Chapter I: Soil Physicochemical Dynamics

1. The Clay–Humus Complex (CHC) : Clay Structure, Humus Formation, and Cation Exchange Capacity (CEC)

The word “soil” has several meanings. In its traditional sense, soil is the natural medium that supports plant growth. Soil has also been defined as a natural body consisting of superimposed layers, or horizons, commonly designated by letters such as O, A, B, E, and C. These horizons are composed of weathered mineral materials, organic matter, air, and water. Soil is distinguished from the Earth’s crust by the significant presence of living organisms. It is sometimes described as “the living skin of our planet.”

Soil constitutes an interface between the lithosphere, atmosphere, and hydrosphere. It is the product of the combined effects of climate, topography, and the activity of organisms—including flora, fauna, and humans who use and cultivate the land—acting on parent materials (rocks and minerals) over time.

Soil consists of three distinct phases :

-**The solid phase,** which comprises mineral constituents (sand, clay, etc.) and organic constituents, including organic matter (OM).

-**The liquid phase**, also known as the soil solution, which consists of water containing dissolved soluble substances, such as salts. These substances originate from the weathering of rocks, the mineralization of organic matter, and anthropogenic inputs, such as the application of soluble or readily solubilizable fertilizers.

-**The gaseous phase**, or soil atmosphere (also referred to as the vapor phase), which contains the same gases as atmospheric air, together with additional gases generated through the decomposition of organic matter.

Table 1 : Nature of the Various Soil Constituents (Solid, Liquid, and Gaseous Phases)

Solid Constituents		**Liquid Constituents**	**Gaseous Constituents**
Mineral constituents	**Organic constituents**	**Soil solution**	**Soil atmosphere**
Fine-earth fraction: -Clay -Fine silt -Coarse silt -Fine sand -Coarse sand	Fresh organic matter: -Components of plant tissues (cellulose, hemicellulose, tannins, etc.) -Animal excreta and dead organisms	Soil water and dissolved substances : -Organic substances (organic acids, sugars, etc.) -Ions in the soil solution : Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, NO_3^{-}, PO_4^{3-}, etc.	Atmospheric gases : N_2, O_2, CO_2 Gases resulting from soil animal activity and decomposition processes: CO_2, H_2, CH_4, etc.
Coarse fragments : -Gravel -Pebbles -Stones -Boulders	Humic substances : -Transformed organic matter		

To understand how these various soil constituents are organized, a vertical section of the soil, known as a soil profile, can be examined to reveal the different layers, which are generally more or less parallel to the soil surface. These layers differ in their composition, colour, structure, and texture (e.g., darker layers generally contain higher amounts of organic matter).

These layers, known as soil horizons, are the result of a range of geological, physical, chemical, and biological processes that have acted on the parent materials over time. Most soils typically exhibit three or four main horizons, commonly designated by the letters O, A, E, B, and C (Figure 1).

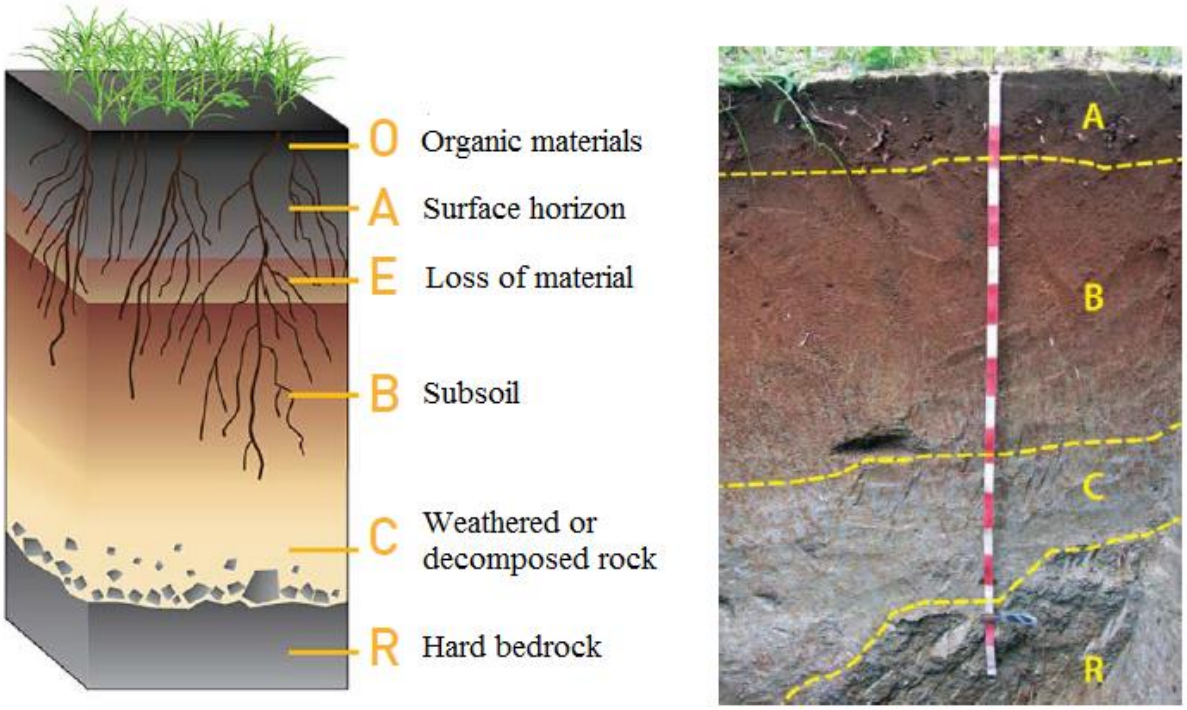

Figure 1 : Schematic representation of a theoretical soil profile, showing in cross-section the different layers or horizons, together with a photograph of a soil profile. It should be noted that other specialized horizons may also occur, such as the S horizon, known as the weathering horizon. This is a weakly developed B horizon characterized by changes in colour and the development of a distinct pedogenic structure, which replaces the original structure of the parent rock. However, there is no significant enrichment in clay or other materials.

