Environmental Quality Monitoring Analysis
Physical and Chemical properties of interest

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Lecture - 8
Partition Constants

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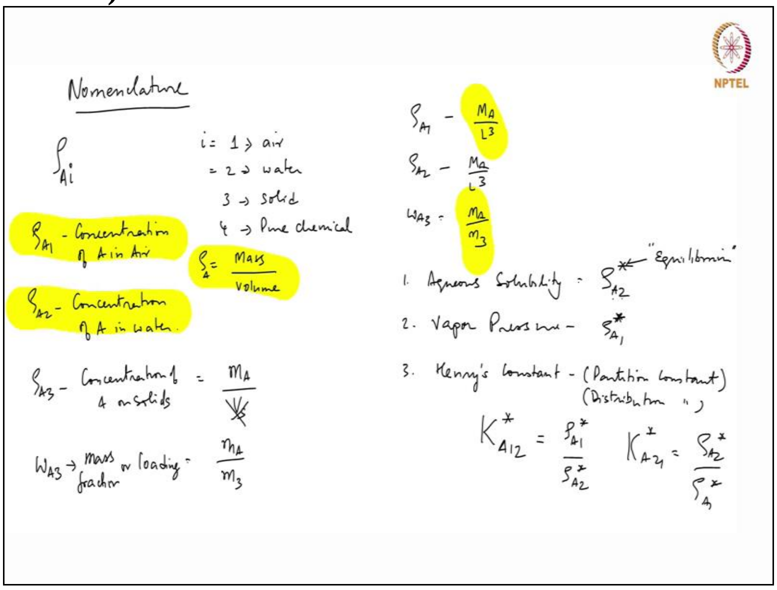

So, we will start today's class with the nomenclature that we are going to follow for the course we have done it in the last class. Ah, our main aim or quantity of interest is concentration. And we are looking at mass concentration. So the mass concentration symbol is Rho of A and in some medium. So, it is concentration of A in water, air from such medium. So here, I have indices for have to put some number here to indicate whether something here is air or water.

So, I will i here, i equals 1 is air, i equals 2 is water the symbol 3 corresponds to solid, 4 corresponds to pure chemical. This is a general nomenclature. So if I write Rho Ai 1 it is Rho it is itself, Rho of A is mass by volume is a density unit. Mass concentration of density rho symbol for density in chemical engineering terminologies we use C. C is concentration in terms of moles per metre cube. That is the convention.

When you write Rho it is of mass so, all our calculation will be in terms of mass. Rho is not convenient since if all our mass per unit whenever we go to the analysis section they are all mass per volume. Mass per volume, we are not working that range, so this is ah, when we say concentration, it is by default in this class is mass concentration. In air when we say Rho A2 this is concentration of A in water.

So, what about soil? In soil, you can also write Rho A3, is concentration of A on solid. But the problem is this means that we are looking at M of A divided by volume of solid. Lot of times volume of solid is not very easy to obtain. If we take soil for instance, it is porous media heterogenous, different sizes. For me to get actual volume is very painful. Ah, because of the properties of soil also and is laborious to do it.

So, instead we do not do this we do a M A over and M3. It is the mass of the solid, it is a mass fraction. Mass fraction symbol is w. Omega or w whatever we can call it. This is Mass fraction, we also call it as loading. WA3 So I would also like to use dimensions instead of using units and all that. So we call in terms of dimensions Rho A1 is MA by l cubed. L is 1 volume of air Rho A2 is MA by l cube again WA3 is MA by M3.

So in this context, when we will when we use when we apply this nomenclature to whatever we did in the last class we have two three physical properties. The first one is aqueous solubility. We call it as Rho A2 but we indicate as an equilibrium property by putting a star there. So, whenever this star appears anywhere it is something, something in equilibrium in something. It relates to equilibrium, some mention of equilibrium is there.

