

# Push-Pull Experiments to Evaluate In-Situ Arsenic Remediation in the Ogallala Aquifer

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## Executive Summary

Arsenic concentrations exceed the U.S. Environmental Protection Agency maximum contaminant level (MCL) for drinking water (10 µg/L) in 220 Public Water Systems in Texas. Conventional treatments for arsenic removal are *ex-situ* treatments, which are costly and produce high concentration arsenic-contaminated sludge which must be disposed of properly.

A pilot study to assess an *in-situ* arsenic remediation treatment was conducted in the city of Andrews wellfield, Andrews County, Texas. This procedure involved adding dissolved iron to the aquifer through water wells. Under oxidizing conditions, the dissolved iron precipitates as iron oxides near the well. Water pumped from the well following iron precipitation flows through the iron-enriched zone and arsenic is adsorbed onto the iron oxides.

Two experiments were conducted in which 24 g and 72 g of Fe were injected into an experimental well. Prior to the experiments, arsenic concentration in the well water was 43 µg/L. Following the first experiment, arsenic concentration in produced water stabilized at 25 µg/L, and after the second experiment arsenic values stabilized at 20 µg/L, representing an approximate 50% reduction in produced arsenic under the test conditions.

These preliminary results suggest that there is potential for treating groundwater arsenic contamination in small public water systems using in situ treatment based on addition of iron to the wells. The reconnaissance tests showed a 50% reduction in arsenic concentration; however, additional testing is required to determine if arsenic concentrations can be reduced to less than the MCL of 10 mg/L and the frequency and volume (mass) of treatment injections required to maintain these low arsenic concentrations needs to be determined for full demand production rates.

## Introduction

Arsenic concentrations exceed the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for drinking water (10 µg/L) in 220 out of 6154 (3.6%) Public Water Systems (PWSs) tested in Texas (1999-2009), with values as high as 185 µg/L. Concentrations in the southern High Plains (SHP) in Texas exceed the MCL in 32% of PWS wells, and approximately 51% of all wells in the southern region of SHP. Elevated arsenic concentration levels represent a potential health hazard as well as a challenge for public water suppliers, who are required to comply with federal drinking water standard regulations. Adverse health effects associated with high arsenic intake by humans are well documented and include several types of cancer (Wu et al., 1989; Bates et al., 1995; Chious et al., 1995; Tsuda et al., 1995; Mazumder et al., 1997), as well as vascular (Chen et al., 1995) and neurological (Abernathy et al., 2003) diseases, among others. Along with food, drinking water represents a primary pathway for arsenic intake.

Arsenic removal from groundwater can be achieved through various methods, including precipitation, adsorption, and filtration. Arsenic removal can be conducted at small and large scales and in different locations, such as *in-situ*, centralized treatment, point of entry (POE), and point of use (POU). All forms of *ex-situ* treatments are costly, require either a centralized treatment plant or installation of distributed systems for POE and POU treatment. Furthermore, *ex-situ* treatment generates waste products with high arsenic concentrations requiring regulated disposal. Conversely, *in-situ* treatment essentially sequesters aqueous arsenic onto the solid phase and decreases or eliminates arsenic concentrations in produced groundwater and eliminates associated waste-disposal issues.

*In-situ* treatment requires high oxygen and iron concentrations (Rott and Kauffmann, 2008; Stollenwerk et al., 2008). These high concentrations can be achieved by aeration of groundwater having low concentrations of dissolved oxygen (DO) and by addition of iron to groundwater having low iron concentrations. A high iron to arsenic ratio ( $\geq 10:1$ ) is required. Precipitation of iron and arsenic sorption occurs in the aquifer. High DO levels in groundwater will oxidize relatively mobile arsenite to the less-mobile arsenate oxyanion form of arsenic while concurrently oxidizing highly soluble ferrous iron to relatively insoluble ferric iron, resulting in a decrease in the groundwater arsenic concentrations (World-Bank, 2005). Rott and Kauffmann (2008) decreased arsenic concentrations from 50 to  $<10$  µg/L (and in some cases as low as 1 µg/L) within 16-19 months by alternating injection and extraction of groundwater from a single well throughout the period. Aerated groundwater can be amended with ferric chloride ( $\text{FeCl}_2$ ) salt which oxidizes and precipitates as iron oxy-hydroxides that subsequently adsorb the oxidized arsenate.

Complexity and cost issues are primarily associated with *ex-situ* treatments, though competing ions and chemical reactions can occur in both *ex-situ* and *in-situ* treatments. Several limitations exist for the different techniques available (Appendix A). The complexity of treatment technologies ranges from simple turn-key systems (i.e., commercially available under-sink POU systems) to those requiring trained personnel to operate high-cost centralized systems (i.e., a reverse osmosis plant). Furthermore, the chemical composition of the influent water is extremely important because competing ions and different chemical reactions influence treatment effectiveness (MWH, 2005).

The objective of this study was to evaluate the effectiveness of an *in-situ* treatment approach to mitigate arsenic concentrations in groundwater produced from the Ogallala aquifer. Push-pull pumping tests were performed to create an iron oxide enriched zone

to adsorb arsenic around an experimental well located in the city of Andrews, in Andrews County, Texas.

## **Study Area**

### ***Regional Hydrogeology***

The push-pull experiment was conducted in the Florey Field, which is one of the PWS well fields for the city of Andrews in Andrews County, Texas (Figure 1). The High Plains or Ogallala aquifer is the major aquifer in the study area (Figure 2), which is equivalent to the Ogallala formation, the dominant geologic unit that makes up the High Plains aquifer. The Ogallala formation is late Tertiary (Miocene–Pliocene) or about 2–12 million years in age (Nativ, 1988). It consists of coarse fluvial sandstones and conglomerates that were deposited in the paleovalleys of a mid-Tertiary erosional surface and eolian sands that were deposited in intervening paleoupland areas (Gustavson and Holliday, 1985). The study area consists of a paleoupland region where the Ogallala formation is thin, resulting in a low saturated thickness and shallow water table. The top of the Ogallala formation is marked in many places by a resistant calcite layer known as the “caprock caliche”. Within much of the study area, the Ogallala formation is overlain by Quaternary-age (Pleistocene–Holocene) eolian, fluvial, and lacustrine sediments that are collectively called the Blackwater Draw formation (Holliday, 1989). The texture of the formation ranges from sands and gravels along riverbeds to clay-rich sediments in playa floors.

In much of the southern High Plains, the Ogallala Formation overlies Lower Cretaceous (Comanchean) strata. The top of the Cretaceous is marked by an uneven erosional surface representing the end of the Laramide orogeny. Cretaceous strata are absent beneath the thick Ogallala paleovalley-fill deposits because they were removed by prior erosion. The Cretaceous sediments were deposited in a subsiding shelf environment and consist of the Trinity Group (including the basal sandy, permeable Antlers Formation); the Fredericksburg Group (limey to shaley formations, including the Walnut, Comanche Peak, and Edwards Formations, as well as the Kiamichi Formation); and the Washita Group (low-permeability, shaley sediments of Duck Creek Formation) (Nativ, 1988). The sequence results in two main aquifer units: the Antlers Sandstone (also termed the Trinity or Paluxy sandstone, about 15 m thick) and the Edwards Limestone (about 30 m thick). These aquifer units constitute the Edwards-Trinity (High Plains) aquifer (Ashworth and Flores, 1991). The limestone decreases in thickness to the northwest and transitions into the Kiamichi and Duck Creek formations.

