Arsenic Adsorption and Desorption in Storrie Lake Sediments

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Abstract

At pH 8, As adsorbed linearly with increased As concentration from 2 to 63 ug/L in the initial solutions. Sediment As adsorption was not affected by the reaction time from 0.25 to 48 hours, indicating that adsorption kinetics occurred rapidly. When the same reaction times and As concentrations were set at pH 5, there was no significant difference in the amount of sediment As adsorbed when compared to the reaction time and the As concentration in solution. Therefore, pH 8 is a more effective adsorptive process than pH 5. Arsenic adsorption and desorption reactions are influenced by other variables such as redox reactions, presence of competing anions, and solid-phase structural changes at the atomic level.

Background and Significance of Study

Over 18,000 people depend on the Gallinas Watershed with three reservoirs, including Storrie Lake, for drinking water. Previous studies found that total recoverable arsenic in stream water samples is strongly correlated with total suspended solids (R^2 = 0.98).   The source originates from Permian and Cretaceous shales that underlie a large area (>50%) of the Gallinas Watershed. Storrie Lake is located in this area where soil arsenic concentrations up to 10 mg/kg (ppm) have been fund (Kaysing, Lindline). It would be helpful to the City of Las Vegas to determine and quantify arsenic adsorption/desorption between the sediment and water. The result will be an indication of potential arsenic contamination in the lake.

Storrie Lake is located 5 miles north of Las Vegas, San Miguel County, New Mexico. It is an artificial reservoir that covers about 1,100 acres. The dam was built in 1921 for the purpose of storing irrigation water, and at present serves as a recreational area and drinking water for the city. The water is diverted to the drinking water treatment plant of Las Vegas for purification. It is fed by flood waters from the Gallinas River, and from the surface runoff in the immediate area.

Overview of Arsenic

Epidemiological studies have shown inorganic arsenic to be carcinogenic, causing higher incidences of respiratory, skin and liver cancers as well as cancers of the GI tract. Arsenic compounds in underlying bedrock and weathered materials are the primary sources in soil and water.

Arsenic (As) is defined as a poisonous metalloid that has three prominent <u>allotropic</u> forms: yellow (molecular non-metallic), black (metalloid) and gray (metalloid). The <u>density</u> of the yellow form is 1.97 g/cm^3; rhombohedral 'gray As' is much denser with a density of 5.73 g/cm^3; the other metalloidal forms are similarly dense. Metalloids usually have properties of metals and nonmetals, but As possesses intermediate electronegativity which results in the formation of oxyacids rather than free cations. Its boiling point (614 ºC) is lower than its melting

(817 ºC) point at atmospheric pressure, resulting in sublimation (O'Neill, 1990; Buckingham, 1984; Goessler et al., 1997; Lippmann, 2001; Thornton and Farago, 1997).

Arsenate is very similar chemically to phosphate and competes for adsorption sites on minerals and even enzyme binding sites. (Frankenberger, 2002). It occurs in several oxidation states (-3, 0, +3, and +5), but +3 and +5 are the most common forms in the environment (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). Like phosphorus, As forms a reactive, gaseous hydride, arsine (AsH_3), which is the most toxic As compound detected in hot springs and anaerobic wastewater treatment facilities (Michalke et al., 2000). When heated in air, it oxidizes to As trioxide. The fumes from this reaction have an odor resembling garlic. This odor can be detected on striking arsenide minerals, such as arsenopyrite, with a hammer. They are brittle semiconductors with a metallic luster.

Speciation determines how As compounds interact with their environment. The behavior of arsenate and arsenite in soil differs with changes in soil physical and chemical properties. Movement in environmental matrices is a strong function of speciation and soil type. In a non-absorbing sandy loam, arsenite is 5–8 times more mobile than arsenate (Gulens et al., 1979). Soil pH also influences As mobility. At a pH of 5.8 arsenate is slightly more mobile than arsenite, but when pH changes from acidic to neutral to basic, arsenite becomes more mobile than arsenate. The mobility of both arsenite and arsenate increases with increasing pH (Gulens et al., 1979). In strongly adsorbing soils, transport rate and speciation are influenced by organic carbon content and microbial population. Both arsenite and arsenate are transported at a slower rate in strongly adsorbing soils than in sandy soils. Appendices A and B show the naturally occurring inorganic and organic As species of environmental significance.

