Soil And Water Chemistry

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> Fisheries science holds the answers to the sustainability of aquatic life and the future of global food security.

Course Name	Soil and Water Chemistry
Lesson 1	Analytical Chemistry: Principles, Applications and Types
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Lesson 1

Objectives:

1. To understand the principles of different analytical chemistry techniques
2. To understand different analytical chemistry concepts

Glossary of terms:

Volumetry: Volumetry is measurement of volume of a solution of known concentration which is used to determine the concentration of the analyte.

Gravimetry: It is a technique through which the amount of an analyte (the ion being analysed) can be determined through the measurement of mass. Gravimetric analyses depend on comparing the masses of two compounds containing the analyte. The principle behind gravimetric analysis is that the mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

Standard solution: Standard solution is the one whose concentration or strength is accurately known. It is also sometimes referred to as “titrant”.

Titration: The Process of adding a standard solution from a volumetric burette to a solution of the unknown concentration in the conical flask until the reaction is just complete is known as “Titration”.

Indicator: The end point or equivalent point of titration is recognized with the help of a chemical reagent called “Indicator”.

Normality: It is a measure of concentration equal to the gram equivalent weight per litre of solution. Gram equivalent weight is the measure of the reactive capacity of a molecule. The solute's role in the reaction determines the solution's normality. Normality is also known as the equivalent concentration of a solution.

Molarity: It is a unit of concentration measuring the numbers of moles of a solute per litre of solution. Molarity is denoted with 'M'. A 1 M solution contains 1 mole of solute per litre of solution.

Molality: It is the number of moles of solute per kilogram of solvent. Solutions expressed in molal concentration are denoted with 'm'. 1 m solution contains 1 mole of solute per kilogram of solvent.

Formality: It is defined as the number of formula mass of any solute dissolved in one litre of solution. A solution is said to be one formal (1 F) if it contains one formula mass of the substance in one litre of solution.

Standard curve: A standard curve also known as Calibration curve, is a type of graph used as a quantitative research technique. Multiple samples with known concentration are measured and plotted on the graph, which then allows similar concentrations to be determined for unknown samples by interpolation on the graph. The samples with known concentration are the standards, and the graph is the standard graph.

Nomograph: These are graphical representations which are used by simply applying a straight edge across the plot through the points on scales representing independent variables, which then crosses the corresponding datum point for the dependent variable; the choice among independent and dependent variable is arbitrary so that each variable may be determined in terms of the others.

E-lecture:

1. What is Analytical Chemistry: Analytical chemistry is application of chemical knowledge for characterising the composition of matter, both qualitatively and quantitatively (the identification of matter under study is performed using qualitative analysis while quantitative analysis is used to determine how much (relative concentration or total amount) of the substance is present in the analyte . Methods used in analytical chemistry are based on chemical and physical principles to study a substance which is to be analysed.

1.1 Classical methods of analytical chemistry:

A) Classical Qualitative methods: These methods can further be divided into

(a) Separation methods &

(b) Identification methods

(a) Separation methods:

i) Precipitation: This is a gravimetric method in which the reactants and products of a chemical reaction are used to analyse a substance. The metallic ions of many elements may enter into a reaction with the negative ions to form a new insoluble substance called the precipitate, which settles to the bottom of the solution. This is filtered out and washed.

ii) Extraction: This is a procedure in which a substance is removed from a matrix, both being in two immiscible phases. The most common technique for extraction of a compound from an aqueous solution is liquid-liquid extraction (LLE). Solid phase extraction (SPE) is a widely used method of sample preparation used to separate and enrich purified components from aqueous solution.

iii) Distillation: This is process of evaporation and condensation by which a component is separated out of a mixture of liquids. It is based upon the difference in boiling points or volatility between the various substances present in the mixture.

(b) Identification methods: These methods are based on colour, odour, melting and boiling points, radioactive or reactive properties of the analyte.

B) Classical Quantitative methods:

(a) Titration method: It includes acid-base or complexometric titration. Acid-base titration helps in quantifying an unknown acid or base in solution by finding its concentration based on the exact amount of corresponding base or acid required to neutralize it. Complexometric titration is a volumetric analysis where end point of titration is the formation of a characteristic coloured complex, which is usually a metal complex.

(b) Gravimetric method: It uses precipitation or volatilization to determine the mass of the analyte from its ionic mass. Precipitation, Volatilization or electroanalytical methods are mostly used.

(c) Coulometric method: These methods help to determine the mass of matter transformed by electrolysis from the amount of electric current used or produced during the reaction.

1.2 Instrumental methods: Instrumental methods are mostly used in advance level of research and the same instrument may be used to separate, identify and quantify the analyte.

A) Instrumental separation methods:

(a) Chromatography: This method uses a mobile phase into which the mixture is introduced, which then passed through the stationary phase. Due to the different rates at which the components of the mixture travel through the stationary phase, they can be separated.

There are different types of chromatography:

(i) Paper or thin layer chromatography

(ii) Gas chromatography

(iii) Ion-exchange and size-exclusion chromatography

(iv) Reversed-phased chromatography, Two-dimensional chromatography, Hydrophobic interaction chromatography

Special Note

High Performance Liquid Chromatography (HPLC) is an advance technique in which the analyte is contained in a mobile phase passed through a stainless-steel column which is between 1 and 25 cm long and less than 1.0 mm to 4.6 mm internal diameter, filled tightly with micro size particles allowing the various components of a complex non-volatile mixture to separate rapidly. The final concentration is determined using computations based on the outputs at varying amounts of organic compound.

(b) Electrophoresis: In this method, an electric field is used to separate particles in a fluid because of development of a charged interface between them.

(c) Field Flow Fractionation: In this technique, a fluid suspension or solution is fed through a narrow channel and a field is applied right angles to it, causing the particles within the field to separate because of their varying mobility in response to the field force.

B) Instrumental qualitative and quantitative methods: These methods may utilize light, electromagnetic, heat and combinations of these to identify the analytes.

(a) Spectrometry: This method can isolate particles based on various properties like mass, momentum or energy. It includes techniques such as ion-mobility spectrometry based on mobility of ionised particles in a carrier gas, or mass spectrometry which measures the ratio of mass to charge of ions.

(b) Spectrophotometry: This method is based on Beer-Lambert law. Here a material or component is identified by its reflection or transmission of light, which depends on the wavelength. Visible, ultraviolet or near-infrared light may be used in this method. This method is widely used to study gases, solids or solutions.

Beer-Lambert Law

This law states that the absorbance of a light absorbing material is proportional to its concentration in solution. The general Beer-Lambert Law is usually written as

$$\mathbf{A} = \mathrm{e}\,l\,\mathbf{c}$$

Where

A is the measured absorbance

e is the *extinction coefficient* of the substance- unique for each substance

l is the sample path length measured in centimetres (i.e. the width of the cuvette almost always 1 cm)

c is the molar concentration of the solution (expressed in terms of molarity)

(c) Potentiometry: It is a method of analysis in which the concentration of an ion or substance is determined by measuring the potential developed when a sensitive electrode is immersed in the solution of the species to be determined. Commonly available pH meters are designed based on this principle.

(d) Conductometry: Conductometry is the measurement of the electrical conductivity of a solution. The main principle involved in this method is that the movement of the ions creates the electrical conductivity. The movement of the ions is mainly depended on the concentration of the ions. Electrical conductivity and Total Dissolved Solids (TDS) of water samples generally determined by instruments designed based on this principle.

(e) Turbidimetry/ Nephelometry: The principle of nephelometry and turbidimetry is based on the on the well-known law of Tyndall Effect. When light is passed through the suspension, part of incident radiant energy is dissipated by absorption, reflection, and refraction while remainder is transmitted. In fact the measurement of the intensity of transmitted light is a function of the concentration of dispersed phase and this becomes the basis of turbidimetric analysis.

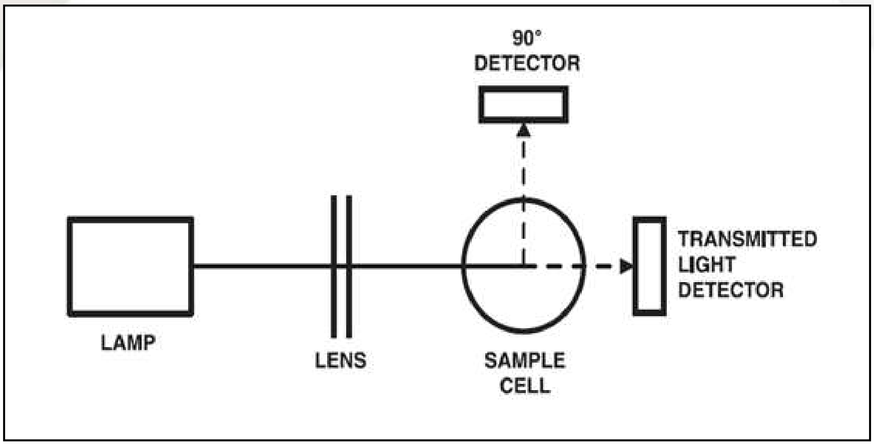


Fig.1. Schematic Diagram of a Nephelometer

(f) Radiometry: Radiometry is the science of measuring light in any portion of the electromagnetic spectrum. In practice, the term is usually limited to the measurement of infrared, visible, and ultraviolet light using optical instruments. Irradiance is the intensity of light and is measured in watts per square meter.

1.3 Volumetry & Gravimetry:

A) Volumetry: It is a widely used quantitative analytical method. It involves measurement of volume of a solution of known concentration which is used to find out the concentration of the analyte.

Some of the widely used volumetric analysis are:

a) Acidimetry: The term acidimetry refers to that part of volumetric analysis whereby an acid solution at known concentration, along with a specific indicator, is used to titrate a base solution and thus work out its concentration.

b) Alkalimetry: The term alkalimetry refers to that part of volumetric chemical analysis which enables us to work out the concentration of an acid solution using an alkaline solution at a known concentration and a suitable indicator.

c) Argentometry: The determination of silver or halides by the precipitation of silver salts is known as argentometric titrations. The sample solution is titrated against a solution of silver nitrate of known concentration. It can be used for measurement of salinity.

B) Gravimetry: Gravimetric analysis is a technique through which the amount of an analyte (the ion being analysed) can be determined through the measurement of mass. Gravimetric analyses depend on comparing the masses of two compounds containing the analyte.

Principle: Mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

For an accurate gravimetric analysis, the following 3 conditions must be met:

i) The ion being analysed must be completely precipitated.

ii). The precipitate must be pure compound.

iii) The precipitate must be easily filtered.

1.4 Standard Solutions: A solution whose strength or concentration is accurately known is referred to as Standard solution.

i) The most accurate and convenient way of preparing a standard solution is to weigh the reagent, dissolve it, and dilute the solution to a definite volume in a volumetric flask. However, this method can only be used if the reagent is a primary standard.

ii) In order for a reagent to be a primary standard, it must be obtainable in pure form (generally at least 99.98% pure), stable both is pure form and in solution, easy to dry and keep dry, and soluble in a suitable solvent.

iii) But many useful reagents do not meet those requirements, so the reagent is dissolved and diluted approximately to the concentration desired. The solution is then standardised by titrating it against a primary solution. This standardised solution is called a secondary standard.

Requirements of a primary standard substance:

- It must be 100% pure and dry.
- It must be 100% soluble in suitable solvent.
- It should not be hygroscopic.
- It should get oxidized by oxygen or affected by CO_2
- The reactions should be stoichiometric and instantaneous.

1.5 Titration & Indicators: Titration is a widely used quantitative analytical technique. The steps involved in titration are as follows:

i) Prepare a solution from an accurately weighed sample to +/- 0.0001 g of the material to be analysed. It is also known as **Analyte**.

ii) Choose a substance that will react rapidly and completely with the analyte and prepare a standard solution of this substance. The concentration of the standard solution should be +/-0.0001 M. It is also known as **Titrant**.

iii) Place the standard solution in a burette and add it slowly to the solution of unknown concentration. This process is called **titration.** Continue the titration until the reaction is complete; that is, until the amount of reactant added is exactly the amount required to react with all the constituent being analysed. This point is called the **equivalence point**, and can be detected by adding an **indicator** to the unknown solution before beginning the titration.

iv) **An indicator** is a substance that gives a visible sign, usually by a colour change, of the presence or absence of a threshold concentration of a chemical species, such as an acid or an alkali in a solution. The point at which the colour change occurs is the end point of titration. An example of indicator is methyl yellow, which imparts a yellow colour to an alkaline solution. If acid is slowly added, the solution remains yellow until all the alkali has been neutralized, whereupon the colour suddenly changes to red. Indicators are classified as acid-base, oxidation-reduction, or specific-substance indicators, every indicator in each class having a characteristic transition range. Some of the commonly used acid-base indicators can be seen in Fig.2.

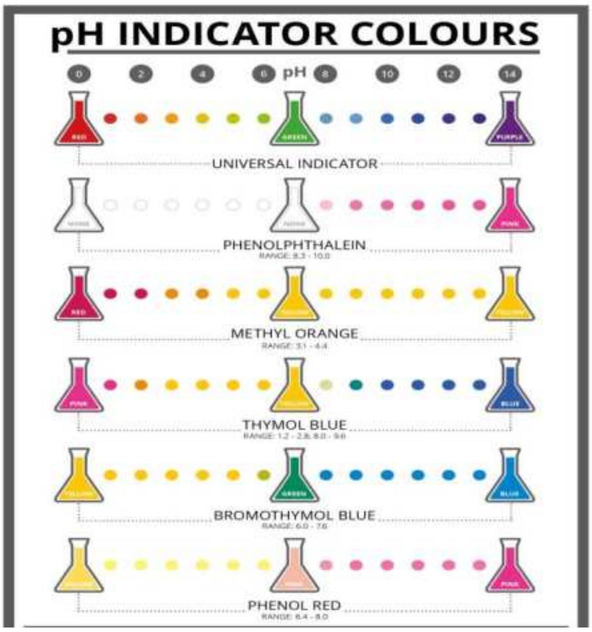


Fig.2. Some common pH indicators (Image courtesy: Compoundchem)

v) Measure the exact volume of standard solution required from burette readings before and after the titration. Since the molarity of the standard solution is known, the number of moles of titrant can be calculated. From a knowledge of the equation for the reaction, the number of moles of constituent present in sample can also be calculated.

1.6 Dilute solutions:

a) Dilution is the process of adding additional solvent to a solution to reduce its concentration. This process keeps the amount of solute constant, but increases the total amount of solution, thereby decreasing its final concentration. Dilution can be done by mixing a solution of higher concentration with an identical solution of lesser concentration. Diluting solutions is a routine process in the laboratory, as stock solutions are often purchased and stored in very concentrated forms. For the solutions to be usable in the lab (for a titration, for instance), they must be accurately diluted to a known, lesser concentration.

b) The volume of solvent needed to prepare the desired concentration of a new, diluted solution can be calculated mathematically. The relationship is as follows:

$M_1V_1 = M_2V_2$

Where

M_1 denotes the concentration of the original solution, and V_1 denotes the volume of the original solution; M_2 represents the concentration of the diluted solution, and V_2 represents the final volume of the diluted solution. When calculating dilution factors, it is important that the units for both volume and concentration are the same for both sides of the equation.

Example:

- 200 ml of a 1.6 M aqueous solution of NaCl is diluted with water to a final volume of 1.0 L. What is the final concentration of the diluted solution?

- $M_1V_1 = M_2V_2$
- (1.6 M) (200 ml) = M_2(1000 ml)
- M_2 = 0.32 M

c) Dilutions can sometimes be visually observed.

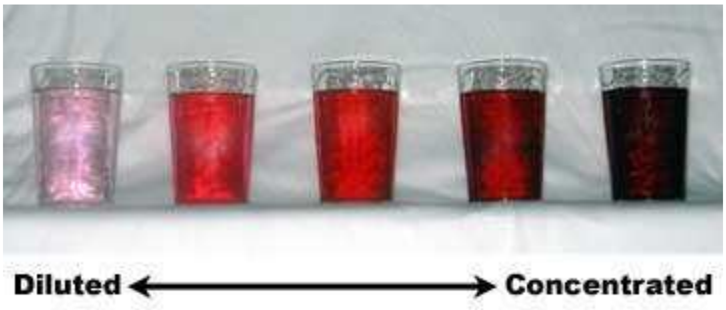


Fig.3. Intense red colour slowly fades as the solutions become more diluted
(Image courtesy*:* Lumen: Introduction to Chemistry)

c**) Serial dilutions:**

Serial dilutions involve diluting a stock or standard solution multiple times in a row. Typically, the dilution factor remains constant for each dilution, resulting in an exponential decrease in concentration. As for example, a ten-fold serial dilution could result in the following concentrations: 1 M, 0.1 M, 0.01 M, 0.001 M, and so on. As seen in this example, the concentration is reduced by a factor of ten in each step.

d) Serial dilutions are used to accurately create extremely diluted solutions, as well as solutions for experiments that require a concentration curve with an exponential or logarithmic scale. Serial dilutions are widely used in experimental sciences, including biochemistry, pharmacology, microbiology, and physics.

1.7 Units of concentration:

a) Most commonly, a solution's concentration is expressed in terms of normality, molarity, molality, formality etc.

b) **Normal solution:** A normal solution contains one gram equivalent mass of the substance in one liter of solution.

$$\text{Normality} = \frac{\text{Mass of the substance in one liter}}{\text{Gram equivalent mass of the substance}}$$

Example: 1.0 N HCl solution contains 36.45 gm of HCl in one litre of d/w

c) **Molarity:** It is a unit of concentration measuring the numbers of moles of a solute per litre of solution. Molarity is denoted with 'M'. A 1 M solution contains 1 mole of solute per litre of solution.

Example: 1.0 M HCl consists of 36.5gm HCl in 1000ml of distilled water

d) Molality: It is the number of moles of solute per kilogram of solvent. Solutions expressed in molal concentration are denoted with 'm'. 1 m solution contains 1 mole of solute per kilogram of solvent.

Example: 1.0 m H_2SO_4 solution contains 98gm of H_2SO_4 in 1000ml of water

e) Formality: It is defined as the number of formula mass of any solute dissolved in one litre of solution. A solution is said to be one formal (1 F) if it contains one formula mass of the substance in one litre of solution.

Example: 1.0 F solution of Oxalic acid ($H_2C_2O_4$, $2H_2O$) contains 126gm. Oxalic acid in one liter of solutions

1.8 Standard Curve: A standard curve also known as Calibration curve, is a type of graph used as a quantitative research technique. Standard curves represent the relationship between two quantities. Multiple samples with known concentration are measured and plotted on the graph, which then allows similar concentrations to be determined for unknown samples by interpolation on the graph. The samples with known concentration are the standards, and the graph is the standard graph.

Example: A standard curve for protein concentration determination.

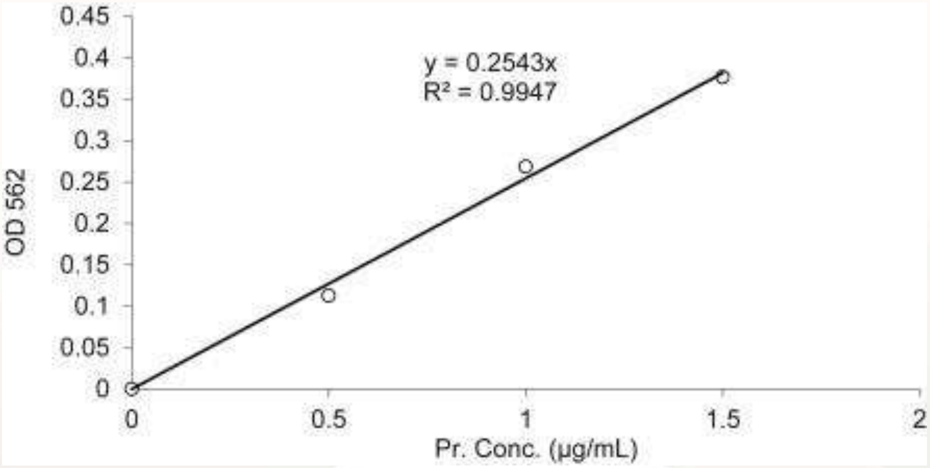
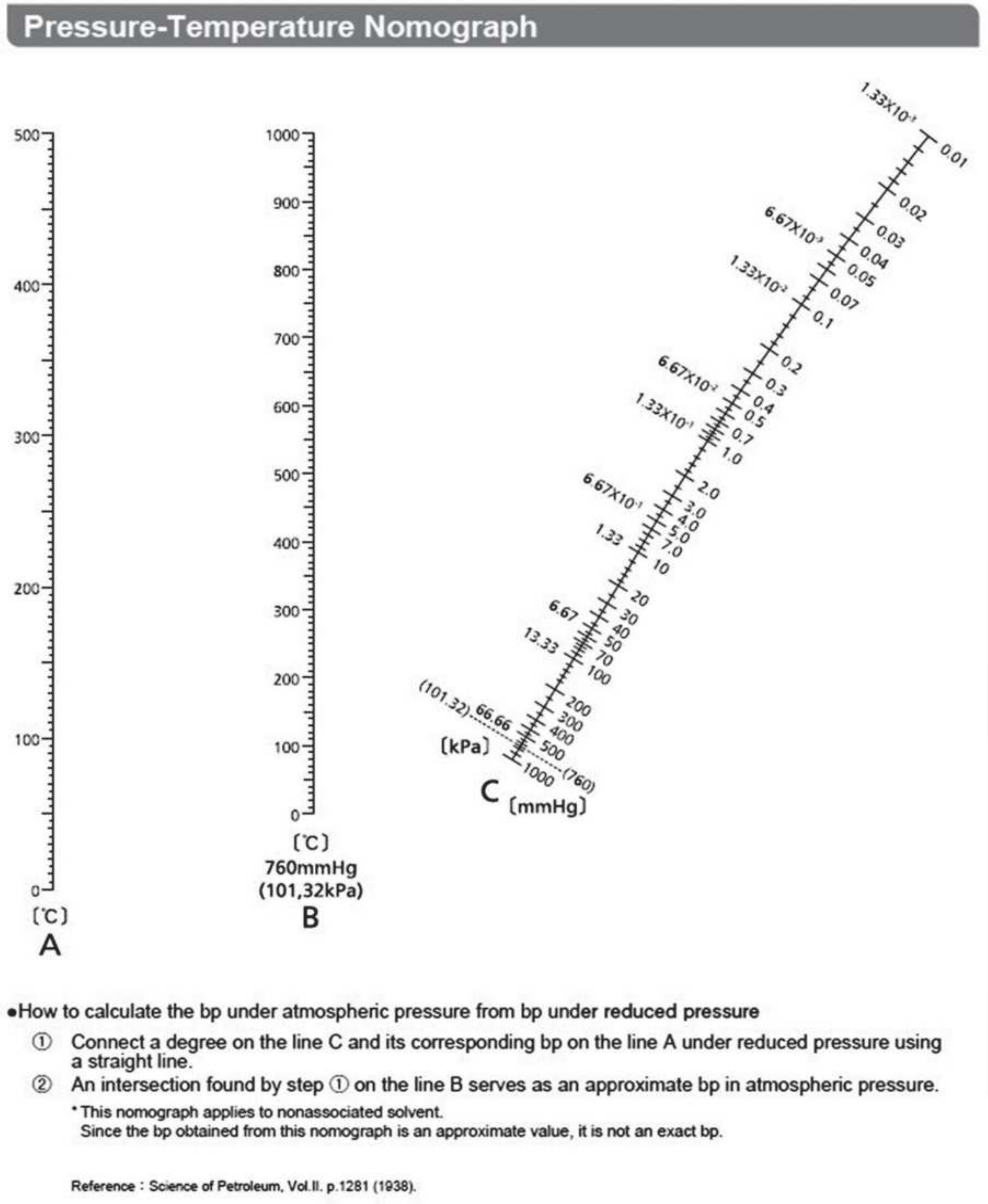


Fig.4. Standard curve example showing protein concentration determination

To calculate the sample concentration based on the standard curve, first we have to find out the concentration (on X-axis) for each sample absorbance (Optical density on Y -axis) using a spectrophotometer on the standard curve; then we have to multiply the concentration by the dilution factor for each sample.

1.9 Nomograph: Nomographs (or nomograms or alignment charts) are graphical representations of mathematical relationships which are used by simply applying a straight edge across the plot through the points on scales representing independent variables, which then crosses the corresponding datum point for the dependent variable; the choice among independent and dependent variable is arbitrary so that each variable may be determined in terms of the others. Common example of nomograms are:

use to compute the lift available for a hot-air balloon, the boiling points of solvents under reduced pressure and the relative forces in a centrifuge. Nomograms provide insight into mathematical relationships, are useful for rapid and repeated application, even in the absence of calculational facilities, and can reliably be used in the field.



●How to calculate the bp under atmospheric pressure from bp under reduced pressure

① Connect a degree on the line C and its corresponding bp on the line A under reduced pressure using a straight line.

② An intersection found by step ① on the line B serves as an approximate bp in atmospheric pressure.

* This nomograph applies to nonassociated solvent.
Since the bp obtained from this nomograph is an approximate value, it is not an exact bp.

Reference : Science of Petroleum, Vol.II. p.1281 (1938).

Fig.5. A Pressure-Temperature nomograph

Course Name	Soil and Water Chemistry
Lesson 2	Chemistry of water
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
University/College Name	Sri Venkateswara Veterinary University,Tirupati

Lesson 2

Objectives:

1. To understand the structure, properties & composition of water

Glossary of terms:

Hydrogen Bond: There is an electrostatic attraction between the oxygen atom of one water molecule and hydrogen of another water molecule which is known as hydrogen bond.

Hydrophilic: Compounds that readily dissolves in water are referred to as Hydrophilic (Greek, "Water-loving").

Hydrophobic: Compounds that do not readily dissolve in water are termed as Hydrophobic.

Amphipathic compounds: Compounds that contain regions that are polar (or charged) and regions that are nonpolar.

Specific Heat: The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius.

Vapourisation: It is a process in which thermal energy make the water molecules loose from the liquid surface and into the gaseous state

Latent Heat of Vapourisation: This is the heat that required for vaporizing 1.0 gm. of water at 100^0C (540 Cal/gm).

Latent Heat of Fusion: The amount of heat required to change water from a solid state to a liquid state with no change in temperature is termed the latent heat of fusion.

Viscosity: It is a measurement of internal molecular friction of a liquid.

Adhesion: It is the tendency to cling to the surface of materials by means of hydrogen bonds of water molecule and oxygen atoms of the other substances.

Cohesion: Cohesion is the property of liquids which offers resistance to being pulled apart or to the formation of new surfaces.

Surface Tension: At the surface of a water mass, the force responsible for resistance is termed Surface Tension.

E-lecture:

1. The Water Molecule: A molecule of water is formed by bonding of two atoms of hydrogen (H) with one atom of oxygen (O) at an angle of 104.5^0. Each hydrogen atom of a water molecule shares an electron pair with the central oxygen atom. The geometry of the molecule is dictated by the shapes of the outer electron orbitals of the oxygen atom. The orbitals form a rough tetrahedron, with a hydrogen atom at each of the two corners and unshared electron pairs at the other two corners as seen in Fig. 1 (a,b). The H-O-H bond angle is 104.5^0 which is < than 109.5^0 of a perfect tetrahedron because of crowding by the nonbonding orbitals of the oxygen atom.

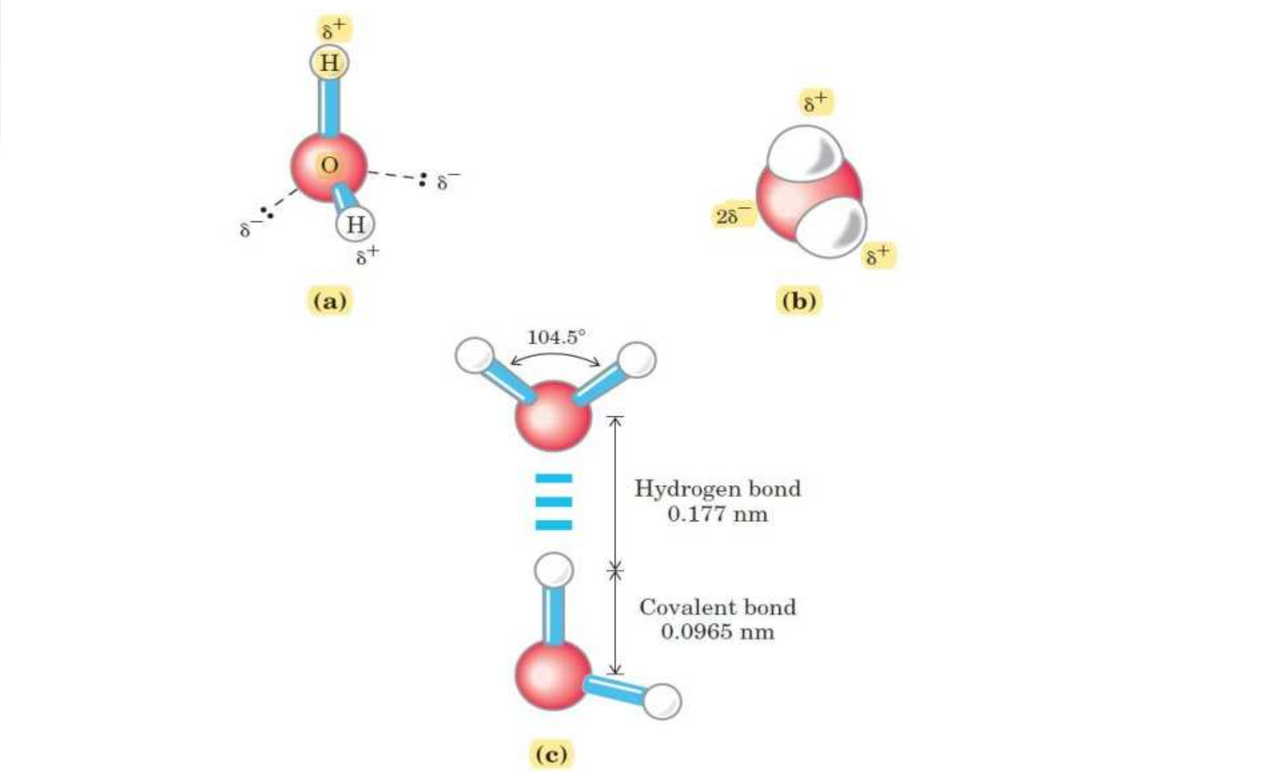


Fig. 1 Structure of the water molecule. The dipolar nature of the H_2O molecule is shown by (a) ball-and-stick and (b) space-filling models. The dashed lines in (a) represent the nonbonding orbitals. There is nearly a tetrahedral arrangement of the outer-shell electron pairs around the oxygen atom; the two hydrogen atoms have localised partial +ve charges (δ^+) and the oxygen atom has a partial negative charge ($2\delta^-$). (c) The H_2O molecules joined by a hydrogen bond (by three blue lines) between the oxygen atom of the upper molecule and a hydrogen atom of the lower one. Hydrogen bonds are longer and weaker than covalent OOH bonds. (Source: Principles of Biochemistry (2008, W.H.Freeman))

A) Hydrogen Bond: The oxygen nucleus attracts electrons more strongly than does the hydrogen nucleus (a proton); that is, oxygen is more electronegative. The sharing of electrons between H and O is therefore unequal; the electrons are more often in the vicinity of the oxygen atom than of the hydrogen. The result of this unequal electron sharing is two electric dipoles in the water molecule, one along each of the HOO bonds; each hydrogen bears a partial positive charge (δ^+) and the oxygen atom bears a partial negative charge equal to the sum of the two partial positives ($2\delta^-$). As a result, there is an electrostatic attraction between the oxygen atom of one water molecule and hydrogen of another as seen in Fig.1(c), called a hydrogen bond.

B) Hydrogen Bonding gives water its unusual properties: Water has a higher melting point, boiling point, and heat of vaporization than most other common solvents (Table 1). These unusual properties are mainly due to attractions between adjacent water molecules that give liquid water great internal cohesion.

Table.1 Melting point, Boiling point, and Heat of Vapourisation of some common solvents

Solvents	**Melting point (^{0}C)**	**Boiling point (^{0}C)**	**Heat of Vapourisation ((J/g)**
Water	0	100	2260
Methanol (CH_3OH)	-98	65	1100
Ethanol (CH_3CH_2OH)	-117	78	854
Propanol ($CH_3CH_2CH_2OH$	-127	97	687
Butanol ($CH_3(CH_2)_2CH_2OH$)	-90	117	590
Acetone (CH_3COCH_3)	-95	56	523
Hexane ($CH_3(CH_2)_4CH_3$)	-98	69	423
Benzene (C_6H_6)	6	80	394
Butane ($CH_3(CH_2)_2CH_3$)	-135	-0.5	381
Chloroform ($CHCl_3$)	-63	61	247

Hydrogen bonds are relatively weak. Those in liquid water have a bond dissociation energy (the energy required to break a bond) of about 23 kJ/mol, compared with 470 kJ/mol for the covalent OOH bond in water or 348 kJ/mol for a covalent COC bond. The hydrogen bond is about 10% covalent, due to overlaps in the bonding orbitals, and about 90% electrostatic.

C) At room temperature, the thermal energy of an aqueous solution (the kinetic energy of motion of the individual atoms and molecules) is of the same order of magnitude as that required to break hydrogen bonds. When water is heated, the increase in temperature reflects the faster motion of individual water molecules. At any given time, most of the molecules in liquid water are engaged in hydrogen bonding, but the lifetime of each hydrogen bond is just 1 to 20 picoseconds (1 ps=10^{-12} s); upon breakage of one hydrogen bond, another hydrogen bond forms, with the same partner or a new one, within 0.1 ps. The sum of all the hydrogen bonds between H_2O molecules confers great internal cohesion on liquid water. Extended networks of hydrogen-bonded water molecules also form bridges between solutes (proteins and nucleic acids, for example) that allow the larger molecules to interact with each other over distances of several nanometers without physically touching.

D) The nearly tetrahedral arrangement of the orbitals about the oxygen atom (Fig. 1 a) allows each water molecule to form hydrogen bonds with as many as four neighboring water molecules. In liquid water at room temperature and atmospheric pressure, however, water molecules are disorganized and in continuous motion, so that each molecule forms hydrogen bonds with an average of only 3.4 other molecules. In ice, on the other hand, each water molecule is fixed in space and forms hydrogen bonds with a full complement of four other water molecules to yield a regular lattice structure (Fig. 2). Breaking a sufficient proportion of hydrogen bonds to destabilize the crystal lattice of ice requires much thermal energy, which accounts for the relatively high melting point of water (Table.1). When ice melts or water evaporates, heat is taken up by the system:

$$H_2O\ (\text{Solid}) \longrightarrow H_2O\ (\text{Liquid})\ \Delta H = +5.9\ \text{kJ/mol}$$

$$H2O\ (\text{Liquid}) \longrightarrow H2O\ (\text{Gas})\ \Delta\ H = 44.0\ \text{kJ/mol}$$

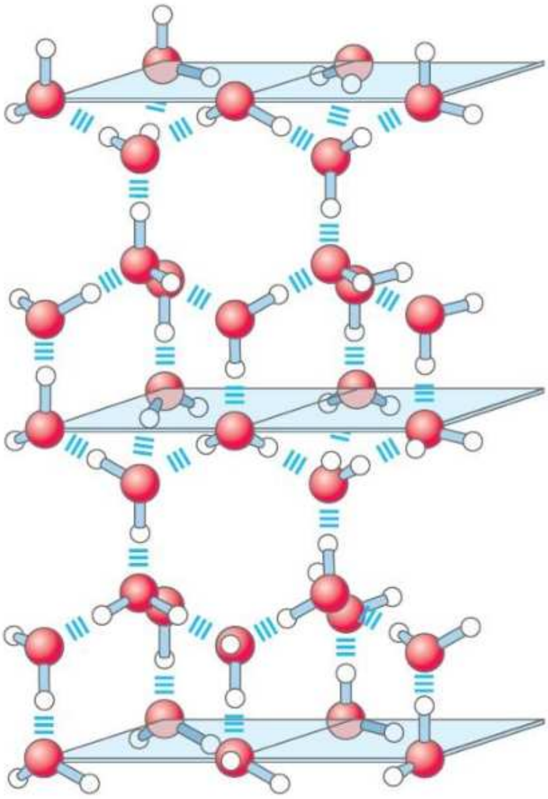


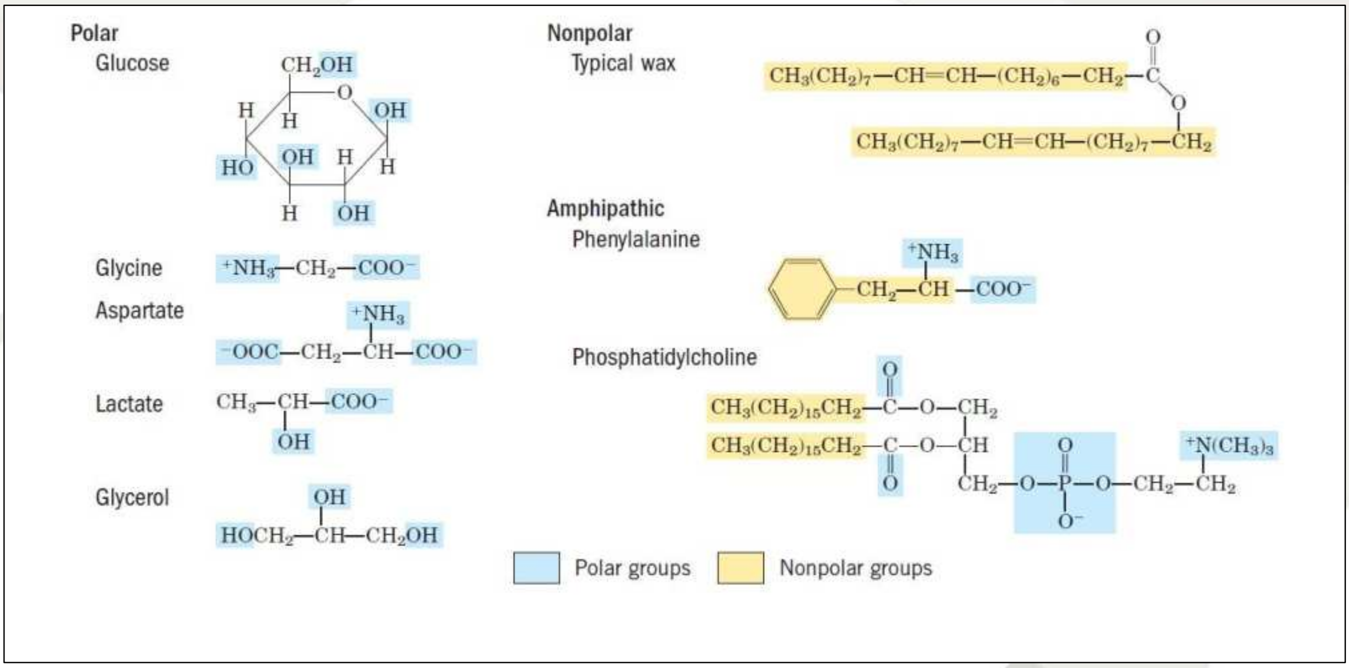
Fig.2 Hydrogen bonding in ice. In ice, each water molecule forms the maximum of four hydrogen bonds, creating a regular crystal lattice. By contrast, in liquid water at room temperature and atmospheric pressure, each water molecule hydrogen-bonds with an average of 3.4 other water molecules. This crystal lattice of ice makes it less dense than liquid water, and thus ice floats on liquid water. (Source: Principles of Biochemistry (2008, W.H.Freeman))

E) During melting or evaporation, the entropy of the aqueous system increases as more highly ordered arrays of water molecules relax into the less orderly hydrogen bonded arrays in liquid water or the wholly disordered gaseous state. At room temperature, both the melting of ice and the evaporation of water occur spontaneously; the tendency of the water molecules to associate through hydrogen bonds is outweighed by the energetic push toward randomness.

F) The water molecule is electrically polar in nature. This is because in the molecular structure of water, both hydrogen atoms are located on the same side rather than being at opposite ends. This means that water molecule is not symmetrical but rather small boomeranged shape. One side of the molecule carries a net negative charge and the other side a net positive charge. This, the molecule is strongly electrically polarized. Water molecule is said to be a permanent dipole, containing a pair of equal and opposite electric charges. High dipolic movement of the water molecule makes water an excellent solvent for ionic compounds.

G) Water readily dissolves most biomolecules, which are generally charged or polar compounds (Table 2); compounds that dissolve easily in water are hydrophilic (Greek, “water-loving”). In contrast, nonpolar solvents such as chloroform and benzene are poor solvents for polar biomolecules but easily dissolve those that are hydrophobic—nonpolar molecules such as lipids and waxes.

Table. 2 Some examples of Polar, Nonpolar and Amphipathic Biomolecules (Shown as Ionic Forms at pH 7) (Source: Principles of Biochemistry (2008, W.H.Freeman))



2. Physical Properties of Water: Table 3 shows some of the basic physical properties of water. Some of these properties are affected by temperature; hence shown at different temperatures. Effect of these properties on water behaviour is also highlighted (Chang, 2010; Ebbing and Gammon, 2009; Manahan, 2000; Venkateswariu, 2003).

Table 3 Physical properties of water

Property	**Value**	**Temperature (^{0}C)**	**Effect & Significance**
Specific heat	1 cal		Water can absorb substantial amount of heat while its temperature rises only slightly.
Density	0.9999	0	Solid form is less dense than its liquid form; ice floats at the surface of liquid water
	1.000 g/mL	3.98	
	0.9971 g/mL	25	
	0.9584	100	
Viscosity	1.79 cP	0	Hot molasses flows much faster than cold molasses
	0.89 cP	25	
	0.28 cP	100	
Surface tension	75.6 dyn/cm	0	Water bugs (striders) seem to skitter
	72.5 dyn/cm	25	
	58.9 dyn/cm	100	

			across this skin as if ice-skating. You can actually float a pin on water, if you carefully lay it across the surface
Dipole moment	1.8546 D		Reflects the polarity of water molecule
Latent heat of fusion	80 cal	0	
Latent heat of vapourisation	540 cal	100	
Boiling point	100^0C (372K) at 1 atm		
Melting point	0^0C (273.2 K)		

2.1 Specific heat: The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius. Unit of specific heat is "Calorie". The calorie is defined as the amount of heat required to raise the temperature of one gram of water by one degree celecius (4.1868 Joule). Water has to absorb 4.184 Joules of heat for the temperature of one gram of water to increase 1 degree celsius (°C). For comparison sake, it only takes 0.385 Joules of heat to raise 1 gram of copper 1°C. Specific heat of water is 1 Cal. In natural waters dissolved substances lower the specific heat.

