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INVESTIGATION OF ARSENIC IN THE TRANSITION ZONE BASIN
OF THE MOJAVE RIVER

A Project
Presented to the
Faculty of
California State University,
San Bernardino

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in
Earth and Environmental Sciences

by
Matthew Edward Howard
December 2012

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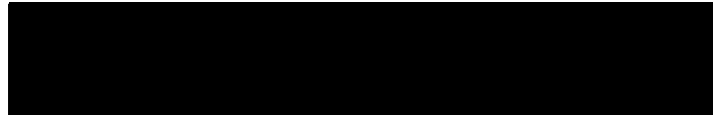
December 2012

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Biochemistry

ABSTRACT

The Purpose of this project was to identify the source(s) of arsenic in the Transition Zone subbasin of the Mojave River. 43 monitoring wells were sampled during September of 2010 and October of 2011. Water quality field parameters recorded in the field include: pH, temperature, electrical conductivity, oxidation reduction potential, salinity, dissolved oxygen, and turbidity. Several laboratory analyses were analyzed in an effort to further the understanding of arsenic in the Transition Zone. These analyses included: arsenic speciation and Scanning electron microscope work with aquifer material. This project is part of an ongoing study of the Transition Zone subbasin and will be used in future work by graduate students and the Mojave Water Agency.

The 43 monitoring wells sampled provided data that confirms a positive correlation between arsenic and pH. Another positive correlation was between arsenic and well depth. There was a negative correlation between arsenic and manganese. There was no correlation between iron and arsenic. Scanning electron microscope analysis provide that low concentrations of arsenic were located on the grains

analyzed, providing strong evidence that aquifer material is the source for elevated arsenic levels. Recommendations for further research would include increasing the water quality data collected and aquifer grains analyzed on the scanning electron microscope.

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CHAPTER ONE

INTRODUCTION

Background

The purpose of this project was to identify the source(s) of arsenic in the Transition Zone of the Alto Subarea of the Mojave River Basin. The Transition Zone is located approximately three miles north-northwest from Victorville, California and encompasses approximately 50 square miles of the high desert. The Mojave River flows seasonally through the transition zone, and year-round through various areas. The objective of this project is to understand the processes by which arsenic is being released from sediment into the groundwater supply.

The project area is located in the arid southwestern desert region of the United States. Limited water supply is a significant issue within the project area, and is supplemented with State Water Project water from northern California. The residents and purveyors in the project area rely on groundwater as the sole source of potable water. This reliance on groundwater makes the study of arsenic in the groundwater vital.

The Transition Zone is a sub-section of the Mojave River watershed. The Transition Zone location is defined as the area between the lower narrows and the Helendale Fault (See figure 1). The Mojave River watershed originates in the San Bernardino Mountains and terminates in the Mojave National Preserve. The Mojave River is approximately 95 miles in length and has numerous smaller tributary watersheds.

In 1972, the U.S. Environmental Protection Agency (EPA) created the Clean Water Act and the Safe Drinking Water Act. The objective of the Clean Water Act is to "Restore and maintain the chemical, physical, and biological integrity of the Nation's Water." These acts set standards for water quality that must be met in order for water to be safe for human consumption. In the Code of Federal Regulations, Title 40, Section 141.62, arsenic is a constituent of concern in the Clean Water Act and the Maximum Contamination Level (MCL) is assigned by the federal and state governments to regulate concentrations of arsenic in drinking water.

According to the California Department of Public Health (CDPH), arsenic is ubiquitous in nature and routinely found in California drinking water supplies. The

CDPH has set the maximum contaminant level (MCL) for arsenic at 10 parts per billion (ppb) or 10 µg/L. CDPH set 10 ppb of arsenic as the maximum allowable limit of arsenic in drinking water. CDPH also set public health goals (PHG), which is the concentration of arsenic that can be consumed throughout a lifetime with no adverse health effects.

Recent Research from the California Office of Environmental Health Hazard Assessment (OEHHA) has concluded that a PHG in drinking water should be 4 parts per trillion or ng/L. (CDPH, 2008)

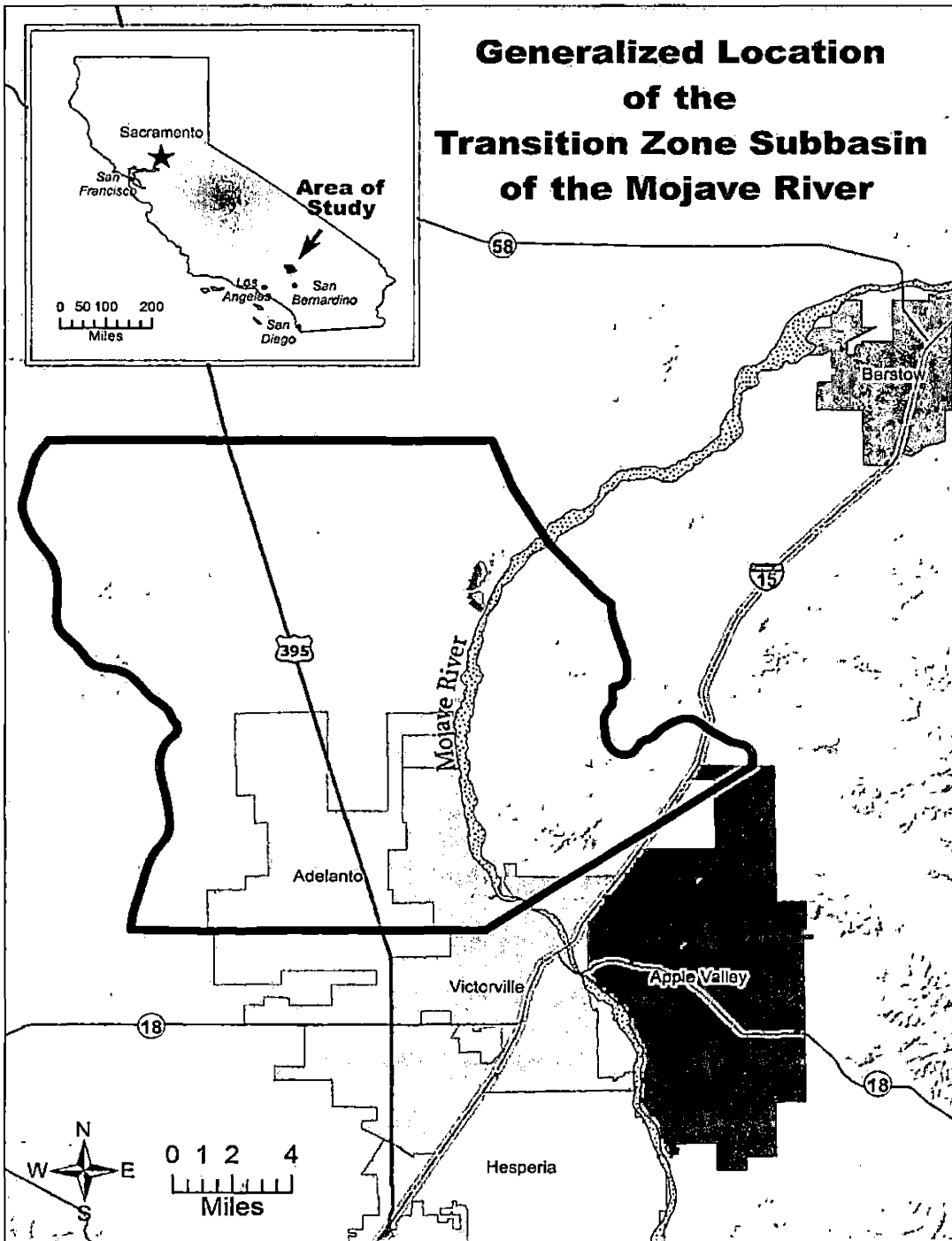


Figure 1. Generalized Location of Transition Zone Subbasin

Project Objective

The objective of this project was to investigate the sources of arsenic in the Transition Zone of the Mojave River Basin. In September 2010 and October 2011 water quality samples were collected and analyzed for multiple analytes. The Mojave Water Agency (MWA) along with the United States Geological Survey (USGS) maintain an extensive monitoring well network along the Mojave River. The samples were collected at varying depths from multiple monitoring wells. Field parameters were monitored to ensure compliance with USGS protocols and sample integrity. Field parameters monitored included: temperature, pH, electrical conductivity (E.C.), salinity, dissolved oxygen (D.O.), oxidation-reduction potential (O.R.P.), flow rate, pumping water level, and turbidity. These parameters were measured to ensure that the samples collected were representative of the groundwater at depth.

The Transition Zone basin of the Mojave River is on a 5-year sampling rotation with the Mojave Water Agency. Historic data from the 2006 MWA sampling event in the TZ was used for preparation of this project. Local residents use groundwater as the water source in the transition zone,

therefore it is important to monitor the water quality in this area.

This project is intended to further the understanding of how arsenic is released from the sediment and into the groundwater in the transition zone of the Mojave River Basin. Throughout the United States there has been arsenic contamination in ground water from human sources. Contamination sources of anthropogenic arsenic are often associated with agricultural activities, manufacturing, and mining. However, previous studies completed in the area suggest that arsenic comes from the in situ aquifer material and is not of anthropogenic nature. Arsenic is detected ubiquitously throughout the Mojave River Basin and in this study it is assumed that the arsenic is not coming from any single point source.

Based on the results of previous water quality sampling events, arsenic concentrations are expected to increase with depth. Previous studies suggest this is associated with sediment mineralogy, increasing age of groundwater with depth (Schlumberger Water Services, 2011), and increased time for water-rock interaction (Hinkle and Polette, 1999).

Elevated arsenic concentration can also be associated with groundwater that has elevated pH values. It has been shown that pH may affect arsenic mobility from aquifer material. Groundwater pH may increase as the depth increases because of the contact time and chemical reactions between the water and aquifer material (Hinkle and Polette, 1999).

Basins of the Mojave River are typically characterized by oxic groundwater conditions and arsenic is expected to be present in the oxidized valence form of arsenate (As^{V}). Arsenic in groundwater is typically in two main valence forms: arsenate (As^{V}) and arsenite (As^{III}). Arsenite (As^{III}) is the predominant form of arsenic in reducing conditions. The valence state can change based on two important factors: oxidation-reduction potential and pH.

Scope

This project investigated the mobility of arsenic in the Transition Zone in the autumn months of September 2010 and October 2011. Water quality sampling took place in fall due to time constraints with other projects, and was not selected for any other reason. During these sampling events 43 water quality samples were collected. All of the water quality samples were analyzed for general minerals, general

physical properties, and metals. In order to fully understand water quality in the TZ basin, monitoring wells selected to be sampled were chosen by geographic distribution and are located throughout the Transition Zone. Monitoring well water quality sampling purge sheets were completed for each sample location and include temperature, pH, electrical conductivity (E.C.), dissolved oxygen (D.O.), salinity, turbidity, oxidation reduction potential (O.R.P.), and depth to water level. Parameters also analyzed at the laboratory included pH, turbidity, electrical conductivity, and oxidation reduction potential.

Water quality samples were collected after field parameters stabilized during purging. Water quality samples were not collected until water quality parameters were stabilized in order to ensure a representative sample that reflects accurate groundwater quality was obtained. After each sample was collected it was immediately put on ice to preserve the sample. The sample and appropriate documentation was then transferred to a laboratory courier who would deliver the sample and appropriate documentation to the laboratory.

Analysis of aquifer material was also performed using a scanning electron microscope equipped with an energy-

dispersive x-ray spectrometer (SEM-EDS). The sediment grains were collected from the drill cuttings of select monitoring wells. The SEM-EDS sample selections were from the monitoring wells that were also analyzed for arsenic speciation. After the aquifer grains were selected, they were examined and analyzed on the SEM-EDS for arsenic.

Limitations of the Study

Scientific projects always have limitations that occur at every step of the project. Training, Audit, and refreshers help to prevent these limitations but variables may occur. The first limitation is monitoring well locations. Sampling design was limited to existing wells sampled that had historical data associated with each well. New monitoring wells were not drilled for this project. This is because of the extensive cost and time it would take to drill a new monitoring well. The addition of specifically placed monitoring wells would fill data gaps that would eliminate any assumptions in data. It is an unreasonable expectation for this project to spend the money and time to drill additional wells.

Another limitation would be pumping influence from nearby domestic and production wells. The TZ sub-basin of the Mojave River is solely reliant on groundwater. Nearby

residences or production wells may have influenced our groundwater samples. During sampling there wasn't evidence of nearby pumping.

