Environmental Quality: Monitoring and Analysis

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Lecture - 10
Soil-Air partition constants

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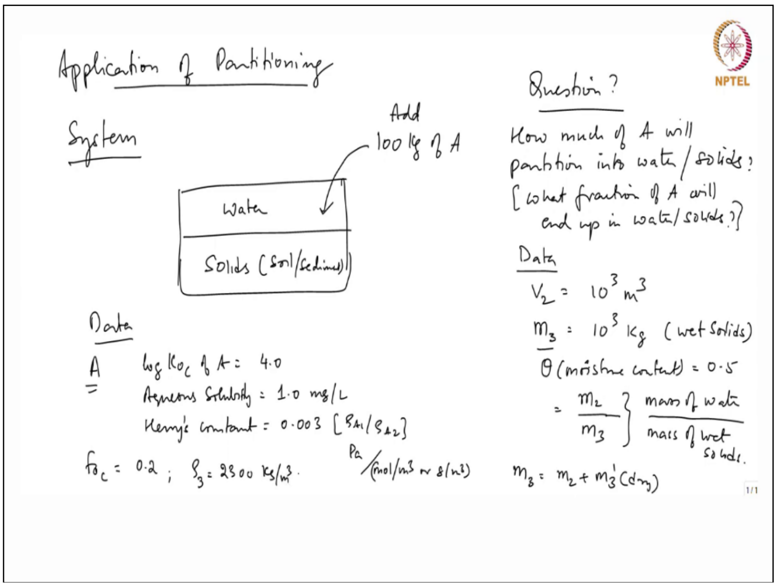


Application of Partitioning

System

Add 100 kg of A

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 ; ρ_3 = 2300 kg/m³.

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

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

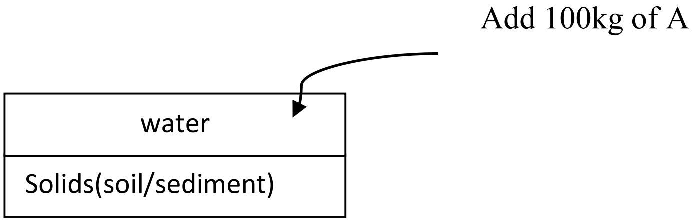
$m_3 = m_2 + m_3'$ (dry)

So, we look at the application of partitioning, so the true application of partitioning constants that we looked at will become more obvious when we start doing transport. But for now, we will look at something very simple which when we will explain that why this is not relevant in its state the way in which we define it but it's very useful in getting some basic information from contaminant fate transport point of view.

At least you will know some very crude information from these kinds of analysis, ok. Now we will expand on this and when we go to fate and transport it will become very useful there, ok. So for example let's take very simple example that I have a system, so I am not going to use systems like soil sediments and all that because it's very impractical. So, let's say I have a system of a closed container which has some soil or sediments. Now let's say it has some solids. This is similar to soil and sediments. And let's say we have water, ok, we will start with these two systems first as of now then we will move on to the third one, ok. Now, into this system I will add, let us say I will add 100 kilograms of some chemical A. So, what do we mean by adding 100 kilograms of A, is say there is the contamination, there is a pollution problem, so somebody dumps 100 kilograms of A into water system which contains water and solid into the system. So very straight forward problem but what we are going to look at some of the calculations that will do;

So the question that we will ask is the following:
How much of A will partition into water/solids? or other words ***what fraction of A will end up in water or the solids?*** ok. So, similar to what we did in the last class for the measurement of partition constant we are we will do 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, so essentially we are asking this question.

So we are saying, so I need to define the system, the system is I'm just given some rough information more information I need about the data that I need is the following, one I need is the volume of water V of 2 let us say it is 10 raise to 3 metre cube 1000 metre cube, ok, so it's a million litres, thousand metre cube. I also have m of 3, mass of 3 the solids is, also let us say it is 10 raise to 3 metre cube or kilograms. I have an additional piece of data so this is what we call as wet solids. So right now, as I have drawn the diagram it looks like it is sediments water on top of earthen solids which means entire solids are water saturated.



