

## **TOPIC: GROUNDWATER ARSENIC POLLUTION**

### **SUB-TOPIC:**

### **PART B: GEOCHEMICAL CONTROLS ON DISTRIBUTION AND MOBILISATION MECHANISMS**

#### **Supporting Transcript**

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*This transcript accompanies associated presentation slides and video content developed for the TIDE project in 2021, with acknowledgements and disclaimer as noted in associated files.*

#### **SLIDE 1**

This is the second lecture on the arsenic pollution series, where we'll be discussing the geochemical controls on arsenic distribution and how arsenic mobilisation mechanisms work.

#### **SLIDE 2**

This lecture will cover the geochemistry of arsenic-contaminated groundwater and we'll be talking about how different minerals, as well as organic matter affect the mobilisation of arsenic

#### **SLIDE 3**

The geochemical controls on arsenic are very dependent on hydrogeochemical setting and can be highly localized, but amongst the general scientific community, there is general agreement on the overriding controls. And it's intuitive to think that understanding what increases arsenic pollution is important to mitigating against high and dangerous levels of arsenic in groundwater. One of the main theories out there is that bioavailable organic matter may facilitate arsenic mobilisation in shallow aquifer systems controlled by reductive dissolution processes, although details of this mechanism remain unclear.

#### **SLIDE 4**

The objectives are to explain the predominant geochemical controls on arsenic mobilisation, to be able to recognize how we can categorize organic matter into different fractions and how this might relate to arsenic mobilization, and also to recognize the role of organic matter in mobilising arsenic from iron (oxyhydr)oxides.

#### **SLIDE 6**

Arsenic exists in two predominant forms in nature and that's arsenate, where arsenic has a oxidation state of +5 and arsenite, where arsenic has a oxidation state of +3. And their occurrence depends on the redox and the pH of the environment that the arsenic is in. That's

shown in this Eh-pe diagram, also known as a Pourbaix diagram, which shows which species is thermodynamically stable at the given conditions. In most environmental systems, arsenite is more mobile and its also harder to remove from the environment.

#### SLIDE 7

We learnt last time that reductive dissolution is the predominant mechanism on controlling arsenic in shallow groundwaters in South and South-East Asia, where the largest portion in the world are affected, and that alkali-desorption can be significant too. So I'm going to focus this lecture on these two mechanisms, but particularly reductive dissolution as it is the predominant control in the most significantly affected areas. Within this mechanism, it's the reduction of what are grouped as iron oxides and hydroxides that is the control for most systems. Arsenic tends to be bound to these groups of minerals, and if they become reduced, they dissolve and release arsenic from their structure. So let's think about basic controls of redox conditions and where we normally find more reducing environments. And that's at greater depths normally, so would we expect to see higher or lower arsenic with depth? Lets have a look.

#### SLIDE 8

This is from a study in Bihar, India. We can see a sharp increase in arsenic from 0-20 m as conditions become more reducing. Oxides are formed in environments with ready sources of oxygen and break down and dissolve in anaerobic conditions. But what triggers the drop-off beyond 20 m? We'll take a look at what could cause this in a second. Importantly, you can see a correlation between iron and arsenic and this shows that this is iron oxyhydroxides being reduced rather than manganese oxides being reduced, which is sometimes the case.

#### SLIDE 10

So iron oxides are a group minerals which include ferrihydrite and goethite amongst other minerals. Arsenic binds to both of these and is released under reducing or alkali conditions. And arsenic is also able to bind to clay minerals including kaolinite, illite and montmorillonite, except there is less arsenic absorbed per unit mass of these clay minerals. Phosphate not a mineral although competes for sorption sites nevertheless and so has an effect here because it can bind to sites on minerals which would otherwise be bound to arsenic. And there have been a lot of studies on phosphate competitive sorption and there is debate to whether phosphate is a major control on arsenic or not -this likely depends on the geochemical setting.

