



2010

## Naturally occurring aqueous arsenic and seawater intrusion on Lummi Island, WA

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**NATURALLY OCCURRING AQUEOUS ARSENIC AND  
SEAWATER INTRUSION ON LUMMI ISLAND, WA**

by

ERICA MARTELL

Accepted in Partial Completion  
of the Requirements for the Degree  
Master of Science

Moheb A. Ghali, Dean of the Graduate School

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## **MASTER'S THESIS**

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**NATURALLY OCCURRING AQUEOUS ARSENIC AND  
SEAWATER INTRUSION ON LUMMI ISLAND, WA**

A Thesis  
Presented to the Faculty of  
Western Washington University

In Partial Completion  
of the Requirements for the Degree  
Master of Science

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Erica Martell  
May 2010

## **Abstract**

Two different types of groundwater contamination may be present in the aquifers on northern Lummi Island, Washington: naturally occurring arsenic and seawater intrusion. Freshwater on northern Lummi Island is stored in bedrock and unconsolidated glacial sediments. The naturally occurring arsenic, sourced from an undetermined stratigraphic layer, varies spatially throughout the island. Additionally, seawater may be intruding into the groundwater supply, which is the primary source of drinking water for the residents of the island. The process of mobilization of the naturally occurring arsenic and the extent of the seawater intrusion has not been fully explored. The purpose of my study was to determine the geochemical, physical, and seasonal influences on concentrations of arsenic and major ions on Lummi Island.

I collected water samples and made *in situ* measurements from wells distributed throughout Lummi Island for geochemical analysis. Statistical analysis was used to test for a relationship between arsenic concentrations and geochemical factors or season. The speciation of arsenic in the groundwater was determined by plotting pH and redox potential measurements on an arsenic species stability diagram. Whole-rock chemical analysis was used to investigate the bedrock source of the arsenic. The extent of the seawater intrusion was determined using major ion analysis, and the source of the ions was interpreted using Piper diagrams. The relationship between aquifers, major ions, and seasonality was explored using multivariate statistical analysis.

Whole rock analysis indicated that the highest arsenic concentration was in the sample taken from the Chuckanut conglomerate. When Eh and pH field measurements were

plotted on an arsenic stability diagram, arsenate was revealed as the dominant species in the groundwater. Speciation calculations in PHREEQC supported the conclusion that arsenate was the dominant species in most water samples. No wells indicated seawater intrusion and some plotted in the freshening region of the Piper diagram. Wells that plotted in the freshening area of the Piper diagram were more likely to have higher arsenic concentrations. Bivariate analysis, principal component analysis, non-metric clustering and Piper plots failed to show a difference in the measured variables between the April and August samples. A positive correlation was found between specific conductance,  $\text{Na}^+$ ,  $\text{Cl}^-$  and total alkalinity and dissolved arsenic, and a negative correlation was found between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and dissolved arsenic. No correlation was observed between dissolved arsenic and Fe or Mn. Multivariate statistics indicated a correlation between the presence of major ions and the dissolved arsenic concentrations.

The positive correlation between alkalinity and dissolved arsenic, negative correlations between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and dissolved arsenic, and no correlations with Fe or Mn is consistent with an arsenic release through a desorption process. The presence of dissolved carbonate and bicarbonate is indicative of a chemical weathering process, which could lead to arsenic desorption, and the charge on  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions can facilitate the adsorption and desorption of dissolved arsenic. Since the Chuckanut sandstone had the highest dissolved arsenic concentrations, a chemical weathering process is most likely occurring within this stratigraphic layer.

No wells in this study exceeded the SMCL (Secondary Maximum Contaminant Level), nor did any wells experience a statistically significant fluctuation in chlorides between the April and August sampling seasons. When the major ions were plotted on a

Piper diagram, all of the wells plotted in either the “fresh” or the “freshening” part of the diagram; none of the samples plotted in the “intruding” or “intruded” area. Because there was no evidence that the wells in my study were experiencing seawater intrusion, the salts must be released from another source.

This relationship between major ions and dissolved arsenic was supported by the multivariate statistical tests principal component analysis and linear discriminant analysis. The principal component analysis successfully classified arsenic into high and low groups, and once trained with a subset of the data, the linear discriminant analysis divided arsenic into high or low categories. The relationship between the major ions and dissolved arsenic can be interpreted from a Piper diagram when the high dissolved arsenic concentrations ( $[As] > 0.07 \text{ mg/L}$ ) is color coded. These water samples all plotted in the freshening region of the Piper diagram. Because chlorides and dissolved arsenic were positively related, specific conductance, used as a proxy for chlorides, could be used as a rough indicator for arsenic.

## **Acknowledgements**

I would like to thank the following people and institutions whose support made this project possible: my graduate advisor Dr. Robert Mitchell for his continual motivation and direction; my committee members Dr. Scott Babcock, Dr. Robin Matthews, and Doug Kelly; Aspect Consulting for allowing me to partner with their firm on this research project; Whatcom Health Department for providing funds to complete the water analysis; the GK-12 program sponsored by the National Science Foundation and WWU that provided both funding and enriched my educational experience; and the Geology Department at Western Washington University and Whidbey Island Rock and Gem Club. I would like make a special acknowledgement to field assistants Pete Kairis, Laurel Kaminski, Chris Ward, Carrie Donnel, Casey Hanell, and Kristie McNeill; Clark Blake for his assistance and knowledge; and to my parents for their encouragement throughout the entire project.



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# 1 Introduction

Lummi Island is an 8.8 square mile elongated island located in the Puget Sound six miles west of Bellingham, Washington (Figure 1). Lummi Island has a relatively small population of approximately 900 permanent and 1500 seasonal residents. The northern and southern halves of the island vary topographically and geologically due in part to an east-west trending normal fault with a 60° north dip that separates these two halves. My study area focuses on the northern half of the island which consists of gently rolling hills, wetlands and a few ephemeral streams (Figure 2). The north half of the island has a low topography with a maximum elevation of 362 feet and contains the majority of the island's residents. Groundwater is used as the primary freshwater source. The southern half of the island has a steep topography with a maximum elevation of 1692 feet. It is excluded from my study because surface water is used as the primary freshwater source (Sullivan, 2005).

Lummi Island is experiencing two different types of groundwater contamination: arsenic and seawater intrusion. In a four year study (1989-1993), the Whatcom County Health Department monitored public wells for arsenic and major ion concentrations. The Health Department identified several public wells with levels of arsenic and chlorides that exceeded the drinking-water standards (Whatcom County Health Department, 1994). The arsenic concentrations varied both spatially and temporally.

Arsenic is a naturally occurring heavy metalloid which is found in groundwater in both oxidizing and reducing environments (e.g., Gotkowitz, 2003; Smedley and Kinniburgh, 2001). It is a known carcinogen and poses health risks when consumed above acceptable limits. Among the adverse health effects are skin, bladder, and kidney cancers (Fazal et al.,

2001). Arsenic is toxic only when ingested; therefore, contaminated waters are an acceptable source for nonpotable uses (U.S. EPA, 1992).

The Environmental Protection Agency (EPA) defines the maximum contaminant level (MCL) for arsenic in drinking water as 10 µg/L (U. S. EPA, 2001). This concentration was implemented in January of 2006, reducing the MCL from the previous limit of 50 µg/L. The arsenic levels in many of the Lummi Island wells that previously did not exceed the MCL now exceed the newer limit of 10 µg/L (Miller, 2005).

Some aquifers on Lummi Island are also susceptible to contamination from seawater intrusion. If water removal is greater than aquifer recharge, wells may experience seawater intrusion as the interface between less dense freshwater and denser seawater moves upwards. The ions contained in seawater pollute freshwater and make it unpalatable (Dion and Sumioka, 1984). Seawater intrusion is typically measured by chloride values since chloride is a relatively non-reactive, highly mobile ion contained within seawater (Dion and Sumioka, 1984). The EPA classifies chloride as a nuisance contaminant and has set a secondary maximum contaminant level (SMCL) at 250 mg/L (U.S. EPA, 1992). A well is contaminated if it has chloride levels greater than 99 mg/L or if it is within 0.5 miles of a chloride contaminated well (Dion and Sumioka, 1984). Between 1989 and 1993, the Whatcom County Health Department sampled 75 wells for major ion analysis and found 9 to exceed the SMCL (Whatcom County Health Department, 1994).

A study of groundwater geochemistry is important in assessing the water quality on Lummi Island. Currently, the method of mobilization of the naturally occurring arsenic and the extent of the seawater intrusion is not fully understood (Whatcom County Health Department, 1994; Aspect, 2006).



## 2 Background

### 2.1 Lummi Island Geology

Freshwater on the northern half of Lummi Island is stored in bedrock and unconsolidated glacial sediments. The bedrock units consist of the Point Migley, Fidalgo Ophiolite and Lummi Formation terranes; and sandstone belonging to the Padden Member of the Chuckanut Sandstone (Figure 3; Figure 4; Figure 5; Blake, 2007). The three accreted terranes comprising the basement rock of Lummi Island differ in origin, lithology, and chemical composition. They are inferred to underlie the entire region and to be unconformably overlain by the Chuckanut sandstone (Lapen, 2000; Sullivan, 2005). Deposited above the Chuckanut sandstone is a sequence of Pleistocene glacial sediments (Figure 4). Wells are generally completed in the Pleistocene glacial deposits in the south end of the island and the Chuckanut sandstone in the north. A few wells in the southeast were completed in accreted terranes (Figure 3; Lapen, 2000; Blake, 2007; Easterbrook, 1971).

The Point Migley terrane outcrops along the northern tip of the island (Figure 5). These rocks are Jurassic in age and consist of pillow basalts, radiolarian chert, ironstone, and limestone. There is an unconformity between the Point Migley terrane and the Chuckanut Sandstone (Blake, 2007).

The Lummi Formation, also known in previous studies as the rocks of the Decatur terrane, outcrops in the south central region of the study area. These are oceanic rocks with a stratigraphic sequence of pillow basalt, metachert, metagreywacke, and metaslate (Lapen, 2000; Blake, 2007). Some pillow structures are visible in the metabasalt (Lapen, 2000). It is hypothesized that the rocks of the Point Migley terrane and the Lummi Formation are

separated by an east-west trending fault in the central northern island; however, at present no conclusive data have confirmed this fault (Figure 5; Blake, 2007). The Fidalgo Ophiolite sequence is located in the southern half of Lummi Island. This sequence is separated from the northern half of the island by an east-west trending fault that separates the topographically different halves of the island (Figure 5). This terrane is a sequence of gabbro and plagiogranite, intrusives and extrusive basalt, siliceous argillite, and ophiolitic breccia, possibly underlain by peridotite (Caulkin, 1959; Lapen, 2000; Blake, 2007).

In order to retain consistency with local data and past studies, I will refer to the Point Migley, Lummi Formation and Fidalgo Ophiolites as one unit called "greenstone." Only a few wells in the region are completed in the greenstone due to the low productivity of the aquifer. The unit has a specific capacity of 0.03 gpm/ft and an average yield of 3 gpm according to drillers' logs (Aspect, 2006). The greenstone aquifer has no primary porosity and is limited to fracture flow (Aspect, 2006).

The Padden Member of the Chuckanut Sandstone, deposited approximately 50 mya in the mid to late Eocene, unconformably overlies the greenstone (Figure 4; Johnson, 1982; Sullivan, 2005). The Padden Member is composed of crossbedded arkosic sandstone with interbedded mudstones, greywackes, shales, and conglomerates. Sulfur minerals, coal, and pyrite are also present (Carroll, 1980, Easterbrook, 1971; Blake, 2007). This unit is continental in origin and was deposited in high energy ancient streams and large floodplains. Fossils are abundant in the shale layers and indicate a more tropical climate (Easterbrook, 1973; Sullivan, 2005; Aspect, 2006).

The Padden Member of the Chuckanut Formation is of varying thickness, with a maximum thickness of approximately 330 ft on Lummi Island (Easterbrook, 1971). The

formation has been folded during tectonic activity into anticlines and synclines generally trending northwest-southeast, plunging northwest (Sullivan, 2005; Aspect, 2006). The greenstone beneath is also inferred to be folded (Aspect, 2006). The sandstone crops out in several places throughout Lummi Island along the northwest shoreline.

The Chuckanut sandstone has limited primary porosity and is assumed to be highly fractured. The sandstone unit has a specific capacity of 0.2 gpm/ft and an average yield of 10 gpm according to drillers' logs (Aspect, 2006).

The Pleistocene glacial deposits form the youngest aquifers on northern Lummi Island. These units vary in thickness with from 0 to 295 ft (Aspect, 2006; Lapen, 2000) and are composed of sand, silt, clay, gravel, and boulders (Schmidt, 1978; Easterbrook, 1971; Easterbrook, 1973). Two distinct aquifers and two aquitards have been differentiated within the glacial deposits (Figure 4; Aspect, 2006). These aquifers and aquitards are defined by the sediment type and size deposited during glacial advances and retreats in the Pacific Northwest. The average specific capacity in the aquifers is 1.8 gpm/ft and the average yield is 12 gpm according to drillers' logs (Aspect, 2006).

The deepest aquifer is composed of undifferentiated sediments resulting from several pre-Vashon glacial advances and retreats. These include the Double Bluff drift, the Whidbey Formation, the Possession drift, and the floodplain and fluvial sediments of the Olympia Stade. This aquifer is coarse grained and unconsolidated (Aspect 2006).

The glacial deposits of the Double Bluff drift and the interglacial Whidbey Formation, and glacial Possession Drift are not exposed on Lummi Island; however, the Double Bluff drift and Whidbey Formation are identified south of Whidbey Island, and the Possession Drift is exposed on Whidbey Island (Easterbrook, 1994). Although these deposits are not

exposed on Lummi Island, they are inferred to be present in the subsurface beneath Lummi Island. It is likely that the deep wells on Legoe Bay Road draw water from this glacial matrix (Figure 2; Figure 3; Figure 4; Aspect 2006). The sediments of the Double Bluff drift and Whidbey Formation were deposited between 250,000 and 100,000 years ago, and the Possession Drift was deposited 80,000 years ago (Easterbrook, 1994). Comprising the more recent portion of the lower glacial aquifer is the floodplain and fluvial sediments of the Olympia Stade interglacial period. The Olympia Stade occurred between 60,000 and 15,000 years ago and preceded the Fraser glaciation. These sediments are composed of sediments ranging from silt and clay sized particles to sandy gravels (Troost, 1999).

The deep, coarse grained aquifer is capped by a fine grained aquitard deposited during the Vashon Stade of the Fraser Glaciation. These sediments were deposited in a low energy environment when rivers and streams entered into a proglacial lake and released their sediment load. The proglacial lake was created when an arm of the continental glacier blocked the Strait of Juan de Fuca. The sediments are composed primarily of silts and clays with a few lenses of sand and dropstones (Easterbrook, 1962; Easterbrook, 1973). Drillers' well logs have identified these deposits as the Cherry Point Silt which is exposed to the north of Lummi Island (Easterbrook, 1973).

Above the fine grained aquitard is the coarse grained Esperance Sand aquifer composed of glacial outwash from the Vashon Stade. The sediments were deposited between 18,000 and 13,000 years ago during the last advance of the continental glacier that reached as far south as Lummi Island (Easterbrook, 1976). The outwash was deposited in front of the glacier during the advance as meltwater carried a sediment load of sandy gravel, coarse to

pebbly sand, gravels, and silts and clays (Lapen, 2000). The sediments were then compacted and consolidated as they were overridden during glacial advance (Easterbrook, 1976).

Two glacial deposits compose the youngest aquitard: Vashon Till and glaciomarine drift (GMD). The Vashon till, deposited during the Vashon Stade, is comprised of unsorted sediments ranging in size from clays to boulders (Lapen, 2000). The sediments are deposited beneath the glacier and compacted by its overriding weight. The GMD consists of two units, Bellingham and Kulshan, and was deposited between 13,600 and 11,000 years ago during the Everson Interstade. These sediments were deposited in a marine environment sourced from overlying glacial ice. The majority of the units are unsorted pebble and boulder drop stones in a silt matrix with some regions of silts and clays (Easterbrook, 1971).

## **2.2 Water Quality**

### **2.2.1 Arsenic**

#### *2.2.1.1 Arsenic Chemistry*

Arsenic can be introduced into groundwater from both natural and anthropogenic sources; however, the main source of arsenic in groundwater are naturally occurring arsenic-bearing minerals and arsenic adsorbed to oxides, sulfides, clay minerals, and organic constituents (Smedley and Kinniburgh, 2001). Arsenic is present in over 200 minerals, often as a substitute anion in sulfide minerals, but is most concentrated in the minerals arsenopyrite, realgar, and orpiment (Smedley and Kinniburgh, 2001). Arsenic occurrence is most common in aquifers with relatively slow groundwater movement where there is ample time for water-rock interactions. Anthropogenic sources tend to be localized, but they can also be transported through an aquifer by groundwater flow. These sources include, but are

not limited to, acid mine waters, agricultural pesticides, and industrial brines (Smedley and Kinniburgh, 2001; U.S. EPA, 2003).

In groundwater, arsenic is found in its inorganic forms as the oxyions arsenite (III) and arsenate (V). As (III) is more commonly found in groundwater since it is prevalent in anaerobic environments; it is also more toxic than As (V) (Bratby, 2006). Arsenic is mobile under both oxidizing and reducing conditions, and speciation is influenced by pH and Eh. Arsenite can occur as the species of  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3^-$ , or  $\text{HAsO}_3^{2-}$ , and arsenate occurs as  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , or  $\text{AsO}_4^{3-}$  (Smedley and Kinniburgh, 2001).

Arsenic can be mobilized through two geochemical processes, adsorption and desorption, and precipitation and dissolution (Hinkle and Polette, 1999). Adsorption and desorption of dissolved arsenic may be controlled by pH, redox reactions, the presence of competitive ions such as bicarbonate, phosphate, silicate, and organic matter, and atomic structural changes of the adsorbing substrate (Gotkowitz, 2003; Smedley and Kinniburgh, 2001; Hinkle and Polette, 1999). Precipitation and dissolution reactions may be controlled by pH, redox reactions, and the chemical composition of the groundwater and aquifer matrix. Since water-rock interactions will consume  $\text{H}^+$ , the pH of groundwater will increase with residence time in an aquifer (Hinkle and Polette, 1999). The redox potential is usually controlled by inorganic elements including available oxygen, carbon, nitrogen, sulfur, and iron; however, microorganisms can also control reduction rates (Smedley and Kinniburgh, 2001).

In groundwater, iron, aluminum, and manganese oxides are closely associated with arsenic concentrations (Vlassopoulos et. al., 2007; Hinkle and Polette, 1999). At near neutral pH, arsenate will be strongly sorbed to the metal oxides; as pH increases, arsenate will

desorb from the mineral oxide surface and be released. Arsenite will adsorb to the mineral oxide surfaces less strongly than arsenate, but it will behave similar to arsenate between pH 6 and 9. Arsenic will adsorb to other mineral surfaces, such as clay minerals, but these adsorption and desorption reactions are not as well characterized (Smedley and Kinniburgh, 2001; Hinkle and Polette, 1999).

The reduction of arsenate to arsenite can mobilize arsenic. When arsenate is reduced to arsenite, the species becomes less strongly sorbed to the mineral surface and may be released into the groundwater. Adsorption and desorption processes can also be facilitated by dissolved bicarbonate, phosphate, silicate, and carbon that compete for adsorption sites. The positively charged calcium and magnesium ions may promote the adsorption of the negatively charged arsenate.

Arsenic can be released through dissolution when arsenic bearing minerals are reduced. This may occur when iron oxide is reduced and dissolved. Arsenic may also be precipitated out of solution with iron oxides in oxidizing conditions (Vlassopoulos et. al., 2007; Hinkle and Polette, 1999).

In areas of arsenic contamination, there is a high amount of spatial variability of the contaminant due to heterogeneities within the aquifer; therefore, arsenic concentration measurements from one well may not be indicative of concentrations in a neighboring well (Ayotte, et al. 1999; Vlassopoulos et. al., 2007). In most aquifers only a small number of wells are likely to be contaminated, making it necessary to test each well within the aquifer (Smedley and Kinniburgh, 2001).

Arsenic concentration in bedrock varies depending greatly on mineral composition of the rock. Generally, concentrations in igneous rocks are low (1.5 mg/kg); however,

greenstone averages about 6.3 mg/kg. Sedimentary rocks have arsenic values slightly above terrestrial sediments, commonly between 5 and 10 mg/kg. Sandstone is typically low with a mean of 4.1 mg/kg, shale averages between 3 and 15 mg/kg, and coal is highly variable with concentrations ranging from 0.3 to 35,000 mg/kg. Unconsolidated sediments range from 3 to 10 mg/kg, with the higher values correlating with the presence of iron and pyrite (Smedley and Kinniburgh, 2001). High dissolved arsenic concentrations in groundwater frequently occur when source rock have arsenic concentrations between 1-20 mg/kg (Smedley and Kinniburgh, 2001).

#### *2.2.1.2 Lummi Island Arsenic Chemistry*

Between 1989 and 1993, the Whatcom County Health Department sampled 24 Lummi Island wells for arsenic analysis and found that 8 of these wells exceeded the 50 µg/L MCL (Whatcom County Health Department, 1994). The arsenic concentrations in many of the Lummi Island wells that did not exceed the previous MCL do exceed the newer limit of 10 µg/L (U.S. EPA, 2001). At the new MCL of 10 µg/L, 13 of the 24 wells in the Whatcom County study exceeded EPA standards. The highest concentrations were within wells completed in the Chuckanut Sandstone, and no link was found connecting past land use with current contamination (Whatcom County Health Department, 1994). It was hypothesized that pyrite within the sandstone was a possible arsenic source. The source of the arsenic and the conditions under which it is mobilized were not investigated (Whatcom County Health Department, 1994).

A later study conducted by Aspect Consulting (2006) also found high concentrations of arsenic within the Chuckanut (Aspect, 2006). Due to the widespread distribution of



arsenic and absence of a clear relationship between concentration and depth, Aspect concluded the arsenic was naturally occurring. I partnered with Aspect and sampled 39 wells on Lummi Island in the spring of 2006 and 44 wells in the fall of 2006. Of the wells sampled, approximately 50% were within the bedrock aquifers and 50% were within the unconsolidated aquifers (Aspect, 2006). Seventy percent of the wells completed in the Chuckanut had arsenic concentrations above the MCL with a median value of 32  $\mu\text{g/L}$ . In 27% of the wells completed in the unconsolidated aquifer exceeded the MCL with a median of 4  $\mu\text{g/L}$ . The wells in the unconsolidated aquifers with elevated arsenic concentrations were located near sandstone aquifer boundaries. It was hypothesized that the contaminated water from the sandstone is recharging the sediments; however, neither the glacial till nor the greenstone were excluded as possible arsenic sources (Aspect, 2006). The concentration of arsenic within the aquifers was highly variable between the two 2006 sampling seasons and the 1994 study (Aspect, 2006).

## ***2.2.2 Seawater Intrusion***

### *2.2.2.1 Seawater Intrusion Background*

Freshwater is less dense than saltwater and rests on saltwater in a lens-like shape. This lens mimics topography in the subsurface with approximately a 1 to 40 ratio between the elevations of the freshwater above sea level to depth below sea level under static water conditions (Freeze and Cherry, 1979). Models such as the Ghyben-Herzberg method use this ratio (1:40) to diagram the freshwater interface (Figure 6). Because seawater and freshwater are miscible there is not a sharp boundary separating the waters, rather there is a mixing zone. This region is not stationary and can migrate vertically due to seasonal groundwater

fluctuations and tidal influences (Figure 7). Moreover, groundwater discharge to the sea can displace the interface seaward. Typically the interface depth is lower in the fall and winter months when aquifer recharge is the greatest, and a shallower depth in the spring and summer during the drier months when there is a greater water demand (Kelly, 2008). This interface can also migrate vertically upwards due to upconing. In this situation, there is a drawdown of the water table and a subsequent upward motion of the mixing zone interface due to well pumping (Figure 7; USGS Fact Sheet 057-00, 2000).

Typically, three processes occur during seawater intrusion: 1) as seawater intrudes, chloride concentrations increase at the contaminated locations; 2) wells at similar depths have a relationship between contaminant and distance to shoreline; and 3) at a specific location chloride concentrations will increase with depth (USGS Fact Sheet 057-00, 2000). However, this model is based on homogeneous materials and may not represent the seawater intrusion within more complex aquifers (Kelly, 2008). Once seawater has intruded an aquifer, it is difficult to flush the seawater out of the system. This is partly due to increased dependence on the water supply by local inhabitants and partly due to the slow motion of groundwater within an aquifer (Dion and Sumioka, 1984). Therefore, prevention is the best solution to seawater intrusion.

#### *2.2.2.2 Seawater Intrusion on Lummi Island*

Sullivan (2005) created a stratigraphic and hydrostratigraphic model of the study area using data collected from 130 driller's well logs, seasonal water level measurements, groundwater chemistry analysis, and well head elevation and positions. Using stratigraphic and physical measurements, Sullivan modeled 12 aquifers and defined their hydraulic properties. With

water chemistry analysis, Sullivan identified wells with elevated salt ions indicative of seawater intrusion. He also provided background chloride reading for several wells and found an average of 40 mg/L for the northern half of the island. Most of the wells that were identified as contaminated in Sullivan's study were within shallow beach-deposit aquifers near the shoreline.

