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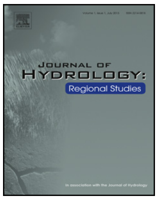

High arsenic (As) concentrations in the shallow groundwaters of southern Louisiana: Evidence of microbial controls on As mobilization from sediments

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ABSTRACT

Study region: The Mississippi Delta in southern Louisiana, United States.
Study focus: The probable role that microbial respiration plays in As release from the shallow aquifer sediments.
New hydrological insights for the region: Shallow groundwaters in southern Louisiana have been reported to contain elevated As concentrations, whereas mechanisms responsible for As release from sediments have rarely been studied in this region. Microbial respiration is generally considered the main mechanism controlling As release in reducing anoxic aquifers such as the shallow aquifers in southern Louisiana and those of the Bengal basin. This study investigates the role microbial respiration plays in As release from shallow aquifer sediments in southern Louisiana through sediment incubation experiments and porewater analysis. Arsenic concentrations were the lowest in the sterilized control experiments, slightly higher in the un-amended experiments, and the highest in the experiments amended with acetate, and especially those amended with both acetate and AQDS (9,10-anthraquinone-2,6-disulfonic acid). Although Fe and Mn generally decreased at the beginning of all the experiments, they did follow a similar trend to As after the decrease. Porewater analysis showed that As and Fe concentrations were generally positively correlated and were higher in the coarse-grained sediments than in the fine-grained sediments. Results of the investigation are consistent with microbial respiration playing a key role in As release from the shallow aquifers sediments in southern Louisiana.

1. Introduction

Naturally occurring arsenic (As) contamination in groundwaters have been reported in many regions of the world, especially the deltas and floodplains in South and Southeast Asia (Berg et al., 2001; Nickson et al., 2000; Polya et al., 2005; Shamsudduha et al., 2008; Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). As of 2009, more than 140 million people worldwide were drinking As-contaminated groundwaters (Ravenscroft et al., 2009). Due to similar geology and sedimentary depositional environments (e.g., organic-rich, fluvial/deltaic deposits) to the modern deltas and floodplains in South

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and Southeast Asia, shallow aquifers and the associated groundwaters in the Mississippi Delta in southern Louisiana are also possibly at risk of geogenic As contamination (Ravenscroft et al., 2009; Yang et al., 2014).

In southern Louisiana, groundwater was first reported in 2003 to contain elevated As concentrations in a study by the United States Geological Survey (USGS) concerning water quality of domestic wells (Tollett et al., 2003). Following the study by Tollett et al. (2003), the Louisiana Department of Environmental Quality (LDEQ) conducted a small scale survey focusing on As concentrations in groundwater from domestic wells in the Cow Island and Forked Island areas of Vermilion Parish in southern Louisiana and the results showed that 20% of the 25 sampled wells contained As concentrations above 10 μg/L, with the highest value reported to be 60 μg/L (Mallett, 2004). In 2011, As was found in domestic wells in Opelousas, Louisiana, with the highest concentration reported being 54 μg/L (Bastien, 2011). More recently, Yang et al. (2014) hypothesized, based on a logistic regression probability model calibrated with geochemical, geologic, and hydrologic data that large regions of southern Louisiana may be underlain by shallow groundwaters with As concentrations exceeding 10 μg/L, the US EPA's maximum contaminant level (MCL) for As in drinking water.

Several possible As sources exist in southern Louisiana, including As from anthropogenic activities. For example, before 1960 cattle dipping vats commonly contained aqueous solutions mixed with As-rich insecticides that were used to control ticks and other insects, and to protect cattle from a disease called "southern cattle fever" (Gresham, 2007). As such, the remnants of the now defunct cattle dip vats may represent a source of As contamination to the underlying aquifer systems. Furthermore, widespread application of arsenical pesticides to cotton fields to control the boll weevil (*Anthonomus grandis*) represents another important legacy source of As to soils and shallow groundwaters across large areas of the southern United States (Potera, 2007). Numerous industrial facilities and Superfund sites located in southern Louisiana could also represent additional possible sources of As contamination to local groundwaters (Gresham, 2007). Finally, historical cemeteries that contain As-embalmed human remains may also contribute As to local groundwaters (Duex and Gresham, 2008). For example, between 1850 and 1910, As was used as a common ingredient in embalming fluids in the United States and it is estimated that as much as 5.4 kg of As was used per body (Borstel and Niquette, 2000). As wood caskets deteriorate with age, the embalmed remains may be directly exposed to the surrounding sediments and cause the downward movement of As into groundwaters (Gresham, 2007; Duex and Gresham, 2008).

Despite the numerous possible anthropogenic sources for As that exist in southern Louisiana, many of the shallow groundwaters that exhibit elevated As concentrations are confined beneath thick layers of clays (up to 10 m thick; Milner and Fisher, 2009) that are expected to act as effective barriers preventing the transport of anthropogenic-sourced As from the ground surface to the underlying groundwater flow systems (e.g., Duex and Gresham, 2008; Milner and Fisher, 2009). For example, in the vicinity of Cow Island and Forked Island, Louisiana, the Chicot aquifer, which can contain high groundwater As concentrations, is overlain by approximately 8 m of clay, which acts as an aquitard preventing contaminants like As from migrating from the surface to underlying groundwaters (Lovelace, 1999; Sargent, 2004; Duex and Gresham, 2008; Prakken and White, 2014). In addition, because the Mississippi Delta shares broadly similar geology, hydrology, and sedimentary depositional environments with the deltas and floodplains of South and Southeast Asia (Yang et al., 2014), we propose that high As concentrations in the southern Louisiana groundwaters reflect the same or similar, naturally occurring biogeochemical processes thought to be responsible for the elevated As concentrations in groundwaters from South and Southeast Asia, namely microbially-driven reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides (e.g., Bhattacharya et al., 1997; Harvey et al., 2002, 2005; Mailloux et al., 2009; McArthur et al., 2001, 2004; Nickson et al., 2000; Islam et al., 2004; Polizzotto et al., 2008; Zheng et al., 2004; Yang et al., 2014). Nonetheless, although multiple examples of As contamination of shallow groundwaters have been reported in southern Louisiana, little attention has focused on the processes that are responsible for the elevated groundwater As concentrations, which likely include anthropogenic and natural causes. For people living in rural areas of southern Louisiana who rely on private wells for drinking waters, the locally elevated groundwater As concentrations may be an unrecognized health risk.

Here, sediment incubation experiments and porewater analysis have been used to investigate the possible role that microbial respiration plays in mobilizing As from sediments to the local groundwaters in southern Louisiana. We hypothesize that reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides by the microbial consortia within the aquifer facilitates As release from sediments to groundwaters in the reducing anoxic shallow aquifers of the Mississippi Delta (e.g., Oremland and Stolz, 2005).