So, it is equilibrium of A with water pure A with water. This is equilibrium concentration of A with water. Similarly, Vapour pressure is Rho A1 Star. Equilibrium of A, is equilibrium concentration of A in air. May be also looked at Henry's constant, Henry's constant is a ratio ratio and we usually have this, this partition constant kind of Concept. This is a partition constant or a distribution constant.

The Difference between Rho A1 is concentration of a chemical in air and that concentration of water 2 is water. So if you look at this. See, you look at this, Rho A1 is concentration of A in air and Rho A2 concentration in water that are representing the concentration of Rho A1? Rho A1 is mathematic format is just a representation. Yah that is a dimension. That is the unit. That is the definition of mass by volume.

So I am writing that MA by L cube. Volume is L cube the dimension is L cube. MA is mass of A and M3 is mass of solid. Mass of A over mass of solid. This is definition dimension of atoms that we are using so that is all. There is no other distribution constant also. We will give generic term K capital K. There is lot of confusion small K capital K application also be careful. So normally when you are writing a problem you have to define whatever whatever is that you defining in words so that there is no confusion.

This is only for convenience there are other symbols people other textbooks use and all that. This is I have found this to be the most because there is a large number of interfacial things this is the most unambiguous representation but there are some text feature evolved some other notation. So they will use that I am not contesting all that. There is no right or wrong with this matter of convenience. This is a matter of convenience sometimes matter of convention.

So I would recommend you do not get stuck with those definitions or those abbreviations. So here we are representing equilibrium of A between two phases which means both the phases have to come in this definition here. So you are not talking about this constant we are talking about the partitioning of A between 1 and 2. One is air and two is water. If you write it like this and we put a star here, it means that it is in equilibrium quantity.

It is the ratio of Rho A1 to that of Rho A2 both of these are in equilibrium with each other. That is already mentioned here. If you want, you can put a star sign here and start here, both of them are in equilibrium. And thus whenever you put a star it sincerely denotes this is equilibrium or something. That is the easy notation for you to remember so that later on when we write look at transport it becomes easier to remember. That is Partition constant, partition constant? There is one air here and this is water.

So this defined as the ratio I put A1and 2 which means one goes to numerator 2 goes to denominator. If I write this as KA 21 star, I will write it as that is all. That makes it unambiguous, whatever partition constant however you define it this is the way it is. Any doubts in this, any questions?

So, sometimes you have this four pure chemical whenever it comes we will discuss that something that is there. We will look at it. In fact, aqueous solubility is like partition constant between pure substance and water, a pure substance its pure substance and vapour. You can write, but ratio of because you cannot write ratio of concentration, concentration does not have any meaning there. Pure phase or something right in terms of activity people write that people write activity in terms of 1 and all that. So we will not get that. So we will stay clear of that.

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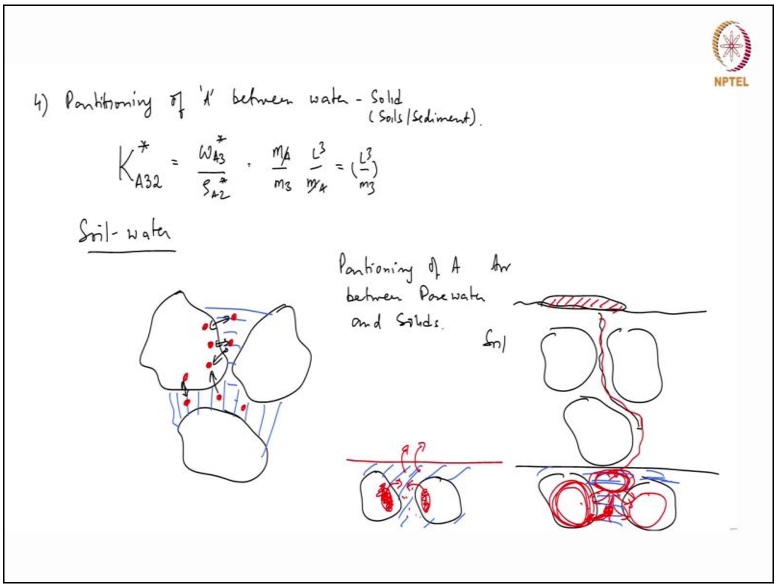

So, now we had properties of aqueous solubility, Vapour pressure and Henry’s concept. The fourth property that we are interested in is the partitioning of a chemical A between water and solid. By solids we mean soils or sediment or any such thing. So, we can write this in terms of here we write as KA. I can write it as 32, arbitrary line I can write it as 32. General convention is people write the KA number as ratio of things.