The Ogallala formation also overlies the Triassic Dockum Group in much of the southern High Plains where Cretaceous sediments are absent (Figure 2). The Dockum Group is generally about 150 m thick and is exposed along the margins of the High Plains. The uppermost sediments consist of red mudstones that generally form an aquitard. Underlying units (Trujillo Sandstone [Upper Dockum] and Santa Rosa Sandstone [lower Dockum]) form the Dockum aquifer. Water quality in the Dockum Group is generally poor (Dutton and Simpkins, 1986). The sediments of the Dockum Group were deposited in a continental fluvio-lacustrine environment that included streams, deltas, lakes, and mud flats (McGowen et al., 1977) related to alternating arid and humid climatic conditions. The Triassic Dockum rocks are up to 600 m thick in the Midland Basin.

## ***Regional Groundwater Arsenic Distribution***

Arsenic concentrations exceed the EPA MCL (10 µg/L) in many wells in the region (Figure 3). Approximately half of the wells in the Ogallala aquifer and one-quarter of wells in the Dockum aquifer in this region (SHP-S) contain arsenic levels above the MCL based on the most recent sample of each well from the TWDB database. Table 1 gives the percentage of wells with arsenic exceeding the MCL (10 µg/L) in each of the major aquifers in the study area.

Although it seems that there is general stratification of arsenic concentrations with depth in the study area (Figure 4), with arsenic concentrations decreasing with depth, the distribution is controlled primarily by location with higher arsenic concentrations in the southern part of the High Plains. When studying each aquifer separately, this stratification is not apparent.

## ***Florey Well Field***

The experimental site is located in the Florey well field (Figures 1 and 5), which is the major water source for the city of Andrews. The water produced from this field is from wells completed in the Ogallala aquifer. Arsenic concentrations in the Florey well field, measured in April 2009, are non-compliant with respect to arsenic in all wells with an average of arsenic concentration of 28 µg/L (Table 2). The PWS wells are screened from 20 ft below surface to the bottom of the well. Depth to water in these wells ranges from ~100 to 115 ft below ground surface.

The geology at Florey well field from geophysical well logs suggests a clay unit at a depth of 153 ft below the land surface that separates the Ogallala aquifer into an upper and lower zone. The upper zone is an unconfined aquifer, and the lower zone is confined by the clay unit.

## **Methods and Materials**

An experimental well was drilled on May 19, 2010 as part of this study to conduct the push-pull tests. The well was constructed of 4.5-in ID PCV completed to a depth of 190 ft and screened from 155 to 190 ft, below a clay unit. The top 155 ft was cased and the annulus was sealed with bentonite grout. The static depth to water in the completed well (141 ft below ground surface) indicates that the clay unit creates a locally confined zone in the aquifer.

Two push-pull experiments were conducted in June 10-12, 2010. During the push phase, an acidified hydrated ferrous chloride (HCl and FeCl<sub>2</sub>·4H<sub>2</sub>O) solution was injected into the aquifer to create a “filter” zone around the well (Figure 6). A 550 gallon-capacity tank was filled using water from a nearby well. The well water in the tank was amended by adding concentrated HCl (37%; 2 L) resulting in a pH of ~3.5 to inhibit iron oxide precipitation in the tank. Hydrated ferrous chloride (86 g total, 24 g Fe) was also added to the water in each amended tank resulting in an Fe concentration of 11.5 mg/L. Bromide (NaBr) was added to (most) tanks as a conservative tracer at a concentration of ~65 mg/L. Natural bromide concentrations in regional groundwater are generally < 1 mg/L.

The tank “slugs” were injected in the well by gravity flow at approximately 30 gal/min. For each experiment, a final un-amended tank volume was injected to displace the amended water from the well and into the surrounding aquifer sediments. This was followed by a

one-hour waiting period to allow time for iron oxide precipitation to occur. The pull phase consisted of pumping and sampling the produced water.

In the first experiment (Exp 1), two tanks, one amended and one un-amended, were injected with a total of 24 g Fe and 1100 gallons. Samples were collected at 200 gallon intervals and a total of 1600 gallons were pumped. In the second experiment (Exp 2), four tanks, three amended and one un-amended, were injected with a total of 72 g Fe and 2200 gallons. Samples were collected at 100 gallon intervals and a total of 4500 gallons were pumped. A total of 96 g of Fe was injected over both experiments. Measurements of pH were performed in the field using an Orion pH meter and alkalinity was measured using a Hach® field titration kit (incremental titration).

Water samples were filtered to 0.45 µm and stored on ice in the field. Samples were analyzed for major anions (F, Cl, and SO<sub>4</sub> following EPA method 300.0) and cations (Ca, Mg, Na, and K following ASTM 6919) by ion chromatography. Samples were analyzed for trace metals (As, V, Mn, Fe, and Sr following EPA method 200.8) by ICP-MS. Samples for ICP-MS analysis were preserved with trace-metal grade HNO<sub>3</sub> (6 N, 1%) in the field. Major anion and cation concentrations were analyzed for all samples while trace metal concentrations were analyzed for every third sample (every 300 gallons). Sampling and analyses followed the approved Quality Assurance Project Plan.

## Results and Discussion

Major anion and cation concentrations measured in the pre-test experimental well water are typical of those in other nearby wells and in wells regionally, with elevated concentrations of As, F, Cl, SO<sub>4</sub>, HCO<sub>3</sub>, Na, Ca, and Mg and with a total dissolved solids (TDS) concentration of about 1000 mg/L (Table 3). Physical parameters measured on the experimental well water prior to the test indicated oxidizing conditions in the aquifer, with a dissolved oxygen (DO) concentration of 9.1 mg/L indicating that the aquifer was essentially oxygen-saturated. This was beneficial for the test in that no aeration of the injection water was required to achieve favorable conditions for iron precipitation and that arsenic was likely already in the oxidized As-V state. Arsenic speciation of groundwater in the southern High Plains also showed that arsenic was in the oxidized As-V state (Scanlon et al., 2009). The aquifer water was also slightly alkaline (pH = 7.70) indicating capacity to neutralize the acid-amended injection water. The measured arsenic concentration (43 µg/L) in the well water was higher than the average value for nearby wells in the Florey field (27 µg/L, Table 2). Other chemical constituents found in the well water indicate ions that could possibly compete with arsenic for the available sorption sites following iron oxy-hydroxide precipitation, particularly vanadium (161 µg/L).

