Environmental Soil Chemistry

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Lecture – 44
Pollutant-Soil Solution Interaction (Contd.,)

Welcome friends to this fourth lecture of our module 9 or week 9 and in this week we are talking about the pollutant and soil solution interactions. So in our previous three lectures we have discussed several aspects of pollutants and their interaction with the soil solution. We have discussed the different dynamics of the pollutants which are soluble in water and how they can interact with different phases.

And also we have discussed the heavy metal dynamics in the soil solution. We have discussed different acid-base equilibria and other solubility equilibria. We have discussed the acid rain effects and also we have discussed solubility of aluminum from the aluminum organic matter complexes and also we have discussed the dissolution of gypsum in the sodic soils. So, in our last lecture while wrapping up we have talked about the ion pair effect in the dissolution of sodium. So let us see what is ion pair?

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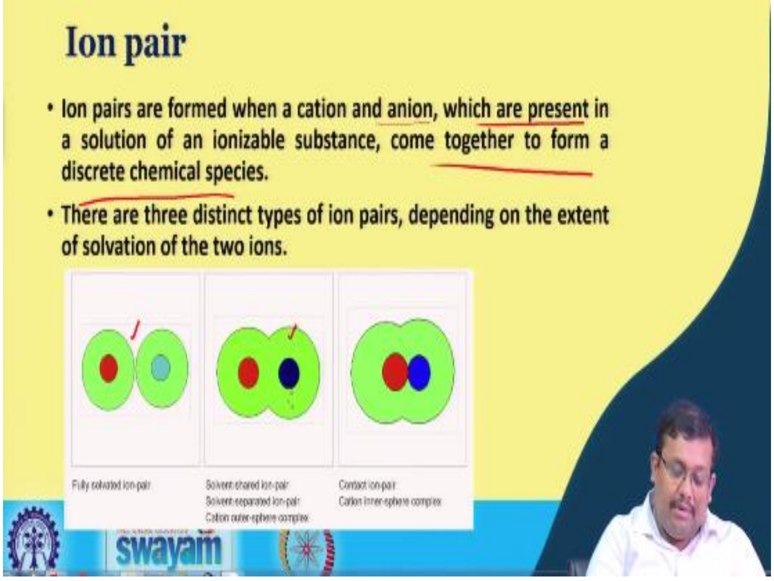

Ion pair

- Ion pairs are formed when a cation and anion, which are present in a solution of an ionizable substance, come together to form a discrete chemical species.
- There are three distinct types of ion pairs, depending on the extent of solvation of the two ions.

Now ion pairs in chemistry ion pairs are basically formed when a cation and anion which are present in a solution of an ionizable substance come together to form a discrete chemical species. So again when the anion or cation which are present in a solution of an ionizable substance come together to form a discrete chemical species and there are three distinct types of ion pairs depending on the extent of solvation of the two ions.

We can see here in this picture once the fully solvated ion pair where this cations or anions are fully solvated and then we can see that solvent shared ion pairs you can see the solvent as shared between these ion pairs or solvent separated ion pair or cation outer sphere complex. So examples are so basically this is solvent shared ion pair and again the third category is basically you can see when the cations and anions are basically in their contact of each other.

So that is called the contact ion pair. So it is fully solvated ion pair, this is solvent share ion pair and this is contact ion pair. So this is ion pair effect has a considerable influence in the gypsum solubility in the sodic soil.

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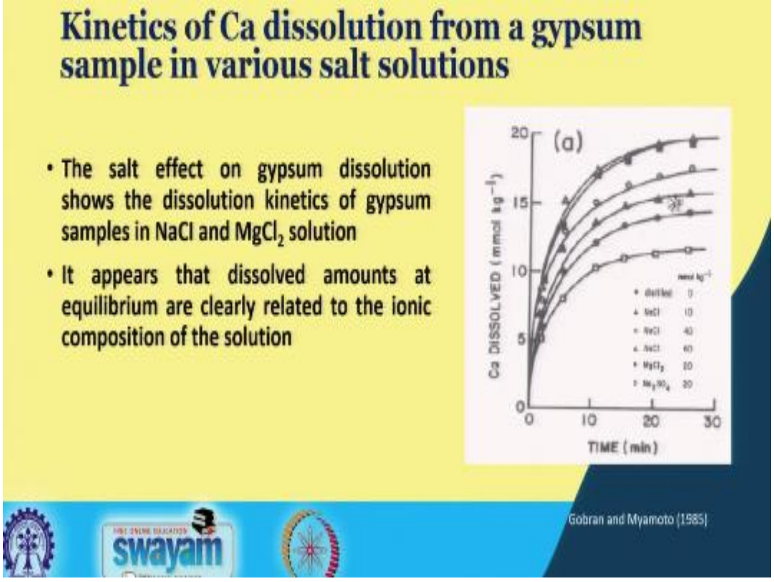

Kinetics of Ca dissolution from a gypsum sample in various salt solutions

- The salt effect on gypsum dissolution shows the dissolution kinetics of gypsum samples in NaCl and $MgCl_2$ solution
- It appears that dissolved amounts at equilibrium are clearly related to the ionic composition of the solution

Gobran and Myamoto (1985)

So if you see the kinetics of calcium dissolution from a gypsum sample in various salt solutions. We can see this type of relationship. This relationship is basically showing the salt effect on gypsum dissolution. In other words, it is calcium dissolution of gypsum. So the salt effect on gypsum dissolution shows the dissolution kinetics of gypsum samples in sodium chloride and magnesium chloride solution.

So you can see here there are different concentration of sodium chloride so for example this one is 10 millimole per kg concentration and also this is 40 millimole per kg concentration and this is 60 millimoles per kg concentration and as far as the magnesium chloride is concerned we can see here this is 20 millimole kg concentration and this is basically sodium sulfate which is showing 20 millimole per kg concentration.

