

SOIL CHEMISTRY AND SOIL FERTILITY

Isam I. Bashour

Faculty of Agricultural and Food Sciences, American University of Beirut, Bliss Street, Beirut, Lebanon.

Keywords: Eutrophication, fertigation, nutrient availability, nutrient toxicity, soil formation.

Contents

1. Introduction
 2. Soil Forming Factors and Processes
 3. Soil Chemical Reactions
 - 3.1. The Inorganic Solid Phase
 - 3.2. The Organic Solid Phase
 - 3.3. The Liquid Phase
 - 3.3.1. Infiltration
 - 3.3.2. Hydrolysis
 - 3.4. The Gaseous Phase
 - 3.4.1. Soil Air Quality
 - 3.4.2. Biochemical Effect of Aeration
 - 3.5. Soil Acidity (pH)
 - 3.6. The Exchange Complex
 - 3.7. Oxidation and Reduction
 4. Soil Fertility and Plant Nutrient Uptake
 - 4.1. Nutrient Fixation and Losses
 - 4.1.1. Macronutrients
 - 4.1.2. Micronutrients
 - 4.1.3. Beneficial Elements
 - 4.2. Fertilizer Application
 - 4.2.1. Solid Fertilizers
 - 4.2.2. Fluid Fertilizers (liquid and suspension)
 - 4.3. Amount and Time of Application
 - 4.4. Fertilizer Mobility in Soils
 - 4.5. Fertilizer Salt Index
 - 4.6. Interactions and Environmental Effects
 - 4.6.1. Inorganic Fertilizers
 - 4.6.2. Organic Pollution Sources
 5. Impact of Soil Chemical Conditions on Land Use and Land Cover
- Glossary
Bibliography
Biographical Sketch

Summary

Soils are formed from the chemical and/or physical breakdown of rocks into

unconsolidated inorganic materials. This weathering process is controlled by the nature of parent material, climate, topography, biota, and time. Soil chemists study the interactions between soil solids, solution and air, and their effect on soil quality and productivity. The inorganic and organic fractions are chemically and physically active, because they work as a reservoir for water and nutrients and improve soil buffering capacity.

Plants absorb three essential elements (C, H, O) from air and water and 13 elements from soil solution in varied quantities. If these nutrients are not available in the soil in sufficient amounts they should be supplied as fertilizers for healthy and economic plant growth. These fertilizers should be placed in the soil in a position that serves the plant to the maximum. They may also be applied on leaves as foliar spray for rapid response.

The effect of fertilizers on the salinity levels of the soil solution and the extent of their movement in the soil should be well understood by farmers to avoid environmental pollution and seed injury. Applying fertilizers, especially N-sources, above recommended levels are potential sources of contamination of soil, water and air. However, trying to approach zero contamination level is unrealistic and may be harmful to food production.

1. Introduction

Soils are a mixture of different phases: solids (inorganic and organic materials, including microorganisms), liquids (water) and air; they all interact and influence each other. Soil chemistry is the discipline which studies these processes and evaluates their effect on soil properties with emphasis on the soil solution, the thin aqueous film surrounding soil particles. These processes are closely linked to soil forming factors and to pedogenesis in general.

The interactions between soil solids and soil solution are very strong and it is not always clear whether some of the ions and water really belong to the soil solution or to soil solids. The physical and chemical interactions of the soil with the atmosphere and the percolating water affect the composition of the atmosphere and the groundwater. These reactions are important for cleaning the environment after natural and human-induced pollution.

Soil chemistry has two branches focusing on inorganic and organic compounds respectively. A clear separation between these reactions is impossible and pointless because they go together and affect each other very much. Studying soil chemistry and soil fertility has been the main interest of people studying plant growth and agricultural production.

In the past, soil fertility was maintained by manure application and crop rotation—at that time the reasons for effective nutrient uptake were not properly understood. Soil fertility assessment is an important goal of soil chemistry and waste management. The ability of the soil to hold, oxidize and precipitate matter is very important for waste recycling and plant nutrition. In this chapter the chemical processes in soils which affect soil formation, soil fertility and nutrient supply will be discussed with emphasis on the

environmental context.