2.2 Latent Heat of vaporization (LHV): Vaporization is a process in which thermal energy make the water molecules loose from the liquid surface and into the gaseous state. Water has an exceptionally high latent heat of vaporization. LHV is the heat that required vaporizing 1.0 gm. of water at 100^0C (540 Cal/gm).

2.3 Latent Heat of fusion: The amount of heat required to change water from a solid state to a liquid state with no change in temperature is termed the latent heat of fusion. 80 calories of heat is required to melt 1g of ice at 0^0C.

2.4 Density of water: Water becomes less dense at high temperature and denser at low temperature. Fresh water reaches its maximum density at the freezing point of water i.e. 3.98 ^{0}C. As it cools below 4^0C, the density decreases i.e. water becomes lighter due to formation of crystalline structure. Density is a function of temperature, pressure and concentration of dissolved or suspended substances.

2.5 Viscosity: It is the measurement of the internal molecular friction of a liquid. Viscosity is concerned with mobility and flow of water. Viscosity of water decreases with increasing temperature.

2.6 Adhesion: Adhesion is the tendency to cling to the surface of materials by means of hydrogen bonds of water molecule and oxygen atoms of the other substances.

2.7 Cohesion: Cohesion is the property of liquids which offers resistance to being pulled apart or to the formation of new surfaces.

2.8 Surface tension: At the surface of a water mass, the force responsible for resistance is termed as Surface Tension. Results from the unsymmetrical activity of water molecules on or below the surface (Fig.3). Surface tension could be defined as the property of the surface of a liquid that allows it to resist an external force, due to the cohesive nature of the water molecules. The surface tension of water is 72.5 dynes/cm at 25°C. It would take a force of 72.5 dynes to break a surface film of water 1 cm long. The surface tension of water decreases significantly with temperature. Species associated with the surface film are known as neuston.

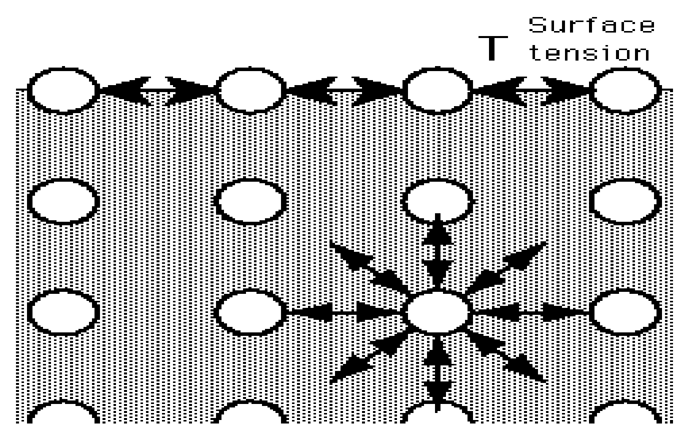


Fig.3 Surface tension of a water mass

3. Chemical properties of water: There are mainly 3 types of chemical reactions that could take place in water: Precipitation, Acid/base, and oxidation-reduction reaction.

- ✓ **Precipitation reaction:** dissolved ions react with each other and form a solid compound or precipitate. A typical precipitation reaction that occurs in water is the formation of calcium carbonate solid when solution of calcium is mixed with solution of carbonate (Davis and Cornwell, 2012).

$$Ca^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)}$$

- ✓ **Neutralisation reaction:** A neutralization reaction is a reaction of an acid and a base that results in an ionic compound and possibly water. When a base is added to an acid solution, the acid is said to be neutralized. The ionic compound that is produced in a neutralization reaction is called a salt (Chang, 2010; Ebbing and Gammon, 2009). The net equation for most acid base reaction is:

$$H^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow H_2O_{(l)}$$

- ✓ **Oxidation-reduction reaction:** It is a reaction in which electrons are transferred between species or in which atoms change oxidation number. The substance that loses the electron is said to be oxidized and it is called a reducing agent. While the substance that accept the electron is said to be reduced and is called oxidizing agent. When one species release electron, another one should be available to accept the electron. Iron pipe corrosion is an example of oxidation–reduction reaction in which iron metal oxidizes and loses two electrons, while hydrogen ions accepts those electrons and reduces to hydrogen gas (Chang, 2010; Davis and Cornwell, 2012; Ebbing and Gammon, 2009)

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$2H^+ + 2e^- \longrightarrow H_{2\ (g)}$$

3.1 pH: The pH of a solution is a measure of hydronium ion (H_3O^+) concentration, which is, in turn, a measure of acidity. In acidic solutions the pH is less than 7, while it is greater than 7 in basic solutions. The pH range in water samples is rarely below 4 or above 10. Determining pH of water is essential as it affects many of the chemical and biological processes that take place in water (Davis and Cornwell, 2012; Venkateswariu, 2003).

3.2 Alkalinity: Alkalinity refers to as buffering capacity of water to neutralise water. It is defined as the sum total of all titratable bases down to about pH 4.5. It is found experimentally by determining how much acid it takes to lower the pH of water to 4. The alkalinity of water is mainly contributed by bicarbonate, carbonate and hydroxide ions.

3.3 Water Hardness: Hardness is the sum total of all polyvalent cations. Practically it is the sum of calcium and magnesium ions which are predominant cations in natural waters. Hardness is expressed in mg/L as $CaCO_3$, as in alkalinity. Both calcium and magnesium have a valence of two when converting to $CaCO_3$. The sum of calcium and magnesium is the total hardness (TH), which is subdivided to carbonate and noncarbonated hardness.

Carbonate hardness is often called temporary hardness because heating the water will remove it. When water is heated, the insoluble carbonates precipitate and tend to form bottom deposits in hot water heaters. Carbonate hardness is equal to the total hardness or alkalinity, whichever is less.

Noncarbonated hardness is correspondingly called permanent hardness because it is not removed when water is heated. Noncarbonated hardness is the total hardness in excess of the alkalinity. If the alkalinity is equal to or greater than the total hardness, there is no noncarbonated hardness (Davis and Cornwell, 2012; Manahan, 2000).

3.4 Sea Water: Chemical analyses of samples from all over the world show that seawater consists of a small quantity of salt dissolved in water. The salt occurs as charged particles, cations and anions, that are dispersed among the molecules of liquid water. Seawater is a chemical solution. The dissolving agent, the liquid water, is the solvent and the dissolved substances, the salt ions, are the solute. Seawater also contains minor to trace amounts of dissolved metals, nutrients, gases, and organic compounds of seemingly infinite variety.

A) Salinity: Average or “normal” seawater has a salinity of about 35‰. This means that the dissolved salt occurs in a concentration of 35 parts per thousand (ppt). That is, the salt comprises 3.5 percent (divide 35 by 1,000, and convert it to a percentage by multiplying it by 100) of the sample, the rest (96.5 percent or 965 parts per thousand) being H_2O molecules.

B) Major constituents: In terms of quantity, the primary solutes in seawater are cations and anions. By weight, chloride (Cl^-) and sodium (Na^+) together comprise more than 85.65 percent (Table 4) of all the dissolved substances in seawater. When these two ions bond chemically into a solid, they form halite and give seawater its most distinctive property—its saltiness. The six most abundant ions—chloride (Cl^-), sodium (Na^+), sulfate ($SO4^{2-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+)—make up over 99 percent of all of seawater’s solutes. The addition of five more solutes to the list—bicarbonate (HCO^{3-}), bromide (Br^-), boric acid (H_3BO_3), strontium (Sr^{2+}), and fluoride (F^-)—elevates the quantity of dissolved ingredients in seawater to 99.99 percent.

Table 4 Major solutes in Seawater

Salt Ion	**Ions in Seawater* (%)**	**Ions by Weight (%)**	**Cumulative (%)**
Chloride (Cl^-)	18.980	55.04	55.04
Sodium (Na^+)	10.556	30.61	85.65
Sulfate (SO_4^{2-})	2.649	7.68	93.33
Magnesium (Mg^{2+})	1.272	3.69	97.02
Calcium (Ca^{2+})	0.400	1.16	98.18
Potassium (K^+)	0.380	1.10	99.28
Bicarbonate (HCO_3^-)	0.140	0.41	99.69
Bromide (Br^-)	0.065	0.19	99.88
Boric acid (H_3BO_3)	0.026	0.07	99.95
Strontium (Sr^{2+})	0.013	0.04	99.99
Fluoride (F^-)	0.001	0.00	99.99
Total	**34.482**	**99.99**	**99.99**

*The gram weight of ions per 1 kg of seawater, or g/kg.

Source: Adapted from Sverdrup, H. U., Johnson, M. W., and Fleming, R. H. *The Oceans* (Englewood Cliffs, N.J.: Prentice-Hall, 1942).

C) Nutrients: Nutrients in seawater are compounds that consist primarily of nitrogen (N), phosphorous (P), and silicon (Si). Representative concentrations of these nutrients in the ocean are listed in Table 5.

Table 5 Near surface nutrient concentration in seawater

Nutrient element	Concentration (ppm)
Phosphorus (P)	0.07
Nitrogen (N)	0.5
Silicon (Si)	3

D) Gases: Gases in seawater include nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), hydrogen (H_2), and the noble gases argon (Ar), neon (Ne), and helium (He) (Table 6). Nitrogen and the three noble gases are inert (unreactive) and rarely involved directly in plant photosynthesis. In contrast, levels of dissolved O_2 and CO_2 are greatly influenced by photosynthesis and respiration of organisms. Therefore, they vary greatly in space and time depending on the activities of plants and animals and are regarded as nonconservative.

Table 6 Quantities of Gas in Air & Seawater

Gas	In Dry Air (%)	In Surface Ocean Water (%)	Water-Air ratio
Nitrogen (N_2)	78.03	47.5	0.6
Oxygen (O_2)	20.99	36.0	1.7
Carbon dioxide (CO_2)	0.03	15.1	503.3
Argon (Ar), hydrogen (H_2), neon (Ne), and helium (He)	0.95	1.4	1.5

E) Trace elements: Most trace elements, such as manganese (Mn), lead (Pb), mercury (Hg), gold (Au), iodine (I), and iron (Fe), occur in concentrations of less than 1 ppm (part per million) (Table 7). Many occur in quantities of less than 1 part per billion (ppb) and even at 1 part per trillion. These low concentrations make certain trace elements difficult and sometimes even impossible to detect in seawater. However, despite their extremely low concentrations, trace elements can be critically important for marine organisms, either by helping to promote life or by retarding or killing life (toxicity).

Table 7 Trace elements in Seawater

Trace element	**Concentration (ppb)**
Lithium (Li)	170
Iodine (I)	60
Molybdenum (Mo)	10
Zinc (Zn)	10
Iron (Fe)	10
Aluminium (Al)	10
Copper (Cu)	3
Manganese (Mn)	2
Cobalt (Co)	0.1
Lead (Pb)	0.03
Mercury (Hg)	0.03
Gold (Au)	0.004

F) Organic compounds: Organic compounds are large, complex molecules produced by organisms. They include substances such as lipids (fats), proteins, carbohydrates, hormones, and vitamins. Typically, they occur in low concentrations and are produced by metabolic (physical and chemical processes in the cell of an organism that produce living matter) and decay processes of organisms.

4.Composition of Waters: In earth crust and atmosphere, water is available in different forms as shown in Table 7.

Table 8 Forms of water in earth's crust and atmosphere

Forms of Water	Percentage (%)
Salt water	97.20%
Freshwater	2.80%
Ice	2.00%
Groundwater	0.62%
Freely available water	0.18 %
Moisture	0.001%

Chemical analysis of water samples from rivers all over the world indicate that they contain a variety of dissolved substances (Table 9). The source of these substances is chemical weathering of rocks on the land. These rocks are made up of an assemblage of minerals composed predominantly of the elements silicon, aluminium, and oxygen. Acidic waters breaks down these rocks into their component elements.

Table 9 Dissolved substances in River water

Substance	Concentration (ppm)	Concentration (%)
Bicarbonate/carbonate (HCO_3^-/CO_3^{2-})	58.8	48.7
Calcium (Ca^{2+})	15.0	12.4
Silica (SiO_2)	13.1	10.8
Sulfate (SO_4^{2-})	1.2	9.3
Chloride (Cl^-)	7.8	6.5
Sodium (Na^+)	6.3	5.2
Magnesium (Mg^{2+})	4.1	3.4
Potassium (K^+)	2.3	1.9
Nitrate (NO_3^-)	1.0	0.8
Iron aluminum oxide [$(Fe, Al)_2 O_3$]	0.9	0.8
Remainder	0.3	0.3

Source: Livingstone, D. A. Chemical composition of rivers and lakes, U.S. Geological Survey, Professional Paper 440-G (U.S. Government Printing Office, 1963).

4.1 Chemistry of Surface Water: Surface water is extremely variable in its chemical composition depending upon the interaction with the rocks on which it flows and in relative contribution of ground water and surface water run-off. The mineral content in river water usually bears an inverse relationship to discharge. The mineral content of river water tends to increase from source to mouth, although the increase may not be continuous or uniform. Other factors like discharge of wastewater from the cities located on the banks, industrial waste etc can also affect the nature and concentration of various chemical constituents in surface water. Among anions, HCO_3 is most important (>50% of the total anions in meq/L). In case of cations, the alkaline earth, viz, Ca predominates. With increasing salinity the hydrochemical facies tends to change from Ca-HCO_3 to mixed cation to Na-HCO_3 and finally to Na-Cl type.

4.2 Chemistry of Ground Water:

a) The quality of ground water is generally considered to be superior to surface water because of the purifying effects of the soil column and vadose zone during the process of percolation. The final composition of groundwater depends on the mineralogic composition of the aquifer framework and contact time or age of the water. According to Mathess (1982), the processes affecting the quality are dissolution, hydrolysis, precipitation, adsorption, ionexchange, oxidation, reduction and bio-chemical mediated reactions. In general, the reactions that control the chemistry of ground water are:

- Introduction of CO_2 gas into the unsaturated zone.
- Dissolution of calcite and dolomite and precipitation of calcite.
- Cation-exchange.
- Oxidation of pyrite and organic matter.

- Reduction of oxygen, nitrate and sulphate with production of sulphide.
- Reductive production of methane.
- Dissolution of gypsum, anhydrite and halite.
- Incongruent dissolution of primary silicates with formation of clays.

b) Ground water that is in perpetual motion, acquires various physical, chemical and biological characteristics as it flows from recharge area to the discharge area. The factors that influence ground water quality are:

- Local geology,
- Land use,
- Climatic conditions particularly pattern and frequency of rainfall
- Anthropogenic activities such as use of fertilizers and pesticides in agriculture,
- Disposal of domestic sewage and industrial effluents and
- Extent of exploitation of ground water resources.

c) The oxygen present in water is used for the oxidation of organic matter that subsequently generates CO_2 to form H_2CO_3. This process goes on until oxygen is fully consumed.

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

d) In addition to these, there are several other basic reactions involving microbiological mediated reactions, which tend to alter the chemical composition of the percolating waters. Percolating water is charged with oxygen and carbon dioxide and is most aggressive in the first part. This water gradually loses its aggressiveness, as free CO_2 associated with the percolating water gets gradually exhausted through interaction of water with minerals.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

$$H^+ + \text{Feldspar} + H_2O \longrightarrow \text{Clay} + H_4SiO_4 + \text{Cation}$$

Some rocks serve as sources of chloride and sulphate through direct solution. The circulation of sulphur, however, may be greatly influenced by biologically mediated oxidation and reduction reactions. Chloride circulation may be a significant factor influencing the anion content in many natural waters.

The list of the chemical constituents present in groundwater in varying proportions are shown in Table 1 (Todd, 1999)

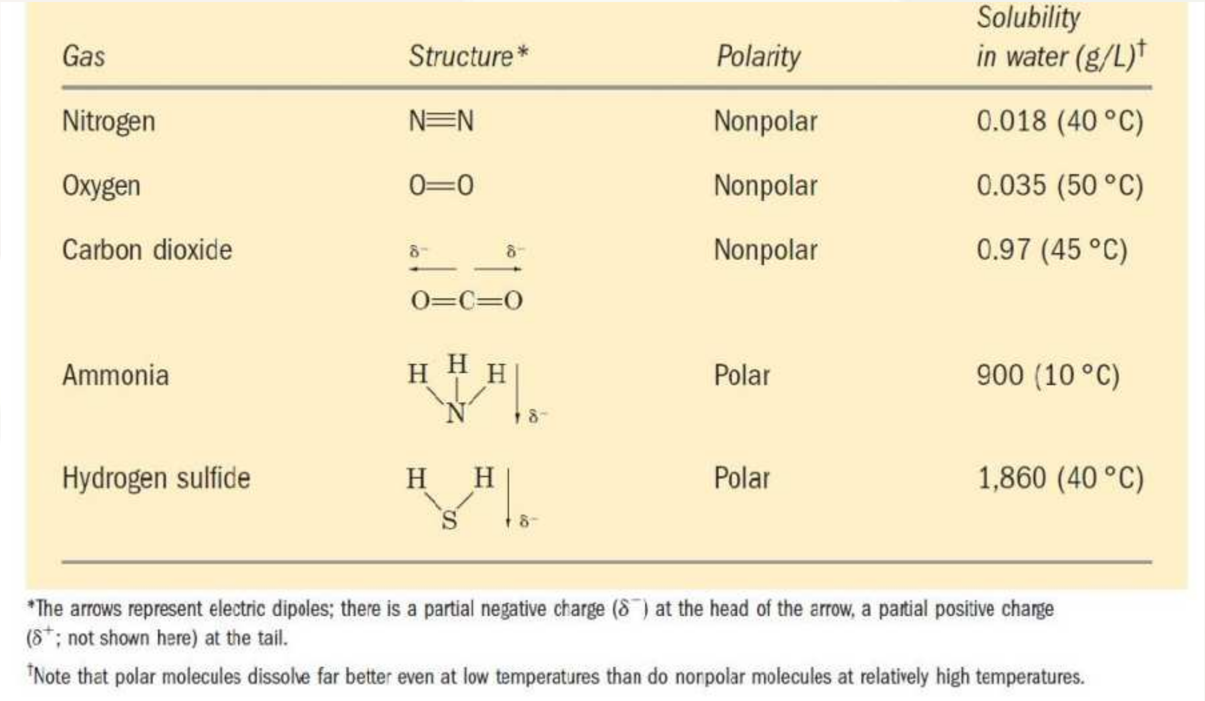
Table 10: Major, Minor & Trace constituents of ground water

Constituent classes	Constituents
Major Constituents (1.0 to 1000 mg/L)	Sodium,Calcium,Magnesium,Bicarbonate,Sulfate,Chl oride,Silica
Secondary Constituents(0.01to10.0 mg/L)	Iron,Strontium,Potassium,Carbonate,Nitrate, Fluoride, Boron
Minor Constituents (0.0001 to 0.1 mg/L)	Antimony,Aluminium,Arsenic,Barium,Bromide,Cadmium,Chromium,Cobalt,CopperGermanium,Iodide,Lead,Lithium,Manganese,Molybdenum,Nickel,Phosphate,Rubidium,Selenium,Titanium,Uranium,Vanadium ,Zinc
Trace Constituents (generally less than 0.001 mg/L)	Beryllium,Bismuth,Cerium,Cesium,Gallium,Gold,Indium,Lanthanum,Niobium,Platinum,Radium, Ruthenium,Scandium,Silver,Thallium,Thorium,Tin,Tungsten ,Ytterbium, Yttrium, Zirconium

4.3 Dissolved gases:

a) Polar gases are generally more soluble in water compared to non-polar gases. The molecules of the biologically important gases CO_2, O_2, and N_2 are nonpolar. In O_2 and N_2, electrons are shared equally by both atoms. In CO_2, each C=O bond is polar, but the two dipoles are oppositely directed and cancel each other (Table 11). The movement of molecules from the disordered gas phase into aqueous solution constrains their motion and the motion of water molecules and therefore represents a decrease in entropy. The nonpolar nature of these gases and the decrease in entropy when they enter solution combine to make them very poorly soluble in water (Table 11). Gases like NH_3 and H_2S which are polar dissolve readily in water.

Table 11: Solubilities of some gases in water (Source: Principles of Biochemistry (2008, W.H.Freeman))



Gas	Structure*	Polarity	Solubility in water (g/L)†
Nitrogen	N≡N	Nonpolar	0.018 (40 °C)
Oxygen	O=O	Nonpolar	0.035 (50 °C)
Carbon dioxide	$\overset{\delta^-}{\longleftarrow}\ \overset{\delta^-}{\longrightarrow}$ O=C=O	Nonpolar	0.97 (45 °C)
Ammonia	H H H N $\downarrow \delta^-$	Polar	900 (10 °C)
Hydrogen sulfide	H H S $\downarrow \delta^-$	Polar	1,860 (40 °C)

*The arrows represent electric dipoles; there is a partial negative charge (δ^-) at the head of the arrow, a partial positive charge (δ^+; not shown here) at the tail.

†Note that polar molecules dissolve far better even at low temperatures than do nonpolar molecules at relatively high temperatures.

b) Gases present in water enters from the atmosphere; very rare gases come from radioactive decay processes with in the sediment in the ocean.

Apart from polarity, dissolution of gases in water mainly depends on

- Temperature of the gas and the solution
- Atmospheric partial pressure of the gas
- Salt content of the solution
- Biological activity

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Course Name	Soil and Water Chemistry
Lesson 3	Acid, base, salts: Hydrogen ions, modern concept of pH and buffer
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
University/College Name	Sri Venkateswara Veterinary University,Tirupati

Lesson 3

Objectives:

To understand the concept of acid, base and salts

To know about the modern concept of pH & buffer

Glossary of terms:

Acid: An acid is a chemical species that donates proton or hydrogen ion and/or accepts electrons.

Base: A base is a chemical species that donates electrons, accepts protons, or release hydroxide (OH^-) ions in aqueous solution.

Salts: Salts are the compounds obtained by neutralization of acid and base.

Buffer: Buffers are aqueous systems that tend to resist changes in pH when small amounts of acid (H^+) or base (OH^-) are added.

pH: pH is defined as negative logarithm of H^+ ion concentration.

Neutral: A pH of 7 is referred to as a neutral pH.

Conjugate acid-base pair: A proton donor and its corresponding proton acceptor make up a conjugate acid-base pair.

Strong Acid: Acids which completely ionised in dilute aqueous solution.

Strong Bases: Bases which completely ionised in dilute aqueous solution.

Dissociation constant: Equilibrium constants for ionization reactions are usually called ionization or dissociation constants, often designated as *K*a.

E-lecture:

1. Acid: An acid is a chemical species that donates protons or hydrogen ions and/or accepts electrons. Most acids contain a hydrogen atom bonded that can release (dissociate) to yield a cation and an anion in water. The higher the concentration of hydrogen ions produced by an acid, the higher its acidity and the lower the pH of the solution. The word *acid* comes from the Latin words *acidus* or *acere*, which mean "sour," since one of the characteristics of acids in water is a sour taste (e.g., vinegar or lemon juice).

Arrhenius, Brønsted-Lowry, and Lewis Acids

There are different ways of defining acids. A person referring to "an acid" is usually referring to an Arrhenius or Brønsted-Lowry acid. A Lewis acid is typically called a "Lewis acid." The reason for the differing definitions is that these different acids don't include the same set of molecules:

- **Arrhenius Acid**: By this definition, an acid is a substance that increases the concentration of hydronium ions (H_3O^+) when added to water. We may also consider increasing the concentration of hydrogen ion (H^+) as an alternative.
- **Brønsted-Lowry Acid**: By this definition, an acid is a material capable of acting as a proton donor. This is a less restrictive definition because solvents besides water are not excluded. Essentially, any compound that can be deprotonated is a Brønsted-Lowry acid, including typical acids, plus amines, and alcohol. This is the most widely used definition of an acid.
- **Lewis Acid**: A Lewis acid is a compound that can accept an electron pair to form a covalent bond. By this definition, some compounds that don't contain hydrogen qualify as acids, including aluminium trichloride and boron trifluoride.

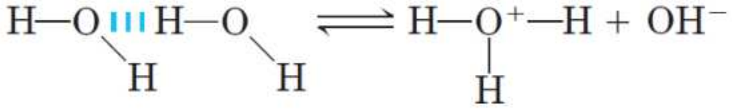
2. Base: In chemistry, a base is a chemical species that donates electrons, accepts protons, or releases hydroxide (OH-) ions in aqueous solution. Bases display certain characteristic properties that can be used to help identify them. They tend to be slippery to the touch (e.g., soap), can taste bitter, react with acids to form salts, and catalyze certain reactions. Types of bases include Arrhenius base, Bronsted-Lowry base, and Lewis base. Examples of bases include alkali metal hydroxides, alkaline earth metal hydroxides, and soap. The word "base" came into use in 1717 by French chemist Louis Lémery. While Lémery may have used the word "base" first, its modern usage is generally attributed to French chemist Guillaume-François Rouelle.

3. Hydrogen ion, modern concept of pH:

3.1 Pure Water Is Slightly Ionized: Water molecules have a slight tendency to undergo reversible ionization to yield a hydrogen ion (a proton) and a hydroxide ion, giving the equilibrium

$$\mathbf{H_2O \rightleftharpoons H^+ + OH^-}$$

Although dissociation product of water is generally shown as H^+, free protons do not exist in solution; hydrogen ions formed in water are immediately hydrated to **hydronium ions** (H_3O^+). Hydrogen bonding between water molecules makes the hydration of dissociating protons virtually instantaneous:



The ionization of water can be measured by its electrical conductivity; pure water carries electrical current as H^+ migrates toward the cathode and OH^- toward the anode. The movement of hydronium and hydroxide ions in the electric field is anomalously fast compared with that of other ions such as Na^+, K^+, and Cl^-. This high ionic mobility results from the kind of "proton hopping" shown in Fig 1. No individual proton moves very far through the bulk solution, but a series of proton hops between hydrogen-bonded water molecules causes the net movement of a proton over a long distance in a remarkably short time. As a result of the high ionic mobility of H^+ (and of OH^-, which also moves rapidly by proton hopping, but in the opposite direction), acid-base reactions in aqueous solutions are generally exceptionally fast.

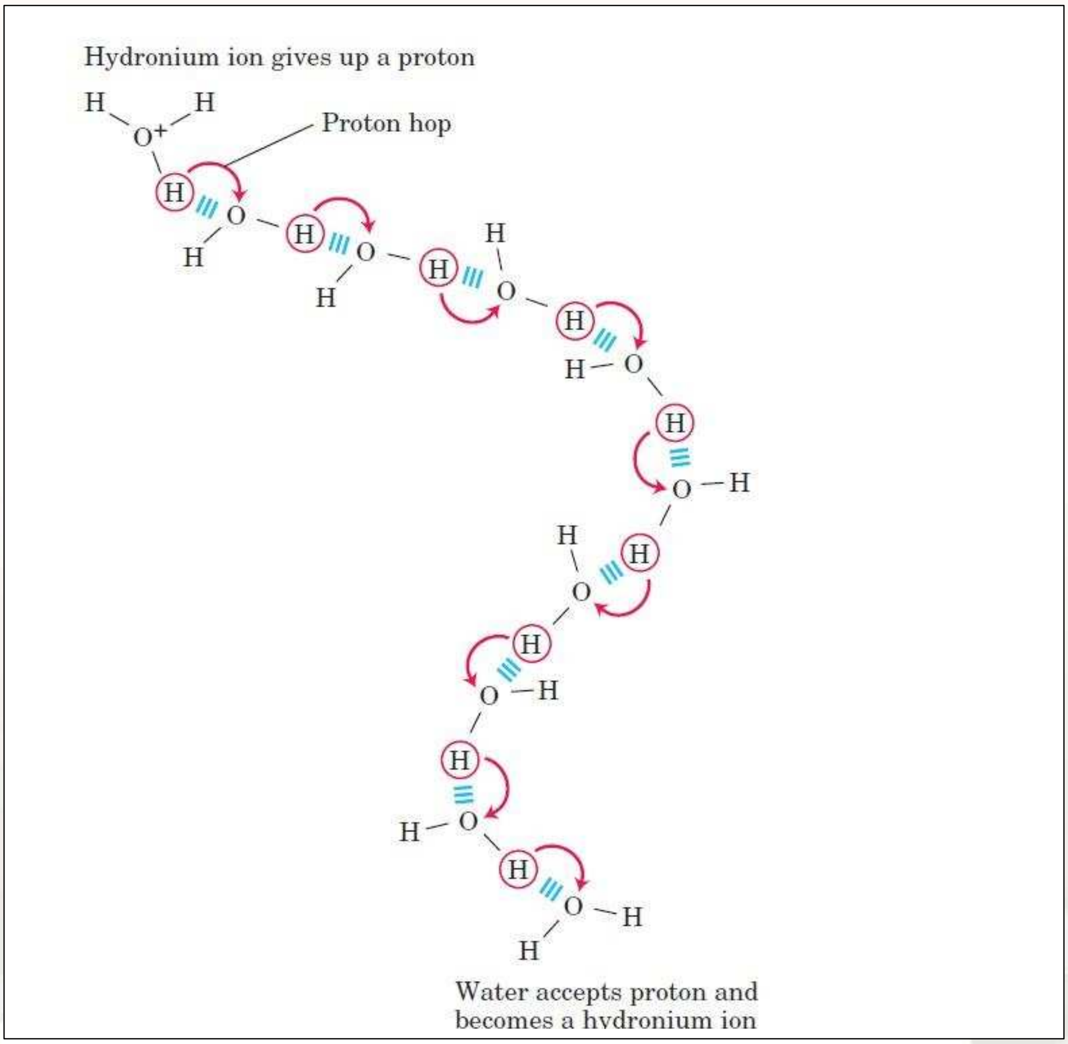


Fig. 1. Proton hopping. Short "hops" of protons between a series of hydrogen-bonded water molecules effect an extremely rapid net movement of a proton over a long distance. As a hydronium ion (upper left) gives up a proton, a water molecule some distance away (lower right) acquires one, becoming a hydronium ion. Proton hopping is much faster than true diffusion and explains the remarkably high ionic mobility of H^+ ions compared with other monovalent cations such as Na^+ or K^+ (Source: Principles of Biochemistry (2008, W.H.Freeman))

Equilibrium constant: The position of equilibrium of any chemical reaction is given by its **equilibrium constant, *Keq*** (sometimes expressed simply as *K*). For the generalized reaction

$$A + B \rightleftharpoons C + D$$

An equilibrium constant can be defined in terms of the concentrations of reactants (A and B) and products (C and D) at equilibrium:

$$Keq = \frac{[C][D]}{[A][B]}$$

3.2 The Ionization of Water Is Expressed by an Equilibrium Constant: The degree of ionization of water at equilibrium is small; at 25 °C only about two of every 10^9 molecules in pure water are ionized at any instant. The equilibrium constant for the reversible ionization of water is

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

In pure water at 25^0C, the concentration of water is 55.5 M (grams of H_2O in 1 L divided by its gram molecular weight: (1,000 g/L)/ (18.015 g/mol)) and is essentially constant in relation to the very low concentrations of H^+ and OH^-, namely, $1x10^{-7}$M. Accordingly, we can substitute 55.5 M in the equilibrium constant expression to yield

$$K_{eq} = \frac{[H^+][OH^-]}{55.5\ M}$$

Which on rearranging becomes

$$(55.5M)K_{eq} = [H][OH] = K_w$$

where K_w designates the product (55.5 M)(K_{eq}), the **ion product of water** at 25 °C.

The value for K_{eq}, determined by electrical-conductivity measurements of pure water, is 1.8×10^{-16} M at 25^0C. Substituting this value for K_{eq} in the above gives the value of the ion product of water:

$\mathrm{Kw} = [\mathrm{H}^+][\mathrm{OH}^-] = (5.5_{\mathrm{M}})\ (1.8 \times 10^{-16}{}_{\mathrm{M}})$

$= 1.0 \times 10^{-14}\ {}_{\mathrm{M}}{}^{2}$

Thus the product $[H^+][OH^-\_]$ in aqueous solutions at 25^0C always equals $1.0 \times 10^{-14}\ {}_{M}{}^{2}$. When there are exactly equal concentrations of $H^+$and OH^-, as in pure water, the solution is said to be at **neutral pH.** At this pH, the concentration of $H^+$and OH^- can be calculated from the ion product of water as follows:

$$\mathrm{Kw} = [\mathrm{H}^+][\mathrm{OH}^-] = [\mathrm{H}]^2$$

Solving for $[H^+]$ gives

$[\mathrm{H}^+] = \sqrt{\mathrm{K_w}} = \sqrt{1 \times 10^{-14}\ \mathrm{M}^2}$

$$[\mathrm{H}^+] = [\mathrm{OH}^-] = 10^{-7}$$

As the ion product of water is constant, whenever $[H\_]$ is greater than 1×10^{-7} M, $[OH\_]$ must become less than 1×10^{-7} M, and vice versa. When $[H^+]$ is very high, as in a solution of hydrochloric acid, $[OH^-]$ must be very low.

3.3 The pH Scale Designates the H^+ and OH^- Concentrations: The ion product of water, *K*w, is the basis for the **pH scale** (Table 1). It is a convenient means of designating the concentration of H^+ (and thus of OH^-) in any aqueous solution in the range between 1.0 M H^+ and 1.0 M OH^-. The term **pH** is defined by the expression

$$\mathrm{pH} = \log\frac{1}{[\mathrm{H}^+]} = -\log[\mathrm{H}^+]$$

The symbol p denotes “negative logarithm of.” For a precisely neutral solution at 25^0C, in which the concentration of hydrogen ions is 1.0×10^{-7} M, the pH can be calculated as follows:

$$\mathrm{pH} = \log \frac{1}{1.0 \text{ x } 10^{-7}} = \log(1.0 \text{ x } 10^{7})$$

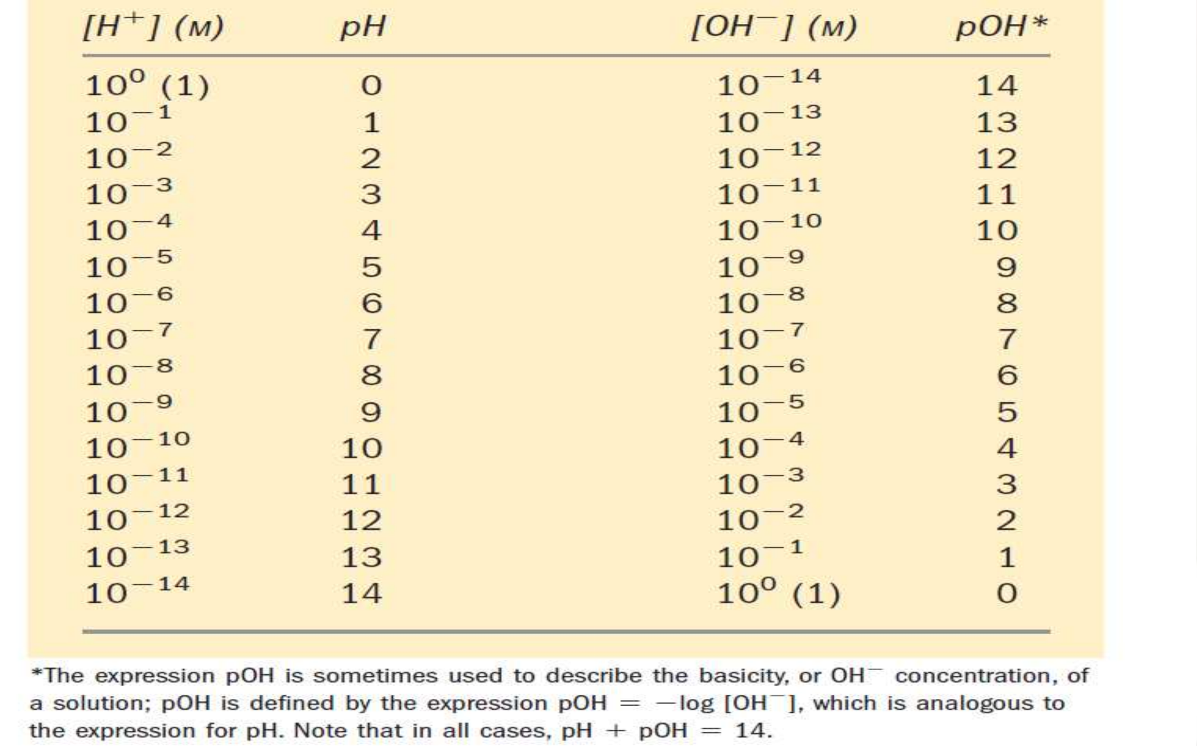
$= \log 1.0 + \log 10^{7}$

$$= 0 + 7 = 7$$

The value of 7 for the pH of a precisely neutral solution is not an arbitrarily chosen figure; it is derived from the absolute value of the ion product of water at 25^{0}C, which by convenient coincidence is a round number. Solutions having a pH greater than 7 are alkaline or basic; the concentration of OH^{-} is greater than that of H^{+}. Conversely, solutions having a pH less than 7 are acidic.

The pH scale is logarithmic, not arithmetic. To say that two solutions differ in pH by 1 pH unit means that one solution has ten times the H^{+} concentration of the other, but it does not tell us the absolute magnitude of the difference. Figure 2 gives the pH of some common aqueous fluids. A cola drink (pH 3.0) or red wine (pH 3.7) has an H^{+} concentration approximately 10,000 times that of blood (pH 7.4).

Table 1 The pH scale



$[H^{+}]$ (M)	pH	$[OH^{-}]$ (M)	pOH*
10^{0} (1)	0	10^{-14}	14
10^{-1}	1	10^{-13}	13
10^{-2}	2	10^{-12}	12
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
10^{-5}	5	10^{-9}	9
10^{-6}	6	10^{-8}	8
10^{-7}	7	10^{-7}	7
10^{-8}	8	10^{-6}	6
10^{-9}	9	10^{-5}	5
10^{-10}	10	10^{-4}	4
10^{-11}	11	10^{-3}	3
10^{-12}	12	10^{-2}	2
10^{-13}	13	10^{-1}	1
10^{-14}	14	10^{0} (1)	0

*The expression pOH is sometimes used to describe the basicity, or OH^{-} concentration, of a solution; pOH is defined by the expression $\mathrm{pOH} = -\log [OH^{-}]$, which is analogous to the expression for pH. Note that in all cases, $\mathrm{pH} + \mathrm{pOH} = 14$.

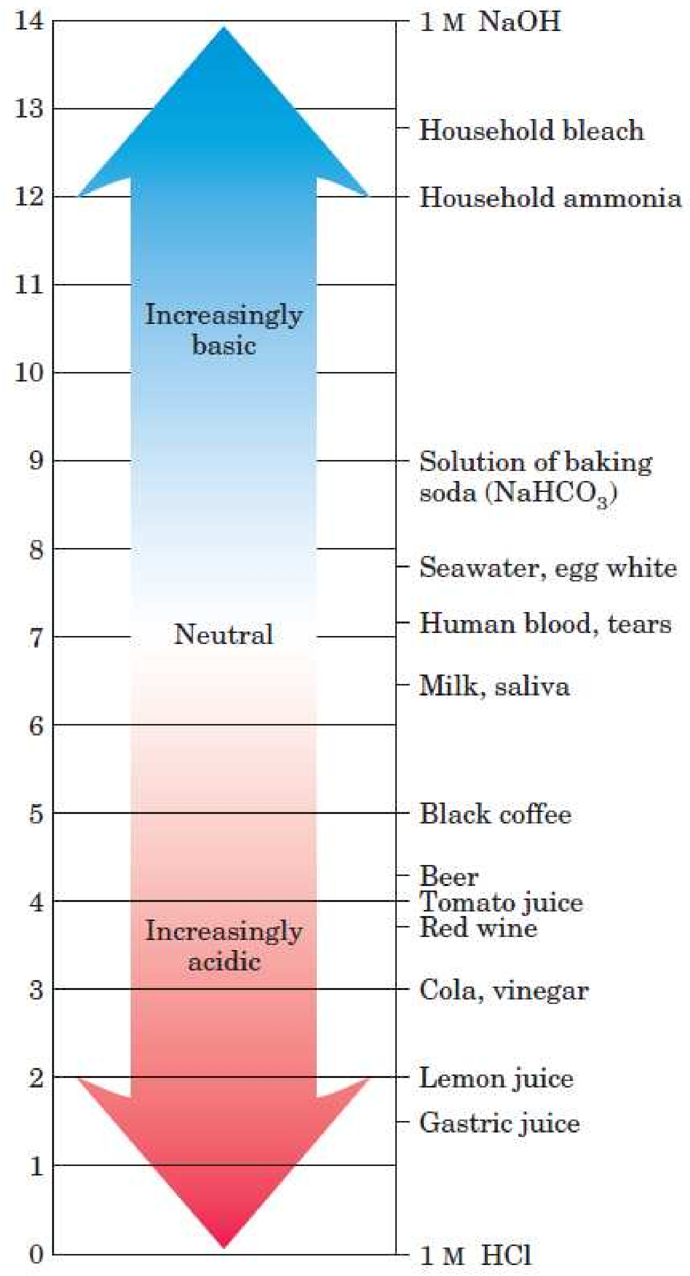


Fig.2 The pH of some aqueous fluids (Source: Principles of Biochemistry (2008, W.H.Freeman))

3.4 Weak Acids and Bases Have Characteristic Dissociation Constants:

Hydrochloric, sulfuric, and nitric acids, commonly called strong acids, are completely ionized in dilute aqueous solutions; the strong bases NaOH and KOH are also completely ionized. On the other hand, weak acids and bases do not completely ionized when dissolved in water.

Acids may be defined as proton donors and bases as proton acceptors. A proton donor and its corresponding proton acceptor make up a **conjugate acid-base pair** (Fig. 3). Acetic acid (CH_3COOH), a proton donor, and the acetate anion (CH_3COO^-), the corresponding proton acceptor, constitute a conjugate acid-base pair, related by the reversible reaction

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3COO^-}$$

Each acid has a characteristic tendency to lose its proton in an aqueous solution. The stronger the acid, the greater its tendency to lose its proton. The tendency of any acid (HA) to lose a proton and form its conjugate base (A^-) is defined by the equilibrium constant (K_{eq}) for the reversible reaction

$$HA \leftrightharpoons H^+ + A^-$$

Which is

$$\mathrm{K_{eq}} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \mathrm{K_a}$$

Equilibrium constants for ionization reactions are usually called ionization or **dissociation constants,** often designated K_a. The dissociation constants of some acids are given in Figure 3. Stronger acids, such as phosphoric and carbonic acids, have larger dissociation constants;
weaker acids, such as monohydrogen phosphate ($HPO4^{2-}$), have smaller dissociation constants.

