Project Number: JYP-1101

LEACHING OF METALS INTO GROUNDWATER – UNDERSTANDING THE CAUSES AND AN EVALUATION OF REMEDIAL APPROACHES

A Major Qualifying Project Report

Submitted to the Faculty of

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Bachelor of Science

Submitted by:

Abigail Albright

Sean Dillon

Julianne Leaver

Erin Saari

Date: February 29, 2012

Approved by:
Professor Jeanine D. Plummer, Civil and Environmental Engineering
Professor Robert W. Thompson, Chemical Engineering

1. Groundwater
2. Contamination
3. Metal Leaching

Abstract

The goal of this project was to determine remedial strategies for the former landfill in Holden, MA to reduce mobility and toxicity of metals. To meet this goal, 16 groundwater and 5 surface water samples were collected at the landfill site. Physical and chemical water quality tests showed reducing conditions (favorable for arsenic dissolution) at 4 of the 16 groundwater wells. Samples were analyzed for arsenic, manganese, lead, iron, and cadmium. Dissolved arsenic was above drinking water standards at one well, but below groundwater standards in all wells. Most of the arsenic was in the particulate form. Remedial strategies to reduce mobility of arsenic were evaluated based on criteria such as cost and long-term effectiveness. The no action/monitor strategy is recommended for this site.

Executive Summary

Groundwater and soil contamination is a common issue at current and former landfill sites. Contaminants such as arsenic, iron, manganese, lead, and cadmium can dissolve from soil and waste material into groundwater in a process known as leaching. The dissolution of these metals is based on the chemistry of the water and the soil. Factors that affect metal mobility include pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), specific conductivity, temperature, and soil conditions (McLean et al., 1992). This contamination may be difficult and costly to clean up, but remedial strategies that reduce metal mobility and toxicity are available.

In the town of Holden, Massachusetts there is a former sanitary landfill, which is possibly causing metal contamination. The former Holden landfill (the landfill) was open from 1955 to 1987 as a municipal landfill for the town of Holden. Between 1980 and 1981 it was noted that there was leaching from the landfill area. This was investigated by the United States Environmental Protection Agency (U.S. EPA) and detectible levels of contamination were found. Between 1980 and 1985, 38 groundwater wells were installed in order to monitor the site. An additional consideration at the landfill site is that the groundwater in the area discharges to the Quinapoxet River, a tributary to the Wachusett Reservoir, which serves as a water supply for greater Boston. In the fall of 2004, Corporate Environmental Advisors Inc. (CEA) began monitoring and working at the former Holden landfill site along with the Massachusetts Department of Environmental Protection (MassDEP) (CEA, 2011). CEA's goals for the landfill site are to further understand the extent of impacts of the landfill as well as to assess the risks posed by the contaminants found at the site.

The Worcester Polytechnic Institute (WPI) chemical engineering major qualifying project (MQP) team assisted CEA in accomplishing their goals. The WPI team's goals were to understand the metals and concentrations present at the landfill site and evaluate remedial strategies in order to determine the most feasible options for the landfill site.

The WPI team participated in the fall 2011 sampling event and collected 16 groundwater samples and 5 surface water samples with the assistance of CEA. At the time of collection, water parameters were recorded including pH, ORP, DO, specific conductivity, and temperature. The unpreserved groundwater samples were taken to the WPI environmental laboratory and analyzed for turbidity, color, metal concentrations, and inorganic anion concentrations. The groundwater samples were tested for both dissolved and digested metal concentrations of arsenic, manganese, lead, iron, and cadmium using an atomic absorption spectrometer. Dissolved metal concentrations refer to the samples tested without the addition of an acid or preservative. Digested metal concentrations refer to the samples treated with 10 M nitric acid which dissolves particulates and provided a total metals concentration. The metal concentrations for the dissolved samples were compared to both U.S. EPA drinking water standards and to MassDEP Groundwater category-3 (GW-3) standards. The digested metal concentrations were not directly compared to these standards, because the samples were acidified. In this study, arsenic was of greatest concern for both the dissolved and digested samples since it is the most toxic metal studied.

For the dissolved samples, one groundwater well had arsenic at 45 parts per billion (ppb), which was above the drinking water standard of 10 ppb, but below the GW-3 standard of 900 ppb. In the digested samples, total arsenic was below detection limits in eight samples. In the remaining 13 samples, levels ranged from 7.049 to 1084 ppb.

A correlation analysis was conducted between all the physical parameters, metal concentrations and inorganic anion concentrations. There was a positive correlation between the depth to the bottom of the well and two parameters, pH and ORP. A geographical analysis was also performed using an analysis of variance (ANOVA) by dividing the samples into three geographical regions: west of the landfill by the River, over the landfill, and east of the landfill. Bromide and ORP were significantly different by region.

Typical remedial strategies were evaluated for their effectiveness and applicability to the landfill site. The remedial strategies that were considered for this project included no action/monitor, recapping, filtration, solidification/stabilization/precipitation, interceptor drain, cut-off trench, permeable wall treatment, ion exchange, chemical treatments, and soil washing. Using the U.S. EPA guidelines for evaluating remedial strategies these strategies were ranked based on the criteria of cost, long term effectiveness, commercial availability, ability to reduce metal mobility, ability to reduce toxicity, and site specific implementation. It was determined that no action/monitor is the recommended remedial strategy for the landfill site. Recapping, filtration, interceptor drains, and ion exchange were recommended if higher concentrations are detected in the future or if a risk assessment concludes that a more aggressive remedial approach is warranted.

Prior to implementing any remedial strategies, it is recommended that the risks posed to human health and the environment by contamination attributable to the landfill be further assessed. It is also recommended that an arsenic background evaluation be performed to determine the naturally occurring concentrations of arsenic. Lastly, the specific type of arsenic compounds present should be determined in order to better characterize risks from metal contamination at the landfill.

Acknowledgements

This project could not have been completed without the contributions and guidance from several individuals. First, we would like to thank our academic advisors, Professor Jeanine Plummer and Professor Robert Thompson, whose supervision and guidance made this project possible. The team would like to thank the entirety of Corporate Environmental Advisors, Inc. (CEA) for sponsoring our efforts, especially Mr. Adam Last, Principal Engineer and Regional Manager at CEA, for his expertise and his continuous assistance. We would also like to thank Mr. Mark Hagie and Mr. John Briggs at CEA for their knowledge and assistance with the field sampling portion of the project. The team would also like to thank Mr. Don Pellegrino and Professor Suzanne LePage of WPI for their assistance in conducting laboratory tests and answering any questions we had. This project would not have been possible without the cooperation of the Town of Holden who allowed our MQP team to use the Former River Street Landfill as a case study. We would like to extend a special thank you to Mrs. Nancy Galkowski, Town Manager and Mr. Jim Zingarelli, Town Engineer of the Town of Holden for their support. Lastly, we extend thanks to Ms. Denise Child of Massachusetts Department of Environmental Protection for her help with our research on the Clinton landfill case study.

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

Solid and hazardous waste can be disposed of in multiple ways, including recycling, composting, and landfilling. Landfills are engineered areas in which solid waste is placed directly into an open area of land (U.S. EPA, 2012). There are currently 3,091 active landfills in the U.S. and over 10,000 former municipal landfills (Zerowaste, 2012). Landfills that were opened after 1950 are of particular concern due to the highly toxic chemicals that have been produced, and likely dumped in landfills, since the 1940s (Zerowaste, 2012). Federal regulations, such as the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act, have improved landfills by monitoring their design, location, operation, and closing (U.S. EPA, 2011g).

The former River Street Sanitary landfill in Holden, MA is located 1,100 feet south of the Quinapoxet River, which serves as a tributary to the Wachusett Reservoir. The former Holden landfill operated between 1955 and 1987, receiving approximately 200 tons of solid waste per week. Between 1955 and 1970, the waste was dumped on the southern side of the site and was burned. The burning stopped after this time frame and solid waste was then dumped on the northern portion of the site until 1987 when the landfill was closed. The United States Environmental Protection Agency (U.S. EPA) noticed leachate from the landfill entering the Quinapoxet River around 1981 during the construction of Route 190. Further investigation was completed between 1980 and 1985 to determine the sources of contamination and potential impacts. The landfill was closed in 1987 and then capped in 1988 (CEA, 2011).

Corporate Environmental Advisors, Inc. (CEA) was hired by the town of Holden to investigate and monitor the former Holden landfill site. CEA monitors groundwater around the landfill and in groundwater seep tributaries to the Quinapoxet River on a semi-annual basis. From past water quality results, three groundwater wells have consistently shown concentrations of arsenic higher than the groundwater standards set by the Massachusetts Department of Environmental Protection (MassDEP, 2011).

In this project, WPI worked with CEA to evaluate the potential impacts from the former Holden landfill and to identify remediation alternatives. This project focused specifically on understanding conditions that promote leaching of metals into groundwater. The main objectives of this project were:

1. To understand the metals and concentrations present at the site; and
2. To evaluate remediation strategies to reduce metal mobility at the former Holden landfill site, thus reducing potential risk to humans and the environment.

These recommendations were made considering various criteria, including the ability to effectively impede metal leaching, cost, and long-term applicability. By accomplishing these objectives, the team presented CEA with remedial alternatives deemed most feasible for the former Holden landfill site.

Chapter 2: Background

Leaching of metals into groundwater from natural or anthropogenic sources has resulted in concentrations that exceed regulatory standards for drinking water. This chapter describes the chemical and physical properties of five metals: arsenic, manganese, lead, iron, and cadmium. Also, this chapter explains natural and anthropogenic sources of these metals. The processes by which the metals leach into the groundwater are described, as well as conditions that affect mobilization. Lastly, this chapter presents a case study of a Massachusetts landfill to better understand the impacts metals contamination in groundwater can have on a community and potential remedial strategies.

2.1 Regulations for Drinking Water and Groundwater

The United States Environmental Protection Agency (U.S. EPA) ensures human and environmental safety through regulations, including those that protect drinking water. The Safe Drinking Water Act (SDWA) sets enforceable limits on various contaminants that may be found in drinking water. The National Primary Drinking Water Regulations (NPDWRs) establish maximum contaminant levels (MCLs) designed to be protective of public health. The National Secondary Standards are secondary maximum contaminant levels (SMCLs) that provide guidelines based on aesthetics and are not enforceable (U.S. EPA, 2011d). Table 1 summarizes U.S. EPA drinking water standards for the five metals of concern in this project.

Table 1: Contaminant Standards in Drinking Waters (U.S. EPA, 2011e)

Metal	Concentration Limit (ppb)	Type of Limit
Arsenic	10	MCL
Manganese	50	Secondary standard
Lead	15	Action level*
Iron	300	Secondary standard
Cadmium	5	MCL

Notes: ppb = parts per billion (micrograms per liter or µg/L)

*The action level is the point at which the water requires a treatment technique (TT) in order to reduce the amount of contamination.

The Massachusetts Department of Environmental Protection (MassDEP) has defined groundwater standards in three categories. The first category, GW-1, defines standards for groundwater that is currently, or will be used as a drinking water source in the near future. The second category, GW-2, includes groundwater that has volatile materials that could potentially migrate into indoor air. Lastly, GW-3 standards exist to monitor possible environmental impacts that contaminated groundwater could have if it was discharged to surface water (MassDEP, 1994). The third category, GW-3, are the standards of interest to this project and are included in Table 2.

Table 2: Groundwater 3 Concentration Standards (MassDEP, 2011)

Metal	GW-3 Concentration Limit (ppb)
Arsenic	900
Manganese	N/A
Lead	10
Iron	N/A
Cadmium	4

2.2 Metal Contamination in Water

Metal contamination in water is a global issue that has affected millions of people. This section describes the chemical properties of five metals, including how they react with other elements, as well as the potential impacts each metal has on human health and the environment.

2.2.1 Arsenic

Arsenic (As) is a highly toxic, semi-metal element that is naturally occurring (Lenntech, 2011a; U.S. EPA, 2011a). Arsenic has an atomic number of 33, with eight possible isotopes. It is most commonly found in its three allotropic forms, which are yellow, black, and grey. The most stable form is a grey, crystalline solid that tarnishes quickly in air and is brittle (Lenntech, 2011b). Arsenic can readily combine with other elements, and inorganic arsenic compounds are formed when arsenic combines with elements such as oxygen, chloride, and sulfur (OSHA, 2004). The arsenic found in groundwater and drinking waters is inorganic arsenic, typically either trivalent arsenate (As (III)) or pentavalent arsenate (As (V)) (Lenntech, 2011c).

When arsenic is in water, oxidation-reduction reactions, coagulation, and adsorption may occur. Adsorption causes arsenic to precipitate with aluminum or iron hydroxides, causing sediments. Arsenic most commonly reacts with moist air, and rarely reacts with dry air. For example, orpiment, an arsenic compound, reacts in water to form arsenious acid and hydrogen sulfide as shown in Reaction 1.

$$As_2S_3 + 6\ H_2O \rightarrow 2\ H_3AsO_3 + 3\ H_2S \qquad \text{(Reaction 1)}$$

Arsenic in its elemental form does not have a high solubility, but arsenic compounds are more likely to be soluble and therefore arsenic exists in various water-based solutions (Lenntech, 2011a).

2.2.1.1 Health and Environmental Impacts

Exposure to levels of arsenic higher than 10 ppb can result in chronic health effects, including cancer of the bladder, lung, skin, kidney, nasal passages, liver, and prostate. This exposure can occur through skin contact and ingestion, but is most often through inhalation.

Non-life threatening effects include stomach pain, nausea, vomiting, diarrhea, partial paralysis, and blindness (U.S. EPA, 2011b). Being exposed to high arsenic levels can also result in skin lesions and anemia. The toxicity of compounds containing arsenic varies, with arsine gas being the most toxic, followed by inorganic arsenic, and then organic arsenic (Gehle, 2009). The lethal dose of inorganic arsenic is 100 parts per million (ppm), whereas the lethal dose of arsine gas is as low as 10 ppm (OriGen, 2000).

2.2.1.2 Populations Affected

Arsenic, stemming from both natural and anthropogenic sources, has been found in groundwater used as drinking water sources. The World Health Organization estimates that over 57 million people in Bangladesh alone drink water that is contaminated with arsenic (Sever, 2011). Natural arsenic contamination in well water has been discovered in over 19 countries, including the United States and Canada (Gehle, 2009).

Figure 1 shows the arsenic concentrations in groundwater throughout the United States. Arsenic is found at the highest concentration (50 micrograms per liter, µg/L, also known as ppb) in areas of California, Oregon, Nevada, Texas and Alaska. Concentrations around 10 µg/L are found throughout western states, the central states, and the northeast, as well as near geothermal activity. These concentration levels were found in at least 25% of samples obtained at each site (Gehle, 2009).

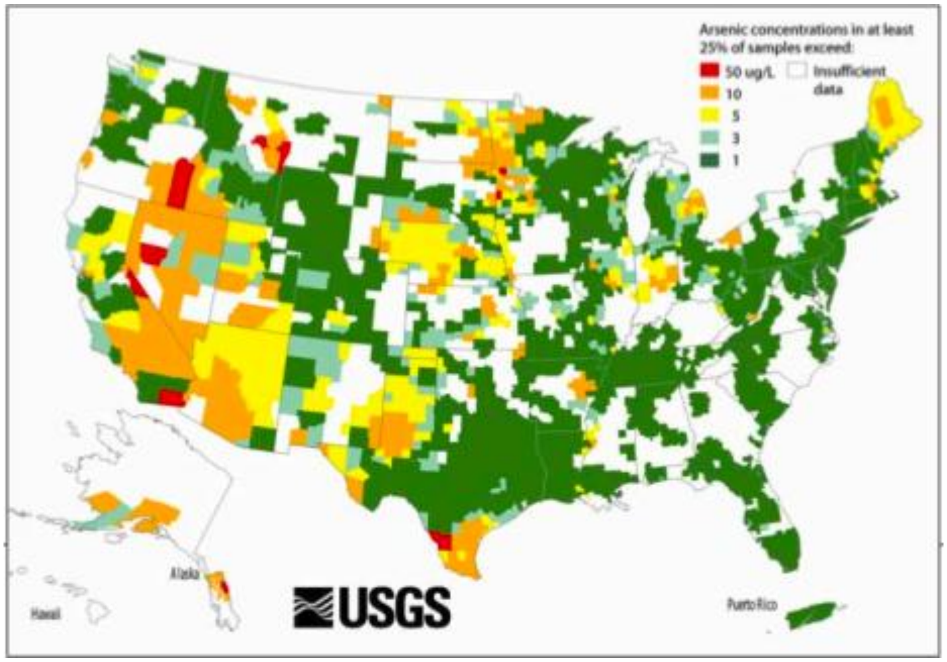


Figure 1: U.S. Geological Survey Map of Arsenic in Groundwater (Gehle, 2009)

2.2.2 Manganese

Manganese is a pinkish-gray chemically active element with an atomic number of 25 and 7 known isotopes. Johann Gahn discovered this hard, brittle metal in 1774. Manganese is easily oxidized because it is highly reactive in its pure form. For example, manganese powder will burn in the presence of oxygen, will rust in water similar to iron, and will dissolve in dilute acids. Manganese is one of the most abundant metals that are naturally present in soils (Lenntech, 2011g). Within soils, manganese is typically present as oxides and hydroxides, which vary with oxidation-reduction reactions affected by the pH (Scheffer et al., 1989).

Manganese has various useful applications. Manganese is used in the formation of inexpensive stainless steel and can be used to decolorize glass. More than 25 million tonnes of manganese are mined every year. Potassium permanganate is a strong oxidizing agent and disinfectant, and is used in drinking water treatment. Lastly, manganese oxide is used in fertilizers, which ensures that plants receive the proper intake that they need to function (Lenntech, 2011g).

2.2.2.1 Health and Environmental Impacts

Manganese is necessary for human survival but toxic when consumed at high concentrations. The secondary standard set by the U.S. EPA for aesthetics is 50 ppb. Manganese is most commonly consumed by eating spinach, grains and rice, eggs, green beans, nuts, and oysters. Manganese deficiency can lead to health issues, including obesity, glucose intolerance, low cholesterol, and blood clotting (Lenntech, 2011g).

Excess manganese can result in adverse health effects. These effects occur in the respiratory tract and in the brain, where symptoms include hallucinations, forgetfulness, nerve damage, bronchitis, schizophrenia, weak muscles, insomnia and manganism. Manganism is a disease that resembles Parkinson's disease. Chronic poisoning has been observed with prolonged inhalation of manganese dust and fumes. Exposure can result in permanent disability (Lenntech, 2011g).

2.2.2.2 Populations Affected

There is an increased risk of exposure to high manganese concentrations for workers in mines and factories if they are working around manganese dusts and fumes. Manganese fumes are released from welding and this chronic exposure can result in neurological effects (U.S. EPA, 2011e).

2.2.3 Lead

Lead was discovered by humans thousands of years ago, however, it is impossible to say the exact date. It is the heaviest element in the carbon family on the periodic table of elements, although it does not share many chemical properties with carbon. Lead was used in the United States in pipes to carry water until 1930, which is believed to cause many harmful health effects (Chemistry Explained, 2011).

Lead is a soft blue-white metal with an atomic number of 82. It is a dense, malleable and ductile metal. Lead does not conduct electricity well (Lenntech, 2011f). It is shiny when first cut, but it tarnishes over time. Lead dissolves quickly into hot acidic compounds. Lead dissolves slowly into water and acidic compounds. Lead does not burn nor does it react readily with oxygen (Chemistry Explained, 2011).

2.2.3.1 Health and Environmental Impacts

Lead has many potential negative effects on human health. Although very low amounts of lead may not be harmful there are known benefits of ingesting any amount of lead. Lead can be either inhaled or ingested. Lead has been known to dissolve from lead solders into drinking water. Water can cause corrosion in pipes containing lead and this risk is increased by water that is slightly acidic. For this reason, the U.S. EPA guideline for pH in public water treatment systems is 6.5 to 8.5. Some of the harmful effects of lead ingestion or inhalation are anemia, high blood pressure, kidney damage, miscarriages, nervous system damage, brain damage, and behavioral and learning disruptions in children (Lenntech, 2011f). Symptoms of lead poisoning include nausea, vomiting, fatigue, and high blood pressure and in more extreme cases, brain damage. These can be chronic or acute health effects (Chemistry Explained, 2011).

2.2.3.2 Populations Affected

Lead poisoning can affect anyone, but children are at much greater risk of lead poisoning than adults because their immune systems are weaker. Children also may put foreign objects in their mouths that may be coated with dirt or paint chips. Lead was used in paints until 1978. In 1978, the United States government banned the use of lead based paint in homes. Many houses built before 1978 still have lead paint on the interior and exterior surfaces and children who ingest this paint may develop lead poisoning. Lead can also be transferred from the exterior of the house to the soil, and it is also possible for children to come in contact with or ingest this soil, and thus the lead it contains. Lead can also accumulate in the body over time and symptoms may not present themselves until a later time. This is most common in factory workers where lead is used in some processes. This type of lead poisoning can also cause nerve or muscle damage (Chemistry Explained, 2011).

2.2.4 Iron

Iron is a silver grey metal with an atomic number of 26. Iron is primarily found as bivalent iron (II), known as ferrous, and trivalent iron (III), known as ferric. Bivalent and trivalent iron react differently and have different properties. In soils, iron is typically found in the trivalent form. When in a soil saturated with water, it is converted to the bivalent form and is capable of being absorbed by plants (Lenntech, 2011e).

Iron reacts with water, air, and dilute acids. Iron will not dissolve in pure water or dry air. When both water and oxygen are present, iron oxidizes, precipitates out of solution and forms rust as shown in Reaction 2.

$$4\mathrm{Fe} + 3\mathrm{O}_2 + 6\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{Fe}^{+3} + 12\mathrm{OH}^- \rightarrow 4\mathrm{Fe(OH)}_3 \text{ or } \mathrm{FeO(OH)} + 4\mathrm{H}_2\mathrm{O} \quad \text{(Reaction 2)}$$

Rust is a red-brown color precipitate. In the presence of dilute acids, iron will also dissolve. This contributes to water contamination because iron present in solution is more mobile (Lenntech, 2011e).

The four main types of iron are ferrous (clear water) iron, ferric (red water) iron, iron bacteria and organic iron. Ferrous iron is the iron most commonly found in drinking water from wells and aquifers. Water containing ferrous iron is clear; however, if it sits for a period time the ferrous iron will precipitate out of the solution due to the oxygen present. Ferric iron is insoluble in water and is noticeably a red brown color when exposed to the atmosphere. Iron bacteria naturally occur in soil and are also found in plumbing, where they form a slimy red-brown substance within the water. They are non-pathogenic and most commonly found under the toilet tank. Finally, organic iron combines with other natural occurring metals and forms large complexes. It is typically found in shallow drinking wells (Colter et al., 2006).

2.2.4.1 Health and Environmental Impacts

Humans can have negative health effects from ingesting too much or too little iron. If drinking water contains a concentration of 3 milligrams per liter (mg/L, also known as parts per million or ppm) or more, it will exhibit rust color, an odor and leave residue on clothes and food; however, this concentration is not harmful to health (Colter et al., 2006). Humans need a certain amount of iron in their diets. On a daily basis, women need 11 grams of iron and men need 7 grams. When people do not ingest enough iron they are anemic. Anemia can cause tiredness, headaches and loss of concentration. If people ingest too much iron, it is stored in the pancreas, liver, spleen and heart. High concentrations of iron in these organs can cause major damage. Typically this only occurs when people ingest water with iron concentrations above 200 mg/L. Iron can cause toxic effects if more than 200 mg is ingested and becomes lethal at doses of 10-50 grams. Also, inhaling iron dust may lead to lung disease (Lenntech, 2011e).

