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ADSORPTION OF ARSENIC ONTO RIVER SEDIMENTS

by

LETICIA AUGUSTA DOS SANTOS FERREIRA

A THESIS

Presented to the Graduate Faculty of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

in

GEOLOGY AND GEOPHYSICS

2022

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ABSTRACT

Previous studies have noted the relationship between shallow groundwater rich in sodium (Na) and bicarbonate (HCO_3) and elevated levels of dissolved arsenic. However, most experimental work on arsenic adsorption in the presence of HCO_3 and differing Na/Ca ratios has proven difficult to extrapolate to natural systems because of differences in tested mineral compositions and component concentrations. In this study, I performed a series of adsorption experiments using river sediments to evaluate the influence of HCO_3 and monovalent/divalent cations on the extent of arsenic adsorption onto natural sediment in groundwater.

Batch adsorption (kinetics, equilibrium, and metal loading) experiments were conducted using river sediments with anions salts (0.1 or 0.01M NaHCO_3 , NaCl , CaCl_2 , or MgCl_2) amended with arsenate and in some cases with natural organic matter (NOM). Arsenate [As(V)] adsorbed strongly onto sediment under all conditions, but the experiments with HCO_3 increased the mobility of arsenic (i.e., less adsorption was observed) relative to systems with chloride (Cl). Systems with divalent cations (e.g., Ca or Mg) adsorbed substantially more arsenic ($\geq 20\%$) than Na-Cl or Na- HCO_3 systems. This may be attributable to the presence of ternary As(V) -divalent cation-mineral surface complexes and/or an electrostatic effect that promotes additional adsorption of arsenic. This study suggests that changes in the bulk chemistry of groundwater, such as the amount of HCO_3 and the ratio of Na/Ca can measurably influence the extent of arsenic adsorption onto river sediments.

ACKNOWLEDGMENTS

This thesis would not have been possible without the guidance and support from several individuals who have contributed one way or another or extended their valuable knowledge and experience in the preparation of my master's degree.

I would like to thank my advisor, Dr. David M. Borrok, for guiding me on a progressive path away from tangents. Dr. Borrok provided an excellent leadership and direction throughout my research project, was always positive and encouraging me to consider different approach in conducting experiments and writing my thesis paper. I acknowledge my thesis committee members Drs David Borrok, David Wronkiewicz, and Katherine Grote guidance for their feedback on this thesis project. I want to thank Dr. Borrok and Dr. Grote for their help with sample collection.

I thank the Geosciences and Geological and Petroleum Engineering Department for funding me as a Graduate Research Assistant. I acknowledge Ninu Madria, a Senior Research from S&T, for her assistance on using ICP-OES. I thank Tasha Hoffman, a PhD candidate from geology and geophysics department for her assistance in the laboratory. I acknowledge Grayson Mejia a participant in S&T's Summer Engineering Research Academy (SERA) for his participation in Arsenic-NOM project. I thank School of Geosciences - University of Louisiana at Lafayette for XRF and XRF analysis of sediment samples.

Last but not the least, I thank my parents, grandma, sisters, and uncle Ni for their constant love and support.

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NOMENCLATURE

Symbol	Description
As(III)	Arsenite
As(V)	Arsenate
HCO_3^-	Bicarbonate
Cl^-	Chloride
Ca	Calcium
CaCl_2	Calcium Chloride
HAsO_4^-	Dissociation form of Arsenic Acid (H_3AsO_4) or Hydrogen Arsenate
HNO_3	Nitric Acid
Mg	Magnesium
MgCl_2	Magnesium Chloride
Na	Sodium
NaCl	Sodium Chloride
NaHCO_3	Sodium Bicarbonate
NaOH	Sodium Hydroxide

1. INTRODUCTION

1.1. OVERVIEW

Arsenic contamination of groundwater is a major health issue and environmental threat (National Research Council (US), 1999; Smedley and Kinniburgh, 2002; Flanagan et al., 2012; Quansah et al., 2015). Long-term exposure to arsenic from drinking water can cause problems such as cancer, skins lesions, damage to cognitive development, cardiovascular disease, and more. The US Environmental Protection Agency Environmental (EPA) suggests that arsenic levels in composited water samples should not exceed 0.002 mg/L (US EPA 2015). Arsenic concentrations in groundwater are hazardously elevated in some parts of the United States and in areas of many other countries including Canada, Bangladesh, Taiwan, and Argentina (e.g., Tseng et al., 1968; Hopenhayn-Rich et al., 1996; Mueller et al., 2001; Smith et al., 2002; Naujokas et al., 2013).

In some cases, increasingly dry climates have led to over pumping of groundwater, which in turn has led to subsidence and other hydrologic changes (Smith et al., 2018). These hydrologic changes have been shown to influence redox processes and may influence the release of arsenic bound within clay interlayers and/or release other elements that impact the degree of arsenic adsorption onto aquifer material (Erban et al., 2013; Ayotte et al., 2016; Smith et al., 2018). Although increases in the concentrations of dissolved arsenic have been documented in regions where groundwater overdrafting is occurring, it remains unclear which geochemical process or processes are most important in leading to increases in arsenic concentrations in groundwater. One of the primary

uncertainties is the degree to which changes in bulk water geochemistry can influence arsenic adsorption under these conditions.

Previous work has shown that the extent of adsorption of dissolved arsenic can be influenced by the presence of competing anions for surface adsorption sites. In fact, several studies have implicated high concentrations of bicarbonate (HCO_3) in groundwater as a key mechanism for enhancing the mobility of arsenic (Appelo et al., 2002; Anawar et al., 2003; Anawar et al., 2004; Arai et al., 2004; Borrok et al., 2018). For example, in the Anawar et al., (2004) investigation, arsenic-rich sediments samples treated with NaHCO_3 effectively mobilized arsenic into groundwater.

Other studies have suggested that the relative abundance of dissolved monovalent (e.g., Na and K) to divalent cations (e.g., Ca and Mg) can impact the extent of adsorption of arsenic. For example, in the Anawar et al., (2004) investigation, the arsenic release in groundwater was greatest in systems with more Na and less in systems with divalent cations (in this case Ba and Mn) even in systems with the same amount of HCO_3 . This phenomenon may be related to changes in the electrostatic double layer of the mineral surfaces or the formation of ternary complexes where divalent cations can help arsenic anions form a complex with negatively charged surface sites (Van Geen et al., 1994; Wilkie and Hering 1996; Redman et al., 2002; Stachowicz et al., 2007). Similar impacts on arsenic adsorption related to the Na/Ca ratio have been identified in experimental studies by Smith et al (2002), Masue et al (2007), and Kanematsu et al (2013).

Although many previous investigations point to the importance of changes in bulk geochemistry (primarily the presence of HCO_3 and the Na/Ca ratio of the solution) in controlling the mobility of arsenic, some experimental investigations have suggested that

these changes may not be important in natural systems (e.g., Mai et al., 2014). For example, Stachowicz et al. (2007) suggested that the competition between HCO_3 and arsenic anions for goethite surface adsorption sites was weak. Moreover, in a column study with an iron coated sand, Radu et al (2005) showed that HCO_3 had relatively little influence on the extent of arsenate adsorption. Part of the reason for these differing opinions regarding the importance of HCO_3 on competition for mineral surface adsorption sites may be the different experimental procedures and conditions employed. Most previous work has concentrated on individual mineral phases as opposed to natural sediments and sometimes the component concentrations used in the experiments were not relevant to those in natural systems. Therefore, the extent to which changes in bulk geochemistry influence the mobility of arsenic under the conditions of most natural groundwater systems remains unclear.

In this study, we addressed this knowledge gap by performing adsorption experiments using natural river sediments under a variety of bulk geochemical conditions to understand (1) how arsenic adsorption onto river sediments behaves in the presence of HCO_3 and dissolved natural organic matter (NOM), and (2) how this adsorption behavior changes with the ratio of monovalent (Na) to divalent (Ca, Mg) cations. We focused on investigating arsenate (As[V]) species because they are dominant in oxidizing shallow groundwaters.

1.2. BACKGROUND

1.2.1. Mechanisms of Arsenic Mobility. Arsenic (As) is a carcinogenic element that is harmful to both human health and environment. Arsenic can be derived from

natural sources (e.g., volcanism and minerals; Y. Mamindy-Pajany et al., 2009) and anthropogenic activities (e.g., mining residues, industrial emissions, wood preserving, coal combustion, and arsenical pesticides; Wang and Mulligan 2006b). In natural systems arsenic exists in oxidation states of III or V. The aqueous speciation of dissolved arsenic depends on the redox conditions and pH. Under oxidizing conditions, As(V) is the dominant arsenic species (Turpeinen et al., 1999; Y. Mamindy-Pajany et al., 2009). The pKa's for the As(V) species - arsenic acid (H_3AsO_4) - are 2.20, 6.97, and 11.53 (Raven et al., 1998). Therefore, under the conditions of most natural groundwater (pH 7.0 to 8.5), the HAsO_4^{2-} is the dominant oxidized form of arsenic. The pKa's for As (III) or arsenite species (H_3AsO_3) are 9.2, 12.1, and 13.4 (Smith et al., 1998; Goldberg and Johnston, 2001), so at neutral pHs neutral or weakly anionic As (III) species are present.

Dissimilatory iron reduction (DIR) is one of the primary mechanisms controlling the mobility of arsenic (Anawar et al., 2003; Lopez-Adams et al., 2021). Lovley and Phillips (1988) first demonstrated that in the absence of oxygen, microorganisms can use Fe (III) or Mn (IV) bound in the structure of minerals as an electron acceptor to oxidize labile organic compounds. This microbial reduction of solid mineral phases results in the release of adsorbed arsenic species.

The mobility of the arsenic after it is released is further determined by the bulk geochemistry of the groundwater (Redman et al., 2002; Anawar et al., 2004; Wang and Mulligan, 2006a; Y. Mamindy-Pajany et al., 2009; Lopez-Adams et al., 2021). Arsenic adsorption mechanisms depend on the geochemistry of the water as well as the mineral or sediments compositions. This is because individual minerals have different types of surface sites and different zero points of charge (ZPCs) which determine their interaction

with arsenic. The ZPC of a mineral defines the pH at which the net charge on the surface equals zero or is neutral. For example, the ZPC for hematite (Fe_2O_3) and goethite (FeOOH) are at pHs of 8.1 and 6.9 respectively (Y. Mamindy-Pajany et al., 2009). Surface charges are positive when solutions are at pHs below the ZPC and negative at pHs higher than the ZPC. If the pH values are higher than the (PZC) value of the mineral surface, then arsenic anion adsorption is not favored (Raven et al., 1998). Based on electrostatic properties, the negative charge of the solid surface will begin to repel the negative charge of arsenic anions. However, if the ZPC is higher than the pH values of the bulk solution, then the mineral surface is positive, and the condition is favorable for arsenic anion adsorption. For this reason, we tend to observe larger amounts of adsorbed As(V) species onto mineral surfaces under lower pH conditions.