So, I have to give you what is the porosity of the solids with its water content, so 'theta' which is the 'moisture content' let us say it is 0.5. So, the definition of moisture content we have to be very careful, there are different definitions of moisture content people use, so in this particular problem I am using moisture content as mass of water over so let's we'll call it as m3, let's not worry about m2 plus m3 we'll just say m3. So, what this means is that it's just mass of mass of water over mass of wet solids.

We have to be very careful you have this whenever definition is done of moisture content this is one way of doing it. The other way of doing this is mass of water over mass of dry solids, ok. And there is a reason why people use dry solids as a reference because dry solids is absolute. Wet solids need not be wet because the way we measure wet solids. Suppose 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 may not have the same moisture content as it is there in situ.

So things are very difficult to determine in terms of as a reference so we are saying moisture content as a reference the 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', yeah, so the dry plus the water is what we are calling as m3. Sometimes m3 is just dry solids whenever the problem changes we will look at that as well. So, this is somewhere you have to be careful because this affects the mass balance and all that, the calculations change based on this.

So you have to be careful in the way this is defined. So right now in this problem we will talk that m3 is wet solids and the moisture content is 50 (.5) on the basis of a wet solids, so you can directly calculate, so if this is wet solids, you know, how much is the water content here, yeah. The other data that I have is pertaining to A, chemical, the log K oc of A is 4.0 let me give you that, the aqueous solubility of A let say is 1.0 milligrams per litre, ok, this is aqueous solubility of A.

The other additional data I have is the, Henry's constant is 0.003 this is the ratio of Rho A1 over Rho A2 (ρ_{A1}/ρ_{A2}), this is the ratio of concentrations. This is the definition; I can have other definitions of Henry's constant. But this is common in environmental literature, so other definition of Henry's constant could be the concentration in the gas phase can be expressed as vapour pressure, partial pressure, whatever is the vapour pressure of the, so there is confusion over vapour pressure partial pressure and all that we will clarify that in a minute, so that is Pascal, ok and water concentration is mole per metre cube. This is one way of doing it or we can have grams per metre cube either of these, mole per metre cubed or grams per metre cubed units are commonly used, ok. So in case you see some of these other units in literature you have to convert from there to here. So using the ideal gas law and all that, we won't do this in the class I will not give you Pascal per metre cubed and all that. We will stick to whatever the ratio of concentration but in general when we are looking at data problems outside in this field, you may have to deal with units like this so you have to convert them into common units. So units are a big problem. So they are all over the place they are not the same system. You have to make sure we are in the same system and then mass balance will work out very nicely otherwise you will make errors and numbers will be 1000 times off sometimes then that will cause major problems, ok, alright.

Here that then we also have additional data about the soil sediments itself. We need ‘foc’, fractional organic carbon in the solids, now let’s it is 0.2, 20% of the solid is fractional is organic carbon this is one definition that we have. The particle density which is Rho of 3 particle density, which means the density of the solids, averaged density of solids also I am giving you it’s just let’s say it is 2300 kilograms per metre cube, ok, done?

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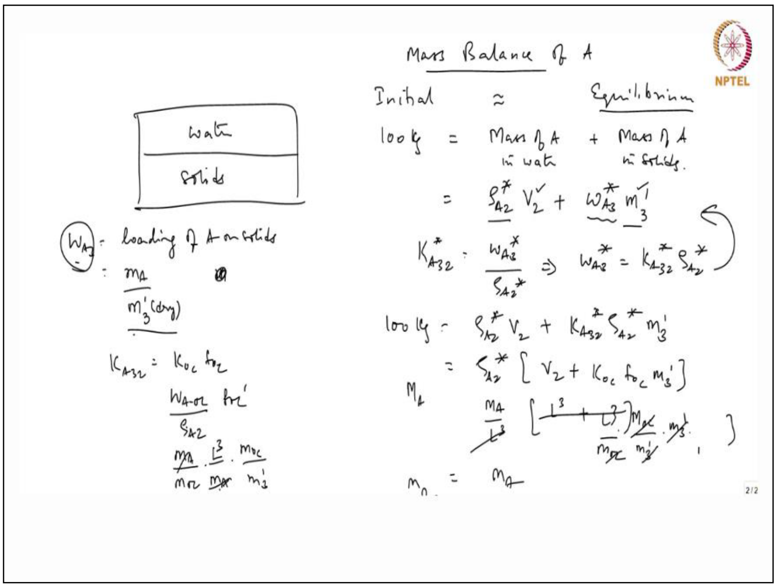

