Sediment Associated Arsenic in Stream and Aquifer Sediments

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Sediment Associated Arsenic in Stream and Aquifer Sediments

by

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Abstract

Arsenic (As) is an element commonly associated with aquifer sediment, with a global concentration 1.7 mg/kg, and can be subsequently released into groundwater. In recent times, increased anthropogenic inputs have contributed to geochemical changes in the subsurface that affect the mobilization of arsenic into subsurface water resources. Concentrations above the EPA’s maximum contaminant level (MCL) of 10 µg/L have recently been reported in many areas across the United States, including Nebraska. The health risk of prolonged exposure to high arsenic concentrations are skin ailments, like hyper pigmentation and keratosis, and cancer. Furthermore, many rural communities, especially in western Nebraska, lack the resources to treat their drinking water supplies. Recent studies have indicated As concentrations above the MCL in Wauneta, NE, a small community in western Nebraska. Wauneta is quite concurrent with other well-studied As contaminated regions but exhibits some important hydrological and geological differences including the presence of oxidizing groundwater, carbonate-rich sediments, and the influence of Frenchman Creek, which flows through the town. Sediment geochemical analyses revealed two sources of As: 1) As derived from Frenchman Creek and 2.) As sourced from the aquifer sediments. Sequential extraction experiments indicate that sediments contain as much as 4.22 mg/kg As and have the potential to contaminate the groundwater up to 99.75 µg/L. Speciation experiments also exhibit high, easily mobilized, sediment associated arsenic concentrations in Frenchman Creek, providing potential for the impact of surface-groundwater interactions on the quality of Wauneta’s drinking water. This is a significant health risk to Wauneta and others using this aquifer for drinking water.
1 Introduction

1.1 Study Description

Arsenic groundwater concentrations above the maximum contaminant level (MCL) have been previously demonstrated in many different locations around the world (Harvey et al., 2002; Islam et al., 2004; Smedley and Kinniburgh, 2002; Welch et al., 2000). Groundwater in many of these areas is mined for drinking and irrigation. Therefore, arsenic concentrations should be of great concern to those who live in these areas as consumption of high doses of arsenic can have adverse health effects such as hyperpigmentation, keratosis and increased risks for cancer (Harvey et al., 2005). Recently, groundwater in Nebraska has been measured above the MCL. For example, the city of Lincoln has experienced arsenic levels in its drinking water as high as 9.8 ppb (Hicks, 2016). Concentrations above the national MCL of 10 ppb have not yet been observed in Lincoln, but these reported concentrations are generally averages and it is likely that many individual wells have exceeded this limit. When arsenic levels surpass the MCL, remediation techniques like water treatment plants (Borgoño et al., 1977) may become necessary. The drilling of new wells that are not in contaminated areas (Nickson et al., 1998) may also be an option, although this is generally not a permanent solution, as areas can easily become contaminated with moving groundwater. Unfortunately, expensive options like water treatment plants, are not feasible for small and/or rural communities in Nebraska like Wauneta, a small town in the southeastern portion of the state, that are experiencing high arsenic concentrations (Snow et al., 2016). For this reason, Wauneta has been working with the Department of Health and Human Services (DHHS) to identify alternative water management strategies to provide the community with higher quality drinking water. In collaboration with the DHHS, the Weber and Snow labs at UNL have been analyzing stream and subsurface sediments
in an effort to identify the source of arsenic and describe mechanisms leading to the mobility of arsenic in groundwater. In order to identify management strategies, it is important to understand the biogeochemical processes that influence arsenic in groundwater.

1.2 Arsenic Background

Arsenic is a ubiquitous element in groundwater that predominately exists in nature in two inorganic forms: Pentavalent As(V) or arsenate, and trivalent As(III) or arsenite (Oremland and Stolz, 2005). As(III) is more toxic to the health of humans as well other organisms like microbes and plants (Aggett and Kriegman, 1988; Duker et al., 2005). Furthermore, As(III) is more mobile in aquatic systems, as it does not tend to adsorb to or incorporate itself with other groundwater minerals (Smedley and Kinniburgh, 2002). Conversely, As(V) is generally found adsorbed onto immobile minerals/sediments in natural waters, but conditions can prevail that mobilize As(V) into the aqueous phase (Manning and Goldberg, 1997). Due to its sorption tendencies, As(V) is regarded as the preferred form due to the fact that is generally immobile in aquifers (Dixit and Hering, 2003; Manning and Goldberg, 1997) and is less toxic. The speciation of arsenic in a system widely depends on other geochemical parameters within the subsurface. One of these is oxidation-reduction potential (ORP) of the water, which drives the oxidation state of elements in a system and is extremely important for arsenic speciation (Cherry et al., 1979).

The speciation of arsenic in a system is extremely dependent on how “reducing or oxidizing” a system is (Smedley and Kinniburgh, 2002). Aerobic systems, or systems high in oxygen, tend to be more oxidizing since oxygen is a thermodynamically favorable electron acceptor. This means that as systems become anoxic, less electron acceptors are present, and thermodynamic equilibrium favors reductive reactions as opposed to oxidations. This is important because As(III) is the more reduced form of Arsenic and tends to exist in higher
concentrations in systems low in oxygen (Oremland and Stolz, 2005). Additionally, organic carbon, which is a common electron donor (Islam et al., 2004) and anthropogenic pollutant, can facilitate this by shifting equilibrium of the system further towards reduction.

