Journal of Hydrology 511 (2014) 509–517

Contents lists available at ScienceDirect

Journal of Hydrology

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

Pathways of arsenic from sediments to groundwater in the hyporheic zone: Evidence from an iron isotope study

Xianjun Xie [a,*], Thomas M. Johnson [b], Yanxin Wang [a,*], Craig C. Lundstrom [b], Andre Ellis [c], Xiangli Wang [b], Mengyu Duan [a], Junxia Li [a]

[a] School of Environmental Studies & State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 430074 Wuhan, China
[b] Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green Street, Urbana, IL 61801, USA
[c] Department of Geological Sciences, California State University-Los Angeles, CA 90032, USA

ARTICLE INFO

Article history:
Received 11 June 2013
Received in revised form 20 October 2013
Accepted 1 February 2014
Available online 10 February 2014
This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Prosun Bhattacharya, Associate Editor

Keywords:
Iron isotope
Arsenic
Hyporheic zone
Groundwater
Dissimilatory iron reduction

SUMMARY

$S_{sulfide}$, Fe content and heavy Fe isotopic signatures of the bulk core sediments all indicate anoxic and sulfidic conditions in the hyporheic zone. The relationship between $S_{sulfide}$ and Fe contents suggests that Fe(III) oxides/hydroxides are transferred between non-sulfidic Fe(II) minerals and Fe(II)-sulfides under anoxic and sulfidic conditions, respectively. The Fe isotope composition provides further evidence that microbial dissimilatory reduction of Fe(III) and the formation of Fe(II)-sulfides and non-sulfidic Fe(II) minerals are the dominant Fe geochemical pathways and take place at different depths in the hyporheic zone. In the upper sections of the Core A and B (with depth less than ≈10 m), microbial Fe(III) reduction and non-sulfidic Fe(II) minerals formation govern the Fe cycling and the Fe isotope composition in hyporheic water and bulk sediments. Microbial Fe(III) and SO_4^{2-} reduction and interaction between produced Fe(II)aq and Fe(II)-sulfides precipitate control δ^{56}Fe values of sediments and water sample in the midsections (≈13–19 m) of the Core A. Conversely, abiotic Fe(III) reduction by HS^- determines the bulk δ^{56}Fe values of core sediments and water in the midsections (≈13–19 m) of the Core B. Microbial SO_4^{2-} reduction is limited and microbial Fe(III) reduction controls the δ^{56}Fe values of water and sediments at the bottom of both cores. The variation of δ^{56}Fe values and the As concentration in hyporheic water are similar at each depth, indicating that As enrichment in the water is strongly associated with the microbial reduction of Fe(III) oxides/hydroxides and the formation of Fe(II)-sulfides and non-sulfidic Fe(II) minerals. The enriched-δ^{56}Fe values of high As water concentrations suggest that microbial reduction of Fe(III) oxides/hydroxides is the dominant process that promotes As mobility in the hyporheic zones.

1. Introduction

Long-term exposure drinking water contaminated with arsenic (As) has been cited as the most widespread threat to human health (Nordstrom, 2002). Recent concern regarding high As concentrations in young alluvial and deltaic aquifers has highlighted the need to carefully examine the mechanism of As enrichment in groundwater (Harvey et al., 2002).

The hyporheic zone is the transition zone between surface water in streams/rivers and groundwater (Runkel et al., 2003). The hyporheic zone is also a barrier that prevents the contamination of near-surface aquifers, which are critical to the production of drinking water. There have been several investigations on nitrate and organic carbon processing that address the potential of hyporheic zones to be efficient bioreactors (Bardini et al., 2012; Lewandowski et al., 2011). Exchanged chemicals enter the sediments with water and can be oxidized or reduced by biogeochemical reactions that are often mediated by the hyporheic microbes. Generally, during these processes, organic matter donates electrons in redox reactions, with nitrate, Fe(III), and sulfate functioning as electron acceptors (Hunter et al., 1998). In the subsurface environment, the biogeochemical cycling of Fe, S and As are closely coupled (O'Day, 2002; Saalfield and Bostick, 2009; Wang et al., 2012; Xie et al., 2009). Thus, the redox cycling of Fe and S in the hyporheic zone favors the undesired mobilization and enrichment of As. Previous studies have indicated the hyporheic zones to be both a source and sink of trace elements, including As (Benner et al., 1995; Harvey and Fuller, 1998; Nagorski and Moore, 1999). Although the mechanisms of As release have been elucidated in other environments, As geochemical behavior in

