SOIL CHEMISTRY

B. G. Lewis

Northwestern University, Evanston, Illinois, USA

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Summary

The chemistry of soil is governed primarily by the colloidal-sized fraction of the soil. This fraction consists of clay minerals, metal oxides and oxyhydroxides, and organic particulates. Contact of these solid phases with the soil solution gives rise to surface reactions that include adsorption, desorption, ion exchange, precipitation, and complexation between the particle surfaces and the molecules and ions in the soil solution. Such reactions are influenced by the net electrostatic charge on the particles, the pH of the soil solution, concentration of other ions, ligands, and molecules, ionic strength of the solution, mechanisms of ionic and molecular binding to the solid phases, and the oxidation-reduction conditions in the soil system. Adsorption mechanisms are discussed on the basis of double layer theory, physisorption, complexation, and hydrophobicity. Microorganisms in the soil also interact with the solid phases and can mediate specific oxidation-reduction reactions. Soil chemical properties and reactions affect soil fertility particularly in terms of effects on nutrient availability. Organic and inorganic soil contaminants can have adverse effects on plant growth and ground water quality; the reactions, fate and transport of these contaminants, and success of remediation methods, are strongly influenced by the physicochemical and biological characteristics of the soil. Methods for restoration and reclamation of disturbed and contaminated soils are also reviewed. Physical and chemical techniques used for physical removal of the contaminated layers or "spots", and disposal of the contaminated material are briefly described. Recently, particular emphasis is made to apply bioremediation for reclamation of contaminated soils, i.e. the use of plants and microorganisms to enhance natural processes for removing or decomposing soil contaminants.

1. Introduction

The soil is one of Earth's life-sustaining components; it serves as physical support, a source of water and nutrients, and a medium in which materials are recycled for future generations of all living things. Technically, soil is defined as the "unconsolidated material on the surface of the earth that shows evidence of life"; it is composed of inorganic and organic materials, water, and air. It is important to distinguish between a "soil" and a "soil sample." A soil is a multilayer porous medium (Figure 1) developed in place by the weathering of the underlying rock or weathering of some other parent material (e.g., alluvium) deposited upon that rock hundreds to thousands of years before. The overall behavior of a soil is dictated by the chemical, physical, and biological composition of each layer of the profile; the latter is the basis of the soil classification system (soil taxonomy) utilized worldwide. A soil sample, on the other hand, is a small portion, removed from the soil profile, and taken to a laboratory for analysis or experimentation. Extrapolation from laboratory data to soil behavior in the field requires caution.

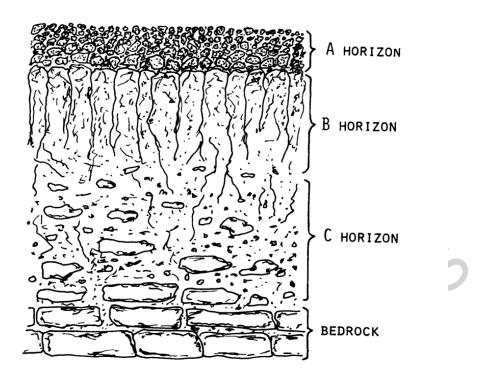


Figure 1. Diagram of a typical soil profile Adapted from Hillel D. (1980). *Fundamentals of Soil Physics*. 413 pp. New York: Academic Press.

2. Soil Composition

Typical dry soil consists of 95 percent inorganic particles and about 5 percent of organic material as coatings on the inorganic particles and as separate phases. Exceptions are histosols, commonly known as peat or bog soils, which contain up to 100 percent organic matter. The inorganic material is a mixture of primary particles (sand, 2–0.02 mm diameter; silt, 0.02–0.002 mm diameter; and clay, less than 0.002 mm diameter as defined by the International Society of Soil Science), metal oxides, and salts. The elemental composition of soil is listed in Appendix 1. Chemically, sand is quartz (SiO₂) silt consists of primary minerals such as feldspars and biotite, and clays are secondary minerals such as kaolinite, montmorillonite, and illite. The proportions of sand, silt, and clay in a soil give the soil its "texture", e.g. loam (Figure 2).

