Title

Geochemical modeling of reactions during the titration of groundwater with arsenic-contaminated and uncontaminated sediments

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by

Jacquelyn Rose Lam

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ABSTRACT OF THE THESIS

Geochemical modeling of reactions during the titration of groundwater with arsenic-contaminated and uncontaminated sediments

by

Jacquelyn Rose Lam

Master of Science in Civil Engineering
University of California, Los Angeles, 2016
Professor Jennifer Ayla Jay, Chair

Titration experiments and geochemical modeling can be performed to study the effects of pH on groundwater chemistry. This study focused on the effect of acidification on mineral dissolution to identify the type of mineral that is responsible for the buffering of pH in groundwater. The study site consists of arsenic- contaminated and uncontaminated regions of the saturated zone of an aquifer. Alkalinity titrations were carried out on contaminated and uncontaminated samples followed by geochemical modeling using PhreeqC Interactive 3.1.7-9213. Artificial groundwater was made for each site in the study region based on constituent data collected by the monitoring wells and then mixed with the associated sediment for 24 hours. During titration, samples were collected at each increment to be analyzed for metals and phosphate. Results show that calcite is likely to be the buffering mineral and the model determined that it is present at 10^{-6} to 10^{-4} moles per 2 liters of solution. This work will be incorporated into a larger model used to predict the transport of arsenic in groundwater under remediation schemes.

The thesis of Jacquelyn Rose Lam is approved.

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1. **Introduction**

Geochemical modeling of contaminated aquifers can be used to predict the transport and behavior of contaminants and to help implement remediation strategies. Effective modeling requires a good understanding of the complex sediment-groundwater system and the numerous relevant geochemical reactions. The behavior of contaminants may be influenced by reactions including precipitation/dissolution, oxidation/reduction, complexation, ion exchange, adsorption and more, which may be heavily influenced by pH changes of the groundwater. For instance, the occurrence of acid mine drainage lowers the pH of groundwater, resulting in the increased mobility of contaminants. To better understand and predict the behavior of contaminants in aquifers, reactive transport models are implemented, taking into account the most predominant reactions governing the fate of the contaminants. In general, it is difficult to predict the exact behavior of contaminants in their natural groundwater environment due to the lack of comprehensive field data and the multifarious mechanisms through which contaminants can be altered, not only via geochemical reactions but by biological mechanisms as well. When studying the influence of minerals on contaminants, “the predictive ability of studies like these will always be limited by irreducible uncertainty in field-scale mineral dissolution kinetics rates and local-scale heterogeneity in aquifer mineralogy” (Keating, *et al.*, 2009).

This study focuses on an arsenic- contaminated site that is currently undergoing evaluation for the appropriate remediation strategy. To better understand the chemical characteristics of the site, alkalinity titration experiments were carried out on a mixture of sediment obtained from different locations at the site and synthesized groundwater matching the characteristics of each location. The goal of this experiment was to help identify the minerals that are likely to be responsible for the buffering of pH and the potential leaching of contaminants which will be useful for analyzing the change in arsenic and other metal concentrations over a wide range of pH values. The geochemical reactions that are of particular interest are the dissolution of carbonates and arsenic adsorption. Furthermore, previous studies by Hafeznezami *et al*. (2016) have been conducted on the adsorption of arsenic to the sediment at the same locations at the predetermined optimum pH level over time. The titration experiment of this study will be compared to previous data that have been collected on arsenic adsorption to establish a relationship between the minerals in sediment responsible for pH buffering, inorganic ions released due to pH changes and the amount of arsenic taken up. These reactions will be modeled and analyzed using modeling tool, PhreeqC Interactive 3.1.7-9213. Since mineralogical data are limited for this experiment, the results of this modeling are to be considered approximations rather than predictions.

2. Background

2.1. Carbonates in Groundwater

Extensive research has been carried out on the kinetics of trace elements concentrations (As, Mn, Pb, Fe, U etc.) due to mineral dissolution and precipitation in groundwater systems. It is well recognized that carbonate mineral precipitation and dissolution are major players in the control of groundwater chemistry, and a great amount of lab experiments as well as modeling work have been done to elucidate this phenomenon. Natural sources of groundwater acidity are the flux of CO_2 into groundwater, the dissolution of carbonate rocks by acidic groundwater, and the production of CO_2 via microbial activity. CO_2- consuming reactions in groundwater tend to be attributed to calcite or plagioclase dissolution (Keating *et al.*, 2010). Understanding dissolution/precipitation of such minerals is important in the study of the relationship between pH changes of groundwater due to these minerals' buffering capacity and the behavior of trace contaminants.

Another key influence of carbonate minerals relevant to this study is their involvement in the leaching of arsenic from its host rocks in aquifer sediment into the groundwater (Kim, *et al.*, 2000). In an anaerobic environment, bicarbonates drive the reductive dissolution of iron oxyhydroxides, also called iron oxides or ferrihydrite, that harbor arsenic species in groundwater, causing the release of arsenic species (Kim *et al.*, 2000). Experiments have shown that the amount of arsenic released is dependent on the concentration of sodium bicarbonate ($NaHCO_3$) and reaction time, with a higher leaching rate in anoxic deionized water and the lowest leaching rate in anoxic groundwater solution (Kim *et al.*, 2000). It is suggested that in anaerobic conditions, arsenic is held primarily in arsenic sulfides (e.g As_2S_3) and sulfosalts and react with bicarbonate to form arseno-carbonate complexes that leach into the water (Kim *et al.*, 2000). The dissolution reactions with bicarbonate and the formation of arseno-carbonate complexes are shown using orpiment (As_2S_3) as an example:

$$\mathrm{As_2S_3 + HCO_3^- \rightarrow As(CO_3)^+ + AsS_2^- + HS^-}$$

$$\mathrm{As_2S_3 + 2HCO_3^- \rightarrow As(CO_3)_2^- + HAsS_2 + HS^-}$$

$$\mathrm{As_2S_3 + HCO_3^- + 2H_2O \rightarrow As(CO_3)(OH)_2^- + HAsS_2 + HS^- + H^+}$$

$$\mathrm{HAsS_2 + H_2O \rightarrow HAsS_2(OH)^- + H^+}$$

(Kim *et al.*, 2000)

High levels of arsenic leaching are found to occur at extreme pH ranges of below 1.9 and between 8 and 10.4 (Kim *et al.*, 2000). High amount of leaching at extremely low pH is explained by acidic leaching and not by the influence of carbonates. Since pKa values indicate that HCO_3^- is dominant between pH 6.3 and 10.3 and $CO3^{2-}$ is dominant above pH 10.3, carbonate ions are likely to be the main leaching agent.

