SOIL CHEMICAL PROCESSES

Soil components interact together chemically on continuous basis such that the soil may be viewed as a chemical system.

Chemical processes and reactions such as solubilization, adsorption and desorption, oxidation and reduction, and ion exchange involve soil colloids, soil solution, and the solid-liquid interface.

Soil colloids

Colloids are particles, which may be a molecular aggregate, with a diameter of 0.1 to 0.001 mm. Colloids go into suspension in a solution — they float around without settling out for great lengths of time. Soil colloids are clays and soil organic matter of particle sizes that are within or approach colloidal dimensions.

Colloids have properties that are important in soil chemistry, such as the ability to adsorb cations because most soil colloids carry negative charges on them. Because of this, they are also referred to as polyanions. Soil colloids are also called micelles.

Soil Solution

The water in the soil is referred to as the soil solution because it contains dissolved materials (cations and ions) as well as suspended colloids of clay and organic matter.

Plants tend to get their nutrients from the soil solution. However, the solution does not contain sufficient nutrients at any one time to last the life of the plant. These nutrients are replenished from the pool of exchangeable nutrients (those that are adsorbed onto colloids). Still more nutrients are held in what is called the stable pool (bound up in solid form as minerals or organic matter).

Adsorption and Desorption

Adsorption is the process by which ions are electrochemically bound to the surface of soil colloids carrying opposite charges. Adsorbed ions are held on the charged edge of the colloidal particles.

Desorption is the process by which the electrochemically bound ions are detached from the surfaces of the colloids. The two processes take place simultaneously giving rise to the phenomenon of ion exchange in the soil.

ION EXCHANGE

Ion exchange refers to the process of exchange of ions between the solid (soil colloid) and the liquid phase of the soil (soil solution). When the process involves positively charged ions (cations), it is denoted as cation exchange. When the process involves negatively charged ions (anions), it is denoted as anion exchange. Cation exchange is most common in soils particularly in soils where the soil colloids (exchange sites) are negatively charged. Anion exchange takes place mainly in acid soils, where the soil colloids are positively charged. Ion exchange also takes place between plant roots and ion in solution or between plant roots and soil colloids when in close contact. The process of ion exchange is vital to nutrient availability for plant uptake.

Cation Exchange Capacity (CEC)

It is primarily the ionic form of nutrients that plants are able to take up into their roots. Many of these nutrients are taken up in the cationic forms, so it is important that the soil be able to supply these. Most soils have at least some ability to hold onto these ions at the negatively charged sites within the soil. The amount that they can hold is denoted as the Cation Exchange Capacity.

Cations that are commonly involved in the cation exchange processes in soil are termed **exchangeable cations**. Cations in the soil are divided into acids and bases. The acids are predominantly hydrogen and aluminum. The bases are primarily calcium, magnesium, sodium, and potassium.

Cation echange capcity (CEC) can be defined as the sum of exchangeable bases plus total soil acidity at a specific pH value, usually 7.0 or 8.0.

When acidity is expressed as salt-extractable acidity, the cation exchange capacity is called the effective cation exchange capacity (ECEC) because this is considered to be the CEC of the exchanger at the native pH value.

b) *Factors influencing CEC*

1. Amount of clay: Higher amounts of clay mean higher CEC.
2. Type of clay: Certain kinds of clay (smectites, montmorillonite) have higher CEC than others (such as kaolinite).
3. Amount of organic matter: Higher amounts of organic matter mean higher CEC
4. pH dependent CEC: Amorphous clay minerals and organic matter have a CEC that varies with pH. As pH increases, so does the CEC. Under acid conditions, these have an anion exchange capacity. For organic matter the rule of thumb is that for every pH unit above 4.5 there is a 1 meq/100g increase for each percent organic matter.

Exchangeable bases*:* These are cations of strong bases (predominantly $Ca^{2+,}$ Mg^{2+}, K^+ and Na^+) adsorbed on the surface of soil colloids. They can be readily replaced with a salt solution.

