Environmental Quality: Monitoring and Analysis
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Lecture - 9
Soil-Air partition constants

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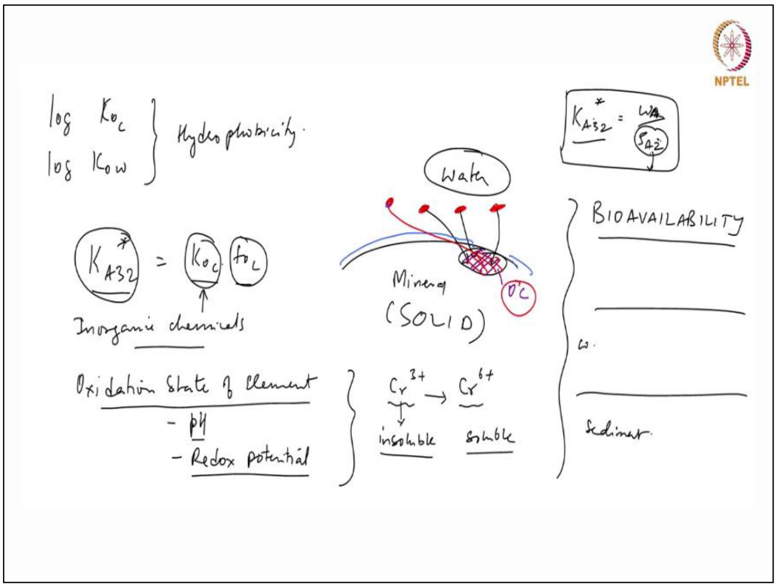

So this issue of log K oc we determine that log K oc and log K ow these are two properties of a chemical which characterise its hydrophobicity? So, so in the context of environmental fate and transport the these these numbers are important from in soil and sediments and will will do an example, immediately following this. So the assumption is like this so if you are writing K A32 star, we will write K A32 star as K oc times foc rather than writing it simply like this. So what we are doing is we are this is the property of chemical itself and this 'f oc' is what we represent site wherever you are taking it from.

So if the very large organic carbon that taking care of this business. The overall partition constant depends on both the organic carbon content and the nature of the chemical, ok. So, this is the number which you actually use in in transport scenario but this is the property of the chemical that is easy for us to quickly get an assessment when you will look at the number itself, you will know that this is likely to be in this phase or this phase you can make quick judgements based on that, ok.

So for the case of inorganic so we said if inorganic chemicals this doesn't apply because when we say for Organic Chemicals the assumption is that all organic compounds will only will only adhere will only bind to organic matter that's present in these things. So, the mineral component in the soil or sediments does not attract. It's not doesn't attract has lesser affinity for organic compounds especially when you have water in the system.

So when there is water, water prefers to adsorb, the surface prefers water than organic compound. You have a mineral surface and of this there is a one component of organic compounds this is organic carbon and rest of it is all mineral, right. So, if there are there are organic compounds here in the water, this is water this will only bind; this can only bind to here the reason is it doesn't not that it does not want to bind on this mineral surface, it cannot bind because this is already occupied by water. The water forms a thin-layer thin layer or just continuum there is if fully saturated it's already there a lot of water is there. So, there is no there is no opportunity or location site on which the mineral can accommodate an organic molecule, ok, so it doesn't allow any water. So the only place the minerals the organic carbon can go through is the organic carbon. This organic carbon phase here that's why this equation become important, it assumes that there is no adsorption there is no binding on the minerals for the organic compound in the presence of water in the system.

For inorganic chemical this doesn't apply, so the inorganic chemicals the nature of binding is very different and it is more to do with the surface charge that is present in the in the system and also its oxidation state surface charge depends on oxidation state and then in what valence it is in. So, the the property that the oxidation state of the inorganic element in some ways determines the where it and what form it is, whether it is the bound; how much it binds to the solid surface are doesn't bind to the solid surface, ok.

And there are no general rules like the 'K oc' and 'f oc' kind of system. The rules are based on oxidation; what determines oxidation state of element several things one is pH, one is the dissolved oxygen content of this, so what is called as a 'Redox Potential'. So, depending on the the amount of; depending on whether the ah ah amount of oxygen that is present in the systems this oxidation state changes, the redox potential changes. So, redox potential for different elements valence states are different and then and it is a function of whatever is there in the system however it is in the system.

So, for soils it is different from soils to sediments because oxygen content is very different and pH is also different. And it's also a function of any biogeochemical activity that is going on in system so it's little more complicated but one example that is very prominent in the case of this why it is important? The oxidation state and therefore the partitioning depending on that the partitioning will change if any of these conditions change.