CHAPTER TWO

PROPERTIES OF ARSENIC IN GROUNDWATER

Arsenic Background

Arsenic is the one of the most common and important contamination threats to our drinking water supply in the United States. Arsenic is a metalloid that occurs naturally in the earth's crust. Arsenic is found ubiquitously throughout groundwater basins in United States. The average concentration of arsenic in the earth's crust is 1.8 $\mu\text{g/g}$. Arsenic exists in different valence states: -3, 0, +3, and +5. Aqueous phase arsenic valence states are limited to arsenate (As^{V}) and arsenite (As^{III}) (Welch et al. 2006).

Arsenic is carcinogenic, mutagenic, and teratogenic and there is positive research that arsenic is not beneficial for the human body (National Research Council, 1999). Arsenic has been linked to cancer of the bladder, lungs, and liver. Arsenic poisoning, or arsenicosis can be seen in many countries such as Bangladesh, India, Mexico, and Thailand (World Health Organization, 2012).

Anthropogenic contamination of arsenic to groundwater usually occurs from runoff from agriculture lands, wood preservatives, and electronic productions wastes. The

largest use for arsenic in the United States is as a wood preservative. The two most common wood preservatives used in the United States are chromated copper arsenate and ammonium copper arsenate (CDPH, 2008). Arsenic is also included in the production of paints, drugs, and soaps. Copper smelting, burning coal, and ore mining contribute to the anthropogenic contamination of arsenic as well (Welch et al, 2006). These industries are not located near the Mojave River, therefore anthropogenic arsenic can be ruled out as a source of arsenic contamination in the Mojave River.

According to Welch et al. (2006) pp. 6, "Most of the arsenic in groundwater comes from the aquifer material" and "Most arsenic is being released from the iron oxide material in an aquifer." Therefore it is hypothesized that arsenic in the Mojave River is of natural sources and originates from aquifer material. Aquifer material can be described as the sediment that interacts with the water table. This interaction involves reactions that exchange chemical species between the aquifer material and aquifer water. Several factors influence the reactions that take place between the aquifer material and aquifer water. The main factors that control reactions between the aquifer

material and aquifer are pH, ORP conditions, and competing ions (Hinkle and Polette, 1999).

pH can be described as the activity of the hydrogen ion, and is measured by a scale from 0 (acidic) to 14 (basic). The pH of natural groundwater can vary from pH 6 to pH 10. This pH range of natural groundwater is dependent on aquifer material geology, aquifer groundwater quality, and groundwater recharge quality. Arsenic has been recognized being pH dependent when looking at sorption and desorption from aquifer material. Sorption is an electrostatic attraction from dissolved arsenic on to the aquifer material surface. Sorption is based on the surface charge of the aquifer material, which can change when pH changes. At a low pH, there is an abundance of hydrogen ions (H^+) which will occupy the available sorption sites. As pH increases, the electro-static attraction between arsenic and the aquifer material diminishes, and arsenic is released. This change in pH is the main driving force in release of arsenic from the aquifer material (Hinkle and Polette, 1999).

According to Hinkle and Polette, (1999) Arsenic in ground water of the Willametter Basin, Oregon, pp. 20

"Arsenate and arsenite adsorb to surfaces of a variety of aquifer materials, including iron oxides, aluminum oxides, and clay minerals. " The interaction between arsenic and aluminum oxides and clay material is weak at the pH found in natural waters.

The interaction between arsenic and iron oxides are vitally important because of the unique electrostatic interactions they share. Iron oxides are common in hydrogeologic environments as a coating on other aquifer materials, which allows the arsenic to dissolve and adsorb based on the pH of the water. At low to neutral pH (pH 3- pH 7.5), there is a net positive charge on the iron oxide which would attract the negative charged species of arsenic: arsenate (As^{v}) and arsenite (As^{III}). The positive attraction would adsorb arsenic onto the iron oxide coating effectively demobilizing arsenic.

At alkaline pH waters (pH 7.0 - pH 10.0) the net charge on the iron oxide becomes increasingly negative as the pH increases. The negative net charge on the iron oxide coating repels the negatively charged arsenic effectively dissolving arsenic from the iron oxide coating. This causes arsenic to dissolve from the aquifer material into the aquifer to be adsorbed onto another piece of aquifer

material or to be pulled into a pumping well. Since iron oxide coating can contain a large amount of adsorbed arsenic (Hinkle and Polette, 1999), if the pH were to increase into alkaline conditions enough arsenic may desorb into the water to cause issues with utility companies and regulatory agencies.

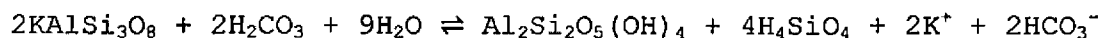
Adsorption and desorption chemistry of arsenic was used in the development of the SONO filter. The SONO filter is used in countries around the world where arsenic tainted water is the only source of water in the area. The SONO filter was invented in 2006 by Abul Hassam, a chemistry professor at George Mason University. The SONO filter is a composition of layered material including sands, charcoal, and composite iron matrix (CIM). This SONO filter was designed to filter arsenic laden water in remote locations around the world. The first SONO filters were used in Bangladesh where groundwater arsenic concentration exceed 5 $\mu\text{g/L}$ - 4000 $\mu\text{g/L}$ and where groundwater pH of Bangladesh ranges from pH 6.5 - pH 7.5. The main component of the SONO lies in the proprietary CIM material, where approximately 92% of the material is iron. Analyses have shown the effectiveness of the SONO filter in removing arsenic from the groundwater of Bangladesh. As mentioned previously,

Bangladesh groundwater arsenic concentration range from 5 $\mu\text{g/L}$ - 4000 $\mu\text{g/L}$ and after the water is run through the SONO filter arsenic concentration ranges from 3 $\mu\text{g/L}$ - 30 $\mu\text{g/L}$. This is reduced in arsenic concentration in effluent water is due to the electro-static attraction between iron oxide and arsenic at this near neutral pH.

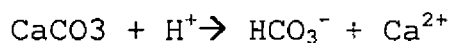
Groundwater pH Buffering

Desorption of arsenic from iron-oxide surfaces becomes favored as pH values become alkaline. Interaction with aquifer material and water has been shown to increase aquifer water pH. One process noted is the silicate hydrolysis, in which feldspars weather into a clay mineral. This weathering involves having dissolved hydrogen ions (H^+) that come from a variety of sources reacting with a group of common minerals called the silicates. Silicates minerals are the largest rock forming group of mineral on earth, which comprise approximately 90% of the earth's crust. There is a variety of elements that make different silicates, such as: Forsterite (Mg_2SiO_4), Almandine ($\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$), or Spessartine ($\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$). The weathering of these silicate minerals neutralizes the hydrogen ion (H^+) and reacts with the silicate to form flat hexagonal sheets called phyllosilicates. Phyllosilicates

are commonly referred to as clays, and act as an aquatard in an aquifer system. Previous studies completed on the upper Mojave River Basin show that the aquifer mineralogy is mainly comprised of quartz, potassium feldspar, sodium feldspar, calcium feldspar, and clays (Schluberger Water Services, 2011). The following reaction depicts how a silicate mineral would undergo hydrolysis to become a phyllosilicate (Reed, 2011):



The weathering of silicate minerals releases HCO_3^- into the system and increases the pH, and because of this silicate hydrolysis the pH of groundwater generally increases with the age of water. Another possible source of elevated pH in groundwater is calcium carbonate dissolution. Calcium carbonate (CaCO_3) is another common mineral found in the earth crust at approximately 4% by weight. Calcium carbonate undergoes a dissolution reaction with hydronium ions (H^+) that dissolve the calcium from the carbonate species. The following is a reaction between calcium carbonate and hydronium ions (H^+):



The dissolution of the calcium carbonate mineral releases bicarbonate and a calcium cation. The bicarbonate mineral buffers the aquifer water and increases the pH.

Groundwater Depth

Groundwater depth can also have an effect on pH. Deep groundwater tends to have long residence time with the aquifer material which tends to have elevated pH. This elevated pH, due to silicate hydrolysis and calcium carbon dissolution, increases the pH over the life span of the water at deeper depths. Another possible effect of the silicate hydrolysis and calcium carbonate dissolution would be the geothermal gradient. The geothermal gradient shows that temperature increases the deeper you go into the earths crust. This heat may act as a catalyst for these and other reactions in deep groundwater basins (Welch, et al. 2006), by increasing the reaction speed and the number of reactions taking place, which would lead to an even higher pH.

Oxidation Reduction Potential

The second main contributing factor to arsenic release from aquifer material is ORP. ORP is the measure of the potential for a chemical species to undergo oxidation reduction reaction. Oxidation can be explained as the loss

of electrons or the addition of oxygen to a chemical species. Reduction can be explained as the gaining of electrons to a chemical species. The ORP measurement is the measurement of the electron activity in a solution and is measured in millivolts (mv). The scale for a ORP measurement ranges from -999 mv to 999 mv. A positive ORP measurement suggests that the solution is oxidizing and a negative ORP measurement suggest that the solution is reducing. ORP readings are designed to help understand the overall state of a solution, and not of one particular species.. Oxidation reduction (Redox) reactions occur in tandem, when one species is oxidized another is reduced, thus determination of one species' oxidation state is not possible with this measurement. The ORP measurement is the net result of all chemical redox species present in solution and the relative concentrations of the oxidized and reduced states of these species.

According to Manning and Goldberg, (1997) pp.21 "Redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility." There are two valance states of arsenic found in natural waters:arsenate (As^{v}) and arsenite (As^{III}). Arsenate (As^{v}) is the most oxidized form of arsenic

found in groundwater. Arsenite (As^{III}) is the more reduced form of arsenic found in groundwater.

The Mojave River has oxic groundwater conditions. Oxic groundwater conditions are described as dissolved oxygen concentrations that are greater than 1 mg/L. This oxic condition will increase the amount of dissolved oxygen in the groundwater which will affect the ORP values. We can expect to see positive ORP measurement because of the oxic conditions found in the Mojave River.

ORP measurements were collected at each monitoring well during sampling as well at the laboratory. The water quality meters used in the field measured ORP in mV. This field ORP measurement is designed to represent redox conditions of the groundwater as a whole and not that of just arsenic. The redox condition may be useful in helping us understand what oxidation state arsenic will be in (see Figure 2). It can be expected that the more positive the ORP measurement is, the more arsenate (As^{V}) would appear in the arsenic speciation analysis result. It would also be expected that the more negative ORP measurement is, the more arsenite (As^{III}) would be expected in the arsenic speciation analysis result.

