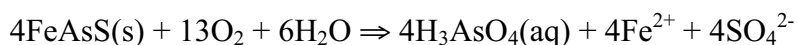


Natural Attenuation of Aqueous Arsenic in Weathered Marine Shale

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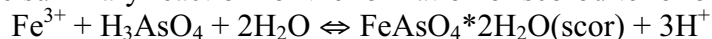
Introduction

Arsenic is a naturally occurring element found in geological materials and soils. Shale of marine origin often contains elevated levels of arsenic. Arsenic in this shale is concentrated in iron sulfide minerals, mainly pyrite (FeS₂) and arsenopyrite (FeAsS). During sulfide mineral formation arsenic precipitates with iron and is incorporated into the mineral structure. The average arsenic concentration in all shales is 15 mg As/kg shale (Dudas, 1987) and samples from five Alberta bedrock marine shale cores reported arsenic concentrations in the 10 to 20 mg/kg range (Alberta Environment, 2000). The average concentration of aqueous arsenic in river water is 2 µg/L. Marine shale is found all over the world including east and west-central Alberta. Oxidative weathering breaks down the arsenic containing pyrite/arsenopyrite minerals releasing arsenic into the surrounding pore water. A summary reaction of the oxidative breakdown of arsenopyrite follows:



Upon the completion of this reaction arsenic is released into solution along with iron and sulfate. Once arsenic is released into solution solubility controlling reactions can remove or limit aqueous concentrations. The two main solubility reactions are precipitation and adsorption.

Precipitation reactions form solid phase arsenic compounds from aqueous solutions. There are many solid phase arsenic precipitate minerals. These precipitation-dissolution reactions and the resulting solid phase compounds determine how much arsenic is in the solid phase and how much is in the dissolved phase. The factors that determine if a precipitate will form include the aqueous concentration of arsenic and the cation arsenic precipitates with. Other factors include the pH and the redox status of the system. Sadiq (1997) has studied arsenic solubility in soil systems and found that through the use of thermodynamic calculations that in oxic, acidic, and suboxic soils, iron-arsenate (scorodite) should control arsenic solubility, provided solution arsenic concentrations are large enough. Scorodite is not stable in alkaline soils. Calcium and Manganese arsenate compounds are the least soluble and most likely arsenate precipitates to form in alkaline soil systems. The summary reaction for the formation of scorodite follows:



Adsorption of aqueous arsenic onto metal oxides and clay minerals is another major geochemical attenuation mechanism in pore, ground, and surface waters. Numerous studies have been conducted that describe the processes involved in arsenic adsorption onto various oxides in aerobic systems. Immobilization of arsenic in soils is due primarily to its sorption on hydrous oxides of Al, Fe, and Mn (McGeehan, 1996, McGeehan et. al., 1994, and Pierce et. al., 1982). Arsenic's oxidation state and the pH of

the system under study are important factors in understanding the adsorption characteristics of aqueous arsenic species. Arsenate adsorption generally increases with decreasing pH, with adsorption maximum occurring near pH 4 on amorphous iron hydroxides (McGeehan, 1996). Pierce and Moore (1982) found a linear declining pattern for arsenic adsorption onto amorphous $\text{Fe}(\text{OH})_3$ with increasing pH, and an adsorption maximum at about pH 4. Arsenate adsorption onto the amorphous iron oxide ferrihydrite was found to be fast at low pH and low arsenic concentrations (Raven et al., 1998). The pH dependent adsorption behavior of arsenic is due to the development of pH dependent surface charge on the solids. As the pH of the system under study decreases, the positive charge and anion exchange capacity of the iron oxide surfaces increases.

Knowing the dominant solubility reaction helps determine the environmental concentration of arsenic. This knowledge also helps in determining arsenic's speciation and possible transportation and fate in groundwater and surface water systems.

