# GROUNDWATER REMEDIATION AT A FORMER OIL SERVICE SITE

A Record of Study

by

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Submitted to the Office of Graduate Studies of Texas A&M University in partial fulfillment of the requirements for the degree of

DOCTOR OF ENGINEERING

May 2005

Major Subject: Engineering
College of Engineering

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#### **ABSTRACT**

Groundwater Remediation at a Former Oil Service Site. (May 2005)

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As an intern with URS Corporation, I participated in several remediation and wastewater treatment projects during the year 2004. A groundwater remediation project was selected to present in this record of study for my Doctor of Engineering degree not only because I spent more time on it than any other project, but also because it represents the broadness and depth of a typical URS remediation project.

In this report, findings from previous environmental investigations were summarized and used for computer modeling and remediation strategy evaluation. Computer models were used to simulate site conditions and assist in remedy design for the site. Current pump-and-treat systems were evaluated by the model under various scenarios. Recommendations were made for the pump-and-treat system to control the contaminant plume.

Various remediation technologies were evaluated and compared for their applicability at the site. A combination of on-site remediation and downgradient plume control was chosen as the site remediation strategy. Treatability studies and additional modeling work are needed for the remediation system design and optimization.

## **DEDICATION**

This record of study is dedicated to my parents, for their love and support.

#### **ACKNOWLEDGEMENTS**

I made up my mind about four years ago to pursue the Doctor of Engineering degree at Texas A&M as an important step for my transition from academia to industries. When it reached the end of the program, I would say that this degree program prepared me very well to work effectively in industry. Thanks to my advisor, Dr. Timothy Kramer and other committee members, I benefited a lot from this program.

Internship with URS Corporation Houston office was a valuable experience for me. Mr. Ken Tyrell and Dr. Tie Li brought me in to this exciting organization. Mr. Pete Conwell serves as my internship supervisor. He showed me how to grow professionally in the consulting business. Dr. Chi-Chung Chang, Mr. John Leethem, Mr. Nish Vasavada, and other project managers gave me the opportunities to work on several exciting projects. They also provided me the inside views on project management, both technical problem-solving skills and management responsibilities.

Special thanks to Dr. Chi-Chung Chang, Mr. Wade Vinson, Mr. Erik Goldman and other team members of this groundwater remediation project. We had a lot of fun working together. While the author has been working on certain parts of the project such as groundwater modeling and remediation technologies under the supervision of Dr. Chi-Chung Chang, this Record of Study is based on the existing URS reports on this project with the input of the project team. The author has no intention to claim any ownership of the materials presented in this Record of Study.

Since the materials contained in this Record of Study are based on several URS reports on this project, URS has the sole ownership of the ideas and design methodologies developed in this Record of Study.

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#### 1. INTRODUCTION

#### 1.1 Internship with URS Corporation

The environmental consulting industry covers a wide range of business lines, such as environmental planning and compliance, hazardous waste management, water and wastewater treatment, and air pollution control. The Environmental Liability Management (ELM) unit of the URS Houston office focuses on environmental compliance related to soil and groundwater. A typical ELM project includes site investigation and characterization, soil/groundwater remediation technology evaluation and selection, preparation and submission of reports following national and state regulations, and the implementation of site remediation.

As one of the world's leading engineering and environmental firms (URS is ranked number one on ENR's list of the top 500 design firms), URS offered me an excellent opportunity to work on all those aspects of environmental compliance projects. As an intern, I am fortunate to get to know and work with some of the best minds in the industry. Thanks to their supports, the objectives listed in my internship proposal and final objectives are met. This valuable experience is important for my future career development. Since joining URS at the beginning of 2004, I have been working on several remediation and wastewater treatment projects as listed below:

This thesis follows the style and format of Environmental Pollution.

- Conducted a site hydrogeology and contaminant fate/transport modeling using
  Visual MODFLOW to simulate groundwater flow and contaminant migration
  at a former oil service site. Calibrated and optimized the model by reviewing
  field hydrogeological data and performing sensitivity analysis. Proposed
  contaminant release scenarios based on modeling results. Provided
  groundwater remediation strategies at the site and preliminary remediation
  system design assistance based on modeling results;
- Reviewed an engineering design of a constructed wetland for the treatment of
  effluent from a secondary wastewater treatment plant. Evaluated the
  performance of the wetland for the removal of nitrogen and phosphorus.
   Constructed kinetic models to simulate BOD, nitrogen, and phosphorus
  transformations in the wetland;
- Conducted conceptual engineering design/calculations and cost estimates for a
  major oil and gas company to treat wastewater generated from its Liquified
  Natural Gas (LNG) facilities. Four wastewater treatment processes were
  considered: activated sludge process (ASP), membrane bioreactor (MBR),
  chemical oxidation, and anaerobic treatment by expended granular sludge bed
  (EGSB) and upflow anaerobic sludge bed (UASB);
- Reviewed the design basis for a Gas-to-Liquids (GTL) wastewater treatment
  plant for a major oil company. Evaluated the feasibility of using thermophilic
  biological technologies to treat GTL wastewater;
- Conducted groundwater remediation technology reviews on Permeable Reactive Barrier and In Site Chemical Fixation (ISCF) for an metalcontaminated site;
- Evaluated different remediation technologies for a private site contaminated by benzene, toluene, ethylbenzene, and xylene (BTEX) and methyl tertiary-butyl ether (MTBE). Conducted cost analyses for different remediation options;

- Conducted a technology review of ISCO (In Situ Chemical Oxidation) for both groundwater and soil remediation at an industrial site contaminated by BTEX and MTBE. Finished a conceptual design for the site remediation by using ISCO;
- Prepared a Response Action Plan (RAP) for a private site as part of Texas Risk Reduction Plan (TRRP) closure requirements;
- Wrote several groundwater monitoring reports for contaminated sites per the requirement of Texas Commission on Environmental Quality (TCEQ) and other regulatory agencies; and
- Conducted soil and groundwater samplings at a land treatment facility (landfarm) that receives refinery wastes at a regular basis.

Among those projects, the first one is the one I spent the most of my internship time working on. It covers a broad range of technical field such as site investigation and delineation, computer modeling, remediation technology screening, cost estimation, treatability study, and engineering system design. For the rest of the report, I will focus on this project and present the findings from previous and current studies. Because it is an on-going project, certain parts of the report are not complete by themselves such as the remediation system design, and more work is either in the planning stage or waiting for the test results. But overall the report reflects the broadness and depth of a typical remediation project conducted at URS.

#### 1.2 Description of the Remediation Site

Due to the nature of this remediation project, both the site name and the exact location cannot be disclosed in this report. A general name, the "Site", will be used throughout the report as the site ID. General information about the Site is provided in the following sections.

The Site structures previously numbered five buildings (three of which remain, as well as the concrete slab of a fourth), sumps, a retaining wall, two oil/water separator tanks with an estimated capacity of 1000 gallons each, and a large storage tank.

Structures from previous operations at the Site are still present, including three contiguous buildings and a retaining wall. Adjacent property includes a municipal water softening plant to the north, an empty field and a railroad line to the south, an out of service bulk gasoline distribution facility to the west, and a maintenance shop and warehouse for storage of city-owned roadway equipment to the east. An aerial photograph of the Site is included as Fig. 1.

#### 1.3 Previous Environmental Investigations

The initial site investigation commenced in 1992. Subsequently, additional site investigations and source removal and control measures were implemented. Highlights from these activities are summarized as follows:

- Soil Sampling in 1992;
- Initial Site Characterization in 1993;
- Phase II Site Investigation in 1994;
- Comprehensive Investigation in 1995;
- Corrective Action Study for Soil in 1999;
- Implementation of Corrective Actions for soil in 2000 and 2001;

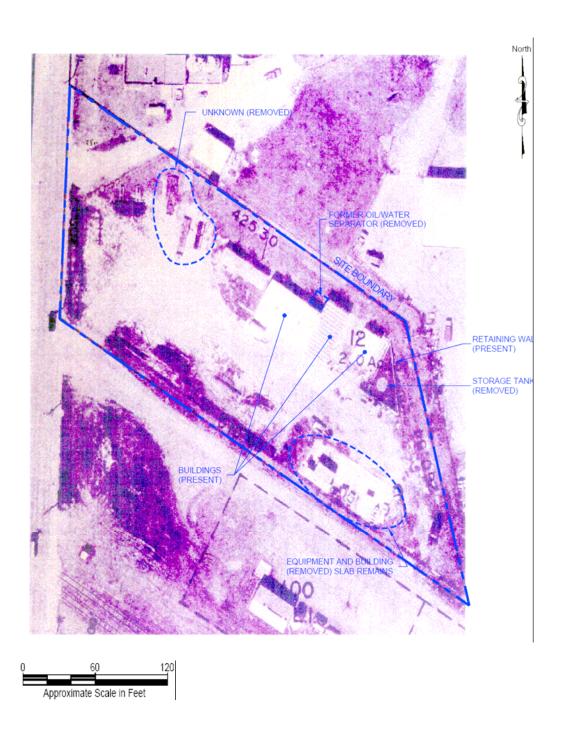


Fig. 1. Site aerial photo

#### 1.4 Past and Present Operations at the Site

The Site was originally used as farm and rangeland before it was sold for industrial use. It was used for storing and loading materials used for enhancing oil recovery from oil-producing limestone formations and as a manufacturing site for specialty products and services related to the stimulation and completion of oil and gas wells. A metal solution was used prior to 1970s' as a corrosion inhibitor at the Site. Presently, the Site is inactive. No known release of any substance has occurred on the Site during its operational history. Specific quantities of substances used or stored on the Site are unknown.