Factors that affect the level of base saturation of a soil include: parent materials, pH of the soil, and rainfall

Base saturation

Base saturation refers to the percentage of exchange sites (negatively charged sites on clay and organic particles) that are occupied with bases (usually Ca^{2+}, Mg^{2+}, K^+ and Na^+) as opposed to ions that make the soil acid (H+ or Al^{3+}). It can also be expressed as the ratio of the quantity of exchangeable bases to the cation exchange capacity.

The value of the base saturation varies according to whether the cation exchange capacity includes only the salt extractable acidity or the total acidity determined at pH 7 or 8. Often expressed as a percent

Anion Exchange

Anions are not adsorbed onto soil particles as much as cations are because clay minerals mostly carry negative charges and most of the exchange sites in organic matter also have negative charges. Some essential plant nutrients.

Anion exchange capacity: The sum of exchangeable anions that a soil can adsorb. Usually expressed as centimoles, or millimoles, of charge per kilogram of soil (or of other adsorbing material such as clay).

Exchangeable anion: A negatively charged ion held on or near the surface of a solid particle by a positive surface charge and which may be easily replaced by other negatively charged ions (e.g. with a Cl^- salt).

Soil pH

Soil pH refers to the negative log of the concentration of hydrogen ions (moles per liter) in the soil. pH generally range in number between 0 and 14.

Soil pH may be classified on the pH scale as: very slightly acidic (6.5 – 7.0), slightly acidic (6.0 – 6.5), moderately acidic (5.5 – 6.0), strongly acidc (4.0 – 5.0), and acid (pH < 4). On the alkaline side, soil may also be classified as very slightly alkaline (7.0 – 7.5), slightly alkaline (7.5 – 8.0), moderately alkaline (8.0 – 8.5), alkali (>8.5).

In acidic soils (pH < 7), H+ ions predominate. In alkaline soils (pH > 7), OH- ions predominate.

Soil acidity

Acidity refers to the condition of the soil when the exchange complex is dominated by hydrogen and aluminum ions. Forms of soil acidity include active acidity, exchange acidity, residual acidity, and total acidity

Active acidity: Refers to the hydrogen ions present in soil solution due to the ionization of organic acids or desorption of H^+ from the surface of soil colloids. This is measured by using pH meters or pH indicator papers

Exchangeable acidity (salt-replaceable): The aluminum and hydrogen that can be replaced from an acid soil by an unbuffered salt solution such as KCl or NaCl.

Total acidity: The total acidity including residual and exchangeable acidity. Often it is calculated by subtraction of exchangeable bases from the cation exchange capacity determined by ammonium exchange at pH 7.0. It can be determined directly using pH buffer-salt mixtures (e.g., $BaCl_2$ plus triethanolamine, pH 8.0 or 8.2) and titrating the basicity neutralized after reaction with a soil.

Soil Alkalinity

Soil alkalinity refers to the condition of the soil when the exchange complex is dominated by OH^- ions, The pH is expressed with values greater than 7.0. Soils with pH > 7 are referred to as alkaline soils. Alkaline soils may be saline or sodic depending on the percentage of the CEC occupied by exchangeable sodium.

A soil is described as **alkali** if

(i) It has a a pH of 8.5 or higher or with an exchangeable sodium percentage greater than 0.15 (ESP>15).

(ii) It contains sufficient sodium to interfere with the growth of most crop plants.

Saline soil: A non-sodic soil so high soluble salt as to adversely affect the growth of most crop plants. Salinity is measured in terms of electrical conductivity of soil extract. The lower limit of saturation extract electrical conductivity of such soils is conventionally set at 4 dS m^{-1}(at 25°C).

Sodic soil: A non-saline soil that contains so high a level of exchangeable sodium as to adversely affect crop production and soil structure under most conditions of soil and plant type. The exchangeable sodium percentage (ESP) of at least 15

Saline-sodic soil*:* A soil containing sufficient exchangeable sodium to interfere with the growth of most crop plants and containing appreciable quantities of soluble salts. The exchangeable sodium ratio is greater than 0.15, conductivity of the soil solution, at saturated water content, of >4dS m-1(at 25°C), and the pH is usually 8.5 or less in the saturated soil.