In Alberta, there are vast areas of arsenic-rich soils. These soils are mapped as the Boundary and Josephine soil series. They contain about ten times as much total arsenic compared to other soils in the interior plains. These soils are derived from and develop on pyrite-bearing marine shales, which have elevated levels of native arsenic. There is a distinct possibility that arsenic is elevated or concentrated in the pore water of these soils and shale. Aquifers composed of weathered marine shale supply water (and potentially arsenic) for human and animal consumption to many Alberta rural residents. Previous studies by CAESA (1997), Alberta Health and Wellness (2000), and Alberta Environment (2000) measured arsenic concentrations in surface and ground water sources throughout Alberta. All of these studies observed water sources with arsenic concentrations exceeding the Interim Maximum Acceptable Concentration (IMAC) of $25\mu\text{g/L}$ in the Canadian Drinking Water Quality Guidelines (Health Canada, 1996). Waters with elevated arsenic concentrations were associated with areas underlain by geologic formations of marine shale bedrock.

The primary objective of this study is to examine the pore water chemistry of the weathered marine shale, which is the parent material of the Boundary soil, and to determine how much arsenic is released from the shale into the surrounding pore water. An equilibration experiment was conducted to accomplish this goal. Another objective of this study is to determine the pore water chemistry of the weathered marine shale amended with glacial till. This mixture will have a higher pH and a different chemical composition than the native marine shale. Using this mixture provides a surrogate of other associated soil parent materials formed by the mixing of calcareous continental till from the last glaciation with the weathered marine shale with elevated arsenic levels. The Josephine soil series is a natural example of a widespread soil developed on this kind of parent material. The influence of the increased pH and additional attendant geochemical reactions (due to the addition of till) on the pore water chemistry of this mixture was studied. A second equilibration experiment was conducted to accomplish this goal. Arsenic spiking experiments were conducted to test if the precipitation of arsenic solid phase compounds limits aqueous arsenic concentrations in both the shale and shale/till systems.

Materials and Methods

The shale samples used in this study were collected from an outcrop of weathered pyritic marine shale belonging to the Cretaceous Age Kaskapau Formation. This weathered shale is the parent geological material for the acid sulfate soils found on the upper portion of this outcrop belonging to the Boundary soil series. This formation is located about 60 km north west of Spirit River, Alberta in Section 08-82-08 W6M. Samples were collected on an east-facing road cut roughly 10 meters below the surface and 10 cm in from the surface of the cut. Samples were collected in late October of 2001, and were stored in large sealed plastic containers and kept in a cooler at 4°C until use. The samples were air-dried and ground with a mortar and pestle and sieved to less than 2mm. The glacial till material was collected in late September of 2001. This till material was collected from the Cca horizon of a typical Orthic Black Chernozemic soil on the Cooking Lake moraine north west of Tofield, Alberta.

The pH of the various samples was taken using a Cole-Parmer glass electrode. A Cole-Parmer digital combination pH/mV/ORP meter was used to process signals from the electrode. The Redox potential of all samples was taken using a combination Cole-Parmer platinum electrode with a calomel reference electrode probe and a Cole-Parmer digital combination pH/mV/ORP meter. All meter Redox (Eh) numbers were recorded in mV and 245mV was added to this number to give actual redox values of the sample (Patrick et al., 1996). Electrical conductivity (EC) of the sample solutions was determined using a YSI model 31 conductivity bridge. Bicarbonates were measured using acid titration (Bundy and Bremner, 1972). All preliminary solid phase arsenic concentrations were determined using the SLOWPOKE (Safe Low Power Critical Experiment) II nuclear reactor at the University of Alberta. X-ray diffraction (XRD) was used to help identify precipitates and certain weathered marine shale fractions. Diffractograms were obtained using a Philips PW 1730 x-ray generator equipped with a curved crystal monochromator. A Dionex series 4000i chromatograph was used to analyze for aqueous phase anions. All aqueous phase cation concentrations were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). A Perkin-Elmer SCIEX Elan Model 5000 ICP quadrupole mass spectrometer (Thronhill, ON) was used for the analysis (Wu et al. 1996).

Two equilibration experiments were conducted using either the marine shale or the marine shale and till mixture. In the equilibration experiments, samples consisted of:

- a. *Equilibration experiment 1*: 65 g of air dried and ground shale and 130 ml of distilled deionized water; or
- b. *Equilibration experiment 2*: 52 g of shale, 13 g of till (80% shale, 20% till) and 130 ml of distilled deionized water.

Sampling times for each experiment was 1, 2, 4, 8, 16, 32, 48, 64 and 128 days from the start of equilibration. At each time, 3 samples (or replicates) were sacrificed for analysis: 9 sampling times * 3 samples sacrificed per time = 27 total samples.