* Corresponding authors. Tel.: +86 27 67883170; fax: +86 27 87436235 (X. Xie). Tel.: +86 27 67883998; fax: +86 27 87481030 (Y. Wang).
E-mail addresses: xjxie@cug.edu.cn (X. Xie), yx.wang@cug.edu.cn (Y. Wang).

http://dx.doi.org/10.1016/j.jhydrol.2014.02.006
0022-1694/

the hyporheic zone has not been quantified, so the effects of hyporheic influences on As mobilization are uncertain. Yet, eliminating the potential threat of As to drinking water requires an understanding of the pathways of As in the hyporheic zone.

Due to the strong association between Fe and As, Fe biogeochemical cycling can provide significant clues to geochemical pathways of As. The Fe biogeochemical cycling between Fe(III) minerals, $Fe(OH)_2$, $FeCO_3$, and FeS in terrestrial environments can be examined using the Fe isotope composition. Fe isotope fractionation has been documented during dissimilatory Fe(III) reduction (Beard et al., 2003; Icopini et al., 2004; Johnson et al., 2005), biotic Fe(II) oxidation (Croal et al., 2004; Herbert and Schippers, 2008; Kappler et al., 2010), abiotic Fe(II) oxidation and precipitation of Fe(III) hydroxides (Balci et al., 2006; Bullen et al., 2001), sorption of aqueous Fe(II) onto Fe(III) hydroxides (Teutsch et al., 2005; Wu et al., 2011, 2010), and the formation of FeS precipitation (Butler et al., 2005), suggesting that Fe isotopes are a useful tool in the study of the biogeochemical cycling of Fe. Research conducted by Johnson et al. (2005) indicated that biogenic magnetite and the Fe-carbonate that forms when microbes oxidize or reduce Fe(III) suggests that the equilibrium $^{56}Fe/^{54}Fe$ fractionation factors are −1.3‰, 0.0‰, and +0.9‰ for Fe(II)aq-magnetite, Fe(II)aq-siderite, and Fe(II)aq-ankerite, respectively, at room temperature. Microbial Fe(III) reduction can cause the $\delta^{56}Fe$ values of Fe(II)aq to be approximately 1.3‰ lighter than the Fe(III) substrate (Beard et al., 2003; Icopini et al., 2004). However, microbial Fe(II) oxidation and precipitation of ferric hydroxides does not result in significant isotopic fractionation between Fe(II)aq and ferric precipitation (Balci et al., 2006). Isotope enriched Fe(II)aq is preferentially adsorbed to the surfaces of Fe(III)(hydr)oxides, resulting in an equilibrium Fe(II)-HFO $^{56}Fe/^{54}Fe$ fractionation factor of −3.17‰ (Wu et al., 2011). However, a study conducted by Crosby et al. (2005) indicated that the $^{56}Fe/^{54}Fe$ isotopic fractionation between aqueous Fe(II) and the outermost layers of Fe(III) on the oxide surface is approximately −3‰, and adsorption cannot result in significant isotopic fractionation between aqueous Fe(II) and Fe(III) oxide. Sorbed Fe(II) have Fe isotope compositions that are similar to those of aqueous Fe(II) at equilibrium (Johnson et al., 2005). However, Fe sulfide precipitation prefers the light isotope with $\Delta^{56}Fe_{FeS-Fe(II)aq}$ values between −0.3‰ and −0.85‰ (Butler et al., 2005).

Thus, As mobilization associated with Fe redox cycling in the hyporheic zone can be demonstrated by Fe isotope data. In this paper, we describe a comprehensive investigation that highlights the mobilization of As in the hyporheic zone based on the Fe isotopes in both sediments and groundwater. This approach provides critical constraints on the Fe pathways and its control on the mobility of As in the hyporheic zones.