The higher arsenic concentration in the experimental well relative to other Florey field wells nearby may be attributed to possible vertical variations in arsenic concentrations and to the short screen interval of the experimental well. The experimental well is screened from 155 to 190 below the land surface and excludes shallower groundwater sources that may have lower arsenic concentrations. The static depth to water in the experimental well (141 ft), which is completed solely below an apparently confining clay layer, is distinctly lower than water levels in other Florey field wells (100-115 ft), which are screened over almost their entire depths. Other area wells thus straddle the clay layer where present and may also produce water from shallower, lower-arsenic

concentration depths. The water used for injection was pumped from a nearby (200 m distance) well that had general overall water chemistry similar to the experimental well water prior to amendment with hydrochloric acid and ferrous chloride (Table 3).

Exp 1 was conducted in one day and included injection of 550 gallons (1 tank) of amended water followed by 550 gallons of un-amended water. After the initial one-hour waiting period, a total of 1600 gallons was pumped and sampled. A pump rate of ~6 gal/min was used during the first 900 gal that increased to ~6.5 gal/min for the remaining 700 gal (Figure 7). Water levels stabilized first at 162 ft below land surface and then at 167 ft below land surface for the two pump rates.

Exp 2 was conducted over two days and included injection of 1650 gallons (3 tanks) of amended water followed by 550 gallons of un-amended water. After the initial one-hour waiting period, the well was pumped and sampled. A pump rate of ~7 gal/min resulted in a stable water level at 162 ft below land surface (Figure 8). The first day, 1500 gal were pumped and the second day 3000 gal were pumped (after ~16 hours of no pumping) resulting in a total of 4500 gal pumped from the well during Exp 2.

The low pH injection water reacted with carbonates in the aquifer that neutralized the acid, raising the pH (Figure 9) and precipitating iron oxides. The oxidizing environment in the aquifer permitted the ferrous iron to remain stable in the solid form, and created an iron oxide coating on sediments in the aquifer. Pumping induced the aquifer water to pass through this “filter zone” around the well, sorbing trace elements such as arsenic and vanadium to the oxides.

The chemistry change in the pumped water is illustrated in Figures 9-15. Although the injected water was extremely acidic (pH ~3.5), the carbonates rapidly neutralized the acid and the lowest pH measured in the pumped water was near neutral at 7.27 in Exp 1, and 6.98 in Exp 2 (Figure 9). Values of pH returned to pre-test values for both experiments.

Bromide concentrations in the first pumped sample of Exp 2 indicate that essentially all (96%) of the water produced initially was injected water, with a concentration (63 mg/L) only slightly below the injected tracer concentration (65 mg/L). (No bromide was included in the un-amended second volume injected in Exp 1.) By the end of Exp 2, the bromide concentration was ~3 mg/L, indicating that approximately 97% of the water produced at that time was non-injected water from the aquifer.

Iron concentrations in the experimental well prior to the test were about 1 µg/L while concentrations in the injected water were about 5 orders of magnitude higher at 11.5 mg/L. The post-injection samples indicate almost 100% precipitation of the Fe, with concentrations that began around 18 µg/L and decreased to about 15 µg/L during Exp 1 (Figure 11). Excluding the first pumped sample during Exp 2, initial concentrations were about 15 µg/L and decreased to 6 mg/L by the end of the experiment. The first pumped sample during Exp 2 had an Fe concentration of 50 µg/L that might have been lowered following a longer waiting period prior to pumping.

Arsenic concentrations were significantly affected during both experiments (Figure 12). The pre-injection value of 43 µg/L decreased to 6 µg/L at the start of pumping and gradually increased to 25 µg/L by the end of Exp 1. The pre-injection value of 28 µg/L prior to Exp 2 decreased to 4 µg/L at the start of pumping and gradually increased to 20



µg/L by the end of pumping. These changes in arsenic concentrations may indicate two processes: first, arsenic co-precipitated with iron oxides which removed approximately 85% of the arsenic from the water. Then, once the precipitation process ended, arsenic was adsorbed onto the precipitated iron oxides and a new equilibrium was reached.

Compared to the pre-test concentration, approximately 42% of arsenic was removed by the end of Exp 1 (with 24 g Fe) and 53% of arsenic was removed by the end of Exp 2 (with 96 g Fe total). Mass balance calculations for arsenic indicate that approximately 140 mg of arsenic was removed from the water pumped in Exp 1 and a total of 620 mg of arsenic was removed during both experiments. Vanadium, which behaves similarly to arsenic and is a competitor for sorption sites, showed a very similar concentration profile to arsenic during both experiments (Figure 13). Approximately 430 mg of vanadium were removed from the water pumped in Exp 1 and a total of 2030 mg of vanadium was removed from the water during both experiments.

Concentrations of other constituents were also affected by the injection. Calcium concentrations increased at the beginning of the experiments due to carbonate dissolution by the acidic injection water (Figure 14). Calcium concentrations stopped increasing after 400 gal were pumped in Exp 1 and after 600 gal were pumped in Exp 2 and decreased gradually thereafter. In Exp 1 the initial calcium concentration was 42 mg/L, which peaked at 105 mg/L and finally stabilized at 75 mg/L. In Exp 2 the initial calcium concentration was 71 mg/L, which peaked at 176 mg/L, and finally stabilized at 87 mg/L. Chloride concentrations also increased at the beginning of the experiments as a result of the added Cl in salt form with the injected Fe ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and from the acid (HCl) used to inhibit Fe precipitation in the 550 gal tank (Figure 15).

## Conclusions

The results of the push-pull treatment tests demonstrate that addition of Fe is effective at decreasing arsenic concentrations in Ogallala aquifer water. Arsenic concentrations in the experimental well were 43 µg/L prior to the experiment and decreased to 20 µg/L by the end of the second experiment. Further experiments should be conducted to determine the economic viability of this approach, including longer-duration tests designed to quantify the frequency and volume (mass) of treatment injections required to maintain arsenic concentrations below the MCL at full demand production rates. These reconnaissance tests suggest that *in-situ* treatment of arsenic is feasible in PWS wells in the Ogallala aquifer and would avoid many of the issues and costs related to *ex-situ* treatment.

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## Tables

Table 1. Summary of study area wells that exceed the MCL for arsenic, by aquifer.

<i>Aquifer</i>	<i>Wells with measurements</i>	<i>Wells that exceed 10 µg/L</i>	<i>% of wells that exceed 10 µg/L</i>
Ogallala	184	102	55%
Dockum	12	3	25%
other	45	19	42%

Table 2. Arsenic concentrations in nearby Florey well field wells.

<i>Well</i>	<i>As (µg/L)</i>
Florey #12	32.8
Florey #14	28.9
Florey #15	28.2
Florey #16	21.8
Florey #18	25.1
Average	27.4

Table 3. Anion, cation, trace metal, and general concentration / parameter values for pre-test water from the experimental well and for the un-amended and amended injection water obtained from a nearby well. The injection water was amended with HCl, ferrous chloride (43 g total, 24 g Fe), and NaBr.