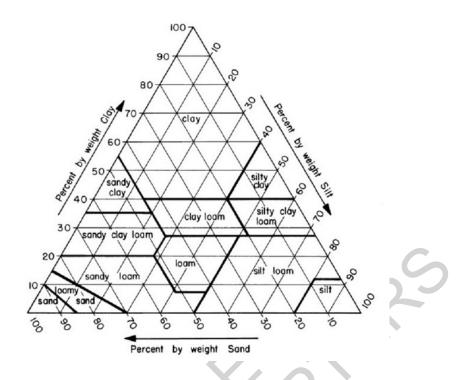


Figure 2. Soil textural diagram Adapted from Hillel D. (1980). *Fundamentals of Soil Physics*. 413 pp. New York: Academic Press.

On the basis of particle size it can be predicted that the colloidal-size fraction (particles less than 0.002 mm diameter) will be the major site of chemical reactions in a soil due to the large specific surface (surface area per unit weight) compared to that of sand or silt fractions. Specific surface of soil particles can range from 20 to 800 m² g⁻¹ for clay, $0.04 \text{ m}^2 \text{ g}^{-1}$ for silt, and 0.007 m² g⁻¹ for sand. The sand and silt fractions of a soil contribute little to chemical behavior but are important to the physical properties of a soil such as its proportion of air and water spaces (porosity), and the rate at which water can be transported from one point in the soil to another (hydraulic conductivity). The focus here is on soil chemical behavior and its basis: soil colloids and their surface reactions with the soil solution.

2.1. The Colloidal Fraction

Soil colloids include clays, metal oxides, and organic particles. The term "clay" can refer to (i) a clay soil (soil with greater than 40 percent clay particles by weight), (ii) a particle size (particles less than 0.002 mm diameter), or (iii) a specific secondary mineral (like kaolinite, montmorillonite, illite). Metal oxides and oxyhydroxides are primarily those of iron, aluminum, manganese, and titanium. Organic colloids are humic substances, that is, remains of plants and animals as well as products of microbial metabolism.

The large specific surface of soil colloids provide sites in which molecules from the soil solution can bind by Van der Waals attractive forces. Soil colloids also have electrostatic surface charge, a property that results in adsorption, binding, and exchange

of ions and molecules on particle surfaces. Surface electrostatic charge originates from isomorphous substitution, ionization of functional groups, or specific adsorption, depending upon the nature of the particle.

2.1.1. Clays

Clays are primarily aluminosilicate secondary minerals, consisting of one to several layers of silica tetrahedra and alumina octahedra (Figure 3). Binding of one layer of silica tetrahedral sheet to one layer of alumina octahedral sheet yields a 1:1 clay mineral; an example is kaolinite, in which the platy minerals stack on each other tightly bonded by hydrogen bonds such that water or other ions can not enter the layers. Such a clay is termed non-expanding. The clay mineral halloysite is a 1:1 kaolin but with water molecules between each 1:1 layer. Monovalent cations can adsorb between these layers. Halloysite is tubular rather than platy.

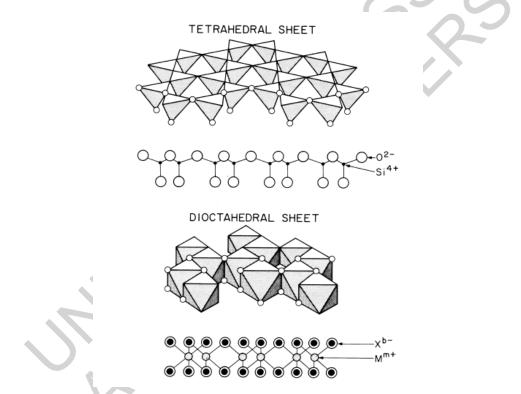


Figure 3. Diagram of SiO₄ tetrahedral and Al(OH)₆ octahedral sheets (X is hydroxyl and M is, e.g., Al). Sections with small open circles on the respective tetrahedra and octahedra are represented below each.
Adapted from Sposito, G. (1984). *The Surface Chemistry of Soils*, 234 pp. New York: Oxford University Press.

