8

Chemical Properties of Soil

The soil is a chemical entity. All the materials there are chemical substances. Soils are composed of solid, liquid, and gas; soluble and insoluble; and organic as well as inorganic substances. There are ions and compounds, salts, acids, bases, minerals, and rock fragments. There are also colloids which are very active chemically. They are very fine soil particles, including humus, fine silicate clays, and oxides and hydroxides of iron and aluminum. Colloids carry electrochemical charges, both positive and negative, and these charges develop by substitution in the lattice structure and dissociation of active groups. These charges hold oppositely charged ions which are replaceable by ions of similar charges in the soil solution. Along with ion exchange properties, two other important indices of soil chemical environment are pH and E_h. Soil pH is the negative logarithm of hydrogen ion concentration in soil suspensions. It denotes the degree of acidity and alkalinity and influences solubility of chemical substances, availability and uptake of nutrients, and growth and activity of soil microorganisms. Some nutrients become unavailable if the soil pH remains at extremely acid or extremely alkaline conditions. The E_h represents the redox potential which indicates the tendency of a soil to be reduced or oxidized. Redox reactions are very important in soil genesis. There are a variety of other chemical reactions occurring all the time in the soil.

8.1 Soils Are Composed of Chemical Elements

Soils contain more than 100 chemical elements, but only a few make their bulk mass. The ranges and median values of different elements in soils are given in Sparks (2003). Median values of oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), and potassium (K) are 49.0, 33.0, 7.1, 4.0, 5.0, 0.5, and 1.4%, respectively. There are small quantities of other elements. Plant nutrients (Chap. 10) such as calcium, magnesium, potassium, phosphorus (P), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), boron (B), and nickel (Ni) are present in the minerals and in the soil solution. Oxygen, silicon, and aluminum occur as constituents of minerals and as oxides. Iron occurs mainly in the form of oxides and hydroxides. Phosphorus is present in soil mainly in the mineral apatite; it also occurs as aluminum and calcium phosphates and as organic compounds such as phospholipids, inositol, and nucleic acids. Nitrogen occurs in soil mainly in the organic form as proteins, peptides, and amino acids. All the micronutrients Mo, Fe, Mn, Zn, Cu, B, and Ni occur in the inorganic form. There are many different soils in nature, and their chemical compositions are also varied.

8.2 Water in Soil with Dissolved Substances Forms Soil Solution

Soil solution refers to the aqueous liquid phase of the soil and its solutes. Solutes include free hydrated ions, ion pairs, ligands, and complexes. One will note that Ca^{2+} is the most prevalent metal cation in the soil solution, which is typical for most soils. Nitrate, chloride, and sulfate are the common anions in more acidic soils, while carbonate can be important in some basic soils. Plants and soil organisms take up the nutrients and elements they need to grow from the soil solution. A plant absorbs ions from the soil solution at the contact of roots. Thus, ions are continuously removed from soil solution by plant roots. Two processes restore the supply of nutrients at this situation. They are the following: (a) movement of more solution from other portions of soil toward the plant root (mass movement) and (b) more ions move through the soil solution toward the root (diffusion). The soil solution is a dynamic entity. Plant roots take up ions from soil solution and release exudates into it. Ions in the soil solution can be sorbed on organic and inorganic components of the soil. Ions can again be desorbed into the soil solution. Some substances in soil solution can precipitate. Weathering of minerals releases soluble ions. Ions are transported through the soil into groundwater or removed through surface runoff

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processes. Microorganisms can remove ions from the soil solution, and when they die and are decomposed, ions are released to the soil solution (Sparks 2003). The concentration of a particular ion in the soil solution is thus changed from time to time. Soils have the natural but variable capacity to replenish the solutes in soil solution. However, the actual concentration of the ion species in the soil solution changes with changes in soil moisture content (Wolt 1994).

8.3 Soil Colloids Are Very Fine Soil Particles

A colloid is an ultramicroscopic substance dispersed evenly throughout another substance; together, both are known as a colloidal system. A colloidal system consists of two separate phases: a dispersed phase (colloidal particle) and a dispersion medium. A colloidal system may be solid, liquid, or gaseous.

The solid phase of the soil comprises of differently sized particles including the colloids. They are formed by weathering minerals as finely divided secondary clay minerals. Many new clay minerals are recrystallized from soluble substances as well. Feldspar, mica, and other primary minerals produce vermiculite, smectite, kaolinite, and other clay minerals. These extremely small mineral particles are visible only by an electron microscope and pass through ultra filters. They are inorganic soil colloids of size <0.002 mm or 2 µm diameter. There are organic colloids as well (humus). Due to their minute size and chemical nature, colloids acquire some properties entirely different from the larger fraction of the soil. Colloids have large surface area and electrical charges on their surfaces. Soil colloids have high nutrient- and water-holding capacities. They are all chemically reactive.

8.3.1 Inorganic Soil Colloids Mainly Include Aluminosilicate Clay Minerals

Clay minerals are commonly hydrous aluminosilicates, usually with appreciable amounts of iron, magnesium, calcium, sodium, and potassium. Clay minerals are generally phyllosilicates (from Gk. *phyllon* meaning leaf) because they are foliated. Clay minerals are basically constituted by organization of silica tetrahedral and alumina octahedral sheets. The basic unit of the silica tetrahedral sheet is the silica tetrahedron composed of one silicon atom surrounded by four oxygen atoms (Fig. 8.1). A tetrahedral sheet is built by sharing basal oxygen of one tetrahedron by its neighboring tetrahedron. On the other hand, the basic unit of the octahedral sheet is the alumina octahedron composed of one aluminum atom surrounded by six oxygen/hydroxyls, giving an eight-sided geometric shape.

In the tetrahedral sheet, some Si may be substituted by Al, and in the octahedral sheet, Al may be substituted by Mg or Fe.

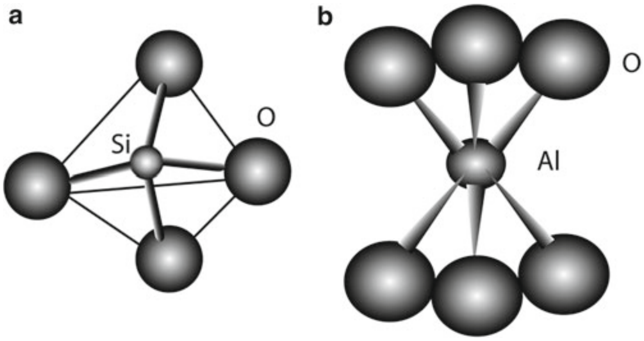

Fig. 8.1 (**a**) Silica tetrahedron and (**b**) aluminum octahedron

In some clay minerals, most Al atoms in the octahedral sheets are substituted by Mg. Al octahedral sheets are known as dioctahedral, and Mg octahedral sheets are known as trioctahedral sheets. Clay mineral crystals are formed either by 1 tetrahedral sheet bound to 1 octahedral sheet (1:1 type clay minerals) or 2 tetrahedral sheets sandwiching 1 octahedral sheet (2:1 type clay minerals). In some clays (such as chlorite), an additional magnesium hydroxide [$Mg_6(OH)_{12}$] sheet is bound to the 2:1 structure. It is, therefore, regarded as 2:1:1 type clay mineral.

8.3.1.1 Major Types of Clay Minerals in Soil

1:1 Type

A layer of 1:1 clay crystal consists of one tetrahedral and one octahedral sheet held tightly together by oxygen atoms mutually shared by silicon and aluminum cations in their respective sheets. These layers, in turn, are held together by hydrogen bonding. Consequently, the structure is fixed, and no expansion ordinarily occurs between layers when the clay is wetted. This is, therefore, known as non-expanding clay. The 1:1 type clay includes the kandite group [$Al_4Si_4O_{10}(OH)_8$], the chief members of which are kaolinite, dickite, nacrite, and halloysite, formed mainly by the decomposition of orthoclase feldspars.

2:1 Type

The 2:1 clay crystal units are characterized by an octahedral sheet sandwiched between two tetrahedral sheets. Three general groups have this basic crystal structure: smectite, vermiculite, and illite. Smectites and vermiculites are expanding type of clay, while illite is non-expanding.

Smectite Group: The smectite group has the general formula $(Na,Ca)_{0.33}$ $(Al,Mg)_2Si_4O_{10}$ $(OH)_2 \cdot nH_2O$. It includes montmorillonite, bentonite, nontronite, hectorite, saponite, and sauconite, formed by the alteration of mafic igneous rocks rich in Ca and Mg. These minerals have high swelling/shrinking potential. Wide cracks commonly form when smectite dominated soils (e.g., Vertisols; Chap. 4) are dried. The dry clods are very hard, making such soils difficult to till.

Vermiculite Group: Vermiculite group has the general formula $(Mg,Fe,Al)_3$ $(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$. In the tetrahedral sheet of most vermiculite, considerable substitution of aluminum for silicon has taken place. For this reason, a high proportion of net negative charge develops in vermiculite. There are many strongly adsorbed cations including Ca^{2+} and Mg^{2+} and water molecules in the interlayer space of vermiculites. They bind the units tightly together. The degree of swelling and shrinking is, therefore, considerably less in vermiculites than in smectites. Vermiculites are considered limited-expanding type of clay minerals, expanding more than kaolinite but much less than the smectites.

