# Environmental Quality: Monitoring and Analysis Prof. Ravi Krishna Department of Chemical Engineering Indian Institute of Technology – Madras

### Lecture – 17 Tutorial

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Environmental Quality: Monitoring & Assessment Problem Tutorial 1

- 1. An industrial facility has a waste tank (20m length, 20m width and 5 m depth) that contains a small amount of solid sludge that is a mixture of inorganic and organic matter. The sludge occupies the tank to a height of 1 m uniformly spread across the cross section. The moisture content of the sludge is 0.4 (mass of water/mass of wet sludge or wet basis). The percentage of organic carbon in the sludge was estimated as 15% on a dry basis and chemical analysis of the sludge showed a loading of 250 mg/Kg-dry solids of a particular hazardous organic chemical A. Mass of wet sludge is 600, 000 Kg. During a rain event, mixing of the sludge with the rain water occurs and the resultant slurry occupies a volume in the tank upto a height of 3m. The contents of the tank are then allowed to settle and the excess supernatant water is removed from the tank. During this transfer 10% of the organic carbon present in the sludge was leached out. Log Koc (A) = 4.0 and Henry's constant = 0.0003 (ratio of concentrations).
- a) What is the expected concentration of A in the "true aqueous" phase in the leachate tank (expressed as mg/L)? Assume that the rain water is free of any organic matter or chemical A. Assume zero evaporation. Explain your answer stating all assumptions. Show clear mass balance calculations along with proper units.
- b) A sample of water is collected from the leachate tank in a 1000 mL glass bottle with a headspace of 200 mL. The sample is extracted using hexane. Do you expect that this value is different from that obtained in part a) and why? What experimental correction or sample pretreatment would have prevented this difference? Explain your answer using algebraic expressions. If possible, calculate the concentration of pure among phase.

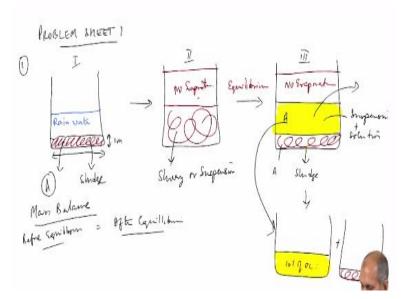
So it says an industrial facility has a waste tank. So one of the things, problem statements are big, it does not mean problem is big, it is just you have to understand, gather information from this problem and fit it into whatever framework we are using. So, we have an industrial facility has a waste tank, I have given you dimensions, contains small amount of solid sludge. Solid sludge means it is water plus solids, mixture of inorganic and organic components and sludge occupies about 1 meter of the tank okay, uniformly spread across.

That is imagine like you should dump mud into a tank, it will occupy the bottom some region. The moisture content of the sledge is 0.4. The percentage of organic carbon in the sludge was estimated as something 15% dry basis, which is 0.15. Chemical analysis of the sludge showed the loading of 250 milligrams per kilogram dry solids of a particular chemical A, some chemical A. The mass of wet sludge is 600,000 kilograms. So, I have given you the volume, I have given you mass, which means you can calculate few things from this information.

Sometimes when I design the problem, I just give some numbers, when you do the calculations, sometimes the numbers are inconsistent. It will violate mass balance. In those cases, you correct it if you know, otherwise you tell me I will correct it okay. So that is the basic idea, right. Now, what I have given is during a rain event, when rain falls into this, it mixes, slurry becomes a suspension with addition of rain water. So overall resultant slurry occupies 3 meters now, originally it was 1 meter and so 2 meters of height is water, extra water that is added.

It is like adding water and mixing stirring up this thing and the contents are then allowed to settle again. So, in the process of this mixing, what do you expect is happening? So, let me write down this problem in terms of the this thing.

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So I have a tank, which is of initially I have some sludge. Let us say I have some sludge and the sludge occupies I think it occupies 1 meter height and some crosssectional area. Now I add water, rainwater, and so the entire thing becomes slurry okay. So this is the physical description of the problem. Then after settling down, what we expect is this again, but now the top portion, this is what I expect. Initially I added the rain water. This is also the suspension. So what has happened between stage, this is let us call it us stage 1, stage 2, and stage 3.

In these 3 stages is what is described in this problem. What has happened in this 3 cases. First there is a certain amount of A is there here, all the A is contained here. When you add rainwater and you mix it, everything is mixing, the water and the solids are mixing together

and now what we have is we have A here and here, both here, A has now distributed itself

into the water and this thing okay. What I am saying is, I am then taking out this water out of

this, okay, all this water is taken out for analysis. I am trying to analyze what is here.

