The main forms of Mo in soil include primary and secondary minerals, exchangeable Mo held by Fe/Al oxides, Mo in soil solution, and organically bound Mo. Although Mo is an anion in solution, the relationships between these forms are similar to those of other metal cations (Fig. 8-17).

Mo in Plants

Mo is absorbed as the weak acid molybdate (MoO_4^{-2}) that can form complexes with other anions such as phosphomolybdate. Mo complexation may explain why Mo can be absorbed in relatively large amounts without any apparent toxicity. Mo content of plants is normally low (0.2–2 ppm), because of extremely low MoO_4^{-2} in solution. In some cases, Mo levels in crops may exceed 300 ppm. Mo toxicity symptoms in plants occurs at >1,000 ppm Mo.

Mo is an essential component of NO_3^- reductase, an enzyme concentrated in chloroplasts, which catalyzes the conversion of NO_3^- to NO_2^-. Mo also is a structural component of nitrogenase, the enzyme essential to N_2 fixation by root-nodule bacteria of leguminous crops, by some algae and actinomycetes, and by free-living, N_2-fixing organisms. Mo concentrations in legume nodules can be >10 times that in leaves. Mo requirement of plants decreases with increasing inorganic N availability. Mo is also reported to have an essential role in Fe absorption and translocation in plants, which explains why a common Mo-deficiency symptom is similar to interveinal chlorosis in Fe deficiency. Deficiency symptoms also include pale green leaf color, stunting, necrosis on leaf edges, and rolled or curled leaves, often appearing on older leaves.

Excessive amounts of Mo are toxic, especially to grazing animals. High-Mo forage may occur in wet, high-pH, and high-OM soils. Molybdenosis, a disease in cattle, is caused by an imbalance of Mo and Cu in the diet when the Mo content of the forage is >5 ppm. Mo toxicity causes stunted growth and bone deformation, but can be corrected by oral feeding of Cu, Cu injections, or Cu application to soil.

Mo in Soil

Mineral Mo The average Mo concentration in the earth's crust is <2 ppm, and typically ranges from 0.2 to 5 ppm in soils. Soil minerals controlling solution MoO_4^{-2} concentration are $PbMoO_4$ and $CaMoO_4$. $CaMoO_4$ predominates in both acidic and calcareous soils.

Solution Mo Mo in solution occurs predominantly as MoO_4^{-2}, $HMoO_4^{-}$, and $H_2MoO_4^{o}$. MoO_4^{-2} and $HMoO_4^{-}$ concentration increases with increasing soil pH (Fig. 8-22). The extremely low concentration of solution Mo is reflected in the low Mo content of plant material. At solution concentrations >4 ppb, Mo is transported to plant roots by mass flow, while Mo diffusion to plant roots occurs at levels <4 ppb.

Factors Affecting Mo Availability

Soil pH MoO_4^{-2} availability, unlike that of other micronutrients, increases approximately tenfold per unit increase in soil pH (Fig. 8-22). Liming to increase soil pH increases Mo availability and prevents Mo deficiency. Alternatively, Mo availability is decreased by application of acid-forming fertilizers such as $(NH_4)_2SO_4$ to coarse-textured soils.

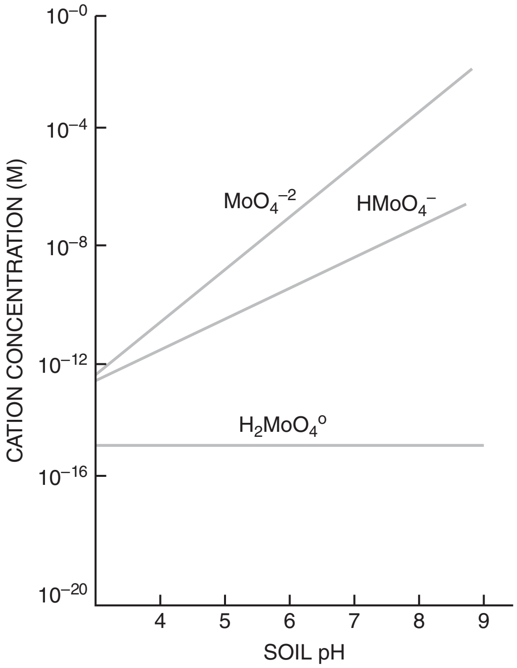


Figure 8-22
Common Mo species in soil solution as influenced by pH.

Soil texture In sandy, low OM soils, MoO_4^{-2} retention is low, increasing the probability of Mo deficiency, especially with high Mo requiring crops (i.e., crucifers, legumes).

Fe/Al Oxides Mo is strongly adsorbed to Fe/Al oxide surfaces, some of which becomes unavailable to the plant. Soils high in Fe/Al oxides (highly weathered soils) tend to be low in available Mo.

Interactions with Other Nutrients P enhances Mo absorption by plants, probably due to exchange of adsorbed MoO_4^{-2}. In contrast, high levels of solution SO_4^{-2} depress MoO_4^{-2} uptake by plants. The antagonism of SO_4^{-2} on MoO_4^{-2} uptake is due to their similar transport mechanism across the cell wall. On soils with marginal Mo levels, application of S fertilizers may induce Mo deficiency.

Both Cu and Mn can also reduce Mo uptake; however, Mg has the opposite effect and will encourage Mo absorption. NO_3^- encourages Mo uptake, while NH_4^+ sources reduce Mo uptake. The effect of NO_3^- uptake may be related to release of OH^- by roots that would increase Mo solubility.

Soil moisture Mo deficiency is accentuated under dry conditions, due to reduced mass flow or diffusion under low-soil-moisture content. Mo availability increases with soil water, where plants grown on poorly drained soils can accumulate excess Mo.

Plant Factors Crops vary in their sensitivity to low solution Mo (Table 8-23). Mo-efficient and Mo-inefficient varieties of alfalfa, cauliflower, corn, and kale have been identified.

Mo Sources

Organic Mo Only small quantities of Mo occur in animal wastes (0.0001–0.0005% Mo), although with most manures, average application rates will provide sufficient plant available Mo. Mo content in municipal waste is usually low, averaging 0.0001% Mo.

Inorganic Mo Mo fertilizers (Table 8-24) are generally applied at low rates (0.03–1 lb/a), depending on application method (Table 8-25). Mo solutions are soil or foliar applied, or applied as a seed coating. Seeds treated with a solution of Na molybdate are widely used because of the low application rates needed. To obtain satisfactory distribution of the small quantities of Mo applied to soil, Mo sources are sometimes combined with

TABLE 8-23
CROP SENSITIVITY TO MO DEFICIENCY

High Sensitivity	Mild Sensitivity	Low Sensitivity	
Alfalfa	Beet	Apple	Grapes
Broccoli	Cabbage	Asparagus	Peach
Brussels sprouts	Citrus	Barley	Potato
Cauliflower	Oats	Beans	Raspberries
Clover	Peas	Blueberries	Rice
Legumes	Radish	Carrot	Ryegrass
Lettuce	Soybean	Celery	Sorghum
Onion	Sugar beet	Corn	Sweet corn
Rapeseed	Tomato	Cotton	Tomato
Spinach	Turnip	Cranberry	Turfgrass
		Flax	Wheat

TABLE 8-24
SOURCES OF MO FERTILIZER

Sources	Formula	% Mo
Ammonium molybdate	$(NH_4)_6Mo_7O_{24}\ 2H_2O$	54
Sodium molybdate	$Na_2MoO_4 \cdot 2H_2O$	39
Molybdenum trioxide	MoO_3	66
Molybdenum frits	Mo silicates	2–3

TABLE 8-25
EXAMPLES OF MO MANAGEMENT FOR SELECTED CROPS

Crop	Mo Source	Rate (lb Mo/a)	Method	Comments
Soybean	NH_4 or Na	0.5–1.0	Broadcast	Effective for 2–3 years
	molybdate	0.03–0.15	Foliar	No residual value
		0.03–0.06	Seed coat	Effective for 3–4 years
Broccoli	NH_4 or Na	0.05–0.15	Foliar	No residual value
	molybdate	0.05	Seed coat	Effective for 3–4 years
Peas	NH_4 or Na	0.03–0.10	Foliar	No residual value
	molybdate	0.03–0.05	Seed coat	Effective for 3–4 years

N-P-K fertilizers. Foliar spray applications with NH_4-or Na-molybdate are also effective in correcting deficiencies.

NICKEL (Ni)

Ni is the latest nutrient to be established (in 1987) as an essential nutrient to higher plants since the recognition of Cl^- in 1954. Ni content of plants normally ranges from 0.1 to 1.0 ppm and is supplied to plants as Ni^{+2}. Ni is the metal component of urease that catalyzes the reaction $CO(NH_2)_2 + H_2O \leftrightarrows 2NH_3 + CO_2$. Apparently, Ni is essential for plants supplied with urea and for those in which ureides are important in N metabolism. Ni is beneficial to N metabolism in legumes. Nodule weight and seed yield of soybeans have been stimulated by Ni.

Ni-deficient plants accumulate toxic levels of urea in leaf tips because of reduced urease activity. Although few Ni deficiencies have been observed in the field, Ni-deficient plants may develop chlorosis in the youngest leaves that progresses to necrosis of the meristem. Ni may also be involved in plant diseases caused by faulty N metabolism.

Ni has been demonstrated as essential to small-grain crops (Table 8-26). The data show increasing barley germination and grain yield with increasing Ni in solution. High levels of Ni may induce Zn or Fe deficiency because of cation competition.

Application of biosolids may result in elevated levels of Ni in crop plants. Plant genes have recently been identified from wild mustard, *Thlaspi goesingense*, which enable plants to accumulate high levels of Ni. Currently over 350 plants are known to hyperaccumulate metals from soil contaminated with Ni, Cu, Zn, Cd, Se, and/or Mn. Tissue concentrations of 1% Ni are 1,000 times greater than normal levels.

TABLE 8-26
EFFECT OF NI SUPPLY ON GERMINATION AND YIELD OF BARLEY

Ni in Solution	Germination	Ni Concentration	Total Grain Wt
(mM)	*(%)*	*(μg/g dry wt)*	*(g dry wt)*
0.0	12	7	7.3
0.6	57	64	7.5
1.0	94	129	8.4

Source: Adapted from Brown et al., 1987, *Plant Physiol.* 85:801.

BENEFICIAL ELEMENTS

In addition to the 17 essential nutrients, several elements are beneficial to some plants but are not considered necessary for completion of the plant life cycle.

Cobalt (Co)

Co in Plants Co is essential for growth of symbiotic microorganisms such as *Rhizobia*, free-living N_2-fixing bacteria, and blue-green algae. Co concentration in plants ranges from 0.02 to 0.5 ppm. N_2 fixation in alfalfa can be enhanced by only 10 ppb Co. Co forms a complex with N, important for synthesis of vitamin B12 coenzyme. Co is also important in the synthesis of vitamin B12 in ruminant animals; thus, soil is an important source of plant Co for animals. Because Co behaves similarly to Fe or Zn, excess Co produces visual symptoms similar to Fe and Mn deficiencies.

Co in Soils Average total Co concentration in the earth's crust is ≈ 40 ppm. Total Co in soils typically ranges from 1 to 70 ppm and averages about 8 ppm. Soils formed on granitic glacial materials are low in total Co, ranging 1–10 ppm. Much higher levels (100–300 ppm) are found in Mg-rich iron minerals. Sandstones and shales are normally low in Co, with concentrations <5 ppm. Co deficiencies in ruminants are often associated with forages produced on soils containing <5 ppm total Co.

Co can be beneficial to some plants grown on (1) acid, highly leached, sandy soils with low total Co; (2) highly calcareous soils; and (3) some peaty soils. Co^{+2} is adsorbed on exchange sites and occurs as clay-OM complexes similar to those of the other metal cations (Fig. 8-15). Solution Co is often <0.5 ppm. Co availability decreases with greater adsorption capacity of Fe/Al oxides. Co availability decreases with increasing soil pH, thus, liming can reduce Co availability. Saturated soil conditions increases soluble Mn^{+2}, which can reduce Co uptake.

Co Fertilizer Co deficiency of ruminants can be corrected by (1) adding it to feed, salt licks, or drinking water; (2) direct injection; (3) using Co bullets (oral tablets); and (4) fertilizing forage crops with small amounts of Co. Co fertilization with 1.5 lb/a $CoSO_4$ every 3–4 years is recommended when extractable soil Mn <500 ppm. With higher soil Co levels, crop fertilization is less effective.

Sodium (Na)

Na in Plants Na is essential for halophytic plants that accumulate salts in vacuoles to maintain turgor and growth. Beneficial effects of Na on plant growth can be observed in low-K soils, because Na^+ can partially replace K^+. Crops with a high Na^+ uptake potential can respond to Na^+ (Table 8-27). The Na demand of these crops appears to be independent of, and perhaps even greater than, their K demand.

TABLE 8-27
NA UPTAKE POTENTIAL OF VARIOUS CROPS

High	Medium	Low	Very Low
Fodder beet	Cabbage	Barley	Buckwheat
Mangold	Coconut	Flax	Maize
Spinach	Cotton	Millet	Rye
Sugar beet	Lupins	Rape	Soybean
Swiss chard	Oats	Rubber	Swede
Table beet	Potato	Wheat	Turnip

Na^+ concentration in leaf tissue varies from 0.01% to 10%. Many C_4 plants require Na, which is specifically involved in water relations. Many C_4 plants occur naturally in arid, semiarid, and tropical conditions, where stomatal closure to prevent water loss is essential for growth and survival. As a result, CO_2 entry is also restricted when stomata are closed. Efficiency of photosynthetic CO_2 conversion is greater in C_4 compared to C_3 plants, where the ratio of CO_2 assimilated to H_2O transpired by C_4 plants is often double that of C_3 plants. It is also noteworthy that C_4 plants are often found in saline habitats.

Sugar beets are particularly responsive to Na, with concentrations in leaf tips $\geq$10%. Na influences water relations and increases drought resistance in sugar beets. In low Na soils, beet leaves are dark green, thin, and dull in hue. Plants wilt more rapidly and may grow horizontally from the crown. There may also be an interveinal necrosis similar to K deficiency. Some of the Na effects may also be due to Cl^-, as NaCl is the common Na source.

Na in Soils Na content in the earth's crust is about 2.8%, while soils contain 0.1–1%. Low Na in soils indicates weathering of Na from Na-containing minerals, thus, the proportion of exchangeable Na^+ to other cations is low in humid-region soils. Na is common in most arid and semiarid region soils, where it exists as Na salts (i.e., NaCl, Na_2SO_4, Na_2CO_3) that accumulate in poorly drained soils, contributing to soil salinity and sodicity. (Chapter 3).

Soil solutions contain between 0.5 and 5 ppm Na^+ in temperate regions. Solution and exchangeable Na^+ varies greatly among soils. Sugar beets respond to fertilization when exchangeable $Na^+ < 0.05$ meq/100g. In arid region soils irrigated with saline waters, exchangeable $Na^+ > K^+$.

Na Sources The important Na-containing fertilizers are:

- K fertilizers with NaCl impurities
- $NaNO_3$ (~25% Na)
- Multiple nutrient fertilizers with Na.

Silicon (Si)

Si in Plants Plants absorb Si as silicic acid ($H_4SiO_4^o$). Cereals and other grasses contain 0.2–2.0% Si, while broadleaves contain 0.02–0.2% Si. Si concentrations of 2–20% occur in Si-rich plants like sedges, nettles, horsetails, and some grasses. Si impregnates the walls of epidermal and vascular cells, where it strengthens tissues, reduces water loss, and retards fungal infection. With large accumulations of Si, intracellular deposits called *plant opals* occur.

Although no biochemical role for Si in plants has been identified, it has been proposed that enzyme-Si complexes form that act as protectors or regulators of photosynthesis and enzyme activity. In sugarcane, Si can suppress the activity of invertase, increasing sucrose production. A reduction in phosphatase activity is believed to provide a greater supply of essential high-energy precursors needed for sugar production and optimum cane growth.

The beneficial effects of Si have been attributed to partial remediation of toxic effects of high soil Mn^{+2}, Fe^{+2}, or Al^{+3}; plant disease resistance; greater stalk strength and resistance to lodging; increased availability of P; reduced transpiration; and improved drought tolerance. Freckling, a necrotic leaf spot condition, is a symptom of low Si in sugarcane. Ultraviolet radiation seems to be the causative agent in sunlight since plants kept under plexiglass or glass do not freckle. Si in sugarcane may act to filter out harmful ultraviolet radiation.

In rice, Si also helps maintain leaf erectness, increases photosynthesis through improved light interception, and results in greater resistance to diseases and insect pests. The oxidizing capacity of rice roots and accompanying tolerance to high Fe and Mn depends on Si. Si additions are beneficial at Si contents of rice straw at $<11\%$. Heavy N rates render rice plants more susceptible to fungal attack due to decreased Si in the straw. Often, Si materials are applied under high fertilizer N use.

Si in Soils Si is the second most abundant element in the earth's crust, averaging $\approx 28\%$, while Si content in soils is 5% to 40%. Unweathered sandy soils can contain $\approx 40\%$ Si, compared with as little as 9% Si in highly weathered tropical soils. Si sources in soil include primary and secondary minerals, where quartz (SiO_2) dominates and comprises $\geq 90\%$ of all sand and silt fractions.

Low Si soils exist in intensively weathered, high-rainfall regions that exhibit low total Si, high Al, low %BS, and low pH. In addition, they all have extremely high P-fixing capacity due to high AEC and Fe/Al oxide content. Plant available Fe^{+2} and Mn^{+2} may also be high in these soils.

$H_4SiO_4^o$ is the principal Si species in solution, where 3–37 ppm solution Si occurs in most soils. Concentrations of <2 ppm Si are insufficient for proper nutrition of sugarcane. Si levels adequate for rice production are ≈ 100 ppm. Solution Si concentration is largely controlled by pH-dependent adsorption reactions, where Si is adsorbed on Fe/Al oxides. Si leaching in highly weathered soils will reduce solution Si and Si uptake.

Si Sources Primary Si fertilizers include:

• Calcium silicate slag ($CaAl_2Si_2O_8$)	18–21% Si
• Calcium metasilicate ($CaSiO_3$)	31% Si
• Sodium metasilicate ($NaSiO_3$)	23% Si

Minimum rates of at least 5,000 lbs/a of $CaSiO_3$ are broadcast applied and incorporated before planting sugarcane (Table 8-28). Annual $CaSiO_3$ applications of 500–1,000 lbs/a applied in the row have also improved sugarcane yields. Liming to increase Ca and decrease acidity does not improve sugarcane production to the same extent as Si fertilization. Rates of 1.5–2.0 t/ha of silicate slag usually provide sufficient Si for rice produced on low-Si soils.

Selenium (Se)

Se in Plants Se is not essential for plants, but it is required by animals. A greater frequency of livestock nutritional disorders caused by low Se occurs after cold, rainy summers than after hot, dry ones. High summer temperatures are amenable to increased Se concentration in forages.

Plant species differ in Se uptake. Certain species of *Astragalus* absorb greater Se than other plants growing in the same soil, because they utilize Se in an amino

TABLE 8-28
SUGARCANE RESPONSE TO SI AT SEVERAL LOCATIONS.

Location	Si Source	Product Rate	Yield	
			Cane	Sugar
		——— t/ha ———		
Mauritius	Electric furnace slag	0	267	27
		6.2	314	34
Hawaii	Electric furnace slag	0	258	22
		4.5	332	32
Hawaii	Ca silicate	0	131	—
		0.83	151	—
		1.66	166	—
Florida	Ca silicate slag	0	138	15
		6.7	175	20

Source: Adapted from Matichenkov and Calvert, 2002, *J. Am. Soc. Sugarcane Tech.* 22:21

acid specific to this species. Plants such as the cruciferae (e.g., cabbage, mustard) and onions, which require large amounts of S, absorb intermediate amounts of Se, while grasses and grain crops absorb low to moderate amounts of Se.

Se in Soil Se occurs in very small amounts in nearly all materials of the earth's crust, averaging ≈ 0.05 ppm in rocks and is found mainly in sedimentary minerals. Se is similar in behavior to S; however, it has five oxidation states. Total Se in most soils ranges between 0.1 and 2 ppm. High-pH, calcareous soils formed from sedimentary shale in semi-arid regions exhibit high-Se soils and produce high-Se vegetation that can be toxic to livestock.

Forms of Se present in soil are:

- *Selenides* $(Se^{-2}) \rightarrow$ largely insoluble, associated with S^{-2} in semiarid region soils where weathering is limited. They contribute little to Se uptake.
- *Elemental Se* $(Se^{o}) \rightarrow$ present in small amounts in most soils. Significant amounts may be oxidized to selenites and selenates by microorganisms in neutral and basic soils.
- *Selenites* $(SeO_3^{-2}) \rightarrow$ exist in acid soils as stable complexes of selenites with Fe oxides. Low solubility of Fe-selenite complexes is apparently responsible for the nontoxic levels of Se in plants growing on acid, high-Se soils. Plants absorb $SeO_3^{-2} < SeO_4^{-2}$.
- *Selenates* $(SeO_4^{-2}) \rightarrow$ frequently associated with SO_4^{-2} in arid-region soils. Other Se forms will be oxidized to SeO_4^{-2} under these conditions. Only limited quantities of SeO_4^{-2} occur in acid and neutral soils. SeO_4^{-2} is highly soluble, readily plant available, and largely responsible for Se toxicity in plants grown on high-pH soils. Most of the water-soluble Se in soils probably occurs as SeO_4^{-2}.
- *Organic* Se $\rightarrow \approx 40\%$ of total Se in some soils occurs as organically complexed Se. Soluble organic Se compounds are liberated through residue decay from Se accumulator plants. Se in plant residue is stable in dry regions, and much of it remains plant available. Organic Se is more soluble in basic than acid soils, which would enhance availability in semiarid-region soils.

Low-Se uptake is usually caused by low total Se or low-Se availability in acid and poorly drained soils. Solution Se is lowest at slightly acid to neutral pH and increases under both more acid and basic soil pH. High soil pH facilitates the oxidation of SeO_3^{-2} to more soluble SeO_4^{-2}. Increased yields with N and S fertilization may lower Se concentration in crops through dilution. There has been some concern about increased incidence and severity of Se deficiencies in cattle due to the negative interaction of SO_4^{-2} on SeO_4^{-2} uptake by crops. Fertilization with S^o products depresses Se uptake less than readily available SO_4^{-2} sources.

Se Sources Although Se deficiency disorders such as muscular dystrophy or white muscle disease in cattle and sheep can be corrected by therapeutic measures, there is interest in Se fertilization to produce forages adequate in Se for grazing animals, rather than to satisfy any particular plant requirements. Se fertilization is acceptable if precautions are taken:

- to avoid Se toxicity to grazing animals, Se topdressing is not recommended.
- high Se levels in edible animal tissue should be prevented.
- protection against Se deficiency should be provided for at least one grazing season following application during the dormant season.

Fertilization with SeO_3^{-2} is preferred because it is slower acting and less likely to result in excessive Se levels in plants. SeO_4^{-2} can be used if rapid Se uptake is desired. Addition of Na_2SeO_3 (1 oz Se/a) is satisfactory for forages. Foliar application of Na selenite (6g Se/a) is an efficient way to increase Se in plants used for animal feed. Se is also present in P fertilizers produced from rock phosphate. Superphosphate containing $\geq$20 ppm Se may provide sufficient Se to plants in Se deficient areas to protect livestock from Se deficiency.

Vanadium (V)

Low concentrations of V are beneficial for growth of microorganisms, animals, and higher plants. Although essential for green algae, there is still no decisive evidence that V is necessary for higher plants. V may partially substitute for Mo in N_2 fixation by *Rhizobia.* It may also function in biological oxidation-reduction reactions. Increases in growth attributable to V have been reported for asparagus, rice, lettuce, barley, and corn. V requirement of plants is $<$2 ppb, whereas normal V concentration in plants averages approximately 1 ppm.

STUDY QUESTIONS

1. Identify the principal micronutrient anion and cation forms absorbed by plant roots.
2. For each micronutrient, describe the influence of soil solution pH on micronutrient availability.
3. For which micronutrients does adsorption to clay and Fe/Al oxide surfaces affect nutrient concentration in solution and plant availability? What adsorption mechanisms are important in calcareous soils?
4. Flooding and submergence influence the solubility and availability of which micronutrients?
5. Explain how microbial activity influences the solubility and availability of micronutrients.
6. How is the availability of micronutrients affected by soil OM?
7. Give examples of nutrient interactions important in micronutrient uptake (a) among heavy metal cations, (b) between N and at least three other elements, (c) between P and at least three other elements, and (d) between K and at least two other nutrients.
8. How do climatic factors influence plant availability of B, Mn, Mo, and Zn?
9. Describe the mechanism that enables Fe-efficient plants to tolerate low-Fe soils.
10. Explain why soluble Fe^{+3} decreases thousandfold and soluble Zn^{+2} decreases hundredfold for every one unit increase in soil pH.
11. Over the normal range in soil pH, solution Fe is 1,000 or more times lower than that required by plants for normal growth. Explain why most soils, regardless of pH, are not deficient in Fe.
12. Explain why soil-applied inorganic Fe fertilizers are less effective in correcting Fe deficiencies in high pH soils, whereas inorganic Zn fertilizers are commonly applied. Describe alternative methods which can be used to correct Fe deficiency.

13. Your agricultural advisor told you that $FeCl_3$ could be soil applied to a calcareous soil because HCl (hydrochloric acid) produced by the following reaction would keep the soil acid and Fe^{+3} in solution: $FeCl_3 + 3H_2O \rightarrow Fe^{+3} + 3OH^- + 3HCl$. Is this good or bad advice? Explain your answer.
14. What deficiencies are best controlled by foliar treatments of micronutrient fertilizers?
15. What micronutrient deficiencies are best corrected soil applications of micronutrients?
16. Acidification of high-pH and calcareous soils in localized zones such as fertilizer bands can be helpful in the treatment of what micronutrient deficiencies?
17. What soil and environmental condition would increase the potential for micronutrient toxicities?
18. Why is the behavior of Mo in soils different from the behavior of the other microelements?
19. Why is Cl^- not commonly deficient in soils?
20. Turf managers frequently use Fe to "green up" fairways. Calculate the quantity of FeEDTA needed to apply 0.3 lbs Fe/1,000 ft^2. If a 0.1% solution were prepared, how many gallons/1,000 ft^2 are needed to apply the same rate of Fe?
21. A grower wants to apply 5 lbs Zn/a. Calculate the amount of $ZnSO_4$ and ZnEDTA needed.
22. For a 18 in. band spacing, how many samples between bands are required for every sample taken on the band?
23. What are micronutrients? How does its deficiency affect the plant growth?
24. What is a chelate? Discuss the chelate dynamics in soil.
25. Explain what is a Chelate Pump in soil, with a diagram.
26. What factors induce Fe deficiency?
27. Give the structures of
    a. EDTA
    b. DTPA and
    c. EDDHA.
28. Explain the Zn cycle.
29. What are the common symptoms of Zn deficiency?
30. Name few common Zn – containing minerals.
31. What leads to Cu toxicity? What are its effects?
32. What are the common sources of Cu.
33. What is crinkle leaf? What is its cause and effect?
34. What factors influence the Mn availability?
35. What is tourmaline?
36. What are the different forms of Se in soil?

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9

Soil Fertility Evaluation

INTRODUCTION

Optimum plant health and productivity of a cropping system depends on an adequate supply of plant nutrients. The quantity of nutrients required by plants varies depending on many interacting factors including:

- plant species and variety
- yield potential
- soil properties
- environment
- management

These factors also influence the quantity of additional nutrients needed to optimize yield. Certainly, continued nutrient removal, with little or no replacement, ensures future nutrient-related yield loss.

When soil does not supply sufficient nutrients for optimum plant growth, nutrients must be applied. The proper nutrient rate is determined by knowing the nutrient requirement of the crop (Table 9-1) and the potential nutrient supply in the soil. Diagnostic techniques, including visual deficiency symptoms, soil and plant analysis, and remote sensing, are used to determine potential nutrient stress and the quantity of nutrients needed to optimize growth. Unfortunately, by the time visual nutrient-deficiency symptoms are observed, a reduction in yield potential has occurred. Therefore, quantifying the capacity of a soil to supply sufficient nutrients before planting or during the growing season is essential for optimum plant growth and yield.

Quantifying nutrient requirements by soil and plant analysis depends on careful sampling and analytical methods calibrated for the representative crops and soils in a specific region. Knowing the relationship between test results and crop nutrient response is essential for providing an accurate nutrient recommendation. Several techniques are commonly employed to assess the nutrient status of a soil:

- nutrient-deficiency symptoms of plants
- tissue analysis of plants growing on the soil
- remote sensing
- soil analysis

PLANT NUTRIENT-DEFICIENCY SYMPTOMS

Visual observation of the growing plant can help identify a specific nutrient stress (see color plates). A nutrient-deficient plant exhibits characteristic symptoms because

TABLE 9-1
TYPICAL NUTRIENT REMOVAL FOR SELECTED AGRICULTURAL AND HORTICULTURAL CROPS[1]

Crop	Yield	N	P	K	Ca	Mg	S	Cu	Mn	Zn
	unit/a	*lbs/a*								
					Grains					
Barley (grain)	60 bu	65	14	24	2	6	8	0.04	0.03	0.08
Barley (straw)	2 ton	30	10	80	8	2	4	0.01	0.32	0.05
Canola	45 bu	145	32	100	7	5	28	—	—	—
Corn (grain)	200 bu	150	40	40	6	18	15	0.08	0.10	0.18
Corn (stover)	6 tons	110	12	160	16	36	16	0.05	1.50	0.30
Flax	25 bu	65	8	29	5	3	12	—	—	—
Oats (grain)	80 bu	60	10	15	2	4	6	0.03	0.12	0.05
Oats (straw)	2 tons	35	8	90	8	12	9	0.03	—	0.29
Peanuts (nuts)	2 tons	140	22	35	6	5	10	0.04	0.30	0.25
Peanuts (vines)	2.5 tons	100	17	150	88	20	11	0.12	0.15	—
Rye (grain)	30 bu	35	10	10	2	3	7	0.02	0.22	0.03
Rye (straw)	1.5 tons	15	8	25	8	2	3	0.01	0.14	0.07
Sorghum (grain)	80 bu	65	30	22	4	7	10	0.02	0.06	0.05
Sorghum (stover)	4 tons	80	25	115	32	22	2	—	—	—
Soybean (grain)	50 bu	188	41	74	19	10	23	0.05	0.06	0.05
Soybean (stover)	3 tons	89	16	74	30	9	12	—	—	—
Sunflower	50 bu	70	13	30	3	3	12	—	—	—
Wheat (grain)	60 bu	70	20	25	2	10	4	0.04	0.10	0.16
Wheat (straw)	2.5 tons	45	5	65	8	12	15	0.01	0.16	0.05
					Forages and Turf					
Alfalfa	6 tons	350	40	300	160	40	44	0.10	0.64	0.62
Bent grass	2 tons	230	22	100	12	5	8	—	—	—
Bluegrass	2 tons	60	12	55	16	7	5	0.02	0.30	0.08
Bromegrass	4 tons	140	22	180	14	15	15	—	—	—
Clover	6 tons	320	40	260	51	22	23	—	—	—
Coastal Bermuda	8 tons	400	45	310	48	32	32	0.02	0.64	0.48
Cowpea	2 tons	120	25	80	55	15	13	—	0.65	—
Fescue	3.5 tons	135	18	160	18	13	20	—	—	—
Orchard grass	6 tons	300	50	320	12	25	35	—	—	—
Red Clover	2.5 tons	100	13	90	69	17	7	0.04	0.54	0.36
Ryegrass	5 tons	215	44	200	13	40	12	—	—	—
Sorghum—Sudan	8 tons	320	55	400	34	47	21	—	—	—
Soybean	2 tons	90	12	40	40	18	10	0.04	0.46	0.15
Timothy	4 tons	150	24	190	18	6	5	0.03	0.31	0.20
Vetch	6 tons	360	38	250	45	32	18	—	—	—
					Fruits and Vegetables					
Apples	500 bu	30	10	45	8	5	10	0.03	0.03	0.03
Bean, dry	30 bu	75	25	25	2	2	5	0.02	0.03	0.06
Bell Peppers	180 cwt	137	52	217	3	43	12	—	—	—
Cabbage	20 tons	130	35	130	20	8	44	0.04	0.10	0.08
Onion	7.5 tons	45	20	40	11	2	18	0.03	0.08	0.31
Peach	600 bu	35	20	65	4	8	2	—	—	0.01
Peas	25 cwt	164	35	105	8	18	10	—	—	—
Potato (sweet)	300 bu	40	18	96	4	4	6	0.02	0.06	0.03
Potato (white)	15 tons	90	48	158	5	7	7	0.06	0.14	0.08
Snap bean	4 tons	138	33	163	8	17	4	—	—	—
Spinach	5 tons	50	15	30	12	5	4	0.02	0.10	0.10
Sweet corn	90 cwt	140	47	136	8	20	11	—	—	—
Tomato	20 tons	120	40	160	7	11	14	0.07	0.13	0.16
Turnip	10 tons	45	20	90	12	6	12	—	—	—

Crop	Yield	N	P	K	Ca	Mg	S	Cu	Mn	Zn
	unit/a					*lbs/a*				
				Other Crops						
Cotton (seed + lint)	1.3 tons	63	25	31	4	7	5	0.18	0.33	0.96
Cotton (stalk + leaf)	1.5 tons	57	16	72	56	16	15	0.05	0.06	0.75
Sugar beet	20 tons	200	20	320	23	50	25	—	—	—
Sugarcane	40 tons	180	40	250	34	25	22	—	—	—
Tobacco (burley)	2 tons	145	14	150	21	18	24	—	—	—
Tobacco (flue)	1.5 tons	85	15	155	75	15	12	0.03	0.55	0.07

[1] divide nutrient removal (lb/a) by yield per acre to obtain lb nutrient/unit yield (i.e. lb/bu or lb/ton)

normal plant processes are inhibited. Visual nutrient-deficiency symptoms are characterized by:

- *chlorosis* → uniform or interveinal yellowing or light green coloring of leaves
- *necrosis* → death of leaf tips, margins, or interveinal regions of leaves
- *reddening* → accumulation of anthocyanins causes red or purple color on leaf margins, interveinal regions, or whole leaves
- *stunting* → reduced plant height, shortened internodes; leaves may remain dark green or exhibit light green or chlorotic symptoms
- *new growth cessation* → death of new shoots, terminal/axillary buds, or flowers; new leaves die back or exhibit rosetting

Each visual symptom is related to a nutrient function in the plant (Chapters 4–8). Most nutrients have several functions, making it difficult to identify the reason for a particular deficiency symptom. For example, with N deficiency, plant leaves become pale green or light yellow (chlorosis). When N is limiting, chlorophyll production and leaf greenness is reduced, allowing yellow pigments (carotene and xanthophylls) to prevail. Several nutrient deficiencies produce pale-green or yellow leaves, thus the symptom must be further related to a particular leaf pattern or location.

Understanding nutrient mobility in the plant is important to accurately identify a specific nutrient-deficiency symptom (Fig. 9-1). With mobile nutrients (N, P, K, Mg, and Mo), symptoms will appear in older leaves first as these nutrients are readily translocated from older leaves to newer growth. Deficiency symptoms will appear in newer growth first with immobile nutrients (Ca, Fe, Mn, Zn, Cu, and Ni). As discussed in Chapters 7-8, S, Cl, and B mobility varies with plant species and therefore is difficult to characterize deficiency symptoms based on mobility.

In addition to leaf symptoms, nutrient deficiencies have a marked effect on root growth (Fig. 9-2). Plant roots receive less attention because of the difficulty in observing them; however, since roots absorb nutrients, inspection of root growth is an important diagnostic tool.

Visual deficiency symptoms can be related to factors other than nutrient stress. Precautions in interpreting nutrient-deficiency symptoms include the following:

- Visual symptoms may be caused by more than one nutrient. For example, N-deficiency symptoms (chlorosis) may be identified, although S deficiency may also be apparent.
- Deficiency of one nutrient may be related to toxicity or imbalance of another. For example, Mn deficiency may be induced by excessive Fe in soils that are marginally deficient in Mn. P addition can induce a Zn deficiency in marginally Zn-deficient soils.

- It can be difficult to distinguish among deficiency symptoms in the field, because disease, insect, or herbicide damage can resemble certain micronutrient deficiencies. For example, leaf hopper damage can be confused with B deficiency in alfalfa.
- A visual symptom may be caused by more than one factor. For example, sugars in corn combine with flavones to form anthocyanins (purple, red, and yellow pigments), and their accumulation may be caused by an insufficient supply of P, low soil temperature, insect damage to roots, or N deficiency.

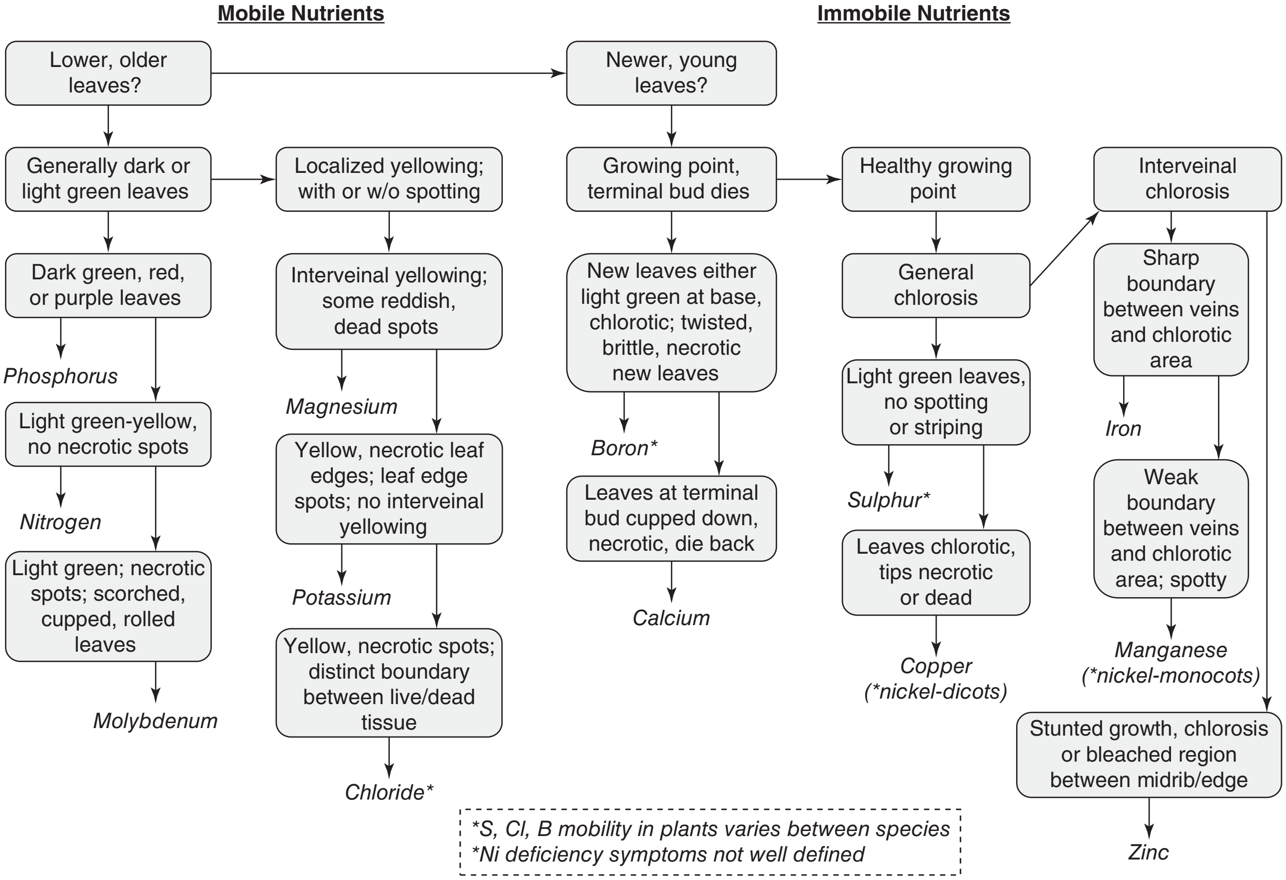
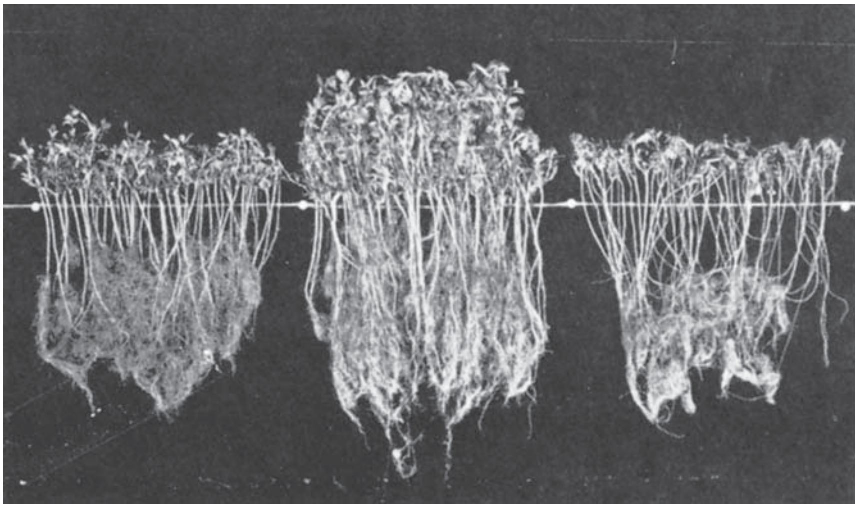


Figure 9-1
Generalized flow chart for distinguishing nutrient deficiency symptoms in plants.

Figure 9-2
Omitting P (left) or K (right) reduces early growth of alfalfa roots and tops in soil deficient in P and K.
(International Plant Nutrition Institute (IPNI)).



Nutrient-deficiency symptoms appear when nutrient supply is so low that the plant cannot function properly. In such cases, supplemental nutrients are needed long before symptoms appear. If the symptom is observed early, it might be corrected during the growing season with foliar or sidedress applications (Chapter 10). However, yield is often reduced below optimum if adequate nutrients are not available at planting. Diagnosis of nutrient deficiency late in the growing season can still be useful in correcting deficiencies the following year.

Nutrient-deficiency symptoms appearing during early growth may disappear as the growing season progresses, or there may be no measurable yield benefit from nutrient additions. For example, P may improve early crop growth, but at harvest, there may be no measurable yield response. Such occurrences are probably related to seasonal effects or to root growth into soil areas with higher fertility levels.

Nutrients may also be present in sufficient quantities under ideal conditions, but in drought, excessive moisture, or unusual temperature conditions, plants may be unable to absorb adequate nutrients. For example, with cooler temperatures, nutrient uptake is reduced because:

- mass flow of nutrients is reduced by decreased growth rate and transpiration
- diffusion rate decreases with declining temperature and a lower concentration gradient
- mineralization of organic bound nutrients is reduced.

More commonly, nutrient-deficiency symptoms may not be visible, although plant nutrient levels may be considerably lower than required for optimum yield (*hidden hunger*). Soil and plant analyses are invaluable tools to identify hidden hunger, verify the specific nutrient causing the deficiency, and guide nutrient management programs to avoid yield loss from nutrient stress. Visual evaluation of nutrient stress should be used only to support or direct other diagnostic techniques (i.e., soil and plant analyses). To assure that nutrients do not limit plant growth, nutrient availability should be high enough to take advantage of optimum growing conditions and to prevent nutrient stress.

PLANT ANALYSIS

Plant analysis methods include tests on fresh tissue in the field and analyses performed in a laboratory. Plant analyses are performed to:

- verify the accuracy of an assessment of visual deficiency symptoms
- identify plant nutrient shortages before they appear as symptoms
- help determine the relative nutrient-supplying capacity of the soil
- quantify the effect of nutrient addition on nutrient concentration in the plant
- study the relationship between plant nutrient status and crop performance (i.e., yield).

Plant analyses help us understand the relationship between plant nutrient content and nutrient availability in the soil. For example, since a nutrient shortage will limit growth, other nutrients may accumulate, regardless of their supply. With low plant N, plant P content may be high. This is no indication, however, that under adequate N supply, P would be adequate.

Tissue Tests

Nutrient analysis on fresh tissue is important in diagnosing nutrient needs of growing plants. With proper tissue testing, it is possible to anticipate or forecast certain nutrient-related production problems while the crop is still in the field.

Tissue tests are easy to conduct and interpret, and some qualitative tests can be made in a few minutes. Because laboratory tests take longer, there is a tendency to guess rather than send samples to the laboratory. It is important to recognize that application of nutrients to correct a nutrient stress identified with a tissue test may not be feasible because:

- the deficiency may have already caused yield loss
- the crop may not respond to the applied nutrient at the specific growth stage tested
- the crop may be too large to apply nutrients
- climatic conditions may be unfavorable for nutrient application

Cell Sap Tests Semiquantitative estimates of plant N, P, and K can be rapidly obtained with simple plant tissue tests conducted in the field. Plant leaves or stems are chopped up and extracted with reagents specific for each nutrient. Plant tissue can also be squeezed with a garlic press to transfer plant sap to filter paper and color-developing reagents are then added. The color intensity of the cell sap/reagent mix is compared with a standard color chart that indicates very low, low, medium, or high nutrient content. Handheld ion-selective sensors and colorimeters are also available but are more expensive.

It is essential to test the plant part that gives the best indication of nutrient status. In general, the conductive tissue of the most recently mature leaf is used for testing. For most vegetable crops leaf petioles are preferred (Table 9-2). Time of day

TABLE 9-2
PETIOLE AND MIDRIB NO_3-N SUFFICIENCY RANGES FOR SELECTED VEGETABLE CROPS ON A DRY WEIGHT AND FRESH SAP BASIS

			NO_3-N	
Crop	Tissue Sample	Growth Stage	*% in dry weight*	*ppm in sap*
Broccoli	Midrib	Buttoning	0.9–1.2	800–1100
Cabbage	Midrib	Heading	0.7–0.9	NA
Carrots	Petiole	Midgrowth	0.75–1.0	550–750
Cauliflower	Midrib	Buttoning	0.7–0.9	NA
Celery	Petiole	Midgrowth	0.7–0.9	500–700
Cucumber	Petiole	First blossom	0.75–0.9	800–1000
		Early fruit set	0.5–0.75	600–800
		First harvest	0.4–0.5	400–600
Eggplant	Petiole	Initial fruit	NA	1200–1600
		First harvest	NA	1000–1200
Lettuce	Midrib	Heading	0.6–0.8	NA
Muskmelon	Petiole	First blossom	1.2–1.4	1000–1200
		Initial fruit	0.8–1.0	800–1000
		First mature fruit	0.3–0.5	700–800
Peppers	Petiole	First flower	1.0–1.2	1400–1600
		Early fruit set	0.5–0.7	1200–1400
		Fruit 3/4 size	0.3–0.5	800–1000
Potato	Petiole	Vegetative	1.7–2.2	1200–1600
		Tuber bulking	1.1–1.5	800–1100
		Maturation	0.6–0.9	400–700
Tomato	Petiole	Early bloom	1.4–1.6	1000–1200
		Fruit 1 in. diameter	1.2–1.4	400–600
		Full ripe fruit	0.6–0.8	300–400
Watermelon	Petiole	Early fruit set	0.75–0.9	1000–1200
		Fruit 1/2 size	NA	800–1000
		First harvest	NA	600–800

NA = not available

Source: Adapted from C. J. Rosen and R. Eliason, 1996, *Nutrient Management for Commercial Fruit & Vegetable Crops in Minnesota,* Univ. of Minnesota, DG–05886-GO.

can affect tissue N concentrations. To reduce variability, samples should be collected in midday. Collect 20–40 plants from deficient areas and compare them with plants from normal areas.

Total Analysis Total analysis is performed on specific plant parts (e.g., petioles, stems, leaves) in a laboratory. After sampling, plant material is dried, ground, and nutrient content determined following wet digestion with concentrated acid or dry ashing in a high-temperature oven. As in cell sap tests, the plant part selected is important, with the most recently matured leaf preferred (Table 9-3). Samples should be kept dry or refrigerated and protected from contamination.

TABLE 9-3
PLANT SAMPLING GUIDELINES FOR SELECTED AGRICULTURAL AND HORTICULTURAL CROPS

Crop	Sampling Time	Plant Part Sampled	Sample #
		Field Crops	
Alfalfa	Early bloom	Top 6 in. or upper 1/3 of plant	20–30
Canola	Before seed set	Newest mature leaf	50–60
Clover	Before bloom	Upper 1/3 of plant	30–40
Corn	Seedling stage	All above-ground material	25–30
Sweet corn	Before tasseling	Fully mature leaf from top of plant	15–20
	Tasseling to silking	Leaf blow and opposite ear	15–20
Cotton	Full bloom	Newest mature leaf from main stem	30–40
Grasses/forage	Stage of best quality	Upper leaves	40–50
Peanuts	Before or at bloom	Newest mature leaf	40–50
Small grains	Seedling stage	All above-ground material	25–40
	Before heading	Uppermost leaf blades	25–40
Sorghum	Before or at heading	Leaf from top of plant	20–30
Soybean	Before or at bloom	Newest mature leaf from top of plant	20–30
Sugar beet	Midseason	Newest mature leaf, center of whorl	30–40
Sunflower	Before heading	Newest mature leaf	20–30
Tobacco	Before bloom	Top fully developed leaf	8–10
		Vegetable Crops	
Asparagus	Maturity	18–30 inches above ground line	10–20
Beans	Seedling stage	All above-ground portions	20–30
	Before or at bloom	Newest mature leaf	20–30
Beets, table	Mature	Young mature leaf	20–30
Broccoli	Before heading	Newest mature leaf	12–20
Brussels sprouts	Midseason	Newest mature leaf	12–20
Cabbage, cauliflower	Before heading	Newest mature leaf, center of whorl	10–20
Celery	Midseason	Petiole of newest mature leaf	12–20
Cucumber	Before fruit set	Newest mature leaf	12–20
Eggplant	Early fruiting	Young mature leaf	15–25
Garlic	Bulbing	Young mature leaf	25–35
Lettuce, spinach	Midseason	Newest mature leaf	15–25
Melons	Before fruit set	Newest mature leaf	15–25
Peas	Before or at bloom	Leaves from node from top	40–60
Peppers	Midseason	Recently mature leaf	25–50
Potato	Before or at bloom	Leaf from growing tip	25–30
Pumpkin/Squash	Early fruiting	Young mature leaf	15–25
Radishes	Midgrowth to harvest	Young mature leaf	40–50
Root crops (carrot, beet, onion)	Before root or bulb enlargement	Newest mature leaf	25–35
Sweet potato	midseason before root enlargement	Leaf from tip center Mature leaves	20–30 25–35
Tomato (field)	Early-midbloom	Leaf from growing tip	15–25
Tomato (trellis or indeterminate)	Midbloom; 1st-6th cluster stage	Petiole of leaf below or opposite top cluster	15–25

(continued)

TABLE 9-3 (CONTINUED)

Crop	Sampling Time	Plant Part Sampled	Sample #
		Ornamentals, Flowers	
Carnation	Newly planted	4th–5th leaf pair from plant base	20–30
	Established	5th–6th leaf pair from plant base	20–30
Chrysanthemum	Before or at bloom	Top leaves on flowering stem	20–30
Poinsettia	Before or at bloom	Newest mature leaf	15–25
Rose	At bloom	Newest mature compound leaf on flowering stem	25–30
Trees and shrubs	Current year growth	Newest mature leaf	30–70
Turf	Active growth	Leaves, avoid soil contamination	2 cups
		Fruit and Nut Crops	
Apple, pear, almond, apricot, cherry, prune, plum	Midseason	Leaves from current year growth-nonfruiting, nonexpanding spurs	50–100
Blueberries	1st week of harvest	Young mature leaf	50–70
Cantaloupe	Early fruiting	Fifth leaf from tip	25–35
Grapes	At bloom	Petioles or leaves adjacent to basal clusters at bloom	50–100
Lemon, lime	Midseason	Mature leaf from last growth flush, nonfruiting terminals	30–40
Orange	Midseason	Spring cycle leaf, 4–7 months old, nonfruiting terminals	25–35
Peach, nectarine	Midseason	Midshoot leaflets/leaves	25–100
Pecan	Midseason	Midshoot leaflets/leaves	25–60
Pistachios	Mid to late season	terminal leaflets, nonfruiting shoots	25–60
Raspberries	Midseason	newest mature leaf, laterals of primocanes	30–50
Strawberries	Midseason	Newest mature leaves	25–40
Walnut	6–8 weeks after bloom	Terminal leaflets/leaves from nonfruiting shoots	25–40
Watermelon	Midgrowth	Newest mature leaf	15–25

Sampling Time

Growth stage is important in plant analysis because nutrient status and demand vary during the season. Nutrient concentration in vegetative parts usually decreases with maturity (Fig. 9-3). Misinterpretation of plant analysis results are common if sampling time is not identified correctly. For example, corn leaves sampled at brown silk would be considered N deficient if compared with third leaf-stage N concentration (Table 9-4). In most agricultural crops, the best sampling times coincide with periods of rapid dry matter and plant nutrient accumulation. Plants from both deficient and normal areas should be sampled to compare results.

Figure 9-3
Variation in nutrient concentration in plant tissue over the growing season (CNR = critical nutrient range).

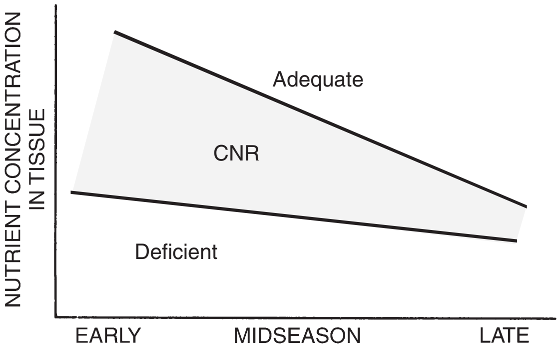


TABLE 9-4
CRITICAL NUTRIENT RANGES FOR SELECTED CROPS

	Corn			
Nutrient	*Whole Plant 24–45 Days**	*Third Leaf, 45–80 Days†*	*Earleaf Green Silks‡*	*Earleaf Brown Silks§*
N, %	4.0–5.0	3.5–4.5	3.0–4.0	2.8–3.5
P, %	0.40–0.60	0.35–0.50	0.30–0.45	0.25–0.40
K, %	3.0–5.0	2.0–3.5	2.0–3.0	1.8–2.5
Ca, %	0.51–1.60	0.20–0.80	0.20–1.0	0.20–1.2
Mg, %	0.30–0.60	0.20–0.60	0.20–0.80	0.20–0.80
S, %	0.18–0.40	0.18–0.40	0.18–0.40	0.18–0.35
B, ppm	6–25	6–25	5–25	5–25
Cu, ppm	6–20	6–20	5–20	5–20
Fe, ppm	40–500	25–250	30–250	30–250
Mn, ppm	40–160	20–150	20–150	20–150
Zn, ppm	25–60	20–60	20–70	20–70

*Seedlings 6 to 16 in. tall; 24 to 45 days after planting.
†Third leaf from top; plants over 12 in. tall; before silking.
‡Seventy to ninety days after planting.
§Grain in developing stage up to "roasting ear."
Source: Schulte and Kelling, 1985, *National Corn Handbook*, NCH-46, Purdue Univ. Coop. Ext. Service.

	Soybean	Small Grain	
Nutrient	*Sufficiency Range**		*Sufficiency Range*
N, %	4.3–5.5	winter / spring grains	1.75–3.0 / 2.0–3.0
P, %	0.3–0.5		0.20–0.50
K, %	1.7–2.5		1.5–3.0
Ca, %	0.4–2.0	barley / all other	0.30–1.2 / 0.20–0.50
Mg, %	0.3–1.0		0.15–0.50
S, %	0.4–0.8		0.15–0.40
Mn, ppm	21–100		25–100
Fe, ppm	51–350		40–250
Zn, ppm	21–50		15–70
Cu, ppm	10–30		5–25
B, ppm	21–55		
Mo, ppm	1.0–5.0		

*Upper fully developed trifoliate leaves sampled before pod set.

(*continued*)

Table 9-4 (Continued)

Alfalfa						
Plant Part	*N*	*P*	*K*	*S*	*Ca*	*Mg*
	%					
Top 6 in.	4.0–5.0	0.20–0.30	1.8–2.4	0.18–0.30	0.8–1.5	0.2–0.3
Upper 1/3	—	0.18–0.22	1.7–2.0	0.20–0.30	—	—
Whole tops	—	0.20–0.25	1.5–2.2	0.20–0.24	1.4–2.0	0.28–0.32
N:S tops	—	—	—	12–17	—	—

Turfgrass							
Nutrient	*Bermuda-grass*	*Coastal Bermuda*	*Creeping Bentgrass*	*Fescue*	*Kentucky Bluegrass*	*Perennial Ryegrass*	*St. Augustine-grass*
N, %	4.0–6.0	1.8–2.2	4.5–6.0	2.8–3.4	2.4–2.8	3.34–5.1	1.9–3.0
P, %	0.25–0.6	0.2–0.3	0.3–0.6	0.26–0.32	0.24–0.3	0.35–0.55	0.2–0.5
K, %	1.5–4.0	1.8–2.1	2.2–2.6	2.5–2.8	1.6–2.0	2.0–3.42	2.5–4.0
Ca, %	0.5–1.0	0.4–0.7	0.5–0.75	0.4–0.6	0.25–0.55	0.25–0.51	0.3–0.5
Mg, %	0.13–0.4	0.2–0.3	0.25–0.3	0.12–0.28	0.28–0.33	0.16–0.32	0.15–0.25
S, %	0.2–0.5	0.28–0.4	—	0.24–0.5	0.26–0.45	0.27–0.56	—
Fe, ppm	50–500	—	100–300	—	—	97–934	50–300
Mn, ppm	25–300	—	50–100	—	—	30–73	40–250
Cu, ppm	5–50	—	8–30	—	—	6–38	10–20
Zn, ppm	20–250	—	25–75	—	—	14–64	20–100
B, ppm	6–30	—	8–20	—	—	5–17	5–10
Mo, ppm	0.1–1.2	—	—	—	—	0.5–1.0	—

TABLE 9-4 (CONTINUED)

	Fruits and Vegetables											
Crop	*N*	*P*	*K*	*Ca*	*Mg*	*S*	*Fe*	*B*	*Cu*	*Zn*	*Mn*	*Mo*
	%						ppm					
Apples	1.9–2.3	0.1–0.4	1.2–1.8	0.8–1.6	0.25–0.45	0.2–0.4	50–200	30–50	6–12	20–50	25–135	> 0.1
Asparagus	2.4–3.8	0.25–0.5	1.5–2.4	0.4–1.0	0.25–0.3	—	40–250	40–100	5–25	20–60	25–160	—
Bean, snap	5.0–6.0	0.25–0.75	2.2–4.0	1.5–3.0	0.25–0.7	—	50–300	20–60	7–30	20–60	50–300	> 0.4
Beets, table	3.5–5.0	0.25–0.5	3.0–4.5	2.5–3.5	0.30–1.0	—	50–200	30–80	5–15	15–30	70–200	—
Blueberries	1.7–2.1	0.10–0.4	0.4–0.7	0.35–0.8	0.12–0.25	0.12–0.3	70–200	25–70	5–20	9–30	50–600	—
Broccoli	3.2–5.5	0.3–0.7	2.0–4.0	1.2–2.5	0.23–0.4	0.3–0.75	50–150	30–100	4–10	20–80	25–150	0.3–0.5
Brussels sprouts	3.1–5.5	0.3–0.75	2.0–4.0	1.0–2.5	0.25–0.75	0.3–0.75	60–300	30–100	5–15	25–200	25–200	0.25–1.0
Cabbage	3.6–5.0	0.33–0.75	3.0–5.0	1.1–3.0	0.4–0.75	0.3–0.75	30–200	25–75	5–15	20–200	25–200	0.4–0.7
Cantaloupe	4.5–5.5	0.3–0.8	4.0–5.0	2.3–3.0	0.35–0.8	0.25–1.0	40	50–300	25–60	7–30	20–200	50–250
Carrot	2.5–3.5	0.2–0.3	2.8–4.3	1.4–3.0	0.3–0.5	—	50–300	30–100	5–15	25–250	60–200	0.5–1.5
Cauliflower	3.3–4.5	0.33–0.80	2.6–4.2	2.0–3.5	0.27–0.50	—	30–200	30–100	4–15	20–250	25–250	0.5–0.8
Celery	2.5–3.5	0.3–0.5	4.0–7.0	0.6–3.0	0.20–0.50	—	30–70	30–60	5–8	20–70	100–300	—
Cucumber	4.5–6.0	0.3–1.3	3.5–5.0	1.0–3.5	0.3–1.0	0.3–0.7	50–300	25–60	5–20	25–100	50–300	—
Eggplant	4.2–5.0	0.45–0.6	5.7–6.5	1.7–2.2	0.25–0.35	—	—	20–30	4–6	30–50	15–100	—
Garlic	3.4–4.5	0.28–0.5	3.0–4.5	1.0–1.8	0.23–0.35	—	—	—	—	—	—	
Grapes	1.6–2.8	0.2–0.46	1.5–2.0	1.2–2.5	0.3–0.4	—	40–180	25–50	5–10	25–100	25–100	0.2–0.4
Lettuce	2.5–4.0	0.4–0.6	6.0–8.0	1.4–2.0	0.5–0.7	—	50–500	30–100	7–10	26–100	30–90	> 0.1
Onion	5.0–6.0	0.35–0.5	4.0–5.5	1.5–3.5	0.3–0.5	0.50–1.0	60–300	30–45	5–10	20–55	50–65	—
Peas	4.0–6.0	0.3–0.8	2.0–3.5	1.2–2.0	0.3–0.7	0.2–0.4	50–300	25–60	5–10	25–100	30–400	> 0.6
Peppers	3.5–4.5	0.3–0.7	4.0–5.4	0.4–0.6	0.30–1.50	—	60–300	30–100	10–20	30–100	26–300	—
Potato (leaf)	3.5–4.5	0.25–0.5	4.0–6.0	0.5–0.9	0.25–0.5	0.2–0.35	30–150	20–40	5–20	20–40	20–450	—
Potato (petiole)	—	0.22–0.4	8.0–10.0	0.6–1.0	0.3–0.55	0.2–0.35	50–200	20–40	4–20	20–40	30–300	—
Pumpkin/Squash	4.0–6.0	0.35–1.0	4.0–6.0	1.0–2.5	0.3–1.0	—	60–300	25–75	6–25	20–200	50–250	—
Radish	3.0–6.0	0.30–0.70	4.0–7.5	3.0–4.5	0.50–1.20	0.20–0.40	50–200	30–50	6–12	20–50	25–130	—
Raspberries	2.2–3.5	0.20–0.50	1.1–3.0	0.6–2.5	0.25–0.80	0.20–0.30	50–200	25–300	4–20	15–60	25–300	—
Spinach	4.2–5.2	0.30–0.60	5.0–8.0	0.6–1.2	0.60–1.00	—	60–200	25–60	5–25	25–100	30–250	> 0.5
Strawberry	2.1–2.9	0.2–0.35	1.1–2.5	0.6–1.8	0.25–0.7	0.2–0.3	90–150	25–60	6–20	20–50	30–100	—
Sweet corn	2.8–3.5	0.25–0.4	1.8–3.0	0.6–1.1	0.2–0.5	0.2–0.75	50–300	8–25	5–25	20–100	30–300	0.9–1.0
Tomato	4.0–6.0	0.25–0.8	2.9–5.0	1.0–3.0	0.4–0.60	0.4–1.2	40–200	25–60	5–20	20–50	40–250	—
Watermelon	2.0–3.0	0.2–0.3	2.5–3.5	2.5–3.5	0.6–0.8	—	100–300	30–80	4–8	20–60	60–240	—

Source: C. J. Rosen and R. Eliason, 1996, *Nutrient Management for Commercial Fruit & Vegetable Crops in Minnesota*, Univ. of Minnesota, DG-05886-GO.

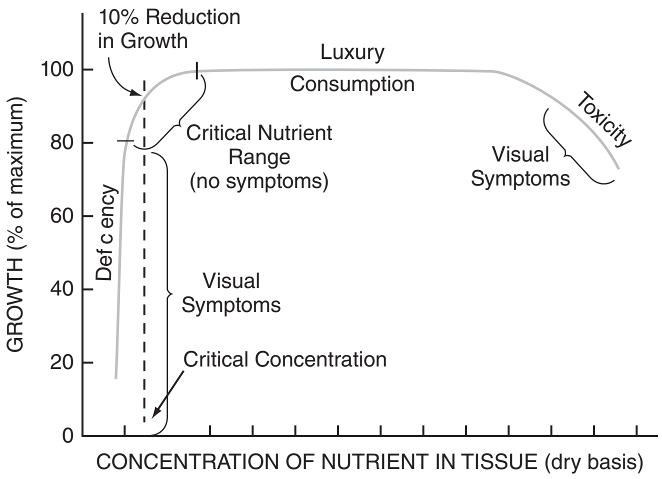


Figure 9-4
Relationship between plant nutrient concentration and plant growth. Critical nutrient range (CNR) represents a small economic yield loss without visual deficiency symptoms.

Interpretation

Plants that are *severely* nutrient deficient exhibit a visual deficiency symptom with substantial yield loss (Fig. 9-4). Plants that are *moderately* deficient usually exhibit no visual symptoms, although yield potential can be reduced. Correcting the deficiency by adding nutrients will maximize growth potential and increase plant nutrient concentration. *Luxury consumption* represents nutrient absorption in excess of that required for optimum growth, but is not detrimental to plant growth. Thus, as nutrient supply increases, plant nutrient concentration increases without an increase in growth. Nutrient *toxicity* occurs when plant growth decreases with increasing plant nutrient concentration.

A critical nutrient concentration (CNC) can be used in interpreting plant analysis results (Fig. 9-5). The CNC is located in that portion of the curve where the plant nutrient concentration changes from deficient to adequate; therefore, CNC is the nutrient level below which crop yield, quality, or performance is unsatisfactory. However, it is difficult to establish an exact CNC since variation exists in the transition zone between deficient and adequate nutrient concentrations. Consequently, critical nutrient range (CNR) is commonly used, which is the range in nutrient concentration at a specific growth stage above which nutrient supply is adequate and below which nutrient deficiency occurs (Fig. 9-5). CNRs have been developed for most of the essential nutrients in many crops (Table 9-4).

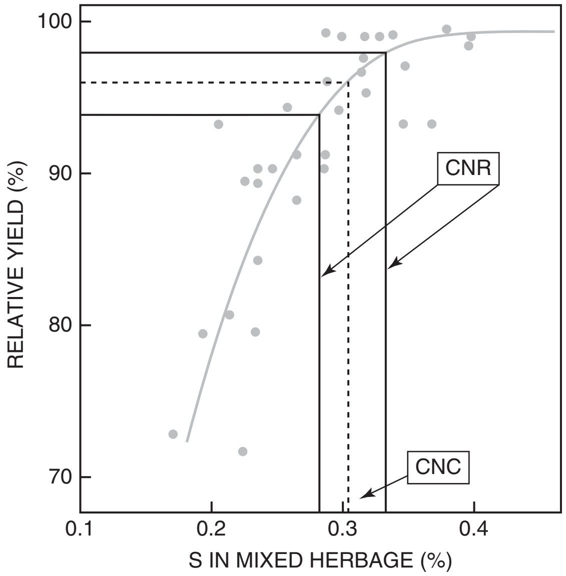


Figure 9-5
Example of critical nutrient concentration (CNC) and critical nutrient range (CNR) for S in forage grass.

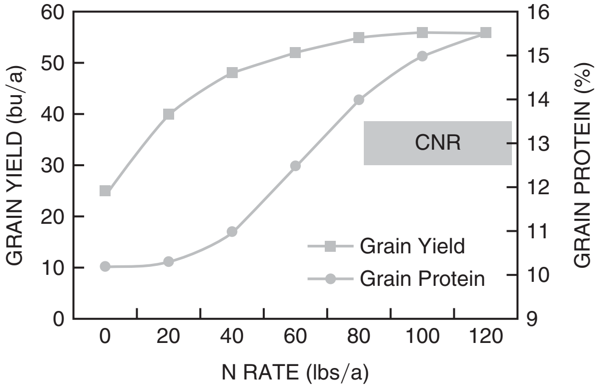


Figure 9-6
Typical grain yield (winter wheat) and plant N (grain protein) response to N rate. CNR ranges between 12.5% and 13.5% grain protein.

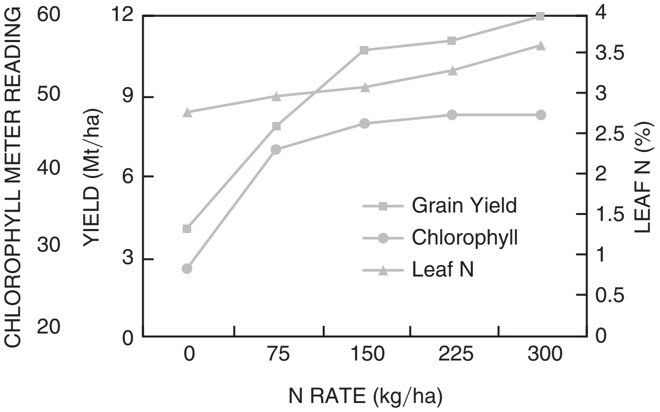


Figure 9-7
Relationship between irrigated corn grain yield, tissue N, and chlorophyll readings at V8 growth stage. CNR is ~3.2–3.7%N. Chlorophyll readings were obtained with a handheld chlorophyll meter.
(Adapted from *Schepers et al., 1992,* Great Plains Soil Fert. Conf., p. 42.)

Relationship Between Yield and Plant Nutrient Content

When a nutrient is deficient, increasing nutrient availability will increase plant growth and nutrient content until CNR is exceeded (Fig. 9-4). For example, applied N increased % N (or grain protein) in wheat (Fig. 9-6) and in corn (Fig. 9-7). Above the CNR, % N in the plant increases with little yield advantage.

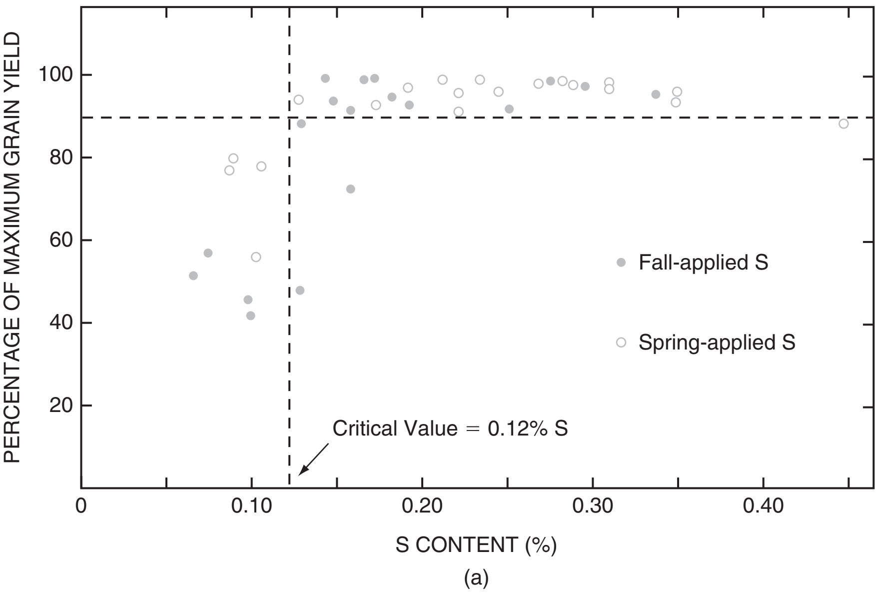
Plant analysis interpretations based on CNR and sufficiency-range concepts have limitations. Unless the crop sample is taken at the proper growth stage, the analytical results will have little value (Fig. 9-3). Also, considerable skill is needed to interpret plant analysis results relative to overall production conditions, as other factors can limit yield and alter nutrient concentration.

Nutrient Ratios

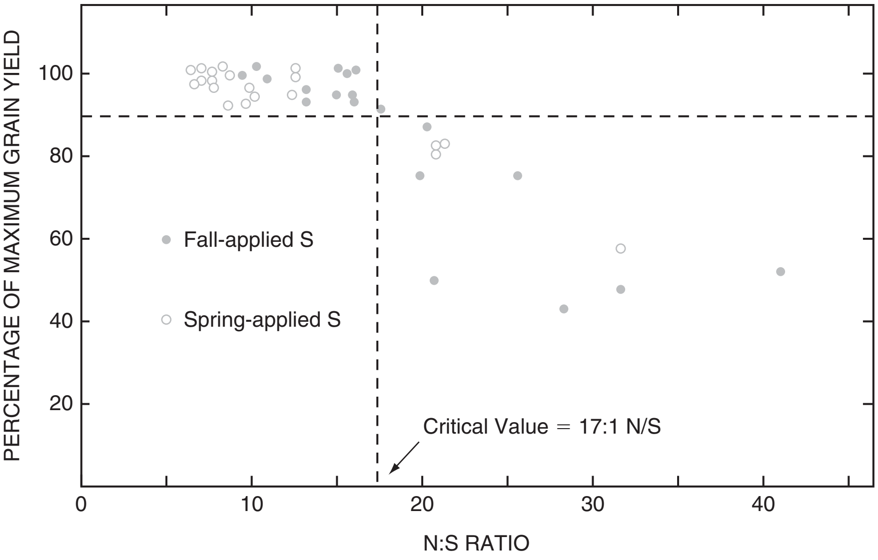
Plant nutrient ratios can be used to assess crop nutrient balance. For example, N:P, N:S, K:Mg, K:Ca, Ca+Mg:K, and other ratios are commonly used. When a nutrient ratio is optimal, optimum yield occurs unless some other limiting factor reduces yield. When a ratio is low, a response to the nutrient in the numerator may be obtained. If the nutrient in the denominator is excessive, yield response to application of the nutrient in the numerator may or may not occur. When the ratio is too high, the reverse is true. Optimum nutrient ratios are established similar to critical levels for individual nutrients (Fig. 9-8). These data illustrate that when S concentration $<0.12\%$ or $N:S > 17$, wheat grain yield will likely respond to S fertilization.

Caution should be exercised in interpreting nutrient ratios. For example, when $N:S = 17$ (Fig. 9-8), three possibilities exist where both N and S are optimal, excessive, or deficient. It is difficult to determine from the ratio alone which situation exists in the plant. When $N:S > 17$, either N could be excessive or S could be deficient. A yield response to applied S occurs only if S is deficient, whereas if N is high and S is normal, additional S may dilute N in the plant. Alternatively, when

Figure 9-8
Relationship between winter wheat grain yield and S concentration (a) and N:S ratio (b). N and S were determined in whole plant samples collected at boot stage.



(a)



(b)

N:S < 17, either N could be deficient or S could be high. With low N, adding N may increase yield and dilute plant S. This example demonstrates why nutrient ratios are difficult to interpret and a yield response is not always obtained when a ratio is outside the optimum range. Interpretation of nutrient ratios should be integrated with CNR information.

Tissue Tests for In-Season N Adjustments Plant analysis is used in many crop systems to determine appropriate nutrient application rates during the growing season. Petiole NO_3–N analysis is advised in cotton production to enhance yield and N-use efficiency (Fig. 9-9). Petiole samples of the newest mature cotton leaf are collected at or near full bloom stage and are either sent to a laboratory for NO_3–N analysis or quick-tested using in-field colorimetric analysis of the petiole tissue sap. For example, if full bloom petiole samples tested 0.2% NO_3–N (Fig. 9-9), then a foliar application of 5 lbs/a N would be recommended. Usually three foliar applications are required to optimize cotton yield. As the cotton plant matures, petiole NO_3–N declines. Thus, it is essential to identify the growth stage accurately.

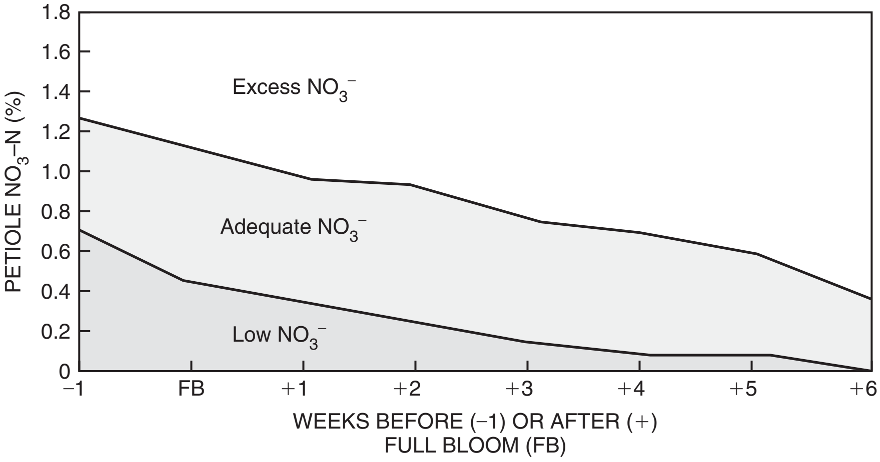


Figure 9-9
Cotton petiole NO_3–N *concentration as influenced by sampling time. Foliar N applications would be recommended when petiole* NO_3–N *is low.*
(Adapted from *Steve Hodges, 1997, Dept. Soil Science, NCSU.*)

In potato, petiole NO_3^- determined 50–55 days after emergence is used as a guide for sidedress or topdress N to maximize yield and recovery of applied N (Fig. 9-10). When petiole NO_3^- concentrations are <1.5–2.0%, additional N is recommended. Petiole NO_3 sufficiency levels will vary depending on crop (Table 9-2) and in some cases the variety (Table 9-5).

In winter wheat, N uptake at mid- (GS25) and late tillering (GS30) are critical growth stages for maximizing yield and N use efficiency (refer to Fig. 10-2). When tiller density is <100 tillers/ft^2 at GS25 and/or N in leaves at GS30 is $<4.5\%$, additional N is required to optimize yield (Fig. 9-11).

Sensor Based Tissue Analysis

Chlorophyll Meters

The chlorophyll meter is a simple, portable diagnostic sensor that measures greenness or relative chlorophyll content in plant leaves. Chlorophyll meters based on either light absorbance or laser technology are available (Fig. 9-12). With absorbance meters, measurements involve placing a handheld sensor on a leaf surface and the quantity of light (~650 nm) transmitted through the leaf is measured (Fig. 9-13). Increasing chlorophyll content decreases light transmitted through the leaves. The sensor displays relative chlorophyll content as SPAD (soil plant analyzer development) values. In practice, chlorophyll readings from nutrient-deficient leaves are compared to readings from

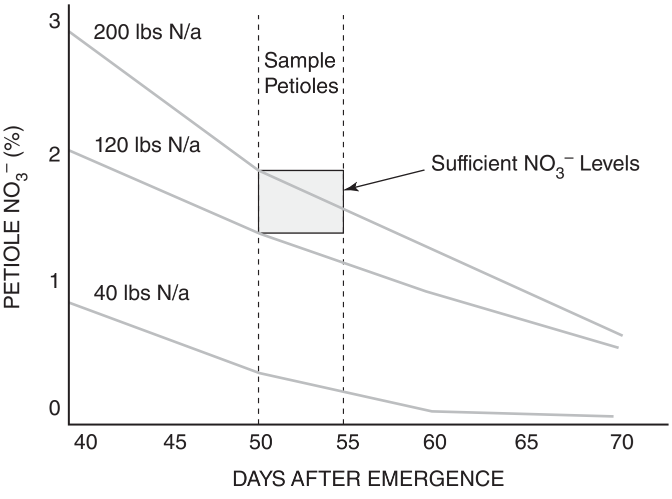


Figure 9-10
Influence of N rate on petiole NO_3^- *concentration. Optimum petiole* NO_3^- *concentration is 1.5–2.0% at 50–55 days after emergence.*
(Adapted from *Wolkowski et al., 1995,* Nitrogen management on sandy soils, *Madison, WI: Univ. Wisconsin Coop. Ext.* Publ. A3634.)

TABLE 9-5
PETIOLE NO_3^- SUFFICIENCY RANGES AT DIFFERENT GROWTH STAGES FOR TWO RUSSET POTATO VARIETIES*

Growth Stage	Description	N Sufficiency Range (%)
	Ranger Russett	
I	Emergence until tuberization	2.0–2.2
II	Tuberization	1.8–2.0
III	Tuber bulking	1.8–2.0
IV	Maturation	1.3–1.5
	Gem Russett	
I	Emergence through tuberization	2.1–2.3
II	Tuberization	2.1–2.3
III	Early tuber bulking	1.6–1.9
IV	Late tuber bulking	1.0–1.3
V	Maturation	0.6–1.1

*To convert NO_3^- to NO_3-N, multiply by 0.226.
Source: Adapted from S. L. Love, 1998, *Cultural Management of Ranger (CIS919) and Gem (CIS1093) Russet Potatoes*, Coop. Ext. System, Univ. of Idaho.

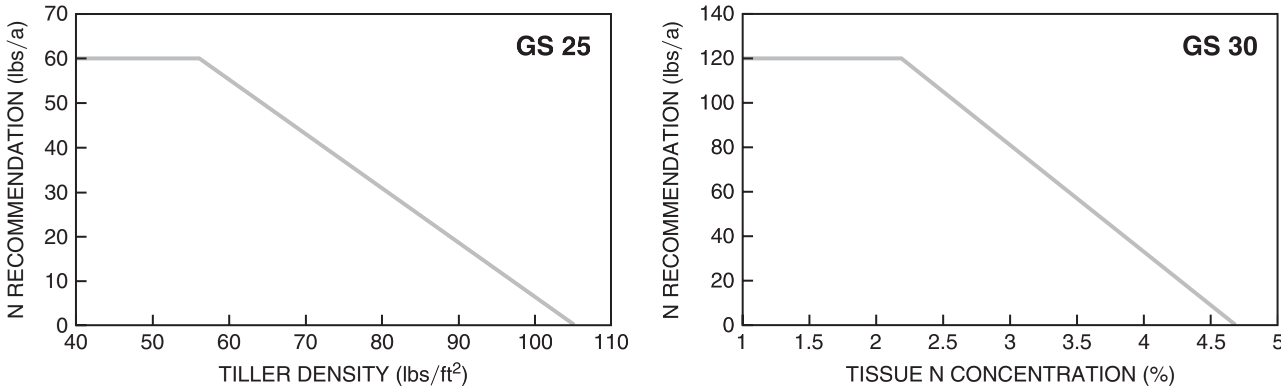


Figure 9-11
Use of tiller density at GS25 and tissue N concentration at GS30 to quantify split N application rates to optimize winter wheat yield and N-use efficiency. (*Alley et al., 1996, Virginia Coop. Ext.*, Publ. No. 424-026.)

Figure 9-12
Handheld chlorophyll meters. Minolta *light absorbance based sensor (left) and* Spectrum *laser based sensor (right).*
(Photo from Spectrum Technologies, Inc, www.specmeters.com).

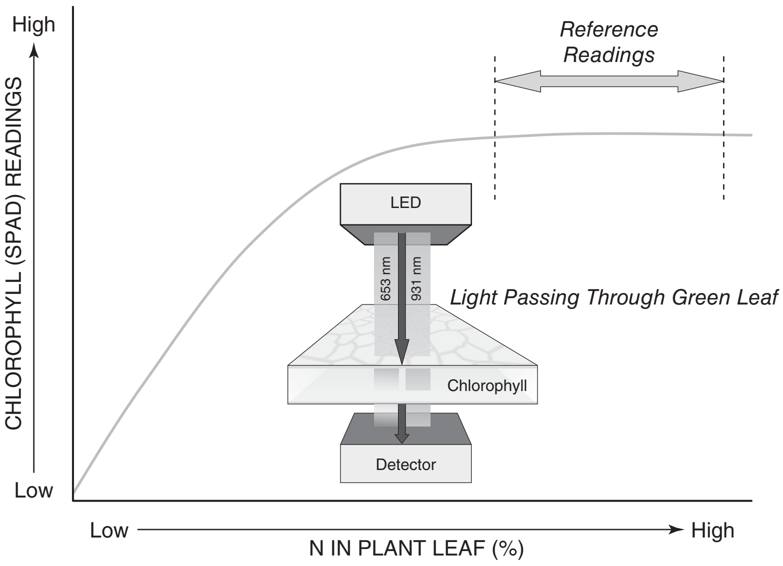


Figure 9-13
Relationship between chlorophyll meter reading (SPAD) and N content in a plant leaf. Proper calibration requires use of "high" N reference areas.

reference plants where nutrients are nonlimiting (Fig. 9-13). A reference strip through the field is established where excessive N is applied to attain high chlorophyll (and N) content in leaves.

Leaf chlorophyll content is highly correlated with % N in the leaf, particularly over the range of yield response to applied N (Fig. 9-7). Increasing N rate increases grain yield and leaf N, but chlorophyll readings do not increase with increasing N applied above that required for optimum yield (Fig. 9-7). Also, chlorophyll readings decrease with plant maturity (Fig. 9-14). For N-management purposes, chlorophyll readings have greater value at an early growth stage because the potential crop response to in-season N applications is greater. The primary advantage of using a chlorophyll meter is its ability to detect nutrient stress before deficiency symptoms are visible.

To help reduce inherent variability in chlorophyll readings in the field, an N sufficiency index (SI) or *relative chlorophyll reading* is calculated:

$$\text{SI} = \frac{\text{(average meter reading from unknown area)}}{\text{(average meter reading from reference area)}} \times 100\%$$

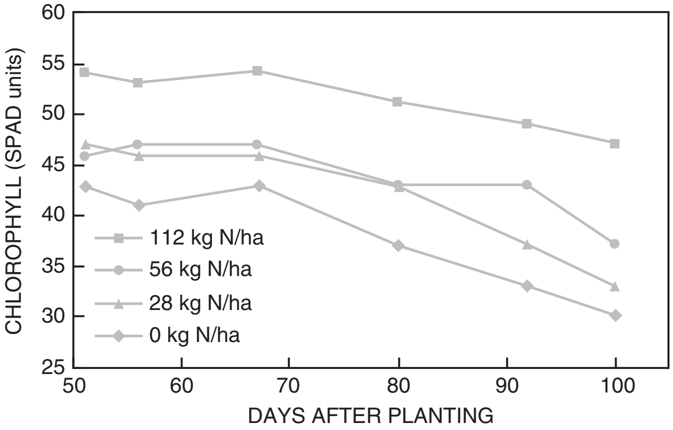
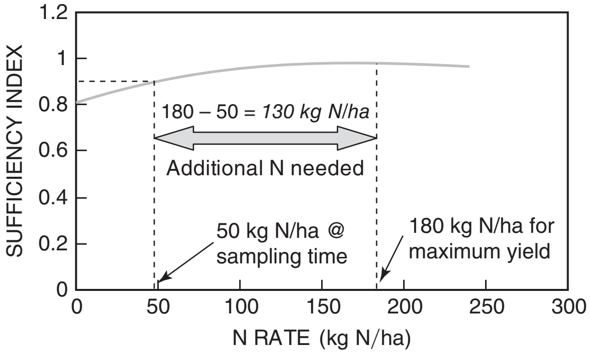


Figure 9-14
Effect of N rate and crop maturity on chlorophyll meter readings in corn.
(Havlin, 1994, unpublished data.)

Figure 9-15
Chlorophyll meter readings at V8 in corn used to predict additional in-season N application rates.
(Adapted from *Varvel et al., 2007, Agron. J. 99:701.*)



When SI < 95%, additional N is required for optimum yield (Fig. 9-15). These data illustrate that SI determined from chlorophyll readings taken at V8 growth stage in corn can be used to estimate the additional in-season N needed to maximize yield.

The chlorophyll meter can also be used to identify S deficiency (Fig. 9-16). Chlorophyll meter values of <45 in the flag leaf indicate S-deficient wheat; these readings are comparable to those for N in wheat and corn (Fig. 9-14).

Chlorophyll meter readings identified K deficiency in cotton, where values <42 represented ≤1% K (Fig. 9-17). However, at this leaf K content, it is usually too late to correct K deficiency and realize optimum yield.