In general, the lowering of pH tends to mobilize trace metals, making the plume more difficult to manage and so the buffering capacity of carbonates is of great interest in studies of trace metal contamination in groundwater. However, this generalization does not apply in some cases such as arsenic contamination, where a reduction in pH creates a favorable surface charge at the adsorption sites for As sorption, but above the pH at which the host mineral dissolves. In this case the buffering of pH by carbonates is not desirable as it indicates greater amounts of required acid for the remediation.

Previous studies of acid mine drainage sites also indicate that the major solid phases influencing pH buffering and metal attenuation are carbonates and hydroxides. A higher pH would favor the precipitation of trace metals, making the addition of limestone and hydrated lime a good in-situ method for treating acid mine drainage (Bain *et al.,* 2001). Previous experiments have demonstrated that minerals responsible for pH buffering in aquifers, even in low quantities, can have an influence on the mobility of metal contaminants (Yong *et al.,* 1993; Rieuwerts *et al.,* 1998; Bain *et al.,* 2001; Knight, 2014). A system that contains calcite will be subject to pH buffering by the dissolution of calcite, resulting in an increase in pH, Ca, and alkalinity (Bain *et al.,* 2001). The increase in pH and alkalinity can subsequently lead to the formation of secondary mineral phases, most commonly Al- and Fe(III)-bearing phases such as siderite, gibbsite, goethite and amorphous iron oxyhydroxide (ferrihydrite), which could slow down the migration of Fe and Al ions (Bain *et al.,* 2001) and increase the amount of heavy metal retention (Yong *et al.,* 1993). The increase in Ca concentration could also result in the precipitation of gypsum

(Bain *et al.,* 2001). Bain's study describes the sequence of buffering in acidic water as follows: as calcite dissolves in the aquifer the pH is buffered near 6, as calcite gets depleted, siderite dissolves and buffers the pH near 5, as siderite gets depleted, the presence of gibbsite will buffer pH near 4 and finally after gibbsite gets depleted, the presence of ferrihydrite will buffer pH near 3. This decreasing pH trend could be due to the emergence of low-pH source water such as from acid mine drainage. While these reactions buffer low pH water, they also release metals that can travel further downstream and re-precipitate at a different location (Bain *et al.,* 2001).

The dissolution of calcite in water and the dissolution of calcite in an acidic environment (below pH 4-5), respectively:

$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$ Log K=-8.31

$$Ksp = \frac{[Ca^{2+}][CO_3{}^{-}]}{1} = 4.9 \times 10^{-9}$$

$CaCO_3 + H+ \leftrightarrow Ca^{2+} + HCO_3^{-}$ Log K=1.855

$HCO_3^{-} + H^{+} \leftrightarrow H_2CO_3$ Log K= 6.4

$$K = \frac{[H^{+}][HCO_3{}^{-}]}{[H_2CO_3]} = 10^{-6.4}$$

The dissolution of gibbsite:

$Al(OH)_3 + 3H^{+} \leftrightarrow Al^{3+} + 3H_2O$ Log K= 8.03

$\text{Log K} = \log a_{\text{Al3+}} + 3\text{pH} = 8.03$

$Al(OH)_3 + 2H^+ \leftrightarrow [Al(OH)]^{2+} + 2H_2O$ Log K= 3.63

Log K = log$a_{Al(OH)2+}$ + 2pH = 3.63

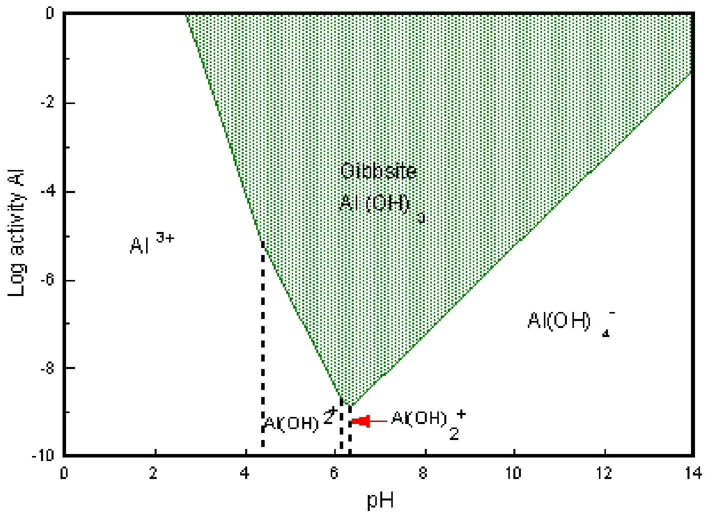
$Al(OH)_3 + H^+ \leftrightarrow [Al(OH)_2]^+ + H_2O$ Log K= -2.52

Log K = log$a_{Al(OH)2}$+ + pH = -2.52

$Al(OH)_3 + H_2O \leftrightarrow [Al(OH)_4]^- + H^+$ Log K= -15.24

Log K = log$a_{Al(OH)4}$- - pH = -15.24

Log activity-pH diagram for gibbsite:



Dissolution of siderite and ferrihydrite ($Fe(OH)_3$), respectively:

