Environmental Quality: Monitoring and Analysis
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Lecture - 10
Soil-Air partition constants

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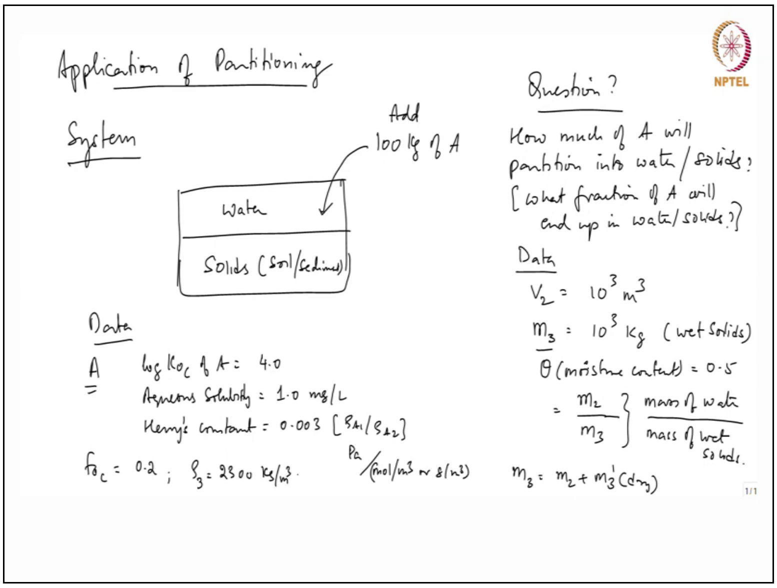

Application of Partitioning

System

Add 100 kg of A

Water

Solids (Soil/Sediment)

Data

A

log K_{oc} of A = 4.0

Aqueous Solubility = 1.0 mg/L

Henry's constant = 0.003 [ρ_{A1}/ρ_{A2}]

Pa / (mol/m3 or g/m3)

$f_{oc} = 0.2$; $\rho_3 = 2300\ kg/m^3$

Question?

How much of A will partition into water/solids?

[what fraction of A will end up in water/solids?]

Data

$V_2 = 10^3\ m^3$

$m_3 = 10^3\ kg$ (wet solids)

θ (moisture content) = 0.5

$= \frac{m_2}{m_3} \Big\} \frac{\text{mass of water}}{\text{mass of wet solids}}$

$m_3 = m_2 + m_3'$ (dry)

Look at the application after partition, application of partitioning constant the partition constancy if we look at it is it is it will become more obvious when we start doing transport. But for now we will look at something very simple and we will explain that why this is not relevant in the in a state in which rain which we define it but it very useful in getting sound basic information from contaminant effect at transport point of view.

We will know some very crude information from this kind of analysis. We will expand on this when we go on the system transfer this is become very useful there. So for example let me check very simple, example that I have a system I am not going to use soil system otherwise it is very impractical. So let us say I have a system of a closed container which has some soil or sediments. Let us say it has some solids. It is similar to soil and sediments.

Let us say we have water we will start with these 2 systems first as of now when we will move on to the third one. Now look at this system I will add, let us say 100 kilograms of some chemical A. So, what do we mean by adding 100 kilograms A there is say that is the contamination is a pollution somebody dumps 100 kilograms of A into water system which contains water and solid into the system. It is very straight forward problem what we are going to look at some of the calculation that will;

So the question that will ask is questions that we will ask is following and the solid other words what fraction other forms of this question what fraction of A blend up in water solid. So, simulate what we did in the last class for the measurement of partition constant during the same thing, but our focus is different here we are looking at how much of a particular chemical will partition into which phase where will it be, essentially asking this question?

So we are saying, so I need to define the system, system is given some of information more information I need about the data that I need is a following I need is the volume of water V of 2 whereas 10 raise to 3 metre cube 1000 metre cube so million litre cube. Also have m of 3 mass of 3 solids is also we say 10 raise to 3 metre cube kilograms. I have additional piece of data to this is what we call as wet solids. Right now I draw the diagram it looks like this sediments water on top of soil which means entire solids are water saturated.

So, I have to give you what is the porosity of the solid with its water content theta which is the moisture content whereas say it is 0.5. So, the definition of moisture content we have to very, very careful different definitions of moisture content people use, so in this particular problem I am using moisture content as mass of water over; so let us call it in the same m3. So, what this m 3 is that is mass of water over mass of wet solid.

