

2.2 Soil Chemistry and Fertility

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Introduction: Soil Chemistry and Fertility

UNIT OVERVIEW

This unit introduces students to the basic concepts of soil chemistry, with an emphasis on how soil chemistry relates to the development and maintenance of soil fertility.

The unit begins with a review of basic chemistry concepts and terminology, including atoms, compounds, ions, and chemical reactions. Soil nutrients essential to plant growth and the processes involved in nutrient uptake are then introduced, with particular attention paid to cation exchange capacity and base saturation as it relates to soil fertility. Soil pH and its effects on nutrient availability is then introduced.

The unit concludes with an overview of the biogeochemical cycles involved in making essential nutrients available to plants; the physiological role of essential plant nutrients; the characteristic symptoms of plant nutrient deficiencies; and the soil amendments used to supply limiting nutrients for organic farming systems.

MODES OF INSTRUCTION

> LECTURE (1 LECTURE, 3.0 HOURS)

The lecture covers basic chemistry concepts and definitions relating to soil chemistry, in particular, nutrient uptake processes and plant nutrients. Each plant nutrient is discussed individually.

> DEMONSTRATIONS

Five suggested demonstrations are designed to be integrated into the lecture. They provide visual representations and analogies for the concepts presented in the outline.

> ASSESSMENT QUESTIONS (1.0 HOUR)

Assessment questions reinforce key unit concepts and skills.

LEARNING OBJECTIVES

CONCEPTS

- Basic chemistry concepts (atomic structure and atomic bonding) and terminology
- Principles and processes involved in cation exchange
- pH and its effects on nutrient availability
- Soil acidity
- Soil alkalinity
- Plant nutrients — what they are, movement in the soil, cycling, their use in plants, and nutrient deficiency problems

SKILLS

This material is primarily conceptual, providing background for the skill-based sessions in Part 1

REQUIRED READINGS (SEE RESOURCES SECTION)

Gurshuney, Grace. 1993. *Start With the Soil*, Chapter 5; Chapter 7, pages 163-173; Chapter 8, pages 187-195; Chapter 9, pages 200-205

Brady, Nyle C., and Ray R. Weil. 1999. *The Nature and Properties of Soils*, Chapter 1, 1.15-1.16 (pp. 23-27); Chapter 16: 16.1-16.4 (pp. 612-625); 16.12 (pp. 645-646)

RECOMMENDED READINGS

Stell, Elizabeth P. 1998. *Secrets to Great Soil*, Chapter 2; Chapter 6; Chapter 7, pp150-157

Parnes, Robert. 1990. *Fertile Soil: A Grower's Guide to Organic and Inorganic Fertilizers*, Chapter 2, pp. 9-19; Chapter 16 (micronutrients)

Lecture Outline: Soil Chemistry and Fertility

for the instructor

A. Pre-Assessment Questions

1. What are some of the essential plant nutrients?
2. How do plants obtain them from the soil?
3. What may happen if levels of one essential plant nutrient are very low or very high?
4. What is soil pH and why is it important to know the pH of your soil?
5. How does the organic matter content of the soil influence soil fertility?

B. Introduction to Basic Chemistry Concepts

1. Atoms and elements
2. Compounds, molecules, and atomic bonds
3. Ions
4. Elements needed by plants
5. Chemical reactions
6. Adsorption vs. absorption
7. Organic vs. organic

C. Soil Colloids

1. Definition
2. Importance

D. Soil Solution

1. Definition

E. Cation Exchange Capacity (CEC) and Base Saturation

1. CEC
 - a) Measurement (meq/100g soil or cmol/kg [new units, numbers are the same])
 - b) Factors influencing CEC
2. Base saturation
 - a) Definitions
 - b) Significance

F. Anion Exchange

1. Introduction
2. Definitions

G. pH

1. What is pH?
2. Effect of pH on nutrient availability and uptake

H. Acidity

1. Definitions

2. Distribution of acid soils
3. Problems associated with acidity
4. Acid soils and liming

I. Alkalinity, Alkali, Salinity, and Sodic Soils

1. Definitions
2. Some elements contributing to alkalinity
3. Salinity (Electrical Conductivity–EC)
4. Sodicity
5. Distribution

J. Soil as a Medium for Plant Growth

1. Nutrient uptake processes

K. Plant Nutrient Requirements

1. Introduction
 - a) Nutrient balance
 - b) Feed the plant or feed the soil
 - c) Macronutrients and micronutrients
 - d) Nutrient cycling
 - e) Mobility of nutrients within the plant
2. Carbon, Hydrogen, and Oxygen
3. Nitrogen
 - a) Physiological role in plant development
 - b) Soil nutrient deficiencies, imbalances, toxicity
 - c) Forms of nitrogen in the soil
 - d) Nitrogen fixation
 - e) Nitrogen and mineralization
 - f) Denitrification
 - g) Immobilization
 - h) Losses of nitrogen through leaching and volatilization
 - i) Supplying nitrogen to the soil
 - j) The nitrogen cycle
4. Phosphorus
 - a) Physiological role in plant development
 - b) Soil nutrient deficiencies, imbalances, toxicity
 - c) The phosphorus cycle
 - d) Phosphorus in soils and factors affecting its availability
 - e) Phosphorus in amendments
5. Potassium
 - a) Physiological role in plant development
 - b) Soil nutrient deficiencies, imbalances, toxicity
 - c) The potassium cycle
 - d) Potassium in soils and factors affecting its availability
 - e) Potassium in amendments

6. Other macronutrients: Calcium, Magnesium, Sulfur

- a) Calcium
- b) Magnesium
- c) Sulfur

7. Micronutrients

- a) Introduction
- b) Boron ($B_4O_7^{2-}$)
- c) Copper (Cu^{2+}),
- d) Iron (Fe^{2+} , Fe^{3+})
- e) Manganese (Mn^{2+})
- f) Molybdenum (MoO_4^{2-})
- g) Zinc (Zn^{2+})
- h) Cobalt (Co^{2+})
- i) Chlorine (Cl^-)
- j) Others

Detailed Lecture Outline: Soil Chemistry

for students

A. Pre-Assessment Questions

1. What are some of the essential plant nutrients?
2. How do plants obtain them from the soil?
3. What may happen if levels of one essential plant nutrient are very low or very high?
4. What is soil pH and why is it important to know the pH of your soil?
5. How does the organic matter content of the soil influence soil fertility?

B. Introduction to Basic Chemistry Concepts

1. Atoms and elements

Elements: basic unit of matter that can't be broken down by chemical means. They are the building blocks of nature. Each element is assigned a symbol of one or more letters derived from its Latin name. For example O is used for oxygen while Fe is used for iron.

Atoms: smallest part of an element that acts like that element.

The components of the atom are the proton, the neutron and the electron. The proton has a positive electrical charge and the neutron has no electrical charge. Protons and neutrons are in the center of the atom in what is called the nucleus. Usually there are an equal number of protons and neutrons +/- 1. Electrons are negatively charged and they orbit the nucleus.

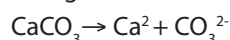
2. Compounds, molecules, and atomic bonds

Atoms combine to form molecules. A collection of like molecules that consist of two or more different kinds of elements is called a compound. Molecules are represented by using the symbols of the elements with subscripts to tell how many there are of each. For example, water is represented as H₂O, which means it has two hydrogen atoms and one oxygen atom.

One way that different atoms can join together is by sharing electrons. This is a type of chemical bond or atomic bond.

3. Ions

A normal molecule has an equal number of protons (+) and electrons (-). Because of this they have a net charge of 0. Frequently, however, an imbalance occurs and the resulting atoms or molecules are called ions. This frequently happens when something dissolves in water. A cation is a positively charged ion (missing electrons), an anion is a negatively charged ion (has surplus electrons). An example is given below. In that example the superscripts indicate the number of ions missing (+) or surplus (-). If no number is given then it means only 1 electron is missing or surplus. A molecule in solution is usually in equilibrium with its constituent ions. In other words, some molecules are breaking into ions while other ions are recombining to form molecules.



Where:

CaCO₃ = Calcium Carbonate

Ca²⁺ = Calcium (cation)

CO₃²⁻ = Carbonate (anion)

4. Elements needed by plants

a) From water and air

Carbon (C), Hydrogen (H), Oxygen (O)

b) From soil

Nitrogen (N), Phosphorus (P), Sulfur (S), Potassium (K), Calcium (Ca), Magnesium (Mg), Copper (Cu), Iron (Fe), Manganese (Mn), Zinc (Zn), Boron (B), Molybdenum (Mo), Cobalt (Co), Chlorine (Cl)

5. Chemical reactions

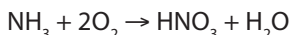
Chemical reactions occur when atoms are rearranged to form new molecules or compounds. For example, carbon dioxide and water can combine to form a sugar (as in photosynthesis). This reaction is written out like this:



(Note that since energy is required to make the reaction happen, this energy is released when the sugars are broken down. This opposite equation is called respiration and it is what happens in our bodies all the time.)