$FeCO_3(s) + 2H^+ = Fe^{2+} + CO_2(g) + H_2O$ Log Ksp= -10.8 to -11.2 (Silva *et al.*, 2001)

$$K_{so} * = \frac{[Fe^{2+}]pCO_2}{[H^+]}$$

$Fe(OH)_3$ (s) + $3H^+ \leftrightarrow Fe^{3+}$ + 3H2O   Log K= 3.2

$$Kso *= \frac{[Fe^{3+}]}{[H+]}$$

Under calcite-buffered and neutral pH environment downgradient of the plume, secondary minerals such as otavite ($CdCO_3$), $Cr(OH)_3$ and smithsonite ($ZnCO_3$) have the potential of forming, but when in contact with low pH water, they will dissolve, releasing aqueous phase metal cations (Bain *et al.,* 2001; Baker *et al.,* 2003; Harris *et al.,* 2003; Murray *et al.,* 2014). Additionally, many studies indicate that oxidation of sulfide minerals (e.g. pyrite) in mine wastes is one of the primary causes of the release of metals such as Co, Cu, Hg and Pb (Blowes *et al.,* 2003; Rios *et al.,* 2008; Murray *et al.,* 2014). Although chemical weathering of plagioclase and aluminosilicates could contribute to the buffering of groundwater, studies by Bain (2001) and Keating (2010) both suggested that their dissolution rates are much slower than that of carbonate minerals above a pH of 4, so it can be assumed that their influence is relatively minor.

Similar to the studies done on acid mine drainage, the buffering capacity of carbonates in this study is vital to understanding how arsenic will behave in the system. However, in this case buffering groundwater at a high pH is undesirable in the treatment of arsenic. Besides favoring the leaching of arsenic at a high pH, it also reduces the sorption of arsenic to iron oxyhydroxides in remediation efforts as will be discussed later. Therefore, alkalinity titrations were performed to study the extent to which calcite will buffer pH changes of groundwater and the amount of acid it will take to overcome the buffering effects.

2.2. Arsenic adsorption

Arsenic species in groundwater existing primarily as arsenite [As(III)] and arsenate [As(V)] are known to be toxic and carcinogenic, posing a threat to public health and the environment. The main source of arsenic in groundwater is arsenic-bearing minerals such as pyrite and arsenic sulfides and sulfosalts (Kim *et al.,* 2000). In an aquifer, the mobility of dissolved inorganic arsenic is largely controlled by sorption to sediment material in the aquifer, mainly oxyhydroxides such as iron oxyhydroxides (ferrihydrite), characterized as poorly crystalline oxides or amorphous oxyhydroxides (Jain *et al.,* 1999). Previous studies have shown a greater amount of sorption on amorphous Fe and Al-hydroxides than crystalline minerals such as hematite (Pierce *et al.,* 1982; Jain *et al.,* 1999; Gu *et al.,* 2002; Dixit and Herring, 2003). Iron oxyhydroxides are known to participate in sorption/desorption reactions and the charge of aqueous iron species varies with pH; $Fe(OH)^+$ dominates in lower pH environment and $Fe(OH)_3$ dominates in neutral or basic pH environment (Keating *et al.,* 2010).

The mechanism of arsenic adsorption occurs via ligand exchange of arsenic species for s-OH_2 and s-OH groups on the surface of adsorption sites, also known as a surface complexation reaction, forming bidentate binuclear complexes (Jain *et al.,* 1999). The level of adsorption is highly dependent on the pH of the environment and oxidation state of arsenic species. In general, ferrihydrite has a greater affinity for arsenic at a lower pH since the negatively charged arsenic species, especially As(V), are drawn to the positively charged hydroxylated surface (Jain *et al.,* 1999). At a low pH, Fe-O-As complex remains partially protonated, which will tend to retain negatively charged arsenic species (Jain *et al.,* 1999). Other studies have shown experimentally that the amount of As(III) adsorbed by ferrihydrite decreases at pH above 7, with a particularly greater pH dependence at high concentrations of As(III) (Pierce *et al.,* 1998). The adsorption of negatively charged arsenic species results in a surface with a net negative charge, thus increasing the pH will reduce further adsorption of more negatively charged arsenic species (Pierce *et al.*, 1998).

Previous studies in the past have had very similar results for the optimum pH range for arsenic adsorption. Pierce's (1998) study observes an optimum adsorption of As(III) at pH 7 and an optimum adsorption of As(V) at pH 4 at concentrations that typically exist in natural water. In another study, maximum adsorption in experiments containing both arsenic species is observed within a pH range of 7 to 9, with a decrease in adsorption at a high pH of 10 to 12 (Carrillo *et al.*, 1998). A more recent study decided that the optimum range of As(V) adsorption is pH 4 to 7 (Dixit and Hering, 2003). When pH exceeds 12, desorption of arsenic species from adsorption sites have been shown to occur (Carrillo *et al.,* 1998). Comparatively, As(III) is less adsorbed onto ferrihydrite than As(V) when subject to the same conditions (Carrillo *et al.*, 1998).

The concentration of arsenic adsorbed is commonly determined using empirical adsorption isotherms, which mathematically relate the concentration of species sorbed to the solid phase to the concentration of adsorbate in aqueous phase at equilibrium. An effective method of simulating the reactive transport of arsenic is via column experiments, but it is a highly time-consuming method. Recently, Hafeznezami *et al.* (2016) performed extensive arsenic adsorption batch experiments on these same samples in order to study the kinetics of arsenic adsorption and test the capability of various empirical adsorption models to describe actual observations. This study confirmed that amorphous ferrihydrite have a greater affinity for arsenic relative to crystalline and recalcitrant ferrihydrite, as shown in Figure 1. The sufficient length of equilibration time for the adsorption of arsenic was determined to be 144 hours (Hafeznezami *et al*., 2016). Hafeznezami's adsorption experiments were maintained at a pH of 7 based on previous studies that determined it to be the adsorption maxima, and the sediment of each site was spiked with different initial concentrations of As(V). Sites 11 and 12 experienced a rapid decline in aqueous phase As(V) for all initial concentrations during the initial 12 hours followed by a gradual decline until they reached equilibrium shown in Figure 2 (Hafeznezami, 2016). Dixit and Hering (2003) also studied the adsorption of As(V) at various initial concentrations, but over a broad pH range of 4 to 10 rather than at a constant pH. Figure 3 shows that for all initial As(V) concentrations, the amount of As(V) adsorbed is at a maximum at near pH 4 and declines at higher pH. For the highest concentration of above 2000 μmol/g the concentration-pH gradient experiences a steep decline from pH 4 to 10 (Fig. 3). For the lowest concentration of below 500 μmol/g, the concentration-pH gradient remains the same from pH 4 to 8 and then declines from pH 8 to 10 (Fig. 3).

