DYNAMICS OF ARSENIC CONCENTRATION AND SPECIATION IN WISCONSIN PRIVATE DRINKING WATER WELLS

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Abstract

Arsenic typically develops in Eastern Wisconsin groundwater as a result of oxidation of sulfide bearing minerals in the limestone bedrock (Schreiber et al. 2000). Naturally occurring arsenic exists in groundwater as oxyanions which have two oxidation states, As(III) and As(V). Under ambient pH conditions As(V) is primarily present as an anion (i.e., $H_2AsO_4^-$) while As(III) tends to be uncharged (i.e., H_3AsO_3), making it much more difficult to remove through the existing treatment techniques such as adsorption and reverse osmosis (RO). Although many studies exist establishing arsenic concentrations across Wisconsin, there is a lack of investigations into the concentrations of each arsenic species as well as minute-scale arsenic dynamics, which is essential for establishing a removal technique. The primary goals of this research were to establish baseline concentrations of each arsenic species, accounting for seasonal variations, and determine how these concentrations could be affected by strenuous water usage. Private drinking water wells were selected at 16 locations across Eastern Wisconsin. The wells were screened at various depths, in multiple geologic units, and contained a wide-range of total arsenic concentrations. Analysis of the speciation data indicated that As(III) was the dominant species of arsenic in all of the wells sampled. Data from the 11 pumping tests that were conducted, showed 9 exhibiting a downward trend in As(III) concentration and an upward trend in As(V) concentration as volume purged increased. The pumping tests also showed a substantial increase in total arsenic in many of the wells as volume purged increased. The results of this study suggest that there is an elevated health risk of consuming water following short-term strenuous water usage and an increased necessity for proper filtration due to dominant As(III) concentrations.

1. Introduction

Elevated arsenic concentrations have been detected in many groundwater systems throughout the world (Smith et al. 1992). Toxicological studies have revealed the acute and chronic effects of inorganic arsenic exposure, including but not limited to: cardiovascular disease, blood disorders, gastrointestinal complications, neurologic disorders, pulmonary disease, renal failure, skin lesions, and cancer (States, 2015). The lethal range of inorganic arsenic in the adult human body is estimated between 1-3 mg As/kg (Ellenhorn et al., 1997), however, lower concentrations can also cause serious health issues.

In Bangladesh, arsenic contamination is considered the largest poisoning of a population in history, with an average concentration of 500 ug/L (ppb) and between 35 million and 77 million people are at risk (Smith et al. 2000). As a result, by the age of 60 years, more than 1 out of 10 people in Bangladesh will have developed skin cancer (Smith et al. 2000). It was estimated that at the previous EPA maximum contamination limit (MCL) of 50 µg/L, the lifetime risk of dying from liver, lung, kidney, and bladder cancer was as high as 13 out of 1,000 persons (Smith et al., 1992). Findings such as these led the EPA to lower their MCL to 10 µg/L in 2001. Households that rely on private domestic wells, however, are responsible for testing their own drinking water, and are often unaware of the risk. In 2017, the United States Geological Survey (USGS) estimated that 44 million people in the United States use private domestic wells for their drinking water and 2.1 million of those people are affected by arsenic concentrations above the EPA MCL (USGS, 2017).

Recognizing the detrimental health effects of arsenic, the Wisconsin Department of Natural Resources (WDNR) began requiring arsenic sampling on private wells (>20,000 locations) during phases of repair, to get a better understanding of the spatial distribution of arsenic concentrations. The data from the research revealed that many counties in Eastern Wisconsin contained wells with arsenic above the EPA MCL (Figure 1), and several wells exhibited concentrations exceeding 1,000 ug/L. The locations from the WDNR study that contained elevated concentrations of arsenic were utilized as references for site selection in this research.

In the Fox River Valley region, located in East-Central Wisconsin, >18% of private water-supply wells exceed the 10 ug/L drinking water standard (Thornburg and Sahai, 2004). Extensive water sampling studies carried out in Outagamie and Winnebago Counties showed that 3% of drinking water wells had arsenic concentrations higher than 50 ug/L and 20% of well had arsenic concentrations higher than 10 ug/L (Riewe, 2000). In Southeastern Wisconsin where limited data is available, the Ozaukee County Public Health Department reported that 24 out of 167 wells tested in 2009 had As concentrations higher than 10 ug/L (Benson, 2009). These concentrations vary extensively from region to region.

The objectives of this research were to determine spatial and temporal variations as well as the speciation and minute-scale pumping variation (dynamics) of arsenic concentrations in private drinking water wells in various aquifers throughout Eastern Wisconsin. It was hypothesized that arsenic concentrations will not behave similarly across all aquifers due to different aquifer materials, so it was essential to obtain a comprehensive list of participants. It is also important to understand when one is most susceptible to high levels of arsenic (i.e., in the morning when no water has been pumped, or afternoon when water use is at a maximum). Thus, concentrations were determined early in the morning prior to use, and 1-hour pump tests were conducted to determine

how these concentrations change with water use. Additionally, the speciation of As was determined through this research.
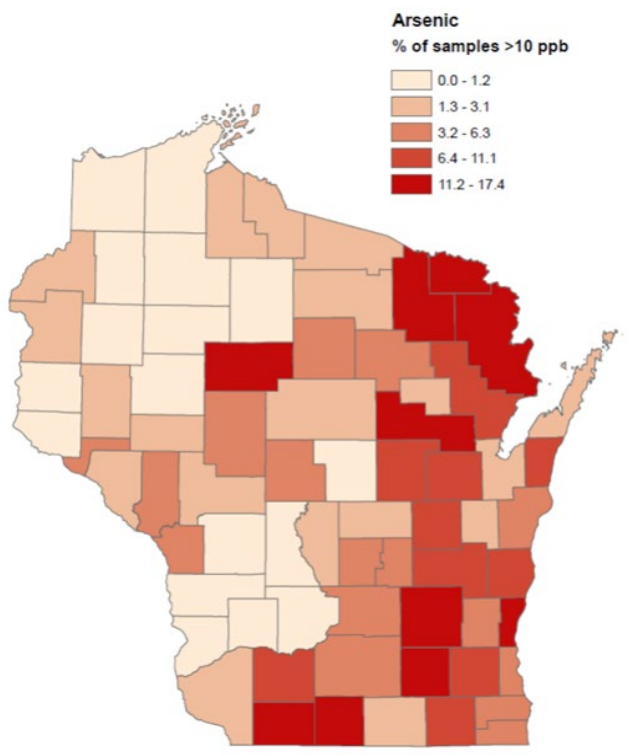

Figure 1. Occurrence of arsenic in Wisconsin private drinking water wells. The map is based on 35,000+ samples and depicts the percent of wells over 10 ppb arsenic in each county. (Wisconsin Groundwater Coordinating Council Report to the Legislature, 2019).

2. Materials and Methods

2.1 Well selection and sampling

This study area was located in eastern Wisconsin, encompassing the region with high-risk aquifers. Sample locations were firstly selected using private well data from the Wisconsin DNR of recent arsenic testing. Letters were mailed to homeowners who had high arsenic concentrations and all respondents received testing. Spatial and aquifer variation were then considered in order to provide a good geographical coverage and sixteen private wells from seven counties were selected (Table 1), representing the Silurian dolomite aquifer in the eastern counties and the shallower Ordovician dolomite and sandstone aquifer in the western counties (Figure 2). The well construction reports are included in the appendix. Seasonal trends were established for each well and several wells were selected to undergo pump tests to determine minute-scale variations in arsenic species and total arsenic concentrations.

Table 1. Well locations, aquifers, and screened intervals.

| Location ID	County	Aquifer	Depth of Water Extracted (ft)
L1	Waukesha	Dolomite	117-265
L2	Ozaukee	Dolomite	48-120
L3	Washington	Dolomite	234-253
L4	Waukesha	Dolomite	107-228
L5	Dodge	Sandstone (Dolomite Above)	62-129
L6	Jefferson	Dolomite	279-322
L9	Outagamie	Dolomite	65-100
L12	Jefferson	Dolomite	54-56
L13	Waukesha	Dolomite	72-145
L14	Waukesha	Dolomite	77-185
L15	Winnebago	Dolomite/Sandstone boundary	42-142
L16	Winnebago	Dolomite/Sandstone boundary	55-104
L17	Winnebago	Dolomite	43-165
L18	Winnebago	Dolomite/Sandstone boundary	43-80
L19	Waukesha	Dolomite	42-145
L20	Jefferson	Dolomite	51-122
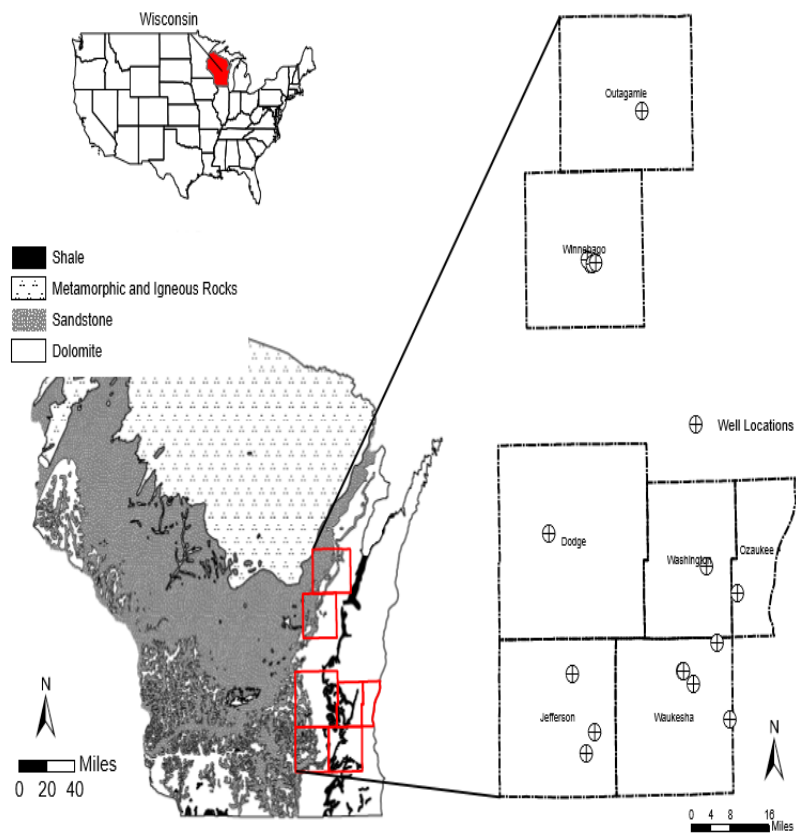
Figure 2. Map of study area. Wisconsin filled in red (top). Wisconsin bedrock map outlining counties in study area in red (left). County map displaying well locations (right).