2.2.4.2 Populations Affected

There are few activities that increase the risk of exposure to high iron levels. Populations around areas of mining have an increased risk. The work from mining these areas can cause iron to enter the soil, potentially contaminating the ground water (Lenntech, 2011e).

2.2.5 Cadmium

Cadmium is a silver-white malleable metal with a molecular weight of 112.4 g/mol and atomic number of 48. Cadmium was discovered by Fredrich Stromeyer in 1817 and is similar to zinc and mercury. Cadmium occurs naturally in the earth's crust as well as being introduced to the environment in fertilizers and pesticides. Cadmium is also part of most zinc compounds and is released into the environment during zinc processing. The main use of cadmium is in batteries. It is also used for coatings, plating, and in the production of plastics (Lenntech, 2011d).

2.2.5.1 Health and Environmental Impacts

Cadmium is a hazardous chemical. Cadmium buildup in the kidneys hinders their filtration systems. This problem can persist because cadmium does not exit the kidneys very quickly and will begin to accumulate. This can ultimately lead to kidney failure. Other adverse health effects from cadmium include stomach pains and infertility, and cadmium is considered a carcinogen. It can also harm the central nervous and immune systems as well as damage DNA.

Inhalation of cadmium can lead to severe damage of the lungs and even death (Lenntech, 2011d). Cadmium has to be ingested or inhaled to be harmful to humans. There are no health effects if cadmium is touched (Illinois Department of Public Health, 2011).

2.2.5.2 Populations Affected

Humans can be exposed to cadmium by food that contains large amounts of it such as liver, cocoa powder, and shellfish. People are typically exposed to cadmium when working in factories that refine cadmium or zinc and lead, for which cadmium is a byproduct. People who live near waste dumps for cadmium can also be at a high risk of exposure (Lenntech, 2011d).

People who smoke cigarettes absorb more cadmium in their bodies. The tobacco helps the cadmium travel into the lungs. People who live in agricultural regions are likely to be exposed to high levels of cadmium because the land may have been fertilized with cadmium or the crops may have been sprayed with cadmium pesticides. The United States is one of the main producers of cadmium (Lenntech, 2011d).

2.3 Metals in the Environment

Anthropogenic (man-made) and natural sources of metals in the environment are discussed in this section. The metal with the most significant health effects that was explored in this project was arsenic. Therefore, sources of arsenic are discussed in depth in this section. The sources of other metals of interest including manganese, lead, iron, and cadmium are discussed as well.

2.3.1 Natural Sources

Metals occur naturally within the environment. They can be found in rock, soils, groundwater, surface water, and the air. This section focuses on the natural presence of arsenic in the environment. Arsenic is the most relevant metal to the project and other metals are discussed briefly.

2.3.1.1 Arsenic

There are three main types of arsenic in nature: airborne, inorganic, and organic. Different sources of arsenic produce different forms of arsenic. Airborne arsenic comes mostly from volcanic activity. Airborne arsenic can have detrimental health effects by polluting the air that people breathe, but it is unlikely to have an effect on drinking water. Organic arsenic can be found in living organisms. Inorganic arsenic compounds contain arsenic as well as other elements however they do not contain carbon. Inorganic arsenic typically originates from geological sources, such as bedrock, and leaches into ground water. Therefore inorganic arsenic is of greatest concern for drinking water (Greenfacts, 2011).

Arsenic can be found in any type of bedrock. Bedrock is classified by the type of chemical compound it contains. Some chemicals found in bedrock react with arsenic and can mobilize it by allowing it to dissolve in water. The seven major types of bedrock include:

1. Carbonate bearing metasedimetary rocks

2. Primarily noncalcareous, clastic deposition rocks with restricted deposition in discrete fault-bounded sedimentary basins of Mississippian or younger age
3. Primarily noncalcareous, clastic sedimentary rocks at or above biotite grade of regional metamorphism
4. Mafic igneous rocks and their metamorphic equivalents
5. Ultramafic rocks
6. Felsic igneous rocks and their metamorphic equivalents
7. Unconsolidated and poorly consolidated sediment (Ayotte et al., 2011)

In two studies done in New England, it was discovered that arsenic commonly occurs in calcareous (containing calcium carbonate) metasedimentary rocks. According to a study by Nielsen et al. (2001), arsenic was detected in calcareous metasedimentary rocks at a 49% frequency, while in all other types of bedrock aquifer it was detected less than 25% of the time. In a similar study in New England, arsenic at levels of 5,000 ppb or greater was detected in 44% of the wells in the lithogeochemical group of metasedimentary bedrock that contained slightly to moderately calcareous and calc-silicate rocks (Ayotte et al., 2011). Twenty eight percent (28%) of the other lithogeochemical groups contained arsenic at those levels. Inorganic arsenic compounds can be found in many different geological sources, but areas where ground waters are surrounded by calcareous metasedimentary rocks are at greater risk because the geochemistry is better for arsenic leaching.

2.3.1.2 Other Metals

Manganese is commonly found in the form of pyrolusite (MnO_2) and also, although less often, as rhodochrosite ($MnCO_3$). It is one of the most abundant metals found in soil (Lenntech, 2011g). Lead can be found naturally in the environment, but pure lead from natural sources is very rare. Zinc, silver and copper ores which contain lead are found much more commonly in the environment than pure lead. Most lead is extracted along with these metals. Lead containing minerals are mined frequently to produce new lead. Some of these minerals include galena (the most abundant lead mineral, chemical formula PbS), cerrussite and anglesite (Lenntech, 2011f). Iron makes up 34.6% of the earth’s mass making it the most abundant element on earth and therefore iron occurs naturally all over the world. About 5% of the earth’s outer crust is iron. Iron is usually found in the form of iron oxides. Some common iron containing minerals are hematite, magnetite, and taconite (Lenntech, 2011e). Cadmium occurs naturally in the earth’s crust. Cadmium is always found along with zinc. Cadmium is also contained in rocks and can be released into rivers through weathering of rocks.

2.3.2 Anthropogenic Sources

Metals that are found naturally in the environment can also be released into the environment by humans, often in higher concentrations than they occur in nature. Metals can be released into the environment via burning of fuels, use of pesticides, disposal practices, and as by products or waste products from chemical processes, such as metal processing.

2.3.2.1 Arsenic

Arsenic and other metals have been introduced into the environment from anthropogenic sources. These sources include past and current production and use of pesticides and wood preservatives. Sources also include metals from mining, such as copper, poultry farming, and sewage sludge disposal (ATSDR, 2007). Figure 2 shows the three major producers of arsenic over the last hundred (Peryea, 2004).

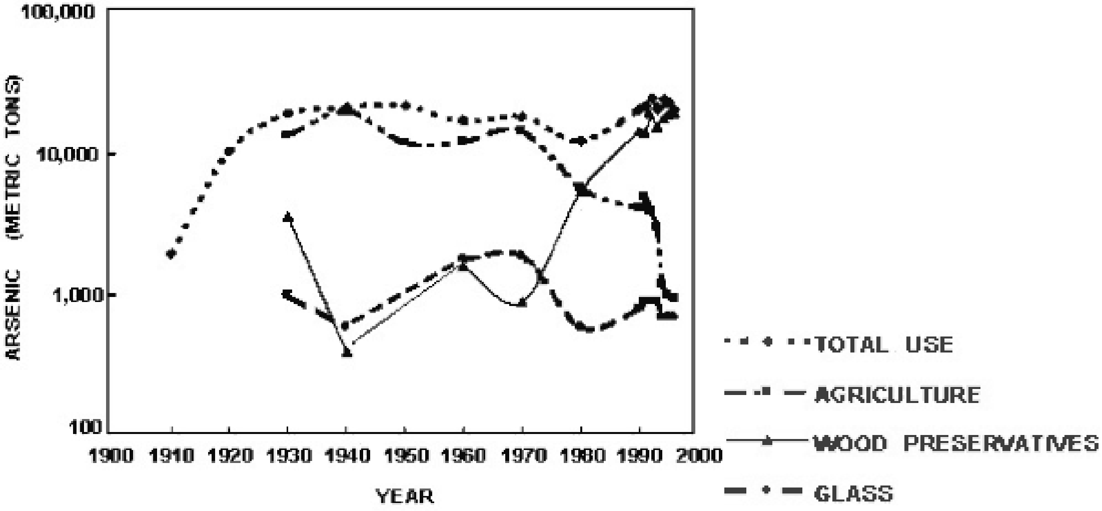


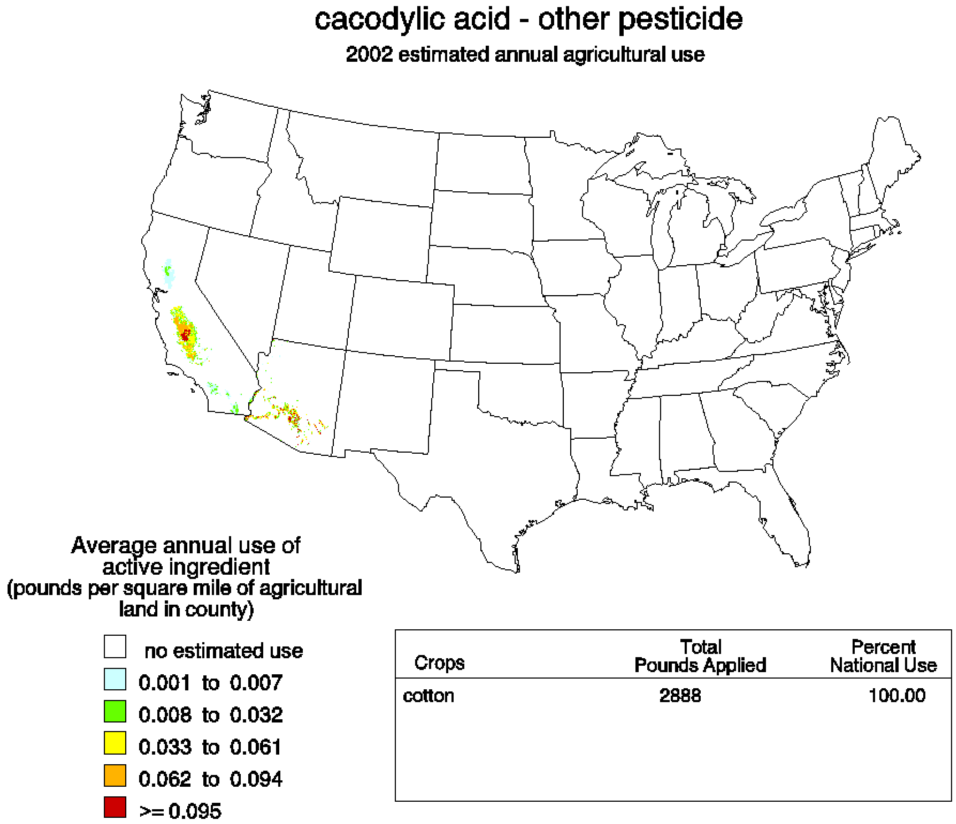
Figure 2: Top Three Producers of Arsenic in U.S. (Welch et al., 2000)

Pesticides are substances used to remove and help prevent pests. Pests include insects, bacteria, rodents, weeds and fungi. Arsenic based substances, such as arsenic sulfides, have been used as insecticides since as early as A.D. 900 in China. The first arsenic-based pesticide used in the United States was copper acetoarsenite pigment, also known as Paris green. Paris green was used to repel the potato beetle in Colorado in the mid-nineteenth century (Peryea, 2004).

The most commonly used arsenical insecticide was lead arsenate. Lead arsenate was used to kill gypsy moths which are common agricultural pests. It was first used in Massachusetts in 1892 and was found to be more effective than Paris green because it adhered to plants longer and better repelled the gypsy moths. In the 1910s, calcium arsenate and aluminum arsenate were introduced as less expensive alternatives to lead arsenate salts. However, lead arsenate was still the most effective insecticide. In 1919, it was discovered that food cleaning methods were not removing arsenic and therefore an alternative to lead arsenate was needed (Peryea, 2004).

In 1948, dichlorodiphenyltrichloroethane (DDT) was developed. Lead arsenate was still used sparingly; however, it was less effective than DDT because most of the moths developed immunity to lead arsenate. In August of 1988, lead arsenate was banned from use in the United States. Even though this arsenical pesticide was banned, other less frequently used pesticides containing arsenic are still used sparingly today, including cacodylic acid, ammoniacal cooper zinc arsenate (ACZA), and monosodium or disodium methanearsonate (MSMA, DSMA). Figure 3 demonstrates the limited use of cacodylic acid in 2002 (Welch et al., 2000).

After the ban on lead arsenate in 1988, the major function of arsenic was wood preservation. Chromated copper arsenate (CCA) was the main chemical used for wood treatment until it was banned in the U.S. in 1996 (Vaajasaari, 2008). Arsenic is also used in the form of arsanilic acid in animal feed to control pathogens. This contributes to high levels of arsenic in fields and agricultural areas that use animal manure as fertilizer. Since pigs and chickens do not metabolize arsenic, most of it is deposited in their feces. The amount of arsenic generated by animal waste has not been documented extensively (Welch et al., 2000).



Crops	Total Pounds Applied	Percent National Use
cotton	2888	100.00

Figure 3: Map of Use of Cacodylic Acid Pesticide in U.S. (USGS, 2002)

Agricultural soils throughout the United States that have been exposed to arsenicals for over 20-40 years have been found to have arsenic concentrations exceeding 100 mg/kg which is 80 mg/kg higher than the MassDEP risk characterization standards (Nelson et al., 2007). Locations that have not been exposed to anthropogenic sources of arsenic will have low concentrations of arsenic within the magnitude of 10 mg/kg or less. Contaminated areas can be problematic for development and clean-up especially since arsenic will settle deep into the soil (Welch et al., 2000).

2.3.2.2 Other Metals

Manganese, lead, iron and cadmium are introduced into the environment from various anthropogenic sources. Manganese is commonly found in fertilizers and fungicides as well as released when steel and iron products are manufactured (Herbal Life Product, 2011). The most common sources of anthropogenic lead are from gasoline automobile exhaust and lead based paint. The volatilized lead can pollute the air as well as the ground via polluted rainfall (Lenntech, 2011f). Iron is used in steel processing, pesticides and herbicides (Suwandana et al., 2011). Cadmium is typically found with zinc which causes it to be released during zinc extraction. Cadmium is also released during manufacturing of pesticides (Lenntech, 2011d).

2.3.3 Determining Sources of Arsenic

According to a study conducted to determine whether or not arsenic in a certain area is naturally occurring or due to a release from an anthropogenic source, three conditions must be demonstrated at the site. The three conditions that must be demonstrated to confirm that the presence of arsenic in the groundwater is naturally occurring are: No past or present anthropogenic sources of arsenic are present at the site; the soil and/or bedrock at the site contain arsenic-bearing minerals or weathering products; and the geochemical parameters in the aquifer are favorable for dissolution of arsenic-bearing minerals and mobilization of arsenic into groundwater (Nelson et al., 2007).

2.4 Metal Leaching Process

The dissolution of metals into ground waters is affected by soil and water conditions. The primary conditions that affect metal solubility are: pH, oxidation/reduction potential, anion/cation exchange, and precipitation and dissolution of metals. Once dissolved in water, metals can be taken up by plants or migrate with the water. Mobile metals have potential to cause contamination issues (McLean et al., 1992).

Oxidation/reduction (redox) reactions are chemical reactions in which valence electrons are transferred between two molecules or ions. The metal that gains electrons is reduced and the metal that loses electrons is oxidized. Redox reactions affect the mobility of metals in the subsurface which is dictated by the redox potential of the subsurface. An absence of oxygen in the subsurface, when metals are gaining electrons, indicates reducing conditions. An excess of oxygen in the subsurface, when metals are losing electrons, indicates oxidizing conditions. In general, oxidizing subsurface conditions favor the retention of metals in soil and reducing conditions increase the mobility of metals (McLean et al., 1992).

The oxidation state of metals impact whether the metals are solid or soluble. For example, Fe (II) is highly soluble while Fe (III) adsorbs to the soil, causing it to precipitate as a solid. Depending on the conditions of the subsurface, Fe can be mobile or stationary. This is also the case for chromium. Hexavalent chromium [Cr (VI)] is highly toxic and soluble; however, trivalent chromium [Cr (III)] is insoluble and less toxic. The mobility of metals in soil and water is also dictated by the oxygen availability of the subsurface (McLean et al., 1992).

The pH of the subsurface affects the mobility of the metals by affecting the sorption/desorption of metals, precipitation/dissolution, complex formation and oxidation/reduction reactions that take place in the subsurface. In general, pH conditions above 7 promote retention of cations in soil and pH conditions less than 7 promote retention of anions (McLean et al., 1992). In an experiment conducted to evaluate the effect of fly ash on the subsurface, it was observed that at pH conditions below 9 the soil cation exchange capacity was reduced and the mobility of Cd and Ni was increased (Chirenje, 1999). Also observed in this experiment was that in a low subsurface pH, the calcium concentration was increased. The low pH allowed $CaCO_3$, which is typically a precipitate, to dissolve. As a consequence of this the concentrations of Cd, Ni, Se, and As increased because they adsorbed to $CaCO_3$ (Chirenje, 1999). As these metals dissolve in water their mobility is significantly increased. From this experiment and other generalizations made by the U.S. EPA, it can be concluded that soils with low pH conditions favor metal leaching (Chirenje, 1999).

The pH of the subsurface also affects adsorption sites. As the pH decreases, the number of negative sites for cation adsorption diminishes and the number of sites for anion adsorption increases (McLean et al., 1992). At a decreased pH, metal cations also compete for available adsorption sites with Al^{+3} and H^+. Certain solid compounds such as Fe and Mn hydrous oxides allow metals to adsorb to soil. When these hydrous oxides dissolve into the water it greatly decreases the ability of metals to adsorb to soil and remain in solid forms. These hydrous oxides dissolve at a pH below 6 and therefore metal leaching is increased at low pH (McLean et al., 1992).

Metals are present in soil in various forms, including uncomplexed metal ions, soluble complexes with ligands, and mobile inorganic and organic colloidal species. A complex is a unit, in which various atoms or molecules are bonded to a centralized metal ion, forming a geometric pattern. The atoms or molecules attached to the metal ion are called ligands. Complexes can be formed with both inorganic and organic ligands, although it is more common that metal ions combine with inorganic ligands. Complexes can exist with an overall positive, negative, or neutral charge, but the metal ion itself will have a lower oxidation state than the free metal. The characteristics of a complex can affect mobility, bioavailability, and toxicity of the metal. Metals that easily form stable complexes are likely to be mobile in the subsurface, whereas metals that do not easily form stable complexes could result in metal retention (McLean et al., 1992).

Many types of surface complexes form between metals and soil. The subsurface must be balanced by ions with an opposite charge as the overall complex. Figure 4 depicts two common mechanisms in which cations form complexes known as outer-sphere and inner-sphere, where outer-sphere is comprised of weaker bonds than the inner-sphere complex. An outer-sphere complex occurs when the metal is surrounded by water and the metal itself is not directly bonded to the surface. These reactions happen rapidly and are reversible with little dependence on the electron configuration. An inner-sphere complex occurs when the metal bonds to the surface, either with ionic or covalent bonding. Water does not need to be present for this complex to form and there is a higher bonding energy associated with this complex. Together, these complexes form a matrix within the soil (McLean et al., 1992).

Anion and cation exchanges contribute to the way metals behave in soils and water. The ion exchange capacity measures the amount of oppositely charged sites available for adsorption. The order and preference of the sorption affinity is dependent on metal properties, surface type, and the physical conditions. Cations with strong bonding capabilities tend to have a higher relative affinity and a higher adsorption capacity. Certain anions precipitate more readily than other anions in clay minerals, oxides, and organic matter. Cations are adsorbed on to specific adsorption sites. Once sites are saturated, they are governed by exchange reactions. The competition for these sites is increased and causes an increased mobility of the cations present, as they compete for the site. Certain adsorption sites favor trace cations and anions because their properties are a better match for the soil than major cations and anions (McLean et al., 1992).

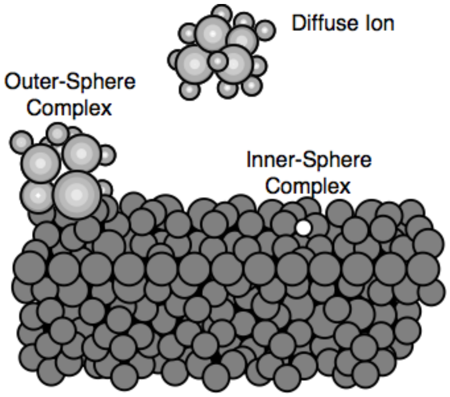


Figure 4: Cation Adsorption Mechanisms (McLean et al., 1992)

Metals within the subsurface solution can be removed from solution through various mass transfer mechanisms. This movement is particularly important to consider for metals such as arsenic and mercury. Metals also can participate in precipitation reactions, where they form solid phases within the soils. The precipitates of metals in soil can be pure solids or mixed solids, which occur from co-precipitation. Precipitation reactions are most common with metals of low solubility. This allows insoluble complexes to precipitate out of the soil without dissolving into groundwater. Inorganic anions commonly form insoluble complexes, which is an advantage to immobilize metals. Solid solution formation tends to occur when the trace element is compatible with that of the host metal. For example, cadmium and calcium are similar in their ionic radii, so cadmium can replace calcium within a carbonate mineral. Adsorption is not affected by these precipitation reactions, but the precipitates can cause an increase in metal concentration and are especially important in waste systems. Thermodynamic data can be used to predict precipitation reactions for metals under given conditions (McLean et al., 1992).

2.4.1 Mechanisms of Groundwater Transport

Groundwater flow patterns can be studied to understand the path of water flow underground. These flow patterns can provide important information when predicting the path of contaminants in groundwater. Additionally, flow patterns can help to determine where groundwater enters a drinking water supply source or breaks through the surface.

As described in section 2.4, contaminants can leach into groundwater. Contaminants can travel through an aquifer in three ways: advection, dispersion, and diffusion. Advection refers to when contaminants flow in the groundwater. Dispersion flow is defined as when a “contaminant at the edges of the mass are deflected away from the mass by particles that obstruct their flow” (Stockton College, 2012). Diffusion is when particles spread from areas of high concentration to low concentration through random motion. An example of this in groundwater is when there is little to no groundwater flow and the contaminants slowly leach into the soil (Stockton College, 2012). Groundwater flow patterns in combination with fate and transport models can be used to best predict the path of contaminants.

2.4.2 Exposure Pathway Evaluation of Contamination

There are five main elements of an exposure pathway that assist in identifying the type and degree of human exposure from a given contaminated source. The first element is the source that can release contaminants into various media. For example, a drum or landfill can release contaminants into the soil or water. The second element is the fate and transport of the contaminant once it has been released into the environment. Each contaminant will move differently through various media. The third element is known as the exposure point or area. This refers to the specific location(s) in which human or environmental receptors may be exposed to the contaminated media. The fourth element is the exposure route which is also known as the means of contact at the exposure point. For example, ingestion and inhalation are types of exposure routes. The last element of an exposure pathway is the population that is potentially exposed to the contaminant (ATSDR, 2005).

In order to best evaluate the exposure at a specific site, conceptual models are commonly used. These models help answer important questions including where the contaminant travels and where the location of greatest risk to receptors is. These models help identify the key elements, beginning with the source of contamination and identifying affected media, safety hazards, and points of exposure. Overall, these methods help to better predict the potential harm that could be caused at the given site (ATSDR, 2005).

2.5 Remedial Strategies for Metal Leaching

Various remedial strategies are outlined in this section to understand common techniques used in preventing and treating metal contamination in groundwater. A general description of and important considerations for each remedial strategy are discussed.

2.5.1 Capping

Capping involves containment, but not removal, of metals contaminated material. Capping is used to stop further interaction between contaminants and surrounding water sources.