2. Soil Forming Factors and Processes

Pedogenesis or soil formation is the production of unconsolidated material by weathering processes and soil profile development. It is reflected in changing soil properties and in the gradual development of soil horizons. These horizons vary in thickness and depth, organic matter content, hardpans, clay movement and deposition, denseness, extent of leaching and a number of other properties. A vertical cross-section of a soil with depth is referred to as a soil profile. More than 15 000 different soils have been described in the world. There are thousands of different minerals that can be mixed in various proportions. Some soils occur in hot wet climates and others in arid dry climates. Some soils have been weathering for many thousands of years and others for much less time. All of these conditions cause differences in final soil development.

Jenny (1941) identified and described five main soil-forming factors which are primarily responsible for soil development. These are: parent material, climate, topography, biological action and time.

Parent Material. Weathering of igneous and metamorphic rocks changes dense solids into porous unconsolidated materials that differ markedly in terms of chemical composition and structure from the parent rocks. The weathering of sedimentary rocks is less striking because the differences between rocks and soils developed from these rocks are often diffuse. Table 1 shows the mineralogical composition of some common soil parent materials.

Compound	Granodiorite (%)	Basalt (%)	Shale (%)	Sandstone (%)	Limestone (%)
SiO ₂	65.1	49.3	58.1	78.3	5.2
K ₂ O	2.4	1.2	4.3	1.4	0.04
TiO ₂	0.5	2.6	0.6	0.2	0.06
Al ₂ O ₃	15.8	14.1	15.4	4.8	0.8
Fe ₂ O ₃	1.6	3.4	4.0	1.1	0.5
FeO	2.7	9.9	2.4	0.3	—
MgO	2.2	6.4	2.4	1.2	7.9
CaO	4.7	9.7	3.1	5.5	42.6
Na ₂ O	3.8	2.9	1.3	0.4	0.05
H ₂ O	1.1	—	5.0	1.6	0.8
P ₂ O ₅	0.1	0.5	0.17	0.08	0.04
SO ₃	—	—	0.6	0.07	0.05
CO ₂	—	—	2.6	5.0	41.5
Total	100	100	100	100	100

Table 1. Average composition of some common parent material rocks.
Source: Bohn *et al.*, (2001).

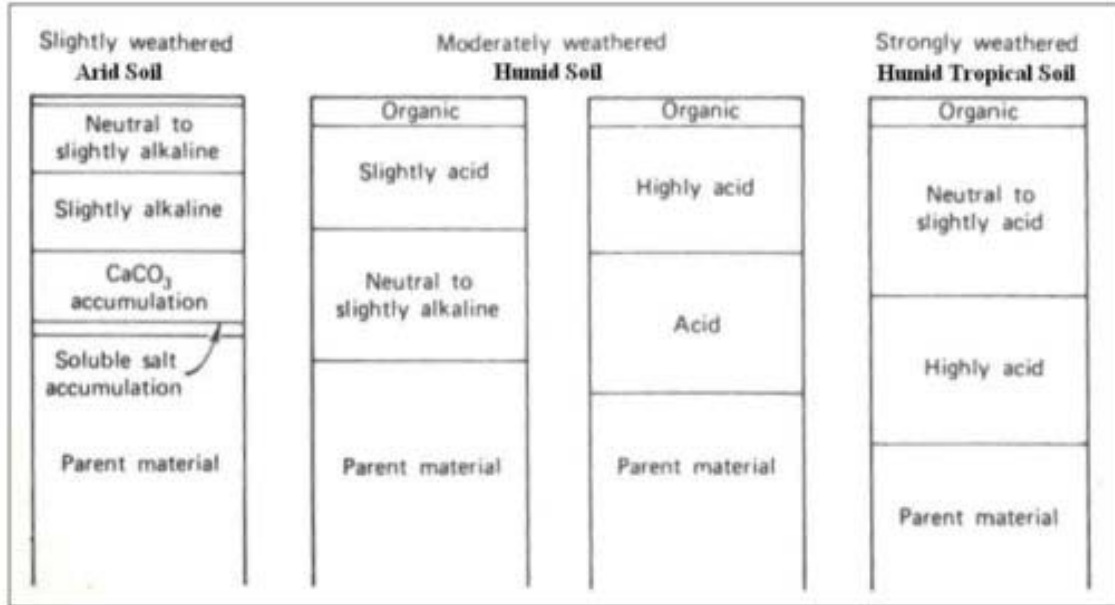


Figure 1. Sequence of soil profiles from arid to humid tropical regions.

Source: Bohn *et. al.* (2001).

Climate. The climate interferes in rock weathering both by its temperature variations (and its influence of internal pressures) and in the amount of water that is available in the rock or soil to dissolve mineral components. Rocks formed beneath the Earth's surface become unstable when occurring at the surface because of the climatic actions referred to above.

