Abundance, size distribution and dissolved organic matter binding of arsenic in reducing aquifer

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ABSTRACT: The interactions between As and dissolved organic matter (DOM) have significant impacts on the environmental behavior of As. Among various interactions, the binary complexes of As bound to DOM and ternary complexes of As bound to DOM with iron (Fe) bridging, are critical to mobility, speciation, toxicity and bioavailability of As. Flow field flow fractionation (FIFFF) offline with high-resolution inductively coupled plasma mass spectroscopy (HR-ICPMS) were utilized to elucidate the As, Fe and DOM complexation in high arsenic, reducing groundwater from Yinchuan plain. The majority (>70%) of As was truly dissolved with molecular size <0.5 nm; while 13% of As and 37% of Fe were bound to colloidal DOM with molecular size between 16–64 nm. The results imply that As-Fe-DOM complex is distributed as moderately large colloids with molecular size between 16–64 nm. However, artefacts due to changes occurring during sample storage and transportation cannot be ruled out. Thus, field ultrafiltration under N₂ atmosphere will be employed in the future to validate FIFFF results.

1 INTRODUCTION

Exposure to elevated levels of As (>10 µg L⁻¹) in groundwater has threatened the health of over 100 million people around the world. High As exposure is primarily due to the presence of As sources in aquifers and mobilization of As from sediment to groundwater in microbially mediated reducing environments. Yet the understanding of factors influencing the concentration and mobility of As, especially the role of dissolved organic matter (DOM), is incomplete. DOM is ubiquitous in natural water system and may affect the mobility of As through a number of mechanisms including binding and surface sorption.

McArthur *et al.*, (2001) postulated that microbial degradation of buried deposits peat leads to the reduction of iron (hydro)oxides (FeOOH) and release of Fe coated As in Bangladesh aquifers. Further, Mladenov *et al.*, (2009) suggested that DOM in reducing groundwater can serve to shuttle electrons and enhance the reductive dissolution of iron (oxy)hydroxide minerals, as evidenced by acceleration of the mobilization of dissolved As in Bangladesh aquifers and Gangetic aquifer of late Holocene. Additionally, DOM and As can form complexation which is relevant to As speciation, mobility and toxicity (Wang & Mulligan, 2006). The associations involve bridging metals and deprotonated functional groups of organic matter (i.e. carboxyl, hydroxyl and sulphhydryl) (Sharma *et al.*, 2010).

Although many laboratory experiments have found evidence for As-(Fe)-DOM complexes in solution, the kinetic and thermodynamic parameters are difficult

to compare due to variable experimental settings in these studies. Further, isolation and determination of this complex in groundwater systems remain scarce. Field (ultra) filtration was conducted for groundwater in the Hetao Basin and the result showed that 20%–40% As is combined with small-size organic colloids and 75% iron is in colloids (Guo *et al.*, 2011). Among various interactions, the binary complexes of As bound to DOM and ternary complexes among As, DOM and Fe, is a mechanism that has emerged to be relevant to mobility of As in reducing aquifers. Here, we explore this possibility as well as isolation of DOM bound of As from Yinchuan Plain where reducing groundwater hosts high levels of As.

2 STUDY AREA AND METHODS

2.1 Study area

Our field site is in Yinchuan alluvial plain where As levels reach 210 µg L⁻¹ and correlate with Fe concentrations >1 mg L⁻¹ in groundwater in the shallow aquifer (depth 4–40 m). Sediment As and Fe concentrations are also high (>10 mg kg⁻¹ and 1% Fe) respectively.

2.2 Method

Three groundwater samples were selected for analysis of colloidal size distributions by coupling on-line flow field-flow fractionation (FIFFF) with detectors including UV-absorbance and fluorescence. The two UV-absorbance detectors measured the absorbance at

254 nm and 280 nm respectively, representing the aromatic and protein content. Fluorescence detectors were set for two indexes FLD1 and FLD2 with Ex/Em of 350 nm/450 nm and 275 nm/340 nm, respectively. Selected elements (As, Fe, S, Mn, and Mg) was determined by HR ICP-MS in off-line fraction samples with RSD < 5%.

3 RESULTS AND DISCUSSION

3.1 Abundance of selected elements in 0.7 μm , 0.4 μm and 0.2 μm filtrates

For all three groundwater samples, negative ORP values, non-detectable nitrate, and strong sulfide smell during sampling suggest that the groundwater has reached Fe and sulfate reducing stage. Concentrations of selected elements in three samples for the 0.7 μm , 0.4 μm and 0.2 μm filtrates are shown in Table 1. The unusually high Fe concentrations in 0.4 μm filtrates for YC-1 and MLW-7 may have been due to the filter leakage.

