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Soil Fertility and Plant Nutrition

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THE BIOLOGICAL, CHEMICAL, AND PHYSICAL FACTORS that control the availability of plant essential and beneficial nutrients as well as potentially phytotoxic and zootoxic microelements are reviewed in this part. Nutrient and elemental availability is important not only as it affects crop plant productivity, but as it determines the potential movement of nutrients outside the boundaries of the crop field and their impact on air and water resources and native ecosystems. The complexity of soil acidity and nutrient interactions as they affect plant uptake and utilization of nutrients are also elaborated in this part. The use of fertilizer nutrients by crop plants, as it is affected by fertilizer material and application timing and placement, are discussed with regard to nutrient mobility and reaction with the soil. Ultimately, the continuum of soil–fertilizer–plant–climate interactions determines the efficiency of nutrient and water use. The economically and environmentally sound management of nutrients and toxic elements is facilitated by accurate soil and plant tissue testing methods that account for all these factors impacting availability.

In addition to C, H, and O, at least 14 mineral elements accumulated by root uptake from the soil are considered essential for most plants (N, P, K, Ca, Mg, S, Cu, Mn, Fe, B, Ni, Mo, Cl, and Zn). N, P, and K are often classified as "major" or "macro" nutrients, because they are frequently deficient in agricultural production, and when deficient they can have substantial impact on crop productivity. Although N and P are accumulated in large quantities by plants, the uptake of P is considerably less, on par with the "secondary" nutrients, Ca, Mg, and S. Silicon may not be essential to complete the life cycle of most plants, but its uptake by some plants, like rice and sugarcane, far exceeds that of N or K, and its impact on productivity of these crops can be great. "Minor" or "trace" elements include both biologically essential "micro" nutrients (Cu, Mn, Fe, B, Ni, Mo, Cl, and Zn) and nonessential elements (e.g., Al, Pb, Cd, and Hg). Plant tissue micronutrient sufficiency levels are quite low; however, at high levels of availability, both essential and nonessential elements can become toxic to plants or animals.

The principles of soil fertility and plant nutrition affecting the growth of plants and impacting the environment are discussed in the following six chapters.

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Bioavailability of N, P, K, Ca, Mg, S, Si, and Micronutrients

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11.1 Bioavailability of Nitrogen

James J. Camberato

11.1.1 Introduction

The focus of this chapter is to illustrate how the fundamental transformations and transport of nitrogen (N) in the soil alter its bioavailability and impact plant productivity and environmental quality. Nutrient bioavailability or availability can be defined in many ways. Of the 10 definitions described by Blackmer (1999), that of Peck and Soltanpour (1990, p. 4) is most appropriate to this chapter: "By plant-available nutrient, one usually means the chemical form or forms of an essential plant nutrient in the soil whose variation in amount is reflected in variations in plant growth and yield."

The transient nature of N in soil and the large quantity accumulated by plants both contribute to the frequent occurrence of N deficiency in nonlegumes. Maximizing N bioavailability from indigenous soil N and added N (fertilizer, manure, legume residues, etc.) to optimize the yield of crop plants was the initial impetus to understanding N bioavailability. Considerable study of N transformations and transport determined that the processes of mineralization and immobilization, nitrification and denitrification, volatilization, and leaching control N bioavailability. With time, it was realized that N losses from agricultural systems via leaching, denitrification, and ammonia (NH_3) volatilization impacted surface and ground water, atmosphere, and noncultivated ecosystems; and much emphasis was then placed on quantifying and understanding these effects as well.

11.1.2 Nitrogen Cycle

Nitrogen bioavailability to plants is dynamic—the result of several interrelated microbial, chemical, and physical processes in soils, which are contingent upon the nature of the soil as well as temperature, moisture, energy, and other factors. The connectivity of these processes is often displayed as "The Nitrogen Cycle" (Section 27.1 of *Handbook of Soil Sciences: Properties and Processes*).

Nitrogen inputs to soils include N fixation, atmospheric deposition, and purposeful nutrient application (fertilizers, manures, etc.). Although dinitrogen gas (N_2) comprises ≈80% of the atmosphere, it can only be utilized by a few species of free-living bacteria and blue–green algae, and specialized N-fixing bacteria that form symbiotic relationships with leguminous plants (Section 27.1 of *Handbook of Soil Sciences: Properties and Processes*). Historically, the majority of reactive N (N molecules other than N_2) arose from microbial N fixation, until the recent (geologically speaking) development of the Haber–Bosch fertilizer manufacturing process (Galloway and Cowling, 2002; Mosier, 2002). The only other natural processes contributing significantly to the oxidative fixation of N_2 are lightning (Noxon, 1976; Liaw et al., 1990), fire, and volcanic activity (Bandy et al., 1982; Huebert et al., 1999).

With the industrial revolution came an increase in atmospheric deposition of reactive N, mostly due to the burning of N-containing substances. More than 90% of the N in organic residues is lost to the atmosphere with burning (Heard et al., 2006), most as NO_x (nitric oxide [NO] and nitrogen dioxide [NO_2]), nitrous oxide (N_2O), NH_3, hydrogen cyanide (HCN), and higher N-compounds (Lobert et al., 1990). On a global scale, atmospheric N deposition from anthropogenic sources has exceeded that from natural sources since the mid-twentieth century (Galloway, 2001) and was recently estimated to be about fourfold that from natural sources (Fowler et al., 2004). Smil (1999) reported wet deposition of 1 kg N ha^{-1} in the United States, west of the Mississippi, 7 kg N ha^{-1} in the coastal Northeast, and as much as 20 kg N ha^{-1} in the Netherlands, northeastern France, and southern England. Although the deposition of reactive N might be viewed positively in its contribution to plant productivity, atmospheric N deposition also contributes to soil and water acidification (Galloway, 2001; Rodhe et al., 2002), eutrophication of surface waters (Fisher and Oppenheimer, 1991; Bergström and Jansson, 2006), and decreased ecosystem diversity (Bobbink et al., 1998; Lee and Caporn, 1998). Additional beneficial and detrimental effects of reactive N in the environment are overviewed in Section 27.5 of *Handbook of Soil Sciences: Properties and Processes* and Galloway and Cowling (2002).

11.1.3 Nitrogen an Essential Plant Nutrient

"Nitrogen is without doubt the most spectacular of all essential nutrients in its effect on plant growth" (Olson and Kurtz, 1982, p. 568). Plant growth responses to increasing N bioavailability are more frequent and larger than to any other essential nutrient. Viets eloquently stated, "No one can claim that N is more essential than any of the other 15 elements known to be needed for higher plants, but on the basis of relative number of atoms needed, N is at the top of the list of those that come from soil or fertilizers," (Viets, 1965, pp. 503–504). Nitrogen is a component of nucleic acids (RNA and DNA), amino acids (proteins and enzymes), and chlorophyll. Detailed information on the role of N in plant nutrition can be obtained from Lea and Morot-Gaudry (2001) and Amâncio and Stulen (2004).

Plant tissue sufficiency concentrations of N differ among plant species and plant parts, ranging from ≈20 to 50 g N kg^{-1} as reported by Olson and Kurtz (1982). Legumes have higher tissue N concentration than nonlegumes, >40 versus <40 g kg^{-1}. Most plant N is in the organic or reduced form, although nitrate (NO_3^-) will accumulate to some extent in some situations (Grunes and Allaway, 1985, pp. 594–597). Aboveground N accumulation may exceed several hundred kilograms per hectare in productive environments, but in most environments N bioavailability limits the growth of nonleguminous plants.

Inadequate N bioavailability reduces overall plant growth and often results in chlorosis (yellowing) of plant tissues, a result of reduced chlorophyll content. Since N is highly mobile in the plant, chlorosis and necrosis of older plant tissues precedes the chlorosis of younger tissues, as N is translocated from older to younger plant parts. Descriptions and photographs of N deficiency on many important grain, sugar, oilseed, vegetable, and fruit crops as well as turfgrasses can be obtained from Bennett (1993). Excess N can also have detrimental effects on plants; including delayed flowering, reduced fruit set, and increased lodging. Excess N can impair the utilization and quality of crop plants, including poor wear tolerance of turfgrasses, reduced sugar concentration of sugar beets, lower tobacco leaf quality, and excessive NO_3^- content of vegetables and forages.

11.1.3.1 Nitrogen Uptake by Plants and Microorganisms

Nitrogen is accumulated by plants from the soil as the anion NO_3^- and the cation NH_4^+. Most plants readily accumulate both inorganic forms, with perhaps the exception of blueberry (*Vaccinium corymbosum* L.; Claussen and Lenz, 1999) and cranberry (*V. macrocarpon* Ait.; Greidanus et al., 1972), which often demonstrate a strong preference for NH_4^+. Some nondomesticated plants may have a preference for NH_4^+ or NO_3^-, depending on their adaptation to soil pH and the predominant form of N naturally occurring in the soil. Species adapted to acid soil environments may prefer NH_4^+ (Atkinson, 1985); the most prevalent form of N in acid soil, whereas less acid-tolerant species may prefer NO_3^- (Gigon and Rorison, 1972). However, many nondomesticated plants, as do crop plants, grow best on a mixture of NH_4^+ and NO_3^- (Rorison, 1985; Falkengren-Grerup, 1995). Nitrogen accumulation by plants can be rapid. Bowman et al. (1989) calculated a rate of ≈35 kg N ha^{-1} day^{-1} for field-grown, moderately N-deficient Kentucky bluegrass (*Poa pratensis* L.). In Maize (*Zea mays* L.), N accumulation rates peaked between 5 and 15 kg N ha^{-1} day^{-1} (Karlen et al., 1987).

Heterotrophic microorganisms accumulate NH_4^+ over NO_3^- when both are present (Jansson et al., 1955; Wickramasinghe et al., 1985; Rice and Tiedje, 1989), but will readily accumulate NO_3^- if it is the only form present (Davidson et al., 1990; Recous et al., 1990). Microorganisms are more competitive for N than plants in the short term. In 24 h ^{15}N uptake studies conducted in a Mollic Haploxeralf, annual grassland plants accumulated NO_3^- and NH_4^+ at rates of 0.6 and 1.0 kg N ha^{-1} day^{-1}, respectively (average for April and February measures), whereas microbial uptake was two- to fivefold higher at 1.1 and 5.3 kg N ha^{-1} day^{-1} (Jackson et al., 1989).

11.1.3.2 Ammonium and Nitrate Nutritional Effects on Plant Growth and Development

Many greenhouse, growth chamber, and hydroponics experiments demonstrated greater N uptake and/or growth of several crop species when provided both NO_3^- and NH_4^+, compared to a preponderance of one N form over the other (Schrader et al., 1972). Since NO_3^- is the predominant form of N available to plants in most cultivated soils, a nitrification inhibitor is often used to increase the proportion of total N that is in the NH_4^+ form. Crops that respond favorably to mixed N nutrition or enhanced NH_4^+ supply include barley (*Hordeum vulgare* L.; Leyshon et al., 1980); sorghum (*Sorghum bicolor* (L.) Moench; Camberato and Bock, 1989); wheat (*Triticum aestivum* L.; Camberato and Bock, 1990); maize (Below and Gentry, 1992); and Italian ryegrass (*Lolium multiflorum* Lam.; Alderman and Streeter, 1997). Unfortunately, this advantage of enhanced NH_4^+ supply has only infrequently been reported in field grown plants (Smiciklas and Below, 1992). Difficulty inhibiting nitrification to enhance NH_4^+ supply or positional availability of NH_4^+ may minimize the advantage to mixed N nutrition in field situations (Bock, 1986). Plants grown in soils where most of the N is derived from soil organic matter and plant residues and in acid or cold soils where nitrification is slowed may accumulate significant amounts of N in the NH_4^+ form without the aid of an artificial nitrification inhibitor. Otherwise, soils have little propensity to accumulate or store bioavailable NH_4^+-N (Chang et al., 1991; Muñoz et al., 2003).

11.1.4 Nitrogen Transformations Affecting Nitrogen Availability

Nitrogen bioavailability to nonleguminous plants is predicated in the presence of NH_4^+ and NO_3^- for root uptake. Thus, indigenous soil N, applied organic N, uric acid, urea, and other N-containing substances are only available to the plant after they are mineralized to NH_4^+ and NO_3^-. Nitrogen mineralization and immobilization (the microbial transfer of inorganic N to organic N) are discussed in detail in Section 27.2 of *Handbook of Soil Sciences: Properties and Processes*. Although NH_4^+ is subject to conversion to NH_3 in a high pH environment and volatilization to the atmosphere if on the soil surface, the loss of NH_4^+ from the soil is considerably less overall than the loss of NO_3^-. Unfortunately, the nitrification of NH_4^+ to NO_3^- (see Section 27.3 of *Handbook of Soil Sciences: Properties and Processes* for details) occurs readily in most soils and the subsequent loss of NO_3^- by leaching and denitrification substantially reduces N bioavailability.

11.1.4.1 Nitrogen Mineralization

The rate and extent of N mineralization determines the bioavailability of organic N sources, most importantly soil organic matter, crop residues, manures, and by-products of municipal waste treatment and industrial processes.

11.1.4.1.1 Soil Organic Matter

Stevenson (1982) reported that >90% of the N in soils is in the organic form. Organic N in the plowed layer of mineral soils ranges from 0.8 to 4.0 g N kg^{-1} (Bremner, 1965, p. 96) representing 1800–9000 kg N ha^{-1}. Thus, a 2% mineralization rate would provide 36–180 kg inorganic-N ha^{-1}, potentially a significant percentage of crop N accumulation. Cassman et al. (2002) determined indigenous N from maize uptake in 55 field experiments in the North-Central United States to typically range between 80 and 240 kg N ha^{-1}, with most providing between 100 and 140 kg N ha^{-1}. Predicting N bioavailability from soil organic N is important to increase the efficient use of fertilizer and added N and to decrease N losses to the environment (Cassman et al., 2002; Mulvaney et al., 2005). The importance of moisture and temperature (Stanford and Epstein, 1974; Kladivko and Keeney, 1987) and pH (Cornfield, 1952; Dancer et al., 1973; Olness, 1999) on N mineralization are well established. Unfortunately, laboratory tests of N mineralization have largely been unsuccessful (Griffin, 2008) in predicting N mineralization in the field, likely because most do not account for the impact of varying temperature and/or moisture in the field on N mineralization. Honeycutt et al. (1991) and Griffin and Honeycutt (2000) improved the incubation-based prediction of N mineralization from soil organic N, fertilizer, crop residue, sludge, and manure by including cumulative thermal units into equations based on soil properties and moisture.

11.1.4.1.2 Crop Rotation and Residue Effects on Nitrogen Bioavailability

Much effort has been placed on determining the cause of lower yield and higher N requirement in continuous maize compared to maize grown after soybean (*Glycine max* L.). Nitrogen availability is an important factor, although many other factors also contribute. Nitrogen uptake by maize grown after soybean in Wisconsin was 51 kg N ha^{-1}, greater than maize grown after maize on two silt loams, but no different in a sandy soil (Bundy et al., 1993). Nitrogen uptake of a second cereal crop grown 2 years after soybean was reduced to 36 kg N ha^{-1} (Vanotti and Bundy, 1995). The authors proffered that the second year reduction in N bioavailability was due to soybean removing more N from the soil than was fixed symbiotically as described by Heichel and Barnes (1984) and others (David et al., 1997; Jaynes et al., 2001). The yield benefit of maize grown after soybean, compared to maize grown after maize, was the same whether the soybean was nodulating or nonnodulating, and was not eliminated by the application of fertilizer N to a silt loam in Wisconsin (Maloney et al., 1999). These findings suggest that the "rotation effect" was not likely a result of N provided directly by the soybean crop, but an enhancement in the maize plant's ability to accumulate and utilize N. However, Gentry et al. (2001), using a similar experimental approach including nodulating and nonnodulating soybean, had a different conclusion. The "rotation effect" was due both to a decrease in N mineralization in continuous maize and to an increase in soil N arising from symbiotic fixation in maize after soybean.

Alternatively, it has been suggested that the effects of crop residues on N bioavailability may arise from their effect on soil temperature. Normal amounts of corn residue or simulated residue lowered soil temperature 0.7°C–1.7°C and resulted in 32 kg ha^{-1} less N than when residues were removed (Andraski and Bundy, 2008). Since the simulated residue (polypropylene snow fence) had a similar effect on soil temperature and N availability as corn stover, it was concluded that temperature, not microbial immobilization, had altered N bioavailability. This seems plausible since only 3–5 kg ha^{-1} of soybean residue–derived N was taken up by maize grown the following season on two Mollisols in Kansas, even though 144–155 kg N ha^{-1} more N fertilizer had to be supplied to maize grown after maize to achieve the same yield as maize after soybean (Omay et al., 1998). Crookston et al. (1991) pontificated that the "rotation effect" was "a somewhat fickle and elusive phenomenon" and was "easier to exploit … than to explain." Twenty years later this statement is still true.

11.1.4.1.3 Cover Crop Effects on Nitrogen Bioavailability

Legumes grown as cover crops differ in N fixation and residual N accumulation (Heichel and Barnes, 1984). Conditions affecting the growth of a cover crop, such as moisture and temperature, also affect its N fixation and recovery of residual N, thereby affecting the potential N contribution to the subsequent crop. The rate and extent of N mineralization from the cover crops determine the bioavailability to the following crop, which is influenced by the composition of the cover crop, placement on or incorporation in the soil, moisture, and temperature. Plant tissue with high C:N and high concentrations of lignin, cellulose, and hemicelluloses decompose and release N slower than plants with lower levels of these constituents (Wagger et al., 1998).

Legumes can fix considerable amounts of N that are significant when compared to the uptake of the subsequent cereal crop. For example, in Delaware, hairy vetch (*Vicia villosa* Roth.) and crimson clover (*Trifolium incarnatum* L.) grown in combination with spring oats (*Avena sativa* L.) or cereal rye (*Secale cereale* L.) accumulated ≈117 kg N ha^{-1} more N in cover crop roots and shoots than when either cereal was grown alone (≈55 kg N ha^{-1}) (Mitchell and Teel, 1977). An average of 90% of the cover crop N was in the top growth and about 33% of the N was released to the following maize crop. Similarly in North Carolina, crimson clover and hairy vetch, compared to a fallow treatment, increased N recovery by the subsequent maize crop ≈42 kg N ha^{-1}; equivalent to about 33% of the aboveground N content of the cover crops (Wagger, 1989a). Cereal rye, in comparison to legume cover crops, reduced N recovery by about 25 kg N ha^{-1} compared to fallow—likely arising from the high C:N of the rye (≈35:1; Wagger, 1989b) and N immobilization. Hairy vetch, big flower vetch (*Vicia grandiflora* W. Koch), and crimson clover grown as winter cover crops in Kentucky accumulated 173, 24, and 20 kg N ha^{-1} more aboveground plant N than cereal rye (36 kg N ha^{-1}), respectively (Ebelhar et al., 1984). Poor growing conditions, including low rainfall, reduce N accumulation. Four cover crop systems grown in the Brazilian Cerrados contributed 25–64 kg N ha^{-1} to the following maize crop in one season, but had no effect in the second season in which cover crop growth and N uptake were reduced by dry weather (Maltas et al., 2009).

Date of planting (growing season length), killing date, and moisture affect N fixation and N recovery of cover crops. A late August planted wheat-hairy vetch mixture grown 30 km south of Vancouver, British Columbia produced 126 kg N ha^{-1}, whereas the same mixture planted 4 weeks later produced only 70 kg N ha^{-1} (Odhiambo and Bomke, 2001). Many researchers have focused studies on the impact of kill date on cover crop N accumulation (Wagger, 1989a, 1989b; Clark et al., 1994, 1997; Odhiambo and Bomke, 2001; Sainju and Singh, 2001). The longer the cover crop is allowed to grow, the greater the amount of N that is fixed or recovered from the soil. Hairy vetch and a vetch-cereal rye mixture accumulated ≈2 kg N ha^{-1} day^{-1} in the aboveground biomass form late March until early May in Maryland (Clark et al., 1997).

Temperature, moisture, and placement of cover crop residues affect N contribution of the cover crop to the subsequent main crop. For several cover crops, faster N mineralization occurred in the first year of a 2 year study, due to higher rainfall (79 versus 15 mm) and higher mean air temperature (29°C versus 25°C) in the first 4 weeks of residue decomposition in North Carolina (Ranells and Wagger, 1996). Nearly complete N release from the hairy vetch cover crop occurred twice as fast in year 1 than year 2, 8 versus 16 weeks. Incorporating legume cover crop residue into a *Typic Paleudalf* in Kentucky increased the rate and extent of N release to the following crop (Varco et al., 1989). Maize recovered 31 kg ha^{-1} more N when hairy vetch was incorporated into the soil compared to when left on the soil surface, 32% versus 20% of the residue N content, respectively.

Nonlegume cover crops can be effective at recovering residual N from a previous crop or a post-growing season manure application. Nitrogen accumulation and subsequent release to the following crop determine bioavailability and environmental impact. In an irrigated *Xeric Torripsamment* sand in eastern Washington, about 29% of the 92–142 kg N ha^{-1}, captured by a mustard (*Brassica hirta* Moench) cover crop from fertilizer applied to a winter wheat-sweet corn-sweet corn rotation was recovered by the following potato (*Solanum tuberosum* L.) crop (Collins et al., 2007).

Cover crops can increase N bioavailability by reducing percolation losses (Weinert et al., 2002) as well as by recovering residual N. An estimated 50% of the 9 cm of winter rainfall was used by cover crops grown on a *Xeric Torripsamment* in the Columbia Plateau of central Washington. Thus, soil mineral N was reduced by 155 kg N ha^{-1} to a depth of 180 cm by cereal rye, wheat, or rapeseed (*B. napus* L.). However, winter water use by cover crops can sometimes reduce yield and N recovery by the subsequent crop, particularly in semiarid regions (Unger and

Vigil, 1998). Bioavailability of cover crop N can be assessed by aboveground N accumulation, with the PSNT soil test for NO_3^- or NO_3^- and NH_4^+ (Vaughan and Evanylo, 1999), or growing degree day predictive methods (Schomberg and Endale, 2004).

11.1.4.1.4 Nitrogen Bioavailability from Animal Manure and Organic N Sources

The term "animal manure" is used to refer to the array of complex substances arising from animal feces, urine, bedding, unused ration, water, medications, and growth promoters. Organic substances used as N sources for crop plants include by-products from vegetable, meat, oilseed, starch and sugar processing, municipal waste treatment (sewage sludge or biosolids), paper manufacturing, and other processes. A thorough discussion of these by-products can be found in Power and Dick (2000). This section will concentrate on N bioavailability from animal manure, although the same principles apply to other organic N sources. Nitrogen forms in manure include NO_3^-, NH_4^+, NH_3, urea, uric acid, and complex organic N compounds. Managing and predicting N bioavailability from manures is more difficult than that from inorganic fertilizer because of the variable composition of these materials and practical considerations that foster less than optimum timing and placement. The transformations of these compounds as affected by application method, timing, soil cation exchange and buffer capacity, and weather determine N bioavailability, but are difficult to predict. Bioavailability estimates for manures generally include availability factors for N that consider inorganic N loss (primarily NH_3 volatilization and NO_3^- leaching), based on application method and timing and an estimate of organic N mineralization. Nitrogen bioavailability from manure may also be represented in terms of "fertilizer replacement value" or "fertilizer equivalency," which does not take into account N loss that both fertilizer and manure N would be subjected to equally.

Manure N availability algorithms for making manure application rate recommendations for 34 states were reviewed and programmed by Joern et al. (2009). They found that 27 different variables were used to determine plant-available manure N and that for any single state 5 to 12 variables are needed to make this determination. While the number of variables required is indeed large, once the manure source is determined, 12 states use only one factor (e.g., total manure N) and 15 states use only two factors (e.g., total manure N and application method) to determine plant-available manure N. All but one state include method of application to determine plant-available manure N; however, only 13 out of 34 states use month of application to determine manure N availability.

Pratt et al. (1973) developed the "decay series" concept to represent manure N bioavailability over multiple growing seasons. The yearly rates of N mineralization in a decay series are given as the fraction of total N (year 1) or residual N (year 2 and beyond) mineralized. For example, if manure were applied containing 100 kg N ha^{-1}, the decay series 0.35, 0.15, 0.10, and 0.05 would predict mineralized N of 35 kg ha^{-1} in year 1 (0.35×100 kg N ha^{-1}), 9.8 kg ha^{-1} in year 2 [$0.15 \times (100 - 35$ kg N $ha^{-1})$], 5.5 kg ha^{-1} in year 3 [$0.10 \times (100 - 35 - 9.8$ kg N $ha^{-1})$], and 2.5 kg N ha^{-1} in year 4 [$0.05 \times (100 - 35 - 9.8 - 5.5$ kg N $ha^{-1})$]. Nitrogen bioavailability from successive annual applications of manure would include N mineralized from previous seasons as well as the current growing season. Thus, if manure containing 100 kg N ha^{-1} were applied annually, N bioavailability in year 4 of the previous example would be 52.8 kg ha^{-1} ($35 + 9.8 + 5.5 + 2.5$ kg N ha^{-1}). The term "mineralized" was used by Pratt et al. (1973) to represent inorganic N released from urea and uric acid as well as slowly mineralizable organic N. Although this concept was originally put forth to estimate actual mineralization, the author's first experimentally based decay series, 0.40, 0.25, 0.06 from a field trial in the Coachella Valley, California, was based on fertilizer equivalency. Not surprisingly, decay series were found to be soil dependent. Dairy manure N bioavailability determined in a 5 year Vermont study was lower on a somewhat poorly drained clay soil (decay series—0.35, 0.15, 0.10, 0.075, and 0.05) than on a well-drained loam soil (decay series—0.60, 0.15, 0.10, 0.075, and 0.05), perhaps due to denitrification losses in the year of application (Magdoff, 1978).

Plant-available N in poultry litter was estimated in incubation studies to be approximately 80% of the inorganic N and 60% of the organic N contents and this provided a reasonable estimate of N bioavailability in two field experiments with maize, conducted in sandy loam Ultisols in Delaware (Bitzer and Sims, 1988). Nitrogen recovered in the second growing season from the 280 kg organic N ha^{-1} added at the highest rate of poultry manure was equivalent to only 31 and 16 kg N ha^{-1} fertilizer N, 11% and 6% of the organic N applied. Camberato and Frederick (1994) found no difference in residual N from poultry manure and fertilizer N applied at comparable N rates. High N availability shortly after poultry manure application and little residual value suggest that poultry manure application timing should be similar to that recommended for inorganic fertilizer to avoid leaching and denitrification losses.

Swine manure is often handled as a slurry or liquid from a lagoon. In this form 60%–80% of the total N content is in the NH_3/NH_4^+ forms (Mikkelsen, 1997). Thus, NH_3 volatilization from surface applications affects bioavailability. Only 40% of the total N content of surface-applied liquid swine manure slurry is considered available in comparison to 70%, when incorporated. Rapid conversion of NH_4^+ to NO_3^- and subsequent leaching and denitrification losses would be similar to those incurred with NH_4^+ fertilizers. Swine manure lagoon sludges have a higher organic N content (75%), thus predicting that organic N mineralization is a main determinant of bioavailability.

Dairy manure has a higher C:N ratio and more organic N than poultry or swine manure. Net nitrification and immobilization from nine dairy manures was more accurately predicted by considering the impact of manure C or neutral detergent fiber on N transformations (Griffin et al., 2005). The fertilizer N equivalency of dairy manure organic N was determined from maize N accumulation in New York to be 21%, 9%, 3%, 3%, and 2% of the original organic N content in years 1–5 after application, respectively (Klausner et al., 1994).

11.1.5 Factors Reducing N Bioavailability

11.1.5.1 Nitrogen Immobilization

Nitrogen can be added to the soil, remain in the rootzone, yet be unavailable to the crop. Immobilization of inorganic N by microorganisms decomposing high C:N crop residues (>20–30:1), such as maize, oat, or wheat stover or other organic materials can render substantial quantities of inorganic N unavailable for periods of time (Alexander, 1977). Substances such as sawdust or other wood-based by-products can have an even greater effect on N bioavailability than crop residues. For example, a papermaking sludge with a C:N ratio of 480:1 immobilized soil N for at least 250 days when added at 267 g sludge kg^{-1} soil (Zibilske, 1987). Ammonium is preferentially used by heterotrophic microflora, but NO_3^- is also immobilized in the absence of NH_4^+ (Recous et al., 1990).

11.1.5.2 Conversion of Ammonium to Nitrate Increases the Potential for Nitrogen Loss

Losses of NH_4^+-N from soil are generally small but NO_3^--N can be lost in large quantities by leaching and denitrification. Thus, nitrification, the conversion of NH_4^+ to NO_3^- by *Nitrosomonas* and *Nitrobacter* (see Section 27.3 of *Handbook of Soil Sciences: Properties and Processes*), is a critical factor that determines N bioavailability in many situations. Many factors affect nitrification rate, including temperature, pH, and soil type.

In laboratory incubations the nitrification rates of four soils increased with increased temperature from near 0°C to 27°C or 35°C, dependent on soil type (Frederick, 1956). The rate of nitrification is increased by increased temperature, but can proceed at relatively high rates with low temperatures in some soils. For example, equal nitrification rates occurred in a clay loam Ultisol incubated at 32°C or 8°C, but only after a 6 week lag period at the lower temperature (Anderson and Boswell, 1964). Nitrification proceeded in a field study in Missouri as soil temperature approached 0°C, albeit at a reduced rate (Kidwaro and Kephart, 1998).

Low soil pH reduces nitrification rate. A fivefold difference in nitrification during a 15-day incubation at 23°C occurred across a range of pH from 4.5 to 6.5 in a *Typic Argiudoll* (Dancer et al., 1973). Liming an acid soil from 5.0 to 7.4 tripled nitrification during a 3–4 week incubation (Frederick, 1956). In Iowa field experiments, 89% nitrification of fall-applied anhydrous ammonia was achieved in mid-April in soils with $pH > 7.5$, but only 39% nitrification occurred in soils with $pH < 6.0$ (Kyveryga et al., 2004).

Nitrapyrin is an effective inhibitor of nitrification (Bundy and Bremner, 1973) that is commonly applied with NH_4^+-containing and NH_4^+-forming fertilizers and manure. The persistence of nitrapyrin ranges from 5 to 50 days and is dependent on soil texture, organic matter, and temperature (Keeney, 1980). The effectiveness of nitrapyrin is greater at lower temperature; therefore, it is often applied with fertilizer after soil temperatures fall below 10°C in autumn for a spring crop (Touchton et al., 1978). Dicyandiamide (DCD) is another commercially available nitrification inhibitor and slow-release N source (Amberger, 1981) that has greater mobility in soil than nitrapyrin. Surface applications of urea and DCD can be moved into the soil with irrigation, shortly after application; but this mobility can also result in separation of DCD from NH_4^+ after urea hydrolysis (Bock et al., 1981).

A nitrification inhibitor can be effective at increasing N bioavailability and reducing NO_3^- leaching and denitrification. Apparent N recovery by maize grown on a sand-textured Ultisol in North Carolina was increased from 17% to 53% by including a nitrification inhibitor with urea versus urea alone (Chancy and Kamprath, 1982). After 22 cm rainfall, substantially more N remained in the upper 55 cm of soil 48 days after application with the nitrification inhibitor, than without. Similarly in a Minnesota study, applying a nitrification inhibitor with urea at 134 kg N ha^{-1} just prior to planting increased maize grain yield 28% on a loamy coarse sand with an available water holding capacity of only 7 cm m^{-1} (Malzer, 1989). Rainfall during the 8 weeks after application averaged 21.5 cm for the 3 years of the study, likely causing substantial NO_3^- leaching when urea was applied without a nitrification inhibitor.

Nitrification inhibitors affect N loss via denitrification as well as via leaching. Bioavailability of fertilizer N applied to a clay loam Ultisol increased when nitrapyrin was added with the fertilizer due to a decrease in denitrification (McElhannon and Mills, 1981). Nitrification of NH_4^+-N in liquid swine manure was complete in 7 weeks without a nitrification inhibitor, but was delayed up to 15 weeks with inclusion of 50 mg nitrapyrin active ingredient per liter of manure (McCormick et al., 1983). Increased N bioavailability was attributed to reduced denitrification as little NO_3^--N was found below the bands of untreated manure.

11.1.5.3 Nitrogen Leaching Reduces Nitrogen Bioavailability

Leaching of NO_3^- from the soil reduces bioavailability to plants and impacts environmental quality. Excess N in surface waters contributes to eutrophication (Keeney and Hatfield, 2008). High NO_3^- and nitrite (NO_2^-) in drinking water and food can cause methemoglobinemia in humans and animals (National Research Council, 1972).

The amount, intensity, and timing of rainfall, evapotranspiration, soil N levels, and many other factors impact the amount of N lost by leaching. In fertilized and manured soils the timing of N uptake by crops in relation to N application and rainfall exceeding evapotranspiration are key factors (Watts and Hanks, 1978). Nitrate movement in sandy soils is thought to occur more or less through the entire soil matrix and, thus, is envisioned as moving downward with the wetting front in proportion to rainfall in excess of evapotranspiration. Nitrogen loss can be substantial and rapid. In structured soil, water moves through an incomplete volume of the soil matrix; thus, NO_3^- is lost from the soil proportional to its concentration and much more slowly and less completely than in sand-textured unstructured soils.

In dry climates and on heavy-textured soils, NO_3^- leaching is limited. Only 7 kg NO_3^--N ha^{-1} $year^{-1}$ of 168 kg N ha^{-1} applied to a field continuously cropped to maize was found in subsurface discharge from loess soils in Iowa (Burwell et al., 1976). Thus, N applied to one crop can "carryover" and be accumulated by the next crop. For example, carryover of fertilizer N from 168 kg N ha^{-1} N applied for maize on a silt loam soil in Wisconsin was about 50% of that applied, ranging from 32 to 106 kg N ha^{-1} using oat to estimate bioavailability (Vanotti and Bundy, 1994). Residual N was highest when N uptake of the maize was reduced by dry weather. Thus, soil NO_3^- testing is often recommended for adjusting N rate recommendations in dry climates (Section 13.2).

In contrast, N leaching occurs readily in warm humid climates on sandy soils, with irrigation, and in heavier-textured soils that are tile drained. A total of 161 kg N ha^{-1} NO_3^--N was leached below 120 cm soil depth in a sandy loam Hapludoll that was irrigated with 50 mm of water each time available soil water decreased to about 50 mm (50% depletion) (Timmons, 1984). Leaching of NO_3^--N from a split application of 185 kg N ha^{-1} beyond 152 cm soil depth in a loamy fine sand Haplustalf was increased by irrigation, 25% above optimum, about 60 mm $year^{-1}$ (Gehl et al., 2005). Only about 10% of the 168 kg N ha^{-1} applied to maize was recovered by wheat (Camberato and Frederick, 1994) or a cereal rye and annual ryegrass (*L. multiflorum* Lam.) cover crop (Shipley et al., 1992).

Nitrate-N leaching occurs in heavier-textured soil if tile drained. Nitrogen leaching ranged from 13 to 61 kg NO_3^--N ha^{-1} $year^{-1}$ in a maize–soybean rotation on Mollisols in Iowa and from 15 to 38 kg N ha^{-1} $year^{-1}$ in silt loam Alfisol (Jaynes et al., 2001). Annual NO_3^--N loss from a tile-drained silt loam *Typic Glossaqualf* in Indiana decreased from 38 to 15 kg N ha^{-1} by including soybean in rotation with corn, reducing N application from ≈300 to ≈200 kg N ha^{-1}, and planting a winter wheat "catch crop" after corn in the rotation (Kladivko et al., 2004). Nitrate leaching from maize grown on Coastal Plain soils in Maryland was reduced to 80% by cereal rye cover crop (Staver and Brinsfield, 1998). Field-scale watershed studies suggested that groundwater NO_3^- was reduced to 60% by the use of cereal rye cover crops.

The environmental benefit of a cover crop is dependent on when the N is mineralized and nitrified and how much is utilized by the subsequent crop. Even though forage and oilseed radish (*Raphanus sativus* L.) were as effective as rapeseed and cereal rye in recovering N from the previous crop, the captured N was released earlier in the spring in Maryland due to winter kill (Dean and Weil, 2009). Thus, high pore water NO_3 in the soil profile under the radishes suggested leaching of NO_3^- from the loamy sand soil was possible unless followed by an early-planted spring crop. Frost-sensitive crops, sudangrass (*S. bicolor* L.) and white mustard, also released N prematurely resulting in soil NO_3^- levels higher than bare fallow (Weinert et al., 2002).

Anion exchange capacity originating at low pH in weathered Alfisols, Ultisols, and Oxisols may slow NO_3^--N loss (Toner et al., 1989; Eick et al., 1999); however, the ability of plants (particularly crop plants) to root into these acid soil layers is questionable due to low Ca availability and/or Al toxicity (Adams and Lund, 1966; Adams and Moore, 1983).

Nitrogen fertilizer, primarily anhydrous ammonia, is often applied in relatively cold and dry climates in late fall for a crop to be planted the following spring. Although nitrification may be limited just after application due to cold soil temperatures, significant nitrification can occur in the spring as the soils warm. Substantial N loss due to leaching and/or denitrification can occur prior to crop N demand. For example, in a corn–soybean rotation, apparent N recovery of anhydrous ammonia applied for corn on a tile-drained Mollisol in southern Minnesota was only 45% for fall-applied N compared to 87% for spring-applied N (Vetsch and Randall, 2004). Nitrate-N loss to tile drainage in this environment was reduced to 14% by spring application in comparison to fall-applied N (Randall and Vetsch, 2005).

11.1.5.4 Denitrification Reduces Nitrogen Bioavailability

Denitrification, conversion of NO_3^- to N_2 or less reduced gaseous N forms (see Section 27.4 of *Handbook of Soil Sciences: Properties and Processes* for details), lowers N bioavailability and contributes to greenhouse gas emissions and global warming. Denitrification losses increase with increasing temperature, but denitrification will occur in winter months with losses to the atmosphere occurring upon thawing (Dusenbury et al., 2008). Anaerobic conditions promote denitrification as do near-neutral soil pH, increasing NO_3^--N (McSwiney and Robertson, 2005; Millar et al., 2010) and soluble C.

Denitrification losses can be agronomically as well as environmentally important on poorly drained soils, with irrigation, application of manures or organic by-products, or reduced tillage. Denitrification losses were substantial on a clay (770 g kg^{-1}) *Typic Humaquept* near Québec City, Canada, on which barley was grown over a 3 year period, ranging from 12 to 45 kg N ha^{-1} during the snow-free season (Rochette et al., 2007). No-tillage, in comparison to moldboard plowing, resulted in a 2.5-fold increase in denitrification due to an increase in water-filled pore space. Denitrification losses in a well-drained loam soil in the same catena as the clay soil were ≤1.5 kg N ha^{-1}. Well-drained soils in dry climates have relatively low denitrification losses. Cumulative denitrification N loss over a 2 year period from four cropping systems in the semiarid northern Great Plains ranged from 0.3 kg N ha^{-1} for alfalfa (*Medicago sativa* L.)-perennial grass to 1.3 kg N ha^{-1} for continuous wheat (Dusenbury et al., 2008).

High rates of N_2O flux from the soil, 0.24–1.06 kg N ha^{-1} day^{-1}, occurred from three vegetable production systems in Santa Barbara County, California (Ryden and Lund, 1980). Peak N_2O emissions followed the first furrow irrigation after N fertilization. Annual emissions were estimated to range from 20 to 42 kg N ha^{-1}. Organic materials high in bioavailable C that stimulate microbial respiration may create an anaerobic microenvironment, creating conditions suitable for denitrification (Rice et al., 1988).

Greater denitrification occurred with alkaline-hydrolyzing fertilizers, anhydrous ammonia, and urea, in comparison to acidic fertilizers, because of increased soil pH and water soluble organic carbon with the alkaline fertilizers (Mulvaney et al., 1997).

Denitrification losses of N from banded urea fertilizer (applied at 218 kg N ha^{-1}) for maize grown on a furrow irrigated, well-drained Aridic Argiustoll in Colorado were 3.2 and 1.7 kg N ha^{-1} in each year of the study (Bronson et al., 1992). Peak N_2O emissions were coincident with irrigation and rainfall and were reduced by slowing the conversion of urea to NO_3^- by including the nitrification inhibitor, nitrapyrin, with the banded fertilizer. Cumulative denitrification N losses from maize grown with 210 kg N ha^{-1} as surface-applied urea, no-tillage, and sprinkler irrigation on two Mollisols in Argentina were 9.8 and 2.1 kg N ha^{-1}, for preplant and sidedress N application, respectively (Sainz Rozas et al., 2001). Most of the N loss occurred when water-filled pore space exceeded 80%.

11.1.5.5 Ammonia Volatilization Reduces Nitrogen Bioavailability

Volatilization of NH_3 from fertilizer and manure can be substantial, easily >25% of the N content of several fertilizer and manure sources (Lauer et al., 1976; Fillery et al., 1984). Direct loss of anhydrous ammonia and aqua ammonia fertilizers can occur through improper soil application (Parr and Papendick, 1966) or application in irrigation water (Gardner and Roth, 1984). Ammonia losses can also occur from fertilizers that do not initially contain NH_3 if they are left on or near the soil surface and conditions are suitable for conversion of NH_4^+ to NH_3. pH and temperature are the two primary factors affecting NH_3 loss. Increasing pH increases NH_3 volatilization because it increases the proportion of ammoniacal-N in the NH_3 form (du Plessis and Kroontje, 1964).

$$NH_4^+ + OH^- \leftrightharpoons NH_3 + H_2O \tag{11.1}$$

Increasing temperature increases the driving force for NH_3 volatilization by decreasing the pK_a for the equilibrium (Koelliker and Kissel, 1988). Wind also increases NH_3 loss (Fillery et al., 1984), as long as it does not impede urea hydrolysis by drying the reaction site.

11.1.5.5.1 Ammonia Volatilization from Fertilizers

Ammonium sulfate or $(NH_4)_2HPO_4$ application to calcareous soils can result in substantial NH_3 loss (Fenn and Kissel, 1973). However, when applied to lower pH soils most NH_4^+-containing fertilizers result in little NH_3 volatilization (Volk, 1959). In contrast, NH_3 volatilization is likely with urea-containing fertilizers in many situations because urea hydrolysis increases pH (Overrein and Moe, 1967) as NH_4^+ is formed.

$$CO(NH_2)_2 + H^+ + 2H_2O \rightarrow 2NH_4^+ + HCO_3^- \tag{11.2}$$

Low buffer capacity soils result in greater NH_3 volatilization due to greater increases in pH and lower retention of exchangeable NH_4^+ (Ferguson et al., 1984).

Ammonia volatilization losses from urea are higher when applied to crop residues (e.g., no-tillage cropping systems), pasture, or turfgrass in comparison to the soil surface, partly because residues and plant tissues have high urease activity (Torello and Wehner, 1983; Dick, 1984), resulting in rapid urea hydrolysis and substantial pH changes on low buffered materials (McInnes et al., 1986). Increased temperature promoted urea hydrolysis (Broadbent et al., 1958; Fisher and Parks, 1958) as well and also increased the proportion of ammoniacal-N in the NH_3 form (Koelliker and Kissel, 1988). Moisture is required for urea hydrolysis to occur (Ernst and Massey, 1960), but losses are enhanced as drying concentrates the NH_4^+ (Hargrove et al., 1977; McInnes et al., 1986). Rainfall of 28 and 33 mm incorporated urea into the soil and halted NH_3 volatilization, whereas irrigation of 2.5 mm increased loss (McInnes et al., 1986). Irrigation or rainfall amount must be sufficient to incorporate the N into the soil so as not to enhance losses (Kissel et al., 2004).

Fertilizer application method and form can affect NH_3 volatilization. Surface application of urea-containing fertilizers greatly enhanced NH_3 volatilization as determined by crop response (Mengel et al., 1982; Touchton and Hargrove, 1982; Fox and Piekielek, 1987). Hargrove (1988) suggested that a depth of 5–10 cm would prevent NH_3 loss from urea on most soils. Banding urea versus a broadcast application generally reduces NH_3 losses as well. Including a urease inhibitor (Schlegel et al., 1986), coating (Matocha, 1976), or encapsulating urea (Knight et al., 2007) also reduce NH_3 volatilization.

11.1.5.5.2 Ammonia Volatilization from Manures

Nitrogen applied to surface-applied manures is subject to NH_3 volatilization losses because potentially volatile N compounds are a significant percentage of the total N content. Urea comprised nearly 70% of the N in urine from ruminants (Bristow et al., 1992). Approximately 30%–50% of the total N content of various poultry manures was uric acid- and urea-N (Nicholson et al., 1996; Fujiwara and Murakami, 2007). Manure pH, which fosters NH_3 and enhances volatilization, may exceed 8.0 (Nicholson et al., 1996), greatly reducing N availability from poultry manures. Nearly 100% of the initial NH_4^+-N content of a poultry litter was lost by NH_3 volatilization in ≈8 days after application in summer when conditions were hot, dry, and windy (Sharpe et al., 2004). However, NH_3 loss in winter was only 10% of the NH_4^+-N content. Rainfall shortly after manure application to the soil surface reduces NH_3 volatilization by transporting volatile N forms into the soil (Cabrera and Vervoort, 1998; Sharpe et al., 2004). Ammonia loss from surface-applied cattle slurry, which was not incorporated, exceeded 40% of the initial NH_4^+-N content, but immediate incorporation with disk harrow, chisel plow, or moldboard plow substantially reduced loss to 5%, 9%, and 1%, respectively (Thompson and Meisinger, 2002). Peak NH_3 loss occurs soon after application (Marshall et al., 1998), so rainfall must also occur soon after application to be effective in reducing NH_3 volatilization.

11.1.5.5.3 Ammonia Volatilization from Plant Tissues

Ammonia volatilization directly from plant tissues can be substantial. Harper et al. (1987) estimated that 21% of the 73 kg ha^{-1}

fertilizer N applied in the spring of the year in Georgia was volatilized from wheat tissue. Direct volatilization of NH_3 from maize tissues in Nebraska was equivalent to 10%–20% of the fertilizer N applied, and apparent total N losses from aboveground plant tissues ranged from 45 to 81 kg N ha^{-1} (Francis et al., 1993). This loss was equivalent to 50%–75% of the unaccounted-for N in ^{15}N balance calculations. Although the results of these studies suggest NH_3 volatilization from plant tissue is substantial, rarely is this loss mechanism considered or quantified in N studies.

11.1.6 Ammonium in the Interlayer of 2:1 Clay Minerals

Ammonium ions occur in the interlayer of 2:1 clay minerals, particularly vermiculite and degraded illite (Nommik and Vahtras, 1982). Often, this phenomenon is referred to as "fixation," implying zero bioavailability. In reality, however, interlayer NH_4^+ exchanges with the soil solution to some degree and is, therefore, available for plant uptake. Fixation of nearly 10 mg kg NH_4^+-N (10% of that added as $(NH_4)_2SO_4$) occurred in less than 1 day in two vermiculitic soils (Broadbent, 1965). Green et al. (1994) found up to 23% of the N applied in urea was fixed as NH_4^+ after 20 days of anaerobic incubation. However, nearly half the fixed NH_4^+ was released during nitrification after 15 days of aerobic incubation (Green et al., 1994). Plant (Li et al., 1990) and microbial (Kelley and Stevenson, 1987) utilization of solution NH_4^+ also resulted in the release of fixed NH_4^+.

11.1.7 Predicting Nitrogen Bioavailability

Blackmer (1999) outlined many indices of N bioavailability; including Mitscherlich "b" and "c" values, Fried and Dean "A" values, Dean "a" values, and several biological and chemical tests for estimating N mineralization. Sims (Chapter 13) overviewed several inorganic N bioavailability tests including the residual inorganic N, preplant soil profile nitrate (PPNT), and the presidedress soil nitrate (PSNT) tests. The recently developed Illinois soil nitrogen test (ISNT), a purported indicator of mineralizable N, was also discussed by Sims. Girma and Raun (Chapter 15) discussed the use of optical sensors to make in-season estimates of N bioavailability by assessing crop canopy size and greenness. Tissue testing and hand-held chlorophyll meters were the precursors to optical sensors (Schepers et al., 1992) and achieved much the same goal. *Adapt-N* is a promising web-based tool used to make N recommendations for maize in New York that dynamically simulates the impact of weather on N transformations and transport to estimate crop N accumulation and predict N need (Melkonian et al., 2008). Given the complexity of the N cycle, the importance of temperature and moisture in affecting N bioavailability, and the economic and environmental costs of errors in N management, it is no wonder a sophisticated tool such as *Adapt-N* is needed to predict N bioavailability and improve N management.

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11.2 Phosphorus Availability

Andrew Sharpley

11.2.1 Introduction

Phosphorus (P) is an essential nutrient for plant growth. The low concentration (100–3000 mg P kg^{-1}) and solubility (0.01–0.10 mg P L^{-1}) of P in soils, however, make it a critical nutrient limiting plant growth. In natural ecosystems, P availability in soil is controlled by the sorption, desorption, and precipitation of P released during weathering and dissolution of rocks and minerals of low solubility. Thus, soil P availability is generally inadequate for crop needs in production agriculture. To meet these needs, P is added as fertilizers or animal manures to buildup or maintain soil P availability at predetermined optimum levels. In this section, P availability is defined as that P in soil or water that is available by desorption and dissolution processes for uptake by plants in terrestrial and aquatic ecosystems.

The components, forms, availability, and cycling of P in soil are conceptualized in Figure 11.1. Complex and interrelated processes determine the amounts and availability of several inorganic and organic forms of P in soil. This section will describe these processes occurring in the soil, how they are affected by agricultural management, how we attempt to optimize soil P availability for crop production, and how this can affect water quality.

11.2.2 Forms and Amounts in Soil

Soil P exists in inorganic (P_i) and organic (P_o) forms (Figure 11.1). Inorganic P forms are dominated by hydrous sesquioxides,

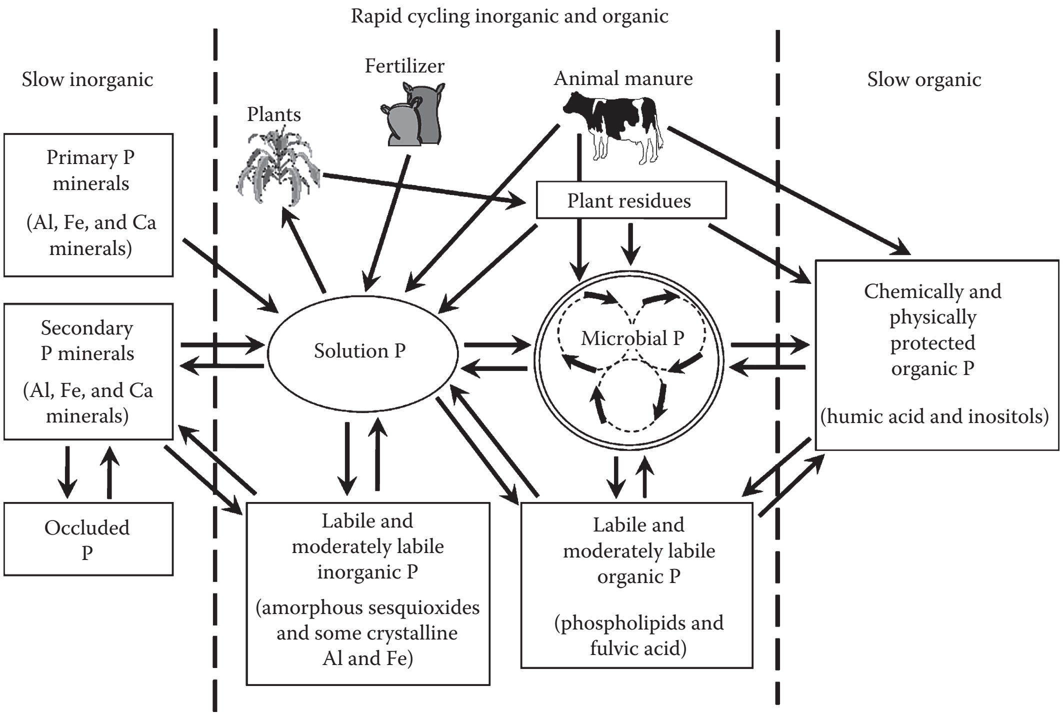

FIGURE 11.1 The soil P cycle: its components, forms, and flows. (Adapted from Stewart, J.W.B., and A.N. Sharpley. 1987. Controls on dynamics of soil and fertilizer phosphorus and sulfur, p. 101–121. *In* R.F. Follett, J.W.B. Stewart, and C.V. Cole (eds.) Soil fertility and organic matter as critical components of production systems. Soil Science Society of America Special Publication No. 19. ASA, CSSA, SSSA, Madison, WI.)

amorphous, and crystalline Al and Fe compounds in acidic, noncalcareous soils, and by Ca compounds in alkaline, calcareous soils (Figure 11.1 and Table 11.1). Organic P forms include relatively labile phospholipids and fulvic acids; more resistant forms comprise inositols and humic acids (Figure 11.1). Forms generalized in Figure 11.1 are not discrete entities, as intergrades and dynamic transformations between forms occur continuously to maintain equilibrium conditions. These approximated forms of P are assigned based on the extent to which sequential extractants of increasing acidity or alkalinity can dissolve soil P (Hedley et al., 1982; Tiessen and Moir, 2007; Zhang and Kovar, 2008).

TABLE 11.1 Average Amounts of Inorganic P (P_i) and Organic P (P_o) in the A1 Horizon of Virgin Calcareous, Slightly Weathered, and Highly Weathered Soils

P Form	Calcareous ($n = 41$)	Slightly Weathered ($n = 40$)	Highly Weathered ($n = 39$)
		(mg kg^{-1})	
Bioavailable P_i[a]	11	21	22
Amorphous Al and Fe-P_i	37	74	109
Ca-P_i	285	85	16
Labile P_o	8	18	34
Protected P_o	28	60	78
Residual P[a]	152	254	179
Total P	521	512	438

Source: Adapted from Sharpley, A.N., H. Tiessen, and C.V. Cole. 1987. Soil phosphorus forms extracted by soil tests as a function of pedogenesis. Soil Sci. Soc. Am. J. 51:362–365.

[a] Bioavailable P_i is resin P_i and residual P is chemically resistant, mineral, and occluded P_i and P_o as designated on Figure 11.1.

In most soils, the P content of surface horizons is greater than subsoil, due to the sorption of added P and greater biological activity and accumulation of organic material in surface layers. However, soil P content varies with parent material, extent of pedogenesis, soil texture, and management factors, such as rate and type of P applied and soil cultivation. These factors also influence the relative amounts of P_i and P_o. In most soils, 50%–75% is P_i, although this fraction can vary from 10% to 90% (Table 11.1). Generally, Ca-P_i decreases with weathering, whereas amorphous Al and Fe-P_i and P_o forms tend to increase, due in part to changes in soil clay fraction from basic primary minerals to Al- and Fe-dominated oxides (Table 11.1).

Phosphorus additions are usually needed to maintain adequate available soil P for plant uptake. The level of these additions varies with both soil and plant type (Pierzynski and Logan, 1993). Once applied, P is either taken up by the crop, becomes weakly (physical) or strongly (chemical) adsorbed onto Al, Fe, and Ca surfaces, or incorporated into organic P (McLaughlin et al., 1988; Ottabong et al., 1997; Zhang and MacKenzie, 1997) (Figure 11.2). As P_i generally supplies most of the P taken up by crops in productive agricultural soils, more attention has been focused on the availability of P_i rather than P_o, following P additions.

Overall, soil pH is the main property controlling the nature of P_i forms, although Al, Fe, Mn, and Ca content determine the

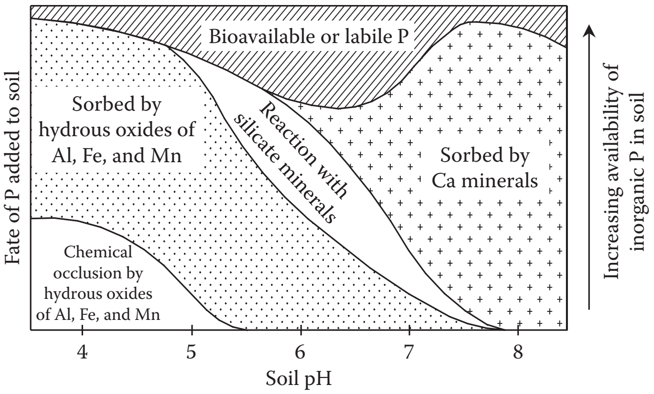

FIGURE 11.2 Approximate representation of the fate of P added to soil by sorption and occlusion in inorganic forms, as a function of soil pH. (Adapted from Buckman, H.O., and N.C. Brady. 1970. The nature and properties of soils. The Macmillan Publishing Co., Collier-Macmillan Limited, London, U.K.)

amounts of these forms (Figure 11.2). In acid soils, amorphous and hydrous oxides of Al, Fe, and Mn dominate P sorption processes, while Ca compounds dominate P sorption and precipitation reactions in alkaline soils. As a result, P availability is greatest at soil pH between 6 and 7 (Figure 11.2). Immobilization of P_i by these processes renders a portion of the added P unavailable for plant uptake (Figure 11.3). Mehlich-3 soil P decreased with time after application of P to a Kingsbury clay (*Aeric Ochraqualfs*; pH of 5.7) and Hagerstown silt loam (*Typic Hapludalfs*; pH of 6.8) incubated at room temperature (25°C) and field moisture (about 30% water). At the same time, P_i becomes more tightly bound with Al and Fe complexes (Figure 11.3). This simple soil-P incubation illustrates why the removal of P_i from soil by crops is generally low. For the United States, an average 29% of P added in fertilizer and manures is removed by harvested crops, ranging from <1% in Hawaii to 71% in Wyoming (National Research Council, 1993). The low recovery reflects the predominance of high P fixing soils in Hawaii.

Even though P_i has generally been considered the major source of plant-available P in soils, the mineralization of labile P_o has also been shown to be important in both low-fertility and high-fertility soils (Stewart and Tiessen, 1987; Oehl et al., 2001; Chen et al., 2002; Condron et al., 2005). Amounts of P_o mineralized in temperate dryland soils range from 5 to 20 kg P ha^{-1} $year^{-1}$ (Stewart and Sharpley, 1987). Mineralization of soil P_o tends to be higher in the tropics (67 to 157 kg P ha^{-1} $year^{-1}$), where distinct wet and dry seasons and higher soil temperatures enhance microbial activity. In contrast, P_o compounds may also become resistant to hydrolysis by phosphatase through complexation with Al and Fe (Tate, 1984).

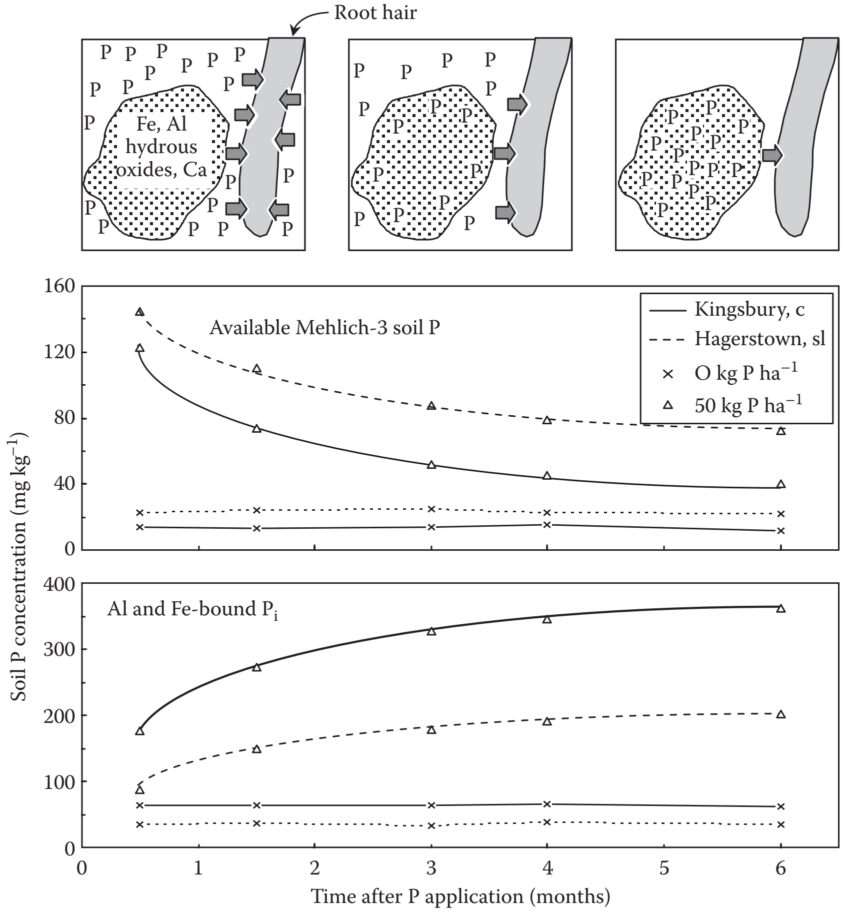

FIGURE 11.3 The change available (Mehlich-3 P) and adsorbed soil P (Al- and Fe-bound) with time after application of P.

11.2.3 Principles of Analysis

The various forms and amounts of P_i and P_o in soil can be estimated by extraction with acids and alkalies that dissolve specific complexes binding P. The most common methods and their background are given by Olsen and Sommers (1982), Turner et al. (2005), Tiessen and Moir (2007), Kovar and Pierzynski (2008). A wide range in methods and principles exists for effective recovery of P based on soil type, environment, and level of detail required. This is particularly true for available soil P_i estimation, which has traditionally been based on acid dissolution (acetic, citric, hydrochloric, lactic, nitric, and sulfuric), anion exchange (acetate, bicarbonate, citrate, lactate, and sulfate), cation complexation (citrate, fluoride, and lactate), or cation hydrolysis (buffered bicarbonate). Several excellent reviews of these methods are available for further reading (Kamprath and Watson, 1980; Fixen and Grove, 1990). In the United States, the most common soil P tests have been Mehlich-1 (Mehlich, 1953), Bray-1 (Bray and Kurtz, 1945), and Olsen P (Olsen et al., 1954); however, most laboratories have converted to the multielement Mehlich-3 (Mehlich, 1984) or AB-DTPA (Soltanpour and Schwab, 1977) extractants, in the past decade (Carter and Gregorich, 2007; Sims, 2008).

It is unlikely that an extractant would exclusively measure a single pool of soil P_i, although some components of extractants are aimed at specific pools. For example, F in the Bray-1 extractant exchanges with Al-bound P_i, with the assumption that this Al-bound P_i contributes to available P in acid soils, while the inclusion of EDTA in Mehlich-3 means this extractant estimates P associated with Fe and Al amorphous complexes. The success of any extractant to estimate available P depends on the appropriateness of the chemical used relative to dominant soil properties controlling P reactivity. Alternative methods utilize P-sinks, such as anion-exchange resins (AER), ion-exchange membranes, and Fe-oxide impregnated paper, to determine the quantity of soil P available to plants with negligible chemical extraction (Sharpley et al., 1994). These methods more closely mimic rhizosphere conditions and often provide comparable or better correlations with crop response than chemical extractants (Table 11.2).

11.2.3.1 Anion-Exchange Resins

AER are the most common P-sink method for assessing available soil P_i. The procedure typically involves the use of chloride saturated resin at a 1:1 resin-to-soil ratio in 10–100 mL of water or weak electrolyte for 16–24 h (Amer et al., 1955; Olsen and Sommers, 1982). To prevent the diffusion of P from the soil to the resin from being the rate-limiting step, resins should be intimately mixed with the soil, which creates difficulties in separating resin from soil for P analysis. Soil can be ground to a smaller size than the resin, but this probably changes soil P release characteristics. Resin and soil may also be separated by enclosing the resin in a mesh bag, which may limit resin–soil contact or float resin from soil in a sucrose solution (Thien and Myers, 1991). Skogley et al. (1990) encapsulated a mixture of anion- and cation-exchange resins in a mesh sphere. Greenhouse studies indicated that the correlation between P uptake by sorghum-sudangrass and resin-sphere results were as good or better than those with the Olsen P soil test (Table 11.2).

11.2.3.2 Ion-Exchange Membranes

A similar approach using ion-exchange resin impregnated membranes has been investigated by several researchers (Abrams and Jarrell, 1992; Qian et al., 1992; Saggar et al., 1992). Impregnation of the resin onto a plastic membrane facilitates separation of the resin beads from the soil and may eliminate the soil grinding step. Also, an extraction time as short as 15 min can be used, without reducing the accuracy of predicted P availability for a wide range of soils (Qian et al., 1992). In pot studies, the resin membranes have provided a better index of P availability than conventional chemical extraction methods for canola and ryegrass (Table 11.2).

11.2.3.3 Iron-Oxide Impregnated Paper

Another P sink that has received attention is Fe-oxide impregnated filter paper (Fe–O strip), which has successfully estimated available P_i in a wide range of soils and management systems (Menon et al., 1989b, 1990; Sharpley, 1991; Chardon, 2008) (Table 11.2).

Wide-spread adoption of P-sink methods for routine soil testing has not yet occurred in the United States, although parts of Brazil have used the method for the last decade (van Raij et al., 1986). As the P-sink methods operate with limited chemical extraction, they are more suited to a wide range of soils, irrespective of management history (Yang et al., 1991; Qian et al., 1992; Somasiri and Edwards, 1992; Myers et al., 2005). Where fertilizer history is unknown and frequent changes in fertilizer type, including rock phosphate, may have been made, it is difficult to choose the appropriate soil test. For example, Olsen P can underestimate and Bray-1 P overestimate P availability in soils amended with rock P, while P-sink methods have provided accurate estimates when KCl rather than $CaCl_2$ is used as the support medium (van Raij et al., 1986; Menon et al., 1989a; Saggar et al., 1992). Even so, detailed field calibration and improvement in standardized methodology will be essential before any of the P-sink approaches can be used routinely to estimate available soil P and make reliable fertilizer recommendations.

Phosphorus isotopes P^{32} and P^{33} have also been widely used to characterize soil P availability. Using laboratory incubation, greenhouse pot, and limited field plot studies, valuable insights have been gained into soil P availability in terms of exchange kinetics, plant-available forms, and the rate, extent, and direction of P cycling in soils. Readers are directed to excellent reviews by Fardeau et al. (1996), Di et al. (1997), and Frossard and Sinaj (1997) for more information.

11.2.4 Cycling in Soil

Dynamic processes involved in P cycling are chemical and biological (Figure 11.1). Chemical processes include precipitation–dissolution and sorption–desorption. Biological processes involve immobilization–mineralization initiated by P uptake

TABLE 11.2 Relationship between Crop Uptake of P and Bioavailable Soil P Determined by P Sink and Chemical Extraction

Crop	Location	Number of Soils	Soil P Test	Correlation Coefficient	Reference
Canola	Saskatchewan	135	IEM	0.92	Qian et al. (1992)
			Olsen	0.87	
Cotton	Brazil	28	AER	0.85	van Raij et al. (1986)
			0.02 M H_2SO_4	0.68	
Maize	Alabama, USA	32	Fe–O strip	0.87	Menon et al. (1989b)
			AER	0.62	
			Olsen	0.81	
			Bray 1	0.74	
Maize[a]	Australia	2	Fe–O strip	0.91	Kumar et al. (1992)
			IEM	0.91	
			Bray 1	0.87	
Maize	Egypt	10	Fe–O strip	0.90	Monem and Gadalla (1992)
			Olsen	0.91	
Maize	Uganda	2	Fe–O strip	0.85	Butewaga et al. (1996)
			Bray 1	0.77	
			Mehlich 1	0.64	
Rice	Brazil	8	AER	0.98	van Raij et al. (1986)
			AB-DTPA	0.41	
Ryegrass[a]	New Zealand	56	IEM	0.92	Saggar et al. (1992)
			Olsen	0.87	
Ryegrass	Finland	32	Fe–O Strip	0.93	Yli-Halla (1990)
			Olsen	0.87	
Sudangrass	Colorado, USA	23	AER	0.92	Bowman et al. (1978)
Sorghum/barley			Olsen	0.88	
WheatI	Australia	2	Fe–O strip	0.96	Kumar et al. (1992)
			IEM	0.97	
			Bray 1	0.98	
Wheat	China	39	Fe–O Strip	0.84	Lin et al. (1991)
			AER	0.83	
			Olsen	0.83	
			Bray 1	0.56	

Note: AEM, anion–exchange membrane; IEM, ion–exchange resin; AB-DTPA, ammonium bicarbonate diethylene triamine pentaacetic acid; PST, resin phytoavailability soil test.

[a] Relationship between relative crop yield and soil P test.

and decay of plants. Also, soil faunal and floral activities often modify the direction, extent, and rate at which these chemical and biological processes occur.

11.2.4.1 Chemical Processes

Precipitation–dissolution processes differ from sorption–desorption in that the solubility product of the least soluble P compound in the solid phase controls dissolution and, thus solution P concentration, whereas solution P controls the amount of P sorbed (Syers and Curtin, 1989). In reality, retention of P by soil material is a continuum between precipitation and surface reactions.

11.2.4.1.1 Precipitation–Dissolution

In general, Ca controls these reactions in neutral or calcareous environments, while Al and Fe are the dominant controlling cations in acidic environments. Apatite is the most common primary P mineral ($Ca_{10}\,(PO_4)_6\,X_2$, where X is F or OH). Apatite dissolution requires a source of H^+ from soil or biological activity and a sink for Ca and P (Mackay et al., 1986; Smillie et al., 1987):

$$Ca_{10}(PO_4)_2X_2 + 12H^+ = 10Ca^{2+} + 6H_2PO_4^- + 2X^- \qquad (11.3)$$

and occurs during soil development due to weathering (Walker and Syers, 1976). Even though the rate of apatite weathering or dissolution will vary with rainfall and temperature, it is still difficult to predict this first step in the P cycle (Pierzynski, 1991; Pierzynski et al., 2005).

Precipitates in Ca systems occur in the following sequence; monocalcium phosphate [$Ca\ (H_2PO_4)_2$], dicalcium phosphate dihydrate ($Ca\ HPO_4\ 2H_2O$), octacalcium phosphate

[$Ca_8H_2(PO_4)_6 \cdot 5H_2O$], and finally hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] or fluorapatite [$Ca_{10}(PO_4)_6F_2$], which have low solubilities and should, thus, control soil solution P concentration (Lindsay et al., 1989; Syers and Curtin, 1989).

In Al- and Fe-dominated soils, few well-crystallized precipitates have been observed. Generally, P reacts with Al oxides to form amorphous Al P or organized phases such as sterretite [$Al(OH_2)_3$ HPO_4 H_2PO_4] and with Fe oxides to such precipitates as tinticite [Fe_6 $(PO_4)_4$ $(OH)_6 \cdot 7H_2O$) or griphite [Fe_3 Mn_2 $(PO_4)_2 \cdot 5(OH)_2$] (Hsu, 1982; Lindsay et al., 1989). Many other amorphous mixed Al–Fe–Si–P compounds have been observed in soils with high P concentrations from phosphatic parent material or large fertilizer or manure applications (Lindsay et al., 1989; Pierzynski et al., 1990b).

11.2.4.1.2 Sorption/Desorption

In most soils, sorption–desorption processes describe P uptake and release by soils that control P availability better than precipitation–dissolution reactions. In this section, the term "sorption" covers surface "adsorption" and subsequent penetration of P into the retaining component or "absorption." Sorption curves or isotherms have been used extensively to describe the relationship between the amount of P sorbed and that remaining in solution (Figure 11.4). For a given solution P concentration, there is a large difference in the amount of P sorbed by the three soil types given as examples. In general, clay content approximates the reactive surface area of a soil responsible for P sorption (Syers et al., 1971; Juo and Fox, 1977; Sharpley et al., 1984a; Hedley et al., 1995). This surface reactivity is a function of the amount and type of hydrous oxides of Al and Fe and reactive Ca components present, other ions (Ca- or Na-dominated), pH of the system, and reaction kinetics.

Even in calcareous soils, hydrous ferric oxides can influence P sorption reactions (Holford and Mattingly, 1975a, 1975b). The types of bonding associated with hydrous oxides and pH dependency have been described in detail by Sample et al. (1980), Uehara and Gillman (1981), and White (1980) (Figure 11.5). Ligand exchange of P at hydrous OH and Fe oxide surfaces results in the formation of monodentate, bidentate, or binuclear complexes (Figure 11.5). As soil solution pH increases, P sorption is decreased by the greater negative charge at the oxide surface and reduced polarization of the Al or Fe–O bond (Figure 11.5).

Soil P sorption has been characterized by parameters calculated from the Langmuir equation:

$$S = \frac{(k S_{\max} C)}{1 + kC} \qquad (11.4)$$

where

S is sorbed P
C is solution P concentration
$S_{\max}$ is the maximum amount of P that can be sorbed
k is an "affinity" constant describing binding energy

Phosphorus sorption maximum is calculated as the reciprocal of the slope of the plot C/S and C and binding energy as the slope/intercept of the same plot (Olsen and Watanabe, 1957; Syers et al., 1973; Graetz and Nair, 2008) (Table 11.3). Equilibrium P concentration is the solution P concentration at which no net sorption or desorption occurs (Figure 11.4 and Table 11.3). These parameters have been widely used to quantify the extent of specific soil reactions and effects of soil types, counter ion and background electrolyte, P source, and soil management on P sorption (Goldberg and Sposito, 1985; Fixen and Grove, 1990). However, the theoretical assumptions of the Langmuir equation were questioned (White, 1980; Barrow, 1989), as sorbed P carries charges that decrease the surface charge and potential of the sorbing surface, leading to large errors in the estimates of $S_{\max}$ (Kuo, 1988). The Freundlich equation often fits data better than the Langmuir equation but does not estimate $S_{\max}$ (Barrow, 1978).

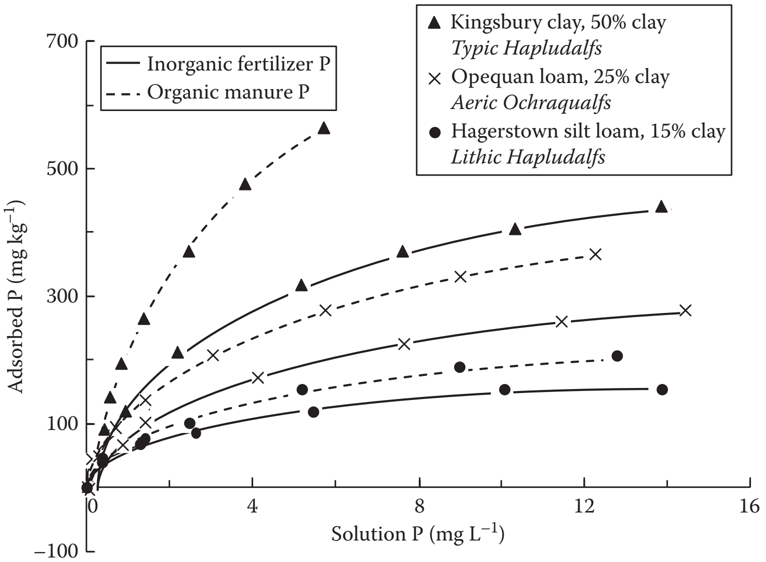

FIGURE 11.4 Phosphorus sorption isotherms as a function of the type of soil and P source.