We have to be very careful whenever definition is done of moisture content this is one way of doing. The other way of doing this is mass of water over mass of dry solid. And the reason why people use dry solids as a reference because dry solids absolute. Wet solids need not be wet the way we measure wet solid. Suppose if I want to measure moisture content. I have to go into this layer take out a sample of water by the time I am analysing it will not have the same moisture content as it is there in situ.

So things are very difficult to determine in terms of reference saying moisture content as a reference denominator is some solid basis. So, the wet solid is here what we are talking about m3 is the; we will call it as m3 dash or m3 dry, dry plus water is what we are calling as m3. Some times m3 just dry solids whenever the problem changes we will look at the raw soil. So, this is somewhere we have to be careful because effective mass balance are that the calculations change based on this.

So you have be careful in the way this is defined. Right now in this problem will talk m3 is wet solid and the moisture content is 50.5 on the basis of a solid, so you can directly calculate this is wet solid. You know, how much is the water contents here. The other data that I have continued is A, pertaining to A chemical the log K oc of A is 4.0 the aqueous solubility of A let say is 1.0 milligrams per litre this is aqueous solubility of A.

The other additional data I have is the; in this constant 0.003 this is ratio of rho A1 on over rho A2 this is the ratio of concentration. This is the definition; I have other definitions of Henry's constant. We will but this is common in environmental literature other definition of Henry's constant could be the concentration of gas phase can be expressed as vapour pressure partial pressure, whatever is the vapour pressure of this is.

The confusion over partial pressure and all that will clarify that in a minute, so that is Pascal and water concentration is mole per metre cube. This is one way of doing it or we can have grams per metre cube either if this mole per metre cube or grams per metre cube this units are commonly used. In case you see some of these other units in Literature your to convert from there to here. Using the ideal gas law and we would not do this in the class I will not give you Pascal per metre cube all that.

We will stick to whatever ratio of concentration but in general when you are looking at data problems outside in this field, you may have to deal with units like this and convert them into common units. So units are a big problem. They all over the place they are not the same system. You have to make sure you are in the same, same system and then mass balance will work out very nicely otherwise you will make errors and numbers will be 1000 times off sometimes because major problems.

Here that then we also have additional data about the soil sediments itself. We need F oc fractional organic carbon in the solids so let us it is 0.2, 20% of the solid fractional organic carbon this is one definition that we have. The particle density which is rho of 3 particle density, which is the density of the solids average density of solid also I am giving it is just 2300 kilograms per metre cube.

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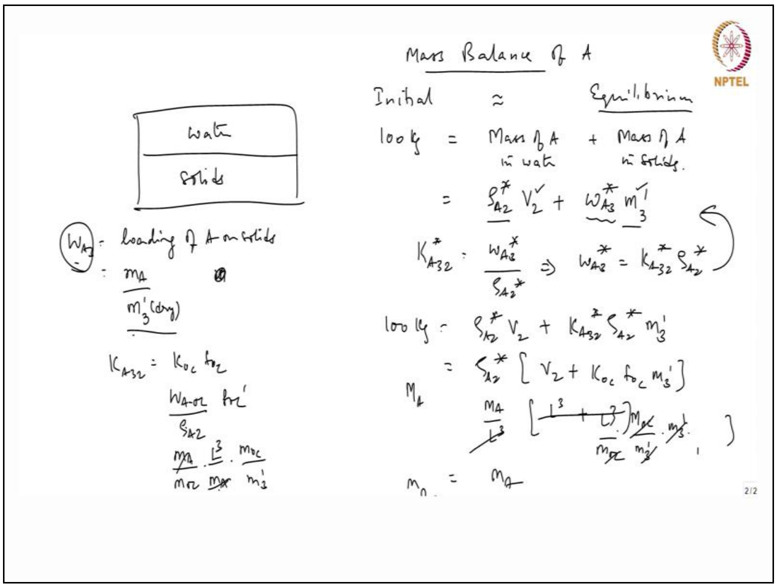
Mass Balance of A

Initial ≈ Equilibrium

100 kg = Mass of A in water + Mass of A in solids.