At the end of the equilibration periods the samples were analyzed for: pH, Redox, EC, Bicarbonates, Anions, and Cations.

Two spiking experiments were done to test whether the precipitation of arsenic solid phase compound occurred and controlled solution arsenic concentrations in the shale and shale/till systems. Arsenic spiking was done using sodium hydrogenarsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$). Initially samples contained either:

- a. 65 g of air dried and ground shale and 130 ml of distilled deionized water; or
- b. 52 g of shale, 13 g of till (80% shale, 20% till) and 130 ml of distilled deionized water.

These mixtures were incubated for a fixed amount of time and a set volume of the solution portion of the samples was removed, filtered (2 μm) and transferred to another container. The arsenic spike was added to this solution and allowed to react. A portion of these solutions was removed for anion and cation analysis. *Spiking Experiment-marine shale*: 9 samples were initially used which contained shale and water. These samples were allowed to react for 7 days and 90 ml of solution was removed from each sample. These solutions were divided in 3 and were spiked with either 4 $\mu\text{g/L}$, 25 $\mu\text{g/L}$, or 100 $\mu\text{g/L}$ of arsenic. These solutions were reacted for 8 days and analyzed for cation and anion concentrations. *Spiking Experiment- Marine shale and till mixture*: 9 samples were initially used containing the shale/till mixture and water. These samples were reacted for 16 days and 90 ml of solution was removed, and divided in 3 and was spiked with either 4 $\mu\text{g/L}$, 25 $\mu\text{g/L}$, or 100 $\mu\text{g/L}$ of arsenic. These solutions were reacted for 8 days and were analyzed for cation and anion concentrations.

Results

Routine chemical and mineral characteristics of the weathered marine shale and the glacial till are summarized in Table 1. There have been numerous past studies investigating acid sulfate soils derived from the same or similar Cretaceous marine shale used in this study (Pawluk and Dudas, 1978; Ross and Ivarson, 1981; Mermut et al., 1985; Dudas et al., 1988). This shale contains large amounts of clay matching amounts found in past marine shale studies, like the 57% found by Pawluk and Dudas (1978) and the 54-60% found by Bulmer (1987). Both of these past studies used soil from the same outcrop used in this study. The most identifiable feature of the marine shale is the low pH (2.75). Oxidation of iron sulfide minerals, specifically pyrite and arsenopyrite, release ferric hydroxides and sulfuric acid. Vegetation associated with the acid sulfate soils derived from this marine shale is often stunted or absent due to this extremely low pH and has been observed in Saskatchewan (Mermut et al., 1985) and in Alberta (Bulmer, 1987). The amount of arsenic associated with the individual particle size and mineral fractions is shown in Table 1. The amount of arsenic in the bulk sample was approximately 35 $\mu\text{g As/g soil}$. This amount falls within the range (5 to 45 $\mu\text{g As/kg soil}$) found by Dudas et al. (1988). There are large amounts of arsenic associated with the sand and the iron oxide fractions. The only remaining iron-sulfide minerals (pyrite or arsenopyrite) that have not undergone complete oxidation are contained in the sand fraction (due to the high density of these minerals). These minerals are the original carriers of arsenic in the shale. These iron sulfides contain large amounts of arsenic that was captured and held in the lattice structure during its formation (Belzile and Lebel, 1986). The amount of total arsenic in the sand fraction is 382 $\mu\text{g As/g sand}$. The sand fraction makes up only 0.33% of the total mass, and only a small portion of this fraction still contains any iron sulfide minerals.

| <i>Characteristic</i> | | <i>Marine Shale</i> | <i>Till(Cca)</i> |
|---|---------------|---------------------|------------------|
| pH | | 2.75 | 7.07 |
| Redox | | 600mV | 483mV |
| EC | | 2.09 dS/m | 0.50 dS/m |
| Carbonates-CaCO ₃ equivalent | | 0 | 8.6%** |
| Texture | Sand | 0.33% | 28%* |
| | Silt | 39.20% | 45%* |
| | Clay | 60.10% | 27%* |
| Initial Solid Phase Arsenic | iron oxides | 305 ug/g soil | - |
| | jarosite | 59.4 ug/g soil | - |
| | sand fraction | 382 ug/g soil | - |
| | silt fraction | 21.8 ug/g soil | - |
| | clay fraction | 34.4 ug/g soil | - |
| | bulk sample 1 | 34.8 ug/g soil | 10.5 ug/g soil |
| | bulk sample 2 | 31.9 ug/g soil | - |