1.1. Clay Structure

Clay are minerals that occur as microscopic sheets or layers, hence the term “phyllites.” They therefore belong, like micas, to the group of phyllosilicates. Each crystal consists of several hundred stacked sheets, each of nanometre-scale dimensions. The structure of the elementary sheet determines the mineral species. Each sheet is composed of two, three, or four layers.

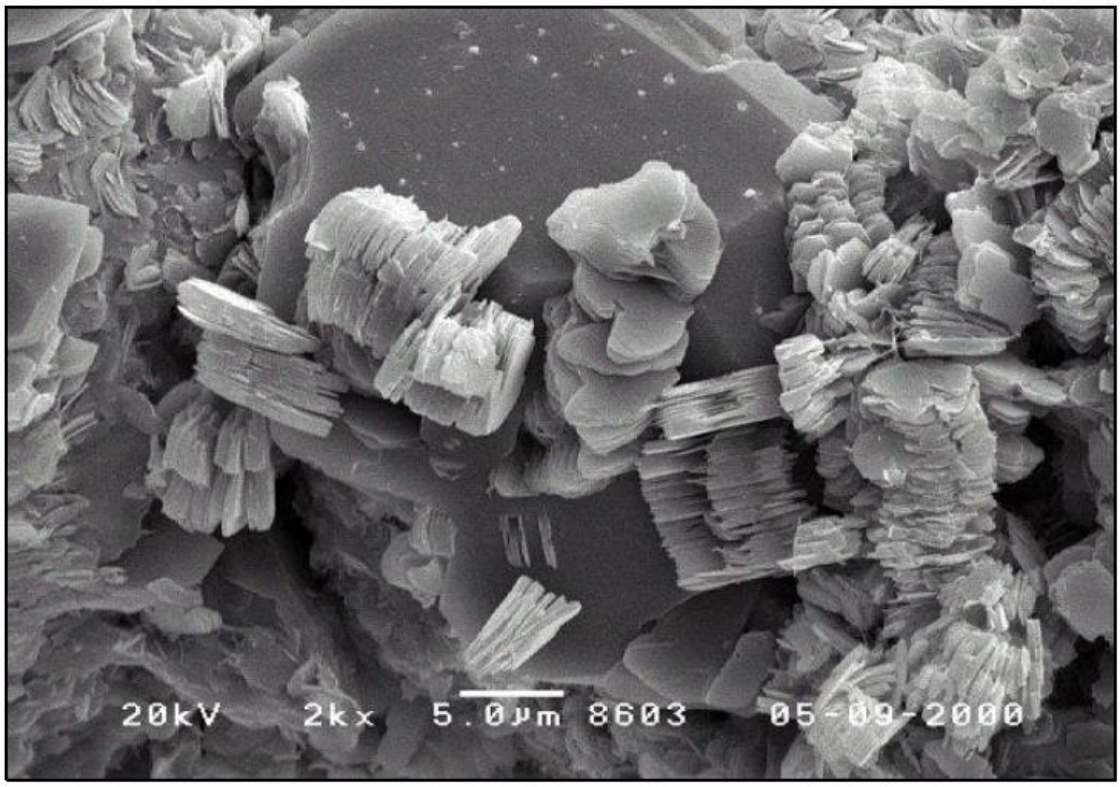

Figure 2 : Sheet-like structure of clay minerals observed by scanning electron microscopy (SEM).

Clay minerals possess a highly organized crystalline structure composed of stacked sheets. Oxygen, aluminium, magnesium, and potassium occur in ionic form. These ions are arranged as spheres, fitting together like pieces of a construction set and held together by electrostatic forces. Some ions may be substituted for others. Each type of structural association represents a group of clay minerals. Moreover, silicon, aluminium, and iron can sometimes substitute for one another without altering the overall structure, resulting in the occurrence of several mineral species. Accordingly, six major groups of clay minerals are recognized, comprising more than fifty mineral species.

Depending on ionic radii, the most common substitutions in phyllosilicates are:

-Si^{4+} may be substituted by Al^{3+} in tetrahedral sites; the ionic radius of Al^{3+} also allows it to occupy octahedral sites.

-Si^{4+} may also be substituted by Fe^{3+} and Ti^{4+}.

-Mg^{2+}, Fe^{2+}, and Mn^{2+} may substitute for one another.

Clay minerals are commonly referred to as “clays” because they possess certain properties, such as swelling, water sorption, and the ability to transform into a mud-like state.