A study completed by Aspect Consulting (2006) expanded upon Sullivan's groundwater (2005) study, further investigating the groundwater flow within the aquifers and the relationship between aquifer type, depth of well completion, and well location with chloride concentrations. I partnered with Aspect and tested 39 wells in the spring and 44 in the fall. These wells included some of the wells that were previously tested by Sullivan. All wells were tested for chloride concentrations, and 17 were tested for major ion analysis. The geochemical analysis from both the spring and fall 2006 sampling periods indicated that the chloride concentrations were highly variable with well completion depth, location, groundwater elevation, and season (Aspect, 2006). This indicates the freshwater interface was more complex than a 1 to 40 ratio; therefore, a simplified model such as the Ghyben-Herzberg model was not used. This supports a heterogeneous groundwater flow system influenced by pumping and fracture flow. This is consistent with other nearby islands, such as Guemes Island to the South, in which seasonal fluctuations have also been observed (Kahle et al., 1995).

### **3 Research Objectives**

The purpose of my study was to determine the geochemical, physical, and seasonal influences on both arsenic and seawater intrusion in the groundwater of Lummi Island, Washington.

I collected water samples from wells distributed throughout northern Lummi Island for geochemical analysis. I used statistical tools to identify any correlations between groundwater chemistry parameters, aquifer matrix, physical groundwater characteristics, and seasonal differences in measurements. I investigated the species of aqueous arsenic by plotting the pH and Eh from field measurements on an arsenic species stability diagram and tested the concentrations of minerals in the bedrock using whole rock analysis. I also investigated seawater intrusion by plotting the major ions on Piper diagrams to determine the distribution and degree of seawater intrusion. The information gathered by my research will be valuable in assessing the sustainability of the Island's finite freshwater resources.

## 4 Methods

### 4.1 Water Sampling

I partnered with Aspect Consulting of Bainbridge Island, Washington (Aspect Consulting) to collect my data. The sampling wells in Northern Lummi Island were identified through voluntary property owner participation. Property owner participation was gained through a public workshop on January 28, 2006 and personal communications (Aspect, 2006). Aspect chose the wells to incorporate a representative sample of all aquifer types throughout the island. Some of these sites included wells sampled in Sullivan's (2004) study. Water samples were collected during April and August of 2006. Thirty-six property owners allowed access to their wells in April, and 41 property owners allowed access in August.

At each well, we measured well head elevation, depth to water level, temperature, dissolved oxygen (DO), pH, Eh, and specific conductance (SC). In addition, we collected a 1 liter water sample for a standard groundwater chemical analysis. Temperature, DO, pH, Eh, and SC were measured using a YSI 556 Multi-Parameter Field Meter (YSI Handheld Multiparameter 556, YSI Incorporated). The meter was calibrated at the beginning of each day from the stock standards for DO, pH, ORP, and SC. To reduce atmospheric contamination, all readings were taken in a flow-through cell, and the water was sampled before a holding tank whenever possible. No samples were taken after the use of a water softener. Measurements were recorded every two minutes beginning after the well pump was first engaged and ending when the DO was within 2% of the previous reading. Once the readings stabilized, the sample bottles were filled and labeled using well number, time of

collection, date, and well owner. These bottles were stored on ice in a cooler for no more than a week.

Elevation and geographic location were measured at each well using a handheld GPS. The GPS measurements were taken only during the first sampling period and were used solely for a general approximation of well head elevation and location. A second set of measurements were taken with a survey grade GPS by Wilson Engineering of Bellingham (Wilson Engineering, LLC).

Field notes were taken at each location. These notes included the location of the well with respect to structures and any abnormalities in data collection. In addition to these parameters, the particular spigot from which water samples were taken was noted. Water samples were taken at the spigot located closest to the well head.

Prior to sampling, water levels were recorded two times at each location with a minimum of 5 minutes between each measurement. A third measurement was taken if there was more than 0.02 ft difference between the first two measurements. If static water levels were not attained within a 30 minute time period, it was recorded in the field notes and excluded from the data set.

The water samples were sent to AmTest Laboratories in Redmond, Washington (AmTest Inc.) to be analyzed. All samples were tested for total As, dissolved As, and Cl<sup>-</sup> (36 samples in April and 41 samples in August). Analysis for additional ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Br<sup>-</sup>) and dissolved metals (Fe, Mn) was performed on specified samples. Including both the April and August sampling seasons, 41 wells (17 in April and 24 August) were sampled for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Fe, and Mn, 10 wells (6 in April and 4 in August) for Br<sup>-</sup>, and 8 wells (7 in April and 1 in August)

for  $\text{PO}_4^{3-}$ . If the concentration of any analyte fell below the detection threshold of the instrument, I set the value in my data set equal to one half of the detection limit of the instrument to prevent null values in my statistical analysis. To accommodate for the censored values, only non-parametric, rank-based statistical methods were used in my analyses (Helsel and Hirsch, 1993).

## **4.2 Whole Rock Analysis**

I collected five rock samples from outcrops on Lummi Island for whole rock analysis (Figure 8). Four samples were taken from the Chuckanut Formation: a shale, a conglomerate, a sandstone, and coal. One additional sample was taken from the greenstone. These samples were crushed and powdered until the grains were clay sized. The samples were sent to ALS Chemex Labs in Vancouver, B.C. (ALS Chemex) for mineral composition analysis.

ALS Chemex Labs tested the rocks for major oxides, trace and ultra trace elements, carbon, and sulfur using atomic emission spectroscopy and atomic emission mass spectrometry, inductively coupled plasma mass spectroscopy, infrared spectroscopy, and Leco sulfur analyzer, respectively. Loss on ignition was performed using a thermal decomposition furnace.

## **4.3 Plotting Arsenic Speciation in Groundwater**

The aqueous species of dissolved arsenic in each water sample were determined by plotting the Eh and pH measurements on an Eh-pH diagram (Smedley and Kinniburgh, 2001). Using PHREEQC software (PHREEQC, Version 2), I calculated the concentrations

of each arsenic species in equilibrium at those Eh-pH conditions. One diagram was created with the April sampling data (n=36), and one diagram was created with the August sampling data (n=41).

#### **4.4 Seawater Ion Plotting with Piper Diagrams**

I used Piper diagrams to characterize the type of water on Lummi Island. For each of the water samples tested for the naturally occurring major seawater ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$ ), I input the relative ion concentrations into AquaChem software (AquaChem, 2005) and used it to create Piper diagrams. Using the Piper diagram I visually identified each water sample as freshwater, mixing, seawater, freshening, and intrusion, using established Piper diagram interpretations. I also created separate diagrams for each rock type with the samples color coded by April/August sampling period and samples color coded by arsenic concentration.

#### **4.5 Statistical Analysis**

##### ***4.5.1 Exploratory Analysis***

Using the statistical program R (R Development Core Team, 2007), I tested for significant correlations between all measured variables at each well site using Kendall's Tau (McBean and Rovers, 1998). My null hypothesis was that there was no statistically significant relationship between any physical or geochemical measurement. Linear diagrams and box plots were used to depict relationships. In this and all following tests, total alkalinity was used in lieu of carbonate and bicarbonate because the two ions are auto-correlated.



#### **4.5.2 Seasonality**

I used multivariate statistics to determine if there was a statistical difference in the measured variables between the April and August 2006 sampling periods. Two multivariate statistical tests were performed: principal component analysis (PCA) and non-metric clustering using Riffle. These tests were performed in the R statistical program (McBean and Rovers, 1998; Matthews and Hearne, 1991).

##### *4.5.2.1 Principal Component Analysis*

I merged the April and August 2006 data sets into a single spreadsheet. For this test, I excluded any wells in the merged dataset for which complete ion analysis was not performed. This totaled 41 samples (17 samples collected in April, and 24 samples collected in August). Using R, I ran PCA on the merged data set using the concentrations of the major seawater ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$ ) as the cluster variables. The correlation matrix was specified in R's "princomp" command. Variance, variable loading on principal component one and two, and ordination by sampling season were graphed. If the data set failed to ordinate into April and August clusters, then it was determined that there was no difference in the measured variables between the seasonal data sets.

#### 4.5.2.2 *Non-Metric Clustering*

The non-metric clustering algorithm Riffle (Matthews and Hearne, 1991) was performed on the merged dataset using all geochemical variables except total As,  $\text{PO}_4^{3-}$ , and  $\text{Br}^-$ . The total As variable was removed because it was redundant with dissolved As. Phosphate and bromide were excluded because only 8 wells were sampled for phosphate and 10 for bromide. Riffle was programmed to cluster the dataset into two groups using the two strongest variables. Since non-metric clustering uses a stochastic algorithm, it was run five times and the proportional reduction in error (PRE) scores were averaged among all five runs. A PRE score is the measure of how well variables can be predicted if the cluster membership is known. A chi-squared test was used to determine if the data successfully clustered into April and August groups.

#### 4.5.3 *Mobilization of Arsenic*

I used multivariate statistics to determine if the measured variables in the merged dataset (April and August 2006) clustered into groups with similar arsenic concentration ranges. Prior to this analysis, the arsenic concentrations were separated into two ranges. The ranges were defined by plotting all the arsenic concentrations and designating the break point as the point prior to the obvious spike (Figure 9). The two range designations were low (<0.07 mg/L) and high (>0.07 mg/L) dissolved arsenic. Three multivariate statistical tests were performed: principal component analysis (PCA), linear discriminant analysis (LDA), and non-metric clustering using Riffle (McBean and Rovers, 1998; Matthews and Hearne, 1991). These tests were performed using the R statistical program.

#### 4.5.3.1 *Principal Component Analysis*

The PCA was run on the merged data set using the major seawater ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$ ) as the cluster variables. Variance, variable loading on principal component one and two, and ordination by sampling season were graphed. The correlation matrix was specified in R's "princomp" command. These graphs were visually analyzed for significant clusters in the data set. If the data set failed to ordinate into high and low arsenic concentration clusters, then it was determined that there was no difference in the measured variables by arsenic concentration.

#### 4.5.3.2 *Linear Discriminant Analysis*

I trained the LDA with the April dataset and used it to predict the dissolved arsenic concentrations (high or low) in the August dataset. The prior probabilities for the high and low dissolved arsenic classifications were calculated as the percentage of rows of each classification in the total April dataset. A chi-squared test was used to determine if the classifications were correct. This process was repeated using the August data to train the LDA to predict dissolved arsenic classifications for the April data set. In order to test the strength of the results, I randomized my dataset and used the LDA to predict dissolved arsenic concentrations using a training model that was created from half of the randomized set.

#### 4.5.3.3 *Non-Metric Clustering*

Non-metric clustering analysis was run on the merged dataset using all geochemical variables except total As, dissolved arsenic,  $\text{PO}_4^{3-}$ , and  $\text{Br}^-$ . The total and dissolved As variables were removed because arsenic was the classifier in this statistical test. In addition,  $\text{PO}_4^{3-}$  and  $\text{Br}^-$  were excluded from this analysis because only a few wells (<7 per season) were tested for these elements. Riffle was programmed to cluster the dataset into two groups using the two strongest variables. Since non-metric clustering uses a stochastic algorithm, it was run five times and the PRE scores were averaged among all five runs. A chi-squared test was used to determine if the data successfully clustered into high and low arsenic groups.

## 5 Results

### 5.1 Water Sampling

The median dissolved arsenic concentration for the merged dataset, was 0.007 mg/L, with a maximum of 0.57 mg/L (Figure 10; Table 1; Table 2). The highest dissolved arsenic concentrations were found in the Chuckanut Sandstone (Figure 11). The median chloride concentration was 18 mg/L, and the minimum and maximum were 7.4 mg/L and 160 mg/L, respectively (Figure 12; Table 1; Table 2). The test results for carbonate, iron, and bromine were mostly below detection limits. Of the 41 wells sampled for Fe, only 10 wells had Fe concentrations above detection limits (Table 1; Table 2).

### 5.2 Whole Rock Analysis

All concentrations of arsenic, iron as  $\text{Fe}_2\text{O}_3$ , and manganese as MnO, varied between samples and the two rock types (Table 3). The greenstone had the highest  $\text{Fe}_2\text{O}_3$  content, and the Chuckanut had the highest MnO and As content. The concentration of arsenic in the rock samples varied from 1.9 ppm in the greenstone to 20.1 ppm in the Chuckanut conglomerate; the concentration of  $\text{Fe}_2\text{O}_3$  in the samples ranged from 1.10% in the coal, to 7.23% in the greenstone; and the concentration of MnO in the samples ranged from 0.10% in the Chuckanut Sandstone to 0.77% in the Chuckanut coal (Table 3).

### 5.3 Plotting Arsenic Speciation in Groundwater

Arsenate, specifically  $\text{HAsO}_4^{2-}$ , was the dominant species in the groundwater samples when samples were plotted in an Eh-pH arsenic stability diagram. In the April sampling

season, 30 samples plotted within the  $\text{HAsO}_4^{2-}$  area of the diagram and 6 samples plotted within the  $\text{H}_3\text{AsO}_3$  area (Figure 13). In the August sampling season, 28 samples plotted within the  $\text{HAsO}_4^{2-}$  area, 8 samples plotted within the  $\text{H}_3\text{AsO}_3$  area, and 5 samples in the  $\text{H}_2\text{AsO}_4^{2-}$  area (Figure 14). Overall, 63 samples plotted as arsenic (V) and 14 samples as arsenic (III), which is also apparent in the PHREEQC calculations (Table 4; Table 5).

#### **5.4 Seawater Ion Plotting with Piper Diagrams**

In the Piper diagram that included both April and August samples, no data points tested for major ions fell within the “intruding” area of the diagram (Figure 15). Six samples in April and 8 in August were in the “freshening” area of the diagram; these samples were more likely to have higher arsenic concentrations (Figure 16; Figure 17). Samples from all rock types fell within the “freshening” area. No seasonal trend in data points was visible between the April and August sampling periods (Figure 15).

Of the wells tested for complete seawater ions, four wells, 226, 232, 245, and 247, had Cl levels that exceeded the conservative background level of 40 mg/L (Figure 12). However, when analyzing the ion ratios on a Piper diagram, none of these four wells indicated intrusion. Bromide concentrations in these wells were not elevated and therefore did not indicate intrusion.

In the wells that did not exceed the background level of 40 mg/L there is also no evidence of seawater intrusion. All of the water samples tested for ions plotted in April and August plotted in either the “fresh” or “freshening” area of the Piper diagram. The wells that were tested for bromide similarly did not indicate seawater intrusion.

No specific seasonal trend can be identified among the data. Wells plotted on the Piper diagrams did not show a consistent directional shift between the seasons. Therefore, it can be interpreted that there is not a seasonal influence in the major ion distribution.

## **5.5 Statistical Methods**

### **5.5.1 Exploratory Analysis**

Among all of the wells sampled, total As, dissolved As, specific conductance, and  $\text{Cl}^-$  were significantly correlated with one another (Table 6; Table 7). Dissolved As was significantly positively correlated with specific conductance,  $\text{Na}^+$ ,  $\text{Cl}^-$ , P, and alkalinity, and negatively correlated with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The strongest correlations with arsenic species were between total arsenic and specific conductance (April:  $P=7.49 \times 10^{-6}$ ,  $\tau=0.53$ ; August:  $P=2.34 \times 10^{-6}$ ,  $\tau=0.52$ ) and between dissolved arsenic and specific conductance (April:  $P=1.38 \times 10^{-5}$ ,  $\tau=0.53$ ; August:  $P=2.95 \times 10^{-5}$ ,  $\tau=0.46$ ; Figure 18). In the merged data set, iron or manganese did not significantly correlate with total or dissolved arsenic. These correlations were consistent for both the April and August sampling seasons (Figure 19; Figure 20).

### **5.5.2 Seasonality**

#### **5.5.2.1 Principal Component Analysis**

In the merged data set, the first two principal components described 62.6% of the variance in the data (Figure 21, Table 8). Principal component 1 was strongly correlated with  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$ , and principal component 2 was strongly correlated with  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,

and total alkalinity (Figure 22). However, the PCA failed to ordinate by sampling season (April and August; Figure 23). These two categories were not distinct in the loadings plot, and considerable overlap occurred.

The randomized merged data set failed to cluster and did not ordinate by sampling season supporting the significance of the non-random clustering. The first two principal components in the randomized set described 45.6% of the variance, with 24.3% of the variance contained within in the first principal component (Figure 24; Figure 25; Figure 26; Table 9).

#### *5.5.2.2 Non-Metric Clustering*

Non-metric clustering failed to cluster the merged data into April and August groups. The PRE scores varied greatly among the five test runs, but the strongest average PRE value was only  $0.363 \pm 0.153$ . None of the runs produced clusters that significantly associated with April or August. The average chi-squared value among the runs was  $0.466 \pm 0.296$ , and the average p-value was  $0.637 \pm 0.137$  (Table 10). There is no statistical difference between the geochemical samples taken in April and August.

### **5.5.3 Mobilization of Arsenic**

#### *5.5.3.1 Principal Component Analysis*

Although the merged data set did not ordinate into April/August groups as described above, the PCA did ordinate the data set into high ( $>0.07$  mg/L) and low ( $<0.07$  mg/L) dissolved arsenic concentration groups (Figure 27). The separation between high and low



arsenic groups was controlled by principal component 1, as evidenced by the loadings plot (Figure 22). Principal component 1 was strongly positively correlated with  $\text{Na}^+$ , and  $\text{Cl}^-$  and strongly negatively correlated with  $\text{Ca}^{2+}$ . The failure of the randomized dataset to cluster successfully, as described above, supports the robustness of this ordination (Figure 28; Table 8)

#### 5.5.3.2 *Linear Discriminant Analysis*

There were 2 high and 15 low dissolved arsenic values in the April data set and 4 high and 20 low in the August dataset used for this analysis. The LDA was limited to using the arsenic values that had complete major ion water chemistry. The prior probabilities for April were 14% high and 86% low; for August they were 22% high and 78% low. Using April as the training dataset, all low values were correctly classified and two high values were misclassified into the low group (chi-squared=5.3455,  $P=0.02078$ ; Figure 29;

Table 11). When the August dataset was used as the training model, one “high” was misclassified and all other values were correctly classified (chi-squared=5.1304,  $P=0.02351$ ; Figure 30,

Table 11). The randomized dataset did not significantly classify the data into high and low groups (chi-squared=0.4,  $P=0.5271$ ; Figure 31; Table 12).

#### 5.5.3.3 *Non-Metric Clustering*

Non-metric clustering failed to cluster the merged data into high and low arsenic groups (Table 13). As described above, the PRE scores were inconsistent among the five test runs. Four of the five runs failed to produce clusters that were significantly associated with high or

low arsenic. The average chi-squared value among the runs was  $1.875 \pm 0.828$ , and the average p-value was  $0.364 \pm 0.166$  (Table 13).

## **6 Discussion**

### **6.1 Whole Rock Analysis**

Of the limited samples examined, the Padden member of Chuckanut formation had the highest arsenic content. The arsenic value in the Chuckanut conglomerate was 20.1 ppm, which is higher than the average arsenic value in sandstone of 4.1 ppm (Smedley and Kinniburgh, 2001). This measurement may indicate that the arsenic is being sourced in the conglomerate layers of the Chuckanut formation, which may account for the localized areas of increased arsenic values in water samples collected from wells completed in the Chuckanut.

A previous study (Whatcom 1994) indicated that the source of arsenic could be pyrite in the Chuckanut conglomerate. Since the Padden member of the Chuckanut sandstone unit was formed in a fluvial environment, the layers in the unit are of variable thickness and discontinuous in areas (Easterbrook, 1973). Therefore, there may be only localized areas that are the source of the arsenic in the groundwater.

Coal may be an arsenic bearing mineral within the Chuckanut and may be influential in the desorption and mobilization of arsenic through redox reactions. The small amount of coal that surrounds the coalified logs found on the island is both low in arsenic and would only introduce a minimal amount of carbon to influence geochemical reactions. Therefore, it is unlikely that this particular source of carbon is influential in arsenic release and mobilization into the aquifer. However, coal veins are known to be present in the Padden member of the Chuckanut, and these have been mapped inland as close as Bellingham and are found in some driller's well logs on Lummi Island (Sullivan, 2005).

## **6.2 Plotting Arsenic Speciation in Groundwater**

Arsenate was the dominant species in the groundwater; however the samples plotted on an Eh-pH arsenic stability diagram should only be used as a proxy for the actual species of arsenic in the groundwater. For an accurate representation of the arsenic species in the groundwater, it would be necessary to test specifically for the chemical composition of the dissolved arsenic. Because I did not test for arsenic species, the plotted samples are used only as a general representation of the arsenic species in the groundwater samples and not the precise arsenic species in each well.

## **6.3 Seawater Ion Plotting with Piper Diagrams**

Slightly elevated chlorides in some wells without any indication of intrusion could suggest chemical weathering. Because the chlorides need to be sourced from somewhere, it is possible that they are being released through geochemical reactions. The wells with elevated chlorides also tended to have elevated arsenic concentrations. This positive relationship between slightly elevated chlorides and elevated arsenic concentrations may indicate that chemical weathering also plays a role in arsenic mobilization.

No wells sampled for ions in my study indicate seawater intrusion, however, this does not rule out the possibility of intrusion of other unsampled wells in other locations on the island. Analysis of other wells by Aspect has indicated that some wells on and near Lummi Point, Point Migley, and Village Point have chlorides elevated above the SMCL of 250 mg/L and may indicate localized intrusion (Aspect, 2006). However, the wells that exceed the SMCL are less than 1,000 feet from the coastline and are limited to localized areas in shallow

beach aquifers. Some of these wells have non-intruded wells nearby. For the wells with elevated chlorides, there is no complete major ion data that could be used to designate the water as intruded or non-intruded. Without these data, it is not possible to determine if the elevated chlorides are from sources such as connate waters, water softeners, or other chloride sources, however, it is likely intrusion.

## **6.4 Statistical Methods**

### **6.4.1 Exploratory Analysis**

Arsenic mobilization in groundwater is most often associated with the presence of Fe and Mn; however, there was no statistically significant correlation between dissolved As, and Fe or Mn (Smedley and Kinneburgh, 2001). Arsenic mobilization may be related to  $\text{PO}_4^{3-}$ ,  $\text{SiO}_2$ , and  $\text{HCO}_3^-$ , as these compounds may compete for adsorption sites when arsenic is released into the groundwater (Smedley and Kinniburgh, 2001). In my study, dissolved arsenic was not correlated with silica or phosphate, but it was positively correlated to total alkalinity. The statistically significant relationship between dissolved arsenic and alkalinity may indicate that alkalinity aids in the desorption/mobilization of arsenic in the groundwater. The negative correlation between dissolved arsenic and with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  is consistent with a desorption process.

Because chlorides and arsenic are correlated, elevated chlorides in a non-intruded area may be an indicator of high arsenic. Since both arsenic and chlorides are have the highest median value in the Chuckanut, it is likely that they are being sourced in this stratum. The lack of correlation between dissolved arsenic and iron or manganese, and the positive correlation between dissolved arsenic and chlorides or alkalinity in the Chuckanut formation

may indicate that desorption related to chemical weathering could be facilitating the release of arsenic into the groundwater. The bedrock matrix (not fractures) would offer a low flow regime that would allow for weathering reactions to occur. It is hypothesized that the Chuckanut serves as a recharge zone for the glacial deposits, which may source the arsenic observed in some glacial aquifers (Sullivan, 2005).

#### *6.4.1.1 Non-Metric Clustering*

Since neither the PCA nor non-metric clustering grouped the merged data by season, it can be concluded that there is no difference between water samples taken in April and August. Similarly, the Piper diagrams did not show a consistent shift in the plotted data points, which would indicate a change of water type between the seasons. This is unusual for water samples taken from areas experiencing seawater intrusion. Areas that are intruded or are becoming intruded typically have highly variable chloride concentrations between samples taken during different seasons. In general, higher chloride concentrations would be expected in the summer when water demand is high and precipitation is low, and lower concentrations in the winter when there is a lower water demand and higher precipitation (Kelly, 2008). The lack of variability observed in this study suggests that seawater intrusion is not occurring. However, it would be interesting to analyze samples taken at other times during the year and from wells that have been observed to exceed the SMCL in the past.

#### *6.4.2 Mobilization of Arsenic*

Both the PCA and the LDA statistical tests indicate that the major seawater ions can be used to group dissolved arsenic into high and low categories. Non-metric clustering failed

to support this grouping. Because non-metric clustering ignores noisy variables, this difference cannot be attributed to the inclusion of the complete data set for non-metric clustering.

Although there is a small data set, the data were significantly ordinated using PCA and significantly classified into high and low groups by the LDA. This indicates that there is a direct multivariate relationship between seawater ions and arsenic concentrations. Similarly, a Piper diagram visually represents the relationship between the major seawater ions. When arsenic concentrations were plotted on the Piper diagram, the high arsenic values were plotted in the lower right side in the “freshening” region. Both the LDA and the PCA statistically support grouping arsenic into high and low concentration groups based on seawater ions, and Piper diagrams visually represent high and low arsenic groups on a tri-linear diagram. Although non-metric clustering produced inconclusive results, PCA, LDA, and the Piper diagrams all support each other in grouping dissolved arsenic into high and low clusters based on seawater ion concentrations.

