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# WESTERN GALLATIN VALLEY ARSENIC DISTRIBUTION PROJECT FINAL REPORT

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## ACRONYMS AND ABBREVIATIONS

As: arsenic

As(III): arsenite

As(V): arsenate

DO: dissolved oxygen

e-tape: electronic tape, also known as a “sounder” or “electronic water level meter”

GLWQD: Gallatin Local Water Quality District

gpm: gallons per minute

MBMG: Montana Bureau of Mines and Geology

MCL: Maximum Contaminant Level

MCLG: Maximum Contaminant Level Goal

mg/L: milligrams per liter, equivalent to ppm in water

ppb: parts per billion, equivalent to  $\mu\text{g/L}$  in water

ppm: parts per million, equivalent to mg/L in water

QA/QC: Quality Assurance/Quality Control

RO: reverse osmosis

SC: specific conductivity

SWL: static water level

t.o.c.: top of casing

TD: total depth

U.S. EPA: Environmental Protection Agency

$\mu\text{g/L}$ : micrograms per liter, equivalent to ppb (parts per billion) in water

## EXECUTIVE SUMMARY

In 2016 the Gallatin Local Water Quality District conducted an arsenic sampling project in the western part of the Gallatin Valley in southwest Montana. Existing data in the GLWQD groundwater database and the Montana Bureau of Mines and Geology Groundwater Information Center database indicated that the area near the Madison Plateau and Camp Creek Hills is a concern due to multiple wells having arsenic levels exceeding the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) of 10 µg/L for arsenic in drinking water. The focus of the sampling project was to better understand the spatial distribution of the problem and inform local residents through education and outreach. Over half of the samples (61%) collected during the project had levels exceeding the arsenic MCL. Samples were also collected for nitrate + nitrite and total iron. Additionally, samples exceeding the arsenic MCL were also submitted for arsenic speciation and total hardness. Speciation results demonstrated that all the samples except for one had arsenic present solely in the form of arsenate, and arsenite was not detected. This makes sense in the context of the field parameter data collected, where 21 out of 23 locations had oxic groundwater conditions (dissolved oxygen  $\geq 2$  mg/L). The single sample that had detectable arsenite was considered to be an outlier due to its unique characteristics in terms of the arsenic level, non-detectable nitrate+nitrite, anoxic conditions, high specific conductivity, and high temperature. We were unable to identify a specific water bearing zone where elevated arsenic is found, possibly because of the geographically large study area and the sparse scattering of the 23 wells that were sampled. The only characteristic or parameter measured that appeared related to the arsenic concentration was temperature, where higher groundwater temperatures were correlated with higher arsenic concentrations. Besides temperature, there was no indicator or predictor of where elevated arsenic might be found. We recommend that all Gallatin County residents using individual domestic wells that live west of the West Gallatin River screen their well for arsenic.

## BACKGROUND

Arsenic (As) is a naturally occurring element that is found in rocks and soil, and is usually combined with other elements to form mineral compounds. Elevated levels of arsenic threaten drinking water supplies in various regions throughout the world, including some areas in southwest Montana. Arsenic can enter waterways and water supplies via the erosion of rock formations, volcanic activity, geothermal discharge, agricultural runoff, mining activities, or certain types of industrial waste runoff. Industrial uses of arsenic in the U.S. include or have included wood preservation, pesticides, and the production of lead-acid batteries and semiconductors. Arsenic naturally present in rock formations can be released to groundwater, as water moves through soil and rock under certain geochemical conditions. Because rivers and streams are connected to groundwater, the arsenic present in surface water can end up in groundwater, and vice-versa.

Under the Safe Drinking Water Act, the current United States Environmental Protection Agency (U.S. EPA) maximum contaminant level (MCL) for arsenic is 10 µg/L or ppb (equivalent to 0.010 mg/L or ppm in water) and the maximum contaminant level goal (MCLG) is 0 µg/L or ppb (0 mg/L or ppm). Historical water quality data from the Montana Bureau of Mines and Geology (MBMG) Groundwater Information Center (GWIC) and the Gallatin Local Water Quality District (GLWQD) groundwater database indicate arsenic above the MCL of 10 µg/L is present in some wells on the west side of the Gallatin Valley, although many wells in this area have not been tested for arsenic at all. It appears that wells located near Manhattan and east towards Belgrade and Bozeman do not have arsenic above the MCL; this is demonstrated on **Figure 1** (on page 8), where there is a fairly distinct geographic separation of groundwater arsenic concentrations.

The locations where arsenic is greater than the U.S. EPA MCL seem to correspond to Tertiary aged sediments on the Madison Plateau and Camp Creek Hills area within the western part of the county (**Figure 1**). Further west, in the Madison River Valley, near the western edge of Gallatin County and the GLWQD boundary, arsenic can be found at ten times the MCL or greater. It is unclear whether the Tertiary sediment arsenic and Madison River Valley arsenic are separate issues. The Madison River headwaters are in Yellowstone National Park, an area known to have arsenic-rich hydrothermal discharge. This geothermal discharge results in arsenic loading to the Madison River, into the irrigated Lower Madison River Valley (west edge of the study area) and into the Missouri River where total arsenic several times the MCL has been reported (Tuck, Dutton and Nimick 1997). Arsenic is also known to be associated with volcanic sediments, and the geologic description of the Tertiary sediments present in the area (primary map unit covering the majority of the area is *Tscmv*: Madison Valley member) indicates that volcanic ash beds are present (Vuke et al., 2014). This geologic map unit representing the Tertiary sediments of interest is shown in **Figure 1** as the beige area on the inset map. Literature describes that soil and rock samples from these Tertiary sediments in the vicinity of the study area were found to have relatively high arsenic concentrations, indicating geologic material is a likely source of arsenic (Nimick 1998).

Another potential source of arsenic to shallow groundwater is pesticides containing arsenic, which were used until the 1980s or 1990s and could have been used on crops in the area. If high soil arsenic levels as a result of pesticide use are present, phosphate fertilizer can increase the potential for arsenic leaching and release arsenic into groundwater (Welch 2000). Recharge on the Madison Plateau is likely a combination of recharge from precipitation (probably a small component in most cases given 10"-15" average annual precipitation in the area), combined with recharge from irrigation water and canal leakage, limited stream recharge, and recharge along the bedrock from the Madison Range to the south. Proportions of these recharge sources surely varies among different water bearing zones and at different locations on the Madison Plateau. Well depths are generally fairly deep in the study area: 100'-300' deep, though some wells are much deeper (400'-800'). Only in the case of many years of application of pesticides containing arsenic along with substantial recharge from irrigation water is this source of arsenic to groundwater in the area plausible.

In order to treat arsenic in drinking water, knowing the oxidation state, or species, is important. Inorganic arsenic is usually found in one of two oxidation states: As(V) (arsenate), or As(III) (arsenite). Both types are hazardous to human health. Chemical reactions that control the movement of arsenic in the environment via adsorption and desorption are complex, and depend on pH, oxidation/reduction reactions, and the other ions and minerals present in the environment. In general, in highly-oxygenated groundwater, As(V) is the predominant species while in anoxic conditions such as those often found in deeper groundwater, As(III) is predominant (Oregon Health Authority n.d.). Nimick (1998) found low concentrations of As(III) compared to As(V) in samples taken from wells east of the Madison River valley in Tertiary sediment.

## **HEALTH EFFECTS OF ARSENIC**

High levels of arsenic in drinking water are associated with adverse health effects. Skin contact with the water is a secondary exposure concern. Of particular concern are persons using private domestic (non-public) wells that receive little to no water quality monitoring, who may not realize they are being exposed to high levels of this odorless and tasteless element. It is important for homeowners that use domestic wells to test their water to determine whether or not it is safe to drink.

Health effects from arsenic can occur due to acute or chronic exposure. Acute toxicity often results from ingestion or inhalation of high levels of arsenic, while chronic poisoning is more commonly associated with arsenic exposure via ingestion of drinking water over a long period of time. Drinking water with high levels of arsenic can lead to a variety of health problems, including effects on the neurological, respiratory, cardiovascular, and gastrointestinal systems (ATSDR 2010). It can cause skin damage, skin lesions, anemia, and an increased risk of many types of cancer including skin, prostate, bladder, liver, and kidney cancer. Other non-cancerous side effects of arsenic poisoning include thickening and discoloration of the skin, stomach pain, nausea, diarrhea, numbness in the

hands and feet, partial paralysis, or blindness. Other negative health effects that have not been listed could also occur.