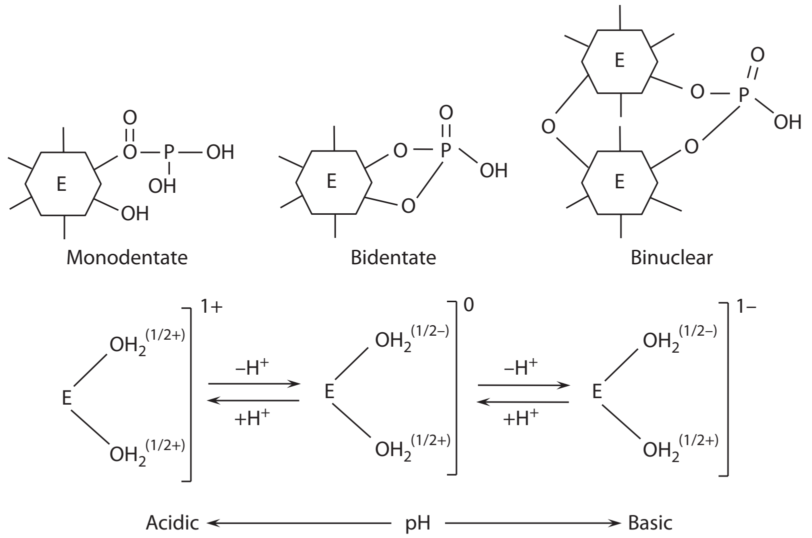

FIGURE 11.5 Types of P bonding associated with hydrous oxides where E is AL or Fe. (Adapted from Fixen, P.E., and J.H. Grove. 1990. Testing soils for phosphorus, p. 141–180. *In* R.L. Westerman (ed.) Soil testing and plant analysis. 3rd edn. SSSA Book Series No. 3. SSSA, Madison, WI.)

TABLE 11.3 Soil P Sorption Properties Calculated from the Langmuir Isotherm as a Function of Soil Type and Source of Added P (Triple Superphosphate and Dairy Manure)

	P Sorption Maxima		Binding Energy		Equilibrium P Concentration	
	Fertilizer	Manure	Fertilizer	Manure	Fertilizer	Manure
Soil Type	(mg kg^{-1})		(L mg^{-1})		(mg L^{-1})	
Hagerstown, sl *Typic Hapludalfs*	172	245	2.17	2.78	0.019	0.044
Kingsbury, c *Aeric Ochraqualfs*	476	909	2.24	3.82	0.069	0.113
Opequon, l *Lithic Hapludalfs*	303	455	1.97	3.09	0.034	0.114

Note: sl, sandy loam; c, clay; l, loam.

Organic anions can compete with P for similar sorption sites on soil surfaces (Yuan, 1980; Hue, 1991; Ohno and Crannell, 1996). However, P sorption can be increased when the addition of organic compounds to amorphous oxides in soil impedes their crystallization and increases specific surfaces (Table 11.3). Also, humic compounds can complex with Fe, Al, and to a lesser extent Ca and sorb P (Levesque and Schnitzer, 1967; Inskeep and Silvertooth, 1988; Frossard et al., 1995).

The release of sorbed P into solution or desorption is not completely reversible. Thus, desorption curves are displaced to the left of the sorption curves. This hysteresis effect is the result of precipitation (Veith and Sposito, 1977), occlusion (Uehara and Gillman, 1981), solid-state diffusion (Barrow, 1983), and bidentate or binuclear bonding with the colloid surface (Hingston et al., 1974).

Several studies have reported that desorption of soil P during a short period of time is a low-activation energy process (Sharpley et al., 1981). The work of Kuo and Lotse (1974) and Evans and Jurinak (1976) reported that the activation energy for P desorption was between 2 and 3 kcal mol^{-1}. The low-activation energies led these researchers to suggest that the desorption of soil P during short reaction times may be limited more by the diffusion of the desorbed P through the stagnant water films present around the soil particles and within the soil aggregates than by the chemical reaction. Although higher-activation energies (20 kcal mol^{-1}) were reported by Barrow and Shaw (1975), they were determined for a longer reaction period (up to 100 days) and represent the transfer of P between desorbable and fixed forms. It has been suggested that there is a continuous range of activation energies for soil P desorption (Posner and Bowden, 1980). During the initial stages of desorption, P held at low-activation energies is desorbed; during the later stages, P held at higher-activation energies is desorbed.

More detailed analysis and review of these chemical processes controlling soil P availability are given by Barrow (1985), Lindsay et al. (1989), Syers and Curtin (1989), Fixen and Grove (1990), Frossard et al. (1995), Condron et al. (2005), and Pierzynski et al. (2005).

11.2.4.2 Biological Processes

Uptake of soluble P by bacteria and fungi, stimulated by the addition of microbial substrates such as litter and crop residues, and release of P as the result of cell lysis or predation (Coleman et al., 1983; Tiessen et al., 1984; Frossard et al., 2000; Jakobsen et al., 2005) are represented in Figure 11.1 as a revolving wheel. This is done deliberately to emphasize the central role of the microbial population in P cycling and availability. For example, if the wheel is stopped or slowed down by lack of C inputs, the supply of P to plants will be limited to the quantity of labile P_i. If the wheel is operating, then solution P is constantly being replenished from labile P_i and P_o forms. Generally, microbial biomass P ranges from 5 to 100 mg kg^{-1} (Srivastava and Singh, 1991; Joergensen et al., 1995; Oberson et al., 1997). As a result, large amounts of P can turnover through microbial biomass annually (He et al., 1997; Oehl et al., 2001; Jakobsen et al., 2005). For example, in a study of P cycling through soil microbial biomass in England, Brookes et al. (1984) measured annual P fluxes of 5 and 23 kg P ha^{-1} $year^{-1}$ in soils under continuous wheat and permanent grass, respectively. Although biomass P flux under continuous wheat was less than P uptake by the crop (20 kg P ha^{-1} $year^{-1}$), annual P flux in the grassland soils was greater than P uptake by the grass (12 kg P ha^{-1} $year^{-1}$).

Within the microbial cell, P exists as a wide variety of compounds, principally RNA (30%–50%), acid soluble P_i and P_o (15%–20%), phospholipids (<10%), and DNA (5%–10%) (Stewart and McKercher, 1982; Condron et al., 2005). If the microbial cell is ruptured or lysed, all these compounds will be released to the soil solution to react with both inorganic and organic soil components to form a host of P_i and P_o compounds of differing solubility or susceptibility to mineralization. The rate of mineralization of P_o forms depends largely on phosphatase activity, which, in turn, can be controlled by solution P concentration (McGill and Cole, 1981; Chen et al., 2002). Stable P_o accumulates in both chemically resistant and aggregate protected forms (Marshall, 1971; Tisdale and Oades, 1982; Condron et al., 2005).

Chemically or physically protected P_o may be slowly mineralized as a by-product of the mineralization of overall soil organic matter or by specific enzyme action in response to the need for P. Therefore, organic matter turnover, as well as solution P_i concentration and the demand for P by microbial and plant components, will be factors controlling the lability of P_o (Richardson, 2000; Turner et al., 2002; Condron et al., 2005). A continuous drain on soil P pools by cultivation and crop removal will rapidly deplete labile P_i and P_o forms and, thereby, reduce available soil P (Hedley et al., 1982; Sharpley and Smith, 1985; Tiessen et al., 1992).

11.2.4.3 Fauna and Flora Processes

The effects of soil fauna (e.g., earthworms and termites) and flora (actinomycetes, bacteria, and fungi) on soil physical, chemical, and biological processes have been extensively studied and reviewed (Reichle, 1977; Lee, 1985; Edwards, 2004). This section outlines the role of the more important of these, earthworms and mycorrhizae, in soil P cycling and their impact on soil P availability.

11.2.4.3.1 Earthworms

Under favorable soil temperature and moisture conditions, earthworms have been found annually to consume 100% of the litter of an evergreen oak forest in Japan (8 Mg ha^{-1} $year^{-1}$ by *A. pheretima*; Sugi and Tanaka, 1978) and mixed deciduous forest in England (3 Mg ha^{-1} $year^{-1}$ by *Lumbricus terrestris*; Satchell, 1967); about 30% of the litter decomposed each year in grass savanna (Lavelle, 1978) and 100% of added cattle manure (17–30 Mg ha^{-1} $year^{-1}$, Guild, 1955). During this consumption, earthworms commonly ingest 100–500 Mg soil ha^{-1} $year^{-1}$ (equivalent to 0.5–3.0 cm of top soil) (Russell, 1973). Consequently, earthworms can have a major influence on soil physical, chemical, and biological properties through incorporation and assimilation of plant litter and associated ingestion of soil material (Lee, 1985; Lavelle, 1988). Egestion as surface and subsurface cast material can rapidly redistribute P in a soil profile, increasing the availability and potential for uptake. Also, earthworm burrowing can allow a greater soil volume to be exploited by plant roots and decrease susceptibility of plants to water stress. Earthworm burrows open to the soil surface increase infiltration rates, enhancing nutrient movement into the profile via macropore flow (Sharpley et al., 1979; Germann et al., 1984; Edwards et al., 1989; Shuster et al., 2003; Dominguez et al., 2004).

The main source of P affected by earthworms is soil organic matter, which includes plant litter in various stages of decomposition, roots, and organic matter in the soil with its complement of microflora and fauna. Ingestion, maceration, and intimate mixing of organic matter with soil increase the rate of humification and mineralization. Although most organic matter undergoes little chemical change during passage through the earthworms' gut, it is finely ground with the increased surface area exposed to microbial activity, facilitating further decomposition. The 5- to 10-fold increase in P content and availability in earthworm casts results from enhanced mineralization of organic P, enrichment of clay-sized particles in casts, and a reduction in P sorption capacity of soil by organic matter blockage (Sharpley and Syers, 1977; Sharpley et al., 1992). Thus, most of the additional P present in casts is held in more physically sorbed than chemisorbed forms, which are readily available to plants.

Both microbial population and activity are increased during passage through the earthworms' gut as a function of the organic matter content of the initial food source (Tiwari, 1979; Gorbenko et al., 1986; Scheu, 1987). Parle (1963) observed that the numbers of bacteria and actinomycetes increased 1000-fold during passage through the gut, and oxygen consumption remained higher in earthworm casts than in soil for 50 days, indicating an increased microbial activity. This enhanced activity is probably responsible for the increased phosphatase activity found in earthworm casts compared to underlying soil (Sharpley and Syers, 1977).

As a result of the incorporation and decomposition of plant material in soil via earthworm activity, soil fertility and productivity can be improved (Lavelle et al., 1989; Edwards et al., 1995; Katsvairo et al., 2002). For instance, Katsvairo et al. (2002) found that earthworm activity contributed to a 15%–40% increase in corn yields in a soybean (*Glycine max* [L.] Merr.)—wheat (*Triticum aestivum* L.)/clover (*Trifolium pretense* L.)—corn (*Zea mays* L.) rotation on a Kendaia—Lima silt loam in Aurora, New York.

Differences in tillage operation and frequency; amount, type, and quantity of residues left on the soil surface; soil type and climate; and application of manures can influence earthworm populations, species composition, and activity (Pankhurst et al., 1995; Edwards and Bohlen, 1996). For example, several studies have reported an increase in the population and activity of earthworms under reduced compared to conventional tillage practices, concomitant with an increase in food or energy supply (Edwards et al., 1989; Trojan and Linden, 1998; Shipitalo et al., 2000).

The application of manure has been shown to encourage the buildup of earthworm populations in cropped soils to a greater extent than in grass, where there tends to be more decaying organic matter (i.e., food) than in cropped soils (Edwards, 1980; Satchell, 1983). For instance, application of dairy manure (50–400 kg P ha^{-1}) to a rape (*Brassica napus* L.)—sugar beet (*Beta vulgaris* L.)—grass rotation increased the numbers of surface feeding *L. terrestris* by directly increasing their food supply and associated microorganisms (Andersen, 1983). Similarly, the application of dairy manure (20 Mg manure ha^{-1} year^{-1} for 14 year) increased earthworm population, diversity, and activity (mainly *Aporrectodea* and *Lumbricus* genus) in a Le Bras clay loam in Quebec (Estevez et al., 1996).

The potential for earthworm activity to incorporate surface applied manures was demonstrated by Chardon et al. (2007). Disappearance of manure patches deposited by grazing cattle, was partially attributed to earthworm activity, with only 15% of dry matter and 22% of total P in manure patches remaining 234 days after deposition on a permanently grassed sandy soil from Heino, the Netherlands (Chardon et al., 2007). While the manure can remain a long-term source of P to soil leachate, the overall risk of P runoff was reduced as the grassland soil could retain most of the P leached from patches.

11.2.4.3.2 Mycorrhizal Associations

Mycorrhizae are widespread under natural conditions, with vesicular-arbuscular mycorrhizae (VAM) most common in agricultural soils (Smith and Read, 1997; Jakobsen et al., 2005). In fact, VAM are formed by approximately two-thirds of all plants species (Fitter and Moyersoen, 1996) and fungi belonging to the recently established phylum Glomeromycota (Schüssler et al., 2001). Three primary mechanisms by which VAM enhances soil P availability are increased physical exploration of the soil, chemical modification of the rhizosphere, and physiological differences between VAM and plant roots (Read, 2002). For example, extensive hyphal growth of VAM reduced the distance for diffusion of P in soil, thereby increasing uptake. This effect is greater when diffusion limits uptake (Gerdemann, 1968; Facelli and Facelli, 2002). Consequently, a greater response to VAM infection has been exhibited in coarse than in fine rooted plant species (Crush, 1973), in high than in low P sorbing soils (Yost and Fox, 1979), and in soils than in solution culture (Howeler et al., 1982). In addition, the generally smaller diameter of VAM hyphae (2–4 μm) compared to root hairs (710 μm) affords a greater absorptive surface area for hyphae and enables entry of hyphae into soil pores and organic matter that cannot be entered by root hairs (Dodd et al., 2000; Drew et al., 2003).

VAM may chemically modify the rhizosphere through exudation of chelating compounds (Jayachandran et al., 1989; Treeby et al., 1989) or phosphatases (Harley, 1989), which could solubilize poorly soluble soil P. It is clear, however, that VAM utilizes the same sources of P as nonmycorrhizal plants (Mosse et al., 1973; Kucey et al., 1989; Blal et al., 1990), but do so more efficiently.

On a unit weight basis, mycorrhizal plants can rapidly absorb larger amounts of P than nonmycorrhizal plants (Bolan et al., 1987). This difference cannot be accounted for by increased surface area of the hyphae alone; it is, therefore, possible that a greater affinity for P in mycorrhizal plants increased absorption rates. It is also possible that the critical or minimum P concentration, below which there is limited net absorption of P, is lower for mycorrhizal than nonmycorrhizal plants because of an increase in physical contact between hyphae and P, thereby reducing P diffusion distance.

For more detailed information on the role of arbuscular mycorrhizae in influencing soil P availability and plant uptake of P, the reader is directed to the excellent review of Jakobsen et al. (2005).

11.2.5 Optimizing Soil Phosphorus Availability

Critical available soil P concentrations are required to maximize crop yields. These soil concentrations can be optimized by P additions, liming, and cultivation. This section discusses how these factors influence soil P availability; the soil testing and recommendation process that quantifies P additions is discussed in the Chapter 14.

11.2.5.1 Critical Concentrations for Plant Production

Estimates of soil P concentrations, above which little or no crop response to P additions is obtained, vary with the extractant used (Kamprath and Watson, 1980). In many neutral to calcareous soils, 10 mg P kg^{-1} Olsen P was adequate for wheat, alfalfa, and cotton (Olsen et al., 1954). For Bray-1 P, the critical level is about 30 mg P kg^{-1} for Midwestern U.S. soils (Thomas and Peaslee, 1973).

Several additional factors influence the availability of soil P. These include temperature, soil compaction, soil moisture, soil aeration, soil pH, type and amount of clay content, and nutrient (including P) status of soil. When soil temperatures are low during early plant growth, P uptake is reduced. Soil compaction reduces pore space, decreasing the amount of water and oxygen, which, in turn, reduces P uptake. The use of liming materials to increase soil pH, and thereby soil P availability, is an old practice, which has been adequately reviewed by several authors (Adams, 1984; Kamprath, 1984; McLean and Brown, 1984). Reducing subsoil acidity has not been highly successful due to physical limitations of mixing lime into subsoils. However, surface applications of gypsum with sufficient time for transport into the subsoil have been shown to increase crop yields, increase subsoil Ca, and decrease exchangeable Al (Sumner et al., 1986; Farina and Channon, 1988). Soils with high clay content tend to fix more P than sandy soils with low clay content. Thus, more P needs to be added to raise the soil test level of clay soils than loam and sandy soils. In addition, the presence of ammonium enhances P uptake by creating an acid environment around the root when ammonium ions are absorbed. High concentrations of ammonium-N in the soil with fertilizer P may interfere with and delay normal P fixation reactions, prolonging the availability of fertilizer P (Murphy, 1988).

11.2.5.2 Phosphorus Additions

Optimizing soil P availability through P additions should consider application rate, timing, type, placement, and residual availability (Singh and Lal, 2005). Because of the immobility of P in most soils, the timing of fertilizer P application is not as critical as its placement. Even so, small amounts of placed starter fertilizer for vegetable crops have successfully reduced the need for much larger broadcast applications of P (Costigan, 1988), and a similar strategy (e.g., foliar applications) may be appropriate for other crops. In efforts to minimize P inputs in sustainable or low-input management systems, there has been renewed interest in the estimation and utilization of residual P availability from fertilizer or manure amendments (Pierzynski et al., 1990a; Yerokum and Christenson, 1990; McCollum, 1991; Linquist et al., 1997; Oberson et al., 1999; Tiessen, 2005).

11.2.5.2.1 Rate

The application of P either as mineral fertilizer or animal manure increases available soil P (Table 11.4). In many areas of intensive crop and livestock operations, the application of P at rates greater than crop removal has increased available soil P content above critical concentrations for crop production (Kellogg et al., 2000; Kleinman et al., 2005; Lanyon, 2005; Sharpley et al., 2005). The increase in available soil P ranged from 5 to 31 mg kg^{-1} for every 100 kg ha^{-1} of fertilizer P added (an average 18% increase; Table 11.4). Barber (1979), Rehm et al. (1984), and McCollum (1991) also observed 13%–28% increases in available P following mineral fertilizer P application. These values are similar to proportional increases following application of beef (7–23 mg kg^{-1}; an average 14%), poultry (14–28 mg kg^{-1}; an average 20%), and swine manure (5–20 mg kg^{-1}; an average 11%) (Table 11.4).

In general, annual applications of manure in crop production systems generally results in crop yields comparable to those obtained with commercial fertilizer, especially when applied based on its N content (Sutton et al., 1982; Lucero et al., 1995; Stevenson et al. 1998; Eghball and Power, 1999; Randall et al., 1999; Schmitt et al., 1999; Macoon et al., 2002). However, long-term N-based applications of manure can result in the accumulation of available soil P to levels greater than optimum for crop production (King et al., 1990; Sharpley et al., 1993, 2004; Sims et al., 1998; Mullins et al., 2005).

11.2.5.2.2 Type

Traditional soluble P fertilizers are ordinary superphosphate, triple superphosphate, ammonium polyphosphate, monoammonium phosphate, and diammonium phosphate (Young et al., 1985). The use of slow release P fertilizers, such as partially acidulated rock P (RP), on soils other than those with low pH, Ca, and P content have also been evaluated (Hedley et al., 1989; Muchovej et al., 1989). For example, in soils of neutral pH, it may be possible to apply a heavy initial dressing of finely ground RP and include a rotation of fine rooted legumes to generate a low pH rhizosphere with low Ca concentrations and, thus, increase RP dissolution. Other methods designed to increase acidity in the immediate RP-soil environment, and thereby its dissolution, include addition of elemental S (Muchovej et al., 1989), NH_4^+ fertilizers, or organic matter such as animal manure and crop residues (Hedley et al., 1989).

Animal manure itself is a valuable resource of P for crop production. The availability of P in manure in some soils may differ from fertilizer P (Table 11.3; Figure 11.4; Hue, 1991; Frossard et al., 1995). As a major proportion of P in manure can be organic (25%–50%), biological processes in soil will play a greater role in determining P availability than for fertilizer P, when applied at equivalent rates of P. In as much, the slower release of P from manure may make it a longer-term source of P to crops than more readily soluble fertilizer P.

Adding manure can cause an increase in soil pH (Kingery et al., 1994; Iyamuremye et al., 1996; Eghball, 2002), due to input of large amounts of Ca (up to 60 g Ca kg manure^{-1}) and the buffering effects of added bicarbonates and organic acids with carboxyl and phenolic hydroxyl groups (Sharpley and Moyer, 2000; Whalen et al., 2000). This suggests that not only the amounts but also form, solubility, and relative availability of soil P for crop uptake and release to overland flow can change with manure application (Wang et al., 1995). In fact, Sharpley et al. (2004) found that the long-term application (10–25 years) of dairy, poultry, or swine manure to 20 sites in New York, Oklahoma, and Pennsylvania resulted in an average increase in soil pH from 5.9 to 6.6, exchangeable Ca from 0.9 to 6.2 g kg^{-1}, organic C from 15.7 to 32.6 g kg^{-1}, and total P from 407 to 2480 mg kg^{-1}, between untreated and treated sites. What was more important to soil P availability was that as Mehlich-3 P increased (22–662 mg kg^{-1}), the proportion that was water soluble (14%–3%) declined as exchangeable Ca increased ($R^2 = 0.81$). Ion-activity products suggested that addition of manure to soil shifts P from Al– and Fe– to Ca–P reaction products, accounting for the relatively greater Mehlcih-3 P but lower water extractability of soil P (Sharpley et al., 2004). This has important implications for agronomic and environmental soil P testing, where acid-based extractants, such as Mehlich-3 and Bray may dissolve Ca–P complexes in manured soils that may not accurately reflect plant availability or potential for release to runoff. For instance, this may explain

TABLE 11.4 Available Soil P of Soil Treated with Fertilizer or Manure for Several Years and Untreated Soil in the U.S. and U.K. Studies

				Available Soil P			
		Added P (kg ha^{-1} Year^{-1})	Time (Year)	Method	Untreated	Treated	
Soil	Crop				(mg kg^{-1})		Reference and Location
Fertilizer							
Portsmouth, fsl *Typic Umbraquult*	Mixed veg.	20	9	Mehlich I	18	73	Cox et al. (1981); North Carolina and Rothamsted
Batcombe, cl *Typic Haploborolls*	Mixed veg.	27	19	Olsen	16	44	
Richfield, scl	Mixed veg.	20	14	Bray 1	12	54	Hooker et al. (1983); Kansas
Aridic Argiustolls		40	14	Bray 1	12	56	
Pullman, cl *Torrertic Paleustolls*	Sorghum	56	8	Bray 1	15	76	Sharpley et al. (1984b); Texas
Keith, sil *Aridic Argiustolls*	Wheat	11	6	Bray 1	22	31	McCallister et al. (1987); Nebraska
Rosebud, sil	Wheat	33	6	Bray 1	24	47	
Aridic Argiustolls		11	6		10	28	
		33	6		10	48	
Beef manure							
Lethbridge, cl	Barley	160	11	Bray 1	22	424	Chang et al. (1991); Alberta
Typic Haploborolls		320	11		22	736	
		480	11		22	893	
Pullman, cl	Sorghum	90	8	Bray 1	15	63	Sharpley et al. (1984b); Texas
Torrertic Paleustolls		273	8		15	230	
Poultry litter							
Cahaba, vfsl *Typic Hapludults*	Grass	130	12	Bray 1	5	216	Sharpley et al. (1993); Oklahoma
Ruston, fsl *Typic Paleudults*	Grass	100	12	Bray 1	12	342	
Stigler, sl *Aquic Paleudalfs*	Grass	35	35	Bray 1	14	239	
Swine manure							
Norfolk, l	Grass	109	11	Mehlich I	80	235	King et al. (1990); North Carolina
Typic Kandiudults		218	11		80	310	
		437	11		80	450	
Captina, sl *Typic Fragiudults*	Grass	101	9	Bray 1	5	121	Sharpley et al. (1991); Oklahoma
Sallisaw, l *Typic Paleudalfs*	Grass	81	15	Bray 1	6	147	
Stigler, sl *Aquic Paleudalfs*	Wheat	37	9	Bray 1	15	82	
Cecil, sl	Grass	160	3	Mehlich I	19	45	Reddy et al. (1980); North Carolina
Typic Kanhapludults		320	3		19	100	

Note: vfsl, very fine sandy loam; fsl, fine sandy loam; sl, sandy loam; sil, silt loam; l, loam; scl, silty clay loam; cl, clay loam; c, clay.

the plateau in the relationship between Mehlich-3 P and runoff dissolved P observed by Torbert et al. (2002). Thus, at high soils P levels Mehclih-3 P is likely extracting some P that may not be immediately released from manured surface soil to runoff.

11.2.5.2.3 Placement

Due to the general immobility of P in the soil profile, fertilizer placement is generally more critical for P than N. Depending on soil and environmental factors, band applications of P may or may not be better than broadcast incorporated applications of P. The effect of P application also varies with soil type. For six soils having a 100-fold variation in P sorptivity, Holford (1989) found that fertilizer P effectiveness, as measured by yield response in the first crop (wheat), residual effect in the second crop (clover), or cumulative recovery of applied P, was consistently greater for shallow banding at 5 cm depth compared to banding at 15 cm or broadcast applications. The almost equal effect obtained by mixing P throughout the soil, regardless of P sorptivity, suggested that the positional availability of P in the root zone is important in maximizing fertilizer effectiveness (Holford, 1989) in addition to reducing P sorption.

Positional availability is also influenced by crop type. In order for banding or restricted fertilizer placement to increase potential root extraction of P, the rate of P absorption and growth of roots in fertilized soil must increase to compensate for roots in unfertilized soil. Increased root growth and P uptake in the P-fertilized volume of soil compared to unfertilized soil has been observed for corn (Anghinoni and Barber, 1980), soybeans (Borkert and Barber, 1985), and wheat (Yao and Barber, 1986). In contrast, several studies have shown that flax does not respond to banded fertilizer due to an inability of its root system to expand and proliferate into and efficiently absorb P from high concentrations in the fertilized zone (Soper and Kalra, 1969; Strong and Soper, 1974). In the case of flax, increased P uptake and yield response was obtained when fertilizer P was placed 2–5 cm directly below the seed, ensuring adequate P levels during early growth (Bailey and Grant, 1989).

Field variability in soil properties, crop-yield potential, and topographic differences can affect site-specific requirements of P. For example, mixing a few fertile soil subsamples with any number of subsamples with marginal nutrient availability can produce misleading analytical results. An example from Nebraska, where scientists extensively sampled a 58 ha cornfield, illustrates this situation (Hergert et al., 1994; Peterson et al., 1994). More than 2000 cores collected from a 58 ha cornfield showed that about 75% of the field would likely respond to P fertilization. Yet, composited annual soil samples indicated a need for little, if any, P fertilizer. Further investigation disclosed the existence of an old farmstead that included a swine feeding operation from 20 years earlier and another area where sheep had been fed in confinement more than 70 years ago.

Integration of the spatial variability of soil properties into fertilizer management and placement decisions will receive greater attention as agronomic response models are developed that incorporate the information now readily available through precision agriculture technology. Such technology, coupled with soil and nutrient management information, will facilitate the correct rate and method of N and P application to meet crop needs.

11.2.5.2.4 Residual Availability

Halvorson and Black (1985) showed that soil test P levels were increased above the initial available P level for more than 16 years, by a one-time P application on a Williams loam (*Typic Argiborolls*) in Montana (Figure 11.6). After the initial increase, available P levels declined for about 12 years and then stabilized at a higher available level than was initially present, thus establishing what appears to be a new equilibrium level of available P. Fixen (1986) reported similar changes in available P levels with time. Crop yields, reported by Halvorson and Black (1985), were also improved by the residual P fertilizer for a period of 16 years (Figure 11.6).

The rate of decline in soil P in high P soils when no further P is added varies with soil type and management (Table 11.5). The rate of decline in available soil P ranged from 0.1 to 30 mg kg^{-1} year^{-1}. McCollum (1991) estimated that without further P, 16–18 years of corn (*Z. mays* L.) or soybean (*G. max* (L.) Merr.) production would be needed to deplete soil P (Mehlich-3 P) in a Portsmouth fine sandy loam (*Typic Umbraquults*) from 100 mg P kg^{-1} to the agronomic threshold level of 20 mg P kg^{-1}. Several authors have found the rate of decrease in available soil P with depletion by cropping when no P is added is inversely related to the soil's P buffering capacity (Holford, 1982; Aquino and Hanson, 1984; Dodd and Mallarino, 2005) or P sorption saturation (available soil P/P sorption maximum; Sharpley, 1996).

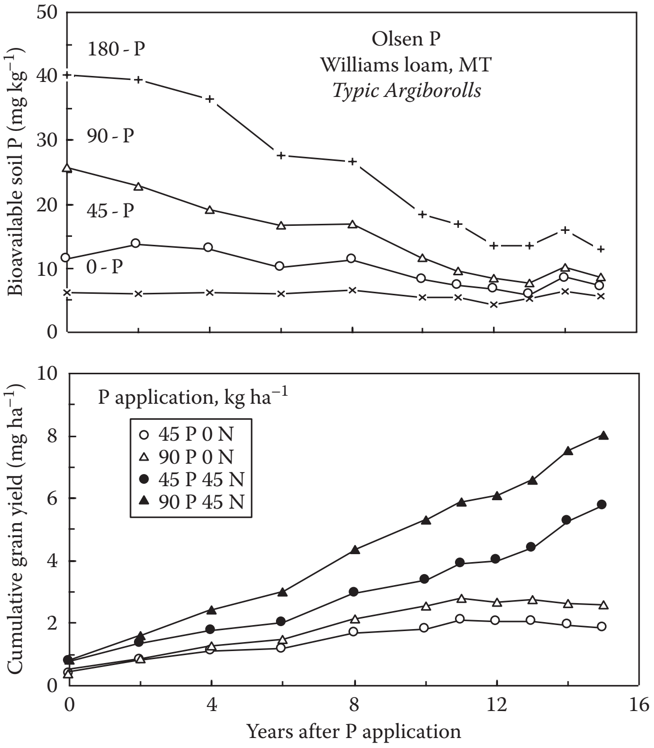

FIGURE 11.6 Changes in bioavailable soil P (Olsen P) and cumulative wheat yields following a single application of fertilizer P. (Data adapted from Halvorson, A.D., and A.L. Black. 1985. Long-term dryland crop responses to residual phosphorus fertilizer. Soil Sci. Soc. Am. J. 49:928–933.)

TABLE 11.5 The Decrease in Available Soil P after P Application Was Stopped in Several North American P Studies

				Available Soil P			
Soil	Crop	Time (Year)	Method	Initial (mg kg^{-1})	Final	Decline ($\text{mg kg}^{-1}\ \text{Year}^{-1}$)	Reference and Location
Thurlow, l	Small grains	9	Olsen	13	4	1.0	Campbell (1965); Montana
Ustollic Haplargids		9		20	4	1.8	
		9		60	6	6.0	
Georgeville, scl	Small grains	7	Mehlich I	3	1	0.1	Cox et al. (1981); North Carolina and Saskatchewan
Typic Hapludult		7		7	2	0.6	
Haverhill, c	Wheat—fallow	14	Olsen	40	25	1.1	
Typic Epiaquolls l		14		74	33	2.9	
		14		134	69	4.6	
Portsmouth, fsl	Small grains	8	Mehlich I	23	18	0.6	
Typic Umbraquults		9		54	26	3.1	
Sceptre, c	Wheat—fallow	8	Olsen	45	18	3.4	
Typic Haploborolls		8		67	18	6.1	
		8		147	40	13.4	
Williams, l	Wheat—barley	16	Olsen	26	8	1.1	Halvorson and Black (1985); Montana
Typic Argiborolls		16		45	14	1.9	
Richfield, scl	Corn	8	Bray 1	12	8	0.5	Hooker et al. (1983); Kansas
Aridic Argiustolls		8		22	14	1.0	
Carroll, cl	Wheat—flax	8	Olsen	71	10	7.6	Spratt et al. (1980); Manitoba
Typic Haploborolls		8		135	23	14.0	
		8		222	50	21.5	
Waskada, l	Wheat—flax	8	Olsen	48	9	4.9	
Typic Haploborolls		8		88	23	8.1	
		8		200	49	18.9	
Waskada, cl	Wheat—flax	8	Bray 1	140	50	11.3	Wagner et al. (1986); Manitoba
Typic Haploborolls		8		320	80	30.0	

Note: fsl, fine sandy loam; l, loam; scl, silty clay loam; cl, clay loam; c, clay.

11.2.5.3 Land Management

11.2.5.3.1 Cultivation

Cultivation and associated fertilizer applications can influence the amount of soil P_i and P_o and should be considered in optimizing soil P availability. Thompson et al. (1954) measured a decrease in P_i and P_o content of 25 surface (0–15 cm) soils from Iowa, Texas, and Colorado, with cultivation. Similarly, Adepetu and Corey (1976) reported that 25% of the P_o content of the surface of a Nigerian soil was mineralized during the first two cropping periods following cultivation. In fact, P_i changes little with crop removal and no fertilizer P application, but available P declines gradually. The net loss from the system through removal in the harvested crop is primarily accounted for by a decrease in P_o. For example, 60 years (1913–1973) of cotton growth on the Mississippi Delta soil, Dundee silt loam (Typic Endoaqualfs), with no reported P added, resulted in no appreciable effect on P_i (Sharpley and Smith, 1983). However, the P_o content of cultivated (93 mg kg^{-1}) compared to virgin analogue (223 mg kg^{-1}) surface soil (0–15 cm) decreased. Mineralization of P_o slowly replenished the P_i pool, which resulted in a 50% reduction in Bray-1 available P. Where cultivation involved P application, P_i and P_o increased 130% and 227%, respectively, while Bray-1 available P increased 84% and P sorption capacity decreased 33% on an average for 8 U.S. agricultural soils (Sharpley and Smith, 1983).

11.2.5.3.2 Remediation of High P Soils

Large amounts of coal combustion by-products are produced annually by power plants in compliance with clean air legislation (U.S. Environmental Protection Agency, 1988). These by-products can be used safely to increase soil pH and reduce subsoil acidity (Stout and Priddy, 1996; Stout et al., 1999; Callahan et al., 2002). Recent research also suggests that two of these by-products—fluidized bed combustion fly ash and flue gas desulfurization gypsum—can greatly reduce water-soluble P levels in soils and surface runoff without appreciably reducing the plant-available P and plant growth; moreover, heavy metals and arsenic in plants or runoff water are not increased (Stout et al., 1998, 2000).

The use of these amendments on critical areas of a watershed has the potential to make large albeit short-term reductions in P loss (Stout et al., 1999).

11.2.6 Water Quality Implications of Soil Phosphorus Availability

Many studies have reported that the loss of dissolved P in surface runoff is dependent on the available P content of surface soil as measured by soil P test extractants (Sharpley et al., 1996; Pote et al., 1999b; Pierson et al., 2001; Torbert et al., 2002; Andraski and Bundy, 2003; Daverede et al., 2003). For instance, runoff P—soil P relationships were developed within a 40 ha watershed (FD-36) in south-central Pennsylvania (Northumberland Co.), where there was a wide range in soil test P concentration as Mehlich-3 P (20–600 mg L^{-1}) (McDowell and Sharpley, 2001; Sharpley et al., 2001). As Mehlich-3 soil P increased, so did the concentration of dissolved P in surface runoff from 2 m^2 plots subjected to a 30 min rainfall of 7 cm h^{-1} (Figure 11.7). Similarly, the concentration of P in subsurface flow is also related to surface soil P (Figure 11.7). Lysimeters of 30 cm depth were taken from the same Pennsylvania watershed and subjected to simulated rainfall (1 cm h^{-1} for 30 min). The concentration of dissolved P in drainage from the lysimeter increased (0.07–2.02 mg L^{-1}) as the Mehlich-3 P concentration of surface soil increased (Figure 11.7; McDowell and Sharpley, 2001; Sharpley et al., 2001). The dependence of leachate P on surface soil P is evidence of the importance of P transport in preferential flow pathways such as macropores, earthworm holes, and old root channels.

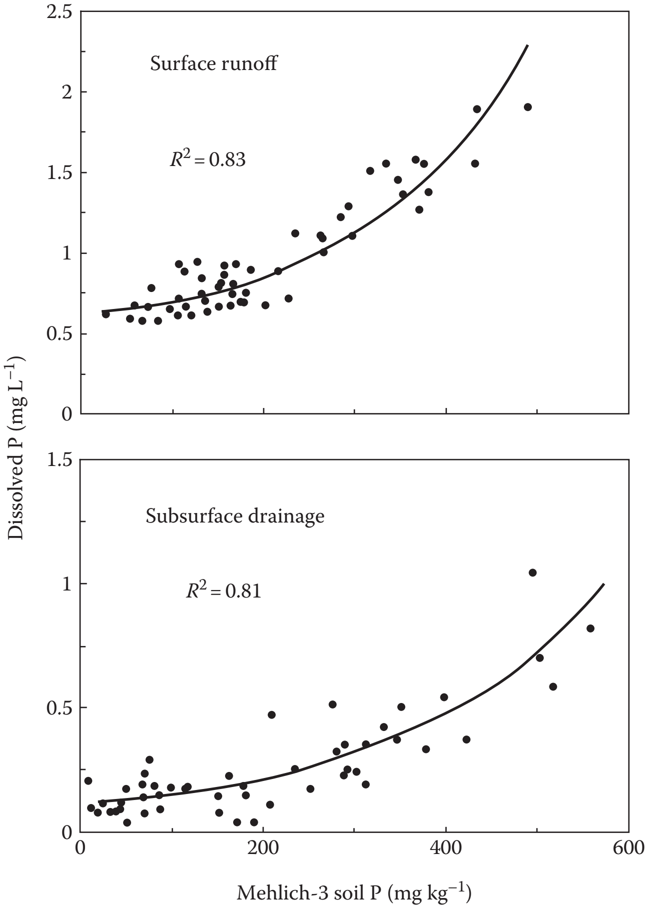

FIGURE 11.7 Relationship between the concentration of dissolved P in surface runoff from 2 m^2 plots and subsurface drainage from 30 cm deep lysimeters and surface soil (0–5 cm depth) Mehlich-3 extractable P concentration from a central PA watershed.

Vadas et al. (2005) conducted a detailed review of the large amount of research published since the late 1990s on the relationship between soil P availability and runoff dissolved P (Table 11.6). Clearly, there was a range in the extraction coefficient representing the slope of the soil P—runoff P relationship or in more simple terms, the extractability of soil P by runoff water. Significant differences among extraction coefficients were not related to any one soil physical, chemical, or management factor (Vadas et al., 2005). The most likely factor influencing soil P extractability was site hydrology, such that a greater proportion of applied rainfall as runoff translated into more P being desorbed from the surface soil and transported in runoff (Vadas et al., 2005). When these studies were combined to include runoff from soil boxes and field plots that were tilled, no-tilled, cropped, and grassed, a single extraction coefficient of 2.0 related Mehlich-3 soil P (mg kg^{-1}) to runoff dissolved P (μg L^{-1}).

This information supports the use of soil test P as a measure of soil P availability in estimating the potential for dissolved P enrichment of runoff, as used in nonpoint source models and more recently in estimating the environmental implications of soil P on runoff P, in relation to impairment of surface waters. Thus, as we move from agronomic to environmental concerns with P, where continued applications of P usually as manure, have led to increased available soil P above optimum levels for crop production, soil P testing is being used to indicate when P enrichment of runoff may become unacceptable. Because of this, a common approach has been to use agronomic soil P standards, following the rationale that soil P in excess of crop requirements is vulnerable to removal by surface runoff or leaching. As agronomic standards already exist for soil test P, this approach required little investment in research and development and can be readily implemented. However, we must be careful how we interpret soil test results for environmental purposes (Figure 11.8).

Interpretations given on soil test reports (i.e., low, medium, optimum, high, etc.) are based on expected crop yield response to P and not on soil P release to surface or subsurface runoff (Sharpley et al., 1994). Some have tried to simply extend crop response levels and say that a soil test that is above the level where a crop response is expected is in excess of crop needs and therefore is potentially polluting (Figure 11.8). However, two factors are of critical importance to the debate on how to use soil test P in environmental risk assessment. First, the gap between crop and environmental soil P thresholds reflects the difference in soil P removed by an acid or base extractant (i.e., Mehlich, Bray, Olsen agronomic tests) and by less invasive water (i.e., simulating extraction of soil P by runoff water), which is soil specific. Secondly, soil P is only one of several factors influencing the

TABLE 11.6 Extraction Coefficients Relating Soil P Availability (mg kg^{-1}) to Runoff Dissolved P (DP; μg L^{-1})

Reference	Location	Land Use	Soil	Number of Observations	Runoff DP	Extraction Coefficient	
						Bray-1	Mehlich-3
Aase et al. (2001)	Indiana	Tilled plots	sl	48	0–0.4	—	—
Andraski and Bundy (2003)	Wisconsin	Cropped plots	sl, cl	126	0–1.0	2.0–13.0	1.3–3.0
Andraski et al. (2003)	Wisconsin	Cropped plots	sl	127	0–0.3	1.9–2.6	1.7
Cox and Hendricks (2000)	North Carolina	Cropped plots	cl, ls	20	0–2.0	—	1.4–3.9
Daverede et al. (2003)	Illinois	Cropped plots	scl	64	0–1.0	0.6–0.8	—
Fang et al. (2002)	Minnesota	Soil boxes	scl, cl, c	10	0–1.0	9.8	5.8
McDowell and Sharpley (2001)	Pennsylvania	Soil boxes, pasture, tilled plots	sl	88	0–1.0	—	1.7–1.9
Pote et al. (1996)	Arkansas	Fescue plots	sl	54	0.2–1.6	2.2	2.6
Pote et al. (1999a)	Arkansas	Fescue plots	sl, sal	36	0–1.2	2.7–4.3	1.6–3.6
Pote et al. (1999b)	Arkansas	Fescue plots	sl	36	0–1.4	—	2.2–2.8
Schroeder et al. (2004)	Georgia	Pasture plots	sal	54	0–1.1	—	1.7–2.0
Sharpley et al. (2001)	Pennsylvania	Pasture tilled plots	sl	—	—	—	2.1
Torbert et al. (2002)	Texas	Bermudagrass plots	sal, cl, c	72	0–1.6	—	0.4–7.0
Turner et al. (2004)	Idaho	Tilled plots	sl, fsl	50	0–0.7	—	1.2–2.8
Weld et al. (2001)	Pennsylvania	Soil boxes	sl	—	—	—	1.5–1.7

Source: Adapted from Vadas, P.A., P.J.A. Kleinman, and A.N. Sharpley. 2005. Relating soil phosphorus to dissolved phosphorus in runoff: A single extraction coefficient for water quality modeling. J. Environ. Qual. 34:572–580.

Note: fsl, fine sandy loam; fas, sandy loam; sl, silt loam; scl, silty clay loam; cl, clay loam; c, clay.

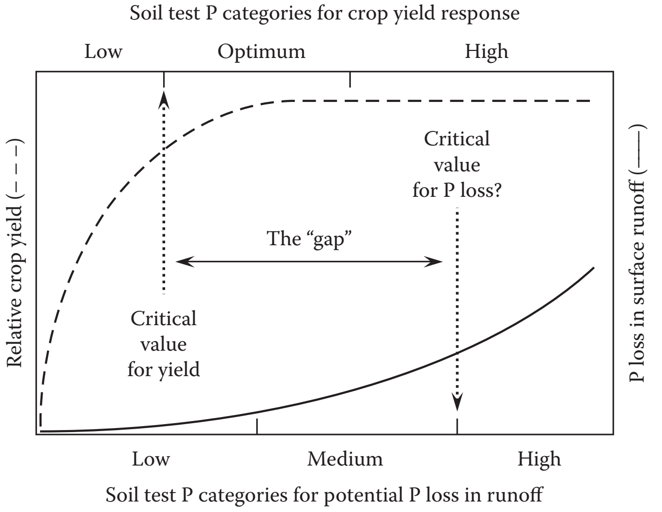

FIGURE 11.8 As soil P increases, so does crop yield and the potential for P loss in surface runoff. The interval between the critical soil P value for yield and runoff P will be important for P management.

potential for P loss; therefore, soil test P should not be used as the sole criteria on which to base P management planning.

11.2.7 Conclusions

The amount and availability of soil P is determined by physical, chemical, and biological processes, which are often managed in attempts to increase or optimize crop uptake of P and yields. In many areas, P cycles have been fragmented by the specialization of agricultural production systems in specific regions. For instance, mineral fertilizer P is imported to areas of crop production from continental United States and overseas deposits, which have been treated to varying degree to increase P solubility. The harvested grain is used to meet human demands, for animal feed, and more recently as biofuel feedstock. In each case, major population areas, confined animal operations, and biorefineries are geographically removed from areas of crop production. For example, most of the corn produced in the Midwest is used as feed in eastern U.S. states. As a result, P is moving from areas where ore deposits are mined, through crop producing regions, and is accumulating in areas of confined animal operations.

Future management of soil P availability must address the impacts that this specialization of agricultural systems is having on regional P requirements and production on a national scale. At the farm scale, however, efforts should continue to find ways of enhancing the efficient use of P, through soil testing, appropriate rates of P application, and utilization of manure sources of P in an increasing number of agricultural production systems. If these goals are not met, soil P availability may become an environmental rather than fertility issue in more areas.

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11.3 Bioavailability of Soil Potassium

Donald L. Sparks

11.3.1 Introduction

The role of K in soils is prodigious. Of the many plant nutrient–soil mineral relationships, those involving K are of major, if not prime, significance (Sparks and Huang, 1985; Sparks, 1999).

Since the middle of the seventeenth century, when J.R. Glauker in the Netherlands first proposed that saltpeter (KNO_3) was the principle of vegetation, K has been recognized as being beneficial to plant growth (Russell, 1961). Glauker obtained large increases in plant growth from the addition of saltpeter to the soil that was derived from the leaching of coral soils. The essentiality of K to plant growth has been known since the work of von Liebig.

Of the major nutrient elements, K is usually the most abundant in soils (Reitemeier, 1951). Igneous rocks of the Earth's crust have higher K contents than sedimentary rocks. Of the igneous rocks, granites and syenites contain 46–54, basalts 7, and peridotites 2.0 g K kg^{-1}. Among the sedimentary rocks, clayey shales contain 30, whereas limestones have an average of only 6 g K kg^{-1} (Malavolta, 1985).

Mineral soils generally range between 0.04% and 3% K. Total K contents in soils range between 3000 and 100,000 kg ha^{-1} in the upper 0.2 m of the soil profile. Of this total K content, 98% is bound in the mineral form, whereas 2% is in soil solution and exchangeable phases (Schroeder, 1979; Bertsch and Thomas, 1985).

Potassium, among mineral cations required by plants, is the largest in nonhydrated size ($r = 0.133$ nm) and the number of oxygen atoms surrounding it in mineral structures is high (8 or 12), which suggests that the strength of each K–O bond is relatively weak (Sparks and Huang, 1985). Potassium has a polarizability equal to 0.088 nm^3, which is higher than for Ca^{2+}, Li^+, Mg^{2+}, and Na^+ but lower than for Ba^{2+}, Cs^+, NH_4^+, and Rb^+ ions (Rich, 1968, 1972; Sparks and Huang, 1985). Ions with higher polarizability are preferred in ion-exchange reactions. Potassium has a hydration energy of 142.5 kJ g^{-1} ion^{-1}, which indicates little ability to cause soil swelling (Helfferich, 1962).

11.3.2 Forms of Soil Potassium

Soil K exists in four forms in soils: solution, exchangeable, fixed or nonexchangeable, and structural or mineral (Figure 11.9). Quantities of exchangeable, nonexchangeable, and total K in the surface layer (0–20 cm) of a variety of soils are shown in Table 11.7. Exchangeable K and nonexchangeable K levels comprise a small portion of the total K. The bulk of total soil K is in the mineral fraction (Sparks and Huang, 1985). There are equilibrium and kinetic reactions between the four forms of soil K that affect the level of soil solution K at any particular time and, thus, the amount of readily available K for plants. The forms of soil K in the order of their availability to plants and microbes are solution > exchangeable > fixed (nonexchangeable) > mineral (Sparks and Huang, 1985; Sparks, 1987, 1999).

11.3.2.1 Solution K

Soil solution K is the form of K that is directly taken up by plants and microbes and also is the form most subject to leaching in soils. Levels of soil solution K are generally low, unless recent

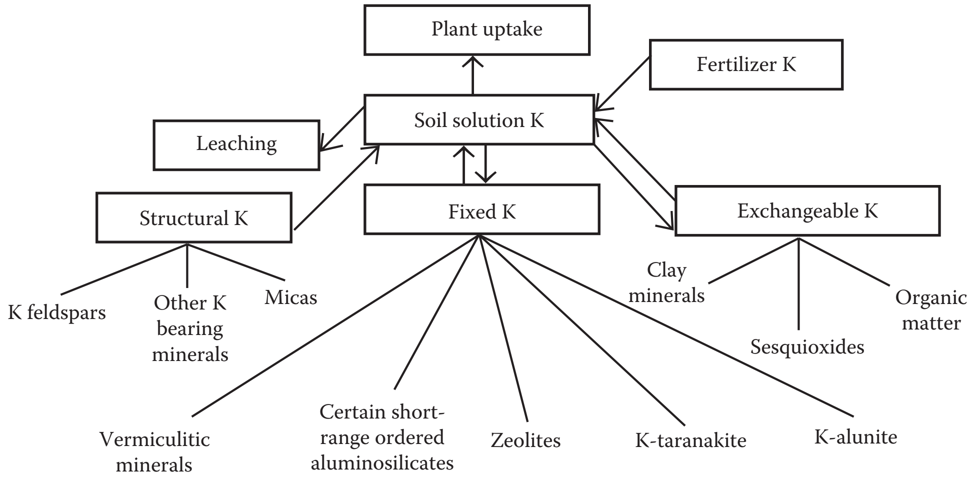

FIGURE 11.9 Interrelationships of various forms of soil K. (From Sparks, D.L., and P.M. Huang. 1985. Physical chemistry of soil potassium, p. 201–276. *In* R.D. Munson (ed.) Potassium in agriculture. ASA, Madison, WI. With permission of American Society of Agronomy.)

TABLE 11.7 Potassium Status of Selected Soils[a]

Origin of Soil	Exchangeable K (cmol$_c$ kg^{-1})	Nonexchangeable K (cmol$_c$ kg^{-1})	Total K (cmol$_c$ kg^{-1})	Source
Alfisols				
Nebraska, USA	0.40	—	—	Soil Survey Staff (1975)
West Africa	0.46	—	3.07	Juo (1981)
Inceptisols				
California, USA	0.40	—	—	Soil Survey Staff (1975)
Maryland, USA	0.20	—	—	Soil Survey Staff (1975)
Mollisols				
Iowa, USA	0.27	—	—	Survey Staff (1975)
Nebraska, USA	0.40	—	—	Survey Staff (1975)
Ultisols				
Delaware, USA	0.33	0.49	22.5	Parker et al. (1989a)
Florida, USA	0.14	0.25	2.71	Yuan et al. (1976)
Virginia, USA	0.11	0.17	6.5	Sparks et al. (1980)
West Africa	0.24	—	8.06	Juo (1981)

[a] Data are for surface soils (0–20 cm depth).

amendments of K have been made to the soil. The quantity of K in the soil solution varies from 2 to 5 mg K L^{-1} for normal agricultural soils of humid regions and is an order of magnitude higher in arid region soils (Haby et al., 1990). Levels of solution K are affected by the equilibrium and kinetic reactions that occur between the forms of soil K, the soil moisture content, and the concentrations of bivalent cations in solution and on the exchanger phase (Sparks and Huang, 1985; Sparks, 1999).

11.3.2.2 Exchangeable K

Exchangeable K is the portion of the soil K that is electrostatically bound as an outer-sphere complex to the surfaces of clay minerals and humic substances. It is readily exchanged with other cations and also is readily available to plants.

11.3.2.3 Nonexchangeable K

Nonexchangeable or fixed K differs from mineral K in that it is not bonded within the crystal structures of soil mineral particles. It is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculites, and intergrade clay minerals such as chloritized vermiculite (Rich, 1972; Sparks and Huang, 1985; Sparks, 1987). Potassium becomes fixed because the binding forces between K and the clay surfaces are greater than the hydration forces between individual K^+ ions. This results in a partial collapse of the crystal structures and the K^+ ions are physically trapped to varying degrees, making K release a slow, diffusion controlled process (Sparks, 1987). Nonexchangeable K also can be found in wedge zones of weathered micas and vermiculites (Rich, 1964). Only ions with a size similar to K^+, such as NH_4^+ and H_3O^+, can exchange K from wedge zones (Chapter 21 of *Handbook of Soil Sciences: Properties and Processes*). Large hydrated cations, such as Ca^{2+} and Mg^{2+}, cannot fit into the wedge zones. Release of nonexchangeable K to the exchangeable form occurs when levels of exchangeable and soil solution K are decreased by crop removal and/or leaching and perhaps by large increases in microbial activity (Sparks, 1980).

Nonexchangeable K is moderately to sparingly available to plants (Mengel, 1985; Sparks and Huang, 1985; Sparks, 1987). Mortland et al. (1956) showed that biotite could be altered to vermiculite by plant removal of K. Schroeder and Dummler (1966) showed that the nonexchangeable K associated with some German soil illites was an important source of K to crops. The ability of plants to take up nonexchangeable K appears to be related to the plant species. Steffens and Mengel (1979) found that ryegrass (*Lolium perenne*) could take up nonexchangeable K longer without yield reductions, while red clover (*Trifolium pratense*) could not. This was attributed to the ryegrass having longer root length, which would allow it to grow at a relatively low K concentration. A similar concentration would result in a K deficiency in red clover. It may be that the difference in root mass, root length, and root morphology between monocots and dicots explains why monocots feed better from nonexchangeable K than dicots (Mengel, 1985).

11.3.2.4 Mineral K

As noted earlier, most of the total K in soils is in the mineral form, mainly as K-bearing primary minerals such as muscovite, biotite, and feldspars. For example, in some Delaware soils, Sadusky et al. (1987) found that mineral K comprised about 98% of the total K (Table 11.8). Most of the mineral K was present as K feldspars in the sand fractions.

Common soil K-bearing minerals, in the order of availability of their K to plants, are biotite, muscovite, orthoclase, and microcline (Huang et al., 1968; Sparks, 1987). Mineral K is generally assumed to be only slowly available to plants; however, the availability is dependent on the level of K in the other forms, and the degree of weathering of the feldspars and micas constituting the mineral K fraction (Sparks and Huang, 1985; Sparks, 1987).

TABLE 11.8 Potassium Status of Delaware Soils and Sand Fractions

		Soils				Sand Fraction	
		$CaCl_2$ Extractable	HNO_3 Extractable	Mineral K[a]	Total K	Total K[b]	
Horizon	Depth (cm)	(cmol$_c$ kg^{-1})					K Feldspars[c] Frequency (%)
Kenansville loamy sand							
Ap	0–23	0.25	0.42	35.02	35.69	30.88	9.5
Bt2	85–118	0.25	0.49	45.30	46.04	33.86	12.0
Rumford loamy sand							
Ap	0–25	0.33	0.49	21.67	22.51	18.62	6.7
BC	89–109	0.21	0.54	23.39	23.96	16.76	8.2
Sassafras fine loamy sand							
Ap	0–20	0.35	0.56	43.54	44.45	28.95	16.0
Cl	84–99	0.13	0.36	45.99	46.68	36.69	24.0

Source: Sadusky, M.C., D.L. Sparks, M.R. Noll, and G.J. Hendricks. 1987. Kinetics and mechanisms of potassium release from sandy soils. Soil Sci. Soc. Am. J. 51:1460–1465. With permission of the Soil Science Society of America.

[a] Mineral K = [(total K) − ($CaCl_2$ ext. K + HNO_3 ext. K)].

[b] These data represent the amount of total K in the sand based on a whole soil basis.

[c] Determined through petrographic analyses of the whole sand fractions and represents the percentage of total point counts in a given sample that were K feldspars. The remaining minerals in the sand fraction were quartz, plagioclase, and opaques.

Sadusky et al. (1987) and Parker et al. (1989a, 1989b) have found that a substantial amount of K is released from the sand fractions of Delaware soils that are high in K feldspars. This finding, along with the large quantities of mineral K in these and other Atlantic Coastal Plain soils, could help in explaining the often observed lack of crop response to K amendments on these soils (Liebhardt et al., 1976; Yuan et al., 1976; Sparks et al., 1980; Woodruff and Parks, 1980; Parker et al., 1989a).

11.3.3 Factors Affecting Potassium Availability

11.3.3.1 Solution-Exchangeable K Dynamics

The rate and direction of reactions between solution and exchangeable forms of K determine whether applied K will be leached into lower horizons, taken up by plants, converted into unavailable forms, or released into available forms.

The reaction rate between soil solution and exchangeable phases of K is strongly dependent on the type of clay minerals present (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980; Sparks and Jardine, 1981, 1984; Jardine and Sparks, 1984) and the method employed to measure kinetics of K exchange (Sparks, 1989, 1995; Amacher, 1991; Sparks et al., 1996). Vermiculite, montmorillonite, kaolinite, and hydrous mica vary drastically in their ionic preferences, ion binding affinities, and types of ion-exchange reactions. Such fundamental differences in these clay minerals account for the varying kinetics of K exchange.

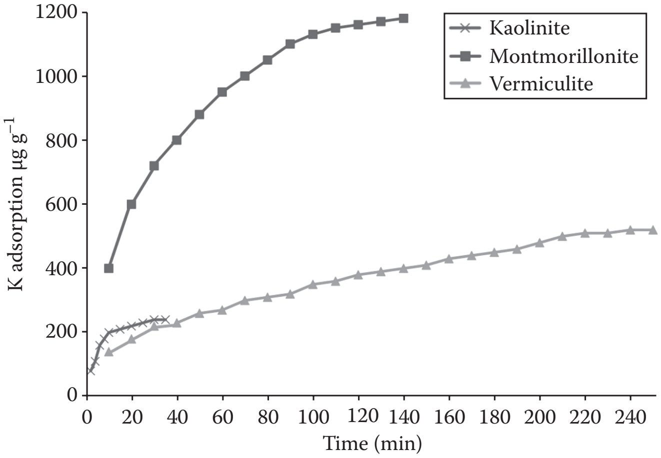

FIGURE 11.10 Potassium adsorption versus time in pure systems. (From Sparks, D.L., and P.M. Jardine. 1984. Soil Sci. 138:115–122. With permission of Wolters Kluwer.)

Kinetics of K exchange on kaolinite and montmorillonite are usually quite rapid (Malcolm and Kennedy, 1969; Sparks and Jardine, 1984; Sparks, 1995, 2002). An illustration of this is shown in Figure 11.10. In the case of kaolin clays, the tetrahedral layers of adjacent clay layers are held tightly by H bonds; thus, only planar external surface and edge sites are available for ionic exchange. With montmorillonite, the inner peripheral space is not held together by H bonds, but instead is able to swell with adequate hydration and thus allow for rapid passage of ions into the interlayer space. Malcolm and Kennedy (1969) found that the rate of Ba exchange on kaolinite and montmorillonite was rapid with 75% of the total exchange occurring in 3 s.

Kinetics of K exchange on vermiculitic and micaceous minerals tends to be extremely slow. Both are 2:1 phyllosilicates with peripheral spaces that impede many ion-exchange reactions. Micaceous minerals typically have a more restrictive interlayer space than vermiculite since the area between layer silicates of the former is selective for certain types of cations (e.g., K$^+$, Cs$^+$). Bolt et al. (1963) theorized the existence of three types of binding sites for K exchange on hydrous mica. The authors hypothesized that slow kinetics were due to internal exchange sites, rapid kinetics to external planar sites, and intermediate kinetics to edge sites.

11.3.3.2 Potassium Fixation

The phenomenon of K fixation or retention significantly affects K availability. The fact that fixation processes are limited to interlayer ions, such as K^+, has been explained in terms of the good fit of K^+ ions (the crystalline radius and coordination number are ideal) in an area created by holes and adjacent oxygen layers (Barshad, 1951). The important forces involved in interlayer reactions in clays are electrostatic attractions between the negatively charged layers and the positive interlayer ions, and expansive forces due to ion hydration (Kittrick, 1966).

The degree of K fixation in clays and soils depends on the type of clay mineral and its charge density, the degree of interlayering, the moisture content, the concentration of K^+ ions as well as the concentration of competing cations, and the pH of the ambient solution bathing the clay or soil (Rich, 1968; Sparks and Huang, 1985).

The major clay minerals responsible for K fixation are montmorillonite, vermiculite, and weathered micas. In acid soils, the principal clay mineral responsible for K fixation is dioctahedral vermiculite. Weathered micas fix K under moist as well as dry conditions, whereas some montmorillonites fix K only under dry conditions (Rich, 1968).

The degree of K fixation is strongly influenced by the charge density on the layer silicate. Those with high charge density fix more K than those with low charge density (Walker, 1957). Weir (1965) noted that K fixation by montmorillonites is limited unless the charge density of the clays is high. Low charge montmorillonite (Wyoming) stays at 1.5 nm when K saturated, unless it is heated (Laffer et al., 1966). Schwertmann (1962a, 1962b) noted that soil montmorillonites have a greater capacity to fix K than do many specimen montmorillonites. Soil montmorillonites have higher charge density and a greater probability of having wedge positions near mica-like zones where the selectivity for K is high (Rich, 1968).

The importance of interlayer hydroxy Al and hydroxy Fe^{3+} material on K fixation was first noted in the classic work of Rich and Obenshain (1955). They theorized that hydroxy Al and hydroxy Fe^{3+} interlayer groups acted as props to decrease K fixation. This theory was later corroborated in the work of Rich and Black (1964) who found that the introduction of hydroxy Al groups into Libby vermiculite increased the Gapon selectivity coefficient (k_G) from 5.7 to 11.1×10^{-2} L $\text{mmol}^{-1/2}$.

Wetting and drying as well as freezing and thawing can significantly affect K fixation (Hanway and Scott, 1957; McLean and Simon, 1958; Cook and Hutcheson, 1960). The degree of K fixation or release on wetting or drying is dependent on the type of colloid present and the level of K^+ ions in the soil solution.

Potassium fixation by 2:1 clay minerals may be strongly influenced by the kind of adsorbed cations or the anions within the system. In studies with the silicate ion, Mortland and Gieseking (1951) found that montmorillonite clays dried with K_2SiO_3 were altered in their swelling properties and fixed K in large amounts. Hydrous mica clays also fixed large amounts of K that could not be removed with boiling HNO_3.

Volk (1934) observed a marked increase in K fixation in soils where pH was raised to about 9 or 10 with Na_2CO_3. Martin et al. (1946) showed that at pH values up to 2.5 there was no fixation; between pH 2.5 and 5.5, the amount of K fixation increased very rapidly. Above pH 5.5, fixation increased more slowly. These differences in K fixation with pH were discussed by Thomas and Hipp (1968). At pH values >5.5, Al^{3+} cations precipitate as hydroxy polycations, which increase in the number of OH groups as pH increases, until they have a form like gibbsite (Thomas, 1960). At this pH (~8), Al^{3+} does not neutralize the charge on the clay and cannot prevent K fixation. Below pH 5.5, Al^{3+} and $Al(OH)_x$ species dominate. Below pH 3.5, H_3O^+ predominates (Coleman and Harward, 1953; Thomas and Hipp, 1968).

The increase in K fixation between pH 5.5 and 7.0 can be ascribed to the decreased numbers of $Al(OH)_x$ species, which decrease K fixation (Rich and Obenshain, 1955; Rich, 1960, 1964; Rich and Black, 1964). At low pH, the lack of K fixation is probably due to large numbers of H_3O^+ and their ability to replace K as well (Rich, 1964; Rich and Black, 1964).

11.3.3.3 Potassium Release

The release of K from micas proceeds by two processes: (1) the transformation of K-bearing micas to expansible 2:1 layer silicates by exchanging the K with hydrated cations and (2) the dissolution of the micas followed by the formation of weathering products. The relative importance of these two mechanisms depends on the stability of micas and the nature of soil environments (Sparks and Huang, 1985).

Release of K from feldspars appears to involve a rapid exchange with H, which creates a thin layer of hydrolyzed aluminosilicate. This residual layer ranges in thickness from several to a few tens of nanometers and seems to cause the initial nonstoichiometric release of alkali and alkaline earths, relative to Si and Al. Following this step, there is continued dissolution, which removes hyperfine particles. After these are removed, further dissolution breaks down the outer surface of the residual layer at the same rate that alkalis are replaced by H at the interface between fresh mineral surfaces and the residual layer. This releases all constituents to the solution. Release is now stoichiometric. Thus, the weathering of feldspars appears to be a surface-controlled reaction (Sparks, 1989).

A number of physiochemical and mineralogical factors govern the release of K from micas by both cation exchange reactions and dissolution processes. These include tetrahedral rotation and cell dimensions, degree of tetrahedral tilting, hydroxyl orientation, chemical composition, particle size, structural imperfections, degree of K depletion, layer charge alterations and associated reactions, hydronium ions, biological activity, inorganic cations, wetting and drying, and other factors (Sparks and Huang, 1985). This review will focus on the latter four factors.

Biological activity promotes K release from micas (Mortland et al., 1956; Boyle et al., 1967; Sawhney and Voight, 1969;

Weed et al., 1969). The organisms deplete the K in the soil solution, and their action may be analogous to that of tetraphenylboron (TPB) in artificial weathering of micas. Furthermore, the overall action of organisms is more complex when organic acids are produced (Boyle et al., 1967; Spyridakis et al., 1967; Sawhney and Voight, 1969).

The importance of organic acids in weathering of rock-forming minerals has been recognized for a long time (Sprengel, 1826; Bolton, 1882; Huang and Keller, 1970). All soils contain small but measurable amounts of biochemical compounds such as organic acids. Furthermore, since the time required for soil formation can extend over a period of centuries, the cumulative effect in a soil of even very small quantities of chelating agents will be considerable. The influence of oxalic and citric acids on the dynamics of K release from micas and feldspars was studied by Song and Huang (1988). They found that the sequence of K release from K-bearing minerals by oxalic and citric acids is biotite > microcline orthoclase > muscovite.

The activity of K^+ ions in soil solution around mica particles greatly influences the release of K from micas by cation exchange. When the K level is less than the critical value, K is replaced from the interlayer by other cations from the solution. On the contrary, when the K level is greater than the critical value, the mica expansible 2:1 mineral takes K from the solution. The critical K level is highly mineral dependent, being much higher for the trioctahedral minerals (Smith and Scott 1966; Newman, 1969; von Reichenbach, 1973; Henderson et al., 1976). The critical levels for muscovite are so low that even the K impurities in laboratory chemicals or dissolved from glassware are often sufficient to prevent any K release (Scott and Smith, 1966).

The nature and concentration of the replacing cations also influences the critical K level of the cations tested in Cl^- solutions. Rausell-Colom et al. (1965) found the critical K levels decreased in the order $Ba^{2+} > Mg^{2+} > Ca^{2+} \approx Sr^{2+}$ for the same concentration of these ions and with a constant mica particle size. The activity of all of these replacing ions in the solution phase must be much greater than that of the K for significant K release to occur. The activity of various cations in the soil solution is governed by other minerals in the soil systems, by pedogenic processes, and by anthropogenic activities.

The release of K upon drying a soil is related to the clay fraction (Scott and Hanway, 1960). When a soil is dried, the degree of rotation of weathered soil minerals, such as micas, may be changed. Thus, the K–O bond may be modified. Dehydration of interlayer cations may permit a redistribution of interlayer cations, because Ca could now compete with K for wedge sites. This seems to account for the release of K from soils upon drying. Rich (1972) found that Virginia soils, which contain hydroxy Al interlayers and appreciable amounts of K, did not release K upon drying. The presence of the hydroxy Al interlayers may block or retard the interlayer diffusion of K ions and may change the b-dimension of micas, the degree of tetrahedral rotation, and the length and strength of the K–O bond.

Other factors that can affect K release from soils are leaching, redox potential (Eh), and temperature. Leaching promotes the K release from K-bearing minerals by carrying away the reaction products. Therefore, leaching accelerates the transformation of minerals, for example, micas, to expansible 2:1 layer silicates and other weathering products if the chemistry of leaching water favors the reaction.

Redox potential of soils could influence K release from micas since it has been pointed out that the tenacity with which K is held by biotite is greater after oxidation of its structural Fe. It appears that, other factors being equal, the extent of the K release from biotite should be less in soil environments that oxidize Fe than in soil environments that reduce it. Major elements in K-bearing feldspars do not exist in more than one valence state; thus, the prevailing Eh of a soil may not be of direct concern to chemical weathering of the feldspars. However, the weatherability of feldspars can be affected by complexing organic acids that are vulnerable to oxidation. Therefore, the stability of feldspars may be indirectly related to the prevailing Eh of a soil.

Increasing temperature has been shown to increase the rate of K release from biotite (Rausell-Colom et al., 1965) and K feldspars (Rasmussen, 1972). Under conditions of leaching of biotite with 0.1 mol NaCl L^{-1}, the rate of K release appears directly proportional to temperature in the range of 293–323 K (Mortland, 1958). Under similar leaching conditions, Mortland and Ellis (1959) observed that the log of the rate constant for K release from fixed K in vermiculite was directly proportional to the inverse of the absolute temperature.

Preheating of micas to high temperatures (1273 K) prior to TPB extraction (Scott et al., 1973) was found to enhance the rate of K extraction from muscovite, to decrease the rate for biotite, and to have little effect on phlogopite, except at very high temperatures. The decrease in K release from biotite by preheating is presumably because of oxidation of Fe at high temperatures. The more rapid rate with muscovite following heating remains unexplained.

11.3.3.4 Leaching of Potassium in Soils

Soil solution K is either leached or sorbed by plants or soils. A number of factors influence the movement of K in soils, including the cation exchange capacity (CEC), soil pH and liming, method and rate of K application, and K absorption by plants (Terry and McCants, 1968; Sparks, 1980).

The ability of a soil to retain applied K is very dependent on the CEC of the soil. Thus, the amount of clay and SOM in the soil strongly influences the degree of K leaching. Soils with higher CEC have a greater ability to retain added K, whereas leaching of K is often a problem on sandy soils (Sparks and Huang, 1985).

Retention of K can often be enhanced in sandy, Atlantic Coastal Plain soils after application of lime, since in such variable charge soils, the CEC is increased as soil pH is increased. Nolan and Pritchett (1960) found that liming a Lakeland fine sand soil (thermic, coated *Typic Quartzipsamment*) to pH 6–6.5 caused maximum retentivity of applied K. Potassium was replaced by Ca on the exchange complex at higher levels of limestone application. Less leaching of K occurred at pH 6.0–6.5 due to enhanced substitution of K for Ca than for Al, which was more abundant at low pH.

Lutrick (1963) found that K leaching occurred on unlimed but not on limed areas when 112–224 kg K ha^{-1} was applied on a Eustis loamy fine sand (sandy, siliceous, thermic Psammentic Paleudult).

Movement of applied K has been related to the method of application. Nolan and Pritchett (1960) compared banded and broadcast placement of KCl applied at several rates to Arredondo fine sand (loamy, siliceous, hyperthermic Grossarenic Paleudult) in lysimeters under winter and summer crops. For the low rate of application, cumulative K removal for both placements was only about 5.0 kg ha^{-1}.

A number of investigations have been conducted to determine the relationship of crop uptake and the rate of K application to leaching of K. Jackson and Thomas (1960) applied up to 524 kg K ha^{-1} prior to planting sweet potatoes (*Ipomoea batatas* L.) on Norfolk sandy loam (fine loamy, siliceous, thermic *Typic Paleudult*). At harvest time, soil and plant K exceeded applied K at the 131 and 262 kg K ha^{-1} rates. However, at the 524 kg K ha^{-1} rate, 38 kg K was unaccounted for by soil and plant K. This deficiency of K was attributed to leaching below sampling depths. During a 2 year study with corn (*Zea mays* L.) on two Dothan (*Typic Paleudult*) soils of Virginia, Sparks et al. (1980) found that 83 and 249 kg of applied K ha^{-1} increased the exchangeable K in the E and B21t horizons of the two soils. These increases were ascribed to leaching of applied K. The magnitude of leaching varied directly with rate of K application. No accumulation of K was found in the top 0.76 m of Leon sand (sandy, siliceous, thermic Aeric Haplaquod) after 40 year of heavy K fertilization (Blue et al., 1955).

11.3.4 Assessing Potassium Extractability and Availability

The extractability and availability of soil and plant K can be assessed by using chemical extractants to quantify the various forms of soil K, soil test extractants, quantity/intensity (*Q/I*) analyses, and plant analysis.

11.3.4.1 Chemical Extractants for Soil K Forms

Methods to determine total K and the other alkali elements in soils use acids or a high temperature fusion to decompose the soil. The most widely employed digestion techniques for total elements in soils and minerals have used combinations of HF and either H_2SO_4 or $HClO_4$ (Helmke and Sparks, 1996).

Exchangeable K is that K that is typically extracted with a neutral normal salt, usually 1.0 M NH_4OAc minus the water soluble K (Knudsen et al., 1982). In soils that are not saline, levels of water soluble K are minimal and can be ignored. However, in saline soils, the levels of water soluble K should be determined from a saturated extract or some similar extract and subtracted from the amount of K determined using NH_4OAc.

It should be noted that in soils that contain weathered vermiculitic and micaceous minerals wedge zones can be present that contain K. This K is not accessible to large index cations such as Ca and Mg, but can be extracted by NH_4, which is of similar size to K. For example, in soils that contain wedge zones, NH_4OAc will extract more K than an extractant like 1 M $CaCl_2$. It is debatable whether this K is truly exchangeable. Thus, in soils containing wedge zones, exchangeable K could be overestimated with NH_4OAc (Sparks and Huang, 1985; Helmke and Sparks, 1996).

There are a number of chemical methods that can be employed to extract nonexchangeable K. These include boiling HNO_3, H_2SO_4, hot HCl, electroultrafiltration, Na TPB with EDTA, and ion-exchange resins such as H and Ca saturated resins (Hunter and Pratt, 1957; Martin and Sparks, 1985; Helmke and Sparks, 1996).

The most commonly used method for extraction of nonexchangeable K is the boiling HNO_3 technique. Most researchers that use this method boil the soil in M HNO_3 for 10 min over a flame, transfer the slurry to a filter, leach the soil with dilute HNO_3, and then determine the concentration in the filtrate. One of the problems with boiling for only 10 min over a flame is that it is difficult to be precise about the correct boiling time, the time it takes for boiling to occur, and the vigor of boiling (Martin and Sparks, 1985). Some workers have attempted to diminish these problems by using a 386 K oil bath for 25 min, including heating time (Pratt, 1965). This modification is particularly useful when large numbers of samples are being analyzed. Of course, one of the major concerns with using a boiling HNO_3 procedure is the potential to cause partial dissolution of mineral forms of K.

Other researchers have used continuous leaching of the soil with dilute acids such as 0.01 M HCl or with dilute salts such as 0.1 M NaCl, repeated extractions with 3, 0.3, and 0.03 M NaCl, Sr salts, hot $MgCl_2$, and sodium cobaltinitrite (Martin and Sparks, 1985).

Cation-exchange resins saturated with H or Ca also have been widely used to measure nonexchangeable K. These resins have high CECs and when saturated with an appropriate cation and mixed with soil and with a dilute solution, they will adsorb released K. One of the major advantages of using cation-exchange resins to extract K is that they act as a sink for the released K and thus prevent an inhibition of further K release. This is a problem with many batch methods that employ dilute acids and electrolytes. One major disadvantage of cation-exchange resins for extracting K is that the resins are expensive and the procedure is time-consuming and tedious.

In order for electrolyte and acid solutions and cation-exchange resins to be effective in extracting K, the K concentration in the solution phase must be kept very low, or K release must be inhibited (Rausell-Colom et al., 1965; Wells and Norrish, 1968; Feigenbaum et al., 1981; Martin and Sparks, 1983, 1985). The critical concentration above which release is inhibited is 4 mg L^{-1} for soils in general, 2.3–16.8 mg L^{-1} for trioctahedral micas in dilute solution, and as low as <0.1 mg L^{-1} for muscovite and illite (Smith and Scott, 1966; Martin and Sparks, 1985). A low enough concentration of solution K can be maintained by employing a continuous flowing extracting or exchanging solution, cation-exchange resins, or Na TPB (Scott et al., 1960).