Here we are writing as KA32, W A 3 over 2. We are writing this in the equilibrium of a chemical between water and solid. So, solid concentration, do not worry about star here. I am putting it now here this indicate that is equilibrium you do not have to put that all the time just have to remember it make it convenient put it otherwise you do not need to, ok. So, here look at it the units are again MA by M3 and this MA is L cube. So the dimension of this is L cube.

Unlike the Henry's constant not Henry’s constant both the units will cancel it will be some number. The ratio of concentration must concentrate. Here it is not so L3 by M3 because of units of metre cube per kilogram or some such thing. Now, this is a General definition.

Partitioning of chemical between water and solids so this is relevant. So when you are looking at soil water systems, for example you have groundwater and you have water here?

I think let me erase the water. I have water in the middle of the solid yah. Suppose if there is a chemical here. You have a chemical here we will call it some Chemical A, this will physical partition to the solid between solid and the ratio in which will exist between this and the water bore water? This is the partitioning of A and the solid. So the system is static or moving slowly are whatever it is.

You do not worry about it right now. It is in equilibrium with its so it is equilibriating between this point. There are other solids sitting here on the surface somewhere and the, there is a exchange between the bore water, chemical in the water and why is this relevant? Relevant because it take the case of , if we take a scenario of say there is somebody there is a soil, air somebody dumps a large quantity of chemical on the soil. So we will put it as this.

So somebody dumps large quantity of chemical in the soil and the so the chemical tries to go down it goes down, it travels down by percolation, going in and is going in all the way say to the groundwater. The groundwater you have again, this is groundwater, so this chemical is travelling, chemical is travelling all the way to the groundwater and depending on its property it will sit there. If it is sitting here under the ground water, what will happen?

Immediately pure phase chemical sitting on ground water, while it is sitting there you just focus on this first, do not worry about this part. We will come to that later. What happened to this? What will happen to the chemical that is sitting in at that first step of bore water? As soon as it comes in contact with bore water what will start happening to it to the the chemical? It will dissolve. It will dissolve into the water it will also comes in contact with the solid.

When it dissolves in water can also come in contact with solid from the water, it can enter the get accumulated on the solid. And it keeps happening as there is pure chemical being supplied from wherever from the source and it keeps accumulating on a solid till a point just like solubility. Some point it cannot accumulate anymore, it reaches equilibrium between concentration that is there in the bore water and the solids and at that some points that will stop.

This is how contamination of solids occurs over a period of time. And then the reverse can happen. When there is lot of chemical that is sitting here, and this chemical here, if this chemical leaves this place, there is non-equilibrium that is setup and chemical from solids will now get into bore water and then move, move away. This is the reverse of this thing. All this takes a long time you will come to all that later.

It takes several decades sometimes to happen for this to happen because processes are very slow. For this reason the presence, the partitioning of chemical between solid and water bore water become very important, very critical in terms of what happened in terms of fate and transport of the chemical in the system.

