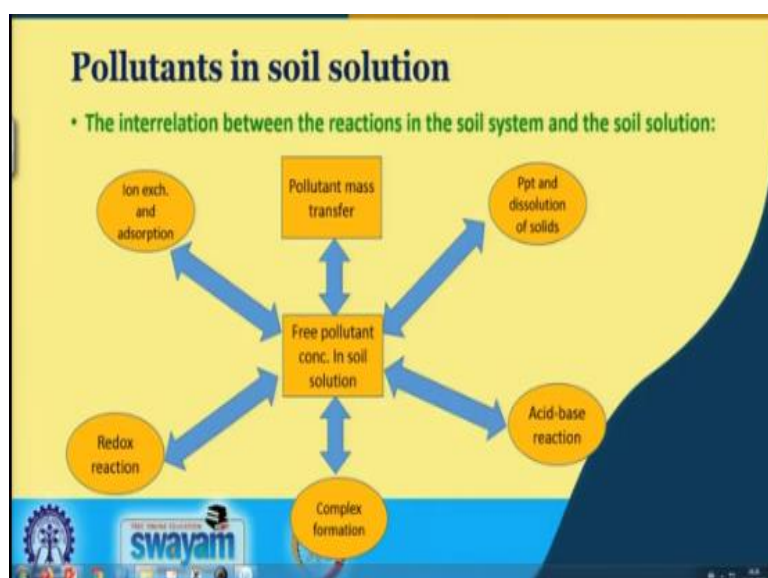


Environmental Soil Chemistry
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Lecture – 43
Pollutants - Soil Solution Interactions (Contd.,)

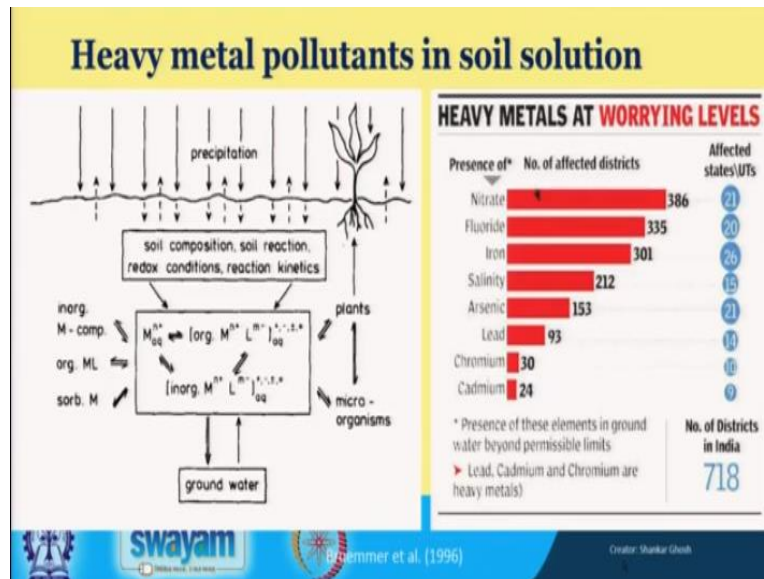
Welcome friends to this third lecture of week 9 of this NPTEL online certification course of environmental soil chemistry and in this third lecture, we will be talking more about some environmental pollution issues. We will be talking about acid rains and also alkaline soils and gypsum dissolution but before going to you know, discuss those things, I just like to give you a quick recap of whatever we have discussed so far.

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So, in our first 2 lectures, we have started with the pollute; discussion with the pollutants in soil solution, I showed you this slide where I showed you that how the free, you know free pollutant concentration in soil solution shows different dynamics and they can be converted to different forms and vice versa, I have shown you this pollutants in soil solution.

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Then, we have discussed what are the dynamics of heavy metal pollutants in soil solution, we have discussed how heavy metals are present in worrying levels in ground water in especially, Indian concern you know, Indian states and union territories are concerned.

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Acid-base equilibria

- The group of reactions covering the transfer of protons governs the **acid-base equilibrium relation**. In this case the proton donor is an acid and the acceptor a base.

acid = base + proton

- With the following equilibrium constant:

$$K_A^0 = \frac{[H^+][Base]}{[acid]}, \text{ where } K_A^0 \text{ is an acidity constant, } [] \text{ are activities.}$$

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Then, we have talked about the in details about the acid base equilibria; we have seen the relevant reaction for 1 acid, 1 base.


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Acid-base equilibria

- $K_A^0 = \frac{[H^+][Base]}{[acid]}$, where K_A^0 is an acidity constant, [] are activities.
- This equation stipulates that for a given ratio of the activities of a particular acid and its conjugate base, the proton activity has a fixed value. In a system where we have a complex of two bases and two acids, the relationship becomes –

$$acid1 + base2 = acid2 + base1$$
- The corresponding equilibrium under this condition is –

$$K_{1,2}^0 = K_{A1}^0 / K_{A2}^0 = \frac{[Base1][acid2]}{[acid1][base2]}$$



And then, we have seen more complex of 2 bases and 2 acids and how this you know, corresponding equilibrium condition changes for these complex 2 acids and 2 bases reaction.