#### 2. RESULTS OF SITE INVESTIGATIONS

This section describes the physical characteristics of the region surrounding the Site. The physical characteristics included in this Section are:

- geology;
- hydrogeology;
- meteorology; and
- ecology.

#### 2.1 Geology

The region where the Site is located is characterized by broad stretches of predominantly treeless flat uplands. The geology of this region is indicative of flood plain/alluvial depositional environments. The upper 20 to 30 feet of soil is characterized by silt and clay deposited during river flood stages. The silt and clay deposits are underlain by fine to very coarse sand and some gravel-sized sediment.

The Site geology consists of crushed limestone fill from ground surface to approximately six inches below ground surface (bgs). The fill material is typically underlain by Quaternary terrace deposits (Qt) of silty clays and clayey silts. The water-producing zone is encountered beneath these silts and clays at an average depth of 24-27 feet bgs, and is composed of fine to very coarse sand, generally coarsening with depth. This sand represents Quaternary alluvial deposits (Qal). The sand zone averages twelve feet in thickness and is underlain by black shale at approximately 42 feet bgs. Both ground surface and subsurface contacts between units dip to the south.

The soils in this region are thick soils of the mollisols (dark, soft grassland soils) type, in an area with a mean annual temperature of +8 to +15°C and a dry climate, usually hot in summer (Brady & Weil, 1996).

Physical properties of the soil include a saturated hydraulic conductivity, Ks, of 16 mm/h - 51 mm/h and a bulk density,  $\rho_b$ , of 1.33 g/cm<sup>3</sup> to 1.53 g/cm<sup>3</sup> (House et al, 2001). Soil moisture contents at the Site ranged from 17 percent to 32 percent by weight. The average soil moisture content is approximately 22 percent by weight. Available water capacity is reported as 0.14 to 0.18 inch of water per inch of soil.

#### 2.2 Hydrogeology

In the region studied, the formation exhibits highly variable thickness due to the dynamic fluvial depositional environments and post-depositional erosion. Recharge occurs as a result of infiltration of precipitation; however, recent trends make it evident that the groundwater table has markedly dropped over the last 40 to 50 years in response to groundwater depletion related to agricultural use.

Potable groundwater is generally found where Quaternary fluvial processes have deposited sand and during periods of vertical aggravation within historic and recent stream channels. Locally, the quantity of groundwater available is a function of the thickness and lateral extent of coarser-grained sediments deposited within the stream valley and of recharge of the aquifer through infiltration of precipitation and infiltration from associated waterways. The Quaternary alluvium generally displays classic upward-fining sequence stratigraphy associated with fluvial depositional environments. The Quaternary alluvium exhibits stratigraphic heterogeneities typical of fluvial depositional environments including variable sand thicknesses, sand lenses, and clay lenses.

Regional groundwater flow is south-southeast. Regional transmissivity values were not available in any of the publications used during this investigation.

Eighteen monitoring wells are located in the vicinity of the City Service Department, as shown in Fig. 2 (the well location map). Groundwater elevations were measured in 2002 and ranged from 1968.05 feet above mean sea level (AMSL) to 1966.27 feet AMSL. Groundwater elevations were re-measured in 2003 and ranged from 1965.2 feet AMSL to 1966.5 feet AMSL. These data indicate that the groundwater flow direction in the area is toward the south-southeast.

The city groundwater pump-and-treat system was installed in 1993, and placed into service in 1995. The purpose of the groundwater pump-and-treat system is to remediate groundwater impacted by petroleum hydrocarbons in the southern portion of the city. The pump-and-treat system consists of a groundwater extraction and treatment system. The groundwater extraction system consists of four groundwater extraction wells (EX-01 through EX-04). The groundwater treatment system consists of a packed tower air stripper followed by activated carbon.

A 24-hour aquifer test was performed, at a flow rate of 25 gpm, on extraction well EX-02 to estimate the transmissivity, hydraulic conductivity, and specific yield of the unconfined aquifer. Drawdown data from four observation well locations were analyzed with the Cooper/Jacob Distance Drawdown method. Using this method, hydraulic properties of the aquifer were estimated to be: average hydraulic conductivity 3.8 x 10<sup>-2</sup> cm/sec (108 ft/day); transmissivity 4,032 ft<sup>2</sup>/day; and specific yield 0.048.

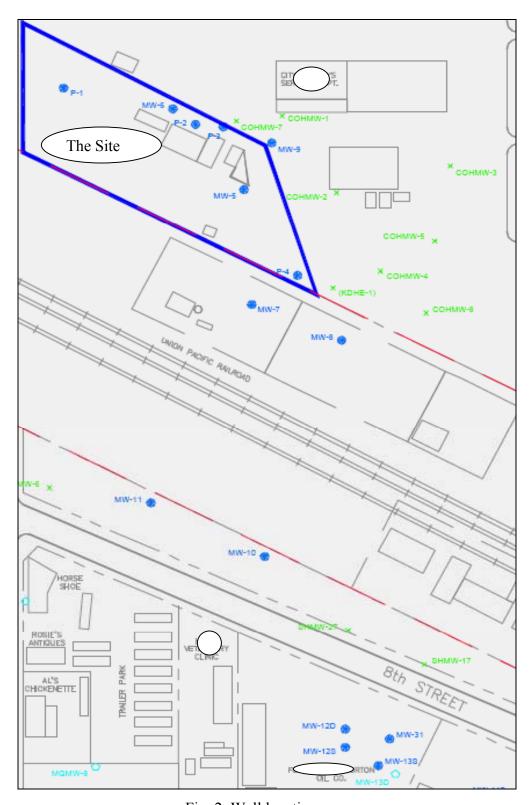


Fig. 2. Well location map

Based on cumulative water-level measurements, the groundwater flow direction beneath the Site is to the south-southeast. During 2002, the estimated groundwater velocity at the Site ranged from 118.2 ft/year to 147.8 ft/year. The depth to groundwater, as measured in 1997, indicated that groundwater levels ranged from 18.88 feet below top-of-casing to 22.86 feet below top-of-casing. The apparent hydraulic gradient was 0.2 feet per 100 feet to the south/southeast.

#### 2.3 Meteorology

The climate in this region is characterized by warm to hot summers, cold winters and light precipitation. The average annual precipitation around this region was 22.68 inches. Mean annual temperature for the region was 53.9 °F.

#### 2.4 Ecology

The Site is located in an industrial section of the City. The Site itself is mowed regularly and does not support any major ecosystem types, nor is it an important refuge for wildlife.

#### 3. SOURCE CHARACTERIZATION

#### 3.1 Chemicals of Concern and Primary Sources

A series of comprehensive soil and groundwater investigations have been conducted at the Site (URS, 2004). Results of these investigations indicate that a metal (a generic name "the metal" will be used throughout this report due to the confidential information requirement by URS) is the primary chemical of concern (COC) at the Site. It is suspected that the primary source of the metal in soil and groundwater at the Site was the release of a metal solution that was used in oil field services as a corrosion inhibitor. The facility operations ceased in 1985, thereby removing the primary source of the metal to soil and groundwater at the Site.

Background metal concentrations in groundwater in this area have been measured as high as 0.028 mg/L up-gradient of the Site.

#### 3.2 Soil Source

Soil affected by historical operations at the Site is suspected to be the secondary source of the metal in groundwater. Delineation of the metal affected soils prior to remedial activities has been conducted in several investigation events.

In order to address the affected soil identified in these investigations, Interim Remedial Measures were performed in 2001. These measures were conducted in order to assure the protection of human health at the Site by removing surface soils exceeding the risk-based criteria for the metal (URS, 2004).

Interim remediation activities were undertaken at the Site, including excavating the former trench area, post-excavation side wall and bottom soil sampling, soil stockpiling,

removal of the stockpiled soil, storm sewer repair, and the installation of the water proof cap over the soil impacted areas. In addition, soil and water drums from previous excavations that were stored onsite were removed, and two oil/water separator underground storage tanks (USTs) were excavated and removed. All known affected areas were removed or capped, eliminating rainwater infiltration to the water-bearing unit. These measures effectively removed the secondary source of the metal to groundwater at the Site.

#### 3.3 Groundwater Source

The source of the metal affecting the groundwater at the Site is likely from historical facility operations. However, the metal has also been detected in groundwater wells upand cross-gradient to the Site. The presence of the metal in these wells could indicate that the metal is naturally occurring in the area, or is being released by some other mechanisms.

As discussed in Section 3.1, the primary source of the metal in the subsurface was removed about 30 years ago when the use of the metal was discontinued. In addition, a soil remediation program significantly reduced the concentrations of the metal leaching to groundwater, effectively eliminating the secondary source of the metal at the Site.