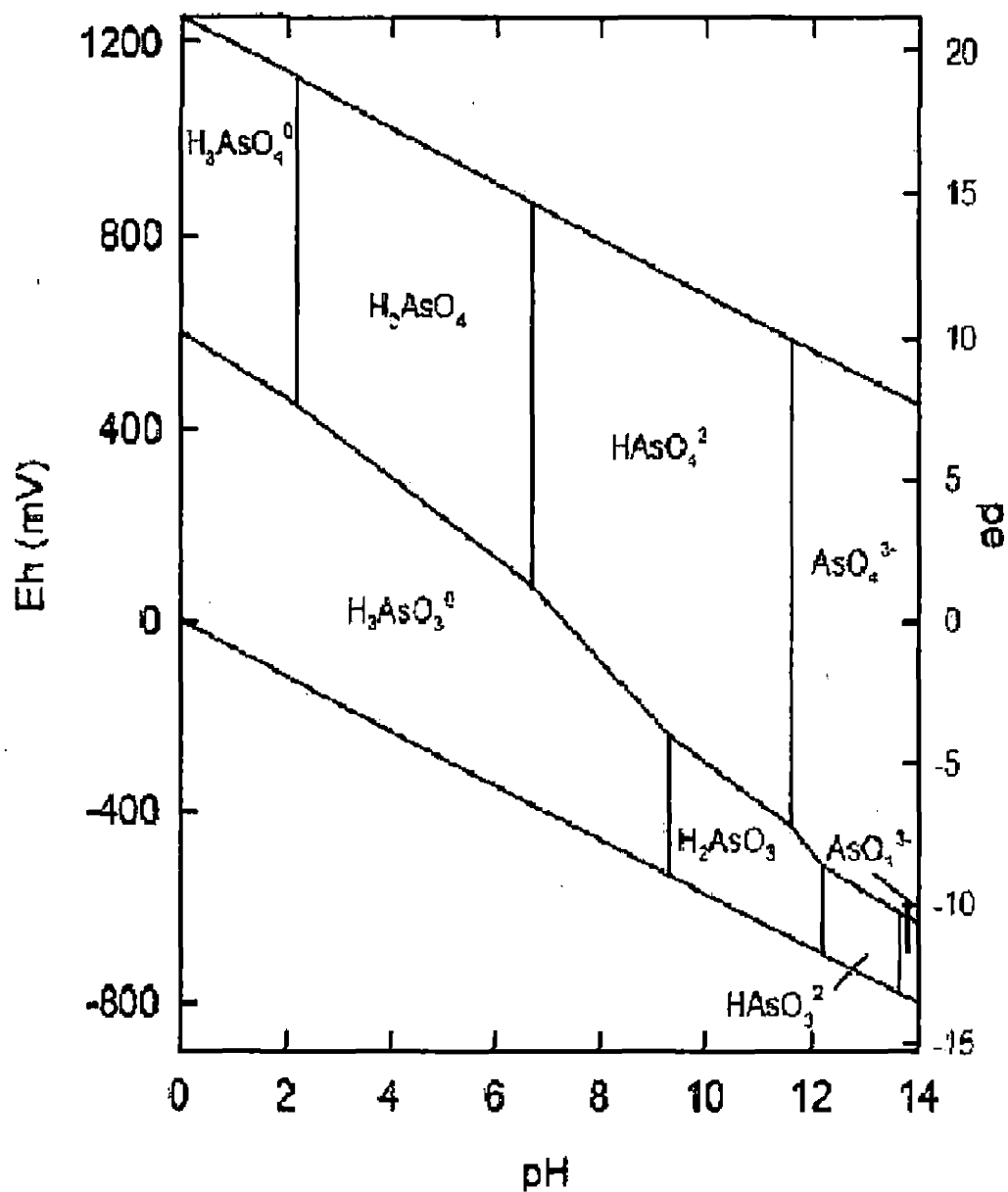


Figure 2. Eh/pH diagram for arsenic (Zang, Nan. *Influence of citrate ligands on ferric hydroxide nucleation at low molar reactions: Application for arsenic removal*. Rice University, 2010.)

Additional analytes were added to the analyte list to further understand arsenic activity. The following analyses were performed for the wells sampled in October 2011: total arsenic, total antimony, total manganese, and total selenium. Total arsenic and total selenium was chosen because according to Chen et al., 1994, "Small iron rich particles with adsorbed arsenic, selenium and other trace elements can pass through traditional filters (.45µm) and subsequently dissolved when the sample is acidified." According to Davis et al, (2000) pp.20 "Arsenic and selenium interact with each other in various metabolic functions and animal models indicate that each element can substitute for the other to some extent." Total manganese was chosen because of the possibility for arsenic to adsorb onto manganese oxide under oxic conditions (O'day, 2004). The additional four analytes added were measured for dissolved and total concentrations.

Scanning Electron Microscope

Analysis was performed on aquifer grains obtained during drilling. Drilling material was organized into trays that separate drilled aquifer material at 10 foot intervals. These grains were selected with the guidance of

Dr. Erik Melchiorre and analyzed using a scanning electron microscope (SEM) equipped with an energy- dispersive x-ray spectrometer (EDS). The SEM was used to take images of the aquifer grains up to 1000 times magnification. The EDS allowed us to quantify the concentration and location of the arsenic. The concentration is measured in weight % from the whole sample size. The SEM-EDS allowed us to maneuver around the aquifer grain and analyze the surface of the grain for chemical composition. The aquifer material and water table interaction occurs on the surface of the aquifer material grains, and it is vitally important to understand how arsenic is bound to the aquifer material.

The SEM-EDS generates an electron source which is then directed toward the sample. As the electrons come into contact with the aquifer material, it excites the electrons of the inner shell of the atoms of the surface of the aquifer grain sample. The inner shell electrons are then excited to a much higher energy level and forced out of the inner shell of electrons. The detection of any element present in the sample is due to a unique photo energy wavelength emitted when that excited inner shell electron returns to a normal state of energy. The unique wavelength is different for every element and thus can be detected and

quantified. The EDS portion of the SEM is an addition that allows for this measurement of chemical composition and element mapping. The SEM-EDS analysis was designated to map arsenic and other minerals to see if there was a positive correlation between certain elements and arsenic.

Aquifer Material

Aquifer material is further described by the stratigraphy of the sample well. The aquifer material changes throughout the TZ basin, which also changes the water quality. There are two distinct aquifers that encompass the TZ basin. The first is the floodplain aquifer; this aquifer consists of new and young alluvial material that is not more than 200 ft in depth. This aquifer receives the majority of the recharge that is received by seasonal flows and discharge from the Victor Valley Wastewater Reclamation Authority (VWVRA). The aquifer material of the floodplain aquifer consists mainly of feldspar rich, clean sand, and is noted by a high resistivity on the borehole electrical log. This stratigraphy makes this floodplain aquifer highly permeable which facilitates recharge (Stamos et al., 2003).

The second distinct aquifer system of the TZ basin is the regional aquifer. The regional aquifer material

consists of older and less permeable material. The regional extends from approximately 200ft to bedrock. The aquifer material consisted mainly of young and older alluvial material. The young alluvial found consists mainly of consolidated gravel and sand. The older alluvial material consists of consolidated sandy clay and silt as noted by a low resistivity on the borehole electrical log. A study done by the United States Geological Survey (USGS) used Carbon-14 analyses to study the age of the water in the regional aquifer. The study showed that the water was recharged nearly 20,000 years ago. The study showed that the regional aquifer has low permeability and water quality issues. (Stamos et al., 2003)

Surface water flow in the TZ basin is seasonal. Perennial flow though the TZ basin occurs sporadically when the San Bernardino Mountains receive more than average annual rainfall. Another source of recharge is the VVWRA, which treats wastewater from the surrounding communities located south of the project area. The discharge of recycled water to the TZ basin can be as high as 15,000 acre feet annually. (Victor Valley water reclamation authority, 2003)

CHAPTER THREE

MATERIALS AND METHODS

Overview

The Transition Zone of the Mojave River was sampled from October 2011 to December 2011. The sampling consisted of selecting 43 monitoring well casings located near the Mojave River in the area of this project. The Monitoring well casings were selected based on a variety of factors that include: proximity to Mojave River floodplain, screen interval depth, and last date sampled.

Each of the 43 wells were sampled following a strict sampling guide outlined in the Mojave Water Agency sampling plan. This plan includes, but is not limited to: specific casing purging requirements, water quality parameter guidelines, and health and safety guidelines.

The sampling techniques used in this project were approved by the USGS, and annual audits are conducted to ensure compliance. Annual audits by a USGS water quality specialist ensure proper sampling techniques. Techniques focus on obtaining a representative groundwater sample, proper decontamination techniques, and measures to prevent contamination of samples.

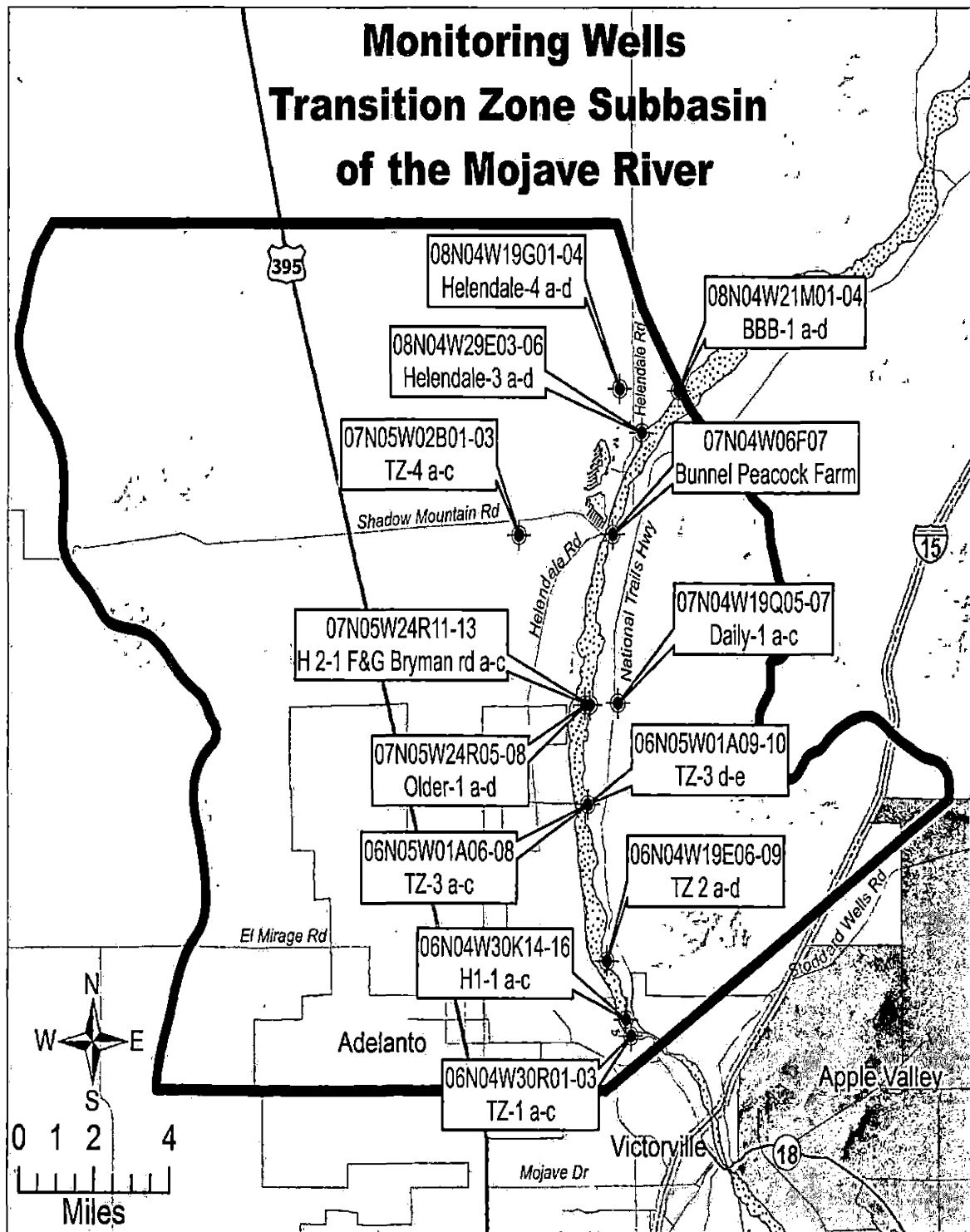


Figure 3. Transition Zone Subbasin Monitoring Well Locations

Well Research

Prior to sampling, research and data collection were done for each well to identify well depth, historic and current static water levels, casing diameter, and previous water quality data. Having the casing specifications made it possible to calculate approximately how much time would be needed to purge and collect a sample from the casing. This was done for each of the wells sampled, and allowed for calculation of how much time was needed for the water quality sampling event.

Review of prior work on these wells revealed that the addition of certain parameters to the analyte list would be scientifically significant, and help meet the project objectives (Noblet, 2011, CSUSB personnel communication). Analytes that were deemed important, included: total arsenic, total antimony, total manganese, and total selenium. Total analyses analyze the raw sample water without filtering, whereas dissolved analyses analyze sample water filtered through a 0.45 μm filter. Previous research has shown that the characteristics of these analytes might have an effect on the activity of arsenic in the TZ basin (Henke, 2009).

The previous water quality data resulted in special considerations of certain casings with sampling issues such as: low-yield wells, water level drawdown issues, elevated turbidity measurements, and/or water quality parameter stabilization issues. Additional sampling time was anticipated for casings identified with any of these issues.

Calculations were made to determine the water column volume inside the casing. The water column in the well is calculated by subtracting the depth to groundwater from the total depth of the well. The casing volume was calculated using the following equation:

$$V = \pi \times (D/2)^2 \times H \times 3_{(\# \text{ of casing volumes removed})} \times 7.48 \text{ gallons/ft}^3$$

Water Quality Sampling

Preparation of the sampling vehicles took place each morning before traveling to the scheduled well. After arriving at the well, equipment set up began. Equipment set up included water quality meter calibration, pump decontamination, and filling out field paperwork. Water quality field parameters were taken from two instruments: a YSI 556mps multi-parameter water quality meter (Figure 4) and a Lamotte 2020e turbidimeter. Field parameters recorded consisted of temperature, pH, EC, salinity, turbidity, ORP,

D.O., and water level. Water quality meters were calibrated each day prior to sampling using National Institute of Standards and Technology (NIST) traceable standards.