One can quantitatively analyze for mineral K (K feldspars and micas) by using a selective dissolution method employing $Na_2S_2O_7$ fusion. The technique and method for calculating the quantities of K feldspars and micas can be found in Helmke and Sparks (1996). A semiquantitative approach for measuring mineral K is to subtract the quantity of nonexchangeable K, using the boiling HNO_3 procedure, from the quantity of total K, using the HF digestion method. One also can quantify K feldspars in the sand fraction of soil, using petrographic analyses (Parker et al., 1989b).

11.3.4.2 Soil Tests for Potassium

Soil test extractants for K were developed to easily and rapidly measure K in soils and to estimate K availability. Based on the amounts of extractable K, recommendations that are based on field test calibrations can then be made on the amount of K that is needed to maximize plant yields. Soil tests for K usually estimate the quantity of solution and exchangeable K, and since acids are usually employed as extractants, some nonexchangeable and mineral K is also extracted (Wolf and Beegle, 1991). The soil tests used to measure extractable K in the United States include Mehlich-1 and Mehlich-3 procedures in the northeastern and southeastern United States, the Morgan and modified Morgan procedures in parts of the northeastern United States, the 1 M NH_4OAc at pH 7 procedure in the north-central United States, and the ammonium bicarbonate-DTPA extraction in the western United States. Procedures for these soil tests are fully described in Helmke and Sparks (1996) and Chapter 14.

11.3.4.3 *Q*/*I* Analysis

Schofield (1947) proposed that the ratio of the activity of cations such as K and Ca was defined by the relation $a_K/(a_{Ca})^{1/2}$ where a is the ion activity. He appears to have been the first person to apply the concepts of quantity (Q) and intensity (I) to the mineral nutrient status of soils (Schofield, 1955).

Beckett (1964a), following the consideration of the Ratio law (Schofield, 1947), suggested that the I of K in a soil at equilibrium with its soil solution could best be defined by the ratio $a_K/(a_{Ca} + a_{Mg})^{1/2}$ of the soil solution. This equilibrium activity ratio for K or AR^K (Beckett, 1964a) has often been used as a measure of K availability to plants (Sumner and Marques, 1966; le Roux and Sumner, 1968).

Beckett (1964c) suggested that exchangeable K is held by two distinct mechanisms. The majority is held by general force fields comparable with those that hold exchangeable Na or Ca. A small proportion is held at sites offering a specific binding force for K but not for Ca and Mg. The electrochemical potential of exchangeable K in the diffuse double layer dictates the chemical potential of K in the soil solution. The K activity is also affected by the difference in electrical potential across the diffuse double layer that surrounds the exchange complex. Thus, no simple relationship exists between the activity of K in soil solution and quantity of K on the exchange phase (San Valentin et al., 1973). Moss (1967) and Lee (1973) note that a soil with a given complement of exchangeable K, Ca, and Mg gives rise to an activity ratio for K (AR^K) in the equilibrium soil solution that will be characteristic of that soil and independent of the soil-to-solution ratio and total electrolyte concentration. Moss (1967) noted that the ratio depends only on K saturation and the strength of adsorption of cations.

However, the relation of the amount of exchangeable K to AR^K must be specified to accurately describe the K status of a soil. Beckett (1964b) noted that different soils showing the same value of AR^K may not possess the same capacity for maintaining AR^K while K is removed by plant roots. Therefore, one must include not only the current potential of K in the labile pool but also the form of Q/I or the way in which potential depends on quantity of labile K present. These findings brought about the classic Q/I curves where the ratio of $a_K/(a_{Ca} + a_{Mg})^{1/2}$ is related to the change in exchangeable K to obtain the effect of quantity (exchangeable K) on intensity. The Q/I concept has been widely promulgated in the scientific literature to investigate the K status of soils (Evangelou et al., 1994).

The traditional method for Q/I analyses involves equilibrating a soil with solutions containing a constant amount of $CaCl_2$ and increasing the amounts of KCl (Beckett, 1964a). The soil gains or loses K to achieve the characteristic AR^K of the soil or remains unchanged if its AR^K is the same as the equilibrating solution. The AR^K values are then plotted versus the gain or loss of K to form the characteristic Q/I curve. From the Q/I plot, one can obtain several parameters to characterize the K status of a soil. The AR^K when the Q factor or ΔK equals zero is a measure of the degree of K availability at equilibrium or AR^K_e. The value of ΔK when $AR^K = 0$ is a measure of labile or exchangeable K in soils (ΔK°). The slope of the linear portion of the curve gives the potential buffering capacity of K (PBC^K) and is proportional to the CEC of the soil. The number of specific sites for K (K_x) is the difference between the intercept of the curved and linear portion of the Q/I plot at $AR^K = 0$ (Beckett, 1964b; Sparks and Liebhardt, 1981; Evangelou et al., 1994).

The traditional method described above is too time-consuming for routine analyses. Advances in ion-selective electrode (ISE) technology have allowed for more rapid Q/I analysis (Evangelou et al., 1994). Parra and Torrent (1983) developed an ISE simplified Q/I method whereby a single K-ISE in an electrochemical cell with liquid junction was employed to quantitate the K concentration (C_K) in equilibrated soil suspensions based on a successive addition procedure. The values of AR^K were estimated based on the expression, $AR^K = (11.5 - 0.3b)\ C_K + 22 \times 10^{-6}$, where b is the CEC ($\text{cmol}_c\ \text{kg}^{-1}$) based on the weight of the soil samples used. The method of Parra and Torrent (1983) is quicker than the traditional Q/I method because equilibration time is reduced to 10 min compared to 24 h for the traditional method. Parra and Torrent (1983) achieved results with their modified procedure that were comparable to the traditional method. Wang et al. (1988) modified the procedure of Parra and Torrent (1983) by making direct measurements of CR_K (concentration ratio: $C_K/(C_{Ca+Mg})^{1/2}$) values with Ca and K-ISEs in an electrochemical cell with or without liquid junction.

11.3.4.4 Plant K Analysis

Plant K analysis will not be discussed in any detail in this review. For extensive discussions on plant analysis, the reviewer

TABLE 11.9 Critical K Concentrations in Agronomic Crops

Crop	Time of Sampling	Plant Part	Critical Concentration[a]
Sugarbeet		Blade	10
Cotton		Leaves	<9–15
Wheat	Jointing (GS6)	Total tops	20–25
	Early boot (GS9)	Total tops	15–20
Rice	Flag leaf to mid-tillering		10–14
Corn	At tassel	Ear leaf	19
	At tassel	Leaves	17–27
	At silk	Sixth leaf from base	13
	At silk	Leaf opposite and just below ear shoot	20
Grain sorghum	Full heading	Second blade below apex	18
Alfalfa		Whole top	8–22
Red clover		Tops	15–22.5
Bermudagrass		Tops	13–15
Orchardgrass		Tops	23–25
Tall fescue		Tops	24–38
Kentucky bluegrass		Tops	16–20

Source: Westerman, R.L. (ed.). 1990. Soil testing and plant analysis. SSSA, Madison, WI. With permission of the Soil Science Society of America.

[a] Critical concentration is that nutrient concentration at which plant growth begins to decrease in comparison with plants above the critical concentration.

is referred to chapters in Westerman (1990). Table 11.9 lists the critical level or concentration of K for various agronomic crops. These levels are usually determined by relating yield (e.g., percentage of the maximum yield or growth rate) to nutrient concentration (g kg^{-1}) for a specific plant part sampled at a given stage of development (Munson and Nelson, 1990). This method is based on the principle that if an element such as K is deficient in a plant, growth rates and yield will be decreased. If one adds increasing amounts of K, the concentration of the element in the plant or plant part increases until an optimum level is attained. Using this approach, growth or yield is expressed as a percentage of the maximum. The zone between the deficient and optimum concentration can be referred to as the transition zone (Ulrich and Hills, 1967). Ulrich and Hills (1967) referred to the transition zone as the zone between nutrient concentrations that produced a 20% reduction in growth or yield and continues to those that cause optimum or 100% in the maximum yield. Dow and Roberts (1982) refer to this latter zone as the critical range where researchers select the yield reduction and nutrient concentrations that are acceptable.

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11.4 Bioavailability of Calcium, Magnesium, Sulfur, and Silicon

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William L. Pan

11.4.1 Introduction

Calcium, Mg, and S are essential mineral elements that are classified as macronutrients. While these three elements generally accumulate in plant tissues in higher concentrations (1.5–35 g kg^{-1}) (Table 11.10) than the micronutrients, they are not as commonly limiting in crop production as N, P, and K. Yet, when the soil bioavailability of Ca, Mg, and S is low, crop yield and quality can be suboptimal, depending on crop species and environmental conditions. Although Si is an essential element in the classical sense for diatoms and algal species of the genera Chrysophyceae and Equisetaceae (Epstein, 1999), it is considered a "beneficial" or "quasiessential" element for many other plant species, most notably rice (*Oryza sativa* L.) and sugarcane (*Saccharum officinarum* L.) (Epstein, 1994).

TABLE 11.10 Calcium and Magnesium Concentrations in Plant Tissue Considered Adequate for Plant Growth

		Range of Concentration		
		Ca	Mg	S
Plant	Tissue	g kg^{-1} Tissue		
Maize	Ear leaf	2.1–10.0	2.0–4.0	1.2–2.5
Rice	Leaves (tillering)	1.6–3.9	1.6–3.9	0.9–3.8
Wheat	Leaves (heading)	2.0–5.0	1.5–5.0	1.5–4.0
Soybean	Leaves	3.6–20.0	2.6–10.0	2.0–4.0
Peanut	Leaves and stem	7.5–20.0	3.0–7.5	2.0–3.0
Cotton	Leaves	19.0–35.0	3.0–7.5	2.9–15.0
Fruit trees	Leaves	14.0–21.0	4.1–6.8	1.3–3.0

Sources: Ca and Mg data adapted from Clark, R., Physiological aspects of calcium, magnesium, and molybdenum deficiencies in plants, in F. Adams (ed.), *Soil Acidity and Liming*, SSSA, Madison, WI, 1984, pp. 99–170; S data compiled from Asher, C.J. et al., Sulfur nutrition of tropical annual crops, in G.J. Blair and A.R. Till (eds.), *Sulfur in South East Asian and South Pacific Agriculture*, The University of New England, Armidale, New South Wales, Australia, 1983, pp. 54–64; Fox, R.L. and Blair, G.J., Plant response to sulfur in tropical soils, in M.A. Tabatabai (ed.), *Sulfur in Agriculture*, ASA, Madison, WI, 1986, pp. 405–434; Kamprath, E.J. and Jones, U.S., Plant response to sulfur in the Southeastern United States, in M.A. Tabatabai (ed.), *Sulfur in Agriculture*, ASA, Madison, WI, 1986, pp. 323–343; Jones, M.B., Sulfur availability indexes, in M.A. Tabatabai (ed.), *Sulfur in Agriculture*, ASA, Madison, WI, 1986, pp. 549–566; Tiwari, K.N., *Sulphur Agric.*, 14, 29, 1990.

The bioavailability of Ca, Mg, S, and Si is governed by the following factors: (1) parent material, (2) ion-exchange reactions, (3) biological transformations, (4) losses from the crop root zone by leaching and crop removal from the field, and (5) replenishment via atmospheric deposition, fertilizer, and soil amendments. Factors influencing Ca and Mg bioavailability are collectively discussed due to the similarity in soil chemical and plant nutritional behavior of these two elements. In contrast, S and Si chemistry in soils and plant nutrition are distinctly different, and are discussed separately in the latter half of the section.

11.4.2 Calcium and Magnesium

11.4.2.1 Overview of Calcium and Magnesium Nutrition

General reviews of the function of Ca and Mg in plants have been written by Clark (1984), Hanson (1984), and Poovaiah and Reddy (1996). A large proportion of Ca is found as Ca pectates in cell walls for structural rigidity, or as Ca oxalate and other organic acids in the apoplasm or vacuoles (Kinzel, 1989; Borchert, 1990). Calcium functions in plants include maintenance of membrane integrity (Caldwell and Haug, 1981) and cell wall stability (Konno et al., 1984), root (Poovaiah and Reddy, 1996) and shoot (Slocum and Roux, 1983) gravitropism, callose deposition (Lerchl et al., 1989), and regulation of several enzymes including α-amylase (Mitsui et al., 1984), protein kinases (Raghothama et al., 1987), and ATPases (Clarkson and Hanson, 1980).

Magnesium functions as an enzyme activator, in addition to serving as the coordinating central cation in the chlorophyll molecule. Magnesium activates numerous plant enzymes by bridging enzymes with ligand groups of substrates to optimize geometric conformation of enzyme systems involving the transfer of phosphate or carboxyl groups (Marschner, 1995). Systems activated by Mg include chlorophyll biosynthesis (Walker and Weinstein, 1991), chlorophyll degradation (Langmeier et al., 1993), photosynthesis (Pierce, 1986), protein synthesis (Cammarano et al., 1972), ATP synthesis (Lin and Nobel, 1971), and ATPases (Balke and Hodges, 1975), some of which are involved in phloem loading of sucrose (Williams and Hall, 1987).

11.4.2.2 Occurrence of Soil Calcium and Magnesium

Calcium and Mg occur in soils primarily in mineral forms and as ions on the exchange complex or in the soil solution. Little Ca or Mg occurs in organic complexes in soils (Mokwunye and Melsted, 1972). The relative amounts of Ca derived from parent materials rank as follows: calcareous sedimentary rock > basic igneous rock > acid igneous rock (Jenny, 1941). Parent materials rank with respect to Mg contents: basic igneous rock > acid igneous rock > sedimentary rock (Metson, 1974). Generally, soils with the highest 2:1 lattice clay content have the highest Mg contents (Mokwunye and Melsted, 1972). Contents of Ca and Mg in soils are presented in Table 11.11.

TABLE 11.11 Contents of Calcium and Magnesium in Various Soils

	Content		
	Ca	Mg	Source
Soil Type	(g kg^{-1})		
Temperate soils	0.7–36	1.2–15	Brady (1974)
Humid region soil	4	3	Brady (1974)
Arid region soil	10	6	Brady (1974)
Peat soils	1.1–48.3		Brady (1974)
Muck soils		0.7–5.7	Millar (1955)

11.4.2.3 Additions and Losses of Soil Calcium and Magnesium

Calcium and Mg accession by soils from atmospheric deposition may be significant in comparison to that removed in crop and forest plants (Johnson and Todd, 1987). Calcium and Mg depositions from precipitation in a Tennessee forest were 6.3 and 0.7 kg ha^{-1} year^{-1}, respectively (Johnson and Todd, 1987). Hedin et al. (1994) estimated atmospheric Ca depositions for Sweden, the northeastern United States, and the Netherlands in the 1990s to be 0.5, 1.0, and 4.2 kg Ca ha^{-1} year^{-1}, respectively. Atmospheric deposition of Mg and Ca has garnered more interest lately because of its potential to increase soil inorganic C and thereby reduce atmospheric CO_2 and global warming. Goddard et al. (2007, 2009) reported the highest deposition in the United States to be 1.0–1.4 kg Mg ha^{-1} year^{-1} in the Pacific Northwest and coastal Florida and to be 2.5–3.6 kg Ca ha^{-1} year^{-1} in the central Midwest–Great Plains region.

Considerable amounts of Ca and Mg are added to soils in the form of limestone (21%–32% Ca, 3%–12% Mg), fertilizers, and animal manures. Fertilizers used to specifically supply Ca to soils include gypsum (22% Ca) and calcium nitrate (19% Ca). Calcium may also be added to the soil incidentally while supplying P as superphosphates (14%–20% Ca). Common Mg-containing fertilizers include Epsom salts (10% Mg) and sulfate of potash magnesia (11% Mg).

Loss of Ca and Mg from the soil occurs through leaching and crop removal. Leaching losses of Ca and Mg from an aspen forest (*Populus tremuloides* Michx.) on *Typic Fragiochrept* soils averaged 39 and 9 kg ha^{-1} year^{-1}, respectively (Silkworth and Grigal, 1982). Cropping with perennial species reduces leaching losses in comparison to annuals. Calcium and Mg leaching losses were 193 and 104 kg ha^{-1}, respectively, from a continuous maize (*Zea mays* L.) rotation but only 64 and 48 kg ha^{-1} from a bluegrass (*Poa pratensis*) sod (Bolton et al., 1970). The application of Ca generally increases the leaching of Mg (Pratt and Harding, 1957), partly because the adsorption affinity for Ca is greater than that for Mg in non-vermiculitic soils (Hunsaker and Pratt, 1971). Leaching of Ca and Mg is accelerated by acidification, resulting from the nitrification of ammoniacal N sources (Schwab et al., 1989; Darusman et al., 1991). Under acid conditions, Al^{3+} and H^+ ions displace Ca^{2+} and Mg^{2+} from the exchange complex enabling leaching to occur.

Plant removals of Ca and Mg from the soil are dependent on the plant species and genotype and the harvested fraction that is removed from the field. The Ca concentration of plants varies considerably, but one generalization can be made: the Ca concentration of dicots, legumes, and crucifers (12–18 g kg^{-1}) is far greater than the 4 g kg^{-1} Ca typically found in grasses (Parker and Truog, 1920). In contrast, the Mg concentration of these groups of plants differs only slightly (~2–4 g kg^{-1}). Several authors have provided compilations of plant mineral composition that may be useful in estimating crop removal of Ca and Mg (Truog, 1918; Beeson, 1941). Magnesium removals were 5, 7, 8, and 16 kg Mg ha^{-1} for snap beans (*Phaseolus vulgare* L.), okra (*Hibiscus esculentus* L.), white potatoes (*Solanum tuberosum* L.), and sweet potatoes (*Ipomoea batatas* (L.) Lam.), respectively (Prince, 1951). More recently, representative uptakes and removals of Ca and Mg for several crops were reported by Buol (1995). Crop removal was in the range of 1–30 kg Ca or Mg ha^{-1} $year^{-1}$. Spring wheat (*Triticum aestivum* L.) accumulated 35 kg Ca ha^{-1} and 13 kg Mg ha^{-1}, whereas sugar beets (*Beta vulgaris* L.) accumulated 104 kg Ca ha^{-1} and 44 kg Mg ha^{-1} (Strebel and Duynisveld, 1989). Barber (1984) reported the total uptake of Mg by maize to be 45 kg ha^{-1}.

Hardwood tree species accumulate substantial amounts of Ca. For example, a mixed oak (*Quercus* sp.) stand grown on *Typic Paleudult* soils contained 1090 kg Ca ha^{-1} (16 kg Ca ha^{-1} $year^{-1}$) in the aboveground plant parts when harvested (Johnson and Todd, 1987). Loblolly pine (*Pinus taeda* L.) grown on the same soils removed only 196 kg Ca ha^{-1}. Both species removed about 45 kg Mg ha^{-1} from the soil (0.6 and 1.5 kg Mg ha^{-1} $year^{-1}$ for mixed oak and pine, respectively). In a more temperate climate, aspen removed 1034 kg Ca ha^{-1} and 95 kg Mg ha^{-1} from *Typic Fragiochrept* soils in northeastern Minnesota (Silkworth and Grigal, 1982).

11.4.2.4 Factors Affecting Availability of Soil Calcium and Magnesium

The activities of Ca and Mg in the soil solution, which directly influence the rates of uptake into plant roots, are dependent on the level of exchangeable cations (Albrecht, 1941) and the type of colloid. Organic matter and 1:1 clays retain Ca less tightly than 2:1 clay minerals, resulting in greater Ca availability at any given level of Ca saturation (Allaway, 1945; Mehlich and Colwell, 1945; Mehlich, 1946).

The affinity of cations for the exchange complex is dependent on the mineralogy of the colloid. For instance, the affinities of Ca and Mg for montmorillonite are similar, but the affinity of Mg for vermiculite is much greater than the affinity of Ca (Wild and Keay, 1964). Soils with exchange complexes arising from organic matter, peat, allophane, kaolinite, and oxides of Fe and Al have a higher affinity for Ca than for Mg (Hunsaker and Pratt, 1971).

The relative abundance of basic cations on the exchange complex affects the plant availability of these ions. Bear et al. (1945) asserted that the ideal base saturation of the exchange complex was 65% of Ca, 10% of Mg, and 5% of K. This concept was termed the basic cation saturation ratio. Although this ideology of soil test interpretation was widely adopted in the Midwestern United States for making fertilizer and lime recommendations (McLean and Brown, 1984), subsequent research demonstrated that a fairly broad range of basic cation saturations would produce equivalent crop yields (Hunter, 1949; Giddens and Toth, 1951; Key et al., 1962; Simson et al., 1979; Osemwota et al., 2007).

The degree of Ca saturation needed to provide sufficient plant-available Ca to crops is dependent on the colloid. Kamprath (1984) concluded from the results of a number of studies that a Ca saturation of about 25%–30% and an exchangeable Ca level of 1.0 $cmol_c$ kg^{-1} in highly weathered soils, dominated by kaolinitic clays and Fe/Al oxides, were adequate for supplying the Ca requirement of most plants. However, other factors such as Al may still limit plant growth at this level of Ca saturation. Soil solution Ca levels in acid soils ranging from 0.38 to 9.3 mM were reported by Kamprath (1978). The soil solution Ca level required for optimum growth of tropical legumes was 0.125 mM, much lower than the 2.0 mM required by temperate legumes (Kamprath, 1978). The soil solution Ca concentration necessary for maximizing cotton (*Gossypium hirsutum* L.) root growth was between 0.04 and 0.34 mM (Howard and Adams, 1965; Adams and Moore, 1983).

11.4.2.5 Calcium and Magnesium Soil–Plant Relationships

The transport of Ca and Mg ions to the root surface occurs by mass flow and diffusion. The soil solution composition and transpiration have been used to estimate the contribution of mass flow to the movement of these ions to plant roots (Barber, 1962). The difference between total nutrient accumulation in the plant and the estimate of that supplied by mass flow gives the relative contribution of diffusion and root interception. From these estimates, Barber (1962) recognized that mass flow could supply more than the required amount of Ca to plant roots of some soil–plant systems, resulting in a buildup of Ca in the rhizosphere that was observed in subsequent experiments (Barber and Ozanne, 1970). He also surmised that in situations where plant Ca demand is high and soil solution Ca is low, the supply of Ca to plant roots can be diffusion limited (Barber, 1962), resulting in a depletion of soluble Ca around the roots (Barber and Ozanne, 1970). Similarly, the mode of Mg transport is cropping system dependent. While mass flow could account for the Mg accumulated by wheat, a majority of Mg moving to sugar beet roots occurred by diffusion (Strebel and Duynisveld, 1989).

The presence of Ca is required throughout the root profile to maintain the integrity of root cell membranes and nutrient uptake (Haynes and Robbins, 1948). Insufficient Ca limits rooting into the subsoil of many Ultisols (Adams and Moore, 1983) and Oxisols (Ritchey et al., 1982) limiting the volume of soil explored and crop access to soil moisture supplies (Sumner et al., 1986; Sumner, 1995). Subsoil horizons in these soils may also be Al and H toxic (Adams and Moore, 1983). The Ca concentration of the soil solution needed to obtain maximum soybean (*Glycine max* (L.) Merr.) root growth increases as pH decreases and Al activity increases (Lund, 1970). The Ca/Al molar ratio of the soil solution was determined to be an excellent indicator of the potential for Al stress in tree species (Cronan and Grigal, 1995).

The effects of liming on soil Ca levels are initially confined to the zone of incorporation (Ritchey et al., 1980; Pavan et al., 1984, 1987). However, gypsum, phosphogypsum, and soluble Ca applications are effective at providing Ca deep into the soil profile. Forty-four weeks after application, soil Ca was increased in the upper 20 cm of a tropical Inceptisol, but phosphogypsum and $CaCl_2$ increased exchangeable Ca to a depth of 80 cm (Pavan et al., 1987). Growth of alfalfa (*Medicago sativa* L.) was increased in an Appling coarse sandy loam (*Typic Hapludult*) by a surface application of gypsum, which increased subsoil Ca and decreased soluble Al (Sumner et al., 1986; Sumner and Carter, 1988; Sumner, 1995).

Low supplies of Ca inhibit the nodulation, growth, and N fixation of bacteria associated with the roots of legumes (Albrecht, 1931; McCalla, 1937). No N fixation occurs unless the Ca saturation is >40% (Albrecht, 1937). The number of nodules and the amount of N fixed increased to 97% Ca saturation. The number of nodules per plant was positively correlated with the total Ca content of the primary root (Sartain and Kamprath, 1978). The Ca requirement for nodulation is greater at low pH and greater than that for the host plant (Alva et al., 1990). Calcium concentration of 0.5 mM maximized nodule number and weight at pH > 5, but 2.5 mM Ca was required at pH 4.5.

The ratio of Ca and Mg to other cations in the soil solution is important in Ca and Mg sufficiency to the plant. Maximum root length of cotton occurred when the activity of Ca exceeded approximately 15% of the total cation activity in the soil solution (Adams, 1966) and when exchangeable Ca was 13% or more of the total exchangeable cations (Howard and Adams, 1965; Adams and Moore, 1983). These relationships were nearly identical for the two soils examined even though the clay mineralogy of one soil was kaolinitic and that of the other was vermiculitic. Other crops respond similarly to the relative activity of Ca in the soil solution. Root growth of soybean (Lund, 1970) and loblolly pine (Lyle and Adams, 1971) were maximized when the ratio of Ca activity to total cation activity in the soil solution exceeded 10%–20%. Magnesium activity expressed as a function of total cation activity in the soil solution was closely correlated with ryegrass (*Lolium perenne* L.) Mg concentration (Salmon, 1964).

Calcium has low phloem mobility, which results in low Ca redistribution from older plant tissues to growing meristems (Jeschke and Pate, 1991), thereby imposing heavy reliance on concurrent Ca uptake and xylem transport to support new growth and development of vegetative and reproductive tissues (Morard et al., 1996). Plant organs with low rates of transpiration (e.g., new leaves, fruits, tubers) and low rates of xylem flow exhibit Ca deficiency disorders such as pod rot in peanut (*Arachis hypogaea* L.) (Cox et al., 1982; Sumner et al., 1988), internal brown spot in potato (Tzeng et al., 1986), blossom end rot in tomato (*Lycopersicon esculentum* Mill.) (Geraldson, 1957), bitter pit in apple (*Malus* sp.) (Perring, 1986), cork spot in pear (*Pyrus communis* L.) (Raese and Drake, 1993), and blackheart in celery (*Apium graveolens* L.) (Geraldson, 1954). Although low soil Ca levels may increase the frequency and severity of Ca deficiency in these crops, the deficiency is more a function of poor Ca translocation within the plant than of low soil Ca levels.

Calcium uptake and translocation occur at greater rates in actively growing meristematic regions than older root sections (Clarkson, 1984; Marschner, 1995). As a result, soil Ca availability must be optimized in the root zone at the time of active root development (Kratzke and Palta, 1986). Since environmental stresses that curtail root meristematic development can inhibit Ca uptake and translocation to shoot meristems, temperature and moisture stresses can exacerbate low soil Ca availability by imposing transient Ca deficiencies during critical periods of crop development. These environmental stresses by soil–Ca interactions explain why these Ca-related disorders are only displayed in some growing seasons. Foliar and fruit sprays, as well as maintenance of adequate soil Ca, are required to completely alleviate Ca deficiency disorders in sensitive crops (Geraldson, 1954, 1957; Raese and Drake, 1993).

11.4.2.6 Crop Response to Calcium and Magnesium Availability

Optimum soil Ca levels for maximizing yield and quality of peanuts are quite high, 538 kg ha^{-1} for small-seeded cultivars, and 1600 kg ha^{-1} for large-seeded cultivars (Walker et al., 1979; Gaines et al., 1989). Adsorption of Ca for kernel development occurs through the shell. Small-seeded cultivars have relatively more surface area per unit mass for Ca adsorption than large-seeded cultivars, hence the lower soil Ca requirement (Sumner et al., 1988). Reduced peanut yield and quality with low soil Ca are, partly due to destruction of pods by *Pythium* and *Rhizoctonia* fungal pathogens (Hallock and Garren, 1968).

Low Mg uptake by forage grasses can induce grass tetany in ruminants (Grunes et al., 1970), while low Ca in wheat forage leads to wheat pasture poisoning (Bohman et al., 1983). Low rates of Mg and Ca uptake due to suboptimal soil Mg and Ca availability can be exacerbated by high K (Thill and George, 1975; Ohno and Grunes, 1985), low soil temperatures (Miyasaka and Grunes, 1990), low P availability (Reinbott and Blevins, 1994), and wet soil conditions (Karlen et al., 1980). A survey of the incidence of grass tetany in the United States showed greater appearance of the problem in areas where soil parent material is naturally low in Mg and in cooler climates (Kubota et al., 1980). This study concurred with earlier findings of a greater incidence of grass tetany when the Mg concentration in forages is < 2.0 g Mg kg^{-1} and the K/(Ca + Mg) equivalent ratio is > 2.2 (Kemp and ‘t Hart, 1957).

Exchangeable Mg levels are often poorly related to crop yield response to applied Mg. Incongruities between exchangeable Mg and crop response primarily arise from two sources: a pool of available Mg in the A horizon soil that is not exchangeable, and an accumulation of available Mg below the A horizon. Nonexchangeable Mg may be an important source of plant-available Mg in some soils. Prince and Toth (1937) noted that only about 3%–4% of the total Mg content of Sassafras loam soil was exchangeable, suggesting fixation of Mg in an insoluble form in the colloidal fraction of the soil. Substantial plant uptake of nonexchangeable Mg occurred in five Coastal Plain soils where only 4%–9% of the total Mg content was in the exchangeable form (Rice and Kamprath, 1968). An additional 4%–10% of the total soil Mg content was extractable with dilute acid and was termed nonexchangeable, but plant available.

Significant fixation of Mg occurred in Oxisols and Ultisols when limed to pH above 7 (Sumner et al., 1978; Grove et al., 1981). Magnesium fixation was nearly 80% in a Bradson soil (*Typic Hapludult*) limed to a pH of 7.2 (Grove et al., 1981). Subsurface accumulations of Mg may also satisfy crop requirements for Mg. Adams and Hartzog (1980) noted that Mg accumulated in the subsoil of Ultisols could explain the lack of crop growth response to applied Mg on soils with extremely low exchangeable Mg in the topsoil. Exchangeable Mg levels were 10-fold greater in the subsoil (60–120 cm) of Wagram loamy sand (Arenic Kandiudult) than in the surface 40 cm (Schmidt and Cox, 1992).

Magnesium deficiencies are intensified by high levels of K or Ca (Welte and Werner, 1963). Severe Mg deficiency of potato and tobacco (*Nicotiana tabacum* L.) and mild Mg deficiencies of sugar beet and barley (*Hordeum vulgare* L.) occurred with heavy applications of K, even though exchangeable Mg levels were considered adequate (Walsh and O'Donohoe, 1945). Magnesium deficiency of citrus occurred when the Mg:K ratio was less than 2.5:1 (Pratt et a1., 1957). Magnesium deficiency of alfalfa occurred when Mg comprised <6% of the exchangeable cations (Prince et al., 1947). Similarly, Mg deficiency of sudangrass (*Sorghum sudanense* [Piper] Stapf) and clover (*Trifolium repens* L.) occurred when soils had <4% of the CEC occupied by Mg (Adams and Henderson, 1962), and in citrus when Mg was <4%–8% of the CEC (Martin and Page, 1969). Exchangeable Mg in excess of 10% of the CEC generally ensures that Mg availability to crops will not be limiting.

When Mg fertilizer applications are made to the soil surface, as in orchards or pastures, or to crops with high Mg requirements, high-solubility fertilizers are more effective than low-solubility materials (Boynton, 1947; Camp, 1947). For example, $MgSO_4$ and MgO increased grapefruit (*Citrus paradise* Macfad.) leaf Mg and alleviated visual symptoms of Mg deficiency within 9 months, whereas effects of $MgCO_3$ were not detected for more than 24 months (Koo, 1971). McMurtrey (1931) reported that considerably more dolomitic limestone was needed than soluble Mg fertilizer to prevent Mg deficiency in tobacco. Foliar applications of $MgSO_4$ can be more effective than soil applications of Mg in correcting Mg deficiency (Scott and Scott, 1951).

11.4.3 Sulfur

11.4.3.1 Overview of Sulfur Nutrition

Sulfur functions in plants have been reviewed by Duke and Reisenauer (1986), DeKok et al. (1993), and Marschner (1995). Sulfur is a structural constituent of organic compounds, some of which are uniquely synthesized by plants, providing animals with essential amino acids (methionine and cysteine) required to synthesize S-containing proteins. Disulfide bonding plays an important role in regulating the 3D conformation of proteins, affecting enzyme function. Sulfur is also contained in vitamins and coenzymes (thiamin, biotin, coenzyme A, and lipoic acid) (Mengel and Kirkby, 1982; Marschner, 1995). Other S-containing compounds include glutathione, an antioxidant (Bergmann and Rennenberg, 1993), and phytochelatin (Grill et al., 1987) as well as glucosinolates, which can serve as natural plant protectants (Schnug, 1993).

11.4.3.2 Occurrence of Soil Sulfur

Soil S exists in organic compounds, and adsorbed and soil solution SO_4^{2-}. Temperate region soils ordinarily contain between 0.1 and 2.0 g S kg^{-1} (Brady, 1974). Representative soils from arid regions contain more S than those from humid regions (0.8 and 0.4 mg kg^{-1}, respectively) (Brady, 1974). The predominant mineral form of S in arid soils is gypsum. Organic S comprises most of the S in most soils (>90% of the total) (Table 11.12). The C:S and N:S ratios of mineral soils vary. The organic pool is composed of three major sources of S (ester sulfates, amino acid S, and C bonded S). Ester sulfate is considerably more labile than C bonded S and is considered an important source of plant-available S. Ester sulfate and C bonded S accounted for 53% and 14% of total organic S, respectively, in 48 surface soils of Ghana (Acquaye and Kang, 1987). Ester sulfate ranged from 35% to 52% of total S in 54 Canadian soils (Bettany et al., 1973), from 20% to 65% in 6 Brazilian soils, and 43% to 60% in 6 Iowa soils (Neptune et al., 1975). Commonly, more than 30% of the total organic S in soils is not identified as either ester sulfate or C bonded S (Neptune et al., 1975; Acquaye and Kang, 1987). Amino acid S has been reported to account for 21%–31% of the total organic S content of two Australian soils (Freney et al., 1972) and 19%–31% of C bonded S in four mineral soils of Scotland (Scott et al., 1981).

Adsorbed SO_4^{2-} occurs on the positively charged exchange sites at the edges of clay minerals, organic matter, and Fe and Al oxides (Chao et al., 1962). The SO_4^{2-} adsorption capacity of a soil is decreased by increased soil pH and P content (Ensminger, 1954;

TABLE 11.12 Total-S, Organic-S, and C:N:S Ratio of Selected Mineral Soils

Origin	Total-S (mg kg^{-1})	Organic-S (mg kg^{-1})	C:N:S[a]	Reference
Saskatchewan, Canada	296	291	79:7.3:1.0	Bettany et al. (1973)
Iowa, U.S.A	319	305	92:8.3:1.0	Neptune et al. (1975)
Oregon, U.S.A	247	235	144:10:1.0	Harward et al. (1962)
Brazil, South America	166	146	139:7.1:1.0	Neptune et al. (1975)
Ghana, Africa	129	121	66:6.8:1.0	Acquaye and Kang (1987)
New Zealand	717	640	91:8.0:1.0	Perrot and Sarathchandra (1987)

[a] Organic C and S for all entries. Total N for all entries, except organic-N for Bettany et al. (1973).

Kamprath et al., 1956). Ultisols, Alfisols, and Oxisols have a high adsorption capacity due to an abundance of Fe and Al oxides and typically low pH. Binding is due to both electrostatic attraction and ligand exchange mechanisms (Marsh et al., 1987; Marcano-Martinez and McBride, 1989) and is highly dependent on the occurrence of positive charge on the soil colloids. Sulfate adsorption occurs rapidly, with nearly complete adsorption in minutes (Rajan, 1978) to days (Marcano-Martinez and McBride, 1989). However, a slower second stage of SO_4^{2-} adsorption also exists, rendering initially adsorbed SO_4^{2-} less available over time (Barrow and Shaw, 1977). Sulfate retention in acid soils is enhanced by Ca (Barrow, 1972; Ryden and Syers, 1976). Marcano-Martinez and McBride (1989) proposed that the stimulation in SO_4 adsorption arose from the bonding of a SO_4–Ca complex to the oxide surface by an O ligand and attraction of the Ca to a negatively charged hydroxyl.

11.4.3.3 Additions and Losses of Sulfur

Major sources of atmospheric S are oceans (24% of the total), soils (35%), volcanic activity (7%), and industry (35%) (Noggle et al., 1986). Sulfur accretion in soils occurs through direct adsorption of S gases and as rainfall. Distance from the source of S determines the amount of deposition. Sulfur in rainfall in Hawaii was exponentially related to distance from the ocean, averaging from 24 to 1 kg S ha^{-1} $year^{-1}$ from the coast to 24 km inland (Hue et al., 1990). As much as 168 kg S ha^{-1} was deposited on soils near industry, whereas urban and rural locations generally received <15 kg S ha^{-1} (Olson and Rehm, 1986). However, clean air legislation in the United States has substantially decreased S emissions from electric utilities and industrial boilers lowering S deposition >30% in the Northeast and Midwest (USEPA, 2010). Although industrial S emissions continue to be reduced in many industrialized countries, thus reducing S deposition (Schnug, 1991), S deposition in some countries remain quite high (Wang et al., 2004). Areas distant from the sea and devoid of industrial sources may have rainfall concentration of <0.1 mg L^{-1} (<0.1 kg S ha^{-1} per 100 mm rainfall) (Fox and Blair, 1986).

The replacement of ordinary superphosphate (12% S) with concentrated superphosphate (1% S) beginning in the late 1940s as the most common P source resulted in an increase in the occurrence of crop S deficiencies in the southern United States (Mehring and Lundstrom, 1938; Jordan, 1964). The use of gypsum as a Ca source for peanuts is another example of incidental S applications to soils. Nutritive applications of S are most frequently applied with N sources. The primary source of S in both liquid and solid N fertilizers is ammonium sulfate (24% S). Ammonium bisulfite (32% S) and thiosulfate (26% S) are also used to provide S in liquid fertilizers. Sulfur sources used in solid fertilizers are potassium sulfate (18% S), potassium magnesium sulfate (23% S), magnesium sulfate (14% S), and ordinary superphosphate. Elemental S is also used sometimes as a slow release source of nutritive S. The S becomes available to plants when the elemental S is oxidized by bacteria to SO_4^{2-} (Starkey, 1966). Oxidation rate is dependent on the size of the S particles, temperature, and moisture (Burns, 1967).

The retention of fertilizer S in surface soils is dependent on rainfall. Nearly 50% of the SO_4^{2-} added to maize was lost from the soil profile by leaching in the subhumid savannah of West Africa (1500 mm rainfall), whereas 100% of that added to a soil in the semiarid savannah (640 mm rainfall) remained in the soil profile to a depth of 105 cm (Friesen, 1991). Nearly all of 56 kg SO_4^{2-} added to Wagram loamy sand (Arenic Paleudult) was leached from the upper 0.45 m of soil with 445 mm of rainfall in 180 days (Rhue and Kamprath, 1973). Leaching losses (24 kg S ha^{-1} $year^{-1}$) exceeded crop removal (15 kg S ha^{-1} $year^{-1}$) even with S inputs from the atmosphere, crop seed, and fertilizer of 37 kg S ha^{-1} $year^{-1}$ and rainfall of 660 mm $year^{-1}$ in clay loam *Typic Eutrochrept* in central Sweden (Kirchmann et al., 1996). Liming and P fertilization decrease S adsorption and increase SO_4-S leaching (Bolan et al., 1988).

Crop removal of S varies by species. Cruciferous forages, alfalfa, and rapeseed (*Brassica napus* L.) accumulate large amounts of S, about 70 kg S ha^{-1} (Spencer, 1975). Sugarcane, coffee (*Coffea arabica* L.), and coconut (*Cocos nucifera* L.) accumulate moderate amounts of S (50 kg S ha^{-1}) (Spencer, 1975), while field crops and forages accumulate between 20 and 30 kg S ha^{-1} annually (Hoeft and Fox, 1986; Kamprath and Jones, 1986).

11.4.3.4 Factors Affecting the Availability of Soil Sulfur

Sulfate uptake by plants from the rooting solution can be saturated at relatively low concentrations of SO_4^{2-}. Soybean growth was optimized with 0.23 mM SO_4-S in nutrient solution (Elkins and Ensminger, 1971). Wheat achieved maximum S accumulation at 0.01 mM SO_4-S in solution (Reisenauer, 1969), while Fox and Blair (1986) concluded that approximately 0.14 mM SO_4-S was required in the soil solution to optimize growth of some tropical and subtropical crops. Early growth of eight agronomic crops was maximized at 0.06 mM in nutrient solution (Hitsuda et al., 2005). Soil reactions that buffer SO_4^{2-} concentrations above these critical soil solution levels are required to optimize S availability. Replenishment of SO_4^{2-} in the soil solution from organic and adsorbed sources is important in determining S supply to the plant (Ribeiro et al., 2001).

Extractable S fluctuates during the year. Tan et al. (1994b) reported that SO_4^{2-} and C-bonded S were inversely related throughout the year in three New Zealand pasture soils (Inceptisols), with the highest proportions of C-bonded S occurring in the winter and SO_4-S predominating in the spring. Although Watkinson and Kear (1996b) found SO_4-S to be constant throughout the year, in contrast to Tan et al. (1994b), they found extractable organic S concentrations to increase in the fall and winter in agreement with the prior study. Conservation tillage was suspected of limiting organic S mineralization in a silt loam Mollisol, resulting in S deficiency of maize (Rehm, 2005).

Sulfate adsorption is negligible in surface soils because little adsorption occurs at soil pH and phosphate levels conducive to crop plant growth (Kamprath et al., 1956). Therefore, most of the effective SO_4^{2-} adsorption in cultivated soils occurs in acid argillic horizons, which often retain enough S to support plant growth. The range in water soluble SO_4-S concentrations of surface horizons of Ultisols was 0.09–0.16 mM and in the argillic horizon, 0.20–0.36 mM (Camberato and Kamprath, 1986). The depth of the argillic horizon, in part, determines the plant availability of S accumulated in that soil layer. When the argillic horizon was >0.45 m deep, S fertilization increased the yield of tobacco in 2 of 10 site years on four Ultisols, but S deficiency did not occur when the argillic horizon was within 0.30 m of the soil surface (Smith et al., 1987). Linear decreases in maize earleaf S occurred as depth to the argillic horizon in two Ultisols increased from 0.2 to 1.0 m (Cassel et al., 1996).

The depth of crop rooting also influences the amount of S accessible to the crop in soils with subsoil accumulations of SO_4^{2-}. The amount of SO_4-S available to tobacco increased during the growing season and was greater than that of cotton on Durham coarse sandy loam soil (Paleudult) with <18 kg SO_4-S ha^{-1} in the upper 0.45 m of soil, but >72 kg SO_4-S ha^{-1} below 0.45 m (Kamprath et al., 1957). Differences in rooting between these crops explained the difference in S supply. Tobacco was previously shown to have 20% of its root activity below 0.45 m at 7 weeks after transplanting, whereas cotton had a much shallower root system with only 2% of its root activity at this soil depth 11 weeks after planting.

If root growth is prevented by impeding soil layers or high Al^{3+} levels, response to S may occur on soils with high levels of subsoil SO_4^{2-}. Failure to disrupt the tillage pan in a *Typic Kandiudult* prevented rooting into an SO_4^{2-} rich subsoil, and wheat grain yield was increased by S fertilization (Oates and Kamprath, 1985). On an adjacent soil that was subsoiled to allow rooting below the tillage pan, wheat obtained sufficient S for maximum crop productivity. Aluminum saturations in excess of 50% were implicated in reducing rooting in the SO_4^{2-} rich subsoil of Aquic Hapludult, resulting in an increase in maize yield with S fertilization (Kline et al., 1989). Limited crop rooting due to shallow soils causes S deficiency of maize and alfalfa in the Midwestern United States (Hoeft and Fox, 1986).

Sulfur commonly limits crop production in the subhumid and humid regions of the Pacific Northwest. Low atmospheric deposition of S (6 kg ha^{-1} $year^{-1}$), low S-containing surface irrigation water and basalt, granite, and volcanic ash parent materials have resulted in soils that have low total S content and low S bioavailability (Rasmussen and Kresge, 1986). Sulfur responses in cereals are dependent on having adequate N availability (Koehler, 1965) and high yield potential (Ramig et al., 1975). High rainfall and winter leaching potential in the humid regions of the Western coastal areas coupled with low S deposition create S deficient conditions in cereal, forage, fruit, and vegetable production (Rasmussen and Kresge, 1986). In contrast, arid soils in the western United States with high accumulations of soluble SO_4^{2-}, low leaching potential under nonirrigated conditions, or that are irrigated with high SO_4^{2-}-containing groundwater respond less frequently to S fertilization.

11.4.3.5 Assessing Levels of Soil Sulfur

Although organic S is the predominant form of S in most soils, many studies have demonstrated that total S or organic S are poorly correlated to crop response to applied S. Measures of extractable S, which may include soil solution, exchangeable, and organically bound SO_4^{2-} and S, have been reasonably successful at predicting response to S fertilization. Differences in the chemical extractant, concentration, temperature, and other procedural factors affect the quantity and form of S extracted from the soil (Anderson et al., 1992). The analytical procedure used to determine S in the extract also influences the quantity of S measured. Turbidimetric and anion-exchange chromatography methods measure only solution SO_4^{2-} levels, whereas inductively coupled argon plasma spectrophotometry measures total S in solution, including solution SO_4^{2-}, ester SO_4^{2-}, and soluble organic S (Anderson et al., 1992). The contribution of S in rainfall to the crop (Hoeft et al., 1973) and subsoil SO_4^{2-}, which are not often quantified, may also be reasons why soil S analysis for predicting crop response is not always reliable. An S deficiency risk index based on atmospheric deposition, annual rainfall and soil type, texture, and pH agreed well with the occurrence of reported S deficiency in cereals (McGrath and Zhao, 2007).

Extractable SO_4-S was not a good indicator of S sufficiency on seven silt loam Mollisols in Minnesota (O'Leary and Rehm, 1991). However, the amount of S mineralized during a 4 or 12 week aerobic incubation was related to maize yield response to S fertilization, indicating the importance of organic S to plant-available S in some soils. Approximately 30% of the S extracted from eight field-moist New Zealand soils was in the soluble organic form, while the remainder was SO_4^{2-} (Tan et al., 1994a). Labile organic-S determined S availability in Oxisols with low and medium S adsorption capacity (SAC), but mineral SO_4-S forms determined S availability in high SAC soils (Ribeiro et al., 2001). Extractable organic S is a good predictor of the amount of labile S. Organic S extracted by potassium phosphate was a better predictor of maximum yield in pastoral soils of New Zealand than initial SO_4^{2-}; SO_4^{2-} mineralized during short-term incubation, organic S extracted by calcium phosphate, or organic S extracted by sodium bicarbonate (Watkinson and Kear, 1996a). Potassium phosphate extracted more organic S from high organic matter soils than the commonly used calcium phosphate extractant. Blair et al. (1991) found that extraction with KCl was superior to either calcium phosphate or sodium bicarbonate as an indicator of pasture response to fertilizer S in 18 soils from northern New South Wales, Australia. Critical levels for the three extractants ranged from 6.5 to 8.4 mg kg^{-1}. The bicarbonate extractant in this case was probably inferior to the others because it overestimated the contribution of available S arising from the ester SO_4^{2-} fraction.

11.4.3.6 Crop Response to Sulfur Availability

Sulfur deficiencies occur worldwide, but are most prevalent in areas where S accretions from atmospheric deposition, the S contents of fertilizers and pesticides, and irrigation water are low, and soils are sandy with low soil organic matter content, and rainfall is plentiful (Tisdale et al., 1986).

Numerous examples of crop S deficiencies and responses to S fertilization are presented by Tabatabai (1986). Recently, the incidence of S deficiency appears to be increasing in the United States as a result of less atmospheric S deposition. Sawyer et al. (2009) in Iowa noted only 3 S deficiencies out of 200 research trials with maize and soybean in 40 years prior to 2005. Since then, about two-thirds of more than 50 maize and of 6 alfalfa trials have responded to S fertilization (Sawyer et al., 2009). Many years of cropping without S fertilization may also contribute to the increased occurrence of S deficiency.

Sulfur deficiencies decrease crop yields and in certain instances also reduce crop nutritional value and quality. Sulfur fertilization of subirrigated meadow vegetation (Nichols et al., 1990) and forage maize (O'Leary and Rehm, 1990) increased dry matter accumulation, but did not affect crop quality. In other instances, S fertilization increased both the protein- and S-containing amino acid content of forages, resulting in increased animal performance (Rendig, 1986). In mixed pastures, S application up to 90 kg S ha^{-1} increased total forage production and the proportion of clover to grass (Jones, 1964). Numerous yield responses of coastal bermudagrass (*Cynodon dactylon* (L.) Pers.) to S fertilization have been documented (Kamprath and Jones, 1986). Alfalfa is the most S responsive crop grown in the Midwest and Northeast regions of the United States (Hoeft and Fox, 1986).

Cyst(e)ine and methionine levels of seeds are increased by S fertilization resulting in more nutritious foods (Rendig, 1986). Baking quality of wheat flour is highly dependent on the S concentration of the grain and is increased by S fertilization (Haneklaus et al., 1992). The S status (Zhao et al., 1995) and baking quality (Zhao et al., 1999) of British wheat decreased substantially in the 12 years after 1981 due to reduced atmospheric S deposition. Bread dough made from S-deficient grain resists extension and has lower extensibility (Moss et al., 1981), which is related to low albumin proteins (Wrigley et al., 1984). Sulfur-containing metabolites influence the flavor of several crops including asparagus (*Asparagus officinalis* L.) and various *Allium* sp. (Schnug, 1990).

11.4.4 Silicon

11.4.4.1 Overview of Silicon Nutrition

The roles of Si in plant nutrition and agriculture have been recently reviewed in Datnoff et al. (2001), Korndörfer and Lepsch (2001), Ma et al. (2001), and Snyder et al. (2007). Uptake of $Si(OH)_4$ (Lewin and Reimann, 1969) appears to be active in Si accumulators such as rice, sugarcane, and bamboo [*Sasa veitchii* (Carrière) Rehder], and passive in others such as oats (*Avena sativa* L.) and other "dryland" Gramineae (Jones and Handreck, 1967), while legumes and other dicots appeared to exclude $Si(OH)_4$. Although concentrations of Si in normal plants range from 1 to 100 g kg^{-1} of dry weight (Epstein, 1999), those in Si accumulators greatly exceed the levels of any essential plant nutrients taken up from the soil (e.g., >200 g Si kg^{-1} dry weight in mature bamboo leaves [Motomura et al., 2002]). Silica gel (hydrated amorphous silica, $SiO_2 \cdot nH_2O$) is present as specialized "skeletal" structures in the epidermal cells and cell walls of many plants (Lewin and Reimann, 1969). These structures when enhanced by Si fertilization may be responsible for increased resistance to plant diseases and insect pests. Solid silica in plant tissue occurs as opal (Jones et al., 1966) in the form of phytoliths, which persist in soil after plant decay.

11.4.4.2 Occurrence of Soil Silicon

Silicon, next to O_2, is the most abundant element in soils, ranging from 2% to 45% and averaging about 31% in the conterminous United States (Shacklette and Boerngen, 1984). Commonly occurring Si minerals include quartz, tridymite, cristobalite, and inorganic and biogenic opal with solubilities ranging from 1 to 70 mg L^{-1} (Wilding et al., 1977). The Si:O ratio is 1:2 in these minerals. Silicon is also a component of other primary and secondary minerals and of the phyllosilicate clay minerals. Silicon occurs in the soil solution as $Si(OH)_4$ at 0.1–0.6 mM levels (Epstein, 1999).

Silicon bioavailability in soil is primarily a function of Si quantity and solubility as determined by weathering and soil pH. $Si(OH)_4$ reacts with Fe, Al, Mn, and other heavy metals to form sparingly soluble silicates (Snyder et al., 2007). $Si(OH)_4$ is sorbed by Fe and Al oxides with the latter sorbing more Si than Fe oxides (Jones and Handreck, 1965). Sorption by both sesquioxides increases with increasing pH (Beckwith and Reeve, 1963; McKeague and Cline, 1963b; Jones and Handreck, 1965). Thus, $Si(OH)_4$ in the soil solution decreases as pH rises (Beckwith and Reeve, 1963, 1964; McKeague and Cline, 1963a, 1963b; Jones and Handreck, 1965). Flooding increases soil solution $Si(OH)_4$, probably due to the reduction of Fe, which releases adsorbed $Si(OH)_4$ (Savant et al., 1997b). Carbonates also sorb Si but not as strongly as sesquioxides (Beckwith and Reeve, 1963). Across 23 paddy soils in China available Si was positively correlated with pH, silt, clay, and $CaCO_3$ content of the soil and negatively correlated with organic matter and amorphous Fe oxide (Liang et al., 1994).

Leaching of $Si(OH)_4$ from the soil profile is a characteristic of soil weathering. Little Si is accrued in soil via atmospheric deposition, but substantial additions may be realized with irrigation. In Hawaii, rainfall and mist Si concentrations were 0.2 and 0.05 mg L^{-1}, respectively, whereas well water contained between 2.5 and 30 mg Si L^{-1} (Fox et al., 1967). From a survey of the literature (Savant et al., 1997a), irrigation water Si concentrations ranged from ~2 to 16 mg Si L^{-1}.

11.4.4.3 Crop Response to Silicon Bioavailability

Silicon application increases crop resistance to disease organisms and insect pests while increasing yield. Rice, sugarcane, and barley show the most consistent response to increased Si bioavailability (Snyder et al., 2007). Beneficial responses occur most often on organic soils (Histisols), highly weathered soils (Ultisols and Oxisols), and sandy Entisols (Datnoff and Rodrigues, 2005).

Silicon increases plant resistance to abiotic stresses including moisture deficit, high temperatures, and salinity (Ma, 2004), while it suppresses several diseases of rice including blast (*Magnaporthe grisea*), brown spot (*Cochliobolus miyabeanus*), and stem rot (*M. salvanii*) (Datnoff and Rodrigues, 2005).

Datnoff (2005) summarized the beneficial effects of Si fertilization in reducing several diseases affecting both warm- and cool-season turfgrasses. Pathogens suppressed include *Bipolaris cynodontis*, *M. grisea*, *Pythium aphanidermatum*, *Rhizoctonia solani*, *Sclerotinia homeocarpa*, and *Sphaerotheca fuliginea*. Reynolds et al. (2009) summarized the indirect and direct impacts of Si augmentation of plants on herbivorous insects. Increased plant Si impacts several insect feeding guilds including lepidopteran borers, folivores, and phloem- and xylem-feeders. Silicon applied to the plant foliage also increased plant resistance to some insect pests (Reynolds et al., 2009).

Yield increases in rice due to Si application ranged from 10% to 30% (Savant et al., 1997b); while in China, wheat was less responsive (4%–9%) than rice (5%–21%) (Liang et al., 1994). These beneficial responses in both crops were partly due to reduced diseases and lodging. Sugarcane responses to Si fertilization in Florida, Hawaii, and Mauritius (Matichenkov and Calvert, 2002) ranged from 17% to 30% in total dry matter and 23% to 58% in sucrose content. Beneficial effects were due to increased disease-, pest-, and frost-resistance. Responses of barley to Si in Russia and England (Snyder et al., 2007) were generally in the range of 10%–20%, but several exceeded 40%.

Slags produced from various metal smelters are often used as sources of Si for crop production. Slag composition can be quite variable in Si concentration ranging from 5%–10% in steel mill to 15%–20% Si in blast furnace slags from pig iron manufacture as well as in other essential elements including Ca, Mg, Mn, and Fe (Savant et al., 1997b). Solubility of Si in slag varies widely (–20% to ~70%) (Savant et al., 1999) with finer particles being more effective than larger pellets as a source of Si for increasing rice plant tissue Si and reducing disease incidence (Datnoff et al., 1992).

Silicon application rates needed to optimize crop yield are substantially higher than those of any other essential plant nutrient. For example, recommended Si fertilization rates (as Ca silicate slag) to optimize rice yield in Florida are 1500 kg Si ha^{-1} at a soil test of <6 mg L^{-1} soil and 1120 kg Si ha^{-1} at 6–24 mg L^{-1} soil (Korndörfer et al., 2001). Suggested rates of slag application for sugarcane production range from 1 to 9 Mg ha^{-1} (approximately 200–1800 kg Si ha^{-1}), dependent on the slag and soil Si concentration (Savant et al., 1999). The high rates of Si application needed to optimize plant bioavailability arise as a result of reduced solubility in the "fertilizer" material, sorption by the soil, and the large quantity needed by the plant. Although significant residual effects of a single Si application have been observed over 5 years of cropping, 50%–75% of that applied was unavailable after 5 years as assessed by chemical and biological techniques (Khalid and Silva, 1978; Khalid et al., 1978), suggesting transformation into unavailable forms. In another study, the residual value of a 3 Mg Si ha^{-1} application for reducing disease and increasing of rice yield in the second growing season was approximately equivalent to 1 Mg Si ha^{-1} applied in that season (Datnoff et al., 1991). Because Si uptake may be as high as 700 kg ha^{-1} for sugarcane, 300 kg ha^{-1} for rice, and 150 kg ha^{-1} for wheat (Snyder et al., 2007), crop removal substantially reduces soil Si (Savant et al., 1997a).

Several soil testing methods to evaluate soil Si sufficiency typically remove a fraction of sorbed Si in addition to water soluble Si. The chemical extractant, solution pH, ionic strength, shaking time, and soil:solution ratio vary among methods and remove different amounts of Si from the soil (Savant et al., 1999). For example, water, phosphate-acetate, acetate, and modified Truog (H_2SO_4) methods were evaluated as potential soil test methods for identifying Si deficient soils for sugarcane production (Fox et al., 1967) with critical values being 9, 50, 20, and 40 mg kg^{-1}, respectively. Although each method extracted different amounts of Si, all methods were equally effective in predicting plant Si accumulation ($r > 0.92$).

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11.5 Bioavailability of Micronutrients

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11.5.1 Introduction

Minor or trace elements include both biologically essential (e.g., Cu, Mn, Fe, B, Ni, Mo, Cl, and Zn) and nonessential (e.g., Pb, Cd, and Hg) elements. The essential elements (for plant, animal, or human nutrition) are required in low concentrations and hence are known as "micronutrients" (Table 11.13). Because the nonessential minor elements are phyto- and/or zootoxic even at low concentrations, they are widely known as "toxic elements" or

TABLE 11.13 Sources of Micronutrients in Soils and Their Functions in Plant and Animal

Micronutrient	Ionic Species in Soil Solution	Sources	Functions
Boron (B)	$H_3BO_3^o$	Fertilizers, rocks, fly ash	Plant: required for cell wall strength and development, cell division, fruit and seed development, sugar transport, and hormone development
Chloride (Cl)	Cl^-	Muriate of potash, micas, feldspars	Plant: controls opening and closing of stomata, balances K in cells, required in photosynthesis, for ionic balance and transport, reduces susceptibility to disease
Cobalt (Co)	Co^{3+}, Co^{2+}, $[Co(H_2O)_6]^{2+}$; $[CoCl_4]^{2-}$	Fertilizers, mafic rock, minerals	Plant: required for N fixation, stem and coleoptiles elongation, leaf disc expansion, curvature of slit stems, opening of hypocotyl hooks, and bud development Nonenzymatic: Cobalamine or vitamin B12—erythropoiesis, granulopoiesis, glucose homeostasis
Copper (Cu)	Cu^{2+}, $Cu(OH)_2^o$, $CuOH^+$, $CuSO_4^o$, $CuCO_3^o$, $Cucl^+$, $CuHCO_3^+$	Fertilizers, fungicides, electrical, paints, pigments, timber treatment, mine tailings	Plant: enzyme activator, major function in: photosynthesis, reproductive stage, respiratory enzymes, indirect role in chlorophyll production, increases sugar content, intensifies color, and improves flavor in fruits and vegetables. Animal: Enzymatic: Cytochrome oxidase—Principal terminal oxidase; Lysyl oxidase—Lysine oxidation; Tyrosinase—Skin pigmentation—Cytocuprein: Superoxide (O_2^-) dismutation. Nonenzymatic: Growth promoter in swine and poultry; lameness control in cattle
Iron (Fe)	Fe^{2+}, $FeCl^+$, $Fe(OH)_2^+$, $Fe\,H_2PO_4^+$, $Fe(OH)_3^-$, $Fe\,(SO_4)_2^-$, $Fe(OH)_4^{2-}$	Fertilizers, iron core, rocks, minerals	Plants: Promotes formation of chlorophyll, enzyme mechanism operates the respiratory system of cells, reactions involving cell division, energy transfer within the plant, a constituent of certain enzymes and proteins, plant respiration, and plant metabolism, and involved in N fixation
Manganese (Mn)	Mn^{2+}, $MnOH^+$, $MnCl^+$, $MnCO_3^o$, $MnHCO_3^+$, $MnSO_4^o$	Fertilizer, rocks	Plant: role in metabolism of organic acids, activates the reduction of nitrite and hydroxylamine to ammonia, role in enzymes involved in respiration and enzyme synthesis, activator of enzyme reactions such as oxidation/reduction, hydrolysis and direct influence on sunlight conversion in the chloroplast, assimilation of carbon dioxide in photosynthesis, synthesis of chlorophyll and in nitrate assimilation, manganese activates fat forming enzymes, formation of riboflavin, ascorbic acid, and carotene, electron transport during photosynthesis, and involved in the Hill Reaction where water is split during photosynthesis Animal: Enzymatic: Arginase—Urea formation; Pyruvate carboxylase—Pyruvate metabolism
Molybdenum (Mo)	MoO_4^{2-}, $HMoO_4^-$, $H_2MoO_4^o$	Fertilizer	Plant: essential for N fixation and nitrate reduction, converting nitrate into amino acids, conversion of inorganic P into organic forms within the plant Enzymatic: Xanthine oxidase—Purine metabolism; Sulfite oxidase—Sulfite oxidation
Nickel (Ni)	Ni^{2+}, $NiSO_4^o$, $NiHCO_3^+$, $NiCO_3^o$	Alloys, batteries, mine tailings	Plant: required for Fe absorption, participate in N metabolism of legume during the reproductive phase of growth, phytoalexin synthesis, and plant disease resistance Nonenzymatic: Increases bone strength in poultry
Selenium (Se)	$HSeO_3^-$, SeO_4^{2-}, SeO_3^{2-}, $MgSeO_4^o$,	Fertilizers, selenide minerals, recycled electronic devices, sulfide ore	Plant: increases the tolerance of plants to UV-induced oxidative stress, delays senescence, promotes the growth of ageing seedlings, regulates the water status of plants under condition of drought Enzymatic: Glutathione peroxidase—Protection against haemoglobin oxidation. Nonenzymatic: Growth promoter
Zinc (Zn)	Zn^{2+}, $ZnSO_4^o$, $ZnCl^+$, $ZnHCO_3^+$, $ZnCO_3^o$	Fertilizers, galvanizing, dyes, paints, timber treatment, mine tailings	Plant: formation of growth hormones (auxin), seed and grain formation, promotes maturity, protein synthesis and transformation, and consumption of carbohydrates Animal: Enzymatic: carbonic anhydrase—CO_2 formation; regulation of acidity; carboxypeptidase—Protein metabolism; alcohol dehydrogenase—alcohol metabolism; cytocuprein—superoxide (O_2^-) dismutation Nonenzymatic: Eczema control in cattle

"heavy metals" or "heavy metalloids" and include both cationic and anionic forms. Both groups can be toxic to plants, animals, and humans above certain concentrations specific to each element and target biota.

Soil represents the major sink for minor elements released into the biosphere through both geogenic (i.e., weathering or pedogenic) and anthropogenic (i.e., human activities) processes. The mobility and bioavailability of minor elements in soils are affected by adsorption onto mineral surfaces, precipitation as salts, formation of stable complexes with organic compounds, and bioaccumulation and biotransformation by microorganisms (Adriano, 2001). Soil is a biologically active integral component of the terrestrial ecosystem in which higher plants, soil constituents, and soil organisms interact, where the available energy in the form of organic and inorganic compounds promotes microbial activity and microbial weathering processes.

Bioavailability, which refers to how much of an element is available to living biota including plants and soil microorganisms, defines the relationship between its concentration in the terrestrial environment and its level that actually enters the receptor causing either a positive or negative effect on the organism. Bioavailability is species-specific because the dose that reaches an organism's target organs or tissues resulting in a biological response varies among receptors (Stokes et al., 2005). Bioavailability often refers to the extent to which an element can desorb, dissolve, or otherwise dissociate from the solid phase in which it occurs to become accessible (i.e., bioaccessibility) for absorption (Alexander and Alexander, 2000).

Chemical bioavailability is now considered an important environmental consideration because availability may be mitigated once the element comes in contact with the soil or sediment. For this reason, both soil fertility status as well as risk assessment of contaminated sites require quantification of chemical bioavailability as is carried out for other nutrients in fertilizer recommendations and risk calculations (Hrudey et al., 1996). In both fertilizer recommendations and contaminated site assessment, bioavailability, which addresses the fundamental issue of exposure of a receptor (plant) to the element in question, is not dictated by the total element concentration in the soil, but rather by the fraction of the total amount that is biologically available. Consequently for the element to become available, it must be desorbed from the soil particle and transported to the root via the soil solution. The amount of an element in soil that is bioavailable depends on a variety of factors including the properties of both the element and the soil environment (Black, 2002; Adriano et al., 2004).

This chapter covers the following aspects of the essential micronutrients (Cu, Zn, Se, Mo, Fe, Mn, Co, Ni, B, and Cl) in relation to their bioavailability in soils: (1) sources and dynamics, (2) indicators and factors affecting bioavailability, and (3) bioavailability implications to soil testing.

11.5.2 Sources of Micronutrients

Just like the major elements such as P and K, micronutrients reach the soil environment through both pedogenic and anthropogenic processes (Tables 11.14 and 11.15). Most micronutrients

TABLE 11.14 Selected References on Micronutrient Concentrations (g kg^{-1}) in Cattle, Poultry and Swine Manure By-Products, and Municipal Biosolids

Sources	Co	Cu	Mn	Mo	Ni	Fe	Se	Zn	References
Cattle manure	—	0.029	0.372	—	0.009	0.009	—	0.067	de Abreu and Berton (1996)
	—	0.139	—	0.002	0.0008	0.002	0.003	0.191	McBride and Spiers (2001)
	—	0.200	0.700	—	—	—	—	0.800	Eneji et al. (2001)
	0.003	—	0.357	—	0.008	0.005	0.0005	0.164	Raven and Loeppert (1997)
	—	0.016	0.149	—	—	—	—	6.480	Wallingford et al. (1975)
	—	0.037	—	—	0.004	0.003	—	0.153	Nicholson et al. (1999)
	—	0.033	—	—	0.006	0.007	—	0.133	Nicholson et al. (1999)
Poultry manure	—	0.400	1.800	—	—	—	—	2.300	Eneji et al. (2001)
	0.313	—	0.246	—	—	—	—	0.327	Wood et al. (1996)
	0.002	0.743	0.607	0.004	0.010	2.760	0.001	0.501	Jackson et al. (1999)
	0.002	0.031	0.166	0.005	—	—	0.0004	0.158	Capar et al. (1970)
	0.006	0.748	0.956	0.006	0.015	1.095	—	0.718	Moore et al. (1998)
	0.008	0.019	0.271	—	0.014	0.013	—	0.252	Bomke and Lowe (1991)
Swine manure	—	1.338	0.869	—	0.012	0.014	—	1.440	de Abreu and Berton (1996)
		1.000	2.100	—	—	—	—	2.900	Eneji et al. (2001)
	—	1.279	0.197	—	—	—	—	0.231	Mullins et al. (1982)
	—	0.374	—	—	0.007	0.003	—	0.431	Nicholson et al. (1999)
Biosolids	0.017	0.294	6.230	0.011	0.075	48.100	0.001	1.250	Jackson et al. (1999)
	—	0.119	0.214	—	0.015	0.324	—	0.328	de Abreu and Berton (1996)
	—	0.089	0.350	—	4.304	0.085	—	0.354	de Abreu and Berton (1996)
	0.010	1.346	0.194	0.014	—	0.003	0.003	2.132	Capar et al. (1970)
	0.004	—	0.142	—	0.031	0.130	0.001	0.450	Raven and Loeppert (1997)

TABLE 11.15 Total and Water-Soluble Micronutrient Concentration (g kg^{-1}) in Fertilizers, Dairy Cattle, Poultry and Swine Manures, and Biosolids

	Dairy Cattle[a]		Poultry[b]		Swine[a]		Sewage Sludge[c]		NPK (15-30-15)[d] Fertilizer	
Element	Total	Water Soluble	Total	Water Soluble	Total	Water Soluble	Total	Water Soluble	Total	Soluble Water
Co			0.0068	0.0031					—	—
Cu	0.356	0.112	0.656	0.314	0.419	0.130	0.148	0.0044	0.700	0.700
Mn	0.345	0.017	0.274	0.006	0.865	0.014			5.000	5.000
Ni	0.009	0.001	0.0087	0.005	0.012	0.003	0.028	0.0001	—	—
Se	—	—	0.0095	0.0038					—	—
Zn	0.765	0.123	0.246	0.018	1.210	0.023	0.330	0.0016	0.600	0.600
Fe									1.500	1.500
Mo									0.005	0.005

[a] Bolan et al. (2003a).
[b] Jackson and Bertsch (2001).
[c] Henry and Harrison (1992).
[d] McCauley (2009).

occur naturally in soil parent materials, chiefly in forms that are not readily bioavailable for plant uptake. Often the micronutrient concentrations released from the soil by natural pedogenic processes are largely related to the origin and nature of the parent material. On the other hand, micronutrients added through anthropogenic activities including fertilization typically have higher bioavailability (Naidu et al., 1996a). Fertilizer and manure additions to agricultural soils are the major sources supplying micronutrients for plant growth (Tables 11.15 and 11.16). Anthropogenic activities, associated with industrial processes, manufacturing and the disposal of domestic and industrial wastes, also contribute to micronutrient enrichment of soils (Adriano, 2001).

11.5.3 Dynamics of Micronutrients in Soils

Micronutrients undergo both chemical and biological transformations including retention, redox and methylation reactions while they are retained in the soil by sorption, precipitation, and complexation, and removed by plant uptake and leaching. Although most micronutrients are not subject to volatilization losses, Se tends to form gaseous compounds through redox and methylation reactions (Frankenberger and Karlson, 1995). When micronutrient solution concentration is low and sorption surfaces large, sorption/desorption processes will govern the soil solution concentration (Tiller, 1989) while the fate of micronutrients in the soil depends on both soil properties and environmental factors.

11.5.3.1 Chemical Transformation Processes

11.5.3.1.1 Sorption and Complexation

Chemical interactions that contribute to micronutrient retention by soil colloids include sorption and complexation with inorganic and organic ligands. Charged ions are attracted to charged soil surfaces by electrostatic and/or stronger covalent bonds (Mott, 1981), which can be specific or nonspecific in nature (Bolan et al., 1999). In nonspecific adsorption, the ion charge balances that on the soil surface by electrostatic attraction while in specific adsorption, chemical bonds form between the ions and the soil surface (Sposito, 1984). Metal ion binding on soil organic matter (SOM) is strongly pH dependent due to competition between metal ions and protons for the available binding sites and to the effect of pH on the electric charge development on SOM. Detailed descriptions of these processes are presented in Chapters 11 and 19 of *Handbook of Soil Sciences: Properties and Processes*.

11.5.3.1.2 Cation-Exchange Reactions

Although most soils have a net negative charge, this charge plays only a minor role in micronutrient reactions in soil. In general, for ions having the same charge, ions with the larger hydrated radius are selectively adsorbed. The many ion exchange selectivity coefficients reported in the literature have been determined in the presence of ligands but the effects of ion-pair formation and complex ions have been generally ignored. Comparisons between reported selectivity coefficients for various systems and exchange reactions can, therefore, not be made with confidence (Sposito, 1984). Very little information is available on the values of the coefficients for ion exchange between dominant and micronutrient cations in soil–water systems.

11.5.3.1.3 Specific Adsorption at Mineral Surfaces

Although most macronutrient cations are weakly retained by soils in exchangeable form, most micronutrient cations are strongly retained as inner sphere complexes with variable charged surfaces by the formation of covalent bonds. Although specific adsorption in the form of inner sphere complexes with variable charged mineral surfaces occurs most readily for metals that hydrolyze in water, such as most of the transition elements (Cu, Fe, Mn, Co, Zn, Ni) and some other divalent

TABLE 11.16 Micronutrient Content of Some Commonly Occurring Fertilizers Used in Agricultural Production

Micronutrient	Fertilizer Compound	Chemical Formula	Concentration (g kg^{-1})
Boron	Boric acid	H_3BO_3	89
	Borax	$NaB_4O_7 \cdot 10H_2O$	110
		NaB_4O_7	214
	Solubor©		175
Cobalt	Cobalt sulfate heptahydrate	$CoSO_4 \cdot 7H_2O$	210
	Cobalt carbonate	$CoCO_3$	460
	Cobalt amino acid chelate	—	20
	Cobalt chelate	CoEDTA	130
Copper	Copper sulfate monohydrate	$CuSO_4 \cdot H_2O$	390
	Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	250
	Copper oxide	CuO	750
	Copper oxy-chloride	$CuCl_2 \cdot 3Cu(OH)_2$ or $Cu_2Cl(OH)_3$	590–700
	Copper chloride	$CuCl_2$	170
	Copper chelate	CuEDTA	80–130
Chloride	Potassium chloride (muriate of potash)	KCl	500
Iron	Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	400
	Ferric sulfate	$Fe_2(SO_4)_3 \cdot 4H_2O$	230
	Ferrous oxide	FeO	770
	Ferric oxide	Fe_2O_3	690
	Ferrous ammonium phosphate	$Fe(NH_4)PO_4 \cdot H_2O$	290
	Ferrous ammonium sulfate	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	140
	Iron ammonium polyphosphate	$Fe(NH_4)HP_2O_7$	220
	Iron chelates	NaFeEDTA	50–140
		NaFeHEDTA	50–90
		NaFeEDDHA	60
		NaFeDTPA	100
	Iron polyflavonoids	—	90–100
	Iron lignosulfonates	—	50–80
	Iron methoxyphenylpropane	—	50
Manganese	Manganese sulfate	$MnSO_4 \cdot 4H_2O$	230–280
	Manganese chelates	MnEDTA	50–120
	Manganous oxide	MnO	410–680
	Manganese methoxyphenylpropane	MnMPP	100–120
	Manganese carbonate	$MnCO_3$	310
	Manganese chloride	$MnCl_2$	170
	Manganese oxide	MnO_2	630
	Manganese frits	—	100–250
Molybdenum	Ammonium molybdate	$(NH_4)_6Mo_7O_{24} \cdot 2H_2O$	540
	Molybdenum frits	Silicates	20–30
	Molybdenum sulfide	MoS_2	600
	Molybdenum trioxide	MoO_3	660
	Sodium molybdate	$Na_2MoO_4 \cdot 2H_2O$	390
Nickel	Nickel plus	Nickel lignosulfonate	54
	Nickel chloride	$NiCl_2 \cdot 6H_2O$	150
Selenium	Sodium selenite	NaSe	450
	Selenium premix	—	2–4
Zinc	Zinc sulfate monohydrate	$ZnSO_4 \cdot H_2O$	360
	Zinc sulfate heptahydrate	$ZnSO_4 \cdot 7H_2O$	224

(*continued*)

TABLE 11.16 (continued) Micronutrient Content of Some Commonly Occurring Fertilizers Used in Agricultural Production

Micronutrient	Fertilizer Compound	Chemical Formula	Concentration (g kg^{-1})
	Zinc oxy-sulfate	$ZnO–ZnSO_4$	380–500
	Zinc oxide	ZnO	500–800
	Zinc chloride	$ZnCl_2$	500
	Basic zinc sulfate	$ZnSO_4 \cdot 4Zn(OH)_2$	550
	Zinc carbonate	$ZnCO_3$	520
	Zn sulfide	ZnS	670
	Zn frits	—	Varies
	Zinc phosphate	$Zn_3(PO_4)_2$	510
	Zinc chelate	NaZnEDTA	60–140
		NaZnHEDTA	60–100
		NaZnNTA	130
	Zn polyflavonoid	—	100
	Zn ligninsulfonate	—	50

micronutrients, adsorption reactions usually involve the formation of an inner sphere complex between the hydroxo-metal ion and the deprotonated negatively charged surfaces of Al, Mn, and Fe oxides. The relative affinities of the metals tend to follow the *Irving–Williams* order:

$$Cu^{2+} > Zn^{2+} > Ni^{2+} \sim Co^{2+} > Fe^{2+} > Mn^{2+}$$

11.5.3.1.4 Adsorption by Soil Organic Matter

Metals can react with SOM by ion exchange, complexation, and precipitation. Although complexation as inner sphere complexes between the cation and SOM coordinating functional groups is thought to be the most important reaction, the difficulties involved in studying SOM preclude accurate separation of the processes in most experiments. The retention of metals by SOM at pH 5.8 decreases in the order (Schnitzer and Khan, 1978):

$$Fe = Al = Cr = Hg = Pb = Cu > Cd > Zn > Ni > Co > Mn$$

Although multiligand complexes can form with simple organic acids, 1:1 complexes occur mainly with ligands of the structurally complex macromolecules in SOM, but two or more donor atoms in the macromolecule may be involved in the complexation reaction. Because electron donors in SOM are mainly O, N, and S, the important binding groups are as follows: –COOH (carboxyl), –OH (enolic and phenolic), –SH (thiol), $–NH_2$ (amino), =O (carbonyl), and –S (thioether). With increasing pH, carboxyl, phenolic, alcoholic, and carbonyl functional groups dissociate, thereby increasing their affinity for cations. This results in SOM having a high affinity for micronutrients cations.

