

SOILS AND FERTILIZERS
MODULE 3
CHEMICAL PROPERTIES OF SOILS

1. Soil Chemistry – General

- a. The study of soil chemistry emphasizes the **soil solution**, which is the thin water film which surrounds soil particles. The soil solution, soil solids, and soil air interact with the rest of the environment as shown in the following figure. The soil solution is the central part because of its intermediary role in most of the soil's reactions and its relations to living organisms and the environment.

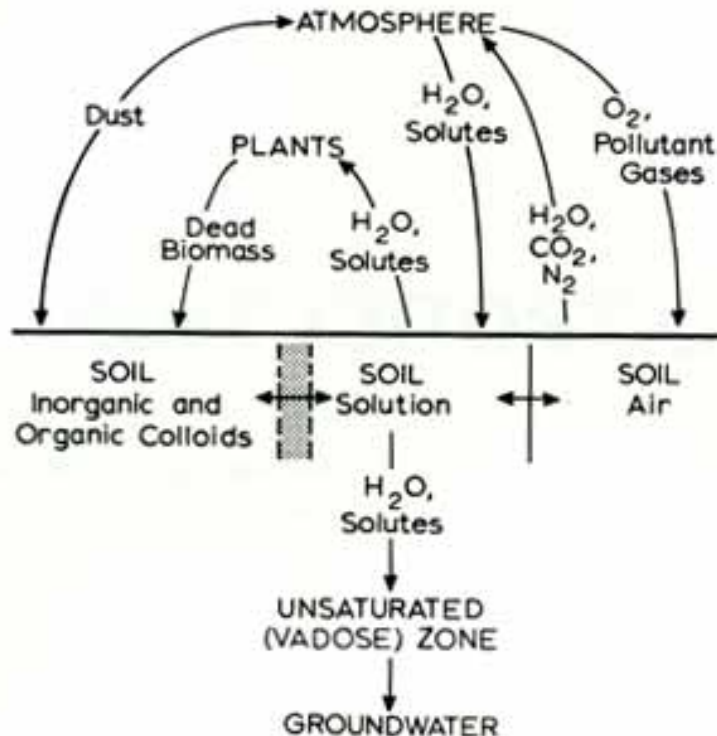


Fig. 1.1 The cycle of mass transfers between the atmosphere, biosphere, the three soil phases, unsaturated (vadose) zone, and groundwater. The shaded area indicates the transition between soil particles and the soil solution.

The chemical interactions of soils with the atmosphere and with water moving through the soil largely determine the composition of the earth's atmosphere and groundwaters. These reactions are also important for cleaning air and water after natural and human-induced pollution.

2. Dissolved ions in the soil solution are the immediate sources of the nutrients required by plants. Ions can enter into the soil solution in the following ways:
 - a. Mineral weathering
 - b. Organic matter decay
 - c. Rain
 - d. Irrigation waters containing salts
 - e. Fertilization
 - f. Release of ions retained by the colloid or clay fraction of soils
3. Soil colloids are the finer size fractions of the soil (clay and organic matter). The term **colloid** means "small particles suspended in a fluid." Colloids are the most chemically active portion of the soil because of their large surface area and the chemical structure of the materials involved.

Larger particles (e.g. sands) do not react extensively with the surrounding fluid (sand grains in water quickly settle out of suspension). Colloidal particles, on the other hand, react strongly with the fluid due to their surface area. Colloidal properties that clays and organic matter impart to soils include:

- a. Retention of ions and molecules
 - b. Water and gas adsorption
 - c. Shrinking and swelling
4. Essential ions (see periodic table)
 - a. The ions in the soil solution that are of primary interest are those which are essential for life, or toxic to life.
 - b. Essential elements for plants can be subdivided into those required in relatively large amounts (the **macronutrients**: hydrogen, carbon, nitrogen, oxygen, magnesium, phosphorus, sulfur, potassium and calcium) and those required in small amounts (the **micronutrients**: boron, chlorine, vanadium, manganese, iron, copper, zinc, and molybdenum).
 - c. The soil is involved in the supply of all essential elements. Though plants obtain their hydrogen, carbon, and oxygen from water and air, the soil supplies water-holding capacity and pore space for O₂ and CO₂ (carbon dioxide).
5. Chemical cycling
 - a. Soil chemistry is an important part of the cycling of elements at the earth's surface. Carbon, nitrogen, and sulfur cycle relatively rapidly among the atmosphere, oceans, and soils. Other elements cycle more slowly between rocks, soils, and oceans. The removal rate from soils is slowed significantly by adsorption, precipitation, and plant uptake.
 - b. Chemical pollution is, in a sense, the diversion of chemical elements from their natural cycles. The carbon, nitrogen, and phosphate in municipal wastes released to water streams are removed from the soil-plant cycle. When air and water are the disposal areas of our wastes, pollution can result because air and water convert waste components back into their