Some studies reported that NOM also influences the geochemistry of arsenic in groundwater (Redman et al., 2002; Wang and Mulligan, 2006a; Sharma et al., 2011). Redman et al. (2002) performed a batch experiment illustrating the competition of NOM with arsenic for adsorption sites onto colloidal hematite. They conducted experiments using water samples containing NOM from Brazil, USA, and New Zealand. They observed significantly altered redox speciation of the free arsenic at the end of every experiment. In addition to promoting redox reactions, NOM may also influence arsenic speciation through the formation of aqueous NOM-arsenic complexes and prevent arsenic from forming surface complexes with minerals Redman et al. (2002). Finally, anionic dissolved NOM may also compete with arsenate anions for mineral surface adsorption sites (Sharma et al., 2011).

Many studies have reported relationships between high concentrations of dissolved arsenic and high concentrations of HCO_3 in shallow groundwater. For example, high concentration of arsenic with elevated concentrations of HCO_3 (up to 650 mg/L) were observed in the groundwater samples from the Bengal delta system in Bangladesh (Anawar et al., 2003). Borrok et al (2018) observed high concentration of arsenic in groundwater rich in Na-HCO_3 in Lower Mississippi River Alluvial Aquifer in Louisiana, USA. Experimental investigations have also supported the role of bicarbonate as a competing anion with arsenic for surface adsorption sites (Van Geen et al., 1994; Appelo et al., 2002; Anawar et al., 2003; Anawar et al., 2004). The Van Geen et al. (1994) investigation suggested that the presence of surface complexes of carbonate led to the release of adsorbed arsenic in groundwater. The competition between HCO_3 and arsenic anions was further illustrated in an experiment using subsurface sediments from Bangladesh (Anawar et al., 2004). These arsenic leaching experiments showed that the presence of increasing amounts of HCO_3 effectively released arsenic that was bound to the sediment (Anawar et al., 2004). Appelo et al (2002) indicated that high alkalinity due to high dissolved CO_2 in a soil zone can solubilize arsenic in groundwater. In this case, bicarbonate or carbonate possibly displaced and released arsenic from arsenic adsorbed mineral surface.

On the other hand, some experimental studies have suggested that the effect of HCO_3 on As(V) adsorption is not meaningful (e.g., Stachowicz et al., 2007; Kanematsu et al., 2013). For example, Radu et al. (2005) showed that the effect of HCO_3 on As(V) sorption onto goethite coated sand in column experiment was weak. Mai et al. (2014) compared differences in arsenic adsorption behavior from the literature on arsenic

adsorption associated with both synthetic minerals and aquifer sediments and concluded that experimental results may not be relevant to natural systems. They suggested that the synthetic minerals from experimental systems may not compare to the minerals in sediments and therefore the impact of bicarbonate on adsorption may not be important in natural systems.

The extent of arsenic adsorption is also impacted by other anions in addition to bicarbonate. These competing anions include phosphates, silicic acid, sulfate, and nitrates (Van Geen et al., 1994; Wilkie and Hering 1996; Redman et al., 2002). Wilkie and Hering (1996) observed a decrease in both As (III) and As(V) adsorption in the presence of sulfate anions. An arsenic sorption study by Smith et al (2002) suggested a competition between phosphorus and As(V) for sorption sites on soil with low Fe-oxides content in comparison to high Fe-oxides soils. However, in the Redman et al. (2002) investigation, the competitive behavior of nitrate, sulfate, and phosphate were undetectable in their sorption experiments.

The effect of the relative amounts of monovalent to divalent cations on arsenic adsorption in groundwater were discussed in several studies (Smith et al., 2002; Ahmed et al., 2004; Anawar et al., 2004; Masue et al., 2007). Smith et al. (2002) reported an increase in arsenate adsorption onto different soils in the presence of Ca in solution relative to systems with Na. Masue et al. (2007) demonstrated that at pH ~8 adsorption of As(V) on coprecipitated Al: Fe-hydroxides increased by up to 40% in the presence of Ca as compared systems with Na. They also reported greater As(V) adsorption with increasing Ca concentrations (Masue et al., 2007). Increasing Na concentrations did result in slightly increased As(V) adsorption, but not nearly as much as in the Ca systems

(Masue et al., 2007). This is because polyvalent cations can act as a cation bridge between negatively charged arsenic anions and mineral surfaces. The formation of ternary complexation is possible when cations are present to help arsenic anions form a complex with negatively charged surface sites (Van Geen et al., 1994; Wilkie and Hering 1996; Redman et al., 2002; Stachowicz et al., 2007). The presence of Ca can possibly enable the formation of ternary As(V) – Ca or Mg – surface complexes. Another possibility could also be that the increasing of Ca concentrations decreased repulsive forces between the negative charge of the hydroxide mineral surfaces and the negative charge of the arsenate oxyanion (Masue et al., 2007; Smith et al., 2002; Masue et al., 2007; Kanematsu et al., 2013). In either case, divalent cation tends to favor arsenic adsorption onto mineral surfaces relative to monovalent cation.

1.2.2. Impact of Climate Change on Arsenic Mobility. Climate change can influence the mobility of arsenic in groundwater by changing redox and bulk geochemical conditions. The alternating redox conditions play an important role in arsenic mobility as the oxidation states influence adsorption mechanisms (Stollenwerk et al., 2007). Hydrological processes which are currently affected by human activities can trigger arsenic release in groundwater (Fendorf et al., 2010). For example, pumping can change the geochemical conditions in the aquifer system (Erban et al., 2013; Ayotte et al., 2016; Smith et al., 2018). Pumping-induced subsidence has led to the release of arsenic contamination in groundwater in the San Joaquin Valley of California. Changes in the water table as the result of overpumping can change the water chemistry and/or compress less permeable layers of the aquifer and release water from clay minerals that may contain high concentrations of arsenic (Smith et al., 2018). Water expelled from interbedded

confining clay could also include dissolved organicNOM or other competing ions that could promote arsenic mobilization (Erban et al., 2013). The dissolved NOM from sediment fosters bacterial activity (Hoffman et al., 2020) that can lead to enhanced DIR (Fendorf et al., 2010; Islam et al., 2004).

Variations in groundwater recharge can also influence contaminant concentrations (Munk et al., 2011; Erban et al., 2013; MacKay et al., 2013). Munk et al. (2011) examined the impact of seasonal groundwater fluctuation in Anchorage, Alaska, and observed higher levels of arsenic during seasons with increased precipitation or snowmelt (high recharge events). In addition, Ayotte et al. (2016) found, that managed aquifer recharged led to decreased amounts of Ca and Mg ions in parts of Central Valley California, which led to increases in the mobility of arsenic in the aquifer.

2. METHODOLOGY

2.1. SEDIMENT SAMPLE PREPARATION

We collected natural river sediment samples in different locations along the Missouri River. Sediment samples were collected in clean air-tight polyethylene bags and later air-dried under room temperature. We used a mortar and pestle to homogenize and powder the dried samples. Stainless steel sieves were used to separate the samples into uniform size ranges. The sizes of the sediment samples used for this investigation were between 0.052 – 0.250 mm. The mineral content in the sediment samples were analyzed at the University of Louisiana at Lafayette using a DIANO 2100E X-ray diffraction (XRD) instrument. A Thermo Scientific Niton portable X-ray fluorescence (XRF) analyzer was used to analyze for elemental concentrations. We measured the organic matter content in our homogenized sediments using the Loss-On-Ignition Method (LOI) (Nelson and Sommers, 1996).

2.2. BATCH ADSORPTION EXPERIMENTS

All apparatus used in the experiments were pre-washed using dilute nitric acid and rinsed with deionized water three times before the experiment. All adsorption experiments were conducted using 30 mL Savillex™ containers. A pre-determined amount of sediment (e.g., 0.1g, 0.5, 1g). was measured and allocated within each container. A pre-determined volume of electrolyte solutions (NaHCO_3 , NaCl , CaCl_2 , or MgCl_2) with dissolved As(V) was added to the containers. The As(V) concentrations were prepared using a potassium acid arsenate salt (H_2AsKO_4). We also performed

control experiments with just the electrolyte and the electrolyte + sediment, to ensure that no detectable concentrations of arsenic were present in the materials utilized for the experiments (Appendix E). The experimental conditions for each adsorption experiments are outlined in Table 2.1.

The initial pH of each mixture was measured and adjusted to values between 4 and 9 using small amounts of 0.01M NaOH or HNO₃. Each reaction vessel was left to equilibrate for two weeks prior to sampling. After this period, the final pH value of each solution was measured. All pH measurements were completed using a a Fisherbrand™ accumet™ Excel XL15 pH meter. The samples were collected by filtering the electrolyte from the sediment using a 20 mL syringe and a 0.45-micron nylon syringe filter. The amount of arsenic adsorbed was calculated by the difference between the initial concentration and the amount of arsenic in the liquid.

The filtered liquid was preserved with a drop of concentrated nitric acid and later analyzed for arsenic concentrations using a Perking Elmer Avio 200 inductively coupled plasma – optical emission spectrometer (ICP-OES). We compared the use of matrix matched standards with standards diluted with NaCl solutions and found that there were no interface effects in either case. As a quality control measure, standards were run as unknowns throughout each experimental run. Using this method, the uncertainty of our analyses was +/- 5% (Appendix E).

2.2.1. NOM Experiments. One subset of adsorption experiments additionally included dissolved natural organic matter (NOM) provided from the International Humic Substances Society (IHSS Upper Mississippi River NOM 1R110N). We used 5 mg/L NOM in all NOM experiments. In addition, we performed a NOM adsorption experiment

without the presence of arsenic. For this experiment we used 0.5 g of sediment with 0.01M NaCl +NOM. The results were evaluated using a Shimadzu TOC – L Analyzer to measure amount of NOM adsorbed onto sediments.

2.2.2. Kinetic Experiments. Kinetic experiments were conducted using the same protocols described above, except that the starting pH was the same for each reaction vessel and samples were collected as a function of time. Experiments were conducted for one month under atmospheric condition. We collected the liquid samples at different time intervals (0.02, 0.08, 0.3, 1, 2, 5, 20, 48, 72, 168, 336, and 672 hours). The purpose of these experiments was to define the time needed for arsenic adsorption to reach equilibrium or steady state. The results from these experiments informed our reaction times for the other adsorption experiments.