Figure 9-16
Relationship between chlorophyll content in flag leaves and shoot dry matter influenced by S supply.

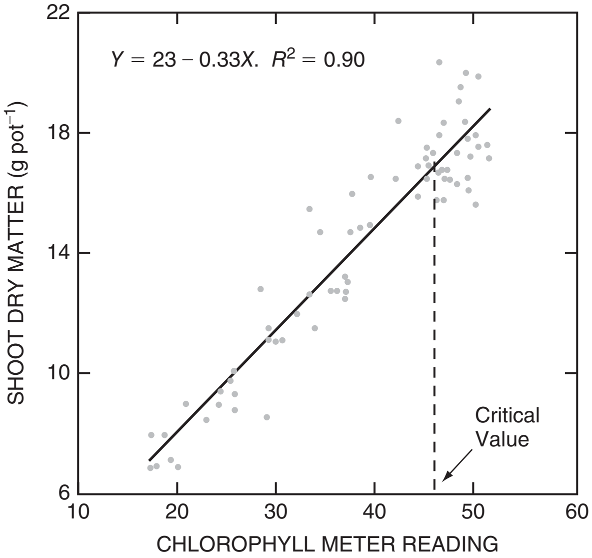


Figure 9-17
Relationship between leaf K content and chlorophyll meter readings with cotton grown over a range of soil K availability.
(Adapted from *Reddy et al., 2000,* Potassium Nutrition of Cotton, *Mississippi State Univ.*, Bull. 1094.)

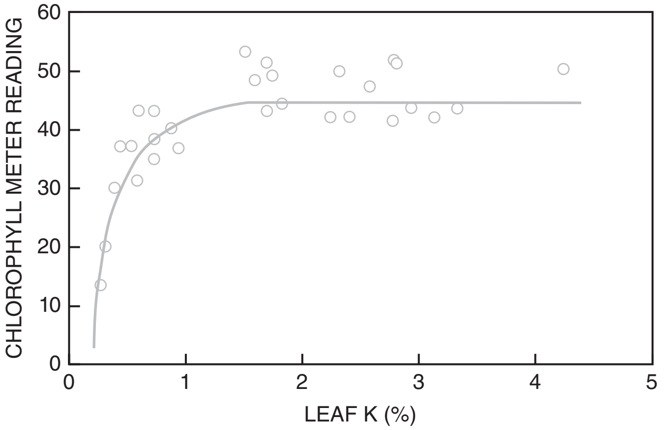


Figure 9-18
An example of a simple color chart to assess N status in wheat.
(Courtesy R. Mutters, UC-Davis.)

Color Charts

In regions where chlorophyll meters are not available, simple, easy-to-use leaf color charts have been developed to assess crop N status and improve N management. Crop N status is periodically assessed by comparing leaf color with panels of critical colors in the chart (Fig. 9-18). Farmers are alerted to the best time for topdressing N as plants begin to show N-deficiency symptoms. Rating of turf quality is often done by means of a color chart.

Remote Sensing

Remote sensing applications in production agriculture have advanced rapidly over the last several decades. Visible and near-infrared sensors are commonly used to detect plant stress related to nutrients, water, and pests. When light energy (green, blue, red, and near-infrared wavelengths) strikes a leaf surface, blue and red wavelengths are absorbed by chlorophyll, while green and near-infrared wavelengths are reflected. Reflected light is monitored by an optical sensor. The contrast of light reflectance and absorption by leaves enables assessment of the quantity and quality of vegetation (Fig 9-19). Chlorotic, N-stressed leaves absorb less light energy. A common index used to evaluate vegetation cover is the normalized difference vegetation index (NDVI) calculated by:

$$\mathrm{NDVI} = \frac{\mathrm{NIR} - \mathrm{PAR}}{\mathrm{NIR} + \mathrm{PAR}}$$

Use of NDVI is based on growing plants strongly absorbing photosynthetically active radiation (PAR) or visible light, while strongly reflecting near-infrared radiation (NIR). NDVI increases with increasing leaf greenness and with green leaf biomass (Fig. 9-19).

NDVI is highly correlated with plant N status; thus, remote sensing of growing crops can be used to identify in-season N requirements. For example, in wheat, NDVI measured at tillering is highly correlated to N uptake (Fig. 9-20). This information is used to predict grain yield potential for purposes of estimating topdress N rates (Fig. 9-21). This method is readily incorporated into real-time, leaf-reflectance-guided variable topdress N applications to increase yield and N-use efficiency.

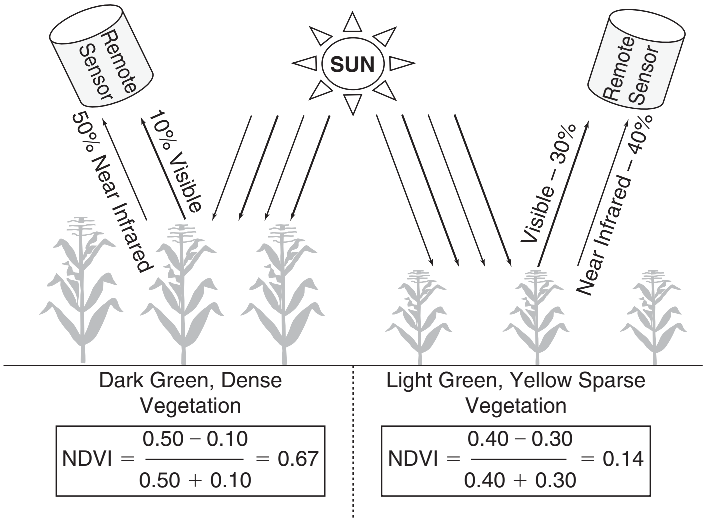


Figure 9-19

Determining the normalized difference vegetative index (NDVI) using an optical sensor. NDVI is calculated from the visible and near-infrared light reflected by vegetation. Dense, dark green vegetation (left) absorbs most of the photosynthetic active radiation or visible light and reflects most of the near-infrared light. Sparse, light green or yellow vegetation (right) reflects more visible light and less near-infrared light. Dense vegetation will reflect much greater near-infrared than visible radiation (high NDVI values), whereas with sparse vegetation reflected near-infrared and visible light are similar (low NDVI values).

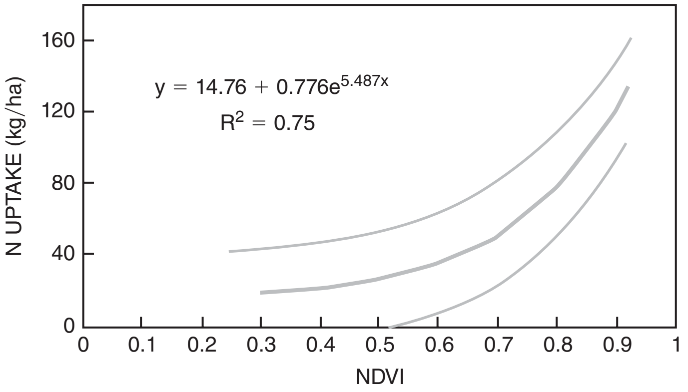


Figure 9-20

Relationship between NDVI at late tillering in winter wheat and plant N uptake. Thin lines represent variation in the data collected from three sites over 3 years.

(*Raun et al., 2002,* Agron. J. *94:815.*)

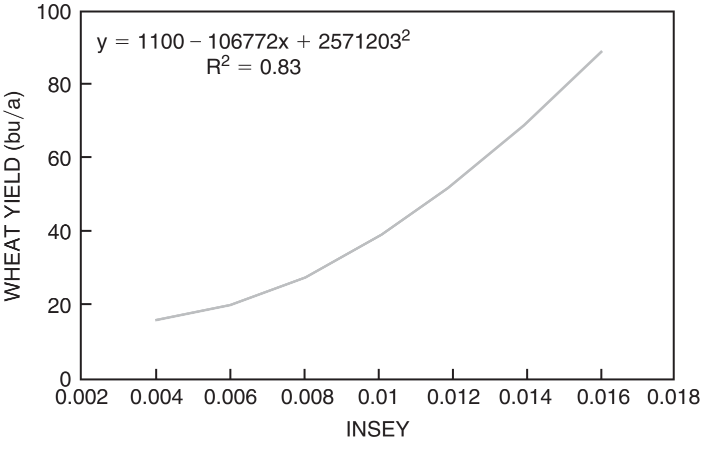


Figure 9-21

Relationship between measured wheat yield and in-season estimated yield (INSEY) determined from NDVI measured at late tillering divided by accumulated growing degree days from planting to late tillering. INSEY is then used to determine N rate required to achieve the estimated yield.

(*Raun et al., 1999,* Agron J. *93:131.*)

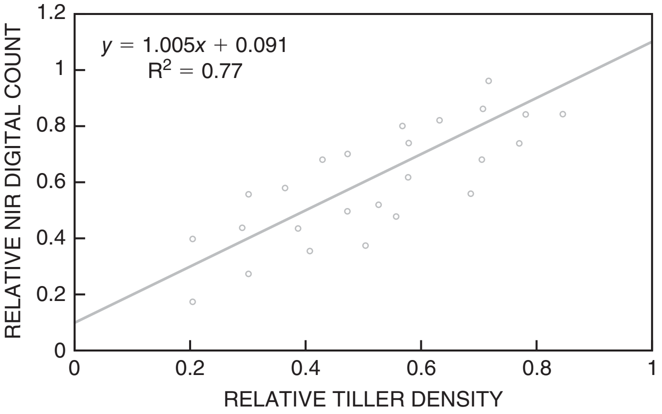


Figure 9-22
Use of aerial NIR photography to determine tiller number in wheat at GS25. Tiller number is used to estimate in-season N requirements.
(*Flowers et al., 2001,* Agron. J. *93:783.*)

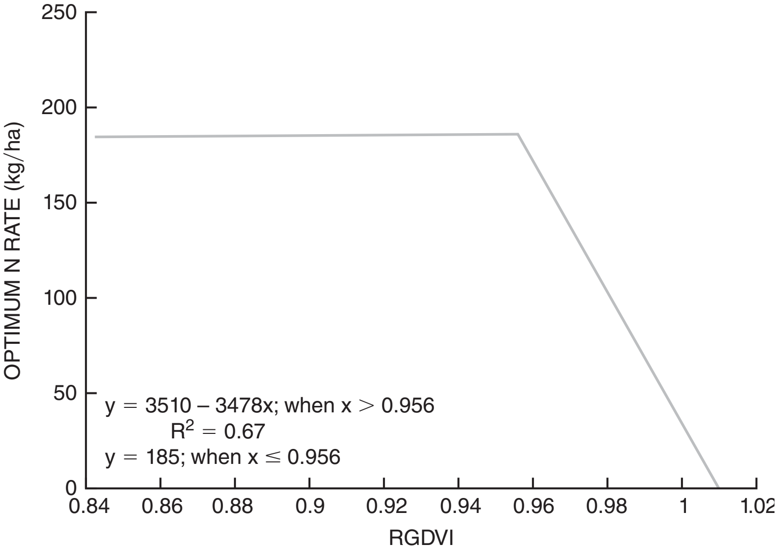


Figure 9-23
Prediction of in-season sidedress N rates for corn using aerial color infrared photography at the pre-tassel growth stage. RGDVI represents the relative green difference vegetation index, which represents the NIR-green values divided by the value for a high N-rate reference plot.
(Sripada, et al., 2005, Agron. J. 95:1443.)

Another method for estimating in-season N requirements involves the use of remote sensing to determine plant biomass. If tiller density is low (<100 tillers/ft^2), N application at GS25 improves grain yield (Fig. 9-11). Tiller number can be determined by remote sensing using aerial infrared photographs at GS25 (Fig. 9-22). These data are then used with tissue N estimated by NDVI to determine optimum N rates applied at GS30. Remote-sensing techniques have also been established to estimate sidedress N rate required at pretassel stage in corn (Fig. 9-23). Field evaluation of this technique demonstrated a 35% reduction in N rate and a 50% increase in N-use efficiency.

Postmortem Tissue Tests

Stalk NO_3^- Test

The stalk NO_3^- test was developed to assess N sufficiency using a corn stalk sample collected at physiological maturity. The postmortem test enables a producer to assess excessive N use, and adjust N rates in subsequent years.

Under low N supply, plants translocate N from the lower leaves and stalk to the younger leaves. With excess available N, corn plants have more N than needed and accumulate NO_3^- in the lower stalks (Fig. 9-24). At 1–3 weeks after physiological maturity (black layer), 8″ stalk sections are taken 6″ above the soil surface from 15 to 20 plants (Fig. 9-25). Areas dissimilar in soil types and management should be

Figure 9-24
General influence of fertilizer N rate on corn stalk NO_3-N concentration.

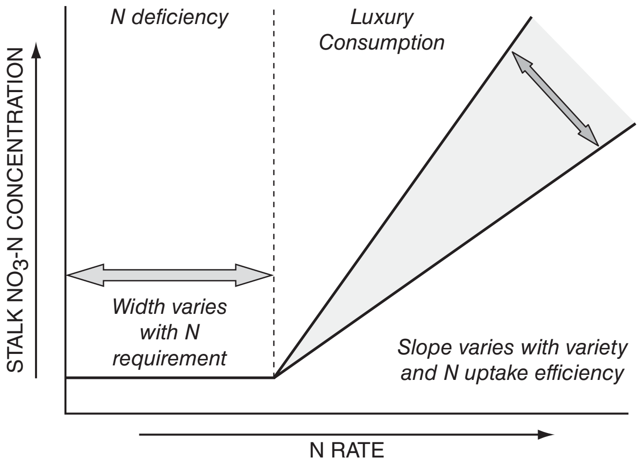
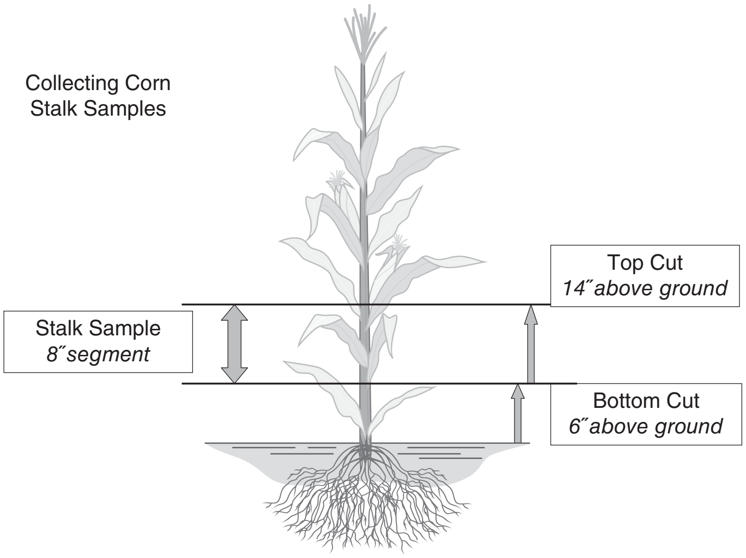


Figure 9-25
Location on corn plant to collect stalk samples.



sampled separately. Samples are air-dried and sent to a laboratory for NO_3-N analysis. General guidelines for interpreting stalk NO_3-N tests are:

Stalk NO_3-N *(ppm N)*	*Plant N Status*	*N Management Recommendation*
0–250	Low	N-deficiency symptoms likely, increase N rate
250–700	Marginal	N rate is close to optimum, slightly increase N rate
700–2000	Optimal	Adequate N
>2000	Excess	Reduce N rate

Many states have evaluated the corn stalk NO_3-N test and have reported similar and consistent results (Fig. 9-26). Reliability of the test is excellent and is especially useful on soils that have a recent history of manure application or forage legumes in the rotation. N mineralization from residual organic N is difficult to quantify, and the stalk N test can help identify the appropriate supplemental N rate.

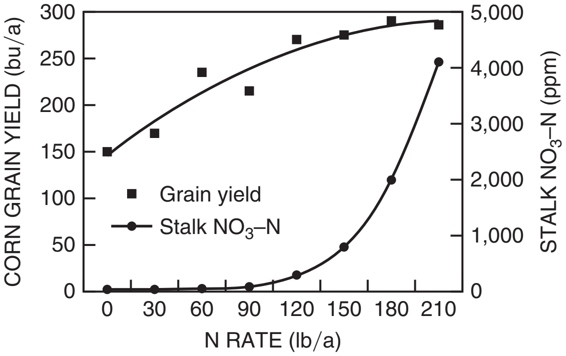


Figure 9-26
Influence of N rate on corn grain yield and stalk NO_3-N at maturity (black layer).
(Adapted from Bongard and Lamb, Univ. of Minn., Dakota Co Extension.)

Grain Analysis

Grain or other harvested plant parts are often collected to provide nutritional information to the grower. For example, wheat grain protein can be used to indicate if additional N was required for optimum yield (Fig. 9-27). When winter and spring wheat grain protein is <11.5% and <13.2%, respectively, additional N is needed to optimize yield.

Grain samples can be sent to a laboratory for analysis, although grain protein sensors have been developed using NIR transmittance that provides inexpensive and rapid results. Sensors can be installed in combines to monitor grain protein as the field is harvested. Grain protein measured spatially illustrates the high spatial correlation between grain protein and soil-profile N content (Fig. 9-28). Because temporal stability of this relationship is greater in regions where annual precipitation is <750 mm, N application rates could be reduced in areas within fields that consistently exhibit high residual soil profile N. While areas of high-profile N content are likely due to either high N mineralization or low yields (low N uptake), grain protein distribution can be used to help delineate variation in N requirements within fields. Although grain analysis can be very helpful in N management, it is a postmortem analysis. However, monitoring grain protein for several consecutive years provides information that improves the accuracy in estimating N requirements.

Figure 9-27
Relationship between grain protein and N sufficiency in winter wheat.
(Goos et al., 1982, Agron J., *74:130–133.)*

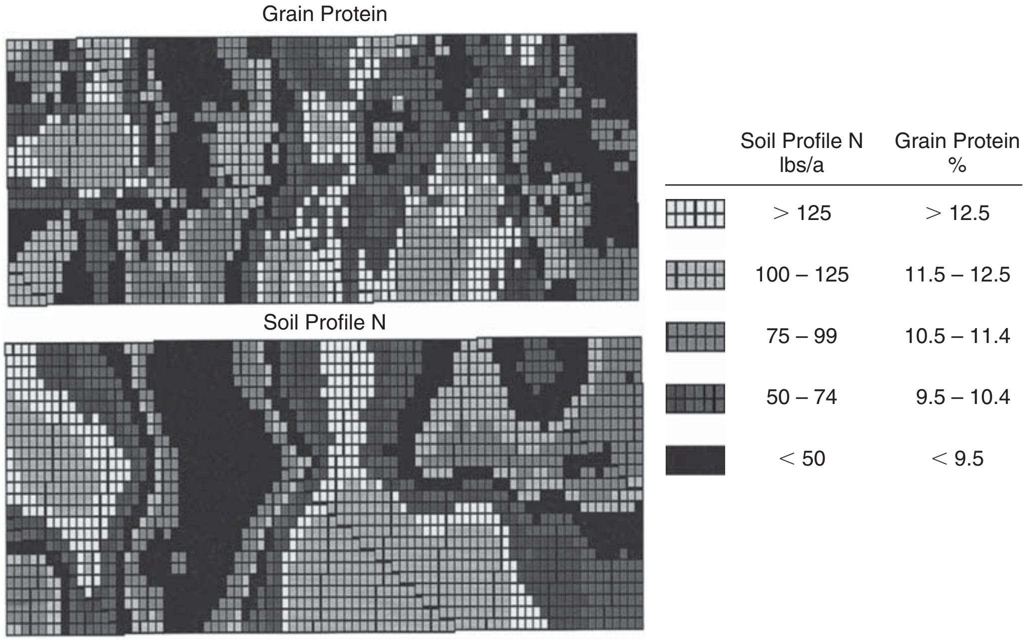


Figure 9-28
Spatial distribution of soil profile N content is similar to that of wheat grain protein content determined with a grain protein sensor mounted on a yield-monitoring combine. Grain protein content is high where soil N is high.

GREENHOUSE AND FIELD TESTS

Greenhouse Tests

Simple greenhouse tests involve growing plants in small amounts of soil to assess nutrient availability. Generally, soils are collected from a field suspected of being deficient in a specific nutrient. For purposes of calibrating soil and plant tissue tests, a wide range of soils that differ in nutrient availability are selected. Selected nutrient rates are applied, and a crop is planted that is sensitive to the specific nutrient being evaluated. Crop response to increasing nutrient rate can be determined by measuring total plant yield and nutrient content. For example, a greenhouse test was used to separate Fe-deficient and Fe-sufficient soils. Soils were selected to represent a range in DTPA-extractable Fe. Sorghum plants show decreasing Fe deficiency as DTPA-extractable Fe increases (Fig. 9-29).

Strip Tests

Narrow field strips where selected nutrient treatments have been applied can help verify the accuracy of nutrient recommendations. The test results must be interpreted with caution if they are unreplicated. Replication of strip tests on several farms is also helpful. Figure 9-30 illustrates how a strip test of several nutrient rates might be located in the field. It is important to place treatments in as similarly uniform areas as possible. If several soil types or conditions occur in the same field, locate treatments so that each soil type occurs equally in each treatment. The use of a yield-monitoring combine to measure and record treatment yields makes strip tests a valuable tool in assessing the accuracy of management recommendations.

Figure 9-29
Greenhouse test used to evaluate the ability of DTPA to separate Fe-deficient and Fe-sufficient soils. Sorghum was used as an indicator crop. Fe stress in sorghum decreased with increasing DTPA extractable Fe (ppm).

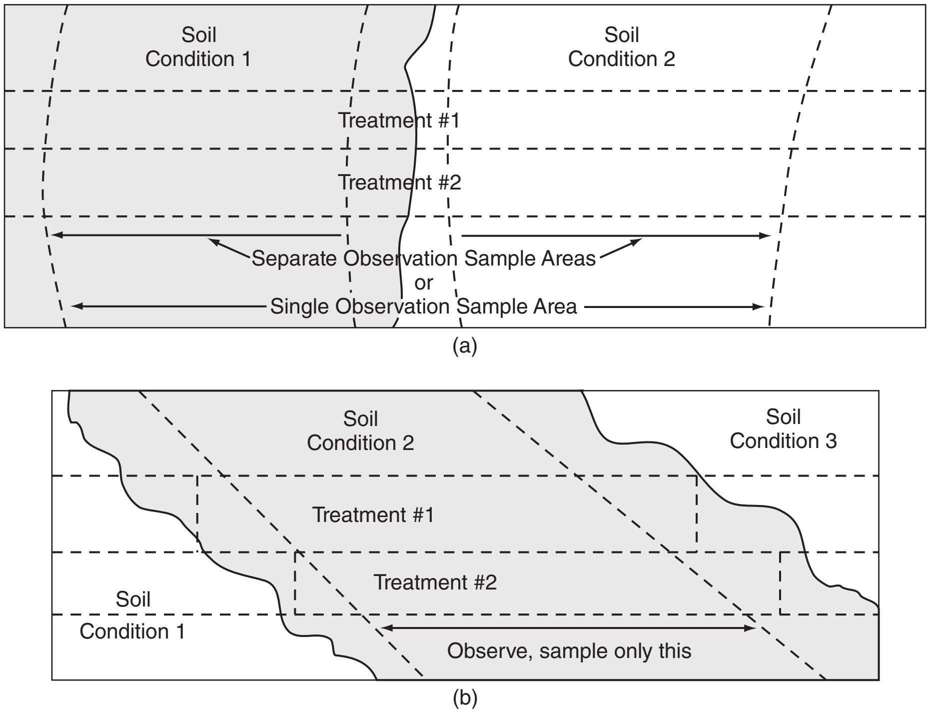


Figure 9-30
Example of strip tests located in a field with two (a) or three (b) soil types or conditions in the field.

Field Tests

Measuring crop response to applied nutrients is commonly done by agricultural scientists developing nutrient recommendations. After specific treatments are selected, they are randomly assigned to an area of land. The treatments are replicated several times to obtain more reliable results and to account for soil variations at the experimental site (Fig. 9-31). For example, when a range of increasing N rates are applied and a crop planted and harvested, the yield results are used in establishing N recommendations (see *Calibrating Soil Tests*). When many similar tests are conducted on well-characterized soils, recommendations can be extrapolated to other soils with similar characteristics.

Field tests are used in conjunction with greenhouse tests in the calibration of soil and plant tests. Field experiments are essential in establishing equations used to provide nutrient recommendations that will optimize crop yield. Plant analysis of samples collected from the various treatments can also help establish CNR.

N RATE TREATMENTS (lbs/a)

0	40	80	120	160	Replicate 1
80	120	160	40	0	Replicate 2
120	80	0	160	40	Replicate 3
40	160	120	0	80	Replicate 4

Figure 9-31
Example of field plot design for evaluating crop response to applied N (left). Five N rates are replicated four times, with N rates randomly placed within each replicate. Photo (right) shows replicated crop rotation study
(USDA-ARS).

SOIL TESTING

A soil test is a chemical extraction of a soil sample to estimate nutrient availability. Soil tests extract part of the total nutrient content that is related to (but not equal to) the quantity of plant available nutrient. Thus, a soil test level represents only an *index* of nutrient availability.

As an index, the nutrient quantity extracted by the soil test is not equal to the quantity of nutrient absorbed by the crop, but they are closely related. For example, Figure 9-32 shows that soil test P varied from 20 to 80 ppm in a ~6a field. If soil test P is related to P availability, then the variability in % P in the crop should reflect the variability in extractable soil P. The spatial distribution of % P concentration in wheat grain reflects the distribution of plant available P as measured by soil test P (Fig. 9-32). Specifically, high and low soil test P results in high and low grain P, respectively. These data demonstrate the ability of a soil test to provide a reliable index of plant available nutrients.

Objectives of Soil Tests

Soil test information can be used to:

1. *provide an index of nutrient availability in soil.* The soil test or extractant is designed to extract a portion of the nutrient from the same "pool" (i.e., solution, exchange, organic, or mineral) used by the plant (Fig. 2-2).
2. *predict the probability of obtaining a profitable response to fertilizer or lime.* Although a response to applied nutrients will not always be obtained on low-testing soils because of other limiting factors, the probability of a response is greater on low-testing soils.
3. *provide a basis for development of fertilizer and lime recommendations.* The basis for nutrient recommendations relies on detailed laboratory, greenhouse, and field studies.

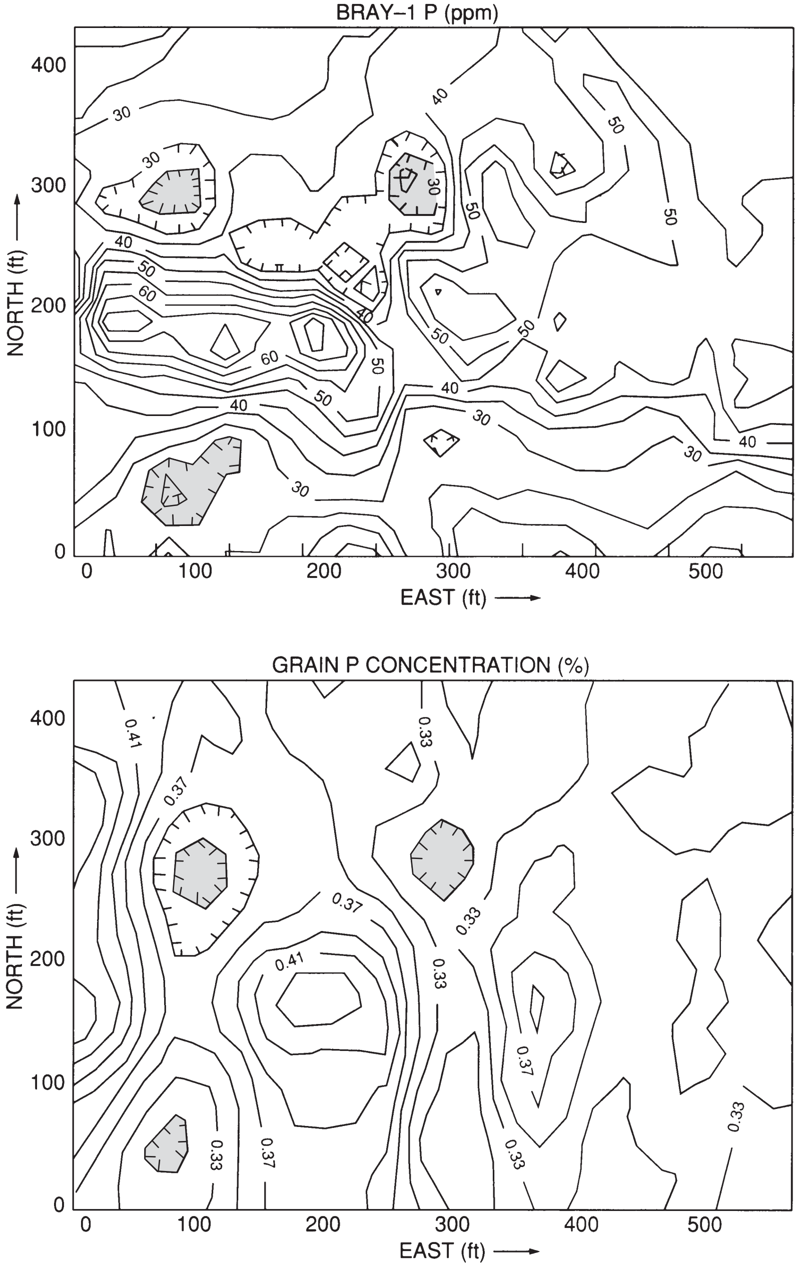


Figure 9-32

Spatial distribution of Bray-1P and wheat grain P concentration over a 6-a field. Areas of high soil test P correspond to areas of high % P in the grain (left center region of both figures). Low Bray-1P levels result in low % P in the grain (see two shaded areas above and one below high soil test P area).

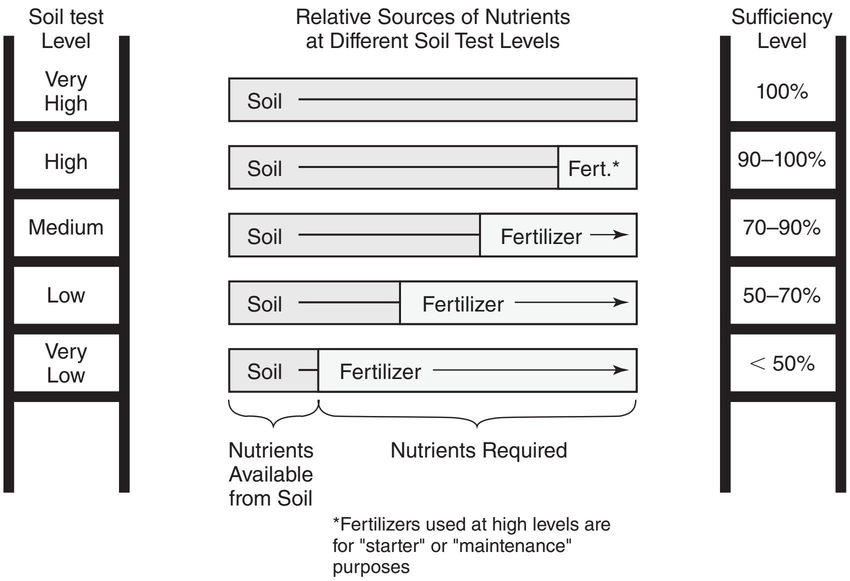
(*Havlin and Sisson, 1990,* Proc. Dryland Farming Conf, *p. 406.*)

The objective of soil testing is to simply help predict the amount of nutrients needed to supplement native soil nutrient supply. For example, a soil testing high will require little or no additional nutrients in contrast to soil with a low test value (Fig. 9-33). Sufficiency levels are commonly used in soil testing, where a high soil test represents 90–100% sufficiency in supplying adequate plant nutrients from the soil. Sufficiency levels decrease with decreasing soil test levels.

The *soil testing–nutrient recommendation system* is comprised of four consecutive steps:

1. Collect a representative soil sample from the field.
2. Determine the quantity of plant available nutrient in the soil sample (soil test).
3. Interpret the soil test results (soil test calibration).
4. Estimate the quantity of nutrient required by the crop (nutrient recommendation).

Figure 9-33
As soil test levels decrease, the capacity of the soil to provide sufficient plant nutrients decreases. High soil test levels represent 90–100% sufficiency in supplying adequate nutrients. A low soil test level represents a 50–70% sufficiency in supplying adequate nutrients.



Soil Sampling

The most critical aspect of soil testing is obtaining a soil sample that is representative of the field. Usually, a composite sample of only one pint of soil (about 1 lb) is taken from a field or sampling area that may represent, for example, a 10a field or about 20×10^6 lbs of surface soil $[(2 \times 10^6 \text{ lb soil/ac} - 6'') \times 10 \text{ ac}]$. Therefore, considerable opportunity exists for sampling errors. If the sample does not represent the whole field, it is impossible to provide a reliable nutrient recommendation. Field sampling errors are much greater than laboratory analysis errors, thus, the accuracy of any nutrient recommendation is entirely dependent on the quality of the sample collected from the field.

Two common methods of collecting soil samples are (1) sampling whole or parts of fields to provide "average" soil test value(s) or (2) sampling to describe spatial variability in soil test values. Field average soil sampling is commonly used, but adoption of site-specific nutrient management technologies requires the spatial distribution of soil test values.

Field Average Sampling Each field should be subdivided into *sampling units* representing a relatively uniform area. Criteria used to delineate a sampling unit include soil types, slope, drainage, or past management (Fig. 9-34). Sampling units

Figure 9-34
Composite samples sent to a laboratory for analysis represent relatively uniform areas within a field.

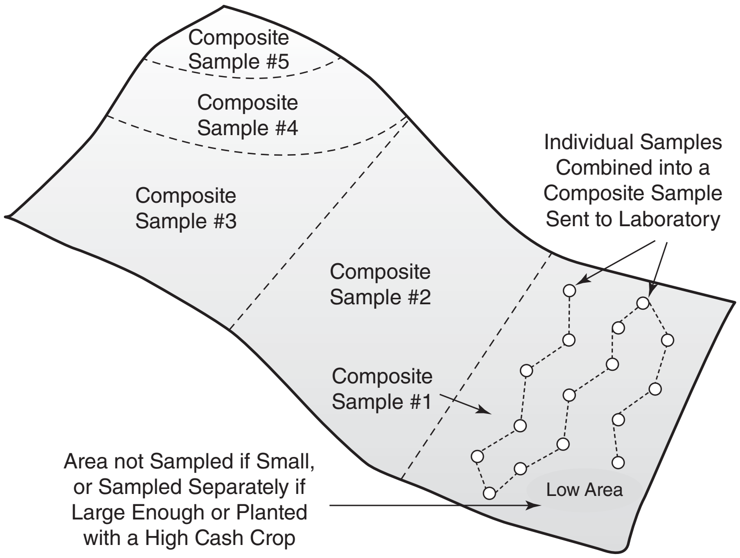


Figure 9-35
Collecting a surface soil sample and placing the 15–40 cores from each sampling unit in the bucket. Mix the contents of the bucket thoroughly and take a subsample to be sent to the laboratory.

vary in size, but usually are <40 ac. Small areas within a sampling unit that are not representative of the unit should be omitted from the sample. Even in a relatively uniform area, variability in soil test levels exists. For example, recent lime or nutrient applications, or previous crop residues, may have been unevenly distributed. A sample taken entirely from areas high in these materials would not represent the field average. To minimize sampling errors, 15–40 sample cores should be collected within the sampling unit (Fig. 9-34). Soil samples within each sampling unit are composited by mixing in a non-galvanized container, and a subsample is sent to the laboratory for analysis (Fig. 9-35). Use of galvanized containers may contaminate the sample with Zn.

With the use of a geographic information system (GIS), sampling units and sampling sites within a unit can be identified. Pertinent digital data used to segregate sampling units include soil survey data (soil types), digital elevation, and an aerial photograph of the field; all are readily available from state or federal agencies. Other known spatial data (soil test data, yield maps, etc.) specific for the field may also be available and could be included. The GIS enables the user to overlay spatial data and delineate sampling units based on uniformity of field and soil characteristics (Fig. 9-36). Sampling points within a sampling unit can also be identified in the GIS. With this information and a global positioning system (GPS) on the soil sampling vehicle, personnel can collect samples from the exact positions identified with the GIS.

On apparently uniform fields, nutrient levels still can be highly variable. More often, soil test values are not normally distributed (Fig. 9-37). When normally distributed, the average or *mean* soil test value is the same as the *mode*, the value that occurs most frequently. If soil test results do not follow a normal distribution, the data are skewed and the mean does not represent the most frequently occurring value or mode. Table 9-6 shows how mean soil test levels were consistently greater than the mode, which represents the largest percentage of the field. Nutrient rates based on mean soil test levels would then be lower than those based on the mode. Most soil test data are lognormally distributed, where > 50% of soil test values are <mean (Fig. 9-37). When this occurs, nutrient needs are underestimated. For example, the skewed distribution of soil test K results in no K recommended when 30% of the field tested low (Fig. 9-38).

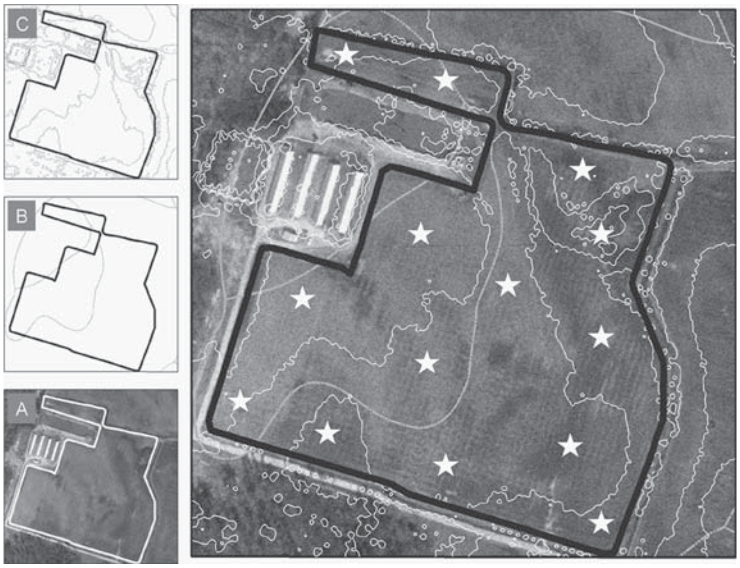


Figure 9-36
Using geospatial data to guide field soil sampling. A represents the digital orthoimagery or aerial black/white photograph of a field, B is the digitized map of soil types obtained from NRCS Soil Survey data, and C is the elevation in the field obtained from remote sensing, where each contour represents a 2m change in elevation. These three data layers are then combined (large photo on the right) to identify locations in the field where soil samples will be collected (areas represented by the "stars").

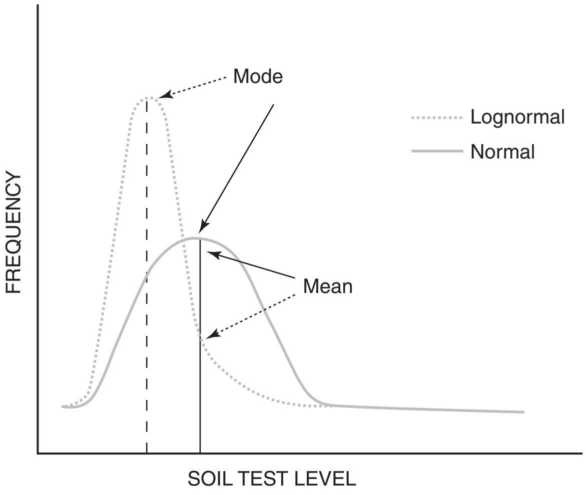


Figure 9-37
Normal and lognormal distributions showing the mean and mode.

TABLE 9-6
STATISTICAL CHARACTERISTICS OF SOIL TESTS FROM 1a SAMPLING GRIDS

Nutrient	Range	Mean	Mode
		ppm	
NO_3-N	2–24	11	8
P	0–104	15	9
K	127–598	276	155
SO_4-S	7–944	480	10

Site-Specific Sampling Use of equipment capable of variably applying nutrients according to variability in soil test levels requires intensive, georeferenced field sampling. Georeferenced sampling refers to the use of a GPS to record the latitude and longitude of each sampling location in the sampling unit.

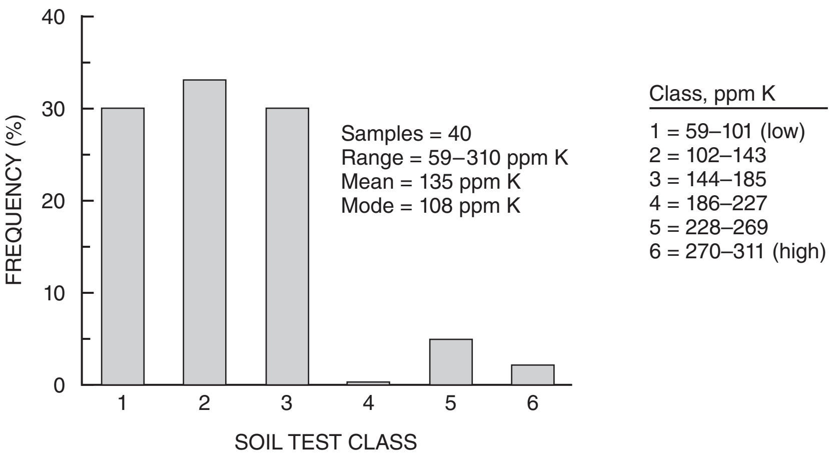


Figure 9-38
Frequency distribution of soil test K from a 220 ft × 220 ft sampling grid. 30% of the field tested low enough to require K (Class 1) and another 33% was marginal in K status (Class 2). If K recommendations were based on the field mean, at least 30% of the field would have experienced K deficiency.
(*Penney et al., 1996,* Proc. Great Plains Soil Fert. Conf, *6:126.*)

Grid Sampling

Grid sampling consists of collecting equally spaced soil samples throughout the field and analyzing each sample separately (Fig. 9-39). Typically 2a to 3a grids are used. Decreasing grid size increases the number of samples collected and associated sampling and analysis costs, but improves the probability of accurately describing the true distribution. For example, in a comparison of grid sizes varying from 0.75a to 7.5a, ≤3a grids adequately describe the spatial variability in soil test P (Fig. 9-40).

Grid samples can be collected as *cell* or *point* samples (Fig. 9-39). With cell sampling, random samples are collected within each grid and composited. With large grids (e.g., 2 acres), compositing samples within a cell will mask variability within the grid. To avoid the averaging that occurs with cell sampling, point samples can be collected (Fig. 9-39). With point sampling, 5–10 individual soil samples are composited from a 10–15 ft diameter circle centered over each intersection of the grid lines. Thus, with point sampling, more within-field variability is quantified.

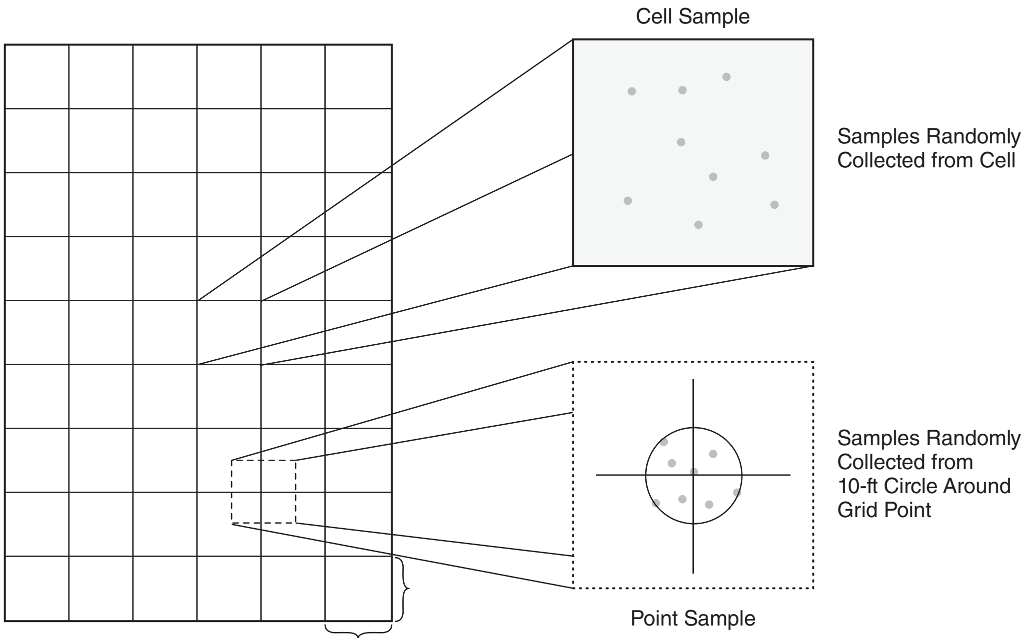


Figure 9-39
Illustration of point and cell sampling schemes used for describing the spatial distribution of soil properties. Grid size commonly varies from 2a to 3a.

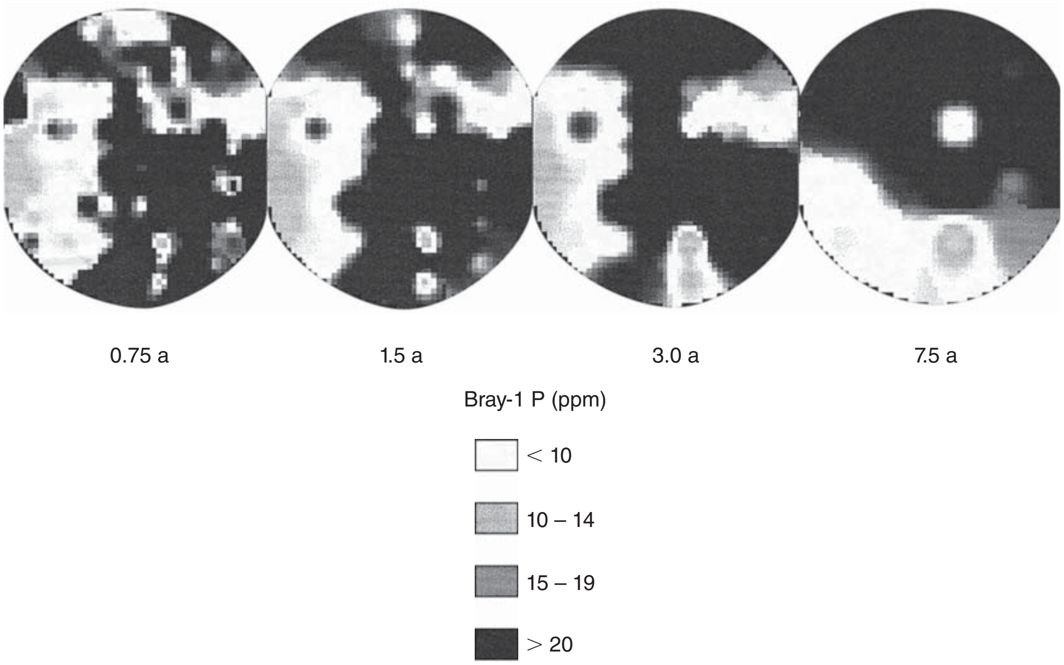


Figure 9-40
Influence of grid size on the spatial distribution of soil test P (Bray-1) levels; ≤3 acre adequately described the variability. (*Havlin et al., 1996,* Agron. Abstracts, *p. 184.*)

Directed Sampling

To reduce the cost of grid sampling, sampling locations can be identified by using other spatially variable parameters in the field. Figure 9-41 illustrates that soil color, OM, and elevation could be used to direct sampling locations needed to accurately quantify the spatial distribution in soil test P. Yield-monitored data and other remote-sensing information could also help direct specific sampling locations. These data also allow development of specific management zones for use in variable nutrient management (Chapter 10).

Other Soil Sampling Considerations

Banded Nutrients

Band application of immobile nutrients (e.g., P and K) often results in higher concentration of residual nutrient in previous fertilizer bands for several years after application. Residual availability depends on application rate, chemical and

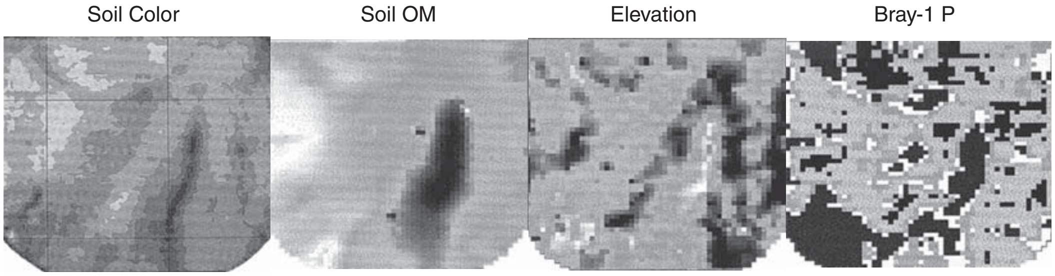


Figure 9-41
The spatial distribution of soil color, using aerial photography, is related to soil OM, elevation, and soil test P. Dark soil color regions correspond to high soil OM, low elevation, and high Bray-1 P. Georeferenced soil sampling could be guided by the soil color map to reduce the samples needed to define variation in Bray-1 P.

(Courtesy of R. Ferguson and J. Schepers, 1995,University of Nebraska).

physical properties of the soil, quantity of nutrient removed by the crop, and time after application. For example, increasing broadcast or band P rate increases soil test P (Fig. 5-34). Band-applied P increased soil test P more than the same rate of broadcast P. Thus, if only the bands are sampled, the soil test P is much higher than if none of the bands are sampled (i.e., if only the between-band areas are sampled). Few guidelines have been established for soil sampling fields in which immobile nutrients have been band applied. In no-till systems where the band is undisturbed and its position is known, the following can be used:

$$S = \frac{8 \times \text{row spacing (in.)}}{12}$$

where S = ratio of off-band to on-band samples. Thus, for 12 in. band spacing, eight samples between bands are required for every sample taken on the band. If the band position is not known, then the sampling intensity should be increased to provide an adequate estimate of the average field soil test level.

Sampling Depth

For cultivated crops, samples are ordinarily taken to tillage depth that can vary from 6 to 12 in. (Fig. 9-42). Tillage generally mixes previous lime and nutrient applications in the tillage layer (Fig. 9-43). When lime and nutrients are broadcast on the surface in lawns, pastures, permanent crops, and no-till systems, considerable nutrient stratification occurs (Fig. 9-43, Table 9-7); where soil samples collected from the upper 4–6 in. depth are recommended. In low rainfall regions, preplant subsoil samples (2–3 ft. depth) are routinely collected to determine NO_3^- content to adjust N recommendations (see *N Soil Tests*).

Sampling Time

Ideally, samples should be taken just before planting or early in the crop growth cycle. However, these times are often impractical due to the time involved in collecting samples, obtaining test results, and applying needed amendments. Consequently,

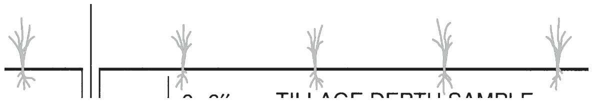


Figure 9-42
Diagram of various soil sampling depths used for nutrient analyses.

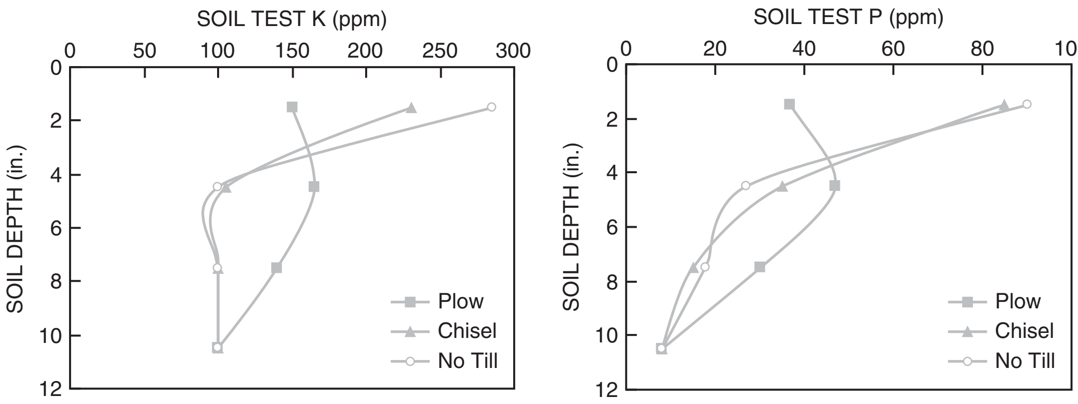


Figure 9-43
Influence of tillage on stratification of soil test K and P. (Adapted from *Mengel, 1990, Agron. Guide AY-268, Purdue Univ.*)

TABLE 9-7
INFLUENCE OF TILLAGE, N RATE, AND SAMPLING DEPTH ON SOIL pH

Yearly N Rate	No-Till		Plow	
lb/a	*0–2 in.*	*2–6 in.*	*0–2 in.*	*2–6 in.*
0	5.75	6.05	6.45	6.45
75	5.20	5.90	6.40	6.35
150	4.82	5.63	5.85	5.83
300	4.45	4.88	5.58	5.43

samples are customarily taken any time soil conditions permit in the noncrop period. Samples for spring-planted crops are often taken after harvest. In drier regions where NO_3^- levels are used to assess soil N status, fall sampling is common.

Generally, soils should be tested every 2–3 years, with more frequent testing on sandy soils. In most instances, this frequency is sufficient to assess soil pH changes and to determine whether the nutrient and lime management program is adequate for optimum productivity. For instance, if soil test P has decreased over time to $<100\%$ sufficiency (Fig. 9-33), P application rate should be increased. If soil test levels have increased to $>100\%$ sufficiency, application should be reduced to maintenance rates (see *Immobile Nutrient Recommendations*).

Soil Tests

The specific chemical extractant used in soil testing varies with the nutrient (Table 9-8). A soil test extractant removes a nutrient from similar reservoirs (i.e., CEC, OM, mineral solubility) that provide nutrients to growing plants (Fig. 2-2).

N Soil Tests NO_3^- occurs predominantly in the soil solution and NH_4^+ exists both in solution and on the CEC. A simple water extract of the soil sample would recover solution $NO_3^- + NH_4^+$. KCl $(1-2\ M)$ is commonly used, where Cl^- replaces small amounts of exchangeable NO_3^- absorbed to AEC and K^+ would remove exchangeable NH_4^+. Increasing KCl extractable NO_3^- decreases N required for optimum yield in regions where NO_3^- leaching potential is negligible (Fig. 9-44).

TABLE 9-8
COMMON SOIL TEST EXTRACTANTS AND SOURCE OF NUTRIENT EXTRACTED FROM THE SOIL

Plant Nutrient	Common Extractants	Nutrient Source
NO_3^-	KCl, $CaCl_2$	Solution
NH_4^+	KCl	Solution/CEC
$H_2PO_4^-/H_2PO_4^-$	NH_4F/HCl (Bray-1P)	Fe/Al-P mineral solubility
	$NH_4F/CH_3COOH/HNO_3$ (Mehlich-P)	Fe/Al-P mineral solubility
	$NaHCO_3$ (Olsen-P)	Ca-P mineral solubility
K^+	NH_4OAc	CEC
SO_4^{-2}	$Ca(H_2PO_4)_2$, $CaCl_2$	Solution/AEC
Zn^{+2}, Fe^{+3}, Mn^{+2}, Cu^{+2}	DTPA, EDTA	Zn, Fe, Mn, Cu mineral solubility
$H_3BO_3^0$	Hot water	Solution
Cl^-	Water	Solution

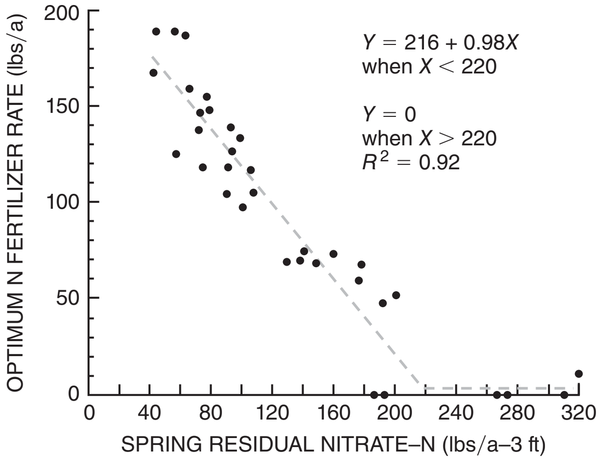


Figure 9-44
Optimum N rates for corn based on preplant soil NO_3^- content (3 ft. sample depth).
(*Bundy et al., 1995,* Wisconsin's Preplant Soil Nitrate Test, *Univ. of Wisconsin, A3512.*)

Preplant Sampling

In many humid regions where annual precipitation exceeds evapotranspiration, leaching and denitrification reduce preplant profile NO_3^- to levels unreliable for use in N recommendations for subsequent crops (Fig. 9-45). However, in regions of the United States where annual precipitation is ≤35″ (Fig. 3-3) and percolation is ≤medium (Fig. 3-5), preplant soil NO_3^- concentration is related to relative yield (Fig. 9-46). As soil NO_3^- increases, the additional N required for optimum yield decreases (Fig. 9-47).

In regions where evapotranspiration exceeds precipitation (Fig. 9-45), measuring preplant profile NO_3^- content is valuable in determining N requirements. Usually a 2 to 3 ft profile sample is collected before planting to provide plant available NO_3^- (Table 9-9). Determining soil profile NO_3^- is essential to accurately estimate additional N requirements (Fig. 9-48).

The Illinois Soil N Test (ISNT) was recently developed to extract a portion of organic N from preplant soil samples (0–12 in. depth) and attempts to estimate potential mineralizable N. The test was developed to detect sites that are nonresponsive to N fertilizer application. Critical ISNT levels are ≈200–250 ppm N. Although results are mixed, the ISNT is generally not predictive of crop response to applied N.

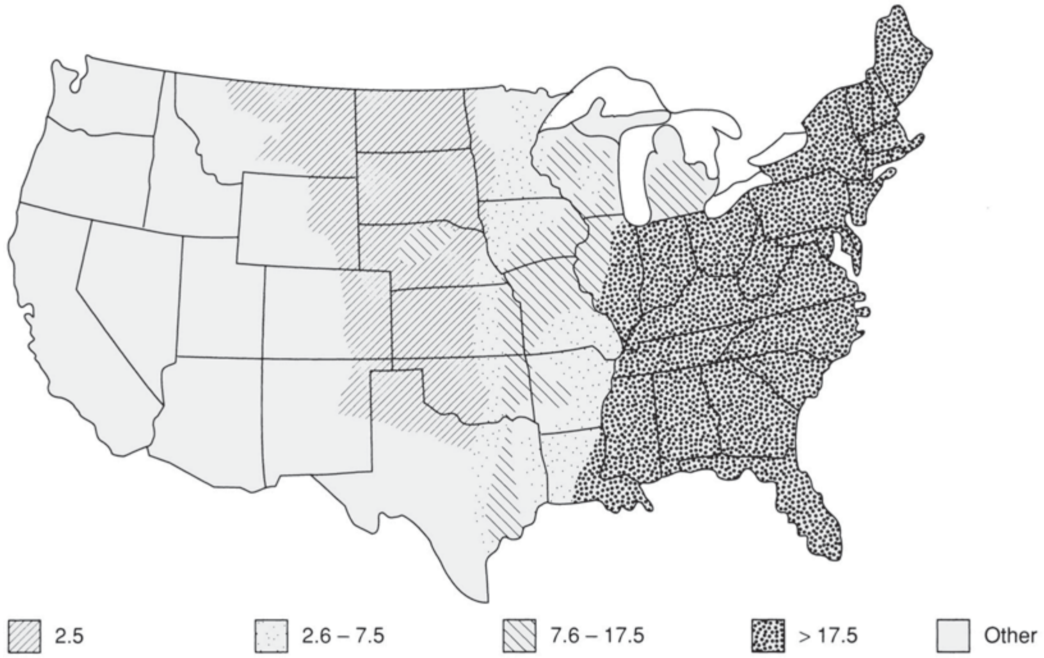


Figure 9-45
Use of residual profile NO_3^- analysis in determining N recommendations is more common in regions where average annual potential percolation below the root zone is <17.5 cm.
(*Hergert, 1987*, SSSA Spec. Publ. No. 21.)

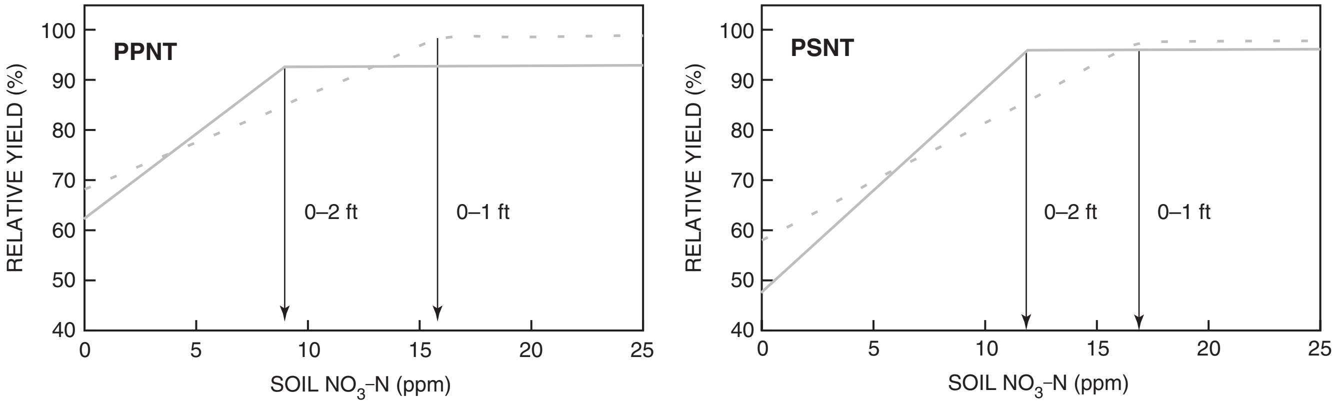


Figure 9-46
Relationship between soil NO_3-N concentration and relative corn yield. Preplant soil NO_3-N test (PPNT) and the presidedress NO_3-N test (PSNT) are based on 0–1 ft soil samples collected before planting and when corn is about 1 ft. tall, respectively. Use of a 0–2 ft sample varies with states. The arrows represent the critical soil NO_3-N concentration above which no additional N is required.
(*Adapted from Bundy et al., 1999, North Central Regional Res.* Publ. No. 342.)

Figure 9-47
Quantity of fertilizer N credit for corn based on preplant soil NO_3-N in a 0–2 ft sample. Generally, higher soil NO_3^- levels occur in cropping systems where manure is utilized or when overwinter or spring precipitation is low.
(Schmitt et al., 1998, Univ. Minnesota, FO-06514-GO.)

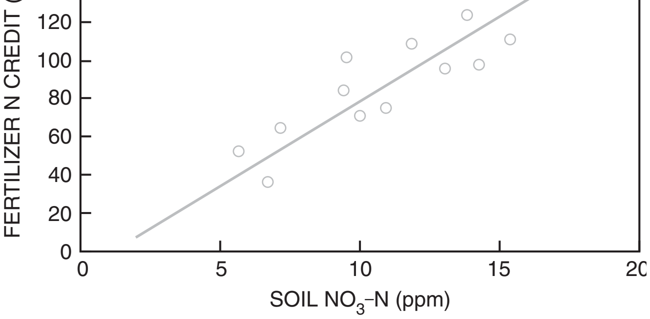


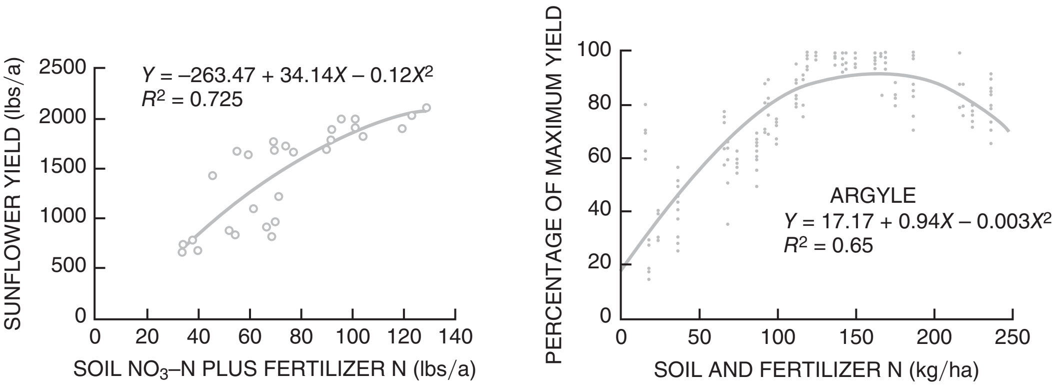
TABLE 9-9
N RECOMMENDATIONS FOR DRYLAND WINTER WHEAT BASED ON SOIL PROFILE NO_3-N AND OM CONTENT FOR A 50 BU/A YIELD GOAL[1]

Soil NO_3-N, ppm[2]		Soil OM, %		
0–1 ft	*0–2 ft*	*0–1.0*	*1.1–2.0*	*> 2.0*
		N rate, lbs/a		
0–3	0–5	75	75	75
4–6	6–9	75	70	50
7–9	10–12	75	45	25
10–12	13–15	50	20	0
13–15	15–18	25	0	0
>15	>18	0	0	0

[1] To adjust N rate for yield goals different from 50 bu/a, add or subtract 25 lbs N/a for each 10 bu/a difference, where maximum rate is 75 lbs N/a.

[2] NO_3-N concentration in the 0-1 or 0-2 ft sample depth.

Source: Davis et al., 2002, *Fertilizing Winter Wheat*, Colorado State Univ. Coop. Ext. No. 0.544.



(a)

(b)

Figure 9-48
Relationship between soil NO_3-N fertilizer N and relative crop yield of sunflower (a) and Kentucky bluegrass (b). *(Black and Bauer, 1992, Proc. Great Plains Soil Fert. Conf.)*

In-season Soil Sampling

Pre-Sidedress Soil NO_3^- *Test (PSNT)* As mineralization and nitrification rates increase in the spring, soil NO_3^- increases, which occurs just prior to maximum N uptake period in corn (Fig. 9-49). Soil NO_3-N determined in surface soil samples (0–12-in. depth) collected between corn rows when corn is about 12 in. tall is related to relative yield (Fig. 9-50). The critical soil NO_3-N concentration below which sidedress N applications are recommended varies between regions, but is approximately 20–25 ppm NO_3-N (Fig. 9-51).

Previous legume crops or manure application greatly influences the quantity of extractable soil NO_3-N (Fig. 9-52). Lower PSNT critical levels (13–15 ppm) are appropriate in semiarid regions due to greater subsoil NO_3-N. In soils amended with organic wastes (manure, sewage sludge, etc.), $NH_4^+ + NO_3^-$ analysis improves prediction of sidedress N response compared to soil NO_3-N alone.

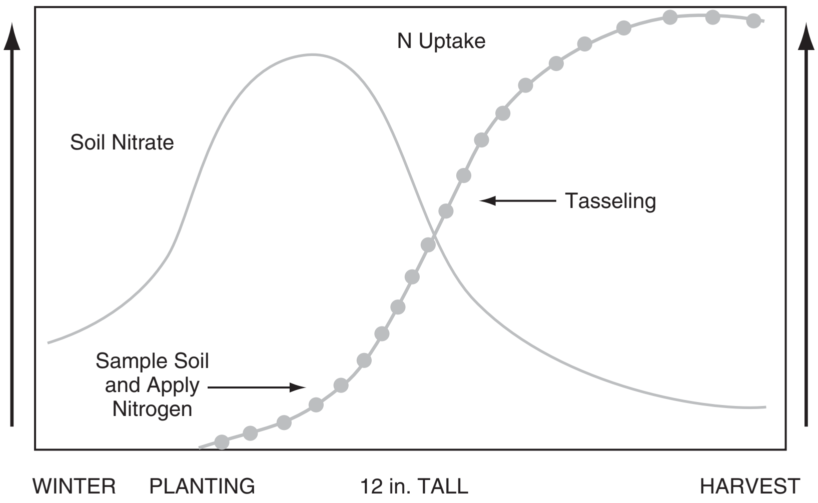


Figure 9-49
General distribution of soil NO_3^- *and N uptake in corn.*

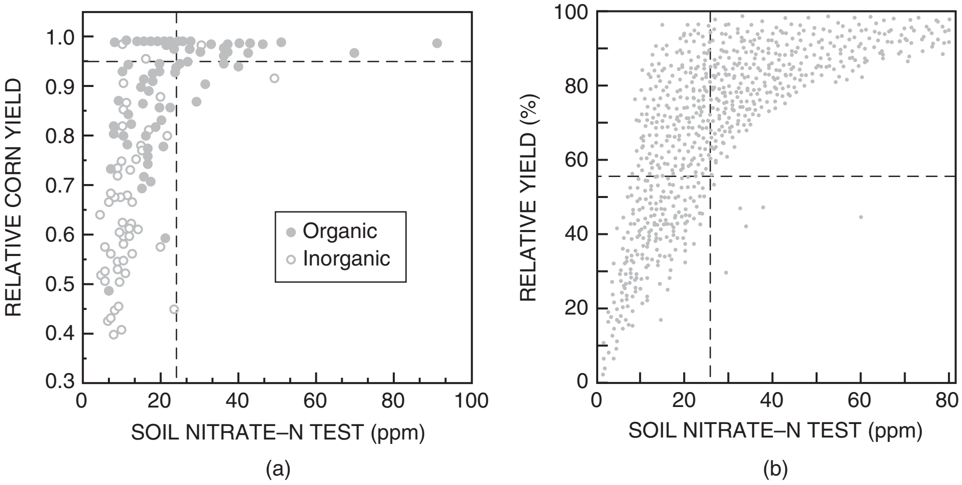


Figure 9-50
Relationship between soil NO_3-N *and relative corn yield in Pennsylvania (a) and Iowa (b). Organic indicates soils with a history of manure or legumes, whereas inorganic indicates soils without this history.* (Beegle, 1982, Proc. Indiana Ag. Chem. Conf.)

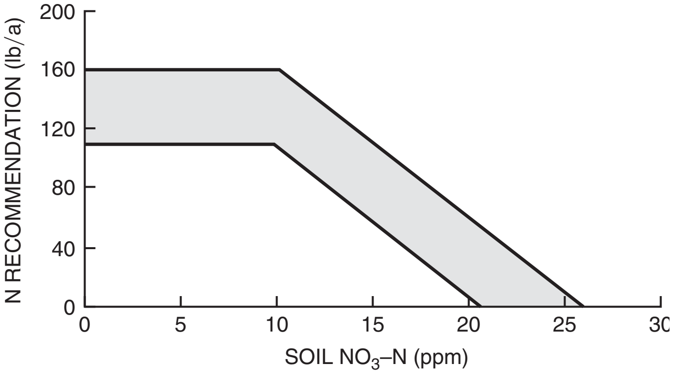
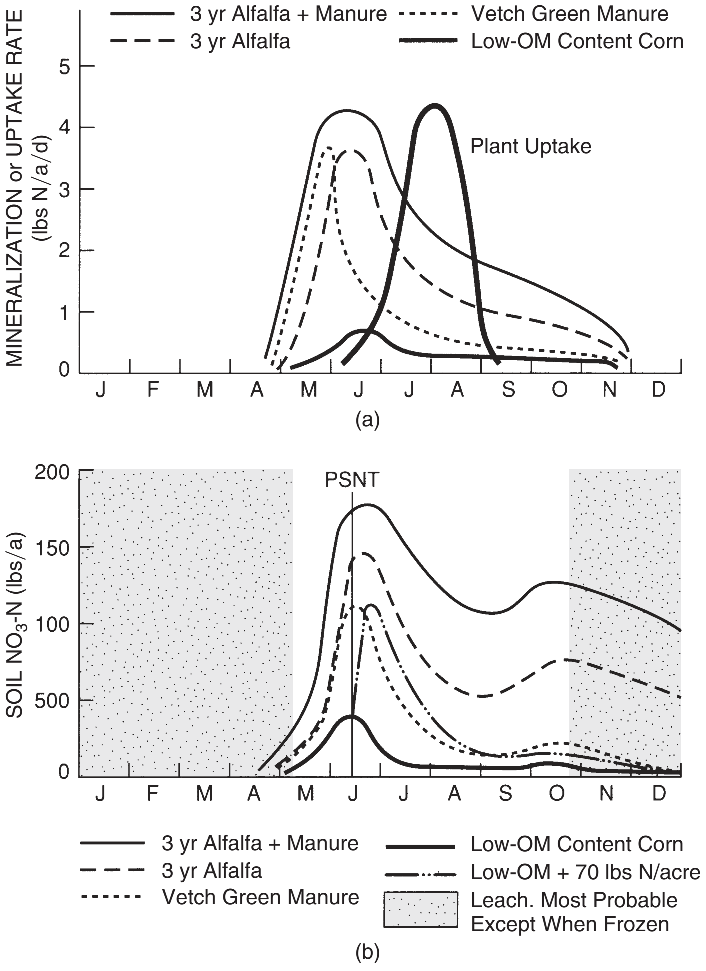


Figure 9-51
Sidedress N recommendations for corn based on PSNT. At 10 ppm NO_3-N *the range in N rates is 110–160 lbs/a, whereas at 20 ppm* NO_3-N *10–60 lbs N/a would be recommended for sidedress application.* (Blackmer et al.,1991, Iowa State Univ. Extension, p. 1381.)



(a)

(b)

Figure 9-52
Synchronization of N mineralization and crop N uptake (a) and subsequent accumulation of NO_3^- (b) as influenced by previous crop and manure.
(*Magdoff, 1991*, Prod. Ag. *4:297–305.*)

PSNT has also been adapted for vegetables where the critical NO_3-N level is similar to that used for corn (Fig. 9-53). Guidelines for in-season soil sampling with vegetables is also similar to corn (Table 9-10).

Other In-Season N Tests As with the PSNT, sampling to determine soil NO_3-N is also useful in adjusting in-season N application rates in wheat (Fig. 9-54).

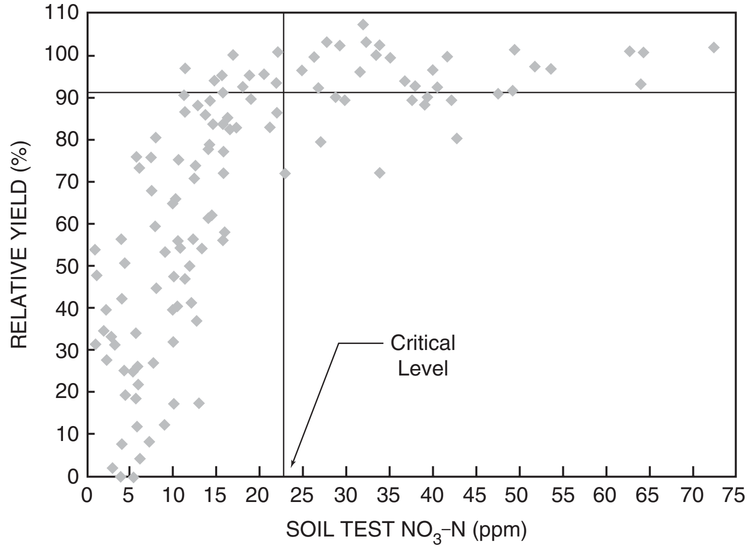


Figure 9-53
Relationship between PSNT and relative yield of cabbage.
(*Heckman, 2003*, Rutgers Coop. Ext. Bull. E285.)

TABLE 9-10
GUIDELINES FOR IN-SEASON SOIL SAMPLING USED FOR PSNT IN VEGETABLES

Crop	Soil Sampling Time
Sweet corn, field corn	plants 6–10 in. tall
Cabbage, cauliflower, broccoli, brussels sprouts	2 wks. posttransplant
Celery	2 wks. posttransplant, repeat in 3–4 wks
Lettuce, endive, escarole	2 wks. posttransplant or after thinning at 2–4 leaf stage if direct seeded
Beet, turnip, rutabaga	after thinning at 2–4 leaf stage
Pumpkin, winter squash, cucumber, muskmelon	vines 6 in. long
Spinach	2–4 leaf stage, repeat after cutting
Irish potato	plants 6 in. tall
Peppers, tomato, eggplant	1st fruit set, repeat after 3–4 wks

Source: Heckman, 2003, Rutgers Coop. Ext. Bull. E285.

New technologies may allow description of the spatial variation in N availability while reducing the dependence on soil sampling and analysis. With a sensor mounted on a yield-monitoring combine, the distribution of grain protein can be measured (Fig. 9-28). As an indicator of N availability, grain protein content is highly correlated with soil-profile N content. These new technologies will ultimately enhance our ability to more accurately predict crop N requirements.

P Soil Tests When solution P decreases with plant uptake, P minerals dissolve or adsorbed P desorbs to resupply soil solution P (Fig. 5-1). Chemical extractants used for P soil tests simulate this process, because they reduce solution Al or Ca. As solution Al or Ca decreases during extraction, native Al-P or Ca-P minerals dissolve to resupply solution Al or Ca. Solution P then concurrently increases, which provides a measure of the soil's ability to supply or buffer plant available P.

The *Bray-1P* soil test is used in acid and neutral pH soils and contains 0.025 M HCl + 0.03 M NH_4F. In acid soils, $Al/FePO_4$ are the primary P minerals controlling P in solution (Fig. 5-12). During extraction, F^- and Al^{+3} precipitate as AlF_3. As Al^{+3} decreases, $AlPO_4 \cdot 2H_2O$ dissolves to buffer the loss of solution Al^{+3}, releasing $H_2PO_4^-$ into solution according to:

Step 1: $3F^- + Al^{+3} \rightarrow AlF_3\downarrow$ [Al^{+3} decreases as AlF_3 precipitates]

Step 2: $AlPO_4 \cdot 2H_2O + 2H^+ \rightarrow Al^{+3} + H_2PO_4^- + 2H_2O$

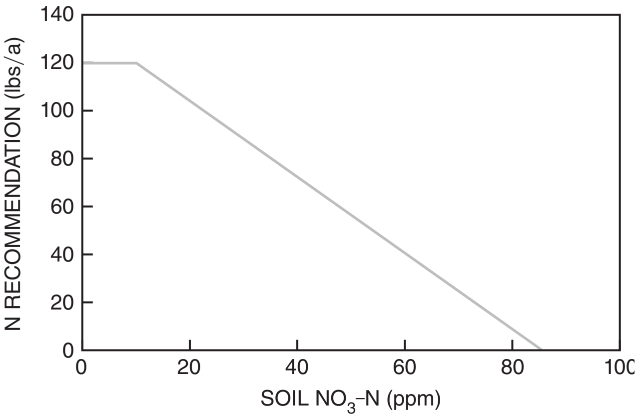


Figure 9-54
Relationship between soil NO_3-N (0–3 ft depth) at mid-tillering (GS 25) and N required for optimum wheat yield.
(*Alley et al., 1996, Virginia Coop. Ext.*, Publ. No. 424-026.)

The subsequent increase in solution $H_2PO_4^-$ during the extraction is measured, which represents an estimate of the soil's capacity to supply plant available P. The HCl in the extractant also dissolves Ca-P minerals present in slightly acid and neutral soils.

Mehlich-3P soil test is also used in acid and neutral soils and contains NH_4F, extracting P in the same manner as the Bray-1P test. A *Mehlich-1* soil test (0.05 M HCl + 0.0125 M H_2SO_4) is used in some regions with more highly weathered, low-CEC soils. The quantity of P dissolved by these dilute acids from Fe-P and Al-P minerals is calibrated with P crop response.

Olsen or *Bicarb-P* soil test is used in neutral and calcareous soils and contains 0.5M $NaHCO_3$ (pH 8.5). In these soils, Ca-P minerals control solution P concentration (Fig. 5-12). The HCO_3^- causes $CaCO_3$ to precipitate during extraction, which reduces Ca^{+2} in solution. Consequently, Ca-P minerals dissolve to buffer solution Ca^{+2} and release $H_2PO_4^-$ into solution by:

Step 1: $HCO_3^- + Ca^{+2} \rightarrow CaCO_3\downarrow + H^+$ [Ca^{+2} decreases as $CaCO_3$ precipitates]

Step 2: $CaHPO_4 \cdot 2H_2O + H^+ \rightarrow Ca^{+2} + H_2PO_4^- + 2H_2O$

As with the Bray-1 and Mehlich-3 tests, the increase in $H_2PO_4^-$ provides a measure of the soil's ability to supply plant available P.

The *Kelowna* (0.015 N NH_4F + 0.25 N HOAc) and *modified Kelowna* (0.015 N NH_4F + 0.5 N HOAc + 1 N NH_4OAc) soil tests are recommended for plant available P on high-pH, calcareous soils in western Canada.

While soil test interpretations differ among regions and crops, the P concentration extracted also varies between tests (Table 9-11). Bray and Mehlich-P tests extract similar quantities of P, while Olsen P test extracts about half as much P. Soil test level indicates the soil P sufficiency level (Fig. 9-33); thus, as soil test P increases, recommended P rate decreases (Table 9-11). No response to P fertilization would occur at high soil test P, where the "high" soil test P level varies with crop (Fig. 9-55). For example, soybean would attain 100% yield at 10 ppm P, while alfalfa would only reach 60% yield at 10 ppm soil test P.

K Soil Tests Exchangeable plus solution K^+ is usually extracted with 1 M NH_4OAc (Table 9-8):

$$\text{Clay-K}^+ + NH_4^+ \rightarrow \text{Clay-NH}_4^+ + K^+$$

The NH_4OAc soil test extracts K^+ in concentrations related to K availability to plants; however, as with P, crops vary in their responsiveness to K (Fig. 9-56). A general calibration for the NH_4OAc soil test is shown in Table 9-12. In soils with high K release and retention properties, this method may extract some K^+ that is unavailable to crops.

TABLE 9-11
CALIBRATIONS FOR THE BRAY-1, MEHLICH-3, AND OLSEN SOIL TESTS[1]

Sufficiency Level	Bray-1	Mehlich-3	Olsen	P Recommendation
	ppm			lbs P_2O_5/a
Very low	<5	<7	<3	50–90
Low	6–12	8–14	4–7	30–50
Medium	13–25	15–28	8–11	10–30
High	26–40	29–50	12–20	0
Very high	>40	>50	>20	0

[1] P sufficiency levels and recommendations represent general values, which vary between region and crop.

Figure 9-55
Response of various crops to Bray-1 P.
(*Olsen et al., 1984,* Nat. Corn Handbook.)

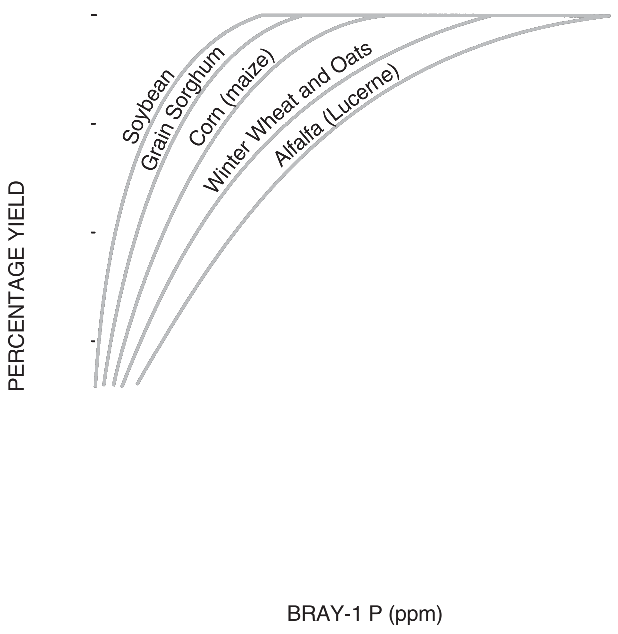


Figure 9-56
Relationship between NH_4OAc *extractable K and relative yield of several crops.*

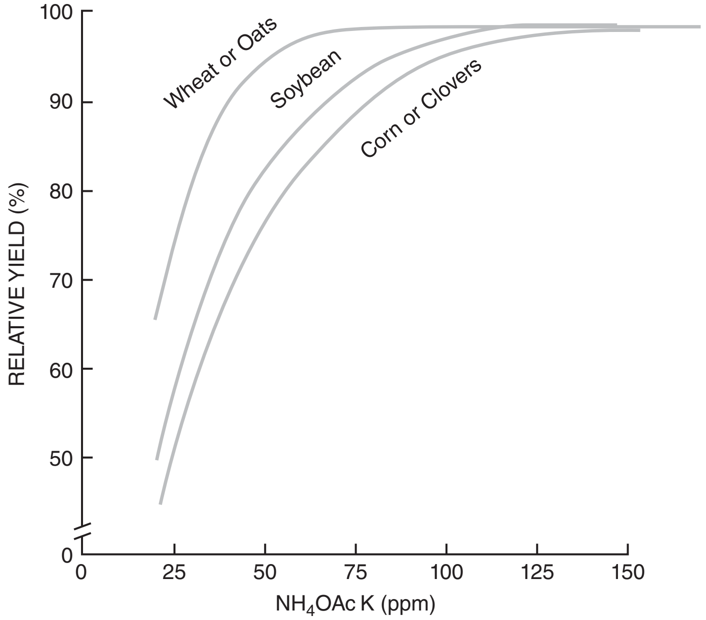


TABLE 9-12
GENERAL CALIBRATION OF THE NH_4OAc-K SOIL TEST[1]

Sufficiency Level	NH_4OAc-K	K Recommendation
	ppm	*lb K_2O/a*
Very low	<40	120–160
Low	41–80	80–120
Medium	81–120	40–80
High	121–160	0–40
Very high	>160	0

[1] K sufficiency levels and recommendations represent general values and will vary between region and crop.

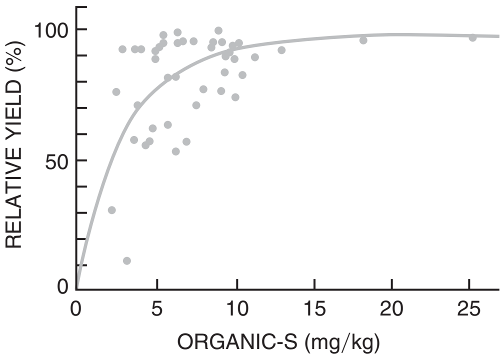


Figure 9-57
Relationship between relative annual yield of pasture and MCP $[Ca(H_2PO_4)_2]$ *extractable organic S.*

S Soil Tests Like NO_3^{-}, SO_4^{-2} is mobile in soil; thus, in humid regions, extractable SO_4^{-2} has not been a reliable measure of S availability. In low rainfall regions; H_2O, $Ca(H_2PO_4)_2$, or $CaCl_2$ extractable SO_4^{-2} have been used with some success. Plant available SO_4^{-2} is supplied by OM mineralization during the growing season. Since organic S represents $\approx$90% of total S in most soils, S soil tests that estimate mineralizable S might be more accurate in identifying S deficient soils. $Ca(H_2PO_4)_2$ or KH_2PO_4 extractable S represents some mineralizable organic S and should be a better indicator of S availability (Fig. 9-57). For example, extraction with 0.2 M KH_2PO_4 satisfactorily measures both available SO_4^{-2} and organic S (Table 9-13).

Where S soil tests are unreliable, recognizing that crop response to S is more likely on coarse-textured, low OM soils is helpful in identifying potential S deficiency. Other factors to consider are (1) crop requirement for S, (2) crop history, (3) use of manures, (4) proximity to industrial S emissions, and (5) S content of irrigation water (Chapter 7).

Fe, Zn, Mn, Cu Soil Tests Chelate-micronutrient relationships and stability in soils are utilized in soil testing for micronutrients. When EDDHA is added to soil, 100% is complexed with Fe over the soil pH range (Fig. 8-7). Therefore, EDDHA might make a good extractant for Fe; however, Fe-EDDHA is so stable that very few other micronutrient cations would be complexed with EDDHA. Although Fe-DTPA is not as stable at high pH as Fe-EDDHA (Fig. 8-7), the other micronutrients (i.e., Zn and Cu) exhibit stability with DTPA, especially at pH > 7 (Fig. 9-58).

