COURSE DETAILS:

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COURSE CONTENT:


Practical: Particle size analysis; pH determination; cation exchange capacity; organic carbon; identifying nutrient deficiency symptoms in plants

COURSE REQUIREMENTS:

This is a compulsory University course. In view of this, students are expected to participate in all the course activities and have minimum of 70% attendance to be able to write the final examination.

READING LIST:


LECTURE NOTES

INTRODUCTION TO SOIL CHEMISTRY

Soil Chemistry is an important branch of soil science. It is fundamental to all soil processes that affect the use of soil. Soil chemistry studies the nature of chemical elements in the soil system in organic and inorganic combinations. It also studies the inter-relationship between these chemical elements and how they relate with three states of matter.
Soil chemistry is regarded as the most central of all the scientific disciplines that interact to make up of the complex web of environmental science.

Significance of soil chemistry
Understanding soil chemistry is very important to crop production in terms of
1) Improving the availability of nutrients to plants
2) To utilize soil microbial organisms to the best advantage
3) To improve the physical conditions of the soil
4) Helps to explain the basic properties of soils as they occur in nature
5) Helps to monitor and follow rapid changes that occur in the soil as a result of the introduction of intensified modern techniques in crop production

SOIL COMPOSITION
Soil may be defined as material of variable depth with a substantial solid content at the Earth’s surface which is undergoing change as a consequence of chemistry, physics and biology processes. Soil essentially consists of three phases; a solid phase, a solution phase and a gas phase.

- The solid phase usually includes an intimate mixture of mineral material, originating from rock, sediment or till, and organic material arising as a consequence of biological activity
- 2. The solution phase, this interact continuously with the solid phase. It originates infiltrating the soil or from rising water or water moving laterally.
- 3. The gas phase, or soil atmosphere composition depends upon biological activity.

SOIL COLLOIDS
- Next to photosynthesis and respiration, no process in nature is more vital to plant and animal life than the exchange of ions between soil particles and plant roots.
- These cation and anion exchanges occur mostly on the surfaces of the finer or colloidal fractions of both the inorganic and organic matter (clay and humans).
- Colloids are substances whose particle size is about 1 to 1000nm when they are mixed with another substance, usually air or water.
- Colloids are action sites for chemical reaction, microscopic, large surface area. The larger the surface area, the better they are for chemical reaction.
- Molecules of some compounds can come within the colloidal range but most colloids consist of aggregate of molecules. Colloids are so ubiquitous in nature and so distinctive that they have common names as fog, smoke, aerosol, foam, emulsion, soil and clay. All are small particles suspended in a fluid. as

General properties of soil colloids
- Size
- Surface area
- Surface charges
- Adsorption of cations and water

Types of soil colloids
There are four major types of colloids present in soil
1. Layer silicate clays
2. Iron and Aluminum oxide clays
3. Allophane and associated clays
4. Humus
(Generally 1, 2, 3 are inorganic while 4 is organic colloids)
Sources of charges on soil colloids
There are two major sources of charges on soil colloids:
1) Hydroxyls and other such functional groups on the surfaces of the colloidal particles that by releasing or accepting H\(^+\) ions can provide either negative or positive charges.
2) The charge imbalance brought about by the isomorphous substitution in some clay structures of one cation by another of similar size but differing in charge.

Permanent charges
- **Negative charges**
  A net negative charge is found in minerals where there has been an isomorphous substitution of a lower charged ion (e.g. Mg\(^{2+}\)) for a higher-charged ion (e.g. Al\(^{3+}\)).
- **Positive charges**
  Isomorphous substitution can also be a source of positive charges if the substituting cation has a higher charge than the ion for which it substitutes.