The LDA has limitations in its ability to use a training data set to classify a second data set. When LDA creates a training set, it has a tendency to “over train” the data. To help compensate for this limitation, it helps to have a large data set. However, having a small data set does not preclude the LDA from producing statistically significant results, although caution should be taken in the interpretation of the data. In this study, I addressed this problem by running LDA twice and by using LDA as a supporting statistical test to other analyses.

## 7 Conclusion

The dominant arsenic species in the groundwater on Lummi Island was arsenate. This was supported by the speciation calculations performed in PHREEQC and the position of the water samples plotted on the arsenic stability diagram. The positive correlation between alkalinity and dissolved arsenic, negative correlations between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and dissolved arsenic, and no correlations with Fe or Mn are consistent with an arsenic release through a desorption process. The presence of dissolved carbonate and bicarbonate is indicative of a chemical weathering process, which could lead to arsenic desorption. Furthermore, the positive charge on the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions can facilitate the adsorption and desorption of dissolved arsenic. Since the Chuckanut sandstone had the highest dissolved arsenic concentrations, a chemical weathering process is most likely occurring within this stratum. Organic matter may be present in the Chuckanut sandstone in coal seams, but the relationship between coal seams and dissolved arsenic was not explored in this study. Iron and manganese did not have any statistical relationship with dissolved arsenic concentrations; therefore, it is unlikely that the arsenic release was related to reductive dissolution of iron or manganese minerals.

When an aquifer is experiencing seawater intrusion, wells show increased chlorides, which often fluctuate throughout the year. No wells in my study that were tested for chlorides exceeded the SMCL, nor did any wells experience a statistically significant fluctuation in chlorides between the April and August sampling seasons. Of the all wells sampled in this study, only four exceeded the conservative chloride background level of 40 mg/L. When the major ions were plotted on a Piper diagram, all of the values plotted in either the “fresh” or the “freshening” part of the diagram; none of the samples plotted in the



“intruding” or “intruded” area. Because there was no evidence that these wells were experiencing seawater intrusion, the salts must be released from another source. Since the Chuckanut sandstone had the highest chloride values, it is likely that the major ions were being sourced in this aquifer. It is possible that the salts were being released through the chemical weathering of the bedrock.

This relationship between major ions and dissolved arsenic was supported by the multivariate statistical tests PCA and LDA. The PCA successfully classified arsenic into high and low groups, and once trained with a subset of the data, the LDA divided arsenic into high or low categories. The relationship between the major ions and dissolved arsenic can be interpreted from a Piper diagram when the high dissolved arsenic concentrations ( $[As] > 0.07$  mg/L) is color coded. These water samples all plotted in the freshening region of the Piper diagram. It is likely that the chemical interactions mobilizing arsenic are related to the presence of the major ions, since these ions may facilitate the desorption of arsenic from mineral surfaces and compete for adsorption sites. Because chlorides and dissolved arsenic were positively related, specific conductance, used as a proxy for chlorides, could be used as a rough indicator for arsenic.

My study was limited to the April and August 2006 sampling periods. It would be interesting to examine changes in water quality data throughout several sampling seasons over multiple years. A larger sample size of wells would allow for a more robust statistical analysis of the water quality data, which could improve the multivariate clustering and reveal other patterns in the data. It would also be helpful to sample wells in or near areas that are considered to be intruded because of high chloride values. These wells could be tested for intrusion and statistically compared to the rest of the data set. A better understanding of the

geochemical reactions could be obtained by directly testing water samples for arsenic species and redox potential by measuring ammonium and nitrate. The chemical environment that controls the mobility of the arsenic can be better understood if the precise arsenic species is known and the redox potential is better characterized. Whole rock analysis should be performed on more rock samples that have been collected from additional locations throughout Lummi Island. In this study, no rock samples were taken from the glacial aquifers and no samples were taken from coal seams. The Chuckanut sandstone, the coalified log, and the greenstone were sampled at only one site.

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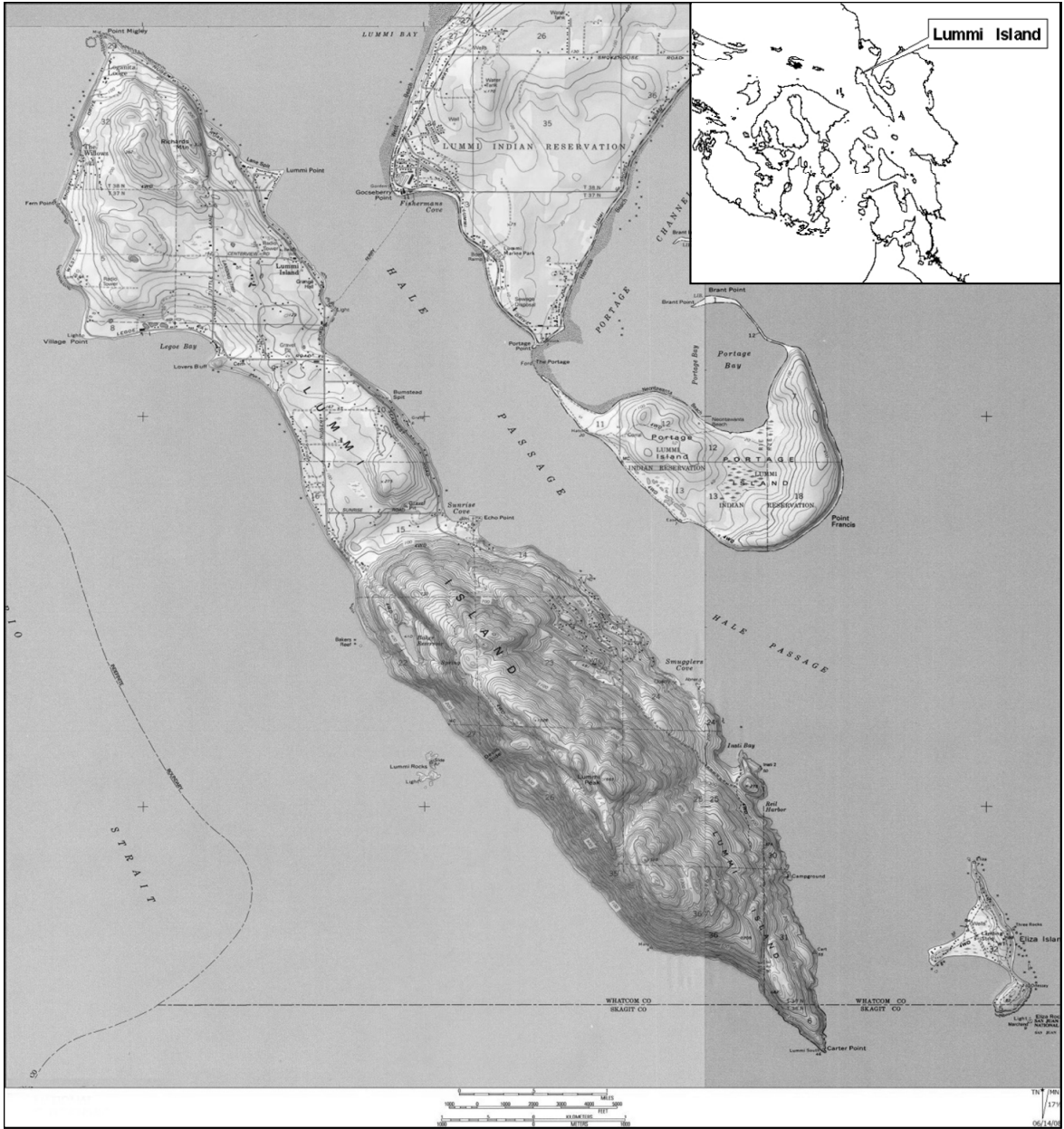
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**Figure 1.** Topographic map of Lummi Island, Washington.

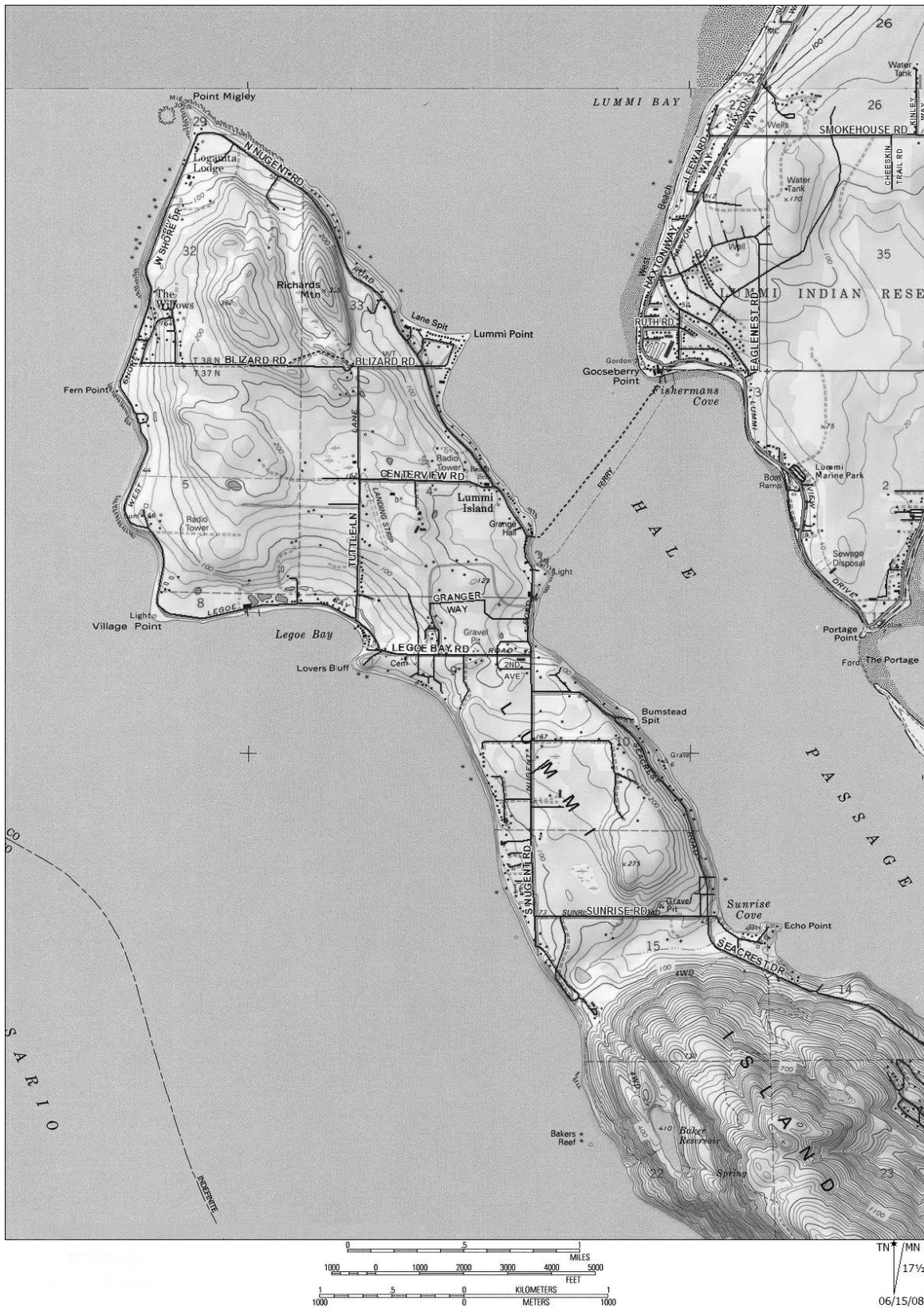
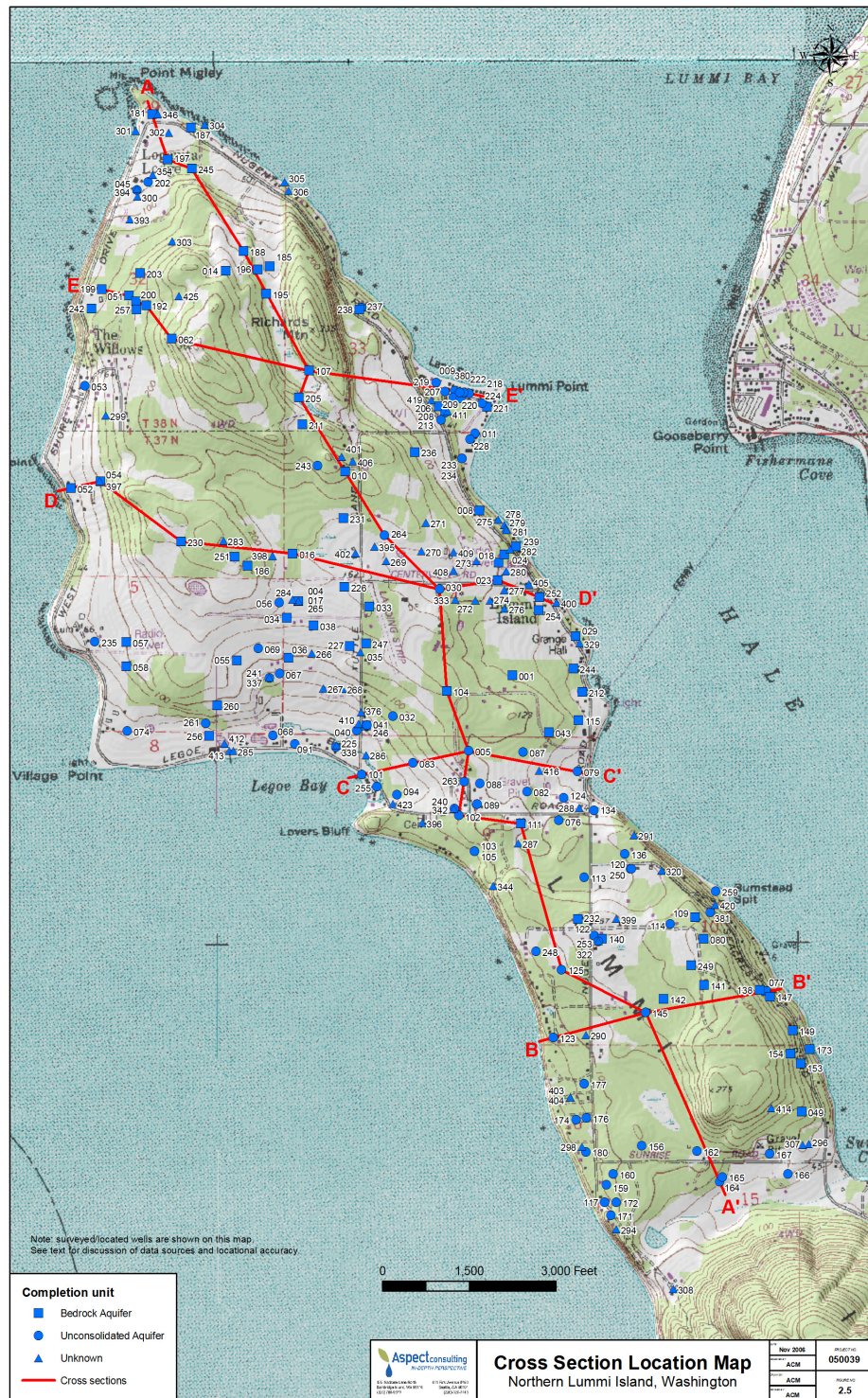


Figure 2. Topographic map of northern Lummi Island, Washington.



**Figure 3.** Cross section location map of northern Lummi Island (Aspect, 2006). Well symbol shape indicates the aquifer type in which the well was completed.



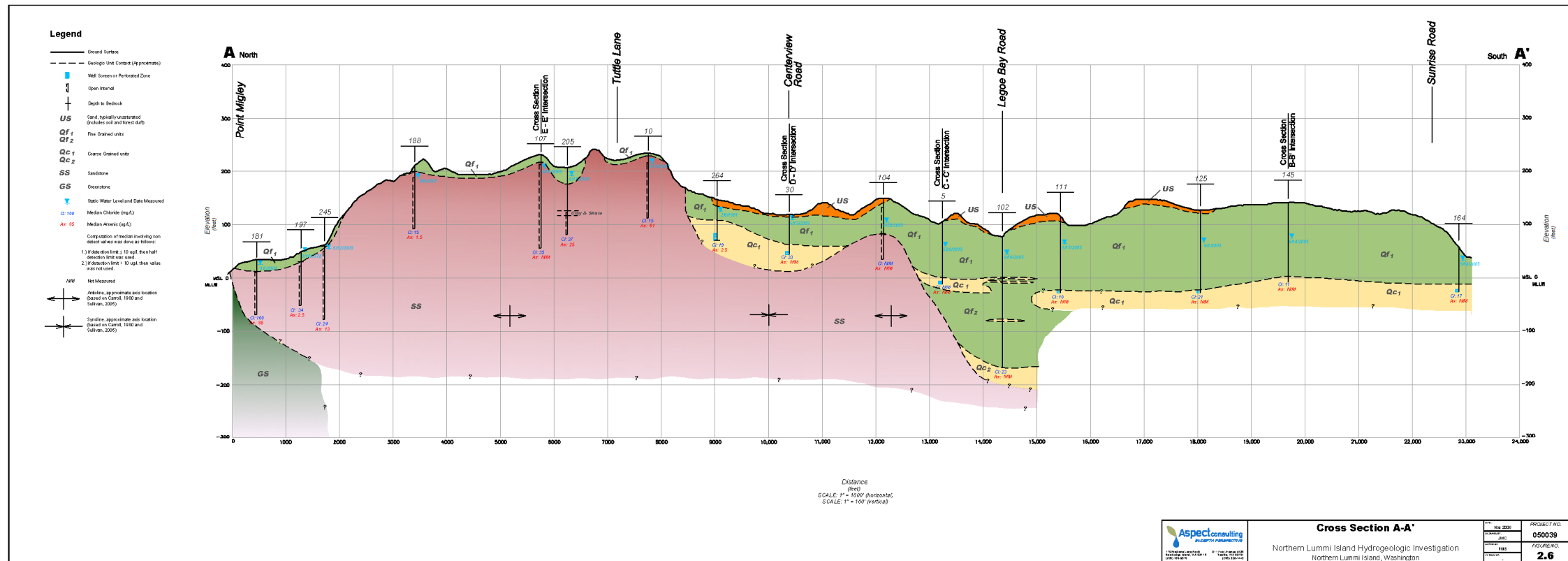
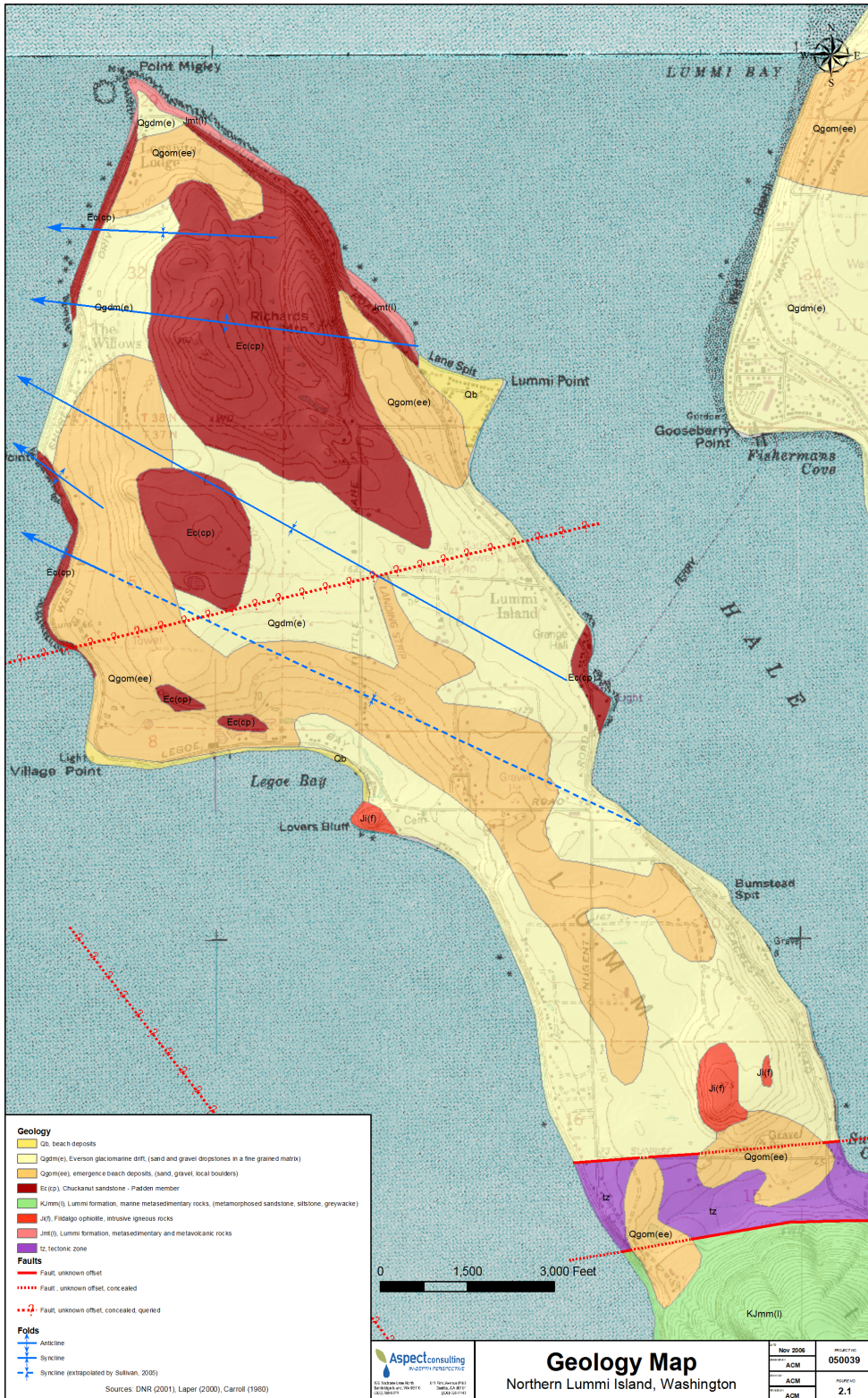
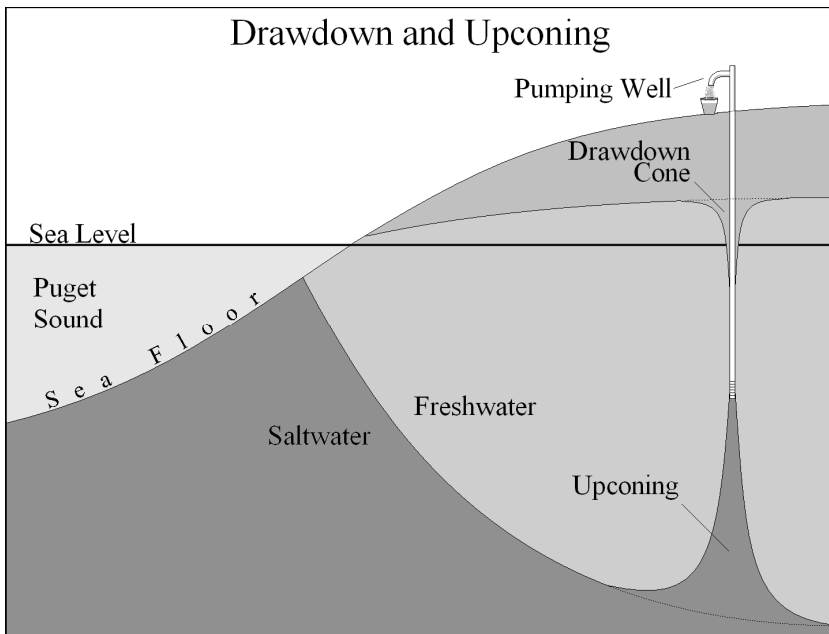


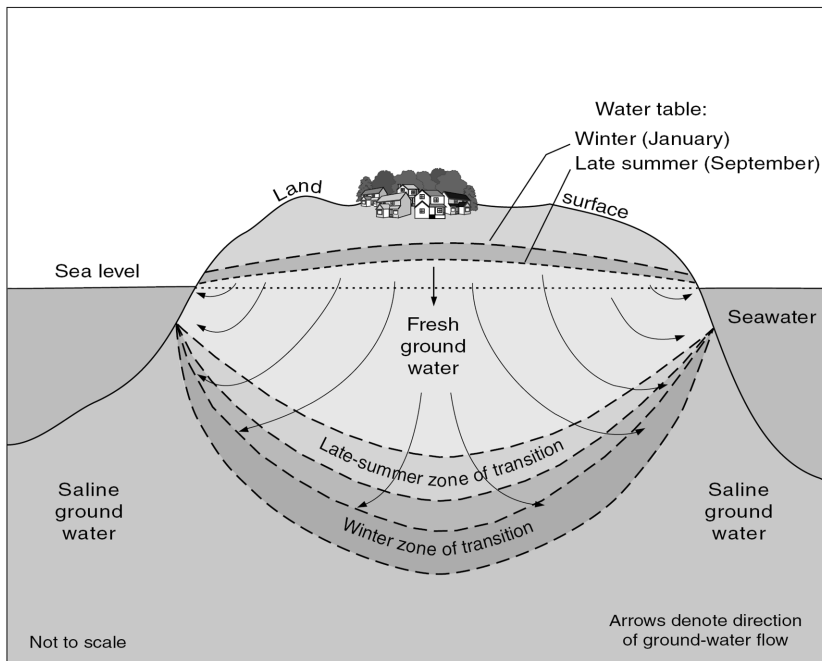
Figure 4. Cross section of Lummi Island from A to A' (Aspect 2006).



