Adsorption and Desorption of Arsenate on Sandy Sediments from Contaminated and Uncontaminated Saturated Zones: Kinetic and Equilibrium Modeling

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Abstract

Application of empirical models to adsorption of contaminants on natural heterogeneous sorbents is often challenging due to the uncertainty associated with fitting experimental data and determining adjustable parameters. Sediment samples from contaminated and uncontaminated portions of a study site in Maine, USA were collected and investigated for adsorption of arsenate [As(V)]. Two kinetic models were used to describe the results of single solute batch adsorption experiments. Piecewise linear regression of data linearized to fit pseudo-first order kinetic model resulted in two distinct rates and a cutoff time point of 14 to 19 h delineating the biphasic behavior of solute adsorption. During the initial rapid adsorption stage, an average of 60-80% of the total adsorption took place. Pseudo-second order kinetic models provided the best fit to the experimental data ($R^2 > 0.99$) and were capable of describing the adsorption over the entire range of experiments. Both Langmuir and Freundlich isotherms provided reasonable fits to the adsorption data at equilibrium. Langmuir-derived maximum adsorption capacity (S_t) of the studied sediments ranged between 29 and 97 mg/kg increasing from contaminated to

uncontaminated sites. Solid phase As content of the sediments ranged from 3.8 to 10 mg/kg and the As/Fe ratios were highest in the amorphous phase. High-pH desorption experiments resulted in a greater percentage of solid phase As released into solution from experimentally-loaded sediments than from the unaltered samples suggesting that As(V) adsorption takes place on different reversible and irreversible surface sites.

Capsule Abstract

The adsorption of As on sandy sediments is described best by a pseudo-second order kinetic model. The Langmuir isotherm model is sensitive to the contamination history of the sediments.

1. Introduction

Consumption of groundwater contaminated with inorganic arsenic (As) is one of the principal pathways for chronic human exposure, increasing the risk of cancers as well as other negative health effects (Kapaj et al., 2006).

Mobility of As in the environment is primarily controlled by adsorption onto solid surfaces including oxides and hydroxides of metals such as iron (Fe) and aluminum (Al), layer silicates and clays, metal carbonates, and solid organic matter. These natural adsorbents have different levels of affinity for As adsorption depending on various factors such as surface properties, aqueous speciation of As, redox condition, pH, and competing ions (Stollenwerk, 2003; Smedley et al., 2002). The mechanism of As adsorption on metal oxides is believed to be through formation of inner-sphere monodentate and bidentate complexes (chemisorption) based on spectroscopic evidence and zeta-potential measurements (Manning and Goldberg, 1996; Hiemstra and Riemsdijk, 1999; Goldberg and Johnston, 2001; Sherman and Randall, 2003; Lakshmipathiraj et al., 2006).

Adsorption of trace level contaminants such as As on solid phases has been described by both mechanistic surface complexation models (SCMs) and empirical isotherms. SCMs predict the adsorption phenomenon by defining complexation reactions and equilibrium constants between solutes and surface functional groups, and incorporating a description of electrical double layer theory. This definition covers the chemical ligand exchange reactions and also accounts for the attractive/repulsive electrostatic forces dependent on the sorbent surface charges (Antelo et al., 2005). Commonly used SCM's include the Diffuse Double Layer model (DDLm), the Constant Capacitance model (CCM), the Triple Layer Model (TLM) and Charge Distribution-Multisite Complexation model (CD-MUSIC).

Empirical adsorption isotherms on the other hand, are mathematical equations that relate the concentration of adsorbed species on the solid phase at equilibrium to the concentration of adsorbate in the bulk solution without describing the chemical and electrostatic mechanisms of retention. Due to ease of use, empirical models are widely used for modeling adsorption data. However, application of empirical models can be challenging due to the uncertainty associated with fitting experimental data and determining adjustable parameters.

Modified empirical isotherm equations have been applied in lieu of using the more complex SCMs (Jeppu et al., 2012) and for application in transport models (Radu et al., 2008).

A great number of studies have focused on use of isotherm equation for describing the adsorption of phosphate on soils and sediments and to a lesser extent on As adsorption. The majority of studies on As adsorption have been conducted on synthetic pure metal oxide minerals or on coated materials for application in water treatment technologies. There are only a handful of studies available on adsorption of As on natural soil and sediment samples (Manning and Goldberg, 1997; Zhang and Selim, 2005; Stollenwerk et al., 2007; Robinson et al., 2011; Jung et

al., 2012; Goldberg and Suarez, 2013;) highlighting the need for further studies. It is worth noting that the methodology and details used for conducting adsorption experiments are critical for interpreting and comparing the data. A search in the published literature shows that there is a wide variety of experimental details among adsorption studies. These experimental details include: reaction time, gas composition, method of pH control, background electrolyte composition and concentration, solid/solution ratio, and method of mixing.

An important yet understudied factor is the kinetics of adsorption on natural sorbents. There is very little information available on kinetics of As adsorption on natural sediments. Many studies have selected arbitrary reaction times for conducting the adsorption experiments without a justification presented. It is necessary to study the kinetics of As adsorption in order to both establish a reaction time sufficient for achieving equilibrium but also for determining the kinetic rate constants. This information will be useful not only in designing equilibrium isotherm experiments but also for modeling other batch and column experiments. Column studies can be very useful for studying the reactive transport of As within a subsurface porous medium however an understanding of the adsorption kinetics will be required for modeling such data.