Sampling events were conducted early in the morning prior to water being used in the household. The first round of sampling events occurred during Wisconsin's winter months (December-March). This sampling event served two purposes: 1) determining the extent of arsenic concentration at each location; and 2) providing the winter concentrations of arsenic. If the well water did not contain arsenic, it was not revisited for a second sampling event. During this sampling event, water was extracted from a spigot, usually located in a building's basement, directly linked to the well (Figure 3). The water that arrived at the spigot was unaltered by any household filtration systems and was most representative of the water at the bottom of the well. The spigot was opened, allowing the water from the holding tank to empty and samples were collected once the pump began to run. The water samples were collected in 250 mL polyethylene bottles. The bottles were filled to the brim, not allowing any oxygen to interact with the sample during travel to the lab. Water quality parameter, including pH, temperature, conductivity, and total dissolved solids (TDS) were determined during this event using a calibrated YSI Professional Plus multiparameter instrument (Figure 4).
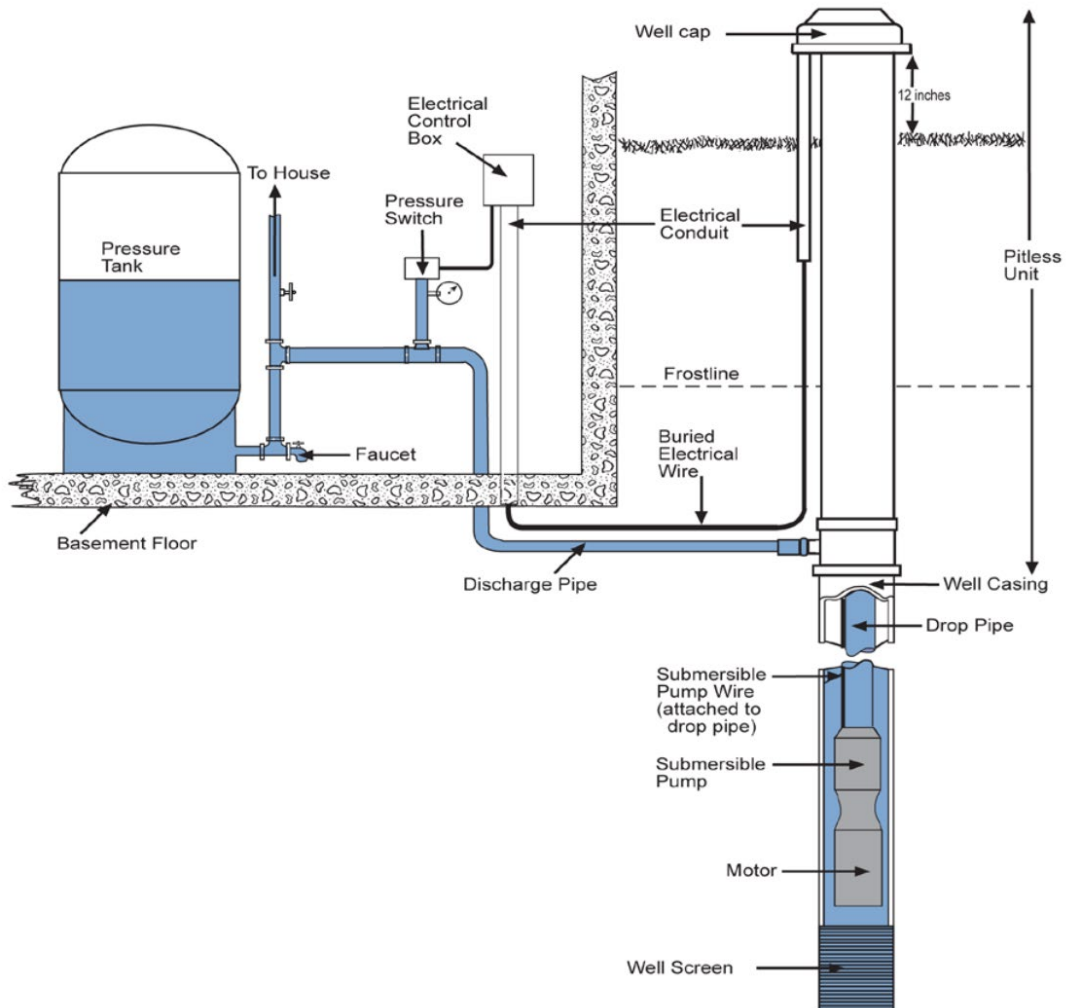

Figure 3. Well Diagram. Reprinted from Minnesota Department of Health "Well Owner's Handbook".

During the first sampling event, water was also tested inside the household from whatever water purification systems were installed. This was done in order to get a better understanding of how the water quality parameters, cations and anions, as well as arsenic concentrations and species were altered by these purification processes. The systems that were in place included: water softeners, carbon filtration, reverse osmosis systems, and in some cases no filtration at all. Results (not included in this report) were provided to the homeowners and recommendations were discussed to limit arsenic exposure.

The second round of sampling occurred over the summer months (May-September) to account for seasonal trends. During this second event, 10 of the wells were pumped to determine how arsenic concentrations changed. The samples collected during the summer event were obtained from an outdoor hose which was also directly linked to the well, without any form of filtration (Figure 4). During this sampling event, field measurements tested for included: pH, temperature, conductivity, and oxidation reduction potential (ORP) using the YSI field instrument.

Figure 4. Measuring field parameters using YSI Professional Plus multiparameter instrument at location L3 (left), 1-hour pump test at location L9 (right).

A third round of sampling was conducted at locations L5 and L6 based upon data analysis of arsenic concentrations. Water was collected similarly to the second round of sampling while another aspect was added: sampling during the period after pumping has ceased. Field measurements remained the same as the second sampling event. Locations L5 and L6 were re-sampled a fourth time, similarly to the third round of sampling, to demonstrate reproducibility.

The wells from locations L1, L2, L3, L5, L6, L9, L15, L16, and L18 were pumped for 1 hour during the second round of sampling. The pumping rates varied at each location, anywhere

from 4 gallons per minute to 15 gallons per minute, depending on the pump configuration for each household. Flow rates were determined by timing how long it takes to fill up a 5-gallon bucket. These tests resulted in volumes between 240 and 900 gallons pumped from the wells over 1 hour. Similar to the winter sampling event, the first sample was collected after the water was removed from the holding tank. Samples were then collected every 20 minutes throughout the duration of pumping.

During the third round of sampling, samples were collected initially, after 30 minutes, and after 60 minutes of pumping. After pumping ceased, samples were collected at 20 minutes, 40 minutes, and 180 minutes at Location L5, and 20 minutes, 40 minutes, and 90 minutes at Location L6. To ensure that the water was not re-disturbed during this portion of sampling, the hose was only turned on long enough to obtain the sample and water quality measures.

During the fourth round of sampling, samples were collected at location L5 and L6 similarly to the third sampling event at location L5 (i.e. initially, 30, and 60 minutes, followed by 20, 40, and 180 minutes post pumping).

A fifth pumping event was conducted at location L6 to determine if arsenic concentrations changed if pumping continued throughout the span of 4 hours.

The collected water samples were preserved on ice and returned to University of Wisconsin Milwaukee (UWM) campus for chemical analysis within 2 hours. We established 'trip blanks' method to determine if arsenic concentrations and speciation's changed from the time that the groundwater was sampled until it was preserved in the lab. In this method, two batches of synthetic solutions were created, the first of which was analyzed for arsenic immediately. The second batch (same solution) was held for 120 minutes prior to analysis, which simulated the furthest return drive time to the lab. These 'trip blanks' consisted of synthetic arsenic mixtures consisting of roughly 50% As(III) and 50% As(V) at concentrations of 5 ug/L, 10 ug/L, 20 ug/L, and 100 ug/L total arsenic. Based upon previous research of arsenic species in groundwater, most aquifers contain some percentage of each species of arsenic (Sorg et al., 2013), which is why these equal mixtures were used. The concentrations of the total arsenic coincide with arsenic data that was previously received from the WDNR. It was established that the changes in arsenic speciation within a 120-minute timeframe are negligible (less than 2%).

2.2 Chemical analysis

Determining iron concentrations in the field was necessary as concentrations between ferrous and ferric iron tend to shift readily when exposed to oxygen. These measurements were made using a Hach DR900 multiparameter portable colorimeter. Ferrous iron reagent powder pillows and Ferrover iron reagent powder pillows were used according to Hach methods 8146 and 8008, respectively. The Ferrover iron reagent powder pillows were used to determine the total iron in solution. To determine the amount of ferric iron, the total ferrous iron concentration was subtracted from the total iron concentration. Iron concentrations were measured throughout the second, third, and fourth sampling events during every period of pumping (initial, 20, 30, 40, and 60 minutes) as well as during the post-pumping periods (20, 40, 90, and 180 minutes). The alkalinity of the initial water samples was quantified through acid titration using a Hach digital titrator test kit using Hach method 8203. This measurement was also conducted in the field as the carbonate ion concentrations would not be representative if exposed to air or agitated excessively. Sulfide concentrations were determined in the fourth round of sampling during each period of pumping (initial, 30, and 60 minutes) as well as during the post-pumping periods (20, 40, 60, 90,

and 180 minutes) according to Hach method 8131.

Other major ions were quantified at the School of Freshwater Sciences lab (SFS) at UWM. The water samples from every sampling period were filtered with a 0.22-micron filter and acidified using 2% optimum nitric acid (HNO_3) in preparation for major cation analysis. Calcium, magnesium, potassium, and sodium were determined from these water samples using an iCE 3300 AAS Atomic Absorption Spectrometer. Major anions (chloride, nitrate, phosphate, and sulfate) were determined using HPLC equipped with a conductivity detector (Xu et al., 2004).

Arsenic concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) following the EPA standard method 200.8 (USEPA, 1994). An anion-exchange method modified from previous studies (Wang and Giammar, 2015; Wilkie and Hering, 1998) was used for separation of As(III) and As(V). Briefly, anion-exchange resin (AG 1-X8 from Bio-Rad, 100 – 200 mesh) was first converted to an acetate form via sequential equilibration with 1 M of NaOH and 1 M of acetic acid. One gram of resin was then wet-packed in chromatography columns (BioRad). An aliquot of a groundwater sample was adjusted to a pH of 6 and passed through two columns of anion-exchange resin (Figure 5).
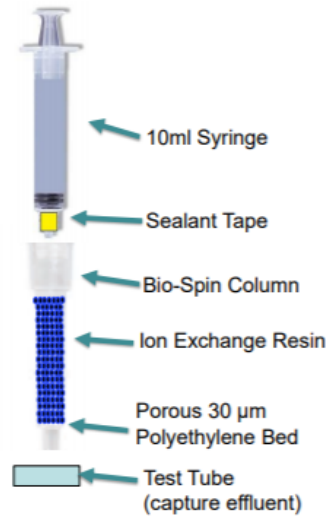

Figure 5. As(III) & As(V) separation process (Trujillo, D., & Wang, Y. 2018)

At a pH of 6, As(V) is primarily present as an anion (i.e., $H_2AsO_4^-$), while As(III) is not charged (i.e., H_3AsO_3) (Figure 6). Thus, neutral As(III) species pass through the column, and anionic As(V) species are retained. Samples before (influent) and after (effluent) column separation were acidified to 1 – 2% HNO_3 for determination of total As and As(III) concentrations, respectively. As(V) concentration were determined as the difference between total As and As(III). This method was validated using a standard addition test of As(III), As(V), and mixtures of As(III) and As(V) samples with predetermined concentrations.
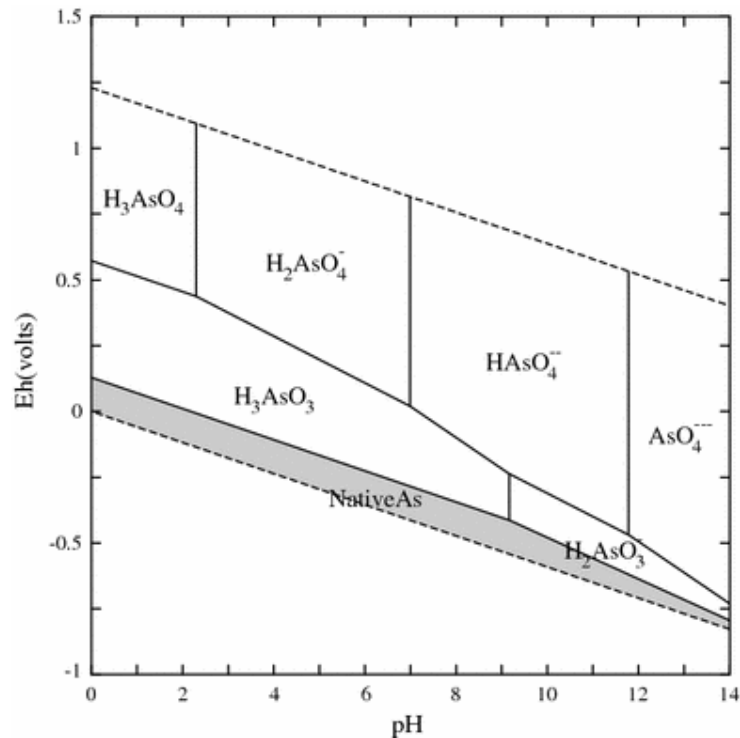
Figure 6. Arsenic Eh-pH Diagram. Reprinted from (Lu and Zhu, 2011).