Based on the removal of the primary (releases from historical operations) and secondary (affected soils) sources of the metal-affected media, concentrations of the metal in groundwater at the Site should demonstrate either a decreasing or stable trend. A qualitative analysis of the metal concentration trends suggested that concentrations in groundwater, in general, are stable or decreasing at the Site and downgradient. Indicated metal concentration trends are illustrated graphically for seven monitoring wells (Fig. 3 through 9). It is probable that the decreasing trend in metal concentrations will continue as the effects of the soil remediation program are more fully realized.

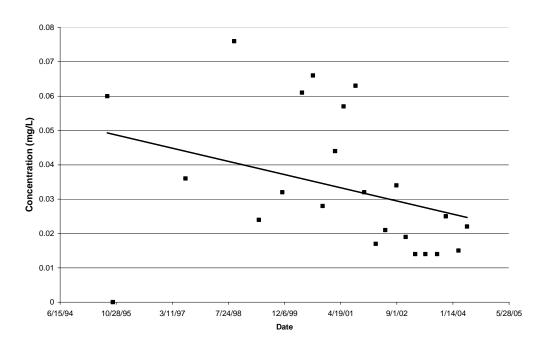


Fig. 3. Metal concentrations in monitoring well A (adapted from URS, 2004)

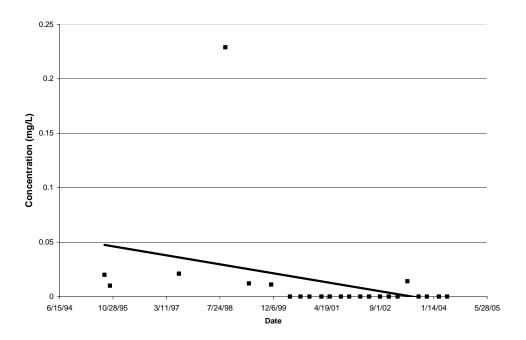


Fig. 4. Metal concentrations in monitoring well B (adapted from URS, 2004)

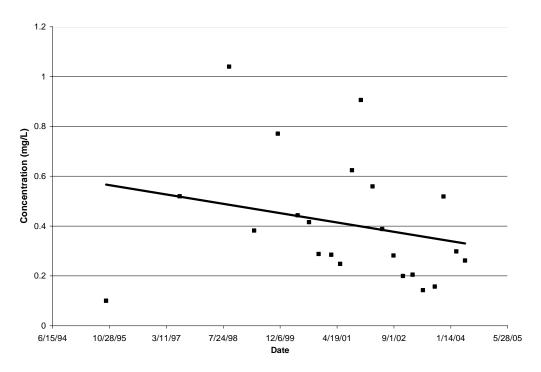


Fig. 5. Metal concentrations in monitoring well C (adapted from URS, 2004)

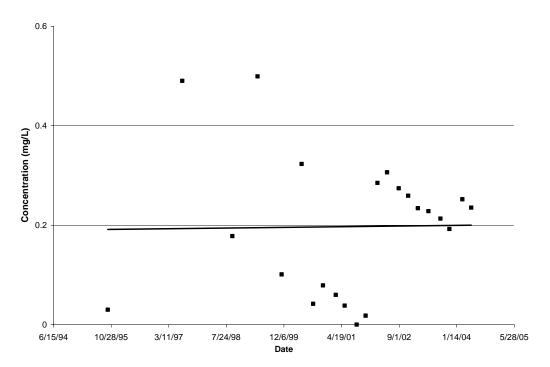


Fig. 6. Metal concentrations in monitoring well D (adapted from URS, 2004)

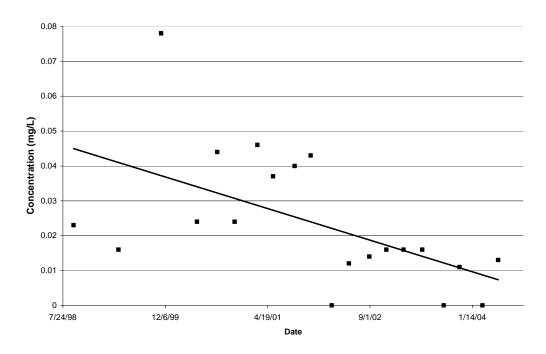


Fig. 7. Metal concentrations in monitoring well E (adapted from URS, 2004)

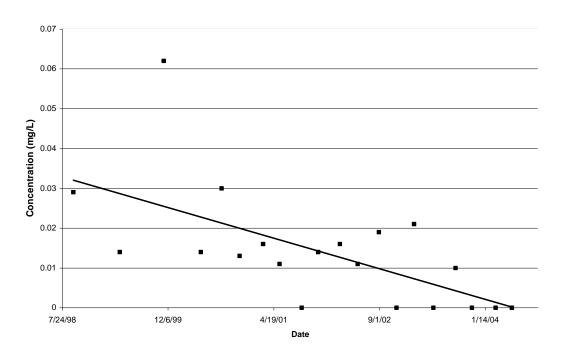


Fig. 8. Metal concentrations in monitoring well F (adapted from URS, 2004)

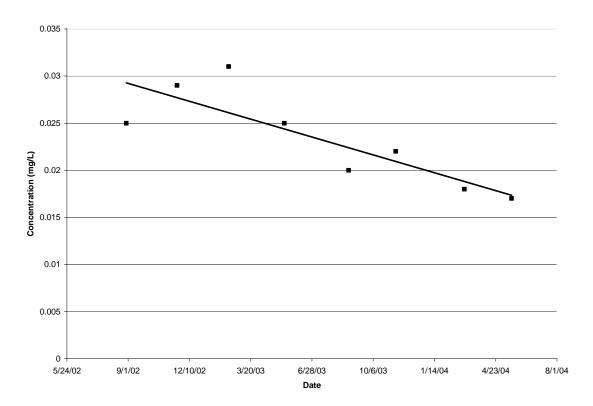


Fig. 9. Metal concentrations in monitoring well G (adapted from URS, 2004)

#### 4. NATURE AND EXTENT CHARACTERIZATION

Surface and subsurface soils and groundwater data from previous site investigations were reviewed in an evaluation of the significant COC fate and transport mechanisms present at the Site. The determination of the nature and extent of COCs was based on soil and groundwater analyses, soil boring lithologies, geoprobe sampling, geochemical field analyses, geophysical surveys, hydrogeological evaluations, topographic surveying and computer modeling. All data were validated using relevant field or laboratory quality control standards to determine whether the data were appropriate to use in groundwater modeling simulations.

#### 4.1 Characteristics of COC in Groundwater

The metal is generally found in groundwater as a molecule complexed with hydrogen and oxygen at two different oxidation states: the higher-state and the lower-state. Of these, the higher-state metal is considered less mobile and generally predominates under oxidizing conditions. The lower-state metal is widely considered to be more mobile and predominates in anoxic, sulfide- or methane-bearing waters.

In this report, mobility refers to the relative partitioning of the metal between the solid and dissolved phases. The lower-state metal is generally considered more mobile than the higher-state metal because the higher state metal tends to partition to the dissolved phase, while the lower-state metal preferentially partitions to the solid phase. Concentrations of the metal in groundwater are governed by the presence of adsorption sites, often in the form of iron oxides, aluminum oxides, clays, or organic carbon. Under oxidizing conditions, the metal tends to be in the higher-state, which will preferentially bind to the adsorption sites, thereby decreasing the metal concentrations in groundwater. However, in the presence of hydrocarbons, groundwater is generally reducing in Eh, which favors the stability of lower-state metal over that of the higher-state metal.

Therefore, reducing conditions generally have the effect of releasing the metal back into the groundwater.

#### 4.2 Affected Soils

As discussed in Section 3.2, impacted soils at the Site are suspected of being a secondary source of the metal in groundwater. Affected soils were delineated at the Site before the interim corrective measures were conducted at the Site. Confirmation sampling data showed that the metal concentrations in the soils remaining at the Site were below the risk-based criteria after the affected soils were removed.

#### 4.3 Groundwater Impact

#### **4.3.1** Background Metal Concentration

In 2001, an investigation into the background concentrations of the metal in the vicinity of the Site was conducted. The results of the study indicate that the metal is found both up-gradient and cross-gradient from the Site. The metal concentrations of 0.028 mg/L were detected in an inactive public water supply well, located approximately 4,500 feet north-northwest of the Site (up-gradient). Concentrations of 0.017 mg/L were detected in a monitoring well, located approximately 1,600 feet southwest of the Site (cross-gradient).

These findings imply that the metal in the area may not all come from the sources described in Section 3, and also there is not necessarily a single continuous area affected by the metal as a COC.

#### 4.3.2 Downgradient Extent

At and adjacent to the Site, the metal concentrations in groundwater range from 0.278 to 0.252 mg/L (2004 data). The railroad runs roughly east-west approximately 100 feet south of the site; no monitoring wells exist in a band approximately 350 feet wide encompassing the railroad right-of-way.

The metal concentrations in a monitoring well located approximately 200 feet west-northwest of the Site has been below detection limits for the metal from the time of its installation in 1998 until sampling was suspended in 2002. Another monitoring well located about 400 feet west-northwest of the Site has been sampled on three occasions from 1998 to 2002, and the metal was below detection limits for all three of these sampling events.