2. Study area

The Mississippi Delta began to form about 7000 years ago when sea-level rise decelerated to less than 1 mm/year, and currently it consists of six recognizable sub-deltas (Blum and Roberts, 2009). The study area is located in a crevasse splay at Napoleonville, Louisiana, along the west bank of Bayou Lafourche, the trunk distributary of the Lafourche sub-delta in the Mississippi Delta (Fig. 1). Bayou Lafourche was a precursor of the modern Mississippi River. Radiocarbon and optically-stimulated luminescence measurements indicated that the Lafourche sub-delta was initiated around 1500 years ago (Törnqvist et al., 1996, 2008), and mostly abandoned by about 600 years ago (Shen et al., 2015). The distributary channel was converted into a stagnant bayou (i.e., Bayou Lafourche) after a dam was built in 1904 at Donaldsonville, where the bayou joined the present-day Mississippi River. Late Holocene stratigraphy of the Lafourche sub-delta has been extensively studied (Fisk, 1952; Frazier, 1967; Törnqvist et al., 1996, 2008), and the results show that the near surface sediments in the study area consist of a widespread layer of woody peat overlain by up to 12 m of over-bank deposits from Bayou Lafourche. Distribution

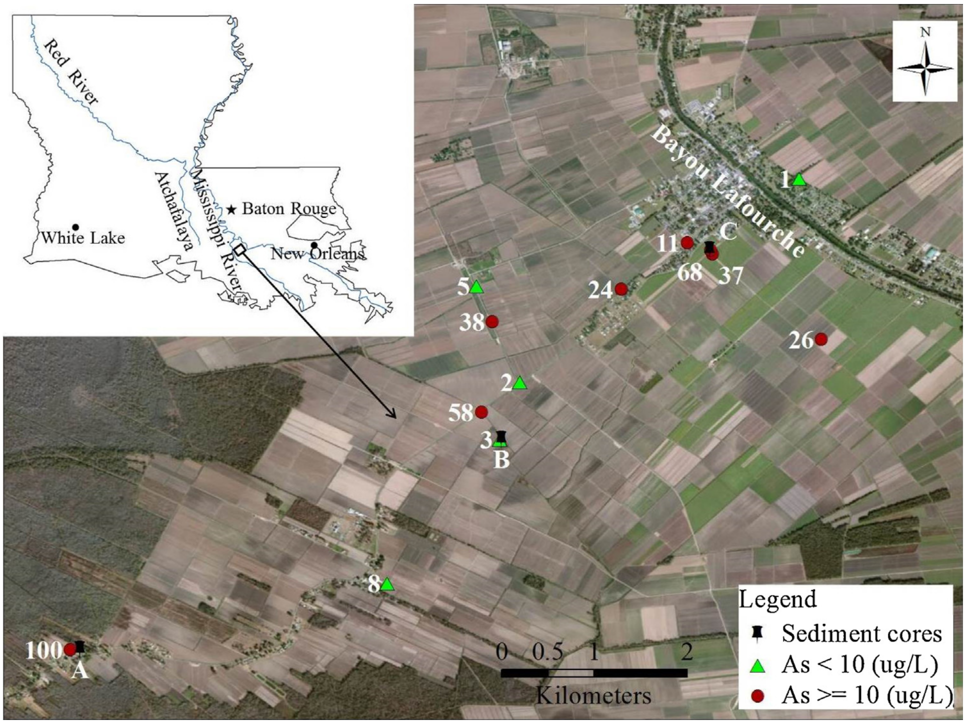

Fig. 1. Google Earth image of the study site showing As concentrations in shallow groundwater (Yang et al., 2014) and the locations of where sediment cores were extracted: A (29°53′40.38N″, 91°5′13.68W″), B (29°54′53.90″N, 91°2′46.70″W), and C (29°56′N, 91°1′34.02″W) in southern Louisiana. Insert map shows the State of Louisiana and the location of the study site relative to the Red River, the Atchafalaya River, and the Mississippi River, as well as the cities of White Lake, New Orleans, and Baton Rouge, Louisiana.

of sandy facies within the overbank deposits generally correlates to the abandoned crevasse channels. Due to relatively high sedimentary organic carbon (SOC) contents and the reducing conditions of the shallow aquifers, we expected that groundwaters in this region would contain elevated As concentrations. Indeed, our previous investigation (Yang et al., 2014) indicated that of the 13 groundwater samples collected from the Lafourche sub-delta, 60% contained As concentrations greater than 10 μg/L (i.e., the US EPA drinking water standard), and the highest value was 100 μg/L (Fig. 1).

3. Materials and methods

3.1. Porewater and sediment collection

Sediment cores were collected with a Giddings soil probe at locations A and B in June, 2013, and using a Geoprobe at location C in September, 2013. The three cores were collected along a transect perpendicular to Bayou Lafourche (Fig. 1). When the probes reached the sampling depths, a PVC core liner (5 cm diameter, 50 cm or 150 cm long) was inserted to collect the sediment core. Right after cores were extruded from the probe, they were immediately capped with PVC caps at both ends and sealed with tape to prevent exposure to O_2.

Rhizon samplers (Rhizonsphere Research Products; http://www.rhizosphere.com/rhizons) were employed to extract porewaters from sediment cores. Rhizon samplers consist of: (1) a 5 cm hydrophilic porous polymer tube with an outer diameter of 4.5 mm and a pore size of 0.15 μm, supported by glass fiber; and (2) a 12 cm PVC tubing with a female luer lock, connected to a 10 mL syringe to create a vacuum (http://www.rhizosphere.com/rhizons). A small hole was created at the surface of the sealed sediment core, into which the 5 cm porous tube of a Rhizon sampler was carefully inserted, and a 10 mL syringe was used to create a vacuum causing porewaters to flow from sediments into syringes. Consequently, porewaters extracted by Rhizon samplers were automatically filtered through a pore size of 0.15 μm. Due to limited quantities of porewaters in sediments, especially the clay-rich sediments, only a total volume of ~15 mL was collected at each depth. We note that colloids with diameters smaller than 0.15 μm could pass through the Rhizon samplers, and potentially influence the analytical results. Nonetheless, owing to the small volumes of porewater that we were able to extract from the sediment cores, additional filtration through smaller nominal pore size filters (e.g., ultrafiltration) was not undertaken in the current study. Future studies may include ultrafiltration studies of shallow groundwaters from the region.

Each porewater sample was subsequently split into three equal aliquots for measuring pH, dissolved organic carbon (DOC), and trace element (i.e., As and Fe) concentrations, respectively. Porewater pH was measured with a micro pH electrode (Fisher Scientific Orion 98633BN). Samples for DOC analysis were acidified to pH <2 with ultrapure HCl (Seastar) and measured

Table 1
Major solute concentration in the 'artificial groundwater' solution used in the incubation experiments.

Major solutes	Concentration (mmol/L)	Reagent	Amount of reagent (mg/L)
PO_4^{3-}	0.002	KH_2PO_4	0.30
NO_3^-	0.001	KNO_3	0.05
Cl^-	2.100	$MgCl_2 \cdot 6H_2O$	53.81
SO_4^{2-}	0.049	$MgSO_4$	5.94
K^+	0.032	K_2CO_3	2.04
Mg^{2+}	0.724	$MgCO_3$	34.58
Ca^{2+}	0.785	$CaCl_2$	87.12
Na^+	3.567	$NaHCO_3$	299.59
HCO_3^-	4.412		

in triplicate using a TOC-5000 analyzer (Shimadzu) with a confidence interval of 0.02 mg/L Carbon (C) at Kansas State University. Porewaters for As and Fe analysis were acidified to pH < 2 with ultrapure HNO_3 (Seastar) and measured by high-resolution (magnetic sector) inductively coupled plasma mass spectrometer (HR-ICP-MS; Thermo Fisher Element 2) following procedures described previously (Datta et al., 2011; Haque et al., 2008; Mohajerin et al., 2014; Sankar et al., 2014).

After porewaters were collected, cores were opened and sediments were transferred into AnaeroPouchbags (Fisher Scientific, Mitsubishi^{TM}), within which a sachet of O_2 absorber (Fisher Scientific, Mitsubishi^{TM}) was included per bag to maintain the anaerobic conditions. Sediments from core A and C were analyzed for SOC using a Vario MicroCube Elemental Analyzer and loss on ignition (LOI), respectively. Sediments from the silt- and sand-rich layers in cores A and C, collected for incubation experiments, were then transferred into a glove box (Plas-Labs "Basic Glove Box" model # 818-GB) where AnaeroPouch bags were opened and sediments subsequently dried under anaerobic conditions in a N_2 atmosphere (Pearcy et al., 2011). Small roots and woody particles were manually removed before sediments were employed for the incubation experiments.