The physical processes related to erosion, freezing and thawing, and heating and cooling break rocks apart. The biggest change comes, however, from a number of chemical reactions, in particular related to the exposure to water, oxygen, CO₂ and organic compounds. In the soil solution (the liquid phase of the soil and its solutes) some ions combine to create new solids that are stable under Earth-surface conditions (secondary minerals). Later, the composition of the soil solution as a whole may change to cause the newly formed minerals to re-dissolve and re-precipitate forming other minerals. Figure 1 represents the course of weathering in a soil profile under arid, humid and humid tropical climates.

Chemical processes affecting rock and soil weathering are more or less intensive depending on the amount of water available. A major result of such processes is the formation of basic cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺). Some soils contain high amounts of cations, others hold less. The difference is due to the nature of the parent rock (basic like basalt or acidic like granite), degree of water availability and leaching of the basic cations. Clay minerals are negatively charged due to isomorphous substitution phenomena (substituting one element for another in the structure of the clay mineral without changing the arrangement of atoms in the mineral) and the pH dependent charges. These negative charges are usually neutralized with positive charges (cations) in soil solution and on the exchange complex. Therefore, an equilibrium should always exist between the negative charge of the soil components and the cations in solution.

When the concentration of basic cations (or exchange complex) in the soil solution decreases their place is occupied by H^+ and/or Al^{3+} , the soil becomes acidic and a hydrolysis of Al^{3+} and Fe^{3+} takes place. When this hydrolysis comes near completion, the surface soil pH returns to near neutrality.

Topography affects soil formation primarily in that it modifies the water and temperature status in the profile. Soils on steep hills have much less water moving down the profile than in land locked depressions that receive runoff water from surrounding higher areas. Oxygen deficiency in water-logged soils results in an accumulation of large amounts of organic material.

The direction in which a slope faces is the slope aspect. In the northern hemisphere, north-facing slopes are shallower than south-facing slopes because they are cooler and receive less direct solar radiation. In arid climates where moisture is limiting, cooler soil temperatures and less evaporation are conducive to deeper soils on north slopes. The opposite is true in the southern hemisphere.

Biota. Living plants and animals and their organic wastes and residues (the biota) have a marked influence on soil development, mainly for two reasons. First because they release acids in the soil, which react with the mineral fraction; and second because larger animals form holes and corridors for water and air penetration. Moreover, decaying organic material forms humus that improves soil structure while humification liberates nitrogen gasses which react with other soil components.

Earthworms, ants, termites, gophers, moles and other burrowing animals are important in soil formation when they exist in large numbers. Soils in a humid forest are rich in decayed humus material and have slowly decomposing organic matter layers on the surface. In contrast, soils in grasslands have well decomposed organic matter which concentrates in a dark layer from the surface to a depth of 30 cm or more into the mineral soil.

Time has an intensifying effect in the sense that the longer a process can be active, the more impact it will have on the changes which it creates in the environment. In Jenny's concept the weathering rate is related to the five factors by the relation:

$$\frac{\Delta \text{Weathering}}{\Delta \text{Time}} = f(\text{climate, topography, parent material, biosphere})$$

The relative importance of each factor in the above equation varies with local and regional conditions. Converting this equation into a quantitative equation is not possible at present because none of the five factors has been described numerically. Under favorable conditions a recognizable soil profile (loose sediments) may develop within 200 years, but under less favorable conditions the time may be extended to thousands of years.

The five forming factors mentioned above interact to produce natural soils. As human populations have grown, they have directly or indirectly created soils on a small scale and affected soil properties. For example, the regular additions of organic matter have

produced soils with thicker A-horizons and increased the phosphorous content. Archeologists rely on high soil organic matter and phosphorous to identify human habitation sites. Changes in landscape, golf courses, strip mining and reconstruction activities are good examples of the effect of man on soil formation.

3. Soil Chemical Reactions

Soil chemical reactions concern in the first place interactions between the inorganic and organic solid phases as well as the liquid and gaseous phases, and the processes related to isomorphous substitution, oxidation, hydrolysis, solution and acidification, as discussed below.