Two monitoring wells located south of the Site, were below detection limits for the metal in 2004; however, the metal was indicated at 0.011 mg/L for one monitoring well in November 2003, and at 0.010 mg/L for the other monitoring well in August 2003. Approximately 1000 feet south-southeast of the Site, the metal was indicated at or above 0.018 mg/L for a monitoring well from its installation in 2002 to the present. Groundwater samples from one monitoring well, approximately 1150 feet south-southwest of the Site, tested at 0.055 mg/L in 2004; prior to that, samples had been below detection limit for the metal in 2003. The concentration range for the wells approximately 1000 feet south of the Site (on the order of 0.01 mg/L) is comparable to that indicated for background wells.

Indicated metal concentration trends are illustrated graphically for 7 monitoring wells south-southeast of the Site in Fig. 3 through Fig. 9.

#### 4.3.3 Lateral Extent of Affected Area

Groundwater samples from monitoring wells located east and southeast of the Site have consistently been below the detection limit for the metal, suggesting that no metal is leaving the Site to the east. These results suggest that the delineation of the maximum eastern cross-gradient extent of the plume has been achieved.

Groundwater samples from a monitoring well located near the northwest corner of the affected area have been below detection limits for the metal for all sampling events except one in 2001 (0.012 mg/L). All groundwater samples taken from a monitoring well, located on the northern side of the Site, have been below detection limits for the metal. For the affected area to the south, only one monitoring well has had indication of the metal once (0.042 mg/L in 2002). These results, coupled with the slight eastern trend to the general groundwater flow direction, suggest that delineation of the maximum western cross-gradient extent of the plume has also been achieved.

#### **4.3.4** Vertical Extent of Groundwater Impact

Groundwater samples collected from the nested wells installed in August 2002 have been collected and analyzed on a quarterly basis since August 2002. Of these wells, none of the deep wells (which extend to the impermeable shale bedrock) have had indications of the metal above detection limits. This suggests that the metal in the groundwater of the affected area is typically found in the upper 10 to 20 feet of the water-bearing unit, above the screened intervals of deep monitoring wells.

#### 4.4 Areas of Uncertainty

Because no well exists in areas from about 150 to 500 feet south of the Site, it is unclear at this time which of the scenarios outlined below is more likely correct.

One possibility is that a single metal plume extends approximately 1000 feet south-southeast from the Site, across the no well areas mentioned above. Field observations indicate an area of reducing groundwater conditions south and east of the Site. Localized indications of the metal downgradient from the Site might be explained by remobilization of the metal in response to these reducing conditions. This scenario is supported by hydrogeological modeling using the conservative Kd value of 1 mL/g, which yields an estimated plume extent of approximately 1000 feet.

A monitoring well located downgradient from the Site had no indication of the metal from the time of its installation in 1998. This suggests that, rather than extending all the way to the southern area, the plume associated with the Site stops some distance north-northwest of this monitoring well. The southern concentrations would then represent a separate plume, perhaps one caused by the re-mobilization of the metal by the reducing conditions. The standard Kd value of 29 mL/g was used in this tow-plume (two-source) scenario. Using this value, the observed plume sizes at the Site correspond closely to those predicted by the two-source model.

#### 4.5 Nature of Impact

The original source is suspected to be a metal solution formerly used at the Site. Presumably, subsequent infiltration allowed this solution to migrate to the soil at the Site and into the groundwater beneath the Site.

Field measurements of Eh and pH conditions from 2003 and 2004 suggest that the metal in the groundwater under the Site exists in the higher-state form; reducing conditions further south indicate that the lower-state metal is the predominant form in groundwater.

Geochemical modeling using Visual MINTEQ confirms that some 99.99% of the metal in the Site groundwater is in the higher-state form.

#### 4.6 Groundwater Modeling

A groundwater model was developed to simulate groundwater flow and fate and transport of the metal at and adjacent to the Site. The groundwater modeling was based on the hydrogeological information generated from the results of previous field investigations, and was used to aid in the designing of groundwater remediation system(s) at the Site. The groundwater model was also used to assess the need for the refinement of an existing groundwater recovery system to contain the metal plume at the city extraction wells. This section summarizes the activities conducted in the development of the groundwater model. Detailed descriptions of the modeling process are included in this report as Appendix.

#### 4.6.1 Modeling Approach

The groundwater modeling approach utilized a step-wise methodology that progressed from a conceptual physical model of the subsurface, to a geochemical model analysis and numerical computer simulation of site-specific scenarios. This allowed delineation of the current site conditions and an evaluation of the effect of the hydraulic control mechanisms. The step-wise process is listed below:

- Development of a subsurface physical model (conceptualization) and numerical model setup;
- Model parameter estimation and generation of model data sets;
- Calibration of the model and establishment of various hydraulic control scenarios;
- Simulation and evaluation of the selected scenarios:
- Evaluation of the effect of the hydraulic control; and
- Preparation of the results of the modeling effort to support the engineering design.

A summary of model configuration and results of the simulations are presented in the following sections. Parameter estimation, model calibration and other detailed modeling information are provided in Appendix.

#### 4.6.2 Configuration and Model Set Up

Site assessment documents and results from previous site investigations were integrated into the model design. The model design included conceptualization, model implementation, evaluation, and prediction of the impact of the hydraulic control. This section discusses the conceptualization of the site and model set up. Based on the preliminary investigation results within and adjacent to the site, a physical site model was configured. The simulated area contains several features that can influence groundwater flow patterns and the location of the hydraulic control. These features are:

- Two hydrogeological layers:
  - An upper, low-permeability clayey layer (hydraulic conductivity K = 0.1134 ft/day); overlying
  - A high-permeability sandy aquifer (K = 31.18 ft/day) with confined/semiconfined conditions;
- Insignificant rainfall recharge into aquifer; and
- Measured groundwater head distribution.

For the numerical analysis, the three-dimensional Visual MODFLOW model was used. The Visual MODFLOW model was developed for groundwater flow and fate and transport simulation by the U.S. Geological Survey. The study area was configured using an 80×50 grid with two layers. Each block of the grid was assigned hydrogeological properties based upon the Site and local area characteristics, as appropriate.

#### 4.6.3 Delineation of COC Extent

Due to the information gap from about 150 to 500 feet south of the Site, the extent of COCs in groundwater could not be fully delineated. With two hypotheses as to the COC distribution at the Site, two sets of fate and transport simulations were modeled to delineate the extent of COCs in groundwater. In order to minimize the uncertainty involved in the model simulation, preliminary geochemical modeling was performed using Visual MINTEQ before using Visual MODFLOW for fate and transport analysis.

Visual MINTEQ is an equilibrium speciation model developed by the EPA and is used to calculate the equilibrium constituent composition of dilute aqueous systems. Visual MINTEQ was run using the specific subsurface conditions encountered at the Site and adjacent areas. In order to verify the effects of oxidizing and reducing conditions in the groundwater at the Site, Visual MINTEQ was run using a series of Eh values from –50 mV to 182 mV. The Eh value of 182 mV was selected to represent the oxidizing conditions encountered in the source area. A conservative Eh of –50 mV was selected to represent the reducing conditions found cross- and downgradient from the source area. Intermediate Eh values of 0 mV and 50 mV were also run in order to investigate the metal speciation under relatively neutral electro-chemical conditions.

The results of the geochemical analyses were used to determine the speciation and relative mobility of the metal in groundwater. In addition, results of the model were used to derive a partition coefficient (Kd). The derivation of the Kd factor was accomplished by first determining the fraction of the metal dissolved in groundwater and the fraction of the metal adsorbed to aquifer solids in the source area. The ratio of these fractions was then used to derive the Kd for the source area.

#### **4.6.4** Modeling Results and Recommendation

Results of the preliminary modeling suggest that 99.99% of the metal is present as the higher-state form in the source area (URS, 2004). Conversely, under reducing conditions, 99.99% of the metal is predicted to be present as the lower-state form. As discussed in Section 4.1, the lower-state is widely considered the more mobile form of the metal; therefore, the concentration of the metal in groundwater is likely to be elevated downgradient of the Site in response to the reducing conditions found in the groundwater there, if the plume reached there or naturally occurred metal was released. This possibility will apply to the remediation options discussed in the following Sections.

Various Kd values were reported in literatures (Baes and Sharpe, 1983). Preliminary geochemical modeling using Visual MINTEQ suggests that the Site-specific Kd value in the source area may be as high as 35 mL/g. In general, the higher the retardation factor, the less mobile the COC will be. Two retardation factors (5.9 and 141.9) were used in the visual MODFLOW model (Appendix). A retardation factor of 5.9 (with a corresponding Kd value of 1.0 mL/g) was used to simulate a more mobile COC (one-source and worst-case scenario). A retardation factor of 141.9 (with a corresponding Kd value of 29.0 mL/g) was used to simulate a less mobile COC (two-source and probable scenario).

For the one-source scenario, the metal might have migrated 1000 feet from the Site after its release from the Site for 50 years. The plume generated from the model under this scenario could match the field data except one monitoring well. There were no detections of the metal in that monitoring well from 1998 to 2002.