2.2.3. Metal Loading Experiments. We prepared six 50mL stock solutions of 0.01M NaCl with pre-assigned concentration of 5, 10, 20, 50, 100, and 200mg/L arsenic and another six 50mL stock solutions of 0.01M NaHCO₃ with equivalent pre-assigned concentrations. We used 0.1 g of sediments with 10mL of each stock solution and performed adsorption tests using the same methods described above only the initial pH of the experiment was not adjusted. After the final pH was measured, we analyzed the arsenic concentration using ICP-OES.

Table 2.1 The experimental conditions described specific component concentrations for each adsorption experiments.

Adsorption experiments	Sediments (g)	Electrolyte solution (mL)	Amount and types of electrolytes	As (V) (mg/L)	NOM (mg/L)
Control experiments	3.0 g	20	0.01M NaHCO ₃	-	-
			0.01M NaCl		
Kinetic experiments	3.0	20	0.01M NaHCO ₃	100	-
	3.0		0.01M NaCl		
	0.5		0.01M NaCl	10	5.0
Adsorption / equilibrium experiments	0.1	10	0.01M NaHCO ₃	10	-
			0.01M NaCl		
			0.01M CaCl ₂		
			0.01M MgCl ₂		
	0.5	10	0.01M NaHCO ₃	10	+/-5
			0.01M NaCl		
			0.01M CaCl ₂		
			0.01M MgCl ₂		
	1.0	10	0.01M or 0.1M NaHCO ₃	10	-
			0.01M or 0.1M NaCl		
0.01M or 0.1M CaCl ₂					
Metal loading experiments	0.1	10	0.01M NaHCO ₃	~7	-
				~11	
				~22	
				~47	
				~101	
				~209	
			0.01M NaCl	~8	-
				~11	
				~21	
				~50	
				~108	
				~212	

3. RESULTS

3.1. SEDIMENT SAMPLE ANALYSIS

The XRD results indicated the presence of crystalline quartz (61 wt.%), plagioclase (23 wt.%), illite (7 wt.%), and orthoclase (4 wt.%) respectively (Figure 3.1). The remaining (5 wt.%) is comprised of a variety of minerals that were present at or below the quantification limit (around 2%) for this method. These included montmorillonite, calcite, muscovite, biotite, and kaolinite. The XRD data are preliminary in nature and are being redone using standards and a more advanced instrument. A semiquantitative XRF analysis on the same samples highlighted the presence of elements that were largely consistent with the XRD results (Figure 3.1, Table 3.1). For example, silica, aluminum, potassium, and calcium were abundant. The presence of more than 2% Fe in the XRF analysis paired with the lack of an Fe mineral phase in the XRD data may suggest the presence of amorphous iron oxide minerals in the sample.

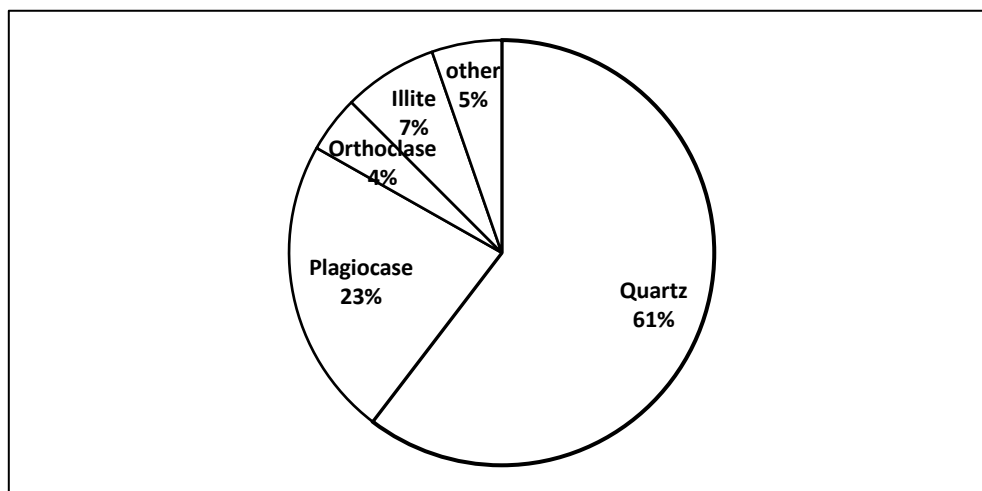


Figure 3.1 XRD analysis of sediment samples. The other category includes trace amounts of montmorillonite, calcite, muscovite, biotite, and kaolinite.

Table 3.1 XRF analysis of the same sediment samples. These analyses were semi-quantitative, so we have included only values estimated to comprise 2% or more of the total, as we have less confidence in the results with lower values. Note that XRF was not able to detect Na or lighter elements.

	wt. %	error (%)
Iron (Fe)	2.15	0.02
Calcium (C)	2.19	0.04
Potassium (K)	1.47	0.02
S (Sulfur)	0.05	0.01
Al (Aluminum)	3.63	0.09
Si (Silica)	26.71	0.13
Magnesium	0.50	0.20

3.2. KINETIC EXPERIMENTS

Kinetic experiments were conducted to determine the equilibrium time of arsenic adsorption onto the natural sediments in the presence of different electrolytes. The extent of arsenic adsorption increased rapidly in all the experiments within 24 hours, then gradually reached a steady state after approximately two weeks (336 hours; Figure 3.2). Although the starting pH for all the samples were similar, the pH changed over the reaction period in slightly different fashions for the different experimental systems. For example, the pH ranges recorded for 0.01M NaCl and 0.01M NaHCO₃, and 0.01M NaCl + 5mg/L NOM were pH= 6.99 - 7.66, pH = 7.18-8.62, and pH= 7.03-7.95 respectively (Appendix A). Hence, the final extents of adsorption cannot be compared directly among these experiments since the pHs are not consistent. Instead, these experiments can only demonstrate that the arsenic adsorption time is roughly similar regardless of the

experimental system and that 336 hours is a sufficient time to achieve equilibrium or steady state.

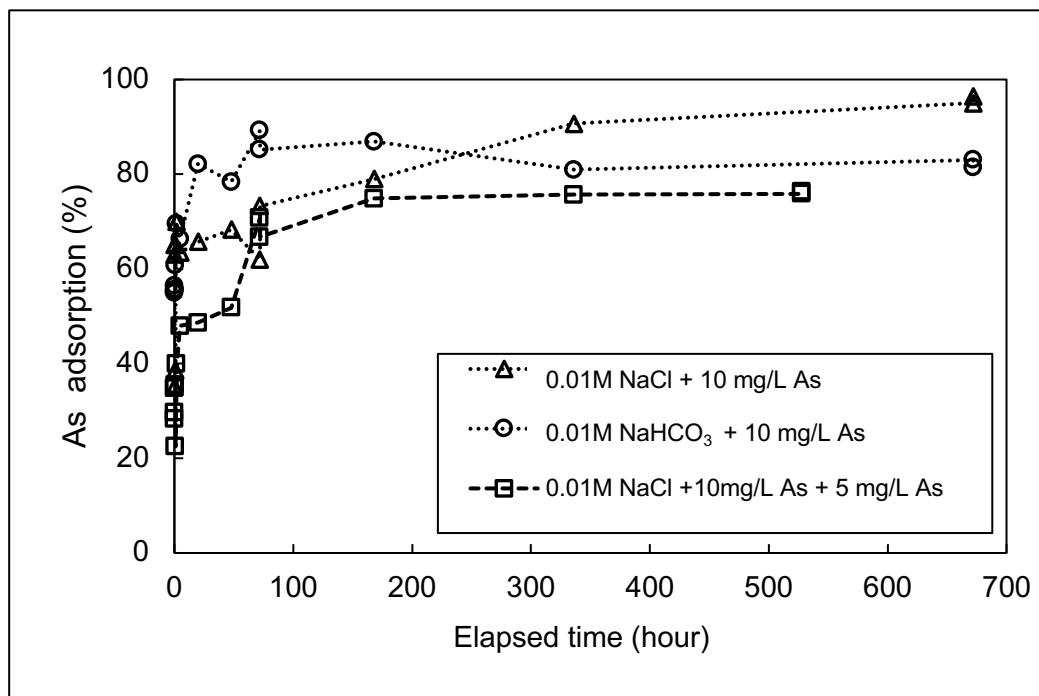


Figure 3.2 Kinetic experiments. The rate of arsenic adsorption over reaction time by 0.01M NaCl \pm NOM and 0.01M NaHCO₃.

3.3. IMPACT OF SEDIMENT TO ARSENIC RATIO

We conducted a series of experiments to evaluate the impact of different sediment amounts relative to arsenic on the extent of adsorption. The overall trend showed that arsenic adsorption decreases with increasing pH. This is because the sites on the mineral surfaces are starting to become negative at higher pH and they are no longer as favorable for the arsenate anion to bind onto. The results showed an increase in arsenic adsorption with increasing sediment - arsenic ratio (Figure 3.3 A-C). For a 10-fold increase in the sediment to arsenic ratio (i.e., the 10g/L to 100g/L sediment experiments) the extent of

arsenic adsorption changed by 60 %, 50%, and 50% at pH 7.0, in the experiments run with 0.01M NaHCO₃, 0.01M NaCl, and 0.01M CaCl₂, respectively (Figure 3.3 A-C).

The degree of changes in arsenic adsorption as a function of sediment to arsenic ratio showed that arsenic adsorption increases with increasing sediment to arsenic ratio. This adsorption characteristics is expected since more sediment provides more surface sites for arsenic adsorption. However, the NaCl system seems to have slightly less of a change from 10 g/L to 100 g/L at pH 7 relative to the system with NaHCO₃. (Figure 3.3 A-B). This is probably because at low sediment to arsenic ratio, in NaHCO₃ system, bicarbonate competes with arsenate anions for adsorption sites. As the sediment to arsenic ratio increases, the changes are more significant in NaHCO₃ because more sites are available for arsenic anions to bind.

3.4. IMPACT OF IONIC STRENGTH

To evaluate the impact of ionic strength on the extent of adsorption, we performed a series of experiments where the amount of sediment (100g/L) and arsenic (10mg/L) remained constant, but we varied the ionic strength of the three electrolytes (NaCl, NaHCO₃, and CaCl₂) from 0.01M to 0.1M. The results showed that the difference in ionic strength had no significant effect on both the NaCl and CaCl₂ solutions (at least under the sediment and arsenic concentrations employed in these experiments; Figure 3.4 A-C). There was, however, a measurable decrease in the extent of arsenic adsorption in the experiment with 0.1M NaHCO₃ relative to the experiment with 0.01M NaHCO₃ (Figure 3.4 A). As the amount of HCO₃ increased 10-fold, arsenic adsorption decreased by about 10% at pH = 7 (Figure 3.4A).