3.2. Sediment incubation

3.2.1. Groundwater recipe

Owing to the small volumes of porewaters extracted from the sediment cores, we were not able to analyze the major ion composition of the shallow groundwaters from the Napoleonville study site. Consequently, we used the average composition of shallow groundwaters from another study site in southern Louisiana (i.e., Cow Island) where major solute concentrations have been quantified to make the "artificial groundwater" solution used for the incubation studies described herein. Specifically, the average concentrations of the major solutes measured in 9 domestic wells were used as the basis to make the "artificial groundwater" solution, and if necessary, bicarbonate (HCO_3^-) was used for charge balance of the averaged cations and anions and to buffer the solution pH at ~8.00. Reagent salts were precisely weighed and transferred to a volumetric flask to which 1 L of de-ionized water (Milli-Q, 18.2 MΩ cm) was added to make a solution that had approximately the same composition as the average shallow groundwaters from the Cow Island site (Table 1). When necessary, the solution was adjusted to pH ~8.00 (i.e., the average pH of the Cow Island groundwaters) using 0.1 N ultrapure HCl (Seastar) or 0.1 N NaOH, and then sterilized in an autoclave for a 20 min cycle at 121 °C and 1.1 atm. After the solution cooled to room temperature (23 ± 2 °C), it was transferred to the glove box, bubbled with N_2 gas using a 25.4 cm gas dispersion tube to strip the dissolved O_2, and then capped and allowed to reach equilibrium under the O_2-free, N_2 atmosphere in the glove box (Pearcy et al., 2011).

3.2.2. Incubation experiments

Prior to incubation experiments, all glass serum bottles (100 mL) and polyethylene centrifuge tubes (10 mL and 50 mL) were acid washed following trace element clean procedures and then sterilized in an autoclave for a 20 min cycle at 121 °C and 1.1 atm (Pearcy et al., 2011). Anaerobic sediment incubations were conducted in the glove box under four conditions: (1) sterilized control (sterilized sediments + 50 mmol/kg 9,10-anthraquinone-2,6-disulfonic acid sodium salt [AQDS]); (2) anaerobic with no amendments; (3) anaerobic + 50 mmol/kg acetate (i.e., sodium acetate); and (4) anaerobic + 50 mmol/kg acetate + 50 mmol/kg AQDS. Acetate represents a labile form of organic carbon that is easily accessible as an electron donor for microbial respiration (e.g., reduction of metal oxides/oxyhydroxides; Crill and Martens, 1986; Islam et al., 2004; Lovley and Chapelle, 1995; Pearcy et al., 2011; Rowland et al., 2007). AQDS is a compound analogous to humic acids, which acts as an electron shuttle to overcome the need for microbes to be in direct contact with poorly soluble electron acceptors such as Fe(III) oxides/oxyhydroxides (Rowland et al., 2007). For sterilized controls, sediments were sterilized in an autoclave for 20 min at 121 °C and 1.1 atm before addition of the sterilized deoxygenated "artificial groundwater" solution. For each experiment, 10 g of the well-mixed sediments from the Napoleonville site and 30 mL of the sterilized "artificial groundwater" solution were added to each bottle. The bottles were then plugged with butyl rubber stoppers and sealed with an aluminum (Al) clamp under the inert N_2 atmosphere within the glove box. Each experiment was prepared in triplicate for six specific reaction periods (i.e., 2, 7, 14, 21, 28, and 35 days).

Table 2
Porewater pH, As, Fe, and DOC concentrations, sediment texture, and sedimentary organic carbon (SOC) at various depths of the sediment cores collected in Napoleonville, southern Louisiana, United States (see Figs. 1 and 2 for sediment core locations and stratigraphy).

Core	Depth (cm)	pH	As (μg/L)	Fe (mg/L)	DOC (mg/L)	Sediment texture[a]	SOC (%)
A	100	7.26	158	6.0	13.6	Silty loam	0.41
	130	8.05	9	0.03	21.9	Silty clay loam	0.56
	160	7.94	74	0.4	12.2	Silty clay loam + silty loam	0.61
B	150	7.35	0.3	0.01	10.6	Silty clay loam	ND
	200	7.28	1	0.01	6.0	Silty loam	ND
	310	7.45	4	0.6	18.2	Silty clay + clay	ND
	460	7.47	5	0.6	21.0	Humic clay	ND
	700	7.73	4	0.9	23.8	Sandy loam	ND
	720	7.26	8	1.5	31.6	Sandy loam	ND
C	150	ND	ND	ND	ND	Silty clay loam	3.99
	270	ND	ND	ND	ND	Silty clay + clay	4.95
	330	ND	ND	ND	ND	Silty loam	3.42
	390	ND	ND	ND	ND	Silty clay loam	4.48
	520	8.12	58	11.1	ND	Sandy loam	2.62
	610	7.15	32	21.5	ND	Sandy loam	2.01
	680	7.00	52	20.2	ND	Sand	1.94
	720	7.10	38	20.4	ND	Sand	2.73
	780	ND	ND	ND	ND	Silty clay loam	4.75

ND—data not determined.

[a] Sediment texture is classified based on USDA soil classification method.

3.2.3. Sample collection and analysis

After each specific reaction period, the solution-sediment slurries were transferred into a 50 mL centrifuge tube and centrifuged for 40 min at 3000 rcf (i.e., relative centrifugal force) to separate sediments from solutions. The supernatant was then filtered through a 0.45 μm syringe filter (EMD Sterivex-HV) into a 15 mL centrifuge tube and immediately acidified with ultrapure HNO_3 (Seastar) to $pH < 2$. After storage in a refrigerator for about two weeks, light gray flocculants formed in most of the filtered and acidified solutions. To identify the flocculants, the filtered and acidified solutions were re-centrifuged for another 10 min to separate the flocculants from solutions. The supernatant was then transferred into a 15 mL centrifuge tube for analysis of As, Fe, and Mn concentrations using HR-ICP-MS following previously described procedures (Datta et al., 2011; Haque et al., 2008; Pearcy et al., 2011). The composition of the flocculants was investigated using a Hitachi S-3400 scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) and an Oxford Inca elemental analyzer. For the SEM-EDS analysis, two drops of the flocculants were placed on an Al stub and heated to evaporate excess water. The dried samples was observed and analyzed at 20 kV. For organic carbon analysis, the flocculants were carefully transferred dropwise into a small silver foil and dried at 60 °C in an oven. The above procedures were repeated until about 10 mg of the dried flocculants were collected, and then the dried samples were analyzed using the elemental analyzer.

4. Results

4.1. Sediment porewaters

Porewater pH values ranged between 7.00 and 8.12 (Table 2), indicating that groundwaters in the Napoleonville region were predominantly neutral to slightly alkaline. Arsenic, Fe, and DOC concentrations in porewaters varied, from 0.3 μg/L to 158 μg/L, from 0.01 mg/L to 21.5 mg/L, and from 6.0 mg/L to 31.6 mg/L, respectively (Table 2).

In core A, porewater As and Fe concentrations were positively associated ($r = 0.92$; Fig. 2a). Both As and Fe concentrations decreased from 158 μg/L to 6.0 mg/L, respectively, at a depth of 100 cm (silty loam) to 9 μg/L and 0.03 mg/L, respectively, at a depth of 130 cm (silty clay loam), and then increased to 74 μg/L and 0.4 mg/L, respectively, at a depth of 160 cm (mixture of silty clay loam and silty loam; Table 2, Fig. 3a). In contrast, As and DOC concentrations in porewaters showed an inverse relationship ($r = -0.74$; Fig. 2b) and exhibited a mirror image pattern with depth (Fig. 3a), such that DOC increased from 13.6 mg/L at 100 cm to 21.9 mg/L at 130 cm, and then decreased to 12.2 mg/L at 160 cm (Table 2, Fig. 3a). Nonetheless, it is important to stress that because of the limited number of porewater samples we were able to extract from core A ($n = 3$), neither the relationships between As and Fe nor As and DOC were statistically significant. In addition to dissolved components, we also measured the SOC content of sediments from core A, which increased from 0.41% at 100 cm to 0.56% at 130 cm and finally to 0.6% at 160 cm. The SOC content was higher in the fine-grained sediments (e.g., silty clay loam) than in the overlying coarse-grained sediments (e.g., silty loam).