Children have an increased susceptibility to arsenic toxicity due to differences in metabolism, increased sensitivity of the developing nervous system, and their decreased ability to detoxify arsenic. Behaviors of children also lead to increased risk of exposure due to hand-to-mouth behaviors, breathing closer to the ground, and playing in potentially contaminated soil (Braaksma, pers. comm., 2016).

## PROJECT GOAL, OBJECTIVES, AND TASKS

The goal of this project was to assess the distribution of arsenic levels that are above or near the U.S. EPA MCL of 10 µg/L (ppb) in groundwater in the western portion of the GLWQD and to educate area residents on results and potential treatment options as needed.

**Objective 1:** Conduct groundwater monitoring from domestic wells to understand the spatial distribution of elevated arsenic in drinking water in the western portion of the GLWQD, near the Camp Creek Hills/Madison Bluffs area. This objective has been met.

**Objective 1 Tasks Completed:** Twenty-three wells were sampled for the project. Of these, twenty one are used for domestic water supply, one is used as a stock well, and one is used for lawn irrigation.

**Objective 2:** Share results with homeowners and conduct an education and outreach workshop. This objective has been met.

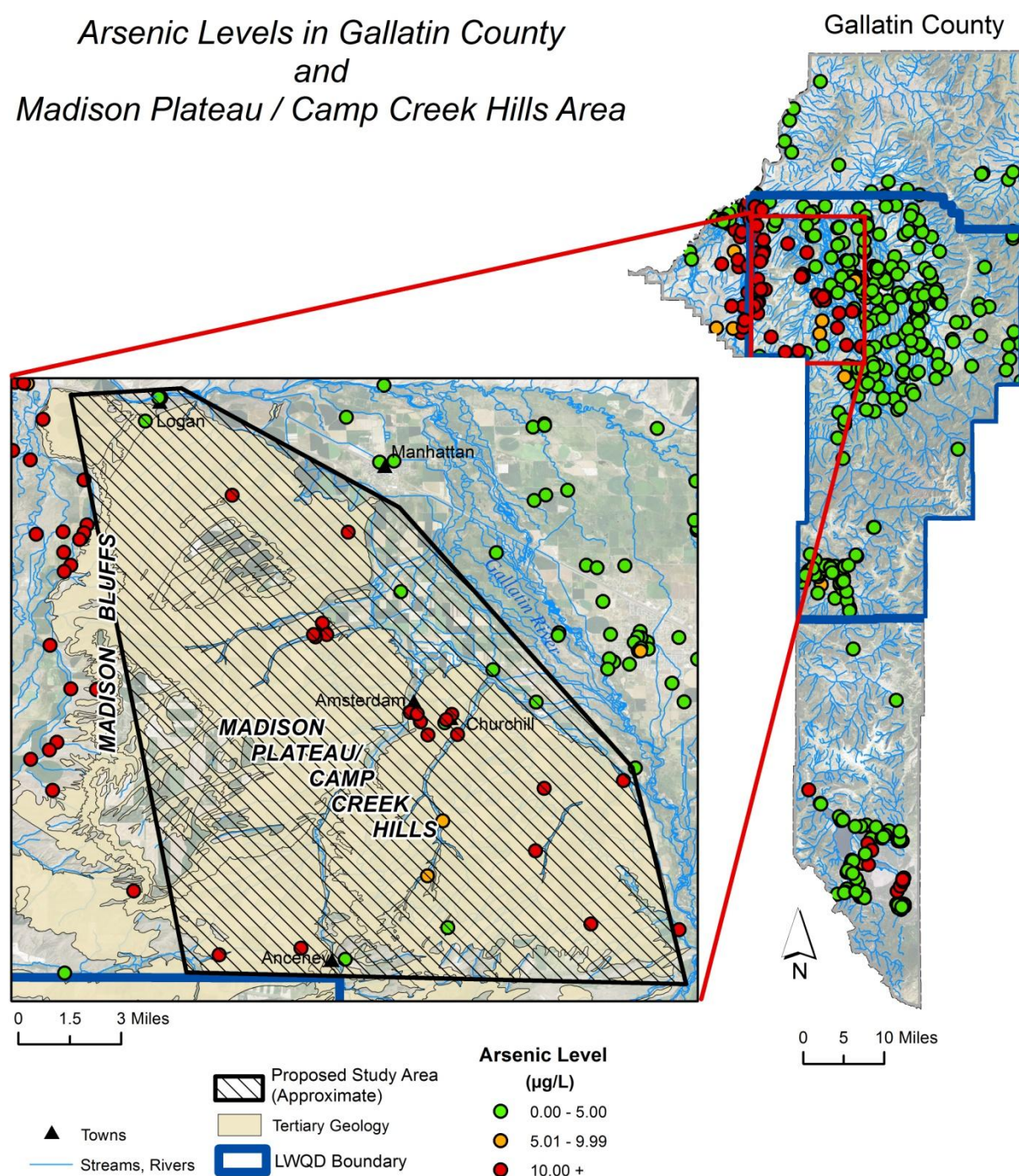
**Objective 2 Tasks Completed:** An arsenic fact sheet was created and mailed to homeowners who participated in the study. The fact sheet has been distributed at GLWQD brochure racks and is available online. Laboratory results and interpretive letters were also mailed to homeowners. An outreach workshop was conducted, which was attended by 31 residents.

## STUDY AREA

The project study area was the western portion of the GLWQD between Anceney to the south, Manhattan and Logan to the north, Four Corners and the Gallatin River system to the east, and the Lower Madison River Valley to the west. The generalized study area is shown within the black polygon on **Figure 1** and covers mostly Tertiary surficial geology (primarily the geologic map unit *Tscmv*: Madison Valley member) shown as the beige area in the western part of the Valley (Vuke, et al. 2014). This area of Tertiary sediments appears to align with where elevated arsenic levels are found in Gallatin Valley.



# *Arsenic Levels in Gallatin County and Madison Plateau / Camp Creek Hills Area*



**Figure 1.** Background groundwater arsenic distribution in Gallatin County using available information from the GLWQD Groundwater Database and the Montana Bureau of Mines and Geology Groundwater Information Center. The inset map shows arsenic levels in the area of interest, the corresponding area of Tertiary geologic sediments, as well as the generalized project study area.



## METHODS

GLWQD Standard Operating Procedures and standardized field forms were used during the project. Static water level measurements were collected using an electronic water level meter (e-tape) upon arrival to the site and during pumping, where possible. In many cases, the static water level based on well logs exceeded the length of the e-tape. At some locations water levels were not measured if there was a high risk of the e-tape getting stuck or tangled in the well. Field parameters were measured at all sites using a YSI 556 or a YSI ProPlus meter and a flow-through cell. A hydrant or spigot as close as possible to the well was selected for purging. Purging the well was conducted by running the hydrant or spigot until field parameters stabilized according to the criteria in **Table 1**:

**Table 1.** Field parameter stabilization criteria.

Parameter	Stabilization Criteria	Reference
pH	+/- 0.1	Puls and Barcelona 1996; Wilde et al., 1998
Specific Conductance (SC)	+/- 3%	Puls and Barcelona 1996
Dissolved Oxygen (DO)	+/- 0.3 mg/L	Wilde et al., 1998

New, laboratory-provided sampling containers were used. Filtration and preservation using laboratory-provided preservatives was completed as needed (**Table 2**).

**Table 2.** Sample volumes, required preservation and filtration, and hold times.

Analyte	Volume Needed and Bottle Type	Preservation	Filtration	Hold Time	Method	Laboratory Reporting Limit
Arsenic, Total	250 mL Plastic or Glass	HNO <sub>3</sub> to pH <2	Unfiltered	6 months	E200.8/A3114B	0.001 mg/L
Arsenic, III & V speciation	250 mL Plastic	HCl to pH <2	Unfiltered	28 days	E1632A Mod.	0.005 mg/L
Nitrate + Nitrite (as N)	50 mL Plastic or Glass	H <sub>2</sub> SO <sub>4</sub> to pH <2, Cool, ≤ 6°C	Unfiltered	28 days	E353.2	0.01 mg/L
Hardness, Total as CaCO <sub>3</sub>	100 mL Plastic or Glass	Cool, ≤ 6°C	Filtered (0.45 µm)	6 months	A 2340 B	1 mg/L
Iron, Total	250 mL Plastic or Glass	HNO <sub>3</sub> to pH <2	Unfiltered	6 months	E200.7/E200.8	0.02 mg/L

Unfiltered grab samples were collected at each site for arsenic, iron, nitrate + nitrite as N, and arsenic speciation. Hardness samples were collected after filtration. All samples were kept chilled on ice and arsenic, iron, and nitrate + nitrite as N were shipped after the day's sampling was completed to Energy Laboratories (a certified drinking water analysis laboratory). Arsenic speciation and total hardness samples were kept chilled until the arsenic results determined which samples should be sent in for further analysis. No hold times were exceeded. Samples with arsenic results greater than or equal to

the MCL, as well as several samples with results just below the MCL (i.e. 8 µg/L or 9 µg/L) were sent for arsenic speciation and total hardness analysis. This information can help assist the participating homeowners with determining the appropriate water treatment system, if they choose to install one.