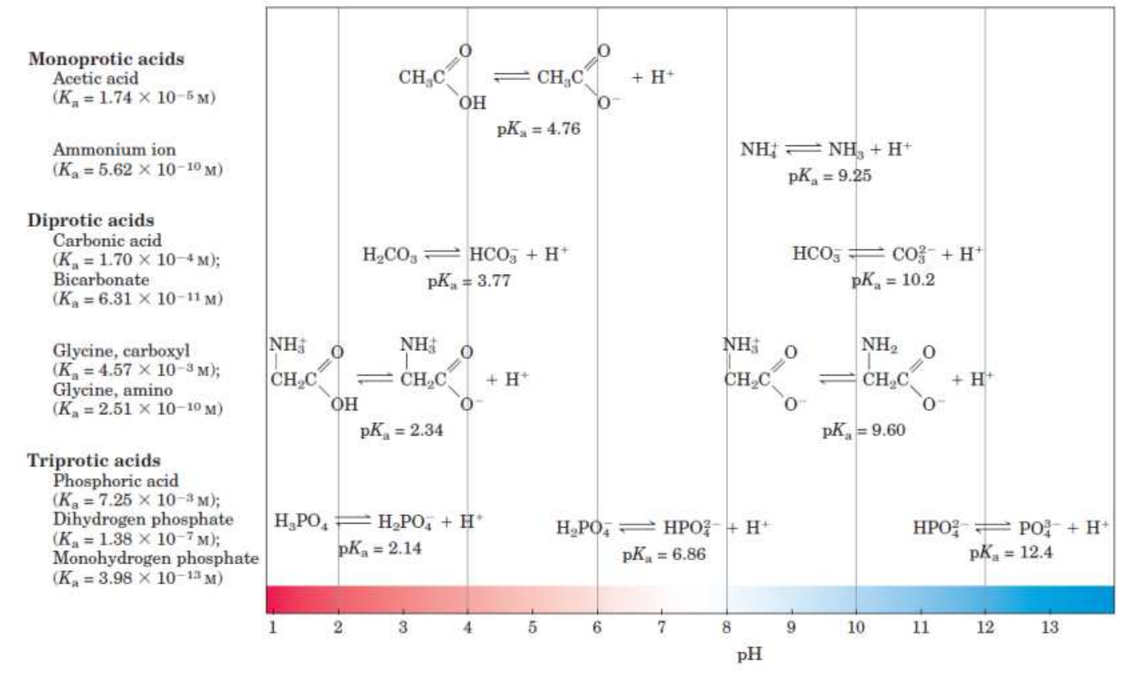


Fig.3 Conjugate acid-base pairs consist of a proton donor and a proton acceptor. Some compounds, such as acetic acid and ammonium ion, are monoprotic; they can give up only one proton. Others are diprotic (H_2CO_3 (carbonic acid) and glycine) or triprotic (H_3PO_4 (phosphoric acid)). The dissociation reactions for each pair are shown where they occur along a pH gradient. The equilibrium or dissociation constant (Ka) and its negative logarithm, the p*K*a, are shown for each reaction. (Source: Principles of Biochemistry (2008, W.H.Freeman))

The values of p*K*a, which is analogous to pH and is defined by the equation

$$\mathrm{p}K_\mathrm{a} = \log\frac{1}{K_\mathrm{a}} = -\log K_\mathrm{a}$$

The stronger the tendency to dissociate a proton, the stronger is the acid and the lower its p*K*a.

4. Buffer: Buffers are aqueous systems that tend to resist changes in pH when small amounts of acid (H^+) or base (OH^-) are added. A buffer system consists of a weak acid (the proton donor) and its conjugate base (the proton acceptor).

4.1 An excellent example of a buffer system is a mixture of equal concentrations of acetic acid and acetate ion, found at the midpoint of the titration curve can be seen in Figure 4, is a buffer system. The titration curve of acetic acid has a relatively flat zone extending about 1 pH unit on either side of its midpoint pH of 4.76. In this zone, an amount of H^+ or OH^- added to the system has much less effect on pH than the same amount added outside the buffer range. This relatively flat zone is the buffering region of the acetic acid–acetate buffer pair.

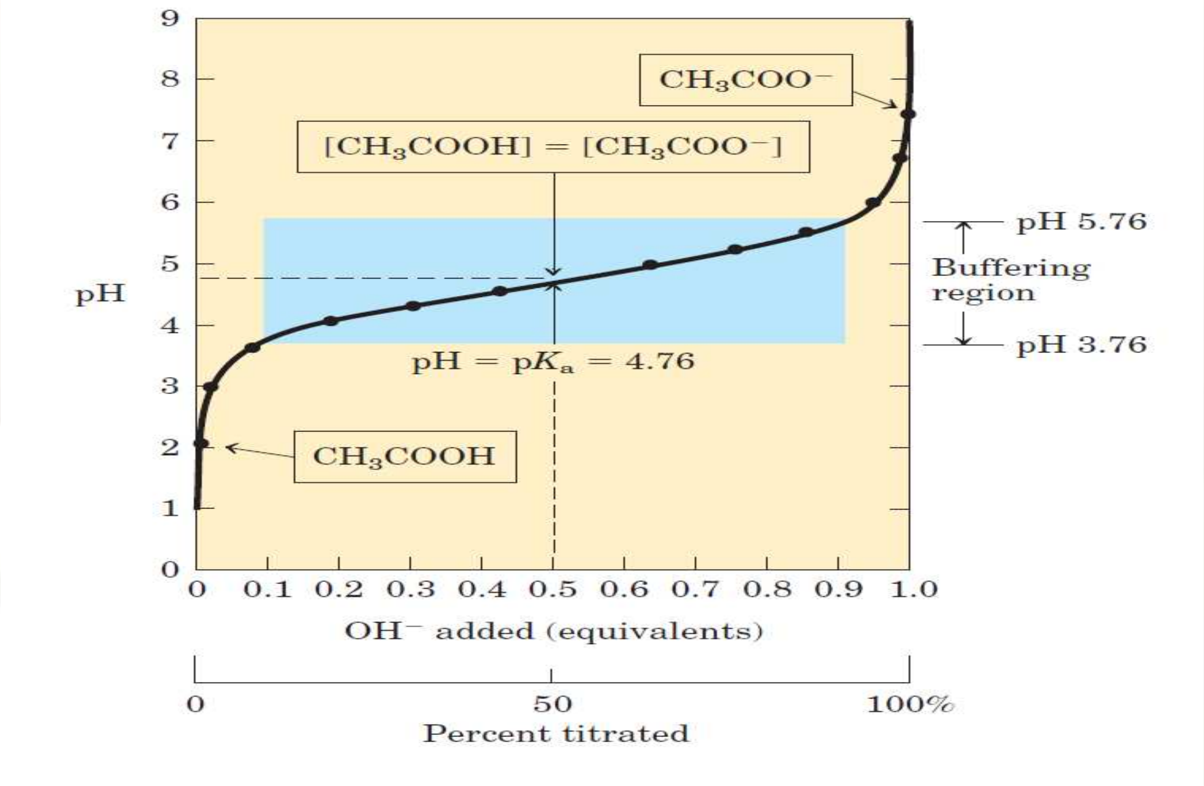


Fig. 4 The titration curve of acetic acid. After addition of each increment of NaOH to the acetic acid solution, the pH of the mixture is measured. This value is plotted against the amount of NaOH expressed as a fraction of the total NaOH required to convert all the acetic acid to its deprotonated form, acetate. The points so obtained yield the titration

curve. Shown in the boxes are the predominant ionic forms at the points designated. At the midpoint of the titration, the concentrations of the proton donor and proton acceptor are equal, and the pH is numerically equal to the p*K*a. The shaded zone is the useful region of buffering power, generally between 10% and 90% titration of the weak acid. (Source: Principles of Biochemistry (2008, W.H.Freeman)

4.2 Buffering results from two reversible reaction equilibria occurring in a solution of nearly equal concentrations of a proton donor and its conjugate proton acceptor. Figure 5 shows how a buffer system works.

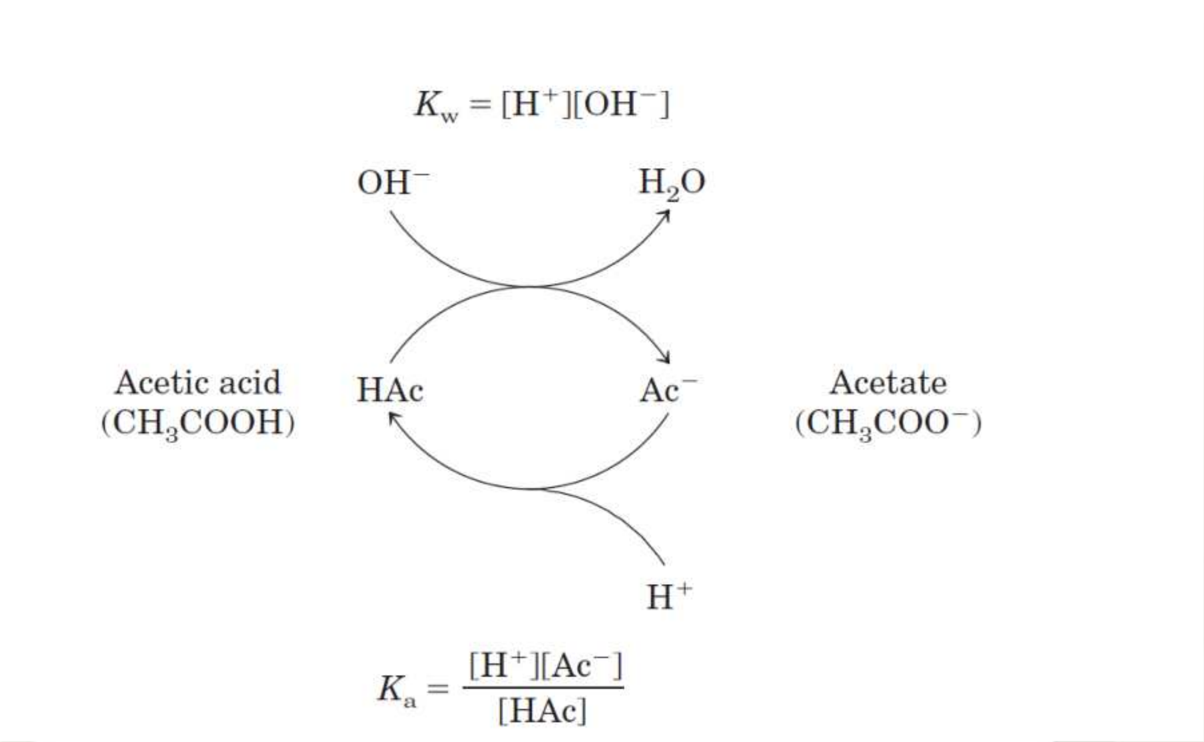


Fig.5 The acetic acid–acetate pair as a buffer system. The system is capable of absorbing either H^+ or OH^- through the reversibility of the dissociation of acetic acid. The proton donor, acetic acid (HAc), contains a reserve of bound H^+, which can be released to neutralize an addition of OH^- to the system, forming H_2O. This happens because the product $[H^+][OH^-]$ transiently exceeds *K*w ($1x10^{-14}$ M^2). The equilibrium quickly adjusts so that this product equals $1x10^{-14}$ M^2 (at 25^0C), thus transiently reducing the concentration of H^+. But now the quotient $[H^+][Ac^-]$ / [HAc] is less than *K*a, so HAc dissociates further to restore equilibrium.

Similarly, the conjugate base, Ac^-, can react with H^+ ions added to the system; again, the two ionization reactions simultaneously come to equilibrium. Thus, a conjugate acid-base pair, such as acetic acid and acetate ion, tends to resist a change in pH when small amounts of acid or base are added. Buffering action is simply the consequence of two reversible reactions taking place simultaneously and reaching their points of equilibrium as governed by their equilibrium constants, K_W and Ka. (Source: Principles of Biochemistry (2008, W.H.Freeman))

4.3 **Suggested reading: Henderson-Hasselbalch equation.**

5. Salts: Salts are the compounds obtained by neutralization of acid and base. These are composed of charged atoms or groups of atoms held together in a crystal lettuce. When these salts are dissolved in a solvent of high dielectric constant such as water or heated to melting point, the crystal forces are weakened and the substances dissociate into the pre-existing charged particles or ions. The resultant solutions are very good conductors of electricity.

Example:

i. $NaCl + H_2O \longrightarrow Na^+ + Cl^-$

ii. $KCl + H_2O \longrightarrow K^+ + Cl^-$

5.1 Hydrolysis of salt: When salts dissolved in water, the resulting solution will be neutral, acidic and alkaline solution depending on the nature of salts.

Hydrolysis is the interaction between the ions of a salt and the ions of water with the production of

i. Strong acids and strong bases-Sodium chloride

ii. Weak acids and strong bases

iii. Strong acid and weak bases

iv. Weak acid and weak base

5.2 Classes of salts:

Class 1 Salt

- Strong acid and strong bases solution remain neutral
- $H_2O \xrightarrow{\qquad} H^+ + OH^-$ (Equilibrium between H^+ and OH^- ions in water)
- In the strong electrolytes of both acid and base neither anions have tendency to combine with neither hydrogen ions nor the cat ions with hydroxyl ions of water

Class 2 Salts

- The salt will completely dissociated in water

  Eg. $MA \xrightarrow{\qquad} M^+ + A^-$

- A salt 'MA' derived from a weak acid (HA) and a strong base (BOH).
- The equilibrium reaction can be written as $A^- + H_2O \xrightarrow{\qquad} OH^- + HA$

Class 3 Salts

- The initial high concentration of cat ions (M^+) will be reduced by combining with the hydroxide ions of water to from a little dissociated base MOH until establishing equilibrium state

  Eg. $M^+ + OH^- \xrightarrow{\qquad} MOH$

Class 4 salts:

- In which both acid and base are weak. Two reactions will occur simultaneously

  Eg. i. $M^+ + H_2O \xrightarrow{\qquad} MOH + H^+$

  ii. $A^- + H_2O \xrightarrow{\qquad} HA + OH^-$

  $M^+ + A^- + H_2O \xrightarrow{\qquad} MOH + HA$

5.3 Hydrolysis constant (K_h) of a salt: Hydrolysis constant of a salt can be expressed as:

$$K_h = \frac{(OH^-) \times (HA)}{(A^-)} \quad \text{or}$$

$$K_h = \frac{(\text{Base}) \times (\text{Acid})}{\text{Un hydrolyzed salt}}$$

5.4 Degree of hydrolysis: It is the fraction of each molecule of hydrolyzed salt at equilibrium. The degree of hydrolysis is largely influenced by

- Changes in temperature
- Conc. of reactants.

Law of Mass action or Law of chemical equilibrium: It is the velocity of a chemical reaction which is proportional to the product of the active masses of the reacting substances.

Hypothetical chemical reaction: $A + B \rightarrow C + D$

- The velocity with which A x D react is proportional to their concentrations.

$$\frac{(C) \times (D)}{(A) \times (B)} = \frac{K_1}{K_2} = K$$

Where K is a equilibrium constant, K_1 x K_2 velocity coefficients

5.5 Types of Salts: 1. Simple salts ,2. Double salts,3. Complex salts, 4. Mixed salts

1. Simple salts

- Salts produced by Acid – base neutralization are called simple salts

i. Normal salt:

- Salts formed by the loss of all replaceable hydrogen (H^+) are called normal salts

Eg. i. Sodium hydroxide ii. Sodium nitrate iii. Sodium chloride etc

ii. Acid salt:

- Salts formed by incomplete neutralization of acids. These salts still contain replaceable hydrogen (H^+).

Eg : i. $NaHCO_3$ (Sodium bicarbonate)

ii. $NaHSO_4$ (Sodium bi-sulphate)

iii. Basic Salts:

Salts formed by incomplete neutralization of acid, polyacidic bases. Salts still contained in one or more hydroxyl groups (OH^-).

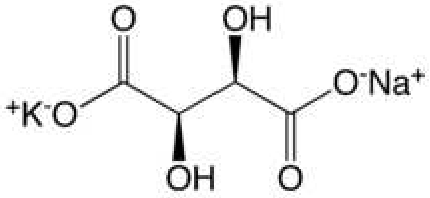
2. Double Salts: Eg : Potash, Aluminum

3. Complex Salts: Eg. $K_4Fe(CN)_6$

4. Mixed Salts

Eg: i) Bleaching powder $Ca(ClO)_2$

ii. Rochell salt – Sodium potassium tartrate



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Course Name	Soil and Water Chemistry
Lesson 4	Water analysis: Collection and preservation of water samples
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University/College Name	Assam Agricultural University, Jorhat
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Lesson 4

Objectives:

1. To learn the principles and procedures of water analysis.
2. To learn the analysis procedures of important physico-chemical parameters of water

Glossary of terms:

1. Physical properties: Physical properties of water are related to the appearance of water, namely, the colour, temperature, turbidity, taste, and odour.

2. Chemical properties: Chemical properties of water generally indicate the chemical reactions displayed by water.

3. Sample: A sample is defined as a portion of material selected from a larger quantity of material.

4. Turbidity: Turbidity refers to an optical property of water that causes light to be scattered or absorbed rather than transmitted through the water in a straight line.

5. Total Solids: Total solids in the water sample represent the dissolved organic matter, particulate organic matter, and dissolved inorganic substances.

6. Alkalinity: Alkalinity refers to buffering capacity of a water body.

7. Hardness: The hardness of a water sample is defined as its content of divalent metallic cations (Ca^{2+} & Mg^{2+}) expressed as equivalent calcium carbonate.

8. Salinity: Salinity of water is the total concentration of soluble salts in a litre of water and expressed as ppt (part of per thousand).

9. Parts per thousand (ppt): A concentration of 1 ppt means 1 mg of solute in 1000 mg of solution, or, 1 g of solute in 1000 g (1000 mL or 1 L) of solution. Symbol ‰ .

10. Parts per million (ppm): A concentration of 1 ppm means 1 mg of solute in 1,000,000 mg of solution, or 1 mg of solute in 1000 g of solution, or 1 mg of solute in 1 kg of solution. This also means 1 mg of solute in 1000 mL or 1 L of solution (remember that 1 mL of water weighs 1 g or 1 L of water weighs 1 kg).

E-lecture:

1. Collection & Preservation of Water Samples: Collection of water sample is an integral part of the total analytical procedure. The amount of water sample collected from a water body should be a true representative of the water body under study. Water samples should always be collected keeping in mind the following points:

- To collect representative sample in suitable volume for analysis
- To maintain water properties original to the sample
- To keep the concentration of all components as in the original sample
- To transport sample with no significant changes in the composition of water

1.1 The frequency of sampling varies with the objective of investigation. However, for routine limnological work samples are collected fortnightly or at monthly intervals. For investigating public health related problems, more frequent sampling should be attempted.

1.2 For collecting surface water samples, a simple bucket or beaker may be used. However, for drawing sub-surface water sample, suitable equipment such as Vandorn sampler, Kammerer sampler or a Reversing bottle (Fig.1) could be used.

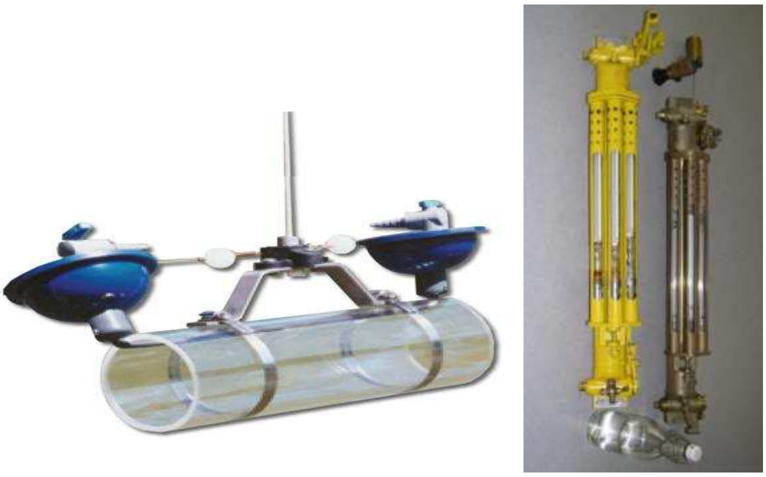

Fig.1. (a) Vandorn sampler (b) Nansen water bottle

1.3 Quantity of sample: Generally, 2 liters or more volume of sample are considered to be sufficient for most of the routine parameters including pigments, TSS, TDS, metals etc.

1.4 When collecting samples directly from a river, stream, lake, reservoir, spring or shallow well, the aim must be to obtain a representative sample. It is thus undesirable to take samples too close to the bank, far from the point of draw-off or near the bottom.

Wells: For collecting samples from wells fitted with a hand or mechanical pump, the pump should first be operated to flush out the remnant water from the pipe-work before a sample is taken.

Sampling in treatment plants: As frequent samples are required to be taken in treatment plants, sampling taps should be provided throughout the plant complex so that all stages of processing could be monitored. If taps are not available, the samples may be taken by lowering the sampling bottle into a tank.

Sampling from taps: Public health and water supply authorities should select sampling sites according to a pre-planned programme. From taps, water should be collected after removing external fittings. Allow some water to run out before collecting water sample.

1.5 Sample containers and labels: Normally, plastic or glass containers are used for collecting water samples. However, each has its own drawbacks. For example, silica and sodium may get leached from glass but not from plastic. Similarly, trace level metals may be adsorbed into the walls of glass containers. For samples having volatile organic, glass bottles are preferred.

Each sample should be labelled bearing details of sample or appropriate code. A field log book should invariably be maintained for recording details of samples and analysis thereof. GPS readings may be incorporated for identification of samples.

1.6 Preservation of samples:

Some water quality parameters get altered if the sample is not analysed quickly. Therefore, it is desirable to make at the site analysis of a few chemical parameters such as dissolved oxygen, carbon dioxide, alkalinity, pH and temperature.

For rest of the analyses, samples could be preserved or stored for a specific time for further analysis in the laboratory.

A summary of special water sampling and handling procedure can be seen in Table 1:

Table 1. Summary of special sampling or handling requirements:

Sl. No.	Parameter	Container	Preservation	Storage period
1.	Acidity	PG(B)	Refrigerate	24 h
2.	Alkalinity	P,G	-do-	24 h
3.	BOD	P,G	-do-	6 h
4.	Boron	P	None required	28 h
5.	Total Organic Carbon (TOC)	G	Analyse immediately or refrigerate, add HCl to pH<2	6 h
6.	CO_2	P,G	Analyse immediately	-
7.	COD	P,G	Analyse as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d
8.	Chlorine	P,G	Analyse immediately	0.5 h
9.	Chlorophyll	P,G	30 d in dark	30 d
10.	EC	P,G	Refrigerate	28 d
11.	Fluoride	P	None required	20 d
12.	Hardness	P.G	Add $HNO_{3\,-}$ to pH<2	6 months
13.	Metals	P(A), G(A)	For dissolved metals filter immediately, add HNO_3 to pH <2	6 months
14.	Ammonia	P,G	Analyse as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d

15.	Nitrite	P,G	Analyse as soon as possible or refrigerate	48 h
16.	Nitrate	P,G	Analyse as soon as possible or refrigerate	12 h
17.	Organic nitrogen	P,G	Refrigerate, add H_2SO_4 to pH<2	7 d
18.	Dissolved oxygen	G, BOD bottle	Analyse immediately	0.5 h
19.	pH	P,G	-do-	2 h
20.	Phosphate	G(A)	Refrigerate	28 h
21.	Salinity	G, Waxseal	Use wax seal	6 months
22.	Silica	P	Refrigerate, do not freeze	28 d
23.	Sulfate	P,G	Refrigerate, add 2 drops 2N Zn	28 d
24.	Taste	G	Analyse as soon as possible	24 h
25.	Temperature	P,G	Analyse immediately	-
26.	Turbidity	P,G	Analyse same day or store in dark upto 24 h, refrigerate	24 h

P= Plastic (polythene or equivalent); G=Glass, P(A)=Rinsed with 1+1 HNO_3; G(B)= Glass borosilicate; G(S)= Glass rinsed

- Refrigerate = storage at 4^0 C in dark.

2. Measurement of physico-chemical parameters of water:

2.1 Measurement of water temperature:

For determination of surface and subsurface water temperature of a water body generally 2 types of thermometers are used.

For measuring surface water temperature, common centigrade thermometer which can measure from 0 to 100^0C is generally used.

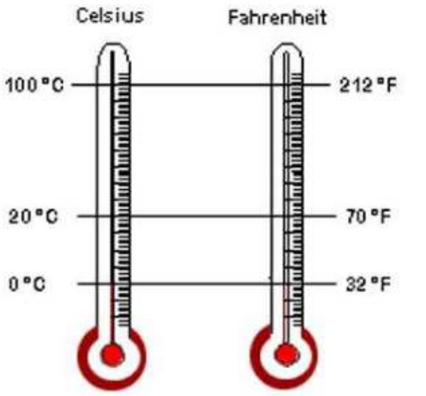

Fig.2 Celsius & Fahrenheit thermometers

For measurement of subsurface water temperature - **reversing thermometer** is widely used.

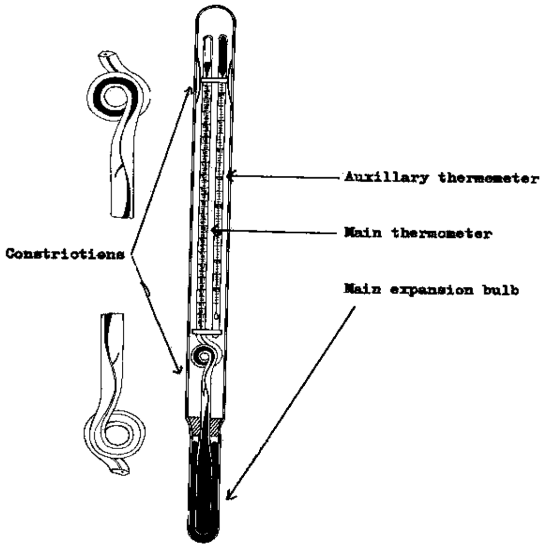

Fig.3 Reversing thermometer

For determining the temperature, dip the thermometer directly into the water, keep it for about one minute or till the reading become constant and note down the temperature immediately. Now a days, electronic thermometers are also available for measurement of water temperature.

2.2 Measurement of transparency/turbidity

Turbidity refers to an optical property of water that causes light to be scattered or absorbed rather than transmitted through the water in a straight line. Turbidity is caused by suspended material (such as soil particles, plankton, and organic detritus) and soluble coloured organic compounds. Turbidity caused by plankton generally is desirable in fish ponds.

Turbidity of a waterbody can be measured by two methods:

A. Using a Secchi disc

B. Using a Nephelometer

1. Secchi disc method

A Secchi disc is a circular metal/ plate with a diameter of 20 cm. The upper surface is divided into four quadrants and is alternatively painted in black and white. A circular iron ring fixed at the centre of the upper surface provides attachment for the graduated rope during operation. At the centre of the lower surface, a weight is attached to facilitate sinking of the disc in proper position (Fig.4). The lower side of the disc is painted in black in order to eliminate reflection of light from that surface.

During use, the Secchi Disc attached to a graduated rope is lowered into the water and the depth at which it disappears is first noted. Subsequently, the disc is gradually taken up and the depth at which it reappears is noted. The average of these two values is taken as the limit (depth) of visibility (d). The disc is operated from the sunny side of boat with the rope supporting the disc held vertically, between 9 a.m. and 3 p.m. when the sun is fairly high in the sky.

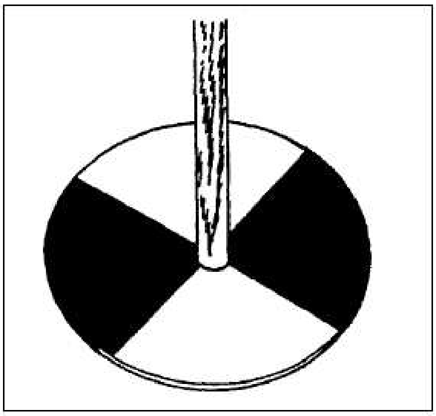

Fig.4 Secchi disc

This method is widely used especially for comparing various waters or same water at different times. As the light penetration in different water bodies is affected by various environmental characteristics, such as plankton density and particulate matter, this method could only be a useful rough index of visibility.

The transparency as a measure of light extinction coefficient (K) is calculated using the following formula of Poole and Atkins:

$$K = \frac{1.7}{d}$$

Where ‘d’ is the depth (m) of Secchi Disc visibility. For turbid waters, however a value of 1.44 is considered instead of 1.7.

For offshore waters $$K = \frac{1.9}{d}$$

For shallow coastal waters $$K = \frac{1.5}{d}$$

2. Nephelometer method:

The principle of operation of a Nephelometer is based on the well-known law of Tyndall Effect. A beam of light passing through a turbid liquid being tested scatters the light, which in turn is collected at right angle by a photocell/ photodiode and indicated on a digital display. The amount of scattered light is proportionate to the turbidity of the solution under test.

Principle:

The source (Tungsten lamp) in combination with optical components produce a converging light beam focussed on turbid solution. The light is scattered by the suspended particles in the solution. The scattered light is sensed by a photocell/photodiode kept at 90 degree in the light path. The amount of light sensed by the photocell/ photodiode is a direct measure of the turbidity of a water sample (Fig.5).

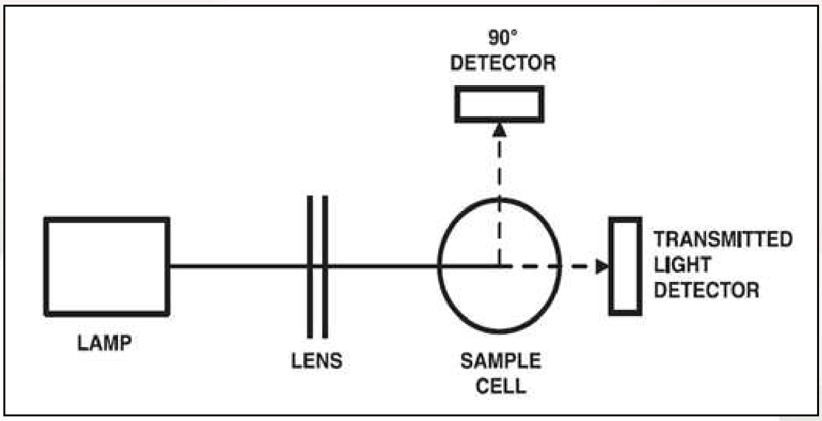

Fig.5 Schematic Diagram of a Nephelometer

Operation of Instrument:

i) Switch the instrument ON and allow 15-20 minutes warm up
ii) Select appropriate RANGE (0 to 1, 10, 100 and 1000 NTU ranges)
iii) Set the CALIB control to maximise clockwise position
iv) Insert the test tube with distilled water into cell holder and cover with light shield.
v) Adjust SET ZERO controls to get zero on the display.

vi) Remove the test tube and replace with test tube containing standard solution.

vii) Adjust CALIB control such that the display indicates as follows:

Range	**STD Solution**	**Display**
0-1 NTU	1 NTU	1.00
0-10 NTU	10 NTU	10.0
0-100 NTU	100 NTU	100.0
0-1000NTU	500 NTU	500

viii) The instrument is now ready for test samples. Insert test tube containing unknown sample in cell holder. The display directly gives turbidity in NTU (Nephelometric Turbidity Unit).

Precautions:

1. Test tubes should be cleaned with detergent and rinsed with distilled water prior to calibration.
2. Test tubes should be inserted in the holder with index marking aligned with markings on the holder top.
3. Test tube should be filled up to mark level.
4. Use high grade distilled water for accurate reading.
5. Keep the tube holder covered with light shield when not in use.

2.3 Measurement of water pH

At field level approximate idea of pH of a water sample can be obtained by using simple **pH paper or Litmus paper**. pH of a water sample can also be measured **colorimetrically** and **potentiometrically**.

pH paper:

pH paper strips are easily available in market and are very handy for getting an approximate idea of pH value of a water sample. The steps involved in determination of pH of a water sample using pH paper (Fig.6) are as follows:

1. Take a single pH strip from the pH book.
2. Dip the pH strip in your water sample and take out quickly.
3. Allow the strip to dry for a minute or so.
4. Compare the colour developed in the pH strip with the standard colours of pH books. Note down the corresponding pH of the matching standard colour.

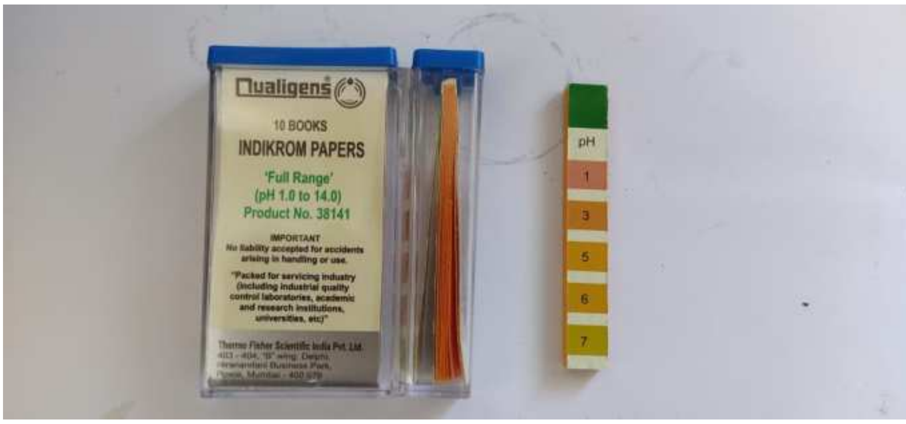

Fig.6 pH paper

Colorimetric measurement:

In physical and analytical chemistry, colorimetry or colourimetry is a technique used to determine the concentration of colored compounds in solution. A colorimeter is a device used to test the concentration of a solution by measuring its absorbance of a specific wavelength of light.

Colorimetric method of pH determination is a field method, less accurate. Easy and simple to operate. In this method pH of a water sample is determined by Lovibond comparator (Fig.7) using universal/

phenolphthalein indicator / phenol red / thymol blue indicator depending on pH range in fresh waters and saline waters.

Fig.7 Lovibond comparator

Potentiometric method:

Potentiometric titration is a technique similar to direct titration of a redox reaction. It is a useful means of characterizing an acid. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution.

The method is more accurate; requires less time; widely used. pH is recorded by immersing the standardized pH meter by following guidelines of the manufacture . pH meter is calibrated with pH values of 4.0, 7.0 and 9.2 standard pH solutions prepared by using the tablets of each pH. Now a days, pH pens are also available which are very handy to use and gives accurate result.

Fig.8 pH meter

2.4 Measurement of Electrical conductivity:

Electrical Conductivity indicates the total concentration of ionized constituents in water. Closely related to the amount of total dissolved solids.EC - used as an index of salt content of water.EC is reciprocal of electrical resistance. In natural water EC values normally ranges from 20 to 1500 mmhos /cm. EC = I/2 R, where R is resistance.

Electrical conductivity is measured using an Electrical conductivity Bridge known as Electrical conductivity meter / whatman conductivity bridge.The conductance of the water sample is measured by immersing the cell of the conductivity meter and recorded the conductance value. By multiplying this value by cell constant value gives EC of the water sample

Calculation: EC (mmhos/an = measured conductivity X cell constant)

2.5 Measurement of salinity/chlorinity:

The halogen compounds present in seawater (chloride, bromide and iodide) readily react with silver to give insoluble silver halides. Fluoride (a halogen ion) does not precipitate with silver. Hence, total quantity of silver required to react with chloride, bromide and iodide is a true measure of chlorinity of seawater. In this method potassium chromate is used as the indicator. **The main principle of this titrimetric method is that silver will not react with chromate till all the halogens (other than fluoride) present in seawater are converted into silver halides.** Since silver chromate has a characteristic brownish red colour, the end point can be precisely noted.

Reagents:

1. **Silver nitrate solution:** 27.25 g of analar/GR/reagent grade silver nitrate is dissolved in a little distilled water and the volume is made up to 1 litre. In the absence of light and evaporation, this reagent is stable at least for one month.

2. **Potassium chromate solution:** 8 g of the salt is dissolved in 100 ml of distilled water. This reagent is stable for several months if it is kept in a refrigerator.

Procedure:

100 ml water sample is taken in a conical flask and 1 ml of chromate solution is added to it. The entire sample now turns yellow. Slowly the silver nitrate already taken in the burette is added. The titration is stopped when the yellow colour vanishes with the formation of a brownish red colour. Values are then tabulated. The titration is repeated with fresh sample till concordant values are obtained.

Calculation:

ml of silver nitrate used (at the time of end point) for the titration of 10 ml = Salinity of the sample.

Salinity of the seawater sample may be expressed by giving the unit $^0/_{00}$ or ppt (parts per thousand). For example, if 35 ml of silver nitrate is required for the titration, the salinity of the water sample will be 35 $^0/_{00}$ or ppt.

Kneudson formula: Chlorinity of a sample can be determined from its salinity using the following formula:

$$S\ ^0/_{00} = 1.80655\ Cl\ ^0/_{00}$$

2.6 Measurement of Total Solids:

The solids invariably represent a portion of water sample and are not lost even upon evaporation. Solids include dissolved organic matter, particulate organic matter, dissolved inorganic substances except gases and CO_2 contained in bicarbonate and particulate inorganic substances. The quantity of total solids (TS) represented by dissolved and particulate organic and inorganic matter is determined by evaporating a water sample and weighing the residue. The amount of total volatile solids (TVS) which is an estimate of dissolved and particulate organic matter on the other hand is measured by determining the weight loss of the residue by ignition from total solids. To determine the amount of total dissolved solids (TDS) which is an estimate of dissolved organic and inorganic matter, the water sample is first filtered to remove the particulate matter and the filtrate is then evaporated and the residue weighed. If the residue obtained from the total dissolved solids is ignited and the weight loss is determined, one may obtain the total volatile dissolved solids (TVDS) which is an estimate of dissolved organic matter in a sample.

Procedure

Total solids (TS)

A 100ml of water sample is taken into a well cleaned and preweighed dish. This is then evaporated in an oven at 103^{0}C for 1 hr. Afterwards, the dish and residue are nd are weighed subsequently.

$$\text{Total solids (mg/l)} = \frac{\text{R-D x 1000}}{\text{Sample Volume (ml)}}$$

Where, R= weight (g) of the evaporating dish and residue
D= weight (g) of the evaporating dish

Total volatile solids (TVS)

The aforesaid dish containing the residue is then placed in a muffle furnace which is maintained at 550^{0}C for about 30 minutes. The dish and residue are cooled in a desiccators before weighing them. The amount of total volatile solids is calculated as follows

$$\text{Total volatile solids (mg/l)} = \frac{\text{R-A} \times 1000}{\text{Sample Volume (ml)}}$$

Where,

R= weight (g) of the evaporating dish and residue before ignition
A= weight (g) of the evaporating dish and residue after ignition

Total Dissolved Solids (TDS)

125 to 150 ml of water sample is filtered through a glass fibre filter placed in a funnel. Then 100 ml of the filtrate is transferred to a preweighed dish. The contents are evaporated as for total solids. The dish and residue are cooled in a desiccators
before weighing.

$$\text{Total dissolved solids (mg/l)} = \frac{\text{R-D} \times 1000}{\text{Sample Volume (ml)}}$$

Where,

R = the weight (g) of the evaporating dish and residue
D = the weight (g) of the evaporating dish

Total volatile dissolved solids (TVDS)

The evaporating dish and residue obtained from the analysis of the total dissolved solids are placed in a muffle furnace maintained at 550^0C for about 30 minutes. The dish and residue are cooled in a desiccator before weighing.

$$\text{Total volatile dissolved solids (mg/l)} = \frac{\text{R-A} \times 1000}{\text{Sample Volume (ml)}}$$

Where, R = the weight (g) of the evaporating residue before ignition

A = the weight (g) of the evaporating residue after ignition

2.7 Measurement of Dissolved Oxygen in Water:

Dissolved oxygen is a vital parameter in the metabolic activity of flora and fauna of aquatic ecosystem. Main source of dissolved oxygen in natural waters are mainly attributed from photosynthetic and respiratory activities of biota and diffusion gradient at the air water interface and distribution by wind driven mixing. It can be measured by a volumetric method known as "Winkler method".

Principle:

Manganous sulphate reacts with potassium or sodium hydroxide to give a white precipitate of manganous hydroxide. In the presence of oxygen, brown manganic basic oxide is formed,

$Mn^{+2}SO_4 + 2KOH$ ---------> $Mn^{+2} (OH)_2 + K_2SO_4$

$2Mn^{+2} (OH)_2 + O_2$ ---------> $2Mn^{+4} O (OH)_2$

Addition of sulphuric acid dissolves the brown manganic oxide yielding manganic sulphate which reacts instantly with iodide to yield iodine.

$Mn^{+4} O (OH)_2 + 2H_2SO_4$ ---------> $Mn^{+4} (SO_4)_2 + 3H_2O$

$Mn^{+4} (SO_4)_2 + 2KI$ ------------------> $Mn^{+2}SO_4 + K_2SO_4 + I_2$

In effect, oxygen oxidizes Mn^{+2} to Mn^{+4} and Mn^{+4} oxidizes I- to I_2. Iodine is then determined titrimetrically with starch as an end point indicator.

Reagents:

1. **Manganese Sulphate (Winkler A)**
2. **Alkaline iodide (Winkler B)**

3. Concentrated Sulphuric Acid

4. Starch indicator (1%)
5. Sodium thiosulphate (0.01 N)

Glasswares:

BOD/ DO bottle (250 ml to 300 ml or 125 ml capacity), pipettes (2 ml capacity), burette, conical flask (250 ml capacity)

Procedure:

When transferring the water sample, the sampler dispensing tube must be placed at the bottom of the sample bottles (BOD bottles) of 125 ml capacity and held below the liquid surface while filling. Liquid should be allowed to overflow the bottle by at least one bottle volume in order to avoid the entrapping of air bubbles. Immediately 2ml of managnous sulphate and 2 ml of alkaline iodide are added one after another. These reagents should be added well below the liquid surface with the sample bottles open for a very short time. The bottle is restoppered without entrapping any airbubbles and carefully tilted, when a precipitate forms and settles at the bottom. At the time of titration, the stopper of the bottle is removed and 2 ml of concentrated sulphuric acid is added. The bottle is again tilted carefully, when the precipitate dissolves and a clear straw yellow solution results. During titration 100 ml of solution is removed from the bottle and is transferred to a 250ml conical flask. This solution is then titrated against 0.01 N sodium thiosulphate solution until a strong pale yellow colour is obtained. At this stage, 3 or 4 drops of 1 percent starch indicator is added and the titration is continued until the disappearance of the blue colour. Water samples collected for the analysis of dissolved oxygen should not be stored for more than eight hours.

Calculation:

$$\text{Oxygen (mg/l)} = \frac{CF \times N \times E \times 1000 \times Vt}{Vs}$$

Where,

CF = Correction factor value

$$\text{Correction factor value} = \frac{\text{Total volume of the stoppered bottle}}{\text{Total volume of stoppered bottle} - 2}$$

N = Normality of thiosulphate (0.01 N)
E = Equivalent weight of O_2
1000 = To convert the value to 1000 ml (or) 1 litre
V_t = Titre value
Vs = Volume of Sample taken for titration

If the oxygen content is to be calculated in ml/l, then the above result should be multiplied by a factor value (0.698). In case of brackishwater and seawater samples, it is customary to express the value of oxygen content in ml/l and in freshwater samples, mg/l .