For core B, porewater As concentrations were positively correlated with Fe ($r = 0.97$) as well as with DOC ($r = 0.96$Fig. 2c and d), both of which were significant at the 99% confidence level, and consequently, all three display similar trends with depth (Fig. 3b). Specifically, As, Fe, and DOC concentrations increased from 0.3 μg/L, 0.01 mg/L, and 10.6 mg/L, respectively,

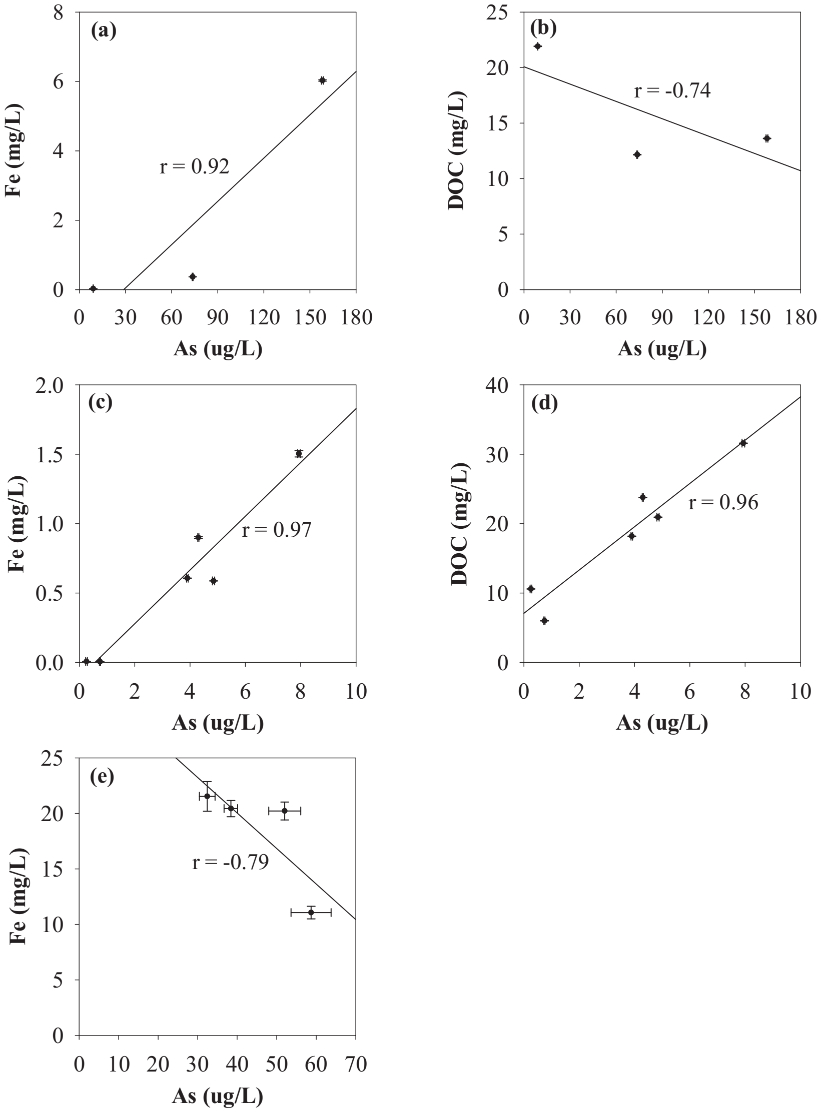

Fig. 2. Scatter plots showing relationships between porewater As, Fe, and DOC concentrations extracted from sediment cores A (a and b), B (c and d), and C (e). Lines represent linear regression of the data in each plot. Analytical uncertainties for many of the analyses are of the same order as the symbols.

at a depth of 150 cm (silty clay loam) to 8 μg/L, 1.5 mg/L, and 31.6 mg/L, respectively, at a depth of 720 cm (sandy loam) (Table 2, Fig. 3b).

In core C, porewater As and Fe concentrations were inversely related ($r = 0.79$, not statistically significant; Fig. 2e), and exhibited different trends as a function of depth (Fig. 3c). Specifically, between depths 520 cm and 720 cm (i.e., interbedded silty loam and fine sand), As concentrations were relatively constant, varying between 32 μg/L and 59 μg/L, whereas Fe concentrations doubled between depths 520 cm and 610 cm, and then remained constant with depth to 720 cm (Table 2, Fig. 3c). Although we were unable to quantitatively measure DOC concentrations in core C, the SOC contents were estimated by LOI. As observed in core A, the SOC contents, as reflected by the LOI measurements, in core C exhibited relatively higher values in the fine-grained sediments (i.e., silty clay loam and silty clay) than in the coarse-grained sediments (i.e., silty loam, sandy loam, and sand) (Figs. 2 and 3).

4.2. Sediment incubation

As mentioned above, upon acidification and cold storage (4 °C for ~2 weeks) prior to analysis, light gray flocculants formed in most of the filtered and acidified experimental solutions. Of the four experiments, the smallest amount of flocculants was produced in solutions from the sterilized control experiments, whereas the largest amount formed in the experiments amended with acetate and acetate + AQDS. Analysis of the flocculants by SEM-EDS and the Elemental Analyzer indicated