<i>Constituent</i>	<i>Experimental well water</i>	<i>Injection water (un-amended)</i>	<i>Injection water (amended)</i>	<i>units</i>
<i>Anions</i>				
F	3.9	3.9	3.9	mg/L
Cl	283	210	270	mg/L
Br	0.9	1.1	65	mg/L
SO <sub>4</sub>	137	153	154	mg/L
HCO <sub>3</sub>	386	230	(0)	mg/L
<i>Cations</i>				
Ca	41.8	72.0	78.2	mg/L
Mg	60.3	75.6	81.7	mg/L
Na	247	97.9	113	mg/L
K	6.4	6.8	6.8	mg/L
Si	25.1	27.3	27.3	mg/L
Sr	1.9	2.7	2.7	mg/L
<i>Trace metals</i>				
As	43	21	10	µg/L
B	192	210	213	µg/L
Fe	1	1	11,500	µg/L
Mn	16	11	11	µg/L
Se	9	11	11	µg/L
V	161	70	70	µg/L
<i>General</i>				
DO	9.2	9.2	-	mg/L
pH	7.7	7.3	3.5	
Temperature	19	19	-	°C
Specific conductance	1293	1305	-	µS/cm

# Figures

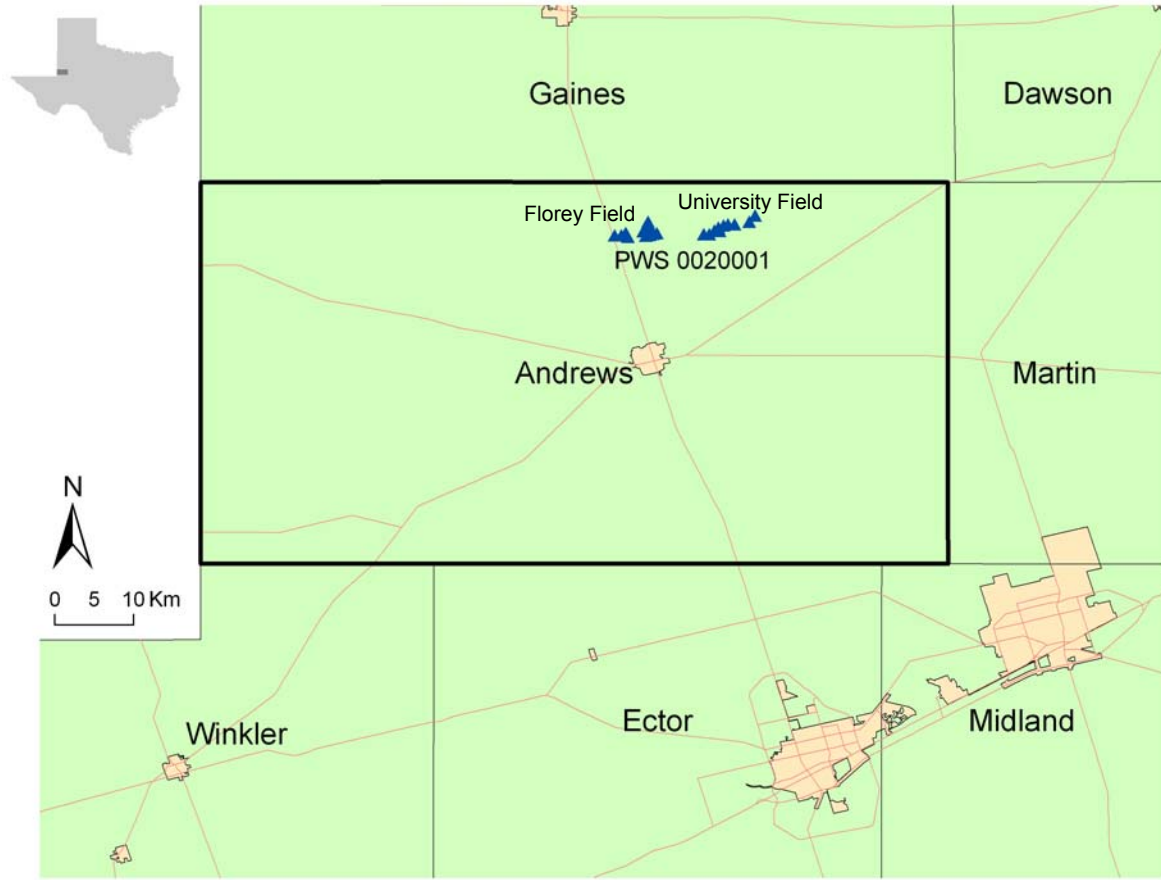
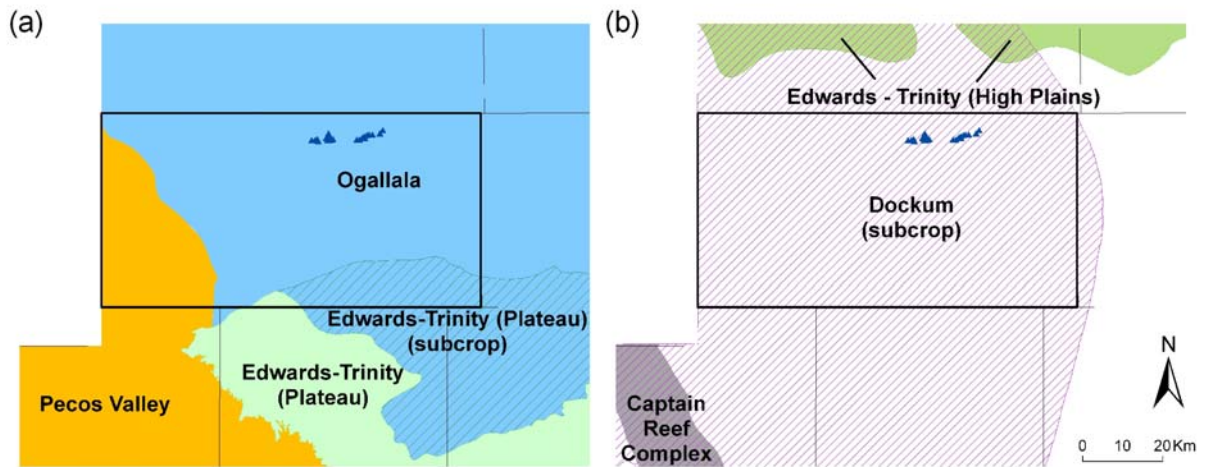


Figure 1. Map showing the locations of the City of Andrews PWS wells.



"Subcrop" indicates a portion of an aquifer that underlies other formations. All other labels indicate a portion of an aquifer that is exposed on the surface.

Figure 2. Aquifers in the study area.