2.8 Measurement of Free CO_2 in water:

Carbon dioxide is present in atmosphere in very small quantity. For this reason, in spite of its high solubility in water, its concentration in most water-bodies is low. It occurs in water in three closely related forms- a) free CO_2, b) bicarbonate ion (HCO_3^-), and c) carbonate ion (CO_3^{2-}). Each form amount present depends on the pH of water. For example, in neutral or acidic waters, high concentration of free carbon dioxide, i.e. in toxic form is frequently found. Most natural waters contain free carbon dioxide. The equilibrium concentration of CO_2 in water is about 0.7 mg/l. However, many waters used for fish culture and most ground waters are supersaturated with carbon dioxide. Essentially, no free carbon dioxide is present in water of pH 8.3 or above. Free CO_2 can be estimated by a volumetric method:

Principle:

Carbon dioxide reacts with NaOH as follows

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

These two reactions indicate the two possible methods for determining carbon dioxide in water, titration with either standard NaOH or with standard Na_2CO_3 to the phenolphthalein end point. For titration with NaOH, 0.0227 N solution is required. For titration with Na_2CO_3 , 0.0454 N solution is required.

Reagents:

1. **Phenolphthalein indicator solution**
2. **Standard sodium carbonate, 0.0454 N**

Procedure:

1. **Collection of sample:** Collect sample so that it does not come in contact with the atmosphere. To minimise exposure to air, a portion of the sample is first siphoned into a 100 ml graduated cylinder through a flexible tube which discharges at the bottom of the cylinder. About, 50 to 75 ml of water may be allowed to overflow from the cylinder before the tube is removed. The excess sample from the cylinder is carefully removed using a pipette. The analysis for CO_2 should be completed within 2 or 3 hours of sample collection.

2. **Titration of carbon dioxide:** Add 4 drops of phenolphthalein indicator solution to 100 ml of sample. If the sample turns pink the pH is above 8.3 and free CO_2 is absent. If the sample remains colourless it contains free CO_2. Samples containing CO_2 must be titrated rapidly with 0.0454 N Na_2CO_3 solution. Stir gently with a stirring rod as Na_2CO_3 is added. A definite pink colour which remains for 30 seconds marks the end point.

   To improve accuracy, a portion of the sample is titrated to the end point and a second 100 ml portion of the sample is taken and the volume of sodium carbonate solution titrate used in the first titration is quickly added. The titration is then continued to the end point.

Calculation:

$$\mathbf{CO_2\ (mg/l) = \frac{(ml\ of\ Na_2CO_3) \times N \times E \times 1000}{Sample\ volume\ (ml)}}$$

Where,
N = Normality of Na_2CO_3
E = Equivalent weight of CO_2 (22)

Guidelines for CO_2 values for fish culture:

1. **12-50 mg/litre- sub-lethal effects include respiratory stress and development of kidney stones (nephrocalcinosis) in some species;**
2. **50-60mg/litre- lethal to many fish species with prolonged exposure.**

2.9 Measurement of Total Alkalinity of water:

The alkalinity of normal freshwater results from bicarbonate, carbonate and hydroxide ions. Alkalinity is measured volumetrically by titration with dilute hydrochloric or sulphuric acid. Two end point indicators, methyl orange and phenolphthalein are commonly employed for alkalinity titrations. Results are expressed as mg/l equivalent of Calcium Carbonate.

Principle:

The water samples containing measurable carbonate ions turn pink to Phenolphthalein indicator (pH about 8.4) and the measurement of alkalinity is done by titrating the sample in two stages. During titration to the phenolphthalein end point, all of the hydroxides and half of the carbonate are neutralised. Reactions are illustrated in equations 1 and 2.

1. $OH^- + H^+$ ----------------> H_2O
2. $CO_3^{2-} + H^+$---------------->HCO_3

Titration to the methyl orange end point (pH-4.5) neutralizes any naturally occurring bicarbonate and that bicarbonate formed by titration of carbonate (eq.3).

3. $HCO_3^- + H^+$ --------------------> $H_2O + CO_2$

Samples negative to phenolphthalein, but positive to methyl orange, contain only bicarbonate. Samples negative to methyl orange have a pH below 4.5 and have no alkalinity.

The entire amount of acid required to titrate a sample of water to pH 4.5 is equivalent to the total alkalinity. The titration to pH 8.3, the phenolphthalein end point, is equivalent to the phenolphathalein alkalinity. Results of the titration to the two end points may also be used to calculate hydroxide, carbonate and bicarbonate alkalinities.

Uptake and release of carbon dioxide by organisms will change the pH and the amount of carbonate, bicarbonate or hydroxide in samples. Therefore, titrations should be done as soon as possible.

Reagents:

1. **Dilute H_2SO_4 (approximately 0.02 N):** Prepare a H_2SO_4 solution of approximately 0.1 N by diluting 3 ml of conc. H_2SO_4 to 1 liter with CO_2-free distilled water. Dilute 200 ml of 0.1 N H_2SO4 to 1 liter with CO_2-free distilled water. The solution is approximately 0.02 N, but it must be carefully standardised to determine its exact normality.
2. **Phenolphthalein indicator solution:** Dissolve 0.5 g phenolphthalein in 50 ml of 95% alcohol. Add 50 ml of distilled water.
3. **Methyl orange indicator solution:** Dissolve 0.05g methyl orange in 100 ml of distilled water.
4. **Standard sodium carbonate, 0.02 N:** Dry a few grams of Na_2CO_3 (primary standard) at 140^0C and cool in a desiccator. Dissolve 1.060g of Na2CO3 and dilute to 1 liter in CO_2- free distilled water. This solution must be used within a few hours of preparation.

Procedure:

1. **Standardisation of dilute sulphuric acid:** Pipet 10 ml of standard 0.02 N Na_2CO_3 solution into a 250 ml beaker. Add 90 ml of CO_2 free distilled water. Add 4 to 8 drops of methyl orange indicator solution. Select a number of drops of methyl orange which allows easy end point detection. Use this number of drops in subsequent drops. Titrate over a white surface to the methyl orange end point with dilute H_2SO_4 solution. At the end point, one drop of acid will change the colour of methyl orange from yellow to orange. Calculate the normality of H_2SO_4 by use of the equation $N_1V_1= N_2V_2$.

2. **Titration of Phenolphthalein alkalinity:** Measure a 100 ml sample unto a 250 ml beaker. Add 2 drops of phenolphthalein indicator solution. If the sample turns pink, it contains phenolphthalein alkalinity. Titrate with standard H_2SO_4 solution until one drop of acid causes the pink colour of the sample to disappear. Save the sample for determination of methyl orange alkalinity.

3. **Titration of methyl orange alkalinity:** Add 4 to 8 drops of methyl orange indicator solution to the same sample used for phenolphthalein alkalinity titration. Titrate over a white surface to the methyl orange end point with standard H_2SO_4 solution.

Calculation:

1. **Phenolphthalein alkalinity as mg/l equivalent $CaCO_3$=**

$$\frac{\text{ml } H_2SO_4 \text{ required for phenolphthalein end point X normality of } H_2SO_4 \text{ X } 50 \text{ X } 1000}{\text{ml of sample}}$$

2. **Total alkalinity as mg/l equivalent $CaCO_3$=**
3.

$$\frac{\text{Total ml } H_2SO_4 \text{ required for methyl orange \& phenolphthalein end points X normality of } H_2SO_4 \text{ X } 50 \text{ X } 1000}{\text{ml of sample}}$$

Inferences:

The data for phenolphthalein and total alkalinity may be used to asses hydroxide, carbonate and bicarbonate alkalinities.

1. Phenolphthalein alkalinity is zero: Sample contains only bicarbonate alkalinity.
2. Phenolphthalein alkalinity less than half total alkalinity: Sample contains both carbonate and bicarbonate alkalinity.
   Phenolphthalein alkalinity x 2 = Carbonate alkalinity
   Total alkalinity – Carbonate alkalinity = Bicarbonate alkalinity

3. Phenolphthalein alkalinity half total alkalinity : Sample contains only carbonate alkalinity.
   Total alkalinity= Carbonate alkalinity
4. Phenolphthalein alkalinity more than half total alkalinity : Sample contains both hydroxide and carbonate alkalinity.
   (Total alkalinity – Phenolphthalein alkalinity) X 2 = Carbonate alkalinity
   Total alkalinity – Carbonate alkalinity = Hydroxide alkalinity

5. Phenolphthalein alkalinity equals total alkalinity : Sample contains only hydroxide alkalinity.
   Total alkalinity = Hydroxide alkalinity.

3.0 Measurement of total hardness in water:

The total hardness of a water sample is defined as its content of divalent metallic cations expressed as equivalent calcium carbonate. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) are the predominant divalent metallic cations in most waters. Alkalinity and hardness values are normally similar in magnitude because calcium, magnesium, bicarbonate, and carbonate ions in water are derived in equivalent quantities from the solution of the limestone in geological deposits. However, in some waters alkalinity may exceed its hardness and vice versa. If alkalinity is high and hardness low, pH may rise to very high levels (>10.5) during rapid photosynthesis. Hardness of a water sample can be estimated by a volumetric method.

Principle

The calcium and magnesium ions of the water sample are titrated with ethylene diamine tetra acetic acid disodium salt (EDTA) to form the stable Ca EDTA and Mg EDTA. A small quantity of Erichrome black-T added to a water sample and buffered at pH 10 would lead to a soluble wine-red complex, with some of the calcium and magnesium ions. During titration, the EDTA will first complex all of the free Ca^{2+} and Mg^{2+} and the solution turns blue. The calcium and magnesium would then dissociate from their complexes with Erichrome black-T to form more stable complexes with EDTA. The following equations summarise the titration.

Ca^{2+} + Mg^{2+} + Ca & Mg Eriochrome Black T (Wine red) + EDTA --->

Ca EDTA + Mg EDTA +Eriochrome black-T (Blue)

Reagents

1. **Buffer solution**
2. **Eriochrome black-T Indicator**
3. **Standard calcium solution (0.01 M)**
4. **Standard EDTA Titrant**

Procedure

A 100 ml of water sample is taken in a flask and to it added 2 ml of the buffer solution. After stirring, 8 drops of Erichrome black-T indicator are added and the solution is titrated against the EDTA solution. A colour change from wine red to pure blue is the end point. The total hardness is calculated as follows.

$$\text{Total hardness (mg/l as } CaCO_3\text{)} = \frac{\text{(ml of EDTA) (M) (100.1) (1000)}}{\text{Sample Volume (ml)}}$$

3.1 Measurement of Ca^{2+} & Mg^{2+} in water:

Ca^{2+} & Mg^{2+} in water can be determined by a flame photometric method. Photoelectric flame photometry, a branch of atomic spectroscopy is used for inorganic chemical analysis for determining the concentration of certain metal ions such as **sodium, potassium, lithium, calcium, magnesium, cesium,** etc. In flame photometry the species (metal ions) used in the spectrum are in the form of atoms. The International Union of Pure and Applied Chemistry (IUPAC) Committee on Spectroscopic Nomenclature has recommended it as flame atomic emission spectrometry (FAES). The basis of flame photometric working is that, the species of alkali metals (Group 1) and alkaline earth metals (Group II) metals are dissociated due to the thermal energy provided by the flame source. Due to this thermal excitation, some of the atoms are excited to a higher energy level where they are not stable. The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques. The subsequent loss of energy will result in the movement of excited atoms to the low energy ground state with emission of some radiations, which can be visualized in the visible region of the spectrum. The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques while the emitting radiation intensity is measured using the emission techniques. The wavelength of emitted light is specific for specific elements.

Parts of a flame photometer

1. Source of flame:

A burner that provides flame and can be maintained in a constant form and at a constant temperature.

2. Nebuliser and mixing chamber:

Helps to transport the homogeneous solution of the substance into the flame at a steady rate.

3. Optical system (optical filter):

The optical system comprises three parts: convex mirror, lens and filter. The convex mirror helps to transmit light emitted from the atoms and focus the emissions to the lens. The convex lens help to focus the light on a point called slit. The reflections from the mirror pass through the slit and reach the filters. This will isolate the wavelength to be measured from that of any other extraneous emissions. Hence it acts as interference type color filters.

4. Photo detector:

Detect the emitted light and measure the intensity of radiation emitted by the flame. That is, the emitted radiation is converted to an electrical signal with the help of photo detector. The produced electrical signals are directly proportional to the intensity of light.

A schematic representation of flame photometer is shown in figure 1,

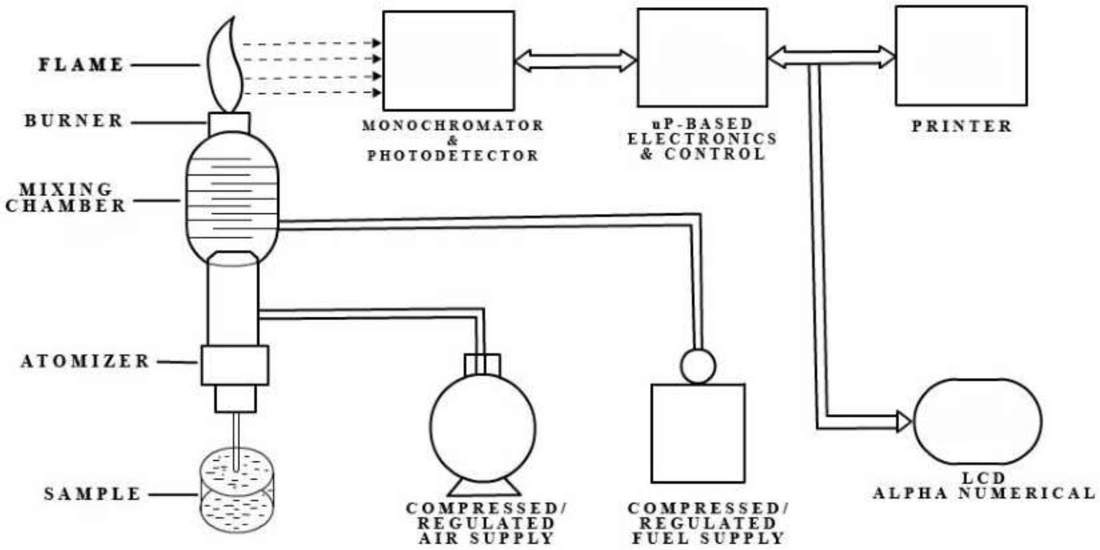

Fig 9: A schematic representation of flame photometer

3.2 Measurement of Nitrogen (Ammonium and Nitrate) and phosphorus in water:

Nitrogen (Ammonium & Nitrate) and Phosphorus in a water sample can be measured with the help of a spectrophotometer. A spectrophotometer is designed based on the principle of Beer-Lambert law.

This law states that the absorbance of a light absorbing material is proportional to its concentration in solution. The general Beer-Lambert Law is usually written as

$$A = elc$$

Where

A is the measured absorbance

e is the *extinction coefficient* of the substance- unique for each substance

l is the sample path length measured in centimetres (i.e. the width of the cuvette almost always 1 cm)

c is the molar concentration of the solution (expressed in terms of molarity)

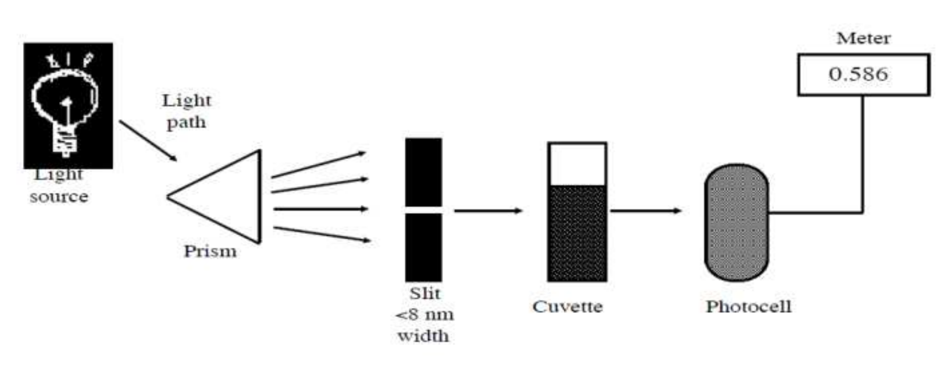

Fig.10 Schematic diagram of a Spectrophotometer

Wavelengths for measurement of Ammonium, Nitrate & Phosphorus in a water sample in a spectrophotometer are as follows:

Ammonia	630nm
Nitrate	543nm
Phosphorus	882nm

Course Name	Soil and Water Chemistry
Lesson 5	Water quality criteria/ requirements for Aquaculture
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
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Lesson 5

Objectives:

1. To learn the principles and procedures of water analysis
2. To learn the analysis procedures of important physico-chemical parameters of water

Glossary of terms:

1. To learn about the congenial water quality criteria/requirements for aquaculture

Glossary of terms:

Ectotherm: Any animal whose regulation of body temperature depends on external sources, such as sunlight or a heated rock surface.

Poikilotherm: These are ectotherms which have no control over their body temperature; their core body temperature conforms to ambient temperature.

Endotherm: These are those animals that maintain a constant body temperature independent of the environment.

Asphyxiation: Stress in fish due to low level of dissolved oxygen in an aquatic ecosystem.

Hypoxia: *Hypoxia* is a condition where not enough oxygen makes it to the cells and tissues in the body.

Nephrocalcinosis: Formation of calcareous deposits in the kidney.

Homeostasis: *It* is a self-regulating process by which an organism tends to maintain stability while adjusting to conditions that are best for its survival.

Lethal effect: Results in death of an organism.

Sub-lethal effect: Effect not enough to cause death but other health problems in an organism.

Stress: The general physiological response of fish to threatening situations, as with all vertebrates, is referred to as *stress.*

Euryhaline: Species that can tolerate wide range of salinity.

Stenohaline: Species that can thrive only on a narrow range of salinity.

Coldwater fish species: Fish species whose congenial temperature range is generally <20^{0}C are referred to as coldwater fish species.

Warmwater fish species: Tropical fish species whose congenial temperature range is 24-30^{0}C are referred to as warm water fish species.

E-lecture:

1. Water quality criteria/ requirements for Aquaculture: Fishes always remains in equilibrium with their environment and potential disease-causing microbes. Alteration in this equilibrium, such as deterioration in water quality can result in fish becoming stressed and vulnerable to diseases. It may ultimately also hamper their growth. Hence, it is essential to know congenial water-quality criteria/requirements for aquaculture.

1.1 Temperature: Fish and crustaceans are poikilotherms. The rates of all biochemical processes are temperature dependent. Within the temperature range that normally occurs in the natural habitat of a particular species, the rate of biochemical processes roughly doubles for **every 10^{0}C increase in temperature.**

Under favourable conditions, optimum temperature range for many coldwater and warm water fishes is 14-18^{0}C and 24-30^{0}C respectively. <12^{0}C lethal for tropical major carps but congenial for cold water fish species; **< 20^{0}C** sub lethal for growth and survival of most of the tropical carps and **> 35^0 C** lethal to most of the fish species (Bhatnagar *et al.* 2004).

1.2 Turbidity: Clay turbidity in water to **30 cm or less may prevent development of plankton blooms**, **30 to 60 cm and as below 30 cm- generally adequate for good fish production** and **if values are > 60 cm there may be increase occurrence of low DO problems.**

According to Bhatnagar *et. al.* (2004**) turbidity in the range from 30-80 cm is good for fish health; 15-40 cm good for intensive culture system and < 12 cm causes stress. Nephelometer reading of 20-30 NTU is considered as suitable for fish culture.**

1.3 Water colour: Abundance of Phyto & Zooplankton are responsible for determination of colour of an aquatic body and Green, Bluish Green/ Brown greenish colour of water indicates good plankton population hence, good for fish health.

1.4 Dissolved Oxygen (DO): This is the most critical and limiting factor in aquaculture. O_2 enters water through photosynthesis by aquatic plants, mainly phytoplankton, and by diffusion at the air-water interface. Critical limits of DO are shown in Fig.1.

The optimum DO content of Pond Water should be in the range of 5mg/L to saturation level for good fish growth. Some of the guidelines for DO for fish production are:

- 5.0 mg/litre- optimum for normal growth and reproduction in tropical waters;
- 1.0-5.0 mg/litre-may have sub-lethal effects on growth, feed conversion and tolerance to disease
- 0.3-0.8 mg/litre-lethal to many species if sustained for a long period.

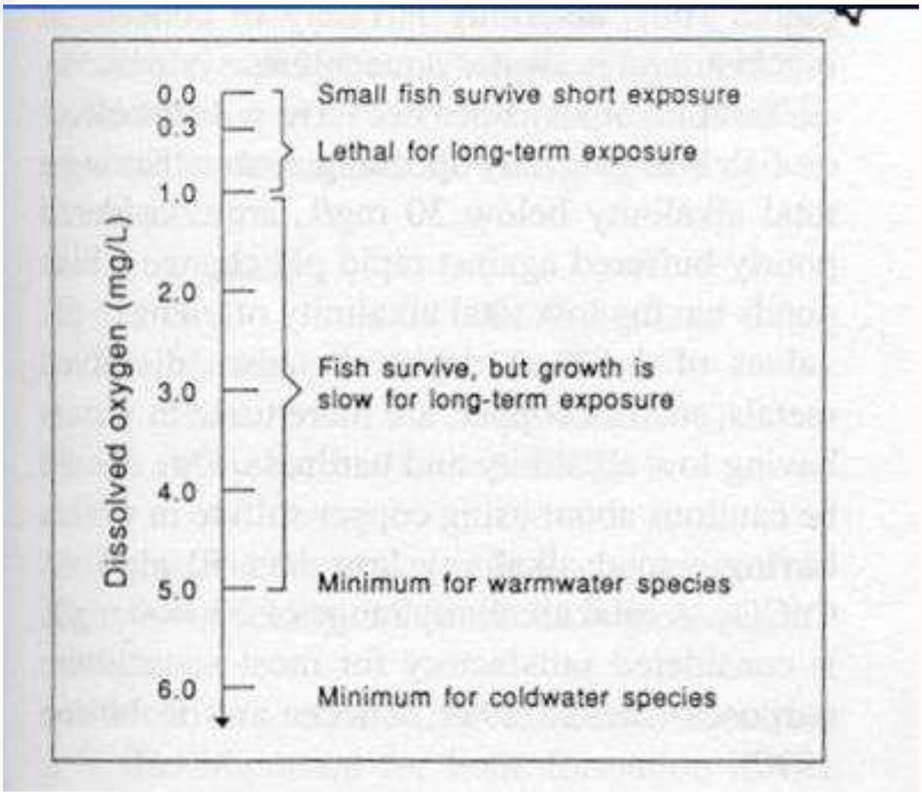

Fig.1. Effects of DO on warm water pond fish (modified from Swingle (1969))

Swingle's assessment of DO requirements of pond fish culture:

"The DO content of warmwater fish habitats shall not be < 5ppm during at least 16 hr of any 24-hr period. It may be < 5ppm for a period not to exceed 8 hr within any 24-hr period, but at no time shall the oxygen content be < 3 ppm. To sustain a coarse fish population, the DO may be <5 ppm for a period not more than 8 hr out of any 24-hr period, but at no time shall the concentration be < 2ppm"

1.5 pH: It is a measure of hydrogen ion concentration in water and indicates how much acidic or basic the water is. CO_2 has an acidic reaction in water. The pH in pond rises during day because of phytoplankton and other aquatic plants remove CO_2 from the water during photosynthesis. It decreases at night because of respiration and production of CO_2 by all organisms. Effect of pH on warm water fish is shown in Fig.2.

- ➢ Water pH affects metabolism and physiological process of fish; it also exerts considerable influence on toxicity of ammonia and hydrogen sulphide as well as solubility of nutrients and thereby water fertility. Guidelines for pH value for fish production are shown in Table 1.

Table 1 Effect of pH on Fish

pH	Effect
4	Acid death point
4-6	Slow growth
6-9	Best for growth
9-11	Slow growth, lethal to fish over long period of time
11+	Alkaline death point

- The gills of fishes are the primary target of reduced pH of the environment as structurally gills are delicate and generally have intimate contact with external environment.
- There are seven major effects of low pH on gill structure/ function as pH declines from a minimum “safe” level of about pH 6 to acutely toxic levels of around pH 4:

i) Inhibition of Na & Cl uptake mechanisms.

ii) Increased ion permeability and diffusional ion efflux

iii) Increased hydrogen ion influx across the gills

iv) Increased mucus production

v) Mucus coagulation & precipitaion

vi) Inhibition of gas exchange across the gills

vii) Damage to gill epithelial layers

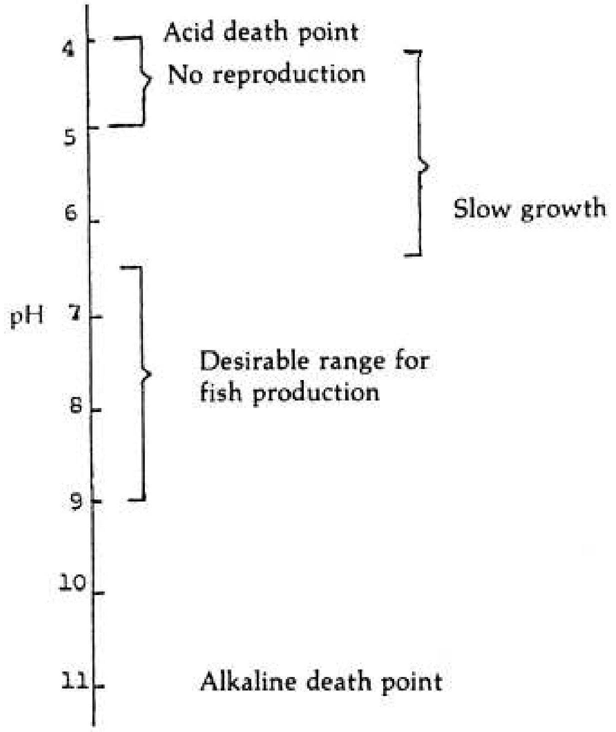

Fig.2 Effect of pH on warm water pond fish

1.6 Free CO_2: CO_2 is present in the atmosphere in very small quantity. For this reason, although it is highly soluble in water, its concentration in most water-bodies is low. It occurs in water in 3 closely related forms: (a) free CO_2, (b) bicarbonate ion (HCO_3^-) and (c) carbonate ion (CO_3^{2-}). Each form amount present depends on the pH of water. As for example, in neutral or acidic waters, high concentration of free CO_2, i.e. toxic form is frequently found.

- Carbon dioxide is important in pond fish culture as:

i) It can be a stressor of aquatic animals

ii) It influences the pH of water

iii) It is a nutrient for plant growth and its availability may limit primary productivity of some aquatic ecosystems.

- In pond fish culture free carbon dioxide **5-8 ppm is essential for photosythetic activity**; **12-15 ppm sublethal to fishes** and **50-60 ppm is lethal to fishes** (Bhatnagar *et al*., 2004).
- High concentrations of dissolved CO_2 **(> 60-80 mg/L**) have a nacrotic effect on aquatic animals and even higher concentrations may cause death. Exposure to lower concentrations may stress fish by interfering with respiration or by causing formation of calcareous deposits in the kidney (nephrocalcinosis). High environmental concentrations of dissolved CO_2 (hypercapnia) reduce CO_2 excretion at fish gills, causing elevated levels of plasma CO_2 and uncompensated respiratory acidosis. These conditions decrease affinity of haemoglobin for oxygen which reduces oxygen uptake by blood at the gills, even if environmental DO concentration are high (Bohr effect).

1.7 Total alkalinity: Alkalinity refers to buffering capacity of water. The alkalinity of normal freshwater results from bicarbonate, carbonate and hydroxide ions.

Guidelines of alkalinity for fish growth are as follows:

- **300 mg/litre- creates stress to fish**
- **75-300 mg/l – ideal for fish**
- **< 75 mg/l- creates stress to fish**

1.8 Total hardness: The total hardness of a water sample is defined as its content of divalent metallic cations expressed as equivalent calcium carbonate. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) are the predominant divalent metallic cations in most waters. Alkalinity and hardness values are normally similar in magnitude because calcium, magnesium, bicarbonate, and carbonate ions in water are derived in equivalent quantities from the solution of the limestone in geological deposits. However, in some waters alkalinity may exceed its hardness and vice versa. If alkalinity is high and hardness low, pH may rise to very high levels (>10.5) during rapid photosynthesis.

Waters are often categorised as follows according to degrees of hardness:

- 0-75 mg/litre- Soft
- 75-150 mg/litre-moderately hard
- 150-300 mg/litre-hard
- > 300 mg/litre- very hard

Guidelines for hardness value for fish growth

- **60 mg/litre- satisfactory for pond productivity and helps protect fish against harmful effects of pH fluctuation and metal ions**
- **<60 mg/litre- creates stress to fish**

- Alkalinity and hardness are not much affected by biological activity or aquacultural operations, and the initial concentrations in ponds are determined by their levels in the water supply; any changes are largely the result of rainfall and evaporation. Desirable level for fish culture generally fall within the range of 75-300 mg/litre.

1.9 Ammonia: Ammonia is the by-product from protein metabolism excreted by fish and bacterial decomposition of organic matter such as waste food, faeces, dead plankton, sewage etc. The unionised form of ammonia (NH_3) is extremely toxic while the ionised form (NH_4^+) is not and both the forms together known as “Total ammonia”.

- Un-ionised ammonia concentrations are determined by total ammonia concentration, pH and water temperature. At any given level of total ammonia, concentrations of un-ionised ammonia are greatest in surface waters on warm, sunny afternoons when pH and temperature are highest. Un-ionised ammonia concentrations decrease at night as Carbon dioxide produced in respiration causes pH to decline.

- The guidelines for unionized ammonia levels for fish growth are:
    - 0.02-0.05 mg/litre-safe concentration for many tropical fish species.
    - 0.05-0.4 mg/litre- sub-lethal effects depending on the species; &
    - 0.4-2.5 mg/litre-lethal to many fish species.

1.10 Nitrite: Nitrite is an intermediate product of aerobic nitrification bacterial process, produced by the autotrophic Nitrosomonas bacteria combining oxygen and ammonia. In most natural water-bodies and in well-maintained ponds, nitrite concentration is low. In water-bodies with high organic pollution and low oxygen concentration, nitrite concentration may increase.

- Nitrite can be termed as an invisible killer of fish because it oxidizes haemoglobin to methemoglobin in the blood, turning the blood and gills brown and hindering respiration also damaging nervous system, liver, spleen and kidneys of fish. This is also known as “Brown Blood Disease”.
- Guidelines for nitrite value for fish growth are as follows:
    - 0.02-1.0 mg/litre- sub-lethal level for many fish species.
    - 1.0-10 mg/litre-lethal level for many warm water fish species.
    - <0.02 mg/litre is acceptable.

1.11 Nitrate: Nitrate (NO_3) is harmless and is produced by the autotrophic Nitrobacter combining oxygen & nitrite. Nitrate levels are normally stabilized in the 50-100 ppm range.

- Nitrate is relatively nontoxic to fish and not cause any health hazard except at exceedingly high levels (>90 ppm).

1.12 Phosphorus: Phosphorus is considered as the limiting nutrient for freshwater pond environment. Almost all of the phosphorus (P) present in water is in the form of phosphate (PO_4) and in surface water mainly present as bound to living or dead particulate matter and in the soil is found as insoluble $Ca_3(P0_4)_2$ and adsorbed phosphates on colloids except under highly acid conditions. It is an essential plant nutrient as it is often in limited supply and stimulates plant (algae) growth and its role for increasing the aquatic productivity is well recognized.

- According to Stone and Thomforde (2004) the phosphate level of 0.06 mg L^{-1} is desirable for fish culture. Bhatnagar et al. (2004) suggested 0.05-0.07 ppm is optimum and productive; 1.0 ppm is good for plankton / shrimp production.

1.13 Hydrogen sulphide: Freshwater fish ponds should be free from H_2S. Hydrogen sulphide is produced by chemical reaction of organic matter that accumulates and forms a thick layer of organic deposit at the bottom. Unionised H_2S is toxic to fish, but ions resulting from its dissociation are not very toxic. Guidelines for H_2S value for fish growth are as follows:

- 0.01-0.5 mg/litre-lethal to fish and any detectable concentration of hydrogen sulphide in water creates stress to fish
- 0.1-0.2 mg/litre-prawns lose their equilibrium and may create sub-lethal stress;
- 3 mg/litre-prawns die instantly.

1.14 Redox potential (oxidation-reduction Eh): It is an index showing status of oxidation or reduction. It is correlated with chemical substances such as O_2, CO_2 and minerals composed of aerobic layers; H_2S, CO_2, NH_3, H_2SO_4 and others comprising anaerobic layer. Microorganisms are correlated with the status of oxidation or reduction. With the degree of Eh, it is indicative of one of the parameters that shows supporting ability of water and soil to fish and prawn biomass.

1.15 Iron: In surface waters, iron occurs in ferrous state II (soluble compounds) or ferric state III (mostly insoluble compounds) forms. Ratio of these two forms depends on the oxygen concentration in the water, pH and on other chemical properties of water. Poorly oxygenated water with low pH, where iron is mainly in the form of soluble compounds may harm fishes. As gill surface of fish tends to be alkaline, soluble ferrous iron can be oxidised to insoluble ferric compounds, which then cover gill lamellae and inhibit respiration.

- In cyprinid culture, it is generally accepted that concentration of iron soluble ionised forms should not exceed 0.2 mg/litre; for salmonids, the limit is 0.1 mf per litre.

1.16 Chlorine: To control bacteria, municipal water supplies are treated with chlorine @1.0mg/litre. If municipal waters are used to culture fish, residual chlorine must be removed by aeration with chemicals such as sodium thiosulphate, or filtration through activated charcoal. Chlorine level as low as 0.02 mg/litre can stress fish.

1.17 Salinity: Salinity refers to the total concentration of all ions in water. The major ions contributing to salinity are calcium, magnesium, sodium, potassium, bicarbonate, chloride and sulphate.

- Ground waters of low salinity (<0.1ppt) are found in inland aquifers composed of sparingly soluble silicate minerals. Limestone aquifers typically yield waters of some higher salinity (0.1-1 ppt), with calcium, magnesium, and bicarbonate being the major ions. High salinities (>15ppt) are typical of groundwaters in contact with halite (NaCl), gypsum ($CaSO_4$), or other soluble minerals. Coastal plain aquifers (and some inland aquifers) derived from marine sediments or subject to seawater intrusion also may have relatively high salinities (from 5 to 35 ppt), with sodium, chloride, and bicarbonate being the major ions.
- Fish are sensitive to the salt concentration of their waters and have evolved a system that maintains a constant salt ionic balance in its bloodstream through the movement of salts and water across their gill membranes. According to Meck (1996) fresh and saltwater fish

species generally show poor tolerance to large changes in water salinity. Often salinity limits vary species to species level. Garg and Bhatnagar (1996) have given desirable range 2 ppt for common carp; however, Bhatnagar *et al.* (2004) gave different ideal levels of salinity as 10- 20 ppt for *Penaeus monodon*; 10-25 ppt for euryhaline species and 25-28 ppt for *Penaeus indicus*. Barman et al. (2005) gave a level of 10 ppt suitable for *Mugil cephalus* and Garg et al. (2003) suggested 25 ppt for *Chanos chanos* (Forsskal).

Table 1: Pond water quality in aquaculture

Sl. No.	Parameter	Acceptable range	Desirable range	Stress
1.	Temperature (^{0}C)	15-35	20-30	<12,>35
2.	Turbidity (cm)	12-30	30-80	<12,>80
3.	Water colour	Pale to light green	Light green to light brown	Clear water, Dark green & Brown
4.	DO (ppm)	3-5	5	<5, >8
5.	BOD (ppm)	3-6	1-2	>10
6.	Free CO_2 (ppm)	0-10	<5, 5-8	>12
7.	pH	7-9.5	6.5-9	<4,>11
8.	Total Alkalinity (ppm)	50-200	75-300	<20, >300
9.	Total Hardness (ppm)	>20	75-300	<20, >300
10.	Ca (ppm)	4-160	25-100	<10, >250
11.	NH_3 (ppm)	0-0.05	0 - <0.025	>0.3
12.	NO_2 (ppm)	0.02-0.2	<0.02	>0.2
13.	NO_3 (ppm)	0-100	0.1-4.5	>100, <0.01
14.	PO_4-P (ppm)	0.03-2	0.01-3	>3
15.	H_2S (ppm)	0-0.02	0.002	Any detectable level

Course Name	Soil and Water Chemistry
Lesson 6	Soil Chemistry: origin and nature of soils, soil colloids, cation exchange, organic carbon, Carbon - Nitrogen ratio, soil fertility
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
University/College Name	Sri Venkateswara Veterinary University,Tirupati

Lesson 6

Objectives:

1. To learn about the basic concepts of soil chemistry
2. To understand the role of soil fertility on overall pond productivity.

Glossary of terms:

Soil Chemistry: Chemical constituents, chemical properties and the chemical reactions

Geologic time: The geologic time scale (GTS) is a system of chronological dating that classifies geological strata (stratigraphy) in time. It is used by geologists, paleontologists, and other Earth scientists to describe the timing and relationships of events in geologic history.

Weathering: Weathering is a term which describes the general process by which rocks are broken down at the Earth's surface into sediments, clays, soils and substances that are dissolved in water.

Magma: It is the molten or semi-molten natural material from which all igneous rocks are formed.

Tectonic plate: Plate tectonics is a scientific theory describing the large-scale motion of seven large plates and the movements of a larger number of smaller plates of Earth's lithosphere

Specific gravity: The specific gravity is the ratio between the density of an object, and a reference substance.

Pedogenesis: The process of formation of soil through weathering and natural erosion of the parent material is called **soil formation or pedogenesis.**

Pedology: The study of soil formation is called **pedology.**

Soil fertility: Nutrient supplying properties of soil.

Soil Science: The science dealing with soil as a natural resource on the surface of the earth, including Pedology (soil genesis, classification and mapping), physical, chemical, biological and fertility properties of soil and these properties in relation to their management for crop production.

E-lecture:

1. Origin and nature of soils:

1.1 Soil: The term SOIL was derived from the Latin Word “SOLUM” Means FLOOR. For a Layman soil is dirt or debris. For an Agriculturist soil is a habitat for plant growth (to grow crops). For a Mining Engineer soil is debris covering the Rocks. For a Civil Engineer soil is a material on which road bed or house bed is formed. For a Home Owner soil is a mellow or loamy or hard material.

- Soil is a three-dimensional body having length, breadth and depth. They form a continuation over the land surface and differ in properties from place to place. Its
  upper boundary is air or water and lower boundary is the rock lithosphere.
- Ruffin and Simonson (1968): Soil is a mixture of Earth’s uppermost mantle of weathered rock and organic matter.

- Buckman and Brady (1969): Soil is a dynamic natural body on the surface of the earth in which plants grow, composed of mineral and organic materials and living forms.

Table 1. Composition of soil on volume basis (Soil components)

Component	Percentage
Mineral matter	45%
Organic matter	5%
Soil water	25%
Soil air	25%

1.2 Definition of soil:

Generally, soil refers to the loose surface of the earth as identified from the original rocks and minerals from which it is derived through weathering process.

- Dokuchaiev (1900): Russian scientist - Father of soil science - Soil is a natural body composed of mineral and organic constituents, having a definite genesis and a distinct nature of its own.

1.3 Soil formation:

- **Weathering:** A process of disintegration and decomposition of rocks and minerals which are brought about by physical agents and chemical processes, leading to the formation of Regolith (unconsolidated residues of the weathering rock on the earth's surface or above the solid rocks). (OR)

  The process by which the earth's crust or lithosphere is broken down by the activities of the atmosphere, with the aid of the hydrosphere and biosphere. (OR)

  The process of transformation of solid rocks into parent material or Regolith.

- **Parent material:** It is the regolith or at least it's upper portion. May be defined as the unconsolidated and more or less chemically weathered mineral material, from which soil are developed.
- **Weathering can be of 3 types:**

- **Physical weathering**—breakdown of rocks from the result of a mechanical action like temperature changes, abrasion (when rocks collide with each other) or frost can all cause rocks to break down.
- **Chemical weathering**—breakdown of rocks through a change in their chemical makeup. This can happen when the minerals within rocks react with water, air or other chemicals.
- **Biological weathering**—the breakdown of rocks by living things. Burrowing animals help water and air get into rock, and plant roots can grow into cracks in the rock, making it split.

Table 2 Different agents of weathering

Physical/Mechanical (disintegration)	**Chemical (decomposition)**	**Biological (disintegration) + (decomposition)**
1.Physical condition of rock	1.Hydration	1.Man & animals
2.Change in temperature	2.Hydrolysis	2. Higher plants & their roots
3.Action of H2O	3. Solution	3.Microorganisms
-fragment & transport	4. Carbonation	
- action of freezing	5. Oxidation	
- alter. Wet & drying	6. Reduction	
- action of glaciers		
4.Action of wind		

5.Atmospheric electric phenomenon		

- **Physical weathering:** The rocks are disintegrated and are broken down to comparatively smaller pieces, without producing any new substances.

A. Physical condition of rocks: The permeability of rocks is the most important single factor. Coarse textured (porous) sand stone weather more readily than a fine textured (almost solid) basalt. Unconsolidated volcanic ash weather quickly as compared to unconsolidated coarse deposits such as gravels.

B. Action of Temperature: The variations in temperature exert great influence on the disintegration of rocks.

i) Fragmentation and transport:

➢ Water beats over the surface of the rock when the rain occurs and starts flowing towards the ocean moving water has the great cutting and carrying force.

➢ It forms gullies and ravines and carries with the suspended soil material of variable sizes.

➢ Transporting power of water varies. It is estimated that the transporting power of stream varies as the sixth power of its velocity i.e the greater the speed of water, more is the transporting power and carrying capacity.

ii) Action of freezing: Frost is much more effective than heat in producing physical weathering.

✓ In cold regions, the water in the cracks and crevices freezes into ice and the volume increases to one tenth As the freezing starts from the top there is no possibility of its

✓ upward expansion. Hence, the increase in volume creates enormous out ward pressure which breaks apart the rocks.

iii) Alternate wetting and Drying : Some natural substances increase considerably in volume on wetting and shrink on drying. **(e.g.) Smectite, Montmorilonite**

iv). Action of glaciers: In cold regions, when snow falls, it accumulates and change into a ice sheet.

➢ These big glaciers start moving owing to the change in temperature and/or gradient.