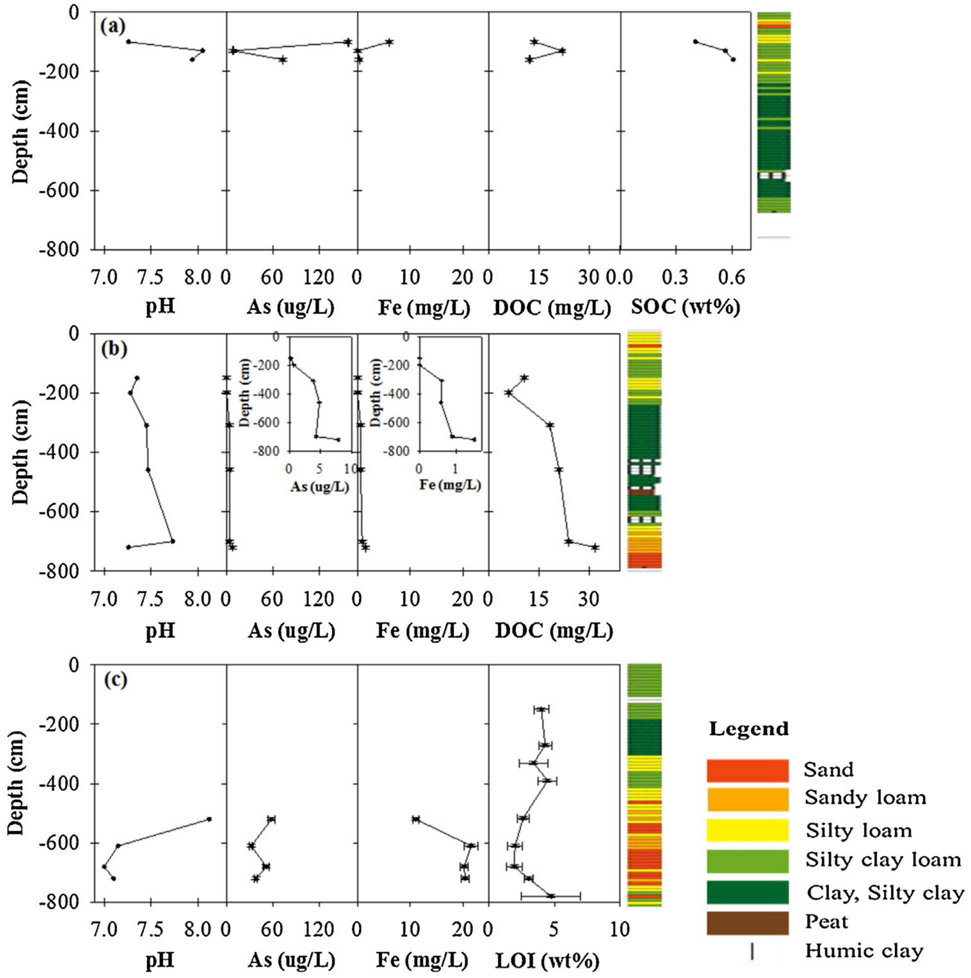

Fig. 3. Results of porewater analysis for pH, concentrations of As (μg/L), Fe (mg/L), and DOC (mg/L) extracted from different depths of cores A (a), B (b), and C (c). Also shown are the cores stratigraphy, SOC and LOI analyses. Analytical uncertainties for many of the analyses are of the same order as the symbols.

that the flocculants were composed of O, Fe, S, Si, and organic carbon (Fig. 4a and b). Aluminum and N are excluded from the analytical results because the sample stub used in SEM-EDS is made of Al and owing to the fact that the solutions were initially acidified with ultrapure HNO_3.

Arsenic, Fe, and Mn concentrations in the experimental solutions are summarized in Tables 3–5, and presented as a function of time in Fig. 5. Concentrations of As, Fe, and Mn were the lowest in the sterilized control experiments, where As, Fe, and Mn ranged from 30 ± 5.4 μg/L to 50 ± 4.3 μg/L, 0.1 ± 0.01 mg/L to 3.0 ± 1.8 mg/L, and 16 ± 5.4 μg/L to 113 ± 22 μg/L, respectively. More specifically, As concentrations remained relatively constant around 49 ± 1.1 μg/L during the initial 21 days of the experiments, and then slightly decreased to 35 ± 3.8 μg/L towards the end of the experiments (Table 3, Fig. 5a). In contrast, Fe and Mn concentrations remained relatively constant around 0.5 ± 0.3 mg/L and 21 ± 6.4 μg/L, respectively, during the initial 14 days, and then increased to 3.0 ± 1.8 mg/L and 113 ± 22 μg/L, respectively, at the end of the experiments (Tables 4 and 5, Fig. 5b and c). At the end of each experiment, the pH of the solutions typically increased to 8.60 in the

Table 3
Summary of As released from sediments during the incubation experiments. Arsenic concentration (μg/L) data represent the mean ± standard deviation of triplicate measurements.

Time (days)	Control	Anaerobic	Anaerobic + acetate	Anaerobic + acetate + AQDS
2	47 ± 8.5	80 ± 2.6	53 ± 4.1	31 ± 1.2
7	50 ± 4.3	54 ± 12	70 ± 22	23 ± 0.7
14	49 ± 5.8	37 ± 2.0	129 ± 24	90 ± 1.9
21	49 ± 2.5	82 ± 5.8	148 ± 14	380 ± 11
28	30 ± 5.4	64 ± 9.7	191 ± 14	360 ± 27
35	35 ± 3.8	72 ± 6.7	197 ± 6.9	337 ± 21

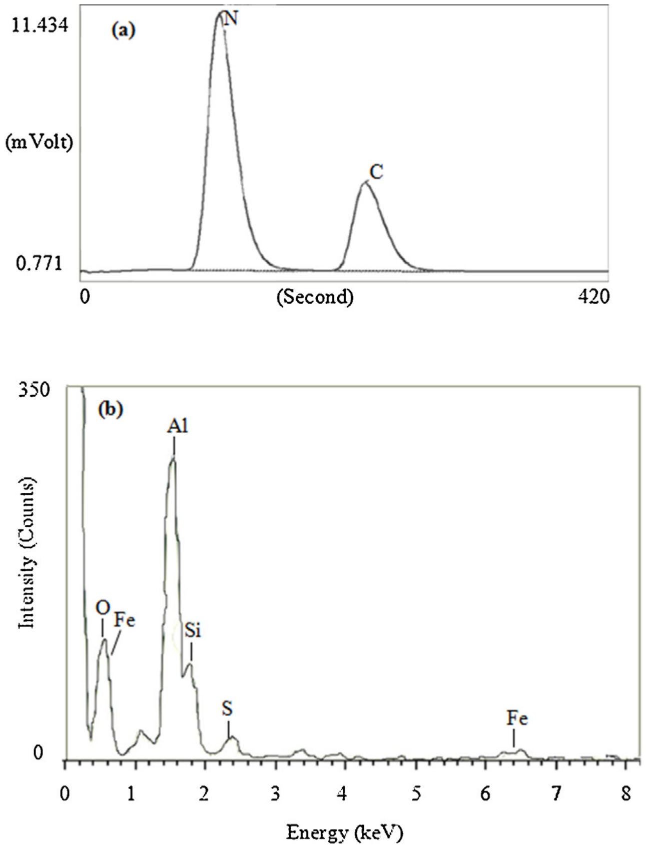

Fig. 4. Results of composition analysis of flocculants by (a) the elemental analyzer (b) SEM-EDS. These qualitative data suggests that the flocculants are chiefly composed of Fe-rich organic matter.

Table 4
Summary of Fe released from sediments during the incubation experiments. Iron concentration (mg/L) data represent the mean ± standard deviation of triplicate measurements.

Time (days)	Control	Anaerobic	Anaerobic + acetate	Anaerobic + acetate + AQDS
2	0.7 ± 0.4	33 ± 0.1	24 ± 1.3	1.6 ± 0.4
7	0.7 ± 0.7	22 ± 9.8	0.6 ± 0.1	0.4 ± 0.2
14	0.1 ± 0.01	8.0 ± 1.8	1.2 ± 0.1	1.1 ± 0.2
21	1.9 ± 0.9	39 ± 6.6	1.9 ± 0.2	7.4 ± 2.1
28	2.9 ± 2.2	40 ± 6.0	1.9 ± 0.3	10.5 ± 2.2
35	3.0 ± 1.8	60 ± 8.8	1.9 ± 0.1	10.9 ± 2.0

Table 5
Summary of Mn released from sediments during the incubation experiments. Manganese concentration (μg/L) data represent the mean ± standard deviation of triplicate measurements.

Time (days)	Control	Anaerobic	Anaerobic + acetate	Anaerobic + acetate + AQDS
2	17 ± 3.8	220 ± 17	164 ± 12	14 ± 1.8
7	30 ± 17	192 ± 80	46 ± 13	30 ± 3.2
14	16 ± 5.4	90 ± 18	69 ± 8.0	103 ± 45
21	61 ± 14	442 ± 45	89 ± 6.9	311 ± 59
28	101 ± 27	589 ± 64	131 ± 12	446 ± 59
35	113 ± 22	857 ± 154	135 ± 3.7	431 ± 63

sterilized control experiments, 8.72 in the un-amended experiments, 8.44 in the acetate amended experiments, and 8.69 in the experiments amended with both acetate and AQDS. The relatively high HCO_3^- concentration of the artificial groundwater solution used in the batch incubations (i.e., 4.4 mmol/L) acted as a relatively effective buffer against dramatic changes in pH values of the experimental solution. The slightly higher pH values of the solutions at the end of each experiment are expected to lead to slightly higher As concentrations in solutions, whereas the opposite effect is expected for Fe and Mn (e.g., Drever, 1988; Johannesson and Tang, 2009).