A field parameter meter was calibrated at the beginning of each day of sampling using standard reference solutions to assure the meters were working properly, and a record of the calibration was recorded on a paper calibration log. Post-sampling drift check of the meter was conducted at the end of each sampling day.

## RESULTS

### Arsenic, Arsenic Speciation, and Field Parameters

Of the twenty-three samples collected during the study, fourteen samples, or 61%, exceeded the U.S. EPA MCL of 10 µg/L for total arsenic. Nine samples, or 39%, were below the MCL. Total arsenic results ranged from 3 µg/L to 161 µg/L, with a mean value of 19 µg/L. All samples collected throughout the project had detectable arsenic. Of the sixteen samples analyzed for arsenic speciation, fifteen of them had arsenic solely in the form of arsenate [As(V)], while arsenite [As(III)] was not detectable.

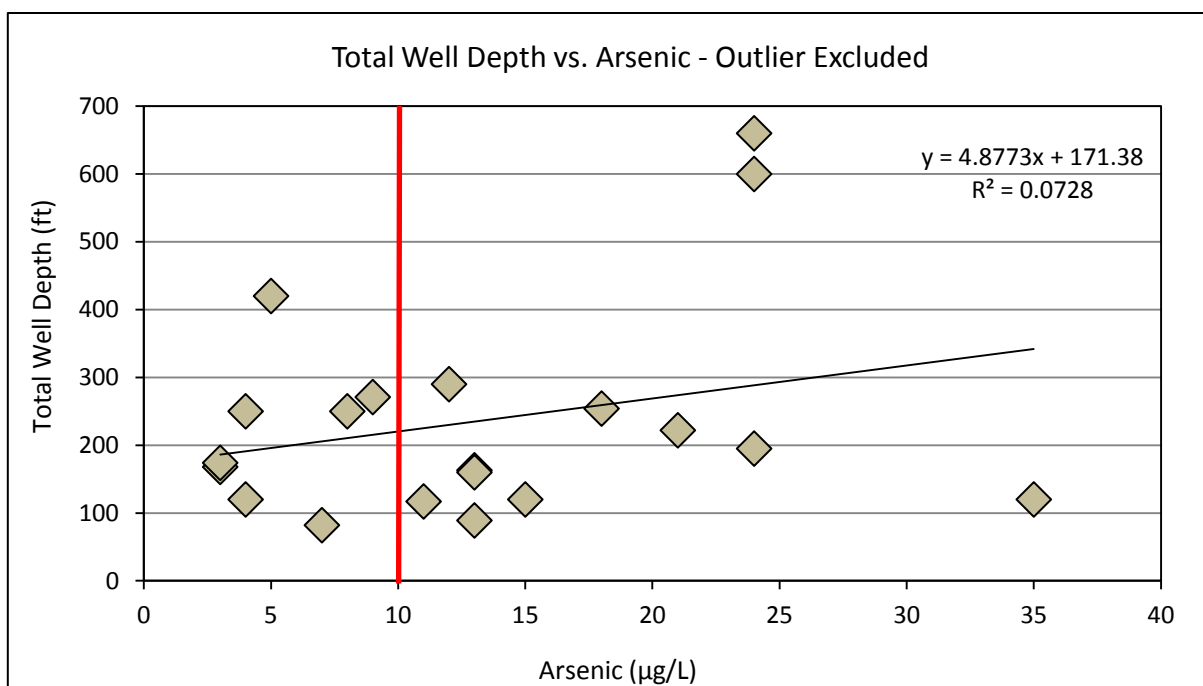
One sample, 051716-02, was an outlier and had nearly equal proportions of arsenite and arsenate. This outlier was the westernmost sampling location, and had the highest arsenic level found throughout the study: a concentration over sixteen times the MCL (161 µg/L). The well from which the sample was collected is located on the edge of the Madison Bluffs and the parcel overlooks the Lower Madison River Valley. This well was an outlier in terms of not only the highly elevated arsenic level but also in terms of temperature, dissolved oxygen, and specific conductivity. This well is presumably hydrologically disconnected from the other sampling locations based on its geochemical characteristics and is not representative of what was otherwise seen in the study. For this reason, most of the figures below exclude this sample. The inclusion or exclusion of the data point is indicated on the figure title.

Well depths were not strongly correlated with arsenic concentrations in the wells sampled (**Figure 2**). Similarly, static water levels were not correlated to arsenic concentrations (**Figure 3**). Groundwater level elevation estimates were calculated using either measured static water levels when available or static water levels listed on the well logs, along with Google Earth<sup>®</sup> ground surface elevation data. There is no evidence of a correlation between groundwater level elevations and arsenic concentration based on the data collected (**Figure 4**). This probably due to the large spatial distribution and scattering of wells sampled, and the lack of uniformity in the geologic depositional layers across the study area. If sampling was condensed to a smaller are, a range of elevations in which wells are withdrawing groundwater with elevated arsenic may be identifiable.

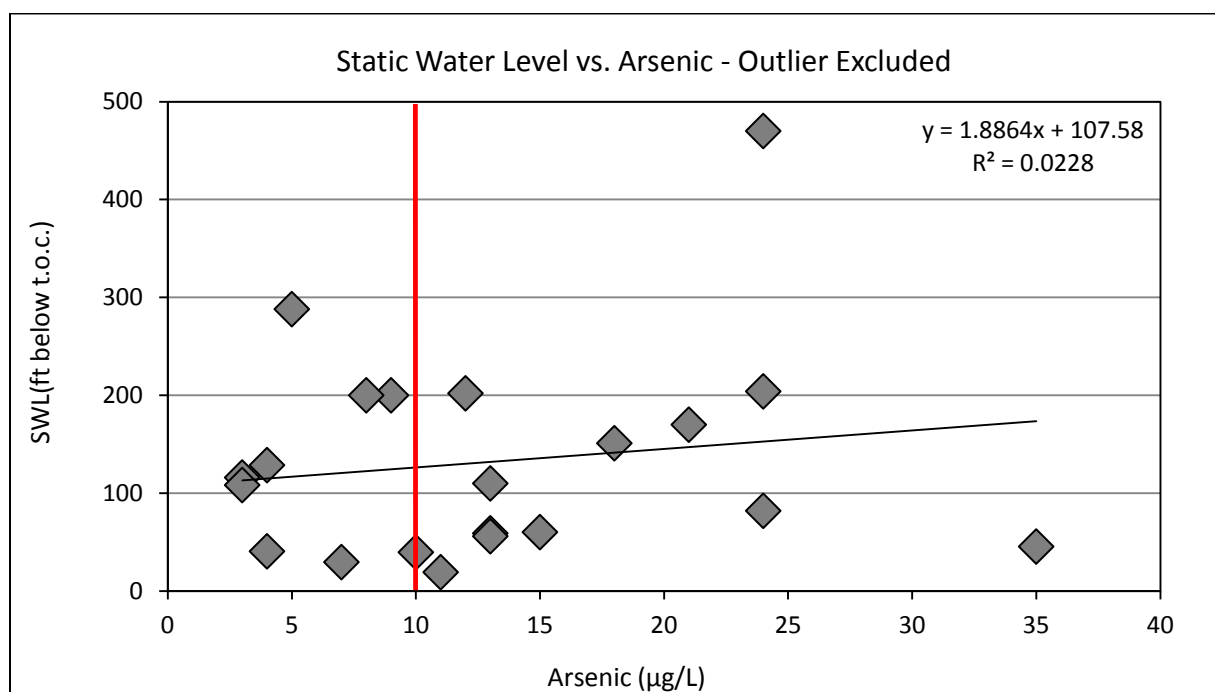
Estimated well completion elevations for all wells used for the project and wells with historical data were calculated based on the total well depths listed on the well logs and Google Earth<sup>®</sup> ground

surface elevation data. This information was compared to arsenic concentrations. There is little to no evidence of a correlation between well completion elevations and arsenic concentrations (**Figure 5**) for all of the available data.