In this study, adsorption of arsenate, As(V), on nine sediments collected from various locations and depths at a study site in Maine, USA was investigated. The objectives of this study were: (1) to characterize the kinetics of As(V) adsorption on sediments; (2) to compare empirical adsorption models for describing the adsorption of As(V) on natural sediments as a function of aqueous concentration; (3) to study the relation between the adsorption capacity of sediments and the solid phase distribution of major elements determined from chemical sequential extractions; and (4) to determine the rates of As(V) desorption from contaminated and uncontaminated sediment.

2. Materials and Methods

2.1. Sediment Samples

The study site is located in Maine, USA and has a history of contamination. A groundwater plume with elevated pH and high levels of PO_4^{3-} and As was detected in the early 1990's. The sample locations in 2014 were categorized by dividing the study site into three areas: 1) an upgradient portion within the plume (impacted upgradient), 2) a downgradient portion within the plume (impacted downgradient), and 3) further downgradient beyond the current extent of the plume (un-impacted). Three sediment samples from different depths of the saturated zone of each area were collected in 2014, making a total of nine distinct samples in this study (Table 1). Sediments from locations within the plume have been in contact with groundwater enriched in As (61-604 $\mu\text{g/L}$). Arsenic levels in groundwater from un-impacted sites were all below 10 $\mu\text{g/L}$. Arsenate [As(V)] is the predominant species in the oxidizing groundwater at this study site. Sediment samples were stored in sealed zip lock-bags upon collection and shipped in coolers on ice. All sediment and groundwater samples were stored refrigerated (4°C) in the dark until use. Sediments were air-dried and <2mm fractions were used in all experiments. The natural pH of sediments was determined by suspending 5 g of sediment in 12.5 mL of de-ionized water and measuring the suspension pH after 1h of shaking and 0.5 h of stabilization. The water and organic content of the sediments were estimated by measuring sequential loss on ignition (105°C for 24h, 440°C for 12 h). Surface areas of samples were measured by N_2 and Kr adsorption isotherm using Micromeritics ASAP 2020 instrument by Brunauer–Emmett–Teller (BET) method. Particle size distribution was determined using the USDA (1972) method by drying 50 g of sediment and soaking in a sodium metaphosphate solution overnight followed by hydrometer measurements at standardized time increments.

2.2. Analytical Methods

All lab-ware and containers were soaked in 1.2N HCl for 24 h and rinsed with Milli-Q water five times prior to use. All solutions were prepared using Milli-Q water (18M Ω) purified by NANOpure deionization system. All chemicals used were of laboratory reagent grade (99.99% pure). pH of solutions was measured using an Acumet Basic AB 15 pH meter, calibrated regularly with standard pH buffer solutions (4, 7, and 10).

Total As concentration in filtered solutions was measured by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) (Perkin Elmer AAnalyst 700) with an electrodeless discharge lamp (EDL). All samples were preserved with 2%v/v HNO₃, refrigerated if not measured immediately, and analyzed in triplicates. 20 μ L of sample plus 5 μ L of matrix modifier (Pd(NO₃)₂ + Mg(NO₃)₂) was used for each measurement. The instrument was calibrated on a daily basis with minimum of five standard solutions (5-100 μ g/L) prepared fresh from an As stock solution (Perkin Elmer). The analyses were conducted in triplicate and the relative standard deviations of measurements were below 5%. All experiments were conducted at least in duplicate. The average value reported and the relative percent difference between the duplicates did not exceed 15%.

2.3. Batch Kinetic Adsorption Experiments

Commonly used empirical isotherm models such as the Langmuir and Freundlich are based on equilibrium assumption, however in natural environments often equilibrium conditions are not achieved. Therefore, understanding the kinetic behavior of As adsorption on natural sediments is important.

Sediments from five locations S-6, S-7B, S-10, S-11, and S-12 were used to study the kinetics of As(V) adsorption at pH 7. In the first round of kinetic experiments, initial As(V) concentrations (C₀) of 0.5, 5, and 10 mg/L were used for S-10, S-6, and S-7B sediments respectively. The

electrolyte solution, solid/solution ratio, shaking and sampling methodology were same as those used for isotherm experiments, mentioned below. Samples were collected between 4 and 144 h reaction time.

In the second round, 25 g of un-impacted sediments S-10 and S-11 were added to 250 mL of background solution with three levels of As(V) (0.5, 1, 2.5 mg/L). These initial concentrations are selected to be relevant to contamination situations encountered in the field. Suspensions were sealed and placed on an orbital shaker and 1 mL samples were withdrawn at different time intervals (0.1-216 h) and syringe filtered (0.45 μ m) into pre-acidified (2% HNO₃) vials. The pH and volumes of the suspensions were kept constant throughout the course of the experiment.