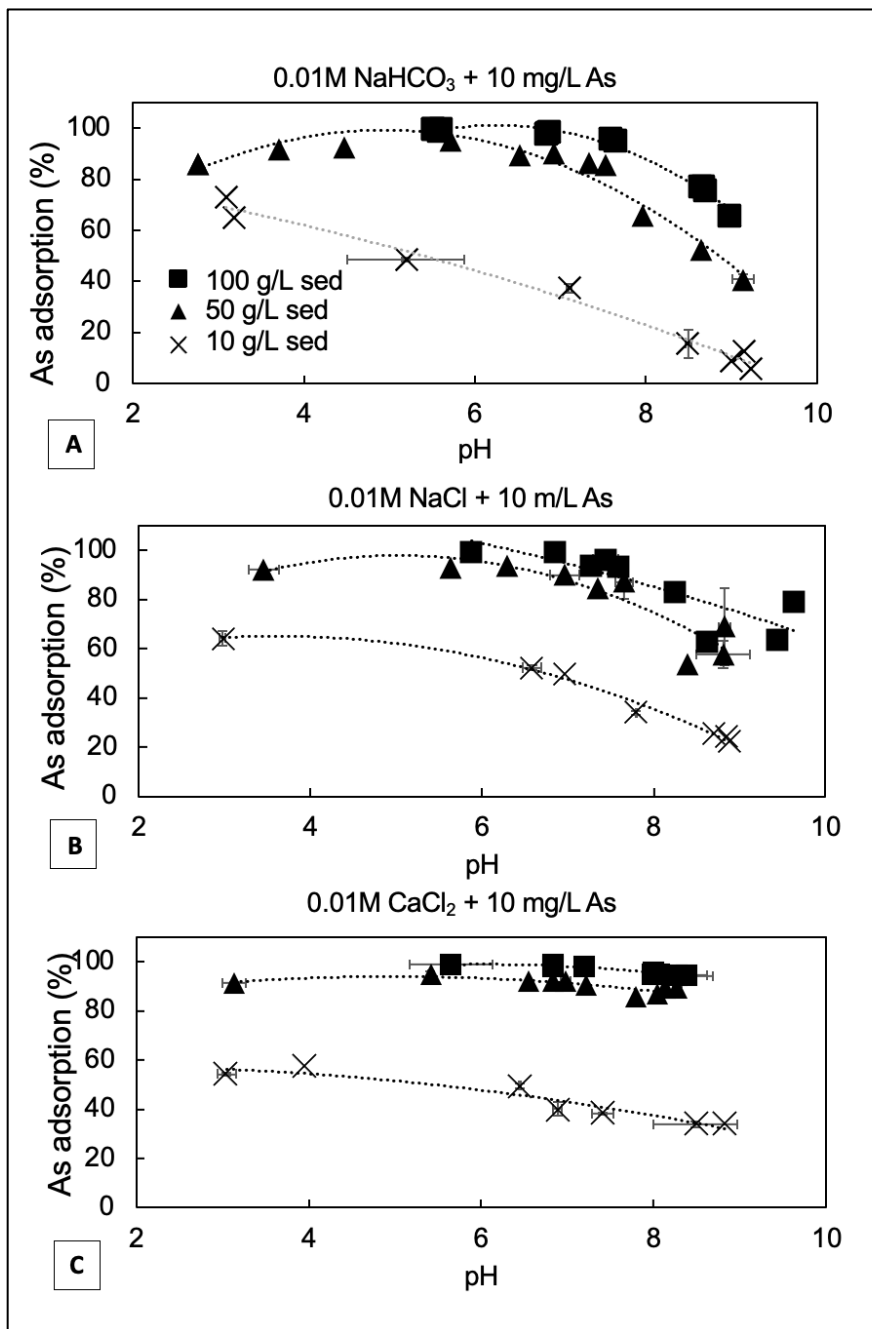


Figure 3.3 Impact of sediment to arsenic ratio. Arsenic adsorption onto (10 g/L, 50 g/L, and 100 g/L sediment concentration) in 0.01M solutions of A) NaHCO₃, B) NaCl, and C) CaCl₂. Error bars represent one standard deviation.

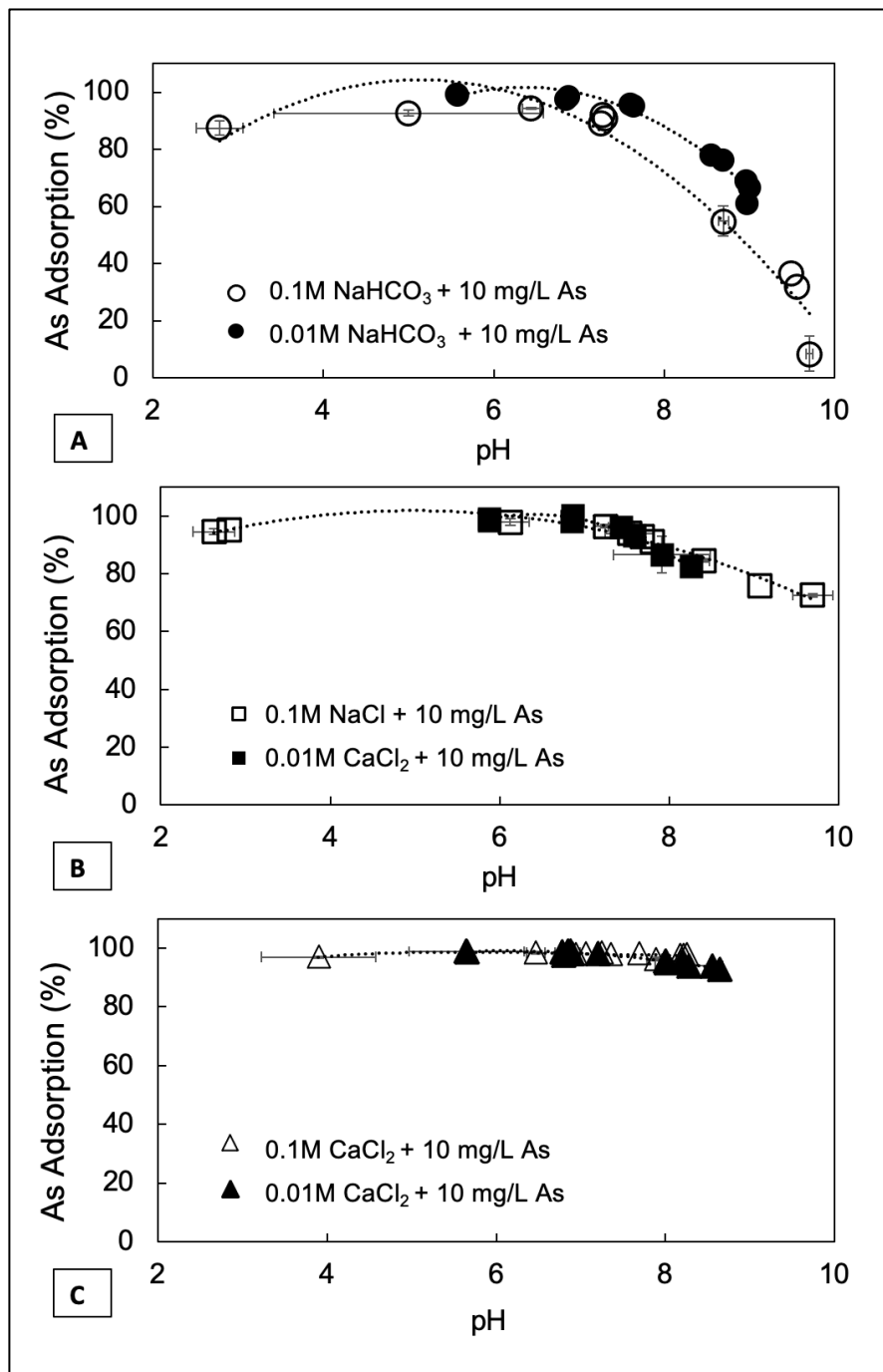


Figure 3.4 Impact of ionic strength. Arsenic adsorption onto 100 g/L sediments in solutions of A) 0.01M and 0.01M NaHCO₃, B) 0.01M and 0.01M NaCl, and C) 0.01M and 0.1M CaCl₂. Error bars represent one standard.

The decrease in the extent of arsenic adsorption in the presence of high levels of HCO_3^- concentration indicates that HCO_3^- competes with arsenate anions for adsorption sites, which implies less arsenic can adsorb to the sediment. Since no significant difference occurred with the Cl systems in our experiments, there was no measurable competition between Cl and arsenate for adsorption sites.

3.5. IMPACT OF ELECTROLYTE TYPES

To study the impact of electrolyte on the extent of adsorption, we conducted a series of experiments using a variety of electrolytes (NaCl , NaHCO_3 , CaCl_2 , and MgCl_2) at different sediment to arsenic ratios. Our experiments showed that the extent of arsenic adsorption increased by 20% or more in the Ca and Mg systems relative to the NaHCO_3 system at pH 7 to 8 (Figure 3.5 A-C; red line represents the extent of adsorption). Both CaCl_2 and MgCl_2 systems also showed more adsorption relative to NaCl systems, suggesting the presence of ternary complexation or an electrostatic effect. The experiments with Na and HCO_3^- increased the mobility of arsenic (i.e., less adsorption was observed) relative to systems with Na (or Ca or Mg) and Cl (Figure 3.5 A-C). The decreased arsenate adsorption in experiments with HCO_3^- electrolyte relative to NaCl or CaCl_2 and MgCl_2 showed that HCO_3^- is an important competing ion with arsenate for adsorption sites (at least under bulk geochemical conditions employed in these experiments). This observation indicates that differences in electrolyte compositions could lead to substantial changes in the extent of arsenic adsorption onto sediments.