**Figure 5.** A geologic map of northern Lummi Island, Washington created by Aspect, which includes outcrops of proposed fault lines (Aspect, 2006).



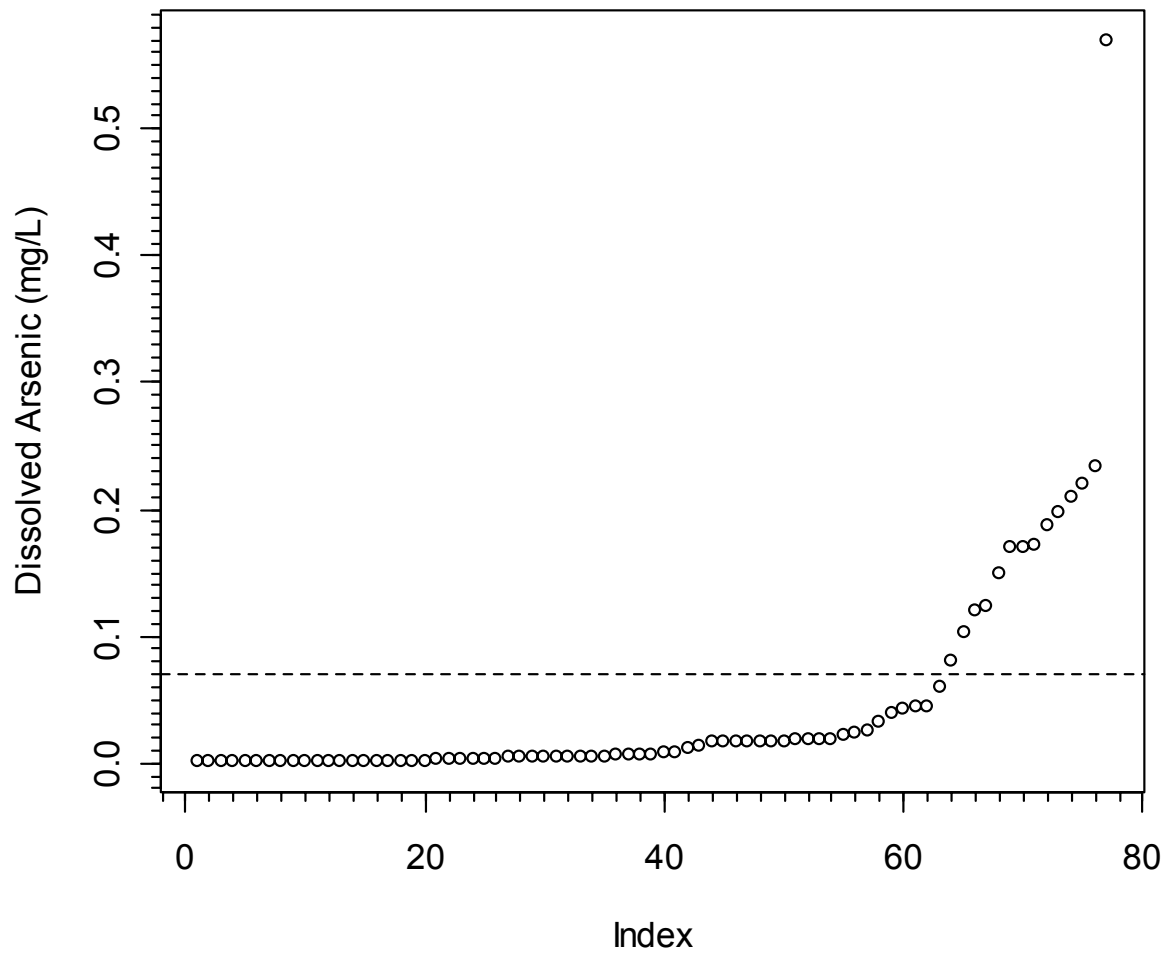
**Figure 6.** Ghyben-Herzberg diagram describing the relationship between the densities of freshwater and saltwater, and how well pumping can locally affect the interface (Kelly, 2005).



**Figure 7.** The zone of transition is typically at a greater depth during the winter compared to the summer months (USGS, 2000).



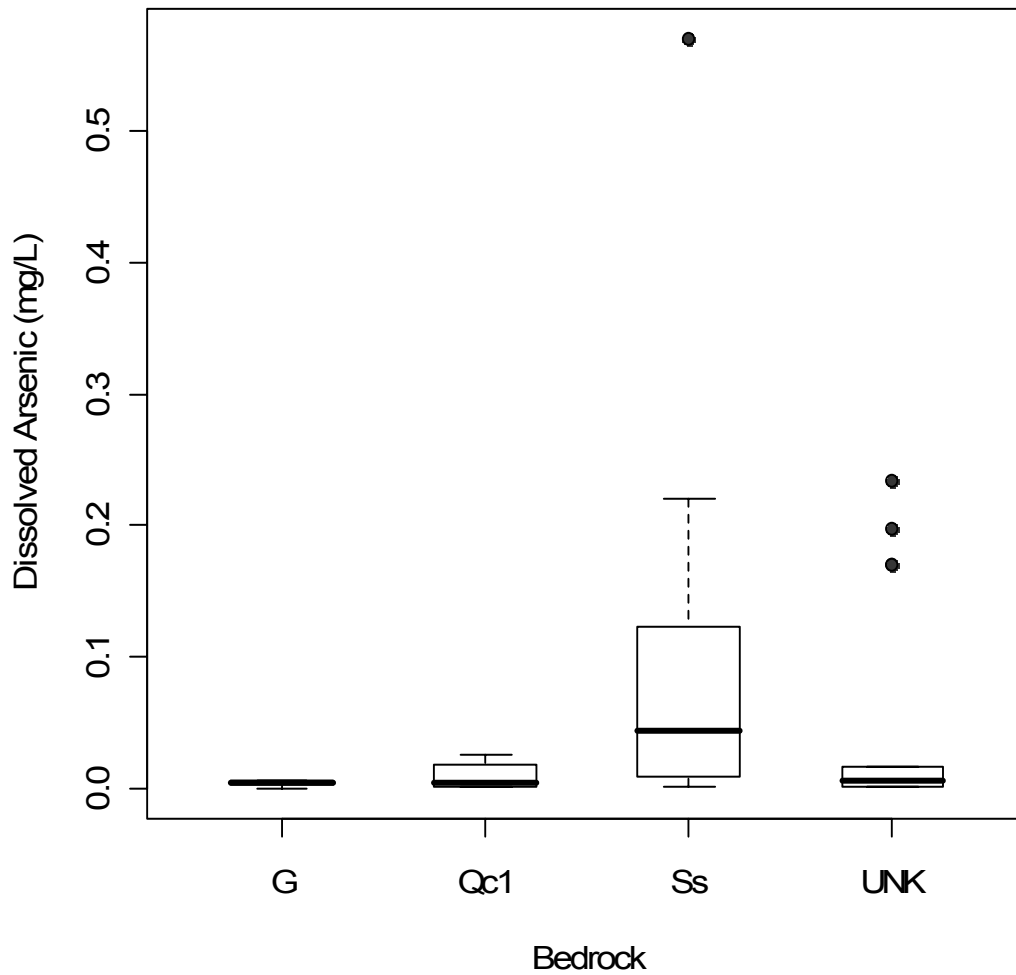
**Figure 8.** Locations on northern Lummi Island from which rocks were collected for whole rock analysis.



**Figure 9.** Break point for the classification of high and low dissolved arsenic in the merged data set. Dissolved arsenic below 0.070 mg/L was classified as “low”, and dissolved arsenic above 0.070 mg/L was classified as “high”.



**Figure 10.** Well location map with arsenic concentrations for April and August sampling seasons. The wells are labeled as: well number/April arsenic concentration/August arsenic concentration. Wells marked with red symbols had an arsenic concentration greater than 0.070 mg/L for at least one sampling season. Wells with blue symbols had arsenic concentrations below 0.070 mg/L for both sampling seasons.

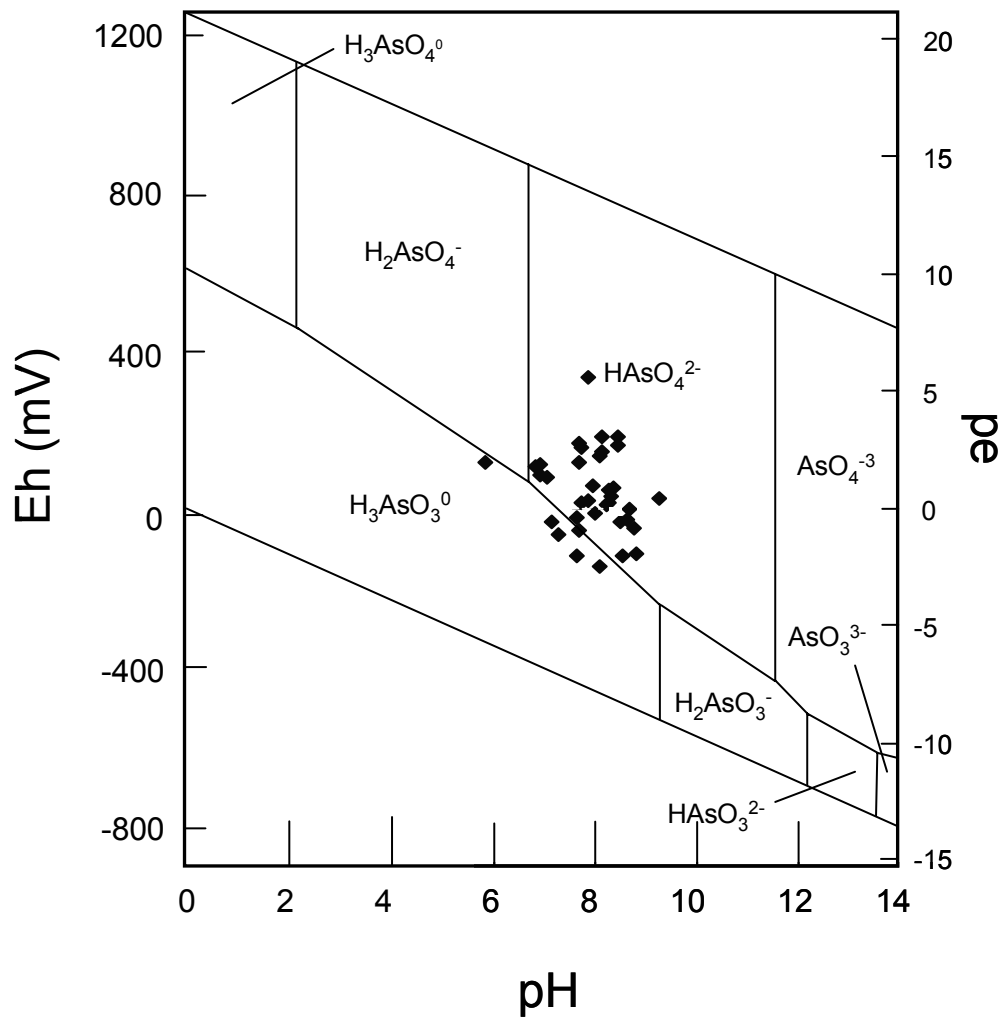


**Figure 11.** Dissolved arsenic concentrations in the merged data set from water samples collected among different aquifer types (G=Greenstone; n=8; Qc1=Glacial Deposits; n=28; Ss=Chuckanut Sandstone; n=25; UNK=Unknown; n=16).

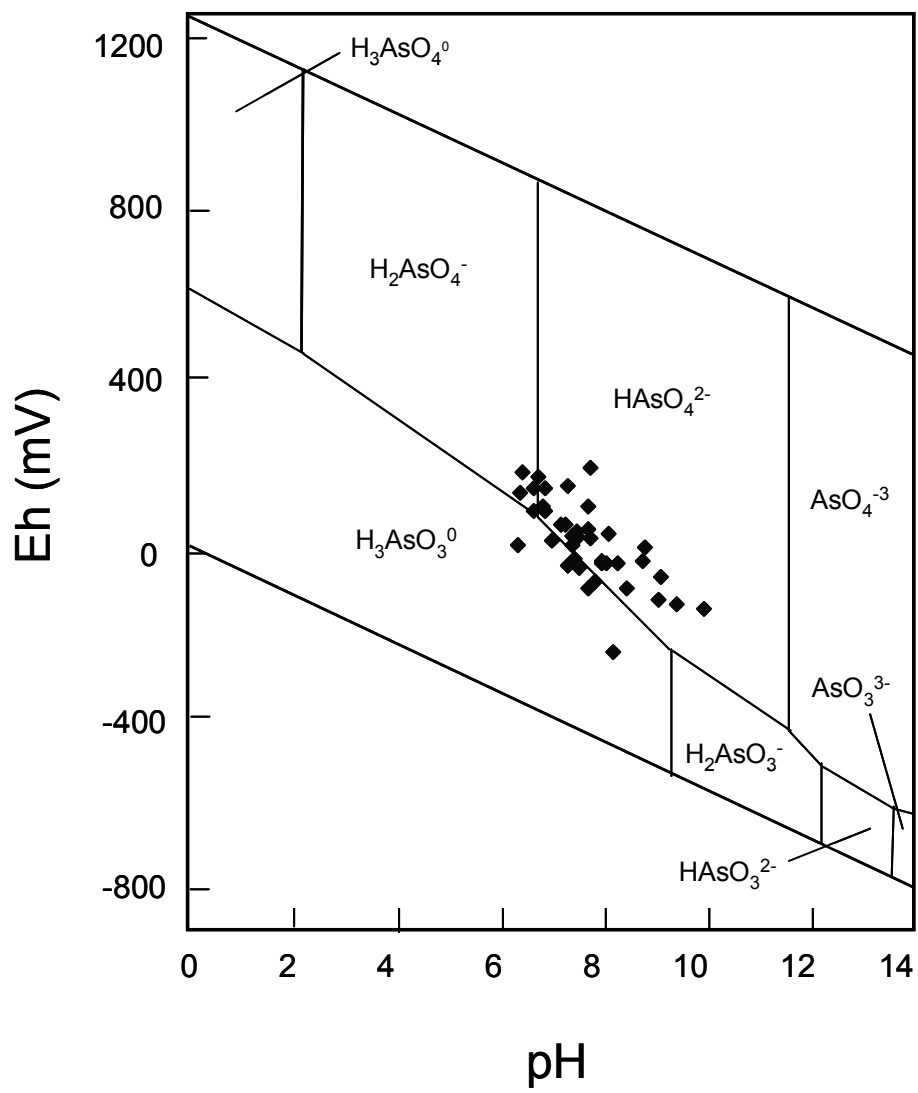


**Figure 12.** Well location map with chloride concentrations for April and August sampling seasons. The wells are labeled as: well number/April chloride concentration/August chloride concentration. Wells marked with red symbols had a chloride concentration greater than 40 mg/L for at least one sampling season. Wells with blue symbols had chloride concentrations below 40 mg/L for both sampling seasons.

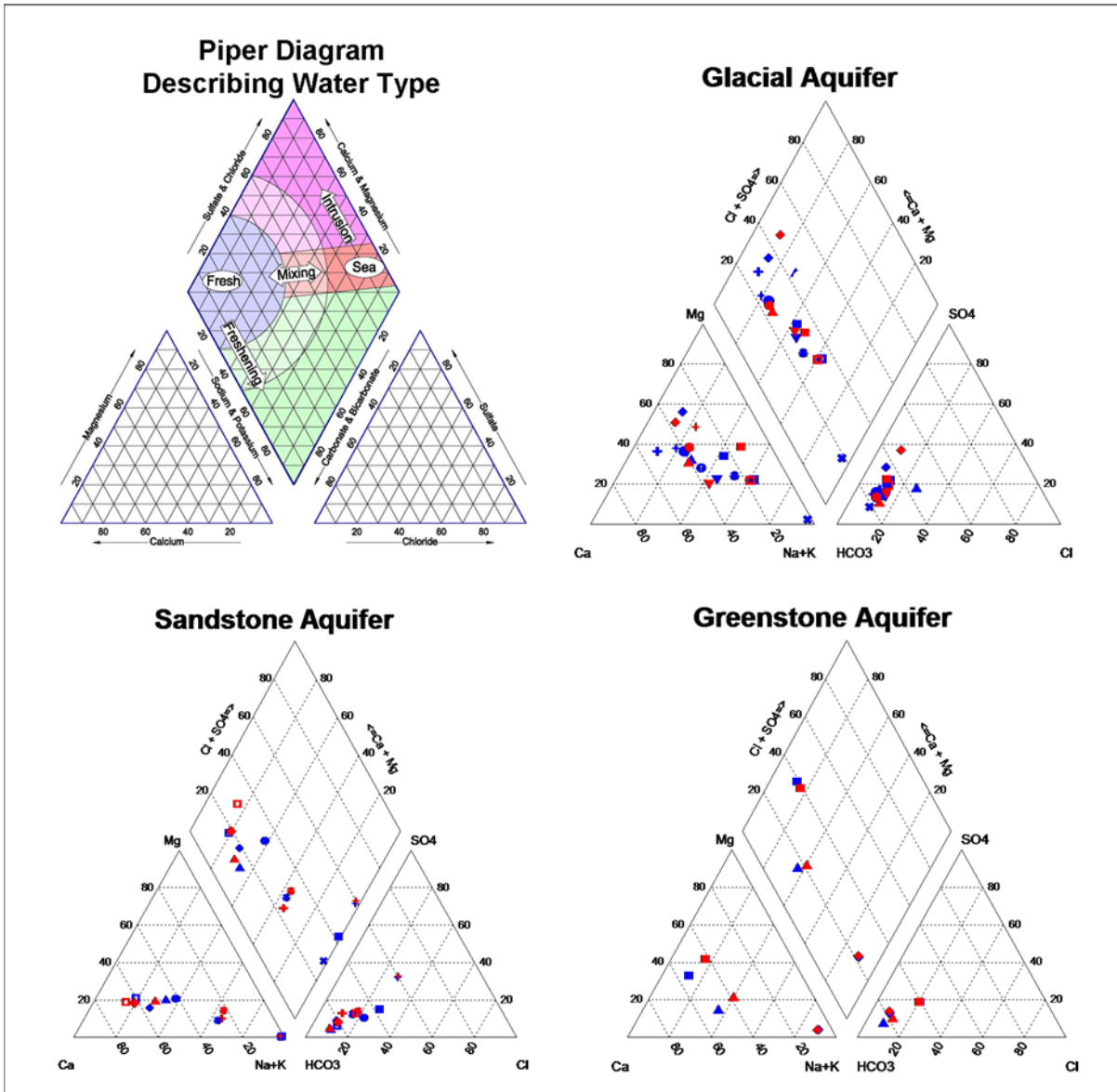




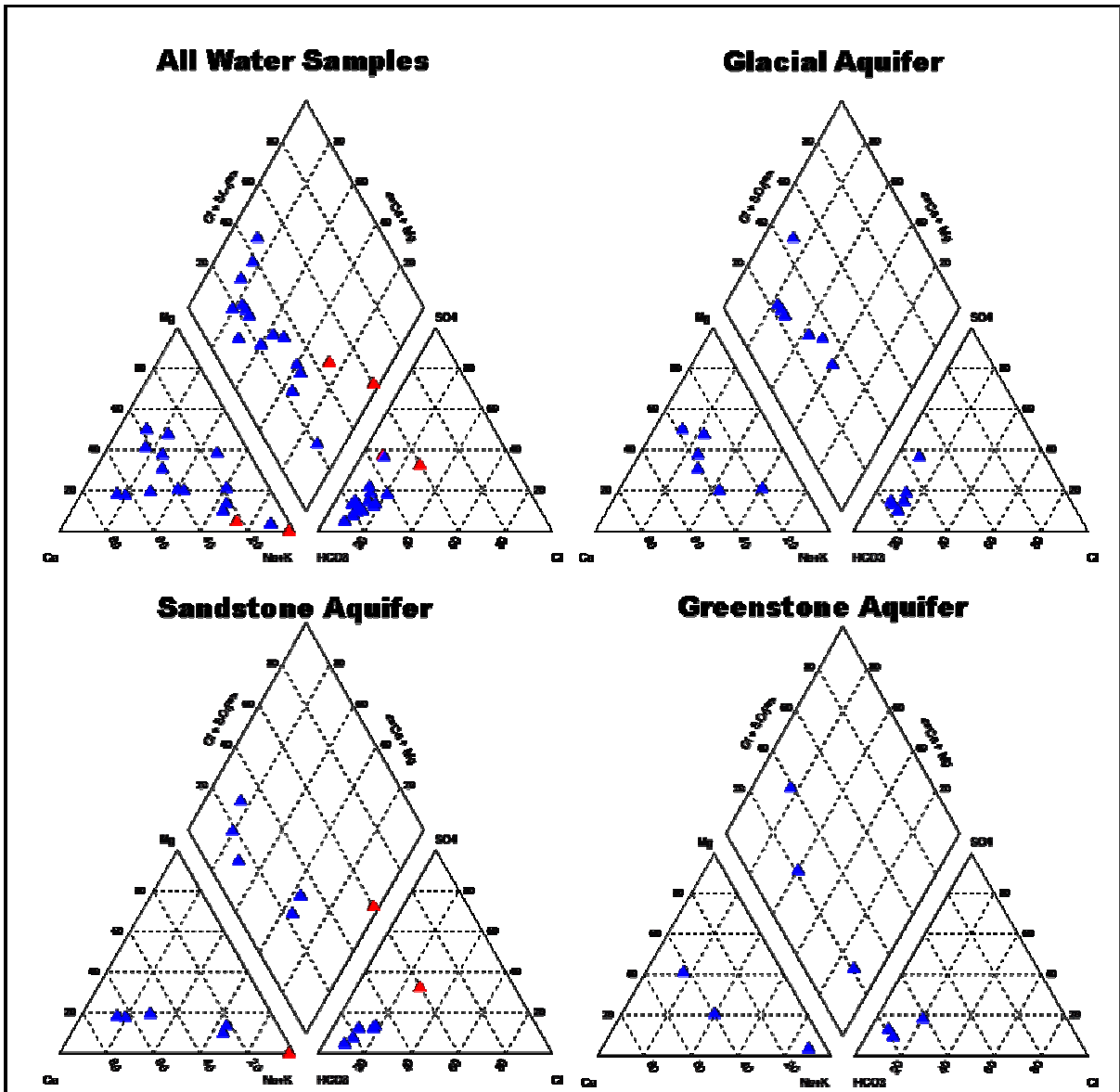
**Figure 13.** April water samples (n=36) plotted on an Eh-pH arsenic stability diagram.