So basically this is showing the calcium dissolution or gypsum dissolution dynamics with respect to time which is basically influenced by different concentration of different salt solution. So it appears that dissolved amount at equilibrium are clearly related to the ionic composition of the solution. So depending on the ionic composition we can see that dissolved amount are at equilibrium.

So what are the other inference from this figure. We can see that the dissolution rate is only apparently different. So we can see the dissolution rates are basically having the similar type of the changes of calcium dissolution rate is showing with respect to time is basically showing the similar type of trend.

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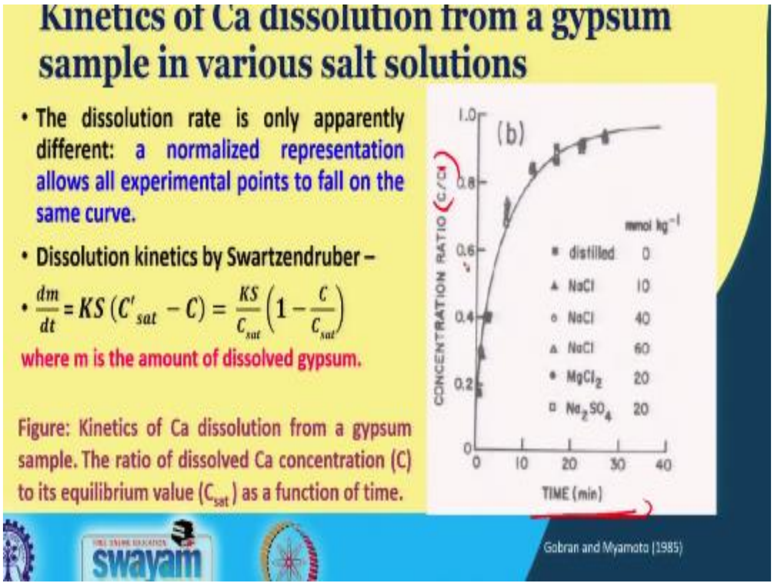

Kinetics of Ca dissolution from a gypsum sample in various salt solutions

- The dissolution rate is only apparently different: a normalized representation allows all experimental points to fall on the same curve.
- Dissolution kinetics by Swartzendruber –
- $\frac{dm}{dt} = KS\,(C'_{sat} - C) = \frac{KS}{C_{sat}}\left(1 - \frac{C}{C_{sat}}\right)$

where m is the amount of dissolved gypsum.

Figure: Kinetics of Ca dissolution from a gypsum sample. The ratio of dissolved Ca concentration (C) to its equilibrium value (C_{sat}) as a function of time.

Gobran and Myamoto (1985)

And if we basically normalize these graphs we can see these representation. So basically in a normalized representation allows all the experimental points to fall on a same curve. So basically all the individual curves when we normalize will basically fall in this curve. So basically we see that the concentration ratio which is denoted by this C / Cl is basically or C / C sorry is basically increase with the passing of time.

So as the time increase there is an increase of this concentration ratio. So basically in this figure it is showing the kinetics of calcium dissolution from a gypsum where the ratio of dissolved calcium concentration to its equilibrium values. So basically this is calcium equilibrium value as a function of time. So we can see these ratio is continuously increasing when you are increasing the time.

So this dissolution kinetics can be expressed by the formula or the relationship given by this Swartzendruber and this relationship basically tells dm / dt = KS multiplied by C dash sat so saturation – C = KS / C sat 1 – C sat. This C basically stands for calcium concentration and this C sat is basically the equilibrium value. So this relationship can be expressed in terms of this relationship this mathematical relation.

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Sludge effect on potentially toxic inorganic trace element solubility

So we have covered the dissolution kinetics of gypsum. Now it is time to discuss another very important issue that is sludge and its effect on potentially toxic inorganic trace element solubility.

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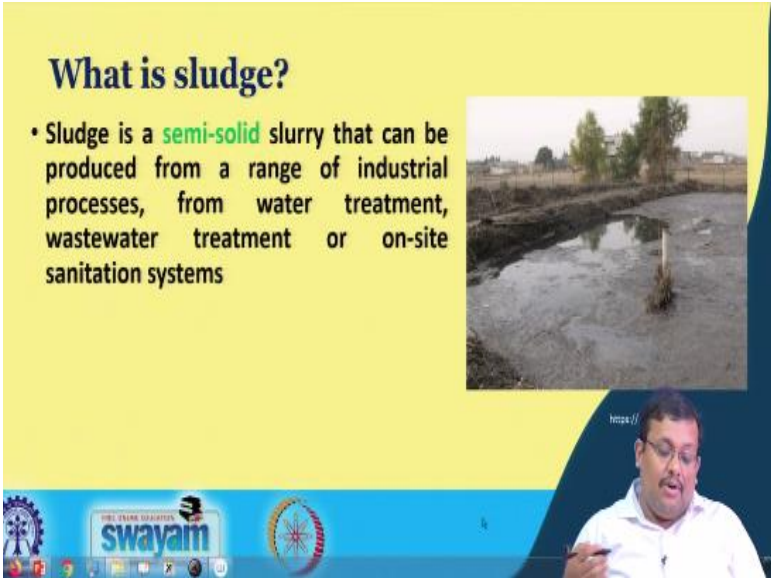

What is sludge?

- Sludge is a semi-solid slurry that can be produced from a range of industrial processes, from water treatment, wastewater treatment or on-site sanitation systems

So all of you must know about the sludge so what sludge you know that it is a semi-solid slurry that can be produced from a range of industrial processes, from water treatment, wastewater treatment or onsite sanitation systems. So you can see this is the semi solid slurry called sludge which can be produced from different industrial processes, anthropogenic processes, water treatment or wastewater treatment or onsite sanitation system.

