

## **Basic principles of groundwater flow and considerations for sampling of arsenic**

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### **ABSTRACT**

Steady-state flow pattern of a hydrogeological system can be characterized using values of hydraulic head, hydraulic conductivity and boundary conditions based on geometry of the system and distribution of recharge. Hydraulic parameters like hydraulic conductivity are defined for representative elementary volume (REV), for which we can determine average value of hydraulic parameters. When appropriate data are available, a suitable groundwater modeling code based on particle tracking procedure can be used to determine flow pattern and residence time of water in a hydrogeological system.

Arsenic, many other metals and metalloids are redox sensitive species. This means that they have different forms with different behavior and toxicity depending on redox conditions in a hydrogeological system. There is generally a vertical (and sometimes lateral) redox zonality in an aquifer. Only discrete depth sampling from piezometers installed at different depth can reveal this zonality. On the other hand, sampling from pumping wells with large screens gives only mixed samples and correct redox zonality and speciation of arsenic can not be determined. It is also necessary to distinguish between filtered and unfiltered samples and properly preserve samples to maintain constant oxidation number of arsenic species until analysis. Speciation of arsenic can be done in the field using the disposable cartridges for selective adsorption of As<sup>5+</sup>.

Keywords: Groundwater, Flow, Sampling, Arsenic, Piezometer, Redox.

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### **1. INTRODUCTION**

Investigation of geochemical behavior of dissolved species in groundwater including arsenic is based on knowledge of groundwater flow pattern. This means that determination of flow pattern is a prerequisite for geochemical investigation.

Let us look at the influence of water sampling locations on the interpretation of geochemical evolution of groundwater (Fig. 1).