**pH-dependent charges**
- **Negative charges**
The pH-dependent charges are associated primarily with hydroxyl (OH) groups on the edges and surfaces of the inorganic and organic colloids. The OH groups are attached to iron and/or Al in the inorganic colloids (e.g. Al-OH) and to the carbon in CO groups in humus (e.g. -CO-OH). Under moderately acid conditions, there is little or no charge on these particles, but as the pH increases, the hydrogen dissociates from the colloid OH group, and negative charge results.
- **Positive charges**
  Under moderate to extreme acid soil conditions, some silicate clays and Fe, Al oxides may exhibit net positive charges. The exposed OH groups are involved. In this case, however, as the soils becomes more acid, (protonation), the attachment of H\(^+\) ion to the surface OH groups takes place.

SILICATE MINERAL CHEMISTRY
The silicate minerals are responsible for the important, physical and chemical properties of most soils. Silicate minerals characteristically contain Si, O\(_2\), and Al.

**Silicon**
It makes up 27.6% of the Earth's crust, second to O\(_2\). Si compound make up of the framework for most soils except tropical soils. It is amphoteric and usually slightly acidic, forming weak acid.

**Definition of clays**
Clays are the active mineral portion of soils dominantly colloidal and crystalline. The crystalline nature of clays is such that they have definite repeating arrangement of atoms which they are composed of. Majority are made of planes of O\(_2\) atoms with Si and Al atoms holding the O\(_2\) together by ionic bonding.

**Classification of clays**
Clays are usually given group names based on their structure or on purely chemical composition. There are 3 groups.
1) **Silicate clays**: These are crystalline clays e.g. Montmorillonite, illite, vermiculite, kaolinite, chlorite. Each crystalline clay is like a particular deck of cards. Each card represent a layer each of which is an exact replication of each other layer.
2) **Amorphous clays**: These are non-crystalline, which have silica, they are mixtures of Si and Al that have not formed well oriented crystals but sometimes have high cation or anion exchangeable capacity.
3) **Sesquioxides**: These consists of groups of Fe, Al and Ti oxides clays. They are present in condition where there is excessive leaching caused by rainfall and sometimes intensive weathering of minerals in humid warm climate. They can be crystalline or armorphous.

**Structures of layer silicate clay**
This implies the basic building blocks of clays. All soil clays are formed from the same 2 basic structural units. It is the way these 2 basic building units are put together that gives the soil clay distinctly different properties. They are:

1) **Silica tetrahedron:** This is a silica dominated sheet is a unit composed of one silicon atom surrounded by four oxygen atoms.

   ![Silica tetrahedron](http://www.unaab.edu.ng)

2) **Aluminum and/or Mg octahedron:** In this unit, an Al or Mg is surrounded by 6 oxygen atoms or hydroxyl groups, the center of which define the apices of an 8-sided solid.

   ![Aluminum and/or Mg octahedron](http://www.unaab.edu.ng)

**MINERALOGICAL ORGANIZATION OF SILICATE CLAYS**

On the basis of the number and arrangement of tetrahedral (silica) and octahedral (Al-Mg) sheets contained in the crystal units or layers, silicate clays are classified into two different groups, 1:1 - type minerals and 2:1 - type minerals.

**1:1 type minerals**

The layer of the 1:1 type minerals are made up of one tetrahedral (silica) sheet and one octahedral (alumina) sheet hence the terminology 1:1 type crystal. Kaolinite is the most prominent member of this group, others are halloysite, nacrite and dickite.

**Characteristics of kaolinite**

1) It has strong H-bonding
2) It does not allow water to penetrate between the layers and have almost no swelling
3) It has low cation exchangeable capacity.
4) Kaolinite exhibits less plasticity (capacity to be molded), stickiness, cohesion, shrinkage or swelling.
5) Kaolinite containing soils make good bases for road beds and building foundations.

**2:1 type minerals**

The crystal unit (layers) of these minerals are characterised by an octahedral sheet sandwiched between two tetrahedral sheets. Four general groups have this basic crystal structure. Two of them, smectite and vermiculite (expanding - type) and the other two fine-grained (illite) and chlorite (non expending).