* based on manual texture

** from Ruhman, 1979

- indicates not analyzed

Table 1. Chemical and Mineralogical Characteristics of the Marine Shale and Glacial Till

The iron oxide fraction also contains elevated arsenic concentrations and is further evidence that the shale has undergone advanced oxidation. These oxides were analyzed by XRD and are amorphous in nature. These oxides are concentrated in planer voids created by the H₂SO₄ dissolution of clay minerals following pyrite/arsenopyrite oxidation (Mermut et al., 1985) and are olive brown to dark reddish brown in color. These cracks allow oxygen and oxygenated water to penetrate into the shale accelerating the oxidation process. Needle shaped gypsum crystals were also present in the voids. Gypsum is another by-product of iron sulfide oxidation. Jarosite (KFe₃(OH)₆(SO₄)₂) and natrojarosite (NaFe₃(OH)₆(SO₄)₂) were also found in the voids. The co-existence of both iron sulfide and jarosite indicates an intermediate stage of oxidation (Mermut et al., 1985).

The change in arsenic concentrations in the shale and shale/till equilibration experiments over the 128-day reaction period is displayed in Figure 1. In the shale equilibration experiment, arsenic concentrations increase up until day 4 (reaching a maximum of 6.84 µg/L) followed by a decrease in concentration until the end of the 4-month equilibration. At the end of the 4 months, the concentration of arsenic dropped down to 1.17 µg/L. Aqueous phase arsenic concentrations in the shale experiment decrease over time. The

downward trend in arsenic concentrations seen in Figure 1 indicates that the concentration of arsenic should remain in the low $\mu\text{g/L}$ range over longer time periods. The kinetics of soil solutions is often slow due to the high degree of complexity and heterogeneity in these solutions. Reaching equilibrium in these solutions takes time and it is likely that the shale and shale/till solutions have not reached equilibrium at the end of the 4-month equilibration. It appears from the data in Figure 1 that a predicted equilibrium solution arsenic concentration in the shale system would be in the $0.0 \mu\text{g/L}$ to $1.2 \mu\text{g/L}$ range. The concentration of aqueous phase arsenic in the shale/till experiment initially rises up until day 4 (a rise of only $1 \mu\text{g/L}$), drops, and then steadily increases until the end of the 4 month incubation period (Figure 1). Arsenic concentrations increase from $1.85 \mu\text{g/L}$ (day 1) to $4.82 \mu\text{g/L}$ (day 128). It appears from the data in Figure 1 that a predicted equilibrium solution arsenic concentration in the shale/till system would be $4.8 \mu\text{g/L}$ or greater.