The cap acts as a physical barrier to restrict contact with contaminated material, to reduce water infiltration through the contaminated material, and to reduce infiltration into the underlying groundwater. It is also used to control gas and odor emissions and create a solid surface so the site may be used for other purposes. Caps do not lower toxicity or remove the contaminants from the site and require periodic inspection and maintenance. According to a study done by the Department of Toxic Substance Control (DTSC) in California, of 188 metal contamination sites evaluated, capping/containment was the most used remedial strategy between 2001 and 2007. Out of those sites analyzed, 60% considered capping, and 16% implemented capping (Burger, 2008). Caps can be single layered or multilayered and can be made of various materials and at differing thicknesses depending on the mobility of the contaminant, climate, and future use of the property. Types of caps are: soil, evapotranspiration (ET), asphalt/concrete, low permeability clay or soil, and geosynthetic/composite (Burger, 2008).

2.5.2 Filtration

Filtration is a precursory or concluding treatment used to remove contaminants from water (Caniylmaz, 2003). In filtration, water is passed through a porous permeable membrane or filter. Suspended particles are too big to pass through the pores while the water flows freely through the filter (Tech Brief, 2011). The effectiveness of filtration often depends on the pore size (Caniylmaz, 2003).

Sediment filters have large pore sizes, generally around 20 microns, but can be larger or smaller (AchaWater, 2011). They are effective at removing suspended matter, but usually ineffective at removing dissolved organic or inorganic materials (Dvorak, 2008). Sediment filters can be used as a pretreatment process to remove large particles that could be damaging to or cause fouling of other processes such as ion exchange resins, which are explained in section 2.5.7 (Caniylmaz, 2003).

Membrane filtration is often pressure-driven, meaning that the driving force for the process is the pressure difference across the membrane. Four general classes of pressure-driven membranes are: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These membranes are classified based on their pore sizes. Of these four, microfiltration has the largest pore sizes, ranging from 0.1 to 10 micrometers. Microfiltration is often used in water treatment processes because of its high recovery rate and low energy requirements compared to other membranes (Caniylmaz, 2003).

2.5.3 Solidification/Stabilization/Precipitation

Solidification/Stabilization/Precipitation (S/S/P) involves mixing a chemical agent into the soil or water to react with the contaminant metal. This reaction causes the metal to precipitate in a solid matrix, decreasing its mobility. A variety of binders, such as lead arsenate, can be used to immobilize metals. This technique is not effective with metals when they are in their anion or organic form.

This technique can be done in situ or ex situ. If done ex situ, the soil must be excavated and the chemical agent added at a facility. The precipitate can then be removed and the soil can be returned to its point of origin. If done in situ, the chemical reagent is added directly into the soil on site. However, this can be more expensive because the precipitate needs to be excavated and disposed of properly because S/S/P does not lower toxicity levels of the metals. A typical large scale S/S/P process can treat between 500 to 1,000 tons of contaminated soil per day (Evanko et al., 1997).

2.5.4 Interceptor Drain

An interceptor drain consists of a gravel trench on top of relatively impermeable soil and is typically placed on a slight slope. This method is commonly used for groundwater collection where ground stability is an issue, such as an area where landslides occur often. Once water enters the gravel trench, it is carried via perforated pipe to a discharge point. The water that enters the trench is contaminated. Since the contaminated water now flows through the trench, the effect of any contaminants on the soil is limited. The water flows to a discharge or collection point where the water then must be removed to a safe area. When the water is present in the trench, other remedial strategies can be employed to reduce contamination (Washington State Department of Ecology, 2011a).

When constructing an interceptor drain, it is important to consider the slope. If the trench is too flat, the water will not flow easily and could clog the trench. Location is also an important factor to avoid introduction of undesired water, such as wastewater, into the drain. This is a good option when the land of interest is already located above a relatively impermeable soil layer (Washington State Department of Ecology, 2011a). These factors show that this option is a poor choice in areas with unstable slopes or on a low bank but good for areas on a bank. Also, it is moderately low cost and its installation and maintenance require the use of heavy equipment. These disadvantages and advantages of an interceptor drain are depicted in Figure 5.

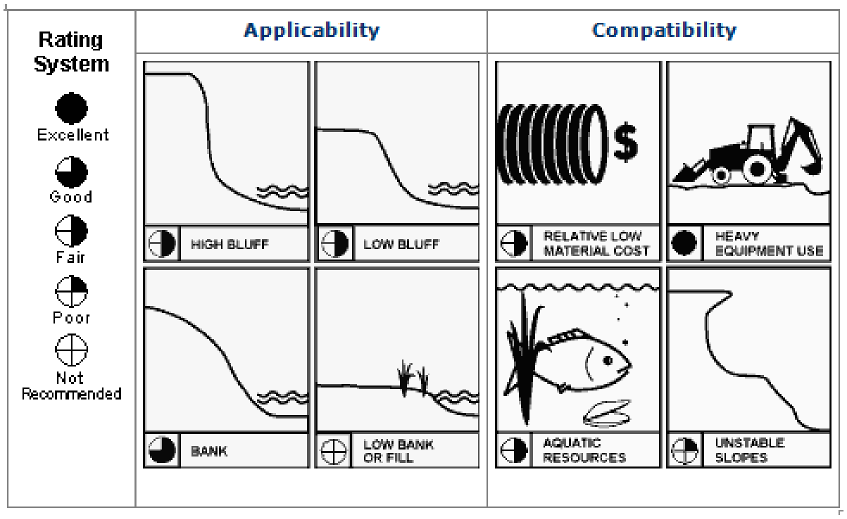


Figure 5: Advantages and Disadvantages of an Interceptor Drain

(Washington State Department of Ecology, 2011a)

2.5.5 Cut-off Trench

Cut-off trenches are used to prevent water seepage into soils. These trenches have been used during the implementation of dams or man-made ponds. Trenches are cut along the centerline of the dam until the trench extends past an impervious material, such as rock, shale, or heavy clay. Then, the trench is filled with heavy clay and compact soil. Cut-off trenches reduce the leakage of contaminated water into soil by the slurry wall, described below. If deep excavation is required, a track hoe or other heavy machinery is required, and therefore work-space is an important consideration (Gentry, 2005).

A major component of cut-off trench is the slurry wall within, which is created by applying slurry to the trench. Slurry is an engineered fluid that is created in a colloidal mixer before being pumped into the trench. This fluid exerts a hydraulic pressure toward the trench walls, preventing a collapse. The most common slurry used is bentonite slurry, which is a combination of bentonite clay and water. A solid, or a "cake," is formed by the slurry, which limits the permeability of the layer. The layer of slurry reduces the leaching potential, which reduces contamination, because the contaminants become caught in the slurry trench and cannot leach into the groundwater. The compatibility between the slurry and contaminants is an important consideration (EarthTech, 2011). If the slurry and chemical are not compatible, then the slurry may not be able to maintain its form under the presence of chemicals that may ruin or deteriorate the material. This could reduce the thickness of the wall, which would reduce the effectiveness of the slurry wall.

2.5.6 Permeable Treatment Wall

A permeable treatment wall is a remedial strategy that removes contaminants by degrading, transforming, precipitating or adsorbing target solutes as the groundwater flows through the wall. Permeable treatment walls are also known as permeable reactive curtains. To install a permeable treatment wall, a trench is typically dug and backfilled with the chosen material for the treatment wall (U.S. Navy, 2011). An advantage of permeable treatment walls is that no pumping or above ground treatment is needed.

Zero valent iron and limestone treatment walls are most common. Zero valent iron permeable treatment walls are typically used to treat systems that have high concentrations of chromium. Low oxidation chemical species serve as electron donors when they come in contact with the treatment wall.

Limestone treatment walls are used to treat systems that are contaminated by lead and acid. Lead and acid are typically a result of battery contamination in landfills. The limestone wall neutralizes the acidic ground water and limits the mobility of metals. If there are anaerobic conditions or high concentrations of iron or aluminum, the effectiveness of the treatment wall could decrease (Evanko et al., 1997). Limestone permeable treatment walls can operate up to 30 years with the proper maintenance (U.S. Navy, 2011).

2.5.7 Ion Exchange

Ion exchange is a remedial approach in which contaminated water runs through a resin containing exchange ions. The exchange ions replace the contaminant ions in the water and the contaminant ions are then transferred to the resin. The resin must be periodically regenerated to maintain its efficiency. Both the spent resin and regeneration water must be further treated and disposed of properly (Siemens, 2011).

Ion exchange technology is used commonly as an arsenic removal method. Ion exchange can remove up to 95% of the arsenic in water (Caniylmaz, 2003). Filtration is commonly performed before ion exchange to remove suspended contaminants such as solids and organics to prevent fouling and damage of the resin (Siemens, 2011).

2.5.8 Chemical Treatments

Chemical treatments are used to detoxify, precipitate or solubilize metals in groundwater and soil, by adding chemicals to the contaminated area. These treatments should be chosen carefully since introducing a new chemical may increase the overall toxicity of the area and could potentially have adverse effects if the wrong chemicals are chosen. Chemical treatments are chosen based on soil and groundwater conditions including other metals present and pH.

Three types of reactions that occur during chemical treatments include oxidation, reduction and neutralization. Each of these reactions can affect the oxidation state of metal atoms, which dictates if the metal is present in solution or as a precipitate. Oxidation reactions change the oxidation state of the metal atom through the loss of electrons. Commercial examples of oxidizing reagents include potassium permanganate, hydrogen peroxide, hypochlorite, and chlorine gas. Chemical treatments can be used to oxidize arsenic, from the more toxic form, arsenic (III), to the less toxic form, arsenic (V). If arsenic is present in the water it can be treated by chemical oxidation to be precipitated out of solution. Arsenic is more likely to precipitate in the presence of Fe (III). Therefore a chemical agent with Fe (III) could be applied to the area (Evanko et al., 1997). Reduction reactions change the oxidation state of metal atoms by adding electrons. Commercial examples of reducing agents are alkali metals (Na, K, etc.), sulfur dioxide, sulfite salts and ferrous sulfate. Neutralization reactions adjust the soil and groundwater pH to be closer to a neutral pH of 7. Typically neutralization is used to precipitate metals from groundwater.

Groundwater containing high concentrations of arsenic usually also contains relatively high levels of iron and manganese. The groundwater chemistry may affect the valence state of Fe and Mn which in turn affects the mobility of As. When Fe and Mn are dissolved under reducing conditions, the arsenic in the water becomes mobilized. Conversely Fe and Mn hydroxides can immobilize arsenic. Arsenic can often be removed as a byproduct of Fe or Mn oxidation filtration because the chemicals used to oxidize Fe and Mn can also oxidize some As (III). For example, oxidizing any soluble Fe (IV) and As (III) allows for the removal of As (V) by iron hydroxides through adsorption/co-precipitation. The As (V) is usually in the form of arsenate, binds to the iron and may be removed. Oxidation of Mn has also been shown to work in some cases. The Mn oxidation removal method can be used for widely varying pH without affecting the efficacy. Some common oxidizing agents are potassium permanganate ($KMnO_4$), chlorine dioxide (ClO_2), and ozone (O_3) (Caniylmaz, 2003).

A more likely scenario in which arsenic is removed by oxidation is one where more arsenic is present than Fe and Mn. In this situation, the oxidation of As (III) becomes important. It is much easier to remove arsenate (AsO_4^{3-}) from water than arsenite (AsO_3^{3-}). As (V) exists primarily in anionic molecules such as $H_2AsO_4^-$ or $HAsO_4^{2-}$. As (III), however, is usually found in neutral form, which makes it more difficult for arsenite compounds to adsorb to mineral sources. Therefore, arsenic is often oxidized to convert As (III), which is found in arsenite compounds, to As (V), which is present in arsenate compounds, and make it easier to remove. This can be done simply by aeration, the addition of oxygen, or by stronger oxidizing reagents such as potassium permanganate, chlorine, hypochlorite, ozone or hydrogen peroxide (Caniylmaz, 2003). Two example of the oxidation of As (III) using permanganate are shown in Reactions 3 and 4.

$$5\mathrm{As}^{3+} + 2\mathrm{MnO_4}^{-} + 16\mathrm{H}^{+} \rightarrow 5\mathrm{As}^{5+} + 2\mathrm{Mn}^{2+} + 8\mathrm{H_2O} \qquad \text{(Reaction 3)}$$

$$5\mathrm{As}^{3+} + 2\mathrm{MnO_4}^{-} + 8\mathrm{H_2O} \rightarrow 5\mathrm{As}^{5+} + 2\mathrm{Mn(OH)_2} + 12\mathrm{OH}^{-} \qquad \text{(Reaction 4)}$$

Reaction 3 works under acidic conditions and Reaction 4 works under basic conditions. Mn (VII) works well to oxidize As (III) regardless of pH which is why potassium permanganate is so commonly used for this application (Na et al., 2007).

2.5.9 Soil Washing

Soil washing is a technique that could use physical separation, chemical treatment, or both to remove metal contaminants from soil. First the soil is excavated and screened to remove large particles which can be placed back at the site. Then the soil is screened a second time to separate the remaining particles by size. The chemical reagent is then added to the soil to dissolve the metal into water. The water is then removed with the dissolved contaminant. Many reagents affect the pH of the soil and the oxidation state of metals. The clean soil is then placed back at the site. Soil washing is inexpensive but only moderately lowers the toxicity and mobility of the metals (Evanko et al., 1997). Since the soil needs to be completely excavated for this technique, it may not be advantageous for large sites.

2.6 Landfill Case Study in Clinton, MA

The South Meadow Road landfill in Clinton, Massachusetts was opened in 1974 after approval from the MassDEP and remained open for thirteen years until it was closed in 1987. The landfill was capped in 1990 and was closed completely with the approval of a capping certificate by the MassDEP in 1995. In 2003, an inspection of the landfill was conducted and a metal leachate was observed discharging down gradient into the South Meadow Pond. The MassDEP issued a Notice of Noncompliance (NON) at this time. The town of Clinton was responsible for replacing the cap or integrating a better remediation method for containing the contaminants in this landfill (Regan, 2009).

In March 2007, an Initial Site Assessment (ISA) and a Comprehensive Site Assessment (CSA) were conducted. These assessments included collecting and evaluating groundwater, surface soil, sediment, and landfill gas samples, for contaminants and potential health risks associated with these contaminants. The contaminants of concern found in this landfill were arsenic, iron, acetone, and iron flocculent (floc). Arsenic was above the drinking water standards in groundwater and also was found in residential wells down gradient from the landfill (Regan, 2009).

A Corrective Action Alternatives Analysis (CAAA) was submitted in 2006 to evaluate several remedial strategies based on U.S. EPA regulations, metal mobility and toxicity, feasibility of incorporation, and cost. The remedial strategies considered for the groundwater were:

1. No further action;
2. Containment;
3. Vertical extraction wells between Clinton and Massachusetts Water Resource Authority (MWRA) landfills and ex-situ treatment and discharge to South Meadow Brook;
4. Collection via trenches and ex-situ treatment and discharge to South Meadow Brook; and
5. Vertical extraction wells between MWRA landfill and South Meadow Pond and ex-situ treatment and discharge to South Meadow Brook.

Before any remedial actions were implemented, bench scale testing was recommended for each of these strategies to evaluate their effectiveness (Regan, 2009).

In order to address the groundwater quality problems in South Meadow Pond, the Board of Selectmen voted unanimously to pursue passive remedial alternatives (Dickhaut, 2011). Examples of passive remedial measures are reconstructing the area around the landfill so that rainwater runoff is diverted away from the landfill, ensuring the landfill is safely capped and is sufficiently impermeable, and closing the area to all vehicles including ATVs (Welsh, 2011).

The town of Clinton hired the engineering company Brown and Caldwell in Andover, MA to assess issues at the South Meadow Pond. For the purpose of collecting data for the passive remedial alternatives, Brown and Caldwell submitted a proposed scope of work. A topographic survey was scheduled for September 2011 to create a topographic map of the current site, the South Meadow Road landfill and the surrounding areas. This map can be used to decide where the land needs to be restructured to meet the required slopes to divert rain water (Podsen, 2011a).

The next phase of this project was to drill and collect soil/groundwater samples in October 2011. It was proposed that up to ten borings be taken to acquire representative samples of all soil types. The initial borings will be used as an investigation as to whether or not to drill more. The drillings are designed to work as representative samples to determine the depth of pollution from the landfill as well as the permeability of the cap and the characteristic groundwater chemistry below the landfill (Podsen, 2011a).

Finally, in early November of 2011 a visual/bathymetric survey was scheduled to be conducted on South Meadow Pond in order to gain a better understanding of both the surface and under the surface water portions of the site (Podsen, 2011a). The data will be used to create a map of the pond to evaluate potential dredging of iron flocculation. The drilling activities for this survey began on December 12, 2011 (Podsen, 2011b). From this event, Brown and Caldwell determined that the landfill cover is more than 4.5 feet thick with trash filling approximately 5 to 14 feet above the water table at all drilling locations (Podsen, 2012). The results of this Comprehensive Site Assessment survey will be analyzed and reported to the town of Clinton, and a meeting with the MassDEP will likely take place shortly thereafter to discuss the proposed passive remedial approaches (Podsen, 2011a).

2.7 Objectives of Project: Landfill Case Study in Holden, MA

The goals of this project were to develop a better understanding of conditions that promote leaching of metals into groundwater and to identify and evaluate remedial alternatives for the former River Street Sanitary Landfill site in Holden, MA, which will henceforth be referred to as “the landfill.” The landfill, which closed in 1987, is in the post-closure monitoring phase. In November 2008, sediment samples near the main seep at the Quinapoxet River revealed high concentrations of arsenic, barium, iron, lead, and manganese. Corporate Environmental Advisors, Inc. is assisting the town of Holden with additional assessment activities to further evaluate the impacts and risks of the discharge from the landfill to the Quinapoxet River. In order to assist CEA in identifying remediation alternatives for the Holden landfill site, the following objectives were completed:

1. Understand the metals and concentrations present at the former Holden landfill site; and
2. Evaluate remediation strategies to reduce metal mobility at the former Holden landfill site, thus reducing potential risk to humans and the environment.

This project aimed to recommend remediation strategies considering various criteria, including the ability to effectively impede metal leaching, cost, and long-term applicability. By accomplishing these objectives, CEA was presented with options to make an informed decision about the appropriate remediation strategy for the former Holden landfill site.

Chapter 3: Methodology for the Holden Case Study

This project assessed metal leaching at the former River Street Sanitary Landfill in Holden, MA. Groundwater and surface water samples were collected from the landfill and the surrounding area. The samples were analyzed for physical and chemical properties that affect metal leaching, such as pH and oxidation-reduction potential (ORP), as well as for metal concentrations. Results were analyzed to determine trends and correlations between parameters in order to identify strategies to reduce leaching.

3.1 Sample Collection

Sampling was conducted with CEA on October 20 - 21, 2011 at the landfill. The landfill occupies 17 acres and is located 300 feet from interstate Route 190. The Quinapoxet River is located approximately 1,100 feet north of the landfill. This river is a tributary of the Wachusett Reservoir, which serves as part of the source water for drinking water in Boston and the surrounding communities, and is used for recreational fishing. A map of the landfill area is shown in Figure 6.

A total of 21 water samples were collected in accordance with Standard Method 1060 (APHA et al., 1995). Groundwater samples were collected from 16 groundwater wells on and around the landfill site. These groundwater wells had water depths ranging from 4.48 to 46.77 feet, which are reported in the results. Five seep water and surface water samples were collected; three samples from the Quinapoxet River and two seep water samples from leachate seepage areas. The sampling locations are noted on Figure 6.

Thirteen of the 16 groundwater samples were collected as follows. First, the groundwater well was uncapped and tubing that was in the well was removed. The water depth of the well was determined with a Solinst interface probe model 122 water level indicator (Solinst, Georgetown, Ontario, Canada). New quarter-inch polyethylene tubing (Nycoil, Randleman, NC) was cut and connected to a peristaltic pump while the other end of the tubing was placed in the well. The peristaltic pump (Pegasis Pump Company, Bradenton, FL) was connected to a YSI 5083 flow cell (YSI, Yellow Springs, OH). The flow cell allowed the water sample to continuously flow from the well through a tube into a cell. A YSI meter was submerged completely in this cell in order to complete field measurements as described in section 3.2. The sample in the cell was not exposed to the atmosphere. After the field measurements were completed, the tubing was redirected from the flow cell to a 250 mL plastic collection bottle labeled with the sampling information. The bottle was filled to the top and then capped.

For three wells, HDOW 9A-C, a check ball valve was used to generate enough pressure to pump the water upwards through dedicated tubing in order to collect samples. These samples were pumped directly into collection bottles. Since the YSI meter did not fit in the 250 mL bottles, an intermediate one liter bottle was used to obtain field measurements. These samples were exposed to the atmosphere for approximately one minute prior to obtaining the measurements.

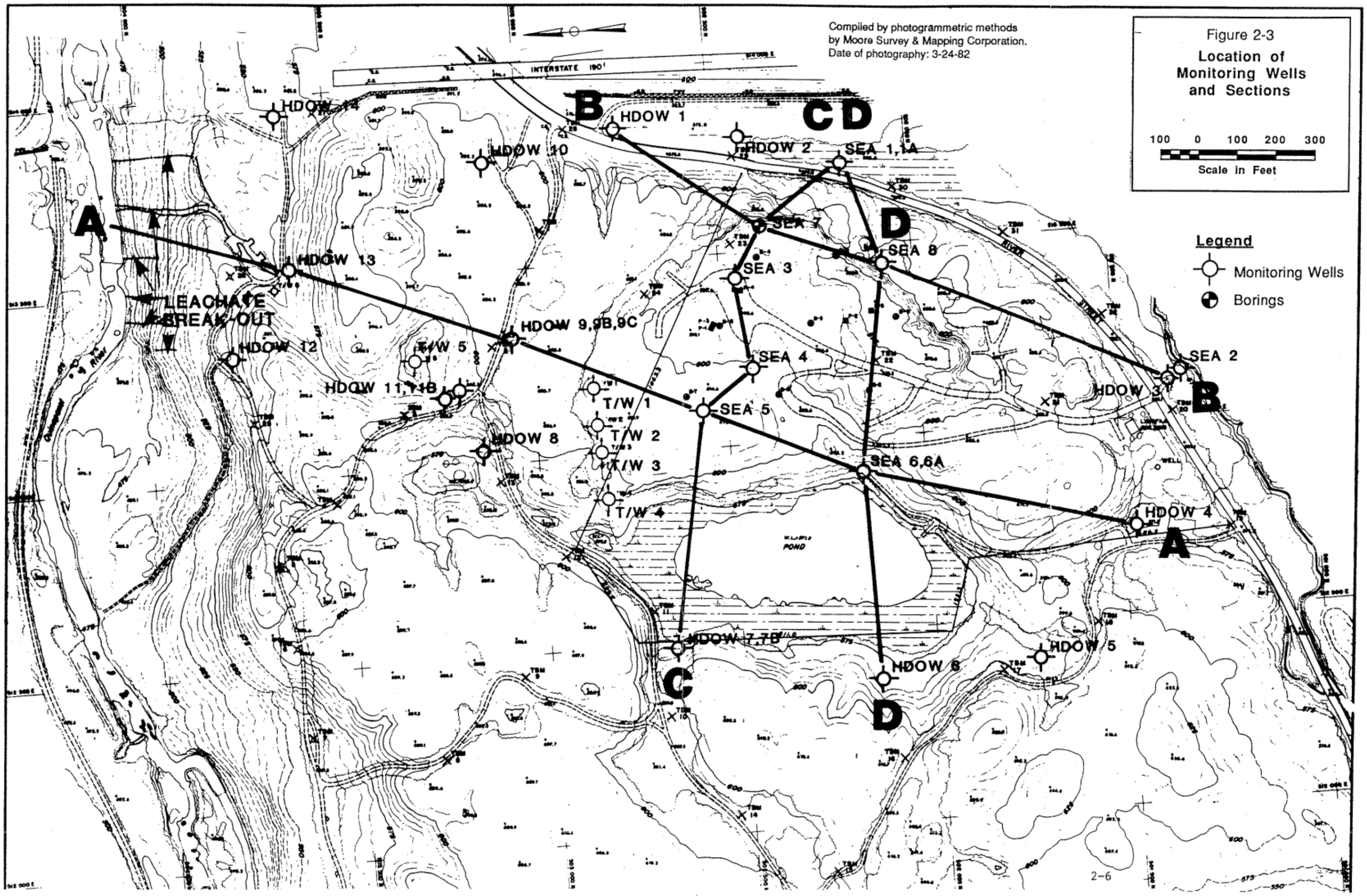


Figure 6: Map of Former Holden Landfill (CEA, 2011)

Five seepage and surface water samples were collected. One seepage sample was collected using one method, and the remaining four samples were collected with a different method. The collection of the leachate at the breakout sample was similar to collection of groundwater samples, using a peristaltic pump placed directly into the surface water and using a flow cell. For the three river samples and Route 190 Seep water sample, the YSI meter was placed directly in the surface water for field measurements. A 250 mL plastic container was placed directly in the river or Route 190 Seep water to collect each sample. The river samples were collected beginning downstream and continued upstream, which helps minimize the disruption of water quality of samples (Town of Plymouth, 2006).