**Expanding minerals**

- The smectite group

**Characteristics of smectites**

1) High plasticity and cohesion
2) Their marked swelling when wet and shrinkage on drying
3) Has high CEC
4) Permeability to water is low.
- **Vermiculites**, these are also 2:1 type minerals, an octahedral sheet being found between two tetrahedral sheets. In most soil verticulites, the octahedral sheet is aluminum dominated (dioctahedral), although Mg-dominated (trioctahedral) vermiculites are also found.

- **Non-expanding minerals**
  Micas and chlorites are the types of minerals in this group.

- **Muscovite and biotite** are examples of unweathered micas often found in sand and silt separates.

- **Soil chlorites** are basically Fe-Mg silicates with some Al present.

**SOIL CHEMICAL PROCESSES**

Soil components interact together chemically on a 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 exchange capacity (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 acid (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., BaCl₂ 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 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: \( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \)

\( \text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} \)

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,

\[
\text{CH}_4 + 2\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + \text{CO}_2
\]

The oxidation state of carbon in CH\textsubscript{4} is +4 while in CO\textsubscript{2} the oxidation number is -4. Thus in the reaction, 8e\textsuperscript{-} 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\textsuperscript{+} (water).**

Water is the main source of proton in the soil.

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-
\]

**Electron acceptors (oxiziders) in soils.**

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

\[
\text{O}_2 + 4\text{e}^- + 4\text{H}^+ = 2\text{H}_2\text{O}
\]

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

\[
\begin{align*}
\text{FeOOH} + \text{e}^- + 3\text{H}^+ &\rightleftharpoons \text{Fe}^{2+} + 2\text{H}_2\text{O} \\
\text{Fe}_2\text{O}_3 + 2\text{e}^- + 6\text{H}^+ &\rightleftharpoons 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \\
\text{MnO}_2 + 2\text{e}^- + 4\text{H}^+ &\rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}
\end{align*}
\]

(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\textsubscript{2} become more soluble and some Fe\textsuperscript{2+} and Mn\textsuperscript{2+} may be removed by leaching.)

\[
\text{SO}_4^{2-} + 8\text{e}^- + 8\text{H}^+ \rightleftharpoons \text{S}^{2-} + 4\text{H}_2\text{O}
\]

(This reaction occurs in swampy areas with H\textsubscript{2}S as the product leading to stinky odour)

\[
\text{NO}_3^- + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{NO}_2^- + \text{H}_2\text{O}
\]

\[
\text{N}_2\text{O} + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{N}_2 \uparrow + \text{H}_2\text{O}
\]

(Nitrite is more toxic than NO\textsubscript{3}, H\textsubscript{2}S is more toxic than SO\textsubscript{4}\textsuperscript{2-} and Fe\textsuperscript{2+}, Mn\textsuperscript{2+} can cause phytotoxicity in rice paddy).

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

\[
\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2} \text{H}_2
\]

**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\textsubscript{2}O\textsubscript{n} for carbohydrate yield a half reaction of oxidation as follows:

\[
\text{CH}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} + \text{energy}
\]

And the other half-reaction would be:

\[
\text{O}_2 + 4\text{e}^- - 2\text{O}_2\text{^{-}} \quad (2)
\]

With oxygen acting as electron acceptor

The overall reaction is:

\[
\text{CH}_2\text{O} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} + \text{energy}
\]

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

\[
\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^- \\
\text{NH}_2\text{H} = \text{N}^{2+} + 3\text{H}^+ + 6\text{e}^- \\
\text{H}_2\text{S} = \text{S}^{2+} + 2\text{H}^+ + 8\text{e}^-
\]

In the reaction (NH\textsubscript{2}\textsuperscript{+} + 2H\textsubscript{2}O = NO\textsubscript{2}\textsuperscript{-} + 8H\textsuperscript{+} + 6e\textsuperscript{-})

\[
\text{H}_2\text{S} = \text{S}^{2+} + 2\text{H}^+ + 8\text{e}^-
\]