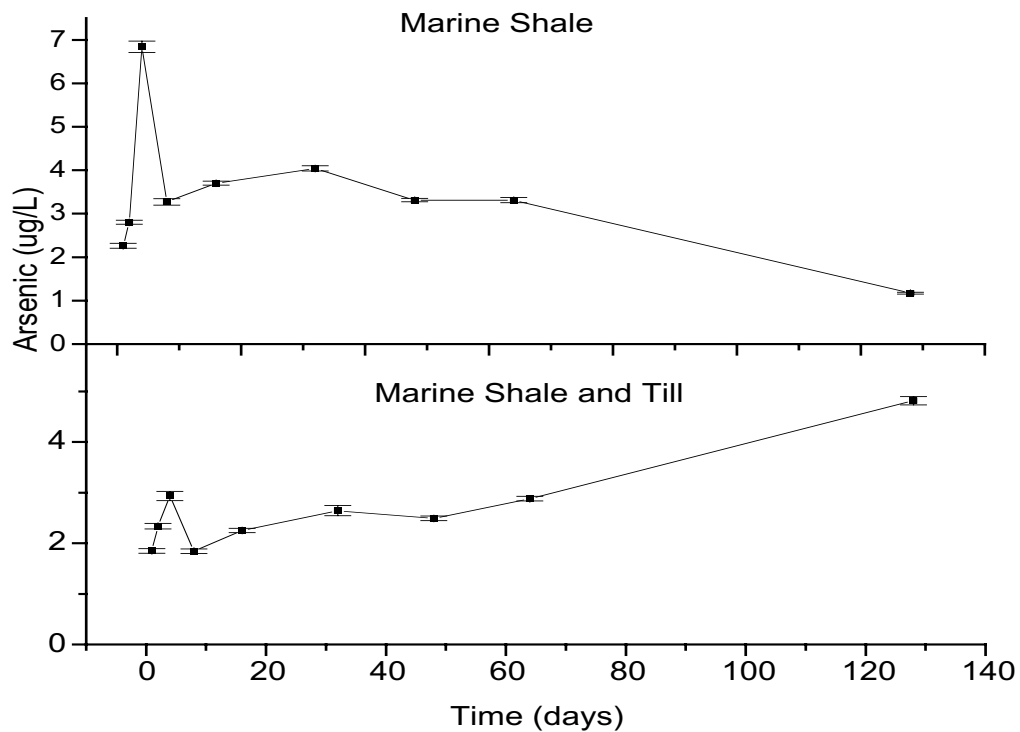


Figure 1. Arsenic Concentration in Pore Water (including errors) vs. Reaction Time in the Shale and Shale/Till Equilibration Experiments

The changes in major cation and anion concentrations over the 4-month equilibrations in the shale and shale/till systems are displayed in Table 2. The change in concentrations of the major solution ions in the shale system indicates the system is in equilibrium or very close to it. The concentrations of Al, Ba, Fe, K, Mg, and SO_4 all remain relatively constant over the latter part of the equilibration. Only the concentration of Mn is still substantially changing (and Ca to a much lesser degree) at the end of the equilibration,

indicating this ion has not reached a state of equilibrium. The common form of molybdenum (in the pH and Eh range of this study) in solution is the oxyanion molybdate (MoO_4^{2-}). This ion has a net negative charge in solution and should theoretically behave in a similar way to aqueous arsenic that is also a negatively charged oxyanion in solution (H_2AsO_4^-). Molybdenum does mimic the changes in arsenic concentration over the last part of equilibration. A recent study by Alberta Health and Wellness (2000) reported a strong relationship in the adsorption and desorption behavior between aqueous arsenic and molybdenum onto the positively charged Fe oxide surfaces. This observed relationship between solution As and Mo in the shale equilibration may indicate that adsorption/desorption reactions are controlling As and Mo solution concentrations in the shale system. Changes in the major solution ion concentrations in the shale/till equilibration (Table 2) indicate a system that has not reached a state of equilibrium at the end of the 4-month equilibration. The Ba, Mn, Mg, and Ca ions are relatively stable at the end of the 4-months indicating the system is in equilibrium with these ions. However, the concentrations of the Al, Na, K, and SO_4 ions are still fluctuating at the end of the equilibration indicating the system is not in equilibrium. There is an increase in solution concentrations of arsenic and Mo near the end of the equilibration. The change in Mo concentration closely mirrors any changes in As concentration over the latter part of the equilibration. This increase in solution concentrations of As and Mo is opposite to the trend (decreasing or stable) observed for all other major solution ions. As mentioned previously a strong relationship in the adsorption and desorption behavior between aqueous arsenic and molybdenum has been reported by Alberta Health and Wellness (2000). Because As and Mo concentration changes mirror each other, it is possible that adsorption/desorption reactions are controlling both ions in the shale/till system.