As previous literature indicated, pH is a major controlling factor in arsenic adsorption, so this titration experiment could provide important information about how the arsenic levels at the site could change with the acidification of groundwater as well as how other minerals at the site could affect this adsorption by buffering the pH. The results of this study could provide insight into whether acidification is a good remediation strategy and the best way to implement this strategy if successful as well as potential consequences that could arise from this modification of conditions. Although there is a high level of predictability in the relationship between pH and the level of arsenic sorption to pure iron oxyhydroxide material in a simplified lab setting, natural groundwater systems are much more complex with the involvement of other reactions and constituents, requiring the aid of experimental work and geochemical modeling to make such predictions.

2.3. Geochemical Modeling Background

In order to effectively perform geochemical and reactive transport modeling for predictive purposes, a detailed mineralogical analysis of the site of interest is required (Bain *et al.,* 2001). Modeling results usually show some deviation from data due to the large simplification of the geochemical system, which means other mineral reactions and behaviors are neglected such as dissolution of secondary minerals, variability in mineral dissolution rates, and also errors in lab measurement, particularly pH measurements (Keating *et al.,* 2010). On the other hand, very simple geochemical models have been created with only the presumed dominating species and reactions with results consistent with the observed data. For instance, in Keating's model, a starting solution of NaCl is titrated with CO_2 in equilibrium with carbonate minerals, in which brine alkalinity and target saturation indices are adjusted until the partial pressure of CO_2 agrees with the measured value at the site, which sufficiently describes the general trend of the data with small amount of variations. Keating (2010)'s modeling of calcite dissolution results reflect that in the absence of calcite dissolution, pH depression is overestimated. Another challenge of modeling oftentimes is the lack of comprehensive information on the trace mineralogy at the site that would determine the future behavior of the trace contaminants (Bain *et al.,* 2001). With the lack of such information, the geochemical modeling that is done can only be treated as a sensitivity analysis with the presumed geochemical parameters as variables until the modeling results reveal the actual controlling parameters through comparison of model trends with observed data (Bain *et al.,* 2001). In this titration experiment, there are no available quantitative data on the minerals present in the samples, so the presumed presence of buffering minerals such as carbonates are variables in this sensitivity analysis. These results would not be enough for predictive modeling, but can be used to assess different potential behaviors and changes in the groundwater chemistry over time (Bain *et al.,* 2001).

In another study of geochemical modeling, an incident of acidic mine drainage is modeled to assess and predict the transport of contaminants in the aquifer. Water that is subject to acidic mine drainage is characterized by low pH and high metal and sulfate concentrations, which are affected by the site-specific mineralogy (Bain *et al.,* 2001). A different reactive transport model, MIN3P was used, which takes into account dissolution-precipitation, aqueous complexation, and oxidation-reduction reactions, yet similarly, it is acknowledged to be "limited by the availability of key geochemical parameters such as the presence and quantities of primary and secondary mineral phases" (Bain *et al.,* 2001), and therefore presents a limitation in the reactive transport model.

To avoid the errors and biases associated with making presumptions about the controlling reactions in adsorption of sediment through the mechanism of ion exchange, some studies utilize a method developed by Spalding and Spalding, which treats sediment material as a quadraprotic acid H4X with four log K values in order to measure cation and anion exchange capacity (Zhang *et al.,* 2008). This method is able to characterize the ion exchange capacity of sediment and the amount of adsorption sites by altering log K values in modeling program, HydroGeoChem v5.0 (HGC5), without assuming what type and initial amount of surface species are responsible for the mechanism (Zhang *et al.,* 2008). However, in this study, ion exchange is expected to have little relevance in arsenic adsorption and the amount of arsenic dissolved in the solutions is too low to warrant such a study, so this method will not be used. For the purpose of this study, PhreeqC will be used to determine how the dissolution of carbonate affects pH and the level of arsenic sorbed.

2.4. Study Site Background

Sediment samples used in this study are collected from six locations at a contaminated aquifer in Maine, USA. The aquifer is divided into three areas spanning the area of the plume and beyond; an impacted upgradient region, an impacted downgradient region and an unimpacted further downgradient region. Site 5 is from upgradient region, Sites 7 and 9 from impacted downgradient region and Sites 10, 11 and 12 from downgradient region beyond the plume. Sediment samples were collected in 2014 from the saturated zone at each location in contact with groundwater contaminated with total measured arsenic ranging from 61 to 604 μg/L. The level of arsenic in the unimpacted region is measured to be below 10 μg/L. The contaminated plume is deemed to be in an oxidizing environment, with As(V) as the predominant species of arsenic. The physical properties of the sediment samples are summarized in Table 1.

3. Methods

3.1. Titration Experiment Methods

Titration experiments were performed to simulate pH reduction in the soils at the field site, as acidification is a proposed remediation scheme. Artificial groundwater was synthesized for each of the six locations of interest, some from the impacted regions and some from the unimpacted region. The artificial groundwater solutions were made by adding salts bearing the major ions, Ca, Mg, K, Na, and HCO_3 to Milli-Q water (18 MΩ) such that their concentrations in solutions match those in the data collected by the monitoring wells at the six locations summarized in Table 2. However, when making artificial groundwater, it must be taken into account that the solution is in equilibrium with air, which would result in a different saturation of atmospheric gasses than that of groundwater residing in the aquifer which is not in equilibrium with air. This difference in saturation would result in a predictably lower alkalinity level. Thus, a modeling program, Visual Minteq 3.1, was used to generate the appropriate concentrations of bicarbonate to add to each solution given the specific atmospheric CO_2 pressure, pH value and concentrations of other ions to be added to the solution. The quantities of salts required were in general too small to be measured and added directly to the final solution, so they were in most cases, added by serial dilution and in a few cases, added directly to the final solution.