Mass Balance of A

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

$m_A = m_A$

water

solids

w_{A3} : loading of A on solids

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

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

$\frac{w_{A-oc} f_{oc}'}{\rho_{A2}}$

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

2/2

So we write mass balance, what is there initially, we are doing mass balance of A in the system, so the mass balance of A in the system is initial and what we did in the calculation in the last class for the partitioning, we are doing 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 this is 100 kilograms, this is what you are adding into the systems. So, if 100 kilogram of A is present you are now putting into your system and then you are seeing where is this 100 kilogram distributed. So, 100 kilograms will now distribute into at equilibrium it’s in the system, so it will distribute into mass of A it it can distribute into mass of A in water plus mass of A in the solids. These are 2 it can distribute in these 2 phases, ok. Now what is the mass of A in the water? It is concentration of A in the water at equilibrium we will call this as ‘Rho A2 e’ into volume of water plus ‘WA 3e’ into mass of the, now here is the tricky part here, ok. Now, this m3 depends on what is the definition of w_{A3}, ok. w_{A3} is what is called as a ‘loading’. w_{A3} is loading of A on solids, now for the reasons I just mentioned it is convenient this is mA divided by some m3, now this m3 has to be dry. Because when you take it for analysis we will see what the analysis procedure is later in the next section. You will realise that if I take a soil or sediment sample by the time I analyse it the moisture content may be different because water may evaporate from your sample in the container and it may change by 5% 10% so the mass does not remain the same.

You don’t want that, we want that all measurements to be based on the basis of some fixed thing whether, no, our reference point is the same does not change, ok. So, for that reasons it is convenient for us to use the dry mass, which is why I think people also use it for moisture content also, but sometimes it is convenient to use wet. So, in this problem it is complicated because of that. And also because when you do dry mass moisture content basis the moisture content goes beyond 1000 100%, fraction will go beyond 100.

Because you can have a lot of water you can have more water than the solids so it’s very nice when we say moisture content as a fraction it is very nice for us to be upper bound 1, ok. People are very uncomfortable when you say 140% moisture content they’ll say what is meaning of 140%? So it’s confusing and that’s why they use wet basis so that everything is there and 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 except that it is odd for sometimes for some calculation, anyway, so here but loading is all the time standard this thing is, this definition which means that here I have to put w3 dash, alright, so what is the definition of w_3 dash here we have theta is m2 divided by the moisture content, m3 dash, yeah, now we want the m3 dash in terms of the moisture content, ok. So typically what we are doing is; I do not want m2 here any way we will calculate it 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, ok, but these 2 unknowns which means we need one more equation to fix this. So since we are saying its at equilibrium we use

$$k_{A32}^{*} = \frac{w_{A3}^{e}}{\rho_{A2}^{e}}$$

$$\Rightarrow \qquad w_{A3}^{e} = k_{A32}^{*}.\rho_{A2}^{e}$$

You can do other way also you can also express in terms of WA3 in both sides and substitute Rho A2 in terms of WA3 also that's also possible but either way.