Illite Group: Illite has the general formula (KH_3O) $(Al,Mg,Fe)_2(Si,Al)_4$ $O_{10}(OH)_2 \cdot H_2O$. It includes hydrous micas, phengite, brammalite, celadonite, and glauconite, formed mainly by the decomposition of some micas and feldspars. They are predominant in marine clays and shales. The K^+, Ca^{2+}, and Mg^{2+} cations in interlayers of illite prevent the entrance of H_2O into the structure. So, the illite clays are non-expanding clays.

2:1:1 Type

This silicate group is represented by chlorites having the general formula $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$. In chlorite clay crystals, the 2:1 layers alternate with a magnesium-dominated trioctahedral sheet. Magnesium replaces a considerable amount of aluminum in the octahedral sheet of the 2:1 layer. Thus, the crystal unit contains two silica tetrahedral sheets and two magnesium-dominated trioctahedral sheets, giving rise to the term 2:1:1 type structure. Important members of the group are clinochlore, chamosite, nimite, pennantite, and cookeite.

Other Clays

Sesquioxide Clays: Sesquioxides are predominant in tropical soils. They are formed by the intensive weathering in humid warm climates. Most of the silica and much of the alumina in primary minerals are dissolved and slowly leached away. The remnant materials, which have lower solubility, are the sesquioxides. Sesquioxides are mixtures of aluminum hydroxide $[Al(OH)_3]$ and iron oxide (Fe_2O_3) or iron hydroxide $[Fe\ (OH)_3]$. Examples of iron and aluminum oxides common in soils are gibbsite $(Al_2O_3 \cdot 3H_2O)$ and goethite $(Fe_2O_3 \cdot H_2O)$. These substances form amorphous to crystalline clay-sized materials.

Allophanes: These clays are common in soils forming from volcanic ash. Almost all of their charge is from accessible hydroxyl ions (OH^-), which can attract a positive ion or lose the H^+ attached. These clays have a variable charge that depends on H^+ in solution.

Distribution of Clay Minerals in Different Soil Orders

Order	Dominant Clay Minerals
Andisols	Allophane, imogolite, hydrated halloysite, and halloysite
Aridisols	Smectites and vermiculites
Vertisols	Smectites
Mollisols	More smectites than kaolinites, some illites
Alfisols	Kaolinites and smectites
Ultisols	Kaolinites, sesquioxides, some smectites
Spodosols	Kaolinites, sesquioxides
Oxisols	More sesquioxides than kaolinites

8.3.2 Organic Colloids Are Derivatives of Humus

Humus or organic colloidal fraction is composed of highly decomposed residues of plant and animal remains (Chap. 7). Organic colloids are amorphous. The structure of soil organic colloid is extremely complex, with many different types of functional groups which can contribute negative and positive charges. Humus colloids consist of modified lignins, polyuronides, and other constituents composed of carbon, hydrogen, and oxygen, along with minor amounts of nitrogen, phosphorous, sulfur, and other elements.

The charge and surface area of humus far exceed that of the crystalline colloids. Humus may contribute from 30 to 90% of the total charge present in the soil even though present in relatively low amounts.

8.3.3 Soil Colloids Have Unique Properties

Because of their tiny size, all soil colloids have a large external surface area per unit mass. Certain silicate clay colloids have extensive internal surfaces as well, which occur between platelike crystal units that make up each particle. The total surface area of soil colloids ranges from 10 $m^2\ g^{-1}$ for clays with only external surfaces to more than 800 $m^2\ g^{-1}$ for clays with extensive internal surfaces.

Soil colloids carry negative and/or positive charges on their surfaces with more negative charges than positive. When an electric current is passed through a colloidal suspension, soil colloids migrate to anode, indicating that they carry a net negative charge. The magnitude of the charge is known as zeta potential. The presence and intensity of charge influence the attraction and repulsion of the particles toward each other. Due to the presence of charges, colloids attract ions of an opposite charge to their surfaces. They attract hundreds of positively charged ions or cations such as H^+, $A1^{3+}$, K^+, Na^+ Ca^{2+}, and Mg^{2+} to satisfy negative charges and SO_4^{2-}, NO_3^-, and $H_2PO_4^-$ to satisfy positive charges. Thus, a colloidal particle is surrounded by a swarm of adsorbed cations. These ions can be replaced by other ions, say K^+ by H^+, in solution. In addition to the adsorbed cations, a large number of water molecules encircle soil colloidal particles. Some are attracted to the adsorbed cations, each of which is hydrated; others are held in the internal surfaces of the colloidal particles.

Cohesion and adhesion are two important physicochemical properties of colloids. Colloids of similar nature tend to stick together. This tendency is primarily due to the attraction of the clay particles for the water molecules held between them. When colloidal substances are wetted, water first adheres to the particles and then brings about cohesion between two or more adjacent colloidal particles. On the other hand, adhesion refers to the phenomenon of colloidal particles sticking to other substances.

When a suspension of colloidal particles is examined under a microscope, the particles seem to oscillate. The oscillation is due to the collision of colloidal particles or molecules with those of the liquid in which they are suspended. Soil colloidal particles with those of water in which they are suspended are always in a constant state of motion. The smaller the particle, the more rapid is its movement. This is known as Brownian movement.

8.3.4 There Are Electric Charges on Soil Colloids

Charges on soil colloids are of two types: (1) permanent charges or charges independent of pH and (2) pH dependent or variable charges. The permanent charges develop on layer silicate clays (except kaolinite) by isomorphous substitution. On the other hand, pH-dependent charges develop on all types of colloids, on layer silicate colloids from broken crystal edges, and on amorphous inorganic colloids, oxides, and hydroxide colloids and humus by dissociation of active groups and association of hydrogen ions (protonation). There may be both negative and positive pH-dependent and ph-independent charges.

8.3.4.1 Permanent Charges

Isomorphous Substitution

During crystallization, some of Si^{4+} atoms in the tetrahedral sheet of crystalline colloids may be substituted by Al^{3+}. One negative charge develops due to this substitution. Si^{4+} and Al^{3+} have comparable ionic radii. This substitution of one atom by another of similar size in a crystal lattice without disrupting or changing the crystal structure of the mineral is called isomorphous (iso—similar, morphous—size and shape) substitution. Al^{3+} in the octahedral sheet may also be substituted by Mg^{2+}, Fe^{2+}, and Zn^{2+}. Thus, substitution of some atoms in crystals by other atoms of similar size but different valence creates positive and negative charges on colloidal surfaces (Fig. 8.2). These charges are not dependent on soil pH and are called permanent charges. Permanent charges develop in such clay colloids as smectite, vermiculite, mica, and chlorite (Sparks 2003).

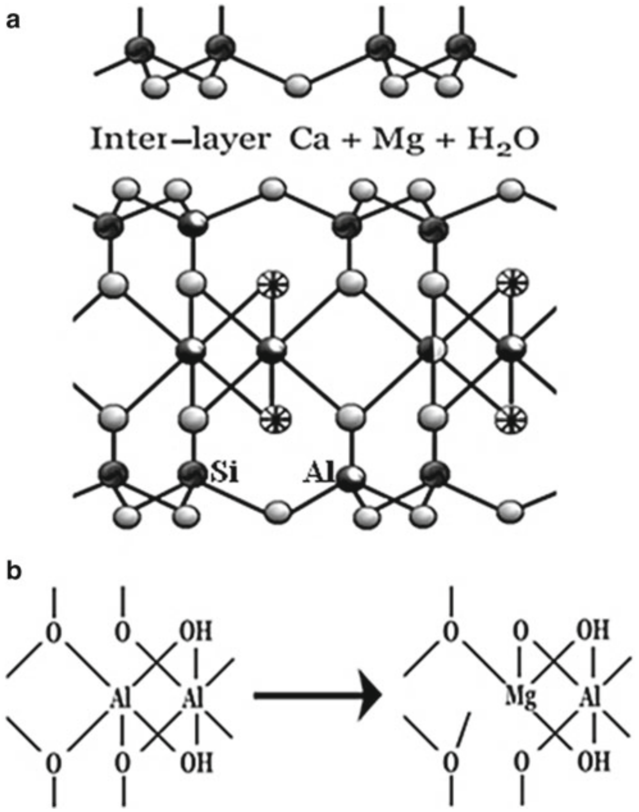

Fig. 8.2 Isomorphous substitution in the silica tetrahedral (**a**) and alumina octahedral sheet (**b**)

Variable Charges

The variable charges in soils change with pH due to protonation and deprotonation of functional groups on inorganic soil minerals such as kaolinite, amorphous materials, metal oxides, oxyhydroxides, and hydroxides and layer silicates coated with metal oxides and soil organic matter (Sparks 2003). In the 1:1 type clay, the negative charges are due to deprotonation of OH at broken edges (Fig. 8.3).

The pH-dependent charges may either be positive or negative depending on the pH of the soil. In acid soils, positive charges develop because of the protonation of the OH group on the surfaces. In alkaline medium, negative charges develop due to deprotonation of the surface O and OH groups (Fig. 8.4).

Humus colloids contain phenolic (–OH), carboxylic (–COOH), amino ($-NH_2$), and some other active groups which undergo protonation and deprotonation depending on the pH of the soil. Positive and negative charges develop due to protonation (in acidic soil) and deprotonation (in alkaline soil), respectively (Fig. 8.5).