Oxidation/reduction reactions are special kinds of reactions that are very common and important in nature. Oxidation occurs when an element or molecule loses an electron and some other element or molecule gains the electron (reduction). The electron donor is said to be oxidized and the electron acceptor is referred to as reduced. The term "oxidized" is used because it is usually oxygen that accepts the electrons (and thus increases in quantity in the new molecule).

A common oxidation reaction occurs in the soil when ammonia is added. Ammonia is oxidized to form nitric acid (notice how oxygen becomes part of the new molecule in this equation). This equation also shows why long-term use of ammonia fertilizers can acidify a soil even though ammonia is a strong base.



(ammonia + oxygen → nitric acid + water)

6. Adsorption vs. absorption

Adsorption and absorption are two terms used in soil science that can get confused.

Adsorption means to be held onto the outside of something. In soils this refers to how ions are held to the edges of mineral and organic particles.

Absorption means to be taken up into something, such as water being taken up by a sponge or nutrients taken into plant roots.

Picture a life raft at sea. Absorbed would be the people in the life raft, adsorbed would be the people hanging to the outside of the life raft.

7. Organic vs. organic

Organic is another confusing term. To the chemist, organic refers to many kinds of compounds containing carbon, which may be natural or synthetic. Many of the synthetic pesticides used are organic by this definition.

Organic also refers to agricultural techniques based on maintaining soil fertility through organic matter. Such systems do not use synthetic organic chemicals, but they may use naturally occurring inorganic soil amendments.

C. Soil Colloids

1. Definition

Colloid: A particle, which may be a molecular aggregate, with a diameter of 0.1 to 0.001 μm . Soil clays and soil organic matter are often called soil colloids because they have particle sizes that are within or approach colloidal dimensions. Colloids go into suspension in a solution — they float around without settling out for great lengths of time.

2. Importance

Colloids have properties that are important in soil chemistry, such as the ability to adsorb cations

D. Soil Solution

1. Definition

Usually the water in the soil is referred to as the soil solution because it contains dissolved materials (cations and ions) as well as suspended colloids of clay and organic matter.

While plants tend to get their nutrients from the soil solution, the solution does not contain sufficient nutrients at any one time to last the life of the plant. Usually these nutrients are replenished from the pool of exchangeable nutrients (those that are adsorbed onto colloids; see CEC, below). Still more nutrients are held in what is called the stable pool (bound up in solid form as minerals or organic matter).

E. Cation Exchange Capacity (CEC) and Base Saturation

1. CEC

Definition: Ability of the soil to adsorb cations

It is primarily the ionic form of nutrients that plants are able to take up into their roots. Many of these nutrients are taken up in the cationic form, so it is important that the soil be able to supply these. Most soils have at least some ability to hold onto these ions at negatively charged sites within the soil. The amount that they can hold is called the Cation Exchange Capacity. The cations are held to the edges of particles within the soil. This is referred to as adsorption. (Use magnets to demonstrate attraction of positive and negative.)

The cations in the soil are divided into acids and bases. The acids are predominantly hydrogen and aluminum. The bases are primarily calcium, magnesium, sodium, and potassium.

A more technical definition of CEC would be:

The sum of exchangeable bases plus total soil acidity at a specific pH value, usually 7.0 or 8.0. When acidity is expressed as salt-extractable acidity, the cation exchange capacity is called the effective cation exchange capacity (ECEC) because this is considered to be the CEC of the exchanger at the native pH value. It is usually expressed in centimoles of charge per kilogram of exchanger (cmol kg^{-1}) or millimoles of charge per kilogram of exchanger.

a) Measurement ($\text{meq}/100\text{g}$ soil or cmol/kg [new units, numbers are the same])

b) Factors influencing CEC

i. Amount and type of clay

Higher amounts of clay mean higher CEC. Certain kinds of clay (smectites, montmorillonite) have higher CEC than others (such as kaolinite).

ii. Amount of organic matter

Higher amounts of organic matter mean higher CEC

iii. pH dependent CEC

Amorphous clay minerals and organic matter have a CEC that varies with pH. As pH increases, so does the CEC. Under acid conditions, these have an anion exchange capacity. For organic matter the rule of thumb is that for every pH unit above 4.5 there is a 1 $\text{meq}/100\text{g}$ increase for each percent organic matter.

2. Base saturation

a) Definitions

In simple terms, base saturation refers to the percentage of exchange sites (negatively charged sites on clay and organic particles) that are occupied with bases (usually Ca^{2+} , Mg^{2+} , K^+ and Na^+) as opposed to ions that make the soil acid (H^+ or Al^{3+}). A more technical definition is the ratio of the quantity of exchangeable bases to the cation exchange capacity. The value of the base saturation varies according to whether the cation exchange capacity includes only the salt extractable acidity (see cation exchange capacity) or the total acidity determined at pH 7 or 8. Often expressed as a percent.

Exchangeable bases: Charge sites on the surface of soil particles that can be readily replaced with a salt solution. In most soils, Ca^{2+} , Mg^{2+} , K^+ and Na^+ predominate. Historically, these are called bases because they are cations of strong bases. Many soil chemists object to this term because these cations are not bases by any modern definition of the term.

b) Significance

Soils with high base saturations are considered more fertile because many of the “bases” that contribute to it are plant nutrients. Usually the base saturation is 100 percent when the pH is above about 6.5. Since rainfall tends to leach bases out of the soil, areas with higher rainfall tend to have lower base saturations than areas with lower rainfall, unless the parent material is high in bases (such as limestone).

F. Anion Exchange

1. Introduction

Anions are not adsorbed onto soil particles to anywhere near the extent that cations are. This is due to the fact that clay minerals only have negative charges and that most of the exchange sites in organic matter also have negative charges.

Many of the anionic nutrients are supplied through organic amendments from which they are released as the organic matter breaks down. Because there is little adsorption of the anions, many (particularly nitrates) are easily leached, which can lead to groundwater contamination. This can even happen in an organic farming situation if it is not well managed.

Nutrients that are usually supplied by anions are nitrogen (NO_3^-), phosphorus (H_2PO_4^- , HPO_4^{2-}), sulfur (SO_4^{2-}), chlorine (Cl^-), boron ($\text{B}_4\text{O}_7^{2-}$) and molybdenum (MoO_4^{2-}).

2. Definitions

Anion exchange capacity: The sum of exchangeable anions that a soil can adsorb. Usually expressed as centimoles, or millimoles, of charge per kilogram of soil (or of other adsorbing material such as clay).

Exchangeable anion: A negatively charged ion held on or near the surface of a solid particle by a positive surface charge and which may be easily replaced by other negatively charged ions (e.g. with a Cl^- salt).

G. pH

1. What is pH?

pH stands for “potential of hydrogen” and it is expressed as the negative of the log of the concentration of hydrogen ions (moles per liter); it is a number between 0 and 14. (Water, H_2O or HOH is usually in equilibrium with its constituent ions, H^+ and OH^- and has a pH of 7.) In acid soils ($\text{pH} < 7$), H^+ ions predominate. In alkaline soils ($\text{pH} > 7$), OH^- ions predominate. Soils with pH of 7 are neutral. (Demonstrate different methods of measuring pH; see pH demonstration in Demonstrations.)

TABLE 1. SOIL REACTION AND pH

REACTION	pH	REACTION	pH
Ultra acid	< 3.5	Neutral	6.6 – 7.3
Extremely acid	3.5 – 4.4	Slightly alkaline	7.4 – 7.8
Very strongly acid	4.5 – 5.0	Moderately alkaline	7.9 – 8.4
Strongly acid	5.1 – 5.5	Strongly alkaline	8.5 – 9.0
Moderately acid	5.6 – 6.0	Very strongly alkaline	> 9.0
Slightly acid	6.1 – 6.5		

2. Effect of pH on nutrient availability and uptake (see Figure 1)

pH does not directly affect plants. It does affect the availability of different nutrients and toxic elements to plants. This is mostly due to the fact that pH changes the form of many of the nutrients and many of the forms are relatively insoluble.

H. Acidity

1. Definitions

Acidity refers to the condition of the soil when the exchange complex is dominated by hydrogen and aluminum ions. There are two forms of soil acidity; their technical definitions are:

Acidity, salt-replaceable: The aluminum and hydrogen that can be replaced from an acid soil by an unbuffered salt solution such as KCl or NaCl. (Also known as exchangeable acidity.)

Acidity, total: The total acidity including residual and exchangeable acidity. Often it is calculated by subtraction of exchangeable bases from the cation exchange capacity determined by ammonium exchange at pH 7.0. It can be determined directly using pH buffer-salt mixtures (e.g., BaCl₂ plus triethanolamine, pH 8.0 or 8.2) and titrating the basicity neutralized after reaction with a soil.