But we are doing this for particular reason you will see why? So now in this equation if I substitute this back into this one we get

$$100\ kg = \rho_{A2}^{e}V_2 + K_{A32}^{*}\rho_{A2}^{e}m_3'$$

$$100\ kg = \rho_{A2}^{e}[V_2 + K_{A32}^{*}m_3']$$

So KA32 is 'Koc' and 'foc' because we are talking about an organic chemical here. We are all talking about organic chemical here no inorganic chemical in this discussion in this particular problem.

$$K_{A32}^{*} = K_{oc}.f_{oc}$$

$$100\ kg = \rho_{A2}^{e}[V_2 + K_{oc}.f_{oc}.m_3']$$

So, you have Koc, foc and m3, ok, you look at the unit here for a minute so when you are doing this kind of calculation sometimes you just want to make sure units are correct, so

$$m_A = \frac{m_A}{L^3}\left[L^3 + \frac{L^3}{m_{oc}}.\frac{m_{oc}}{m_3'}.m_3'\right]$$

units of left hand side are mA dimensions mA this is m A by L cubed, yeah. This is L cubed plus this is m of oc by m of 3 dash into m of 3 dash divided by, ah this is K oc is wA 3 again by Rho A2, oc sorry.

Student: sir, what is the difference between star and equilibrium?

Professor: same, you can write star also. So I've just mentioned equilibrium so I kept equilibrium. you can write star it's the same thing, there is no it's just the nomenclature, that's all.

Whenever I write star star is where 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 at equilibrium that is the only definition but sometimes I will just write it as Rho A2 it is not if understood that equilibrium you just write it as that, ok.

Sometimes Rho A2 star is also solubility. So, we have solubility also in this problem that is why kind of keep it separately that is also equilibrium this is also equilibrium this is different equilibrium that is different equilibrium. So there is lot of nomenclature problems that is why I have I put 'e' here. So now here we see that if you look at the units here

$$K^{*}_{A32} = K_{oc}.f_{oc}$$

$$K^{*}_{A32} = \frac{w_{Aoc}}{\rho_{A2}}.\frac{m_{oc}}{m'_3}$$

$$= \frac{m_A}{m_{oc}}.\frac{L^3}{m_A}.\frac{m_{oc}}{m'_3}$$

This is dimensionally consistent.

So, we have this equation here

$$100\ kg = \rho^{e}_{A2}[V_2 + K_{oc}.f_{oc}.m'_3]$$

$$\rho^{e}_{A2} = \frac{100\ kg}{[V_2 + K_{oc}.f_{oc}.m'_3]}$$

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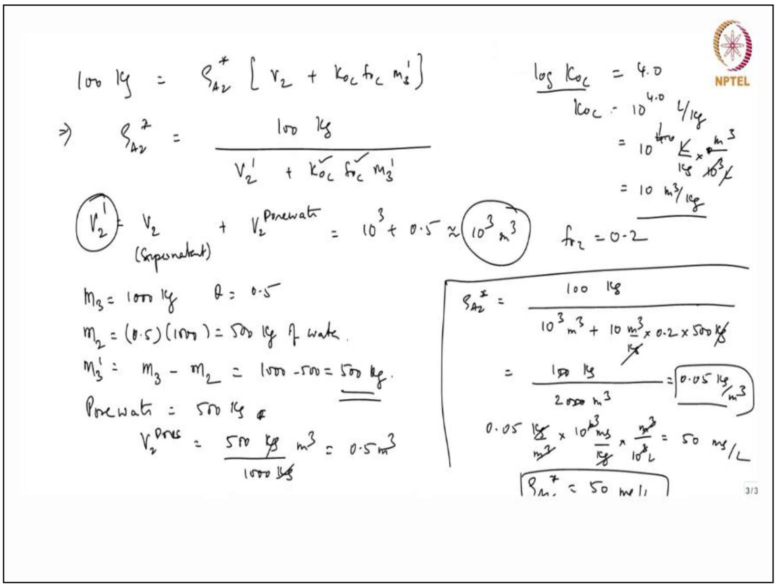

$$100\,kg = \rho_{A2}^{*}\left[V_2 + K_{oc} f_{oc} m_3'\right]$$

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

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

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

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

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

Porewater $= 500\,kg$

$$V_2^{Pores} = \frac{500\,kg}{1000\,kg}\,m^3 = 0.5\,m^3$$

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

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

$= 10^{\cancel{4.0}\,1}\,\frac{L}{kg} \times \frac{m^3}{10^3\,L}$

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

$f_{oc} = 0.2$

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

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

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

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

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 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 there is this water and this water is connected to this water, yeah. So if you look, the solids are here and pore water is here and this pore water is connected to the water on top of it.

