Colloid-associated export of arsenic in stream water during stormflow events

E. Neubauer [a], F. von der Kammer [a], K.-H. Knorr [b,1], S. Peiffer [b], M. Reichert [b], T. Hofmann [a,*]

[a] Department of Environmental Geosciences, University of Vienna, Althanstraße 14, 1090 Vienna, Austria
[b] Department of Hydrology, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany

ABSTRACT

Significant correlations between arsenic concentrations and those of iron and natural organic matter (NOM) have been found in run-off from wetlands. This has been suggested to be a result of mobilization of arsenic-NOM colloids. The aim of this study was therefore to elucidate the possible association of iron and arsenic with colloids in surface water from a small, forested catchment area. The impacts that groundwater levels prior to stormflow events and the chemistry of the hydraulically active soil layers have on the release and formation of colloids, such as NOM and iron (oxy)hydroxide colloids, were also investigated.

At baseflow, the NOM, iron, and arsenic concentrations in the stream water were relatively low (<650 $\mu mol \cdot L^{-1}$, <5.5 $\mu mol \cdot L^{-1}$, and 8–16 $nmol \cdot L^{-1}$, respectively), and the pH was close to deep groundwater (4.6–5.5). At low groundwater levels prior to stormflow events, the discharging stream water was fed by anoxic groundwater from the deeper layers of the peat, and by deep, oxic groundwater. The iron/DOC ratio in the stream water was high, and iron was present as iron-NOM colloids and precipitated as iron (oxy)hydroxide colloids. Arsenic was dissolved and associated with NOM, and the conditional distribution coefficients of arsenic binding to NOM ($logK_D$ values) were relatively high (around 3 $L \cdot mol^{-1}$).

When initial groundwater table levels were high before stormflow events, the stream was fed by shallow peat layers rich in NOM, iron, and arsenic during the event. The iron/DOC ratios were low and most of the iron was present in iron-NOM colloids in the stream water. The pH of the stream water was also lower under these conditions, and the $logK_D$ values of As-NOM associations in the stream water were accordingly lower (<3 $L \cdot mol^{-1}$). Large quantities of dissolved arsenic (<1000 $g \cdot mol^{-1}$) were exported under these conditions.

Our data reveal that the $logK_D$ values of As-NOM associations decreased with increasing discharge as a consequence of decreasing pH. The $logK_D$ values for arsenic-NOM associations in this study are higher than those reported elsewhere in published literature, which had been derived from laboratory tests with NOM and arsenic. The formation of ternary complexes with ferric iron may therefore have enhanced the binding of arsenic to NOM within the studied stream.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

It is widely recognized that bioavailable forms of arsenic can have adverse effects on human health (Smedley and Kinniburgh, 2002). Arsenic is, however, ubiquitous at trace concentrations in virtually all environmental media (Adriano, 2001). Peatlands, which cover about 3% of the Earth's surface (Limpens et al., 2008), can accumulate arsenic originating from both natural and anthropogenic sources, depending on the type and setting of the wetlands (La Force et al., 2000; Matschullat, 2000; González et al., 2006; Huang and Matzner, 2007a, 2007b; Cloy et al., 2009). Under oxic conditions dissolved arsenic occurs mainly as inorganic arsenate, and when oxygen is depleted it can be chemically and microbially reduced to arsenite. Aerobic and anaerobic microorganisms can also transform arsenic into arsenic-organic compounds (Bentley and Chasteen, 2002).

Primary sorbents for arsenic in wetlands and surface water include iron and manganese oxides and (oxy)hydroxides, sulfides, and natural organic matter (NOM, La Force et al., 2000; Bostick and Fendorf, 2003; Blodau et al., 2008; Dousova et al., 2012; Hoffmann et al., 2012; Langner et al., 2012; Pokrovsky et al., 2012; Neubauer et al., 2013a). The retention of arsenic and its release into solution is related to redox reactions, such as the precipitation and dissolution of arsenic-bearing iron (oxy)hydroxides (La Force et al., 2000; Smedley and Kinniburgh, 2002; Bosch et al., 2010; Davranche et al., 2012) and sulfides (Kirk et al., 2004; Langner et al., 2012). NOM may compete with arsenic for sorption sites on minerals (Redman et al., 2002; Kumpulainen et al., 2008), and may stabilize arsenic-bearing mineral colloids (Bauer and Blodau, 2009). As wetlands are characterized by a high NOM content, a large proportion of the