In the reaction (H\textsubscript{2}S + 4H\textsubscript{2}O = SO\textsubscript{4}\textsuperscript{2-} + 10H\textsuperscript{+} + 8e\textsuperscript{-})

**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 CO₂ 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 $\text{NH}_4^+$ to NO$_2^-$ and NO$_2^-$ to NO$_3^-$, oxidation of H$_2$ to H$_2$O, Oxidation of S to H$_2$S and H$_2$SO$_3$. 

\[
\text{NH}_4^+ + \frac{1}{2}O_2 \rightarrow \text{NO}_2^- + 2H^+ + H_2O \quad \text{Nitrosomonas sp}
\]
\[
\text{NO}_2^- + H_2O \rightarrow \text{NO}_3^- + 2H^+ \quad \text{Nitrobacter sp}
\]

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 microorganisms develop under the influence of specific soil treatments 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°C and these are termed mesophiles, however, some are able to tolerate extreme temperatures these are Psychrophiles (0 to 20°C) and Thermophiles (40 to 65°C).

**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 $10^5$- $4 \times 10^6$ 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 actinomycetes cause plant diseases eg potato scab disease.

**Algae**

These are sub-divided into two groups:

1. Green algae (True algae)
2. Blue-green algae (Cyanobacteria)

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

The blue-green algae do not possess nucleus, cell wall composed of a substance called 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.

**MICROBIOLOGY OF THE RHIZOSPHERE**
The microbial population is altered both quantitatively and qualitatively by the presence of plant roots. The microorganisms that respond to the presence of root is distinctly different from other soil community, the plant creates a habitat for organisms. In turn the plant is highly affected by the populations it stimulated since the root zone is the site from which inorganic nutrients are obtained and through which pathogens must penetrate. Consequently, interaction between the macro and microorganism in this region has considerable effect on crop production and soil fertility.

**Rhizosphere:** The rhizosphere is not a well define or uniform part of the soil, instead it represents a poorly defined zone with a microbiological gradient in which the maximal effect of root and microorganism is in the soil nearest to the root. Outer-rhizosphere and inner-rhizosphere had been used to define zones of influence. The inner-rhizosphere is the root surface and its adhering soil and can be referred to as rhizosplane. While the outer rhizosphere beyond this zone but still under the influence of the plant root is referred to as rhizosphere. The rhizosphere is a region of highly favourable habitat for the proliferation and metabolism of numerous microbial types. A vast microbial community occurs near and on the surface of roots and root hairs. Bacteria are found to be localized in colonies and chains of individual cell, Fungi and actinomycetes are observed but not as frequently as bacteria. The rhizosphere effect is measured quantitatively by the R/S ratio. This is defined as the ratio of microbial numbers per unit weight of rhizosphere soil R, to the number in a unit weight of adjacent non-rhizosphere soil. The rhizosphere effect is usually greater for bacteria than other soil microorganisms.

**Influence of Plant on Microorganism:** The microbial population is affected in many ways by the growing plant, and microbial reactions important to fertility are more rapid in the root environment.

1. The most important contribution to the rhizosphere microorganisms is provision of excretion products and sloughed-off tissue to serve as a source of energy, carbon, nitrogen, and growth factors.
2. Plants assimilate inorganic nutrient within the rhizosphere and therefore lower the concentration available for microbial development.
3. Microorganisms are affected by root respiration which alters the pH or the availability of certain inorganic nutrients by the evolution of carbon dioxide.
4. Root penetration improves soil structure and brings about aeration for microbial development.
5. In the presence of nitrates denitrification may result in the root region thus increasing release of nitrous oxide and nitrogen gas.
6. The presence of certain plants, reduce the population of nitrifying microorganisms.
7. The cellulolytic organisms increase in number in response to availability of large quantity of cellulosic tissues in the sloughed-off plant materials and the product of their metabolism provide carbonaceous substrates for other organisms.
8. Some root excretions aid the germination of the resting structures of several fungi by providing them with sources of energy. This stimulus to germination is particularly important to plant pathogens that are not vigorous competitors and remain in the resting stage because of nutrient shortage or fungistasis.
9. Roots may liberate antimicrobial agents, in some instances these are antifungal substances. The production of high quantity of carbon dioxide may inhibit germination or affect fungi in other ways.

