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Do Fe-oxides control the adsorption of arsenic in aquifers of the Red River floodplain, Vietnam?

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Abstract

Adsorption of As(III) to aquifer sediments from the Red River floodplain, Vietnam, has been studied with the aim of identifying controlling parameters for the adsorption. The adsorption capacity differs between similar sediments, indicating that it is not related to bulk components of the sediment but rather that certain properties of the sediments are important for the adsorption. Normalizing the adsorption of As(III) to the content of Fe-oxides in the sediments results in almost identical adsorption isotherms, indicating that Fe-oxides are the main adsorbents for As(III) in these three reduced aquifer sediments. This is further strengthened by adsorption experiments carried out with sediments leached for Fe-oxides, as this resulted in reduced adsorption capacity and despite the difference in adsorption capacity of the untreated sediments, the adsorption capacity became identical after Fe-oxide leaching. The importance of Fe-oxides for As(III) adsorption to reduced aquifer sediments has implications for the mobility of As(III) in the groundwater aquifers, as it will vary spatially and also over time, as the Fe-oxides in the sediment are reduced.

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1. Introduction

Elevated concentrations of arsenic (As) in the groundwater of the floodplains in South and South East Asia affect the health of millions of people. In the Red River floodplain, Vietnam, it is estimated that 10 million people are exposed to high arsenic groundwater¹. The mobility of As in the groundwater aquifers of South East Asia is controlled by adsorption² and a data compilation of As(III) adsorption isotherms on both oxidized and reduced

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aquifer sediments from Bangladesh and Vietnam showed very similar adsorption isotherms for four of the five datasets, suggesting that As(III) adsorption is controlled by a bulk sediment component³.

To further investigate the controlling parameters for As(III) adsorption to aquifer sediments, new As(III) adsorption experiments have been carried out with reduced aquifer sediments from the Red River floodplain, Vietnam. The new results are compared to the results in the above mentioned data compilation, especially the results from the field locality Nam Du, Vietnam³.

2. Material and methods

2.1. Sediment characterization

Sediment cores were collected in stainless steel tubes using a piston corer and stored frozen within the tubes. Sediments were collected at the previously described sites Phu Kim and the H-transect located about 30 km NW of Hanoi, Vietnam⁴. Both aquifer sediments consist of grey, fine grained sand with silt and clay and were collected from the reduced part of the aquifers. The sediments were characterized by chemical extractions, XRD and specific surface area (N₂-BET). The chemical extractions were carried out in parallel under constant flushing of N₂ and consisted of a) 1 mM HCl at pH 3 using an automatic titrator to keep pH constant while dissolving carbonates and phosphates and b) 0.1 M ascorbic acid + 0.2 M ammonium oxalate at pH 3 to dissolve Fe-oxides including crystalline oxides such as goethite and hematite, as described in⁴. XRD and BET was conducted on untreated sediment samples and sediment samples after treatment with 0.1 M ascorbic acid + 0.2 M ammonium oxalate.

2.2. Batch adsorption experiments

Batch adsorption experiments were carried out inside an anaerobic glovebox with a 4% H₂ in a N₂ atmosphere in the presence of Pd catalysts. The concentration of hydrogen in the batches was minimized by bubbling solutions and batches with pure N₂. Batches were sealed with thick rubber stoppers, crimped and stored inside the glovebox, shaken manually several times per day.

Batch adsorption isotherms experiments were carried out as described in³ using a matrix solution of 10 mM PIPES and 50 mM NaCl with pH adjusted to the desired pH (6.2, 7.0 or 7.5). As(III) stock solution was added stepwise and samples of the aqueous phase were taken 24 h after addition of As(III). Aqueous analyses were carried out as described in³. In short As(V) and As(III) were separated using disposable anion exchange cartridges within the glove box and measured by ICP-MS. The concentration of Fe(II) and PO₄ was measured spectrophotometrically in each sample throughout the experiment.

After the adsorption experiment the sediment was chemically extracted with 0.1 M ascorbic acid + 0.2 M ammonium oxalate for 48 hours, thoroughly rinsed inside the glovebox and subsequently used for a second series of batch adsorption isotherm experiments.

3. Results

3.1. Sediment extractions

Results from the chemical extractions show that the two sediments of this study and the sediment from Nam Du³ vary in the amount of Fe extracted. The largest pool of Fe-oxides (calculated as the difference in Fe extracted with the two methods) is seen in the Nam Du sediment (75.2 μmol/g)³, the Fe-oxide pool in the H-transect is slightly lower (63.4 μmol/g), and substantially lower in Phu Kim (20.1 μmol/g).

The specific surface area of the three sediments show the same trend as the pool of Fe-oxides; Nam Du having the largest surface area, followed by the H-transect and with the Phu Kim sediment having the lowest specific surface area. Leaching the H-transect and Phu Kim sediments with 0.1 M ascorbic acid + 0.2 M ammonium oxalate, to remove the Fe-oxides, results in even lower, but nearly identical specific surface area.

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