$= \rho^*_{A2} V_2 + w^*_{A3} m'_3$

$K^*_{A32} = \frac{w^*_{A3}}{\rho^*_{A2}} \Rightarrow w^*_{A3} = K^*_{A32} \rho^*_{A2}$

$100\ kg = \rho^*_{A2} V_2 + K^*_{A32} \rho^*_{A2} m'_3$

$= \rho^*_{A2} [V_2 + K_{oc} f_{oc} m'_3]$

M_A

$\frac{m_A}{\cancel{L^3}} [\cancel{L^3 + L^3} \cdot \frac{\cancel{M_{oc}}}{\cancel{m_{oc}}} \cdot \frac{\cancel{m'_3}}{\cancel{m'_3}}]$

$m_A = m_A$

water

solids

w_{A3} : loading of A on solids

$: \frac{m_A}{m'_3 (dry)}$

$K_{A32} = K_{oc} f_{oc}$

$\frac{w_{A\text{-}oc} f'_{oc}}{\rho_{A2}}$

$\frac{\cancel{m_A}}{m_{oc}} \cdot \frac{L^3}{\cancel{m_A}} \cdot \frac{m_{oc}}{m'_3}$

So we write mass balance, what is there initially, initially we are doing mass balance of A in the system, the mass balance of A in the system is initial and what we did in the calculation last class for the partitioning between partitioning. The assumption in partition is when we say partitioning constant we are saying it is at equilibrium always so initial and then we are saying that at equilibrium the total amount of A is conserved nothing is happening to, it stays as it is.

So what is the total amount of A initially is 100 kilograms this is what you are adding into the systems. So, 100 kilogram of A is present you are putting into your system and then you asking where is this 100 kilogram distributed. So, 100 kilogram will not distributed into at equilibrium in the system will distribute into mass of A in water + mass of A in the solids these are 2 it can distribute in this 2 phases. Now what is the mass of A in the water it is concentration of A in the water at equilibrium we will call it as rho A2 e into volume of water + WA 3e into mass of A.

Now here is the tricky part here. Now this m3 depends on what is the definition of WA 3? WA 3 is what is called as a loading. WA 3 is loading of A on solids for the reasons I just mentioned it is convenient. This is mA divided by some m3, which m3 has to be dry. Because when you take it analysis we will see what the analysis procedure is later in the next session. You will realise that if I take a soil of sediment sample by then analysed for moisture content different because water evaporate from your sample in the container and it may change by 5% 10% is the mass does not remain the same.

You would not want that, we want that all measurements to be based on the basis of some fixed thing whether reference point is the same does not change. So, for that reasons it is convenient for us to use the drying mass, which is why I think people also use it for moisture content also, but sometimes it is convenient to use. So, this problem it complicated because of that. Also because when you have 2, dry mass moisture content based the dry mass goes beyond 100% fraction will go beyond 100.

Suppose we can have a lot of water more water than the solid it is very nice when you say fraction moisture content of a fraction is very nice for us to be upper bound 1 the people are say 140% moisture content they say what is meaning of 140%? So it is confusing and that is why they uses wet bases for everything is there in the fraction of water in the solid is whatever something, so usually below that. So, if you use dry basis moisture content will go beyond 100% it is nothing wrong in it expect that it is odd for sometimes for some calculation.

So here loading is all the time standard is there, this definition which means that if you put W3 dash, so what is the definition of W3 dash here what we have theta is M2 divided by the moisture content m3 dash we want m3 dash in terms of the moisture content. So typically what we are doing is; I do not want m2 here any way we will calculate the hard way. This is the definition we will leave it like this.

Now we have; we do not know either of these 2 quantities. We know this we can calculate this, we will calculate that in a minute but these 2 unknowns there is one more equation to fix this. Since we are saying its equilibrium we use KA 32 star = WA 3 equilibrium by Rho A2 equilibrium which means that WA 3 equilibrium equals KA 12 star into rho A2 equilibrium. You can do other way also you can also express in terms of WA 3 in both sides and substitute rho A2 in terms of WA 3 also that is also possible but either way.

We are doing this for particular reason you will see why? So now in this question if I substitute this back into this one we get 100 kilograms equals to rho A2 equilibrium V2 + KA 32 star rho A2 equilibrium into m3 dash which makes rho A2 equilibrium into V2. Now KA 32 it is wet solid completely wet solid. So KA 32 is K oc and F oc talking about organic chemical here. We are all talking about organic chemical here no inorganic chemical in this discussion in this particular problem.

So, you K oc F oc and m3, you look at the unit here for a minute so I am doing calculation sometimes you just want to make sure units are correct, unit of left hand side is mA dimensions mA this is m A by L cube. This is L cube + m of 3 by m of 3 dash into m of 3 dash divided by; K oc is WA 3 again by rho A2, K oc sorry same you can write star also. So I just mention equilibrium you can put equilibrium, you can write star is the same thing, there is no it is nomenclature.