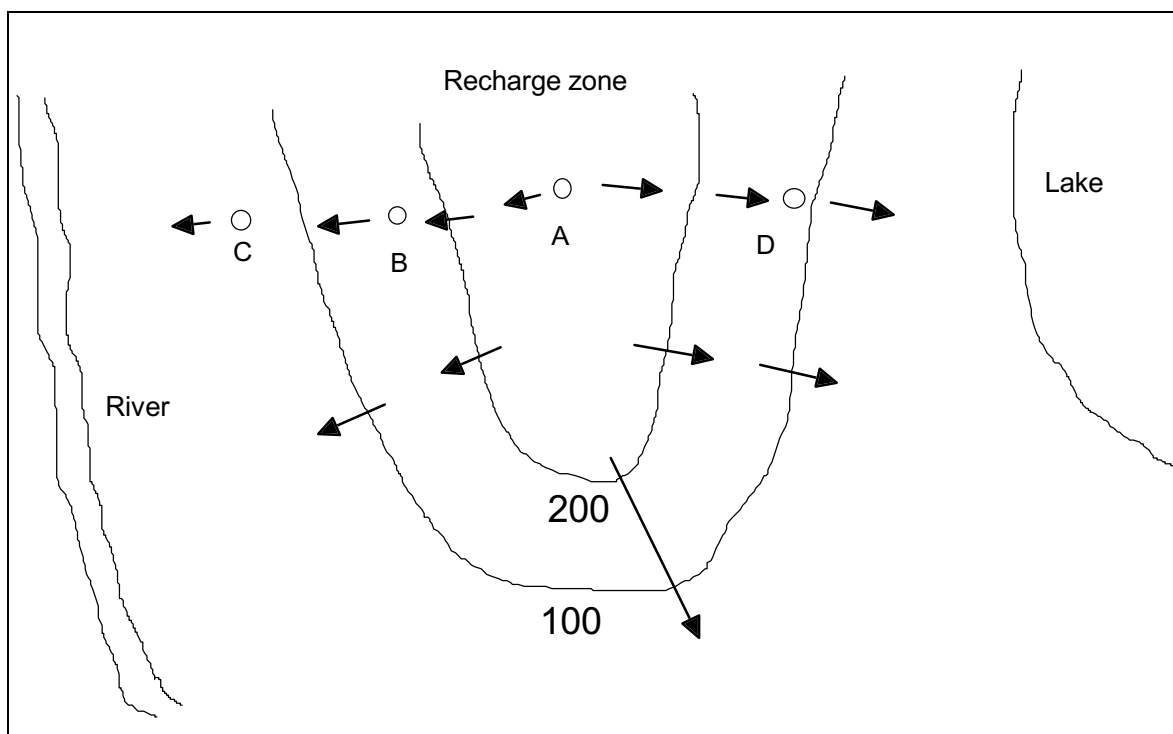


Figure 1. Geochemical sampling of a hypothetical flow system.

This is planar view of a simple flow system where recharge area represented by point A. From point A groundwater flow is diverted in 2 directions: towards river and points B and C and in the opposite direction, towards point D and lake. When we investigate geochemical evolution of water, we can compare points A and B (and also C), but comparison of C and D does not make much sense from viewpoint of geochemical evolution.

Groundwater movement is described by Darcy's Law expressed in its common form as:

$$v = k.I/n_e$$

where  $v$  is groundwater velocity,  $k$  is hydraulic conductivity,  $I$  is hydraulic gradient and  $n_e$  is effective porosity. Hydraulic conductivity characterizes transmitting properties of porous media and is defined for representative elementary volume (REV). The REV is a volume of porous media for which we can define average hydraulic parameters (DOMENICO AND SCHWARTZ, 1990). Steady-state flow in homogeneous porous media ( $k = \text{const.}$ ) is described by Laplace's equation, expressed in 2-D as

$$(\partial^2 h / \partial x^2) + (\partial^2 h / \partial y^2) = 0$$

However, a porous media is rarely homogeneous and the effect of variable hydraulic conductivity has to be taken into account. Thus, for determination of flow pattern we need to know the distribution of hydraulic head, hydraulic conductivity, and boundary conditions for investigated system including recharge. There are several programs like FLOWPATH and Visual MODFLOW available for flow modeling which can be used to determine hydraulic head distribution. These programs are combined with particle tracking codes, which determine direction and velocity of flow in an investigated flow domain.

## **2. REDOX ZONES**

There is a vertical component of flow in recharge and discharge areas. In lateral flow zones hydraulic head is constant along a flowpath. However, in the case of redox sensitive species like metals, nitrates and also arsenic there is vertical redox stratification in an unconfined aquifer even in zones of lateral flow. For example, in the case of nitrate contamination high concentrations of nitrate generally occur at shallow depth, close to water table together with detectable oxygen concentration. On the other hand, high  $\text{Fe}^{2+}$  concentrations occur deeper, in the anoxic zone of aquifer. Groundwater pumping wells have large screen zone (sometimes >40 m) to give maximum yield from water-transmitting formation (Fig. 2b). This means that when we sample groundwater from a pumping well, several redox horizons are mixed. In that case,  $\text{Fe}^{2+}$  can be oxidized to  $\text{Fe}^{3+}$  and precipitate as  $\text{Fe}(\text{OH})_3$ . During precipitation dissolved metals including arsenic are adsorbed on  $\text{Fe}(\text{OH})_3$ . Resulting sample has much lower concentrations of  $\text{Fe}^{2+}$ , arsenic and dissolved  $\text{O}_2$  than groundwater in the aquifer. In that case, concentrations of nitrate are also lower because there will be dilution of nitrate within the pumping well. This means that discrete depth sampling from piezometers installed at different depth is necessary. This is accomplished by installation of a piezometric nest with several short screen piezometers (Fig. 2a) opened in different depth.

## **3. SAMPLING FOR ARSENIC**

When we sample for species with several oxidation numbers, perfect preservation of a sample is essential. Arsenic has  $\text{As}^{3+}$  and  $\text{As}^{5+}$  forms and samples with high arsenic concentrations generally also have elevated  $\text{Fe}^{2+}$  concentrations. It is necessary to prevent oxidation of  $\text{Fe}^{2+}$

to  $\text{Fe}^{3+}$  and its precipitation in the form of  $\text{Fe}(\text{OH})_3$ . This mineral phase is a very efficient scavenger for arsenic. Thus, samples have to be filtered and acidified in the field.