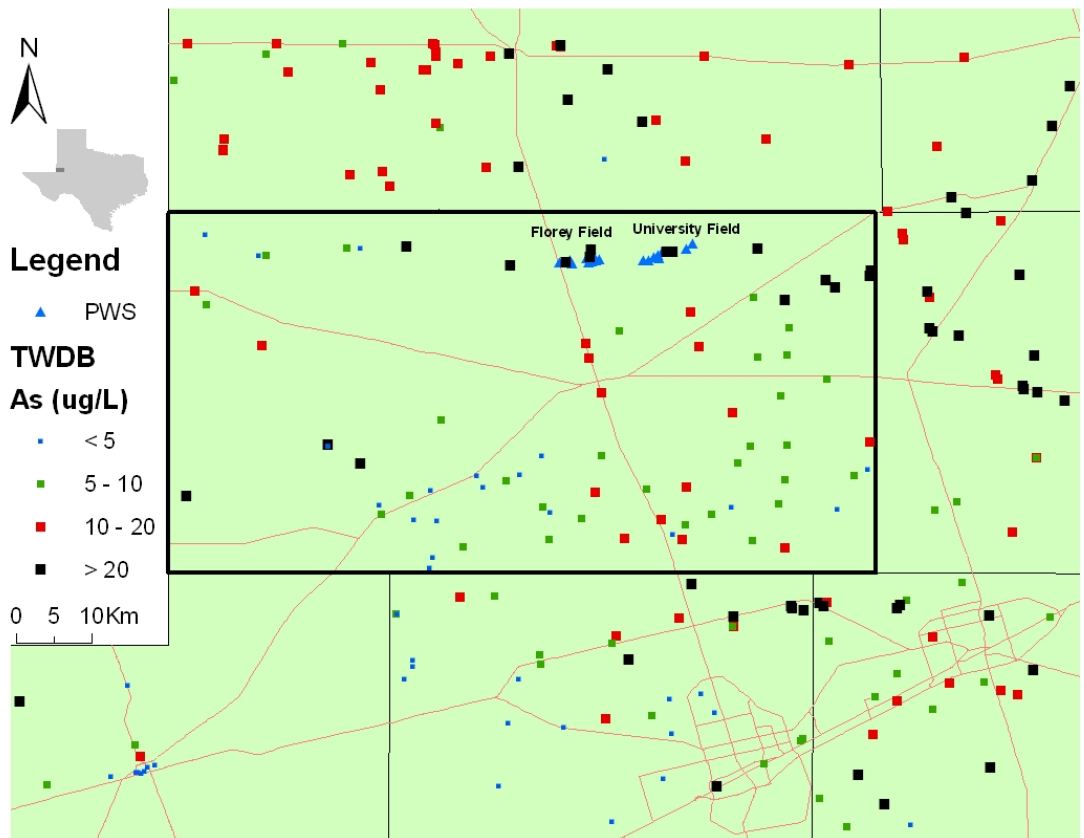


Figure 3. Spatial distribution of groundwater arsenic concentrations in the study area (TWDB database).

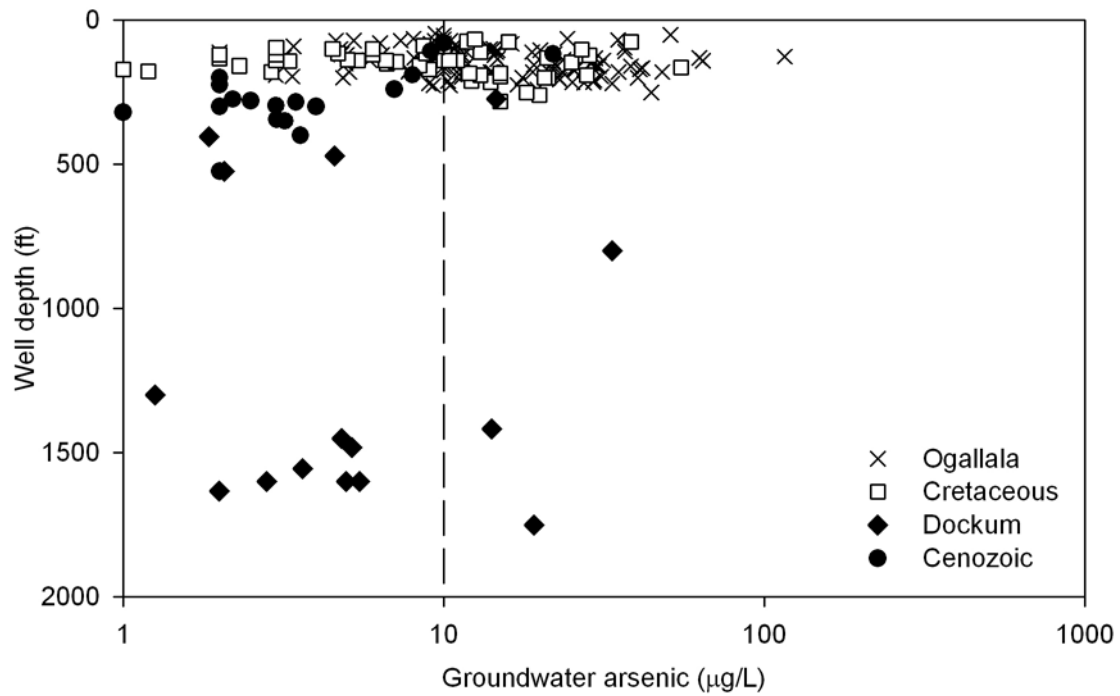


Figure 4. Relationship between groundwater arsenic concentrations and well depth by aquifer in the study area (TWDB database). (Cretaceous includes the Edwards-Trinity High Plains and Antlers aquifers, Cenozoic represents the Cenozoic-Pecos Alluvium aquifer.)



Figure 5: Google Earth image of the Florey well field, located approximately 10 miles north of Andrews, Texas. The locations of the experimental push-pull well and the injection source water well (F #12) are shown.