The first six groups consist of sheet-structured minerals:

-**Minerals of the kaolinite group:** kaolinite, halloysite, dickite, and nacrite are two-layer minerals. They consist of one tetrahedral layer with a silicon-centered structure and one octahedral layer with an aluminium-centered structure. The structural chemical formula is $Si_2Al_2O_5(H_2O)_2$. The interlayer spacing is 7 Å. Kaolinite is used for paper coating and in the manufacture of porcelain.

-**Illites**, named after the U.S. state of Illinois, are three-layer minerals consisting of an octahedral layer with an aluminium-centered structure sandwiched between two tetrahedral layers with silicon-centered structures. The structural chemical formula of illite is $KAl_2(OH)_2(AlSi_3(O,OH)_{10})$. The interlayer spacing is 10 Å.

-**Smectites**, from the Greek word *mektos*, meaning "I cleanse," or the montmorillonite group, named after Montmorillon in the Vienne department of France, have the same three-layer structural arrangement as illites. The chemical formula of smectites is $Si_8Al_4O_{22}(H_2O)_2(H_2O)_n$. The interlayer spacing ranges from 14 to 17 Å. In this group, the sheets are thin and weakly bonded to one another, allowing water and organic matter to enter the interlayer space. This property accounts for the term "expanding clays."

-**Bentonite** is a colloidal clay whose name derives from Fort Benton, Wyoming, USA. Also known as "fuller's earth," it can be regarded as a smectite, consisting predominantly of montmorillonite, $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2(H_2O)_n$ (approximately 80%), which accounts for its high water-retention capacity.

-**The chlorite group** derives its name from the Greek word *chloros*, meaning "pale green" or "yellowish green," referring to the colour of chlorine gas. Chlorites are green clays used for various medicinal applications. Their sheets are closely bound to one another by hydrated groups containing magnesium, aluminium, and iron. The interlayer spacing is approximately 14 Å.

-**Vermiculites** derive their name from their worm-like appearance after heating, from the Latin *vermiculus*, meaning "little worm." The water contained between their sheets can be removed by heating to temperatures above 300 °C. The interlayer spacing consequently decreases from 14 to 10 Å. Vermiculites are used in the construction industry as insulating materials.

Table 2 : Different Types of Clay Minerals and Their Characteristics

Mineral species	**Chemical formula**	**Number of layers**	**Interlayer spacing**	**Type**
Kaolinite	Si2Al2O5(H2O)2	Two-layer minerals	7 Å	Non-expanding
Illite	$KAl_2(OH)_2 \cdot (AlSi_3(O,OH)_{10})$	Three-layer minerals	10 Å	Non-expanding
Smectite (or montmorillonite)	$Si_8Al_4O_{22}(H_2O)_2 \cdot (H_2O)_n$	Three-layer minerals	10–17.5 Å	Expanding
Bentonite	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot (H_2O)_n$	Three-layer minerals	-	Expanding
Chlorite	$(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$	Three-layer minerals	14 Å	Non-expanding
Vermiculite	$(Mg,Ca)_{0.7}(Mg,Fe,Al)_6(Al,Si)_8O_{22}(OH)_4 \cdot 8H_2O$	Two-layer minerals	10-14 Å	Expanding