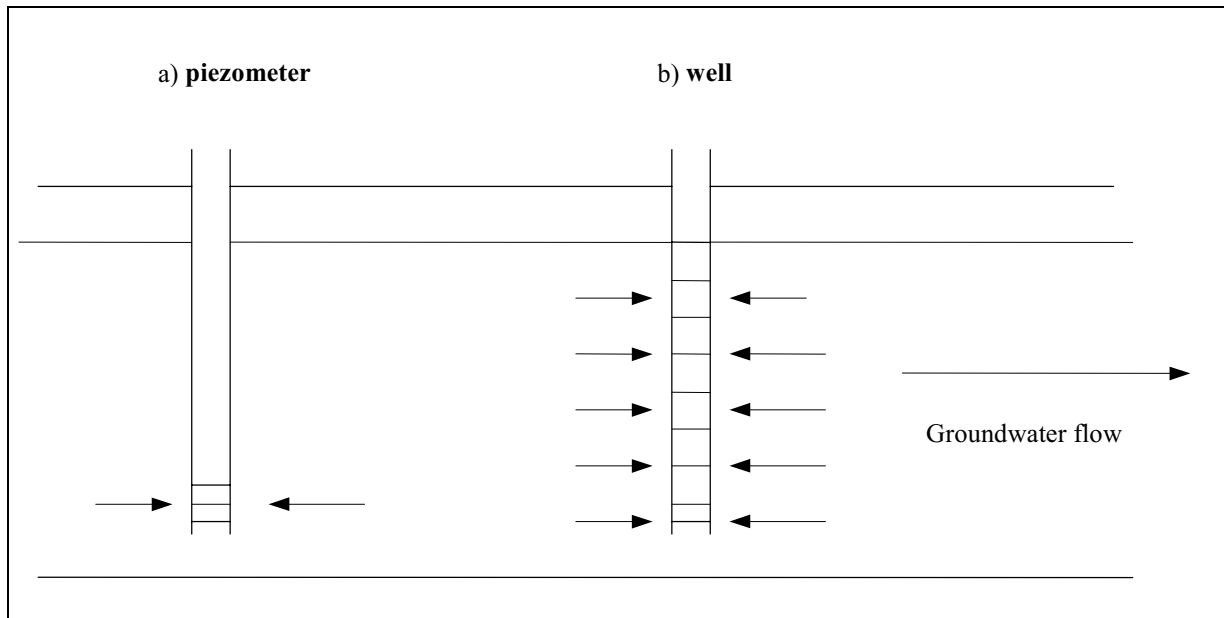


Figure 2. Piezometers and wells.

Let us imagine a sample with significant concentrations of  $\text{Fe}^{2+}$ ,  $\text{As}^{3+}$  and  $\text{As}^{5+}$ , and a certain concentration of  $\text{Fe}^{3+}$  in colloidal form as  $\text{Fe}(\text{OH})_3$ .

### 3.1 Unfiltered and unacidified samples: First sampling scenario

If the sample is not acidified and filtered, then  $\text{Fe}^{2+}$  will be converted to  $\text{Fe}^{3+}$ , and will precipitate as  $\text{Fe}(\text{OH})_3$ . The  $\text{As}^{5+}$  will be adsorbed on precipitated  $\text{Fe}(\text{OH})_3$ . Adsorption affinity for  $\text{As}^{5+}$  is stronger than for  $\text{As}^{3+}$ , thus the ratio  $\text{As}^{3+}/\text{As}^{5+}$  of remaining arsenic will be altered. Water samples are commonly filtered in a laboratory prior to analysis, thus the  $\text{Fe}(\text{OH})_3$  including its fraction precipitated after sampling will be lost with adsorbed  $\text{As}^{5+}$  and also  $\text{As}^{3+}$ . The results of water analysis will show underestimated concentrations of total Fe,  $\text{As}^{5+}$  and  $\text{As}^{3+}$ . The ratio  $\text{As}^{5+}/\text{As}^{3+}$  will also be different compared to the sampled groundwater.