Micronutrients are known to form organic complexes that affect their sorption onto soil particles (Adriano, 2001; He et al., 2005). For example, Bolan et al. (2003a) demonstrated that the addition of organic manures increased the complexation of Cu in soils. Additionally, they observed that while Cu^{2+} adsorption measured as the change in the total Cu in soil solution was not affected by biosolid addition, Cu complexation measured as the change in free Cu^{2+} concentration, increased with increasing level of biosolid.

Modeling of the binding of metals to humic materials as in MINTEQA2 is in its infancy with most work having been conducted on organic matter dissolved in surface waters rather than on SOM (Susetyo et al., 1991). More research is needed to develop suitable models that quantify metal retention by SOM.

The extent of micronutrients-organic complex formation, however, varies with a number of factors including temperature, steric factors, and concentration. All these interactions are controlled by solution pH and ionic strength, nature of the micronutrients species, dominant cation, and inorganic and organic ligands present in the soil solution.

11.5.3.1.5 Precipitation

At high pH and in the presence of SO_4^{2-}, CO_3^{2-}, OH^-, and HPO_4^{2-}, precipitation appears to be the predominant process when micronutrient cation concentrations are high (Naidu et al., 1996b). This occurs when the ionic product in the solution exceeds the solubility product of that phase. In normal soils, precipitation is not very important, but in heavy metal contaminated soils, the precipitation process can play a major role in remediation, especially under alkaline pH. Increasingly, addition of phosphate is being used to precipitate excessive levels of micronutrients such as Zn (He et al., 2005).

11.5.3.1.6 Leaching and Runoff

Micronutrients occur in solution either as free ions or soluble complexes that are prone to leaching. L'Herroux et al. (1997) showed that repeated applications of swine manure slurry increased the concentrations of Mn, Co, and Zn in drainage water manyfold. Similarly, Moore et al. (1998) found increased soluble Cu and Zn in runoff with increasing metal loading through poultry manure application, obtaining a strong relationship between dissolved organic carbon (DOC) and soluble Cu and Zn in the runoff.

However, pretreating the manure with $Al_2(SO_4)_3$ decreased runoff losses of these micronutrients as a result of sorption onto $Al(OH)_3$ formed upon hydrolysis of $Al_2(SO_4)_3$.

Migration of micronutrients in soils after manure slurry applications is greatly enhanced by DOC (Japenga et al., 1992; del Castilho et al., 1993; Li and Shuman, 1997; Hsu and Lo, 2000). Acidification due to nitrification from applied manures releases micronutrients from the solid phase (Japenga et al., 1992; del Castilho et al., 1993). Thus, while organic matter in manure by-products may provide some buffer against metal bioavailability, it does not prevent the metal from being more mobile.

11.5.4 Biological Transformation Processes

11.5.4.1 Plant Uptake and Bioaccumulation

Micronutrients are applied to overcome deficiencies, thereby increasing crop production. When micronutrients in soil are deficient, yield responses to fertilizer and manure are often observed due to increased uptake. Typical examples of yield responses to micronutrients in several crops are presented by Mortvedt (1999). Although plant uptake is a major sink for micronutrients, only a small fraction of that applied to soil is ever taken up because the greatest proportion is immobilized.

Microorganisms can bioaccumulate micronutrients from substrates containing very low concentrations. Bacteria produce large quantities of extracellular polymers with anionic properties that remove soluble micronutrients ions from solution (Srinath et al., 2002) while many fungal products, such as glucans, mannans, melanins, chitins, and chitosans can act as efficient biosorption agents (Blackwell et al., 1995). Thus, microorganisms are competitors with plant roots for these nutrients.

11.5.4.2 Oxidation/Reduction

Redox reactions, both chemical and biological, affect the bioavailability of micronutrients such as Fe, Mn, and Se. In agricultural soils, the reduced forms of Fe^{2+} and Mn^{2+} are most available while Se is more available in the oxidized [Se(VI)] form. Because of the great heterogeneity in the pore space of most soils, zones of reducing and oxidizing conditions are often in close proximity to one another allowing roots to access the available forms at different points in the soil. Application of manures to soils that are subject to reducing conditions (very wet) can result in losses of micronutrients such as Mn by leaching (L'Herroux et al., 1997), while micronutrients such as Co sorbed on sesquioxides under oxic conditions (McLaren et al., 1984) can be released due to manure-induced reduction of these oxides. Temporary flooding of alfalfa fields often result in substantial yield decreases due to the induced Mn^{2+} toxicity from the reducing conditions.

11.5.4.3 Methylation/Demethylation

While some metals (As, Hg, and Se) can be methylated and lost by volatilization (Cernansky et al., 2009), none of the plant-essential micronutrients are involved. Thus, this process is only of interest in metal contaminated sites.

11.5.5 Bioavailability of Micronutrients in Soils

11.5.5.1 Definition

The bioavailability of an element in the soil environment is defined as the fraction of the total that is present in the soil solution and on the solid phase that is available to the plant (Naidu et al., 2008). Considerable controversy exists as to "what constitutes the bioavailable fraction," including the definition itself and the methods used for its measurement. For instance, microbiologists often regard the bioavailable fraction as the concentration that can induce a change either in morphology or physiology of the organism, whereas plant scientists regard the plant-available pool as the bioavailable fraction, which is the definition that will be used here. Physical accessibility of micronutrients for uptake occurs either through movement of ions to roots by diffusion and mass flow or through root extension to the site of the nutrient. Chemical accessibility requires that nutrients remain in the soil solution in the form in which they are taken up (Marschner, 1995). Because the transformation of micronutrients in soils is a dynamic process, bioavailability changes with time.

11.5.5.2 Indicators of Bioavailability

Micronutrients occur in various fractions in soils that include the following (Shuman, 1991):

1. Structural components of primary and secondary minerals (e.g., Mn in manganous oxide)
2. Precipitated in inorganic forms, including those occluded by Fe, Al, and Mn oxides (e.g., Zn)
3. Complexed by organic matter (e.g., Cu)
4. Incorporated into organic matter including microbial biomass (e.g., B, Se)
5. Specifically adsorbed onto silicate clay minerals and Fe, Al, and Mn oxides (e.g., Zn)
6. On clay and organic exchange sites
7. Water soluble as free and complexed inorganic and organic ions

Despite only small amounts of micronutrients being present in exchangeable (6) and water soluble fractions (7) from which uptake occurs, they are continuously replenished from other less-soluble fractions, ensuring continuity of supply. Micronutrient bioavailability in soils can be assessed using chemical and biological tests.

11.5.5.2.1 Chemical Tests

11.5.5.2.1.1 Single Extraction A range of chemical extractants including mineral acids (e.g., 1 M HCl), salt solutions (e.g., 0.1 M $CaCl_2$), buffer solutions (e.g., 1 M NH_4OAc), and chelating agents (e.g., DTPA) have been used to predict micronutrient bioavailability in soils (Sutton et al., 1984; Payne et al., 1988; Sims and Johnson, 1991) but chelating agents, such as EDTA and DTPA are usually more reliable (Sims and Johnson, 1991), since they are more effective in removing potentially bioavailable fractions. However, they do not actually measure availability (Beckett et al., 1983a, 1983b). For example, although the

DTPA-extractable Cu was linearly related to Cu application rate, no relation with corn grain or leaf tissue Cu existed (Payne et al., 1988). Nevertheless, because DTPA-extractable micronutrients increase with metal level in soil (Wallingford et al., 1975; Haleem et al., 1992; Martinez and Peu, 2000), which is related to crop uptake (Wallingford et al., 1975; Mullins et al., 1982; Bibak, 1994; Duffera et al., 1999), DTPA-extractable micronutrients and plant uptake may in some cases be fortuitously related (Beckett et al., 1983a, 1983b).

11.5.5.2.1.2 Sequential Fractionation Sequential fractionation schemes are often used to examine the redistribution or partitioning of micronutrients in various chemical forms that include soluble, adsorbed (exchangeable), precipitated, organic, and occluded. Although the extraction procedures vary between chemical fractionation schemes, generally the solubility and bioavailability of micronutrients in soils decrease with each successive step in the scheme (Basta and Gradwohl, 2000). Specific chemical pools measured by chemical fractionation have been correlated with plant uptake and have been successful in predicting micronutrient availability in soils (Shuman, 1991). Because chemical extraction is matrix dependent, validation for different micronutrients sources, such as inorganic fertilizer, and organic biosolid and manure by-products must be carried out.

The diversity of reagents used to extract specific metal forms from soils makes comparison of results difficult (Table 11.17). Even when the same reagent is employed, the efficiency of extraction depends on the nature of sample, its particle size distribution, duration of extraction, pH, temperature, strength of extractant, and solid:solution ratio (Miller et al., 1986). Because chemical reagents used for extraction may themselves alter the indigenous speciation of micronutrients, milder extractants are usually more selective albeit less efficient for specific fractions than more aggressive reagents, which may extract other forms as well (Lake et al., 1984; Ross, 1994).

Redistribution of micronutrients as measured by fractionation techniques depends on their source. While fertilizer-applied micronutrients tend to remain in soluble and exchangeable form, those applied in manure are in the organic-bound form. For example, after fractionation of metal-organic components in a manure-amended soil, del Castilho et al. (1993) found that strongly bound organic–metal complexes (Cu and Zn) were mostly associated with hydrophobic acids (phenols) and neutrals (hydrocarbons) while the weakly bound micronutrients were complexed with hydrophilic neutrals (i.e., carbohydrates).

11.5.5.2.1.3 Diffusive Gradient Thin Film Diffusive gradient thin film techniques physically mimic the removal of metals by a plant by having a layer of chelating resin behind a diffusive layer (usually a gel faced with a filter membrane) that is in contact with the soil solution. This chemically and physically well-defined system introduces a sink for ions in the soil, which results in a concentration gradient in the soil solution adjacent to the device and a consequent supply of ions from the solid phase into the locally depleted solution (Smith et al., 2007).

11.5.5.2.1.4 Isotopic Techniques Methods, such as isotopic dilution and the isotopic exchange kinetics (IEK) method have been shown to measure phytoavailable elements in soils (Hamon et al., 2008; Hedley, 2008). Isotopic dilution techniques consist of spiking soil with the metal before cropping after which the specific activity (isotope:nonisotope ratio) of the plant and soil solution are measured; from this, the amount taken up from the isotopically exchangeable pool can be calculated, allowing for a good estimation of the amount of phytoavailable element.

The IEK technique, which is used to study isotopic exchange as a function of time, can be employed in conjunction with other techniques to describe the transfer of Co (Wendling et al., 2009), Cu (Ma et al., 2006), Zn (Sinaj et al., 1999; Zhang et al., 2006), Ni (Echevarria et al., 1998), and Se (Goodson et al., 2003) in soils and is very useful in describing plant availability in terms of quantity/intensity (Q/I) concepts (Hamon et al., 2002).

The labile pool of an element in soil, whether determined by radioactive or stable isotopes, can be considered as a relatively unambiguous assessment of the chemical and biological reactivity of that metal in soil compared with fractions isolated by chemical extractants (Hedley, 2008). However, it should be recognized that isotopic exchange determinations are based on the assumption that the added spike (radioisotope or stable isotope) remains 100% available for exchange. Any fixation ("irreversible" sorption) of some of the spike by reactive soil phases will result in an overestimate of the size of the labile pool (Hamon et al., 2002).

11.5.5.2.2 Biological Tests

11.5.5.2.2.1 Phytoavailability Plant availability of micronutrients largely depends on the source, soil type, and plant species (Martinez and Peu, 2000). While the application of micronutrient fertilizers usually increases the uptake of the elements by plants, application of manure by-products can both increase or decrease micronutrient concentrations in plants. For example, addition of farmyard manure increased the uptake of soil Co and Mn by winter wheat (Bibak, 1994), while acidification of soils by manure increased the B and Zn concentrations in the soil solution and uptake by maize (Jahiruddin et al., 2001). On the other hand, three annual of applications of ~24 kg Cu ha^{-1} as Cu-enriched swine manure increased Cu concentration in the corn ear leaf, but did not affect either corn grain yield or grain Cu concentration (Kornegay et al., 1976). Similarly, the uptake of Se from Se-enriched cattle manure was found to be less than that from an inorganic source (Ajwa et al., 1998) and the addition of cattle manure decreased the concentration of borate anions in soil solution and the subsequent plant uptake of B (Yermiyahu et al., 2001).

11.5.5.2.2.2 Microbial Availability Long-term applications of biosolids to agricultural land can reduce microbial activity in soils as a result of high concentrations of micronutrients (McGrath, 1994). In contrast, only limited studies have examined the direct effect of manure-borne micronutrients on microbial activity. Huysman et al. (1994) showed that in soils receiving

TABLE 11.17 Selected References on the Array of Reagents Used to Partition the Chemical Forms of Micronutrients Derived from Various Sources in Soils

		Fraction/Form							
Source	Element	Soluble	Exchangeable	Adsorbed	Organic	Oxide	Carbonate	Residual	Reference
Fertilizers	Zn	1 mol L^{-1} NH_4NO_3 (pH 7.0)			0.1 mol L^{-1} $Na_4P_2O_7$ (pH 10)	0.1 mol L^{-1} $NH_4OH \cdot HCl$ in 0.01 mol L^{-1} HNO_3	1 mol L^{-1} NaOAc pH 5.0		Gonzalez et al. (2008)
	Cu		0.01 $Ca(NO_3)_2$		0.7 M NaOCl (pH 8.5)	0.2 M NH_4O_x, 0.2 Oxalic acid, 0.1 M Ascorbic acid		HNO_3, $HClO_4$, HF (3:1:10)	McLaren and Ritchie (1993)
	B	Hot water							Haddad and Kaldor (1982)
	Mn	H_2O	NH_4OAc						Rayment and Verrall (1980)
	Mn		1 M $MgCl_2$ (pH 7)			0.1 M $NH_2OH \cdot HCl$ (pH 2)	1 M NaOAc (pH 5)		Nádaská et al. (2009)
	Co, Mn		0.01 M $Ca(NO_3)_2$		3% NaOCl (pH 8.5)	0.1 M $NH_2OH \cdot HCl$		HNO_3	Li et al. (2001)
	Ni	H_2O	1 M $MgCl_2$		30% H_2O_2	0.175 M $(NH_4)_2C_2O_4$—0.1 M $H_2C_2O_4$	0.5 M NaOAc + 0.5 M HOAc		Rahmatullah et al. (2001)
	Se	1 M $MgCl_2$		1 M NaH_2PO_4		10 M HF		Acid	Lim and Goh (2005)
Manures	Cu	0.05 M $CaCl_2$		2% CH_3COOH	0.1 M $K_4P_2O_7$	0.175 M $(NH_4)_2C_2O_4$		HCl, HNO_3, HF	Payne et al. (1988)
	Cu	0.5 M $CaCl_2$		2% CH_3COOH	0.1 M $K_4P_2O_7$				Mullins et al. (1982)
	Cd, Cu, Ni, Zn,		1 M $MgCl_2 \cdot 6H_2O$		0.02 M HNO_3; 30% H_2O_2, 3.2 M $(NH_4)_2C_2O_4$	0.04 $NH_2OH \cdot HCl$ in 25% CH_3COOH	1 M NaOAc	HCl, HNO_3	Narwal and Singh (1998)
	Cd, Pb, Zn	H_2O	0.5 M KNO_3		0.05 M NaEDTA	0.5 M NaOH		4 M HNO_3	Pierzynski and Schwab (1993)
	Cd, Cr, Cu, Ni, Pb, Zn	0.1 M $CaCl_2$			0.5 M NaOH		0.05 M NaEDTA		Canet et al. (1997)
	Cd, Pb, Zn	H_2O	1 M $Mg(NO_3)_2$		0.7 M NaOCl	0.1 M $NH_2OH \cdot HCl$ (Mn oxide); 0.2 M $(NH_4)_2C_2O_4 - 2$ M $H_2C_2O_2$ – ascorbic		HCl, HNO_3, HF	Li and Shuman (1997)
	Cu, Zn	1 M NH_4NO_3			H_2O_2	$(NH_4)_2C_2O_4 - 2$ M $H_2C_2O_2$		4 M HNO_3	Han et al. (2001)
	Cu	H_2O	0.5 M $Ca(NO_3)_2$	0.44 CH_3COOH	O.1 M $K_4P_2O_7$	0.275 $(NH_4)_2C_2O_4$	0.1 M $NH_2OH \cdot HCl$	HCl, HNO_3, HF	Miller et al. (1986)

swine manure for 5 years, there was no effect of Cu on anaerobic bacteria or fungal activity, but aerobic Cu-resistant bacteria increased with increasing soil DTPA Cu concentration, indicating that this may provide a sensitive measure of Cu bioavailability in soils. Application of swine and cattle manure slurries to grasslands acidifies soil while increasing total C and N contents, resulting in significant decreases in microbial biomass C and N. This suggests a decrease in the microbial turnover rate of C and N in manure-amended soil, apparently caused by increased solubilization of Cu, Ni, and Zn (Christie and Beattie, 1989). Organic complexation of Cu and other metals in biosolids and manures may be the main reason for the lower level of toxicity to soil biota of this form compared to inorganic salts, indicating that both microbial and plant toxicity is largely controlled by the free metal ion concentration (van Rhee, 1975; Brookes and McGrath, 1984; McGrath, 1994).

11.5.6 Factors Affecting Bioavailability of Micronutrients in Soils

11.5.6.1 Soil Interactions

Properties of the soil and its ambient solution determine the dynamic equilibrium between micronutrients in solution and solid phases, thereby affecting their bioavailability. Micronutrients interact with particulates by metal ion adsorption at surface sites, ion exchange with clay minerals, binding with organic-coated particulate matter or organic colloidal material, and by adsorption of metal–ligand complexes. All of these interactions are controlled by application of various soil amendments, pH, ionic strength, nature of the metal species, dominant cation, and inorganic and organic ligands present in the soil solution.

11.5.6.1.1 pH

Soil pH has a marked effect on metal adsorption increasing from <20% to 100% within the narrow pH range of 3–5 for all metals except those that form oxyanions (Forbes et al., 1976; Kinniburgh and Jackson, 1981; Christensen, 1984; Brümmer et al., 1988; Tiller, 1989; Naidu et al., 1994). This pH range, called the adsorption edge, generally occurs 2–3 pH units below the value of the pK for the hydroxide solubility constant of the hydrated metal ion and is partly a function of the experimental conditions (Barrow, 1986). This pH effect on adsorption of micronutrients depends on initial solution concentration, nature of soil constituents, and metal retention capacity of soils. Increased adsorption of metal ions with increasing pH is due to both increased negative surface charge density (Naidu et al., 1994) and increased concentration of the MOH^+ species in the soil system (Hodgson et al., 1964). As discussed above, at pH values less than the value of the point of zero net charge (pznc), an increase in soil pH leads to a marked increase in the negative electrostatic potential of a variable charge system, which promotes cation adsorption. However, the precise nature of this interaction between metal ions and particle surfaces is unclear as different mechanisms have been proposed to explain the increasing metal adsorption with pH. For example, the rapid increase in adsorption of Zn within the adsorption edge was attributed to abrupt changes in the concentration of $ZnOH^+$ species as the pH increases toward the pK_1 of the hydrolysis of Zn^{2+} (Barrow, 1986).

11.5.6.1.2 Ionic Strength

The effects of ionic strength on the adsorption of metals by soils are not as well understood as those of pH (Petruzzelli et al., 1985; Naidu et al., 1994). The effect of ionic strength on metal adsorption by soils depends on the surface properties of the particles being more pronounced in variable than permanent charge soils. Metal adsorption decreases with increasing ionic strength for permanent charge minerals (Garcia-Miragaya and Page, 1976; Schindler et al., 1987; Boekhold et al., 1993).

11.5.6.1.3 Index Cation and Solution Composition

Cation adsorption by soils is a competitive process in which the degree to which any cation is adsorbed depends on the concentrations and identity of the other cations present (Bolan et al., 1999). This phenomenon has practical implications on the behavior of micronutrients in soils because the concentration of several metal cations (e.g., Na^+, Ca^{2+}, and Mg^{2+}) in soil solution ranges from <0.01 M in Oxisols to >0.1 M in saline sodic soils. Such changes in ionic strength and metal ion concentration can enhance the mobility and, thus, the bioavailability of micronutrients in soils, for example, by liming or gypsum application, both of which increase Ca^{2+} ions that can compete with micronutrients for adsorption sites.

11.5.6.1.4 Inorganic and Organic Ligands

Ligands play important roles in numerous soil chemical processes such as mineral weathering, control of dissolved micronutrient concentrations, and dissolution and plant availability of micronutrients (see Harter and Naidu, 1995). The soil solution also contains inorganic ligand ions such as Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- whose concentrations vary considerably with soil type from >0.1 M in saline to <0.001 M in highly weathered soils. Such variations in ligand ion concentrations modify both the nature and surface interactions of the metal species present, leading to marked variability in metal bioavailability.

Dissolved organic material consists of a range of low molecular weight compounds including water soluble humic and fulvic acids, which are dominant except in the rhizosphere where simple organic compounds may dominate. Despite extensive studies of metal ions with organic matter (Stevenson, 1991), the values of the reaction constants need to be improved because only limited efforts have been directed toward understanding the role of low molecular weight organic acids in the dynamics of metals in the soil solution; this is due partly to the commonly held, but incorrect, belief that such organic material is rapidly degraded, and therefore short-lived, and partly to difficulty assaying the low concentrations of organic acids present. In the vicinity of plant roots, dissolved organic matter concentrations, often reaching millimolar levels, are high due to root exudates and microbial activity (Harter and Naidu, 1995), greatly enhancing the bioavailability and uptake of soil P, Cu, Fe, Mn, and Zn (Braum and Helmke, 1995). The role of plant and microbial exudates on metal reactions in soils is an area that lacks information and is an active area of research.

11.5.6.2 Soil Amendments

A number of amendments can change micronutrient bioavailability either through mobilization that releases the micronutrient into soil solution for plant uptake or through immobilization where the micronutrient concerned is removed from soil solution either by adsorption, complexation, and precipitation, rendering the micronutrient unavailable for plant uptake and leaching to groundwater.

11.5.6.2.1 Chelating and Complexing Agents

When a micronutrient ion combines with an electron donor containing two or more donor groups, a complex or coordination compound with one or more rings called a micronutrient chelate is formed. A "chelate" (Greek, *chela* meaning claw) is so named because these species can coordinate at several or all positions literally wrapping themselves around a central micronutrient ion. Chelating agents, which have a high affinity for micronutrients ions such as Fe, Cu, and Zn, can be used to enhance the solubilization of micronutrients by the formation of soluble micronutrients chelates such as EDTA, EDHA, DTPA, and EHPG (Table 11.16). The effectiveness of a chelate in mobilizing soil micronutrients depends on several factors, including species, micronutrient:chelate ratio, thermodynamic stability constants, presence of competing cations, soil pH, stability of the micronutrient–chelate complex, the ageing, and the extent of micronutrient on soil constituents (Grčman et al., 2001). Synthetic chelates appear to mobilize micronutrients from the exchangeable, organic, and carbonate-bound fractions, but not from the oxide fraction (Elliott and Shastri, 1999). The use of chelating agents may induce the solubilization of other than the target micronutrients, which may become phytotoxic (e.g., Al and Mn).

11.5.6.2.2 Phosphate Compounds

Phosphate compounds can enhance the immobilization of micronutrients in soils by various processes including direct adsorption by P compounds, phosphate anion-induced adsorption, and precipitation with solution P as phosphates (Bolan et al., 2003b). Because the phosphate anion is very effective in desorbing certain oxyanions, such as selenite and molybdate, it is often used as an extractant to measure the amount of adsorbed oxyanions (James et al., 1995; Aide and Cummings, 1997). Phosphate also competes strongly with molybdate (MoO_4^{2-}) for adsorption sites, thereby resulting in increased desorption of the latter (Barrow, 1973; Xie et al., 1993).

Interaction of P with micronutrients also occurs within the plant. For example, increasing levels of P can induce or accentuate symptoms of Zn deficiency in plants grown in soils or culture media low in available Zn (Loneragan et al., 1979; Cakmak and Marschner, 1987). This disorder is commonly known as "P-induced Zn deficiency," which is the most widely examined P-trace element interaction in soil–plant systems (Loneragan and Webb, 1993). Five plausible mechanisms involving P, which may operate separately or concurrently, can cause decreases in Zn concentrations in the plant, depending upon plant species and environmental conditions (Loneragan et al., 1979; Loneragan and Webb, 1993): (1) dilution of tissue Zn by growth promoted by P addition, (2) inhibition of Zn uptake by roots as a result of competition with the cations accompanying the P, (3) increased P-induced Zn adsorption by Fe and Al oxide-rich variable charge soils, (4) greater Zn requirement in shoots induced by P additions, and (5) inactivation of Zn within the shoot in the presence of high P levels (Loneragan and Webb, 1993).

11.5.6.2.3 Liming Materials

Although liming is primarily aimed at ameliorating soil acidity, bioavailability of Zn, Mn, Cu, and other cationic micronutrients can be reduced as a result of decreased mobility by increased sorption/precipitation and competition between Ca^{2+} and micronutrients ions on the root surface for uptake (Brown et al., 2009). Because liming also increases Mo (molybdate) mobility in soils by decreased sorption on soil surfaces, Mo in soil solution available for uptake is increased.

11.5.6.2.4 Organic Composts

The most important organic fertilizers are biosolids and animal manures. Unlike biosolid application, regulations governing livestock and poultry manure are generally based on total N and P loading so that excessive amounts of some micronutrients are inadvertently applied (Cu and Zn in swine and As in poultry manure) (Bolan et al., 2004), requiring pretreatment to reduce bioavailability. For example, treatment of poultry manure with alum [$Al_2(SO_4)_3$] decreases the concentrations of water-soluble Zn and Cu. Organic amendments increase the CEC of soils, thereby resulting in increased micronutrients adsorption.

Micronutrients form both soluble and insoluble complexes with organic materials, a process that depends on the nature of the organic matter (Bolan et al., 2003a). With increasing pH, carboxyl, phenolic, alcoholic, and carbonyl functional groups on SOM dissociate, thereby increasing the affinity of ligand ions for micronutrient cations. For example, addition of manure increases the adsorption and complexation of Cu by the soil with DOC being primarily responsible (Bolan et al., 2003a).

11.5.7 Bioavailability Implications for Soil Testing and Risk Assessment

11.5.7.1 Soil Testing and Crop Response

While most soil testing focuses on the bioavailable fraction of micronutrients for fertilizer recommendation purposes, most risk assessment models assume that the target element is 100% available, which is clearly not the case; consequently, a number of soil tests have been developed to predict micronutrient availability. Descriptions of micronutrient deficiency symptoms and the soil conditions in which deficiencies are likely to occur are presented in Table 11.18 while selected references on crop responses to micronutrients are presented in Table 11.19. In this section, we focus on Zn, Mn, Cu, Fe, B, Cl, Mo, and Ni that are essential for crop growth, development, and yield.

TABLE 11.18 Deficiency Symptoms and Crop Response to Micronutrients

Micronutrient	Deficiency Symptoms	Crop Response
Boron	B deficiencies symptoms vary with plant species including impaired meristem activity (dieback of young growth, malformed leaves often manifest as "witches broom"), impaired cell wall development (cracking of stem and petioles), and poor pollen tube development (reduced seed set, fruit fall, and deformed fruit)	B deficiency occurs on a wide range of soils (coarse-textured, highly weathered, shallow, volcanic ash, and thin soils over calcareous material) and crops
Cobalt	Co is essential for N fixation in plants Deficiency causes ill-health in ruminants. Co deficiency is associated with vitamin B12 decreases in animals	Co deficiency occurs in acidic and highly leached soils, soils derived from granites, calcareous, and peat soils Co is usually administered directly to animals
Copper	Catalyst for several enzymes Deficiency effects new growth with wilting, withering of youngest growth Cu deficiency in grain crops is known as reclamation disease, wither-tip, yellow-tip, or blind ear. In woody plants, such as citrus, this is known as dieback or exanthema	Cu deficiency occurs in: peat and muck soil; alkaline and calcareous soils, especially sandy soils or those with high levels of free $CaCO_3$: highly leached soils; or soils heavily fertilized with N, P, and Zn fertilizers Cu deficiency is corrected mostly by soil application rather than foliar application; Cu is also applied as a fungicide spray
Iron	A major element for chlorophyll production. Deficiency turns new leaves pale yellow or white while the veins remain green Difficult for plants to absorb and moves slowly within the plant. High soil pH prevents plants absorption of Fe	Fe deficiency is caused by imbalance of metallic ions (Cu and Mn), excessive P, a combination of high soil pH, high lime application, high soil moisture, cool temperature, and high levels of bicarbonate in the rooting medium Fe deficiency can be corrected by direct application of Fe fertilizer to soils or as foliar application
Manganese	Works with plant enzymes to reduce nitrates before producing proteins Mn deficiency turns young leaves a mottled yellow or brown Mn deficiency is called gray speck in oats, yellow disease in spinach, speckled yellow in sugar beets, marsh spot in peas, crinkle leaf in cotton, stem streak necrosis in potato, streak disease in sugarcane, mouse ear in pecan, and internal bark necrosis in apple	Mn deficiency occurs in: shallow peaty soils overlying calcareous subsoils; alluvial soils and marsh soils derived from calcareous parent materials; poorly drained calcareous soils with high organic matter; acid sandy mineral soils that are low in native Mn or high lime application Mn deficiency is corrected by soil application of Mn fertilizers or by foliar application
Molybdenum	Mo is an essential constituent of enzyme necessary for N_2 fixation. Deficiency causes leaves to turn pale, with scorched-looking edges, and irregular growth. Mo deficiency is known as whiptail disease in brassica plants and yellow spot disease in citrus. Mo deficiency is frequently associated with legume crops as Mo is an essential constituent of N_2 fixation	Mo deficiency occurs in acid sandy soils, highly podsolized soils, highly weathered tropical soils and well drained sandy soils Mo deficiency can be corrected by soil application, foliar spray, and seed treatment with Mo; lime application can overcome Mo deficiency
Nickel	A constituent of four enzymes: urease, methyl coenzyme M reductase, hydrogenase, and carbon monoxide dehydrogenase Without Ni, toxic levels of urea accumulate, leading to the formation of necrotic lesions. In tomato, chlorosis in the youngest leaf leading to necrosis of their meristematic tissues; in cereals (wheat, oats, and barley) growth depression, premature senescence and decreased Fe levels	Occurs mainly in woody perennials such as pecan and coffee. Can be induced as a result of complexation by glyphosate. Foliar sprays are effective in overcoming deficiency
Selenium	Essential for higher animals; Se deficiency causes muscular dystrophy or white muscle disease	Se deficiency occurs in strongly leached soils
Zinc	Zinc is required in a number of enzymes and plays an essential role in DNA transcription Deficiency produces stunting, yellowing, and curling of small leaves A typical symptom of deficiency is the stunted growth of leaves, commonly called "little leaf" and is caused by the oxidative degradation of the growth hormone auxin	Zn deficiency is caused by: low Zn content in soils, high lime application, or unavailability of Zn to the plant, and metabolic disorder within plants (e.g., imbalance between Zn and P) Zn deficiency can be overcome by soil and foliar application and avoiding imbalance between Zn and P

Source: Adriano, D.C., *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metal(loid)s*, 2nd edn., Springer, New York, 2001.

11.5.7.1.1 Diagnosis and Prognosis of Micronutrient Deficiencies or Toxicities

Dry matter and grain yield of a crop are determined by the ability of the roots of plants to extract micronutrients from the soil at rates that are nonlimiting for crop growth. Therefore, the amount of nutrient taken up by a crop is a measure of availability. Analysis of selected plant parts (e.g., leaves, young growth), or whole shoots (Smith, 1980), is used as a diagnostic tool to identify micronutrients that may be limiting growth in contrast to soil tests that estimate the available pool. Plant analysis as a diagnostic tool is discussed in detail in Chapter 13.

TABLE 11.19 Selected References for Crop Responses to Micronutrients

Micronutrient	Crop Species	Application Rate	Observations	Reference
Cu	Barley (*Hordeum vulgare* L.) and wheat (*Triticum aestivum* L.)	50 kg Cu ha^{-1}	Application levels about 4–5 times the usual for crop application. However, no detrimental effects in yield reduction or phytotoxicity in wheat. For barley, 50 kg Cu ha^{-1} decreased yield by 12% in the first year. The Cu levels in plants were <9 mg kg^{-1}	Gupta and Kalra (2006)
	Wheat	6.7–13.4 kg Cu ha^{-1}	Application of Cu increased grain yield	Rehm (2008)
	Wheat and barley	0.7–2.1 kg Cu ha^{-1}	Application of Cu increased grain yield and concentrations of wheat and barley grown on neutral to acidic soils	Gartrell and Glencross (1968)
Zn	Barley and wheat	50 kg Zn ha^{-1}	Zn applications of 50 kg ha^{-1} for 2 years resulted in crop tissue Zn levels as high as 105 mg kg^{-1} did not cause any phytotoxicity in cereals	Gupta and Kalra (2006)
	Rice	13.5 kg Zn ha^{-1}	Zn at 13.5 kg ha^{-1}, increased dry matter, tissue Zn concentration and grain yield	Slaton et al. (2005)
	Wheat and barley	0.7–2.1 kg Zn ha^{-1}	Application of Zn increased grain yield of wheat and barley grown on neutral to acidic soils	Gartrell and Glencross (1968)
Fe	Soybean and Pigeon pea	20 kg Fe ha^{-1}	Application of Fe at 20 kg Fe ha^{-1} increased grain yield of soybean and pigeon pea by 9% and 414%, respectively	Hodgson et al. (1992)
	Soybean	400 g Fe EDTA (5.5% Fe and 2% EDTA) ha^{-1}	The Fe application with 80 kg N ha^{-1} gave the highest seed yield	Caliskan et al. (2008)
Co	Faba bean (*Vicia faba* L.)	20 mg L^{-1} Co as foliar spray	Co application at 20 mg L^{-1} increased grain yield by 218% and total protein by 48%	Hala (2007)
Mn	*Lupinus angustifolius* L.	1.7 kg Mn ha^{-1} in 200 L foliar application	Foliar Mn prevented deficiency, and increased grain yield	Hannam et al. (1984)
	L. angustifolius L.	3.5–15 kg Mn ha^{-1}	Soil application increased grain yield, decrease amount of split seed at maturity	Brennan (1999)
Ni	Tomato	30 mg Ni kg^{-1} soil	This level, increased quality of fruit and auxin and gibberlin contents	Gad et al. (2007)
	Pecan (*Carya illinoinensis* [Wangenh.] K. Koch)	10–100 mg L^{-1} (plus urea and surfactant)	Decreased "water-stage fruit-split" symptom of pecan reducing crop losses	Wells and Wood (2008); Malavolta and Moraes (2007)
Mo	Tobacco	1.1 kg Mo ha^{-1}	This level of Mo and lime at 7.3 or 14.6 t ha^{-1} increased yield by 16%–22%	Khan et al. (1994)
Se	Wheat	20 g Se ha^{-1}	Se fertilization at 20 g ha^{-1} increased grain Se content by four- to sevenfold	Stroud et al. (2010)

11.5.7.1.2 Soil Analysis to Assess Available Micronutrient Pool

The objectives of a micronutrient soil test are to (1) group soils into classes for fertilizer recommendations, (2) predict the probability of a response to an application, and (3) evaluate soil productivity (Fitts and Nelson, 1956). A good soil test should (1) extract all or a proportionate fraction of the available form or forms of a nutrient, (2) accurately and in a timely manner measure the amount of the nutrient extracted, and (3) be correlated with the growth and response of each crop to each micronutrient under various conditions (Sims and Johnson, 1991). A detailed discussion of soil testing is presented in Chapter 13.

11.5.7.1.2.1 Zinc Zinc deficiency is widespread throughout the world, probably the most common micronutrient deficiency across a range of crop species (Takkar and Walker, 1993). Usually, Zn deficiency in plants occurs in calcareous (high pH) soils because of low Zn availability or in coarse-textured (sandy), highly leached, acid soils because of their low total Zn content. Antagonisms between Zn and several other essential elements (e.g., P, N, and Cu) can also lead to Zn deficiencies (Loneragan and Webb, 1993). Recommended amounts of Zn fertilizer range from about 1 to 15 kg Zn ha^{-1}. Some crops particularly sensitive to inadequate soil Zn are corn, soybean, rice (*Oryza sativa*), field bean (*Vicia faba*), and citrus (*Citrus spp.*).

The sources of Zn used as fertilizers are presented in Table 11.16 with zinc sulfate crystal or granular form being the most common (Mortvedt and Gilkes, 1993). Zinc oxide has low effectiveness in the granular form as it is insoluble in water (Mortvedt, 1991). Because water solubility of the Zn source is important, at least 50% water solubility is required to be effective on calcareous soils (Gangloff et al., 2002; Westfall et al., 2002). However, in acid soils, a wide range of products, including the oxide and sulfate, are equally effective as fine powders mixed thoroughly with the soil (Mortvedt and Gilkes, 1993).

11.5.7.1.2.2 Copper Usually, Cu deficiency occurs on highly leached, acid soils (low total Cu content), on coarse-textured (sandy) soils, and soils rich in organic matter. Recommended amounts of Cu fertilizer range from about 1 to 25 kg Cu ha^{-1}. Because amounts of Cu in excess of crop requirements are often applied particularly in manures and fungicides, Cu has a long residual effect in the soil and remains bioavailable for some considerable time after application; consequently, frequent applications are not required (Gartrell, 1981; Brennan, 2006).

Although soil applications are the commonest method used to correct Cu deficiency (Gartrell, 1981; Martens and Westermann, 1991), foliar sprays are effective in citrus, wheat, corn, and soybean (Martens and Westermann, 1991). Because some fungicides usually supply more Cu than is required by the crop, repeated applications can result in soil accumulation (Graham and Webb, 1991). Inorganic sources applied to the soil such as, Cu oxide, sulfate, carbonate, nitrate, and chloride are effective in correcting deficiencies in crops (Gartrell, 1981).

Bioavailability of Cu fertilizers is affected by (1) the method of placement, (2) ability of the Cu product to produce Cu^{+2} ions in the soil or rhizosphere, (3) reactions of Cu with soil, and (4) different requirements of plant species due to differences in growth rate, efficiency of absorption, or translocation in the plant. Because Cu is immobile in the soil, its availability is greatly influenced by the number of granules per unit volume of soil and the position in which they are placed. Banding Cu is more effective than topdressing, without incorporation into the soil. Copper fertilizer is ineffective in soil profiles that contain few absorbing roots, for example, dry soil. Applied at the same rate, large granules (fewer granules per unit volume) are much less effective than fine material (Gartrell, 1981).

11.5.7.1.2.3 Manganese Usually, Mn deficiency is associated with well-drained neutral to alkaline soils, and those rich in organic matter. In addition, because of their low total Mn content, highly leached, coarse-textured (sandy) acid soils are also frequently deficient for some crop species. Recommended amounts of Mn fertilizer range from about 2 to 20 kg Mn ha^{-1}. Manganese has a short residual effect in most neutral to alkaline soils, because the bioavailable Mn^{+2} is rapidly oxidized to MnO_2. On the other hand, for sweet lupin (*Lupinus angustifolius* L) grown on acid sandy soils, the effect of 7.5 kg Mn ha^{-1} has lasted for some considerable time after application, while that of 50 kg Mn ha^{-1} persisted for about 17 years (Brennan et al., 2001). Foliar application is the most efficient and effective method of correcting Mn deficiency in various crops grown on a range of deficient soils. Manganese deficiency is frequently encountered in cereals, cotton, peanuts, soybeans, and a range of fruits and vegetables (Martens and Westermann, 1991).

Band placement of manganese sulfate fertilizer is more effective than broadcasting at the same rate for soybean (*Glycine max*) (Mascagni and Cox, 1985) and sweet lupin (Brennan, 1999) because concentration in the band reduces the rate of oxidation of Mn^{+2} to less available forms. Foliar sprays and band application of Mn sulfate were equally effective for soybeans (Mascagni and Cox, 1985). Soil moisture affects Mn availability with the seed-applied Mn being effective under adequate soil moisture but not drought conditions in soybean (Alley et al., 1978). For some crops (peanut [*Arachis hypogaea*], soybean, and wheat) and conditions, multiple rather than single foliar sprays are required (Cox, 1968; Hallock, 1979; Nayyar et al., 1985). The timing of the foliar spray in relation to crop development stage is also important for soybean (Gettier et al., 1984), corn (Mascagni and Cox, 1984), and sweet lupin (Brennan et al., 2008).

11.5.7.1.2.4 Iron Usually, Fe deficiency is a common problem in numerous crop species grown on alkaline soils containing free $CaCO_3$ in the soil profile (Marschner, 1995). In many cases, the problem stems from various factors that inhibit Fe absorption by plant roots or impair its utilization in metabolic process in Fe-inefficient species. Although rare, acid soils with deficient levels of Fe do occur, for example, in Florida and other similar areas (Welch et al., 1991). Recommended amounts of Fe fertilizer range from about 20 to 100 kg Fe ha^{-1} (Martens and Westermann, 1991). Iron has a short residual effect in most alkaline soils, because Fe^{+2} is rapidly converted to unavailable forms. Foliar application is more effective at correcting Fe deficiency in various crops grown on a range of deficient soils. Iron deficiency is frequently encountered in a range of Fe-sensitive crops and/or Fe-inefficient cultivars (Welch et al., 1991). Growing Fe-tolerant species or varieties is an effective method for controlling Fe deficiency in crops grown on soils where Fe availability is low (Chen and Barak, 1982).

Because soil–fertilizer contact is limited in band placement, iron sulfate fertilizer banded in the soil is more effective than broadcasting at equal rates. However, Fe sulfate is frequently broadcast on pastures (*Trifolium subterannean* L.) where Fe deficiency has been induced by overliming acid soil (Brennan and Highman, 2001). Several other methods such as (1) mixing of Fe sulfate and sulfuric acid (Wallace, 1988; Martens and Westermann, 1991), (2) inclusion of organic residues with Fe sulfate (Mostaghimi and Matocha, 1988), and (3) inclusion of K_2SO_4 with Fe sulfate that corrected Fe deficiency in peanuts (Shaviv and Hagin, 1987) have been used to reduce the conversion of applied Fe to unavailable forms. Foliar sprays of inorganic (e.g., Fe sulfate) and organic Fe sources (e.g., Fe chelates) are very effective in correcting Fe deficiency (Martens and Westermann, 1991). Foliar applications of Fe sulfate are more effective than soil application of Fe chelate (FeEDDHA). Iron is less available in well-aerated soils due to insolubility of Fe(III) oxides; but availability can be promoted by increasing soil moisture that produces loci where some reduction of Fe(III) to Fe^{2+} can take place (Bjerre and Schierup, 1985). However, excessive soil moisture in calcareous soils may intensify Fe deficiency mainly due to the buildup of HCO_3 in the soil solution (Moraghan and Mascagni, 1991). Plant residues, manures, biosolids, charcoal, coal, and a range of by-products from manufacturing (e.g., polyflavoids and lignosulfonates) have been effective in alleviating Fe deficiency (Chen and Barak, 1982).

11.5.7.1.2.5 Boron Boron is an essential micronutrient where the range between deficiency and toxicity is smaller than for most other micronutrients. Plants respond to the activity of B in solution rather than to adsorbed B making the rate of desorption, which follows a first-order rate equation, important in B supply to the root. The bioavailability of B is determined by pH, texture, moisture, temperature, SOM, and clay mineralogy (Goldberg, 1997) while the adsorbing surfaces of importance are sesquioxides, clay minerals, lime, and organic matter. Boron adsorption increases initially with pH on both mineral and organic surfaces up to pH 8–10 and then decreases. Consequently, overliming acid soils can cause a temporary deficiency due to higher adsorption at high pH (Reisenauer et al., 1973). The roles of B in the plant include sugar transport, cell wall synthesis and structure, pollen tube growth, pollen viability, carbohydrate synthesis, respiration, and membrane integrity while excess B can cause impairment in a range of cellular functions, such as phenol and ascorbate metabolism, free radical generation, and detoxification (Cakmak and Romheld, 1997); but its primary role is still unknown. These changes may be direct or indirect functions of B deficiency.

Boron deficiency occurs on a wide range of soils (coarse-textured, highly weathered, shallow, volcanic ash, and shallow soils over calcareous material) and crops (alfalfa [*Medicago sativa*], beets [*Beta vulgaris*], peanut [*A. hypogaea*], brassicas [*Brassica* spp.], coffee [*Coffea* spp.], oil palm [*Elaeis guineensis*], cotton [*Gossypium* spp.], sunflower [*Helianthus annuus*], apple [*Malus domestica*], and grape [*Vitis vinifera*]) (Shorrocks, 1997) as well as many vegetable crops.

Deficiency symptoms vary with plant species including impaired meristem activity (dieback of young growth, malformed leaves often manifest as "witches broom"), impaired cell wall development (cracking of stem and petioles), and poor pollen tube development (reduced seed set, fruit fall, and deformed fruit). The main B sources used to correct B deficiency are borax ($NaB_4O_7 \cdot 10H_2O$ [11% B], NaB_4O_7 [21.4% B]), boric acid ($B(OH)_3$ [17.5% B]), and a range of crushed ores containing variable amount of B (Shorrocks, 1997). Boric acid and Solubor® (17.5% B), products readily soluble in cold water, are used as foliar applications. For annual crops, 1–2 kg B ha^{-1} is the recommended rate (Shorrocks, 1997).

Boron toxicity commonly occurs in arid and semiarid environments on alkaline and saline soils (Nable et al., 1997). Continued application of irrigation water with high levels of B can lead to toxicity. The typical symptoms of B toxicity are leaf burn, chlorotic, and necrotic patches often on the margins and tips of older leaves (Bennett, 1993).

11.5.7.1.2.6 Chloride Chloride (Cl^-) is essential for many plant functions such as a chemical balancing agent for K^+ during the opening and closing of stomata, photosynthesis, cation balance and transport within the plant, counteracting the effects of fungal infection, and competing with NO_3^-, thus promoting the uptake of NH_4-N (Boyer et al., 1954; Fixen, 1993; Talbott and Zeiger, 1996). Deficiency symptoms vary with plant species including wilting and leaf chlorosis while toxicity manifests itself as leaf margin scorching, leaf drop in excessive situations, and leaf area reduction and thickening, resulting in reduced growth.

Because Cl^- is highly soluble in water, leaching losses occur, where rainfall is high and soil drainage is good. If Cl^--containing fertilizers (e.g., muriate of potash [KCl]) are not regularly used, Cl^- deficiency can occur. In coastal regions with rough surf, atmospheric deposition of Cl^- can be high, decreasing with distance from the coast. Chloride competes with other anions (e.g., NO_3^-, SO_4^{2-}) although little data are available on the specific interactions and competition between each anion.

11.5.7.1.2.7 Nickel Recently Ni, which has been shown to be an essential element for plants, is required in miniscule amounts as a piconutrient. It plays a vital part in the translocation of N in ureide-transporting woody perennials such as pecans (*Carya illinoensis*) and coffee (*Coffea arabica*) where a deficiency of Ni disrupts ureide, amino, and organic acid metabolism but its physiological role is poorly understood (Bai et al., 2006). In addition, it confers disease resistant on plants although much work needs to be done in this field (Wood and Reilly, 2007). Nickel appears to play a key role in the production of secondary plant metabolites that influence resistance to disease. Most soils contain adequate amounts of Ni but under certain specific conditions, for example, where glyphosate that strongly complexes Ni has been used as a herbicide, deficiencies can be induced (Yamada, 2010). Consequently, deficiency symptoms manifest themselves as those of N. Research in this field is still in its infancy.

11.5.7.1.2.8 Molybdenum Because Mo occurs in the soil solution as MoO_4^{2-}, it interacts with other anions, particularly phosphate and SO_4^{2-} to reduce Mo uptake. In addition, it is strongly sorbed on sesquioxide surfaces at pH values below 7, decreasing 100-fold for each unit drop in pH. Thus, Mo deficiencies are mainly found on acid soils where bioavailability is low (Gupta, 1997). Consequently, liming acid soils can often supply sufficient Mo to meet the needs of many crops including legumes, which are most sensitive to deficiency. In legumes, because Mo is required by the Rhizobia in the fixation of N, deficiency of Mo is manifest as those of N. In addition, it is an activator for the nitrate reductase enzyme, crucial to the N nutrition of crops. Where Mo deficiency occurs, correction can be achieved by relatively small applications (~100 g Mo ha^{-1}) as foliar sprays in the form of sodium or ammonium molybdate.

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12

Soil Acidity and Liming

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12.1 Introduction

About 26% of the global ice-free land surface is occupied by soils with pH_w (pH determined in water) values of 6.5 or less, of which two-thirds have potential Al toxicity problems. Subsoil Al problems are estimated to encompass 16% of the ice-free land surface (Eswaran et al., 1997). Naturally, acid soils are found in regions where rainfall exceeds evapotranspiration (Jenny, 1941); H^+ and eventually Al^{+3} replace basic cations lost from exchange sites through excess water transport. Most of the acid soils belong to the Alfisols, Histosols, Oxisols, Spodosols, and Ultisols orders of the U.S. Soil Taxonomy (Buol et al., 1997).

Agricultural and industrial processes also contribute to soil acidification. The conversion of ammonium to nitrate produces H^+, which can require up to 3.6 kg $CaCO_3$ to neutralize the acidity produced by each kg of N (Adams, 1984). Plants excrete H^+ from roots when cation uptake exceeds that of anions (Tang and Rengel, 2003). Legumes have excess cation uptake when most of their N is supplied via atmospheric fixation. Neutralization of acidity produced by N-fixing legumes can correspond to 54–550 kg $CaCO_3$ ha^{-1} $year^{-1}$ (Bolan et al., 1991; Coventry and Slattery, 1991). Major sources of acid precipitation are atmospheric emissions of nitrogen and sulfur compounds from burning processes and their eventual transformation into nitric and sulfuric acids (Alewell, 2003).

12.2 Nature of Soil Acidity

Soils with pH_w values <5.5 have appreciable amounts of exchangeable Al^{3+}. The proportion of cation exchange sites occupied with Al^{3+} and the concentration of Al in the soil solution increase with declining soil pH. In mineral soils, the soil solution Al concentration and the %Al saturation of the cation exchange capacity (CEC) approach zero between pH values of 5.5 and 5.8 (Kamprath, 1984; Sumner and Yamada, 2002). Organic soils have significant quantities of both exchangeable Al^{3+} and H^+. Aluminum binds to organic matter in nonexchangeable forms, such that soil solution Al concentrations in organic soils are less than in mineral soils at the same pH value (Evans and Kamprath, 1970). At pH_w 5, organic soils have very little Al in the soil solution and Ca concentrations are high enough to overcome H^+ competitive effects on Ca uptake. Hydrolysis of the Al^{3+} in the equilibrium soil solution impacts the soil solution H^+ concentration and pH (Thomas and Hargrove, 1984).

Exchangeable acidity is extracted from soils with neutral unbuffered salt solutions such as KCl, to minimize changes in soil pH (Thomas and Hargrove, 1984). Soils also contain acidity, which is not extracted with neutral unbuffered salt solutions but is titrated with base. This nonexchangeable acidity represents the acid buffering capacity of soils, and includes Al bound to organic matter, H^+ associated with carboxyl groups of organic matter, hydroxy Al, and hydrated oxides of Fe and Al (Kamprath, 1978).

12.3 Acid Soil Constraints to Plant Growth

Plant growth in acid soils can be limited by a combination of toxicities (H^+, Al^{3+}, and Mn^{2+}) and nutrient deficiencies (namely Ca, Mg, Mo, and P) (Kamprath, 1984; Sumner and Yamada, 2002). Responses to lime can involve amelioration of a combination of factors, wherein experiments in hydroponics often provide insight into the magnitude of individual constraints.

12.3.1 Hydrogen Toxicity

Visual root symptoms of excess H^+ usually occur at $pH < 4.6$ and entail stunted growth, brownish color, and little lateral root development. At low pH and low Ca^{2+} concentrations, root membranes are damaged, leading to loss of organic substrates and absorbed cations. Root injury due to H^+ can reduce the uptake of Ca, Mg, and K (Islam et al., 1980; Foy, 1984). Increasing solution Ca^{2+} concentration alleviates root injury due to H^+ (Lund, 1970; Moore, 1974; Runge and Rode, 1991; Sanzonowicz et al., 1998). Low pH has detrimental effects on rhizobium survival, legume host plant root infection, and nodule initiation (Andrew, 1978).

12.3.2 Aluminum Toxicity

Aluminum toxicity is a major constraint to plant growth in acid soils. The immediate and visible evidence of Al toxicity is a reduction in root length, which limits plant access to water and nutrients. Aluminum interferes with various root growth processes, namely, disruption of regulatory signals in root cap cells (Bennet and Breen, 1991), interference with cell division, enzyme activities, DNA replication, and P availability at membranes (Foy, 1984; Silva et al., 2002).

Concentrations of soil solution Al^{3+} that reduce crop growth are in the micromolar range (Kamprath, 1984). Soil solution Al^{3+} concentrations are related to the percentage of Al^{3+} saturation of the soil cation exchange sites, with a marked increase in solution concentration when Al^{3+} saturation exceeds 50% (Kamprath, 1978; Kamprath and Smyth, 2005). Determination of Al^{3+} and other cations in soil solutions is tedious and time consuming. It is simpler to measure exchangeable cations and diagnose Al^{3+} toxicity based on the %Al saturation of the cation exchange sites (Kamprath, 1970, 1978). A realistic measure of the soil cation exchange at a given pH value, the effective cation exchange capacity (ECEC), is the sum of exchangeable Ca^{2+}, Mg^{2+}, K^+, Na^+, and unbuffered salt-extractable acidity (Coleman et al., 1959).

Tolerance to Al differs significantly among plant species and cultivars within species. Reviews of field lime trials suggested that cassava yields were not depressed by %Al saturation values of <75%, whereas best yields for most trials with cotton, mung bean, and wheat were at 0% Al saturation; however, critical Al saturation levels among trials with different varieties ranged from 0% to 40% with corn and soybean and 0% to 60% with upland rice (Osmond et al., 2007). There are various proposed mechanisms of Al tolerance, which can be both internal and external to plants (Taylor 1991; Kochian, 1995). Internal tolerance involves detoxification after Al^{3+} is absorbed, whereas external mechanisms imply the prevention of Al^{3+} uptake and transport. Proposed exclusion mechanisms by various investigators include immobilization of Al^{3+} at the cell wall, low root CEC, selective permeability of the plasma membrane, changes in rhizosphere pH, exudation of Al-chelating compounds, and Al^{3+} efflux. Internal mechanisms may also include chelation of Al^{3+}, compartmentalization in vacuoles and Al-tolerant enzymes (Silva et al., 2002).

12.3.3 Manganese Toxicity

Acid soils with large contents of Fe and Al oxides often contain quantities of Mn that are toxic to plants (Kamprath, 1984). Plant growth is reduced through excess accumulation of Mn in aboveground plant tissues. Plant symptoms of Mn toxicity vary among species, but include marginal chlorosis and necrosis of leaves, leaf puckering and necrotic spots on leaves (Foy, 1984). Soil solution levels of Mn^{+2} are difficult to predict, because they are influenced by total soil Mn content, soil pH and redox potential. Although solubility decreases with increasing pH, Mn toxicity may occur above a soil pH of 5.5 under the appropriate reducing conditions (Sumner and Yamada, 2002). Improved plant growth upon liming soils above pH 5.5, where soil solution and exchangeable Al^{3+} are reduced to essentially zero, is often associated with the alleviation of Mn toxicities (Kamprath, 1984; Sumner and Yamada, 2002).

12.3.4 Calcium and Magnesium Deficiencies

Acid soils with high %Al saturation have limited amounts of Ca^{2+} and Mg^{2+} in either the exchangeable form or in the soil solution. The supply of adequate Ca^{2+} and Mg^{2+} for normal plant growth may also be constrained in soils with low CEC due to their limited capacity to retain these cations (Kamprath, 1984). An external supply of Ca^{2+} is essential for normal root development (Rios and Pearson, 1964; Ferguson and Clarkson, 1976; Clarkson, 1984). The addition of $0.1\,cmol_c$ Ca kg^{-1} (20 mg Ca kg^{-1}) to an Oxisol initially containing $0.02\,cmol_c$ Ca kg^{-1} (4 mg Ca kg^{-1}) increased wheat seedling length by over 50%, regardless of whether the Ca was supplied as lime, calcium chloride or calcium phosphate (Ritchey et al., 1983). In a review of lime experiments in the tropics, Kamprath (1984) suggested that an exchangeable soil Ca level of $1.0\,cmol_c\,kg^{-1}$ as a minimum value for good plant growth. Plant growth responses to Mg are often linked to conditions of low soil exchangeable Mg^{2+} and/or less than 5% Mg saturation of the CEC and pH values ≤5 (Adams, 1984; Kamprath and Foy, 1985; Kamprath and Smyth, 2005).

The susceptibility of peanut to Ca deficiency is associated with its below ground fruit development. The fruit absorbs most of its Ca from the surrounding soil solution. In the absence of adequate ambient soil Ca, shelling percentage is reduced due to poor fruit development (Cox et al., 1982; Adams, 1984). Soil Ca is often supplemented for peanut by applications of lime and gypsum.

12.3.5 Phosphorus and Molybdenum Deficiencies

Investigations regarding improvement of soil P solubility with liming provide conflicting results, as indicated in several reviews of the subject (Kamprath and Foy, 1985; Sumner and Yamada, 2002). However, there is general agreement that neutralization of exchangeable Al^{3+} increases root growth, exploration of a greater soil volume, and access to more soil P. In acid soils Al^{3+}

at the root surface precipitates P and reduces P transport to plant tops; neutralization of Al $^{3+}$ by liming increases transport of P to plant tops (Kamprath and Smyth, 2005).

Molybdenum is an essential nutrient for N fixation in legumes. The availability of soil Mo is a function of Mo content, pH and MoO_4^{2-} absorption by hydrous oxides of Fe and Al (Adams, 1984; Kamprath and Foy, 1985). In a review of lime and Mo experiments, soil solution Mo increased two- to threefold as soil pH was increased up to values of 6–7; likewise, soybean yields without Mo treatment increased with liming and approached yields of seed Mo treatments at pH values above 6 (Sumner and Yamada, 2002). With Mo added via seed treatments, there was no soybean yield response to lime above pH values of 5.3–5.5 where most of the exchangeable Al^{+3} is neutralized. Increased solubility of Mo with increasing pH is attributed to OH^- displacement of adsorbed MoO_4^{2-} on hydrous oxides of Fe and Al (Barrow, 1978).

12.4 Lime Requirement Methods

For extensive reviews and comparisons between lime requirement methods, the reader is referred to articles by van Lierop (1990), Sims (1996), and Sumner (1997). Some of the most commonly used methods are discussed herein.

12.4.1 Soil–Lime Incubations

Increasing rates of lime are mixed with fixed quantities of soil and equilibrated in a moist state for weeks or months. Lime required to achieve a given soil pH or exchangeable Al^{3+} level can be related to measurements of other soil chemical and physical attributes. Although time and costs of this method are not conducive to lime recommendations via routine soil testing, it is widely used to test and verify most of the rapid lime tests in current use across a number of soils with a range of chemical and physical characteristics within a given region of interest.

12.4.2 Buffer pH Methods

A given volume of a buffer solution is equilibrated with a fixed weight or volume of soil, and pH of the soil–buffer mixture is measured. The molarity of the buffer solution is known and the decrease in its pH, after mixed with soil, is a measure of the soil acidity that must be neutralized by a base in order to achieve a targeted soil pH.

Buffer pH methods used to determine lime requirements in different regions of the United States are described in Table 12.1. Each method was developed for representative soil types in a given region. The composition of the buffer solutions is different and has pH values ranging from 6.6 to 8.0. The targeted soil pH values after liming range from 6.0 to 7.0 among the various methods and the amount of lime required for a pH decrease of 0.1 in the buffer–soil mixture, relative to that of the initial buffer solution, ranges from 0.1 to 0.6 ton of $CaCO_3$ ha^{-1}. Several investigators have recently proposed modifications to existing methods (Huluka, 2005; Sikora, 2006; Sikora and Moore, 2008) or new buffer methods (Liu et al., 2005).

TABLE 12.1 Characteristics of Buffer pH Methods Used to Determine Lime Requirements in the United States

Method	Buffer pH	Target Soil pH	Intended Soil Use	Lime/0.1 Buffer pH Decrease ton $CaCO_3$ ha^{-1}
Adams and Evans	8.0	6.5	Low CEC Ultisols	0.1
Mehlich	6.6	6.0	Neutralize exch. Al^{+3}, Ultisols	0.16
SMP	6.8	6.8	High exch. Al^{+3} Alfisols	0.6
		6.4		0.5
		6.0		0.4
Woodruff	7.0	6.5–7.0	Mollisols	0.5

Source: Adapted from van Lierop, W. 1990. Soil pH and lime requirement determination, p. 73–126. *In* R.L. Westerman (ed.) Soil testing and plant analysis. 3rd edn. SSSA, Madison, WI.

12.4.3 Exchangeable Aluminum

Lime requirements are based on the amount of exchangeable Al^{3+} extracted from soils with neutral unbuffered salt solutions such as KCl (Kamprath, 1970). Adding lime to mineral soils on an equivalent basis to the amount of exchangeable Al^{3+} raises soil pH to 5.3–5.6 and reduces soil solution Al^{3+} concentration and exchangeable Al to near zero (Kamprath, 1984; Sumner and Yamada, 2002). Lime neutralizes exchangeable acidity, but also reacts with the nonexchangeable acidity that includes Al bound to organic matter and H associated with carboxyl groups of organic matter, hydroxy Al, and hydrated oxides of Fe and Al. Therefore, lime requirements to achieve 0% Al saturation of the ECEC, based on exchangeable soil acidity, include a lime equivalence factor that is greater than 1.0 and usually in the range of 1.5–4.0 (Kamprath, 1984; Sumner, 1997).

There are several proposed modifications of the basic lime requirement determination based on exchangeable Al. Cochrane et al. (1980) proposed the following adjustment that accounts for differential acid tolerance among crops and cultivars:

$$\text{CaCO}_3\text{ equivalent (ton ha}^{-1}\text{)} = \text{LF}\left[\text{Al} - \frac{\text{TAS(Al + Ca + Mg)}}{100}\right] \tag{12.1}$$

where

LF is the product of 1.5 equivalents of $CaCO_3$/equivalent of exchangeable Al plus the conversion to a 20 cm layer for a hectare of soil

Al, Ca, and Mg are exchangeable cations extracted with a neutral unbuffered salt

TAS is the %Al saturation tolerated by the crop or cultivar

This approach seeks to only neutralize the quantities of exchangeable Al that exceed the %Al saturation tolerated by the crop. Although useful in regions where lime materials are expensive, data on exchangeable Ca and Mg, and %Al saturation tolerated by the intended crop must also be known in addition to soil exchangeable Al.

In soils with low ECEC, lime required to neutralize the exchangeable acidity may not be sufficient to correct Ca and Mg deficiencies. Therefore, lime requirements may include considerations of minimum targets for soil exchangeable Ca and Mg as illustrated by the following adjustment proposed by Sousa and Lobato (2002) to ensure that soil Ca + Mg achieves a value of $2\,\text{cmol}_c\,\text{dm}^{-3}$ after liming:

$$CaCO_3\text{ equivalent (ton ha}^{-1}) = 2(\text{Al}) + (2 - (\text{Ca} + \text{Mg})) \quad (12.2)$$

12.4.4 Comparison of Lime Requirement Methods

Given the combination of soil factors associated with a potential acidity constraint, Sumner and Yamada (2002) proposed grouping acid soils into two general categories: soils with pH values <5.2–5.4 where Al and Mn toxicities are the primary constraints to crop growth, and soils with pH values >5.4 where liming impacts crop growth through improved availability of nutrients, namely Ca, Mg, Mo, and P. In the first category, increasing soil pH via liming resolves the toxicity problems, whereas nutrient inputs without liming are an alternative remedial strategy to nutrient availability problems in the latter group. An understanding of the types of acidity constraints in the soils of interest can help in determining the most appropriate remedial strategy.

Differences in soil factors contributing to an acidity constraint and crop species/cultivar tolerances to Al and Mn toxicities reduce the likelihood that a given target pH value can be used to estimate lime requirements under a variety of circumstances. Therefore, it is important that lime requirement methods should be calibrated with crop performance data under field conditions for the representative crops and soil types of interest in a given region (Sumner, 1997). Liming mineral soils to a pH value of 6 ensures neutralization of exchangeable Al (around pH 5.4–5.6) and reduces the frequency for repeated applications of lime as the soil re-acidifies through N fertilizer inputs and plant secretion of H^+. Unless Mn toxicity is an issue, liming of acid soils to pH values above 6 will decrease the solubility of Cu, Fe, Mn, and Zn and potentially induce their deficiencies in soils where availabilities are adequate at lower pH values (Kamprath, 1971; Lucas and Knezek, 1972). Modest levels of soil acidity (pH values of 5.0–5.5) can also have economically beneficial impacts by reducing the incidence of pests and diseases such as soybean cyst nematode (*Heterodera glycine*) (Garcia et al., 1999) and scab disease (*Streptomyces scabies*) in potato (Keinath and Loria, 1989).

12.5 Lime Material Characteristics and Application

Various materials derived from natural deposits or industrial by-products can be used for liming. Calcium carbonate (calcitic limestone) and calcium-magnesium carbonate (dolomitic limestone) are frequently used crystalline compounds from natural deposits. Marls are soft, unconsolidated calcium carbonates that may contain some clay impurities. Calcium oxide (burnt or quick lime) and calcium hydroxide (hydrated lime) are white powders that are caustic when wet and difficult to mix uniformly with soil. Basic slag (calcium silicate) is a by-product of the steel industry often containing appreciable amounts of Mg and P. Several factors to consider when selecting and applying lime materials are described in the following sections.

12.5.1 Neutralizing Value

The neutralizing value represents the amount of acid neutralized by a unit weight of lime material. Pure calcium carbonate serves as a standard and has the calcium carbonate equivalent (CCE) value of 100%. The CCE values of several pure liming materials are given in Table 12.2. Most liming materials have impurities, which reduces their CCE value. Lime requirement estimates are often based on 100% CCE and the actual application rate needs to be adjusted for the CCE value of the selected lime material.

12.5.2 Fineness of Liming Materials

Upon contact with acid soils, lime particles dissolve and release Ca^{2+} and HCO_3^-, which leads to neutralization of H^+ and Al^{3+}. The reaction rate depends on the surface area of the lime particles in contact with the soil. Therefore, it is desirable that small particles are close together so that their zones of neutralization overlap in a short time.

Calcitic and dolomitic limestones are ground to increase the number of particles per unit of soil. Most ground lime materials contain a range of particle sizes from very fine to sand-sizes, which comply with state or province regulations on particle size distribution. A fineness factor for the lime material is the sum of the products of percentages of lime material in each size fraction and its corresponding efficiency factor. Depending on regional regulations, fractions greater than a certain size have

TABLE 12.2 Neutralizing Value (CCE %) of Pure Liming Materials

Material	% $CaCO_3$ Equivalence
Calcium carbonate, $CaCO_3$	100
Calcium-magnesium carbonate, $CaMg(CO_3)_2$	109
Calcium oxide, CaO	179
Calcium hydroxide, $Ca(OH)_2$	135
Calcium silicate, $CaSiO_3$	86

Source: Havlin, J.L., J.D. Beaton, S.L. Tisdale, and W.L. Nelson. 2005. Soil fertility and fertilizers: An introduction to nutrient management. 7th edn. Pearson Education, Inc., Upper Saddle River, NJ.

an efficiency factor of zero (e.g., >2 mm) and this value increases to a maximum of 1.0 with decreasing particle fineness (e.g., <0.4 mm) (Havlin et al., 2005). Calcitic limestones are softer than dolomitic limestones; thus, a given size fraction of the former dissolves at a faster rate (Kamprath and Smyth, 2005).

12.5.3 Effective Calcium Carbonate Rating

Effective Ca carbonate rating (ECC) is the product of the CCE and fineness factor for the liming material. The selection among available lime materials often involves comparing costs of sources per unit ECC and whether Mg inputs (via dolomitic limestone) are needed.

12.5.4 Lime Incorporation into the Soil

Lime should be mixed with the volume of soil to which one intends to neutralize acidity. In conventional tillage systems, lime recommendations often assume a soil depth of 15–20 cm. Thorough mixing can be achieved by broadcasting and incorporating half of the lime by disk or plow, followed by inversion and broadcasting and disking the remainder. In no-till systems, however, lime is surface applied and initial acid neutralization will be limited to the 0–5 cm soil depth. Surface applications without incorporation of lime rates to neutralize soil acidity in a 15–20 cm soil depth can lead to excessively high soil pH values and associated nutrient deficiencies in the 0–5 cm soil depth.

The effectiveness of surface-applied lime in ameliorating subsoil acidity below the 0–5 cm depth is an important consideration in no-till systems, especially when root elongation is constrained and crops lose access to soil reserves of water and nutrients. Sumner (1995) has reviewed an extensive collection of investigations regarding amelioration of subsoil acidity through surface application of lime and gypsum. The investigations entail a variety of soil types, climatic regimes, and rates of lime or gypsum. Likewise, the subsoil depth to which lime or gypsum moved was quite variable, although the process of detectable movement was gradual and entailed months and years after surface applications. In some instances, the changes in subsoil acidity consisted of increased exchangeable Ca and Mg without improvements in soil pH values. Although increases in solution Ca^{2+} concentration at constant pH can ameliorate Al^{3+} rhizotoxicity to some extent (Alva et al., 1986; Horst, 1987; Wright and Wright, 1987; Noble et al., 1988; Sanzonowicz et al., 1998), absence of an increased subsoil pH suggested that alkaline anions (HCO_3^- and/or OH^-) were not associated with the downward transport of basic cations from the surface applied lime (Sumner, 1995). In cases where subsoil pH also increased with downward movement of Ca^{2+} and Mg^{2+}, Sumner (1995) proposed two potential processes: (a) downward movement of NO_3^- and plant secretion of OH^- when NO_3^- uptake from subsoils leads to an excess of anion over cation uptake; and (b) complexation of toxic Al^{3+} by downward movement of soluble organic components. The former process supports frequent observations that subsoil Ca^{2+}, Mg^{2+}, and pH increased more rapidly when surface applications of lime were complemented with acidifying fertilizers. The trade-off, however, is a faster acidification of the surface soil when ammoniacal N sources are used.

Several investigators have compared the residual effects of an initial surface application of lime with and without supplementary lime applications in succeeding years (Blevins et al., 1978; Edwards and Beegle, 1988; Godsey et al., 2007). In all cases, lime rate had a greater effect than frequency of lime application in reducing acid characteristics of the subsoil. Nevertheless, frequent surface applications of lime in no-till systems will avoid detrimental effects on crop growth through acidification of the surface soil layers.

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13

Soil Fertility Evaluation

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13.1 Introduction

13.1.1 Soil Fertility: A Modern Definition

Soil fertility is a scientific discipline that integrates the basic principles of soil biology, soil chemistry, and soil physics to develop the practices needed to manage nutrients in a profitable, environmentally sound manner. Historically, the study of soil fertility has focused on managing the nutrient status of soils to create optimal conditions for plant growth. Fertile, productive soils are vital components of stable societies because they ensure that we are able to grow the plants needed for food, fiber, animal feed and forage, medicines, industrial products, energy, and for an aesthetically pleasing environment. Beyond management of soil nutrients, the study of soil fertility rests on two other fundamental principles. First, optimum nutrient status alone will not ensure soil productivity. Other factors such as soil moisture and temperature, soil physical condition, soil acidity and salinity, and biotic stresses (disease, insects, weeds) can reduce the productivity of even the most fertile soils. Second, modern soil fertility practices must stress environmental protection as well as agricultural productivity; that is, we must prevent the pollution of our soils, air, and water as we strive to optimize the nutrient status of soils for plant growth.

13.1.2 Soil Fertility Evaluation: Purpose, General Principles, and Practices

Soil fertility evaluation is a central feature of modern soil fertility management. The fundamental purpose of soil fertility evaluation has always been to quantify the ability of soils to supply the nutrients required for optimum plant growth. Knowing this, we can optimize the nutrient management practices needed to achieve economically optimum plant performance. Related, equally important goals are as follows: (1) to identify other factors that reduce soil productivity (e.g., acidity, salinity, elemental phytotoxicity) and (2) to determine if the intended use of the soil may negatively impact the quality of our environment.

The general principles and practices of soil fertility evaluation are derived from or influenced by many other disciplines (e.g., soil science, plant physiology, plant genetics, crop science, plant pathology, entomology, climatology, hydrology, statistics). This chapter, and other publications (Black, 1993; Tisdale et al., 1993; Foth and Ellis, 1997; Havlin et al., 2004), describes these principles and practices in great detail. At heart, however, we seek to evaluate the fertility of a soil by observations and tests and then to use this information to predict the response of plants, and the larger environment, to our nutrient management efforts. The actual practices that constitute soil fertility evaluation include an impressive array of field and laboratory diagnostic techniques and a series of increasingly sophisticated empirical and/or theoretical models that quantitatively relate these indicators of soil fertility to plant response. Diagnostic techniques include long-standing practices, such as chemical and biological soil tests, visual observations of plant growth for nutrient deficiency or toxicity symptoms, and chemical analyses of plant tissues. New approaches include passive or active optical sensing technologies and geographic information systems (GIS) that facilitate landscape scale, site-specific assessments of soil fertility. Computerized expert systems allow us to rapidly relate these indicators of soil fertility to quantitative or qualitative assessments of plant performance (e.g., yield, composition, quality, color, health) and thus to rapidly adjust soil management practices for the most efficient use of nutrients. These advances in computing, GIS, and sensing technologies have allowed us to better describe and address the temporal and spatial variability of soil fertility.