The analysis of laboratory samples will involve both experimental and analytical quality assurance (QA)/quality control (QC) checks. Experimental checks include the collection of laboratory blanks and replicate samples. Analytical QA/QC checks include instrument calibration, check standards, and method blanks. Internal standard will be spiked to each sample before injection to address the instrumental variation. Groundwater samples were also sent to other laboratories for sample confirmation.

3. Results and Discussion

3.1 Total arsenic concentration and arsenic speciation

The water quality field parameters as well as arsenic concentrations from the first round of sampling events are summarized in Table 2. Of the 16 private wells that were sampled in the first round, 7 wells exceeded 10 ug/L As, 4 wells contained between 5 ug/L and 10 ug/L As, and 5 wells had concentrations less than 5 ug/L As. Of the wells that exceeded 10 ug/L, one well contained 764.83 ug/L arsenic, >75 times larger than the EPA MCL. The wells that contained less

than 5 ug/L (L4, L12, L17, L19, and L20) were not revisited for a second sampling event due to the insignificant arsenic concentrations.

Table 2. Water quality measures and total arsenic concentrations at 16 well locations during winter sampling events.

Location ID	Date Sampled	pH	Conductivity (us/cm)	Temperature (°C)	TDS (ppm)	Alkalinity (mg/L)	Arsenic (ug/L)
L1	12/20/2018	7	910	14.3	457	214	9.27
L2	1/10/2019	7	787	12	397	354	9.00
L3	1/17/2019	7	500	11.4	254	206	6.80
L4	1/19/2019	7	794	12.3	398	--	2.96
L5	2/9/2019	6.5	625	13.3	311	344	14.25
L6	1/31/2019	6.5	655	10.1	330	336	21.13
L9	2/28/2019	6.5	551	11.1	278	373	39.77
L12	2/7/2019	6.5	939	11.6	473	--	0.24
L13	3/1/2019	7	1087	11.8	548	--	8.05
L14	3/1/2019	6.5	707	12.3	352	--	12.74
L15	6/30/2019	6.5	696	11.6	352	379	764.83
L16	3/15/2019	6.5	945	12.4	485	388	17.80
L17	3/18/2019	6.75	1113	11.5	569	--	0.11
L18	3/18/2019	6.75	725	12.4	363	307	51.17
L19	3/19/2019	6.75	1280	12.2	638	--	0.20
L20	4/26/2019	7	647	12.6	325	--	0.51

Sample locations that were visited twice (winter and summer), due to elevated arsenic concentrations, were included in (Table 3). During the winter sampling events, 10 out of 11 of the wells were dominated by As(III) while in the summer all 11 wells were dominated by As(III). During the winter, the average percent As(III) species was 76.81% while in the summer the average increased to 86.29% As(III). Location L14 was the only well that exhibited dominated As(V) species during all sampling events. The only well that showed a decrease in As(III) percentage from winter to summer was location L15, which also exhibited the highest arsenic concentrations during all tests.

Table 3. Seasonal arsenic speciation at 11 well locations.

Location ID	Winter Sampling Event			Summer Sampling Event		
	As(III) %	As(V) %	Total As (ug/L)	As(III) %	As(V) %	Total As (ug/L)
L1	74.8	25.2	9.3	91.1	8.9	10.8
L2	76.2	23.8	9.0	100.0	0.0	9.5
L3	76.9	23.1	6.8	83.8	16.2	7.7
L5	73.5	26.5	14.3	94.5	5.5	13.6
L6	88.8	11.2	21.1	90.8	9.2	19.0
L9	82.4	17.6	39.8	81.9	18.1	39.5
L13	79.0	21.0	8.0	100.0	0.0	9.3
L14	45.6	54.4	12.7	62.3	37.7	10.9
L15	85.7	14.3	764.8	65.8	34.2	618.9
L16	81.9	18.1	17.8	91.4	8.6	17.8
L18	80.3	19.7	51.2	87.6	12.4	44.4
Average	76.8	23.2	86.8	86.3	13.7	72.9

The wells (e.g., well L15) that had highest arsenic concentrations were screened at or near the sulfide cement horizon. Wells screened within the Ordovician, Sinnipee dolomite appeared to have the greatest variation in values, some being insignificant and one approaching 40 ug/L arsenic. The wells that were screened within the eastern Silurian dolomite did not contain very high concentrations, however all contained values at or near the EPA MCL.

Under circumneutral groundwater conditions As(V) is primarily present as an anion (i.e., $H_2AsO_4^-$) while As(III) tends to be uncharged (i.e., H_3AsO_3), making it much more difficult to remove from water. Walker et al. (2008) demonstrated that while >95% of As(V) can be removed through reverse osmosis (RO), the removal efficiency was generally <45% when more than 50% of the arsenic exists as As(III). Not only is As(III) unable to be removed through standard arsenic treatment processes, it is also considered more toxic than As(V) (USEPA 2001). Thus, when developing an efficient, cost-effective removal strategy for arsenic form drinking water, it is important to determine both the total concentration and speciation of arsenic.

Previous research based upon thermodynamics shows that As(V) is favored in oxic waters while As(III) is favored in anoxic water (Anderson and Bruland 1991; Mok and Wai 1990; Smedley and Kinniburgh 2002; Welch et al. 1988; Welch et al. 2000). It is also important to recognize that under natural conditions in a limestone/dolomite aquifer, the oxidation of As(III) into As(V) occurs very slowly due to high bicarbonate concentration (buffer) controlling the pH (Shafer et al. 2007).

One study examined spatial variations in arsenic species across the United States, determining that one species of arsenic is dominant (>80% As(III) or As(V)) in nearly all the wells that were sampled (59 out of 65 wells) (Sorg et al. 2013). Of the 65 sites, 31 were dominated by As(V) and 28 were dominated by As(III). Our results showed that As(III) is the dominant form of arsenic in the selected wells. This speciation finding should be included in the design, implementation and regulation of arsenic removal technology at household level because tradition filtration techniques tend to exhibit low removal efficiency for As(III).

Arsenic concentrations in the private wells are dependent on the geologic unit that each well is screened in. In portions of southeastern Wisconsin, many wells are screened in the shallow sand and gravel aquifer. This Pleistocene aquifer is present due to glacier retreat, leaving behind hundreds of feet of aquifer material in some areas. This aquifer is often susceptible to surface contamination due to its proximity to the surface as well as its high permeability. This aquifer also contains natural contaminants, arsenic being one of them. Root et al. (2010) researched the solid-phase geochemistry of this region and determined that the upper portions of the sand and gravel aquifer have between 2-4 mg/kg of arsenic. Tests were also conducted on the lower portions of this unit and average concentrations between 4-8 mg/kg were detected, with one concentration being 21 mg/kg. Another study conducted in this aquifer showed only 8 out of 136 wells sampled exceeding the EPA MCL for arsenic, with a maximum concentration of 32 ug/L (Root 2005). The main mechanism for arsenic release in this aquifer is through microbially mediated reductive dissolution of arsenic-bearing Mn and/or Fe-(hydr)oxides, such as goethite, due to the presence of solid-phase organic matter (Root 2005). The (hydr)oxides incorporate arsenic as an impurity. Reductive dissolution may appear in this aquifer in the following form (Shafer et al. 2007):

$$4FeOOH + CH_2O + 7H_2CO_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 6H_2O \ (1)$$
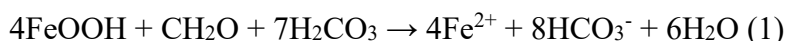
Other mechanisms such as diagenesis and desorption may also play a role in the arsenic release, however the combination is difficult to determine due to the complexity of these processes. Although this mechanism readily releases arsenic into the groundwater, it tends not to occur at high levels. This reductive release mechanism is less relevant to the wells selected for this research as all the wells are screened beneath the sand and gravel layer.

Below the sand and gravel aquifer in Eastern Wisconsin lays a Silurian aquifer comprised of dolomite. This dolomite is dated back to the Middle and Late Paleozoic Era, and the rock in this aquifer was deposited in open and marginal marine environments (Luczaj et al., 2015). This aquifer is thickest in the region that borders Lake Michigan and becomes thinner westward. This dolomite layer and the subsequent underlying layers tend to dip towards the east at approximately 5 to 7 m/km (Luczaj, 2013). This aquifer is underlain by the Maquoketa Shale, an aquitard which restricts downward groundwater flow to the deeper Ordovician layers. Within the dolomite aquifer, groundwater flows through fractures, pores, vugs, and caves. The level of interconnectedness of these features determines the extent to which the groundwater travels. Due to the spatial variability of these features in the subsurface, groundwater yields vary as well as the presence of source minerals that are responsible for arsenic. The source minerals that contain solid phase arsenic are primarily sulfide bearing minerals such as goethite, pyrite, and marcasite (Schreiber et al., 2003, Shafer et al. 2007). The release mechanism of arsenic in this aquifer is abiotic oxidative dissolution of the sulfide minerals where arsenic resides as an impurity, represented by the following formula (Schreiber et al., 2003):

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4H^+ + 4SO_4^{2-} \ (2)$$
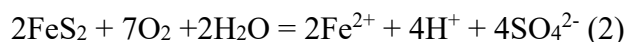
In situations where oxidative dissolution occurs, oxygen, nitrate, and ferric iron serve as electron acceptors, and positive correlations are anticipated between arsenic, sulfate, metals, and residual elements within the sulfide minerals (Schreiber et al., 2003). Elevated arsenic concentrations in wells installed within this unit often vary from household to household depending on factors such as well depth and proximity to vugs and fractures that contain goethite, pyrite, and marcasite. Because arsenic concentrations often remain around or below the MCL in this aquifer, few studies have pursued this system for arsenic research even as recent data are

suggesting growing health concerns. Based on well construction reports, most of the wells included in this research are primarily screened within the dolomite aquifer and the total arsenic concentrations varied between 8.0 and 40 ug/L.

Another aquifer which is present throughout much of Wisconsin is the Cambrian-Ordovician sandstone and dolomite aquifer. Alternating layers of sandstone and dolomite make up this aquifer system which was created by alternating shallow and deep marine environments between 443 and 485 million years ago (Luczaj, 2013). A large portion of the water wells in the state are installed within this aquifer, primarily in the central portion of the state where sandstone dominates the subsurface. Arsenic contamination is a significant concern in portions of East-Central Wisconsin (Fox River Valley), where the Sinnipee dolomite and St. Peter sandstone reach the surface. Previous work in this region establishes high concentrations of arsenic in a mineralized layer between the Sinnipee dolomite and St. Peter sandstone, termed as the Sulfide Cement Horizon (SCH) (Screiber et al. 2000). The location of the SCH suggests that the mineralization occurred due to the preferential flow of fluids through the top of the sandstone unit. The SCH is found at various depths with various thicknesses, however its stratigraphic position is consistent. Schreiber (2000) conducted rock and mineral analysis on this unit to determine its contents, finding that arsenic is present up to 1% by weight, including some samples that contained greater than 400 mg/kg arsenic. Consistent to previous studies, our results showed that wells screened within the Cambrian-Ordovician sandstone and dolomite aquifer tend to have high arsenic concentrations (up to 765 ug/L).