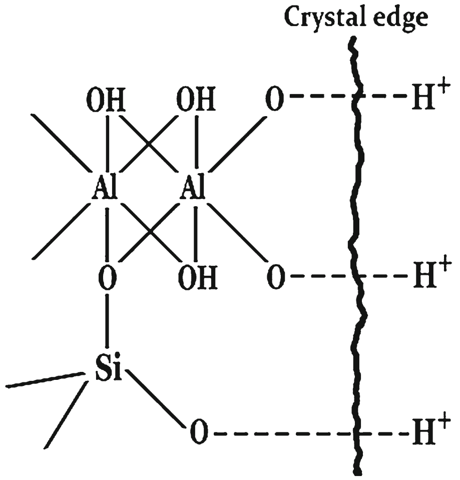

Fig. 8.3 pH-dependent charge at the broken edge of 1:1 clay

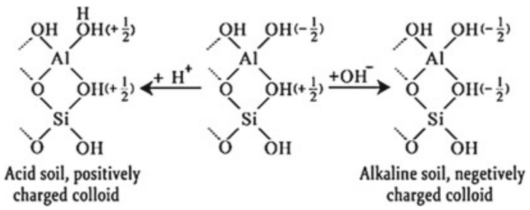

Fig. 8.4 Protonation and deprotonation of clay colloids and associated charge development

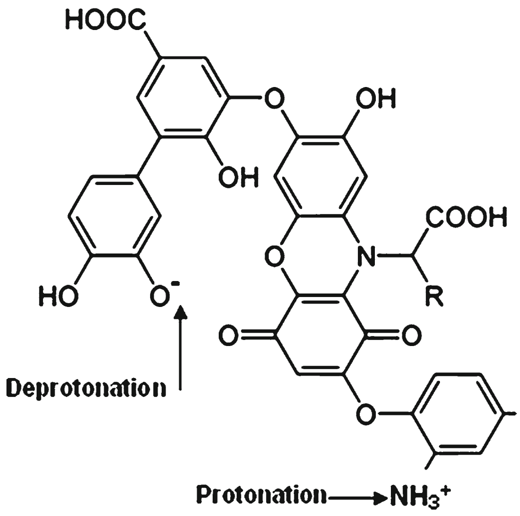

Fig. 8.5 Part of a humus molecule with protonation and deprotonation

8.4 The Soil Is a Seat of Diverse Chemical Reactions

Many diverse chemical reactions occur simultaneously in the soil. These reactions govern the solubility, availability, and mobility of important soil constituents and those introduced into the soil and groundwater system (Gee et al. 1999). Soil is a very complex chemical system, and it is difficult to predict the nature of reactions that may occur in soil at any given time. It depends on the soil environment (water, oxygen, pH, etc.) and biological activity. Many soil reactions are biologically mediated (Mulder and Cresser 1994; Gee et al. 1999). The most important chemical reactions in soils include oxidation, reduction, hydrolysis, hydration, carbonation, dissolution, chelation, precipitation, adsorption, and ion exchange. Examples of oxidation, reduction, hydrolysis, hydration, and carbonation were given in connection with biogeochemical weathering in Sect. 2.14.3. Examples of oxidation–reduction reactions are also given in connection with properties of submerged soils in Chap. 13. Oxidation and reduction of N, P, S, Fe, and Mn and hydrolysis of minerals leading to the release of nutrients are important aspects of plant nutrition (Chap. 10). Here dissolution, chelation, precipitation, adsorption, and ion exchange reactions are explained.

8.4.1 The Equilibrium Constant Represents the Solubility Product in Dissolution Reactions

Many chemical compounds are said to be insoluble, but they are actually slightly soluble in water. Moreover, the soil solution in most aerobic soils is acidic in nature; so, some minerals are slowly dissolved, although in a very low amount, in soil water. Dissolution of calcium carbonates, gypsum, oxides of Fe and Mn, and minerals is very important in relation to soil genesis, soil chemistry, and plant nutrition. During dissolution of primary minerals and formation of clay minerals, and other dissolution reactions, a solid exists in equilibrium with its solution. Thus, decomposition of kaolinite and formation of gibbsite and dissolution of lime in soil, etc., obey solubility laws (Tan 2011).

If we consider that the chemical compound to be dissolved in soil is BA and during dissolution some B^+ and A^- ions are produced, then at equilibrium, the equilibrium constant according to the law of mass action, K, is called the solubility product K_{sp}. The solubility product is defined as the product of ion concentrations in a saturated solution of a difficultly soluble solid. The dissolution reaction can be written as

$$BA \leftrightarrow B^+ + A^-,$$

Since the activity of a pure solid is unity at equilibrium, $K_{sp} = (B^+)(A^-)$

For dissolution of iron oxides such as goethite, hematite, and ferrihydrite in soils, K_{sp} values are usually extremely low ($(Fe^{3+})(OH^-)^3 = 10^{-37}$–$10^{-44}$. However, for each mineral type, K_{sp} may increase by several orders of magnitude with decreasing crystal size (Schwertmann 1991). Because the K_{sp} values are generally very small, they are often expressed in terms of ten raised to certain negative powers. For convenience, the solubility product (K_{sp}) can be expressed as pK_{sp} defined by $pK_{sp} = -\log K_{sp}$. Visconti et al. (2010) reported that reliable values for gypsum and calcite solubility products (pKs) in a water-saturated salt-affected soil were 4.62 and 8.43, respectively.

8.4.2 Chelation Is the Complexation of Metals with Organic Substances

Chelation is the process by which metals are bound to ligands or functional chelate groups. Chelates are organic molecules that can form inner-sphere complexes with divalent hard metals and heavy metals (Evangelou 1998). Some well-known synthetic chelating agents are EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriamine pentaacetic acid), CyDTA (cyclohexanediaminetetraacetic acid), EDDA [ethylenediamine-di(O-hydroxyphenyl)acetic acid], or Chel-138. These chelating agents are widely used in chemical industries and in remediation of metal contamination of the environment. There are also many natural chelating agents. All chelating agents have active groups capable of associating with the metal ion on adjacent carbon atoms. Such groups include amine, carboxyl, R_2CH–OH, R_2C=O, and RCH_2–SH. So, organic acids, amino acids, amines, and sugars can all be chelating agents if they meet the steric requirements (rearrangement of electrons in atoms or molecules affecting reactivity) for ring formation (Evangelou 1998). Figure 8.6 shows chelation of metal (M) with citrate. The common metals that form chelates in soils are Fe^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Ca^{2+}, and Mg^{2+}. Heavy metals such as Cd also frequently form chelate complexes.

8.4.3 Precipitation Is the Separation of Substances from Solution

Precipitation in soil is the formation and separation of an insoluble solid from soil solution due to a chemical change. Three types of precipitation reactions are usually found to take place in the soil system: (1) precipitation of an element due to its supersaturation in the soil solution, (2) surface precipitation, and (3) coprecipitation of elements. These reactions can potentially control the mobility of metals in soil.

A solution containing more solute than allowed at equilibrium is a supersaturated solution. Such solutions are unstable, and any further addition of solute will cause its precipitation. Precipitation from soil solution is common for Al, Fe, Si, Mn, Ca and Mg, and trace elements. Surface precipitation is the three dimensional growth of a solid on the surface of a soil particle. It occurs when the soil particle becomes increasingly covered by solid precipitate from the soil solution. Often trace elements, such as Pb, Cr, and As, will precipitate on a soil particle and become immobilized. The thermodynamic reasons for surface precipitate formation are the following: (1) the solid surface may lower the energy of nucleation by providing sterically similar sites (McBride 1991), (2) the activity of the surface precipitate is <1 (Sposito 1986), and (3) the solubility of the surface precipitate is lowered because the dielectric constant of the solution near the surface is less than that of the bulk solution (O'Day et al. 1994). The surface precipitates can form (1) through polymeric metal complexes that form on mineral surfaces and through the sorption of aqueous polymers (Chisholm-Brause et al. 1990) and (2) on a surface when the solution becomes saturated and the surface acts as a nucleation site. Coprecipitation is the incorporation of trace element into mineral structure during solid solution formation and recrystallization of minerals. The opportunity for coprecipitation is higher with Fe and Mn oxides than Al oxides or aluminosilicates. The reason for this is the higher solubility of the former two minerals under anaerobic conditions. Soil reduction generates the soluble ions, Fe^{2+} and Mn^{2+}, which then reoxidize to Fe^{3+} and Mn^{4+}, again form the insoluble oxides once the soil is aerated. Coprecipitation of trace metals may occur during these cycles of alternating reduction and oxidation (McBride 1994).