2.4. Batch Adsorption Isotherm Experiments

Single solute adsorption experiments were conducted in duplicate by equilibrating 3g of sediment samples with a background electrolyte solutions (0.1M NaCl, 5mM HEPES) in polypropylene centrifuge tubes using a 1 g:10 mL solid/solution ratio. Sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O, Sigma-Aldrich, ACS reagent grade) was used to prepare stock solutions (1000 ppm) and the serial dilutions needed. Initial concentrations (C₀) used in the experiments were 0.05, 0.1, 0.5, 1, 2.5, 5, 10, 15, and 30 mg/L.

Arsenate adsorption on environmental surfaces is more favorable in the pH range 4 to 7 (Dixit and Hering, 2003) and tends to be limited at higher pH values due to increased repulsive forces between the negatively charged As oxyanion species and the predominantly negatively charged solid particles. Several studies on soils and sediments have shown adsorption maxima for As species near pH 7 (Stollenwerk et al., 2003), therefore the adsorption experiments in this study were conducted at pH 7 in order to obtain estimations for the maximum adsorption capacities at a commonly observed pH value in subsurface systems.

pH of the suspensions was adjusted prior to addition of As(V) and maintained at 7 throughout the experiment by addition of 0.1N HCl or 0.1N NaOH. Preliminary kinetic tests showed that a mixing time of 7 days was needed to reach equilibrium. The suspensions were placed on rotary shakers in room temperature (25°C) for the course of the experiment. At the end of the 7-day experiment, the sediments were separated from solutions by centrifuging the suspensions at 7800 rpm for 15 minutes. Supernatants were syringe-filtered through 0.45 µm disposable MCE filters (EMD Millipore), acidified with HNO₃ (2%), and refrigerated until analysis.

In preliminary experiments few methods such as use of chemical buffers and maintaining a constant gas pressure were tested. The method selected for the adsorption experiments in this study was to use 5mM of HEPES buffer in the electrolyte solution. The electrolyte solution was added to the sediment and the pH of the suspension was adjusted after 1h and again after 12 h of shaking time and prior to addition of As(V). Kanematsu et al. (2012 and 2013) have used 1mM of HEPES in conducting As(V) adsorption isotherm experiments and have demonstrated that HEPES buffer does not affect the data even at low concentrations.

2.5. Sequential Extraction and Desorption Experiments

Three chemical extraction steps were conducted on the sediments sequentially in order to characterize the solid distribution of As and other major elements. The amorphous Fe oxides were extracted by hydroxylamine-hydrochloride for 0.5 h (0.25 M NH₂OH. HCl in 0.25 M HCl at 50° C) followed by a 72-h hydroxylamine extraction targeting the more crystalline Fe phases. The last step was the hot acid total digestion (EPA 3050B). The extracted solutions were analyzed for Al, As, Ca, Fe, and P by ICP-MS.

Desorption experiments were carried out on all nine fresh sediment samples as well as on selected sediments following the completion of adsorption isotherm experiments. In order to induce high-pH desorption, sediments were equilibrated with 1.44x10⁻² M NaHCO₃ / 2.8x10⁻³ M

Na₂CO₃ (pH 9.5) for 7 days using the 1:10 ratio (Kohler et al., 2004). The 7-day reaction period was determined based on the results of preliminary kinetic experiments. These preliminary experiments were conducted with and without presence of phosphate (5 mg/L) in the system.

3. Results

3.1. Arsenic Adsorption Kinetics

Results of the preliminary experiments on S-6, S-7B and S-10 sediments (data not shown) indicated that 144 h is a sufficient equilibration time for the adsorption experiments on sediments.

Results for un-impacted S-11 and S-12 show a rapid initial adsorption within the first 12 h followed by a more gradual rate until equilibrium was reached at approximately 216 h. The gradually slower adsorption observed over time is related to the decrease in the difference between the concentration in solution and surface (Banerjee et al., 2008). The amount of As(V) remaining in solution versus time at different initial concentrations for sediments S-11 and S-12 is displayed in Figure 1.

Both sediments demonstrated similar overall patterns; however, S-11 exhibits a range of 12 to 22% higher adsorption rate compared to S-12 over the course of the experiment. This finding is consistent with the higher maximum sorption capacity determined for S-11 from isotherm experiment results, which will be presented in following sections.

The equilibrium adsorption rates decrease with increasing initial aqueous phase As concentration. In case of S-11, maximum adsorption achieved at the three initial As(V) levels of 0.5, 1, and 2.5 mg/L, were 96%, 93%, and 80% respectively. Sediment S-12 achieved smaller equilibrium adsorption rates of 89%, 77% and 54% at the three levels used.

Percentage of the total As(V) adsorption achieved in the first 12 h was 80%, 70%, and 64% for S-11 and 67%, 63%, and 60% for S-12 indicating a decreasing trend with increasing initial

concentration. The percentages of total adsorption that occurred after 48h were 6%, 12%, 19% for S-11 and 14%, 17%, 18% for S-12. These result indicate that the As(V) adsorption kinetics become slower with increasing concentration in solution and therefore the adequate reaction time needed for reaching equilibrium state in such studies is an important factor at higher initial concentrations.

There are several kinetic models which have been implemented in the literature for fitting adsorption data on different solid surfaces (Ho and Mckay, 1998; Zhang and Selim 2005; Banerjee et al., 2008; Maji et al., 2008; Oke et al., 2008; Guo et al., 2010; Neupane et al., 2014). These models will be presented below and compared for fitting the data for S-11 and S-12 sediments.