Buffering capacity of soil

This is the ability of soil to resist changes in pH. The buffering capacity of soil depends on the CEC, the texture and the base saturation. The higher the CEC and base saturation, the higher the buffering capacity. Clayey soils also have higher buffering capacity than sandy soil.

Liming

Liming is the application of liming to soil with intention of reducing its acidity. Liming materials are substances that when added to soil are able to increase the pH.

Liming requirement is the amount of liming material required to raise the pH of the soil to a specified level. It is experimentally determined.

Examples of liming materials are oxides, hydroxides, carbonates and silicate of Ca, Ca and Mg. The anion present in the substance reduces the activity of Al

The effectiveness of liming material is measured by the neutralizing value

OXIDATION –REDUCTION REACTIONS IN SOIL

Oxidation and reduction reactions are two reactions occurring simultaneously. These reactions are common in the soil. Oxidation is a reaction which involves gain of oxygen, or loss of hydrogen or electron. Reduction on the other side is the reaction which involves loss of oxygen, or gain hydrogen or electron. Oxidation – reduction reactions generally involve transfer of electrons from one substance to another (no bonding formed or broken).

Oxidizing agents (oxidizers) accept electrons from other substances.

Reducing agents (reducers) donate electrons to other substances.

Example: $Fe^{3+} + e^-$ $\quad$ Fe^{2+}

$H_2O_2 + 2e^- + 2H^+$ $\quad$ $2H_2O$

Source of electrons in soils.

Carbon atoms of organic matter are the main source of electrons in soils

Carbon has a wide range of oxidation states.

For example in the reaction,

$CH_4 + 2O_2$ $\quad$ $2H_2O + CO_2$

The oxidation state of carbon in CH_4 is +4 while in CO_2 the oxidation number is -4. Thus in the reaction, $8e^-$ are released

Other sources of electron in soil include nitrogen and sulfur atoms which can also exhibit several oxidation states. The availability of electrons usually controls the oxidation/reduction reactions and is expressed as redox potentials.

Soil microbes often serve as catalysis for the release of electrons from a substance.

Source of H^+ (water).

Water is the main source of proton in the soil.

H_2O $H^+ + OH$

Electron acceptors (oxidizers) in soils.

Electron acceptors in soil include oxygen, Fe, Mn, sulphate and nitrate ions. Oxygen is the most common electron acceptor under aerobic condition.

$O_2 + 4e- + 4H+ = 2H_2O$

Fe and Mn accept electrons under anaerobic conditions (in the absence of oxygen). Their reactions include the following

$FeOOH + e- + 3H^+$ $Fe^{2+} + 2H_2O$

$Fe_2O_3 + 2e- + 6H^+$ $2Fe^{2+} + 3H_2O$

$MnO_2 + 2e- + 4H^+$ $Mn^{2+} + 2H_2O$

(Common in soil where oxygen has been excluded such as in flooded soils.

In seasonally flooded soils (for example the fadama), minerals such as FeOOH and MnO_2 become more soluble and some Fe_{2+} and Mn_{2+} may be removed by leaching).

$SO4^{2-} + 8e- + 8H^+$ $S^{2-} + 4H_2O$

(This reaction occurs in swampy areas with H_2S as the product leading to stinky odour)

$NO_{3-} + 2e- + 2H^+$ $NO_2 + H_2O$

$N_2O + 2e- + 2H^+$ $N_2\uparrow + H_2O$

(Nitrite is more toxic than NO_{3-}, H2S) is more toxic than $SO4^{2-}$ and Fe^{2+}, Mn^{2+} can cause phytotoxicity in rice paddy).

In the absence of any other electron acceptors H^+ (protons) can serve as electron acceptor in the aqueous system.

$H^+ + e-$ $\frac{1}{2} H_2$

Electrons donors (reducers) in soils.