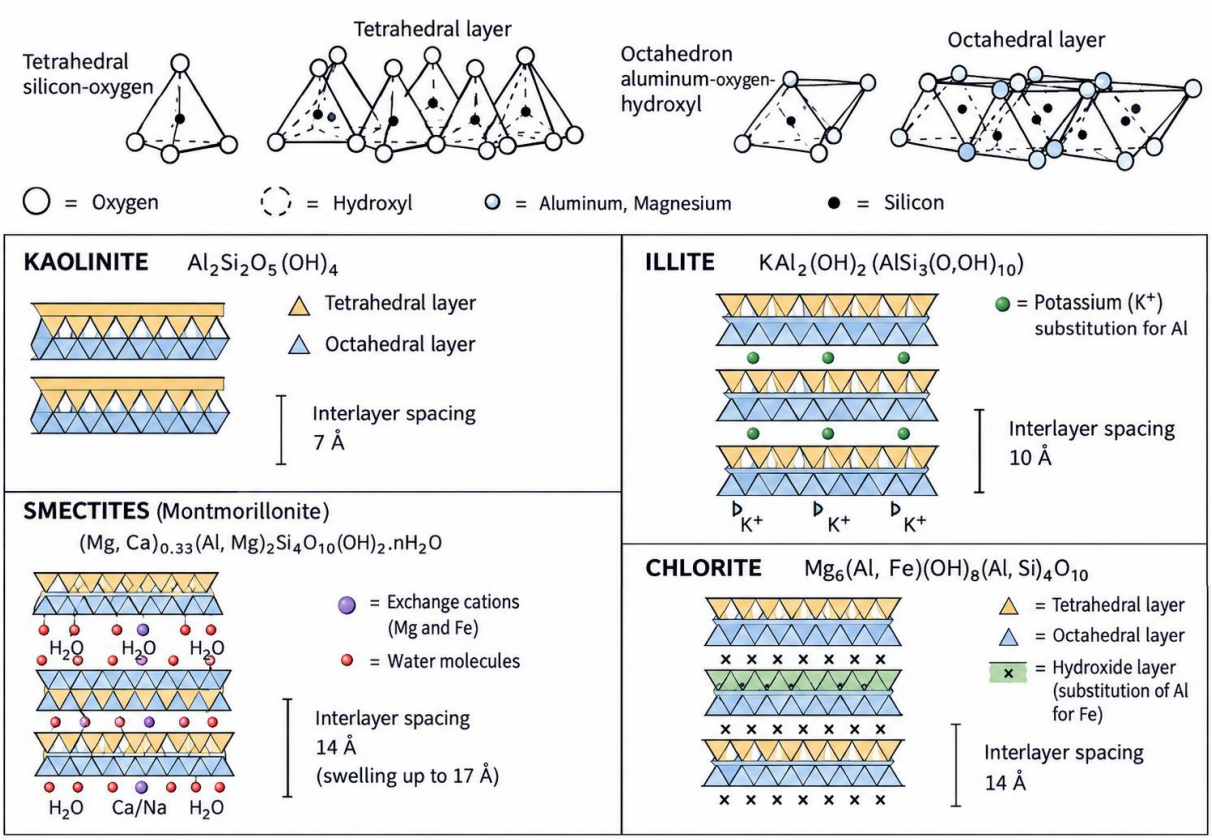

Figure 3 : Crystal structures of clay minerals.

Origins of Clay Minerals

Clay minerals do not generally form as primary minerals in igneous or metamorphic rocks associated with the internal geodynamics of the Earth. Rather, they are primarily associated with the external geodynamics of the Earth, particularly with sedimentary rocks and with weathering products (alterites) derived from the alteration of various types of rocks, including igneous and metamorphic rocks. Clay minerals therefore form mainly at or near the Earth's surface.

Clays are both weathering-derived and detrital minerals resulting from the alteration of primary silicate minerals. This process can be represented as follows :

Primary silicates (quartz, feldspars, pyroxenes, amphiboles, etc.) + percolating water → stable silicates (quartz) or incompletely altered minerals (feldspars) + secondary minerals (clay minerals and Fe and Al hydroxides) + ion-enriched solutions.

Depending on the nature of the parent rock (basic or acidic), climatic conditions (warm and humid), and topography (depressions or summits), which influence drainage conditions, different types of clay minerals may form.

1.2. Humus Formation

The decomposition of organic debris, whether of plant or animal origin, under the action of various agents, leads to the formation of humic substances. This organic material may be deposited on the soil surface, for example through natural litterfall, senescence, or crop residues, or incorporated into the soil by humans and/or animals.

The death of living organisms, together with their waste products and secretions, contributes organic matter to the soil. This material is referred to as "fresh" organic matter before undergoing transformation into humus. Plant-derived materials account for almost the entire contribution (99%) to humus formation.

Soil organic matter therefore initially consists of fresh or relatively undecomposed materials. The fresh organic matter that contributes to humus formation includes:

-sugars, starches, and other water-soluble carbohydrates;

-hemicelluloses;

-cellulose, a polysaccharide formed through the condensation of glucose molecules;

-lignins, which are condensation products of polyphenols;

-tannins;

-fats, waxes, and oils;

-proteins and their derivatives;

-mineral constituents (ash), including P, S, K, and Ca.

Soil organic matter subsequently contains more highly transformed products, known as humic substances. Together with fresh organic matter, these substances constitute humus in the strict sense of the term.

Humic substances are organic macromolecules or "colloids," that is, extremely fine particles that do not form a true solution in the aqueous soil solution but rather a colloidal suspension. These colloids are highly reactive and are composed mainly of carbon, oxygen, hydrogen, and nitrogen, with smaller amounts of sulfur and phosphorus.

Humic substances are classified according to their molecular size and their solubility in aqueous media. Two major fractions are distinguished: humic acids and fulvic acids:

-**Humic acids** constitute a significant proportion of the dissolved organic carbon in the soil solution. They represent one of the major fractions of humus. They are relatively immobile but can interact to varying degrees, depending on their type, with other soil constituents, particularly clay minerals. In this case, they are referred to as grey humic acids. The complex formed between humic substances and clay minerals, known as the clay–humus complex, is highly stable.