So you can see this is frequently this can be frequently seen especially in urban areas. So this is a potential source of pollutant because it carries huge load of different organic and inorganic pollutants in the inorganic pollutants the heavy metals and trace elements are important and as far as organic chemicals are concerned there are different toxic organic chemicals which are loaded in this sludge.

So obviously the interaction of sludge with the soil system is very important and needs to be learned if we want to have a comprehensive idea about the pollutant and soil solution interaction.

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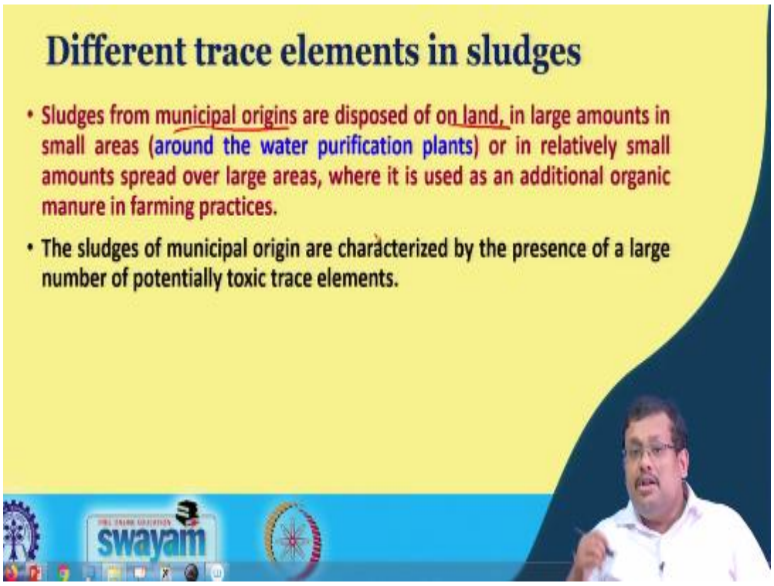

Different trace elements in sludges

- Sludges from municipal origins are disposed of on land, in large amounts in small areas (around the water purification plants) or in relatively small amounts spread over large areas, where it is used as an additional organic manure in farming practices.
- The sludges of municipal origin are characterized by the presence of a large number of potentially toxic trace elements.

So what are the different trace elements in the sludges? I have already told you that the sludge contains different trace elements. So sludge from municipal origins are disposed of land and in large amount in small areas around the water purification plants or in relatively small amount spread over large areas where it is used as a additional organic manure in farming practices.

So again this large are basically generated from this municipal origins and disposed of on the land in large amounts in the small areas. So for example nearby some water purification plants or in relatively small amount spread over the larger areas basically as a mean of addition of organic manure for farming practices. The sludge of municipal origin are characterized by the presence of a large number of potentially toxic trace elements. Now this municipal sludge are loaded with different heavy metals or trace elements which can create considerable toxicity in the soil.

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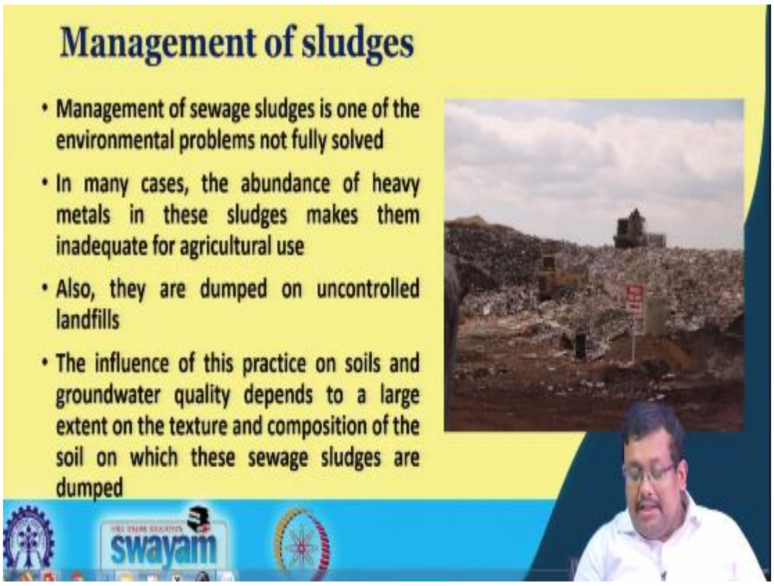

Management of sludges

- Management of sewage sludges is one of the environmental problems not fully solved
- In many cases, the abundance of heavy metals in these sludges makes them inadequate for agricultural use
- Also, they are dumped on uncontrolled landfills
- The influence of this practice on soils and groundwater quality depends to a large extent on the texture and composition of the soil on which these sewage sludges are dumped

So let us see those if we consider the management of the sludges. The management of sewage sludge is one of the environmental problems which are not fully solved yet obviously there are some problems. So the management of sewage sludge is a big challenge for the environmental scientist. Now in many areas the abundance of heavy metals in this sludges make them inadequate for agricultural use.

Obviously you do not want to add this in terms of manure in the field to create further problem, to encourage the bio accumulation. So, in many cases these abundance of these heavy metals are the reason that is why due to the presence of huge amount of organic matter which is considered to increase which is expected to increase the natural fertility of the soil it is not generally used because of the presence of this heavy metals.

Also they are dumped on uncontrolled landfills. So landfills are the regions where you can see the municipal solid waste are basically dumped. So in this dumped in this uncontrolled dumped sides or landfills you can see huge amount of this municipal sludges are being dumped. So the influence of this practice on the soils and groundwater quality depends to a large extent on the texture and composition of the soil on which this sewage sludges are dumped.

It is quite natural because of the different soil physical chemical properties the movement of heavy metals or other organic chemical from this sludge is impacted by the physical condition or physico-chemical condition of the soil on which it is dumped. If the soil texture based on the soil texture the movement or mobility of these heavy metals can be influenced and also the organic chemicals also can move through the soil column based on the different soil properties.