13.1.3 Soil Fertility Evaluation for Agricultural and Nonagricultural Systems

The study of soil fertility evolved within ecosystems devoted primarily to the production of agricultural crops, particularly plants grown for food, forage, fiber, and industry. Tisdale et al. (1993) traced the relationship of soil fertility management to food production as far back as 2500 BC. The importance of soil fertility to world agriculture continues today as a spiraling world population and a diminishing arable land base create unprecedented pressures on scientists and practicing agriculturalists to produce more food per unit area of land than ever before. Advances in plant genetics and breeding and other agricultural technologies (e.g., irrigation) are increasing agricultural productivity. However, higher crop yields mean greater depletion of soil nutrient supplies, which eventually must be balanced by increased nutrient inputs to maintain the fertile soils needed by our societies. Given this, it is apparent that soil fertility evaluation will play an increasingly important role in the future of global agriculture as we seek to identify new lands that can be brought into production and to maximize the production from existing soils. Land uses other than traditional "production" agriculture also require a thorough, in-depth evaluation of soil fertility for maximum economic and environmental efficiency. Examples are horticultural systems, disturbed lands needing reclamation, and soil conservation and remediation practices.

Horticulture includes an extremely diverse range of situations where nutrients must be managed, often quite intensively. Vegetables for fresh market and processing, greenhouses and nurseries growing ornamental and vegetable plants for urban areas, golf courses, public gardens, parks, athletic facilities, and the managed landscapes around commercial businesses, governmental offices, and cities are only a few examples. The types of plants and growth media ("soilless" growth media are often used for horticultural plants) common to these situations are staggering in breadth and variability, challenging the ability of scientists to provide a systematic process for soil fertility evaluation.

Land reclamation can be equally diverse in terms of the nature of the growth media and the types of plants. Soils at land reclamation sites (e.g., surface mining, highway construction, landfills) are often highly disturbed by human activity and possess extremely unfavorable chemical and physical characteristics, including very low soil fertility. In many cases the soils used to revegetate disturbed lands are in fact subsoils, geologic materials, or low-quality soil materials imported from nearby borrow pits. In other cases, "synthetic" soils, created from by-products such as biosolids, coal ash, composts, and poor quality soil must be used. Evaluating the fertility status of soil-like materials such as these, with reference to the growth of grasses, shrubs, and trees must often proceed in the absence of a database relating soil nutrient status and/or other soil properties to plant performance.

Related, but slightly different problems are faced when evaluating the fertility of soils used for conservation purposes, such as grassed waterways, terraces, buffer strips, constructed wetlands, and wildlife habitats. In cases such as these, where the goal is not maximum yield but a stable vegetative cover, the objective may often be low to moderate soil fertility, not agronomically optimum nutrient values. Preventing excessive growth of invasive species is also usually a goal in these settings, and many invasive plants become more competitive if soil fertility is high. Finally, the need to ensure optimum soil fertility in soil remediation programs is a new, but increasingly important aspect of soil fertility evaluation. The goals of these programs may be enhancing microbial degradation of an organic contaminant, such as an oil spill, or phyto-remediation (plant-based remediation of a contaminated soil) of an inorganic contaminant, such as cadmium (Cd), lead (Pb), or zinc (Zn) from the soil near an industrial site (Berti and Cunningham, 1994; McCutcheon and Schnoor, 2003).

13.1.4 Soil Fertility Evaluation: Environmental Issues

Environmental quality is inextricably linked with soil fertility. Just as it is essential that we manage soils to optimize plant productivity, it is equally important to manage soil fertility to avoid or minimize the pollution of our waters, atmosphere, and food chain. A wealth of scientific research has clearly documented that some essential plant nutrients can also contribute to environmental problems. Nitrogen (N), arguably the most important plant nutrient, is known to cause human and animal health problems if nitrate-N (NO_3-N) leaches to ground waters used for drinking water supplies. Ammonia-N (NH_3-N) from fertilizers and animal manures can volatilize to the atmosphere as a gas and, upon redeposition in rainfall, cause soil acidification in forest ecosystems. Nitrous oxides (NO_x) produced by the microbial conversion of NO_3-N in soils to gaseous forms of N (NO, N_2O) have been implicated in ozone depletion and global warming. Eutrophication of surface waters, defined as "…enrichment of surface waters by plant nutrients… regarded as a form of pollution as it restricts the potential uses of impacted water bodies" (Foy and Withers, 1995), can be caused by phosphorus (P) and N entering these waters in soil erosion and runoff, or, in the case of NH_3-N by aerial deposition in rainfall. Soil salinity problems can result when the plant nutrients calcium (Ca), magnesium (Mg), potassium (K), sulfate-sulfur (SO_4-S), and chloride (Cl) or nonessential elements such as sodium (Na) accumulate to excess in soils, particularly in arid regions.

Efforts to enhance soil fertility by use of society's wastes or by-products as nutrient sources can also directly or indirectly affect environmental quality. Modern industrialized societies face increasing pressures to land apply wastes to avoid the costs and undesirable environmental impacts of landfilling and incineration. Lesser developed countries often must use wastes and wastewaters as fertilizers and for irrigation because of a lack of resources, equipment, and infrastructure. For example, the use of municipal biosolids (e.g., sewage sludge, compost) as soil amendments is beneficial because it recycles plant nutrients while building soil organic matter. However, this practice is carefully regulated in most countries because biosolids may contain nonessential elements that can be phytotoxic or can accumulate in the food chain, impacting human, animal, or ecosystem health. Additionally, most land application programs for biosolids (and animal manures) base application rates on the amount of N needed for optimum crop yields. However, the unfavorable N:P ratio in most organic wastes, relative to the N:P ratio in harvested crops, usually means that P accumulates in waste-amended soils to concentrations much higher than required for crop production. This creates an environmental dilemma because the beneficial use of organic wastes as N sources causes the build-up of P in soils and the likelihood that significant amounts of P will be lost to surface waters in erosion and runoff (see Section 11.2). Other municipal, agricultural, or industrial by-products that have been shown to have beneficial effects on some aspect of soil fertility and/or productivity often create similar dilemmas. Materials such as papermill sludges, municipal composts, wood ashes, coal combustion by-products (e.g., flue gas desulfurization gypsum, coal fly ash) are all sources of plant nutrients. However, if managed improperly, they can also create unfavorable soil pH values, excessive soluble salts, and cause microbial or chemical immobilization of plant nutrients.

Soil fertility evaluation is more complex today because of the need to balance productivity and environmental protection for a wider and more diverse range of land uses, as illustrated conceptually in Figure 13.1. This chapter presents a critical analysis of

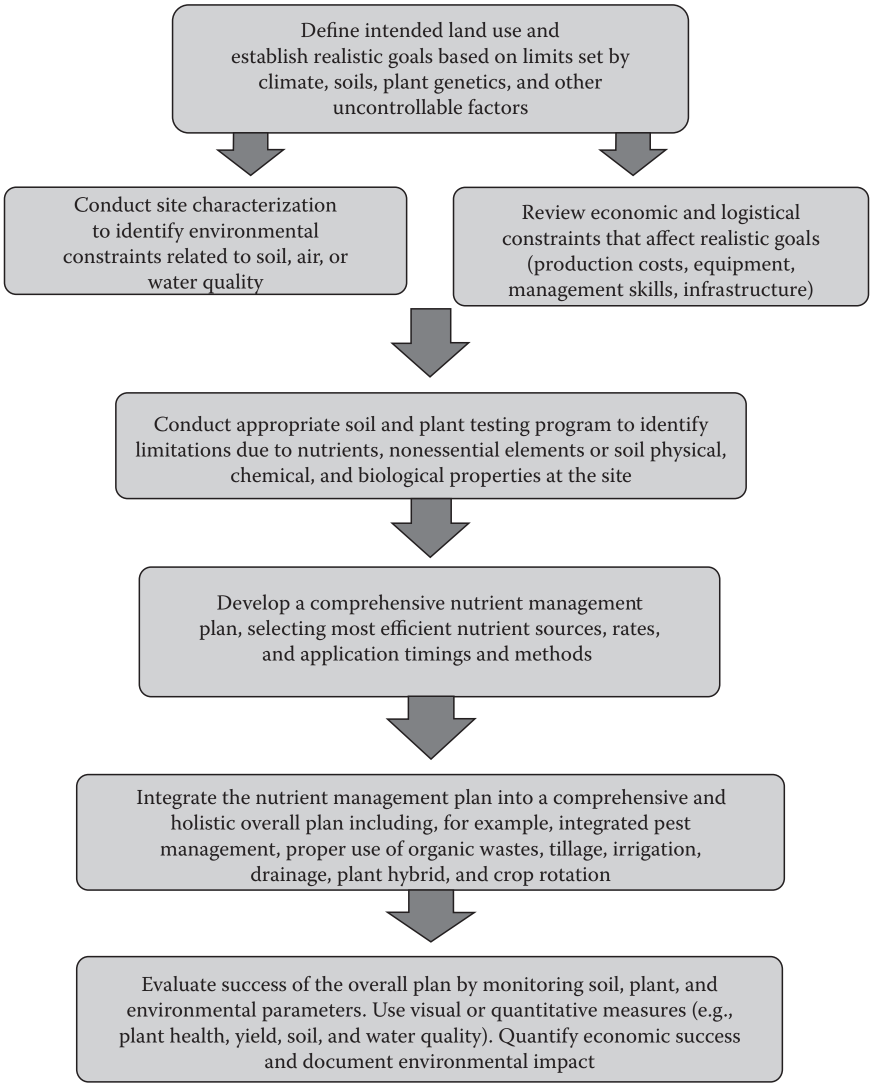

FIGURE 13.1 Conceptual summary of the process of soil fertility evaluation.

the major techniques used in soil fertility evaluation—soil and plant testing, focusing not only on current practices but on the recent advances in science, technology, and interpretive philosophies that will shape soil fertility evaluation in the future.

13.2 Soil Testing

13.2.1 Soil Testing: Historical Overview

Soil testing is defined as "…rapid chemical analyses to assess the plant-available nutrient status, salinity, and elemental toxicity of a soil…a program that includes interpretation, evaluation, fertilizer and amendment recommendations based on results of chemical analyses and other considerations" (Peck and Soltanpour, 1990). The use of soil testing represents perhaps the most significant practical application of our knowledge of soil science to land use management and should be viewed fundamentally as an interpretive process, not simply as a series of laboratory methods. The purpose of soil testing is to provide a quantitative basis to guide soil management decisions, usually, but not always, for agricultural systems (e.g., agronomy, horticulture, silviculture) where plant growth and performance (yield) are the ultimate measures of success. Soil testing has applications to other systems as well; particularly to those where the goal is protection of human health or the environment. Advancing soil testing in nonagricultural systems requires a thorough review of the technical aspects of soil testing and the basis by which we evaluate its success, since plant production is not the issue of greatest importance.

Early efforts at soil testing began in the nineteenth century but systematic studies of the relationship between soil testing and plant growth did not occur until the 1920s. As with soil fertility in general, soil testing evolved within an agricultural setting; hence, its principles and practices have been markedly influenced by the needs and interests of production agriculture. The original purpose of soil testing was rather straightforward—to determine if soils were deficient in nutrients and, based on field studies of crop response to fertilizers and manures, to make recommendations for the nutrient rate, source, and method that would most effectively overcome the limitations caused by the nutrient deficiency. Organized soil testing programs began to be established in the United States in the late 1940s as chemical soil tests were developed that could rapidly assess nutrient availability in soils. The broader infrastructure of soil testing originated first with universities, where research and Extension scientists conducted the laboratory, greenhouse, and field studies needed to verify the accuracy and reliability of soil test methods. Following close upon these studies was the educational aspect of soil testing—publications that described how to test soils and report forms that provided users (primarily farmers) with results and recommendations. Today soil testing is an international activity operating in both the public and private sectors. In the United States, numerous regional and national soil testing organizations, often including public and private soil testing laboratories, are in place to review and revise soil testing methods, update soil test interpretations and recommendations, and ensure the analytical proficiency of soil testing laboratories. Information on the activities and publications of these vitally important advisory and overview groups is available from the web sites of the Soil Science Society of America (SSSA) (https://www.soils.org/), the Soil and Plant Analysis Council (http://www.spcouncil.com/), and the North American Proficiency Testing Program (http://www.naptprogram.org/).

13.2.2 Soil Testing: Assessing Elemental Availability in Soils

One of the fundamental tenets of soil testing is that only a proportion of the total quantity of an element in a soil will be available for assimilation by a biological organism. This means that measuring total elemental concentration in soils is usually of little value. Instead we must have testing methods that can extract (complex, dissolve, desorb, exchange, hydrolyze) a percentage of the total soil nutrient pool that is proportional to the quantity that will become available to the organism of interest during the time period of concern. The term *labile* is often used to describe the chemical and biological forms of an element that are in rapid equilibrium with the soil solution and are thus most likely to be available for biological assimilation. A similar term, *bioaccessible*, is often used when the primary interest is in testing contaminated soils for potentially toxic elements, particularly metals such as arsenic, copper, chromium, and lead, where the main concern is human exposure via ingestion or dermal contact. Much of soil testing research has focused on the development of chemical extracting solutions that can selectively remove labile and bioaccessible elements from the soil in a rapid and reproducible manner.

13.2.2.1 Assessing the Availability of Essential and Nonessential Elements

Insofar as soil fertility is concerned we are most interested in the availability of the 13 elements known to be essential for plant growth that are primarily obtained from soils (N, P, K, Ca, Mg, S, B, Cl, Cu, Fe, Mn, Mo, Zn) as opposed to those obtained from air (C, O) and water (H, O). When we consider human, animal, and environmental health, we have two other concerns. First is the potential environmental impact of essential plant nutrients found in soils that may be transported to other ecosystems (e.g., soil P movement to surface waters). Second is the fate of essential and nonessential elements added to soils in fertilizers or other soil amendments (biosolids, composts, industrial by-products, manures) that may impact human health should they enter the food chain, drinking water supplies or natural ecosystems or become toxic to plants if they accumulate to high concentrations in soils. The nonessential elements of greatest concern are aluminum (Al), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), and selenium (Se). Potentially toxic essential elements are Cu, Mo, and Zn.

The most common means to assess the availability of elements in soils is with chemical soil test extractants, which are typically dilute solutions or mixtures of acids, bases, salts, and chelates. Biological techniques (e.g., bioassays based on microbial growth) have been used to a limited extent but are generally too expensive and time-consuming for routine use. The most effective concentrations and relative proportions of the reagents in a chemical extracting solution were usually determined empirically by comparison of the amount of an element extracted from the soil with some type of biological response (usually yield) by a target organism (usually a plant). The nature and diversity of chemical solutions used in soil testing is illustrated by comparing the Mehlich 1 soil test, a dilute mixture of two strong acids (0.05 M HCl + 0.0125 M H_2SO_4), the ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA) soil test, a dilute combination of a base (1 M NH_4HCO_3) and a chelating agent (0.005 M DTPA), and the Bray P_1 soil test, a dilute mixture of a strong acid (0.025 M HCl) and a complexing ion (0.03 M NH_4F).

Soil testing extractants developed for plant nutrients have also been used, with some success, to assess the risk of plant uptake of nonessential elements (O'Connor, 1988, Risser and Baker, 1990; Gaskin et al., 2003; Sukkariyah et al., 2005) or loss of these elements in surface runoff (Zhang et al., 2003). Other soil testing methods are also used for these elements, although not to measure biological availability. Examples include a method to measure total sorbed metals that is often used to monitor the accumulation of elements in the soil up to some defined regulatory limit (EPA-3050; U.S. Environmental Protection Agency, 1986) and the toxicity characteristic leaching procedure (TCLP), sometimes used to determine if a soil is sufficiently polluted with an element or organic compound to be considered a hazardous waste. Recent advances in environmental soil testing for some metals (As, Cd, Pb, Zn) have used extracting solutions that simulate the biological activity within the human digestive system, referred to as the physiologically based extraction test (PBET) (Ruby et al., 1996; Fendorf et al., 2004; Brown et al., 2007).

13.2.2.2 Influence of Soil Properties and Environmental Conditions on Elemental Availability

One of the major challenges in the evaluation of soil fertility is the need to develop tests (chemical or otherwise) that can estimate nutrient availability in soils of widely differing biological, chemical, and physical properties. Decades of soil science research have proved that the availability of elements in soils depends both on soil properties that are essentially permanent (e.g., the percentages of sand, silt, and clay, oxides of Fe and Al, carbonates, and organic matter) and on those that are more sensitive to natural and anthropogenic inputs (pH, cation exchange capacity [CEC], oxidation–reduction status). Elemental availability can also be markedly affected by broader soil properties (drainage class, nature of soil horizons, slope) and by the soil environment (aeration, moisture, temperature). Therefore, if we wish to estimate the present availability of essential and/or nonessential elements in a given soil, and how this availability will change following some management practice, we must also have a good understanding of the basic properties of that soil and of the environmental conditions likely to be present during the time interval of interest.

Two approaches are used to integrate soil properties and environmental conditions with elemental availability provided by soil testing. First, we can directly test soils for some of these properties and use this information to modify our assessment of biological availability. The most common examples of this are soil pH and organic matter content; other parameters (e.g., CEC, texture, oxides, carbonates) are usually too time-consuming to measure routinely. Second, we can obtain information on soil properties that are difficult to measure and on environmental conditions simply by asking a few key questions of the individual submitting the soil sample for analysis. Knowledge of geographic location, soil series, drainage class, slope, and historical information on previous soil management practices (e.g., fertilization, liming, crop rotation) can be invaluable when evaluating soil productivity and thus crop nutrient requirements. Our ability to integrate information such as this into management recommendations has markedly improved due to the now widespread use of computers in soil testing and with the increased ease of using GIS that are capable of "layering" different data bases to provide a more holistic view of the relationship between soil fertility and land use.

13.2.3 Soil Testing: Overview of the Major Components

All modern soil testing programs have four basic components: (1) soil sample collection, handling, and preparation; (2) soil analysis; (3) interpretation of analytical results; and (4) recommendations for action. For soil testing to be successful, each component must be conducted properly, keeping the overall objective (e.g., plant production or environmental protection) firmly in mind, and with an awareness of the potential sources of error that can occur at each step.

13.2.3.1 Soil Sample Collection and Handling

Collection of a sample that is representative of the entire area of interest, whether it is a farm field, a lawn or garden, or a severely disturbed soil at a construction or mining site, is the most important step in any soil testing program. Proper handling of the sample, once collected, is also important to avoid contamination or changes in elemental concentrations due to improper storage and/or the use of incorrect techniques to prepare the soil sample for analysis (drying, grinding, sieving). An effective soil sampling and handling program must be based on an understanding of the natural and anthropogenic sources of soil variation, the proper method of sample collection (depth, time of year, sampling tools), and the sources of error in sample handling and preparation.

13.2.3.1.1 Understanding and Compensating for Variability

A high degree of natural variability in soil chemical and physical properties can exist even within a very small area. The origin of this variability is the soil forming process in which parent material, climate, relief (topography), biota, and time act together to produce soils that are fundamentally different, not only in terms of topsoil properties, but throughout the entire soil profile. Sample collection should reflect this natural variability, to the extent that it is likely to significantly influence the intended use of the soil. In some cases the differences between adjacent soil series in a large field may be pronounced and require not only different soil samples, but entirely different soil and crop management practices. In other situations differences are minor and collecting additional samples and/or altering management practices is not economically justifiable. Information on the spatial distribution of soil series in an area is available in soil surveys such as those published and now available on the internet (http://soils.usda.gov/survey/printed_surveys/) by the U.S. Department of Agriculture's Natural Resources Conservation Service (USDA-NRCS). Internet access to soils information, at least in the United States has increased significantly in the past decade and much useful information is now available at the NRCS "Soil Data Mart" (http://soildatamart.nrcs.usda.gov/). The Soil Data Mart can quickly allow users to determine where soil tabular and spatial data are available and then to download these data and a variety of reports for individual soil survey areas. Consulting soil surveys is a first step in identifying natural sources of variability to consider in a soil sampling program. A simple follow-up to reviewing these soil surveys is to visually inspect the areas of interest, particularly during periods of plant growth or major seasonal changes in climate, to determine how natural soil variability is affecting land use. New technologies are now available to integrate soil survey information and qualitative data on soil spatial variability into GIS-based land use planning including the use of remote sensing and global positioning systems (GPS), to link soil sample location to soil series. For agronomic crops yield, monitoring devices can now be installed on harvesting equipment, providing a spatially based data set that relates soil fertility, soil series, and plant performance (see Section 13.4). Natural variation can often be overshadowed by the variability in soil fertility caused by human activities. Many soil management practices, such as the method of fertilizer or organic waste application, the tillage method, land leveling for irrigation, terracing, and even the year-to-year selection of what plants will be grown and where, can produce marked differences in soil nutrient status and other soil properties. These differences can be even more pronounced in nonagricultural settings, such as land reclamation projects, where soil disturbance can be severe and by-products may be used as soil amendments at unusually high rates. It is also important to remember that anthropogenic as well as natural soil variability can occur in three dimensions. For example, changing from conventional tillage to no-tillage can result in surface accumulation of P and a decrease in pH at the soil surface as well. Therefore, such factors should be accounted for when designing a soil sampling program. Similarly, nutrient management practices that involve subsoil tillage or injection of soil amendments (e.g., lime, fertilizer, manures) can extend spatial variability below the topsoil, a factor that should not be ignored in the soil sampling process.

Many other examples could be cited to make the point that spatial variability in soil properties, natural or anthropogenic, is inevitable. What is more important, however, are the practices that can be used to compensate for any known source of variability. James and Wells (1990) suggested that soil sample collection basically occurs under either uniform or nonuniform conditions and that sampling techniques should reflect this. Uniform fields are those that are reasonably similar in physical properties (e.g., slope, aspect, drainage, soil series,) and management practices (e.g., crop rotation, fertilizer/manure management history, tillage, irrigation). In many agricultural settings this is a rather common scenario. The proper approach to use for uniform fields is to collect a random, composite sample. This is normally done by following a "zig-zag" path across the area to be sampled, collecting enough soil samples to minimize the influence of any localized nonuniformity (Figure 13.2). Typically this involves collecting about 25–30 separate soil cores from a uniform area <8 ha (~20 acres), ensuring that field corners and edges are included in the sample. Individual soil cores are combined into one composite sample that represents the entire area by crushing and mixing and the composite sample is submitted for analysis.

Nonuniform fields were defined by James and Wells (1990) as those with a high degree of either macro-variation (significant variation between sample points separated by >2 m) or meso-variation (significant variation between sample points separated by 0.05–2 m). For areas with high macro-variation a nonrandom sampling process must be followed to characterize the average value for the soil properties of interest and to understand the spatial location of extreme values. This prevents skewing of average soil test results for an area by samples that are extremely high or low in some soil property. It also allows for more site-specific application of fertilizers, organic wastes, lime, etc. at appropriate rates, thus avoiding under- or over-application of these soil amendments. Nonrandom sampling requires a large number of soil samples and is usually done by establishing a field sample grid with a spacing of 15–30 m between grid intersection points. A composite soil sample is collected at each grid point by combining 8–10 soil cores collected from a 1 m diameter circle placed around the sample point. Grid spacing is a function of the intended land use and the anticipated degree of macro-variation. Note that a 15 and 30 m grid spacing will result in about 45 and 12 composite soil samples per ha, respectively, considerably more than the one sample per 8 ha associated with random sampling. Grid sampling has become more common in recent years with the advent of GIS and GPS technology and its use in precision agriculture (see Section 13.4). For areas with significant and identifiable meso-variation, as might occur when fertilizers are consistently placed in bands across a field, a more intensive random sampling pattern can be used to ensure that the average value is not skewed by either the very high value present in the fertilizer band or the lower value for the bulk soil located between the bands. The number of soil cores to be collected in these situations will usually be four or five times as great as those needed for a random, composite sample (i.e., as many as

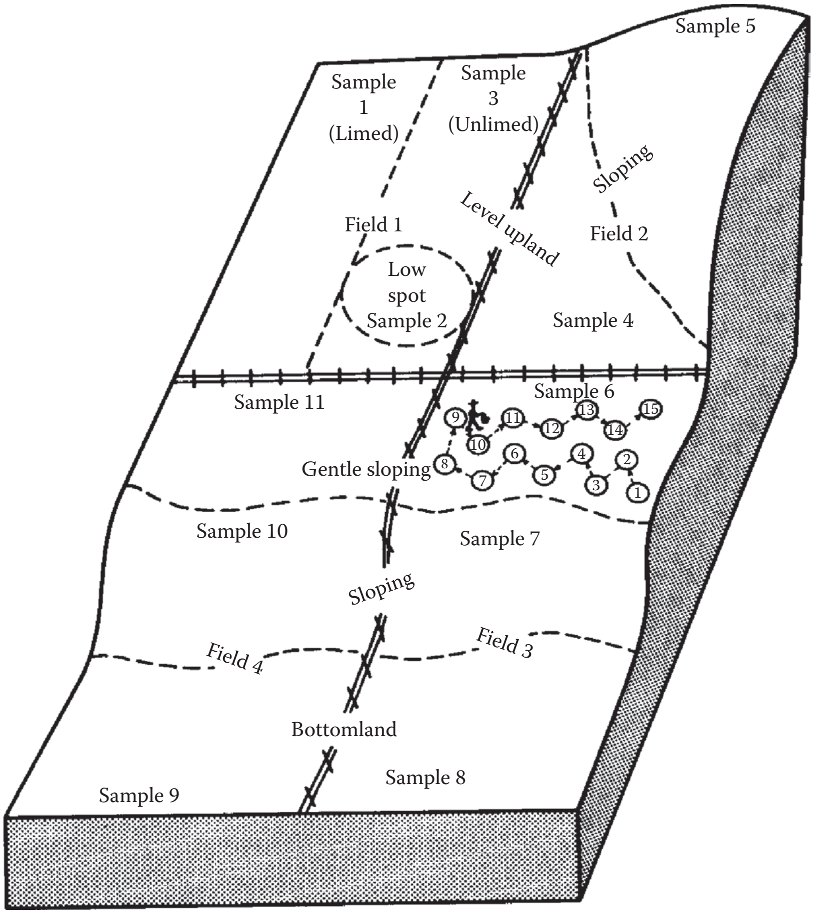

FIGURE 13.2 Illustration of soil sampling practices for uniform fields [Courtesy of Nebraska Agricultural Extension Service].

1–2 soil samples per ha). Finally, it should be noted that random and nonrandom sampling techniques are not appropriate for all aspects of soil fertility evaluation, particularly true for elements that are more mobile in the soil profile (e.g., NO_3-N and SO_4-S).

13.2.3.1.2 Soil Sampling Methods

The most important factors to consider in the soil sampling process are the depth of sampling, the time of year to sample, and the frequency of sampling. The depth to sample depends on the objectives of the soil fertility evaluation, including the crop to be grown, the nutrient of interest, the type of soil test to be performed, and the basis for resulting fertilizer recommendations. Soil samples for routine soil tests of plant nutrient availability and lime requirement are usually obtained from topsoils (0–20 cm depth). There are, however, a number of important exceptions to this general rule such as when soil tests are conducted for mobile soil nutrients (NO_3-N and SO_4-S), or to estimate the effect of pH on herbicide activity in no-till cropping systems, or for soil fertility evaluation for shallow or deep-rooted crops, or to monitor the leaching of potential pollutants downward in the soil profile. Shallow soil sampling is most often recommended for conservation tillage systems where nutrients and lime are not incorporated with the soil by plowing, for permanent pastures and/or turf where root systems rarely extend below a depth of 10 cm, and to estimate the potential for P loss in erosion or runoff in watersheds where eutrophication is an important environmental concern (sample to 0–5 cm). Finally, it is important to review the source of soil test interpretations or fertility recommendations before deciding on a soil sampling depth. In the United States, recommendations often originate from a local or regional Land Grant University and different universities may have calibrated the same tests to different sampling depths. The recommended depth for subsoil sampling varies with the intent of the test. For example, subsoil testing for NO_3-N in arid regions may require that samples be taken to as deep as 1 m (60 cm is often recommended). Testing sandy soils in humid regions for SO_4-S may require a subsoil sample from the B horizon (usually 20–60 cm) where SO_4-S can accumulate by sorption to clays and Fe/Al oxides. Care should be taken to minimize contamination of the subsoil sample by topsoil when collecting subsoil samples, which can seriously influence results and subsequent recommendations.

The proper time of year to collect a soil sample and the frequency of soil sampling should also be considered. Soil samples can be collected at any time of the year when the ground is not frozen, although the ideal time is shortly before making a land management decision because this gives the most current indication of soil properties (fertility, pH). In general, for most agricultural systems routine soil tests for lime and fertilizer recommendations are normally collected 3–6 months prior to planting a crop. This usually provides sufficient time for management decisions to be made and implemented in a timely manner. For example, if a soil test should recommend that limestone is needed to correct a problem with soil acidity, it is important to know this several months in advance of planting because of the time required for the limestone to react in the soil and raise the soil pH to the desired value. Soil testing well in advance of planting also allows time to change the plants to be grown if soil test results indicate that growing conditions are inappropriate for the plant specified. An exception is the pre-sidedress nitrate test for corn (PSNT) (see Section 13.2.4.4), which must be collected when corn plants are about 30 cm in height.

The frequency of soil testing varies somewhat with intended land use, such as the plants to be grown and the nutrient management practices required. Ideally, soils should be sampled at the same time of year (e.g., spring or fall) and at no more than 2–3 year intervals. Sampling at the same time of year minimizes the effect of seasonal variations on soil pH, which decreases during the summer as soluble salts increase in the soil from fertilization and mineralization of organic matter. Some studies have shown similar decreases in P and K during the year, with lower values reported in the fall than spring.

13.2.3.1.3 Soil Sample Handling

Proper handling of soil samples is necessary to prevent contamination and to minimize extreme changes in elemental concentrations or pH between the soil in the field and the sample that is analyzed in the laboratory. Handling includes the actual process of collecting soil cores, the mixing needed to prepare a composite sample, transporting the sample from the field to the laboratory, and the drying, grinding, sieving, and storing that occurs in the laboratory. A variety of tools are available to collect soil cores, including handheld soil probes and augurs, hydraulic soil coring devices, shovels, and hand trowels. The major consideration is to use sampling and mixing tools made of materials that will not contaminate the soil (e.g., stainless steel or plastic). Once collected, individual soil cores from the area of interest are composited by combining them in a clean container, preferably made of plastic to avoid contamination from painted or galvanized metal surfaces, mixing well, and removing a subsample that represents the entire mixture. During the sampling process avoid contamination from dirty or rusty sampling and mixing devices, fertilizer materials, galvanized metals (source of Zn), and paper bags that may contain boron (B). Soil samples should be delivered to the testing laboratory as soon as possible after collection to minimize any changes in elemental concentration that may take place prior to drying. The greatest concern is with NO_3-N, which can increase when soils are kept for extended periods in a warm, moist state (from mineralization of organic N and nitrification of exchangeable NH_4-N), or decrease when soils are maintained in a warm, wet state (from denitrification of NO_3-N). Once received by the laboratory, soil samples are normally dried at low temperatures (ambient to 50°C; avoid higher temperatures), ground and sieved, typically to pass a 2 mm screen. The samples are then ready for analysis.

13.2.3.2 Soil Analyses: Overview of Chemical, Physical, and Biological Methods

Chemical analysis of soils is based on the principle that chemical solutions can rapidly, reproducibly, and inexpensively assess soil nutrient supplying capacity and other soil properties that affect plant growth (pH, soluble salts, organic matter). The most common chemical methods used are extraction and equilibration; others include titration (for acidity) and chemical or thermal oxidation (for organic matter).

Chemical extraction is almost always conducted with dried, ground, and sieved soil samples. For most soil tests the process involves scooping or weighing a small representative portion of the soil sample (from 1 to 10 cm^3 or g) into an extracting vessel (flask, beaker, extraction bottle), adding a known volume of chemical extracting solution (from 10 to 100 mL), shaking rapidly for a short time period (from 5 to 30 min), filtering the sample, and analyzing the filtrate for the elements of interest. For example, extraction by the Mehlich 3 soil test, one of the most widely used extracting solutions in the United States involves scooping 2.5 cm^3 of air-dried, sieved (2 mm) soil into a 100 mL plastic extraction bottle, followed by the addition of 25 mL of the Mehlich 3 solution (0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA). The soil suspension is shaken for 5 min on a reciprocating shaker, filtered into 25 mL plastic vials, and analyzed by either atomic absorption spectrophotometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), or colorimetry to determine the concentration of each element in the soil extract. The principles of these instrumental methods are described in the Soil Science Society of America (SSSA) monograph *Methods of Soil Analysis*: *Chemical Properties*, Part 2 (Sparks, 1996).

Soil chemical properties are not always assessed by extraction methods. Another common chemical testing method is equilibration, in which a solution is added to the soil, the resulting suspension is shaken (or sits) for a short time period, and some property of the soil suspension is measured. This approach is used to measure soil pH and lime requirement, by use of an electrode that determines the chemical activity of hydrogen ions in a soil–water suspension (pH) or in a suspension of soil and a chemical buffer solution (lime requirement). A similar approach is used to measure soil soluble salts where a conductivity cell or bridge measures the specific conductance of a soil–water suspension. Some soil testing laboratories use titrimetric techniques to measure soil acidity by first extracting soil with a neutral salt solution (e.g., 1 M KCl), followed by titration of the acidic extractant with a dilute base (e.g., 0.1 M NaOH). Soil organic matter tests originally used wet chemical oxidation to estimate organic matter from the amount of carbon in soils that could be oxidized by $K_2Cr_2O_7$. Environmental concerns about the use and disposal of chromium (Cr) have caused most laboratories to now use high temperature oxidation (360°C) to estimate organic matter from weight loss upon ignition of a soil sample.

Most soil testing methods have been standardized by regional and national soil testing organizations and the SSSA. Consequently, numerous publications provide detailed, recommended methods (e.g., soil drying, grinding, sieving; preparation of extracting solutions; proper soil:solution extraction ratio, shaking rate, time and filtration method; and appropriate instrumental method). These publications are both national (Sparks, 1996; Jones, 1999; USDA-NRECS, 2004; Carter and Gregorich, 2007) and regional (SRIEG-18, 1992; NEC-67, 1995; NCR-13, 1998) in scope. Closely following these recommended methods is essential to accurately assess soil fertility.

13.2.3.3 Interpretation of Soil Testing Results

Interpretation of soil testing results may be defined as quantitatively relating the results of a soil analysis to the probability that a soil management activity will have the desired result. For soil fertility evaluation this means using soil test results to accurately predict crop yield without nutrient addition and the probability of a profitable plant response when fertilizers or other soil amendments (e.g., lime, manures, composts) are added. Interpreting soil test results for land uses where the desired result is not economically optimum plant yield (e.g., aesthetic value of ornamental plants in a horticultural setting; biodegradation of an organic pollutant in a bioremediation system; inactivation of a heavy metal in a polluted soil) requires that we are able to identify measures of success that can be quantitatively related to a soil test value and to soil management practices.

Soil test interpretation for agricultural systems begins with research that proves a statistical correlation exists between a soil test value and some aspect of plant response (e.g., nutrient concentration in the plant, crop yield). If the soil test and plant response are correlated the next step in interpretation is soil test calibration. The main goal of soil test calibration is to rate soils in terms of the probability that nutrient additions will be profitable (e.g., to divide the population of soil test values into responsive and nonresponsive categories; Table 13.1 and Section 13.2.6).

13.2.3.4 Recommendations Based on Soil Testing

Soil test recommendations must integrate soil test data with many other factors such as climate, economics, soil and crop management practices, management ability of the soil test user, and any considerations imposed by environmental protection. Soil test values tell us nothing about these other factors, instead we must rely on other sources of information, basic scientific principles, practical experience, and professional judgment to integrate them, with soil test results, into a reasonable recommendation.

The recommendation process starts with knowledge of the intended land use and factors that affect recommendations vary in importance with land use. Production agriculture recommendations usually include the rate, timing, and method of application of fertilizers, liming materials, and other soil amendments such as biosolids and manures. In this situation, where the goals are economically optimum crop yields and minimal environmental impact, recommendations are based on (1) current soil

TABLE 13.1 Generalized Soil Test Categories and Recommendations Based on Crop Response and Environmental Impact

Category Name	Category Definition	Recommendations
Crop response		
Below optimum (very low, low, medium)	The nutrient is considered deficient and will probably limit crop yield. There is a high to moderate probability of an economic yield response to adding the nutrient	Nutrient recommendations are based on crop response and will build soil fertility into the optimum range over time. Starter fertilizer may be recommended for some crops
Optimum (sufficient, adequate)	The nutrient is considered adequate and will probably not limit crop growth. There is a low probability of an economic yield response to adding the nutrient	If soils are tested annually, no nutrient additions are needed for the current crop. For other than annual soil testing, nutrient applications are often recommended to maintain the soil in the optimum range. Starter fertilizer may be recommended for some crops
Above optimum (high, very high, excessive)	The nutrient is considered more than adequate and will not limit crop yield. There is a very low probability of an economic yield response to adding the nutrient. At very high levels, there is the possibility of a negative impact on the crop if nutrients are added	No nutrient additions are recommended. At very high or excessive levels, remedial action may be needed to prevent phytotoxicity or environmental problems
Environmental response		
Potential negative environmental impact (very high, excessive)	Soils testing at this level or above have higher potential to cause environmental degradation and should be monitored closely. The likelihood of environmental problems depends on other site-specific characteristics (e.g., slope, hydrology, rainfall). This soil test level is independent of the crop response categories above and may be above or below the optimum level based on crop response	If other site factors minimize environmental impact, some nutrient additions may be recommended according to crop response guidelines. If other site factors indicate a potential environmental impact is likely, nutrient additions including starter fertilizer are not recommended. Remedial actions may be required to protect the environment

Source: Adapted from Beegle, D. 1995. Interpretation of soil test results, p. 84–91. *In* J.T. Sims, and A.M. Wolf (eds.) Recommended soil testing procedures for the Northeastern United States. Bull. no. 493. University of Delaware, Newark, DE.

test values and any other soil characteristics that affect a recommendation, such as soil drainage class; (2) the crop to be grown and the realistic yield potential for that crop; (3) soil test calibration data that indicate the degree of response expected to any soil amendment; (4) the source of nutrients and/or lime to be used and any restrictions on application method and timing that exist; (5) soil management history, such as the use of animal manures, biosolids, or growth of a leguminous cover crop; and (6) environmental parameters that may require modification of standard recommendations, such as soil leaching potential and depth to ground water and/or soil erosion and runoff potential and proximity to surface waters sensitive to eutrophication.

Not surprisingly, given the rather subjective nature of many components of the soil test recommendation process, several different recommendation philosophies have evolved for agricultural systems. These philosophies, contrasted in detail in Section 13.2.6, vary mainly in the approach used to maintain soil fertility in the range needed for optimum crop production. Some recommend more liberal and more frequent applications of nutrients to ensure that nutrient deficiency does not limit crop production. Others are more conservative, relying heavily on soil tests as the basis for any nutrient addition, often recommending that no nutrients be added when soils are in the optimum or excessive range. The decision on which philosophy to follow is primarily based on the current economics of production. However, for nutrients known to have environmental impacts (N, P), environmental-based recommendations to protect ground and surface water quality, even if the result is suboptimum crop performance, are now mandated or at least being considered in many regions.

13.2.4 Soil Testing Methods for Plant Nutrients

The intent of this chapter is to briefly describe, for each plant nutrient, (1) the major soil processes affecting the nutrient that are relevant to soil testing, (2) current soil test methods and recent advances in research, and (3) any factors that should be taken into consideration when conducting soil tests or interpreting soil test results. Other chapters in the *Handbook of Soil Science* provide reviews of nutrient cycling and should be consulted as necessary.

13.2.4.1 Phosphorus

13.2.4.1.1 Soil Phosphorus

Phosphorus in soils occurs in inorganic and organic forms that primarily originated from the weathering of calcium phosphate minerals, the most common being apatite ($(Ca_{10}(X)_2(PO_4)_6$, where X is either F, Cl, OH, or CO_3). Approximately 30%–50% of the total P in most soils is found in the organic fraction. Chemical weathering of soil minerals and mineralization of organic matter release P into the soil solution where it exists in very low concentrations (0.003–0.3 mg P L^{-1}, average of ~0.05 mg P L^{-1}) almost exclusively as phosphate ions. In acid soils, dihydrogen phosphate ($H_2PO_4^-$) is the prevalent ion while hydrogen phosphate (HPO_4^{2-}) is the main phosphate species found above pH 7.2. Once in solution, phosphate can be assimilated by biological organisms; sorbed (chemically bound) to soil colloids such as clays, oxides of Fe and Al, and $CaCO_3$; precipitate as an insoluble compound by reaction with Al and Fe in acid soils or Ca in calcareous soils; or be lost in surface or subsurface runoff. Phosphorus can be released back into the soil solution by mineralization of organic compounds, desorption of P from soil colloids, or the dissolution of solid phases of P. Plant available forms of soil P are mainly those found in the soil solution, sorbed by soil colloids, or precipitated as relatively soluble minerals. Mineralization of organic P and dissolution of very stable P minerals proceeds too slowly in most soils to provide a large percentage of the available P required for plant growth. Desorption (and dissolution) of P occurs when plant uptake decreases the P concentration in the soil solution, thermodynamically favoring the release of sorbed or solid phase P. Soil tests for P were designed to simulate this process, extracting P from sorbed forms and metastable precipitates by four processes: (1) acid dissolution, (2) anion exchange, (3) cation complexation, and (4) cation hydrolysis (Kamprath and Watson, 1980). For example the Bray P_1 soil test, developed for slightly acid and neutral soils where Al-P and Ca-P are major sources of plant available P, is a mixture of 0.025 M HCl + 0.03 M NH_4F. The F^- ion forms a strong complex with Al^{+3} in solution, causing dissolution of Al-P compounds, and the dilute HCl dissolves a proportion of the Ca-P and lesser amounts of Al-P and Fe-P. Together, NH_4F and the HCl cause labile pools of soil P to release P into solution, similar to what would occur in soils in response to the depletion of soil solution P by plant uptake. In near neutral soils, the F^- also reacts with Ca to form CaF_2, enhancing dissolution of Ca-P. The Olsen soil test (0.5 M $NaHCO_3$, pH 8.5) functions similarly in calcareous soils where HCO_3^- precipitates soluble Ca as $CaCO_3$ causing release of P from $CaHPO_4$. Soil P tests may also extract organic P either by direct acid hydrolysis of organic P esters or by enhancing P release from organo-metallic complexes (Al-OM, Fe-OM). Note that soil tests based on soluble P alone are not an accurate index of a soil's P supplying capacity because they do not reflect the capacity of the solid phase to replenish the solution phase as P uptake occurs. Nor would soil tests using very strong chemical reagents that cause extensive dissolution of mineral phases or oxidation of organic matter because they would overestimate plant available P.

Current soil testing methods for P: the soil testing methods commonly used for P today are shown in Table 13.2 and were reviewed extensively by Fixen and Grove (1990). The Bray P_1, Ca-lactate, Morgan, and Olsen soil tests are only used to extract P while Mehlich 1, Mehlich 3, and AB-DTPA (NH_4HCO_3 + DTPA) are multielement soil tests used to extract P, K, Ca, Mg, and some micronutrients (Cu, Fe, Mn, Zn). As a general rule, the acidic extractants (Bray, Mehlich 1, Mehlich 3, Morgan) are used on acid soils and the alkaline extractants (AB-DTPA, Olsen) on calcareous soils. A number of studies, however, have shown that the Olsen P test may be an accurate test for a broader range of soils.

TABLE 13.2 Summary of Soil Testing Methods Currently Used for Phosphorus (P)

Soil Test	Extractant Composition	Comments, Critical Values,[a] and Sources
AB-DTPA	M NH_4HCO_3 + 0.005Af DTPA—pH 7.5	Multinutrient extractant primarily used with alkaline soils. Critical value: ≥8 mg kg^{-1} (Soltanpour and Schwab, 1977)
Bray P_1	0.03 M NH_4F + 0.025 M HCl	Used only to extract P on acid soils with moderate CEC. Critical value: ≥30 mg kg^{-1} (Bray and Kurtz, 1945)
Mehlich I	0.05 M HCl + 0.0125 M H_2SO_4	Multinutrient extractant used on acidic, low CEC soils. Critical value: ≥25 mg kg^{-1} (Mehlich, 1953)
Mehlich III	0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA—pH 2.5	Multinutrient extractant suitable for wide range of soils. Well correlated with Bray P_1, Mehlich I, and Olsen P. Critical value: ≥50 mg kg^{-1} (Mehlich, 1984)
Morgan and modified Morgan	Morgan: 0.7 M $NaC_2H_3O_2$ + 0.54 M CH_3COOH + —pH 4.8 modified Morgan: 0.62 M NH_4OH + 1.25 M CH_3COOH—pH 4.8	Multinutrient extractant primarily used in the northeast United States for acid, low CEC soils. Not suitable for calcareous soils. Critical value: ≥4–6 mg kg^{-1} (Morgan, 1941)
Olsen	0.5 M $NaHCO_3$—pH 8.5	Originally developed as P extractant for alkaline soils in the western United States; now also used for acid and neutral soils. Critical value: ≥10 mg kg^{-1} (Olsen et al., 1954)
Egner	P-CAL: 0.01 M Ca lactate + 0.02 M HCl P-AL: 0.10 M NH_4 lactate + HOAc—pH 3.75	Multinutrient extractant used in Europe and Scandinavia but not in the United States. (Egner et al., 1960)

[a] Critical value is defined as the soil test concentration above which the soil test level is considered optimum for plant growth and responses to additions of the nutrient are unlikely to occur. Critical values cited in this table are approximate, can be affected by soil type and crop, and were obtained from several sources.

Two soil testing approaches for P, the P_i soil test and ion exchange resins, do not remove P from soils by chemical extraction. The P_i test was developed and evaluated in the late 1990s and early 2000s and showed considerable promise, but still has not been adopted as a routine soil test (Myers et al., 1995, 1997, 2005; Chardon et al., 1996; Menon et al., 1997). In this method, the soil is equilibrated with 0.01 M $CaCl_2$ in the presence of an Fe-oxide-coated filter paper strip, which acts as an "infinite sink" for soil P. Phosphorus in solution is sorbed to the strip, causing desorption of labile P from the soil. After a specified equilibration period (usually 2 h) the strip is removed, rinsed lightly to remove soil particles, and sorbed P is extracted from the strip by shaking for 2 h with a 1 M H_2SO_4 solution. Ion exchange resins have been used for many years in soil P research to study the desorption of soil P (Amer et al., 1955; Sibbesen, 1978; Wolf et al., 1985; van Raij et al., 1986; Sharpley et al., 1989; Abrams and Jarrell, 1992; Mallarino and Atia, 2005; Saavedra et al., 2007). These studies have shown that anion exchange resins saturated with Cl or HCO_3 and suspended with soils in aqueous suspensions can accurately estimate labile P in soils of widely differing properties. Resins simulate root uptake by removing P from solution by surface sorption processes, with the rate of P sorption controlled by diffusion (Kuo, 1996). Despite this research, ion exchange resins have not been adopted as routine soil tests for P in the United States primarily because of practical difficulties such as separating the resin from the soil after the equilibration process. To overcome these obstacles Skogley et al. (1990) developed an encapsulated ion exchange resin technique for use by routine soil testing laboratories as a multinutrient soil test (commonly referred to as the phytoavailability soil test, or PST; see also Skogley, 1994). Similar efforts have occurred in other countries such as Brazil, where van Raij (1994) successfully adapted ion exchange resin beads for use as multinutrient soil tests by routine soil testing laboratories. Ion exchange resins and chemical extractions can also be used as environmental soil P tests, to identify soils with a higher potential for P loss in soil erosion and surface or subsurface runoff (see Section 13.2.7).

13.2.4.1.2 Considerations in Soil Testing for P

The soil testing process for P is rather straightforward. Soil samples for P can be collected at any time during the year because P is relatively immobile in most soils. The standard sample depth is 0–20 cm, except for permanent pastures and turf (0–10 cm). In fields where the use of banded fertilizers containing P is a common practice it may be necessary to significantly increase the number of soil samples collected per unit area to overcome the high meso-variation that can be present (see Section 13.2.3.1). For situations where the transport of P to surface waters by erosion and runoff is a concern samples should be collected from the 0–5 cm depth, since runoff waters only interact with the upper few centimeters of the soil surface (Sharpley and Smith, 1989; Sharpley et al., 1996). There are no special handling or storage requirements for samples collected for P analysis—air drying, grinding, and sieving with a 2 mm screen is the standard approach. Analysis of P in soil extracts can be done colorimetrically by the molybdenum blue method, which primarily measures orthophosphate (Murphy and Riley, 1962) or by ICP-AES, which measures orthophosphate and some organic P. Note that ICP-AES values for soil test P can often be 5%–10% higher than those measured colorimetrically.

Interpretation of analytical results for P must consider the fact that P moves to roots primarily by diffusion, a process that is highly dependent upon soil moisture and temperature. It is not uncommon to see early season P deficiency in crops grown in soils that are rated as "optimum" or "excessive" in P. Low soil temperatures and dry soil conditions can inhibit diffusion, root growth, and plant uptake of P, creating a temporary P deficiency that often disappears as soils warm and receive rainfall or irrigation. In most cases, if soils have optimum concentrations of plant available P, early season deficiencies have no significant negative effects on crop yield. For the most part, however, soil P tests are interpreted using the sufficiency level approach described in Table 13.1.

13.2.4.2 Soil Testing for Potassium, Calcium, and Magnesium

13.2.4.2.1 Soil K, Ca, and Mg

The cycling and plant availability of K, Ca, and Mg are sufficiently similar that these three nutrients can be considered together for the purposes of soil fertility evaluation. The primary sources of plant available K, Ca, and Mg are soil minerals, which release these ions into solution during the weathering process.

Major K-bearing minerals include the feldspars (orthoclase, microcline, sanidine) and micas (biotite, muscovite, phlogopite). Total K concentrations in soils average 1.9%, but can range from 0.03% in organic soils (peats, mucks), to 0.3% in very sandy soils, to as high as 3.0% in mineral soils derived from feldspars and micas. Once mineral dissolution has occurred, soil K is primarily found in soluble, exchangeable, and nonexchangeable forms. Potassium in the soil solution ranges in concentration from 1 to 80 mg K L^{-1} (average = 2–5 mg K L^{-1}) and is in rapid equilibrium with exchangeable K that is retained by electrostatic attraction to the negatively charged cation exchange sites located on clays and soil organic matter. Usually, less than 5% of the total CEC of a soil is occupied by exchangeable K. Soluble and exchangeable K are the major sources of plant-available K in most soils but together represent less than 1%–2% of total soil K. Nonexchangeable K, also referred to as "fixed" K, is found within the interlayers and on the edges of 2:1 expanding clay minerals and is viewed as a slowly available reserve of K for plant uptake. Soluble K is <1% of exchangeable soil K and can be quickly depleted by plant uptake or leaching. The ability of soils to maintain an adequate concentration of K in solution by releasing K from exchangeable and nonexchangeable forms is referred to as the K buffer capacity and is an important measure of soil fertility. The K buffer capacity of soils depends largely upon the amount and types of clay minerals present and to a lesser extent on soil organic matter content. Soils with higher percentages of clay, especially 2:1 clays, have higher K buffer capacities than sandy or organic soils and more ability to maintain soluble K in an optimum range for plant growth.

Major mineral sources of soil Ca are carbonates, feldspars, and phosphates. The most important Ca-bearing mineral is anorthite ($CaAl_2Si_2O_3$; a plagioclase feldspar), except in calcareous soils of arid regions where calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) dominate. Total soil Ca varies widely, from <0.1% in highly weathered, tropical soils to as high as 25% in calcareous soils. Typical total soil Ca values in noncalcareous, humid, temperate soils are from 0.7% to 1.5%; total Ca values >3% indicate the presence of $CaCO_3$. In most soils, Ca is the dominant exchangeable cation, occupying 20%–80% of the total CEC. Consequently, soil solution concentrations of Ca are quite high relative to most other plant nutrients, ranging from 30 to 300 mg Ca L^{-1} in noncalcareous soils.

Plant available Mg originates from the weathering of minerals such as biotite, dolomite, hornblende, olivine, and serpentine. Total soil Mg varies from <0.1% in coarse, sandy soils of humid regions to 4% in fine-textured soils formed from Mg-bearing minerals. As with K and Ca, soluble and exchangeable Mg are most important to plant growth. Exchangeable Mg occupies from 4% to 20% of total soil CEC and soluble Mg ranges from 50 to 120 mg Mg L^{-1} in temperate region soils.

13.2.4.2.2 Current Soil Testing Methods for K, Ca, and Mg

Soil chemical extraction is by far the most common approach used today to test soils for plant-available K, Ca, and Mg and most extracting solutions simultaneously extract and analyze soluble and exchangeable K, Ca, and Mg (Table 13.3). Haby et al.

TABLE 13.3 Summary of Soil Testing Methods Currently Used for Potassium (K), Calcium (Ca), and Magnesium (Mg)

Soil Test Extractant	Extractant Composition	Comments, Critical Values,[a] and Sources
Ammonium acetate	M NH_4OAc, pH 7.0	Used for >50 year as soil test for K, Ca, and Mg (Chapman and Kelley, 1930; Schollenberger and Simon, 1945). Suited for wide range of soils, but primarily used in midwestern and western states of the United States. Critical values for K, Ca, and Mg vary widely based on soil type (pH, CEC, clay mineralogy) and crop and reportedly range from K: 110–200 mg kg^{-1}; Ca: 250–500 mg kg^{-1}; and Mg: 30–60 mg kg^{-1} (Haby et al. 1990)
AB-DTPA	M NH_4HCO_3 + 0.005 M DTPA—pH 7.5	Multinutrient extractant primarily used with alkaline soils (Soltanpour and Schwab, 1977)
Mehlich I	0.05 M HCl + 0.0125 M H_2SO_4	Multinutrient extractant used on acidic, low CEC soils (Mehlich, 1953)
Mehlich III	0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA—pH 2.5	Multinutrient extractant suitable for wide range of soils (Mehlich, 1984)
Morgan and modified Morgan	Morgan: 0.7 M $NaC_2H_3O_2$ + 0.54 M CH_3COOH +—pH 4.8 Modified Morgan: 0.62 M NH_4OH + 1.25 M CH_3COOH—pH 4.8	Multinutrient extractant primarily used in the northeast United States for acid, low CEC soils. Not suitable for calcareous soils (Morgan, 1941)

[a] Critical value is defined as the soil test concentration above which the soil test level is considered optimum for plant growth and responses to additions of the nutrient are unlikely to occur. Critical values cited in this table are approximate, can be affected by soil type and crop, and were obtained from several sources.

(1990) surveyed soil testing laboratories in the United States and Canada and reported that the most common soil test for K, Ca, and Mg was ammonium acetate (1 M NH_4OAc, pH 7.0), which has been used in the United States since the 1930s. Since then, multielement soil testing extractants, such as AB-DTPA and Mehlich 3 have gained wide popularity and are fast becoming the standard soil test method for K, Ca, and Mg. The more widespread use of multielement extractants can be attributed to the fact that many soil testing laboratories formerly used one extracting solution for P (e.g., Bray P_1), another for K, Ca, and Mg (e.g., 1 M NH_4OAc, pH 7.0), and another for micronutrients (e.g., DTPA). Converting to multielement extractants thus reduced the cost and time of analysis. Most soil test extractants for K, Ca, and Mg displace these cations from exchange sites on soil colloids with a replacing cation, usually NH_4^+ (NH_4OAc, AB-DTPA), Na^+ (Morgan), H^+ (Mehlich 1) or a combination of cations (Mehlich 3, Modified Morgan). All extractants also remove any solution K, Ca, and Mg present in the soil. Acidic soil tests (e.g., Mehlich 1, Mehlich 3) may also extract some nonexchangeable K from soils containing 2:1 clays because the H^+ ion is small enough to enter the interlayers of these minerals and displace K from interlayer exchange sites. Acidic extractants may also overestimate exchangeable Ca and Mg in arid region calcareous soils because they may dissolve Ca- and Mg-bearing minerals. One recent advance in soil K testing has been the use of sodium tetraphenylboron (NaTB) to extract plant available K. Cox et al. (1999) showed in greenhouse studies that a 5 min NaTB soil extraction was well correlated with plant K uptake and suggested that NaTB effectiveness was due to its ability to extract both exchangeable and nonexchangeable K. Fernández et al. (2008) in a field study with soybeans found NaTB to work reasonably well but that is was not as effective overall as 1 M NH_4OAc at predicting plant K uptake.

A few alternatives to chemical extraction have been used for routine evaluation of plant available K, Ca, and Mg. Two that have received the most interest have been ion exchange resins, used in a few U.S. states and some South American countries (van Raij et al., 1986; Skogley, 1994), and electro-ultrafiltration (EUF), which has primarily been used in Europe (Nemeth, 1979; Haby et al., 1990). The basic principles of ion exchange resin techniques were discussed earlier in Section 13.2.4.1. The EUF method combines electrodialysis and ultrafiltration and has been used as a multielement extractant for NH_4^+, NO_3^-, P, K, Ca, Mg, Na, S, B, Mn, and Zn. In this approach, a soil suspension is stirred in a central compartment attached to cells on each side containing platinum electrodes. Microfiber filters separate the soil suspension from the electrodes. Voltage is applied to the electrodes and vacuum filtration is used to withdraw water and dissolved ions from the central cell after specified time intervals that characterize different forms of plant nutrients (e.g., the 0–5 min extraction is soluble K, the 5–10 min extraction is exchangeable K, and the 10–30 min extraction reflects K buffering capacity). Solutions collected at the anode and cathode sides of the EUF device are combined and analyzed by standard instrumental techniques. While EUF has been shown to be an effective method to simultaneously extract plant-available nutrients, it is rather slow and expensive and not as widely used as chemical soil tests (Haby et al., 1990; van Lierop and Tran, 1985).

13.2.4.2.3 Considerations in Soil Testing for K, Ca, and Mg

Soil samples for K, Ca, and Mg analysis are collected following the standard approaches described in Section 13.2.3.1. The most important exception is with K where subsoil samples are sometimes recommended for soils with a very sandy surface horizon and a shallow B horizon (zone of clay accumulation). In these situations subsoil K has been shown to be an important source of plant available K and testing the surface horizons alone may underestimate the true K supplying capacity of the soil. This is particularly true if the B horizon has a high percentage of 2:1 clays that can act as a reservoir of slowly available, nonexchangeable K. Subsoil samples are rarely tested for Ca and Mg. Samples should be collected at the same time each year to minimize the effect of natural, seasonal changes in K concentrations caused by processes such as leaching, freezing, and thawing, biological transformations (uptake, mineralization, biocycling of K from subsoils to topsoils), and seasonal differences in soil moisture content.

Soil sample handling, particularly drying method, can markedly and unpredictably alter extractable K. Air-drying will usually cause an increase in exchangeable K except in soils that have very high K values, where drying results in K fixation into nonexchangeable forms, thus decreasing soil test K. Changes caused by drying are greatest in fine-textured soils dominated by 2:1 clays. While it can be argued that soil tests for K would best be conducted on field-moist soils, virtually all laboratories air-dry soils to ease handling, grinding, sieving, mixing, and weighing of a representative subsample. These advantages outweigh the changes in extractable K that occur during drying; however, soils to be analyzed for K should only be air-dried at moderate temperatures (<50°C) because oven-drying, particularly at >60°C greatly enhances the release of K from soils. Analyses of soil extracts for K, Ca, and Mg can be conducted by either AAS or ICP-AES.

Interpretation of soil test results for K, Ca, and Mg follows the sufficiency level approach (Table 13.1) with only a few minor modifications related to soil type, plant to be grown, and soil/crop management. Soil test K interpretations are often modified based on the CEC of the soil. Soils with higher CEC values will often have a higher "critical value" (point above which crop response is not expected and thus no fertilizer is recommended). As an example, the critical value for soil test K in Alabama (Mehlich 1 soil test) increases from 40 to 80 mg K kg^{-1} as CEC increases from 4.5 to 9.0 cmol kg^{-1}. Subsoil K is occasionally considered when interpreting the results of a soil test for K, usually by the use of indirect information on subsoil properties, such as soil survey data on horizonation (e.g., depth to B horizon), texture, and clay mineralogy. Other factors that may alter a soil test-based recommendation for K fertilization include crop and yield goal that affect K removal, tillage practices, and climate, which affects release of K from K-bearing minerals.

Modification of the results of a soil test for Ca or Mg by inclusion of other information is unusual. In general, maintaining soils in an adequate pH range for plant growth by use of the proper type of liming material is adequate to maintain Ca and Mg fertility in most soils.

13.2.4.3 Sulfur

13.2.4.3.1 Soil S

The total S content of temperate zone soils ranges from 0.005% to 0.04%, more than 90% of which is found in organic forms. Total S values can be much higher in arid and semiarid regions where soils can accumulate soluble and mineral forms of sulfate-S (SO_4-S), such as gypsum ($CaSO_4 \cdot 2H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), and mirabilite ($Na_2SO_4 \cdot 10H_2O$). Important S-bearing minerals in humid regions are pyrite (Fe_2S), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$). Sulfur originating from burning fossil fuels, particularly coal, or S emissions from volcanic activity, wetlands, and oceans can also be added to the soils by wet or dry atmospheric deposition.

The plant available form of S is the sulfate anion (SO_4^{2-}-S), which originates from the dissolution of soluble salts and minerals containing S, oxidation of elemental S, and mineralization of organic S. Solution SO_4-S can be taken up by plants, immobilized in microbial biomass, sorbed by soil colloids, precipitated in an insoluble mineral form by reaction with Ca, Mg, or Na, or leached to subsoils. If plant roots penetrate to subsoils, sorbed SO_4-S can be released into solution and absorbed. Under reducing conditions, SO_4-S can be converted to H_2S gas and lost from the soil by volatilization or precipitated as metal sulfide minerals such as pyrite. Traditionally, S deficiency has been considered uncommon except with high yielding crops grown on deep sandy soils with low organic matter contents or on soils that developed from parent materials low in S. Organic matter mineralization and wet deposition of SO_4-S resulting from the burning of fossil fuels typically have provided enough plant available S for most crops. Concentrations of SO_4-S in the soil solution (A horizon) of most temperate zone soils ranged from 5 to 20 mg SO_4-S L^{-1}, higher than the 3–5 mg SO_4-S L^{-1} required for the optimum growth of most plants. However, recently, S deficiencies have been reported globally due to a combination of factors, the primary factor being a marked decrease in S deposition due to air pollution control measures. Sulfate deposition has clearly decreased over the past 20 years as indicated by the National Atmospheric Deposition Program (NADP, 2008). For example, the average total wet deposition of sulfate at the Huntington Wildlife Station in Essex County, New York, United States, was 22 kg-SO_4 ha^{-1} for the period of 1979–1983 and decreased 43% to 14 kg-SO_4 ha^{-1} for the period of 2003–2007 (NADP, 2009). This decrease in atmospheric deposition combined with increased crop yields and decreased agronomic S inputs are expected to contribute to increasing S deficiencies in crops (McGrath and Zhao, 1995). These predictions have been supported by recent studies showing increased yield responses to S fertilization in previously nonresponsive soils (Chen et al., 2008).

13.2.4.3.2 Current Soil Testing Methods for S

Due to the historic lack of crop response to S fertilization, less effort has been directed toward the development and calibration of soil tests for S than for P and K. Soils tested for S are normally sampled from the A horizon, except in sandy, low organic matter soils with shallow B horizons that can be a significant reserve of plant available SO_4-S. In these situations soil testing laboratories may request a subsoil sample because the subsoil may have enough available S for plant growth.

Soil testing for S relies on chemical extraction. More than 20 extracting solutions have been developed and evaluated as S soil tests, including water and various concentrations of dilute acids (HCl), dilute salts (e.g., $CaCl_2$, LiCl, NaCl, NH_4Cl), acetates (e.g., NH_4OAc, MgOAc, NaOAc), and phosphates (e.g., $Ca(H_2PO_4)_2$, KH_2PO_4) (Johnson and Fixen, 1990). Most extractants remove soluble and sorbed forms of SO_4-S, along with a small percentage of organic S, as these are the soil fractions regarded as plant available. In arid regions where the concentration of SO_4-S is often quite high due to the accumulation of sulfate salts, extraction with deionized or distilled water is used to identify S deficiency. In humid regions, the use of an extractant that contains a replacing anion such as phosphate is often more successful. One of the most widely used extracting solutions for S is a 500 mg P L^{-1} solution of $Ca(H_2PO_4)_2$, sometimes in combination with 2 M HOAc. The phosphate ions displace sorbed SO_4-S, the Ca ions cause flocculation of the soil allowing for ease of analysis of S by either colorimetric or turbidimetric means, and the HOAc extracts some organic S. Recently there has been interest in using Mehlich 3 as a S soil test to eliminate the need for a separate extraction to determine available S. Once extracted, SO_4-S can be analyzed by colorimetry, titrimetry, ion chromatography, and ICP-AES. The most common analytical techniques are turbidimetry (if S is determined alone) and ICP-AES (for S alone and in multielement analyses). A review of the advantages and disadvantages of analytical methods for S is given by Tabatabai (1996).

13.2.4.3.3 Interpretation of S Soil Tests

Sulfur soil testing is a moderately reliable approach to determine the S fertility status of a soil but is best used in conjunction with other information, such as plant analysis, knowledge of soil type and plant yield potential, soil organic matter content, and inputs of S from sources other than fertilizers (e.g., manures, crop residues, rainfall, and irrigation waters). A major concern with soil testing for S is that inputs of S from the atmosphere or irrigation waters, which can be more than the rates of S fertilizer recommended, are not accounted for by soil testing. In situations where S deficiency is probable, based on knowledge of the soils, crops, and management practices it may be more economical to apply a small amount of S fertilizer (10–15 kg S ha^{-1}) than to incur the costs of soil testing for S.

13.2.4.4 Soil Testing for Nitrogen

Nitrogen deficiency is the most common soil fertility problem for nonlegumes. Nitrogen (N) is also well known to negatively impact water and air quality. However, despite the importance of N to agricultural production and environmental quality we have not yet developed a widely accepted method to routinely and rapidly test soils for plant available N, particularly in humid regions. The reasons for this center around the complex transformations undergone by N in soils, referred to as the soil N cycle. A summary of the key aspects of the N cycle most relevant to soil testing follows; C.4 and D.1 in the *Handbook of Soil Sciences*, and elsewhere (Keeney, 1982; Keeney and Nelson, 1982; Power and Schepers, 1989; Tisdale et al., 1993; Pierzynski et al., 1994; Foth and Ellis, 1997; Schepers and Raun, 2008) provide thorough treatments of N cycling, management, and environmental impacts.

Most of the N available for biological assimilation by plants and animals originated from the atmosphere, which is 78% N_2 by volume. Only a small fraction of the global N supply is in soils where total N values typically range from 0.05% to 0.15% and most of the N (>98%) is organic in nature. Atmospheric N is converted to forms of N that can be directly or indirectly used by plants by symbiotic or nonsymbiotic biological N fixation. Bacteria of the genera *Rhizobium* and *Bradyrhizobium* can form symbiotic relationships with plants to assimilate N_2 from the atmosphere while nonsymbiotic N fixation can be conducted by free-living algae, bacteria, and actinomycetes. Electrical discharges and industrial processes that combine N_2 with H from natural gas to produce the ammonia (NH_3) used in fertilizer manufacture also convert atmospheric N to fixed forms that can be used by plants. The burning of fossil fuels and volcanic eruptions are also atmospheric sources of N to soils.

The key components of the soil N cycle are as follows: (1) mineralization, in which soil organic N is converted to inorganic NH_4-N by microbial decomposition; (2) immobilization, in which soil microorganisms assimilate NH_4-N and NO_3-N from the soil solution for population growth and biomass production—essentially the reverse of mineralization; (3) nitrification, in which certain soil bacteria convert NH_4-N to NO_3-N, a rapid process in most well-aerated soils; (4) ion exchange in which NH_4-N is retained by cation exchange sites on soil clays or organic matter (including fixation within the interlayers of 2:1 clays as nonexchangeable NH_4-N) and NO_3-N is retained by any positively charged sites present on soil colloids (rarely of consequence in most soils); (5) denitrification, in which soil bacteria that are more active under reduced conditions convert NO_3-N to gaseous forms of N (N_2O, NO, N_2), which are then lost from soils to the atmosphere; (6) volatilization, in which NH_4-N is converted to gaseous NH_3-N under certain alkaline conditions (high pH) and lost to the atmosphere; and (7) leaching, in which NO_3-N moves downward in the soil profile with percolating waters.

Plants absorb N from the soil solution as NH_4-N and NO_3-N. An accurate soil test for N, therefore, must be able to predict how all components of the soil N cycle that affect the availability of NH_4-N and NO_3-N can be integrated into a quantitative assessment of a soil's N supplying capacity. This is a complex task given the dependence of N cycling on biological activity and environmental conditions (temperature, moisture, rainfall). The fact that the main form of inorganic N in most soils is NO_3-N further complicates the matter given the leachability of NO_3-N and its sensitivity to loss as a gas via denitrification.

13.2.4.4.1 Current Soil Testing Methods for N

Soil testing for N differs markedly between arid and humid regions. In arid (or semiarid) regions evapotranspiration usually exceeds precipitation and inorganic forms of soil N are not as susceptible to leaching or denitrification. For this reason a soil sample collected from a crop's rooting zone shortly before the start of the growing season and analyzed for residual inorganic N (the NH_4-N and NO_3-N remaining from the past year's mineralization, fertilization, and organic waste applications) accurately measures plant available soil N. Nitrogen inputs are then reduced in proportion to the amount of residual inorganic N. In most cases soil samples for residual inorganic N must be collected to deeper depths (as much as 180 cm, minimum of 60 cm) than for standard soil testing (20 cm). Soil samples tested for residual inorganic N are often only analyzed for NO_3-N since this is usually the dominant form of inorganic N in most soils. The best time to take a soil sample for residual inorganic N is usually just before planting or early in the growing season, although in very cold and dry areas, where mineralization and leaching are minimal, samples can be collected the preceding fall or winter.

After sample collection, proper handling is critical to avoid changes during storage that affect the amount of inorganic N present. Moist soils stored under warm conditions can mineralize or immobilize a significant amount of inorganic N; very wet samples can lose NO_3-N by denitrification. To avoid problems soil samples should be rapidly air-dried at ambient temperatures by spreading the soil in a thin layer. Extraction of inorganic N is usually accomplished by shaking a dried, ground soil sample for 30 min to 1 h with a salt solution (e.g., 2 M KCl, 0.01 M $CaSO_4$, 0.04 M $(NH_4)_2(SO_4)$), followed by filtration. The most common methods to determine NH_4-N and NO_3-N in soil extracts are automated colorimetry and ion chromatography. Other, less commonly used methods are steam distillation, ion specific electrodes, and microdiffusion techniques. Details on the various methods used to measure inorganic N in soils are given by Bundy and Meisinger (1996) and an extensive review of chemical extraction methods to assess soil N availability was recently prepared by Griffin (2008).

Soil testing for N in humid regions is a more complex process and a less accurate predictor of soil N fertility, and consequently most soil testing laboratories in humid regions do not offer routine soil N tests. The greater rainfall and warmer temperatures in humid areas can cause rapid seasonal changes in the amount of inorganic N present in the soil profile making direct measures of residual inorganic N estimates of plant available N less reliable.

The general consensus on soil testing for residual inorganic N in humid regions is that this practice has value if conducted at or near planting and if samples are collected to a reasonable depth in the soil profile (not just the topsoil). If residual inorganic N values are high, reductions in N inputs should be made. Bundy et al. (1992) reported on the use of the preplant soil profile nitrate test (PPNT) in the upper Midwestern United States where moderate rainfall and cooler winter temperatures make this approach more likely to be successful than in warmer, higher rainfall humid regions. The economically optimum N fertilizer rate for corn (*Zea mays*, L.) was shown to decrease in a near-linear manner with increasing PPNT values in soil samples collected to a depth of 1 m. Another situation where residual inorganic N testing has been successful in humid regions has been with short-season crops where there is less likelihood that significant losses of residual inorganic N will occur.

In general, the most promising advance in soil N testing in the humid regions of the United States has been the presidedress soil nitrate test (PSNT) originally developed for corn and later used for a wider range of agronomic and vegetable crops (Magdoff et al., 1984; Bock and Kelley, 1992). The PSNT was conceived and evaluated to address the problem of overfertilization of corn with N in the Northeastern United States, particularly in fields with histories of manure and legume use where residual organic N would likely provide an appreciable percentage of the total N requirement for many nonleguminous crops. The PSNT has four basic tenets: (1) all fertilizer N for corn except for a small amount banded at planting, should be applied by sidedressing when the crop is beginning its period of maximum N uptake, usually early June; (2) soil and climatic conditions prior to sampling integrate the factors influencing the availability of N from the soil, crop residues, and from previous applications of organic wastes; (3) a rapid sample turn-around (<14 d) by a testing laboratory is possible, thus allowing time for farmers to collect the soil sample, submit it to the laboratory, have it an analyzed, receive the results and recommendations, and then apply (or not apply) sidedress N before the corn crop becomes too large for equipment to move through the field; and (4) farmers will normally only sample to a depth of 30 cm, the recommended depth for the PSNT sample. In practice a PSNT sample is collected early during corn growth, when the corn plants are ~30 cm in height. The sample is air-dried rapidly, or oven-dried at <60°C, after spreading the soil in a thin (<1 cm) layer. Extraction and analysis for NO_3-N proceed as described above for residual inorganic N. However, while the PSNT actually measures inorganic soil N, it is not a measure of residual inorganic N, but an indirect, field-based expression of a soil's capacity to provide an adequate supply of inorganic N during the growing season (i.e., of the soil N mineralization potential). The PSNT has been evaluated in over 300 field studies in the Northeastern and Midwestern United States and has been repeatedly shown to be successful in identifying N sufficient soils (Magdoff et al., 1990; Bock and Kelley, 1992; Meisinger et al., 1992; Sims et al., 1995; Jaynes et al., 2004; Muñoz et al., 2008). Some of the logistical difficulties associated with the need for rapid sample analysis have been overcome by the development of "quicktest" kits and specific ion electrodes that can be used in the field (Jemison and Fox, 1988).

Recently, the Illinois soil N test (ISNT) has been proposed as a means to identify fields where corn would not be responsive to N fertilization. Initially, Mulvaney et al. (2001) found that soils that did not respond to fertilizer N mineralized larger quantities of N and this mineralization was correlated to a decrease in soil amino sugar N. However, the fractionation of soil N developed by Mulvaney and Khan (2001) to determine amino sugar N is too cumbersome for routine soil analysis. Therefore, Khan et al. (2001) developed a simpler method for estimating amino sugar N, which has come to be known as the ISNT. The ISNT estimates amino sugar N and has been found by some to reasonably identify soils where no response to fertilizer N would be expected in corn. The procedure as described by Khan et al. (2001) requires incubation of 1 g of air-dried soil with 10 mL of 2 M NaOH in a 472 mL wide mouth jar. The sample is heated for 5 h at 48°C–50°C on a hot plate. Ammonium and amino sugar N is then liberated as NH_3 and collected in an H_3BO_3 indicator solution. After its original publication, the method underwent modest modifications including a recommendation to rotate the sample jars on the hot plate (Mulvaney et al., 2004) or to enclose the hot plate and incubation vessels in a box (Klapwyk and Ketterings, 2005) in order to reduce spatial variability within the hotplate.