**Influence of Microorganisms:** The microorganisms in the rhizosphere may have either favourable or detrimental influence on plant development. Since the microflora is so intimately related to the root system any beneficial or toxic substances produced can cause an immediate and profound response.

1. Microorganisms may favour the growth of higher plant by affecting the availability of various nutrient elements essential for plant growth, most especially carbon, nitrogen and phosphorus.
2. The production of CO$_2$ in the rhizosphere and the formation of organic or inorganic acids aid in the solubilization of inorganic plant nutrients. This is particularly so with insoluble phosphate containing compounds.

3. At the same time, the vast population of microorganisms demands some anions and cations for their own development leading to immobilization of N and P.

4. Aerobic bacteria remove O$_2$ from the environment and add CO$_2$ and either of these processes may reduce root elongation and development or diminish the rate of nutrient and water uptake.

5. Microorganisms may favour plant growth through the production of specific growth stimulating or growth regulating substances such as auxins and phyto hormones eg indole acetic acid, gibberelins and cytokinins.

6. Some microorganisms are parasitic to plants or produce certain toxic substances which are injurious to plants.

7. Antibiotics may be produced in the rhizosphere and this may affect the growth of root pathogens and even the development of diseases in the above tissues if translocated to stem and intravascular system. Antibiotics are also known to affect the physiology of plant.

8. Some groups of microorganisms form symbiotic relationship with higher plant, eg certain fungi form mycorrhizal association with higher plants and the numbers of free living nitrogen fixing organisms are quite high on the root surface.

MYCORRHIZA
This is the symbiotic association between fungi and root of higher plants, the association is beneficial to most organisms. Mycorrhizas are classified into several groups.

**Ectomycorrhiza:** This association consists of septate fungal cells infecting roots of trees and shrubs. The fungi form compact mantle or sheath over the root surface and penetrate between the cells of the root cortex to form a complex intercellular system called the Hartig net. The ectomycorrhizal fungi produce auxins responsible for some morphological differences between mycorrhizal and nonmycorrhizal roots. Many fungi from classes Basidiomycetes, Ascomycetes, Zygomycetes and Mushrooms form ectomycorrhiza. It is usually difficult and sometimes impossible to plant seedlings of trees in grassland soils or other new areas, particularly in forest establishment without introduction of the fungi partner.

**Ectendomycorrhiza:** This is similar to ectomycorrhiza except that the external mantle of fungi sheath may be much reduced or absent, the Hartig net is well developed and the hyphae also penetrate the host cells.

**Ericaceous mycorrhizas:** These include the mycorrhizas associated with Arbutus, Ericales and Monotropaceae.

**Arbutoid mycorrhizas** are formed as mantle which serve as storage organ, when Hartig net is present it penetrates the outer layer of the cortical cells. The septate hyphae form intracellular coils that eventually disintegrate within the cell.

**Ericoid mycorrhiza** occurs between the ericaceous plants and a fungus called Pezizella. The fungus forms multiple coils within the cells and up to 42% of the root cells can be occupied by the fungal hyphae.

**Monotropoid Mycorrhiza:** A member of the Basidiomycetes called Boletus infects both the monotropa and the roots of neighboring trees. The seed of monotropa is very small it will initiate germination but will not develop further until infected with Boletus. Phosphate and glucose can be translocated by the fungi over a distance of 1 to 2 m to the tissue of monotropa.