So one example is following so we one of the permanent we example give is Cr 3+ and Cr 6+, yeah. So Cr 3+ is chromium valency of 3+, valency of 6+ this is usually present in an insoluble form and this is present in a soluble form which means it is in the water in presence of water Cr 6+ is likely to be more in the water than Cr 3+. Cr 3 + if it is there it will be as an insoluble form. This not adsorption, this is the way it is, so Cr 3+ is becomes precipitate Cr 3+ present in the form of precipitate either as chromium trioxide or some such it forms an oxide or it forms another combination or something else that is present in the in the soil and sediments.

It is present in the insoluble form. And when there is a conversion due to some activity, if there is conversion from Cr 3+ or Cr 6+ it comes into the soluble form. Even in the case of organic compounds when we look at the K A32, when we look at KA 32 star the implication of KA 32 star is that it determines how much of chemical is present in the in the water, right. Why is that important? Why are you very worried about being present in the water? It is the property, so like solubility, if the solubility is very high or its vapour pressure is very high, so in the case of water we take solubility as high or the KA 32 is is is some value it it implies that there is a value, there is a concentration that exist in water, ok. So why is this important? Why why do we need to know how much this is, the value of this is determined by how much, is this value? Why is this important? This is what is the, let us look at this two two of these numbers.

So, will will I think we will get back to this in a few minutes I think will make little more context that time, ok. Along with this concept of hydrophobicity, the the significance of numbers like KA 32 is in another term that we commonly used in again in Pharmacology and Toxicology and in Environmental Sciences is this thing called 'Bioavailability', ok. Bioavailability means it is it can be seen in different contexts, from a context of human health and fate and transport and exposure what it means is that, say there is there is a sediment, ok and there is water on top of it.

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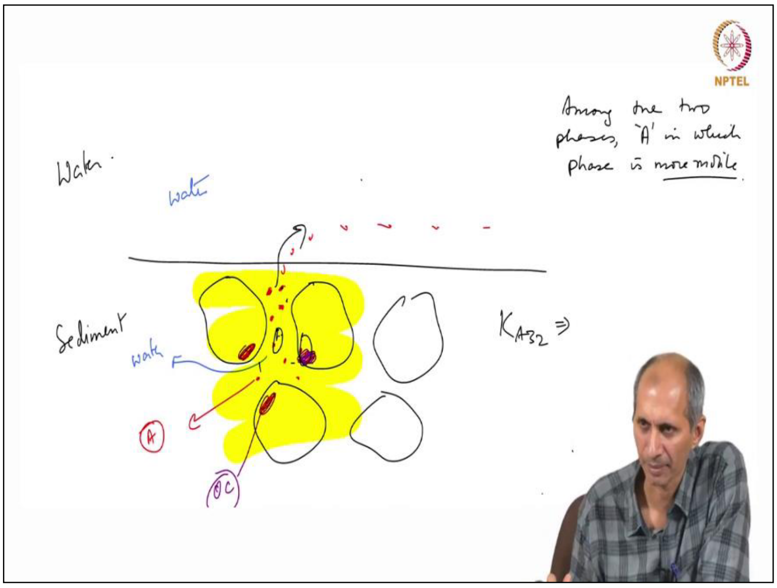

And we have, I will draw it, write down separately again, so there is sediment here and there is water on top of it and there is a lot of solids and among the solids you have some organic phase and you have also a lot of the; what is the implication of this diagram. If I have drawn this, this this is the chemical A, this is the organic carbon and this is all water. What is the implication of this from exposure point of view? The value of KA 32, the value of K 32 how does that influence this, what is happening in the system? If there is when we say KA 32 in the system, what does it determine? Say if we are taking this particular system. If I take if I take this system, yeah, what is the value of KA 32 determine, in the system?

KA 32 is the equilibrium of A between the solid and the water, so which means it will determine, what is the distribution of the chemical between these two phases. So, we can find out what is the concentration of A in the pore water, So how does that matter, why is it important? It is important from the point of view that which of these phases is more likely to move from one place to another place? Which is more mobile?

We asked this question, is more mobile, among the two phases, on the solid phase A that is sitting on the solid phase or A that is sitting here which is more mobile?

Students: water

Professor: the water, yeah, for that reason this this can move much more easily from one phase to another from one place to another place because there is a continuum here. There is water here and there is water here it can move out this chemical can go out and travel somewhere else and reach a receptor.

There is the possibility of reaching receptor much more. So, that's the reason the bioavailability can be interpreted in this form in which it is now accessible to some receptor, some fish, some animals or some human beings downstream somewhere, somewhere away from the system. Where it can move from here to there and therefore it becomes mobile and that that is bioavailability available for biological activity. On the other hand, we also use the term bioavailability in the context of treatment.