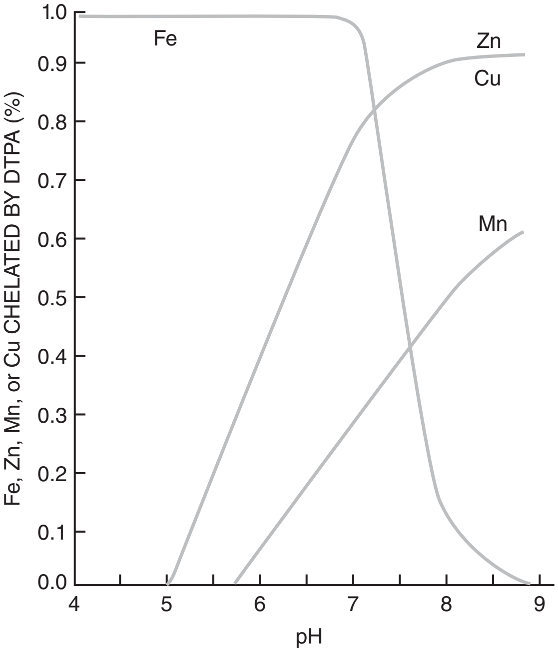
Knowledge of chelate stability in soil provides the basis for developing the DTPA soil test for Fe, Zn, Cu, and Mn, which is used in most soil-testing laboratories. EDTA is less effective in extracting micronutrients because it has a high affinity for Ca. In soils with pH > 6.5, EDTA would be approximately 100% complexed with Ca, with little remaining capacity to complex Fe, Zn, Cu, and Mn.

TABLE 9-13
INTERPRETATION OF SO_4 AND ORGANIC S SOIL TEST VALUES

Soil S Status	SO_4^{-2}	Organic S	S Recommendation
	ppm	*ppm*	*lb S/a*
Deficient	0–6	0–10	10–20
Adequate	7–12	10–20	0
Above optimum	>12	>20	0

Source: Sulphur Institute, 1994.

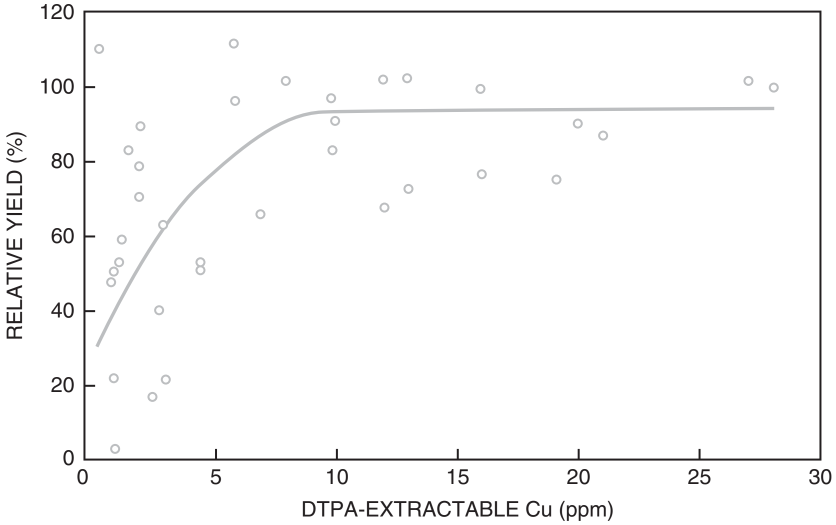
Figure 9-58
Influence of soil pH on the amount of Fe, Zn, Mn, or Cu chelated with DTPA. Over the pH range of most soils (pH 5–8), DTPA complexes micronutrients in quantities related to crop response.



Before chelate relationships were developed, the most common micronutrient soil test was based on an acid extraction, usually HCl. Although some laboratories still use acid-extractable micronutrient soil tests, the DTPA test is preferred. Excellent correlations exist between DTPA-extractable micronutrients and relative crop yield (Fig. 9-59). For example, DTPA effectively separates Zn-deficient from nondeficient soils (Fig. 9-60). About 90% of the soils testing < 0.65 ppm Zn responded to Zn, whereas 100% above this level did not respond. The DTPA soil test has been calibrated for most crops, and the general interpretation for DTPA-extractable micronutrients is shown in Table 9-14.

B, Cl, and Mo Soil Tests Extraction with hot water is the most common soil test for B. Critical levels for most crops are ≤ 0.5 ppm B. When hot water-extractable B is >4–5 ppm, B toxicity can occur. Like NO_3^-, Cl^- is soluble, so extraction with water is used. Soil samples should be taken to at least a 2 ft depth. The critical water-extractable Cl^- level is 7–8 ppm for most crops. No reliable Mo soil test has been

Figure 9-59
Relationship between DTPA-extractable Cu and relative barley yield.



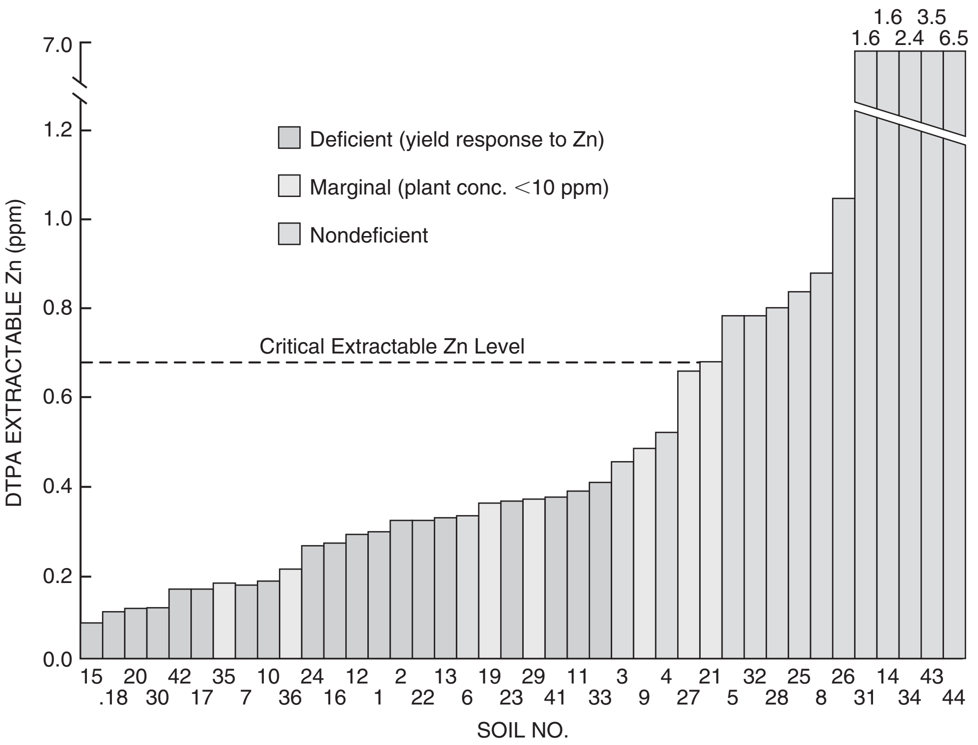


Figure 9-60
Corn response of 40 soils to Zn as a function of DTPA soil test levels.
(Havlin and Soltanpour, 1981, SSSAJ, 45:70–75.)

TABLE 9-14
DTPA-EXTRACTABLE FE, ZN, MN, AND CU FOR DEFICIENT, MARGINAL, AND SUFFICIENT SOILS

Sufficiency	Fe	Zn	Mn	Cu
		ppm		
Low (deficient)	0–2.5	0–0.5	0–1.0	0–0.4
Marginal	2.6–4.5	0.6–1.0	—	0.4–0.6
High (sufficient)	>4.5	>1.0	>1.0	>0.6

developed, although both water and NH_4-oxalate extracts have been used. Fortunately, Mo deficiency is uncommon in the United States.

Multinutrient Soil Tests With the advance of analytical instruments capable of measuring elements simultaneously, soil tests have been developed that simultaneously extract macro- and micronutrients. Components of the Mehlich-3 soil test and their functions in extracting nutrients include:

- 0.2 N CH_3COOH (acetic acid) → buffers solution at pH 2–3 to limit CaF_2 precipitation.
- 0.25 N NH_4NO_3 (ammonium nitrate) → NH_4^+ exchanges for cations on CEC.
- 0.013 N HNO_3 (nitric acid) → dissolves some Ca-P + micronutrient containing minerals.
- 0.015 N NH_4F (ammonium fluoride) → extracts P; NH_4^+ exchanges for cations on CEC.
- 0.001 M EDTA → complexes Fe, Zn, Cu, and Mn.

For calcareous soils, the NH_4HCO_3-DTPA soil test is based on:

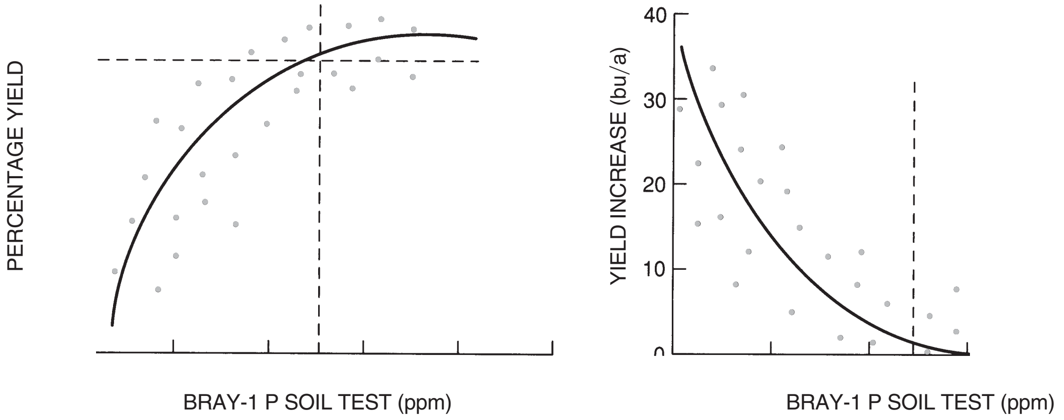
- 1.0 M NH_4HCO_3 (ammonium bicarbonate) → NH_4^+ exchanges for K^+; HCO_3^- extracts P.
- 0.005 M DTPA → complexes Fe, Zn, Cu, and Mn.

Calibrating Soil Tests

To identify the optimum nutrient application rate from soil test results, soil tests must be calibrated against crop responses to applied nutrients in field experiments conducted over a wide range of soils and climate conditions. Yield responses from various rates of applied nutrients can then be related to the quantity of available nutrients indicated by the soil test. An accurately calibrated soil test (1) correctly identifies the degree of nutrient deficiency or sufficiency and (2) supports the estimated nutrient rate required to optimize crop productivity.

Controlled experiments are initially conducted in the greenhouse to provide information about (1) the ability of a soil test to extract a nutrient in quantities related to crop uptake (i.e., to identify the best extractants), and (2) the relationship between soil test level and relative yield. Figure 9-29 shows crop response to a range of DTPA extractable Fe levels. When DTPA Fe is > 4.5 ppm, normal growth is observed.

After greenhouse studies have been completed, field calibration experiments are conducted on the major soil series and crops in the region. For example, if a P soil test is being calibrated (Fig. 9-31), 4–6 P rates will be applied and crop response quantified by measuring yield (e.g., forage, grain, fruit) and P content in the whole plant or plant part. Yield response data can be expressed as *% yield* or *yield increase* (Fig. 9-61); % yield represents the ratio of yield in unfertilized soil to yield obtained where P is nonlimiting (fertilized soil). For example, 70% yield means that the unfertilized crop yield is 70% of that obtained at optimum P applied. Yield increase represents the increase obtained with optimum fertilization. Thus, as soil test P increases, % yield increases to 100%, or where no difference in yield is observed between fertilized and unfertilized soil. Alternatively, as soil test P level increases, yield increase to P fertilization eventually declines to zero.



(a) (b)

Figure 9-61
Relationship between % yield (a) or yield increase (b) and Bray-1 P soil test level. The vertical dashed line represents the critical soil test level, or the soil test level below which crop response to added nutrient is expected. Vertical dashed lines represent the CL.

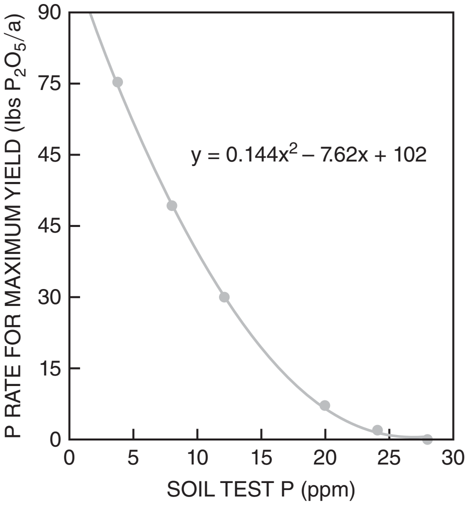


Figure 9-62
Influence of soil test P level on P recommendation.

Generally, when % yield reaches 95–100% or when yield increase reaches 0–5%, the critical soil test level (CL) is obtained (Fig. 9-61). The CL represents the soil test level above which no yield response to fertilization will be obtained. Soil test CLs vary among crops, climatic regions, and extractants. For example, CLs for the Bray-1, Mehlich-3, and Olsen P tests are approximately 25, 28, and 11 ppm, respectively (Table 9-11).

Soil test calibration studies also provide data to establish fertilizer recommendations. For example, at each field location, P rate required for optimum yield can be determined and displayed (Fig. 9-62). Increasing soil test level corresponds to decreasing P rate required for optimum yield. These diagrams are used to establish nutrient rates associated with very low, low, medium, and high soil test levels; however, an equation is commonly used to describe the relationship (Fig. 9-62).

Interpretation of Soil Tests Many soil test reports, in addition to reporting the nutrient concentration, provide the interpretation or nutrient sufficiency (very low, low, medium, high, or very high). The probability of a response to fertilization increases with decreasing soil test level (Fig. 9-63). While nutrient availability is only one factor influencing plant growth, the probability of a response to applied nutrients increases with decreasing soil test level.

Soil test interpretation involves an economic evaluation of the relation between soil test level and nutrient response. However, actual nutrient response may vary due

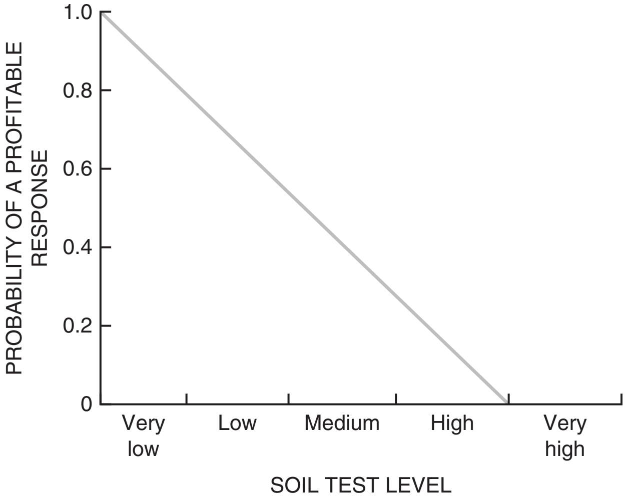
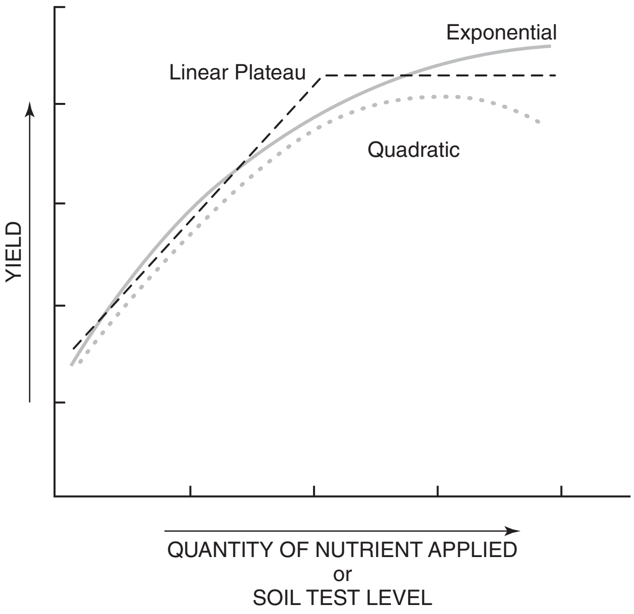


Figure 9-63
The probability of obtaining a profitable response from nutrient addition decreases with increasing soil test level.

Figure 9-64
Common models used to describe crop response to increasing soil test level or to rate of applied nutrients.



to any factor (i.e., weather, pests, and management) that limits yield (Fig. 1-11; Fig 1-12).

Many soil test laboratories provide one recommendation, assuming best production practices for the region, and producers make adjustments as necessary. As technology and management practices improve, yield potential and recommendations increase. For the grower, the goal is to maintain plant nutrients at a level for sustained productivity and profitability, which means that nutrients should not be a limiting factor at any stage, from plant emergence to maturity.

Nutrient-Response Functions The most common models used in fitting nutrient-response data are given by (Fig. 9-64):

Linear-plateau model:

$$Y = b \quad \text{plateau portion with slope} = 0$$
$$Y = mx + b \quad \text{linear portion with slope} = m$$

Exponential model:

$$Y = e^x$$

Quadratic model:

$$Y = a + bx - cx^2$$

where Y = yield, x = nutrient rate, and a, b, and c are constants or coefficients. All of these equations have been used to describe yield response to both immobile and mobile nutrients.

The model selected for use in describing crop response to increasing soil test level will influence the established critical level (Fig. 9-65). Regardless of the model, crop response will vary with the crop (Fig. 9-55), yield potential (Fig. 1-12), soil test level (Fig. 9-66), previous crop (Fig. 4-13), year (discussed later), and other management factors (Chapter 10).

Nutrient Recommendations

Nutrient Mobility Soil test interpretation for purposes of making nutrient recommendations is influenced by the mobility of the nutrient. With mobile nutrients, crop yield is proportional to the total quantity of nutrient present in the root zone, because

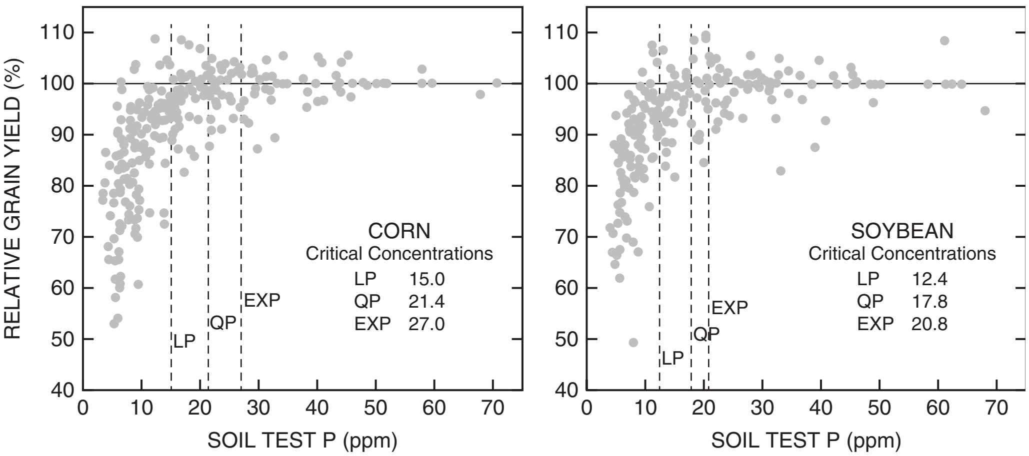


Figure 9-65

Relationship between soil test P and relative yield of corn and soybean (24 years, three locations) in Iowa using linear-plateau (LP), quadratic (QP), exponential (EXP) models. Dashed lines represent critical soil test P levels for each model. (Dodd and Mallarino, 2005, SSSAJ/69:1118–1128)

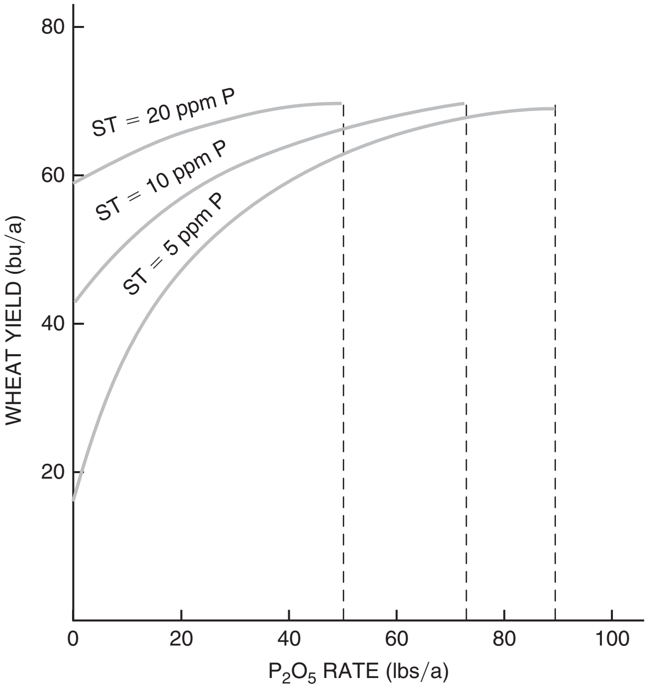


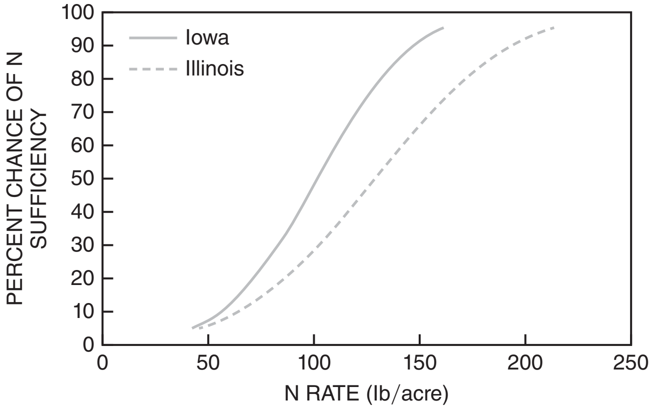
Figure 9-66

Wheat yield response to P_2O_5 rate at three soil test (ST) P levels.

of minimal interaction with soil constituents (Fig. 2-20). Recall that for NO_3^-, SO_4^{-2}, and Cl^-, a 2–3 ft profile sample is important for accurately assessing mobile nutrient availability (Fig. 9-47). In contrast, yield response to immobile nutrients (e.g., $H_2PO_4^-$, K^+, Zn^{+2}) is proportional to the concentration of nutrients near the root surface because these nutrients strongly interact with or are buffered by soil constituents (Fig. 2-20).

Crop response to increasing nutrient concentration is generally linear until the yield potential for the given environment is achieved or is limited by nutrient depletion or other yield limiting factors (Fig. 1-12). For example, if profile N soil test indicated available N was ≈70% sufficient, equivalent to 100 lb N/a, then for 100% sufficiency additional N would be recommended (Fig. 9-67).

Figure 9-67
Influence of N rate on relative N supply (sufficiency) to corn.
(Nafziger et al., 2004, North Central Ext.-Ind. Soil Fert. Conf. Des Moines, IA)



Mobile Nutrient Recommendations With mobile nutrients, soil test buildup and/or maintenance programs are not viable, because these nutrients are readily mobile in the root zone in many soils. Preventing potential NO_3^- transport below the root zone, while providing sufficient N for profitable crop production, requires accurate N recommendations and management (Chapter 10). N recommendations are usually based on yield goal, where the N required to produce each unit of yield is known (i.e., 2.0 lbs N/bu of winter wheat, see Table 9-1). This concept is also evident when in-season N is recommended because better-than-average growing conditions increased yield potential above initial estimates provided before planting.

N recommendations require knowledge of the quantity of N needed by the crop and supplied by the soil. N recommendations are based on:

$$N_{REC} = N_{CROP} - N_{SOIL} - (N_{OM} + N_{PC} + N_{MN})$$

where, N_{REC} = N recommendation
N_{CROP} = crop yield goal × N coefficient
N_{SOIL} = preplant soil NO_3^- content
N_{OM} = soil OM mineralization
N_{PC} = previous legume crop N availability
N_{MN} = manure N availability

N_{CROP} represents N required by the crop and involves estimating yield and lb N/ unit of yield (N coefficient). Underestimating the yield goal can cause considerable yield loss due to underfertilization. Alternatively, overestimating yield goal results in overfertilization, which can greatly increase profile N content after harvest and increase N leaching potential. Unfortunately, growers often overestimate yield goal and thus apply excess N. The N coefficient also varies among crops, regions, and climates (Table 9-1). The N coefficients for corn, usually ranges from 0.9 to 1.7 lbs N/bu (1.2 lbs N/bu average), and for winter wheat, 1.8 to 2.4 lbs N/bu (2.0 lbs N/bu average), are used to estimate N_{CROP}. Thus, with 60 bu/a wheat yield goal, total N required by the crop is 120 lbs N/a.

The N_{CROP} estimate is reduced by potential available soil N. After adjustments for soil profile NO_3^- content, if present, N_{CROP} is adjusted for potential mineralizable N available from N_{OM}, N_{PC}, and N_{MN}. N_{MN} varies with rate applied and time after application (Chapter 10). Generally, 50% of manure N is available in the first year, 25% in the second year, and none in the third year. N_{PC} depends on the legume, legume yield, and length of time after the legume crop was rotated to a nonlegume crop (Chapter 4, Chapter 12). N_{PC} from forage legumes is generally greater than grain legumes, although low-yielding forage legumes can fix less N_2 than high-yielding grain legumes (Table 4-7). When nonlegume crops are grown on soils previously cropped to a forage legume, N_{PC} decreases with time (Fig. 4-12). Thus, N_{REC} is lower in the first year following the legume compared with subsequent years.

Few N_{REC} models include N_{OM} because of the difficulty in accurately estimating soil OM mineralization under variable climate conditions from year to year. Although many tests have been evaluated, they have not always been highly correlated with N_{OM}. Some models reduce the N coefficient to account for N_{OM}. Alternatively, some N_{REC} models use % soil OM as an indicator of N_{OM} (Table 9-9). Credits for N_{OM} generally range from 20 to 80 lbs N/a.

N_{REC} Based on Average N Response Data

Most N_{REC} systems are based on field trials that quantify crop response to a wide range of N rates (Fig. 9-31). The N response data over many soils, soil and crop management inputs, and years are combined to develop an average N response equation that uses average yield goals and average N coefficients (lb N/bu grain). For example, in western Minnesota, the N recommendation model for corn is:

$$N_{REC} = [1.2 \text{ lb N/bu} \times \text{YG}] - \text{STN} - N_{PC}$$

where, N_{REC} = N recommendation (lb N/a)
YG = crop yield goal (bu/a)
STN = preplant soil NO_3^- content (0–2 ft depth) (lb N/a)
N_{PC} = previous crop N credits (lb N/a)

In most situations, the N rate needed for optimum yield varies greatly between years (Fig. 9-68). In this example, optimum N rate varied between 121 and 230 lb N/a (Table 9-15). The N coefficient (lb N/bu) also varied between 0.7 and 1.3 lb N/bu. If the average optimum N rate (165 lb N/a) were recommended, then the correct N rate would have been applied in 2 of 6 years (2001 and 2003), excess N applied in 2 years (2000 and 2002), and insufficient N applied in 2 years (1999 and 2004). Since there is a greater economic loss to underfertilizing than overfertilizing (Chapter 11), N recommendations are increased above averages supported by N response studies (Fig. 9-68). For example, if the N coefficient were increased to 1.2 lb N/bu, then the N recommendation would be 208 lb N/a ($173 \text{ bu/a} \times 1.2 \text{ lb N/bu}$), resulting in excess N applied in 4 of 6 years. In addition, N use efficiency (NUE; % N applied that is recovered in the grain) averaged 60% (Table 9-15). Using 208 lb N/a, the NUE decreases to 48%, which increases fertilizer N left in the soil after harvest and potential for N leaching below the root zone.

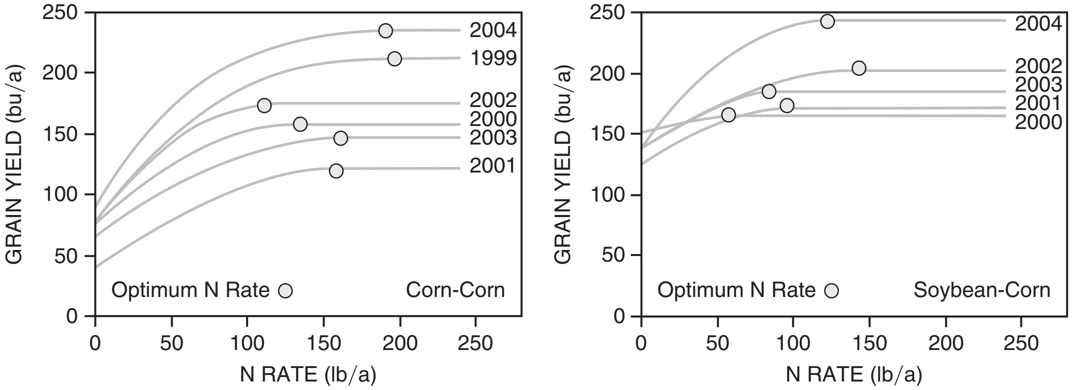


Figure 9-68

Variation in corn grain yield response to N following corn (left) and soybean (right) (1999–2004). Optimum N rate represents maximum net return to N at 0.10 price ratio (i.e. $0.44/ lb N: $4.40/bu).

(*Adapted from* Sawyer et al., 2006, PM 2015, Iowa State Univ.)

Table 9-15
Annual Variability in Continuous Corn Yield Response to N[1]

Year	Yield No N	Optimum Yield	Optimum N rate	N Coefficient[2]	NUE[3]
	bu/a		lb/a	lb N/bu	%
1999	75	212	200	0.94	64
2000	75	156	143	0.92	56
2001	42	121	162	1.34	45
2002	75	170	125	0.74	74
2003	65	147	164	1.12	49
2004	84	230	198	0.86	69
Average	**69**	**173**	**165**	**0.99**	**60**

[1] Data from Fig. 9-68; Sawyer et al., 2006.

[2] Optimum N rate / optimum yield.

[3] NUE → % fertilizer N recovered in grain at optimum N rate
→ [(fertilized yield * 1.5 %N - unfertilized yield * 1.2 %N) / optimum N rate] * 100
→ yield in lb/a = bu/a * 56 lb/bu

1.2 and 1.5% grain N assumed for unfertilized and fertilized grain, respectively.

This example illustrates the difficulty in accurately estimating optimum N rates for a given year. While year-to-year variation in growing season environment greatly contributes to the error in predicting N rates, these conditions also greatly influence soil mineralizable N. Therefore, using technologies that enable in-season N rate adjustments (see *Tissue Tests for In-Season N Adjustments* and *In-season Soil Sampling*) to improve the accuracy of estimated N requirements can significantly decrease the amount of excess N applied, which will increase NUE and profitability, while reducing potential N loss to the environment. (Fig. 9-69).

N_{REC} Based on “Delta” Yield

To address the difficulty in estimating N rate based on average yield goal and the large variation in N response between years (Fig. 9-68), a *delta yield* approach has been developed. Delta yield is the difference between unfertilized yield and yield at optimum N rate. The unfertilized yield provides a biological estimate of soil N supply. For example, there is a poor correlation between optimum yield and N rate, due to yearly variation in N response; however, optimum N rate is highly correlated to *delta yield* or optimum yield–unfertilized yield (Fig. 9-70). Determining delta yield for a field requires an unfertilized strip and the producer would measure yield in the fertilized and unfertilized area over several years. With the commonly available yield monitors, *delta yield* can be easily determined using strip test procedures (Fig. 9-30). Clearly the *delta yield* method of determining N recommendations is an improvement over using average yield goals.

Immobile Nutrient Recommendations With immobile nutrients, crop yield potential is limited by the quantity of nutrient available at the soil-root interface (Fig. 2-20). Generally, solution concentrations of immobile nutrients are low, and replenishment occurs through exchange, mineralization, and mineral solubility reactions (Fig 2-2). If nutrient uptake demand exceeds the soils capacity to replenish solution nutrients, then plant growth and yield will be limited. Immobile nutrient recommendations are based on sufficiency levels determined through soil testing (Fig. 9-33). Soil tests for immobile nutrients provide an index of nutrient availability that is generally independent of environment.

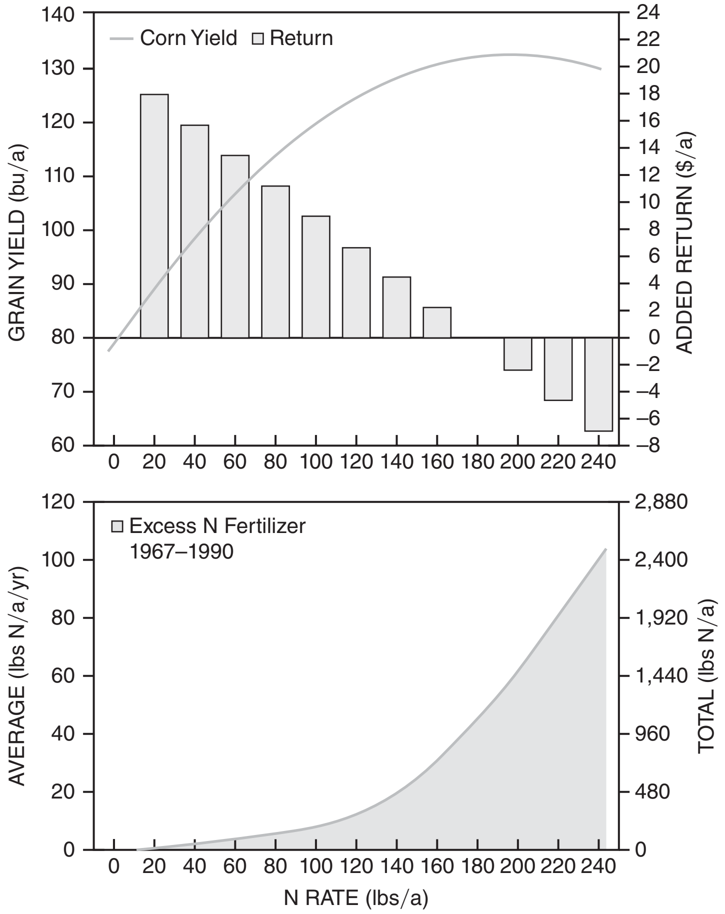


Figure 9-69

Effect of N rate on corn yield, economic return, and amounts of excess N applied. (Vanotti and Bundy, 1994,J. Prod. Agric. 7:243.)

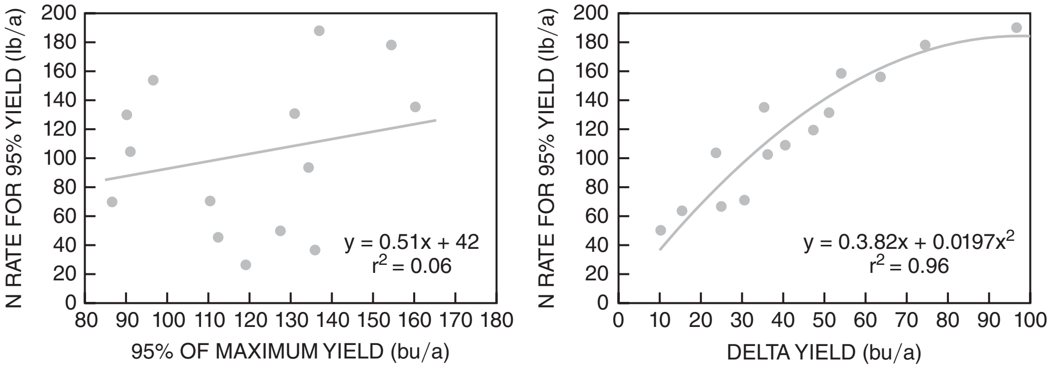


Figure 9-70

Relationship between optimum corn yield and N rate needed for optimum yield (left) *and* delta yield *and optimum N rate (right)* (Kachanoski et al., Better Crops 80 (1):20–23).

Some immobile nutrient recommendation models account for yield potential similar to N recommendations (Table 9-16). Incorporation of yield potential into P or K recommendations is based on *replacement* of nutrients removed as a function of yield level. For instance, 70 bu/a wheat production would deplete soil test P if no P were applied or P were applied for 40 bu/a yield potential. Alternatively, P rates applied for 70 bu/a production are inappropriate for 40 bu/a yields. Significant soil test P buildup would occur with overfertilization.

TABLE 9-16
N, P, AND K RECOMMENDATIONS BASED ON CORN YIELD POTENTIAL

	Yield Potential (bu/a)		
	100	140	180
	N Rate (lb/a)		
	110	160	220
Bray-1 P (ppm)	P_2O_5 Rate (lb/a)[1]		
5	85	100	115
10	60	75	90
15–30	35	50	65
35	20	25	35
45	0	0	0
NH_4OAc-K (ppm)	K_2O Rate (lb/a)[2]		
50	195	210	220
75	145	160	170
100	95	110	120
125–155	45	60	70
165	25	30	35
175	0	0	0

[1] Values represent P soil test maintenance recommendations, where P rate will increase or decrease if buildup or drawdown of soil test P is advised, respectively.
[2] Values represent K rates for a CEC = 20 meq/100 g, where K rate increases with increasing CEC or decreases with decreasing CEC.
Source: Vitosh et al., 2002, Coop. Ext. Service Bulletin E–2567, Ohio State Univ., Columbus, OH.

With any immobile nutrient management program, soil must be sampled periodically to determine whether the soil test level is decreasing or increasing (Fig. 5-33). These data show that soil test P declined with ≤50 lbs P_2O_5/a. In contrast, P soil test was maintained at or slightly above the initial level with annual applications of 100 lbs P_2O_5/a. Soil test P level increased with 150 lbs P_2O_5/a applied initially and every 3 years, and then subsequently declined with crop removal.

Basic Cation Saturation Ratio (BCSR)

The *basic cation saturation ratio* (BCSR) approach in soil testing for immobile nutrient recommendations assumes that maximum yields can only be achieved by maintaining an ideal cation saturation percentage or ratio of Ca^{+2}, Mg^{+2}, and K^{+} on the CEC. Using "ideal" exchangeable cation levels of 65% Ca, 10% Mg, 5% K, and 20% H, the "ideal" ratios suggested are:

Ca:Mg	6.5:1
Ca:K	13:1
Mg:K	2:1
K:Ca+Mg	1:15

In some regions "ideal %" is expanded to optimum saturation ranges of 65–85% for Ca, 6–12% for Mg, and 2–5% for K.

The BCSR maintenance approach differs from the sufficiency approach (Fig 9-33) by an emphasis on *fertilizing the soil* rather than *fertilizing the crop*. Using BCSR, nutrient rates are based on maintaining specific cation ratios on the CEC. Once ideal levels are attained, nutrient rates equal to crop nutrient removal are applied to maintain ideal cation ratios. Using the sufficiency level approach, nutrient rates are based on maintaining plant nutrient levels in soil that provide optimum nutrient availability to plants. Below a defined soil test sufficiency or CL, crops will respond to the applied nutrient; plants will not respond if soil test levels are above the CL.

Most field crop studies show that BCSR approach has little impact on crop response, and suffers from the disadvantage in that if the cation ratio is optimum, a nutrient deficiency may still exist. For example, if two soils have an optimum Ca:Mg ratio of 6.5:1, one soil could have 65% Ca and 10% Mg, while the other soil has 13% Ca and 2% K and exhibit Ca deficiency. Therefore, sufficient supply of available cations in the root zone is more important than the cation ratio in determining optimum nutrient recommendations. Most soil testing laboratories use the *sufficiency level* approach to establish nutrient recommendations.

Soil Test Maintenance—Buildup

Decisions to maintain, draw down, or build up a soil test level are based on understanding the CL for the specific nutrient and crop (Fig. 9-71). When the soil test is <CL, buildup or sufficiency programs are recommended, depending on factors such as land ownership, fertilizer costs, and other economic considerations. For example, P or K rates based on sufficiency levels (very low, low, medium) are recommended with short-term (<2–3 years) land rental. If fertilizer costs are high, sufficiency rates might be advisable until costs decrease.

Generally, annual applications of 10–30 lbs P_2O_5/a are required to increase soil test P 1 ppm, depending on soil properties influencing P fixation capacity (Chapter 5). Similarly, 5–30 lbs K_2O/a are needed to increase soil test K level 1 ppm, depending on CEC.

When soil test is >CL, continued applications to further increase soil test are not needed and continued crop removal will draw down the soil test level. Although this can be a viable option, soil test levels can decline rapidly; thus, annual soil testing is recommended (Fig. 9-72). These data illustrate both drawdown and buildup of soil test P relative to the CL. When soil test is at or slightly above the CL, soil test level can be maintained by P or K rates that replace P or K crop removal. In some 2-year and *double crop* (2 crops/year) rotations, the first crop can be fertilized at sufficient rates for both crops.

In cropping systems utilizing annual manure applications, fertilizer nutrients are likely not needed, unless soil, crop, and environmental conditions suggest that a response to starter nutrients is warranted (Chapter 10). When soil tests indicate very high sufficiency levels of P or K, no further additions of these nutrients should be made because of increased risk to water quality (Fig. 9-73). Regardless of the

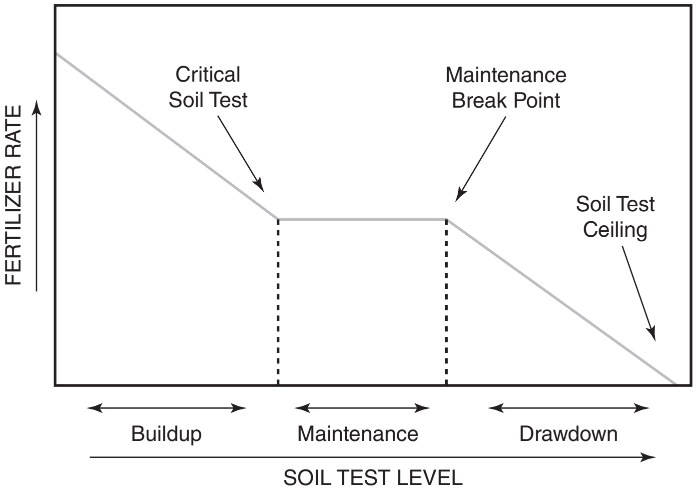


Figure 9-71
Diagram of buildup/maintenance approach to P and K recommendations.

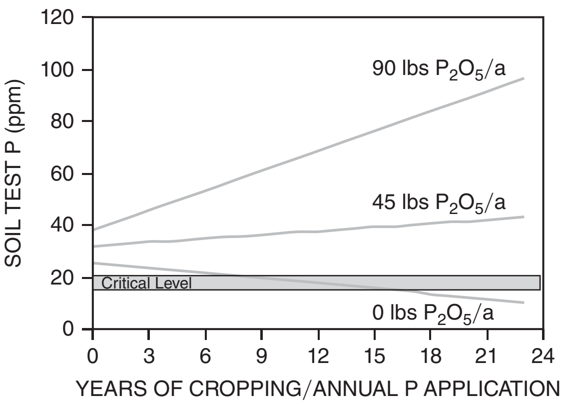


Figure 9-72
Influence of P rate and cropping on soil test P over time. Approximately 25 lb P_2O_5/a is needed to maintain initial soil test P level.
(Dodd and Mallinaro, 2005, SSSAJ/69:1118).

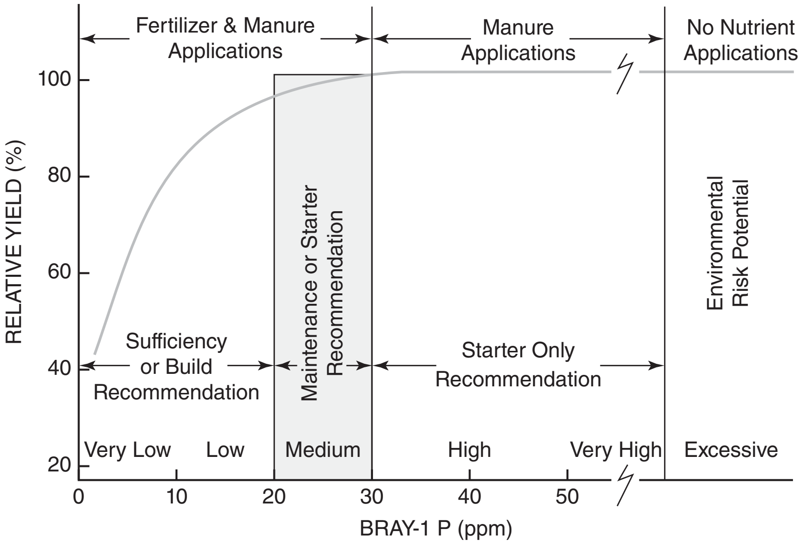


Figure 9-73
Example of buildup and maintenance rates of P based on soil test level.
(*Leikam et al., 2003,* Better Crops, *87:6–10*).

management program selected for immobile nutrients, decisions must be based on the information provided from periodic or annual soil testing that accurately monitors change in soil test level with time as nutrients are added and removed. Soil test history will guide adjustments in rates depending on whether soil test levels are increasing or decreasing. Soil test P or K buildup substantially above the CL is unnecessary, and with P, poses a potential risk to water quality (Chapter 12). Alternatively, decreasing soil test levels below the CL that reduces yield is economically unsustainable and should be avoided.

STUDY QUESTIONS

1. What factors must be taken into consideration in interpreting tissue tests?
2. Describe the difference between critical nutrient concentration (CNC) and critical nutrient range (CNR).
3. Identify the potential problems in interpreting plant nutrient ratios in diagnosing nutrition problems.
4. Can any part or growth stage of crops be used in plant analysis? Why or why not?
5. How can plant analysis be useful in soil fertility management? Provide several examples.
6. Describe the use of in-season tissue analysis to improve N management.
7. Would you apply a given nutrient if there were only 50% chance of obtaining a response? A 25% chance? Why or why not?
8. Describe the important information that can be used to develop a sampling plan. How frequently should it be resampled?

9. What is the primary advantage of point sampling over cell sampling?
10. Explain how selected spatial data can be used to develop a soil sampling plan.
11. When is deep soil sampling appropriate?
12. How does band application of immobile nutrients complicate soil-sampling procedures?
13. Why are N soil tests less reliable in high rainfall areas?
14. Describe the theoretical basis for the following soil tests.
    a. NH_4OAc-K
    b. $NaHCO_3$-P
    c. Bray-1P
    d. $Ca(H_2PO_4)_2$-S
    e. DTPA
    f. PSNT
15. What are the essential components of an N-recommendation model? Which factors are measured and which are estimated?
16. List five factors that affect the recommended nutrient rate and describe how each factor affects the recommendation.
17. Using diagrams/figures, show how you can establish the "critical level" of a nutrient in the soil and in a plant or plant part.
18. Describe the main steps in the soil testing/fertilizer recommendation process. What are the relative errors involved in each step? What can be done to reduce these errors?
19. Briefly outline how soil tests are developed and how fertilizer recommendations are established.
20. 20 grams of NH_4NO_3 (34% N) is added to 400 grams of soil. Calculate
    a. % N in soil
    b. lb N/afs
    c. ppm NO_3 added
    d. ppm NH_4 added
    e. ppm N added
21. A grower sampled his okra leaves 8 weeks after emergence and sent them into a lab for analysis. The results showed 0.25% P. The critical level for P in okra is 0.32% (sampled at 4 weeks after emergence). Give two reasons why the grower should not apply P to this crop.
22. Profile NO_3-N is determined prior to planting. The laboratory reported the following data. How many lb N/a–4 ft are present in the profile? If the sample were combined into one 4 ft sample, calculate the ppm N.

Soil Depth	ppm NO_3-N
0–6 inches	3.5
6–12 inches	4.0
1–2 feet	3.0
2–3 feet	1.5
3–4 feet	1.0

23. 200 lb N/a was applied by a farmer. Calculate
    a. lb NH_3/a
    b. lb UAN/a
    c. lb urea/a
24. A farmer applies 20 25–lb bags of fertilizer (15% N content) to 2500 ft^2 lawn. Calculate the lb N/a applied.
25. Why is it important to evaluate soil fertility?
26. Highlight on the plant nutrient – deficiency symptoms with reference to N, P, K, Ca, Mg, S, Cu, Mn and Zn.
27. What is the effect of nutrient deficiency on the leaf and root growth with respect to
    a. Chlorosis
    b. Necrosis
28. Give a generalized overview of the nutrient deficiency symptoms in plants with a flow chart.
29. What are the reasons for reduced nutrient uptake?
30. What are the advantages of plant analysis?
31. Write a note on tissue tests. What are its benefits?
32. What are the similarities and differences of cell sap and total analyses?
33. Plot the relationship between plant nutrient concentration and plant growth and explain the curve to indicate the various stages of the deficiency, luxury and toxicity.
34. What is a chlorophyll meter? What is the principle behind its working?
35. What is N sufficiency index? How is it calculated?
36. What is a colour chat? What is its use?
37. Express NDVI. How is the index calculated?
38. How is a postmortem tissue test performed?
39. Explain the various models used in fitting nutrient-response data.
40. What is the difference between point sampling and cell sampling?

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10

Nutrient Management

Efficient nutrient management programs supply plant nutrients in adequate quantities to sustain maximum plant growth and yield while minimizing environmental impacts of nutrient use. Substantial economic and environmental consequences occur when nutrients limit plant productivity. Ensuring optimum nutrient availability through effective nutrient management practices requires knowledge of the interactions between the soil, plant, and environment.

PLANT CHARACTERISTICS

Nutrient Utilization

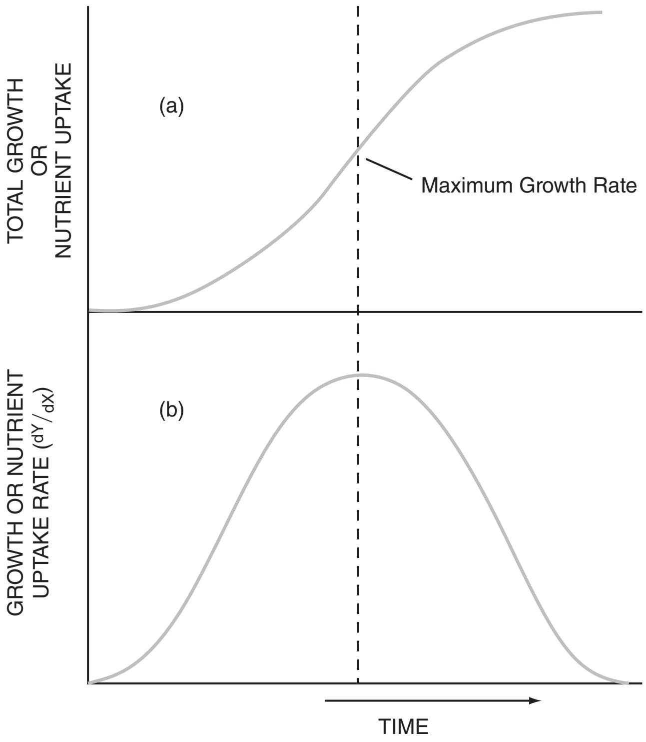
The quantity of nutrients required by plants (Table 9-1) varies depending on plant characteristics (crop, yield level, variety or hybrid, planting rate), environmental conditions (moisture and temperature), soil characteristics (soil properties, soil fertility, and landscape position), and soil and crop management. Although these interacting factors affect plant nutrient uptake and recovery of applied nutrients, nutrient accumulation during the growing season generally follows plant growth (Fig. 10-1). The shape of the curve varies among plants, but nearly all plants exhibit a rapid or exponential increase in growth and nutrient accumulation rate up to a maximum, followed by a period of decline. Some plants exhibit rapid nutrient uptake and growth early in the growing season, while other plants exhibit maximum growth rate much later (Fig. 4-14).

Regardless of the shape of the growth curve, nutrients are needed in the greatest quantities during periods of maximum growth rate. Thus, nutrient management plans are designed to ensure adequate nutrient supply before the exponential growth period (Fig. 10-2). In this case, N should be applied preplant or split applied before the stem extension phase. All the immobile nutrients, including P and K, should be applied before planting. Knowledge of crop-uptake patterns facilitates improved management for maximum productivity and recovery of applied nutrients.

Roots

Since nutrients are absorbed by roots, understanding root characteristics is important in nutrient management. Root systems are usually either fibrous or tap, and both occur with annuals, biennials, or perennials. The roots' ability to exploit soil for nutrients and water depends on their morphological and physiological characteristics. Root radius, root length, root surface/shoot

Figure 10-1
Graphical representation of cumulative plant growth (a) and plant growth rate (b) of a typical annual plant.



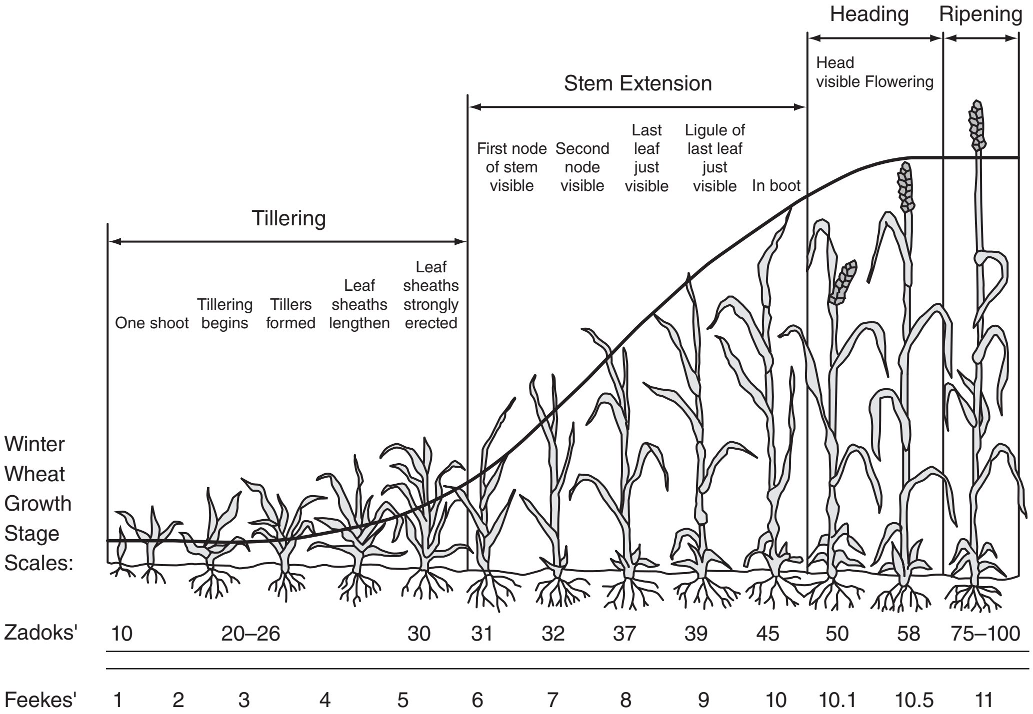


Figure 10-2
N-uptake pattern (solid line) of winter wheat throughout the growing season.
(Alley et al., 1996, Virginia Coop. Ext., Publ. No. 424–026.)

weight ratio, and root hair density are the main morphological features (Table 10-1). The presence of mycorrhizae is also important.

Plant Species Knowledge of rooting characteristics is important to understanding water and nutrient extraction by plants from soil. The primary plant root systems include *fibrous* roots characterized by a dense mass of similarly sized roots (mostly

TABLE 10-1
TYPICAL ROOTING DEPTHS OF SELECTED CROPS

<1.5 ft	1.6–3.0 ft	3.1–6.0 ft	>6.0 ft
Vegetables	Small grains	Corn	Alfalfa, clovers
Berry crops	Soybean	Sorghum	Sunflower
Lawn grasses	Annual legumes	Biennial clover	Cotton
	Potato	Perennial grasses	Sugar beet
			Safflower
			Tree fruits

monocots), or taproots (mostly dicots) characterized by one main root from which smaller branch roots emerge (Fig. 10-3). Fibrous-rooted plants generally exhibit extensive root systems, exploring greater soil volume for H_2O and nutrients. Many taprooted crops have smaller root systems that reduce the accessible quantity of H_2O and nutrients. For example, fibrous root length density (cm root/cm^3 soil) can be 5–10 times larger than with taproots. With either root system, early root growth occurs mainly in the topsoil, increasing with plant age in the subsoil. Some taprooted crops (i.e., alfalfa, clovers) may penetrate >10 ft if soil conditions are favorable (Fig. 10-4). One advantage deep-rooted crops have is they loosen compact subsoil by root penetration and subsequent decomposition. Also, deep-rooted legume species in pastures provide more animal feed during drought periods than do shallow-rooted grasses.

With either taprooted or fibrous-rooted plants, most of the total root mass is in the surface soil (Fig. 10-4). However during dry periods, surface root growth can decrease in favor of deeper growth (Fig. 10-5). Root growth can also be limited by soil compaction (Fig. 10-6).

Root systems of the same species tend not to interpenetrate, which suggests an antagonistic effect (Fig. 10-7). Thus, with narrow row spacing and high populations, the characteristic root pattern is altered and there may be deeper rooting if soil conditions permit.

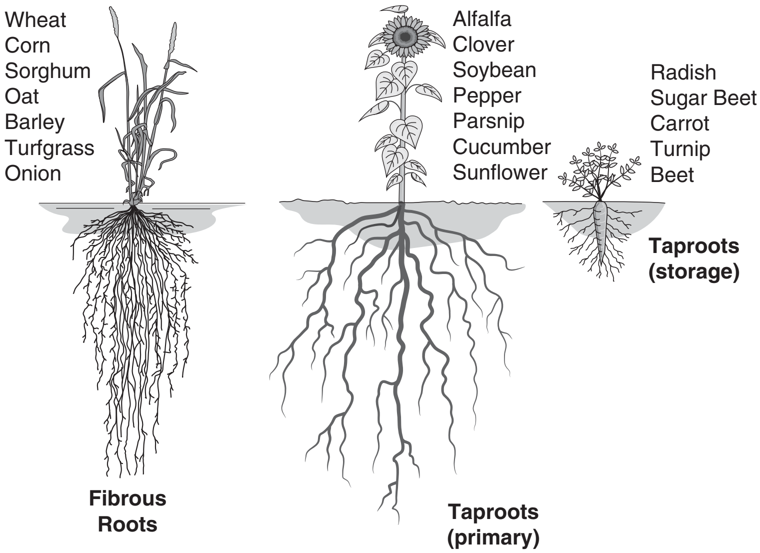


Figure 10-3
Selected examples of plants with fibrous *and* taproot *systems.*

Figure 10-4
Alfalfa (a), dryland wheat (b), irrigated wheat (c), potato (d), and lettuce (e) root distribution. Grid lines are 1 ft apart.

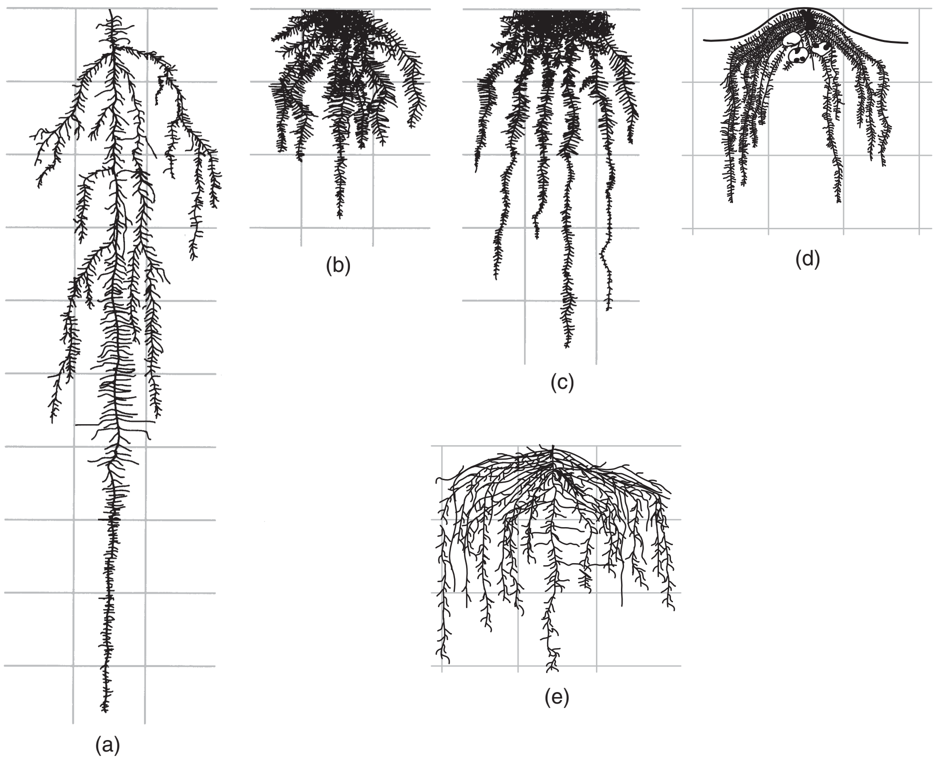
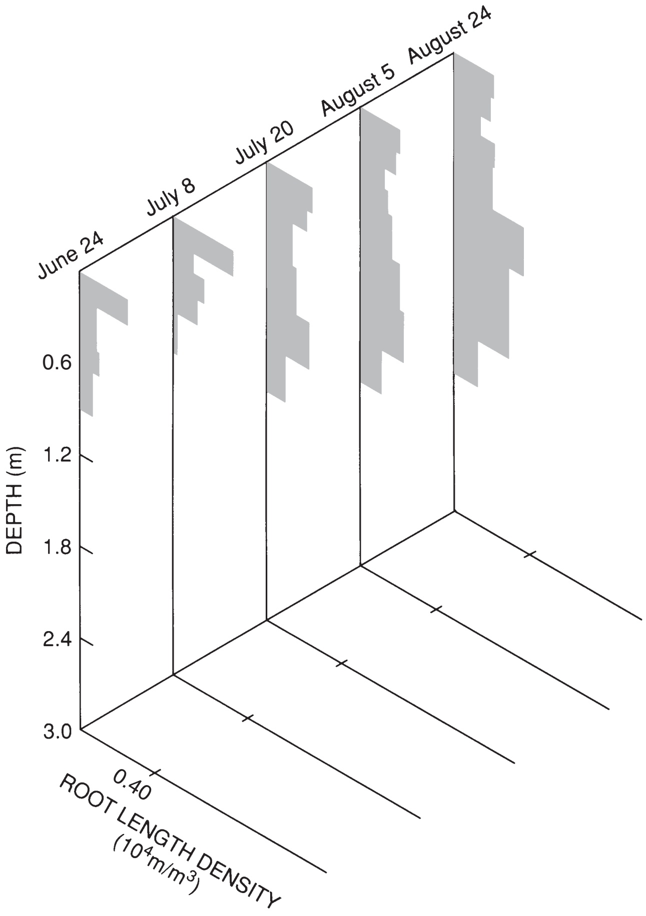


Figure 10-5
Root development in soybean, where subsoil root growth expands later in the season due to more favorable soil moisture.
(*Taylor, 1980,* Agron. J. *72:543.*)



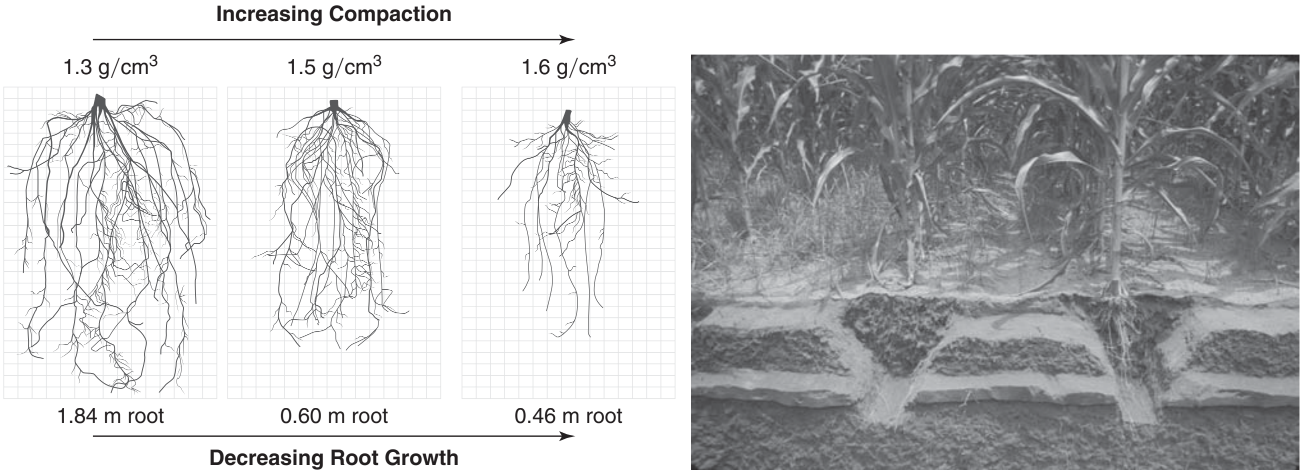


Figure 10-6
Soil compaction increases bulk density (g/cm^3), which decreases root growth (m). Photo of tillage-related soil compaction effect on corn root growth. (Courtesy USDA, Nat. Soil Dynamics Lab.)

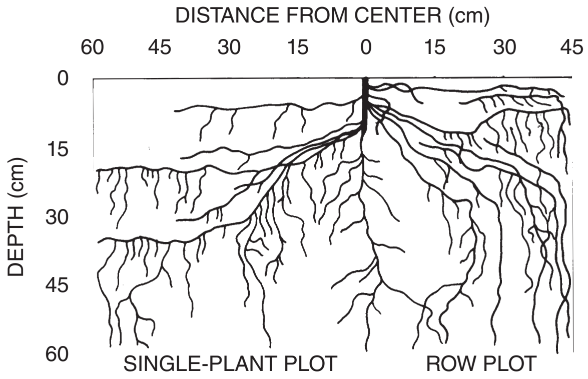


Figure 10-7
Influence of neighboring soybean roots on root growth. Single-plant plot *represents root distribution with only one soybean plant in the plot area, and* row plot *represents typical row-planted soybean illustrating the influence of neighboring roots on root growth.*
(Raper and Barber, 1970, Agron. J., 62:581.)

Nutrient Extraction Since roots occupy about 2% of the soil-root volume, interactions between roots and soil greatly influence nutrient uptake. Since most of the root mass is in the surface soil, nutrients placed near actively growing roots will be readily taken up. With fibrous root crops (i.e., small grains), nutrients placed on the surface or with or to the side of the seed optimize growth due to secondary root growth above the seed. With taprooted plants (i.e., peas, lentils, beans), few roots grow above the seed, thus subsurface band application of nutrients below the seed often improves growth compared to surface-applied nutrients. High nutrient rates placed with the seed are not recommended due to potential salt damage (see "Salt Index"). Storage taproot crops (Fig. 10-3), with generally smaller root volume, access less soil volume for nutrients and require additional nutrient application. Likewise, many of these crops also require supplemental irrigation, depending on annual rainfall.

Generally, divalent cation requirement is higher in dicots than in monocots compared to monovalent cations. The relative absorption of cations and anions influences release of H^+ or HCO_3^- by the root. Acidity develops from H^+ released in response to absorption of NH_4^+ or other cations, while pH increases with release of HCO_3^- and/or OH^- following NO_3^- uptake. Changes in rhizosphere pH affect the solubility and availability of many plant nutrients.

Mycorrhizal fungi colonize roots of most plants and function primarily by enhancing nutrient and H_2O uptake. *Ectomycorrhiza* predominately infect tree species, while *vesicular-arbuscular* mycorrhiza (VAM) colonize most other plants, although plants vary in the degree of fungal colonization. As new roots develop, mycorrhizal fungi colonize or enter the root and develop extensive structures extending into and beyond the rhizosphere influenced by root hairs (Fig. 5-6). Plants with a high dependency on VAM generally exhibit (1) low root surface area due to low root branching, (2) few or short root hairs, (3) slow root growth rate, and (4) reduced root exudation. Under low soil nutrient availability, VAM-infected roots explore a substantially larger soil volume from which to absorb nutrients and H_2O (Figs 5-7 and Fig. 10-8). In many cases, excessive P fertilization can reduce mycorrhizal influence on plant growth (Fig. 10-9).

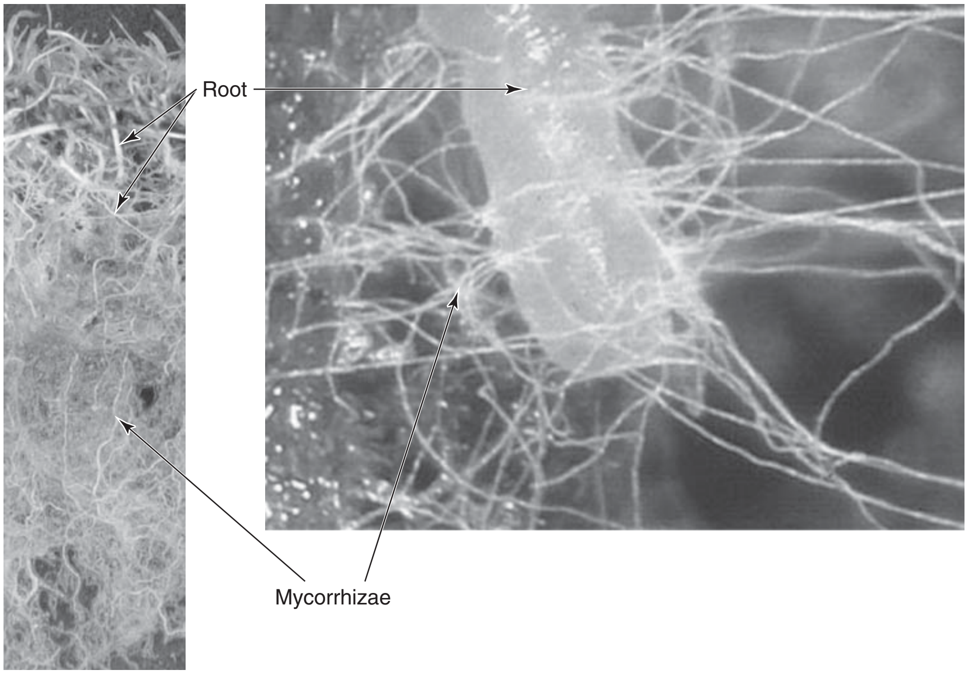


Figure 10-8
Example of mycorrhizal colonized root.
(USDA)

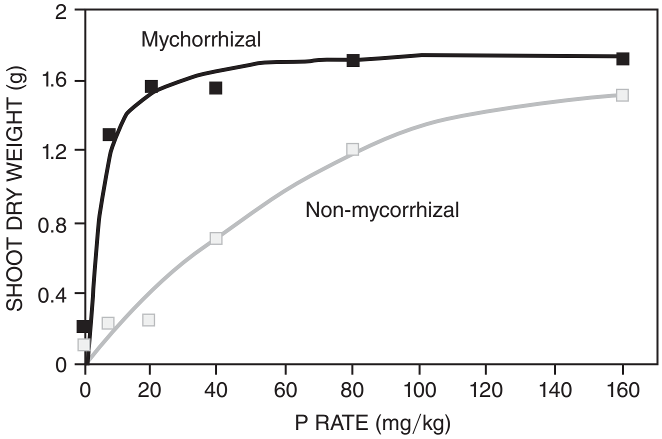


Figure 10-9
Example of increased P uptake by Cassia pruinosa *colonized with VAM. At higher P availability, P uptake is similar between VAM-infected and uninfected plants.*
(*Jasper et al., 1994, in C. E. Pankhurst [ed.],* Soil biota in sustainable farming systems *[pp. 9–11], CSIRO Publ., East Melbourne.*)

SOIL CHARACTERISTICS

Roots must fully exploit soil to obtain nutrients and H_2O for optimum productivity. Since crop yield is directly related to the availability of stored soil water and nutrients, soil physical conditions that restrict root growth will reduce yield potential (Fig. 10-6).

Soil tillage can improve seed placement into moist soil, seed germination, and seedling growth; however, tillage can also influence root growth and distribution (Fig. 10-10). With reduced tillage, root growth can be enhanced by more favorable soil H_2O availability due to greater surface residue cover compared to full tillage. Increased tillage also increases compaction. In some soils, no-tillage can restrict root growth because of increased bulk density compared to reduced tillage.

Attempts to loosen plowpans or heavy subsoils are not always successful. Subsoiling is most effective when the subsoil is dry so that shattering of the soil occurs; however, in most cases, there is a rapid resealing of the subsoil (Fig. 10-11). One cultivation with a disk or similar implement may eliminate any effect of subsoiling.

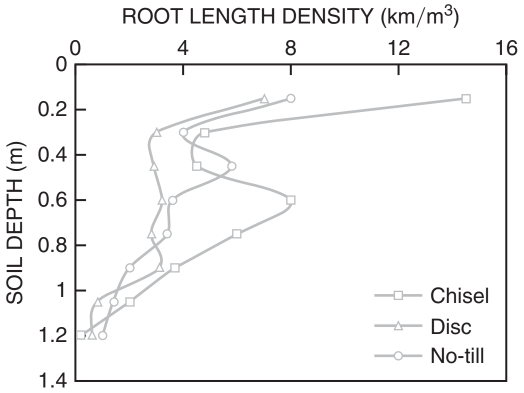


Figure 10-10
Tillage effects on corn root distribution. Discing left less residue on soil surface, reducing plant available H_2O and increased compaction. Root growth is reduced in No-till due to increased soil bulk density.
(Newell and Wilhelm, 1987, Agron. J., 79:160–165.)

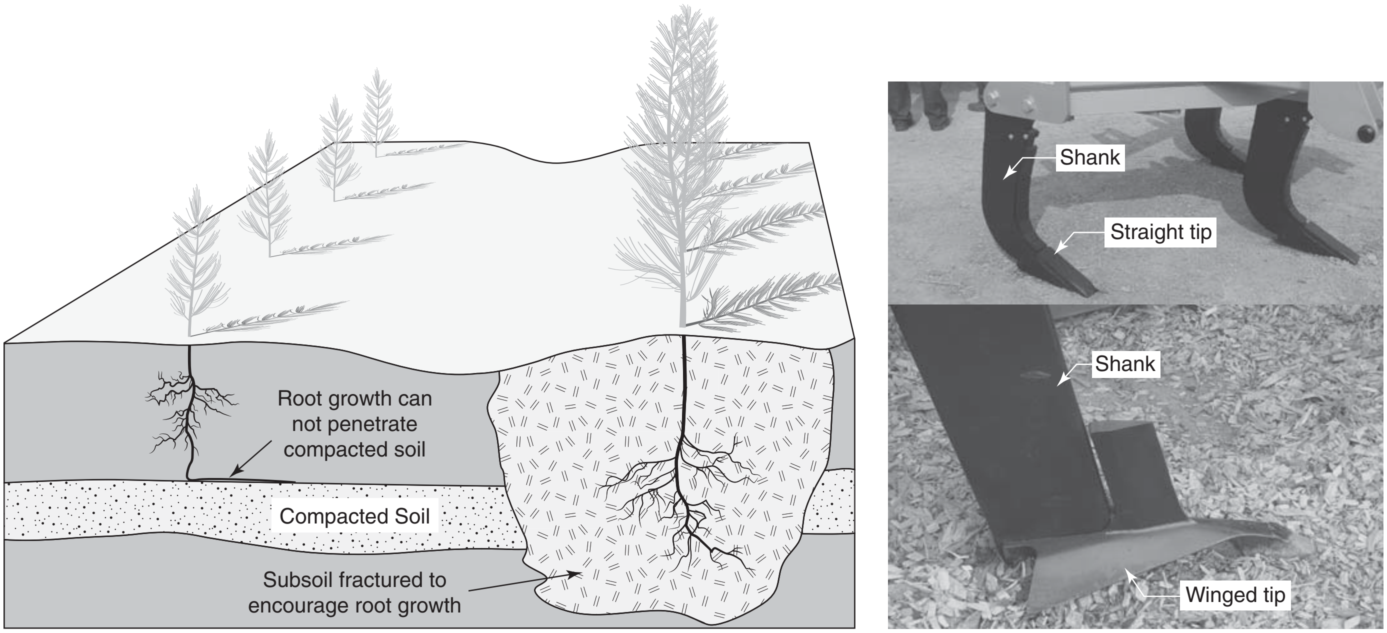


Figure 10-11
Subsoiling can improve root growth below compacted soil layer. Photos illustrate subsoiler shanks. (Courtesy U.S. Forest Service.)

Figure 10-12
Effect of soybean root length on grain yield.
(Barber and Silberbush, 1984: Spec. Publ. No. 49, p. 86, Madison, Wis: ASA.)

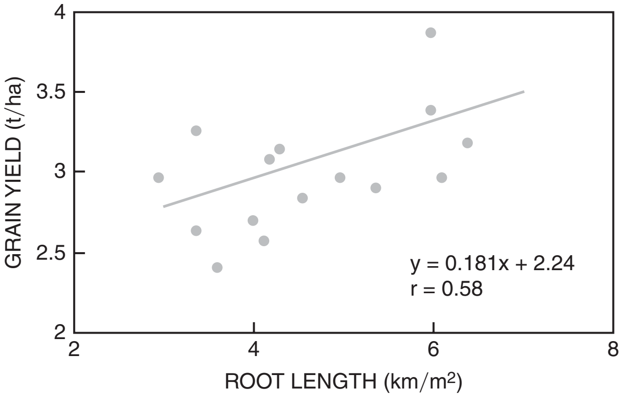
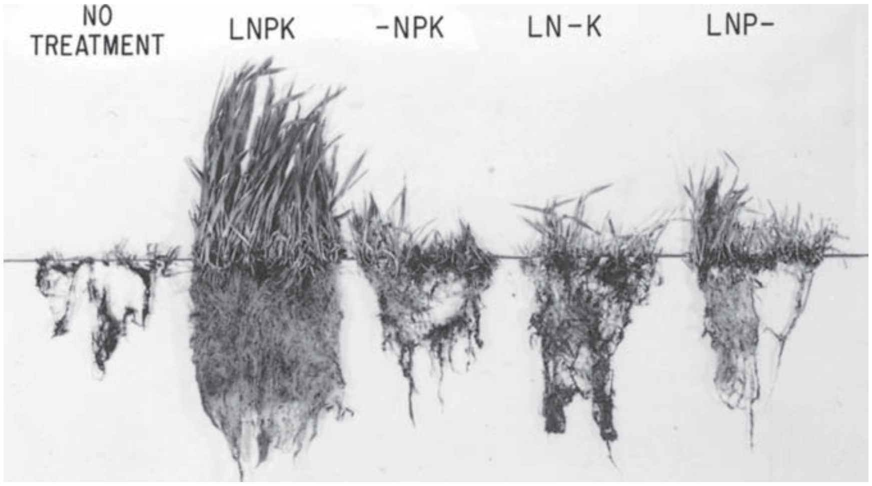


Figure 10-13
Influence of lime (L), N, P, and K on root growth and tillering in wheat grown on a low pH and N-, P-, and K-deficient soil.
(International Plant Nutrition Institute (IPNI))



In drought-prone areas with root-restrictive soil layers, subsoiling can increase rooting depth and plant available H_2O, especially in crops such as soybean, cotton, and many vegetable crops that have limited ability to penetrate even moderately compacted soil layers.

Plant Nutrient Effects

Numerous soil physical and chemical factors influence root growth and absorption of H_2O and nutrients in quantities sufficient for optimum productivity. Any management factor that improves the soil environment for healthy root growth will enhance plant growth and yield (Fig. 10-12). Adequate nutrient supply in the topsoil encourages a vigorous and extensive root system (Fig. 10-13). Stimulation of root development is related to N and P buildup in the cells, which hastens cell division and elongation.

Plants cannot absorb nutrients from dry soil; thus, shallow applications of nutrients may be less effective under drought. Generally, nutrients should be placed where stimulation of root growth is wanted; therefore, deep placement may be necessary in frequently droughty soils (Fig. 5-4). While it is not necessary to fertilize the entire soil volume occupied by roots, fertilized soils exert a strong influence on root growth (Fig. 10-14).

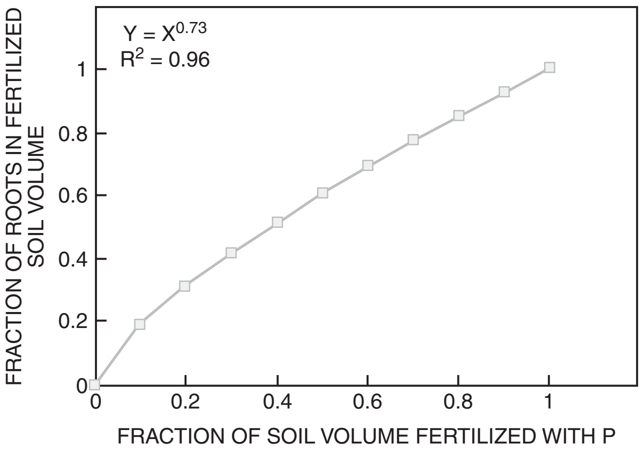


Figure 10-14
Relationship between fraction of the soil volume fertilized with P and fraction of total roots in fertilized soil volume.
(*Adapted from Mullins, 1993, Fertilizer Res., 34:23–26.*)

NUTRIENT PLACEMENT

Determining proper placement of applied nutrients is as important as identifying the correct rate (Chapter 9). Placement decisions involve knowledge of crop and soil characteristics, whose interactions determine nutrient availability. Numerous placement methods have been developed, and the following factors should be considered with nutrient placement decisions:

1. *Optimum nutrient availability from plant emergence to maturity.* Vigorous seedling growth (i.e., no early growth stress) is essential for obtaining the desired plant growth and yield potential. Merely applying nutrients does not ensure that they will be absorbed by the plant.
2. *Prevent salt injury to the seedling.* N, K, or other soluble salts close to the seed may be harmful, although salt injury potential depends on nutrient source, rate, and crop sensitivity to salts.
3. *Convenience to the grower.* Timeliness of all crop management factors is essential for realizing yield potential and maximum profit. In many areas, delay in planting after the optimum date reduces yield potential. Consequently, growers often reject nutrient placement options to avoid delays in planting, even when they may increase yield. Placement decisions influence yield potential; thus, planting date and nutrient placement effects on yield must be carefully evaluated.

Nutrient Placement in Soil

Fertilizer placement options generally involve surface or subsurface applications *before*, *at*, or *after* planting (Fig. 10-15). Placement practices depend on the crop and crop rotation, degree of deficiency or soil test level, nutrient mobility in the soil, degree of acceptable soil disturbance, and equipment availability.

Preplant

Broadcast

Nutrients are applied uniformly on the soil surface over the entire target area before planting, and can be incorporated by tilling or cultivating (Fig. 10-16). In no-till cropping systems, there is no opportunity for incorporation; thus, broadcast N applications will reduce N recovery by the crop due to potential immobilization, denitrification, and volatilization losses (Table 4-21).

Broadcast application errors commonly occur with spinner spreader applicators if proper overlap distance is not followed (Fig. 10-17). Overlap distance can be about

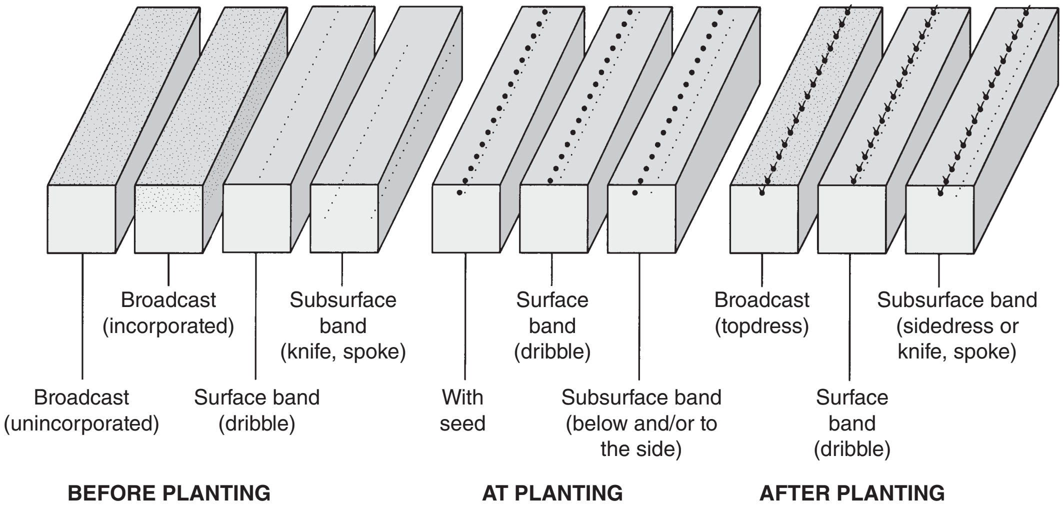
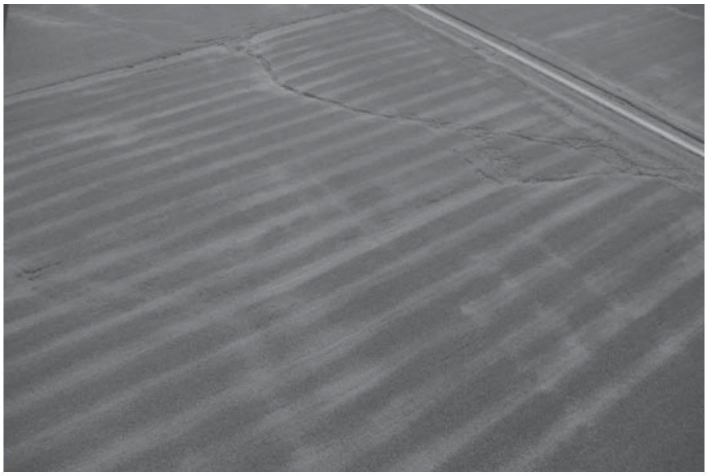


Figure 10-15
Illustration of various nutrient placement options in soil.

Figure 10-16
Broadcast application of solid fertilizers before planting with a spinner spreader (left) and air boom spreader (right).

Figure 10-17
Uneven N fertilizer application with a spinner spreader is probably the cause of the streaks in this photo. Dry N fertilizer with broken granules is difficult to spread evenly with this type of spreader, and is becoming increasingly common as dry N fertilizer use increases.
(Courtesy Peter Scharf/University of Missouri, photo by Henrietta Christensen.)



30% of application width depending on particle size distribution and other material characteristics; however, with pneumatic or air applicators, little overlap is needed (Fig. 10-18).