Whenever you write star, normally you write star or usually you write star for some reason I wrote it as equilibrium. You can write it as star also the same thing. There is no description universal description you can all write it as which means there are all equilibrium that is the only definition but sometimes I will write it as rho A2 it is understood that equilibrium you just write it as such. Sometimes rho A2 star is also solubility.

So, we have solubility in this problem that is why kind of keep it separately that is also equilibrium this is also equilibrium this is different equilibrium this is different equilibrium. There is lot of nomenclature problems that is why I have put me here. So now you here we see that you look at the unit share this is a L cube volume is L cube, K oc is L cube by M oc. If you go back to the back to the definition of K oc, K oc is the WA oc divided by rho A2 this is a definition of K oc, if you recall our discussion into K oc, so W oc is M of As divided by M of oc and this is m of A by denominator is the concentration mA by L cube.

So, this is M oc by m3+ F oc M oc M oc cancel L 3 by M oc is what K oc, so if you write dimensions like this then you know, if you missing something they are all the dimention this cancel this cancel L3 L3 this cancel with this, mA on the right side and mA on the left side dimensionally it is consistent. So, we have this equation here rho A2 into V2 + K oc F oc m3.

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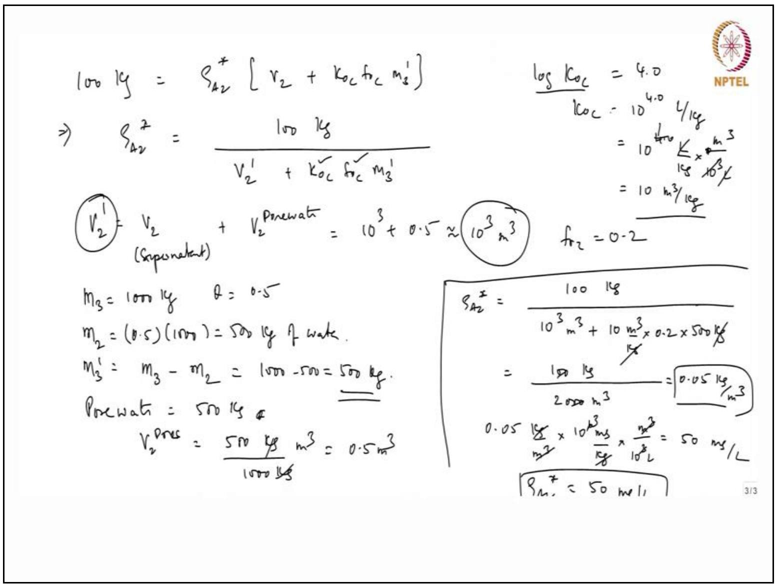

$100\ kg = \rho_{A2}^{*}\left[V_2 + K_{oc} f_{rc} m_3'\right]$

$\Rightarrow \rho_{A2}^{*} = \dfrac{100\ kg}{V_2' + K_{oc} f_{rc} m_3'}$

$\boxed{V_2'} = \underset{(\text{Supernatant})}{V_2} + V_2^{\text{Porewater}} = 10^3 + 0.5 \approx \boxed{10^3\ m^3}$

$m_3 = 1000\ kg \quad \theta = 0.5$

$m_2 = (0.5)(1000) = 500\ kg$ of water.

$m_3' = m_3 - m_2 = 1000 - 500 = \underline{\underline{500\ kg}}.$

Porewater $= 500\ kg$

$V_2^{\text{Pores}} = \dfrac{500\ kg}{1000\ kg} m^3 = 0.5\ m^3$

$\underline{\log K_{oc}} = 4.0$

$K_{oc} = 10^{4.0}\ L/kg$

$= 10^{4.0} \dfrac{L}{kg} \times \dfrac{m^3}{10^3 L}$

$= \underline{10\ m^3/kg}$

$f_{rc} = 0.2$

$\rho_{A2}^{*} = \dfrac{100\ kg}{10^3\ m^3 + 10 \frac{m^3}{kg} \times 0.2 \times 500\ kg}$

$= \dfrac{100\ kg}{2000\ m^3} = \boxed{0.05\ kg/m^3}$

$0.05 \dfrac{kg}{m^3} \times 10^6 \dfrac{mg}{kg} \times \dfrac{m^3}{10^3 L} = 50\ mg/L$

$\boxed{\rho_{A2}^{*} = 50\ mg/L}$

This is the water, all are water now here I have 2 possibilities our system we say this is definition of the problem is important. The way you want you want to see it is a solid. This is really solid plus water in this problem what we are saying is there is a continuum and this is water and this water and connected to this water. If you look at solid here and pore water is here and this pore water is connected to the water on top of it.