So the material that is here can travel here so when we are saying it's equilibrium, we are truly talking about equilibrium between the water and this thing. So, now I have to write this water is the water that is there inside the pore also not just V2 that's 10 raised to 3 metre cube is not enough I have to see this, take the water content inside this that's where the equilibration occurs first and then it moves out and it equilibrates further, ok. Transport part we will talk later.

But right now what do you mean by equilibrium is this entire system which consists of 2 components which is solids and the water and the water may be anywhere, it can be inside the liquid are there. This is our very broad theoretical equilibrium definition. Now, I can take the system the reason I am saying this is true is if I can take the system I can shake it. So I get a big mixture and I mix the solids and I mix the pore water and other water and the solid everything together and it becomes one giant slurry all the water is now seems connected, it seems more institutively connected.

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

So we know that V 2 dash is V2, just the supernatant plus V 2 pore, ok.

$$V_2' = V_2^{supernatant} + V_2^{pore\ water}$$

The V2 porewater, now what do we know? we know that the m3 is 1000 kilograms, we also know theta is 0.5 which means the water content inside the solids is 0.5 into 1000 is 500.

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

$$m_2 = 0.5 * 1000\ kg\ = 500kg\ of\ water$$

$$m_3' = m_3 - m_2 = 1000 - 500 = 500$$

This 500 kilograms of water inside the solids, ok, which means m3 dash is 1000 kilograms - 500 kilograms, m3 dash is the m3 minus m2 which is 1000 minus equals 500kilograms.

So, pore water is 500 kilograms which is the volume of pore water is 500 kilograms divided by the density of water is 1000 kilograms per metre cubed. Small number compared to the volume of water, large volume of water, so you may even neglect it if you don't think it is important compare to. So it's a best example of numbers are off it can really be off, but in a big system like lake or something numbers are huge. Solid numbers are very big. Because the density of solids is 2.5 times that of water and the mass is very big, ok, so that is I think just an example how to do calculations. So now this becomes 10 raise to 3 plus 0.5.

$$V_2' = V_2^{supernatant} + V_2^{pore\ water} = 10^3 + 0.5$$

You can ignore this 0.5 if you want; it's just a nuisance in your calculations 1000 plus 0.5, 1000.5 you can say it doesn't matter. You can see the difference I will say it approximately equal 10 raise to 3, but in some systems it may become very important, ok. Especially when you have a slurry and all that it becomes important so you have to take that into account any way. So, our volume is still 10 raise to 3 metre cube, yeah. Now m3 plus you also know it's 500 kilograms, so now we will plug in all these values in here Rho A2 star equals 1000 kilograms divided by now the value of K oc;

Log K oc is 4; K oc is 10 raise to 4 the units are litre per kilogram,

$$\log(K_{oc}) = 4$$

$$K_{oc} = 10^4$$

just I had mentioned this to you when we were discussing K oc. So when we say log K oc this number is always the units are **litres per kilogram** which means I convert it to metre cube per kilogram it becomes 10 metre cube per kilogram because I am working in metre cube per kilograms I do not want litre in between. So I will convert all of these to the same units.

So, we now do the final calculation,

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

$$= 0.05\frac{kg}{m^3}$$

Yeah, now you have a concentration of 0.05 Kilogram per metre cube, is the problem done? Now we have to check one thing 0.05 kilogram per metre cubed multiplied by 10 raise to 6 milligrams per kilogram into 10 raise to 3 litres per metre cube.

$$= 0.05\frac{kg}{m^3} * \frac{10^6 mg}{kg} * \frac{m^3}{10^3 L}$$

What will this give you what will this give 0.05 into 10 raise to 3 is 50 milligrams per litre, so this is your answer Rho A2 star is 50 milligrams per litre. Anything wrong with this answer, this Rho A2 star is 50 milligrams per litre according to this calculation, now what is Rho A2 star it is the concentration of A in water? So what is the next thing you have to check, the reason I am asking you this if you think the answer is correct and go back and check. What will you check immediately whenever you get concentrations of water you check it and compare against, I have given you data in the problem.