2. Distribution of acid soils

Acid soils usually occur where there is sufficient rainfall or other sources of precipitation to leach the bases out of the soil. When this happens, the exchange complex becomes dominated by hydrogen (lowers pH) and aluminum (toxic). In the U.S. there is a fairly strong correlation between precipitation and pH, with soils receiving more than about 30 inches of annual precipitation having a pH less than 6. (See map on page 163 of *Start with the Soil*.)

3. Problems associated with acidity

Aluminum toxicity: Aluminum is the third most common element in the earth's crust. It becomes more available at low pH's, and can be toxic to plants.

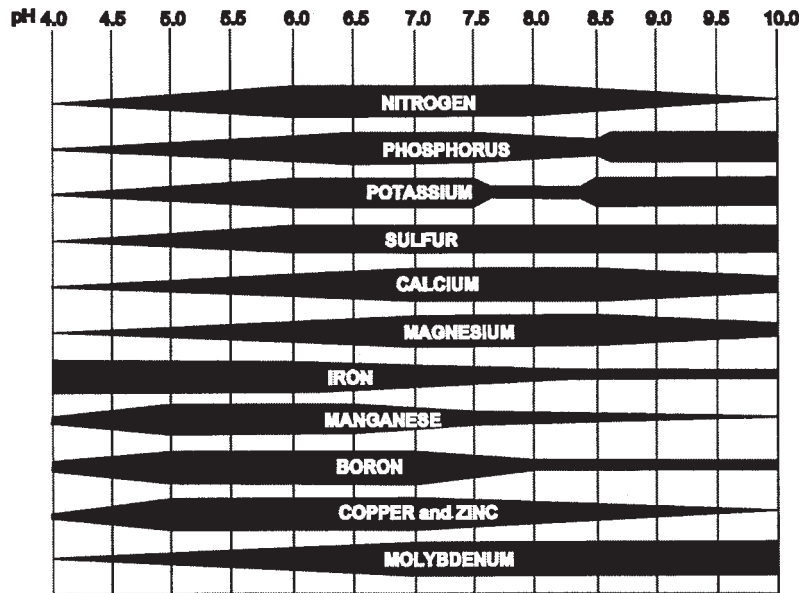
Manganese toxicity: This may occur in soil that are high in Mn and that have a pH less than 5

4. Acid soils and liming

Lime (calcium carbonate) is added to acid soils to raise the pH. Calcium replaces hydrogen and aluminum on exchange sites. For a good reference on liming, get the Soil Quality Technical note Number 8 from the website:

www.statlab.iastate.edu/survey/SQL/agronomy.shtml

FIGURE 1. NUTRIENT AVAILABILITY AT DIFFERENT pH VALUES. MAXIMUM AVAILABILITY IS INDICATED BY WIDEST PART OF BAR.



I. Alkalinity, Alkali, Salinity, and Sodic Soils

1. Definitions

Alkalinity, soil: The degree or intensity of alkalinity in a soil, expressed by a value >7.0 for the soil pH

Alkali soil: (i) A soil with a pH of 8.5 or higher or with an exchangeable sodium percentage greater than 0.15 (ESP >15). (ii) A soil that contains sufficient sodium to interfere with the growth of most crop plants. See also saline-sodic soil and sodic soil

Saline soil: A nonsodic soil containing sufficient soluble salt to adversely affect the growth of most crop plants. The lower limit of saturation extract electrical conductivity of such soils is conventionally set at 4 dS m^{-1} (at 25°C). Actually, sensitive plants are affected at half this salinity and highly tolerant ones at about twice this salinity.

Sodic soil: A nonsaline soil containing sufficient exchangeable sodium to adversely affect crop production and soil structure under most conditions of soil and plant type. The sodium adsorption ratio of the saturation extract is at least 13.

Saline-sodic soil: A soil containing sufficient exchangeable sodium to interfere with the growth of most crop plants and containing appreciable quantities of soluble salts. The exchangeable sodium ratio is greater than 0.15, conductivity of the soil solution, at saturated water content, of $>4 \text{ dS m}^{-1}$ (at 25°C), and the pH is usually 8.5 or less in the saturated soil.

2. Some elements contributing to alkalinity

Calcium: Calcium is common in many soils in arid areas. It helps the soil to form aggregates. (Because it has a $+2$ charge (divalent), it can bind to two clay or organic particles). (Acid demonstration in Demonstrations)

Magnesium: Behaves similarly to calcium in helping to form aggregates.

Potassium: An important plant nutrient

Sodium: Toxic to plants at high levels

3. Salinity (Electrical Conductivity—EC) (see Salt Crust Example and Conductivity Demonstration in Demonstrations)

Salinity refers to the presence of salts. Since saline soils conduct electricity, it is usually measured as Electrical Conductivity—EC. The units for EC are mmhos/cm or dS/m (millimhos per centimeter or decisiemens per meter). A soil is considered saline if it has an $EC > 4$ (though some plants cannot tolerate even this much). Saline soils mainly occur in dry areas. The reason plants cannot tolerate salinity is either due to the toxic effect of certain salts or to the fact that salts can hold on to the water so tightly that the plants cannot get it. Non-saline water may not infiltrate saline soils very easily. When irrigating saline soils with water that has a low salt content, it may be necessary to add gypsum to the water so that it will infiltrate the soil.

In order for there to be salts in the soil, there must be a source for them. For example, in many parts of California there are old marine beds, which contain salts that have been lifted into various mountain ranges. Also, feldspars usually contain some sodium that is released upon weathering. (The granite that makes up much of California is a source of such feldspars.) If there is sufficient rainfall to leach out these salts and if there is a watershed to carry the salts out to the ocean, then these salts won't be a problem. However, in many parts of California there is usually not enough precipitation to accomplish this and also, in many places, there are closed basins that do not drain to the ocean. Frequently, in these areas there are playas—salty basin floors that may hold intermittent, saline water.

The salts that usually contribute to soil salinity are magnesium (Mg^{2+}), sodium (Na^+), calcium (Ca^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}).

4. Sodicity

Sodicity refers to the presence of sodium. Many saline soils are also sodic (though it is possible for a soil to be sodic and not saline). Sodium is toxic to plants. It also causes soil particles to disperse (separate), which causes cracking and sealing of the soil surface. Sodium in the soil is usually expressed in the term Sodium Adsorption Ratio (SAR), which reflects the degree to which the exchange sites in the soil are occupied by sodium (rather than other cations). A soil with a SAR greater than about 13 is considered to be sodic. Sometimes the term Exchangeable Sodium Percentage (ESP) is used instead. An ESP of 15 is roughly equivalent to a SAR of 13.

Sodic soils can be reclaimed with a two step process. First the sodium is flushed from exchange sites by adding amendments containing calcium (such as lime, gypsum or dolomite) or by adding sulfur followed by calcium. (The sulfur is converted to sulfuric acid by microbial activity. The acid reacts with lime to free calcium.) The next step is to leach out the sodium salts by providing water in excess of what the plant needs. This excess amount of water is called the leaching fraction.

5. Distribution

Alkaline soils usually occur where there is insufficient rainfall to leach the bases out of the soil, that is, where annual evapotranspiration is greater than the precipitation. (See map on page 167 of *Start with the Soil*.)

J. Soil as a Medium for Plant Growth

1. Nutrient uptake processes

(This section is adapted from material produced by the University of Saskatchewan)

Imagine you are a tiny creature trying to move around in the soil. Can you imagine the millions of pores of all sizes and shapes, many of which are blocked by organic matter and mineral particles? The surfaces of these pores are very active and are capable of adsorbing ions and organic molecules. Once you have found your way around, the system changes with each wet-and-dry, or freeze-and-thaw cycle. Maybe a burrowing animal drops by and creates a real mess of your little world. In short, the soil is a constantly changing system that has numerous barriers to the movement of organisms and chemicals.

In terms of soil fertility we are greatly interested in the soil physical system. For a nutrient to be available for the plant to take up it must first be in the proper chemical form to pass the root membrane and most importantly it must be available at the root surface.

The movement of nutrients in soil is dependent on

- their concentration in soil solution;
- how strongly they are adsorbed by clays and organic matter,
- and how fast they can move.

For any given nutrient if we know how it moves in soil then we can use this information to formulate and place fertilizers.

As an example: phosphorus exists in soil solution as the orthophosphate ion (H_2PO_4^- or HPO_4^{2-}) in very low concentrations and is strongly adsorbed by the soil surfaces. In contrast, nitrogen usually has a much greater concentration in soil solution (usually as NO_3^-), and is very weakly adsorbed. Knowing these facts we then can determine that we must place phosphorus fertilizers very close to the seed to be effective, whereas nitrogen can be broadcast over the surface of the soil where it can be washed down to plant roots.

Nutrients move through the soil to plant roots in three ways

- Root Interception
- Mass Flow
- Diffusion

Each nutrient will have one or more of these methods of movement depending on its chemical form and soil physical and chemical conditions.