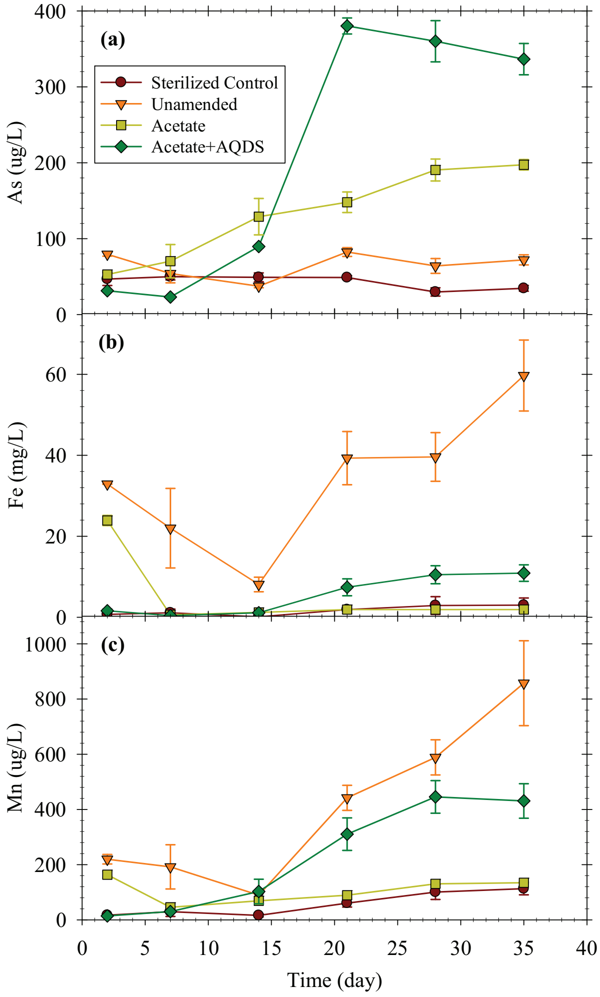

Fig. 5. Concentrations of (a) As (µg/L), (b) Fe (mg/L), and (c) Mn (µg/L) in the experimental solutions from the sterilized control experiments, the un-amended experiments, the acetate amended experiments, and the experiments amended with both acetate and AQDS. Symbols and error bars represent the mean and standard deviations of the triplicate analyses of each experiment.

For the un-amended (i.e., anaerobic, no added acetate or AQDS) experiments, As, Fe, and Mn concentrations in solutions were generally higher than for the sterilized control experiments (Tables 3–5, Fig. 5a–c). For example, As, Fe, and Mn concentrations ranged from 37 ± 2.0 µg/L to 82 ± 5.8 µg/L, 8.0 ± 1.8 mg/L to 60 ± 8.8 mg/L, and 90 ± 18 µg/L to 857 ± 154 µg/L, respectively. The concentrations of all three trace elements initially decreased in solutions over the first 14 days, and generally increased thereafter (Fig. 5a–c). Compared to the sterilized control experiments, the relative increases in Fe and Mn concentrations were much more pronounced than for As, which remained relatively constant around 73 ± 7.4 µg/L (i.e., the average ± σ (standard deviation) for day 21, 28, and 35) after doubling in concentrations between days 14 and 21 (Fig. 5a–c). The un-amended experiments are the closest representation of the field conditions, and As and Fe concentrations in the un-amended experimental solutions are comparable to As (i.e., mean ± σ = 34 ± 45 µg/L) and Fe (i.e., mean ± σ = 6.4 ± 8.7 mg/L) in porewaters collected from the coarse-grained sediment layers within cores A and C.

In the acetate amended experiments, As concentrations increased almost monotonically over the course of the experiments and attained higher concentrations in solutions at the end of the experiments than either the sterilized control experiments or the un-amended experiments (Fig. 5a). For example, As concentrations increased from 53 ± 4.1 µg/L at day 2 to 197 ± 6.9 µg/L at day 35, or at a rate of ~4.4 µg/L/d (i.e., µg/L per day). In contrast, Fe and Mn concentrations in solutions decreased over the first 7 days, and then exhibited relatively constant concentrations for the remainder of the experiments (Fig. 5b and c). Compared to the un-amended experiments, As concentration in solutions were roughly twice as high in the acetate amended experiments, whereas Fe and Mn experienced substantial decreases, especially after the initial decreases in the acetate amended solutions.

The experiments amended with both acetate and AQDS exhibited the greatest As release as indicated by the highest As concentrations attained (i.e., 380 ± 11 µg/L) in these solutions (Table 3, Fig. 5a). Arsenic, Fe, and Mn concentrations in solutions exhibited similar trends as a function of time, which followed broadly "S-shaped" curves over the 35 day course of the experiments (Fig. 5a–c). More specifically, the release rates of As, Fe, and Mn between day 7 and day 21 were 25.5 μg/L/d, 500 μg/L/d, and 20.1 μg/L/d, respectively, whereas between day 21 and day 35, the release either stopped (e.g., As, with a release rate of −3.1 μg/L/d) or decreased (e.g., Fe, with a release rate of 250 μg/L/d, and Mn exhibited a release rate of 8.6 μg/L/d). Decreases in release rates led to a plateau in As, Fe, and Mn concentrations by the end of the experiments. For example, the mean ± σ of As, Fe, and Mn from day 28 to 35 were 348 ± 24 μg/L, 10.7 ± 2.1 mg/L, and 438 ± 61 μg/L, respectively (Tables 3–5).

5. Discussion

5.1. Arsenic in the Napoleonville groundwaters

Reductive dissolution of Fe(III) oxides/oxyhydroxides is generally considered the primary mechanism controlling As release from sediments to groundwaters in the reducing anoxic aquifers of South and Southeast Asia (Harvey et al., 2005; Mailloux et al., 2009; McArthur et al., 2004; Nickson et al., 2000; Polizzotto et al., 2008; Zheng et al., 2004). The positive relationship between As and Fe concentrations in porewaters extracted from cores A ($r = 0.92$) and especially core B ($r = 0.97$, $p < 0.01$) at the Napoleonville site supports the probability that reductive dissolution of Fe(III) oxides/oxyhydroxides also plays an important role in As release from sediments to shallow groundwaters at the Napoleonville site in southern Louisiana. In contrast, DOC and particularly SOC were inversely related to As and Fe in porewaters from core A (Fig. 3a). Closer examination of the stratigraphy of core A revealed that porewater As and Fe concentrations were the lowest within the fine-grained sediment layer (i.e., silty-clay), and substantially higher in the coarse-grained sediment layer (i.e., silt and silty loam) above and directly below the clay layer (Fig. 3a). Furthermore, DOC concentrations in porewaters were the highest in the clay-rich layer and substantially lower in the silt-rich layer above and below the clay layer. Sedimentary organic carbon (SOC) as estimated by LOI is also generally higher in the fine-grained sediments where As was relatively low compared to the coarse-grained sediments (Fig. 3a).

Taken together the field data from the Napoleonville site suggest that the fine-grained, clay-rich sediments act as a source of labile DOC that fuels microbial reduction of Fe(III) oxide/oxyhydroxides by respiratory microbes, and subsequent release of sorbed and/or co-precipitated As to the shallow groundwaters. More specifically, we submit that fermentative bacteria within the fine-grained, clay-rich layers degrade SOC to produce small, labile forms of DOC such as acetate, lactate, and propionate. These labile, short-chain fatty acids subsequently diffuse from the clay-rich sediment layers into the overlying and underlying coarse-grained silt- and sand-rich layers, where they act as electron donors for Fe-reducing bacteria (e.g., Chapelle and Bradley, 1996; McMahon and Chapelle, 1991). The Fe-reducing bacteria solubilize Fe by reductive dissolution of Fe(III) oxide/oxyhydroxides, which also liberates adsorbed and/or co-precipitated As to the local shallow groundwaters.