Figure 4. YSI 556 Water Quality Instrument

Containers used for this sampling included one liter translucent high density polyethylene (HDPE) bottles preserved with 8 mL 1:1 hydrochloric acid, 125mL unpreserved translucent HDPE poly bottle, and one liter translucent HDPE unpreserved bottle. The one liter

translucent HDPE bottles preserved with 8 mL 1:1 hydrochloric acid was used for analysis of arsenic speciation. The 125mL unpreserved translucent HDPE bottle was used for analysis of hydrogen and oxygen isotopes. The one liter translucent unpreserved HDPE bottle was used for analysis of general minerals, dissolved metals, and inorganic species.

During equipment set up and sampling activities, nitrile gloves were worn to prevent contamination of sampling equipment and water quality samples. New gloves were put on before and after handling the pump, water quality meters, calibration solutions, sample bottles, and collecting water level measurements.

A Groundfos Redi-Flo 2 submersible pump was used for purging and sampling activities (Figure 5). Prior to use at each well, the pump was decontaminated by placing the pump into a 0.1% Liquinox/deionized water solution for five minutes, then placing the pump into a deionized water wash for five minutes, followed by a separate deionized water rinse for five minutes. Disposable, food grade polyethylene tubing was attached to the pump for purging and sampling. New tubing was used at each well. The tubing was attached to the pump power cord using plastic zip ties.

The plastic zip ties were attached at 25 ft. intervals until desired depth was reached. The pump was placed at a depth of one foot above the screen zone or historic sampling depths were used. Historic sampling depths is the depth the pump was placed the last time the well was sampled and if applicable was used to save sampling cost and time.

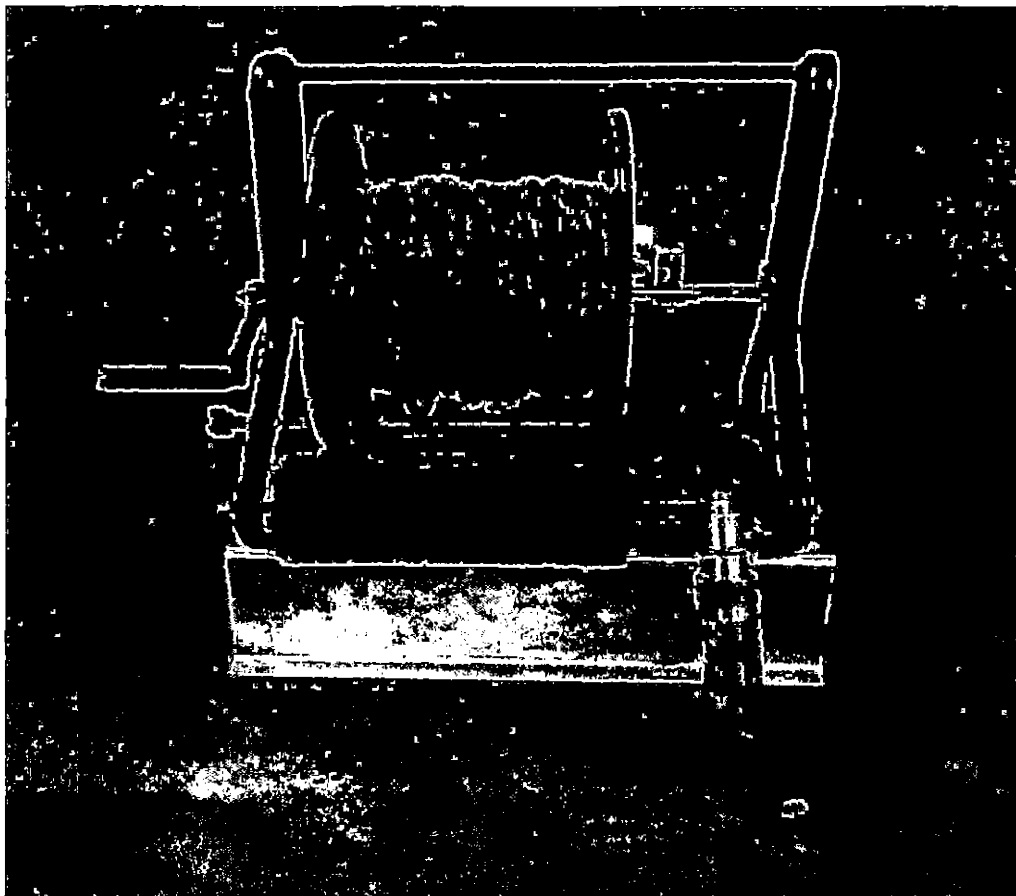


Figure 5. Grundfos Redi-Flo 2 Submersible Pump

Prior to starting the pump, the static water level and total depth of the well were measured. A calibrated electronic water level meter was used to measure the depth to water in the well. The total depth of the well was measured using a manual total depth sounder. These values were necessary to calculate the total amount of water needed to purge and collect a representative groundwater sample. An environmental industry standard of three casing volumes was considered acceptable to remove the majority of the stagnant groundwater from the casing. Water quality parameters were measured and recorded at intervals of five to fifteen minutes during purging activities. Stable water quality parameters indicate that stagnant groundwater inside the casing has been removed and replaced with water from the surrounding formation. Water quality parameters were considered stable when three consecutive measurements taken three to ten minutes apart were recorded and water quality parameters meet the criteria in Table 1.

These parameter guidelines are set to ensure that the sample taken is representative of formation water and not of stagnant groundwater inside the casing.

Pump start time was recorded, and parameter measurements were taken every five to fifteen minutes. The

pump rate was determined on total gallons to be purged, total depth, and historic sampling data.

Table 1. Water Quality Parameter Stabilization Criteria

Parameter	Units
pH	+/- 0.1 pH Units
Specific Conductance	If groundwater \leq 100 μ S/cm, readings must be within 5% If groundwater $>$ 100 μ S/cm, readings must be within 3%
Dissolved Oxygen	+/- 0.3 mg/L
Temperature	+/- 0.2 $^{\circ}$ C
Turbidity	<5 NTU

Once the parameters were stable and three well volumes had been purged, a sample was taken. The sample was collected inside a polyethylene sample chamber to ensure atmospheric constituents did not contaminate the sample. The tubing was then cut using pre-cleaned stainless steel tubing cutters before the flow meter. Cutting the tubing before the flow meter is necessary to ensure that any possible contamination can be ruled out from the flow meter, flow cell, or valves used. The sample is then collected inside a sample chamber to prevent possible contamination from the outside air.

The sample bottle was then sealed and put into a zip-lock bag and placed on ice to preserve the sample and to

maintain sample integrity. Once the samples were on ice, the cut tubing was then reinserted into the flow meter and a post sample parameter measurement taken. This is to ensure that water quality parameters were stable during the time of sampling. The parameters must follow the guidelines after taking the sample as well.

The pump was then removed from the casing and decontaminated. The entire process was repeated for each well casing.

A Chain of Custody form was then filled out to legally bind the samples to the technician, until that technician gives the samples to the laboratory courier. The Chain of Custody is then signed by each party and the samples are legally in the courier's procession. The laboratory courier then transported the samples to Test America Laboratories, where the samples were analyzed for the selected analytes.

Analysis

After the lab had completed the prescribed analyses, a report was generated and data analysis began. Data analysis included reviewing the water quality reports for: positive correlation between certain analytes and dissolved arsenic concentrations, trends of arsenic speciation at depth and spatially, trends in arsenic concentrations relative to pH

and ORP values, and trends in iron and manganese concentrations both spatially and at depth. Identifying trends and finding positive correlation between analytes is the key to understanding how arsenic is being desorbed and adsorbed.

The arsenic speciation analysis was completed on eight monitoring wells (Figure 6). Eight monitoring wells were selected for arsenic speciation by Standard Method 7063 (EPA SW-846, 2012). Wells were selected based on elevated arsenic concentrations identified during previous water quality data. The wells were also selected by general location and proximity to one another. The wells selected for cross sectional analysis and interpretation extend for roughly two miles in a north-south direction along the Mojave River bed. The monitoring wells selected for arsenic speciation analysis: TZ-3 (a-d), H2-1 (a-b), and Older 1 (a, c, & d) had screened intervals that give information from the shallowest (95.8 ft.) depth to the deepest (705.1 ft.) depth. This sampling schematic would give a cross section where arsenic speciation could be analyzed at 8 different depths between a two mile section of the Mojave River. This cross-section of data could then be used to translate up and down the river to portray a TZ basin

arsenic release system, and find certain depths and water quality characteristics that could predict the location of groundwater with elevated arsenic concentrations.

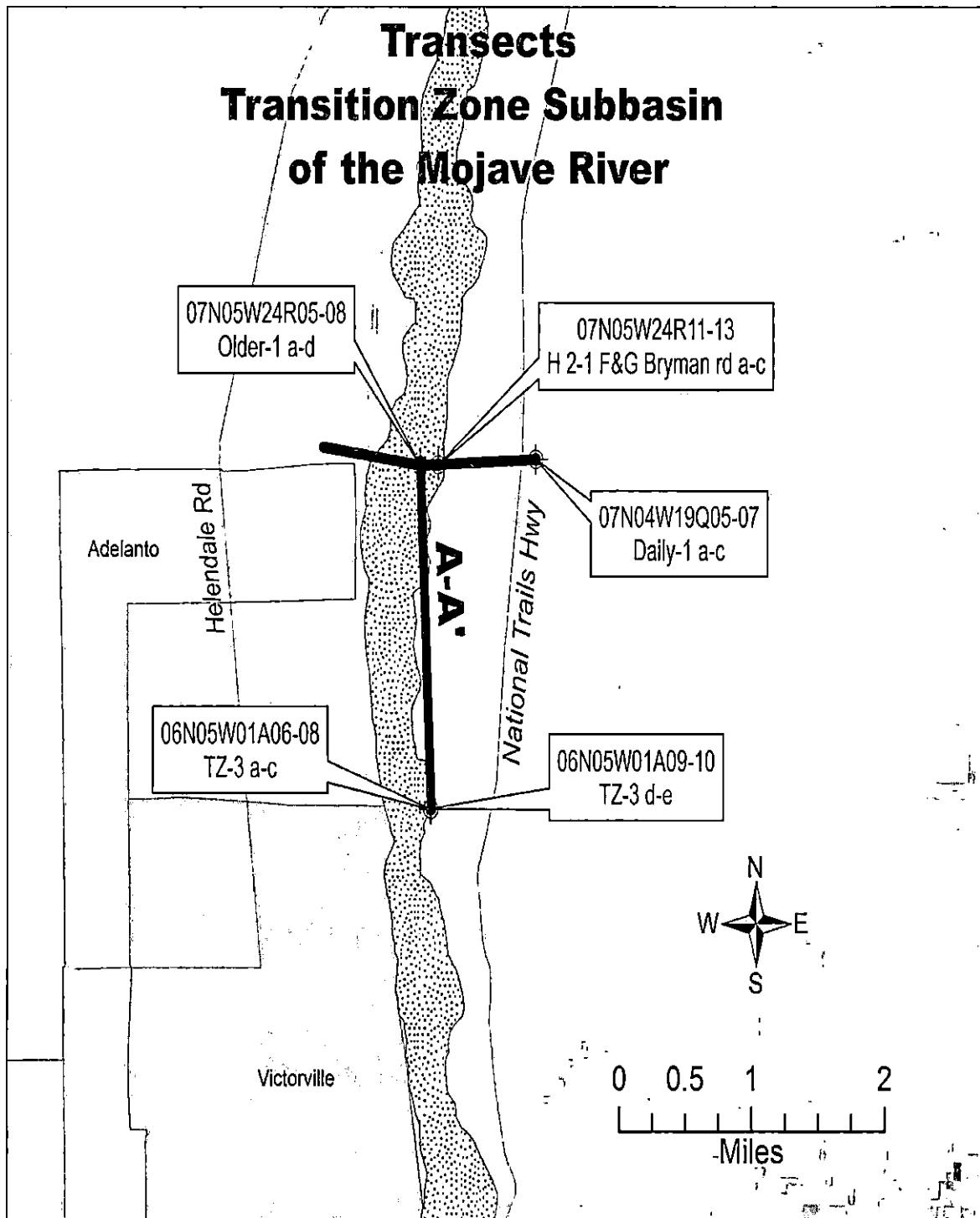


Figure 6. Arsenic Speciation Transects Map

Oxidation Reduction Potential Comparison

An ORP study was conducted on the first five samples taken during the project. A head to head ORP comparison between a 1 liter clear HDPE bottle and a 250 mL amber organic analysis bottle. Research has shown that field ORP measurements may yield useful information on what predominate species of arsenic can be expected. During the sample collection a 250 mL amber glass bottle without headspace was used to compare against standard 1 liter clear poly bottle with headspace. The laboratory then ran the ORP analysis for each bottle. This comparative analysis would reveal if the headspace left in the 1 liter clear poly bottle contributed to the oxidization of arsenic. This comparative analysis was only done for the first five samples.