Clays with 2 layers of silica tetrahedral sheets with a layer of alumina octahedral sandwiched between them are termed 2:1 clay minerals, of which montmorillonite is an example. The layers of montmorillonite are held together loosely by water molecules and thus can expand to hold more water molecules and hydrated ions.

A third group are the 2:1:1 clays (the chlorites) that are 2:1 in terms of silica and alumina, but have, in addition, a hydroxide interlayer. The interlayer sheet is bound to the 2:1 clay electrostatically, and the tetrahedral layer is bound to the interlayer sheet by hydrogen bonds.

Other groups of clay minerals include the illite, mica, intergrade, interstratified, allophane, and fibrous groups. Identification of the various clay minerals in soil is usually carried out by x-ray diffraction techniques after the clay fraction has been separated from the soil and cleaned to remove surface coatings.

Surface charge on aluminosilicate clays arises typically from isomorphous substitution, that is, substitution of, for example, Al^{3+} for Si^{4+} in the tetrahedral layer, or Mg^{2+} for Al^{3+} in the octahedral layer of the clay mineral lattice without appreciable change in the shape or dimensions of the lattice. The result is a net negative charge, usually on the basal plane of the mineral; the charge is essentially constant because the lattice substitutions tend to be permanent. In some clays, such as kaolinite, there can be a variable charge at broken edges where functional groups such as O and OH can protonate or deprotonate, leaving a net positive or negative charge at that site. The hydroxide sheet of chlorites tends to have a positive charge because there are less than three OH⁻ per Al³⁺.

Aluminum oxides	Iron Oxides		
Bayerite α -Al(OH) ₃	Akaganeite β-FeOOH		
Boehmite γ-AlOOH	Ferrihydrite Fe ₁₀ O ₁₅ .9H ₂ O Feroxyhyte δ-FeOOH		
Diaspore α-AlOOH			
Gibbsite γ-Al(OH) ₃	Goethite α-FeOOH		
	Hematite α -Fe ₂ O ₃		
	Lepidocrocite γ-FeOOH		
	Maghemite γ -Fe ₂ O ₃		
	Magnetite Fe ₃ O ₄		
Manganese Oxides	Titanium Oxides		
Birnessite δ -MnO ₂	Anatase TiO ₂		
Pyrolusite β-MnO ₂	Rutile TiO ₂		

2.1.2. Metal Oxides and Oxyhydroxides

Table 1. Oxides, oxyhydroxides, and hydroxides in soils Adapted from Sparks D.L. (1995). *Environmental Soil Chemistry*. 267 pp. New York: Academic Press.

Oxides of aluminum, iron, and manganese do not typically occur in large quantities in temperate region soils but can be present to a greater extent in tropical and highly weathered soils (Table 1). They have high specific surface and react readily with ions in the soil solution. They can occur as discrete solid phases, as coatings on clays and organic colloids, and as mixed gels. The most common aluminum oxides are gibbsite and boehmite, an oxyhydroxide. The most common iron oxide is goethite. Birnessite,

the most common oxide of manganese in soil, acts as a natural oxidant for certain metals, e.g. As^{3+} and Cr^{3+} .

Surface charge on metal oxides usually results from ionization of functional groups, mainly hydroxides and oxyhydroxides, resulting in surfaces with variable charge whose sign is reversible and depends on protonization and deprotonization of the sites. The pH of the surrounding medium and the pH of zero charge (PZC) of the particle affect the sign and magnitude of the charge (see below). Another source of surface charge typical of metal oxides and oxyhydroxides is termed specific adsorption. For example, an anion such as orthophosphate, HPO_4^{2-} , can bind as an inner-sphere complex (no intervening water molecules between the ion and the surface) to a surface hydroxyl group of an oxide particle (iron oxide, for example), resulting in negative charge at that site (Figure 4).