**Orchidoid mycorrhizas:** Orchid seedlings are very small and the seedlings pass through a seedling stage during which they are unable to photosynthesize. Since the seeds are too small to contain reasonable reserves, a germinating embryo does not develop further unless it receives an outside supply of carbohydrates or is infected by a compatible mycorrhizal fungus. The infection in orchids spreads from cell to cell, with hyphae coils taking up a large portion of the volume of infected cells.
The intracellular hyphae have a limited live and degeneration can occur as early as 30 to 40 hours after initiation of infection and is usually complete within 11 days. Fungi genera involve include *Rhizoctonia, Marasmius, Armillaria* and *Fomes*. Parasitism of host plant can occur as in monotropoid mycorrhizas. However unlike monotropoid mycorrhizas, a Hartig net, well developed fungal sheath and specialized haustoria are absent.

**Arbuscular mycorrhizal fungi (AMF):** These are the most common forms of mycorrhizas it involves fungi classified as Zygomycetes. The aseptate hyphae infect the root cells of nearly all cultivated plants, forest trees, shrubs and herbaceous species. No visible structural change is observed on the root except on onion where a sight yellowing of the root is observed. Internal vesicles constituted by fungal hyphae expansion filled with lipids are used for storage. There is another internal structure in the root cortex called arbuscule, this consist of finely branched hyphae and persist within the plant cell for 4 to 10 days. After which they are digested by the plant cell and new ones are formed in other cells. Nutrient transfer occurs between the finely branched fungal mycelium and plant cell membranes. Some fungi hyphae and resting spores extend externally in the soil. Five major genera of the family Endogonaceae form AMF, these are; *Glomus, Gigaspora, Acaulospora, Sclerocystis* and *Scutellospora*. They are distinguished by the morphology of their resting spore.

**FUNCTIONS OF MYCORRHIZAS**

1. The major contribution of the fungus is in nutrient uptake and translocation, especially of phosphorus and sometimes nitrogen.
2. Mycorrhizal plants have the capacity to withstand or tolerate drought better than non-mycorrhizal plants.
3. The plants are protected from pathogens, nematodes and heavy metal concentrations in the rooting zone.
4. The fungi partners obtain carbon from the plant.
5. Mycorrhizal fungi have aggregating effect especially on coarse soil.
6. The production of phyto-hormones such as cytokinins may have positive effect on plant growth.
BIOLOGICAL NITROGEN FIXATION

Nitrogen fixation is the conversion of atmospheric nitrogen to plant available nitrogen. It can be brought about by electrical discharge (lightning) or other ionizing phenomena of the upper atmosphere (Haber process). The fixed nitrogen is added to the soil as a component of precipitation.

\[ \text{200 atms} \]
\[ \text{\( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \rightarrow \text{NH}_4\text{OH} \)} \]
\[ 450^\circ\text{C, Catalyst} \]

Most of the nitrogen fixed into the soil is however accomplished by biological nitrogen fixation. There are two types of biological nitrogen fixation; Symbiotic nitrogen fixation and Non symbiotic nitrogen fixation.

Non Symbiotic nitrogen fixation

This biological nitrogen fixation is carried out by organisms which live freely in soil as represented by two groups of microorganisms; bacteria and blue-green algae (cyanobacteria).

Bacteria genera involve in nitrogen fixation could be aerobes, facultative anaerobes and anaerobes.

Examples of aerobic bacteria include, species of \text{Azotobacter} and \text{Beijerickia}.

Examples of facultative anaerobe include species of \text{Azotobacter} and \text{Beijerickia}.

Examples of anaerobe include species of \text{Clostridium}.

For the blue-green algae, the examples include species of \text{Nostoc}, \text{Plectonema} and \text{Anabaena}.

These nitrogen fixers add between 0.2 and 5 kg N/ha/annum, whereas most crop plants require 50 – 200 kg N. This process is therefore thought to be of little significance agronomically. However, the process is of value in rice paddies where blue - green algae, which depend on photosynthesis freely, fix nitrogen. The process is highly influenced by the population of nitrogen fixers in the soil and this in turn is dependent on soil pH.