Selecting additional important analytes, along with the arsenic speciation analysis and the aquifer material analysis, gave important information on the concentration and distribution of arsenic in the TZ basin.

Scanning Electron Microscope Analysis

Analysis of aquifer material was completed using an Hitachi S-2700 scanning electron microscope equipped with an EDAX energy- dispersive x-ray spectrometer (EDS) (Figure

7). The grains were selected from the drilled material from select monitoring wells sampled. Samples were selected from trays of drilled aquifer material. Under the guidance of Dr. Erik Melichorre, grains were selected based on color and size. The colors that were observed to be containing iron were black and orange. The samples were then mounted on a carbon coated stage and then coated with carbon. The carbon coating is necessary when analyzing non-conductive samples. Resolution and signal quality are better when a carbon coat is applied to the sample. The samples are then placed in the SEM-EDS, and a vacuum evacuates all the air from the SEM-EDS. Evacuation is necessary because of contamination from elements in the air.

Once the samples were loaded and the SEM-EDS was evacuated, sample analysis began. The SEM-EDS was controlled by a computer that would allow the user to navigate around the grain and perform analytical measurements on different parts on the grain. The analytical measurements detected elements in weight % of sample.

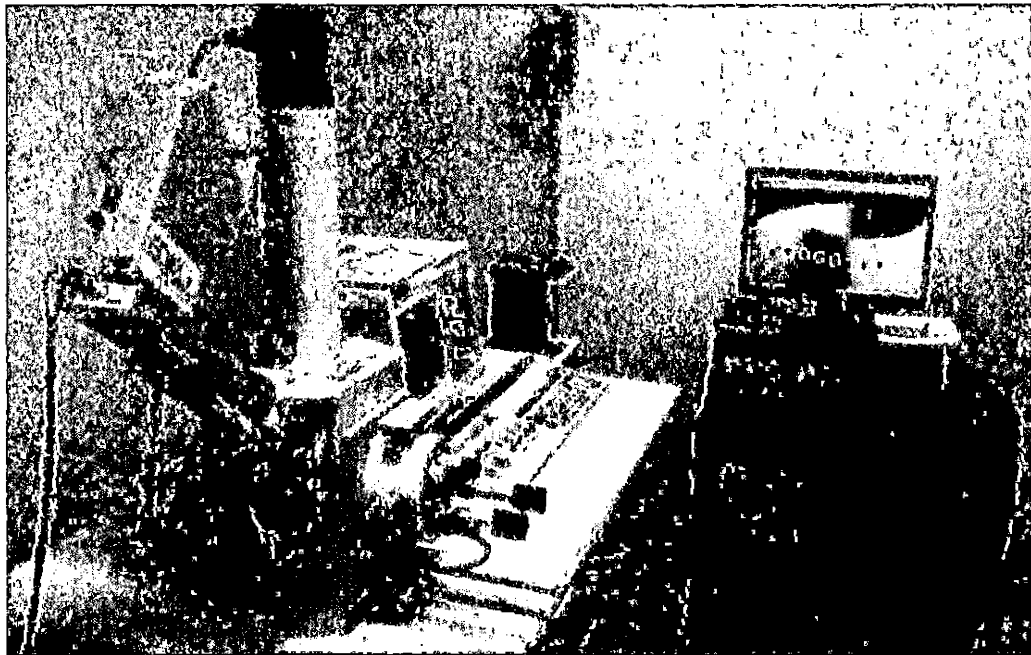


Figure 7. Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy

The weight % was then converted into parts per million. This analysis was performed on 12 different grains from specific wells with historical and current elevated arsenic.

CHAPTER FOUR
FINDINGS AND RESULTS

Sampling and Lab Data

43 monitoring wells were sampled for this project. Monitoring wells were assigned and labeled using the rectangular system for the division of land. The monitoring wells were identified by township, range, and section. This is the state of California well number system and each well is assigned a state well number (SWN). Along with the SWN, a well is given a common name, describing a unique characteristic about the well. Below is a list of all of the monitoring wells sampled along with total depth, screen perforations, and common name.

Table 2. Monitoring Wells Sampled. Continued on following page.

SWN	Common Name	Total Depth (ft)	Screen Perforations (ft)
08N04W19G01	Helendale-4-a	318.8	295 - 315
08N04W19G02	Helendale-4-b	242.1	220 - 240
08N04W19G03	Helendale-4-c	173	150 - 170
08N04W19G04	Helendale-4-d	102.3	80 - 100

Table 2. Monitoring Wells Sampled. Continued on following page.

SWN	Common Name	Total Depth(ft)	Screen Perforations(ft)
06N05W01A06	TZ-3-a	705.1	690.1 - 700.1
06N05W01A07	TZ-3-b	466.3	451.3 - 461.3
06N05W01A08	TZ-3-c	317.5	302.5 - 312.5
06N05W01A09	TZ-3-d	105	90 - 100
06N05W01A10	TZ-3-e	55	40 - 50
07N05W02B01	TZ-4-a	625.8	600 - 620
07N05W02B02	TZ-4-b	322.9	300 - 320
07N05W02B03	TZ-4-c	136.1	110 - 130
07N05W24R05	Older-1-a	550.9	510 - 550
07N05W24R07	Older-1-c	149.7	130 - 150
07N05W24R08	Older-1-d	50.9	45 - 50
07N05W24R11	H 2-1 F&G Bryman rd-a	157.1	140.6 - 150.6
07N05W24R12	H 2-1 F&G Bryman rd-b	95.8	80 - 90
07N05W24R13	H 2-1 F&G Bryman rd-c	24.3	4 - 19
07N04W06F07	Bunnell Peacock Farm	29.6	15 - 25
06N04W19E06	TZ 2-a	794.3	785 - 795
06N04W19E07	TZ 2-b	180.1	165 - 175
06N04W19E08	TZ 2-c	53.9	40 - 50
06N04W19E09	TZ 2-d	25.2	10 - 25
06N04W30K14	H1-1-a	122.9	108.3 - 118.3
06N04W30K15	H1-1-b	72.1	52 - 67
06N04W30K16	H1-1-c	31.6	6 - 26
06N04W30R01	TZ-1-a	207.1	190 - 200
06N04W30R02	TZ-1-b	155.8	140 - 150
06N04W30R03	TZ-1-c	109.3	93 -103
07N04W19Q05	Daily-1-a	591.9	534 - 574
07N04W19Q06	Daily-1-b	275.2	256 - 276

Table 2. Monitoring wells sampled

SWN	Common Name	Total Depth(ft)	Screen Perforations(ft)
07N04W19Q07	Daily-1-c	148.2	130 - 150
08N04W21M01	Helendale-1-a	371.6	350 - 370
08N04W21M02	Helendale-1-b	230	210 - 230
08N04W21M03	Helendale-1-c	142.2	120 - 140
08N04W21M04	Helendale-1-d	42.2	30 - 40
08N04W29E03	Helendale-3-a	311.7	289 - 309
08N04W29E04	Helendale-3-b	213	190 - 210
08N04W29E05	Helendale-3-c	134	110 - 130
08N04W29E06	Helendale-3-d	43.9	30 - 40

There were four additional analytes added for 2011 sampling event. The analytes were: total arsenic, total manganese, total selenium, and total antimony. There were twelve wells sampled in October 2010 that were not analyzed for the four additional analytes: Helendale-1, Helendale-3, and Helendale-4. The other 31 wells were sampled in November 2011. Three duplicate samples were collected at wells: TZ-2(D), H2-1(A), and TZ-4(B). These duplicates were collected as quality assurance and quality control samples.

Arsenic

Dissolved arsenic was identified in 36 of the 43 wells sampled. Out of the 36 wells that had dissolved arsenic concentrations, 15 of the wells had concentrations above the MCL of 10 ppb. The average dissolved concentration identified in the 36 wells was 22.7 ppb.

Total arsenic was identified in 27 of the 31 wells sampled, in which 15 of wells had total arsenic concentrations above the MCL of 10 ppb. Out of the 31 wells sampled for both total and dissolved arsenic, concentrations differed in 22 of the wells. The average difference between wells sampled for total and dissolved arsenic was 2.7 ppb. Five of the wells had total concentrations of arsenic that was lower than the dissolved concentrations of arsenic. These concentrations show that the majority of the arsenic in the samples is in the dissolved in the water.

Elevated arsenic concentrations can be identified in relation to depth. Dissolved arsenic concentrations increased as the depth of the well increased, and decreased in shallower wells (Figure 9). Total arsenic concentrations also increased with depth as the difference between total

and dissolved arsenic concentrations was approximately 2.7 ppb.