So soil texture and composition are very, very important for the mobility of these heavy metals, trace elements or organic chemicals from the soil to groundwater. If the texture is sandy obviously there will be more movement of these toxic or organic chemicals or heavy metals down to the groundwater and ultimately creating the groundwater pollution.

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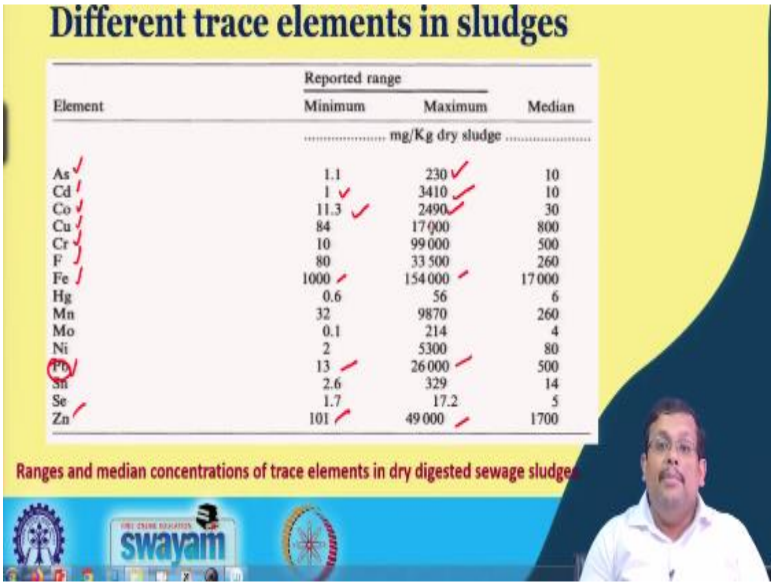

Different trace elements in sludges

Element	Reported range Minimum	 Maximum	Median
	.... mg/Kg dry sludge		....
As	1.1	230	10
Cd	1	3410	10
Co	11.3	2490	30
Cu	84	17 000	800
Cr	10	99 000	500
F	80	33 500	260
Fe	1000	154 000	17 000
Hg	0.6	56	6
Mn	32	9870	260
Mo	0.1	214	4
Ni	2	5300	80
Pb	13	26 000	500
Sn	2.6	329	14
Se	1.7	17.2	5
Zn	101	49 000	1700

Ranges and median concentrations of trace elements in dry digested sewage sludges

So different trace elements in the sludges if you see here one table which is published by chainy in 1983 we can see that these are the concentration of different heavy metals and trace elements Pb is a heavy metal and so these are the trace elements and if you see the concentration, they generally show a wide range of variability starting from if you consider arsenic it shows wide range of variability from 1.1 PPM or milligram per kg of dry sludge to 230 PPM.

Then cadmium which varies from 1 to 23410 and copper which varies from 11.3 to 2490 and so on and so forth. As compared to lead in respect to the lead you can see wide variation starting from 13 PPM to 26,000 PPM. In case of zinc it varies from 101 to 49,000 PPM. So 49,000 PPM means 4.9% which is quite high. So, similarly iron from 1,000 PPM to 154,000 PPM. So you can see that how this sludges shows the wide variability of this trace elements sometimes which is beyond the permissible limit and these are the median values of those data.

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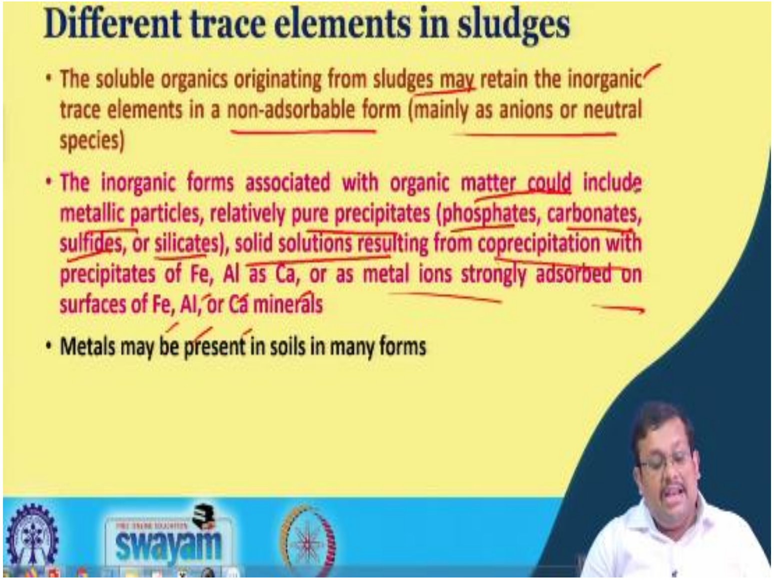

Different trace elements in sludges

- The soluble organics originating from sludges may retain the inorganic trace elements in a non-adsorbable form (mainly as anions or neutral species)
- The inorganic forms associated with organic matter could include metallic particles, relatively pure precipitates (phosphates, carbonates, sulfides, or silicates), solid solutions resulting from coprecipitation with precipitates of Fe, Al as Ca, or as metal ions strongly adsorbed on surfaces of Fe, Al, or Ca minerals
- Metals may be present in soils in many forms

So the soluble organics which are originating from sludges may retain the inorganic trace elements in a non absorbable form which is mainly as anion or neutral species. So the soluble organics which are also originating from sludge may retain in the inorganic trace elements. These inorganic trace elements basically retain in the sludge is non-adsorbable form mainly as anions or neutral species.

Now the inorganic forms associated with organic matter could include different forms what are those. Metallic particle it could be metallic particles relatively pure precipitates what are those relatively pure precipitates phosphates, carbonates, sulfides or silicates. So you can see these are the relatively pure precipitates like phosphate, carbonates, sulfides and silicates which you can see are associated with the organic matter in the sludge.