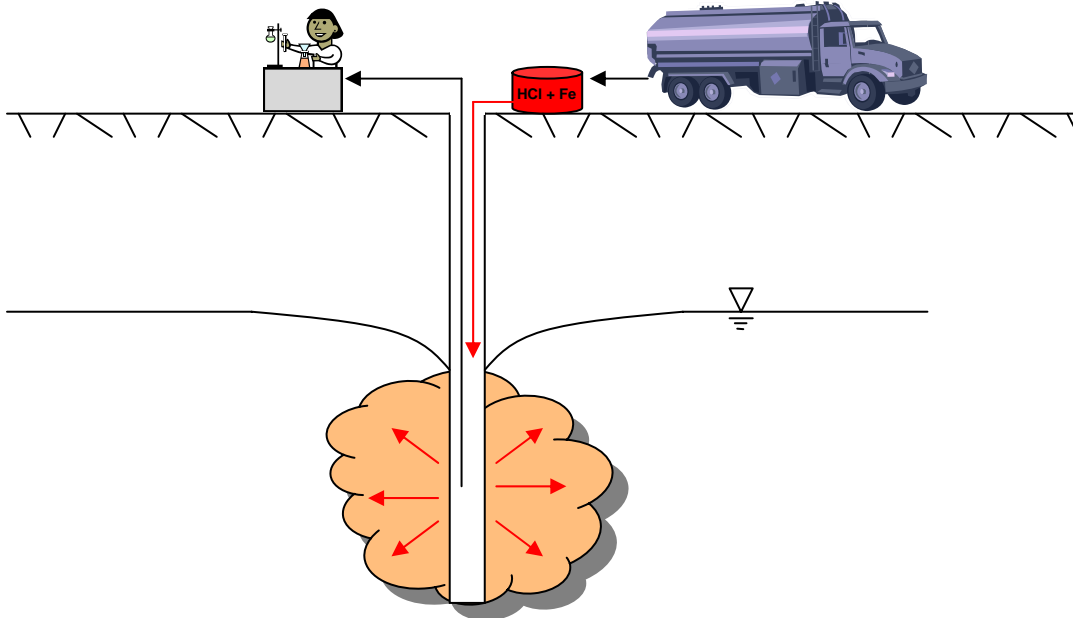


Figure 6. Schematic diagram of the push-pull test procedure. Water, produced either from the injection well or another well, is amended with HCl and  $\text{FeCl}_2$ , and injected into the treatment well. The injected water enters the formation surrounding the well bore where alkaline water and carbonate sediments neutralize the acid and oxidizing conditions result in Fe precipitation in the form of Fe oxy-hydroxides. The precipitated Fe provides sorption sites for arsenic as the natural formation water flows to the well during subsequent pumping.

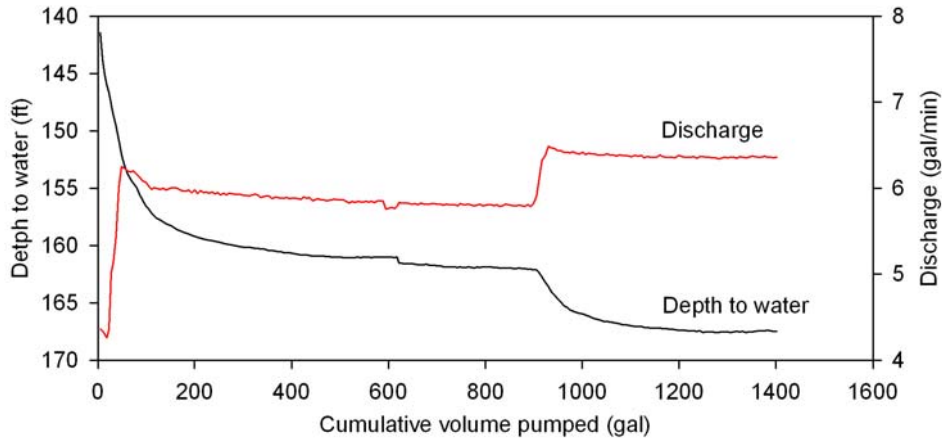


Figure 7. Experiment 1 depth to water and discharge rate versus cumulative volume pumped.

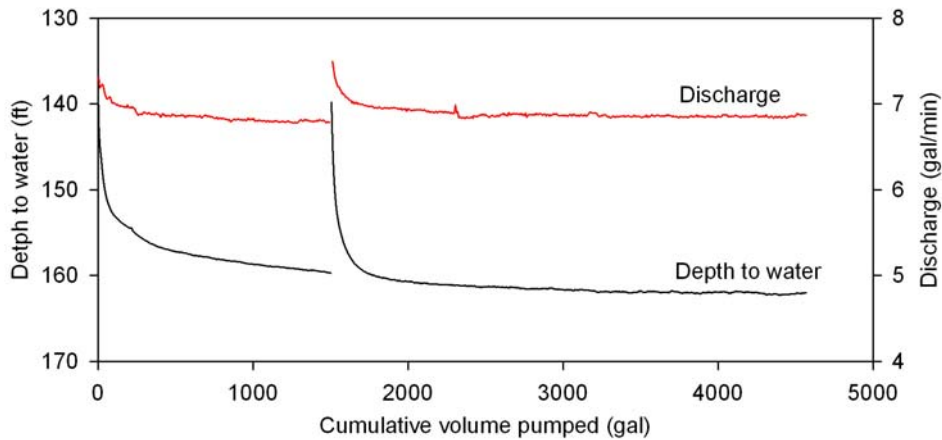


Figure 8. Experiment 2 depth to water and discharge rate versus cumulative volume pumped.

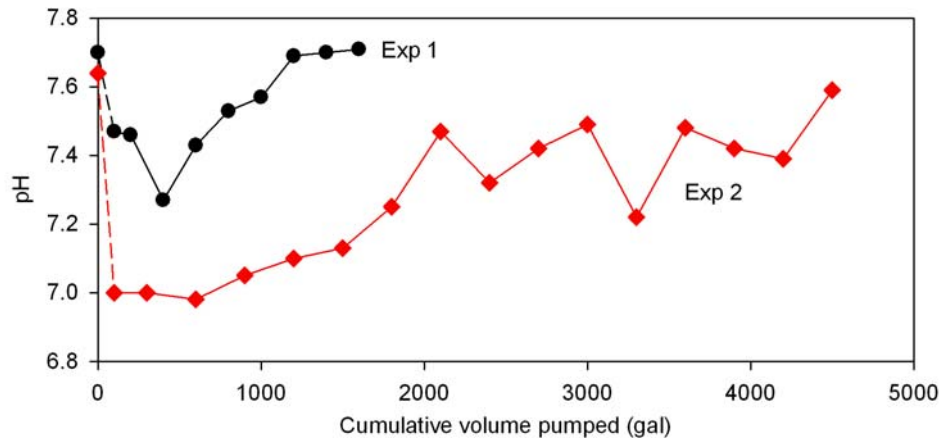


Figure 9. Variations in pH during experiments 1 and 2. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment. The results indicate that the injected acidic water (pH = ~3.5) was rapidly neutralized. Values of pH returned to pre-test values for both experiments.



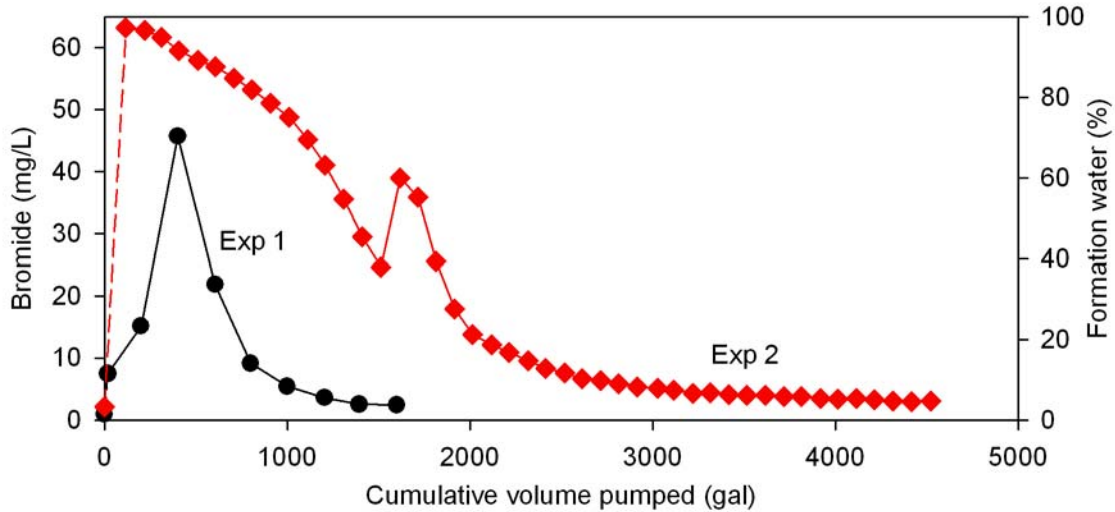


Figure 10. Variations in bromide concentrations during experiments 1 and 2. Bromide was added to only the amended tank in experiment 1 and to all tanks in experiment 2. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment. The axis on the right (Formation water) represents the percentage of formation (non-injected) water produced (during Exp 2 only) based on the injection water bromide concentration of 65 mg/L and formation water (background) bromide concentration of 1 mg/L.