Prior to the final experiment, two smaller scale pre-experiments were run to get an estimation of the amount of acid required to titrate the pH of each site to 4.5 and to determine the estimated alkalinity corresponding to each pH increment. A 1:20 ratio of groundwater to sediment was used for the pre-experiments. The first pre-experiment involved 10 g of sediment in 200 mL of groundwater and the second pre-experiment involved 25 g of sediment in 500mL of groundwater. Only 10mL of samples were taken out at each pH increment to perform the alkalinity test.

For the final experiment, serial dilutions were made with 5 mL transfer from one vial to the next making up a final volume of 30 mL. The final volume of groundwater solution made for each site was 2 liters in either 2 liter glass beakers or 2 liter glass Erlenmeyer flasks. The pH level of each site was also adjusted by adding 0.1 N HCl or 0.1 N to 1N NaOH and measured using an Acumet Basic AB 15 pH meter to match the pH measured by the monitoring wells. Prior to the addition of sediment, an initial alkalinity test was performed for each of the sites to serve as a baseline against which the following alkalinity values will be measured after reaction with the sediment and titration with 1 N HCl. According to the predetermined sediment to groundwater ratio of 1:40, 50 g of sediment from each site was measured and added to the groundwater solution and stirred with a magnetic stir bar at a moderate speed to create a slurry for 24 hours to allow equilibration with the solution.

After 24 hours of mixing, the sediment was allowed to settle and the pH was measured and adjusted with 0.1N to 1N NaOH if it fell below the intended pH value. Based on the difference between the starting pH value and the end point of pH 4.5, six incremental pH values were determined. Small increments of 1N HCl between 3μL to 1000 μL was pipetted into the mixture to reach the next desired pH value depending on the requirement of the specific solution. After acidification, a 45 minute mixing time with a magnetic stir bar was given between increments, with adjustments made during that period if the pH deviated too much. The total amount of acid added was recorded at each increment. After 45 minutes of mixing, the pH was measured and recorded. After that, 10 minutes of settling was allowed and then the pH was measured again since pH readings fluctuate over time. Some sites experienced a greater amount of fluctuation than others. The final pH values used to summarize the data are the averages of the two pH measurements taken right after mixing and after 10 minutes of settling. The purpose of letting it settle was also to prevent significant loss of sediment during the extraction of samples following the pH measurements. After settling, one 10 mL sample was obtained for the alkalinity test, one 25 mL sample was obtained and preserved in sulfuric acid for phosphate analysis and one 50mL sample was obtained and preserved in nitric acid for metals analysis. All of these samples were filtered with 0.45 μm polytetrafluoroethylene (PTFE) syringe filters.

The alkalinity test was performed by first, adding 100 μL bromocresol-green methyl-red indicator to the 10 mL sample and then titrating with 0.02N sulfuric acid while the sample was continuously stirred with a magnetic stir bar. The volume change and the number of drops of sulfuric acid added were recorded for the calculation of alkalinity. These procedures were performed at each increment.

At the end the experiment, there were seven alkalinity values and six values for the amounts of acid added to each site, corresponding to each pH value, used to graph the experimental data. The sample bottles for all six sites were then sent to a third- party lab for phosphate and metals analysis. The phosphate analysis was performed using EPA Method 365.4, which measures total phosphorus with an autoanalyzer. The metals analysis was performed using EPA Method 200.7, which measures trace elements in water by inductively coupled plasma-atomic emission spectrometry.

3.2. PhreeqC Modeling Methods

Based on the metal analysis data collected by the third-party laboratory, Ca had the highest concentration compared to the other metals measured, including Fe, Mg, and Mn. This data is shown in Table 3. Thus, it was hypothesized that calcite plays a major role as a buffering agent at this site. The geochemical models in PhreeqC are generated by first, inputting the list of cationic and anionic species that were added to the groundwater, the initial pre-acidification pH, initial pre-acidification alkalinity measured in the experiments, and a consistent temperature of 25°C under the section of “Solution”. Under the section of “Equilibrium Phases”, calcite was added with a presumed initial amount in millimoles. The simulation of the alkalinity titration was generated by inputting the total amount of 1N HCl added for the site in the titration experiment in 20 reaction steps under the section of “Reaction”. The amount of calcite was adjusted by trial and error to match the observed experimental data shown in Figure 4.

4. Results

In general, all of the sites require very low amounts of calcite, between 1E-6 and 1E-4 moles in order to achieve the amount of buffering seen in the experimental data. It is important to note that atmospheric CO_2 is left out of the models. The addition of atmospheric CO_2 in the models resulted in much greater pH levels than observed in the experiments as shown in Fig. 5 for Site 10. The results of the titration simulation with added calcite all achieved very close matches to experimental data trends. In general, all of the sites experienced strongest buffering between pH 6 to 7 characterized by a shallow or nearly flat slope compared to the rest of the titration curve. For instance, the graph in Site 10 of Figure 4 shows that buffering occurs between pH 5.5 and 6.5 for both the experimental and model plots. The RMSE is evaluated for all sites to determine the goodness of fit of the models, with values ranging from 0.2905 to 0.947, with most values falling between 0.50 and 0.56.

The concentration of arsenic obtained from lab analysis ranges from 0.00045 to 0.0053 mg/L across all samples, which is too low for modeling the adsorption mechanism of sediment. Although the arsenic content is below the level of concern, it may be notable to point out that in every case there is a decreasing trend of aqueous arsenic species concentration as pH decreases. This trend corresponds to the expected increase in arsenic adsorption with acidification.