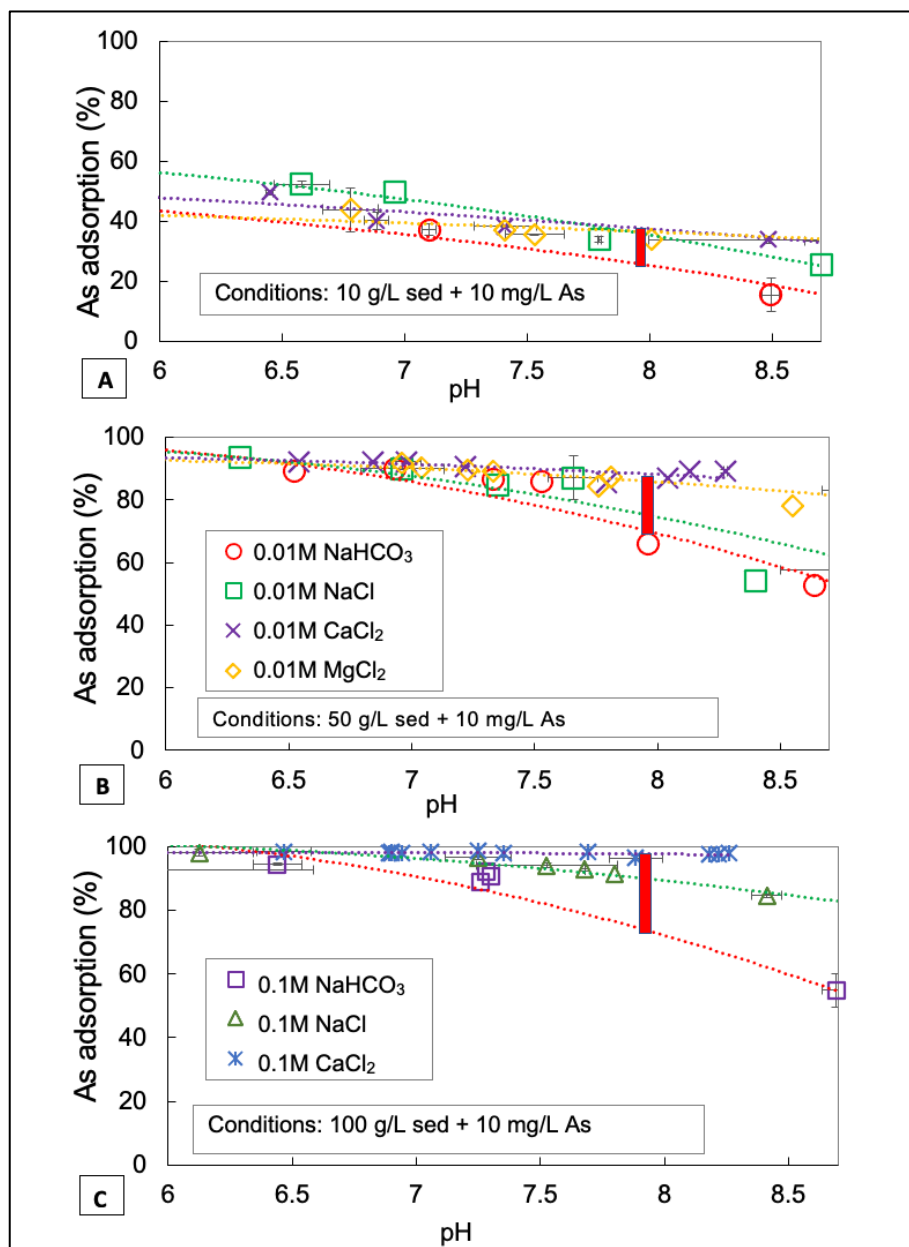


Figure 3.5 Impact of electrolyte types (0.01M NaCl, NaHCO₃, CaCl₂, and MgCl₂) on arsenic adsorption. Red lines represent difference between Na – HCO₃ and Ca/Mg solutions. Error bars represent one standard deviation.

3.6. IMPACT OF NOM

To evaluate the impact of NOM on arsenic adsorption, we performed a series of arsenic adsorption experiments with NOM under a variety of conditions. The results

showed that NOM had no significant effect on the rate (Figure 3.2) or extent of arsenic adsorption in all the electrolyte solutions (Figure 3.6 A-D). In the NOM adsorption experiments without arsenic present, only 10 to 20% of the NOM adsorbed onto sediments (Figure 3.7; Table C.2 in Appendix C). The relatively weak adsorption of NOM onto the sediments was not enough to impact the adsorption of arsenic under these conditions.

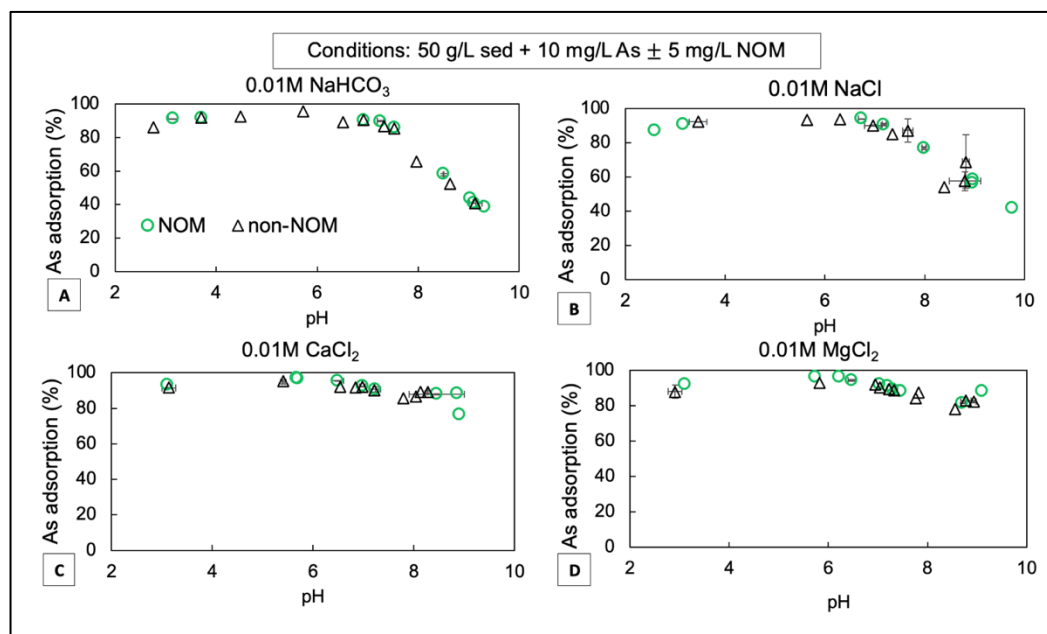


Figure 3.6 Impact of NOM on arsenic adsorption. The symbol legend is the same for all panels. Error bars represent one standard deviation.

3.7. METAL LOADING EXPERIMENTS

To test the maximum arsenic adsorption capacity of the sediments we performed a series of metal loading experiments. Although the results showed that the experiments with NaHCO₃ systems had lower adsorbed As (V) (~ 0.1 to 0.2 mg/g) relative to Na-Cl experiments (Figure 3.8), the pH values for the two systems were slightly different such

that comparisons of the extent of adsorption are not possible. The change in the adsorption relationship from linear to a flattening curve suggests that the sites might be reaching saturation at around ~ 0.7 mg/g for NaHCO_3 and 0.8 mg/g for NaCl (Figure 3.8). The adsorption sites for arsenic appear to be more limited in the NaHCO_3 system relative to NaCl system. This may reflect the competition of HCO_3^- with arsenate for mineral surface sites.

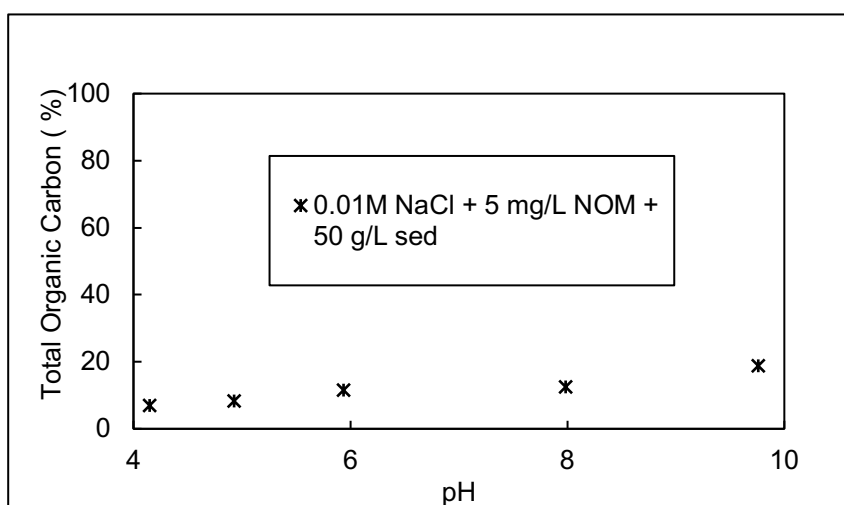


Figure 3.7 TOC analysis results

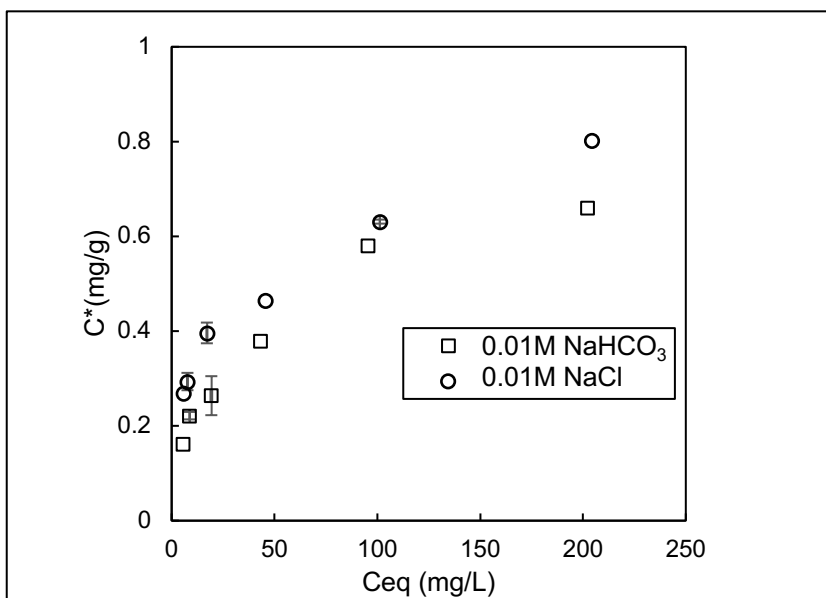


Figure 3.8 Metal loading experiments. Total dissolved As (from ~7 to 212 mg/L) in a 0.01M NaCl or NaHCO_3 solutions with 10 g/L sediment concentration. C^* is the amount of arsenic adsorbed onto sediment. C_{eq} is the concentration after equilibrium time with respect to the initial total dissolved As (Appendix D). Error bars represent one standard deviation.