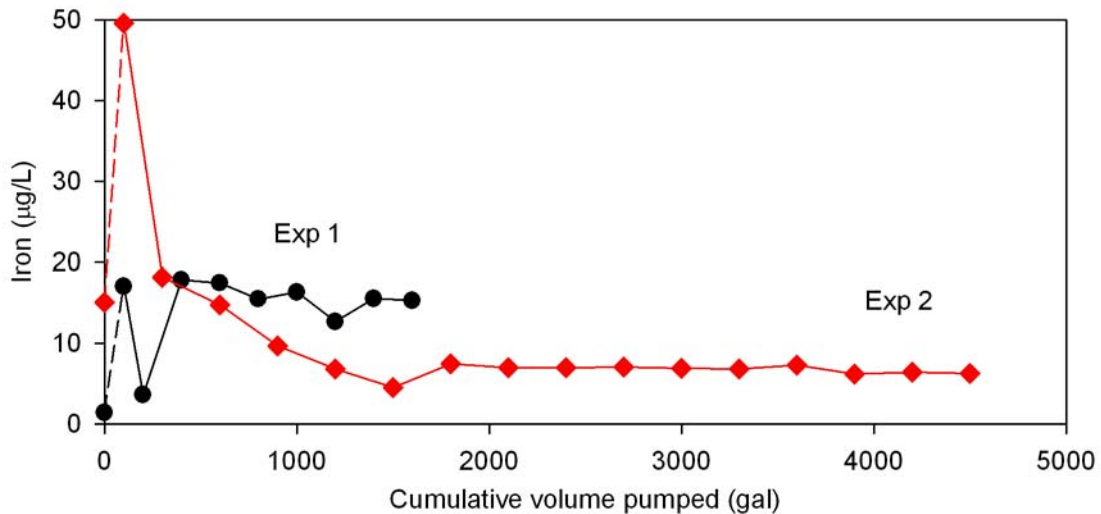


Figure 11. Variations in iron concentrations during experiments 1 and 2. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment. Iron concentration in all injected water was 11.5 mg/L, with a total of 96 g of iron injected over both experiments. Concentrations in the produced water indicate that essentially all of the iron precipitated in the aquifer.

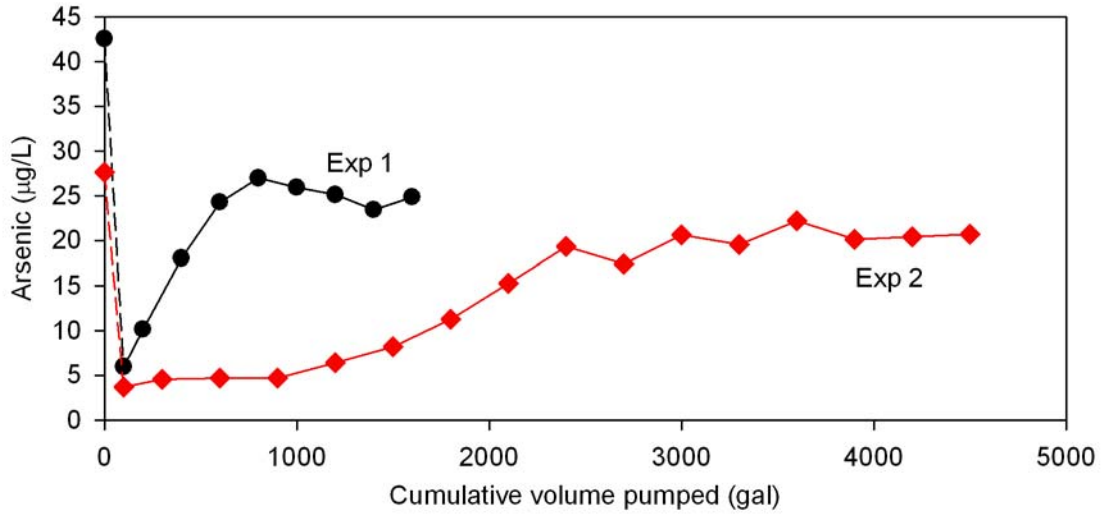


Figure 12. Variations in arsenic concentrations during experiments 1 and 2. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment.

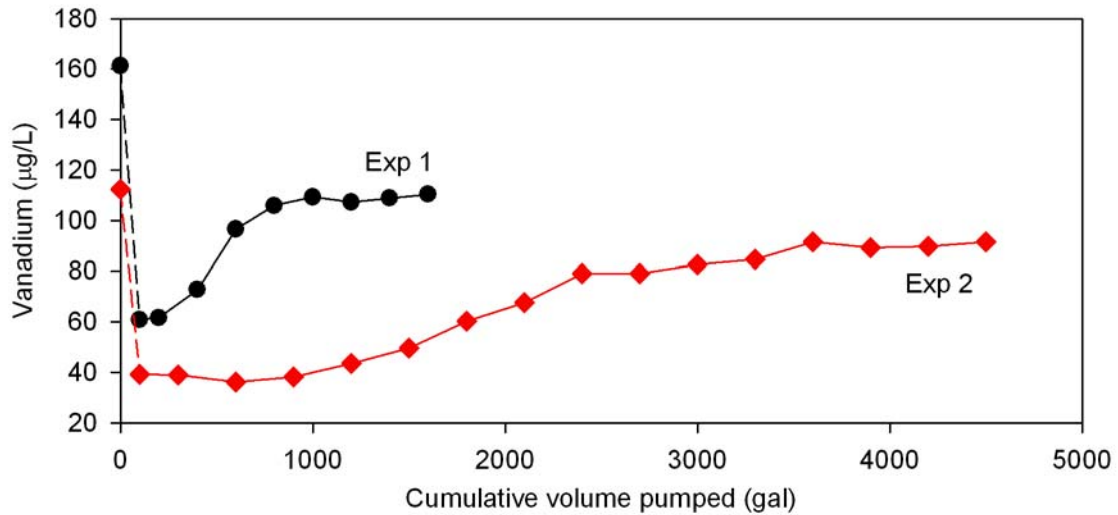


Figure 13. Variations in vanadium concentrations during experiments 1 and 2. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment.