Some material can travel here material as such can travel here when you assigning equilibrium here, truly talking about equilibrium between the water and the missing. So, now I have to write this water, the water that is there inside the pore also not just we to 10 raise to 3 metre cube is not enough I have to say take the water content inside single. That is where the equilibration occurs first and it equilibrates further travel part we will talk later.

Right now what do you mean by clearing this entire system which consists of 2 components which is solids and the water in the water anywhere it can be inside the liquid are there in; this is our very broad theoretical equilibrium definition. Now, I can take the system that I am saying this is true if I can take the system I can shake it. So I get a big mixture and mix solid and a mixture pore water and other water and the solid everything together and it become one giant flurry all the water is now seems connected no institutively connected.

But in this particular system I am saying that solids are sitting there and water is on top of it. It looks as of the solid separate systems and water, but they are all connected. The water is a continuum that is going from the pore into the supernatant the water here. So, we add all this water together in this number here. So, now this calculation everything is known we know this and we know this, we need calculate V2 dash and m 3 little bit of calculation that we need to do.

We know that V 2 dash is V2 it is supernatant plus V 2 pore, V2 porewater how do we know we know that m3 is 1000 kilograms and we also know theta is 0.5 which means the water content inside the pore inside the solid is 0.5 into 1000 is 500 kilograms of water inside the solid, which means m3 dash is 1000 kilograms - 500 kilograms m3 dash is the which is 1000 - 500 = program; is the problem I say 1000 into 10 raise to 3 kilograms is given.

So, pore water is 500 kilograms which is volume of pore water 500 kilograms divided by the density of water 1000 kilograms per metre cube small number compare the volume of water, large volume of water, you may even neglect it if you do not think it is important compare to. Usually this is an examples test examples of number really half, in a big system like layer are something numbers are huge. Solid numbers are very big.

The density of solids 2.5 times that of water and mass is very big, so that is a example, just example to do calculation. So now this becomes 10 raise to 3 + 0.5. You can ignore this 0.5 if you want; it is just a nuisance in your calculations 1000 + 0.5, 1000.5 it does not matter. You can see the difference that if I will say approximately equal 10 raise to 3, but in some systems it may become very important. Especially if have flurry and all that it is very important you have to examine the account any way. So, our volume is 10 raise to 3 metre cube. Now m3 plus you also not 500 kilogram, so nor we will plugin all this values in here rho A2 star = 1000 kilograms divided by now the value of K oc;

Now K oc is 4; K oc is 10 raise to 4 the unit are litre per kilogram, just we are mentioned this when we are discussing K oc. When you say K log KC this number is always the unit are litres per kilogram convert it to 10 raise to 4 litres per kilogram into 10 raise to 3 litres per metre cube it becomes 10 metre cube per kilogram I am working in metre cube per kilogram I do not want metre in between. So I will convert all of this to the same unit.

So, this is, so now we do the final calculation rho A2 star equals 100 kilograms divided by 10 raise to 3 metre cube + K oc is 10 raise to 10 metre cube per kilogram into F oc is 0.2, this i F oc into m raise to 3 is 500 kilogram so this will be 5000, 5000 into 0.2, 1000 again it is 2000 meter cube correct the calculation check the calculation it is right now check with the calculator. Now you have concentration of 0.5 Kilogram per metre cube problem done. Now we have to check one thing 0.05 kilogram per metre cube multiplied by 10 raise to 6 milligrams per kilogram into 10 raise to 3 litres per metre cube.

How much this give you 0.05 into 10 raise to 3 is 50 milligram per litre this is your answer rho A2 star 50 milligrams per litre. Anything wrong with this answer, this rho A2 star 50 milligram per litre according to this calculation, now what is rho A2 star it is the concentration of A in water? What is the next to check, the reason I am asking you is think the answer is correct and go back and check. Check immediately whenever you get concentration of water you check it and compare again, I have given you data in the problem.

What is data? Solubility, solubility is given as 1 milligram per litre and we have calculator rho A2 is 50 milligram per litre, so it is possible?