Similar to the eastern dolomite aquifer, the primary mechanism for the release of arsenic from this layer is promoted by abiotic oxidation of the sulfide-bearing minerals. One of the primary causes for oxidation of this aquifer is by well water usage, resulting in the lowering of the water level. Schreiber (2000) determined that the proximity of the air-water interface to the SCH plays a big role in the concentration of the arsenic in the well water, finding highest concentrations where the air-water interface was within 15m of the SCH. Typically the air-water interface is above the SCH (Figure 7), however during periods of excess pumping, the water level may be drawn below the SCH, introducing oxygen into the system, releasing arsenic. Other forms of oxidation in this unit include regional recharge, vertical leaking, and dewatering (Screiber et al. 2000).
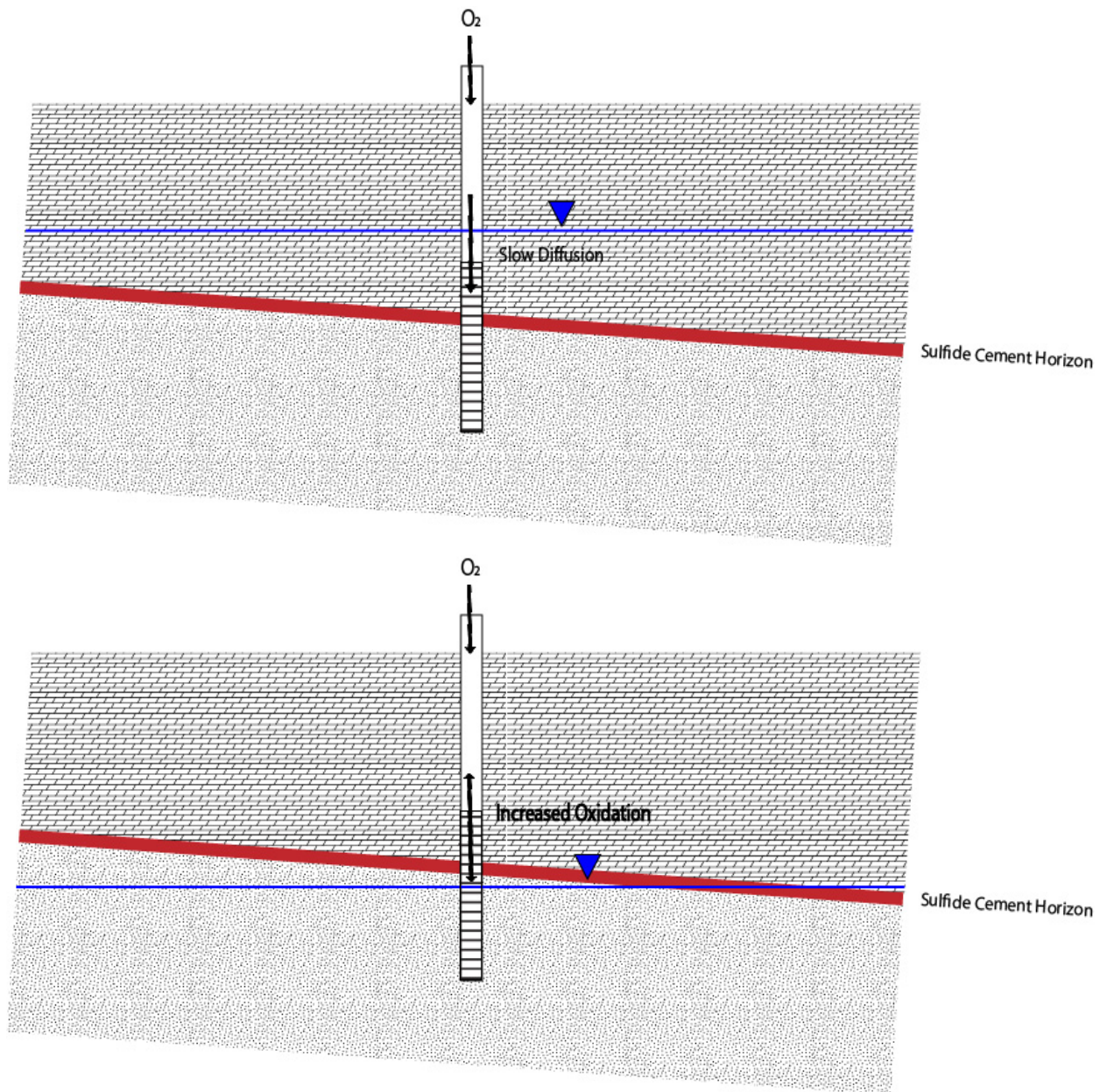
Figure 7. Potential release of arsenic through the oxidation of sulfide cement horizon via borehole interaction: static conditions (top), oxidizing conditions (bottom).

3.2 Dynamics of arsenic concentration and speciation during water pumping

To further understand and quantify the effect of well pumping and water level fluctuation on arsenic concentration and speciation, we monitored arsenic dynamics during typical water use. For three wells (L5, L6 and L15), arsenic concentration increased by more than 15 ug/L. Wells L5 and L15 were presumably drawing water from at or near the SCH, while L6 was drawing water from the Sinnipee dolomite, near the SCH. Pump tests were conducted on wells L5 and L6, 3 and 4 times, respectively, and well L15 once (Figures 8-10).

Well L5 displayed a trend in which arsenic concentrations increased substantially throughout the first 200 gallons of pumping and then appeared to level off or even decrease towards the conclusion of the test (Figure 8). This trend was consistent across all three pump tests, with the August test displaying the lowest concentration variations and the October test displaying the greatest variations. The most substantial increase in arsenic (October) was 27.93 ug/L after 180 gallons of pumping (30 minutes).
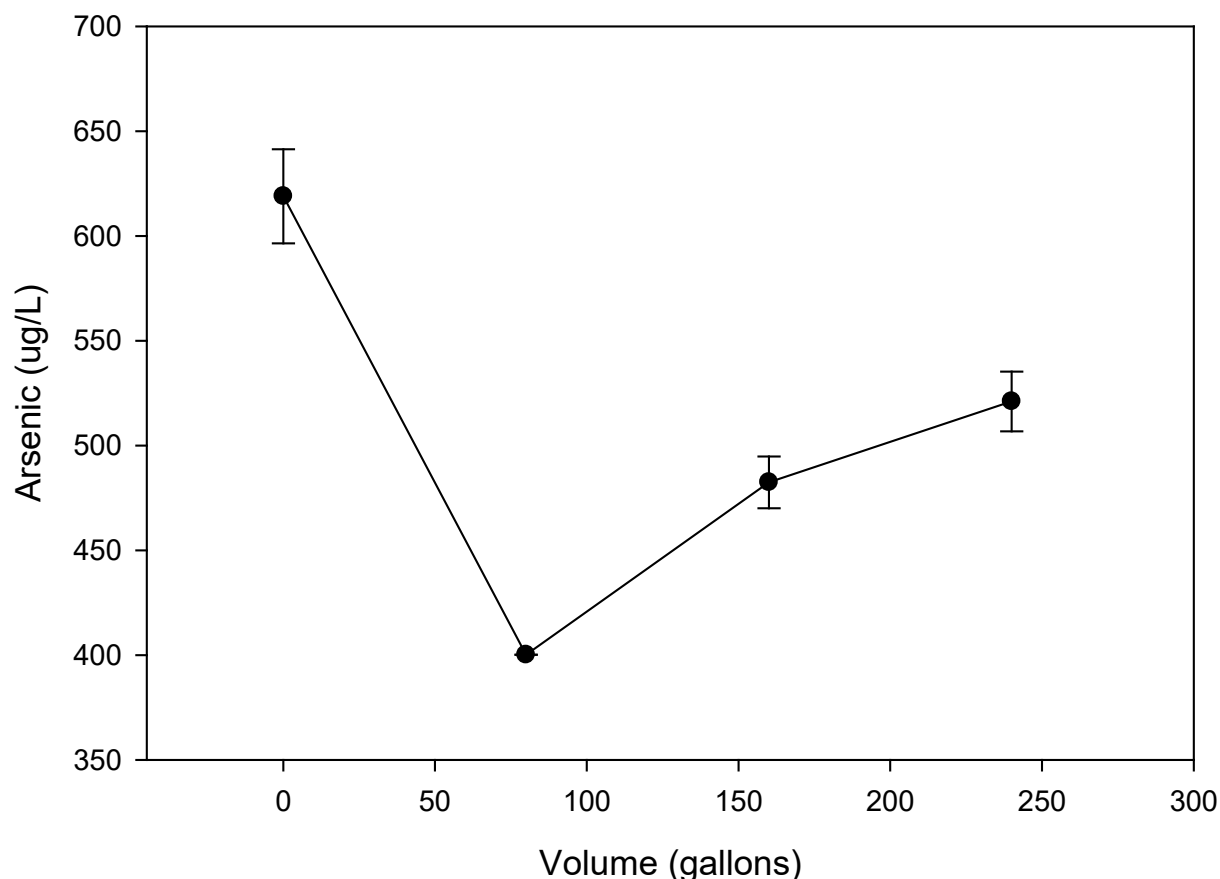
Location L5 Pump Tests vs Arsenic
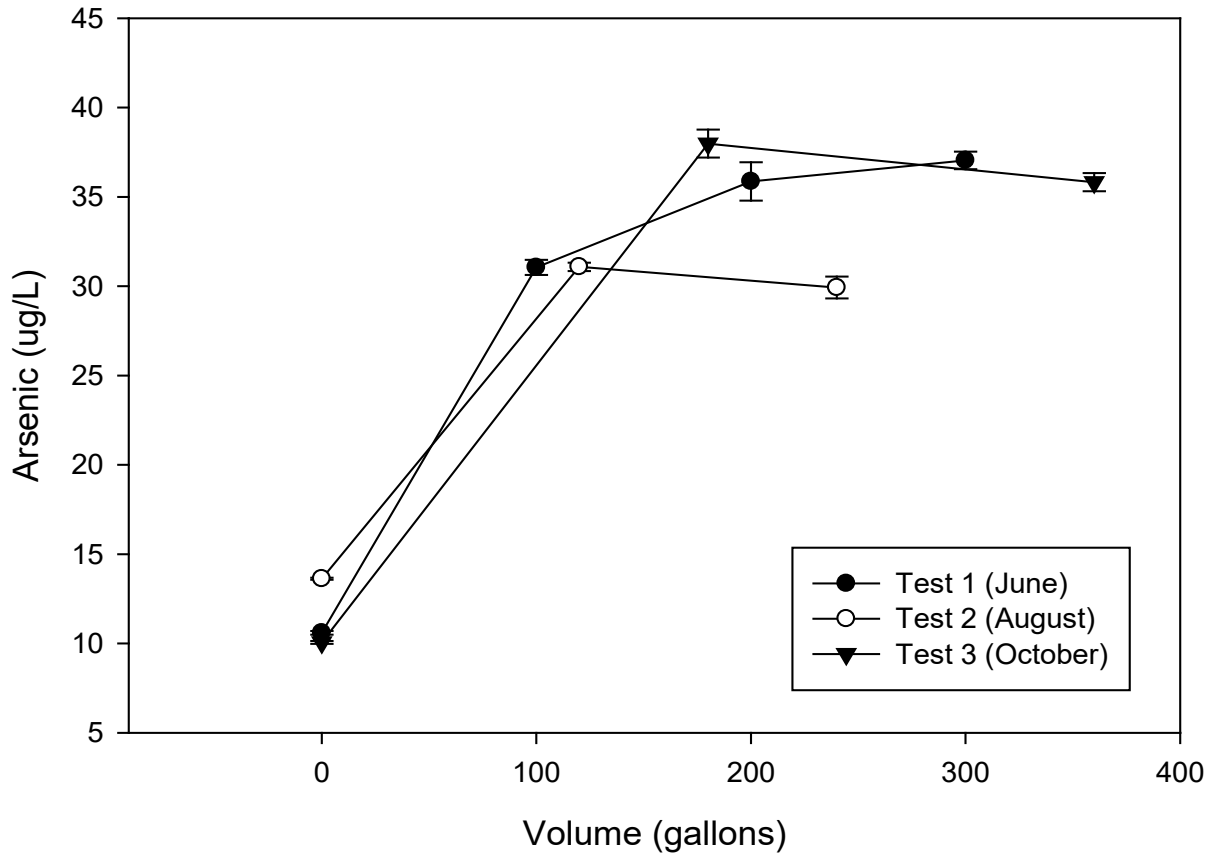
Figure 8. Three pump tests conducted at location L5. Comparing volume pumped (gallons) to total arsenic concentration (ug/L).