| Time days | Al ug/L | Ba ug/L | Ca mg/L | Fe ug/L | K mg/L | Mg mg/L | Mn ug/L | Mo ug/L | Na mg/L | SO_4 mg/L |
|---------------------|------------|------------|------------|------------|-----------|------------|------------|------------|------------|-----------------------|
| Shale | | | | | | | | | | |
| 1 | 59553 | 12.8 | 594 | 6323 | 18.5 | 3.1 | 338 | 0.4 | 1.1 | 11557 |
| 32 | 86659 | 4.7 | 500 | 111720 | 1.1 | 8.6 | 462 | 0.5 | 2.7 | 1930 |
| 64 | 87983 | 6.3 | 553 | 21891 | 0.2 | 7.5 | 575 | 0.5 | 1.9 | 1826 |
| 128 | 88384 | 6.8 | 529 | 13823 | 0.4 | 7.5 | 403 | 0.2 | 1.8 | 1951 |
| Shale / Till | | | | | | | | | | |
| 1 | 5.6 | 9.5 | 702 | <50 | 5.0 | 29.8 | 98.6 | 3.8 | 3.2 | 486 |
| 32 | 3.0 | 6.8 | 658 | <25 | 2.2 | 37.8 | 128 | 9.9 | 3.9 | 141 |
| 64 | 314 | 14.0 | 608 | <15 | 2.5 | 38.0 | 498 | 8.2 | 2.9 | 77.2 |
| 128 | 225 | 13.7 | 599 | <25 | 1.4 | 35.7 | 476 | 17.1 | 1.9 | 92.6 |

Table 2. Changes to Selected Chemical Properties Over the 4-Month Equilibration in the Shale and Shale/Till Systems (numbers are an average of 3 replicates).

The 2 spiking experiments were conducted to test if the precipitation of an arsenic solid phase compound(s) controls or limits aqueous phase arsenic concentrations. Figure 2

shows the results of the shale spiking experiment. The *before* arsenic concentration represents the arsenic spike (either 4, 25, 100 $\mu\text{g/L}$) and any natural background arsenic present in the soil solution. The *after* arsenic concentration represents the total amount of arsenic in the solution after the spiking and 8 days of further equilibration. Figure 3 shows the results of the spiking experiment in the shale/till mixture.

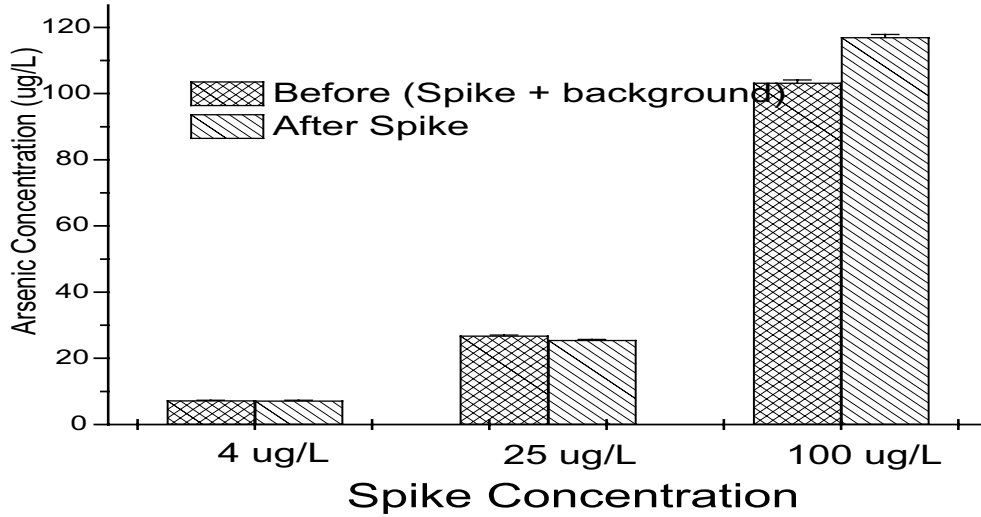


Figure 2. Concentration of Solution Arsenic in the Shale System *Before* (which includes the arsenic spike concentration and any natural background arsenic) and the Concentration of Solution Arsenic *After* 8 Days of Equilibration with the Spike.