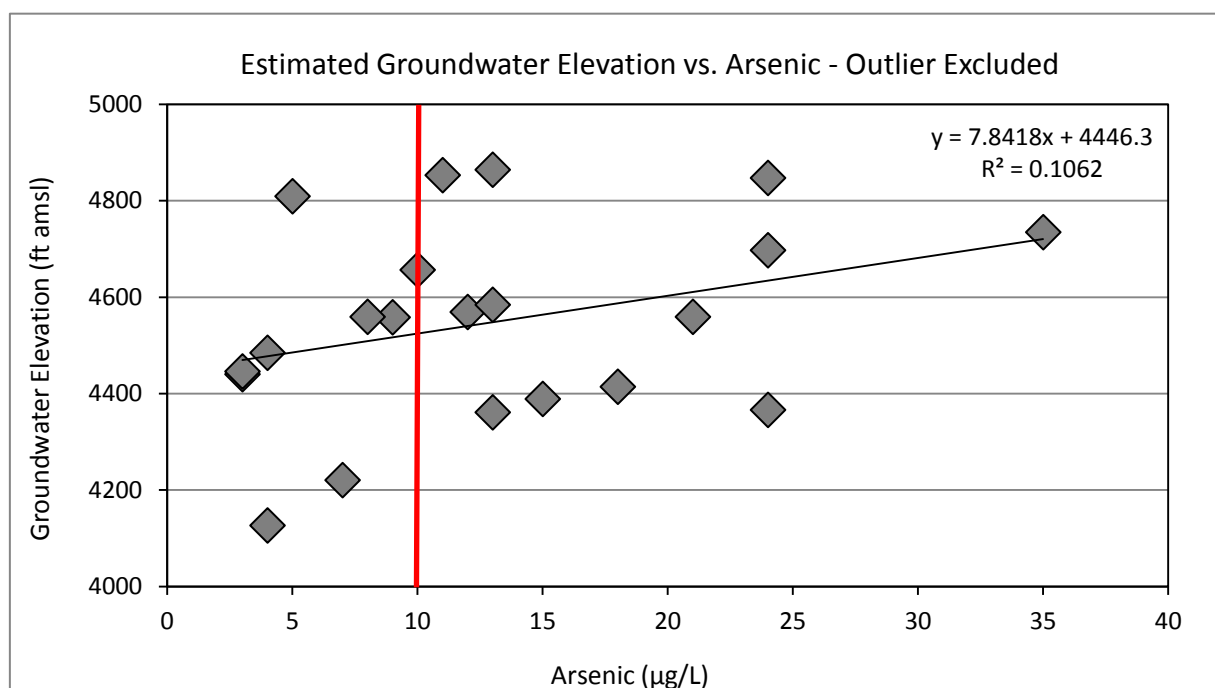
Groundwater temperature was measured in the field after wells were purged and when field parameters had stabilized (**Table 1**). There is sufficient evidence to indicate that there is a relationship between arsenic concentrations and groundwater temperatures when data was compared for all wells except for the outlier based on a p-value of 0.021 (**Figure 6**). The relationship between arsenic concentration and temperature is also shown on **Figures 7** with the outlier included. Other field parameter measurements collected were dissolved oxygen, pH, and specific conductivity, none of which had a correlation to the arsenic concentrations found throughout the study. Nearly all field parameter measurements of dissolved oxygen indicated oxic groundwater conditions (>2 mg/L), with the exception of the outlier sample (sample ID 051716-02 with a dissolved oxygen concentration of 0.25 mg/L) as well as one additional sample (sample ID 051616-01 with a dissolved oxygen concentration of 1.32 mg/L).



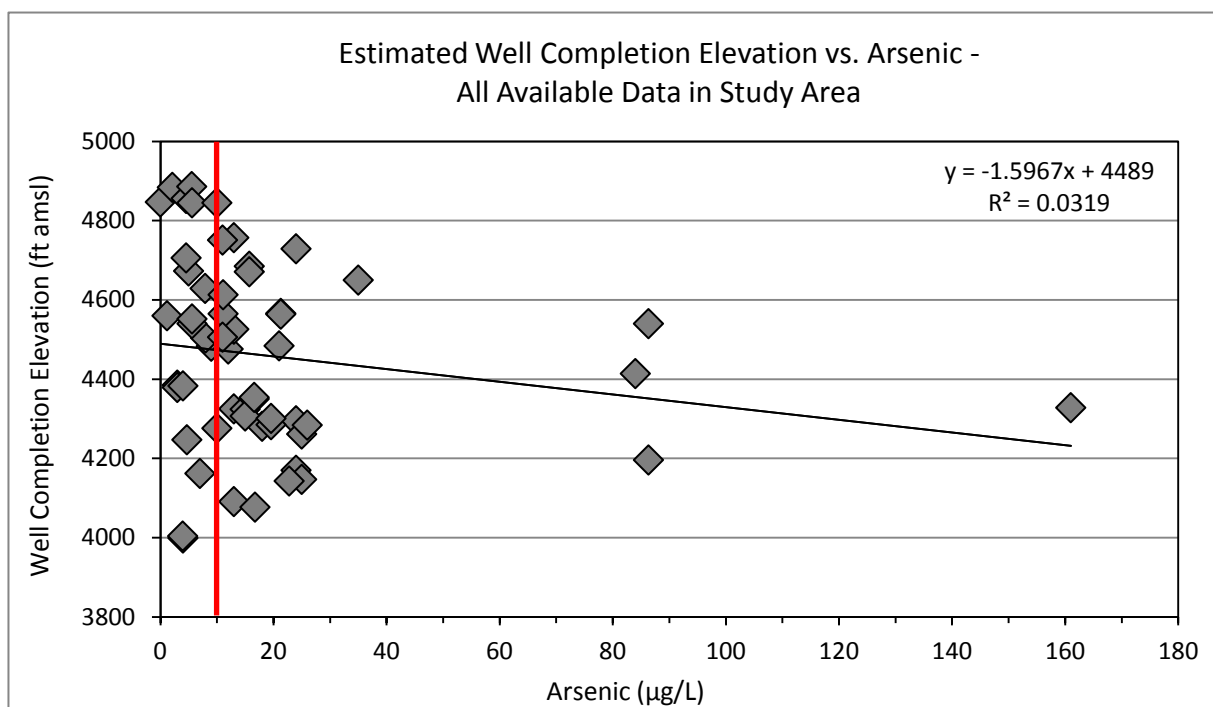
**Figure 2.** Well depth and arsenic concentrations plotted along with a linear line-of-best-fit and the resulting equation and  $R^2$  value. The data shown here excludes the outlier sample (051716-02). The red vertical line represents the arsenic MCL. There is inconclusive evidence of a correlation between total well depth and arsenic concentration given an ANOVA p-value of 0.238.



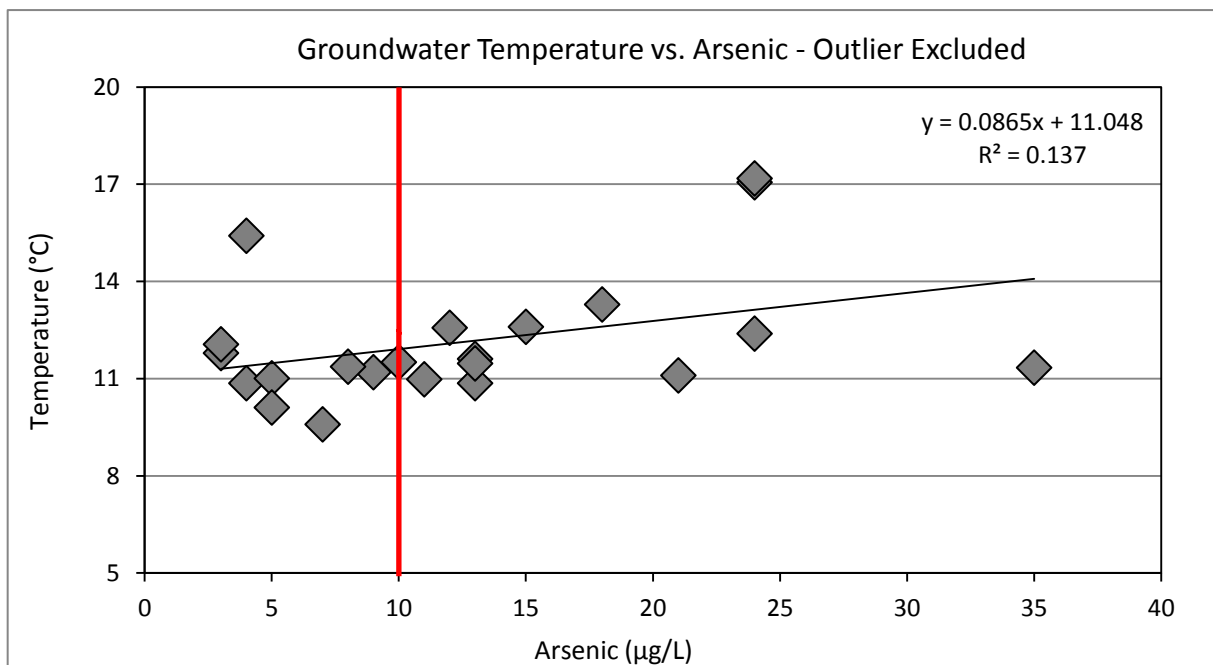
**Figure 3.** Static water levels and arsenic concentrations plotted along with a linear line-of-best-fit and the resulting equation and  $R^2$  value. The data shown here excludes the outlier sample (051716-02). The red vertical line represents the arsenic MCL. There is no evidence that a correlation between static water levels and arsenic concentrations exists in the data given an ANOVA  $p$ -value of 0.518.