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Acid-base equilibria

- The corresponding equilibrium under this condition is –

$$K_{1,2}^0 = K_{A1}^0 / K_{A2}^0 = \frac{[Base1][acid2]}{[acid1][base2]}$$
- The soil solution being an aqueous system, H_2O is the ever-present acceptor.
- For example, during the dissociation of an acid in the soil solution, H_3O^+ will be one of the dissociation products and the acid strength of the H acid relative to H_3O^+ will be a measurable parameter.
- In a dilute solution, the activity of the hydrated protons equals that of H_3O^+ and the pH value characterizes the H-ion activity.
- Under these conditions, substituting for pH gives:

$$pH - pK_A = \log \frac{[Base]}{[Acid]}$$





Then you know, we have discussed what is the importance of these hydronium ions, H_3O^+ as far as the you know, dissociation of acids is concerned.

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pK_A value :

- The pK_A value is one method used to indicate the strength of an acid. pK_A is the negative log of the acid dissociation constant or K_A value. A lower pK_A value indicates a stronger acid. That is, the lower value indicates the acid more fully dissociates in water
- For example, the pK_A of acetic acid is 4.8, while the pK_A of lactic acid is 3.8. Using the pK_A values, one can see lactic acid is a stronger acid than acetic acid.





And also we have discussed about the pK_A value remember, you know pK_A is the negative logarithm of the acid dissociation constant K_A. So, a lower pK_A value indicates a stronger acid and we have seen the example of acetic acid and lactic acid, where the lactic acid has a lower pK_A value and as a result, lactic acid is stronger than you know, lactic acid is stronger than that of acetic acid.

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Precipitation-dissolution

- Under various physicochemical conditions, a process of dissolution and precipitation of minerals in water occurs.
- This reaction is more common for the natural systems and plays a lesser part in the fate of pollutants.
- The extent of the dissolution or precipitation reaction for systems that attain equilibrium can be estimated by considering the equilibrium constant.







Now, if you consider you know, we have also discussed precipitation dissolution the reactions.

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Precipitation-dissolution

- The precipitation of chemicals can only occur at super saturation, since dissolution ends only at water saturation.
- In the soil medium the dissolution reaction is a heterogeneous chemical reaction.
- It is necessary to characterize the solubility in terms of a solubility product with an equilibrium constant which can characterize the solubility as well as predict how solution variables can change the solubility.



And you know, we have seen different conditions of precipitation and dissolution, what is the condition of getting so, you know precipitation, what is super saturation, what is under saturation we have discussed all these things.

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Precipitation-dissolution

- The dissolution in water of an electrolyte comprising a cation A^{+n} and an anion B^{-m} behaves according to the following reaction:

$$A_m B_n (S) = m A^{+n} (aq) + n B^{-m} (aq)$$

where (s) and (aq) stand for the solid and the aqueous phase, respectively.

- The equilibrium condition is


$$[A_m B_n (S)] = [A^{+n} (aq)]^m [B^{-m} (aq)]^n$$




which gives the conventional solubility expression

$$K_{so} = [A^{+n} (aq)]^m [B^{-m} (aq)]^n$$

where K_{so} is the solubility product, and [] activities.

- This formula assumes that the activity of the pure solid phase is set equal to unity











And then in terms of this you know dissolution of in water of an electrolyte comprising these cations and anions, we have discussed this example, in terms of the solubility product constant and the activities of those anions and cations.

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Precipitation-dissolution

- It is considered that a possible test to determine whether a solution is over or under saturated would be to check whether the dissolution free energy of the solid chemical is positive, negative or zero, and to compare the ion activity product (IAP) with K_{so} .
- The state of saturation of the solution with respect to a chemical in solid state is defined:
 - $IAP > K_{so}$ (Over saturated)
 - $IAP = K_{so}$ (Equilibrium, saturated)
 - $IAP < K_{so}$ (under saturated)



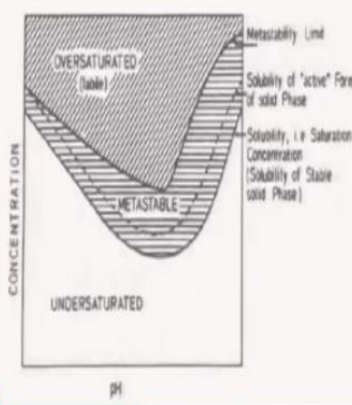




So, we have seen that ion activity product, how these ion activity products linked with this solubility product to infer whether the solution, when there will be over saturation or saturation or under saturation and in this 3 condition, how this precipitation and dissolution will occur.




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Precipitation-dissolution

- Oversaturation leads to the precipitation of the chemical
- A chemical substance can exist in more than one crystalline form but, except at a transition temperature, only one is thermodynamically stable for a given chemical composition of the system
- The metastable forms are more soluble than the stable ones



Yaron et al. (1996)

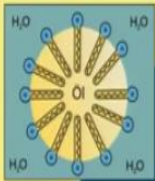








Then, we have seen the relationship between pH and concentration; I have shown you the zones of under saturation, zones of over saturation as well as the metastability limits and metastable zones.