#### SLIDE 11

These plots are showing us the percentage of arsenic adsorbed on the surface of two iron oxides in comparison to pH, goethite a major control on arsenic whilst hematite, although not one of the main sorbents of arsenic, can be used to exemplify the differing properties of the iron oxides across different pHs. We can see that beyond around pH 8, the adsorption capacity decreases. And this is effectively the mechanism for alkali-desorption – at higher pHs, arsenic is desorbed, leaving the iron oxide carrier as a solid phase. This is different to reductive

dissolution because here the solid-phase carrier dissolves. Arsenic also desorbs from clays at higher pHs.

#### SLIDE 12

So now we can look at the other major control on arsenic and that is organic matter

#### SLIDE 13

Lets first look at how we characterize organic matter and group it into different types and sources. We can divide organic matter in a number of different ways due to the heterogeneous and complex nature of organic substances. We can divide it up into that that is bound to sediment, organic matter that is petroleum-derived and then organic matter that is relatively young and from a surface source like sewage or farm waste, which we call surface-derived organic matter. This could make its way into groundwater through ponds, wetlands and can likely be influenced by groundwater pumping, which may draw this material down. We've also got organic matter derived from the decay of plant material. The reactivities and bioavailabilities between these three groups is thought to be very different and has been given a lot of attention in the study of geochemical reactions in groundwater involving organic matter. So how does organic matter contribute to arsenic mobilisation?

#### SLIDE 14

Bioavailable organic matter is a major control on arsenic because it is able to act as an electron donor to facilitate microbially-controlled reductive dissolution of iron oxides. And the type of organic matter is thought to be really influential to this process. Very young, labile organic matter is thought to be more reactive than more mature organic matter, and so we think that surface-derived sources could be contributing more to mobilisation than mature, sediment-bound or petroleum-like organic matter, but this is still quite up for debate.

#### SLIDE 15

A potential research question could be whether the reason for arsenic in groundwater dropping off beyond 20 m in the Bihar study, is to do with the presence of total dissolved organic matter, or a particular type of organic matter, decreasing beyond this point.

#### SLIDE 16

Additionally, organic matter is also able to compete with arsenic for sorption sites on iron oxides, which means more arsenic is freely available if there is organic matter present. Although to confuse it a bit more arsenic can also sorb to the organic matter itself, which will reduce the amount of freely available arsenic. But overall, this is a major control on arsenic occurrence in groundwater and there has been a lot of work to pinch down which type of organic matter has the greatest influence on mobilisation.

#### SLIDE 17

And one such theory is that the influx of surface-derived, labile organic matter, from sewage or the ingress of river water, is facilitating the mobilisation of arsenic along the banks of the Ganges River and elsewhere in the world. It is thought that an increase in irrigation and municipal pumping can also draw organic matter from the river and from the surface. And this theory is currently being put to the test, through the characterization followed by the modelling of organic matter, to see if this is indeed a plausible mechanism.

#### SLIDE 19

So to summarize this mini-lecture, the speciation of arsenic is important to consider as it affects the mobility of arsenic in groundwater. Iron (oxyhydr)oxides can be thought to regulate the release of arsenic in most of As-affected groundwaters and finally organic matter, particularly its type, is thought to play a significant role in the mobilisation of groundwater arsenic and more work is being done to find out more about this.

#### SLIDE 20

Now onto a learning exercise.

#### SLIDE 21

For the learning exercise, I'd like you to number one, list and describe two geochemical controls on arsenic mobilisation. Number two, can you explain how organic matter is thought to increase arsenic concentration in groundwater and then suggest how might the type of organic matter may affect this, which is something we discussed. Feel free to rewind the video to help you answer these.

#### SLIDE 23

Here are the references that were used for these slides.

#### SLIDE 24

And again, I refer you to these best practice guides for some good information on arsenic in groundwater and how it can be controlled.

#### SLIDE 25

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