Geochemistry of Arsenic

Arsenic is ubiquitous in nature, and As levels are often elevated by mining and industrial and agricultural activities (Meharg et al., 1994 and 2002). Naturally occurring As is commonly found in volcanic glass in volcanic rocks of rhyolitic to intermediate composition; adsorbed to and coprecipitated with metal oxides, especially iron oxides; adsorbed to clay-mineral surfaces; and associated with sulfide minerals and organic carbon (Welch et al., 1988). Sulfide minerals can contain As either as a dominant mineral-forming element or as an impurity; sulfide minerals are found in North America in the Western Cascades (U.S. Geological Survey, 1969). Arsenic compounds are constituents in over 200 minerals, ranging in concentrations from a few parts per million to percentage quantities. These are classified as arsenates (60%), sulfides and sulfosalts (20%), with arsenides, arsenites, silicates and elemental As composing the remainder. Table 1 shows some common arsenicals (O'Neil, 1990).

Table 1. Common Arsenicals.

	Examples	Chemical Formula
Arsenates	Scorodite	$FeAsO_4 \cdot 2H_2O$
	Mimetite	$Pb_5(AsO_4) \cdot Cl$
Sulfosalts	Tennantite	$(Cu,Fe)12As_4S_{13}$
	Energite	Cu_3AsS_4
Sulfides	Realgar	AsS, As_2S_2
	Orpiment	As_2S_3
	Arsenopyrite	$FeAsS$
Arsenites	Trippkeite	$CuAs_2O_4$

Arsenic is common in many mineral deposits, such as iron pyrite, galena, and chalcopyrite and is less common in sphalerite. Arsenopyrite is the most abundant As mineral (Thornton and Farago, 1997; O'Neill, 1990).

Arsenic in Sediment and Soil

Arsenic in underlying bedrock and weathered materials is the primary source in soil. The process of weathering may free As from rock in the form of arsenious acid and As acid salts. Generally, soils contain higher levels of As than rocks. Unpolluted soils usually contain from 1-40 mg/kg of As. Due to the affinity of As towards organic matter, sandy soils and granitic soils may have lower concentrations, while alluvial and organic soils may have much higher levels (Table 2). Soil and groundwater affected by geothermal activity tend to have higher concentrations of As, indicating that geothermal heat can also force As from minerals in the ground (Kabata-Pendias and Pendias, 1984; O'Neill, 1990; Thornton and Farago, 1997). High levels of As are present in some agricultural soils due to extensive use of arsenicals in pesticides, herbicides, and fungicides (Yan-Chu, 1994). Historical use of inorganic arsenicals, such as $NaAsO_2$, in agriculture has resulted in contaminated orchard soils. In Spain, these soils are frequently used for tomato and bean growing (Carbonell-Barrachina, 1992, 1995a, 1995b).