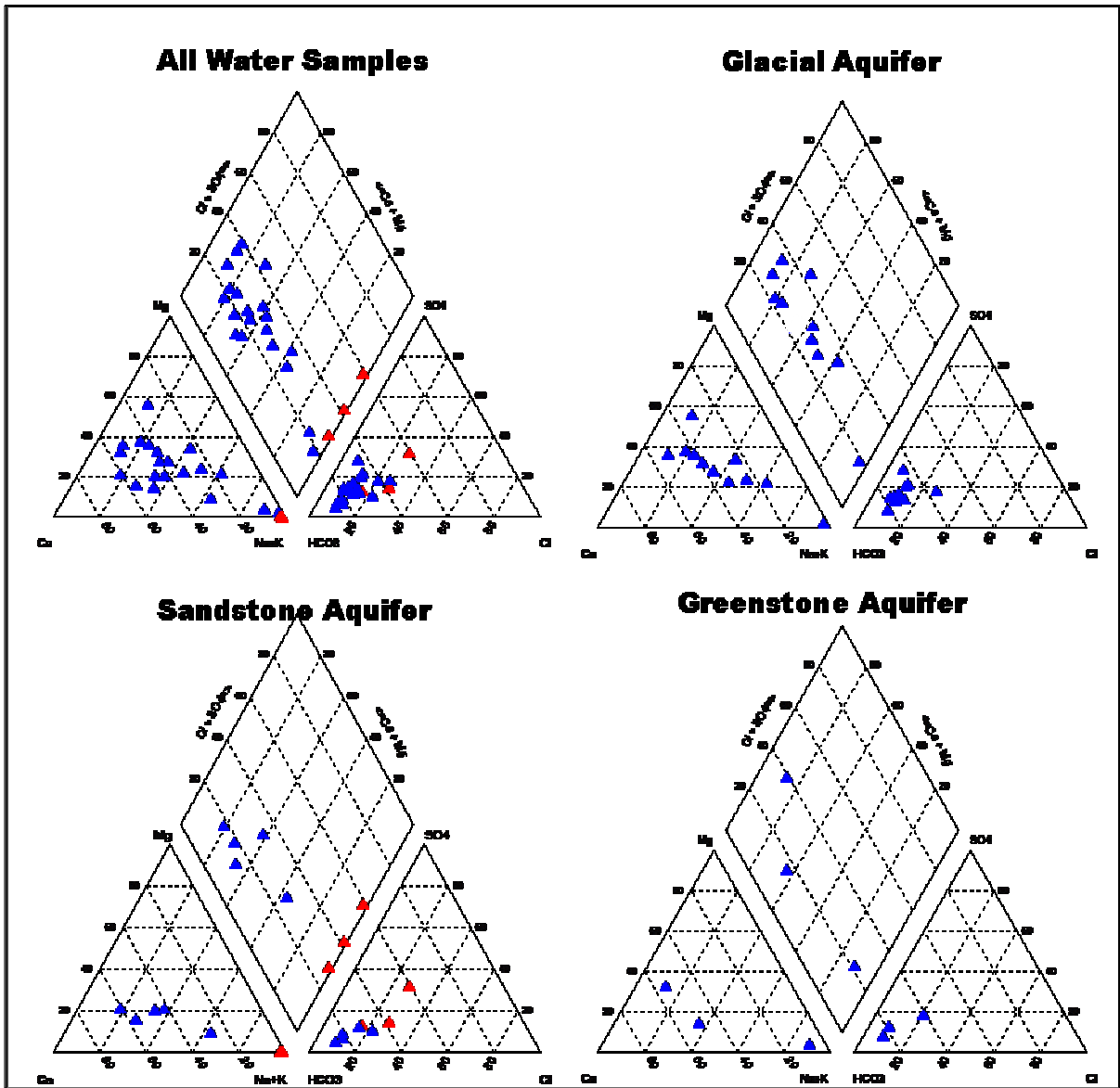
**Figure 14.** August water samples (n=41) plotted on an Eh-pH arsenic stability diagram.



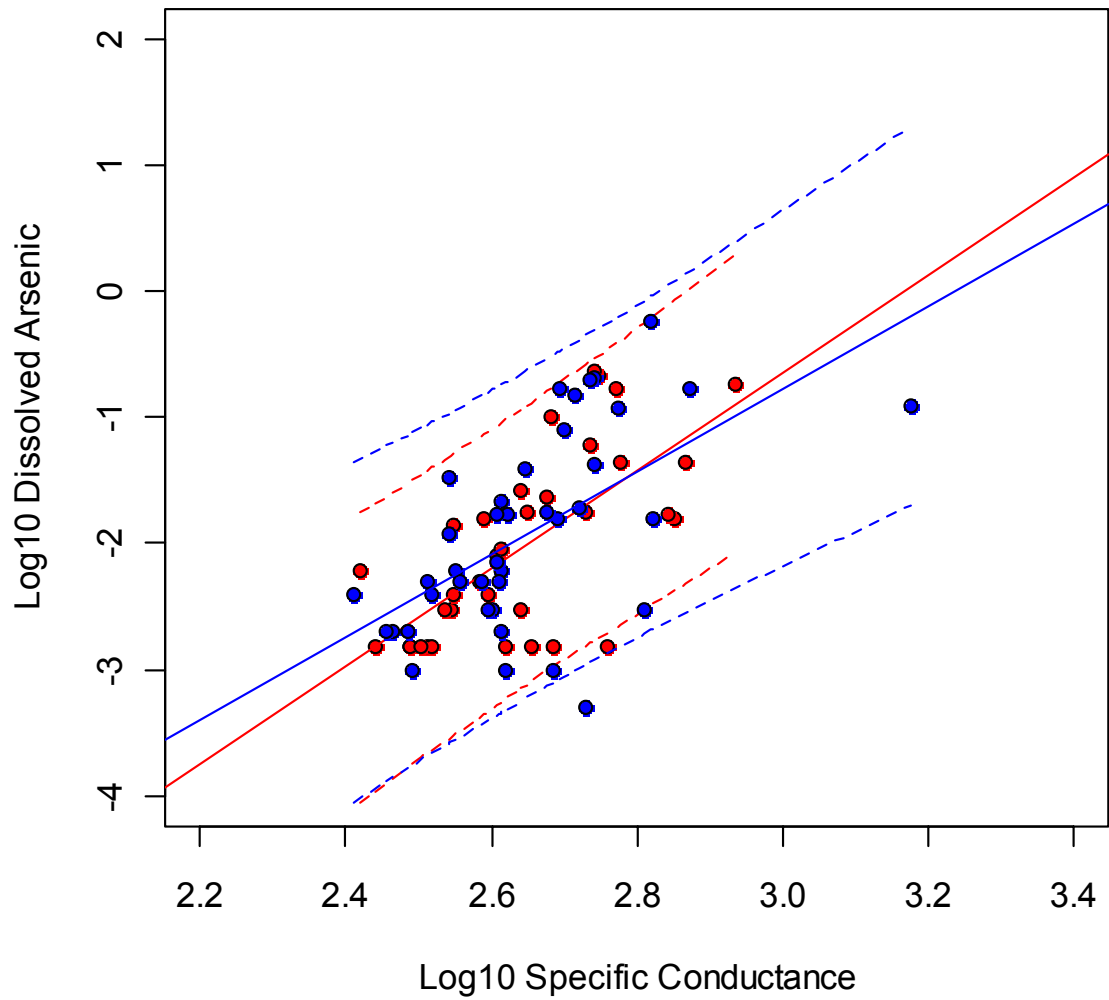
**Figure 15.** Piper diagram describing major ions in relation to seawater intrusion (Kelly, 2008), and Piper diagrams for bedrock types on northern Lummi Island. Each well is given an individual symbol and color coded by season. Red indicates the April sampling season and blue indicates the August sampling season.



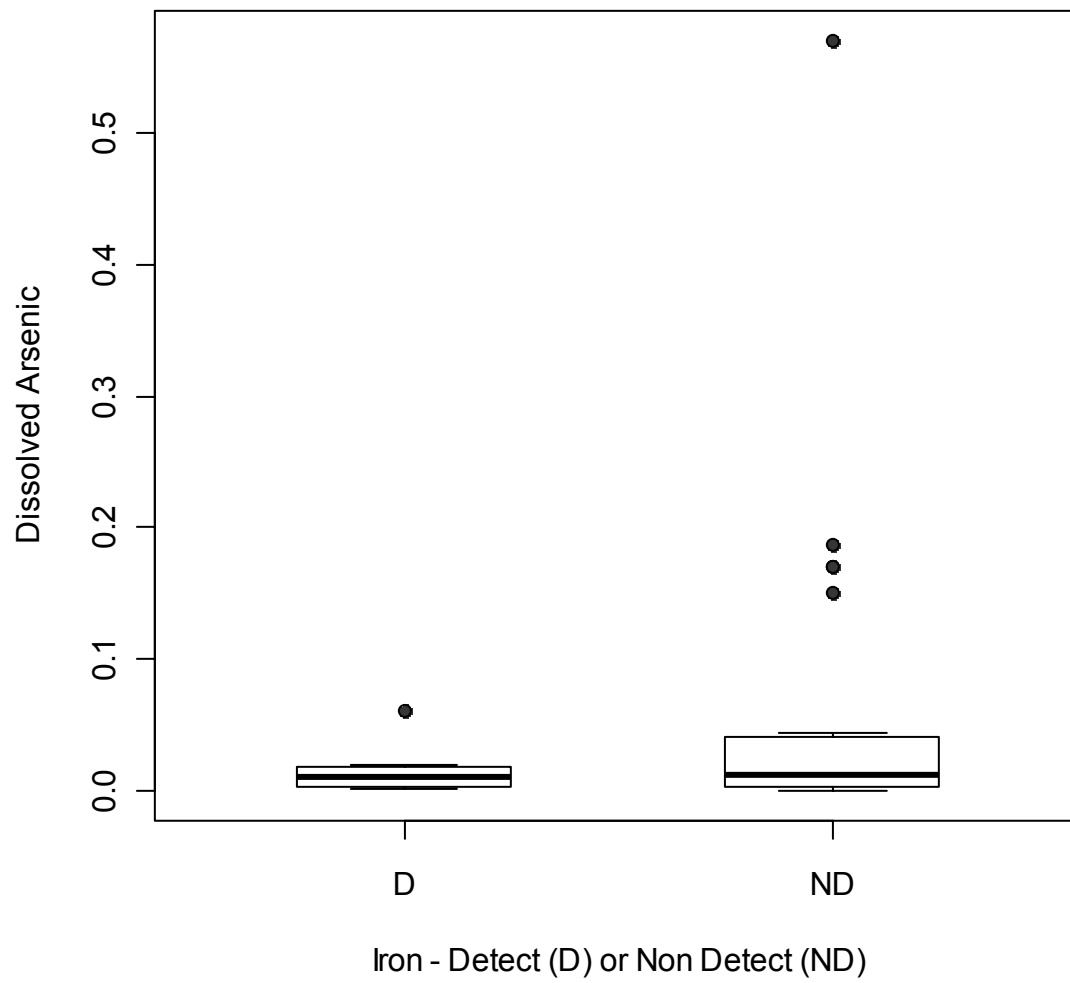
**Figure 16.** April water samples plotted on Piper diagrams by aquifer type and color coded by arsenic concentration group (Red: [As] > 0.07 mg/L and Blue: [As] < 0.07 mg/L; Glacial: n=13; Sandstone: n=11; Greenstone: n=4).



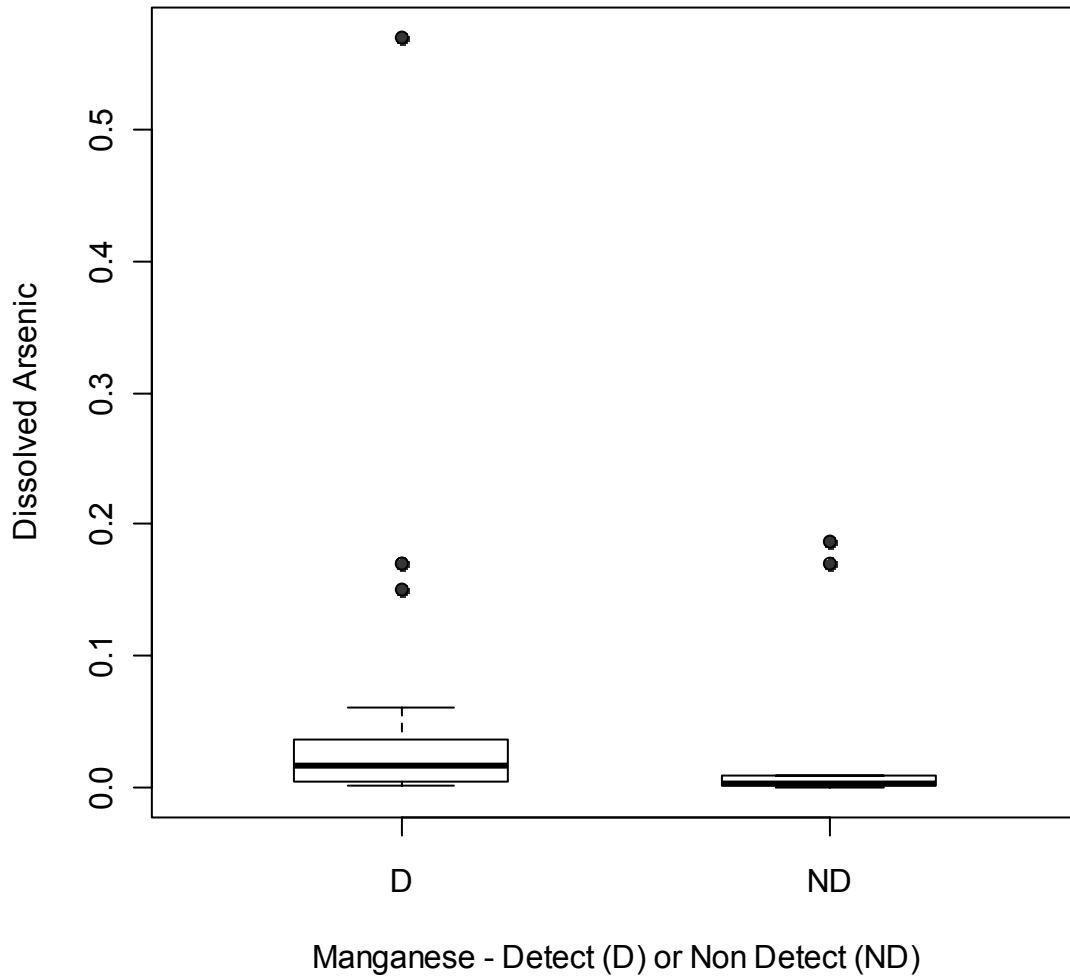
**Figure 17.** August water samples plotted on Piper diagrams by aquifer type and color coded by arsenic concentration group (Red: [As] > 0.07 mg/L and Blue: [As] < 0.07 mg/L; Glacial: n=15; Sandstone: n=14; Greenstone: n=4).



**Figure 18.** A correlation diagram describing the relationship between dissolved arsenic and specific conductance. Red indicates the April sampling season and blue indicates the August sampling season. The dashed lines represent the 95% confidence intervals for each season.

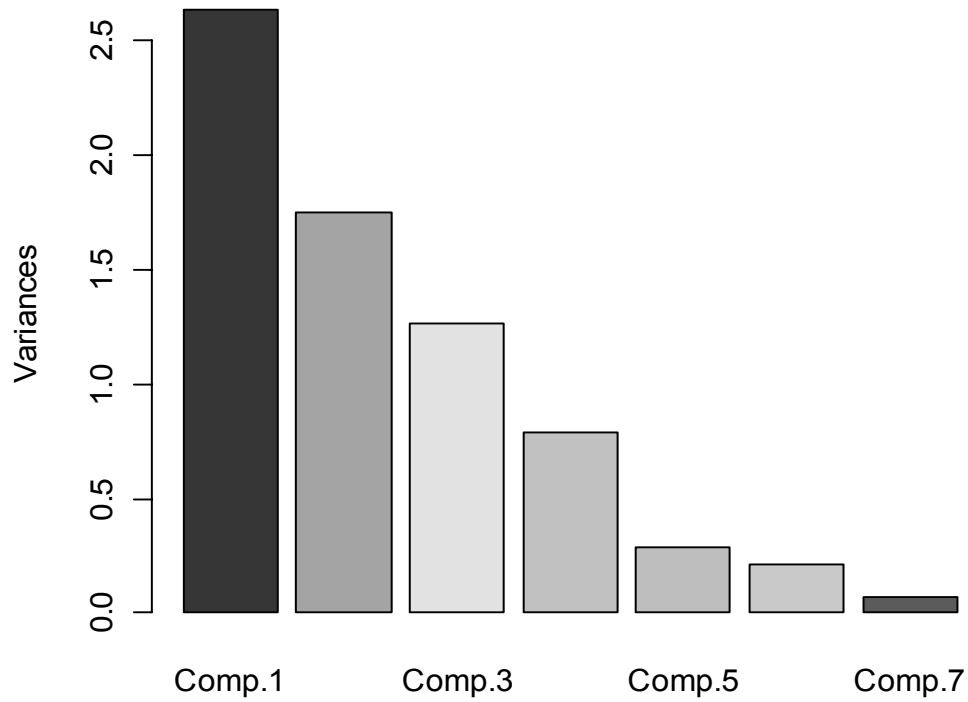


**Figure 19.** Dissolved arsenic concentration for detect (D; n=10) and non-detect (ND; n=31) iron groups.

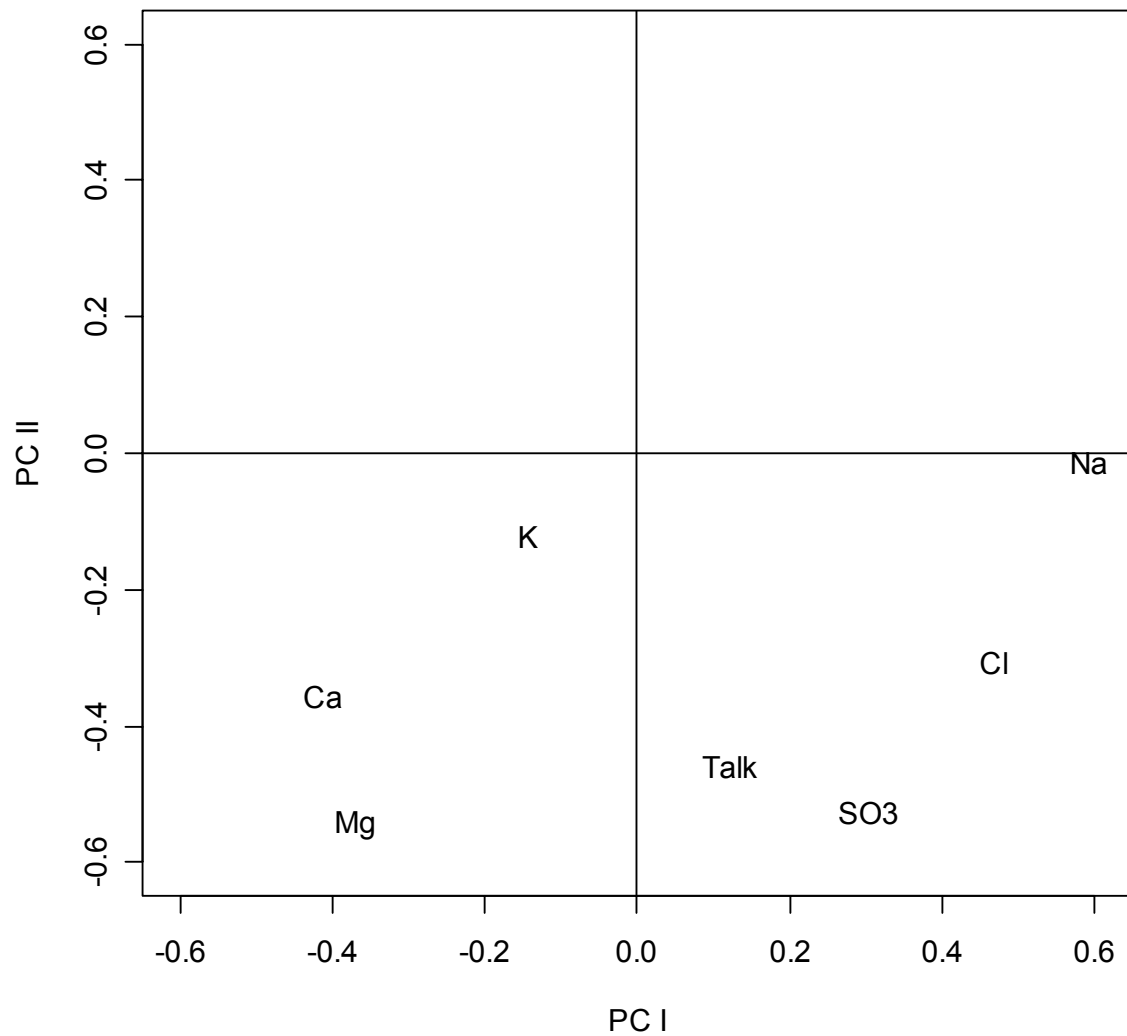


**Figure 20.** Dissolved arsenic concentrations for detect (D; n=32) and non-detect (ND; n=9) manganese groups.

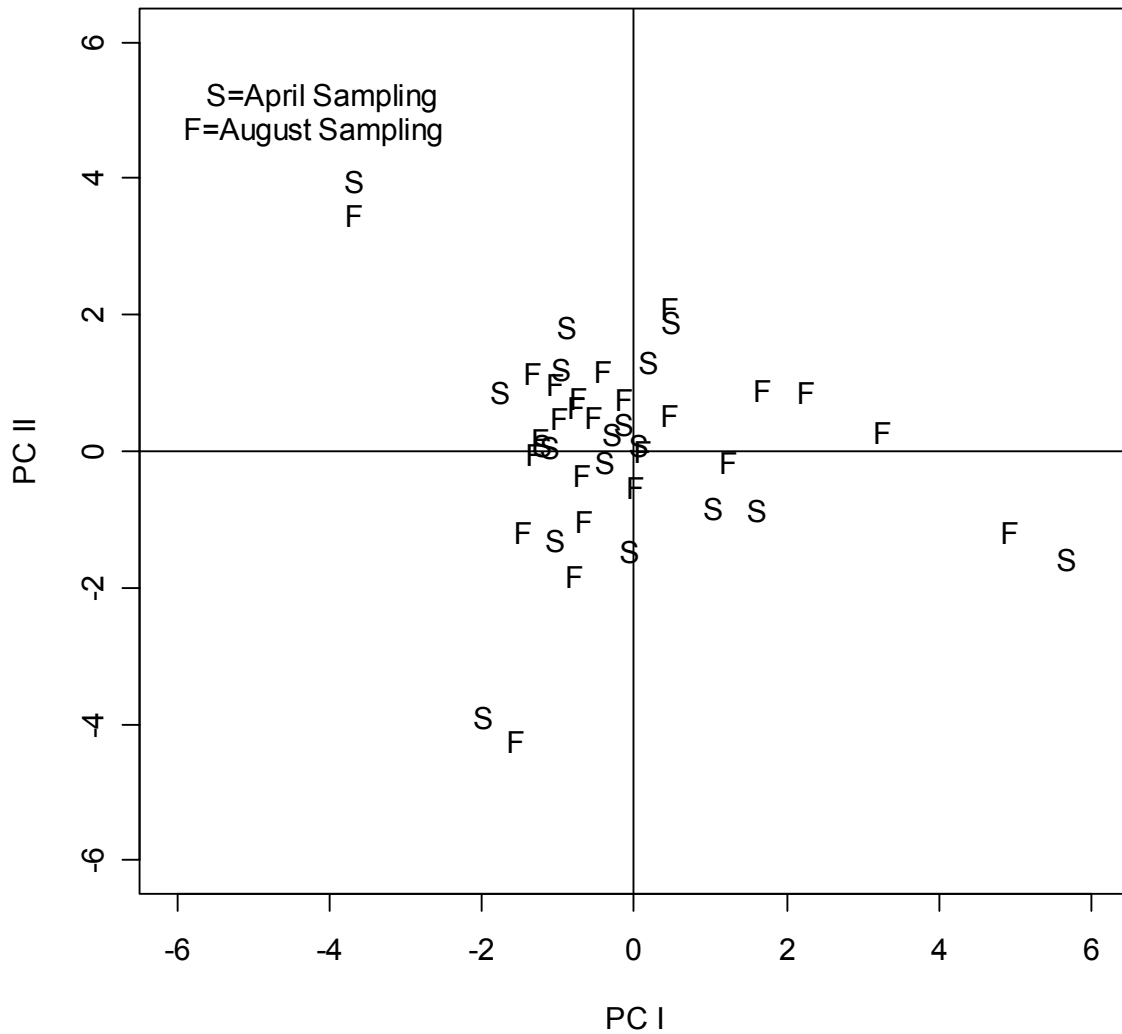




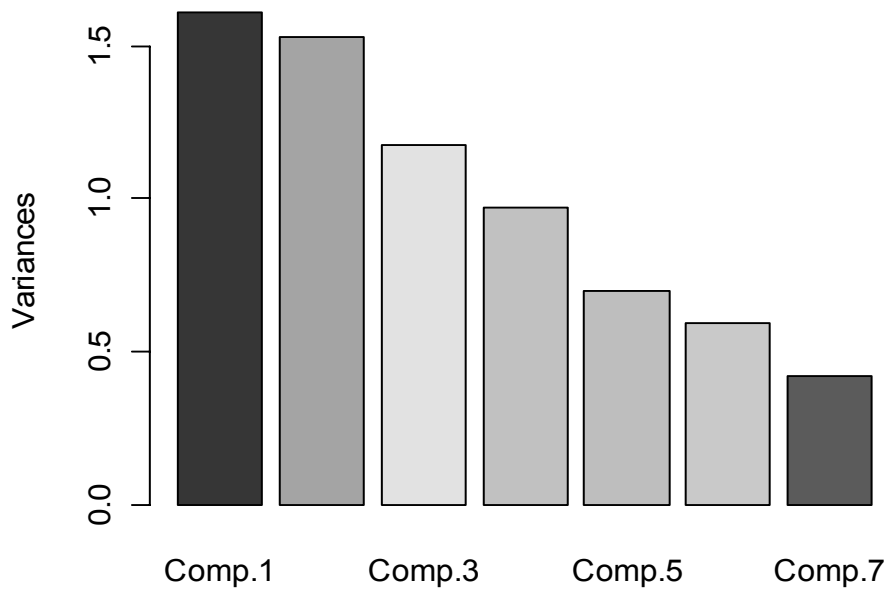
**Figure 21.** The variance described by the first seven principal components when analyzing the combined dataset using PCA. This loadings chart visually represents the amount of the variance that can be described by each principal component.