3.2 Abundance of elements from FIFFF

The asymmetrical FIFFF system (AF2000, Postnova) was equipped with a 0.3 kDa polyether sulfone ultra-filtration membrane and a 0.35 mm spacer with 1 mL of injection volume. A mixed solution with 10 mM NaCl (aq) and 5 mM H_3BO_3 (aq) and pH of 8 (adjusted with NaOH), which was optimized to have the highest recovery and reasonable separation, was used as the carrier solution. Four fractionations with increasing molecular sizes were collected during FIFFF; smallest colloids of 0.5–8 nm, small colloids of 8–16 nm, medium size colloids of 16–64 nm and large colloids of 64–700 nm (Table 1). Concentration in the dissolved fraction (<0.5 nm) was estimated by subtracting the sum of all the colloidal fractions from the total As in <700 nm fraction (Table 1).

Dissolved fractions accounted for the majority of As in YC-1, YC-5 and MLW-7 yet most Fe was found as colloids (Table 1). The medium sized colloidal fraction (16–64 nm) accounted for 12.3% (19.4 $\mu\text{g L}^{-1}$), 12.3% (29.3 $\mu\text{g L}^{-1}$) and 13.4% (34.7 $\mu\text{g L}^{-1}$) of total As concentrations in three samples.

Fractograms from the FIFFF analysis suggested that humic-like DOM (represented by Ex/Em of 350 nm/450 nm) in smaller molecular size, mostly <3 nm but protein-like DOM (characterized by Ex/Em of 275 nm/300 nm) in a wider size spectrum containing both nano-colloidal <4 nm and larger colloidal sizes in the 4–8 nm and >20 nm levels. The different sized DOM components may have different affinity for different forms of As during their interactions, which can be elucidated by simultaneous analysis of both DOM and As in different molecular size fractions. Concerned with sample preservation artefacts, field ultrafiltration under N_2 atmosphere will be employed during future sampling to evaluate reducing groundwater As–organic matter interaction.

Table 1. Concentrations of selected elements of three samples in the 0.7 μm , 0.4 μm and 0.2 μm filtrates (in blue), and 64–700 nm, 16–64 nm, 8–16 nm and 0.5–8 nm fractionations. The concentrations in the dissolved fraction (<0.5 nm) were estimated by subtracting the sum of all the colloidal fractions from the total concentrations in <700 nm fraction.

Sample ID	Size internal (nm)	As ($\mu\text{g L}^{-1}$)	Fe (mg L^{-1})	S (mg L^{-1})	Mn (mg L^{-1})	Mg (mg L^{-1})
YC-1	<700	157.5	1.52	242.9	0.09	97.5
	<400	163.3	2.54	240.2	0.31	97.2
	<200	168.2	1.69	236.6	0.23	95.7
	64–700	10.3	0.71	0.9	0.04	0.57
	16–64	19.4	0.53	2.0	0.03	0.46
	8–16	3.5	0.07	0.5	0.01	0.12
	0.5–8	1.7	0.10	1.1	0.00	0.14
	<0.5	122.6	0.11	238.4	0.01	96.2
	<700	236.5	0.28	42.6	0.18	30.5
	<400	231.5	0.28	45.2	0.18	31.2
YC-5	<200	233.2	0.32	52.5	0.14	35.9
	64–700	12.8	0.08	0.0	0.01	0.08
	16–64	29.1	0.11	0.0	0.01	0.18
	8–16	13.9	0.01	44.6	0.00	0.04
	0.5–8	3.0	0.03	102.0	0.00	0.03
	<0.5	177.7	0.05	–104.0	0.16	30.2
	<700	259.5	0.16	0.8	0.17	15.1
	<400	262.3	0.28	0.4	0.16	15.1
	<200	255.0	0.12	0.8	0.04	15.5
	64–700	13.9	0.14	0.8	0.01	0.07
MLW-7	16–64	34.7	0.80	2.4	0.02	0.36
	8–16	14.9	3.0	0.2	0.12	0.08
	0.5–8	5.5	0.07	0.2	0.01	0.02
	<0.5	190.5	–3.8	–2.9	0.01	14.55

ACKNOWLEDGEMENTS

The study is supported by National Natural Science Foundation (No. 41772265). Special thanks are extended to Tingwen Wu from China Geology Survey.

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