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Effects of mixed solvents and surfactants

- Many of the potentially toxic organic chemicals reach the soil in a mixture of solvents or in formulations with dispersing agents (**surfactants**)
- The objective of such a formulation is to increase the solubility of the active compound in a solvent such as water
- In a solvent which forms nearly ideal solutions with another, and when the solubility of a third substance is limited to a low value by its crystal stability, the logarithm of its solubility is nearly a linear function of the mole fraction composition of the solvent









Then we have started a, we discussed an important aspect that is effect of mixed solvents and surfactants, we have discussed the you know, we have discussed the structure of the surfactants and how their solubility, how they act as a dispersing agent to increase the solubility of non-polar, you know non polar molecules in the water. So, what is their implication as far as the solubility of toxic organic chemicals like pesticides in water and their movement from one part of the environment to another part of the environment is concerned, we have discussed in details.

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Effects of mixed solvents and surfactants

- In the case of a pair of solvents in which the solubilities of the third substance differ greatly, these solvents - due to their different solvent powers - are generally much less soluble in one another and form miscible solutions which are far from linear











Then we have seen the effects of mixed solvents and surfactants.

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Effects of mixed solvents and surfactants

- The amount of solute dissolved in a mixture of two equal amounts of the solvents is **very much less than proportional** to the amount expected to be dissolved by the more powerful solvent.
- In the case of a powerful organic solvent miscible with water, a more nearly linear slope for the log solubility vs. solvent composition relationship is obtained if the composition is plotted as volume fraction rather than mole fraction.



We have discussed when there is a cosolvent in the water, how this mixture affects the, you know solubility of a third substance.

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Solvents and surfactants interaction


- Yalkowsky and Roseman (1981) and Rubino and Yalkowsky (1987) suggest the following equations for relating the solubility (S_m) of a nonpolar solute in a binary mixture of an organic solvent and water to that in pure water (S_w):




$$\log S_m = \log S_w + \sigma_s \cdot f_s$$

With,

$$\sigma_s = (A \log K_{ow} + B)$$

- where f_s is the volume fraction of the cosolvent in the binary mixed solvent.
- A and B are empirical constants dependent on cosolvent properties and K_{ow} is the organic solvent-water partition coefficient of the solute.











We have discussed this in terms of this, you know relationship between the solubility in a mixture of solvents, which is basically the summation of solubility in pure water plus this you know, this component that is sigma s you know, f_s , where this sigma s is basically you know taking this form $A \log K_{ow}$, where K_{ow} is the organic solvent water partition coefficient and A and B are basically the empirical constant depend on cosolvent properties.

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Cosolvent

- In chemistry, cosolvents are substances added to a primary solvent in small amounts to increase the solubility of a poorly-soluble compound.










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Multiple solvents and surfactants interaction

- We know that $\log S_m = \log S_w + \sigma_s \cdot f_s$.
- Extrapolating this equation to a complex mixture of multiple solvents-solute

$$\log S_m = \log S_w + \sum \sigma_i f_i$$
- where the subscript i indicates the i-th cosolvent.
- The solute mixtures of interest could comprise
 - a) two hydrophobic organic chemicals, or
 - b) one hydrophobic + one ionizable organic chemical.








So, we have discussed about the cosolvent and you know based on that what are the compositions, possible composition of this solid mixture we have discussed.

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Multiple solvents and surfactants interaction



- $\log S_m = \log S_w + \sum \sigma_i f_i$
- Crystalline salts of many organic acids and bases often have a maximum solubility in mixtures of water and water-miscible solvents.
- The ionic part of such a dissociable molecule requires a strongly polar solvent such as water to initiate dissociation.



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Solvents and surfactants interaction

- A mixture of water-miscible solvents hydrates and dissociates the ionic fraction of the solutes, and the water-miscible organic solvent accepts the remaining pollutants at a higher concentration than would either solvent alone.
- The deliberate use of a water-insoluble solvent as cosolvent in the formulation of toxic organic chemicals can lead to the increased solubility of hydrophobic organic chemicals in the aqueous phase and, consequently, to a potential increase in their transport from land surface to groundwater.

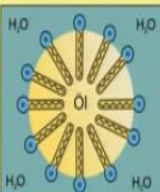






Then, we have discussed the solvent and surfactant interactions.

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Solvents and surfactants interaction in soil and ground water

- An increase in solubilization in water of nonpolar organic chemicals is obtained when surfactants are present in the water solution
- The solvent power of surfactants is much greater than that of a simple cosolvent
- The surfactant molecules are aggregated, forming a cluster of 20-200 units or more.
- The hydrophobic "tails" are extended to the interior of the cluster and the hydrophilic "heads" are oriented to the exterior, in contact with the water phase









How these hydrophobic tails are extended into the interior of the cluster in the hydrophilic heads are oriented to the exterior in contact with the water phase and how they affect the dissolution of non-polar compound in the polar water solvent.