For the two-source scenario, one metal release source was from the Site, and the other source from the south of the Site. With a retardation factor of 141.9 and groundwater velocity at 120 ft per year, it is anticipated that the metal will migrate less than 1 foot per year downgradient from the Site.

Because of the relatively recent period of data collection, direct measurements of the metal migration rate cannot be calculated, and neither scenario can be validated with current data sets.

#### 4.6.5 Assessment of Existing Groundwater Recovery System

The focus of the groundwater modeling was first to simulate groundwater flow patterns under current site conditions and then to predict groundwater flow patterns under the influence of the proposed pumping systems. Each simulation for the modeling of current site conditions was calibrated using the field measurements (e.g. groundwater level measurements in the wells and the metal concentration data). After the model parameters had been calibrated with field measurements, proposed features for the pumping system were integrated into the model to evaluate the potential effect of these extraction wells.

#### 4.6.6 Recommendation for Existing Groundwater Recovery System

From the Visual MODFLOW simulation results, a minimum pumping rate of 5,500 - 7,000 GPD (about 9-13% of the designed pumping rates for the three extraction wells) for each extraction well is needed to control the plume. Below that pumping rate, the plume will pass the city extraction wells and continue to travel downgradient. A system with the appropriate pumping rate will ensure that it has the capability to capture a theoretical fast-moving, widespread plume (one-source scenario, with low retardation). Any slower plume would be captured by this system as well. See Appendix for a detailed discussion on the simulation results.

Table 1 specifies the pumping rates in gallons per day (gpd) for each extraction well to ensure adequate capture.

The groundwater modeling will continue to be fine-tuned as more field data is collected. It is anticipated that a pump test will be conducted to further characterize the aquifer near the extraction wells.

Table 1 Recommended pumping rates for extraction wells

	Screen Interval	Recommended Pumping Rates
Well ID	(feet bgs)	(gpd)
EX-01A	34 to 44	5,500 – 7,000
EX-02	35 to 45	No pumping
EX-03A	35 to 45	5,500 - 7,000
EX-04	35 to 45	5,500 - 7,000

### 5. IDENTIFICATION OF REMEDIES

This section is a summary of the remediation technologies that are potentially applicable at the Site based on the URS (2004) report. While this section focuses on the groundwater remediation, a brief discussion on the soil remediation is necessary to understand the remediation strategy screening and remediation system design.

### 5.1 Soil Remediation

Interim Corrective Measures in soil were implemented in 2000 and 2001 to assure the protection of human health at the Site. Although data at the Site indicates concentrations in soil meet the risk-based criteria at the surface, further remedial options are evaluated in this section for soils that remain in place.

The interim corrective measures fulfill the requirements stated in EPA OSWER Directive 9200.4-17P: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites (EPA, 1999). This directive concerns the remediation of COC sources. The interim corrective measures were also conducted to reduce soil metal concentrations to levels that do not impact human health. The possibility of "no further action" has been evaluated on the basis that effective soil remediation has already been completed in accordance with the aforementioned EPA regulations.

To ensure that any exposure to the metal from the Site is negated, the possibility of applying for Environmental Use Controls (EUCs) has been evaluated. An EUCs preventing future removal of the impermeable cap and future installation of water supply wells in the area of impacted groundwater would serve to remove the possibility of exposure to the metal.

#### 5.2 Groundwater Remediation Alternatives

Various remediation alternatives were evaluated for groundwater remediation at the Site. Groundwater remediation alternatives are divided into in-situ strategies, ex-situ strategies, monitored natural attenuation, and augmenting the existing pumping system. These remediation technologies include the following:

- In-Situ Strategies
  - o Electrokinetics (EK)
  - o Phytoremediation
  - Air Sparging
  - o Metal Removal Curtain
  - o Iron Co-Precipitation
- Ex-Situ Strategies
  - Iron Co-Precipitation
  - Adsorption
  - Modified Lime Softening
  - o Reverse Osmosis
  - o Ion Exchange
- Monitored Natural Attenuation (MNA)
- Augmentation of Existing Pumping System

#### **5.2.1** In-Situ Strategies

#### 1) Electrokinetics (EK)

This technology involves the application of a low-intensity current to affected soil or water. Anions migrate to an anode, where pump & treat or other remediation methods are employed. Test studies generally involve anodes and cathodes no further than 30 ft. apart. The Site (approx. 200 ft. long) would therefore require multiple sets of anodes and cathodes. Soil applications may cost up to \$70 per treated ton. This system also has

a poor maintenance record according to the EPA. EK is a temporary way to reduce the lateral extent of a plume. It is not suitable as a permanent remediation strategy.

## 2) Phytoremediation

Phytoremediation is a non-invasive technique based on the preferential uptake of a given COC by certain plants, which could conceivably be harvested and disposed of as hazardous waste after on-site COC concentrations have been reduced to acceptable levels.

Certain plants such as the Brake Fern (Pteris vittata) have demonstrated the ability to accumulate metals in their tissues. Ferns typically thrive in climates with warmer winter temperatures than the areas around the Site typically enjoys. The Brake Fern, however, has been successfully used for metal remediation at the Brownsfields property near Trenton, New Jersey, where winter temperatures are comparable to those at the Site.

The limiting factor in the use of the Brake Fern at the site is the relatively shallow root system, which is unlikely to effectively remediate an aquifer that extends approximately 20 to 50 ft. bgs.

### 3) Air Sparging

The injection of air into an aquifer impacted with metals can lead to the precipitation of the metal-bearing iron floccules, removing dissolved metals from the groundwater. This strategy was employed at the Brooks Landfill in Wichita, Kansas to reduce metal concentrations to less than 0.01 mg/L (American Academy of Environmental Engineers, 1999). The base cost for this remedial strategy is estimated at \$150,000-\$350,000 per acre treated.

The limiting factor in this technology is that dissolved iron concentrations sufficient to remove metals must be initially present in the water. At the Site, background concentrations of dissolved iron are too low to effectively remove the metal to the acceptable level. The addition of iron would be necessary at the Site in order to achieve satisfactory remediation results. Air delivery equipment is needed and will add to the treatment cost.

### 4) Metal Removal Curtain

In situations where the metal is impacting the groundwater, a metal removal curtain, which can be any of several adsorptive media such as activated alumina, iron filings, iron-coated sand, etc., is sometimes installed downgradient from the source area. Contaminants that pass through the curtain is adsorbed onto the wall medium and immobilized. All of the normal limitations of adsorption methods apply; these limitations are detailed in Section 5.2.2.

Potential problems associated with metal removal curtain installation include, but are not limited to:

- Correct length and orientation of the proposed curtain to ensure adequate interception of impacted groundwater;
- Extensive on-site excavation would impact the neighborhood, and may have a negative effect on public opinion;
- Groundwater flow rates in the area may be potentially higher than an effective wall could accommodate;
- Appropriate wall thickness;
- Waste disposal; and

 Most appropriate medium for use in the wall. Assuming an iron-coated sand suspended in a slurry of guar or other biodegradable polymer, the correct proportion of iron and sand will need to be calculated.

If the issues cited above are addressed, the installation of a metal removal curtain or a similar engineered remediation system is a viable option.

### 5) Iron Co-Precipitation

Metals can be removed from groundwater by co-precipitation with iron compounds. Iron co-precipitation can be used for metal remediation both in-situ and ex-situ. If this technology is used in-situ, it is also referred to as "in-situ chemical fixation."

For in-situ applications, an iron salt solution (e.g., ferric/ferrous sulfate or chloride) or zero-valent iron would be injected into the impacted groundwater. The metals in groundwater adsorbs to the surfaces of hydrated iron compounds such as ferrihydrite (hydrous ferric oxide). Portion of the two ions may also precipitate out as a solid "floc." The resulting solid is left in-situ; the metal is immobilized in the floc. Annual monitoring is needed to assure that the metal concentrations in excess of the EPA MCL are not leaching from the remaining floc. If the metal is found to be leaching from the flow, re-application of the technique may be necessary.

Ferric/ferrous chloride and sulfate are the primary iron salts used with this technology. Other adsorption media such as activated alumina are sometimes employed. Activated alumina is ineffective when pH is less that 6, and has the additional disadvantage of introducing aluminum to the aquifer.

Eh and pH values from wells impacted with the metal concentrations greater than 0.01 mg/L suggest that most of the metal at the Site is likely in the higher-state form, which

has a greater affinity for positively-charged iron adsorption sites and is less likely to require additional oxidation.

One viable in-situ alternative at the Site would focus on the use of iron salt for the coprecipitation of hydrated ferric iron and the metal. Alternatively, a zero-valent iron slurry or nano-scale iron compound could be used. The feasibility of this strategy would be determined by a detailed analysis of groundwater chemistry and a pilot-scale study.

#### **5.2.2** Ex-Situ Strategies

Barring effective in-situ remediation or natural attenuation (either over time in-situ, or during off-site transport), it is necessary to ensure that the metal concentrations in water entering the public water supply system from the Site do not exceed the risk-based criteria set by the state. A pump and treat strategy would need to be employed to reduce the metal concentrations to acceptable levels.