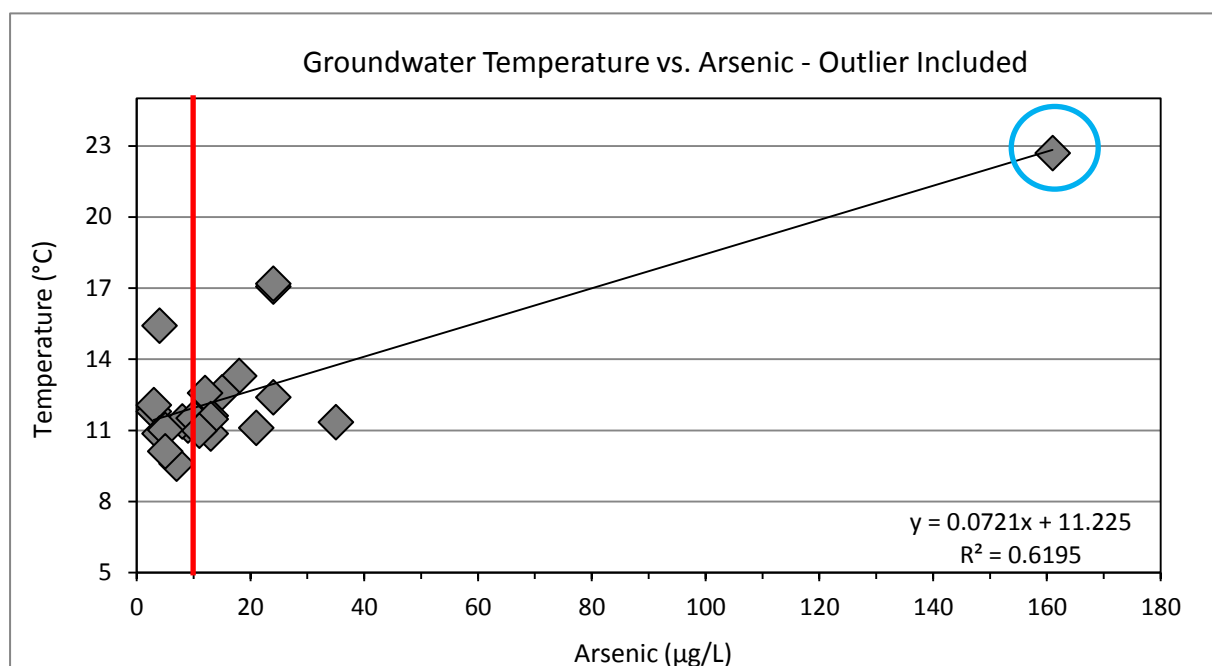
**Figure 4.** Estimated groundwater elevations and arsenic concentrations plotted along with a linear line-of-best-fit and the resulting equation and  $R^2$  value. The data shown here excludes the outlier sample (051716-02). The red vertical line represents the arsenic MCL. There is no evidence that a correlation between groundwater elevations and arsenic concentration exists in the data given an ANOVA  $p$ -value of 0.296.



**Figure 5.** Estimated well completion elevations and arsenic data plotted for all available data within the project area (including the recently collected project data and historical data). The linear line-of-best-fit through the data is shown along with the resulting equation and  $R^2$  value. There is little or no evidence of a correlation between well completion elevation and arsenic concentration given an ANOVA  $p$ -value of 0.129.



**Figure 6.** Groundwater temperature and arsenic data plotted along with a linear line-of-best-fit and the resulting equation and  $R^2$  value. The data shown here excludes the outlier sample (051716-02). The red vertical line represents the arsenic MCL. There is moderately convincing evidence that there is a correlation between groundwater temperature and arsenic concentration in the study area given an ANOVA  $p$ -value of 0.021.



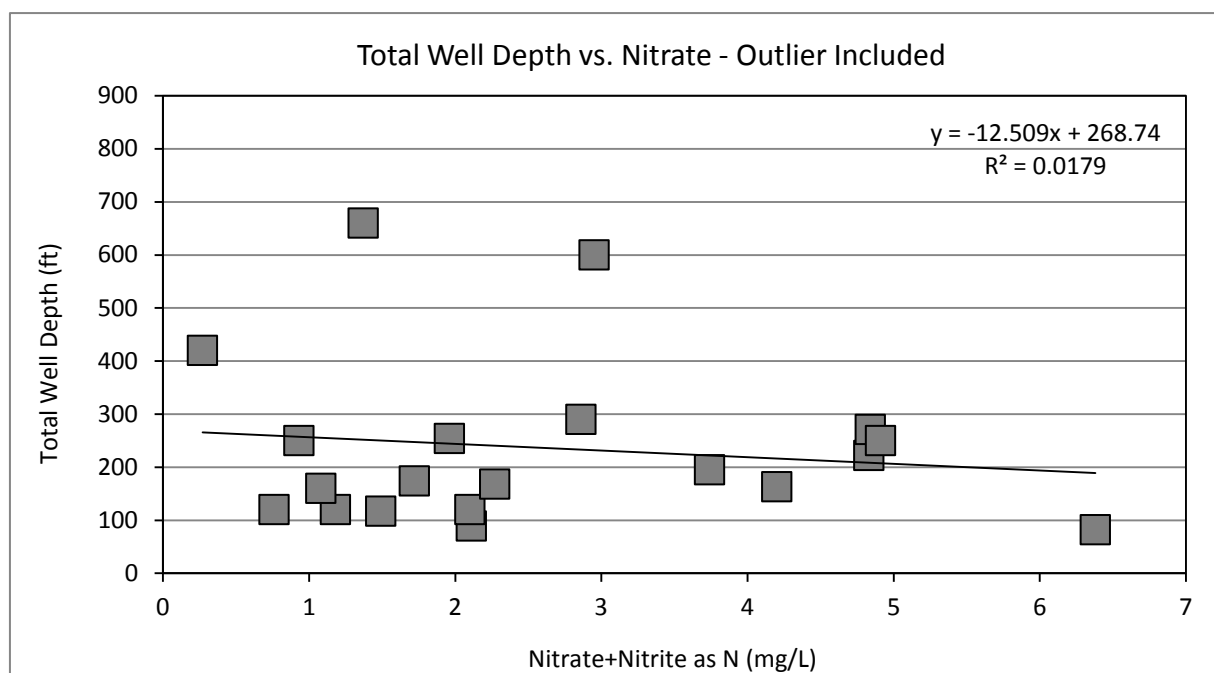
**Figure 7.** Groundwater temperature and arsenic data plotted for all project results, along with a linear line-of-best-fit and the resulting equation and  $R^2$  value. The red vertical line represents the arsenic MCL. The blue circle indicates the outlier sample collected in the study.

## Nitrate

Nitrate + nitrite as N (hereafter referred to as “nitrate”) was analyzed for each location sampled in the study. Given the oxic conditions measured, it is unlikely that any nitrite was present. Nitrate is a drinking water contaminant of concern with a U.S. EPA MCL of 10 mg/L and is also an indicator analyte that can help detect various water quality issues such as agricultural runoff, or a problem with a septic or wastewater treatment system. Nitrate ranged from not detectable to 6.38 mg/L, with a mean value of 2.52 mg/L for samples with detectable levels. Background nitrate is generally considered 2 mg/L or less. Of the twenty-three samples collected, eleven samples (48%) had nitrate less than 2 mg/L, and twelve samples (52%) were between 2 and 6.5 mg/L. All samples were below the MCL of 10 mg/L. Well depth was not correlated with nitrate concentrations in the wells sampled (**Figure 8**).

