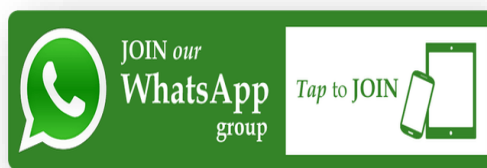


Chapter 3

Soil Chemistry

- ✓ Soil chemistry is the study of the chemical characteristics of the soil. Soil chemistry is affected by mineral composition, organic matter and environmental factors.
- ✓ **Soil Colloid** – The colloidal state refers to a two-phase system in which one material (or materials) in a very finely divided state is dispersed through a second.
- ✓ In general, the range of true colloids is from 2 nm to 200 nm.
- ✓ The scattering of light by colloids is called Tyndall scattering or simply “**Tyndall effect**”.
- ✓ Due to unbalanced impact of solvent molecules on colloid particles, these particles move in a zig-zag way in the soil solution which is called “**Brownian movement**”.
- ✓ A typical value of CEC of humic colloids (which is pH dependent) 200 - 250 c. mol (p^+) kg^{-1} or even higher.
- ✓ The tetrahedral unit is SiO_4^{-4} in which the silicon ion is equidistant from the 4 oxygen ions.

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- ✓ The octahedral unit consists of an Al, Fe or Mg ion, surrounded by equidistantly spaced 6 oxygen or hydroxyl ions in the form of an octahedron.
- ✓ When Al is present, say in gibbsite structure, $\text{Al}_2(\text{OH})_6$, two thirds of the ionic positions are filled to become the unit is called “**Di octahedral structure**”. With divalent cations, as in brucite $\text{Mg}_3(\text{OH})_6$, all the octahedral positions are filled to give a “**Tri octahedral structure**”.
- ✓ 1:1 minerals – Dimorphic minerals.
- ✓ 2:1 minerals – Trimorphic minerals.
- ✓ 2:2 minerals – Tetramorphic minerals.
- ✓ The 1:1 types of clays include kaolinite, halloysite, anauxite, nacrite and dickite. To illustrate the properties of 1:1 silicate clays we will focus on kaolinite, which is by far the most common in soils.
- ✓ **Kaolinite** – The most widely occurring clay mineral in soils is kaolinite, which is the simplest mineral among all the clay minerals. This is the dominant type of clay mineral in red and laterite soils. In this mineral units are held together very rigidly by hydrogen bonding. Basal spacing of kaolinite is $7.2 \text{ \AA}^0$ (0.72 nm). On the other hand kaolinite mineral can have an anion exchange capacity as high 43 me/100 g at an acidic equilibrium pH of 4.7
- ✓ **Montmorillonite** – Montmorillonite is best example for 2:1 type expanding clay mineral. A Montmorillonite crystal unit consists of a single gibbsite octahedral sheet sandwiched between two silicon tetrahedral sheets. The crystal units are held together by very weak oxygen-oxygen linkages.
- ✓ Vermiculite has high CEC on volume base and high surface area among all clay minerals.
- ✓ Layer charge highest for Mica and Chlorite.

- ✓ AEC highest in Kaolinite.
- ✓ Illite is non expanding 2:1 clay mineral and which is also called hydrous mica.
- ✓ Montmorillonite is 2:1 type expanding clay mineral.
- ✓ Vermiculite is slightly expanding 2:1 clay mineral.
- ✓ Chlorite (had brucite sheet) is example for 2:2 or 2:1:1 mineral.
- ✓ CEC on weight base highest in humus.
- ✓ A number of techniques have been developed to identify clay minerals such as X-ray diffraction analysis (XRD technique), Electron diffraction analysis, Differential thermal analysis, Electron micrograph, Surface area determination, Cation exchange capacity determination, Elemental chemical analysis and Y-index.
- ✓ Ethylene glycol (EG) or ethylene glycol monoethyl ether (EGME) adsorption is recommended to determine total, internal and external surface areas of clay minerals.
- ✓ Molecular ratio of silica/sesquioxide ($\text{SiO}_2/\text{R}_2\text{O}_3$) where R_2O_3 stands for Fe_2O_3 and Al_2O_3 was used extensively to ascertain whether the soil clay was dominantly kaolinitic or montmorillonitic. In the former, the ratio is less than 2 (for kaolinite) where as in the latter ratio is higher than 2 (for montmorillonite).
- ✓ The content of K_2O in illite varies from 6 - 10 %.
- ✓ The Y-Index was proposed by “**Martin and Russell**”.
- ✓ Y-Index has proved to be useful to assess the dominating type of clay mineral in soil.
- ✓ The laws governing structural characteristics of the phyllosilicates are known as Goldschmidt’s Laws – Law I and Law II.

