

Is organic matter a source or redox driver or both for arsenic release in groundwater?



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ABSTRACT

Arsenic (As) contamination in groundwater is a global public health issue, because groundwater is the main source of drinking water worldwide. Arsenic contamination in groundwater is directly or indirectly associated with organic matter (OM). Therefore, this study investigated the role of OM in mobilization of As in the subterranean aquifers. The reduced concentrations of terminal electron acceptors (dissolved O₂, NO₃⁻, and SO₄²⁻), enhanced concentrations of dissolved organic carbon (DOC), HCO₃⁻ and NH₄⁺ ions, and strong correlations between NH₄⁺ and DOC indicate the reducing geochemical environment of aquifer in Bangladesh, where DOC might have originated from microbial oxidation of sedimentary OM, humic substances, surface derived terrestrial OM and petroleum. Groundwater samples exhibit variations in the concentrations of DOC (0.20–5.09 mg/l), fluorescence intensity and As depending on the depth and locations of the sampling site suggesting that the aquifers have different characteristics and different sources of DOC. The DOC concentrations in the upper aquifer (up to 41 m) are higher than those in the middle and lower aquifers (>55 m) suggesting that the recent inflow of surface derived terrestrial OM with recharge water and petroleum in the shallow parts of the aquifer promoted the peak of high dissolved As, where older water mixes with recent recharge water containing organic carbon. Hydrogeochemical data and sediment geochemistry indicates that As mobilization from the sediment occurs through the microbial-mediated reductive dissolution of iron oxyhydroxide, where OM is the main redox driver facilitating As release into groundwater. Organic matter can strongly influence the solubility and mobility of As mainly through redox reactions, competitive adsorption, desorption and complexation reactions. Furthermore, based on the results of sediment and groundwater geochemistry, and As speciation in plant tissue, it can be concluded that OM is not only a redox driver, but also one of the sources of As in groundwater.

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1. Introduction

Close association is found between arsenic (As) and organic matter (OM) in sediments of the Bengal delta plains and other parts of the world (McArthur et al., 2001; Anwar et al., 2003). Moderate to strong positive correlations between As, Fe, HCO₃⁻, NH₄⁺ and dissolved organic carbon (DOC) in groundwater suggest that As mobilization mainly occurs via microbially mediated reductive dissolution of As bearing Fe(III) oxides by OM (Nickson et al., 1998; Anwar et al., 2003; Islam et al., 2004). Strong correlations between As, Fe and OM in subsurface sediments also provide further evidence for the above mechanisms in the Bengal delta plains (Anwar et al., 2003; Rowland et al., 2006). Some previous

studies indicated that infiltration of surface-derived OM or *in situ* OM from within the sediment, or from other sources into the shallow aquifer may stimulate the activity of microbial communities, thereby leading to a reduction of iron oxyhydroxide and As release (Akai et al., 2004; Anwar et al., 2006; Rowland et al., 2006). Arsenic mobilization mechanisms may vary with location and depth, depending on hydrogeological and redox conditions.

Organic matter is presumed to be carrier of As and to control the mobility, diagenetic cycling, transport, aggregation, and deposition of As and other trace elements in soils, sediments, biogenic deposits and groundwater of most delta plains (McArthur et al., 2001; Bauer, 2008). Natural OM plays a key role as a source of energy for micro-organisms in the aquatic environment (Anwar et al., 2003, 2006; Akai et al., 2004; Lapworth et al., 2008). Humic materials in sediments occur as insoluble macromolecular complexes bound together by metals and metalloids (Stevenson, 1985). Fulvic acids (FAs), a part of humic substances, are organic

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polyelectrolytes that are ubiquitous in soils and surface waters (Rook, 1977). Humic substances originating from the soil zone by flushing and leaching with recharge water during spring runoff, precipitation, and storm events in summer and fall generally reflect the oxidizing conditions, while those originating from sedimentary OM indicate the reducing conditions of aquifer (Artinger et al., 2000; Buckau et al., 2000). However, recent study by Schäfer et al. (2005) suggests that shallow recharge groundwater and deep brine derived FAs exhibit a similar C_{arom}/C_{aliph} ratio (1.1–1.4), indicating invariance in the backbone structure against higher residence time and variation in geochemical conditions.

Very few studies have been published regarding characterization of DOC, its fluorescence property and role of OM as a source of As and redox driver for As mobility in groundwater. Therefore, further investigation is needed for clear-cut understanding regarding the mechanism of As mobilization in groundwater of the Bengal delta plain and other parts of the world. Is OM (1) a source of As and redox driver, or (2) only redox driver to control the geochemical condition and reductive dissolution of iron oxyhydroxides/oxide for As mobility in groundwater? It is still now a big question for As biogeochemistry in groundwater. Therefore, the aims of this study are (1) to elucidate the answer of the above questions based on our own results and the previous publications, and (2) to determine the hydrogeochemistry, sources and fluorescence property of DOC, and role of OM as a source of As and redox driver in groundwater.