Root Interception

When you are hungry, if no one brings you food, you need to go out and get it. The roots of plants are constantly expanding (opening up blocked pores as they do so) and they grow from areas of depleted nutrients (e.g., because of plant uptake) to other regions where nutrients are more concentrated. These nutrients may be adsorbed on soil surfaces or locked in fertilizer pellets.

Although many plants such as cereals and grasses have a very extensive root system, they only can contact less than 5% of the soil volume. The root interception mechanism is very valuable, however, because root growth can extend to areas where mass flow and diffusion take over. For example, a root could grow within a few millimeters of some soil phosphorus pellet. Although the root does not technically bump into the nutrient and intercept it, the root is close enough for diffusion to occur. In some cases, the presence of mycorrhizal fungi increases the nutrient-absorption capacity of root systems (see Unit 2.3, Soil Biology and Ecology).

Mass Flow

Growing plants are continually absorbing water from the soil profile. Dissolved in this water are soluble nutrients. These nutrients are transported along with the water to the root surface. Nutrients that are strongly adsorbed to the soil surfaces, like phosphorus, would never get there. But nutrients, like nitrogen, that are held very weakly by soils readily move along with the water. Nutrients that move by mass flow are those that have a high concentration in soil solution relative to the plant requirements, e.g. nitrate and sulfate.

Diffusion

The random movement of ions in response to thermal energy is called diffusion. Imagine you have a tank of water with a removable barrier in the middle. On one side of the barrier you have ink, the other side pure water. When you remove the barrier very slowly you will see the ink and water mixing due to random movement of molecules. This is the process of diffusion. Similarly if we place a particle of fertilizer into soil it will slowly dissolve and the solution will spread out slowly and mix with the soil solution. How slow is diffusion? Phosphorus will rarely move more than a few millimeters from a fertilizer granule in a whole growing season! It very important that we place this fertilizer so that the root can intercept it. Diffusion is the dominant mechanism of movement for phosphorus and most of the micronutrients.

K. Plant Nutrient Requirements

1. Introduction

a) Nutrient Balance

Before we begin our discussion of nutrient requirements, we need to consider the concept of balance. Even though it is easier to consider one nutrient at a time, it is important to think of plant needs holistically. Supplying one nutrient while ignoring other plant needs (nutrients and environmental factors) may not benefit the plant at all and, in fact, may be bad for the crop.

Justus von Liebig (1803–1873) analyzed plant samples and proposed a law of the minimum. This law states that plant growth is proportional to the amount available of the most limiting plant nutrient. For example, if I supply nitrogen sufficient to produce 70 bushels of wheat per acre but only supply enough phosphorus for 50 bushels per acre, then I will get only 50 bushels per acre (providing everything else is sufficient). This concept has since been expanded to include not only nutrients but also such things as water, temperature and other soil factors.

As important as Liebig's contributions are, they do not go far enough in addressing the situation holistically. In the above example, for instance, nitrogen that is applied in excess of what the crop will consume is in danger of being leached into the groundwater where it will become a pollutant. Also, application of too much of any one nutrient can be injurious. For example, if too much nitrogen is supplied to tomatoes relative to the amount of phosphorus supplied, the tomatoes may grow very pretty plants but not produce any fruit.

The advantage of organic farming and gardening is that natural and organic soil amendments, unlike many synthetic ones, frequently supply many more nutrients than the primary one for which it is used, especially in regard to micronutrients.

b) Feed the plant or feed the soil

One of the main distinctions of organic farming and gardening is its emphasis on feeding the soil rather than on feeding the plant (which most contemporary agricultural practices do). The idea is that if the soil is happy, the plant will be happy. However, we still need to keep in mind the nutrient needs of the plant, because the plant may need some nutrient of which the soil is perfectly content to do without.

The reason for this is that most soils are well suited to supply the needs of the native vegetation. And while a soil may have no problem supporting, let's say, southern hardwoods, it may be ill prepared to nurture a field of corn.

c) Macronutrients and micronutrients

Plant nutrients are divided into two categories. Macronutrients are those that build up the bulk of the plant and so are needed in large quantities. Micronutrients are needed in small quantities, but are no less important. However, deficiencies of these are less likely to occur. Macronutrients include nitrogen, phosphorus, potassium, sulfur, calcium, and magnesium. Micronutrients include boron, copper, iron, manganese, molybdenum, zinc, chlorine, and cobalt.

d) Nutrient cycling

The amount of each chemical element in the world (with some exceptions) is fixed. Consequently, if we remove all of one element from a location, it's not going to be available there anymore unless it gets put back. This is a very important consideration in soil chemistry and plant nutrition. Many nutrients never leave the farm and are recycled through the use of things like manures and compost. But many nutrients are exported from a farm (in the crop or down the sewer, for example), and there needs to be a way to replace those nutrients in the soil. Looking at things this way, farming and gardening are nothing more than moving ions and nutrients around.

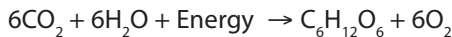
Some of the details of different nutrient cycles will be considered further when individual nutrients are discussed.

e) Mobility of nutrients within the plant

Some nutrients are mobile within plants; others remain where they are. This affects how nutrient symptoms appear. Nutrients that are mobile can move from older leaves to newer, growing tissues when there is a deficiency of them. Consequently, when these are lacking, symptoms appear in the older (lower and inner) leaves first. Nutrients that are immobile cannot be translocated to young, new growth. As a result, deficiency symptoms will appear in younger (upper and outer) tissues first. Nutrients that are mobile include nitrogen, potassium, phosphorus, magnesium, molybdenum, and zinc. Nutrients that are immobile include sulfur, calcium, iron, manganese, boron, and copper.

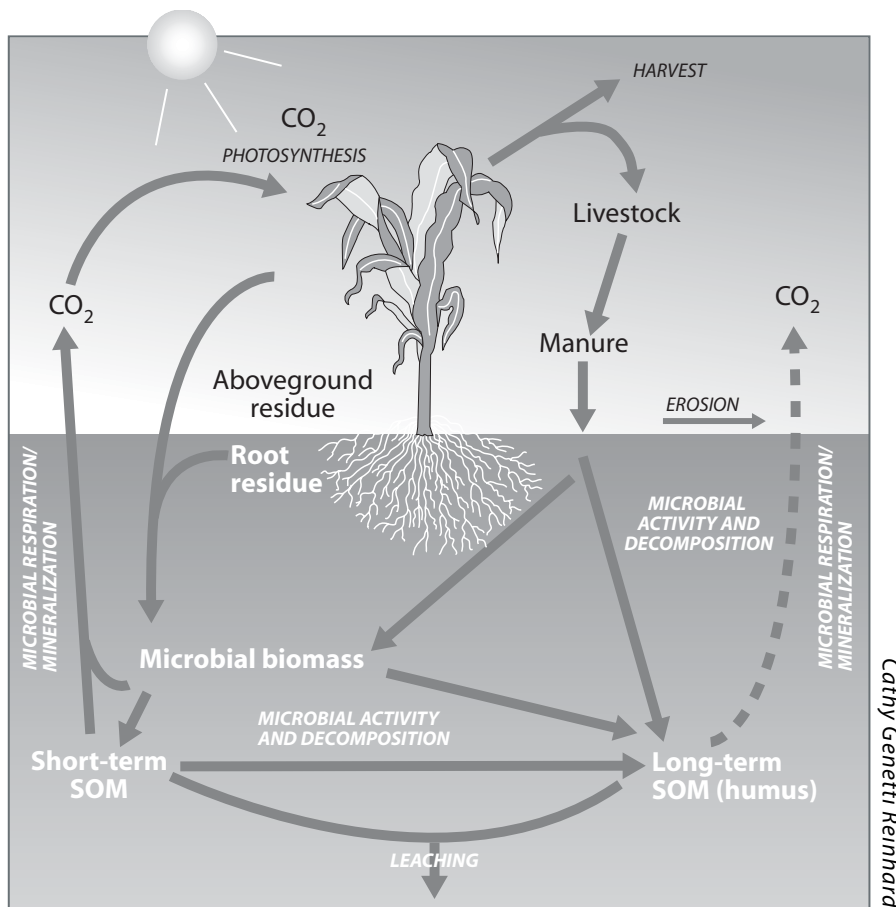
2. Carbon, hydrogen, and oxygen

Most of the bulk of plants and animals is made up of carbon, hydrogen and oxygen. A common term for these compounds is carbohydrates. Plants get these elements primarily from air (carbon dioxide—CO₂) and water (H₂O). This happens in the leaves of plants during photosynthesis:



Carbon is the core element of the large organic molecules that comprise all living things. It combines with elements such as hydrogen, oxygen, nitrogen, sulfur, phosphorus and other carbon atoms to form not only carbohydrates, but also fats, proteins and other compounds. In recent years there has been renewed interest in carbon due to its purported role in global warming. In some areas they are practicing carbon sequestration—an attempt to build up reserves of carbon in the soil to keep it from being released to the atmosphere as greenhouse gases.