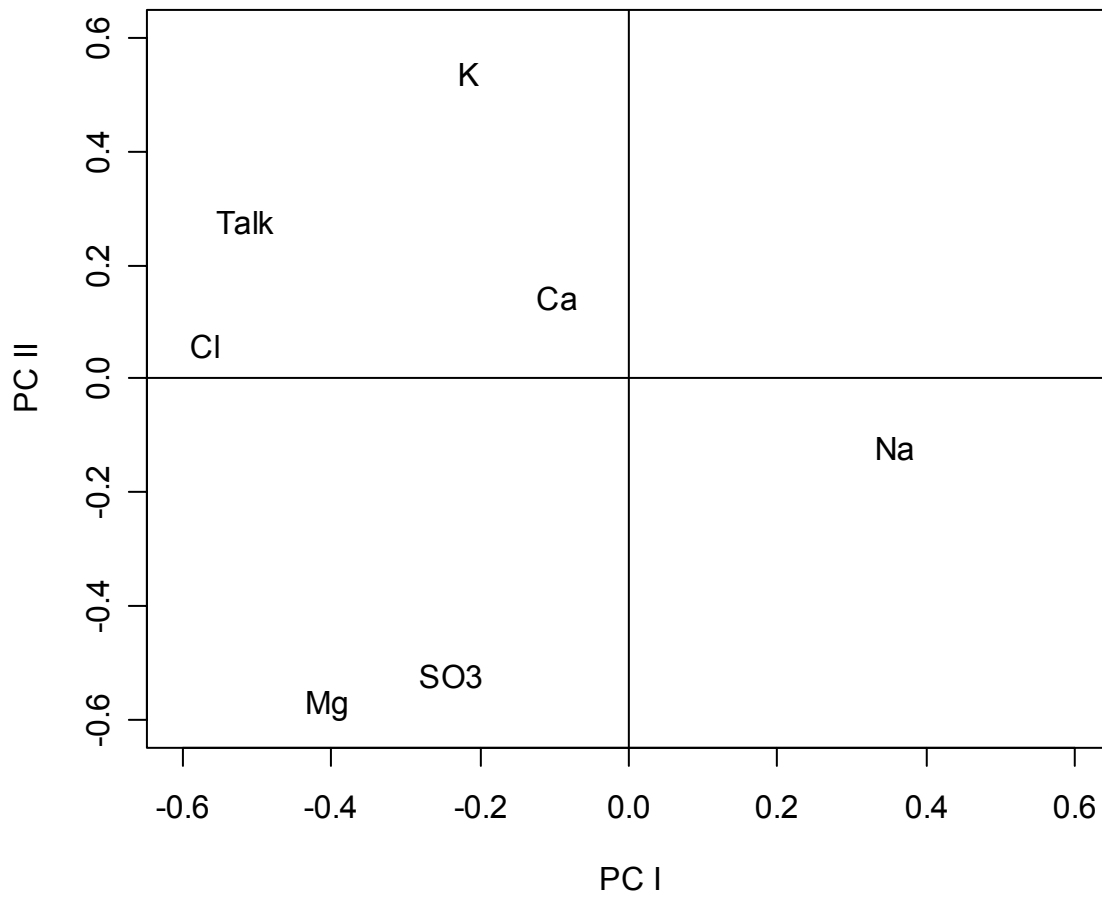
**Figure 22.** The variable loadings along principal component one and principal component two for the combined April and August data set. This depicts the relationship between each measured variable and the first two principal components in multivariate space.



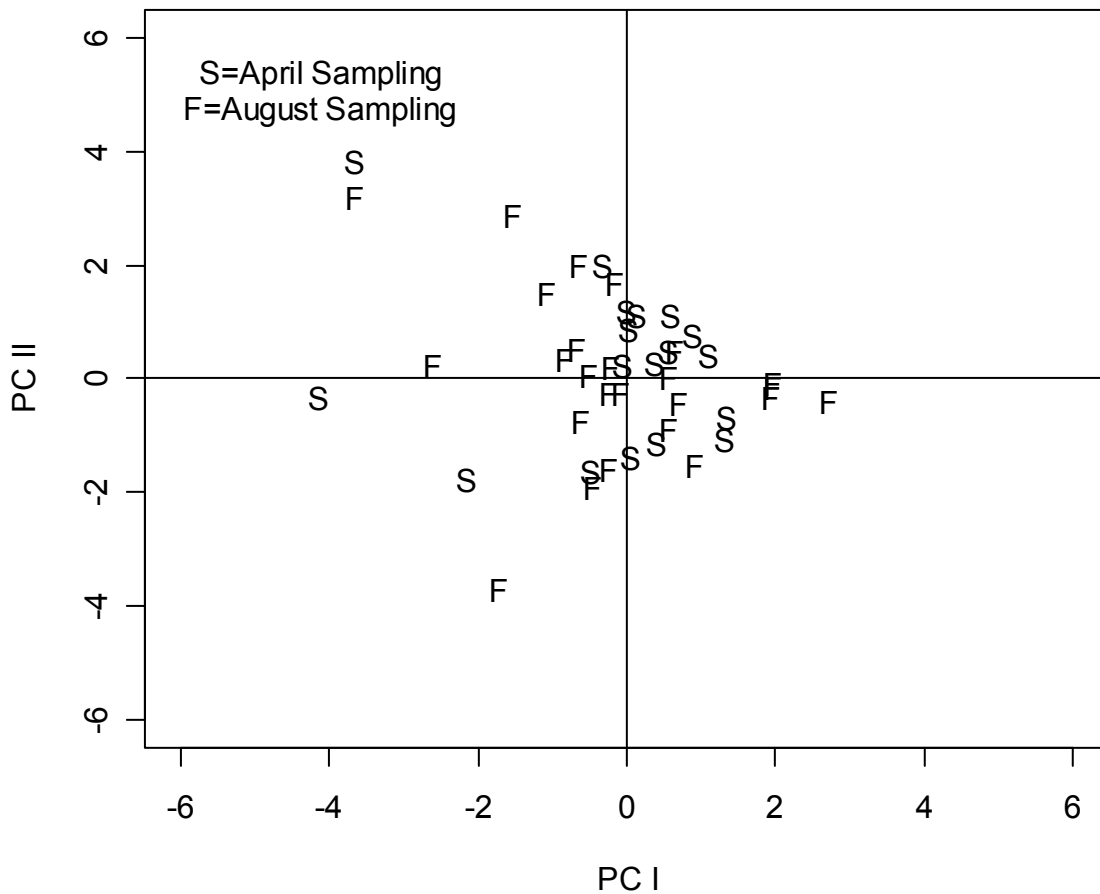
**Figure 23.** The ordination along principal component one and principal component two using the combined April (S) and August (F) data set. The lack of distinct clustering of variables along the first two principal components suggests that the data does not ordinate well.



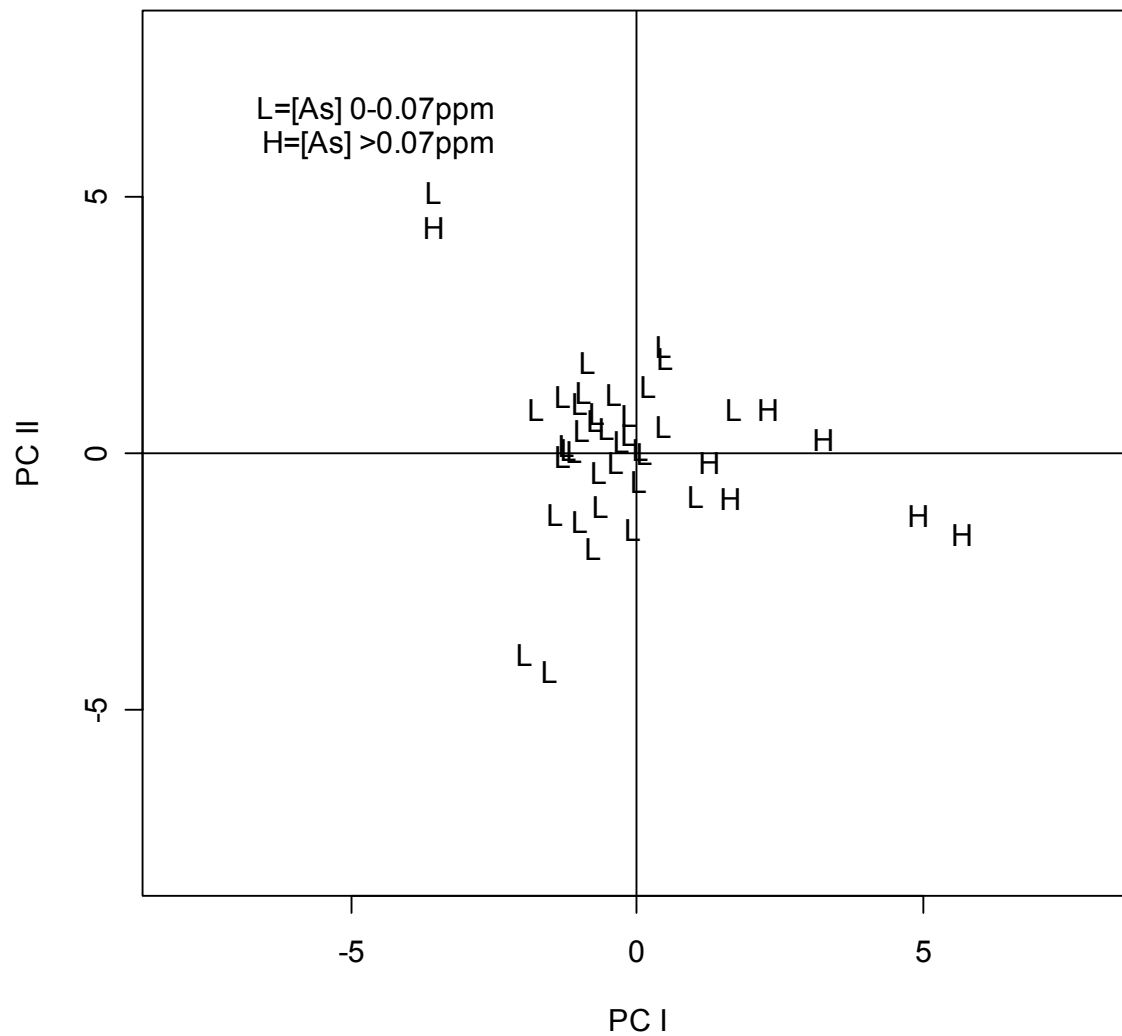
**Figure 24.** The variance described by the first seven principal components when analyzing the randomized dataset using PCA. This loadings chart visually represents the amount of the variance that can be described by each principal component.



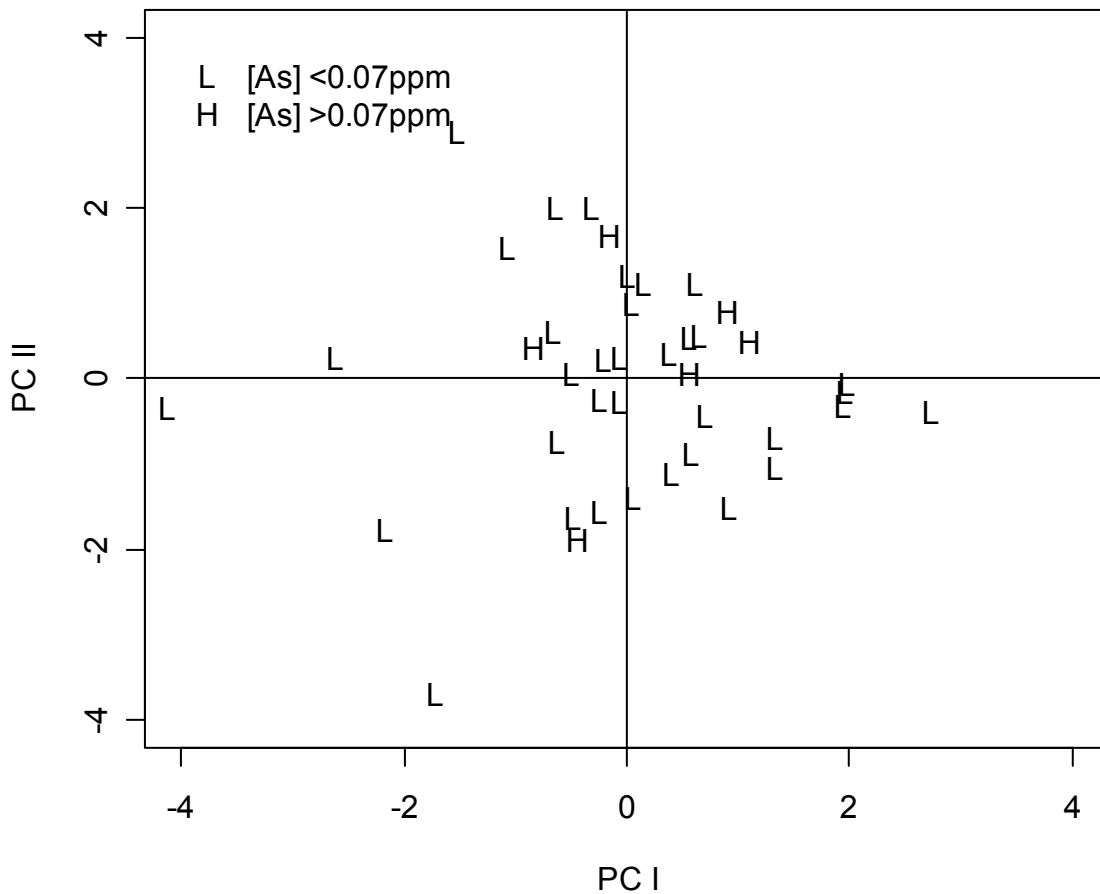
**Figure 25.** The variable loadings along principal component one and principal component two for the randomized data set. This depicts the relationship between each measured variable and the first two principal components in multivariate space.



**Figure 26.** Ordination along principal component one and principal component two using the randomized April (S) and August (F) data set. The lack of distinct clustering of variables along the first two principal components suggests that the data does not ordinate well.

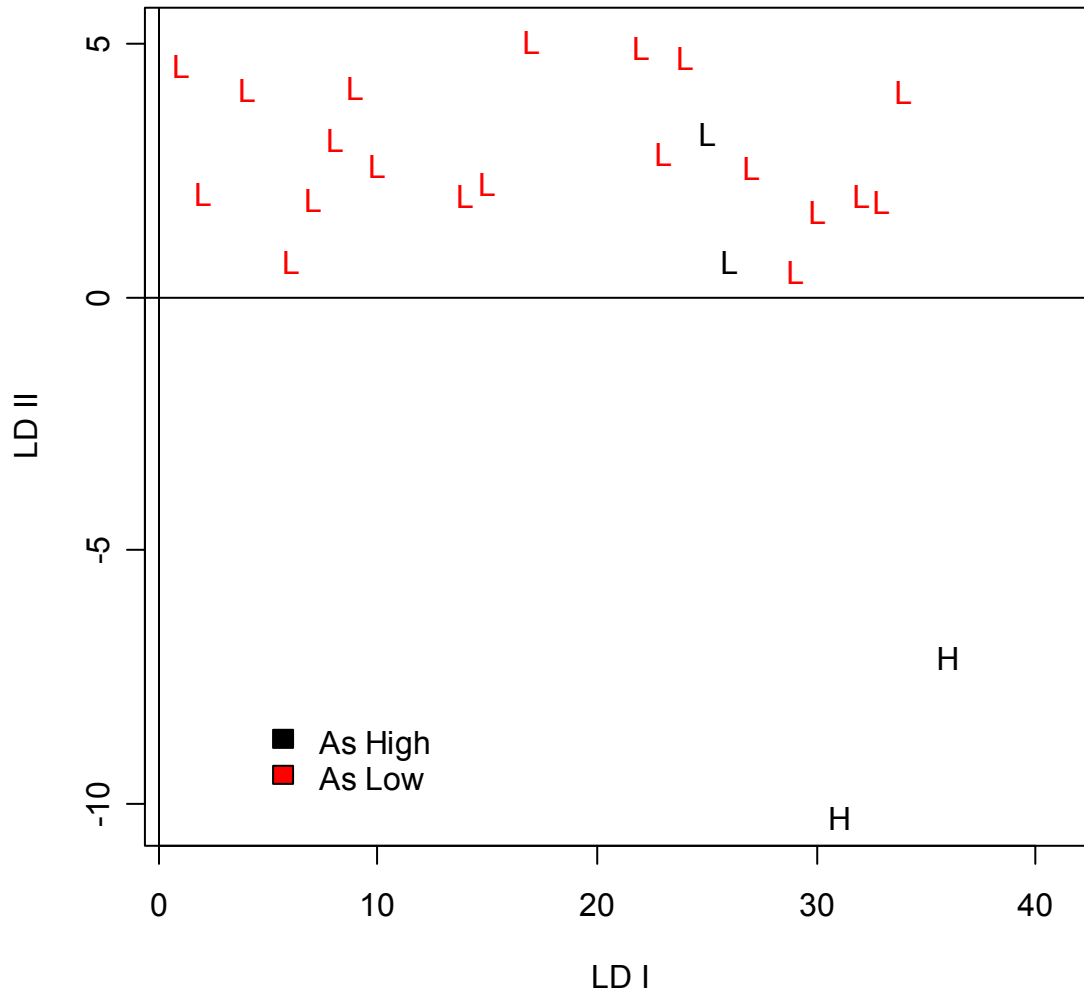


**Figure 27.** Ordination along principal component one and principal component two into “high” (H) and “low” (L) arsenic groups using the combined April and August data set. The distinct clustering of variables along principal component one suggests that the data ordines well.

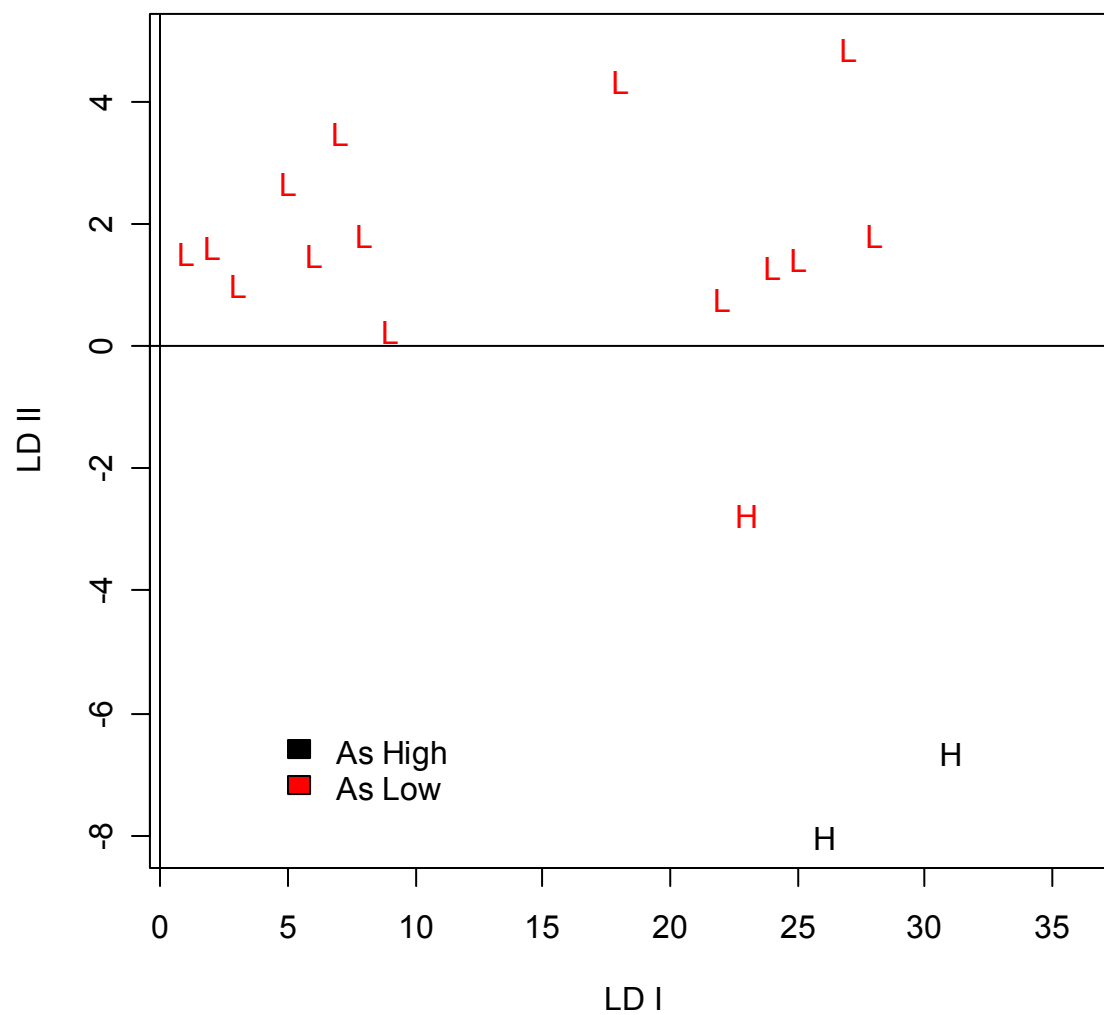


**Figure 28.** Ordination along principal component one and principal component two into “high” (H) and “low” (L) arsenic groups using the randomized data set. The lack of distinct clustering of variables along the first two principal components suggests that the data does not ordinate well.

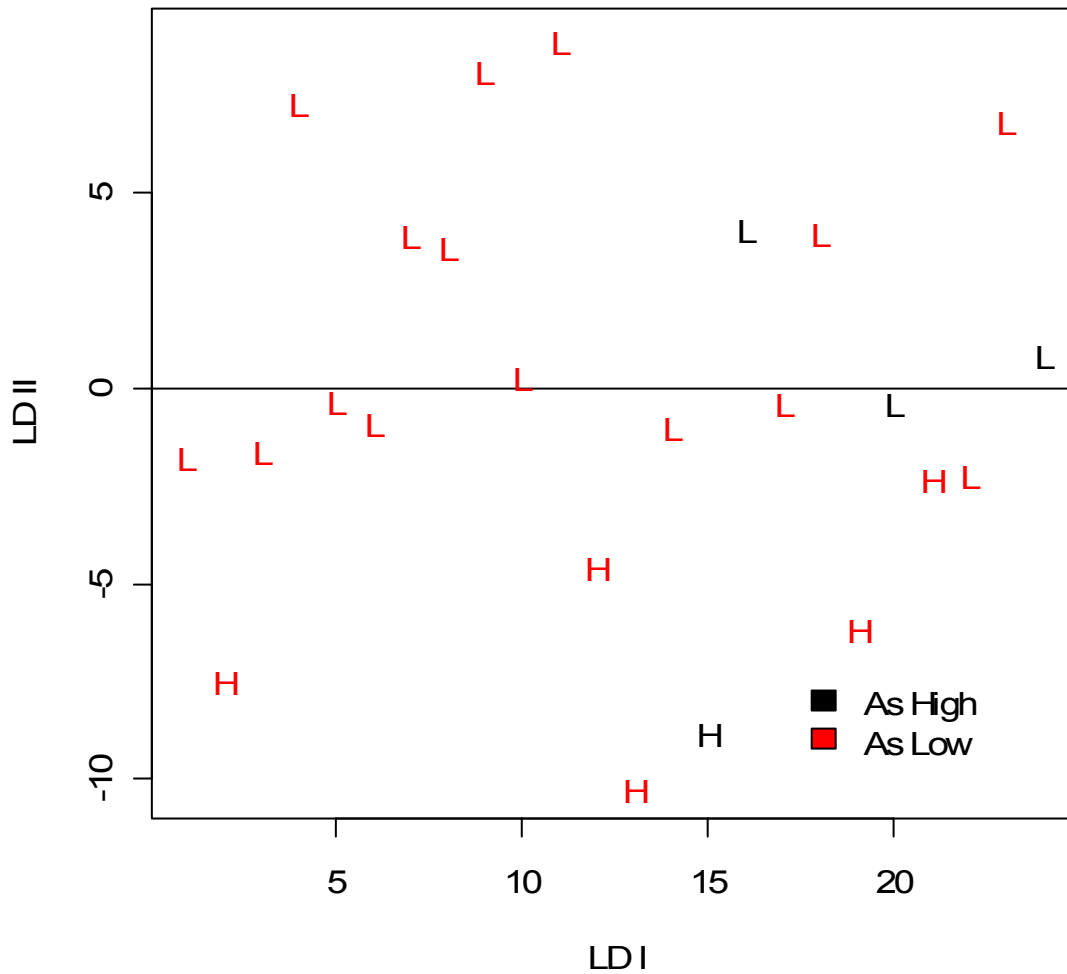




**Figure 29.** Classification of the August data set into “high” (H; [As] > 0.070 mg/l) and “low” (L; [As] < 0.070 mg/L) dissolved arsenic groups along linear discriminant I and linear discriminant II using the April data as the training set.



**Figure 30.** Classification of the April data set into “high” (H; [As] > 0.070 mg/l) and “low” (L; [As] < 0.070 mg/L) dissolved arsenic groups along linear discriminant I and linear discriminant II using the August data as the training set.