So this water is now taken out and the sludge is remaining like this. So sludge remains as it

is. What I have also given in the problem is that this contains 10% of the organic carbon

originally which was there in this sludge, just is now removed 10% of that organic carbon

from there. So, this is the setup of the problem okay. Anybody has doubt? Question about

this, how this happens? Now, very simple question that I am asking is what is expected

concentration of A in the true aqueous phase here, in this one, yeah.

What has happened is you have had rainwater which is mixed with, it has suspended, re-

suspended all the sludge and it has caused contamination of water and the water is being

drained out and this water is now we were trying to find out what is there in the water. How

much A is there in the water? So, we do a mass balance in which of these systems? For true

aqueous phase on which of these 1, 2, or 3, which one will you do a mass balance on?

"Professor - Student conversation starts." Three, one all of them are the same. They all

have the same thing, but what is we are doing mass balance at equilibrium, initial and

equilibrium yeah. "Professor – student conversation ends." We are likely we are doing it at

3, but we can also, it is 2 and 3 are equivalent in some sense, you keep mixing it, you keep

mixing it, it is really 2 because that is the state of equilibrium. Then you wait for a long time

for it to settle down and we are assuming that there is equilibrium and this equilibrium is

attained between these 2 stages and it stays there, nothing else is happening.

So, we are also assuming that nothing is going out, no evaporation, it is that what I have

assuming 0 evaporation, no evaporation. So in a real case scenario, you will not see that. In a

real scenario, it will not come to equilibrium because it will evaporate okay. So, no

evaporation, our system is only this, only the slurry water and solid. So the mass balance that

you will write will be in terms of, so what will be the mass balance? It will be before

equilibrium, after equilibrium okay.

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So what is that before equilibrium? Where is the A? We are doing mass balance for component A, where is the A? You are going to write algebraic expressions, you do the calculations on your own. "Professor – student conversation starts." In the sludge. In the sludge, so how will you express it? All the mass of A, so mass of A in sludge, now mass of A in water equals after equilibrium in water. "Professor – student conversations ends." Now we are saying rainwater, we make assumptions here. One assumption that we make here is this rainwater contains no A, this need not be true okay.

Rainwater can contain some things depending on where it is, how it is being processed, because it is in contact with particulate matter. So, it is a complicated problem. Sometimes rainwater will bring what is called as wet deposition, whatever is the particulate matter in the atmosphere, it will all be dumped into your, it will come with the rain, okay? So, it may add pollution to your existing system, where it is cleaned it may add more stuff into that. So, a lot of that is called as a wet deposition.

Our assumption is that we are not considering wet deposition, there is no A, that is simple. You can add all these complicated cases if you have enough information about system, that is all. You can do it later if you know how to work this, which means that this is 0 okay. "Professor – student conversation starts." Sir, since Henry's constant is there whether we need to consider at air also? We are not, right now we are saying no evaporation. So, if you have evaporation, we will do that problem later. Evaporation is evaporation of water or evaporation of air. Both, but right now, our concern is only water, the A now.

So, evaporation of water occurs, then a lot of other things will change. So, those are complexities that that the system will have subsequently. "**Professor** – **student conversation ends.**" So, we are now only trying to understand the process of estimating the solute. The water also will change, can evaporate. So, we are modeling water and air evaporation separately. So, now it is mass of A in the sludge. What is mass of A in the sludge? This one. Algebraically, how will you define it?

This is 0, there is only thing that is before equilibrium all the A is in the sludge. How do you express concentration of A in a solid Sludge? Using WA3 into m 3 equals at equilibrium it will be WA3 star m3 plus into V2. This is the mass balance, very simple, similar to what we did in class for the other one. Only difference here is now we are changing, we are not adding pure chemical or anything, it is already there in a system, it is redistributing because there is additional water that was added.

Now, this is known, we will call it as WA3 0 which is given. This is given to you, this and this we do not know, so, we have to calculate m3 and V2 yeah. This constitutes a biggest effort in the problems like this. Calculating of V2 and m3, it involves a little bit of work. So, here what we have already is, we have given mass of, what is given this mass of wet solids. So, you have to understand one thing whenever we say m3, in previous classes we have discussed, m3 is usually dry.