Weathering at the Earth's surface usually takes place under oxidizing conditions, forming oxyanions of the pentavalent oxidation state. Under reducing conditions, arsenate (+5) is slowly converted to arsenite (+3). In terms of thermodynamic stability, the pentavalent forms of As acid (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$ and AsO_4^{-3}) predominate at normal soil pH values of 4-8. Redox potential (Eh) values of less than +300 mV at pH = 4 and −100 mV at pH = 8 (in the absence of complexing species and methylating organisms) tend toward the thermodynamic stability of arsenious acid (H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{-2}$) of the trivalent oxidation state (O'Neill, 1990; Thornton and Farago, 1997). Figure 1 summarizes As speciation in soil under various Eh-pH values at 25°C, 1 atmosphere (Ringwood, 1996).
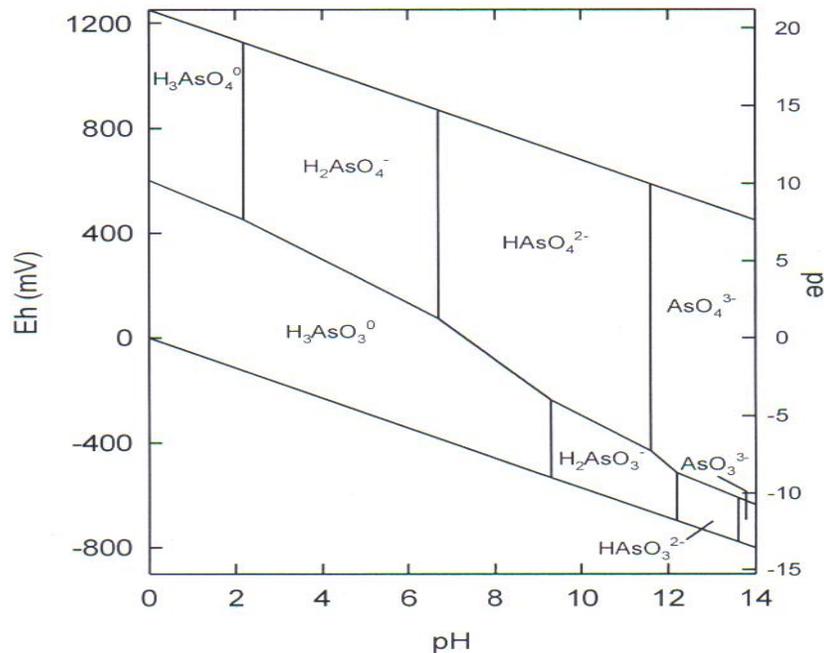
Figure 1. Arsenic Speciation Diagram with Respect to Eh-pH Values (Ringwood, 1996).

Soil As can undergo a variety of reactions: oxidation-reduction (Brannon and Patrick, 1987; Masscheleyn et al., 1991) and methylation-demethylation (Brandon and Patrick, 1987). Methylated As oxyacids can be produced by a variety of microorganisms, and their presence has been reported in a wide range of soils, sediments, and waters (Masscheleyn et al., 1991). Inorganic arsenicals may also change oxidation states (solely or in combination with the inorganic processes described above) via metabolism by soil microorganisms, including yeasts and bacteria. This metabolism occurs on the surfaces of soil particles or suspended particles in aqueous environments. Resulting products under aerobic conditions may be monomethylarsonic acid ($CH_3AsO(OH)_2$), dimethylarsinic acid (or cacodylic acid, $(CH_3)_2AsO(OH)$) and trimethylarsenic oxide ($(CH_3)_3AsO$), and under anaerobic conditions, volatile and highly toxic and flammable methylarsine gases: trimethylarsine ($(CH_3)_3As$) and dimethylarsine ($(CH_3)_2AsH$). Trimethylarsine gas is spontaneously flammable in air (Chapman and Hall, 1984). Clay minerals, organic matter and the presence of iron and aluminum oxides interfere with As oxidation rates and solubility as well as leaching rates. Arsenic's oxidation states largely govern its soil reactions according to the above factors. Mobility is dependent on the stability of the parent minerals and the electrochemical properties of the elements involved. Arsenic sorbed to Fe and Al containing minerals is the exception to this, becoming available if these soils are hydrolyzed with the reduction of soil potential (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). The World Health Organization (WHO) has listed naturally occurring inorganic and organic As species of environmental significance (WHO, 2001).

Table 2. Arsenic in Surface Soils of the United States (Kabata-Pendias and Pendias, 1984).