Also the sludge contains solid solutions resulting from co precipitation with precipitates of iron, aluminum and calcium or as metal ion strongly adsorbed on the surfaces of the iron, aluminum and calcium minerals. So you can see that this trace elements can be present in the sludge in different forms and also metals maybe present in soils in many forms. So basically you can see that either they can be this trace elements can be present as metallic particles or precipitates or solute solutions or co precipitation or strongly adsorbed. So there are different forms in which they are present in the sludge and ultimately creating the environmental problem.

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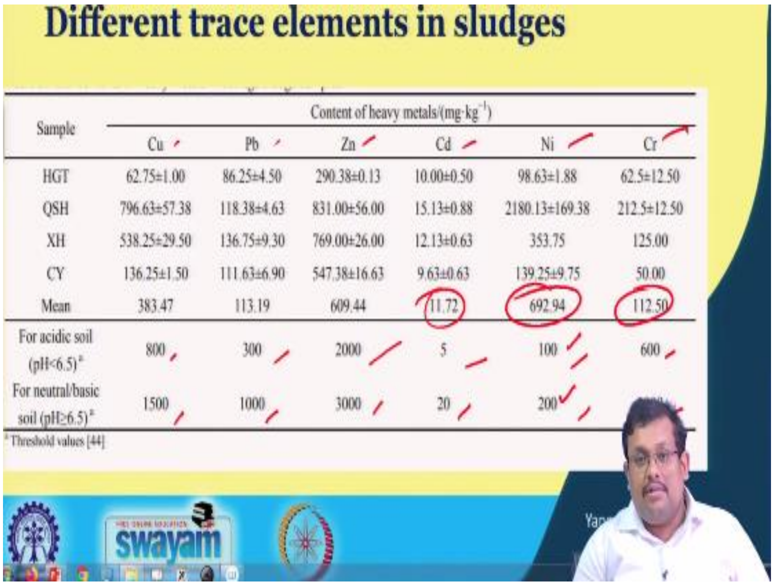

Different trace elements in sludges

Sample	Content of heavy metals/(mg·kg^{-1})					
	Cu	Pb	Zn	Cd	Ni	Cr
HGT	62.75±1.00	86.25±4.50	290.38±0.13	10.00±0.50	98.63±1.88	62.5±12.50
QSH	796.63±57.38	118.38±4.63	831.00±56.00	15.13±0.88	2180.13±169.38	212.5±12.50
XH	538.25±29.50	136.75±9.30	769.00±26.00	12.13±0.63	353.75	125.00
CY	136.25±1.50	111.63±6.90	547.38±16.63	9.63±0.63	139.25±9.75	50.00
Mean	383.47	113.19	609.44	11.72	692.94	112.50
For acidic soil (pH<6.5)^a	800	300	2000	5	100	600
For neutral/basic soil (pH≥6.5)^a	1500	1000	3000	20	200	[illegible]

^{a} Threshold values [44]

So this is another data which we can see that produced by Yang et al in 2017. We can see that the content of heavy metals for example copper, lead, zinc, cadmium, nickel and chromium how they are varying in different parts of the study area. So we can see that for acidic soil these are the threshold values that means the permissible values for example 800 PPM for copper, 300 PPM for lead, 2,000 PPM for zinc, 5 PPM for cadmium, 100 PPM for nickel and 600 PPM for chromium.

And for neutral and basic soil the corresponding values are 1,500 PPM for copper, for lead it is 1,000 PPM for zinc it is 3,000 PPM, for cadmium it is 20 PPM, for nickel it is 200 PPM, for chromium it is 1,000 PPM. So if we consider the mean values which they calculate from different areas you can see that as far as the cadmium is concerned it is showing higher than the threshold value for the acidic soil in case of acidic soils.

And also the nickel concentration is quite high which is around 600 mean nickel concentration is 692.94 PPM which is quite high than the threshold values of both acidic soil as well as the neutral or basic soils. As far as the chromium is concerned the values are less than the threshold values of acidic soil. So obviously that shows the wide variation of different heavy metals which are present in the sludge and how they can sum of them above the threshold limits permissible threshold limits.

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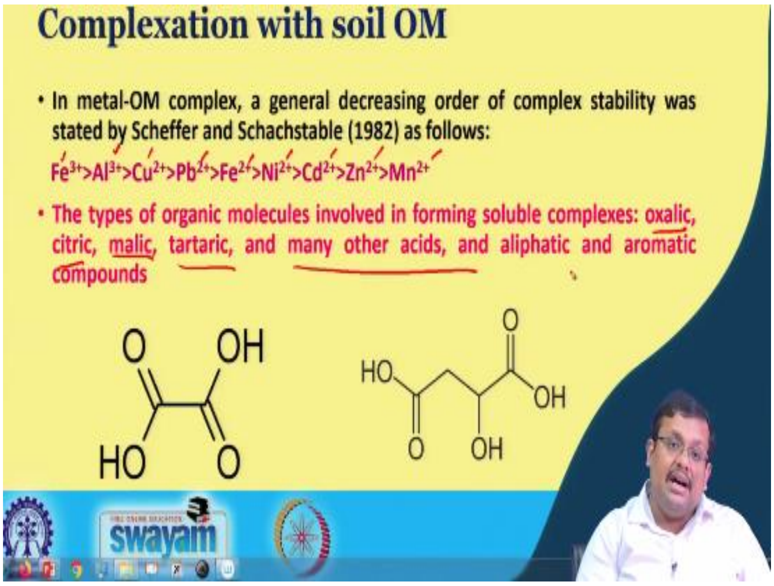

Complexation with soil OM

- In metal-OM complex, a general decreasing order of complex stability was stated by Scheffer and Schachstable (1982) as follows: $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Fe^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+}$
- The types of organic molecules involved in forming soluble complexes: oxalic, citric, malic, tartaric, and many other acids, and aliphatic and aromatic compounds

Now if you see the complex session with soil organic matter you know in the metal organic metal complex a general decreasing order of complex stability was stated by this so two scientist Scheffer and Schachstable in 1982 and this is decreasing order of complex stability can be found when the highest of Fe3 + aluminum 3 + then copper, then lead, then Fe2 + or ferrous, nickel, cadmium, zinc and manganese.