However, it is not possible to draw significant conclusions about pH influence on arsenic adsorption due to the miniscule experimental values.

5. Discussion

For all of the sites, excluding atmospheric CO_2 unexpectedly resulted in much better model fits compared to including it in the models. Equilibration with CO_2 in the models led to a very narrow departure from the initial pH during the titration, compared to the larger deviations from initial pH in the experimental data. This could be due to the insufficient equilibration time during the experiments; however, further studies on this phenomenon would be required for a more conclusive statement. A closed system tends to experience greater pH changes during acidification than an open system (Salminen et al., 2007). The kinetics of CO_2 transport from gas to liquid phase is a relatively slow process (Lower, 1999), so the 24-hour mixing of groundwater and sediment in containers covered with paraffin film may not be enough time for the solution to equilibrate with atmospheric CO_2. Thus, it may be erroneous to consider the solutions in the experiment as open systems.

The discrepancies between the model and experimental plots may also be due to the limited equilibration time allowed between pH increments. In most of the models, the trend towards the lowest pH values tends to maintain above that of the experimental data (Fig. 4). Allowing an extended mixing time between increments during the acidification of groundwater solutions is likely to result in higher pH values near model predictions since the pH of most of these sites were observed to have a strong tendency to resist pH reduction. For this experiment, 45 minutes of mixing was allowed between increments due to time constraints. In general the RMSE values indicate a good fit between model and experimental data. For the same reason as mentioned previously, conducting the experiment with extended mixing time could improve the RMSE values, reflecting better model fits.

6. Conclusion

Performing titration experiments together with the aid of geochemical modeling is a powerful combination that allows an extensive study of geochemical reactions and the behavior and fate of metals in groundwater. In groundwater, carbonates play an important role as a buffering agent against acidification, but can also leach metals during dissolution. In this study site, calcium carbonate was determined to be the primary mineral responsible for the buffering observed during the titration experiments between pH 6 and 7, which is near the buffering range cited in other literature, although some literature reported lower ranges between pH 5 and 6.

Since the remediation strategy for this study site involves acidification of groundwater in order to increase ferrihydrite's affinity for arsenic, the buffering effect of calcium carbonate could pose a problem. A large amount of acid might be required to overcome the buffering capacity, especially if the initial pH of the groundwater is already high (> pH 9) as observed in Site 5. However, previous literature has suggested that the optimum pH range of adsorption is between pH 7 to 9, which is beyond calcium carbonate's observed buffering region according to the experimental results so it may not have a significant influence on the acidification process. Contrary to expectations, incorporating atmospheric CO2 into the models resulted in greater pH values than the observed data. This phenomenon could be due to insufficient equilibration time during experiments. Future experiments should increase pre-acidification solution equilibration time to two or more days and increase incremental acidification mixing time to an hour or more.

Due to limited available data and limitations in modeling programs, it is important to conduct sensitivity analyses to determine the validity of simplifications made in geochemical modeling to avoid large errors in prediction.

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Appendices

Appendix A: Figures

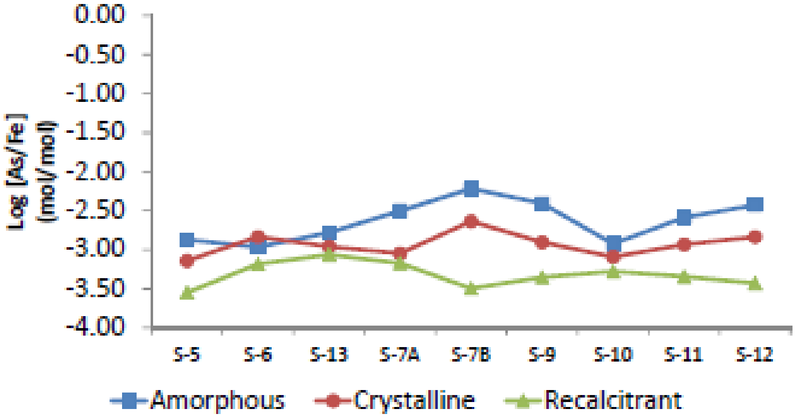

Fig. 1. Molar ratios of As/Fe extracted from different solid phases. (Hafeznezami *et al.,* 2016)

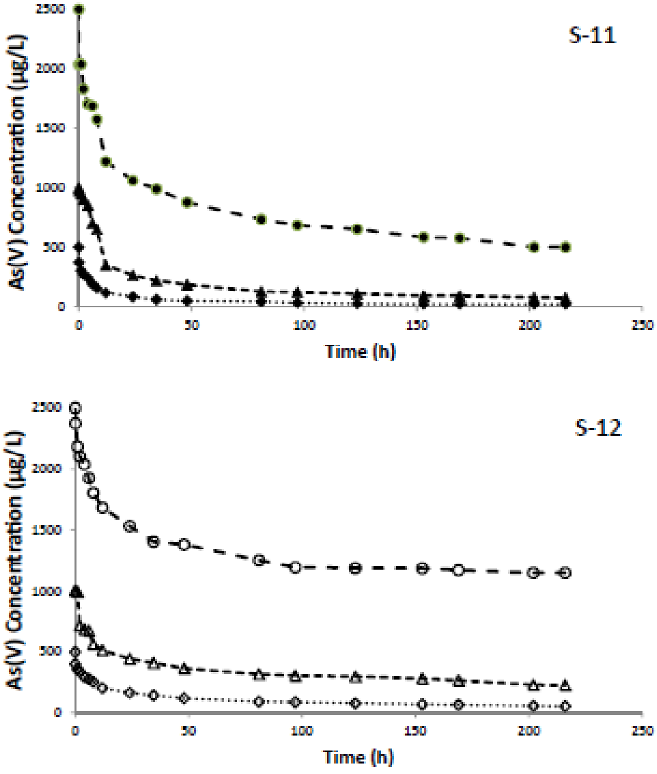

Fig. 2. Aqueous phase As(V) concentration in S-11 and S-12 treated with initial concentrations of 0.5, 1, and 2.5 mg/L. (Hafeznezami *et al.,* 2016)