- ✓ **Goldschmidt's Law I** - In an ionic crystalline compound, Isomorphous replacement of one cation by another, without incurring any change in the order of the crystal pattern, is permitted provided that the radii of the cation replaced and the cation substituting it agree within 15 %.
- ✓ **Goldschmidt's Law II** - This law also called "**Radius Ratio Law**". When the number of anions surrounded a central cation such that they satisfy the charge completely, the number of anions that can be so accommodated around the cation depends on the radius of the central cation to that of the surrounding anions. Thus, this ratio of ionic radii governs is known as "**Coordination number**".
- ✓ **Isomorphous Substitution** – Negative charge developed in layer silicate clay minerals by Isomorphous substitution. Isomorphous substitution is the substitution of one ion with another ion in a mineral without a significant change in the crystal structure.
- ✓ Generally Exposed edges, Isomorphous substitution and Anion exchange are important sources for negative charge in silicate clays.
- ✓ The pH at which net surface charge of the soil colloids is zero is called zero point charge or ZPC (here positive charge is equal to total negative charge, resulting in the zero net charge).
- ✓ Among the functional groups, carboxylic groups are acidic groups with higher dissociation constant than other organic as well as inorganic S-OH groups. The carboxylic groups dissociate at the lower pH giving rise to the development of the negative charges. Phenolic and enolic groups dissociate at the higher pH to produce negative charges. Unlike inorganic S-OH groups, organic COOH and OH groups do not associate with H^+ at lower pH, meaning there by that net positive charge does

not develop on the organic colloids. Thus soils rich in organic matter may not have a zero point charge.

- ✓ The thickness of diffuse double layer decreases as the electrolyte concentration in the water increases at equal equivalent concentrations of electrolyte.
- ✓ Divalent cations decrease the thickness of double layer more strongly than that of monovalent cations, and trivalent more strongly than divalent.
- ✓ The double layer is thicker if the exchangeable ions are sodium (Na^+) and potassium (K^+) than calcium and magnesium.
- ✓ DDL thickness will be more due to presence of sodium than potassium (That is why soils containing more sodium show high pH resulting from more thicker diffuse double layer).
- ✓ “With increasing the electrolytic concentration four times, DDL thickness reduces to half”.
- ✓ The potential difference between the fixed layer and freely mobile portion of DDL (Diffuse Double Layer) is known as “**Zeta potential**”.
- ✓ Due to decrease in pH the zeta potential can be reduced resulting from the reduction of negative charge on the clay micelle and also from the replacement of sodium or other monovalent cations with hydrogen (H^+) ion.
- ✓ Ion exchange in soil system refers to exchange of equivalent amounts of ions between two phases in equilibrium in contact in a reversible process.
- ✓ The experimental evidence of cation exchange was provided around 1850 by Thompson, followed by J. Thomas Way.
- ✓ Colloidal material of the soil with effective particle diameters of less than 20 microns being the most important site for causing the ion exchange phenomena.

- ✓ **Inverse Ratio Law** was given by Matson.
- ✓ Adsorption is defined as a phenomenon by which an increase in concentration or an accumulation of an ion species on a solid occurs due to ion exchange or other reactions. Desorption is a phenomenon by which the replacement or release of an adsorbed ion occurs.
- ✓ The weight of one hectare furrow slice (depth of 0-15 cm layer) is 2.2×10^6 kilograms.
- ✓ Famous Physical Chemist C. E. Marshall had emphasized that the CEC is the second most important in nature, surpassed in fundamental importance only by the photosynthetic process of green (CEC is next to photosynthesis).
- ✓ **ECEC (Effective Cation Exchange Capacity)** – It is the sum of exchangeable bases (Ca^{+2} , Mg^{+2} , K^{+} and Na^{+}) as extracted by 1 M NH_4OAc (one molar ammonium acetate at 7 pH) and 1 M KCl extractable Al^{+3} .
- ✓ In most soil laboratories, CEC of a soil is determined by extraction with 1 N neutral ammonium acetate (1N NH_4OAc).
- ✓ Surface Charge Density = $\text{CEC} / \text{Specific Surface Area}$.
- ✓ On the basis of experimental data, the preference of different anions for the positive sites has been found to follow the order - $\text{SiO}_4^{-4} > \text{PO}_4^{-3} > \text{SO}_4^{-2} > \text{NO}_3^{-} = \text{Cl}^{-}$.
- ✓ Kaolinite mineral can have an anion exchange capacity as high 43 me/100 g at an acidic equilibrium pH of 4.7.
- ✓ The repulsion of anions by the negatively charged sites leads to a local deficit of anions near a clay particle in comparison with the equilibrium solution. The deficit has been termed as “**Negative adsorption**”.
- ✓ Negative adsorption also called “Anion exclusion”.