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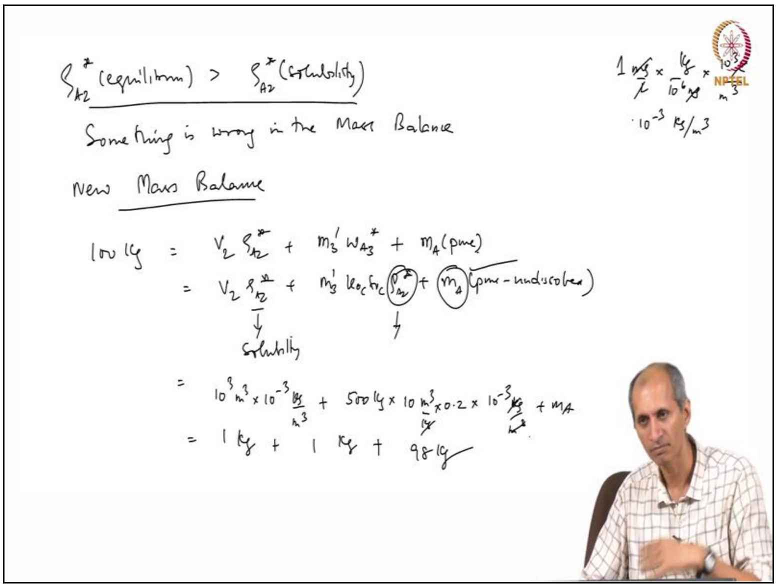

ρ_{A2}^* (equilibrium) > ρ_{A2}^* (solubility)

Something is wrong in the Mass Balance

New Mass Balance

$$100\ kg = V_2 \rho_{A2}^* + m_3' w_{A3}^* + m_A(\text{pure})$$

$$= \underset{\text{Solubility}}{\underset{\downarrow}{V_2 \rho_{A2}^*}} + m_3' k_{oc} f_{rc} \boxed{\rho_{A2}^*} + \boxed{m_A} (\text{pure - undissolved})$$

$$= 10^3\ m^3 \times 10^{-3} \frac{kg}{m^3} + 500\ kg \times 10 \frac{m^3}{kg} \times 0.2 \times 10^{-3} \frac{kg}{m^3} + m_A$$

$$= 1\ kg + 1\ kg + 98\ kg$$

$$1 \frac{mg}{L} \times \frac{kg}{10^6\ mg} \times \frac{10^3\ L}{m^3}$$

$$10^{-3}\ kg/m^3$$

Rho A2 star at equilibrium is greater than rho A2 star solubility, not possible, you cannot have concentrations greater than solubility, what is wrong, and where is the mistake. In this kind of problems mistake can be, at anyone place it is happened in the beginning, what is the fundamental calculation or basis for all our calculation the mass balance. So something is wrong in the mass balance what can be wrong with the mass balance?

You have to thing from the; using this statement is true. What will happen, concentration if a partition into water and solids water concentration is 50 milligram that means solubility is only one since it cannot accommodate the water cannot accommodate more than 1. So, where will the chemical go? The solid but this is equilibrium between solid and water it cannot partition more than this, where does the rest of the chemical go, no.

In this problem we are not in this problem we are not allowing evaporation. If it evaporates it is different issue. That is a big problem that we will see later in the course. But in the system I have water and solid. Let me give you clue, pure solid yeah. If you add solubility of let us say particular salt is 35 grams per litre. I have a 1 litre water bottle and I had 50 grams into this. At equilibrium what will you fine? This is the solubility 35 grams per litre. I have 1 litre water bottle at 50 grams of salt into it and take it and I make it to equilibrium.

At equilibrium what will I find? I will find 35 grams in the water and rest of 15 grams as salt pure substance does not dissolve in stays at the bottom same thing happened here. When you do is calculation means that it is not water concentration higher than solubility, which means it is not possible some of it as remain as pure chemical. We redo the mass balance, now the balance is 100 kilograms is now V 2 into rho A2 star + m3 dash into + mA pure un-dissolved solid.

So, then how many unknowns, 3 unknowns, do we have 3 unknowns. How many unknowns we have in the equations now? This equation has rho A2 star + m3 K oc F oc rho A2 Star + mA pure un-dissolved. How many unknowns are there in this equation? What is now solubility and this is solubility only one unknown equation and only this is only one equation. This is known as from the previous analysis that we know that now its solubility goes to limitable solubility rest of it stays as chemical.

So, this is maximum, maximum whatever is remaining stays as pure substance. So here we do the calculation again, you can do the calculation the same number that we had before 10 raise to 3 metre cube into 1 milligram per litre, so we do 1 milligram per litre into 10 raise to 6 milligram per kilogram into metre cube, 10 raise to 3 kilogram per metre cube this is 500 1001 1 kilogram 6.2 kilogram check the calculation it is 1.