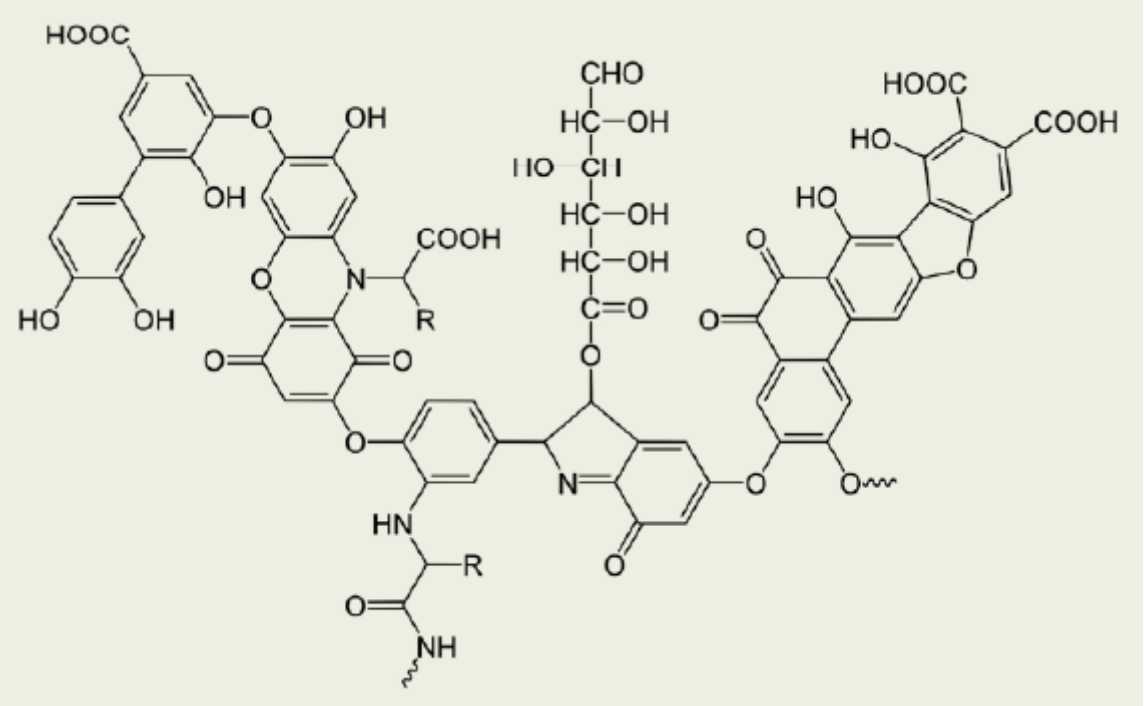

Figure 4: Schematic representation of a humic acid.

-**Fulvic acids**, which are more mobile, constitute the major fraction of dissolved organic carbon in natural waters. They are rapidly transported by infiltrating water, which carries the clay minerals and iron with which they are associated. Through this mechanism, fulvic acids are considered major agents of iron leaching. They can chelate several soil minerals and thereby facilitate their uptake by plants.

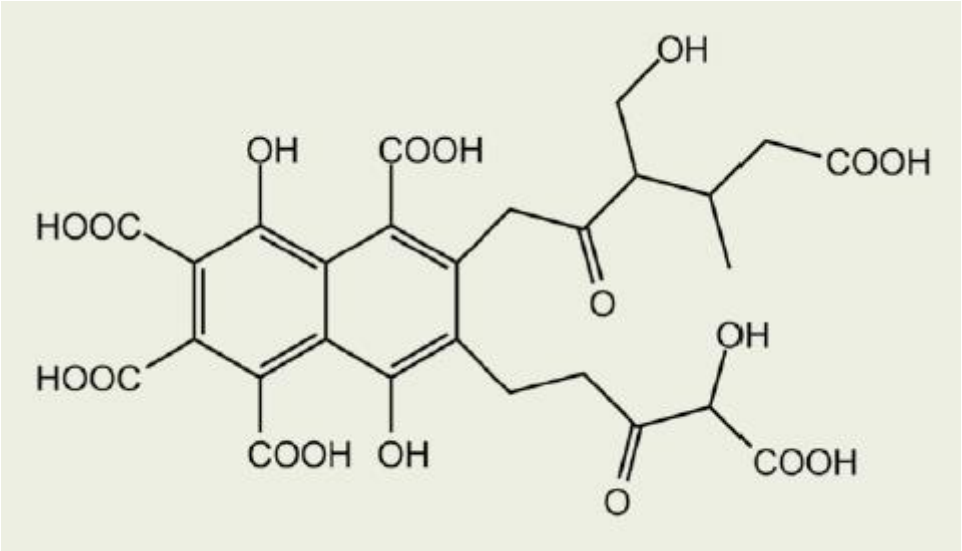

Figure 5: Schematic representation of fulvic acid.

Factors Affecting the Rate and Quality of Decomposition

❖ Environmental factors:

-Aeration

-Temperature

-Moisture

-Soil or substrate pH

-Presence of potential inhibitors that may hinder the metabolism of decomposer organisms (e.g., heavy metals, biocides, etc.)

❖ Factors related to the quality of the organic matter introduced into the system:

-Size and shape of organic residues

-Carbon-to-nitrogen (C/N) ratio of organic residues or of the bulk soil: The C/N ratio is very high in fresh plant material (50–150 in straw) and decreases throughout the decomposition process, eventually stabilizing at around 10 in humus. It is generally accepted that the higher the C/N ratio of a material, the more slowly it decomposes in the soil; however, the humus formed tends to be more stable.

C/N < 15 : Nitrogen is released, and the rate of decomposition increases; it reaches its maximum at a C/N ratio of 10.

15 < C/N < 20 : The nitrogen requirements are adequately met, allowing efficient decomposition of the carbonaceous organic matter.

C/N > 20 : There is insufficient nitrogen to support carbon decomposition. Competition occurs between nitrogen uptake by plants and the immobilization of organic matter by soil microorganisms, resulting in the phenomenon known as "nitrogen hunger." Nitrogen is therefore withdrawn from the soil reserves. Mineralization is slow and releases only a small amount of mineral nitrogen into the soil.

❖ The composition of organic matter influences its rate of decomposition.

The decomposition rate varies according to the relative proportions of the following compounds, listed in order from the most rapidly to the most slowly decomposed:

-Sugars, starches, and simple proteins

-Hemicellulose

-Cellulose

-Fats, waxes, oils, and resins

-Lignin, phenolic compounds, chitin, etc.

Properties of Humus

Humus has the following properties :

-It improves soil structure.

