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

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\textit{S}dissulfide-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 \textit{S}dissulfide 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 \textasciitilde 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\textsubscript{4}\textsuperscript{2-} reduction and interaction between produced Fe(II)aq and Fe(II)-sulfides precipitate control \textit{δ}\textsuperscript{56}Fe values of sediments and water sample in the midsections (\textasciitilde 13–19 m) of the Core A. Conversely, abiotic Fe(III) reduction by HS\textsuperscript{-} determines the bulk \textit{δ}\textsuperscript{56}Fe values of core sediments and water in the midsections (\textasciitilde 13–19 m) of the Core B. Microbial SO\textsubscript{4}\textsuperscript{2-} reduction is limited and microbial Fe(III) reduction controls the \textit{δ}\textsuperscript{56}Fe values of water and sediments at the bottom of both cores. The variation of \textit{δ}\textsuperscript{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-\textit{δ}\textsuperscript{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.

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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; Saafield 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
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, FeCO₃, 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(II) has been documented during dissimilatory Fe(III) reduction (Yu et al., 2013). Fe isotope fractionation can be used to determine the origin of Fe in soils and sediments (Butler et al., 2005). 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). Enriched Fe(II)aq is preferentially adsorbed to surfaces of Fe(III)(hydr)oxides, resulting in an equilibrium Fe(II)-HFO ⁵⁶Fe/⁵⁴Fe fractionation factor of ∼3.17‰ (Wu et al., 2011). However, a study conducted by Crosby et al. (2005) indicated that the ⁴⁰Fe/⁴⁴Fe 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 ⁸⁸Fe/⁸⁶Fe values of Fe(II)aq 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 Province, 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 HNO₃) 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 geochemical 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 spectrometry (ICP-MS) (POEMSIII) after digestion by HNO₃, HF and HClO₄ 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 glove-box filled with N₂. Using a syringe, 8 mL of 1 M CrO₃-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 H₂O followed by 8 M HNO₃ and H₂O. After separation, the purified Fe fraction was evaporated to dryness and dissolved using 2% HNO₃ for isotope analysis. The water samples for Fe isotope measurement were evaporated and then purified using the same methods as for solid samples.
The Fe isotope composition was determined by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Nu Plasma Nu Instrument) equipped with a Cetac ASX-110 automatic sampler and a DSN-100 Desolvating Nebulizer System at the Department of Geology at the University of Illinois at Urbana-Champaign (UIUC). Procedural blanks were prepared and found to contribute to less than 0.1% of the Fe content in the samples. Fe isotopic ratios were reported in delta notation as defined by the following relationship:

\[
\delta^{56}\text{Fe} = \frac{\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{sample}}}{\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{standard}}} - 1 \times 1000.
\]

The measured $^{56}\text{Fe}/^{54}\text{Fe}$ isotope ratio for IRMM-014 was used as the standard. Instrument mass bias was corrected for by the standard bracketing approach.

3. Results

3.1. Hydrochemistry and iron isotopes of hyporheic water

A total of six hyporheic water samples were collected from the study site. The physio-chemical parameters and iron isotope compositions are presented in Table 1. The hyporheic waters were characterized by strong reducing and weak alkaline conditions with ORP and pH values ranging from −211.4 mV to −167.2 mV and from 7.20 to 7.70, respectively. The water samples had high As concentrations, varying between 12 µg/L and 132.3 µg/L. The hyporheic water samples from well 1 had relatively higher As concentrations than those from well 2. In well 1, high As concentrations were detected in the samples from the shallow (10 m depth) and deep (20 m depth) water samples. However, high As concentrations were only observed in the deep sample (20 m) in well 2. HS$^-$ was detected in all of the samples with a concentration ranging from 2 to 9 µg/L. It is interesting to note that high As hyporheic water samples generally contained low HS$^-$ concentrations in both wells (Table 1). Fe concentrations in water samples ranged from 206 to 863 µg/L. Like HS$^-$, Fe concentrations were generally low in the high As samples (Table 1). Concentrations of Mn in water samples varied between 0.20 and 1.68 mg/L and had a close association with As (Table 1). The observed correlation between As and Mn could be due to the fact that they both easily co-exist with iron oxides/hydroxides via sorption (Xie et al., 2012). The $\delta^{56}\text{Fe}$ values in the hyporheic water samples ranged widely (from 0.04‰ to 0.71‰). Unlike HS$^-$ and Fe, the $\delta^{56}\text{Fe}$ values were relatively higher in the samples with high As (Table 1).