FIGURE 2. THE CARBON CYCLE (ADAPTED FROM MICHIGAN STATE UNIVERSITY EXTENSION BULLETIN E-2646)



Cathy Genetti Reinhard

3. Nitrogen (N)

a) Physiological role in plant development

Plants take up nitrogen either as the ammonium ion (NH_4^+) or nitrate (NO_3^-). Most organic compounds in plants contain nitrogen, including amino acids, nucleic acids, many enzymes and energy transfer materials such as chlorophyll, ADP, and ATP. N is necessary for the production of sugars such as is found in sweet ripe fruit. Growing plants must have nitrogen to form new cells. Consequently, plants cannot function without nitrogen.

b) Soil nutrient deficiencies, imbalances, toxicity

Nitrogen deficiency symptoms include:

- Slow growth, stunted plants
- Yellow-green color (chlorosis)
- Firing (burnt look) of tips and margins of leaves beginning with more mature leaves
- Low protein content of crops

Symptoms of nitrogen excess include:

- Dark green, succulent, vegetative growth at the expense of seed production in grain crops, fruit production in tomatoes and some tree crops and sugar content in beets
- Watery potatoes
- Frost damage if there is too much succulent growth when frost hits
- Weakened stems (lodging)
- Flowering or fruiting delayed
- Boron or copper deficiency due to inhibited uptake of these nutrients

c) Forms of nitrogen in the soil

Nitrogen occurs in the soil in various forms

- Nitrogen gas in the soil air (N_2)
- Nitrate (NO_3^-)
- Nitrite (NO_2^-)
- Ammonium (NH_4^+)
- Ammonia (NH_3)—a gaseous (volatile), transitory form
- In various other forms as part of complex organic molecules frequently as an amine group ($-\text{NH}_2$)

d) Nitrogen fixation

Nitrogen gas makes up about 70% of the atmosphere. It is a very stable form of nitrogen, but it is unavailable to plants. Certain bacteria (Rhizobium) and actinomycetes (Frankia) are able to transform nitrogen gas into nitrate. This is called biological nitrogen fixation (as opposed to industrial nitrogen fixation carried out by chemical factories). The microbes form symbiotic relationships with plants in which the plants provide food to them and they provide nitrogen to the plants. Rhizobium is a genus of bacteria that work almost exclusively in plants of the bean (legume) family. Frankia are actinomycetes that are active with plants such as alder (*Alnus* spp.), bayberry (*Myrica* spp.), ornamental "olives" (*Elaeagnus* spp.), ceanothus (*Ceanothus* spp.) and Australian pine (*Casuarina* spp.). There are also some species of free-living cyanobacteria that are able to fix nitrogen. These frequently form cryptobiotic or microbiotic crusts that can be important parts of desert ecosystems. Some nitrogen fixing cyanobacteria live in conjunction with other organisms to form lichens.

In many cases, there may not be sufficient Rhizobium or Frankia in the soil to give a good boost to the crop. Or it may be that the type of Rhizobium is not the right species for the crop you are planting (not all Rhizobium species work with all species of legumes). In this case it may be necessary to inoculate the seed when the crop is planted. Inoculants are supplied by many of the companies that sell legume seed.

Inoculating legume seed does not mean that it will not be necessary to supply additional nitrogen to the crop. The Rhizobium themselves will need nitrogen to get started and the crop must have sufficient nitrogen to last until the Rhizobium are producing enough. Also, Rhizobium need sufficient phosphorus, iron, molybdenum, and cobalt in order to live.

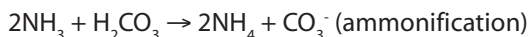
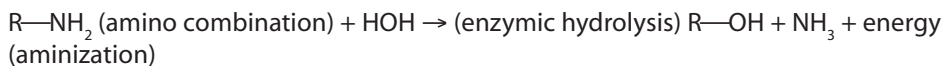
Nitrogen can also be fixed by lightning (with the nitrates then being carried to ground by rainfall), combustion (as in nitrous oxides in auto exhaust), or through synthetic processes (as in the manufacture of nitrogen fertilizers).

TABLE 2. COMPARISON OF NITROGEN FIXATION SOURCES.
VALUES ARE IN MILLIONS OF METRIC TONS PER YEAR ON A GLOBAL BASIS (APPROXIMATE VALUES)

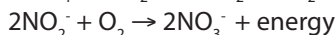
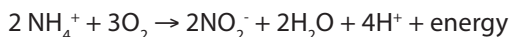
NON BIOLOGICAL		BIOLOGICAL	
Industrial	~50	Agricultural land	~90
Combustion	~20	Forest and other land	~50
Lightning	~10	Seas	~35
TOTAL	~80		~175

e) Nitrification and mineralization

Mineralization (aminization and ammonification) is the release of ammonium ions from decomposing organic matter. Many microbes are capable of doing this, so an environment that is favorable to microbial growth makes for fairly rapid ammonification. The ammonium that is produced is held in the soil solution, adsorbed onto cation exchange sites, or taken up by plants. An example of a mineralization reaction is:



Nitrification is a two stage process in which ammonium is transformed into nitrate (which is more readily taken up by plants). This, too, depends on microbial activity, but there are specific bacteria involved. *Nitrosomas* spp. (and a few others) oxidize ammonium to nitrite and *Nitrobacter* spp. oxidize nitrite to nitrate.



f) Denitrification

Nitrogen can be lost from wet soils where anaerobic (oxygen free) conditions occur. Under these conditions specialized bacteria can get their oxygen from nitrate (rather than oxygen), releasing nitrogen gas back into the atmosphere. This process is called denitrification. Though nitrogen can be lost from the ecosystem this way, denitrification can be a very useful function where excesses of nitrate occur in the soil. Note that even well drained soils may have parts that become anaerobic at some times.

To minimize denitrification one should maintain good aeration (structure) in the soil, keep the pH near neutral, avoid over-fertilization with nitrate, and incorporate residues in the upper few inches of the soil where there is more oxygen

g) Immobilization

Nitrogen is unavailable to plants (immobilized) when it is in the organic form. Usually, rates of mineralization in the soil are higher than rates of immobilization. However, if organic matter added to the soil has less than 1.5% N, the rate of immobilization will temporarily exceed the rate of mineralization, decreasing the amount of N available to plants.

- h) Losses of nitrogen through leaching and volatilization
Nitrogen is one of the easiest nutrients lost from the system. Nitrogen, especially ammonia, is easily volatilized. Amendments left on the soil surface will rapidly lose the nitrogen value. Volatilization is higher with warmer temperatures.

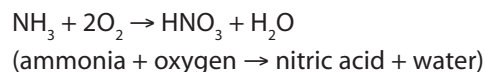
Nitrogen is also easily leached. This is not only a loss to the crop because the nitrates can contaminate the ground water, making it toxic. Leaching is most likely to occur in sandy soils, fallow areas, or in soils low in organic matter.

“The more one tries to force nitrogen into the soil, the greater are the chances of nitrogen losses” (Parnes, 1990, p. 75)

- i) Supplying nitrogen to the soil.

There are many ways that nitrogen can be supplied to the soil. These include green manures, crop rotation with leguminous crops, and amendments. Amendments that can be used to supply nitrogen include animal manures, guano, cottonseed meal, bone meal, hoof and horn meal, bloodmeal, peanut shells, and fish emulsion.

Care must be taken when using amendments high in ammonia (such as fresh poultry manure). Ammonia is a strong base that can “burn” plants. However, its use over an extended period of time will acidify the soil as bacteria oxidize the ammonia to form nitric acid. The chemical formula for this is:



- j) The nitrogen cycle (see Figure 3)

4. Phosphorus (P)

- a) Physiological role in plant development

Phosphorus is present in all living cells. It is used by plants to form nucleic acids (DNA, RNA) and is used in the storage of energy trapped by photosynthesis and its transfer.

Phosphorus also stimulates early growth and root formation and it hastens maturity (bloom time) and promotes seed production and size. It is used in protein synthesis and it is found in legume nodules.

- b) Soil nutrient deficiencies, imbalances, toxicity

Phosphorus must be balanced with nitrogen both in the plant and in the soil. In the soil, P and N compete to be taken up. Because N is highly mobile and P is one of the least mobile nutrients (both in the plant and in the soil), excessive N can cause a P deficiency even if there is enough P in the soil for the crop.

In the plant, N is required to trap energy, but P is required to facilitate its transfer. Also, N is a primary ingredient of protein but P is required for its synthesis.

