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Association between arsenic and different-sized dissolved organic matter in the groundwater of black-foot disease area, Taiwan

Ting-Chien Chen [a], Zeng-Yei Hseu [b, *], Jiin-Shuh Jean [c], Mon-Lin Chou [c]

[a] *Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 92101, Taiwan*
[b] *Department of Agricultural Chemistry, National Taiwan University, Taipei 10617, Taiwan*
[c] *Department of Earth Sciences, National Cheng Kung University, Tainan 70101, Taiwan*

HIGHLIGHTS

- The complexation of As and DOM was demonstrated by using the fluorescence technique.
- Arsenic was mainly partitioned into the small sized-dissolved organic matters.
- All fractional DOMs were considered as microbial sources.
- The formation of As–Fe-DOM complex was significant in the smaller sized-DOMs.

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ABSTRACT

The formation of an arsenic (As)-dissolved organic matter (DOM) complex is important in driving the release of arsenic in groundwater. This study collected groundwater samples from a 20 m deep well throughout 2014 and separated each into three subsamples by ultrafiltration: high molecular weight-DOM (HDOM, 0.45 μm–10 kDa), medium molecular weight-DOM (MDOM, 10–1 kDa), and low molecular weight-DOM (LDOM, <1 kDa) solutions. The fractional DOM was measured with a three-dimensional excitation-emission matrix (EEM) via fluorescence spectroscopy. A fluorescence quenching method was used to calculate the apparent stability constant (K_s) between arsenic and the fractional DOM. Based on the EEM records, three fluorescence indicators were further calculated to characterize the DOM sources, including the fluorescence index (FI), the biological index (BI), and the humification index (HI). The experimental results indicated that arsenic in the groundwater was mainly partitioned into the MDOM and LDOM fractions. All fractional DOMs contained humic acid-like substances and were considered as microbial sources. LDOM had the highest humification degree and aromaticity, followed by MDOM and HDOM. The As and DOM association could be formed by a Fe-bridge, which was demonstrated by the K_s values and fourier transform infrared (FTIR) spectra of the DOM. The formation of As–Fe-DOM complex was only significant in the MDOM and LDOM.

1. Introduction

The International Agency for Research on Cancer has listed arsenic as a group 1 carcinogen. The element arsenic exists in a multitude of different chemical species in biological tissues, soils, waters, and minerals. Many are inter-convertible under a range of conditions observed in terrestrial and marine environments. These species can be considered as inorganic (arsenate and arsenite) or organic (including monomethylarsonic acid [MMA], dimethylarsinic acid [DMA], tetramethylarsonium [TMA], asenobetaine (AB) and arsenosugars) (Chen et al., 1994). The inorganic arsenic species, arsenate As(V) and arsenite As(III), are generally more acutely toxic than the organic ones and are redox sensitive (Aposhian et al., 2004). The interchange of As(V) and As(III) can be driven chemically through changing the redox potential and pH, as well as by the presence of chemical oxidants and reductants (Cherry et al., 1979). In groundwaters, arsenic is generally predominant in inorganic species, which is approximate 95% of the total arsenic (Shraim et al., 2002). Additionally, the species variation is still controlled by inorganic and organic materials and

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* Corresponding author.
E-mail address: zyhseu@ntu.edu.tw (Z.-Y. Hseu).

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mineral surface (Masscheleyn et al., 1991).

Groundwaters from large areas of West Bengal, Bangladesh, and southeastern Asia are heavily enriched with geogenic arsenic. This has prompted a reassessment of the factors controlling the distribution of arsenic in the natural environment and the ways in which arsenic may be mobilized (Smedley and Kinniburgh, 2002). In Taiwan, drinking groundwater with a high concentration of geogenic arsenic has been confirmed to be associated with black-foot disease (BFD), which was common in southwestern Taiwan in the 1960s (Tseng et al., 1968). Nath et al. (2011) reported that the mean arsenic concentration was 208 $\mu g\ L^{-1}$ with the range from 13 to 575 $\mu g\ L^{-1}$ in this area. However, the maximum concentration of arsenic in drinking water that is recommended by the World Health Organization (WHO) is 10 $\mu g\ L^{-1}$ (WHO, 1993). The limit of As in drinking water in Taiwan is also 10 $\mu g\ L^{-1}$ (Environmental Protection Administration of Taiwan (1998)). The use of groundwater for drinking has been prohibited in the BFD areas for four decades, but groundwater continues to be used for irrigation and aquaculture. Therefore, the environmental risk still exists (Hsu et al., 2012).

Recent studies suggest that the overall controlling factor driving the release of arsenic in groundwater is the reactivity of the dissolved organic matter (DOM), because the formation of As-DOM complexes is important in regulating the transport, transformation, and bioavailability of arsenic in the environment (Huang et al., 2012; Selim Reza et al., 2012; Majumder et al., 2014a). In natural settings, the DOM parent material is primarily derived from terrestrial and aquatic macro- and micro-organisms. Guo et al. (2011) demonstrated the crucial role of colloidal dissolved organic carbon (DOC) on arsenic mobility in groundwater Hetao Basin in Inner Mongolia.