-It increases soil resistance to the erosive effects of rainfall and wind.

-It can retain water and gradually release it to plants, thereby increasing water-holding capacity and ensuring water availability over a longer period.

-It can retain nutrients in the soil and gradually release them to plants over a longer period.

-It contains important nutrients, including nitrogen (N), phosphorus (P), and potassium (K), which become available to plants following decomposition.

Agents of Humification

Soil biota, including bacteria and fungi, and soil fauna (e.g., woodlice, ants, springtails, earthworms, slugs, millipedes, etc.) fragment and transform plant and animal residues. As agents of humification, they act successively within a complex trophic network whose functioning remains only partially understood to this day.

1.3. The Clay–Humus Complex and Cation Exchange Capacity (CEC)

From a chemical perspective, clay minerals and humus would not normally be expected to bind together because both clay and humus micelles carry predominantly negative electrical charges and therefore naturally repel one another. Nevertheless, certain soil organisms, such as soil fungi and earthworms, can contribute to the formation of such complexes by promoting the association of clay minerals with humus.

Both structures, which carry negative charges, would normally repel each other. However, they are closely associated through positively charged “cationic bridges” and “biological binding agents”:

-Calcium has a stabilizing effect. It is interposed between humus and clay mineral layers, forming highly stable calcium bridges and promoting soil structure aeration.

-Magnesium also forms cationic bridges, but contributes to soil structure compaction.

-Iron hydroxide bridges may also form; however, they are less stable than calcium bridges.

-soil biological activity plays a fundamental role in the stabilization of the clay–humus complex (CAH). Certain organic molecules, particularly glomalin, coat and stabilize soil aggregates, making them more resistant to water. Glomalin is mainly produced by arbuscular mycorrhizal fungi, while earthworm activity also contributes to aggregate formation. During digestion,

earthworms mix organic matter (humus) with mineral particles (clay), promoting the formation of stable CAH aggregates that resist water-induced degradation.

The clay–humus complex (CAH) is a structure formed by clay minerals and humus. Humus, the stable fraction of soil organic matter, is relatively resistant to mineralization and contributes significantly to soil structural stability.

The stability of the complexes depends mainly on:

-Type of clay: its particle size, density of negative charges, and ability to bind organic molecules influence complex stability.

-Type of bridging cation: stability depends on the cation's valence and ionic radius. Monovalent cations generally form less stable complexes than polyvalent cations.

-Type of humus: stability varies according to the nature of humic compounds; the greater their degree of polycondensation, the more stable the complex.

The clay–humus complex (CAH) can retain exchangeable cations from the soil solution on its surface through its adsorptive capacity. These cations can be exchanged with the soil solution and taken up by plants, thereby serving as a major reservoir of the soil's chemical fertility. This property is known as the cation exchange capacity (CEC).



Figure 6 : Role of the clay–humus complex (CAH): it retains cations and prevents their loss through leaching; the CAH thus retains and stores these elements.

- **Cation Exchange Capacity (CEC) of Soil**

When mineral salts dissolve in soil water, they dissociate into positively charged cations and negatively charged anions. Because clay particles and humus carry negative charges, they adsorb and retain cations on their surfaces. Humus has a higher adsorption capacity than clay.

The cation exchange capacity (CEC) represents the number of negatively charged sites available for cation adsorption on soil clay and humus.

Hydrogen ions (H^+) are strongly retained by the clay–humus complex. Under acidic conditions, H^+ occupies most exchange sites and can displace other cations. Near neutral pH, essential cations such as Ca^{2+}, Mg^{2+}, K^+, and Na^+ can be exchanged between the clay–humus complex and the soil solution.

These exchangeable cations are continuously available in the soil solution and constitute an important pool of mineral nutrients that can be taken up by plants.

2. Soil Solution : Solubility Equilibria, Ion Adsorption/Desorption, and Bioavailability

Soil Solution

The liquid phase of soil is commonly referred to as the soil solution**.** In chemistry, a solution is defined as a homogeneous mixture consisting of a solvent and one or more solutes.

In soils, water is the only solvent. The terms soil water or soil moisture are commonly used to refer to the soil solution. It contains dissolved substances such as ions, salts, CO_2, O_2, other gases, and various inorganic and organic compounds. Some of these substances occur as colloids, including organic colloids such as carbohydrates, lignin, and humic substances, and inorganic colloids, mainly clay particles (≤ 2 μm).

Table 3 : Median Concentration of Nutrient Elements in Soil Solutions.

Nutrient	mmol L^{-1}	mmol L^{-1}	ppm
Nitrogen (total)	0.46	0.014	0.05
Phosphorus	0.0004	0.0002	0.005
Sulfate	0.18	0.16	1.67
Potassium	1.28	0.09	3.5
Calcium	1.87	0.8	32
Magnesium			25

Solubility Equilibria And Ion Adsorption/Desorption

The movement and availability of solutes in the soil solution are influenced by their interactions with clay minerals, organic matter, and other soil components. Ions present in the soil solution may be sorbed onto organic and inorganic surfaces and subsequently released through desorption. Their concentrations are also regulated by mineral dissolution and precipitation processes. When the soil solution becomes supersaturated with respect to a mineral, precipitation may occur until equilibrium is reached, whereas undersaturation may promote mineral dissolution and the release of ions into the solution.