3.2. Geochemistry and iron isotopes of core sediments

As presented in Table 2, the core sediments had Fe concentrations ranging from 17.27 to 39.14 mg/g and $\delta^{56}\text{Fe}$ values ranging from 0.04‰ to 0.48‰. Arsenic contents in the sediments varied
between 10.29 and 46.92 mg/kg, values which are higher than the 10 mg/kg typical of modern unconsolidated sediment (Smedley and Kinniburgh, 2002). The core sediments also had high TOC (0.65–3.19%) and $S_{\text{sulfide}}$ (0.25–0.63%) contents. As observed in our previous study (Xie et al., 2013, 2012), there was a positive correlation between As and Fe content in the sediments. It is interesting to note that two trends can be observed from the Fe versus $S_{\text{sulfide}}$ plot (Fig. 2B): (1) Fe content increases with $S_{\text{sulfide}}$ from samples taken at 10 m, 14 m and 20 m from two wells. The most depleted-Fe isotope composition of core sediments.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth (m)</th>
<th>As (mg/kg)</th>
<th>Mn (mg/L)</th>
<th>Fe (mg/g)</th>
<th>TOC (%)</th>
<th>$S_{\text{sulfide}}$ (%)</th>
<th>$\delta^{56}\text{Fe}$</th>
<th>SD</th>
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<tr>
<td>A1</td>
<td>5.8</td>
<td>25.79</td>
<td>26.88</td>
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<td>1.36</td>
<td>0.34</td>
<td>0.35</td>
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<tr>
<td>A2</td>
<td>8</td>
<td>28.93</td>
<td>39.14</td>
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<td>2.56</td>
<td>0.43</td>
<td>0.30</td>
<td>0.77</td>
</tr>
<tr>
<td>A3</td>
<td>10</td>
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<td>24.92</td>
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<td>1.67</td>
<td>0.35</td>
<td>0.27</td>
<td>0.037</td>
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<tr>
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<td>12.8</td>
<td>21.80</td>
<td>25.43</td>
<td>0.974</td>
<td>2.17</td>
<td>0.38</td>
<td>0.19</td>
<td>0.058</td>
</tr>
<tr>
<td>A5</td>
<td>13.8</td>
<td>14.09</td>
<td>22.47</td>
<td>0.667</td>
<td>1.96</td>
<td>0.34</td>
<td>0.29</td>
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</tr>
<tr>
<td>A6</td>
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<td>24.98</td>
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<td>0.37</td>
<td>0.41</td>
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<td>B1</td>
<td>8.5</td>
<td>31.11</td>
<td>37.99</td>
<td>0.936</td>
<td>2.24</td>
<td>0.35</td>
<td>0.04</td>
<td>0.063</td>
</tr>
<tr>
<td>B2</td>
<td>10.2</td>
<td>17.56</td>
<td>24.79</td>
<td>0.580</td>
<td>1.69</td>
<td>0.38</td>
<td>0.42</td>
<td>0.036</td>
</tr>
<tr>
<td>B3</td>
<td>13.4</td>
<td>18.27</td>
<td>17.27</td>
<td>0.540</td>
<td>2.32</td>
<td>0.41</td>
<td>0.36</td>
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</tr>
<tr>
<td>B4</td>
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<td>27.29</td>
<td>35.29</td>
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<td>1.74</td>
<td>0.63</td>
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<td>21.23</td>
<td>29.76</td>
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<td>0.52</td>
<td>0.36</td>
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<tr>
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<td>–</td>
<td>–</td>
<td>1.71</td>
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<tr>
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<td>21.71</td>
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<td>0.26</td>
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<tr>
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<td>13.45</td>
<td>26.50</td>
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<td>0.26</td>
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</tr>
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<td>C4</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>2.59</td>
<td>0.32</td>
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</tr>
<tr>
<td>C5</td>
<td>20.4</td>
<td>18.92</td>
<td>25.44</td>
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<td>1.06</td>
<td>0.38</td>
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<tr>
<td>D1</td>
<td>8.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.41</td>
<td>0.30</td>
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</tr>
<tr>
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<td>10.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.19</td>
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<td>0.22</td>
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</tr>
<tr>
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<td>30.50</td>
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<td>1.41</td>
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<tr>
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<td>0.25</td>
<td>0.26</td>
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</tr>
</tbody>
</table>