Well L6 also exhibited a trend in which arsenic concentrations increased consistently throughout the 1-hour, 300-gallon pump test, and never appeared to level out (Figure 9). Consistent with well L5, well L6 had the greatest variations in arsenic concentrations in October, and the lowest variations in June. The most substantial increase in arsenic (October) was 15.64 ug/L after 300 gallons of pumping (1-hour). The release mechanism responsible for total arsenic in well L6 appears to be occurring at a slower rate than that of well L5.

14
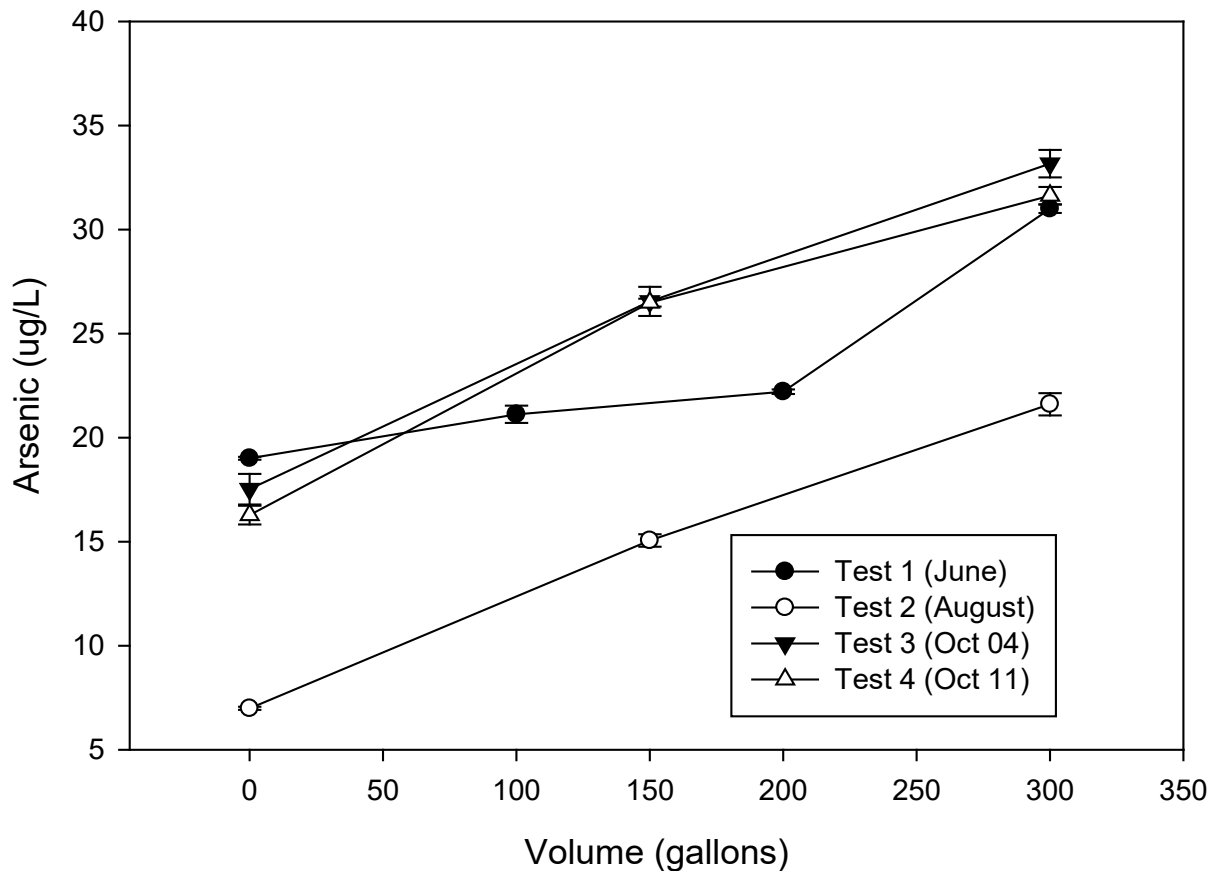
Figure 9. Four pump tests conducted at location L6. Comparing volume pumped (gallons) to total arsenic concentration (ug/L).

Well L15 exhibited a trend unlike wells L5 and L6, in which total arsenic concentration decreased (218.79 ug/L) during the first 20 minutes (80 gallons) of pumping (Figure 10). Following the initial decrease, arsenic concentrations began to increase as the test continued, 120.87 ug/L for the remaining 40 minutes (160 gallons) of pumping. The release mechanism in well L15 is much more sensitive to pumping than that of wells L5 and L6. Well L15 also had the highest arsenic concentration among all the wells included in this research. It appeared that for this well, the initial pumping, which may draw water from surrounding areas, led to a dilution effect on arsenic concentrations. The continuation of the pumping, however, led to release of arsenic, which in turn caused a substantial increase in arsenic concentrations. Thanks to findings from this research, the owner of L15 decided to switch to municipal water supply during the study period of this research, which limited our capability to perform more details studies on arsenic dyn amics.

Figure 10. Pump test conducted at location L15. Comparing volume pumped (gallons) to total arsenic concentration (ug/L).

Tests were also conducted on wells L5 and L6 to determine how arsenic concentrations rebounded after pumping had ceased (Figure 11). Well L5 displayed decreasing arsenic concentrations after pumping ceased in both tests. Arsenic concentrations returned to initial values after 3 hours during the August test, and appeared to be more gradual in decline in October, decreasing 64% of the way back to initial concentration. Well L6 displayed decreasing arsenic concentrations in tests 1 and 3 where pumping ceased, however values did not return to initial concentrations. Arsenic values decreased 33% and 52% of the way back to initial concentrations, respectively. Test 2 displayed arsenic concentrations as a result of continuous usage throughout the post-pump 3-hour period. The homeowner continued to use water for household activities such as laundry (~50 gallons), and arsenic concentrations failed to decrease.
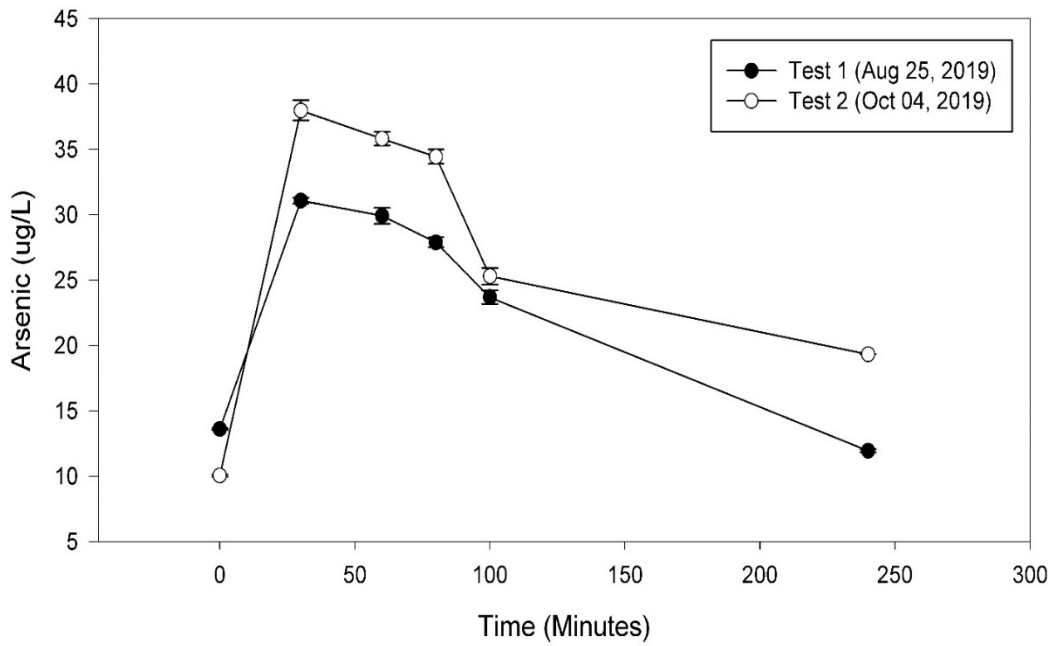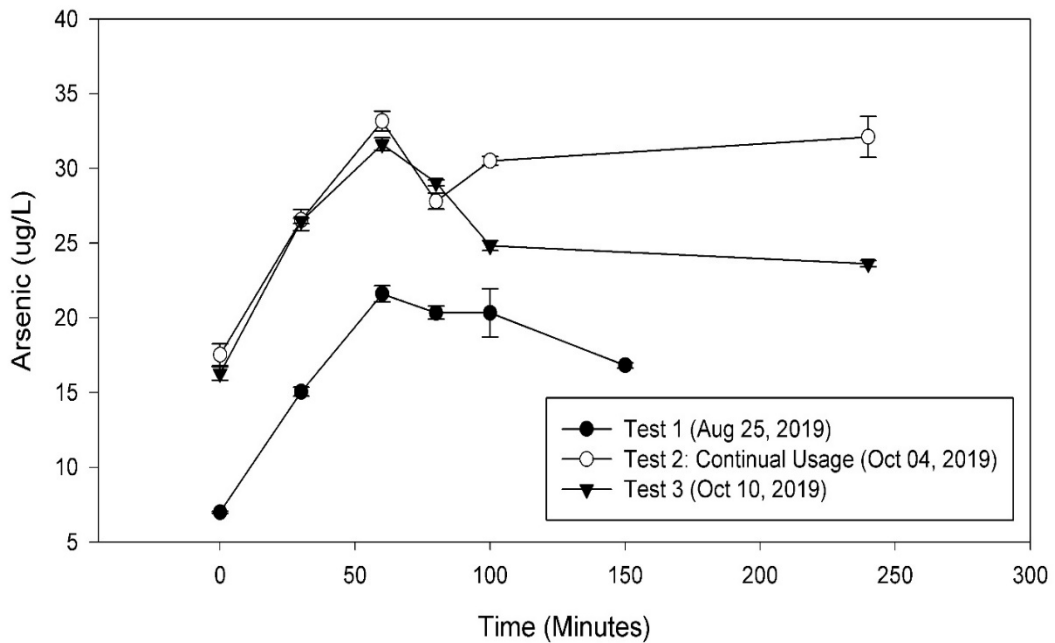
Figure 11. Arsenic concentrations following 1-hour pump tests. Well L5 (top) and Well L6 (bottom) show rebounding arsenic values. Vertical dash-dot line shows stoppage of pumping.