There are however, other geochemical parameters that control the speciation of arsenic. The presence of certain molecules, iron and aluminum, for example, have been demonstrated as being very significant in arsenic redox cycling (Islam et al., 2004; Manning and Goldberg, 1997; Nickson et al., 2000). Iron, specifically, being the fourth most abundant element in the earth’s crust, plays a vital role in arsenic cycling. Reduction of arsenic has been demonstrated to track that of iron in subsurface systems (Islam et al., 2004). Thus, iron geochemistry in a system can be a good indicator of the mobility of arsenic in areas with high concentrations. Although speciation is important when considering the mobility of arsenic in a system, it can sometimes change rapidly based on other environmental conditions (Cherry et al., 1979; Neil et al., 2012; Polizzotto et al., 2008). Consequently, it is important to consider other mechanisms of mobilization when studying arsenic. Geochemical iron cycling has been well described by Weber et al., 2006

The sorption of arsenic on to and off of aquifer minerals has been demonstrated as an important mechanism in the mobilization of arsenic in sediments (Welch et al., 2000). Iron has already been discussed as being influential in the speciation of arsenic but the incorporation of arsenic with iron hydroxides is widely regarded as the most important process to arsenic mobility in many subsurface systems (Manning and Goldberg, 1997; Nickson et al., 1998; Smedley and Kinniburgh, 2002; Welch et al., 2000). Iron hydroxides (Fe(III) bearing minerals) have a high affinity for As(V) which tends to sorb to the surfaces of these minerals. As reducing conditions prevail in a system iron hydroxides dissolve and the reduction of Fe(III) to Fe(II) occurs. As(V)
is released as a result of this dissolution, increasing arsenic concentration in the system. Furthermore, as Fe(II) increases, the formation of Fe(II) minerals becomes more favorable. These minerals, like goethite, have less adsorption sites and the previously released arsenic cannot be re-adsorbed to newly formed minerals. Additionally, since the system is now more reducing, As(V) is converted to As(III), increasing its solubility and toxicity (Nickson et al., 1998). This process is very common in aquifers with high arsenic concentrations (Harvey et al., 2002), and further demonstrates the importance of iron in arsenic mobilization.

Along with iron, other minerals like nitrate, phosphate and bicarbonate, have all been demonstrated to play important roles in arsenic mobilization (Kim et al., 2000; Smith et al., 2017). Nitrate, a common contaminant associated with agriculture and wastewater runoff (Nolan and Weber, 2015), has been demonstrated to be a favorable electron acceptor in aquatic systems. Presence of nitrate in aquifers has been observed to facilitate the oxidation of Fe(II) to Fe(III) (Senn and Hemond, 2002; Smith et al., 2017; Weber et al., 2006). This causes the formation of iron hydroxides which, as previously discussed, provide sorption sites for arsenic and other ions. As(V) is then sorbed to these minerals and arsenic levels are lowered. Furthermore, the fact that nitrate is a strong electron acceptor promotes oxidizing conditions and can facilitate the reduction of As(V) to As(III). Conversely, the oxidation of As(III) to As(V) in the presence of nitrate has also been demonstrated (Smith et al., 2017), which has been identified as a potential management strategy for high As systems.

Phosphate, on the other hand, inhibits the attenuation of arsenic. Phosphate competes with arsenic for sorption sites on aquifer minerals and is generally associated with increasing arsenic concentrations (Hug et al., 2001; Roberts et al., 2004). This is due to the fact that phosphate forms inner-sphere complexes with oxide minerals, much like arsenic. (Kanematsu et
al., 2013). Smith and colleagues (2017) demonstrated that high concentrations on nitrate can inhibit the facilitative effects of phosphate on arsenic mobilization, even when phosphate is in higher than average concentrations. This is an important consideration because nitrate and phosphate contamination are associated with agricultural pollution, which is common in the area considered in this study.

Another co-contaminant that competes with arsenic for sorption sites is silicic acid. It associates itself with oxides, much like phosphate (Kanematsu et al., 2013), but can do so via multiple processes. In low concentrations it tends to bind via polymerization, but in high concentrations, which is more common in groundwater, it will adsorb in the same manner as arsenic and phosphate (Swedlund and Webster, 1999). It has also been demonstrated that while not as efficient as phosphate at adsorbing to Fe oxides, it generally exists in higher concentrations in groundwater (Meng et al., 2000), making it a strong contributor to arsenic mobilization in aquifers.