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Solvents and surfactants interaction in soil and ground water

- The interior retains a normal nonpolar solvent power for nonpolar crystalline solutes.
- This type of dissolving action has been called solubilization despite the fact that it is not an appropriate name with regard to the mechanism involved
- The solubility of a crystalline solute of low water solubility cannot increase continuously with the expansion of the micelle



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Solvents and surfactants interaction in soil and ground water

- The limitation comes from the fact that the micelle cannot increase indefinitely in size without modifications of its structure and properties due to reorientation of surfactant molecules
- Example - the presence in municipal disposal sites of surfactants which can, in this way, enhance the solubilization of hydrophobic organic substances and their transport through soils.

Surfactant molecule

Emulsion of water in oil Emulsion of oil in water

Dispersion of solid in water Polymeric surfactant at oil/water

We have discussed all these things.

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Temperature effect in solubility

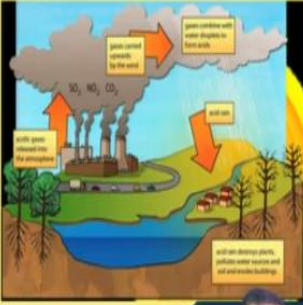
- The solubility in water of most inorganic and organic pollutants increases with temperature
- The temperature not only has a direct effect on chemical solubility in the soil aqueous phase but also has an indirect effect on the reactions
- The seasonal variation of temperature might affect the solubility of toxic chemicals in the soil solution

And also finally, we have discussed the temperature effect in the solubility, you know remember that the solubility in water of the most inorganic and organic pollutants increases with the temperature and the temperature not only has a direct effect on chemical solubility of the in the soil aqueous phase but also has an indirect effect on the reactions.

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Acid rains and soil system

- A classical example of a man-induced effect on the acid-base equilibrium in the soil liquid phase is the acid rain effect
- Acidic precipitation can be caused by natural (volcanoes) and man-made activities, such as from cars and in the generation of electricity
- The precursors of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion



<https://www.bbc.co.uk>

So, today we are going to start with the acid rains details about; detailed discussion about the acid rains and you know how they interact with the soil system and what is the relationship between acid rain and soil system. So, a classical example of man induced effect on the acid base equilibrium in the soil liquid phase is the acid rain effect. Now, we have already briefly talked about the acid rain effect in our previous lecture.

Remember that when there is an acidic precipitation and this acidic you know, we call it acid rain and this acidic precipitation generally occurs when there is a reaction of different gases with the water vapour which is present in the atmosphere creating different acids. So, acidic precipitation can be caused by natural volcanoes, as you can see it is a natural volcanoes and man-made activities.

So, man-made activities; what are the man-made activities? So, they can be you know, this gas can generate for example sulphur dioxide; this sulphur dioxide can be generated from the car exhaust you know and in the also, generation of the electricity also they can produce these gases. So, this acidic active you know, these gases when go to the you know, atmosphere and mix with you know water vapour, then it they produce the acidic rain.

Now the precursors of acid rain formation results from both natural sources such as volcanoes and decaying vegetation's and manmade sources you know, primarily emission of sulphur dioxide and this sulphur dioxide basically emit from different automobiles and nitrogen oxides you know, the nitrogen oxides can be represented as NO_x , resulting from fossil fuel combustion.

So, this when we you know, when we burn the fossil fuel either petroleum or coal, they basically you know generate the sulphur dioxide and nitrogen oxides and this sulphur dioxide as you can see these acidic gases released into the atmosphere and you know, for example sulphur dioxide, nitrogen dioxide and carbon dioxide. They can be also generated from the smokestack of you know industrial you know, industrial release.

So, gas carries to; after they are released these gases carried upwards by the wind and goes combined with the water droplet to form different acids. We are going to see the chemical reactions which are responsible for forming those acids and ultimately, then you know come back ultimately in the form of acid rain. So, acid rain basically what happens when there is an acid rain, acid rain basically destroy plants, pollutes water sources and erode different buildings and so these are some of the ill effects of the acid rains. So, we have seen that the precursor of this acid rain formation the mainly, the gases; sulphur dioxide and nitrogen oxides are forming as a result of fossil fuel combustion.

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Acid rains and soil system

- The burning of fossil fuels (coal and oil) by power-production companies and industries releases sulfur into the air that combines with oxygen to form sulfur dioxide (SO_2)
- Exhausts from cars cause the formation of nitrogen oxides in the air. From these gases, airborne sulfuric acid (H_2SO_4) and nitric acid (HNO_3) can be formed and be dissolved in the water vapor in the air

The diagram illustrates the process: smokestacks and cars release pollutants (SO_2 , NO_2 , CO_2) into the air. These gases combine with water droplets to form acid rain. The acid rain falls on a landscape, polluting water sources and eroding buildings.