4. Discussion

4.1. Iron isotopes in hyporheic water

Total of six hyporheic water samples were collected at specific depth of 10 m, 14 m and 20 m from two wells. The $\delta^{56}\text{Fe}$ values of water at various depths in well 1 mirrored the bulk $\delta^{56}\text{Fe}$ values in Core A (Tables 1 and 2). Although the Fe-reducing bacteria preferentially release light Fe from silicates and Fe-oxides (Brantley et al., 2001., 2004; Emmanuel et al., 2005), enriched-$\delta^{56}\text{Fe}$ values in bulk sediments can produce relatively enriched-$\delta^{56}\text{Fe}$ values of Fe(II)aq due to Rayleigh distillation. Accordingly, the bulk sediment $\delta^{56}\text{Fe}$ values in Core A can account for the observed vertical variation of $\delta^{56}\text{Fe}$ values of water in well 1. The high $\delta^{56}\text{Fe}$ value and low Fe concentration in the water sample from well 1 at 10 m depth could be due to a moderate reduction of enriched-$\delta^{56}\text{Fe}$ Fe[III] minerals in hyporheic sediments at the same depth. Taken together, the low $\delta^{56}\text{Fe}$ value and high Fe and HS concentrations in the water sample from well 1 at 14 m depth and the Fe concentrations and $\delta^{56}\text{Fe}$ values in core sediments suggest that there was intensive reduction of Fe(III) and $SO_4^{2-}$. High concentration of Fe and HS can result in the formation of Fe sulfide precipitate and depletion of $\delta^{56}\text{Fe}$ in water samples according to the study conducted by Butler et al. (2005). It is well documented that FeS precipitate can retain a large amount of As (Smedley and Kinniburgh, 2002; Han et al., 2011; Wolthers et al., 2005). Therefore, this group of reactions may account for the high HS and Fe and low As and $\delta^{56}\text{Fe}$ values in water at 14 m in well 1 (Table 1). The high $\delta^{56}\text{Fe}$ value in the water sample at 20 m can be attributed to reduction of the lithogenic Fe oxides/hydroxides with high $\delta^{56}\text{Fe}$ values in the corresponding sediments. However, this appears inconsistent with the low Fe concentrations measured in water from the bottom of the well 1. The microbial reduction of Fe(III) does not necessarily release all of the Fe(II) into groundwater because some is retained in the solid phase (Fredrickson et al., 2013, 2012, 2011).
Therefore, high Fe concentrations would not be expected along with the microbial reduction of Fe(III) minerals at the bottom of well 1. The vertical distribution of As concentrations and $\delta^{56}$Fe values in water samples from well 1 were strikingly similar (Fig. 3A). It is well known that Fe(III) oxides and hydroxides are the critical sequesters in sediments in the study area (Xie et al., 2008, 2013), and the close relationship between Fe and As contents in the bulk core sediments offers further evidence for this (Fig. 2A). Therefore, the high As concentrations at 10 m and 20 m in well 1 can be attributed to the microbial reduction and dissolution of As-bearing Fe(III) minerals, such as Fe(III) oxides/hydroxides.