- ✓ Langmuir Adsorption Theory is the basic theory of adsorption of gases on solids.
- ✓ Freundlich Isotherm is one of the most widely used adsorption equations to describe the experimental data on adsorption of ionic or molecular species in soil.
- ✓ The theory of Brunauer, Emmet and Teller (BET) extends Langmuir derivation to obtain an equation for “**Multilayer adsorption**”.
- ✓ Ratio between the cations on soil surface and CEC is termed as the relative base saturation and when expressed on percentage basis, it is termed as the percent base saturation or base saturation percentage (BSP)
- ✓ At pH 7.0 percent base saturation is about 80 and each unit decrease in pH, base saturation decreases by about 20 %.
- ✓ If base saturation percentage is more than 80 which indicates highly fertile soil, while if it is between 50 - 80 % which indicates medium fertile soil and if it is less than 50 % less fertile soil.
- ✓ The sequence of tenacity with which ions will be adsorbed is called “Hofmeister series or lyotropic series”. For the alkali ions, the selectivity has been often found to increase in the same order of lyotropic series namely $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ and alkaline earth ions it follows the sequence $\text{Mg}^{+2} < \text{Ca}^{+2} < \text{Sr}^{+2} < \text{Ba}^{+2}$. Lyotropic series in respect of adsorbability is given as $\text{Al}^{+3} > \text{Ca}^{+2} > \text{Mg}^{+2} > \text{K}^+ = \text{NH}_4^+ > \text{Na}^+$.
- ✓ **Activity Coefficient** – It is the ratio between the activity (chemical) and the concentration of a substance in solution. When concentration is corrected by a factor which is always less than 1 and that factor is called activity coefficient. This can be expressed by $a = f \times c$.

-
- ✓ Activity in the soil solution phase can be calculated easily by Debye-Huckel equation
 - ✓ Concept of Root CEC was given by Devaux.
 - ✓ The cation exchange capacity of roots of different plant species ranges from less than 10 to almost 100 me/100 g of soil. The exchange properties of roots appear to be attributable mainly to carboxyl groups (-COOH) present in pectic substances.
 - ✓ Complementary ion effect is defined as the influence of one adsorbed ion on the release of another ion from the surface of a colloid.
 - ✓ Gapon constant values commonly range from 0.010 - 0.015.
 - ✓ For heterovalent exchange, the equations proposed by Vanselow and Gapon are widely used and both are based on "law of mass action".
 - ✓ Krishnamoorthy, Davis and Overstreet (KDO) proposed "Nearest Neighbour Model" and Jenny proposed "Oscillation volume".
 - ✓ F. G. Donnan in 1911. Donnan membrane equilibrium belongs to mass action equations.
 - ✓ **Jarusov's Rule** (Complementary ion principle) – The exchangeability of a given ion was not a constant, but was a function of its amount in relation to the amount and kind of other cations present.
 - ✓ Electrons, small negatively charged components of atoms of all substances.
 - ✓ Protons, positively charged particles of much greater mass than electrons.
 - ✓ The unit of mass in the International System of Units (SI) is the kilogram (kg).
 - ✓ Gram atomic weight = atomic weight in grams.

- ✓ The number of atoms in 1 gram atomic weight of any element is as 6×10^{23} . This number is known as Avogadro's number and is used for a number of calculations, such as calculating the weight of one atom.
- ✓ **Normality** - The number of equivalent weights of a substance dissolved in 1 litre (L) of a solution determines the normality (**N**) of the solution- in other words, "Normality" is the strength of the solution. If one equivalent is dissolved in 1 L of a solution, the solution has a strength of 1 N (one normal). If two equivalents are present in 1 L of solution, the solution is 2 N. The symbol N is usually italicized, or when a capital letter is used underscored or underlined (**N**), to distinguish it from the symbol N, the nitrogen element.
- ✓ **Molarity** (M) is defined as the number of moles of a substance per litre of solution. Molality (m), on the other hand, is the number of moles per kilogram (kg) of water, and formality (f) is the number of moles of a substance per kg of solution.
- ✓ Another chemical unit, which is sometimes used in soil chemistry, is the mole fraction. The latter is defined as the ratio of the number of moles of a given substance to the total number of moles of all constituents in solution, including the number of moles of water if it is an aqueous solution.
- ✓ Radioactivity, discovered for the first time in 1896 by Henri Becquerel, involves a spontaneous disintegration of certain types of elements or atoms to form other elements or atoms.
- ✓ Half-life is a measure of the rate of decay of radioactive material. It is the length of time during which the material loses one-half of its radioactivity, or the time required for decomposition of one-half of the atom. In the latter sense, the term half-life has now been adopted for measuring the persistence of pollutants in soils.