To consider the heterogeneity of DOM, a molecular weight separation method has been employed to evaluate arsenic distribution in individual fractions of DOM in groundwater (Majumder et al., 2014a). The toxicity of arsenic is dependent on not only arsenic speciation but also the As-DOM complex. The small molecular weight DOM and arsenic complexes could enhance the inhibition of plasmin activity as compared with either DOM or arsenic alone (Hseu et al., 2001). Both arsenic and small molecular weight DOM occurred in high concentrations in the Bangladesh groundwater, and thus their combined effects may enhance arsenic poisoning (Tareq et al., 2013).

DOM absorbs light in a broad range of wavelengths (λ), contrary to inorganic compounds, which are more common in natural waters. Therefore, spectroscopic techniques can provide information about the source and composition of the DOM present in these systems. Chromophoric DOM, the fraction that absorbs UV and visible light, controls how the optical properties of the natural waters can be examined (Birdwell and Engel, 2010). Fluorescence spectroscopy is a highly selective technique for analyzing organic substances because only those compounds containing moieties with conjugated bonds are observed. Fluorescence characteristics can reflect origins and various degrees of humification or diagenesis of DOM (Hudson et al., 2007). Additionally, fluorescence quenching is an available method for rapid determination of the binding parameters between DOM and metal ions (Wu et al., 2011). DOM and humic substance (HS) contained ionizable functional groups, such as carboxylic and phenolic groups, which are well-known metal chelators. Therefore, fluorescence quenching titration (FQT) is one of widely applied methods to quantify the metal binding characteristics of DOM or HS (Ohno et al., 2008; Yamashita and Fjaffe, 2008; Wu et al., 2011, 2012; Hur and Lee, 2011a,b). The stability constants of As with mangrove DNA complexes had been determined by FQT method (Majumder et al., 2014b). The FQT is a simple and non-destructive method (Ohno et al., 2008; Yamashita and Fjaffe, 2008; Wu et al., 2011, 2012; Hur and Lee, 2011a). The assumption of FQT technique is that only 1:1 metal/ligand complexes are formed. The stability constants of metal-DOM complexes have been typically determined based on a single pair of the excitation and the emission wavelengths for a DOM sample.

Significant differences observed in arsenic concentrations among various molecular weight DOM fractions have indicated that molecular weight is a fundamental DOM property and potentially affects the binding behavior between DOM fractions and arsenic (Tareq et al., 2013). However, only a few studies have documented the formation of As-DOM complexes in groundwater, although this complexation may critically affect the mobility and toxicity of arsenic species (Liu and Cai, 2010, 2013). By using the approaches of fluorescence spectroscopy to infer the relative contributions of different DOM sizes, this study explored the binding of arsenic with molecular weight fractions of DOM in the groundwater of the BFD area on the Chianan Plain, Taiwan. The aims of this study were to: (1) link fluorescence intensities with different wavelengths and their derived indicators to the relative contributions of fractional DOM, (2) estimate the source and stability of these DOMs in the groundwater, and (3) calculate the apparent stability constants of arsenic-DOM complexes with different molecular weights in the groundwater by using the fluorescence quenching.

2. Materials and methods

2.1. Study area description

In the BFD area on the coastal alluvial Chianan Plain in southwestern Taiwan, arsenic concentration commonly exceeded 10 $\mu g\ L^{-1}$ in the groundwater (Nath et al., 2011; Selim Reza et al., 2012). An investigation of shallow groundwater quality on the Chianan Plain revealed that high As concentrations were found in both aquifers and aquitards in this area (Liu et al., 2006), and thus the origin of As for this study is geological, i.e., As release is due to the reduction dissolution of Fe-oxyhydroxide minerals in the aquifer (Nath et al., 2011). The Chianan Plain covers an area of 2100 km^2 and is a tectonically active subsiding depression formed at the foreland of an actively uplifting mountain belt in the east (Liu et al., 1997), which comprises recent alluvium deposits. Two major rivers, the Pachang and Tsengwen, flow into the plain from the northeast to the west. During the Pleistocene and Holocene eras, fast erosion in the upstream caused a sharp change of river gradient, which resulted in the deposition of muddy sediments in the upper plain. The uppermost layer (approximate 210 m thick) is composed mainly of unconsolidated sediments (such as clay, silt and fine sand) derived from a thick (5000 m) sequence of slightly consolidated Pliocene marine mudstones which outcropped in the east (Ho, 1986).

2.2. Characterization of groundwater

This study selected a 20 m deep well (23°12′4.02″N, 120°10′50.7″E) to obtain groundwater samples in different seasons (March, May, September, and November) 2014. Before sampling, at least three well bore volumes of groundwater were pumped to ensure removal of standing water. In each season, three replicates were obtained for analysis. Temperature, dissolved oxygen, electrical conductivity (EC), pH, and redox potential (Eh) later corrected with respect to standard hydrogen electrode were measured in a flow-through cell every 5 min during well purging by using portable meters (Horiba U-50, Japan) before filtration.

Groundwater for DOC, As, and Fe analyses was collected in prewashed polyethylene bottles. Each sample was filtered through a 0.45 μm cellulose nitrate filter (Millipore Isopore Membrane