## Iron

Iron was analyzed because of its potential interference with reverse osmosis or adsorptive filter treatment systems when it is present at high levels. Concentrations in the study ranged from not detectable to 1.11 mg/L, with a mean value of 0.20 mg/L for samples with detectable levels. The U.S. EPA has set a MCL for iron of 0.3 mg/L based on aesthetic effects of taste, appearance, and fixture staining. Of the twenty-three samples collected, ten samples (43.5%) had non-detectable iron, ten samples (43.5%) had detectable iron less than the secondary U.S. EPA MCL of 0.3 mg/L, and three samples (13%) had concentrations exceeding the MCL.



**Figure 8.** Total well depth and nitrate plotted along with a linear line-of-best-fit and the resulting equation and  $R^2$  value. No nitrate samples exceeded the MCL of 10 mg/L. There is no evidence that there is a correlation between total well depth and nitrate given an ANOVA  $p$ -value of 0.180.

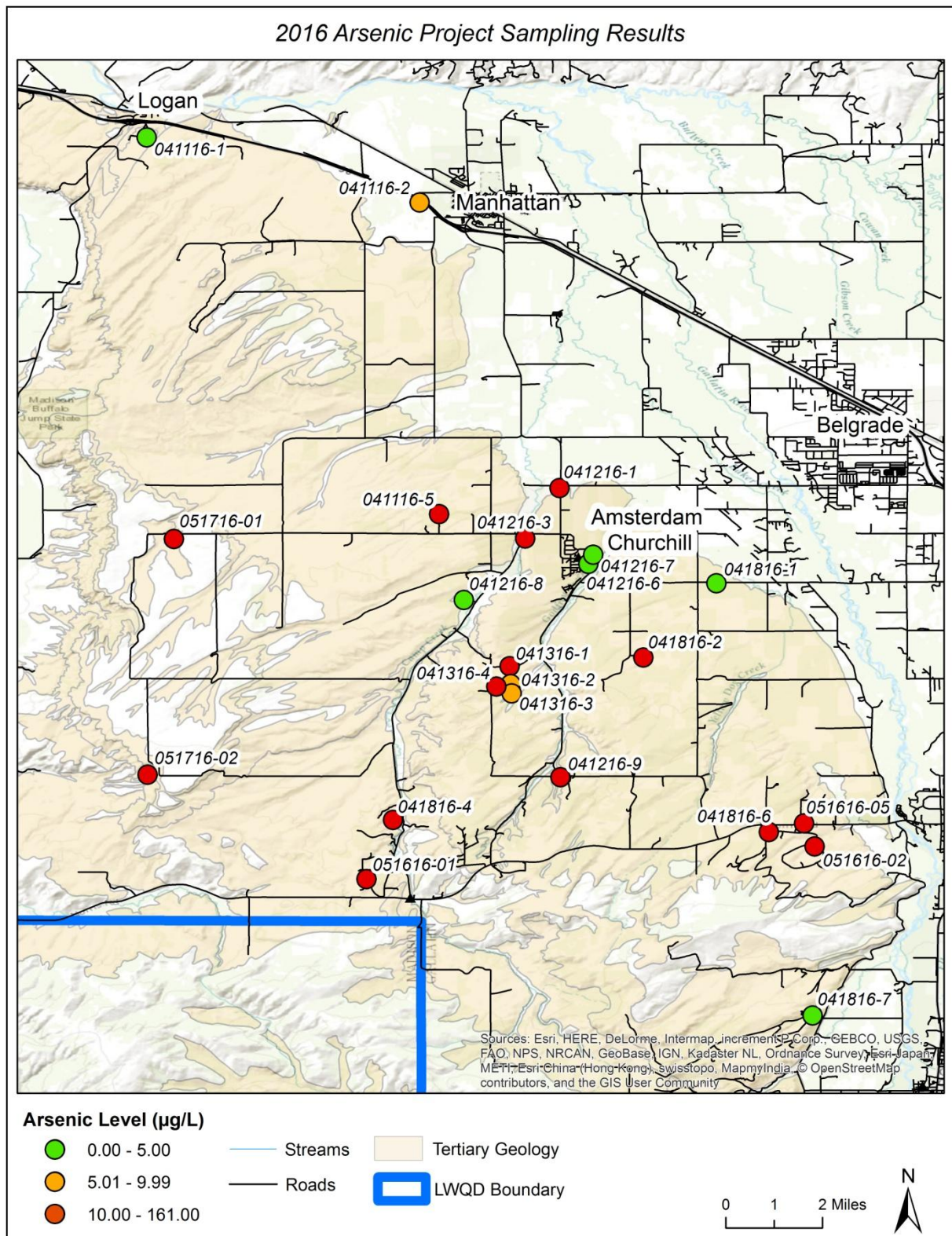
### Hardness

Samples were analyzed for total hardness only if the arsenic concentration was close to or exceeded the MCL. The water hardness results or levels were provided to help homeowners evaluate potential treatment systems. Very hard water can negatively interfere with a reverse osmosis system’s function over time and may result in a reduced volume of water passing through the membrane. Of the sixteen samples submitted, hardness results ranged from 89-275 mg/L, which is considered moderately hard water at the lower end and very hard water at the upper end of the range of results. Mean hardness was 183 mg/L (very hard water).

### Spatial Variability

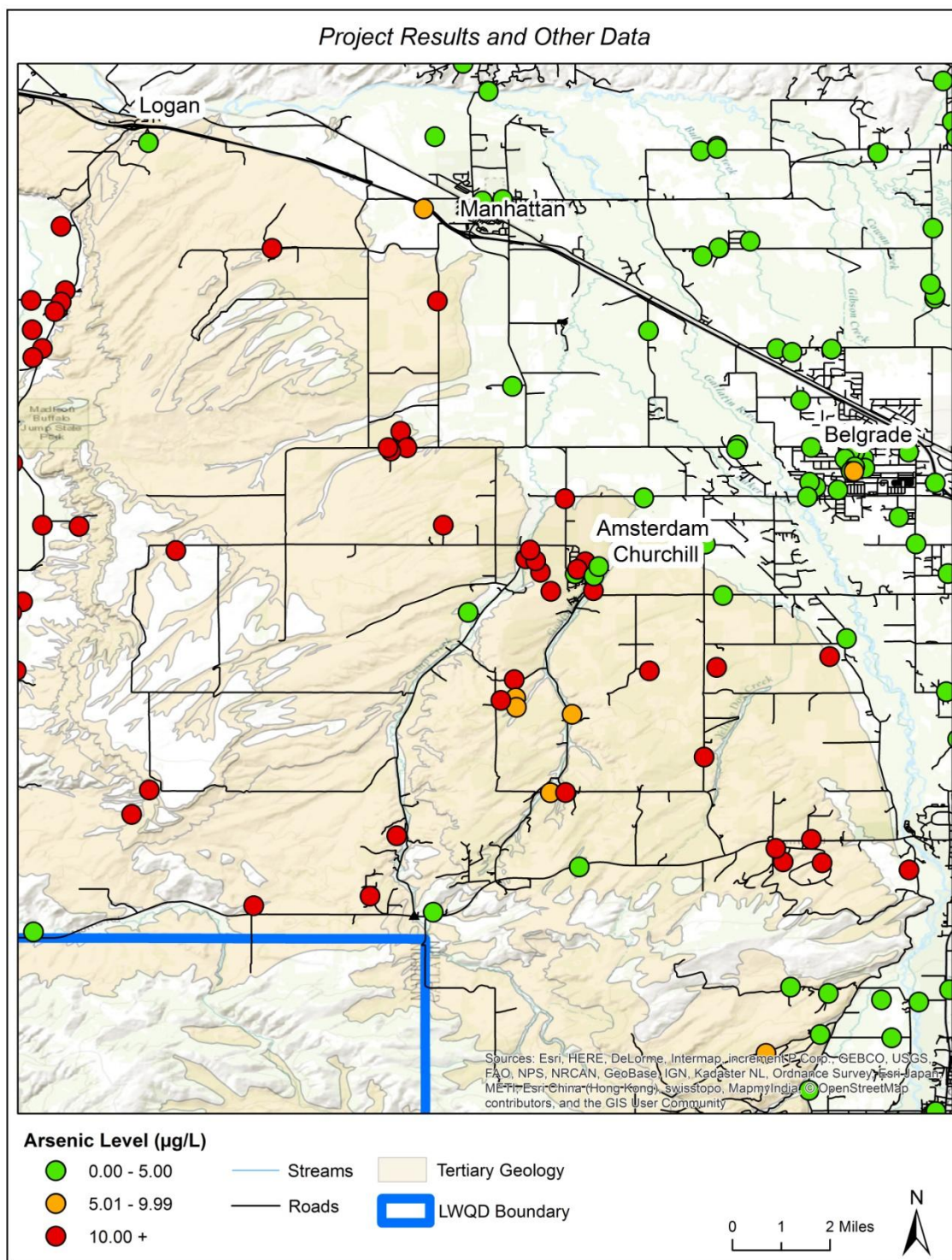
The sampling conducted for the project supported the idea that the area of arsenic contamination in groundwater is consistent with the area mapped as Tertiary geology in the western part of Gallatin County. Although not all wells in the area that were sampled revealed arsenic levels that were greater than the MCL, more than half of them did (see red dots on **Figure 9**). All available data, including preexisting historical data and project results are shown on **Figure 10**.