- ✓ Half-life of ^{14}C is only 5370 years.
- ✓ **The Nernst equation** was formulated by Walther Hermann Nernst (1864 – 1941), a German physical chemist (Wahl, 2005). Known also for his Nernst–Thompson rule, explaining the ionization process, and for the Heat Theorem as reflected in the Third Law of Thermodynamics, for these and many other contributions Nernst was awarded the Nobel Prize for electrochemistry in 1920. This provides a means for the determination of the redox potential of a half-cell reaction and can also be used to calculate the electromotive force of the whole electrochemical cell.
- ✓ **Henry's rule** indicates that the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid.
- ✓ When compounds dissolve, the energy is released, a phenomenon called heat of solution. The ions are then hydrated and the corresponding release of energy is called heat of hydration. In thermodynamic language, it is the increase in enthalpy due to formation of a hydrate. In contrast, when clay particles are hydrated, the energy released is called heat of wetting.
- ✓ **Biological oxygen demand (BOD)** -This is defined as the amount of oxygen consumed by microorganisms in the process of decomposition of organic matter during a 5 - day incubation period. The test was developed in England, where it was believed that dissolved organic matter not decomposed within 5 days would be transported into the sea.
- ✓ **Chemical oxygen demand (COD)** -This is defined as the amount of oxygen consumed in the chemical oxidation of organic matter by potassium dichromate in the presence of sulphuric acid. The analysis for oxidation of organic C is known today as the Walkley – Black method.

- ✓ **Total oxygen demand (TOD)** - This is the amount of oxygen consumed in the catalytic oxidation of carbon. The amount of CO_2 produced in the reaction is measured.
- ✓ The attraction of soil solids (matrix) for water provides a matrix force, and that part of the water potential attributed to the matrix force is called matric potential. Taylor and Ashcroft (1972) reported that the matric potential is similar to the capillary potential and replaces terms such as soil moisture tension, soil moisture suction, or matric suction.
- ✓ The Debye - Huckel theory, developed by Peter Debye and Eric Huckel in 1923, is simply a concept conveying the behaviour of ionic solutions, in which electrical potential fluctuations due to ions are practically very small.
- ✓ The term ionic strength is used as a measure of the strength of ionic concentrations in the solution. The concept was introduced by Lewis and Randall (1921) to assess the combined effect of the activities of several electrolytes in solution on a given electrolyte.
- ✓ Lignin is considered, second to cellulose, the most abundant biopolymer in nature.
- ✓ Cyclosilicates - Tourmaline, benitoite.
- ✓ Inosilicates - Amphibole, pyroxene, hornblende.
- ✓ Nesosilicates - Garnet, olivine, zircon, topaz.
- ✓ Phyllosilicates - Chlorite, vermiculite, illite, kaolinite, smectite.
- ✓ Sorosilicates – Epidote.
- ✓ Tectosilicates - Feldspars, quartz, Zeolite.
- ✓ Members of the kaolinite group are kaolinite, dickite, nackrite, and halloysite. Except for halloysite, the other minerals are nonexpandable in water. Upon heating, it is irreversibly dehydrated, and the mineral is then called metahalloysite.

- ✓ The illite minerals are micaceous types of clay. However, in contrast with the true micas, which are primary minerals or primary formation, illites are of secondary origin. They are also known under the names “**hydrous mica**” or “**soil mica**”. The term illite is suggested for the fine-grained minerals in this group, whereas the coarser particles are frequently called hydrous mica.
- ✓ Vermiculite name is derived from vermiculare or vermicularis (Latin: “wormlike,” or “to breed worms”), because upon heating, the mineral becomes elongated, twisted, and curled. After heating, it usually expands to 20 to 30 times its original size.
- ✓ The Fe-rich chlorite is called **chamosite**, and Mg-rich chlorite is known as **clinochlore**.
- ✓ Several of the different types of clay minerals may be stacked together as a packet. This process is called interstratifications and such clays are referred to as interstratified clays or mixed-layer clays.
- ✓ In general, solubility of silica minerals is related to the packing density of the silica tetrahedra. The solubility increases in the following order: Quartz < cristobalite < opal < amorphous silica.
- ✓ The x-ray diffraction (XRD) method is perhaps the most widely used technique in the identification of clays.
- ✓ Isomorphous substitution is believed to be a major source of negative charges in 2:1 layer clays.
- ✓ The negative charge of the clay surface is thus screened by an equivalent swarm of counter ions that are positive. The negative charge on the clay surface and the swarm of positive counter ions are called the electric double layer.