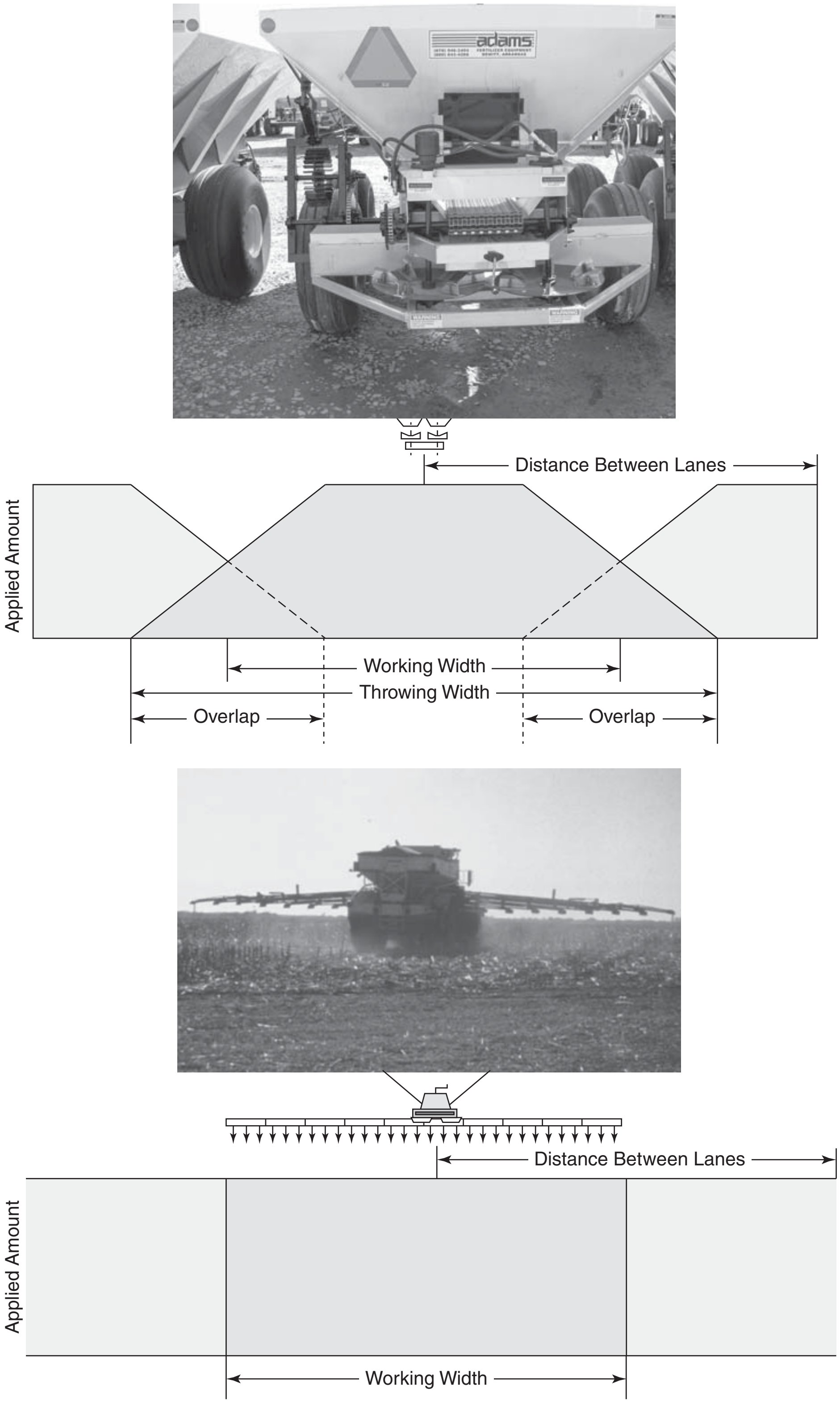


Figure 10-18 *Relative application overlap width needed for uniform nutrient application with spinner spreader applicators (top photo/diagram). Little overlap is needed with pneumatic applications (bottom photo/diagram).* *(Adams Fertilizer Equipment Manufacturer)*

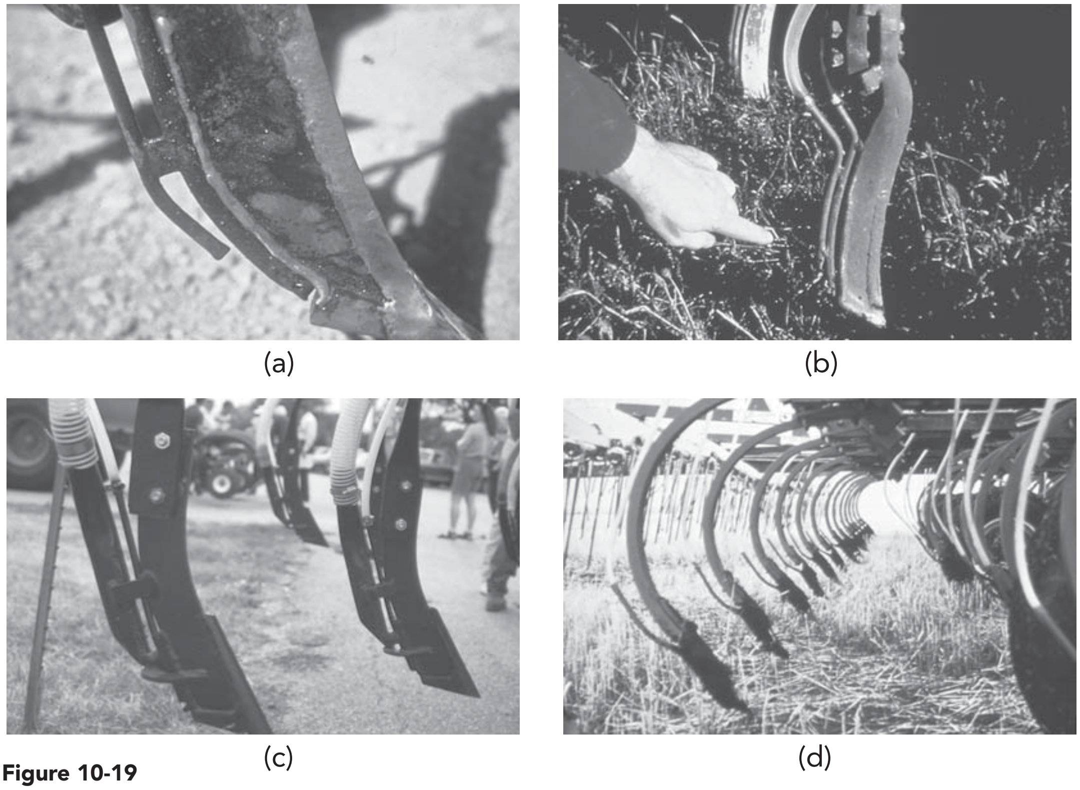


Figure 10-19
Examples of injection knives for subsurface band application of nutrients in conventional and reduced tillage cropping systems. Knife (a) is designed to place anhydrous NH_3 *(front tube) and liquid P or 10-34-0 (rear tube) simultaneously. As the* NH_3 *is converted from a liquid under pressure to a gas, the* NH_3 *tube freezes. The ~1 cm separation between tubes behind the knife prevents liquid P tube from freezing during application. Knife (b) is similar to (a) except that the backswept design reduces topsoil disturbance during application. Knife (c) is also similar to (a) except that dry P sources (i.e., TSP, MAP, DAP) are delivered through the large hose by forced air. Knife (d) represents a typical application knife mounted on a chisel plow shank.* *(Photos (a) and (b) courtesy of L. S. Murphy.)*

Subsurface Band

Crop recovery of nutrients can be increased by placing below the soil surface where soil moisture might be more favorable for nutrient uptake. Subsurface placement depth varies between 2 and 8 in., depending on the crop, nutrient source, and application equipment. In full and reduced tillage systems, a knife applicator is commonly used to apply nutrients below the soil surface (Fig. 10-19). A cutting coulter in front of the liquid injection knife is important in heavy surface crop residue (Fig. 10-20). When injecting nutrients, a disk implement will disturb less residue than a knife implement. In semi-arid regions, the commonly used sweep plow tillage implement can also be equipped to apply nutrients (Fig. 10-21).

Subsurface point or spoke injection of fluid fertilizers can be effective in high surface residue cropping systems, especially with application of immobile nutrients (Fig. 10-22). Point injection of N in no-till systems is also more efficient than broadcast N. Point injection can be used in turf systems to simultaneously fertilize and aerate.

Surface Band

Surface band–applied fertilizers can be effective before planting (Fig. 10-23). However, if not incorporated, dry surface soil conditions can reduce nutrient uptake, especially with immobile nutrients. Surface band N applications can improve N availability compared with broadcast application in some soils and cropping systems.

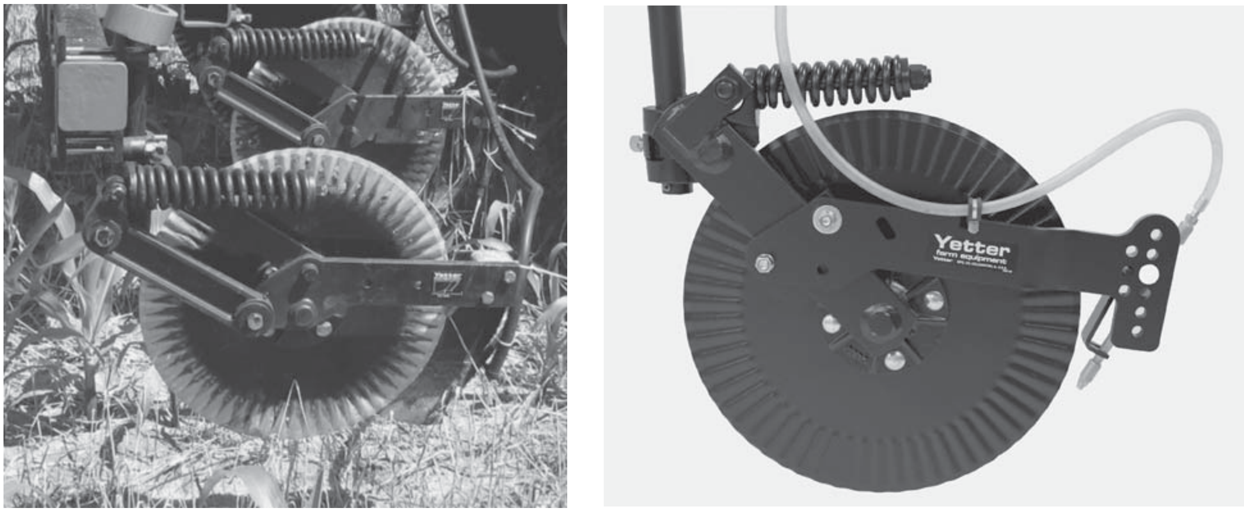


Figure 10-20
Cutting coulter in front of a liquid knife (left) or high pressure liquid injection (right). *(Right Photo: Courtesy Yetter Mnfg, Inc.; Left Photo: Courtesy Wade E. Thomason, Virginia Tech)*

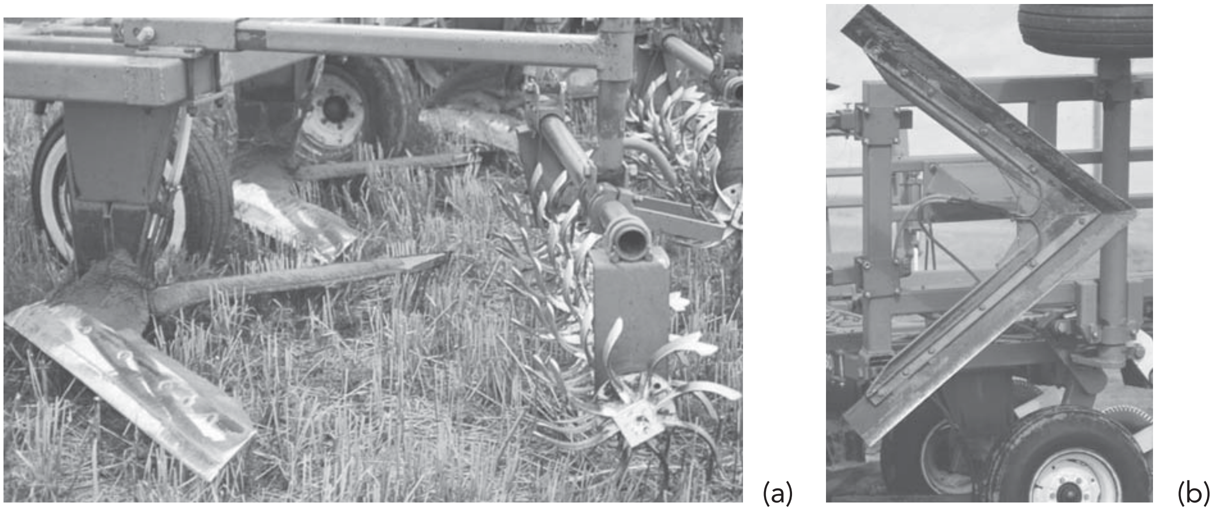


Figure 10-21
The sweep plow is a common tillage implement in semi-arid regions (a) that provide weed control with little residue incorporation by operation about 3–4 in. below the soil surface. Sweep plows can be equipped to apply anhydrous NH_3 *and/or liquid N or P sources through a steel tube placed under the sweep blade (b) with injection orifices spaced every 12 in.*

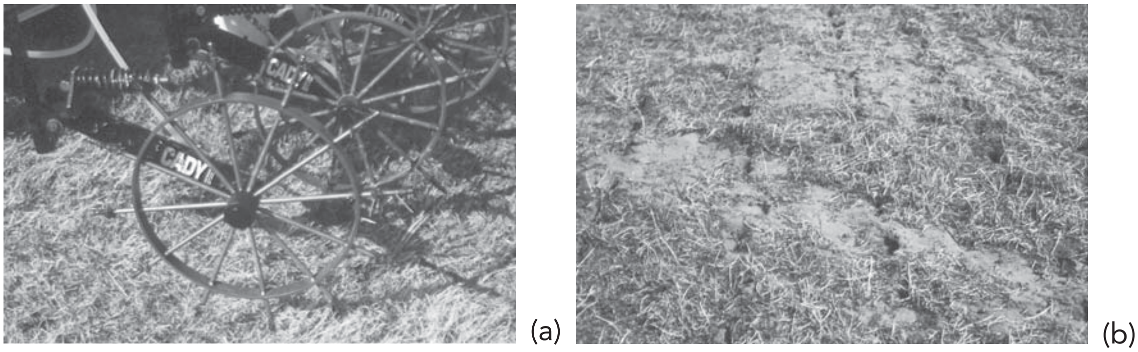


Figure 10-22
Point or spoke injector for application for fluid fertilizers in no-tillage systems. Injection depth varies from 2 to 6 in. depending on surface soil texture and moisture content, with little disturbance of surface residues.
(Courtesy Spike Wheel Systems.)

Figure 10-23
Surface-band application of liquid fertilizers before planting.
(Courtesy L. S. Murphy.)

At Planting

Subsurface Band

Solid and fluid fertilizer placement can occur at numerous locations near the seed (Fig. 10-24). Commonly called a *starter*, fertilizer is applied 1–4 in. directly below and/or to the side of the seed, depending on equipment and crop (Fig. 10-25). Single pass or direct seeding that includes application of as much fertilizer as is feasible without harming seed reduces operating costs but increases planting time.

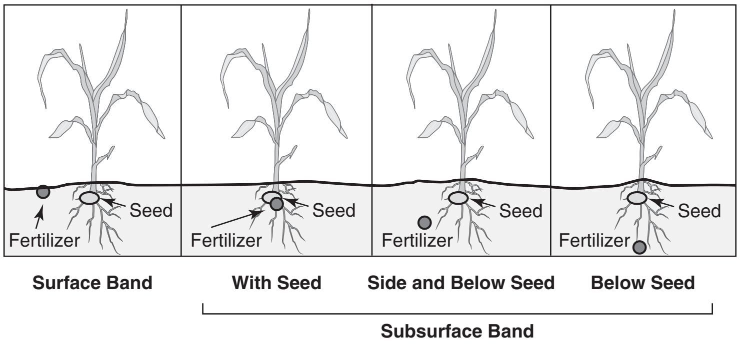


Figure 10-24
Options for at-planting band application of nutrients at or below the soil surface.

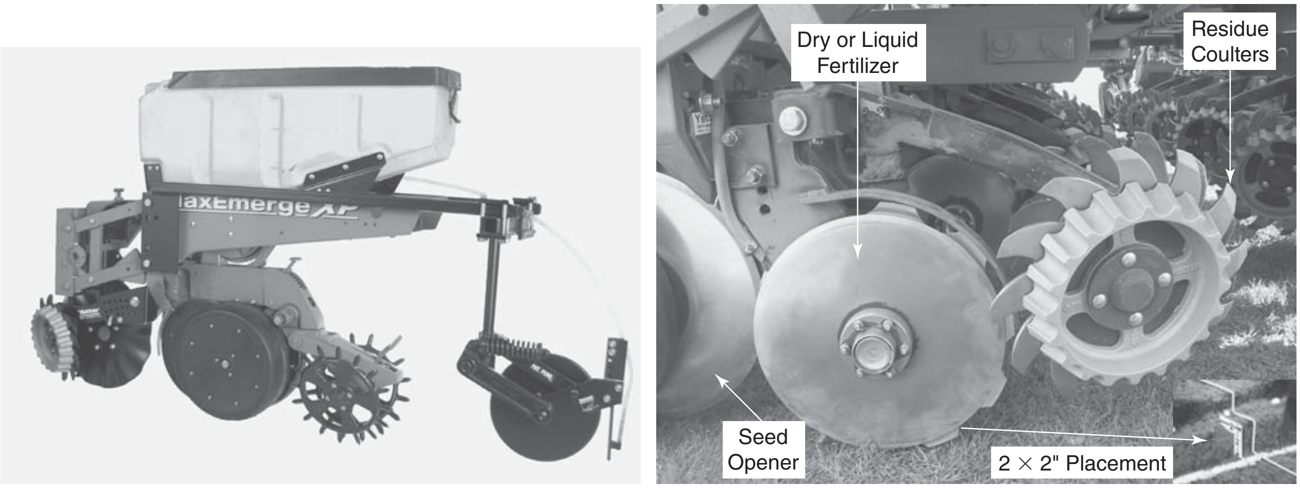


Figure 10-25
Example of subsurface nutrient placement at planting illustrating 2 × 2 in. placement (see photo inset). Residue coulters are required for subsurface application in high surface residue systems.
(Courtesy Yetter Mnfg. Inc.)

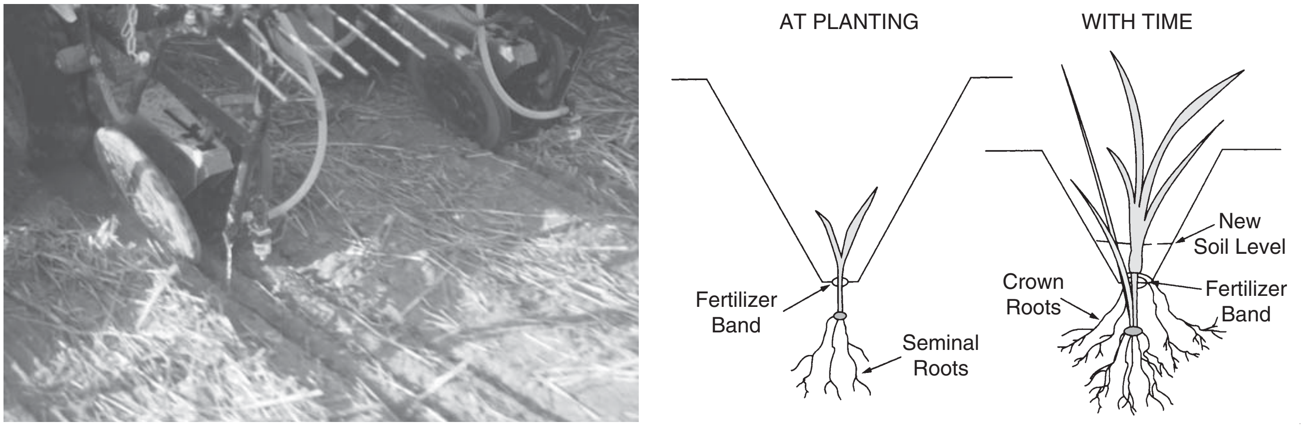


Figure 10-26
Surface band or dribble application of fluid fertilizer. In this case fertilizer is applied over the row after the press wheel. Application beside the row at planting is also possible. With surface-band application of nutrients, soil will slough into the furrow left by the planter press wheel and bury the fertilizer. (Westfall et al., *1987*, J. Fert. Issues, *4:114–121.*)

Seed Band

Fertilizer application with the seed (in the seed row), commonly referred to as a *pop-up* application, is a subsurface band generally used to enhance early seedling vigor, especially in cold, wet soils (Fig. 10-24). Usually low nutrient rates are applied to avoid germination or seedling damage. Fluid or solid sources can be used.

Surface Band

Fertilizers can be surface applied at planting in bands directly over or to the side of the row (Fig. 10-23; 10-24). Application over the row can be effective for placement of immobile nutrients with a hoe opener because soil can slough off over time and bury the fertilizer band. Thus, the surface-applied band becomes a subsurface band placed slightly above the seed (Fig. 10-26).

After Planting

Topdress

Topdress N applications are common on permanent or close seeded crops (i.e., turf, small grains, pastures); however, N immobilization in high-surface-residue systems can reduce recovery of topdress N (Fig. 10-27). Topdressed P and K are not as

Figure 10-27
Topdress application of nutrients to small grain. *(CropCare, Paul B Zimmerman Inc.)*

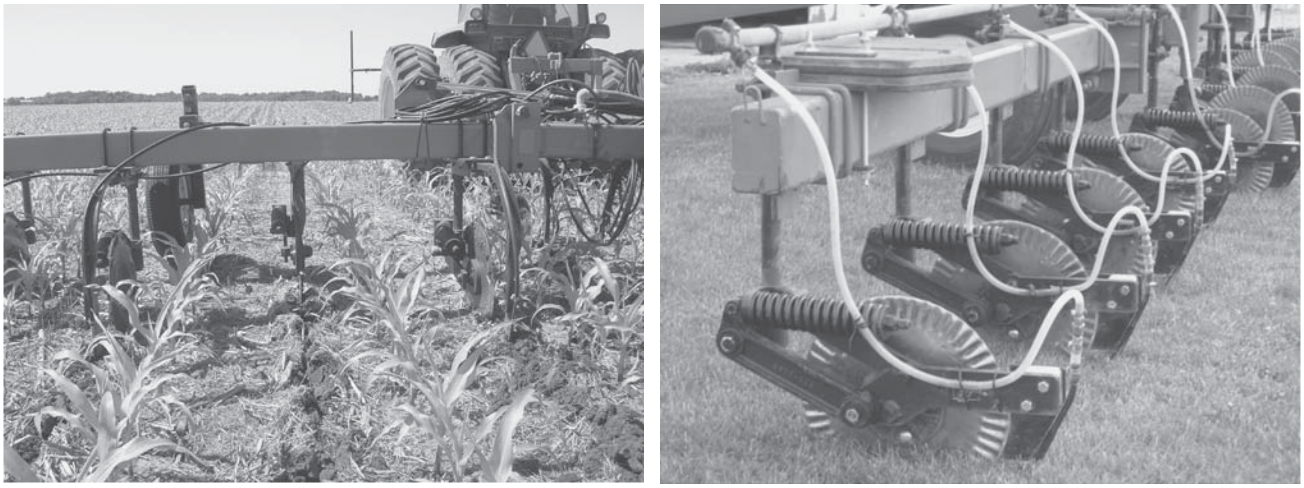


Figure 10-28
Sidedress application of N to corn (left) and subsurface application in grass (right). *(Right photo: Dr. Peter Scharf, University of Missouri; Left photo: Courtesy Yetter Mnfg. Inc.)*

effective as preplant applications. Both solid and liquid sources can be used. Topdress granular urea in corn and sorghum may damage the crop due to urea granules deposited in the "whorl." The dissolving urea places high salt concentration near the growing point. Topdress fluid fertilizers may also damage the crop if applied above recommended rates.

Sidedress

Sidedress N application is very common with row crops (i.e., corn, sorghum, cotton) and is done with a standard knife (Fig. 10-20; 10-28) or point injector applicator (Figs 10-22). Anhydrous NH_3 and fluid N sources are most common. Fluid sources also can be surface band applied beside the row after planting. Sidedress applications increase flexibility since applications can be made almost any time equipment can be operated without damage to the crop. Sidedress placement is particularly suited for spatially variable N application using remote sensors mounted on the applicator to guide application rate (see *Variable Nutrient Management*).

Subsurface sidedress applications with a knife too close to the plant can cause damage by either root pruning or nutrient toxicity (i.e., anhydrous NH_3). Sidedress application of immobile nutrients (e.g., P and K) is not recommended because most crops need P and K early in the season.

Anhydrous NH_3 converters are often used to reduce the need for deep injection and pre-application tillage to ensure soil closure behind the injection knife. Converters serve as depressurization chambers for compressed anhydrous NH_3 stored in the applicator tank. Anhydrous NH_3 freezes as it expands in the converters, separating liquid NH_3 from the vapor and greatly reducing pressure. The temperature of liquid NH_3 is about −26°F. Approximately 85% of the anhydrous NH_3 turns to liquid; the remainder stays as vapor. The liquid flows by gravity through regular application equipment into the soil. Vapor collected at the top of the converter is injected into the soil in the usual manner.

High NH_3, NH_4^+, and NO_2^- concentrations can severely damage germinating seedlings. Deeper injection offsets the harmful effects of high NH_3 rates. Closer injection spacing would also reduce the injurious effect of high NH_3 rates.

Figure 10-29

Nutrient application with or near the seed enhances wheat seedling vigor and growth (left—16 lb P_2O_5/a) and grain sorghum maturity (right—12 lb P_2O_5/a). Starter P applied as 7-21-7 on a low P soil. (Fluid Fertilizer Foundation)

Specific Placement Considerations

Band Applications

Vigorous seedling growth is essential to maximum crop productivity. Often a small amount of nutrients with (*pop-up*) or near (*starter*) the seed at planting promotes increased root growth and formation of large, healthy leaves (Figs 10-29 and 5-5). Starter or pop-up applications include N, but should also include P, K, and S, especially with soil testing low to medium in P and K, and low OM soils. With cool, wet spring conditions, reduced nutrient availability can be caused by reduced:

- mineralization of N, P, S, and micronutrients
- mineral dissolution rate
- nutrient diffusion rate
- nutrient absorption by the plant

The advantage of early stimulation depends on the crop, variety, soil test levels, and seasonal conditions. Some factors to consider are:

- *Resistance to pests.* A vigorous young plant is more insect and disease resistant.
- *Competition with weeds.* A vigorous early crop growth advances canopy coverage of soil surface important for reducing light penetration and soil temperature that reduces weed germination. Reduced weed pressure improves herbicide effectiveness and reduces cultivation frequency. Reduced H_2O use by weeds and soil H_2O evaporation enhances H_2O availability to crops.
- *Advanced maturity.* Early crop vigor, especially with P, can advance crop maturity that enables earlier harvest and/or lower grain-moisture content at harvest (Fig. 10-29). Early maturity can be important in northern climates, where adverse fall weather may interrupt and delay harvest. With vegetable and fruit crops, a delay of only 3–4 days may result in a producer missing an early, higher value market.

Salt Index. High concentration of soluble salts in contact with germinating seeds reduces germination and seedling growth. Plasmolysis occurs when the salt concentration outside root cells exceeds the cellular salt concentration, resulting in H_2O diffusing out of the cell. As a result, the cell's membrane shrinks away from the cell wall, partially collapsing the cell. H_2O transport across cell membranes from high H_2O concentration (inside cell) to lower H_2O concentration (outside the cell) causes the plant to exhibit symptoms similar to drought stress.

Fertilizers are categorized for their salt injury potential by the *salt index*, determined by placing the material in soil and measuring the osmotic pressure of the soil solution. The *salt index* is the ratio of the increase in osmotic pressure produced by the fertilizer to that produced by the same weight of $NaNO_3$, based on a relative value of 100 (Table 10-2).

N and K salts have much higher salt indices and are more detrimental to germination than P salts when placed close to or in contact with the seed (Fig. 10-30). High NH_4^+ concentrations following application of NH_4^+ sources increases osmotic pressure of the soil solution, and favors temporary accumulation of NO_2^-, which is toxic to plants. Some N sources contribute more to germination and seedling damage than is explained by osmotic effects. NH_3 is toxic and can move freely through the cell wall, whereas NH_4^+ cannot. Urea, DAP, $(NH_4)_2CO_3$, and NH_4OH will cause more damage than MAP, $(NH_4)_2SO_4$, and NH_4NO_3.

TABLE 10-2
SALT INDEX FOR COMMON FERTILIZER MATERIALS

Material	Analysis[1]	Salt Index[2]	Partial Salt Index[3]
	N Sources		
NH_3	82.2	47.1	0.572
NH_4NO_3	35.0	104.1	3.059
$(NH_4)_2SO_4$	21.2	88.3	3.252
$NH_4H_2PO_4$-MAP	11.0		2.453
$(NH_4)_2HPO_4$-DAP	18.0		1.614
Urea	46.0	74.4	1.618
UAN	28.0	63	2.250
UAN	32.0	71.1	2.221
$NaNO_3$	16.5	100	6.080
KNO_3	13.8		5.336
	P Sources		
$Ca(H_2PO_4)_2$-CSP	20.0	7.8	0.390
$Ca(H_2PO_4)_2$-TSP	48.0	10.1	0.210
MAP	52.0	26.7	0.405
DAP	46.0	29.2	0.456
APP	34.0	20	0.455
	K Sources		
KCl	60.0	116.1	1.936
KNO_3	50.0	69.5	1.219
K_2SO_4	54.0	42.6	0.852
Sul-Po-Mag	22.0	43.4	1.971
$K_2S_2O_3$	25.0	68.0	2.720
KH_2PO_4	34.6	8.4	0.097
	S Sources		
$(NH_4)_2S_2O_3$	26.0	90.4	7.533
$(NH_4)_2S_x$	40.0	59.2	2.960
$CaSO_4 \cdot 2H_2O$	17.0	8.2	0.247
$MgSO_4 \cdot 7H_2O$	14.0	44.0	2.687
	Organic Sources		
Manure salts	20.0	112.7	4.636
Manure salts	30.0	91.9	3.067

[1] %N in N carriers, $\%P_2O_5$ in P carriers, and $\%K_2O$ in K carriers.

[2] Relative to $NaNO_3$.

[3] Salt index of a mixed fertilizer is the sum of the partial salt index per unit (20 lb) of nutrient times the units due to each source in the mixture.

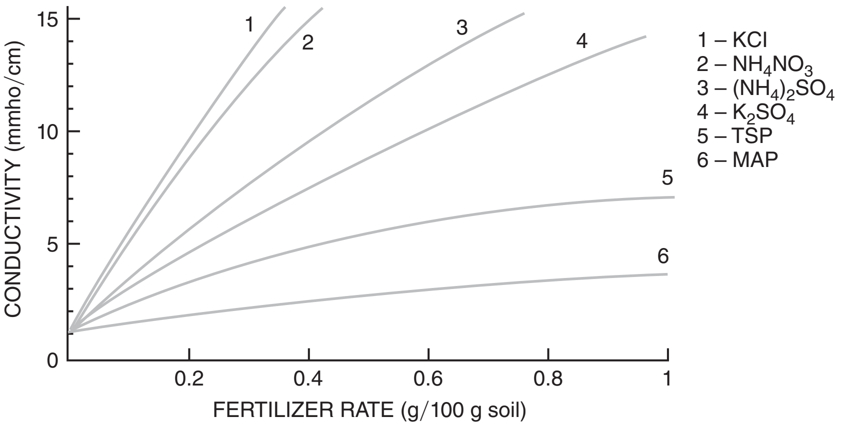


Figure 10-30
Effect of N, P, and K fertilizers on solution conductivity in a silt loam soil.
(*Chapin et al., 1964, SSSAJ/28:90.*)

Mixed fertilizers also vary widely in salt index depending on sources used. Higher analysis mixed fertilizers generally have a lower salt index per unit of plant nutrient than lower analysis fertilizers because they usually comprise higher analysis sources. For example, to furnish 50 lb N/a, 240 lb of $(NH_4)_2SO_4$ would be required, whereas with urea, 110 lb would be required. Hence, higher analysis fertilizers are less likely to produce salt injury than equal amounts of lower analysis fertilizers. In addition, increasing row width increases quantity of fertilizer applied in a row, assuming that equal rates are applied. For example, with the same fertilizer rate, fertilizer placed per unit length of row is double in 30-in. rows than in 15-in. rows (Table 10-3). In general, total N + K_2O should not exceed about 10 lb/a applied with the seed (Fig. 10-31); however, this value varies widely with crop and soil conditions. Primary factors affecting the potential for salt damage include:

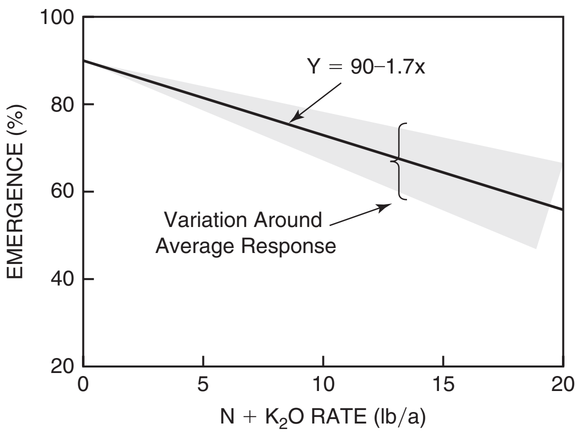
1. *Soil properties.* Soil moisture at seeding and in the first week after seeding can influence extent of salt damage. Toxic fertilizer effects are diluted with soil H_2O content at or near field capacity. Fine-textured soils not only hold more H_2O than coarse-textured soils, but clay surfaces also adsorb more NH_4^+ from soil solution, reducing toxic effects of N sources. Dry, calcareous, eroded hilltops with low soil OM are especially prone to salt injury from seed row urea fertilizer placement, partially due to elevated levels of NH_3.
2. *Crop type.* Cereals generally exhibit greater salt tolerance with seed row fertilizers than legumes and oilseed crops. Within cereals, salt tolerance with oats > barley > wheat. With oilseed crops, soil tolerance with flax > canola. Most

TABLE 10-3
SUGGESTED MAXIMUM N + K_2O RATES APPLIED WITH CORN AND SMALL GRAIN SEED

	N + K_2O (lb/a)[1]	
Row Spacing (in.)	*Medium- to Fine-Textured Soils*	*Sandy or Dry Soils*
6–8	30	21
10	24	17
12	20	14
15	16	11
20	12	8
30	8	6
40	6	4

[1] Reduce rates 30% for grain sorghum; no seed placed N + K_2O with soybean, sunflower, field bean, sugar beet. No urea or UAN with the seed.
Source: Kansas State Univ. Extension.

Figure 10-31
Average effect of salt rate applied with the seed on corn emergence. Emergence decreased ~1.7%/lb (N + K_2O)/a. Variation around average response is due to soil moisture conditions (rainfall) after planting. Increasing soil moisture reduced the salt damage and increased emergence.
(*Adapted from Raun et al., 1986,* J. Fert. Issues, *3:18–24.*)



legumes and other broadleaf crops are much more sensitive to elevated salt concentration near the seed.

3. *Risk factors.* The safest rate is probably no fertilizer with the seed. In some conditions, high rates of seed placed fertilizer can cause minimal injury, yet in other situations, the same rates cause extensive damage. Seed or seedling mortality may not always lead to lower yield, as thin stands may tiller and produce addition yield; however, delaying maturity by several days or more can reduce yield. With reduced plant population because of seed placed fertilizer damage, increased weed growth can reduce crop yield.

To avoid potential seedling damage, broadcast application or placement to the side and below the seed is an effective method (Fig. 10-32).

Broadcast Applications

Broadcast applications usually involve large amounts of lime and/or nutrients in buildup or maintenance programs. The advantages of broadcast nutrients include:

- application of large amounts of fertilizer is accomplished without danger of plant injury
- if tilled into the soil, distribution of nutrients throughout the tillage layer encourages root exploration of the soil for H_2O and nutrients

Figure 10-32
Comparison of fertilizer placed with the seed and 1.5 in. below and to the side of the seed at planting on seedling emergence. Adding K to the blend substantially reduced emergence when banded with the seed compared to below and beside the seed.
(*Lawton et al., 1964,* Agron. J., *52:326.*)

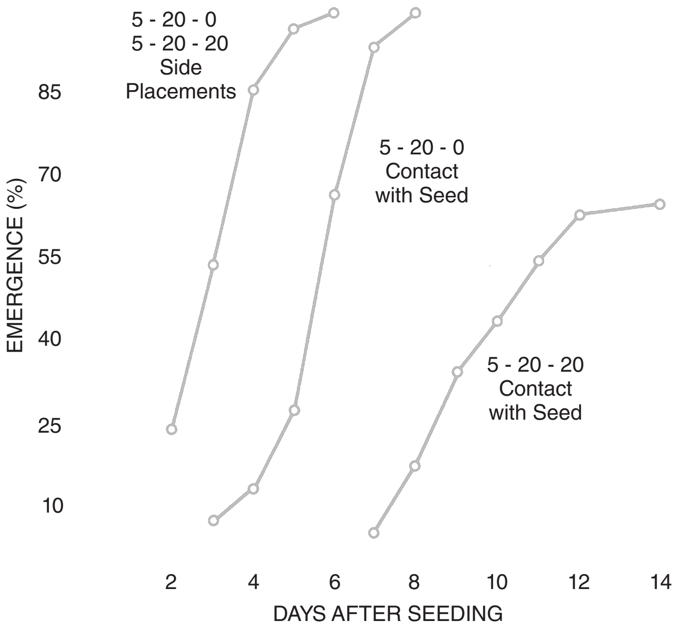


TABLE 10-4
EFFECTS OF UNEVEN BROADCAST APPLICATION OF N-P-K FERTILIZER ON CROP YIELD

	Soybeans	Corn	Barley
Spread Pattern		*Yield (kg/ha)*	
No fertilizer	1,278	2,059	592
Uniform	1,345	8,060	2,809
Nonuniform	1,264	7,271	2,540

- labor is saved during planting, as fertilizer application can be extended through fall, winter, or early spring periods
- practical means of applying maintenance nutrient rates, especially in forage, turf, and no-till cropping systems

Uniform and accurate spreading of fertilizer and lime is essential for effective utilization by the crop (Figs 10-17 and 10-18; Table 10-4). Several disadvantages of broadcast application include:

- in reduced tillage systems, nutrient stratification (Fig. 9-43) can reduce soil test levels below 4–6 in. depth where broadcast applications would be relatively ineffective (depending on nutrient mobility in soil)
- broadcast N in high surface residue systems can reduce plant available N by increased N immobilization, volatilization, and denitrification (Chapter 4)
- broadcast, incorporated nutrients increase soil erosion potential through loss of protective surface residue cover (Chapter 12)

Specific Nutrient Considerations

Nitrogen

Total N requirements for most crops are generally not supplied with starter or pop-up applications due to potential risk to the crop. Many recommendations suggest ≤50–60 lb N (or N + K_2O) in a 2 × 2 in. placement, depending on crop and soil texture. Lower rates are used for salt-sensitive crops and in coarse-textured soils. For large N use crops, starter N with the remaining N broadcast or band applied optimizes plant growth and yield (Fig. 10-33). Thus, most N is applied either before planting or side dressed after planting or both to increase N efficiency. Prediction of sidedress N rates can be improved by use of remote sensing or PSNT (Chapter 9). With vegetable and other small taprooted crops, broadcast N usually provides sufficient N to meet crop demand, although positive responses to subsurface band–applied N occur, especially

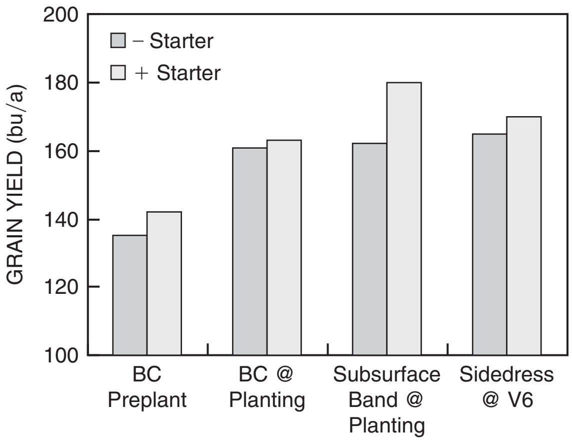
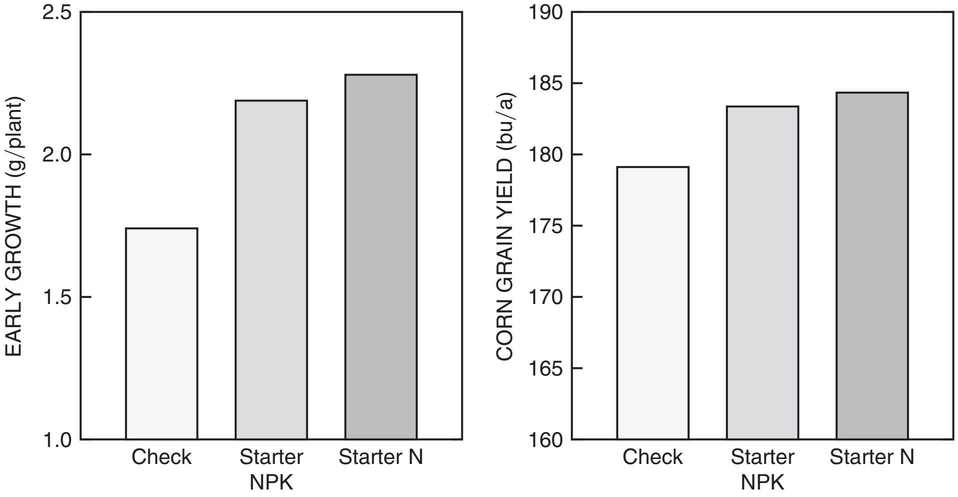


Figure 10-33
Effect of N placement with and without starter N. Broadcast (BC) N was applied preplant and at planting (160 lb N/a); starter N rates were 20 lb N/a.
(Havlin, unpublished data).

Figure 10-34
Starter response in corn on soils high in soil test P and K.
(Adapted from Mallarino, 2003, Intergrated Crop Mgmt. Conf. Iowa State Univ.)

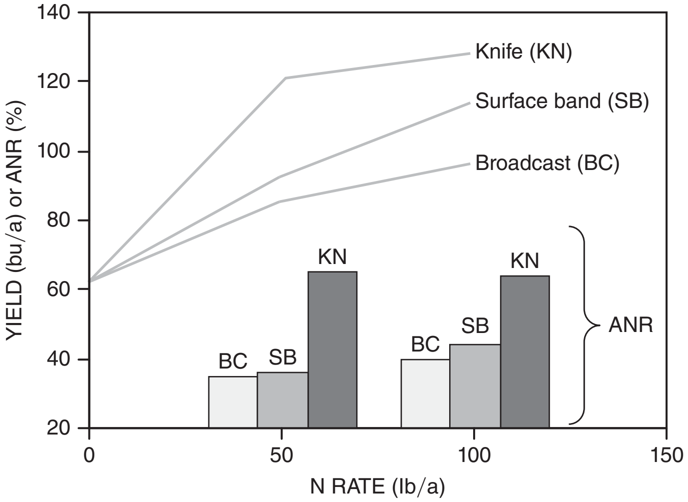


with high surface residues. Split N applications (preplant + sidedress or topdress) generally enhance vegetable yield and quality.

Most starter materials contain multiple nutrients, because crop response to mobile and immobile nutrients can occur in high-testing soils in cool, moist conditions. However, in many high P and K soils, starter response is commonly due to N, especially if the remaining N is sidedress applied after planting or applied fall preplant where a portion of the N can be lost by leaching below the seedling root zone or denitrified (Fig. 10-34). Under conditions conducive to nitrification, the addition of a nitrification inhibitor can improve the crop response to starter N (Chapter 4).

Yield increases from band-applied nutrients are generally greater under no-till systems than under full tillage systems. Conservation tillage maintains greater surface residue cover, resulting in cooler and wetter conditions at planting, reducing nutrient availability and plant growth. A large portion of broadcast N in reduced-tillage systems can be immobilized by surface crop residues (Chapter 4). Therefore, maximizing crop recovery of fertilizer N requires placement below the residue (Fig. 10-35). Similarly, low rates of broadcast N are generally ineffective in permanent grass pastures and native grassland due to considerable N immobilized by high C/N grass residue (Fig. 10-36).

Figure 10-35
Influence of N rate and placement on no-till grain sorghum yield and apparent N recovery (ANR) in the grain. Placing N below surface crop residue increased yield and % recovery of applied N compared with broadcast and surface band N.
(Adapted from Lamond et al., 1989, Rep. of Prog., Kansas State Univ.)



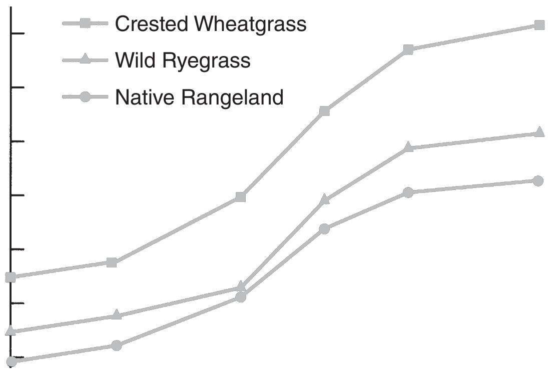


Figure 10-36
Effect of broadcast N fertilization on permanent grassland and native rangeland.
(Adapted from Leyshon and Kilcher, 1976, Proc. Soil Fert. Workshop. Publ. 244, Univ. Saskatchewan, Sask.)

Phosphorus

Since P is relatively immobile in soil compared to N and K, placement near roots is usually advantageous. For example, in establishing forage crops in low P soils, surface or subsurface band–applied P is generally superior to broadcast, although higher broadcast P rates would likely have improved seedling growth (Fig. 10-37). Subsurface band application of P at planting also enhances crop response compared to broadcast P in shallow-rooted and/or taprooted vegetable crops especially grown in short seasons, in cooler temperatures, and on low P soils.

Surface applications after the crop is planted will not place P near the root zone and will be of little value to annual crops in the year of application. In perennial forage crops, subsurface band applications are generally not feasible, and surface band and broadcast applications at higher rates will maintain adequate P availability as P can be absorbed by plant crowns and very shallow roots. Subsurface P applied with a spoke wheel applicator is an excellent alternative to surface application in established perennial crops (Fig. 10-22).

When properly placed, band-applied P can enhance plant growth and yield potential compared with broadcast P (Table 10-5; Fig. 10-38). In this case, subsurface band P greatly increased tiller number, which is directly related to number of heads and final grain yield. Increasing broadcast P to three times band P did not produce the same growth at late tiller stage. Band P placement increased root growth and

(a)

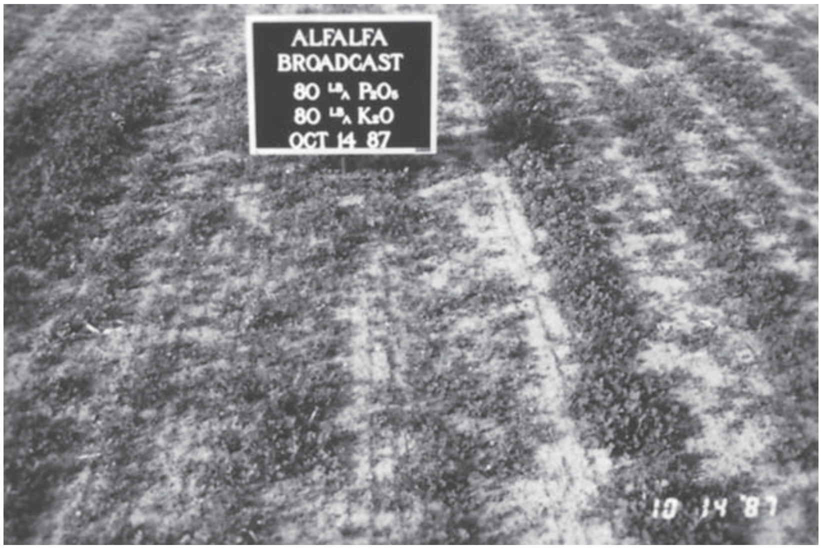


Figure 10-37
Alfalfa response to P and K placement in the establishment year; P_2O_5 and K_2O were applied at 80 lb/a by (a) broadcast, (b) surface band or dribble, and (c) subsurface band or knife applications before planting. Early alfalfa growth is enhanced with band-applied P and K compared with broadcast.
(Courtesy of D. Sweeney, 1989, Kansas State University.)

Figure 10-37
(Continued)

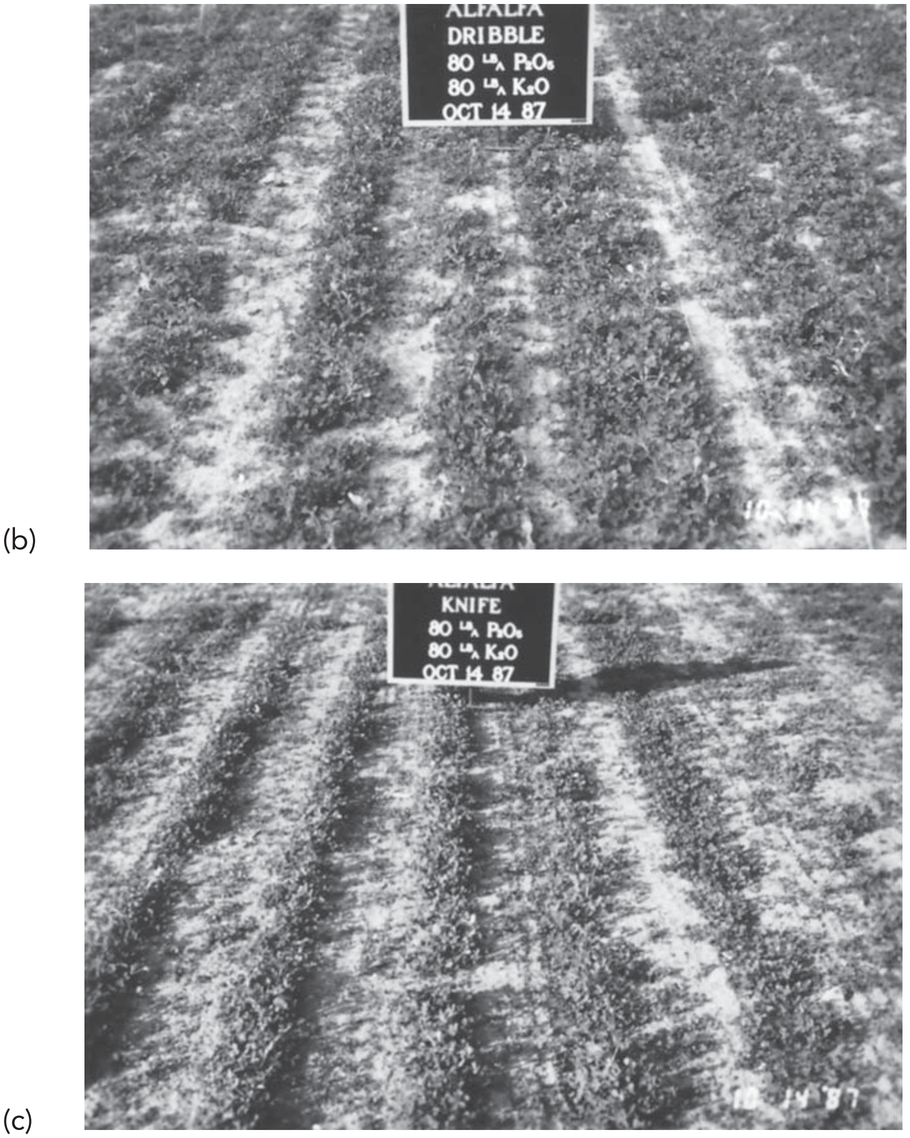


TABLE 10-5
NO-TILL WINTER WHEAT RESPONSE TO P RATE AND PLACEMENT

P Placement[1]	P Rate	Tillers	Dry Matter Full Tiller[1]	Dry Matter Harvest	Grain Heads	Grain Yield
	lb P_2O_5/a	#/ft^2	lb/a	lb/a	#/ft^2	bu/a
	0	11	280	4,978	43	34
Broadcast	15	14	370	5,906	51	40
	45	17	475	8,131	61	53
Subsurface	15	29	1,053	7,754	63	49
band	45	32	1,096	8,641	70	58

[1] Broadcast unincorporated; band applied 1 in. below seed; full tiller = Feekes growth stage 5 (Fig. 10.2).
Source: Havlin, 1992, Proc. Great Plains Soil Fert. Conf.

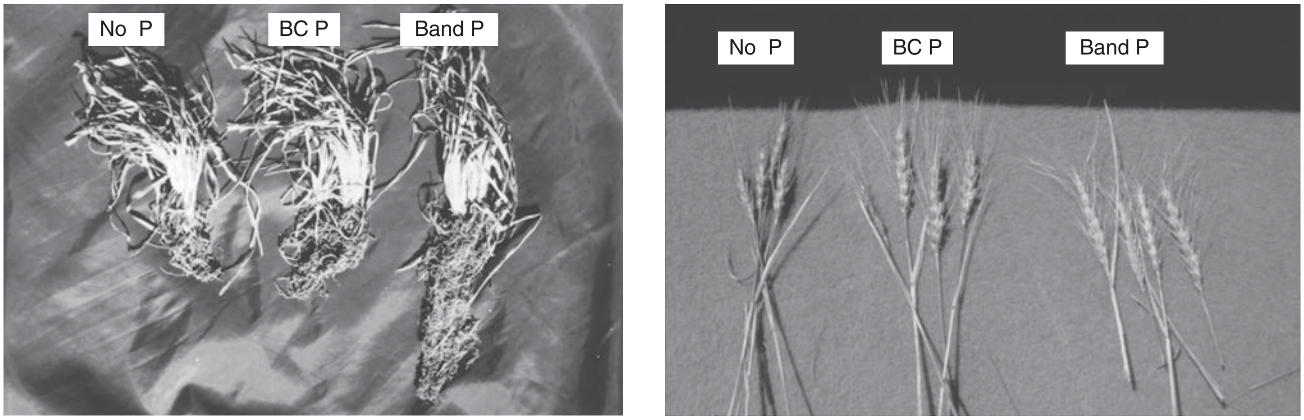


Figure 10-38
Influence of P placement on winter wheat root growth (left) and grain head size (right). P rate was 45 lb P_2O_5/a broadcast applied and subsurface band applied 1 in. below the seed (~ 2.5-in. below soil surface). (Havlin, 1988, Kansas State Univ.)

head size (Fig. 10-38). Similar responses to P placement in corn and soybeans occur (Table 10-6). Grain moisture content with starter P decreased, which illustrates more advanced maturity (Fig. 10-29).

NH_4^+ added to P fertilizer has beneficial effects on P availability (Fig. 10-39). Although dual application of N + P may not increase yield in all soils, positive responses have frequently been observed (Fig. 10-40).

TABLE 10-6
EFFECT OF P RATE AND PLACEMENT ON PLANT HEIGHT, GRAIN YIELD, AND CORN GRAIN MOISTURE

		Plant Height, in.		Grain Yield, bu/a		Grain
Placement	P Rate, lb/a	Corn	Soybean	Corn	Soybean	Moisture, %
Broadcast	0	14.6	7.1	115	37	27.0
	20	16.5	8.3	124	40	26.1
	40	15.4	7.5	119	40	26.6
	80	17.3	9.8	123	40	25.6
Starter	0	14.2	7.1	117	35	27.0
	20	27.2	10.2	135	39	24.8
	40	26.8	10.2	132	39	22.5
	80	30.7	10.2	146	45	24.2

Source: Fixen et al., *1984, Better Crops,* vol. 72.

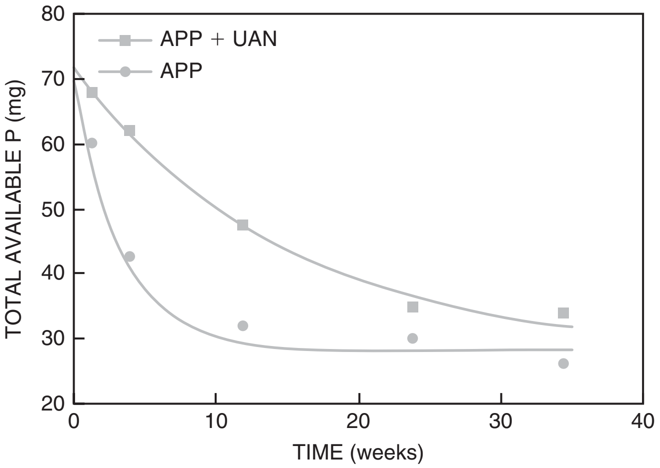
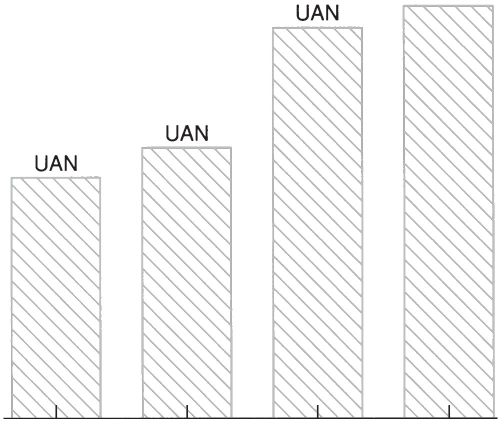


Figure 10-39
Influence of NH_4^+ (UAN) added to P fertilizer (APP) on plant available P with reaction time in soil.
(Djinadou et al., 1995, SSSAJ, 59:49–58.)

Figure 10-40
Winter wheat response to dual N-P application compared with N and P applied separately. BC and SB represent broadcast and seed-banded P, respectively, while UAN was knife applied separately. DL represents dual N-P.
(Leikam et al., 1983, SSSAJ, 47:530.)



When all of the P is either banded or broadcast, the relative efficiency is related to both soil P status and P application rate. In general, differences in crop response between subsurface band and broadcast P decline with increasing soil test P (Fig. 10-41). Although responses to starter P decreased with increasing soil test P, small increases can occur with high soil test P (Fig. 10-42), likely related to cool, wet spring soil conditions. In most cases, early plant growth response to starter P is greater than responses in final yield.

Figure 10-41
Influence of soil test P level on the ratio of broadcast (BC) to band (BD) P rates required for equal grain yield.
(Peterson et al., 1981, Agron. J., 73:13–17.)

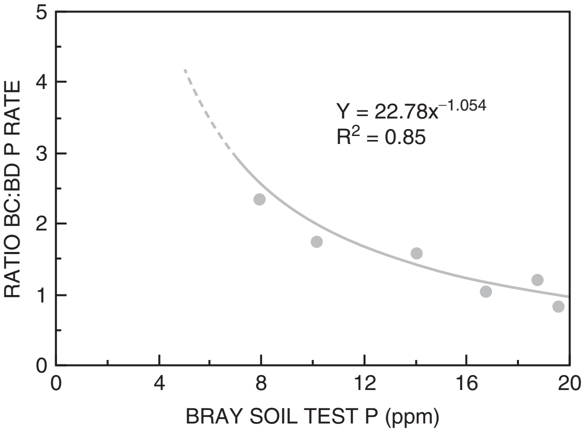
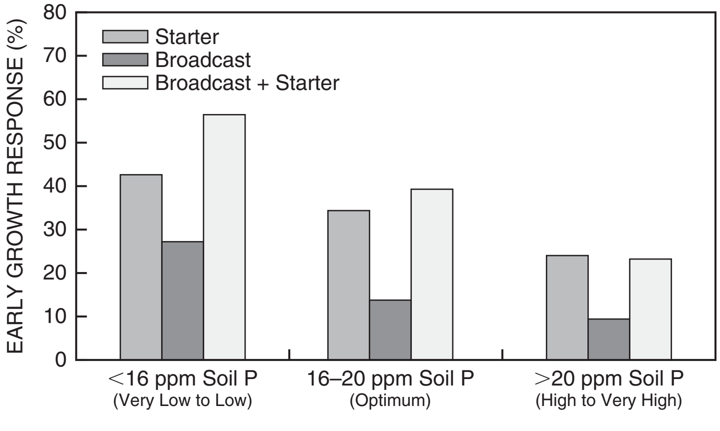


Figure 10-42
Influence of soil test P on relative response to starter P in corn.
(Mallarino, 2003, Intergrated Crop Mgmt. Conf. Iowa State Univ.)



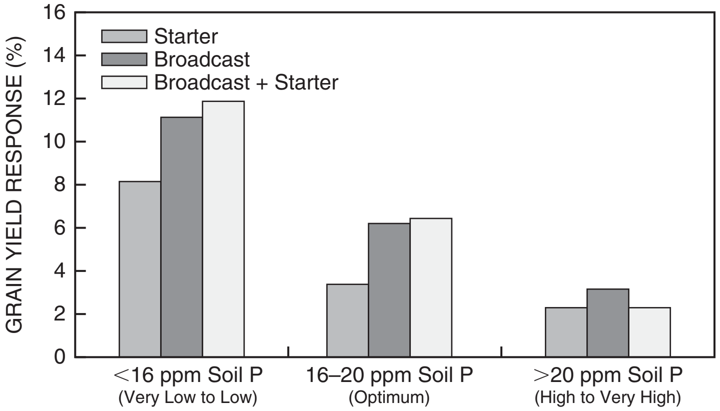


Figure 10-42
(Continued)

Even with band placement, crops during any one season generally recover <20% of applied P. In contrast, typical N and K recovery can be about 40–60%. Band P placement reduces fertilizer–soil contact, resulting in less fixation than broadcast P (Chapter 5). Therefore, band P should increase crop recovery compared with broadcast P. Although generally the most efficient use of limited quantities of P is at planting and the highest return will be obtained by band applications, there may be some advantage in building up soil fertility in a long-term fertilizer program. Generally, use of starter P only will result in gradual decrease in soil test P. Maintaining high crop yield can require increasing soil test P to medium or higher sufficiency levels (Fig. 10-43).

Plant response to starter nutrients can be difficult to predict, but responses dominantly depend on soil test levels, tillage system, soil environmental conditions near the seedling, and proximity of nutrients to the seed. As with most band placement methods, the probability of a response commonly decreases with increasing soil test level. With medium-high soil tests, yield response to starters is often related to cool, wet conditions in fine-textured soils where early season nutrient diffusion may not meet early plant growth demand. In addition, starter responses are often more frequent in conservation tillage systems where cool, wet soil conditions persist through early crop growth. Figure 10-44 provides a general summary of observable crop responses to band versus broadcast P and selected conditions affecting the response.

Potassium

Relative to P, K is more mobile in soil, and placement responses are generally not as large as P. K fertilizers (mostly KCl) applied at ≥10 lb K_2O/a in direct-seed contact commonly reduces germination and seedling growth, especially in salt-sensitive crops.

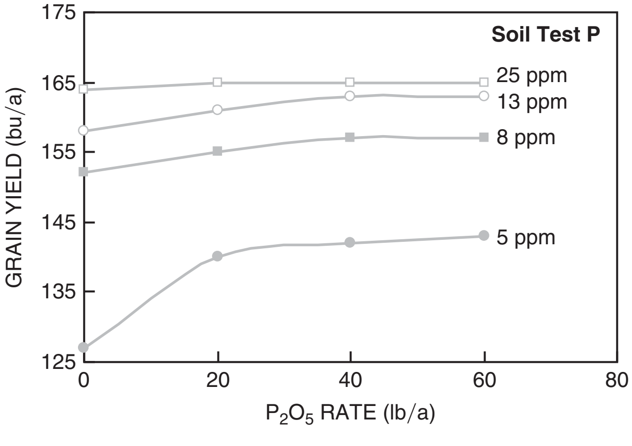
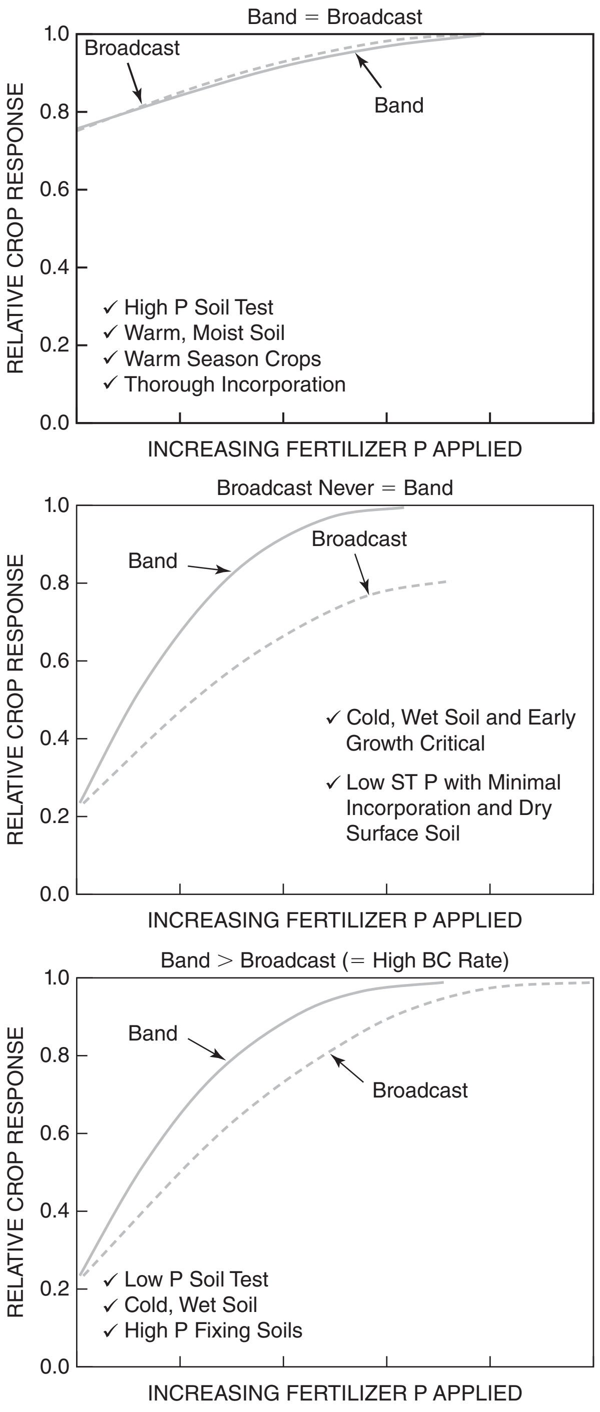


Figure 10-43
Increasing soil test P above medium sufficiency (~ 13 ppm Bray P) optimized corn yield with 20 lb P_2O_5/a starter.

(Adapted from Franzen and Gerwing, 1997, North Central Regional Res. Publ. No. 341.)

Figure 10-44
General differences in crop response to increasing P rate and P placement methods. Typical soil and environmental factors affecting P placement response are shown.
(Adapted from Fixen and Leikam, 1988, Proc. Great Plains Soil Fert. Workshop, 2:37–51.)



K placed in a 2 × 2 in. band generally avoids salt toxicity effects on plant growth. In contrast, salt-tolerant crops such as barley and other small grains can respond to 15–30 lb K_2O/a placed with the seed.

Depending on the crop, broadcast K is usually less efficient than banded K; however, as soil test K increases, there is generally less difference between placement methods. The importance of placement also decreases as higher K rates are used. Starter responses from K, similar to those from N and P, occur with many crops planted under cool, wet conditions, even on high K soils.

K responses in reduced and no-till systems are likely due to cool, wet conditions and low subsoil K (Fig. 10-45). K responses are less unlikely to occur in years when warm, spring conditions persist.

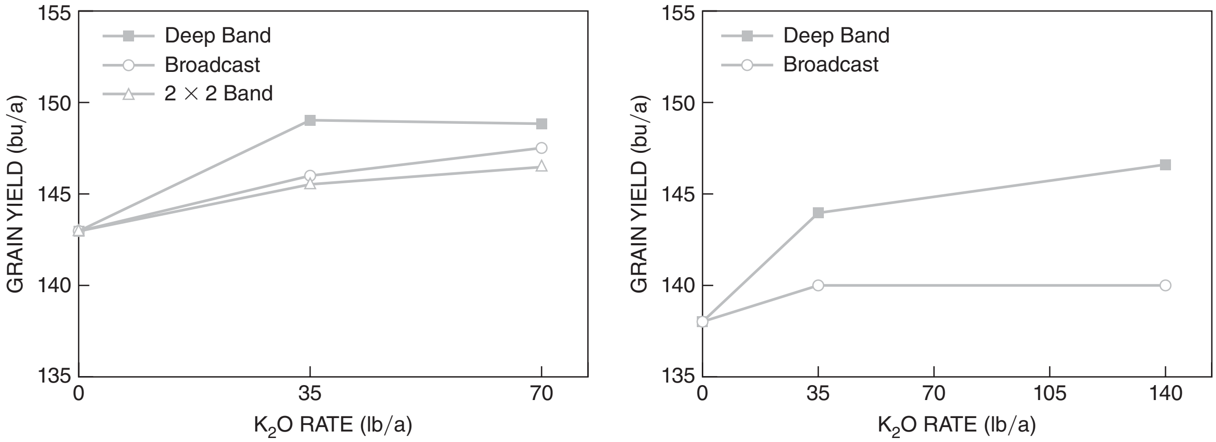


Figure 10-45

Corn yield response to K placement methods in no-tillage (left) and ridge-tillage (right) systems.

(Adapted from Mallarino and Sawyer, 2003, Integrated Crop Mgmt. IC-490, Iowa State Univ.)

Compacted soils often respond to subsurface band-applied K (Table 10-7). These data show starter K response even in high K soil. Although cotton is a high K use crop, yield increases from deep placement of fertilizer K have not consistently increased yield above broadcast K with subsoiling (Table 10-8). Subsoiling without

TABLE 10-7
EFFECTS OF SOIL COMPACTION, SOIL TEST K, AND K MANAGEMENT ON CORN (1985–87) AND ALFALFA (1992–94) YIELDS

			Yield	
Compaction	Soil Test K[1]	K Mgmt.[2]	Corn	Alfalfa
t			*bu/a*	*t/a*
<5	Optimum	0	142	11.1
		+	158	11.3
	Very high	0	153	11.0
		+	158	11.5
19	Optimum	0	126	9.2
		+	158	10.3
	Very high	0	141	9.2
		+	148	10.3

[1] optimum soil test K~115 ppm, very high soil test K > 200 ppm.

[2] 45 lb K_2O/a starter, 300 lb K_2O/a broadcast.

Source: Wolkowski, 2000, New Horizons in Soil Sci. Univ. Wisc., Madison.

TABLE 10-8
EFFECT OF IN-ROW SUBSOILING AND DEEP K PLACEMENT ON SEED COTTON YIELD

In-Row Subsoil Tillage[1]		Tillage + K Management[1]		
No	Yes	BC K – Subsoiling	BC K + Subsoiling	Deep Band K
		lb/a		
2,169	2,625	2,399	2,708	2,711

[1] Subsoiling and deep K (75 lb K_2O/a) placed ~12 in. deep.

Source: Mullins et al., 1994, Agron. J., *86:136–139.*

K produced nearly the same cotton yield as deep band K, illustrating the impact of compacted soil on K nutrition. Soils exhibiting the greatest response to deep placement of K generally have subsoil with low to very low soil K.

Micronutrients

As crop yields continue to increase, greater frequency of micronutrient deficiencies can be expected. Specific micronutrients are applied in areas known to be severely deficient or to crops with especially high micronutrient requirements. The micronutrient may be added to a mixed starter fertilizer, applied separately as a broadcast application or foliar spray, or added as a seed coating. Micronutrients added to N-P-K fertilizer should be placed in bands 2 in. away from the seed to prevent fertilizer injury. Micronutrients are commonly added to APP and other P sources used in starter applications. Continued use of soil- or foliar-applied B to permanent crops can elevate B availability to potentially toxic levels (Chapter 8).

Application Timing

Timing of nutrient application depends on cropping system, climate, specific nutrient, and soil. Sometimes nutrients are applied during the year when they may not be the most efficient agronomically, but are more favorably priced or better suited to workload on the farm. Despite these considerations, growers should apply nutrients at a time that will maximize recovery by the crop and reduce potential losses to the environment.

Nitrogen N loss mechanisms must be considered in selecting the time of application (Chapter 4). It is desirable to apply N as close to peak crop N demand as possible; however, this is seldom feasible except with early in-season applications. Because of N mobility in soils, the amount and distribution of rainfall are important considerations. As annual rainfall increases, N-leaching potential increases, especially if the crop is not growing vigorously or in coarse-textured soils. In addition, conditions conducive to denitrification are likely to occur when soils become waterlogged.

In warm climates, soil temperatures are more optimum for nitrification during a greater portion of the year. Thus, fall N applied before spring planting would be more subject to nitrification and leaching. In cooler climates, NH_4^+ sources can be applied in the fall, after soil temperature drops below 50°F, except on sandy or organic soils. However, compared with fall-applied NH_4^+, spring applications are 5–10% more efficient on fine- and medium-textured soils and 10–30% more efficient on coarse-textured soils. Nitrification and/or urease inhibitors can be used to improve N efficacy in warm, sandy soils. For spring-planted crops, maximum crop recovery of applied N often occurs when growers preplant (fall or early spring) apply 20–40% of total N and the remaining N as in-season sidedress or topdress during early crop growth.

With fall-planted small grains, all or most of the N is commonly applied in late summer or fall (preplant). In warm, humid regions, yields will be somewhat below those obtained by topdressing some of the N in early spring because of N losses by leaching, denitrification, and/or volatilization. In some regions, the soil may be too wet for machinery to be operated in early spring, thus fall-applied N may be the only option. For fall-planted crops, maximum crop recovery of applied N often occurs when growers preplant apply 20–40% of total N and the remaining N as in-season topdress before jointing (Fig. 10-2).

With many vegetable and small fruit crops, application of total N needed by the crop is not generally recommended. Split applied N is common, where 30–50% of the total N is applied preplant and the remaining N rate applied at planting and/or after emergence (Table 10-9).

TABLE 10-9
EXAMPLE N RECOMMENDATIONS FOR VEGETABLE CROPS

		Split N Timing[1]		
Crop	Total N	*Preplant*	*At Planting*	*After Emergence*
	lb/a			
Asparagus (new)	100	50 BC-inc		50 sidedress @ 6-in. height
Asparagus (established)	80			40 pre-harvest 40 post-harvest
Lima beans	30		30 2 × 2	
Snap beans				
Carrots, Horseradish Parsnip	100	50 BC-inc		50 topdress (4–6 weeks)
Table beets, Rutabagas	80		30 2 × 2	50 topdress (well established)
Broccoli, Cabbage, Brussels sprouts, Cauliflower	130	50 BC-inc		40 sidedress (3 & 6 weeks after transplant)
Sweet corn	130	50 BC-inc	30 2 × 2	50 sidedress
Cucumbers slicing	70		30 2 × 2	40 topdress
Cucumbers pickling	60	30 BC-inc		30 topdress
Muskmelons, Watermelons	90	90 BC-inc (plastic)	45 band (no plastic)	45 sidedress (no plastic)
Peas	40	40 BC-inc		
Peppers	120	40 BC-inc		40 sidedress (3 weeks after transplant) 40 sidedress (3 weeks after 1st harvest)
Radishes Turnips	50	50 BC-inc		
Tomatoes (processing)	75	50 BC-inc		25 sidedress
Tomatoes (fresh market)	120	60 BC-inc		30 sidedress (3 + 6 weeks after transplant)
Rhubarb	100	50 early spring		50 sidedress

[1] BC-inc = broadcast incorporate; 2 × 2 = starter at planting.
Source: Extension Bull., E-550B, Mich. State Univ.

Phosphorus In general, P should be applied just before or at planting because of the conversion of soluble P to less available forms. The magnitude varies greatly with the P-fixation capacity of the soil (see Chapter 5). On soils low to moderate in P-fixation capacity, broadcast P in the fall for a spring-planted crop is an effective method. On low P and/or high P fixing soils, band-applied P as close to planting as possible is the most efficient and should maximize crop recovery of P. On medium to high P soils, the time and method are less important and maintenance applications are advised. Similarly with vegetable crops, recommended P should be applied before or at planting.

Potassium K is commonly applied and incorporated before or at planting, which is usually more efficient than sidedress. Because K is relatively immobile compared to N, sidedress K is less likely to move to the root zone to benefit the current crop. Fall-applied K is more dependable than either P or N applied in the fall- to spring-planted crops because fewer loss mechanisms exist with K. In some crop rotations, K may be broadcast only once or twice in the rotation. Fall incorporation of K is generally made before planting K responsive crops, such as corn and legumes.

Maintenance application on forage crops can be made almost any time. Fall applications are generally desirable, because the K will have time to move into the root zone. On hay crops, application is recommended after the first cutting and/or before the last cutting. With vegetable crops, recommended K should be applied before or at planting.

Nutrient Application to Foliage and Through Irrigation

Foliar Application Soluble nutrients may be applied directly to leaves to remedy obvious (visual) nutrient deficiencies or prevent hidden hunger (not visual) that can seriously impair crop yield or quality (Fig. 10-46). Foliar application can be an excellent supplement to soil-applied nutrients. Generally, horticultural crops have higher value encouraging careful monitoring of plant nutrient status; thus, foliar nutrients are commonly applied to high value crops (i.e., fruits, vegetables). The quantity of nutrients absorbed depends on factors related to the specific nutrient, crop, climate, and application technique. General advantages and disadvantages of foliar nutrients include:

Advantages

- Nutrient response can be high if the plant is severely deficient.
- Foliar-applied micronutrients can meet much of the plant need.
- Can be combined with foliar pesticide applications.
- With tree crops, foliar application is the most efficient means of correcting a deficiency.

Disadvantages

- Absorption time can be short depending on nutrient and environmental conditions.
- Quantity of macronutrients delivered or absorbed is relatively small.
- Compatibility with pesticides is variable (review pesticide label).
- Solution concentration is generally small, requiring repeated application.
- Time of day, weather conditions, and plant age influences nutrient absorption rate.

In addition to these constraints, foliar-applied nutrients must first enter the leaf surface before entering leaf veins and translocating throughout the plant (Fig. 10-47). The primary resistance to absorption is through the waxy cuticle layer. The cuticle has a high pore density (10^{10} pores/cm^2) where most pores are <1 nm diameter.

Figure 10-46

Foliar fertilization of winter wheat. *(Left photo: CropCare/PBZ LLC A Paul B Zimmerman Inc.)*

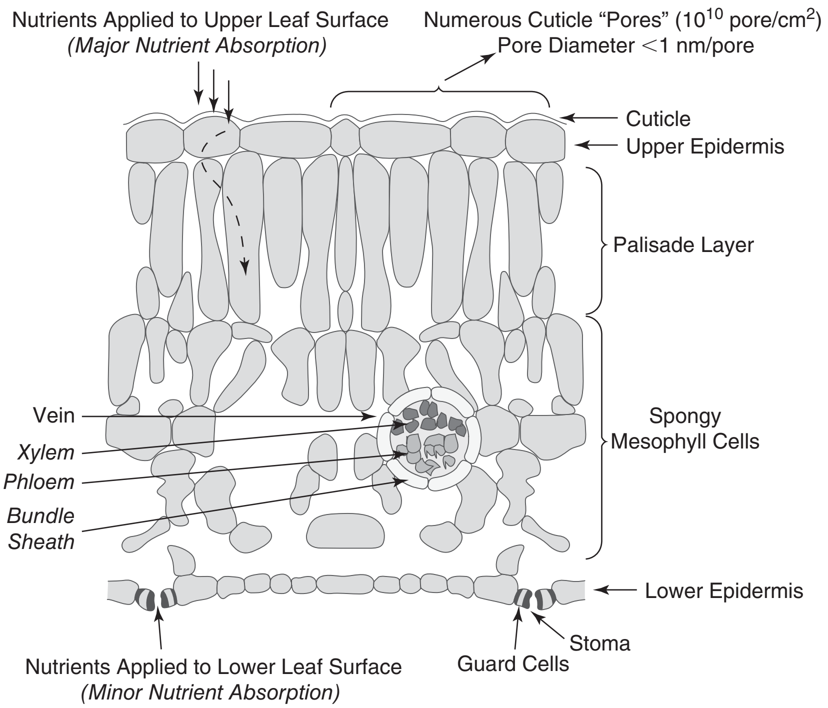


Figure 10-47
General structure of a leaf illustrating nutrient absorption through cuticle in upper leaf surface (primary absorption site) and through stoma in lower leaf surface (minor absorption).

Most ions <0.5 nm radius can physically enter through cuticular pores, unless a cation is applied with a chelate (>1nm diameter).

Nutrient	*Hydrated Diameter (nm)*
K^+, NH_4^+	0.33
Ca^{+2}	0.41
Mg^{+2}, Zn^{+2}	0.43
*Urea	0.44

**Non-hydrated*

Membranes within cuticular pores have a net (−) charge, increasing from the leaf surface through the inner cuticle, encouraging cation over anion absorption and transport. Since urea is uncharged, transport through the cuticle is not influenced; thus, urea absorption is generally greater than other N sources (NH_4^+ or NO_3^-). Cuticle pore density is also high within the guard cells, which accounts for greater foliar nutrient absorption in plants with high stomata density. The dominance of cuticular over stomatal absorption is evidenced by the general observation that nutrient absorption is higher at night when stomata are closed than during the day when stomata are open.

With macronutrients, foliar applications do not *replace* soil applications; however, foliar nutrient application can be effective with micronutrients. For example, B is rapidly absorbed and can readily correct B deficiencies in many crops. Fall foliar application of B in perennial fruits and other woody plants can increase B in the successive crop; however, excessive B can accumulate in soil and woody plants contributing to potential B toxicity in successive crops. Foliar Zn, Mn, and Fe are effective in correcting deficiencies if applied several times during the season depending on the crop.

With macronutrients, late season foliar N applied to small grains and other monocots can increase grain N or protein as late season N is rapidly translocated to developing grain. Foliar application of urea increases N nutrition in grapes, apples, citrus, pineapple, and other tree crops, because N is absorbed more rapidly than with soil applications. Foliar P application is used less than foliar N because most

P compounds (with N) cause leaf damage when sprayed in quantities large enough to increase plant P. In contrast, foliar Ca generally does not correct Ca deficiency as Ca is not readily translocated in the vascular system. However, repeated foliar Ca applications throughout the season can reduce Ca deficiency in fruit and vegetable crops.

Nutrients supplied through leaves can increase short-term nutrient utilization, quickly correcting nutrient deficiencies compared to soil application. Often the response is temporary due to the small amount of nutrient applied or absorbed through the leaf. To achieve full benefits from foliar feeding, proper nutrient application relative to specific crop need or growth stage is essential. Many other factors (time of day, specific nutrient, etc.) affect absorption and translocation of nutrients applied to leaves. Important guidelines to maximize absorption of foliar applied nutrients include:

- Foliar nutrients should be applied before plant demand to ensure optimum response.
- Plants with severe nutrient deficiency can respond quickly to foliar application.
- Plants with "hidden hunger" may exhibit a yield response.
- Correcting macronutrient deficiencies is difficult because of relatively high nutrient requirement relative to nutrient absorption rates through leaves. Excessive foliar nutrient application can cause leaf "burning" (Fig. 10-48).
- Multiple applications repeated at short intervals (every 2–3 weeks) may be needed.
- After application, rapid drying of nutrient solution on the leaf surface decreases absorption; thus, application when leaves are wet (early morning or late evening) increases absorption and response.
- Application to both upper and lower leaf surfaces (nozzle orientation and pressure) increases nutrient absorption.
- Crops that exhibit no other stress than the nutrient in question will respond more favorably to foliar application; heat or moisture stress reduces nutrient absorption rate.
- Leaf cuticle thickness increases with plant age; thus, foliar nutrient application late in the growing season will be less effective.
- Nutrient absorption rates vary with specific nutrient, climate condition at application, and plant age (Table 10-10).
- Nutrient absorption can also be reduced by physical droplet runoff from leaf immediately after application and rainfall washing nutrients off leaves shortly after application.

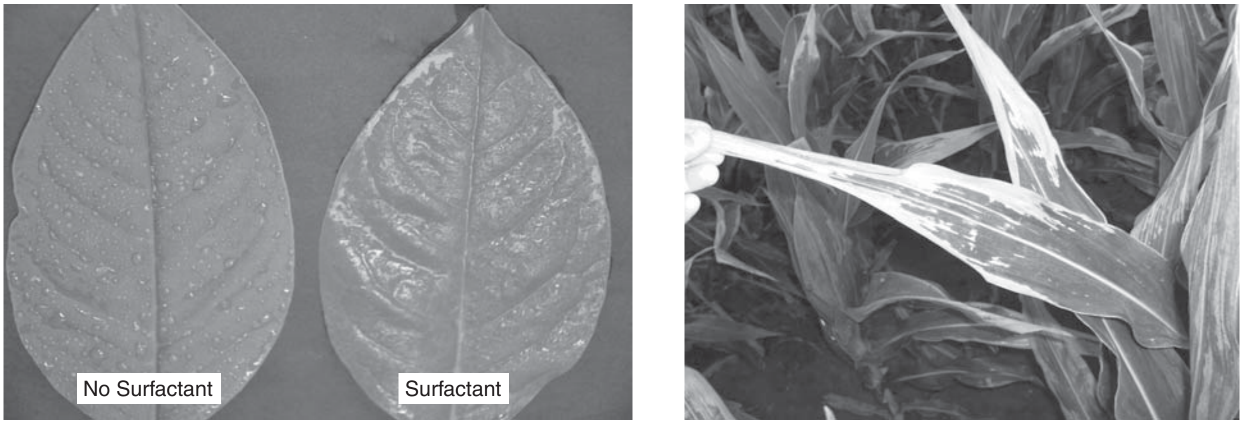


Figure 10-48

Use of a surfactant in the foliar nutrient solution reduces surface tension increasing leaf surface wetting and nutrient absorption in the leaf (left). Foliar nutrients at high rates may cause leaf damage (right).

TABLE 10-10
GENERAL NUTRIENT ABSORPTION RATES IN A PLANT LEAF

Nutrient	Time for 50% Uptake
NH_4^+, NO_3^-	2–6 hrs
Urea	0.5–2 hrs
$H_2PO_4^-$	5–10 days
K^+	0.5–2 days
Ca^{+2}	1–4 days
SO_4^{-2}	5–10 days
Mg^{+2}	0.5–1 day
Fe^{+3}	6–8 days
Mn^{+2}	1–2 days
Zn^{+2}	1–2 days
MoO_4^{-2}	10–20 days
$H_3BO_3^o$	1–2 hrs

Source: Adapted from Wittwer and Teubner, *1959, Annu. Rev. Plant Physiol., 10:13–32.*

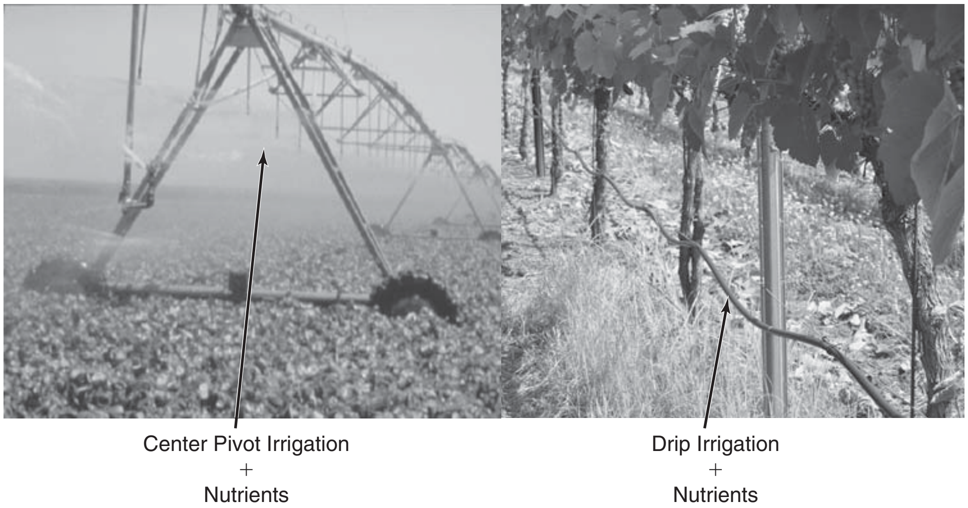
Although foliar application rates vary widely with nutrient and crop, nutrient concentrations <1–2% in the product solution are generally used to avoid injury to foliage (Table 10-11). Because of the hydrophobic leaf surface, due to cuticle wax and presence of leaf hairs in some plants, surfactants are often added to the foliar nutrient solution to reduce surface tension, increasing wetting of leaf surface that increases absorption (Fig. 10-48). Surfactants increase contact between leaf and the aqueous solution and increase permeability of the external wax barrier. Both ionic and non-ionic surfactants are available, where non-ionic surfactants are generally more effective. The narrow cuticle pore diameter and (−) surface charge within the pores likely reduces transport of anionic, high molecular weight chelates like EDTA.