What is the data? Solubility, solubility I have given you as 1 milligram per litre and we have calculated Rho A2 is 50 milligrams per litre, so is it possible?

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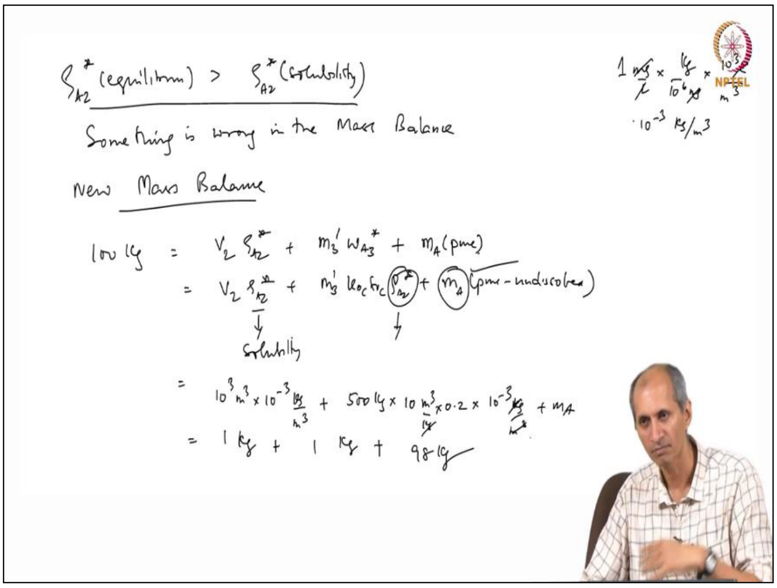

ρ^*_{A2} (equilibrium) > ρ^*_{A2} (solubility)

Something is wrong in the Mass Balance

New Mass Balance

$$100\ kg = V_2 \rho^*_{A2} + m_3' w^*_{A3} + m_A(pure)$$

$$= \underset{\substack{\downarrow \\ solubility}}{V_2 \rho^*_{A2}} + m_3' K_{oc} f_{oc} \underset{\downarrow}{\boxed{\rho^*_{A2}}} + \boxed{m_A}(pure - undissolved)$$

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

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

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

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

Rho A2 star at equilibrium is greater than Rho A2 star solubility,

$$\rho^*_{A2}(equilibrium) > \rho^*_{A2}(solubility)$$

it’s not possible, you cannot have concentrations greater than solubility, so what is wrong, where is the mistake. If in these kind of problems mistake can be only at anyone place it can be right at the beginning, what is the fundamental calculation or the 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 think this statement is true. If this is true what will happen, concentration, if it partitions into water and solids, the water concentration is 50 milligrams per litre but the solubility is only one it means the water cannot accommodate more than 1 So, where will the chemical go? This is equilibrium between solid and water it cannot partition more than this, where does the rest of the chemical go? Evaporate? No. In this problem we are not allowing evaporation. If it evaporates that's the different issue. That's a big problem that we will see later in the course. But in this system we only have water and solid right now. Let me give you a clue, pure solid ah? Pure solid, yeah. If you add solubility of let's say particular salt is 35 grams per litre, ok. I have a 1 litre water bottle and I add 50 grams into this. At equilibrium what will you find? If this is the solubility, it's 35 grams per litre. I have 1 litre water bottle and I add 50 grams of salt into it and I'll shake 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 it does not dissolve it stays at the bottom so the same thing has happened here. When you do this calculation it's means that it's not water concentration higher than solubility, which means it is not possible some of it has to remain as pure chemical, right. So we now redo the mass balance, 100 kilograms is now V 2 into Rho A2 star plus m3 dash into plus mA pure un-dissolved solid.