The $\delta^{56}$Fe values in well 2 differed from those in well 1 because they increased with depth from 0.04‰ to 0.56‰ (Fig. 3B). The $\delta^{56}$Fe value in water at 10 m (0.04‰) are consistent with the bulk $\delta^{56}$Fe value of sediments from Core B at 8.5 m (0.04‰) (Tables 1 and 2), indicating that Fe does not experience significant redox cycling. It is worthy of noting that water sample from well 1 at 14 m had similar $\delta^{56}$Fe value with sediment samples from 13.4 m depth. Importantly, the sample also contained high concentration of Fe (620 µg/L) and HS⁻/CO₃⁻ (8 µg/L). Sulfide can directly react with Fe(III) oxides, hydroxides and oxyhydroxides to abiotically reduce Fe(III) to Fe(II) under high concentrations of HS⁻ conditions (Yao and Millero, 1996). No significant isotopic fractionation can be expected between Fe(II)aq and the residual Fe(III) minerals in this process. At the same time, high concentration of Fe and HS⁻ resulted in the formation of Fe sulfide precipitate and sequester As from water (Smedley and Kinniburgh, 2002; Han et al., 2011; Wolthers et al., 2005). Thus, the observed iron isotopic and hydrochemical characteristics can be attributed to HS⁻ abiotical reduction of Fe(III) minerals. In contrast, the relative enriched-$\delta^{56}$Fe value of water sample in well 2 at 20 m (0.56‰) indicates Fe(III) minerals have experienced an intensive microbial redox cycling. Therefore, the vertical distribution of As concentrations and $\delta^{56}$Fe values apparently supports that As levels in water from well 2 governed by abiotical and microbial Fe(III) reduction.

4.2. Iron content and iron isotope of core sediments

As in our previous study on sediments with high As (Xie et al., 2013, 2012), we again observed a close association between As and Fe content in hyporheic core sediments (Fig. 2A). Iron oxyhydroxides are common in aquifer sediments that have high As concentration (Root et al., 2007). The main mineral phases of iron oxyhydroxides are hematite, goethite, lepidocrocite, maghemite, magnetite, and ferrhydrite in unconsolidated sediments (Zhang et al., 2003). Arsenic can form inner-sphere adsorption complexes on Fe(III) oxyhydroxides, including ferrhydrite (Ona-Nguema et al., 2005), goethite (Farquhar et al., 2002; Ona-Nguema et al., 2005), lepidocrocite (Ona-Nguema et al., 2005), hematite (Ona-Nguema et al., 2005), and maghemite (Cances et al., 2008).
In addition, iron sulfide minerals, such as troilite, pyrite and mackinawite are commonly found in sediments under reducing conditions (Thamdrup and Canfield, 1996; Thamdrup et al., 1994). Iron sulfides have been clearly demonstrated to be effective in removing As from water under anoxic conditions (Han et al., 2011; Wolthers et al., 2005). Our SEM-EDS results revealed the existence of unevenly distributed As-bearing Fe sulfide in sediments (Fig. 4). Therefore, the close association observed between As and Fe concentrations (Fig. 2A) may be related to the occurrence of iron oxyhydroxides and sulfides in hyporheic sediments.