Pump tests were also utilized to demonstrate variations in arsenic species. Wells L5, L6, and L15 all exhibited increasing arsenic concentrations, thus the concentration of one or both of the arsenic species must increase as well. Although arsenic species was dominated at all locations by As(III), during the pump tests As(V) appeared to increase more substantially than As(III) (Figures 12-14). By the conclusion of the pump tests, many of the C/C_o values for As(V) were 1.5 – 2 times greater than that of As(III). As(V) did not appear to deviate greatly from As(III) until after approximately 150 gallons of pumping. The increase in As(V) C/C_o values can be attributed to oxidation from borehole during pumping. Redox sensitive ions such as SO_4^{2-} and Fe^{3+}, however, did not show a substantial trend during pumping.
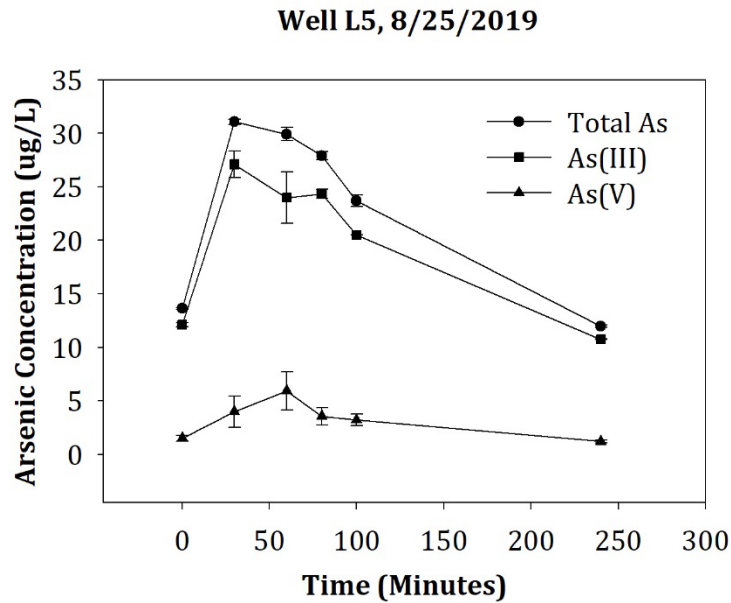
Figure 12. Well L5 arsenic species (C/C_o) variation through pumping. Pumping stopped at 60 minutes for water level to recover.
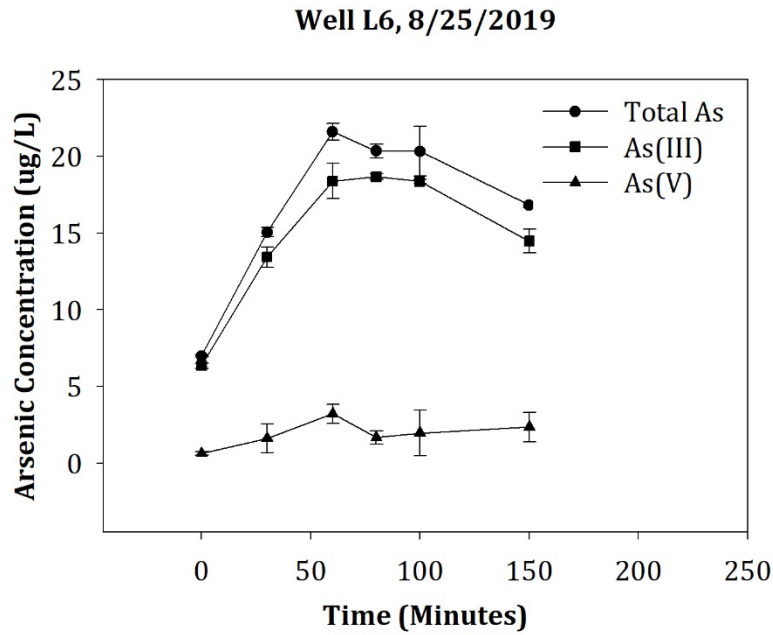
Figure 13. Well L6 arsenic species (C/C$_o$) variation through pumping. Pumping stopped at 60 minutes for water level to recover.
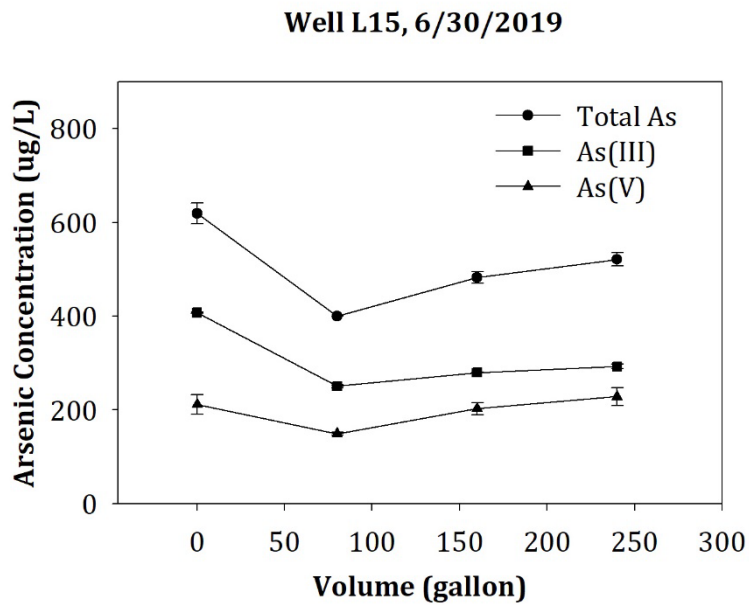

Figure 14. Location L15 arsenic species (C/Co) variation through pumping.

The behavior of arsenic in other wells, such as L3, L9, and L18, were similar to wells L5, L6 and L15, albeit the magnitude of the increase in arsenic concentration was less significant. Based upon well construction reports, it was inferred that well L3 was drawing water from the Eastern Silurian dolomite, well L9 was drawing water from the Sinnipee dolomite, and well L18 was drawing water from at or near the SCH.

Briefly, well L3 did not show a trend in total arsenic concentration for the first 20 minutes of pumping, however a 2.31 ug/L increase occurred between 20 and 40 minutes (120 and 240 gallons) and a slight decrease in concentration for the last 20 minutes of the test. The arsenic trend coincided directly with sulfate concentration, which is conducive of oxidizing conditions (Figure 15). This is the only well where the dynamics of arsenic was correlated with the dynamics of sulfate, the product of sulfide oxidation by oxygen.
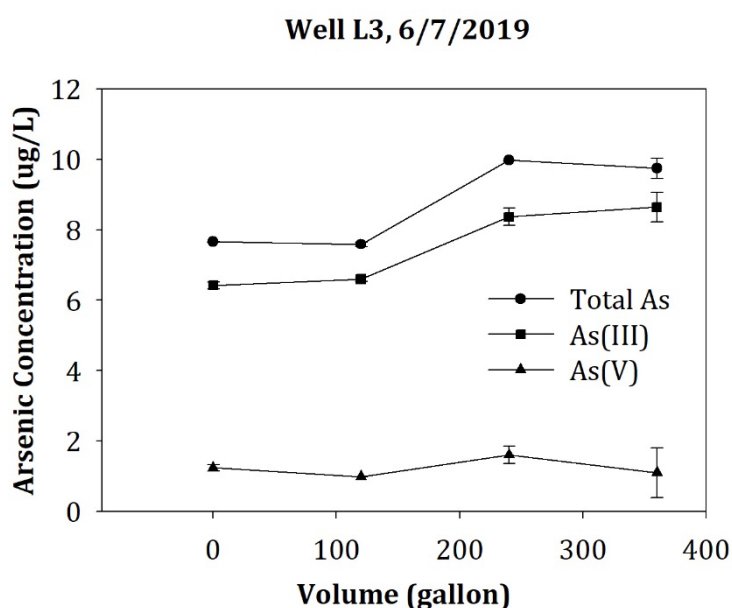
Figure 15. Pump test conducted at location L3.

Well location L9 exhibited an increase of arsenic by 6.2 ug/L through the first 40 minutes (280 gallons) of pumping followed by a slight decrease for the remainder of the test (Figure 16). At the beginning of this pump test arsenic concentrations were already 4 times greater than the EPA MCL and became more dangerous as the test continued. There did not appear to be a trend with respect to the redox ions or water quality measures through pumping, rather most concentrations remained unchanged making it difficult to infer the reason for arsenic increase.
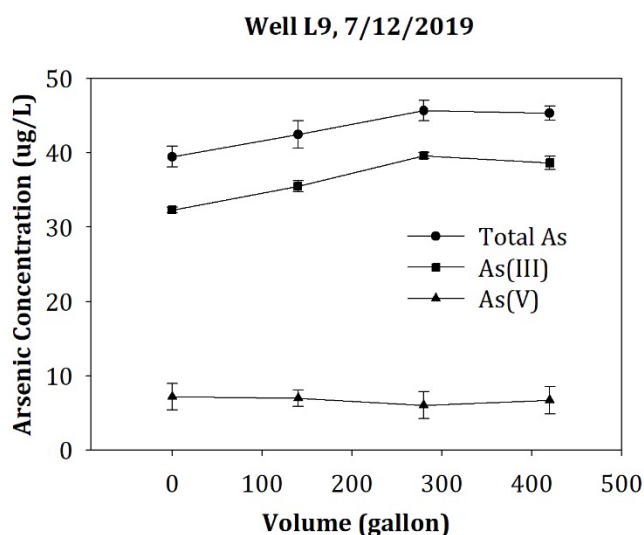
Figure 16. Pump test conducted at location L9.

Well L18 displayed an increase in total arsenic of 4.72 ug/L during the first 20 minutes (100 gallons) of pumping followed by a slight decrease for the remaining 40 minutes of the test (Figure 17). Like well L9, arsenic concentrations were over 4 times the EPA MCL at the beginning of the test and increased towards more dangerous levels as the test continued. Similar to the other wells, it did not show many trends with respect to water quality measures or redox ions.
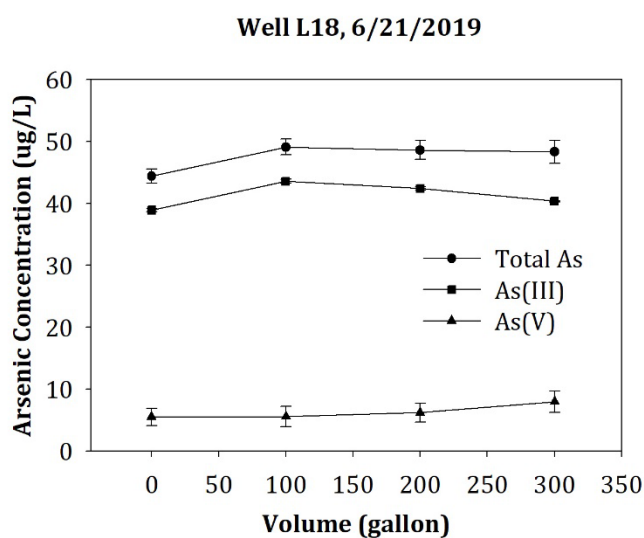
Figure 17. Pump test conducted at location L18.

Pump tests were also utilized to demonstrate variations in arsenic species at these three wells (Figures 15-17). Although As(III) was the dominant species in each well during each test, variations occurred throughout the pump tests. Arsenic C/C_o values for As(III) and As(V) were not consistent in these wells. Well L3 displayed a trend in which As(III) C/C_o values were dominant for the first 20 minutes, followed by As(V) for the second 20 minutes, and As(III) became dominant in the final 20 minutes. Based upon this trend, there appeared to be a relationship between As(III) C/C_o values and total As concentration. As As(III) C/C_o values became more significant, total arsenic concentrations appeared to increase and vice versa.