This WA3 is on the basis of dry. So, you will look at that, the definition as given is the loading of 250 milligrams per kilogram dry solid, so WA3 is always on dry basis, which means by that definition, m3 is dry solid. It is a very hassle free way of doing it because dry solid will always there, no, nothing will happen to them. The moisture content may go away, as in this case the moisture content is changing. You are adding water and removing water and all those things is being done.

So, in those case, our mass balance is simple by keeping, we are keeping track of it by way of m3 only. So, mass of wet solids is m3 + m2. Now this m2, this particular we will call it as m2 dash because this m2 is the pore water. In other words, you can write this thing as, I can remove this and say its m2 of 3, because it is the water mask associated with the solid, yeah. What is given m2 of is a wet solid mass is given as 600,000 kilograms yeah. What is also given is the, I have not given some information I think you need that.

"Professor – student conversation starts." Moisture content. Moisture content is given 4, theta is given 0.4, which means m3 divided by m3 + m23 is given as 4, sorry m2. So, now I have volume of 2 is 240 meter cube. Total volume is 20 by 20 by 1 which is 400 meter cube. Total volume of 1 meter height of the sludge, total volume of the sludge at this point is 400 meter cube. So m3 is 360,000 kilograms that is the balance that is remaining in this. So, for now we do not need to do anything else, we can do the problem using this.

But in some cases you need to calculate the reverse if the moisture content is not given or anything, you need to estimate the water content. So you need the volume occupied by the solid, which means I need particle density of solid, from mass I will calculate particle density, using particle density to calculate volume of solids V3 and then use whatever is balance volume occupied by, for example, in soil you have water and air and if you have water, volume occupied by solid plus volume occupied by water plus volume occupied by air, all of these constitute the full volume in the system.

Water saturation systems are much easier to handle. So we have this and this, okay. So now we do the mass balance, you have 250, let us go to the next page.

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WA30 m3 = WA3 star m3 + rho A3 star V2, we have 250 milligrams per kilogram dry multiplied by 360 kilogram equals here I will write now, WA3 star by rho A2 star = koc foc. So therefore this will become WA3 stars becomes koc foc into rho A2 star. This is my equation for now, okay. What is this? This is the concentration of A in the aqueous phase,

true aqueous phase. Now the slurry also contains what is mentioned in the problem, the also contains 10% of the organic carbon.

Organic carbon is a solid phase in the suspension, but that is not water, it is still solid, okay, there is chemical still sitting on it and all that will come on under this term, it is still part of the solid. Only thing we are saying is that, that is why we said when we say we want to consider, we are considering this one other than 3, they are the same, 2 and 3 are the same except that equilibrium has happened and this the solids have settled down, we are still assuming that organic carbon is still there.

So, we are not changing the system, we are not changing the equilibrium or system or anything okay. Everything is there as it is. No evaporation, no water is removed, nothing is added to it. So, the concentration of rho A2 that is present in this state should be the same here before settling and after settling as long as equilibrium has been achieved. If you keep it stirred long enough, for it to come to equilibrium, whatever the concentration that is there when in the suspended state will still be retained when you are settling all the solid out.

This is usually as long as you do not have anything else in the system. You do not add more carbon or your do not evaporate anything else, you are not disturbing the equilibrium. So, in our problem assuming that to be true. So, this rho A2 star is the true aqueous phase. Sorry this is not, this is other way, m3 is here, V2 is here into koc, koc in the problem is 10. So it is 10 raised to 1. So koc is 10 raised to 1 meter cube per kilogram. This log koc is 10 raised to 4 liter per kilogram.

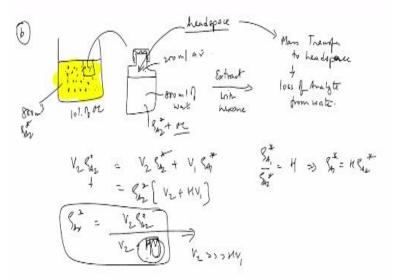
So therefore, this is 10 here, foc is 0.15 yeah, then 10 into 0.15 + 240 meter cube. This is meter cube per kilogram, so the kilogram, kilogram get canceled milligrams. So your aqueous phase concentration will be in milligrams per meter cube whatever you are getting. You can calculate that, whatever this value is okay. So look at the magnitude of this number versus this number, you can see that a lot of it is still in the solids. It will shift towards the water, so the water volume becomes very large.