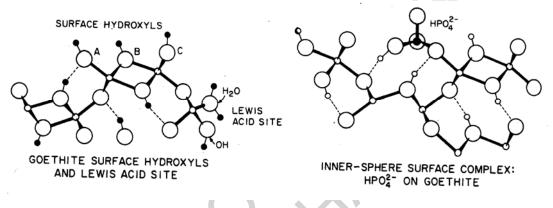


Figure 4. Specific adsorption of orthophosphate on iron oxide Adapted from Sposito, G. (1984). *The Surface Chemistry of Soils*, 234 pp. New York: Oxford University Press.

2.1.3. Organic Colloids

Soil organic matter can occur as soluble organic compounds or as organic particulate phases, commonly known as humus, and/or as coatings on clays and metal oxides. Humus includes humic substances, non-humic substances, and products of microbial metabolism. Soil organic colloids have high specific surface (up to 900 m² g⁻¹) and large amounts of negative surface charge (150 to 300 cmol kg⁻¹) due to ionization of functional groups such as carboxyl, phenolic, alcoholic, and carbonyl. This material thus can bind, or is a source of, plant nutrients, metal ions, and xenobiotic compounds (e.g. pesticides and other contaminants). Due to the variable nature of organic matter in soil, identification of individual compounds is not routinely done; rather, a definition of soil organic matter groups is determined operationally.

2.2. The Soil Solution

The soil solution refers to the aqueous phase permeating the pores of a soil; its chemical behavior is governed by the rules of aqueous chemistry except that the presence of colloids, both organic and inorganic, adds reactions involving adsorption and desorption, ion exchange, mineralogical dissolution and precipitation, and ion uptake

and exudation by plant roots. Reactions typical of the soil solution itself include oxidation and reduction, complex formation, dissolution and precipitation, and acidbase. Soil solutions include dissolved salts (approximately 0.02 N in a typical soil), soluble organic compounds, metal organic and inorganic complexes, enzymes and other soluble biochemicals. The pH of typical soil solutions range from 4 to 9, and govern the mobility and availability of nutrients and contaminants to plants as well as enzymatic activity of soil microorganisms (see *Influence of Colloids and Sediments on Water Quality*).

2.2.1. Soil Solution Effects on Particle Surface Charge

The surface charge on a colloid results in attracting or repelling ions in the adjacent solution phase, and thus governs the nature and extent of ionic and molecular binding to the particle. Regardless of the nature of the particle, it can be modeled as a solid sphere, with a uniform charge distributed over its surface, surrounded by water containing ions in solution. Distribution of these ions on and around the particle can be quantified by "double layer" theory, a simplified version of which is illustrated here (Figure 5).

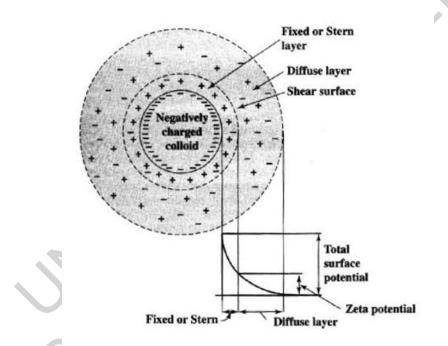


Figure 5. Schematic diagram of the double layer and electric potential around a negatively charged colloidal particle
 Adapted from Sawyer C.N., McCarty P.L., Parkin, G.F. (1994). *Chemistry for Environmental Engineering*, 608 pp. New York: McGraw-Hill.