natural cycles only slowly. Soil, on the other hand, has enormous surface area and catalytic activity, plus a supply of oxygen and water with which to deactivate pollutants. Soil degrades most wastes quickly and returns components to their natural cycles, thereby minimizing environmental disturbance by human activities.

6. Properties of Clays and Clay Minerals

a. Layer silicate clays (found in less-weathered soils)

- i. Shape - Laminated, that is, made up of layers of plates or flakes that are crystalline (having an ordered internal arrangement).
- ii. Surface area - External surface area is very large (10 m² per gram), but internal surface area is even larger (up to 800 m² per gram). The internal surface occurs on interfaces between the plate-like crystal units that make up each clay particle.
- iii. Electronegative charge and adsorbed cations - The colloidal clay particles ordinarily carry a net negative charge. Consequently, hundreds of thousands of positively-charged ions, or **cations**, are attracted to each clay particle (e.g. H⁺, Al³⁺, Ca²⁺, Mg²⁺, etc.). The term that describes how the cations are "attached" to the clay is **adsorption**.

b. Iron and aluminum oxides and hydroxides (found in more highly-weathered soils)

- i. The small amount of clay found in most southwest Florida soils is most likely of this type (gives the soil a yellowish or reddish color). Some have crystalline structure, some do not.
- ii. Cation adsorption by these clays is much lower than for layer silicates because the amount of negative charge carried is much less.

7. Adsorbed cations

- a. Although all cations may be adsorbed by soil colloids, in humid regions the cations Ca, Al, and H are the most numerous.
- b. Reason: Ions are not all held with equal "tightness" by the colloids. The order of strength of adsorption when they are present in equal quantities is Al > H > Ca > Mg > K > Na. Consequently, the native quantity of these ions adsorbed to the colloids in uncultivated soil are in the same order, and the general case in southwest Florida soils is for Al, H, and Ca to dominate. This distribution can be altered by common farming practices, e.g. liming or addition of fertilizers.

8. Cation Exchange

- a. The various cations adsorbed by soil colloids are subject to replacement by other cations through a process called **cation exchange**. Exchangeable ions are defined as those released from the soil by a salt solution; soluble salts, on the other hand, can be removed by water alone.

- b. Example of cation exchange under natural conditions - Hydrogen ions (H^+) generated as organic matter decomposes can displace Ca^{2+} and other cations from the colloidal complex. Under these conditions, the soil tends to become more acid.
- c. Influence of lime and fertilizer - Cation exchange reactions are reversible, so if limestone or other calcium compound is applied to an acid soil, the reverse of the above exchange occurs. The Ca ions replace the H^+ and Al^{3+} ions, and the soil pH is raised. If sulfur or other acid-forming material is added to an alkaline soil, H^+ replaces the metal cations on the soil colloids and the soil pH decreases. If an application of a water-soluble fertilizer such as muriate of potash (KCl) is made, K^+ may be adsorbed on the colloid and will replace an equivalent quantity of Ca^{2+} , H^+ , and other metals than appear in the soil solution. The K remains in an available condition but is less subject to leaching.
- d. Cation Exchange Capacity (CEC) - the sum total of the exchangeable cations that a soil can adsorb (expressed as milliequivalents per 100 grams of soil, or centimoles of positive charge per kilogram of soil). CEC can range from as little as 1 meq/100 g soil for extremely coarse-textured soils to 50-60 meq/100 g soil for fine-textured soils containing large amounts of clay and organic matter.

(Note: Soils can also adsorb negatively-charged ions (anions) such as chloride, sulfate, or nitrate, and can adsorb uncharged molecules, e.g. pesticides. However, the magnitude of adsorption for these species is generally much less than for cations.)