If I take this and add, so if the order of magnitude of this for example 36, this 3.6 into 10 raised to almost 5 multiplied by 1.5. See the order binary is 10 raised to 5 and this is 240. For this to significantly distribute itself into the water, you need to have a lot of water, you keep

adding more water and more and more water when the water then increases its capacity, the capacity to take chemical in the water becomes higher and higher, okay. So, it also depends on the value of koc. If the koc is small, log koc is 1, this number will become very small.

So, the distribution of the chemical between the two phases, this phase and this phase really depends on the volume of water as well as the koc and the mass of sediment and all. So, this must balance is very clear, can see which direction the problem will go if I increase volumes of water or if I decrease certain other numbers and so and so. So, you calculate the number here okay.

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Part B relates to analysis chemical analysis. So, when we say true aqueous phase, there is a reason for when we call it as true aqueous phase, okay and it relates to part B. So in part B, suppose I am, what I am saying is I have this case where this 2 meter cubed, no not 2 metered cubed whatever this, there is additional water now, so there is some additional. So sorry, I have mistake, none of you pointed out. "**Professor – student conversation starts.**" Rain water. Rain water, yeah. How much is rainwater? 800 meter cube, yeah. So, this is not to 240, this is huge, 1040 sir, yeah. "**Professor – student conversation ends.**"

This is of the pore water, V2 rain water is 20 by 20 by 2, this is 800 meter cube. So therefore, the total V is 1040, this is bigger than this. So therefore this one, so what we are doing is now after separation, we are taking out that 800 and going back into a different chamber. We are retaining the original pore water, letting it settled down to its original capacity, and we are

pulling out all 800 into here, in the next one, this is 800 meter cube of rho A2 star, but it also contains 10% of the organic carbon originally there in the other one.

Now here, we are still not exposed it to water, now here is where I am exposing it to air and I am asking what will be the transfer there. Now there will be a shift in equilibrium, again you are redoing the equilibrium here because we are now exposing it to air okay. So the organic carbon is here, the organic carbon have nothing to do with evaporation because equilibrium has already been achieved and this organic carbon that is there here has already participated in the equilibrium.

If you add new organic carbon into the system, it will re-equilibrate it, but as long as you are not adding anything new, nothing will happen. What are you adding now here in the problem that says? I have a sample from this volume, I am taking a small sample, let us say I am taking a small sample of water into a glass bottle, 1 liter glass bottle with the headspace of 200 ml. What I am doing is I am taking a 1 liter bottle, I am collecting the 800 ml of water and 200 ml air, this term headspace is used in chemical analysis.

Headspace means this is the headspace, this is called headspace. You take a bottle, you do not fill it up fully and you close it. There is some region that is on top of the liquid that is called as headspace. We make use of this in chemical analysis, we will discuss that in the next section, so it is capped, its closed it is a closed container. Now you can imagine what will happen in system. This contains rho A2 star plus some organic carbon, some fraction of organic carbon is there in this okay, little bit of organic carbon there in this and this contains air.

So the sample is extracted, now here is the kicker here. So I am extracting, I am adding extract with hexane, which means I am doing this. So, what do I need to do to extract with hexane, the sample? I have to open the bottle. When I open the bottle, what will happen? Because there is headspace, some amount of the A that is in the water has now has gone partition into air and that will escape, that will go away essentially okay. So, what we are saying is when you have headspace, there is mass transfer into air into headspace and therefore there is loss of analyte from water.

How much of analyte loss is there in water? Which means that the original concentration is rho A2 here, what will be the concentration there? It is a very simple calculations, it is the mass balance again. The original mass balance is again V2 rho A2 = V2 rho A2 + V1 rho A1 star. This rho A2 is the rho A2 star from the previous problem, okay. Now, rho A1 star by rho A2 star is Henry's constant, which means that we have rho A1 star = H rho A2 star, rho A2 star into V2 + H into V1.

This is your concentration. Now, what has happened is because the denominator if HV1 this is 0, it will be the same because how we have some volume of air and some Henry's constant that is acting on it, this denominator is greater than V2, therefore you will get a small decrease in the concentration as you compare to rho A2. So, rho A2 to initial whatever is going into the system, into the sample, the original true aqueous sample okay. This is all imaginary problem okay, none of these things will happen in real life. "Professor - student conversation starts" At this time we need not to consider the organic evaporation.

We will come to that, here no, the organic when you are talking about evaporation, where is evaporation occurring from? Evaporation occurs only from water. "Professor – student conversation ends." Henry's constant relates true aqueous phase, true vapor phase, particulate matter is all under a different equilibrium. Now, if I keep the water exposed to continuously to air, then evaporation is occurring and the water will deplete, and then there is a change in the equilibrium between the aqueous phase and the organic carbon.