Carbonate, which is present in high concentrations in this area, has been demonstrated as being important to the mobilization and toxicity of As in aquatic systems. The presence of carbonate has been shown to increase leaching of arsenic previously incorporated with sulfides (Kim et al., 2000). Many studies have indicated the effectiveness of the bicarbonate ion as an oxidizing agent and thus, a method of dissolving arsenic containing molecules (Evangelou et al., 1998; Lázaro et al., 1997; Nicholson et al., 1988). These studies have linked arsenic leaching from common arsenic containing molecules, like arseno-sulfides and arseno-pyrites, to increased concentrations of bicarbonate. It was also exhibited by Kim et al., 2000 that arseno-carbonate complexes are more likely to contain As(III) than As(V), meaning that these complexes already contain the most toxic form of arsenic. The mobilization process described by these studies are
in contrast to previously described mechanisms for arseno-pyrites, in which As(V) must first
dissolve off the mineral and then be reduced to As(III). Arseno-carbonate complexes have also
been demonstrated to be extremely stable in aquatic systems (Simon et al., 2015), interjecting the
argument that these complexes are some of the most stable forms of inorganic arsenic in the
systems in question. Furthermore, similar to phosphate and silicic acid, carbonate can compete
with As for sorption sites on Fe oxides (Kanematsu et al., 2013). It does so to a lesser extent
than that of previously mentioned competitors but, carbonates competitive nature should be
taken into account along with its influence on other As mobilizing processes. Although pH has
not been linked directly to arsenic cycling, it plays a key role in weathering and sorption patterns
in aquatic systems. Since carbonate ions control buffering in most natural waters (Stumm and
Morgan, 2012), their presence plays a decisive role in the stability of minerals of which arsenic
incorporates itself. This, in addition to carbonates oxidizing capability and its affinity for Fe
oxides, makes their consideration crucial when studying arsenic in aquatic systems.

It is also important to consider the biotic portion of subsurface systems when studying
arsenic. Many of the reactions described above either consume or yield energy, as there is a
transfer of electrons involved. Microorganisms sometimes exclusively rely on this energy
transfer to carry out their cellular functions (Oremland and Stolz, 2005). The reduction of iron,
which has been discussed in detail above, again plays a role in arsenic mobilization, this time
through microbial metabolisms. The process of iron reduction is commonly facilitated by
microorganisms in the subsurface and is thought to be one of the most important reactions for
microbial metabolisms (Weber et al., 2006). This is important in high arsenic systems because
although iron reduction is highly utilized by microorganisms, it tends to be utilized very quickly
by the microbial population. This leaves a need for further energy sources. After all of the iron
in a system is reduced, microbes move on to other elements and arsenic reduction generally follows that of iron (Islam et al., 2004). It should also be noted that this process is facilitated further with high amounts of organic carbon acting as an electron donor. Organic carbon can be added to systems by many processes but it is a common co-product of many agricultural practices (Kong et al., 2005), wastewater disposal (Glassmeyer et al., 2005) and solid waste leachate (Carpenter et al., 2012). Metal reducing microbes account for as much as 90% of the oxidation of organic matter (Canfield et al., 1993) and in turn, reduction of appreciable amounts of trace metals including As. Thus, their consideration is important when examining arsenic mobilization.

1.3 Statement of Purpose

As described above, there are many mechanisms that control arsenic mobilization in aquatic systems. Consequently, understanding the source of arsenic in a contaminated system can provide much of the information necessary for determining the dominant mechanisms driving its release. **Due to this, the objective of this study is to identify the sedimentary sources and geochemical species of arsenic.** This will be achieved by 1) identifying the dominant species of As in sediments collected from each sampled location, 2) classifying the sources of arsenic from the sediment and 3) quantifying the amount of arsenic that is adsorbed to the sediment.
II. Materials and Methods

2.1 Site Description

Wauneta is a small town in the southeastern corner of Chase County (40.4165° N, 101.3712° W). The city of Wauneta has recently been experiencing high levels of Arsenic in its Public Water Supply (PWS). Water for public use in Wauneta originates from the High Plains aquifer and is collected via screened wells illustrated in Figures 1 and 2. Another area of interest here is Frenchman Creek, which runs east through the northern part of Wauneta (Figure 1). Frenchman Creek is a spring fed stream that originates in Phillips County in Colorado, and runs east through Chase, Haynes and Hitchcock Counties in Nebraska before ending at the Republican River. High arsenic levels have also been observed in the creek’s water. The underlying geology of Wauneta consists of five zones. The first of which being an alluvial zone consisting of mostly stream gravel, sand silt, and clay. The next containing discontinuous sands separated by muds. The next containing calcareous sands with limestone beds and the final two consisting of clay overlying mixed clay/gravel zones and organic shales overlying bedrock of bentonite and gypsum. The previously described zones, areas from which the sediment cores were collected, and public water supply schemes are illustrated in Figure 2.

2.2 Sediment and Groundwater Collection

Sediment cores were collected using a geo-probe (Geospec Drilling®) utilizing a direct-push method in areas close to the public water supply (PWS) wells. The sediment core for Frenchman creek was obtained by drilling into the north bank of the stream (5 in Figure 1). During collection, drilled cores were ejected into polycarbonate liners which were flushed with 100% argon gas to preserve geochemistry.
The water samples for this study were collected from PWS wells and Frenchman Creek (Figure 1). These samples, along with other samples from irrigation wells were collected and analyzed for physiochemical parameters. All and soil samples were stored under an anoxic atmosphere at 4°C and transported to the Weber Lab for processing which was done in an anoxic glove-bag (5%H₂/19%CO₂/balance N₂).