Dead and decaying organic materials and soil organic matter constitute the electron donors and soil organic matter. Organic matter and plant material denoted by the formula $(CH_2O)_n$ for carbohydrate yield a half reaction of oxidation as follows

$CH_2O\ C^{4+} + H_2O + 4e-$ (1)

And the other half-reaction would be

$O_2 + 4e-\ 2O_{2-}$ (2)

With oxygen acting as electron acceptor

The overall reaction is:

$CH_2O + O_2$ $CO_2 + H_2O$ + energy

Inorganic electron donor in soil include ammonia, hydrogen sulphide and ferrous iron

$Fe^{2+} = Fe^{3+} + e-$

$NH_3 = N^{3+} + 3H^+ + 6e-$

In the reaction ($NH_4^+ + 2H_2O = NO_2^- + 8H^+ + 6e-$)

$H_2S = S^{6+} + 2H^+ + 8e-$

In the reaction ($H_2S + 4H_2O = SO_4^{2-} + 10H^+ + 8e-$)

SOIL ORGANIC MATTER

Soil organic matter is the fraction of soil solid that is of plant and animal origin. It consists of plant and animal remains in various stages of decomposition and synthesis.

Soil organic matter is generally grouped into two – humic substances, and non-humic substances

Soil organic matter can be fractionated, both physically and chemically. Physical fractionation is done by its particle sizes gives the particulate organic matter (light fraction of size greater than 50 microns), and the non-particulate organic matter (< 50 µm). Particulate organic matter chemically consists of non-humic substances and still retains the original chemical structure of its precursor as well as the chemical compounds.

Humic substances are further divided, based on the molecular weight, solubility in mineral acid (HCl) or alkali (NaOH), into :

Fulvic acid – soluble in both acid and alkali, low molecular weight,

Humic acid – soluble in alkali but insoluble in acid, medium molecular weight

Humin – insoluble in both acid and alkali, high molecular weight

Importance of soil organic matter

Most tropical soils are highly weathered, highly leached, erodible and low in cation exchange capacity and nutrient reserve. Soil organic matter constitute largely less than 5 %, except in forest lands, but play significant roles in the productivity of tropical soils. The roles of soil organic matter include:

- Supply of plant nutrients – N, P, S, micronutrients *etc* – in balanced proportion
- Nutrient retention
- Soil pH buffer
- Binding agent for structural aggregation of the soil
- Water retention
- Immobiliztion of toxic elements, heavy metals, and pesticides

SOIL ORGANISMS

The soil is a very complex medium where many chemical, biological, biochemical, geochemical, biogeochemical and physical processes take place.

The soil is also the medium where plants obtain most of their nutrients.

The soil has a vast population of living organisms including micro and macro flora, micro and micro fauna, insects etc.

The activities of some of these organisms are detrimental to plants, particularly the disease causing organisms.

The activities of most are however beneficial to crops particularly with regards to soil aggregation, nutrient cycling, biological nitrogen fixation, nutrient uptake, disease control/prevention and production of growth hormones.

These organisms interact with one another in the soil giving rise to diverse relationships/interactions such as symbiosis, parasitism, commensalism, protocooperation, neutralism, competition.

The soil microorganisms constitute the highest populations of soil organisms and because of their enzymatic capabilities, they are more important in soil processes than other soil organisms.

Classification of Soil Microorganisms

Soil microorganisms can be classified based on physiology or nutrition, mode of respiration and origin

A. Physiological/Nutritional Classification: Microorganisms need food as sources of energy to enable them carry out their activities, for growth and multiplication. Microorganisms differ in their nutrition requirements, whereas some organisms can use the same source of food as carbon and energy, others require different sources as carbon and energy.

On this basis microorganisms are divided into

a. Autotrophs/Lithotrophs: These are organisms that can use CO_2 as the sole source of carbon.

Based on the source of energy they are further classified as;

i. Photoautotrophs/Photolithotrophs: These are organisms deriving their energy from sun through the process of photosynthesis. Such organisms contain a pigment known as chlorophyll which enable them convert CO2 to carbohydrate in the presence of sun energy eg Algae.

ii. Chemoautotrophs/Chemolitotrophs: These are organisms which derive their energy from carrying out biochemical oxidations. These organisms release energy from the reactions eg oxidation of NH_4^+ to NO_2^- and NO_2^- to NO_3^-, oxidation of H_2 to H_2O, Oxidation of S to H_2S and $H_2SO_3^-$.