3.1.1. Pseudo-first Order Kinetic Model

The pseudo-first order equation has been used in two forms based on the aqueous concentration (Banerjee et al., 2008), and based on the solid sorption capacity (Maji et al., 2008). These two forms are briefly described below and applied to the results.

In the aqueous based model, the adsorption reaction can be considered as

where C_{aq} stands for concentration of adsorbate in solution (eg. As_{aq}), S represents a generic surface site, and $S-C_s$ is the cocnetration of adsorbed species. Given the fact that the concentration of adsorbent is orders of magnitude greater than the solute and remain unchanged, the pseudo-first order equation can be expressed as

$$\frac{dC_t}{dt} = -k'_1 C_t$$

where C_t is the aqueous concentration at time t and k'_1 is the pseudo-first order rate constant (h^{-1}).

Integrating and applying the boundary conditions at $t=0$ and $t=t$ results in the form

$$\ln \left[\frac{C_t}{C_0} \right] = -k'_1 t$$

where C_0 is the initial solute concentration at $t = 0$. The model can be fitted using plot of $\ln[C_t/C_0]$ versus time and linear regression. Analysis of the results (Figure 2) indicates that two distinct slopes are present. A piecewise linear regression method was applied in STATA 12.0 (StataCorp LP, College Station, TX) using least-squares estimation to fit the results and estimate the cutoff time point (t_c) which refers to the time at which the slope change occurs. The piecewise linear regression method yields satisfactory fitting of the data ($R^2 > 0.98$, $RMSE \leq 0.15$, $P < 0.01$) for S-11 and S-12 sediments at the three C_0 levels studied. The average cutoff time point is 18.4h for S-11 and 16.6h for S-12. The t_c parameter and the two slopes (kinetic rate constants) derived are presented in Table 2. It can be seen that the rate constants after t_c are one order of magnitude smaller than the rate constants before t_c illustrating the transition from the initially fast to the slower and gradual adsorption rate.

The second form of pseudo-first order model based on Lagergren equation (Singh et al., 1988) and considering the adsorbed concentrations is written as

$$\frac{dq_t}{dt} = k'_1(q_e - q_t)$$

where q_t and q_e are the adsorbed concentration (mg kg^{-1}) at time t and at equilibrium (ie. adsorption capacity). After integrating and applying boundary conditions the equation becomes

$$\ln[q_e - q_t] = \ln[q_e] - k'_1 t$$

Therefore a linear plot of $\ln[q_e - q_t]$ versus time would indicate a good fit for this model. However as indicated by others (Ho and McKay, 1998), this model in most cases does not fit the data well over the entire range of contact time. In addition, the main disadvantage of this model is that it depends on adsorption capacity (q_e) to be known which in most cases is not effectively known

and this subsequently introduces uncertainty to the model. In order to fit to data, one needs to either assume or determine the value of equilibrium sorption capacity (q_e) which could become problematic in some cases.

The pseudo-first order Lagergren model was applied to the data in this study using the equilibrium adsorption capacity at the final time point, however both linear and piecewise linear regressions did not improve the fits ($R^2 < 0.94$).

3.1.2. Pseudo-second Order Kinetic Model

The pseudo-second order equation does not have the disadvantage mentioned for the Lagergren equation and can be used to determine the parameters without prior knowledge of sorption capacity (Ho et al., 2006).

A number of studies have used the pseudo-second order reaction model (Jang et al., 2003; Ho and Ofomaja, 2006; Oke et al., 2008; Guo et al., 2010) to fit adsorption kinetic data. The kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k'_2(q_e - q_t)^2$$

where k'_2 is the rate constant of pseudo-second order adsorption ($\text{kg mg}^{-1} \text{ h}^{-1}$). Applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, the integrated and rearranged equation can be written as

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k'_2 q_e^2}$$

Therefore, a linear plot of t/q_t versus time would indicate that data follow this kinetic model. Figure 3 shows that the pseudo-second order model provides excellent fits to the experimental data ($R^2 > 0.99$, $P < 0.01$) in all cases.

Term $k'_2 q_e^2$ can be regarded as the initial adsorption rate, h ($\text{mg kg}^{-1} \text{ h}^{-1}$) as $t \rightarrow 0$. Table 3 lists the parameters derived from the pseudo-second order kinetic model. The values of k'_2 for As(V)

adsorption ranged between 0.07 and 0.006 kg/mg.h at Site 11 and between 0.04 and 0.01 kg/mg.h at Site 12 decreasing with increase of C_0 .

3.2. Adsorption Isotherms

The most commonly used adsorption isotherms are the Langmuir and Freundlich equations which are empirical but with rational basis. The Langmuir equation is based on these assumptions: only a monolayer surface coverage is considered, adsorption takes place at independent sites, and adsorption sites are equivalent.

The advantage of the Langmuir isotherm over the Freundlich isotherm is the ability to derive a maximum sorption capacity parameter which makes it more appealing for application in soils and sediments adsorption studies. However, the premise of a homogenous adsorbent surface, essential to the Langmuir isotherm, is not a valid assumption for heterogeneous materials such as soils and sediments. On the other hand, the Freundlich model allows for multi-layer adsorption and includes an empirical parameter (n) that accounts for heterogeneity of surface sites with different adsorption energies.