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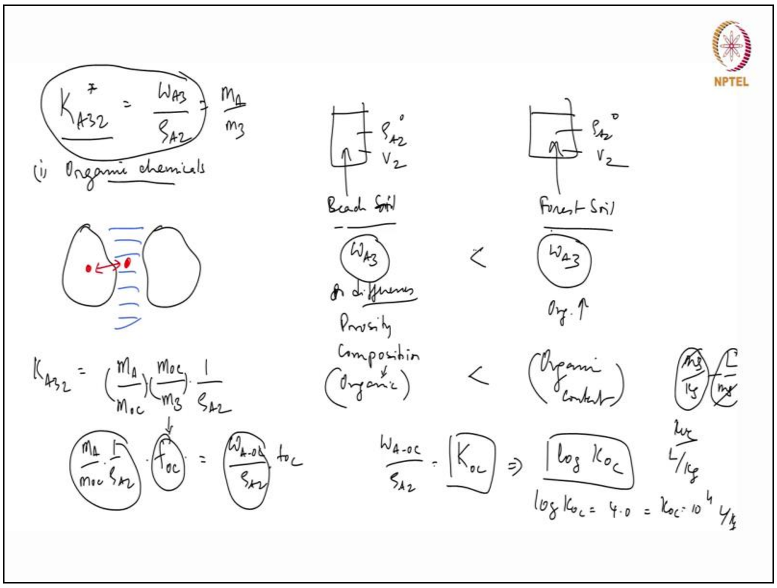

So, if you looking at the KA 32 WA by Rho A2 now, you have 2 conditions, 2 possibilities year one is for Organic Chemicals. This is true for organic or inorganic chemicals. Either of this can partition. Inorganic and organic both can partition for a large amount of discussion we have organic chemicals so we start with that first. So, organic chemicals, organic chemical is there in water and it is in contact with the solid, it is partitioning of organic chemical between sing a solid.

So now we have to invoke what is the solid material one of the this things here, if I want to measure, I want to get the partition constant of any chemical here, suppose I look at partition constant of a chemical in IIT, what is the partition constant of chemical say Bangalore or Hyderabad or Delhi? What do you think the number will be? Will the number be different or same? I am talking about partition constant.

Henry's constant is it the same or different in different places. Henry's constant is different in Chennai and Delhi and Hyderabad our aqueous solubility is the the same. What about KA 32 star? Same, how do you know? On what basis do you say that? This ratio of KA32 star WA3 Rho A2 the ratio, the equilibrium ratio. KA 32 on what basis are you saying that? If this is true, what else has to be true?

Let us say that I take a soil sample from Marina beach, the beach, beach and soil sample from inside the campus here and I put it to make a solution of chemical A. Take one Same solution a start with Rho A20 start with Rho A20 in this case I add beach soil in this case I add forest soil same concentration, same volume.

When I put the 1 gram of beach soil and one gram of forest soil, in both cases I shake it, at the end of some period of time say 2 days or 3 days, how much of the chemical would you think will be on the soil in the case of the beach and the soil in case of the forest? Which one would be higher? SO if I want to estimate WA3 here and WA3 here, which one do you think will be greater? Will they be the same?

Do you understand the problem what I have posed? I have added the same amount of chemical in the water phase in the initial here and have added the same amount of solid in both cases, but I had different solids: one is from the beach other in the forest file. You think it will be same or different? Why, why will it be different? Properties of the soil are different. What properties of soil are different, likely to be different?

Porosity ok, anything else, what composition? What is specifically in composition? What do you think will? So if A is organic chemical, what do you think will, will be the factor determining factor? Which one will be higher? This or this? From your general observation of beach soil what is the difference between beach soil and the forest soil? No, no, soil. I will go to the beach and take soil and go out and take.

Water content may or may not be different. Is there anything else, major compositional difference? Pores. Somebody said something, could not hear, any other difference, big difference? Loose ok I can make this also loose, I can make this also loose like a property this thing. Ah so it will be of more organic content. So if you have organic content, the composition one of the main thing is organic content for Organic chemicals.

You have to recall some discussion that we had earlier about organic matter. Which one of this will be greater: So, the organic content of forest soil is higher organic content of beach is less than organic content of the forest soil. WA3 what you think how do you think will behave? It will be more in the beach why? Organic content is less why will be more in the beach? Organic content is high what does it imply?