**Figure 9.** Sampling locations that were used for the project area are shown on the map above. Green and orange dots indicate arsenic levels below the MCL, while red dots indicate arsenic samples that exceed the MCL.





**Figure 10 (left).** All available arsenic data for the study area is shown on the map at left, including historical data and results from this project. Green and orange dots indicate arsenic levels below the MCL, while red dots indicate arsenic levels that exceed the MCL.

## QA/QC

Quality Assurance/Quality Control (QA/QC) samples including blanks and duplicates were collected and submitted to the laboratory for total arsenic, total iron, and nitrate + nitrite as N. Duplicates for arsenic speciation and hardness were also submitted. The QA/QC sample results are shown in **Table**

3. No detections for any of these analytes were found in any of the three blank samples submitted. Iron duplicate data exceeding the relative percent difference of 25% was flagged prior to submission into the Montana Department of Environmental Quality water quality (MT eWQX) database. Laboratory QA/QC reports were provided when data was received from the lab.

**Table 3.** Results of the project QA/QC for water chemistry samples. Red highlighting indicates arsenic concentrations greater than the MCL, while blue text indicates the iron duplicates exceeded 25% relative percent difference.

<u>Sample ID</u>	<u>Sample Type</u>	<u>Arsenic (µg/L)</u>	<u>Nitrate + Nitrate as N (mg/L)</u>	<u>Iron (mg/L)</u>	<u>Hardness (mg/L)</u>	<u>As(III) (mg/L)</u>	<u>As(V) (mg/L)</u>
041116-2	SAMPLE	7	6.38	0.39	--	--	--
041116-3	DUPLICATE	6	6.45	0.03	--	--	--
041216-1	SAMPLE	13	2.11	0.06	138	ND	0.015
041216-2	DUPLICATE	13	2.13	0.02	138	ND	0.015
041216-3	SAMPLE	15	2.10	0.53	200	ND	0.016
041216-4	DUPLICATE	16	2.14	0.18	202	ND	0.016
041816-2	SAMPLE	13	4.20	ND	261	ND	0.014
041816-3	DUPLICATE	13	4.16	ND	261	ND	0.012
041816-4	SAMPLE	10	1.09	ND	129	ND	0.009
041816-5	DUPLICATE	10	1.08	ND	--	--	--
051616-02	SAMPLE	11	1.49	0.06	167	ND	0.010
051616-03	DUPLICATE	11	1.49	0.05	--	--	--
051716-02	SAMPLE	161	ND	0.08	273	0.074	0.076
051716-03	DUPLICATE	164	ND	0.09	--	--	--
041116-4	BLANK	ND	ND	ND	--	--	--
041216-5	BLANK	ND	ND	ND	--	--	--
051616-04	BLANK	ND	ND	ND	--	--	--

## EDUCATION AND OUTREACH

As components of Objective 2 of the project, several outreach tasks were completed. An arsenic fact sheet was developed and is distributed at the Gallatin County Courthouse, at the GLWQD office, and is available online at [www.glwqd.org](http://www.glwqd.org). Laboratory results and interpretive letters were mailed to all homeowners who were involved with the project, along with informational fact sheets and postcard invitations to the project workshop. A project workshop was conducted on June 15, 2016 at the Manhattan Bank in Churchill. A total of 31 residents came to the workshop, where well test kits along with informational handouts were distributed to all interested residents.

One Bozeman Daily Chronicle article was published announcing the workshop and the project, and two television news stations reported on the project. The project generated a great deal of phone call inquiries and office walk-in traffic seeking well test kits. The number of well test kits handed out in a one-week period during and following the project workshop exceeded the average number of test kits handed out over several months. The outreach component of this project was highly successful.

## DISCUSSION/CONCLUSION

The arsenic data compiled for the entirety of Gallatin County suggests that most wells in the area on the west side of the Gallatin Valley have elevated levels of arsenic ( $\geq 10 \mu\text{g/L}$ ) in groundwater. Wells in the Quaternary alluvium just east of the study area such as near Manhattan and Belgrade do not have arsenic MCL exceedances. Currently, there is no way to predict or identify which wells are likely to have high arsenic within the area evaluated in this study, therefore all wells in the area should be screened.

The elevated arsenic in this area is likely from a naturally occurring geological source, though is probably not connected to the Madison River Valley alluvial aquifer, which is known to have arsenic levels above the MCL (often five or ten times greater than the MCL). The most recent geologic map for the area (Vuke et al., 2014) indicates that volcanic ash is present within the Tertiary sediments that cover most of the Madison Plateau. Because volcanic ash is known to be an arsenic source, this is probably the primary source of elevated arsenic in area groundwater.

It remains unclear whether there is a distinct aquifer where elevated arsenic is present, or whether the various water bearing zones in the area all have the same problem. The large geographic scale of the project area and the spatial variability in sedimentary depositional layers complicate the ability to resolve this. Further studies with one or more small focus areas and a higher density of sampled wells at different depths may help answer this question. Additionally, no clear trends between arsenic levels and other factors were identified in this study with the exception of groundwater temperature.

This study showed that nearly all of the arsenic in samples was in the form of As(V) (arsenate). The possibility of a transformation between As(III) to As(V) occurring during sample collection or transfer cannot be ruled out, but standard sampling procedures to avoid this were followed. Because oxic conditions in groundwater were present, it is not surprising that speciation results indicated As(V) was the predominant form of arsenic in the study.

Nimick (1998) noted that along the Madison River bluffs to the east of the Lower Madison River Valley (west edge of the study area in this project) there exists exposed travertine rock (indicating previous geothermal flow) as well as two active geothermal springs. These indicators of geothermal activity make sense when considering the location of the outlier sample (sample ID 051716-02) and the outlier's many unique geochemical characteristics, including temperature and oxygen conditions. Based on this information, it appears that a different hydrogeologic situation is present in a portion of the far western edge of the study area.

To conclude, the study revealed that elevated arsenic in domestic wells on the west side the Gallatin Valley is a common concern. Arsenate [As(V)] was the form of arsenic present in all samples collected in the study except for one outlier where arsenate [As(V)] and arsenite [As(III)] were present in nearly equal proportions. Iron and nitrate were analyzed and vary from well to well. The secondary MCL for iron (0.3 mg/L) was exceeded in three samples. No nitrate samples exceeded the MCL of 10 mg/L. Total water hardness analysis indicated that water in the area ranges from moderately hard to

very hard. No factors correlated with the arsenic concentrations with the exception of temperature. Based on all available data there is a distinct difference in arsenic concentrations that lines up with mapped geology in the Gallatin Valley where wells in Quaternary alluvium do not exceed the MCL and most wells in Tertiary sediments to the west do. The source is naturally occurring and probably from volcanic sediment. More work is needed to identify one or more distinct aquifers where this elevated arsenic is present.

## **RECOMMENDATIONS**

Based on the results of this study, we recommend that residents in Gallatin County who live west of the Gallatin River test their well water for arsenic at least once and consider repeating this screening every 5 years, in addition to annual nitrate and bacteria (total coliform and *E. coli*) testing. If arsenic in drinking water exceeds 10 µg/L, we recommend retesting to confirm the results and then installing a treatment system with the help of a water treatment specialist. Additional data outside of this project suggests that homeowners using private domestic wells in the Big Sky, Three Forks, or West Yellowstone areas should also consider testing their well water for arsenic at least once.