In the case of core B, the majority of porewater samples were extracted from the clay-rich sediments, and only the deepest porewater samples (depth >700 cm) were from the coarse-grained sediments (i.e., silt loam, sandy loam, and sand). Consequently, As and Fe concentrations in porewaters were generally low (As <5 μg/L and Fe <1 mg/L) for all but the deepest sample (Table 2, Fig. 3b), compared to what was observed in porewaters from core A. In contrast, DOC concentrations in porewaters were generally high in core B, but similar in magnitude to DOC concentrations (≥20 mg/L) also measured in porewaters from the clay-rich sediments in core A. The combination of the stratigraphic data and porewater chemistry from core B are also generally consistent with the above proposed model, whereby microbial respiration that leads to As mobilization is chiefly limited to the coarse-grained sediments, where DOC, derived from fermentation of SOC in the clay-rich sediments and subsequent diffusion of labile DOC, drives microbial respiration in the coarse-grained sediments.

In the case of core C, porewater As and Fe concentrations are generally an order of magnitude higher than in core B (Fig. 3c). A critical difference between the porewater samples from cores C and B is that all of the porewater samples from core C were extracted from the coarse-grained sediments (i.e., silt, silty loam, sandy loam, sand), as compared to the porewater samples from core B that were mainly extracted from the fine-grained sediments (i.e., silty clay and clay). Compared to core B, the 10-fold higher As and Fe concentrations in porewaters from core C suggests that microbial reduction of Fe(III) oxides/oxyhydroxides in the coarse-grained sediments is the dominant process controlling As mobilization to the porewaters. This hypothesis is further supported by the SOC data, which exhibited higher values in the fine-grained sediments as compared to the underlying coarse-grained sediments.

Overall, the data presented for the Napoleonville sediment cores and associated porewaters support the above proposed model that As release from sediments is largely confined to the coarse-grained sediments where microbial respiratory processes dominate over fermentation, and also, that the organic carbon fueling microbial Fe(III) (and possibly sulfate) reduction is sourced from the clay-rich layers within these sediments (Bethke et al., 2008; Chapelle and Bradley, 1996; McMahon and Chapelle, 1991). Future detailed field sampling at the Napoleonville site and other locations in southern Louisiana are underway to test this mechanism of As mobilization.

5.2. Incubation experiments

As suggested by our field data from Napoleonville, Louisiana (Fig. 3), and many studies in South and Southeast Asia, As mobility is strongly affected by reduction of As-bearing Fe(III) oxides/oxyhydroxides in the reducing anoxic aquifers

(Harvey et al., 2005; McArthur et al., 2004; Nickson et al., 2000; Polizzotto et al., 2008). Consequently, factors that influence Fe mobility, such as DOC (e.g., humic and fulvic acids) concentrations are also expected to affect As mobility in groundwater systems (Redman et al., 2002; Catrouillet et al., 2014). For example, Fe(II) released by reductive dissolution of Fe(III) oxides/oxyhydroxides can bind with humic acids to form Fe(II)-organic complexes (Catrouillet et al., 2014) and further facilitate reduction of Fe(III) oxides/oxyhydroxides and subsequent As release to groundwaters. Because this process can lead to decreases in Fe concentrations and increases in As concentrations in solutions, it may be another plausible explanation for the commonly observed decoupling of Fe and As concentrations in groundwaters (Horneman et al., 2004; van Geen et al., 2004; Radloff et al., 2007). The flocculants formed in the filtered and acidified solutions from the incubation experiments described herein contain Fe, O, S, and organic carbon (Fig. 4). Thus, the composition of the flocculants and the fact that they only formed in the experimental solutions upon acidification, strongly suggests that they represent Fe- and S-rich, organic compounds like humic acid. The formation of these putative organic flocculants likely removed some Fe, Mn, and possibly even As from solutions in the incubation experiments, which may also explain the decoupling of As from Fe in some of these experiments (e.g., Fig. 5a–c). Although we suggest that this same mechanism may explain the decoupling between As and Mn reported in some of our experiments (Fig. 5), because the Mn contents of the flocculants were too low to be detected by the SEM-EDS, we cannot evaluate this possibility.

The sterilized control experiments exhibited the lowest As (except at day 14), Fe, and Mn concentrations of all the experimental solutions (Tables 3–5; Fig. 5). Because the sediments used in these experiments were initially sterilized, the results largely represent the effect of abiotic processes on As mobility. This "pool" of As is consistent with readily exchangeable As that is weakly adsorbed onto mineral surfaces in the sediments (Pearcy et al., 2011). Another factor that may also affect As release from the sterilized sediments is that autoclaving may have changed the sediment properties, resulting in aggregation of sediment particles and consequent reduction of sediment surface area (Lotrario et al., 1995; Trevors, 1996). Additionally, sterilization by autoclave may increase the degree of crystallinity of initially amorphous Fe(III) oxides/oxyhydroxides, which can subsequently inhibit As release from sediments (Radloff et al., 2008). Nonetheless, the release of the readily exchangeable As "pool" caused by abiotic processes is fast, and was completed within the first 2 days of the experiments, after which As concentrations remained relatively constant at $49 \pm 0.6\ \mu g/L$ (the average for day 7, 14, and 21) until day 21 (Fig. 5a). The fast release of As from the sterilized Napoleonville sediments is consistent with our previous study of As release from sterilized sediments collected from the Aquia aquifer in Maryland, USA (Pearcy et al., 2011), as well as a number of other investigations of sediments from South and Southeast Asia (Islam et al., 2004; Radloff et al., 2007; Rowland et al., 2007). Arsenic concentrations in the sterilized solutions exhibited a decrease (e.g., 30%) after day 21, which may reflect re-adsorption of As onto un-reacted Fe(III) oxides/oxyhydroxides (Oremland and Stolz, 2005), clay minerals, and/or the newly formed Fe(II)-S-organic flocculants. Unfortunately, as in the case for Mn detection by SEM-EDS in the flocculants, the As content of the flocculants was also too low to be detected by SEM-EDS. Considering the variability in the measurements by HR-ICP-MS, Fe and Mn released in the sterilized control experiments were low and remained relatively constant for the first 14 days, and then exhibited a slight increase until the end of the incubation. The gradual Fe and Mn release could be due to abiotic dissolution of newly formed secondary Fe and Mn minerals including magnetite (Fe_3O_4), siderite ($FeCO_3$), and rhodochrosite ($MnCO_3$) during the experiments (Lloyd, 2003; Coker et al., 2006).

Arsenic released in the un-amended experiments was generally higher (i.e., by up to a factor of 2) than the sterilized control experiments (Table 3). Because As released from the sterilized sediments only reflects abiotic processes, the higher amount of As released in the un-amended experiments must represent the amount of As mobilized by both abiotic and biotic processes in the incubation experiments. We propose that the additional As release in the un-amended experiments reflects biotic release by microbial respiration that can occur using the natural organic carbon content of the particular sediment aliquot (Fig. 5b; Pearcy et al., 2011). Consequently, the additional As released in the un-amended experiments is consistent with microbial mediated release of As in addition to release of the readily exchangeable As "pool" by, for example, desorption and/or ion-exchange processes. The amounts of Fe and Mn released from the un-amended sediments were also substantially higher than the sterilized sediments (Tables 4 and 5). The large increases in Fe and Mn concentrations in the un-amended solutions are consistent with the notion that microbial reduction of Fe(III)/Mn(III) oxide/oxyhydroxides and the subsequent releases of Fe(II) and Mn(II) have occurred in these experiments. Another possible explanation of the As concentrations increase in the un-amended experiments is that the adsorbed or co-precipitated As(V) associated with Fe(III)/Mn(III) oxides/oxyhydroxides is being directly reduced to As(III) and subsequently mobilized into solutions (Oremland and Stolz, 2005). Future investigations that include As speciation analysis of the solutions and sediments are needed to test this hypothesis.