Then these options will happen, all that will happen, so we will talk about it later. For right now, the organic carbon is just a passive observer, it has nothing to do, it does not participate in evaporation yet in this equilibrium this thing. You can write if you want equilibrium for all the 3 okay. It is correct, it is a full valid way of doing it, I am ignoring it because I would not expect to see a big change, but if you have to write, the correct way of doing this, will be moc multiplied by or we will recall it as m3 WA3 + m3 WA3, but this A3 is only organic carbons.

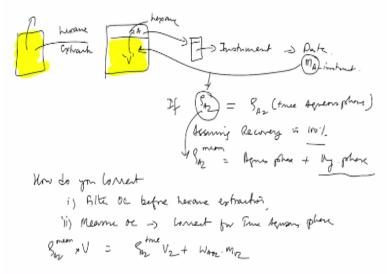
So, whole bunch of calculations you have to do. The amount of organic carbon you are taking in 1 liter is very small. So, we are now essentially neglecting that portion, any big change is happening here, but you are right, that is the correct way of doing it. There will be a very small change in that very likely, but just to make this point that because you have headspace,

because you have allowed volume of air and with a significant H. So, again this number here depends on the magnitude of Henry's constant.

Henry's constant is big, you expect this number to be big or the volume of air to be big, similar to what we did in the rainwater and the sludge case, right. So, you will get some change. The answer is, do we expect any change? Answer is yes because some amount of chemical will now partition into air, how much that depends on the value of Henry's constant and the volume of air and it may not be significant at all. You may see that the value is about 2.4 and the other value is 2.399, so insignificant that is the call you have to make whether it is relevant or not.

So, you can also look at the magnitude of HV1 and V2, if you think if V2 is much larger than HV1, you ignore this term and move on, assume that to be true, but be assured that for different volumes, it may matter. So this is the illustration of the losses that we were talking about in the case of chemical analysis in last class. Now, second part of that question. yeah.

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The question is if I extract with hexane and I will get, so what will I get when I extract with hexane? So, I take the sample, water sample which is this, extraction which will mean that I am adding a little bit of hexane, yeah. So, all the A is now gone to hexane and this hexane I am taking into a smaller vial and then transferring it to some analytical instrument and I will get data. I will get a concentration of a mass of A that corresponds to this volume. So, I can get a concentration of A in this.

So, mass of A from the instrument analyzed by the instrument using recalibration graph and all that, then the volume of liquid I am taking the sample from, the entire sample, I can get a concentration. This will give me a concentration. My question is will this number which is measured, will it be the same as the rho A2 true aqueous phase that you estimated in part 1? "Professor – student conversation starts." Why not one of you shaking your head? Why not? It is not possible expect complete amount of this changing. Let us assume we have done all that.

Let us assume we have done all calling over, assuming recovery is 100% where that is a different issue. Assume recovery 100%, I know all assuming I have calculated recovery. My question is very different, question is, is this rho A2 represent the rho A2 that you estimated in your calculation? Because some amount escaped into air. All that is accounted for. That organic part is, so what is organic part do? That also has a concentration so that also will include yeah.

So, what you are measuring is the hexane is you are extracting everything. You are extracting this rho A2 measured includes the aqueous phase plus the organic phase. It is significant amount of chemical sitting on organic phase the koc is very large, 10% of the original organic phase is still a large amount. So, it is very likely that you will see a large concentration if you take the entire water sample as it is and extract it, against the concentration you have estimated based on the calculation true aqueous phase okay.

So, how do you correct for this experimentally? We filter the concentration. You can filter. "Professor – student conversation ends." One is filter the oc before hexane extraction. Sometimes it is very difficult to do okay. So, the other option is to measure the oc and then correct using the mass balance, same mass balance. Now, this mass balance will be whatever value you have now got corresponds to both the phases, you have to distribute it. You say this is the total amount of mass that is contained in this volume equals volume of water plus whatever is there.

So, correct for true aqueous phase by doing this. So, we have rho A2 measured multiplied by total volume equals rho A2 true aqueous phase multiplied by volume plus WAoc multiplied by mass of oc. "**Professor** – **student conversation starts.**" Every time during extraction, the concentration, I mean the compound A gets extracted even from the carbon or even from the

solid? It will, if you do not separate it. "Professor - student conversations ends." It

depends on what your objective is again.