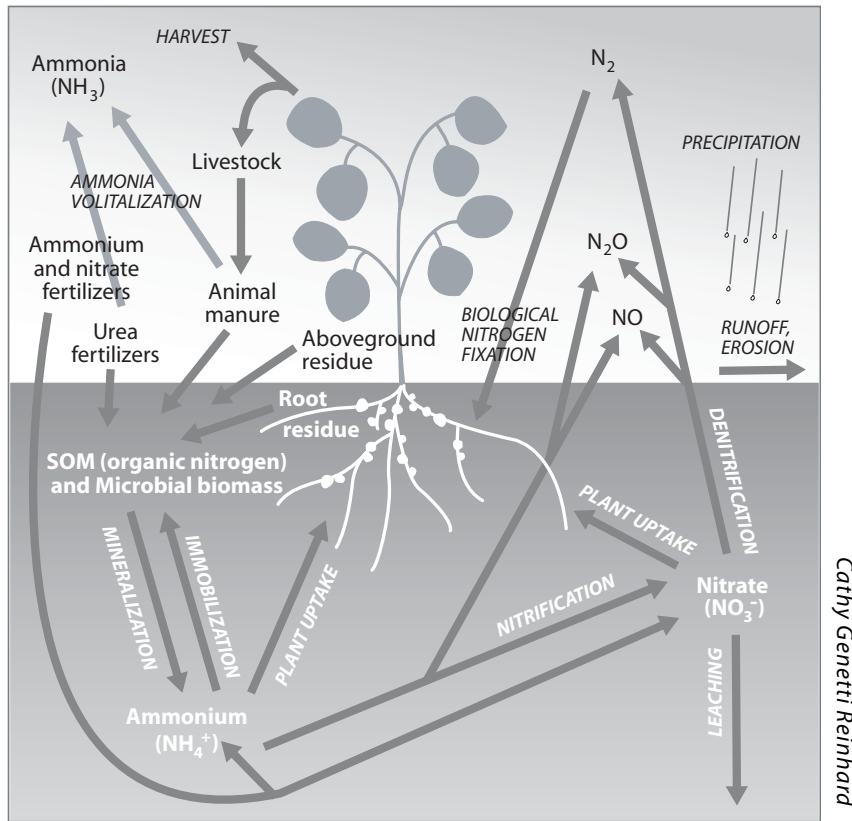
CARBON-NITROGEN RATIOS

Microbial action can either mineralize or immobilize nitrogen. The main factor in determining which will happen is the carbon to nitrogen (C:N) ratio. Microbes use carbon (from organic matter) for bodybuilding as well as for energy. The nitrogen entering their bodies needs to be in a fixed ratio to the amount of carbon. The critical range of the C:N ratio is ~22:1 to 25:1. Ratios wider than this (caused by the addition of residues with a C:N ration higher than this) will cause N to be immobilized. Narrower ratios will permit N to be freed as organic matter decomposes. Most plant residues have C:N ratios of 20:1-100:1; the bodies of microorganisms have a C:N ratio of 4:1 to 9:1. Usually the organic matter in the soil stabilizes with a C:N ratio somewhere between 8:1 to 15:1.

NITRATE TOXICITY

When nitrate is consumed, it is converted (reduced) to nitrite in the anaerobic (oxygen depleted) conditions in the gut. This nitrite gets absorbed into hemoglobin molecules, which reduces their oxygen carrying capacity (a cause of “blue-baby syndrome”). Nitrate can also react with amino acids to form nitrosamines, which are carcinogenic.

FIGURE 3. THE NITROGEN CYCLE (ADAPTED FROM MICHIGAN STATE UNIVERSITY EXTENSION BULLETIN E-2646)



Phosphorus deficiency symptoms include:

- Slow growth, stunted plants
- Purplish coloration on foliage of some plants
- Dark green coloration with tips of leaves dying
- Delayed maturity
- Poor grain, fruit or seed development

c) The phosphorus cycle (see Figure 4)

Phosphorus is not easily leached from the soil as it remains bound to soil particles. Consequently, the main losses of P from the system are either by export of crops or by soil erosion. Most phosphate pollution of lakes and streams is from sediment that is high in P.

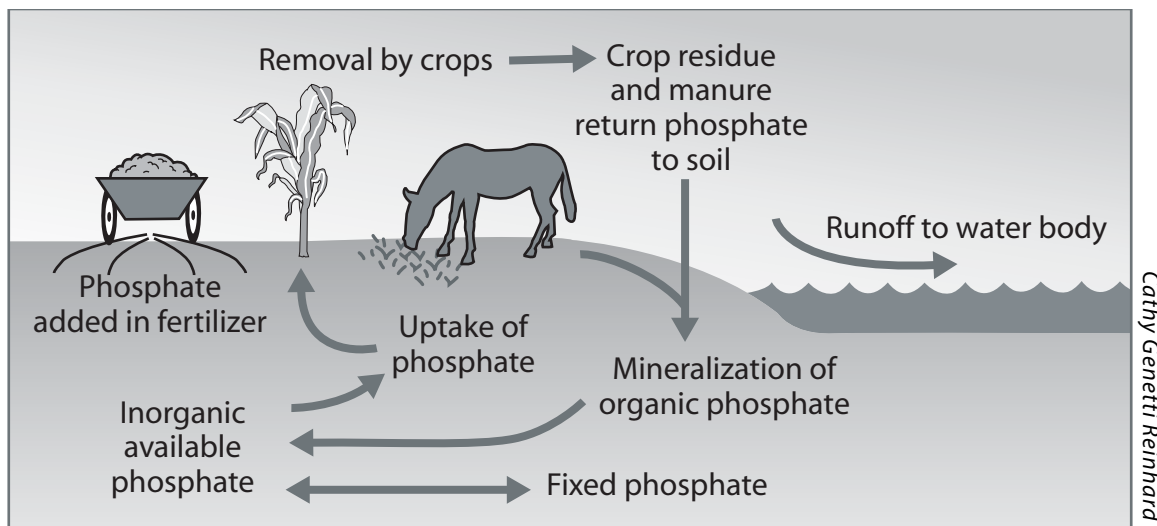
d) Phosphorus in soils and factors affecting its availability

Phosphorus is taken up as H_2PO_4^- or HPO_4^{2-} or PO_4^{3-} depending on pH. H_2PO_4^- is more available in very acid conditions while PO_4^{3-} is more available in very alkaline conditions. Most of the total P in the soil is tied up in compounds with limited solubility. In neutral to alkaline soils, it is usually bound as calcium phosphate, while in acid soils it forms iron and aluminum phosphates. Maximum availability occurs between pH 6.5 and 7.2.

Some soils are capable of fixing (binding nearly irreversibly) phosphorus when the P gets bound with reactive forms of iron, aluminum, and manganese. The fixing capacity of a soil is largely dependent on the amount and types of clay present in the soil. Clays made up of iron, aluminum, and manganese oxides or allophane have high P fixing ability. These clays are commonly found in warm humid climates (oxisols and ultisols) and areas affected by volcanic ash (Andisols). Usually these conditions are dealt with by adding enough P to the soil to satisfy its P fixing ability.

FIGURE 4. THE PHOSPHORUS CYCLE

(ADAPTED FROM WWW.EXTENSION.UMN.EDU/DISTRIBUTION/CROPSYSTEMS/)



Phosphorus is highly immobile and roots only take up what is only a fraction of an inch away, so if the P is not close to the root, it will not be available. Maintaining adequate moisture throughout the growing season will facilitate P movement. Phosphorus availability is also affected by temperature. In cool temperatures P may show as deficient in plants even though there is enough present for the plant needs. As temperatures warm, deficiency signs may go away. Organic P tends to be more available than inorganic, so use of organic amendments, along with promoting biological activity, will make P more available.

e) Phosphorus in amendments

The best source of phosphorus to use in the garden is “recycled” — compost and manures. Compost and manures are fairly low in P content but may have more available P than some other sources. Poultry manure has the highest amounts. Organic amendments should have a pH between 6.5 and 6.8 to maximize availability. If these are not sufficient to meet needs, bone meal (finely ground bones from slaughterhouses) or colloidal or rock phosphate are some sources that are high in phosphorus. The negative side to bonemeal is that it is usually dependent on large-scale confined animal operations. Colloidal and rock phosphates come from non-renewable sources. Another drawback to bone meal and rock phosphate is that, while they are P rich, the phosphorus is slowly available and most of what is applied serves more for crops to be planted in following years.

5. Potassium (K)

a) Physiological role in plant development

Potassium is essential for the movement of sugars within the plant and for starch formation. It is necessary for the opening and closing of stomata by guard cells, controlling water use by the plant. It encourages root growth and helps build disease resistance. It is involved with photosynthesis and enzyme activity. It helps regulate metabolic activity and is involved in protein synthesis. Potassium promotes larger and better-quality fruits and grains. In some plants, more potassium is required than any other nutrient.

b) Soil nutrient deficiencies, imbalances, toxicity

Potassium deficiency symptoms include:

- Slow growth
- Tip and marginal "burn" starting on more mature leaves. As severity of the deficiency increases, this condition progresses toward the top of the plant.
- Weak stalks, plants lodge easily
- Small fruit or shriveled fruit and seeds
- Reduced disease and pest resistance
- Increased sensitivity to drought, frost, and salts
- White or yellow spots develop along the edges of clover leaves, in severe cases these join to give a scorched appearance.