9. Cation Exchange and Availability of Nutrients

- a. Exchangeable cations generally are available to both higher plants and microorganisms. Through cation exchange, hydrogen ions from the root hairs or microbe replace nutrient cations from the exchange complex. They enter the soil solution where they can either be absorbed by plant roots, or be removed with drainage water.
- b. Factors affecting nutrient availability:
 - i. Relative amount of cation on the colloid surface (the higher the proportion of the cation in question, the easier it will be for the plant to obtain it)
 - ii. Competition between nutrients; influence of associated ions (Example: magnesium availability to plants has been shown to be limited by excessive quantities of exchangeable calcium)

10. Soil Acidity, Alkalinity, and pH

- a. One of the most important chemical properties of the soil is its pH - that is, whether it is acid, alkaline, or neutral. Since microorganisms and higher plants respond so markedly to their chemical environment, the importance of soil pH has long been recognized.

- b. Acid soils originate in regions where rainfall is high enough to leach exchangeable **basic cations** (e.g. Ca^{2+} , Mg^{2+} , K^+ , Na^+) from the surface soil. Alkaline soils occur where basic cations have remained, or where calcareous (calcium carbonate) parent materials have dominated. In acid soils, hydrogen (H^+) and aluminum (Al^{3+}) dominate in the soil solution; in alkaline soils, hydroxyl (OH^-) ions dominate.
- c. Soil pH - a measure of the concentration of hydrogen or hydroxyl ions in the soil solution. The pH scale runs from 0 to 14, and is logarithmic (i.e. a soil at pH 4 is 10 times more acidic than a soil at pH 5 and 100 times more acidic than a soil at pH 6). pH 7 is neutral, i.e. the concentration of hydrogen and hydroxide ions are equal. Lower than pH 7, acid conditions exist; higher than pH 7, alkaline conditions exist.
- d. Sources of hydrogen ions (acidity)
 - i. Aluminum oxides and hydroxides in the soil
 - ii. Sulfur or sulfides
 - iii. Fertilization with nitrogen in the ammonium (NH_4^+) form
 - iv. Decomposing plant residues and organic wastes
- e. Sources of hydroxyl ions (alkalinity)
 - i. Carbonate ions from limestone
 - ii. Irrigation water pumped from limestone aquifers
 - iii. Calcareous parent material

11. Percent Base Saturation

This parameter is sometimes shown on soil test reports. It is defined as:

$$\text{Percent base saturation} = \frac{\text{Sum of basic cations}}{\text{CEC}}$$

Acid soils have low percent base saturation. As the soil pH increases from liming, percent base saturation increases.

12. Salt Index and salt-affected soils

- a. Soluble salt problems in Florida arise from two common sources: saltwater effects in coastal areas, including saltwater intrusion of wellfields (where the predominant ions are sodium and chloride), and salt effects due to over-fertilization (where the predominant highly-soluble ions are potassium, chloride, ammonium, nitrate, and sulfate). Historically, soil testing labs have reported soluble salt levels in terms of **parts per million (ppm)** of dry soil. This approach does not work well outside of Florida, but has served Florida agriculture well because of the uniform sandy nature of the state's mineral soils. However, recent efforts have emphasized the use of **electrical conductivity (EC)** measurements to un-isolate Florida's growers and agricultural industry from what the rest of the world uses to

measure salinity. The EC measurement of a water extract of the soil is termed the **salt index**.

- b. Excessive soluble-salt effects on plant growth can be classified into osmotic (related to total salt levels) effects and specific-ion effects. The latter include the effects of ions which are particularly harmful to sensitive species, such as sodium and chloride. This effect is generally less severe than the osmotic effect. Osmotic effects are commonly inferred from the EC of a soil extract, with the EC being proportional to the soluble salt concentration and generally negatively correlated with plant growth.
 - c. The salt index of the soil will vary as rainfall or crop uptake removes soluble salts from the root zone, or as fertilizer salts or salts from irrigation water are added to the soil.
 - d. Conversion between ppm soluble salts and salt index:
$$\text{Soluble Salts (ppm)} = \text{Salt Index} \times 180$$
13. How Soil Chemical Properties Relate to Citrus Production in Southwest Florida
- a. Soils have low CEC due to low content of clay and organic matter; thus, the soil cannot be counted on to hold fertilizer cations from leaching. Nutrients need to be applied more frequently in smaller amounts to avoid leaching losses.
 - b. Native soils used for citrus production are usually inherently acid at the surface. Liming is necessary to avoid aluminum and copper toxicity.
 - c. Soils where alkaline materials have been brought to the surface present a different problem. Micronutrient nutrition is difficult on these soils.