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So, the burning of this fossil fuels like coal and petroleum by power production companies as we have seen here power production companies and industries release this sulphur into the air and combines with the oxygen into in the form of sulphur dioxide, so that is how a sulphur dioxide gas is produced. Now, exhaust from the cars cause the formation of nitrogen oxides in the air, from these gases you know airborne sulphuric acid.

For example, from this you know, from this sulphur dioxide, these airborne sulphuric acid and nitric acid, this nitric acid can form from this nitrogen oxides can be formed and dissolve into the water vapour in the air.

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Acid rains and soil system

1. Sulphuric acid and nitric acid are the major agents of acid rain.

a) Formation of Sulphuric acid:

$$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$$

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \text{ (Sulphuric acid)}$$

b) Formation of nitric acid

$$2\text{NO} + 3(\text{O}) \rightarrow \text{N}_2\text{O}_5$$

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \text{ (Nitric acid)}$$

2. Hydrochloric acid, nitrous acid and carbonic acid also contribute to acid rains.

a) Formation of carbonic acid

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \text{ (Carbonic acid)}$$

b) Formation of nitrous acid

$$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2$$

$$\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$$

$$\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2 \text{ (Nitrous acid)}$$

The diagram shows a factory emitting smoke containing SO_2 , NO , and CO_2 . These gases combine with water droplets in the air to form acid rain. The acid rain falls on a landscape with trees and a lake, where it can damage plants and pollute water sources.

So, these are some of the reactions which are responsible for producing the acid rains, so let us see. So, sulphuric acid and nitric acids are the major agents of the acid rains, they are the strong acids. So, let us consider the formation of sulphuric acid, as we have seen that sulphur dioxide, this sulphur dioxide which is produced by burning of the fossil fuels when they exhaust and then basically, reacts with the oxygen to form sulphur trioxide.

This sulphur trioxide when reacts with the water vapour, they will produce H_2SO_4 or sulphuric acid similarly, formation of nitric acids, here you can see nitric oxides, these nitric oxides when reacts with the oxygen, they produce N_2O_5 and this N_2O_5 when reacts with water vapour they produce this nitric acid and so you know, hydrochloric acid, nitrites and then nitrous acid and carbonic acids are also can contribute to acid rain.

So, major contribute of these acid rains are sulphuric acid and nitric acid, apart from that hydrochloric acid, nitrous acid and carbonic acids also contribute to acid rains. How carbonic acid form; we create is generated, this carbonic acid is generated because of the carbon dioxide reaction with the water vapour, as you can see here the carbonic acids, carbon dioxide when reacts with the water vapour, it produces the carbonic acid.

Formation of nitrous acids; so here you can see nitric oxides when it reacts with the ozone, it produce nitrogen dioxide and oxygen and you know these nitric oxides also can react with this nitrogen dioxide to produce this N_2O_3 and this N_2O_3 when reacts with the water vapour, it produces this nitrous acid. So, what we can see; we are seeing that the sulphur dioxides or the nitrogen oxides which are exhausting from which are emitting due to the industrial activities as well as the burning of the fossil fuels or car exhaust anthropogenic activities.

They basically undergoes to different reactions, chemical reactions and ultimately they reach into the atmosphere, mix with the water vapour and then form the acid and comes back into the soil in the form of acid rain.

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Acid rains and soil system

- If an acid rain reaches alkaline soils, the rain acidity is neutralized by the existing bases and the pH of the soil solution remains unchanged
- Where the buffering effect is lacking, the acid rain induces an increase in the acidity of the soil
- Although acid-rain gases may originate in urban areas, they are often carried for hundreds of miles in the atmosphere by winds into rural areas. That is why forests and lakes in the countryside can be harmed by acid rain that originates in cities

<https://www.scribd.com/>

The slide features a yellow background with a blue header and footer. The title 'Acid rains and soil system' is in bold blue text. The bullet points are in black text, with the first point's key phrase underlined. A photograph of a forest with dead, skeletal trees is on the right. The footer includes the Swamy logo and a circular emblem.

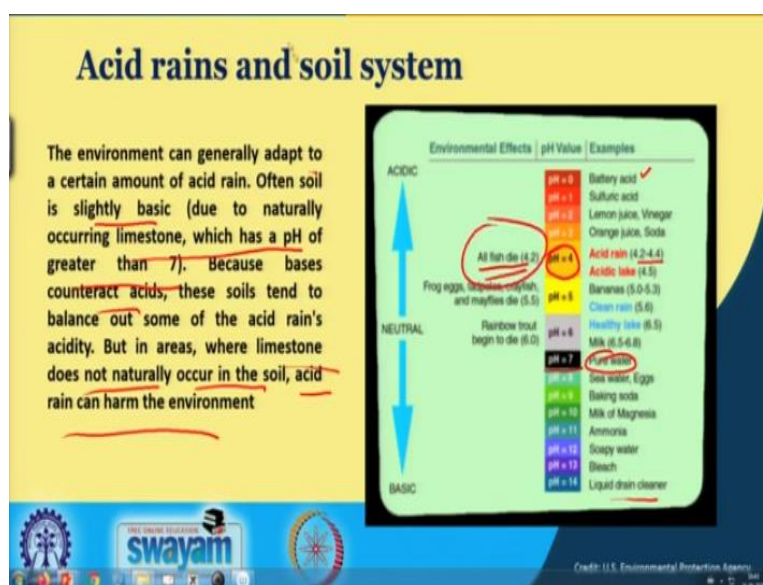
Now, if an acid rain reaches alkaline soils, the rain acidity is neutralized by the existing bases and the pH of the soil solution remains unchanged. So, again you know, if you know so to simplify this, when the acid rain which is basically acidic in nature, when reaches the alkaline soil, the rain acidity is neutralized because of the presence of the you know, bases in the alkaline soil by, in the alkaline soils and pH of the soil solution remains unchanged, so there is basically neutralization.