Fertigation Application of nutrients, primarily N, P, K, and S, through an irrigation system (*fertigation*) is feasible where supplemental irrigation is essential for production of a crop or landscape. In environments where evapotranspiration exceeds

TABLE 10-11
RECOMMENDED SOLUTION CONCENTRATIONS USED IN FOLIAR NUTRIENT APPLICATION

		Solution Concentration
Nutrient	Source	*lb product/100 gal*
N	UAN	5–7
	NH_4NO_3, $(NH_4)_2SO_4$, NH_4Cl	3–5
P	APP	3–4
K	KNO_3, K_2SO_4	6–10
	KCl, $K_2S_2O_3$	2–4
Ca	$CaCl_2$, $Ca(NO_3)_2$	6–10
Mg	$MgSO_4 \cdot 7H_2O$, $Mg(NO_3)_2$	8–10
Fe	$FeSO_4 \cdot 7H_2O$	4–10
Mn	$MnSO_4 \cdot H_2O$	4–6
Zn	$ZnSO_4 \cdot 7H_2O$	3–5
Cu	$CuSO_4 \cdot 5H_2O$	0.5–1
B	Sodium borate—$Na_2B_4O_7 \cdot 10H_2O$	0.5–2
Mo	Sodium molybdate—$Na_2MoO_4 \cdot 2H_2O$	0.2–0.3

Figure 10-49
Center pivot irrigation system equipped to apply nutrients to vegetables during the growing season (left) and drip irrigation on grapes (right) equipped for fertigation.



growing season precipitation, nutrients can be injected into the irrigation stream to meet crop nutrient demand. Fertigation is utilized in furrow, center pivot (overhead sprinkler), and microirrigation (drip) systems (Fig. 10-49). Fertigation is common in microirrigation systems because of their frequency of operation and because H_2O application is carefully metered. Fertigation enables uniform nutrient/H_2O distribution in the root zone, optimizes nutrient application timing with respect to crop demand, reduces nutrient application costs, and often reduces nutrient application rates. Fertigation equipment varies widely with application (agronomic or landscape), but each comprises a metering system to inject nutrients into the irrigation H_2O delivered to the field or site (Fig. 10-50).

In order to be injected, nutrient sources must be H_2O soluble. Granular sources must first be completely dissolved prior to injection. Fertilizer materials differ widely in H_2O solubility, with solubility depending on the physical properties of the fertilizer as well as on irrigation H_2O temperature, pH, and salt content. Most dry nutrient fertilizers are coated with conditioners to prevent absorption of moisture by the granules. Use of coated granular fertilizers can cause plugging problems; thus, only fluid grade

Figure 10-50
Irrigation and nutrient injection system needed to deliver H_2O and nutrients to irrigation nozzles or emitters.
(Adapted from Schwankl, 2008, Univ. California-Davis.)

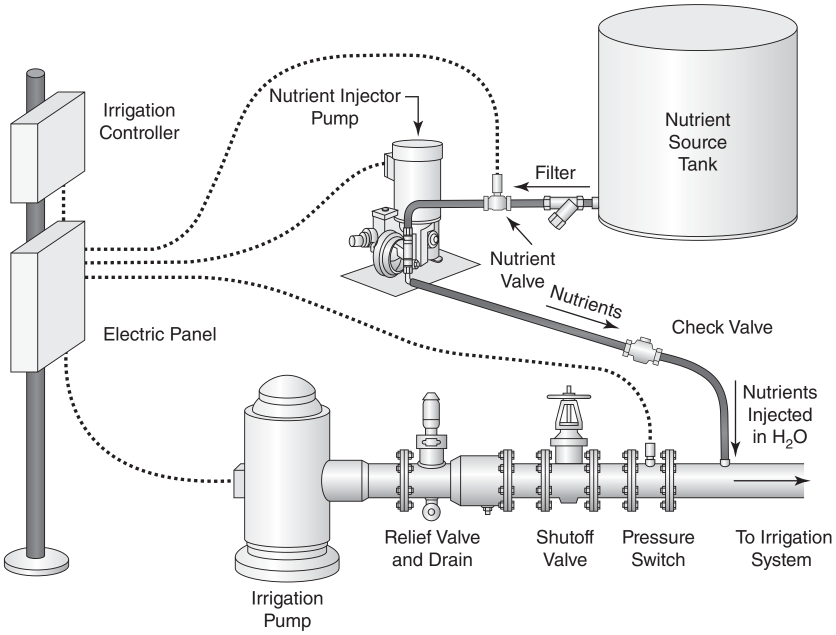


TABLE 10-12
SELECTED FERTILIZERS COMMONLY USED IN FERTIGATION SYSTEMS

Source	Common Name	Precautions
$NH_4NO_3 \cdot H_2O$	AN-20	Do not mix with urea-H_2SO_4 or other concentrated acids
$(NH_2)_2CO \cdot NH_4NO_3$	UAN-32/28	Do not mix with CAN-17 or other Ca sources
$Ca(NO_3)_2 \cdot NH_4NO_3$	CAN-17	Do not mix with SO_4^{-2} or $S_2O_3^{-2}$ sources; mix with NO_3^- & Cl^- salts
$(NH_2)_2CO \cdot H_2SO_4$		Do not mix with AN-20
$(NH_4)_2S_2O_3$	ATS	Do not mix with CAN-17 or other Ca sources
$(NH_4)_2S_x$	APS	S can precipitate if mixed with aqua NH_3
K_2SO_4		Can cause some precipitates
$K_2S_2O_3$	PTS	
KCl		Do not use on fruit and tree crops (Cl toxicity)
H_3PO_4		
$(NH_4)_3HP_2O_7 \cdot NH_4H_2PO_4$	APP	Do not mix with >300 ppm Ca/Mg H_2O

(100% H_2O soluble) sources should be used. To avoid this problem, liquid sources are commonly used except for fluid grade KCl and K_2SO_4 (Table 10-12).

Injection of anhydrous NH_3, UAN, or other free NH_3-containing N sources to irrigation waters high in Ca^{+2}, Mg^{+2}, and HCO_3^- may precipitate $CaCO_3$ and/or $MgCO_3$, causing scaling and plugging problems in irrigation equipment. Their formation can be prevented by the addition of H_2SO_4, $(NH_4)_2S_2O_3$, or other acid solutions. Fertigation of P is common, although APP combined with irrigation H_2O containing >300 ppm Ca or Mg will cause Ca/Mg-P to precipitate and plug the irrigation system. Solution grade K sources are H_2O soluble and can be mixed with N and P sources. The exception is K_2SO_4, which is less soluble than KCl or KNO_3; thus, most use $K_2S_2O_3$ (liquid) or dissolve KCl. Many of the N and K sources contain S, and Cl^- or SO_4^{-2} salts are commonly used for most micronutrients (Chapter 8). With Ca/Mg, Cl^- and SO_4^{-2} salts are commonly used; however, special equipment is needed to dissolve and agitate the less-soluble SO_4^{-2} salts.

Uniform fertigation of nutrients is accomplished with properly designed irrigation systems and skilled irrigation management, since dissolved nutrients are delivered with the water. Poor nutrient distribution can occur with flood or furrow irrigated systems and with low nutrient rates. Under furrow irrigation, a large proportion of the nutrients may be deposited near the inlet and uneven infiltration may result in nutrient moving below the root zone. To prevent nutrients from becoming inaccessible to crops through either leaching below the root zone or accumulating at or near the soil surface, they should be introduced toward the middle of the irrigation period and application should be terminated shortly before completion of the irrigation. For these reasons, furrow and flood fertigation is less common. With sprinkler fertigation systems, as with topdress applications (Fig. 10-27), it is critical to follow labeled product rates to prevent excessive nutrient application on leaves that may cause significant leaf burn and yield loss.

Variable Nutrient Management

Variable or *site-specific* nutrient management can improve nutrient use efficiency by distributing nutrients based on spatial variation in yield potential, soil test levels, and other spatially variable factors that influence soil nutrient availability and crop nutrient demand. Pre-season and in-season assessments of spatial information are two variable nutrient management approaches used to guide nutrient application decisions.

Pre-Season Approach Geospatial information is acquired before nutrients are applied and the crop is planted in a given field, and commonly includes:

- previous crop yield data obtained from a yield monitor combine
- soil test data obtained from grid, cell, or zone sampling
- digital orthophoto quarter quads (DOQQ) (b/w aerial photographs)
- aerial or satellite provided NDVI
- digital elevation
- soil electrical conductivity (EC correlated to soil texture, soil depth, salinity, etc.)

These spatial data are stored and analyzed within a GIS and interpreted for relationships influencing crop yield that can be used to guide spatially variable nutrient rate decisions (Fig. 10-51). For example, the spatial distribution in soil test P based on grid sampling (Fig. 9-39) and associated P sufficiency levels (Fig. 9-33) are used to establish variable P recommendations in the same way field average P recommendations are developed (Fig. 10-52). Fertilizer P is then applied through a computer-controlled variable rate applicator according to the variable P rate map (Fig. 10-53). With uniform P application, low soil test P areas are underfertilized while high soil test P areas are overfertilized (Fig. 10-54). Similar responses to variable application of K and lime are also common. Yield loss due to underfertilization decreases profitability more than overfertilization because the value of lost yield exceeds the cost of the excess fertilizer input.

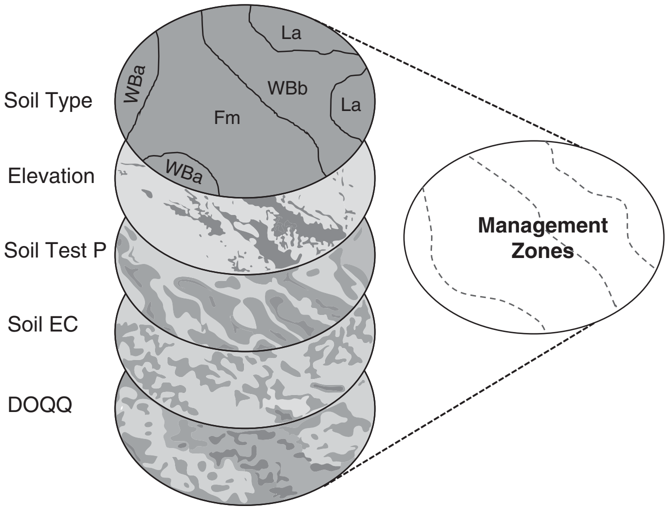


Figure 10-51
Spatial information on a field site, soil, and crop used to develop nutrient prescription maps to guide spatially variable nutrient application. Selected data layers can be used to identify management zones.

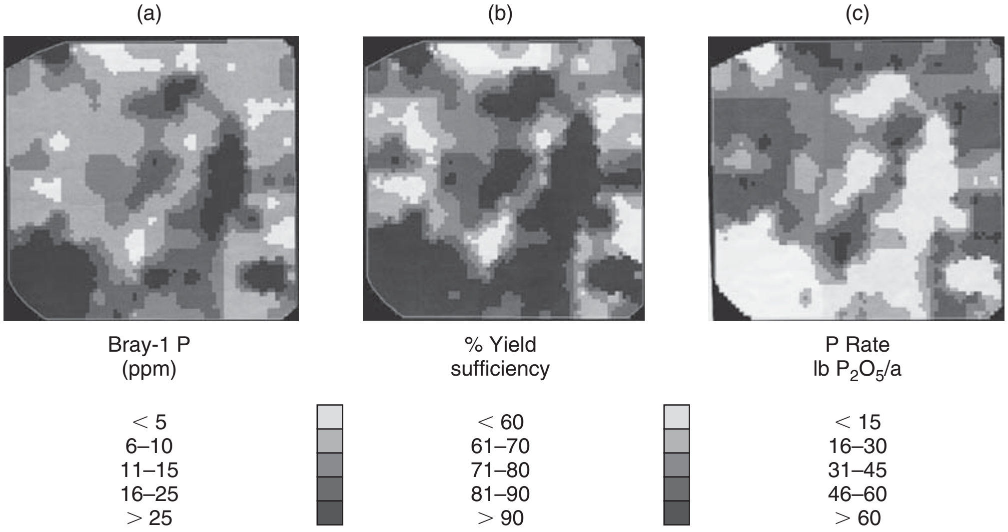


Figure 10-52
Spatial distribution of soil test P determined from sampling 120 acre field on 2 acre square grids (a). These data were used to develop the P sufficiency map (b). Ultimately, a variable P recommendation map is established (c). The light areas represent low soil test P (a), low % P sufficiency (b), and low P recommendations (c).

Figure 10-53
Typical variable fertilizer applicator capable of applying several nutrient sources at various rates based on spatially distributed soil test levels (left) and the variable rate controller in the vehicle (right).

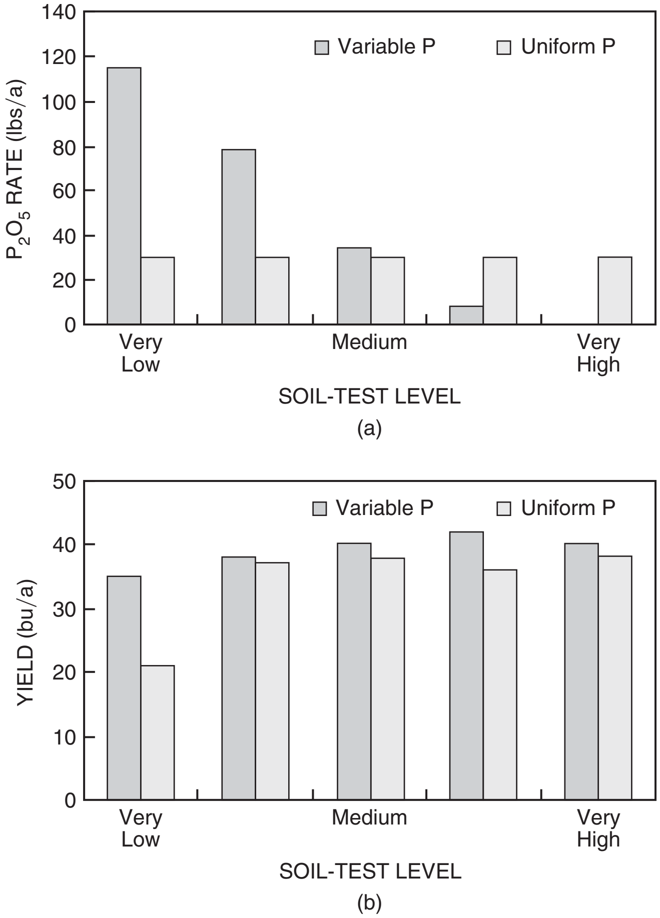


Figure 10-54
Comparison of variable and uniform P application on soybean yield. Applying a uniform P rate of 30 lb P_2O_5/a (a) resulted in significant yield loss on very low P areas (b). On very high P areas, overapplication occurs with uniform P management (a).

Establishing *management zones* within a field based on specific spatial data can also be used to develop variable nutrient recommendations (Fig. 10-51). These spatial data commonly include aerial photography of soil color (correlated with surface soil OM), previous yield maps, electrical conductivity, elevation, soil type, and other spatial information (Fig. 10-55). Although variability in weather conditions influences yield potential between years, in years when high yield management zones do not perform as expected, over- and underapplication of nutrients would increase compared to years when management zones perform as expected (Fig. 10-56). With N, overfertilization may have negative impacts on N transport below the root zone (Table 10-13).

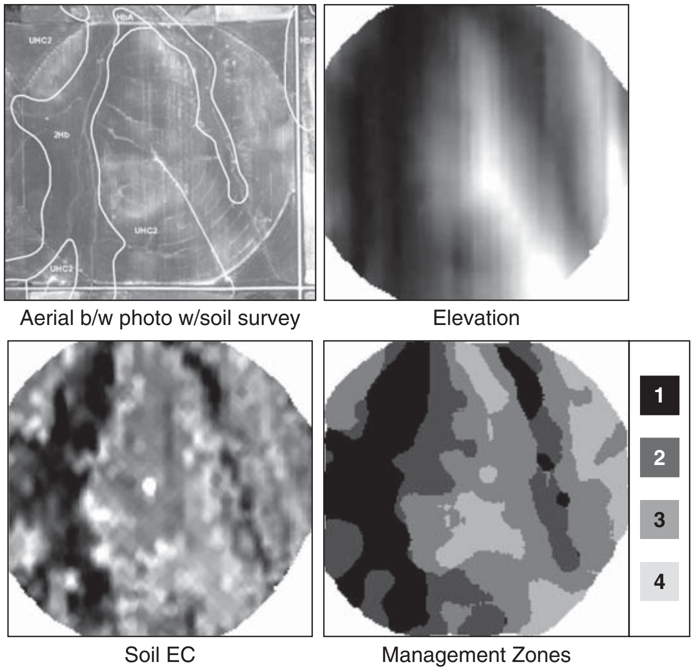


Figure 10-55
Use of b/w aerial photography, *where dark colors represent areas of higher surface soil OM than lighter color areas and where digitized* soil survey *data were superimposed over the b/w photo;* elevation, *where elevation increases from dark to light colored areas; and* electrical conductivity, *where soil EC increases from dark to light. These spatial data were used to delineate soil* management zones *that represent areas of similar crop yield potential. The dark-colored zones exhibit higher yield potential (Fig. 10-56) and would require higher nutrient application rates than light-colored areas.*
(*Schepers et al., 2004,* Agron. J., *96:195.*)

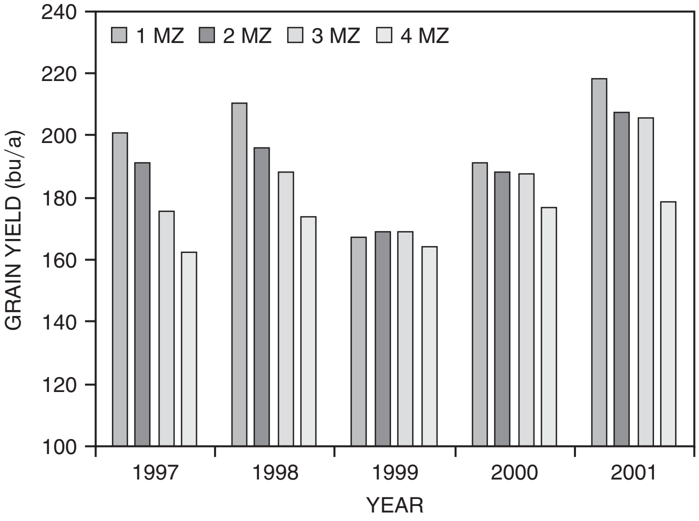


Figure 10-56
Average corn yields of four management zones (MZ) over five crop seasons (see Fig. 10-55).
(*Schepers et al., 2004,* Agron. J., *96:195–203.*)

Table 10-13
Comparison Between Uniform and Variable N Management in a 40a Field on Average N rate, Total Urea Use, Spring Wheat Yield, and Soil Profile NO_3-N (0–2 ft) After Harvest

N Management	Average N Rate	Urea Applied	Yield	Soil NO_3-N
	lb/a	*lb*	*bu/a*	*lb/a*
Uniform	70	6,087	44.0	41.1
Variable	57	4,944	45.6	32.0

Source: D. Franzen, North Dakota State Univ.

Pre-season variable nutrient management is common with immobile nutrients and lime. Many growers realize enhanced crop productivity and profitability with adoption of grid or zone soil sampling to variably apply P, K, and lime. With mobile nutrients like N, where N rates are based on estimated yield goals determined from crop yield maps, the spatial distribution of crop yield can vary greatly between years (Fig. 10-57). Thus, it is difficult to utilize annual yield maps to reliably establish the spatial distribution in yield goals needed to prescribe variable N rates. Technologies used to establish *in-season* N recommendations will likely be more efficient than N recommendations determined through pre-season variable N management techniques.

In-Season Approach Growing plants are often the best indicator of N availability (Chapter 9). Remote sensing (light reflectance) provides an excellent opportunity to quantify crop N status and additional N need that varies throughout a field (Fig. 9-19). Thus, in-season N management decisions can be guided by real-time or on-the-go crop N status (canopy reflectance) assessment, interpretation, and N application. Crop canopy reflectance provides a relative measure of leaf chlorophyll content, where NDVI is highly correlated to crop N status, N uptake, and crop yield (Figs 9-20, 9-21, and 10-58). Therefore, vehicles equipped with canopy sensors can quickly assess variability of crop N status and apply the economic optimum N rate, reducing both under- and overapplication errors (Fig. 10-59). While in-season crop N assessment coupled with variable N application technologies are rapidly evolving, research has clearly established in-season variable N management is an effective means of increasing crop N use efficiency (Table 10-14).

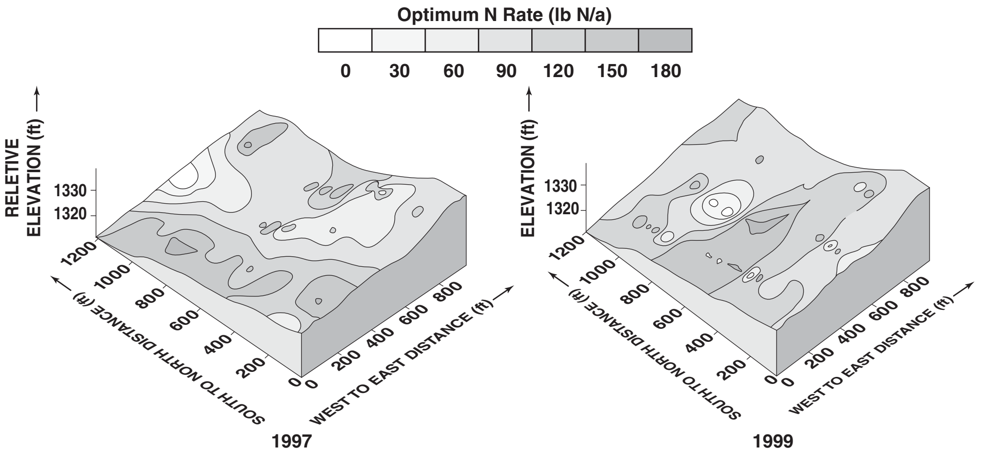


Figure 10-57
Variation in economic optimum N rate between years for a 30-acre corn field. Field topographic features are illustrated.
(*Malzer data [Univ. Minn.] from Doerge, 2002,* Crop management, *doi:10.1094/CM-2002-0905-01-RS.*)

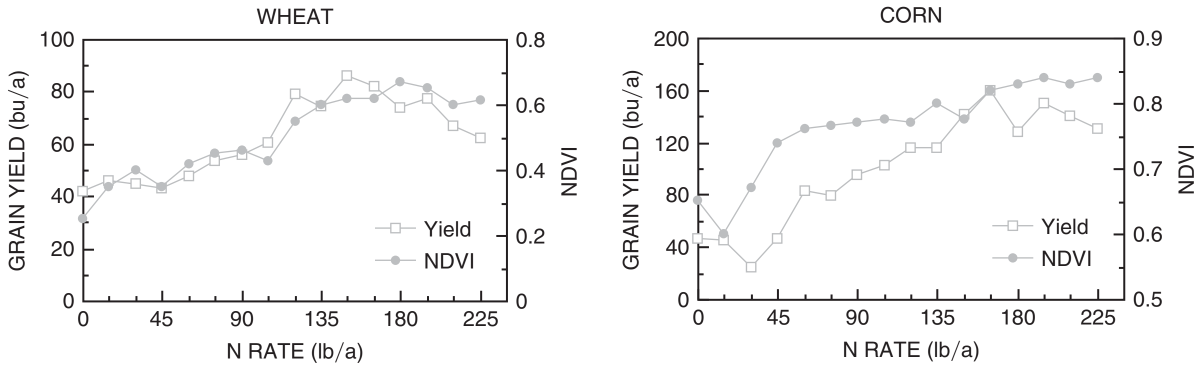


Figure 10-58
Relationship between NDVI and grain yield in wheat and corn. (*Raun et al., 2008,* Agron. J., *100:1088–1093.*)

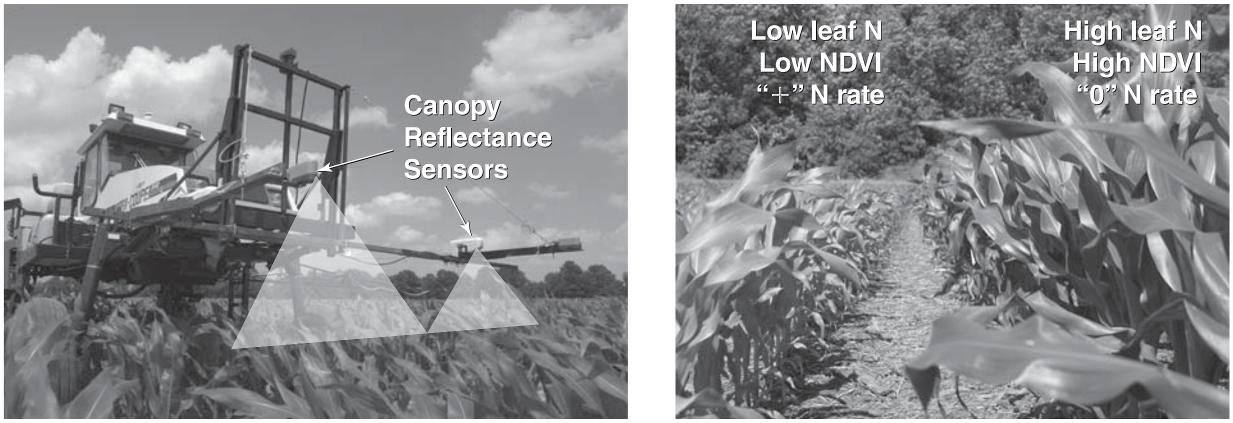


Figure 10-59
In-season N application to corn using canopy reflectance sensors to determine NDVI and variable N application rate.
(Right photo: Newell R. Kitchen, University of Missouri; Left photo: Newell Kitchen/USDA-ARS)

TABLE 10-14
EVALUATION OF PREPLANT AND IN-SEASON UNIFORM N WITH PREPLANT + VARIABLE IN-SEASON N USING CANOPY REFLECTANCE (NDVI)

	N Application				N Use	
Treatment	*Preplant*	*In-season*	*Total*	**Yield**	**Efficiency**	**Net Return**
		lb/a		*bu/a*	*lb N/bu*	*$/ac*
Uniform N	73	20	92	34.6	2.66	82
NDVI-based N	56	23	79	39.8	1.98	100

Source: Courtesy B. Raun, Okla. State Univ.

Since a portion of the total crop N requirement should be applied before planting, utilizing both *pre-* and *in-season* variable N management will spatially match crop N need with N application rate. A pre-season estimate of total fertilizer N is used to determine preplant N rate and to establish potential ranges for in-season N rates, which are then dynamically determined through monitoring crop N status. Only through in-season variable N application can the spatially optimum N rate be applied, increasing N use efficiency throughout the field.

OTHER NUTRIENT MANAGEMENT CONSIDERATIONS

Utilization of Nutrients from the Subsoil

Utilization of subsoil nutrients depends on the ability of roots to explore subsoil, which depends on the crop, and on soil physical (i.e., compaction, drainage, aeration) and chemical properties (i.e., soil acidity, exchangeable Al). Most humid-region subsoils are acidic and low in fertility, which contribute very little to total nutrient uptake by crops (Fig. 10-60). Deep-rooted crops (e.g., alfalfa, sweet clover, grasses) increase available P in the surface by upward transfer from the subsoil as the organic residues are returned and decomposed. Surface horizons of forest soils are commonly higher in nutrients than the subsoil horizons because of upward transfer and accumulation.

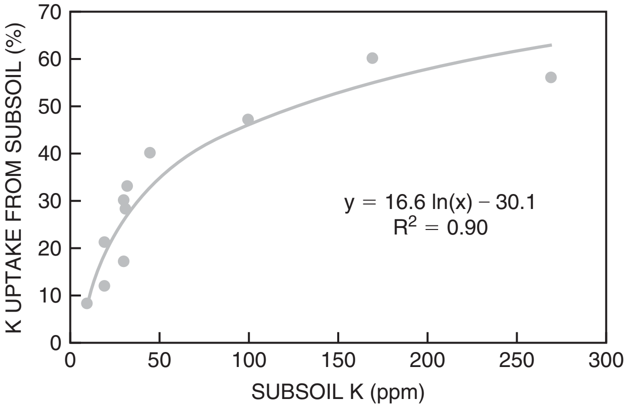


Figure 10-60
Effect of increasing subsoil K content on K uptake by wheat.
(*Adapted from Kuhlman, 1984,* Plant & Soil, *127:129.*)

Loess or alluvial soils can be high in K and P throughout the profile and can be utilized by deep-rooted plants, causing some difficulty in correlating surface soil test results for P or K. When subsoil P or K is considered, the relation between extractable P or K and crop response can be improved. Some regions have established relative subsoil nutrient availability for major soil series to improve the accuracy of nutrient recommendations (Fig. 10-61).

In calcareous soils, soil test K is usually high in both surface soil and subsoil, but most subsoils are low in P and many micronutrients. P and micronutrient fertilization of the surface soil is generally adequate to increase P and micronutrient availability.

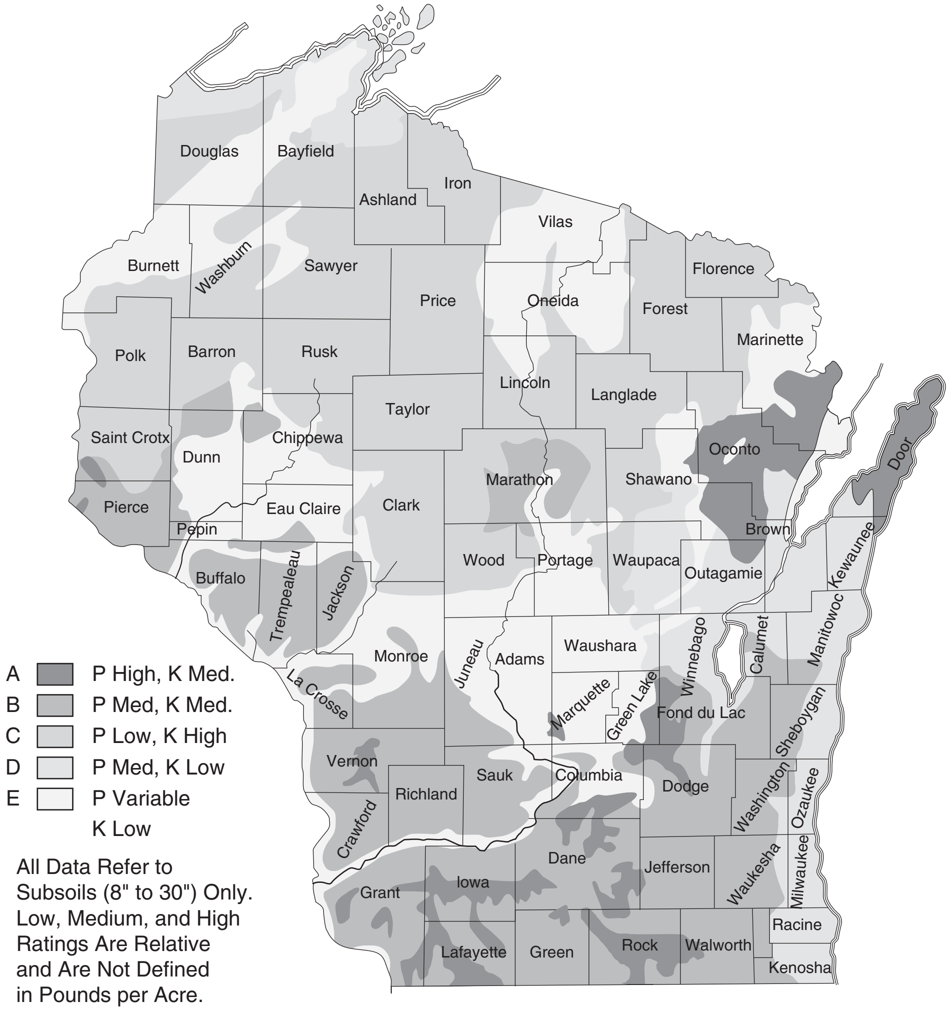


Figure 10-61
Relative P and K availability in subsoils of major soil series in Wisconsin.
(*Kelling et al., 1999,* Optimum soil test levels for Wisconsin, *Univ. of Wisconsin Coop. Ext. A3030.*)

TABLE 10-15
EFFECT OF SUBSOILING AND DEEP INCORPORATION OF P AND K ON BARLEY YIELD (1974–77)

Tillage/Fertilizer	Grain Yield
	bu/a
None	50.3
Subsoiled alone	63.2
Subsoiled + P + K	73.5
P + K to topsoil	49.9

Source: Adapted from McEwan and Johnston, 1979, *J. Agr. Sci.* (Camb.), 92:695.

Subsoil application of nutrients can enhance nutrient availability and root development in the fertilized zone. Lime added to acid subsoil will not only reduce Al, Fe, and Mn in solution, but also increase Ca and Mg supply (Chapter 3). In some cases, subsoiling alone can increase crop yields, although subsoil incorporation of fertilizers can further increase yields (Table 10-15). Subsoiling to 10–20-in. depth increased 4-year mean barley yield by 24%, and subsoil incorporation of P + K increased barley yield an additional 20%. In some soils, deep tillage (24–36 in.) can improve root growth and crop yield without subsoil fertilization, mostly due to access to subsoil H_2O. If the plant is utilizing water from 24 to 36 in. in contrast to only 12-in. deep, the probability of drought stress is reduced. Under some conditions, turning up heavy clay subsoil material may cause the surface to seal off more rapidly and decrease infiltration.

Residual Fertilizer Availability

Depending on nutrient mobility in soil, a portion of applied nutrients will remain in the soil after harvest, depending on rate applied, crop nutrient removal, and the soil. Residual N availability is related to buildup of profile NO_3-N and soil OM especially with continued animal waste applications (Chapters 4 and 9). With fertilizer N in humid regions, residual profile N generally does not accumulate due to leaching and denitrification losses of residual fertilizer N (Fig. 9-45). However, in moderate to semi-arid climates, fertilizer N recommendations should include residual N (Figs 9-46 and 9-47; Table 9-9). With substantial surface residue cover, recommended N rates also depend on N placement (Fig. 10-62). Like N, residual fertilizer S in moderate to semi-arid climates also can accumulate in subsoil; however, in highly weathered soils, SO_4^{-2} can be retained in subsoil by adsorption to AEC (Fig. 3-37).

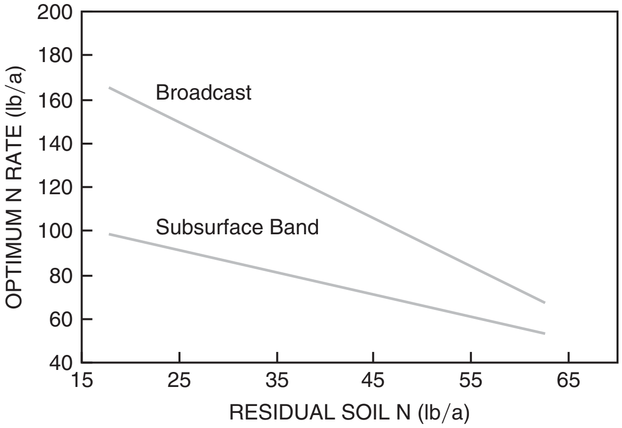


Figure 10-62
Influence of residual soil N and N placement on optimum N rate for dryland wheat in western Kansas.
(*Adapted from Schlegel et al., 2003, Agron. J., 95:1532–1541.*)

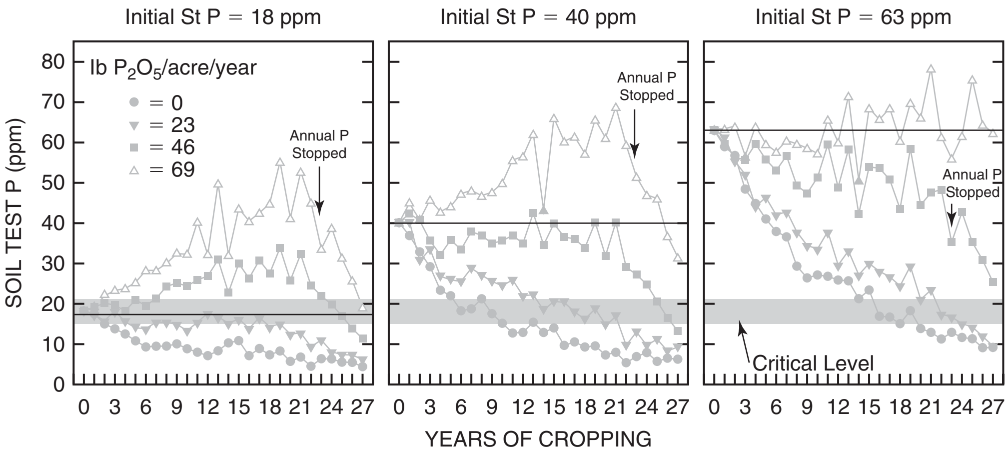


Figure 10-63

Effect of long-term P fertilization and cropping (corn-soybean) on soil test P (St P). Critical soil test P levels (shaded bar) are 15–21 ppm for corn and 12–18 ppm for soybean.

(*Adapted from Dodd and Mallinaro, 2005, SSSAJ/69:1118.*)

For immobile nutrients, residual availability can be observed for many years depending on the rate applied and the soil buffer capacity (Fig. 10-63). Generally, as fertilizer application rate increases, the residual value also increases. In many cases, the cost of fertilization is charged to the crop treated. However, residual fertilizer availability should be included in evaluation of fertilizer economics. The residual availability potential for immobile nutrients can be accurately determined through soil testing.

MANAGEMENT OF ORGANIC NUTRIENTS

Animal Manure

Recycling of organic wastes is a primary function of soil, and prior to development of fertilizers, animal manures were a major source of nutrients for crop production. Some of the beneficial effects of manure use are:

- a source of plant available nutrients
- increased soil OM, CEC, and buffer capacity
- increased mobility and availability of P and micronutrients due to OM complexation
- increased soil H_2O and nutrient holding capacity
- improved soil structure, decreased bulk density, and increased infiltration
- increased soil pH and reduced Al^{+3} toxicity in acid soils by complexation with OM

Table 10-16 illustrates the improvement in soil quality factors with long-term application of animal manure. Greater attention is being given to effective disposal

TABLE 10-16
EFFECTS OF 11 YEARS OF MANURE ADDITIONS ON SOIL PROPERTIES

Application Rate	OM	CEC	pH	P	K	Pore Space
t/a/y	*%*	*meq/100 g*		—— *ppm*	——	*%*
0	4.3	15.8	6.0	6	121	44
10	4.8	17.0	6.2	7	159	45
20	5.2	17.8	6.3	14	191	47
30	5.5	18.9	6.4	17	232	50

Source: Magdoff and Van Es, 2009, *Building soils for better crops (3rd ed.), Sustainable Agric. Network Handbook Series Book 10* (http://www.sare.org/publications/bsbc/bsbc.pdf, accessed March 24, 2011).

of manures because of increased use of confinement production systems and associated manure distribution problems, and increased risk of ground and surface water contamination by NO_3^- and $H_2PO_4^-$ associated with long-term manure application.

Manure is applied to about 16 million acres of U.S. cropland, which represents about 5% of total cropland. While confined animal feeding operations occur in nearly every state, they are concentrated in the southwest (beef and dairy), southern plains (beef), upper Midwest (dairy and poultry), and the southeast (poultry and hogs) (Fig. 10-64). In principle, manure could be spread on far more cropland, mitigating risks that arise from excessive concentrations of manure (Fig. 10-65). These data show the large capacity of soils (mollisols) and crops (corn) in the Midwest to utilize manure N, whereas the highly

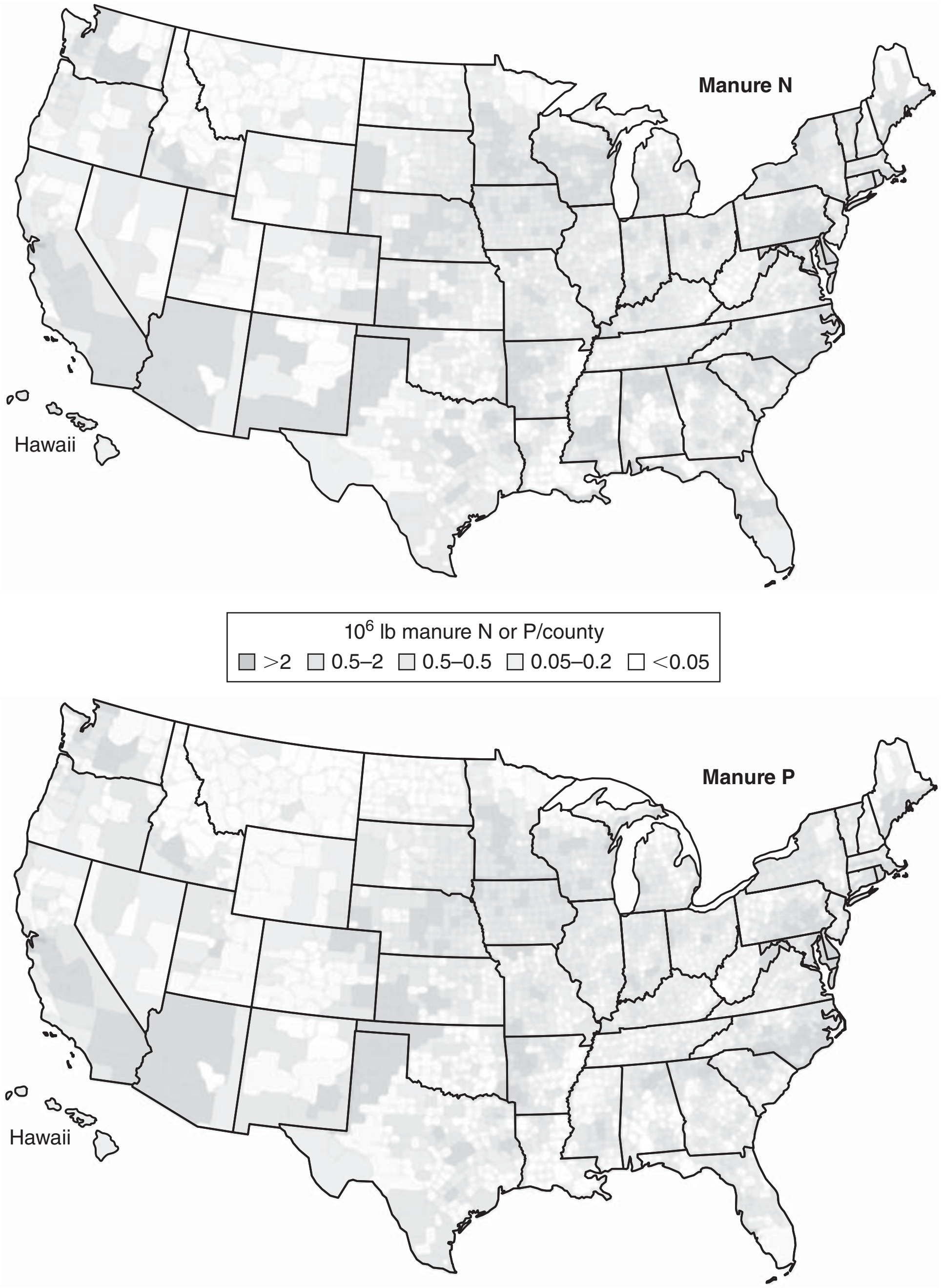


Figure 10-64
Total manure N and P available for application from confined livestock operations.
(Kellogg et al., 2000, USDA-NRCS, Publication No. nps00-0579.)

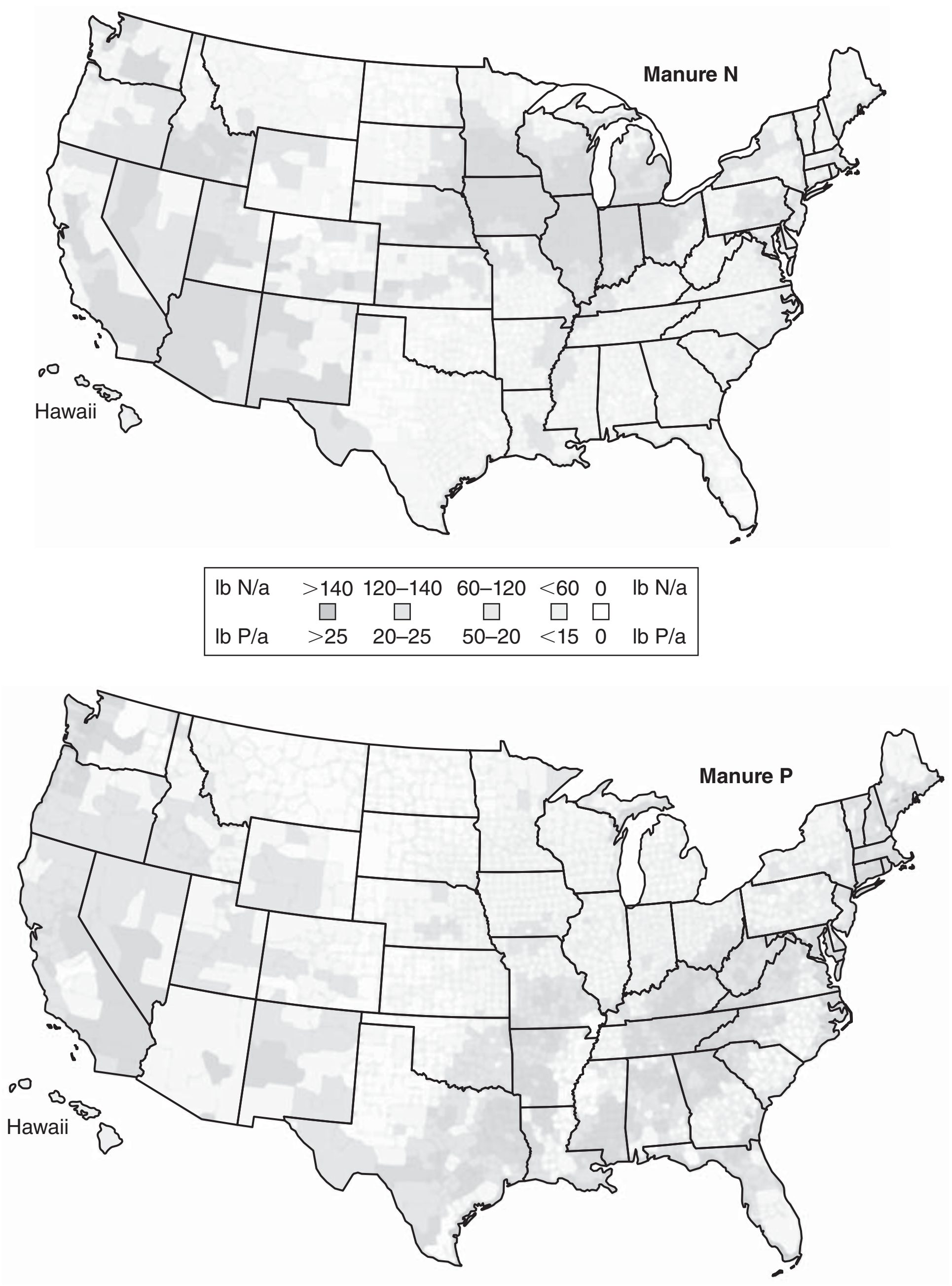


Figure 10-65
Capacity of cropland to assimilate N and P in manure.
(Kellogg et al., 2000, USDA-NRCS, Publication No. nps00-0579.)

weathered, low P soils in the southeast can utilize substantial manure P. Over 70% of manure nutrients are applied to eight crops, with the majority applied to corn from dairy, beef, and swine manure (Table 10-17). Peanuts receive a large proportion of poultry manure because peanuts are dominantly grown in the southeast where extensive poultry production occurs. Unfortunately, large quantities of manures are produced in localized areas, and it is cost prohibitive to transport manure nutrients to other cropland regions. Many areas in the United States produce more nutrients than can be locally utilized by crops (Fig. 10-66). As a result, many crop fields near confined animal feeding operations have received animal wastes for many decades, increasing the risk of N and P transport to surface and ground waters (Chapter 12). Typical manure nutrient rates applied to crops in the United States is shown in Figure 10-67.

TABLE 10-17
DISTRIBUTION OF ANIMAL MANURE TO MAJOR AGRONOMIC CROPS IN THE UNITED STATES

	Manure Source					
Crop	Dairy	Beef	Swine	Poultry	Other	All
	$ac \times 10^3$					
Barley	54	36	4	4	2	100
Corn	5,612	1,617	1,161	472	224	9,086
Cotton	67	101	0	228	1	397
Oats	218	139	8	3	7	375
Peanuts	0	8	0	44	0	52
Sorghum	1	37	7	1	0	46
Soybeans	354	327	139	132	30	982
Wheat	107	250	26	12	6	401
All	6,413	2,515	1,345	896	270	11,439

Source: USDA, 2006, *Manure use for fertilizer and for energy/report to Congress* (http://www.ers.usda.gov/Publications/AP/AP037/AP037b.pdf, accessed March 25, 2013).

Maximizing crop recovery of soil-applied manure nutrients depends on the manure nutrient content, application method and time, and short- and long-term availability of manure nutrients. Manure nutrient content varies, depending on:

- animal type and diet
- type and amount of bedding
- manure moisture content
- storage and handling method

Nutrient content of typical animal wastes varies between regions and local values should be used in estimating the quantity of nutrients applied with a specific manure rate (Table 10-18; Chapter 4). In most cases, just prior to application, manure samples should be collected and sent to a laboratory for analysis.

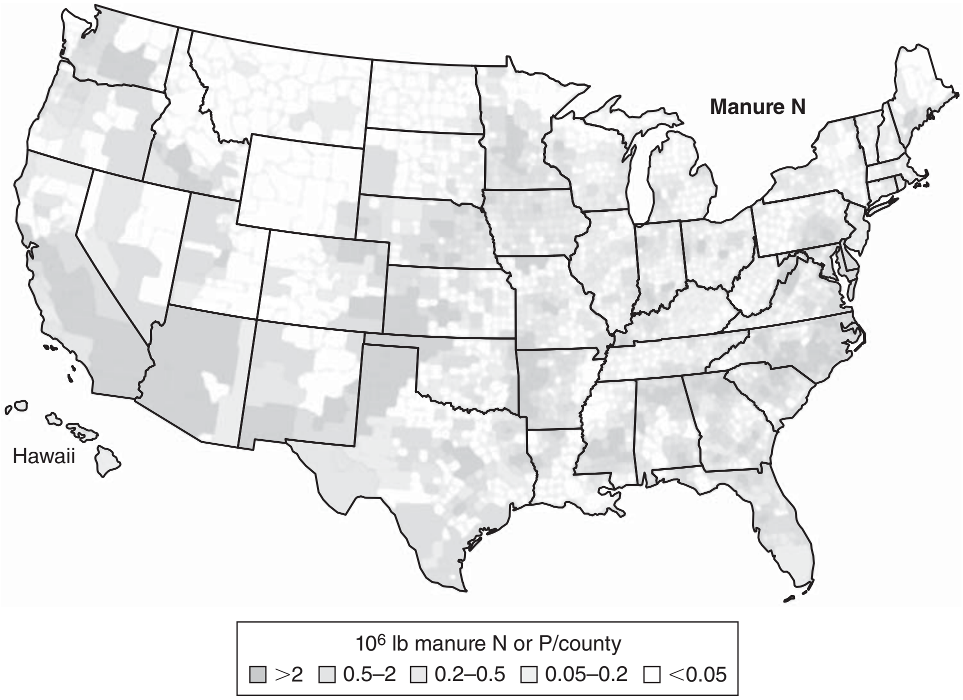


Figure 10-66
Manure N and P in excess of crop need.
(Kellogg et al., 2000, USDA-NRCS, Publication No. nps00-0579.)

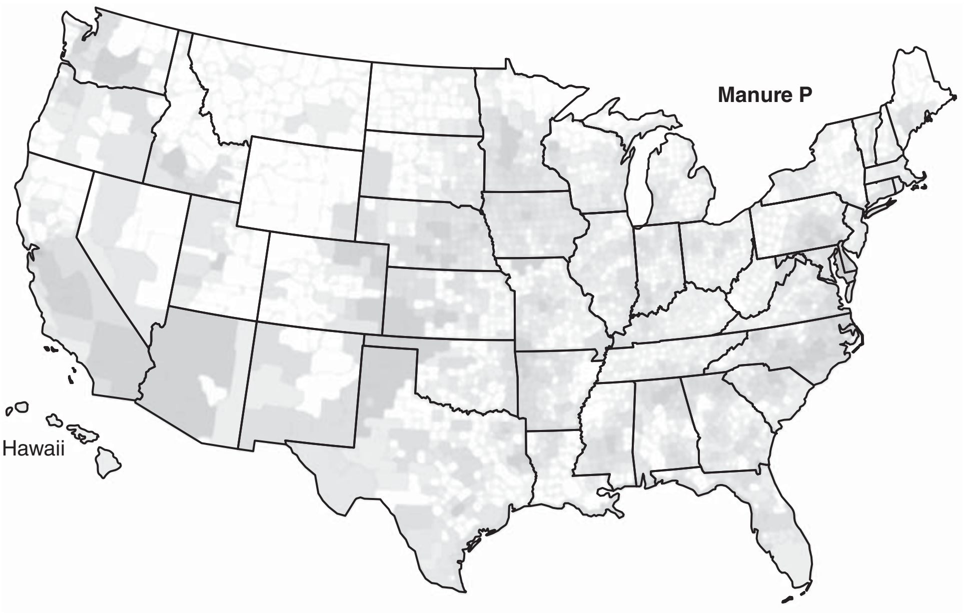


Figure 10-66
(Continued)

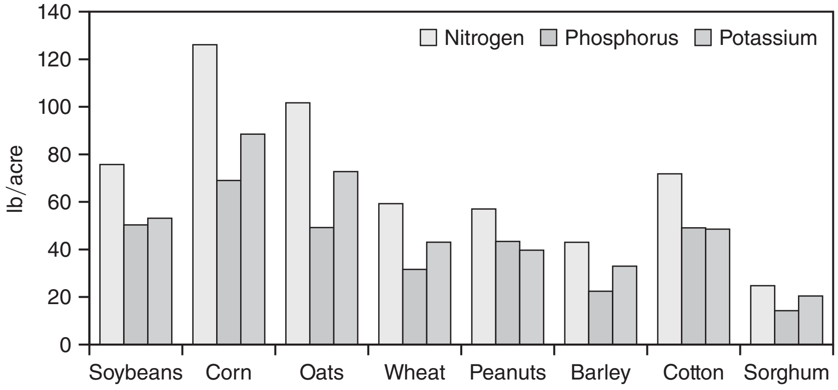


Figure 10-67
Average macronutrient rates applied in manure to major agronomic crops in the United States.

(USDA, 2006, Manure use for fertilizer and for energy/report to Congress, http://www.ers.usda.gov/Publications/AP/AP037/AP037b.pdf, accessed March 25, 2013.)

TABLE 10-18
APPROXIMATE DRY MATTER AND NUTRIENT COMPOSITION OF SELECTED ANIMAL MANURES

			Nutrients (lb/ton)			
			N			
Livestock Type	Waste Handling System	Dry Matter %	*Available*[1]	*Total*[2]	P_2O_5	K_2O
		Solid Handling Systems				
Swine	Without bedding	18	6	10	9	8
	With bedding	18	5	8	7	7
Beef cattle	Without bedding	15	4	11	7	10
	With bedding	50	8	21	18	26
Dairy cattle	Without bedding	18	4	9	4	10
	With bedding	21	5	9	4	10
Poultry	Without litter	45	26	33	48	34
	With litter	75	36	56	45	34
	Deep pit (compost)	76	44	68	64	45

(continued)

TABLE 10-18 (CONTINUED)

Livestock Type	Waste Handling System	Dry Matter %	Nutrients (lb/ton)			
			N			
			Available[1]	*Total*[2]	P_2O_5	K_2O
		Liquid Handling Systems				
Swine	Liquid pit	4	20	36	27	19
	Oxidation ditch	2.5	12	24	27	19
	Lagoon	1	3	4	2	<1
Beef cattle	Liquid pit	11	24	40	27	34
	Oxidation ditch	3	16	28	18	29
	Lagoon	1	2	4	9	5
Dairy cattle	Liquid pit	8	12	24	18	29
	Lagoon	1	2.5	4	4	5
Poultry	Liquid pit	13	64	80	36	96

[1] Primarily NH_4-N, which is plant available during the growing season.

[2] NH_4-N plus organic N, which is slow releasing.

Application conversion factors: 1,000 gal = ~4 t; 27,154 gal = 1 acre-inch

Source: Sutton et al., 1985, Univ. of Minn. Ext. Bull. AG-FO-2613.

Four primary methods used for field application of manure include:

- broadcast solid manure
- broadcast slurry or liquid manure with a vehicle or irrigation system
- subsurface band or injection of slurry or liquid
- surface band-applied preplant or in-season

Methods for handling and storing manure will affect manure nutrient content. Common manure disposal methods include both dry and liquid manure sources (Fig. 10-68). Liquid waste systems have been developed where manure is diluted with water and stored in pits or lagoons and distributed. N-volatilization losses in liquid systems can be substantial (Table 10-19). In an open lot, about 50% of the N is lost. In a lagoon, much of the P settles out and is lost from the liquid applied on the land.

Manure application methods particularly affect N-volatilization losses that reduce the quantity of plant available N applied in the manure (Table 10-20). N losses are greatest with liquid systems and with broadcast solids or liquids. Immediate incorporation will minimize N volatilization (Fig. 10-69). In most cases, little or no N is available if incorporation occurs later than 5–8 days after application. Subsurface application maximizes N availability from manure, but increases application costs. The effectiveness of injected liquid manure can be improved by adding nitrification inhibitors to maintain NH_4-N.

In addition to NH_4^+ present in the manure (Table 10-18), organic N will slowly mineralize over time to supply plant available N. Depending on the manure source, 20–30% of organic N will mineralize the first year after application, decreasing in subsequent years (Table 10-21). The classic studies in England demonstrated substantial residual N availability of continued applications of high manure rates (Fig. 10-70). Even though maintenance of 100% relative yield required annual manure applications, residual effects were observed nearly 40 years after waste applications were stopped.

Figure 10-68
Manure application methods including dry manure spreader (upper left), liquid spreader (upper right), subsurface liquid injection (lower right), and traveling high pressure liquid gun (lower left). (USDA)

TABLE 10-19
EFFECT OF ANIMAL WASTE HANDLING AND STORAGE METHOD ON N LOSSES

Handling/Storing Method *Solid Systems*	N Loss (%)[1]	Handling/Storing Method *Liquid Systems*	N Loss (%)[1]
Daily scrape and haul	15–35	Anaerobic pit	15–30
Manure pack	20–40	Oxidation ditch	15–40
Open lot	40–60	Lagoon	70–80
Deep pit (poultry)	15–35		

[1] Based on composition of waste applied to the land versus composition of freshly excreted waste, adjusted for dilution effects of the various systems.
Source: Sutton et al., 1985, Univ. of Minn. Ext. Bull. AG-FO-2613.

TABLE 10-20
EFFECT OF MANURE APPLICATION METHOD ON N-VOLATILIZATION LOSSES

Method of Application	Waste	N Loss (%)[1]
Broadcast without cultivation	Solid	15–30
	Liquid	10–25
Broadcast with cultivation[2]	Solid	1–5
	Liquid	1–5
Subsurface knife	Liquid	0–2
Irrigation	Liquid	30

[1] % total N in waste applied that was lost within 4 days after application.
[2] Cultivation immediately after application.
Source: Sutton et al., 1985, Univ. of Minn. Ext. Bull. AG-FO-2613.

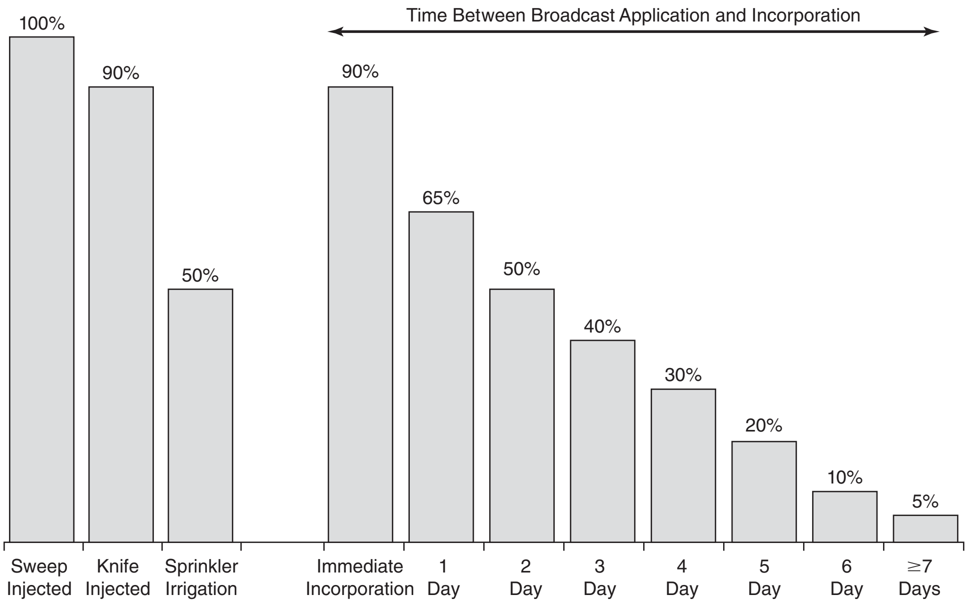


Figure 10-69
Influence of manure application method and length of time between application and incorporation on % plant available N of the original manure N. The majority of the decrease in %N availability is due to N-volatilization losses.
(Leikam and Lamond, 2003, Kansas StateUniv. Coop. Ext. MF2562.)

TABLE 10-21
ESTIMATED QUANTITY OF PLANT AVAILABLE N FROM THE ORGANIC N APPLIED IN MANURE OVER 3 YEARS

Manure Source	Year 1	Year 2	Year 3
		% N Mineralized	
Liquid manure	30	12	6
Solid manure	25	12	6
Compost	20	6	3

Source: Leikam and Lamond, 2003, Kansas State Univ. Coop. Ext. MF2562.

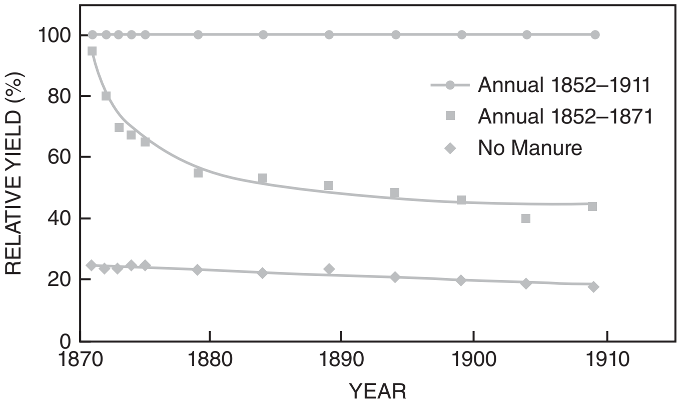


Figure 10-70
Barley yield influenced by long-term manure application. Annual manure application of 30 Mt/ha from1852 to 1911. N availability for mineralizable organic N from manure applied from 1852 to 1871 persisted for 40 years after manure applications were halted in 1871.
(Hall, 1917, The book of the Rothamsted experiments [2nd ed.], E.P. Dutton and Company, N.Y.)

Estimating *plant available N* (PAN) in manure is provided in the following examples:

Solid beef manure (without bedding)—broadcast, incorporate 2 days after application

Total N = 11 lb/t (Table 10-18)
Organic N = 7 lb/t
NH_4-N = 4 lb/t
NO_3-N = negligible

PAN = 4 lb NH_4-N/t × 50% = 2.0 lb available NH_4-N/t (Fig. 10-69)
+7 lb organic N/t × 25% = 1.7 lb plant available organic N/t (Table 10-21)
3.7 lb PAN/t

Liquid swine manure (lagoon)—knife injected

Total N = 4 lb/1,000 gal (Table 10-18)
Organic N = 1 lb/1,000 gal
NH_4-N = 3 lb/1,000 gal
NO_3-N = negligible

PAN = 3 lb NH_4-N/1,000 gal × 90% = 2.7 lb available NH_4-N/1,000 gal (Fig. 10-69)
+1 lb organic N/1,000 gal × 30% = 0.3 lb plant available organic N/1,000 gal (Table 10-21)
3.0 lb PAN/1,000 gal

Many comparisons have been made between the effects of manure on crop production and those obtained from the application of equivalent amounts of N, P, and K in commercial fertilizers. Long-term studies comparing manure and fertilizer sources demonstrate similar crop productivity (Figs 10-71 and 10-72).

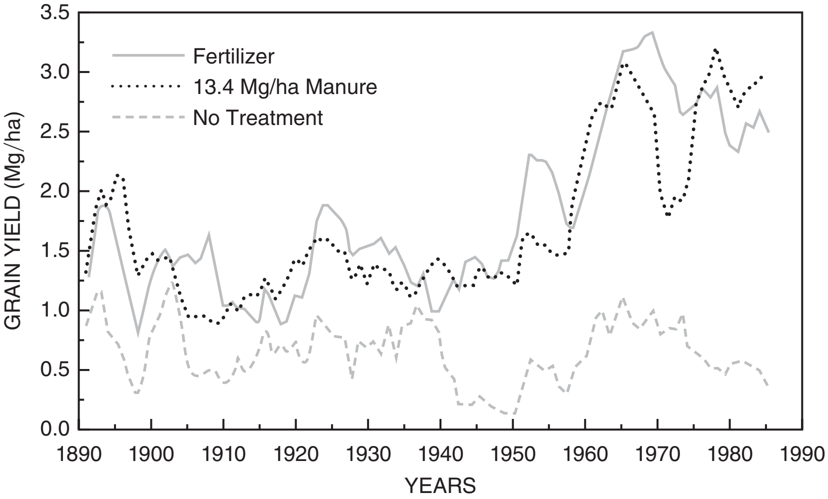


Figure 10-71
Long-term continuous wheat production between manure and fertilizer nutrient sources (1890–1990).
(Sanborn Plots, University of Missouri.)

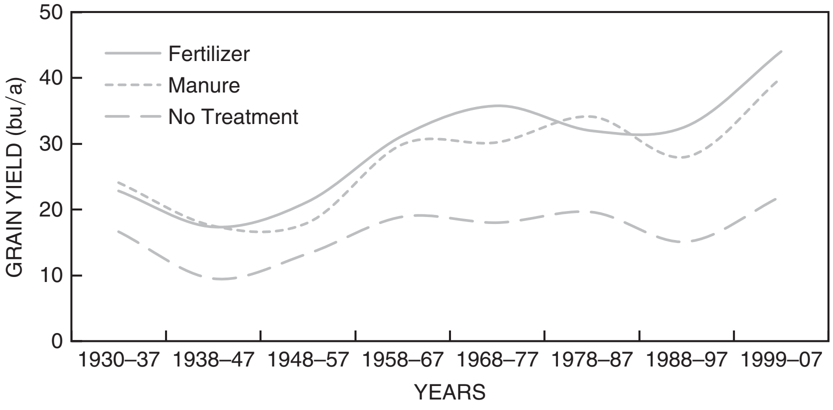


Figure 10-72
Comparison of manure and fertilizer sources on winter wheat yield (1930–2007).
(MagruderPlots, Okla. State Univ.)

Distribution of manure by grazing animals presents a problem in the maintenance fertilization of pastures. For N, which does not remain in effective concentrations for more than a year, about 10% of a grazed area is effectively covered annually. In contrast, residual effects of P from animal wastes may last for 5–10 years. In general, nearly all of a pasture area will receive deposits of manure in a 10-year period. K retention in soil is intermediate between N and P, and manure-applied K is effective to some degree for about 5 years. During this period, about 60% of a pasture will have been covered. With low stocking rates, animal excreta will essentially have no effect on soil fertility. On highly productive pastures with a high carrying capacity, excreta may have a beneficial effect on soil fertility over a period of time.

Producers interested in using manure as a nutrient source in cropping systems should consider:

- high transportation costs potentially result in continued application of manure close to the source, where overapplication is common
- nutrient content in manure is highly variable, causing considerable uncertainty in quantifying nutrient rates applied
- high variability in mineralization of organic N in manure combined with year-to-year environment effects on N mineralization causes uncertainty in estimated N availability to crops
- increased soil compaction can occur with manure application equipment
- possible nutrient imbalances; for example, manure rates based on crop N requirements will result in P applications three to five times the crop requirement (Table 5-14)

Composted Feedlot Manure Composting is being adopted in many regions as an alternative means for handling large volumes of manure produced at confined animal feeding operations. This approach has many benefits, including reduction in mass and volume of material as well as reductions in weed seed viability and fly breeding potential, plus avoiding malodors from land application of manure. N and C losses as high as 30–60%, respectively, accompanied by reductions of 20–30% in dry matter are observed in typical windrowing compost (Fig. 10-73). Consequently, compost bulk density is 3-4 fold higher than manure, reducing transportation costs.

Figure 10-73
Composting animal manure.

Biosolids

Sewage wastes that have undergone treatment to meet specific standards can be used as an agricultural soil amendment and are referred to as *biosolids*. Biosolids are nutrient-rich materials from the treatment of municipal wastewater and contain nutrients beneficial to plants and some heavy metal elements that must be monitored in soils and in plants. Interest in disposal of biosolids is increasing because of increasing population-generated wastes, and the need to recycle these materials as energy and fertilizer costs continue to increase. Use of biosolids can benefit agricultural production because of the relatively high OM and nutrient content and is an effective alternative to more costly methods of disposal, such as burning or burying (landfills).

Land application of biosolids is regulated by federal and state governments. Prior to land application, biosolids are treated to reduce pathogens, odor, and heavy metal content.

The United States divides biosolids into two grades: *class A* biosolid has been treated to reduce bacteria prior to application to land; *class B* biosolid has not. Class A biosolid is the most rigorous, with no application site restrictions (i.e., all crops, lawns, gardens, and public accessible areas). Class B biosolid receives less rigorous treatment, with site restrictions related to crop harvest, animal grazing, and public access. Biosolids are also treated with lime, partial composting (aerobic and anaerobic), and dehydrated to reduce odor and the potential to attract flies and other disease-transmitting organisms (vector attraction reduction).

Like manure, biosolids contain both inorganic and organic N (Table 10-22). Biosolid application rates to crops are determined by crop N requirement and biosolid N content similar to manure rates. Most of the inorganic N occurs as plant available NH_4^+. During and after application, the quantity of NH_3 volatilized depends on application method (Table 10-23). Subsurface application or immediate incorporation will minimize N volatilization losses and increase plant available N.

As with manure, organic N will slowly mineralize to provide plant available N. Because of variation in organic N content, biosolid application rate, and yearly variation in environment controlling N mineralization rate, it is difficult to assess

Table 10-22
Typical Elemental Analysis of Biosolids on a Dry Weight Basis

Component	Concentration	Component	Concentration	Cumulative Loading Limit
	%		*ppm*	*lb/a*
Organic C	50–60	Hg	1–15	15
Organic N	3–6	Zn	700–2,800	2,464
$NH_4^+ + NO_3^-$	1–2	Cu	500–1,500	1,320
P_2O_5	2–4	Mn	50–400	–
K_2O	0.2–0.3	B	20–85	–
Ca	3	Cd	5–50	34
Mg	1	Pb	50–300	264
S	0.9	Ni	20–400	370
Fe	1–3	As	15–50	36
		Se	5–70	88

Source: Stehouwer, 2011, Penn. State Univ. (http://cropsoil.psu.edu/extension/esi/biosolids-use, accessed March 25, 2013).

TABLE 10-23
EFFECT OF BIOSOLID APPLICATION METHOD ON NH_3 VOLATILIZATION

Application Method	NH_3 Loss (%)
Broadcast	40–60
Broadcast and incorporation within 3–4 days[1]	10–30
Subsurface band or injection	<2

[1] Increasing time between application and incorporation increases NH_3 loss.

the annual contribution of organic N mineralization to plant available N. First-year N mineralization rates range between 10 and 40% depending on the biosolid source (Table 10-24). When waste is applied annually, N mineralization contributions from both current and past applications must be considered in estimating plant available N. The declining amounts of mineralizable N with time from previous biosolid applications are considered in the determination of total PAN:

$$
\begin{aligned}
\%\text{PAN} = {} & \text{NO}_3\text{-N} \\
& + \%\ \text{volatilization loss} \times \text{NH}_4\text{-N} && \text{(Table 10-23)} \\
& + \text{mineralization rate (1st year)} \times \text{organic N*} && \text{(Table 10-24)} \\
& + \text{mineralization rate (past years)} \times \text{organic N*}
\end{aligned}
$$

where $\text{*Organic N} = \text{Total N} - \text{Inorganic N}\ (\text{NO}_3\text{-N} + \text{NH}_4\text{-N})$

Like animal waste, biosolids applied at agronomic N rates often results in P and micronutrient application in excess of crop requirement. Eventual buildup of these elements can pose environmental concerns. In contrast, K content in biosolids is low, and supplemental fertilizer K may be needed if soil test K is below the CL.

Biosolid application is regulated to *lifetime loading rates* determined by cumulative application of eight elements (Table 10-22). Cumulative loading represents the maximum total amount (lb/a) of each element that can be applied to a field. Background concentration of the eight elements is documented prior to biosolid application. With each biosolid application, the lb/a of each element applied is added to the initial background level. Biosolid application to a field is prohibited when lifetime loading rate has been reached. It is essential that appropriate application and soil management techniques be used to protect the environment and human health.

TABLE 10-24
N MINERALIZATION RATES FOR VARIOUS BIOSOLID MATERIALS OVER THREE CROPPING SEASONS AFTER APPLICATION

	% N Mineralization		
Sludge Type	*Year 1*	*Year 2*	*Year 3*
Unstabilized	40	20	10
Lime stabilized	30	15	7
Aerobic digestion	30	15	7
Anaerobic digestion	20	10	5
Composted	10	5	2

NUTRIENT MANAGEMENT IN TURF

Turfgrass production is a rapidly growing component of agriculture. Regardless of its use in residential or recreational environments, effective nutrient management is essential to turfgrass quality, durability, and aesthetic appeal. A comparison of relative nutrient contents of several turfgrasses is provided in Table 9-1. The primary difference between most agricultural crops and turfgrass is that most of the nutrients applied to turf systems are not removed, but recycled through soil OM components as the residues are degraded (Fig. 4-2). Most of these nutrients ultimately become plant available in subsequent years. In addition to soil tests, plant tissue can be sampled to assess nutrient status and adequacy of the fertilization program. Samples are collected by clipping leaves slightly above the soil surface several days after regrowth (Table 9-3). Nutrient sufficiency ranges are provided in Table 9-4.

Nitrogen

N requirements of turfgrass are greater than any other nutrient, which is similar to other agronomic crops (Table 9-1). Adequate N maintains a desirable dark-green leaf color, prolific tillering or shoot density, and some tolerance to other nutrient and pest stresses. Excessive N accumulation in turf increases growth and H_2O use, enhances susceptibility to diseases, and reduces tolerance to heat stress. Reduced root, stolon, and rhizome growth with increased heat and water stress results in thin, uneven growth patterns.

The goal of an efficient N management program is to provide adequate N to support vigorous growth without overfertilization. Recommended annual N rates depend on the turfgrass species, desired turfgrass quality, and soil type. N contribution from the irrigation water should also be factored into the N recommendation. Most turfgrass N recommendations range between 1 and 8 lb/1,000 ft^2 (40–350 lb N/a) annually (Table 10-25). Because N is mobile in the soil, two to four applications throughout the season are recommended. More frequent applications result in higher quality and longer periods of dark-green color. Because of the midspring to midsummer and mid- to late-fall active growth pattern in cool-season grasses (e.g., bluegrass, ryegrass, and fescue), maintaining high forage quality requires three to four applications of 1 lb/1,000 ft^2 in late fall and early spring (Table 10-25). Warm-season grasses (e.g., bermuda grass and zoysia) exhibit active growth from midsummer through midfall. N is applied in midspring (1 lb/1,000 ft^2), followed by monthly applications through early fall. Low N rates ($<$1.5 lb/1,000 ft^2) should be used with soluble N sources to maximize N recovery by the plant and to minimize N leaching. Higher rates can be used with slow release N sources (Tables 4-23 and 4-24).

Continued use of N fertilizers will depress soil pH (Table 3-5). Monitor soil pH changes with periodic soil testing and apply lime to maintain soil pH at 6–6.5.

Phosphorus

Although used in smaller amounts than N, P is important for early seedling vigor, stand establishment, and spring regrowth (Chapter 5). P is especially important for establishing new turfgrass areas. In low P soils, increasing P availability improves N utilization and recovery. P deficiencies are uncommon in established turfgrass, where clippings are usually left on the surface, and many mixed turf fertilizers contain P. Soil testing is the best tool to identify low P soils and the need for P fertilization. Where soil test P is high, fertilizers that contain P are not necessary. Overapplication of P will increase surface loss of soluble P, which can degrade surface H_2O quality (Chapter 12).

TABLE 10-25
OPTIMUM ANNUAL N APPLICATION RATES AND TIMING FOR SELECTED TURFGRASS SPECIES[1]

Turf Species	Annual N Rate *lb/1,000 ft²*	Number of Applications *1*	*2*	*3*	*4*
Fine leaf fescue	1–2	EF	EF, ES	EF, ES, LF	EF, ES, MR, LF
Tall fescue	2–4	EF	EF, ES	EF, ES, LF	EF, ES, MR, LF
Perennial ryegrass	2–4	EF	EF, ES	EF, ES, LF	EF, ES, MR, LF
Kentucky bluegrass	2–4	EF	EF, ES	EF, ES, LF	EF, ES, MR, LF
Bermuda grass	4–8	ES	ES, MR	ES, ER, LR	ES, ER, MR, LR
St. Augustine grass	2–4	ES	ES, MR	ES, ER, LR	ES, ER, MR, LR
Zoysia	2–4	ES	ES, MR	ES, ER, LR	ES, ER, MR, LR

[1] E=early; M=mid; L=late; S=spring; R=summer; F=fall

Potassium

Turfgrass can require as much K as N, although N is usually the most limiting. Using adequate N without K enhances plant susceptibility to diseases and drought stress. With high N rates, higher K rates are required to maintain turfgrass quality. Balanced N and K nutrition encourages root, stolon, and rhizome growth important for maintaining optimum turf density; H_2O use efficiency; winter hardiness (in northern climates); and tolerance to heavy traffic. An N:K ratio of 2:1 in leaf tissue is considered normal. Early fall-applied K improves winter hardiness in northern climates, while early spring-applied K preceding heat or water stress periods is beneficial in southern climates. Fertilizers with a 1:1 ratio of N:K will supply adequate K in most cases. K fertilizers have higher salt indices than most N and P sources; thus, caution is recommended with applications at germinating and seedling growth stages (Table 10-2). The salt index with K_2SO_4 is lower than other K sources.

Sulfur

Turfgrass usually requires more S than P. Adequate S nutrition is important for protein and chlorophyll synthesis that greatly contributes to a healthy, dark-green color (Chapter 7). S-deficiency symptoms are often mistaken for N stress. S is also essential for maximizing recovery of N and K, which is important in reducing N leaching potential. Annual S rates are 0.5–2 lb/1,000 ft^2, either as a single application in early spring or split applied with N in the spring and fall. Split applications of S reduce the potential for S leaching, especially in sandy soils (Chapter 7).

Micronutrients

Dark-green turf color is also related to Fe and Mg nutrition, since these nutrients function in chlorophyll synthesis. Early spring and midsummer applications are recommended. Soil testing provides the best guide to identifying soils low in plant available micronutrients. Foliar-applied Fe can enhance turf greenness, even with adequate Fe availability.

NUTRIENT MANAGEMENT PLANNING

Adoption of *best management practices* (BMPs) for nutrients should increase plant productivity (yield and quality), increase profitability, maintain or improve soil fertility and productivity, and avoid damage to the environment. The basic requirements of good soil fertility, nutrient availability, and efficient plant use of applied nutrients include:

- optimal soil pH for the specific plant grown
- sufficient soil OM for improved soil structure, H_2O holding capacity, nutrient supply, and microbial activity
- porous soil structure with no limits to root growth, infiltration, or drainage
- removal or neutralization of toxic elements (Al in strongly acid soil, Na in saline/alkali soils, or heavy metal contaminants)

Implementation of BMPs for plant nutrients can be challenging due to many uncontrollable variables; however, efficient nutrient management should start by avoiding common mistakes:

- less than optimum soil pH, OM, and soil structure reduce nutrient supply, plant growth, and nutrient use efficiency (NUE)
- unrealistic yield goals may cause overapplication of nutrients reducing NUE and increasing risk of nutrient loss from the root zone
- not using or misuse of readily available soil and plant nutrient diagnostic techniques
- failure to recognize high nutrient requirements of selected plants
- unbalanced nutrient availability may cause hidden hunger that reduce plant yield
- while nutrient additions may be recognized, optimum nutrient response and NUE will be realized only with the optimum rate, source, placement, and/or application timing of recommend nutrients

A nutrient management plan must be developed for each field and includes the following information.

Field and Soil Map

A field map illustrating field boundaries, soil types, and elevation enables assessment of crop land areas, proximity to water bodies, water wells, residences, and other objects. Yield history of each manageable subfield area is essential to identifying potential productivity that influences nutrient availability, retention, and need.

Soil Testing and Plant Analysis

Accurate soil test information depends on a quality soil sampling plan guided by the field and soil map (Chapter 9). This information provides the foundation for assessing the soil's ability to supply plant available nutrients and establish nutrient recommendations. Plant analysis information from previous crops should be reviewed for areas with nutrient levels below or above their critical range.

Crop and Crop Rotation

Previous crop and yield level is important information, especially with legumes. Low legume yield in the previous year will provide less legume available N than a high yielding legume crop. Surface residue condition and specific crop will guide nutrient placement decisions.

The intended crop will determine the general nutrient requirements. Recognize specific plants with high requirements for certain nutrients.

Yield Expectation

Realistic yield expectations are essential to estimating nutrient needs. Historical yield records for each field provide the best record for determining expected yield level. Overestimating yield results in overapplication of nutrients with potential negative impacts on environment, while underestimating yields results in underapplication of nutrients and loss of yield and profitability.

Nutrient Sources

If soil physical conditions are not optimum, increasing soil OM may be warranted. Quantifying nutrient content (and mineralization rate) of organic amendments is essential to balanced nutrient supply and meeting the projected nutrient need of the plant. Selection of fertilizer sources is based on crop need, soil properties, and cost. Selected nutrient sources should optimize nutrient supply just ahead of peak nutrient demand.

Recommended Rates

Recommended rates are determined through evaluation of expected yield potential, native soil nutrient supply, and efficiencies of crop recovery of applied nutrients. Most soil testing laboratories provide recommended nutrient rates. While these recommendations are good guides, adjustments should be made to satisfy requirements for specific field conditions. Match the nutrient rate to crop need (Fig. 10-74). Excess nutrients may enhance losses to the environment, while too little reduces yield and/or quality. Utilize appropriate diagnostic tools (crop scouting, soil and plant analysis, field tests, variable rate technology, record keeping, etc) to evaluate nutrient sufficiency. Documenting nutrient response of previous crops is essential to quantify the most efficient nutrient rate for the intended crop.

Application Timing

Nutrient application timing depends on the specific nutrient and the crop growth pattern. Mobile nutrients should be applied just prior to the maximum uptake or growth period. This may require in-season split applications or controlled release sources (N) to maximize nutrient use efficiency. With immobile nutrients, preplant applications are generally recommended.

Placement Method

Many placement options exist that greatly influence nutrient availability and crop recovery of applied nutrients. For example, broadcast N with surface residue cover reduces N recovery by the crop. Band-applied P can substantially increase yield in low P soils compared to broadcast P. Placement decisions are based on specific nutrient and intended crop.

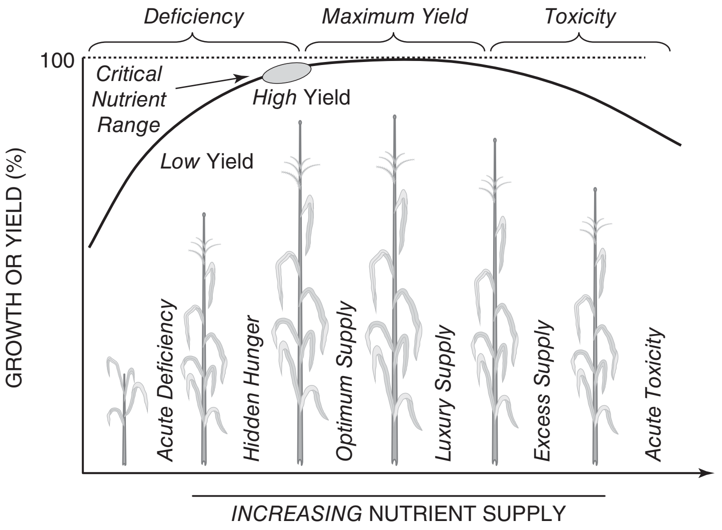


Figure 10-74
Optimum nutrient supply is essential for maximizing plant growth and nutrient use. Nutrient addition beyond critical nutrient range does not increase plant growth and reduces nutrient use efficiency.

Proximity to Nutrient-Sensitive Areas

Assessment of the field and potential nutrient transport will help prevent nutrients from entering unwanted areas (e.g., streams, ponds, groundwater, water wells). Use of riparian buffers, grassed waterways, conservation tillage, and other management practices reduces potential nutrient transport off the field (Chapter 12).

Assessment and Revision

After each crop season, the nutrient management plan should be evaluated relative to crop productivity and profitability. Adjustments should be made with any nutrient-related decrease in yield or quality.

Regardless of the nutrient source (organic or fertilizer), adopting nutrient BMPs will help ensure efficient nutrient supply to the target crop, which should minimize offsite impacts of nutrient use.

While recycling and use of all available organic nutrient sources is beneficial to both the supplier and user, fertilizer nutrients are essential to meet the growing global population demand for food, fiber, feed, and other products generated from plant materials.

STUDY QUESTIONS

1. Why is root growth stimulated in response to plant nutrients in infertile soil? What root characteristics influence the ability of crops to exploit soil for moisture and nutrients?
2. Describe soil conditions that might affect depth of rooting.
3. Why might the nature of the root system of the crop being grown affect the decision to build up the fertility level of the soil versus applying fertilizer in the row? How would the economic status of the farmer affect the decision?
4. Explain how band and broadcast applications complement each other in encouraging efficient crop production.
5. Explain why crops are more likely to experience salt injury on a sandy soil than on a silt loam.
6. Why can P materials be placed close to the seed or plant? Why is it usually important that P be close to the seed or young plant?
7. You have the choice of broadcasting and plowing down, broadcasting and disking in after plowing, or subsurface band apply. Which method would be most desirable for N and P? Explain fully.
8. Under what conditions is surface broadcast P and K taken up by the plant?
9. Why does NH_4-N applied with P cause more P to be absorbed by the plant?
10. What are the risks associated with fall N fertilization?
11. Explain how mycorrhizas function and their influence on nutrient use.
12. What is meant by *residual nutrient availability*? Using Figure 10-63, estimate the number of years required for soil test P to decline below the critical level if no P is applied in each soil.
13. Are there residual benefits from NO_3-N in soils? What conditions would you expect to measure residual N?
14. There are three philosophies of managing immobile nutrients: buildup, maintenance, and drawdown. Describe situations where each would be the most appropriate management.
15. What is foliar fertilization? Discuss any limitations.
16. What is fertigation and what are its advantages and drawbacks?
17. How is the distribution of plant nutrients in the root zone modified by tillage?
18. Explain why deeper placement of plant nutrients is likely to give a greater response than shallow placement in some areas.
19. Explain why conservation tillage often requires a change in nutrient management. Why might higher rates of N be required for no tillage compared to conventional tillage?
20. Ten grams of NH_4NO_3 (34% N) is added to 3,000 g of greenhouse soil. Calculate the following:
    a. mg NH_4NO_3 added
    b. mg N added
    c. ppm N added
    d. ppm NO_3 added
    e. ppm NH_4 added
    f. %N in soil after adding N
    g. lb N/afs

22. A farmer wants to apply 160 lb N/a. Calculate the following:
    a. lb NH_3/a
    b. kg NH_3/ha
    c. lb urea/a
    d. lb UAN/a
    e. gal UAN/a (assume 10.8 lb/gal)
23. A homeowner applies 3 lb N/1,000 ft^2. Calculate the lb N/a applied.
24. A golf green manager applied N to each green at 75 lb N/a. Each green is 600 ft^2. Calculate the following:
    a. lb N/green
    b. lb UAN/green
    c. gal UAN/green
25. A homeowner applies ten 40-lb bags of fertilizer (10% N content) to a 2,000 ft^2 fescue lawn. Calculate lb N/a applied and indicate whether this is a normal, high, or low N rate.
26. Broadcast N usually is less efficient than subsurface N in high surface residue cropping systems. Using the following data, calculate the %N recovery for each system. What caused the difference? [%N recovery $=$ (N uptake$_{\text{fertilizer + soil}}$ $-$ N uptake$_{\text{soil only}}$)/N rate $\times$ 100.]

