

Arsenic transfer and speciation in volcanic materials

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Arsenic (As) is one of the most carcinogenic and toxic substances in both surface and ground waters posing threats to millions of people. The distribution of dissolved arsenic among possible compounds, referred to as speciation of arsenic, is the most important factor controlling its toxicity, bioavailability and mobility.

The concentration of As in high temperature geothermal waters, wastewater from geothermal plants, volcanic pollution and street runoff in Iceland is such that it can be harmful to sensitive ecosystems. Thus it is of great importance to understand the speciation of As in these waters and the processes controlling its mobility in the Icelandic surface- and groundwater environment.

The present research is conducted in a laboratory environment under controlled conditions (pH, redox, temperature and solution composition). Distribution of dissolved arsenic species is measured as well as species interactions with porous media, such as volcanic ash, organic materials and Andosols (volcanic soils). The research is the PhD project of Bergur Sigfússon at the University of Aberdeen in collaboration with the Institute of Earth Sciences, University of Iceland.

Experimental setup constitutes of a) batch experiments and b) column experiments. Batch experiments enable estimation of K_d values (distribution of species between surfaces and solution at equilibrium) and retardation factors, R (retardation of species compared to water due to interaction with the solid materials) for individual arsenic species. Those empirically determined values can be incorporated into hydrological models of groundwater movement. Column experiments are carried out in a closed environment and are used to validate K_d and R values obtained from batch experiments. Arsenic occurs primarily on two oxidation states, III and V which are not stable under atmospheric conditions and hence the reduced form of arsenic is always measured immediately by Flow Injection Analysis Hydride Generation Atomic Absorption spectrometry (FIA-HG-AAS).

Preliminary results report interactions between As^{III} and As^V and basaltic glass at pH 3 and 10.05. The zero point of charge for basaltic glass is predominantly close to 7.0 which means the glass is positively charged at pH values below 7 and negatively charged above that same pH.

Table 1 displays experimentally determined K_d and R values for As(III and V) interacting with basaltic glass at different pH. K_d values from 0-1 indicate none (0) to complete (1) surface sorption. A R value of 1 indicates no retention of a given chemical with regards to water and R=2 indicates half the flow rate of a chemical compared to water.

Table 1

pH	Oxidation state	K _d	R
3.00	III	0.43	1.15
3.00	V	0.97	1.94
10.05	III	0.27	1.26
10.05	V	0.074	1.01

1) At pH 3 the reduced form of As is predominantly the uncharged species H₃AsO₃ and is therefore not retained strongly on the surface of glass. 2) The predominant oxidised form at pH 3 is H₂AsO₄⁻ which is strongly adsorbed on the positively charged glass. 3) At pH 10, the reduced form is mainly H₂AsO₃⁻ that is repelled from the negatively charged surface of the glass. 4) The oxidised form at pH 10 is primarily HAsO₄⁻² which is strongly repelled from the glass due to its -2 charge resulting in low adsorption at the glass's surface and insignificant retention compared to water flow. Preliminary results from column experiments agree well with those results but further data have to be acquired before those values can be incorporated into groundwater movement models.

Future work includes the study of a) interaction between Icelandic Andosols and organoarsenic species, b) effect of sulphur on arsenic speciation and c) measurements of arsenic surface species on volcanic materials.

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