Ions with charge opposite to that of the surface are strongly bound to the surface by the Coulombic force, and is called the "fixed" or Stern layer. Outside the Stern layer, the ions are more diffuse (the Guoy-Chapman layer). As the Coulombic force decreases with the square of the distance from the particle surface, ions of opposite charge under Brownian motion in the solution, are more diffusely attracted, while ions of the same charge as the particle surface are repelled with decreasing force. At infinite distance (the bulk solution), the cations and anions are at electroneutrality. Although this is not the

whole story (there are several models of double-layer theory), this model may help to understand some aspects of adsorption and ion exchange in soil. One difference between this simplified model and more refined models, for example, is the identification of "inner sphere" and "outer sphere" complex charges. The inner sphere complex charge arises from inner-sphere complexes, i.e. ion-pairs that have direct, short-range bonding between the ion and the particle, with no water molecules in between. Outer sphere complex charge arises from outer-sphere complexes, i.e. ion pairs that have at least one water of hydration between the ion and the particle; bonding is Coulombic and long-range.

The total surface electric potential due to the particle charge can not be measured directly but can be calculated if surface charge density (electrostatic charge per unit area of particle) is known. The zeta potential (Figure 5), which is sometimes used as an approximation of the surface potential, can be experimentally determined by measuring the electrophoretic mobility of the particle in an electric field. The extent (thickness) of the double layer (x in cm) can be estimated from the ionic strength (I) of the solution, i.e.

 $x\approx 2.8\!\times\!10^{-8}\times I^{-0.5}$

(1)

Thus, in a typical soil solution, with ionic strength about 0.02 M, the thickness of the double layer is estimated to be 2 nm. In high-ionic strength solutions such as sea water (~ 0.7 M), the diffuse layer is about 0.3 nm thick.

1

Mineral	PZC	Mineral	PZC
α -Al ₂ O ₃	9.1	β-MnO ₂	7.2
α-Al(OH) ₃	5.0	SiO ₂	2.0
γ-ΑΙΟΟΗ	8.2	ZrSiO ₄	5.0
CuO	9.5	Feldspars	2-2.4
Fe ₃ O ₄	6.5	Kaolinite	4.6
Fe(OH) ₃ amorphous	8.5	Montmorillonite	2.5
MgO	12.4	Albite	2.0
δ -MnO ₂	2.8	Chrysotile	>10

2.2.2. Solution pH and Points of Zero Charge

Table 2. Approximate values of points of zero charge (PZC) of soil minerals. Values are not necessarily comparable, as they were determined by different investigators under different conditions.

Adapted from Stumm W., Morgan J.J. (1981). *Aquatic Chemistry*, 780 pp, New York: John Wiley and Sons.

The sign and magnitude of the surface charge on a soil colloid is determined by the nature of the particle and by the pH of the solution surrounding the particle particularly in the case of metal oxides. Understanding this phenomenon is essential to predict the fate and transport of contaminants in soil, e.g. if it is assumed that Pb^{2+} in the soil will be bound tightly to the soil due to the assumed negative charge on the soil particles, the prediction will be incorrect if there is charge reversal on clays and metal oxides in the

soil under the pH conditions of the soil solution. Approximate points (pH) of zero charge of common soil minerals are listed in Table 2.

If the pH of the colloid suspension is equal to the *PZC* (pH of zero charge), then the particles have no net charge; if pH < PZC then the particles have a net positive charge; if pH > PZC, then the particles have a net negative charge.

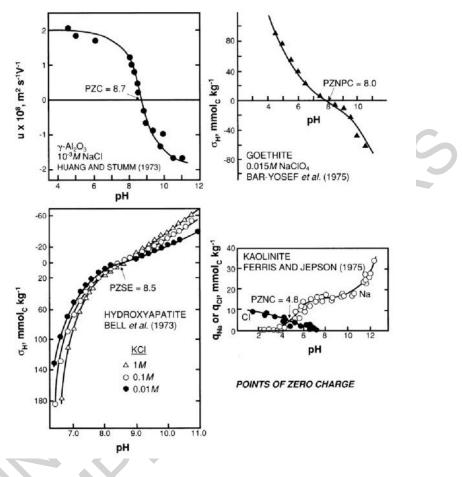


Figure 6. Examples of various points of zero charge. μ (top left) is electrophoretic mobility Adapted from Sparks D.L. (1995). *Environmental Soil Chemistry*. 267 pp. New York: Academic Press.