It is noteworthy that two sample groups can be detected from the Fe vs. Ssulfide plot (Fig. 2B). In the first group (Group 1), Fe contents increase with increasing Ssulfide. Under reducing environment, Fe(II) can be presented as Fe(II)-sulfides, such as troilite, pyrite and mackinawite, and Fe(II) sulfide has been commonly observed in sulfidic sediments (Thamdrup et al., 1994; Thamdrup and Canfield, 1996). The occurrence of Fe sulfide in sediment is also supported by our SEM–EDS result (Fig. 4). Therefore, the close relationship between Fe and Ssulfide contents can be attributed to the formation of Fe(II)-sulfide in the hyporheic zone. In the second group (Group 2), Fe contents change significantly even as the Ssulfide content remains stable. The hyporheic zone is regarded as a hotspot of biogeochemical reactions (Lautz and Fanelli, 2008). As mentioned above, Fe(III) oxyhydroxides are common in sediments (Zhang et al., 2003). Thus, microbial Fe(III) reduction may be expected in the hyporheic zone and have been documented in previous studies (e.g., Lovley et al., 1991). Generally, FeCO3 (siderite) and amorphous FeS preferentially precipitate in anaerobic conditions due to microbial Fe(III) reduction (Matsunaga et al., 1993). Most of the produced Fe(II) is believed to occur as authigenic, non-sulfidic, secondary Fe(II) minerals, such as Fe(II) hydroxides or siderite, which is commonly observed in environments that are strongly reducing and have sulfide deficits (Lovley et al., 1987). Although no direct evidences, our extraction experiment results indicated the occurrence of secondary Fe(II) phases in sediments (Xie et al., 2013). Thus, all of the core sediments included in Group 2 may be due to a transformation between Fe(III) and non-sulfidic, secondary Fe(II) minerals, such as Fe(II) hydroxides or siderite, a transformation that is catalyzed by microbes.

To further examine the formation of Fe(II) sulfides and non-sulfidic Fe(II) minerals, the relationship between Fe contents and δ56Fe values in the core sediments is presented in Fig. 5. We calculated the evolution of δ56Fe values during Fe(II)-sulfides precipitation and dissimilatory Fe(III) reduction. The low δ56Fe value (0.04‰) in core sediments is close to bulk δ56Fe value for soils and lithogenic Fe-sources (Emmanuel et al., 2005; Poitrasson and Freydier, 2005). Therefore, the microbial dissimilatory Fe(III) reduction and the mixing models of lithogenic Fe oxides/hydroxides and Fe(II)-sulfides precipitation assume that the δ56Fe value for lithogenic sources is 0.04‰. From Fig. 5, it can be seen that all of the core sediments fall near but slightly shift to the right of the calculated lines for dissimilatory Fe(III) reduction and Fe(II)-sulfide precipitation. This indicates that the bulk Fe isotope composition of core sediments can be explained by microbial dissimilatory Fe(III) reductions and the mixing of Fe(II)-sulfides precipitation with lithogenic Fe oxides/hydroxides. Microbial Fe(III) reduction does not necessarily release all Fe(II) into groundwater because some is retained on the solid phase (Fredrickson et al., 1998). Isotope-enriched Fe(II) is preferentially adsorbed to the Fe(III)(hydr)oxides surfaces (Wu et al., 2011). Similarly, the equilibrium δ56Fe/δ54Fe fractionation factor between Fe(II)aq and mackinawite was measured as −0.32‰ by Wu et al. (2012). Thus, the bulk δ56Fe values of core sediments that are slightly shifted from the anticipated dissimilatory Fe(III) reduction and Fe(II)-sulfides precipitation curves in Fig. 5 may be related to the adsorption of Fe(II) to Fe(III) oxides/hydroxides and the surfaces of Fe(II)-sulfides.

Cores A and B were drilled to understand the two dimensional distribution of Fe isotopes and the transformation of Fe-bearing minerals in the hyporheic zones. Core A exhibits a well-defined minimum δ56Fe value of 0.19 at the middle depth at 12.8 m, while maximum δ56Fe values occur at the upper (0.41‰) and lower (0.35‰) ends of the core (Fig. 6A). In the uppermost section of Core A, the δ56Fe value (0.04‰) was very low and close to the bulk δ56Fe values for soils and lithogenic Fe-sources (Emmanuel et al., 2005; Poitrasson and Freydier, 2005). This suggests that the lithogenic Fe-sources did not undergo significant reduction by microbes.

