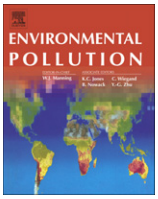
Environmental Pollution 159 (2011) 1398–1405

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Arsenic strongly associates with ferrihydrite colloids formed in a soil effluent

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Natural concentrations of competing (in)organic species in soil-derived solutions do not impede the strong and quantitative association between As and colloidal ferrihydrite.

ARTICLE INFO

Article history:
Received 2 July 2010
Received in revised form
22 December 2010
Accepted 3 January 2011

Keywords:
Iron hydroxide
Phosphate
Silicate
Carbonate
Dissolved organic matter

ABSTRACT

Arsenic mobility may increase in liquid phase due to association with colloidal Fe oxides. We studied the association of As with Fe oxide colloids in the effluent from water-saturated soil columns run under anoxic conditions. Upon exfiltration, the solutions, which contained Fe^{2+}, were re-aerated and ferrihydrite colloids precipitated. The entire amount of effluent As was associated with the ferrihydrite colloids, although PO_4^{3-}, SiO_4^{4-}, CO_3^{2-} and dissolved organic matter were present in the effluent during ferrihydrite colloid formation. Furthermore, no subsequent release of As from the ferrihydrite colloids was observed despite the presence of these (in)organic species known to compete with As for adsorption on Fe oxides. Arsenic was bound via inner-sphere complexation on the ferrihydrite surface. FTIR spectroscopy also revealed adsorption of PO_4^{3-} and polymerized silica. However, these species could not impede the quantitative association of As with colloidal ferrihydrite in the soil effluents.

1. Introduction

Arsenic is known for its human toxicity (Kapaj et al., 2006), and its mobility and availability in soil, groundwater and surface water remains a hazard to major public health. Arsenic strongly adsorbs on or co-precipitates with synthetic Fe oxides (Dixit and Hering, 2003; Ford, 2002; Fuller et al., 1993; Grafe et al., 2001, 2002) and Fe oxides formed in nature (Fritzsche et al., 2006; Rancourt et al., 2001). The strong adsorption of inorganic As(III) and As(V), which are the relevant species in natural waters (Smedley and Kinniburgh, 2002) and in soils and aquifers (Bissen and Frimmel, 2003), can be explained with the formation of inner-sphere surface complexes with hydrous Fe oxides. This was shown for goethite (Manning et al., 1998; Sun and Doner, 1996), akageneite (Waychunas et al., 1993), lepidocrocite (Farquhar et al., 2002) and ferrihydrite (Goldberg and Johnston, 2001; Jain et al., 1999; Raven et al., 1998). Colloids are defined as dispersed molecules or polymolecular particles that have a dimension roughly between 1 nm and 1 μm at least in one direction (IUPAC, 1997). When considered as carrier (Kretzschmar et al., 1999), dispersed Fe oxide colloids facilitate the transport of As and thus enhance its mobility in the liquid phase (Bauer and Blodau, 2009). Thus, the stabilization of Fe oxides at colloidal dimension may counteract remediation strategies that base on As immobilization by concurrent sedimentation with Fe oxides (Lin and Puls, 2003). However, owing to the presence of a wide variety of dissolved organic and inorganic compounds, significant interferences on the association of As with Fe oxides can be expected in natural systems. Dissolved organic species (Bauer and Blodau, 2006; Grafe et al., 2001, 2002; Redman et al., 2002) and inorganic ions such as PO_4^{3-}, SiO_4^{4-}, and CO_3^{2-} (Holm, 2002) compete for the adsorption on Fe oxide surfaces and may cause the release of already adsorbed As species. Humic acids and natural organic matter (NOM) also change the speciation of As (Buschmann et al., 2005; Redman et al., 2002), which affects its adsorption on Fe oxides (Dixit and Hering, 2003; Pierce and Moore, 1982). Arsenic was found to form complexes with NOM (Redman et al., 2002) and to bridge Fe(III)–OM complexes (Ritter et al., 2006; Sharma et al., 2010). It was rather associated with colloidal OM than with colloidal Fe oxide in surface waters (Pokrovsky and Schott, 2002). However, no association between As and lake-water OM was found in a recent study (Metreveli et al., 2010). Furthermore, water-soluble soil organic matter (Eusterhues et al., 2008; Schwertmann, 1966), models of microbial polysaccharides (Mikutta et al., 2008) and inorganic ions (Kaegi et al., 2010; Voegelin et al., 2010) affect the structure and crystallinity of Fe oxides precipitating in soil. Consequently, the composition, reactivity and surface properties of natural Fe oxides differ significantly from those synthesized in the laboratory (Gunnars et al., 2002; Perret et al., 2000). Natural OM (Barnes et al., 2009; Gunnars et al., 2002), humic acids (Mylon et al., 2004) and microbial polysaccharides (Mikutta et al., 2008) also retard the

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doi:10.1016/j.envpol.2011.01.001

aggregation of Fe oxides and therefore stabilize them at colloidal dimension. Consequently, the presence of organic and inorganic solutes has two major effects on the association of As with Fe oxides in natural systems such as soils and groundwater: i) it changes physical (e.g., particles size, specific surface area) and chemical (e.g., reactivity, structural defects) properties of Fe oxides forming in these environments, and ii) the solutes compete with As for interaction with the Fe oxides.