	Broadcast N	*Subsurface N*	*Unfertilized*
N rate	100 lb N/a	100 lb N/a	0 lb N/a
Grain yield	98 bu/a	110 bu/a	75 bu/a
Test weight	56 lb/bu	56 lb/bu	56 lb/bu
% grain N	2.1	2.4	1.8

27. A biosolid has the following analysis: 0.5% NO_3-N, 0.8% NH_4-N, and 6% total N. The material was broadcast and immediately incorporated. Using Tables 10-23 and 10-24, estimate PAN.
28. Explain the growth curve of a plant.
29. What is meant by nutrient management?
30. What is meant by soil tillage?
31. What is meant by nutrient placement? What factors should be considered in determining proper placement of applied nutrients?
32. Illustrate the various possible nutrient placement options in soil diagramatically.
33. What are the advantages of broadcast placement? Briefly explain, why it is considered as an effective method that prevents potential seedling damage.
34. What are the disadvantages of broadcast application?
35. What is the principle of fertigation?
36. List some of the beneficial effects of manure use.
37. What are the commonly used methods for field application of manure?
38. What is total PAN? How is it determined? Give the formula and explain.
39. What are the salient features of a nutrient management planning?
40. What do you mean by crop rotation?
41. How does the placement method influence the nutrient availability and crop recovery of applied nutrients?

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11

Nutrient Interactions and Economics

NUTRIENT INTERACTIONS

Adequate plant nutrition depends on nutrient supply and nutrient balance. Nutrients interact when increasing one nutrient influences nutrient uptake or translocation of another nutrient. Thus, assessing nutrient interactions requires understanding relationships between soil nutrient supply and plant growth, and between plant nutrient concentrations and plant growth.

Although interactions between nutrients can be positive, negative, or neutral, it is usually negative interactions that are the most documented. An interaction occurs when plant response to two or more inputs is different than the sum of responses to the individual inputs (Fig. 11-1). A *zero* interaction occurs when cumulative plant response is the simple addition of responses to individual inputs:

- response to nutrient A $= 100$
- response to nutrient B $= 50$
- response to A $+$ B $= 150$

Positive (synergistic) interactions occur where the combined response to two limiting nutrients is greater than the sum of the individual responses:

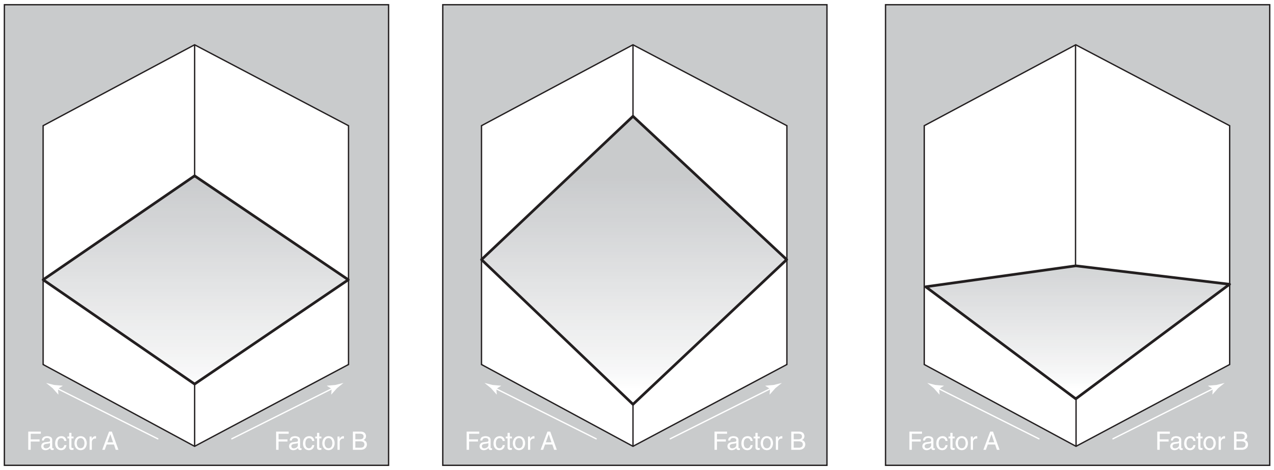
- response to nutrient A $= 100$
- response to nutrient B $= 50$
- response to A $+$ B > 150

Negative (antagonistic) interactions result when plant response to the combined nutrients is less than the response to the two inputs applied separately:

- response to nutrient A $= 100$
- response to nutrient B $= 50$
- response to A $+$ B < 150

Negative interactions are often observed by either a deficient or toxic plant nutrient concentration (Fig. 9-4) caused by an imbalance in soil nutrient supply. Many antagonistic interactions can be avoided by maintaining a balanced nutrient supply. Assessment of nutrient ratios can be misleading since the same nutrient ratio can occur when both nutrients are deficient or both are excessive.

Nutrient interactions frequently influence plant growth when (1) two nutrients are deficient, or (2) there is an excessive supply of one nutrient, while another is



Zero Interaction

Growth response to Factor A and Factor B is additive. The additional growth or yield realized by adding Factor A and B is equal to the sum of the responses of each factor individually.

Positive Interaction

Growth response to 2 factors is greater than the sum of the responses of the factors individually. The influence of either factor alone will be much less than the influence applied together.

Negative Interaction

Growth response to Factors A and B combined increases yields less than when they are applied separately.

Figure 11-1
Influence of zero, positive, and negative interactions between two factors on crop growth.

marginally sufficient. In the first case, positive nutrient interactions are often observed, as both yield and nutrient concentration increase with increasing balanced nutrient supply. In the second case, nutrient deficiency (second nutrient) is induced by excess nutrient supply (first nutrient). Yield increases from an application of one nutrient can reduce the concentration of the second nutrient, but the greater plant growth results in greater uptake [yield × nutrient concentration (%)] of the second nutrient. This dilution effect should be distinguished from an antagonistic effect, which occurs only if the nutrient concentration decreases below the critical range (Fig. 9-4).

Many interactions are not observed with average yields; however, under high yield environments, nutrient demand is greater and nutrient interactions are more likely. Nutrient responses are influenced by many crop (variety, plant population, row spacing, etc.), soil (plant available water, tillage, compaction, etc.), and environment factors that must be carefully managed to optimize plant productivity and nutrient use efficiency. Future increases in agricultural productivity will likely be related to manipulation of interactions between numerous management inputs and other plant growth factors. It is essential that growers recognize and take advantage of nutrient interactions.

Interactions Between Nutrients

Macronutrients N-P and N-K interactions are commonly observed. For example, under low pH, grain yield responses to N and P are substantially reduced compared to responses on optimum pH soil (Fig. 11-2). Crop response to N is greatly reduced when P is limiting, where adequate N and P supply substantially increases grain yield compared to N or P applied alone (Table 11-1). In addition to grain yield response, recovery of applied N is increased and residual fertilizer NO_3-N in the soil profile

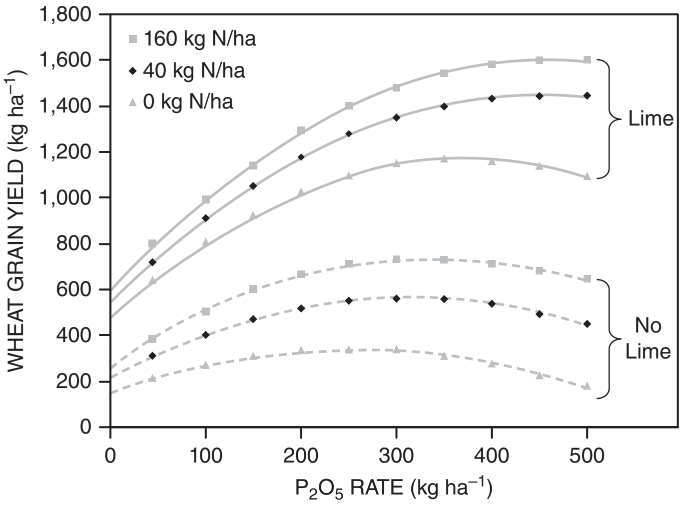


Figure 11-2
Influence of lime application on wheat yield response to broadcast N and P on an acid sandy soil. About 8 t/ha lime increased soil pH from 4.4 to 6.2.

(*Adapted from Goedert, 1987, In Sanchez et al. (Eds.).* Mgmt. Acid Tropical Soils Sust. Agric. Proc. *[pp. 109–127]. IBSRAM Inaugural Workshop, Bangkok, Thailand.*)

TABLE 11-1
N-P INTERACTION ON CORN, WHEAT, AND GRAIN SORGHUM YIELD

Corn			Wheat			Grain Sorghum		
N Rate	P_2O_5 Rate	Yield	N Rate	P_2O_5 Rate	Yield	N Rate	P_2O_5 Rate	Yield
lb/a		*bu/a*	*lb/a*		*bu/a*	*lb/a*		*bu/a*
0	0	41	0	0	32	0	0	45
200	0	50	30	0	42	90	0	87
0	160	58	30	30	45	0	30	88
200	160	123	60	0	38	90	30	101
			60	60	58			

Source: Adapted from *Better Crops*, 1999, 83(1):11–13.

is decreased with application of N + P on low P soils (Fig. 11-3). N rate required for optimum yield was higher with 40 lb P_2O_5/a (160 lb N/a) compared with no P (80 lb N/a). When both N and P were adequate, fertilizer N recovery was approximately 75% compared with 40% without adequate P fertilization. Maximizing crop recovery of fertilizer N reduced profile NO_3-N after harvest (Fig. 11-3). The rooting depth is approximately 4–5 ft and without adequate P supply a significant quantity of applied N moved below the root zone. Thus, adequate N and P supply

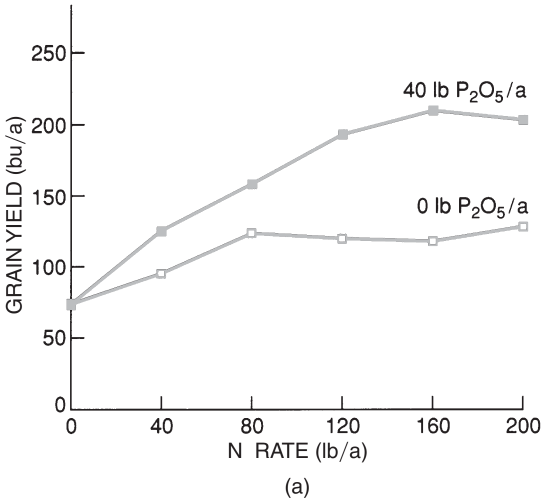
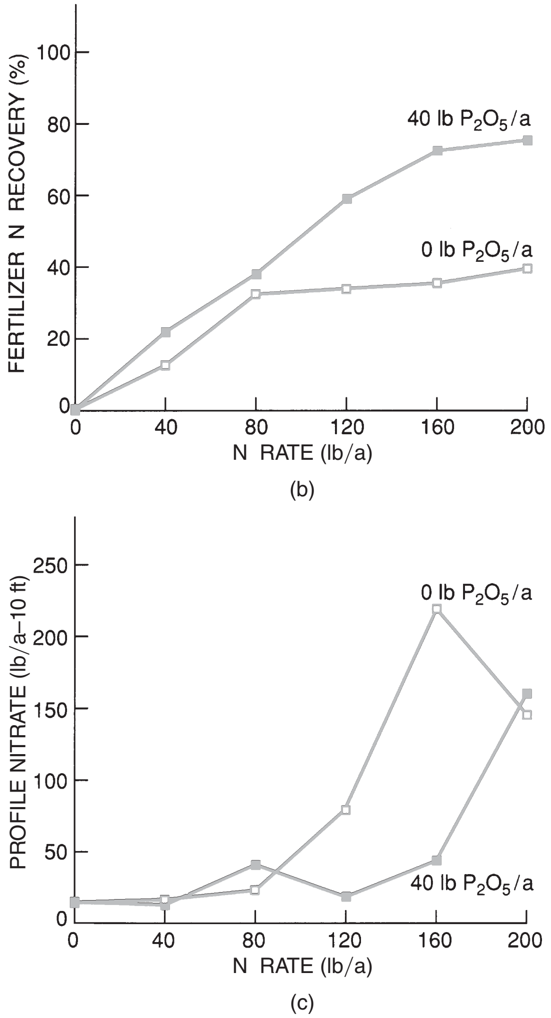


Figure 11-3
Interaction of N and P fertilization on irrigated corn grain yield (a), fertilizer N recovered in the grain (b), and profile NO_3 after harvest (c).

(*Schlegel et al., 1996,* J. Prod. Agric., *9:114–118.*)

Figure 11-3
(Continued)



will optimize yield and maximize fertilizer N recovery while minimizing environmental impact of N use.

N-P interactions are observed with many different crops (Table 11-2). Positive N-K interactions on grain yield are also commonly observed with increasing K fertilization or

TABLE 11-2
N × P INTERACTION ON YIELD AND N USE EFFICIENCY (NUE) IN SELECTED CROPS

Crop (kg N/ha-kg P_2O_5/ha)	Parameter[1]	Fertilizer Treatment *Unfertilized*	*N Only*	*P Only*	*N + P*
Wheat	Grain yield	1,750	4,187	1,947	5,057
(120–60)	NUE		20		26
Rice	Grain yield	2,940	5,530	3,243	6,190
(120–60)	NUE		22		25
Corn	Grain yield	1,190	4,750	2,250	6,750
(120–60)	NUE		36		45
Sorghum	Grain yield	2,270	3,670	3,450	5,500
(120–60)	NUE		12		17
Sunflower	Grain yield	1,470	1,995	1,672	2,426
(60–30)	NUE		9		13
Field pea	Grain yield	2,180	2,592	2,422	3,028
(40–30)	NUE		10		15

[1] Grain yield (kg/ha); NUE (kg grain/kg N).

Source: Adapted from Aulakh and Malhi. 2004. In Mosier et al. (Eds.). *Agriculture and the nitrogen cycle.* Washington, D.C.: Island Press.

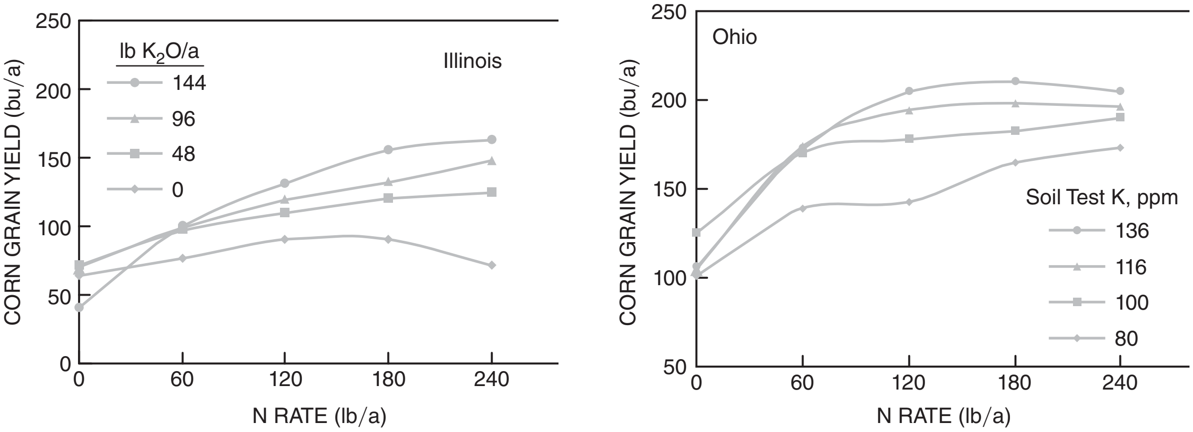


Figure 11-4
Influence of K fertilization (Illinois) and soil test K (Ohio) on corn response to N. (Better Crops, *1998, 82[3]:12–13.*)

TABLE 11-3
P-K INTERACTION ON SOYBEAN, WHEAT, AND COASTAL BERMUDA GRASS YIELD

Soybean			Wheat			Coastal Bermuda Grass		
P_2O_5	K_2O	Yield	P_2O_5	K_2O	Yield	P_2O_5	K_2O	Yield
lb/a		*bu/a*	*lb/a*		*bu/a*	*lb/a*		*lb/a*
0	0	26	0	0	52	0	0	2.69
30	0	31	60	0	77	100	0	3.26
0	120	46	0	80	64	0	300	2.65
30	120	55	60	80	91	100	300	4.57

Source: Adapted from *Better Crops*, 1999, 83(1):11–13.

soil test K (Fig. 11-4). Similar P-K interactions are also common, where plant response is considerably lower with P or K alone compared to P + K (Table 11-3).

Micronutrients Interactions with micronutrients can be dramatic. For example, on a soil testing low in P and Zn, adding P without Zn decreased yield by 12 bu/a, while adding Zn without P decreased yield by 22 bu/a (Fig. 11-5). When both nutrients were applied, a positive interaction occurred, increasing yield by 44 bu/a. Similar responses with P applied on marginally Fe-deficient calcareous soils are also common.

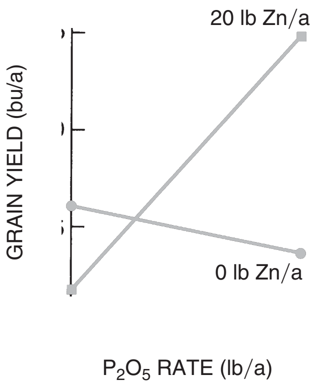


Figure 11-5
Interaction of P and Zn fertilization on corn yield.
(*Ellis, 1967,* Kansas Fert. Handbook, *Kansas State Univ., Manhattan, Kans.*)

Depending on plant species, soil, and environmental conditions, excessive Mg^{+2} can have an antagonistic effect on K^{+} absorption, while excessive K^{+} supply can reduce absorption of Ca^{+2} and Mg^{+2} (Fig. 11-6). While negative Ca-Mg and Ca-K interactions have been observed, they are less frequent or pronounced as K-Mg interactions. Increasing Ca supply has little influence on macronutrient cations, but can substantially reduce absorption of Mn, Fe, and Zn (Fig. 11-7). Increasing Ca concentration enhances oxidizing ability of roots decreasing Mn, Fe, and Zn solubility.

Many nutrient interactions influence plant growth and nutrient content; only a few examples have been provided. The most probable nutrient interactions in a given cropping system involve nutrients that are deficient or marginally deficient.

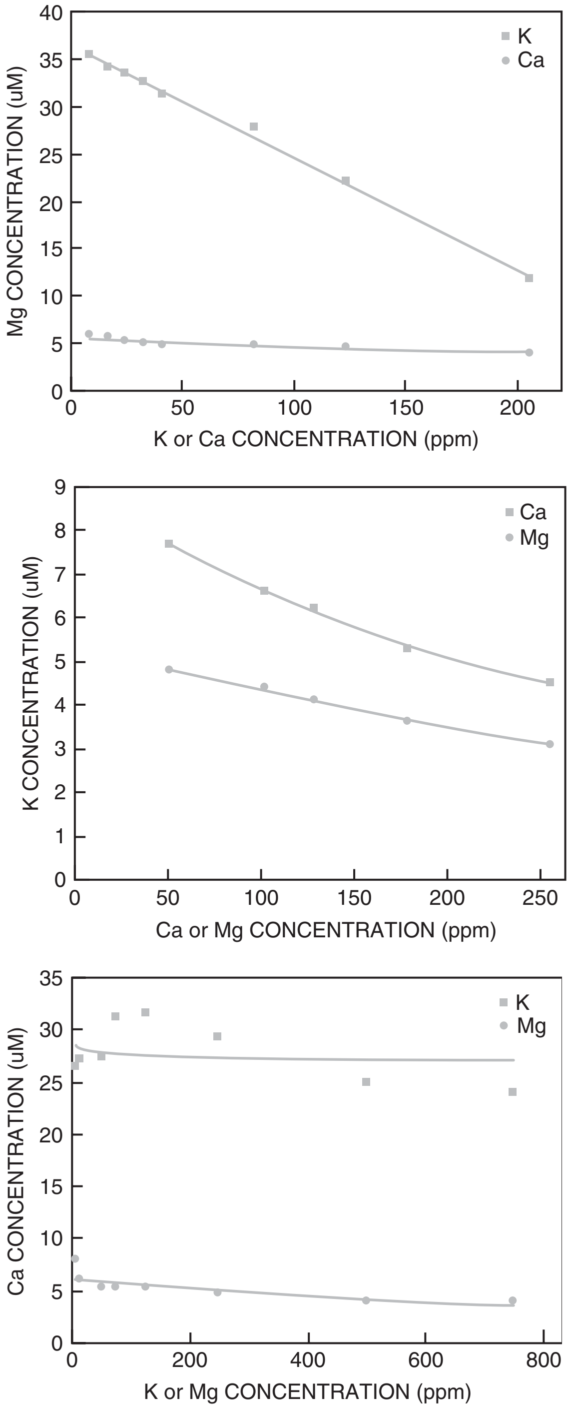


Figure 11-6

K, Ca, and Mg interactions in rice seedlings grown in solution culture.

(*Adapted from Fageria, 2001,* J. Plant Nutr., *24:1269–1280.*)

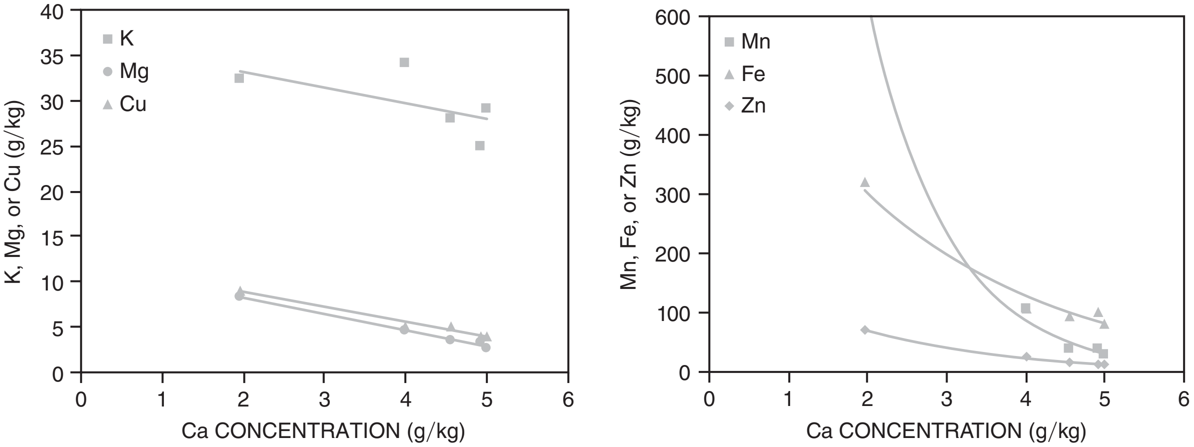


Figure 11-7

Influence of increasing Ca supply on macro- and micronutrient uptake in dry bean grown in soil.

(*Adapted from Fageria, 2001,* J. Plant Nutr., *24:1269–1280.*)

Therefore, a good soil testing program will enable the grower to anticipate potential nutrient interactions.

Nutrient–Crop Management Interactions

Population (row spacing) Increasing plant population may not increase yield without increasing available nutrients, while increasing nutrient supply without sufficient plant population to utilize the additional nutrients may also not increase yield. For example, under low rainfall and N supply (0 lb N/a), increasing plant population decreased corn yield due to substantially greater crop N demand relative to N supply (Fig. 11-8a). As N supply increased, higher plant populations provided higher plant yield compared to low population. In a year with greater plant available H_2O, increasing population resulted in increased plant yield at all N rates (Fig. 11-8b). In contrast, under lower moisture conditions, both plant population and optimum N rates are substantially lower (Fig. 11-8c). In addition, no interaction was observed between population and N supply.

With increasing plant population, it may be necessary to adopt narrower row spacing to optimize light distribution through the crop canopy. Equidistant plant spacing decreases individual plant competition for sunlight, H_2O, and nutrients, which can enhance plant growth and yield potential. This is especially important under limited plant available H_2O, where high populations planted in wide rows increases within row competition for available H_2O. In an environment with greater

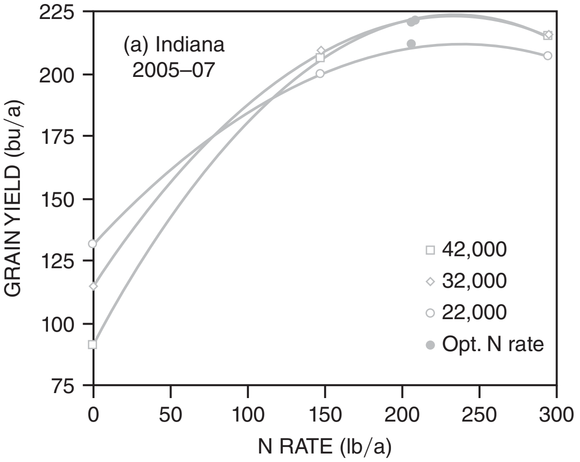


Figure 11-8

Plant population × N rate interaction as influenced by environment. Optimum N rate is based on a 0.1 price ratio. In (c), N supply = soil N + applied N.

(*Adapted from Boomsma et al., 2009,* Agron J., *101:1426–52 [a, b]; Blumenthal et al., 2003,* Agron. J., *95:878–83 [c].*)

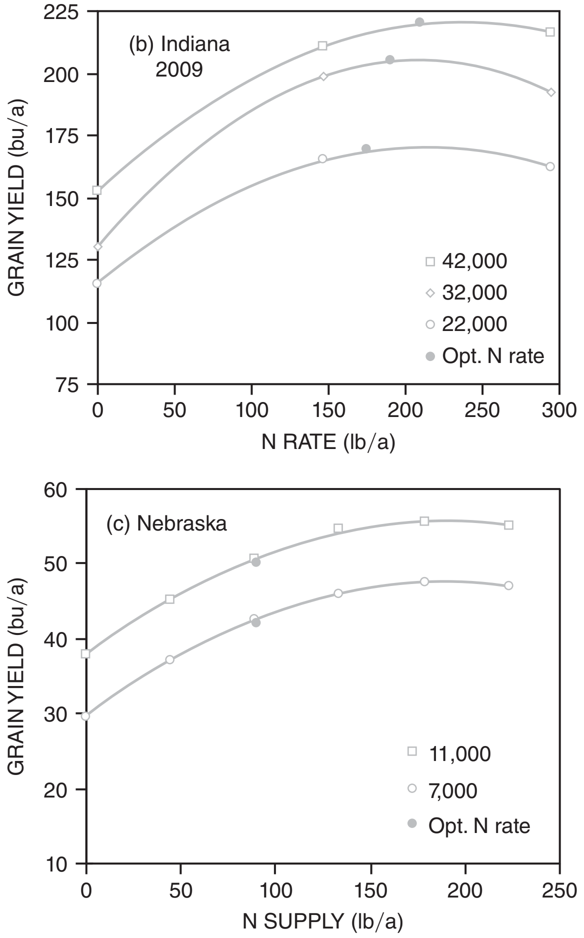


Figure 11-8
(Continued)

plant available H_2O, the advantage to narrow row spacing would likely be reduced. Generally, the advantage to narrow row spacing is greater in northern latitudes where sunlight can be relatively more yield limiting than in southern climates.

Variety or Hybrid Within a given environment, one hybrid or variety may produce a greater response to applied nutrients than another (Fig. 11-9). This is especially true with N × hybrid response as they vary greatly depending on growing season

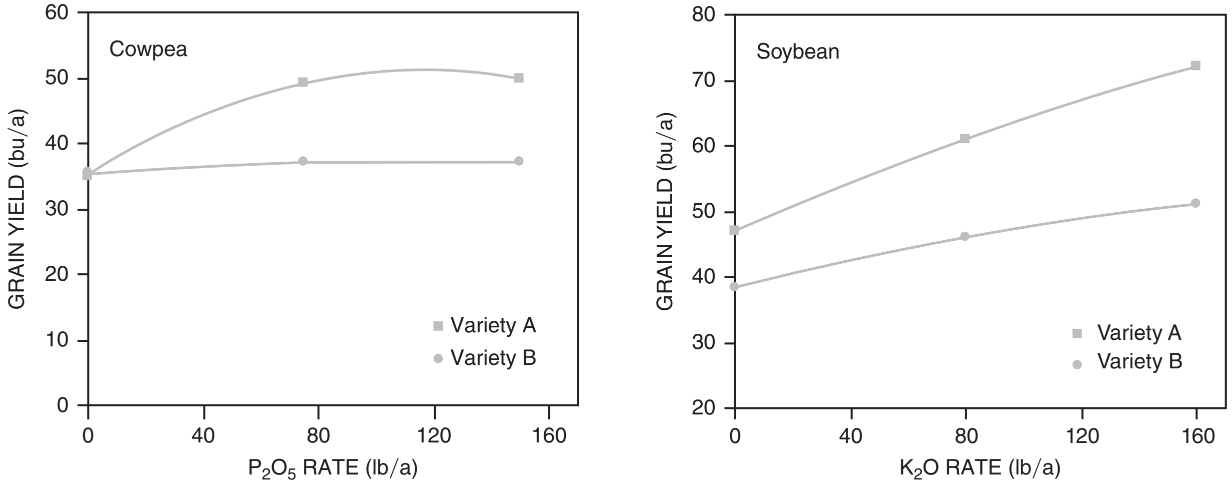


Figure 11-9
Variety × nutrient interaction effect on cowpea and soybean grain yield. (Adapted from Magani and Kuchinda, *2009*, Agron. J., *101:1387*; *Terman, 1977*, Agron. J., *69:234*.)

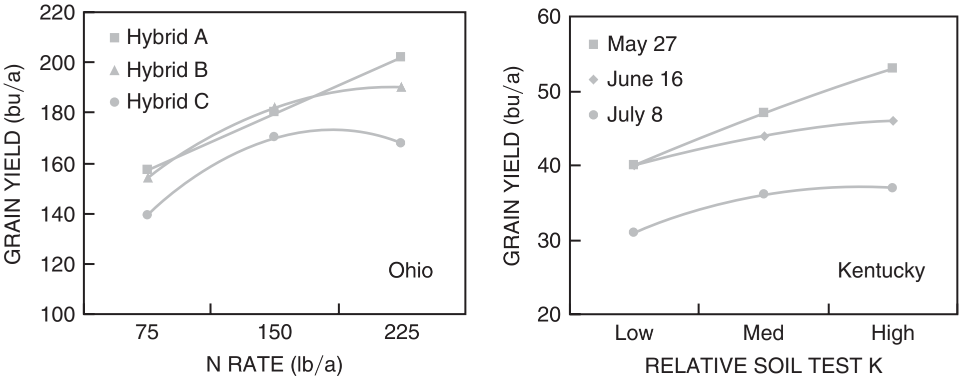


Figure 11-10
Variety × N interaction in corn (Ohio) and planting date × K in soybean (Kentucky).

(Adapted from Thomison et al., 1994, Fluid J., 94[2]:10–11; Peaslee, Univ. of KY, personal comm.)

moisture and temperature (Fig. 11-10). Because nutrient response between varieties is difficult to predict, on-farm evaluations of varietal responses to nutrients should be conducted to optimize productivity and nutrient use efficiency (Fig. 9-30).

Planting Date Earlier planting dates extend the growing season for spring-planted crops, which generally increase yield potential. For example, soybean yield response to increasing soil test K level was greater with earlier planting (Fig. 11-10). Similar planting date interactions with both N and P are common. Cooler soil temperatures experienced with early planting can temporarily reduce nutrient supply, especially in northern latitudes, requiring a starter nutrient application to ensure nutrient supply meets demand associated with high yield potential (see “Application Timing” in Chapter 10).

Nutrient–Soil Management Interactions

Plant response to fertilization can be greatly increased if nutrients are applied properly (Chapter 10). Under reduced and no-tillage systems, surface accumulation of residue and nutrients combined with cooler temperatures and higher moisture in the spring can influence nutrient use. In many cropping systems, especially with low soil test P and/or K, nutrients applied below the soil surface often enhance plant growth and yield (Figs 10-38; 10-44). Positive interaction of N and P was also shown in wheat with N-P placement (Fig. 10-40).

In general, higher rates of N and perhaps S are required under no-till systems than under conventional tillage. Under no-till, broadcast N is partially immobilized and/or denitrified (Fig. 10-35). To avoid fertilizer N interactions with surface residues, N must be placed below the residue to reduce N immobilization, denitrification, and/or volatilization losses, improving plant recovery of applied N and reducing residual profile N after harvest. In some environments, yield potential is greater under no-till systems, requiring more N and other nutrients.

The importance of exploiting interactions in maximizing productivity and profitability cannot be overemphasized. When one practice or group of practices increases yield potential, nutrient requirement increases. As production agricultural technologies (genetics, management, etc.) advance, they will be successful only if the technology is integrated in a manner that allows the expression of positive interactions.

Nutrient–Water Interactions

Soil H_2O supply influences nutrient availability and use, while nutrient supply can influence H_2O use (Fig. 11-11). Even in regions where annual precipitation exceeds evapotranspiration, H_2O stress frequently limits plant growth potential and plant nutrient demand. With excessive nutrient application, early plant vigor (growth) increases use of limited H_2O supply, ultimately reducing yield. In addition, nutrient deficiencies, pests, and other stresses reduce the plants’ ability to use H_2O efficiently, which reduces crop productivity.

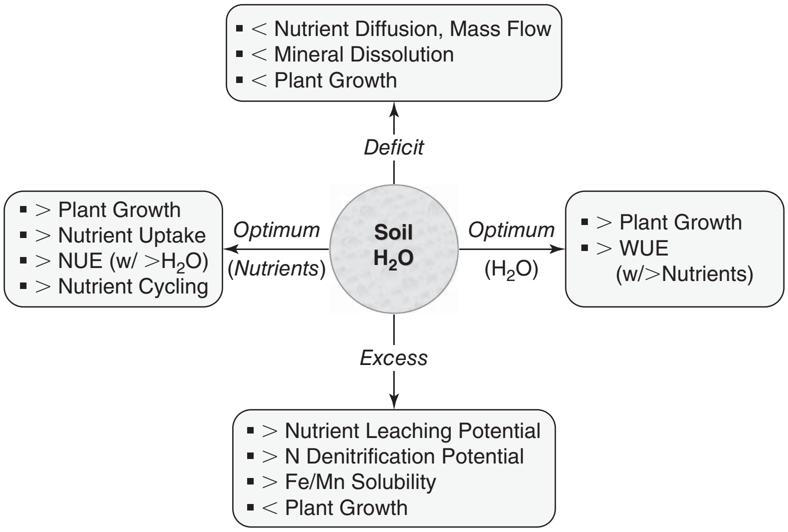


Figure 11-11
Influence of soil H_2O content on nutrient supply and plant growth.

Increasing industrial and residential H_2O use will reduce availability for irrigated agricultural uses increasing reliance on non-irrigated (dryland) crop production. Increasing H_2O use efficiency is a major challenge to agriculture; thus, growth factors that increase yield generally improve H_2O use efficiency.

Water Use Efficiency Water use efficiency (WUE) represents crop yield per unit of H_2O used from soil, precipitation, and irrigation. WUE varies between season and management level (Fig. 11-12). Crops also vary greatly in WUE (Table 11-4). Because H_2O use is required to produce the first unit of plant biomass, a minimum quantity of both biomass and H_2O is required to produce harvestable yield. Thus, when measuring WUE based only on grain yield, for example, yield versus H_2O use lines have a negative Y intercept (Fig. 11-13).

Yields of crops have increased greatly in the past 30 years on essentially the same amount of H_2O, which is related to improved genetics and soil/crop management practices. For example, tillage systems that leave large amounts of surface residues conserve H_2O by:

- increased infiltration
- reduced runoff
- decreased evaporation from soil surface
- increased snow collection (standing residue)

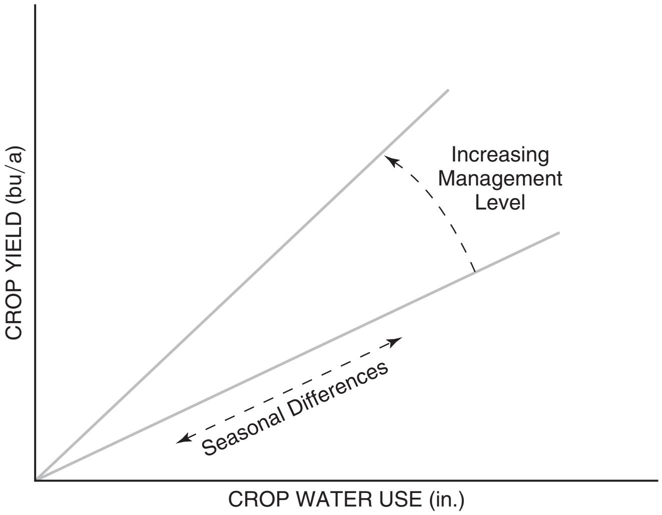


Figure 11-12
Conceptual diagram of growing season and management effects on water use efficiency (crop yield/water use).
(*Adapted from Hatfield et al., 2001, Agron. J., 93:271.*)

TABLE 11-4
WATER USE EFFICIENCIES (WUE) FOR SELECTED CROPS AND THE ESTIMATED MINIMUM QUANTITY OF WATER REQUIRED TO PRODUCE FIRST UNIT OF GRAIN

Crop	WUE	H_2O Required to Produce First Bushel
	lb grain/a/in. H_2O	*In.*
Corn	580	9.1
Wheat	390	6.8
Millet	240	3.5
Safflower	190	9.2
Sunflower	165	5.3

Source: Neilsen, 1995, Cons. Tillage Fact Sheet No. 2-95, USDA-ARS, USDA-NRCS.

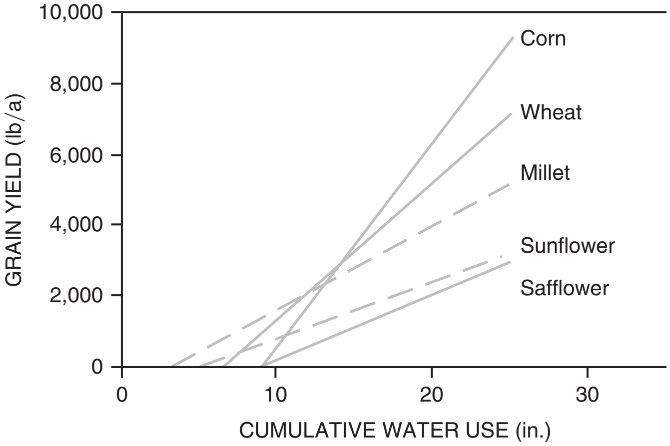


Figure 11-13
Water use efficiencies for selected dryland crops. The points where lines cross the X axis represent the minimum quantity of water required to produce the first unit of grain (actual values in Table 11-4).
(Adapted from Neilsen, 1995, Cons. Tillage Fact Sheet No. 2-95, USDAARS, USDA-NRCS.)

Although irrigation can stabilize production, yields may still be limited by other factors (Figs 1-11 and 1-12). For example, if yield potential is doubled with irrigation, then nutrient demand would double. Consequently, the crop must obtain more nutrients from native soil supply, manures, or fertilizers. With optimum nutrient availability, WUE is generally greater under irrigation than under dryland conditions, where H_2O may limit yield potential and crop response to nutrients (Fig. 11-14).

Water and Nutrient Absorption With vigorous plant growth, most crops rapidly deplete soil H_2O in shallow surface layers. As surface soil H_2O is depleted, the plant extracts H_2O from the lower three-fourths of the root depth (Fig. 11-15). Under nutrient stress, root growth may be limited and the plant may not extract H_2O from lower soil depths, limiting plant growth. If an extra 2–4 in. of subsoil water is accessed, the crop may tolerate drought without appreciable yield loss. In areas with dry subsoil, increased fertilization will not help crops penetrate subsoil.

Water is essential to nutrient uptake by root interception, mass flow, and diffusion (Chapter 2). Roots intercept more nutrients, especially Ca^{+2} and Mg^{+2}, in a moist soil than in a dry soil because root growth is more extensive. Mass flow of soil H_2O transports most of the NO_3^-, SO_4^{-2}, Ca^{+2}, and Mg^{+2} to roots. Nutrients diffuse from areas of high to low nutrient concentration but over short distances. Diffusion rate depends partly on soil H_2O content; therefore, thicker H_2O films or higher nutrient content increase nutrient diffusion (Fig. 11-11).

Figure 11-14
Relationship between irrigated and dryland winter wheat yield and water use efficiency (WUE).
(*Musick et al., 1994*, Agron. J.,*86:980.*)

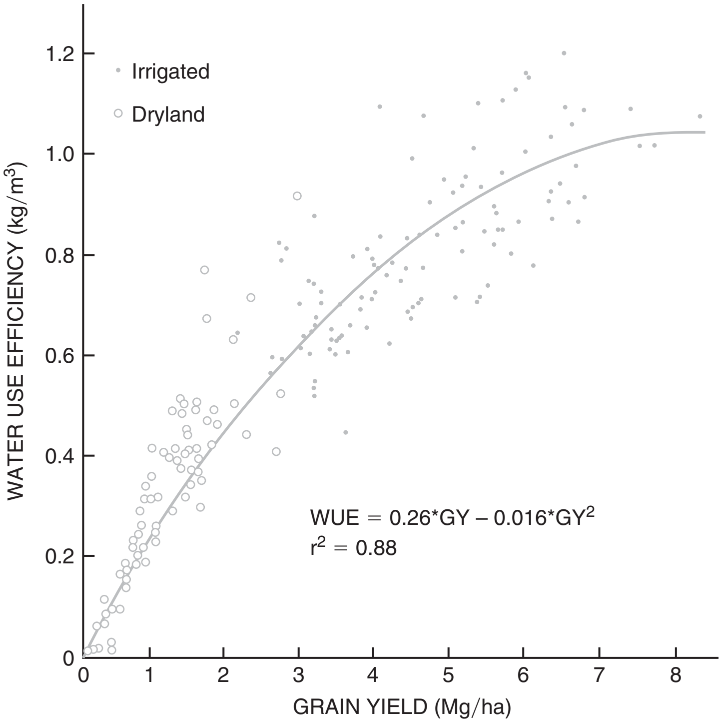
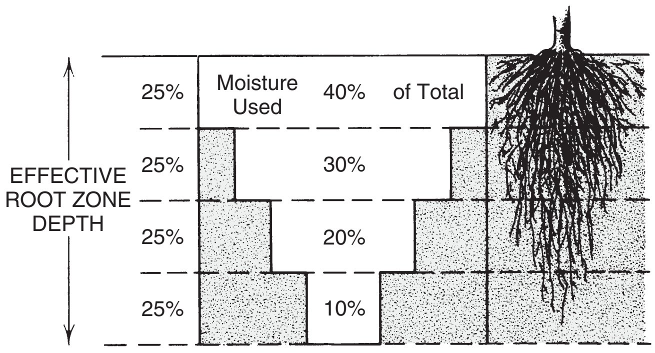


Figure 11-15
The top 25% of the root zone is the first to be exhausted of available moisture. Certain management practices, including adequate nutrient availability, encourage a deeper root system to extract moisture from the lower root zone.



Nutrient absorption is directly affected by soil H_2O content, and indirectly by the effect of H_2O on metabolic activity, degree of soil aeration, and solution salt concentration. Plant growth and yield potential is greater with normal or higher moisture availability; however, even in dry seasons, adequate nutrient availability greatly increases yield and WUE (Fig. 11-16).

Adequate nutrient supply is critical for efficient crop H_2O use and enhanced crop tolerance to low soil H_2O supply. The following factors are relevant:

- adequate nutrient supply favors expanded root growth; if roots explore an additional 1 ft. depth, 1–2 in. of H_2O can be obtained
- under low soil H_2O, nutrient diffusion is reduced because H_2O films are thin, increasing diffusion path length
- low soil H_2O exerts a physiological effect on roots reducing elongation, turgidity, and density of root hairs, decreasing nutrient uptake
- adequate K nutrition aids stomata closure during drought, reducing transpiration H_2O loss
- adequate nutrition encourages rapid canopy development that reduces soil H_2O evaporation

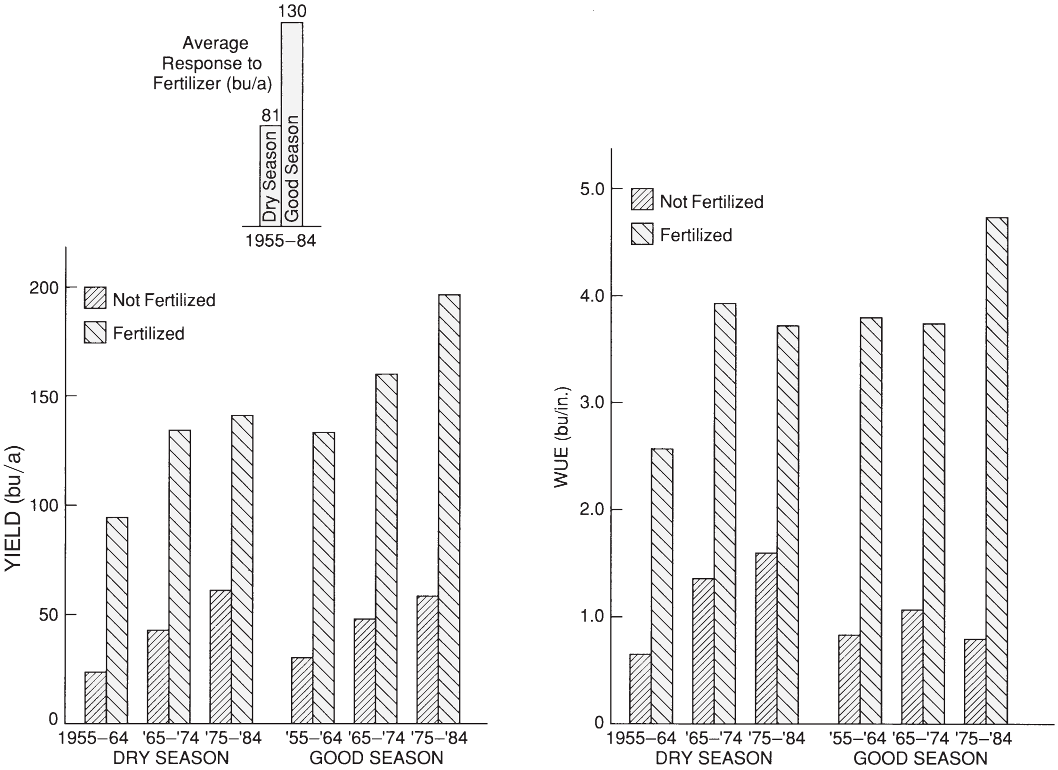


Figure 11-16

Long-term influence of fertilization on corn grain yield and WUE. (Morrow plots, Univ. Illinois).

(*Adapted from Potash & Phosphate Inst., 1990,* Fert. Improves Water Use.)

- adequate nutrition advances maturity that may initiate flowering, pollination, and grain fill before summer periods of drought and high temperatures
- plant residues increase with increasing yield, increasing surface residue cover, which increases infiltration, reduces runoff, and lowers wind speeds at the soil surface, all of which increase potential H_2O availability

Dryland (non-irrigated) Cropping Systems

In many climates, available soil H_2O frequently limits plant growth and yield. In semi-arid and arid regions, fallowing (extended non-crop periods) is commonly practiced to store additional precipitation. In crop-fallow systems, increased soil H_2O conservation by maximizing surface residue cover (no-till) will reduce the dependence on fallowing and enable more intensive cropping (Fig. 11-17). These data illustrate that wheat yields in a wheat-fallow rotation are not greatly increased due to the extra soil H_2O conserved under no-till; however, additional stored soil H_2O enabled production of two crops in 3 years and three crops in 4 years compared to one crop in 2 years. Total WUE increased $>50\%$ in the 3-year rotation compared with the 2-year rotation.

N availability is usually not reduced as much as P and K; however, under drought conditions, N mineralization is reduced, in addition to reduced uptake of soluble N. Generally, the commonly observed positive $H_2O \times N$ interaction is related to (1) increasing N supply will not increase yield without sufficient plant available H_2O and (2) increasing stored soil H_2O will not greatly increase production without adequate N (Fig. 11-18). Similarly, increasing N supply increases WUE.

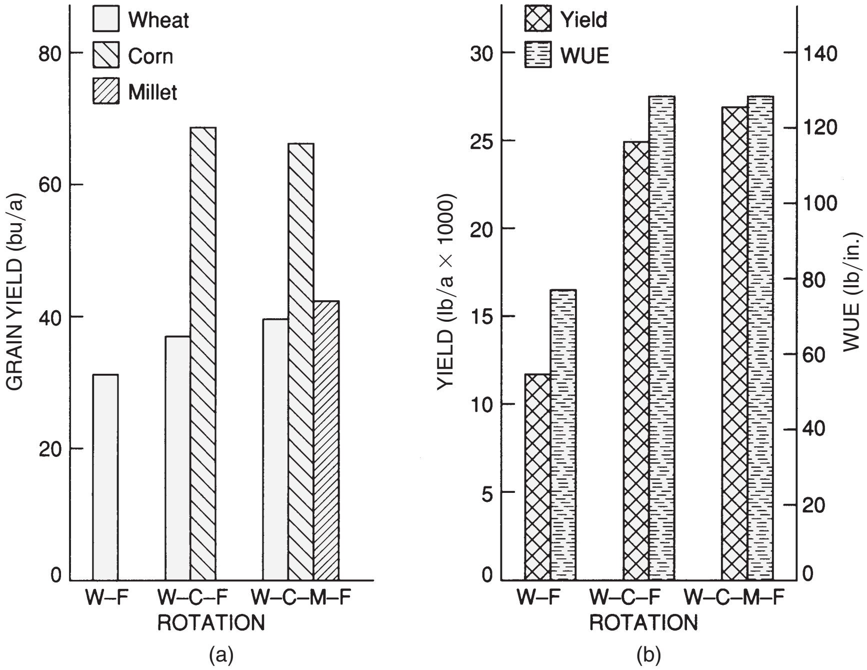


Figure 11-17
Influence of decreasing fallow (F) frequency on wheat (W), corn (C), and millet (M) grain yield (a) and on total grain production and H_2O use efficiency (b) in a 12-year cycle. (*Peterson et al., 1992,* Proc. Great Plains Soil Fert. Conf., pp. 47–53.)

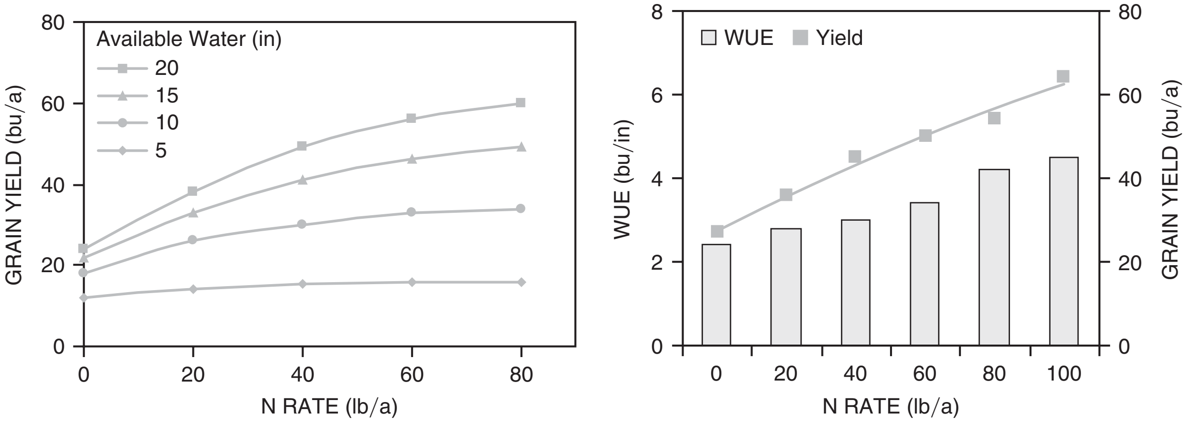


Figure 11-18
Interaction between plant available H_2O (soil H_2O + growing season rainfall) and N on dryland winter wheat yield (left) and N rate on wheat grain yield and water use efficiency (right) (*Havlin, unpublished data*).

Sufficient P and K nutrition is critical for maximizing plant growth under reduced soil H_2O availability, where increasing drought stress increases P and K response (Fig. 11-19). The P/K × H_2O interaction is related to:

- P/K diffusion is reduced under low H_2O content; P/K fertilization increases concentration in the H_2O films and increases diffusion
- subsoil P/K < surface soil in many soils; under drought stress, roots explore lower P/K subsoil, contributing to increased plant response to P/K

Micronutrient diffusion to plant roots is also reduced under low soil H_2O. Since plants require a much smaller quantity of micronutrients, drought stress effects are not as great. Temporary B deficiency can occur under dry soil conditions attributed to both restricted B mineralization and crop uptake in surface soil. Low soil H_2O can also induce Mn and Mo deficiencies. Increased soil moisture results in

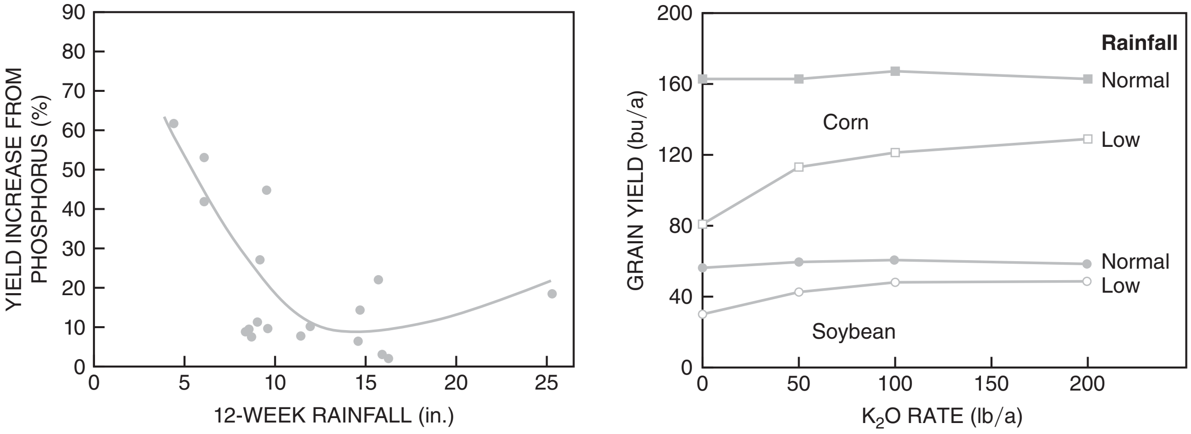


Figure 11-19

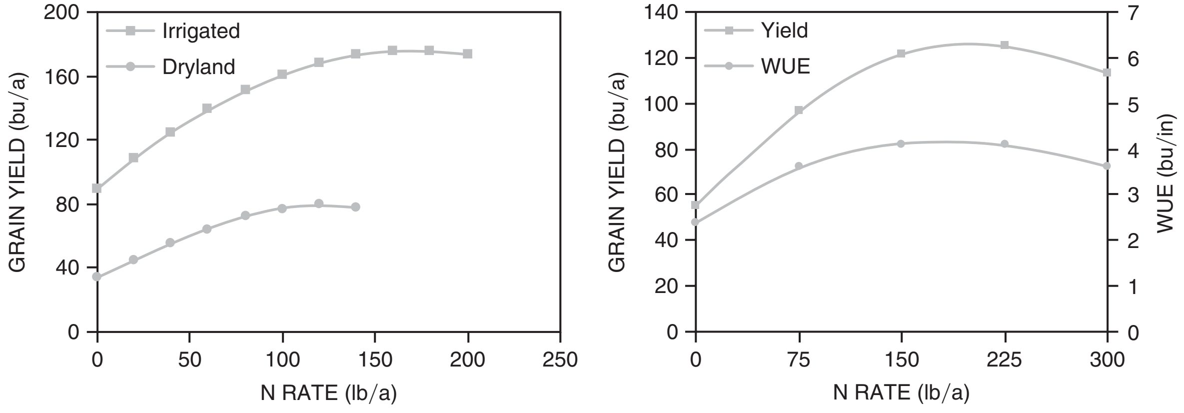
Influence of growing season rainfall on soybean response to P (left) (Barber, 1971, Better Crops) *and corn and soybean response to K (right).* (Johnson and Wallingford, 1983, Crops and Soils, 36:15).

greater amounts of Mo uptake. Mn becomes more available under moist conditions because of conversion to more soluble forms.

Irrigated Cropping Systems

Nutrient × H_2O interactions under irrigated systems are often similar to dryland systems, except the interactions operate at higher yield levels (Fig. 11-14). Fertility is one of the important controllable factors influencing H_2O use in irrigated soils. Generally, crop response to N is much greater under irrigation, where H_2O is non-limiting (Fig. 11-20). When N is deficient, increasing N fertilization will increase yield, total H_2O use, and WUE. In sandy soils, excessive irrigation may leach soluble nutrients (e.g., NO_3^- and $H_2BO_3^0$), which can reduce nutrient supply.

When irrigating crops with ground or surface waters, it is essential that water samples are sent to a laboratory for nutrient analysis. For example, in western regions of the United States, irrigation water may contain salts, S, and many other constituents that must be accounted for in the nutrient management plan. Salts are particularly problematic (Chapter 3); however, substantial nutrients can also be added to



(a)

(b)

Figure 11-20

Influence of N supply on irrigated and dryland corn yield (a) and on wheat yield and WUE (b). (Schlegel and Havlin, 1995, J. Prod. Ag., 8:181–185; PPI, 1990.)

crops through irrigation. For example, if a H_2O analysis shows 10 ppm SO_4-S and 12-in. irrigation H_2O is applied during the growing season, the quantity of S applied is calculated by:

$$10\text{ ppm S} = \frac{10\text{ lb S}}{10^6\text{ lb H}_2\text{O}} \times \frac{43{,}560\text{ ft}^2}{\text{a}} \times 1\text{ ft H}_2\text{O} \times \frac{62.4\text{ lb H}_2\text{O}}{\text{ft}^3} = 27\text{ lb S/a}$$

This amount of S meets or exceeds S requirement of most crops (Table 9-1).

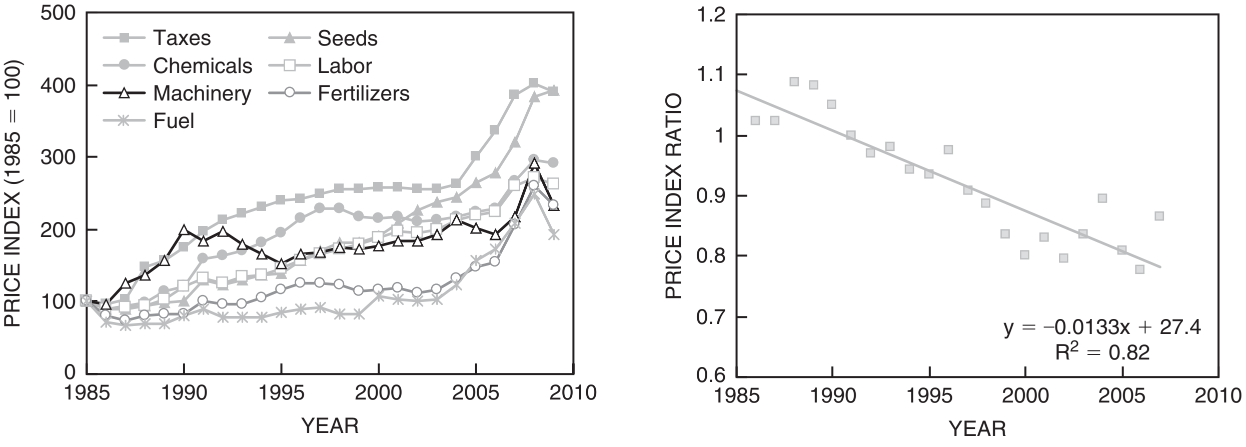
ECONOMICS OF NUTRIENT USE

World fertilizer use increased ≈30% over the last decade, due to increased nutrient use in China and other rapidly developing nations (Fig. 1-9). To meet world food demands in the next 40 years (Chapter 1), increased agricultural productivity will require increased inputs, especially fertilizers. As higher nutrient rates are utilized, it is essential that nutrients are applied to maximize recovery by the crop. Higher crop yields represent the greatest opportunity for reducing per-unit production costs.

To obtain a given level of production, growers vary fertilizer, labor, machinery, and other inputs. Actual input use depends on relative costs and returns. Although production costs vary between years, costs generally increase over time. The relative costs of many farm inputs have increased more than the costs of fertilizers and chemicals (Fig. 11-21). Unfortunately, the input prices paid by growers have increased much more than the output prices received (Fig. 11-21). Therefore, it is imperative that growers achieve optimum productivity through efficient and cost-effective use of only those inputs that ensure positive net returns.

Maximum Economic Yield

Maximum economic yield represents the yield level where the last unit of input pays for itself and is less than maximum yield (Fig. 11-22). Maximum economic yields vary among management levels, although on most farms they are often higher than those generally achieved. To maximize profits, higher yields are essential; however, achieving the highest yield will not result in the greatest return per unit of added input.



(a) (b)

Figure 11-21
Index of prices paid for selected inputs (a) and the ratio of prices received to prices paid (b).
(USDA-National Agric. Statistics Service, 2011, http://quickstats.nass.usda.gov/ and http://www.nass.usda.gov/Charts_and_Maps/Agricultural_Prices/.)

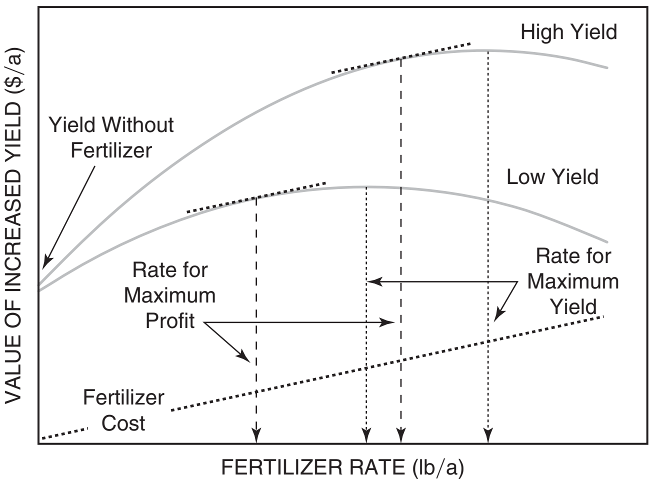


Figure 11-22
Diagram representing fertilizer economics associated with high and low yield levels. Fertilizer rate for maximum yield occurs where the slope of the response curve is equal to 0 or is parallel with the x-axis. Fertilizer rate for maximum profit occurs where the slope of the response curve is parallel to the fertilizer cost line.

Management practices that increase crop yield per unit of land area will lower per unit production cost, since management (tillage, planting, input application, etc.) costs associated with a low or high yield crop are relatively similar. *Fixed* costs (land, buildings, machinery, labor, seed, etc.) are independent of production level, whereas *variable* costs (fertilizers, harvesting, handling, etc.) vary with yield.

Inputs that increase yield increase production cost/a, but decrease cost/bu and increase net return (Table 11-5). Key factors in obtaining the most efficient use of inputs are weather and the management skill of the producer. With superior management, higher nutrient rates are generally required (Fig. 11-22). Selected management practices that enhance yield include:

- *timeliness:* important in planting, tillage, nutrient application, equipment adjustment, pest control, scouting, and harvesting
- *variety selection:* large differences in yield, disease resistance, quality, and responsiveness to inputs exist among varieties and hybrids
- *plant population-row spacing:* optimum utilization of light energy through the canopy and plant available soil H_2O requires equidistant plant spacing
- *pest control:* identifying pest problems early improves effectiveness of pesticides
- *crop rotation:* rotating crops may not only reduce weed, disease, and insect problems but also improves soil structure and reduces N inputs when legumes are included
- *tillage:* reduced tillage in many environments increases water availability

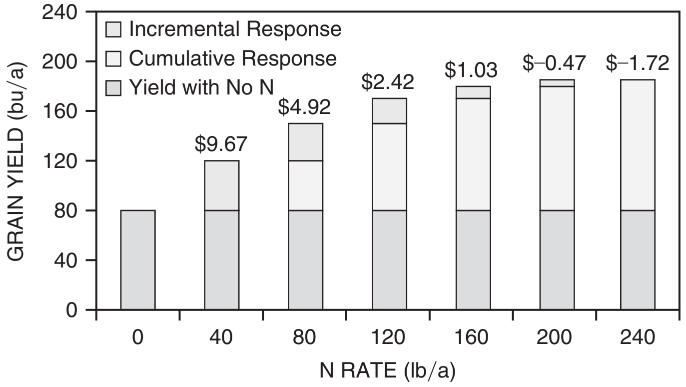
Producers recognize the importance of maximizing net return per unit of land. With adequate cash or credit, producers select input levels that earn the greatest

TABLE 11-5
EFFECT OF INCREASING CORN YIELD ON PRODUCTION COSTS AND NET PROFIT/A

Grain Yield	Production Costs		Net Profit[1]
bu/a	*$/a*	*$/bu*	*$/a*
130	350	2.69	235
160	390	2.44	330
190	410	2.16	445
220	420	1.91	570

[1] Revenue-variable costs assuming $4.50/bu.

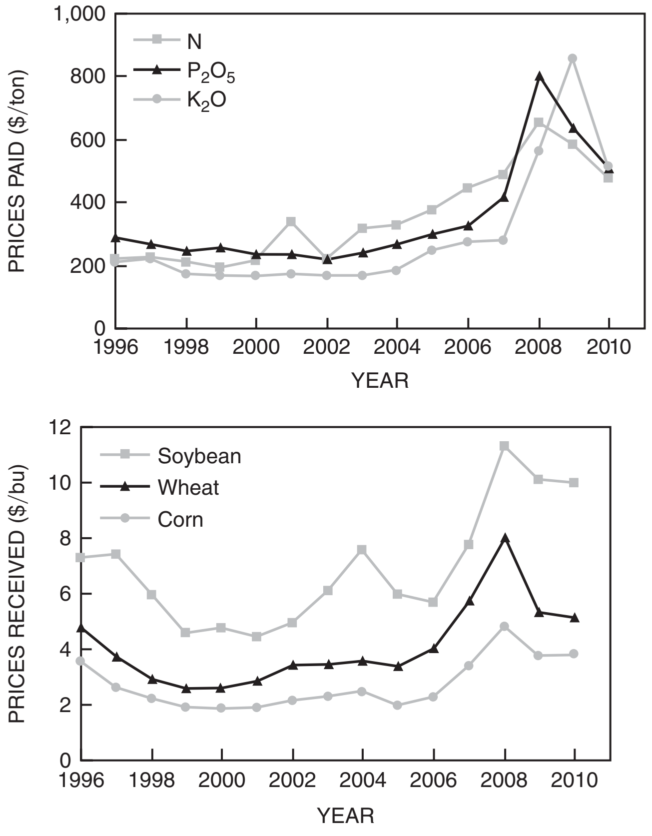
Figure 11-23
Diminishing returns to N application. The dollar values on top of each bar represent the net return per added dollar invested in N.



net return per acre. In general, as nutrient rate increases, the return per dollar spent decreases as a result of reduced response for each successive incremental input. Eventually, no further response to additional nutrients is realized. This principle is called the *law of diminishing returns* (Fig. 11-23). When a nutrient is deficient, the first nutrient increment results in a large yield increase. The next increment may also give an increase, but not as proportionately large as the first. Consequently, responses to additional increments continue diminishing to the point where the last incremental yield value just equals the input cost, which represents the nutrient rate for maximum profit.

Nutrients costs and crop prices can vary widely (Fig. 11-24). When fertilizer prices increase and crop prices decrease, the nutrient rate for maximum return should be adjusted. To assess the influence of changing crop and nutrient prices, the nutrient rate required for maximum yield and maximum profit can be estimated from

Figure 11-24
Annual variation in fertilizer costs and commodity prices in the United States.
(USDA-NASS, 2011, http://quickstats.nass.usda.gov/.)



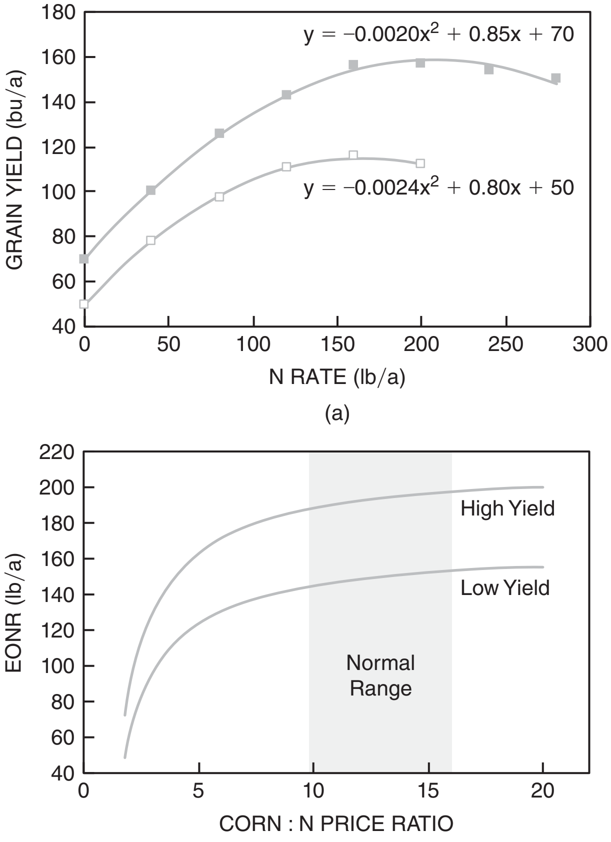


Figure 11-25
Example yield response to N relationships with high and low corn yield levels (a). Influence of corn : N price ratio on economic optimum N rate (EONR). Shaded area in (b) represents the typical range in corn price : N cost ratio.

typical yield response to applied nutrient relationships. For example, assume the yield response to N function for a *high yield* is (Fig. 11-25a):

$$Y = -0.0020X^2 + 0.85X + 70$$

where $Y =$ grain yield (bu/a)
$X =$ N rate (lb/a)

N rate for maximum yield:

- set the first derivative of the response function equal to zero
- solve for X

$$\frac{\mathrm{d}Y}{\mathrm{d}X} = -0.004X + 0.85$$

$$0 = -0.004X + 0.85$$

$$X = \frac{0.85}{0.004} = 212 \text{ lb N/a}$$

- N rate for maximum yield represents that point on the yield (bu/a) curve where the slope $(\mathrm{d}Y/\mathrm{d}X) = 0$ (Fig. 11-26a).

N rate for maximum profit:

- set the first derivative of the response function equal to the ratio of fertilizer N cost (i.e., \$0.45/lb N) to grain price (i.e., \$4.50/bu)
- solve for X

$$\frac{dY}{dX} = -0.004X + 0.85 = \frac{\$0.45}{\$4.50}$$

$$-0.004X + 0.85 = 0.10$$

$$X = \frac{0.75}{0.004} = 188 \text{ lb N/a}$$

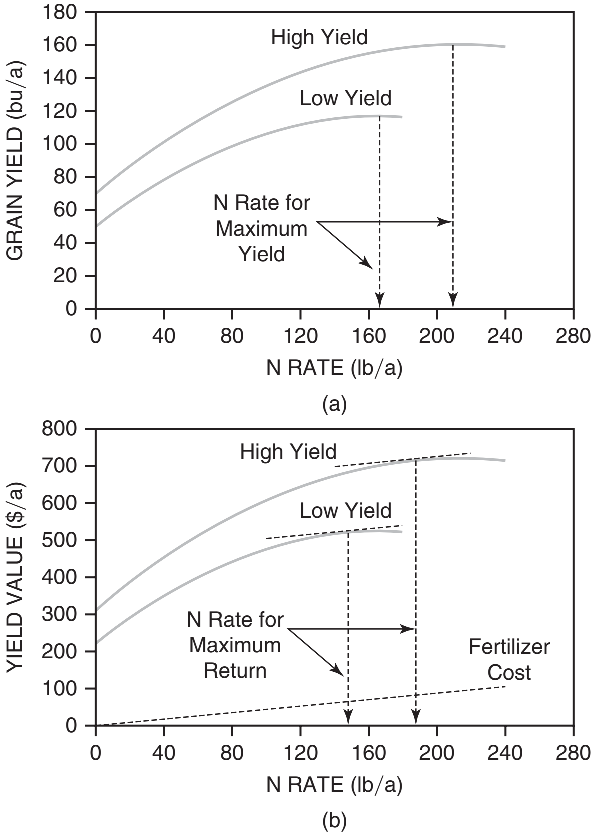


Figure 11-26
Graphical representation of the N rate for maximum yield (a) and N rate for maximum return to applied N (b), using the high and low yield functions in Figure 11-25a.

The N rate for maximum profit represents the point on the yield value ($/a) curve where the slope is parallel to the fertilizer cost line (Fig. 11-26b).

For the low yield response function (Fig. 11-25a), the N rate for maximum yield and profit are 167 lb N/a and 146 lb N/a, respectively (Fig. 11-26).

The nutrient rate required for maximum return to applied nutrient depends on nutrient cost and crop price (Fig. 11-24). For example, as N cost increases with a given corn price, the N rate for maximum profit decreases (Table 11-6). Alternatively, as corn price increases with a given N cost, the N rate for maximum profit increases. If prices remain within a commonly observed range of 10:1–15:1 (Fig. 11-25b), price changes have relatively minor effects on N rate for maximum profit (12 lb N/a range). However, if large fluctuations occur in N cost or crop price, adjustments in N rate can be considered. For example, with $6/bu corn and $0.30/lb N, optimum rate is 200 lb N/a, whereas at $3.00/bu corn and $0.60/lb N, optimum rate is 163 lb N/a.

Additional Benefits from Maximum Economic Yields

Energy Efficiency

Higher yields are an effective means of improving energy efficiency in agriculture. Higher yields require more input energy/a, but less energy cost/bu or ton. Some costs are the same regardless of yield level. For example, it takes just as much fuel to till a field yielding 60 bu/a of soybean as one yielding 90 bu/a.

Reduction in Soil Erosion

Raindrops strike soil with surprising force, dislodging particles and increasing soil erosion. However, crop canopies and residues absorb raindrop energy maintaining or increasing infiltration, reducing runoff, and decreasing soil loss. Wind erosion and soil moisture depletion are also decreased by the presence of heavy surface crop residues. Highly productive cropping systems are essential to soil conservation and productivity because crop canopy development is advanced and more top and root

Table 11-6
Effect of Crop Price and Fertilizer Cost on N Rate for Maximum Return to Applied N, Based on "High Yield" N Response Function in Figure 11-25

	N Cost ($/lb)						
Crop Price	**0.30**	**0.35**	**0.40**	**0.45**	**0.50**	**0.55**	**0.60**
$/bu				*lb N/a*			
3.00	188	184	180	175	171	167	163
3.50	191	188	184	180	177	173	169
4.00	194	191	188	185	182	178	175
4.50	196	193	191	188	185	182	179
5.00	198	195	193	190	188	185	183
5.50	199	197	195	192	190	188	186
6.00	200	198	196	194	192	190	188

Note: "Shaded" cells represent the N rate associated with a corn : N price ratio = 10:1; the "outlined" area represents a commonly observed range in price ratio = 10:1–15:1.

residues are produced. Conservation tillage practices leave more residues on the surface greatly reducing soil erosion (Chapter 12).

Soil Productivity

Increasing soil OM is a long-term process; however, the productivity benefits of raising OM can be substantial (Chapter 12). In areas of higher temperatures and lower moisture, it is more difficult to increase OM; however, larger amounts of decomposing residues improve soil physical conditions and water infiltration that increases water availability to plants, while reducing runoff and erosion.

Other Nutrient Economic Issues

Unit Price of Nutrients

Growers are interested in the most economical nutrient source. Wide variations in the cost per unit of nutrient occur commonly related to increased foreign demand for fertilizers and increased natural gas and other energy costs. Growers should choose a fertilizer source based on the cost per unit of nutrient in the formulation. For example, if urea (45-0-0) costs $400/ton and UAN (30-0-0) costs $320/ton, the unit cost ($/lb N) is:

Urea

$$2{,}000 \text{ lb urea} \times 0.45 = 900 \text{ lb N}$$
$$\$400/900 \text{ lb N} = \$.44/\text{lb N}$$

UAN

$$2{,}000 \text{ lb UAN} \times 0.30 = 600 \text{ lb N}$$
$$\$320/600 \text{ lb N} = \$.53/\text{lb N}$$

Mixed fertilizers contain more than one nutrient. To compare costs of several mixed fertilizers, the cost per unit of one or more nutrients is assumed or based on the cost of the single nutrient source used in the mixed fertilizer formulation. The assumed cost of these nutrients is subtracted from the total fertilizer cost, and then the remaining cost is used to determine the cost per pound of the nutrient in question. For example, if DAP (18-46-0) costs $650/ton, assume the N cost is $0.44/lb for *urea* in the above example. The unit cost ($\$/\text{lb } P_2O_5$) is:

$$2{,}000 \text{ lb fertilizer} \times 0.18 \text{ N} = 360 \text{ lb N}$$
$$2{,}000 \text{ lb fertilizer} \times 0.46 \text{ P} = 920 \text{ lb } P_2O_5$$

DAP cost attributed to N:

$$\$.44/\text{lb N} \times 360 \text{ lb N} = \$158.40$$

P_2O_5 *cost in DAP:*

$$\$650 - \$158.40 = \$491.60$$
$$\$491.60/920 \text{ lb} = \$.53/\text{lb } P_2O_5$$

If TSP (0-46-0) costs \$400/ton, the unit cost ($\$/\text{lb } P_2O_5$) is:

$$2{,}000 \text{ lb fertilizer} \times 0.46 = 920 \text{ lb}$$
$$\$400/920 \text{ lb} = \$.43/\text{lb } P_2O_5$$

The cost of P_2O_5 in 18-46-0 is greater than in 0-46-0.

Similar calculations are used when comparing common-blended fertilizer made from the concentrated sources shown above (i.e., 3-9-9, 10-10-10). For example, a 5-10-10 costs \$180/ton and 10-10-10 costs \$220/ton. Assuming the same P and K costs, the 5-10-10 costs \$1.80/lb N and the 10-10-10 costs \$1.10/lb N.

In addition to the actual fertilizer cost, growers also consider cost of transportation, storage, and labor used in fertilizer application. These costs may be difficult to evaluate, but if the nutrient price from one source is the same as another source, growers will purchase the one requiring less labor. Higher analysis sources generally are the least expensive sources.

Residual Effects High crop yields are impossible with low levels of fertility. Soil nutrient supply can be easily controlled; however, the initial cost of building soil fertility from low to high levels may discourage growers if viewed as an annual rather than long-term investment. Residual nutrient availability from past applications should be included in analyses of nutrient economics. Usually the entire cost of fertilization is charged to the current crop, whereas lime cost can be amortized over 5–7 years. With high rates of fertilization; however, residual effects can be substantial, especially with immobile nutrients (Fig. 10-63).

At optimum N rates, about 10–20% may be residual for next year's crop, provided that it is not leached below the root zone. The residual value of P and K can vary from 25 to 60%, depending on rate applied, crop removal, and soil properties influencing P and K availability.

The lower figure would apply when hay, straw, or stover is removed, or with high P or K fixing soils. Buildup of immobile nutrients is a capital investment that can be amortized over years. For example, soil test P buildup from 20 to 30 lb/a (Bray-1 P) requires 100 lb/a, assuming 10 lb P_2O_5/a per 1 lb/a Bray-1 P. The initial cost is \$45.00/a (\$0.45/lb P_2O_5); however, using a 5-year payoff, the annual payment would be \$9/a/yr with interest. A yield increase of 2 bu/a of \$5/bu corn or 1 bu/a of \$10/bu soybean would pay for the investment.

Soil Fertility Effects on Land Value When buying land, the producer may choose high- or low-priced property. The higher priced land is generally more productive, is fertile, and has better improvements. The lower priced land may actually be a good buy, provided the land is not severely eroded or has no other physical limitations to productivity. Low-priced land is usually infertile and may need considerable lime and/or nutrients. Adequate liming and fertilization, as indicated by soil tests and combined with other good practices, can rapidly increase productivity. Expenditures to improve fertility may be included in the land cost, where \$100 − 200/a for liming and nutrient buildup may be expected. Thus, with proper management, it is possible to increase land productivity and value, with the cost amortized over years.

Liming Lime applications guided by soil testing and plant requirement are essential for maximum returns from fertilizer (Fig. 11-2). Net returns from liming are high when applied where needed, where returns vary with lime rate, lime cost, yield response to liming, and crop price. In spite of a high return, lime is often neglected in the fertility program because (1) responses to lime are often not as visual as those obtained with N, P, or K unless the soil is particularly acidic and (2) liming effects last for 5–7 years and returns are not all realized the first year.

Animal Wastes Soil enriching benefits from manure, in addition to those from nutrients, are related to the OM that improves soil structure and moisture relations; increases mobility of P, K, and micronutrients; and stimulates microbial activity. There is considerable variability in manure, depending on methods of storing and handling; however, with current fertilizer, labor, and equipment costs, it is usually profitable for the grower to use livestock manure. Because manure is largely an N-P fertilizer, the highest returns are obtained on non-legume crops. Hauling charges can be reduced by applying it on fields close to the source and using commercial fertilizer on more distant fields. With this strategy, risk of overapplication and N and P loss to surface and ground waters is increased. Composting of manure significantly lowers hauling costs, enabling it to be transported to greater distances (Chapter 10).

STUDY QUESTIONS

1. What is a positive interaction? Why are interactions more critical at higher yield levels?
2. Explain why it is impossible to obtain a full response from an applied nutrient if the level of another nutrient is inadequate.
3. Describe the importance of adequate P or K supply on N response.
4. Explain the greater response to P or K in dry years and in wet years.
5. Define water use efficiency (WUE). Why is it so important in agriculture? List factors that affect WUE.
6. What is the effect of adequate plant nutrients on WUE? Why does this effect occur?
7. Explain the effect of adequate nutrients on increasing the extent of the root system. Why is this important in drought periods?
8. How might placement of nutrients affect uptake in a dry year?
9. What is maximum economic yield and how is it determined?
10. Using Figure 11-22, describe why fertilizer rate for maximum profit is less than that required for maximum yield. Describe how fertilizer rate for maximum profit is calculated. Show how the fertilizer rate for maximum profit can be determined graphically.
11. Why does the level of management affect the return from a given level of fertilization?
12. What are some of the yield improving practices that cost little or nothing? How do they influence returns from high-cost inputs?
13. The function $Y = 90 + 0.6X - 0.0025X^2$ describes the crop response to fertilizer N.
    a. Calculate the N rate for maximum yield.
    b. Calculate the N rate for maximum profit ($4/bu; $0.40/lb N).
    c. Grain price drops 20% and fertilizer cost increases 20%. Calculate N rate for maximum profit. Why is the answer different than in part b?
15. Calculate the nutrient cost per lb of N, P_2O_5 and K_2O, when the fertilizer cost is
    a. TSP (0–46–0) $ 500/ton
    b. KCl (0–0–60) $ 800/ton
    c. NH_3 (82–0–0) $ 200/ton

16. If urea (45–0–0) costs $ 500/ton and UAN (30–0–0) costs $ 350/ton, what is the unit cost ($/lb N).
17. If DAP (18–46–0) costs $ 700/ton, what is the unit cost ($/lb P_2O_5) in the above problem. Assume the N cost is $ 0.50/lb for urea.
18. If the function $y = 100 + 0.5x - 0.0005x^2$ describes the crop response to fertilizer N, calculate the N rate for maximum yield.
19. Comment on
    a. N-P interaction
    b. N-K interaction
    c. P-K interaction
20. What are the benefits of a good soil testing program?
21. Discuss the influence of Ca supply on macro – and micronutrient uptake in dry bean grown in soil.
22. Discuss the influence of (i) soil water on nutrient availability & use and (ii) nutrient supply on H_2O use.
23. Explain the essentiality of water in nutrient absorption.
24. What is the principle of law of diminishing returns?
25. Discuss the various management practices followed to increase the crop yield per unit land area.
26. What is liming? How does lime application maximise the returns from fertilizers?

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12

Agricultural Productivity and Environmental Quality

The strength and longevity of any civilization depends on the ability to sustain and/or increase the productive capacity of its agriculture. Soil and crop management practices should achieve *sustained* profitable production. Sustainable agriculture encompasses soil and crop productivity, economics, and environment and can be defined by:

> *The integration of agricultural management technologies to produce quality food and fiber while maintaining or enhancing soil productivity, farm profitability, and environmental quality.*

Achieving agricultural sustainability depends on many agronomic, environmental, and social factors. Common criteria used to assess sustainable farming systems include:

- maintain short-term profitability and sustained economic viability
- maintain or enhance soil productivity
- protect environmental quality
- maximize efficiency in use of resources
- ensure food safety, quality of life, and community viability

Soil management practices that contribute to or encourage soil degradation will reduce soil productivity and threaten agricultural sustainability (Fig. 12-1). Alternatively, soil conservation is essential to enhancing soil productivity and long-term sustainability.

SOIL HEALTH OR QUALITY

Many interrelated physical, biological, and chemical properties determinely the *health* of a soil. Most of these properties are relative easy to measure and should be periodically assessed to guide soil and crop management decisions that can sustain crop productivity (Table 12-1). Improving soil health can have a large influence on profitability by:

- increasing plant vigor and yield
- reducing risk of yield loss during stress (e.g., drought, pests pressure)
- reducing input costs (e.g., less tillage, fertilizer, and pesticides use)

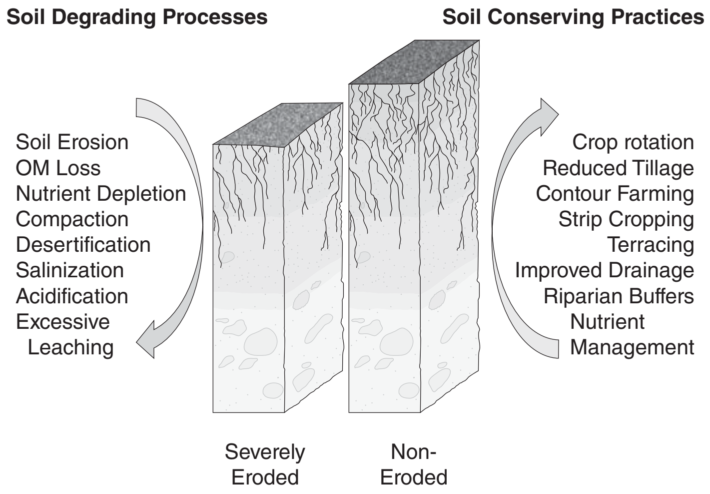

Figure 12-1
Soil productivity is reduced by soil degradating processes and improved by soil conservating practices.

TABLE 12-1
MEASURABLE SOIL PROPERTIES USED AS INDICATORS OF SOIL HEALTH

Measurement	Process Affected
Topsoil depth	Root volume, H_2O/nutrient availability
Soil OM	Nutrient cycling, H_2O/pesticide retention, soil structure, porosity
Infiltration	Runoff, erosion, leaching potential, plant available H_2O
Aggregation	Soil structure, infiltration, erosion, root growth
Bulk density	Root penetration, H_2O/air-filled pore space, microbial activity
Microbial biomass	Biological activity, nutrient cycling, pesticide degradation
Soil pH	Nutrient availability, pesticide absorption and mobility, root growth
Salinity, sodicity	Soil structure, infiltration, crop growth
Nutrient availability	Plant growth, environmental hazard

Management practices that degrade a natively productive soil reduce crop yield and producer profitability (Fig. 12-2). When a soil is not functioning to its full capacity, changes in many physical, biological, and chemical soil properties can be observed or measured (Table 12-2). For example, dryland wheat yields declined until growers adopted technologies that improved soil productivity and wheat yield (Fig. 12-3).