➢ On moving, these exert tremendous pressure over the rock on which they pass and carry the loose materials

➢ These materials get deposited on reaching the warmer regions, where its movement stops with the melting of ice

C. Action of wind:

✓ Wind has an erosive and transporting effect. Often when the wind is laden with fine material viz., fine sand, silt or clay particles, it has a serious abrasive effect and the sand laden winds itch the rocks and ultimately breaks down under its force.

D. Atmospheric electrical phenomenon: It is an important factor causing break down during rainy season and lightning breaks up rocks and or widens cracks.

➢ **Chemical weathering:** Decomposition of rocks and minerals by various chemical processes is called chemical weathering. It is the most important process for soil formation. Chemical weathering takes place mainly at the surface of rocks and minerals with disappearance of certain minerals and the formation of secondary products (new materials). This is called chemical transformation.

Feldspar + water $\longrightarrow$ clay mineral + soluble cations and anions

- **Chemical processes of weathering:**

A. Hydration: Chemical combination of water molecules with a particular substance or mineral leading to a change in structure. Soil forming minerals in rocks do not contain any water and they undergo hydration when exposed to humid conditions.

B. Hydrolysis: Most important process in chemical weathering. It is due to the dissociation of $H_2 O$ into H^+ and OH^- ions which chemically combine with minerals and bring about changes, such as exchange, decomposition of crystalline structure and formation of new compounds. Water acts as a weak acid on silicate minerals.

C. Solution: Some substances present in the rocks are directly soluble in water. The soluble substances are removed by the continuous action of water and the rock no longer remains solid and form holes, rills or rough surface and ultimately falls into pieces or decomposes. The action is considerably increased when the water is acidified by the dissolution of organic and inorganic acids. (e.g) halites, NaCl

$NaCl + H_2O \longrightarrow Na^+, Cl^-, H_2O$

(dissolved ions with water)

D. Carbonation: Carbon di oxide when dissolved in water it forms carbonic acid.

$2H_2O + CO_2 \longrightarrow H_2CO_3$

This carbonic acid attacks many rocks and minerals and brings them into solution. The carbonated water has an etching effect up on some rocks, especially lime stone. The removal of cement that holds sand particles together leads to their disintegration.

$CaCO_3$+ H_2CO_3 $\xrightarrow{\hspace{6em}}$ $Ca(HCO_3)_2$
(Calcite) (Calcium bicarbonate)
Slightly soluble Readily soluble

E. Oxidation: The process of addition and combination of oxygen to minerals. The absorption is usually from O_2 dissolved in soil water and that present in atmosphere. The oxidation is more active in the presence of moisture and results in hydrated oxides. (e.g) minerals containing Fe and Mg.

F. Reduction: The process of removal of oxygen and is the reverse of oxidation and is equally important in changing soil colour to grey, blue or green as ferric iron is converted to ferrous iron compounds. Under the conditions of excess water or water logged condition (less or no oxygen), reduction takes place.

$2Fe_2O_3^{-}O_2$ $\xrightarrow{\hspace{6em}}$ 4FEO
(Haematite) **(Ferrous oxide)-reduced form**

In conclusion,

- during chemical weathering igneous and metamorphic rocks can be regarded as involving destruction of primary minerals and the production of secondary minerals.
- In sedimentary rocks, which is made up of primary and secondary minerals, weathering acts initially to destroy any relatively weak bonding agents (FeO) and the particles are freed and can be individually subjected to weathering.

➢ **Biological weathering:**

A. Man and Animals: The action of man in disintegration of rocks is well known as he cuts rocks to build dams, channels and construct roads and buildings. All these activities result in increasing the surface area of the rocks for attack of chemical agents and accelerate the process of rock decomposition. A large number of animals, birds, insects and worms, by their activities they make holes in them and thus aid for weathering.

B. Higher Plants and Roots: The roots of trees and other plants penetrates into the joints and crevices of the rocks. As they grew, they exert a great disruptive force and the hard rock may broken apart. (e.g) pipal tree growing on walls/ rocks.

C. Micro- organisms: In early stages of mineral decomposition and soil formation, the lower forms of plants and animals like, mosses, bacteria and fungi and actinomycetes play an important role.

1.4 Formation, Transportation & Deposition of parent material: The formation, transportation and deposition of parent material is shown in Fig.1.

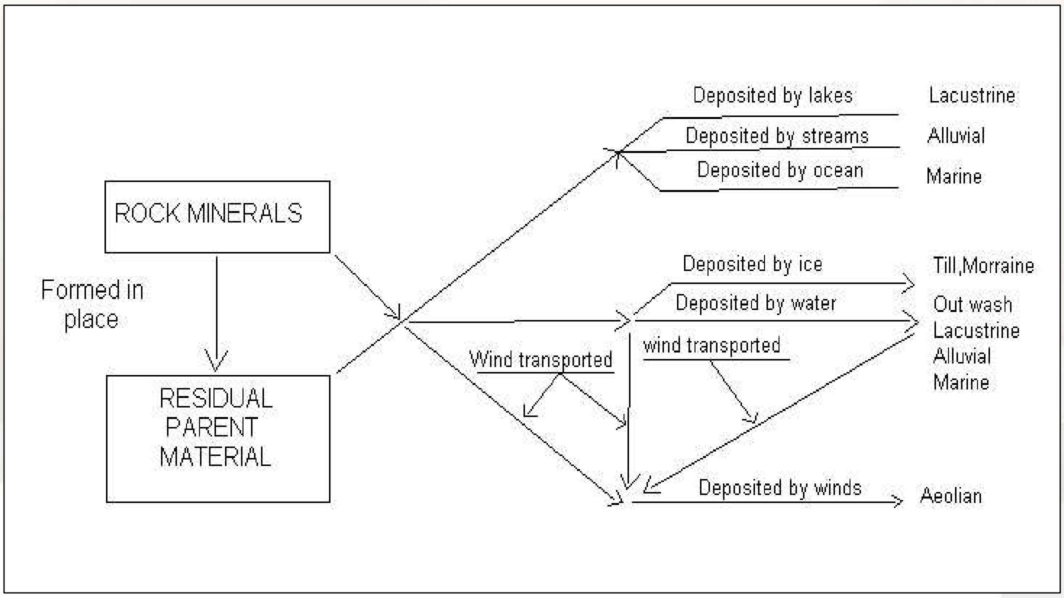

Fig.1 How various kinds of parent's material are formed transported & deposited

1.5 Products of Weathering

Rock Type	Soil Type
Granite	Silty sand
Basalt	Clayey soil
Shale / Slate	Clay/silt
Sandstone	Sand
Limestone	Clay/silt

1.6 Transportation / Deposition

Transporting Agent	Soil Type
Gravity	Colluvial
Water	Alluvial
Streams	Fluvial
Rainfall	Pluvial
Ice	Glacial
Wind	Aeolian

1.7 Factors influencing soil formation:

- Climatic condition - particularly temperature and precipitation
- Living organism - especially native vegetation
- Nature of parent material – texture & structure of soil
- Chemical & mineralogical composition of soil
- Topography of the area
- Time of soil formation

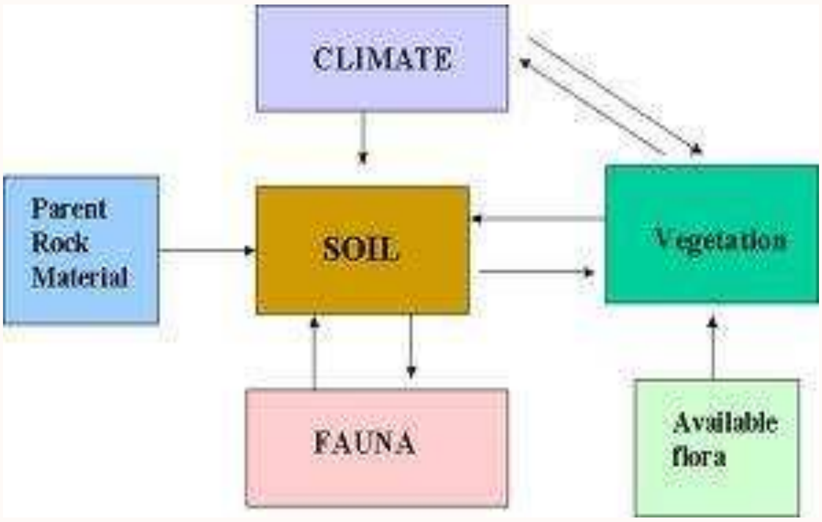

Fig.2 Different factors influencing soil formation

1.8 Soil Profile: The vertical cross-section of the soil, made of layers running parallel to the surface is called **soil profile.** Each layer of the profile is known as **soil horizon.**

The different layers of soil are:

a) O-Horizon

-The O horizon is the upper layer of the topsoil which is mainly composed of organic materials such as dried leaves, grasses, dead leaves, small rocks, twigs, surface organisms, fallen trees, and other decomposed organic matter.

-This horizon of soil is often black brown or dark brown in colour and this is mainly because of the presence of organic content.

b) Topsoil or A horizon

-It is the darkest layer of the soil because it has the highest proportion of organic material and is known as the humus layer.

-This layer consists of both organic matter and other decomposed materials.

-The topsoil is soft and porous to hold enough air and water.

- In this layer, the seed germination takes place and new roots are produced which grows into a new plant.

-This layer consists of microorganisms such as earthworms, fungi, bacteria, etc.

c) Subsoil or B horizon

-It is the subsurface horizon, present just below the topsoil and above the bedrock.

- It is comparatively harder and compact than topsoil.

-It contains less humus, soluble minerals, and organic matter.

-It is a site of deposition of certain minerals and metal salts such as iron oxide.

-This layer holds enough water than the topsoil and is lighter brown due to the presence of clay soil.

- **The A and B horizons together are referred to as the Solum or True Soil**

d) C-Horizon

The C horizon referred to as the **soil parent material** - occurs beneath the solum and extends downwards to the bed rock

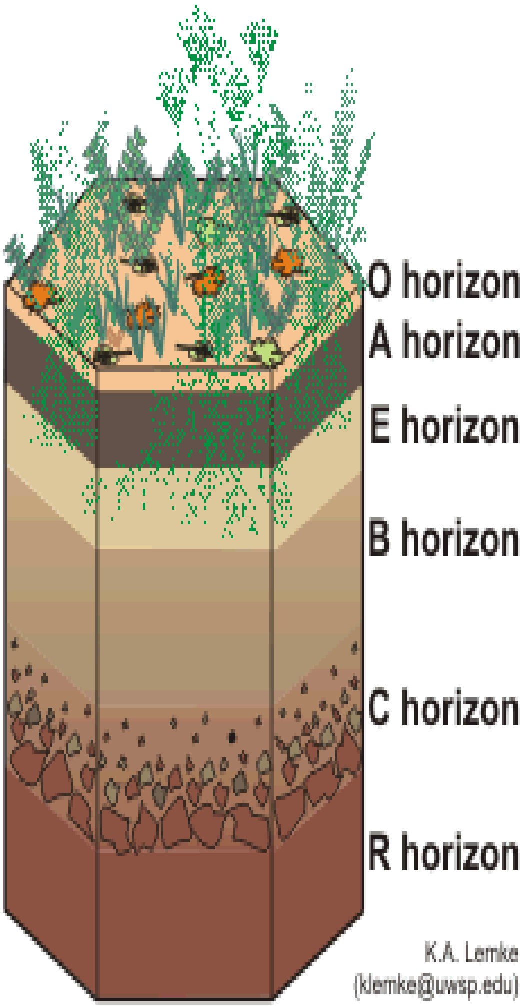

Fig.3 Soil Profile

Important Point

Mineral Matter: Mineral matter is inorganic material and began as rock. Soil generally has mineral particles of different sizes. These particles are labelled sand, silt, or clay, based on their size. Sand is the largest, silt is the mid-size and clay is the smallest soil particle.

Organic Matter: Organic matter, which accounts for about 5% of the soil, is partially decomposed plant and animal matter. Most organic matter is from plant leaves, roots, and stems which gives soil its dark color. Organic matter improves aeration and water holding capacity and contributes to the soil's fertility.

Pore Spaces: Pore spaces are the gaps between solid soil particles. They are occupied by water or air. The amount of water and air found in the soil fluctuates constantly. When the soil is wet, the amount of water occupying pore spaces is greater than the amount of air. Conversely, when the soil is dry, the amount of air is greater than the amount of water.

Living Organisms: An abundance of life can be found in soil. Earthworms, insects, bacteria, fungi, and other organisms inhabit soil. Bacteria and fungi play an important role in breaking down organic matter to release nutrients. Earthworms, ants, crawfish, moles, and other organisms tunnel through the soil improving the soil tilth.

Tilth is the ease with which soil can be worked. Tilth enhances drainage and improves air exchange.

2. Soil colloids: Soil colloids are the most active constituent of the soil and it determine the physical and chemical properties of the soil. They are very small particles which are one-thousandth of a millimetre (0.0001 mm; 0.0004 in) small. Some colloids are minerals, whereas others are organic. Mineral colloids are usually refine clay particles. Under a microscope, they display thin, plate-like bodies. When these particles are well mixed in water, they remain suspended indefinitely, turning the water murky. Organic colloids are tiny bits of organic matter that are resistant to decay. The predominant soil colloids are soil clays and humus.

2.1 Properties of soil colloids:

a) Colloidal particles are always in motion because of charge particles.

b) Colloidal particles are transformed from a liquid into a soft semisolid or solid mass by adding an opposite charged ion.
c) Colloidal particles have ability to absorb gases, liquid and solid from their suspension.
d) Colloidal particles never pass through a semipermeable membrane.
e) Colloidal particles have the properties of cohesion and adhesion.

2.2 Importance of soil colloids: Soil colloids are important because their surfaces attract soil nutrients dissolved in soil, water as positively charged mineral ions, or cations. Some cations are needed for plant growth, including calcium (Ca^{++}), Magnesium (Mg^{++}), Potassium (K^+), and sodium (Na^+). They need to be dissolved in a soil-water solution to be available to plants when they are in close contact with root membranes. The fertility of the soil-water solution for plants is based on the capability of the soil to hold and exchange cations; this is referred to as the cation-exchange capacity. Without soil colloids, most vital nutrients would be leached out the soil by percolating water and carried away in streams.

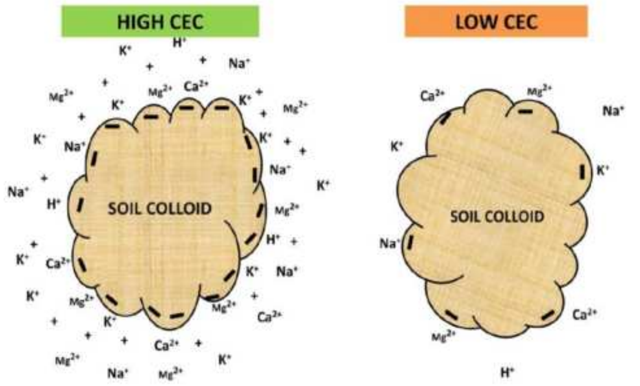

Fig.4 Solid colloids with high and low negative charges.

2.3 Types of Soil Colloids:

a) **Crystalline silicate clays** (Phyllosilicates→ tetrahedral and octahedral crystal sheets).
b) **Non-crystalline silicate clays** [Dominantly amorphous clays (allophane and imogolite)].
c) **Iron and aluminium oxides** [Dominantly gibbsite (Al-oxide) and goethite (Fe-oxide)]

d) Organic (humus) colloids [Non-crystalline colloids dominated by long C-chain molecules]

Important Note

- **Phyllosilicates** are sheet Silicate minerals, formed by parallel sheets of silicate tetrahedral with Si_2O_5 or a 2:5 ratio.
- The most important amorphous colloid is allophane.
- **Allophane** is an amorphous to poorly crystalline hydrous aluminium silicate clay mineraloid developed from volcanic ash. Its chemical formula is Al_2O_3 2 $SiO_3.H_2O$
- Highly weathered clay soil are found in tropics and subtropics which contain Iron and Aluminum oxides such as Gibbsite Al $(OH)_3$ and Geolite (FeoOH).
- Some features of **Organic (humus) colloids**-
  a) It is colloidal in nature i.e it holds water - up to 10 times its own weight
  b) It has a high cation exchange capacity (CEC) - typically 300-800 meq/100g
  c) It is 'sticky and glue-like' - it aggregates other soil components (eg sand & clay) creating tilth.
  d) It is resistant to biological decomposition - lasting typically 10-100 years but often 1000 years.

3. Cation exchange: Cations are positively charged ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), sodium (Na^+) hydrogen (H^+), aluminum (Al^{3+}), iron (Fe^{2+}), manganese (Mn^{2+}), zinc (Zn^{2+}) and copper (Cu^{2+}). Cation exchange consists of an interchange between cations adsorbed on changed surface and cations in the soil solution. To make a room for more Ca^{2+} on colloids, proportions of all the other adsorbed cations must be released into solution. At the new equilibrium concentration of all ions other than Ca^{2++} decrease on colloids and concentration of all cations increase in solution.

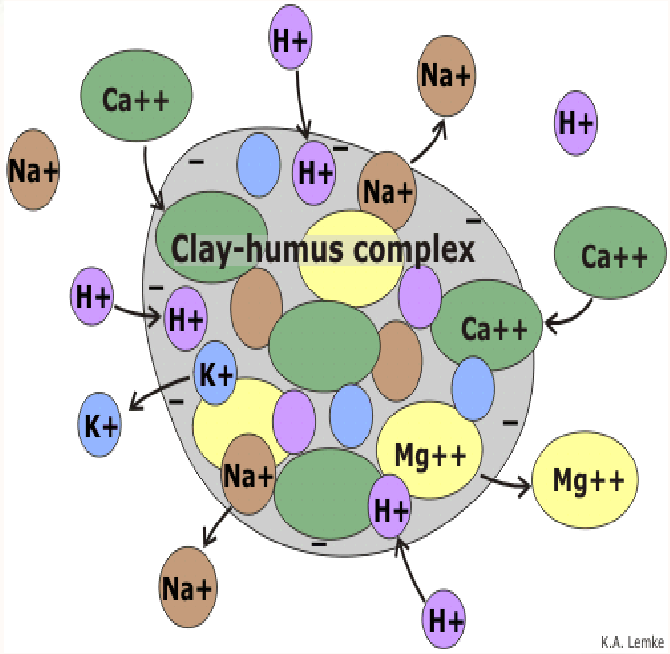

Fig.5 Cation exchange

3.1 Cation Exchange Capacity (CEC): The capacity of the soil to hold on to these cations called the cation exchange capacity (CEC). These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces (negative soil particles attract the positive cations). The cations on the CEC of the soil particles are easily exchangeable with other cations and as a result, they are plant available. Thus, the CEC of a soil represents the total amount of exchangeable cations that the soil can adsorb.

The total number of cations a soil can hold--or its total negative charge--is the soil's cation exchange capacity. The higher the CEC, the higher the negative charge and the more cations that can be held.

➢ CEC is measured in millequivalents per 100 grams of soil (meq/100g). A meq is the number of ions which total a specific quantity of electrical charges. In the case of potassium (K^+), for example, a meq of K ions is approximately 6 x 10^{20} positive charges. With calcium, on the other hand, a meq of Ca^{++} is also 6 x 10^{20} positive charges, but only 3 x 10^{20} ions because each Ca ion has two positive charges.

➢ Following are the common soil nutrient cations and the amounts in pounds per acre that equal 1 meq/100g:

- Calcium (Ca^{++}) - 400 lb./acre
- Magnesium (Mg^{++}) - 240 lb./acre
- Potassium (K^{+}) 780 lb./acre
- Ammonium (NH_4^{+}) - 360 lb./acre

➢ **Relationship between CEC & Liming practices:** Recommended liming practices will vary for soils with widely differing cation exchange capacities. For instance, soils having a high CEC and high buffer capacity change pH much more slowly under normal management than low-CEC soils. Therefore, high-CEC soils generally do not need to be limed as frequently as low-CEC soils; but when they do become acid and require liming, higher lime rates are needed to reach optimum pH.

4. Organic carbon: Organic carbon (OC) enters the soil through the decomposition of plant and animal residues, root exudates, living and dead microorganisms, and soil biota. Soil Organic Matter (SOM) is the organic fraction of soil exclusive of non-decomposed plant and animal residues. Nevertheless, most analytical methods do not distinguish between decomposed and non-decomposed residues. SOM is a heterogeneous, dynamic substance that varies in particle size, C content, decomposition rate, and turnover time.

Soil Organic Carbon (SOC) is the main source of energy for soil microorganisms. The ease and speed with which SOC becomes available is related to the SOM fraction in which it resides. In this respect, SOC can be partitioned into fractions based on the size and breakdown rates of the SOM in which it is contained (Table 3). The first three fractions listed are part of the active pool of SOM. Carbon sources in the active pool are relatively easy to break down.

SOM contains approximately 58% C; therefore, a factor of 1.72 can be used to convert OC to SOM. There is more inorganic C than Total Organic Carbon (TOC) in calcareous soils. TOC is expressed as percent C per 100 g of soil.

Table3 Size and breakdown rates of various soil organic matter fractions

Soil Organic Matter Fraction	**Particle Size (mm)**	**Turnover Time (years)**	**Description**
Plant residues	≥ 2.0	< 5	recognizable plant shoots and roots
Particulate organic matter	0.06 – 2.0	< 100	partially decomposed plant material, hyphae, seeds, etc
Soil microbial biomass	variable	< 3	living pool of soil organic matter, particularly bacteria and fungi
Humus	≤ 0.0053	< 100 – 5000	ultimate stage of decomposition, dominated by stable compounds

- **Importance of SOC:** SOC is one of the most important constituents of the soil due to its capacity to affect plant growth as both a source of energy and a trigger for nutrient availability through mineralization. SOC fractions in the active pool, previously described, are the main source of energy and nutrients for soil microorganisms. Humus participates in aggregate stability, and nutrient and water holding capacity.

- OC compounds, such as polysaccharides (sugars) bind mineral particles together into microaggregates. Glomalin, a SOM substance that may account for 20% of soil carbon, glues aggregates together and stabilizes soil structure making soil resistant to erosion, but porous enough to allow air, water and plant roots to move through the soil. Organic acids (e.g., oxalic acid), commonly released from decomposing organic residues and manures, prevents phosphorus fixation by clay minerals and improve its plant availability, especially in subtropical and tropical soils. An increase in SOM, and therefore total C, leads to greater biological diversity in the soil, thus increasing biological control of plant diseases and pests. Data also reveals that interaction between dissolved OC released from manure with pesticides may increase or decrease pesticide movement through soil into groundwater.
- **Pond soil with**
  - **<0.5% OC - Unproductive.**
  - **0.5-1.5% OC- Medium productive**
  - **1.5-2.5% OC- Highly productive**
  - **>2.5% OC- Not suitable for fish production (as it may lead to excessive bloom of microbes and oxygen depletion in the water).**

5. C:N ratio: This ration of soil, influences activity of soil microbes. This, in turn, affects rate of release of nutrients from decomposing organic matter. The rate of breakdown (mineralization) is very fast, moderately fast and slow at **the C:N ratio in the range of <10, 10-20 and >20 respectively. In general, C:N ratio between 10 and 15 is considered favourable for aquaculture and of 20:1 or narrower gives good results.**

6. Soil Fertility: The nutrients essential for plant growth is determines soil fertility. Nitrogen, phosphorus and potassium are major nutrients required by phytoplankton of pond environment. Inorganic fertilizers can be applied to provide these nutrients. The appropriate dose depends on the amount of individual nutrients present in the pond soil in available form. Generally, relatively small amounts of potassium are needed in fish-ponds. But newly constructed ponds or those situated on poor soil may need potassium also. **The single most critical nutrient for maintenance of pond fertility is available phosphorus content of soil and water. Pond soils with 30 ppm, 30-60 ppm, 60-120 ppm and > 120 ppm available phosphate (P_2O_5) were considered to have poor, average, good and high fertility, respectively. Ponds with <250ppm available soil nitrogen are considered to have low productivity while concentration in the range 250-500 ppm and >500 ppm are considered to be medium and highly productive.**

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Course Name	Soil and Water Chemistry
Lesson 7	Soil Types and their Distribution Physical, Properties of Soil Reaction
Course Revisor Name	Dr. Rajdeep Dutta
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Lesson 7

Objectives:

1. To learn about different soil types and their distribution
2. To learn about different physical properties of soil
3. To understand about different soil reactions

Glossary of terms:

Ultisols: These types of soils are red in colour, rich in clay, acidic in nature that support a mixed group of vegetation prior to cultivation. Naturally these soils are suitable for forestry, but can be converted to agriculturally productive with the application of lime and fertilizers, and are stable materials for construction projects.

Alfisols: These are soils found in semi-arid to humid areas, typically under a hardwood forest cover. They have a clay-enriched subsoil and relatively high native fertility. "Alf" designates aluminium (Al) and iron (Fe).

Vertisols: These are clay-rich soils that shrink and swell with changes in moisture content. During dry periods, the soil volume shrinks and deep wide cracks form. The soil volume then expands as it wets up. Originated from from Latin verto meaning "turn".

Entisols : These soils that do not show any profile development except A horizon. It has no diagnostic horizons, and most are basically unaltered from their parent material, which can be unconsolidated sediment or rock.

Inceptisols: These soils form quickly through modification of parent material. They are considered to more developed than Entisols. Inceptisols have no accumulation of clays, iron oxide, aluminium oxide or organic matter. They have an ochric or umbric horizon and a cambic subsurface horizon.

Aridisols: The term derived from the Latin aridus, for "dry", and solum form in an arid or semi-arid climate. These soils are seen in deserts and xeric shrublands, which occupy about one third of the Earth's land surface.

Mollisols: The terminology derived from Latin mollis meaning "soft". These are the soils of grassland ecosystems which are characterized by a thick, dark surface horizon. This fertile surface horizon, known as a mollic epipedon, results from the long-term addition of organic materials derived from plant roots.

Histosols: These soils form in decaying organic matter, in low, wet places, like the bogs or the marshes below, organic matter accumulates below the water table and decomposes more slowly than it accumulates. Over time, thick accumulations of this material can form.

E-lecture:

1. Soil types and their distribution:

1.1 SOIL TYPES:

Soil can be classified into four types namely

1. **Sandy Soil:**

   The first type of soil is sand. They consist of small particles of weathered rocks. They are one of the poorest types of soil for growing plants as they are low in nutrient and have poor water holding capacity. They are usually formed as a result of the breakdown and fragmentation of rocks like granite, limestone and quartz.

2. Silt Soil:

They are comparatively smaller particles in comparison with sandy soil and is made up of rocks and other mineral particles. They are smaller than sand but larger than clay.

3. Clay Soil:

Clay is the smallest particle amongst the types of soil. They are tightly packed against each other with little or no air space. They have a strong water holding capacity. Clay is the densest type of soil which does not drain well or provide space for plant roots to flourish.

4. Loamy Soil:

It is a combination of sand, silt and clay such that the beneficial properties from each are included. For instance, their ability to retain moisture, nutrients. This soil is also referred to as the agricultural soil.

Fig.1. Different types of Soils

The United States Department of Agriculture System and International Soil Science Society System (ISSSS) categorized soil based on size as:

SL. NO	SOIL TYPE	SIZES (mm)	
		USDAS	ISSSS
1	**Very coarse sand**	2.00-1.00	--
2	**Coarse sand**	1.00-0.50	2.00-0.20
3	**Medium sand**	0.50-0.25	--

4	**Fine sand**	0.25-0.10	0.20-0.02
5	**Very fine sand**	0.10-0.05	--
6	**Silt**	0.05-0.002	0.02-0.002
7	**Clay**	<0.002	<0.002

1.2 Parent geological formations of soils of India: Soils of India have inherited their fundamental characters from their parent geological formations.

a) Archean System of Rocks: These rocks are very complex and of different origin. They have been extremely metamorphosed. Occur in Karnataka, Andhra Pradesh, Tamil Nadu, Eastern Ghat mountains, Orissa, Madhya Pradesh, West Bengal, Assam and central Himalayan ranges and Meghalaya.

b) Dharwar System of Rocks: The archean system of rocks were disintegrated and decomposed. Occurs in southern India, champaner system of rocks in Gujarat and Aravalli system of rocks in Rajasthan.

c) Cuddapah system of Rocks: The azoic era ended with intense earth movement when the products of weathering of rocks were removed from the high lands and were deposited in valleys in layers which were subsequently cemented to form the sedimentary rocks that were subsequently folded and metamorphosed to form a system of rocks which is known as the Cuddapah system of rocks which occur mainly in the Cuddapah district of Andhra Pradesh, Chhattisgarh district of Madhya Pradesh and Sundargarh district of Orissa.

d) Vindhyan System of Rocks: They occur in very large area which extends from Dehri-on-Sone in Bihar to Gwalior and Hoshangabad and from Chittorgarh to Agra.

e) Gondwana System of Rocks: Gondwana rocks are mostly sandstones of different kinds and shales and contain fossils.

f) Deccan Trap Rocks: These rocks are of porphyritic texture. These are found in Maharashtra, Madhya Pradesh, Andhra Pradesh & Kutch (Gujarat).

g) Mesozoic & Tertiary Groups of Rocks: These groups of rocks comprises of Triassic, Jurassic & cretaceous system of rocks. They mostly occur in Himachal Pradesh, Gujarat & Rajasthan.

h) Pleistocene & Recent Geological Formations: Clay, silt and sand were deposited during Pleistocene and recent period. Laterisation took place towards the closure of the Pleistocene period. Types of these rocks are:(i) Alluvium, (ii) Loess, (iii) Desert Sand & (iv) Laterite

1.3 Soil groups of India: Soils of India have been divided into 24 groups as reported by Raychaudhury & Govinda Rajan (1971) (Table 1). The main differentiating characters as given by Govinda Rajan and Gopala Rao (1978) are as follows:

a) Red and Yellow Soils: Micaceous quartzite, schists, phyllites, hornblende-schists, gneisses etc. have been weathered to form the red and yellow soils which are fairly well drained and of reddish yellow to yellowish brown colour and of fine texture and of slightly acidic to neutral reaction. The yellow colour of some of these soils is due to higher degree of hydration of ferric oxide than in red coloured soils.

b) Red Sandy Soils: Silica rich granites, granitoid gneisses, quartzites, sandstones have been weathered to form acidic (pH 4.5 to 6.5 in most cases) red sandy soils. The clay is coated with coloured haematite or yellow coloured limonite. These soils contain ferruginous gravels containing alumina and silica and also bits of quartz.

c) Red Loamy Soils: Rocks like granites, gneisses, charnokites, diorites, containing feldspars, micas, pyroxenes, amphiboles etc, have been weathered to form red loamy soils of loamy to silty clayey to clay loam texture. Mostly these soils are slightly acidic to neutral in reaction. Those red loamy soils which have been formed from weathering of anorthite bearing rocks may be alkaline in reaction.

d) Laterite Soils: Mostly basic rocks have been weathered in hot-humid climate when basic elements and silica have been leached down and hydrous oxides of iron and aluminium have been left behind. The laterite soils thus formed are devoid of weatherable minerals. Their clay mineralogy is dominated by kaolinites and hydrous oxides of iron and aluminum. Some of them possess oxic horizon while some other possess plinthite.

e) Deep Black Soils: Basaltic traps have been weathered to form deep black soils of more than one metre depth, up to 2 m depth or even more. Deep blacks are also known as regurs. They are of uniform texture in their surface and sub surface layers. Their texture varies from silty clay to clay. They may contain up to 60% clay.

f) Medium Black Soils: Varieties of rocks such as basaltic traps, Dharwar schists, basic granites, gneisses, hornblende- and chlorite-schists have been weathered to form medium black soils of depth varying from 50 cm to 120 cm and silty clayey to clayey texture. Medium black soils are fairly well drained, moderately rich in humus and contain lime.

g) Shallow Black Soils: Deccan trap rocks have been weathered to form shallow (30 to 50 cm depth) black soils of colour varying from dark brown to dark yellowish brown and of granular to weakly blocky structure. $CaCO_3$ occurs in them in the form of modules or grains. Their solum merges with the disintegrating Deccan trap rock.

h) Mixed Red & Black Soils: Mixed red and black soils have been found in intricate pattern in certain areas where red soils occur in elevated areas and black soils occur in low lying areas. In predominantly black soil area red soils occur at the higher elements of the slope and black soils occur at the lower elements of the slope. Black soils have been formed from weathering of intrusive basic rocks or basalt in the midst of a granitic, granitoid-gnessic or sandstone areas or red soils.

i) Alluvial Soils: Products of weathering of rocks constituting the mountains have been washed down which subsequently flows down in the form of rivers, the Indus, the Ganges and the Brahmaputra and their tributaries in north India and Godvari, Krishna, Kaveri and Mahanadi in south India and deposit them along their courses. These sediments are old at many places. However, fresh materials are being continually being deposited particularly along the course of the rivers and the areas adjacent to it.

j) Deltaic Alluvium: The deltaic alluvium represents the heterogenous sediments brought by waters flowing down the river systems- the Ganges, the Mahanadi, the Godavari, the Krishna, and the Cauvery and deposited at the mouths of these river systems.

k) Coastal Alluvium: Soils of coastal region are recent deposits of fluvial origin. Their texture varies from sandy clay to silty clay and clay. They do not manifest horizonation in most of the cases. They are usually deep, bright and reddish brown, and yellowish brown to grey and dark grey in colour. They are poorly drained in most of the places and poor in plant nutrients.

l) Highly Calcareous Alluvial Soils: These soils are pale brown to yellowish brown in colour, sandy loam to loam in texture, alkaline in reaction and low in available phosphorus and potassium. They occur in the north eastern districts of Uttar Pradesh and extend to the north western region of Bihar.

m) Coastal Sands: Certain coastal areas have been covered by deep sandy soils devoid of horizons largely due to the sandy nature of their parent material.

n) Calcareous Sierozemic Soils: These soils are deep, light coloured and clayey in texture in which clay has been illuviated in their middle horizons. A $CaCO_3$ layer occurs below 150 cm depth. Their clay mineralogy is dominated by 2:1 type of clay mineral. They are neutral to alkaline in reaction and deficient in phosphorus.

o) Gray Brown Soils: These have been developed under semi arid condition, are largely of alluvial origin and of coarse texture i.e. sandy loam. However, their B horizon is of finer texture. CaCO3 occurs throughout the soil depth especially 60 to 90 cm depth. Soils are neutral to alkaline in reaction. Smectites dominated their clay mineralogy. They are poor in available N & P.

p) Desert Soil-Regosols: A & B horizons have been weakly developed or are absent in desert soil regosol of depth >50cm. They are low in organic matter and may contain considerable amount of weatherable minerals and are yellowish brown to pale brown in colour. Some of them contain high amount of salt.

q) Desert Soil-Lithosols: These are shallow soils occurring in desert condition as seen in western Rajasthan. Red sandstones lie exposed at the surface and remain covered with a thin spread of gravel or shallow layer of sand. Strong wind continue to blow rapidly enough to continuously shift the sandy soil materials leaving very little scope for profile development.

r) Tarai Soils: They occur along the foot of the Himalayan mountain ranges extending from northern Uttar Pradesh to northern Bengal. The products of weathering of rocks constituting the Himalayan mountain ranges had been brought down by the water flowing down the Himalayan mountain ranges and were deposited at the foot of the Himalayan mountain ranges to form the Tarai soils which are of sandy loam or silty loam texture at their surfaces while clay had been illuviated at their subsurface. They are moderately fertile and hence covered with dense vegetation.

s) Brown Hill Soils: Sandstones, grey micaceous sandstones and shales have been weathered in the sub-Himalayan region to form brown hill soils under an annual rainfall of 10160 mm to 11780 mm after removal of the original coniferous vegetation. The surface soil is dark brown in colour and loam to silty clay loam in texture and moderately rich in organic matter. The B horizon is 50 to 80 cm thick and silty loam to clay in texture. The surface soils tend to be acidic in reaction. Compact grey and dark brown clay loam has made the lower horizon below 100 cm from the surface which is slightly acidic in reaction and overlies the weathered parent material from sandstones and shales.

t) Sub- Mountain Soils (Podzolic): The top soil up to 10 to 15 cm depth is dark brown in colour and sandy loam in texture with loose undecomposed organic matter. The next lower layer from 15 cm to 50 cm depth is dark brown in colour, and sandy clay loam in texture and is rich in humus. The next underlying layer up to 100 cm depth is brown to reddish brown in colour and compact sandy clay in texture. The lower layers are mixed with weathered gravels of the parent material. These soils are acidic in reaction.

u) Mountain Meadow Soils: Sandstones and shales have been weaithered at very high altitude of the Himalayas (where trees do not grow) to form moderately shallow soils under grass vegetation which add organic matter to the soil. The relatively low temperature helps to build up the organic matter level of the soil. Partially weathered rock pieces and gravels have been found admixed with the soil.

v) Saline & Alkali Soils: Saline soils are characterised by the occurrence of soluble salts mostly sodium chloride and sodium sulphate in high amounts and flocculated condition. Soil minerals have weathered to release the soluble salts which move upwards along with the capillary movement of the soil solution and accumulate at the surface in the form of saline efflorescence. Alkaline conditions are mainly due to sodium carbonate and bicarbonate, the occurrence of high amount of which deflocculates the clay and make the soil impervious.

w) Peaty and Saline Peaty Soils: These soils form from brackish water sediments containing sulphides (Iron sulphides). When they remain saturated with water they may be slightly acidic in reaction. When these soils are drained, sulphides are oxidised to form H_2SO_4. The soil becomes extremely acidic in reaction. Organic matter accumulates due to poor drainage.

x) Skeletal Soils: The Vindhyan formation sandstones have been weathered to form shallow (7 to 15 cm thick) soils of pale brown to dark brown colour and sandy loam to loam texture soil erosion has obliterated horizonation of these soils.

Table 1. Soil Groups of India, their Distribution and Classification According to U.S.D.A Comprehensive Classification System

* A-Assam,AP-AndhraPradesh,B-Bihar,D-Delhi,G-Goa, GJ-Gujarat,H-Haryana,H.P.-Himachal Pradesh,JK-Jammu & Kashmir, K-Kerala, KT-Karnataka,M-Maharashtra,MP-Madhya Pradesh, O-Orissa,P-Punjab,PO-Pondicherry,R-Rajasthan,TN-Tamil Nadu,UP-Utter Pradesh,WB-West Bengal.

Soil Group	Area Sq. km.	Distribution*	Equiv. USDA Comprehensive Classification		
			Order	Sub- order	Great group
1. Red & Yellow	403651	MP,O,B	Ultisols	Aquult-ustults	Ochraquults Haplustults Rhodustults
2. Red Sandy	330590	TN,KT,AP,B,WB	Alfisols	Ustalfs	Haplustalfs Rhodustalfs
3. Red loamy	213271	AP,TN,KT,KR,MP,O,R	Alfisols	Ustalfs	Paleustalfs Rhodustalfs
4. Laterite	130066	TN,KT,KT,AP,O,M,G,A,WB,GJ	Ultisols	Aquults Udults Ustults	Plinth & quults Plinthudults Plinthustults
5. Deep black	112060	M,AP,KT,MP,GI,R	Vertisols	Usterts Uderts	Pellusterts Chromusterts Pelluderts
6. Medium black	430383	M,MP,GJ,AP,KT,R	Vertisols	Usterts	Pellusterts Chromusterts
7. Shallow black	31532	M	Entisols Inceptisols	Orthents Tropepts	Ustorthents Ustropepts
8.Mixed red & black	162265	KT,TN,M,MP,AP,B	Association of Alfisols & Vertisols		
9. Alluvial i) Recent ii) old	356720	UP,P,B,WB,A,H,AP,GJ,JK,KT,MP,R,D	Entisols Alfisols Inceptisols	Aquents Fluvents Ustalfs Ochrepts	Haplaquents Ustifluvents Udifluvents Haplustalfs Ustochrepts
10. Deltaic Alluvium	87045	TN,AP,O,WB	Entisols Alfisols	Psamments Aqualfs	Quartzi Psamments Tropaqualfs

11. Coastal Alluvium	54403	TN,K,KT,AP,M,GJ,WB,A	Entisols	Aquents	Haplaquents
12. Alluvial Soils Highly Calcareous	13611	UP,B	Entisols	Orthents	Calciorthents
13. Coastal sands	4534	O,TN,AP,PO	Entisols	Psamments	Ustipsaments
14.Calcarreous Sierozemic	45080	p	Aridisols	Orthids	Calciorthids
15. Grey Brown Soils	101572	GJ,R	Aridisols	Orthids	Calciorthids
16. Desert Regosol	154423	R,G,H	Aridisols	Orthids	Calciorthids
17. Deserty Lithosol			Entisols	-	Lithic Entisols
18.Tarai	28919	UP,B,WB	Mollisols	Aquolls	Haplaquolls
19. Brown Hills	81242	UP,HP,GJ,JK,KT,P,WB	Ultisols	Humults	Palehumults
20. Sub-Montain (Podzolic)	76695	UP,JK,HP	Alfisols	Udalfs	Hapludalfs
21. Mountain Meadow	59790	JK	Mollisols Inceptisols	Borolls Ochrepts	Cryoborolls Cryochrepts
22. Saline and Alkali	17377	UP,H,P,M,KT,GJ,R		Orthids Argids	Salorthids Salargid Natrargids
23. Peaty and Saline Peaty	2720	KT,WB	Histosols	-	-
24. Skeletal	79151	MP	Entisols	-	Lithic Entisols

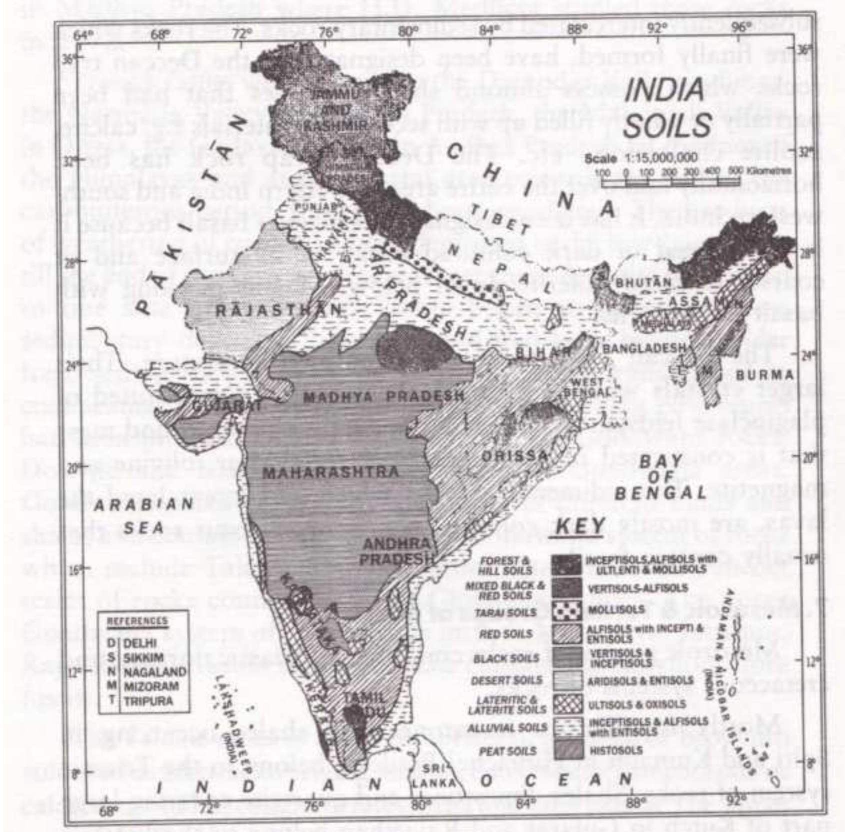


Fig. 1. Soil Map of India (Source: "Introductory Pedology" by J.L.Sehgal)

2. Physical properties of soil:

2.1 Soil colour: Soil colour gives an indication of the various processes going-on in the soil as well as the type of minerals in the soil. For example the red colour in the soil is due to the abundance of iron oxide under oxidised conditions (well-drainage) in the soil. Dark colour is generally due to the accumulation of highly decayed organic matter. Yellow colour is due to hydrated iron oxides and hydroxide. Black nodules are due to manganese oxides; mottling and greying are associated with poor drainage and/or high-water table. Abundant pale yellow mottles coupled with very low pH are indicative of possible acid sulphate soils. Colours of soil matrix and mottles are indicative of the water and drainage conditions in the soil and hence suitability of the soil for aquaculture.

