Characteristics and compound-specific carbon isotope compositions of sedimentary lipids in high arsenic aquifers in the Hetao basin, Inner Mongolia[☆]

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ARTICLE INFO

ABSTRACT

Organic matter, as an electron donor, plays a vital role in As mobilization mediated by microorganisms during reductive dissolution of Fe/Mn oxides in shallow aquifers. However, the specific types and sources of organic matter involved in biogeochemical processes accelerating As mobilization are still controversial. Both sediment and groundwater samples were collected at different depths from aquifers of the Hetao Basin, a typical inland basin hosting high As groundwater. Sedimentary lipids and their compound-specific carbon isotope ratios were analyzed to evaluate characteristics and sources of organic matter. Results show that sedimentary As were well correlated with Fe and Mn oxides, suggesting that As exist as Fe/Mn oxide bound forms. Groundwater As far exceeded the drinking water guide value of 10 μg/L. Moreover, As concentrations in shallow groundwater were relatively higher. Lipids in clay were mainly originated from terrestrial higher plants, while that in fine sand samples were derived from terrestrial higher plants, microorganism and petroleum. Shallow fine sand samples were also characterized by evident in-situ biodegradation. Compound-specific carbon isotope compositions of sedimentary lipids showed that short-chain n-alkanes and n-alkanoic acids had more positive $\delta^{13}C$ values compared to long-chain compounds, especially in shallow fine sand samples. $\delta^{13}C_{TOC}$ were also low in shallow fine sand samples. These results jointly indicate that these lipids in shallow fine sand samples acted as carbon source for indigenous microorganism and the short-chain components were particularly more vulnerable to biodegradation, which may contribute to high As concentrations in shallow groundwater. The new findings provide the first evidence that short chain length n-alkyl compounds afforded a source of potential electron donors for microbially mediated As mobilization process in the shallow aquifers.

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1. Introduction

High arsenic (As) groundwater is widely distributed throughout the world (Nordstrom, 2002). In China, many inland basins host high As groundwater, including the Yinchuan basin, the Hetao basin, the Datong basin, and the Songnen basin (Smedley et al., 2003; Guo et al., 2014). Long-term intake of high As groundwater

seriously affects people's health. Microbially mediated reduction of As-containing Fe(III) oxy-hydroxide minerals and As(V) dissimilatory reduction have been widely accepted for As release mechanisms (Nickson et al., 1998; Berg et al., 2001; Ravenscroft et al., 2001). As an electron donor, organic matter plays an important role in these microbial processes (Oremland and Stolz, 2003; Islam et al., 2004; Postma et al., 2007).

Organic matter, which contributes to As mobilization in shallow reducing aquifers, can originate from multiple possible sources, including external sources such as surface ponds (Lawson et al., 2013, 2016) and wetlands (Stuckey et al., 2015), and internal sources such as peat-layers (Goodbred and Kuehl, 2000; McArthur et al.,

2004; Shrivastava et al., 2015). The sedimentary organic matter is an important carbon source, accounting for a large proportion of total organic carbon. Although most of bioavailable organic matter may have been exhausted during the long-term deposition process, sedimentary organic matter would be bioavailable for microorganisms and subsequently fuel microbially reductive release of As under special conditions, such as in situ perturbations (Neumann et al., 2014).

As an important pool of sedimentary organic matter, lipids not only accelerate As release by acting as an electron donor (Rowland et al., 2007, 2009), but also serve as biomarkers of complex carbon pools in sediments (Diefendorf and Freimuth, 2016). Previous studies showed that microbially-derived and petroleum-derived hydrocarbons were potential carbon sources for microbially-mediated reduction of Fe(III) oxides and As mobilization (Ghosh et al., 2015a, 2015b). On the other hand, lipids (including *n*-alkanes, *n*-alkanoic acids and *n*-alkanols) are biomarkers of sources of organic carbon. For example, high molecular weight *n*-alkanes with an odd-over-even predominance of the carbon chain length (calculated as a proxy of carbon preference index (CPI) (van Dongen et al., 2008)) are known to originate from higher plants (Eglinton and Hamilton, 1963, 1967), while petroleum-derived *n*-alkanes have the weak odd-over-even predominance of *n*-alkanes. Therefore, the *n*-alkane distribution patterns can be used to distinguish between higher plant-derived organic matter and mature petroleum-derived organic matter. Similarly, the petroleum-derived hopanes and steranes are also applied to distinguish the maturity of organic matter (Peters et al., 2005).

Although contents of organic matter including lipids in high As-groundwater aquifers are generally low, several studies have been carried out to investigate sources and bioavailability of organic matter by using the lipid distribution patterns in high-As groundwater systems, i.e. Bangladesh (Rowland et al., 2006; Ghosh et al., 2015a, 2015b), Vietnam (Al Lawati et al., 2012), Taiwan (Al Lawati et al., 2013), and Datong basin (Xie et al., 2012). All studies showed the mixture pools of sedimentary organic carbon in high As-groundwater aquifers, including higher plants, microbial cell wall, and petroleum origins with different bioavailability. Based on microcosm experiments, Rowland et al. (2009) concluded that the bioavailable petroleum-derived *n*-alkanes is of potential importance in triggering As mobilization.