To the best of our knowledge, the effects of dissolved OM (DOM) and inorganic ions derived from mineral soils under (near-)natural conditions on the interaction between As and colloidal Fe oxides have not been studied yet. A soil column outflow experiment with its realistic liquid-to-solid ratio plus the use of a low ionic influent allow obtaining a solution that can be expected within soils and at exfiltration springs from waterlogged soil. Variable flow regimes, i.e., alternating flow and no-flow periods, account for non-equilibrium processes (Wehrer and Totsche, 2003), which induce the temporal variable concentrations of OM and inorganic ions characteristic of natural solutions.

Our study provides insights into the association of As with ferrihydrite colloids that precipitated from a soil effluent. We assessed the effect of effluent DOM, PO_4^{3-}, SiO_4^{4-} and CO_3^{2-} on the association of As with colloidal ferrihydrite during its precipitation as well as after long-term exposure of the ferrihydrite colloids to these effluent constituents.

2. Material and methods

2.1. Soil column experiments

Duplicate soil columns (stainless steel, volume 1000 cm^3, length 15.5 cm) were filled with approx. 760 g of soil material sieved <2 mm from the topsoil horizon (Ah) of a Gleyic Fluvisol (IUSS Working Group, 2006) from a site near Muldenstein (Saxony-Anhalt, Germany). The bulk density within the columns was comparable to the bulk density found in situ (approx. 0.8 g cm^{-3}). The fine-textured, silty-clayey material contained fairly high amounts of pedogenic Fe oxides (dithionite-extractable Fe, 12.1 mg g^{-1}; oxalate-extractable Fe, 10.0 mg g^{-1}) and organic C (OC, 79.8 mg g^{-1}), but no inorganic C. Periodical flooding by the nearby Mulde river caused the accumulation of As (dithionite-extractable As, 0.27 mg g^{-1}) from former mining areas in the upstream Ore Mountains (Brandt, 2003; Klemm et al., 2005). The soil columns were fed with 1 mM NaCl or 1 mM LiBr influent solution (Merck, Darmstadt, Germany) under water-saturated conditions with a low pore water velocity ($\nu = 0.22$ cm h^{-1}; equivalent to the exchange of approximately 0.3 pore volumes d^{-1}). The soil effluent was allowed to re-aerate after being discharged from the soil columns.

2.2. Characterization of the soil column effluent

Owing to the water-saturated conditions within the soil column and the resulting limitation in O_2 supply, Fe^{2+} was formed by microbial Fe reduction of pedogenic Fe oxides and was subsequently mobilized within the soil columns (S1, Supplementary data). After the discharge from the soil column and direct contact with the atmosphere, O_2 was available for re-oxidation of effluent Fe^{2+}, which resulted in the formation of effluent Fe oxide colloids.

Effluent pH was analyzed potentiometrically (Sentix 41 + pH 197i, WTW, Weilheim, Germany) in unfiltered samples. After acidification ($pH < 2$), organic C (OC) was measured in unfiltered and filtered samples (0.45 μm Acrodisc PES, Pall Scientific, East Hills, USA) by combustion (TOC-5050A, Shimadzu, Kyoto, Japan). Non-purgeable inorganic C was calculated as the difference between the C concentration in acidified samples (equals OC) and the concentration in non-acidified samples with previous purging with C-free synthetic air (4 min). Iron, As, Si, and P were analyzed in 0.45 μm-filtered samples and in acidified unfiltered samples by inductively coupled plasma optical emission spectrometry (ICP-OES; Vista Pro, Varian, Palo Alto, USA). Acidification was conducted by adding HCl (32%, p.a., Merck) to achieve a final concentration of 1 M HCl in the samples followed by shaking overnight. We assume P, analyzed by ICP-OES, present as PO_4^{3-} since PO_4^{3-} concentrations were too low for a reliable detection with ion chromatography.

Hydrodynamic diameters (d_H) of the effluent colloids were analyzed by dynamic light scattering (DLS) by non-invasive detection in backscattering mode (Nano ZS, Malvern Instruments, Malvern, UK) in 0.45 μm-filtered and in unfiltered effluent. The interpretation of d_H is based on the intensity of light scattering and was derived from fitting a single exponential to the correlation function (equals Z-average). Two measurements were conducted per sample. The number of runs per measurement ranged between 13 and 23 in dependence on the total scattering intensity. The collection time per run was 10 s. Only d_H from measurements that reproducibly met the quality criteria were used for the interpretation. For filtered and unfiltered samples, the average polydispersity index (PdI) was 0.168 (±0.054, $n = 39$) and 0.293 (±0.089, $n = 33$) while the average intercept of the autocorrelation function was 0.96 (±0.02, $n = 39$) and 0.96 (±0.01, $n = 33$), respectively. Ultrapure water ($R = 18.2$ MΩ, DOC < 1 μg L^{-1}, Elix + Milli Q, Millipore, Billerica, USA) was used throughout the whole experiments and subsequent analyses.