**Figure 31.** Classification of the random data set into “high” (H; [As] > 0.070 mg/l) and “low” (L; [As] < 0.070 mg/L) dissolved arsenic groups along linear discriminant I and linear discriminant II using a subset of the randomized data as the training set.

**Table 1.** Chemical analysis for water samples collected in April and August (Aspect, 2006). All values in mg/L unless otherwise noted. All values represent dissolved constituents unless otherwise noted.

Well ID	Date	Time	Arsenic		Major Ions									Arsenic Research Parameters						Intrusion	Field Parameters				
			Total As	As	Ca	Mg	K	Na	Sulfate	Carbonate	Total Alkalinity	Bicarbonate	Cl	Fe	Mn	P	S	SiO <sub>2</sub>	Total Phosphate		Br	Temp (°C)	Specific Conductivity (uohm/cm)	Dissolved Oxygen (mg/L)	pH
10	4/12/06	12:40	0.065	0.044	73	17	0.52	47	12	< 1	260	260	16	< 0.100	0.0760	0.01	4.0	28	0.014		10.2	598	2.18	6.87	106.7
	8/30/06	12:50	0.048	0.043	60	16	0.54	50	11	< 1	260	260	17	< 0.005	0.0385	0.03	3.5	28			10.23	553	1.45	7.54	-24
14	4/14/06	15:20	0.003	0.003	22	7.3	5.2	23	11	< 1	110	110	9.8	0.239	< 0.0100	< 0.01	3.8	20	< 0.005		16.77	351	2.01	8.05	-6
	8/31/06	14:45	0.006	0.006	44	7.9	7.2	33	13	< 1	180	180	11	< 0.005	0.0026	< 0.01	4.2	20			15.84	410	1.08	7.27	51.6
23	8/29/06	13:15	0.130	0.120									53							< 0.42	12.53	593	1.45	6.99	81.8
53	4/13/06	10:38	0.004	< 0.003	26	12	1.4	20	21	< 1	190	190	20	< 0.100	< 0.0100	0.01	7.1	21			10.33	325	5.96	7.79	158.7
	8/30/06	12:10	0.001	0.001	26	13	1.8	21	23	< 1	90	90	25	< 0.005	< 0.0005	0.02	7.5	21			12.44	310	5.94	6.51	122.9
54	4/15/06	13:00	0.026	0.026									39								9.6	438	7.35	7.8	19.1
	8/30/06	15:45	0.021	0.022									34								15.01	411	9.46	8.04	-35.5
62	4/13/06	9:05	0.019	0.016	56	10	1.6	19	15	< 1	190	190	15	< 0.100	0.0520	0.01	5.0	19			9.43	389	2.09	8.18	182
	8/30/06	10:49	0.039	0.033	44	7.5	2.0	24	13	< 1	150	150	11	< 0.005	0.1420	0.01	4.3	20			13.99	348	0.97	6.86	159.5
76	4/12/06	14:45	0.016	0.016	65	54	10	19	88	28	190	162	18	0.681	0.0730	0.04	29	31	< 0.05		10.35	711	4.78	7.68	-117.1
	8/29/06	17:31	0.005	0.003	50	54	9.6	18	86	< 1	250	250	17	< 0.005	0.0877	0.01	29	26			10.28	644	0.59	8.23	-238.1
79	4/14/06	16:45	0.008	0.008	32	20	8.1	20	22	< 1	160	160	13	< 0.100	0.0440	0.18	7.5	28	0.18		11.49	405	1.07	8.01	61.1
	8/31/06	10:57	0.006	0.007	37	20	8.2	20	26	< 1	160	160	12	< 0.005	0.0823	0.18	8.6	34			11.94	404	0.63	7.77	91.7
88	4/13/06	17:05	0.022	0.018	11	19	15	36	42	< 1	160	160	16	< 0.100	0.0330	0.30	14	27			11.01	446	0.47	8.29	10.2
	8/30/06	15:35	0.017	0.017	23	20	16	38	37	< 1	160	160	17	< 0.005	0.0491	0.34	12	30			11.79	418	0.48	7.56	38.8
109	4/13/06	15:44	0.004	0.004	5.3	1.6	2.5	69	17	24	150	126	7.7	0.117	< 0.0100	0.05	5.6	18	0.049		11.07	352	5.32	8.83	-48.6
	8/29/06	16:44	0.004	0.005	4.9	1.6	2.3	71	14	30	140	110	7.4	0.005	0.0021	0.06	4.7	19			14.36	325	5.03	9.13	-68.1
113	4/12/06	15:41	< 0.003	< 0.003									9.8							< 0.05	9.96	308	0.43	7.33	-61
	8/31/06	12:10	0.002	0.002									9.1								10.92	292	0.52	7.62	-43.4
122	8/29/06	14:30	0.004	0.004									22								16.00	330	4.1	7.79	40.5
141	4/14/06	15:55	0.006	0.006									11								11.18	262	2.92	8.39	55.1
	8/30/06	16:40	0.004	0.004									11								15.10	257	4.41	7.82	19.5
160	4/13/06	15:05	0.019	0.018									15								10.66	536	0.64	8.73	2.5
	8/31/06	11:15	0.019	0.019	2.1	1.5	5.9	120	16	20	220	200	15	0.094	0.0070	1.82	5.5	22			10.70	524	0.14	8.76	-29.7
162	4/14/06	10:50	0.003	< 0.003									17								10.48	485	0.7	7.74	-50.9
	8/31/06	10:30	0.002	0.001	59	25	3.1	14	35	< 1	190	190	17	< 0.005	0.0088	0.02	12	23			10.99	485	0.27	7.41	-41.4
166	4/13/06	14:50	< 0.003	< 0.003									0								10.55	308	5.00	8.34	17.7
	8/30/06	18:30	0.002	0.002									13								11.23	286	4.77	7.56	28
180	8/31/06	12:15	0.017	0.017	20	12	15	41	23	< 1	150	150	16	0.005	0.0456	0.34	7.7	29			10.67	404	0.13	8.33	-35.8
181	8/29/06	16:15	0.198	0.123									100							< 0.42	13.48	1502	2.45	7.47	6.2
188	4/13/06	17:30	< 0.003	< 0.003									12							< 0.05	9.62	276	5.2	8.87	-109.7
	8/30/06	10:38	0.004	0.005									15							< 0.05	16.91	385	2.13	7.12	16.8
195	4/12/06	13:05	0.224	0.220									19								8.89	559	4.22	8.5	184.1
	8/29/06	15:10	0.220	0.210									20								10.62	553	1.4	7.88	-76.4
203	4/13/06	11:35	< 0.003	< 0.003									21								10.14	330	1.86	5.91	119
	8/29/06	17:12	0.002	0.001									20								10.19	417	1.16	6.46	6.7
205	8/30/06	12:05	0.025	0.016	43	13	7.4	41	22	< 1	180	180	35	< 0.005	0.0460	0.03	7.4	24			10.13	491	0.44	8.01	-27.8
208	4/14/06	10:17	0.004	< 0.003	16	16	2.1	13	20	< 1	130	130	8.9	0.182	0.0670	0.04	6.5	24			10.77	307	3.77	7.92	335.4
	8/31/06	13:23	0.003	0.002	30	16	2.2	14	18	< 1	120	120	7.5	0.146	0.131	0.03	6	27			14.99	305	2.47	7.47	24.5

**Table 2.** Chemical analysis for water samples collected in April and August (Aspect, 2006). All values in mg/L unless otherwise noted. All values represent dissolved constituents unless otherwise noted.

Well ID	Date	Time	Arsenic		Major Ions									Arsenic Research Parameters						Intrusion Br	Field Parameters				
			Total As	As	Ca	Mg	K	Na	Sulfate	Carbonate	Total Alkalinity	Bicarbonate	Cl	Fe	Mn	P	S	SiO <sub>2</sub>	Total Phosphate		Temp (°C)	Specific Conductivity (uohmn/cm)	Dissolved Oxygen (mg/L)	pH	ORP
225	4/12/06	11:58	0.007	0.005																	11.28	383	3.23	7.75	119.5
	8/29/06	12:18	0.005	0.006	31	13	4.9	26	18	< 1	150	150	16	< 0.005	0.0350	0.09	6.0	20	0.071		13.29	355	3.04	8.5	-93.9
226	4/12/06	10:55	<b>0.050</b>	<b>0.044</b>																	10.44	736	12.7	6.98	116.3
	8/29/06	15:08	<b>0.560</b>	<b>0.570</b>	1.3	0.07	0.19	140	28	80	220	140	39	< 0.005	0.0033	0.05	9.3	12			14.61	661	13.61	7.56	20.1
227	4/13/06	11:40	<b>0.115</b>	<b>0.103</b>																	9.82	480	7.75	8.6	-114.6
	8/29/06	13:46	<b>0.160</b>	<b>0.150</b>	1.6	0.10	0.32	120	24	40	210	170	23	< 0.005	0.0034	0.08	7.9	12			14.23	518	3.74	9.42	-128.6
232	4/13/06	13:20	< 0.003	< 0.003	40	24	1.8	17	46	< 1	190	190	37	< 0.100	< 0.0100	< 0.01	15	17		< 0.05	11.17	574	4.36	8.54	-31.4
	8/30/06	16:49	< 0.001	< 0.001	69	25	1.8	18	43	< 1	180	180	36	< 0.005	< 0.0005	0.01	14	17			10.90	538	3.77	8.16	29.5
239	4/12/06	14:01	<b>0.074</b>	<b>0.060</b>	28	7	5.9	81	35	< 1	260	260	22	0.110	<b>0.0850</b>	0.01	12	20			10.96	545	1.24	7.19	-27.3
	8/30/06	17:35	<b>0.080</b>	<b>0.080</b>																	11.01	502	0.18	7.76	-94.1
240	4/14/06	17:25	<b>0.022</b>	<b>0.023</b>	18	13	14	61	36	< 1	160	160	18	< 0.100	0.0240	0.41	12	220	0.41		11.39	475	0.87	8.31	52.7
	8/31/06	10:00	<b>0.018</b>	<b>0.018</b>	16	13	15	61	41	< 1	160	160	18	0.023	0.0436	0.43	14	26			11.18	474	0.52	7.83	184.3
245	4/14/06	12:25	0.009	0.009	14	5.6	6.1	44	21	< 1	130	130	20	< 0.100	< 0.0100	0.01	7.1	16		< 0.05	10.3	411	2.17	7.09	84.8
	8/30/06	13:08	0.042	<b>0.039</b>	27	5.4	6.9	68	23	< 1	170	170	22	< 0.005	0.0011	0.02	7.5	14			10.56	444	1.14	6.97	133.7
247	4/12/06	16:34	<b>0.188</b>	<b>0.187</b>	3.2	0.47	0.36	180	110	< 1	170	170	68	< 0.100	< 0.0100	0.12	38	14	0.12	< 0.05	11.11	863	0.52	8.67	-26.1
	8/29/06	13:09	<b>0.170</b>	<b>0.170</b>	2.7	0.25	0.33	160	92	40	190	150	59	< 0.005	0.0073	0.12	31	14		2.5	11.09	746	0.07	9.9	-138.5
257	4/13/06	9:55	0.005	0.003	69	12	1.0	18	14	< 1	98	98	14	< 0.100	<b>0.160</b>	< 0.01	4.5	21			9.44	436	1.43	7.73	165.7
	8/30/06	10:10	0.004	0.005	57	12	1.0	20	11	< 1	180	180	15	< 0.005	<b>0.0946</b>	0.02	3.8	22			13.28	408	1.32	6.57	172.9
264	4/12/06	13:59	0.006	0.004	33	11	1.7	43	27	< 1	160	160	19	< 0.100	0.0180	0.03	8.9	21			10.63	393	3.32	8.48	162.9
	8/29/06	12:25	0.003	0.003	26	11	1.6	41	23	< 1	150	150	18	< 0.005	0.0115	0.03	7.7	21			11.00	400	2.74	6.95	92.6
268	4/15/06	14:15	<b>0.014</b>	<b>0.014</b>																	10.30	353	7.22	7.93	22.4
	8/29/06	11:22	<b>0.014</b>	<b>0.012</b>	26	12	5.5	26	20	< 1	150	150	13	< 0.005	0.0078	0.12	6.7	19			15.62	347	5.64	8.1	-35.7
300	4/13/06	13:30	< 0.003	< 0.003																	10.68	319	6.51	6.98	86.3
	8/30/06	14:20	0.002	0.002																	11.01	306	6.65	6.79	81.2
354	4/13/06	14:00	<b>0.206</b>	<b>0.171</b>	22	3.1	6.9	81	100	< 1	180	180	18	< 0.100	< 0.0100	0.02	35	19	0.017		10.28	589	0.4	7.7	-18.4
	8/30/06	18:10	<b>0.170</b>	<b>0.170</b>	26	2.8	6.6	86	67	< 1	170	170	19	< 0.005	0.0042	0.02	22	20			12.00	494	1.42	7.35	50.6
393	4/12/06	16:00	<b>0.020</b>	< 0.003																	10.66	451	2.03	8.19	144.9
	8/30/06	13:45	0.010	0.002																	11.46	409	2.11	6.95	87.3
398	4/14/06	13:35	<b>0.234</b>	<b>0.234</b>																	10.28	551	1.28	9.31	29.9
	8/29/06	18:30	<b>0.192</b>	<b>0.198</b>																	12.36	545	2.92	8.82	0.2
399	4/14/06	11:19	< 0.003	< 0.003																	9.85	417	5.21	8.37	35.3
	8/29/06	16:16	0.001	0.003																	13.50	393	2.96	9.05	-116.4
402	4/12/06	9:35	<b>0.019</b>	<b>0.017</b>																	11.15	696	0.74	8.14	-140.5
	8/29/06	11:35	<b>0.016</b>	<b>0.016</b>																	12.18	662	0.99	7.38	142.7
425	4/12/06	15:18	0.004	0.003																	10.11	344	3.34	8.16	136.7
	8/30/06	11:38	0.004	0.005																	10.34	360	1.04	6.75	135.1

**Table 3.** Rock analysis for samples taken on Lummi Island, Washington (G=Greenstone; Cg=Chuckanut Conglomerate; Sh=Chuckanut Shale; C=Coalified log in Chuckanut; Ss=Chuckanut Sandstone).

Rock Type	ME-ICP06 (%)													C-IR07 (%)	S-IR08 (%)
	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	Cr2O3	TiO2	MnO	P2O5	SrO	BaO	C	S
G	55.10	17.70	7.23	5.04	3.54	6.53	0.09	<0.01	0.52	0.11	0.09	0.02	0.01	0.07	0.12
Cg	80.20	8.33	3.00	0.92	0.82	1.57	1.68	<0.01	0.30	0.07	0.06	0.06	0.08	0.16	0.08
Sh	64.60	13.60	6.53	1.28	2.05	1.84	1.80	0.01	0.69	0.13	0.09	0.06	0.12	0.41	0.04
C	11.15	1.65	1.10	43.40	0.49	0.48	0.14	<0.01	0.07	0.77	0.07	0.01	0.01	13.20	0.05
Ss	69.50	12.70	4.29	2.10	1.28	3.04	1.98	0.01	0.49	0.10	0.07	0.07	0.11	0.11	0.02

Rock Type	ME-MS81 (ppm)														
	Ag	Ba	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Ga	Gd	Hf	Ho	La
G	<1	55.6	8.3	24.5	20	0.06	53	2.27	1.40	0.61	15.2	1.98	1.9	0.47	4.1
Cg	<1	689.0	38.4	68.4	30	5.86	18	2.57	1.47	0.89	10.3	3.41	2.1	0.51	19.6
Sh	<1	1105.0	40.4	16.0	90	9.82	41	3.73	2.18	1.02	18.0	4.32	4.0	0.73	20.7
C	<1	49.7	11.1	2.7	10	0.11	<5	1.79	1.05	0.49	4.1	2.0	0.4	0.36	7.7
Ss	<1	942.0	40.9	10.6	50	8.15	10	2.72	1.54	0.98	14.8	3.43	3.4	0.51	21.3

Rock Type	ME-MS81 (ppm)														
	Lu	Mo	Nb	Nd	Ni	Pb	Pr	Rb	Sm	Sn	Sr	Ta	Tb	Th	Tl
G	0.2	<2	2.3	5.9	15.0	<5	1.2	1.2	1.7	1.0	209.0	1.2	0.3	0.3	<0.5
Cg	0.2	<2	11.4	18.6	25.0	9.0	4.6	43.0	3.4	1.0	467.0	7.1	0.5	4.5	<0.5
Sh	0.3	<2	9.5	20.6	39.0	11.0	5.1	56.5	4.3	2.0	468.0	0.8	0.7	5.4	<0.5
C	0.1	<2	1.0	7.3	5.0	<5	1.5	3.3	1.6	1.0	68.9	0.1	0.3	0.4	<0.5
Ss	0.2	<2	6.4	18.8	20.0	10.0	4.8	44.3	3.7	1.0	577.0	0.5	0.5	4.7	<0.5

Rock Type	ME-MS81 (ppm)								ME-MS42 (ppm)						OA-GRA05 (%)	TOT-ICP06 (%)
	Tm	U	V	W	Y	Yb	Zn	Zr	As	Bi	Hg	Sb	Se	Te	LOI	Total
G	0.21	0.12	191	70	11.8	1.46	71	75	1.9	0.02	0.057	0.07	0.5	0.01	3.21	99.2
Cg	0.21	1.38	58	269	12.8	1.40	47	77	20.1	0.08	0.187	0.26	0.4	0.03	2.79	99.9
Sh	0.31	2.34	127	15	18.8	2.18	108	156	10.4	0.17	0.025	0.43	0.5	0.02	6.08	98.9
C	0.14	0.24	35	10	12.0	0.97	13	20	5.3	0.02	0.028	2.49	0.8	0.01	38.80	98.1
Ss	0.22	1.53	84	6	13.2	1.50	60	129	5.1	0.04	0.021	0.18	0.4	0.01	2.78	98.5

**Table 4.** The concentration of each arsenic species in solution in well samples from the April data set. All values are in mg/L.

Well	As(III)	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	H <sub>4</sub> AsO <sub>3</sub> <sup>+</sup>	HAsO <sub>3</sub> <sup>-2</sup>	AsO <sub>3</sub> <sup>-3</sup>	As(V)	H <sub>2</sub> AsO <sub>4</sub> <sup>-2</sup>	HAsO <sub>4</sub> <sup>-</sup>	AsO <sub>4</sub> <sup>-3</sup>	H <sub>3</sub> AsO <sub>4</sub>
10	0.0010	0.0016	4.7E-06	1.09E-10	3.53E-14	3.05E-23	0.0430	0.0263	0.0543	2.94E-07	1.28E-06
14	7.19E-06	1.14E-05	6.57E-07	5.09E-14	1.01E-13	1.69E-21	0.0030	0.0050	0.0007	1E-06	1.09E-09
53	2.99E-10	4.9E-10	1.2E-11	3.97E-18	7.52E-19	5.43E-27	0.0015	0.0023	0.0006	2.11E-07	1.59E-09
54	0.0003	0.0005	1.12E-05	3.65E-12	6.94E-13	4.98E-21	0.0257	0.0388	0.0095	3.65E-06	2.59E-08
62	2.01E-11	3.19E-11	1.84E-12	1.05E-19	2.72E-19	4.66E-27	0.0160	0.0273	0.0028	6.11E-06	3.16E-09
76	0.0160	0.0264	0.0005	2.75E-10	2.44E-11	1.37E-19	1.49E-05	2.12E-05	6.77E-06	1.54E-09	2.47E-11
79	3.76E-07	6.06E-07	2.57E-08	2.96E-15	2.84E-15	3.56E-23	0.0080	0.0131	0.0019	2.1E-06	3.36E-09
88	4.05E-06	6.3E-06	5E-07	1.62E-14	1.03E-13	2.41E-21	0.0180	0.0314	0.0025	9.46E-06	2.21E-09
109	7.33E-07	9.64E-07	2.66E-07	7.12E-16	1.9E-13	1.55E-20	0.0040	0.0073	0.0002	7.7E-06	4.31E-11
113	0.0015	0.0025	2.07E-05	5.83E-11	4.44E-13	1.1E-21	5.4E-06	5.89E-06	4.23E-06	1.89E-10	3.44E-11
141	1.63E-08	2.49E-08	2.5E-09	5.07E-17	6.52E-16	1.94E-23	0.0060	0.0106	0.0007	4.04E-06	4.73E-10
160	1.61E-07	2.22E-07	4.79E-08	2.07E-16	2.67E-14	1.7E-21	0.0180	0.0329	0.0009	2.71E-05	3.05E-10
162	0.0012	0.0019	4.22E-05	1.76E-11	2.38E-12	1.54E-20	0.0003	0.0005	0.0001	4.01E-08	4.25E-10
166	1.29E-07	2E-07	1.74E-08	4.56E-16	3.93E-15	1.02E-22	0.0015	0.0026	0.0002	8.79E-07	1.47E-10
188	2.81E-05	3.67E-05	1.05E-05	2.48E-14	7.66E-12	6.48E-19	0.0015	0.0027	5.61E-05	2.99E-06	1.31E-11
195	1.47E-11	2.2E-11	2.6E-12	3.49E-20	7.87E-19	2.79E-26	0.2200	0.3945	0.0191	0.0002	1.04E-08
203	0.0014	0.0023	7.24E-07	1.4E-09	5.96E-16	5.63E-26	0.0001	1.4E-05	0.0003	1.71E-11	5.64E-08
208	9.28E-17	1.51E-16	5.05E-18	9.07E-25	4.38E-25	4.34E-33	0.0015	0.0024	0.0004	3.04E-07	9.21E-10
225	2.48E-08	4.08E-08	9.43E-10	3.63E-16	5.66E-17	3.87E-25	0.0050	0.0074	0.0020	6.47E-07	6.28E-09
226	0.0002	0.0003	1.22E-06	1.68E-11	1.19E-14	1.34E-23	0.0438	0.0316	0.0505	4.58E-07	9.23E-07
227	0.0235	0.0341	0.0053	4.29E-11	2.09E-09	9.63E-17	0.0796	0.1439	0.0055	8.61E-05	2.41E-09
232	9.01E-07	1.32E-06	1.88E-07	1.91E-15	6.92E-14	2.9E-21	0.0015	0.0027	0.0001	1.45E-06	6.03E-11
239	0.0589	0.0984	0.0006	3.17E-09	1.01E-11	1.86E-20	0.0011	0.0011	0.0010	2.52E-08	1.19E-08
240	1.47E-07	2.28E-07	1.92E-08	5.58E-16	4.22E-15	1.05E-22	0.0230	0.0403	0.0030	1.28E-05	2.59E-09
245	0.0002	0.0003	1.56E-06	1.3E-11	1.95E-14	2.8E-23	0.0088	0.0073	0.0092	1.37E-07	1.3E-07
247	2.37E-05	3.34E-05	6.39E-06	3.58E-14	3.19E-12	1.81E-19	0.1870	0.3404	0.0110	0.0002	4.14E-09
257	6.79E-10	1.12E-09	2.29E-11	1.04E-17	1.2E-18	7.31E-27	0.0030	0.0044	0.0013	3.48E-07	4.04E-09
264	1.24E-12	1.85E-12	2.24E-13	3.07E-21	7E-20	2.5E-27	0.0040	0.0072	0.0004	3.3E-06	2.1E-10
268	3.27E-05	5.32E-05	1.79E-06	3.12E-13	1.55E-13	1.55E-21	0.0140	0.0222	0.0040	2.87E-06	8.19E-09
300	6.04E-05	0.0001	3.88E-07	5.29E-12	3.84E-15	4.34E-24	0.0014	0.0010	0.0017	1.51E-08	3.04E-08
354	0.0503	0.0828	0.0016	8.27E-10	8.4E-11	4.95E-19	0.1207	0.1738	0.0530	1.32E-05	1.84E-07
393	2.4E-11	3.79E-11	2.36E-12	1.22E-19	3.79E-19	6.98E-27	0.0015	0.0026	0.0003	6.09E-07	2.86E-10
398	1.85E-09	1.72E-09	1.39E-09	4.21E-19	2.91E-15	7.04E-22	0.2340	0.4355	0.0032	0.0014	2.76E-10
399	2.82E-08	4.34E-08	3.94E-09	9.24E-17	9.21E-16	2.48E-23	0.0015	0.0026	0.0002	9.26E-07	1.28E-10
402	0.0168	0.0267	0.001512	9.7E-11	2.21E-10	3.69E-18	0.0002	0.0003	3.15E-05	6.09E-08	4.02E-11
425	1.31E-10	2.09E-10	1.18E-11	7.24E-19	1.73E-18	2.91E-26	0.0030	0.0051	0.0005	1.11E-06	6.5E-10

**Table 5.** The concentration of each arsenic species in solution in well samples from the August data set. All values are in mg/L.