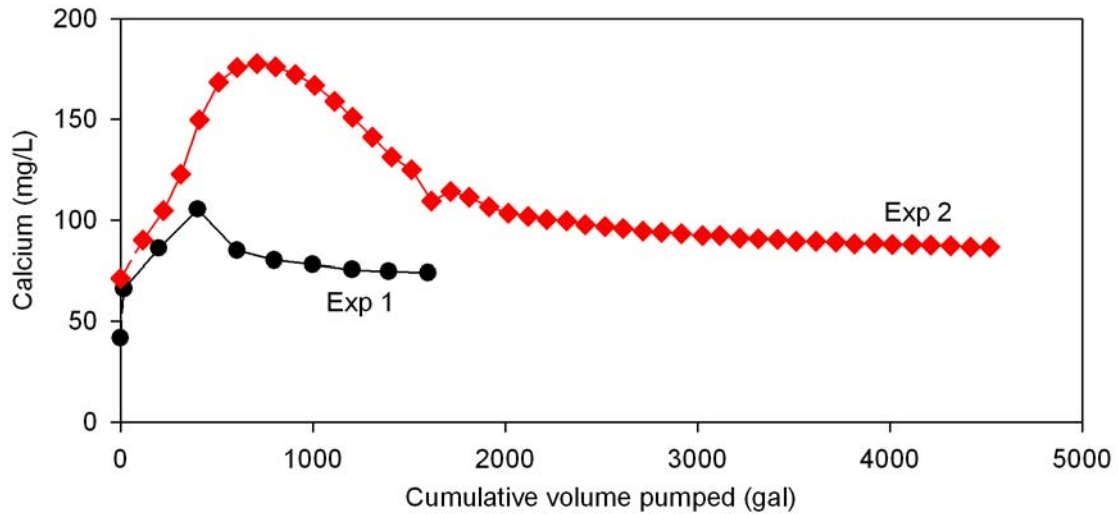


Figure 14. Variations in calcium concentrations during experiments 1 and 2. The HCl in the injected water reacted with calcite and resulted in calcium concentrations that initially increased and then decreased as pumping continued. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment.

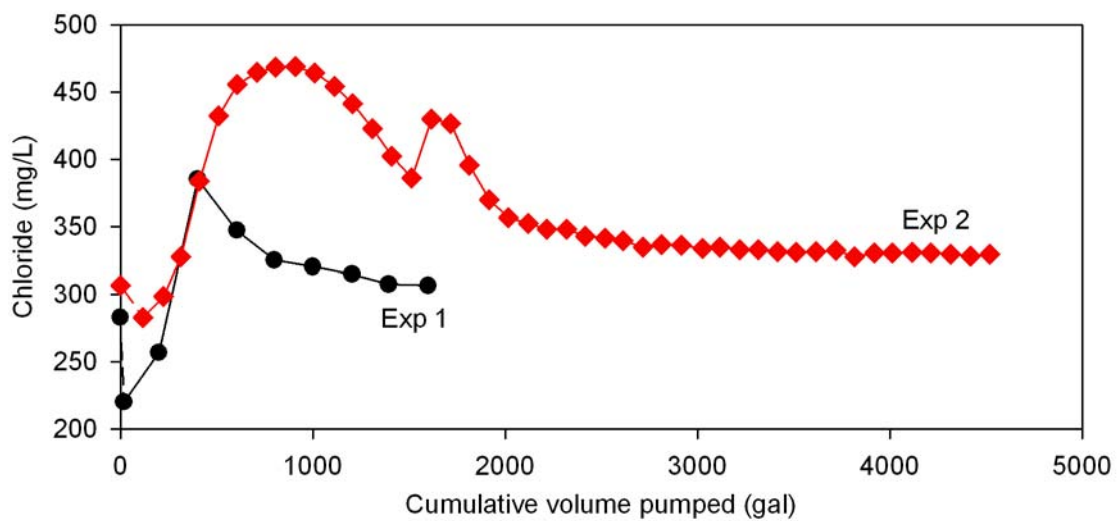


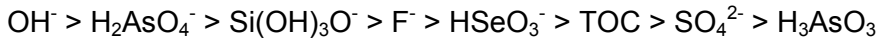
Figure 15. Variations in chloride concentrations during experiments 1 and 2. Concentrations associated with 0 volume pumped represent pre-test conditions for each experiment.

# Appendix A

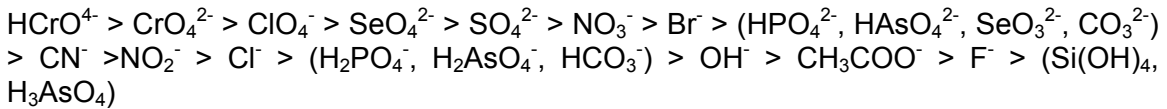
## Competing ions:

Many treatments are based on the affinity of a pollutant to adsorp/exchange. Presence of competing ions in the effluent may decrease the ability to remove pollutants (Table A1). The presence of 10 mg/L silica could decrease the sorption process of arsenic by up to 70% (Meng et al., 2000).

Ion hierarchy, in the order of competing ion selectivity, varies according to the treatment method used and reaction carried out. Sorption methods, such as activated alumina, have the following hierarchy of competing ions (USEPA, 2000):



An ion hierarchy in relation to affinity for resin exchange of a Strong Base Anion (SBA) selectivity (ion exchange resin) causes ions higher in the hierarchy to flush out other ions from the resin. The hierarchy of competing ions in relation to arsenic and fluoride is (MWH, 2005; USEPA, 2000):



## Chemical reactions:

Other problems that may occur include fouling of membranes. Potential fouling could be caused by scaling and by corrosive damage. Scaling occurs when certain ions react in the water and precipitate. These scales clog the membranes and decrease efficiency. Silica and sulfate are the main ions that might precipitate. High TDS may also decrease efficiency of different treatments. High chloride concentrations poses a different risk in membrane processes. The corrosive nature of chloride may damage the membranes. Therefore, it is important to decrease chloride concentrations before running the water through a reverse osmosis plant.

Table A1: Competing ions and their concentration limits for treatment.

Treatment	Cl <sup>-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	PO <sub>4</sub> <sup>3-</sup> (mg/L)	Si (mg/L)	Fe <sup>3+</sup> (mg/L)	TDS (mg/L)	TOC (mg/L)	Turbidity (NTU)
AA	250		360		30	0.5	1000	4	0.3
IX		5	50				500		0.3
IBS			50	1	10				0.3
RO	300		100	5	20		1800		5

AA – activated alumina; IX – ion exchange; IBS – iron based sorpents; RO – reverse osmosis. TDS, total dissolved solids; TOC, total organic carbon.

The operation of reverse osmosis on water with substantial amounts of silica is only feasible if there is chemical pretreatment to prevent excessive fouling by this refractory deposit. Precipitation, coagulation, and flocculation should be used to remove silica (Sheikholeslami and Bright, 2002).