Future work could include a more focused study with samples from many wells in a smaller area to identify which distinct aquifers have elevated arsenic. However, given the rural nature of this part of the Gallatin Valley, the number of wells available in an area is a limiting factor, along with the homeowner response rate. Other work could include sampling in Big Sky to resolve whether elevated arsenic is a contaminant of concern in certain aquifers in the area.

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## **APPENDICES**

### **APPENDIX A**

#### **FIELD SAMPLING EQUIPMENT AND SUPPLIES LIST**

- 3 clean garden hoses
- 2 hose splitters with flow control valve
- Extra hose connection gaskets
- 2, 5-gallon buckets
- Cell phone or stopwatch
- YSI 556 or ProPlus™ multiparameter meter and flow-through cell, hose connector
- Extra C cell batteries
- Peristaltic pump
- Disposable 0.45 µm standard capacity filters
- Disposable syringes for water filtration
- Bleach spray bottle (~200 ppm chlorine refilled weekly)
- Paper towels
- Energy Laboratories sample bottles (with labels) and cooler(s), preservatives, chain-of-custody forms, shipping labels
- Ice
- Gallon size ziplock bags
- Packaging tape
- Deionized water for sample blanks (from MSU Center for Biofilm Engineering)
- 2 electronic tape sounders
- Adjustable crescent wrenches
- 7/16" wrench
- Screwdriver
- Flashlight
- Clipboard
- Field forms



- Field notebook
- Well logs and maps
- Writing utensils
- Calculator
- Stop watch
- Parameter stabilization summary sheet
- Aerial map of sampling area with addresses, roads labeled
- Nitrile disposable gloves
- Tool box
- Paper towels
- Kim-wipes

## **APPENDIX B**

### **SAMPLING PROTOCOL AND PROCEDURE DETAILS**

Sampling protocols were followed using the GLWQD Standard Operating Procedures for Groundwater Sampling. This section provides sampling guidelines and describes general and specific procedures, methods and considerations to be used and observed when collecting groundwater samples for laboratory analysis of general inorganics:

A YSI ProPlus or 556 multiparameter field meter connected to a flow-through cell is used for collecting field parameter data (pH, specific conductance, dissolved oxygen, temperature). The meter is calibrated each day prior to going into the field following manufacturer instructions and recorded in a calibration log. End of the day drift checks are also recorded in the calibration log.

The following procedures are to be followed for each sampling site:

1. Water supply taps, including hydrants near the well and taps on the house are located.
2. A site sketch is drawn on the Site Visit Form showing major features such as home and road locations.
3. The wellhead is located and the well cap removed. If the well is in a location where it could be exposed to contamination (debris from shrubs or bushes), the open well is immediately covered with a clean plastic bag. Well cap and casing condition is noted (sanitary well cap present, signs of insects, etc.) and recorded on the Site Visit Form.
4. The static water level (SWL) is obtained from the well using an electronic tape sounder that has been disinfected with a bleach water solution and dried with clean paper towels prior to deployment in the well. If the well pump is running, the SWL is recorded as a “pumping” water level.
5. A splitter valve is then connected to the tap/spigot and a clean garden hose attached to one half of the splitter. The splitter valve is opened to only the hose portion. The tap/spigot is turned on and the hose connection adjusted to eliminate water leakage at the splitter connection. Water is pumped into a five-gallon bucket. Flow rate (gpm) is monitored using a stopwatch and recorded on the Site Visit Form.

6. The YSI meter with flow-through cell is then connected to the discharge line of the other side of the hose splitter valve. Water quality parameters are recorded every 5 minutes on the Site Visit Form until stabilized using the following criteria:

Parameter	Stabilization Criteria	Reference
pH	+/- 0.1	Puls and Barcelona 1996; Wilde et al., 1998
specific conductance (SC)	+/- 3%	Puls and Barcelona 1996
dissolved oxygen (DO)	+/- 0.3 mg/L	Wilde et al., 1998

7. Several well volumes are purged and a pumping water level is then recorded on the Site Visit Form a minimum of one time during the purging process.
8. Once water quality parameters stabilize, the tap/spigot is turned off and all hoses and tubing are removed.
9. A clean five gallon bucket is filled with water, and syringes and filters are used to hand-filter and collect a water hardness sample from the bucket. Samples are preserved as appropriate and stored on ice.
10. All sample bottles that do not need filtration are triple rinsed with native water directly from the outdoor hydrant prior to sample collection. Samples are preserved as needed then placed in a one-gallon Ziploc bag and stored in a cooler on ice.
11. Syringes and filters used for filtration are disposed of.
12. The electronic tape sounder is decontaminated between sites.
13. Pertinent information from the Site Visit Form is recorded in a field notebook.
14. Samples are shipped to the laboratory via overnight carrier along with a completed chain of custody form. Duplicate samples for arsenic speciation and hardness are refrigerated and stored until shipment on ice to the laboratory.

#### **Equipment Decontamination Procedures**

Samples were collected directly from the outdoor hydrant at each sampling location. Because no pump tubing was used, decontamination of tubing and containers was not needed.

For the electronic tape sounder:

1. Rinse with a dilute bleach/water solution.

## APPENDIX C

### TABULATED PROJECT DATA

<u>Sample ID</u>	<u>Total Depth (ft)</u>	<u>SWL (ft, from well log or measured)</u>	<u>Measuring Point Elev. (ft amsl)</u>	<u>Ground Surface Elev. (ft amsl)</u>	<u>Well Completion Elev. (ft amsl)</u>	<u>Temp (°C)</u>	<u>SC (µS/cm)</u>	<u>DO (mg/L)</u>	<u>pH (SU)</u>	<u>Arsenic (µg/L)</u>	<u>Nitrate + Nitrite as N (mg/L)</u>	<u>Iron (mg/L)</u>	<u>As(III) (µg/L)</u>	<u>As(V) (µg/L)</u>	<u>Hardness (mg/L)</u>
041116-1	250	129	4252	4255	4005	15.41	429	2.95	7.27	4	0.93	Not Detected	--	--	--
041116-2	82	30	4247	4250	4168	9.59	531	8.15	7.20	7	6.38	0.39	--	--	--
041116-5	254	151	4563	4565	4311	13.29	364	7.96	7.37	18	1.96	0.03	ND	21	140
041216-1	89	59	4415	4420	4331	11.61	512	8.72	7.06	13	2.11	0.06	ND	15	138
041216-3	120	60	4444	4449	4329	12.60	599	8.38	7.46	15	2.1	0.53	ND	16	200
041216-6	168	116	4556	4556	4388	11.79	490	7.32	7.4	3	2.27	Not Detected	--	--	--
041216-7	174	108	4552	4554	4380	12.06	544	7.51	7.36	3	1.72	0.15	--	--	--
041216-8	120	41	4521	4525	4405	10.86	454	8.83	7.35	4	0.76	Not Detected	--	--	--
041216-9	120	45	4776	4780	4660	11.34	437	8.95	7.2	35	1.18	Not Detected	ND	36	166
041316-1	222	170	4725	4729	4507	11.10	559	8.91	7.57	21	4.83	Not Detected	ND	19	115
041316-2	271	200	4756	4758	4487	11.20	749	7.91	7.25	9	4.84	0.03	ND	8	275
041316-3	250	200	4756	4759	4509	11.37	750	7.77	7.29	8	4.91	Not Detected	ND	8	269
041316-4	290	202	4769	4771	4481	12.57	556	9.24	7.35	12	2.86	0.05	ND	11	189
041816-1				4521		11.01	415	8.53	6.77	5	2.43	Not Detected	--	--	--
041816-2	163	110	4692	4694	4531	10.86	706	9.50	7.48	13	4.20	Not Detected	ND	14	261
041816-4		40	4692	4696		11.51	334	8.15	7.48	10	1.09	Not Detected	ND	9	129
041816-6	160	56	4916	4920	4760	11.47	436	10.81	7.44	13	1.08	1.11	ND	8	170
041816-7	420	288	5093	5097	4677	10.11	343	8.10	7.41	5	0.27	0.06	--	--	--
051616-01	600	204	4898	4901	4301	17.06	552	1.32	7.03	24	2.95	0.03	ND	27	89
051616-02	117	19	4869	4872	4755	10.98	383	11.27	7.17	11	1.49	0.06	ND	10	167
051616-05	195	82	4925	4929	4734	12.39	668	11.74	7.50	24	3.74	0.05	ND	24	219
051716-01	660	470	4829	4836	4176	17.18	414	6.31	7.37	24	1.37	Not Detected	ND	23	135
051716-02 (outlier)	800	724	5129	5134	4334	22.69	861	0.25	7.01	161	Not Detected	0.08	74	76	273