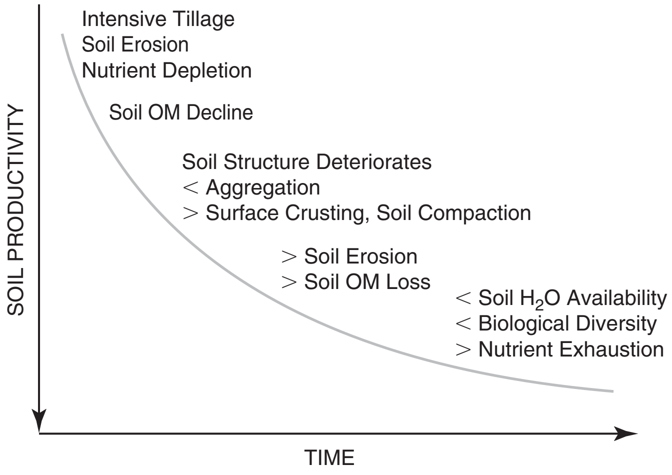

Figure 12-2
Soil management practices that degrade soil health ultimately reduce the soils ability to support crop production.

TABLE 12-2
SOIL FACTORS THAT NEGATIVELY INFLUENCE SOIL HEALTH

Soil Properties		
Physical	*Chemical*	*Biological*
Compaction	Nutrient depletion	Low microbiological activity
Low infiltration	Excessive acidity	Low organism diversity
Poor drainage	High salinity or sodicity	Low organic matter
Erosion	Heavy metal contamination	High pest or pathogens
Poor aggregation	Pesticide contamination	High weed seed bank
Surface crusting		
Low plant available H_2O		
Shallow soil depth		

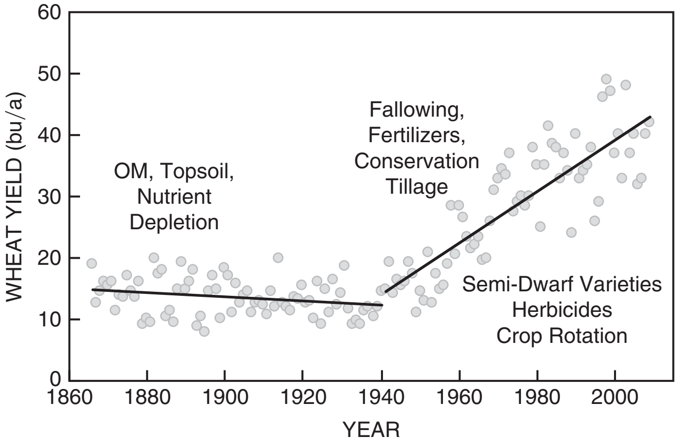

Figure 12-3
Relative changes in dryland wheat productivity in the United States. (USDA-NASS, 2010.)

Although all of the soil properties inherent in soil health are important, soil OM content is the most critical, because of its influence on many characteristics of a productive soil (Table 12-3). For example, increasing soil C increases aggregate stability

TABLE 12-3
CHARACTERISTICS OF SOIL OM AND ASSOCIATED EFFECTS ON SOIL AND PLANTS

Property	Effect on Soil	Effect on Plant
Color	Imparts dark color	> surface soil temperature advances germination & seedling growth (depending on residue cover)
H_2O retention	Holds ~20 times its weight in H_2O	> H_2O holding capacity, > plant available H_2O esp. in sandy soils
OM-clay interaction	Cements soil particles into aggregates	Improves soil structure & porosity, enhances gas exchange, infiltration, root proliferation in soil
CEC	Increase CEC 20 - 70%	> nutrient retention and availability
Mineralization / immobilization	Nutrient cycling	Increases nutrient availability, retains/conserves nutrients
Buffer capacity	pH and nutrient buffering	Buffer pH and nutrient changes in solution
Chelation	Stable metal (M^{n+}) complexes	Enhances micronutrient availability
Solubility	Insoluble humus-clay complexes, many soluble low m.w. organic compounds	Soluble compound-nutrient complexes leach nutrients from surface to subsoil areas
OM-organic molecules	Pesticide bioactivity, persistence	Influences pesticide degradation

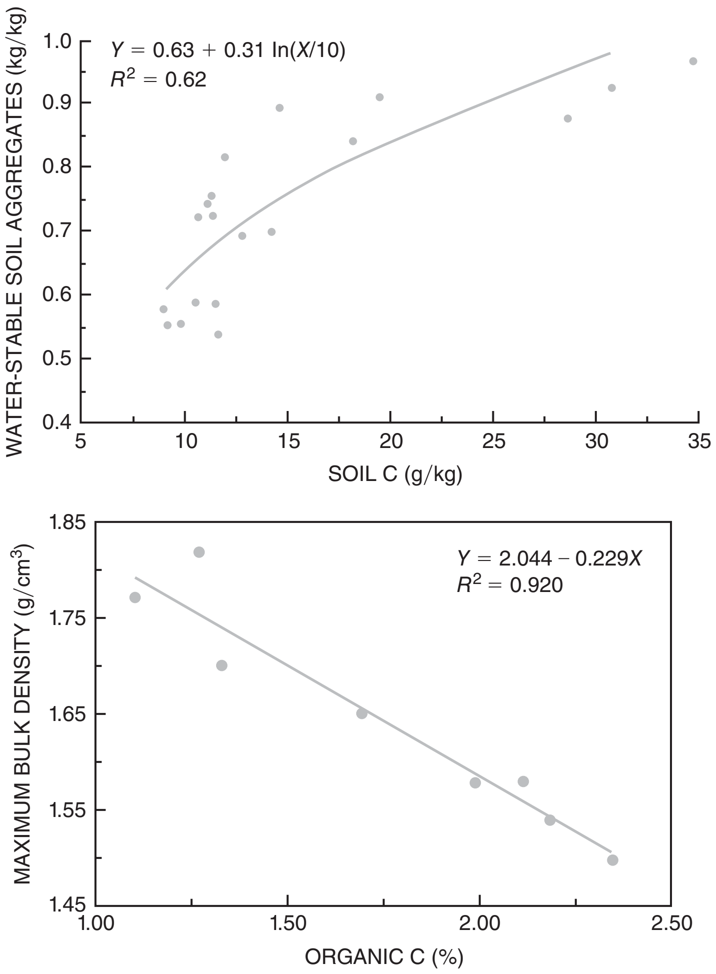

Figure 12-4
Influence of soil C on aggregate stability (top) and soil bulk density (bottom).
(USDA-NRCS, 2005.)

and reduces bulk density, which increases infiltration, improves root proliferation through the soil, and improves soil resistance to water and wind erosion (Fig. 12-4).

The steady-state OM level depends on soil and crop management practices influencing C accumulation and loss (Fig. 12-5). If management practices are changed, a new OM level is attained that may be lower or higher than the previous level. Maintenance of OM for the sake of maintenance alone is not a practical approach to farming. It is more realistic to use a management system that will give sustained profitable production without degradation of OM.

When a virgin soil is cultivated, OM decline is rapid during the first 10 years and then decreases at gradually diminishing rates for several decades (Fig. 12-6). Increased aeration by soil tillage stimulates microbial oxidation of soil organic C and increases loss of OM-rich topsoil by water and wind erosion. Many studies have suggested that under continuous cultivation, soil OM declines approximately 50% in 40–70 years, depending on the environment and quantity of residue returned. Eventually, an apparent equilibrium is reached, where soil OM gains equal losses.

Several long-term studies demonstrate the exponential declines in soil OM after virgin soils are tilled (Fig. 12-7). These data show that OM decreased ≈40% after 45 years in a conventionally tilled wheat-fallow system. Maintenance of 2% OM occurred with annual application of 10 t/a manure (C and N added), whereas annual application of 40 lb N/a had little influence on OM. Reducing C input by burning crop residue further decreased soil OM. The influence of C and N balance on grain yield is also evident (Fig. 12-7).

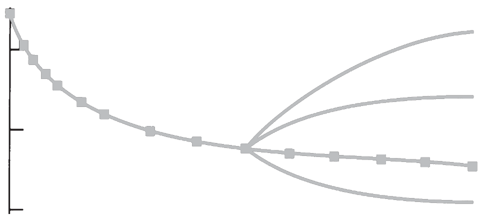

Figure 12-5
Hypothetical decrease in soil OM with time. At 50 years, changes in soil and crop management can either maintain (A), decrease (B), or increase (C, D) soil OM. (A) represents no change in cropping system; (B) represents a change that would accelerate OM loss (i.e., more intensive tillage); (C) might represent adoption of reduced tillage or a crop rotation that produces more residue; (D) might reflect the change in OM following adoption of a high-yield no-till system or rotations that return large quantities of residue.

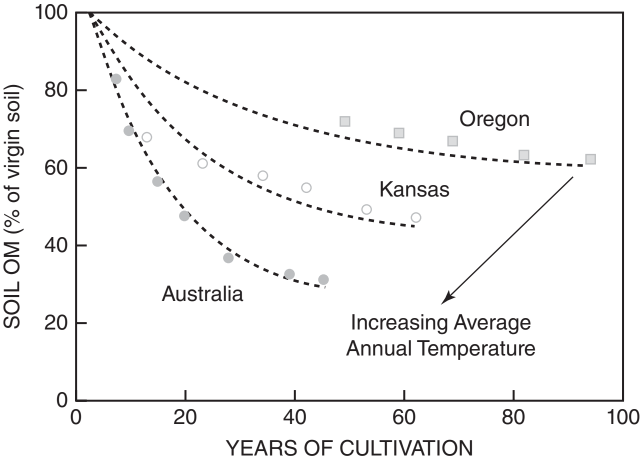

Figure 12-6
Decline in soil C with time since initial cultivation in corn and wheat cropping systems. Increasing temperature regime increases rate of OM oxidation.

(Adapted from Paustian et al., 1997, Mgmt. Controls on Soil C., p. 25, CRC Press, Boca Raton, Fla.)

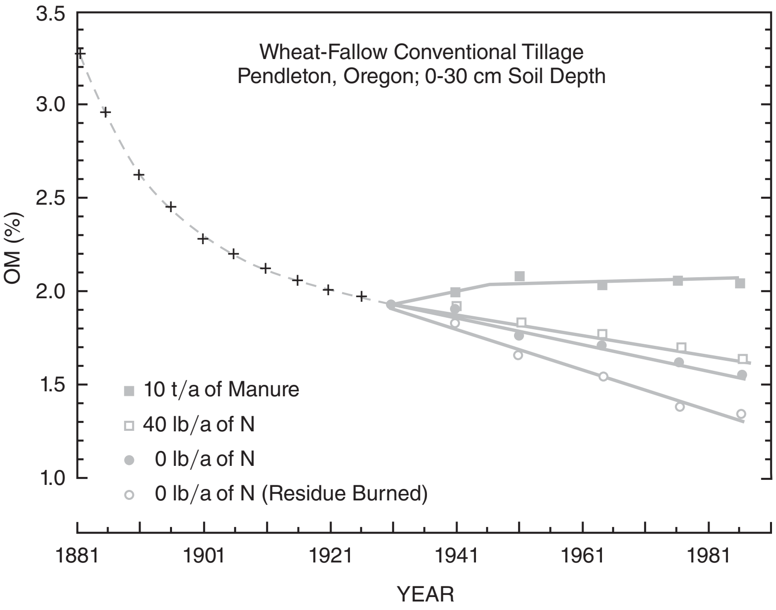

Figure 12-7
Effects of increasing or decreasing C and N (manure or fertilizer N) inputs on soil OM (top) and grain yield (bottom) in a wheat-fallow cropping system.

(Rasmussen, 1989, USDA-ARS, Bull. 675.)

Figure 12-7
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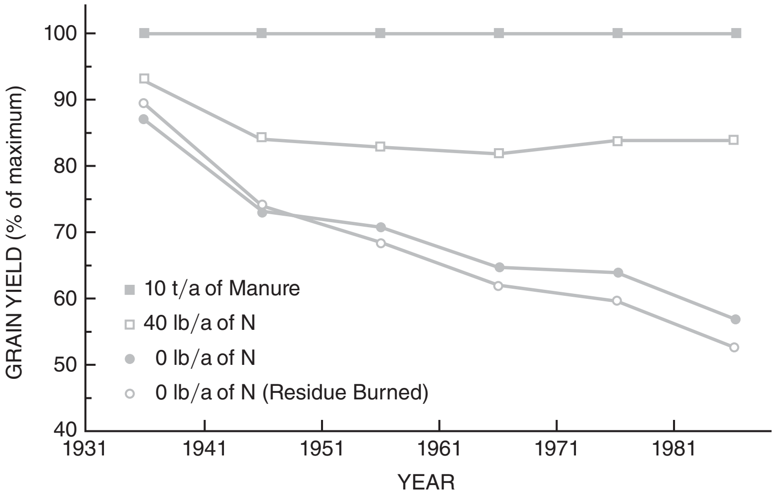
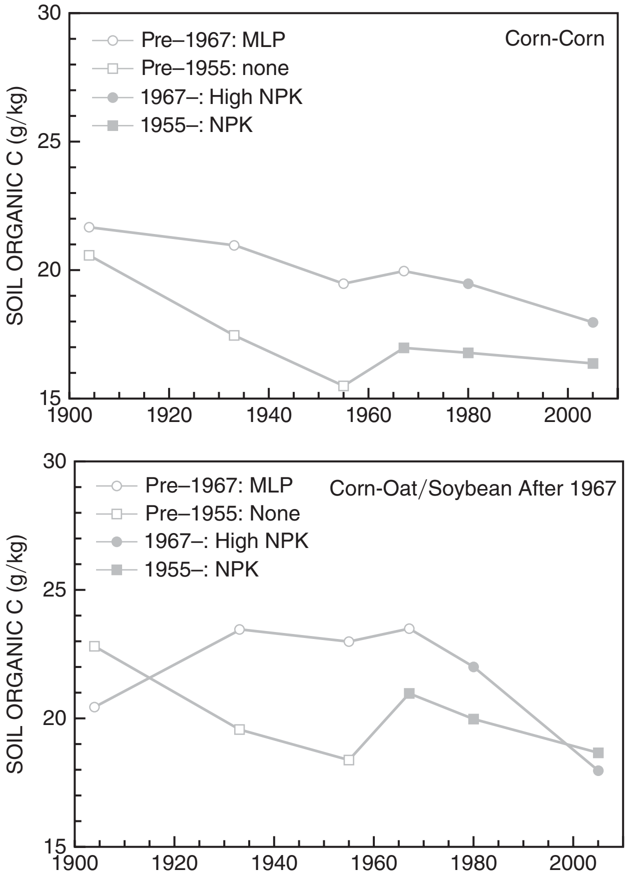


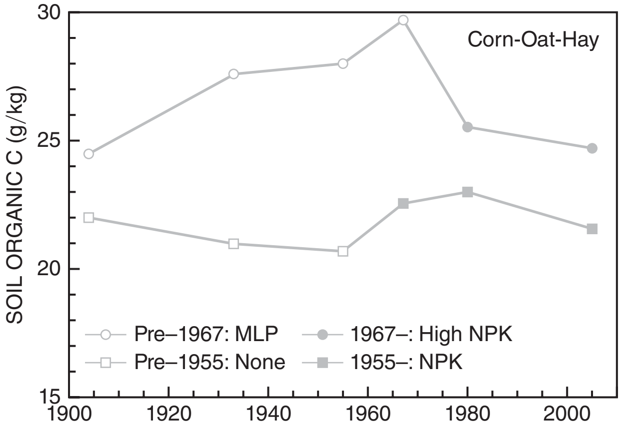
Long-term rotation and nutrient management effects on soil OM are well documented (Fig. 12-8). Generally, soil OM increases with rotations compared to continuous cropping due to higher residue C returned associated with higher yields. Also, ≈100 years of annual manure addition increased soil OM compared with no manure applied. Interestingly, when manure application was replaced with fertilizer N, soil OM declined.

Similarly, dryland crop rotations increased soil OM with increasing cropping intensity or reduced dependence on fallowing (Fig. 12-9). Soil OM increased as more residue was produced in the wheat-corn-fallow and wheat-corn-millet-fallow systems compared with the wheat-fallow-wheat system.

Figure 12-8
Long-term influence of crop rotation and nutrient management on soil C. Open circles (○) represent manure, lime, and P (MLP) applied during 1867–1966 and replaced with NPK from 1967 to 2005 (●). Open squares (□) represent no amendments used during 1867–1955 and replaced with NPK from 1955 to 2005 (■).

(*Khan et al., 2007*, J. Environ. Qual., *36:1821–1832.*)





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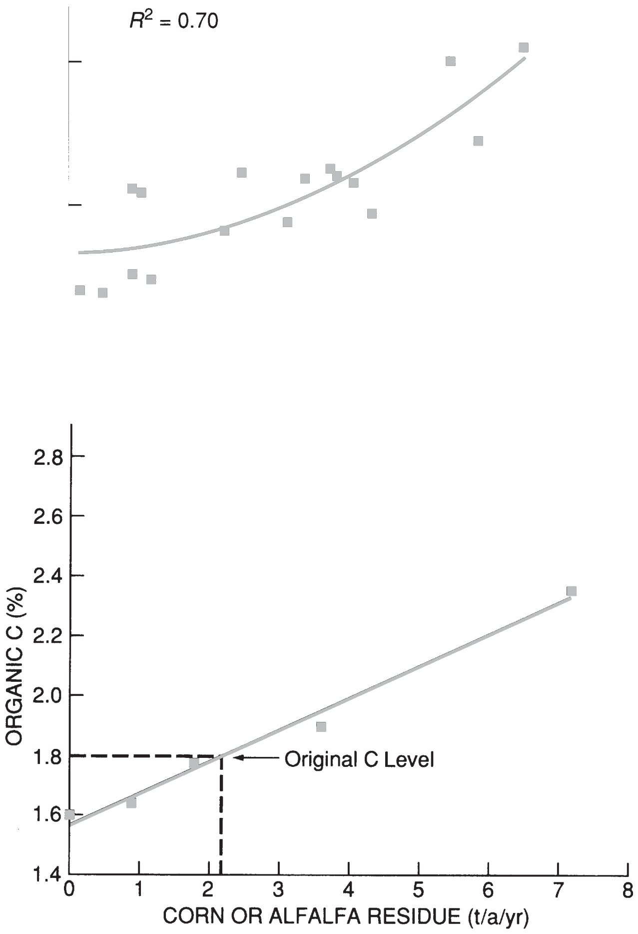


Figure 12-9
Increasing no-till cropping intensity increased OM compared with wheat-fallow-wheat systems (top). W, wheat; C, corn; M, millet; F, fallow. (Peterson and Westfall, 1990, Proc. Great Plains Soil Fert. Conf.) *Influence of corn or alfalfa residue incorporated into the soil for 11 years on soil C (bottom).* (*Larson et al., 1972,* Agron. J., *64:204.*)

Generally, the quantity of residue returned to the soil will have a much greater effect on increasing soil OM than residue N content. Figure 12-9 shows that even though N content of alfalfa is much greater than corn, the original soil C content was maintained with either corn or alfalfa residue. Increasing residue produced and returned with either crop increased soil organic C. Soil organic C would have been greater if all of the alfalfa residue had been left on the soil surface.

Soil OM transformations are very dynamic. Intensive tillage systems, fallowing, and low crop productivity, combined with physical soil loss by erosion, decrease soil OM content over time (Fig. 12-5). Increasing soil OM requires reducing tillage intensity and increasing the quantity of CO_2 fixed by plants and returned to the soil. Increasing C input or sequestration depends on the interaction between more productive rotations and reduced tillage.

Many factors determine whether soil OM is increased or decreased by cropping systems. The key is to keep large amounts of crop residues (stover and roots) cycling through the soil. Continued good management, including adequate fertilization, helps to maintain the cycle. Sustaining soil productivity for future generations ultimately depends on maintaining optimum soil OM levels.

SOIL EROSION EFFECTS ON CROP PRODUCTIVITY

Soil erosion represents the greatest threat to sustained soil productivity. Physical soil loss by water and wind (Fig. 12-10) reduces soil productivity by:

- decreasing topsoil thickness and rooting depth
- decreasing OM and microbial activity, which decreases nutrient supply
- decreasing depth to higher subsoil clay content, which decreases infiltration and plant available H_2O

Loss of soil productivity through soil erosion and other soil-degrading processes occurs throughout the world; in developed regions, producers have afforded adoption of many soil conservation technologies (Table 1-3). While the extent of soil erosion has decreased in the U.S., approximately 30% of cropland still exceeds acceptable soil loss tolerance (Fig. 12-11).

Figure 12-10
Examples of water (top) and wind (bottom) erosion in farm fields.

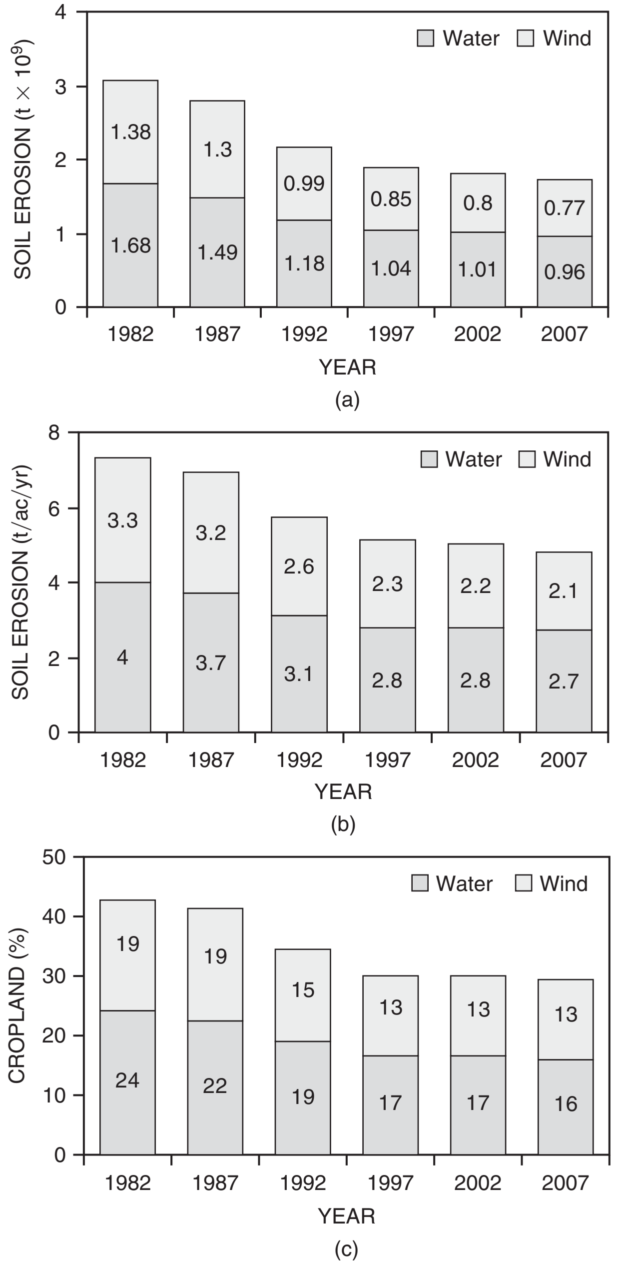


Figure 12-11
Trend in total annual soil erosion loss (a), average annual soil loss per acre (b), and % cropland exceeding soil loss tolerance (c) in the United States. Soil loss tolerance or "T" represents maximum annual soil erosion without a loss in crop productivity.
(USDA-Natural Resource Cons. Serv., 2009.)

Soil erosion is a *symptom* of poor soil and crop management. Although growers may recognize or observe soil erosion on their lands, they may not be overly concerned because crop yields have substantially increased since the 1950s (Fig. 12-3). One should not confuse increasing crop yields with increasing soil productivity, because yield increases are primarily due to technological advances in crop breeding and genetics, fertilizers and nutrient management, pesticides and pest management, and other agronomic technologies.

Water and wind erosion of topsoil can reduce productivity by exposing less-productive subsoil (Table 12-4). For example, the productive capacity of eroded Ulysses soil is less than that of eroded Harney soil because the latter is a deeper soil and has a greater OM content in the subsoil, which improves nutrient availability and H_2O holding capacity (Fig. 12-12). As a result, the yield loss associated with increasing soil loss is also greater in the Ulysses than in the Harney soil (1.8 vs. 0.8 bu/a/in. topsoil, respectively). On many eroded subsoils, reduced soil OM and H_2O availability are common factors limiting productivity (Table 12-4; 12-5).

TABLE 12-4
INFLUENCE OF SOIL EROSION ON SURFACE SOIL PROPERTIES IN THREE INDIANA SOILS

Soil Series	Erosion Level	Clay	OM	PAW[1]	P
			%		*lb/a*
Corwin	Slight	19.6	3.03	12.9	62
	Moderate	20.8	2.51	9.8	61
	Severe	23.0	1.86	6.6	41
Miami	Slight	15.4	1.89	16.1	95
	Moderate	18.1	1.64	11.5	86
	Severe	22.1	1.51	4.8	68
Morley	Slight	18.6	1.91	7.4	81
	Moderate	23.0	1.76	6.2	66
	Severe	28.4	1.60	3.6	50

[1] PAW = plant available soil H_2O.
Source: USDA-NRCS, 1998, Soil Quality-Agronomy Tech. Note No.7.

Clearly, loss of topsoil exposes subsoils with physical, biological, and chemical properties less suitable for optimum crop production. As subsoil characteristics (<depth, >% clay, <pH, <OM) become less suitable for crop growth, increasing inputs or management will have less effect on yield (Fig. 12-13).

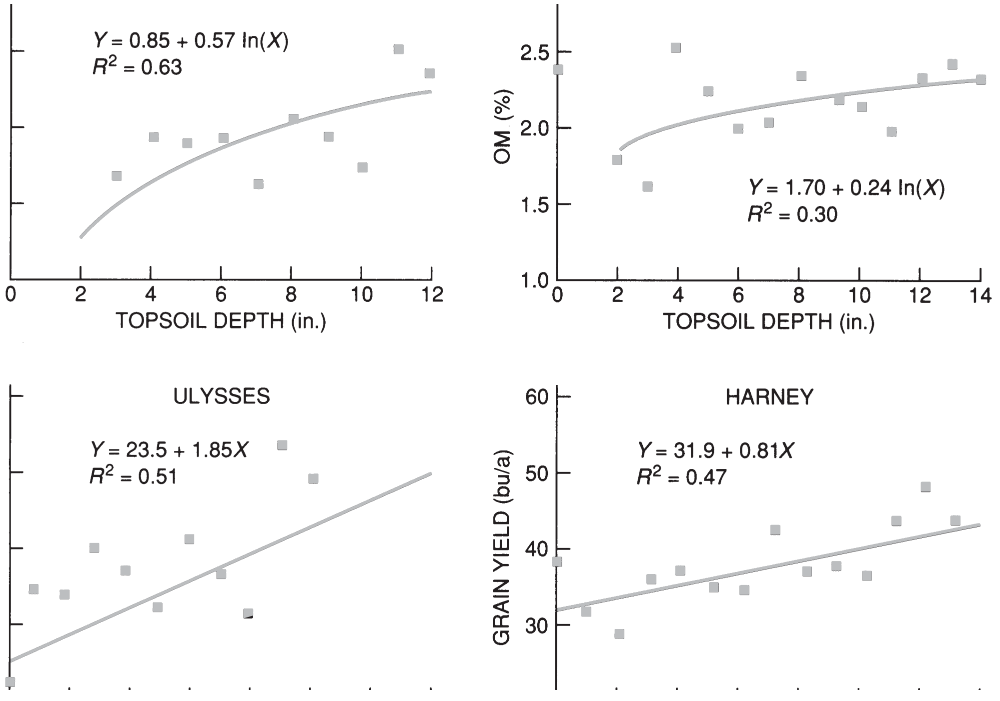


Figure 12-12
Loss of topsoil by wind and water erosion reduces soil OM, which contributes to wheat grain yield loss. Loss in productivity varies between soils, depending on initial topsoil depth and productivity of the subsoil. Compared with the Ulysses soil, the Harney soil has a deeper topsoil; thus, productivity is not reduced as much as the Ulysses soil under equivalent topsoil loss. (Havlin et al., 1992, Proc. Great Plains Soil Fert. Conf.)

TABLE 12-5
INFLUENCE OF SOIL EROSION ON CROP YIELD LOSS AND THE DOMINANT SOIL PROPERTIES AFFECTING CROP PRODUCTIVITY IN SELECTED U.S. SOILS

			Factors Related to Yield Loss					
Location	**Erosion Level**	**% Yield Loss**	**<H_2O** *Holding Capacity*	*<pH*	*>Bd*	*> % Clay*	*< OM*	*< Rooting Depth*
Indiana	Moderate	5	■			■		
	Severe	15	■			■	■	■
Iowa	Moderate	7					■	■
	Severe	16	■				■	
Michigan	Moderate	11		■				
Minnesota	Moderate	3	■				■	
Missouri	Severe	22						
Nebraska	Moderate	7	■		■	■		
	Severe	9	■		■	■		
N. Dakota	Severe	20		■	■	■	■	
S. Dakota	Moderate	4		■		■		■
	Severe	16	■	■	■			■
Wisconsin	Moderate	8	■					
	Severe	6	■					

Source: USDA-NRCS, 1998, Soil Quality-Agronomy Tech. Note No.7.

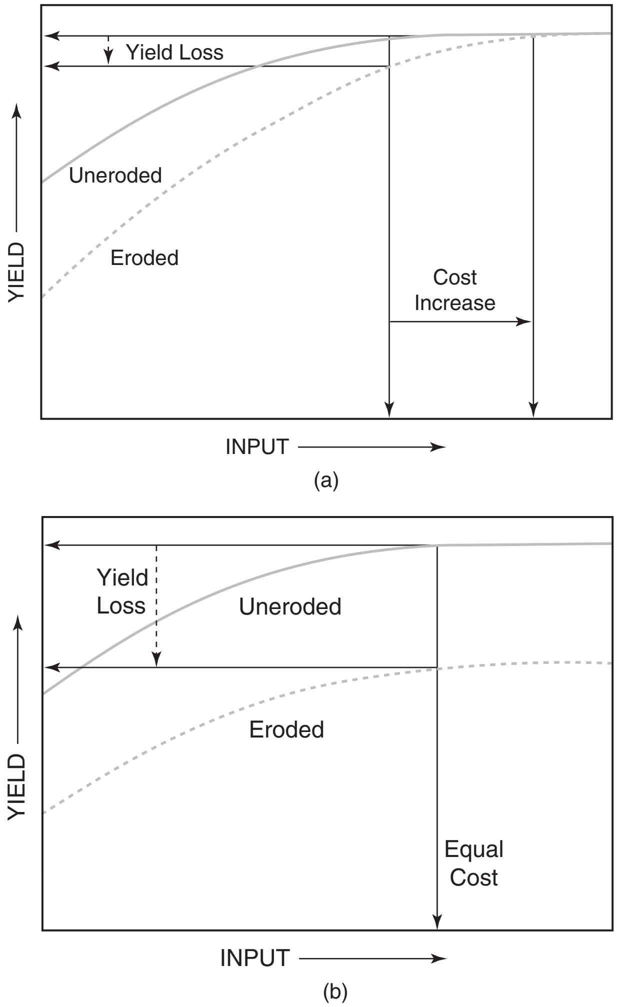
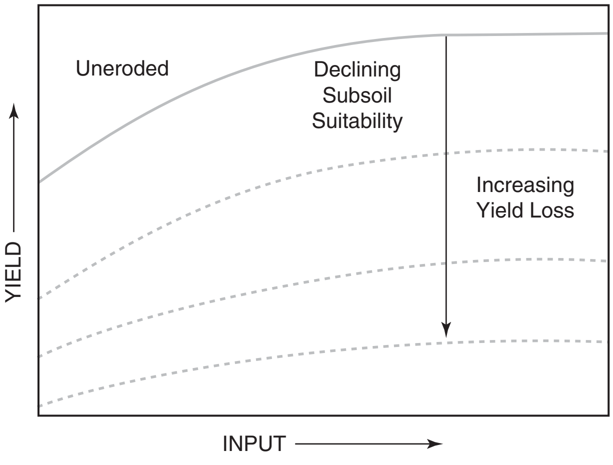


Figure 12-13
Effect of degree of erosion and exposed subsoil properties on crop productivity. (a) represents moderate erosion (topsoil loss) or a subsoil with soil characteristics where increasing inputs would produce similar yield as an uneroded soil. (b) represents severe erosion and/or subsoil characteristics that results in a crop yield loss regardless of input level. (c) illustrates how declining subsoil suitability to support crop growth decreases yield potential.

Figure 12-13
(Continued)



(c)

Profitable crop production on eroded soils is an important agricultural problem that severely limits our ability to meet world food demand (Chapter 1). It is imperative that crop production systems minimize the destructive effects of water and wind erosion.

MANAGEMENT PRACTICES ESSENTIAL TO SOIL HEALTH

Conservation Tillage

Crop residue management (tillage) systems have been developed to leave more crop residue on the surface to reduce soil and/or water loss compared with conventional or full tillage systems wherein all residues are incorporated into the soil after harvest and/or before planting. *Conservation tillage* broadly refers to tillage systems that leave ≥30% of the soil surface covered with residue after planting. Specific advantages include:

- > crop yield, except in level, fine-textured, poorly drained soils
- < soil erosion by water and wind
- > soil OM, aggregation, infiltration, and soil H_2O stored
- < surface soil evaporation
- > acreage of sloping land that can safely be used for row crops
- < labor, machinery, and fuel costs

Several disadvantages include:

- > potential for rodents, insects, and diseases in some systems
- < soil temperatures in spring, resulting in slower germination and early growth
- > management ability is required

Several unique conservation tillage methods that require specialized equipment include (Fig. 12-14):

> *no-tillage*—all crop residue left on soil surface; soil disturbance occurs only with planters and/or application of nutrients (subsurface band, Chapter 10). With heavy surface cover, no-till is not well-suited for poorly drained soils
>
> *strip tillage*—a narrow strip tilled before or at planting, incorporating residue only in the narrow strip allowing for increased soil temperature and decreased soil H_2O at planting compared to no-till

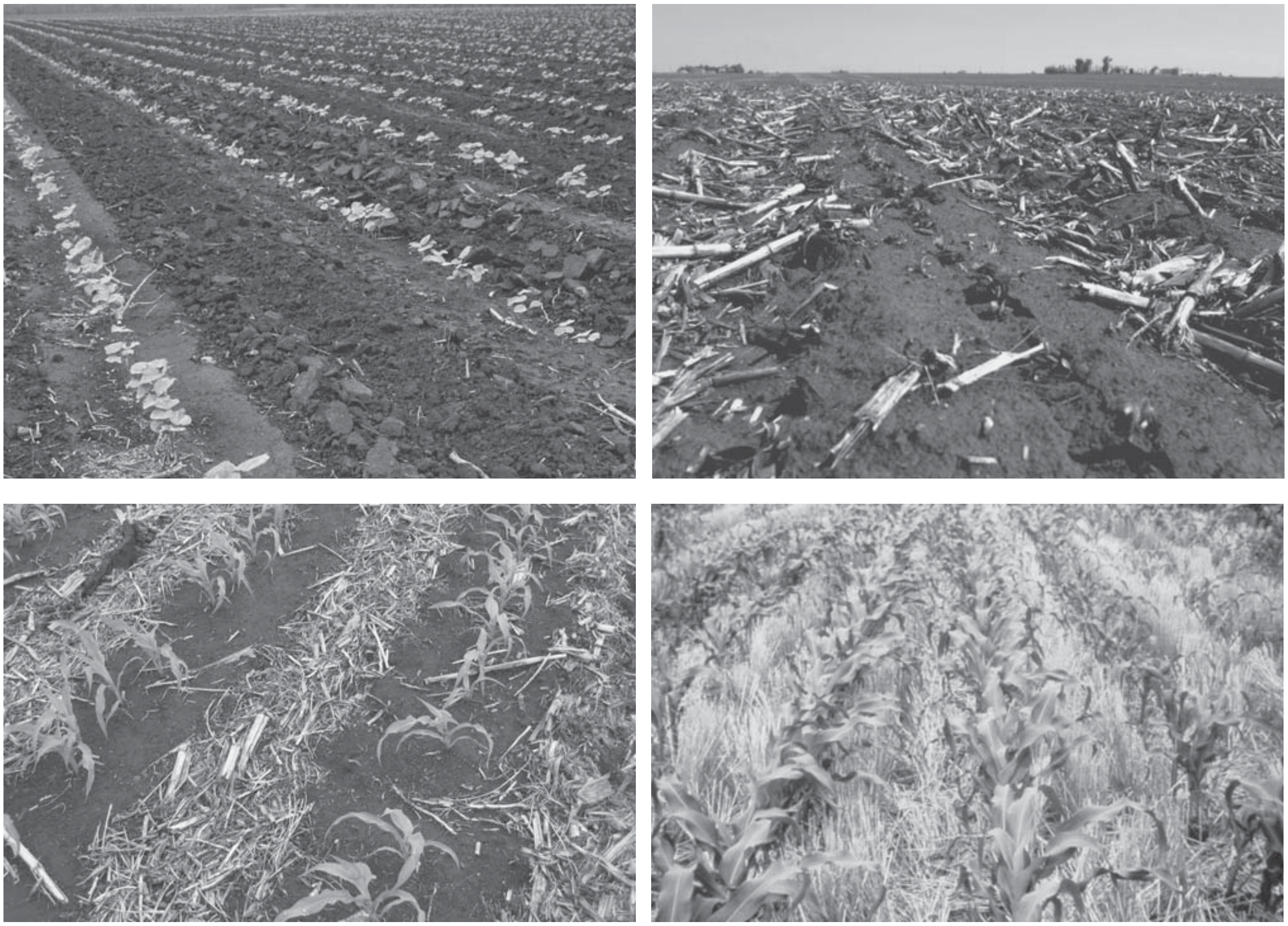


Figure 12-14
Tillage systems influence surface residue cover and erosion control. Upper left-full tillage (no residue cover); upper right-ridge tillage; lower left-strip tillage (courtesy L. Stahl, Univ. of MN), *lower right-no tillage.* (Other photos courtesy of USDA.)

ridge tillage—a single-pass tillage-planting operation; planter units work on ridges made the previous year during cultivation, after harvest, or preplant; planter pushes old residue into the area between the rows; practice useful on poorly drained, clay soils (Fig. 12-15)

Conservation Tillage Effects on Soil Erosion The quantity of surface residue remaining after tillage operations depends on crop residue type and amount, and tillage characteristics (e.g., specific implement, number of passes, tillage depth, speed of travel). Figure 12-16 illustrates the relationship between residue cover and residue mass. Low residue producing crops (e.g., soybean, sunflower, cotton, peanuts) provide little surface cover compared with small- and coarse-grain crops.

The quantity of residue required to prevent or minimize soil erosion depends on:

- soil characteristics (e.g., texture, OM, surface roughness, structure, depth, slope percentages, and slope length)
- residue characteristics (e.g., type, quantity, orientation)
- rainfall characteristics (e.g., quantity, duration, and intensity)
- wind characteristics (e.g., velocity, direction, gusts, and duration)

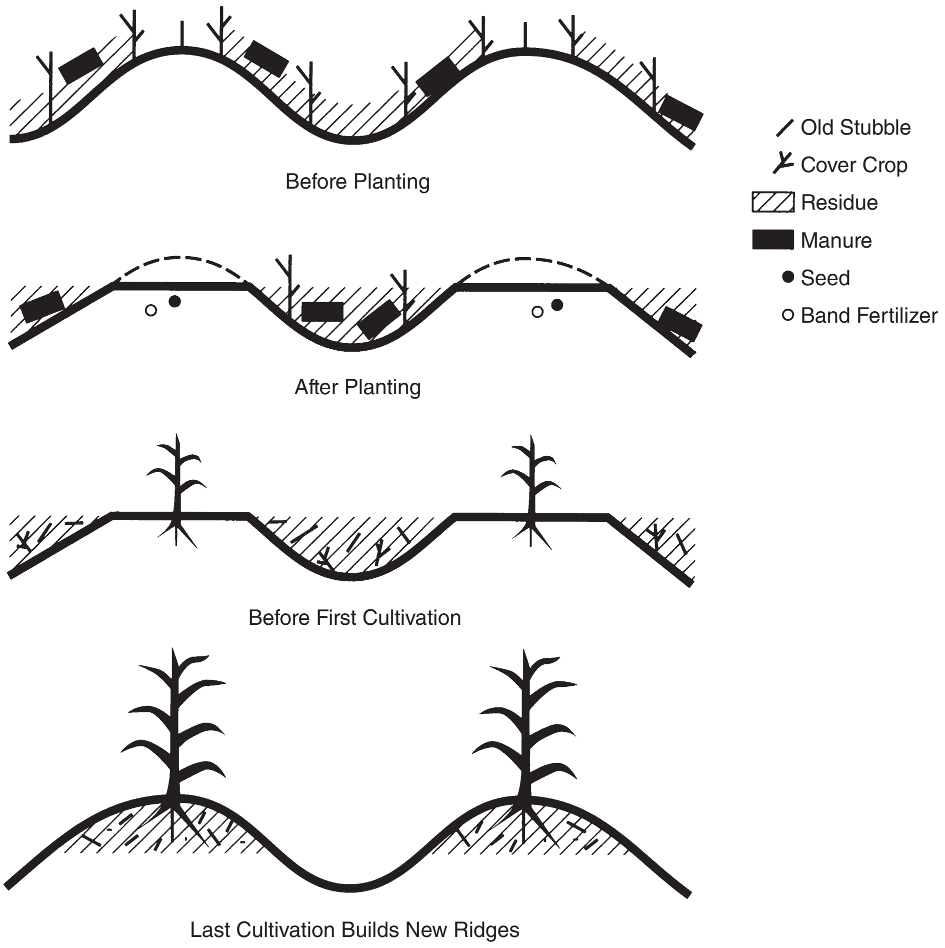


Figure 12-15
Ridge tillage production system. The planter tills 2–4-in. soil in 6–8-in. band on top of ridges. Seeds are planted on top of ridges, and soil from ridges is mixed with crop residue between ridges. Soil on ridges is generally warmer than soil on flat fields or between ridges. Warm soil facilitates crop germination. Crop residue between ridges also reduces soil erosion and increases moisture retention. Mechanical cultivation during the growing season helps to control weeds, reduces need for herbicides, and rebuilds ridges for the next season.

In general, as surface residue cover increases, soil erosion potential decreases (Fig. 12-16). At about 30% residue cover, soil loss is about 20% of that observed under bare, fallow (no crop, no residue cover) conditions that maximize erosion potential. Thus, increasing surface residue cover decreases soil detachment by water and wind, and soil erosion loss. (Fig. 12-17). While reducing tillage intensity increases surface residue cover, surface cover was much less after planting soybean than corn, resulting in considerably greater soil loss (Table 12-6). In addition, soil loss is generally greater with tillage up/down the slope

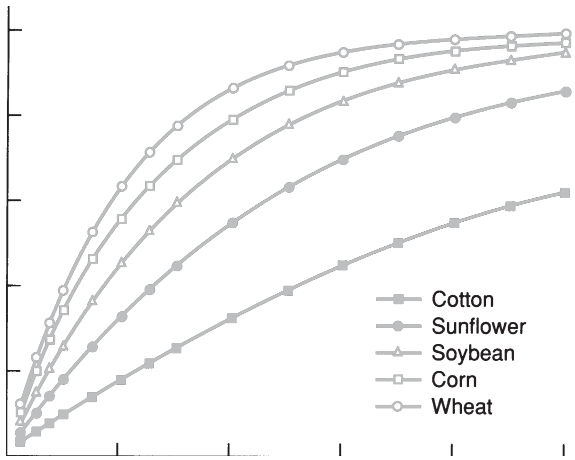


Figure 12-16
Relationship between residue mass and % surface cover for selected crops (top). Relationship between soil loss with residue cover divided by soil loss from bare soil (soil loss ratio) and % surface residue cover (bottom).
(USDA-NRCS, 1998.)

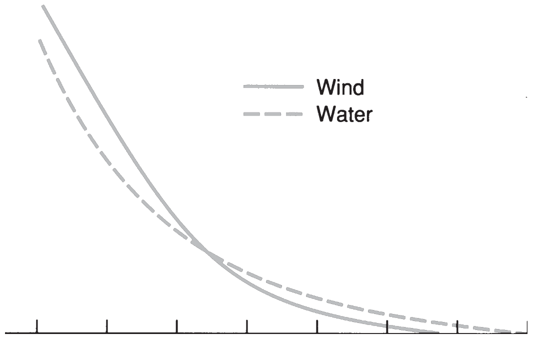


Figure 12-16
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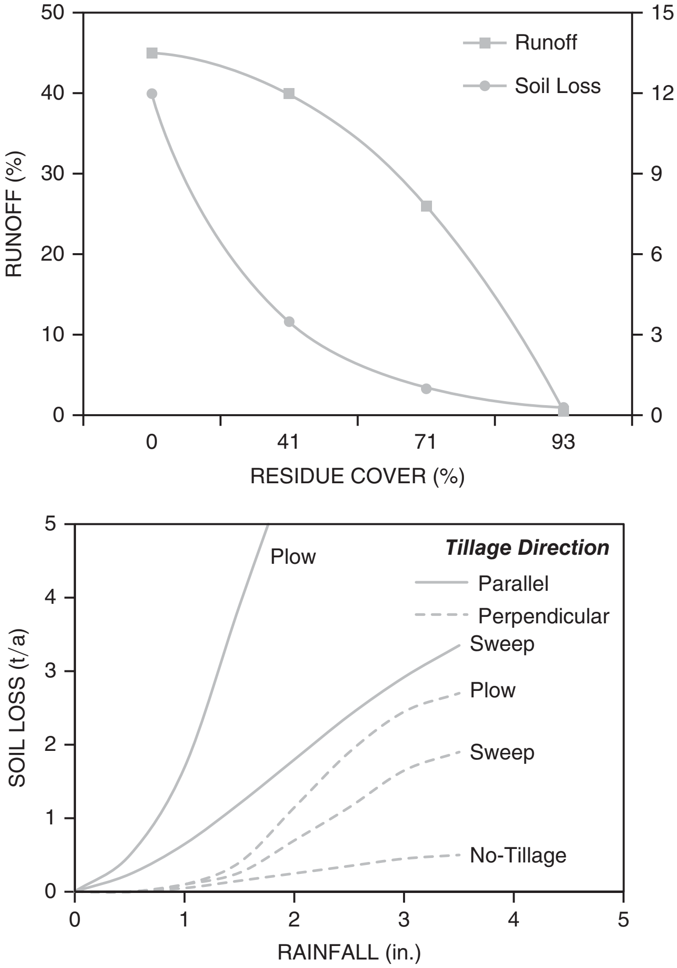


Figure 12-17
Surface residue cover effects on runoff (% of rainfall) and soil loss (top) and influence of tillage direction (relative to slope) and intensity on soil loss (bottom).
(*J. Mannering, 1996, personal communication; adapted from Dickey et al., 1981,* Neb Guide, *181–554, Univ. of Neb.*)

compared to tillage on the contour. The same relationship can be seen in Figure 12-17; however, no-tillage (100% residue cover) provides the largest soil erosion protection.

Conservation Tillage Effects on Nutrient Supply Decreasing tillage intensity and increasing surface residue cover will influence soil temperature and H_2O, which affects microbial activity, nutrient supply, and ultimately plant growth. Soil temperatures are generally lower under conservation tillage than under full tillage due to the insulating effect of the residues (Fig. 12-18). Decomposition of crop residue and soil OM, with subsequent release of plant nutrients (e.g., N, P, S), is restricted by low soil temperatures. Low soil temperatures may also retard root growth and nutrient

TABLE 12-6
INFLUENCE OF TILLAGE INTENSITY AND DIRECTION ON SURFACE RESIDUE COVER AND SOIL LOSS

	Tillage Up/Down Slope				Tillage On Slope Contour			
	Surface Cover, %		*Soil Loss, t/a*		*Surface Cover, %*		*Soil Loss, t/a*	
	Previous Crop				Previous Crop			
Tillage System	*Corn*	*Soybean*	*Corn*	*Soybean*	*Corn*	*Soybean*	*Corn*	*Soybean*
Fall plow	7	1	9.8	18.3	4	2	5.7	11.4
Fall chisel	25	12	6.7	13.5	50	11	0.6	3.3
No-tillage	69	26	1.1	6.0	85	59	0.5	1.7

Note: Indiana soils, ~4.5% slope, 35 ft slope length, 5-in. simulated rainfall.
Source: Siemens and Oschwald, 1976, *ASA*, 76:2552.

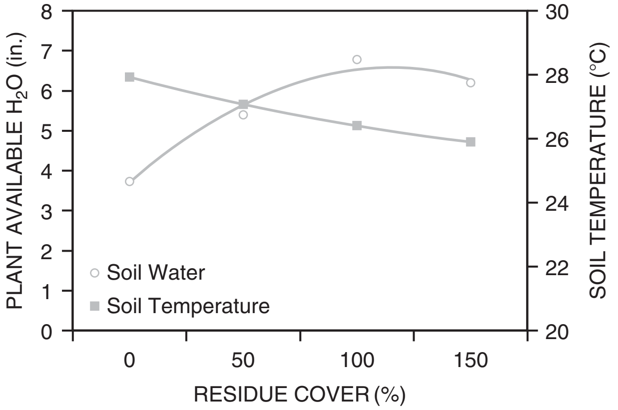


Figure 12-18
Increasing surface residue cover increases plant available H_2O (in./5 ft rooting depth) and decreases surface soil temperature (average growing season maximum soil temperature @ 2 in depth). The 150% residue cover established by adding the residue removed from the 50% residue treatment.
(Doran et al., 1984, SSSAJ/, 48:640–645.)

diffusion to plant roots, although the temperature difference is generally only a few degrees.

Increasing surface residue cover by reducing tillage can increase plant available H_2O by decreasing runoff, increasing infiltration, and reducing evaporation from the soil surface (Fig. 12-18). The H_2O conservation value of reduced tillage is particularly critical in semi-arid regions. Increasing residue cover with no-till systems can increase total H_2O stored, consequently improving yield and WUE compared with residue incorporation (Table 12-7).

TABLE 12-7
TILLAGE EFFECTS ON WATER STORAGE, SORGHUM GRAIN YIELD, AND WUE IN A WHEAT-SORGHUM-FALLOW CROPPING SYSTEM

	Precipitation				
Tillage System	*Total*	*Storage*	**GrainYield**	**Crop H_2O Use**	**WUE**
	In.	*%*	*bu/a*	*In.*	*bu/in.*
Disk	5.9	15.2	29	12.5	2.3
Sweep	6.7	22.7	37	12.8	2.9
No-till	8.5	35.2	47	13.8	3.4

Source: Unger and Weise, 1979, *SSSAJ*/43:582.

The influence of tillage on soil temperature and moisture dramatically influences microbial activity (Fig. 12-19). Mixing air and plant residues into the surface soil with tillage increases soil aeration and temperature, stimulating aerobic microbial decomposition of residue and soil C, while increasing nutrient mineralization. The net tillage effect is increased OM mineralization, resulting in gradual OM loss over time (Fig. 12-6; 12-20). Reducing tillage intensity reduces OM mineralization and C loss; thus, soil OM levels can be sustained. As discussed earlier, N applications combined with high-residue-producing cropping systems can increase soil OM, although 5–8 years of continuous no-till systems may be needed before effects are measurable. The increase in soil OM occurs predominantly in the surface 2 in., although increased OM can be measured deeper in the profile after decades of continuous no-till cropping.

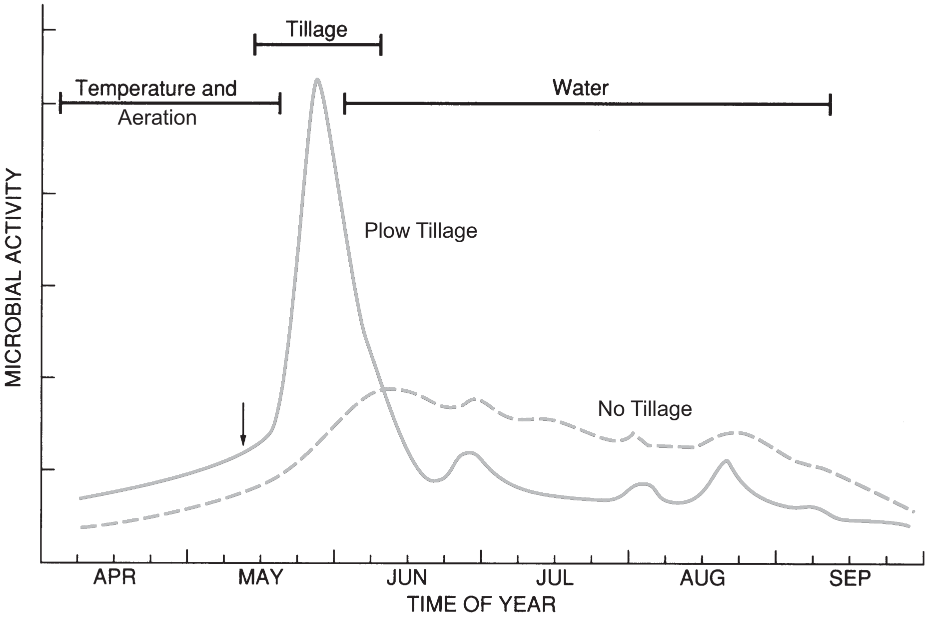


Figure 12-19
Hypothetical relationship between relative microbial activity and time of year in a plowed and a no-till soil; factors controlling activity are shown on top of the graph; the arrow indicates time of plowing.
(J. Doran, personal communication.)

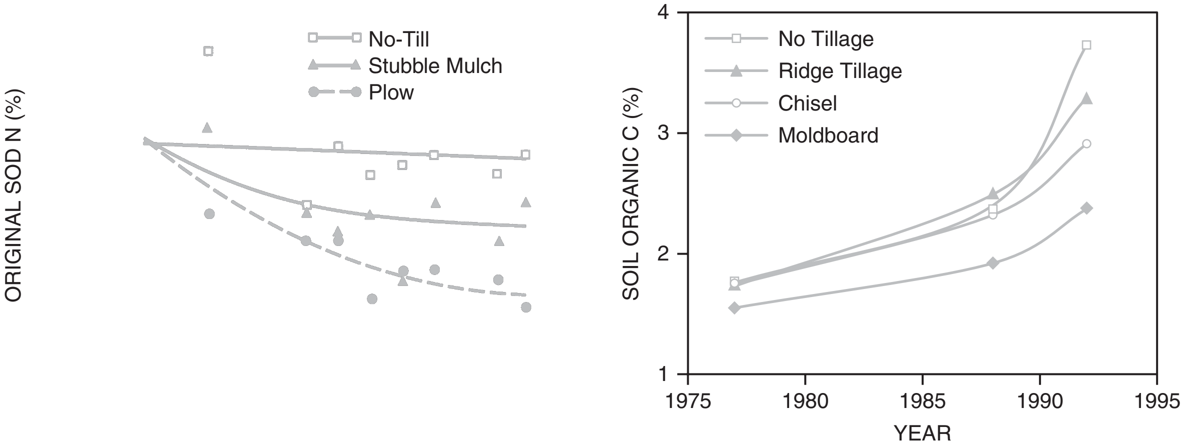
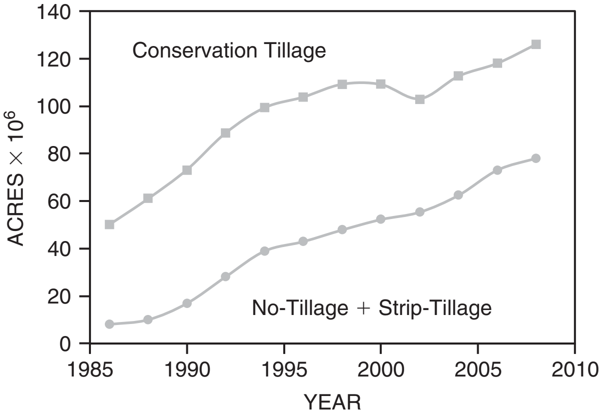


Figure 12-20
Influence of tillage on soil N, measured as % of total N in undisturbed prairie soil (left). (Lamb et al., 1985, *SSSAJ*, 49:352).
Decreasing tillage intensity increased soil C. The increase in C with moldboard plow tillage is due to an increase in yield (right).
(*Power et al., 2001*, J. Environ. Qual., *30:1866–1880.*)

Figure 12-21
Adoption of conservation tillage systems in the United States.
(USDA-CTIC, 2008.)



Adoption of Conservation Tillage Systems Currently, over 60% of the cropland in the U.S. is under some form of conservation tillage (Fig. 12-21). No-till cropping will continue to increase, where ≈50% of U.S. cropland in the next 20 years will be under no-till systems. The attractive features of no-tillage systems are:

- row crop production on sloping lands is more feasible, with less loss of soil, nutrients, and H_2O
- increased infiltration and reduced evaporation reduces drought stress and increases WUE
- energy, time, labor, and machinery costs are reduced

Crop Rotation

The increased supply of inexpensive N in the 1960s encouraged non-legume cropping systems on soils where erosion was not a serious problem. Most cropping systems are currently used because of favorable economics. The most common example where most producers in a large geographical area use the same crop rotation is the corn-soybean rotation in the Midwest United States. The overwhelming use of this 2-year rotation indicates powerful economic or social factors influencing cropping decisions. The primary factors include government program incentives, crop insurance policy, agronomic research focused on corn-soybean, and economics related to high global demand for these grains and lower production costs related to similar machinery and equipment. The Morrow plots at the University of Illinois clearly document the benefit of long-term rotation (and adequate nutrient supply) on crop productivity compared to continuous cropping (Table 12-8). In the Midwest, corn yield is often increased ≈10–20% in rotation with soybean than with continuous corn (Fig. 4-10). Similarly, soybean yield in rotation with corn is also higher than in continuous soybean. Corn-soybean rotation costs about 10–15% less to produce than continuous corn, primarily due to increased productivity with lower N cost.

Crop rotations are commonly used to diversify income, spread labor requirements throughout the year, and spread crop loss risk associated with weather and pests over two or more crops. Rotations are primarily used to increase crop productivity and enhance soil health by:

- reducing wind and water erosion of topsoil
- maintaining or increasing soil OM
- increasing soil N supply with legumes in the rotation
- utilizing residual nutrients applied to previous crop
- deep-rooted legumes and other crops may improve soil structure, water infiltration, and nutrient redistribution from subsoil to surface soils

TABLE 12-8
AVERAGE CORN YIELDS IN THE MORROW PLOTS SINCE 1967

Fertility Treatment	Continuous Corn	Corn-Soybean	Corn-Oat-Hay	Treatment Mean
	bu/a			
Unamended	47	79	100	*76*
Manure[1]	82	108	124	*105*
Manure[2]	92	125	147	*121*
U-NPK[3]	127	153	168	*150*
M-NPK[4]	141	157	164	*154*
H-NPK[5]	139	160	161	*153*
Rotation mean	*105*	*131*	*144*	

[1] Manure applied at 4 t/a/y to continuous corn, 6 t/a/y applied before corn in corn-soybean and corn-oat-hay rotations. Plant density is 8,000 plants/a in manure and unamended plots.

[2] Manure amendment rates are the same as above, plant density is 16,000 plants/a.

[3] No manure, 200 lb N/a as urea; plots testing <45 lb P/a and 336 lb K/a amended with 49 and 93 lb/a TSP and KCl.

[4] Manure and N, P, and K applied as in U-NPK.

[5] Plots that had received manure until 1967 were amended with only 300 lb N/a as urea, and P and K were maintained at >112 and 560 lb/a of P and K.

Source: Aref and Wander, 1997, *Advances in Agron.*, 62:153–197.

- reducing weed, insect, and disease pressure
- labor is more broadly distributed and income is diversified

While these factors can increase crop yield, a response to crop rotation above that attributed to these factors can be observed. The specific mechanism(s) causing this *rotation effect* is difficult to identify (Fig. 4-13). In this example, corn yield increased following wheat or alfalfa, where the response is not attributed to N.

In some regions, crop options may be limited because of climatic constraints or market opportunities; thus, growers continuously produce an adapted crop that maximizes profit potential. Dryland continuous wheat-fallow in the Great Plains region is an example.

Numerous long-term experiments have demonstrated that, in general, rotations increase long-term crop and soil productivity compared with continuous cropping (Fig. 12-22).

The reasons for the production advantage with rotation cropping compared with continuous cropping depend on the crops involved, environment, and other

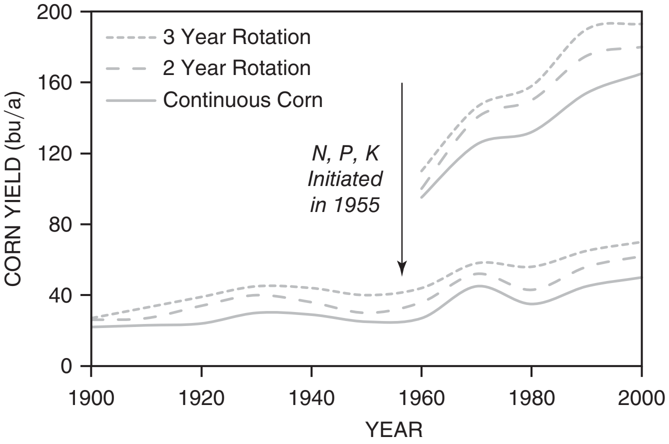


Figure 12-22
Long-term crop rotation effects on corn yield (2 year = corn-soybean; 3 year = corn-oat-soybean)

(*Adapted from Darmody and Peck, 1997*, Soil organic c changes in morrow plots, *p. 165, CRC Press, Boca Raton, Fla.*)

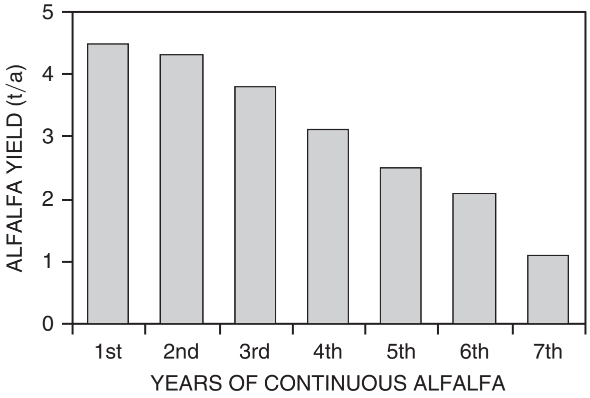


Figure 12-23
Reseeding alfalfa into alfalfa over 7 years illustrates an allelopathic decrease in alfalfa production.
(USDA-NRCS, 2009.)

interacting factors. In some cases, a crop may have a harmful effect on the subsequent crop, especially if it is the same crop. *Allelopathy* is the term used to describe the antagonistic action on like or different species. Substances released from roots and foliage or formed during the decomposition of residues can have toxic and inhibitory properties. The comparison of continuous corn versus a corn-soybean rotation is an example. Seeding alfalfa following alfalfa is often unsatisfactory (Fig. 12-23). With time, continuous wheat yields generally decrease in many regions due to allelopathic effects and increased disease and insect pressures.

Crops vary considerably in their macro- and micronutrient demand and in root morphology that influences nutrient removal from the soil profile. For example, deep-rooted crops absorb nutrients from the subsoil. As their residue decomposes in the surface soil, subsequent shallow-rooted crops may benefit from the redistribution of nutrients.

Crop Rotation Planning Widespread use of a single, simple, rotation usually leads to problems with insects, diseases, and resistant weeds, which are increasingly observed in corn-soybean (U.S. Midwest), wheat-canola (Canadian Prairies), or wheat-lupine (Australia). Use of pesticides and genetic engineered crops can be effective, although they are expensive inputs. Increasing diversity and length of rotations is also effective depending on the economics of each crop in the rotation.

Designing a crop rotation sequence should include basic agronomic principles including:

- 2-season interval between the same crop often increases rotation productivity
- specific crop rotation sequence is established to reduce volunteer plants from the previous crop
- crop options, especially with forages, within the rotation are enhanced with live-stock diversified farming systems
- vegetable crops are a viable alternative for increased profits, but required high investments in equipment and labor
- the desire to increase diversity and intensity needs to be balanced with profitability
- previous crop residue quantity, distribution, and architecture that influence pre-plant tillage and planting the subsequent crop should be considered
- previous crop residue types and management influence infiltration, in-field snow collection, evaporation, and other factors affecting soil H_2O storage critical in semi-arid regions
- to recover residual nutrients applied to a previous crop, include crops with fast germination and root development, deeper rooting depths to reach deep profile nutrients, and crops with high nutrient demand
- varying crop rotation sequence may reduce pest pressure and the probability of developing resistant, tolerant, or adapted pest species

TABLE 12-9
EXAMPLE CROPS TO INCLUDE IN CROP ROTATION PLANNING

Cool Season			Warm Season		
Grass	*Broadleaf*	*Vegetable*	*Grass*	*Broadleaf*	*Vegetable*
Barley[1]	Alfalfa	Asparagus	Corn[1]	Amaranth	Bush beans
Durum wheat	Clovers	Beets	Sorghum[1]	Buckwheat[1]	Pole beans
Oats[1]	Canola	Broccoli	Sudangrass[1]	Chickpea	Lima beans
Spring Wheat[1]	Crambe	Brussel sprouts	Millet[1]	Dry Edible beans	Cantaloupe
Winter Wheat[1]	Field pea	Cabbage	Sweet Corn	Potatoes	Cucumber
Winter Rye	Flax[1]	Cauliflower	Corn silage	Safflower	Eggplant
Triticale[1]	Lentils	Carrots	Popcorn[1]	Sunflower	Okra
	Lupine	Celery		Soybean	Peppers
	Mustard	Horseradish			Pumpkins
	Sugarbeets	Onions			Squash
		Peas			Snap beans
		Spinach			Sweet potatoes
		Turnips			Tomatoes
		Lettuce			Watermelon
		Radish			Zucchini
		Carrots			
		Mustard			

[1] High-residue-producing crop.

The crop sequence should contain different crop types (Table 12-9) such that:

- 2-crop sequence should contain a warm season and a cool season crop
- 3-crop sequence should contain a warm season and a cool season crop, neither of which may be grown in consecutive years
- 4-crop sequence should contain two different crop types, neither of which included in $>50\%$ of the sequence
- $\geq$5-crop sequence can have 2–3 consecutive years of the same crop type
- with legume-based rotations, legume should be grown immediately prior to non-legumes with high N requirements

Crop Rotation Effects on Soil Erosion and Soil Health Generally, crop rotations that include forage crops in the sequence and/or utilize no-tillage to maximize surface residue cover increases soil surface protection from soil erosion (Fig. 12-24). As discussed previously (see "Conservation Tillage"), increasing residue produced and left on the soil surface will increase infiltration, while reducing runoff and soil loss. Some of the influences of crop rotations on soil erosion are:

- increasing canopy denseness and/or residue cover enhances protection from wind and rain, reduces evaporation, and increases yield
- decreasing the proportion of row crops in the sequence relative to close-growing or solid seeded crops (e.g., small grains, forages) decreases erosion potential

Crop sequences designed for fields/soils with a high erosion potential should provide good plant cover and return large amounts of surface crop residue. Crop rotation can greatly improve soil structure and health of many medium- and fine-textured soils, especially if managed with conservation tillage. Pasture grasses and legumes in rotation exert significant beneficial effects on soil physical properties. When soils

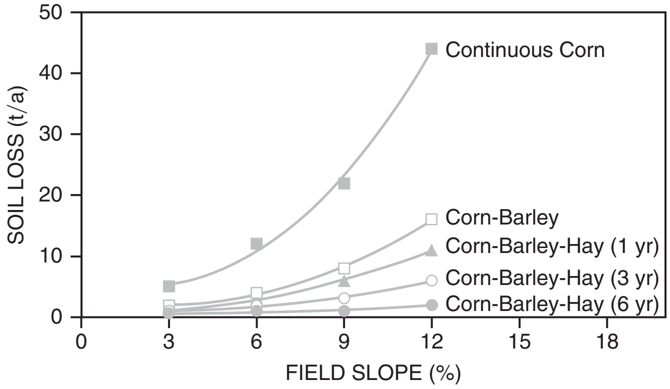


Figure 12-24
Influence of crop rotation sequence and field slope on soil erosion loss. Hay grown following corn-barley for 1, 3, and 6 years.

previously in sod are plowed, they crumble easily and readily shear into a desirably mellow seedbed. Internal drainage can be improved so that ponding and the time needed for drainage of excess H_2O is reduced.

Crop Rotation Effects on Pest Control With most diverse crop sequences, pest pressure can be considerably lower than under monoculture. For example, reducing root-rot diseases in wheat and other cereals requires crop rotation, together with resistant varieties, clean seed, and field sanitation practices (Table 12-10). Legumes, other dicotyledons, and even cereals such as oats, barley, and corn are often suitable alternate crops in place of wheat when take-all disease occurs. However, under irrigation, this disease can be severe, even in wheat following other crops. Corn root rots and the severity of several seedling diseases have been reduced in rotations. Susceptible crops should be grown on the same field only once every 3–4 years. For example, due to serious loss in canola yields from at least three widespread diseases, minimum 3–4-year rotations are recommended. Cereals and grasses are suitable rotational crops because they are not susceptible to diseases of cruciferous crops. Few important bacterial or viral diseases are controlled by crop rotation.

TABLE 12-10
EXAMPLES OF HOW CROP ROTATION CAN REDUCE INCIDENCE OF COMMON DISEASES IN SELECTED CROPS

Disease	Crops Affected
Bacterial blights	Wheat, barley, grasses, rye
Black rot, blackleg	Cabbage, pumpkin
Clubroot	Radish, cabbage
Common root rot	Wheat, barley, grasses
Ergot	Rye, wheat, grasses
Fusarium rot	Asparagus, spinach, lettuce
Fusarium wilt	Peas, muskmelon, squash, tomato
Net blotch	Barley
Rust (sunflower)	Sunflower
Scab	Wheat, barley, corn, rye
Sclerotinia (white mold)	Sunflower, dry beans safflower, soybean, potato, canola
Septoria (different species)	Wheat, barley
Smut (corn)	Corn
Take-all	Wheat, barley
Tan spot	Wheat, durum
Verticillium wilt	Potato, sunflower, safflower

Note: The frequency of including these crops in a rotation sequence varies between 2 and 7 years.

Crop rotation is important for control of nematodes in annual crops. Grass crops are commonly used in rotation to control root-knot nematodes. Acceptable yields of irrigated cotton can be obtained following 2 or more years of root knot–resistant alfalfa.

The role of crop rotation in weed control depends on the weed and the ability to control it with available cultivation and/or herbicides. If all of the weeds can be conveniently and economically controlled with herbicides, then crop rotation is not a vital part of a weed control program. However, there are situations in which rotations are necessary for control of a troublesome weed. For example, downy brome and jointed goat grass can severely reduce yields in a wheat-fallow system. Improved herbicides have reduced the negative effects of these and other grasses in grass crops; however, crop rotations with broadleaf crops enhance weed control through rotation of herbicides and reduced potential of weed resistance to specific compounds. Continuous use of the same herbicides can potentially cause development of weeds resistant to the specific herbicide.

Rotation was once a common practice for insect management, but its use declined with the development of economically effective insecticides. Interest in rotations has increased because of insect resistance to certain chemicals and increased costs. Rotation can be helpful where insects have few generations each year or where more than one season is needed for the development of a generation. For example, northern corn rootworm can be a serious problem in continuous corn. Rotation with soybean reduces the need for insecticide control. Rotation is only partially successful in reducing damage by cotton bollworm.

Cover Crops and Green Manure Crops

Cover crops are planted after crop harvest to protect the surface soil from erosion during the non-crop periods (Table 12-11). These crops may be a non-legume, a legume, or a mixture of the two. If the cover crop is incorporated into the soil with tillage prior to planting the primary crop in the rotation, it becomes a green manure crop (Fig. 12-25). Often a green manure crop is planted similarly to a cash crop

TABLE 12-11
COMMON COVER CROPS USED IN MAJOR CROP REGIONS OF THE UNITED STATES

Region	Cover Crops	Benefits to Cash Crop	Limitations to Cash Crop
Pacific Northwest	Winter pea, brassicas, wheat, triticale	Improve H_2O retention & soil structure, reduce erosion	Cover crop H_2O use, planting and germination in heavy residues
Pacific	Small grains, field pea, vetches	Reduce intercrop tillage, suppress weeds & pathogens	Cool soil temperatures reduce vigor, slow cover crop re-growth
Northern Plains	Rye, winter pea, sweet clover, sorghum-sudangrass	Improve H_2O retention, reduce wind erosion, increase soil C	Cover crop H_2O use, slow soil warming following cover crops
Southern Plains	Small grains	Improve H_2O storage, reduce wind erosion	Cover crop H_2O use
Midwest	Rye, red clover, hairy vetch, sweet clover	Reduce erosion, suppress weeds, recover N	Short cover crop season, establishment constraints
Mid-South	Small grains	Reduce erosion, improve soil structure	Crop establishment in clay soils w/high residue
Northeast	Rye, wheat, oats, ryegrass, hairy vetch, crimson clover, winter pea, brassicas	Reduce erosion, improve soil H_2O, N source	Cost, establishment constraints, H_2O use
Southeast	Small grains	Increase OM, less erosion, improve H_2O storage	Cost, excess H_2O at crop planting

Figure 12-25
Rye grass cover crop in a corn field (left) and rye-hairy vetch green manure crop (right).
(Left Photo: Copyright Michigan State University Board of Trustees; Right Photo: Danielle Treadwell, University of Florida - IFAS)

(normal growing season) and is used primarily as a soil amendment and a nutrient source for the subsequent crop in the rotation. Using the normal growing season for a green manure crop instead of a cash crop will increase the green manure crop yield and quantity of nutrients returned to the soil. Since the field is not in production of the cash crop, the economic loss must be considered.

Cover and green manure crop benefits to subsequent crops include:

- providing N from a legume included in the cover or green manure crop
- weed suppression through allelopathic effects
- decreased soil erosion
- potentially greater plant available water through increased infiltration and less soil H_2O evaporation (cover crop water use may reduce soil water for next crop)
- small grains or other cover crops can be grazed in late fall and winter when the amount of growth and soil conditions permit; grazing allows additional return from cover crop

One important reason for using green manure legume crops is that they supply additional N, depending on yield and N content (Table 12-12). Increasing the quantity of N produced in the legume cover crop increased yield of unfertilized corn

TABLE 12-12
COMMON GREEN MANURE CROPS USED IN TEMPERATE REGIONS AND THE RANGE IN YIELD AND N CONTENT

	Yield	N Content
Green Manure Crop	*t/ha*	*kg/ha*
	Legumes	
Black lentil	1.0–2.5	35–65
Blue lupine	2.0–5.0	20–35
Yellow trefoil	0.6–12	15–220
Burr medic and snail	0.5–3.0	15–75
Gamma medic	1.2–2.5	10–25
Alfalfa	0.5–3.0	20–150
Barrel medic	1.2–4.0	35–130
Yellow sweetclover	3.0–5.5	15–55
Field pea or Austrian winter pea	3.0–5.0	60–160
Berseem clover	2.0–8.0	75–180

TABLE 12-12 (CONTINUED)

Green Manure Crop	Yield *t/ha*	N Content *kg/ha*
Legumes		
Kura clover	6.0–10	55–140
Alsike clover	2.5–6.0	45–135
Crimson clover	4.0–7.0	110–180
Balansa clover	2.5–4.5	35–70
Red clover	0.4–3.5	20–110
White clover	0.8–4.0	10–90
Persian clover	1.7–4.0	12–25
Hairy vetch	1.5–9.0	60–240
Non-Legumes or Mixtures		
Oat	3.0–5.0	80–82
Mustard	2.0–4.0	62–72
Buckwheat	2.0–4.0	52–65
Ryegrass	0.5–5.0	10–50
Field pea	0.5–7.0	35–180
Oilseed radish	2.5–3.5	15–45
Rye	1.5–4.0	20–70
Wheat	4.0–10	40–80
Hairy vetch and rye	3.0–6.0	50–180
Crimson clover and rye	2.5–8.0	50–170

Source: Cherr and Scholberg, 2006, *Agron. J.*, 98:302–319.

(Table 12-13). The grain yield after fallowing was greater than following the wheat cover crop because of N mineralization during the fallow period.

Allowing the cover or green manure crop to grow to its reproductive stage will increase yield and the quantity of N fixed and returned to the soil (Fig. 12-26). Legume green manure crops can contribute large quantities of N to subsequent non-legume crops (Table 12-13).

In rotations where crops return little residue, maintenance of soil productivity may be particularly difficult. Thus, lengthening the rotation to include green manure crops could be beneficial. The acreage of corn and sorghum silage is increasing in some areas, which leaves the soil with almost no surface residue. Oats or rye seeded immediately after harvesting or seeded by airplane before harvesting will help to protect the soil and increase the residue returned.

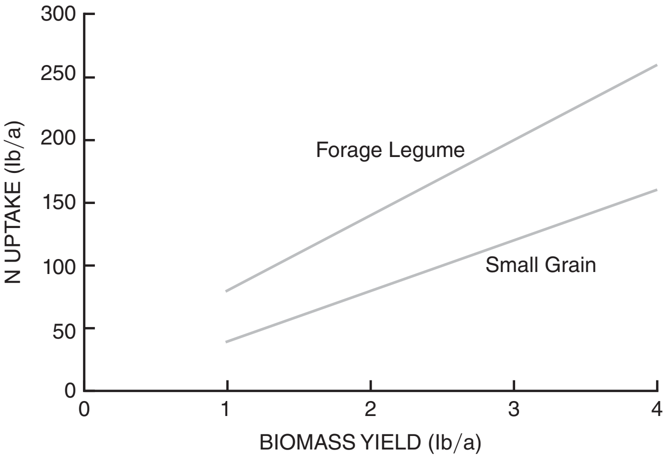


Figure 12-26
Effect of biomass yield on N uptake in corn following hairy vetch (forage legume) and rye (small grain) green manure crops.

TABLE 12-13
DRY MATTER AND N CONCENTRATION OF VARIOUS COVER CROPS AND THEIR INFLUENCE ON CORN GRAIN YIELD

Cover Crop	Dry Matter	N Content	Grain Yield 0 *lb N/a*	Grain Yield 200 *lb N/a*
	lb/a	*lb/a*	*bu/a*	*bu/a*
Fallow	—	—	63	161
Wheat	1,178	35	32	121
Winter pea	1,423	61	132	165
Hairy vetch	2,526	113	156	168
Crimson clover	2,883	102	143	172

Source: Neely et al., 1987, *Role of legumes in conservation tillage systems*, p. 49, Soil Cons. Soc. Am., Ankeny, Iowa.

Protection against erosion is one of the most important benefits of winter cover crops, depending on the distribution of rain and erosion potential during the year. The effect of cover crops on soil loss is reduced if soil erosion occurs when winter cover crops are incorporated in early spring.

For perennial crops such as grapes, peaches, and apples planted on steep slopes, continuous cover is important in reducing erosion. Since the trees and the cover crops occupy the land simultaneously, care must be taken, particularly in young orchards, to prevent competition for H_2O and nutrients. In regions of high overwinter rainfall, cover crop recovery of residual plant nutrients will aid in controlling potential environmental problems.

ENVIRONMENTAL QUALITY

As plant nutrients cycle through the soil-plant-atmosphere continuum, some will be recovered through plant uptake, incorporated into OM, adsorbed to mineral and OM surfaces, and precipitated as solid minerals (Fig. 2-1). The remaining nutrients can be transported from the field through runoff and subsurface lateral flow toward streams and rivers, and by leaching to groundwater (Table 12-14; Fig. 12-27).

TABLE 12-14
SOIL PROCESSES POTENTIALLY INFLUENCING SURFACE WATER, GROUNDWATER, AND AIR QUALITY

Soil Process	Impact on Water and Air Quality
OM mineralization	Release of soluble nutrients and other compounds subject to erosion or leaching
Soil erosion	Transport of nutrients and other chemicals dissolved in H_2O and adsorbed to sediments in surface H_2O runoff
Leaching	Transport of dissolved nutrients and other chemicals in percolating H_2O through soil pores and rapid transport of H_2O and solutes from soil surface through macropores (root and organism channels, cracks) to groundwater
Denitrification Volatilization	Chemical or biological transformation of dissolved NH_4^+, NO_3^-, and SO_4^{-2} to gases released to the atmosphere

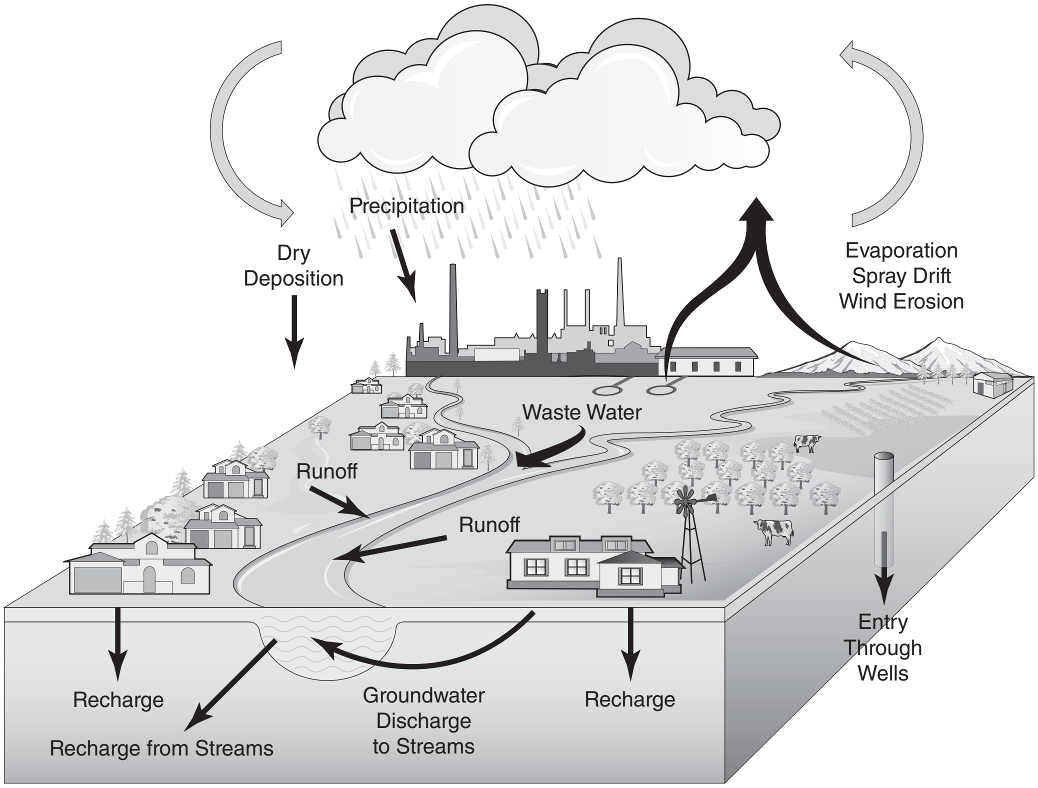


Figure 12-27

Diagram of the hydrologic cycle showing potential pathways of nutrients to surface water, groundwater, and the atmosphere. (*Gilliom et al., 2006,* The quality of our nation's waters—pesticides in the nation's streams and ground water, 1992–2001, *U.S. Geological Survey Circular 1291, p. 172.*)

Gaseous losses of N and S to the atmosphere also occur (Chapters 4 and 7). While it is impossible to utilize nutrients in agriculture without some loss or transport to surface water, groundwater, and the atmosphere, careful management of applied nutrients can minimize their loss to the environment.

Surface- and Groundwater Quality

Nutrients and sediments from agriculture commonly impair inland surface waters (Table 12-15). Organic compounds, metals, and nitrates are the primary contaminants of groundwater. The nutrients of primary environmental concern in agriculture are N and P.

It is important to recognize that nutrient movement to surface- and groundwater occurs in natural ecosystems. Water quality standards for drinking water have been established for all elements that adversely affect health when present in high concentrations (Table 12-16). Approximately 2% of groundwater wells used for drinking water exceed the primary drinking water standard of 10 ppm NO_3-N. Several adverse health effects occur in humans or animals due to excessive N in the environment (Table 12-17). Although rare, the most notable health effect of high NO_3^- water is low blood O_2 in human infants, called methemoglobinemia (Table 12-18). Infants have a low tolerance for NO_3-N compared to adults.

Another impact of nutrient loss from fields is nutrient enrichment or *eutrophication* of surface waters with P and N. Eutrophication is a natural process that typically occurs as a water body ages; however, accelerated eutrophication is usually due to anthropogenic causes. Nutrient additions to surface water stimulate excessive

TABLE 12-15
MOST COMMON POLLUTANTS AND SOURCES THAT IMPACT WATER QUALITY OF INLAND SURFACE WATERS IN THE UNITED STATES

Rank	Rivers	Lakes	Estuaries
		Pollutants	
1	Siltation	Nutrients	Nutrients
2	Nutrients	Metals	Bacteria
3	Bacteria	Siltation	Toxic organic chemicals
4	O_2-depleting substances	O_2-depleting substances	O_2-depleting substances
5	Pesticides	Noxious aquatic plants	Oil and grease
		Sources	
1	Agriculture	Agriculture	Industrial discharges
2	Municipal point sources	Unspecified nonpoint sources	Urban runoff/storm sewers
3	Hydrologic modification	Atmospheric deposition	Municipal point sources
4	Habitat modification	Urban runoff/storm sewers	Upstream sources
5	Resource extraction	Municipal point sources	Agriculture

Source: U.S. EPA, 2008.

TABLE 12-16
WATER QUALITY STANDARDS FOR HUMAN AND LIVESTOCK CONSUMPTION

Element	Human	Livestock
	ppm	
Pb	<0.1	0.05
Mo	—	0.01
As	<0.05	0.05
Se	<0.01	0.01
Zn	<15	<20
Cd	<0.01	0.01
Ba	<1.0	—
Ca	<200	<1,000
Hg	<0.01	0.002
NO_3-N	<10	<50
NH_4-N	<0.05	—
Cl	400	<1,000

Source: US-EPA, 2005.

phytoplankton and algae growth. As algae die, they sink to the lake or river bottom and decay encouraging microbial growth. The decay process releases more nutrients and depletes the water of dissolved O_2. Eutrophication results in several negative impacts on water quality and ecology of the water bodies, including:

- reduced light penetration due to increased algae growth decreases productivity of plants living in the deeper waters that are important for producing O_2
- use of O_2 by microorganisms decomposing dead algae
- reduced dissolved O_2 causes death of desirable fish that requires high concentrations of dissolved O_2, with a shift to less desirable fish species

TABLE 12-17
POTENTIAL ADVERSE ENVIRONMENTAL AND HEALTH IMPACTS OF N

Impact	Causative Agents
	Human Health
Methemoglobinemia	Excess NO_3^- and NO_2^- in water and food
Cancer	Nitrosamines from NO_2^-, secondary amines
Respiratory illness	Peroxyacyl nitrates, alkyl nitrates, NO_3^- aerosols, NO_2^- , HNO_3 vapor in urban atmosphere
	Animal Health
Environment	Excess NO_3^- in feed and water
Eutrophication	Inorganic and organic N in surface waters
Materials and ecosystem damage	HNO_3 aerosols in rainfall
Stratospheric ozone depletion	N_2O from nitrification, denitrification, stack emissions

TABLE 12-18
GUIDELINES FOR USE OF WATER WITH KNOWN NO_3-N (OR NO_3^-) CONTENT

NO_3^-	NO_3-N	Interpretation*
ppm		
<45	<10	U.S. Public Health Service standard as safe for humans and livestock
45–90	10–20	Safe for adults and livestock; not safe for pregnant women or infants
90–180	20–40	Humans and some livestock at risk, especially young or those in high-risk category; monitor nitrates in livestock feed
>180	>40	Hazardous to humans and livestock; do not use for drinking or cooking without treatment

- increasing costs of water purification if used for human consumption
- reduced esthetics and recreational use of water

N and P reaching surface water are from nonpoint agricultural sources, primarily from land-applied animal wastes and fertilizer (Table 12-15). Guidelines have been established for N and P loading rates for rivers and streams (Table 12-19).