4. DISCUSSION

4.1. EFFECT OF HCO_3 ON ARSENIC ADSORPTION

Our results demonstrated that the presence of high levels of bicarbonate can significantly displace arsenic for adsorption sites on mineral surfaces in natural sediments. Although we observed an increase of the extent of adsorption as we increase the sediment to arsenic ratio, the overall extent of adsorption in NaHCO_3 solutions was lower relative to solutions with NaCl and CaCl_2 (Figure 3.3 A-C). Furthermore, when we increased the amount of HCO_3 by 10-fold, the extent of arsenic adsorption decreased by 10% at pH 7 (Figure 3.4A). The ionic strength of the other electrolytes had no significant effect on the extent of arsenic adsorption (Figure 4B-C). Finally, the relationships found in the metal loading experiments suggest that HCO_3 was taking up some fraction of the available surface sites in the river sediment.

Our results agreed with investigations that demonstrate the importance of HCO_3 on the extent of arsenic adsorption (Van Geen et al., 1994; Appelo et al., 2002; Anawar et al., 2003; Anawar et al., 2004). However, it is easy to see how changes in experimental condition could shift our findings such that they would seem to agree with Radu et al. (2005), Stachowicz et al. (2007), Kanematsu et al. (2013), and Thi Hoa Mai et al. (2016) who all suggested that the effect of HCO_3 on arsenic adsorption onto mineral surface is negligible. Also, most of these previous studies used synthetic iron oxide minerals in their experiments (Radu et al., 2005; Stachowicz et al., 2007; Kanematsu et al., 2013), while we used river sediment. We believe that the adsorption behavior of arsenic in our experiments is more relevant to natural systems because river sediments have many

minerals with differing surface properties. Therefore, in natural systems, we would expect to see higher concentrations of dissolved As in the presence of groundwater rich in HCO_3^- .

4.2. EFFECT OF DIVALENT CATION ON ARSENIC ADSORPTION

In our study, the presence of Ca and Mg increased the extent of adsorption by 20% or more relative to Na systems (Figure 3.5 A-C). One interpretation could be that divalent systems (e.g., Ca, Mg) favor As(V) adsorption because of an electrostatic effect that promotes additional adsorption of arsenic. Divalent cations are more effective in reducing repulsive potential between negative charges of mineral surfaces relative to monovalent cations (Masue et al., 2007). Smith et al., (2002) explained that natural water with Na system was ineffective in raising the Fe-oxides surface charges and was less effective for arsenic adsorption, whereas Ca divalent cations counteracted negative Fe-oxide surface charges, promoting arsenic adsorptions (i.e., specifically for arsenate). For this reason, we observed larger amounts of adsorbed arsenic onto sediments in Ca or Mg systems and the differences were more pronounced at high pHs when the mineral surface sites start to become negatively charged.

A separate but related explanation could be that Ca and Mg served as a cation bridge to form ternary surface complexes with arsenate and mineral surfaces. The co-adsorption of metal cations and ligands to the same site on mineral surface is an example of ternary surface complexation. The divalent cations can act as a cation bridge to form As(V) – divalent cation – mineral surface complexes. In the case of our experiments, Ca or Mg may be capable of forming ternary complexations with mineral surfaces because

of the +2 charge can be shared with both arsenic anions and negative charge of mineral surfaces. Conversely, Na as a monovalent system is not capable to form ternary complexation because the +1 charge can only satisfy one negative charge; therefore, Na is not as efficient as Ca or Mg in this regard. For this reason, monovalent system tends to have lower arsenic adsorption than divalent system.

4.3. IMPLICATION FOR CLIMATE-DRIVEN CHANGES IN ARSENIC

Variation in climate can affect groundwater recharge amounts and pathways, which can influence the concentrations of HCO_3^- and the Na/Ca ratio of groundwater (Munk et al., 2011; Erban et al., 2013; MacKay et al., 2013). Because the extent arsenic adsorbs onto sediments depends on this water geochemistry, changes in the concentration of competing ions such as HCO_3^- will greatly influence the adsorption of arsenic. Increasing the amount of HCO_3^- and the ratio of Na/Ca can occur through a variety of natural weathering and ion exchange pathways or through hydrological processes impacted by human activities (Fendorf et al., 2010). For example, managed aquifer recharge can also affect the amount of Ca or Mg in the groundwater. Lower amounts of these cations could result in increases in dissolved arsenic. For example, the decreased amounts of Ca and Mg ions in parts of Central Valley California has led to more arsenic released in the aquifer (Ayotte et al., 2016).

5. CONCLUSION

Kinetic experiments demonstrated that the rate of arsenic adsorption onto river sediments reached equilibrium in about two weeks with or without NOM present. Batch adsorption experiments showed that arsenic adsorbs strongly onto river sediment under all conditions, but that experiments with Na and HCO_3 increase the mobility of arsenic by limiting surface adsorption relative to systems without HCO_3 and higher amounts of Ca or Mg. Higher amounts of HCO_3 (0.01M vs. 0.1M) increased the competition for adsorption sites, leading to lower levels of arsenic adsorption. The presence of Ca or Mg increased the extent of arsenic adsorption ($\geq 20\%$) relative to systems with only monovalent cations (e.g., Na). This adsorption behavior can be attributed to ternary complexation and/or an electrostatic effect that promotes additional adsorption of arsenic. NOM adsorbed weakly onto the sediment and had no significant effect on arsenic adsorption.

Results from this study suggest that the bulk chemistry of groundwater, specifically the amount of HCO_3 , and ratio of divalent to monovalent cations can substantially influence the extent of arsenic adsorption in natural systems. This has implications for regions where the chemistry of shallow groundwater is being impacted by climate change and anthropogenic activities such as overpumping.

APPENDIX A.

TABLES OF KINETIC EXPERIMENTS DATA

Table A.1. Kinetic Experiments (NaCl)

X g sediment	3			
Y mL liquid	20			
0.01 M NaCl electrolyte				
X mg/L arsenic	114.8285029			
Sample #	Time (hrs)	pH	Amount adsorbed (mg/L)	% adsorbed
1	0.02	7.3	74.8	65.1
2	0.08	7.38	72.4	63.1
3	0.33	7.66	40.3	35.1
4	1	7.54	44.3	38.6
4-duplic	1	7.5	74.9	65.2
5	2	7.4	80.3	69.9
6	5	7.36	72.8	63.4
7	20	7.3	75.5	65.7
8	48	7.18	78.4	68.3
9	72	7.26	71.1	61.9
9-duplic	72	7.3	84.1	73.3
10	168	7.26	90.7	79.0
11	336	6.99	104.2	90.7
12	672	7.26	109.1	95.0
12-duplic	672	7.47	110.8	96.5

Table A.2. Kinetic Experiments (NaHCO₃)

X g sediment	3			
Y mL liquid	20			
0.01 M NaHCO ₃ electrolyte				
X mg/L arsenic	119.8909			
Sample #	Time (hrs)	pH	Amount adsorbed (mg/L)	% adsorbed
1	0.02	7.77	66.0	55.0
2	0.08	7.83	66.5	55.5
3	0.33	7.85	67.7	56.4
4	1	7.7	66.8	55.7
4-duplic	1	7.75	72.8	60.7
5	2	7.85	83.4	69.6
6	5	7.71	79.6	66.4
7	20	7.8	98.5	82.2
8	48	7.71	94.0	78.4
9	72	7.72	107.0	89.2
9-duplic	72	7.18	102.2	85.2
10	168	8.3	104.2	86.9
11	336	8.54	97.1	80.9
12	672	8.62	99.6	83.0
12-duplic	672	8.57	97.6	81.4

Table A.3. Kinetic Experiments (NaCl +NOM)

Kinetics				
X g sediment	0.5			
Y mL liquid	10			
0.01 M NaCl electrolyte				
X mg/L arsenic	10.002			
Any other ingredient such as NOM (mg/L)	5			
Sample #	Time (hrs)	pH	Amount adsorbed (mg/L)	% adsorbed
1	0.02	7.03	7.0	29.7
2	0.08	7.22	7.2	28.3
3	0.33	7.28	6.5	34.8
4	1	7.21	6.5	35.5
4-duplic	1	7.36	7.7	22.5
5	2	7.34	6.0	39.9
6	5	7.45	5.2	47.9
7	20	7.52	5.1	48.7
8	48	7.58	4.8	51.8
9	72	7.95	2.9	70.8
9-duplic	72	7.63	3.3	66.8
10	168	7.6	2.5	74.8
11	336	7.65	2.4	75.7
12	528	7.71	2.4	75.9
12-duplic	528	7.82	2.4	76.4

APPENDIX B.

TABLES OF ADSORPTION (EQUILIBRIUM) EXPERIMENTS DATA

Table B.1. Equilibrium Experiments (0.01M NaHCO₃)

X g sediment	1						
Y mL liquid	10						
X mg/L arsenic	~10						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.95	3.3	69.0	9.0	65.6	0.0	3.9
1-dupli	9.00	3.5	66.6				
1-triplica	8.98	4.1	61.3				
2	8.54	2.4	77.8	8.6	76.8	0.1	1.1
2-duplic	8.67	2.5	76.8				
2-triplic	8.70	2.6	75.7				
3	7.64	0.5	95.2	7.6	95.2		
4	7.60	0.4	95.9	7.6	95.9		
5	6.87	0.2	98.4	6.9	98.4		
6	6.85	0.2	97.8	6.9	97.8		
7	6.84	0.3	97.4	6.8	97.4		
8	5.61	0.1	99.4	5.6	99.4		
9	5.58	0.1	98.9	5.6	98.9		
10	5.51	0.0	99.5	5.5	99.5		

Table B.2. Equilibrium Experiments (0.01 M NaCl)

X g sediment	1						
Y mL liquid	10						
X mg/L arsenic	~10						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.43	0.8	63.5	9.4	63.5		
2	9.64	0.5	78.8	9.6	78.8		
3	8.62	0.8	62.9	8.6	62.9		
4	8.18	1.6	84.4	8.2	82.9	0.1	1.4
4-duplic	8.25	1.8	82.6				
4-triplicate	8.3	1.9	81.8				
5	7.26	0.6	93.8	7.3	93.8		
6	7.53	0.7	93.0	7.6	93.2	0.1	0.3
6-duplic	7.64	0.7	93.3				
7	7.6	0.4	96.4	7.4	96.3	0.2	0.4
7-duplic	7.4	0.4	95.8				
7-triplic	7.31	0.3	96.7				
8	6.86	0.0	100.0	6.9	98.9	0.0	1.1
8-duplic	6.85	0.2	97.9				
8-triplic	6.85	0.1	98.6				
9	5.87	0.1	98.7	5.9	99.1	0.0	0.6
9-duplic	5.87	0.1	98.8				
9-triplic	5.88	0.0	99.8				