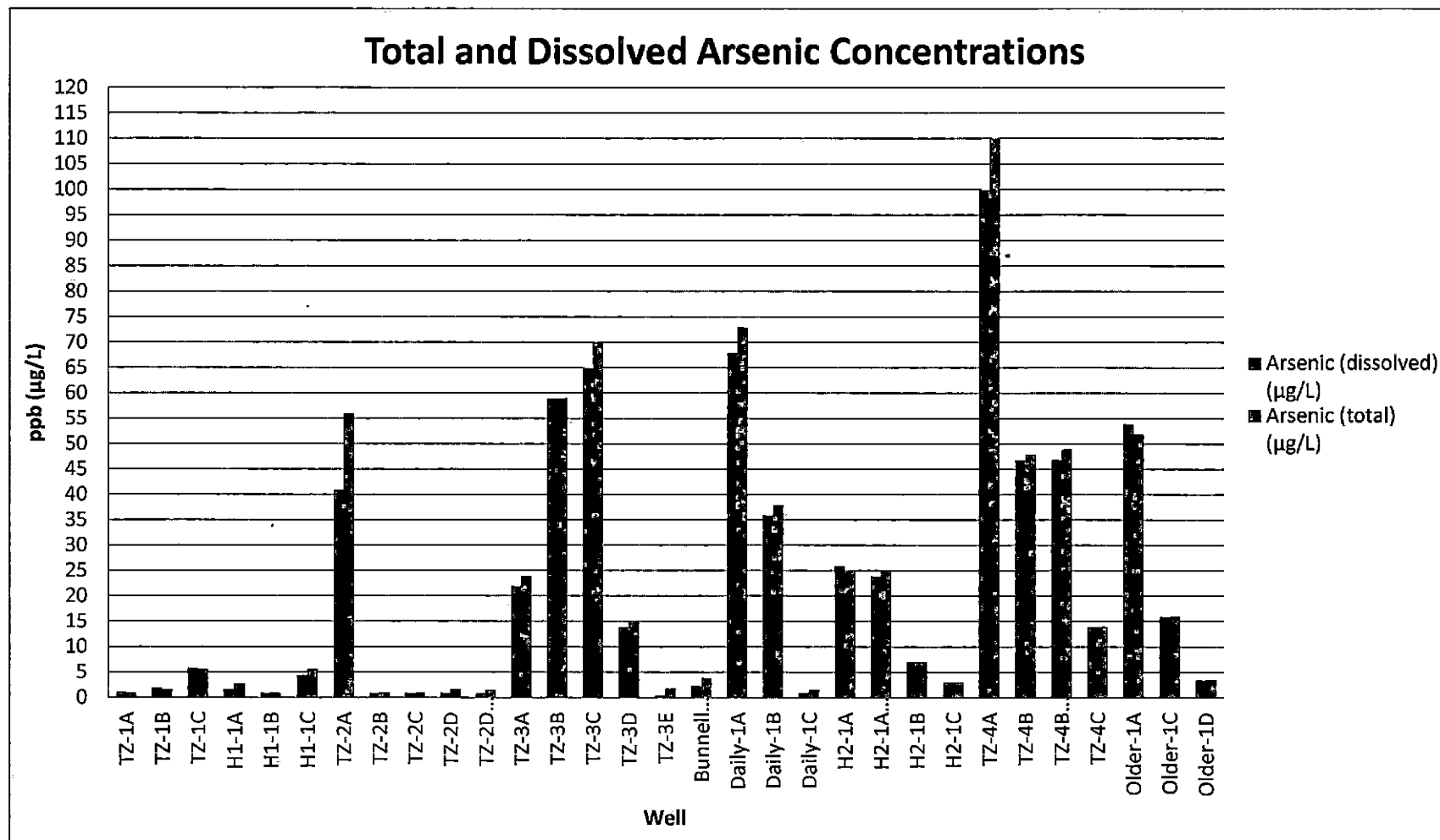


Figure 8. Total and Dissolved Arsenic Concentrations by Well

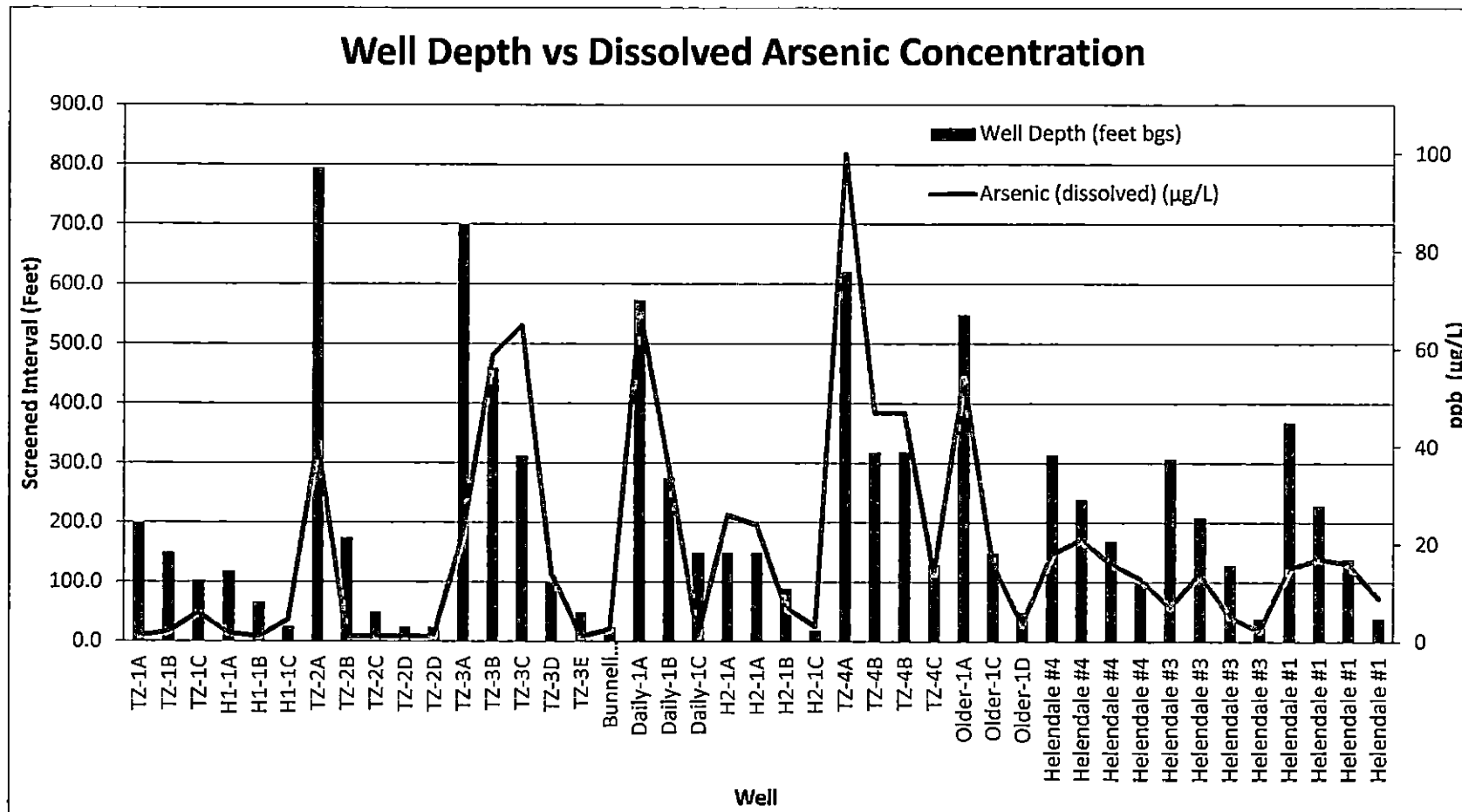


Figure 9. Dissolved Arsenic Concentrations Based by Well Depth

Arsenic Speciation

Arsenic speciation analyses were completed on eight wells. Arsenite (As^{3+}) concentrations ranged from 3.4 ppb to 16 ppb. Arsenate (As^{5+}) concentrations ranged from 12 ppb to 47 ppb. It is seen that arsenite (As^{3+}) concentrations dominate when the pH is less than 8.0, whereas Arsenate (As^{5+}) concentrations are not detected. Arsenate (As^{5+}) concentrations dominate with pH above 8.0, while arsenite (As^{3+}) concentrations are not detected. These results show that in deeper wells with elevated pH, Arsenate (As^{5+}) is the primary oxidation state of arsenic. At shallow wells, with less alkaline pH, arsenite (As^{3+}) is the primary oxidation state of arsenic. The weathering of aluminosilicates and carbonate minerals may increase the pH in the regional and floodplain aquifer, leading to increased arsenic desorption. The regional aquifer is comprised of ancient water that has had a thousand years of time to react with aquifer material resulting in a pH values above 7.5.

Arsenic speciation results also follow a trend with well depth. The two shallow wells analyzed for arsenic speciation revealed only arsenite (As^{3+}), while the deeper wells sampled revealed arsenate (As^{5+}) as the dominate

oxidation species. The ORP measurements for the wells selected for arsenic speciation ranged from 330mV to 450mV. There was no observable trend with the ORP results and the arsenic speciation results.

Table 3. Arsenic Speciation, pH, and Oxidation Reduction Potential Results

Common Name	Screened Interval (feet)	Arsenite (As ³⁺) (µg/L)	Arsenate (As ⁵⁺) (µg/L)	Redox Potential (Eh) (mV)	pH
TZ-3A	700.1	3.4	15	440	8.3
TZ-3B	461.3	15	34	430	8.7
TZ-3C	312.5	<2.0	47	440	8.4
TZ-3D	100	16	<8.0	450	7.8
H2-1A	150.6	<2.0	18	380	8.3
H2-1B	90	5.8	<2.0	330	7.1
Older-1A	550.0	<2.0	29	410	8.2
Older-1C	150.0	<2.0	12	410	8.0

pH

pH was measured for all of the 43 wells sampled. The pH range of the wells sampled was between 6.5 and 9.0, with the average pH of approximately 7.8. At pH levels 6.5-7.0 there were no detectable levels of arsenic. pH levels between 7.0-7.5, arsenic levels increase to a maximum of 9.0 ppb. With pH levels 7.5-8.5, arsenic concentrations continue to increase to a maximum of 68 ppb. Lastly pH levels above 8.5, arsenic concentrations increase to a maximum of 100 ppb.

Arsenic concentrations generally increased when greater alkaline conditions were encountered. There were two wells where arsenic concentrations did not increase with pH: TZ-1(A-C) and TZ-2(B-D). TZ-1(A) was a low yielding well, which took two consecutive days and approximately twelve hours to obtain a sample. TZ-1 (A) was pumped very slowly (<1.0 gpm) and had excessive drawdown. TZ-1 (B) was also a low yielding well, taking approximately 4 hours to purge three casing volumes. Low flow sampling was performed on TZ-1 (C) due to excessive drawdown. The pump was placed one foot into the screen zone, and pumped at a slow rate (<0.2gpm).

These low yielding wells reveal that the wells are placed in low yielding sediments that may not represent typical groundwater conditions for wells completed in higher yielding aquifer zones. This could have affected the arsenic and pH relationship we typically see in other wells. Arsenic concentration increased with pH in the other wells sampled.

TZ-2(B-D) also did not show the typical relationship between arsenic and pH. TZ-2(B-D) did not exhibit any uncharacteristic field conditions while sampling, and was sampled within the field parameter sampling criteria.

Trends in pH vs. well depth can be observed as the pH increases as depth increases in a well, and the pH decreases the shallower the well (figure 10).

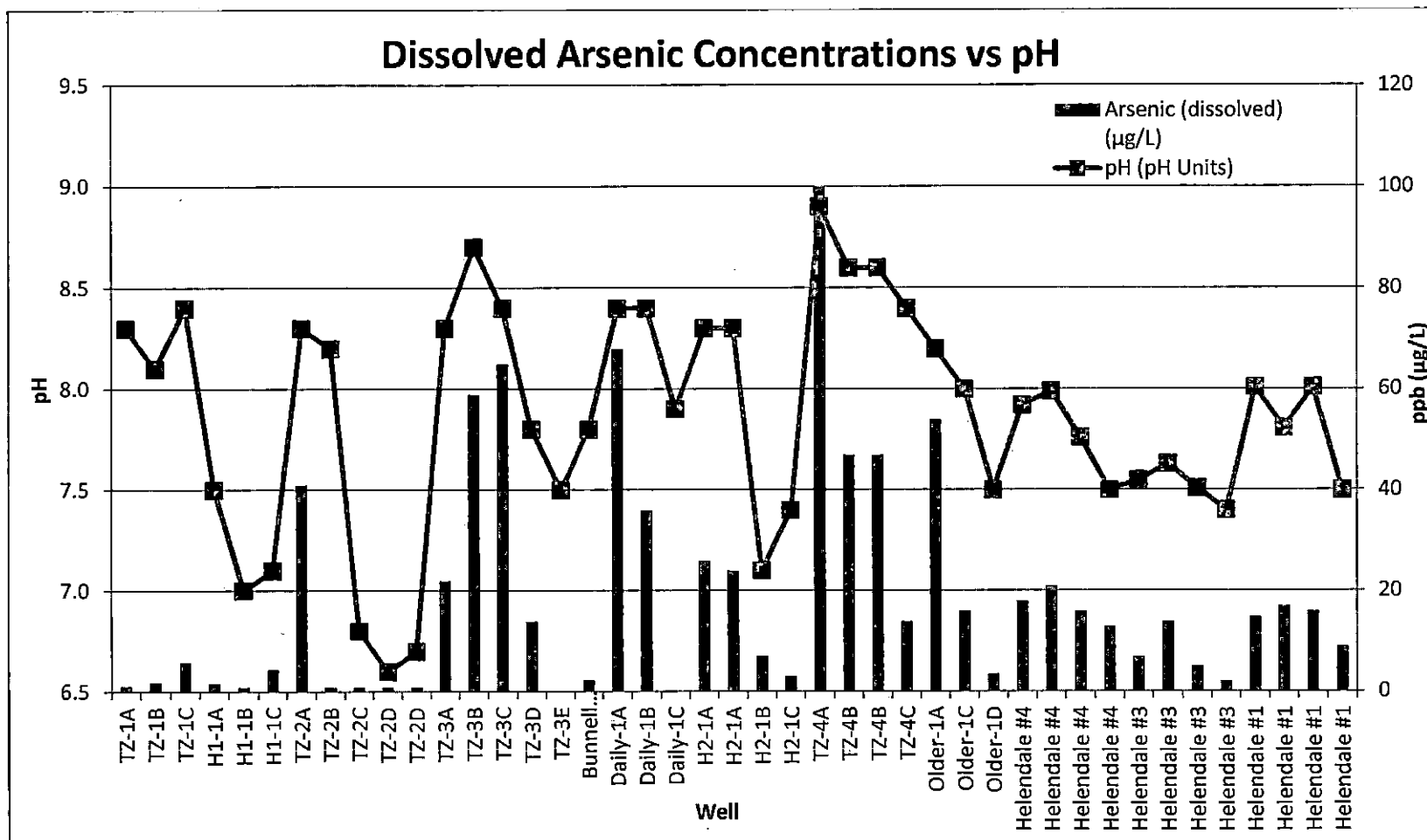


Figure 10. Dissolved Arsenic Concentration versus pH by Well

Oxidation Reduction Potential

Oxidation reduction potential (ORP) was measured at each well. Based on the oxic groundwater of the Transition Zone we expect to see all of the ORP values to be positive. ORP measurements ranged from 180mV to 540mV. The average ORP measurement from the 43 wells sampled was 401.0, displaying oxic conditions throughout the TZ subbasin. There wasn't a noticeable trend between ORP and arsenic concentrations (Figure 11).