Symbiotic nitrogen fixation

This is the production of plant available N from atmospheric nitrogen by organisms that live in association with plant roots. These bacteria reside in the roots of legumes causing swellings known as nodules in legume roots. They derive their food and nutrients from the legumes and in turn supply the legumes with nitrogen fixed from the atmosphere. This symbiotic relationship is most common between legumes and \text{Rhizobium} species. Examples of legumes include trees such as \text{Acaasia}, \text{Mimosa} and \text{Cassia}, shrubs such as \text{Cesalpina} and \text{Indigofera} as well as crops such as cowpea, soybean, groundnut, pigeon pea, etc. The Rhizobium species are host specific and when the right species are not present in the soil, where the legume is grown, nodulation may not occur and even when some nodules are formed nitrogen fixation may not occur at all or at significant level. Therefore, under certain conditions Rhizobium inoculation is recommended.

Grain legumes are capable of fixing about 150 kg N/ha/annum, an amount that meets the nitrogen requirement of many crop plants.

Mechanism of nitrogen fixation

The central reaction according to which biological nitrogen fixation proceeds and the enzyme responsible for the reaction are the same in all organisms (Symbiotic and non-symbiotic).

\[ \text{N}_2 + 6\text{e}^- + 8\text{H}^+ + 12\text{ATP} \rightarrow 2\text{NH}_4^+ + 12\text{ADP} + 12\text{pi} \]

A molecule of nitrogen gas reduced to ammonia requires energy to proceed. It is estimated that 12 moles of ATP are required for 1 molecule of \text{N}_2, which is reduced to 2 molecules of ammonium.

The enzyme responsible for nitrogen fixation is called \text{Nitrogenase}. It consists of two proteins (i) Iron protein also called Azoferreredoxin or Component II or Azofer (ii) Molybdenum iron protein also called molybdo-ferredoxin or Component I or Azofermo. The individual component does not catalyse any reaction only the combined system of both proteins is regarded as an enzyme.

Both of the nitrogenase proteins are Iron-sulphur components. The iron protein is the smaller of the two with molecular weight ranging from 50,000 – 70,000. It is rapidly but reversibly inactivated by oxygen. The molecular weight of molybdenum iron protein range from 100,000 – 300,000 and also reversibly inactivated by oxygen.

Factors influencing nitrogen fixation

Biological factors
1. There has to be appropriate organism-host relationship or compatibility, because not all rhizobia can form nodules in all legume roots.
2. The plant should be nutritionally healthy to carry out optimal photosynthesis so as to obtain enough carbon for itself and the organism.
3. Infection by other organisms should be minimal, e.g., infection of roots by nematodes.

Chemical factors
1. High soil nitrogen content discourages nitrogen fixation.
2. Soil pH has a profound influence on the process, soil pH of 6 – 7.5 favour nitrogen fixation.

Physical factors
Aeration is important as most of the organisms involved are heterotrophic and aerobes. However, the presence of oxygen could retard the process, since it is a reduction process.
The presence of a pigment called Legume haemoglobin salvages the problem by binding $O_2$ thereby rendering it inactive, to be released only when needed. A cross section of an active nodule is reddish brown due to the presence of legume haemoglobin.

Agronomic importance of nitrogen fixation
1. In symbiotic nitrogen fixation the organisms live inside plant root, nitrogen fixed is immediately assimilated into products needed by plants such as amino acids, amines etc. In non-symbiotic fixation, the nitrogen is fixed into soil and absorbed by plants.
2. When ploughed in as green manure or incorporated as crop residues, the nitrogen synthesized into organic N can be mineralized as nitrates and be of benefit to crops that will be subsequently grown in the soil.
3. In mixed cropping, when legumes and non-legumes are grown in mixture, the non-legume benefit from nitrogen fixed by legumes.

Nitrogen fixation is so important that where it is suspected that the appropriate strains of rhizobia are not present in the soil, legume seeds are inoculated with such strains.