$NH_4^+ + 1^1/_2O_2$ --- $NO_2^- + 2H^+ + H_2O$ *Nitrosomonas sp*

$NO_2^- + H_2O$ --- $NO_3^- + 2H^+$ *Nitrobacter sp*

b. Heterotrophs: These are organisms that organic compounds as their carbon and energy source. They derive both carbon and energy from the same source. Most of the microorganisms belong to this class, in addition to carbon other nutrients like N, K, P, Na, Mg, Ca, Fe, etc which they need are obtained from organic matter.

B. Classification Based on Respiration: Based on mode of respiration, soil microorganisms can be classified as aerobes, anaerobes and facultative anaerobes.

Aerobes: These organisms require free oxygen for their respiration they cannot survive in the absence of oxygen. Most bacteria, all fungi and actinomycetes fall into this class.

Anaerobes: These organisms can grow optimally only in the absence of molecular oxygen, this group incorporates many bacteria eg *Clostridium*.

Facultative Anaerobes: These organisms can survive either in the presence or absence of oxygen. Although they need oxygen, they do not necessarily need to have access to molecular oxygen. They can survive by extracting the required oxygen from an oxygen rich compound such as nitrates or sulfates, the compounds are reduced thus changing their availability to plants.

C. Classification Based on Origin of Microorganisms: Based on their origin bacteria are classified as;

Autochthonous or Indigenous microorganisms: These are the original residents in the soil, their numbers are constant, they do not usually respond to additions of organic matter and they grow very slowly. They may have developmental stages used to endure in soil for a long period without being active metabolically.

Allochthonous or Zymogenes or Invaders: These miroorganisms develop under the influence of specific soil treatemts such as addition of organic matter, fertilization or aeration. They do not contribute significantly to soil processes.

Transient Microorganisms: These microorganisms are introduced into the soil intentionally eg Rhizobium sp, mycorrhizal fungal or unintentionally eg through diseased plants. They die rapidly or may survive in the soil for a period of time in the presence of host plant or animal

BACTERIA

These are unicellular organisms without organelles or nucleus they are one of the simplest forms of life. The size ranges from 1-5 microns. The shape vary from cocci (round shaped), to bacilli (rod shaped) and to spiral.

In terms of population they probably the most numerous microbes whose population range from a few hundreds to 3 billion per gram soil.

They are very versatile in their metabolic activities some can use simple inorganic materials as enery source while other are heterotrophic. Some bacteria need oxygen for their respiration others are anaerobic and some can adapt to presence or absence of oxygen.

Importance:

1. Bacteria are very important in the general decomposition of organic matter in soil

2. They carry out specific functions important in nutrient cycling such as nitrification

3. A group of bacteria are important in in nitrogen fixation- conversion of atmospheric nitrogen to plant available forms.

4. Some soil bacteria cause diseases

Growth Conditions: Bacteria can survive under diverse environmental conditions.

Optimum pH condition for bacteria growth is slightly acidic to neutral, however some groups survive under highly acidic conditions and they are termed **acidophilic bacteria**.

The optimum temperature range for most bacteria is 25 to 35^oC and these are termed **mesophiles**, however, some are able to tolerate extreme temperatures these are **Psychrophiles** (0 to 20^oC) and **Thermophiles** (40 to 65^oC).

FUNGI

They have well developed organelles including nuclei, mitochondria, they are more developed than bacteria.

The most important characteristic of fungi is the possession of a filamentous body consisting of strands of hyphae. The mycelium can be sub-divided into cross-wall called septa, however there many non-septate fungi.

They about 5 µm in diameter the population range between 0.1 – 1 million propagules per gram of soil

Almost all fungi are heterotrophic in nature and all are aerobic thus they do not occur in diverse environment as bacteria.