# 1) Iron Co-Precipitation

Iron co-precipitation is the same as described in Section 5.2.1, except that the water would be treated in tanks instead of in-situ. Once treated above ground, it would be possible to capture the resulting metal-bearing "floc" for disposal.

#### 2) Adsorption

Groundwater containing the metal can be filtered through any of a number of media in order to cause the metal to adsorb onto the media surface. The application of adsorption by one of the adsorption media, activated alumina, is most effective at a pH of approximately 6. The groundwater pH at the Site would have to be lowered after pumping, but before filtration. Disposal of the spent media is problematic, and there are

concerns related to aluminum concentrations in treated water exceeding drinking water standards.

A less-expensive alternative to activated alumina involves filtration through iron filings or iron-coated sand. This alternative has also been used to remove the Site COC from groundwater.

### 3) Modified Lime Softening

At high pH, lime can be used to effectively remove metals from water, but this technology is not used for water systems with more than 500 service connections; the feasibility of this alternative would have to be evaluated on that basis as well.

One step in water treatment involves lime softening, therefore this strategy would merely duplicate one already in-place.

### 4) Reverse Osmosis

Reverse osmosis involves straining pumped groundwater through a membrane to remove COCs. This method is not practical at the Site because of the cost, the large volume of rejected water, and the relatively low success rate in meeting the MCL.

### 5) Ion Exchange

In ion exchange, water is filtered through a reactive medium. While the water is being filtered, the metal is exchanged for non-hazardous ions. The base cost ranges from \$6000 per year for a 0.01 million gallons per day (mgd) system to more than \$50,000 per year for a system with flow rates up to 1 mgd.

Sulfate (SO<sub>4</sub><sup>2-</sup>) ion and other anions compete with the metal for exchange onto the medium; EPA specifies sulfate concentrations should be less than 120 mg/L if this technology is to be effectively employed. Background sulfate measurements around the Site range from 60 mg/L to 240 mg/L. The upper sulfate concentration is double the recommended maximum. Ion exchange technology cannot be employed in compliance with EPA guidelines at the Site.

# **5.2.3** Monitored Natural Attenuation (MNA)

Monitored natural attenuation (MNA) relies on natural processes to reduce COC concentration over time. Indicated metal concentration trends are illustrated graphically in Fig. 3 through 9. Linear trend lines on these figures showed the metal concentrations on Site and downgradient are decreasing over time.

The use of MNA assumes that pumping at the extraction wells is sufficient to prevent further plume migration, as detailed in the EPA OSWER Directive 9200.4-17P: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites (EPA, 1999). The hydrogeological modeling described in Section 4 determined that the pumping rate of the extraction wells should be at least 10-20% of design capacity (approximately 7,000 gallons per day per well) in order to assure that the metal does not migrate past the extraction wells. Given that it may not be possible to ensure that these pumping rates are maintained, a contingency plan (consisting of additional pumping wells, to be installed in the event that the public water supply may be impacted by the metal) will be worked out to ensure that no further plume migration occurs.

Continued monitoring for the metal in monitoring wells downgradient of the extraction wells should provide warning if the extraction wells prove insufficient to prevent further plume migration.

MNA, in conjunction with continued pumping at the extraction wells to prevent further plume migration and EUCs restricting the installation of additional drinking-water wells in the affected area, is a viable groundwater remediation strategy. MNA is discussed further in Section 6.

### **5.2.4** Augmentation of Existing Pumping System

The use of MNA (as discussed in Section 5.2.3) is contingent on the effective interception and treatment of affected groundwater by the city extraction wells. That alternative assumes that the pumping rate is maintained at approximately 7,000 gpd per operating well (10-20% of design capacity). Should adequate capture (as indicated by analysis of samples from nearby and down-gradient wells) or treatment still be insufficient despite pumping, one or more additional extraction wells should be installed to supplement the existing system.

### 6. EVALUATION OF REMEDIES

Based on the URS (2004) report, most remedial strategies for the Site groundwater discussed in Section 5.2 have been eliminated from consideration because they are comparatively ineffective or impractical for the Site. Four strategies may be viable. These strategies are discussed in greater detail below; they are:

- Metal Removal Curtain;
- In-situ iron co-precipitation;
- MNA in conjunction with plume interception; and
- Augmentation of the existing pumping system.

A detailed comparative analysis was conducted for each of the selected remedial strategies. The strategies were compared using the following evaluation criteria:

- Overall Protection of Human Health and the Environment;
- Compliance with Federal and State ARARs;
- Long-term Effectiveness and Permanence;
- Reduction of Toxicity, Mobility, and Volume through Treatment;
- Short-term Effectiveness;
- Implementability;
- Cost; and
- Community Acceptance.

#### **6.1** Metal Removal Curtain

Installation of a metal removal curtain or similar engineered remediation system is discussed in Section 5.2.1. This strategy involves the installation of an iron-bearing curtain on the downgradient side of the Site to intercept impacted groundwater, capturing the metal in the reactive media (iron-coated sand or iron filings).

At the Site, the base of the transmissive zone is approximately 40 feet bgs; the permeable wall would be approximately 200 feet long. Assuming a trench of 2 feet in thickness and a 20-foot thick aquifer, a minimum of 8,000 cubic feet of reactive media would be required.

Table 2 is a summary of the evaluation of the metal removal curtain system, followed by a detailed analysis on this system.

Table 2

Evaluation of the metal removal curtain system	
Overall Protection of Health and the Environment	High
Compliance with State and Federal ARARs	High
Long-term Effectiveness and Permanence	Moderate
Reduction of Toxicity, Mobility, and Volume Through Treatment	High
Short-Term Effectiveness	High
Implementability	High
Cost	\$1.93 M
Community Acceptance	Moderate

<sup>\*</sup> Adapted from URS reports on this project

 Overall Protection of Human Health and the Environment – High: Oxidizing groundwater Eh values have been reported for the Site, and most (99%+) of the metal should be in the more readily adsorbed form, and effective removal is expectable.

- Compliance with Federal and State ARARs High: Similar applications at other sites showed that this technology is in compliance with the federal and state guidelines.
- Long-term Effectiveness and Permanence Moderate: Adsorptive media will lose its capacity of intercepting the metal and may need to be regenerated after several years.
- Reduction of Toxicity, Mobility, and Volume through Treatment High:
   Through adsorption of the metal onto the reactive curtain, toxicity would be reduced in groundwater leaving the Site.
- *Short-term Effectiveness* High: once installation is completed.
- *Implementability* High. Similar permeable walls have been installed at more rugged locations to depths of up to 100 feet.
- Cost A system similar to the metal removal curtain and of approximately the same length and half the depth, composed of iron filings and installed using a continuous excavation method, cost an estimated \$500,000 to install (University of Waterloo, 1997). A similar application reviewed by the EPA involved a \$1.2 million initial outlay. A rough cost estimate for a metal removal curtain system as described here, with monitoring and reporting costs, totals approximately \$1.9 million (a breakdown is given in Section 7.0). Removal and/or replacement of spent media would require additional cost outlays.
- Community Acceptance Moderate: Although the wall would be installed on the Site itself, noise and dust would almost certainly affect adjacent properties.
   Trenchless metal removal curtain installation method may be used to minimize the impact.

Conclusion – This option will be evaluated further in the implementation
phase; it will be discussed further as a possible recommended option in Section
7.0.

# 6.2 In-Situ Iron Co-Precipitation

This strategy typically involves the injection of an iron salt solution such as ferric or ferrous sulfate. The metal in groundwater adsorbs to the iron surfaces forming a hydrated ferric iron. The two ions precipitate out as a solid "floc", effectively immobilizing the metal. Natural filtration of the water through the aquifer will ensure that the resulting floccules remain on-site.

Table 3 is a summary of the evaluation of the In-Situ Iron Co-Precipitation system, followed by a detailed analysis on this system.

Table 3
Evaluation of in-situ iron co-precipitation system

Evaluation of in situ non co precipitation system	
Overall Protection of Health and the Environment	High
Compliance with State and Federal ARARs	High
Long-term Effectiveness and Permanence	Unknown
Reduction of Toxicity, Mobility, and Volume Through Treatment	High
Short-Term Effectiveness	High
Implementablility	Unknown
Cost	\$1.5 million
Community Acceptance	Moderate-High

<sup>\*</sup> Adapted from URS reports on this project

- Overall Protection of Human Health and the Environment High: By immobilizing the metal *in-situ*, the absence of the metal in drinking water supplies downgradient is assured.
- Compliance with Federal and State ARARs High. An EPA (1991) review of a similar technology assumes an 80% removal efficiency for metals. At the

Site, oxidizing redox conditions and neutral pH give reason to believe that a higher recovery rate is likely. Reducing conditions downgradient of the Site implies that this treatment would be less effective if employed to the south of the Site.