The effluent properties were related to the number of exchanged pore volumes, which is a dimensionless measure for the portion of mobile water within the soil compared to the total volume of the soil column.

2.3. Exposure of effluent Fe oxide colloids to soil effluent solutes

Aggregation experiments were conducted with the soil effluent Fe oxide colloids to investigate the potential release of associated As after 70 d exposure to the effluent with its organic and inorganic solutes.

After storage for 70 d in dark at 4 °C in the soil effluent they precipitated from, the soil effluent Fe oxide colloids had a d_H of approx. 70 nm, which was also the d_H after the initial colloid formation. The unaltered d_H excluded the ripening of the Fe oxide colloids during storage. Owing to their low size, the Fe oxide colloids could entirely pass a 0.45 μm filter (S2, Supplementary data). An aggregation would increase the particle size and thus potentially decrease the Fe concentration in the filtrate. If Fe and As concentrations in the filtrates decreased equally, it would indicate that the entire As was associated with the Fe oxide colloids. Arsenic that is not colloid-associated would not be removed by filtration after complete aggregation of the Fe oxide colloids to sizes exceeding the filter cutoff. To achieve the aggregation of the colloids, four electrolyte solutions containing either 2.5 mM Ca^{2+} ($CaCl_2 \times 2H_2O$, p.a., Sigma–Aldrich, St. Louis, USA), Ba^{2+} ($BaCl_2 \times 2H_2O$, p.a., Merck), or Mn^{2+} ($MnCl_2 \times 2H_2O$, p.a., Merck) were added separately to aliquots of the 70 d old soil column effluent that contained the nano-sized Fe oxide colloids.

The solutions were gently shaken on a horizontal shaker at 30 rpm (SM25, Edmund Bühler, Hechingen, Germany) at 24 °C after addition of the electrolyte solutions. Turbidity is given as formazine attenuation units (FAU) based on the absorption of light at $\lambda = 860$ nm (Cary 50, Varian, Palo Alto, USA). The DLS measurements were carried out as described above. Owing to a high polydispersity in unfiltered samples, which evolved during the aggregation of the soil effluent Fe oxide colloids, the interpretation of d_H was relied on the results from the 0.45 μm-filtered samples. There, the highest average PdI was detected in the $BaCl_2$-treatment with 0.247 (±0.057, $n = 7$) while the mean intercept of the autocorrelation function was 0.95 (±0.01, $n = 7$). The average PdI of the remaining treatments did not exceed 0.200 while the average intercept was approx. 0.95. Both the turbidity and DLS measurements were conducted instantaneously after sampling. The analysis of Fe and As in 0.45 μm-filtered, acidified samples was conducted in accordance to the procedures described above.

2.4. Fourier-transform infrared (FTIR) spectroscopy

The Fe oxide colloids, which have been characterized by FTIR spectroscopy, were obtained from the effluent of a soil column experiment that was operated under identical conditions as described above. The colloid characterization required the conversion from suspension to solids. To avoid precipitation of salts during freeze-drying (Alpha 1–4 LSC, Christ, Osterode, Germany), the effluent was dialyzed against H_2O beforehand (Spectra/Por 6, 2 kDa molecular weight cutoff; Spectrum Laboratories, Rancho Dominguez, USA). Fourier-transform IR spectra were recorded using a Nicolet iS10 spectrometer (Thermo Fisher Scientific, Waltham, USA). We mixed freeze-dried and mortared samples with KBr (FTIR grade, Alfa Aesar, Karlsruhe, Germany) at a ratio of 1:200 and pressed it to pellets at 31 MPa for 10 min. The pellets were studied in transmission mode in the mid-infrared range with 16 scans per spectrum at a resolution of 4 cm^{-1}. Beside effluent OM that was associated with the Fe oxide colloids, significant amounts of DOM exceeding 2 kDa were retained inside the dialysis tube. Consequently, an OM fraction was also present in the solids although not necessarily associated with colloidal Fe oxides. A further Fe oxide-free OM spectrum was obtained from an effluent fraction collected directly in HCl (32%, p.a., Merck) to obtain a final concentration of 1 M HCl (pH approx. 0). The acidified effluent fraction was dialyzed and freeze-dried like the non-acidified effluent fractions. We checked the persistency of the dialysis tube in HCl, and we did not detect cellulose resulting from dissolution of the tube. The acidic conditions inhibited the oxidation of effluent Fe^{2+} (Lamb and Elder, 1931; Singer and Stumm, 1970). Consequently, no Fe oxides precipitated during the freeze-drying since dialysis removed all Fe^{2+} from the effluent. We recorded a reference spectrum of $NaAsO_2$ (Sigma–Aldrich). Baseline correction and height normalization were applied to all spectra.

2.5. Replicate soil column

All treatments and methods were applied identically to the effluent fractions of both replicate soil columns. These data revealed identical trends in effluent composition and precipitation of As-bearing Fe oxide colloids, thus proving the reproducibility of the effects discussed in this contribution. Data from only one soil