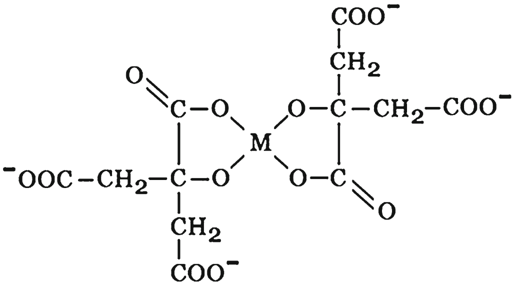

Fig. 8.6 Metal citrate chelate

8.4.4 Adsorption Is the Attraction of Gas, Liquid, or Solid on Surfaces of Colloids

Adsorption is the adhesion of atoms, ions, or molecules of gas, liquid, or dissolved solids to a surface (Brandt et al. 1993). The substance that is adsorbed is called adsorbate, and the surface on which adsorption takes place is called the adsorbent. This process creates a film of the adsorbate on the

Table 8.1 Common adsorbents and adsorbates in soil

Common adsorbents in soil	Common adsorbates in soil
Silicate clays, hydrated oxides of iron and aluminum, humic substances, coated surface, closed or open pore	Cations: Ca^{2+}, Mg^{2+}, K^+, Fe^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+}, Cd^{2+}, H^+
	Anions: $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, CrO_4^{2-}, HCO_3^-
	Dissolved organics

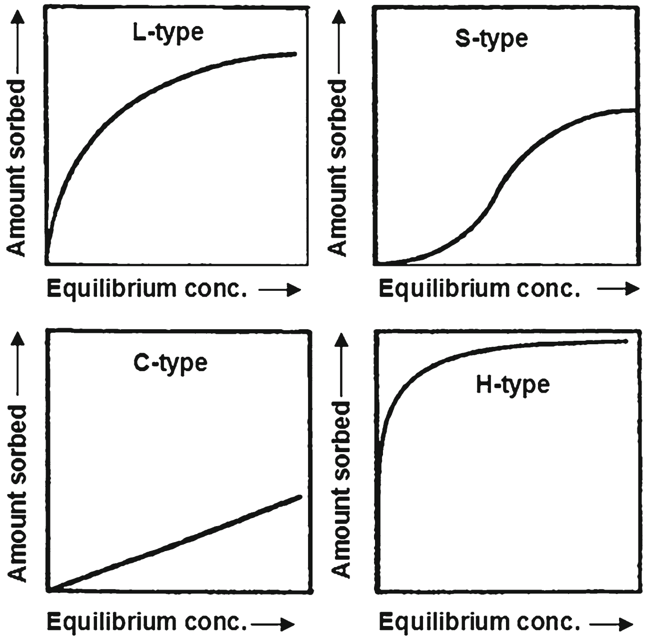

Fig. 8.7 General types of adsorption isotherm

surface of the adsorbent. Soil solids particularly the colloids act as adsorbents, and ions, polar molecules, and colloids themselves may be adsorbate. Clay and humus colloids are electrically charged particles, and against these charges, water, ions, and other colloids may be adsorbed. A list of common adsorbents and adsorbates in soil is provided in Table 8.1.

8.4.4.1 Adsorption Models

Adsorption is a reversible reaction. At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction. Two major techniques commonly used to model adsorption equilibrium processes are (1) the Freundlich technique and (2) the Langmuir technique. Both of these techniques involve adsorption isotherms. An adsorption isotherm is a curve that describes the relation between the activity or equilibrium concentration of the adsorptive and the quantity of adsorbate on the surface at constant temperature. Adsorption isotherms are classified into four types, L-, S-, C-, and H-type, depending on their general shape (McBride 1994). These types are shown in Fig. 8.7. The L-type shows high-affinity adsorption between the adsorbate and adsorbent; S-type describes the adsorbate–adsorbate interactions on the adsorbent, often referred to as clustering of the adsorbate with solution ligands; C-type indicates partitioning, which suggests interaction between a generally hydrophobic adsorbate with a hydrophobic adsorbent; and the H-type is basically an extreme case of the L-type isotherms.

8.4.4.2 Freundlich Adsorption Isotherm

Freundlich equation is an empirical model used frequently in adsorption studies in soils. Freundlich developed this model in 1909 to describe adsorption of gas molecules on solid surfaces. This model shows the relationship between the concentration of a solute on the surface of an adsorbent and the concentration of the solute in the liquid. The equation can be expressed as

$$q = K_d C^{\frac{1}{n}},$$

where q is the amount of adsorption (adsorbate per unit mass of adsorbent), C is the equilibrium concentration of the adsorptive, K_d is the distribution coefficient, and n is a correction factor. The equation produces an L-type curve. By plotting the linear form of the above equation, $\log q = 1/n \log C + \log K_d$, the slope is the value of $1/n$ and the intercept is equal to $\log K_d$. The main disadvantage of this model is that it does not predict an adsorption maximum. The single K_d term in the Freundlich equation implies that the energy of adsorption on a homogeneous surface is independent of surface coverage (Sparks 2003).

8.4.4.3 Langmuir Adsorption Isotherm

Langmuir equation is another model used commonly for explaining relationships between amount of adsorption and the equilibrium concentration of adsorbates in soil. Langmuir (1918) developed this model to describe the adsorption of gas molecules on a planar surface. Fried and Shapiro (1956) and Olsen and Watanabe (1957) applied this model first to soils in relation to phosphate adsorption. Like Freundlich equation, it is best applicable at low concentrations. The equation can be written as

$$q = \frac{kCb}{1 + kC},$$

where q and C have the same meanings as mentioned earlier, k is a constant related to the binding strength, and b is the maximum amount of adsorptive that can be adsorbed. This equation also produces an L-type curve. The Langmuir model is criticized because most of the original assumptions that Langmuir had made for developing this model are not valid in a heterogeneous system like soil. The assumptions were the following: (1) adsorption occurs on planar surfaces that have a fixed number of identical sites that can hold only one molecule (monolayer coverage), (2) adsorption is reversible, (3) there is no lateral movement of molecules on the surface, and (4) the adsorption energy is the same for all sites and independent of surface coverage (i.e., the surface is homogeneous) (Harter and Smith 1981).

8.4.4.4 Surface Complexation Models

Surface complexation models based on a molecular description of the electric double layer are being used at present to characterize adsorption. The electric double-layer theory is also a century older. According to this theory, a diffuse layer of adsorbate ions is formed adjacent to the charged surface (adsorbent). Gouy (1910) and Chapman (1913) derived an equation describing the ionic distribution in the diffuse layer. The countercharge (charge of opposite sign to the surface charge) can be a diffuse atmosphere of charge or a compact layer of bound charge together with a diffuse atmosphere of charge. The surface charge and the sublayers of compact and diffuse counterions constitute the double layer. Schofield (1947) applied the diffuse double-layer theory in soil science to study the thickness of water films on mica surfaces (Evangelou 1998). Further discussions on this theory are not within the scope of this book. Readers may get details of the electric double-layer theory in Bolt (1982). Surface complexation models include (1) the constant-capacitance model (CCM), (2) the triple-layer model (TLM), (3) the Stern variable surface charge–variable surface potential model (VSC–VSP), (4) the generalized two-layer model, and (5) one *pKa* model (Goldberg 1992).

8.4.4.5 Free Ion Activity Model

The free ion activity model is used generally to describe bioadsorption of metal ions by plant cell membranes. The free ion activity model assumes that (1) the cell membrane is the primary site for metal interactions, (2) interaction of metal ions with the plasma membrane results from surface complexation reaction which occurs rapidly leading to the establishment of pseudo-equilibrium between metal species in the bulk solution and at the membrane surface, (3) the concentration of free sites remains virtually constant, and (4) the nature of the membrane remains constant during exposure to the metal ion. The model is consistent with experimental results for systems involving divalent trace metals, a fixed pH, and a known ligand concentration. Several formulations of the free ion activity model have been tried in connection with metal ion uptake by plants but often satisfactory results are not found (Hough et al. 2005).

8.4.5 Ion Exchange Is the Replacement of One Ion from Colloidal Surface by Another

Adsorbed cations on colloids can be replaced by other cations in solution (Fig. 8.8). Similarly, one anion can replace another anion. This phenomenon is known as ion exchange. Ion exchange mechanism is used in many ways to remove ions from solution and to separate ions of various kinds from one another. It is widely utilized in the scientific laboratory for purifications and for analysis of unknown mixtures. Ion exchange materials such as zeolites are also employed commercially to purify water and medically to serve as artificial kidneys, and for other purposes.

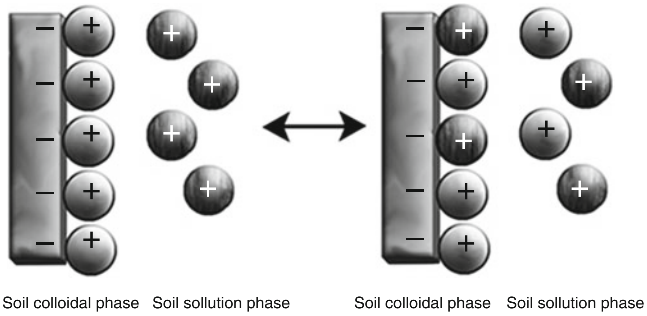

Fig. 8.8 Exchange of ions between colloidal phase and solution phase

There are cation exchange and anion exchange. The most commonly adsorbed cations on soil colloids are H^+, Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+, while the most common adsorbed anions are Cl^-, SO_4^{2-}, NO_3^-, $H_2PO_4^-$, and HCO_3^-. These adsorbed ions are loosely held and are exchangeable. This phenomenon of exchange of ions between the colloidal surfaces and solution is known as ion exchange. Ion exchange is of two types: cation exchange and anion exchange.

Cation exchange takes place when one of the cations in the soil solution replaces one of the cations on the soil colloid. Cation exchange capacity (CEC) is the capacity of unit mass of soil to hold and exchange cations at pH 7.0.