After each sample was collected, field measurements were completed with methods described in section 3.2. Each container with the sample was then placed in a cooler with icepacks and transported to the WPI laboratory for additional analysis, as described in section 3.3.

3.2 Field Testing

As mentioned in section 3.1, field measurements were conducted at the time of sample collection. A YSI 650MDS Multi-Probe Field Meter (YSI, Denver, CO) was used to measure pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), specific conductivity, and temperature after the reading was stabilized. For 13 of the 16 groundwater samples, a flow cell was used to ensure accurate readings. For 3 of the 16 groundwater samples, the samples were exposed to air for approximately one minute prior to measurement. It is likely that pH, specific conductivity, and temperature were not significantly affected by this sampling technique. However, exposure to oxygen in the air may have altered both the DO and ORP readings. Table 3 provides a summary of the parameters tested and the associated methods from Standard Methods (APHA et al., 1995).

Table 3: Field Testing Parameters and Methods

Parameter	Method	Standard Method Number
pH	Electrochemical Method	4500 - H^+ B
ORP	Oxidation-Reduction Potential Measurement in Clean Water	2580 B
DO	Membrane Electrode Method	4500-O G
Specific conductivity	Conductivity Cell	2510 B
Temperature	Field Thermometer	2550 B

3.3 Laboratory Testing

Water samples were transported to the laboratory for further analysis of chemical and physical properties that affect the mobility of metals. The parameters tested in the laboratory included metal concentrations, inorganic anion concentrations, turbidity, and color. The methods and holding times are shown in Table 4. As shown in the table, the actual holding times for metal and inorganic anion concentrations were less than the acceptable holding time. However, the actual holding time for turbidity and color was longer than the acceptable time. Turbidity measurements have a short holding time of two days in order to limit the effect microbial decomposition would have on the result (APHA et al., 1995). Microbes are not typically found in groundwater at significant amounts, and therefore, a longer holding time likely did not affect the turbidity measurements (American Ground Water Trust, 2008). The color was not recorded until after an acceptable holding time, however, it is not believed to have affected the results. All samples were stored at 4°C prior to analysis. Additional background information on the sampling techniques and specific laboratory tests can be found in the Appendix A.

Table 4: Laboratory Testing Parameters and Methods

Parameter	Method	Standard Method Number	Holding Times (days)	
			Allowed	Used
Turbidity	Nephelometric method	2130	2	42
Color	Visual method	2120	2	26
Metal Concentrations	AA furnace or AA flame	3110 Individual Metals- 3500	180	28
Inorganic anion concentrations	Ion chromatography anions	4110 B	42	28

Quality assurance and quality control measures were taken for metal concentrations, inorganic anion concentrations, and turbidity. First, blank samples were used as standards or quality control checks. For metals, calibration curves included standards listed in Table 5. For anions, one standard for each anion was used to create a calibration peak (see section 3.3.2). For turbidity, no blank samples were used. The instrument had been calibrated three weeks prior to measurements. Duplicate samples were tested and average results were reported. The AA instrument automatically measured each sample twice and reported each value along with the mean. The ion chromatograph only measured each sample once. Five random samples, of the twenty-one samples, were tested twice. Since these samples showed precise measurements between the two tests, the instrument was determined to provide precise results, and therefore duplicate measurements were not completed on all samples.

3.3.1 Metal Concentrations

The concentrations of five metals (arsenic, manganese, lead, iron, and cadmium) were determined using an AAnalyst 300 atomic absorption spectrometer (Perkin Elmer, U.S.). The samples were analyzed in two ways: as dissolved samples and as digested (total) samples. The dissolved samples represent the concentrations of metals present in the aqueous phase, as received. The digested samples were prepared to show the total concentration of metals present in the aqueous and particulate phases. For dissolved samples, each sample was shaken for 5 seconds. Then, the sample was passed through a Millex (Millipore, Billerica, MA) syringe driven filter (0.45 micron) into a 50 mL centrifuge tube. The syringe used was 20 mL (BD, Franklin Lakes, NJ). Samples were then stored at 4°C until the samples were ready to be tested. To create the digested samples, 50 mL of each sample was mixed with 5 mL of 10 M nitric acid. Samples were placed on a hot plate at 175°F for 24 hours to reduce the volume to 25 mL. Then, reagent-grade water (ThermoScientific, Marietta, OH) was added to increase the volume to 50 mL each. These samples were then passed through a Whatman #4 filter paper (Whatman, Piscataway, NJ) to fill 20 mL tubes.

Standard solutions for arsenic, cadmium, manganese, lead, and iron were made from standard stock solutions. These stock solutions were purchased at concentrations of 1000 μg/mL from UltraScientific, SCP Science, or Perkin Elmer. To make a standard solution, a specific volume of the stock solution was placed in a volumetric flask and then filled to mark with reagent-grade water. For example, to prepare a 1 ppm standard solution of iron, 50 μL of the 1000 μg/mL iron stock solution was placed in a 50 mL volumetric flask and filled with reagent-grade water. The standards used are summarized below in Table 5.

Table 5: Standards Used for Each Metal for AA

Metal	Dissolved Standards	Digested Standards
Arsenic	5, 10, 20 ppb	5, 10, 20, 50 ppb
Manganese	0.1, 0.2, 0.5, 1, 3, 5, 20 ppm	0.1, 0.2, 0.5, 1, 3, 5, 20 ppm
Lead	5, 10, 20 ppb	5, 10, 20 ppb
Iron	0.2, 0.5, 1, 3, 5 ppm	0.2, 0.5, 1, 3, 5, 20 ppm
Cadmium	5, 10, 20 ppb	5, 10, 20 ppb

An HGA 850 Furnace (HGA, Germany) was used to quantify concentrations of arsenic, cadmium, and lead. Two milliliters of each of the dissolved samples was put into AA sampling vials using a pipette. A calibration blank, standards, and the 21 sample vials were placed in the AA furnace sample holder. A NIST (National Institute Standard Technologies) sample was also placed in the holder. A lamp was chosen depending on which metal was being analyzed. The furnace AA is automatic, where the needle placed itself in a cleaning solution and placed itself in and gathered a matrix modifier and then the sample. After collecting the sample, the needle went into the furnace. The instrument ran every sample twice through the furnace. Each of these results was reported along with the mean concentration detected. The procedure was repeated for the digested samples.

Flame AA was used to measure manganese and iron in order to avoid contamination of the furnace. Running the AA with the flame eliminates the possibility of contamination because there is no graphite that could absorb the metal, as with the furnace. Iron easily contaminates the furnace and could provide inaccurate concentration results if samples were analyzed by the furnace. First the flame was turned on. A small tube that was connected to the flame was then placed into the centrifuge tube, where it collected the sample. The sample was then passed through the flame, allowing the instrument to measure the metal concentrations burnt in the process. A detailed description of flame AA can be found in the Appendix A. The procedure for flame AA was repeated for each of the dissolved and digested samples.

3.3.2 Inorganic Anion Concentrations

Dissolved samples were analyzed on a Dionex 2100 RFIC ion chromatograph (Dionex, Sunnyvale, CA). The instrument column operated at 30°C.   The eluent generator utilized 38 mM potassium hydroxide and the suppressor ran at 113 mA. Prior to running any samples, the instrument ran with blank samples and then various standards. The standards were 20 ppm for fluoride, 200 ppm for phosphate, and 100 ppm for bromide, chloride, nitrite, nitrate, and sulfate. Digested samples were not analyzed for ion chromatography because the acid could damage the instrument. Samples were taken from the previously prepared dissolved bottles and placed in 5 mL cuvettes using a pipette. These cuvettes were placed in the ion chromatograph and the instrument ran the measurements, where it analyzed the samples for inorganic anions, including fluoride, chlorine, sulfate, bromide, nitrate, and phosphate.

3.3.3 Turbidity

Samples were analyzed for turbidity using a HACH 2100N Turbidimeter (Hach, Loveland, CO). Samples were analyzed as received from sampling. The first sample was placed in a vial, capped, and gently inverted two times for consistency. The outside of the 30 mL vial was wiped clean with a kimwipe. The vial was placed in the turbidimeter, where the result in NTU was displayed. This process was repeated for each sample. In between each sample, the 30 mL turbidity vial was rinsed with reagent-grade water.

3.3.4 Color

The color of each sample was recorded. This process was a visual method where general color of the aqueous phase sample was indicated, as well as the presence of any sample in the particulate phase. The color for digested samples was also noted.

3.4 Data Analysis

The data collected while sampling was analyzed by several different methods. The data were analyzed geographically using maps, and analytically using Microsoft Excel. Remedial strategies were also evaluated to determine the most appropriate alternatives.

3.4.1 Geographical Analysis

The parameters obtained through testing were analyzed visually using a map of the landfill area. These parameters collected from the 21 locations were divided into smaller ranges and each range was assigned a color. The colors were then used to mark geographically which wells fell into each range. This visual representation of data was designed to determine if there were any noticeable geographical trends, for example, if a certain cluster of wells contained high total lead, or if the pH was low along a line between two portions of the map.

3.4.2 Statistical Analysis

A statistical analysis was conducted on the data to show if there was any statistically significant correlations or variance between the data obtained in both the field and laboratory. A correlation analysis was done between all of the parameters, metal concentrations, and ions. The wells were then divided into three geographical regions and an analysis of variance (ANOVA) was conducted between these regions for all of the parameters, metal concentrations, and ions. A correlation analysis was also conducted between the metal concentrations obtained by CEA and the team's digested metal concentration results.

3.4.3 Evaluation of Remedial Strategies

In order to determine which remedial strategies are most appropriate to accomplish the specified goals, an evaluation was completed according to "The Feasibility Study: Detailed Analysis of Remedial Action Alternatives," a U.S. EPA document that details the method of determining appropriate remedial alternatives (U.S. EPA, 1990). Figure 7 shows general guidelines to develop remedial action alternatives. This method includes understanding results of the site of interest and analyzing a list of alternatives to treat the site, as well as developing a feasibility study for each recommended action. Each remedial strategy was researched and described in section 2.5. Each remedial alternative was ranked based on six criteria: cost, long-term effectiveness, commercial availability, ability to reduce mobility of metals, ability to reduce toxicity, and site specific implementation. Rankings ranged from 1 to 5, where a value of 1 represented a weak candidate for that criteria and a 5 represented it was the best candidate in that criterion. After each remedial strategy was ranked for each criterion, the criteria were weighted according to the importance of that criterion in determining appropriate remedial strategies. The rankings were added for each remedial strategy, giving a total number out of a possible 35. These totals were then used to determine recommendations for the site.

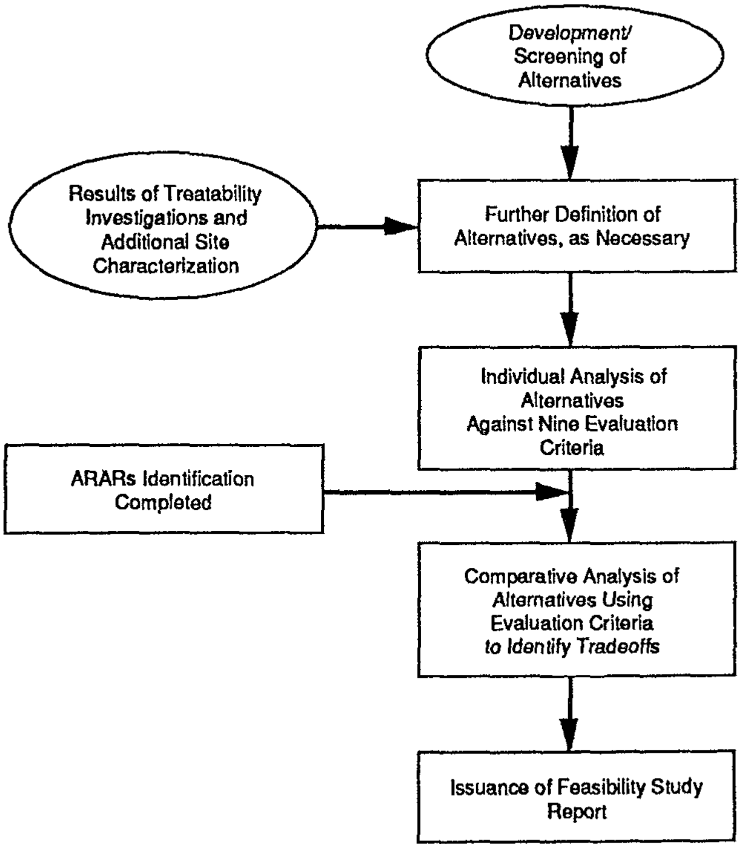


Figure 7: Guidelines for Evaluation of Remedial Alternatives (U.S. EPA, 1990)

Chapter 4: Results and Discussion

The purpose of this project was to understand the metals and concentrations present at the former River Street Sanitary Landfill in Holden, MA, and to evaluate remediation strategies to reduce metal mobility, thus reducing potential risk to humans and the environment at this site. In order to accomplish these goals, 16 groundwater and 5 surface water samples were collected at the site. This chapter presents site observations and sampling results, as well as geographical and statistical analyses of the data. Then, remedial alternatives were compared to criteria, such as cost and long-term effectiveness, in order to determine feasible remedial strategies for the landfill site.

4.1 Site Observations

The former River Street Sanitary Landfill in Holden, MA was studied for this project. The landfill covers an area of approximately 17 acres. The top of the capped landfill was relatively flat and was vegetated with grass, when the team sampled on October 20-21, 2011. This area appeared to be regularly maintained and was marked off for model airplane runways. This area is used as a runway and flight area by the Quinapoxet Model Flying Club as a MassDEP approved post-closure use. The area directly surrounding the landfill is wooded.

Field sampling was conducted at the landfill using previously installed groundwater wells. The groundwater wells were located on the capped landfill and in the surrounding area. Samples were also collected from three points in the Quinapoxet River: upstream of the landfill, downstream of the landfill, and around the main seep mixing area. The main seep mixing area is the area where water from the main leachate seep mixes with the waters of the Quinapoxet River. The downstream location is located under Interstate I-190 at the bottom of a rocky embankment.

The landfill is located on River Street in Holden, Massachusetts. The nearest residents on River Street are located greater than 500 feet from the landfill and do not have access to municipal water because there is no available public potable water distribution in this area. These residences have private wells. However, there are no private wells within 500 feet of the landfill (MassDEP, 2012).

4.2 Sampling Results

This section presents the physical observations and analytical results for the 21 water samples collected at the landfill. In Table 6, the physical properties of the samples are presented including the depth to water table in the well, depth to bottom of well, and color. It is pertinent to know the depth to groundwater in the wells in order to evaluate if the depth of the water is correlated to metal leaching. The statistical analysis of this is presented in section 4.4. The results show that the samples were collected from wells with various water depths ranging from 4.48 to 46.77 feet, as well as from surface waters. The three samples from the river were slightly cloudy. One sample, HDOW 13, was black, and most others were light brown or orange in color.

Table 6: Physical Properties of Wells and Color of Samples

Well ID	Well vs. Surface Sample	Depth to Water in Well (ft)	Depth to Bottom of Well (ft)	Color
SEA 1	Well	11.86	17.15	Orange and brown particles
SEA 2	Well	10.01	27.09	Slightly cloudy
SEA 2A	Well	4.48	14.15	Clear
SEA 6	Well	18.94	46.00	Slightly cloudy with some particles
SEA 6A	Well	18.95	26.64	Bright orange with particles
QR1	Surface	N/A	N/A	Slightly cloudy
QR2	Surface	N/A	N/A	Slightly cloudy
QR3	Surface	N/A	N/A	Slightly cloudy
190 Seep	Surface	N/A	N/A	Clear
Leachate at the breakout	Surface	N/A	N/A	Light brown with particles
HDOW 5	Well	29.81	0	Light brown with few particles
HDOW 6	Well	10.04	0	Clear
HDOW 7A	Well	9.66	51.08	Cloudy with particles
HDOW 7B	Well	9.56	0	Light brown with particles
HDOW 8	Well	19.03	47.06	Brown with particles
HDOW 9A	Well	46.77	84.4	Light brown with foam top
HDOW 9B	Well	43.66	74.65	Bright orange with particles
HDOW 9C	Well	43.76	55.58	Bright orange with particles
HDOW 12	Well	7.53	31.70	Yellow
HDOW 13	Well	5.47	13.13	Black
HDOW 14	Well	4.51	32.50	Light brown

Physical and chemical water quality measurements included temperature, specific conductivity, DO, pH, ORP, and turbidity, which are shown in Table 7. These parameters are significant in order to understand the factors that may contribute to metal leaching in groundwater. These parameters can affect the solubility of the metals in the water and indicate how many particles are present within the samples that were collected.

The temperature of the samples ranged from 10.4 to 13.9°C. Thus, all temperatures were within a 4°C range. The specific conductivity ranged from 0.019 to 1.80 mS/cm, with only two samples having a result higher than 1 mS/cm. In a study of a former refinery in Carson City, MI, total dissolved solids and specific conductivity were analyzed. It was shown that eight uncontaminated groundwater samples had an average specific conductivity value of 0.576 mS/cm at an average depth of 8.7 feet (Atekwana et al., 2003). This shows that the specific conductivity values obtained at the landfill site are typical of uncontaminated groundwater values.

Table 7: Physical and Chemical Properties of Water Samples

Well ID	Temp (°C)	Specific Conductivity (mS/cm)	DO (mg/L)	pH	ORP (mV)	Turbidity (NTU)
SEA 1	11.57	1.799	0.70	6.65	-118.6	119
SEA 2	10.98	0.311	1.52	6.73	-65.0	159
SEA 2A	12.42	0.303	1.50	6.15	-43.6	41.6
SEA 6	12.96	0.069	1.27	6.60	-47.7	356
SEA 6A	13.86	0.428	1.85	6.47	-57.2	1032
QR1	12.51	0.105	10.21	7.74	34.8	2.64
QR2	12.44	0.107	10.79	8.07	37.3	1.86
QR3	12.36	0.129	10.63	7.56	53.5	2.14
190 Seep	11.97	0.826	7.60	6.92	75.1	0.153
Leachate at the Breakout	12.21	0.376	3.02	6.68	55.7	49.6
HDOW 5	11.47	0.831	1.08	6.67	10.3	163
HDOW 6	12.09	0.019	2.71	6.94	1.3	33.5
HDOW 7A	13.81	0.049	2.74	7.26	-7.4	19.3
HDOW 7B	13.90	0.031	0.78	6.83	-22.4	20.4
HDOW 8	10.98	0.167	0.83	6.86	-54.7	198
HDOW 9A	11.40	1.508	3.82	8.15	-12.8	215
HDOW 9B	11.46	0.423	7.89	8.30	10.0	505
HDOW 9C	12.45	0.308	8.79	7.19	63.1	385
HDOW 12	10.39	0.136	0.70	6.89	-56.5	56.4
HDOW 13	11.37	0.384	0.38	6.98	-42.9	627
HDOW 14	11.72	0.403	0.53	6.48	-43.4	91

The DO of the landfill water samples ranged from 0.7 to 10.8 mg/L, with the highest values being the surface water samples QR1, QR2, and QR3. The remaining surface water samples (190 seep and leachate at the breakout) were also elevated compared to most of the groundwater samples. The DO for wells HDOW 9A, 9B, and 9C were higher than most well samples. The collection method used for these three wells, described in section 3.2, allowed samples to be exposed to the oxygen in the atmosphere prior to measurement, making them inaccurate. The range of DO for landfill groundwater well samples only (excluding HDOW 9A, 9B, and 9C) was 0.38 - 2.74 mg/L. This is consistent with typical groundwater DO levels, which range from 0.11 - 2.99 mg/L (Center for Earth and Environmental Sciences, 2012). The pH of all samples collected at the Holden site was within the range of 6.15 to 8.30, which is relatively neutral. The ORP (oxidation-reduction potential) of the landfill samples ranged from -120 mV to 80 mV, with the surface samples having the highest (most positive) results, with the exception of HDOW 9C. This is consistent with typical groundwater ORP values, ranging from -400 mV to 600 mV (Nielson, 2006). The turbidity ranged from 0 to 1032 NTU, with the highest sample collected from well SEA 6A. All samples with higher values of turbidity showed discoloration.

As mentioned in section 3.3.1, samples were tested for metal concentrations both as dissolved and digested samples. The dissolved samples represent the concentrations of metals present in the aqueous phase, as received. The digested samples were prepared to show the total concentration of metals present in the aqueous and particulate phases. These results are displayed in Table 8 and Table 9, respectively. The AA instrument detects concentrations based on comparison to the standard solutions. Therefore, the lowest standard used for each metal acted as a detection limit.

For the dissolved samples, one groundwater well had a higher level of arsenic than the drinking water maximum contaminant level (MCL) of 10 ppb (U.S. EPA, 2011d). The remaining fifteen wells and five surface water samples had arsenic concentrations less than the detection limit of 5 ppb (lowest standard used), and therefore less than the drinking water standard. As mentioned in section 2.1, manganese and iron do not have maximum contaminant levels for drinking water. Instead, the U.S. EPA has defined secondary standards, which are 50 and 300 ppb, respectively (U.S. EPA, 2011d). All 21 samples showed levels higher than the secondary standard for manganese and 11 for iron. Secondary standards are for aesthetics and do not infer that samples are harmful. As mentioned in section 2.2.4.1, iron is not harmful unless it is at concentrations closer to 200 ppm, which is 200,000 ppb (Lenntech, 2011e). No samples showed detectable concentrations of lead or cadmium (see Appendix B for metals concentrations). No concentrations for arsenic, lead, or cadmium were higher than the GW-3 standards. There are no GW-3 standards for manganese and iron.