Soil Type	[As] Range (ppm dry wt.)	[As] Mean (ppm dry wt.)
Sandy soils and lithosols on sandstones	<0.1-30.0	5.1
Light loamy soils	0.4-31.0	7.3
Loess and soils on silt deposits	1.9-16.0	6.6
Clay and clay loamy soils	1.7-27.0	7.7
Alluvial soils	2.1-22.0	8.2
Soils over granites and gneisses	0.7-15.0	3.6
Soils over volcanic rocks	2.1-11.0	5.9
Soils over limestone and calcareous rocks	1.5-21.0	7.8
Soils on glacial till an drift	2.1-12.0	6.7
Light desert soils	1.2-18.0	6.4
Silty prairie soils	2.0-12.0	5.6
Chernozem and dark prairie soils	1.9-23.0	8.8
Organic light soils	<0.1-48.0	5.0
Forest soils	1.5-16.0	6.5
Various soils	<1.0-93.2	7.0

Lake Sediment Sampling and Experimental Design

Storrie Lake sediment samples were collected with a stainless steel Petite Ponar dredge 150mm x 150mm (6" x 6") and sample volume 2400 mL at sampling site location 35°39'57.69"N; 105°14'15.77"W. The sampling site was near the dam of the reservoir at a depth of approximately 4.5 m.

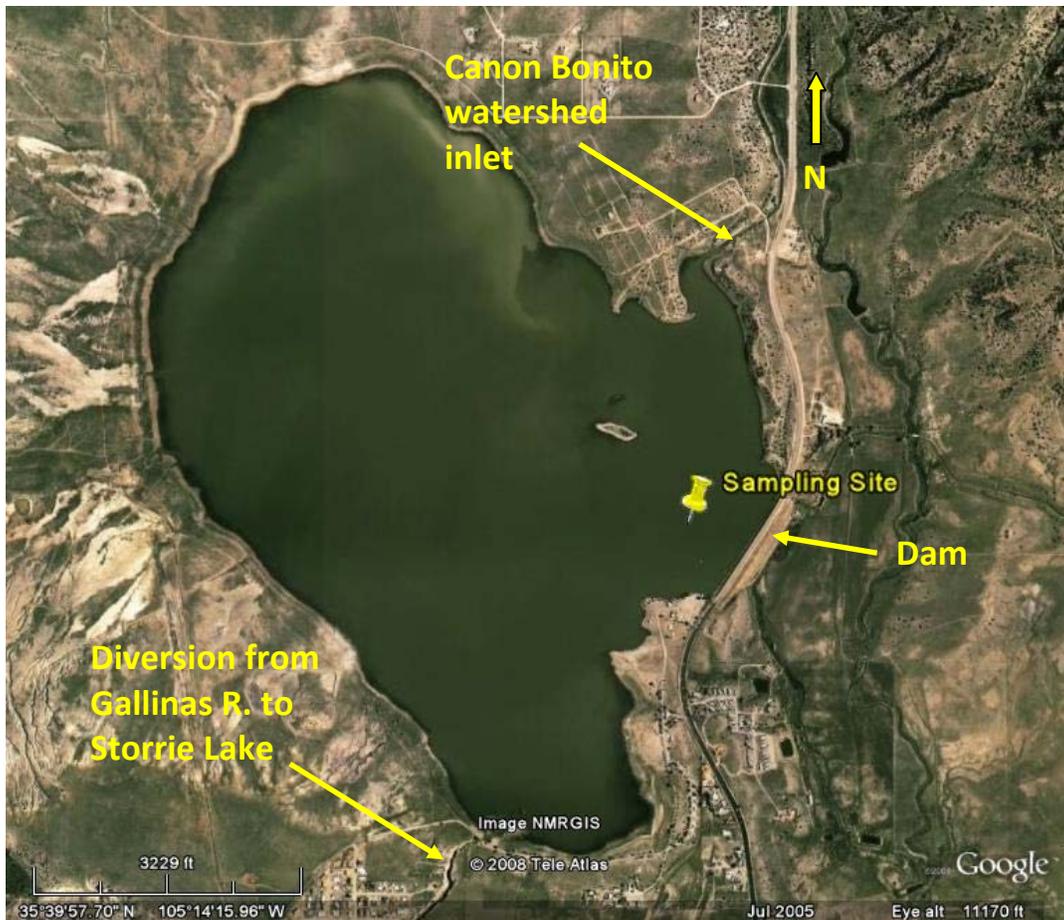**Figure 2. Storrie Lake with sampling equipment.**

Figure 3. Storrie Lake and sampling location.