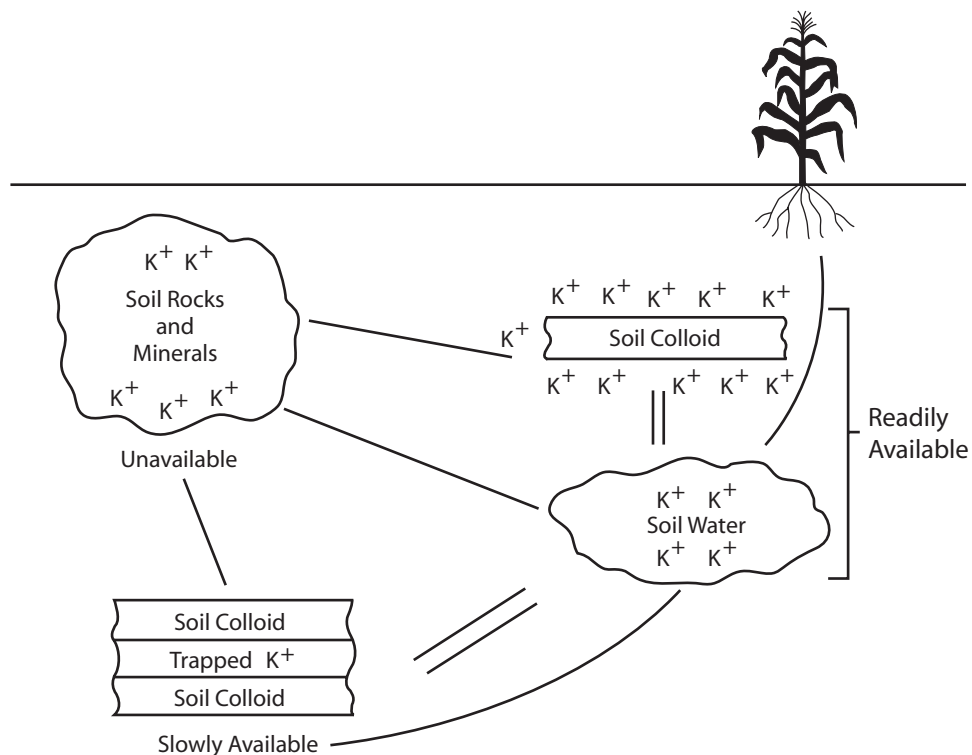
Excess potassium can cause:

- Magnesium deficiency
- Calcium deficiency in acid soils

c) The potassium cycle (see Figure 5)

FIGURE 5. THE POTASSIUM CYCLE

(FROM WWW.AGCENTRAL.COM/IMCDEMO/07POTASSIUM/07-06.HTM)



d) Potassium in soils: Factors affecting its availability

Plants take up potassium in the form of potassium ions (K^+). They may take up potassium that is adsorbed onto exchange sites (exchangeable K) or potassium that is dissolved in the soil solution. Consequently, in dry areas (where there is less soil solution) exchangeable K tends to be more important than dissolved K. Because K dissolves readily, it is highly mobile in the soil. However, it can get trapped between layers of expanding clays. Potassium tends to remain in ionic form within cells and tissues.

Potassium is present in feldspars and is released upon weathering of the minerals. Soils formed from feldspar-rich materials (such as granite or granitic alluvium) have a large supply of potassium to draw from. Even though a soil test may not show much potassium in such soils, it is usually released in sufficient quantities for plant growth. (Since much of the Sierras and southern California mountains are granitic, soils formed in these areas or in alluvium from these areas tend to have sufficient potassium.)

e) Potassium in amendments

Potential sources of potassium include wood ashes, granite dust, seaweed, greensand and langbeinite (Sulfate of Potash-Magnesia or Sul-Po-Mag). Greensand and langbeinite are non-renewable resources. Granite dust is also non-renewable, but granite occurs in such huge quantities over such extensive areas that using it should not be an issue. Wood ashes may increase the soil pH to undesirable levels and may not be available in large enough quantities.

Potassium in organic residues tends to be more highly available than that supplied by inorganic sources. So even though the total quantity of potassium supplied by these residues may be less, it may be more effective. With a steady program of recycling these residues, K is not likely to be deficient. Usually if the C:N ratio is high, the K:N ratio is also high.

6. Other macronutrients: Calcium, magnesium, sulfur

a) Calcium (Ca)

Plants take up calcium in its ionic form (Ca^{2+}). Calcium is an essential part of cell wall structure and it must be present for the formation of new cells both in the tops and in the roots. Calcium also helps control movement into and out of cells. It also reacts with waste products precipitating them or chelating them to render them harmless to the plant.

Calcium is normally so abundant that it usually only needs to be added to very acid soils where lime is required. However, excessive irrigation can leach calcium from the soil in sufficient quantities to bring about deficiency symptoms in plants. Plant roots are relatively inefficient at taking up calcium from the soil so the amount extracted is usually small compared to what is in the soil. Excess calcium can lead to a deficiency of magnesium or potassium.

Sources of calcium include poultry manure, wood ashes, seashells, lobster shells, legume hay (which has no liming value), limestone, and gypsum.

Calcium is not mobile in plants. Young tissue is first affected when there is a deficiency.

Deficiency symptoms include:

- Death of growing points (terminal points) on plants. Root tips are also affected.
- Abnormal dark green appearance of foliage
- Premature shedding of blossoms and buds
- Weakened stems (causes cell membranes to lose permeability and disintegrate)
- "Blossom end rot" of tomatoes
- Short, thick, bulbous roots

b) Magnesium (Mg)

Plants take up magnesium in its ionic form (Mg^{2+}). Magnesium is required for photosynthesis since it is contained in chlorophyll molecules. It helps in the assimilation of carbon dioxide during photosynthesis. Magnesium is also an activator for many plant enzymes required in growth processes. Magnesium is necessary for every operation that involves phosphorus in the plant and it also influences nitrogen metabolism.

Magnesium is generally available throughout the western states (where it is drier) but it is often more deficient than calcium. Magnesium, like calcium, is easily leached in humid areas. Soils with low CEC's cannot hold much Mg. It is important to have a balance of magnesium, potassium, and calcium so that no one of these elements dominates the cation exchange sites in the soil. Soils derived from serpentine often have a high Mg to Ca ratio. This makes the soil unsuitable for many plants and the worst areas are barren of vegetation.

Sources of magnesium include plant residues, fresh poultry manure, dolomitic limestone, and langbeinite (Sul-Po-Mag—see section on phosphorus)

Magnesium is mobile within plants and can be translocated from older tissue to younger tissue during conditions of deficiency. Symptoms of magnesium deficiency include:

- Interveinal chlorosis (yellowing) in older leaves
- Curling of leaves upward along margins
- Marginal yellowing with green "Christmas tree" area along midrib of leaf
- Stunted growth
- Ripe fruit is not sweet

c) Sulfur (S)

Plants take up sulfur in the form of the sulfate ion SO_4^{2-} . Sulfur is also sometimes absorbed from the air through leaves in industrial areas where sulfur is emitted into the atmosphere.

Atmospheric sulfur can also come from volcanoes, sea spray and hydrogen sulfide (H_2S) emissions from swamps and oilfields.

As a constituent of three amino acids (cystine, methionine, and cystine), sulfur is very important for protein synthesis. Sulfur is also essential for nodule formation by nitrogen fixing bacteria on the roots of legumes. Sulfur is also present in oil compounds that give plants such as garlic and onions their characteristic odor. (Vidalia onions, known for their sweetness, come from an area that has low sulfur soils.)

The use of organic residues in amounts to satisfy other nutrient requirements will usually provide sufficient sulfur. Other sources of sulfur include animal manures (sulfur is usually well balanced with respect to nitrogen), langbeinite (Sul-Po-Mag—see section on phosphorus), gypsum, and pure sulfur from natural sources (granular is preferred since sulfur dust is an explosion hazard).