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

So, but then how many we have now 3 unknowns, do we have 3 unknowns. How many unknowns do we have in the equations now? So I will write this equation as Rho A2 star plus m3 K oc f oc Rho A2 Star plus mA pure-undissolved.

$$100\,kg = \rho_{A2}^{e}V_2 + m_3' K_{oc} f_{oc} \rho_{A2}^{e} + m_A(pure - undissolved)$$

How many unknowns are there in this equation? RhoA2 star now is solubility, this is solubility so we have only one unknown (mA-pure) equation this is only one equation. So this (ρ_{A2}^{e}) is known that's from our previous analysis that we know that now its solubility it goes to limit solubility rest of it stays as chemical.

$$100\,kg = 10^3 m^3 . 10^{-3}\frac{kg}{m^3} + 500kg \times 10\frac{m^3}{kg} \times 0.2 \times 10^{-3}\frac{kg}{m^3} + m_A(pure)$$

$$100\ kg = \ 1kg + 1kg + 98kg)$$

So, this is maximum whatever is remaining stays as the pure substance, ok. So here we do the calculation again, you can do the calculation the same numbers that we had before 10 raised 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 minus 3 kilogram per metre cube this is 500 thousand thousand one 1 kilogram it's .2 kilogram check the calculation it is 1.

That's 1 na? yeah, 1 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 balance will change entirely. So 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, we 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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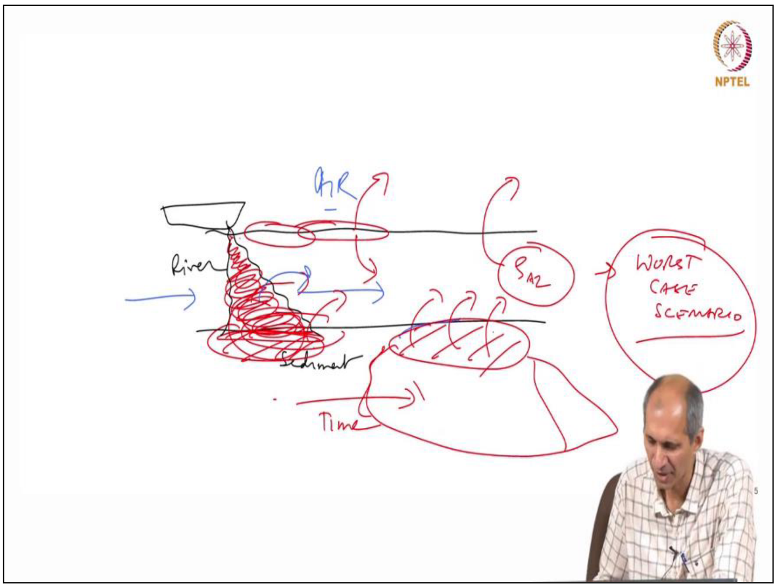

So, in a real scenario what may happen is the following suppose I have a river say I have a lake, I will take river it is even more complicated then I have sediment, somebody so there is a boat carrying chemical. This chemical dumps this barge dumps a large amount of chemical into the water say tonne,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

If it is heavy denser than water it will come down and sink on the top of sediment it will land on the top of sediment and sit there. Now here, from here it starts; now river is flowing right, the river water is flowing and there is also air that is 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 so with time you are going to find this.

But while this is happening, while a leak is happening there is some amount of transfer that has happened to the water already that is one. Second is the transfer will happen from the sediment to water over a period of time because the water is moving. Then it can also happen; transfer can happen from water to air if this is volatile, ok. And then this is also moving out this is spreading downwards all these things can happen so the system may never come to equilibrium as we speak in this problem.