A

![Image](https://example.com/image1)

B

![Image](https://example.com/image2)

**Fig. 4.** Scanning electron microscopy image and energy dispersive X-ray spectrum (EDS) of Fe sulfides in sediment. The point for EDS analysis was marked in B.
between −0.3‰ and −0.85‰. Moreover, microbial Fe(III) reduction can cause δ^{56}Fe values of Fe(II)aq to be lighter than the Fe(III) substrate (Beard et al., 2003; Icopini et al., 2004). As a result, the extensive microbial Fe(III) reduction that accompanies SO_{4}^{2−} reduction and organic matter oxidation in the hyporheic zones can produce a Fe isotope composition depleted in secondary Fe(II) minerals such as carbonates and sulfides and result in a gradual decrease in the bulk δ^{56}Fe values of the core sediments. However, the low HS巯 concentrations in the hyporheic water (Table 1) suggest that a significant amount of Fe(II)-sulfide is not formed in the upper sections of the cores. Therefore, the decrease in δ^{56}Fe values observed in the upper sections can be explained by extensive Fe(III) mineral reduction and the formation of non-sulfidic secondary Fe(II) minerals.

It is interesting to note that δ^{56}Fe values increase in the deeper sections of Cores A and B. According to the sequence of redox reactions (Borch et al., 2010), reduction of amorphous Fe(III) hydroxides occurs before the reduction of SO_{4}^{2−} to HS巯, which is followed by the reduction of crystalline Fe oxide/hydroxides, such as α-FeOOH(s). Hence, there may be extensive microbial reduction of sulfates after amorphous Fe(III) hydroxides are reduced at a specific depth. High concentrations of HS巯 were detected in water samples at 14 m in both cores, indicating an extensive reduction of SO_{4}^{2−} to HS巯. As a result, the Fe(II)-sulfides may be produced, as appears apparent in Figs. 2, 4 and 5. According to an experimental study of Fe isotope fractionation during the precipitation of FeS by Butler et al. (2005), the kinetic Fe isotope fractionation of zeroage FeS is ΔFe(II)−FeS = −0.85‰, and the FeS in contact with Fe(II)aq became progressively heavier in isotopes (ΔFe(II)−FeS = −0.3‰ at equilibrium). Recently, Wu et al. (2012) obtained an equilibrium δ^{56}Fe/δ^{56}Fe fractionation factor of −0.32‰ between Fe(II)aq and mackinawite. Therefore, under strong reducing conditions, Fe(II)-sulfides in contact with Fe(II)aq may account for the increase in δ^{56}Fe value in the deeper sections of both cores. In addition, according to the Rayleigh distillation, the intensive microbial reduction of crystalline Fe oxide/hydroxides that accompanies SO_{4}^{2−} reduction may also enrich the δ^{56}Fe in residual Fe oxides/hydroxides. Hence, for each depth level, Fe concentration and isotope composition in the hyporheic zone sediments are controlled by the extensive reduction of Fe(III) and SO_{4}^{2−} by microbes and by the formation of secondary sulfidic and non-sulfidic Fe(II) minerals.

4.3. Implications for arsenic mobilization in the hyporheic zone

We constructed a conceptual model of Fe geochemical pathways and As mobilization that incorporates data on the sulfide and Fe contents and δ^{56}Fe value of the bulk core sediments in hyporheic water (Fig. 7). In the hyporheic zone, the δ^{56}Fe of the bulk core sediments and hyporheic water at each depth is governed by the intensity of microbial Fe(III) and SO_{4}^{2−} reduction and the formation of secondary sulfidic and non-sulfidic Fe(II) minerals. In the upper sections (with depth less than 10 m) of the hyporheic zone, Fe(III) reduction catalyzed by microbes is the dominant biogeochemical reaction. The reduction of As-bearing Fe(III) minerals can release As into the hyporheic water and formation of non-sulfidic Fe(II) minerals. This explains the high As and low Fe concentration and high δ^{56}Fe value in water at 10 m in well 1. Under strongly reducing conditions, intense SO_{4}^{2−} reduction and Fe-sulfide precipitation will prevail in the midsections (13–19 m) of the hyporheic zone. Because it is sequestered by the Fe(II)-sulfides, As concentration is limited in water at corresponding depths. This may explain the low As concentrations in