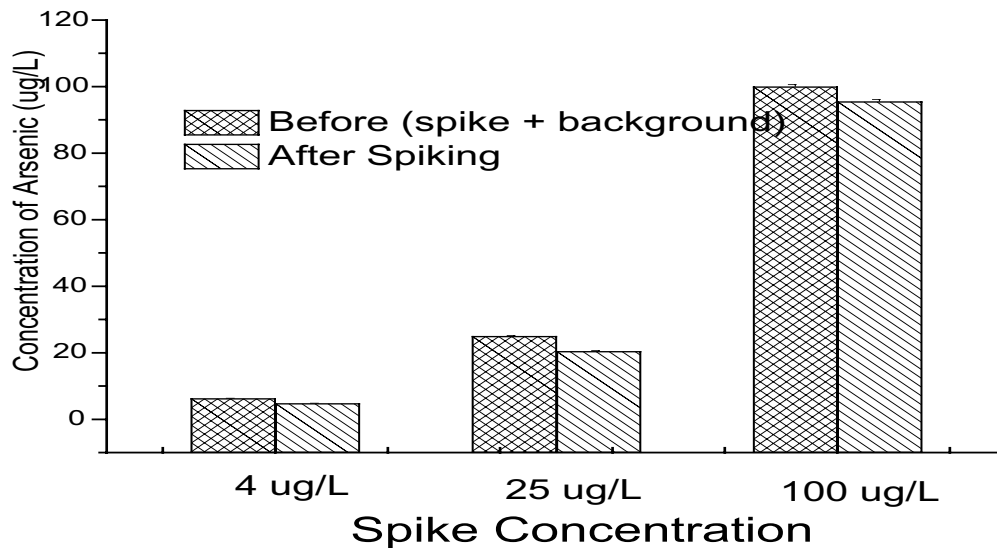


Figure 3. Concentration of Solution Arsenic in the Shale/Till System *Before* (which includes the arsenic spike concentration and any natural background arsenic) and the Concentration of Solution Arsenic *After* the 8 Day Equilibration with the Spike.

Discussion

The highly weathered marine shale used in this study contains naturally elevated arsenic concentrations in the 30 mg As/kg shale range. This shale is almost fully oxidized as indicated by the co-existence of jarosite and minute traces of iron sulfides (Mermut et al., 1985). Most of the arsenic in this shale has been released from the host mineral (iron sulfide). Throughout the world, natural arsenic contamination of pore, ground, and surface water released from surrounding marine shale formations is common. In fact, elevated solution arsenic concentrations were expected in this study because of the high concentrations of As in the marine shale and because most of the arsenic had already been released from the original host mineral. However, elevated solution concentrations of arsenic were not found in the equilibration experiments. In the 4-month marine shale equilibration, the concentration of solution arsenic reached a maximum of 7 $\mu\text{g/L}$ and the concentration was about 1 $\mu\text{g/L}$ at the end of the 4-month equilibration. This value is well below the 25 $\mu\text{g/L}$ guideline value set out in the Canadian Guidelines for Drinking Water Quality (Health Canada, 1996). The amount of arsenic released from the shale into the solution phase was 10,000X less than the total solid phase arsenic concentration initially found in the shale. At the end of the 4-month equilibration solution arsenic concentrations were dropping, and the predicted aqueous arsenic concentration once the system has reached equilibrium should be below 1 $\mu\text{g/L}$. It appears that the amount of aqueous arsenic in the boundary soil and its associated parent material will be extremely small (less than 1 $\mu\text{g/L}$) under constant aerobic conditions.

Glacial till (Cca) was added to the shale in the second equilibration experiment. Glacial till was added to increase the pH and any changes to solution arsenic concentrations were determined. Determining and understanding changes to solution arsenic in this mixture is important for two reasons:

- a. boundary soils derived from the shale are used for crop production often with lime amendments added to adjust the pH to aid in plant growth; and
- b. there are large areas of soils developed on marine shale admixed with calcareous glacial till.

The concentration of solution arsenic in the shale/till equilibration increased towards the latter part of the 4-month equilibration. The concentration of arsenic after day 64 increased until the end of the 4-month equilibration in the shale/till mixture unlike the decreasing trend in solution arsenic concentrations observed in the shale system after day 64. The addition of till resulted in increased aqueous arsenic concentrations due to the increased pH and additional attendant geochemical reactions of the new mixture. At the end of the 4-month equilibration, the amount of solution arsenic in the shale/till system was 4X greater than in the shale system alone. The increase in solution arsenic in the higher pH shale/till mixture is not unexpected. One of the main ways arsenic is removed from solution is through adsorption reactions. These reactions are less effective as the pH of the system under study increases. The positive charge of iron oxides/hydroxides that adsorbs the negatively charged arsenic oxyanions diminishes as pH increases. Anion exchange capacity is pH dependent (iron hydroxide/oxides have a Zero Point of Charge when the surface of the oxide has neither a net positive or net negative charge, ranges from 6.5 to 8.0) which results in the shale/till mix having a lower anion exchange

capacity than the shale alone. The lower anion exchange capacity in the shale/till mix means less arsenic adsorption and larger solution arsenic concentrations, which is what was observed in the equilibration experiment. Amphoteric clays (iron and aluminum oxyhydroxides) in the shale carry a pH-dependent charge. At pH values above the ZPC (the shale/till mix), these minerals would have a low anion exchange capacity which results in less adsorption and higher aqueous phase anion (H_2AsO_4^-) concentrations. For pH values below the ZPC (the shale system alone) these minerals would have a higher anion exchange capacity that results in increased adsorption and lower aqueous phase anion (H_2AsO_4^-) concentrations.