2. Materials and methods

2.1. Sampling

The study site, which is well known to be contaminated by natural sources of As, is located on the south bank of the Sanggan River, in Shanxi Provence, China (Fig. 1). The hydraulic gradient drives groundwater towards the river at this location, and it is influenced by rainfall and irrigation, leading to seasonal variability in groundwater discharge rates. The groundwater–surface water exchange is expected to be intense due to the significant seasonal fluctuation of surface water levels. Monitoring has indicated that the interactions between groundwater and surface water primarily occur at less than 20 m distance from the river bank (Yu et al., 2013).

In this study, four 20 m sediment cores were collected using rotary techniques at distances of 0 m (Core A), 10 m (Core B), 40 m (Core C) and 80 m (Core D) from the river (Fig. 1). The sediment samples were collected at various intervals down to the bottom of the boreholes. The cores were capped immediately with PVC pipe, wax-sealed and stored at 4 °C in the dark. Previous work on sediment cores from the study site indicates that the lithology of the sediments is a very homogenous composition of fine sands and silts (Xie et al., 2013). Based on the lithologies, monitoring wells were installed in Core A and Core B at depths of 10 m, 14 m and 20 m to obtain a two dimensional distribution of the hyporheic water composition. Water is pumped to the surface through plastic tubing. Slow pumping and immediate filtration using syringes keeps the ambient air out of the samples and minimizes the oxidation of dissolved Fe(II) to particulate Fe(III) oxides prior to acidification and storage. Chemical and physical parameters, such as pH oxidation and redox potential (ORP) and temperature (T), were measured on the site using portable meters made by Hach Instruments. HS^- was determined using a spectrophotometer (DR2800, HACH) for methylene blue assay. Two filtered (<0.45 μm) acidified samples (acidified to pH < 2 using ultra-pure HNO_3) were collected in 50 mL HDPE bottles for the laboratory analysis of their chemical composition, including As and Fe concentrations and Fe isotopic ratios.

2.2. Analytical method

The trace metal ion concentrations in groundwater, including As and Fe, were measured by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer ELAN DRC-e) at the School of Environmental Studies at the China University of Geosciences in Wuhan. Sample replicates were chosen at random, and all fell within 5%. The field and laboratory blanks were below detection limits for the trace hydrochemical components. Core sediments were air dried, crushed and passed through a 200 mesh. The concentrations of Fe, Mn and As in the sieved sediments were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Intrepid II XSP, Thermo Elemental) and inductively coupled plasma mass spectroscopy (ICP-MS) (POEMSIII) after digestion by HNO_3, HF and $HClO_4$, respectively. The bulk geochemistry of sediments was determined at the State Key Laboratory of Biogeology and Environmental Geology at the China University of Geosciences in Wuhan. For S concentrations, approximately 0.5 g of wet sediment was added to a serum bottle with a trap tube containing 2.5 mL of 10% zinc acetate solution in a glovebox filled with N_2. Using a syringe, 8 mL of 1 M Cr^{II}–HCl solution and 4 mL of 12 M HCl were then injected into the sealed serum bottles. After 20 h of rotation at 200 rpm, the ZnS suspension was homogenized by a sonicating water bath and determined by methylene blue assay in a HACH DR2800 spectrophotometer. The total organic carbon (TOC) in the sieved sediment was determined using an elemental analyzer (Vario TOC, Elementar) after the inorganic carbon was removed with diluted HCl. In addition, one polished thin section of sediment from Core A at ≈15 m depth was chosen for mineral phase analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (Quanta 200, FEI).

The digested sediment samples were purified for mass spectrometry by ion exchange chromatography in a clean room. Samples for Fe isotopic composition measurement were dried down and resuspended in 0.4 mL 8 M HCl. The solution was then passed through an HCl-conditioned anion exchange resin (Bio-Rad AG1-X8) for Fe purification. Matrix elements were removed by washing with 8 M HCl. Fe was eluted using 0.5 M HCl and H_2O followed by 8 M HNO_3 and H_2O. After separation, the purified Fe fraction was evaporated to dryness and dissolved using 2% HNO_3 for isotope analysis. The water samples for Fe isotope measurement were evaporated and then purified using the same methods as for solid samples.