2.3 Sediment Processing (Moisture, pH, and ORP)

Following collection, sediments of interest were processed for basic parameters in anoxic conditions (glove-bag described above). First, sediments were weighed initially, and ground with a mortar and pestle (light to medium pressure). They were then put through a 2mm sieve to remove all gravel and large particles. Material that passed through the sieve was weighed again, and the difference was used to calculate a “Sand, Silt, and Clay” percentage. Next, moisture content was calculated. Approximately 5 g of each sediment was weighed and left to dry in a dehumidifying atmosphere. After 14 days of drying, the sediment was weighed again and the difference was used to calculate moisture percentages. For pH and ORP (Oxidation-Reduction Potential) bench meters were used on a 1g sediment-2.5 mL DDI water slurry. Sand, silt and clay percentages ranged from 54.91% to 99.93%, with the majority of samples containing more than 90% sand, silt and clay. Moisture content ranged from 5.6% to 23.34% (creek bed sediments), although most locations contained between 10 and 15% moisture by mass. All pH levels were under 7, but were all close to neutral (6.22-6.75). ORP values were quite sporadic, with many sediments being very oxidizing and many being very reducing. All previously mentioned parameters are described in Table 2.

2.4 Arsenic Speciation
In order to obtain available total arsenic, As(III) and As(V) concentrations, a filtration method was used. Artificial groundwater (AGW) (described in Table 1) was prepared to mimic actual groundwater chemistry, which was obtained from Snow et al., 2016. This solution was mixed with sediment at a (solid to solution ration) SSR of 1:10 and agitated on an orbital shaking table for 96 hours to further replicate actual groundwater geochemistry. Aliquots were then centrifuged and filtered through a 0.45µm PVDF filter to obtain the liquid phase from sediment. Half of each collected volume was then acidified and stored for analysis. The remaining effluent from aliquots was then passed through a Supel-Select SAX (SAX) filter, which are known to retain As(V) (Yalçin and Le, 2001). Sample passed through these filters were then quantified for arsenic and compared to sample collected before SAX filtration.

Upon completion of these experiments, inductively coupled plasma-mass spectrometry (ICP-MS) analysis was used for As quantification.

2.5 Arsenic Source Classification (Fractionation)

In order to identify the geochemical sources of As in these sediments, a fractionation experiment was performed that classified arsenic into different categories that are based on ease of dissolution from sediment. Arsenic from each sediment (same depths as speciation extractions) was extracted via the processes described below, based on a study performed by Haque et al., 2008. The components used and each fraction extracted are described in Table 3. Each amendment (excluding the final H₂O₂/HNO₃ extraction, which was only performed once) was performed in duplicate to ensure total extraction of each fraction.

**Fraction 1 (Non-specifically sorbed As):** For each sediment, 1 g of sediment was added to a 30 mL centrifugation tube and was amended with 15 mL of 0.05 M (NH₄)₂SO₄. These aliquots
were placed on an orbital shaking table at 180 rpm and were agitated for 4 hours at standard temperature and pressure. It was then centrifuged for 10 min. at 4,000 rpm, filtered (0.45µm), and stored at 4°C after being acidified with HNO₃. Analysis of the filtered and acidified extractant (same methodology used for speciation experiments) was completed after all fractionation was completed. The remaining sediment was used for the next fractionation.

**Fraction 2 (Specifically sorbed As):** Remaining sediment from fraction 1 was amended with 15 mL of 0.05 M NH₄H₂PO₄. These aliquots were agitated for 16 hours in the same manner as fraction 1. The aliquots was then filtered, acidified and stored for analysis (This will be the same for all remaining amendments). Remaining sediment was used in the next fractionation.

**Fraction 3 (As with amorphous and Poorly-crystalline hydrous oxides and Fe and Al):**
Remaining sediment from fraction 2 was amended in 15 mL of a 0.2 M NH₄-oxalate buffer solution at a pH of 3.25. These aliquots were agitated in the same manner as previous fractions for 4 hours. A wash step was employed after this fraction was processed by re-amending sediment with the 3.25 pH, 0.2 M NH₄-oxalate buffer. The aliquots, at an SSR of 1:12.5, were placed on a shaker table at 180 rpm for 10 min in the dark to prevent the dissolution of crystalline Fe-oxides via the catalyzing effect of light. After shaking, effluent from the wash step was processed like previous fractions and added to the effluent from fraction 3. Remaining sediment was used in the next fractionation.

**Fraction 4 (As with well-crystalline hydrous oxides of Fe and Al):** Remaining sediment from fraction 3 was amended with 15 mL of a 3.25 pH, 0.2 M NH₄-oxalate buffer solution + 0.1 M Ascorbic acid. The aliquots were placed in a 96±3°C water bath, and were agitated by hand every minute, for 30 minutes. Another wash step was implemented after this extraction (wash step same as fraction 3).
Fraction 5 (Residual Phases): Residuals from fraction 4 were amended with a 25 mL of HNO₃ and 2 ml 30% H₂O₂, and were microwave digested. The aliquots were then centrifuged and filtered, and remaining sediment was amended with 30% H₂O₂ and microwaved digested again. Again, effluent from this was centrifuged and filtered. The two effluents were combined before being stored for analysis.

All effluent collected from this experiment was quantified using the same methods as previous experiments.