2. Materials and methods

2.1. Study area and sample collection

Groundwater samples were collected from tube-well waters at Sonargaon thana, Narayanganj district that is about 25 km furthest to the south-east of Dhaka city, Bangladesh. This study site covers an area of about 16 km². The aquifer comprises of alternating sandy and silty layers and consists of late Pleistocene–Holocene alluvial sediments of the Bengal delta. The samples were collected randomly and filtered with Whatman (0.7 μm pore size) GF/F filters.

2.2. Chemical analysis

After filtration, two different procedures of sampling were adopted for DOC measurement and fluorescence study: 25 μl of 6 N HCl solution was added to filtrate to remove dissolved inorganic carbon (DIC) for DOC determination, while no acid was added for fluorescence measurement. For later analysis, samples were stored in a freezer (−35 °C) to prevent microbial oxidation. Dissolved organic carbon was measured by high temperature catalytic oxidation method (HTCO) using a Shimadzu TOC 5000A, total organic carbon analyzer. Standards were prepared from reagent grade potassium hydrogen phthalate (KHP) in Milli-Q water. Fluorescence properties of water samples were determined by a spectrofluorometer (F-4500, Hitachi Ltd). Scanning range was 225–400 nm for excitation (Ex) and 225–500 nm for Emission (Em). Standards were prepared from reagent grade Quinine Sulfate Monohydrate (QSM) using diluted sulfuric acid. After standard measurement, the excitation-emission matrix (EEM) for groundwater samples was determined within the above excitation-emission (EE) range. The detailed method of sample collection, preservation and analysis of DOC and fluorescence are described in Anwar et al. (2003).

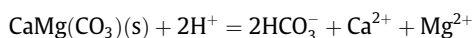
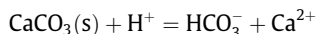
Major anions and cations in groundwater samples were measured by Dionex QIC Analyzer, and IC 20 Ion Chromatography (Dionex Corp.), respectively. The HCO_3^- concentration was determined

using charge balance between the other ions (especially major cations and anions). Arsenic was measured by inductively coupled plasma mass spectrometry (ICP-MS) (PMS 2000, Yokogawa analytical system). The instrument was linearly calibrated from 1.0 to 40 μg/l with custom multi-element standards (SPEX Industries) yielding a minimum r^2 of 0.9996. Arsenic, major cations, anions and DOC data of groundwater from Sonargaon thana are taken from Anwar et al. (2003). However, these data have been statistically analysed in a different method than those used in the previous publication, and explained to discern the different viewpoints than those described in Anwar et al. (2003).

3. Results and discussion

3.1. Geochemical weathering and relationship of DOC with chemical parameters

High concentrations of ammonium ion (NH_4^+), HCO_3^- and correlation between NH_4^+ and DOC concentrations (Fig. 1a) suggest the source of NH_4^+ and DOC from re-mineralization of humic-type sedimentary organic matter (SOM) derived from terrestrial (higher plant) sources (Sholkovitz, 1973; Rowland et al., 2006; Anwar et al., 2010) resulting in the reduction of oxidizing agents like O_2 , NO_3^- , or SO_4^{2-} (Buckau et al., 2000) and reducing geochemical condition in groundwater of Bangladesh. The use of agrochemicals (nitrogen containing fertilizers) may contribute a part of the total NO_3^- and NH_4^+ ions in groundwater that cannot be excluded. The concentrations of DOC here show very weak relationship with HCO_3^- (Fig. 1b). In contrast, calculation of molar ratio and strong correlation of calcium with HCO_3^- (Fig. 2a) in groundwater samples reflect that dissolution of sedimentary calcite and dolomite is more dominant process (McArthur et al., 2001) than other processes (e.g., degradation of OM) to release HCO_3^- in groundwater of this study area (Stumm and Morgan, 1996) as follows:



The correlation between the concentrations of dissolved magnesium and HCO_3^- (Fig. 2b) is weaker than that between calcium and HCO_3^- (Fig. 2a). The concentrations of NO_3^- ions are inversely related with DOC concentration (Fig. 1c) in groundwater. The concentration of DOC is inversely related with those of Na^+ and Cl^- (Fig. 1d and e) suggesting that they might be produced from the two different geological sources. The source of DOC in groundwater is terrestrially derived SOM, whereas the source of Cl^- from marine origin. However, in groundwater of Bangladesh, SO_4^{2-} concentration is very low, and in most cases below detection limit (<0.2 mg/l) that is attributed to the reductive depletion of SO_4^{2-} by *Desulfovibrio* microbial oxidation of SOM under reducing condition (Schubert et al., 2000) that produced the negative relationship between SO_4^{2-} and DOC concentration (Fig. 1f). However, few samples showed high concentration of sulfate due to the recent recharge of saline water. The As-rich pyrite is rarely found in sediments of the Bengal delta (Akai et al., 2004) that is produced via diagenetic alteration of sediments rich in organic matter by sulfate reducing bacteria in the anoxic environment (McCreadie et al., 2000).

3.2. Transport of surface derived OM in groundwater and arsenic release

Groundwater samples exhibit variations in the concentrations of DOC depending on the depth and locations of the sampling site (Fig. 3a), suggesting that the aquifers may have different

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