In the current study, these commonly used isotherm equations are applied to model the adsorption data.

3.2.1. Freundlich Isotherm

The Freundlich isotherm is one the most commonly used empirical models to fit adsorption data (Lin and Wu, 2001; Badruzzaman et al., 2004; Zhang and Selim, 2006; Boddu et al., 2008) and is expressed as

$$S = K_f C^n$$

where K_f is the Freundlich constant, C and S stand for equilibrium solution (mg L^{-1}) and sorbed (mg kg^{-1}) concentrations, and n is a dimensionless parameter representing heterogeneity of the sorption sites. This parameter is usually less than one and accounts for the different adsorption

sites. At $n=1$, the Freundlich equation becomes a linear adsorption model and K is the partition coefficient. The Freundlich equation is generally linearized in order to fit data as follows

$$\log S = n \log C + \log K_f$$

The Freundlich isotherm model was applied to the experimental adsorption data (Figure S.1, supplementary material) and the adjusted parameters are presented in Table 4. The Freundlich isotherm fit the data well and the fitting parameter n ranged from 0.42 to 0.59 with a mean of 0.49. A positive correlation ($R^2 = 0.62$, $P = 0.01$) between the derived Freundlich constant and the amorphous Fe content was found suggesting the importance of Fe oxides in adsorbing As.

3.2.2. Langmuir Isotherm

Parameters derived from the Langmuir equation describe the adsorption affinity (K , L mg^{-1}) and maximum adsorption capacity (S_t , mg kg^{-1}).

$$S = S_t \frac{KC}{1 + KC}$$

Conventionally, the Langmuir equation would be transformed to a linear form and fitted to the data. However, as shown by Bolster and Hornberger (2008), linearized forms of the Langmuir equation needlessly limit modeling of adsorption data and therefore their use in soil and sediment studies should not be pursued. These limitations include sensitivity to variability in low levels of S , clumping of data points, overestimation and underestimation of correlation between the transformed linearized variables.

Results of the Langmuir model non-linear regression fits to the experimental data for six of the studied sites are illustrated in Figure 4. Table 5 lists the parameters derived from Langmuir fits using least squares regression analysis. The S_t values ranged between 29 and 97 mg/kg with the un-impacted sites having higher average capacity than the sites within the plume. The affinity constant K ranged between 0.2 and 2.7 L mg^{-1} .

The un-impacted sites (S-10, S-11, S-12) yielded the highest S_t values and consequently largest number of surface sites for As(V) adsorption. On the other hand, the impacted upgradient sites (S-5, S-6, and S-13) where the highest levels of historical contamination have occurred are the least adsorptive sites with smallest S_t values.

3.3. Desorption Experiments

Preliminary desorption kinetic experiments were conducted on selected sediments from the three major areas of the site (S-5, S-9, S-11). Similar to the adsorption experiments, a minimum equilibrating time of seven days was needed to reach steady state for dissolved concentrations of As(V). These experiments were conducted with and without the addition of 5 mg/L $\text{PO}_4\text{-P}$. As expected, presence of PO_4 increased the desorption rates between 13 to 43% (Figure S.2, supplementary material).

Desorption experiments conducted on the sediments after the conclusion of isotherm experiments showed that an average of 48 % of the adsorbed As(v) was released back into the solution from the solid phase across the spiked concentration levels. Significantly smaller rates of As(V) desorption were observed from the original samples as shown in Table 6. The difference in desorption rates between fresh and spiked sediments could be attributed to the role of different surface sites involved in reversible and irreversible adsorption reactions.

Comparison between the rates of desorption from fresh sediments and sediments spiked with As(V) indicate that the majority of solid phase As is present in non-reactive sites further suggesting that the attenuation of mobile As in the plume by the sediments have been relatively insignificant. The desorption experiments were conducted 7 days after the conclusion of adsorption experiments. Studies have shown that the adsorbed species diffuse into the solid matrix of sorbent phases over time. Only a weak correlation ($R^2 = 0.55$, $P = 0.02$) between the

amount of As desorbed from sediments and solid phases associated with the amorphous Fe oxides exists.

3.4. Sequential Extractions

Percentages of solid phase distribution of As, Fe and P for the nine studied sediments are presented in Figure 5 (data for Al and Ca presented in Figure S.3, supplementary material).

Amorphous and crystalline extractions accounted for between 19 and 36% of the total Fe content. Majority of P extracted from sediments was associated with the amorphous phase and crystalline fraction only represented 3 to 10% of the solid P content.

None of the sediments studied exhibited levels of As greater than the global average concentration of 1-10 mg/kg. This indicates that the inhibiting geochemical factors such as the high pH and significant phosphate competition present at this site, limited the adsorption of As(V) mobilized into the groundwater by the sediments in the path of the contaminated plume. The As/Fe and P/Fe molar ratios for the three extracted fractions are compared in Figure 6. The density of As in the amorphous fraction is generally higher than in the crystalline and recalcitrant fractions. Amorphous phases are known to have high affinity for adsorption and accumulation of As and other contaminants. A similar trend is observed for phosphate with higher P/Fe ratios observed in the amorphous fraction and the majority of total solid phase P was present in that fraction. Comparison between P/Fe and As/Fe ratios indicates that phosphate is adsorbed or associated with the amorphous phase at a much higher density than As and therefore is outcompeting As.