Soil colour is described by the parameters called **hue, value and chroma.**

- **Hue represents the dominant wave length or colour of the light; value,**

refers to the lightness of the colour; chroma, relative purity or strength of the colour.

- The colour of the soil in terms of the above parameters could be quickly determined by comparison of the sample with a standard set of colour chips mounted in a note-book called Munsell Soil Colour Charts (Munsell Soil Colour Charts, 1973). In these charts, the right hand top corner represents the Hue; the vertical axis, the value; and the horizontal axis, the chroma.

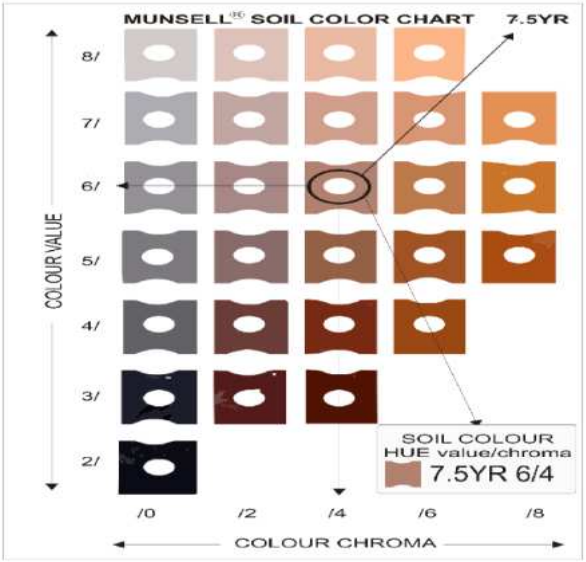
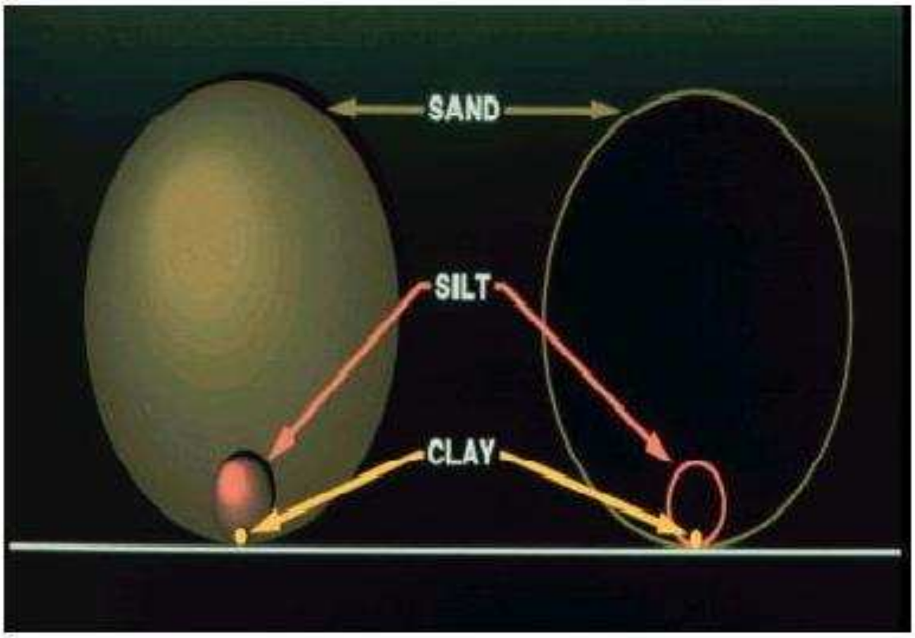


Fig.2 Munsel Soil Colour Chart

2.2 Soil Texture: The relative size of soil particles is expressed by the term texture, which refers to the fineness or coarseness of the soil. Texture is determined by the relative proportions of sand, silt and clay. The soil size groups are called as soil separates- sand (coarsest), silt and clay (the smallest)

- The rate and extent of many important physical and chemical reactions in soil are governed by texture because it determines the amount of surface on which the reactions can occur. Texture determines water intake rate (infiltration), water storage, ease of tilling the soil, the amount of aeration and fertility of the soil.



Relative sizes of sand, silt, and clay.

Fig.3 Different soil fractions

Table 2 Some characteristics of soil separates

Separate	**Diameter (mm)^a**	**Diameter (mm)^b**	**Number of Particles per Gram**	**Surface Area in 1 Gram, sq cm**
Very coarse sand	2.00-1.00	-	90	11
Coarse Sand	1.00-0.50	2.00-0.20	720	23
Medium Sand	0.50-0.25	-	5700	45
Fine Sand	0.25-0.10	0.20-0.02	46,000	91
Very Fine Sand	0.10-0.05	-	7,22,000	227

Silt	0.05-0.002	0.02-0.002	57,76,000	454
Clay	<0.002	<0.002	90,260,853,000	8,000,000

[a] United States Department of Agriculture System

[b] International Soil Science Society System

- **Particle size higher than 2.00 mm. in dia. are excluded from soil texture**
- **Stones and gravels make little or no contribution to the basic soil properties especially in water holding capacity and release of plant nutrients**

➢ **Naming of Soil Texture:** The words sand, silt, clay and loam are used to name soil texture. Loam refers to a mixture of sand, silt and clay and exhibits the properties of each fraction equally. Most soils are mixture of various mineral particles. Based on the proportions of various particles contained in them, soil can be grouped into five textural groups.

✓ ***Fine Textured Soils:*** Contains > 40% clay, may be sticky plus plastic when wet and hold considerable water + plant nutrients. Shows higher plasticity & cohesion.

✓ ***Coarse-textured Soils:*** Loose - sandy gravel soil lack the capacity to adsorb water but keep little to sufficient moisture and nutrients for plant growth. There is lacking of fertility and water holding capacity in this soil

✓ ***Medium textured Soils:*** It is a mixture of sand, silt and clay high enough to hold water and plant nutrients.

✓ ***Moderately fine textured Soils:*** It contains high % of clay. It is moderately sticky & plastic when wet, it may form a crust on the surface if organic matter is low. It shows high moisture holding capacity.

- ✓ ***Moderately Coarse Soils:*** It includes sandy loam to very fine sandy loam.

- ➢ On the basis of relative % of soil particles viz. sand, silt & clay, all these 5 textural soil groups include 11 textural classes. Soil containing at least 30% of clay is ideal for fish pond construction.

Table 3 Textural classes proposed by U.S. Bureau of soils

	Textural group	**Range in relative % of mineral particles**		
		Sand	**Silt**	**Clay**
1.	Sandy Soil	80-100	0-20	0-10
2.	Sandy Clay	50-70	0-20	30-50
3.	Sandy Clay Loam	50-80	0-30	20-30
4.	Sandy Loam	50-80	0-50	0-20
5.	Silty clay	0-20	50-70	30-50
6.	Silty clay loam	0-30	50-80	20-30
7.	Silt loam	0-50	50-100	0-20
8.	Clay	0-50	0-50	30-100
9.	Clay loam	20-50	20-50	20-30
10	Loam	30-50	30-50	0-20
11	Loamy sand	70-90	0-30	0-15

2.3 Soil Structure: Natural aggregates (units of soil) are called peds and they vary in their water stability. Peds are natural groups of primary particles that occur and persist within the soil and broken into any shape by ploughing. Peds are absent in soils having low content of clay.

- **Soils are described by three characteristics**

  Type (shape)
  Class (size)
  Grade (strength of cohesion).

There are **four types** of soil structure.

- **Plate like**
- **Prism like**
- **Column like**
- **Block like,**
- **Sphere like**

Platy

In platy structure, the units are flat and platelike. They are generally oriented horizontally. A special form, lenticular platy structure, is recognized for plates that are thickest in the middle and thin toward the edges. Platy structure is usually found in subsurface soils that have been subject to leaching or compaction by animals or machinery. The plates can be separated with a little effort by prying the horizontal layers with a pen knife. Platy structure tends to impede the downward movement of water and plant roots through the soil.

Prismatic

In prismatic structure, the individual units are bounded by flat to rounded vertical faces. Units are distinctly longer vertically, and the faces are typically casts or molds of adjoining units. Vertices are angular or subrounded; the tops of the prisms are somewhat indistinct and normally flat. Prismatic structures are characteristic of the B horizons or subsoils. The vertical cracks result from freezing and thawing and wetting and drying as well as the downward movement of water and roots.

Columnar

In columnar structure, the units are similar to prisms and are bounded by flat or slightly rounded vertical faces. The tops of columns, in contrast to those of prisms, are very distinct and normally rounded. Columnar structure is common in the subsoil of sodium affected soils. Columnar structure is very dense and it is very difficult for plant roots to penetrate these layers. Techniques such as deep plowing have help to restore some degree of fertility to these soils.

Blocky

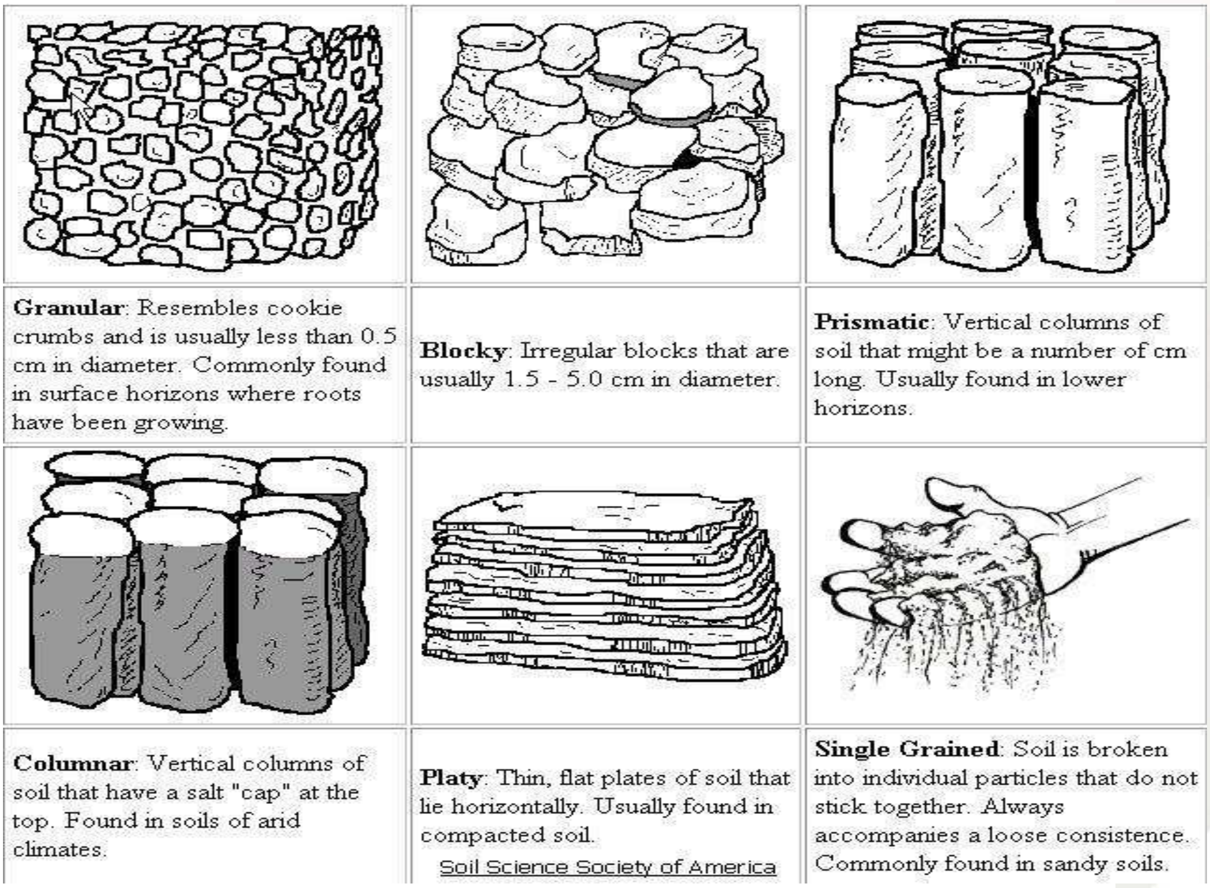
In blocky structure, the structural units are blocklike or polyhedral. They are bounded by flat or slightly rounded surfaces that are casts of the faces of surrounding peds. Typically, blocky structural units are nearly equidimensional but grade to prisms and to plates. The structure is described as angular blocky if the faces intersect at relatively sharp angles; as subangular blocky if the faces are a mixture of rounded and plane faces and the corners are mostly rounded. Blocky structures are common in subsoil but also occur in surface soils that have a high clay content. The strongest blocky structure is formed as a result of swelling and shrinking of the clay minerals which produce cracks. Sometimes the surface of dried-up sloughs and ponds shows characteristic cracking and peeling due to clays.

Granular

In granular structure, the structural units are approximately spherical or polyhedral and are bounded by curved or very irregular faces that are not casts of adjoining peds. In other words, they look like cookie crumbs. Granular structure is common in the surface soils of rich grasslands and highly amended garden soils with high organic matter content. Soil mineral particles are both separated and bridged by organic matter breakdown products, and soil biota exudates, making the soil easy to work. Cultivation, earthworms, frost action and rodents mix the soil and decreases the size of the peds. This structure allows for good porosity and easy movement of air and water. This combination of ease in tillage, good moisture and air handling capabilities, and good structure for planting and germination, are definitive of the phrase *good tilth*.

Structureless

Some soils lack structure and are referred to as structureless. In structureless layers or horizons, no units are observable in place or after the soil has been gently disturbed, such as by tapping a spade containing a slice of soil against a hard surface or dropping a large fragment on the ground. When structureless soils are ruptured, soil fragments, single grains, or both result. Structureless soil material may be either single grain or massive. Soil material of single grains lacks structure. In addition, it is loose.



Granular: Resembles cookie crumbs and is usually less than 0.5 cm in diameter. Commonly found in surface horizons where roots have been growing.

Blocky: Irregular blocks that are usually 1.5 - 5.0 cm in diameter.

Prismatic: Vertical columns of soil that might be a number of cm long. Usually found in lower horizons.

Columnar: Vertical columns of soil that have a salt "cap" at the top. Found in soils of arid climates.

Platy: Thin, flat plates of soil that lie horizontally. Usually found in compacted soil.

Soil Science Society of America

Single Grained: Soil is broken into individual particles that do not stick together. Always accompanies a loose consistence. Commonly found in sandy soils.

Fig.4 Types of Soil Structure

2.4 Soil porosity: Pore space is an empty space as an error. Portion of the soil volume not occupied by solids, either mineral or organics is referred to as soil porosity. The volume percentage of total pore space in a soil is known as soil porosity. Pores in the soil - result of irregular shapes of primary particles and their aggregation. Sandy soils contain less pore space while clay loam and clay soils contain high total pore space and hold large amount of water. Clay soil may have 50-60% pore space whereas sandy soils have low pore space to be about 30%. Clay soils possess greater total porosity than the sand.

Total porosity is calculated by the data on bulk density and partial density. The relationship between partial density (Dp), bulk density (Db) and pore size (p) is given by

$$\% \text{ Pore space} = \frac{D_p - D_b \times 100}{Dp}$$

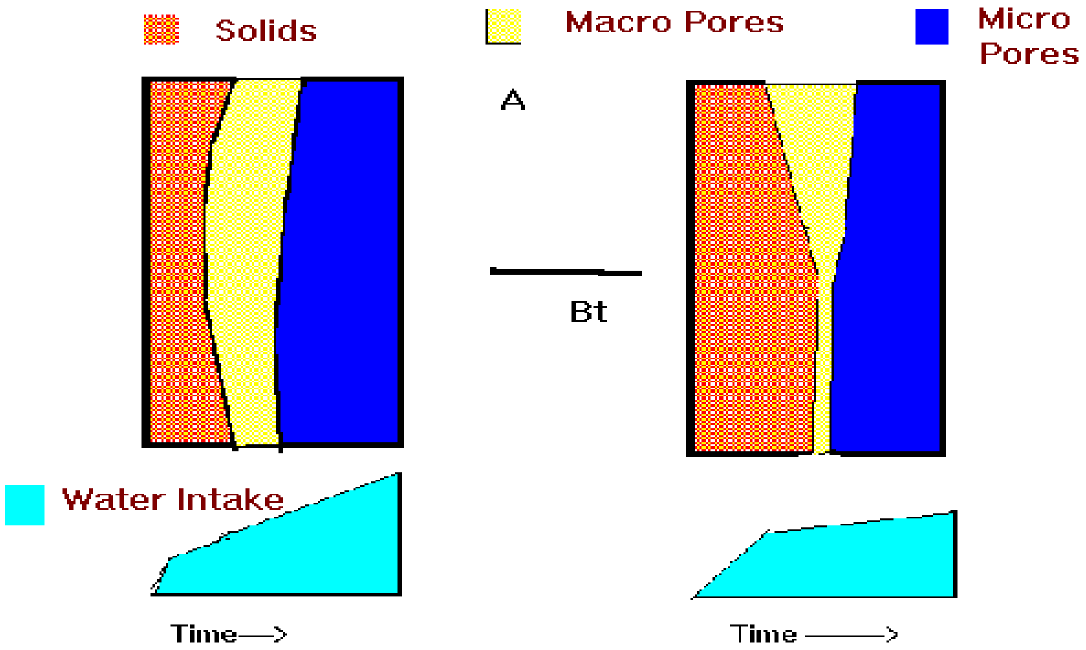


Fig. 5 Water intake of Micro and Macro pores

2.5 Bulk density: -The soil bulk density (BD), also known as dry bulk density, is the weight of dry soil (M_{solids}) divided by the total soil volume (V_{soil}). It is exprseed as gm/cm^3.

The total soil volume is the combined volume of solids and pores which may contain air (V_{air}) or water (V_{water}), or both. The average values of air, water and solid in soil are easily measured and are a useful indication of a soils physical condition.

Soil BD and porosity (the number of pore spaces) reflects the size, shape and arrangement of particles and voids (soil structure). Both BD and porosity (V_{pores}) give a good indication of the suitability for root growth and soil permeability and are vitally important for the soil-plant-atmosphere system

-It is generally desirable to have soil with **a low BD (<1.5 g/cm^3**) for optimum movement of air and water through the soil.

2.6 Water holding capacity: Water in the soil - contains nutrients in solution - for plant growth and their physiological process. The amount of water that a soil can store in the form that is available for plant use is known as the available water-holding capacity of the soil. Most soil profiles can store between 5-25 cm available water. Fine textured soils generally have high water holding capacity as small particles have a large total surface and large volume spaces. Loose sandy soils have large pore spaces and can hold much air and little water. Clay soils influences water holding capacity of soils. Organic matter can hold a weight of water in excess of its own weight 100 to 150 %. Loamy soil can hold water as it contains about 50% pore space by volume.

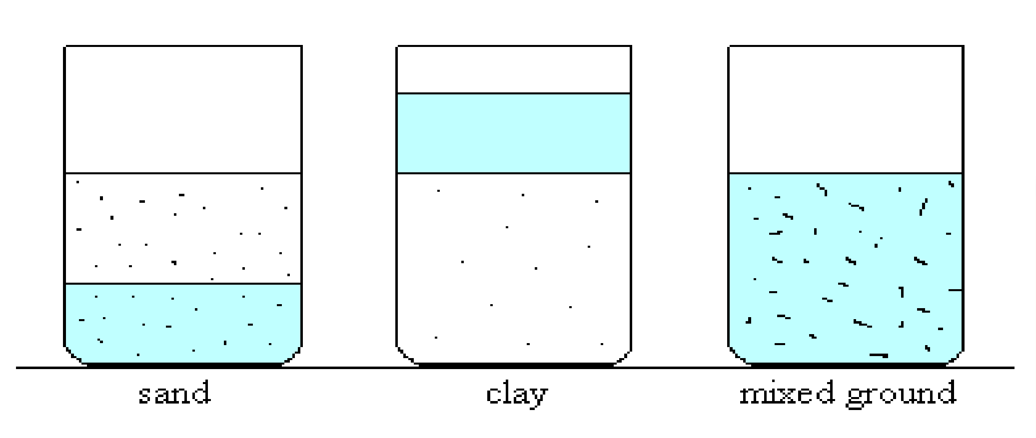


Fig.6 Permeability of different types of soil components. In blue the distribution of water.

3. Soil reaction

2.1 Acidity:

- Soil acidity is measured in pH units. Soil pH is a measure of the concentration of hydrogen ions in the soil solution.

- The lower the pH of soil, the greater is the acidity. pH is measured on a logarithmic scale from 1 to 14, with 7 being neutral.

- Pond soils with pH below 7.5 should be limed with the amount of liming material applied based on either the results of a lime requirement test or soil pH.

- Most minerals are more soluble in acid soils than the neutral or slightly alkaline soils.
- Mineral soils (pH 6.5) is considered suitable for agricultural crop whereas organic soils (pH 5.5) are considered as unsuitable for agriculture.

-Acidic ponds do not respond well to fertilization and liming is the only way to improve water quality with acid soil and it is the soil that must be corrected for lasting effect, rather than the pH of the water.

2.2 Alkalinity:

-Alkalinity refers to the total amount of bases in water/soil, expressed in mg/l of equivalent calcium carbonate.

-This parameter is a measure of the bases like, bicarbonates (HCO_3^-), carbonates (CO_3-) and, in rare instances, hydroxide (OH^-).

-Total alkalinity is the sum of the carbonate and bicarbonate alkalinities.

Causes of soil alkalinity:

1. **Presence of soil minerals** producing **Sodium carbonate** (Na_2CO_3) and **Sodium bicarbonate** ($NaHCO_3$) upon weathering.

2. **Industrial and domestic waste** such as Sodium carbonate, Sodium bicarbonate (baking soda), Sodium sulphate, Sodium hydroxide (caustic soda), Sodium hypochlorite (bleaching powder), etc. in huge quantities during their production process or consumption enhancing water sodality.

3. **Coal-fired boilers / power plants,** when using coal or lignite rich in limestone, produce ash containing calcium oxide. CaO readily dissolves in water to form slaked lime– $Ca(OH)^{2-}$ and carried by rain water to rivers / irrigation water.

4. Use of **softened water in irrigation** (surface or ground water) containing relatively high proportion of sodium bicarbonates and less calcium and magnesium.

2.3 Conductivity:

-Soil electrical conductivity (EC) is a measure of the amount of salts in soil (salinity of soil). It is an important indicator of soil health.

-It affects crop yields, crop suitability, plant nutrient availability, and activity of soil microorganisms which influence key soil processes including the emission of greenhouse gases such as nitrogen oxides, methane, and carbon dioxide.

-Excess salts hinder plant growth by affecting the soil-water balance.

-Arid and semi-arid climates naturally have a higher salt content.

-Salinity is influenced by humans through cropping, irrigation and land management practices.

$$\sigma_b = \sigma_s + \sigma_w \frac{\theta^{n+2}}{\theta_s}$$

Here σ_b is the bulk conductivity which is measured by the probe, σ_s is the bulk surface conductivity, σ_W is the conductivity of the pore water, θ is the volumetric water content, θ_s is the saturation water content of the soil and n is an empirical parameter with a suggested value around 0.5.

-The SI unit for electrical conductance is the Siemen, so electrical conductivity has units of S/m.

2.4 Redox potential (oxidation-reduction E_h):

- Redox potential is a measure of the tendency of a chemical species to acquire electrons from or lose electrons to an electrode and thereby be reduced or oxidised respectively.
- It is an index indicating status of oxidation or reduction.
- It is correlated with chemical substances such as O_2, CO_2 and minerals composed of aerobic layers, H_2S, CO_2, NH_3, H_2SO_4 and others comprising anaerobic layer. Microorganisms are correlated with the status of oxidation or reduction.

Course Name	Soil and Water Chemistry
Lesson 8	Submersed Soils: Wet Lands, Peat Soils, Fluxes Between Mud and Water, Methane and Hydrogen Sulphide Formation
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
University/College Name	Sri Venkateswara Veterinary University,Tirupati

Lesson 8

Objectives:

1. To learn about characteristics of submerged soils, saline soils, alkali soils, acid sulphate soils and problems associated with these soils

2. To learn soil reclamation procedure

Glossary of terms:

Wet lands: Surfaces which remain under water most of the time.

Peat soils: *Peat soils* are formed from partially decomposed plant material under anaerobic water saturated conditions.

Saline soil: S*aline soil* is *defined* as one that inhibits the growth of most crops because of the higher concentration of neutral soluble salts in it.

Alkali soils: These are clay soils with high pH (> 8.5), a poor soil structure and a low infiltration capacity.

Reclamation: The process of claiming something back.

Anaerobic: Absence of oxygen.

Decompose- Breakdown or cause to break down into simpler constituents.

Acid sulphate soil: Acid sulphate soil is a name given to soils or sediments containing iron sulphides.

E-lecture:

1. Submerged Soil:

Submerged soil are those soils that have been saturated with water for a prolonged period of time annually which gives the soil the distinctive grey horizons as a result of oxidation-reduction processes:

A. Partially oxidised A horizon high in organic matter.
B. Mottled zone in which oxidation and reduction alternate
C. Permanently reduced zone which is bluish green in colour.

1.1 Wet land soil

Wetland soils differ from terrestrial soils in that they are anaerobic. The absence of oxygen produces characteristic differences especially in colour and texture. Wetland soils are composed mostly of organic matter as the dead organic matter does not decompose well under water.

Fig.1 Wet land soil

1.2 Peat soils:

The organic materials that accumulate in swamps and marshes are called peat. Peat is composed primarily of the partially decomposed remains of wetland plants along with lesser amount of mineral material. It is usually olive green to black in color in its natural state and often exhibits an odorous smell.

Peat sometimes known as turf, is an accumulation of partially decayed vegetation or organic matter. Soils consisting primarily of peat are known as histosols. Peats are formed in wetland conditions, where flooding or stagnant water obstructs the flow of oxygen from the atmosphere, resulting in the slow rate of decomposition. These soils are formed when plant materials does not fully decay in acidic and anaerobic conditions.

Peat soil can be categorized into 3 classes based on its decomposition state as **sapric, hemic** and **fibric.**

Fig. 2 Peat soils

-Sapric materials are the most decomposed and are defined those having less than 1/6 of the total organic content. **Fibric** materials are those having ¾ or more identifiable plant materials, while **hemic** are those that does not meet the requirement of both either sapric or fibric material.

Types of peat soils

There are 3 types of peat soils namely

1. Sedimentary peat
2. Fibrous peat
3. Woody peat.

- **Sedimentary peat**

Sedimentary peats are those that usually accumulates in deeper water. They are the fine textured matrix of olive green to gray color with little to no identifiable plant remains. As their name suggest, sedimentary peat are deposited in lakes or deeper ponds. The organic content varies but it often exceeds 50% by weight. Sedimentary peat is often soft, spongy and somewhat gelatinous in its natural wet state. Moisture capacity is as high as 4-5 times of dry weight. It has low shear strength and high consolidation potential.

➢ Fibrous peat

Fibrous peat is the source of sedimentary peat and the organic portions of sand, silt, and clay. It is dark brown in color and is composed of the remains of aquatic, semi aquatic and shore line emergent plant growth. It is deposited as shoreline deposits in ponds, lakes, and wet basins. It has very low shear strength and high consolidation potential.

➢ Woody peat

Woody peat is less common than fibrous peat but is found in conjunction with that material. It is a swampy deposit accumulating at the surface above the fibrous peat. It is brown or black in color. It is formed as emergent woody vegetations become established either on concentration or accumulation of fibrous peat or directly in shallow wet basins.

Physical Properties of Peat Soils

1. Color : Dark Brown
2. Bulk density : Lower than Mineral soil
3. Water capacity : High 2-3 times
4. Structure : Highly adsorptive, low plasticity & cohesion highly porous, easy for cultivation
5. Buffering : Residential to pH change
6. Lime loss : High as cat ion is very active
7. Strength of acid : Lower pH
8. Colloidal nature : Surface area increases due to soil colloids

Uses of Peat Soils

- As a manure – used in nurseries, green house and lawns
- As a bedding material-used in stables litters, poultry houses,

- As a packing material-as it is a good insulation capacity.
- As a fuel-as rich in carbon coal like Dutch, Germen peat.
- Industrial purpose
- Field soils- United States for soil amendments

1.3 Bog Lime or Marl:

Bog lime or Marl is a gray to white deposit of fresh calcium carbonate occurring as a bottom deposit in lakes or marshes. It often contains some soft shell and some plant remains and generally exhibits an odorous smell. Marl is formed as a precipitate from the water having high calcium carbonate content. Marl is formed due to the deposition and decomposition of mollusks shells, aquatic plants such as mosses, algae (chara). Marl may be dugout, dried and pulverized and used as agricultural lime. It is an alkaline peat soil and it is not desirable for aquaculture activities.

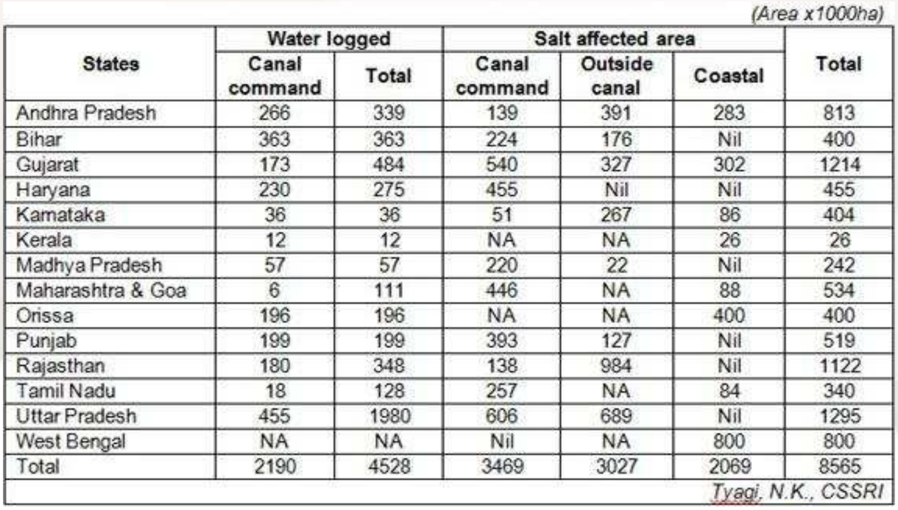
Fig. 3 Bog Lime or Marl

1.4 Fluxes between muck and peat soil:

Muck soil is easily identifies by their black colour as a results of the high concentration of tannins. Muck soils are made up of 20-80% organic matter. Soil fertility is tied directly to the decomposition of plant residues, dead microbes, and detritus. Because of the presence of greater composition of organic matter, muck soil are more fertile than mineral soils. Muck soil also consist higher percentage of mineral matter than peat because of the decomposition of organic material. The oxidized material is called muck to distinguish it from the unoxidized peat.

2. Salt affected soils: The salt-affected soils occur in the arid and semiarid regions where evapo-transpiration greatly exceeds precipitation. The accumulated ions causing salinity or alkalinity include sodium, potassium, magnesium, calcium, chlorides, carbonates and bicarbonates. The salt-affected soils can be primarily classified as saline soil and sodic soil. The state-wise distribution of salt affected soils in India is presented in the following table.

Table 1 Extent and distribution of Salt affected soils in India



(Area x1000ha)

States	Water logged		Salt affected area			Total
	Canal command	Total	Canal command	Outside canal	Coastal	
Andhra Pradesh	266	339	139	391	283	813
Bihar	363	363	224	176	Nil	400
Gujarat	173	484	540	327	302	1214
Haryana	230	275	455	Nil	Nil	455
Karnataka	36	36	51	267	86	404
Kerala	12	12	NA	NA	26	26
Madhya Pradesh	57	57	220	22	Nil	242
Maharashtra & Goa	6	111	446	NA	88	534
Orissa	196	196	NA	NA	400	400
Punjab	199	199	393	127	Nil	519
Rajasthan	180	348	138	984	Nil	1122
Tamil Nadu	18	128	257	NA	84	340
Uttar Pradesh	455	1980	606	689	Nil	1295
West Bengal	NA	NA	Nil	NA	800	800
Total	2190	4528	3469	3027	2069	8565

Tyagi, N.K., CSSRI

2.1 Saline soils

Saline soils defined as soils having a conductivity of the saturation extract greater than 4 dS m^{-1} and an exchangeable sodium percentage less than 15. The pH is usually less than 8.5. Formerly these soils were called *white alkali* soils because of surface crust of white salts.

Fig.4 Saline soils

Formation

The process by which the saline soil formed is called Salinization. Saline soils occur mostly in arid or semi arid regions. In arid regions saline soils occur not only because there is less rainfall available to leach and transport the salts but also because of high evaporation rates, which tend further to concentrate the salts in soils and in surface waters.

Major production constraints

Presence of salts leads to alteration of osmotic potential of the soil solution. Consequently water intake by plants restricted and thereby nutrients uptake by plants are also reduced. In this soil due to high salt levels microbial activity is reduced. Specific ion effects on plants are also seen due to toxicity of ions like chloride, sulphate, *etc.*

Management of saline soils

The reclamation of saline soils involves basically the removal of salts from the saline soil through the processes of leaching with water and drainage. Provision of lateral and main drainage channels of 60 cm deep and 45 cm wide and leaching of salts could reclaim the soils. Sub-surface drainage is an effective tool for lowering the water table, removal of excess salts and prevention of secondary salinisation. of ions like chloride, sulphate, *etc.*

- **Irrigation management**

Proportional mixing of good quality (if available) water with saline water and then using for irrigation reduces the effect of salinity. Alternate furrow irrigation favours growth of plant than flooding. Drip, sprinkler and pitcher irrigation have been found to be more efficient than the conventional flood irrigation method since relatively lesser amount of water is used under these improved methods.

- **Fertilizer management**

Addition of extra dose of nitrogen to the tune of 20-25% of recommended level will compensate the low availability of N in these soils. Addition of organic manures like, FYM, compost, etc helps in reducing the ill effect of salinity due to release of organic acids produced during decomposition. Green manuring (Sunhemp, Daincha, Kolingi) and or green leaf manuring also counteracts the effects of salinity.

- **Crop choice / Crop management**

Crops are to be chosen based on the soil salinity level. The relative salt tolerance of different crops is as follows:

Table 2 Relative tolerance of crops to salinity

Plant species	**Threshold salinity (dS m^{-1})**	**Plant species**	**Threshold salinity (dS m^{-1})**
Field crops		**Vegetables**	
Cotton	7.7	Tomato	2.5
Sugarbeet	7.0	Cabbage	1.8
Sorghum	6.8	Potato	1.7

Wheat	6.0	Onion	1.2
Soybean	5.0	Carrot	1.0
Sugarbeet	7.0	Cabbage	1.8
Groundnut	3.2	**Fruits**	
Rice	3.0	Citrus	1.7
Maize	1.7	-	-
Sugarcane	1.7	-	-

Soil / cultural management

Planting the seed in the centre of the raised bed / ridge may affect the germination as it is the spot of greatest salt accumulation. A better salinity control can be achieved by using sloping beds with seeds planted on the sloping side just above the water line. Alternate furrow irrigation is advantageous as the salts can be displaced beyond the single seed row. Application of straw mulch had been found to curtail the evaporation from soil surface resulting in the reduced salt concentration in the root zone profile within 30 days.

3. Alkali / Sodic soils

Alkali or sodic soil is defined as a soil having a conductivity of the saturation extract less than 4 dS m^{-1} and an exchangeable sodium percentage greater than 15. The pH is usually between 8.5 – 10.0. Most alkali soils, particularly in the arid and semi-arid regions, contain $CaCO_3$ in the profile in some form and constant hydrolysis of $CaCO_3$ sustains the release of OH^- ions in soil solution. The OH^- ions so released result in the maintenance of higher pH in calcareous alkali soils than that in non – calcareous alkali soils.

Formation

Soil colloids adsorb and retain cations on their surfaces. Cation adsorption occurs as a consequence of the electrical charges at the surface of the soil colloids. While adsorbed cations are combined chemically with the soil colloids, they may be replaced by other cations that occur in the soil the soil colloids. While adsorbed cations are combined chemically with the soil colloids, they may be replaced by other cations that occur in the soil solution. Calcium and magnesium are the principal cations found in the soil solution and on the exchange complex of normal soils in arid regions. When excess soluble salts accumulate in these soils, sodium frequently becomes the dominant cation in the soil solution resulting alkali or sodic soils.

Major production constraints

Excess exchangeable sodium in alkali soils affects both the physical and chemical properties of soils.

a) Dispersion of soil colloids

b) Specific ion effect

Reclamation of alkali / sodic soils

Physical Amelioration

This is not actually removes sodium from exchange complex but improve physical condition of soil through improvement in infiltration and aeration. The commonly followed physical methods include

- Deep ploughing is adopted to break the hard pan developed at subsurface due to sodium and improving free-movement water. This also helps in improvement of aeration.
- Providing drainage is also practiced to improve aeration and to remove further accumulation of salts at root zone.
- Sand filling which reduces heaviness of the soil and increases capillary movements of water.
- Profile inversion – Inverting the soil benefits in improvement of

physical condition of soil as that of deep ploughing.

Chemical Amelioration

Reclamation of alkali / sodic soils requires neutralization of alkalinity and replacement of most of the sodium ions from the soil – exchange complex by the more favourable calcium ions. This can be accomplished by the application of chemical amendments (the materials that directly or indirectly furnish or mobilize divalent cations, usually Ca^{2+} for the replacement of sodium from the exchange complex of the soil) followed by leaching to remove soluble salts and other reaction products. The chemical amendments can be broadly grouped as follows:

- *Direct Ca suppliers:* Gypsum, calcium carbonate, phospho-gypsum, etc.
- *Indirect Ca suppliers*: Elemental Sulphur, sulphuric acid, pyrites, $FeSO_4$, etc

Among them gypsum is, by far, the most commonly used chemical amendment. Calcium carbonate is insoluble in nature which of no use in calcareous sodic soils (have already precipitated $CaCO_3$) but can be used in non calcareoussodic soils (do not have precipitated $CaCO_3$) since pH of this soils are low at surface and favouring solubilisation of $CaCO_3$. Some of indirect suppliers of Ca *viz.* Elemental sulphur, sulphuric acid, iron sulphate are also used for calcareous sodic soils. These materials on application solubilise the precipitated $CaCO_3$ in sodic soils and releases Ca for reclamation.

Other sources Distillery spent ash

Distillery spent wash is acidic (pH 3.8-4.2) with considerable quantity of magnesium. About 2 lakh litres of distillery spent wash can be added to an acre of sodic soil in summer months. Natural oxidation is induced for a period of six weeks with intermittent ploughing once in a month. In the second month (after 45-60 days) fresh water may be irrigated and drained. Such a treatment reduces the pH and exchangeable sodium percentage.

Distillery effluent

Distillery effluent contains macro and micronutrients. Because of its high salt content, it can be used for one time application to fallow lands, About 20 to 40 tonnes per ha of distillery effluent can be sprayed uniformly on the fallow land. It should not be allowed for complete drying over a period of 20 to 30 days. The effluent applied field has to be thoroughly ploughed two times for the oxidation and mineralization of organic matter. Then the crops can be cultivated in the effluent applied fields by conventional methods.

Pulp and paper mill effluents

Pulp and paper effluents contain lot of dissolved solids and stabilized organic matter and if properly treated can safely be used for irrigation with amendments *viz.* pressmud @ 5 tonnes ha^{-1}, fortified pressmud @ 2.5 tonne ha^{-1} or daincha as in situ green manure.

Crop choice

Rice is preferred crop in alkali / sodic soil as it can grow under submergence, can tolerate fair extent of ESP and can influence several microbial processes in the soil. Agroforestry systems like silviculture, silvipasture *etc.* can improve the physical and chemical properties of the soil along with additional return on long-term basis. Some grasses like *Brachariamutica* (Para grass) and *Cynodondactylon* (Bermuda grass) *etc.* has been reported to produce 50% yield at Exchangable Sodium Percentage (ESP) level above 30.

The sodicity tolerance ratings of different crops is given in Table2.

Table 3 Sodicity Range of different crops

ESP (Range)	Crop
2-10	Deciduous fruits, nuts, citrus, avocado
10-15	Safflower, black gram, peas, lentil, pigeon pea
16-20	Chickpea, soybean
20-25	Clover, groundnut, cowpea, pearl millet
25-30	Linseed, garlic, cluster bean
30-50	Oats, mustard, cotton, wheat, tomatoes
50-60	Beets, barley, sesbania
60-70	Rice

*Relative yields are only 50% of the potential in respective sodicity ranges.

Table 4 Relative tolerance of fruit trees to sodicity

Tolerance to sodicity	ESP	Trees
High	40-50	Ber, tamarind, sapota, wood apple, date palm
Medium	30-40	Pomegranate
Low	20-30	Guava, lemon, grape
Sensitive	20	Mango, jack fruit, banana

4. Saline Alkali or Sodic Soils: Saline-alkali / sodic soil is defined as a soil having a conductivity of the saturation extract greater than 4 dS m^{-1} and an exchangeable sodium percentage greater than 15. The pH is variable and usually above 8.5 depending on the relative amounts of exchangeable sodium and soluble salts. When soils dominated by exchangeable sodium, the pH will be more than 8.5 and when soils dominated by soluble salts, the pH will be less than 8.5.

Formation

These soils form as a result of the combined processes of salinisation and alkalization. If the excess soluble salts of these soils are leached downward, the properties of these soils may change markedly and become similar to those of sodic soil.