Table 8: Metal Concentrations for Dissolved Samples

Well ID	As (ppb)	Mn (ppb)	Fe (ppb)
SEA 1	BDL	**2695**	**5146**
SEA 2	BDL	**181**	70
SEA 2A	BDL	**155**	98
SEA 6	BDL	**158**	107
SEA 6A	BDL	**11060**	**6549**
QR1	BDL	**70**	**391**
QR2	BDL	**67**	**394**
QR3	BDL	**72**	**418**
190 Seep	BDL	**326**	161
Leachate at the Breakout	BDL	**1309**	156
HDOW 5	BDL	**543**	213
HDOW 6	BDL	**109**	202
HDOW 7A	BDL	**107**	210
HDOW 7B	BDL	**145**	**601**
HDOW 8	BDL	**2094**	231
HDOW 9A	**45.42**	**187**	269
HDOW 9B	BDL	**1761**	**624**
HDOW 9C	BDL	**1412**	**483**
HDOW 12	BDL	**1376**	**486**
HDOW 13	BDL	**3444**	**609**
HDOW 14	BDL	**2692**	**1176**

*BDL = below detection limit

*Bold indicates above drinking water standard

As mentioned in section 3.3.1, digested samples were prepared by adding 5 mL of 10 M nitric acid to samples as collected. Because acid was added to the samples, these metal concentrations cannot accurately be compared to drinking water standards or Groundwater 3 (GW-3) standards defined by the MassDEP in section 2.1. It was noted that the digested samples had overall higher metal concentrations. This increase in concentrations can be attributed to the inclusion of the particulate phase in these measurements, whereas the dissolved samples only measured the concentrations in the aqueous phase. The digested samples displayed concentrations higher than GW-3 standards for lead in 9 groundwater wells and 1 surface water sample (QR 2 at the river). Since the dissolved sample did not show a high concentration at QR 2, this area may not be of immediate concern. However, QR 2 should continue to be monitored since it is a surface water sample. Only one digested sample showed a concentration of cadmium higher than the GW-3 standard. One sample showed concentrations higher than the GW-3 standard for arsenic and there are no current GW-3 standards defined for manganese and iron (see Appendix B for metals concentrations).

Table 9: Metal Concentrations for Digested Samples

Well ID	As (ppb)	Pb (ppb)	Cd (ppb)
SEA 1	BDL	BDL	BDL
SEA 2	7.049	**90.25**	BDL
SEA 2A	BDL	BDL	**8.403**
SEA 6	55.86	**21.78**	BDL
SEA 6A	676.8	7.267	BDL
QR1	BDL	BDL	BDL
QR2	BDL	**36.42**	BDL
QR3	BDL	BDL	BDL
190 Seep	BDL	BDL	BDL
Leachate at the Breakout	86.28	6.979	BDL
HDOW 5	82.59	**13.96**	BDL
HDOW 6	BDL	6.48	BDL
HDOW 7A	BDL	BDL	BDL
HDOW 7B	14.79	**10.07**	BDL
HDOW 8	177.7	9.465	BDL
HDOW 9A	720.4	**14.29**	BDL
HDOW 9B	187.6	**11.64**	BDL
HDOW 9C	177.0	**16.05**	BDL
HDOW 12	105.5	BDL	BDL
HDOW 13	**1084**	**33.64**	BDL
HDOW 14	41.12	**35.55**	BDL

*BDL = below detection limit

*Bold indicates above GW-3 standard

The inorganic anion concentrations for dissolved samples were determined using an ion chromatograph, and these results are presented in Table 10. These results indicate that fluoride, chloride, and sulfate are present at almost all of the sampling sites, with the majority having higher concentrations of chloride and sulfate than fluoride. The U.S. EPA has defined secondary standards for fluoride, chloride, and sulfate in drinking water are 2 ppm, 250 ppm, and 250 ppm, respectively (U.S. EPA, 2011d). No samples had concentrations of fluoride and sulfate above their defined secondary standards (see Appendix B). The concentrations displayed in Table 10 show that two samples, SEA 1 and HDOW 9A, has chloride concentrations higher than the secondary standard. No other samples were above the secondary limit for chloride. As mentioned, secondary standards are not enforced guidelines and do not indicate a health risk but rather may cause cosmetic effects (U.S. EPA, 2011d). The EPA defines a Maximum Contaminant Level (MCL) for nitrate in drinking water at 10 ppm (U.S. EPA, 2011d). All samples tested indicate concentrations below this standard. The U.S. EPA has not defined MCLs or secondary standards for pure bromide and phosphate.

Table 10: Inorganic Anion Concentrations for Dissolved Samples

Well ID	Chloride (ppm)	Fluoride (ppm)	Sulfate (ppm)	Bromide (ppm)	Nitrate (ppm)	Phosphate (ppm)	Total (ppm)
SEA 1	**570.72**	0.05	7.33	0.31	0.67	0.00	579.08
SEA 2	76.62	0.18	11.20	0.00	1.37	0.00	89.37
SEA 2A	76.84	0.17	11.74	0.00	0.28	0.00	89.02
SEA 6	1.80	0.06	1.37	0.00	0.13	0.00	3.36
SEA 6A	1.50	0.03	5.78	0.43	0.50	0.00	8.24
QR1	20.55	0.07	7.45	0.00	0.32	0.00	28.39
QR2	20.87	0.07	7.40	0.00	0.33	0.40	29.06
QR3	23.11	0.07	7.37	0.00	0.34	0.00	30.89
190 Seep	214.97	0.13	9.08	0.23	1.53	0.00	225.93
Leachate at the breakout	40.70	0.07	6.63	0.21	0.00	0.00	47.61
HDOW 5	1.15	0.85	7.49	0.00	0.00	0.00	9.49
HDOW 6	3.29	1.16	0.00	0.00	0.00	0.00	4.45
HDOW 7A	1.31	0.07	1.43	0.00	0.39	0.00	3.20
HDOW 7B	0.00	1.50	0.06	0.00	0.00	0.24	1.80
HDOW 8	12.00	0.18	3.19	0.00	0.00	0.00	15.38
HDOW 9A	**258.33**	0.17	0.61	1.00	0.00	0.00	260.11
HDOW 9B	27.08	0.04	1.25	0.00	0.00	0.00	28.39
HDOW 9C	41.83	0.04	0.71	0.00	1.84	0.00	44.42
HDOW 12	5.23	0.11	2.06	0.00	0.19	0.00	7.59
HDOW 13	10.23	0.14	3.15	0.00	0.00	0.00	13.52
HDOW 14	97.57	0.21	5.88	0.14	0.13	0.00	103.92

4.3 Geographical Analysis

The groundwater wells with the highest digested arsenic concentrations were found to be on gradient A on Figure 6. Gradient A shows the groundwater flow pattern at the Holden landfill site. The water flows in the northwest direction towards the Quinapoxet River (SEA, 1986). As seen on this map, the groundwater well HDOW 13 is closest to the river. Of the 21 samples tested, the groundwater in HDOW 9A had the highest concentration of dissolved arsenic (45.42

ppb). The two wells that had the highest digested lead concentrations were SEA 2A and QR2. SEA 2A is located far from the river; however, QR2 is a river sample.

Color coded maps for each parameter are shown in Appendix B. Each parameter was divided into appropriate ranges, where each range was assigned a color. The sample ID numbers were highlighted according to the color that represented the value of the sample. These maps allowed observations about pH, temperature, DO, and ORP to be made in relation to the geographical location of the sampling. As previously mentioned, the pH ranged from 6.15 to 8.30. Samples with pH values towards the higher side of this range (8.30) were along the Quinapoxet River as well as in HDOW 9A and 9B. The majority of the other pH values were close to 7. The samples with the lowest values (around 6.15) were observed to be the groundwater wells furthest from the Quinapoxet River including SEA 1,SEA 2A, SEA 6, SEA 6A and HDOW 5.

The dissolved oxygen concentrations of the surface water samples, including the Quinapoxet River, were the highest (>10 mg/L). This was expected since the water was exposed to the atmosphere. The dissolved oxygen concentrations of the groundwater samples were low (<2 mg/L) since the water was not directly exposed to the atmosphere.

The most positive oxidation reduction potentials were found to be near the river, in the 190 seep and HDOW 9C samples. The most negative oxidation reduction potentials were found to be at HDOW 8, HDOW 12, SEA 1, SEA 2, and SEA 6A.

4.4 Statistical Analysis

The data from the groundwater wells and river samples was statistically analyzed to determine correlations and differences. Table 11 and Table 12 show the results of a correlation analysis conducted in Microsoft Excel between all of the physical parameters, metal concentrations, and inorganic anion concentrations. Calculated correlation coefficients were compared to critical correlation values. A table of the correlation values and the critical correlation values can be found in Appendix B.

There was a positive correlation between depth to the bottom of the well and two other parameters, pH and ORP. There was also a positive correlation between depth to the groundwater table in a well and the two parameters, pH and ORP.

The temperature of the samples did not correlate with any of the parameters or the metal concentrations present in the wells. All of the temperatures were within a 4°C range. None of the digested samples showed a correlation to the physical and chemical water quality parameters (DO, pH, ORP, temperature, specific conductivity). The dissolved samples indicated a positive correlation between the metal concentrations of arsenic, lead, cadmium, and iron and specific conductivity. Out of the 21 samples measured, 20, 21, 21, and 5 samples indicated concentrations lower than the lowest standard used for arsenic, lead, cadmium, and iron, respectively. This indicates that metal concentrations were potentially instrument background noise, and the correlation may not be valid.

To determine if there were differences in water quality based on location, the landfill was divided into three regions and an analysis of variance (ANOVA) was conducted. Region 1 was near the river west of the landfill. Region 2 was over the landfill. Region 3 was east of the landfill. The sample sites in region 1 were QR1, QR2, QR3, 190 Seep, HDOW 12, HDOW 13, HDOW 14, and leachate at the breakout. The sample sites in region 2 are HDOW 9A, B, C, HDOW 5, and HDOW 8. The sample sites in region 3 are SEA1, SEA 2, 2A, SEA 6, 6A, HDOW 6, and HDOW 7A, B. ORP and bromide were found to be significantly different among the three regions. Of the 21 samples, bromide was detected in 5 samples. All of the other parameters, metal concentrations, and inorganic anion results were not significantly different for the three regions.

Table 11: Correlation Analysis between Parameters and Metal Concentrations

	Depth to Water	Depth to Well	Temp.	Specific Conduct-ivity	DO	pH	ORP	As (Diss.)	Pb (Diss.)	Cd (Diss.)	Fe (Diss.)	Mn (Diss.)
Depth to Water	1											
Depth to Well	**+Y**	1										
Temperature	N	N	1									
Specific Conduct.	N	N	N	1								
DO	N	N	N	N	1							
pH	**+Y**	**+Y**	N	N	**+Y**	1						
ORP	**+Y**	**+Y**	N	N	**+Y**	**+Y**	1					
As (Dissolved)	**+Y**	**+Y**	N	**+Y**	N	**+Y**	N	1				
Pb (Dissolved)	N	N	N	**+Y**	N	N	N	N	1			
Cd (Dissolved)	N	N	N	**+Y**	N	N	**-Y**	N	**+Y**	1		
Fe (Dissolved)	N	N	N	**+Y**	N	N	**-Y**	N	**+Y**	**+Y**	1	
Mn (Dissolved)	N	N	N	N	N	N	N	N	N	N	**+Y**	1
As (Digested)	N	N	N	N	N	N	N	**+Y**	N	N	N	**+Y**
Pb (Digested)	N	N	N	N	N	N	N	N	N	N	N	N
Cd (Digested)	N	N	N	N	N	N	N	N	N	N	N	N
Fe (Digested)	N	N	N	N	N	N	N	N	N	N	N	**+Y**
Mn (Digested)	N	N	N	N	N	N	N	N	N	N	**+Y**	**+Y**
Fluoride	N	N	N	N	N	N	N	N	N	N	N	N
Chloride	N	N	N	**+Y**	N	N	N	N	**+Y**	**+Y**	**+Y**	N
Sulfate	N	**-Y**	N	N	N	N	N	N	N	N	N	N
Bromide	**+Y**	**+Y**	N	N	N	**+Y**	N	**+Y**	N	N	N	N
Nitrate	**+Y**	N	N	N	N	N	N	**-Y**	N	N	N	N
Phosphate	N	N	N	N	N	N	N	N	N	N	N	N
Total ions	N	N	N	**+Y**	N	N	N	N	**+Y**	**+Y**	**+Y**	N
Turbidity	N	N	N	N	N	N	N	N	N	N	**+Y**	**+Y**

*Y indicates a statistically valid correlation, + positive correlation, - negative correlation

Table 12: Correlation Analysis Continued

	As (Dig.)	Pb (Dig.)	Cd (Dig.)	Fe (Dig.)	Mn (Dig.)	Fluoride	Chloride	Sulfate	Bromide	Nitrate	Phosphate	Total
As (Digested)	1											
Pb (Digested)	N	1										
Cd (Digested)	N	N	1									
Fe (Digested)	**+Y**	N	N	1								
Mn(Digested)	**+Y**	N	N	**+Y**	1							
Fluoride	N	N	N	N	N	1						
Chloride	N	N	N	N	N	N	1					
Sulfate	N	N	**+Y**	N	N	N	N	1				
Bromide	**+Y**	N	N	N	N	N	N	**-Y**	1			
Nitrate	N	N	N	N	N	N	N	N	N	1		
Phosphate	N	N	N	N	N	N	N	N	N	N	1	
Total	N	N	N	N	N	N	**+Y**	N	N	N	N	1
Turbidity	**+Y**	N	N	**+Y**	**+Y**	N	N	N	N	N	N	N

*Y indicates a statistically valid correlation, + positive correlation, - negative correlation

4.5 Natural vs. Anthropogenic Sources of Arsenic at the Former Holden Landfill

It was evaluated whether the arsenic at the landfill is from natural or anthropogenic sources. For the source to be natural, the first condition (see section 2.3.3) is that there can be no past or present anthropogenic sources of arsenic at the site (Nelson et al., 2007). A landfill qualifies as an anthropogenic source of arsenic; therefore, this condition was not met at the former Holden landfill site. The landfill was capped in 1988. Capping is a remedial strategy that is designed to prevent metal leaching from the capping area. Even with a cap it is possible for arsenic to seep through the bottom of a landfill and into the surrounding area if the landfill waste is in contact with groundwater. At the former Holden landfill, only one well sampled contained a high concentration of dissolved arsenic (0.045 mg/L). It is possible that arsenic could have leached from the landfill to this well. It is also possible that the arsenic originated from natural sources; however since there is a known former anthropogenic source of arsenic onsite, this cannot be confirmed.

The second condition for the source to be natural is that the soil and or bedrock at the site contain arsenic-bearing minerals or weathering products (Nelson et al., 2007). According to the subsurface maps provided in the comprehensive site assessment scope of work for the Holden site, the soil below the landfill area was classified as fine medium sand, fine coarse sand, sand and gravel, and fine sand trace silt (CEA, 2011). To conclude if the soil or bedrock in the area contains arsenic-bearing minerals, it is necessary to perform soil borings and conduct soil tests. Without data about the concentrations of arsenic in the soil and bedrock in the area, the second condition cannot be confirmed.

The third condition to confirm a natural arsenic source is that the geochemical parameters in the aquifer must be favorable for dissolution of arsenic-bearing minerals and mobilization of arsenic into groundwater (Nelson et al., 2007). Under reducing conditions arsenite, is more mobile than arsenate. Reducing conditions include low dissolved oxygen and oxidation-reduction potential and a pH<9.0. At the site examined by Nelson et al. (2007), the highest average arsenic concentrations were detected under reducing conditions with less than 1.2 mg/L of dissolved oxygen, and pH between 7.0 and 8.0.

Most of the pH values at the former Holden landfill site were relatively neutral (6.15 to 8.3) but not between 7.0 and 8.0. Therefore, samples with pH values in the range of 6.8 to 8.2 were also included under the definition of reducing conditions for the landfill. Under this new criteria, four wells contained all three criteria ($6.8<pH<8.2$, $DO<1.2$mg/L, and negative ORP). The wells were HDOW 7B, 8, 12, and 13. Table 13 indicates when a sample had a pH, DO, or ORP within the specified range, indicating which samples favored reducing conditions. As shown in this table, conditions to promote the leaching of arsenic-bearing minerals are present at the landfill site. This could not be used as proof that the source of the arsenic is natural; however, natural arsenic could be mobilized if it is present.

Based on Nelson et al. (2007), there are three conditions required to conclude that arsenic comes completely from natural sources at a site. There is a former landfill at the site, which qualifies as a former source of arsenic. There was not enough evidence to say with certainty that the arsenic present came entirely from anthropogenic sources. However, it is likely that at least some of the arsenic detected was of anthropogenic origin.

Table 13: Reducing Conditions Geochemistry at Holden Site

Well ID	6.8<pH<8.2	DO<1.2 mg/L	ORP<0 mV
SEA 1		▨	▨
SEA 2			▨
SEA 2A			▨
SEA 6			▨
SEA 6A			▨
QR1	▨		
QR2	▨		
QR3	▨		
190 Seep	▨		
Leachate at the Breakout			
HDOW 5		▨	
HDOW 6	▨		
HDOW 7A	▨		▨
HDOW 7B	▨	▨	▨
HDOW 8	▨	▨	▨
HDOW 9A	▨		▨
HDOW 9B			
HDOW 9C	▨		
HDOW 12	▨	▨	▨
HDOW 13	▨	▨	▨
HDOW 14		▨	▨

*Gray shaded boxes indicate measurement within the specified range

Nelson et al. (2007) presents the theory that reducing conditions are favorable for arsenic dissolution from soil into groundwater. Four of the groundwater wells at the former Holden landfill were consistent with reducing conditions. Although the geochemistry may be favorable for leaching of arsenic, only one well (HDOW 9A) showed a concentration of dissolved arsenic higher than drinking water standard (0.045 mg/L). Concentrations of digested arsenic above the drinking water standard (0.015 to 1.084 mg/L) were observed in 12 of the 21 wells. Since the concentrations of arsenic of the digested samples were significantly higher than the dissolved samples, it was indicated that the arsenic is principally contained in the particulate phase. It was not apparent why the arsenic has not leached from the particulate matter into the groundwater when the conditions appeared to be favorable for dissolution from soil to groundwater.

4.6 Results Conclusion

From the physical and chemical water quality tests conducted, only one well had an arsenic concentration over the U.S. EPA drinking water standard for the dissolved (or as collected) samples, and no dissolved samples had metal concentrations above GW-3 standards. The digested samples cannot accurately be compared to the U.S. EPA drinking water standards or GW-3 standards since they were not filtered to remove particulate matter prior to being acidified, however, these samples showed one arsenic concentration, ten lead concentrations, and one cadmium concentration higher than the GW-3 standard. Geographically, the samples collected near the river did not have any metal concentrations over the GW-3 standards, with the exception of one river sample (QR2) that had a lead concentration of 36.42 ppb (U.S. EPA standard is 15 ppb; GW-3 standard is 10 ppb). All other samples from the Quinapoxet River and other surface water samples did not have dissolved metal concentrations over the U.S. EPA drinking water or GW-3 standards.

Correlations were made between physical parameters and the depth to the water in the well and depth of the well. There was also a correlation between four of the five dissolved metals and specific conductivity. However since most samples were below detection limits for metals, correlations may not be valid. The metal concentrations for the digested samples were higher than the dissolved samples; this shows that the metal contaminants present are in the particulate phase and not in solution. If most of the metals are not leaching into the water, the remedial strategies that are applicable are affected. Based on these results, the team evaluated remedial strategies to address the one well with high dissolved arsenic and to prevent further leaching of metals from the landfill. These remedial alternatives are discussed in Chapter 5.

Chapter 5: Evaluation of Remedial Strategies

This study has shown that the landfill groundwater and surface water samples contained contamination which is primarily arsenic, principally in the particulate phase. There was one groundwater well that showed levels of dissolved arsenic higher than the drinking water standards. When the samples were digested, arsenic levels were detected in 12 of the groundwater wells and in one surface water source, the leachate seepage. A goal of this project was to determine the most cost effective and feasible remedial strategy to implement at the landfill site in order to reduce mobility and toxicity of the contamination. Remedial strategies that reduce arsenic mobility and toxicity were researched. To fully evaluate remedial strategies, soil testing data and determination of the arsenic forms contained in the sediment should be obtained. These data were not available at the time of this study.

In order to provide recommendations for remedial strategies based on current data, remedial strategies were compared. The remedial strategies were divided into three groups: no action, in situ treatment and ex situ treatment. Then, each strategy was ranked based on criteria as shown in Table 14. Cost was given a higher weight than other criteria because it was determined to be the most important factor by the sponsor of this project. The total weighted score is the sum of the ranking in each criterion multiplied by the weighting. The total possible weighted score is out of 35. Information on each of the remedial strategies is provided in the following sections. Each remedial strategy was evaluated based on current data and more research should be conducted before a remedial strategy is implemented.

5.1 No Action/Monitor

The data showed that only one groundwater well, HDOW 9A, contained a concentration of arsenic (45.42 ppb) higher than the U.S. EPA drinking water standard in the as collected (dissolved) sample. There are no buildings or private drinking water wells within 500 feet of this well (MassDEP, 2012). The surface waters in the area did not contain detectable concentrations of dissolved arsenic, manganese, lead, iron, or cadmium. This information suggested that there was little to no risk to humans or the environment at the present time. The no action/monitor option is the least expensive option since it does not cost any additional money to implement.

Although there were no detectable concentrations of dissolved metals in the surface waters, the leachate breakout area contained a high concentration of arsenic in the digested sample (86.28 ppb). Humans and animals are more likely to come in contact with surface water than groundwater. For this reason, further evaluation of the potential risks posed by contaminated media within the affected region should be performed to determine if restricting access to this area is warranted. This could be accomplished by constructing a fence around the leachate at the breakout area (the area on the site where the groundwater breaks through the surface).

The no action strategy has been used in other cases, such as the Clinton landfill. However, this strategy does not prevent or inhibit metal leaching. It also does not reduce the toxicity of contaminants. Monitoring is used to assess changes in metal concentrations over time.

If the contamination spreads or becomes harmful to humans or the environment, other strategies may be necessary.

5.2 In situ

In situ remediation by definition occurs on site. In situ remediation includes physical and chemical processes (Terrapex, 2009). Chemical processes, such as oxidation and solidification/stabilization/precipitation, are generally used to reduce the toxicity of metals or make them easier to remove by changing the metals from a liquid to a particulate phase. Physical processes include capping and filtration, and are used to remove contaminants or reduce their mobility. In the case of the former Holden landfill site, most of the arsenic is in the particulate phase, which is easier to remove by physical remediation strategies than dissolved arsenic. Chemical processes designed to convert arsenic to forms that are more easily removable from water are not effective when the arsenic is already in the particulate phase; therefore, physical processes are more relevant. As shown in Table 14, all of the physical in situ treatments, such as capping and filtration, outrank the chemical processes, such as oxidation and chemical in situ treatments.

5.2.1 Recapping

One of the highest rated in situ remediation techniques in Table 14 was recapping the landfill. Capping is a physical in situ treatment designed to reduce the mobility of contaminants. The landfill was capped in 1988. The cap was made of impermeable clay and was 12 inches thick (Appiah, 2011). The wells that were found to have high total arsenic (digested samples) in the groundwater near the landfill are outside of the capped zone (see Appendix A). This indicates that either high arsenic concentrations were present in the groundwater before the landfill was capped, the cap may have failed to prevent the leaching of arsenic from the landfill, or the arsenic is derived from some source other than the landfill. Recapping the landfill would be relatively inexpensive at $175,000/acre (FRTR, 2012), and would theoretically prevent further leaching of arsenic.

Some disadvantages to recapping the landfill are that it will not reduce the toxicity of the metals and it is not guaranteed to effectively prevent metal leaching. It does not address arsenic concentrations currently in groundwater and soil. If the current leaching of metals is not due to a failure in the cap, but due to naturally occurring arsenic leaching into the groundwater, then adding another cap may not prevent metal leaching. It may be feasible to make adjustments to the current cap in order to make it more effective.

5.2.2 Filtration

Filtration is a physical in situ treatment that involves physical separation of particles from a solution. Filtration could reduce the toxicity in the groundwater at the landfill site, because most of the contaminants are in the particulate phase and could be filtered out. However, most of the particulate phase contamination occurs in the groundwater compared to the surface water. Therefore, a pump and treat system would be needed to extract the groundwater, and the treated water would need to meet water quality standards of the water body into which it is discharged.