Sulfur deficiency problems can occur if concentrated fertilizers for other nutrients are used that are free of sulfur. Symptoms of sulfur deficiency include:

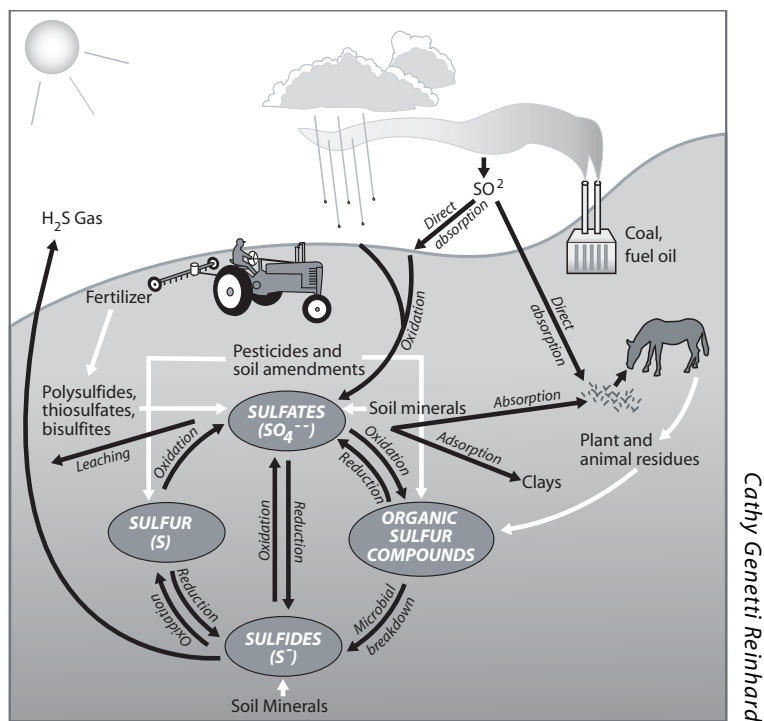
- Young leaves light green to yellowish in color. In some plants older tissue may be affected also.
- Small and spindly plants
- Retarded growth rate and delayed maturity
- Interveinal chlorosis on corn leaves

7. Micronutrients

a) Introduction

Micronutrients are those plant nutrients that are needed only in small quantities compared to other (macro-) nutrients. This fact, however, does not diminish their importance. The effects of micronutrients on plants are difficult to understand, partly because of their interrelationships with each other and partly due to how the plants respond to micronutrients individually.

FIGURE 6. THE SULFUR CYCLE



The response of many plants to micronutrients is almost an all or nothing affair. As long as the concentration of the micronutrients falls within a certain range, the response of the plant is the same, regardless of the exact concentration of the nutrient. If the concentration of the nutrient falls above this range, toxicity problems occur and if the concentration is below the range, the plants become deficient in the nutrient.

Interrelationships of micronutrients are many. For example, nitrogen fertilization can cause a deficiency of iron or copper. Prolonged phosphorus fertilization can lead to an iron deficiency. Excess phosphorus can lead to manganese deficiency. Sulfur and copper can cause molybdenum deficiencies, while the availability of molybdenum is increased by phosphorus. Iron, copper, manganese, and zinc compete with each other.

Availability of micronutrients is highly dependent on soil pH and organic matter. At certain pHs, micronutrients can get bound to inorganic compounds and become unavailable. Organic matter can diminish the effect of pH. If micronutrient levels become too low, organic matter can often supply them. Copper, iron, manganese, and zinc can get bound to soluble organic compounds that are readily available to plants. These are called chelates. If micronutrient levels get too high, organic matter can bind them up so they don't become toxic.

b) Boron ($B_4O_7^{2-}$)

Boron is required in minute quantities by plants, but in spite of this, there may not be sufficient boron in some soils. Boron can also become toxic in amounts not much higher than that needed by the plants. Boron toxicity is most frequently a problem in soils formed at the bottoms of enclosed basins in arid areas where groundwater evaporates through the soil, leaving salt concentrations near the surface (playas). Boron is needed for protein synthesis; for starch and sugar transport; to regulate nitrogen and carbohydrate metabolism; for root development and fruit and seed formation; for differentiation of meristem cells; and for water uptake and transport. Boron contributes more than any other micronutrient to the quality of produce. Boron is non-mobile in plants and so a continuous supply is necessary at all growing points.

Symptoms of boron deficiency include:

- Death of terminal growth, causing lateral buds to develop and producing a “witches’-broom” effect
- Thickened, curled, wilted and chlorotic leaves
- Soft or necrotic spots in fruit or tubers
- Reduced flowering or improper pollination

c) Copper (Cu^{2+})

Copper occurs as impurities in crystal structures of clays and other minerals. It may also occur in other compounds in the soil. As these materials weather the copper is released, after which it is adsorbed onto exchange sites from where it may be taken up by plants or leached from the soil. Consequently, soils formed from highly weathered materials may be deficient in copper. Copper is fairly abundant and deficiencies rarely occur. Also, since copper can be highly toxic at low levels, amendments should not be used except where the need for it has been established.

Copper is a catalyst for respiration and an activator of several enzymes. It is important for carbohydrate and protein synthesis. It may also play a role in carotene production.

Symptoms of copper deficiency include:

- Stunted growth
- Dieback of terminal shoots in trees
- Poor pigmentation
- Wilting and eventual death of leaf tips
- Formation of gum pockets around central pith in oranges

d) Iron (Fe^{2+} , Fe^{3+})

Plants require iron in larger amounts than any other micronutrient. It is used in chlorophyll synthesis; in oxidation-reduction during respiration; and as a constituent of various enzymes and proteins. It also serves as an activator for nitrogen fixation.

Iron is a very abundant in the soil, but some of its forms are so insoluble that plants may suffer a deficiency in spite of its abundance. (Like being stranded in the ocean and being thirsty for want of fresh water.) This is particularly true at pH levels above 7; where there is a high content of lime or manganese; or where there is poor aeration (though Fe requires some period where oxygen is lacking). Some plants, such as peppers, are more susceptible than others. Treatment may consist of adding iron in a form that won't be bound up in the soil or by lowering the pH.

Symptoms of iron deficiency include:

- interveinal chlorosis—a yellowing of the leaves between the veins
- twig dieback
- death of entire limbs or plants

e) Manganese (Mn^{2+})

Manganese is used in the metabolism of nitrogen and inorganic acids; for the formation of vitamins (carotene, riboflavin and ascorbic acid); for the assimilation of carbon dioxide during photosynthesis; and in the breakdown of carbohydrates. Manganese may be oxidized in the soil to form MnO_4^- . High manganese levels may induce iron deficiency.

Symptoms of manganese deficiency include:

- Interveinal chlorosis of young leaves. Gradation of pale green coloration with darker color next to veins. No sharp distinction between veins and interveinal areas as with iron deficiency.
- Development of gray specks (oats), interveinal white streaks (wheat), or interveinal brown spots and streaks (barley)

f) Molybdenum (MoO_4^{2-})

As with boron, molybdenum is needed only in minute quantities. Molybdenum is needed for nitrogen fixation and for reducing nitrate nitrogen to the amine form (plants take up nitrate- NO_3^- but use it to create amines $-\text{NH}_2$ for amino acids). Because of this a molybdenum deficiency can cause a nitrogen deficiency in plants. Molybdenum has been found in quantities sufficient to be toxic to livestock in forage grown in inland desert areas such as the San Joaquin Valley and Nevada. Molybdenum levels tend to be low in highly leached soils.

Symptoms of molybdenum deficiency include:

- Stunting and lack of vigor (induced nitrogen deficiency)
- Marginal scorching and cupping or rolling of leaves
- "Whiptail" of cauliflower
- Yellow spotting of citrus

g) Zinc (Zn^{2+})

Zinc occurs as impurities in crystal structures and in other compounds in the soil. As it is released by weathering, it is adsorbed onto exchange sites from where it may be taken up by plants or leached from the soil. Consequently, soils formed from highly weathered materials (such as quartz and sandstone) may be deficient. Soils formed from igneous rocks tend to have higher levels of zinc. Zinc is used in the formation of growth hormones; for protein synthesis; and in seed and grain maturation and production.

A well-aerated soil is necessary for zinc availability.

Symptoms of zinc deficiency include:

- Decrease in stem length and a rosetting of terminal leaves
- Reduced fruit bud formation
- Mottled leaves (interveinal chlorosis)
- Dieback of twigs after first year
- Striping or banding on corn leaves

h) Cobalt (Co^{2+})

Cobalt occurs as impurities in crystal structures and in other compounds in the soil. As it is released by weathering, it is adsorbed onto exchange sites from where it may be taken up by plants or leached from the soil. Consequently, soils formed from highly weathered materials may be deficient. Cobalt has not yet been shown to be essential to higher plants, but it is essential in the symbiotic relationship between legumes and Rhizobia.

i) Chlorine (Cl^-)

Minute amounts of chlorine are essential to some plants. Even touching plants with sweaty hands may be sufficient to provide sufficient chloride. Chlorine is required for photosynthetic reactions in plants. However, the quantities needed are so small and chlorine is so abundant that deficiencies never occur in nature.

Symptoms of chlorine deficiency include:

- Wilting, followed by chlorosis
- Excessive branching of lateral roots
- Bronzing of leaves
- Chlorosis and necrosis in tomatoes and barley

j) Others

Other micronutrients that may be of importance are:

i. Silicon

Silicon gives plants mechanical strength and may help minimize water loss and increase disease resistance

ii. Vanadium

Vanadium is not used directly by plants but seems to be required by soil organisms, which, in turn, benefit the plants

iii. Selenium, iodine and chromium

These elements are important to human and animal health. If they are present in the soil they can be taken up by plants and become available to plant consumers.