There is often some confusion in regard to nomenclature appearing in the literature on zero points of charge, and can be clarified by defining four components that make up the total net charge on a particle, $\sigma_{\rm p}$.

$$\sigma_{\rm P} = \sigma_{\rm O} + \sigma_{\rm H} + \sigma_{\rm IS} + \sigma_{\rm OS} \tag{2}$$

where $\sigma_{\rm O}$ is permanent charge due to structural substitutions, $\sigma_{\rm H}$ is net proton charge (difference between the moles of protons and moles of OH ions complexed by surface functional groups, $\sigma_{\rm IS}$ is inner-sphere complex charge, and $\sigma_{\rm OS}$ is outer-sphere complex charge. The total net charge on a particle must be balanced by the charge of the

diffuse swarm of ions in the surrounding solution, σ_D , such that the sum of the two is zero. Important pH values can now be defined (Figure 6):

- PZC is point of zero charge equal to the pH at which $\sigma_{\rm P} = 0$
- PZNPC is point of zero net proton charge equal to the pH at which $\sigma_{\rm H} = 0$
- PZNC is point of zero net charge equal to the pH at which $\sigma_{IS} + \sigma_{OS} + \sigma_D = 0$, i.e. the pH at which the difference between the cation exchange capacity and anion exchange capacity is zero.
- PZSE is point of zero salt effect equal to the pH at which the potentiometric titration curves intersect regardless of the background solution ionic strength.

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Hillel D. (1980). *Fundamentals of Soil Physics*. 413 pp. New York: Academic Press. [Soil physical properties, soil water – energy state, saturated and unsaturated flow; the solid phase with emphasis on clays and their physical chemistry; soil structure; gaseous phase, composite properties and behavior, soil stress-strain relations, strength, compaction, and consolidation; solutes and salinity. Has worked out example problems that are very good for self-study, but no additional problems that can be assigned. Best text book to introduce students to soil physical principles over a single quarter of a school year. A nice bonus are the epigrams at the start of each chapter that put the subject in perspective for the students.]

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Biographical Sketch

Barbara-Ann Gamboa Lewis is Associate Professor of Environmental Engineering and Science in the Department of Civil and Environmental Engineering at Northwestern University, Evanston, Illinois, USA. She obtained her B.Sc. in Chemistry (1953) from the Philippine Women's University in Manila, and her M.Sc. (1963) and Ph.D. (1971) degrees in Soil Science from the University of California, Berkeley. Her dissertation focused on the biochemical transformations of selenium in higher plants. Prior to graduate study, she was Soil Chemist for 8 years at the Bureau of Soils in the Department of Agriculture, Republic of the Philippines, studying phosphate fixation in soils, and uptake of Cs-137 by plants. After her Ph.D., she was Environmental Scientist at Argonne National Laboratory in Illinois, USA (1972 to 1979), assessing the impact of nuclear and fossil fuel electric power generation on environmental quality. Her research at Argonne included microbial dispersion of microorganisms from power plant cooling towers, and occurrence of asbestos fibers in cooling tower effluent. In 1979, she joined the faculty at Northwestern University where she teaches environmental chemistry, ecotoxicology, and soil science. Her research work has centered on restoration of land disrupted by acidic coal-cleaning refuse, uranium mill and other mining wastes, quantification of radium uptake and radon emission by vascular plants, and most recently, modeling the transport of radon in water, soils, and vegetation. She has several teaching awards from the McCormick School of Engineering at Northwestern University, she has held the Krebs Chair for Environmental Engineering and Economics, and was awarded the Palladium medal for Engineering and Conservation by the American Association of Engineering Societies. She was recently awarded a NASA Faculty Fellowship at the Jet Propulsion Laboratory in Pasadena, California, where she investigated the use of Raman spectrophotometry in the search for life in extreme environments.