4. Discussion

4.1. Effect of Time

While the pseudo-second order kinetic model provided the best fit to the experimental data and was capable of describing the adsorption over the entire range of experiments, the pseudo-first

order kinetic models indicate that adsorption of As(V) on sediments takes place in two distinct phases. Initially the reactive sites are occupied quickly, indicated by a fast initial adsorption rate and then a more gradual adsorption continues until an equilibrium is reached at approximately 7 days.

The reaction times used in adsorption studies can vary widely (Limousin et al., 2007) depending on the type of solid surfaces studied. The adsorption of As species on variety of pure solids such as synthesized and natural minerals, or synthetic adsorbent materials for application in water treatment has been extensively studied. The reaction times applied in these kinds of studies are generally between 4 and 48 hours (Manning and Goldberg, 1996; Dixit and Hering, 2003; Kundu et al., 2004; Kanel et al., 2005; Gimenez et al., 2007; Bauer and Blodau, 2006) while several studies have used longer reaction times reporting between 5 and 18 days to reach equilibrium (Badruzzaman et al., 2004; Dadwhal et al., 2011).

However, there is greater variability among the reaction times used in adsorption studies on soils and sediments as these surfaces are heterogeneous and more complex. Zhang and Selim (2005) performed batch isotherm experiments on soils for 24 h while Goldberg and Suarez (2013) used a reaction time of 2 h when studying As(V) adsorption on alluvial sediments. Manning and Goldberg (1997) studied As(III) and As(V) adsorption on three different soil types by equilibrating suspensions for 16 h, citing Pierce and Moore (1982) that showed 99% of adsorption take place within 4 h. Stollebwerk et al. (2007) conducted batch experiments and determined that As adsorption on oxidized sediments collected from Bangladesh reaches equilibrium in 2 days. For their batch As(V) adsorption isotherm experiments, Robinson et al. (2011) equilibrated the sediment and solution mixtures for 14 days. Borgnino et al. (2012) reported adsorption of As(V) on clastic sediments reaching equilibrium after 140 h (6 days).

Kinetic results in this study show that although a significant amount of total adsorption occurs within the initial 14-19 hours of reaction, the gradual increase in the adsorbed As(V) concentration between 48 h and final equilibrium is significant (6-19%). Therefore it is necessary to conduct preliminary kinetic experiments in order to determine the required reaction time for reaching adsorption equilibrium when studying sediments.

4.2. Adsorption Isotherms

The adsorption process is a highly pH dependent phenomenon, therefore requiring that pH of sediment suspensions remain constant at the target level throughout the adsorption experiment. Due to the heterogeneity of sediment grains and potential presence of carbonate minerals such as calcite in the solid matrix and significant buffering, this task becomes more challenging when conducting experiments on natural samples. The experimental methodology used in this study was successful in obtaining reproducible adsorption results by maintaining a constant pH and solid/solution ratio throughout the duration of the experiments.

The maximum adsorption capacity determined in the isotherm experiments is an important finding that can be incorporated in surface complexation and reactive transport models. In this context, the Langmuir isotherm is preferred over the Freundlich equation as it includes the S_t fitting parameter. Results of this study show that the Langmuir isotherm can be used in practical environmental applications such as assessing the natural attenuation of sediments at a contaminated site.

A difficulty in interpreting the adsorption experimental data with the Langmuir isotherm model is making an appropriate distinction between the monolayer adsorption capacity of the sediments and multilayer retention resulted from surface precipitation occurring at higher concentrations of solutes. Lack of an explicit plateau indicating the saturation of surface sites as the solute

concentration increases is a common phenomenon in adsorption studies. Additional experimental evidence such as using spectroscopic techniques are needed for determining the sorption mechanisms at the solid-solution interface. Therefore it is important to have a rational basis for selecting the range of aqueous concentrations in an adsorption experiment in order to avoid possible overestimation or underestimation of adsorption capacities.

There have been several modifications to the Langmuir equation to account for the effects of pH, competition for sorption sites, pre-adsorbed solutes and heterogeneity of adsorbent phases (Jeppu et al., 2012; Zhou et al., 2005; Bradl, 2004; Rau et al., 2003; Turiel et al., 2003). An example is the Langmuir-Freundlich isotherm which includes an index of heterogeneity (n) that can vary from 0 to 1 depending on the heterogeneity of the sorbent medium. However, the Langmuir-Freundlich equation is often too flexible due to higher number of fitting parameters (S_t , K , n) and results in non-unique solutions (Chu, 2002).

4.3. Effect of Chemical and Physical Properties on Adsorption Capacity

Strong positive correlations between As adsorption and Fe, Al, and clay content of soils have been reported in the literature (Smedley and Kinniburgh, 2002).

In order to investigate relationships between the chemical and physical characteristics of the sediments and the adsorption capacity values derived from the Langmuir models, univariate linear regression analyses were conducted. The parameters studied were sediments particle size distribution, natural pH, Surface area measurement (BET), concentration of dissolved As(V) at each sample site, solid phase distribution of Al, As, Ca, Fe and P.