8.4.5.1 Cation Exchange Capacity

CEC is the sum total of the exchangeable cations that a soil can adsorb. The unit of CEC is $cmol_c\ kg^{-1}$. CEC of a soil is the function of the amount and type of colloids. Different types of clay minerals contain different number of charges and cation exchange capacity. Among soil colloids, humus has the greatest CEC (100–300 $cmol_c\ kg^{-1}$). Among inorganic colloids, allophanes, vermiculites, and montmorillonite have CEC values higher than 100 $cmol_c\ kg^{-1}$. However, different types of soil colloids have different cation exchange capacities (Table 8.2).

Exchangeable cations remain in equilibrium with cations in solution. When concentration of a cation increases in soil solution, for example, by fertilizer addition, exchange of ions between colloid surfaces and solution takes place to reach a new equilibrium. The replacing power of cations varies with the type of ion, its size and degree of hydration, valence, and concentration. It is controlled by a number of factors; so no single order of replacement can be given. Usually the replacing power of monovalent cations are in the following

Table 8.2 Cation exchange capacity of different soil colloids

Type of colloids	CEC, $\text{cmol}_c\ \text{kg}^{-1}$
Kaolinite	1–10
Montmorillonite	80–120
Vermiculite	120–150
Chlorite	20–40
Gibbsite, goethite	1–10
Humus	100–300

http://www.plantstress.com/Articles/min_deficiency_i/soil_fertility.pdf

order: $H^+ > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and for divalent cations: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. In case of mixture of cations as they exist in normal soils, the replaci ng power remains in the following order: $Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > Na^+$.

The factors affecting cation exchange capacity include soil texture, organic matter, nature of clay, and pH. CEC increases as the soil becomes heavier in texture (more clayey). CEC also increases with organic matter content. Soils with montmorillonite and vermiculite clay have much higher CEC than soils with kaolinite clay. As the number of negative and positive charges on most soil colloids varies with pH, it is customary to measure CEC at pH 7.0.

An Approximate Estimate of CEC of Tropical Soils

A fair estimate of CEC of tropical soils (Oxisols, Ultisols, some Inceptisols, and Entisols) may be obtained from their organic matter and clay contents by the thumb rule:

Add 1 $\text{cmol}_c\ \text{kg}^{-1}$ for each 10% clay (tropical soils are dominated by kaolinite and oxides of Fe and Al; they may have a maximum of 10 $\text{cmol}_c\ \text{kg}^{-1}$ CEC). Add 3 $\text{cmol}_c\ \text{kg}^{-1}$ for each 1% organic matter (humus has a maximum of 300 $\text{cmol}_c\ \text{kg}^{-1}$ CEC).

If a tropical soil, for example, contains 30% clay and 2% organic matter, its CEC may be around -

$$30 \times 1/10 = 3\ \text{cmol}_c \text{kg}^{-1} \text{for 30\% clay}$$

$$3 \times 2 = 6\ \text{cmol}_c \text{kg}^{-1} \text{for 2\% organic matter}$$

$$(3+6) = 9 \text{cmol}_c \text{kg}^{-1} \text{CEC for the soil}$$

The soil has an approximate CEC of 9 $\text{cmol}_c\ \text{kg}^{-1}$.

8.4.5.2 Total Exchangeable Bases

Total exchangeable bases (TEB) are the sum of exchangeable cations excluding Al^{3+} and H^+. TEB may be obtained by subtracting exchangeable H^+ and Al^{3+} from CEC or by summing up exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+. In calcareous soils, the sum of the cations ($\sum Ca^{2+}$, Mg^{2+}, K^+, Na^+) is invariably equal to the CEC because any deficit of cations on the exchange surfaces can be made up by Ca^{2+} ions from the dissolution of $CaCO_3$ (White 2006). In noncalcareous soils, however, $\sum Ca^{2+}$, Mg^{2+}, K^+, Na^+ is less than CEC. Often, TEB is taken to be a more meaningful index than CEC of soil's ability to provide plant nutrients. Usually, the higher the TEB is, the more fertile is the soil. Most base cations are essential nutrients for plant growth. Their predominance as exchangeable cations follow the order: $Ca^{2+} > Mg^{2+} > K^+$.

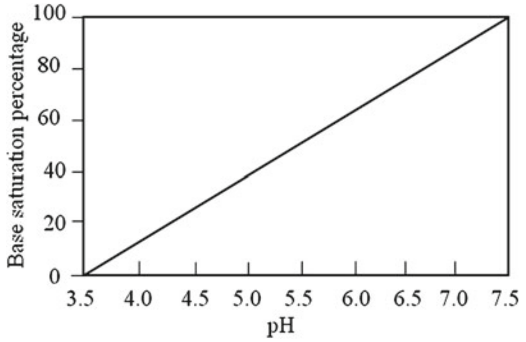

Fig. 8.9 Relationship of base saturation percentage with pH of soil

8.4.5.3 Base Saturation Percentage

Base saturation is the proportion of CEC occupied by bases. It is usually expressed as percentage.

$$\text{BSP} = \frac{\text{TEB}}{\text{CEC}} \times 100$$

$$\text{Again, BSP} = \frac{\text{CEC} - \text{exchangeable acidity}}{\text{CEC}} \times 100$$

If CEC of a soil is 10 $\text{cmol}_c\ \text{kg}^{-1}$ and the exchangeable acidity is 2 $\text{cmol}_c\ \text{kg}^{-1}$, then base saturation percentage, BSP, is 80. Such a soil must have a pH value above 7.0 because bases prevail in neutral to alkaline solution. Base saturation is roughly correlated with soil pH in many acidic to neutral soils, ranging from 20 to >60% as the pH increases from 5 to >7 (Fig. 8.9).

A high CEC does not necessarily mean high nutrient-supplying capacity, because most exchange sites remain satisfied with H and Al in acid soils. CEC and BSP together indicate better the fertility of soils. Soils with base saturation percentage lower than 50 are called dystrophic soils. They are medium to low fertility soils. Soils with base saturation percentages higher than 50 are eutrophic soils. They are high fertility soils. Alfisols have higher and Ultisols have lower exchangeable base status.

8.4.5.4 Exchangeable Sodium Percentage and Sodium Adsorption Ratio

Excessive exchangeable sodium deteriorates soil physical conditions. Soil particles, particularly colloids, remain dispersed when saturated with exchangeable Na^+. Soil aggregates are dispersed into their constituent individual soil particles. Sodium-saturated soils are impervious and have high pH (as high as 10).

$$\mathrm{ESP} = \frac{\text{Exchangeable Na}^{+}}{\mathrm{CEC}} \times 100$$

A soil is said to be sodic when it contains ESP > 15. Sodic soils are often compacted, macroporosity is greatly reduced, and water infiltration slows to the minimum. Wet sodic soil has poor infiltration and drainage, and when it dries, it becomes quite hard. Surface soil crust and hardsetting are common. In the subsoil, soil sodicity leads to decreased permeability to water and air and poor soil drainage over time. Another important index of sodicity in soil is the sodium adsorption ratio or SAR. A soil is said to be sodic if it contains SAR greater than 13. SAR is obtained by

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\dfrac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2}}{2}}}.$$

Na^+, Ca^{2+}, and Mg^{2+} are exchangeable sodium, calcium, and magnesium, $\mathrm{cmol_c\ kg^{-1}}$, respectively. Seilsepour et al. (2009) observed a relationship between SAR and ESP as

$$\mathrm{ESP} = 1.95 + 1.03\,\mathrm{SAR}.$$

Sodic soils are considered as problem soils (Chap. 11).

8.4.5.5 Anion Exchange

Colloids contain some positive charges against which anions such as SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-, and $H_2PO_4^-$ can be adsorbed. Any one of these anions or all can be replaced by a suitable anion. In other words, like cation exchange capacity, soils have anion exchange capacity (AEC) as well. But adsorbed nitrate is very readily replaced by other anions so that little nitrate is found adsorbed in any given time. Nitrate leaching from arable soils has become a serious problem of groundwater pollution and health hazard. Phosphate sorption is also a mechanism of reducing leaching of phosphate. Movement of phosphate from agricultural fields has eutrophicated many adjacent surface water reservoirs. Issues related to nitrate and phosphate leaching are discussed in Chap. 10.

8.5 Soil Reaction Is the State of Acidity or Alkalinity in a Soil

Soil reaction is denoted by soil pH. The term pH was taken from French "pouvoir hydrogene" meaning "power of hydrogen." Sorenson (1909) defined pH as the negative logarithm of hydrogen ion activity which is equal to the hydrogen ion concentration in very dilute solution. The H^+ ion concentration is expressed in moles per liter:

$$\mathrm{pH} = -\log[\mathrm{H}^{+}]$$

The pH scale ranges from 0 to 14, with a value of 7 at neutrality. A pH value less than 7 indicates acidity, while a value greater than 7 indicates alkalinity. The lower the pH, the higher is the acidity. Similarly, alkalinity increases as the pH rises. Soil pH generally lies within 4–10; however, acid sulfate soils (Chap. 11) may have pH values as low as 2. Good quality agricultural soils have pH values around 6.0–7.0. Since the pH scale is logarithmic, a difference of 1 unit pH is actually a ten-fold difference. For example, a soil with pH 5 is ten times more acid than a soil with pH 6.