Since its release, the effectiveness of the ISNT has received mixed reviews within the soil science literature. Klapwyk and Ketterings (2006) reported that when used in combination with soil organic matter the ISNT appeared to do a good job of identifying corn fields that may be responsive to additional N fertilizer. However, Barker et al. (2006) reported that the ISNT was not able to distinguish between responsive and nonresponsive Iowa soils. A strong correlation was found between the ISNT and total soil N, hydrolysable NH_4-N, and hydrolysable NH_4 + amino sugar-N. They concluded that the ISNT extracted a consistent fraction of soil total N and as a result was not able to predict potentially labile soil N fractions. As a result, the authors recommended against the use of the ISNT to guide N fertilization in Iowa corn production. Similarly, in an on-farm N fertilizer response trial conducted by Spargo et al. (2007), the ISNT was found to extract a consistent percentage of total soil N and was deemed a poor predictor of labile soil N. Osterhaus et al. (2008) conducted 80 corn N response experiments in Wisconsin and reported that ISNT values were not related to the observed economically optimum N rate and that the ISNT had no ability to separate N-responsive from unresponsive sites. They suggested that the ISNT measures a constant fraction of soil organic N instead of measuring the readily available N pool, as would be required for an accurate soil N test designed to predict soil N supplying capability and corn N response. In contrast to these studies, Lawrence et al. (2009) found that adjusting ISNT values based on soil organic matter content (as estimated by loss-on-ignition [LOI]) resulted in accurately identifying 83% of the N responsive sites in a 34-site field study using corn planted after grass-legume sod. They emphasized the importance of the timing of soil sample collection (within 5 weeks of sod plowdown) and the need to include N credits for sod decomposition to the successful use of the ISNT. These mixed results indicate that the ISNT should be used with caution, and perhaps in conjunction with other soil measurements (e.g., organic matter); it is, however currently offered as a routine soil N test by some commercial and state soil testing laboratories.

13.2.4.4.2 Considerations in Interpretation of Nitrogen Soil Tests

Most recommendations for the amount of N required for optimum plant growth are not based on soil N testing, but on field calibration studies quantifying plant performance in response to N inputs (fertilizers, manures, biosolids, etc.). Widespread, commercial-scale use of soil N testing today is confined to certain areas and crops, such as the PSNT and ISNT for corn in humid regions or residual inorganic N testing for grain crops in arid regions. Recommended N rates for the major grain crops, such as corn, wheat (*Triticum aestivum*, L.), and sorghum (*Sorghum bicolor* [L.] Moench) are initially determined from equations using the expected, realistic yield goal and a conversion factor appropriate to that crop. For example, for corn, the fertilizer N rate recommended in many U.S. states is arrived at by directly multiplying the realistic yield goal by an empirically determined factor that ranges from 17 to 18 kg fertilizer N per Mg of expected yield (equivalent to 1.0–1.2 lb fertilizer N per bushel of expected yield). Modifications (reductions) to this recommendation are then made based on PSNT values, residual soil inorganic N, the previous or intended use of other N sources (animal manures), documented N inputs from other sources (high NO_3-N irrigation waters), and credits for N supplied by a previous legume crop in the rotation (e.g., alfalfa, soybeans). Tisdale et al. (1993) summarized the general approach used to make N recommendations:

$$N_{\text{fertilizer}} = N_{\text{crop}} - N_{\text{soil}} - (N_{\text{organic matter}} + N_{\text{previous crop}} + N_{\text{organic waste}}) \tag{13.1}$$

$N_{\text{fertilizer}}$ is the amount of N needed from fertilizers, manures, biosolids, etc.
N_{crop} is the crop N requirement at realistic yield goal
N_{soil} is the residual soil inorganic N (NH_4-N + NO_3-N)
$N_{\text{organic matter}}$ is the N mineralized from soil organic matter
$N_{\text{previous crop}}$ is the residual N available from previous legume crops
$N_{\text{organic waste}}$ is the residual N available from previous organic waste use such as animal manures, biosolids, wastewater irrigation, etc.

In some cases, an N availability index, based on soil organic matter content, soil texture (indication of leachability and moisture holding capacity), and climate (indicated by crop being grown) is used to estimate soil N supplying capacity. Fertilizer N recommendations are adjusted accordingly with fine-textured soils with higher organic matter contents presumed to provide more plant available N from mineralization and thus to need less fertilizer N. Mathematical models have also been developed to predict crop N requirements but with only limited success because of the amount of site-specific information required for the models to function with any degree of accuracy (Tanji, 1982).

Interpretations of N soil tests are done routinely and with reasonable success. However, soil N testing may be improved by use with plant analysis or other techniques now available to quantify plant N status in the field, such as remote sensing or leaf chlorophyll meters (LCMs). Plant N testing methods are discussed in Section 13.3; some environmental aspects of soil N testing are discussed in Section 13.2.7.3.

13.2.4.5 Soil Testing for Micronutrients (B, Cl, Cu, Fe, Mn, Mo, Zn)

Micronutrients are essential elements normally present in plants at very low concentrations (<100 mg kg^{-1}) and include boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn). The following overview of micronutrient cycling focuses on soil properties and processes most relevant to soil testing and reflects the fact that four micronutrients exist in soils as cations (Cu^{2+}, Zn^{2+}, $Fe^{2+,3+}$ and Mn^{2+}) while three are found as an uncharged molecule ($H_3BO_3^0$) or anions [$B(OH)_4^-$, Cl^-, MoO_4^{2-}].

Plant available Cu in soils originated from the weathering of igneous and sedimentary rocks. The main Cu bearing primary minerals are chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), and bornite ($CuFeS_4$). Soil total Cu concentrations typically range from 1 to 40 mg kg^{-1} and concentrations in the soil solution are quite low, from 10^{-8} to 10^{-9} M. More than 99% of the Cu in the soil solution is found as Cu^{2+} complexed with organic matter; above pH 6.9 the dominant inorganic form of Cu is $Cu(OH)_2^0$. Soluble Cu is in equilibrium with Cu complexed by organic matter, exchangeable Cu retained on the CEC sites of soil colloids, and Cu sorbed, occluded, or coprecipitated by soil oxides. Sorption of Cu by organic matter is the primary reaction controlling the plant availability of Cu although Cu solubility is also highly pH dependent, decreasing 100-fold for each unit increase in pH.

Plant available Zn in soils also originates from the weathering of igneous and sedimentary rocks and total soil Zn concentrations usually range from 10 to 300 mg kg^{-1}. The major Zn bearing minerals in soils include franklenite ($ZnFe_2O_4$), smithsonite ($ZnCO_3$), and willemite ($ZnSiO_4$). Zinc concentrations in the soil solution range from 2 to 70 µg L^{-1} (ppb) and Zn^{2+} is the major species below pH 7.7. Approximately 50%–60% of soluble Zn is complexed with organic matter. Plant available Zn also includes exchangeable Zn and Zn sorbed by clays, oxides, and carbonates. As with Cu, the solubility of Zn is highly dependent upon soil pH, decreasing markedly above pH 6.0–6.5 (Wear and Evans, 1968).

Iron is one of the major constituents of the earth's crust (~5%) and total Fe contents in most soils are quite high, ranging from 1,000 to 10,000 mg kg^{-1}. Major mineral forms of Fe include olivene ($(Mg,Fe)_2SiO_4$), pyrite (FeS), siderite ($FeCO_3$), hematite (Fe_2O_3), and goethite (FeOOH). Plant available forms of Fe include those that are sorbed by clays and organic matter. Soil solution concentrations of Fe in equilibrium with these minerals are very low and depend greatly upon soil pH, ranging from 10^{-6} M in very acid soils to <10^{-20} M in soils above pH 7.0. The form and solubility of Fe in the soil solution also depends upon soil redox potential; in well-aerated, oxidized soils, ferric Fe (Fe^{3+} or $Fe(OH)_2^+$) predominates, while in reduced, waterlogged soils the major inorganic species is ferrous Fe (Fe^{2+}). Each unit increase in pH decreases the solubility of Fe^{3+} by 1000-fold, but only decreases soluble Fe^{2+} by 100-fold. Of relevance to soil testing for Fe is the fact that the total concentrations of soluble inorganic Fe in most soils are too low to meet the nutritional needs of most plants, even under very acid soil conditions, yet plants are able to obtain adequate Fe for growth. Research has shown that natural organic compounds in soils (chelates) and exuded from plant roots play an important role in preventing the precipitation of Fe as insoluble compounds by forming Fe-chelate complexes that can move to plant roots by mass flow or diffusion. At the root surface, Fe dissociates from the chelate and is taken up by the plant.

Plant available manganese (Mn) in soils originates from the weathering of minerals such as pyrolusite (MnO_2), hausmannite (Mn_3O_4), manganite (MnOOH), rhodochrosite ($MnCO_3$), and rhodonite ($MnSiO_3$). Total soil Mn concentrations are from 20 to 3000 mg kg^{-1} while soluble Mn is usually between 0.01 and 1.0 mg L^{-1}, existing primarily as Mn^{2+} in equilibrium with MnO_2 in oxidized soils and $MnCO_3$ in reduced soils. Exchangeable, sorbed, and organically complexed Mn are the forms important to plant availability. As much as 80% of soluble Mn in some soils is complexed with organic matter. Soil properties and processes affecting Mn solubility include soil pH, complexation/chelation, and redox potential. Manganese solubility decreases about 100-fold as pH increases by one unit and also increases markedly when soils become reduced and Mn oxides (e.g., MnO_2) dissolve.

Plant available boron (B) originates in most soils from the weathering of sedimentary rocks (e.g., shales) and tourmaline (a highly insoluble borosilicate mineral). Total soil B concentrations usually range from 2 to 200 mg kg^{-1} with <5% available to plants. Unlike Cu, Zn, Fe, and Mn, which exist primarily as divalent cations, B in soils is found as undissociated $H_3BO_3^0$ (pH 5–9) or as the $B(OH)_4^-$ anion (dominant species at pH > 9.2). Major sources of plant available B in soils include those that are sorbed by soil clays and oxides or hydroxides of Fe/Al and the B complexed by organic matter. The uncharged nature of the $H_3BO_3^0$ molecule makes it highly mobile in many soils, particularly those low in clays, oxides, and organic matter. However, B availability is well known to decrease at pH > 6.5–7.0 because of an increased affinity of soil clays and oxides for the $B(OH)_4^-$ anion.

Molybdenum is present in soils at very low levels, with total Mo values ranging from 0.2 to 5.0 mg kg^{-1} and soil solution concentrations <0.5 μg L^{-1}. Plant available Mo is anionic in nature, existing in most soil solutions as $HMoO_4^-$ or MoO_4^{2-}, species strongly sorbed by Fe/Al oxides under acidic conditions and/or complexed by organic matter. Unlike all other micronutrients, Mo availability increases with soil pH, due to the greater solubility of several Mo-bearing minerals at pH values >7.0 and to a decreased affinity of most soils for Mo.

Chloride occurs mostly in igneous and metamorphic rocks and, once weathered, is found in soils as precipitates and soluble salts such as NaCl, $MgCl_2$, and $CaCl_2$ and in the soil solution as the Cl^- anion. Dissolution of these salts is the primary process controlling Cl^- availability to plants. Soil solution concentrations of Cl^- vary widely as a function of soil type and geographic location, ranging from <0.5 to >6000 mg L^{-1} in soils from arid regions. Chloride is very mobile in most soils, analogous in many ways to NO_3-N, and significant retention of Cl^- only occurs in highly acid soils that can develop positive, pH-dependent electrostatic charge on 1:1 clay or Al/Fe oxides.

13.2.4.5.1 Current Soil Testing Methods for Micronutrients

Soil tests for micronutrients have historically been conducted as special tests, restricted to situations where soil properties or crop characteristics indicated an economic response to micronutrient fertilization was possible. Consequently, for many years, and even today, separate soil tests were used for each micronutrient, or for groups of micronutrients with similar properties. However, the advent of multielement extractants, such as Mehlich 3, DTPA, and AB-DTPA, and of instruments capable of rapid, simultaneous analysis of soil extracts for several elements (ICP-AES) has increased the use of micronutrient soil testing in many areas of the world.

Soil sampling, handling, and storage for micronutrient soil testing are conducted following the standard techniques outlined in Section 13.2.3. Soil samples are almost always collected from topsoils (0–15 or 0–20 cm). The major consideration for micronutrients is the need to avoid contamination of the soil sample during sample collection, handling, and storage. For example, galvanized sampling tools and mixing buckets and some rubber stoppers contain Zn, metal surfaces on equipment used for grinding and sieving samples may contain Cu, Fe, and Zn, borosilicate glassware should be avoided during the extraction of B from soils as should the use of paper bags and boxes that may contain B in glues, and many common laboratory reagents contain Cl. Sample drying, the length and force of soil grinding, the speed of shaking during the extraction process, and the type of extraction vessel and soil:solution ratio have been shown to affect the quantity of extractable Cu, Fe, Mn, and Zn in some soils (Soltanpour et al., 1976, 1979). Given these somewhat unpredictable potential sources of error, following standardized methods for soil sampling, handling, preparation, and extraction is a vital aspect of micronutrient soil testing. Only a small amount of contamination or a slight alteration in procedure can badly skew a soil analysis, resulting in an erroneous recommendation.

Chemical extraction is the standard approach to assess micronutrient availability in soils. The major types of micronutrient soil tests used for Cu, Fe, Mn, and Zn are dilute acids and extractants that contain chelating agents. Less commonly used tests include neutral salts, which remove only small quantities of most micronutrient cations, and reducing agents, such as hydroquinone, used only for Mn (Table 13.4). In general, soil tests have been designed to remove soluble micronutrient forms

TABLE 13.4 Summary of Major Soil Testing Methods, Interacting Factors, and References for Micronutrient Soil Tests

Micronutrient	Soil Test and Critical Range	Comments and Interacting Factors Used in Soil Test Interpretation
Boron[a]	Hot water: 0.1–2.0 mg kg^{-1} Mehlich III: 0.7–3.0 mg kg^{-1}	Hot water is the most widely used method. Interacting factors include crop yield goal, pH, soil moisture, texture, organic matter, and soil type
Copper	AB-DTPA: 0.5–2.5 mg kg^{-1} DTPA: 0.1–2.5 mg kg^{-1} Mehlich I: 0.1–10 mg kg^{-1} Mehlich III: 0.3–15 mg kg^{-1} 0.1 M HCl: 0.1–2.0 mg kg^{-1}	AB-DTPA and DTPA are used for alkaline soils, Mehlich III for alkaline and acid soils, and Mehlich I and 0.1 M HCl for acid, low CEC soils. Interacting factors include crop type, organic matter, pH, and % $CaCO_3$.
Iron	AB-DTPA: 4.0–5.0 mg kg^{-1} DPTA: 2.5–5.0 mg kg^{-1}	AB-DTPA and DTPA are used for alkaline soils (Fe deficiency is very rare with acid soils). Interacting factors include pH, % $CaCO_3$, CEC, organic matter, and soil moisture
Manganese	AB-DTPA: 0.5–5.0 mg kg^{-1} DTPA: 1.0–5.0 mg kg^{-1} Mehlich I: 5.0 mg kg^{-1} at pH 6 10 mg kg^{-1} at pH 7 Mehlich III: 4.0 mg kg^{-1} at pH 6 8.0 mg kg^{-1} at pH 7 0.1 M HCl: 1.0–4.0 mg kg^{-1}	AB-DTPA and DTPA are used for alkaline soils, Mehlich III for alkaline and acid soils, and Mehlich I for acid, low CEC soils. Interacting factors include pH, texture, organic matter, and % $CaCO_3$
Molybdenum	Ammonium oxalate—pH 3.3: 0.1–0.3 mg kg^{-1}	Soil testing for Mo is rarely done. Interacting factors are pH and crop
Zinc	AB-DTPA: 0.5–1.0 mg kg^{-1} DTPA: 0.2–2.0 mg kg^{-1} Mehlich I: 0.5–3.0 mg kg^{-1} Mehlich IH: 1.0–2.0 mg kg^{-1} 0.1 M HCl: 1.0–5.0 mg kg^{-1}	AB-DTPA and DTPA are used for alkaline soils, Mehlich III for alkaline and acid soils, and Mehlich I and 0.1 M HCl for acid, low CEC soils. Interacting factors are pH, % $CaCO_3$, P, organic matter, % clay, and CEC

Sources: Martens, D.C., and W.L. Lindsay. 1990. Testing soils for copper, iron, manganese, and zinc, p. 229–264. *In* R.L. Westerman (ed.) Soil testing and plant analysis. 3rd edn. SSSA Book Series No. 3. SSSA, Madison, WI; Sims, J.T., and G.V. Johnson. 1991. Micronutrient soil tests, p. 427–476. *In* J.J. Mortvedt et al. (eds.) Micronutrients in agriculture. 2nd edn. SSSA, Madison, WI.

[a] References: Hot water B, Berger and Truog (1940); Mehlich 3 B, Shuman et al. (1992).

(including organically complexed) by solvent action, to displace exchangeable and sorbed forms by ion exchange and desorption reactions with other cations or with hydrogen ions (H_3O^+), to partially dissolve soil minerals or oxides that contain precipitated and occluded forms, and to dissociate or chelate micronutrient cations that are complexed by solid phases of organic matter. In most cases all four cations are extracted and analyzed simultaneously. The most common instrumental techniques used for micronutrient cations are AAS and ICP-AES.

Dilute acids (0.025–0.1 M) have been used for decades as soil tests for micronutrient cations, most successfully on acidic soils because they are not adequately buffered to extract sufficient quantities of micronutrients from calcareous soils. These extractants work primarily by dissociation, displacement, and partial acidic dissolution of cations from soil clays, oxides, and organic matter. The most common dilute acid soil tests today are the Mehlich 1 (dilute double acid: 0.0125 M H_2SO_4 + 0.05 M HCl) and 0.1 M HCl. The Mehlich 1 is a multielement extractant for macro- and micronutrients used in the southeastern and mid-Atlantic United States, and in South America. The 0.1 M HCl soil test has been used for a wider range of soils, primarily as an extractant for Zn, Cu, and Mn.

The other major category of soil tests for micronutrient cations is extractants containing chelating agents, most commonly DTPA and EDTA. Chelating agents reduce the activity of free metal ions in the soil solution by forming metal-chelate complexes, much as occurs in the rhizosphere of a plant. Replenishment of free ion concentrations in the soil solution (during the extraction process) by release from solid phases in the soil (clays, oxides, organic matter) occurs in response to the formation of the soluble metal-chelate complex. The amount of a micronutrient extracted by a chelate-based soil test therefore reflects both the initial quantity present in the soil solution and the ability of the soil to maintain that concentration. Chelate-based extractants thus simulate nutrient removal from the soil by plant uptake and replenishment of the soil solution by labile solid phases. Most chelate-based soil tests were developed for specific physiographic regions and soil types and are buffered at specific pH and ionic strength values to avoid the release of micronutrients from nonlabile solid phases in the soil. Hence, it is important to use them only for the soil type and conditions for which they were originally calibrated. For example, the DTPA soil test, commonly used for calcareous soils, is buffered at pH 7.3 and contains 0.01 M $CaCl_2$ to prevent the dissolution of carbonate minerals that might contain occluded or precipitated Cu, Fe, Mn, and Zn. Clearly, since the DTPA was developed for calcareous soils it would be inappropriate for highly acid soils without careful calibration and perhaps modification of the extractant composition (Lindsay and Norvell, 1978; Norvell, 1984; O'Connor, 1988). EDTA has been successfully used on a wide range of soils either alone or in multielement soil tests (i.e., 0.001 M EDTA is in the Mehlich 3 soil test and the modified Olsen soil test: 0.5 M

$NaHCO_3$ + 0.01 M EDTA, pH 8.6) (Viro, 1955). Similarly, DTPA is included in the AB-DTPA extractant (1 M NH_4HCO_3 + 0.005 M DTPA, pH 7.6) now widely used in the western United States.

Soil tests for the anionic or uncharged micronutrients (B, Mo, and Cl) have received less attention than those for micronutrient cations because of the relatively rare nature of crop response to fertilization with these elements. Most soil tests have focused on methods that remove soluble, sorbed, or organically complexed forms of these micronutrients.

The most common soil test used for B has been the hot water extraction method of Berger and Truog (1940) in which soil is boiled with water or 0.01 M $CaCl_2$, using a reflux condenser, removing soluble B and organically complexed B. Although shown to be a reasonably good predictor of plant response to B, the cumbersome, time-consuming nature of the Berger and Truog soil test has made its routine use difficult. Research by Mahler et al. (1984) using boiling plastic pouches, by Gestring and Soltanpour (1984) with the ammonium bicarbonate + DPTA soil test, and by Shuman et al. (1992) with the Mehlich 3 extractant has identified some practical alternatives to the original hot water method. Molybdenum is usually extracted with acid ammonium oxalate, primarily via a desorption reaction with the added oxalate, while deionized water or any dilute salt solution (e.g., 0.01 M $Ca(NO_3)_2$, 0.5 M K_2SO_4) can be used as a soil test extractant for Cl because of its high solubility in most soils.

Considerations in interpretation of micronutrient soil tests: Micronutrient deficiencies are, for the most part, associated with specific combinations of soil and plant factors that are reasonably well understood (Tisdale et al., 1993). Copper deficiencies are most common on soils that are extremely high in organic matter (peats, mucks) or with high pH, calcareous soils, while deficiencies with the other micronutrient cations (Fe, Mn, Zn) are almost always confined to calcareous or overlimed soils and sensitive crops. Boron deficiency is most frequently observed on sandy, low organic matter soils or following extremely dry periods that reduce the mineralization of organic matter and thus the release of organically bound B. Molybdenum deficiency rarely occurs except with very acid soils and then only with crops that are highly sensitive to low concentrations of soil Mo (e.g., legumes, crucifers, citrus). Chloride deficiencies are very unusual and confined to certain physiographic regions, such as the Northern Great Plains of the United States.

The critical value approach is the most widely used method to interpret the results of a micronutrient soil test (Tables 13.1 and 13.4). However, when micronutrient deficiencies are a definite concern, it has usually been shown that the predictive value of a micronutrient soil test can be improved by evaluation of more than one soil property or by knowledge of the crop to be grown. For instance, soil tests for Mn and Zn are much more accurate when soil pH is known; other examples of interacting factors that can improve soil test interpretation for micronutrients are given in Table 13.4. In some cases, quantitative "availability indexes," usually multiple regression equations based on the soil test result and another soil property, are calculated and used in place of the critical value approach.

Finally, several micronutrients can be toxic to plants if present in soils at high concentrations. The most common micronutrient phytotoxicities occur with Mn in highly acid soils ($pH < 5.2$) and B where only a slight over-application of fertilizer B can cause phytotoxicity. Although unusual, Cu and Zn can occasionally become phytotoxic in soils amended with agricultural, municipal, and industrial waste products, such as animal manures (pig and poultry), municipal biosolids, and some by-products of mining industries, if recommended or mandated management practices are not strictly followed (Sukkariyah et al., 2005). Critical phytotoxic levels based on micronutrient soil tests are much more difficult to establish than deficiency values and are usually highly specific to the plant that is grown and soil type.

13.2.5 Soil Testing Methods for Soil Chemical, Physical, and Biological Properties

The availability of essential and nonessential elements to plants, their potential to become phytotoxic, or to cause environmental problems via leaching, erosion, runoff, and/or volatilization depends upon soil physical, chemical, and biological properties. Some of these properties are routinely measured by soil testing laboratories; others are only measured on selected soil samples. Some are rarely measured at all but can be inferred from other soil properties or from information in USDA-NRCS Soil Survey manuals. Since the focus of this chapter is soil fertility evaluation, only the soil properties that are most relevant to plant growth are discussed (soil pH, lime requirement, organic matter, and soluble salts).

13.2.5.1 Soil pH

Soil pH is an index of the hydrogen ion activity in the soil solution that is in equilibrium with H retained by soil colloids (clays, organic matter, oxides) (van Lierop, 1990). It is a measure of the degree of acidity or alkalinity of a soil and is commonly measured electrometrically using a pH meter equipped with glass and reference electrodes (Thomas, 1996). Soil pH is one of the most useful pieces of information for soil fertility evaluation and management because it provides information on (1) the solubility, and thus potential availability or phytotoxicity of some plant nutrients and nonessential elements and (2) the relative biological activity of plants and soil microorganisms. The solubility of most micronutrients, and several nonessential trace elements (e.g., Cd, Ni, Pb) for plant uptake is highly pH dependent because the solubility of the solid phases containing these essential elements changes with soil pH. For most elements, solubility increases as the soil becomes more acidic; exceptions include P, which is most available at pH ranges between 5.5 and 7.5, and Ca and Mo, which are most available at higher pH values ($pH > 7.0$). Other processes important to nutrient and nonessential element retention in soils (e.g., cation exchange, sorption/desorption) also vary with pH. Acid soil infertility is most severe at pH values < 5.5 and is caused by the increased solubility and toxicity of aluminum (Al) and Mn and by the decreased plant availability of Ca, Mg, Mo, and P. Soil N availability is less under acidic conditions because the bacteria responsible for mineralization of soil organic N are most active at neutral or slightly acid soil conditions. Alkaline soil infertility is most common in calcareous or overlimed soils and results from the reduced availability of several important nutrients including P, B, Cu, Fe, Mn, and Zn due to the decreased elemental solubility (P, Cu, Fe, Mn, Zn) or greater sorption (B) that occurs at higher pH values.

13.2.5.2 Lime Requirement

Soil pH is an index of the soil chemical environment and its general suitability for plant growth. Soil pH, however, provides no information on the amount of soil amendment needed to correct problems with acid or alkaline soil infertility. To determine the rate of lime (or acidulent) needed, it is necessary to measure the buffer capacity of the soil (ability of the soil to resist a change in pH). For acid soils, lime requirement is defined as the amount of agricultural limestone or other basic material needed to increase the soil pH from an unacceptably acidic condition to a value that is considered optimum for the desired use of the soil (Sims, 1996). The acidification requirement is similar to lime requirement and refers to the amount of acidulent (usually elemental sulfur or aluminum sulfate) needed to decrease soil pH to an optimum value. The lime requirement of a soil can be measured by a number of methods, but the most common is the use of soil-buffer equilibrations to determine "buffer pH" (Sims, 1996). A buffer pH measurement is conducted by adding a chemical solution buffered at a high pH (pH 7.5–8.0) to a soil sample, allowing the soil and buffer to equilibrate, and then measuring the pH of the soil-buffer suspension. The decrease in buffer pH that occurs when the acidity in the soil reacts with the buffered chemical solution is an index of the amount of soil acidity that must be neutralized by liming to adjust the soil to the desired pH. Field calibrations between buffer pH measurements and changes in soil pH upon liming are essential to the development of a buffer pH test. The most common buffer pH solutions in the United States are the Shoemaker–McLean–Pratt ([SMP], pH 7.5), the Adams–Evans ([AE] pH 8.0), and the Mehlich (pH 6.6). Recently, environmental and toxicity concerns about chromium and paranitrophenol, constituents of the SMP buffer, led Sikora (2006) to propose a modified SMP buffer. Chemicals chosen to replace chromium and p-nitrophenol were 2-(N-morpholino) ethanesulfonic acid monohydrate (MES) and imidazole. The new buffer is adjusted to pH 7.7. A study comparing soil-buffer pH with the new buffer versus the SMP buffer using 255 Kentucky and 87 soils from throughout the United States showed that the two methods were highly correlated ($r^2 > 0.97$). Similar concerns with the toxicity of paranitrophenol, exist for the AE buffer. Consequently, Sikora and Moore (2009) developed the Moore–Sikora (MS) buffer, which contains no hazardous chemicals and was shown to be highly correlated ($r^2 > 0.98$) with results from the AE buffer. The buffer has been successfully used by Clemson University (South Carolina) for 4 years but the authors suggest further field studies are needed prior to its widespread adoption in other regions of the United States. Another lime requirement technique involves extraction of exchangeable acidity or exchangeable Al^{3+} from a soil with a salt solution (e.g., 2 M KCl), followed by titration of the extract with a standardized base. This is a rapid, inexpensive method that is well adapted to highly acidic, aluminous soils in areas with limited supplies of limestone. Application of sufficient limestone to neutralize 1.5–2.0 times the amount of exchangeable acidity is often adequate to eliminate some of the more serious limitations associated with acid soil fertility (e.g., Al toxicity). Finally, Liu et al. (2005) have shown success with a direct titration method to determine lime requirement based on an initial pH reading in 0.01 M $CaCl_2$ and a second reading following the addition of one dose of $Ca(OH)_2$, followed by extrapolation to the target pH. The more widespread availability of automatic titration systems suggests this approach should receive further investigation.

13.2.5.3 Organic Matter

The organic matter content of a soil is extremely important to soil fertility and many soil testing laboratories now include organic matter as a standard component in the routine soil test (which usually consists of pH, buffer pH, organic matter, and soil test extractable P, K, Ca, Mg). Soil organic matter is the nonliving organic material in the soil and includes both nonhumus (fresh plant, animal, and microbial residues) and humus (amorphous, highly stable, dark colored, organic material). Although organic matter is only a small percentage of most topsoils (1%–5%) and is present at very low levels in subsoils (<0.5%), consideration of organic matter in soil fertility evaluation is critical because it (1) provides plant nutrients, especially N, B, P, and S, as microorganisms decompose organic matter; (2) acts as a chelate, particularly important in maintaining micronutrient cations in a plant available form; (3) effectively complexes Al, reducing its phytotoxic effects in many soils; (4) has a high water holding capacity by weight and thus helps minimize the effects of moisture stress on plants; (5) is the predominant source of pH dependent CEC in most soils and thus contributes to the overall capacity of soils to retain nutrients and nonessential elements; (6) is a significant source of pH buffering, preventing marked and often undesirable changes in soil pH due to anthropogenic inputs; and (7) acts as an aggregating agent, cementing smaller soil particles together and thus improving soil structure, resulting in better aeration and more prolific root growth. Despite the many important roles soil organic matter plays in soil fertility, only recently soil testing laboratories have begun to measure and routinely report this soil property. The long-standing, traditional approach used to estimate soil organic matter content was to measure organic carbon (C) by wet chemical oxidation using dichromate ($Cr_2O_7^{2-}$) as the oxidant. Soil organic matter was then calculated from an empirically derived relationship between organic matter and organic C. This method was too time consuming to use on a routine basis and also generated a significant amount of high Cr waste; hence, it was primarily used as a special test. Most soil testing laboratories now estimate soil organic matter content by the "loss-on-ignition" (LOI) method in which a soil sample is "ignited" in a high temperature oven at ~360°C–400°C for several hours or overnight. The weight loss upon ignition is assumed to be proportional to soil organic matter content. Usually, an empirical relationship between LOI and some direct measure of organic matter (e.g., dichromate oxidation) is used to calculate estimated organic matter content. The LOI method is well suited to modern soil testing laboratories that wish to include an estimate of soil organic matter content in the routine soil test. Advances in electronic weighing and data acquisition and processing have resulted in LOI becoming an efficient, reasonably accurate approach to estimate soil organic matter.

13.2.5.4 Soluble Salts

Soil salinity, defined as the presence of excessive levels of dissolved inorganic solutes in the soil solution, is a global problem and directly affects soil fertility. Soils high in soluble salts, either naturally or due to inputs of salts in fertilizers and irrigation waters, can negatively affect plant growth in several ways. Specific ion toxicities can occur, particularly if high concentrations of Na, Cl, and B are present, causing direct injury to plants, especially young seedlings. Saline soils also disrupt plant water relations by decreasing the osmotic potential of the soil solution, thus making it more difficult for plants to extract water from soils, even to the point of causing plant injury and death. Measuring soluble salts is a fairly easy task but is usually done as a special test even in arid regions where soil salinity is a common problem. Rapid tests for soluble salts are done by measuring the electrical conductivity of a soil:water extract at a 1:2 or 1:5 soil:solution ratio. A more time consuming test, but one that better represents the soluble salts concentration in the soil solution is the saturated paste extract, obtained by mixing soil and deionized water to the point of saturation, followed by filtration and analysis of the extract for electrical conductivity.

13.2.6 Soil Testing: Interpretation and Recommendations

Interpretation is a systematic process, relying primarily on statistical evaluation of research comparing soil test parameters with plant performance, or other indexes of the success of a land use program. Recommendations arising from soil test interpretation must not only be quantitative in nature but also include professional judgment since it is not possible to identify all the factors that control plant performance from analysis of a single soil sample. Individuals responsible for nutrient management recommendations must be thoroughly familiar with the process of soil testing and with all aspects of the intended land use, including soil types, plants to be grown, climate, crop management practices, and any economic or environmental factors that may restrict a recommendation.

13.2.6.1 Correlation and Calibration of Soil Tests

Interpretation of soil analyses begins with soil test correlation, defined as "…the process of determining whether there is a relationship between plant uptake of a nutrient or yield and the amount of nutrient extracted by a particular soil test" (Corey, 1987). To be of value, a soil test must first be shown by laboratory, greenhouse, and field research to be statistically correlated with some measure of plant performance. Greenhouse studies are usually the first step in soil test correlation and can rapidly and inexpensively assess the potential value of a soil test for widely differing soils and plants. The standard approach is to obtain samples of soils representative of the range of soil types where the soil test will be used, measure the amount of soil test extractable nutrient (or nonessential element) in each soil, grow plants in the soils under controlled greenhouse conditions, where moisture, light, and spatial variability are minimized, and then measure plant yield and elemental composition. Statistical correlation and regression methods are then used to assess the relationship between soil test level and plant response. Correlation analysis determines if the change in plant yield or nutrient composition is proportional to the amount of nutrient extracted by a soil test. If a high degree of correlation exists, regression analysis will provide a predictive equation that reliably estimates plant yield or elemental composition at each soil test value. In some cases, multiple correlation and regression analysis are used to develop a predictive equation that quantifies the relationship between plant performance and more than one soil property (e.g., soil test value and pH, organic matter, texture, etc.).

If a soil test is significantly correlated with plant performance in the well-controlled greenhouse environment, field experiments are then conducted to determine how accurate the test will be under normal growing conditions. For greatest reliability, field trials should be conducted at many locations with a range of soil types and soil test values for the nutrient of interest. The trials should be done for several years and should include multiple rates of the nutrient being investigated. Experiments should be replicated at least three times and other variables besides the nutrient being studied that affect plant performance should be controlled to the extent possible (e.g., using irrigation to minimize soil moisture stress, pesticides to prevent insect damage and weed competition, and fertilization or liming to ensure that other nutrients do not limit plant growth and yield). Correlation analysis is again used to determine if there is a statistically significant relationship between the soil test value for a nutrient and plant response. Field experiments usually have poorer correlation coefficients than greenhouse studies because (1) they are conducted at fewer locations due to the time and expense required, and (2) uncontrolled variability is usually present that affects the soil test-plant performance relationship in an unpredictable manner. Recently, the costs and time required to conduct field and greenhouse studies have caused a greater reliance on laboratory correlation studies as a means to evaluate new soil test extractants. For example, several laboratory studies have compared the Mehlich 3 multielement soil test with earlier soil tests (Hanlon and Johnson, 1984; Wolf and Baker, 1985; Sims, 1989). Many of these studies reported highly significant correlations between nutrients extracted by Mehlich 3 and those extracted by the Mehlich 1, Bray P_1, 1 M NH_4OAc, and EDTA, indicating that the Mehlich 3 could be as reliable a means to evaluate soil fertility as the existing soil test. However, while laboratory-based correlation studies may be acceptable for the preliminary evaluation of new soil tests, they should not be used as the sole means to determine soil test reliability. It is fundamental to soil test correlation that the amount of an element extracted by the soil test be correlated with what is of actual interest, usually plant yield or elemental composition (Fixen and Grove, 1990).

The next step in soil test development is calibration, defined as "…ascertaining the degree of limitation to crop growth or the probability of a growth response to applications of a nutrient at a given soil test level" (Dahnke and Olson, 1990). The purpose of calibration studies is to categorize soil test levels in terms of the probability of economic response to applications of a nutrient or for their potential to affect the environment. Traditionally, soil test results have been categorized as very low, medium, high, and very high. More recently, the terms "optimum" and "excessive" have been used to describe soil nutrient status and some regions, such as the northeastern United States have identified two separate classes of soil test category—"crop response" and "environmental impact" (Beegle, 1995). Tisdale et al. (1993) suggested that probability of an economic response to fertilization with P and K for a soil rated as "low," "medium," "high," and "very high" in either nutrient would be 70%–95%, 40%–70%, 10%–40%, and <10%, respectively. Several of the more important approaches used in soil test calibration are briefly described below; for a more thorough review of this subject, refer to Dahnke and Olson (1990) and Black (1993).

The calibration process is essentially an effort to mathematically model the relationship between soil test level and plant response to nutrient additions, which is almost always nonlinear. Consequently, curvilinear regression models (exponential, quadratic, quadratic-plateau) are often used to identify the point where plant performance is optimal (e.g., the plateau yield, usually associated with 93%–95% of maximum attainable yield) and then to determine the soil test value associated with optimum yield, which is referred to as the critical level or critical value (Figure 13.3a). Curvilinear models are often based on relative yield or percent yield, defined as the yield obtained without addition of the nutrient being studied divided by the yield attained at that location when no other factors are limiting. Relative yield data from field trials in the region of interest are combined and plotted against the soil test value from the control treatment for each trial and the critical level is determined mathematically or graphically. Use of relative yields minimizes the influence of uncontrolled variables and allows for more effective interpretation of data collected over many different years, locations, soils, climates, and management settings. Once the critical value has been identified, soil test values below this level are subdivided into categories that are associated with the probability of crop response (e.g., low, medium, optimum) and the nutrient rate required for an optimum yield. It is important to note that critical soil test levels may vary between soils, crops, and climatic regions and will usually differ between soil test extractants. For instance, critical soil test P values by the Bray P_1, Olsen, Mehlich 1, and Mehlich 3 soil tests are about 30, 12, 25, and 50 mg kg^{-1}, respectively (Jones, 1999).

Another calibration approach used to identify critical soil test levels is the Cate–Nelson method (Figure 13.3b; Cate and Nelson, 1965). In this approach, relative yield is plotted against soil test value and the data are subdivided graphically into four quadrants either visually, using professional judgment, or mathematically (Nelson and Anderson, 1977) by placing a horizontal line at the optimum relative yield (93%–95% of maximum yield) and a vertical line at the soil test value that minimizes the number of points in the upper left and lower right quadrants. If the soil test under consideration is reliable, there will be few points in the upper left or lower right quadrants. Points in the upper left quadrant would mean that a low soil test value was associated with a high relative yield; points in the lower right quadrant are those where a high soil test value was associated with a low yield. Both of these are inconsistent with the basic premise of soil testing, that is, a soil test can accurately and reliably separate responsive from nonresponsive sites. If most points are in the lower left or upper right quadrants, then the soil test accurately predicts plant performance, that is, low soil tests have low relative yields and high soil tests have high relative yields.

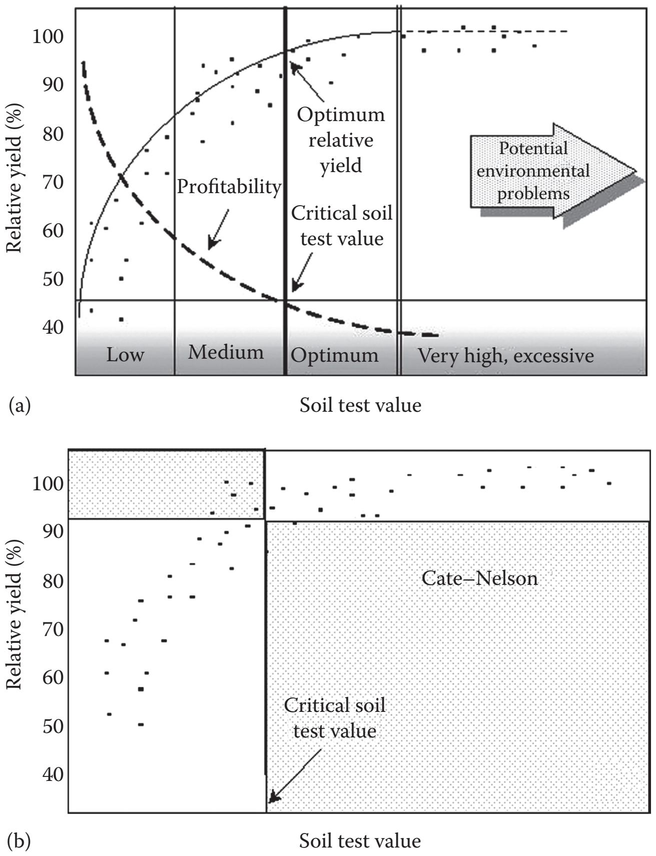

FIGURE 13.3 Generalized illustration of the principles of soil test correlation and calibration using (a) curvilinear models and (b) the Cate–Nelson approach.

As shown in Figure 13.4, the mathematical approach used to model the relationship between plant performance (relative yield) and rate of nutrient added can affect the determination of the economically optimum nutrient rate. Thorough discussions of the mathematical models used to interpret soil test results are provided by Black (1993).

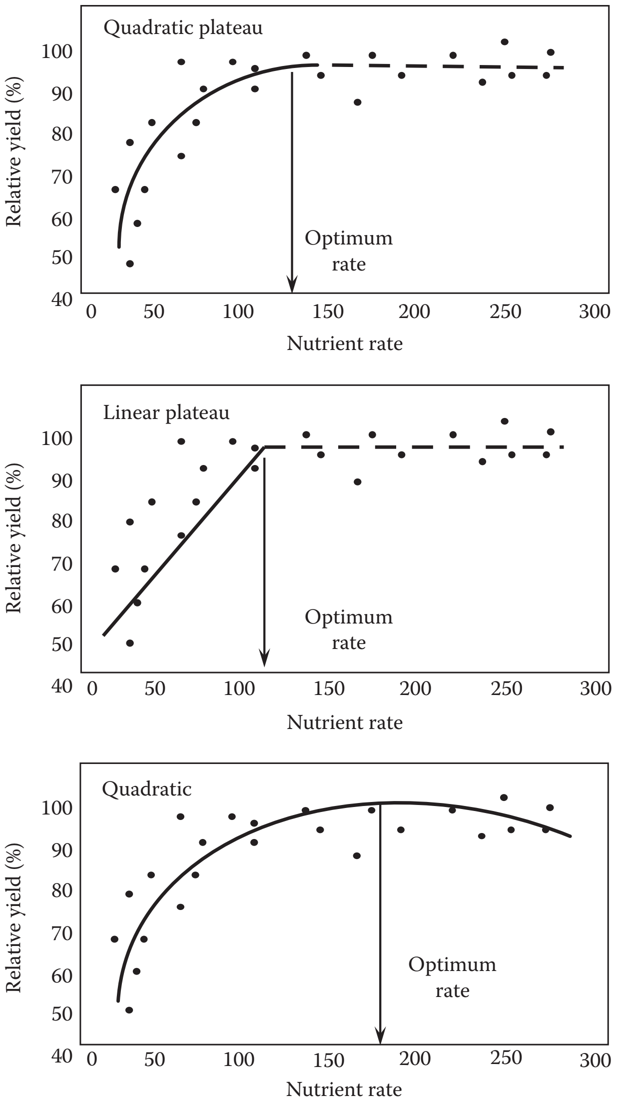

FIGURE 13.4 Illustration of the influence of type of mathematical model selected on the identification of the nutrient rate required for optimum yield.

13.2.6.2 Recommendation Philosophies for Soil Test Interpretation

The final phase in soil test development is the recommendation process in which the actual amount of nutrient to be applied, the application method, and the timing of the application are specified in detail. Individuals making a nutrient recommendation must integrate the quantitative information from soil test calibrations (e.g., the probability and magnitude of response likely to occur at a given soil test value of the nutrient) with other, more subjective aspects of nutrient management. Individuals skilled at making efficient recommendations are able to combine soil testing information with their professional experience, judgment, and scientific understanding of the system of interest in a manner that optimizes the profitability of nutrient use while minimizing any potential impacts on environmental quality. Given the subjective nature of this process, it is not surprising that several different recommendation philosophies have evolved and now receive widespread use. The two most common philosophies, for agricultural crops, are "rapid build-up and maintenance" and "sufficiency level." Both philosophies are more commonly used with "immobile" plant nutrients, those that do not readily leach from topsoils or the root zone (P, K, Ca, Mg, Cu, Fe, Mn, Mo, Zn), than with "mobile" nutrients (B, Cl, NO_3-N, SO_4-S) where more comprehensive soil test approaches, such as subsoil testing, must be relied upon.

The rapid build-up and maintenance approach recommends that soil fertility be built to an optimum level as rapidly as possible, usually within 2 years. Following this initial "build-up" of soil fertility, "maintenance" nutrient applications are made annually at rates equal to the amounts removed in the harvested portion of the crop. This philosophy is sometimes referred to as "fertilization of the soil" and proceeds somewhat independent of soil testing since nutrient applications are made each year, regardless of soil test results. As noted by Dahnke and Olson (1990), "…the rapid build-up and maintenance concept discounts the inherent nutrient delivery capacity of a soil's native mineral reserves which, with most soils other than sands is large for most nutrients" and "Complete adherence to this system… would eliminate the need for further soil testing." While still used, economic and environmental questions about the appropriateness of this recommendation philosophy persist (Olson et al., 1987).

The most widely used recommendation philosophy today is the "sufficiency level" approach, which "…promotes the idea that a measurable soil test level exists below which responses to added fertilizer are probable and above which they are not" (Eckert, 1987). This approach is also sometimes referred to as "fertilization of the crop" and is a more conservative approach than rapid build-up and maintenance because nutrients are only recommended when soil test values are below the critical soil test level and are applied proportionate to the soil test category (i.e., more nutrients are added to soils that are rated low than those that are rated medium). The sufficiency level approach also inherently includes a build-up phase, but once soil fertility is in the optimum range, nutrient additions cease, or are minimal, until subsequent soil testing indicates that soil fertility has declined to the point where an economic response to further nutrient inputs is likely. There is no evidence to support the contention that the sufficiency level approach causes unnecessary depletion of soil nutrient reserves; in fact most studies have shown that adhering to this philosophy results in a slight buildup of soil fertility. Consequently, most soil test calibration research supports the use of the sufficiency level concept for soil test recommendations.

13.2.7 Environmental Soil Testing

13.2.7.1 Overview of the Principles and Purposes of Environmental Soil Tests

Soil testing has traditionally been used to evaluate the soil limitations to agronomic crop performance imposed by nutrient deficiencies (or pH, soluble salts, etc.) and to guide the recommendation process so that these limitations could be eliminated economically and without impacting the quality of our environment. In recent years, interest has grown in environmental soil testing, defined here as "quantitative analysis of soils to determine if environmentally unacceptable levels of nutrients, nonessential elements or organic compounds are present." Environmental soil testing is a much more ambiguous process than agricultural soil testing because it is usually quite difficult to quantify the meaning of the term "environmentally unacceptable." Absent a clear, quantitative measure of success, such as crop yield for agricultural soil testing, the entire process of soil testing, from sample collection to recommendation, becomes more diffuse and more complex. Nevertheless, the rising interest in environmental protection in many areas of the world has prompted an increased effort to use soil testing as an index of the risks posed by soils to other sectors of the environment, particularly ground and surface waters. Given this, it is appropriate to consider the most effective means to restructure soil testing practices to meet environmental goals (Sims et al., 1997).

In the broadest sense, the goals of environmental soil testing are the same as those of routine, agricultural soil testing—rapid, accurate, and reproducible soil analysis by the most appropriate methods, and a reasonable interpretation of results related to environmental risk. Factors to consider when developing an environmental soil testing program are discussed next, using two reasonably common examples, potentially toxic trace elements and plant nutrients that are known to degrade water quality. In both cases, it is critical to consider the conceptual differences in interpretation of an environmental soil test, illustrated in Figure 13.5, compared to an agricultural interpretation (Figure 13.3).

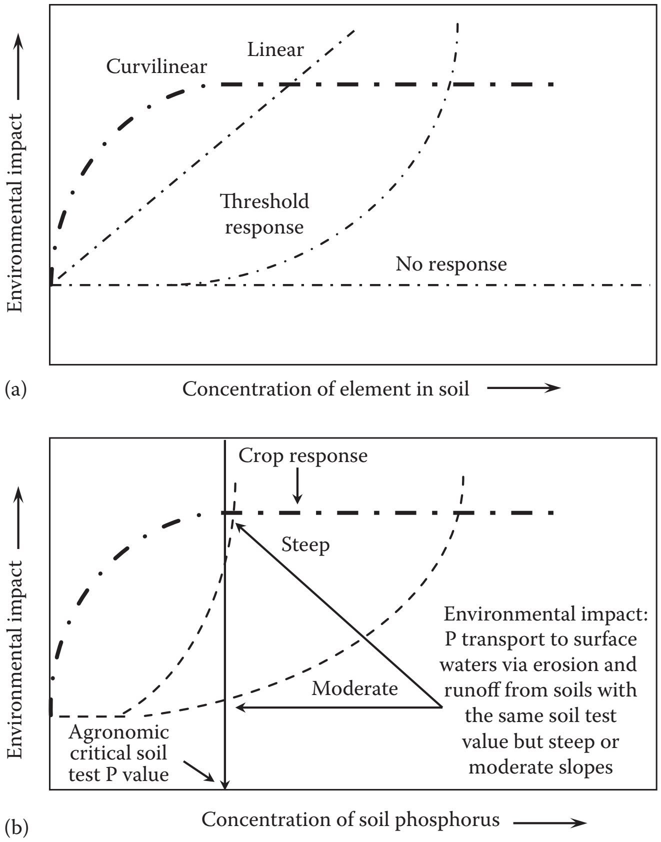

FIGURE 13.5 Illustration of points to consider in interpretation of environmental soil tests. As seen in (a) increasing the concentrations of soil nutrients or nonessential elements can induce no environmental response, cause a response once a threshold is reached, or have a linear or curvilinear effect on the environmental parameter of interest. In (b) crop response to increasing soil concentrations of a nutrient is contrasted with the environmental impact of that element, which can be modified by other soil properties. For example, crop response to inputs of phosphorus (P) is normally curvilinear, while the impacts of P on surface waters due to erosion and runoff can follow a threshold response. Soils with the same soil test P value, but varying slopes (steep or moderate) will have differing environmental impacts. (Figure a adapted from Pierzynski, G.M., Sims, J.T., and Vance, G.F. 1994. Soils and environmental quality. Lewis Publishers, CRC Press, Boca Raton, FL.)

13.2.7.2 Soil Testing for Potentially Toxic Trace Elements

Soil testing for potentially toxic trace elements is an environmental issue because some plant nutrients (Cu, Mo, and Zn) and nonessential elements (As, Cd, Cr, Hg, Ni, Pb, Se) have been shown to be toxic to either plants, animals, or humans. Soils may contain naturally high concentrations of one or more of these elements (very unusual), or concentrations may increase as a result of some anthropogenic activity such as the intentional addition of wastes as beneficial soil amendments (e.g., animal manures, municipal sewage sludges, industrial by-products). Some soils may be highly polluted with toxic elements due to mismanagement of potentially beneficial wastes, by an accidental spill or discharge, or as a result of an industrial activity such as mining or smelting. Note that contamination and pollution are not the same. Contamination occurs when a substance is present at concentrations higher than would occur naturally but no adverse effect on an organism is apparent while pollution implies not only an elevated concentration in the soil, but clearly documented adverse effects on some organism (Pierzynski et al., 1994).

Soil testing for potentially toxic trace elements begins with an understanding of the nature of the risk involved—what organisms may be affected, by what pathway, and by which elements. Primary areas of concern in general are direct soil ingestion, phytotoxicity, plant uptake and food chain contamination, and water pollution from erosion, runoff, or leaching. Direct soil ingestion is normally only a concern for Pb and with young children who are most likely to ingest soil or inhale dust from high Pb soils. Phytotoxicity is rarely an issue with Pb except in highly polluted soils at industrial sites but is a greater concern with Cu, Cr, Ni, and Zn. Food chain contamination and human health effects are most often associated with Cd and Hg and water quality concerns with As, Cu, Hg, and Se. Knowledge of the nature of the risk and the element of concern helps to determine the most effective soil sampling protocol. In the case of Pb in urban soils where human health is the concern, it may be advisable to collect very shallow soil samples (<2 cm) since this is the soil depth most likely to be ingested. A similar depth would be useful if runoff or erosion were the issue since rainfall primarily interacts with only the uppermost few cm of the soils. However, if concerns exist about ground water pollution, sampling into subsoil horizons, perhaps to a depth of 1–2 m would be recommended to determine if elemental leaching is occurring. For elements where the main concern is phytotoxicity and food chain contamination, the normal sampling depths associated with the crops to be grown are usually acceptable (e.g., 0–20 cm). If remediation of the site is the goal, either by soil removal, soil washing, or soil amendment, then systematic deep sampling (e.g., 0–5, 5–10, 10–20, 20–40, 40–60, 60–100 cm) is recommended to determine the depth of soil contamination and thus the extent of remediation required. Careful consideration should also be given to the soil sample handling and preparation steps to avoid contamination from any sampling and mixing tools or grinding and sieving devices (e.g., stainless steel, used in many electric grinding device contains Cr and Ni) and to protect the health and safety of the individual taking the sample. The method of analysis to be used varies with the intent of the test. If the goal is to assess biological availability (e.g., plant uptake, human ingestion) then many dilute acid or chelate-based soil test extractants, or the PBET mentioned earlier (Section 13.2.2.1) may be suitable, providing due consideration is given to the most appropriate test for the intended land use or human health concern (O'Connor, 1988). Interest, and field research, using the PBET has increased in recent years as the need to remediate metal-contaminated sites has grown. Areas of particular interest are simplifying the methodology to adapt the PBET for routine testing and standardizing the interpretation of PBET results. For example, Fendorf et al. (2004) simplified the PBET method by reacting 0.5 g soil and 50 mL of 1 M glycine, adjusted to pH 3 for 1 h in a 35.6°C water bath. They found this method accurately tracked decreases in bioaccessibility of As, Cr, and Pb in a wide range of surface and subsoils from the United States. Other simplifications of the PBET have been evaluated by Yoon et al. (2007) in studies of method to immobilize Pb and reduce leaching, by Brown et al. (2007) in research on the use of soil amendments to reduce Pb bioavailability at a U.S. Environmental Protection Agency (USEPA) Superfund site, by Brown et al. (2003) in studies of factors controlling Pb bioavailability in urban soils, and by Moseley et al. (2008) in investigations of the use of phosphate soil amendments to reduce Pb bioaccessibility in industrial and firing range soils. However, if the goal is to quantify the extent of accumulation of an element, relative to normal soils or natural background levels, or to monitor this accumulation over time, methods that determine or approximate total elemental content are recommended. One example is USEPA Method 3050 that successively digests a soil sample with concentrated HNO_3, H_2O_2, and HCl to measure "total sorbed metals" by acidic dissolution of clays, oxides, and carbonates and oxidation of organic matter; elements associated with silicates are not dissolved. Therefore, for a true measure of total elemental content of a soil sample, complete digestion of the soil with strong acids (e.g., HNO_3-$HClO_4$ for Cd, Hg, and Pb), by carbonate fusion (Cr, Ni), or by alkaline oxidation techniques (As, Se) is required. Given the costs and difficulty of measuring total elemental content of trace elements in soils it is often advisable to use rapid soil testing methods as surrogate monitoring techniques (Sims and Johnson, 1991).

Interpretations and recommendations for soil tests for potentially toxic trace elements are considerably more difficult than for agricultural systems and are often very site and element specific. As mentioned above, the main difficulty lies with soil test calibration—establishing a quantitative relationship between an agreed upon measure of environmental risk and the amount of an element measured by the soil test. In most cases, this has been done by the use of complex risk assessment models that first identify the "target organism" of concern (e.g., human vs. plant) and then evaluate all possible pathways by which the target organism may be exposed to the risk factor (the toxic trace element). If possible, a "most sensitive pathway" is identified, defined as the lowest soil concentration level at which an adverse effect on the organism would be likely to occur (e.g., soil ingestion vs. consumption of contaminated drinking water). Regulatory upper limits may then be established for that pathway, which can be monitored by the soil testing methods described above. This approach was used by USEPA in the formulation of the national rule for the disposal and utilization of municipal sewage sludges, which established regulatory limits for the total amount of several trace elements that could be applied to agricultural soils via land application of these sludges (Ryan and Chaney, 1993). Additional information on the methods used to interpret soil testing results is found in U.S. Environmental Protection Agency (1989), Risser and Baker (1990), and Pierzynski et al. (1994).

13.2.7.3 Soil Testing for Plant Nutrients with Water Quality Impacts

Soil testing for plant nutrients that can degrade water quality is focused primarily on N and P because of their well-documented effects on ground (N) and surface (N, P) water quality. The principles, practices, and problems of soil testing for N were described in Section 13.2.4.4. Other than the methods described in that section (e.g., the PSNT and ISNT), which focus on identifying sites with an adequate N supply and thus avoiding unnecessary applications of fertilizers or organic sources of N (manures, sludges), there are no other approaches currently available for use in an environmental soil testing program for N. Environmental soil testing for P, however, is a considerably different matter. Growing international concerns about the role of P in the eutrophication of surface waters stimulated a large research effort on environmental soil testing for P beginning in the late 1980s and continuing even today. The focus of this effort has been the use of soil testing alone, or as a component of site indexes and nonpoint source pollution computer models, to identify soils that are most likely to be significant nonpoint sources of P pollution of streams, rivers, ponds, lakes, and bays. Some aspects of environmental soil testing for P are described below, illustrating the changes needed in soil sampling, analysis, and interpretation when surface water protection, not agricultural production, becomes the primary goal. Readers are referred to several reviews for more detailed information on this topic (Sims, 1993; Sharpley et al., 1996; Sibbesen and Sharpley, 1997; Sims, 1997; Tunney et al., 1997; Maguire and Sims, 2002).

13.2.7.3.1 Establishing Upper Critical Limits for Soil P Using Soil Testing Methods

One approach proposed for environmental soil testing for P is to simply establish an upper critical limit for soil P using currently available agronomic soil testing methods (e.g., Bray P_1, Mehlich 1, Mehlich 3, Olsen P). Soils that exceeded the upper critical limit for soil test P would no longer receive P inputs from any source (e.g., fertilizers, manures, biosolids) and would be targeted as priority areas for soil and water conservation practices to prevent P loss in erosion, runoff, and leaching. Two reasons are usually given to justify the need for this upper critical limit. First is that an extensive body of research shows that soils that are overfertilized with P relative to crop requirements will create an increased risk of nonpoint source pollution of surface waters (Sharpley, et al. 1994; Sims et al., 1997, 1998, 2002; Tunney et al., 1997). Second is the concern that continuing to apply P to soils well beyond values that are needed for crop production contradicts the principles of sustainable development and sustainable agriculture. The rationale underlying this second concern is the fact that P is obtained from a finite natural resource base, at a cost to society, and that agricultural practices that waste this resource are inconsistent with sustainability. Despite these concerns, until recently there was a reluctance to establish upper critical limits using soil test P measurements primarily because (1) agronomic soil tests were not originally designed or calibrated for environmental purposes and thus there was uncertainty concerning their accuracy at identifying soils with the potential to contribute environmentally significant amounts of P to waters by runoff or leaching and (2) there would be an unjustified reliance upon agronomic soil test P alone by environmental regulatory agencies attempting to control nonpoint source pollution of surface waters, ignoring the complex interaction between soil P and the transport processes and soil/crop management factors that control the movement of P from soil to water.

Because of these questions and concerns, the most appropriate means to use existing agronomic soil P tests, or new soil test methods, to identify soils with a high risk of P transfer to water has received intense research interest in the past decade. Results of many laboratory and field studies conducted in the 1990s and 2000s have clearly shown that agronomic soil P tests are often well correlated with other measures of soil P that suggest increased risks of P loss, such as water soluble P, the equilibrium P concentration in the soil solution (EPC_0), easily desorbable P (e.g., P extracted by Fe-oxide filter paper strips), and algal-available P (Gartley and Sims, 1994; Sibbesen and Sharpley 1997; Sims 1997; McDowell and Sharpley, 2001; Vadas et al., 2005). Additional studies of the relationships between agronomic soil test P and dissolved P concentrations in overland flow or leachate provided direct evidence for increased risks of P loss from overfertilized soils (Heckrath et al., 1995; Westermann et al., 2001; Maguire and Sims, 2002; Little et al., 2007). In some cases, this relationship was near-linear, while in others there appeared to be a "change point" above which there was a more rapid increase in dissolved P concentrations in runoff or leachate with increases in soil test P. Research has also shown that maintaining soil test P in the optimum range for plant growth minimizes dissolved P losses. When combined with information on soil erosion, soil test P can also be used to assess the risk of particulate P loss to water, as is done by risk assessment tools such as the P Site Index, as discussed below.

"Environmental soil P testing," however, is not confined to the use of agronomic soil P tests. It may mean the use of completely different methods for soil sampling, analysis, and interpretation than those done for agricultural purposes. Or, it may mean that an environmental or regulatory interpretation is now being applied to results of an agronomic soil P test, such as establishing an upper limit for soil test P beyond which no further P additions can be made. Changes in soil sample collection may include sampling to a shallower depth (0–5 cm) if overland flow is of greatest concern or to the depth of the mean high water table (e.g., 50–150 cm) if P leaching and subsurface flow is the main pathway for P loss. Different analytical methods may be used such as assessment of the degree of soil P "saturation" (DPS), water-soluble P, easily desorbed P, "algal available" P, and quick tests for P sorption capacity. For example, a DPSox method based on acid ammonium oxalate extraction of P, Al, and Fe was developed in the Netherlands to identify soils where P leaching to shallow groundwaters is a risk. Oxalate extractable P (Pox) represents the amount of P currently sorbed by the soil and oxalate Al and Fe (Alox, Feox) are proportional to the P sorption capacity of noncalcareous soils. The molar ratio of Pox to [α (Alox, + Feox)] is thus an indication of soil P saturation (where α is a parameter used to convert (Alox + Feox) to estimated soil P sorption capacity and typically ranges from 0.4 to 0.6). Upper limits for DPSox of 25%–40% are most commonly used today. Research has found increases in water-soluble and desorbable P in soils above these DPSox values, suggesting a greater risk of P loss to surface waters and shallow groundwaters from P-saturated soils. Research has also shown that DPS measured by the Mehlich 3 (M3) soil test is well correlated with DPSox and also with P concentrations in leachate and overland flow (Sims et al., 2002). The Mehlich 3 soil P test is widely used in the United States and Canada, and some soil testing laboratories now report a soil P fertility assessment (M3-P) and soil P saturation (M3-DPS) using one soil extraction. In addition to using soil P saturation to predict dissolved P losses, research has also shown that using the "safe P storage capacity" (SPSC) of a soil can be accurately estimated using Mehlich 1 or Mehlich 3 DPS values (Nair and Harris, 2004; Chrysostome et al., 2007). The SPSC concept is used to determine how much additional P loading can occur before dissolved P losses become an environmental concern, particularly important in settings where manures or biosolids are regularly applied to soils.

With the possible exception of the M3-DPS test, environmental P tests would probably not be conducted on every sample submitted as part of a nutrient management plan. Instead, they would be part of a more intensive testing procedure used when agronomic soil test P values were considered high enough to warrant further investigation. Even more important, most soil scientists recommend that environmental soil P tests not be used alone, but as a component of a more holistic risk assessment process, such as the P Site Index (Heathwaite et al., 2005) a risk assessment tool that integrates soil P with P transport and management practices to characterize the potential for P loss at a site. For instance, the states of Delaware and Maryland in the United States require that a P Site Index be conducted for fields with an agronomic soil test P (Mehlich 3) value >150 mg P kg^{-1}. Nearly every state in the United States has developed and adopted a P Site Index as the preferred means to assess the risk of P loss from agricultural fields to surface waters, as opposed to the use of a soil P test alone. Many P Site Indices are now available on the internet, such as a very comprehensive index developed by the University of Wisconsin (see http://wpindex.soils.wisc.edu/).

13.3 Plant Testing

Soil fertility evaluation does not rely upon soil analysis alone. Many techniques now exist to assess soil fertility by characterizing the growth and elemental composition of plants. These include visual diagnosis, in-field evaluation techniques, laboratory analysis of plant tissues, and remote sensing. Plant analysis includes both rapid in-field tissue testing and total elemental analysis of plant samples, normally conducted in the laboratory. In both cases, the underlying premise is that the plant concentration of an element is proportional to the availability of the nutrient in the soil and thus is an index of soil fertility. Visual diagnosis and remote sensing do not actually determine the nutrient concentration in a plant, but instead rely upon changes in plant color or growth as indexes of soil fertility.

13.3.1 Visual Diagnosis of Deficiency Symptoms

With experience it is possible to identify visual symptoms that result from nutrient deficiencies. Examples include severely stunted growth and purpling of older leaves (P), chlorosis and necrosis of leaf margins (K), interveinal yellowing of newer leaves by Fe and Mn and of older leaves by Mg, and distorted meristems and blackened internal tissues (B). In general, visual diagnosis should be verified by soil and plant analysis, prior to taking corrective actions. Tisdale et al. (1993) cited four reasons for this: (1) the symptom may be caused by a deficiency of more than one nutrient; (2) the deficiency of one nutrient may be caused by an excess of another; (3) other factors, such as insect and disease injury, can create symptoms similar to nutrient deficiencies; and (4) the symptom may be caused by more than one growth factor (e.g., P deficiency can occur in cold, wet soils that have optimum P fertility levels—the deficiency disappears when soils warm). Other factors to consider are the fact that the same symptom may be caused by different nutrients in differing plants. For example, purpling of older leaves, typically due to P, can be caused in cruciferous plants by S deficiency. The location of a deficiency on the plant can assist in proper identification of the cause. Nitrogen and S can both cause yellowing of plant leaves; however, because N is more mobile in most plants than S, its deficiency symptoms usually occur on older leaves, while S deficiencies are seen as a more overall yellowing. Calcium and most micronutrients (B, Cu, Fe, Mn, Zn) are rather immobile in plants; hence, their deficiencies usually occur on new growth, compared to some of the more mobile macronutrients (N, P, K, Mg) where deficiency symptoms are observed on older plant parts. Finally, for many plants, by the time a nutrient deficiency symptom can be accurately diagnosed, it is either too late for corrective action (unless nutrients can be added via fertigation or sidedressing) or unwise because the deficiency has already damaged the plant beyond the point where nutrient additions can profitably correct the problem.

13.3.2 In-Field Evaluation of Plant Nutritional Status

In addition to visual diagnosis, there are several “in-field” diagnostic techniques that can be used to provide semiquantitative information on plant nutritional status. The most common is the use of rapid tissue testing kits for the colorimetric analysis of plant sap. The color that develops after addition of the appropriate chemical reagents to sap is proportional to the concentration of the nutrient (usually only N, P, and K are tested in these kits). The entire process takes only a few minutes much less than required for total elemental analysis of a plant tissue by an analytical laboratory, which can require a week or more. In general, because of its semiquantitative nature, rapid tissue testing should only be used as a guide, and not as the sole basis for nutrient management recommendations. Tisdale et al. (1993) also cautioned that rapid tissue testing must (1) only be done with the correct plant part, sampled at the proper time of year and, for some nutrients (e.g., NO_3-N), at the proper time of day because nutrient concentrations change during the day; (2) be done in a comprehensive manner, continuing the testing throughout the growing season, not as a one-time activity; (3) focus on periods of maximum vegetative growth and reproductive stages to best assess a fertilizer program; (4) be the average value from the analysis of at least 10–15 plants and be collected from areas of normal and deficient plant growth.

One advance in field-scale plant N testing is the LCM, a small, hand-held spectrometer that directs a beam of light corresponding to the wavelength absorbed by the chlorophyll molecule through a plant leaf, while the leaf is still on the plant. The meter essentially measures leaf “greenness,” which has been shown in numerous studies to be correlated with leaf chlorophyll content, plant N, and the likelihood of an economic response to N fertilization. The LCM allows for rapid, ongoing monitoring of plant N nutrition and is particularly well suited to irrigated crops where N can be added via the irrigation system according to LCM results. Since other nutrients affect leaf greenness, especially S, the LCM must be used with caution and with soil N testing where possible to avoid recommending N fertilization when some other factor is responsible for the observed chlorosis (Schepers et al., 1992). Nevertheless, the LCM is an important advance in the field-scale evaluation of plant N nutrition, particularly for agronomic crops.

Remote sensing has long been recognized as a relatively inexpensive method for mapping, monitoring, and classifying vegetative cover. As discussed earlier, the high spatial and temporal variability of soil N has limited development of reliable soil tests for determination of soil N supplying capacity. However, remote sensing shows potential to overcome the shortfalls of traditional plant and soil analysis due to its ability to characterize spatial variability down to resolutions of just a few meters and to identify nutrient deficiencies in real time while applying fertilizers or other nutrient sources. Numerous vegetative indexes have been developed using knowledge of plant spectral reflectance and absorbance characteristics. For example, plants scatter or reflect the majority of near infrared (IR) radiation that they intercept due to internal cellular structures. Conversely, chlorophyll absorbs the majority of red (R) light intercepted to provide energy for photosynthesis. One such index is the normalized differential vegetation index (NDVI):

$$\mathrm{NDVI} = \frac{\mathrm{IR} - \mathrm{R}}{\mathrm{IR} + \mathrm{R}} \tag{13.2}$$

The NDVI has been widely used to assess land use, monitor crop phenology, and to estimate yields by numerous researchers. More recently, NDVI has been used to relate predicted yield to N requirements of various crops during the growing season (Shanahan et al., 2001; Chang et al., 2003). Nonetheless, remote sensing has often been of limited use in agriculture due to the cost and time associated with collection and processing of remote sensing data generated by satellites or fixed wing aircraft. However, recently portable, active optical sensors have become commercially available. These sensors emit their own light and can be hand-held or mounted on equipment, overcoming many of the shortfalls associated with satellite- and aircraft-based sensors that are reliant on reflected sunlight and vulnerable to atmospheric conditions. These sensors have been shown to reliably predict crop yields and multiple algorithms have been developed to relate various indexes to crop N requirements (Raun et al., 2005; Thomason et al., 2007). Moreover, the sensors can be used to control variable rate N application in real-time, significantly increasing N use efficiency. As sensing technologies continue to develop, they are likely to represent perhaps the most significant advance in the evaluation and adjustment of crop nutrient status.

13.3.3 Plant Analysis

13.3.3.1 Plant Analysis: Basic Principles

Plant analysis is defined as "…the determination of the elemental composition of plants, or a portion of the plant, for elements essential for growth. It can also include determining elements that are detrimental to growth or animals or humans through our food chain" (Munson and Nelson, 1990). The components of a plant analysis program are similar to those used for soil testing: (1) collection of a representative sample from a plant, or the whole plant, at the proper stage of plant development; (2) proper handling of the sample to avoid contamination or damage that could affect interpretation of results, followed by accurate sample analysis using standardized laboratory methods; (3) correlation and calibration studies that establish quantitative relationships between plant analysis and plant performance; and (4) economically and environmentally sound nutrient management recommendations to correct any nutrient deficiencies. Key factors to consider in each step are described below. Many references provide detailed descriptions of the protocols used for plant sampling, handling, and laboratory analysis; hence, these topics will not be discussed (Plank, 1989; Jones and Case, 1990; Westerman, 1990; Mills and Jones, 1997).

13.3.3.2 Plant Analysis: Interpretation of Analytical Results

The two most widely used methods for interpretation of plant analysis are (1) the critical nutrient concentration or range (CNC or CNR) and (2) the diagnosis and recommendation integrated system (DRIS), which relies primarily on nutrient ratios, emphasizing the importance of nutrient balance in the plant to optimum plant performance.

Interpretation by the CNR approach relies, as with soil testing, mainly on correlation and calibration studies that show there is a statistically significant relationship between the nutrient concentration in a plant and plant response to additions of the nutrient (Figure 13.6). In most cases plant analysis results are compared to optimum CNRs, with analytical values expressed in percentages (for major nutrients) and parts per million (mg kg^{-1} or $\mu\mathrm{g}\ \mathrm{g}^{-1}$ for micronutrients), on a dry weight basis. Nutrient concentrations below the CNR are considered deficient, those above it adequate or optimum; the CNR represents a transition zone between these two categories. The CNC is defined as the nutrient concentration where plant performance changes from suboptimum and unsatisfactory to optimum. Because the CNC is a single value that can be difficult to determine experimentally, given the uncertainties and variations associated with field studies, and because it can

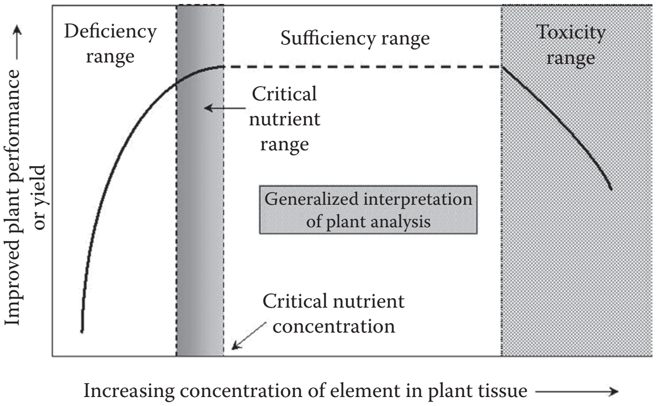

FIGURE 13.6 Illustration of the critical nutrient range approach for plant analysis interpretation.

vary somewhat within a plant species due to genetic differences among hybrids, the CNR approach is more commonly used to interpret plant analysis results. Extensive research conducted to determine CNRs for most plants with economic value clearly show that the CNR for a plant depends upon growth stage and plant part that is sampled (Mills and Jones, 1997). Therefore, comparisons of plant analysis results with CNR values are only valid if the plant sample is taken at the same growth stage and from the same plant part used in the calibration studies conducted to determine CNRs. Interpretation of plant analysis results by this method, therefore, requires careful adherence to recommended protocols for sampling, handling, and analysis.

The balance of nutrients within a plant is often more important than the concentration of any individual nutrient. The DRIS system focuses on nutrient balance as an alternative to the CNR approach to plant analysis interpretation. One advantage of the DRIS system, compared to the CNR, is that nutrient ratios in plants tend to be more constant throughout the growing season than individual nutrient concentrations. Use of DRIS, therefore, allows for greater flexibility in the time of plant sample collection as samples do not necessarily have to be taken at a specific growth stage. The DRIS system first establishes norms for all nutrient ratios (N:P, N:K, P:K, N:S, P:S, etc.) associated with maximum crop yield. These norms can be developed from reviews of the scientific literature or by widespread sampling of a crop in a given physiographic region. As much as possible, all factors that affect crop yield are measured at the time of plant sample collection (soil test values, pest pressure, climate, cultural practices, etc.). In this way, an integrated relationship can be established between the DRIS norms, crop yield, and the other growth-limiting factors. Interpretation of plant analysis via the DRIS system can be done graphically or mathematically by the calculation of DRIS indices. The DRIS system has received intense interest and considerable research in the past decade. Computer programs that can rapidly calculate DRIS indices have been developed from this research, resulting in wider use of DRIS by plant analysis laboratories. Readers are referred to Beaufils (1973), Sumner (1979, 1981), Escano et al. (1981), Amundson and Koehler (1987), Karlen et al. (1988), Walworth et al. (1988), Munson and Nelson (1990), and Beverly (1991) for examples of the use of DRIS.