Depending on soil conditions, water may move relatively freely, while the movement of solutes may be more restricted. Dissolved ions can also be transported through the soil profile toward groundwater or removed through surface runoff. Evaporation and soil drying may promote the upward movement and concentration of ions. Microorganisms can take up ions from the soil solution, while the decomposition of organic matter and microbial residues can subsequently release these ions back into the solution. Gases may also be exchanged between the soil solution and the soil atmosphere, either by dissolving in the solution or being released into the gaseous phase.

The soil solution serves as the principal medium for most chemical and biochemical reactions in soil and provides plant roots and soil organisms with water and essential inorganic nutrients.

- **Bioavailability**

Bioavailability refers to the degree to which chemicals present in soil or sediment are accessible to and can be absorbed, metabolized, or otherwise interact with biological organisms. It is a complex process involving several stages, beginning with the release or desorption of a chemical from soil or sediment particles and followed by its transport and availability at the biological receptor. The resulting concentration at the site of interaction determines the extent to which the chemical can exert biological effects.

-The first process, environmental availability, or bioaccessibility, refers to the fraction of a contaminant that can be released from soil or sediment into the surrounding water and potentially become accessible to organisms. It is mainly governed by desorption processes and can involve rapidly, slowly, and very slowly desorbing fractions. These differences arise from the strength and location of contaminant binding sites and from diffusion through water films, pores, and organic matter. Consequently, some contaminants may remain strongly bound to soil particles for very long periods, limiting their release and bioavailability.

- The second process, environmental bioavailability, refers to the uptake of dissolved and desorbable chemical compounds from sediment by organisms. This process occurs through partitioning mechanisms governed by the chemical activity of the compounds. It is related to concepts such as chemical potential and fugacity. In contrast, strongly bound and non-desorbable compounds are generally not available for this partitioning process and therefore have limited bioavailability.

- The third process, known as toxicological bioavailability, refers to the processes that occur after a toxic substance enters an organism. It involves toxicokinetic processes such as internal

transport, distribution, metabolism, and excretion, ultimately determining the concentration of the substance at its target site and its potential to produce observable biological effects.

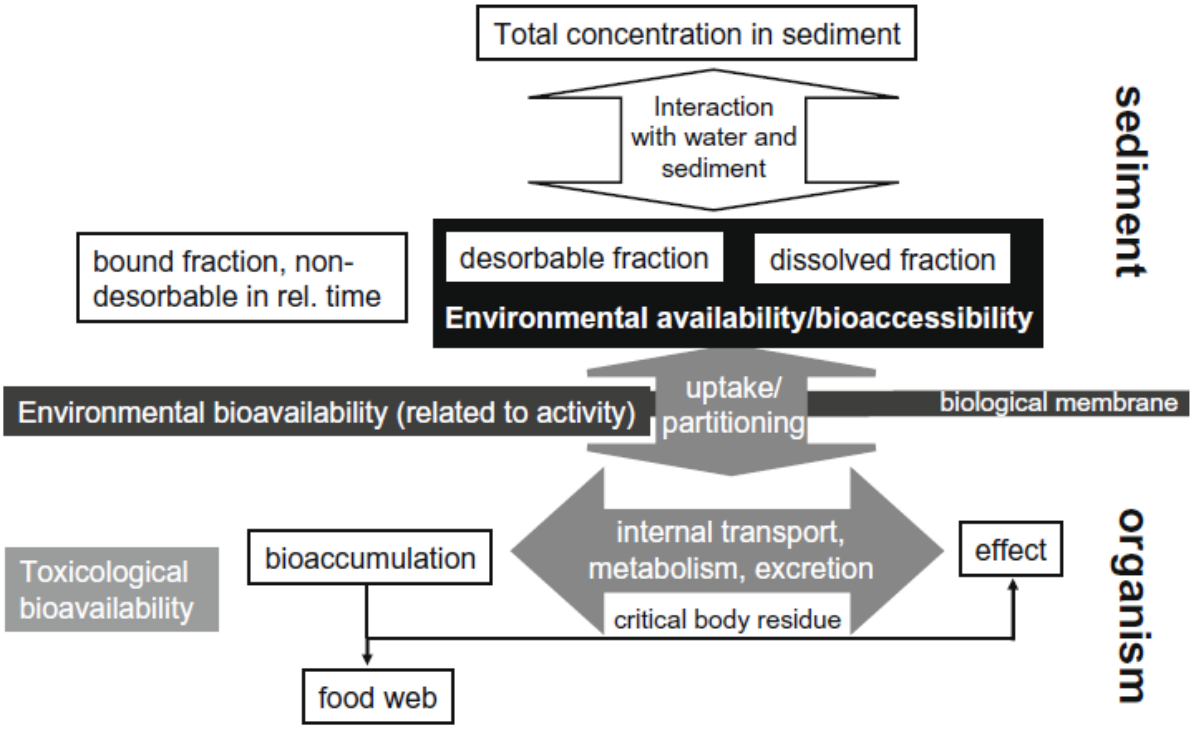

Figure 7 : Overall scheme of bioavailability.