8.5.1 Soil pH Is Measured from Soil–Water Suspensions

For soil pH measurement, a suspension is made with soil and distilled water at a ratio of 1:1 or 1:2 or 1:2.5 (20 g air dry soil with 20 or 40 or 50 ml distilled water, respectively). The 1:2 ratio is more frequently used. Usually, air dry soil (field moist soil will also do) is mixed with distilled water by occasional stirring for equilibration for half an hour, and the pH reading is recorded by a pH meter. Soil pH value increases by about 0.5 units as the soil–water ratio increases from 1:1 to 1:2. Therefore, it is customary to mention the ratio of measurement along with the pH value.

Soil pH is sometimes measured in a 0.01 M calcium chloride suspension of soil in order to counteracting calcium release from the soil exchange complex. Soil pH value thus obtained is generally lower than that recorded in a suspension made up with distilled water. Since pH of distilled water is itself acidic, soil pH is sometimes measured in suspension made with neutral 1 N KCl solution.

8.5.2 The pH Value May Be Estimated from H^+ and OH^- Ion Concentrations

In any dilute solution, the product of H^+ and OH^- ion concentrations is 10^{-14}. Therefore, pH may be calculated if concentration of any one of H^+ or OH^- ion is known. For example, if the concentration of OH^- ions in a dilute aqueous solution is 10^{-9} g L^{-1}, its pH may be calculated as follows:

$$\begin{aligned}
[\mathrm{H}^{+}] \times [\mathrm{OH}^{-}] &= 10^{-14} \\
[\mathrm{OH}^{-}] &= 10^{-9}\,\text{moles L}^{-1} \\
\text{So,}\,[\mathrm{H}^{+}] &= 10^{-5}\,\text{moles L}^{-1} \\
\mathrm{pH} &= -\log[\mathrm{H}^{+}] \\
&= -\log 10^{-5} \\
&= 5\log 10 \\
&= 5 \times 1 = 5.
\end{aligned}$$

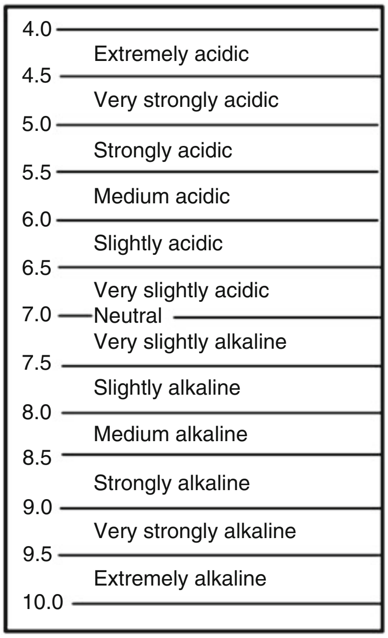

Fig. 8.10 Categories of acidity and alkalinity in soil

The pH of the soil is 5.

In any solution, the H^+ ion concentration decreases as the OH^- ion concentration increases.

8.5.3 Soils Are Classified into Different Categories of Acidity and Alkalinity on the Basis of pH

Soils are classified into several categories of acidity and alkalinity on the ranges of soil pH (Fig. 8.10).

However, for practical purposes, a soil pH range of 6.5–7.5 may be considered as neutral.

8.5.3.1 Sources of Acidity in Soil

(a) Precipitation reacts with carbon dioxide of the atmosphere; the carbonic acid thus formed is a weak acid which gives natural rainwater a pH of about 5–6. Precipitation adds acidity continuously to soils.
(b) Respiration by roots and other organisms produces carbon dioxide that also forms carbonic acid (H_2CO_3). It contributes H^+ to the soil solution.
(c) CO_2 is also produced by decomposition of organic matter in soil.
(d) Organic acids are formed by partial decomposition of organic matter.
(e) Oxidation of mineralized nitrogen and sulfur produces nitric and sulfuric acid, respectively.
(f) Soils may be acidified by fertilizers, particularly nitrogen, when used for long time in excess of crop needs.
(g) Greater precipitation results in more plant growth, causing more respiration and organic matter mineralization. Rainwater leaches soluble bases and increases soil acidity. So, soils of humid regions are more acidic than arid or semiarid soils.
(h) Soils may inherit acidity from the parent materials.
(i) Some soils may contain acid-forming compounds such as pyrite (FeS_2) which is oxidized in aerobic conditions to form H_2SO_4. These soils are called acid sulfate soils which may have pH as low as 2.0. Acid sulfate soils are formed when seawater or sulfate-rich water mixes, in the absence of oxygen, with land sediments containing iron oxide and organic matter. Mangroves, salt marshes, floodplains, swamps, wetlands, estuaries, and brackish or tidal lakes are ideal areas for acid sulfate soil formation (Lovell 2006).
(j) Aluminum ions generate soil acidity, particularly in soils that are already acidic. Al^{3+} ions cause hydrolysis during which H^+ ions are released into the soil solution.

$$\mathrm{Al^{3} + H_2O = Al(OH)_2{}^{+} + H^{+}}$$

(hydroxy aluminium)

(k) Hydroxy-aluminum may occupy exchange sites releasing H^+ from clay surfaces or may further be hydrolyzed to produce more hydrogen ions.

$$\mathrm{Al(OH)_2{}^{+} + 2H_2O = Al(OH)_3 + 2H^{+}}$$

(Gibbsite)

(l) Crop harvest results in base export along with harvested parts and may be responsible for some soil acidity in continuously cropped areas.
(m) Acid rains may bring some acid to soils.

8.5.3.2 Sources of Alkalinity in Soil

(a) Soil parent materials may be calcareous for the presence of free $CaCO_3$. Presence of lime or calcium carbonate in soil may be tested with dilute HCI which evolves carbon dioxide gas. Calcium carbonate produces OH^- ions on hydrolysis and contributes to alkalinity in soils. In calcareous soil, carbonate hydrolysis controls soil pH. If the soil remains calcareous, carbonate hydrolysis maintains a pH that ranges from 7.5 to 8.5 or more.

$$\mathrm{CaCO_3 + H_2O = Ca^{2+} + HCO_3{}^{-} + OH^{-}}$$

(b) Soils that contain Na_2CO_3 may have soil pH as high as 10, which is caused by the greater solubility of Na_2CO_3 and greater production of OH^- by hydrolysis.
(c) The weathering of many primary minerals contributes to soil alkalinity. For example, the hydrolysis of anorthite produces a moderately strong base $Ca(OH)_2$.

$$\underset{\text{(anorthite)}}{3\mathrm{CaAl_2Si_2O_8}} + 6\mathrm{H_2O} = \underset{\text{(aluminosilicate)}}{2\mathrm{HAl_4Si_6O_{10}}} + 3\mathrm{Ca(OH)_2}$$

(d) Calcium and magnesium are alkaline earth metals, and potassium and sodium are alkali metals. These cations are called basic cations, and their predominance makes soils neutral to alkaline.

(e) Soils that contain high exchangeable Na (>15% exchangeable sodium percentage ESP, or >13 sodium adsorption ratio, SAR) may have soil pH values above 10.

Table 8.3 Aluminum sensitivity/tolerance of some plants

Categories	Plants
Highly sensitive	Durham wheat, barley, lentils, chickpeas, lucerne, strawberry, Berseem, buffelgrass, tall wheatgrass
Sensitive	Canola, red clover, Balansa clover, white clover
Tolerant	Whistler, diamond bird wheat, ryegrass, tall fescue, Subterranean clover, chicory
Highly tolerant	Narrow-leaf lupins, oats, triticale, cereal rye, cocksfoot, Paspalum, yellow and slender serradella, consol lovegrass

8.5.4 Plant Growth Depends on Soil pH

Soil pH affects plant growth mainly by their roles on other soil properties including nutrient availability, elemental toxicity, and microbial activity. Although H^+ ions may exert some direct corrosive effect on root membranes at very low pH (Islam et al. 1980; Foy 1984), effects of soil pH on plants are mainly indirect. Plants suffer in acid soils from deficiency of Ca, Mg, P, and Mo and toxicity of Al, Fe, and Mn.

8.5.4.1 Nutrient Availability

Plant roots absorb soluble and exchangeable nutrient ions from soil. Soluble and exchangeable ions in soil remain in equilibrium at any given time. Since soil pH regulates the solubility of elements and compounds in soil, it also governs the availability of plant nutrients in soil. When soil pH decreases from 6.5, that is, as the soil becomes more acidic, the solubility of some elements including Fe, Al, Mn, Cu, and Zn increases and of some others, for example, Ca, Mg, and Mo decreases. On the other hand, when soil pH rises from 7.0, solubility of Ca, Mg, and Mo increases and that of Fe, Al, Mn, Cu, and Zn decreases. Aluminum, although highly predominant in soil, is not an essential element for plants. In strongly acid soils (pH below 5), solubility of Al along with Fe and Mn increases to such an extent that they become toxic to many plants. Moreover, plants may suffer from Ca and Mg deficiency in acid soils.