Nitrogen Although NO_3^- naturally occurs in all waters, NO_3^- loading of surface- and groundwaters can be greatly elevated from N added to agricultural systems. Although fertilizer, legume, and manure N sources are used to meet N requirements of crops, fertilizer N is considered the primary cause of contamination of surface- and groundwater, due to its predominance as an N source (Fig. 4-1). Fertilizer N lost directly through runoff is relatively small because its solubility and mobility results in immediate movement into the root zone in most soils. In general, crops recover 40–60% of fertilizer N in the first year. The remaining N stays in the soil as NO_3^-, immobilized to organic N, denitrified as N gases, volatilized as NH_3, and leached as NO_3^- below the root zone (Fig. 4-2). High N recovery by the crop (low residual N available for leaching after harvest) will occur with a readily available N source applied to a crop that can utilize it quickly. Split N applications and/or slowly

TABLE 12-19
GENERAL GUIDELINES FOR N AND P LOADING INTO RIVERS AND STREAMS

Risk Level	Total N	Total P
	mg/L or ppm	
Low	<0.5	<0.05
Intermediate	0.5–1.0	0.05–0.10
High	>1.0	>0.10

Note: Total P in streams should not exceed 0.05 mg/L directly entering lakes or reservoirs; total P should not exceed 0.1 mg/L in streams not discharged directly into lakes or reservoirs.
Source: U.S. EPA, 2003.

available N provides N throughout the crop N uptake period, which improves fertilizer N recovery and reduces N leaching potential. Thus, applied at appropriate rates, fertilizer N can exhibit a lower potential for leaching than manure, biosolid, or legume N because a portion of the organic N in these materials will mineralize during periods of low plant growth and N uptake (Fig. 4-14). Thus, organic N can often contribute more to nonpoint source contamination of surface- and groundwater than fertilizer N at equal application rates.

NO_3^- leaching is normal; excessive NO_3^- loss is unacceptable. For NO_3^- leaching to occur, soil H_2O must contain NO_3^- and move below the root zone (Chapter 4 (Nitrate Leaching)). Water transport below the root zone generally occurs in regions where rainfall or irrigation exceeds evapotranspiration (Fig. 12-28). In addition, soil profile characteristics are important in determining the quantity of NO_3^- transported below the root zone (Fig. 12-29). In these examples, the time required for NO_3^- to reach groundwater is very short (3–9 months) in a sandy soil with a shallow *vadose zone*, which represents the material below the rooting depth but above the aquifer. With similar vadose zone thickness, time required for transport to

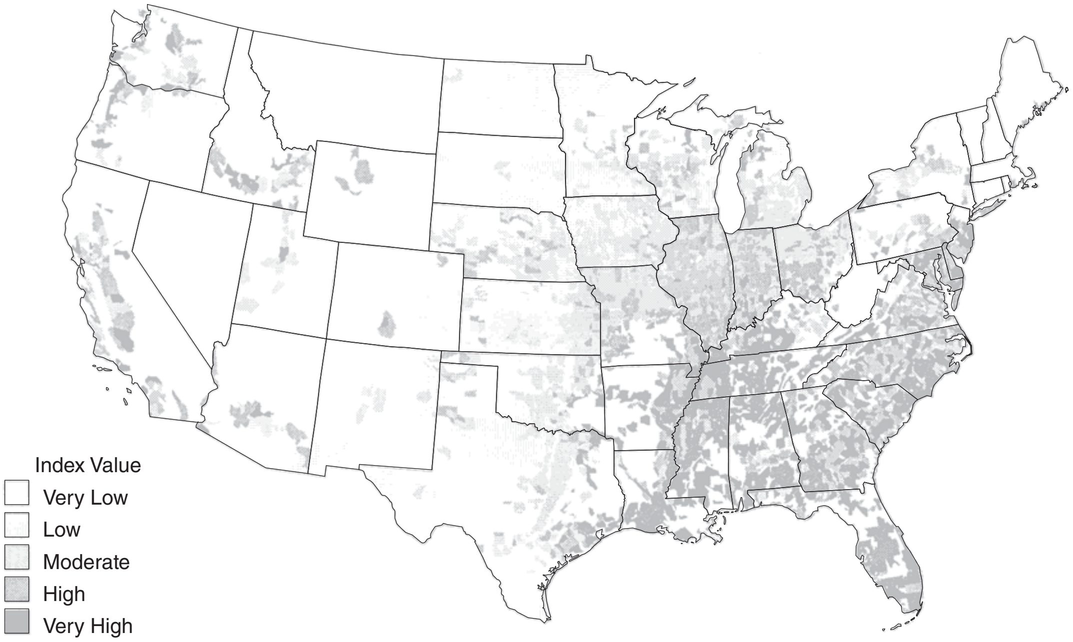


Figure 12-28
Groundwater vulnerability index for N. (USDA, 1996.)

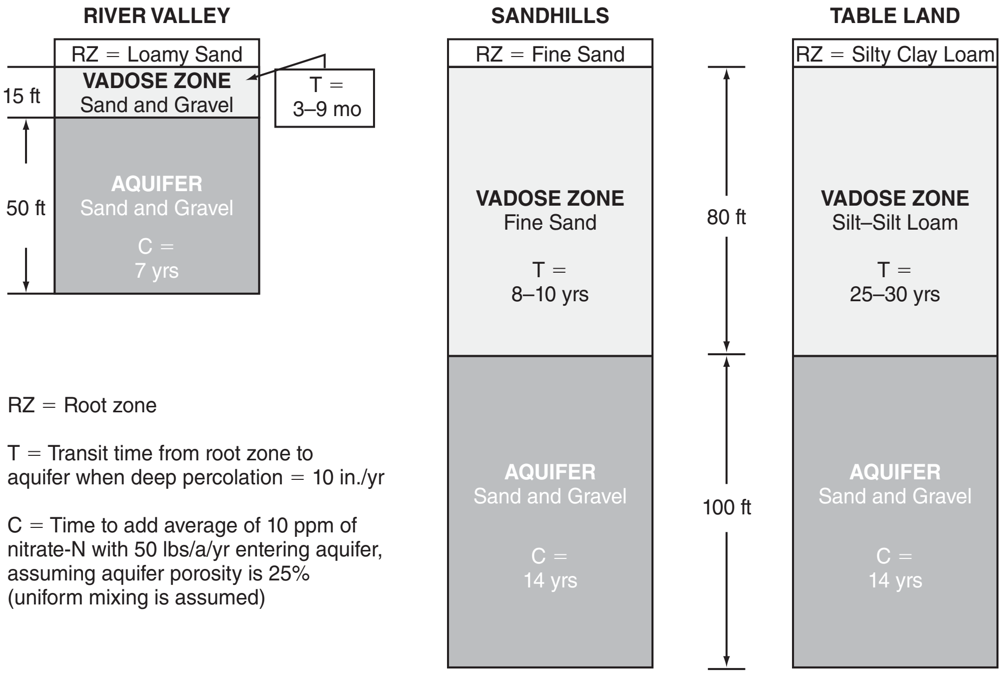


Figure 12-29

Summary of NO_3-N *transit times and aquifer contamination times for three example situations.*

(Watts, 1992, Univ. of Nebraska.)

groundwater can be two to three times longer in fine-textured soils compared with sands (Fig. 12-29).

In fields with subsurface drainage tiles, excess soil H_2O containing NO_3^- is transported to nearby surface water (Fig. 12-30). N management can influence NO_3^- concentration in the soil after harvest and in the drainage effluent (Fig. 4-32; Table 12-20).

Irrigated cropping systems can contribute to nonpoint source NO_3^- contamination, especially with excessive irrigation combined with high N-application rates. With furrow irrigation systems, more water is applied at the beginning than at the end of the furrow, increasing the quantity of water transport below the root zone during irrigation (Fig. 12-31). After irrigation, NO_3^- leaching is greater down field.

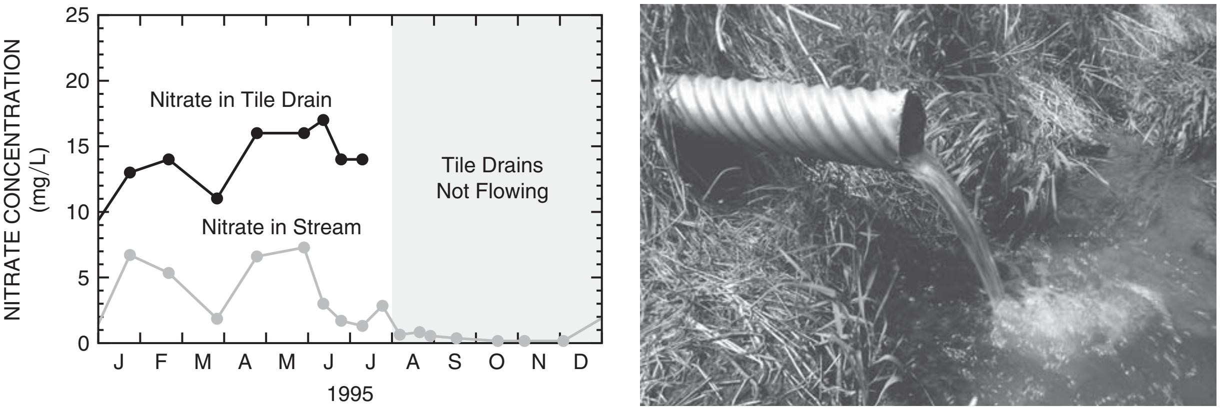


Figure 12-30

Illustration of a drainage tile transporting soil water containing NO_3^- *from a field to nearby surface water.*

(USGS, 2010, Circ. 1350.)

TABLE 12-20
INFLUENCE OF N RATE ON CORN YIELD AND NO_3-N IN THE SOIL PROFILE (4 FT) AND IN DRAINAGE WATER

N Rate	Grain Yield	Soil Profile N	Drainage NO_3-N
lb/a	*bu/a*	*lb/a*	*ppm*
60	153	13	11
120	199	23	14
60 + 60	180	28	15
180	207	40	18

Note: N was applied preplant, whereas the split N treatment (60 + 60) was applied preplant and at eight leaf stage.
Source: Jaynes and Colvin, 2006, *Agron. J.*, 98:1479–1487.

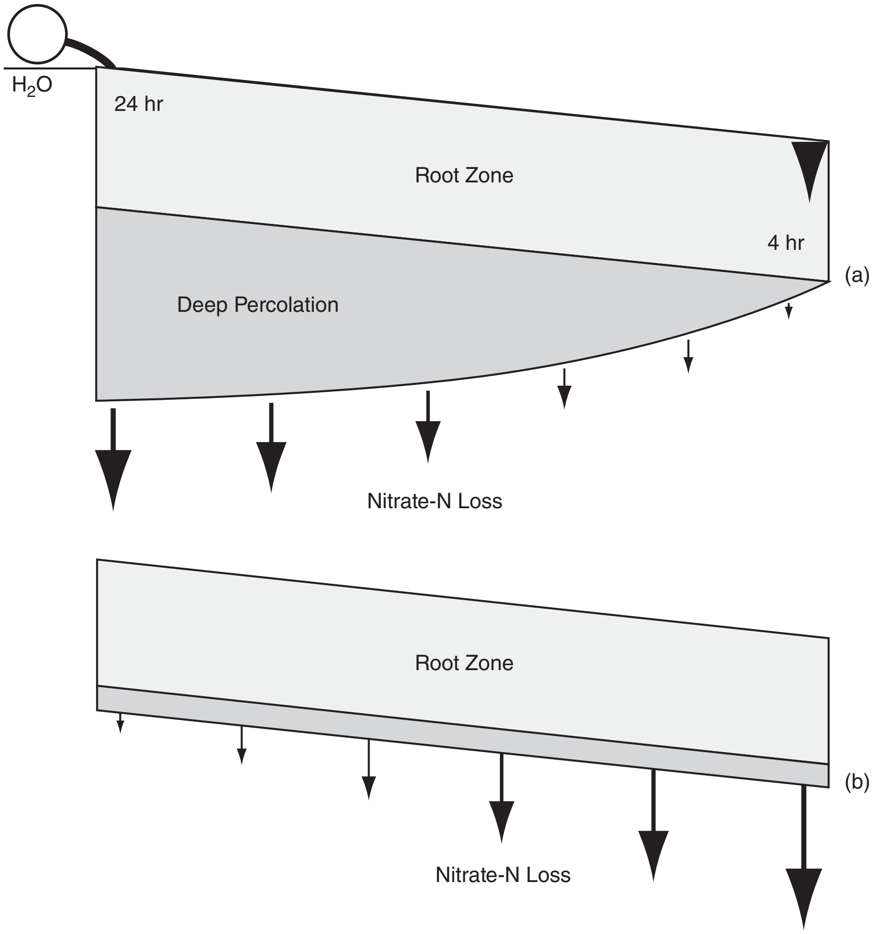


Figure 12-31
NO_3^- *leaching pattern during the irrigation season (a) and off-season (b) for long set times and/or long irrigation runs.*
(Watts, 1992, Univ. of Nebraska.)

NO_3^- leaching can be as problematic under center-pivot systems with similar over-irrigation and/or over-fertilization (Fig. 12-32).

N Best Management Practices (BMPs)

Many site, environment, and management factors interact to reduce potential NO_3^- contamination of surface- and groundwaters. Understanding the principles involved in N availability and transport to surface- and groundwaters is essential for identifying the BMPs for reducing the impact of N use on water quality. Figures 12-33 and 12-34 illustrate how these principles direct appropriate best management strategies.

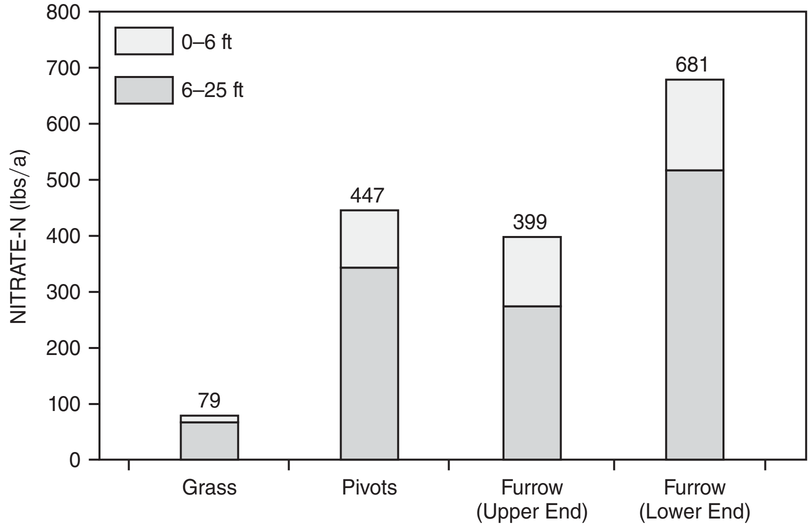
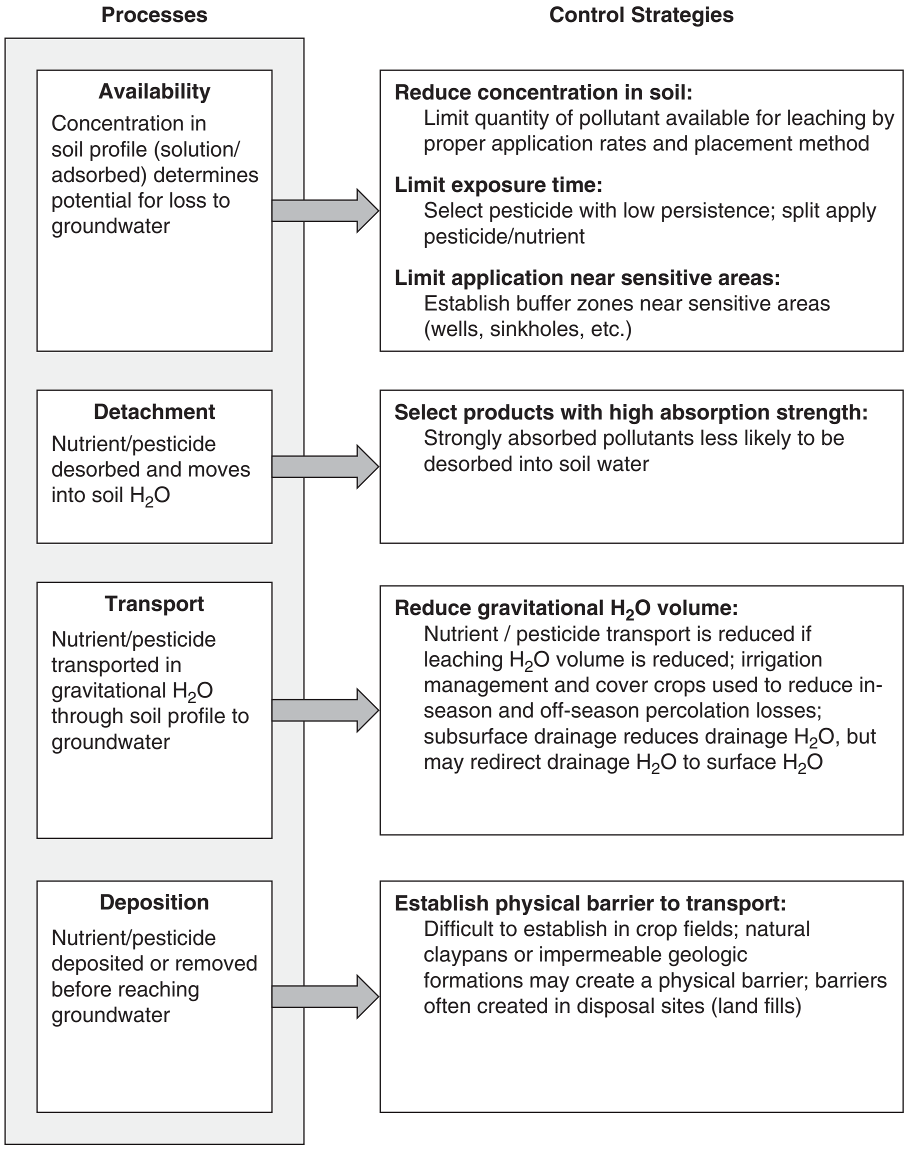


Figure 12-32
Average lb/a of NO_3-N *in deep soil samples under 4 center-pivot and 10 furrow-irrigated corn fields.*
(Watts, 1992, Univ. of Nebraska.)



Availability
Concentration in soil profile (solution/adsorbed) determines potential for loss to groundwater

Reduce concentration in soil:
Limit quantity of pollutant available for leaching by proper application rates and placement method

Limit exposure time:
Select pesticide with low persistence; split apply pesticide/nutrient

Limit application near sensitive areas:
Establish buffer zones near sensitive areas (wells, sinkholes, etc.)

Detachment
Nutrient/pesticide desorbed and moves into soil H_2O

Select products with high absorption strength:
Strongly absorbed pollutants less likely to be desorbed into soil water

Transport
Nutrient/pesticide transported in gravitational H_2O through soil profile to groundwater

Reduce gravitational H_2O volume:
Nutrient / pesticide transport is reduced if leaching H_2O volume is reduced; irrigation management and cover crops used to reduce in-season and off-season percolation losses; subsurface drainage reduces drainage H_2O, but may redirect drainage H_2O to surface H_2O

Deposition
Nutrient/pesticide deposited or removed before reaching groundwater

Establish physical barrier to transport:
Difficult to establish in crop fields; natural claypans or impermeable geologic formations may create a physical barrier; barriers often created in disposal sites (land fills)

Figure 12-33
Processes and control strategies of nutrient and pesticide losses to groundwater.

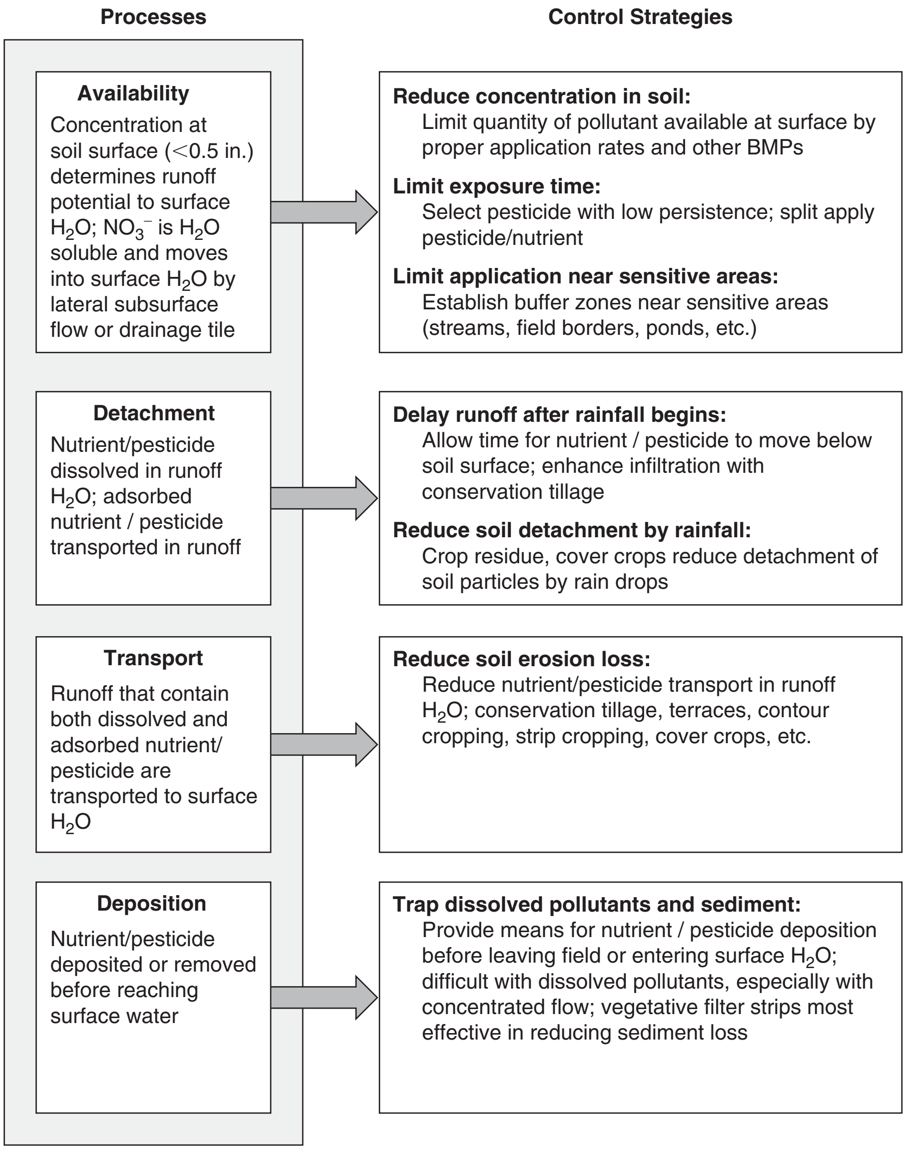


Figure 12-34
Processes and control strategies for nutrient and pesticide entry into surface water.

Processes	Control Strategies
Availability Concentration at soil surface (<0.5 in.) determines runoff potential to surface H_2O; NO_3^- is H_2O soluble and moves into surface H_2O by lateral subsurface flow or drainage tile	**Reduce concentration in soil:** Limit quantity of pollutant available at surface by proper application rates and other BMPs **Limit exposure time:** Select pesticide with low persistence; split apply pesticide/nutrient **Limit application near sensitive areas:** Establish buffer zones near sensitive areas (streams, field borders, ponds, etc.)
Detachment Nutrient/pesticide dissolved in runoff H_2O; adsorbed nutrient / pesticide transported in runoff	**Delay runoff after rainfall begins:** Allow time for nutrient / pesticide to move below soil surface; enhance infiltration with conservation tillage **Reduce soil detachment by rainfall:** Crop residue, cover crops reduce detachment of soil particles by rain drops
Transport Runoff that contain both dissolved and adsorbed nutrient/ pesticide are transported to surface H_2O	**Reduce soil erosion loss:** Reduce nutrient/pesticide transport in runoff H_2O; conservation tillage, terraces, contour cropping, strip cropping, cover crops, etc.
Deposition Nutrient/pesticide deposited or removed before reaching surface water	**Trap dissolved pollutants and sediment:** Provide means for nutrient / pesticide deposition before leaving field or entering surface H_2O; difficult with dissolved pollutants, especially with concentrated flow; vegetative filter strips most effective in reducing sediment loss

BMPs for N can be categorized into those essential for groundwater and surface water (Table 12-21). Understanding the impact of each N BMP requires knowledge of how N transformations in soils influence native and added N availability (Chapter 4), crop N requirements (Chapter 9), and N management for optimum productivity and maximum recovery by the plant (Chapter 10). The material developed in these chapters provides the foundation for nutrient management plans that incorporate appropriate BMPs. An environmentally sound N management plan involves evaluation of all native N sources (soil OM, irrigation water, legume N, etc.) to accurately assess additional N requirements (Chapter 9). For example, if estimated crop N requirement is the same under two different systems, recognition that residual NO_3^- is greater under one system than the other results in a lower N recommendation.

The most important factor in reducing NO_3^- leaching potential is to minimize the quantity of soil profile NO_3^- after harvest and to establish the next crop with a root system extensive enough to recover residual profile NO_3^-. Important N BMPs include the following.

N Rate. The most important N BMP is identifying the correct N rate required to optimize yield (Chapter 9). When N rate exceeds yield potential, residual NO_3^- may leach if H_2O is sufficient to move below the root zone (Fig. 4-33; 4-34). Significant

TABLE 12-21
BEST MANAGEMENT PRACTICES FOR CONTROLLING N ENTRY INTO SURFACE- AND GROUNDWATERS

	Nitrogen
Conservation practices	Conservation tillage, terraces, contour cropping reduces total N loss by reduced sediment loss Runoff/leaching losses of NO_3^- not consistently affected Increased stored H_2O can increase NO_3^- movement below root zone
Crop rotation	Legumes reduce N needed in subsequent non-legume crop Legumes and other deep-rooted crops utilize residual fertilizer N
Cover crops	Cover crops grown in non-crop periods utilize residual fertilizer NO_3^-
Riparian buffers	Buffers trap sediment containing NH_4^+ and organic N Denitrifies residual fertilizer NO_3^- in subsurface flow Although minor, buffer plants take up some NO_3^-
Soil testing	Preplant soil tests are useful in drier climates With spring NO_3^- leaching and/or denitrification potential, late spring or pre-sidedress N tests can determine additional N need
N rate	Use realistic expected yields based on yield history for each field Use appropriate soil tests to determine residual N (if needed) Credit manure, legume residual N and N in irrigation H_2O
N timing	Split N applications increase crop recovery of applied N b/c N rates applied close to periods of high crop N demand If some N is fall applied, delay till soil temperatures $<50°F$
N placement	Subsurface band N reduces volatilization loss Band apply N in ridge to reduce N leaching Subsurface band N with surface residue cover
N source	Select N source based on N loss potentials and crop value, consider controlled release N
Application precision	Variable rate N, combined with intensive soil analysis or crop sensing can adjust N rates to match crop productivity
Inhibitors	Nitrification inhibitors maintain NH_4^+ longer, reducing leaching and denitrification Urease inhibitors temporarily maintain NH_4^+, reducing volatilization
Plant analysis	Tissue tests can confirm N deficiencies and hidden hunger Chlorophyll sensors are reliable in assessing plant N status Grain protein, stalk NO_3^- are useful post-mortem tests to assess N supply
Irrigation management	Irrigation scheduling based on soil moisture estimates and potential evapotranspiration is essential Sprinkler systems apply H_2O uniformly, reducing NO_3^- leaching Furrow irrigation efficiency improved by adjusting set time, stream size, furrow length, water every other row, use surge valve Fertigation supplies N during high crop demand
Controlled drainage	Reduce residual fertilizer NO_3^-
Constructed wetlands	Surface or drainage tile H_2O directed to constructed wetlands to denitrify NO_3^-
Pest management	Minimize yield loss from pests to ensure final yield matched N rate

NO_3^- accumulation occurs only when N rate exceeds that required for optimum yield (Fig. 12-35). N recommendations should be evaluated for each individual situation.

N Timing. Substantial reduction in total applied N susceptible to N leaching occurs with split N applications compared with a single application (Fig. 12-36). The use of sensor-based in-season N applications can be used to split apply N (Fig. 10-59).

N Placement. Subsurface N application can reduce soluble N loss in surface runoff, but also reduces N loss by volatilization (Chapter 4). In permanent pasture or turf systems, subsurface applications are less desirable than surface broadcast applied

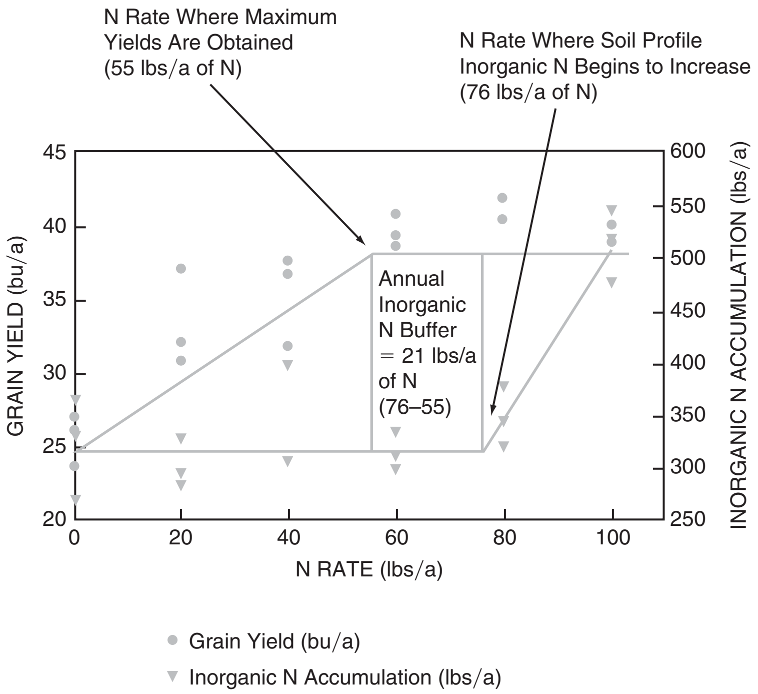


Figure 12-35
The relationship between inorganic N accumulation and annual N applied and the estimated soil-plant N buffering zone, which represents the proportion of applied N that is immobilized and does not contribute to inorganic N accumulation.
(*Raun and Johnson, 1995,* Agron. J., *87:827.*)

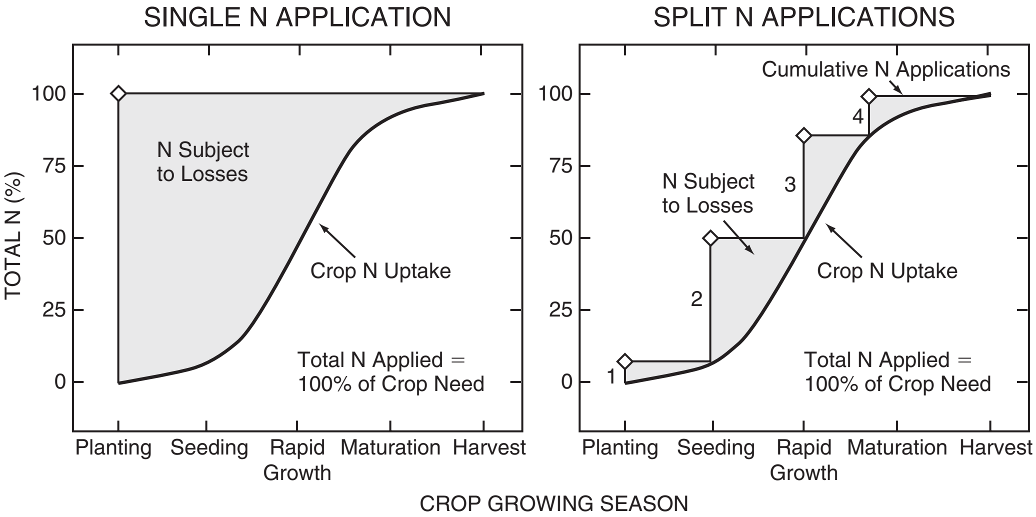


Figure 12-36
General estimations of potential soil N losses occurring when N fertilizer is applied in a single or in split applications. (*Waskom et al., 1994,* BMPs for irrigated agric., *Colorado Water Resources Institute Report No. 184.*)

N; however, spoke-wheel and other innovative application technologies offer opportunities to maximize recovery of N by the crop (Chapter 10). In reduced-tillage systems, which are critical to ensuring long-term soil and crop productivity, subsurface application of N is essential to maximizing crop recovery of applied N and reducing N immobilization by high-C-containing crop residues.

Crop Rotation. There are several issues relative to cropping systems that can influence N management decisions. Figure 12-37 illustrates that, except for fallow systems that produce the largest amount of leachable N (no N uptake during periods of N mineralization), rotations that include legumes may contribute more leachable N than non-legume-based systems, unless high N rates are used in the non-legume rotations. Table 12-22 shows that soybean in the rotation increased soil profile NO_3^- as well as NO_3^- below the root zone.

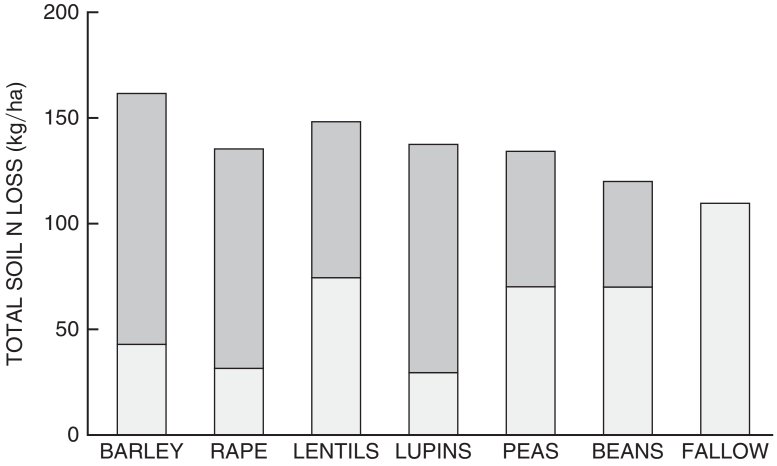


Figure 12-37
Total soil N loss during and following a spring wheat crop grown in rotation with selected legumes, non-legumes, and fallow. (■) represents N uptake by the wheat crop in relation to apparent leaching losses (□) during the autumn/winter following wheat harvest.

TABLE 12-22
COMPARISON OF SOIL PROFILE NO_3-N WITH SOIL SOLUTION NO_3-N BELOW THE ROOT ZONE

Treatment	Soil Profile (0–0.45-m depth) May, June, July[1]	Soil Solution (1.2–1.5-m depth) June, July, August
	mg/kg (mg/L)	*mg/L*
Corn (1990)		
No-till	14 (56)	9
Tilled	19 (77)	10
Wheat (1991)		
No-till	4 (16)	4
Tilled	6 (24)	10
Beans		
1990	26 (105)	12
1991	33 (133)	27

[1] Used different times to compensate for the time necessary for the soil solution to flow from the surface to the 1.2–1.5-m depth.
Source: Meek et al., 1994, *SSSAJ*/58:1464.

When soil tests suggest that significant, residual soil profile NO_3^- is present after harvest, cover crops may recover significant quantities of NO_3^- to reduce N transport to groundwater.

N from Organic Wastes. Organic N sources contribute to plant available N as efficiently as fertilizer N. Unfortunately, if N rates exceed crop N requirement, N mineralization after the peak N uptake period may contribute to leachable N. Figure 12-38 illustrates that increasing poultry manure or municipal biosolids rate greatly increases soil profile NO_3^-. Compared with split applications of fertilizer N, manure N can result in greater profile NO_3^- content after harvest (Table 12-23).

Riparian Buffers. Although retaining surface residue cover through conservation tillage systems can substantially reduce soil erosion, riparian buffer zones are effective in reducing NO_3^- in subsurface flow and in filtering sediments and nutrients in surface runoff water (Fig. 12-39). Depending on the width of the grass and/or forest buffer, 60–95% reduction in sediment can occur (Table 12-24). Reduction of N and P in surface runoff ranges 10–80%; the wider the buffer area, the greater the deposition of nutrients.

Figure 12-38
Influence of poultry manure N application (a) and municipal biosolids (sludge) or fertilizer N application (b) on soil profile NO_3-N. 1x and 3x represent one and three annual applications, respectively.

(Scott et al., 1995, Arkansas Agric. Exp. Bull. 947.)

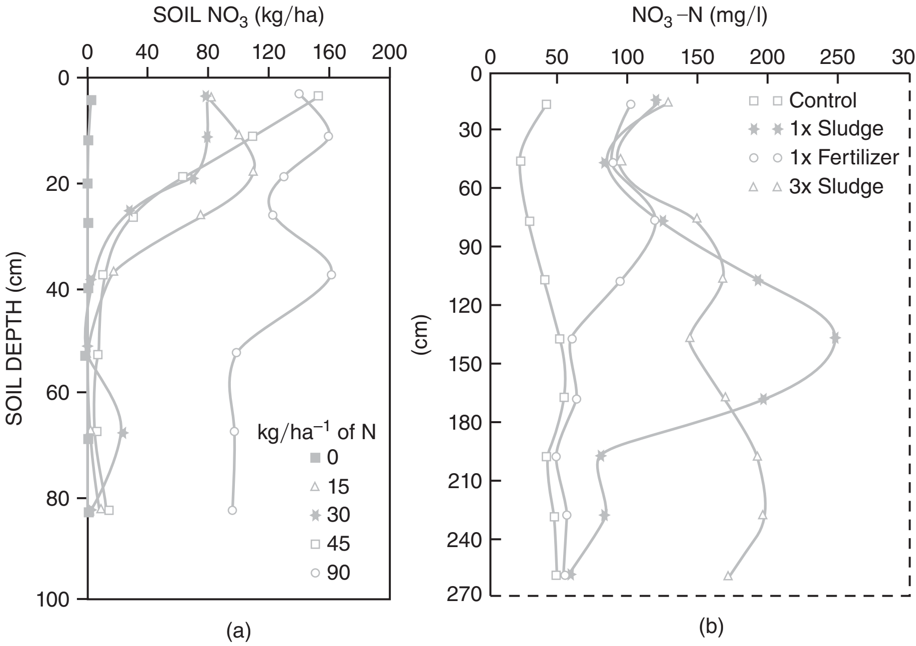


Table 12-23
N Management Effects on Corn Yield and NO_3-N Concentration in Soil Water

N Source	N Rate	N Timing	Grain Yield	Soil Water NO_3-N[1]
	lb/a		*bu/a*	*ppm*
Anhydrous NH_3	150	Spring	177	12
Anhydrous NH_3	75 + 75	Spring + sidedress	173	10
Hog manure	196[2]	Spring	184	41

[1] Measured at 5-ft depth by suction lysimeters at the end of second year.

[2] Estimated available N. Total N applied was 315 lb/a, half being inorganic and half organic; 100% availability from inorganic N in year of application.

Source: Griffith, 1989, *Better Crops*, 73:23.

Figure 12-39
Schematic of the two-zone riparian forest buffer system.

(Modified from Lowrance et al., 1995, U.S. EPA, Washington, D.C., 903-R-95–004.)

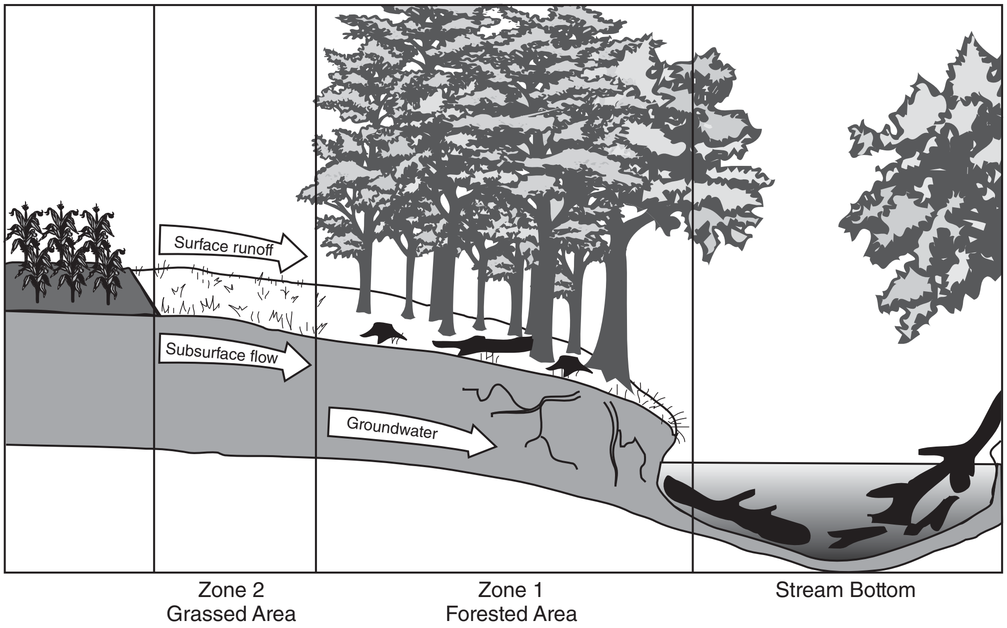


TABLE 12-24
EFFECTS OF RIPARIAN BUFFERS ON REDUCTIONS OF SEDIMENT AND NUTRIENTS FROM FIELD SURFACE RUNOFF

Buffer		Sediment			N[1]			P[1]		
Width	*Type*	*Input*	*Output*	*Reduction*	*Input*	*Output*	*Reduction*	*Input*	*Output*	*Reduction*
m		*mg/L*		*%*	*mg/L*		*%*	*mg/L*		*%*
4.6[2]	Grass	7,284	2,840	61	14.1	13.6	4	11.3	8.1	29
9.2[2]	Grass	7,284	1,850	75	14.1	10.9	23	11.3	8.6	24
19.9[3]	Forest	6,480	660	90	27.6	7.1	74	5.0	1.5	70
23.6[4]	Mixture	7,284	290	96	14.1	3.5	75	11.3	2.4	79
28.2[5]	Mixture	7,284	188	97	14.1	2.8	80	11.3	2.6	77

[1] $N = NO_3 - N + NH_4 - N$ (dissolved + adsorbed) + organic N (soluble + particulate); P = dissolved + particulate.
[2] Calculated from masses of total suspended solids, total N, total P, runoff depth, and plot size (22 × 5 m).
[3] Surface runoff concentrations at 19 m into forest.
[4] 4.6-m grass buffer +19-m forest.
[5] 9.2-m grass buffer +19-m forest.
Source: Lawrence et al., 1995, U.S. EPA, Washington D.C., 903-R-95–004.

The reduction in NO_3^- concentration in subsurface flow occurs through denitrification, *not plant N uptake* (Fig. 12-40). Anaerobic denitrifying microorganisms obtain C from roots in the buffer zone and convert NO_3^- to N_2 gas. In many crop fields, soil solution NO_3^- concentration can range 15–40 ppm N after harvest. Figure 12-41 shows that denitrification reduces NO_3^- concentration to <10 ppm N, depending on buffer width.

N BMP Summary

Although the range of options for BMPs should be evaluated for each site, the decisions on which management practices are utilized depend on the skill of the manager and the particular situation (Table 12-21). While conservation practices are important in efficient use of N, identifying the right N *rate*, using the correct *timing* or split N applications, identifying the optimum N *source*, and using the right application method or *placement* will dramatically improve N utilization by the target crop.

Producer adoption of BMPs is essential to maximizing profit and minimizing the impact of N use on H_2O quality. Our continued ability to produce sufficient food for an expanding population depends on continued increases in crop yield per unit land area. Under increasing production pressure, conservation of our limited natural resources (quantity and quality) can only occur with full adoption of existing

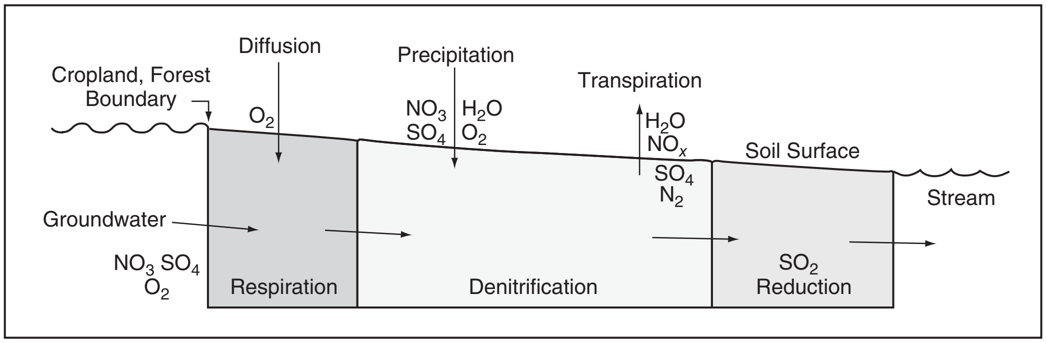
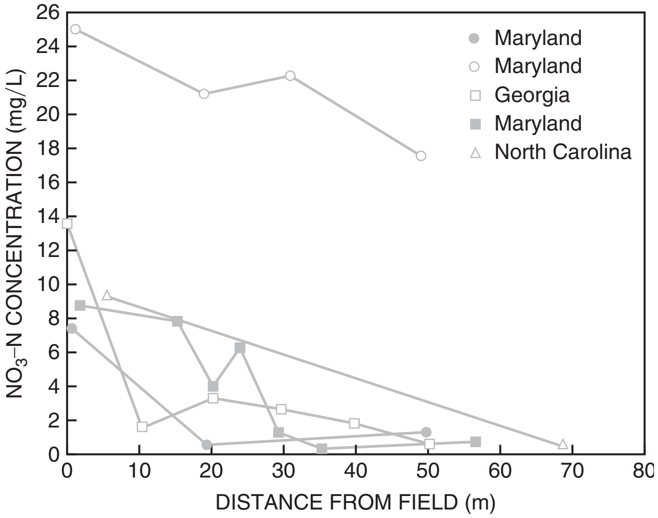


Figure 12-40
Conceptual model of below-ground processes affecting groundwater nutrients in riparian forest.
(*Correll and Weller, 1989,* Freshwater, wetlands and wildlife, *pp. 9–23, U.S. Dept. Energy.*)

Figure 12-41
Nitrate concentrations in groundwater beneath riparian forests.
(*Osmond et al.,* Selected agric. best mgmt. practices to control N, *NC Agric. Res. Service Tech. Bull. 311 NC State Univ.*)



BMPs and continued development of new agricultural technologies that will improve crop N use efficiency essential to reducing environmental risks associated with N use.

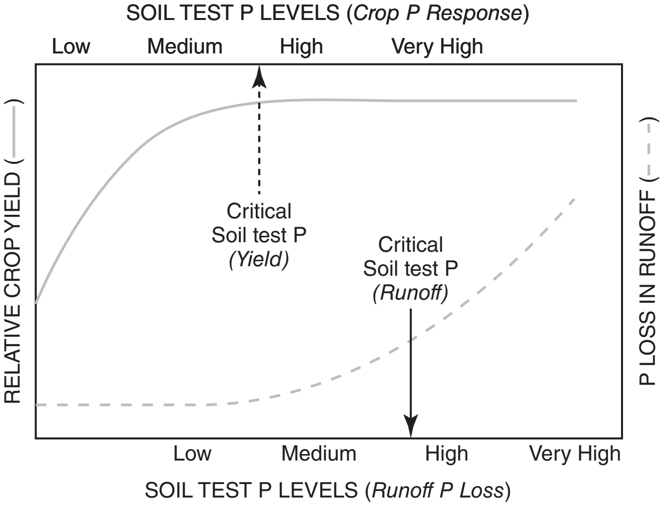
Phosphorus While industrial wastes, municipal wastes, and urban runoff contribute to P loading in certain watersheds, P applied directly to cropland though fertilizers and animal wastes can be primary contaminant sources in watersheds with predominately agricultural land uses.

In general, about 20% of fertilizer P is recovered by crops during the first growing season after application. When P is applied at recommended rates, soil test P levels generally remain the same or increase slightly with time depending on P rate, soil type, and crop removal. When animal waste application rates are based on crop N requirement, P rates can be three to five times the crop P requirement (Table 5-14). Continued long-term application of P exceeding crop requirement will increase soil test P and subsequent risk of P loss to surface- and groundwater (Fig. 12-42). P transport and loss to surface- and groundwaters involves (1) soluble P loss in runoff water, (2) P adsorbed to eroding sediments, (3) soluble P loss in leaching water, and (4) P losses related to the type of waste P and method of application.

Soluble P in Surface Runoff

Total soluble P in surface runoff transported to a stream or other water body depends on the quantity of runoff and its P concentration (Fig. 12-43). Dissolved P in runoff

Figure 12-42
Comparison of agronomic and environmental interpretation of soil test P. As the agronomic soil test P increases above the level where crop response to added P is not expected, dissolved P concentration in runoff increases to levels that could potentially contaminate surface water.



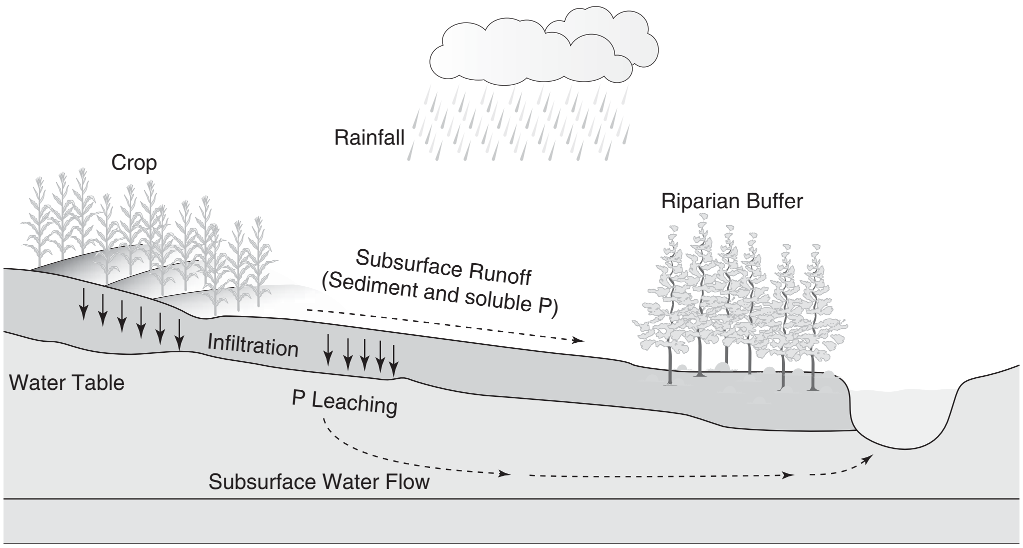


Figure 12-43
Diagram of major pathways of P transport to surface- and groundwater.

is directly related to soil test P. Since P is adsorbed more strongly in clay soils, higher soil test P is required for a given runoff P concentration in clay soils compared to sandy soils (Fig. 12-44). This difference is related to P being held less tightly in the sand compared to the clay soil because of differences in P adsorption capacity.

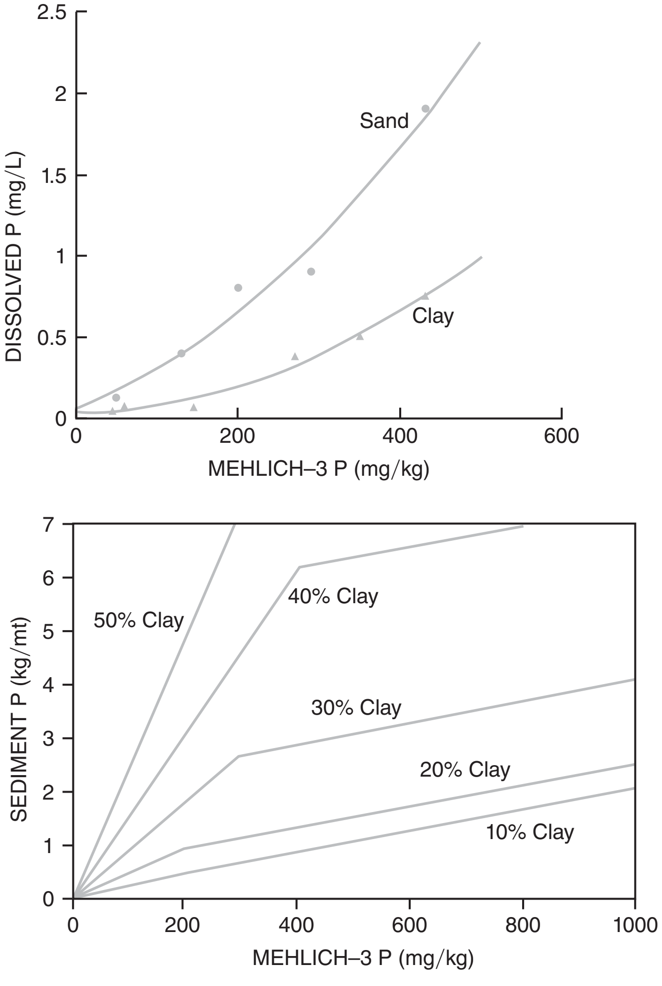


Figure 12-44
Influence of soil test P and soil texture on dissolved P (top) *and sediment bound P* (bottom) *in surface runoff water.*
(*Cox and Hendricks, 2000,* J. Environ. Qual., *29:1582.*)

The quantity of runoff H_2O with an individual storm event depends on characteristics of the rainfall (quantity, intensity, and duration), surface soil conditions (residue cover, soil physical properties including H_2O content) that influence infiltration, subsoil properties that influence percolation, and H_2O table depth. During rainfall, H_2O enters the soil through large, surface-connected macropores. H_2O then diffuses vertically and horizontally into a network of micropores by capillary action or soil moisture tension (SMT). After soil macropores are filled, H_2O moves through micropores toward the highest SMT. H_2O infiltration or transport rate is governed by the number, size, and continuity of the pore network. The presence of old root channels, earthworm and other organism burrows, and natural subsoil structural macropores can substantially increase H_2O infiltration and transport of dissolved P through the profile; however, their presence and influence are difficult to quantify.

P Adsorbed to Sediments Transported by Water

Although receiving less attention, P can be removed from surface soils in windblown clay and OM sediments containing adsorbed P. With H_2O erosion, P adsorbed to clay and OM tranported beyond the field edge is a function of (1) soil erosion rate, (2) amount of sediment deposition within the field, and (3) quantity of P adsorbed to the eroding soil particles (Fig. 12-43). The amount of P adsorbed to soil depends primarily on soil test P and clay content (Fig. 12-44). As soil test P and clay content increase, the quantity of adsorbed P and potential sediment-bound P loss increases.

P in Leaching Water

There is potential for P to leach below the root zone and be transported to surface waters through shallow subsurface groundwater flow (Fig. 12-43). Since P is strongly adsorbed to clays, P leaching would occur only when % P saturation is increased to very high levels though continued applications of P exceeding crop requirement (Fig. 12-42). Although P leaching is frequently greater in sandy soils (low P adsorption capacity), P leaching can occur in some clay soils through macropore flow.

P leaching commonly occurs in sandy soils where high rates of manure are applied over extended periods (Fig. 12-45). Increasing the manure rate increases potential P transport through the profile (Fig. 12-46). The P leaching potential increases with increasing soil test P level and sand content.

Waste Source Effects

During runoff events, soils with low erosion potential can contribute to high-soluble P loss due to differences in waste source properties and their interaction with soil

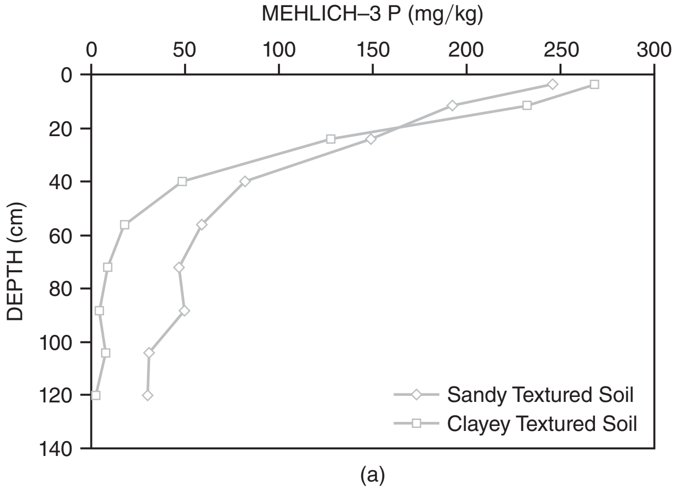
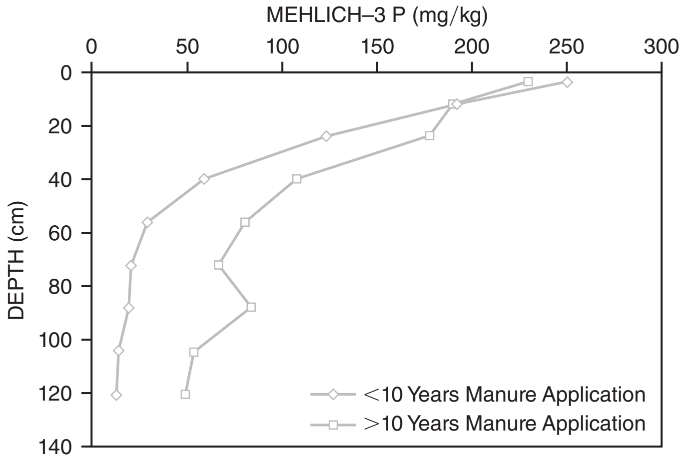


Figure 12-45
Influence of soil texture (a) and duration after surface waste application (b) on P leaching in a sandy soil.
(Ham et al., 2000, Ph.D. Diss., NC State Univ.)



(b)

Figure 12-45
(Continued)

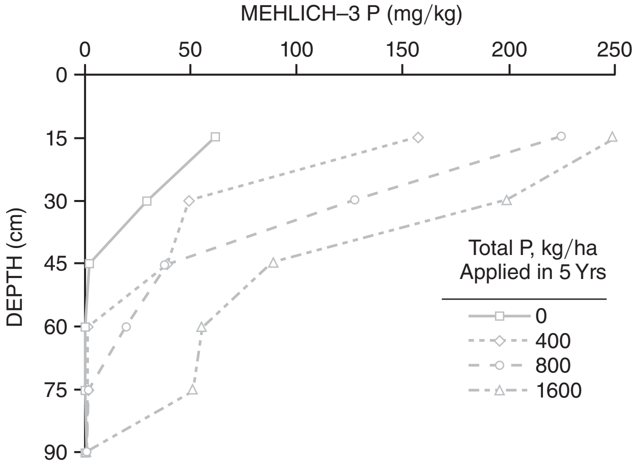


Figure 12-46
Effect of total P applied as swine effluent during a 5-year period on distribution of Mehlich-3 P.

(*Reddy et al., 1980,* J. Envir. Qual., 9:86.)

particles. The primary waste source characteristics that influence P delivery to a surface water body are total P and soluble P concentrations (Table 12-25).

Total P content of waste sources varies widely with animal species, diet, and method of waste handling and storage. In general, P content in common waste sources follows the order: poultry and turkey > beef > swine > dairy. Increasing P in the animal diet will increase P content in the waste. Total P concentration within a waste source varies depending on the waste handling system, where generally dry litter > liquid > slurry > sludge. Inorganic P comprises 60–90% of total P in animal wastes, where about 25–80% of total P is water soluble (Table 12-25).

Waste sources with high P solubility result in a high proportion of total P infiltrating into soil, reducing potential soluble surface P loss. Generally, runoff P loss is highest during the first runoff event following waste application, with P loss decreasing with subsequent runoff events. Waste materials with high % solid content will remain on the soil surface until decomposed or dissolved with rainfall. H_2O-soluble P content is a useful indicator of potential P runoff or leaching. While both soluble and particulate P are transported in runoff water to the field edge, a proportion of mobile P is retained in the field by adsorption of soluble P to eroded sediment and deposition before reaching the stream or water body edge.

P BMPs

Many soil and crop management factors interact to determine potential P transport from fields to surface- and groundwaters (Table 12-26). Reducing potential P loss requires understanding and managing P availability and sediment detachment,

TABLE 12-25
SELECTED SOURCES OF ANIMAL WASTES AND THEIR P CONTENT

Waste Source	Total P[1]	Soluble Fraction[2]	Soluble P[3]	Nonsoluble P[4]
Beef				
Lagoon liquid, kg P/ha-cm	15.0	0.80	12.0	3.0
Lagoon sludge, g P/L	2.7	0.60	1.6	1.1
Slurry, g P/L	1.2	0.75	0.9	0.3
Dairy				
Lagoon liquid, kg P/ha-cm	15.0	0.80	12.0	3.0
Lagoon sludge, g P/L	1.2	0.60	0.7	0.5
Scraped, kg P/t	1.4	0.60	0.8	0.6
Slurry, g P/L	0.7	0.75	0.5	0.2
Swine				
Lagoon liquid, kg P/ha-cm	10.3	0.80	8.2	2.1
Lagoon sludge, g P/L	2.6	0.40	1.0	1.6
Slurry, g P/L	1.2	0.60	0.7	0.5
Broiler				
Fresh manure, kg P/t	3.6	0.25	0.9	2.7
House litter, kg P/t	17.3	0.25	4.3	13.0
Stockpiled litter, kg P/t	17.5	0.25	4.4	13.1
Layer				
High-rise manure, kg P/t	12.3	0.60	14.8	9.8
Lagoon liquid, kg P/ha-cm	8.9	0.80	16.2	4.1
Lagoon sludge, g P/L	4.9	0.50	2.5	2.4
Slurry, g P/L	3.1	0.60	1.9	1.2
Undercage manure, kg P/t	6.9	0.50	3.5	3.4
Turkey				
Stockpiled litter, kg P/t	15.9	0.25	4.0	11.9
House litter, kg P/t	11.5	0.25	2.9	8.6

[1] Concentration units vary with waste source.
[2] Wt. basis.
[3] Soluble P = Total P × Soluble fraction.
[4] Nonsoluble P = Total P × Soluble P.

transport, and deposition processes (Figs 12-33 and 12-34). Important P BMPs include the following.

P Rate. Regardless of the P source, once soil test P reaches the agronomic optimum level for the specific cropping system and soil, P rates that further increase soil test P increase potential for P loss (Figs 9-73 and 12-42).

P Placement. Subsurface P placement reduces P susceptible to runoff loss compared to surface applications (Fig. 12-47). Broadcast P applications to pastures or no-till crops results in greater soluble P loss than in cultivated soils, due to reduced P soil contact. As the time interval between application and incorporation increases, potential runoff P loss increases. Incorporation within 2–3 days after application is recommended. Subsurface P applications will not reduce potential soluble P loss by leaching.

P Timing. Application of P in relation to probability of rainfall is an important factor in managing loss of surface-applied fertilizer or waste P to surface water. Runoff P can be reduced by applying waste during periods of low rainfall probability, with greater reductions occurring on soils with high P adsorption capacity. Surface P application just prior to a rainfall event can lead to significant P losses in runoff. Relative to P supply to crops, all recommended P should be applied before planting to maximize crop response (Chapter 10).

TABLE 12-26

BEST MANAGEMENT PRACTICES FOR CONTROLLING P ENTRY INTO SURFACE- AND GROUNDWATERS

	Phosphorus
Conservation practices	Conservation tillage, terraces, contour cropping, cover crops reduce total P loss by reduced sediment loss Conservation practices consistently reduce runoff P loss Runoff P loss higher in no-till with surface-applied fertilizer or manure P, incorporating/injecting P below soil surface reduces P loss
Riparian buffers	Buffers trap sediment and adsorbed P Buffers constructed/maintained for sheet flow of runoff through buffer
Soil testing	Preplant soil tests are essential to determine agronomic rates
P rate	Reduce rates in high runoff risk areas Consider P content of manure rather than solely N content Use P index tool to assess environmental risk of continued P use
P timing	Avoid fertilizer and manure application to frozen or wet soil Apply all P preplant
P placement	Incorporate or inject P sources, band apply P in low P soils Starter P can usually supply maintenance P requirements for row crops
P source	Select P source for ease of placement and P fixation potential
Application precision	Variable rate P application is recommended if >20% field is P responsive
Plant analysis	Tissue tests can confirm P deficiencies and hidden hunger
Irrigation management	Surface crop residue in furrow irrigated crops reduces sediment and P loss
Manure management	Determine P content to calculate appropriate P rate Low P soils benefit most from manure applications Consider risk factors such as nearness to streams, slope, presence of wells, sinkholes, surface tile inlets, and residences when selecting fields for manure application Manure amendments such as alum reduce soluble P losses in runoff
Animal feed management	Balance livestock rations so supplemental P is not excessive Low phytate corn or phytase enzyme in rations reduces manure P

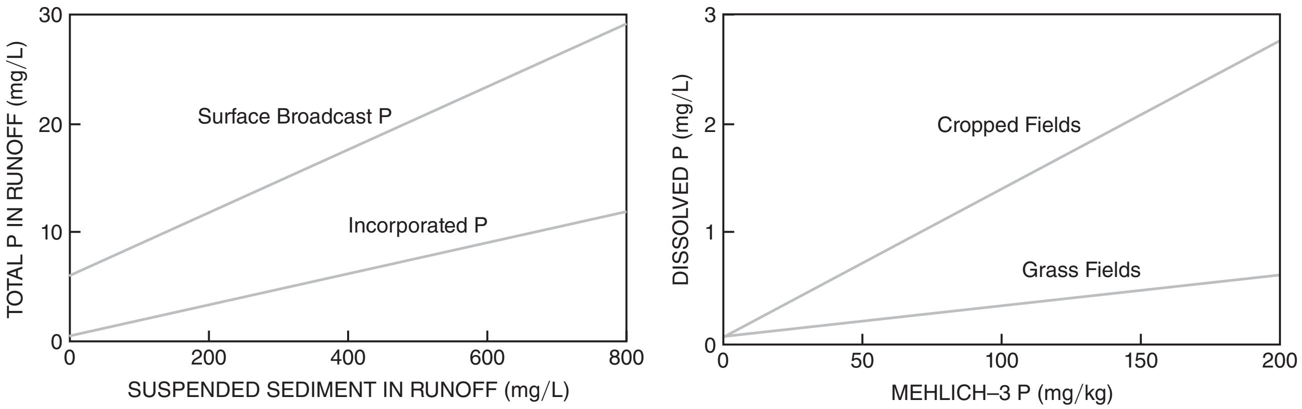


Figure 12-47

Influence of sediment content in runoff and surface broadcast or incorporated P in manure or fertilizer on total P concentration in runoff (left) *and the effect of soil test P and cropping system on dissolved P in runoff* (right). *Cropped fields represent wheat with residue incorporated with a moldboard plow and grassed fields representative of short grass pasture.*

(*Kleinman et al., 2002,* J. Envir. Qual., *31:2026.*)

Table 12-27
Soil and Crop Management Factors That Reduce Annual Estimated Sediment Loss

Conservation Practice	Relative Reduction[1]
Terraces	High
Vegetative filter strips[2]	Medium
Permanent pasture	High
No-tillage (standing residue)	High
No-tillage (residue removed)	Medium–low
50% residue incorporation	Medium
75% residue incorporation	Low
Contour tillage	Low
Contour conservation tillage	Medium–low
Contour cropping (conventional tillage)	Medium–low
Contour cropping (no-tillage)	Medium–high
Contour strip cropping (conventional tillage)	Medium
Contour strip cropping (no-tillage)	High

[1] Relative reduction in sediment transport to the field edge as influenced by conservation practices.
[2] Narrow (<1 m) permanent grass strips planted on the contour. As with terraces, the steeper the slope, the smaller the interval between strips.

Soil Conservation Practices. Table 12-27 illustrates the relative effectiveness of selected conservation practices in reducing sediment transport, which would reduce sediment-bound P loss. Generally, increasing surface residue cover will decrease soluble and sediment P transport (Fig. 12-47). Because there are many interacting factors that influence soil erosion control, it is difficult to generalize. For example, terracing is one of the most costly conservation practices to implement and consequently is not commonly used unless slopes are >5–7%. However, when properly designed and maintained, terraces can substantially reduce effective slope length, thus reducing the erosive kinetic energy associated with runoff compared to longer slopes. Conservation practices also have cumulative effects. For example, contour cropping and/or contour strip cropping combined with terracing can be more effective than contour cropping or strip cropping alone. If these systems are implemented with no-tillage management, the potential sediment and P loss can be greatly reduced (Fig. 12-17).

Sediment P Trapping Practices. Riparian buffers between the field edge and the surface water body can be effective in trapping sediment P, further reducing P loss (Fig. 12-43). Sediments must be evenly distributed within the buffer to maintain long-term effectiveness in reducing sediment P. Vegetative buffers can remove 20–80% of sediment P in surface runoff (Table 12-24). Increasing buffer width increases sediment P removed (Fig. 12-48). Although buffers are effective in trapping sediment, they are less effective in trapping soluble P.

Several in-field conservation structures can also help reduce sediment P delivery to the stream edge by 10–50%. These include controlled drainage structures, sediment basins, and ponds; ponds will generally maintain standing H_2O throughout the year, while sediment basins do not.

Soluble P Retaining Practices. Unlike sediment P, there are few conservation practices that can reduce soluble P in runoff prior to reaching the stream edge. However, any soil management practice that increases infiltration and decreases runoff (conservation tillage or water control structures) can reduce transfer of soluble P to surface H_2O.

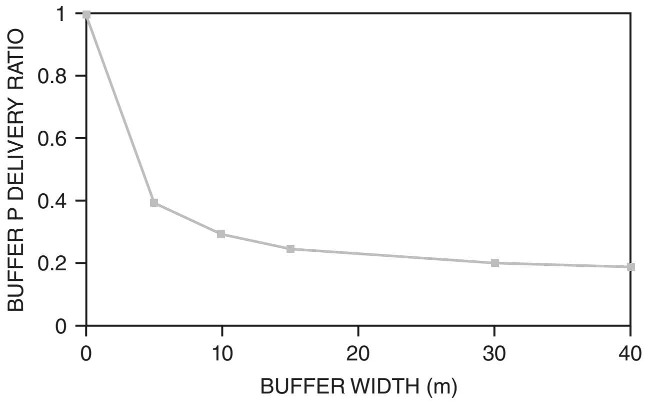


Figure 12-48
Effect of buffer width on delivery of sediment P.
(Daniels and Gilliam, 1996, SSSAJ/ 60:246.)

P in Animal Feed. About 65% of P in feed grains (corn and soybean) occurs as relatively undigestable phytate-P or phytic acid (Fig. 5-20). Since undigested phytate-P will be excreted by the animal, supplemental P as $CaHPO_4$ is added to the diet to meet P nutritional needs.

Phytase is an enzyme that facilitates hydrolysis of phytate-P into digestible inorganic P $(H_2PO_4^-)$. Added to the feed ration, phytase improves grain P digestibility, reducing the need for supplemental P. Phytase in diets can reduce manure P in poultry 25–35% and in swine 25–60%, which represents a significant reduction in potential P loss associated with land-applied wastes. In addition, advances in barley, corn, and soybean genetics have resulted in low phytate-P hybrids and varieties. Currently, these new genetics have shown reduced yield potential relative to traditional high phytate-P genetics. With continued developments, such as the combination of high-yielding low-phytate genetics and phytase supplemented diets, the manure-P applied to fields can be reduced by 30–40%, decreasing potential applied-P impact on water quality.

P Loss Assessment Tools

Recently, changes in nutrient management guidelines suggested by the USDA resulted in development of methods or tools to estimate the quantity of P delivered to surface- and groundwaters. These P loss assessment tools require a technical service provider to understand fate and transport of P applied to soils that involve (1) P adsorbed to eroding sediments, (2) soluble P in runoff water, (3) soluble P in leaching water, and (4) P losses related to the specific waste sources and management. In addition, the potential P loss associated with fertilizer or waste P applications can be estimated. P loss assessment tools enable the user to assess the impact of adoption of P BMPs on reducing potential P loss, and thus will reduce the risk of P use on water quality.

Air Quality

Naturally occurring greenhouse gases include H_2O vapor, CO_2, methane (CH_4), nitrous oxide (N_2O), and others. Although CO_2 is a dominant anthropogenic greenhouse gas, agriculture contributed $\approx$6% of total U.S. gas emissions. While agriculture is not a major contributor to CO_2 emission, it is not predominately involved in CO_2 sequestration.

Agricultural soil and crop management contribute to greenhouse gas emission through numerous processes, where CH_4 and N_2O are the major sources. CH_4 and N_2O emissions have increased only slightly over the last two decades (Fig. 12-49). CH_4 emissions are dominated by animal intestinal gas (*enteric fermentation*), manure application, and rice cultivation, while N_2O emissions are dominated by agricultural soil management (mostly fertilizer N) and manure N application (Fig. 12-50). With manure management, CH_4 and N_2O are dominantly produced by anaerobic decomposition of manure and urine.

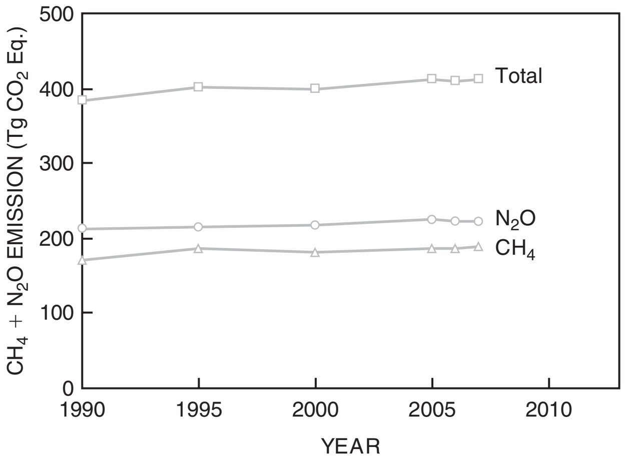


Figure 12-49
Trend in CH_4 *and* N_2O *emissions from all agriculture related sources in the United States from 1990 to 2007. Quantity in teragram* (10^{12} g) *of gas equivalent to* CO_2 *(Tg* CO_2 *Eq.).*
(U.S. EPA, 2009, EPA 430-R-09-004.)

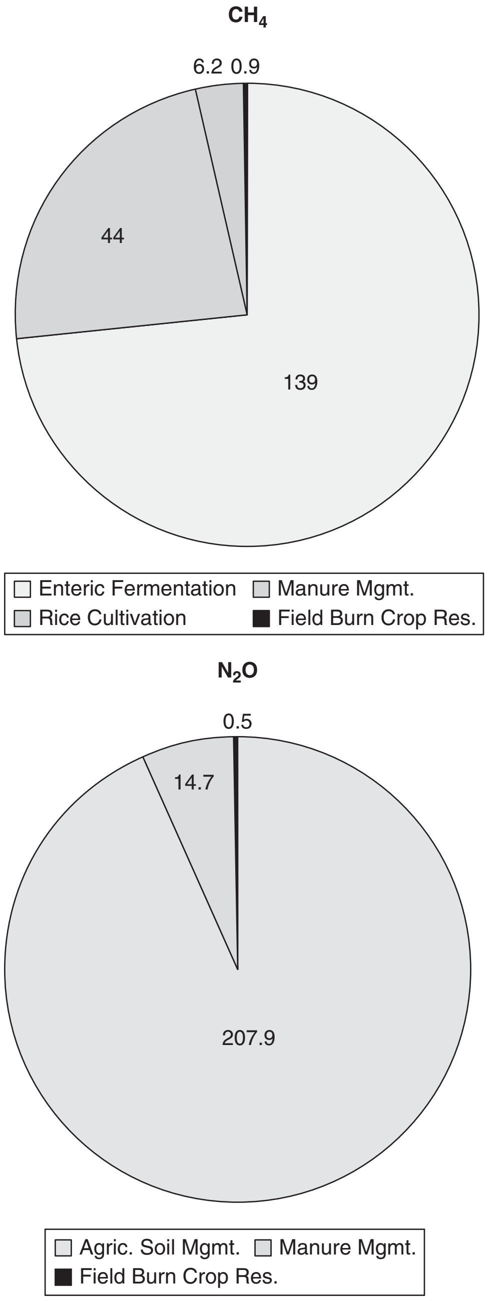


Figure 12-50
Primary sources of CH_4 *and* N_2O *emissions (Tg* CO_2 *Eq.) from agriculture in the United States.*
(U.S. EPA, 2009, EPA 430-R-09-004.)

N_2O is released naturally from soils through nitrification and denitrification reactions (Chapter 4). Increasing mineral N in soils increases the amount of N available for nitrification and denitrification, and ultimately N_2O emission. Mineral N is increased either directly or indirectly (Fig. 12-51). Direct sources include fertilizer, manure, or biosolid N applications; crop residue degradation; drainage/cultivation of organic soils; and, to a lesser extent, nonsymbiotic N_2 fixation (Chapter 4). Soil management practices (e.g., tillage, drainage, fallowing) can also contribute to N emission through N mineralization and nitrification.

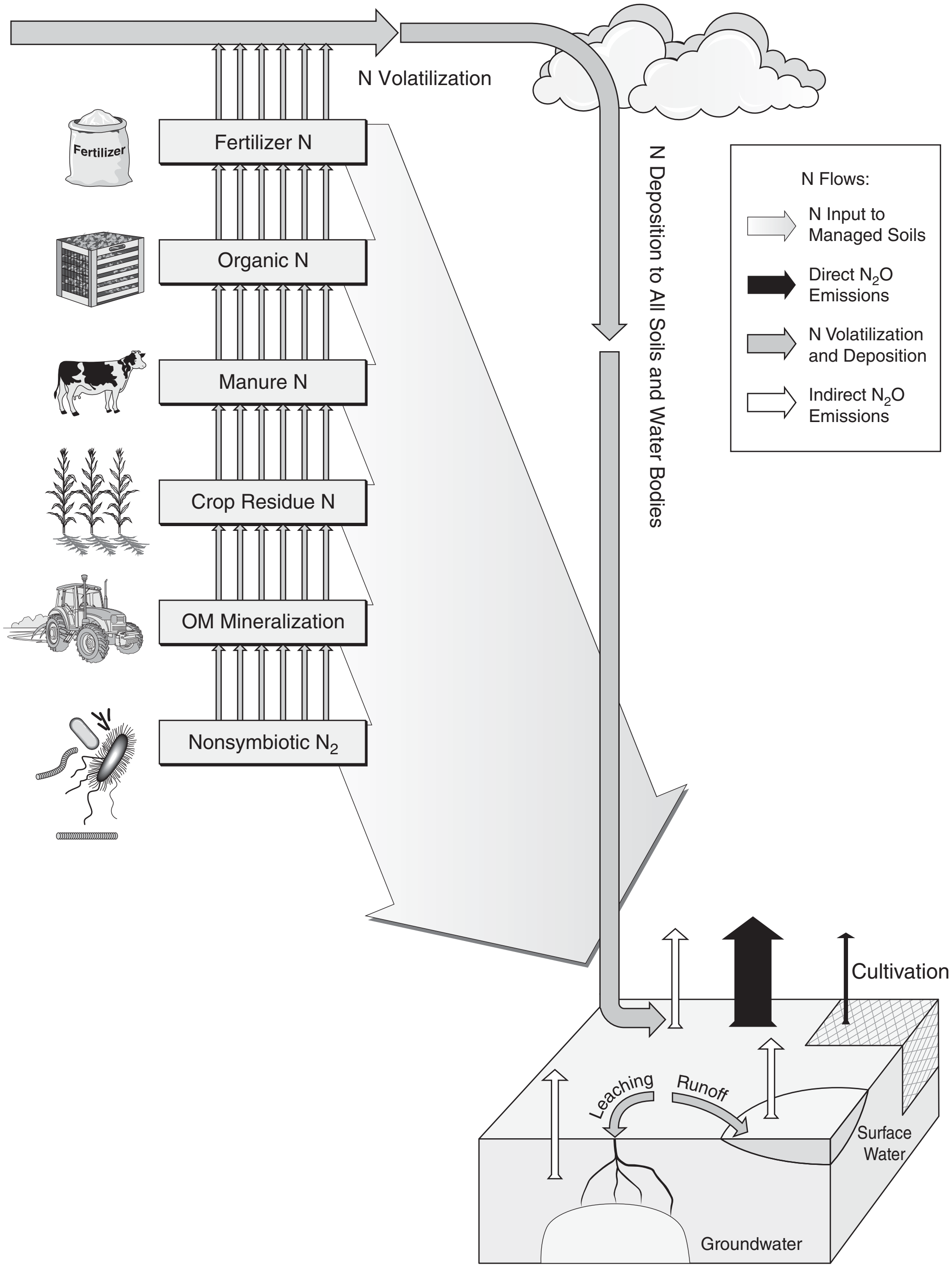


Figure 12-51

Agricultural N sources and direct and indirect pathways (arrows) of N_2O *emissions from soils.*

(Adapted from U.S. EPA, 2009, EPA 430-R-09-004.)

Figure 12-52
Trend in N_2O emissions from all sources in the United States from 1990 to 2007. Agriculture soil management represents about 67% of the total.
(U.S. EPA, 2009, EPA 430-R-09-004.)

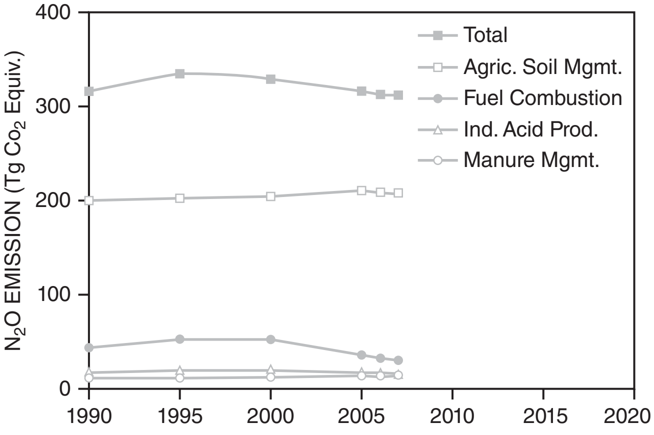
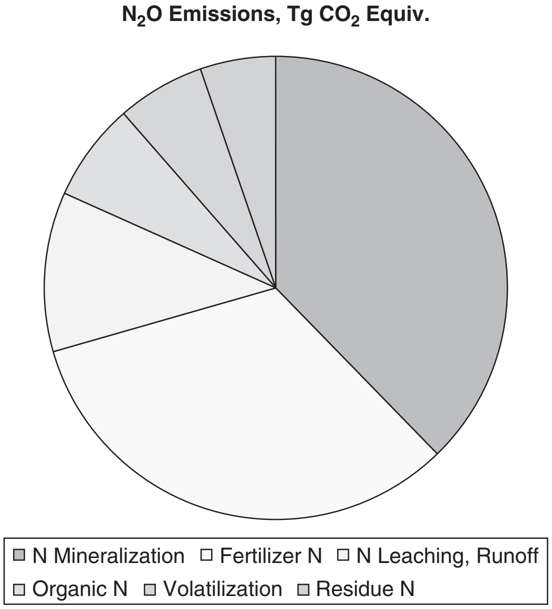


Figure 12-53
Primary sources of N_2O emissions from agricultural cropland in the United States.
(U.S. EPA, 2009, EPA 430-R-09-004.)



Management of agricultural soils produces approximately 67% of all N_2O emissions in the United States, with fuel combustion and manure application contributing substantially lower amounts (Fig. 12-52). The dominant sources of N_2O emission are related to agricultural management of cropland and, to a lesser extent, grasslands. Within agricultural cropland, N mineralization and fertilizer N application comprised over 70% of N_2O emission (Fig. 12-53).

While it is difficult to mitigate agricultural N source contributions to greenhouse gas emissions, N management guidelines are effective (Table 12-28). Many of these N BMPs are similar to those identified in Table 12-21. Dominant BMPs include identifying the right N *rate*, using the correct *timing* or split N applications, identifying the optimum N *source*, and using the right application method or *placement* to improve N utilization by the target crop and reduce N loss to the environment.

EPILOGUE: AGRICULTURAL CHALLENGES AND OPPORTUNITIES

Meeting food security needs for a growing population (estimated to be 9.5 billion in 40 years) will require ≈50–70% increase in food production on approximately the same or less agricultural land area used today (Chapter 1). Land managers must

TABLE 12-28
SELECTED N MANAGEMENT PRACTICES THAT MAY REDUCE N LOADING TO THE ATMOSPHERE

Source	Management	Impact
N fertilizer	Soil testing, plant analysis, crop sensing	Improves N rate estimate, reduces over-fertilization
	N timing	N applied synchrony with crop N demand, limit N application in non-crop periods
	N placement	N banding increases NUE, reduces volatilization
	N source	Additives to N sources reduce nitrification, denitrification, and volatilization
	Cover crops, green manure, legume rotations	Cover crops reduce residual soil N, green manure and legumes provide biologically fixed N reducing N loss
Manure N	Waste storage	Anaerobic waste storage reduces N_2O loss by removed substantial N to atmosphere during storage, net effect is small
	Waste disposal	Subsurface banding reduce N loss
Non-crop N addition	Crop N use	Manage similar to crop N management
	Riparian buffers	Riparian buffers essential to reduce N leaching and subsequent N_2O loss at streamside
	Animal facility	NH_3 loss from confined animal housing contributes NH_4^+; NH_3 emission from waste storage reduced with anaerobic systems

adopt economically viable technologies that maintain, enhance, or protect the productive capacity of our soil resources to ensure future food, feed, and fiber supplies. While organic nutrient sources are important to meeting the nutritional needs of diverse cropping systems, inorganic fertilizer nutrients will remain the predominant nutrient source. The challenge to the agricultural community is to ensure maximum recovery of applied nutrients, regardless of source, through use of diverse soil, crop, water, nutrient, and other input management technologies to maximize plant productivity. Accomplishing this will significantly reduce nutrient losses to the environment. Protecting water and air quality is essential to the health of diverse ecosystems on Earth, which directly impact our quality of life.

The study of soil fertility and nutrient management is a large and critical component of our agricultural systems. Throughout the text, the relationships between nutrients and other essential inputs and management factors were presented. Sustaining the productivity of agriculture demands a thorough and functional understanding of the interactions between nutrients, water, plant growth, and many other factors that influence plant health and yield. Hopefully you will continue your search for new knowledge and experiences that will help secure a productive agriculture.

STUDY QUESTIONS

1. Why are long-term yield trends likely to be misleading as a measure of soil productivity? What might happen to yield trends if plant breeding studies ceased?
2. What is the aim of a crop and soil management program? How does it relate to agricultural sustainability?
3. Discuss the yield response to rotation and nutrient amendments in the Morrow Plots relative to long-term crop and soil productivity.
4. Loss of surface soil varies considerably with the soil. How does soil erosion influence crop yield and explain how soil fertility depletion might accelerate soil erosion.
5. List the advantages of rotations and monoculture.
6. In what ways may N, P, and K be lost other than by crop removal? In what ways other than fertilization may the supplies be increased?
7. Using your local conditions, design two crop rotations that maximize profitability while

(1) increasing soil OM over time and (2) reducing N fertilizer or manure use.

8. Which cover or green manure crops would work best in your area? Identify the advantages and disadvantages to the use of cover/green manure crops.
9. Define conservation tillage and outline its advantages and disadvantages.
10. What soil and environmental conditions would be most and least suited for no-tillage?
11. Describe how BMPs protect surface and subsurface water quality.
12. Compare and contrast the essential components of N and P BMPs.
13. How do riparian buffers function to enhance water quality?
14. Nitrate leaching into the groundwater has become an increasingly sensitive issue among both rural and urban constituents. You have been asked to give a short presentation to an urban consumer group on agricultural technologies that reduce the potential for fertilizer N movement to groundwater. What management technologies would you identify/discuss?
15. Identify the primary source of greenhouse gas emissions from agriculture.
16. A farmer uses conventional tillage on a 2% OM soil (0–6 in. depth). How much total soil N does the farmer lose each year, if the soil loss by erosion is 25 t/ac/yr.
17. Describe the pathways of P loss in agricultural soils.
18. How does P source and management influence potential P loss?
19. P is strongly adsorbed to soil clays. How is it possible that P can leach in soils?
20. What are the common criteria used for assessing sustainable farming system?
21. What factors determine the soil health?
22. How improving soil quality will lead to increase in profitability?
23. Explain how soil productivity is reduced by soil degradation processes and improved by soil conservation processes.
24. Explain the influence of soil erosion on surface soil properties.
25. List down the specific advantages and disadvantages of conservation tillage.
26. Write a note on types of tillage methods.
27. What is the relation between crop rotation and pest control?
28. What is eutrophication? What is its cause and effect?

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