arsenic may be bound to NOM; there is spectroscopic evidence that arsenic can bind to NOM via sulfhydryl groups (Langner et al., 2012) and that ternary complexes can form between NOM, arsenate, and ferric iron (Mikutta and Kretzschmar, 2011).

Arsenic concentrations in streams draining wetlands are affected by the mobilization of dissolved arsenic in soil during heavy rain events, by fluctuating water tables and superficial flow (Huang and Matzner, 2007a; Rothwell et al., 2009; Rothwell et al., 2011), and by the erosion of sediments (Rothwell et al., 2008). Significant correlations have been found between arsenic concentrations and those of iron and NOM in run-off from wetlands (Kalbitz and Wennrich, 1998; Huang and Matzner, 2007a; Rothwell et al., 2009). It has thus been suggested that the correlation between arsenic and NOM is a result of mobilization of arsenic-NOM colloids (Rothwell et al., 2009), but detailed studies are lacking. Furthermore, previous investigations have shown that NOM mobilization from riparian wetland soils into stream water is affected by season and by hydrological conditions (Strohmeier et al., 2012; Jirsa et al., 2013). Temporal variations in NOM export are a direct consequence of the composition of the hydraulically active layers in the soil profile and their respective discharge patterns (Knorr, 2012; Strohmeier et al., 2012). It has been suggested that future changes in the hydrological regime will influence the dynamics of NOM export (Strohmeier et al., 2012), which might in turn influence the dynamics of iron and arsenic export.

So far, no investigations have been carried out on the impact that hydrological conditions and soil chemistry have on colloid-associated arsenic export. Therefore, we investigated the export of arsenic from a small, forested catchment during stormflow events, with a high temporal resolution. Our objective was to elucidate the possible association of iron and arsenic with colloids in surface water, and to relate the release and formation of colloids, such as NOM and iron (oxy)hydroxide colloids, to fluctuating groundwater levels prior to the event, and to the chemistry of the hydraulically active soil layers. We hypothesized that iron and arsenic speciation is governed by complexation with NOM under stormflow conditions, because the stream is then fed by shallow peat layers rich in NOM, while under baseflow conditions, oxidation of ferrous iron and precipitation at the soil/stream water interface may affect iron and arsenic speciation.

2. Materials and methods

2.1. Site description and hydrogeological model

The investigations were carried out in the Lehstenbach catchment, within the German Fichtelgebirge mountains (50°08′N, 11°52′E; Gerstberger et al., 2004). The catchment area covers 4.2 km^2 at an elevation between 695 and 877 m.a.s.l. (Lischeid et al., 2007). The mean annual air temperature is 5 °C and the mean annual precipitation is approximately 1150 mm (Huang and Matzner, 2007b). Wetland soils of bog and fen type cover 30% of the area (Huang and Matzner, 2006) and are moderately to highly decomposed (3 to 9 on the von Post index of peat decomposition) with low C/N ratios (17 to 30, Goldberg et al., 2008).

Upland soils are mainly Dystric Cambisols and Haplic Podzols (FAO classification) of sandy to loamy texture, developed over deeply weathered granitic bedrock (Huang and Matzner, 2007b). The regolith overlying the granitic bedrock is 40 m thick and consists of sand, loam, gravel, and granite boulders (Lischeid et al., 2007). The catchment is drained by a dense network of natural streams and artificial ditches.

During baseflow conditions the stream is fed by discharging shallow, anoxic groundwater and deep, oxic groundwater. During stormflow, near-surface flow in the organic-rich upper 30 cm soil layer contributes significantly to the stream's discharge (Lischeid et al., 2007). Near-surface layers have higher hydraulic conductivity (Frei et al., 2010) and drain more quickly and efficiently because the hydraulic

conductivity in the soil profile decreases exponentially with increasing depth ("transmissivity feedback": Bishop et al., 2004; Frei et al., 2010).