Organic content is part of the soil of the solid phase, what does it imply? Organic content, you say, what can it do? Where else do you use organic solids any application that you are aware of? Agriculture, something more, common. What do you use in Agriculture for? That is even an application. With reference to water, do we use organic solids for anything? May be in water treatment, ah activated carbon, what do you use it for?

Water, treatment means what exactly? Absorption means what is the more general description of absorption? If I do not know the word absorption, how can I describe it? What is absorption? Removal of yah, removal of activated carbon is used there for specific reason. Why do have carbon? So if we look at the organic property or organic carbon, large background, backbone of carbon so it likes carbon.

If organic carbon content is high, carbon likes other organic chemicals. This is, this is true. More or less if you have a large organic content it is likely to attract organic compounds. So you are likely to find that if the organic content is high here, you are also going to find this in the same direction. Large amount of organic Chemicals are also likely to go to the forest soil. So, this is, this leads to more accumulation this has, then you have problem.

If you want to describe KA32 for a particular chemical I have to then go and get the organic content of all the this things and I have to refer to I have to do an experiment to actually get what is the, so I cannot have a uniform property, I cannot say KA32 of a chemical between two particular soil KA32 of a chemical itself I cannot classify because I need to know about the organic carbon content and it that also information I need.

So, this is we will use this in calculations, but this is not a, you cannot use it as a property of a chemical. But from this observation what people have looked that is that I can write this KA32 as WA3 just now we have also determined the organic carbon content is different. So we will write this as instead of KA32, will write this KA organic carbon divided by yah so we will write it even more expendables.

We will say M of A divided by M of OC, M of OC divided by M3 divided by, if I break up the numerator into two terms here, we are writing is WA3 is m of A3 right, m of A3 if we write that in terms of this. So this first time here is the second term here is content organic carbon containing some amount of mass of carbon divided by mass of the solid. So we will give this, we call it as fractional organic carbon and this term here, when becomes it is a mass of organic chemical A over the mass of organic carbon.

This number here becomes a little more normalised. So what it says is if I know what the organic carbon is in general I can now say that there is absorption of a particular chemical partitioning of an organic chemical, organic carbon with reference to water is should be more or less the same. I am removing this F OC out of the 3 equations I am separating it out. So what I will do is instead I will write MOC, MA by MOC into 1 by Rho A2.

This makes it as W A2 OC by Rho A2 into F OC. If I do this, this number here is a normalised partition constant. So it does not depend on the amount of organic carbon. It depends on the type of organic carbon. You understand? So, here again we discussed in class that there is likely to be variability in organic carbon itself, but then, collection of a lot of data of people of figured out that the organic carbon has a certain range in which it behaves.

Composition does not change a whole lot unless exceptional conditions. So people have measured this. So, they have measured this KA32 using experiments like what we have described here. And then have broken it up. They have also measured the organic carbon and have normalised it, they have broken, separated the organic carbon content and the ratio of the WA OC this number this quantity.

WA OC by Rho A2 is now called as KOC KAOC is power definition but this is KOC. It is a generalised term in Literature as KOC. KOC is the partitioning of chemical between organic carbon and water with the assumption that organic carbon is a same throughout the entire world which may or may not be true. This is first exercise is that we you have to do. I will ask to go and get organic carbon lock KOC, for, for different chemicals. You will see the range of KOCs it is not one number. It will vary and varies for good reason.

The reason that we have mentioned need not be the same everywhere, depending on origin of organic carbon this composition, will change and therefore the number will also change partitioning velocity change and it is more complicated than what we give. But this is a convenient methodology to do this. So, KOC is the, is the physical property that can be listed if you are saying that organic carbon has a certain property.

So when people measure organic accuracy of a new chemical you need a reference right? Where do I get organic carbon from? I have to get it from I can get it from India, I can get from China, from the US, or Europe, Africa anywhere. Organic carbon which means I get soil from different places and extract the organic carbon and then use it. So, people of standards, standards to which you measure KOC of a particular chemical, use those standard matrices.