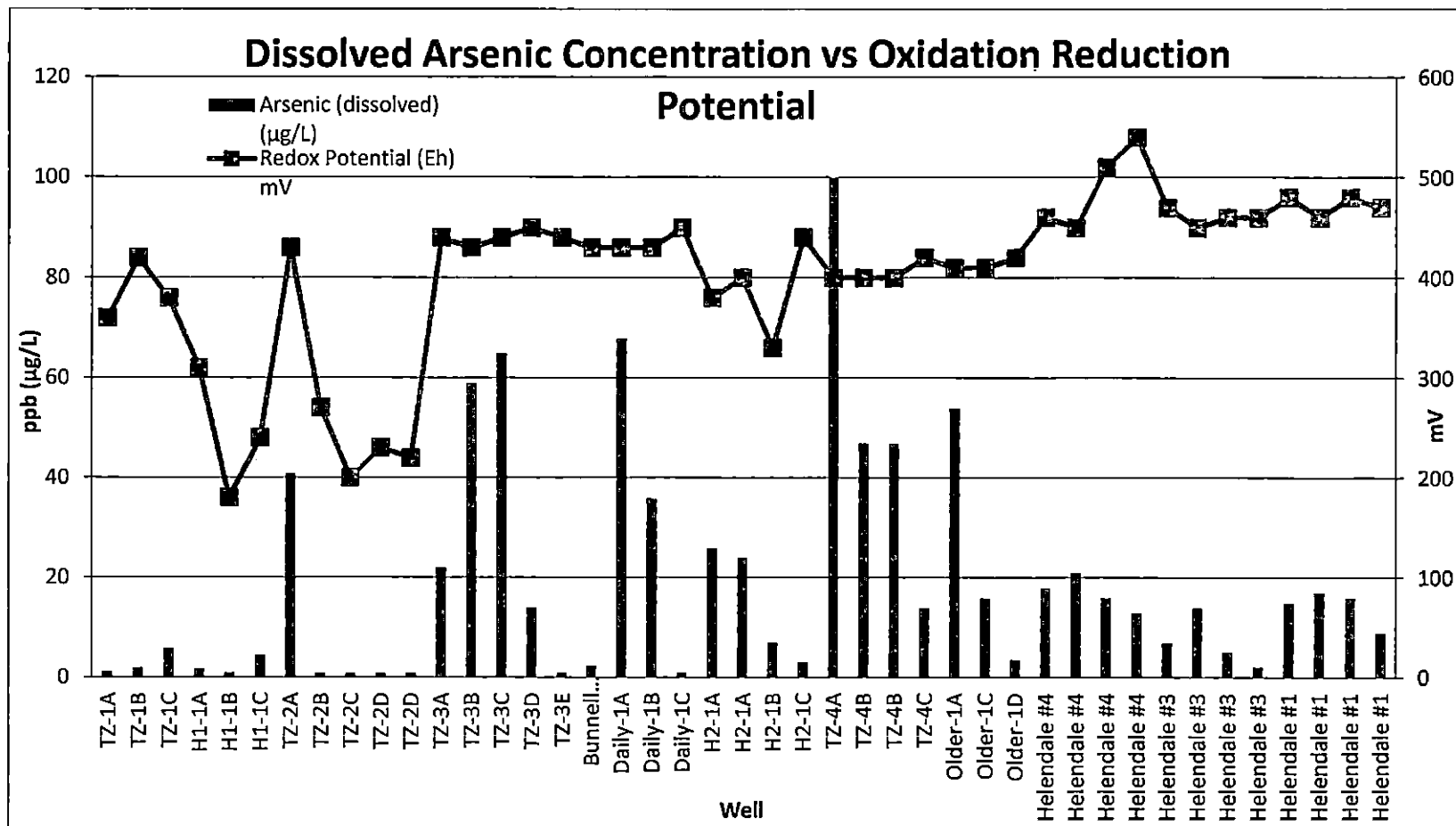


Figure 11. Dissolved Arsenic Concentration versus Oxidation Reduction Potential by Well

Iron

There were four iron analyses performed on each well: Total iron, dissolved iron, ferrous iron (Fe^{2+}), and ferric iron (Fe^{3+}). Total iron concentrations exceeded 0.10 mg/L (ppm) in 25 of the wells. Dissolved iron concentrations surpassed 0.10 ppm in 9 of the wells. Higher concentrations in total iron over dissolved iron shows that iron is principally colloidal and therefore filtered out in the lab.

Ferrous iron (Fe^{2+}) concentrations surpassed 0.10 ppm in 9 of the wells. Ferric iron (Fe^{3+}) concentrations exceeded 0.01 ppm in 23 of the wells. Ferrous iron is generally soluble in groundwater, while ferric iron is generally insoluble in groundwater. This might explain why total iron concentrations were consistent throughout 25 of the wells. These total iron concentrations could have adsorbed arsenic on to iron rich colloidal material, which would explain a small difference in total and dissolved arsenic concentrations.

Manganese

Dissolved manganese was analyzed for all 43 wells (figure 12). 29 of the wells had detectable concentrations of manganese, ranging from 1.4 ppb to 5,300 ppb. The

average dissolved manganese concentration of all 29 wells was 667.2 ppb. The average dissolved manganese concentration is high because five wells exceeded manganese concentrations of 1,000 ppb.

Total manganese was analyzed for 31 of the wells sampled. 30 of the wells had detectable amounts of manganese, ranging from 1.0 ppb to 5,000 ppb. The average total manganese concentration was 610.1 ppb. There was a noticeable manganese difference in the wells analyzed for both total and dissolved. Out of the 31 samples, there were six samples that had lower total manganese than dissolved manganese, this might be due to random error at the laboratory or filter clogging during filtration. The average difference between total and dissolved manganese was 59.3 ppb.

Manganese also had a unique relationship with well depth (figure 12). Shallower wells displayed an increase in manganese concentrations, and deeper wells displayed a decrease in manganese concentrations.

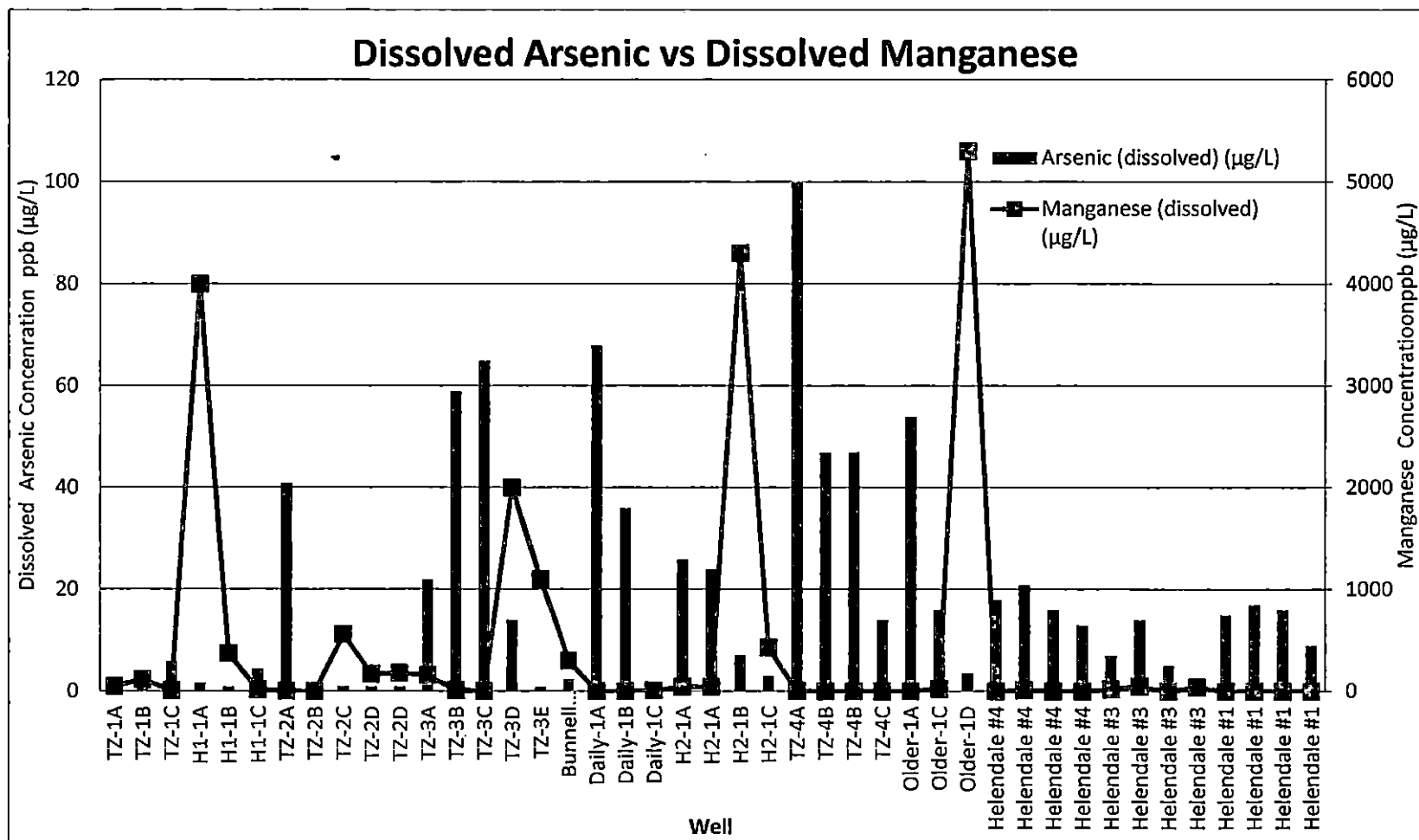


Figure 12. Dissolved Arsenic Concentrations versus Dissolved Manganese Concentrations by Well

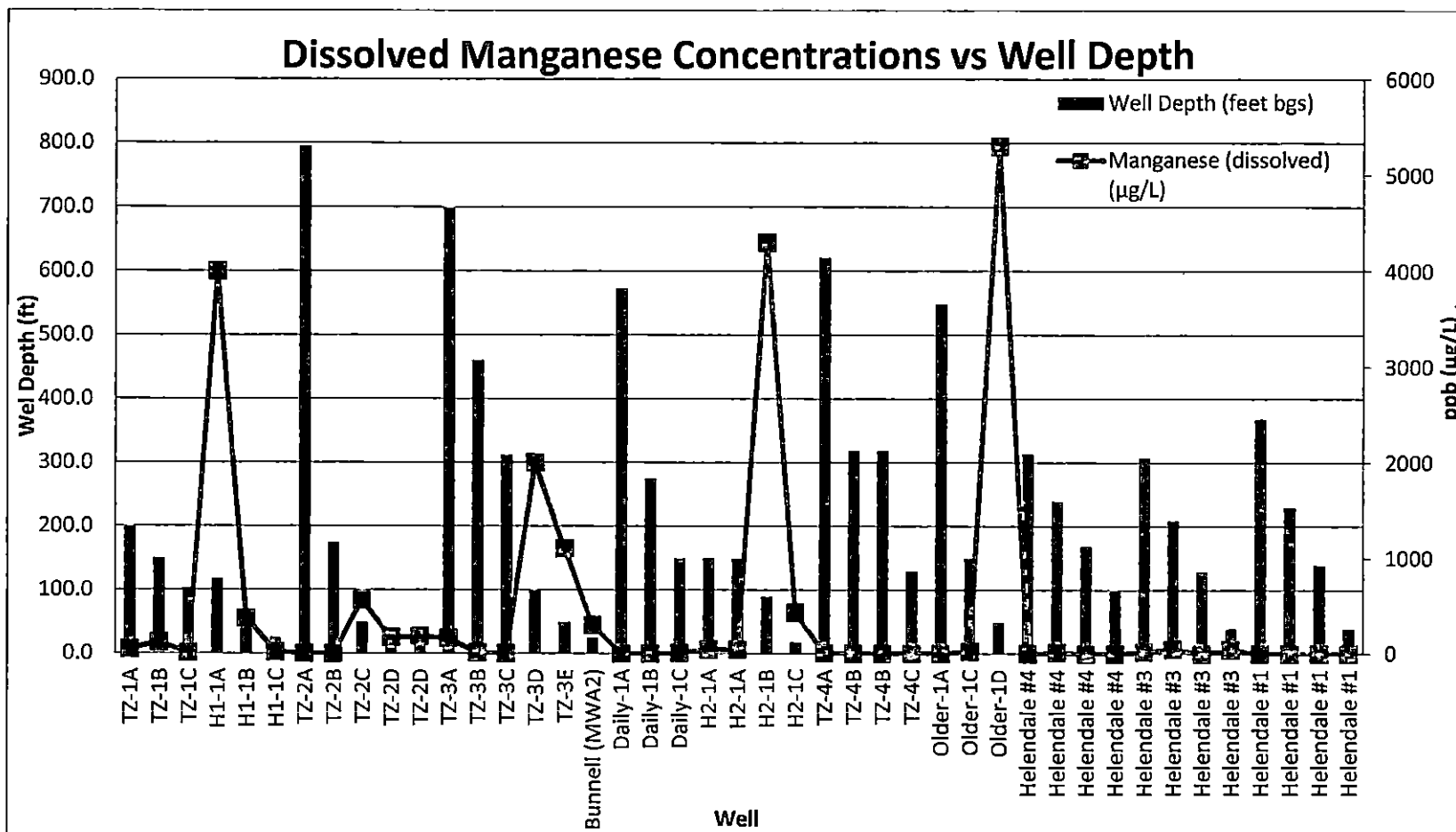


Figure 13. Dissolved Manganese Concentrations versus Depth by Well

Antimony

There wasn't any detectable dissolved or total concentration of antimony in any of the wells sampled during this sampling event.