Where the buffering effect is lacking, let us consider a soil where the buffering effect is you know for example, the soil which has low amount of clay or low amount of organic matter, these soils are lacking their buffering capacity. So, when there is an acid rain in this type of soil, the acid rain induces an increase in the acidity of the soil, so although acid rain gases may originates in urban areas, they are often carried for 100's of miles in the atmosphere by

winds into the rural areas that is why forests and you know and lakes in the countryside, the rural areas can be harmed by acid rains that originate in the cities.

As you can see here this is a photograph of acid rain effect in the forest which is published by USGS, so you can see this, due to the acid drain a large tract of forest area are getting you know are getting affected and plants are getting defoliated. So, this is basically the interaction of acid rains in the soil solution.

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So the, if we see the pH of the you know acid rain, so obviously these chart or these graph will give you a better idea, this chart will give you better idea, so we can see in case of battery acid which is highly extremely acidic, the pH will be 0, whereas liquid drain cleaner which has the highly basic, are having the pH 14. When we are talking about pH 7 that is the pH of a pure water.

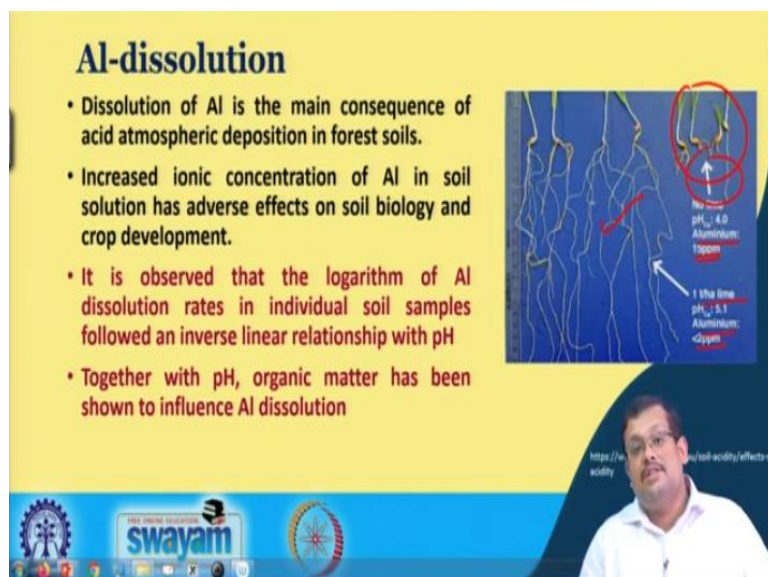
So, if we consider the acid rain you know, this acid and has a pH varies from 4.2 to 4.4 and so basically near about pH 4, we can see the as you know, the pH of an acid drain cleaner. So, basically these acid rain is highly acidic and as a result of these very low pH, all fish which are you know present in the aquatic body basically dies. So, this is basically giving an idea about the pH of the acid rain.

So, the environment can generally add up to a certain amount of acid rain and you know often soil you know, when the often the soil is slightly basic due to the naturally occurring limestone which is a pH greater than 7, now because bases counteract the acids which have

already discussed in the last slide. So, base is basically counteracts acid and this soils tends to balance out some of the acid rain's acidity.

But in areas, where limestone does not naturally occur in the soil or in the areas where the soil lacks the normal buffering capacity, acid rain can harm the environment as you can see here.

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Al-dissolution

- Dissolution of Al is the main consequence of acid atmospheric deposition in forest soils.
- Increased ionic concentration of Al in soil solution has adverse effects on soil biology and crop development.
- It is observed that the logarithm of Al dissolution rates in individual soil samples followed an inverse linear relationship with pH
- Together with pH, organic matter has been shown to influence Al dissolution

The diagram shows a cross-section of soil with roots. A red circle highlights a root tip in a region labeled 'pH = 4.0 Aluminium: 10ppm'. An arrow points to another root tip in a region labeled '1 the time pH = 5.1 Aluminium: <1ppm'. A URL 'https://www.swayam.academy' is visible in the bottom right corner of the slide.