Importance:

1. Fungi are important in decomposition of organic residues in soil

2. They are especially important in decomposing woody material which many bacteria cannot decompose.

3. They are important in processes leading to humus formation

4. They play important roles in the formation of stable aggregates

5. Some soil fungi cause plant and animal diseases

6. Some fungi form symbiotic association with roots of higher plants.

ACTINOMYCETES

Structurally, these organisms lie between bacteria and fungi, they bear similarity to bacteria in terms of cell size and structure characteristic and they are filamentous organisms like fungi.

They are the next populous in soil after bacteria, the number ranging from 10^5- $4x10^6$ cell/g of soil

The organisms prefer moist and well aerated soil. They are sensitive to acidic condition, optimum pH ranging from 6 – 7.5

Importance

1. They are important in decomposition of organic matter, especially cellulose, chitin and phospholipids

2. Some actinomycetes produce antibiotics eg *Streptomyces sp*

3. Some actinimycetes cause plant diseases eg potato scab disease.

ALGAE

These are sub-divided into twogroups:

1. Green algae (True algae)

2. Blue-green algae (Cyanobacteria)

Morpologically, the true algae have nucleus, cell wall compose mainly of cellulose and chloroplast distributed within the various organelles.

The blue-green algae do not possess nucleus, cell wall compose of a substance call muramic acid. They have a blue pigment called Phycocyanin distributed throughout the cytoplasm.

Nutritionally, algae are autophototrophic.

Importance

1. Some algae are capable of nitrogen fixation, these can be especially important in some ecological condition eg rice paddies.

2. They form symbiotic associations with fungus (lichens) and fresh water fern (azolla). Lichens are important in early stages of pedogenesis while azollas are important in fertility management of rice paddies

NEMATODES

These are of microscopic size they are like worms round and spindle-like in shape.

The importance of nematodes in soil is not all that related to soil fertility but that some are pathogenic to some agricultural crops. They usually infect the roots of such plants thereby interfering with normal physiology and obstructing water and nutrient uptake. The plants infected are mostly horticultural crops like tomatoes, carrots, ornamental and fruit trees.

EARTHWORMS

These are the first known larger animals in the soil. They thrive best in moist soil with abundant supply of organic matter.

They are very important in the fertility of the soil because they aid in humus formation by in jesting some organic debris and later egesting same as worm cast. The worm cast usually contains high amounts of organic matter, N, Ca, Mg and P.

Earthworm help in the process of soil formation by building new top soil every year. Study has shown that earthworms contribute about 2 cm thick layer of soil every ten years.

Earthworm is also important because of the burrowing activities the channels they leave behind are very effective in surface drainage and aeration.

Earthworm also helps to improve soil water infiltration thereby preventing erosion.

TERMITES

The presence of termites is one of the characteristics of most tropical soils. Termites exhibit very great diversity in their feeding habits; some feed on organic residues, some on wood and some cultivate fungi in their nest.

There are different forms of termite nests, some build huge nests about 3 meters in height and 12 meters in diameter.

The population of nests per hectare can be very high, in some cases they can make up to 20 % of the landscape and as many as 3,000 per hectare especially during rainy season.

Importance: This is under physical, chemical and pedological aspects of the soil.

Physical Effects:

1. They carry only finer particles, thereby leading to increase in the finer structure of the soil.
2. The mound materials are more stable and better aggregated than the surrounding soil thus affecting the structure of the soil.

3. Because of the numerous underground channels they create, the bulk density of the soil is reduced.

4. Also because the mound contains finer particles like clay and high organic matter, the water holding capacity is increased.

Chemical Effects:

1. The soil pH is higher in the mound material because of accumulation of $CaCO_3$.

2. Organic matter is higher than in adjacent soil.

3. The termite mound contain higher amount of Mg, P, Ca and K, thus important in soil fertility.

Pedological Effect:

1. The activities of termites in bringing finer particles from the sub-soil to the surface contribute to formation of gravel and soil free horizon.

2. Up to 560 kg per hectare per year of soil materials can be turned over through the activities of termites, thus helping in soil formation.

3. It has been shown that activities of termites lead to the formation of 3 cm thick of soil every 100 years.