Once we have mentioned in the last class called the humic acid and Folic acid and all that, so we use one of those. So, there are standards available in the market, but you can buy and you can report KOC based on that. When you look at the experiment data experimental data for KOC people will mention what is the organic carbon that they have used. They have used one type of ah OC or naturally occurring OC or synthetic compound which mimics organic carbon all these are possible.

So, this is log and usually represented as log because KOC, because KOC is a big number and you can imagine even if I have a few milligrams of organic carbon solubility's of lot of chemicals is small, but they are organic there, there like they like organic phase. So, they all will go there and they will stick there. That is the reason why we use them as absorbent because KOC is very big. Partitioning from water to the solid is very high.

That is the reason we use it as absorption for that is why soil is considered to be a naturally purifying medium because while, before it goes to ground water it has to go through all the layers in which there are organic carbon that will remove, absorb a lot of this chemical and so the number is big. Instead of writing 10000 and 20000 all that they just convert into log of KOC. So, again the KOC has units, it is the same unit as that.

So, the nomenclature, the convention KOC is usually in litres per kilogram. KOC has unit of litres per kilogram because it is coming from milligrams per kilogram and milligrams per litre. This is the concentration units of any chemical on solid any concentration unit of chemical in water. This is usually there, so therefore we cancel, sorry if we cancel these you get litre per kilogram. That is general convention.

When you see only log KOC, if you say log KOC of 4 which means KOC is 10 raise to 4 litres per kilogram unless otherwise specified normally. Sometimes people will just give you the KOC and different units 10 raise to 4 litres per kilogram is 10 metre cube per kilogram. They will give you 10 meter per kilogram and that is also valid. But if there is a mention of only Log KOC then it is assumed that units of KOC are litres per kilogram.

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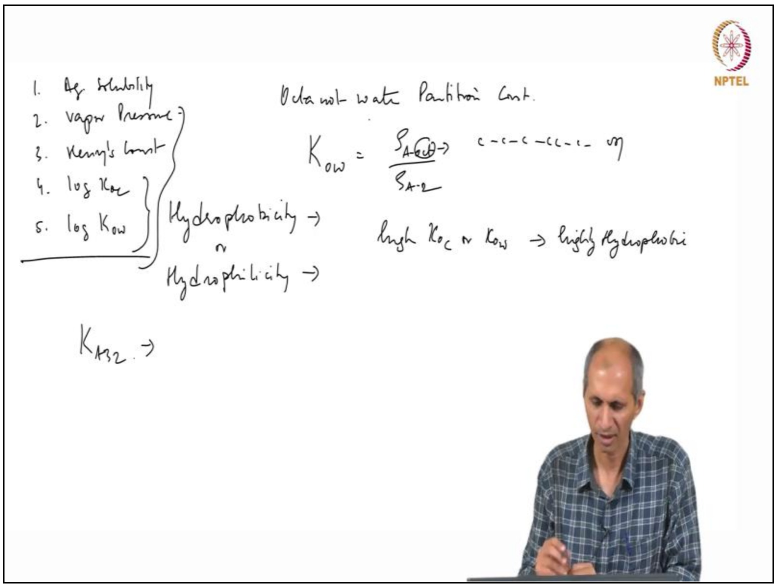

So, in association with log KOC we have no properties of we have aqueous solubility, we have vapour pressure, we have Henry’s constant, we have log KOC. So in association with log of KOC, log KOC generally gives the affinity the tendency of a chemical to bind to an organic phase. This is a general assumption. There is a larger implication of this before environmental scientist came about and invented log KOC because it pertains to soil and sediments and all.

In Pharmacology, in toxicology people look at this number differently. What they look at is if you are eating a medicine or a poison how toxic a particular material is if it is through a different, different route inhalation or oral route. They look at the binding of this particular chemical is accumulation in the human body in your tissue and this they call as bioaccumulation.