Selenium

There were only two wells with detectable concentrations of selenium: TZ-4B and TZ-4C. All of the wells were analyzed for dissolved selenium, and 31 of them analyzed for total selenium. These wells that had concentrations of selenium are located approximately two and a half miles west of the Mojave River. The total selenium concentrations for TZ-4B and TZ-4C were, 2.0 ppb and 2.3 ppb respectfully.

SEM-EDS Analysis

Twelve grains were analyzed using the SEM-EDS. Multiple analyses on one grain were performed because of the inconsistent nature of the grains. The elements that were selected to be scanned on the SEM-EDS were: silicon, sodium, potassium, calcium, aluminum, arsenic, iron, chromium, manganese, sulfur, and titanium. The results varied from grain to grain (Table 4). There were common trends that were noticed while analyzing the grains:

- 1) On every grain there was silica and aluminum present. This suggests that all of the grains were a derivative of an aluminosilicate mineral. Weathering of aluminosilicates may have an effect on pH, which can effect arsenic concentrations.
- 2) Arsenic was detected at low weight % content in most grains, while there were select grains that had arsenic exceeding 5%. Varying weight % of arsenic was found on the same grain without displaying any trend.
- 3) Iron was detected in a majority of the samples analyzed, varying in concentrations from .57 weight % to 90.6 weight %. The iron oxide coating on aquifer material that is interacting with arsenic is not evenly distributed around the grain. The iron is located more in concentrated areas across the grains analyzed.
- 4) Traces of the other elements were found sporadically on the grains, without showing any trend with arsenic.

Table 4. Scanning Electron Microscope Electron Dispersive
X-ray Spectrometer Average Weight Percent Results

Grain	Average Wt % aluminum	Average Wt % silica	Average Wt % arsenic	Average Wt % iron
Grain # 1	6.71	78.62	0.09	1.17
Grain # 2	11.79	75.87	0.04	4.39
Grain # 3	14.82	65.22	0.22	9.06
Grain # 4	6.09	61.65	0.4	6.46
Grain # 5	7.45	55.52	0.16	1.1
Grain # 6	11.18	62.36	0.13	5.36
Grain # 7	8.61	40.61	0.65	41.04
Grain # 8	5.89	24.62	0.04	56.98
Grain # 9	23.7	49.19	1.33	3.29
Grain # 10	28.65	48.46	1.35	1.61
Grain # 11	20.58	51.12	1.43	7.27
Grain # 12	28.66	40.99	3.18	7.32

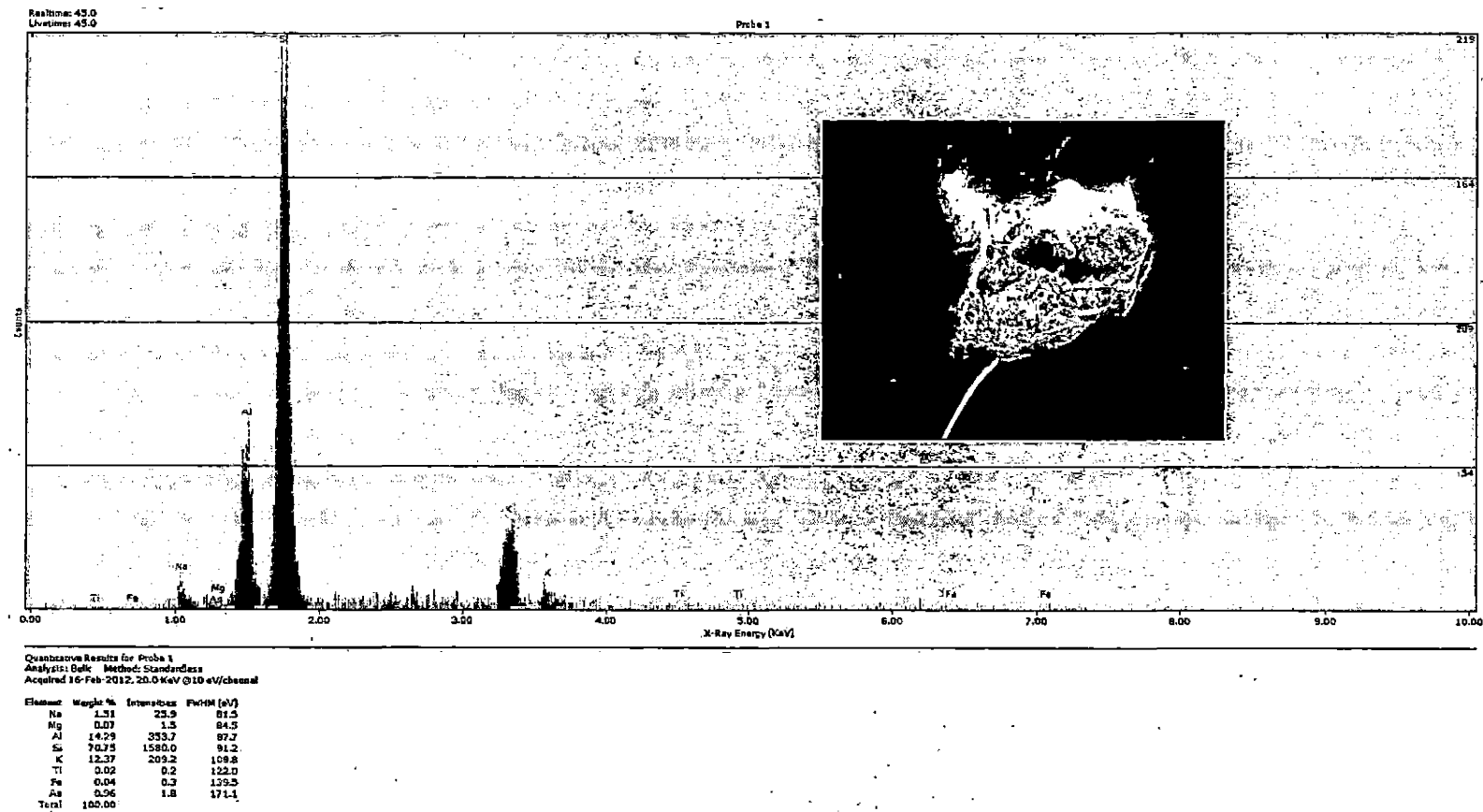


Figure 14. SEM-EDS Display of Sample Grain from TZ-3(A)

CHAPTER FIVE

DISCUSSION

Arsenic

Elevated arsenic concentrations were measured in the TZ subbasin of the Mojave River. The water quality results, with supporting evidence from the SEM-EDS results, show that the arsenic is coming from the aquifer material and not from anthropogenic sources. Total and dissolved arsenic concentrations are relatively close, with an average of 2.7 ppb difference. This small difference between the two phases shows that a majority of the arsenic is in the dissolved phase rather than the whole phase.

Total arsenic concentrations may be skewed due to a turbidity spike in the sample, resulting in an increase of total arsenic concentration. Turbidity was filtered out at the lab, but iron-rich minerals smaller than $0.45\mu\text{m}$ containing arsenic may not have been filtered out. This is supported by the presence of ferric iron (Fe^{3+}) concentrations in 23 of the wells.

Arsenic concentrations are directly related to pH and well depth. pH increased as the depth increased resulting

in higher arsenic concentrations. The pH increase is assumed to be caused by weathering of alumino-silicate material throughout the TZ basin. The deeper wells located in the regional aquifer may have lower transmissivity values, which allows time for aquifer material to interact with the aquifer water resulting in alkaline pH values. The shallower wells are located in the floodplain aquifer which is directly influenced by flow patterns in the Mojave River. The wells located in the floodplain aquifer typically have pH values that are near neutral to slightly alkaline. One possible explanation for the neutral and slightly alkaline pH values is contact time between the aquifer material and aquifer water. Perennial flow in the TZ basin may result in a flushing of the floodplain aquifer, reducing the time the aquifer water has to react with the aquifer material. This aquifer flushing effects arsenic concentrations in the floodplain aquifer. Arsenic concentrations follow a trend with depth. Arsenic concentration generally increased as depth and pH increased.

Arsenic Speciation

Arsenic speciation results were dependent on well with alkaline pH, arsenate (As^{5+}) was the predominate arsenic

species. The results show that around pH 8.0, arsenate (As^{5+}) sorption decreased. This is likely due to the increasing negative charge on iron material as pH increased, which decreased the sorption between iron and negatively-charged arsenate (As^{5+}). In the shallower wells sampled with slightly lower, relatively neutral, pH conditions, arsenite (As^{3+}) was the predominate arsenic species. This is likely due to the increased desorption of arsenite (As^{3+}) from iron at this pH. As the pH increases, negative charges on iron material also increase and the less negatively-charged arsenite (As^{3+}) adsorbs to the iron material. The reverse effect happens when the pH decrease to neutral to slightly alkaline, arsenate (As^{5+}) adsorbs to iron material and arsenite (As^{3+}) desorbs.

Well Depth and pH

The arsenic levels increase as depth increases in the aquifer. The arsenic concentrations also show a strong correlation with pH. Arsenic concentrations generally increased as the pH increased. There are a few wells that had non-detect concentrations of arsenic when the pH increased. These wells were located furthest south in the TZ basin.

Oxidation Reduction Potential

The ORP measurement values do not correlate with arsenic or arsenic speciation results. Trends between arsenic concentrations were expected during sampling but were not observed.

Iron

23 of the wells had ferric iron (Fe^{3+}) concentrations exceeding 0.1 ppm, this explains that small iron rich material were present as colloidal material. This iron rich colloidal material may vary in size based on the dissolved iron and ferrous iron concentrations found in nine wells. Smaller iron rich colloidal material may have passed through the 0.45 μm filter used for dissolved analyses, while large colloids may have been filtered out. Arsenic concentrations did not display positive correlations with any iron analyses.

Manganese

There was an inverse relationship between dissolved arsenic and dissolved manganese. When the manganese was present the arsenic was not and vice versa. Another noticeable trend was between manganese concentrations and depth. Elevated concentrations of

manganese only appear in shallower wells generally less than 100 ft. in depth.

There were five wells that had elevated manganese concentrations: H1-1(A), TZ-3(D-E), H2-1(B), and Older-1D. These wells have depths less than 100 feet, with the exception of H1-1(A) that has a depth of 118 feet. Based on these results it appears that there are concentrated manganese deposits in the floodplain aquifer. Manganese concentrations and ORP did not have any relationship:

SEM-EDS Analysis

THE SEM-EDS analysis yielded useful information regarding the chemical composition of aquifer material in the TZ subbasin. Arsenic was detected in low weight % concentrations around the grains analyzed. This shows that arsenic is present on the aquifer grains in low concentrations, with the ability to desorb to the aquifer water and exceed the 10 ppb MCL for arsenic. Iron was detected on a majority of the grains in concentrated areas with no observable trend. Aluminum and silica were present in large concentrations on every grain. This explains that alumino-silicate material is buffering the aquifer water to alkaline conditions.

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