3.1. The Inorganic Solid Phase

The inorganic (or mineral) fraction is composed of particles with a diameter ranging from colloidal size (<2 μm) to gravel size (>2 mm), and includes primary and secondary soil minerals. In most soils, the sand and silt fractions consist mainly of quartz and feldspars and lesser quantities of other primary minerals such as micas, pyroxenes, amphiboles and olivine. The minerals in the clay fraction are mainly secondary and include carbonates (CaCO₃ and Ca.MgCO₃); S-minerals (CaSO₄.2H₂O and FeS₂); silicates and various oxides. Jackson and Sherman (1953) grouped clay minerals as summarized in Table 2. The most important secondary minerals in the clay fraction are the layer silicates because they have a great influence on soil properties.

A typical layer silicate may be a combination of two types of structural units (Si-tetrahedral sheet and Al, Mg, Fe²⁺, Fe³⁺ octahedral sheet). These two sheets are bounded together by a layer of shared oxygen. In the 1:1 layer silicates (kaolin groups) are formed from the superposition of a tetrahedral sheet upon an octahedral sheet (C-spacing = 0.72 nm). In the 2:1 layer silicates (pyrophyllite group); the unit layer is one octahedral sheet sandwiched between, and sharing oxygen atoms with, two tetrahedral sheets (c-spacing = 0.93 nm). A more in-depth discussion on these topics can be found in *Soil Mineralogy*.

Relative degree of soil development	Prominent minerals in soil clay fraction
1	Gypsum, sulfides, and soluble salts
2	Calcite, dolomite, and apatite
3	Olivine, amphiboles, and pyroxenes
4	Micas and chlorite
5	Feldspars
6	Quartz
7	Muscovite
8	Vermiculite and hydrous micas
9	Montmorillonite
10	Kaolinite and halloysite
11	Gibbsite and allophone
12	Goethite, limonite, and hematite

13	Titanium oxides, zircon, and corundum
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Table 2. Sequence of clay mineral distribution with increasing soil development

Source: Jackson and Sherman, 1953.

Layer silicate clays have negative charges. The major source of the negative charge arises from replacement of either Si^{4+} or Al^{3+} cations with cations of lower charge (*isomorphic substitution*). Isomorphic substitution occurs during the formation of minerals and is thus largely unaffected by present environmental conditions. It is uniformly distributed over the surface of clay minerals. Another source of negative charge on clay minerals is associated with the “broken edges” of the layer silicates and is affected by the pH of the soil solution; hence the term *pH-dependent charge*.

Under acid conditions (low pH) broken edges are positively charged because of the excess of H^+ ions associated with the exposed Si-OH and Al-OH groups. As the pH of the soil solution increases, some H^+ ions are neutralized and the negative charge on the broken edge increases. Only about 5 to 10% of the negative charge on 2:1 clays is pH dependent, while the majority of the 1:1 clay minerals are pH-dependent.

3.2. The Organic Solid Phase

The organic fraction of the soil consists of dead plants, animal residue and living organisms. The decomposed organic fraction is the most active portion of the soil. It promotes good soil structure, good air and water relations, a large reservoir of carbon, a source of CEC and soil buffering capacity (the ability of a soil to re-supply and ion to the soil solution).

Humus is the decomposed organic material that has been transformed into a relatively stable form by soil microorganisms. The composition of soil humus is complex and incompletely understood. The heterogeneous mixture of molecules range in molecular weight from a few hundred to over 300 000. Both humic and fulvic acids are the product of soil organic matter decomposition. Humic acid molecular weight is much larger than that of fulvic acid.

Soil humus is highly colloidal and amorphous; its surface area is larger than the surface area of the silicate clays. Therefore, it affects the colloidal properties of the soil and its adsorptive capacities more than the silicate minerals (the larger the surface area of the colloids the more reactive the material). The negative charge of humus is mainly due to the dissociation of H^+ from fractional groups leaving a negative charge on the functional groups, and is strongly pH dependent ($\text{R-COOH} \rightarrow \text{R-COO}^- + \text{H}^+$). No soil organic matter fraction possessing a net positive charge has been found at normal pH values. Some groups in humus have positive charges, but the overall charge on the humus remains negative and has the ability to retain cations and anions in exchangeable forms. Therefore, soils containing larger amounts of decomposed organic material (humus) are usually fertile, have high CEC values, high water holding capacity and are well aggregated.