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**Fig. 5.** Relationship between Fe-concentration and Fe-isotope composition observed in Fe-oxohydroxide-coated sands in core sediments. The red line is the calculated theoretical relationship between Fe-concentration and Fe-isotope composition during a dissimilatory Fe(III) reduction. The blue line is the calculated theoretical relationship between Fe-concentration and Fe-isotope composition during Fe(II)-sulfide precipitation and mixing with lithogenic Fe in core sediments. The line for dissimilatory Fe(III) reduction is calculated using the initial conditions of δ^{56}Fe = 0.04‰, Fe content is 37.99 mg/g, and the isotopic fractionation factor is 1.003. The mixing line between Fe(II)-sulfides and lithogenic Fe-sources is calculated using initial conditions of δ^{56}Fe = 0.04‰ and a Fe content of 37.99 mg/g for lithogenic Fe-sources. δ^{56}Fe = 0.39‰ for Fe(II)-sulfides, which is computed based on a Δ^{56}Fe_{FeS−Fe(II)} of −0.32‰ (Wu et al., 2012) and a Δ^{56}Fe_{FeS−Fe(II)} of 0.71‰ (the measured iron isotope composition in this study). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 6.** The vertical distribution of bulk δ^{56}Fe values of core sediments in Cores A and B.
water at 14 m in both cores. However, Fe isotope compositions in water at this depth may be controlled by different processes in Core A and B. In core A, interaction between Fe(II)aq and produced Fe sulfide can be used to account for the low δ56Fe value in water sample. However, relative enriched-δ56Fe value in water sample from Core B may be due to HS⁻ abiotical reduction of Fe(III) minerals under high HS⁻ concentration environment. According to the sequence of redox reactions (Borch et al., 2010), reduction of SO₄²⁻ to HS⁻ is followed by the reduction of crystalline Fe oxide/hydroxides. At the SO₄²⁻ reduction stage, most of SO₄²⁻ is likely used up, and then the formation of Fe(II)-sulfides will be limited. Subsequently, the reduction of crystalline Fe oxide/hydroxides can promote the mobilization of As. As a result, high As concentrations can be detected in water samples at ≈20 m depth in both Cores A and B.

5. Conclusions

As and Fe are strongly associated in bulk core sediments, which is likely due to the presence of iron oxyhydroxides and sulfides in the hyporheic zone. The relationship between Fe and S_{sulfide} in core sediments indicates that microbes catalyze transformations between Fe(III) and non-sulfidic Fe(II) minerals and Fe(II)-sulfides in the hyporheic zone at the study site. The relationship between Fe contents and δ56Fe values of bulk core sediments further explain the formation of Fe(II)-sulfides and non-sulfidic Fe(II) minerals. The bulk δ56Fe values of core sediments are shifted slightly to the right in plots of the calculated dissimilatory Fe(III) reduction and Fe(II)-sulfides precipitation curves. This is likely due to the adsorption of Fe(II) to the surfaces of Fe(III) oxides/hydroxides and Fe(II)-sulfides. The large variation and vertical distribution of δ56Fe values in Fe(II)-sulfides precipitation indicates intensive abiotic and microbial reduction of Fe(III) and SO₄²⁻ and precipitation of Fe(II)-bearing non-sulfidic and sulfidic phases takes place at different depths in the hyporheic zone. The δ56Fe values and As concentrations in water at each level are closely associated with the Fe(III) oxides/hydroxides reductions and the formation of Fe(II)-sulfides and non-sulfidic Fe(II) minerals. The enriched-δ56Fe values in water with high levels of As imply that microbial reduction of Fe(III) oxides/hydroxides promotes As mobility in the hyporheic zones. Low As water from Core A at 14 m with low δ56Fe value and high HS⁻ and Fe concentration can be attributed to the formation of Fe(II) sulfides. However, low As hyporheic water with high δ56Fe value and high HS⁻ and Fe concentration in Core B may be related to HS⁻ abiotic reduction of Fe(III) oxides/hydroxides and Fe(II) sulfides formation.

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