Two studies were designed to determine the sediment adsorption/desorption capacity. Five initial concentrations of 2, 8, 18, 63, µg/L As (V) were prepared in 0.01M KNO_3 background solution to maintain a constant ionic strength. The pH of all the samples were modified to that of the lake, which has an average pH of 8. In the second study, the pH of each of the As concentrations (2, 28, 33, 63 µg/L) were changed to 5. The batch experiment consisted of mixing approximately 6 g of sediment to 28 mL of arsenate solution in 50mL centrifuge tubes. Each treatment was performed in triplicate and shaken in a reciprocal shaker at 150 rpm. After reaction times of 0.25, 6, 24, and 48 hours in study 1, the samples were centrifuged at 4000 rpm. The reaction times were changed to 2, 8, 12, and 24 hours in study 2. Inductively Coupled Plasma Mass Spectrometer (ICP-MS; at NMSU, Dr. April Ulery) was used to determine the residual arsenic content in solution.

Results and Discussion

Study 1 indicated a significant increased in As adsorbed with increased As concentration (P = 0.00001) (Figure 4). Sediment As adsorption is not affected by the reaction time (P = 1.000) indicating that adsorption kinetics occurred rapidly (Figure 5). Therefore, if Storrie Lake should

experience a spike in arsenic level, As will be continuously adsorbed by the sediment, until equilibrium is reached.

Statistical analysis of study 2 showed that there is no significant difference in the amount of sediment As adsorbed when compared to the reaction time (P = 0.06) and the As concentration in solution (P = 0.41).

Comparing both studies, study 1 is a more effective process because much more As is removed from solution than study 2. Therefore, pH played a very important role in adsorption. When the pH was changed from 8 to 5, the adsorptive capability of the sediment decreased significantly.