This bioaccumulation also results is determined by, by looking at the theory there is that most of the blood and all that all the food goes in it gets digested it is going in more or less aqueous solution and it is partitioning between different portions of the tissue as it is going. So, if a chemical has a very high partitioning between water, water base, aqueous base system and very high organic liquid tissue is considered to be a liquid based this thing, fats and tissue and all that.

So, people look at that partitioning. And they can have different numbers. They can have KA some bio some tissue and water. They can do it at different levels. They can taken take some animals they just dump the animals into water put a chemical and after finding time they will see how much of chemical is gone into, into the animal into, into fish or something else. That is one bulk thing you can look.

Or you can take a particular tissue you can probe which part of the tissue how much accumulation happening on the tissue itself. So, this bioaccumulation factor is also base is just like the log KOC. It is the ratio of two concentrations. In this context people have what is called KOW. This is a normalised number instead of using lipids, they use Octanol. Octanol is used as a surrogate for lipids. ok

So, it is octanol water partition constant. This is KOW equals now you will just write it as Rho A Octanol versus Rho A water? This is how it has been determined originally. So they will not use W when they use for some liquid. Octanol is a liquid when you doing the test outside. But in the human body, in the body, tissue is solid. So measurement of that is very difficult. So what people have done is they need a common basis to which in, in which they can estimate accumulation factor.

So KOW or Octanol factor constant is considered to be a good circuit of lipids which means it has reasonably long Chain and then it has OH group 8 carbons. OH group it looks like the organic carbon. Organic carbon is a long chain hydrocarbon with polar groups at the end. Octanol is not that long but some numbers represented by some they have chosen it on some bases and based on analysis of lipids, how they.

So, it is not the actual number that will be there in the human body, but it is notiona, it gives you a scaling, gives you a some kind of comparison of what? What does it give you? If you look at log KOC and log KOW both of them will give you a quick ideas if you compare the log KOC and KOW they have different Chemicals, organic chemicals. It very quickly looking at the values you can tell whether its chemical will bind to an organic phase or will stay more in the water, whether it likes the oil, likes the organic carbon or like the water.

So this, we come up with another term called Hydrophobicity or Hydroelicity. Hydrophobicity means it does not like water. Now Hydrophilicity means it does not like the carbon. SO, this is a scale of hydrophobic behaviour. The chemical is hydrophobic means high KOC or KOW means highly hydrophobic. For relative things, there is no absolute terms hydrophobicity. There is no absolute, there is relative one chemical versus another chemical.

One of them will or you can that chemical which has log KOC or KOW of 1 versus KOC or KOW of 4 which means it is 1000 times more than that. So, this one will accumulate 1000 times more than that. So, they will do this on the basis of that, it also gives you some idea of how much hydrophobicity can be enough if you want to design a particular chemical especially for this is used a lot in Pharmacology.

As we discussed Pharmacology looks at how much of accumulation in the body is medicine.
You need the medicine to bind to a particular site in order to work. So chemical is not at all hydrophobic and hydrophilic then it will not accumulate anywhere. It will go out or pass out body will send it out without any absorption or accumulation. So there are various applications to this, both environmental as well as system.

The property of KOC is used as an index to see whether discreetly, quick reference. You can look at all these properties and say where the chemical is going to be.If I look at all these properties, it will quickly give a qualitative way of this chemical likely to be more in air or in water or not been water in the sediment soil it will come out very slowly. You can make very quick decision as to where your attention should be, focus should be, on, on remediation or treatment or whatever that you need to do subsequent decision to it.

So these are all important properties and most of the chemical structure are concern to us this property is listed. So, these last 2 pretty much except last four most of them is organic chemicals is the focus. The first one you have both organic and inorganic. The partition constant KA 32 we are worried about it from both organic and inorganic. Both of them will partition, but the KOC theory only applies to organic Chemicals. It does not apply to inorganic chemical.

So we will talk about inorganic chemical tomorrow. What happens and then how does KA32 changes for that? But you cannot generalise it like that. You still have to, you have to find out you have to find out other set of conditions. It is not very easy you have to do it very site specific. There is no generalised theory based on for that.