Management of saline alkali soils

The reclamation / management practices recommended for the reclamation of sodic soil can be followed for the management of saline – sodic soil.

5. Acid Sulphate Soils:

Acid sulphate are drained coastal wetland soils that have become acid ($pH<4$) due to oxidation of the pyritic minerals in the soil. Undrained soils containing pyrites need not be acid and they are called potential acid sulphate soils.

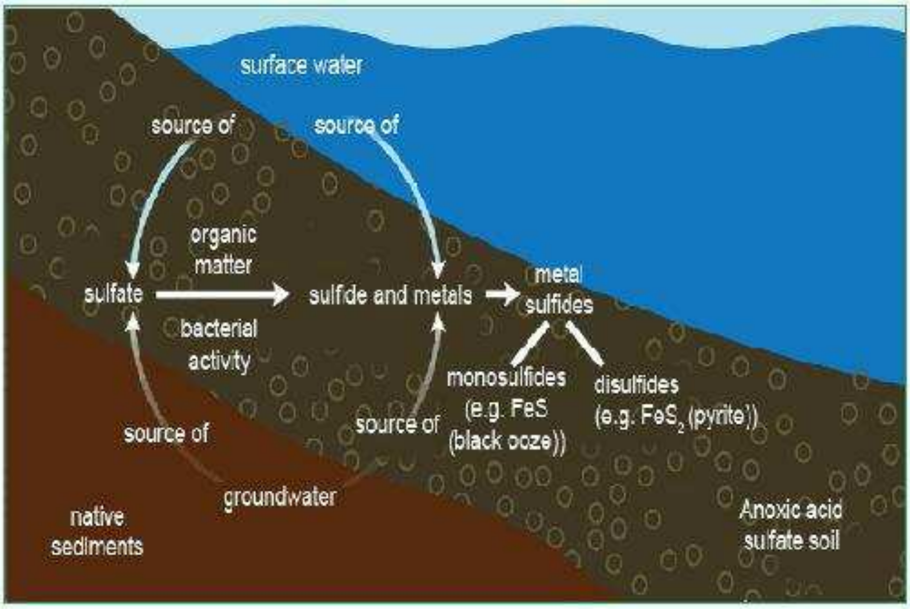


Fig.7 Formation of iron pyrite

Types of acid sulphate soils

Potential acid sulphate soils

ASS which have not been oxidised by exposure to air are known as potential acid sulfate soils (PASS). They are neutral in pH (6.5–7.5) , contain unoxidised iron sulfides, are usually soft, sticky and saturated with water and are usually gel-like muds but can include wet sands and gravels have the potential to produce acid if exposed to oxygen

Actual acid sulphate soils

When PASS are exposed to oxygen, the iron sulfides are oxidised to produce sulfuric acid and the soil becomes strongly acidic (usually below pH 4). These soils are then called actual acid sulfate soils (AASS). They have a pH of less than 4, contain oxidised iron sulfides, vary in texture and often contain jarosite (a yellow mottle produced as a by-product of the oxidation process).

Fig.8 Acid Sulphate Soil

Occurrence in India

Soil with sufficient sulphides (FeS_2 and others) to become strongly acidic when drained are termed acid sulphate soils or as the Dutch refer to those soils *cat clays*. When allowed to develop acidity, these soils are usually more acidic than pH 4.0. Before drainage, such soils may have normal soil pH and are only *potential acid sulphate soils.* Generally acid sulphate soils are found in coastal areas where the land is inundated by salt water. In India, acid sulphate soil is, mostly found in Kerala, Orissa, Andhra Pradesh, Tamil Nadu and West Bengal.

Formation of Acid Sulphate Soils

Land inundated with waters that contain sulphates, particularly salt waters, accumulate sulphur compounds, which in poorly aerated soils are bacterially reduced to sulphates. Such soils are not usually very acidic when first drained in water.

When the soil is drained and then aerated, the sulphide (S^{2-}) is oxidized to sulphate (SO_4^{2-}) by a combination of chemical and bacterial actions, forming sulphuric acid (H_2SO_4). The magnitude of acid development depends on the amount of sulphide present in the soil and the conditions and time of oxidation. If iron pyrite (FeS_2) is present, the

oxidized iron accentuates the
acidity but not as much as aluminium in normal acid soils because the iron oxides are less soluble than aluminium oxides and so hydrolyze less.

Characteristics

Acid sulphate soils contain a *sulphuric horizon* which has a pH of the 1 : 1 soil : water ratio of less than 3.5,plus some other evidences of sulphide content (Yellow colour).

Such strong acidity in acid sulphate soils results toxicities of aluminium and iron, soluble salts (unless leached), manganese and hydrogen sulphide (H_2S) gas. Hydrogen sulphide (H_2S) often formed in lowland rice soils causing akiochi disease that prevents rice plant roots from absorbing nutrients.

Management of Acid Sulphate Soils

Acid sulphate soils from mine spills and coastal mangroves contain high levels of pyrite (FeS_2 1-6%). As long as sediments containing pyrites are submerged and anaerobic, they remain reduced and change little. However, as they are drained and exposed to air, they oxidize and form sulphuric acid. Sulphuric acid reduces water pH when pond is filled. In ponds, problems with acid sulphate soils usually originate in pond-dykes. Pond bottoms are usually flooded and anaerobic, so sulphuric acid doesnot form. However, dykes dry and sulphuric acid formed during dry period enters pond through run-off water after rains. Acidity on dykes can be controlled by liming (0.5-1.0 kg/m^2) and by establishing good cover with an acid-resistant grass species.

A procedure for rapid reclamation of ponds with acid sulphate involves drying and filling of soil to oxidize pyrite, filling pond with water and holding water till pH drops to below 4, and then draining pond; repeat procedure till pH stabilizes at or above 5, and then lime pond with 500 kg of $CaCO_3$/ha.

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Course Name	Soil and Water Chemistry
Lesson 9	Soil analysis: collection and preparation of soil samples
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
University/College Name	Sri Venkateswara Veterinary University,Tirupati

Lesson 9

Objectives:

1. To learn the principles and procedures of soil analysis.
2. To learn the analysis procedures of important physico-chemical parameters of soil

Glossary of terms:

Soil sampling: It is the process of taking a small sample of soil, which is then sent to a lab to determine its physical, chemical and biological properties.

Soil core: A cylindrical sample of soil for tests and examination. Undisturbed soil samples may be obtained by the use of special appliances, which allow extraction of soil cores of diameter usually 1-1/2 in (3.8 cm) or 4 in (10.2 cm).

Composite sample: A mixture of individual samples (grab samples) collected over a specific period of time.

Sieving: Itis a simple technique for separating particles of different sizes in soil analysis.

Calibration: Calibration is defined as the process of assessment and refinement of the accuracy and precision of a method.

Soil auger: It is an instrument used for collection of soil samples

Hydrometer: An instrument used for measuring the relative density of liquids based on the concept of buoyancy.

Saturation capacity of soil: It is the maximum amount of water a soil is capable of holding under standard conditions.

1. Soil Analysis:

Soil analysis is a useful tool to ensure the efficient use of applied plant nutrients. Soil tests provide a means for assessing the fertility status of a soil, but do not provide a direct measure of the actual quantity of plant nutrients in the soil. Instead, soil tests measure the quantity of a nutrient element that is extractable from a soil by a particular chemical extracting solution. A soil testing programme has 4 phases as follows:

1. Collection of soil samples.
2. Chemical analysis of soil samples.
3. Calibration and interpretations of the results of chemical analysis, and
4. Nutrient/Fertilizer recommendation.

1.1 Collection of soil samples:

The greatest challenge in soil sampling is obtaining a sample that reflects to the true fertility of the field. Most fields are highly variable, especially when the topography is rolling. However, even level fields that appear uniform can be highly variable. Certain general principles which should be followed to make soil sampling correct is:

1. A series of cores taken according to some systematic grind layout of the area of equal diameter and comparable depth should be composited.
2. Separate soil cores should be analysed or replicate sets of composites made to determine statistical significance of results on the final composite.
3. The number of cores to be composited will depend on the variability of the soil, the degree of accuracy desired, the particular element or elements to be determined.
4. Cultivated soils are generally more variable than virgin soils, and acidic/saline are extremely variable.
5. Separate composite samples representing different segments of the soil profile or root zone should be taken.

6. Contamination from soil surface materials should be avoided (crop residue, manures, fertilizers, etc.), also contamination of one soil depth.

Using a soil probe, soil auger, or spade can collect surface soil samples; however, for collecting subsoil samples, a spade is not very satisfactory. A post hole digger can be used for collecting deep samples, but requires some special techniques.

Fig 1. Tube auger

Fig2. Screw auger

Fig 3. Collection of soil sample using soil probe

Use of soil probe or tube is the most desirable tool for collecting soil samples. It will give a continuous core with minimal disturbance of the soil. The cores can be divided for the various depths. There should be very little contamination of subsoil samples with surface soil when using a soil probe. A soil probe cannot be used when soil is wet, too dry, or frozen. Soil probes cannot be used in soils that contain gravel. The soil auger can be used in soils that are frozen or contain gravel; however, great care must be taken to obtain representatives samples and to avoid mixing of soil from different depth. The use of soil auger in wet, sticky soils will result in mixing soil from different depths. A soil auger will not effectively gather dry, powdery soils. Use a soil auger only when a soil probe cannot be used.

Procedure for soil sampling:

- Equipments required are spade, auger, polythene bucket and scale.
- Determine the soil unit (or plot).
- Make a traverse over the soil unit.
- Clean the site (with spade) from where soil sample is to be collected.
- Select the sites at random (20-30) in a zigzag (or criss cross) manner of cultural operations and natural trends of change such as slope.
- Enough cores should be taken to represent the whole sampling area adequately.
- Dig soil with spade.
- Standing on opposite side, again insert the spade into soil.
- A lump of soil is removed.
- A pit of V shape is formed. Its depth should be 0.15cm or 0-22.5 cm or 0-30 cm.
- Take out the soil slice of ½ inch thick from both the exposed surface of the pit from top to bottom. To collect the soil slice spade maybe used.
- Collect the soil samples in a polythene bucket.
- The core should be of same volume and represent the same cross section of the sampling volume.
- There should be no chemical interactions of soil material composited that are significant to the objectives.
- The soil unit selected for one composite sample should be homogeneous for the objectives of the analysis.

The chemical analysis of the soil profiles is made for information on the chemical processes of soil development and long-range soil fertility. The soil profiles to be sampled are selected:

a. To represent agriculturally important soils.

b. To represent soil development factors functionally.
c. To represent the sequence of mineral weathering functionally.

Selecting soil types to represent the soil development and chemical weathering functionally simplifies the interpretation of results and provides the maximum of useful information per determination on the processes responsible for soil properties. A sequence of soil type is selected to isolate the effect of a single factor in so far as possible (such as soil types in sequence, climosequence, chronosequence, biosequence, lithosequence, catena, etc.).

1.2 Proper sampling depth:

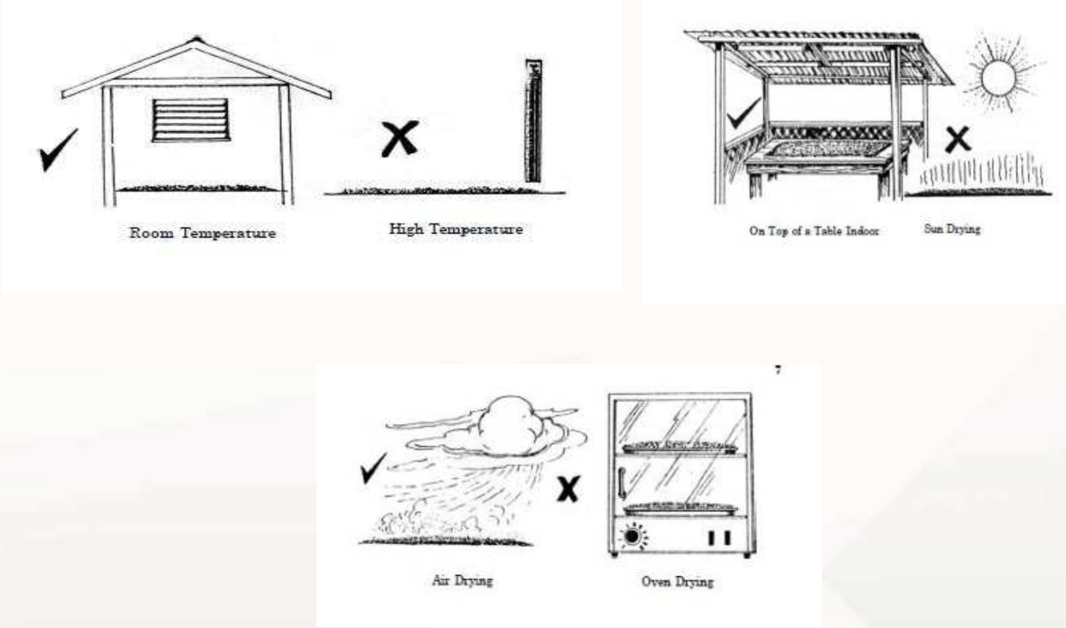
Surface (0-15cm depth) samples are frequently used for determining the soil pH, lime requirement, organic matter, phosphorous, potassium, sulphur, and available micronutrients. Soil test correlations and calibrations for these tests are based on surface samples. Usually, the tillage layer is considered to be 0-15cm or the 0-20cm depth.

1.3 Time of sampling:

Winter is a good time for soil sampling except for testing for nitrate-nitrogen in sandy soils. However, soil samples can be collected any time except during rainy season from the farmers fields. Delaying sampling until spring provides for soil moisture replenishment from fall, winter and early spring precipitation, reflect the nitrate nitrogen distribution more accurately for when the crop is growing.

1.4 Drying:

Moist, well mixed soil samples are transferred to paper bags, cardboard boxes or aluminium trays of convenient size. The open sample container is then placed in a drying rack or cabinet equipped with exhaust fans to expedite air movement and moisture loss. This is specially critical for potassium analysis, which can be significantly influenced by drying temperatures. If nitrate analyses are involved, the soil should be dried or frozen within 12 hours of sampling. Spreading them out on a clean paper or cloth and blow-drying them with a fan can dry such samples. When sample volume is not adequate to justify artificial drying, samples maybe spread on clean surfaces, such as paper plates. Initial crushing of soil clods will decrease the time required for drying at room temperatures.



Photographic illustration of how to dry soil

1.5 Crushing and Sieving:

The nature of analyses to be done, in addition with the presence of rocks or limestone concretions, determines the initial steps to crushing. Crush samples designated for mechanical analyses with a wooden rolling pin after removing all stony materials from the soil. Crush other samples with a flail-type grinder, a power driven mortar and pestle, or some other crusher, which is designed to minimize contamination through carryover from one sample to another. If micronutrients are to be analysed, it is important that all surfaces coming in contact with the soil be stainless steel, plastic or wooden, preferably in the order listed. Samples should be crushed until a major portion of the sample will pass 2 mm opening sieve.

Crushing to pass a finer mesh sieve may be desirable for analysis utilizing less than one gram of soil.

Fig. 5 Sieving

1.6 Analysis of Soil Samples:

For complete analysis, the following determinations are generally made:

Sl. No	PHYSICAL PARAMETERS	Sl. No	CHEMICAL ANALYSIS
1	Apparent specific gravity or bulk density.	1	Analysis of HCl extract or fusion with Na_2CO_3 for Al, Fe, Ca, Mg, P and K.
2	True specific gravity or particle density.	2	pH
3	Pore space	3	Electrical conductivity of saturation paste
4	Aggregrate analysis	4	Organic matter
5	Moisture retention at 1/3 atmosphere and 15 atmosphere	5	Exchangeable cations such as Ca, Mg, K and Na.

6	Mechanical analysis of soils (% coarse sand, fie sand, silt and clay content)	6	DTPA extractable cationic micronutrients (Fe, Mn, Cu and Zinc).
7	Moisture (%)	7	Lime requirement
8	Loss on ignition (%)	8	Total nitrogen
9	Calcium carbonate (%)	9	Available N, P, K.
		10	Available boron and molybdenum.

Most of the soil testing laboratories in our country is analysing soil samples for pH, organic carbon (%), available N, P, K. Now the emphasis is given for the analysis of available secondary nutrients, micronutrients and lime requirement of acidic soils.

1.7 Calibration and Interpretation of the result of chemical analysis:

For the calibration of soil test data, a group of soils ranging in soil fertility from low to high in respect of the particular nutrient are selected and the test crop is grown of these soils with varying doses of that particular nutrient with basal dose of other nutrients.

The most common method is to plot soil test value against the percentage yield and to calculate the relationship between soil test values and per cent yield response.

% Yield = (A-B) × 100/A

Where,

A= the crop yield with adequate nutrient

B= the yield of control without the addition of the particular nutrient under study.

The lower the soil test value of particular nutrient, the higher is the response to the added fertilizer nutrient. Assessment of nutrient requirement for different crops for different soils for fertilizers recommendation can be done by soil test crop response correlation studies.

Based on the contents of available nutrients, soil test values (N, P, K), can be grouped into classes of low, medium, and high.

The ratings of nutrient used in India by the State Soil Testing Laboratories is given in the table below.

Table 1. Rating charts of soil test values (Muhr *et al.,* 1965).

NUTRIENT	**CATEGORY OF NUTRIENT AVAILABILITY**		
Organic carbon (%)	<0.50	0.5-0.75	>0.75
Available P (Kg/ha)	<10	10-25	>25
Available potassium (Kg/ha)	<120	120-280	>280

The Nutrient Index (NI) of Soil is Calculated as Follows:

NI= (L + 2M + 3H)/Total number of soil samples tested

Where,

L, M and H indicate the number of soil samples falling into low, medium and high category of nutrient availability.

The value of NI arbitrarily chosen below 1.5, 1.5-2.5, and above 2.5 as an index of nutrient stats indicate the low, medium and high category of nutrient availability, respectively.

The different categories of soil fertility indices are most commonly interpreted on the basis of the probability of an economic response to adding additional nutrients. Soil testing for every three years is recommended with this approach.

Table2 Soil testing interpretation for different categories of nutrient availability

CATEGORY	DEFINITION AND INTERPRETATION
BELOW OPTIMUM	• Indicates that the nutrient is probably deficient and that the deficiency will likely limit crop growth. • High probability of a profitable return from correcting a low level. • Recommendations for a soil testing “below optimum” are increasing the soil in test level above optimum and to maintain it that level.
OPTIMUM	• Indicates that the nutrient is probably adequate and will likely not limit growth in a typical growing season. • There is a low probability of a profitable return from increasing the soil test level above optimum. • Recommendations for a soil testing “optimum” are designed to offset crop removal in order to maintain the nutrient inthe optimum range. • If testing is done on an annual basis, no maintenance fertiliser is needed when soil tests in the optimum range.
ABOVE OPTIMUM	• Indicates that the nutrient is more than adequate and will not limit crop growth. • Very low profitability of a profitable return from applying additional nutrients to a soil testing “above optimum”. • No fertilizer is recommended on these soils. Too much of a plant nutrient may cause a nutrient imbalance in the soil and as a result, in the plant, which may adversely affect plant growth and environmental quality.

1.8 Nutrient/fertilizer recommendation:

The main objective of the soil testing is to recommend the fertilizer for efficient and economic crop production. Soil tests give the relative level of a nutrient in the soil and must be calibrated to relate its level to the likely response to application of fertilizer. Output for different crops for different doses of fertilizers are obtained from the response curves.

The quantity of a nutrient taken up by the crop to produce the target yield can be estimated. The following equation is used to solve the needed fertilizer rate to get the targeted yield.

$X= (Y-Z)/R$

Where,

X= is the amount of the element to be supplied by fertilizer.

R= is the proportion of the element applied recovered by the crop.

Y= is the estimated amount taken by the crop.

Z= is the estimated amount supplied by the soil.

2. Determination of soil parameters

2.1 Determination of Soil Texture:

Soil texture refers to the relative percentage of sand, silt and clay in a soil. Natural soils are comprised of soil particles of varying sizes. Texture is an important soil characteristic because it will partly determine water intake rates (absorption), water storage in the soil, and the ease of tillage operation, aeration status etc. and combinedly influence soil fertility. The determination of the percentage of the soil separate present in a sampler is called particle-size analysis.

a. **Determination of soil texture by feel.**

In the field, texture is commonly determined by the sense of feel. The soil is rubbed between thumb and fingers under wet conditions. Sands feel gritty and its particles can be easily seen. The silt when dry feels like flour and talcum powder and is slightly plastic when wet. Clayey particles feel very plastic and exhibit stickiness when wet and are hard under dry conditions.

Place approximately 25g of soil in the palm and add water drop after drop and kneed to break down structure. Soil is at the proper consistency when plastic and mouldable like moist putty. Place the soil ball between thumb and forefinger and push the soil to form a ribbon and its extension over the forefinger until it breaks from its own weight and observe the following

OBSERVATION	**TEXTURE**
No formation of ball No formation of ribbon	Sand Sandy loam
If the ribbon is < 2.5cm long and break and the thoroughly wetted sample feels: 1. Gritty 2. Smooth 3. Neither gritty or smooth	Sandy loam Silt loam Loam
If the ribbon is between 2.5-5cm long and break and the thoroughly wetted sample feels: 1. Gritty 2. Smooth 3. Neither gritty or smooth	Sandy clay loam Silty clay loam Clay loam
If the ribbon is between 5 cm long more than and the thoroughly wetted sample feels: 1. Gritty 2. Smooth 3. Neither gritty or smooth	Sandy clay Silty clay Clay

b. Determination of soil texture by hydrometer method (Buoyoucous, 1927).

The percentage of silt and clay are determined by treating a weighed soil sample with a sodium compound (usually sodium polyphodphate or sodium oxalate) and dispersing it by means of a shaker or an electric mixture. Dispersion breaks the soil aggregrates apart so the particles act individually in the analysis. The suspension of dispersed soil is transferred to a tall cylinder and shaken end over end a few times, the place upright. The particles fall through the water, and sand soob settles from the upper few centimetres, leaving behind silt and clay. The percentage of sand, silt and clay can be determined from the data obtained in the proceeding analyses.

Apparatus:

- Buoyoucous soil hydrometer.
- Mechanical shaker
- Thermometer
- 1L measuring cylinder
- Stirrer/Plunger

Reagents:

- 5% sodium hexametaphosphate: w/v aqueous
- 30% H_2O_2 reagent grade
- 2 N HCl: 16.7 ml CONC. HCl dissolved in 100 ml volumetric flask in water.
- 1N NH_2OH

Procedure:

1. Take 50g of soil sample in a 500 ml conical flask.
2. Treat the soil with H2O2 to destroy the organic matter.
3. Add 200ml of distilled water and 100ml of sodium hexametaphosphate soln and mix well with the stirrer and keep the suspension for 4-5 hrs or overnight.

4. Shake the suspension vigorously several timers on a mechanical shaker.
5. Transfer the dispersed soil medium into a 1 litre measuring cylinder and make the volume to 1L.
6. Place a rubber stopper over the mouth of the cylinder, and shake it vigorously, back and forth, for 1 minute.
7. Place the cylinder on a table and note the time immediately.
8. Immediately place the hydrometer in the suspension.
9. Record the reading exactly 4 minutes after placement of hydrometer.
10. Reinsert the hydrometer at the end of 2 hrs and note the hydrometer reading.

Calculation:

A. % SILT + CLAY = value of 1st reading × 2
B. % CLAY = value of 2nd reading × 2
C. % SILT = A – B
D. % SAND = 100 – (Silt-Clay)

c. Estimation of soil textural classes:

The textural class of the soil corresponding to specified percentage of sand, silt, and clay can be determined from the triangle given below.

The triangle is divided into 12 areas containing all possible proportions of sand, slit and clay. The numbers on the three scales are angled to indicate the slopes of the lines to which they apply. The intersection of lines in the figures for sandy clay loam represents 30% clay (along a horizontal line), 10% silt (along a line parallel to the left side opf the triangle), and 60% sand (along a line parallel to the right side of the triangle). Line maybe similarly traced on the triangle to show the soil textural classes having different percentage of sand, silt and clay.

Sometimes, the point representing the texture of a soil sample happens to fall exactly on the line between two textural names. It is customary to use the name of the finer fraction when this happens. For example, a sample containing 40% clay, 30% silt, and 30% sand is called clay rather than clay loam.

Fig. 6 Soil Triangle of textural analysis

2.2 Determination of Maximum Water Holding Capacity or Saturation Capacity

Principle:

Maximum water holding capacity (MWHC) or saturation capacity of a soil is the maximum amount of water a soil is capable of holding under standard conditions (Piper, 1950). Under this condition, the total pores i.e., both micro- and macro-pores are filled with water. If the moisture content is increased further, percolation starts, i.e., the excess water begins to flow down under the action of gravity. The saturation capacity varies with the soil. It increases with the presence of greater quantities of silt, clay, organic matter and colloidal matter.

Apparatus/Equipment

Soil sampling auger, Mortar and pestle, 2.0 mm sieve, Keen-Raczkowski box (or keen box) with perforated bottom and ring, Filter papers, Spatula, Water tray, Electronic balance , Drying oven, Desiccators, Soil core sampler.

Procedure:

1. Collect the soil sample from the desired depth using soil sampling auger.
2. Air-dry the sample, break the aggregates in a mortar and pestle as far as possible and pass through a 2.0 mm sieve.
3. Mix the sieved material thoroughly and preserve it for filling the Keen box.
4. Cut out a Whatman No. 1 or 44 filter paper in such a way that it exactly fits at the perforated bottom of the Keen box.
5. Take the weight of the Keen box along with the filter paper placed inside on the perforated bottom (A).
6. By means of spatula, transfer the soil in small lots into the keen box so as to fill the box. For uniform packing, tap the box gently with each addition of soil during filling process. When the box is full, slice of the extra quantity with the help of the spatula. Tap the box, add a little more quantity of soil and again remove the surplus stuff to ensure a level surface.
7. Place the keen box containing soil in a water tray for saturation overnight. On next day remove the box, wipe it dry from outside. Take their weights along with the soil (B). After weighing, place the box in an oven at 105°C and dry it to a constant weight. Cool the brass box in a dessicator and weigh (C).
8. Instead of Keen’s box, undisturbed soil cores can also be used for this purpose. In this case, first the weight of and empty core is recorded (A). After collecting soil in this core with the help of a core sampler, the core filled with soil is kept on a filter paper inside a tray filled with water and saturated through capillary action. After saturation, the

moist weight of the core with soil (B) is recorded after removing the extra water. Then this core is dried in oven at 105^0 C till constant weight and the dry weight (C) is recorded.

9. Apply a correction for the amount of water absorbed by the filter paper as follows. Weigh five filter papers together. Saturate them with water. Roll gently a glass rod over them to squeeze out water uniformly. Weigh again. Calculate the average amount of water held by the paper (D).

Calculation:

Calculate the maximum water holding capacity with the following equation:

MWHC (%) = ((B-C-D)/(C-A)) × 100

Procedure for calculating saturation capacity of undisturbed soil in rings of core sampler

1. During sampling by core auger, soil retained in the two rings on both side of core can be used for saturation capacity determination.
2. The ring containing soil should be covered at the bottom by wrapping the bottom with a filter paper followed by putting a rubber band around it to keep the cover intact in its position.
3. Then it should be kept in a tray containing water until the sample gets completely saturated.
4. Transfer the wet soil from the ring in the pre-weighed can and weigh it.
5. Keep it in oven at 105 ^{0}C for a day and determine the oven dry weight of the can +soil.
6. Calculate saturation % by using the following formula:
   % saturation = $100 \times [(W_{\text{wet soil+can}} - W_{\text{dry soil+can}})/ (W_{\text{dry soil+can}} - W_{\text{can}})]$
   Where, $W_{\text{wet soil+can}}$,W_{can} and$W_{\text{dry soil+can}}$ are weights of wet soil +can, empty can and dry soil+can, respectively.

2.3 Determination of Soil pH:

Determination of pH is actually a measurement of hydrogen ions activity in soil – water system. The pH value of a soil is an indication of soil reaction i.e. acidic, neutral or alkaline. The nutrient availability is governed by soil reaction. It is maximum at neutral pH and decreases with increase in acidity or alkalinity. Thus, pH value gives an idea about the availability of nutrients to plants.

Principle :

The pH is usually measured by pH meter, in which the potential of hydrogen ion indicating electrode (glass electrode) is measured potentiometrically against calomel saturated reference electrode which also serves as salt bridge. Now a day, most of the pH meters have single combined electrode. Before measuring the pH of the soil, the instrument has to be calibrated with standard buffer solution of known pH. Since, the pH is also affected by the temperature, hence, the pH meter should be adjusted to the temperature of the solution by temperature correction knob.

Reagents :

Standard buffer solutions: These may be of pH 4.0, 7.0 or 9.2 and are prepared by dissolving one standard buffer tablet in 100 ml distilled water, It is necessary to prepare fresh buffer solution after few days. In absence of buffer tablet, a 0.05 M potassium hydrogen phthalate solution can be used which gives a pH of 4.0 (Dissolve 10.21 g. of A.R. grade potassium hydrogen phthalate in distilled water and dilute to 1 litre. Add 1 ml of chloroform or a crystal of thymol per litre as a preservative).

Procedure :

(a) Soil to water ratio of 1:2 (pH2)

Take 20 g soil in 100 ml beaker and add 40 ml. of distilled water to it. The suspension is stirred at a regular interval for 30 minutes. Determine the pH by immersing electrodes in suspension. For soils containing high salts, the pH should be determined by using 0.01M calcium chloride solution. (Dissolve 0.110 g of $CaCl_2$ in water and dilute to 1 litre).

Fig. 7 pH meter

(b) Saturates soil paste (pHs)

Add small amount of distilled water to 250g of air dried soil. Stir the mixture with a spatula. At saturation, the soil paste glistens and flows slightly when the container is tapped it slides freely and ensures cleanly off the spatula. After mixing, allow the sample to stand for an hour. If the paste has stiffened markedly or lost its glistening, add more water or if free water has collected on the surface of the paste, add an additional weighed quantity of dry soil and mix it again. Then insert the electrode carefully in the paste and measure the pH.

(c) Saturation extract (pHe)

The soil is extracted using vacuum extractor and the pH is measured in the saturation extract.

Categories of soil pH values:

Soil pH	Interpretation
< 5.0	Strongly Acidic
5.1 – 6-5	Slightly Acidic
6.6 – 7.5	Neutral
7.6 – 8.0	Mild Alkaline
> 8.0	Strongly Alkaline

2.4 Determination of Soil Conductivity:

Calibration of Instrument Using 0.01 N KCl Solution:

- Dissolve 74.5 g KCl in 100 ml conductivity water free from CO_2. This is the standard reference solution whose conductance is 1412 µS/ cm at 25^{o}C.
- Take this KCl solution in a 100 ml beaker; the electrode was dipped in it. If the conductivity meter does not read 1412 µS/ cm, then adjust the instrument to read 1412.

PROCEDURE:

- 5 g of the soil is weighed into a beaker and to that add 25 mL distilled water.
- Stirred well for about 5-10 minutes and is allowed to settle for sometimes.
- The distillate is taken into another beaker and is used for conductivity measurements.
- Thoroughly rinse the cell one or more times with the sample.
- Read the sample conductivity directly from the conductivity meter.

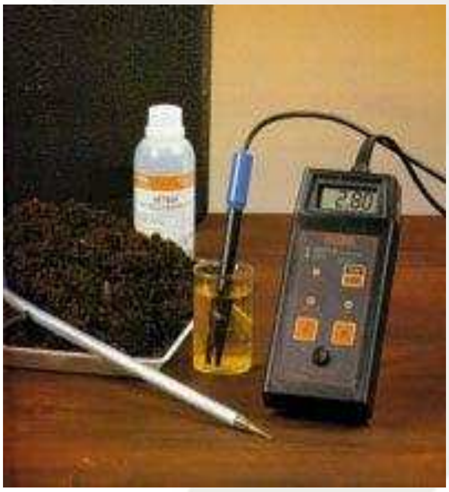


Fig. 8 Conductivity meter

2.5 Determination of Soil Organic Carbon:

Principle:

Organic carbon present in soil is directly correlated to the nitrogen availability to the plants and its determination is most frequently carried out as an indicator of the soil quality. Oxidizable matter in a soil sample is oxidized by $Cr^2O_7^{2-}$, and the heat generated when two volumes of H_2SO_4 are mixed with one volume of 1 N $K_2Cr_2O_7$ solution facilitates the reaction. The excess $Cr_2O_7^{2-}$ is determined by titration with standard iron sulphate solution, and the quantity of substances oxidized calculated from the amount of $Cr_2O_7^{2-}$ reduced. Carbon is not the only element that is oxidized by chromic acid ($H_2Cr_2O_7$), but H^+ also reacts:

$$2\ H_2Cr_2O_7 + 12H^+ + 6\ H_2SO_4 = 2Cr_2(SO_4)_3 + 14\ H_2O$$

The presence of H^+, therefore, increases the amount of dichromate required for oxidation. However, the carbon present in the carboxyl group does not require dichromate to get oxidized and thus lower amount of dichromate required for oxidation.

$$R\text{- }COOH \rightarrow RH^+\ CO2$$

It is generally accepted that opposite effects of H+ and carbon(in carboxyl group) balance each other.

Reactions:

$$4Cr_6{+}{+}3C^0 = 4Cr^{3+}+3C^{4+}$$

$$2\ H_2Cr_2O_7+3C^0+6\ H_2SO_4 = 2Cr_2(SO_4)_3+3CO_2+8H_2O$$

In the oxidation of organic carbon the change in valance from 0 to +4 (in CO). the equivalent weight of C in this oxidation reaction is 12/4. Thus 1 ml of 1N $K_2Cr_2O_7$ will oxidized 3mg or 0.003gm of C. This explains the factor 0.003 used in calculation.

Reagents:

1. 1N potassium dichromate: dissolve 49.04gm potassium dichromate in distilled water and diluted to 1 litre.

2. 0.5N Ferrous Sulphate: Dissolve 140gm of $FeSO_4.7H_2O$ in distilled water, add 40ml concentrated H_2SO_4, cool and dilute to 1 litre. This reagent should be standardized every day before use.
3. 0.25 N O- Phenanthroline ferrous complex indicator: Dissolve 1.485 hm of O- Phenanthroline monohydrate and 0.695 gm of $FeSO_4.7H_2O$ in distilled water and dilute to 100 ml (also available directly as prepared solution). Colour change from pale blue to chocolate red.

OR

Diphenylamine indicator prepared by dissolving 0.5 gm diphenylamine in a mixture of 100 ml concentrated H_2SO_4 (C.P) and 20 ml water. Colour change – blue to green.

In the oxidation of Fe^{+2} to Fe^{+3} the redox potential changes from 0.94 to 1.40 and the end point of titration is at about 1.3 O- phenanthroline changes its colour from pale blue to chocolate red at redox potential of 1.14 and and therefore suits for this titration. On the other hand diphenylamine changes ist colour at a redox potential of 0.76 and can be used only when phosphoric acid and sodium fluoride are used to complex Fe^{+3}. By lowering the concentration of Fe^{3+} the end point is sifted to a redox potential of about 0.76 and diphenylamine can be used as an indicator.

4. Concentrated sulphuric acid, sp. Gr. 1.84 C.P.
5. Concentrated phosphoric acid, 85% c.P. (to be used only with diphenylamine indicator)
6. Sodium flouride(NaF) (to be used only with diphenylamine indicator)

Procedure (Walkley and Dark Method, 1934):

Take a suitable amount of soil (2.0g for soil having 1% O.M., 0.5gm for mountail soils and 0.5gm for peats) having passed a 80 mesh sieve in a 500ml Erlenmeyer flask and add 10 ml 1N $k_2Cr_2O_7$ solution. Swirl gently to mix the reagent with soil thoroughly. Now add slowly along the sides of the flask 20 ml of concentrated H_2SO_4. Mix acid with soil by rotating the flask on an asbestos sheet for 30 minutes to allow the oxidation to proceed. Now add 100 ml of water and one drop of O- phenanthroline indicator. Add 10 ml H_3PO_4 and 0.2 gm NaF if diphenylamine (1-2 drops) indicator is used.

Titrate the content of flask with $FeSO_4.7H_2O$ solution. Add $FeSO_4.7H_2O$ solution freely from the burette until the contents of the flask turn dull green, then start adding it drop by drop until colour changes to chocolate red. Simultaneously, carry out a blank determination. If more than 8 ml of dichromate are reduced, the determination should be repeated with lesser amount of soil.

Observations:

Sample/blank	ml of 0.5 N $FeSO_4$ solution used
Blank	
Sample	

Calculations:

ml of 1N $K_2Cr_2O_7$ reduced=

$$\frac{[(\text{Blank reading} - \text{sample reading}) \times \text{ml K2Cr2O7 taken initially}(10)]}{\text{Blank reading}}$$

- Organic Carbon(OC) in soil (%)= (S×0.003×1.3*×100)/ weight of soil sample in gm
- Organic Matter (OM) in soil (%)= Organic Carbon(%) × 1.724**
- Organic Carbon(OC) in soil (gKg^{-1})= Organic Carbon(%) × 10

(*Based on 77% recovery,**Based on the 58% carbon in soil organic matter)

Organic carbon g ha^{-1} in surface 0-15 cm soil= Organic carbon in soil(g kg ha^{-1})× 2.24×10^6

= Organic carbon in soil(g kg^{-1})× 2.24×10^3 kg ha^{-1}

(Taking the weight of surface 0-15 cm soil as 2.24×10^6)

Discussion:

1. Importance of soil organic matter in soil fertility management.
2. Limits of soil organic carbon(%) as a measure of available N are: low <0.5; medium 0.5-0.75; high >0.75 (Subba Rao, 1995)
3. Carbon sequestration by soil.
4. Functions of reagents:

(i) Potassium dichromate - In the presence of sulphuric acid it makes chromic acid, which is strong oxidizing agent for C.

(ii) Ferrous sulphate - For reducing the potassium dichromate not reduced by soil organic carbon and thus to find out the exect amount of potassium dichromate reduced by the soil organic carbon.

(iii) O- Phenanthroline – ferrous complex –it is the indicator for ferrous sulphate – potassium dichromate titration.

(iv) Diphenylamine – same as at number (iii).

(v) Phosphoric acid – to complex Fe^{3+}in the Ferrous sulphate – potassium dichromate titration when diphenylamine is used as an indicator.

(vi) Sodium flouride – same as at number(v).

Precautions:

Nitrates and chlorides under certain circumstances interface in this procedure. Nitrates interface only when their concentration exceeds 5% of the carbon content. The interference due to chlorides can be corrected either by the use of silver sulphate or by making a correction if thde amount of chloride presents are known. When the amount of chloride is less than the molecular equivalent C, 1.025 g of silver sulphate should be dissolved in 1000 ml of H_2SO_4. If silver sulphate is not used the corrections for chlorides can be made as under:

Corrected organic C(%)= Uncorrected organic C(%) – (%) Cl/12

Numerical Exercises:

1. A 1.0 gm soil sample when reacted with 10 ml $K_2Cr_2O_7$ and concentrated H_2SO_4 for 30 minutes required 15.4 ml $FeSO_4.7H_2O$ solution. $FeSO_4.7H_2O$ when titrated in blank required its 22.2 ml titrate 10 ml $K_2Cr_2O_7$ and concentrated H_2SO_4. Calculate OC and OM content in soil.
2. A soil contains 1.2% OM and C:N ratio in soil is 10. Calculate kg ha^{-1} of OC and present in 0 – 15 cm soil depth. Take the weight of surface soil from 0 – 15 cm depth for 1 ha as 2.24×10^6 kg.

2.6 Determination of Soil Nitrogen:

Nitrogen is one of the major elements required for life. It will stimulate above ground growth, and produces the rich green colour that is the characteristic of healthy plants, because of this Nitrogen is essential for plant life. 78% of the atmosphere is covered by molecular Nitrogen (N_2); this form of Nitrogen cannot be used by animals. This molecular Nitrogen must first combine with Oxygen or Hydrogen to produce compounds such as Ammonia or Nitrate, or some other organic form of Nitrogen. This is called Nitrogen Fixation. Some Nitrogen Fixation occurs by lightning and some other by blue green algae. However, the bulk of Nitrogen Fixation is preferred by bacteria living in the soil. Some of the Nitrogen Fixation bacteria were living free in the soil, while the others were living within the root nodules of some plants such as soya bean, peanut, beans, clover, alfalfa, etc. Because of Ammonia or Ammonium is produced by the decomposition process, the decomposition of materials in the forest is also a source of Nitrogen. The movement of Nitrogen from the atmosphere into inorganic forms, followed by the incorporation of Nitrogen into plant matter is represented as the **Nitrogen Cycle.**

The rate of plant growth is proportional to the rate of nitrogen supply. If the soil is deficient in Nitrogen, the plants become stunted and pale. However, an excess of Nitrogen can damage the plants just as over-fertilizing the lawn can burn and damage the grass.

Apparatus:

Kjeldahl Digestion Assembly, Ammonia Distillation Assembly.

Fig. 9 Kjedahl Digestion Assembly

Principle:

The Kjeldahl method permits the available nitrogen to be precisely determined in the plant and in the soil. The method of determination involves three successive phases which are,

1. Digestion of the organic material to convert nitrogen into HNO_3.
2. Distillation of the released Ammonia into an absorbing surface or medium.
3. Volumetric analysis of the Ammonia formed during the digestion process.

Digestion:

Digestion of the organic material is carried out by digesting the sample with Con. H_2SO_4 in the presence of $CuSO_4.H_2O$ as a catalyst and K_2SO_4 which raise the digestion temperature. The organic material decomposes into several components i.e.,

$C \rightarrow CO_2$, $O \rightarrow H_2O$ and $N \rightarrow NH_3$

In the organic matter, some nitrates are present, most of which are lost during the digestion. The loss may be disregarded for most soils. Since the amount of NO_3^- - N is far lesser than the Organic Nitrogen.

$2\ C_6H_3(OH)NH_2COO + 26\ H_2SO_4 \rightarrow (NH_4)_2SO_4 + 25\ SO_2 + 14\ CO_2 + 28H_2O$

Distillation:

The Ammonia content of the digest is determined by distillation with excess NaOH and absorption of the evolved NH_3 is in standard HCl.

$(NH_4)_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ NH_3 + 2\ H_2O$

$NH_3 + HCl \rightarrow NH_4Cl$

Volumetric Analysis:

The excess of standard HCl is titrated against standard NaOH using Methyl Red as an indicator. The decrease in the multi equivalence of acid as determined by acid-base titration, which gives a measure of the N content of the sample. The end point is determined by a change of colour from pink to yellow.