13.4 Soil Fertility Evaluation: The Future

The principles and practices used to assess soil fertility continue to evolve and it is clear that the process of soil fertility evaluation will take on new dimensions in the next decade. Given this, two important questions should be considered now. First, how should newly emerging technologies for the evaluation of soil fertility be assessed and integrated with current practices? Second, it is clear that in the past decade soil fertility evaluation has expanded well beyond production agriculture to address new challenges, especially those related to environmental protection and human health. Given this, how can we best apply the results of “environmental” soil tests to assess the value of best management practices intended to protect or restore the environment or reduce soil-related human health risk?

13.4.1 Precision Agriculture and Remote Sensing

The past decade has seen the development of several new technologies that have the potential to significantly alter soil fertility evaluation and management. The two most important and closely related examples are “precision agriculture” and remote sensing (defined as “… the science of obtaining information about an area through analysis of data acquired by devices not in contact with the area”; Hergert, 1997). Precision agriculture, also referred to as site-specific management, has become an increasingly accepted and widespread approach to farming that allows us to (1) precisely map soil fertility in a field or on a farm at great detail (typically in 1 ha grids) through the use of hand-held or equipment-mounted GPS that use signals from a network of satellites to instantaneously locate a position on the earth’s surface; (2) use variable rate application equipment, equipped with GPS and “on-the-go” sensors of soil nutrient status, to supply nutrients in accordance with these maps; and (3) generate GPS-based maps of crop yields. Factors related to yield that cannot easily be measured by soil and plant testing can be obtained from other computerized data bases (e.g., soil series from soil surveys) or be assessed using remote sensing (e.g., plant health, soil moisture, irrigation and drainage, pest pressure). The most commonly used remote sensing devices today include cameras and other imaging systems mounted on aircraft or satellites. Other, more recent examples are sensors mounted on ground equipment (e.g., tractors, pesticide applicators) or on large permanent structures (irrigation systems, electrical towers). Remote sensing devices acquire electromagnetic energy that is emitted or reflected from plants (or bare soils) and convert this energy into data that can be used in soil fertility evaluation. Each combination of soils, plants, environmental conditions, and management practices has a characteristic spectral “signature”—a specific spectrum of radiation—that can be used to diagnose soil fertility problems. As an example, IR aerial photography has been used for many years to assess plant performance because healthy green plants reflect large amounts of IR radiation while plants damaged by insects, drought, or nutrient deficiencies do not. As with traditional approaches to soil fertility evaluation, the ultimate value of these increasingly sophisticated technologies lies in our ability to interpret the results. Indeed one of the problems with precision agriculture is that vast quantities of spatially located data can be generated very quickly, creating an information overload that can confuse or obscure interpretation. Research is now underway to develop “expert systems” that use computerized GIS to integrate the various “layers” of data in a meaningful way, thus guiding a more holistic approach to crop management, of which soil fertility evaluation is only a part. Some areas in precision agriculture where research is needed include the following: (1) an economic analysis of the value of the additional information obtained by extensive, GPS-based grid soil sampling, relative to traditional, less intensive techniques; (2) a reevaluation of current soil test calibration and correlation models given the enormous, large-scale data bases that are rapidly becoming available; (3) the most effective and rapid means to obtain "ground truth"—verification of the accuracy of remote sensing devices and "on-the-go" sensors as indicators of soil fertility; and (4) the value of site-specific management techniques for application other than crop production, such as minimizing N and P losses via leaching and runoff, irrigation scheduling, erosion control practices, and more efficient use of wastes and by-products. Readers are referred to Robert et al. (1995), Pierce and Sadler (1997), and Bongiovanni and Lowenberg-Deboer (2004), Srinivasan (2006) for reviews of precision agriculture and site-specific management and to the following Web sites from universities and private industry for examples of the latest advances in this field: (1) Australian Centre for Precision Agriculture, http://www.usyd.edu.au/agric/acpa/; (2) Cranfield University (United Kingdom) Centre for Precision Farming, http://www.cranfield.ac.uk/sas/naturalresources/index.jsp; (3) The Ohio State University, http://precisionag.osu.edu/; (4) Purdue University Site Specific Management Center, http://www.agriculture.purdue.edu/ssmc/; and (5) Precision Ag, http://www.precisionag.com/.

13.4.2 New Directions and Uses for Soil Fertility Evaluation Techniques

The formal, institutionalized practice of soil fertility evaluation originated to serve the needs of production agriculture, a function that continues to be of unquestioned importance today. However, some of the needs of the agricultural sector are changing as, for example, in developed countries where the potential environmental impacts of soils that have become over-enriched with nutrients or contaminated by wastes and by-products from industry and urban area has begun to supersede the need to identify and correct nutrient deficiency problems. At the same time, those responsible for nonagricultural land uses are beginning to see the potential value of practices originally developed to optimize soil fertility for crop production. There are several challenges that must be overcome if the process of soil fertility evaluation is to evolve and respond to needs such as these. First is the establishment of better and more direct interfaces between nontraditional users of soil and plant testing and researchers with expertise in these areas. This will help to clarify when, where, and how it is appropriate to use current soil fertility evaluation techniques for purposes other than those for which they were originally designed. It will also provide insight into the advances in soil science research needed to more effectively address the problems faced by those charged with protecting air and water quality, preventing further damage or restoring soil quality to lands disturbed by erosion, salinization, construction, surface mining, and similar activities, and remediation of soils polluted by anthropogenic activities. Second, is the need for the public and private organizations responsible for soil fertility evaluation to recognize the contribution they can make to solving land management problems that are not solely directed at profitable crop production. This will require better interactions with (1) researchers who have developed many new soil testing methods that have value in these areas but that have not been adopted by routine soil testing laboratories; (2) new clientele who often have unusual problems and limited understanding of the principles and practices of soil and plant testing; and (3) a wide range of technical and regulatory agencies and not-for-profit environmental groups who have the responsibility or interest in the protection and restoration of air, water, and soil quality. Strengthening these interfaces will provide the research base essential to support nontraditional uses of soil fertility evaluation techniques and the educational component needed to ensure that only the appropriate analytical methods are used and that proper interpretations of the results are made. This research should then help guide the design and implementation of best management practices that can minimize nutrient loss from land to water, stabilize (or remove) elements in soils that may be toxic to humans or other organisms, and restore ecosystems degraded by nonpoint pollution.

In conclusion soil fertility evaluation is a vital, integral part of global agriculture and plays an increasingly important role in many nonagricultural land uses, especially those related to nonpoint source pollution. Successful application of the principles and practices described in this chapter will increase the profitability and minimize the environmental impacts of nutrient use—the fundamental goal of soil fertility management. Appropriate integration of newly emerging technologies with current practices will further enhance our ability to evaluate soil fertility and make sound nutrient management decisions. Expanding the process of soil fertility evaluation to more fully include nonagricultural settings, and especially to situations where environmental protection or land restoration are the goal, is perhaps the greatest challenge we face today.

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14

Fundamentals of Fertilizer Application

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14.1 Introduction

Efficiency of nutrient application is one of the major factors affecting the overall effectiveness of a fertilizer program. There are a number of ways that the efficiency of fertilizer use can be measured, such as the percent of the applied nutrient taken up by the plant or the increase in crop yield per unit of applied nutrient. But regardless of the measure used, a number of interacting factors determine the efficiency of a given fertilizer application. The relative mobility of the nutrient of concern in the soil is foremost in importance. Nitrogen (N) is an excellent example of a nutrient that is mobile in the soil and easily lost from the root zone. Devising an application system that can provide N to the crop when it is needed is the challenge in many cropping situations. Sulfur, B, and Cl are other nutrients considered to be mobile in soils. Compared to N usage, uptake of these nutrients is rather small. However, management decisions regarding time and method of application may still be needed to ensure optimum utilization.

Phosphorus, on the other hand, is generally considered to be relatively immobile in soils. While loss of P from the root zone limiting P availability to crops may be unlikely, P is subject to a number of reactions and transformations, which can reduce P availability to the plant. Placement techniques that minimize the effects of these transformations and enhance P availability are potentially valuable to crop managers.

In choosing appropriate application technology, a number of characteristics of the system beyond nutrient mobility must also be considered. These include the nature of the crop being fertilized, weather and climate, soil properties, the form in which the nutrient is applied, the method of application utilized, and the timing of the fertilizer application in relation to nutrient needs of the crop. By understanding how these individual factors interact, one can devise an efficient system of nutrient delivery requiring the least possible amounts of fertilizer, yet achieving optimum growth and subsequent yield.

To arrive at useful and effective decisions with respect to fertilizer application, it is necessary to have some understanding of how plant nutrients get to the root system. There is general agreement that nutrients reach a root by three primary mechanisms: mass flow, diffusion, and root interception.

Mass flow is somewhat self-descriptive. Nutrients dissolved in the soil solution/water move to the surface of the root as water is taken up by the plant. Mobile nutrients such as N, S, B, and Cl, and immobile nutrients present in high concentrations in the soil solution such as Ca and Mg move to the root surface with soil water through mass flow. Diffusion is a process whereby soil nutrients move from an area of high concentration to an area of lower concentration near the root surface created through nutrient uptake. Immobile nutrients such as P, K, and the micronutrient metals move to the surface of the root by diffusion. Diffusion takes place over relatively short distances (<1 mm). Fertilizer application methods, which create zones/areas of high nutrient concentration such as fertilizer banding, can facilitate diffusion. However, only the portions of the root system in, or in direct contact with the high nutrient availability zones are impacted.

Root interception is simply the process where the root intercepts plant nutrients as it grows through the soil. Both mobile and immobile nutrients are made accessible for nutrient uptake by this process.

14.2 Application of Mobile Nutrients

Of the 14 mineral nutrients considered essential for plant growth, N, S, B, and Cl are generally considered to be mobile in soils. Because of the differences in magnitude of uptake and sources available for use in a fertilizer program, the application of each will be discussed separately.

14.2.1 Nitrogen

Application of N is a major concern in the production of most nonlegume crops. When developing an N fertilization program today, the modern grower is faced with decisions about (1) the rate of N to apply, (2) fertilizer source or sources to use, (3) when to apply N to ensure adequate amounts present at key crop growth stages, (4) method of application, and (5) the use of compounds such as nitrification or urease inhibitors, or specialty fertilizer products such as coated urea to prevent N loss.

14.2.1.1 Nitrogen Sources

There are numerous sources of N that have been used for crop production over the years. The three N sources most commonly used for field crop production in the United States today are anhydrous ammonia (82-0-0), urea-ammonium nitrate solutions (28-, 30- or 32-0-0), and granular urea (46-0-0). In addition, significant amount of ammonium nitrate (33-0-0) and ammonium sulfate (21-0-0-24S) are also applied in some areas. Nitrogen is also added as a secondary component in many multiple nutrient fertilizers. These include the dry granular ammonium phosphates diammonium phosphate, DAP (18-46-0), monoammonium phosphate, MAP (11-52-0), and liquid ammonium polyphosphates (10-34-0 and 11-37-0). Many by-product N sources are also marketed as fertilizers, such as dry or liquid ammonium chloride. The choice of the source of fertilizer N is dependent on a number of factors such as the local availability of a specific product, cost of the product per unit of N, safety issues related to using the product, application equipment available and cost of application, time required and availability of custom application, N loss potential of the soils in that particular field, cropping system and residue cover, rooting patterns of the intended crop, and other individual factors.

The relative advantages of one fertilizer N source over another has been widely debated and consequently studied at length. In most studies with field crops, when care was taken to prevent N loss, most N sources have an equal effect on yield when used at rates that supply the same amount of N. Where differences have been observed, the differences can generally be explained by some factor that makes a particular source susceptible to N loss in that particular application. Examples would include (1) a surface application of urea in a high pH or high residue situation leading to N loss from ammonia volatilization; (2) the broadcast surface application of urea ammonium nitrate (UAN) solutions to a soil covered with large amounts of a wide C:N residue such as wheat straw or corn stalks resulting in N immobilization; (3) preplant applications of granular ammonium nitrate for corn on a sandy soil prone to leaching loss; (4) or an early fall preplant application of anhydrous ammonia for corn on a poorly drained soil prone to denitrification in a humid climate.

In each of these examples, N loss could have been reduced and the source successfully used through incorporation of the fertilizer or the addition of a urease inhibitor with the urea in example 1; placement of the UAN below the wide C:N residue through subsurface banding in example 2; use of a high N starter fertilizer followed by sidedressing with the ammonium nitrate in example 3; and delaying the application of the fall preplant ammonia to spring, and/or adding a nitrification inhibitor such as nitrapyrin to reduce denitrification in example 4. As these examples show, N source selection when developing an N management plan is not a decision that can be made independently of many other factors such as N loss potential from leaching, denitrification, immobilization and ammonia volatilization, application equipment available and time available for application, safety, and cost.

14.2.1.2 Time of N Application

The optimum time for N applications to agronomic crops generally revolves around three key factors, (1) the intended crop, architecture of the root system, nutrient uptake pattern, and when physiologically it demands N for key stages in crop growth, (2) the potential for N loss at that particular site, as a function of both climate and soils, and (3) time available for nutrient application in the cropping system. Using time of application as a management tool to avoid loss of N fertilizer will be discussed in detail in the following section.

Growth and development of the crop, and especially of the root system, are important factors to consider in timing decisions. Because of the downward mobility of NO_3-N in soils, more frequent applications of fertilizer N have been most effective for shallow rooted crops such as edible beans and potatoes, especially on sandy soils. Nitrogen uptake by crops is also not constant throughout the growing season. For crops such as wheat, barley, oats, and corn, for example, the rate of N uptake is slow during the early part of the growing season, accelerates before anthesis, and stops or decreases rapidly after pollination. Therefore, N fertilizer should be supplied in such a way as to meet the minimal needs of the young seedling, while providing the majority of the N throughout the later stages of vegetative growth, but be completed before grain fill is started. In the case of corn on sandy soils, where NO_3-N can move quickly below the root zone, a preplant or starter application to support early growth followed by a sidedress application at the four to eight leaf stage is generally adequate on nonirrigated sites. Under high-yielding irrigated environments, additional N applications prior to tasseling can be beneficial, both to ensure adequate N for grain fill, and to reduce the movement of NO_3-N below the root zone facilitated by the application of irrigation water.

With winter wheat, an application of N at seeding, either through broadcasting N or applying N with the planting equipment to enhance fall growth and tillering, followed by a topdress application applied between green-up and "jointing," or initiation of stem elongation, is common. In the high-yielding, intensive management systems used in the Mid-Atlantic and Ohio River Valley regions of the United States, multiple topdress applications are commonly made. In regions where winter wheat is a dual purpose crop used for both forage production and grain, higher rates of N applied prior to or at planting to stimulate fall and winter vegetative growth, followed by a heavy topdressing in early spring to stimulate grain production is common.

On well-drained medium to fine textured soils, timing of the applications of fertilizer N is more flexible for deep rooted crops such as corn and wheat in many environments. In many of these situations, time of application has little effect on yield, as long as adequate N is present to meet the needs of the crop at key physiological growth stages such as ear or head initiation/development. Nitrogen loss and environmental concerns may also be minimal in many environments. In these situations, applying N in a single application prior to planting can be a reasonable system to use for many crops.

Timing of needed fertilizer N is also an important consideration in the production of forage grasses. Because cool season species such as tall fescue and smooth brome grass produce most of their dry matter in late spring and early summer, fertilizer N should be applied before this season of rapid growth. How the forage is utilized, whether harvested for hay or used for grazing, and whether the N is applied alone or in combination with other nutrients can also influence the time of N application. When using cool season grasses for hay, making a single application of N in the early spring before or at green-up is common. When making a combined application of N with P, a late fall application to stimulate tillering and root growth is preferable in many environments. In environments where cool season grasses are used for grazing, especially fall grazing, or a second cutting of hay is made, splitting the N application with the majority of the N and any needed P applied in the fall or early spring followed by an application of the balance of the N in mid- to late summer to stimulate fall growth, can be beneficial.

In contrast, the majority of the growth of warm season species occurs when temperatures are high and therefore application of fertilizer N should be delayed until after the initiation of the warm season grass growth to minimize stimulation of cool season invasive grass and weed species. In the case of high-yielding, intensively managed species such as Bermuda grass, multiple applications of N are generally more efficient than single, early season N applications.

14.2.1.3 Managing Fertilizer N to Prevent Losses

Nitrogen is lost from agricultural soils primarily by (1) leaching, (2) denitrification, and (3) ammonia volatilization. In addition, N can be transformed to unavailable forms through immobilization and ammonium fixation. Detailed reviews of each of these processes can be found in Section 27.1 of *Handbook of Soil Sciences: Properties and Processes*, Hauck (1984), Scharf and Alley (1988), and Schepers and Raun (2008). However, some basic fundamental concepts will be discussed to facilitate the understanding of how application techniques may minimize the impact of these processes.

Leaching is simply the downward transport of NO_3^- (and NH_4^+ in low cation exchange capacity [CEC] soils) with water. Leaching occurs when water reaching the soil surface from precipitation and/or irrigation exceeds evaportranspiration (Nelson and Uhland, 1955). Leaching is a special concern in the more humid climate of the eastern United States, where precipitation exceeds evapotranspiration by 150–500 mm annually, or where irrigation is used. Soil water-holding capacity also plays an important role in determining the importance of leaching losses. Soil with a high water-holding capacity, such as silt loams, can accumulate large quantities of water before NO_3^- is transported below the root zone. Thus, soils with high water-holding capacities are much less prone to leaching losses than coarse textured, low water-holding capacity soils. Tile drainage, such as is commonly used in the midwest, can enhance leaching by providing a shallow outlet for drainage to surface water sources.

Denitrification is a microbial process by which soil bacteria (facultative anaerobes) utilize the O in NO_3^- and NO_x and N_2 gases are released into the soil atmosphere and are subsequently lost. A number of factors or conditions interact to impact the rate of denitrification. These include energy sources such as soil organic matter (SOM), crop residue, and animal manure, moisture/O_2 availability, temperature, and pH (Wijler and Delwhiche, 1954; Bailey and Beauchamp, 1973; Burford and Bremner, 1975; Rolston et al., 1978). Denitrification is the primary N loss process and is a major concern for finer textured poorly drained soils, or soils with high seasonal water tables.

Ammonia volatilization is the gaseous loss of free NH_3 to the atmosphere from soil and fertilizers. There are three general situations where NH_3 volatilization is a significant loss problem. When NH_4^+-based fertilizers such as ammonium sulfate are broadcast on the surface of high pH or alkaline soils and not incorporated, some NH_4 is converted to NH_3, which can volatilize to the atmosphere. This only occurs in significant amounts with $pH > 7$. When urea-based fertilizers are applied to soils, the naturally present urease enzyme hydrolyzes the urea to NH_3. The hydrolysis reaction generates enough OH^- ions to temporarily raise the pH of the soil around the urea fertilizer, which, in turn, causes NH_3 volatilization. Volatilization of N from urea is enhanced if urea is applied to a soil surface covered with crop residue or vegetation, as in a no-till corn field or a pasture or hayfield. Ammonia volatilization in cases one (volatalization from ammonium sulfate at high pH) and two (volatalization from urea) is exacerbated by the evaporation of water from the soil surface. The third situation deals with the addition of urea- or NH_4-based fertilizers to flooded rice paddies. A diurnal fluctuation in pH due to algal utilization of CO_2 results in a rapid rise in water pH reaching a maximum of 7–10 during midday. The high pH favors the conversion of NH_4 to NH_3, and its volatilization. In all cases, incorporation of urea- or NH_4-based fertilizers into the soil effectively stops volatilization (Ernst and

Massey, 1960). Unfortunately, incorporation is not always possible so alternative management strategies are sometimes utilized.

There are a number of alternative application strategies that can be used to reduce leaching loss of N from agricultural soils. Probably the most commonly used is timing of fertilizer applications to match periods of rapid utilization by crops. The use of sidedressing, delaying applications of N fertilizers until the crop is established and taking up N, or the use of split applications to avoid N leaching losses is common for crops such as corn, wheat, and cotton, particularly on sandy soils. An example of how time of N application has been used to enhance N use efficiency on coarse textured soils by reducing leaching losses can be found in Evanylo (1991).

The use of nitrification inhibitors and slow-release fertilizers is an alternative strategy to application timing as a means of reducing N loss from leaching. While the use of nitrification inhibitors has proven to be a successful means of reducing N loss on fine textured soils in the Eastern Corn Belt (Huber et al., 1982; Stehouwer and Johnson, 1990; Mann, 1995), they have shown mixed results in irrigated areas and the western Corn Belt (Maddux et al., 1985; Cerrato and Blackmer, 1990). A number of slow-release fertilizer products have been studied and have potential for reducing N loss from leaching in coarse textured soils.

Many of the same strategies that are used to avoid leaching losses can be used to avoid losses from denitrification, namely, timing of application, the use of slow-release fertilizers, and nitrifications inhibitors. However, one important difference among soils where these problems occur must be emphasized. Soils prone to high rates of leaching loss tend to be well drained, with low water-holding capacity. These soils dry rapidly after a leaching event and a farmer has a high probability of being able to drive across these fields in a short period of time. Many of these fields may be irrigated, which allows for the application of fertilizer N with irrigation water (fertigation). Soils prone to high rates of N loss through denitrification are not usually irrigated and tend to be poorly drained and slow to dry and trafficability is reduced. Thus, while sidedressing or split N applications are excellent tools to reduce N loss from denitrification, they entail risk to the grower who chooses to use them on poorly drained soils. This is a risk that additional N may not be applied in a timely manner.

Nitrification inhibitors are useful tools for reducing N loss in soils prone to denitrification. A number of studies in fine textured soils of the eastern Corn Belt have shown responses to the use of nitrification inhibitors with fall or spring preplant applied N (Frye et al., 1981; Huber et al., 1982; Stehouwer and Johnson, 1990).

Incorporation of the urea-N into the soil is the most effective strategy for reducing N loss from NH_3 volatilization (Ernst and Massey, 1960). While this is not always possible with no tillage systems, a number of tools have been developed to allow injection or banding of N fertilizers in these production systems. A number of studies have demonstrated that injection of N fertilizers into the soil and below the surface residue in corn and grain sorghum greatly enhances N use efficiency (Mengel et al., 1982; Lamond et al., 1991). Irrigation water can also be used to incorporate urea into the soil to reduce NH_3 volatilization (Mengel and Wilson, 1988).

Choosing a nonvolatile N fertilizer source is another alternative (Bandel et al., 1980; Fox and Hoffman, 1981). Ammonia volatilization losses from ammonium nitrate and ammonium sulfate are negligible compared to those from urea or urea-based products (Keller and Mengel, 1986).

Urease inhibitors are another management tool available to reduce NH_3 production until after the urea has been incorporated into the soil by rain or irrigation water. At present, one urease inhibitor, N-(n-buty1) thiophosphoric triamide (NBPT) is commercially available in the United States. Research has shown that urea impregnated with NBPT is a viable alternative to a nonvolatile N source such as ammonium nitrate. Coated urea products, such as polyurethane coated urea are also useful in reducing NH_3 volatilization.

14.2.2 Sulfur

Sulfur, like N is mobile in soils, yet its transformations and chemistry differ considerably from many of the reactions associated with N. Because S is mobile, many of the best management practices suggested for use of fertilizer N are also appropriate for the management of fertilizer S. Compared to N, S is utilized in relatively small amounts by actively growing crops. Various research projects have evaluated the effect of rate and management of S fertilizers on production and quality of a variety of crops. Specific management practices associated with optimum production vary with the crops that are grown.

The legumes, (alfalfa, clovers, soybeans) and canola remove relatively large amounts of S from the soil system while other crops (corn, small grains, forage grasses) remove smaller amounts. Options for placement of fertilizer S also vary with the intended crop.

Approximately 90% of the total S in soils is found in SOM, which can supply substantial amounts of S for crop production. Traditionally, research has shown that crops grown on fine textured soils with a high SOM do not respond to the application of fertilizer S. On the other hand the use of fertilizer S has produced dramatic increases in yield when applied to crops grown on sandy soils with a low SOM content (Section 11.4). Recent reductions in the atmospheric deposition of S may be altering this relationship however. Reports of S fertilizer responses appear becoming more widespread in recent years.

14.2.2.1 Sulfur Sources and Methods of Application

Application of S in a fertilizer program is most frequently associated with the production of alfalfa and other perennial legumes, corn, and small grains. As reported by Hoeft and Walsh (1975), alfalfa responds favorably to annual topdress applications of fertilizer S. Products containing elemental S (>90% S) or SO_4 form can be used for this method of application. The most common dry sources of SO_4-S are ammonium sulfate (24% S) and the double salt of potassium and magnesium sulfate (22% S). If K is needed in a fertilizer program for alfalfa, the double salt is a logical choice for topdress applications. Cogranulated ammonium phosphate products containing both elemental and SO_4 forms of S are also available and would be logical products to use if P were needed. Perennial grasses have also responded to annual topdress applications in situations where S is needed in a fertilizer program (Lamond et al., 1995). In general, annual applications of fertilizer S are suggested for all perennial crops whenever there is a need for S in the fertilizer program. Although legumes such as alfalfa generally remove substantial amounts of S from soils, soybeans have not responded consistently to S fertilization. Yield increases have been noted when fertilizer S is applied on very sandy soils (Matheny and Hunt, 1981) but not on fine textured soils (Brown et al., 1981; Sweeney and Grande, 1993). Sulfur needed for soybeans can be either broadcast before planting or applied in a band at planting. There is no research information to suggest that one method of application is superior.

When corn is grown on sandy soils where responses to S fertilization might be expected, the needed S can either be broadcast and incorporated before planting or applied as a starter fertilizer at planting (Hoeft et al., 1985; Kline et al., 1989). In general, rates of applied S are doubled if S fertilizer is broadcast and incorporated before planting rather than applied in a band near the seed at planting. There is general agreement that the use of split applications of N fertilizers is a best management practice for corn production on irrigated sandy soils. In evaluating the timing of S applications for sandy soils, however, a single application at planting has been as effective as split applications during the first half of the growing season (Rehm, 1993). When wheat and other small grains are considered, responses to S fertilization are not frequently reported. The majority of responses reported have been for the silt loam soils of the Pacific Northwest where broadcast applications have been popular (Ramig et al., 1975; Mahler and Maples, 1987). Responses have also been observed in wheat recently in the sandy, low SOM soils of the central and southern Great Plains.

When fluid fertilizers are used for production of annual crops, S can be supplied as ammonium thiosulfate (26% S) or potassium thiosulfate (17% S). Although these fluid materials are best suited for a band application at planting, caution should be used because germination can be impaired if ammonium thiosulfate is placed in contact with the seed. The safety of potassium thiosulfate when placed in contact with the seed has not been fully documented. Fluid fertilizer containing S can also be injected into irrigation water. This is not a preferred practice and should be limited to correcting identified S deficiencies.

14.2.2.2 Managing Sulfur to Prevent Losses

When present as SO_4-S, downward movement through soils can occur during either heavy rainfall or over-irrigation. The rate of downward movement of SO_4-S is, however, not as rapid as that of NO_3-N. Unless excessive amounts of irrigation water are applied to sandy soils, leaching of SO_4-S should be of minor concern. Because SO_4-S is not associated with problems of water quality, its loss by leaching is of economic concern, which can be minimized by applying fertilizer S, when needed, in a band close to the seed at planting.

14.2.3 Boron

This essential nutrient is also mobile in soils. Boron, which is found in soils as uncharged H_3BO_3, is not strongly sorbed by soil particles and is susceptible to leaching. Boron is classified as a micronutrient because small amounts are required for optimum crop production. The majority of the research conducted with B fertilization on agronomic crops has focused on the production of alfalfa (Brown, 1972), corn (Touchton and Boswell, 1975), small grains (Gupta et al., 1976), cotton, and peanut. Positive responses have not been consistent and are limited to unique soils and/or situations. As with N and S, annual applications of B are suggested often as broadcast preplant applications with annual crops or topdress applications or foliar applications on perennials, such as alfalfa.

Since B applied with the seed can cause germination problems and seedling injuries, especially for oilseeds, broadcast applications incorporated before planting are suggested for all annual crops and placement of B in contact with the seed should be avoided. Foliar application of B is routine for many crops, including cotton (Roberts et al., 2000) and peanut (Gascho and Davis, 1995).

14.2.4 Chloride

Chloride, like B, is mobile in soils behaving like NO_3-N in terms of leaching (Endelman et al., 1974). Although not studied intensively, responses to this nutrient have been documented for corn (Heckman, 1995), sorghum (Mengel et al., 2009), and small grain production in limited situations, and especially where applications of potassium chloride are not routinely made (Fixen et al., 1986a, 1986b; Engel et al., 1994). Because $C1^-$ is mobile, placement should have little effect on crop response to this nutrient. In contrast to the management of N, there is no indication that split applications would be superior to a single application at or before planting. Common sources for Cl^- include many soluble salts such as KCl, $CaCl_2$, $MgCl_2$, and NaCl, and NH_4Cl.

14.3 Application of Immobile Nutrients

Nutrients such as P, K, Ca, Mg, Zn, Cu, Fe, and Mn that are strongly sorbed by soil components are immobile and do not move easily through soils (Chapter 11). Unless there are substantial losses of soil from the landscape, there are usually no significant losses of immobile nutrients from the soil system other than through crop removal. There are situations however, where nutrients normally considered immobile can move through a soil profile. Two examples are leaching of K^+ and Mg^{2+} in soils with a low CEC and leaching of Mn^{2+} and Fe^{2+} through very sandy soils that are poorly drained.

Placement consideration: Fertilizer placement becomes a major management consideration in the overall management of immobile nutrients with the following options available.

14.3.1 Broadcasting

Broadcasting with or without soil incorporation is the most commonly used method of application for immobile nutrients. Throughout the United States, a very high percentage of P and K fertilizers are applied in this manner. With this placement option, especially when coupled with incorporation through tillage, essentially 100% of the top few cm of topsoil comes in contact with the applied fertilizer. Some of the advantages of broadcast applications are as follows: (1) it is fast and easy; (2) there are several opportunities for application that can reduce the workload at critical times during the year; (3) there is high probability that crop roots will come in contact with fertilized soil especially when incorporated with some form of tillage; and (4) when soils have low CEC, there are more potential sites for adsorption and subsequent retention of K and Mg. Some of the disadvantages of this placement option are as follows: (1) thorough mixing with tillage increases the probability of fixation and reduced availability; and (2) it is difficult to achieve a uniform application of low rates of fertilizers that supply the immobile nutrients.

14.3.2 Banding

Banding fertilizer is a mechanical technique in which some device is used to open a furrow or trench and the fertilizer is applied in a band below the soil surface. With most band applications, <1% of the top soil (15 cm) volume comes in contact with the fertilizers. The common band placement options include (1) placing a low rate of fertilizer in close proximity to the seed to enhance availability of nutrients to young plants (starter); (2) placing a low rate fertilizer in direct contact with the seed at planting (pop-up); and (3) concentrating fertilizer in the root zone to overcome fixation reactions and create zones of high fertility.

In North Carolina, Nelson et al. (1959) compared various band placement options to broadcast applications of P for corn and cotton production. Using low rates of P on P-responsive sites, they found that band placement enhanced early growth and resulted in better utilization of the applied P. There were, however, no differences in yield. Barber (1958) established a long-term study in Indiana and evaluated both the direct and residual responses to broadcast and band placement of P fertilizers. He found that band applications provided the greatest response when the P soil test was low, and that the advantage decreased as the soil test for P increased. This study also showed that the production of optimum corn yields required both broadcast and banded application of P fertilizer at low soil test P levels. Welch et al. (1966a, 1966b) found similar results with the application of both P and K in Illinois. With low fertilizer rates on responsive soils, band application resulted in more efficient utilization of immobile nutrients. However, highest yields were obtained by combining both band and broadcast application at higher rates. For soils with higher soil test values, response to fertilizer was smaller and placement had only limited effects on use efficiency and yield.

The primary advantages of banded application of immobile nutrients are as follows: (1) it creates a zone(s) of enhanced nutrient availability by minimizing contact between soil and fertilizer and (2) it is a simple and efficient method of applying small amounts of fertilizer. Disadvantages include (1) only a limited portion of the root system has high probability of coming in contact with the fertilizer; (2) damage to germination can occur when high rates of some fertilizer products are placed too close to the seed; and (3) the cost of equipment used in banding can be high.

With the continued expansion of no-till production systems, and introduction of strip-till systems, the use of deep banding to place fertilizer 15–20 cm deep below the row area has gained considerable interest. This practice avoids the concentration of nutrients near the soil surface, vertical nutrient stratification, which commonly occurs with broadcast applications when not accompanied with incorporation. In most deep banded situations, a tine or shank device is pulled through the soil doing some tillage with the fertilizer released at some depth below the surface. The depth of placement used varies from 10 to 30 cm. The volume of soil mixed with the fertilizer varies widely, but is still limited in most cases. In most cases, the crop is then planted into the tilled strip, directly over the fertilizer band. Work to date has shown only limited response to deep banding of P and K as compared to traditional starter fertilizer application or broadcasting similar rates of fertilizer in corn, soybean, and wheat production in the United States (Bordoli and Mallarino, 1998; Rehm and Lamb, 2004; Martin, 2009).

14.3.3 Strip Application

In strip application, a compromise alternative to band and broadcast applications, the fertilizer supplying the immobile nutrients is placed in a band on the soil surface that is then incorporated with some tillage. By varying the width of the surface band and the type of tillage used for incorporation, 5%–15% of the volume of the surface soil is mixed with the fertilizer. While the level of nutrient availability in the treated zone may be lower than with other banding options, a much larger portion of the root system can potentially come in contact with the fertilizer. This has enhanced uptake of immobile nutrients. Nelson et al. (1959) were the first to test this concept with corn and cotton and found that a combination of in-row or seed-placed phosphate with stripping resulted in the best utilization of P by young seedlings. In a 5 year study with P and K, Barber (1974) found that strip application produced significantly higher corn yields when compared to either banding or broadcasting equivalent rates.

14.3.4 Point Fertilization

In its simplest form, this consists of opening a hole in the soil with a stick or hoe, and placing a quantity of fertilizer into the soil near the crop to be fertilized. An early study conducted by

Coe (1926) in Iowa compared broadcast application to hill placement, or short bands of fertilizer 7.5–15 cm long and 3–4 cm wide at the same depth as the seed. He concluded that banding the fertilizer in the hills was equal or superior to broadcasting, if contact between fertilizer and seed was avoided, and suggested that the fertilizer should be placed to the side of and below the seed. When used at moderate rates, fertilizer could be placed in the hill with the seed, but at high rates, the fertilizer should be split with part applied in the hill and part broadcast.

The point system is commonly used today in the production of perennial shrub or tree crops. Holes are dug near the outer edge of the canopy (drip line) of trees and fertilizer placed in those holes. Tree stakes, solid blocks of fertilizer shaped to facilitate pushing them into the ground, can also be placed at points along the outer edge of the canopy. In many developing countries, a whole is dug near or in a hill of corn or sorghum and a small quantity of fertilizer is added to maximize nutrient utilization and to minimize competition from weeds. Large individual granules of fertilizer (super granules) have been developed specifically for this purpose. With a point application system, only a very small portion of the soil, generally much <1%, will come in contact with the fertilizer.

14.3.5 Application with Irrigation Water

Fluid fertilizer can be injected into irrigation water but in the case of immobile nutrients, particularly P, this method of application has limited use. Research evaluating this placement has been reviewed by Mikkelsen (1989).

14.3.6 Foliar Application

Although the majority of nutrients needed for growth and development of plants enter through the root system, beneficial effects of foliar fertilization have been reported. For example, Shafer and Reed (1986) studied the foliar absorption of 31 organic and inorganic compounds. Much of the research effort on foliar fertilization has been summarized by Alexander and Schroeder (1987).

14.4 Placement of P and K Fertilizers

The efficiency of use of the immobile nutrients has been the focus of field and greenhouse research projects for many years. In most cases, these studies have focused on the relative advantages or disadvantages of banding versus broadcasting of P and K fertilizers. The impact of the placement of immobile nutrients on uptake by crops and subsequent yield has been studied in both the laboratory and the field. Mechanistic models to explain some of the complex relationships that influence crop response to fertilizer placement were developed by Claassen and Barber (1976), Anghinoni and Barber (1980), and Barber and Cushman (1981).

Using 33 diverse soils to test the Barber–Cushman model, Kovar and Barber (1987, 1988, 1989) found that the concentration of P in the soil solution was the soil parameter that had the greatest effect on P uptake. When P fertilizer was placed in contact with small volumes of soil, banding produced the largest increase in soil solution P for each unit of applied fertilizer. However, the number of roots that can come in contact with the increased solution P is limited by banding. Since roots have a finite capacity to take up nutrients, it is possible that although banding increases the concentration of P in the fertilized zone, restricted root volume in contact with the high P zone could limit uptake. Using the Barber–Cushman model to predict the optimum volume of soil that should be fertilized, they found that the optimum volume varied substantially from a low of about 3% to a maximum of 15%–20%. Borkert and Barber (1985) found a very close relationship between predicted and measured P uptake by soybeans as a function of soil volume fertilized in a pot experiment. Barber (1995) concludes "Placement of P is most important in soils low in available P that sorb or fix large quantities of added P." Phosphorus placement also becomes more important as the rate of applied P decreases.

Although the quantity of P taken up by crops is only a fraction of that of K, fertilizer placement effects are similar for both. The use efficiency of banded K for corn is greater at low soil tests value for K with the difference between banded and broadcast diminishing as soil test K increases (Welch et al. 1966a, 1966b).

14.4.1 Field Comparison of Placement Options

Field comparisons between band and broadcast applications of P and K fertilizers show that banding, especially for P fertilizers, produced greater yield increases when equal rates were used for both. The results summarized by Welch et al. (1966a, 1966b) are typical of many of the results reported.

Working with several forage crops, Sheard (1980) concluded that the banded application of 30 kg P ha^{-1} increased seedling growth as much as fivefold regardless of the species and soil test for P. Working with oats grown on contrasting soils in a greenhouse, Sleight et al. (1984) concluded that the beneficial effects of banding are obtained mainly from placing all the immobile nutrients where contact by active roots is likely, rather than from an increase in availability that may be obtained from the decreased soil/fertilizer contact associated with banding.

Some research utilizing a wide range of application rates has shown that rate can influence the effect of placement. Barber (1958, 1959) has shown that at high fertilization rates, broadcast applications may give higher yields than band applications while Welch et al. (1966a, 1966b) have demonstrated that the optimum combination of banding and broadcasting can be a complex interaction of application rate and soil test level.

With P and K fertilizers, the most frequent placement is to the side of and below the seed at planting (starter fertilizer). In the midwest United States, starter fertilizer has consistently affected early season growth more than yield (Randall and Hoeft, 1988). Starter fertilizer application has consistently been more beneficial in no-till than conventional or clean till corn (Reeves and Touchton, 1986; Mengel, 1992). This benefit, in part, may be attributed to the fact that in no-till the soil is generally cooler in the spring and has a higher bulk density and thus early root growth is inhibited. Starter fertilizer effects are generally found to be greatest when soil temperatures are lowest (Kitcheson, 1968).

Earlier planting dates typically coincide with cooler soil temperature resulting, in slower root growth and metabolism. Although crops typically respond to starter fertilizer under these planting conditions, starter can also increase growth and grain yield on late planted corn, when soil temperatures were very warm (Farber and Fixen, 1986). This was also found to be true on Coastal Plain soils where inherent soil strength inhibits root growth and exploration (Karlen et al., 1984).

Much debate has focused on which nutrients in a starter fertilizer are responsible for the increased early season growth and subsequent increased grain yield, particularly under no-till. In Wisconsin, Motavalli et al. (1993) obtained a response to starters containing N and P in only 1 of the 3 years where manure had been applied. In Illinois, under conventional tillage on a soil with high residual P, an N and P starter fertilizer increased early season growth without increasing final plant dry weight or yield (Bullock et al., 1993). In Indiana, N was the most important nutrient in the starter solution on soils containing adequate levels of P and K (Mengel, 1992). In Alabama, Karim and Touchton (1983) found N primarily responsible for increased growth 14 days after emergence, but P appeared to have the greatest effect at 28–42 days. Wright (1985) found improved yields and earlier maturity in Florida when using a starter fertilizer containing N and P on a high P soil.

Occasionally, fertilizer will be broadcast at planting specifically to enhance early growth. With no-till corn at several locations, Mann (1995) showed that broadcast applications of 44 kg N ha^{-1} as urea-ammonium nitrate solution negated the response to N containing starter fertilizer in no-till corn. This broadcast application of fluid N, many times used as a carrier for burndown herbicides, has become a common practice in some areas of the midwest United States where large corn planters do not routinely have starter fertilizer attachments.

While N and P are the two nutrients most commonly used in starter fertilizers, a number of others are routinely applied including K, S, Mg, and Zn. Starter fertilizer bands provide a convenient delivery system for micronutrients in many crops. For example, Miner et al. (1986) obtained a response to Mn applied in a starter on an Atlantic Coastal Plain soil that was Mn deficient due to excessive liming. The low dissolution pH of common starter fertilizer materials such as MAP can enhance the availability of micronutrient metals such as Zn, Mn, Cu, and Fe. The addition of S compounds in starter fertilizer bands can further lower pH and provide an even greater increase in metal solubility.

In general, the band application of immobile nutrients has proven to be a cost effective method of fertilizer placement, particularly when soil tests values are in the low or very low range. Either band or broadcast applications have been effective when P or K soil test values are in the medium or high range. A combination of broadcast and band applications seem to be most valuable at lower soil test values.

The effect of placement of immobile nutrients has also been evaluated for small grain production. As with corn, band applications have been superior to broadcasting, particularly at lower rates of fertilizer (Sander et al., 1990). The distance between bands is not a concern when immobile nutrients are applied with a drill but could pose a problem when phosphate is applied in a subsurface band before planting small grains. Comparing spacing of 25, 30, and 50 cm, Maxwell et al. (1984) reported that spacing affected P uptake by young plants but had no effect on grain yield.

The residual effects of both broadcast and banded applications of phosphate are also important for small grain production. Following the harvest of spring wheat, Selles (1993) measured greater availability of P in soil samples collected directly over the band. When P was banded in soil having a range of soil test levels established by previous broadcast applications, Alessi and Power (1980) reported that the effects of the combination of band and residual effects of previous broadcast applications are additive.

Starter fertilizer usually involves the application of a small amount of fertilizer close to the seed at planting for the purpose of enhancing the early season growth of crops. In some cases, the starter fertilizer is placed directly in the seed furrow. This pop-up or in-furrow placement should only be used with crops, such as corn and small grains, which are relatively salt tolerant. There are a number of reports of injury to corn seedlings from fertilizer placed in direct contact with the seed (Coe, 1926; Allred and Ohlrogge, 1963; Creamer and Fox, 1980), sometimes resulting in stand reductions (Mengel, 1992; Gordon and Whitney, 2001). The amount of fertilizer that can be placed safely on or in contact with seed varies with crop, row spacing, soil moisture, properties of the fertilizer, and climate. For corn in Indiana, a maximum fertilizer rate of 5.6 kg N plus K ha^{-1} on silt loam or heavier soils is recommended for seed placement (Mengel, 1992). Similar recommendations can be found from many Land Grant Universities. The use of seed-placed fertilizer is a common practice for small grain production and no damage has been reported unless excessive, uneconomical fertilizer rates are used. An exception is urea containing fertilizers. Urea is particularly harmful to seed, due to the formation of free ammonia upon hydrolysis and it is not recommended for placement with the seed. Soybeans are much more sensitive to seed placed, pop-up fertilizer and this practice has severely reduced germination and subsequent yield (Clapp and Small, 1970; Hoeft et al., 1975). Consequently, seed placement of fertilizer is not recommended, regardless of rate, with soybeans.

14.4.2 Fertilizer Placement in Conservation Tillage Systems

The principles for placement of P and K fertilizers (Section 14.4.1) were developed primarily in production systems using a moldboard plow for primary tillage. Because of the emphasis on soil conservation, tillage systems are changing to minimize soil disturbance resulting in less incorporation of broadcast P and K fertilizers with a subsequent reduction in the redistribution of nutrients in crop residues (Larson, 1964).

The stratification of immobile nutrients in the conservation tillage production systems has been documented for a variety of soils (Cruz, 1982; Weil et al., 1988; Robbins and Voss, 1991; Rehm et al., 1995; Hollanda et al., 1998). In no-till or reduced till systems, extremely high levels of immobile nutrients can accumulate in the top 4 or 5 cm of soil because of lack of incorporation of fertilizers and nutrient cycling through the nutrient containing residues remaining on the soil surface. Interestingly, this stratification is not restricted to no-till and ridge-till but is also found with chisel plowing and shallow tillage systems (Cruz, 1982; Hollanda et al., 1998).

In addition to vertical stratification, horizontal stratification can also occur. Work in Indiana clearly shows that the nutrients can accumulate near the old row area when the crop row is consistently placed in the same area, a controlled traffic system. Thus, nutrient stratification can occur in both vertical and horizontal planes. Unless a substantial portion of the root system develops near the soil surface, in the zone of nutrient enrichment, and the root environment is conducive to nutrient uptake, stratification can reduce the amount of nutrients available for uptake by the actively growing crop. A number of studies have shown that roots do concentrate in fertilized zones of soil, particularly in areas of high P (Barber, 1995) and this can be near the soil surface, especially in more humid climates (Cruz, 1982; Kaspar et al., 1991; Hollanda et al., 1998). Thus, the effect of nutrient stratification near the soil surface could be either a negative or positive factor influencing nutrient uptake and is highly dependent on the environment. Schwab et al. (2006) used moldboard plowing to redistribute P in a number of highly stratified soils in Kansas; however, no increased yield was observed.

The advantages of band applications of starter fertilizer for corn in no-till planting systems have been discussed earlier. However, a number of studies have documented the importance of subsurface or deep banding for ridge-till and no-till planting in the northern Corn Belt (Rehm et al., 1995). However, the response to deep banding has not been universal as many studies have obtained no or mixed results in recent years. In one study, placement of P and K had a significant effect on corn yield when soil test levels for P and K were in the low range, but not when they were high. Highest yield responses generally resulted from a combination of subsurface band with a starter fertilizer (Rehm et al., 1988). In contrast, responses observed by Bordoli and Mallarino (1998) appeared more closely related to deficient rainfall in late spring and early summer than with soil test K. Often corn yield advantages to deep band placement of P and K were small (Bordoli and Mallarino, 1998; Mallarino and Murrell, 1998) and would rarely offset the higher application costs (Bordoli and Mallarino, 1998).

A similar range of response to placement of immobile nutrients has been found for other crops grown in conservation tillage production systems. Yields of grain sorghum, for example, were improved when P and K fertilizers were knifed in below the soil surface rather than broadcast on the surface (Sweeney, 1989). Yield increases from this knife placement were larger where soil test values for P and K were in the low rather than the medium range.

Nutrient stratification has not always been associated with reduced yields and response to alternative fertilizer placement techniques, however. In a long-term tillage in Indiana, moldboard plow, chisel plow, ridge-till, and no-till systems were included, in both a continuous corn monoculture and a corn/soybean rotation (Griffith et al., 1988). Extensive stratification of P, K, and acidity, both vertical and horizontal, was found within the surface 30 cm of soil in both rotations (Cruz, 1982; Hollanda et al., 1998). However, differences in corn yields among tillage systems were relatively small in the corn/soybean rotation (<4%), but rather large differences (<17%) were found in the continuous corn yields from 1980 to 1995, indicating that stratification of nutrients alone was not a significant yield limiting factor.

Yibirin et al. (1993) evaluated the effect of mulch on the response of corn to banded K and concluded that its benefits decreased as the amount of mulch on the soil surface increased. The mulch apparently increased soil moisture and reduced soil temperature near the soil surface, thereby increasing root development and subsequent K uptake from that zone.

In contrast to other crops, yield of winter wheat grown in no till planting systems in the Great Plains was not affected by P placement when soil test values for P were in the medium range (Halvorson and Havlin, 1992). The absence of a placement effect may be a consequence of the distribution of roots closer to the soil surface when compared to the corn and grain sorghum crops and a root environment more conducive to nutrient uptake during key periods of growth.

14.5 Calcium and Magnesium

Like P and K, these nutrients are relatively immobile in most agricultural soils. In contrast to K, however, uptake of Ca and Mg by crops is considerably less. As a result, the necessity for these nutrients in fertilizer program is diminished to special or localized situations. Therefore, research that has focused on the application of these two nutrients has not been extensive.

In most agricultural soils, Ca dominates the CEC, which satisfies the Ca requirements of most crops (Mortvedt and Cox, 1985). Under acid conditions, the Ca content of the soil decreases, while the H and A1 content increases. The addition of calcitic or dolomitic limestone to correct acidity problems is the primary means by which Ca is supplied to crops. With the exception of the peanut crop (Section 11.4); Ca deficiency is much more common in fruit and vegetable crops such as tomato, apple, and lettuce (Shear, 1975).

Like Ca, availability of Mg to plants decreases under acid soil conditions due to both a pH effect and loss of Mg through leaching from the root zone (Mortvedt and Cox, 1985). Increasing the pH of the soil, even with calcitic lime, can increase Mg availability (Christenson et al., 1973). Dolomitic limestone is the preferred Mg source in areas where it is available.

Applications of $MgSO_4$ or KMg $(SO_4)_2$ fertilizers are made on low Mg soils when dolomitic lime is not available. Soil tests are commonly used to estimate the need for Mg. In the midwest United States, Mg applications for most field crops are recommended when the exchangeable Mg levels are <50 mg kg^{-1} (Vitosh et al., 1995). General recommendations are to apply dolomitic lime if the soil is acid or to apply either 55 kg ha^{-1} soluble Mg, or 0.5 ton dolomitic lime ha^{-1} if the soil pH is adequate.

Since both Ca and Mg are not routinely added to fertilizer programs, the effectiveness of placement of these nutrients for agronomic crops has not been investigated. If lime is routinely used in a crop rotation, these nutrients should not generally be needed in a fertilizer program.

14.6 Micronutrients

The management of the remaining five micronutrients (Zn, Fe, Cu, and Mo), which are taken in small amounts by crop, will be discussed individually.

14.6.1 Zinc

A deficiency of Zn is most likely to occur on sandy soils formed from parent material low in Zn (Krauskopf, 1972), highly weathered tropical soils, highly calcareous soils, and organic soils (Schulte and Walsh, 1982). Overliming (Rehm and Penas, 1982), application of high rates of P (Murphy et al., 1981), and removal of surface soil by erosion, land leveling, and terracing (Frye et al., 1978; Grunes et al., 1961) are management practices that can enhance Zn deficiency.

Crops differ in their sensitivity to Zn deficiency. Corn, edible beans, and sorghum are highly sensitive; barley, sugar beet, soybean, and Sudan grass are moderately sensitive; and wheat, alfalfa, and most forage grasses are not sensitive to Zn deficiency (Laboski et al., 2006). While Zn deficiency can be corrected through either soil or foliar application, soil applications are more common for agronomic crops (Martens and Westerman, 1992) and foliar applications in the fruit and vegetable industry.

Relatively high rates of Zn, broadcast as $ZnSO_4 \cdot 7H_2O$, are commonly used to correct a Zn deficiency in agronomic crops. Other inorganic sources include ZnO and Zn frits, which are not readily available for crop uptake unless finely ground. Application rates vary depending on the demands of the crop being grown, soil properties that could affect Zn availability, and the native supply of Zn in the soil. Higher application rates are commonly needed on calcareous than noncalcareous soils (Wiese and Penas, 1979). Higher rates are also recommended for soils with low levels of extractable Zn (Leikam et al., 2003). Lower rates of Zn are normally applied in band than broadcast applications because of the reduced Zn-soil contact, which slows the reversion of Zn to less available forms and the lowered pH in the band when Zn is applied in combination with N or N–P fertilizers. In addition to inorganic sources, a number of organic Zn sources are used for band applications. These include Zn EDTA, Zn lignosulfate, Zn acetate, and Zn citrate. The chelated materials are commonly used for foliar applications.

14.6.2 Manganese

Manganese deficiencies in crops are found in high organic matter, slightly acidic, and poorly drained sandy soils. Soybeans, wheat, barley, and oats are highly sensitive to Mn deficiency while corn, sugar beets, alfalfa, and forage grasses are moderately sensitive (Vitosh et al., 1994). The availability of Mn is highly influenced by the total Mn content of the soil, drainage, oxidation state, SOM content, and pH. Soil pH is the most important soil property controlling the availability of Mn to plants, which decreases as pH increases. Over liming soil frequently produces Mn deficiencies (Gilbert et al., 1926; Blair and Prince, 1936; Sherman et al., 1942; Snider, 1943; Sanchez and Kamprath, 1959). The fact that Mn availability is influenced by so many factors has led to confusion concerning the effectiveness of various methods of Mn application. Positive yield responses from broadcast application of $MnSO_4$ or MnO, banding of Mn products at planting, banding of Mn in conjunction with an acid forming fertilizer, and foliar application of $MnSO_4 \cdot 7H_2O$ have been used successfully as a means of correcting Mn deficiencies in a number of crops (Gilbert and McLean, 1928; Evans and Purvis, 1948; Anderson and Carstens, 1973; Alley et al., 1978; Gettier et al., 1984; Mascagni and Cox, 1985a, 1985b).

Broadcast applications of Mn were found to be ineffective or less effective than banding as a means of correcting Mn deficiency across a broad range of soils (Harner, 1942; Steckel, 1946; Randall et al., 1975; Gupta, 1986; Eck, 1995). Mascagni and Cox (1985a) found that optimum yield of soybeans were obtained on Atlantic Coastal Plain soils by banding 3 kg Mn ha^{-1} compared to broadcasting 14 kg Mn ha^{-1}. Randall et al. (1975) found similar results in Wisconsin, although an additional foliar application was required for optimum yield when deficiencies were severe. Excellent results have also been obtained when Mn is band applied in conjunction with acid forming fertilizers (Mederski et al., 1960; Petrie and Jackson, 1984) or banding an acid forming fertilizer alone (Steckel et al., 1948).

Foliar applications of Mn have also been used to correct Mn deficiency. Although applications of <1.0–5.0 kg Mn ha^{-1} as $MnSO_4 \cdot 7H_2O$ are commonly recommended (Laboski et al., 2006; Vitosh et al., 1994), the number of applications required has not been unequivocally established. Eck (1995) found a single application of 1.1 kg Mn ha^{-1} adequate for correcting Mn deficiency in soybeans in Indiana while Mascagni and Cox (1985a, 1985b) found that up to three applications were required.

14.6.3 Iron

Like Mn, Fe availability to plants is controlled by a number of soil factors including pH, free $CaCO_3$ content, SOM content, and redox potential. The reader is referred to reviews by Moraghan and Mascagni (1992) and Lindsay (1992) for a detailed discussion of these factors. Iron deficiency (chlorosis) is common in soybeans and grain sorghum on calcareous soils (Martens and Westerman, 1992). Because of large differences in tolerance to Fe chlorosis among and within plant species, development of tolerant cultivars has been possible. Because broadcast applications of inorganic sources of Fe to the soil are not effective in controlling or correcting Fe chlorosis, foliar sprays using chelates such as iron ethylene diamine-N,N′-bis(2-hydroxyphenyl) acetic acid (FeEDDHA) are generally recommended in field crops but multiple applications may be required. Band applications of iron, the application of animal manure and seed treatments of iron have all been used successfully.

14.6.4 Copper

Copper deficiency occurs most commonly on organic soils, but can also occur where sandy soils are highly weathered, on mineral soils with a high SOM content, and on calcareous mineral soils (Martens and Westerman, 1992). Crops differ greatly in their susceptibility to Cu deficiency with wheat, oats, Sudan grass, and alfalfa being highly sensitive; barley, corn, and sugar beet moderately sensitive; and soybeans and most forage grasses tolerant to Cu deficiency (Vitosh et al., 1994).

While a number of fertilizers to supply Cu are available, $CuSO_4 \cdot 5H_2O$ is the most common fertilizer material used because of low cost and high water solubility. Karamanos et al. (1986) evaluated a number of Cu fertilizers and their effect on crop production. Copper oxide was generally ineffective in the year of application but residual effects alleviated Cu deficiency, while $CuSO_4 \cdot 5H_2O$ and chelated products were effective in the year of application. However, there was no residual effect from the application of chelated materials. Applications of animal manure or biosolids containing Cu will also correct deficiencies. Swine manure is an excellent source of Cu in many areas because of the high levels of Cu fed to growing pigs. Soil application is the preferred method of correcting Cu deficiency because of the good residual effects from Cu fertilization. Copper fertilizers are most commonly broadcast at or before planting but can also be banded. Common rates for soil application for field crops are 2.2–3.3 kg Cu ha^{-1} banded or 33–66 kg Cu ha^{-1} broadcast (Schulte and Kelling, 1999). Foliar applications can be used during the growing season to correct Cu deficiencies with chelated materials being favored.

14.6.5 Molybdenum

Molybdenum is required for NO_3 reduction reactions in plants and the symbiotic fixation of N by legumes. Deficiencies of this nutrient have been reported for a number of crops grown on acid soils in the Great Lakes and southern regions and coastal areas of the United States, as well as in New Zealand and Australia. Deficiencies are usually observed with the legume crops.

Molybdenum deficiencies can be corrected by liming, by soil or foliar application of Mo or with seed treatment. While Mo toxicity in plants is rare, high concentrations of Mo in forages may induce Cu deficiency in animals (Miltmore and Mason, 1971). Therefore, care must be exercised in making Mo applications. Application methods that utilize the lowest effective Mo rate, generally seed treatment, are preferred.

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15

Nutrient and Water Use Efficiency

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15.1 Introduction

Nutrient use efficiency (NUE) is an important aspect of plant nutrient management. While discussion of NUE of all essential elements is desirable, because over 10^8 ton of nitrogen (N) fertilizer is produced annually, 60% of which is used in cereals, we will focus on N as an example of a mobile nutrient from both production and environmental perspectives. Phosphorus (P) will represent immobile nutrients. The importance of spatial and temporal variability on improved nutrient and water use efficiency (WUE) will also be discussed. This will highlight the need for better mid-season management practices that can ultimately decrease nutrient loss from different causes. The approaches used to improve NUE of N and P can be applied to other plant nutrients. Recent technological advances that improve WUE will be further highlighted.

15.2 Nutrient Use Efficiency

NUE can be defined in several ways (Moll et al., 1982; Gourley et al., 1994; Baligar et al., 2001; Cassman et al., 2002; Mosier et al., 2004; Fixen, 2006; Roberts, 2008) and at times some definitions are misleading. Roberts (2008) and Cassman et al. (2003) discussed different types of NUE calculations and demonstrated each with data compiled from Asia and the United States. For example, fertilizer use efficiency of 21% or 100% can be calculated using the same input data but different computation methods (Roberts, 2008).

15.3 Bray's Nutrient Mobility Concept: What's Nutrient Efficiency Got to Do with It?

Bray's mobility concept (Bray, 1954) remains a benchmark paper for those truly interested in improving NUE of mobile and immobile nutrients. Further discussion will focus on how this has been applied in precision agriculture, and how Liebig's Law of the Minimum (van der Ploeg et al., 1999) continues to be relevant, especially for those scientists focused on yield prediction as a tool for improved nutrient management.

The term "mobility" in the field of soil fertility and plant relationships refers to the overall process whereby plant nutrient ions reach sorbing root surfaces (Bray, 1954). Bray (1954) proposed that the availability of soil nutrients for plant use might be strongly influenced by their level of mobility in the soil and classified nutrients as mobile or immobile. He also conjectured that the volume of soil from which roots sorbed nutrients also

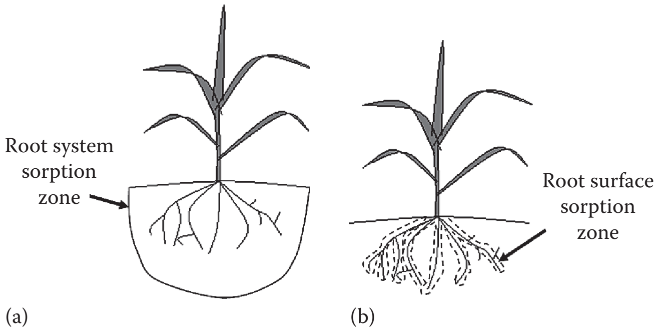

FIGURE 15.1 Root system sorption zone of mobile nutrients (a) and root surface sorption of immobile nutrients (b). (Adapted from Bray, R.H. 1954. A nutrient mobility concept of soil plant relationships. Soil Sci. 78:9–22.)

determined the soil fertility requirements of a plant. Bray's concept of soil nutrient mobility was plausible in the field of soil nutrient–plant relationships.

Bray identified two distinct types of soil sorption zones of plants. The first one is the large volume of soil occupied by the major part of the plant root system called the root system sorption zone (Figure 5.1a) from which mobile nutrients, like nitrate-N (NO_3^-–N), are taken up in large quantities by plants. This results in their "net" requirement being almost equal to the crop content at maturity. Mobile nutrients act as a "limiting nutrient" in the context of the "Law of the Minimum."

The second sorption zone is a relatively thin layer of soil adjacent to each root surface (root surface sorption zone, Figure 5.1b) from which immobile nutrients can be removed by the plant. From this zone, the roots effectively obtain relatively immobile nutrients like P. The sum of these small root surface sorption zones represents only a small part of the soil. Hence, plant roots access only a small fraction of the relatively immobile nutrients present. The amount of nutrient that must be present in the soil to support maximum crop yield is many times larger than the crop nutrient content (Cornforth, 1968). Variation in yield might affect the plant's ability to obtain the relatively immobile nutrients. However, the soil nutrient level needed to support a wide range of plant yield does not vary with yield, because the plant's ability to obtain the nutrient is proportional to its yield.

Bray's mobility concept was a combination of the Mitscherlich percent sufficiency concept (Bray, 1958; Johnson, 1991) and Liebig's Law of the Minimum. Bray showed that Liebig's Law of the Minimum concept applied for mobile nutrients like NO_3^-–N, and that Mitscherlich's percent sufficiency concept worked for immobile nutrients like P and potassium (K). In Liebig's theory of plant response, if all nutrients were adequate except one, then yield would increase in direct proportion to increasing the availability of the deficient nutrient. Bray's concept of how plants responded to soil nutrient availability could be represented as a straight-line response for a nutrient that is 100% mobile in the soil and a curvilinear response for relatively immobile nutrients.

When plants are grown close together, as in intensive agriculture, it becomes clear that the volume of soil from which plants extract mobile nutrients may overlap, while soil volumes supplying immobile nutrients do not. Thus, plants will compete among each other for mobile nutrients if they are closely spaced (Cornforth, 1968; Darrah et al., 2006). As cropping systems increase yield by planting more densely, there will be a direct increase in demand by the crop for the mobile nutrients and it will be necessary to add more of the mobile nutrient to eliminate the competition among plants.

On the other hand, there is no competition among plants for extracting immobile nutrients even when growing close together. This is because the plant root is extracting immobile nutrients from an extremely small volume of soil, often only the soil within a millimeter or two from the root surface (Cornforth, 1968; Eghball and Sander, 1989). As plants grow, they obtain additional supplies of an immobile nutrient by developing more roots that will explore new volumes of soil. If a soil is 100% sufficient in supplying an immobile nutrient for a dry-land crop yield of 3.8 ton ha^{-1} corn (*Zea mays* L.), then it will also be 100% sufficient if the field is irrigated and the yield is 11.3 ton ha^{-1} (Johnson, 1991). Sufficiency of immobile nutrients is independent of yield level. The most limiting of the mobile nutrients will determine the maximum possible yield (as in Liebig's "Law of the Minimum"). Deficiencies of immobile nutrients reduce the potential yield of a site or field (Raun et al., 1998), by a "percent sufficiency" factor, and identify the ultimate potential yield.

In contrast to what Bray documented, Sollins et al. (1988) argued that there are circumstances in which mobile nutrients become immobile. They indicated that variable-charge (v-c) and permanent-charge (p-c) soils differ in the dynamics of nutrient mobility and this dynamic is more complex in v-c than in p-c soils. For example, as the pH of v-c soils decreases, cation exchange capacity (CEC) decreases and anion exchange capacity (AEC) increases. If AEC exceeds CEC, cations such as ammonium (NH_4^+) and K considered as relatively less mobile will be more mobile than anions such as NO_3^-.

Putting into perspective the concept of mobility of nutrients and NUE, it is clear that access of plant roots to nutrients is restricted by the mobility of a nutrient. Nutrient mobility also determines the potential for loss from the nutrient cycle, which consequently affects NUE. The efficiency of nutrient acquisition by roots is dependent on nutrient mobility. Most of the cutting edge nondestructive yield prediction methods such as sensor-based nutrient management depend heavily on this concept.

15.4 Status of Nutrient Use Efficiency

Excessive use of nutrients can lead to environmental pollution and unnecessary fertilizer cost to producers (Cassman et al., 2003). Fertilizer use efficiency (NUE of applied inorganic N, P, and K fertilizers) was reported to be about 50% or lower for N, less than 10% for P, and close to 40% for K in the 1980s (Baligar and Bennett, 1986; Shaviv and Mikkelsen, 1993). Unfortunately, fertilizer use efficiencies have not increased substantially since then. Fertilizer N recovery efficiencies from researcher managed experiments for major grain crops have been reported to range from 46% to 65% (Roberts, 2008) where crops are grown under optimal management practices. For field managed plots, average N recovery did not surpass 30% and 40% under rainfed and irrigated conditions, respectively (Ladha et al., 2005). Globally, cereal N use efficiency is only 33% (Raun and Johnson, 1999; Davis et al., 2003). In corn and sorghum [*Sorghum bicolor* (L.) Moench], Muchow (1998) reported maximum N use efficiency (calculated as grain yield per unit N uptake) of 61 and 48 kg grain^{-1} kg^{-1} N absorbed, respectively.

Phosphorus use efficiency (PUE) is dependent on the method of placement and soil type (Peterson et al., 1981; Sander et al., 1990, 1991). Sander et al. (1990, 1991) reported that PUE averaged 8% when P was broadcast and incorporated and 16% when P was either knifed with anhydrous ammonia or applied with the seed in winter wheat (*Triticum aestivum* L.). Of course, this depends on residual soil P level (Peterson et al., 1981). Several studies (Giskin et al., 1972a, 1972b, 1972c; Bond et al., 2006) showed that P use efficiency of crops decreased with high level of soil residual P level. Residual P can be high due to high soil organic matter or high availability of P from previous applications attributed to low P fixing capacity of a soil. At both soil pH extremes where P could be precipitated, it is likely to see high crop P response, which may not translate to high PUE (Giskin et al., 1972a; Harrison and Adams, 1987).

It is worth mentioning the distinction between NUE and effectiveness. The highest NUE always occurs at the lower parts of the yield response curve, where fertilizer inputs are lowest. There must be a balance between optimal NUE and optimal crop productivity. In fact, in winter wheat, Wuest and Cassman (1992) and Sowers et al. (1994) demonstrated a decrease in N use efficiency with increased N fertilizer rates. Specifically, management systems designed for high protein harvest (Fowler, 2003) in cereals have resulted in low use efficiency since high protein harvest requires higher rates of fertilization than does grain production (Fowler et al., 1990). This suggests that effectiveness of fertilizers in increasing crop yields and optimizing farmer profitability should not be sacrificed for the sake of efficiency alone (Fixen, 2006; Roberts, 2008).

15.5 Causes of Low Nutrient Use Efficiency

One of the major causes of low NUE is the fact that the elemental cycle of most plant nutrients have sinks for loss; meaning one or more forms of a nutrient will leave the cycle through man-made or natural processes. For instance, N can be lost directly from the root system/rhizosphere area by denitrification, volatilization, and leaching or after plant uptake, by ammonia (NH_3) volatilization from plant tissues. Nitrogen losses via denitrification range from 10% to 70% of applied fertilizer N resulting in reduced efficiency (Avalakki et al., 1995; Jambert et al., 1997; Pu et al., 1999). According to Pu et al. (1999), denitrification is a major problem when large amounts of residue are left on the soil. Likewise, Hargrove and Kissel (1979) reported that in a laboratory study using urea, 13%–31% of the applied N was lost as NH_3. Hamid and Mahler (1994) and Mahler and Hamid (1994) reported 4.9%–37.8% loss of surface applied urea fertilizer to the atmosphere through NH_3 volatilization in Northern Idaho soils.

Nitrate leaching occurs more so in well-drained soils than poorly-drained soils and when precipitation/irrigation water exceeds water storage capacity (Stout et al., 2000). Leaching losses increase with increased fertilizer rate especially when the N application rate exceeds the amount required for optimum crop growth (Hauck and Tanji, 1982). Estimates of NO_3^- leaching from different soils and cropping systems ranged from 4 to 80 kg ha^{-1} year^{-1} (Hauck and Tanji, 1982; Dowdell et al., 1984; Jemison and Fox, 1994; Davis et al., 2003).

Ammonia losses to the atmosphere from plant tissues can contribute substantially to decreases in N use efficiency. Francis et al. (1993) reported that 52%–73% of the total unaccounted N was attributed to loss of NH_3 from plant tissue. The authors further showed that N loss from plants increased from 49 to 78 kg N ha^{-1} as N fertilizer rate increased from 50 to 150 kg N ha^{-1} (with 50 kg N ha^{-1} increment). Lees et al. (2000) estimated net plant N loss (determined as the difference of forage N uptake at flowering from total N in the grain and straw at maturity) of 3–42 kg N ha^{-1}. They also found that plant N loss was highest for the highest N rate. Similarly in wheat, Harper et al. (1987) reported that 21% of applied fertilizer N was lost as NH_3, of which 11.4% was from the soil and plant soon after fertilization, and 9.8% from leaves between anthesis and maturity.

Phosphorus fixation by Fe and Al oxides in acid soils and by Ca in alkaline soils and loss of P by erosion in all soils contribute to low PUE. PUE is improved by maintaining soil pH in the optimum range (Blair et al., 1971) to minimize these P fixation reactions. For P, the amount needed to satisfy the precipitation reactions in soils prone to P fixation is a major problem for increasing its use efficiency. It has been reported that only 20%–30% of the P fertilizer applied will be available for crop use and the percentage decreases the longer P is in contact with the soil before plant uptake can occur (Janssen et al., 1987). Soil inorganic P undergoes a very complex system of reactions and compound formation depending on soil pH, type and amount of soil minerals, amount of P in the soil, and several other factors (Sharpley and Sisak, 1997; Slaton et al., 2002). To improve PUE with a reduced input of fertilizer, it is necessary to first develop a strategy to reduce the amount of P fertilizer fixed (Jarvis and Bolland, 1991; Helyar, 1998). Phosphorus fertilizer placement could be critical due to the limited root surface sorption zone as demonstrated by Bray (1954).

15.6 Strategies to Improve Nutrient Use Efficiency

Improving NUE requires the development and adoption of integrated crop and nutrient management methods (Alcoz and Hons, 1993; Arregui and Quemada, 2008) in a sustainable way. Such methods include:

- Appropriate fertilizer application rate (Cochran et al., 1978; Campbell et al., 1993), timing (Bundy, 1986; Shanahan et al., 2004), placement methods (Black and Reitz, 1972; Mahler et al., 1994; Barbieri et al., 2008), and sources (Pan et al., 1984; Salsac et al., 1987; Huffman, 1989)

- Use of inhibitors for N fertilizer (Bremner and Douglas, 1973; Schlegel et al., 1986; Shaviv and Mikkelsen, 1993)
- Foliar applications (Dion et al., 1949; Harder et al., 1982; Mosali et al., 2006; Girma et al., 2007b)
- Cover crops and crop rotations (Raun and Johnson, 1999; Schomberg et al., 2006)
- Tissue and sensor based nutrient management methods (Blackmer et al., 1994; Stone et al., 1996; Raun et al., 2002)
- Use of traditional crop breeding and biotechnology (Kamprath et al., 1982; Bufogle et al., 1997; Kanampiu et al., 1997)

The different methods that must be integrated to maximize NUE are discussed in detail next.

15.6.1 Adjusting Rate, Timing, Placement, and Source of Fertilizer Application to Increase Nutrient Use Efficiency

15.6.1.1 Rate of Nutrient Application

Fertilizer application rate plays an important role in NUE but should be combined with other methods designed to improve NUE. In response to efficiency, environmental, and economic concerns, researchers made significant progress in improving optimum fertilizer rates. Fertilizer application rate evolved from less accurate blanket "recommendation domain," based to site-specific variable rate application (VRA) systems today. Regardless, all fertilizer rates are determined from measurements taken from soil, crop or both.

Worldwide statistical-based nutrient response curves have been widely used for establishing optimum fertilizer rate. Linear or quadratic nutrient response curves and their variants such as liner-plateau, linear-linear, and quadratic-plateau have been fitted to yield data (Neeteson and Wadman, 1987; Cerrato and Blackmer, 1990; Bullock and Bullock, 1994; Girma et al., 2007c). Other nutrient response curve models were also tested but found to be unreliable. For example, for potato (*Solanum tuberosum* L.), Bélanger et al. (2000) compared quadratic, exponential, and square root response models and found that both exponential and square root models were weaker than the quadratic model in determining economically optimum N rate in Atlantic Canada. This approach is affected by temporal and spatial variability (Bullock and Bullock, 1994; Makowski et al., 2001; Liang et al., 2008), varies with change in price of both fertilizer and economic yield (Babcock, 1992), and would not help for in-season fertilization decision. Mechanistic models were also evaluated for predicting N fertilizer requirements (Geist et al., 1970) but were not adopted simply because they were based on too many theoretical assumptions and were not user friendly.

Soil test-based N and P recommendation has been employed in many parts of the United States and elsewhere. For N, total soil N or soil test NO_3^- (Soltanpour et al., 1989) were widely used. Two types of soil test NO_3^-, namely, preplant soil NO_3^-–N test (PPNT) and presidedress soil NO_3^-–N test (PSNT) were employed for drier (Bundy and Meisinger, 1994) and humid areas (Meisinger et al., 1992; Andraski and Bundy, 2002) of corn growing states, respectively. However, PSNT was criticized for lack of correlation with actual crop response and nutrient demand, and resulted in large variability (Andraski and Bundy, 2002). More importantly, the method failed to identify non-N responsive soils when applied to different soils. To overcome these problems, the Illinois soil N test (ISNT) method was developed. This method employs diffusion analytical procedure to measure alkali-hydrolyzable amino sugar, which was highly and inversely correlated with fertilizer N response of corn yield (Khan et al., 2001; Mulvaney et al., 2001). This method has been reported to work in several corn growing states (Khan et al., 2001; Mulvaney et al., 2005; Williams et al., 2007). Yet, in other areas, the method did not improve the prediction of fertilizer N requirements (Barker et al., 2006; Marriott and Wander, 2006; Laboski et al., 2008; Osterhaus et al., 2008) or found to be as good as total soil N (Spargo et al., 2009).

Since the last 20 years, the focus of nutrient rate determination shifted to in-season application rate methods aided by destructive and nondestructive plant tissue analysis (Turner and Jund, 1991; Scharf et al., 2006; Hawkins et al., 2007; Zhang et al., 2008), soil test, and remote sensing (Solie et al., 1996; Raun et al., 2001; Barker and Sawyer, 2010). The latter will be discussed in detail under "sensor-based variable rate nutrient management." Soil test methods such as ISNT discussed above are useful but less convenient for producers as the methods require laboratory testing that might take time. Soil testing remains one of the most accurate methods for determining nutrient requirements, however. At the heart of each in-season N rate decision tool is a level of spatial and temporal accuracy of measurements that aide in increasing NUE of crops. Nondestructive in-season tissue analysis methods used instruments such as chlorophyll meters. Chlorophyll meter readings were correlated with soil NO_3^- or plant tissue N concentration to estimate nutrient needs of crops thereby improving NUE. Both success (Schepers et al., 1992; Hussain et al., 2000) and lack of success (Piekkielek and Fox, 1992; Bavec and Bavec, 2001) with this method were reported. In paddy rice (*Oryza sativa* L.) in the Philippines, greater agronomic efficiency of N fertilizer was obtained with the use of chlorophyll meter sufficiency indices compared with preset timing schemes commonly practiced (Hussain et al., 2000). A study conducted in corn growing areas of north-central United States concluded that chlorophyll meter readings were strongly related ($R^2 = 0.53–0.79$) with economical optimum N rate (EONR) and suggested the method can be applied with reasonable accuracy in wide range of environments (Scharf et al., 2006). Unlike these reports, Piekkielek and Fox (1992) and Bavec and Bavec (2001) showed that the relationship between chlorophyll meter reading and grain yield was weak and growth stage dependent. According to Waskom et al. (1996) portable chlorophyll meter was effective for determining N need but must be accompanied by soil test to determine actual N. Schepers et al. (1992) and Hawkins et al. (2007) used relative chlorophyll meter values to establish N rates in corn.