Arsenic adsorption and desorption reactions are influenced by other variables such as redox (reduction/oxidation) reactions, presence of competing anions, and solid-phase structural changes at the atomic level.
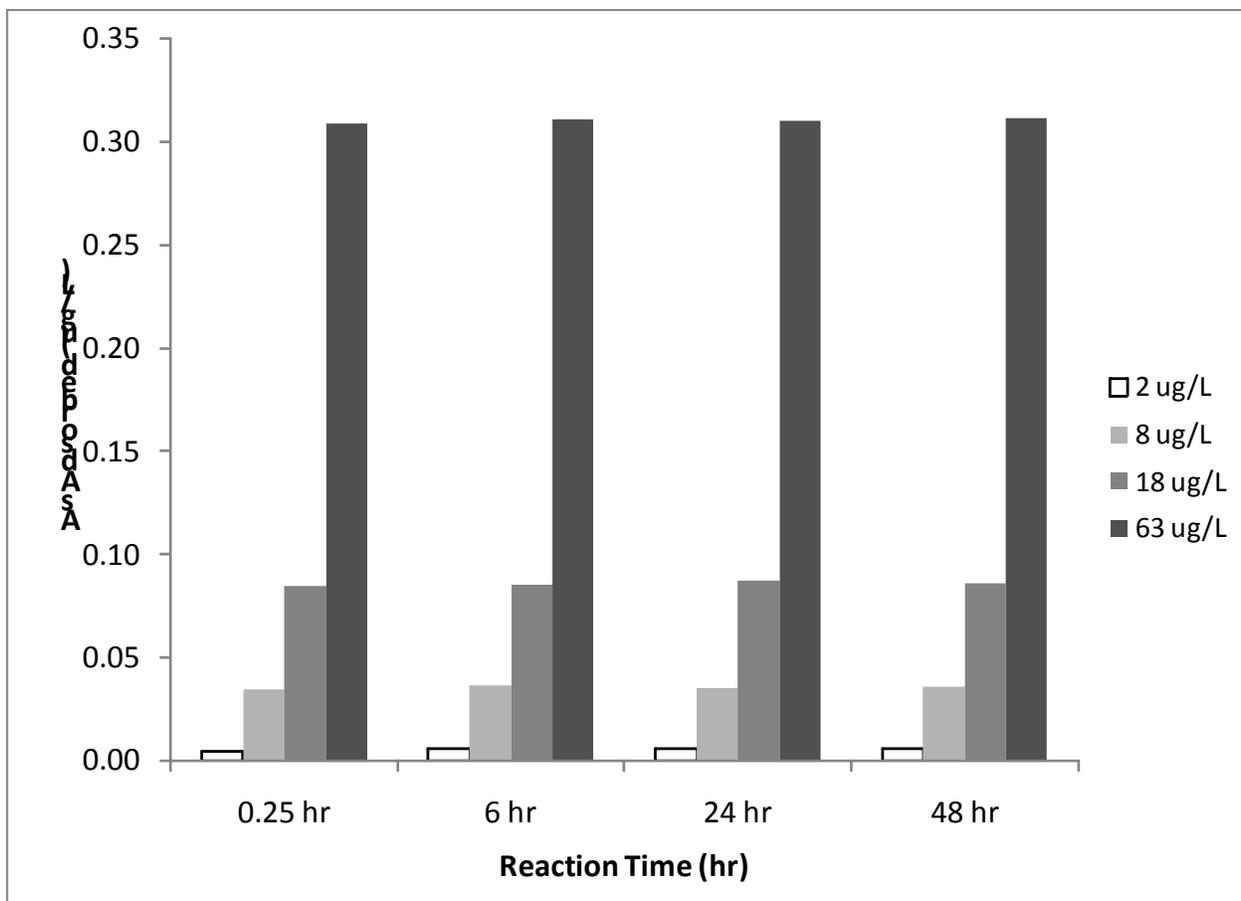

Figure 4. Sediment arsenic adsorption vs. initial standard solution concentrations; pH 8 (study 1). Adsorption results between all standards were significantly statistically different.
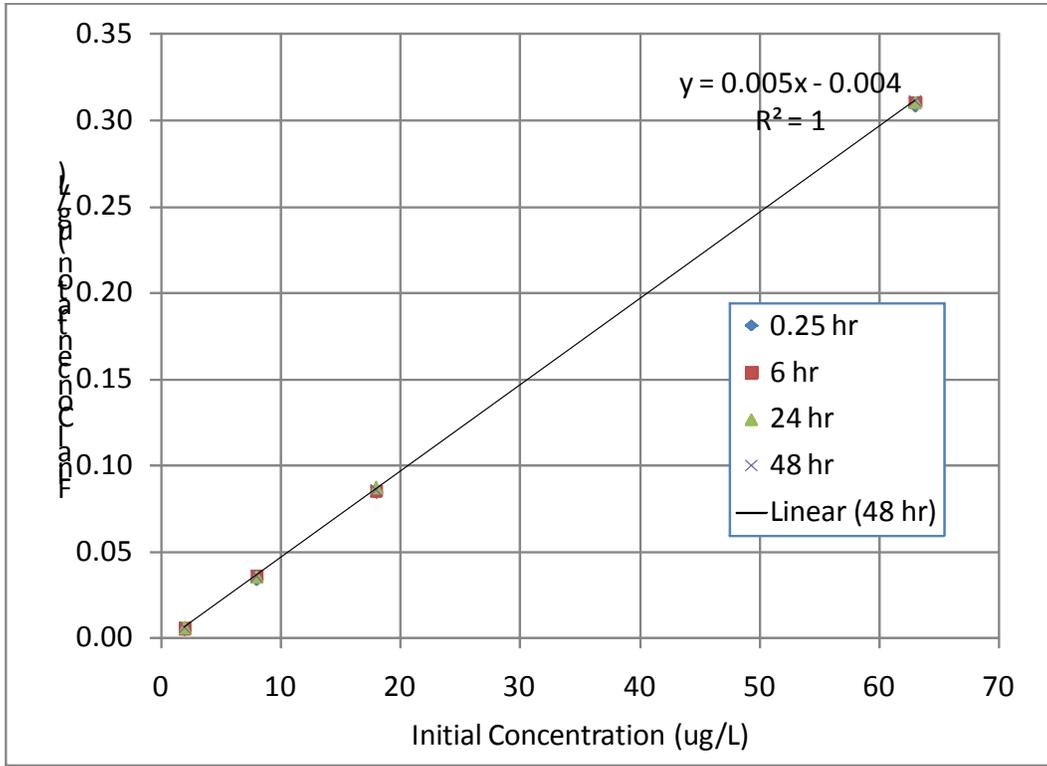
Figure 5. Final solution concentration vs. initial solution concentration; pH 8 (study 1).