3.3. The Liquid Phase

The liquid phase is also called soil water, soil moisture or soil solution. It is composed of water, dissolved substances and colloidal materials that are located in the macro- and micro-pores. Water is held in pore spaces by forces of attraction exerted by the soil matrix, ions and surface tension in the capillaries. The two major reactions responsible for holding water in soils are adhesion and cohesion. Adhesion is the attraction of solid surfaces to water and cohesion is the mutual attraction between water molecules. The water held in the soil constitutes the reserve water supply for plant use between additions of water by rain or irrigation. The forces holding water in soil, expressed in terms of energy levels such as matric (ψ_m), osmotic (ψ_o) and pressure potential (ψ_p) are collectively called water potential (ψ_w). The formula for water potential is written as follows (Tan, 2000):

$$\Psi_w = \Psi_m + \Psi_o + \Psi_p$$

Water moves in soils from high to low potentials. The water potential (Ψ_w) has a negative value because the attraction by matric and osmotic forces reduces the free energy level of soil water, i.e. soil water held by the soil matrix and solutes can't move freely.

The water potentials can be expressed in terms of positive values (suction force which is called soil moisture tension) that can be expressed in pounds / inch², cm of water, bars and pF. The unit cm of water is the basic unit; it is defined as the force equal to the weight of the height of a water column in cm. It is interpreted in the same way as cm Hg is interpreted for barometric pressures. A moisture tension of zero cm indicates the presence of excess water and of 10 000 000 cm means that the soil is dry. A more detailed discussion on this topic can be found in *Soil Physics*. The following terms are important in the context of this paper:

pF = log cm H₂O;

pF = 0 means no tension i.e. soil is saturated with water and

pF = 7 means very high tension i.e. soil is dry

At field capacity, the soil moisture tension = 0.333 bars = **pF** of 2.54

3.3.1. Infiltration

The term infiltration refers to the entry of liquid (water) into the soil. It is driven mainly by the attraction of water to dry pores and surfaces (from high to low potential). Gravity helps in downward infiltration. The boundary between wet and dry soil is called the wetting front. Ahead of the wetting front the soil stays at its original water content and behind the front, it is close to saturation. The depth of water penetration is often easy to feel by pushing a rod into the soil or by placing a tensiometer set at the required depth.

The infiltration rate is usually limited by the rate at which water is applied. It is important that the infiltration rate be higher than the rate of irrigation or rain to prevent water ponding. Ponding can increase runoff, erosion and unevenness of watering. This is common with heavy irrigation or prolonged rain. The rate of infiltration depends on

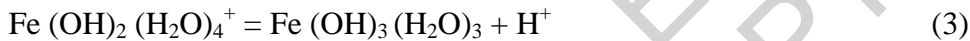
soil properties such as texture, structure, porosity and mineralogy. Infiltration slows down as it proceeds and the wetting front is further extended. It will slow even more if the wetting front meets an impermeable compacted, clayey or cemented subsoil layer. This must be taken into account in deciding how much irrigation water to apply. During heavy rainstorms, runoff accelerates as infiltration slows down. This is why one long storm contributes more than many short storms to watershed yield, stream flooding and soil erosion.

3.3.2. Hydrolysis

The attraction of cations for water molecules is so strong that the cation's charge tends to repel H^+ ions from the water ligands in the solvation sphere:



This reaction is called hydrolysis, because it splits a water molecule according to the formulae:



The uncharged $Fe(OH)_3(H_2O)_3$ species is less water soluble than the charged ions. Once it loses the water molecules it precipitates as $FeOOH$. The $FeOOH$ molecules are more stable than $Fe(OH)_3$.

The hydrolysis reactions (1, 2, 3 and 4) oversimplify the actual mechanism of hydrolysis of Fe. The hydrolyzed ions associate and form polynuclear ions, which get enlarged with further hydrolysis. These ions exist as soluble ions in water for a long time before they precipitate as solids.

The hydrolysis of Fe^{3+} can happen to Al^{3+} and all other cations in soil, but the extent varies widely. Ions in water interact with water molecules and with each other. These interactions affect the chemical potential of the soil solution and the movement of ions in percolated water through a soil profile to produce different soils under different climates as explained in section 2.

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Biographical Sketch

Isam Bashour is a professor and chairperson of the Land and Water Resources Department, Faculty of Agricultural and Food Sciences, American University of Beirut, Lebanon. He holds a PhD in soil Science and Plant Nutrition (1977) from the University of California-Davis.

He has been active for more than twenty five years in teaching, research and consultation in the fields of soil fertilization, reclamation and crop management in arid and semi-arid regions. He developed and

formulated acidic fertilizers in different forms: granular, suspension, liquid and soluble powder. His research has mainly focused on soil fertility of various crops and fruit trees with emphasis on fertigation. He also has written many technical reports to FAO, NGOs and national agencies in the Near East.

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