$2\ HCl + 2\ NaOH \rightarrow 2\ NaCl + H_2O$

Procedure:

- Weigh 50 g of processed soil sample in 500 mL Kjeldahl flask.
- Add 1 g $CuSO_4$, 10 g K_2SO_4 and 30 mL Con. H_2SO_4.
- Shake the contents of the flask until through mixing and allowing to stand for at least 30 minutes with frequent shaking or until complete solution results.
- Digest the content until greenish colour appears. K_2SO_4 raises the boiling point of the acid. So that the loss of acid volatile solution is prevented. $CuSO_4$ $5H_2O$ is digestion accelerator which catalyses the speed of digestion process.

- The reagents sometimes contain impurities so run a blank with the same quantities of reagents and subtract the blank value from the value of the soil digest.
- Digestion is effected on the Kjeldahl digestion rack with low flame for the first 10 – 30 min until the frothing stops and then gradually more strongly until the sample is completely charred. The heat is gradually raised until the acid reaches approximately one third the way up the digestion-flask. The flame is not allowed to touch the flask above the part occurred by the liquid. Excessive boiling may cause volatilization of the acid before the organic matter is oxidized.
- Cool the content and dilute to about 100 mL with distilled water. Swirl the flask for about 2 minutes and transfer the fluid part to a 1000 mL distillation flask.

- Wash the residue left in the Kjeldahl flask with 4 or 5 lots of 50 – 60 mL distilled water, decanting the washings into the distillation flask.
- Add a few, glass bead to prevent bumping.
- Fit the flask with two neck joints to one neck dropping funnel is connected for adding 40 % NaOH while to the other neck Kjeldahl trap, which is used to trap the NaOH coming with the distillate. The trap is connected to the condenser with a delivery tube which dips into 50 mL of 0.1 N HCl contained in a conical flask, with one or two drops of methyl red indicator.
- Add about 125 mL (or 100 ml if bumping is a problem) of 40 % NaOH solution till the content are alkaline in reaction (about 5 times the volume of Con. H_2SO_4 used during the digestion). Heat the RB flask.
- Allow the ammonia formed to be absorbed in standard HCl. Wash down the end of the tube. 150 mL distilled water is added to the conical flask. When no more ammonia is received (test with a red litmus paper turning blue) stop the distillation.

- Titrate the excess of the acid with 0.1 N NaOH solution till the pink colour changes to yellow.
- From the titre value calculate the multi equivalence of the acid participating in the process of ammonia absorbing during digestion.

Calculation:

i. **Blank**

Volume of HCl taken for blank = a mL

Volume of NaOH used = b mL

Volume of HCl consumed by liberated NH_3 present in blank = a – b = z mL

ii. **Sample**

Volume of HCl taken for sample = v mL

Volume of NaOH used = u mL

Volume of HCl consumed by liberated NH_3 present in sample = v – u = w mL

Volume of HCl consumed for NH_3 liberated by sample only = w – z = y mL

1000 mL 1N HCl = 1000 mL 1 N NH_3 = 17 g NH_3 = 14 g N

1 mL 1N HCl = 1 mL 1 N NH_3 = 0.014 g N

1 mL 0.1 N HCl = 1 mL 0.1 N NH_3 = 0.0014 g N

Weight of Nitrogen in 5 g of Sample = y x 0.0014 g N = q g N

% of N in sample = $\frac{q \times 100}{5}$

= p %

2.7 Determination of Phosphorous in Soil:

Principle :

Phosphorus is extracted from the soil with 0.5 m $NaHCO_3$ at a nearly constant pH of 8.5. The phosphate ion in solution treated with ascorbic acid in an acidic medium provides a blue colour complex. Measurement of the quantitative determination of phosphorous in soil (Olsen's *et al.*, 1954).

Reagents :

- **0.5 M Sodium bicarbonate ($NaHCO_3$) solution:** Dissolve 42 g of $NaHCO_3$ in distilled water to get one litre solution and adjust the pH of the solution to 8.5 by small quantity of NaOH.
- **Activated Charcoal:** Darco G-60 (P- Free).
- **5N Sulphuric acid (H_2SO_4) Solution:** Add 141 ml of con. H_2SO_4 to 800 ml of distilled water. Cool the solution and dilute to one litre with distilled water.
- **Reagent A:**
- ➢ Dissolve 12.00 g of ammonium paramolybdate in 250 ml of distilled water.
- ➢ Dissolve 0.2908 g of potassium antimony tartrate ($KSbO.C_4H_4O_6$) in 100 ml distilled water.
- ➢ Above both solution mix thoroughly and made one litre in volumetric flask with the help of distilled water.
- ➢ Add these dissolved reagents to one litre of 5N H_2SO_4.
- **Ascorbic acid working solution (Reagent B):** Dissolve 1.056 g of ascorbic acid in 200 ml of **reagent A** and mix. This ascorbic acid (**reagent B**) should be prepared as required because it does not keep more than 24 hours.
- **Standard phosphate solution**: Weigh 0.4393 g of potassium dihydrogen phosphate (KH_2PO_4) into one litre volumetric flask. Add 500 ml of distilled water and shake the contents until the salt dissolves. Dilute the solution to one litre with distilled water to get 100 ppm P solution. Dilute 20 ml of 100 ppm P solution to one litre to get form working solution of 2 ppm.

Preparation of standard curve:

- Take different concentration of P (0, 1, 2, 3, 4, 5, etc ml of 2 ppm standard P Solution) in 25 ml volumetric flasks.
- Add 5 ml of the 0.5M $NaHCO_3$ extracting solution to each flask, and acidify with 5N H_2SO_4 drop by drop.
- Add about 10 ml distilled water and 4 ml of reagent 'B', then shake the solution.
- Make the volume 25 ml by distilled water.
- The intensity of blue colour is read on spectrophotometer at 660 nm wavelengths after 10 minutes.
- Plot the curve by taking P concentration on X axis and colorimeter reading on Y axis.
- Repeat the process till you get straight line relationship.
- Calculate the factor i.e. 1 colorimeter reading is equal to how much ppm of phosphorus?

Procedure :

- Take 2.5 g of soil sample in 150 ml conical flask and 0.5 g Darco G-60 activated charcoal.
- Then add 50 ml of 0.5 M $NaHCO_3$ solution and shake the solution for 30 minute in a shaker. Similar processes run for a blank without soil.
- Filter the suspension through the Whatman no. 40 paper.
- Take 5 ml aliquot of the extract in a 25 ml volumetric flask, and acidify with 5N H_2SO_4.
- Add small quantity of distilled water, and then add 4 ml of reagent B.

Fig.10 Spectrophotometer

- The intensity of blue colour is read on spectrophotometer at 660 nm wavelengths after 10 minutes.

OBSERVATIONS :

1	Weight of soil sample	2.5 gm
2	Volume of extract used	50 ml
3	Volume of filtrate used	5 ml
4	Absorbency	R
5	Absorbency from standard curve	A
6	Concentration of P for absorbency A	B ppm

CALCULATION:

Available P (Kg ha^{-1}) = $\frac{R \times F \times 50 \times 2.24}{5 \times 2.5}$

Where, F (factor) = B/A

LIMIT OF AVAILABLE PHOSPHOROUS IN SOIL:

VERY LOW	Less than 5 P kg ha^{-1}
LOW	5-10 P kg ha^{-1}
MEDIUM	10-20 P kg ha^{-1}
HIGH	20-40 P kg ha^{-1}
VERY HIGH	More than 40 P kg ha^{-1}

2.8 Determination of Lime Requirements

It may appear that the amount of calcium carbonate necessary to raise the total alkalinity of a pond to a specified level can be calculated directly. Using such a logic, the amount of calcium carbonate needed to raise the total alkalinity (remember that total alkalinity is expressed as equivalent $CaCO_3$) of a 1ha ×1m deep pond from 5-20 mg/l would be 15mg for each litre of water or 15 g for each cubic meter. As the pond contains 10000 m3, a total of 150kg of calcium carbonate would be required. However, this amount of calcium carbonate would scarcely change the total alkalinity of a pond volume of 10000m3. Most of added limestone would react with acidity in the bottom soil and be lost from the water (Greene, 1971).

Soil acidity from exchangeable aluminium:

Soil texture-pH method

The cation exchange capacity (CEC) of soils increases with increasing clay content, and at the same pH, a clayey soil normally will have a higher lime requirement than a loamy soil. A loamy soil will have a higher lime requirement than a sandy soil. Also, for soils of similar texture, the lime requirement increases a ph decreases. Schaeperclaus (1933) modified the soil texture-ph method for use in aquaculture ponds as given in the table below.

Lime requirement (kg/ha as $CaCO_3$)			
Mud pH	Heavy loams or clays	Sandy loam	Sand
<4.0	14,320	7160	4475
4.0-4.5	10,740	5370	4475
4.6-5	8950	4475	3580
5.1-5.5	5370	3580	1790
5.6-6	3580	1790	895
6.1-6.5	1790	1790	0
>6.5	0	0	0

Dose Effect Experiment:

Hickling (1962) evaluated the effects of different application rate of agricultural limestone o water quality in ponds at Malacca.

Table: Relationship between liming rate and total alkalinity in pond water.

Agricultural limestone (Kg/ha)	Total alkalinity (mg/l)
0	10
560	20
1120	28
1680	37
2240	45
4480	68

Direct Calculation:

This method requires that the CEC and pH have been measured and that data for estimating base unsaturation from soil pH are available for soils in the area. The amount of calcium carbonate needed to increase the base unsaturation enough to provide the desired soil ph can be estimated from the fraction of the exchangeable acidity that must be neutralised to effect the necessary change in pH.

Buffer Method:

This method was intended for use by soil testing laboratories in estimating lime requirements of agricultural soils. The pH change caused by the addition of a known quantity of soil to a buffered solution is used to estimate the exchange acidity of a soil. Each pH change of 0.1 unit in 20ml of the Adams Evan buffer solution corresponds to 0.08 meq of soil acidity.

$$\text{Acidity to be neutralised} = \text{Exchange acidity} \times \frac{Initial\ base\ unsaturation - Desired\ base\ unsaturation}{initial\ base\ unsaturation}$$

The factor multiplied by the exchange acidity represents the proportion of the exchange acidity that must be neutralised to produce the desired pH.

The laboratory aspects of Adam Evans buffer method for determining lime requirement of ponds flows:

1. Prepare a *p*-nitrophenol buffer of pH 8.0±0.1 by dissolving 20g of *p*-nitrophenol, 15g of boric acid, 74g of potassium chloride, and 10.5 g of potassium hydroxide in distilled water and diluting to 1000ml in a volumetric flask. Adjust the pH with acid or base if necessary before diluting to volume.
2. Dry the mud sample in air and pulverize the dry mud so that it will pass a 20 mesh screen.
3. Weigh 20 g of dry, pulverised mud into a 100 ml beaker, add 20 ml of distilled water and stir intermittently for 1 hr. Measure the pH of the mud water mixture with a glass electrode and record. Next, add 20 ml of the p-nitrophenol buffer to the same mud water mixture

and stir intermittently for 20 minutes. After setting the pH meter at pH 8 with a 1:1 mixture of *p*-nitrophenol buffer and distilled water, read the ph of the mud water buffer mixture while stirring vigorously.

4. With the two ph values, select the appropriate lime requirement from the table given below. If the ph of the mud water buffer mixture is below 7, repeat the analysis with 10g of dry mud add double the liming rate from the given table.
5.

Table: Lime requirement (in Kg/ha $CaCO_3$; neutralising value= 100%) to increase total hardness and total alkalinity of pond water to 20mg/l or more.

Mud pH	$CaCO_3$ (Kg/ha) according to mud pH in buffered solution									
	7.9	7.8	7.7	7.6	7.5	7.4	7.3	7.2	7.1	7.0
5.7	91	182	272	363	454	544	635	726	817	908
5.6	126	252	378	504	630	756	882	1008	1134	1260
5.5	202	404	604	806	1008	1210	1411	1612	1814	2016
5.4	290	580	869	1160	1449	1738	2029	2318	2608	2829
5.3	340	680	1021	1360	1701	2042	2381	2722	3062	3402
5.2	391	782	1172	1562	1948	2344	2734	3124	3515	3906
5.1	441	882	1323	1765	2205	2646	3087	3528	3969	4410
5.0	504	1008	1512	2016	2520	3024	3528	4032	4536	5040
4.9	656	1310	1966	2620	3276	3932	4586	5242	5980	6552

4.8	672	1344	2016	2688	3360	4032	4704	5390	6048	6720
4.7	706	1412	2116	2822	3528	4234	4940	5644	6350	7056

Soil Acidity from Sulphide Oxidation:

Ponds constructed on sites where coal has been removed by strip mining are acidic because of the oxidation of iron pyrite in bottom muds and on watersheds. Likewise, the oxidation of iron pyrite causes the acidity of pond soils constructed on potential acid sulphate soils.

The lime requirement of sulphides in acid sulphate soil material can be estimated by hydrogen peroxide oxidation. The hydrogen peroxide oxidizes the sulphides to sulphuric acid and the amount of sulphuric acid formed is determined by titration with standard sodium hydroxide. To obtain the total lime requirement of an acid sulphate soil, both the acidity from pyroxide oxidation and the exchange acidity must be summed.

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Course Name	Soil and Water Chemistry
Lesson 10	Soil and Water Amendments & Environmental Ameliorative
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Lesson 10

Objectives:

1. To learn about different soil & water amendments

2. To learn about environmental ameliorative

Glossary of terms:

Soil amendments: These are organic or inorganic matter added to the soil to improve texture, water retention, drainage or aeration.

Environmental ameliorative: These are substances use to repair environmental problems of soil.

Compost: Composting is the biological decomposition of organic materials by microorganisms under controlled, aerobic conditions to a relatively stable humus-like material called compost.

Mulch: A *mulch* is a layer of material applied to the surface of soil.

Humus: The organic component of soil, formed by the decomposition of leaves and other plant material by soil microorganisms.

Manure: *It* is organic matter that is used as organic fertilizer in agriculture.

Micronutrients: These are essential plant nutrients that are found in trace amounts in tissue, but play an imperative role in plant growth and development.

Soil deodorizer: These are agents used for Suppressing the explosive generation of spoilage and decaying odors from soil.

1. Soil Amendment:

-Soil amendments are organic or inorganic matter added intentionally to the soil to improve texture, water retention, drainage or aeration.

-In case of sandy or rocky soil amendments are required to improve the texture and add water retention properties.

- Clay soils require the addition of material to improve texture, aeration and drainage.

Fig.1 Different types of soil amendments

1.1 Common inorganic amendments:

Amendment	Function/Purpose
Sand or Profile Soil Conditioner	To improve aeration and drainage
Lime or Sulfur	To raise or lower pH
Vermiculite, a natural balsamic mineral and perlite made from heated amorphous volcanic glass	Increases aeration, improves texture and assists in water retention.

1.2 Common organic amendments:

Amendment	Function/purpose
Manures	To add nutrients
Mulch	Mulch helps soil retain its moisture
Compost	Improves the texture of the soil, increases aeration, promotes both water retention and drainage as well as adds valuable nutrients necessary for plant growth.
Humus	Humus offers stability to imbalanced soil and rectifies deficiencies while maintaining its own balance
Peat Moss	It increases the ability of the soil to retain water and is ideal for sandy or rocky soil. It is ideal for stabilizing clay soils as well.
Wood products like wood chips and shavings	To improve soil, but may create a nitrogen deficiency.

Advantages

- Soil amendments improve the physical properties resulting in better conditions for water storage, root development and soil ecosystems
- Soil amendments enhances soil aeration
- Soil amendments can be produced locally, especially organic amendments (e.g. compost), which are cheap to produce

Disadvantages

- Wood products can tie up nitrogen in the soil

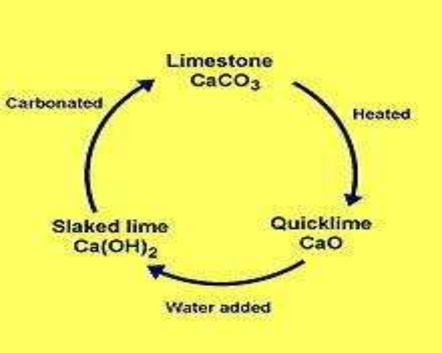
- The incorporation of the soil amendment (especially of organic amendments) can be time consuming
- If too many nutrients or organic matter are put into the soil, they can be released and cause an outflow of nutrients into the groundwater and surrounding rivers and lakes, which can result in water pollution

Factors to be considered in selecting in soil amendment:

- The soil texture
- Salt contents
- Soil salinity and plant sensitivity to salts
- Salt content and pH of the amendment

1.3 Common Materials Used as Soil Amendment:

- Lime, manures, fertilizers, micronutrients, zeolites, alum, gypsum.
- Lime is a calcium-containing inorganic mineral composed primarily of oxides, and hydroxide, usually calcium oxide and/ or calcium hydroxide.



Types of lime:

-Agricultural lime ($CaCO_3$)

- Quick lime (CaO)

- Slaked lime $Ca(OH)_2$

Liming materials:

-They are substances containing Ca and Mg compounds capable of neutralizing acidity.

-The most common liming materials are oxides, hydroxides and carbonates of Ca and Mg having higher percentage of Ca compared to Mg.

Chemical changes due to different liming materials, which occur, may be represented as follows:

$CaO + 2H^+ \rightarrow Ca^{2+} + H_2O$
$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O$
$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$
$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2O + 2CO_2$

-The effectiveness of liming material depends on their neutralizing capacity, particle size and physical properties.

-Pure $CaCO_3$ can be considered to have a neutralizing value of 100%, and is used as the standard.

Benefits of liming

- Liming establishes a strong pH buffer system, and thereby prevent sudden fluctuation in environment, that is considered detrimental for aquatic life.
- Lime reduces turbidity caused by suspended silt and clay particles and humic substances.
- Toxic and caustic actions of liming materials kill bacteria as well as fish parasite in their various stages of life cycle and thus render fishes less liable to disease.
- The pH of acidic soil raised by liming increases microbial activity, and thus favors mineralization of nitrogen and other nutrients through decomposition of organic matters.

Methods of application of liming material:

- Agricultural lime is generally used in fish ponds.
- It is low priced and does not create any harmful effects, compared to oxides and hydroxides, which are used under specific conditions for control of diseases.

- Liming should be applied on to pond bed when it is desired to improve pond bottom or to control parasites.
- But for controlling precipitation of water and removal of turbidity in acid water, liming materials are broadcasted on the water surface.
- Newly constructed ponds should be limed prior to filling with water.
- Maintenance of desired ph of soil is rather difficult by liming due to relationship between reserve and exchange acidity of soil, so frequent applications of lime in split doses are considered effective to achieve desired results.

LIME DOSES AT DIFFERENT pH LEVEL

pH	Soil condition	Dose (kg/ha)
4.0 -4.5	Highly acidic	1000
4.5-5.5	Medium acidic	700
5.5- 6.5	Slightly acidic	500
6.5- 7.5	Near neutral	200

1.4 Manures:

-Manure is organic matter that is used as organic fertilizer in agriculture.

-Most manure consists of animal faeces; other sources include compost and green manure.

-Manures contribute to the fertility of soil by adding organic matter and nutrients, such as nitrogen, that are utilised by bacteria, fungi and other organisms in the soil.

1.5 Types of Manure:

a) Animal manure

-Cattle manure is a good source of nitrogen as well as organic carbon.

- Chicken litter, is very concentrated in nitrogen and phosphate and is prized for both properties.
- It can improve the soil structure (aggregation) so that the soil holds more nutrients and water, and therefore becomes more fertile.

Fig.2 Animal manure (Cow dung)

Table 1 Nutritive value of different animal manures

Animal	Excreta	Moisture (%)	Organic matter (%)	Nitrogen (%)	Phosphorus (P_2O_5 %)	Potash (%)
Cattle	Faeces	80-85	14.0	0.3	0.2	0.1
	Urine	92-95	2.3	1.0	0.1	1.4
Pig	Faeces	85	15.0	0.6	0.5	0.4
	Urine	97	2.5	0.4	0.1	0.7
Chicken	Faeces	78	25.5	1.4	0.8	0.6
Duck	Faeces	81	26.2	0.9	0.4	0.6
Rabbit	Faeces	10	37.0	2.0	1.3	1.2
Goat	Faeces	10	-	2.7	1.7	2.9

b) **Compost** -Composting is the natural process of recycling organic matter, such as leaves and food scraps, into a valuable fertilizer that can enrich the soil.

-Anything that grows decomposes eventually; composting simply speeds up the process by providing an ideal environment for bacteria, fungi, and other decomposing organisms (such as worms, sowbugs, and nematodes) to do their work.

Fig.3 Compost made from vegetable peel

- The resulting decomposed matter, which often ends up looking like fertile garden soil, is called compost.

c) Green manure

-Green manure is a term used to describe specific plant or crop varieties that are grown and turned into the soil to improve its overall quality.

-When these plants are incorporated into the soil, it breaks down, eventually releasing important nutrients, such as nitrogen.

Fig.4 Green manure

1.6 Fertilizer:

-There are many commonly used fertilizers produced for a variety of applications. Fertilizer manufacturers are required to list the grade on each fertilizer container by the percent of nitrogen (N), phosphorus (P) as phosphoric acid (P_2O_5) and potassium (K) as potassium monoxide (K_2O).

-Additions of phosphorus in ponds usually provide a much greater increase in fish production than from either nitrogen or potassium.

-Liquid fertilizers are generally superior to the traditional granular form fertilizers in promoting rapid growth of plankton algae in farm ponds. This is because the nutrients are immediately in solution, making them more rapidly available to the algae.

-Also, smaller applications of liquid fertilizers (more as concentrates) can be used which may reduce the cost and labor of application but still improve the effectiveness of pond fertilization.

Types of Fertilizer:

a) Nitrogen Fertilizers

1. Organic

2. Inorganic

DAP $(NH_4)_2$ HPO_4	21%N (53%P_2O_4)
Ammo. phos $NH_4H_2PO_4$	11% (48%P_2O_4)
Urea $CO(NH_2)_2$	42-.45%
Amm.Nitrate NH_4NO_3	33%
Amm.Sulphate$(NH_4)2SO_4$	21%
Anhydrous ammonium (Liquid NH_3)	82%

b) Phosphate Fertilizers

1. Super phosphate Ca $(H_2PO_4)_2$ (Principle P. fertilisers)	16-50(P_2O_5),	7- 22 %(P)
2. Di ammonium phosphate $(NH_4)_2HPO_4$	46-53(P_2O_5)	20-23% (P)

3. Rock Phosphate 25-30(P_2O_5)11-13% (P)

c) Potassium Fertilizers

Pot.Chloride	KCl	40.50(K_2O)	40.42%K
Pot.Sulphate	K_2SO_4	4	
Pot nitrate	KNO_3	44(K_2O)	37%K
Muret of potash	KCl	20-70(K_2O)	19-25%K

d) Sulfur Fertilizers

- Ammonium Sulphate
- Potassium Sulphate

Application Methods

-Liquid fertilizers generally weigh about half again as much as water. Because they are heavier than water, they must be diluted with water or applied into turbulence so that they mix with the pond water and don't sink to the bottom.

- One method of application of liquid fertilizer is to dip it slowly into the water from the bow of a boat driven by an outboard motor so that the wake of the boat and the action of the propeller will mix fertilizer into the water before it has a chance to sink.

-It can also be applied by pouring it directly into the turbulence caused by the outboard motor

1.7 Micronutrients: Micronutrients are compounds that are only required in minimal amounts which aid in the growth, development, and maintenance of the body.

Zinc, cobalt, manganese and copper play a significant role in aquaculture.

Zinc: Zinc can be highly beneficial for fish growth mainly of silver carp and *Catla catla*.

-The recommended dose for zinc are as follows:

30 kg zinc sulphate/ha/yr for soil having **0.5 ppm** available zinc

20 kg zinc sulphate/ha/yr for soil having **0.5- 0.75 ppm** available zinc

10 kg zinc sulphate/ha/yr for soil having **0.75-1.00 ppm** available zinc

-Zinc is required for the synthesis of DNA and RNA, and is therefore, essential for cell proliferation.

- For fish, zinc is second in quantitative importance, next to iron.

-At the same time excessive environmental zinc can have severe impacts upon the survival and growth of aquatic organisms.

Cobalt:

-It plays an important role in nitrogen fixation by rhizobium and it is also a constituent of Vit B_{12}

-Cobalt @10 kg cobalt chloride/year as micronutrient fertilizer could be highly beneficial for fish growth especially of silver carp and mrigala.

Manganese:

-It plays an important role in photosynthesis and heterotrophic growth of plankton.

-Application of manganese increase plankton to about 15% by weight.

-Manganese concentration in natural surface water seldom reaches 1.0 mg/l and is usually less than 0.2mg/l.

-Higher concentration of manganese is toxic to aquatic organism.

Copper:

-Copper is mainly applied to aquacultural ponds to control algal bloom, to kill organisms, which produces odourous compounds responsible for off flavor in fish and shrimp and to control fish disease.

-The maximum admissible copper concentration in water for the protection of fish is in the range of 0.001 -0.02 mg/l depending upon the physical and chemical properties of the water and the species of the fish.

-Excess concentration of water is toxic to the aquatic species effecting bronchial function and growth inhibition.

Zeolite:

-Zeolite is a naturally occuring deposit (i.e. rock) that has a fairly unique structure which is highly porous whilst also allowing for rapid uptake and loosing of charged particles.

-When placed in water zeolite filters ammonia out of the water and holds it inside its' porous structure.

-As ammonia is highly toxic to fish this is a very useful way of reducing ammonia concentration in water.

-Zeolite is often used when transporting fish for a period of several hours to avoid the ammonia accumulation in the bags or transport tank from reaching toxic levels.

-It can also be used when setting up a new recirculating system or tank to maintain low ammonia levels while the biofilter is maturing.

-Occassionally zeolite is used in reef aquarium to polish the water of unwanted particles other than ammonia

. **Fig.5 Zeolite**

Alum:

-Alum is the most effective for clearing clay turbidity from a pond.

-It can be sprinkled as a powder over the water surface, through a waterfall, or through a skimmer intake.

-Alum also reduces dissolved inorganic phosphate levels through the precipitation of insoluble aluminium phosphate, reducing phytoplankton growth.

-The use of alum may therefore necessitate the addition of lime to correct total alkalinity and pH if these parameters fall below acceptable levels.

Fig.6 Alum

Gypsum:

-It is used to increase the total hardness of waters beyond that possible with lime, although it does not neutralise acidity.

-The low cost and high solubility of gypsum makes it ideal for use in the maintenance of calcium levels in hatchery situations.

Fig.7 Gypsum

Important Notes

- Excess lime reduce the availability of iron phosphorus, manganese, boron, zinc and sulfur and also potassium.
- The most commonly used amendments for alkaline soil are gypsum and sulfur.
- Carbon, Hydrogen, Oxygen (Air and Water), N, P, K Ca Mg S (Soil solids) **macro nutrients.**
- Fe, Mn, Bo, Mb Cu, Zn, Cl^-, Cobalt are essential **micro nutrients.**
- Ca^{++} and Mg^{++} - applied as lime and are known as **lime elements.**

2.0 Environmental Ameliorative

2.1 Chlorination:

-Chlorine disinfection is a point-of-entry treatment that kills pathogens, including certain viruses and bacteria that retard the growth of fishes. Moreover, chlorination can offer residual disinfection throughout the household water distribution system.

-Hypochlorus acid and hypochlorite (free chlorine residual) are responsible for disinfecting power of chlorine products in pond water.

-But , chlorination of waters containing fish or prawn is dangerous and unbeneficial.

-It is possible to disinfect bottoms of empty ponds and water in newly filled but unstocked ponds, by applying chlorine products.

-When this is done, enough chlorine should be applied to overcome chlorine demand to provide 1 mg/l or more of free chlorine residuals. The residuals will detoxify naturally in few days so to stock ponds safely.

How Chlorination Works?

-The effectiveness of chlorination depends on various factors, including water temperature, water pH, water turbidity, general water quality and contact time.

-The contact time is the time available to complete the reaction between the chlorine and untreated water. A longer contact time results in more effective disinfection.

-As the chlorine concentration increases, the required contact time decreases. Chlorination is more effective at a high temperature and a low pH.

-Particles in the water decrease the effectiveness of chlorination, as microorganisms may ‘hide’ behind particles and avoid disinfection.

-The quality of the untreated water affects the chlorine demand. Chlorine readily combines with other components dissolved in water, including iron, manganese, hydrogen sulfide, microorganisms, plant material, ammonia, and organic color such as that from decaying peat moss. These things ‘use up’ chlorine so it is important to add sufficient chlorine to meet the demand and still provide residual disinfection.

-Chlorine is available in two formulations, as a dry powder or pellet (calcium hypochlorite), or as a liquid (sodium hypochlorite).

-Chlorine solutions from powders should be prepared frequently since the strength of the solution decreases gradually after mixing. To avoid hardness deposits on equipment, manufacturers recommend using softened or distilled water when mixing chlorine solutions.

2.2 Deodorizer:

-In a confined aquaculture pond, gradual accumulation of unutilized feed, dead algae, faecal matter etc. raises the organic load at the pond bottom.

-This load absorbs all the available oxygen at pond bottom, by way of oxidation process and creates anaerobic condition.

-In the absence of oxygen, noxious gases like hydrogen sulphide (H_2S), ammonia (NH_3), nitrite (NO_2-) etc. become more stable and these depleted dissolved oxygen conditions trigger stress to the cultured species and cause severe health problems ultimately leads to mortality if timely action is not taken.

Few odorizer used in aquaculture are:

a) **Tetra San:** It is a versatile and powerful water sanitizer for use as an effective disinfectant in Aquaculture ponds. It improves the total aquatic environment. By way of reducing the load of pathogenic flora and fauna in Aquaculture facilities (farms and hatcheries) and also as a deodorizer for use in Aquaculture ponds.

b) **Yuka G:** Yuka G contains Yucca schidigera blended with suitable probiotics and enzymes in granular form.

Benefits:

- Reduces ammonia and other irritant gases
- Reduces waste odor
- Improves sludge characteristics for better
- Overall improvement in pond environment
- Easy application

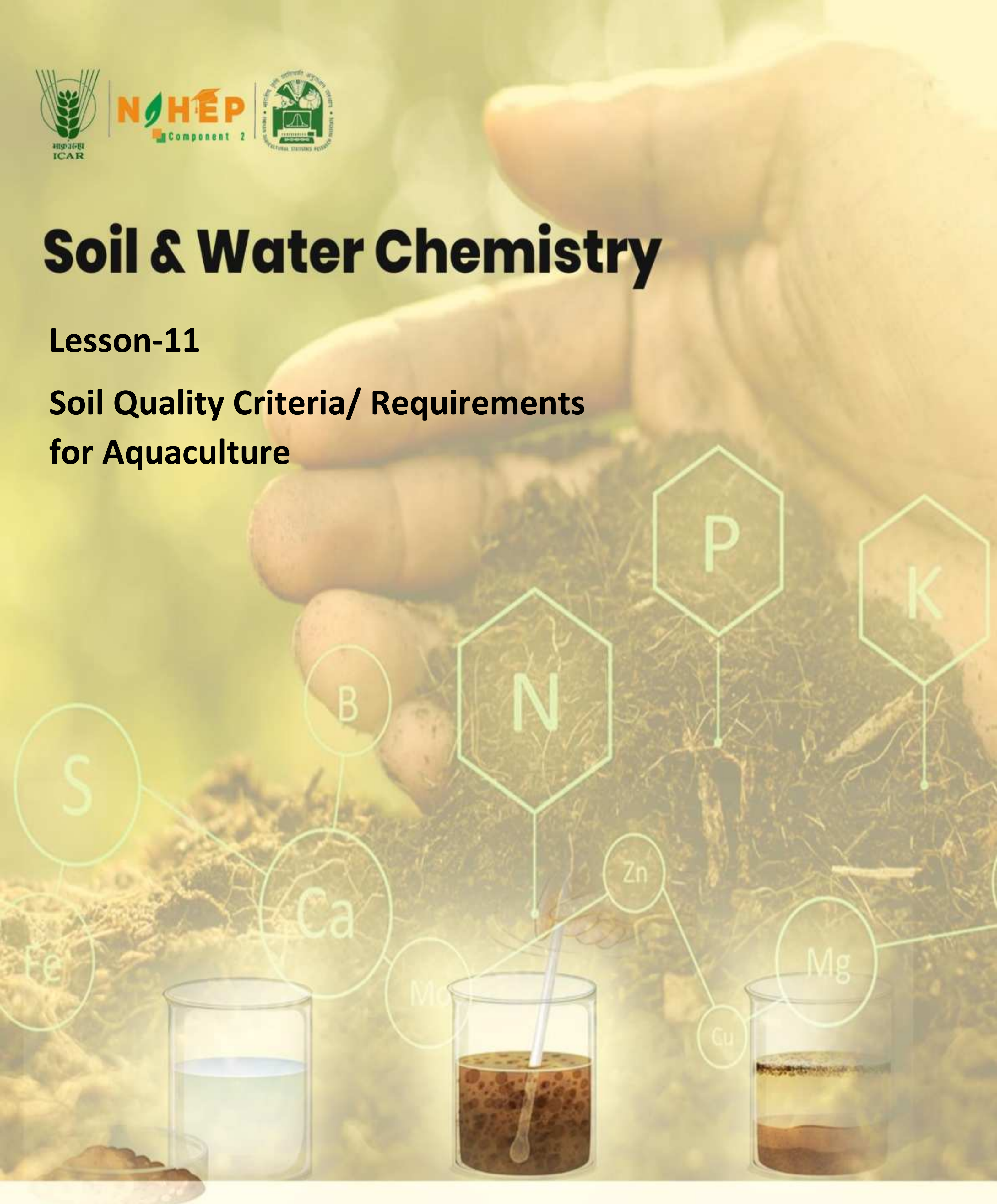
Dosage:

- Shrimp ponds: 500 gms/ha
- Fish/other species ponds: 500 gms/ha
- Packaging: 500 gm bottle

Common Causes of Smelly Pond Water & Odours:

1) **Stagnant Pond Water (Low aeration)**
2) **Poor Water Filtration**
3) **Pond Sludge (Bottom muck)**
4) **Overgrowth of Algae**
5) **Dead pond fish or plants**

2.3 Bacterial formulation: Microbial formulations have a potential to restore the fertility of degraded soil through diverse processes, viz., by increasing the nutrient availability through nitrogen fixation and mobilization of essential elements (**phosphorus, iron and potassium**) to the plants and repairing the soil structure by improving its aggregation and stability. Microbial formulations also help in disease management. Success rate of these formulations in the field depends on their antagonistic or synergistic interaction with indigenous microbes, organic carbon content, soil properties (physical and chemical) and soil amendments. A consortium of microorganisms, with or without organic fertilizer, is more beneficial to restore soil fertility and organic matter content of agricultural soil than a single inoculum. Agricultural practices also play a great role in the establishment of these microbial formulations.



Soil & Water Chemistry

Lesson-11

Soil Quality Criteria/ Requirements for Aquaculture

Content

DESIGNED AND DEVELOPED UNDER THE AEGIS OF
NAHEP Component-2 Project “Investments In ICAR Leadership In Agricultural Higher Education”
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Lesson 11	Soil Quality Criteria/ Requirements for Aquaculture
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Lesson 11

Objectives:

1. To learn about optimum soil quality criteria/requirements for aquaculture

Glossary of terms:

Pond Productivity: The quantum of natural food produced in a pond is the result of interplay of various factors viz., climate and fertility status of pond soil and water. Phytoplankton being the primary producers in aquatic environment depends upon all these factors. Increase in primary production means an increase in pond productivity.

Tilling: Tilling is the act of preparing the soil for planting.

Mineralisation: It is defined as conversion organic compounds into inorganic compounds through various decomposition procedures.

Organic fertilizer: These are *fertilizers* derived from animal matter, animal excreta (*manure*), human excreta, and vegetable matter (e.g., compost and crop residues).

Inorganic fertilizer: In inorganic or mineral fertilizers, the nutrients are inorganic salts, obtained by extraction and/or physical and chemical processes. The three primary plant nutrients are nitrogen, phosphorus and potassium.

Organic soil: Organic soil is a soil that is created by the decomposition of plant and animal materials to create a nutrient and mineral rich mini-ecosystem with microorganisms that feed and breathe life back into the soil.

Phytoplakton: These are microscopic algae found in aquatic bodies which act as primary producers.

Zooplankton: These are plankton of animal origin found in water bodies act as secondery producers.

1.0 Soil Quality and their requirements for Aquaculture:

Soil is one of the important factors that determine the productivity of a pond. The production of various primary food organisms depends largely on the availability of different nutrients. The availability of most nutrient in an aquaculture pond depends mostly on the prevailing condition of the bottom soil, for which it is sometimes called **"Chemical Laboratory of the pond".**

Some criteria or requirement for aquaculture are as follows:

1.1 Texture

Nature and properties of the parent material forming soil determine soil texture. Many important physic-chemical properties for fertility of fish ponds are influenced to a great extent by the proportion of different size fraction of soil. **An ideal pond should not be too sandy to allow leaching nor be too clayey to keep all the nutrients absorbed.**

1.2 Soil acidity

Soil can either be acidic, alkaline or neutral. pH range of 6-8 is considered ideal. Soil which are acidic does not respond well to fertilization. Liming is the only way to improve water quality in ponds with acidic soil and it is the pH of the soil that must be corrected for lasting effects rather than pH of water.

1.3 Bottom-soil oxidation

Dissolved oxygen cannot move rapidly into water-saturated soil, and pond soils become anaerobic below the depth of a few millimetres. **Aeration and water circulation are beneficial in improving bottom-soil oxidation**, but surface layer of the soil may still become anaerobic in intensive fish culture ponds. When redox potential is low at the soil surface (anaerobic condition), hydrogen sulphide and other toxic microbial metabolites diffuse into pond water. Sodium nitrate can serve as a source of oxygen for microbes is poorly oxygenated environments; the redox-potential will not drop enough for formation of hydrogen sulphide and other toxic metabolites.

1.4 Drying pond bottoms

When pond bottoms are dried between crops, evaporation of water from soil-pores and cracking of soil enhances aeration and favours microbial decomposition of soil organic matter. Excessive drying makes soil too dry for even microbial activity; a drying period of 2-3 weeks is usually adequate. Tilling of dry soil with a disk harrow can improve aeration, but tilled bottoms of aerated ponds should be compacted before refilling to reduce tendency of erosion.

1.5 Good practices for bottom soil management: Major concerns in pond bottom soil-management are low soil pH, high soil-organic matter, loss of oxidized layer, and accumulation of soft sediments. Some good practices for protecting soil quality are shown in Table 1.

Table 1. Good management practices for pond bottom-soil quality

Problem	Preventive measures
Low soil pH	• Neutralise acidity of new pond bottom - soil before initiating aquaculture. • In old ponds that have never been limed, apply agricultural limestone according to soil pH. • Use urea and ammonium fertilizers conservatively as they are acid forming • Monitor total alkalinity of pond-waters and soil pH to assure that total alkalinity is >75ppm in fish ponds and pH is >7, • After initial correction of soil pH, apply agricultural limestone to bottoms of empty

	ponds @1000kg/ha during fallow period between crops. If ponds are full, apply to water.
High soil organic matter	• Select sites without organic soil • Where soils are organic, apply agricultural limestone and urea (200-400kg/ha) to encourage degradation of organic matter during fallow periods. Repeat after each crop. • Use moderate stocking rates to avoid high inputs of nutrients and organic matter in fertilizers, manures and feeds. • Dry ponds between crops, apply agricultural limestone according to soil pH and till heavy-textured soils to encourage oxidation of organic matter by bacteria. • In areas, where pond bottom soils cannot be dried, apply nitrate fertilizer at 20 to 40 g/m^2. • Monitor soil organic matter concentrations annually. >3% organic carbon (about 6% organic matter) suggest excessive organic matter.
Loss of oxidized layer	• Where a surface layer high in organic matter has developed in bottom soils, use turning plough to bury this layer and expose higher quality soil. • Monitor appearance of soil. The upper few millilitres should be of natural soil colour or brownish, A gray or black colour at surface indicates reduced (anaerobic) conditions. • Use a rake or chain to scarify surface soil during crop if it appears anaerobic • Remove accumulation of organic matter from corners of ponds

	• Maintain adequate plankton to restrict light and prevent mats of benthic algae. • Remove soft sediment from ponds.
Excessive accumulation of soft sediment	• If water supply has high concentrations of suspended solids, pass water through a settling basin before putting it in ponds. • Establish grass cover to minimise erosion on watersheds and embankments of ponds. • Use proper side slopes and compaction when constructing new ponds or renovating old ones. • In ponds with mechanical aeration, install aerators to prevent water currents from eroding insides of embankments. • If sites of active erosion are observed, measures for lessening erosion should be installed. These measures may include installation of rip-rap, proper sloping and compaction, grass cover, etc. • When ponds are empty between crops, remove sediments from deep areas and place them on areas from which eroded. Proper sloping and compaction, establishment of grass above water level, or installation of rip-rap will lessen erosion potential. • Do not leave ponds empty longer than necessary during rainy season to prevent erosion of soil from shallow area with deposition of soil in deeper areas. • If bottom of heavily aerated ponds are tilled between crops, compact bottoms with heavy roller before refilling.

	• Do not allow livestock to walk on pond embankments or wade in shallow water-edges. • Avoid operating equipment that will cause ruts and other inundations in pond bottoms. • Monitor pond bottoms for soft sediment and remove such sediments periodically instead of waiting until a severe problem develops.

1.6 Chemical properties of bottom soil: Some important chemical properties of soil in pond that influence nutrient management of ponds are:

1. **Soil reaction (pH):** pH is one important factor that influence the productivity of a pond as it control most of the chemical reactions in the pond. **pH of near neutral and slightly alkaline is considered ideal for fish production.**
2. **Organic carbon content:** Organic carbon acts as a source of energy for bacteria and other microbes that release nutrient through various biochemical processes. **Pond soils with < 0.5% organic carbon are considered unproductive while those with 0.5-1.5% and 1.5-2.5% have medium and high productivity respectively, while > 2.5% is also not suitable for fish production as it may lead to eutrophication and oxygen depletion.**
3. **Carbon: Nitrogen ratio:** This ratio influences activity of soil microbes which in turn affects rate of release of nutrient from decomposing organic matter. **Rate of mineralisation is very fast, moderately fast and slow at C:N ratio range of <10, 10-20 and more than 20 respectively. Carbon nitrogen ratio of between 10-15 is considered favourable for aquaculture.**
4. **General nutrient status:** Nitrogen, phosphorous and potassium are major nutrients required by phytoplankton. The single most critical nutrient of pond productivity is phosphorous content of soil and

water. **Pond soil with 30ppm, 30-60ppm and 60-120ppm and more than 120ppm available phosphate are considered poor, average and good and highly productive respectively. Nitrogen content of <250ppm are considered low in productivity while concentration range of 250-500ppm and above 500ppm are considered medium and highly productive.**

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ICAR, New Delhi, 2011.*Handbook of Fisheries & Aquaculture*, DKMA, ICAR, New Delhi, 1116.