When we do water treatment and solid treatment we are looking at bioavailability is looking specifically at the the amount of chemical that is available for microbes to degrade. Degradation of microbial degradation occurs mainly in the aqueous phase in the presence of water they don't perform very well if you have dry conditions and all that. So, the transfer of chemicals from solid phase to a microbe occurs through water. The water is the medium by which it occurs therefore that is also a context in which we can look at bioavailability.

So, the term bioavailability is important so in the case of chromium, things like chromium it becomes more bioavailable if it is in the soluble form than it is insoluble form, right. So any condition that will convert Cr 3+ to Cr 6+ will make it more mobile, which is the reason Cr 6+ is considered to be more toxic Cr is Cr because Cr 6+ more mobile it is what you are you will measure away from a particular site, if you are measuring chromium in water it should usually is Cr 6+.

If you have solid phase you measure Cr 3+ and 6+ because there is 6 and 3, 6 will be here and 3 will be here. If I take entire thing and measure you will get total chromium it will be in combination of 6 and 3 I only do it here. If it is pure aqueous phase is only this Cr 6+, ok. So, this becomes an important constituent in terms of partition. So partitioning constant is important from from a view of bioavailability and then for inorganic compound this bioavailability is influenced by other factors such as pH and oxidation reduction potential and its oxidation state and all that and any other conditions that will influence it, ok.

So lot of times what happens is there is say chromium is sitting as an insoluble form in sediment because it is deep under the water. Now you go and dig it up and you churn it and stir it up. You are introducing oxygen into the system and there gonna be transformation of all the things which are in a lower oxidation state now get to higher oxidation state and they can become more mobile. So, this is generally the, so for inorganic elements you have to measure the partition constant separately each one if you are going to look at; It's more complicated it is not as straight forward as K oc and f oc. It is possible to get a relationship between the partitions constant verses other factors but people usually don't do that they will go to each site and measure the hard way. There is no unifying single normalising parameter for a case of inorganic elements but there are also a lot a lot of inorganic elements of interest. We are looking at a few heavy metals Chromium, arsenic, Mercury and few of them there are there are not a whole lot.

So, that's the practical aspect is there and there is a very vast subject in aquatic chemistry, biogeochemistry of aquatic systems where people look at all these things in different systems in lake systems, in river systems in groundwater, in sediments and in oceans so all of these elements that are present in each one of these systems have a different biogeochemistry because there is a different set of biological presence there.

And they are all participating in it, so fairly complex system and so we will look at one chemistry, we look at mercury, we will look at mercury in a particular system and then study everything related to that the inorganic chemistry of mercury in that system, ok.

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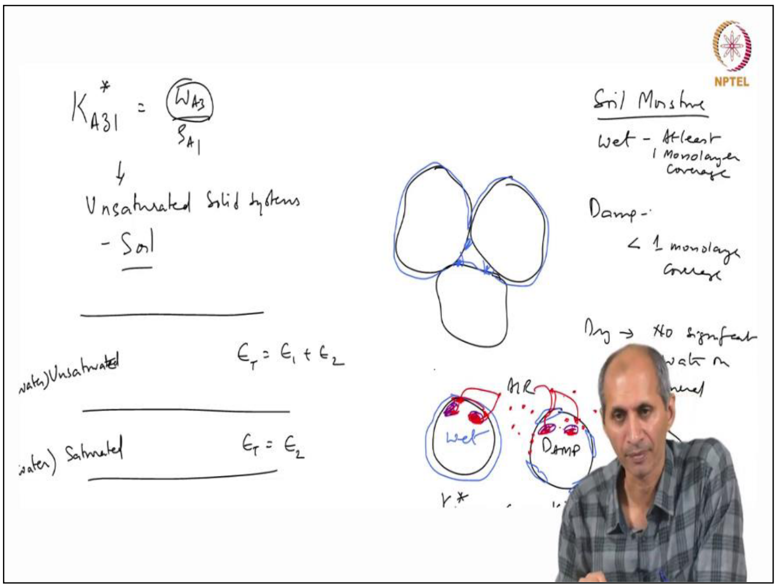

So, now we look at the another number which we call as KA 31 star so from the definition of what we have been talking about. This is wA3 divided by Rho A1. So, what is this correspond to so this is the solid we are talking about solid and air which system does this corresponds to? Which environmental system thus this corresponds to, KA 32 corresponds to groundwater saturated groundwater and sediment systems where everything is water we are interested in water.