If your objective is to estimate evaporation and all that, evaporation will not occur from the

carbon, it will occur mainly from the aqueous phase only. So, your estimate will go a little bit

off, but if you do not care, if you say as it is the water I just want to know how much is there.

So, for example, if this water somebody supplying this water for drinking, you are drinking

everything right, your intake contains everything, so then you may not want to correct for it,

you may want to actually measure what is the total concentration here along with, the organic

carbon you cannot see sometimes.

The water sample, it looks very almost clear, but it may contain organic carbon very small

amount. So what in terms of if you are not having a filtration mechanism before drinking

water, whatever is if I am unable to filter my water, I would like to measure the concentration

of that including the organic carbon also because I am ingesting organic carbon also from a

risk assessment point of view that is also important, I need to know that.

But if I am doing calculations like this, if evaporation and mass transfer calculations, you are

interested in the true aqueous phase, this will give you a wrong estimate of that. So, again, we

come back to this question of what is the objective of your analysis. So, all of these are right

and all of these are you know you have to use it in the correct spirit of how you want to do

this calculation. The third part, any questions on this? Every step, you do mass balance, that

is all simple, this is of understand is there.

So a problem I am giving here is very artificial, never happens almost like this because we

are never at equilibrium in most of systems. We are always in some state of unsteady state,

something is happening all the time. It is very difficult, very rarely do we get equilibrium in

environmental systems. So, you need to understand the purpose of having equilibrium. Why

is it useful? We discussed that a few classes ago.

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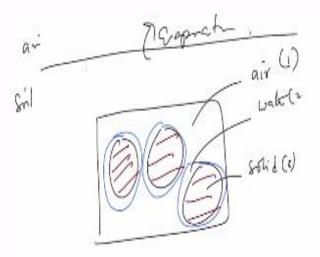
c) In the measurement of the concentration of A in the leachate water, ImL of 100 mg/L solution of a surrogate B was added to 1L sample before extraction procedures. The sample was extracted with 50 mL hexane and 40 mL of this extract was concentrated to 1 mL and 1µl of it was injected into an analytical instrument. The response of B obtained was 80,000 units. Calibration of B in the analytical instrument provided was Response = 60000m, where m is the mass of the analyte in ng and Response was in arbitrary units. Estimate the extraction efficiency based on the surrogate analysis.

- 2. Estimate the minimum water sample that is required for the measurement of total suspended solids (TSS) in the range of 10-30 mg/L using a method of filtration followed by gravimetric analysis of the filters. A 4-digit balance (least count of 0.1mg) is being used to weigh the filters to obtain gravimetric measurements of the filter paper. Standard deviation of random measurements of the filter paper was obtained as 5.4 mg.
- 3. Soil with moisture content of 10% (wet basis and considered as wet) is measured to have a contamination of chemical A with a loading of 100 mg/kg. What is the expected concentration of A in the pore vapor. Assuming no evaporation is taking place from the soil, what is the fraction of chemical on the solid phase and the vapor phase. Assume any other properties relevant to the calculation.

So the third part, part c is something that we did last Thursday and Friday in the surrogate analysis, so we do not have time for it, we will do it tomorrow. We will work on that problem tomorrow. And question number 2, I think this we did it last class, I think the illustration of minimum detection limit and all that, we did this. So question number 2, the minimum water sample required we did this in class, illustration of sampling volume and all that, minimum detection limit was used, so you already know that.

Question number 3 soil with moisture content of 10% with wet basis and considered as wet is measured to have a contamination. So, this is extension of the problem that we did it in class when we were discussing, first time when I did mass balance calculation, we did it with wet water saturated soil. We did it with sediment, this is now with soil, which means that this has water and air both together. So, you have to do the mass balance for all the 3 phases together assuming no evaporation since we are not considering.

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See when we say evaporation in this problem we are saying that there is a soil mass, there is soli, and there is water in between somewhere and the rest of it is air, this is the solid. So, we have phase 3, this is water phase 2, this is air 1. See this entire volume is filled with these 3 phases. Now, we have to distribute the chemical among these 3 phases that the mass balance has been written. What we say no evaporation means, somewhere far away there is a soil air interface

I am not assuming this evaporation, which in real cases is always happening, continuously happening, there is no equilibrium, but we for the purposes of this problem, we are trying to look at this okay. Any questions on this? So tomorrow, we will do the other problem. We will just go over that, any other questions if you have, and if you have no questions, I will move on to my next topics, which is not there in the exam, but we will start, instrument methods for chemical analysis. We will start one by one then.