Filtration costs \$13.5-46.6/10,000 gallons water treated and could be used at the head of the tributary to treat the groundwater that is feeding the surface water if the particulate phase in the surface water becomes a problem (FRTR, 2012).

5.2.3 Other In Situ Techniques

Some other physical in situ techniques include the cutoff trench, interceptor drain, and permeable treatment wall methods. These methods can reduce the toxicity or mobility of the metals. Cutoff trenches and interceptor drains are not overly expensive, costing approximately \$540-750/m^2 and \$60-250/m, respectively (FRTR, 2012). Permeable treatment walls are among the most expensive treatments, costing \$1,267/m (FRTR, 2012). The cutoff trench could be effective in bringing the contaminants to the surface; however, an extra step of removing the collected contaminants would be required. Other considerations for installing a cutoff trench include the ownership of the property where the trench would be located, and future maintenance and monitoring requirements.

Chemical in situ processes have already been mentioned and are not recommended. The contaminants that are present are for the most part in the particulate phase and chemical treatments, such as oxidation or solidification/stabilization/precipitation, will not be effective. These techniques are usually used in situations with high dissolved levels of contaminants, or in cases where the contaminants are in the most toxic form and oxidation can reduce the toxicity of the compound. In situ chemical treatments are not recommended for this project.

5.3 Ex situ

Ex situ remediation involves removing contaminated soil or water from the site. The contaminated soil or water must be treated and disposed of properly. This can be accomplished by disposing of the soil or water off-site, onsite treatment, and reintegration to the subsurface.

5.3.1 Ion Exchange

Ion exchange is an ex situ separation technique. It is cost effective around \$3-8/10,000 gallons treated and is commercially available (FRTR, 2012). Ion exchange reduces the toxicity of the water because it removes the contaminant from the water. Once the resin reaches capacity, the resin needs to be regenerated and the regeneration water needs to be properly treated and disposed of. Ion exchange resins can be damaged by particles in the water. A potential solution to this problem would be to use a physical separation technique prior to ion exchange, such as filtration. As discussed earlier, filtration would be an effective remedial strategy for the former Holden landfill site since it was determined that most of the contamination was contained in the particulate matter. Therefore ion exchange may not be needed after filtration.

5.3.2 Soil Washing

Soil washing is an ex situ process that involves digging up soil, taking it off site for treatment and returning it to the site. This is a poor option for several reasons. First, it is a costly option at \$187/m^3 and possibly involving removing the existing cap (FRTR, 2012). Also, soil washing is a treatment for the soil. No soil tests have been performed at the former Holden landfill site; therefore, there are no data to support the need for this remediation method. The affected area is also very large, spanning 17 acres and most of it is wooded. Soil washing is not a feasible option because of the physical size and geography of the site.

Table 14: Evaluation of Remedial Strategies (1 = worst; 5 = best)

Remedial Strategy	Type	Criteria (Weight)						
		Cost (x2)	Long-term Effectiveness (x1)	Commercial Availability (x1)	Reduce Mobility Metals (x1)	Reduce Toxicity (x1)	Site specific Implementation (x1)	Total weighted score
No Action/Monitor	None	5	1	5	1	1	5	23
Recapping	In situ	4	2	5	4	2	4	25
Filtration	In situ	3	3	4	4	4	3	24
Solidification/Stabilization /Precipitation	In situ	2	2	4	2	2	2	16
Interceptor Drain	In situ	4	3	3	3	4	3	24
Cut Off Trench	In situ	3	3	3	3	4	3	22
Permeable Treatment Wall	In situ	3	3	3	3	4	3	22
Chemical Treatment	In situ	1	2	4	2	4	3	17
Oxidation	In situ	2	2	4	2	4	3	19
Soil Washing	Ex situ	2	4	4	3	3	1	19
Ion Exchange	Ex situ	3	4	4	4	4	3	25

Chapter 6: Conclusions and Recommendations

This section summarizes the conclusions made in this project, as well as presents recommendations for future work.

6.1 Conclusions

The objective of this project was to gather data on metals at the Former River Street Sanitary Landfill in Holden, MA, and to evaluate remedial strategies to reduce metal mobility at this site. Samples were collected from 21 groundwater wells and surface water locations on and near the landfill.

Only one well at the former Holden landfill (the landfill) had a concentration of dissolved arsenic over the drinking water standard (HDOW 9A). This well did not contain arsenic concentrations above the GW-3 standard, however, so it is not of high concern. Twelve water samples contained digested arsenic concentrations above the drinking water standard and one of them was above the GW-3 standard. However, the arsenic will most likely stay in the particulate phase in the natural environment. None of the surface waters contained dissolved concentrations of arsenic above the detection limit (0.005 mg/L). The leachate at the breakout contained digested arsenic above the drinking water standard but below the GW-3 standard. There is a small possibility for the leachate to be harmful because it is at the surface and humans could come in contact with is. This possibility could be reduced by prohibiting access to the leachate breakout from the general public.

Eleven remedial strategies were evaluated on their cost, commercial availability, ability to reduce toxicity, ability to reduce mobility and the ability to implement them at the landfill site. There are few contaminants dissolved in the groundwater, therefore, chemical treatments were not strongly considered, because physical treatment processes would be more effective in removing contamination. Most of the contamination occurred in the groundwater and in locations that are not accessible to humans. There are no drinking water sources within 500 feet of the contaminated groundwater wells and by the time the water reaches the Quinapoxet River, the concentrations are below the drinking water standards for both digested and dissolved arsenic. Therefore, the no action/monitor option is feasible, and is the best option based on its low cost.

6.2 Recommendations

Based on the findings of this project, we recommend the no action/monitor remedial strategy as the best available option at this time. The data showed that none of the samples collected at the former Holden landfill contained dissolved concentrations of arsenic above the GW-3 standard. Only one groundwater well contained a concentration of arsenic above the U.S. EPA drinking water standard. At the time of collection, this well was not a drinking water source nor was it within 500 feet of a drinking water source; therefore it does not currently pose a threat to human health.

We recommend that the potential risks posed by contaminated media in the area directly around the leachate at the breakout be further evaluated to determine if restricting access by humans and most animals to this area is warranted. Only one surface water sample, the leachate at the breakout area, contained a detectable concentration of digested arsenic (86 ppb). This concentration of arsenic is not known to be harmful to human health. This breakout is in a small area and can be enclosed easily and cost effectively.

We recommend that filtration, recapping, interceptor drains and ion exchange also be considered as viable remedial strategies to be implemented. Twelve samples obtained from the landfill site contained concentrations of digested arsenic above the U.S. EPA drinking water standard. One groundwater well contained a higher concentration than the GW-3 standard. It has been noted that there are no standards for digested (unfiltered) water samples because natural groundwaters and surface waters do not come in contact with strong acids and the existing standards are based on filtered samples. The removal of the arsenic in the particulate phase could be achieved by physical separation techniques. Chemical treatments are usually used to make dissolved contaminants easier to remove.

We recommend that soil samples be collected from the landfill site because soil testing can provide useful information for further study of the site. The focus of this project was groundwater and surface water samples, which are useful in determining the contaminants present and their dissolved concentrations in water, as well as the chemical properties of the water. Soil samples are useful in other ways. Soil borings can provide information about the bedrock and soil type, which could help determine whether there are high concentrations of natural arsenic, or other metals, in the area. Soil samples may also provide more information about where the metals are leaching from and whether or not the concentration of arsenic in the soil itself is of concern.

We recommend that further testing be performed at future sampling dates to determine the specific arsenic compounds present and to obtain accurate DO readings for every groundwater well at the landfill site. The toxicity of arsenic present at the site can be better understood with speciation data on arsenic. Dissolved oxygen has been identified as a potential indicator of conditions favorable for the leaching of arsenic.

Chapter 7: References

AchaWater. *What is filtration and water filter purifiers.* Retrieved 12/9/2011 from http://www.achawater.com/water-filters-purifiers.html

Agency for Toxic Substances and Disease Registry (ATSDR). *Public Health Assessment Guidance Manual. Chapter 6: Exposure Evaluation: Evaluating Exposure Pathways.* November 30, 2005. Retrieved 2/8/2012 from http://www.atsdr.cdc.gov/hac/phamanual/ch6.html

Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological profile for Arsenic*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. 2007.

American Ground Water Trust. *Public Information Pamphlet #10 Bacteria and Water Wells.* 2008. Retrieved 2/14/2012 from http://www.agwt.org/info/bacteria.htm

American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). Standard Methods for the Examination of Water and Wastewater. (19th edition). September 1995. Washington, DC: APHA

Atekwana, E. A., Atekwana, E. A., Rowe, R. S., Werkema, D. D. Jr., Legall, F. D.. *The Relationship of Total Dissolved Solids Measurements To Bulk Electrical Conductivity in an Aquifer Contaminated with Hydrocarbon.* April 14, 2003. Retrieved 2/7/2012 from http://www.epa.gov/esd/cmb/pdf/JAG-TDSpublished.pdf

Ayotte, J. D., Nielsen, M. G., Robinson, J., Gilpin R. & Moore, R. B. *Relation of arsenic, iron, and manganese in ground water to aquifer type, bedrock lithogeochemisty, and land use in the new england coastal basins.* Retrieved 9/5/2011 from http://pubs.usgs.gov/wri/wri994162/pdf/3introduction.pdf

Burger, K., Carpenter, P., Chan, K., Finch, M., Muniz-Ghazi, H., Oudiz, D., Shaddy, K., Sotelo, J. *Proven Technologies and Remedies Guidance: Remediation of Metals in Soil*. Department of Toxic Substances Control California Environmental Protection Agency. N.p. Retrieved 12/9/2011 from http://www.dtsc.ca.gov/PublicationsForms/upload/Guidance_Remediation-Soils.pdf.

Caniylmaz, S. *Arsenic removal from groundwater by fe-mn oxidation and microfiltration* 2003. Retrieved 12/5/2011 from http://d-scholarship.pitt.edu/9748/1/Caniyilmaz.Sevil_Dec2005.pdf

Chasteen, T. *Atomic Absorption Spectroscopy*. Sam Houston State University. N.p. 2000. Retrieved 9/20/2011from http://www.shsu.edu/~chm_tgc/primers/pdf/AAS.pdf.

Chemistry Explained. *Lead, chemical element - overview, discovery and naming, physical properties, chemical properties, occurrence in nature, isotopes.* Retrieved 9/17/2011 from http://www.chemistryexplained.com/elements/L-P/Lead.html

Colter, A. and Mahler, R.L. *Iron in drinking water*. Pacific Northwest Extension Publication, Retrieved 9/26/2011 from http://www.cals.uidaho.edu/edComm/pdf/pnw/pnw589.pdf

Corporate Environmental Advisors, Inc. (CEA). *Comprehensive Site Assessment Scope of Work: Former River Street Sanitary Landfill.* September 1, 2011. West Boylston, MA.

Dickhaut, M. R. Correspondence to Ms. Lynne Welsh 09 Aug. 2011. Re: Town of Clinton-South Meadow Road Landfill. Department of Environmental Protection 627 Main Street Worcester, MA, 01608

Dvorak, B. *Drinking water treatment: sediment filtration.* 2008. Retrieved 12/4/2011 from http://www.ianrpubs.unl.edu/live/g1492/build/g1492.pdf

EarthTech. *Slurry Trench Cut-Off Walls*. Retrieved 12/5/2011 from http://www.earthtech.net/commercial/services_solutions_slurrytrench.php

ENVCO Environmental Equipment. *Dip sampler*. Retrieved 09/10/2011 from http://www.envco.co.nz/catalog/product/liquid-samplers/dip-sampler.html

ENVCO Environmental Equipment. *Kemmerer bottles.* Retrieved 9/13/2011 from http://www.envcoglobal.com/catalog/water/water/limnology/water-quality-sampling/water-sampling-bottle/surface-water-sampling/ke

ENVCO Environmental Equipment. *Van dorn bottle samplers.* Retrieved 9/13/2011 from http://www.envcoglobal.com/catalog/water/water/limnology/water-quality-sampling/water-sampling-bottle/surface-water-sampling/va

Evanko, C. and Dzombak, D.. *Remediation of Metals-Contaminated Soils and Groundwater*. Technology Evaluation Report. Groundwater Remediation Technologies Analysis Center, Retrieved 9/27/2011 from http://www.clu-in.org/download/toolkit/metals.pdf

Federal Remediation Technologies Roundtable (FRTR). *Remediation Technologies Screening Matrix and Reference Guide, Version 4.0.* Retrieved 2/8/2012 from http://www.frtr.gov/matrix2/section1/toc.html

Gehle, K. M. *ATSDR Case studies in environmental medicine: Arsenic toxicity*. Retrieved 9/6/2011 from http://www.atsdr.cdc.gov/csem/arsenic/docs/arsenic.pdf

Gentry, A. *Cut-off trench helps prevent water seepage*. Retrieved 12/5/2011 from http://www2.ljworld.com/news/2005/jan/25/cutoff_trench_helps/

Greenfacts. *Scientific Facts on Arsenic*. Retrieved 9/5/2011 from http://www.greenfacts.org/en/arsenic/l-3/arsenic-2.htm

Herbal Life Product. *Manganese.* Retrieved 10/08/2011 from http://herballifeproduct.net/index.php/dietary-minerals/manganese

Illinois Department of Public Health. *Cadmium*. Environmental Health Fact Sheet. Retrieved 9/12/2011. http://www.idph.state.il.us/envhealth/factsheets/cadmium.htm

Intertek. *Thermogravimetric analysis.* Retrieved 9/25/2011 from http://www.intertek.com/analysis/thermogravimetric/

Kneas, K. *Operating Instructions for the use of the PE AAnalyst 300 Atomic Absorption Spectrophotometer*. Elizabethtown College Department of Chemistry. N.p., Retrieved 9/20/2011 from http://users.etown.edu/k/kneask/Instrument Operating Procedures_files/PE_AA.pdf.

Lenntech (2011a). *Arsenic (As) and water.* Retrieved 9/7/2011 from http://www.lenntech.com/periodic/water/arsenic/arsenic-and-water.htm

Lenntech (2011b). *Arsenic (As) –Chemical properties, health and environmental effects*. Retrieved 9/6/2011 from http://www.lenntech.com/periodic/elements/as.htm

Lenntech (2011c). *Arsenic in groundwater*. Retrieved 9/6/2011 from http://www.lenntech.com/groundwater/arsenic.htm

Lenntech (2011d). *Cadmium (Cd) - Chemical properties, health and environmental effects.* Retrieved 9/17/2011 from http://www.lenntech.com/periodic/elements/cd.htm

Lenntech (2011e). *Iron (Fe) - chemical properties, health and environmental effects.* Retrieved 9/6/2011 from http://www.lenntech.com/periodic/elements/fe.htm

Lenntech (2011f). *Lead (Pb) - Chemical properties, health and environmental effects.* Retrieved 9/17/2011 from http://www.lenntech.com/periodic/elements/pb.htm

Lenntech (2011g). Manganese (Mn) *–Chemical properties, health and environmental effects.* Retrieved 9/17/2011 from http://www.lenntech.com/periodic/elements/mn.htm

Lowry, R. W., & Dickman, D. *Oxidation reduction potential explained : ORP.* Retrieved 9/25/2011 from http://www.rhtubs.com/ORP.htm

Ma, G. and Wilson, G. *Flame Atomic Absorption Spectrometry*. Environmental Sampling & Monitoring Primer. N.p., Retrieved 9/20/2011 from http://www.cee.vt.edu/ewr/environmental/teach/smprimer/aa/aa.html

Massachusetts Department of Environmental Protection (MassDEP) Bureau of Waste Site Cleanup and Office of Research and Standards. *Background Documentation for the Development of the MCP Numerical Standards.* April 1994.

Massachusetts Department of Environmental Protection (MassDEP). *MCP Numerical Standards*. Retrieved 11/20/2011 from http://www.mass.gov/dep/cleanup/laws/standard.htm.

McLean, J. E., & Bledsoe, B. E. *Ground water issue: Behavior of metals in soil.* No. EPA/540/S 92/018) U.S. EPA.

Middle Tennessee State University (MSTU). *Correlation Values for Pearson.* Retrieved 1/28/2012 from http://frank.mtsu.edu/~dkfuller/tables/correlationtable.pdf

Na, L., Maohong, F., Johannes, V. L., Basudec, S., Honqun, Y., Huang, C.P. *Oxidation of As(III) by potassium permanganate.* January 2007.

Nelson, J. R., Batchelder, G. L., Radville, M. E., Albert, S. A., 2007, *Proceedings of the Annual International Conference on Soils, Sediment, Water and Energy,* Using Multiple Lines Of Evidence To Demonstrate That Elevated Arsenic Groundwater Concentrations Are Naturally Occurring, *Volume 12*, Article 7.

Nielsen, M. G., & Robinson, G. R. J. *Abstract 50336:Relation of Arsenic Concentrations in Ground Water to Bedrock Lithology in Eastern New England.* Retrieved 9/5/2011 from http://www.geosociety.org/absindex/annual/1998/50336.htm

Occupational Safety & Health Administration (OSHA). *Arsenic.* Retrieved 9/14/2011 from http://www.osha.gov/SLTC/arsenic/index.html

OriGen. *Toxic effects of Arsenic*. August 2000. Retrieved 11/14/2011 from http://www.origen.net/tox.html.

Peryea, F. J. *Historical use of lead arsenate insecticides, resulting soil contamination and implications for soil remediation*. TreeFruit Soil & Nutrition. N.p., Retrieved 9/5/2011 from http://soils.tfrec.wsu.edu/leadhistory.htm.

Podsen, D. W. Correspondence to Ms. D. Lynne Welsh. 09 Sep. 2011 (2011a). Clinton Landfill South Meadow Road. Massachusetts Department of Environmental Protection 627 Main Street Worcester, MA, 01608

Podsen, D. W. Correspondence to Ms. D. Lynne Welsh. 29 Nov. 2011 (2011b). Clinton Landfill South Meadow Road. Massachusetts Department of Environmental Protection 627 Main Street Worcester, MA, 01608

Podsen, D. W. Correspondence to Mr. Michael Penny. 13 Jan. 2012. Clinton Landfill South Meadow Road. Massachusetts Department of Environmental Protection 627 Main Street Worcester, MA, 01608

Regan, J. J. Correspondence to Michael Ward. 16 January 2009. CAAA Permit. Central Regional Office, Worcester, MA.

Scheffer F., and Schachtschabel, P. Lehrbuch der Bodenkunde. *Oxides and Hydroxides.* 1989. Enke Verlag, Stuttgart. Retrieved 9/18/2011 from http://www.soils.wisc.edu/courses/SS325/oxides.htm#mn

SEA Consultants Inc.. *Hydrogeologic Investigation and Design of Closure*. September 1986. Cambridge, MA.

Sever, M. *Arsenic leaching into water from soil.* Geotimes. Retrieved 9/4/2011 from http://www.agiweb.org/geotimes/feb06/NN_arsenicleaching.html

Siemens Water Technologies. *Arsenic removal from groundwater.* Retrieved 12/9/2011, from http://www.water.siemens.com/en/applications/groundwater_remediation/arsenic-removal/Pages/default.aspx

Stockton College. *Contaminant Transport Modeling.* Retrieved 2/8/2012 from http://www.stockton.edu/~epsteinc/webber/contrans.htm

Suwandana, E., Kawamura, K., & Soeyanto, E. (2011). *Assessment of the heavy metals and nutrients status in the seawater, sediment and seagrass in banten bay, indonesia and their distributional patterns*. Journal of Fisheries International, *6*(1), 18.

Tech Brief. *A national drinking water clearinghouse fact sheet.* Retrieved 12/9/2011 from http://www.nesc.wvu.edu/pdf/dw/publications/ontap/2009_tb/filtration_DWFSOM51.pdf

Terrapex Environmental Ltd. *In-Situ/Ex-Situ Remediation.* 2009. Retrieved 1/24/2012 from http://www.terrapex.com/in-situ-ex-situ-remediation.asp

Tissue, B. *Atomic-Absorption Spectroscopy (AA).* The Chemistry Hypermedia Project. N.p., 2000. Retrieved 9/20/2011 from http://www.files.chem.vt.edu/chem-ed/spec/atomic/aa.html.

Town of Plymouth: Environmental Management Division. *Surface Water Sampling Standard Operating Procedure.* January 2006. Retrieved 2/7/2012 from http://www.plymouth-ma.gov/Public_Documents/PlymouthMA_EnvironManage/Surface%20Water%20Sampling_Plymouth_appF.pdf

University of Minnesota Soil Testing Laboratory *Recommended Chemical Soil Test Procedures for the North Central Region.* Retrieved 9/12/2011 from http://soiltest.cfans.umn.edu/methods.htm

U.S. Environmental Protection Agency (2011a). *Arsenic rule.* Retrieved 9/11/2011 from http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations.cfm

U.S. Environmental Protection Agency (2011b). *Basic Information about Arsenic in Drinking Water.* Retrieved 10/10/2011 from http://water.epa.gov/drink/contaminants/basicinformation/arsenic.cfm

U.S. Environmental Protection Agency (2011c). *Compliance.* Retrieved 10/3/2011 from http://www.epa.gov/nrmrl/wswrd/dw/arsenic/compliance.html

U.S. Environmental Protection Agency (2011d). *Drinking Water Contaminants.* Retrieved 10/3/2011 from http://water.epa.gov/drink/contaminants/index.cfm

U.S. Environmental Protection Agency (2011e). *Drinking Water Health Advisory for Manganese.* EPA-822-R-04-003 Retrieved on 10/3/11 from http://www.epa.gov/ogwdw/ccl/pdfs/reg_determine1/support_cc1_magnese_dwreport.pdf

U.S. Environmental Protection Agency (2011f). *Region 9 surface water sampling general.* Retrieved 9/10/2011 from http://www.epa.gov/region6/qa/qadevtools/mod5_sops/surface_water_sampling/general/r9surface-wtr-sampling.pdf

U.S. Environmental Protection Agency. *Standard Operating Procedure: Soil Sampling*. Emergency Response Team. U.S. EPA Contract 68-C4-0022. February 18, 2000. Retrieved 9/7/2011 from http://www.epa.gov/region6/qa/qadevtools/mod5_sops/soil_sampling/ertsop2012-soil.pdf

U.S. Environmental Protection Agency (2011g). *Waste Disposal.* April 15. 2011. Retrieved 2/11/2012 from http://www.epa.gov/region7/waste/solidwaste/waste_disposal.htm#federal_regs

U.S. Environmental Protection Agency. *Wastes-Non-Hazarsous Waste-Municipal Solid Waste.* February 10, 2012. Retrieved 2/11/2012 from http://www.epa.gov/osw/nonhaz/municipal/

U.S Geological Survey (USGS). “Cacodylic acid-other pesticide”. Retrieved 9/12/2011 from http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=02&map=m8017

U.S. Navy. Naval Facilities Engineering Command. *Permeable Reactive Barriers (Treatment walls).* Retrieved 12/6/2011 from http://portal.navfac.navy.mil/portal/page/portal/NAVFAC/NAVFAC_WW_PP/NAVFAC_NFESC_PP/ENVIRONMENTAL/ERB/PRB

Vaajasaari, K. *Anthropogenic arsenic sources*. Risk Assessment and Risk Management Procedure for Arsenic in the Tampere Region. N.p., Retrieved 9/5/2011 from http://projects.gtk.fi/ramas/research/anthropogenic.html.