### 3.2 Unfiltered and acidified samples: Second sampling scenario

The sample is acidified below pH about 2.8, but not filtered. If there was not any colloidal  $\text{Fe}(\text{OH})_3$  prior to acidification, then everything is fine. There will not be precipitation of

Fe(OH)<sub>3</sub> in the sampling bottle later, and, thus, there will not be adsorption of metals either. The concentrations of As<sup>3+</sup> and As<sup>5+</sup> will be preserved.

However, if there was a significant portion of Fe(OH)<sub>3</sub> colloids in water prior to sampling, then the colloids will be dissolved due to the acidification below pH 2.8, releasing Fe<sup>3+</sup> and adsorbed arsenic. In that case, concentrations of iron and arsenic may be overestimated, compared to the concentrations in bulk water.

### *3.3 Filtered and acidified samples: Third sampling scenario*

In this case, the colloidal Fe(OH)<sub>3</sub>, if present, is removed by filtration and concentrations of dissolved species are preserved. They should correspond to their concentrations in the sampled water.

## **4. RECOMMENDATIONS FOR SAMPLING**

### *4.1 General considerations*

If there was no pumping prior to the sampling, then it is necessary to pump or bail about three volumes of well or piezometer prior to sampling. Values of pH and temperature are measured immediately after recovery of a sample from a well or piezometer. The pH-meter must be calibrated in the day of sampling. The measurements of dissolved oxygen, alkalinity and the Eh in the field are strictly recommended. The Eh-meter should be checked with Zobell's solution and measured Eh values have to be corrected with respect to the hydrogen electrode (correction is 244 mV for 25°C).

### *4.2 Sampling for principal cations and metals*

Samples are filtered through 0.45 µm membrane on-line filter and then acidified with pure HCl to pH below 2.0. If possible, a headspace in sampling bottle should be avoided. If there is suspicion that colloidal iron might be present, then several duplicate samples are taken. One sample is filtered and acidified, and second sample is not filtered, but acidified. In the second case the colloidal iron will be dissolved, releasing adsorbed metals (see Sec. 3.2). The difference in concentrations between filtered and not filtered samples can be attributed to the influence of colloids. Oxidation of As<sup>3+</sup> to As<sup>5+</sup> is considered as a relatively slow process (CHERRY ET AL. 1979). However, in ideal case it is useful to separate As<sup>3+</sup> from As<sup>5+</sup>

immediately in the field using the Disposable Cartridges<sup>®</sup>, special on-line filters (MENG AND WANG, 1998) following acidification. In that case only As<sup>3+</sup> passes through filter and total arsenic (regardless of later oxidation) analyzed from separate bottle represents As<sup>3+</sup>.

#### *4.3 Sampling for anions*

Samples are filtered through 0.45 µm membrane filters, but they are not acidified. When we sample for reduced sulfur species (H<sub>2</sub>S, HS<sup>-</sup>, S<sup>-2</sup>), they should be precipitated in the field in separate bottle using cadmium acetate CdAc.

### **5. CONCLUSIONS**

Determination of flow pattern is necessary for geochemical evolution investigation including behavior of arsenic. This is accomplished by collection of hydraulic head and hydraulic conductivity data and application of flow modeling/particle tracking code.

Vertical redox zonation occurs commonly in aquifers. Sampling of groundwater from pumping wells causes mixing of water within a well and alters both hydrogeochemical parameters and concentrations of dissolved species. Thus, discrete depth sampling from short screen piezometers is necessary to obtain data for meaningful geochemical interpretation.

Samples have to be preserved to avoid changes of water chemistry between sampling and analysis. Hydrogeochemical parameters like pH, Eh and temperature have to be measured in the field.

### **6. REFERENCES**

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