It is worth noting that only using the lipid distribution patterns to reflect the source of organic matter is still subject to some limitations. It is difficult to efficiently determine its source by the traditional lipid distribution patterns under complex environments with multiple inputs of lipid compositions or microbial reworking. Compound-specific carbon isotope analysis is a widely-used technology, which can be utilized to better distinguish among sources (Tanner et al., 2010) and reflect organic matter transformation and degradation process in the past (Schmidt et al., 2004; Quénéa et al., 2006; Philp, 2007; Amelung et al., 2008). In particular, using the ^{13}C-labeled alkanes and kerogen to trace the microbial processes, Rizoulis et al. (2014) found that *n*-alkanes act as electron donors in anaerobic processes for Fe(III) and As(V) reduction, which stimulate the release of As.

However, compound-specific carbon isotope compositions of lipids in high-As groundwater aquifer sediments are still unknown, and whether they are efficiently used to trace transformation and degradation of organic matter in aquifers is worth investigating. Therefore, it is necessary to combine lipid distribution patterns and compound-specific carbon isotope compositions to better understand the sources of organic matter in high As groundwater aquifers and their roles in As mobilization.

The Hetao basin is one of the typical high As groundwater-affected areas. Although previous studies have shown that As mobility was caused by both dissimilatory reduction of Fe oxides (Guo et al., 2013) and microbial sulfate reduction and microbial disproportionation of sulfur intermediates (Guo et al., 2016), the sources of bioavailable organic matter are not tagged. Therefore, the main objectives of this study are to 1) investigate geochemical characteristics of lipids in aquifer sediments from the Hetao Basin; 2) characterize compound-specific carbon isotope compositions of representative lipids (*n*-alkanes and *n*-alkanoic acids); 3) to evaluate origins of lipids and their possible linkages to microbial processes for As mobility.

2. Material and methods

2.1. Study area and sample collection

The Hetao basin is located in the west of Inner Mongolia, to the south of the Langshan Mountains, the north of the Yellow River, the east of the Ulan Buh Desert, and the west of Wuliangsu lake, where high As groundwater has been found since 1990s (Tang et al., 1996; Guo et al., 2008; He et al., 2008; Deng et al., 2009). Groundwater mainly occurs in the Quaternary aquifer sediments, which mostly originated from alluvial, alluvial–pluvial and fluvial–lacustrine of Langshan mountains and the Yellow River (Guo et al., 2008).

A borehole BH02 (40°59′45.3″N, 106°58′25.1″E), being locating in a typical high-As groundwater area of the flat plain, was drilled by rotary drilling to collect sediment samples up to about 89 m below land surface (bls) in 2012 in the northwest of the basin (Fig. 1), which is located in the front of the Langshan mountains. Sampling interval was normally around 2.0 m, and additional samples were collected near lithological boundaries. Sixty-seven sediment samples were collected from the borehole. Before sampling, drilling mud was not used. After being taken from borehole, fresh sediment samples were immediately packed with the foil paper and kept in ultrapure N_2-filled PVC bags on site in order to minimize the exposure to oxygen. After collection, sediment samples were transported to laboratory at 4 °C, and then stored at −80 °C in the laboratory.

After sediment sampling, a multilevel well was installed in the borehole at depths of 5, 7.5 10, 20, 30, 40, 50, 60, 70, 75 m bls. Establishment of the multilevel well (ten piezometers) was described in Guo et al. (2012). All piezometers had screening length around 0.5 m and were apart from each other by backfilling the sediments drilled from the similar depths. Ten groundwater samples were collected from those piezometers of the multilevel well in July 2014. At the time of the groundwater sampling, parameters, including water temperature, EC, pH, and ORP, were measured using a multi-parameter portable meter (HI 9828, HANNA), which was calibrated by a standard solution before using. Concentrations of NH_4-N, S^{2-}, and Fe(II) were determined by a portable spectrophotometer (DR2800, HACH), with 1, 10 phenanthroline, 5 aminosalicylic acid, and methylene blue methods, respectively. Groundwater alkalinity was measured in the field with a bromocresol green-methyl red indicator by HACH Model 16900 digital titrator.

Groundwater was sampled after pumping until the water temperature, electrical conductivity (EC), pH, and ORP were stable. Water samples for laboratory analysis were filtered through 0.22 μm filter membranes in the field. Samples for trace element and major cation analysis were collected in 100 mL HDPE bottles and acidified to pH < 2 by addition of 6 M ultrapure HNO_3. Water samples for anion analysis were fully filled in 10 mL HDPE bottles and sealed with parafilm.