So this is basically showing the decreasing order of complex stability. So obviously iron has the highest and manganese has the lowest. So the type of organic molecules which are involved in forming the soluble complexes are basically oxalic acids, citric acids, malic acids, tartaric acid and many other acids and aliphatic and aromatic compounds and these acid basically complex with these heavy metals in the sludge.

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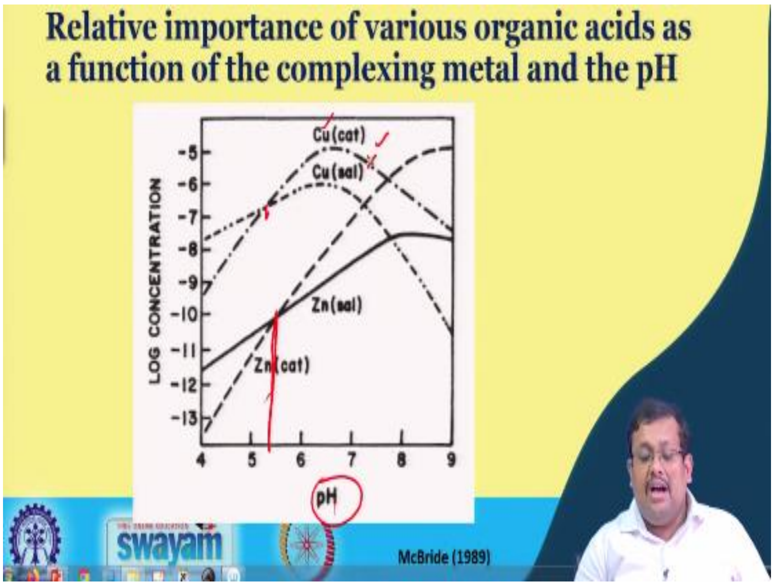

Relative importance of various organic acids as a function of the complexing metal and the pH

McBride (1989)

So another important graph is there which was shown by Mcbride in 1989 which shows the relative importance of various organic acids as a function of the complex session of metal and pH we can see the log of concentration if you plot that in the y axis and pH in the x axis that shows there are two metals one is zinc another is copper and there are two types of organic complexes that is catechol complex and salicylate complex for both the elements.

We can see that up to pH around 5.5 the concentration the binding capability of zinc salicylate is higher than that zinc catechol and then when these threshold level is achieved then this zinc catechol showing the higher complexing ability than that of zinc salicylate. In case of copper it shows for the same at pH4 it shows quite high complexing capacity where up to pH around 5 these copper salicylate shows higher binding capacity or complex forming capacity.

However, when the pH goes beyond 5 then the complexing capacity of copper catechol is increased than copper salicylate. So that shows the importance of pH for determining the complex formation of different organic acids with the metals and this plays a very important role for these metal dynamics of the heavy metals in the sludge when they are dumped into the soil surface.

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Complex formation at different pH

- Cu (catechol)$_2^{2+}$ dominates over the Cu (catechol)$_2^0$ species above pH 7.6
- Cu is predicted to be almost totally complexed with catechol at high pH
- Catecholate ligand is a better electron donor than salicylate

So if you see that the copper catechol 2 + so basically this species basically dominates over the copper catechol 2 0 species above pH 7.6. So if you see that pH 7.6 around this pH 7.6 this copper catechol dominates over copper catechol 2 0 species and copper is precipitated to be almost totally complex with catechol at high pH and catecholate ligand is better electron donor than that of salicylate ligand.

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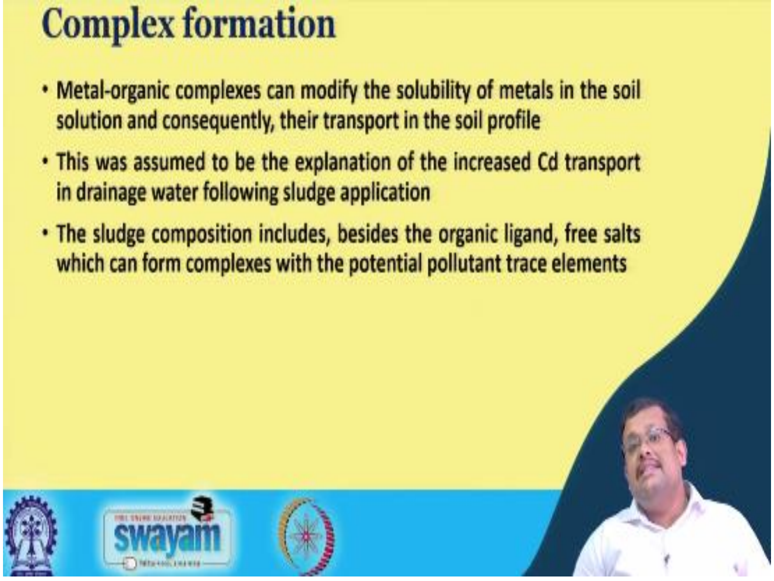

Complex formation

- Metal-organic complexes can modify the solubility of metals in the soil solution and consequently, their transport in the soil profile
- This was assumed to be the explanation of the increased Cd transport in drainage water following sludge application
- The sludge composition includes, besides the organic ligand, free salts which can form complexes with the potential pollutant trace elements

Also we have seen that the metal organic complex can modify the solubility of metals in the soil solution and consequently their transport in the soil profile and this basically this solubility modification was assumed to be the explanation of the increased cadmium transport in drainage water following the sludge application. Remember the sludge composition basically includes besides the organic ligands free salts which can form the complexes with the potential pollutant trace elements.