No statistically significant relation between the sediment characteristics and adsorption capacity was found among all samples studied. However, generally the adsorption capacity of studied sediments increased with the distance from the contamination origin and towards downstream areas with the un-impacted sediments having the highest derived Langmuir S_t .

Although there were no significant relationships observed between sediment characteristics and adsorption capacity, there was a trend for increased adsorption capacity of sediments with higher amorphous Al and Fe oxide content, and BET surface area at the downstream and unimpacted sites (Figure 7).

The observed trends are that the adsorption capacity tends to increase with increasing Fe and Al content and BET surface area as expected. However these factors do not adequately describe the variation of adsorption capacity values across all sites. The lack of statistically significant correlation between the adsorption capacity and sediment physical/chemical parameters could be due to the fact that the studied sediments have generally similar characteristics and also the relatively limited number of samples.

These results indicate that predicting the adsorption capacity of heterogeneous phases such as sediments may not be solely possible based on general chemical and physical characteristics, and may require incorporation of data from additional mineralogical and spectroscopic studies.

As illustrated in Figure 6, P/Fe ratios were lowest in the three un-impacted sites (S-10, S-11, and S-12) where the highest adsorption capacity for As was observed. The fact that the contamination plume has significant phosphate concentrations (8-9 mg/L) reinforce the evidence for competitive adsorption at the impacted sites. The main parameter correlating with the As adsorption capacities observed in this study is the location and historical exposure of the sediment to the contamination plume. It can be inferred that the elevated phosphate levels in the plume have decreased the adsorption capacity of sediments for As by occupying the available surface sites.

5. Conclusions

Understanding the rates and controlling factors for adsorption of contaminants such as As on natural sediments aids in effective design and implementation of remediation schemes for contaminated soils and groundwaters. However, there are many challenges associated with interpretation of the experimental adsorption results on heterogeneous sorbents using the empirical models.

In this study, the pseudo-first order equation was not capable of fitting the kinetic adsorption data over the entire range of reaction time as also indicated by other studies (Guo et al., 2010; Banerjee et al., 2008; Oke et al., 2008). However, piecewise linear regression model was applied to fit the plots of $\ln [C/C_0]$ versus time in order to estimate the reaction rate (k_1) for two distinct stages of reaction and describe the biphasic behavior of solute adsorption. Pseudo-second order kinetic model provided the most accurate fit to the experimental data without requiring knowledge of a pre-determined equilibrium adsorption maximum.

The highest level of As(V) adsorption capacity observed among the studied sediments was an S_t value of 97 mg/kg at Site 10, with which is located in the un-impacted zone of the study site. Only moderate correlations were observed between the maximum adsorption capacity and sediment chemical compositions such as Fe and Al content or physical properties such as BET surface area.

The sequential extractions provided evidence that the highest As/Fe molar ratio exists in amorphous phases with exception of one sediment. Also, the majority of P on solid phase is present in the amorphous phase outcompeting As.

Lower rates of desorption were observed from fresh sediments versus sediments loaded with As(V), indicating that the existing solid phase As was mostly associated with non-reactive or

irreversible surface sites as opposed to more reactive surface sites occupied during the isotherm experiments.

The adsorption maximum capacities and kinetic rates derived from this study can be used in reactive transport models to simulate column experiments for better assessing in-situ remediation strategies.

517 **Figures**

Figure 1. As(V) concentration remaining in solution versus time for S-11 and S-12 with different initial concentrations (C_0) of 0.5, 1, and 2.5 mg/L

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Figure 2. Plots of $\ln(C/C_0)$ versus time for S-11 with (A) $C_0=0.5$ mg/L, (B) $C_0= 1$ mg/L , (C) $C_0=2.5$ mg/L, and for S-12 with (D) $C_0= 0.5$ mg/L, (E) $C_0=1$ mg/L , (F) $C_0=2.5$ mg/L. Dashed lines represent piecewise linear regression fits.

Figure 3. Plots of t/q versus time for S-11 and for S-12. Lines represent linear regression fits.

Figure 4. Langmuir isotherm fits to adsorption data for impacted upgradient sites (S-5 and S-13), impacted downgradient sites (S-7B and S-9), and un-impacted sites (S-10 and S-11).

Figure 5. Solid phase distribution (%) of As, Fe, and P among the three extracted phases (amorphous, crystalline and recalcitrant).

Figure 6. Molar ratios of As/Fe and P/Fe extracted from the different solid phases.

Figure 7. Comparison between the Langmuir S_t parameter and adsorptive chemical and physical characteristics of sediments (amorphous Fe, amorphous Al, and BET surface area). Bars represent the sediment characteristics and lines with markers represent the Langmuir S_t parameter.