Well	As(III)	H <sub>3</sub> AsO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	H <sub>4</sub> AsO <sub>3</sub> <sup>+</sup>	HAsO <sub>3</sub> <sup>-2</sup>	AsO <sub>3</sub> <sup>-3</sup>	As(V)	H <sub>2</sub> AsO <sub>4</sub> <sup>-2</sup>	HAsO <sub>4</sub> <sup>-</sup>	AsO <sub>4</sub> <sup>-3</sup>	H <sub>3</sub> AsO <sub>4</sub>
10	0.0311	0.0517	0.000706	7.44E-10	2.48E-11	1E-19	0.0119	0.0154	0.0068	8.07E-07	3.43E-08
14	0.0001	0.0002	2.29E-06	6.69E-12	5.63E-14	1.51E-22	0.0059	0.0061	0.0049	1.99E-07	4.84E-08
23	0.0047	0.0078	3.3E-05	4E-10	3.66E-13	4.57E-22	0.1153	0.0847	0.1312	1.34E-06	2.39E-06
53	5.74E-05	9.62E-05	1.34E-07	1.49E-11	4.9E-16	2.01E-25	0.0009	0.0003	0.0015	1.61E-09	8.02E-08
54	0.0008	0.0012	6.31E-05	5.48E-12	8.79E-12	1.34E-19	0.0212	0.0352	0.0048	6.62E-06	8.02E-09
62	6.78E-06	1.14E-05	3.77E-08	7.83E-13	3.31E-16	3.23E-25	0.0330	0.0201	0.0417	2.43E-07	1.04E-06
76	0.0030	0.0047	0.0003	1.39E-11	5.48E-11	1.09E-18	2.87E-08	4.95E-08	4.46E-09	1.28E-11	4.57E-15
79	2.26E-07	3.72E-07	9.24E-09	3.15E-15	5.99E-16	4.39E-24	0.0070	0.0104	0.0027	9.74E-07	8.13E-09
88	0.0002	0.0003	5.16E-06	4.65E-12	2.05E-13	9.2E-22	0.0168	0.0222	0.0093	1.27E-06	4.54E-08
109	1.89E-07	1.95E-07	1.23E-07	7.22E-17	2.05E-13	3.78E-20	0.0050	0.0093	0.0001	2.13E-05	1.39E-11
113	0.0017	0.0028	4.67E-05	3.32E-11	2.04E-12	1.02E-20	0.0003	0.0004	0.0002	2.88E-08	6.92E-10
122	2.94E-06	4.8E-06	1.47E-07	3.89E-14	1.21E-14	1.08E-22	0.0040	0.0060	0.0015	6.57E-07	4.39E-09
141	1.32E-05	2.15E-05	6.83E-07	1.63E-13	5.76E-14	5.33E-22	0.0040	0.0061	0.0014	6.95E-07	3.84E-09
160	1.56E-06	2.13E-06	4.92E-07	1.85E-15	2.95E-13	2.02E-20	0.0190	0.0348	0.000922	3.07E-05	2.81E-10
162	0.0010	0.0016	1.67E-05	3.12E-11	4.52E-13	1.4E-21	3.7E-05	4.36E-05	2.59E-05	1.73E-09	1.77E-10
166	6.25E-05	0.0001	1.54E-06	1.42E-12	5.96E-14	2.62E-22	0.0019	0.0026	0.0011	1.44E-07	5.23E-09
180	9.82E-05	0.0002	1.3E-05	3.55E-13	2.89E-12	7.34E-20	0.0169	0.0296	0.0021	9.7E-06	1.73E-09
181	0.0249	0.0413	0.0005	7.01E-10	1.92E-11	7.51E-20	0.0981	0.1219	0.0622	5.95E-06	3.79E-07
188	0.0026	0.0043	2.95E-05	1.64E-10	5.38E-13	1.06E-21	0.0024	0.0021	0.0024	5.03E-08	3.38E-08
195	0.1853	0.3021	0.0092	1.99E-09	7.2E-10	6.48E-18	0.0247	0.0386	0.0078	4.47E-06	1.8E-08
203	0.0010	0.0017	1.9E-06	2.91E-10	5.56E-15	1.86E-24	8.82E-07	2.61E-07	1.39E-06	1.14E-12	8.38E-11
205	0.0009	0.0015	5.86E-05	7.12E-12	6.07E-12	7.22E-20	0.0151	0.0247	0.0037	3.81E-06	6.28E-09
208	8.98E-05	0.0001	2.1E-06	2.52E-12	7.86E-14	3.23E-22	0.0019	0.0024	0.0012	1.2E-07	7.5E-09
225	0.0004	0.0006	9.01E-05	1.01E-12	3.34E-11	1.39E-18	0.0056	0.0100	0.0005	5.19E-06	2.71E-10
226	0.0177	0.0293	0.0005	4.04E-10	2.29E-11	1.16E-19	0.5523	0.7362	0.3012	4.61E-05	1.51E-06
227	6E-05	4.52E-05	5.53E-05	8.62E-15	1.8E-10	6.5E-17	0.1499	0.2793	0.0016	0.0013	1.09E-10
232	7.93E-08	1.26E-07	7.37E-09	4.36E-16	1.12E-15	1.94E-23	0.0005	0.0008	8.97E-05	1.9E-07	1.09E-10
239	0.0790	0.1298	0.0030	1.13E-09	1.84E-10	1.27E-18	0.0010	0.0015	0.0004	1.31E-07	1.2E-09
240	3E-10	4.9E-10	1.36E-11	3.63E-18	9.75E-19	7.99E-27	0.0180	0.0276	0.0062	2.9E-06	1.62E-08
245	4.53E-05	7.59E-05	2.83E-07	4.06E-12	2.72E-15	3E-24	0.0390	0.0277	0.0453	3.93E-07	8.49E-07
247	5.95E-06	2.34E-06	7.62E-06	1.48E-16	6.46E-11	6.32E-17	0.1700	0.3155	0.0006	0.0040	1.32E-11
257	3.54E-06	5.93E-06	9.83E-09	7.97E-13	4.28E-17	2.08E-26	0.0050	0.0018	0.0075	1.12E-08	3.63E-07
264	9.19E-05	0.0002	5.57E-07	8.62E-12	5.23E-15	5.59E-24	0.0029	0.0020	0.0034	2.75E-08	6.78E-08
268	0.0002	0.0004	2.16E-05	1.39E-12	3.56E-12	6.39E-20	0.0118	0.0198	0.0023	4.35E-06	3.44E-09
300	0.0004	0.0007	1.72E-06	5.55E-11	1.12E-14	8.27E-24	0.0016	0.0009	0.0021	8.14E-09	6.04E-08
354	0.0047	0.0078	7.39E-05	1.74E-10	1.83E-12	5.15E-21	0.1653	0.1849	0.1250	6.6E-06	9.91E-07
393	8.44E-05	0.0001	5.22E-07	7.92E-12	5E-15	5.44E-24	0.0019	0.0013	0.0023	1.84E-08	4.49E-08
398	7.23E-07	9.44E-07	2.69E-07	7.16E-16	2.01E-13	1.69E-20	0.1980	0.3639	0.0083	0.0004	2.23E-09
399	1.11E-05	1.24E-05	6.25E-06	5.5E-15	8.32E-12	1.24E-18	0.0030	0.0055	7.43E-05	1.03E-05	1.19E-11
402	2.6E-07	4.34E-07	4.43E-09	9.03E-15	1.18E-16	3.56E-25	0.0160	0.0184	0.0116	7.01E-07	8.63E-08
425	2.95E-05	4.95E-05	1.1E-07	4.39E-12	6.3E-16	4.15E-25	0.0050	0.0025	0.0068	2.13E-08	2.11E-07



**Table 6.** P-values for correlations between variables in the merged April and August data set.

	Temp	Specific Cond.	DO	pH	ORP	Total As	As	Ca	Mg	K	Na	SO <sub>4</sub>	Total Alkalinity	Cl	Fe	Mn	P	S	SiO <sub>2</sub>	Total PO <sub>4</sub>
Temp		0.2620	0.6630	0.6760	0.4470	0.8810	0.5170	0.0441	0.1880	0.9730	0.6290	0.4650	0.0222	0.6000	0.1320	0.1170	0.1780	0.4720	0.2790	0.5480
SC	0.2620		0.0054	0.3650	0.0609	7.47E-11	3.72E-09	0.6530	0.9640	0.7190	0.0049	0.0001	3.27E-07	3.61E-07	0.5470	0.7020	0.7860	0.0001	0.5200	0.5480
DO	0.6630	0.0054		0.6860	0.2750	0.0498	0.0792	0.7190	0.9280	0.0028	0.1920	0.1920	0.3360	0.2040	0.4270	0.0955	0.1540	0.1810	0.0627	0.7200
pH	0.6760	0.3650	0.6860		6.74E-05	0.1660	0.1290	0.0057	0.3220	0.9820	0.1700	0.1670	0.9010	0.8390	0.1810	0.1430	0.0066	0.1600	0.2550	0.5480
ORP	0.4470	0.0609	0.2750	6.74E-05		0.6950	0.2630	0.1260	0.6360	0.5740	0.1050	0.0559	0.0718	0.7050	0.6650	0.2900	0.1410	0.0465	0.2740	0.9050
T. As	0.8810	7.47E-11	0.0498	0.1660	0.6950		0.0000	0.0569	0.0024	0.8480	4.71E-07	0.1170	0.0022	0.0003	0.5710	0.8920	0.0582	0.1200	0.4420	0.5480
As	0.5170	3.72E-09	0.0792	0.1290	0.2630	0.0000		0.0222	0.0010	0.6850	3.19E-08	0.1460	0.0051	0.0020	0.5630	0.8390	0.0184	0.1400	0.3540	0.3990
Ca	0.0441	0.6530	0.7190	0.0057	0.1260	0.0569	0.0222		1.73E-05	0.7530	1.45E-05	0.1490	0.1600	0.5650	0.3290	0.0032	0.0006	0.1400	0.0246	0.5330
Mg	0.1880	0.9640	0.9280	0.3220	0.6360	0.0024	0.0010	1.73E-05		0.0331	1.77E-07	0.3210	0.8920	0.5200	0.9520	0.0038	0.7770	0.3550	3.38E-07	0.9010
K	0.9730	0.7190	0.0028	0.9820	0.5740	0.8480	0.6850	0.7530	0.0331		0.5580	0.0529	0.2570	0.2030	0.6380	0.3380	0.0361	0.0502	0.0016	0.3990
Na	0.6290	0.0049	0.1920	0.1700	0.1050	4.71E-07	3.19E-08	1.45E-05	1.77E-07	0.5580		0.2370	0.1740	0.0098	0.6210	0.0078	0.0157	0.2410	0.0232	0.9050
SO <sub>4</sub>	0.4650	0.0001	0.1920	0.1670	0.0559	0.1170	0.1460	0.1490	0.3210	0.0529	0.2370		0.0663	5.42E-05	0.7000	0.2550	0.1070	0.0000	0.6930	0.0610
T. Alk	0.0222	3.27E-07	0.3360	0.9010	0.0718	0.0022	0.0051	0.1600	0.8920	0.2570	0.1740	0.0663		0.0047	0.3760	0.9640	0.5230	0.0646	0.7250	1.0000
Cl	0.6000	3.61E-07	0.2040	0.8390	0.7050	0.0003	0.0020	0.5650	0.5200	0.2030	0.0098	5.42E-05	0.0047		0.1220	0.0061	0.8470	0.0001	0.0326	0.3150
Fe	0.1320	0.5470	0.4270	0.1810	0.6650	0.5710	0.5630	0.3290	0.9520	0.6380	0.6210	0.7000	0.3760	0.1220		0.2230	0.8650	0.7540	0.3650	0.2510
Mn	0.1170	0.7020	0.0955	0.1430	0.2900	0.8920	0.8390	0.0032	0.0038	0.3380	0.0078	0.2550	0.9640	0.0061	0.2230		0.8030	0.2890	5.39E-05	0.5950
P	0.1780	0.7860	0.1540	0.0066	0.1410	0.0582	0.0184	0.0006	0.7770	0.0361	0.0157	0.1070	0.5230	0.8470	0.8650	0.8030		0.0912	0.0519	4.96E-05
S	0.4720	0.0001	0.1810	0.1600	0.0465	0.1200	0.1400	0.1400	0.3550	0.0502	0.2410	0.0000	0.0646	0.0001	0.7540	0.2890	0.0912		0.6840	0.0610
Si	0.2790	0.5200	0.0627	0.2550	0.2740	0.4420	0.3540	0.0246	3.38E-07	0.0016	0.0232	0.6930	0.7250	0.0326	0.3650	5.39E-05	0.0519	0.6840		0.6150
T. PO <sub>4</sub>	0.5480	0.5480	0.7200	0.5480	0.9050	0.5480	0.3990	0.5330	0.9010	0.3990	0.9050	0.0610	1.0000	0.3150	0.2510	0.5950	4.96E-05	0.0610	0.6150	

**Table 7.** R values for correlations between variables in the merged April and August data set.

	Temp	Specific Cond.	DO	pH	ORP	Total As	As	Ca	Mg	K	Na	SO <sub>4</sub>	Total Alkalinity	Cl	Fe	Mn	P	S	SiO <sub>2</sub>	Total PO <sub>4</sub>
Temp		-0.0874	0.0339	-0.0326	-0.0592	-0.0118	0.0513	-0.2200	-0.1450	-0.0037	0.0531	-0.0801	-0.2580	-0.0417	-0.1810	-0.1720	0.1510	-0.0789	-0.1200	0.2140
SC	-0.0874		-0.2170	0.0706	-0.1460	0.5150	0.4670	0.0493	-0.0050	-0.0393	0.3090	0.4240	0.5750	0.4040	-0.0725	-0.0421	0.0306	0.4230	-0.0715	0.2140
DO	0.0339	-0.2170		0.0315	0.0848	-0.1550	-0.1390	0.0394	-0.0100	-0.3270	-0.1430	-0.1430	-0.1080	0.1010	0.0957	-0.1830	-0.1600	-0.1470	-0.2070	-0.1430
pH	-0.0326	0.0706	0.0315		-0.3100	0.1090	0.1200	-0.3030	-0.1090	0.0025	0.1510	0.1520	0.0140	-0.0161	0.1610	-0.1610	0.3060	0.1540	-0.1270	0.2140
ORP	-0.0592	-0.1460	0.0848	-0.3100		-0.0310	-0.0886	0.1670	0.0522	-0.0614	-0.1780	-0.2090	-0.2030	-0.0301	0.0521	0.1160	-0.1650	-0.2180	0.1220	-0.0714
T. As	-0.0118	0.5150	-0.1550	0.1090	-0.0310		0.8710	-0.2110	-0.3390	0.0212	0.5590	0.1740	0.3490	0.2890	-0.0690	0.0150	0.2150	0.1730	-0.0864	0.2140
As	0.0513	0.4670	-0.1390	0.1200	-0.0886	0.8710		-0.2530	-0.3680	0.0447	0.6130	0.1610	0.3180	0.2500	-0.0703	-0.0225	0.2680	0.1630	-0.1040	0.2860
Ca	-0.2200	0.0493	0.0394	-0.3030	0.1670	-0.2110	-0.2530		0.4770	-0.0347	-0.4790	-0.1590	0.1590	-0.0639	-0.1180	0.3250	-0.3860	-0.1630	0.2510	-0.1820
Mg	-0.1450	-0.0050	-0.0100	-0.1090	0.0522	-0.3390	-0.3680	0.4770		0.2360	-0.5820	0.1100	0.0156	-0.0722	-0.0074	0.3220	-0.0324	0.1030	0.5760	0.0364
K	-0.0037	-0.0393	-0.3270	0.0025	-0.0614	0.0212	0.0447	-0.0347	0.2360		-0.0645	0.2130	-0.1280	-0.1410	0.0568	0.1060	0.2370	0.2160	0.3530	0.2860
Na	0.0531	0.3090	-0.1430	0.1510	-0.1780	0.5590	0.6130	-0.4790	-0.5820	-0.0645		0.1310	0.1550	0.2880	-0.0600	-0.2950	0.2740	0.1300	-0.2550	0.0714
SO <sub>4</sub>	-0.0801	0.4240	-0.1430	0.1520	-0.2090	0.1740	0.1610	-0.1590	0.1100	0.2130	0.1310		0.2080	0.4490	-0.0468	-0.1260	0.1820	0.9870	-0.0443	0.5710
T. Alk	-0.2580	0.5750	-0.1080	0.0140	-0.2030	0.3490	0.3180	0.1590	0.0156	-0.1280	0.1550	0.2080		0.3230	-0.1100	-0.0052	-0.0744	0.2100	-0.0406	0.0000
Cl	-0.0417	0.4040	0.1010	-0.0161	-0.0301	0.2890	0.2500	-0.0639	-0.0722	-0.1410	0.2880	0.4490	0.3230		-0.1890	-0.3060	-0.0220	0.4380	-0.2410	0.2960
Fe	-0.1810	-0.0725	0.0957	0.1610	0.0521	-0.0690	-0.0703	-0.1180	-0.0074	0.0568	-0.0600	-0.0468	-0.1100	-0.1890		0.1480	-0.0211	-0.0380	0.1120	-0.3560
Mn	-0.1720	-0.0421	-0.1830	-0.1610	0.1160	0.0150	-0.0225	0.3250	0.3220	0.1060	-0.2950	-0.1260	-0.0052	-0.3060	0.1480		0.0284	-0.1170	0.4530	0.1610
P	0.1510	0.0306	-0.1600	0.3060	-0.1650	0.2150	0.2680	-0.3860	-0.0324	0.2370	0.2740	0.1820	-0.0744	-0.0220	-0.0211	0.0284		0.1910	0.2230	1.0000
S	-0.0789	0.4230	-0.1470	0.1540	-0.2180	0.1730	0.1630	-0.1630	0.1030	0.2160	0.1300	0.9870	0.2100	0.4380	-0.0380	-0.117	0.1910		-0.0456	0.5710
Si	-0.1200	-0.0715	-0.2070	-0.1270	0.1220	-0.0864	-0.1040	0.2510	0.5760	0.3530	-0.2550	-0.0443	-0.0406	-0.2410	0.1120	0.453	0.2230	-0.0456		0.1480
T. PO <sub>4</sub>	0.2140	0.2140	-0.1430	0.2140	-0.0714	0.2140	0.2860	-0.1820	0.0364	0.2860	0.0714	0.5710	0.0000	0.2960	-0.3560	0.161	1.0000	0.5710	0.1480	

**Table 8.** The PCA analysis for the merged April and August data set.

**Importance of Components**

	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5	Comp.6	Comp.7
Standard deviation	1.622169	1.322160	1.125174	0.887901	0.532910	0.458562	0.267964
Proportion of Variance	0.375919	0.249730	0.180860	0.112624	0.040571	0.030040	0.010258
Cumulative Proportion	0.375919	0.625648	0.806508	0.919132	0.959702	0.989742	1

**Component Loadings**

	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5	Comp.6	Comp.7
Ca	-0.412	-0.351	0.407	0.140	-0.385	0.559	-0.247
Mg	-0.369	-0.540	-0.146	0.119	0.264	-0.539	-0.420
K	-0.142	-0.119	-0.778	-0.332	-0.484	0.129	
Na	0.590	-0.209	0.173	-0.759			
SO3	0.303	-0.522	-0.297	0.306	0.417	0.448	0.283
Talk	0.122	-0.456	0.328	-0.759	0.291		
Cl	0.468	-0.301	0.112	0.379	-0.609	-0.377	0.146

	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5	Comp.6	Comp.7
SS loadings	1	1	1	1	1	1	1
Proportion of Variance	0.143	0.143	0.143	0.143	0.143	0.143	0.143
Cumulative Proportion	0.143	0.286	0.429	0.571	0.714	0.857	1.000

**Sample Size**

Season	As Concentration
April 24	High 6
August 17	Low 35

**Table 9.** The variance described by the first 8 principal components in the randomized merged data set.

**Importance of Components**

	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5	Comp.6	Comp.7	Comp.8
Standard deviation	1.438525	1.297537	1.140577	1.055655	0.850039	0.678493	0.661325	0.459839
Proportion of Variance	0.258669	0.21045	0.162615	0.139301	0.090321	0.057544	0.054669	0.026432
Cumulative Proportion	0.258669	0.46912	0.631734	0.771035	0.861356	0.9189	0.973568	1

**Table 10.** PRE scores,  $\chi^2$  values, and predicted groups for 5 runs of non-metric clustering analysis on the merged data set. The data was clustered into two groups, April and August.

Trial	Temp	SC	DO	pH	ORP	Ca	Mg	K	Na	SO3	Talk	Cl	P	S	Si	Fe	Mn	Das
#1	0.0000	0.0526	0.0526	0.1316	0.6316	0.3158	0.3947	0.3599	0.4474	0.3947	0.4211	0.0789	0.3947	0.3947	0.3421	0.3034	0.3421	0.0263
#2	0.1316	0.6053	0.1842	0.0526	0.0789	0.3684	0.3947	0.4132	0.3947	0.3684	0.1316	0.3947	0.3947	0.3947	0.3591	0.4474	0.3684	
#3	0.1053	0.2632	0.4211	0.1053	0.0000	0.0263	0.0526	0.0132	0.0263	0.0263	0.0263	0.4211	0.0263	0.0263	0.0000	0.0000	0.0526	0.1842
#4	0.0789	0.8684	0.3421	0.0526	0.2368	0.1053	0.0263	0.0398	0.0263	0.0263	0.0000	0.2895	0.0263	0.0263	0.0789	0.0395	0.0789	0.6842
#5	0.0263	0.0000	0.1053	0.0263	0.0000	0.8684	0.8947	0.9733	0.8947	0.8947	0.8684	0.0789	0.9474	0.8947	0.8947	0.8885	0.8947	0.0789
Average	0.0684	0.3579	0.2211	0.0737	0.1895	0.3368	0.3526	0.3599	0.3579	0.3474	0.3368	0.2000	0.3579	0.3474	0.3421	0.3181	0.3632	0.2684

Trial	$\chi^2$	p-value
#1	1.560	0.212
#2	0.015	0.903
#3	0.627	0.428
#4	0.015	0.903
#5	0.112	0.738
Average	0.466	0.637

Group	Trial #1		Trial #2		Trial #3		Trial #4		Trial #5	
	1	2	1	2	1	2	1	2	1	2
April	24	17	21	20	23	18	21	20	22	19
August	15	21	18	18	16	20	17	19	17	19

**Table 11.** The LDA classification of the data into “high” (H; [As] > 0.070 mg/l) and “low” (L; [As] < 0.070 mg/L) dissolved arsenic groups.

**Predict Fall**

Training	H	L	
	H	2	0
	L	0	15
			$\chi^2 = 8.7314$
			p-value = 0.003128
Prediction	H	L	
	H	2	2
	L	0	20
			$\chi^2 = 5.3455$
			p-value = 0.02078

**Predict Spring**

Training	H	L	
	H	4	0
	L	0	20
			$\chi^2 = 17.34$
			p-value = 3.125e-05
Prediction	H	L	
	H	2	0
	L	1	14
			$\chi^2 = 5.1304$
			p-value = 0.02351

**Table 12.** The LDA classification of the randomized data into “high” (H; [As] > 0.070 mg/l) and “low” (L; [As] < 0.070 mg/L) dissolved arsenic groups.

Training	H	L	
	H	2	0
	L	0	15
			$\chi^2 = 8.7314$
			p-value = 0.003128
Prediction	H	L	
	H	1	3
	L	5	15
			$\chi^2 = 0.4$
			p-value = 0.5271

**Table 13.** PRE scores,  $\chi^2$  values, and predicted groups for 5 runs of non-metric clustering analysis on the merged data set. The data was clustered into “high” ([As] > 0.070 mg/l) and “low” ([As] < 0.070 mg/L) dissolved arsenic groups.

Trial	Temp	SC	DO	pH	ORP	Ca	Mg	K	Na	SO3	Talk	Cl	P	S	Si	Fe	Mn
#1	0.079	0.000	0.105	0.026	0.079	0.868	0.895	0.920	0.947	1.000	0.868	0.132	0.895	1.000	0.895	0.889	0.895
#2	0.000	0.553	0.132	0.158	0.658	0.053	0.000	0.000	0.000	0.000	0.026	0.079	0.026	0.000	0.026	0.013	0.079
#3	0.026	0.053	0.105	0.079	0.000	0.868	0.895	0.973	0.895	0.895	0.868	0.026	0.895	0.895	0.947	0.889	0.895
#4	0.474	0.211	0.000	0.026	0.526	0.158	0.237	0.147	0.184	0.184	0.211	0.026	0.184	0.184	0.132	0.192	0.132
#5	0.079	0.000	0.105	0.026	0.079	0.868	0.895	0.920	0.947	1.000	0.868	0.132	0.895	1.000	0.895	0.889	0.895
Average	0.1316	0.1632	0.0895	0.0632	0.2684	0.5632	0.5842	0.5920	0.5947	0.6158	0.5684	0.0789	0.5789	0.6158	0.5789	0.5741	0.5789

Trial	$\chi^2$	p-value
#1	2.345	0.126
#2	4.504	0.034
#3	0.122	0.727
#4	0.059	0.809
#5	2.345	0.126
Average	1.875	0.364

	Trial #1		Trial #2		Trial #3		Trial #4		Trial #5	
Group	1	2	1	2	1	2	1	2	1	2
High	4	10	11	3	6	8	8	6	4	10
Low	35	28	27	36	33	30	31	32	35	28