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Impact of redox processes on metal solubility

- The dissolution of trace elements into the soil liquid phase and their redistribution into the porous media between the land surface and the groundwater is also affected by the redox reactions occurring in the soil medium.
- The redox process could occur in the whole soil profile under saturation or drying conditions
- In unsaturated soils the processes of reduction and oxidation proceed simultaneously at the aggregate soil level - reduction into the soil aggregate and oxidation at the aggregate surface

So let us see the impacts of redox process on metal solubility. So if we see that the dissolution of the trace elements into the soil liquid phase and their redistribution into the porous media between the land surface and the groundwater is also affected by the redox reactions. We have already discussed this redox reactions extensively in our previous lectures.

So the redox process could occur in the whole soil profile under the saturation or the drying conditions. Now in case of unsaturated soil the process of reduction and oxidation these redox reaction proceed simultaneously at the aggregate soil level and reduction into the soil aggregates and oxidation at the aggregate surface obviously at the aggregate surface that is more in direct contact with the air.

So obviously there will be oxidation and in the aggregate when there is less contact with the external oxygen or air then obviously there will be reduction. So we can see in an unsaturated soil the process the redox process basically goes side by side simultaneously at the aggregate soil level and you can see this is the picture of redox reactions which is undergoing in the soil which is you can see the coloration the change in coloration in the soil as a result of redox processes. So this shows very important implication for metal solubility.

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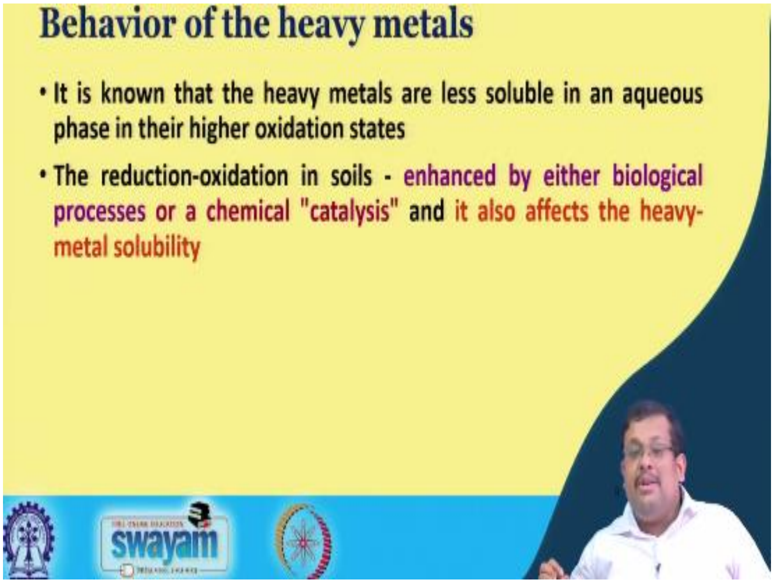

Behavior of the heavy metals

- It is known that the heavy metals are less soluble in an aqueous phase in their higher oxidation states
- The reduction-oxidation in soils - enhanced by either biological processes or a chemical "catalysis" and it also affects the heavy-metal solubility

Now it is known that the heavy metals are less soluble in an aqueous phase in their higher oxidation states. So the reduction oxidation in soils are basically enhanced by either biological processes or a chemical catalysis and it is also affects the heavy metal solubility. So we know that the heavy metals when they are present in the higher oxidation states they are less soluble in aqueous phase.

So when the redox reaction in the soil are basically biologically mediated so these biological or chemical catalysis is generally used to enhance this redox process it also affects the heavy metal solubility by changing the oxidation status. So this is how the redox potential or redox reaction has a profound influence on the heavy metal solubility and this is playing a very important role for heavy metal contamination when you are applying the sludge in the soil surface and their mobility.

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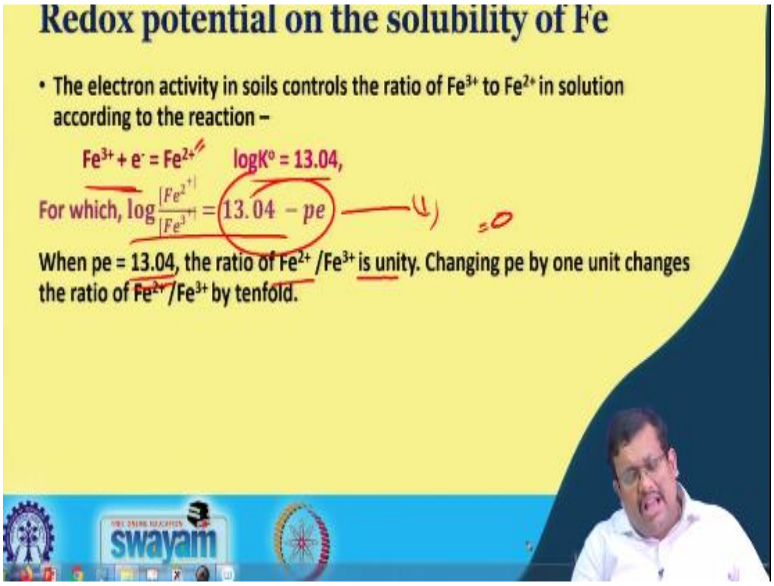

Redox potential on the solubility of Fe

- The electron activity in soils controls the ratio of Fe^{3+} to Fe^{2+} in solution according to the reaction –

$Fe^{3+} + e^{-} = Fe^{2+}$ $\log K^{o} = 13.04$,

For which, $\log \frac{[Fe^{2+}]}{[Fe^{3+}]} = 13.04 - pe$ —— 1) $=0$

When pe = 13.04, the ratio of Fe^{2+}/Fe^{3+} is unity. Changing pe by one unit changes the ratio of Fe^{2+}/Fe^{3+} by tenfold.