Well L9 displayed a trend in which As(III) C/C_o values increased while As(V) values decreased through the first 40 minutes of pumping, followed by As(III) values decreasing and As(V) values increasing for the remaining 20 minutes of pumping. Comparing this trend to that of total arsenic, total arsenic concentrations reflected As(III) C/C_o values, increasing as As(III) C/C_o increased and vice versa.

Well L18 displayed a trend in which As(III) C/C_o values increased more substantially than As(V) values for the first 20 minutes of pumping, followed by decreasing As(III) values and increasing As(V) values for the remaining 40 minutes of pumping. The increasing C/C_o trend of As(V) species is consistent with the first group of wells (Figures 15-17); however, when comparing total arsenic concentrations to As(V) C/C_o values, there appeared to be a trend more representative of the wells in this group (i.e. increasing As(III) C/C_o = increasing Total As).

Wells L5, L6 and L15 exhibited most substantial increases in arsenic concentrations (>15 ug/L), and were approximately screened at or near the location where the SCH is anticipated to be located, between the Sinnipee dolomite and St. Peter Sandstone units. In the SCH there is a concentrated band of mineralization consisting of pyrite and marcasite (sulfide minerals). Previous research conducted in this region involving arsenic isotopic signatures found nearly identical $\delta^{34}S$ values in the SCH and in the groundwater, suggesting that oxidation of these sulfide minerals is the dominant mechanism (Schreiber et al. 1999). Although there were many variables that are responsible for arsenic release, one of the most important variables is the location of the water level. If during pumping, water levels were drawn below the SCH exposing the pyrite and marcasite to air, oxidation of those minerals could increase the concentration of arsenic in the water (Schreiber et al. 1999).

Other wells such as L16 and L18 appear to be screened at or near the SCH however do not exhibit significant changes in arsenic concentration during pump tests. Based upon well construction reports, water levels in these wells are much higher than the approximate level of the SCH, which doesn't favor oxidation via water level decrease as a mechanism for arsenic release. Rather, changes in arsenic concentration observed through pumping are more likely attributed to dissolved oxygen being introduced via disturbance of the borehole while pumping. It is important to note, although total arsenic concentration did not increase substantially in the aforementioned wells due to water table proximity, arsenic concentrations are still typically above the EPA MCL due to proximity to the SCH.

4. Conclusions

This study examined the minute-scale pumping dynamics and speciation of naturally occurring arsenic in groundwater in the eastern Silurian dolomite and the Cambrian-Ordovician sandstone and dolomite across eastern Wisconsin. This study investigated private drinking water wells to determine if water usage, via 1-hour pump tests, results in higher arsenic concentrations,

as well as which species of arsenic dominates the groundwater and how the species concentrations change with pumping. A better understanding of these dynamics is critical for determining long-term exposure, health risks, and design and implementation of water treatment techniques.

This study concluded that arsenite (As(III)) was the dominant arsenic species present in the eastern Silurian dolomite and Cambrian-Ordovician sandstone and dolomite. During the winter, As(III) dominated the groundwater samples by an average of 76.8%, while in the summer, As(III) dominated by an average of 86.3%. Wells that contained arsenic had an average total arsenic of 86.8 ug/L in the winter, and an average total arsenic concentration of 72.9 ug/L in the summer. The highest arsenic concentration detected in this study was 764.83 ug/L, occurring in Winnebago county located in east central Wisconsin (Fox River valley).

Furthermore, total arsenic concentrations were primarily associated with the geologic unit in which each well is screened, coupled with the location of the water level in relation to the source minerals. Wells which exhibited substantial increases in arsenic concentration (>15 ug/L) during 1-hour pump tests, were screened at or near the SCH with the water table in close proximity. Substantial arsenic increases were accompanied with increasing As(III) and As(V) concentrations during pumping, indicative of sulfide mineral oxidation. Wells which exhibited moderate increases in arsenic concentration (1 ug/L<As<15 ug/L) during 1-hour pump tests, were screened either at or near the sulfide cement horizon while the water table wasn't in close proximity; or they were screened in the Sinnipee dolomite with the water table in close proximity.

Post-pump analysis conducted on wells demonstrating substantial arsenic increase showed that arsenic concentrations decrease towards initial values with time. During one post-pump test at well L5, arsenic concentrations returned to initial values after a 3-hour period of non-use. Other post-pump analyses conducted at wells L5 and L6 showed arsenic concentrations not returning to initial values after 3 hours of non-use, however decreasing substantially. One test was conducted where water use continued inside the house throughout the 3-hour post-pump period and arsenic values remained substantial throughout.

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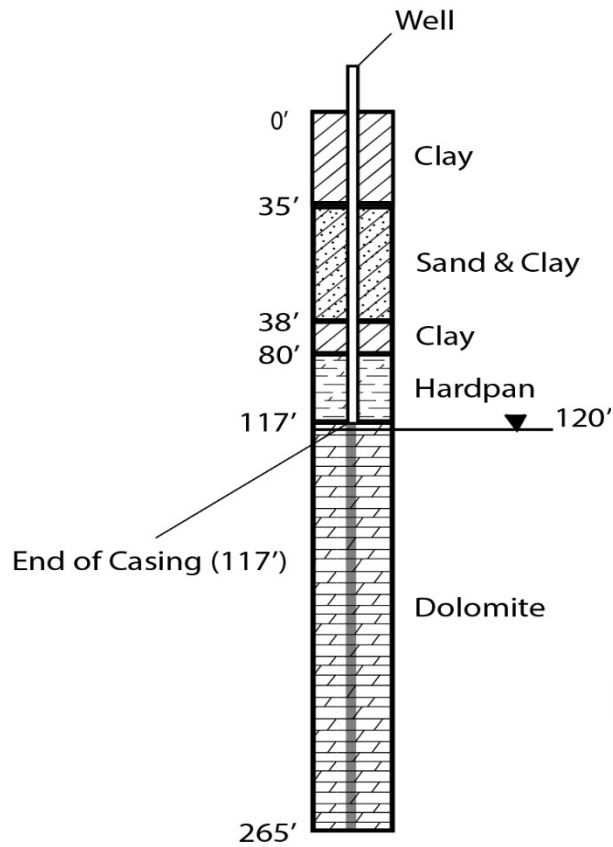
APPENDIX. Well Construction Reports

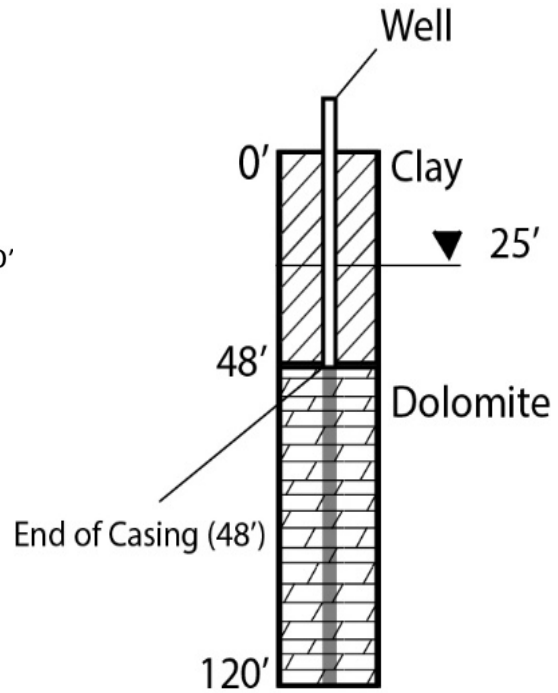*Figure A1. Location L1 well construction report.*

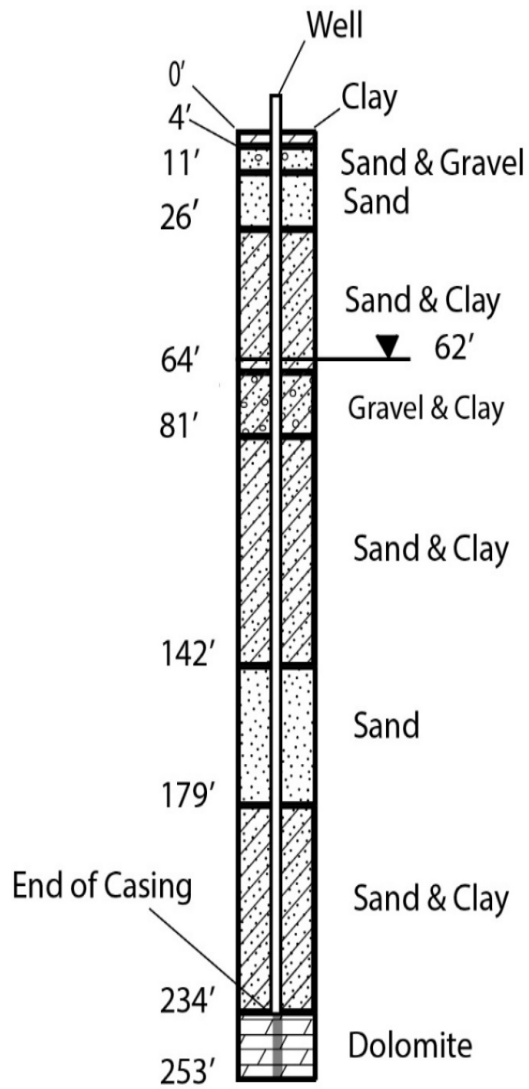*Figure A2. Location L2 well construction report.*
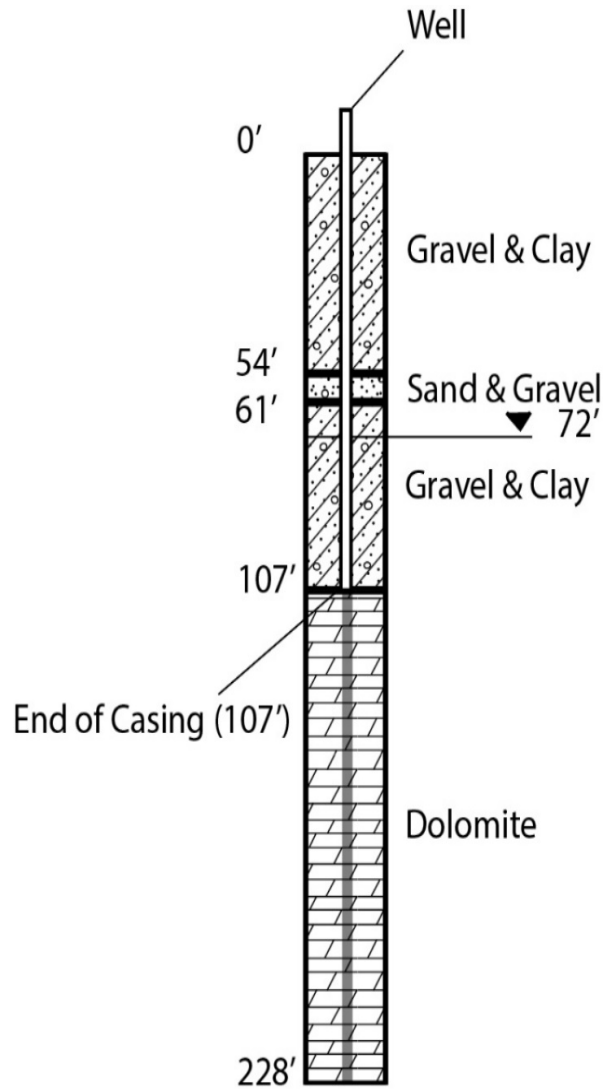
Figure A3. Location L3 well construction report.