Table B.3. Equilibrium Experiments (0.01M CaCl₂)

X g sediment	1						
Y mL liquid	10						
X mg/L arsenic	~10						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.64	0.8	92.7	8.6	92.7		
2	8.55	0.7	94.0	8.4	94.7	0.2	1.0
3	8.2	0.5	95.4				
4	8.11	0.6	94.7	8.3	94.1	0.4	0.8
4-duplic	8.74	0.8	93.2				
4-triplicate	7.99	0.6	94.4				
5	7.98	0.5	95.3	8.0	95.3		
6	8.06	0.5	95.1	8.1	95.1		
6-duplic	8.01	0.4	95.8	8.0	95.8		
7	7.19	0.2	98.2	7.2	98.0	0.0	0.3
7-duplic	7.2	0.2	98.0				
7-triplic	7.21	0.2	97.7				
8	6.8	0.3	97.5	6.8	98.1	0.1	0.5
8-duplic	6.74	0.2	98.4				
8-triplic	6.95	0.2	98.5				
9	6.88	0.1	98.9	6.8	98.9	0.1	0.1
9-duplic	6.84	0.1	98.9				
9-triplic	6.78	0.1	98.7				
10	6.13	0.1	98.8	5.6	98.9	0.5	0.1
10-duplic	5.64	0.1	98.9				
10-triplic	5.17	0.1	98.8				

Table B.4. Equilibrium Experiments (0.1M NaHCO₃)

X g sediment	1						
Y mL liquid	10						
X mg/L arsenic	~10						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.66	5.5	18.4	9.7	8.4	0.0	6.1
1-duplic	9.73	5.9	13.0				
1-triplic	9.76	6.2	7.7				
1-quadrup	9.67	6.5	3.9				
1- quint	9.7	6.4	4.8				
1-sextupli	9.7	6.5	2.7				
2	9.5	5.6	36.6	9.5	36.6		
3	9.55	6.1	31.8	9.6	31.8		
4	8.71	2.2	54.4	8.7	54.9	0.1	5.3
4-duplic	8.74	2.4	49.9				
4-triplicate	8.63	1.9	60.4				
5	7.26	0.4	89.0	7.3	89.0		
6	7.28	0.3	92.1	7.3	92.1		
7	7.3	0.3	90.9	7.3	90.9		
8	6.51	0.2	94.6	6.4	94.3	0.1	0.4
8-duplic	6.37	0.2	94.1				
9	6.12	0.2	93.3	5.0	92.6	1.6	1.0
9-duplic	3.88	0.2	91.9				
10	2.59	0.4	85.6	2.8	87.4	0.3	2.5
10-duplic	2.98	0.3	89.2				

Table B.5. Equilibrium Experiments (0.1M NaCl)

X g sediment	1						
Y mL liquid	10						
X mg/L arsenic	~10						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.07	2.6	76.1	9.1	76.1		
2	9.53	3.0	72.2	9.7	72.5	0.2	0.5
2-duplic	9.86	3.0	72.9				
3	8.47	1.7	84.4	8.4	84.6	0.1	0.6
3-duplic	8.42	1.7	84.2				
3-triplic	8.35	1.6	85.3				
4	7.8	0.9	91.4	7.8	91.4		
5	7.68	0.8	92.5	7.7	92.7	0.0	0.2
5-duplic	7.68	0.8	92.8				
6	7.65	0.7	93.7	7.5	94.0	0.3	0.7
6-duplic	7.73	0.7	93.5				
6-triplic	7.2	0.6	94.8				
7	7.1	0.3	97.1	7.3	96.5	0.1	0.5
7-duplic	7.35	0.4	96.2				
7-triplic	7.3	0.4	96.3				
8	5.97	0.1	98.7	6.1	98.0	0.2	1.1
8-duplic	6.28	0.3	97.2				
9	2.81	0.5	95.1	2.8	95.1		
10	2.8	0.4	95.4	2.6	94.7	0.2	1.1
10-duplic	2.45	0.6	93.9				

Table B.6. Equilibrium Experiments (0.1M CaCl₂)

X g sediment	1						
Y mL liquid	10						
X mg/L arsenic	~10						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.18	0.2	97.6	8.2	97.6		
2	8.22	0.2	97.6	8.2	97.6		
3	10.05	0.4	96.4	10.1	96.4		
4	8.26	0.2	97.8	8.3	97.8		
5	7.81	0.3	96.7	7.9	96.3	0.1	0.6
5-duplic	7.96	0.4	95.9				
6	7.69	0.2	98.2	7.7	98.2		
7	7.35	0.2	98.0	7.4	98.0		
8	7.25	0.1	98.6	7.3	98.6		
9	7.06	0.2	98.2	7.1	98.2		
10	6.9	0.2	97.9	6.9	97.9		
11	6.9	0.2	98.1	6.9	98.1		
12	6.94	0.2	98.0	6.9	98.0		
13	6.89	0.2	98.1	6.9	98.1		
14	6.34	0.1	98.4	6.5	98.4	0.1	0.4
14-duplic	6.51	0.1	98.8				
14-triplic	6.55	0.2	98.0				
15	3.3	0.3	97.1	3.9	96.9	0.7	0.3
15-duplic	4.63	0.3	97.2				
15-triplic	3.76	0.3	96.6				

Table B.7. Equilibrium Experiments (0.01M NaHCO₃)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~11.5						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.31	7.0	38.4	9.1	40.7	0.1	2.1
1-duplic	9.1	6.7	41.0				
1-triplic	9.03	6.4	43.5				
1-quadr	9.11	6.8	40.1				
2	8.64	5.4	52.5	8.6	52.5		
3	7.96	3.9	65.8	8.0	65.8		
4	7.33	1.5	86.7	7.3	86.7		
5	6.93	1.1	90.0	6.9	90.0		
6	7.53	1.6	85.7	7.5	85.7		
7	6.52	1.2	89.3	6.5	89.3		
8	5.72	0.5	95.5	5.7	95.5		
9	3.71	0.9	91.8	3.7	91.8		
10	4.48	0.8	92.4	4.5	92.4		
11	2.76	1.4	86.3	2.8	86.3		

Table B.8. Equilibrium Experiments (0.01 M NaCl)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~11.0						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.16	5.6	49.1	8.8	57.6	0.3	5.5
1-duplic	9.09	4.9	55.4				
1-triplic	8.7	4.4	60.2				
1-quadr	8.42	4.1	63.2				
1-quint	8.67	4.4	59.9				
2	8.9	5.4	50.8	8.8	68.9	0.1	15.7
2-duplic	8.78	2.4	78.4				
2-triplic	8.79	2.5	77.4				
3	8.4	5.1	53.9	8.4	53.9		
4	7.72	2.2	79.7	7.7	87.1	0.1	7.0
4-duplic	7.71	1.3	87.9				
4-triplic	7.54	0.7	93.6				
5	7.35	1.7	84.7	7.4	84.7		
6	6.84	1.1	89.7	7.0	89.9	0.2	0.2
6-duplic	7.08	1.1	90.0				
7	6.3	0.7	93.7	6.3	93.7		
8	5.63	0.7	93.0	5.6	93.0		
9	3.33	0.8	92.1	3.5	92.1	0.2	0.0
9-duplic	3.58	0.8	92.1				

Table B.9. Equilibrium Experiments (0.01M CaCl₂)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~11.6						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.06	1.1	90.4	8.2	88.2	0.1	2.8
1-duplic	8.27	1.3	88.6				
1-triplic	8.28	1.2	89.6				
1-quadr	8.13	1.2	89.1				
1-quint	8.02	1.9	83.3				
2	7.79	1.7	85.5	7.8	85.5		
3	7.22	1.1	90.5	7.2	90.5		
4	7.02	0.9	92.3	7.0	92.2	0.1	0.1
4-duplic	6.94	0.9	92.2				
5	6.84	0.9	92.0	6.8	92.0		
6	6.54	0.9	92.0	6.5	92.0		
7	5.43	0.7	94.2	5.4	95.0	0.0	1.2
7-duplic	5.39	0.5	95.9				
8	3.23	0.9	91.8	3.1	91.6	0.1	0.3
8-duplic	3.04	1.0	91.3				

Table B.10. Equilibrium Experiments (0.01M MgCl₂)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~10.9						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.89	2.1	81.9	8.9	82.3	0.1	0.6
1-duplic	8.97	2.0	82.7				
2	8.7	1.9	83.0	8.8	82.9	0.1	0.1
2-duplic	8.85	2.0	82.9				
3	8.55	2.5	78.1	8.6	78.1		
4	7.81	1.4	87.4	7.8	87.4		
5	7.76	1.8	84.3	7.8	84.3		
6	7.33	1.3	89.0	7.3	89.0		
7	7.23	1.2	89.4	7.2	89.4		
8	6.96	0.9	91.9	7.0	91.9		
9	7.04	1.1	90.4	7.0	90.4		
10	5.81	0.8	92.9	5.8	92.9		
11	2.94	0.9	91.8	2.9	88.0	0.1	3.7
11-duplic	3.03	1.4	87.6				
11-triplic	2.76	1.7	84.5				

Table B.11. Equilibrium Experiments (0.01M NaHCO₃ + NOM)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~10						
Any other ingredients such as NOM?(mg/L)	~5						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.22	5.8	42.5	9.2	42.5		
2	9.43	6.4	37.2	9.4	37.2		
3	9.41	6.4	37.1	9.4	37.1		
4	8.51	4.2	58.3	8.5	57.9	0.0	0.6
4-duplic	8.5	4.3	57.5				
5	7.3	1.0	89.6	7.3	89.7	0.1	0.2
5-duplic	7.21	1.0	89.9				
6	5.99	0.5	95.1	6.0	95.1		
7	6.22	0.6	94.0	6.2	94.0		
8	3.08	0.8	91.2	3.1	91.2	0.1	0.0
8-duplic	3.21	0.8	91.2				
9	5.11	0.5	94.7	5.1	94.7		