Comprehensive data on arsenic dynamics in different compartments of the catchment (soil, soil pore water, precipitation, throughfall, and litterfall) has been published in recent years (Huang and Matzner, 2006, 2007a, 2007b; Blodau et al., 2008), and arsenic concentrations in the stream water have been related to concentrations in these compartments by a mass balance study (Huang and Matzner, 2007a). Previously it has been shown that As(V) and As(III) dominate over organic arsenic species such as monomethylarsonic acid, dimethylarsinic acid, and arsenobetaine in run-off (Huang and Matzner, 2007a), despite relatively high concentrations of organic arsenic species in soil solutions from the wetland (up to 70% of the total arsenic; Huang and Matzner, 2006).

2.2. Water sampling and data logging

Run-off in the stream was sampled at the catchment outlet using an autosampler (6712, Teledyne ISCO, Lincoln, USA). Four stormflow events were sampled between May and September 2011 over periods of 36 to 94 h, with a sampling interval of 1 to 8 h (May/June, July I, July II, September, Table 1). Sampling started during baseflow conditions and covered the rising and falling limb of the hydrograph until baseflow discharge was again established. The only exception was the July II sampling, which started when the discharge was already rising. Discharge at the catchment outlet was logged at 15 minute intervals using a pressure transducer (Levelogger Gold, Solinst Ltd., Georgetown, Canada). The groundwater level was recorded in well GM1b, which is located close to the stream-sampling site.

2.3. Chemical analysis

Cooled samples were sent to the laboratory at the Department of Environmental Geosciences at the University of Vienna (Austria), and stored at 4 °C until analysis. Analysis was typically performed within one week of arrival of the samples. The pH was measured in the laboratory (WTW SenTix electrode, Weilheim, Germany). Samples were filtered through 0.2 μm cellulose acetate filters before analysis (Sartorius Stedim, Sartorius, Göttingen, Germany).

Samples for major element and trace element analysis were microwave-digested prior to analysis. Briefly, 20 mL from each sample was digested with 5 mL 65% HNO$_3$ (Suprapur grade, Merck, Darmstadt, Germany) and 1 mL H$_2$O$_2$ (Suprapur grade, Merck, Darmstadt, Germany) in a microwave (Anton Paar, Microwave 3000, Graz, Austria) at 175 °C for 15 min. The digested samples were then diluted with ultrapure water to 100 mL, and stored in 100 mL PE bottles until analysis, which was by ICP-OES (Perkin Elmer Optima 5300 DV, Waltham, USA) and ICP-MS (Agilent 7700×, Waldbronn, Germany, LOD Fe:0.18 μmol·L^{-1}, As: 0.13 nmol·L^{-1}). The iron concentrations in selected unfiltered samples were compared to the concentrations in filtered samples of the September event. The analysis revealed that between 10 and 20% of the total iron was filtered off with the 0.2 μm filters.

Dissolved organic carbon (DOC) measurements were performed using a TOC-V$_{CPH}$ total organic carbon analyser (Shimadzu, Duisburg, Germany, blank 50 μmol·L^{-1}, precision 3%). Anion concentrations were measured using ion chromatography (ICS-1000, Dionex, Vienna, Austria, LOQ 0.1 mg·L^{-1}).

Subsamples of the 0.2 μm filtered water were ultrafiltrated using a Millipore stirred ultrafiltration cell (Merck Millipore, Billerica, USA), equipped with a regenerated cellulose filter (1000 g·mol^{-1} nominal molecular weight cut-off (NMWCO), determined by the manufacturer: Merck Millipore, Billerica, USA). The ultrafiltration apparatus and the membrane were rinsed with MilliQ water before usage. The first 2 mL were discarded. Ultrafiltrates were acidified with a volume equivalent to 4% of the sample volume with 5 N HNO$_3$ (Suprapur grade, Merck, Darmstadt, Germany) and were used for ICP-OES and