2.6 Arsenic Desorption

In order to determine the amount of As adsorbed to the surfaces of these sediments, a desorption experiment was also carried out. For the desorption experiment, a CARB Solution (14.4 mM NaHCO₃ + 2.8 mM Na₂CO₃) was used as eluent (Hafeznezami et al., 2016). Using this solution, aliquots were prepared in anoxic conditions at a 1:10 SSR for 6 sediment depths. This experiment utilized fewer depths because it was more resource intensive and more costly. The selected areas (starred in Table 1) were selected because they were likely to provide an all-encompassing idea of the processes occurring in this area based on preliminary data. A total of 60 aliquots were placed on an orbital shaker table (180 rpm) and one of each sediment was removed at 7 different time lengths (0.5 hr. 2 hr. 4 hr. 8 hr. 24 hr. 48 hr. 96 hr. and 384 hr.). These aliquots were centrifuged, filtered and acidified in the same manner as previous experiments. ICP-MS analysis was also used for element quantification with these samples.
III. Results and Discussion

3.1 Arsenic Speciation

Concentrations from the speciation experiment are exhibited in Figure 2. Besides FCA, which showed a total As concentration of 11.08 ppb, all sediments exhibited total concentrations below the MCL (10 ppb). Sediments in this experiment were agitated under docile conditions compared to what is possible in nature, and because of this, little mobilization was expected, meaning it is entirely possible that more easily mobilized As exists in these sediments. Total As concentrations range from 11.08 ppb to 0.93 ppb. As(V) concentrations ranged from 8.63 ppb to 0.22 ppb. As(III) concentrations ranged from 4.73 ppb to 0.34 ppb (All described in Table 4). While FCA had exhibited more total As than other wells by more than a factor of two, its majority was in the pentavalent state. While all As can cause health issues in high enough concentration (Smedley and Kinniburgh, 2002), this can be taken as a positive with respect to the drinking water quality of the stream.

Of the sampled wells, PWS 1 (the closest well geographically to the creek) exhibits the highest As concentrations. This implies a potential influence of the creek on the underlying groundwater, and provides evidence for surface-groundwater interactions in this system. Furthermore, The dominant species in PWS 1 is As(III) suggesting that if the creek is influencing the groundwater, it is possible that labile As(V) in the creek is changing geochemically as it passes through the subsurface.

3.2 Geochemical Sources of Arsenic in Sediment (Fractionation)

Fractionation experiments were done on sediments from each PWS well and Frenchman Creek to access the extent of As susceptible to mobilization in the presence of different
geochemical parameters. Table 3 outlines the chemical composition of each fractionation and total concentrations of As mobilized from each sediment after agitation are presented in Figure 4. This graph depicts total As mobilized from sediment in a normalized fashion with respect to the extractant used in each fraction. Fractions 1, 2 and 3 were determined to be “Easily mobilized As” as it is possible to observe chemical parameters in nature that would cause this arsenic to mobilize. Higher percentages of this “easily mobilized As” (represented in red) were observed in Frenchman Creek and PWS 1. Individual concentrations of As from each fraction were variable depending on sampling location and depth but were highest in Frenchman Creek (17.05 ppb-76.99 ppb). Remaining concentrations are presented in Table 5.

While overall concentrations of As were much higher in Frenchman Creek compared to the PWS wells, the fact that sediments PWS 1 showed higher percentages of easily mobilized As and higher overall concentrations as compared to PWS 2 and PWS 4 was quite concerning. Of the drinking water wells in Wauneta, PWS 1 is the closest geographically to Frenchman Creek. This furthers hypotheses drawn from previous experiments that the As rich Frenchman Creek is having an effect on groundwater used for drinking through surface-groundwater interactions.

When it comes to the individual mechanisms that mobilize As in these sediments, each sample area differs slightly. While incorporation in strongly crystalline oxides (not easily mobilized) is common in all wells, the dominant section of the easily mobilized fraction is different in each sampled location. No discernable trends are available here but, almost all easily mobilized As is either strongly sorbed to sediment minerals and weakly incorporated in crystalline oxides, or some combination of the two. When comparing these results to those of other studies done on As fractionation, interesting comparisons can be drawn. While work by Kumar et al., 2016 done in India on As, indicate similar percentages of sediment associated As
as “easily mobile” the vast majority of this was in fraction 2 (As with amorphous and Poorly-crystalline hydrous oxides of Fe and Al). In our experiment, this fraction is a major source of As in some locations but, fraction 2 (Specifically sorbed As) was common as well. This indicates that easily mobilized As in this system is more dynamic than other high-As locations.

3.3 Desorption Mechanics

The results of the desorption study are presented in Figures 5, 6 and 7. While As concentrations did go up quite substantially in all cases, no samples appeared to reach equilibrium (the point where adsorption and desorption rates are the same). This is unusual when compared to other studies. When Hafeznezami et al., 2016 performed an As desorption study in Maine, USA, they indicated equilibrium times of a maximum of 7 days. Our aliquots were agitated for up to 16 days and did not exhibit equilibrium even after this time-step. As desorption has been studied quite extensively (Feng et al., 2013; Hafeznezami et al., 2016; Raven et al., 1998) and many different equilibration times have been reported. These times however, are very dependent on the geochemistry of the system and the parameters of our system could be having an effect on As sorption.