At low pH (<5.5), phosphorus is precipitated with Al, Fe, and Mn as their polyphosphates. At high pH (>8.0), P is precipitated with Ca. Both at soil acidity and alkalinity, P availability is reduced to deficiency levels. The predominance of the three ionic forms of P ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) is regulated by pH. Phosphorus as $H_2PO_4^-$ is more available than other forms, and it predominates at pH near 6.5. Availability of P is usually higher in the pH range of 6.5 and 7.0. Boron deficiency may also occur in strongly acidic and strongly alkaline soils. Availability of macronutrients (Ca, Mg, K, P, N, S) and Mo and B is restricted at low pH. On the other hand, availability of most micronutrients (Fe, Mn, Zn, Cu, Co) increases at low pH. The most satisfactory plant nutrient levels occur at a pH range of 5.5–6.5. Alkaline soils may have problems with deficiencies of such nutrients as zinc, copper, boron, and manganese. Soils with an extremely alkaline pH (greater than 9) are likely to have high levels of sodium which may deteriorate soil physical properties and exert toxicity on plants.

8.5.4.2 Toxicity of Al, Fe, and Mn

Toxicity of Al occurs due to predominance of Al^{3+} and $Al(OH)^{2+}$ ions in soils at pH below 5.2. $Al(OH)^{2+}$ is more toxic than Al^{3+}, and it predominates in soil at pH 4.5. Absorbed Al is accumulated in plant roots, impairing their normal functioning. Aluminum may block the uptake of Ca and may precipitate P in plant body. Aluminum may interfere with P metabolism including ATP and DNA functions. Plant roots become stunted with little branching; root tip and lateral roots become brown. Plants suffering from aluminum toxicity produce symptoms in leaves that resemble P deficiency.

Iron and manganese are essential nutrients, but their concentrations in very acidic soils may create toxicity to plant roots. Reduced forms of Fe and Mn which are predominant in O_2-depleted or waterlogged soils are more toxic than their oxidized forms. Toxicity by oxidized Fe frequently occurs in soils of pH below 4.0. Mn toxicity is likely in soils having 200–5,000 mg kg^{-1} Mn. Manganese concentrations in the range of 0.2–12 mM have been reported to produce severe growth limitations in solution culture studies of species such as cotton (*Gossypium hirsutum* L.) [Kennedy and Jones 1991], sweet potato (*Ipomoea batatas* L.) [Mortley 1993], sorghum (*Sorghum bicolor*) [Mgema and Clark 1995], and wheat (*Triticum aestivum* L.) [Taylor et al. 1991]. Aluminum sensitivity of some plants is shown in Table 8.3.

8.5.4.3 Microbial Population and Activity

Soil pH influences the microbial population, thereby regulating the biochemical transformations of mineral and organic materials in soils. Among bacteria, actinomycetes, and fungi, only fungi can thrive well in acid soils, and they outnumber bacteria and actinomycetes in such soils. Many fungal diseases of plant roots appear in acid soils. Organic matter decomposition, nitrogen mineralization, nitrification, and nitrogen fixation are reduced by soil acidity.

From the above discussion, it appears that growth and yield of crops are hampered by soil acidity and alkalinity. Some plants can tolerate acidity; they are tolerant to excess Al, Fe, and Mn or need less Ca, Mg, and P for normal growth. Management of acid and alkaline soils is discussed in Chap. 11. The following steps may, however, be taken if the soil is acidic or alkaline:

- Choose a set of crops suitable for the soil pH level.
- Adjust pH of the soil to the desired level by liming (if the soil is acidic) or acidifying (if the soil is alkaline).
- Ensure adequate irrigation and drainage to leach acids or bases.

8.5.5 Plants Have Preferences for pH

Plant species differ in their optimal soil pH requirement. Some crops may thrive best in very acid or alkaline soils, but most agriculturally important crops do well on soils of neutral pH (6.5–7.5). Legumes such as alfalfa, sweet clover, and soybeans are among these crops because the bacteria *Rhizobium* that fix nitrogen in their nodules proliferate best on neutral soils. Crops such as corn, sorghum, wheat, and cool-season grasses tolerate a wider pH range, including moderate acidity as well as neutral pH conditions. Soil pH preference of some plants is given below (Jett 2005):

pH range	Suitable crops
4.5–5.5	Azalea, camellia, rhododendron
5.5–6.0	Blackberry, chicory, gooseberry, magnolia, pineapple, potato, oats, rosemary
5.5–6.5	Apple, avocado, barley, cranberry, capsicum, melon, turnip, strawberry, wheat
6.0–6.5	Broad bean, bean, carrots, lemon, lentil, olives, parsley, pear, pumpkin, raspberry, soybean, squash, watermelon, white clover
6.0–7.5	Asparagus, broad bean, broccoli, cabbage, cauliflower, celery, cherry, chrysanthemum, cucumber, dahlia, French bean, garlic, grape, horse radish, lettuce, mulberry, mustard, onions, peach, pear, peas, peppers, plum, radish, spinach, sweet corn, tomato, turnips
6.5–7.5	Alfalfa, asparagus, avocado, barley, sugar beet, beetroot, grapevine, mushroom, spinach

8.5.6 Acidity May Be Active or Reserve

There are two types of soil acidity: active acidity and potential or reserve acidity. Active acidity of soil is based on the concentration of hydrogen ions in the soil solution, while reserve acidity is due to the amount of hydrogen and aluminum ions attached to clay and organic colloids in the soil. Reserve acidity is also known as exchangeable acidity. By soil pH, we measure the active acidity. Reserve acidity can be determined by replacing the adsorbed hydrogen and aluminum.

8.5.7 Soils Have Some Capacity to Resist Change in pH

Buffering capacity is the ability of a solution to resist changes in its pH on addition of small amount of acid or alkali. Some soils have high buffering capacity, that is, their pH values tend to remain unchanged upon addition of a considerable amount of acid or alkali. This quality of soil can be easily demonstrated by making a soil–water suspension and adding dilute acid slowly from a burette in it under a pH electrode. The pH reading will not change after addition of some acid in the beginning, pH will very slowly go down after some time, and when the buffering capacity is diminished, the pH reading will sharply fall. This resistance in the beginning is due to buffering capacity of the soil. Buffering substances in soil include weak acids and weak bases in soil solution; soluble acidic anions such as NO_3^-, HCO_3^-, and SO_4^{2-}; basic cations such as Ca^{2+} and Mg^{2+}; and exchangeable cations and anions and active groups on humus. Soils with high clay and organic matter content (i.e., higher CEC) have high buffering capacity. Calcareous soils often have high buffering capacities because free $CaCO_3$ effectively neutralizes acid.

Soils with a high buffering capacity need a great deal of liming or acidifying effort to alter pH. This is good if the soil has a desirable pH, but it can be a problem if the soil needs pH modification.

8.6 Redox Potential Is the Tendency of a Substance to Accept Electrons

Soils contain a variety of electron acceptors and electron donors. An electron acceptor is a chemical entity that accepts electrons transferred to it from another chemical entity. An electron acceptor is an oxidizing agent that, by virtue of its accepting electrons, is itself reduced in the process. Prominent oxidizing agents in soil are O_2, NO_3^-, Fe (III), Mn (IV), SO_4^{2-}, and CO_2. An electron donor donates electron during an oxidation–reduction reaction, and by donating electrons, it becomes oxidized. Electron donors are reducing agents, and prominent ones in soil are H_2, S, S^{2-}, Fe (II), Mn (II), CH_4, and organic compounds. However, oxidation is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.

Reduction is the gain of electrons or a decrease in oxidation state. A common redox reaction in soil is given below:

$$\mathrm{Fe}(\mathrm{OH})_3 + \mathrm{e}^- + 3\mathrm{H}^+ \Leftrightarrow \mathrm{Fe}^{2+} + 3\mathrm{H}_2\mathrm{O}$$

This reaction proceeds to the left (oxidation) if the soil is aerobic, and it proceeds to the right (reduction) if the O_2 supply in soil is low. This reaction or any oxidation–reduction reaction can be divided into two half reactions: one in which a chemical species undergoes oxidation and one in which another chemical species undergoes reduction. The driving force is the reduction potential if a half reaction is written as a reduction. If the half reaction is written as oxidation, the driving force is the oxidation potential related to the reduction potential by a sign change.

The redox potential is a measure of the affinity of a substance for electrons. It indicates the electronegativity of substances. Substances less electronegative than hydrogen have negative redox potentials, and substances more electronegative than hydrogen have positive redox potentials. The redox potential or oxidation–reduction potential (ORP) of a compound is measured under standard conditions against a standard reference half-cell. In biological systems, the standard redox potential is defined at pH = 7.0 versus the hydrogen electrode and partial pressure of hydrogen = 1 bar (IUPAC 2003). Redox potential is denoted by E_h and expressed in volts (V) or millivolts (mV).

8.6.1 Aeration Governs Redox Potential in Soil

Redox potential indicates the oxidation status of the soil. It varies within a wide range depending on the aeration in the soil. It may range from 100 to −300 mV in O_2-depleted soils and may be as high as 800 mV in very well aerated soils. According to Jackson (2005), well-oxidized soils, moderately well-oxidized soils, poorly oxidized soils, much-reduced soils, and extremely reduced soils may have redox potential values around 500, 300, 100, −200, and −300 mV, respectively. Thus, redox potential decreases with the depletion of oxygen level in soils. The sequence of reactions and stepwise lowering of E_h are shown in Chap. 13 on Wetland Soils.