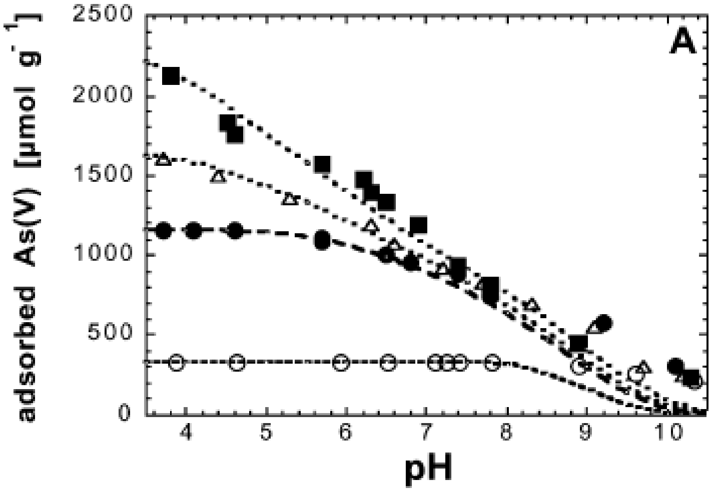

Fig. 3. As(V) adsorption onto amorphous iron oxide (HFO) at various initial concentrations over pH. (Dixit and Hering *et al.,* 2003)

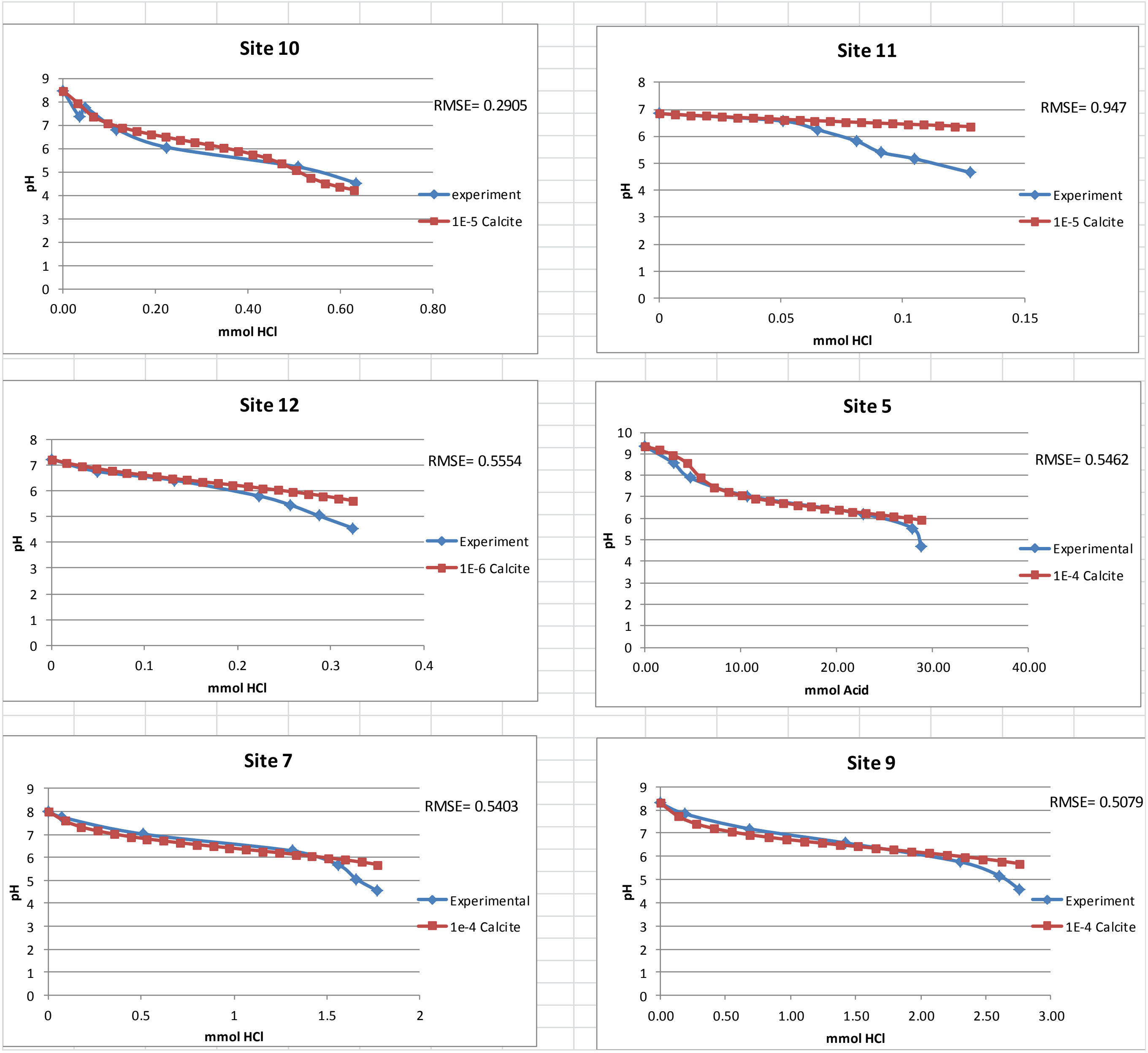

Fig. 4. Fitting PhreeqC titration modeling results with calcite as a parameter onto experimental data for all six sites.