3. pH and Redox Potential : Influence on the Chemical Speciation of Elements and Toxicity (e.g., Aluminum Toxicity in Acidic Soils)

- **Soil Acidity (pH)**

Acidity is defined by the concentration of H^+ ions in the soil water and is measured by pH, which determines the degree of acidity or alkalinity. In acidic soils, the concentration of H^+ ions exceeds that of OH^- ions. Conversely, in alkaline soils, OH^- ions are more abundant than H^+ ions in the soil solution. A neutral soil contains equal concentrations of H^+ and OH^- ions. These conditions are characterized by the soil pH.

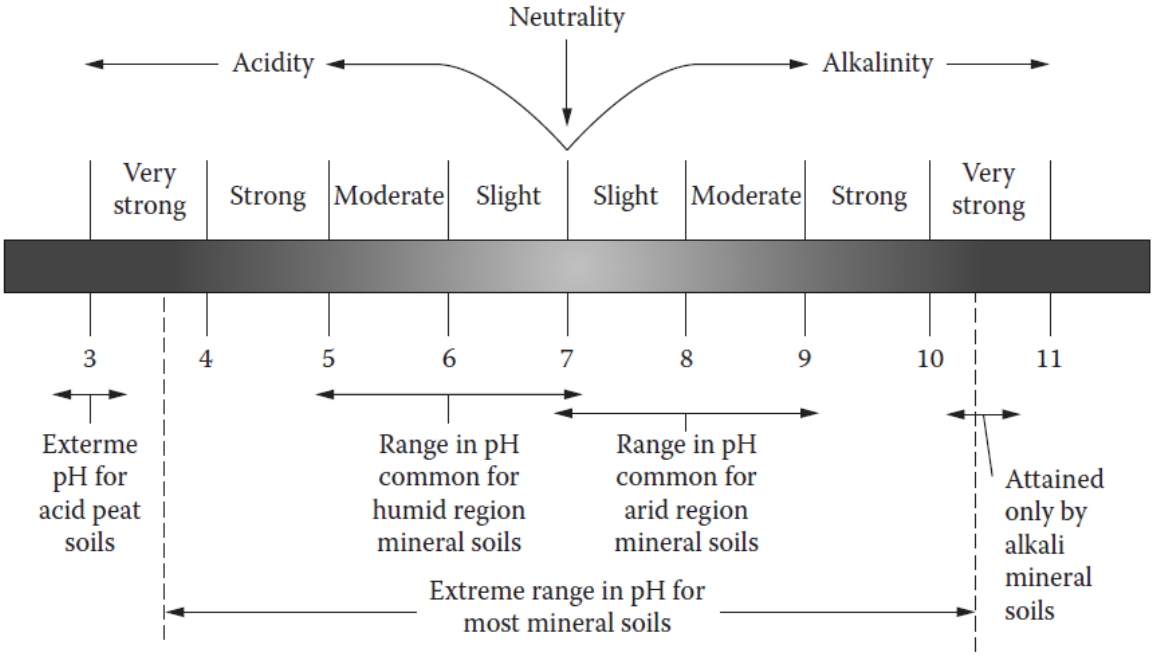

Figure 8 : Soil pH ranges and soil reaction classes.

Soils naturally tend to become acidic over time as mineral cations are progressively replaced by H^+ ions. This process is influenced by several factors, including soil properties and buffering capacity. Clay-rich soils generally have a greater capacity to resist changes in pH, a property known as soil buffering capacity. Loss of calcium through decalcification can also promote acidification, as Ca^{2+} is progressively replaced by H^+ ions. Climate conditions may further contribute to soil acidification. In addition, certain fertilizers, particularly those containing ammonium, nitrates, or phosphates, can increase soil acidity.

- **Redox Potential**

Soil redox potential is a measure of the oxidation–reduction processes occurring in the soil. It reflects the availability of electrons and the balance between oxidation, which involves the loss of electrons, and reduction, which involves their gain. In soils, the oxidation of organic matter is one of the major processes that supplies electrons. These electrons can subsequently be transferred to other compounds, promoting their reduction and leading to the formation of products such as CO_2 and water.

Exemple :

$$4Fe(OH)_3 + 12H^+ + 4e^- \rightarrow 4Fe^{2+} + 12H_2O(\text{reduction})$$
$$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-(\text{oxidation})$$
$$4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_2O$$

- **Influence on the Chemical Speciation of Elements and Toxicity**

-In fully aerobic soils, oxygen acts as the primary electron acceptor, resulting in the formation of CO_2 and H_2O. Soil redox potential is governed by the balance between oxidation and reduction processes and is closely related to soil respiration and carbon cycling. It can therefore serve as a useful indicator of soil conditions, particularly the availability of oxygen and the dynamics of labile carbon pools, which are important components of soil health.

-Redox potential can also serve as an indicator of nutrient availability and soil biological processes. Similar to pH, which reflects proton availability, redox potential (Eh) reflects the availability of electrons and can strongly influence the chemical forms and availability of nutrients. Managing soil redox conditions is particularly important in flooded soils, such as rice paddies, where appropriate redox conditions can help limit the accumulation of toxic elements such as arsenic and cadmium while improving the availability of essential elements such as manganese.

-Soil acidification can lead to metal toxicity. Unlike essential nutrients, metals become more soluble and therefore more readily available for uptake under acidic conditions. A common example is aluminum (Al) toxicity. As soil pH decreases, H^+ and Al^{3+} increasingly occupy exchange sites, thereby increasing the risk of aluminum toxicity. At the same time, the concentration of Ca^{2+} decreases, which can negatively affect soil structure.