15.6.1.2 Time of Nutrient Application

The time of application of fertilizer has a significant role in achieving increased NUE for both mobile and immobile nutrients. Providing a mobile nutrient, like N, just prior to a plant's rapid uptake phase increases NUE. The growth stages at which rapid N uptake occurs are well defined for cereals. For winter wheat, Girma et al. (2011) reported that more than 61% of the maximum total N accumulated at later stages of growth could be accounted for by Zadoks 30 (pseudostem) growth stage. Therefore, in wheat, Zadoks 30–32 (2 nodes detectable) was the best time to topdress N to increase use efficiency and optimize final yield (Raun and Johnson, 1999; Girma et al., 2011).

In corn, a steady increase in dry matter (DM) and N accumulation was observed between the V4 (4th leaf collar fully unfolded) and V8 (8th leaf collar fully unfolded) corn growth stages, after which a fast increase in N uptake was measured between V8 and R2 (blister) (Shanahan et al., 2004). Walsh (2006) recommended topdressing/sidedressing N at or before the V10 (10th leaf collar fully unfolded) growth stage to supply the growing corn with adequate N when it is required in the greatest quantities. Similarly, Ma et al. (1999) reported that only a limited amount (20%) of the total plant N was accumulated by V6 (6th leaf collar fully unfolded), and most of the N (60%) was accumulated between V6 and R1 (silking stage). Three studies, Licht and Al-Kaisi (2005), Freeman et al. (2007a), and Girma et al. (2011), reported that greater than half of the total N was accumulated between V8 and VT (tasseling) in corn. These research findings suggest that topdressing or splitting N between V8 and VT growth stages in corn can increase N use efficiency.

Applying a small portion of the N at planting and the remainder of the N just before the rapid growth phase in the spring (a split application) was effective for increasing N use efficiency of wheat (Alcoz and Hons, 1993; Mahler et al., 1994). López-Bellido et al. (2006) reported that in spring wheat, preplant application of 150 kg N ha^{-1} resulted in 13% recovery of N fertilizer, while recovery was as high as 42% when applied at the beginning of stem elongation. For winter cereal crops grown in dry climates, splitting N applications may not increase N use efficiency because N losses are minimal (Arregui and Quemada, 2008). Similarly, in Minnesota, Jokela and Randall (1997) found that nonirrigated corn did not respond to timing of fertilizer N application.

Synchronizing time of N fertilizer with peak crop demand reduces N loss to the environment as well as improves crop yield and N use efficiency (Randall et al., 1997; Karlen et al., 1998). Preplant application of fertilizer especially several months before planting does not seem rational in relation to fertilizer dynamics in the soil. From an environmental health perspective, sidedressing N midseason can significantly reduce NO_3^- leaching into ground water (Bundy, 1986). Also, sidedress N reduces the N that can move by runoff into watersheds impairing quality of surface waters (Allen, 2002). According to Sanchez and Blackmer (1988), 50%–60% of fall-applied N fertilizer is lost from the soil through several of the pathways that lead to N loss from the soil. A winter wheat study conducted to assess the effect of split N applications on N use efficiency using ^{15}N showed that splitting recovered 7%–16% more fertilizer than fall applications (Sowers et al., 1994).

15.6.1.3 Placement of Nutrient

For both mobile and immobile nutrients, the method of application and placement significantly influences the efficiency of the nutrient (Mahler et al., 1994; Barbieri et al., 2008; Kapoor et al., 2008). Generally, subsurface or surface band applications of solid urea and urea ammonium nitrate (UAN) liquid fertilizers in high residue cropping systems can be used to avoid N tie-up in crop residues or N loss by NH_3 volatilization (Mahler et al., 1994). Incorporation of broadcast urea, UAN, and manure into the soil where tillage is practiced can assist in avoiding NH_3 volatilization and run-off losses (Campbell et al., 1993; Freeman et al., 2007b). Banding P is the best strategy instead of broadcasting (Bordoli and Mallarino, 1998).

Tillage and crop residue greatly influence NUE, especially for N. In a no-tillage production system, grain yield improved by 32% when 60 kg N ha^{-1} was banded 8–10 cm below the seed row and 15% when banded between the rows compared to surface broadcast urea (Rao and Dao, 1996). Adaptation of subsurface placement of N fertilizer for no-till winter wheat has the potential to significantly improve N availability to plants and thereby improving N use efficiency and reducing environmental and economic risks (Rao and Dao, 1996). Similarly, crop residue can increase or decrease NUE based on the quantity of residue retained, and type of crop and tillage (Eagle et al., 2000; Kravchenko and Thelen, 2007). In rice, Eagle et al. (2000) reported that straw retention lowered N use efficiency compared with straw removal or burning. Of course, in a no-till setting with total or partial residue retention, fertilizer N use efficiency could be low due to immobilization (Black and Reitz, 1972).

For immobile nutrients the application of all fertilizer at planting is a common practice. NUE can be improved by placing the fertilizer close to the root sorption zone in bands (Sanchez et al., 1991; Jacobsen et al., 1997). PUE is lower when broadcast, compared to banded, because of greater fixation of soluble fertilizer P when broadcast or due to low soil test P (Bell and Black, 1970). For sweet corn (Sanchez et al., 1991) in a low soil test P soils, the relative P fertilizer efficiency was greater than 3:1 for band to broadcast ratio. However, some reports refute the advantage of banding over broadcast P (Borges and Mallarino, 2001, 2003). Borges and Mallarino (2001) found little difference between broadcast and band P on yield and P uptake of corn. In a soybean study, band P had higher P uptake than broadcast for only 3 out of 14 sites (Borges and Mallarino, 2003).

15.6.1.4 Source of Nutrients

Another factor that has a considerable effect on NUE is the nutrient source or form used, which determines the risk of loss and availability of the nutrient. It has been generally agreed that maintaining N in the immobile NH_4^+ form, rather than in the mobile NO_3^- form, will increase N use efficiency. Tsai et al. (1992) suggested that the use of NH_4^+–N fertilizers can reduce leaching and denitrification losses and allow extended availability for late season uptake. Uptake was increased by 35% when N was supplied as NH_4^+ based N sources (Wang and Below, 1992). The N use efficiency of NH_4^+–N based N fertilization has been tied to reduced energy cost for assimilation in an actively growing corn crop compared with NO_3^-–N (Pan et al., 1984; Salsac et al., 1987; Huffman, 1989; Randall and Mulla, 2001). While source of fertilizer plays a crucial role in improving NUE, it should be used as a component of a sustainable nutrient management plan and not as a sole strategy as presented in most reports.

15.6.2 Urease and Nitrification Inhibitors for N Fertilizers

A strategy for slowing down urea hydrolysis and nitrification has been recommended as a method to improve N use efficiency of urea containing fertilizers (Shaviv and Mikkelsen, 1993). Urease inhibitors were reported to delay urea hydrolysis in soils and reduce gaseous loss of urea N as NH_3 (Bremner and Douglas, 1973; Schlegel et al., 1986). Bremner and Douglas (1973) showed that gaseous loss of urea N as NH_3 from urea applied on sandy soil incubated at 20°C for 14 days was reduced from 61% to 0.3% by addition of 2,5-dimethyl-p benzoquinone inhibitor. Likewise, using ammonium lignosulfonate as a urease inhibitor, NH_3 loss from surface-applied urea was reduced up to 85% of the amount lost with plain urea (Al-Kanani et al., 1994).

Nitrification inhibitors (NIs) slow the soil conversion of the less mobile NH_4^+–N form to the leachable NO_3^-–N form. These compounds are especially useful on coarse textured soils where leaching is likely and on fine textured soils where excess water can cause denitrification losses of NO_3^-–N (Shi and Norton, 2000). The use of an NI can be helpful with both preplant and sidedressed N applications. In spring wheat in the northern Great Plains, Goos and Johnson (1999) reported that the apparent N uptake efficiency of grain and straw was 50%–56% with the use of nitrapyrin and ammonium thiosulfate as NI compared to 24% for the control. In corn, Walters and Malzer (1990) reported a significant improvement in N fertilizer use efficiency with NI with the application of 90 kg N ha^{-1} as urea. The use of inhibitors as effective tools for reducing N loss requires certain conditions to be fulfilled. However, the use of inhibitors by themselves may not always translate to improved efficiency. For example, a study in winter wheat and barley (*Hordeum vulgare* L.) revealed that use of fertilizer with an NI (3,4-dimethylpyrazole phosphate, DMPP) did not improve N use efficiency (Arregui and Quemada, 2008).

15.6.3 Foliar Fertilization for Improving Nutrient Use Efficiency

It has been more than six decades since scientists proved the benefits of foliar uptake of nutrients through leaves and other green tissue parts using radioactive and isotopically tagged nutrients (Dion et al., 1949). Studies showed foliar fertilization is more efficient and reduces potential environmental impact than soil fertilization (Harder et al., 1982; Mosali et al., 2006; Girma et al., 2007b). Dixon (2003) reported that foliar-applied nutrients can be 4–30 times more effective than soil applied nutrients. This high efficiency is related to increased enzymatic activities in plant cells with foliar application. Others reported that foliar fertilization was 8–10 times more efficient than root uptake (Wittwer et al., 1963). Foliar applications have provided a highly efficient alternative for supplying nutrients to plants, particularly micronutrients, which are needed in small quantities and are subject to reduced availability when soil applied.

At present, foliar N in corn is not a viable option because of the higher temperatures present throughout the growing season. Liquid N fertilizer sources, such as UAN, adhere to the leaf, when applied directly to the leaves. This coupled with the high temperature of the summer can result in leaf burn (Lohry, 2001). However, many new products are currently available that can be applied foliar, and that have limited leaf burn including urea triazone and urea formaldehyde solutions. In corn, the alternative to foliar application to increase NUE is a traditional sidedress application.

Foliar P fertilization can increase P use efficiency in comparison to soil-applied P because P fixation in the soil is avoided. Averaged over 6 site years, Mosali et al. (2006) reported 80% PUE in winter wheat when applied foliarly at 2 kg P ha^{-1} between stem elongation and heading. Similarly, in rainfed corn, Girma et al. (2006) reported 35% more PUE than soil applications of P when 2 kg P ha^{-1} was applied to the foliage at the V8 growth stage of corn. With new fertilizer formulations and application technologies, the use of foliar fertilization to increase NUE tool may increase in the future.

15.6.4 Use of Cover Crops and Crop Rotation

The use of winter cover crops can help prevent NO_3^-–N leaching in high rainfall areas. Cover crops absorb residual nutrients and return them to the soil for the following crop. Guillard et al. (1995) found that N use efficiency was increased in corn-rye (*Secale cereale* M. Bieb) and oat (*Avena sativa* L.)-tyfon (*Brassica* spp.) cropping systems with the application of 112 kg N ha^{-1}. Pikul et al. (2005) reported N use efficiency of 49, 67, and 70 kg corn grain yield kg^{-1} N for continuous corn, corn-soybean (*Glycine max* L. (Merr.)), and corn-soybean-wheat-alfalfa (*Medicago sativa* L.) rotation systems, respectively, with application of moderate N (N rate predicted to achieve 5.3 Mg ha^{-1} corn yield). In irrigated or high-rainfall production regions, soybean-corn rotations have high N use efficiency and can reduce the amount of residual N available for leaching when compared to continuous corn (Huang et al., 1996). Unfortunately, rotations are not easily adopted by farmers who have become accustomed to monoculture production systems since a new crop often requires purchase of additional equipment and learning to integrate new cultural practices. In irrigated agriculture, the use of high N rates as a substitute for more N use efficient rotation systems (corn-soybean) must be weighed against the increased potential for NO_3^-–N loss (Anderson et al., 1997).

Nitrogen use efficiency for wheat following legumes was 32% and 21% greater than that of wheat following fallow and continuous wheat, respectively (Badaruddin and Meyer, 1994). In another study, Badaruddin and Meyer (1990) found that N use efficiency of wheat was greater following alfalfa or hairy vetch (*Vicia villosa* Roth.) green manure crops than fallow. Average corn N use efficiency derived from soybean and alfalfa residue for the whole plant and grain was 43% and 30%, respectively, (Hesterman et al., 1987). Wheat-corn-fallow production systems are promoted instead of wheat-fallow where only 420 mm precipitation is received per year (Kolberg et al., 1996). The more intensive systems (growing more crops in a given period of time), require greater fertilizer N inputs but are higher in total yield and economically advantageous (Kolberg et al., 1996; Anderson, 2005). More intensive dryland cropping systems lead to increased WUE and better maintained soil quality (Halvorson and Reule, 1994; Anderson, 2005). Alternative dryland systems proposed include spring barley, corn, and winter wheat grown in rotation with adequate N fertilization instead of continuous winter wheat-fallow (Halvorson and Reule, 1994).

15.6.5 Sensor-Based Variable Rate Nutrient Management

Sensor-based variable rate nutrient management employs spectral radiance in red and near-infrared (NIR) regions of the electromagnetic spectrum as a tool to detect the health of an actively growing plant (Lukina et al., 2001). This tool was introduced in nutrient management for cereals particularly in wheat and corn in the mid-1990s. Blackmer et al. (1994) found strong correlation between reflected radiation and relative grain yield at later vegetative growth stages. Stone et al. (1996) demonstrated that an index developed from red and NIR reflectance could be an excellent predictor of total N uptake of a crop at early stages of winter wheat growth. This technique allowed the accurate prediction of fertilizer N requirement, thus improving crop N use efficiency (Raun et al., 2002; Teal et al., 2006).

The technologies that emerged from measurement of normalized difference vegetation index (NDVI), the Greenseeker® (Trimble Navigation Limited, Sunnyvale, CA), and Crop Circle™ (Holland Scientific, Inc., Lincoln, NE) sensors have a functional algorithm developed from measurements based on yield potential and responsiveness of the crop to N fertilization (Johnson and Raun, 2003; Mullen et al., 2003; Solari et al., 2008; Sripada et al., 2008). The specific growth stages at which N uptake and N use efficiency increased have been identified. Accordingly, for winter wheat, the stage between Zadoks 30 and 32 is recommended. In corn, sensor measurements were well correlated with predicted yield when measurements were obtained between V8 and V12 (Teal et al., 2006; Freeman et al., 2007a). Using this technology, N use efficiency in wheat was increased by 10%–20% and savings in fertilizer was about $\$20\,\mathrm{ha}^{-1}$ (Raun et al., 2009). Research in China found that a sensor-based system for determining optimum N rate for winter wheat resulted in 61% N use efficiency, surpassing the soil test-based and farmer methods by about 10% and 48%, respectively (Li et al., 2009).

The variable rate sensor-based system can be used to manage both temporal and spatial variations, which directly influence NUE. It was reported, following extensive soil sampling, optical sensor measurements of plants, and geostatistical analysis, that the spatial scale of N availability in wheat was about $1\,\mathrm{m}^2$ (Raun et al., 1998, 2002; Chung et al., 2008). When N management decisions are made on areas of $<1\,\mathrm{m}^2$, the variability that is present beyond that resolution can be detected using optical sensors (Solie et al., 1996; Stone et al., 1996). Simple methods that can manage temporal variability and increase N use efficiency have also been evaluated. The N-rich strip or N reference strip is becoming instrumental since it is simple and can be used with or without a sensor (Girma et al., 2007a; Raun et al., 2008).

Although the use of optical sensors for improving N use efficiency has shown great promise, and there is no doubt about its contribution to improving N use efficiency, the need to develop empirical algorithms for use on different soil types, crop management systems, and climates has limited its adoption (Samborski et al., 2009).

15.6.6 Biotechnology and Variety Selection for Improving NUE

NUE is under genetic and physiological influence of a given crop and is modified by the environment (Baligar et al., 2001). Both biotech and conventional breeding can be used to identify or modify plant traits that can contribute to improvement in NUE. However, there is not much data available in this regard. The early study of N use efficiency was facilitated by identifying individual components that elucidated both uptake and utilization efficiency (Bruetsch and Estes, 1976; Moll et al., 1982). Differences among corn hybrids for N use efficiency are largely due to variation in the utilization of accumulated N before anthesis, especially under low N supply (Moll et al., 1982; Eghball and Maranville, 1991).

Wheat varieties with a high harvest index (grain produced divided by the total dry biomass) and low forage yield have low plant N loss and increased N use efficiency (Kanampiu et al., 1997). Furthermore, N assimilation after anthesis is needed to achieve high wheat yields (Cox et al., 1985) and high N use efficiency. Higher N use efficiency has also been observed in rice varieties with high harvest index (Bufogle et al., 1997). Work by Karrou and Maranville (1993) suggested that wheat varieties that produce more seedling DM with greater N accumulation are not necessarily the ones that use N more efficiently. Genetic selection is often conducted with high fertilizer N input in order to eliminate N as a variable; however, this can mask efficiency differences among genotypes to accumulate and utilize N to produce grain (Kamprath et al., 1982). This is consistent with Earl and Ausubel (1983), noting that high yielding varieties of corn, wheat, and rice released during the Green Revolution were selected to respond to high N inputs. Consequently, continued efforts are needed where plant selection is accomplished under low N, often not considered to be a priority by plant breeders and uncharacteristic of agricultural experiment stations.

15.7 Water Use Efficiency

Water is the single most important regional and global resource management challenge. In rainfed regions, water runoff, surface evaporation, low soil water holding capacity, and random precipitation are major problems constraining WUE among many factors (Kemper, 1993; Hatfield et al., 2001; Condon et al., 2002). Despite its wide use, the word WUE does not reflect losses for which intervention strategies are being developed. Some prefer to use the term "biomass to water ratio (BWR)" to reflect the biomass produced per unit of water used by a crop (Morison et al., 2008). But more importantly, the variation in units used to describe WUE when the term is used in association with different spatial and temporal scales as well as type of yield (biological or economic) calls for careful interpretation of WUE values.

Generally, WUE is the ratio between the amount of water that is used for an intended purpose and the total amount of water input within a spatial domain of interest (Guerra et al., 1998). In this review, we are interested in WUE as it is related to crop biomass production (total DM or economic yield). In view of this, the definition given by Viets (1962) and later modified by Tanner and Jury (1976) is appropriate. Accordingly, WUE is defined as

$$\text{WUE} = \frac{\text{Dry matter or economic crop yield}}{\text{Water used to produce the economic yield}} \tag{15.1}$$

The unit for this computation is usually kg m^{-3}.

According to World Water Assessment Program (WWAP, 2009), agricultural use accounts for 70% of freshwater withdrawals from different sources. It has been quantified that the process of photosynthesis takes 400–2000 L (average of 1600 L) of evapotranspiration (ET) to produce 1 kg of wheat crop (CAWMA, 2007) depending on climatic conditions and the genetics of crop cultivars. Given this, crop WUE has doubled in the last 40 years (CAWMA, 2007).

It is anticipated that agricultural WUE will improve from 52% in 2003 to 66% in 2050 (FAO, 2008). During the same period, crop water consumption will increase by 64%–83%; almost doubling from its current annual consumption of 7130 km^3 (CAWMA, 2007) due to changing weather conditions characterized by unpredictable growing seasons (FAO, 2006). However, population growth, urban expansion, bioenergy, and other economic developments are decreasing the quantity of water available for agricultural use (Müller et al., 2008). Quality of water due to salinization of ground and surface water remains a major problem. In the United States, about 87.5% of crop production is rainfed and this constitutes about 32% of arable land (World Bank, 2007). This clearly demonstrates the need to improve the WUE of this large sector. Current and future water use strategy in crop production must account for these emerging global undertakings (Angus and van Herwaarden, 2001).

15.8 Critical Factors Affecting Water Use Efficiency by Crops

There is not a single factor that controls WUE of crops. It is rather many factors that interactively and simultaneously influence water use. Soil physical and chemical properties (e.g., texture, structure, water holding capacity, salinity, and organic matter), soil management practices (e.g., tillage, residue management, planting date, etc.,), crop and crop genetics, as well as climate are among the factors that determine WUE. However, climate is likely the most influential variable. Seasonal distribution and amount of rainfall, wind, and light intensity are some of the climatic factors that limit WUE by crops. In wheat in Argentina, Abbate et al. (2004) found that WUE was greater when water was limited due to shortage of rainfall than when adequate. They hypothesized that this could be due to stomatal closure when vapor pressure deficit was highest. Genetics (crops and varieties of crops) is another factor that determines the amount of water that can be efficiently used for production of DM. Although crops adapt to specific growing conditions in a given agroecology, some are better users of available water and more efficient in translating it to DM than others (Richards, 2004; Bessembinder et al., 2005; Mueller et al., 2005). For example, Bessembinder et al. (2005) attributed the WUE of crops to their morphology (e.g., leaf angle), anatomy (e.g., leaf cuticle composition), phonology (e.g., growing degree days), and physiology (e.g., protein and fat concentration in different plant parts).

15.9 Strategies to Improve Water Use Efficiency

It is intuitive that it is not possible to manipulate climate but what is possible is to manipulate soil conditions and crop and variety traits to better cope with changes in climate and increased WUE. Therefore, strategies to increase WUE by crops should employ soil and crop management practices and genetic improvements of crops and crop varieties. The intervention needed varies for irrigated and dryland systems. For example, in an irrigated setting, WUE can be achieved by increasing the output per unit of water, reducing losses of water to unusable sinks, reducing water degradation, and reallocating water to higher priority uses (Howell, 2001). In dryland systems, soil and crop management practices can be used to conserve and increase WUE.

15.9.1 Tillage and Residue Management

Conservation tillage, crop residue management, and mulch play a pivotal role in water conservation and improving crop water use. In addition to its benefit for building soil organic matter and reducing soil erosion, no-till has emerged as a useful practice for conserving soil moisture when practiced with appropriate cultural practices (Machado et al., 2008). Such cultural practices include row spacing and seeding rate. For example, WUE was increased by 6% with row spacing of 9 cm compared to 36 cm in no-till wheat (Tompkins et al., 1991). These authors investigated the interaction of seeding rate and row spacing on WUE under no-till and found 9 kg grain yield cm^{-1} higher WUE with seeding rate of 140 kg ha^{-1} and 9 cm row spacing compared to 35 kg ha^{-1} seeding rate and 36 cm row spacing. In corn, no-till increased WUE by 0.96 kg grain yield ha^{-1} mm^{-1} (Norwood, 2000) suggesting reduced irrigation water demand. Reduced tillage and residue retention improved infiltration and enhanced storage of precipitation that in turn increased DM produced per unit of water.

Mulching can improve WUE through its effect on increased water storage of a soil and reduction of evaporation from surface soil. Ji and Unger (2001) found that mulched soils had 10% higher water storage capacity than bare soils when 5 mm simulated rain was applied with ET of 6 mm day^{-1}. They further showed that 2 Mg ha^{-1} mulch is needed to maintain 10% or more water storage with simulated rain water of 10 mm and ET of 12 mm day^{-1}. Similarly, in north China, Zhang et al. (2005) reported that over 12 seasons, mulching improved WUE of corn by 8%–10%. The timing of irrigation also increased WUE for corn and winter wheat in this environment, where 73% of 480 mm precipitation falls during the winter wheat cropping season (Zhang et al., 2005). Beginning irrigation at jointing stage of winter wheat was preferable as prejointing irrigation of all tillers including infertile tillers could reduce crop WUE. However, in a more arid Arizona environment (277 mm seasonal precipitation), irrigation may not be delayed until jointing without yield penalty (Jama and Ottman, 1993). Burning of stubble had no effect on WUE of double cropped wheat and soybean (Daniels and Scott, 1991). In Washington, the interaction of crop residue and tillage showed that soil-stored water level was the same when conventional or no-till were practiced following undisturbed standing wheat residue in the winter (Kennedy and Schillinger, 2006). In a grain sorghum study, Unger and Jones (1981) reported that averaged over 3 years, 8 ton ha^{-1} straw mulch increased WUE by 19% compared with no mulch. These findings suggest that surface residue retention and the amount of soil disturbance are key factors in water conservation.

15.9.2 Crop Rotations Cover Crops and Fallow System

In many parts of the United States, double cropping and other alternatives to continuous corn have been evaluated. Crop-fallow systems have been effective in conserving precipitation water for subsequent crops, in a way, contributing to higher WUE. However, the newer cropping systems can also be as good as or even better than the crop-fallow system in conserving water. In the central Great Plains, Tanaka et al. (2005) reported that wheat WUE was improved 18%–56% with the inclusion of broadleaf crops in a grass-based system. However, in a study designed to identify the most water efficient production system in Texas, Jones and Popham (1997) found that soil water content at planting of the next crop in no-till was increased by 29 mm in a continuous wheat cropping system compared with stubble mulch.

In a study that compared forage and grain systems, Nielsen et al. (2005) found that WUE (kg DM ha^{-1} mm^{-1}) was highest for pea followed by millet and lowest for corn. However, corn grain WUE was second to millet while pea had the lowest grain WUE. In Mediterranean environment, rotation involving barley and wheat with rapeseed (*Brassica napus* L.) and vetch (*Vicia sativa* L.) increased biomass WUE by 7 kg DM mm^{-1} ha^{-1} compared with monoculture barley (Álvaro-Fuentes et al., 2009). Also, precipitation use efficiency is greater for corn grown in rotation when compared to continuous corn (Varvel, 1994).

15.9.3 Crop/Variety/Hybrid Selection

Crop improvement through conventional breeding coupled with appropriate agronomic management has significantly contributed to increased water use by crops and crop varieties under both rainfed and irrigation systems (Richards et al., 2002). However, much work is needed to identify specific physiological and agronomic traits that can significantly control water utilization in crops.

It is a well-established fact that crops vary in their ability to extract soil water and reduce transpiration allowing them to survive in dry environments. In dryland areas of the Great Plains, sorghum and sunflower (*Helianthus annuus* L.) removed 19 mm more water from subsurface soil compared with corn and soybean (Norwood, 1999).

Howell et al. (1998) did not find a difference in grain and DM WUE of two corn hybrids (short and full season) but seasonal ET was reduced with a short season hybrid by 129 mm compared with a full season hybrid. In grain sorghum, Unger (1991) found that hybrids significantly differ in WUE. He concluded that highest yielding cultivar had the highest WUE.

Molecular biology could play a significant role in untangling this in the future. In Australia, isotope discrimination techniques had helped in identifying varieties with high transpiration efficiency (Richards, 2004). Other traits that could be sources of WUE improvement include increased root length (Proffitt et al., 1985; Payne, 2000; Ehdaie et al., 2003) and leaf canopy architecture (Schakel and Hall, 1979; Osborne et al., 1998). Under drought conditions, leaflets of cowpeas [*Vigna unguiculata* (L.) Walp] positioned paraheliotropically (becoming more vertical) in the afternoon to reduce transpiration (Schakel and Hall, 1979). Recently, in rice, researchers identified a mutant that reduced the indole-3-acetic acid (IAA) at the lamina joint, shoot base, and nodes enhancing drought tolerance (Zhang et al., 2009).

15.9.4 Soil Physical and Chemical Properties

Soil physical and chemical properties play a crucial role in soil water conservation and WUE in crops. For example, two decades ago, Stout et al. (1988) studied the effect of N supply and soil physical properties on WUE in tall fescue (*Festuca arundinacea* Schreb.). They found that when rainfall was adequate and evenly distributed over the crop growing season, N supply controlled WUE. In contrast, when rainfall was erratic, water holding capacity controlled WUE.

Soil organic matter is a critical component of soil that "conditions" soil, improving water infiltration rate and water-holding capacity. It serves as a reservoir of water and supplies them to crops when needed, indirectly increasing WUE of crops. With a high level of organic matter soil tilth is improved, and aggregate size tends to be large and bulk density low (Allison, 1973; Six et al., 1998).

Water use by crops is influenced by salt level in irrigation water and the soil itself. In arid climates, irrigation water usually contains a large quantity of salts that over time accumulate in the soil and limit water availability in the root zone. Various strategies have been proposed to address this problem (Ma et al., 2008). Recently variable rate precision irrigation has been investigated. Al-Kufaishi et al. (2006) assessed the feasibility of applying spatially variable irrigation under a center pivot system and found that the loss of water was higher for the uniform application scenarios than that for the VRA scenarios for applications of 20 and 30 mm. Under precision irrigation, water and associated solute movement are designed to vary spatially within the root zone and salt accumulation or leaching of nutrients that influence water balance in the root zone (Mmolawa and Or, 2000; Raine et al., 2007). Many current irrigation systems are open and have relatively low efficiencies of water application (Hagin and Lowengart, 1995, 1999). In addition, water quality relative to management practices has been largely ignored.

15.9.5 Modeling as a Tool for Improving Water Use Efficiency

Since the 1980s, crop production decision support models have been advocated. Models, particularly mechanistic models that strive to simulate water and nutrient transport, and DM production as a function of management and climatic factors are becoming beneficial. Through continued research today there are several models that can be used in decision making regarding water use in specific environments and cropping systems. For example, the AquaCrop model developed by FAO was found to be a good predictor of crop productivity, water requirement, and WUE under water-limiting conditions for maize in different environments (Heng et al., 2009). The SORKAM model predicted an increase in sorghum WUE in the southern High Plains of Texas when a later maturing sorghum cultivar was planted in mid-May at irrigation levels of 3.75 and 5.0 mm day^{-1} (Baumhardt et al., 2007).

15.9.6 Nutrient and Water Interactions

It is well documented that WUE cannot be achieved without addressing fertility constraints. WUE has been constrained by the supply of both N and P. Selles et al. (1992) suggested that soil testing laboratories should modify their fertilizer recommendations according to different levels of available water, rather than the traditional dry, normal, and wet classes used. Halvorson et al. (2004) demonstrated that precipitation use efficiency of winter wheat increased with N rate reaching peak after 56 kg N ha^{-1}. Optimal leaf N concentration promoted higher WUE (Heitholt et al., 1991), and low leaf N led to poor WUE in N limited and drought stressed wheat in the southern Great Plains. NUE and WUE were improved when nutrients were placed beneath the surface of the soil at a depth of 15 cm in turfgrass (Murphy and Zaurov, 1994). Inefficient water use can result if N fertilizer is applied during the vegetative phase since it increases transpiration loss by reducing the soluble carbohydrate reserves available for translocation to grain (Angus and van Herwaarden, 2001).

Likewise, increasing soil P availability resulted in increased water use in both water-stressed and non-water-stressed conditions (Payne et al., 1992; Brück et al., 2000). Another study showed that N and P fertilization was related to WUE (Payne et al., 1995). Generally, in non-water-limiting conditions, WUE was improved with higher rates of both nutrients.

15.10 Conclusions

Nutrient and WUE have a lot to do with energy production and use in agriculture. Improving both NUE and WUE can contribute to efficient and productive agricultural system. Improving NUE requires the use of best management practices in a sustainable way and managing both spatial and temporal variability. There is no single factor that can serve as a silver bullet to improve NUE. Variable rate nutrient management systems, foliar fertilization, and biotechnology are some of the new best management practices (BMPs) that may result in huge improvement in N and other NUE in crops. WUE like NUE will always play a pivotal role in agricultural production. But unlike NUE, WUE, especially in dryland environments is a function of temporal or climatic variability. In the vast majority of rainfed production environments, weather changes dramatically from year to year. As a result, WUE changes from year to year and in these environments it is highly unpredictable. Thus, management systems that can buffer or dampen the effects or impact of water play an increasingly important role.

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16

Nutrient Interactions in Soil Fertility and Plant Nutrition

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Nutrients interact during numerous biological, physical, or chemical processes along the soil–root–shoot continuum such that the level of one nutrient alters the availability, uptake, or plant response to another nutrient (Zhang et al., 2006). Given the very nature of ionic balance in plant nutrition and the ionic interactions in soil chemistry and fertility, virtually all soil–plant processes involve nutrient interactions, making a comprehensive review a boundless task. This review will focus on key concepts and provide examples to illustrate them. The availability and flow of any given nutrient through the continuum are constantly influenced by the activity and form of other nutrients, and the nature and rate of these interactions are sufficiently complex that they are sometimes beyond our current ability to measure and quantify their impacts. The nutrient interactions that are most often recognized and documented have for the most part been observed in soil fertility experiments that characterize crop nutrient uptake and growth response to one or more nutrients added to the system. Thus, this review will focus on the examples of nutrient and other elemental (e.g., heavy metals) interactions documented in the soil fertility literature, with subsequent discussion of plausible chemical and biological mechanisms of those same interactions along the soil–root–shoot continuum as described in the soil chemistry, soil microbiology, and plant nutrition literature.

Nutrient interactions will be delineated as to their specificity, specific or primary interactions being those in which two nutrients directly react in a chemical or biological process. Nonspecific or secondary nutrient interactions occur when the uptake of one nutrient is indirectly affected by the activity of another nutrient through a series of intermediate plant processes.

16.1 Historical Perspective

Our modern concepts of plant nutrient essentiality and their interactions coevolved with the development of modern chemical principles, as described in reviews by Browne (1944), Ihde (1964), Tisdale et al. (1985), Wild (1988), Black (1993), and Epstein and Bloom (2005). The Law of the Minimum (LM), popularized by Justus von Liebig in the mid-nineteenth century but first succinctly stated by Carl Sprengel, recognized a basic fundamental nature of interactions among these essential nutrients. Sprengel conducted experiments on mineral salts extracted from organic matter and soils and published a list of mineral elements essential for plant growth (van der Ploeg et al., 1999). Furthermore, he wrote in 1828 "…when a plant needs 12 substances to develop, it will not grow if any one of these is missing, and it will grow poorly, when one of these is not available in a sufficiently large amount as required by the nature of the plant."

Liebig subsequently stated in 1855 as part of his LM that "by the deficiency or absence of one necessary constituent, all the others being present, the soil is rendered barren for all crops to the life of which that constituent is indispensible" (Wild, 1988). These pioneers of plant nutrition research established a basic concept of nutrient codependence.

The LM and the concept of plant response to a most limiting nutrient was later modeled by Mitscherlich when he published his "Law of Diminishing Returns" (Mitscherlich, 1909). The model depicts a plant yield (y) exponential response to increasing nutrient availability from fertilizer and soil (x + b) that rises to a plateau (the shape of the rise defined by constant [c] as it nears a maximum potential yield [A]). As Black (1993) summarized, while many other empirical polynomial models have been used to represent yield response to nutrient availability, the

Mitscherlich model is unique in that the variables represent biological concepts. The nonfertilizer soil nutrient supply (b), the nutrient use efficiency represented by the rise to the maximum (c), and the maximum yield (A) are all influenced by the status of other growth factors, including other essential nutrients (Figure 16.1).

Comparative analysis of two-way nutrient responses provides insight into the nature of interactions between those nutrients. Historically, there has been considerable debate whether "c" is constant for a given species response to a specific nutrient (N1). Mitscherlich contended that "c" was in fact inherently constant, but van der Pauw (1952) statistically reanalyzed Mitscherlich's data and found a sizable variation in "c" values. Furthermore, subsequent experiments provide compelling evidence and argument for variable "c" values for a given nutrient, notably when a second nutrient (N2) interacts to change the true plant availability of the nutrient N1 or N2 competes with N1 for uptake (see Black, 1993). In retrospect, these two possibilities of having constant or variable "c" need not be mutually exclusive. It is plausible that the alteration of factors "c," "A," or both depends on the nature of the interaction between growth factors and whether they are primary or secondary in the nature.

For the purpose of this review, primary nutrient interactions are defined as specific chemical and biochemical interactions between two nutrients occurring in the bulk soil, soil solution, rhizosphere, or root cell surface that affects the activity, bioavailability, or ion transport of one or both nutrients. In contrast, secondary nutrient interactions are defined as nonspecific nutrient interactions mediated by general physiological responses such as compensatory root growth (Drew and Saker, 1975) to one nutrient that indirectly influence the uptake and assimilation of a second nutrient. Examples of primary and secondary nutrient interactions are listed in Table 16.1.

The constancy or variability of "A" is dependent on whether the second nutrient N2 is supplied in limiting or nonlimiting levels. Obviously, if N2 is nonyield limiting at all levels, then maximum yield "A" will remain unaffected by variation in N2. The constancy or variability of "c" is dependent on the specific or nonspecific nutrient interactions that can alter the nutrient use efficiency of N1. For example, changes in "c" in response to the level of N2 may reflect specific primary chemical interactions affecting nutrient activities that represent their immediate bioavailability as reflected by the ionic activity of the absorbed nutrient form, and how changes would affect nutrient uptake and utilization. Nonspecific secondary interactions, mediated through indirect effects on general plant growth, root, or rhizosphere bacterial activities, might also alter "c" by changing the plant's overall demand for N1 or by changing the N1 nutrient uptake or utilization efficiency. Four hypothetical scenarios, portrayed in Figure 16.1 with modeled yield responses to nutrient 1 (N1) as affected by nutrient 2 (N2) levels, are represented by Mitscherlich equations.

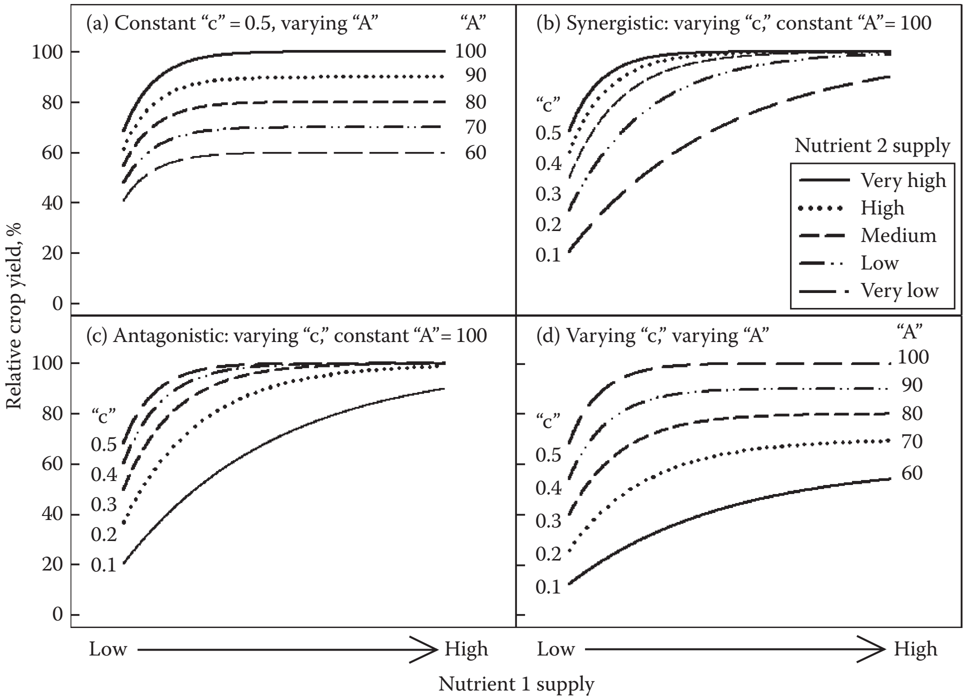

FIGURE 16.1 Depiction of four interaction scenarios between two nutrients (1 and 2) as modeled with the Mitscherlich equation. The legend in Panel (b) indicates level of nutrient 2 supply for all panels. Values for "A" and "c" for each level of nutrient 2 are included in each panel where appropriate. Panel (a): The classic "Mitscherlich" response depicting proportional yield increases in response to incremental levels of nutrients 1 and 2. Panel (b): Increasing levels of nutrient 2 increase the utilization efficiency of nutrient 1 (synergistic). Panel (c): Increasing levels of nutrient 2 decrease the utilization efficiency of nutrient 1 (antagonistic). Panel d: The classic "Law of the Minimum" response, where nutrient 1 is initially most limiting thus nutrient 2 has no effect on crop yield; but with increasing levels of nutrient 1, nutrient 2 has increasing impact on crop yield.

TABLE 16.1 Examples of Primary (Specific) and Secondary (Nonspecific) Nutrient Interactions

Primary	Secondary
Cation–anion exchange	Increased yield potential and nutrient demand
Cation–anion precipitation	Altered nutrient uptake or utilization efficiency
Ion pairing	Modification of rhizosphere chemistry, biology
Ion uptake synergism or antagonism	Modification of soil solution ionic strength

Scenario 1 (Figure 16.1a) depicts Mitscherlich's concept of variable "A" and constant "c." This scenario occurs when N1 and N2 are both initially present at yield-limiting levels, responding simultaneously to incremental increases in both nutrients. Since N2 does not affect N1 bioavailability or uptake and utilization efficiencies, the shape of the rise ("c") to "A" is unaffected. This type of response is referred to as the "Mitscherlich (MTS) response" (Zhang et al., 2007).

Scenario 2 (Figure 16.1b) depicts a specific interaction affecting "c" but not "A" in which N2 levels specifically (e.g., ion uptake synergism) or nonspecifically (e.g., increased root proliferation) increase "c" by improving the N1 uptake or utilization efficiency, while "A" remains unchanged.

Scenario 3 (Figure 16.1c) represents the opposite situation of scenario 2, whereby an increased level of nutrient N2 inhibits the uptake of nutrient N1 due to specific ion antagonism at the N1 influx porter or due to specific or nonspecific reduction in N1 bioavailability. Nutrient 2 is present in nonyield limiting supply, so there is no change in "A," but more N1 supply is required to reach "A" due to the antagonism of N2, which reduces the N1 nutrient use efficiency and shifts "c" to a lower value.

Scenario 4 (Figure 16.1d) depicts situations in which both N1 and N2 are initially limiting, but if N1 is the most limiting nutrient, then the crop will primarily respond to N1 until it reaches a level in which it is no longer the most limiting nutrient and then the crop will respond to increases in N2. The "A" increases with N2 levels, but "c" values decrease. This represents the spirit of Liebig's LM, and has thus been referred to as the LM type response (Zhang et al., 2007) or the Liebig response.

Interactions amongst growth promoting factors were described by Bloom et al. (1985), in the context of a "Multiple Limitation Hypothesis (MLH)," to occur in resource allocation terms, whereby plants invest resources into homeostatic mechanisms for acquiring the most growth limiting resources it needs, at the expense of acquiring less limiting resources. Zhang et al. (2007) applied MLH to nutrient interactions by surmising that a response to a nutrient should increase with increased availability of other nutrients, similar to the MTS response, provided they are not toxic. Rubio et al. (2003) examined 60 responses of *Lemna minor* to combinations of N, P, K, and Mg, and found 23 LM responses, 17 MLH responses, and 20 undefined responses. Type of response was highly dependent on the nutrient pairings. In contrast, Wood et al. (1972) examined 69 experiments and found that 49 matched the LM response and only eight were classified as MTS. These researchers assumed that either of the two theories—MLH or MTS—(Figure 16.1a) or LM (Figure 16.1d) would represent the nature of all nutrient responses and nutrient interactions. However, in both studies there were undefined responses that could not be characterized by either theory. In retrospect, these undefined responses could be rationalized with scenarios 2 (Figure 16.1b) or 3 (Figure 16.1c) in which N1 use efficiencies are altered by specific or nonspecific nutrient interactions.

16.2 Conceptual and Quantitative Frameworks of Nutrient Interaction Mechanisms

Fried and Broeshart (1967) published a conceptual framework depicting nutrient flow through the soil solid–soil solution–root–shoot continuum. They contended root uptake would be the rate-limiting step at equilibrium, a supposition soon after contested (Nye, 1977) and largely disproven with numerous subsequent experiments (see Barber, 1995; Silberbush, 1996) demonstrating that nutrient delivery from and through the soil to the plant root is often rate limiting for sparingly soluble nutrients. A corollary to that concept would be that nutrient interactions affecting availability and mobility are most often important for relatively immobile nutrients such as P and K, whereas nutrient interactions affecting the root uptake and utilization processes are most often important for mobile nutrients such as Ca and NO_3-N.

The essential contribution of the Fried–Broeshart model was that it provided the conceptual basis for subsequent quantitative soil-nutrient uptake models (Baldwin and Nye, 1974; Claassen and Barber, 1976; Rengel, 1993; Barber, 1995; Silberbush, 1996; Claassen and Steingrobe, 1999; Hopmans and Bristow, 2002). These models attempt to simulate soil processes affecting nutrient solubility and movement to plant roots, integrated with simulations of root growth and nutrient uptake. For the sake of simplicity, most models are single nutrient based and have not included modules to account for the multitude of nutrient interactions that can occur along the continuum. Exceptions include a multi-ion uptake model published by Bouldin (1989) that stresses the importance of maintenance of electrical neutrality through balanced cation–anion movement through the system. Relative ratios of cations [K/(Ca + Mg)] on exchange sites and in solution were incorporated into the model. Koenig and Pan (1996b) demonstrated how single ion nutrient uptake models can be used to assess potential effects of soil nutrient interactions on crop nutrient uptake, by modeling cation exchange-driven shifts of quantity/intensity (Q/I) relationships that affect the bioavailability of the absorbed nutrient. Calcium exchange for NH_4 increases solution NH_4 concentrations, a limiting factor in NH_4 diffusion rates to and into plant roots (Table 16.2). This proposed mechanism for Ca-stimulated NH_4 uptake was suggested as an alternative hypothesis to prior theories on membrane level Ca-NH_4 synergies (Fenn et al., 1987; Fenn and Taylor, 1990).

TABLE 16.2 Soil Supply Parameters Used in the Simulation of NH_4 Uptake and Predicted NH_4 Uptake over a 10 d Period for Rice (*Oryza sativa* L.) and Corn (*Zea mays* L.) as Influenced by Ca

					10 Day N Uptake	
	C_s	C_l	B	D_e	Rice	Corn
Condition	mg N kg^{-1}	mg N L^{-1}	L kg^{-1}	cm^2 s^{-1}	mg N	
−Ca	100	12	5.44	2.10×10^{-7}	415	27
+Ca	100	32	1.79	6.39×10^{-7}	506	29

Source: Koenig, R.T., and W.L. Pan. 1996b. The influence of calcium on ammonium quantity-intensity relationships and ammonium availability in soil. Soil Sci. Soc. Am. J. 60:492–497.

C_s, exchangeable NH_4; C_l, solution NH_4; b, soil buffer capacity for NH_4; D_e, effective diffusion coefficient for NH_4.

16.2.1 Nutrient Interactions at the Soil Solid–Solution Interface

Primary nutrient interactions occur at the different stages of the soil–plant continuum (Table 16.1), generally related to cation–cation, anion–anion, or cation–anion chemical interactions.

Chemical and biological interactions affecting nutrient equilibria and flow rates between the labile fraction of the soil solid and solution phases influence solution ionic activities and transport to plant roots (Degryse et al., 2009). Cation availability is reduced by adsorption to negatively charged organic matter, oxides, and clay minerals. Precipitation with reactive anions also reduces soluble cation availability. Sorption into the labile pool occurs within hours following addition, whereas slower "fixation" reactions reduce the labile pool. Fixation of K and NH_4 into interlayers of 2:1 layer silicates or "fixation" of metal cations during diffusion into hydroxides or precipitates, ion adsorption, and biological immobilization all remove nutrients from the soil solution, potentially reducing their immediate availability to the plant root. Conversely, depending on the reversibility of these reactions and the solubility of the compounds, those nutrients are held in reserve, preventing nutrient leaching. Upon depletion from the soil solution or with a shift in chemistry or biology affecting the equilibria, these nutrients can be solubilized later in the growing season. For example, the availability of soluble anions promotes cation desorption, solubility, and mobility (Sakuri and Huang, 1996).

The importance of ion composition of the soil solution including cationic micronutrients (McGeorge, 1924), elemental toxicities (Magistad, 1925), and P forms (Pierre and Parker, 1927) as a critical factor in plant response to soil conditions has been recognized for more than a century (Adams, 1974; Sparks, 1984). Solid phase–solution phase solubility, as affected by solubility products of salts and by ion exchange reactions were first characterized with solubility diagrams proposed by Aslyng (1954). Ion activities, as affected by nutrient interactions, were calculated according to the Debye–Huckel equation and related to root growth (Howard and Adams, 1965, Adams, 1966; Adams and Lund, 1966). Subsequently, recognition of nutrient interactions of ion pair formation refined estimates of ion activities (Bennett and Adams, 1970). Tedious iterative calculations of specific ion activities were automated in computer programs such as GEOCHEM (Sposito and Mattigod, 1980) and MINTEQ (Brown and Allison, 1987) despite the fact that these activities are as Sposito (1984) characterized, an immeasurable "thermodynamic illusion." Nevertheless, these models promoted more extensive research that demonstrated correlations between specific ion activities in soil solutions with root growth and ion uptake (Hough et al., 2005). Nutrient interactions in soil solutions that can affect specific ion activities are thereby manifested in this model by either contributing to or interfering with (1) the formation of insoluble precipitates or sorption of ion pairs (e.g., Bolan et al., 1993; Pearce and Sumner, 1997), (2) the formation of soluble ion pairs (e.g., Kinraide and Parker, 1987), or (3) a buildup of ionic strength, which inversely affects ion activities (e.g., Kalis et al., 2008).

16.2.2 Specific Nutrient Interactions at the Solution–Root Interface

Primary and secondary nutrient interactions in the rhizosphere involve both chemical and biological processes. The ion uptake models described above assume ion uptake by plant roots is related to ion concentration or ion activity in the soil solution of the rhizosphere. Thus, primary nutrient interactions in the rhizosphere affecting ion activities would affect plant uptake and plant response. Root metabolism resulting in differential depletion or accumulation of nutrients in the rhizosphere, rhizosphere pH modification, and root release of complexing organic compounds all potentially change the rhizosphere chemistry affecting ion activities (Marschner, 1995; Hinsinger, 1998). In addition, secondary nutrient effects on rhizosphere microbial activities also influence the forms, activities, and uptake of other nutrients.

Much of our knowledge of nutrient interactions at the root surface affecting ion uptake has been derived from solution-grown plants with varied nutrient compositions (Reid, 1999; Epstein and Bloom, 2005). Not coincidentally, ion uptake response to increasing ion activity in the rooting solution resembles crop response to increasing nutrient supply in the field. The diminishing rise to a maximum characterized by the MTS equation is reflective of similarly shaped ion uptake responses to nutrient supply at the root surface, typically characterized by single or multi-phased Michaelis–Menten kinetics. Likewise, some field level nutrient interactions have similar patterns of antagonism or synergism of ion uptake at cellular or root levels (see Epstein and Bloom, 2005). These interactions are expressed in changes in the shape of the rise to maximum, defined by K_m, and/or in changes in V_{max} (Wang et al., 1993). Like-charged ions tend to be antagonistic, while mobile counter-ions can facilitate greater uptake.

Molecular ion transport mechanisms of major nutrients have recently been reviewed (Miller et al., 2009). Families of membrane-bound protein transporters of N, P, and S have been identified, classified, and mapped to gene sequences. Plant regulation and control mechanisms of ion transporters coordinate relative uptake rates among nutrients to maintain internal nutrient balance during shifting nutrient availability regimes (Hesse et al., 2004).

16.2.3 Cation–Cation Interactions

Cation interactions that influence ion uptake rates occur at each stage of the soil–plant continuum. Cation exchange interactions with negatively charged clay and organic matter affect quantities held in reserve, solution cation activities (intensity), and flux rates to plant roots. The Q/I ratio is a measure of this relationship between solid and solution phase, and is a key parameter (buffer power, "b") of soil nutrient uptake models (Barber, 1995; Claassen and Steingrobe, 1999). The Barber and Cushman (1981) model predicted that when the total concentration of a cation in soil is held constant and buffer capacity is reduced in the presence of other exchangeable cations, then the cationic activity in solution increases, which, in turn, can drive an increase in cation uptake rates.

Cation exchange also occurs at the root surface on negative sites residing in the cell wall and plasmalemma. Inflow of cations through the root apoplasm by diffusion or mass flow is influenced by exchange properties of carboxylic groups of cell wall structural components such as polygalacturonic acid (Marschner, 1995). These exchange sites harbor a reserve pool of cations for membrane transport (Epstein and Leggett, 1954). Root cation exchange capacity (CEC) differs among species, and dicotyledonous plants are generally higher in exchange capacity than monocotyledonous plants. As in soils, selective binding of multivalent cations over monovalent cations occurs at the cell wall surface, increasing the concentration of divalent and trivalent cations in the apoplasm of species with high root CEC. The importance of this exchange phenomenon is inferred from correlations between root CEC and cation uptake selectivity differences among plant species (Crooke and Knight, 1962; Haynes, 1980). Conceptually, the cation selectivity on the root exchange sites influence the ratio of cations at the sites of membrane transport. Reid (1999) cautioned that research focused on cell wall electrostatic properties may have overshadowed more important charge properties of the plasmalemma. He argues that the membrane charge is more important due to proximity to the transport sites. Optimal calcium effects of increasing apparent K_m of Rb uptake by yeast cells (Gage et al., 1985) was offered as evidence for this influence of interacting cations on membrane adsorption and absorption. These electrostatic binding interactions in the cell wall and plasma membrane are thought to play an important role in trace element uptake and toxicity as well (Yermiyahu and Kinraide, 2005).

Calcium has long been recognized for its special synergistic role in facilitating ion uptake (Viets, 1944), which is commonly attributed to its positive maintenance of membrane integrity and subsequent membrane transport selectivity of other ions (Marschner, 1995; Epstein and Bloom, 2005). Membrane stabilization is achieved by calcium bridging of carboxylate and phosphate groups of the membrane phospholipids (Caldwell and Haug, 1981). Zinc nutrition has also been linked to membrane integrity and ion retention by roots (Welch et al., 1999). Ca and Mg can reduce the phytotoxicity of Cu, Zn, Al, Na, and H by reducing the electrostatic attraction of the root plasma membrane for these cations (Kinraide et al., 2004).

Commonly, a deficiency in one cationic nutrient will increase the uptake of other cations of similar properties. Direct interference of one cation on the porter-binding of a substrate cation has long been offered as a principle mechanism of cation antagonistic competition between like-charged cations (Epstein, 1972). Aluminum toxicity can be manifested as a primary mechanism of competitive inhibition of divalent cation uptake (Rengel and Robinson, 1989; Rengel, 1990) or secondary effects on root growth and general reduction of nutrient absorptive capacity (Foy, 1988). Primary interference of Al on Mg uptake is rapid (Rengel, 1990) and these types of cation interactions may also be attributed to altered surface charge potential of the cell wall (Gage et al., 1985). Antagonistic interactions among K/Na (Mohammadi et al., 2008; Luan et al., 2009), may relate to both transporter activity and synthesis (Yao et al., 2010). In the field, low K can result in increased Na uptake (Yoshida and Castenada, 1969). Antagonism between NH_4/K is also well recognized during the seedling (Vale et al., 1987; Hoopen et al., 2010) and reproductive (Pan et al., 1986) stages of cereal crops, with this interaction also involving a competition between the two cations for porter sites (Hoopen et al., 2010).

Cation–cation interactions also occur during internal plant transport and mobilization processes (Morgan and Jackson, 1976). For example, excess K is well known to suppress forage Mg accumulation, due to altered Mg translocation from root to shoot (Ohno and Grunes, 1985). Welch et al. (1999) demonstrated that Zn sufficient wheat had lower phloem movement of Cd to the grain compared to Zn deficient plants. Similar observations were made of Zn influences on Mn movement in root phloem (Pearson and Rengel, 1995).

Cation–cation antagonism in micronutrient and heavy metal uptake is also well documented. Calcium-inhibited Zn uptake and translocation was noted in wheat (Hart et al., 1998). Cadmium uptake can be increased (Girling and Peterson, 1981) or decreased (Honma and Hirata, 1978; Cataldo et al., 1983; Keltjens and van Beuschichem, 1998) by the addition of other metals depending on the resulting ratios of Cd and competing metals in solution. Rice accumulated more Fe and Mn under Zn deficient conditions (Sajwan and Lindsay, 1986), and Mn uptake by this crop has also been correlated to Mn/Fe activity ratios, suggesting an antagonism between Mn and Fe (Moore and Patrick, 1989). Excess Cu-induced Fe deficiency in wheat (Aurelia et al., 2008). Zinc deficiency stimulated root exudation and enhanced mobilization of both Zn and Cu that might stimulate cationic micronutrient uptake (Degryse et al., 2008).

16.2.4 Cation–Anion Interactions

Nutrient interactions between cations and anions may either increase or decrease nutrient use efficiency, depending on the dominance of reactions affecting their bioavailability in precipitation/adsorption/dissolution and ion pairing reactions relative to their role in providing ionic balance during uptake and translocation of those nutrients. For example, NH_4/metal interactions depend on opposing reactions at the solid–solution interface versus the solution–root interface. In solution culture experiments, NH_4 antagonizes heavy metal uptake (Chaudhry and Loneragan, 1972) due to cation binding interference in the plasma membrane. In contrast, soil experiments demonstrated that the mobility of the chloride NH_4 salt had the greatest positive influence on increasing Cd absorption by plants compared to less soluble anions, SO_4 and PO_4 (Bingham et al., 1983, 1984; Ohtani et al., 2007), overshadowing possible effects of cation–cation antagonism. The presence of chloride optimized the response to enhanced NH_4 supply in wheat, either by helping to facilitate transport to, or into the root (Koenig and Pan, 1996a). In contrast, cation composition of soils influences phosphate solubility and precipitation, whereby Ca promotes P precipitation while Na increases solution P (Curtin and Syers, 2001).

The formation of soluble ion pairs increases total nutrient concentration in the soil solution, potentially facilitating greater nutrient transport to root surfaces, but at the same time, may affect the activity of charged species that directly interact with roots. For example, the formation of soluble $AlSO_4^+$ was proposed by Kinraide and Parker (1987) to decrease Al toxicity in wheat due to decreased Al^{3+} activity.

At the root surface, the presence of soluble anions can increase cation uptake. For example, Ca uptake by corn roots in solution was greater from NO_3 and Cl salts compared to SO_4 (Maas, 1969).

High P-induced Zn deficiency is often cited in the literature as an important anion–cation antagonism (Jones, 1991), but direct evidence of this type of interaction is sparse (Hernandez and Killorn, 2009) and Zn responses on high P soils have not shown Zn deficiencies (Mallarino and Webb, 1995).

16.2.5 Anion–Anion Interactions

Similar to cation–cation interactions, anions interact at the soil surface as well as the root cell surface to affect anion uptake by plants. Anion concentrations in soil solution influence anion adsorption of variable charged clays (Roy et al., 1986; Manning and Goldberg, 1996) whereby competing anions may increase soil solution anionic concentrations and increase plant uptake. For example, the addition of CO_3 and SO_4 salts to calcareous soil increased PO_4 availability and movement (Olatuyi et al., 2009).

In addition, anions can interact by competing at anion membrane channels that facilitate uptake (White and Broadley, 2001). Leggett and Epstein (1956) demonstrated that Se interferes with SO_4 influx while other anions have no effect. Anion antagonism is best exemplified by mutual antagonisms between Cl and NO_3. High Cl supply inhibits NO_3 uptake and high NO_3 reduces Cl uptake (Mengel and Kirkby, 1987). Interactions vary at high and low affinity porter sites in the root cell membrane (Siddiqi et al., 1990). Inhibition of N uptake by NaCl is often attributed to the role of Cl in antagonizing NO_3 absorption in a scenario 3 type response (Figure 16.2; Massa et al., 2009).

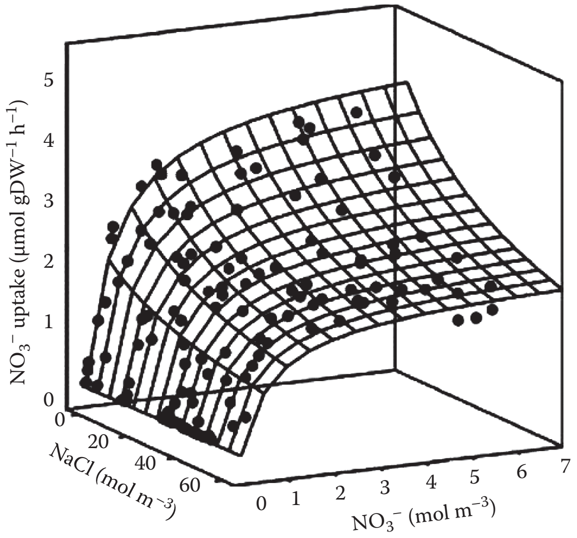

FIGURE 16.2 NaCl and NO_3 effects on NO_3 uptake in *Rosa*. (With kind permission from Springer Science+Business Media: Massa, D., N.S. Mattson, and H.J. Lieth. 2009. Effects of saline root environment (NaCl) on nitrate and potassium uptake kinetics for rose plants: A Michaelis-Menten modeling approach. Plant Soil 318:101–115.)

16.2.6 Secondary, Nonspecific Nutrient Interactions

Nutrients can have secondary effects on the uptake of other nutrients through their alteration of microbial activities in the rhizosphere, plant root activity, and rhizosphere chemical or biochemical modification (Marschner et al., 1987). In contrast to specific nutrient interactions, the uptake of multiple nutrients is affected by these secondary interactions. Furthermore, interactions between any of the macronutrients that have major influence on plant growth and development will include secondary effects on sink demand for other nutrients and/or via increased root proliferation and nutrient absorption capacity (Forde and Lorenzo, 2001; Williamson et al., 2001). Classic nonspecific nutrient interactions include N interactions with other nutrients, when the level of N bioavailability influences growth, yield potential, and corresponding demand for other nutrients.

An example of microbially mediated secondary nutrient interactions involves P-deficiency enhanced wheat responses to arbuscular mycorrhizal fungal inoculation, which increases Zn and Cu uptake and accumulation due to increased sorptive area, but not Fe and Mn (Mohammad et al., 1995). Kothari et al. (1991) suggested that the mycorrhizae decrease the potential for Mn reduction in the rhizosphere by lowering the number of Mn reducing bacteria. Furthermore, Zn binds to polyphosphates, a major P transport form in mycorrhizal hyphae, adding a primary nutrient interaction to this complex system.

Another prominent example of a nonspecific interaction is the rhizosphere acidification of plant roots in response to a nutrient deficiency, which, in turn, affects the solubility and bioavailability of pH-sensitive nutrients such as P and the cationic micronutrients (Marschner et al., 1987). Nitrogen form during N_2 fixation or NH$_4$ and NO$_3$ uptake by plants has the largest impact on cation–anion balance of absorbed charge, which is counterbalanced by net efflux of H$^+$ during excess cation uptake or OH$^-$ equivalents during excess anion uptake (Riley and Barber, 1971; Israel and Jackson, 1982). More recently, rhizosphere acidification has been observed to be a light-mediated reaction, seemingly tightly coupled to photosynthesis and energy transport to roots (Rao et al., 2002). Acidification of the rhizosphere then has secondary effects on nutrient availability and determines the propensity of certain species to utilize sparingly soluble Ca-phosphates (Shen et al., 2004; Zhou et al., 2009) and cationic micronutrients (Tills and Alloway, 1981). Manganese-deficient grass species are predisposed to take-all disease caused by *Gaeumannomyces graminis* var. *tritici* (Graham and Rovira, 1984), and NH$_4$ nutrition-induced acidification and reduction of Mn to the plant-available Mn^{2+} form improves Mn nutrition and reduces disease incidence (Brennan, 1992; Heckman et al., 2003).

Secondary micronutrient interactions can be utilized agronomically to enhance micronutrient uptake. Recent efforts to biofortify food crops with enhanced micronutrients place greater importance in recognizing mechanisms influencing micronutrient uptake, accumulation, and balance in designing agronomic systems (Zhang, 2009). Several researchers have recognized the benefits of intercropping Graminaceae and dicotyledonous crops in improving Zn and Cu accumulation in the dicot plant. This has been demonstrated in wheat/chickpea and lentil (Gunes et al., 2007) and maize/peanut (Zao et al., 2000). It is proposed that the Graminaceae crop, using strategy I in producing phytosiderophores under Fe deficiency to solubilize and acquire Fe and Zn in the comingled rhizosphere of both plant species, thereby enhances the cationic micronutrient uptake of both plants. The supply of FePO$_4$ was shown to increase Ca and Zn uptake in wheat, possibly due to a rhizosphere acidification response (Li et al., 2004).

Nitrogen and S fertility synergistically interact to affect crop grain yield (Wang et al., 1976; Randall et al., 1981), grain protein and grain quality (Randall et al., 1990), N utilization efficiency (Mahli and Gill, 2002), and N use efficiency (Salvagiotti and Miralles, 2008). Optimization of S nutrition increases N use efficiency, mainly by increasing N uptake efficiency in grass species (Brown et al., 2000; Figure 16.3, Salvagiotti et al., 2009). These responses align with scenario 1 (see Figure 16.1a).

In Brassica crops, yield and oil content (Ahmad et al., 1999), glucosinolate (Kim et al., 2002; Schonhof et al., 2007), and isothiocyanate (Gerendas et al., 2008) concentrations are influenced by relative supplies of N and S. Moderate N and S availability optimized production of benzyl-isothiocyanate in cress (Gerendas et al., 2008). In contrast to the previously cited improved nutrient use efficiency responses of grass species, Jackson (2000) observed a Liebig-type N × S interactive response in canola (scenario 4, see Figure 16.1d), in which N was initially more limiting than S, and yield response to S was apparent only at higher N supply (Figure 16.4b). In soil in which S availability was lower (Figure 16.4a), added S increased yield potential, which in turn increased N demand and the N supply required to obtain "A."

The field observations of N and S fertility interactions are well reflected at the cellular and root levels (Reuveny et al., 1980; Hesse et al., 2004). Mineral nutritional studies have revealed the uptake and assimilation of N and S are coregulated by the substrate ions and their assimilatory products (Clarkson et al., 1989; Koprivova et al., 2000; Hesse et al., 2004). Sulfate uptake and assimilation are regulated by O-acetylserine, a cysteine precursor that is in itself regulated by N availability and assimilation (Koprivova et al., 2000). Excess cysteine production when S is high or N is limiting will repress S uptake and assimilation (Zhao et al., 1999). Conversely, N uptake and assimilation is depressed during S starvation (Clarkson et al., 1989; Prosser et al., 2001) as arginine and asparagine accumulate with reduced cysteine and methionine production (Thomas et al., 2000; Prosser et al., 2001).

Nonspecific N–P interactions are commonly observed if for no other reason that they are typically the two most limiting nutrients in crop production and therefore demonstrate additive

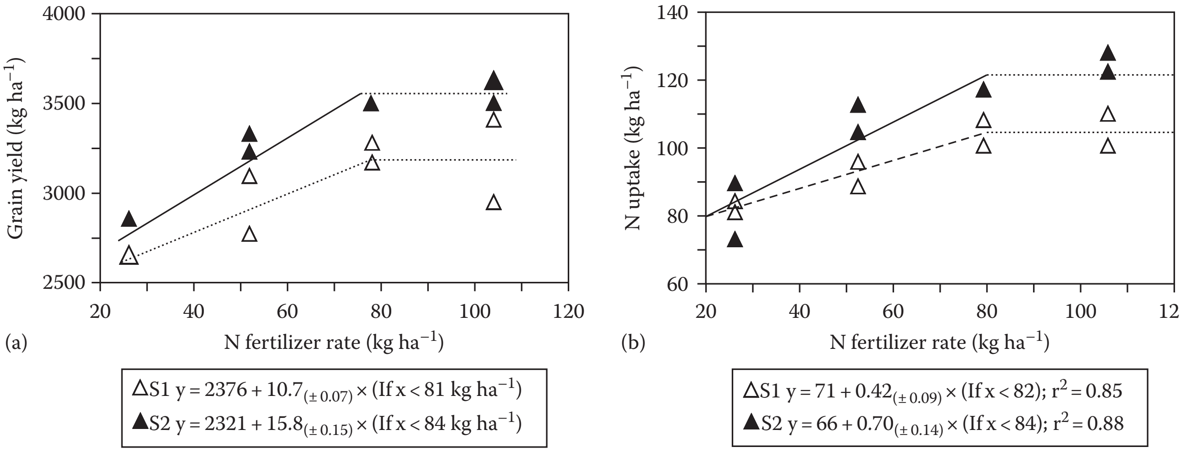

FIGURE 16.3 Wheat (a) grain yield and (b) N uptake responses to N fertilizer rate at two S levels. (From Salvagiotti, F., J.H.M. Castellarín, D.J. Miralles, and H.M. Pedrol. 2009. Sulfur fertilization improves nitrogen use efficiency in wheat by increasing nitrogen uptake. Field Crops Res. 113:170–177. Copyright (2009), with permission from Elsevier.)

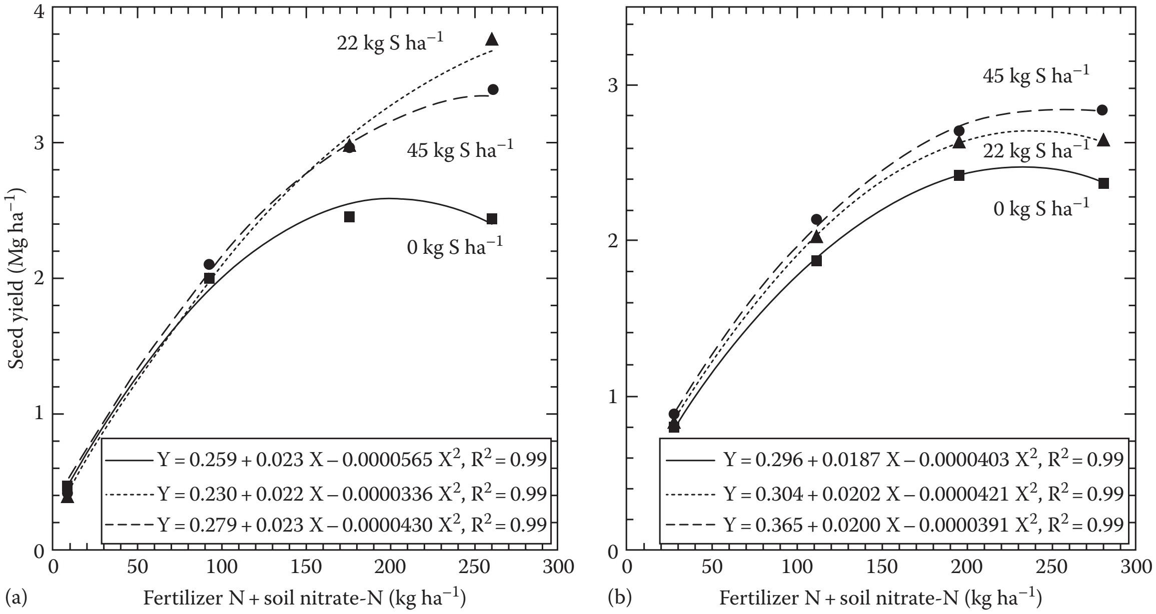

FIGURE 16.4 Canola responses to N and S fertility at two rainfed sites at (a) Sunburst, MT with a lower residual S soil and (b) Conrad, MT with a higher residual S soil. (From Jackson, G.D. 2000. Effects of nitrogen and sulfur on canola yield and nutrient uptake. Agron. J. 92:644–649. With permission from Soil Science Society of America.)

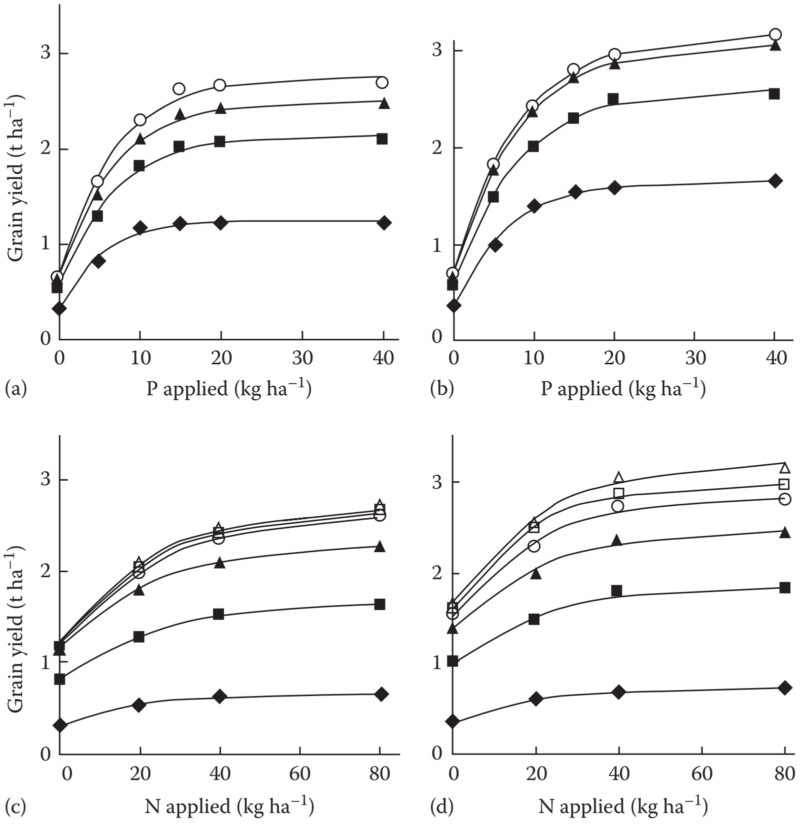

FIGURE 16.5 Canola (a, c) and wheat (b, d) responses to fertilizer P at increasing levels of N (a, b) and to fertilizer N at increasing levels of P (c, d). Nitrogen rates for panels (a) and (b) were 0 (◆), 20 (■), 40 (▲), and 80 (●) kg ha^{-1}. Phosphorus rates for panels (c) and (d) were 0 (◆), 5 (■), 10 (▲), 15 (○), 20 (□), and 40 (△) kg P ha^{-1}. (From Brennan, R.F., and M.D.A. Bolland. 2009. Comparing the nitrogen and phosphorus requirements of canola and wheat for grain yield and quality. Crop Pasture Sci. 60:566–577. With permission from CSIRO Publishing, http://www.publish.csiro.au/nid/40/paper/CP08401.htm)

or synergistic yield effects in bringing both nutrients to sufficient levels of availability. Mechanisms of N–P interactions have been ascribed to all stages of the soil–plant continuum (Miller, 1974). Brennan and Bolland (2009) demonstrated classic Liebig-type responses (see Figure 16.1d) to P at varying levels of N (Figure 16.5a and b) suggesting P was more critically limiting than N in these soils. Nitrogen level did not substantially alter the optimal level of P. The same data plotted differently exhibited an MTS-type response (see Figure 16.1a) to N at varying levels of P in canola and wheat (Figure 16.5c and d), suggesting there were limited specific interactions between the two nutrients that affected their bioavailability and that P availability was at least as critically limiting as N, such that optimization of P increased the N supply required to obtain "A." However, in other instances, a Liebig-type response (see Figure 16.1d) to N and P is observed (Nuttall et al., 1992) in which the level of N increased the optimal level of P supply.

16.3 Conclusions

Nutrient interactions are important factors to consider in accurately predicting nutrient responses in soil fertility management. Both primary and secondary interactions will influence nutrient use, uptake, and utilization efficiencies. Interactions occur at all points along the soil–plant continuum, and multinutrient quantitative models are needed to assess the relative importance and influence of individual interactions that are at times in synchrony and sometimes counter-opposing. Full recognition of the nature of these interactions will better allow us to understand the nature of variable yield responses to nutrient supplies. Shapes of nutrient response curves are influenced by the relative severity of the deficiencies of the interacting nutrients, the specificity with which the nutrients interact in influencing their relative availabilities and ability to react with root membrane surfaces, and their relative ability to influence plant internal processes and overall nutrient demand.

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