$y = 0.005x - 0.004$

$R^2 = 1$

- 0.25 hr
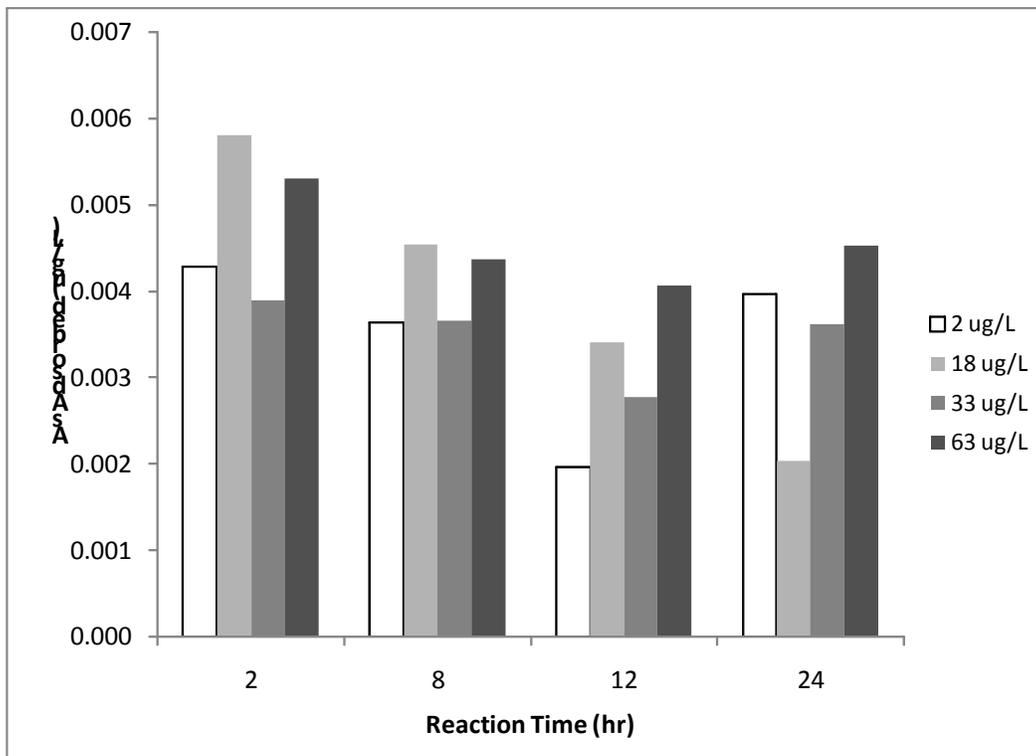- 6 hr
- 24 hr
- 48 hr
- Linear (48 hr)

Figure 6. Sediment arsenic adsorption vs. initial standard solution concentrations; pH 5 (study 2). Adsorption results between all standards were significantly statistically different.

- 2 ug/L
- 18 ug/L
- 33 ug/L
- 63 ug/L

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