For the un-amended anaerobic incubation experiments, the As, Fe, and Mn concentrations follow similar trends over the course of the experiments, decreasing during the first 14 days and then increasing until the end of the experiments (Fig. 5). The initial decreases in As, Fe, and Mn concentrations in solutions may reflect re-adsorption of the previously released readily exchangeable As (e.g., the sterilized controls) as well as loss of all three trace elements onto the newly formed organic flocculants. Nonetheless, with the increase of reaction time, microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides appear to dominate, causing increases in As, Fe, and Mn concentrations after day 14. Compared to the sterilized control experiments, the near doubling of As release in the un-amended sediments strongly suggests that microbial respiration plays an important role in mobilizing As from these sediments. As mentioned above, the un-amended incubation experiments are perhaps most similar to the situation observed in the majority of the porewater/sediment samples from the Napoleonville study site in terms of the comparable As and Fe concentrations in solution. Nevertheless, the chief exceptions are the porewaters from sediment core A, for which As concentrations attain substantially higher values (i.e., up to 158 μg/L; Table 2, Fig. 3), and groundwaters from the same vicinity as core A, where we report an As concentration of 100 μg/L (Fig. 1). Indeed, the As concentrations of these groundwaters and the acetate amended incubation experiments described below are supportive of the notion that diffusion of labile organic carbon from the interlayered clay-rich sediments is required at the Napoleonville site to generate porewater As concentrations that can exceed ∼100 μg/L.

Addition of acetate substantially accelerates microbial respiration (Islam et al., 2004; Pearcy et al., 2011; Radloff et al., 2007, 2008), resulting in greater As release to the experimental solutions than observed in either the sterilized control experiments or the un-amended experiments (Fig. 5c). Addition of acetate also *appeared* to accelerate the formation of Fe- and S-rich organic flocculants, which led to decreases in Fe and Mn concentrations in solutions (i.e., the decrease took 14 days in the un-amended experiments, compared to only 7 days in the acetate amended experiments). However, to address such questions additional experiments will be necessary to closely monitor the timing of the formation of the organic flocculants, the corresponding solution concentrations of As, Fe, and Mn, as well as the changing concentrations of these trace elements within the flocculants as they form and precipitate. With sufficient acetate as electron donor, microbe-facilitated reduction of other electron acceptors such as sulfate and arsenate may co-occur with Fe(III)/Mn(III) reduction, causing continuous As release into solutions even at times when the hypothesized scavenging of Fe and Mn by the organic flocculants is occurring (e.g., the first 7 days). After 7 days; however, microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides appeared to dominate (Tables 4 and 5), and As concentrations increased with increasing Fe and Mn concentrations until the end of the experiments (Table 3).

Addition of AQDS to the acetate amended experiments also appeared to accelerate the formation of Fe- and S-rich organic flocculants, which again may explain the associated decreases in Fe and Mn concentrations in solutions (i.e., finished in 7 days for Fe and 2 days for Mn). After the initial decreases in Fe and Mn concentrations, microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides again appeared to dominate, as suggested by the increases in these metals in solutions (Tables 4 and 5). Arsenic concentrations also started to increase after day 7 until day 21, and then remained relatively constant until the end of the experiments. Both Fe and Mn concentrations generally increased until day 28 and then reached a plateau at the end of the experiments. The "plateauing" of As, Fe, and Mn concentrations suggests that either the maximum amounts of available Fe, Mn, and As that can be mobilized by microbial respiration in the Napoleonville sediments have been reached by ∼days 21/28, or that the acetate added in the sediment incubations has been completely consumed, where upon microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides gradually stops after day 21. The fact that the amounts of Fe and Mn released from the sediments in the un-amended experiments were much higher than the amended experiments suggests that given a constant labile DOC source, it is possible that additional amounts of As could be mobilized from sediments due to microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides. Thus, the addition of the electron shuttling compound (AQDS) appears to have further stimulated microbial respiration in these sediment incubations compared to the analogous experiments with only acetate added.

Compared to the un-amended experiments, the amended (i.e., acetate and acetate + AQDS) experiments attained much higher As concentrations in solutions. These results are consistent with the addition of acetate and AQDS acting to facilitate increase in microbial respiration and hence, As mobilization by 2-fold (e.g., 197 μg/L) in the acetate amended experiments and 4-fold (i.e., 380 μg/L) in the experiments amended with both acetate and AQDS at the end of the experiments (Table 3). Furthermore, results of the incubation experiments support the conclusion of our field sampling and analysis, which strongly suggest that microbes play an important role in mobilizing As from sediments to shallow groundwaters at the Napoleonville site in southern Louisiana.

6. Conclusions

Arsenic and Fe concentrations in porewaters from Napoleonville, Louisiana, varied by an order of magnitude between the coarse-grained silt- and sand-rich sediment layers (e.g., As up to158 μg/L) and the fine-grained clay-rich sediment layers (e.g., As <10 μg/L). Porewater samples high in As concentrations were generally associated with high Fe and DOC concentrations. Therefore, results of porewater analysis support the hypothesis that As mobilization from sediments mainly occurs in the coarse-grained sediments where microbial reduction of Fe(III) oxides/oxyhydroxides dominates the As mobilization, and also, DOC fueling microbial Fe(III) reduction is sourced from the clay-rich layers (Bethke et al., 2008; McMahon and Chapelle, 1991). Incubation experiments using sediments from the Napoleonville site support the hypothesis that microbial reduction of Fe(III) oxides/oxyhydroxides is the chief mechanism controlling As release from sediments to shallow groundwaters at the study site in southern Louisiana. Specifically, As concentrations in the experimental solutions were low in the sterilized control experiments, slightly higher in the un-amended experiments, and the highest in the experiments amended with acetate and acetate + AQDS. Compared to the un-amended experiments, addition of acetate and AQDS resulted in an increase in As concentrations by a factor of 2 (i.e., acetate) to 4 (i.e., acetate + AQDS). However, addition of acetate and AQDS in the amended experiments resulted in the formation of Fe- and S-rich organic flocculants in the experimental solutions, which appeared to have scavenged Fe and Mn, and perhaps even As, from solutions, leading to lower than expected concentrations of these trace elements (especially Fe and Mn) in the experimental solutions. Although As release did not exactly follow the same trend as Fe and Mn, As concentrations generally increased with increasing Fe and Mn concentrations in solutions. Results of the incubation experiments support our hypothesis that microbial reduction of As-bearing Fe(III)/Mn(III) oxides/oxyhydroxides is the primary mechanism causing As release from sediments to groundwaters at the Napoleonville site in southern Louisiana.

Published concentrations of As in groundwaters and aquifer sediments from southern Louisiana are currently limited, and the mechanisms controlling As mobilization from aquifer sediments in this region are likely complex and diverse. Therefore, future investigations should focus on: (1) determination of As concentrations and speciation in both groundwaters and aquifer sediments from the Mississippi Delta region; (2) identification of competing chemical reactions that affect As concentrations and speciation in both aqueous and the solid phases of the aquifer matrix (e.g., Oremland and Stolz, 2003); (3) ascertaining historical use and loading of anthropogenic As sources to the environment; and (4) assessing factors that can be used as parameters for predicting natural groundwater As distribution (Yang et al., 2014). Because groundwaters are important domestic and municipal water source in southern Louisiana, a better and complete understanding of As distribution in groundwaters is essential to the health of the local population.

Conflict of interest

None.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ejrh.2015.11.023.

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