- Long-term Effectiveness and Permanence Unknown: For the Site aquifer conditions, there is some question as to whether the injection would (a) cover the requisite area and (b) allow normal permeability in the injection area. In theory, the metal will be immobilized permanently, barring major changes to the pH and/or redox potential of the aquifer. Should these factors change radically (for example, in response to a major hydrocarbon spill), permanence cannot be assured.
- Reduction of Toxicity, Mobility, and Volume through Treatment High.
- Short-term Effectiveness High.
- Implementability Unknown: Not possible without first obtaining a full
  dissolved ion characterization of the aquifer, and second, performing a pilotscale study.
- Cost A complete estimate, including costs for materials, reporting, monitoring, etc. (as detailed in Section 7.0), might run as high as \$1.5 million. These estimates assume that the metal will be immobilized in-situ indefinitely. In the event that the injected media are subsequently excavated, total costs will be substantially higher.
- *Community Acceptance* Moderate-High: Assuming excessive iron concentrations in the out-flowing water are not encountered.
- Conclusion Iron co-precipitation is a viable option for remediation of the
  metal in groundwater at the Site. This option will be evaluated further in the
  implementation phase; it will be discussed further as a possible recommended
  option in Section 7.0.

#### **6.3** MNA

MNA is discussed in Section 5.2.3. The feasibility of this strategy depends on the application of EUCs for the source area while natural attenuation is taking place. In addition, this remedy assumes that the pumping rate of the extraction wells will be at least 10-20% of the design capacity (approximately 7,000 gallons per day per well) in order to prevent affected groundwater from migrating past the extraction wells, or, barring that, that an effective contingency plan is in place to ensure that no further migration can occur.

The affected water does not constitute wildlife habitat because it is below ground, and prevention of further plume migration will ensure that nearby surface water is not impacted.

The use of affected water as a municipal water source is an immediate and essential concern because it is the remaining route for potential exposure. The application of MCLs "at the tap" (as per EPA compliance requirements) means that sporadic indications above MCL in individual monitoring wells in the past is not a compliance issue. Instead, the post-treatment drinking water must be below the MCL.

According to EPA, "the MCLs set under the Safe Drinking Water Act are generally the applicable or relevant and appropriate standard" (EPA, 1988). Further, "if MCLs are applicable, they are applied at the tap" (ibid.).

The combination of diluting the affected water and the lime softening treatment applied at the water treatment plant, will result in compliance with the EPA National Primary Drinking Water Regulations (Title 40, Sec. 141.23), and with the requirements dictated by the Safe Drinking Water Act. Should pumping of the existing wells prove

Moderate

Moderate Moderate

Moderate

Low

High

insufficient, additional pumping wells will be installed according to the contingency plan that will be prepared if MNA is chosen as the remedy at the Site.

Table 4 is a summary of the evaluation of the proposed MNA, followed by a detailed analysis on it.

rable 4
Evaluation of MNA
Overall Protection of Health and the Environment
Compliance with State and Federal ARARs

Tal-1- 4

iance with State and Federal ARARs Long-term Effectiveness and Permanence Reduction of Toxicity, Mobility, and Volume Through Treatment **Short-Term Effectiveness Implementability** Cost \$1.2 million for

15 years Community Acceptance Unknown

- *Overall Protection of Human Health and the Environment* Moderate: Although for the short term concentrations of the metal in the water at the Site would be above the EPA MCL, the metal would probably not pose a threat to human health. Downgradient from the Site, concentrations of the metal would remain well below MCL in post-treatment drinking water (the applicable route of exposure in this case).
- Compliance with Federal and State ARARs Moderate: Quarterly testing of the post-treatment drinking water must be undertaken to assure that the metal concentrations are below the MCL.
- Long-term Effectiveness and Permanence Moderate: Assuming that the existing treatment and dilution remain in effect.
- *Reduction of Toxicity, Mobility, and Volume through Treatment* Moderate: Lime softening treatment at the water treatment plant should result in a

<sup>\*</sup> Adapted from URS reports on this project

decrease in the metal concentrations. Rather than a decrease in volume being a goal, an increase in volume from additional drinking water sources helps assure that the overall concentrations in the community drinking water remain below the MCL by dilution.

- Short-term Effectiveness Low: MNA is generally a long-term proposition.
- *Implementability* High: Essential elements already in-place.
- Cost Costs associated with continued monitoring, and of maintaining the existing extraction well system, remain in effect. Additionally, EUCs involve a \$10,000 fee. Additional monitoring and reporting costs would increase this figure to an estimated \$80,000 per year. Assuming monitoring of 15 years duration, total costs could be up to \$1.2 million. These estimates do not include costs associated with the contingency plan, which will be discussed in Section 7.0.
- Community Acceptance Unknown: Presumably, as long as drinking water is
  demonstratively safe according to EPA standards, community acceptance is not
  an issue. However, the existence of the metal in the groundwater on-site that
  has not been treated, even if this metal poses no threat to the drinking water
  supply or environment, may cause public concern.
- Conclusion By itself, this possibility is not recommended. However, in
  conjunction with remediation of elevated metal concentrations at the Site and
  adequate pumping rates of the city extraction wells to ensure full plume
  interception, many of the aspects of this strategy are useful.

### 6.4 Augmentation of Existing Pumping System

Augmentation of the existing pumping system is discussed in Section 5.2.4. This strategy assumes that the proposed pumping rate of the operating wells (at least 7,000

gpd each, or 10-20% of design capacity) is not achieved, or else is still insufficient for adequate capture, despite modeling predictions. Alternatively, the possibility that treatment at the city water plant is inadequate to remove the metal to below 0.01 mg/L must be provided for. In either case, a strategy of pumping system augmentation would involve the installation of one or more additional wells, and an associated pump-and-treat system.

Table 5 is a summary of the evaluation of this proposed remediation strategy, followed by a detailed analysis on it.

Table 5

Evaluation of augmentation of existing pumping system	
Overall Protection of Health and the Environment	High
Compliance with State and Federal ARARs	High
Long-term Effectiveness and Permanence	Moderate
Reduction of Toxicity, Mobility, and Volume Through	High
Treatment	
Short-Term Effectiveness	Moderate
Implementability	Moderate
Cost	\$4 million for 15 years
Community Acceptance	Moderate

<sup>\*</sup> Adapted from URS reports on this project

- Overall Protection of Human Health and the Environment High: This
  alternative would control the movement of groundwater and reduce the metal
  concentrations in recovered groundwater through treatment. Worker exposure
  during installation and operation of the pumping and treatment system would
  be minimal.
- Compliance with Federal and State ARARs High: Recovered groundwater would be treated to meet the MCL.

- Long-term Effectiveness and Permanence Moderate: Mobility is controlled only while pumping system is operational. The metal would be permanently removed from recovered groundwater through treatment.
- Reduction of Toxicity, Mobility, and Volume through Treatment High:
   Mobility, toxicity, and volume would be reduced through the combination of pumping and treatment.
- Short-term Effectiveness Moderate: Installation of a pumping system would begin affect the flow of groundwater immediately upon commencement of pumping. However, the metal removal rates are anticipated to be low.
- Implementability Moderate: the location and quantity of additional extraction
  wells need to be decided before the implementation of this strategy. Access to
  certain areas is complicated by public streets and a railroad right-of-way.
  Radius of influence for pumping system would be good in the alluvial waterbearing zone.
- Cost The metal removal from groundwater would require a batch or continuous flow process and daily maintenance. A more detailed cost estimate, involving an initial outlay of approximately \$250,000, is presented in Section 7.0. Adding estimated monitoring and reporting costs, an additional cost of \$250,000 per year is a reasonable estimate. Assuming 15 years of operation, costs could exceed \$4 million. These estimates assume that the post-treated water could be pumped using the city system to the city water treatment/distribution plant. If piping to the plant would need to be installed as well, initial and maintenance costs would increase considerably, and implementability would be poorer than shown.
- *Community Acceptance* Moderate. This alternative would control the movement of groundwater and treatment would reduce the amount of the metal in recovered groundwater. But overall it is a long-term strategy.

Conclusion – Installation of a pumping system would aid in reducing the
amount of metal contained in groundwater and would control the movement of
groundwater. Due to the cost of treatment, however, implementation of this
alternative is not recommended unless the metal concentrations greater than the
MCL are observed at downgradient monitoring wells during semiannual
monitoring.

This alternative will be retained as a contingency measure in the event that the metal concentrations above the MCL are detected despite the activities recommended in Section 7.

### 7. RECOMMENDED REMEDY

# 7.1 Description of Recommended Remedy

The use of iron co-precipitation or installation of metal removal curtain system at the Site (Sections 6.1 and 6.2) does not address the indications of the metal in groundwater south of the Site. Likewise, MNA and interception of affected water by the city extraction wells could be a prohibitively long-term strategy if active remediation is not undertaken. Regardless of the source or sources of the metal in groundwater at and near the Site, a remedy addressing both metal-affected areas is warranted.

The recommended remedy is a combination of two of the strategies discussed in Sections 5 and 6. For the Site area, installation of a metal removal curtain system or the use of iron co-precipitation is recommended, in order to remediate affected groundwater. For the downgradient area, plume interception using the existing pumping system and MNA is recommended. This recommended corrective action is outlined in more details below.

### 1) Installation of metal removal curtain system or Iron Co-Precipitation

Two options remain under consideration for intercepting the metal in groundwater in the source area: (1) a wall or trench containing a slurry of zero-valent iron and sand in guar or biodegradable polymer would be installed to the base of the aquifer across the south end of the Site; or (2) in-situ iron co-precipitation using a series of injection wells installed in the source area. In both instances, adsorption of the metal onto the iron would occur as groundwater passes through the area heading south. This strategy would prevent elevated metal concentrations from leaving the source area. The two methods will be further evaluated in order to assure that the most efficient and cost-effective alternative is selected. Bench and pilot scale studies are necessary to achieve this goal.