It is 1? Yes it is 1 kilogram in water 1 kilogram in the solid rest 98 kilograms is in pure phase. So, if I change the numbers volume of mass of solid or mass of volume of liquid this weak balance will change entirely. This is a very artificial problem in this case what we are imposing in the problem is that we are not allowing any other contact, where are assuming that contact is happening between the pore water and the main water everything is nice.

We are not concerned really about how long it will take, in the time scale this will happen other process may also happen.

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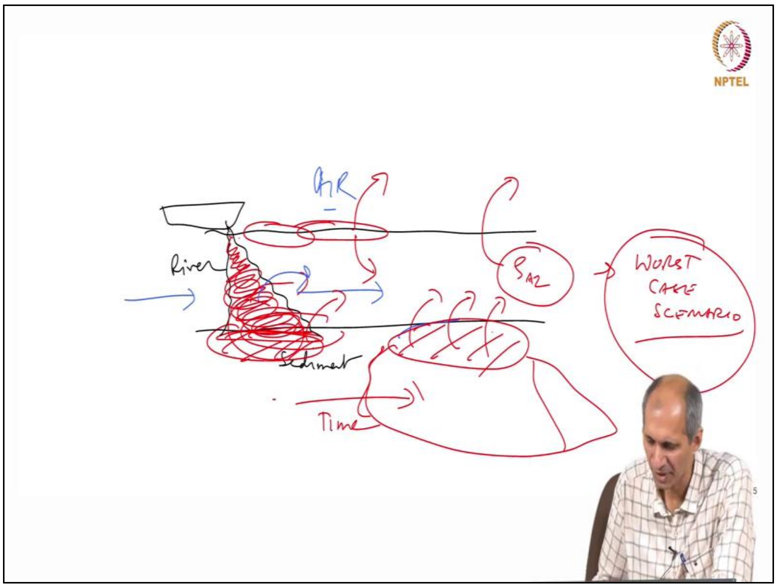

So, in real scenario what may happen if the following suppose I have a river I have a lake, I will take river it is even more complicated then I have sediment somebody; so there is a boat carrying chemical. This chemical dumps this barge dumps large amount of chemical into the water say tonne, 1000 kilograms it happens often. Like in oil spill, oil tanker breaks all the water comes in all the; oil comes into the water.

If it is heavy denser than water it will come down and sync on the top of sediment land on top of it and sit there. Now here, from here it starts; now river is flowing, river water is flowing and it is also air in contact with it. Lot of things happening simultaneously, this chemical is now transferring from as it is coming down. So, after period of time is the barge is gone. So you will only find with time you are going to find this.

But why this is happening, this is happening there is some amount of transfer that happened to the water already that is one. And second is transfer is happen from the sediment to water over a period of time so water is moving. It can also happen; water to air is this is volatile. And then this is also moving out this is spreading downwards all things are happens when the system and never come to equilibrium as we speak in this problem.

But it is driven by equilibrium, the mass transfer happen because there is an equilibrium state and we will come to talk about transport, so equilibrium is important. Why the equilibrium? If we are we are saying in this scenario that you will never achieve equilibrium. What is equilibrium then what is the importance of equilibrium from the environment point of you? What I am saying here is the concentration of rho A2 in the water here. It will never achieve equilibrium.

Then why are we interested in equilibrium? Its maximum concentration, it is what we called as worst case scenario. Why are we talking about worst case scenario because sometimes we do not know what happening. You are not sure what happening at least can say nothing can happen beyond. This is the worst. Even if I do not know any science I know any transport phenomena from nothing. I do not know what happening underwater and approximately what is the depth of water and what is the soil content at the depth of water; and what is the worst case scenario?

When we plan for worst case scenario, for example in the earlier problem I know lot it are still sitting a pure chemical and does not gone into the soil. What can you do? We must taken out rest of are very small one kilogram 1 kilogram may be ti is not important because it is Esy to handle later on. In the previous problem if we find that this number. In the water you find attached 50 kilograms and here you find it as 30 kilograms then you have problem.

Lot of it in the water and this thing, the percentage is very high then you have to deal with the water much more. So, the way we treat water will be different from the we treat the solids and the chemical. So the same kind of scenario can exist when this chemical is a mixture of what we call as a; is the chemical is denser than water and also lighter than water, which means you will have another layer here.