Table B.12. Equilibrium Experiments (0.01M NaCl + NOM)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~10						
Any other ingredients such as NOM?(mg/L)	~5						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.76	6.4	41.6	9.8	41.6		
2	8.96	4.8	56.6	9.0	56.6		
3	8.97	4.6	58.3	9.0	58.3		
4	8.01	2.6	76.2	8.0	76.8	0.0	0.9
4-duplic	7.96	2.5	77.4				
5	7.16	1.0	91.0	7.2	90.5	0.0	0.6
5-duplic	7.22	1.1	90.1				
6	6.79	0.7	93.9	6.7	93.8	0.1	0.2
6-duplic	6.69	0.7	93.7				
7	3.16	1.0	90.6	3.2	90.6		
8	2.59	1.4	87.3	2.6	87.3		

Table B.13. Equilibrium Experiments (0.01M CaCl₂ + NOM)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~10						
Any other ingredients such as NOM?(mg/L)	~5						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.91	2.6	76.5	8.9	76.5		
2	8.87	1.3	88.3	8.9	88.3		
3	8.07	1.4	87.8	8.5	87.9	0.5	0.2
3-triplic	8.84	1.3	88.1				
4	7.31	1.2	89.7	7.2	90.7	0.1	1.4
4-duplic	7.16	0.9	91.6				
5	7	0.8	92.7	7.0	92.7		
6	6.57	0.5	95.6	6.5	95.5	0.1	0.1
6-duplic	6.41	0.5	95.4				
7	5.7	0.4	96.5	5.7	96.5		
8	5.68	0.3	96.9	5.7	96.9		
9	3.12	0.8	93.0	3.1	93.0		

Table B.14. Equilibrium Experiments (0.01M MgCl₂ + NOM)

X g sediment	0.5						
Y mL liquid	10						
X mg/L arsenic	~10						
Any other ingredients such as NOM?(mg/L)	~5						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.75	2.0	81.5	8.7	81.5	0.0	0.0
1-duplic	8.68	2.0	81.5				
2	9.1	1.3	88.0	9.1	88.0		
3	7.31	1.2	88.8	7.3	88.8		
4	7.47	1.3	88.1	7.5	88.1		
5	7.2	1.0	91.0	7.2	91.0		
6	7.04	0.9	91.8	7.0	91.8		
7	6.52	0.7	93.8	6.5	94.1	0.1	0.5
7-duplic	6.42	0.6	94.5				
8	3.11	0.8	92.1	3.1	92.1		
9	5.74	0.4	95.9	5.7	95.9		
10	6.22	0.4	96.1	6.2	96.1		

Table B.15. Equilibrium Experiments (0.01M NaHCO₃)

X g sediment	0.1						
Y mL liquid	10						
X mg/L arsenic	~11						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	9.23	10.5	5.6	9.2	5.6		
2	9.15	9.6	12.8	9.2	12.8		
3	9	10.2	8.7	9.0	8.7		
4	8.47	9.0	19.4	8.5	15.5	0.0	5.6
4-duplic	8.52	9.9	11.6				
5	7.12	6.8	38.5	7.1	37.2	0.0	1.8
5-duplic	7.08	7.1	36.0				
6	5.68	5.7	48.1	5.2	48.6	0.7	0.6
6-duplic	4.71	5.6	49.0				
7	3.09	2.9	73.0	3.1	73.0		
8	3.18	3.8	65.0	3.2	65.0		

Table B.16. Equilibrium Experiments (0.01M NaCl)

X g sediment	0.1						
Y mL liquid	10						
X mg/L arsenic	~12.6						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed	pH	% adsorbed
1	8.88	9.7	22.4	8.9	22.4		
2	8.7	9.4	25.5	8.7	25.5		
3	8.84	9.6	24.1	8.8	24.1		
4	7.8	8.3	34.5	7.8	33.9	0.0	0.9
4-duplic	7.79	8.4	33.3				
5	6.96	6.3	49.6	7.0	49.6		
6	6.66	5.9	53.0	6.6	52.3	0.1	1.0
6-duplic	6.5	6.1	51.6				
7	2.95	4.7	62.2	3.0	64.2	0.0	2.9
7-duplic	3	4.2	66.3				

Table B.17. Equilibrium Experiments (0.01M CaCl₂)

X g sediment	0.1						
Y mL liquid	10						
X mg/L arsenic	~12.7						
XXX equilibration time	2 weeks						
				average		std	
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed	pH	% adsorbed		
1	8.83	8.3	34.3	8.8	34.3		
2	8.14	8.3	34.7	8.5	33.8	0.5	1.1
2-duplic	8.83	8.5	33.0				
3	7.5	7.9	38.1	7.4	38.4	0.1	0.3
3-duplic	7.32	7.8	38.6				
4	6.92	7.8	38.3	6.9	40.3	0.0	2.8
4-duplic	6.85	7.3	42.3				
5	6.46	6.4	48.9	6.5	49.6	0.0	0.9
5-duplic	6.44	6.3	50.2				
6	3.96	5.3	57.3	4.0	57.3		
7	3.12	5.8	53.9	3.0	54.3	0.1	0.7
7-duplic	2.97	5.7	54.8				

Table B.18. Equilibrium Experiments (0.01M MgCl₂)

X g sediment	0.1		
Y mL liquid	10		
X mg/L arsenic	~9.9		
XXX equilibration time	2 weeks		
Sample #	pH	Amount adsorbed (mg/L)	% adsorbed
1	8.7	4.9	33.4
2	8.8	4.8	36.9
3	8.0	4.5	34.2
4	7.5	4.5	35.6
5	7.4	4.4	37.0
6	6.8	4.7	44.0
7	3.0	4.8	46.5

APPENDIX C.

TABLES OF LOI AND TOC-L ANALYSIS DATA

Table C.1. OM-LOI Method Calculation

	Total amount (Excluded beaker)	After 105 °C for 24hr (Excluded beaker)	After 360 °C (Excluded beaker)
Sample amount	5.0019g	4.9967 g	4.9448 g
	OM-LOI (% wt. loss)	$\frac{4.9967\text{ g} - 4.9448\text{ g}}{4.9967\text{ g}} \times 100 = 1.038\%$ of NOM	

Table C.2. TOC-L Analyzer Data and Calculation

Condition: 0.01M NaCl + 5 mg/L NOM + 50 g/L sed		
	amount in liquid (ppm)	x / 5 ppm NOM * 100%
pH		
4.15	0.4	7.0
4.93	0.4	8.3
5.94	0.6	11.7
7.99	0.6	12.7
9.76	0.9	18.8

APPENDIX D.

TABLES OF METAL LOADING EXPERIMENTS DATA

Table D.1. Metal Loading Experiments (0.01M NaHCO₃)

Metal loading experiments							
X g sediment	0.1						
Y mL liquid	10						
0.01M NaHCO ₃ electrolyte							
X mg/L arsenic	various concentration						
XXX equilibration time	2 weeks						
Sample #	Initial Conc. or Total dissolved As(mg/L)	Amount of As in remaining liquid or Conc. After two weeks (Ceq) (mg/L)	Amount adsorbed, (mg/L)	Avg C*(mg/g)	Std C*	Avg Ceq	Std Ceq
1	7.10	5.47	1.62	0.16		5.47	
2	10.97	8.80	2.16	0.22	0.01	8.75	0.08
2-duplic		8.79	2.18				
2-triplic		8.66	2.31				
3	21.93	19.31	2.61	0.26	0.04	19.29	0.41
3-duplic		19.69	2.24				
3-triplic		18.87	3.06				
4	47.19	43.40	3.79	0.38		43.40	
5	101.28	95.49	5.80	0.58		95.49	
6	208.86	202.27	6.59	0.66		202.27	

Table D.2. Metal Loading Experiments (0.01M NaCl)

X g sediment	0.1						
Y mL liquid	10						
X mg/L arsenic							
XXX equilibration time	various concentration						
	2 weeks						
Sample #							
1	Initial Conc. or Total dissolved As(mg/L)	Amount of As dissolved in remaining liquid or Conc. After two weeks (Ceq) (mg/L)	Amount adsorbed (mg/L)	Avg C*(mg/g)	Std C*	Avg. Ceq	Std Ceq
2	8.4	5.7	2.7	0.27		5.73	
2-duplic	10.6	7.7	3.0	0.29	0.02	7.68	0.18
2-triplic		7.5	3.1				
3		7.9	2.7				
3-duplic	21.1	17.0	4.1	0.40	0.02	17.12	0.22
3-triplic		17.0	4.1				
4		17.4	3.7				
5	50.3	45.6	4.7	0.47		45.61	
5-duplic	107.5	101.2	6.3	0.63	0.00	101.23	0.04
6		101.3	6.3				
	212.4	204.3	8.0	0.80		204.34	

APPENDIX E .

METHOD VALIDATION AND EXPERIMENTAL CONTROLS

E. 1. Experimental Control

We performed experimental control to ensure no detectable concentration of arsenic were present in our sediment samples.

Table E. 1. Control experiments

Electrolytes	Sediment concentration	As detected (ppm) by ICP
0.01M NaCl	3.0 g	0.00
0.01M NaHCO ₃	3.0 g	0.00

E. 2 Method Validation

We run arsenic analysis on reagent (0.01M NaCl and NaHCO₃) mixed with 3.0 g of sediments to test whether any arsenic trace elements in the sediment samples. Based on the results, on average trace amount of arsenic is almost negligible in the sediment samples.

In our experiment, we did continuous testing by repeating the same standard as an unknown at least for 3 or 4 times for each experiment. If we get the same values over time, it means a good result. We always used a reagent blank as a blank. In our case, we used 0.01 M NaCl as the blank since we also used it to dilute our standards. We also did recovery testing by analyzing the standards as unknowns and using the matrix-matched standards and reagent. The average differences are about ~5% between the standards and the standards as unknowns (Table E.2)

Table E.2. Calculation for % differences for standards and standards as unknowns.

Experiments	Known standards (ppm)	Unknowns (detected by ICP-OES) (ppm)	Differences (%)
Kinetic experiments	1.0077	1.0	1.60%
	1.0077	1.0	1.50%
	1.0077	1.0	1.60%
Equilibrium experiments	1.0077	1.0	1.50%
	1.0077	1.0	1.60%
	1.0077	1.0	1.50%
	1.0077	1.0	1.30%
	1.0077	1.0	0.10%
	3.0061	3.0	0.80%
	3.0061	3.0	3.50%
NOM-Equilibrium	3.0061	2.9	7.50%
	2.0087	2.0	3.43%
	2.0087	2.0	0.74%
	2.0087	1.9	6.14%
Metal loading experiments	2.0087	1.9	6.02%
	2.0087	1.8	19.52%
	2.0087	1.8	23.09%
		2.1	9.68%
		Average	5.06%

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