8.6.2 There Is a Relationship Between pH and E_h of Soils

From the generalized redox reaction,

OX. (oxidizer) + ne^- + mH^+ = Red. (reducer) + m/n H_2O, the Nernst reaction can be written as

$$E_h = E_h^0 - \frac{RT}{nF}\ln\frac{(\mathrm{Red})}{\mathrm{Ox}}\left(H^+\right)^m,$$

where E_h^0 is the standard electrode potential, R is the gas constant, T is absolute temperature (Kelvin), and F is Faraday constant.

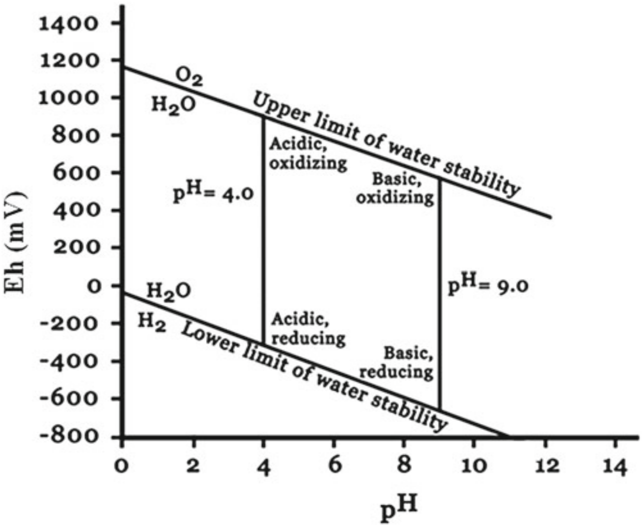

Fig. 8.11 The generalized pH–Eh relationship curve

$$\text{At } 25^\circ\text{C}, \left(\frac{RT}{F}\times 2.303\right) = 0.059\ \text{V, then}$$

$$E_h = E_h^0 - \frac{0.059}{n}\log\frac{(\mathrm{Red})}{(\mathrm{Ox})} - 0.059\frac{m}{n}\mathrm{pH}.$$

Thus, E_h increases with the increase in activity of the oxidized component, decreases with increasing activity of the reduced component, and increases with an increase in H^+ ion activity or reduction in pH (Fig. 8.11). If the ratio of proton to electron (*m*/*n*) is equal, there is a predicted 0.059 V change in E_h per unit change in pH. Since the pressure of hydrogen in surface environments could not exceed 101 kPa, the maximum possible reducing potential in the presence of water would be

$E_h = -0.059\ \mathrm{pH} - 0.03\log(1) = -0.059\ \mathrm{pH}$ (DeLaune and Reddy 2005).

Study Questions

1. What are the types of chemical reactions that occur in soils? Differentiate between precipitation and adsorption. How adsorption is related with ion exchange?
2. What are the types of colloids in soils? Distinguish between 1:1 and 2:1 clay colloids in respect of structure, swelling, and surface charge. Show the distribution of clay minerals in different soil orders.
3. What is the significance of electric charges on colloid surfaces? What is the difference between permanent and variable charges? How do charges develop on smectites and vermiculites?
4. Explain CEC, AEC, BSP, and SAR. Indicate the problems of low base status and sodicity. Why BSP in calcar-

eous soils is high? What will be the dominant cations in a soil with very low BSP? How will be its effect on soil reaction?

5. Define pH. What are the sources of H^+ ions in soil? How does soil pH affect nutrient availability and toxicity? Explain Eh and discuss its relationship with pH.

References

Bolt GH (1982) Soil chemistry. B: Physico-chemical models, 2nd rev edn. Elsevier, Amsterdam

Brandt RK, Hughes MR, Bourget LP, Truszkowska K, Greenler RG (1993) The interpretation of CO adsorbed on Pt/SiO_2 of two different particle-size distributions. Surf Sci 286:15–25

Chapman DL (1913) A contribution to the theory of electrocapillarity. Philos Mag 25(6):475–481

Chisholm-Brause CJ, O'Day PA, Brown GE Jr, Parks GA (1990) Evidence for multinuclear metal-ion complexes at solid/water interfaces from X-ray absorption spectroscopy. Nature 348:528–530

Delaune RD, Reddy KR (2005) Redox potential. In: Hillel D (ed) Encyclopedia of soils in the environment. Academic, New York

Evangelou VP (1998) Environmental soil and water chemistry principles and applications. Wiley, New York

Foy CD (1984) Physiological effects of hydrogen, aluminum, and manganese toxicities in acid soil. In: Adams F (ed) Soil acidity and liming. American Society of Agronomy, Madison

Fried M, Shapiro G (1956) Phosphate supply pattern of various soils. Soil Sci Soc Am Proc 20:471–475

Gee W, Shober A, Anderson B (1999) Chemical reactions in soils. http://www.cee.vt.edu/ewr/environmental/teach/gwprimer/group01/intro.html. Accessed 7 Oct 2011

Goldberg S (1992) Use of surface complexation models in soil chemical systems. Adv Agron 47:233–329

Gouy G (1910) Sur la constitution de la charge électrique à la surface d'un electrolyte. Ann Phys (Paris) (IV) 9:457–468

Harter RD, Smith G (1981) Langmuir equation and alternate methods of studying "adsorption" reactions in soils. In: Dowdy RH, Ryan JA, Volk VV, Baker DE (eds) Chemistry in the soil environment, Special publication no 40. American Society of Agronomy, Madison

Hough RL, Tye A, Crout N, McGrath SP, Zhang H, Young S (2005) Evaluating a free ion activity model applied to metal uptake by Lolium perenne L. grown in contaminated soils. Plant Soil 270(1):1–12

http://www.plantstress.com/Articles/min_deficiency_i/soil_fertility.pdf. Accessed 8 Nov 2011

Islam AKMS, Edwards DG, Asher CJ (1980) pH optima for crop growth. Results of a flowing solution culture experiment with six species. Plant Soil 54:339–357

IUPAC (2003) IUPAC compendium of chemical terminology. International Union of Pure and Applied Chemistry, Research Triangle Park

Jackson ML (2005) Soil chemical analysis – advanced course, Rev 2nd edn. Parallel Press, University of Wisconsin, Madison

Jett JW (2005) pH preference of plants. http://www.wvu.edu/~agexten/hortcult/homegarden/pHpref.pdf. Accessed 9 Oct 2011

Kennedy CW, Jones JE (1991) Evaluating quantitative screening methods for manganese toxicity in cotton genotypes. J Plant Nutr 14:1331–1339

Langmuir I (1918) The adsorption of gases on plane surface of glass, mica, and platinum. J Am Chem Soc 40:1361–1382

Lovell J (2006) Guidelines for environmental assurance in Australian horticulture. Horticulture Australia Ltd., Sydney

McBride MB (1991) Processes of heavy and transition metal sorption by soil minerals. In: Bolt GH, Boodt MFD, Hayes MHB, McBride MB (eds) Interactions at the soil colloid-soil solution interface 190:149–176. Kluwer, Dordrecht

McBride MB (1994) Environmental chemistry of soils. Oxford University Press, New York

Mgema WG, Clark RB (1995) Sorghum genotypic differences in tolerance to excess manganese. J Plant Nutr 18:983–993

Mortley DG (1993) Manganese toxicity and tolerance in sweet potato. Hortic Sci 28:812–813

Mulder J, Cresser MS (1994) Soil and solution chemistry. In: Moldan B, Cerny J (eds) Biogeochemistry of small catchments, a tool for environmental research. Wiley, Chichester

O'Day PA, Brown GE Jr, Parks GA (1994) X-ray absorption spectroscopy of cobalt (II) multinuclear surface complexes and surface precipitates on kaolinite. J Colloid Interf Sci 165:269–289

Olsen SR, Watanabe FS (1957) A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci Soc Am Proc 21:144–149

Schofield RK (1947) Calculation of surface areas from measurements of negative adsorption. Nature 160:408

Schwertmann U (1991) Solubility and dissolution of iron oxides. Plant Soil 130(1&2):1–25

Seilsepour M, Rashidi M, Khabbaz BG (2009) Prediction of soil exchangeable sodium percentage based on soil sodium adsorption ratio. Am-Eur J Agric Environ Sci 5(1):01–04

Sorenson SPL (1909) Enzyme studies II. The measurement and the importance of the hydrogen ion concentration in enzyme reaction. Coml Rend Tran Lab (Carlsberg) 8:1–168

Sparks DL (2003) Environmental soil chemistry, 2nd edn. Academic, Amsterdam

Sposito G (1986) Distinguishing adsorption from surface precipitation. In: Davis JA, Hayes KF (eds) Geochemical processes at mineral surfaces. Am Chem Soc Symp Ser 323:217–229

Tan KH (2011) Principles of soil chemistry, 4th edn. CRC Press, Boca Raton

Taylor GJ, Stadt KJ, Dale MRT (1991) Modelling the phytotoxicity of aluminum, cadmium, copper, manganese, nickel, and zinc stress using the Weibull frequency distribution. Can J Bot 69:359–367

Visconti F, De Paz JM, Rubio JL (2010) Calcite and gypsum solubility products in water-saturated salt-affected soil samples at 25 °C and at least up to 14 dS m^{-1}. Eur J Soil Sci 61:255–270

White RE (2006) Principles and practice of soil science: the soil as a natural resource, 4th edn. Blackwell Publishing, Malden

Wolt J (1994) Soil solution chemistry. Wiley, New York