Washington State Department of Ecology (2011a). *Groundwater Interceptor Drains.* Retrieved 9/22/2011 from http://www.ecy.wa.gov/programs/sea/pubs/95-107/groundwater.html

Washington State Department of Ecology (2011b). *Sampling and Testing for Residential Lead Abatement*. Retrieved 9/12/2011 from http://www.ecy.wa.gov/programs/hwtr/demodebris/pages2/leadsample.html#Soil

Weiss, J., & Weiss, T. *Handbook of ion chromatography* Wiley-VCH. Retrieved 9/10/2011 from http://onlinelibrary.wiley.com/doi/10.1002/9783527619610.fmatter/pdf

Welch, A.H., Westjohn, D.B., Helsel, D.R., and Wanty, R.B., 2000, *Arsenic in ground water of the United States-- occurrence and geochemistry: Ground Water* 38 (4): 589-604.

Welsh, D. L. Correpondence to Christopher McGown 22 Jul. 2011. Clinton Landfill South Meadow Road. Town of Clinton Landfill 242 Church Street Clinton, MA, 01510

Zerowaste. *Landfills: Hazardous to the Environment*. Retrieved 2/11/2012 from http://www.zerowasteamerica.org/Landfills.htm

Appendix A: Supplemental Background Information

Background research on sampling techniques and laboratory tests used are discussed in depth in this section. Although this project did not participate in soil sampling, the method is described below.

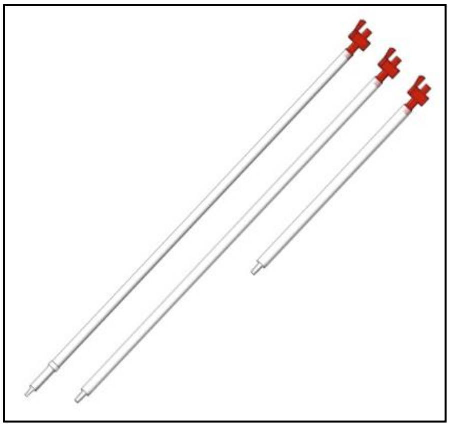
Water Sampling

Collecting and analyzing water samples is a necessary step in determining the type and extent of contamination in a body of water. In order to perform such an analysis it is necessary to collect, store, transport and test each sample in a safe, consistent method which will not bias the sample. There are many different situations in which water samples may be taken; therefore there are multiple techniques for sampling. The EPA has a Standard Operating Procedure (SOP) to ensure regardless of the method used it is used correctly and consistently evaluated. The EPA SOP applies to samples taken from streams, rivers, lakes, ponds, lagoons and surface impoundments, either at the surface or at any depth below the surface (U.S. EPA, 2011f).

Before a sample can be collected there are preparatory steps that must be taken. For safety reasons the site should be surveyed prior to sampling to ensure that the health and safety of all those involved can be assured. Permission to sample should be obtained well in advance and a schedule should be coordinated with staff, clients, and the regulatory agency. Plastic stakes, flags, or buoys should be used to mark all of the proposed sampling locations. Prior to sampling, appropriate equipment must be obtained, in working order and properly cleaned to prevent contamination. Some of the most common methods for collecting water samples are the direct method, the dip sampler method and the discrete depth sample method (U.S. EPA, 2011f).

The direct method uses sample collection bottles to collect surface water samples. Pre-preserved sample bottles may not be used as collection bottles in the direct method because the preservative may be diluted while collecting a sample. In the direct method, the collector uses appropriate means to access the sampling location including a small boat, pier, or by wading. Wading is only acceptable in small streams with noticeable currents. Samples must be taken upstream. In the direct method the collector submerges the closed collection bottle, opens the bottle under water and allows water to fill the bottle. The collector then closes the bottle under the surface of the water. This is the preferred method of surface sampling if it is safe to do so. The collector directly interacts with the water to be tested in the direct method. For this reason, any samples that must be taken in an area where contact with contaminants is a concern cannot be taken using the direct method (U.S. EPA, 2011f).

In the dip sampler method the collector uses a long transparent tube with valves on each end called a dip sampler (see below). There are two ways to sample using a dip sampler. If an all-layer sample is required the dip sampler must be lowered into the water with the bottom valve opened, allowing water from all layers to flow into the sampler. The valve must then be closed and the dip sampler withdrawn from the water. The contents of the dip sampler can then be removed into a storage bottle or container. If a target sample is required the only difference in procedure is that the sampler is lowered into the water with the valve closed. The valve is then opened at the desired depth until water fills the dip sampler and then the valve is closed (ENVCO Dip sampler, 2011).



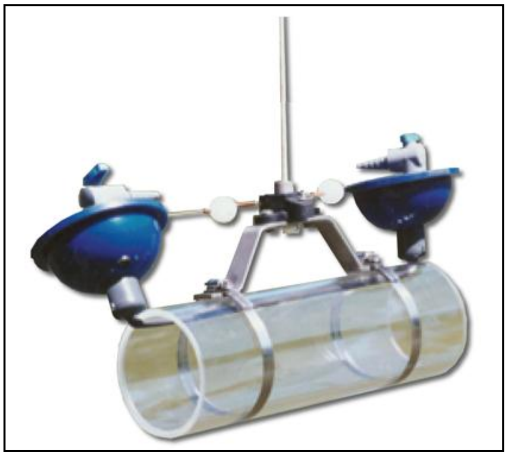
Dip sampler, long transparent tubes with two valves (ENVCO Dip Sampler, 2011)

Kemmerer and Van Dorn samplers are both types of discrete depth samplers (U.S. EPA 2011f). Kemmerer samplers are collection cylinders usually made of metal, such as stainless steel, brass, or plastic. Two rubber stoppers are placed on the sampler one on each side of the tube. The cylinder is oriented vertically when lowered into the water (U.S. EPA, 2011f). An example of a Kemmerer sampler can be seen below.

Kemmerer sampler (ENVCO VanDorn, 2011)

Van Dorn samplers are also cylinders with two stoppers on the ends, usually made of plastic. The difference between Van Dorn and Kemmerer samplers is that Van Dorn samplers are oriented in the horizontal direction (U.S. EPA, 2011f). An example of a Van Dorn bottle can be found below. The procedure for the discrete depth sample method is the same for both Kemmerer and Van Dorn samplers. The sampler is lowered with the ends open to allow water to flow in. When the sampler reaches the desired depth a messenger is sent down via a rope to close the ends. The sampler is then withdrawn from the water. Water is removed via a valve on the sampler; however the first 10 to 20 mL should be disposed of to clear the valve of contamination.

Attachments are also available to transfer samples to dissolved oxygen bottles (U.S. EPA, 2011f).



Van Dorn sampler (ENVCO VanDorn, 2011)

Other common water sampling instruments include peristaltic pumps to take samples of water columns, and storm water samplers for collecting storm water.

Soil Sampling

Consistent soil sampling procedures are necessary to ensure accurate and viable results for soil testing. Tools typically used for collecting soil samples are spades, shovels and trowels (Washington State Department of Ecology, 2011b). The best practice is to designate different tools for each type of sample that is being collected. If this is not possible, the tools must to be cleaned before each collection (U.S. EPA, 2000). After each use, the tools should be cleaned, decontaminated and wrapped in Aluminum foil (Washington State Department of Ecology, 2011b).

Soil testing methods require multiple samples that are processed before tests can be completed. For soil sampling, it is necessary to determine how many samples are needed for the testing and divide them up appropriately. For soil sampling, stainless steel or plastic tools are used to prevent contamination of the samples (University of Minnesota, 1988, Washington State Department of Ecology, 2011b). It is especially important to avoid galvanized containers, cast iron mortars, rubber stoppers and brass screens (University of Minnesota, 1988). For best preservation, the sample should be mixed in the bucket to ensure it is homogenous within the container (Washington State Department of Ecology, 2011b). The samples should be labeled and numbered (University of Minnesota, 1988). A designated control sample should also be labeled (University of Minnesota, 1988). Typically samples need to be dried overnight under a heating element and a fan to keep moisture low (University of Minnesota, 1988).

Common Metal Laboratory Tests

This section explores common laboratory tests that were utilized in analyzing samples.

Atomic Absorption Spectroscopy

One of the most common methods for determining the metals present in a collected sample and the concentrations of those metals is Atomic Absorption Spectroscopy (AAS). AAS (Figure 7) has been used to identify elements since the 1950s (Ma, 1997).

Atomic Absorption Spectroscopy Machine (Tissue, 2000)

Each element has a unique electron configuration and produces a unique line spectrum. In the AAS, the element is atomized and sent through a flame where the atoms are excited, causing these atoms to advance to higher orbitals. Each element absorbs light at specific wavelengths while in this excited state. An element can be identified by looking at the specific wavelengths produced by each sample when a beam of light is shone on this atomized element. The concentration of the metal can be determined by measuring the amount of light absorbed by the sample and using Beer-Lambert Law. Beer-Lambert Law is an equation that represents the linear relationship between absorption and concentration (Tissue, 2000).

$$A = a_{\lambda} \times b \times c$$

A is measured absorbance, a_{λ} is an absorptivity coefficient, b is the path length and c is the wanted concentration (Tissue, 2000).

The different parts of the AAS are the hollow cathode lamp, nebulizer, flame, monochromator, and photomultiplier tube (PMT). The hollow cathode lamp is used to produce a beam of light. This beam of light shines on the atoms and excited the atom. This lamp can be tuned so it will produce a specific wavelength to detect a specific metal. The nebulizer is used to make the sample into an aerosol. It is also where the element, fuel (usually acetylene), and oxidant (air or nitrous oxide) are mixed together. The flame is used to get rid of ions, break down the element and excite the element. The monochromator is tuned to pick up wavelengths of the element of interest and the PMT identifies the intensity of the wavelengths omitted (Chasteen, 2000).

AAS requires a large amount of energy to fuel the flame and power the machine. In order to eliminate wasted energy a blank with the desired material can be run through before the actual experiment to determine the wavelength of this material. The correct hollow cathode lamp must be installed for the metal going to be analyzed (Kneas, 2009).

Ion Chromatography

Ion chromatography is a form of liquid chromatography that can be used for water analysis. Ion chromatography is able to measure the concentrations of major cations and major anions in water samples. Samples are loaded into the ion chromatograph and run through a pressurized column where they are absorbed. After the sample is absorbed by the tower an ion extraction liquid called eluent is passed through the column to absorb and separate the ions. The ion concentrations in the sample are determined by the retention time of different species (Weiss et al. 2011).

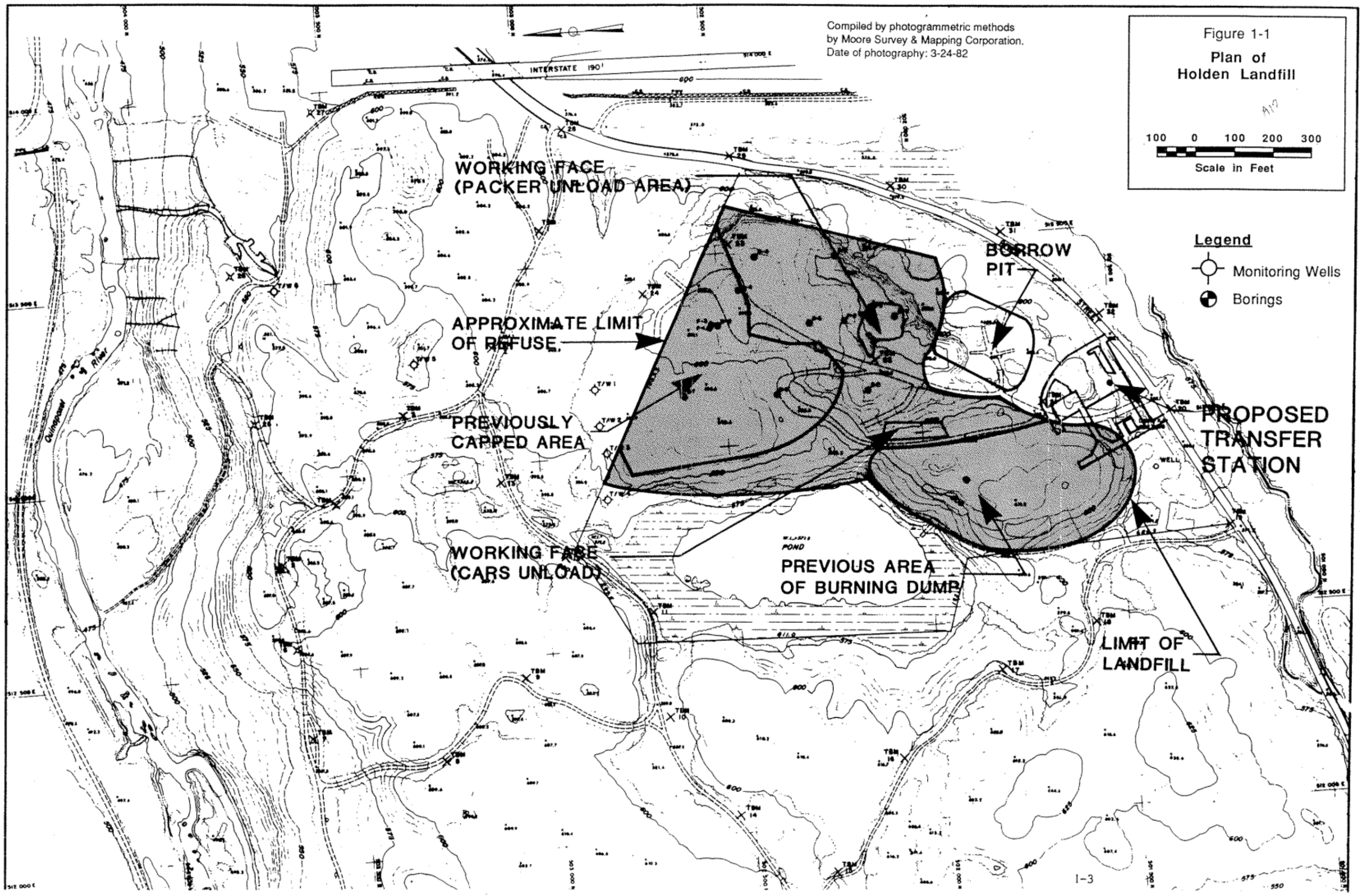
Oxidation Reduction Potential

Oxidation Reduction Potential (ORP) is a measurement of the electrical potential of an oxidation-reduction, or redox, reaction. ORP demonstrates the quantity of oxidation (adding of oxygen to form an oxide) and reduction (removing of oxygen) that is possible under certain conditions. An ORP meter consists of an electrode with a metal half-cell for measuring, and a reference half-cell. When the electrode is inserted into a sample containing oxidizing or reducing agents a voltage is generated by the transfer of electrons across the measuring surface. Most pH meters have a millivolt setting that can be used to measure ORP (Lowry et al., 2011).

Thermogravimetric Analysis

Thermogravimetric analyzers (TGA) have many different applications. TGA analyzers heat samples to cause physical changes in material or force reactions. TGA measures change in mass due to decomposition, dehydration or oxidation of a sample with temperature or time. TGA can be used to determine the moisture content of soil samples by measuring the change in mass due to dehydration of the sample (Intertek, 2011).

Map of former Holden landfill (CEA, 2011)



*Gray shaded area indicates former landfill area. Note this is a similar map to Figure 6 but indicates the landfill area.

Appendix B: Additional Physical and Chemical Water Quality Results

Metals Concentrations

These tables represent output data from the AA for various metal concentrations. None of these concentrations were found to be higher than both the U.S. EPA drinking water standards of the GW-3 standards defined by the MassDEP. If the metal concentration of the sample is less than the standard solution used then the concentration cannot be accurately detected. Therefore negative concentrations could be attributed to potential background noise of the instrument. As noted in Table 8 and Table 9, concentrations lower than the lowest standard used were "Below Detection Limit." The following two tables show all concentrations as reported by the AA for the dissolved and digested samples, respectively.

Well ID	Dissolved				
	As (ppb)	Pb (ppb)	Cd (ppb)	Fe (ppm)	Mn (ppm)
SEA 1	0.226	3.335	2.6	**5.146**	**2.695**
SEA 2	0.161	0.103	0.822	0.07	**0.181**
SEA 2A	0.763	0.267	0.361	0.098	**0.155**
SEA 6	1.746	0.167	0.158	0.107	**0.158**
SEA 6A	-0.297	0.131	-0.013	**6.549**	**11.06**
QR1	1.093	0.36	0.076	**0.391**	**0.07**
QR2	1.286	0.291	0.038	**0.394**	**0.067**
QR3	1.366	0.398	-0.065	**0.418**	**0.072**
190 Seep	0.791	0.65	0.082	0.161	**0.326**
Leachate at the breakout	0.228	0.2	0.13	0.156	**1.309**
HDOW 5	4.019	0.13	-0.002	0.213	**0.543**
HDOW 6	-0.318	0.126	-0.021	0.202	**0.109**
HDOW 7A	1.418	0.119	0.189	0.21	**0.107**
HDOW 7B	3.048	0.393	0.069	**0.601**	**0.145**
HDOW 8	0.804	0.001	0.067	0.231	**2.094**
HDOW 9A	**45.42**	1.758	0.243	0.269	**0.187**
HDOW 9B	1.325	0.175	-0.029	**0.624**	**1.761**
HDOW 9C	0.178	0.099	0.263	**0.483**	**1.412**
HDOW 12	0.88	-0.027	-0.036	**0.486**	**1.376**
HDOW 13	1.314	0.066	0.032	**0.609**	**3.444**
HDOW 14	0.236	0.08	0.171	**1.176**	**2.692**

*Bold indicates concentrations higher than drinking water standards

Well ID	Digested				
	As (ppb)	Pb (ppb)	Cd (ppb)	Fe (ppm)	Mn (ppm)
SEA 1	2.281	3.332	3.261	12.53	2.44
SEA 2	7.049	**90.25**	1.591	9.872	0.282
SEA 2A	2.201	3.426	**8.403**	3.187	0.215
SEA 6	55.86	**21.78**	0.553	19.78	0.372
SEA 6A	676.8	7.267	0.053	64.21	10.65
QR1	0.221	4.83	0.347	0.643	0.161
QR2	-0.661	**36.42**	0.995	0.713	0.171
QR3	-0.648	2.555	0.633	0.567	0.17
190 Seep	-0.048	3.939	0.475	0.238	0.367
Leachate at the breakout	86.28	6.979	0.622	13.42	1.314
HDOW 5	82.59	**13.96**	0.844	12.71	0.718
HDOW 6	4.872	6.48	0.412	2.775	0.207
HDOW 7A	4.967	3.382	0.476	2.15	0.191
HDOW 7B	14.79	**10.07**	0.278	4.993	0.207
HDOW 8	177.7	9.465	0.518	19.17	2.11
HDOW 9A	720.4	**14.29**	0.905	20.37	0.297
HDOW 9B	187.6	**11.64**	0.535	45.29	2.453
HDOW 9C	177.6	**16.05**	0.732	39.08	1.505
HDOW 12	105.5	2.946	0.336	10.71	1.395
HDOW 13	**1084**	**33.64**	0.358	86.56	4.62
HDOW 14	41.12	**35.55**	1.347	10.94	2.578

*****Bold indicates concentrations higher than GW-3 standards

Colors of Samples

These pictures show the 21 samples collected at the former Holden landfill and allow for a visible representation of their color.

SEA 1, SEA 2, SEA 2A, SEA 6, SEA 6A

QR1, QR2, QR3, QR3 B (190 Seep), Leachate at the breakout

HDOW 5, HDOW 6, HDOW 7A, HDOW 7B, HDOW 8

HDOW 9A, HDOW 9B, HDOW 9C, HDOW 12, HDOW 13, HDOW 14

Geographical Analysis Maps

These maps include a color code that depicts a range for each parameter. The maps were used to determine if there was a visible trend in different regions or locations around the landfill that had similar values of a specific parameter of interest.