Furthermore, there is also a possibility that microorganisms are having an effect on As mobility here. As discussed earlier, if in high enough demand, microbes in the subsurface are capable of changing As geochemistry in anoxic environments (Islam et al., 2004). Further work will need to be done to elucidate what is causing these discrepancies.

3.4 Limitations and Recommendations

During the course of these experiments, several discrepancies related to our results were observed. Cost was a major limiting factor for us, and due to this, we could not afford to prepare
replicate samples. If these experiments were to be performed again and cost allows, we would advise preparing samples with multiple analytical replicates. This would improve our confidence in the results provided by instrumentation.

Another issue that arose was related to the desorption experiment. It is a consensus that other factors are playing into our sample’s lack of equilibrium but, the time steps at which we chose to sample made elucidating further upon this difficult. A lack of data at later time-steps, when As concentrations are unusually increasing or decreasing, inhibits us on making conclusions on what is causing these discrepancies. If this study were to be repeated, an emphasis on sampling at later time-steps would be necessary. There were also unconventional increases and decreases in concentration early in the experiment. Analytical replicates could also improve confidence in results here.

IV. Conclusions

4.1 Experimental Conclusions

This preliminary study on sediment and groundwater beneath the small town of Wauneta, NE begins to clarify the processes controlling As mobilization and speciation in surface waters and the subsurface. This work begins to answer fundamental questions regarding As in this system and its implications on the citizens of Wauneta. Our conclusions are as follows:

I: The speciation of As in this system is variable depending on geographic location and depth below the surface. It is also entirely possible that As species are changing as it travels through the system. While As(III) is more toxic than As(V), both cause adverse health effects and should...
be considered a threat when being consumed in concentrations above the MCL. From and attenuation standpoint, only approaches that mitigate both species should be considered.

II: The sedimentary sources of As here are also variable from location to location. While much of the As identified in the sediment is in “difficult to mobilize” fractions, sampled depths within PWS wells exhibit as much as 65% of the total As in the “easily mobilized” fractions. Furthermore, the sources of easily mobilized As in this system differ from other studies (Kumar et al., 2016). Our findings exhibit As distributed more randomly across easily mobilized fractions. This arbitrariness provides a significant health risk, as more geochemical processes need to be taken into account when considering attenuation strategies.

III: Results of several experiments performed here indicate that Frenchman Creek is having an effect on As levels in Wauneta’s groundwater. PWS 1 (the closest well to the creek) exhibits higher overall concentrations than other wells and more As that is easily mobilized from the sediment. If surface/groundwater interactions prove to be a major factor in labile As in groundwater, this knowledge could give good indications on where safe drinking water could be located.

IV: Results of the desorption study are inconclusive, as no sampled locations appeared to reach equilibrium. This could be due to several factors that will need to be investigated with future studies.

4.2 Future Work

This study provides a small glimpse into the complex system of As geochemistry in Western Nebraska. Further research needs to be done to understand what processes are controlling the release of As in small towns like Wauneta. The most important component that
needs to be studied now is the role of microorganisms. One of our hypotheses related to the inconclusive results of the desorption experiment is that microbes are influencing As mobility against the natural geochemical gradient we would expect in a natural subsurface system. Understanding the role these organisms play could be instrumental to identifying attenuation and alternate management strategies for struggling communities like Wauneta.

Additionally, while the results of the desorption experiment were inconclusive, adsorption mechanics need to be quantified to obtain a total understanding of sorption in this system. Many of the studies mentioned above (Feng et al., 2013; Hafeznezami et al., 2016; Kumar et al., 2016; Manning and Goldberg, 1997; Nickson et al., 2000; Swedlund and Webster, 1999), all contain both desorption and adsorption data. In order to truly compare data recovered here to the literature, more research on As sorption is necessary.

Finally, as conclusions drawn here point toward surface-groundwater interactions as a major contributor to As mobility in Wauneta, groundwater modelling research may be necessary to explicate exact As plume movements, as well as to confirm our conclusions. This could also be beneficial when providing Wauneta with attenuation strategies, as knowing the location and movement specifics of an As plume would make advising drilling sites for new wells very easy, although this would need to be constantly monitored to consistently provide citizens with safe drinking water.
Figure 1: Map of Wauneta, NE located in Chase County. Green dots indicate sampling locations. 1-PWS 1, 2-PWS 2, 3-PWS 4, 4-Creek water sampling location, 5-Creek sediment core location.
Figure 2: From Snow et al., 2016. Underlying geology and initial As and Fe concentrations of sampling wells.
Figure 3: Results of speciation study. Light shade represents As (V) and dark shade represents As (III)
Figure 4: Normalized depiction of fractionation results. Red sections indicate As that is mobilized relatively easily and blue sections indicate As that is difficult to mobilize. Top-left: Frenchman Creek, top-right: PWS-1, bottom-left: PWS-2, bottom-right: PWS-4.
**Figure 5:** Results of Desorption Study for Frenchman Creek.