But it is driven by equilibrium, the mass transfer will happen because there is an equilibrium state and we will come that when talk about transport, ok. So this equilibrium is important. What is this equilibrium? If we are we are saying in this scenario that we will never achieve equilibrium. What is equilibrium then what is the importance of equilibrium from an environmental point of view? What I am saying here is the concentration of Rho A2 in the water here. If it will never achieve equilibrium. Then why are we interested in equilibrium? The maximum concentration. It’s a 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’s happening. We are not sure what’s happening then we can at least can say this is the worst case scene nothing can happen beyond this. This is the worst, ok. Even if I do not know any science I know any transport phenomena nothing. I do not know what happening underwater and I know approximately what is the depth of water and I know what is the soil content organic content I can at least say what is the worst case scenario?

So then we can plan for worst case scenario, for example in the earlier problem I know that lot it is still sitting as pure phase it has not gone into the soil. What can you do? You can just take it out you can just pick it out the rest of it is very small one kilogram 1 kilogram may be it is not important, ok it is easy to handle it later on. Suppose in the previous problem if we find that this number, in the water you find it as 50 kilograms and here you find it as 30 kilograms then you have a problem. Because a lot of it is in the water and this thing, so percentages are very high because 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 pure chemical. So a same kind of scenario can exist if 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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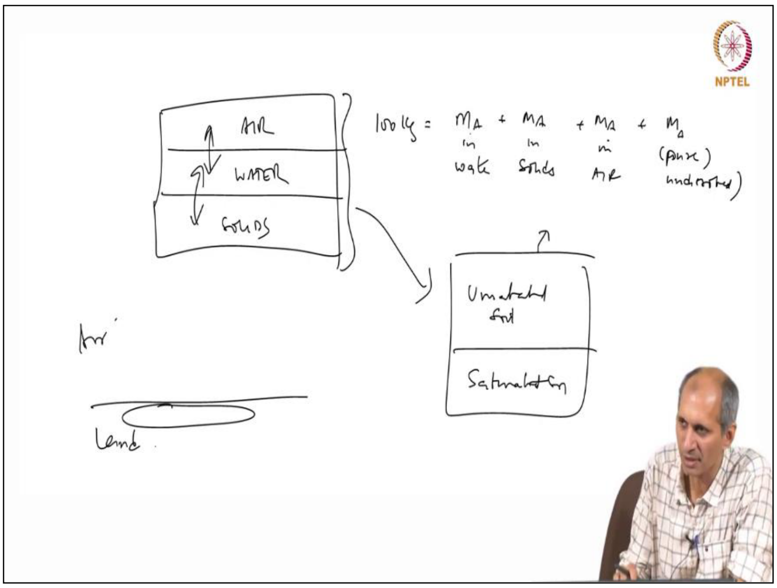

So if I add and assume that there is nice transfer between all the 3 phases, how well happens is again as I said it may take long time for it to happened it may never happen it may take you know, an impractical amount of time that we do. But this is what we study and we neglect we can ignore some components, we say that it will take 1000 years for this to move into air or anything so let's not consider air at all, we will just look at water and solid and that be done with it and 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 38 percent is in the in the sediments you will ignore the air, say that’s not important not even bother about it.

Let’s not worry about air pollution now, will worry about the water and the other 2 things. So this is quick decision making from a regulatory point of you that is that is useful, so 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 plus mass of A in air plus mass of A pure un-dissolved and if you can add any other phase. If there is something else there you can add that also.

This will constitute the worst case scenario distribution. So, that is very important concept people talk about in fate and transport. This is the first analysis people do if they have information. Now this is not as simple as it looks here in the environmental systems, because for example as a example I mentioned in river systems it’s not static, the volume of water is changing because as dissolution is occurring you are carrying system is changing its volume, right. So then we have to take a different approach to it.

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

So I can 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 all these 3 phases, I have soil, solids I have water and I have air. So within this system there 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, ok. So the system definition has to be done properly. And that’s the big challenge and that requires experience of knowledge of the environmental system itself. So you can’t arbitrarily take air and next problem that will come if you are taking air outside, if I’m 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 kilometres height 50 kilometres height it’s unbound, right there is boundaries to that but we’ll discuss that later.

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