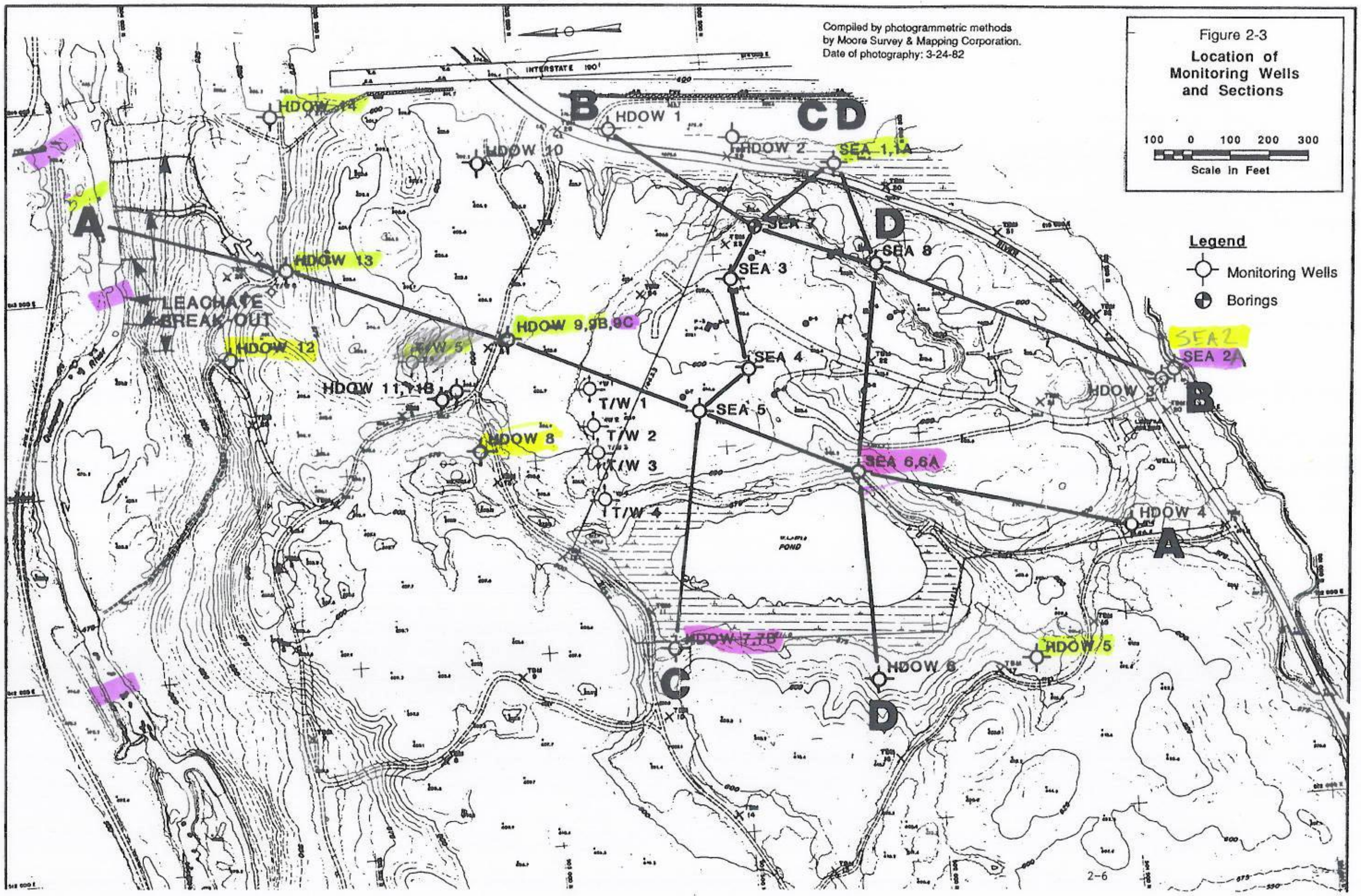
Temperature

10 - 11 🟨

11.01 - 12 🟩

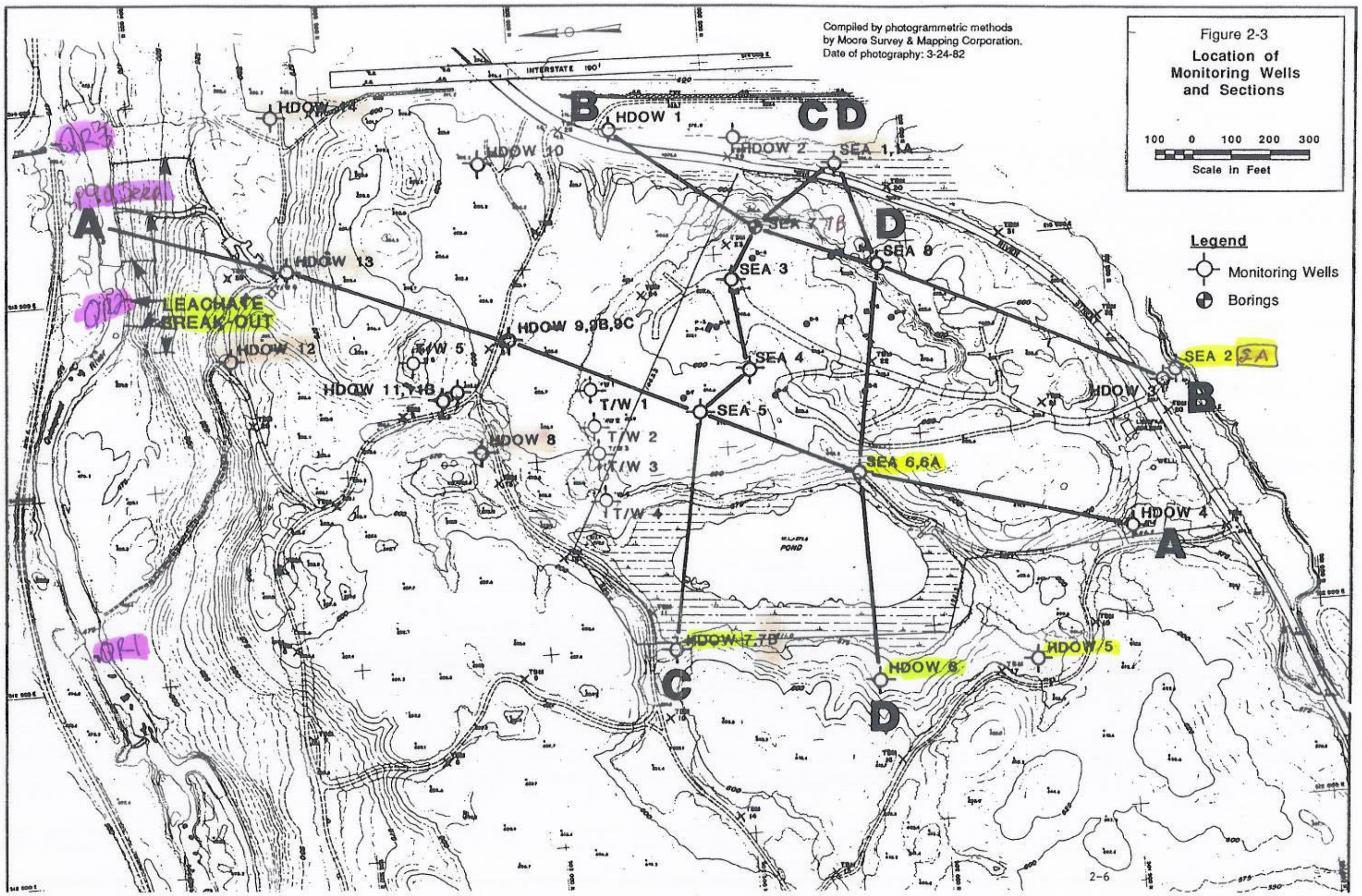
12.01 - 13 🟪

13.01 - 14 🟪



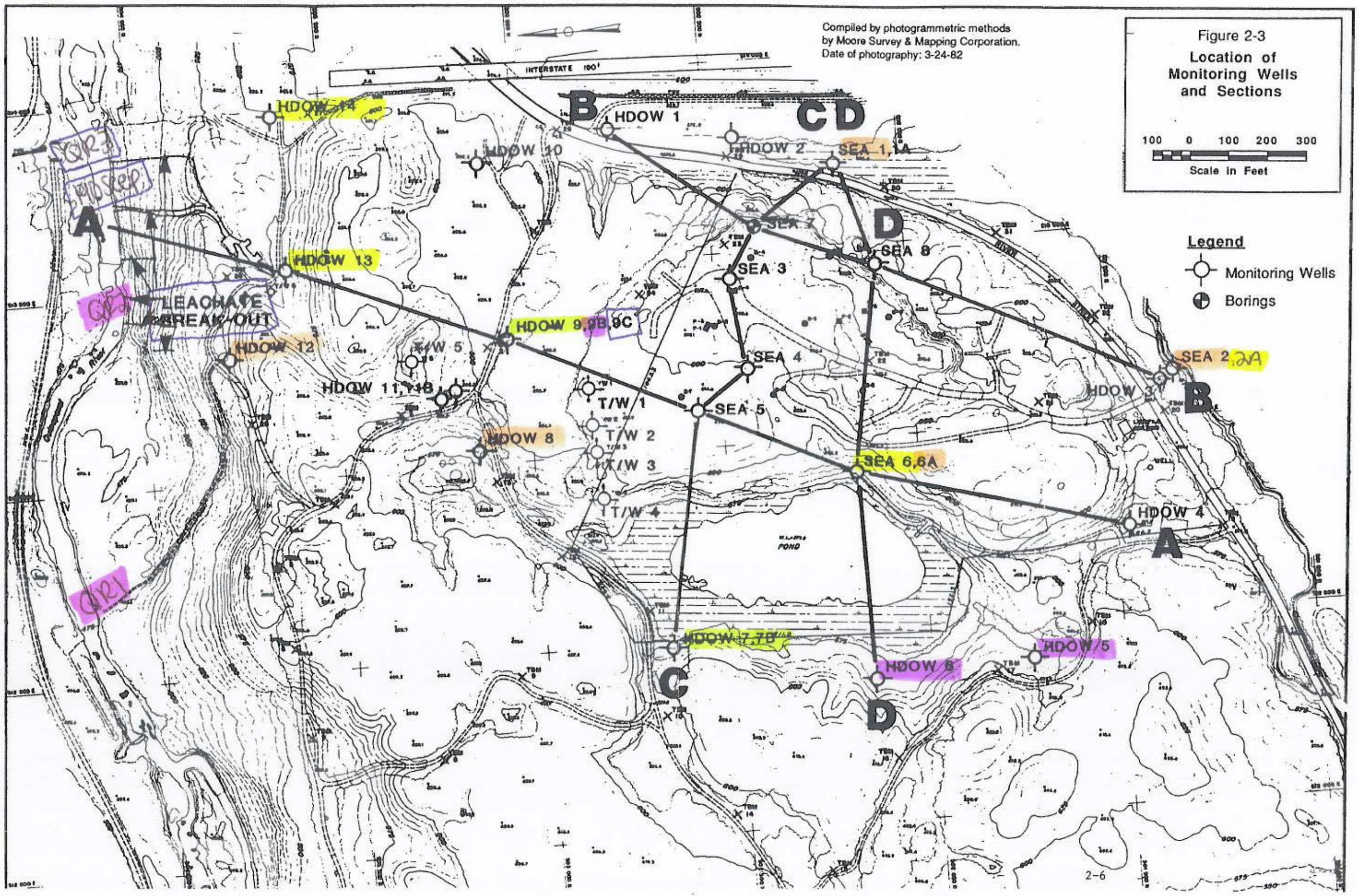
Dissolved Oxygen

🟫 0.3-1
🟨 1-2
🟩 2-3.07
🟪 7-9
🟪 9-10.8



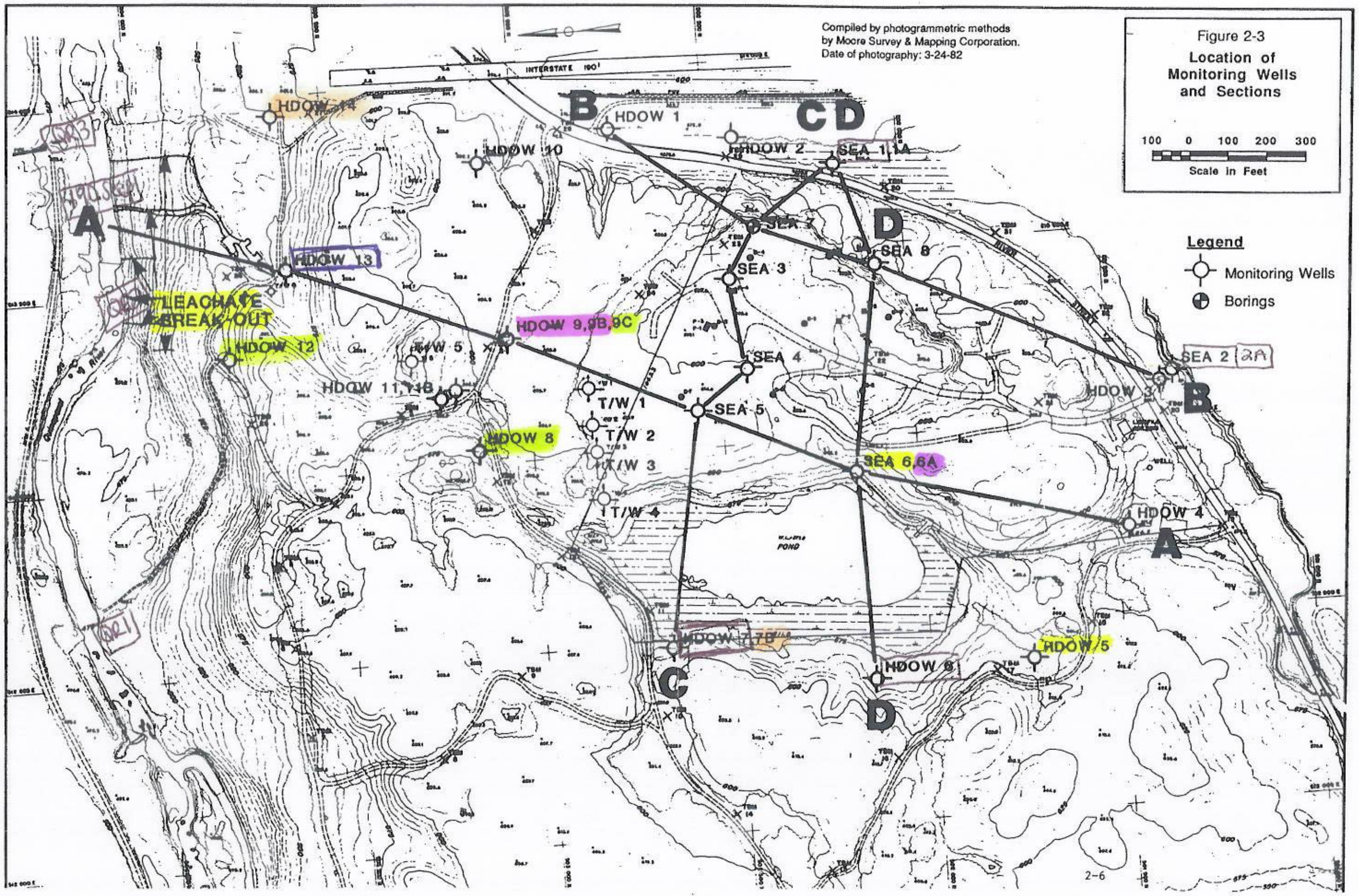
ORP

🟧 less than -50 MV
🟨 -50 to -25 MV
🟩 -25 to 0 MV
🟪 0 to 25 MV
🟪 25 to 50 MV
🟦 over 50 MV



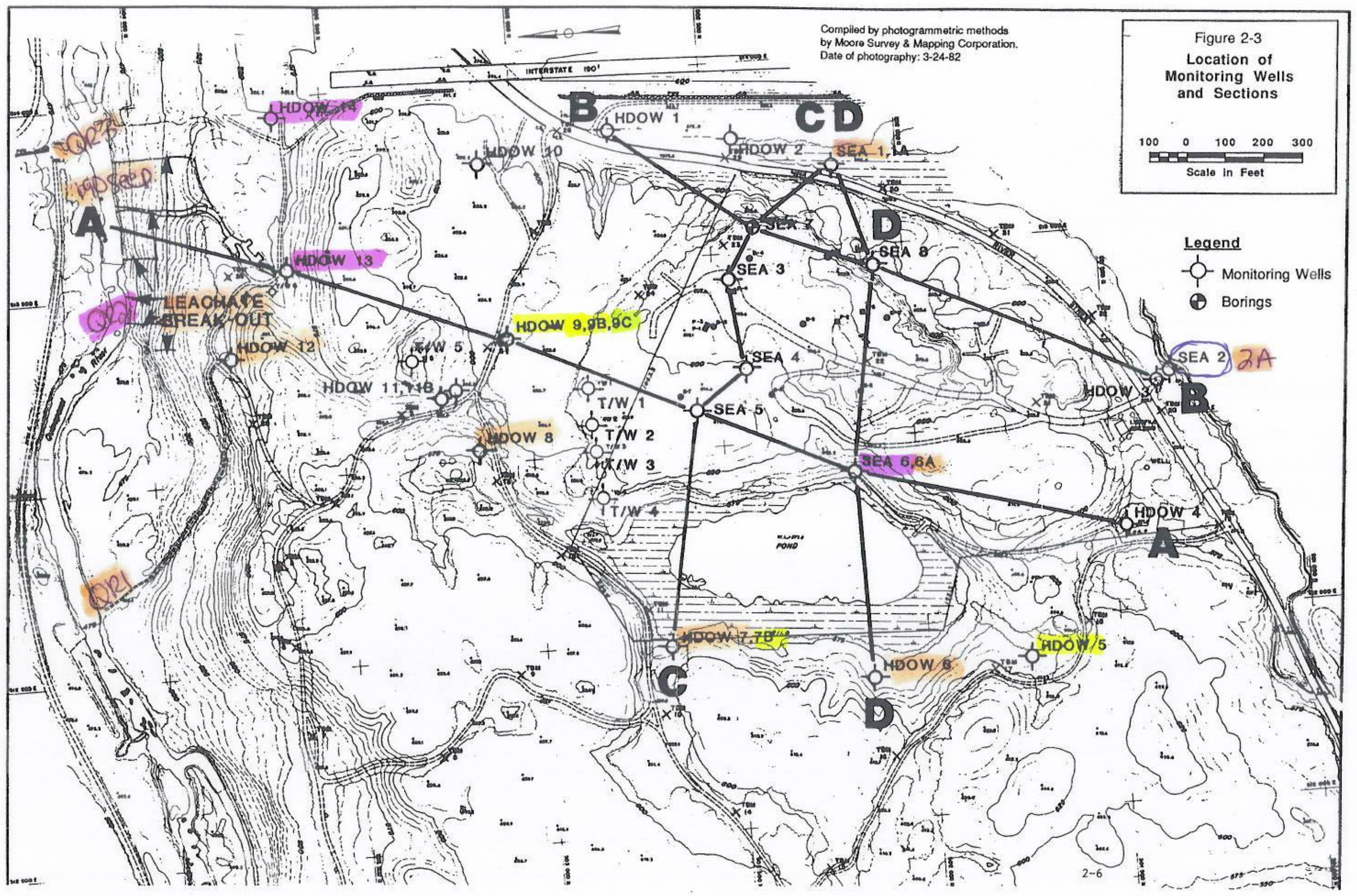
Digested
Arsenic

- 🟪 Below 10 ppb
- 🟧 10-50 ppb
- 🟨 50-100 ppb
- 🟩 100-200 ppb
- 🟪 600-700 ppb
- 🟪 700-800 ppb
- 🟦 over 1000 ppb



Digested
Lead

🟧 under 10 ppb
🟨 10-15 ppb
🟩 15-20 ppb
🟪 20-30 ppb
🟪 30-40 ppb
🟦 over 40 ppb



Compiled by photogrammetric methods
by Moore Survey & Mapping Corporation.
Date of photography: 3-24-82

Figure 2-3
Location of Monitoring Wells and Sections

Statistical Analysis

This section provides the statistical analysis output used to determine if correlations existed between various parameters.

Table of critical correlation values for comparison of correlation values (MSTU, 2012)

	# of Samples	*Critical Correlation Value*
Temp	21	0.413
Specific Conductivity	21	0.413
DO	18	0.444
pH	21	0.413
ORP	21	0.413
As (Diss)	21	0.413
Pb (Diss)	21	0.413
Cd (Diss)	21	0.413
Fe (Diss)	21	0.413
Mn (Diss)	21	0.413
As (Dig)	21	0.413
Pb (Dig)	21	0.413
Cd (Dig)	21	0.413
Fe (Dig)	21	0.413
Mn (Dig)	21	0.413
Fluoride	21	0.414
Chloride	20	0.423
Sulfate	20	0.423
Bromide	6	0.707
Nitrate	13	0.514
Phosphate	2	(Not enough samples)
Total ions	21	0.413
Turbidity	21	0.413

The following three tables present statistical values between parameters. The critical correlation values in the table above were used to determine if a correlation does exist.

	Depth to Water	*Depth to Well*	*Temp*	*Specific Cond.*	*DO*	*pH*	*ORP*
Depth to Water	1.000						
Depth to Well	0.854	1.000					
Temp	-0.094	0.000	1.000				
Specific Conductivity	0.350	0.103	-0.320	1.000			
DO	0.779	0.675	0.139	-0.150	1.000		
pH	0.723	0.853	-0.084	0.037	0.714	1.000	
ORP	0.599	0.640	0.195	-0.249	0.770	0.457	1.000
As (Diss)	0.528	0.608	-0.157	0.522	-0.002	0.436	0.006
Pb (Diss)	0.129	-0.003	-0.119	0.856	-0.057	0.088	-0.326
Cd (Diss)	-0.143	-0.337	-0.165	0.659	-0.242	-0.225	-0.536
Fe (Diss)	-0.076	-0.345	0.247	0.413	-0.208	-0.259	-0.476
Mn (Diss)	-0.036	-0.298	0.192	0.126	-0.260	-0.286	-0.357
As (Dig)	0.208	0.033	-0.101	0.238	-0.221	0.114	-0.197
Pb (Dig)	-0.139	-0.174	-0.283	-0.090	-0.127	-0.041	-0.224
Cd (Dig)	-0.267	-0.423	-0.050	0.198	-0.190	-0.375	-0.301
Fe (Dig)	0.233	-0.076	-0.047	0.085	-0.192	-0.003	-0.216
Mn (Dig)	-0.021	-0.293	0.160	0.108	-0.256	-0.247	-0.348
Fluoride	-0.169	-0.152	0.196	-0.161	-0.302	-0.188	-0.007
Chloride	0.044	-0.093	-0.214	0.879	-0.121	-0.050	-0.335
Sulfate	-0.421	-0.694	-0.151	0.113	0.101	-0.332	0.024
Bromide	1.000	0.894	-0.152	0.521	0.122	0.897	-0.109
Nitrate	0.711	0.285	-0.157	0.276	0.243	0.009	0.349
Phosphate	0	0	-1.000	1.000	1.000	1.000	1.000
Total ions	0.055	-0.109	-0.246	0.878	-0.091	-0.047	-0.322
Turbidity	0.299	-0.015	0.135	0.074	-0.174	-0.068	-0.268

	As (Diss)	*Pb (Diss)*	*Cd (Diss)*	*Fe (Diss)*	*Mn (Diss)*	*As (Dig)*	*Pb (Dig)*	*Cd (Dig)*	*Fe (Dig)*	*Mn (Dig)*
Pb (Diss)	0.386	1.000								
Cd (Diss)	-0.027	0.834	1.000							
Fe (Diss)	-0.120	0.461	0.486	1.000						
Mn(Diss)	-0.154	-0.005	0.036	0.834	1.000					
As (Dig)	0.423	0.017	-0.167	0.266	0.544	1.000				
Pb (Dig)	-0.032	-0.189	0.103	-0.164	-0.069	0.070	1.000			
Cd (Dig)	-0.041	0.245	0.389	0.028	-0.142	-0.211	-0.034	1.000		
Fe (Dig)	0.009	-0.122	-0.103	0.377	0.677	0.850	0.115	-0.215	1.000	
Mn (Dig)	-0.153	-0.040	-0.001	0.791	0.992	0.616	-0.044	-0.163	0.758	1.000
Fluoride	-0.003	-0.107	-0.164	-0.169	-0.223	-0.152	-0.072	-0.111	-0.229	-0.229
Chloride	0.293	0.955	0.861	0.427	-0.008	-0.049	-0.091	0.308	-0.149	-0.047
Sulfate	-0.309	0.072	0.256	0.083	-0.037	-0.329	0.262	0.528	-0.344	-0.073
Bromide	0.945	0.330	-0.078	-0.061	-0.085	0.815	-0.093	-0.114	0.260	-0.074
Nitrate	-0.442	0.068	0.168	-0.068	-0.054	0.038	0.274	-0.123	0.209	-0.052
Phosphate	-1.000	-1.000	-1.000	-1.000	-1.000	-1.000	1.000	1.000	-1.000	-1.000
Total ions	0.282	0.944	0.863	0.428	0.007	-0.042	-0.073	0.329	-0.138	-0.032
Turbidity	-0.001	-0.124	-0.101	0.569	0.825	0.725	0.087	-0.206	0.905	0.869

	Fluoride	*Chloride*	*Sulfate*	*Bromide*	*Nitrate*	*Phosphate*	*Total ions*	*Turbidity*
Chloride	-0.168	1.000						
Sulfate	-0.177	0.175	1.000					
Bromide	0.153	0.153	-0.882	1.000				
Nitrate	-0.011	0.220	0.087	0.029	1.000			
Phosphate	-1.000	0	1.000	0	0	1.000		
Total ions	-0.209	1.000	0.232	0.142	0.224	1.000	1.000	
Turbidity	-0.242	-0.167	-0.270	0.223	0.108	-1.000	-0.150	1.000

Anova p-values significant values

	Anova P-value
Temp	0.065
Specific Conductivity	0.455
DO	0.106
pH	0.068
ORP	0.043
As (Diss)	0.167
Pb (Diss)	0.714
Cd (Diss)	0.229
Fe (Diss)	0.302
Mn (Diss)	0.855
As (Dig)	0.630
Pb (Dig)	0.912
Cd (Dig)	0.340
Fe (Dig)	0.607
Mn (Dig)	0.924
Fluoride	0.354
Chloride	0.786
Sulfate	0.230
Bromide	0.003
Nitrate	0.071
Phosphate	(not enough samples)
Total ions	0.871
Turbidity	0.435

A correlation analysis was done between CEA's digested data and WPI's digested data. Arsenic, lead, and manganese were statistically similar. For CEA and WPI's data both cadmium and iron were below the detectable limit for all the samples. CEA reported low values as being less than their lowest standard, whereas WPI reported output values from the AA. This affected the statistical correlation, which is shown in the table below.

CEA correlation with team's digested metal concentration data	
Metal contaminate	Correlation Value
Arsenic	0.80512
Lead	0.23
Cadmium	0.03976
Iron	0.90913
Manganese	0.99214

Cost of Remedial Strategies

Remedial Strategy	Cost
No Action	N/A
Recapping	$175,000/acre
Filtration	$ 13.5 -45.6/10,000 gallons treated
Solidification/Stabilization/Precipitation	$190 -330/m^3
Interceptor Drain	$60 – 250/m
Cut Off Trench	$540 -750/m^2
Permeable Treatment Wall	$1,267/m
Chemical Treatment	$1,582/m^3
Oxidation	$150/10,000 gallons treated
Soil Washing	$187/m^3
Ion Exchange	$3 – 8/10,000 gallons treated

*The cost was estimated based on values found by the Federal Remedial Technology Roundtable (FRTR, 2012). This only includes the cost of implementation and maintenance but does not include labor costs.