**Figure 6:** Results of Desorption Study for PWS 1.

**Figure 7:** Results of Desorption Study for PWS 4.
<table>
<thead>
<tr>
<th>AGW Chemical Makeup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>NH₄Cl</td>
</tr>
<tr>
<td>NaHCO₃</td>
</tr>
<tr>
<td>NaNO₃</td>
</tr>
<tr>
<td>MgCl₂.6H₂O</td>
</tr>
<tr>
<td>CaCl₂.2H₂O</td>
</tr>
</tbody>
</table>

Table 1: Species present in AGW used in adsorption experiments.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth</th>
<th>Sand Silt Clay</th>
<th>Moisture</th>
<th>pH</th>
<th>ORP</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC – A*</td>
<td>Creek Bed</td>
<td>90.61</td>
<td>23.34</td>
<td>6.46</td>
<td>243</td>
</tr>
<tr>
<td>FC – B*</td>
<td>10-11</td>
<td>54.91</td>
<td>12.80</td>
<td>6.67</td>
<td>-145</td>
</tr>
<tr>
<td>FC - C</td>
<td>15.0 - 17.5</td>
<td>91.79</td>
<td>11.52</td>
<td>6.75</td>
<td>144</td>
</tr>
<tr>
<td>FC - D</td>
<td>25.0 - 27.5</td>
<td>68.94</td>
<td>6.61</td>
<td>6.68</td>
<td>-502</td>
</tr>
<tr>
<td>FC - E</td>
<td>5.0 - 7.5</td>
<td>93.94</td>
<td>28.73</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PWS - 1A*</td>
<td>17.5-20</td>
<td>97.88</td>
<td>5.60</td>
<td>6.65</td>
<td>394</td>
</tr>
<tr>
<td>PWS - 1B*</td>
<td>112.5-113.5</td>
<td>83.08</td>
<td>10.72</td>
<td>6.71</td>
<td>30</td>
</tr>
<tr>
<td>PWS - 1C</td>
<td>42.5 - 44.0</td>
<td>61.91</td>
<td>8.80</td>
<td>6.75</td>
<td>230</td>
</tr>
<tr>
<td>PWS - 1D</td>
<td>81.0 - 82.5</td>
<td>97.76</td>
<td>10.93</td>
<td>6.71</td>
<td>-526</td>
</tr>
<tr>
<td>PWS - 1E</td>
<td>62.5 - 65</td>
<td>99.93</td>
<td>20.61</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PWS - 2A</td>
<td>30.0 - 31.0</td>
<td>97.85</td>
<td>13.02</td>
<td>6.74</td>
<td>-521</td>
</tr>
<tr>
<td>PWS - 2B</td>
<td>65.0 - 66.0</td>
<td>96.11</td>
<td>7.05</td>
<td>6.72</td>
<td>-240</td>
</tr>
<tr>
<td>PWS - 2C</td>
<td>81.0 - 82.5</td>
<td>98.96</td>
<td>11.53</td>
<td>6.45</td>
<td>-479</td>
</tr>
<tr>
<td>PWS - 4A*</td>
<td>61-62.5</td>
<td>97.47</td>
<td>11.67</td>
<td>6.22</td>
<td>340</td>
</tr>
<tr>
<td>PWS - 4B*</td>
<td>112.5-114</td>
<td>79.35</td>
<td>14.86</td>
<td>6.31</td>
<td>389</td>
</tr>
<tr>
<td>PWS - 4C</td>
<td>101.0 - 102.5</td>
<td>99.20</td>
<td>11.52</td>
<td>6.85</td>
<td>-514</td>
</tr>
<tr>
<td>PWS - 4D</td>
<td>138.5 - 140.0</td>
<td>96.69</td>
<td>12.89</td>
<td>6.71</td>
<td>-509</td>
</tr>
</tbody>
</table>

Table 2: Sediment Properties. Samples marked with a * denote those used in adsorption experiments.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fraction</th>
<th>Extractant</th>
<th>Extraction Condition</th>
<th>SSR</th>
<th>Wash Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Non-specifically sorbed As</td>
<td>0.05 M (NH₄)₂SO₄</td>
<td>4h shaking, 20 °C</td>
<td>1:15</td>
<td>------</td>
</tr>
<tr>
<td>2</td>
<td>Specifically sorbed As</td>
<td>0.05 M NH₄H₂PO₄</td>
<td>16h shaking, 20 °C</td>
<td>1:15</td>
<td>------</td>
</tr>
<tr>
<td>3</td>
<td>As with amorphous and Poorly-crystalline hydrous oxides of Fe and Al</td>
<td>0.2M NH₄-oxalate buffer @ pH 3.25</td>
<td>4h shaking in dark, 20 °C</td>
<td>1:15</td>
<td>0.2M NH₄-oxalate buffer @ pH 3.25, SSR 1:10, 10 min shaking in dark</td>
</tr>
<tr>
<td>4</td>
<td>As with well-crystalline hydrous oxides of Fe and Al</td>
<td>0.2M NH₄-oxalate buffer @ pH 3.25 + 0.1 M Ascorbic acid</td>
<td>30 min shaking in water bath, 96±3 °C</td>
<td>1:15</td>
<td>0.2M NH₄-oxalate buffer @ pH 3.25, SSR 1:10, 10 min shaking in dark</td>
</tr>
<tr>
<td>5</td>
<td>Residual phases</td>
<td>HNO₃/H₂O₂</td>
<td>microwave digestion</td>
<td>1:25</td>
<td>------</td>
</tr>
</tbody>
</table>
## Table 3: Descriptions of fractionation treatments