- ✓ When a colloidal suspension is placed in an electrical field, the colloidal particles move in one direction (toward the positive pole). The counter ions move in another direction (toward the negative pole). The electric potential developed at the solid–liquid interface is called the zeta potential.
- ✓ Adsorption is defined as the concentration of constituents at the colloidal surfaces. The curve relating the concentrations of adsorbed materials at a fixed temperature is called the adsorption isotherm.
- ✓ If the soil–water potential decreases, soil–water content also decreases. The latter may cause water to move out of the cell, ultimately producing a phenomenon called cytoplasmolysis.
- ✓ The cation exchange capacity of sesquioxides is 2 - 4 meq / 100 g of soil.
- ✓ Under certain conditions, the adsorbed cations are held so strongly by clays that they cannot be recovered by exchange reactions. These cations are called fixed cations.
- ✓ The repulsion of anions from colloidal surfaces possessing negative charges is called negative adsorption.
- ✓ Bolt (1976) reported a decreasing order of preferential adsorption among the different anions –
 $\text{SiO}_4^{4-} > \text{PO}_4^{3-} \gg \text{SO}_4^{2-} > \text{NO}_3^- = \text{Cl}^-$.
- ✓ Phosphate anions can be attracted to soil constituents with such a bond that they become insoluble and difficult to obtain by plants. This process is called phosphate retention and phosphate fixation, which can occur biologically or chemically. Some call it chemical fixation of phosphate.
- ✓ The term phosphate potential is introduced by Schofield (1955) to be used as an index for availability of soil phosphorus. Similarly, as with the definition of soil water potential, the phosphate potential is defined as the amount of work that must

be conducted to move reversibly and isothermally an infinitesimally small amount of a phosphate ion from a pool of phosphates at a specified location at atmospheric pressure to the point under consideration.

- ✓ Bronsted and Lowry defined independently, in 1923, that an acid is a compound capable of donating a proton (proton donor). On the other hand, any compound capable of accepting a proton is considered a base (proton acceptor). This acid-base concept is also known as the proton concept.
- ✓ **Lewis Concept** - According to this theory, an acid is a compound that can accept an electron pair (electron-pair acceptor). A base is a compound that can donate an electron pair (electron-pair donor). Hence, any substance that has an unshared pair of electrons is a base, and any compound that can react with that pair of electrons is an acid. This is also called the electron concept.
- ✓ When a liquid is dispersed in a gas medium, it also forms an aerosol, like spray and fog, but when it is dispersed in a liquid it is called an emulsion.
- ✓ Hymatomelanic acid soluble in alkali and alcohol mediums but insoluble in acid mediums.
- ✓ Humic acid and humin both are insoluble in alcohol medium.

Table–1 CEC (C. mol. P⁺ kg⁻¹ (or) meq / 100 g of soil)

1	Sesquioxides	2 – 4
2	Kaolinite	3 – 15
3	Montmorillonite	80 – 100
4	Illite	15 – 40
5	Vermiculite	80 – 150
6	Humus	150 – 300

Table - 2 [C –AXIS SPACING (A°)]

S. No	Name of the mineral	Spacing
1	Kaolinite	7.2
2	Montmorillonite	14
3	Halloysite	10.25
4	Illite (or) Mica	10
5	Vermiculite	10 - 15
6	Chlorite	14

NOTE: 1 nm = 10 A°

Table - 3 HUMIC COMPOUNDS

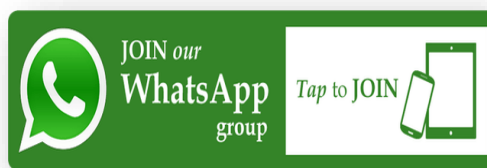
S. No	Fraction name	Molecular weight	Soluble medium
1	Fulvic acid	Low	Soluble both in alkali and acid medium
2	Humic acid	Medium	Soluble in alkali medium only
3	Humin	High	Insoluble in both acid and alkaline mediums

Table – 4 Y - INDEX

S.No	Name of the mineral	Y-index value
1	Kaolinite	0 - 5
2	Illite	5 - 25
3	Montmorillonite	> 25

□□□□□

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