Arsenic spiking experiments were conducted to test if a metal-arsenate solid phase compound is controlling aqueous arsenic concentrations. After spiking, the final aqueous phase arsenic concentrations will be the indicator of whether the precipitation of an arsenic solid phase compound controls solution arsenic concentrations. Spiking was done on the removed solution portion of the samples to eliminate any possible adsorption to the shale and/or till solid phases that would interfere with the formation of arsenic solid phase precipitates. If the concentration of arsenic after spiking does not converge or drop down to the same concentration, then chemical precipitation does not exert a control on aqueous phase arsenic concentrations. This final concentration (or activity) would represent a point on the lowest equilibrium line from a metal-arsenate activity ratio diagram for the least soluble metal-arsenate precipitate in equilibrium with aqueous arsenic restoring a state of equilibrium in the system. The precipitation of a solid phase compound (metal-arsenate in this case) only allows a specific or maximum aqueous concentration of the ion(s) that form the precipitate. Any ion concentration above this maximum results in a system that is over-saturated, and the precipitation of the solid will occur, resulting in a lowering of the aqueous ion concentration, restoring equilibrium in the system. No drop in arsenic concentration was observed after spiking in the shale system indicating chemical precipitation does not control aqueous arsenic concentrations in the 4-month shale equilibration experiment under continual oxidizing conditions. This experiment indicates equilibrium with an arsenic solid phase does not exist and arsenic solubility and aqueous activity is likely controlled by adsorption. This is consistent with the literature that states adsorption onto iron oxides/hydroxides is the dominant force removing aqueous arsenic in systems with solution arsenic concentrations of less than 0.01 moles/L. No uniform drop in arsenic concentration was observed after spiking in the shale/till mixture indicating chemical precipitation does not control aqueous arsenic concentrations over the 4-month equilibration before the system has reached equilibrium under continual oxidizing conditions. It is likely that adsorption controls aqueous arsenic concentrations.

Conclusion

The concentration of aqueous arsenic released from the shale at the end of the 4-month equilibration under aerobic conditions as the system approached equilibrium is 1.2 $\mu\text{g/L}$. There was an overall drop in aqueous arsenic concentrations in the shale system under aerobic conditions over the 4-month equilibration. The concentration of aqueous arsenic released from the shale/till mixture under aerobic conditions at the end of the 4-month equilibration as the system approached equilibrium was 4.8 $\mu\text{g/L}$. There was an increase

in solution arsenic concentrations in the shale/till mixture under aerobic conditions over the 4-month equilibration. The concentration of solution arsenic in the shale/till system was 4X higher than the concentration in the shale system at the end of the 4-months. This study indicates the addition of lime to a Boundary soil raising pH to aid plant growth will increase the amount of aqueous phase arsenic.

The average concentration of aqueous arsenic in river water is 2 µg/L. The current Canadian guideline value for arsenic in drinking water is 25 µg/L. The concentration of aqueous arsenic in the shale system is extremely low (about 1 µg/L) and in the shale/till system is low (about 5 µg/L). This study indicates that the amount of arsenic released from the marine shale (surrogate for the Boundary soils) and from the shale/till mixture (surrogate for the Josephine soils) is low and should not contribute to the build up of arsenic in the surrounding surface or groundwater provided the system remains oxidized. Arsenic spiking experiments were conducted to determine if the precipitation of an arsenic solid phase compound(s) occurred and controls or limits aqueous arsenic concentrations. These experiments determined that no arsenic solid phase compounds were precipitating and controlling aqueous arsenic concentrations in either the shale or the shale/till systems over the 4-month equilibrations under constant aerobic conditions.

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