Which is floating on the water which can evaporate directly and it will also dissolve in this thing, and another layer dissolving, which is complications all kinds of sceneries can exist. So, the property of the chemical in terms of the partitioning in terms of solubility in terms of density and all that is important in assessing making a preliminary assessment of what we call a worst case scenario. This is usually the how far you are from the worst case scenario is depends on the other information in a system.

What is the flowing system or it is a static system, it is lake it is not going anywhere is sitting there. Over a period of time it will reach equilibrium and if it evaporating also then equilibrium may not go out completely but you are also evaporating then you have asses what is happening there. So, all this are; so in the earlier problem I can add third phase not air. In this problem; in this system here I can add third phase air and problem will change significantly.

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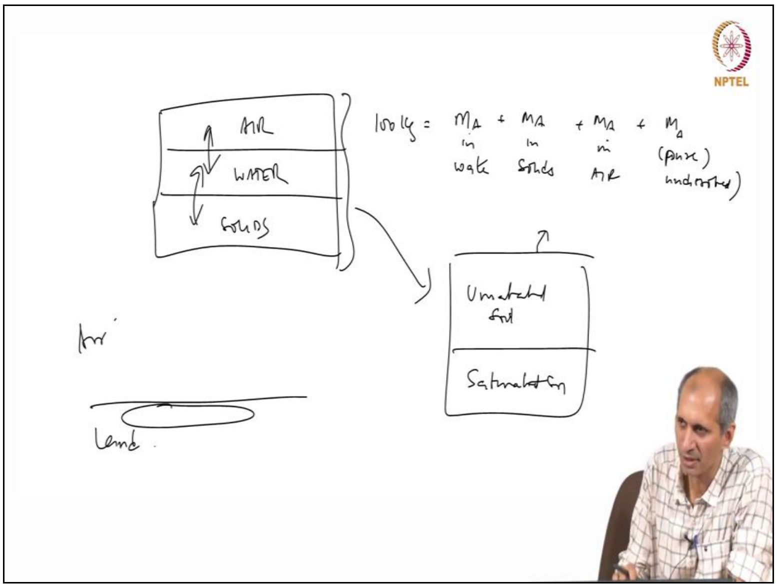

So if I add and assume that there is nice transfer between all the 3 phases, how well happens is again as I said it may take long time for ever happened it may take impractical amount of time. But this is what we study and neglect we can ignore some component, so it will take 1000 years for just to move into air or anything not consider air at all, just this look at water and solid and that will done with it. That depends on this mass balance the worst case mass balance that you say that 0.5% is in the air 60% is in water and 49, 48% is in the in the sediments you ignore there is not important not even bother about it.

Does not worry about air pollution now will worry about the water and the other 2 things? So this is this is quick decision making from a regulatory point of you that is that is useful, simple mass balance. So, if you are writing 3 system like this. We can write again 100 kilograms equals mass of A in water plus mass of A in solids mass of A in air mass of A pure un-dissolved and if we have nay other phase. If there is something else is there you can add that also.

This will constitute the worst case scenario of distribution. So, that is very important concept people talk about system transport. This is the first analysis people will do to have information.

This is not as simple as it looks in environmental systems, because For example I mention in river systems is not static. The volume of water is changing as dissolution occurring. Your caring system is changing volume. Then we have to take a different approach to it.

We cannot use this can approach. But in system like lake and groundwater systems are not moving very fast are not moving at all. So you can do this kind analysis and definitely for air you cannot do it all air is not static. It is changing is constantly moving. So it is very impractical for me to look at air here. But this system what we have written here is is very valid for soils, unsaturated and saturated soil.

This entire system I can say is all inside soil. I can take a system where I have saturated soil and unsaturated soil. Among these 2 I have always 3 phase I have soil, solids I have water and air. Within this system is not much movement. You can assume that the equilibrium may be achieved in reasonable amount of time before it gets to the surface and start moving out. So the system definition has to be done properly. That is big challenge and that requires experience of knowledge of the environmental system itself.

And you cannot arbitrarily take care and next problem that will come you are taking air outside, if I am taking this is land and air. If I dump 1000 kilograms of material on the road somewhere, if I want to calculate what is worst case scenario, what will take the volume of air? I have no idea. Volume of air I can take 1 kilometre height 2 kilometre height 50 kilometre height and unbound there are boundaries to that but we discuss it later.

But that is also moving my scope of reference will come with changing constantly. So we do not deal with this kind of problems in that sense there we approach it differently. This is useful in for scenarios and certain kinds of decision making.