So if we see the redox potential of the solubility of iron we know that the electron activity in soil controls the ratio of Fe3 + to Fe2 + in solution according to the reaction that is we know that according to the reaction Fe3 + there is electron then it will be converted to ferrous. So ferric will be converted to ferrous by after accepting an electron and here the log K value is basically 13.04.

Now we know that the logarithm of these reduced species over oxidized species equal to this log K0 – pe we already know that. So basically in putting these value of log K will get this reaction let us consider this reaction 1. So logarithm of Fe2 + over Fe3 + = 13.04 – pe. Now when the pe value is 13.04 obviously so these total right hand side will become zero. So obviously in that condition these ratio that is Fe2 + to Fe3 + is becoming unity.

And so basically changing pe by one unit basically changes the ratio of Fe2 + to Fe3 + by tendfold. So this is basically the redox potential on the solubility of Fe. So similarly we can see the implication of redox potential on the solubility. So basically when the Fe3 + converts to Fe2 + obviously their solubility is increased Fe2 + is more soluble ferrous is more soluble than ferric. So this is how when the change in the redox potential results in the changes in the solubility of iron.

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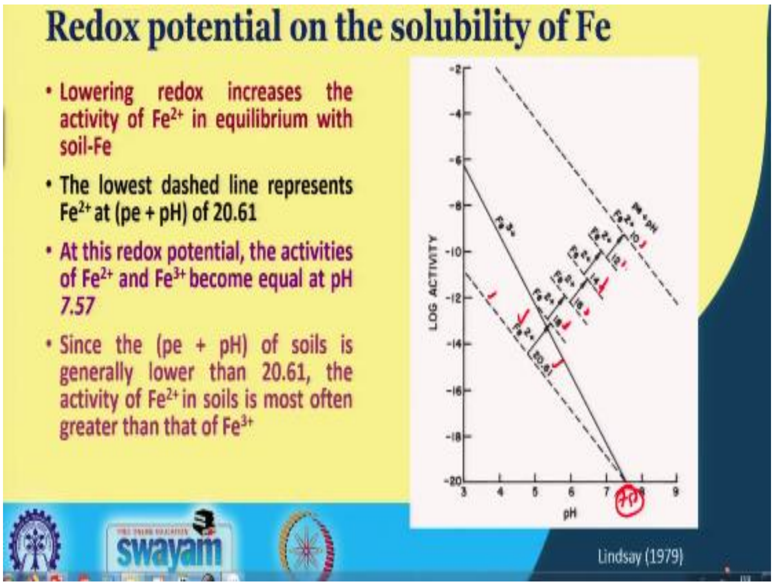

Redox potential on the solubility of Fe

- Lowering redox increases the activity of Fe^{2+} in equilibrium with soil-Fe
- The lowest dashed line represents Fe^{2+} at (pe + pH) of 20.61
- At this redox potential, the activities of Fe^{2+} and Fe^{3+} become equal at pH 7.57
- Since the (pe + pH) of soils is generally lower than 20.61, the activity of Fe^{2+} in soils is most often greater than that of Fe^{3+}

Lindsay (1979)

So this is also showing a very good relationship between the pH and the activity of Fe2 + and Fe3 + irons. So it is clear that as we decrease the redox then there is an increasing the activity of Fe2 + in the equilibrium with soil iron. So basically when we are reducing the redox that means the redox potential is decreasing. When the redox potential is decreasing the activity of Fe2 + in equilibrium is increasing because their solubility is increasing.

We know that iron will be convert Fe3 + or ferric will be converted to ferrous Fe2 + by accepting an electron. So basically when there is reduction occur when the redox potential is decreasing the Fe3 + will be converted to Fe2 + and a result of that their solubility will increase and their activity will increase. So the lowest dashed line as you can see in this picture this lowest dashed line.

This is the lowest dashed line this represents this Fe2 + at this pe + pH value of 20.61. Now at this redox potential the activity of Fe2 + and Fe3 + become equal at pH 7.57. So this is the pH 7.57 when the activity of this Fe2 + and Fe3 + becomes equal. Now remember that from this graph that the pe + pH value as you can see this is pe + pH values of soil is generally lower than that of 20.61.

As you can see 18, 16, 14, 20, 12 and 10 so this pe + pH values of soil is generally lower than 20. 61 and the activity of Fe2 + in soils is basically is most often greater than that of Fe3 +.

This graph shows us this implication. So basically when we are reducing the low redox potential it is increasing the Fe2 + activity in the soil solution. Here we can see the lowest dashed line represents the Fe2 + at pe + pH of 20.61.

At this redox potential these activities of ferrous and ferric become equal at pH value of 7.57 we can see here it is becoming equal and since the pe and pH of the soils this pe + pH in the soil is generally lower than that of 20.61 as you can see 18, 16, 14, 12 and 10 and the activity of this ferrous in soil is most often greater than that of Fe3 +. So this is the relationship between logarithm activity and the pH of the soil solution.

So friends we have learned some important aspects of sludge and how different trace elements are present in the sludge and what are the different conditions which are influencing their mobility in the sludge, what are the sludge management, what is the difficulties in the sludge management, why we are not applying the sludge as a manure in the agricultural fields. So I think you have gathered some new knowledge from this lecture. Please feel free to email me if you have any queries I will be more than happy to answer your queries.

So let us wrap up our lecture here and in our last lecture of week 9 we will be talking more about polycyclic aromatic hydrocarbons and their properties and how their solubility some insights on their solubility in different solvents. So let us wrap up our lecture here and let us meet in our last lecture of week 9 to discuss polycyclic aromatic hydrocarbons in details and their different properties and their interaction with different solvents. Thank you very much.