So, let us talk about another important thing, so we have completed the acid rain, let us talk about another important thing that is aluminium dissolution. Now, aluminium is a you know, aluminium is an element which you can see or aluminium is a metal which you can see in high concentration in acidic condition. Now, remember that the dissolution of aluminium is the main consequence of acid atmospheric deposition in forest soils.

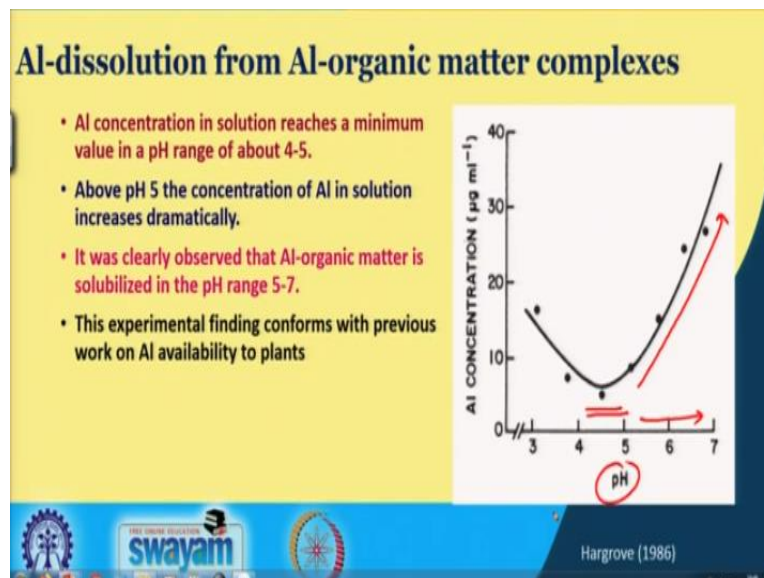
So, increase in ionic concentration of aluminium in soil solution has adverse effects on soil biology and crop development. So, basically again the dissolution of aluminium in the, is the main consequence of acid atmospheric deposition of forest soil. As a result of acid deposition or acid rain, the aluminium activity in the soil solution quite increase and these ionic activity you know increase ionic activity of aluminium has an adverse effect on soil biology and crop development.

This picture can give you a better idea about the you know ill effects of aluminium concentration in the soil solution, as you can see here these are you know, the roots which are grown with an aluminium concentration of less than 2 ppm, whereas and here also, here the

aluminium is here 15 ppm. Now, here the difference basically is here in this case we are applying 1 ton per hectare lime and here we are not applying lime to neutralize the acidity.

So, obviously when we are adding lime to neutralize this acidity, we can see that there is normal growth of the roots however, when there is no application of lime obviously their concentration of aluminium increases which adversely affect the root growth which you can see in this picture. So, it is observed that the logarithm of aluminium dissolution rates in the individual soil samples followed an inverse linear relationship with pH. Now, remember that together with pH, organic matter has been shown to influence the aluminium dissolution, how? Let us see in our next slide.

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So, this graph basically shows the relationship of aluminium concentration in microgram per ml and pH, so here basically this graph is showing aluminium dissolution from aluminium organic matter complexes. So, one thing is clear that aluminium concentration in solution reaches a minimum value in a pH range of about 4 to 5. So, in this region the aluminium concentration in the solution reaches a minimum value.

Now, above this pH 5, the concentration of the aluminium in solution increases dramatically as you can see it is increasing with the steep slope and it is clearly observed that aluminium organic matter is solubilized in the pH range of 5 to 7. So, obviously when there is a solubilisation, aluminium concentration in the soil solution will increase and this experimental finding conforms with previous work of aluminium availability with the plants.

So, these basically shows the aluminium dissolution from aluminium organic matter complexes and how this dissolution of this aluminium, from these aluminium organic matter complexes are influenced by the pH of the soil solution.

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Alkaline soils and gypsum dissolution

- Soil salinization could affect the soil properties as well as the gypsum balance
- The distribution of gypsum depends on the natural constituents or on the human activities

<https://agropedia.org/soil-for-clay-soil/>

The slide features a yellow background with a blue footer. The footer contains logos for 'swayam' and 'INDIA RISE, CHINA FEAR'. A photograph of a person in a blue shirt and shorts standing in a field of brown soil is positioned to the right of the text. A small inset photo of a man in a white shirt is in the bottom right corner.

So, another important thing which we need to discuss is the alkaline soils and gypsum dissolution. Now, you know what are the alkaline soil; alkaline soils are those soils in which the exchange complex is saturated with the sodium ions and as a result of the saturation of the sodium ions you know, the soil becomes alkaline in nature. The alkaline soil are having high pH and the alkali soils or alkaline soils are not good for crop production.

Why? Because they have unfavourable physical conditions, what are those unfavourable physical conditions; due to the presence of sodium, the soil particles are dispersed, they do not form the aggregates and as a result of that, the zeta potential is quite high. As a result of high zeta potential, the flocculation never occurs and these individual particles basically block the entry of moisture or soil water through infiltration or exchange of gases from the atmosphere to the soil air.