566 **Tables**567 **Table 1.** Chemical and physical properties of sediments

Sediment	Depth	pH	Surface Area (m ² /g)	Clay (%)	Sand (%)	Silt (%)	USDA Classification	Water Content (%)	Organic Content (%)	Notes
Impacted Upgradient										
S-5	23-27.5	9	2.44	6.19	89.81	4.00	sand	22.1	2.3	brown fine sand
S-6	29-37	9.2	3.45	12.39	69.78	17.84	sandy loam	11.2	1.7	gray sandy till
S-13	34-44	9.1	2.1	4.15	94.57	1.28	sand	21.6	2.4	brown fine to medium sand
Impacted Downgradient										
S-7A	43-49	8.3	2.7	9.51	78.48	12.01	sandy loam	22.2	2.1	brown fine sand
S-7B	49-58	8.3	1.43	4.18	92.54	3.28	sand	9.7	2.1	brown coarse sand
S-9	47-56	8.1	1.92	7.50	88.50	4.00	loamy sand	22.5	2.2	brown fine to coarse sand
Un-impacted										
S-10	51-58	8.7	3.9	9.50	88.50	2.00	loamy sand	21.9	1.7	gray fine to medium sand
S-11	46-56	7.7	2.93	5.20	92.50	2.30	sand	15.4	2.4	brown fine to medium sand
S-12	48-58	7.7	1.26	6.85	90.66	2.49	sand	22.5	2.3	brown fine to medium sand

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569 **Table 2.** Pseudo-first order kinetic model parameters obtained from piecewise linear regression.

Sediment	S-11					S-12				
	R ² *	RMSE**	t _c (h)	K' _{1 < t_c} (h ⁻¹)	K' _{1 > t_c} (h ⁻¹)	R ² *	RMSE**	t _c (h)	K' _{1 < t_c} (h ⁻¹)	K' _{1 > t_c} (h ⁻¹)
C ₀ = 0.5 mg/L	0.9832	0.15	17.83	-0.0950	-0.0068	0.9914	0.07	18.00	-0.0533	-0.0053
C ₀ = 1 mg/L	0.9880	0.12	19.34	-0.0813	-0.0063	0.9885	0.08	14.19	-0.0554	-0.0032
C ₀ = 2.5 mg/L	0.9915	0.05	17.92	-0.0405	-0.0038	0.9892	0.04	17.52	-0.0268	-0.0013

570 *P < 0.01

571 ** Root mean square error (RMSE) is a measure of average difference between modeled and experimental data and

572 indicates goodness of fit.

573 **Table 3.** pseudo-second order kinetic model parameters obtained from linear regression.

Sediment	S-11				S-12			
	R ² *	h (mg/kg.h)	K' ₂ (kg/mg.h)	q _e (mg/kg)	R ² *	h (mg/kg.h)	K' ₂ (kg/mg.h)	q _e (mg/kg)
C ₀ = 0.5 mg/L	0.9998	1.69	0.0717	4.85	0.9987	0.76	0.0377	4.49
C ₀ = 1 mg/L	0.9965	0.80	0.0083	9.84	0.9975	0.89	0.0145	7.82
C ₀ = 2.5 mg/L	0.9975	2.60	0.0063	20.28	0.9989	1.92	0.0100	13.87

574 * $P < 0.01$

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576 **Table 4.** Freundlich adsorption isotherm model parameters.

	Freundlich Parameters		
	K _f (mg/kg)(L/mg) ⁿ	n	R ² *
S-5	11.64	0.4852	0.9625
S-6	21.29	0.5077	0.9652
S-13	9.96	0.586	0.9591
S-7A	29.77	0.4745	0.9086
S-7B	14.16	0.4157	0.9592
S-9	13.58	0.5209	0.9497
S-10	24.58	0.4972	0.9755
S-11	27.04	0.4808	0.9446
S-12	14.83	0.4579	0.958

577 * $P < 0.01$

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583 **Table 5.** Langmuir adsorption isotherm parameters.

Sediment	Langmuir Parameters		
	Fit 1		
	K(L/mg)	S _t (mg/kg)	R ² *
S-5	1.03	28.53	0.962
S-6	1.12	52.23	0.976
S-13	0.25	42.31	0.948
S-7A	2.74	67.05	0.956
S-7B	0.12	70.64	0.949
S-9	0.15	72.23	0.969
S-10	0.28	97.20	0.974
S-11	0.40	91.84	0.956
S-12	0.26	74.12	0.94

* $P < 0.05$

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585 **Table 6.** Arsenic desorption rates from original and As-loaded sediments (before and after
586 adsorption experiments)

Sediment	Desorbed from fresh samples		Desorbed from sediments loaded with As (% of adsorbed)							
	(mg/kg)	(% of As in Amorphous phase)	C ₀ (mg/L)							
			0.05	0.1	0.5	1	2.5	5	10	15
S-5	0.07	4.3	-	-	-	-	49.8	44.6	55.2	50.7
S-6	0.26	16.3	-	-	-	-	45.4	54.3	58.8	51.6
S-13	0.08	4.4	-	-	-	-	68.9	42.4	41.9	38.3
S-7A	0.99	21.6	-	-	-	-	41.6	53.2	46.7	50.1
S-7B	0.50	9.2	-	-	-	-	55.6	49.7	43.9	33.2
S-9	0.47	13.7	50.2	52.3	48.3	49.2	-	52.0	39.1	35.5
S-10	0.25	16.4	32.9	34.1	49.1	42.4	-	56.5	57.2	52.7
S-11	0.46	10.0	68.1	42.4	44.7	38.7	-	53.8	60.4	48.7
S-12	0.32	9.1	-	-	-	-	-	44.2	38.7	34.8

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