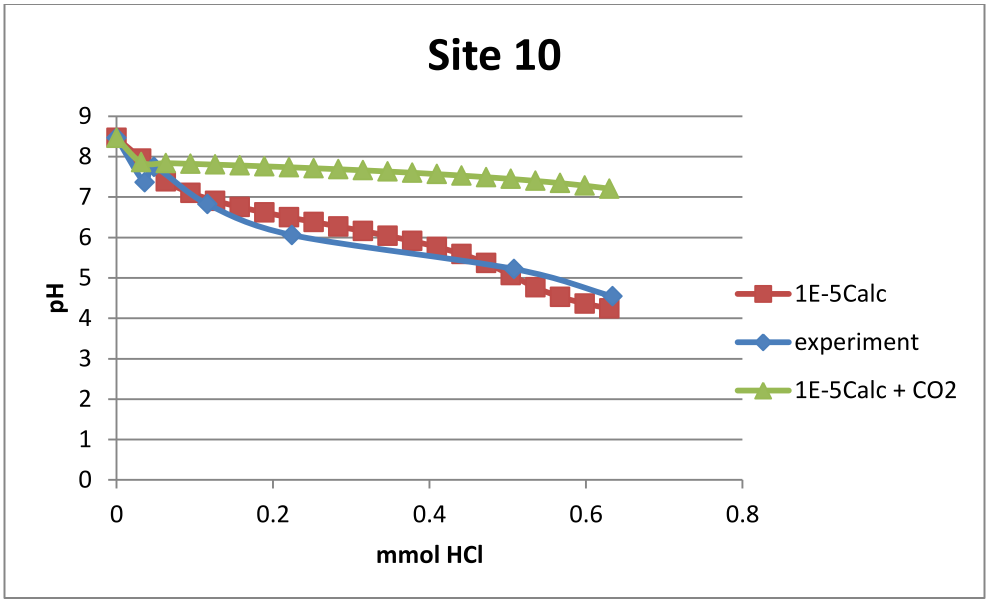

Fig. 5. Comparing titration models for Site 10 with and without equilibration with atmospheric CO_2.

Appendix B: Tables

Table 1. Physical properties of sediments

	Sites					
	S 5	S 7	S 9	S 10	S 11	S 12
Sediment type	brown, fine	brown fine to coarse	brown fine to coarse	gray fine to medium	brown fine to medium	brown fine to medium
Depth (feet)	23-27.5	49-58	47-56	51-58	46-56	48-58

Table 2. Initial concentrations of various ions in artificial groundwater for different sites.

	Site 10	Site 11	Site 12	Site 5	Site 7	Site 9
	g/L	g/L	g/L	g/L	g/L	g/L
Na	0.01237054	0.003816902	0.031434	0.371097	0.029636	0.107761
K	0.00328	0.00228	0.00593	0.00072	0.001	0.001
Ca	0.0274	0.0108	0.0781	0.000418	0.000959	0.000779
Mg	0.00613	0.00443	0.0158	0.00062	0.000231	0.000245
Cl	0.08379146	0.038508539	0.225674	0.020986	0.048974	0.0263
HCO3	0.1098	0.06344	0.244	0.95429	0.05737	0.09265

Table 3. Lab analysis of metals and phosphate in samples of each site in mg/L.

Site 10

	Phos	As	Ca	Fe	Mg	Mn
	(mg/L)					
pH						
8.46	<0.10	0.0014	24.1	0.139	5.74	0.00375
7.36	<0.10	0.0012	24.8			
7.745	<0.10	0.0013	25.8		5.94	
6.825	<0.10	0.0011	26.1			
6.06	<0.10	0.0014	26.4		6.08	
5.22	<0.10	<0.0008	27.0			
4.54	<0.10	<0.0009	27.6	0.505	6.09	0.0534

Site 5

	Phos	As	Ca	Fe	Mn	Mg
	(mg/L)					
pH						
9.34	<0.10	0.0015	1.11	0.128	0.354	0.00336
8.57	<0.10	0.0014	1.04			
7.885	<0.10	0.0014	1.07		0.344	
7.04	0.11	0.0016	1.22			
6.195	0.1	0.0015	1.40		0.414	
5.54	0.15	<0.0009	1.69			
4.7	0.22	0.0012	2.25	0.055	0.556	0.048

Site 11

	Phos	As	Ca	Fe	Mg	Mn
	(mg/L)					
pH						
6.84	<0.10	<0.0008	9.76	0.152	3.82	0.0171
6.565	<0.10	<0.0009	9.57			
6.245	<0.10	<0.0008	9.90		3.68	
5.825	<0.10	<0.00045	10.1			
5.41	<0.10	<0.0007	10.6		4.13	
5.165	<0.10	<0.0006	10.6			
4.655	<0.10	<0.0006	11.7	0.105	4.45	0.0814

Site 7

	Phos	As	Ca	Fe	Mg	Mn
	(mg/L)					
pH						
8	<0.10	0.0052	0.814	0.194	0.214	0.00235
7.75	<0.10	0.0053	0.810			
7.015	<0.10	0.0050	0.851		0.218	
6.28	<0.20	0.0049	0.973			
5.685	<0.10	0.0036	1.16		0.278	
5.055	<0.10	0.0025	1.45			
4.535	<0.10	0.0029	2.07	0.206	0.419	0.0525

Site 12

	Phos	As	Ca	Fe	Mn	Mg
	(mg/L)					
pH						
7.23	<0.10	<0.0007	155	0.612	15.5	0.0337
6.76	<0.10	<0.00045	152			
6.415	<0.10	<0.00045	153		15.2	
5.8	<0.10	<0.0008	151			
5.46	<0.10	<0.0008	150		14.9	
5.035	<0.10	<0.00045	149			
4.55	<0.10	<0.0007	154	0.726	15.4	0.0564

Site 9

	Phos	As	Ca	Fe	Mg	Mn
	(mg/L)					
pH						
8.29	<0.10	0.0053	0.607	0.072	0.195	0.00618
7.83	<0.10	0.0050	0.630			
7.18	<0.10	0.0051	0.710		0.215	
6.57	<0.10	0.0047	0.832			
5.755	<0.10	0.0047	0.971		0.274	
5.155	<0.10	0.0046	1.23			
4.585	<0.10	0.0049	1.76	<0.020	0.419	0.0616