And as a result of that these alkaline soils are not good for crop growth, so these alkaline soils need to be reclaim you know, for the reclamation of this alkaline soil the you know, farmers generally use gypsum which is basically calcium sulphate dihydrate and these since the salinization or alkalinisation could affect the soil properties as well as the gypsum balance. So, the distribution of gypsum depends on the natural constituents or on the human activities.

So, generally to counteract the ill effects of alkaline soil we generally apply gypsum; gypsum is basically calcium sulphate dihydrate and this gypsum, the calcium from the gypsum can replace the sodium in the exchange complex and as a result, the clay start you know starts to flocculate or forming the aggregate. So that is why we generally apply the gypsum in the alkaline soil. As you can see here in this picture you know farmers are spreading the gypsum, dusted gypsum in the alkaline soil.

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Alkaline soils and gypsum dissolution

- The dissolution of gypsum in the soil profile could be changed as a result of alkalinity
- The effective solubility of gypsum depends on the soil solution and exchange phase composition
- The dissolution exchange reaction –
$$2\text{NaX} + \text{CaSO}_4 = \text{CaX}_2 + 2\text{Na}^+ + \text{SO}_4^{2-}$$



So, the dissolution; let us consider the dissolution of the gypsum in the alkaline soil, so the dissolution of the gypsum in the alkaline soil profile could be you know, change as a result of alkalinity. Now, the effective solubility of gypsum basically depends on the soil solution and exchange phase composition. So, let us see how it occurs, so the dissolution of exchange reaction, dissolution exchange reaction as you can see, so the exchange complex was previously saturated by sodium ions.

So 2, let us consider these 2 sodium ions was attached or adsorbed into the mixture into the clay surface and when we are applying the calcium sulphate, the calcium basically replace this sodium which basically comes into the soil solution. So, as a result of that the calcium binds the you know soil particles and forming the aggregate.

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Sodic water and gypsum dissolution

- Irrigation with sodic water brings an increase in the exchangeable Na^+ in the soil complex
- Under such conditions, the dissolution of CaSO_4 will increase, to compensate for the Na^+ which is exchanged with Ca^{2+} in the soil

<http://www.agriculture.gov.in/sodict>

So, the sodic soils or alkali soils are basically, you know the sodium saturated soils, so irrigation with sodic water, if we just do the irrigation with sodic water brings an increase in the exchangeable sodium in the soil complex and creates the unfavourable condition as you can see in this picture and so under such conditions, the dissolution of calcium sulphate will increase to compensate for the sodium which is exchanged with the calcium in the soil.



As you can see this is an ill effect of you know of the sodic soil, as you can see here the exchange complex has nil sodium, here it has got slightly higher sodium content and in this condition they have moderate sodium concentration in the exchange complex and here it has severe sodium concentration in the exchange complex. So, you know as you can see from this slide, from this soil to this soil, there is a, you know continuous increase in sodium concentration.

As a result of that you can see here the degree of dispersion is continuously also increasing with the increase in sodicity, so here this soil is you know highly aggregated and these soils are increasingly disaggregated. So, under such conditions when these you know when the sodicity is increasing in the soil, you know the dissolution of calcium sulfate is also increased because this calcium from this calcium sulphate competes from the exchange site in the soil and thereby replace those sodium from the exchange site to form the aggregates or you know to form the flocculates. So, this is basically the dissolution of gypsum in sodic soils.

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Sodic water and gypsum dissolution

- It has been reported that effective gypsum solubility is enhanced through ion-pair formation and electrolyte effects
- Under these conditions, the amount of water required for dissolution of gypsum in alkaline soils is likely to be much less than commonly inferred from gypsum solubility in water



It has been reported that effective gypsum solubility is enhanced through ion pair formation and electrolyte effects, under this conditions the amount of water required for dissolution of gypsum in alkaline soil is likely to be much less than commonly inferred from gypsum solubility in water. Again, the effective gypsum solubility is enhanced through the ion pair formation.

What is ion pair we will discuss and the electrolyte effects, in this conditions the amount of water which is generally required for dissolution of gypsum in alkaline soil, you know here we will require much less than commonly you know what we see which is required for gypsum solubility in the water. So, let us wrap up our lecture here, in this lecture we have discussed the acid rain effect and their interaction with the soil system.

Also, we have seen the sodic soil and how the gypsum solubility is influenced in the sodic soils and also we have seen the aluminium, you know aluminium solubility from the organic matter complexes, aluminium organic matter complexes and how they are impacted by variable pH. So, I hope that you have learnt something new in this lecture, let us wrap up this lecture here.

And the next lecture will be discussing more about you know ion pair effects, what is ion pair which I have discussed here, what is the ion pair and other aspects of pollutant and soil solution interactions. So, feel free to email me or feel free to let me know, if you have any questions, I hope that you know these are pretty self-explanatory, if you need any explanation

just let me know and feel free to email me, I will be more than happy to answer your queries.

Thank you very much, let us meet in our next lecture.