## Table 4: Results of As Speciation Experiment. Excluding percentages, values reported in parts per billion (ppb).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total As</th>
<th>As III</th>
<th>As V</th>
<th>% As III</th>
<th>% As V</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC - A</td>
<td>11.08</td>
<td>2.45</td>
<td>8.63</td>
<td>22.14%</td>
<td>77.86%</td>
</tr>
<tr>
<td>FC - B</td>
<td>2.09</td>
<td>1.58</td>
<td>0.51</td>
<td>75.70%</td>
<td>24.30%</td>
</tr>
<tr>
<td>1 - A</td>
<td>5.42</td>
<td>4.73</td>
<td>0.69</td>
<td>87.36%</td>
<td>12.64%</td>
</tr>
<tr>
<td>1 - B</td>
<td>1.61</td>
<td>1.39</td>
<td>0.22</td>
<td>86.37%</td>
<td>13.63%</td>
</tr>
<tr>
<td>4 - A</td>
<td>0.93</td>
<td>0.34</td>
<td>0.59</td>
<td>36.32%</td>
<td>63.68%</td>
</tr>
<tr>
<td>4 - B</td>
<td>1.32</td>
<td>0.91</td>
<td>0.41</td>
<td>68.68%</td>
<td>31.32%</td>
</tr>
</tbody>
</table>

## Table 5: Results of As Fractionation Experiment. Values reported in ppb.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC - A</td>
<td>3.76</td>
<td>17.53</td>
<td>4.26</td>
<td>3.90</td>
<td>26.85</td>
<td>56.30</td>
</tr>
<tr>
<td>FC - B</td>
<td>0.48</td>
<td>1.38</td>
<td>4.22</td>
<td>3.84</td>
<td>2.57</td>
<td>12.49</td>
</tr>
<tr>
<td>FC - C</td>
<td>1.75</td>
<td>0.43</td>
<td>12.90</td>
<td>6.99</td>
<td>16.27</td>
<td>38.33</td>
</tr>
<tr>
<td>FC - D</td>
<td>0.63</td>
<td>1.44</td>
<td>1.54</td>
<td>5.74</td>
<td>7.71</td>
<td>17.05</td>
</tr>
<tr>
<td>FC - E</td>
<td>1.55</td>
<td>20.37</td>
<td>16.15</td>
<td>26.83</td>
<td>12.10</td>
<td>76.99</td>
</tr>
<tr>
<td>PWS - 1A</td>
<td>1.03</td>
<td>5.63</td>
<td>5.18</td>
<td>3.20</td>
<td>1.60</td>
<td>16.64</td>
</tr>
<tr>
<td>PWS - 1B</td>
<td>0.03</td>
<td>1.06</td>
<td>1.03</td>
<td>1.14</td>
<td>1.96</td>
<td>5.22</td>
</tr>
<tr>
<td>PWS - 1C</td>
<td>3.77</td>
<td>2.51</td>
<td>3.51</td>
<td>8.00</td>
<td>7.29</td>
<td>25.08</td>
</tr>
<tr>
<td>PWS - 1D</td>
<td>2.85</td>
<td>4.63</td>
<td>8.26</td>
<td>7.42</td>
<td>15.33</td>
<td>38.48</td>
</tr>
<tr>
<td>PWS - 1E</td>
<td>1.51</td>
<td>6.05</td>
<td>1.81</td>
<td>4.94</td>
<td>8.66</td>
<td>22.97</td>
</tr>
<tr>
<td>PWS - 2A</td>
<td>0.98</td>
<td>4.14</td>
<td>3.66</td>
<td>7.21</td>
<td>12.43</td>
<td>28.42</td>
</tr>
<tr>
<td>PWS - 2B</td>
<td>0.53</td>
<td>3.35</td>
<td>1.96</td>
<td>5.82</td>
<td>5.57</td>
<td>17.23</td>
</tr>
<tr>
<td>PWS - 2C</td>
<td>2.13</td>
<td>2.35</td>
<td>11.57</td>
<td>8.90</td>
<td>12.77</td>
<td>37.72</td>
</tr>
<tr>
<td>PWS - 4A</td>
<td>0.43</td>
<td>1.07</td>
<td>1.69</td>
<td>8.50</td>
<td>3.06</td>
<td>14.75</td>
</tr>
<tr>
<td>PWS - 4B</td>
<td>0.48</td>
<td>0.69</td>
<td>1.68</td>
<td>2.44</td>
<td>3.45</td>
<td>8.74</td>
</tr>
<tr>
<td>PWS - 4C</td>
<td>1.46</td>
<td>1.98</td>
<td>13.46</td>
<td>7.83</td>
<td>16.01</td>
<td>40.73</td>
</tr>
<tr>
<td>PWS - 4D</td>
<td>0.89</td>
<td>2.59</td>
<td>7.98</td>
<td>6.58</td>
<td>11.20</td>
<td>29.23</td>
</tr>
</tbody>
</table>

Table 5: Results of As Fractionation Experiment. Values reported in ppb.
Appendix B: References


Hicks, N. (2016) City to study rising arsenic level in city drinking water. Lincoln Journal Star.