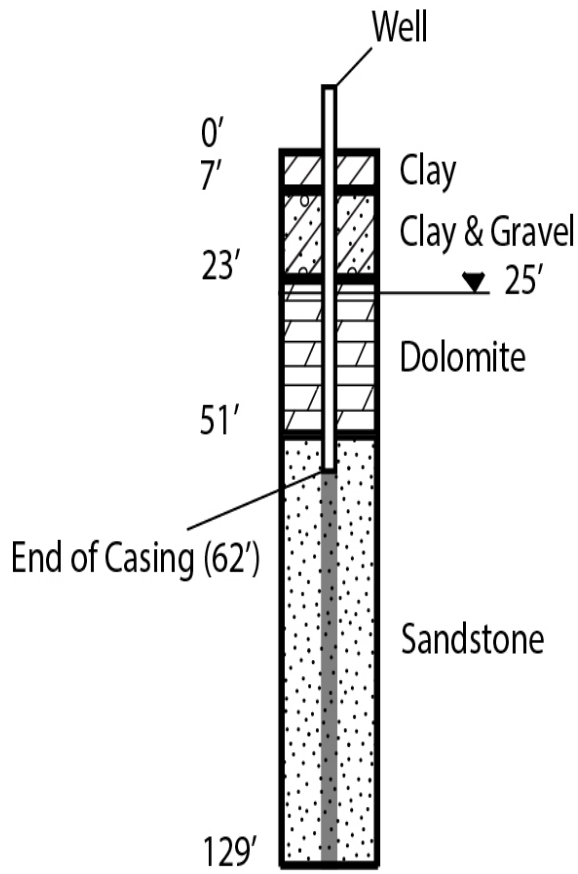*Figure A4. Location L4 well construction report.*

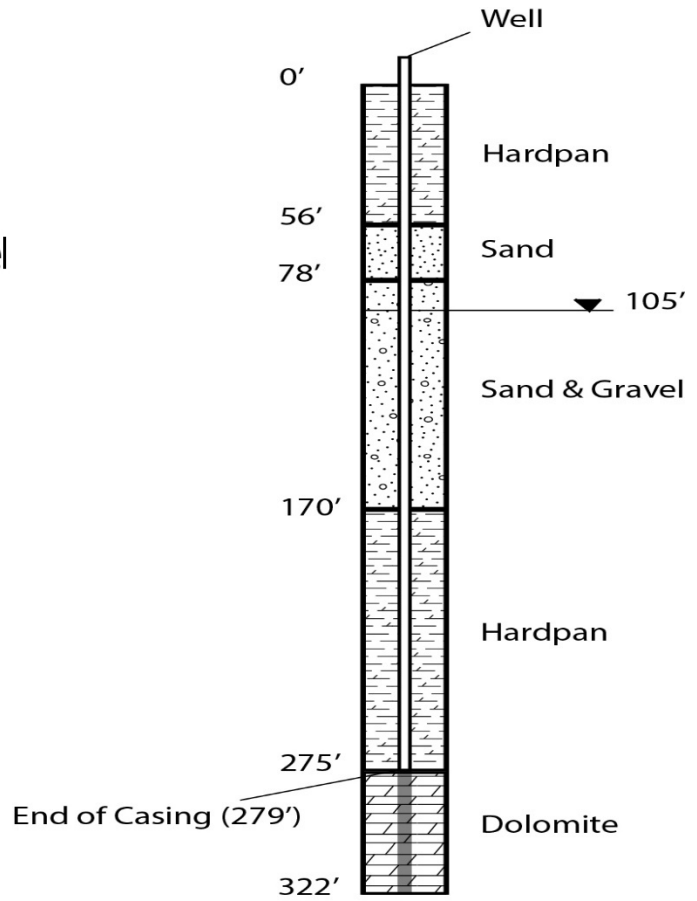*Figure A5. Location L5 well construction report.*

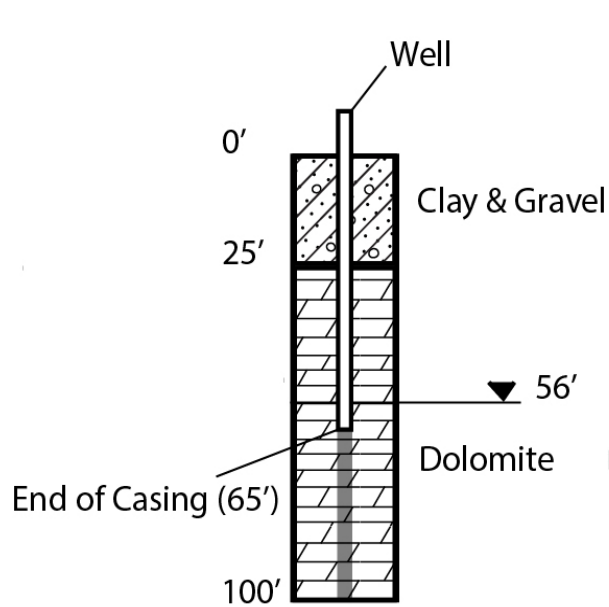*Figure A6. Location L6 well construction report.*
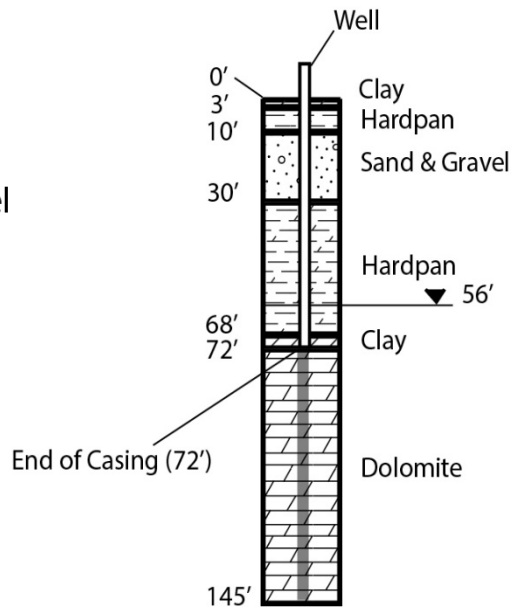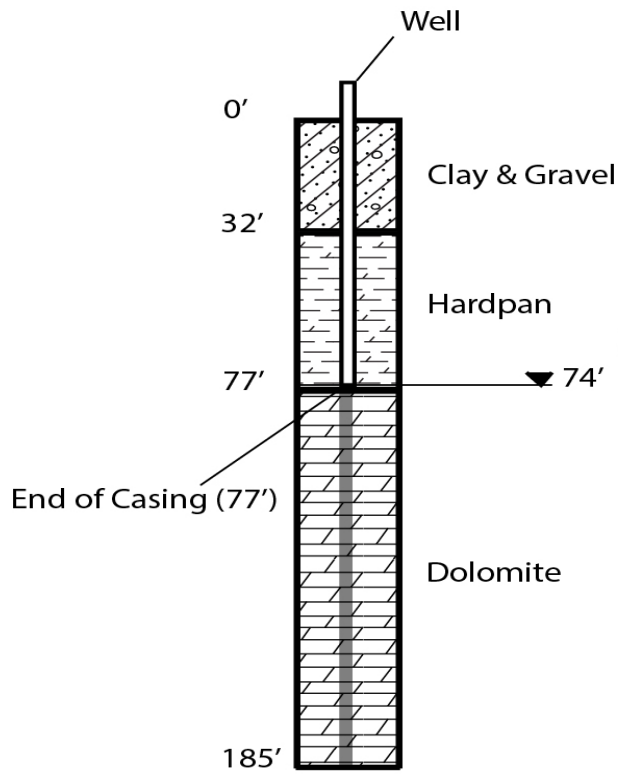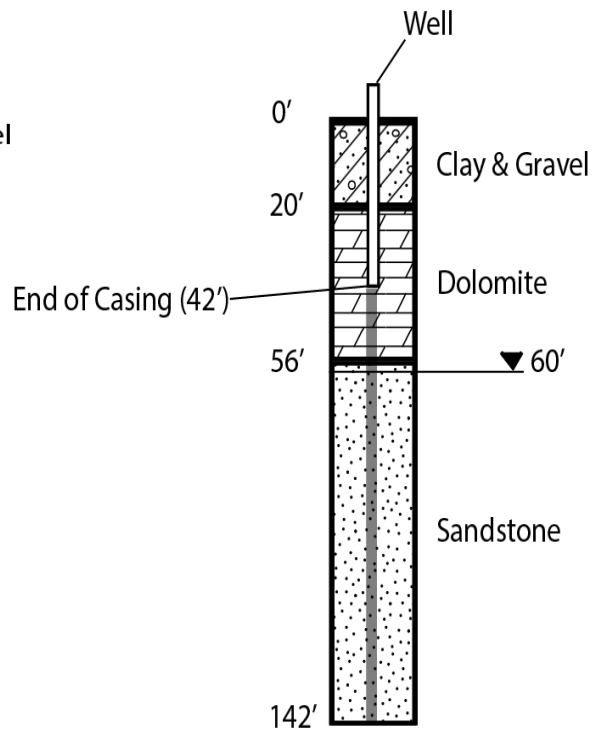

Figure A7. Location L9 well construction report.

Figure A8. Location L13 well construction report.

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Figure A9. Location L14 well construction report.

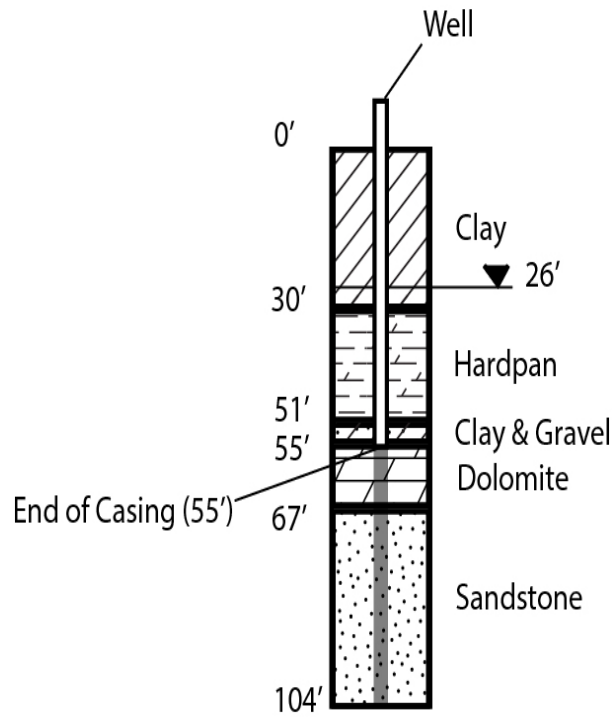*Figure A10. Location L15 well construction report.*
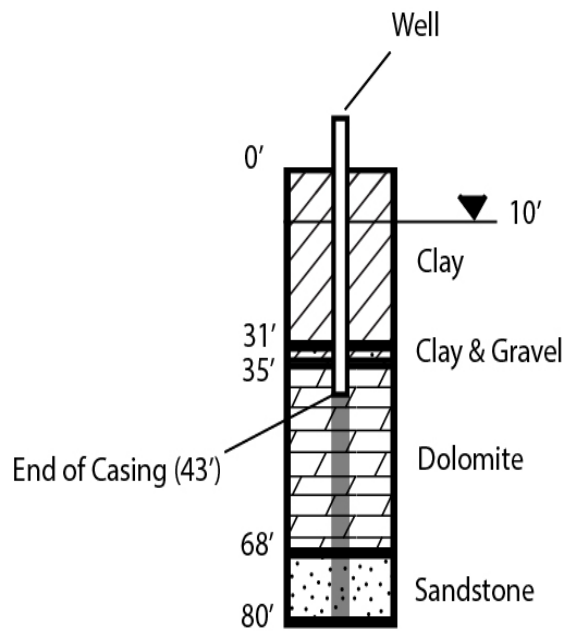

Figure A12. Location L16 well construction report.

Figure A12. Location L18 well construction report.

30