### 2) Capture and Monitoring of Groundwater Downgradient

Pumping of the extraction wells should be at least 7,000 gallons per day (gpd) (10-20% of design capacity) for each of the operating wells. Groundwater modeling indicated that this would ensure complete capture of metal-bearing water south of the Site, preventing further plume migration. Dilution and treatment of the captured water would result in compliance with all applicable guidelines.

Monitoring of existing wells, and of post-treated water, should continue on a quarterly basis. If the metal is detected in concentrations above the MCL in post-treated water, immediate re-sampling and analysis should be undertaken to verify the results. Should the metal concentrations be non-compliant with the guidelines, results should be verified, and additional pumping wells should be installed to intercept and treat affected water (as discussed in Section 6.4).

#### 7.2 Cost Estimates

Cost estimates for metal removal curtain and iron co-precipitation systems are provided in Section 7.2.1 and 7.2.2, respectively. Cost estimate for groundwater capture and monitoring is provided in Section 7.2.3.

#### 7.2.1 Metal Removal Curtain

A breakdown cost estimate for the metal removal curtain system is provided in Table 6.

Table 6 Cost estimate of the metal removal curtain system

TASK	COST	
Planning & design	\$40,000	
Dissolved ion characterization of the aquifer	\$60,000	
Bench-scale testing	\$100,000	
Construction of curtain	\$800,000	
Data validation/evaluation	\$5,000	
Reporting	\$15,000	
Monitoring (2 years)	\$360,000	
Monitoring (thereafter): \$80,000/yr. x 5 years	\$400,000	
Water & soil disposal	\$150,000	
Total:	\$1,930,000	

<sup>\*</sup> Adapted from URS reports on this project

# 7.2.2 Iron Co-Precipitation

A breakdown cost estimate for the Iron Co-Precipitation system is provided in Table 7.

Table 7
Cost estimate of iron co-precipitation system

TASK	COST	
Dissolved ion characterization of the aquifer	\$60,000	
Data validation/evaluation	\$7,000	
Reporting	\$15,000	
Pilot-scale study planning, design, permitting	\$20,000	
Construction for pilot-scale study	\$40,000	
Pilot-scale study operation & reporting	\$130,000	
Full-scale remediation	\$325,000	
Monitoring (1 <sup>st</sup> years)	\$360,000	
Monitoring (2 <sup>nd</sup> year)	\$120,000	
Monitoring (thereafter): \$80,000/yr. x 5 years	\$400,000	
Total:	\$1,477,000	

<sup>\*</sup> Adapted from URS reports on this project

### 7.2.3 Capture and Monitoring Groundwater Downgradient

A breakdown cost estimate for the proposed groundwater capture and monitoring system is provided in Table 8.

Table 8
Cost estimate of groundwater capture and monitoring system

TASK	COST	
Installation of 3 additional extraction wells	\$40,000	
Waste disposal	\$20,000	
Installation of treatment systems	\$115,000	
Testing and startup	\$20,000	
Evaluation, reporting, project oversight	\$55,000	
Operation & maintenance: \$140,000/yr. x 15 years	\$2,100,000	
Monitoring & ongoing evaluation: \$110,000/yr. x 15 years	\$1,650,000	
Total:	\$4,000,000	

<sup>\*</sup> Adapted from URS reports on this project

### 7.3 Treatability Study and System Design

Treatability study is necessary for remediation system design and implementation because site-specific conditions need to be taken into account for the remediation technology to work properly at the Site and achieve the desired results. Both batch tests and column/pilot-scale tests will be conducted to select the appropriate Site remediation technology and provide data for system design and optimization.

Visual MODFLOW and Visual MINTEQ simulations will be used to assist remediation system design. They are very useful tools to simulate various scenarios with varying system design variables and control mechanisms. Based on the information generated from both treatability study and computer modeling, a solid engineering system design for the Site remediation is expectable.

### 8. CONCLUSIONS

Site investigations generated information about the Site geology and hydrogeology, which are important for remediation technology screening and remediation system design. This information was also used to set up the computer models to simulate Site conditions and evaluate remediation strategies.

It was decided that the Site COC is a metal based on the environmental investigation and monitoring results. The primary source of the metal at the Site was suspected to be the release of a metal solution that was used in oil field services as a corrosion inhibitor for acidizing oil wells, but the possible contribution of naturally occurred metal to the elevated COC concentration at and adjacent to the Site could not be excluded due to the reducing environmental around the Site.

Computer simulations by Visual MODFLOW and Visual MINTEQ were conducted to simulate Site conditions and assist in evaluating remediation strategies for the Site. Based on the simulation results, it is recommended that a minimum pumping rate of 5,500 - 7,000 GPD for each extraction well is needed for the city pump-and-treat system to control the COC plume. The plume control mechanisms were simulated under two possible COC release scenarios: one-source and two-source releases. Pumping effects on the plume migration were also evaluated by the model.

The metal contaminated groundwater is the main concern at the Site. Various remediation alternatives were evaluated for groundwater remediation at the Site including in-situ strategies, ex-situ strategies, MNA, and augmenting the existing pumping system. After a thorough analysis and comparison of these remediation options, Metal Removal Curtain and In-Situ Iron Co-Precipitation systems stand out as the potential remedies for the Site groundwater. Combined with MNA and possible

pumping system augmentation at downgradient of the Site, total control of the COC plume is achievable.

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### **APPENDIX**

### SITE SIMULATION BY VISUAL MODFLOW

#### 1.0 Site Conditions

### 1.1 Site Hydrogeology

The Site geology consists of crushed limestone fill from ground surface to approximately six inches below ground surface (bgs). The fill material is typically underlain by Quaternary terrace deposits (Qt) of silty clays and clayey silts. The water-producing zone is encountered beneath these silts and clays at an average depth of 24 feet bgs, and is composed of fine to very coarse sand, generally coarsening with depth. Based on cumulative water-level measurements, the overall groundwater flow direction beneath the Site is to the south-southeast. During 2002, the estimated groundwater velocity at the Site ranged from 118.2 to 147.8 ft/year. The depth to groundwater, as measured in 1997, indicated that groundwater levels ranged from 18.88 to 22.86 feet below top-of-casing. The apparent hydraulic gradient was 0.2 feet per 100 feet to the south/southeast.

### 1.2 Site COC Extent

A series of comprehensive soil and groundwater investigations have been conducted at the Site. Results of these investigations indicate that a metal is the primary chemical of concern (COC) at the Site. It is suspected that the primary source of the metal in soil and groundwater at the Site was the release of a metal solution that was used in oil field services. The use of the metal at the Site was discontinued prior to 1973, and facility operations ceased in 1985, thereby removing the primary source of the metal to soil and groundwater at the Site.

At and adjacent to the Site, the metal concentrations in groundwater samples from the May 2004 sampling event ranged from 0.278 to 0.252 mg/L. Two monitoring wells located downgradient of the Site were below detection limits for the metal in March 2004; however, the metal was indicated at 0.011 mg/L for one monitoring well in November 2003, and at 0.010 mg/L for the other one in August 2003. Approximately 1000 feet south-southeast of the Site, the metal in groundwater was indicated at or above 0.018 mg/L for one monitoring well from its installation in August 2002 to the present.

As discussed above, the source of the metal affecting groundwater at the Site is likely from historical facility operations. However, the metal has also been detected in groundwater wells up- and cross-gradient to the Site. The presence of the metal in these wells could indicate that the metals is naturally occurring in the area, or is being released by some other mechanisms.

# 2.0 Modeling Approach

The groundwater modeling approach utilized a step-wise methodology that progressed from a conceptual physical model of the subsurface, to a geochemical model analysis and finally this numerical computer simulation of site-specific scenarios. This approach allowed delineation of the current site conditions and an evaluation of the effect of the hydraulic control mechanisms. The step-wise process is listed below:

- Development of a subsurface physical model (conceptualization) and numerical model setup;
- Model parameter estimation and generation of model data sets;
- Calibration of the model and establishment of various hydraulic control scenarios;
- Simulation and evaluation of the selected scenarios;
- Evaluation of the effect of the hydraulic control; and
- Preparation of the results of the modeling effort to support the engineering design.

# 3.0 Model Setup

MODFLOW was developed by USGS to simulate a wide variety of groundwater systems. Due to its extensive publicly available documentation and its rigorous USGS peer review, MODFLOW has become the worldwide standard groundwater flow model. Visual MODFLOW is the new development of MODFLOW with features such as 3-D presentation. The main objective in applying Visual MODFLOW is to simulate site-specific hydrogeological conditions in order to better understand contaminant fate and transport in the subsurface.

Groundwater flow within the aquifer is simulated in Visual MODFLOW using a block-centered finite-difference approach. Layers can be simulated as confined, unconfined, or a combination of both. Flows from external stresses such as flow to wells, recharge, evapotranspiration, flow to drains, and flow through riverbeds can also be simulated. Visual MODFLOW was developed using a mathematical finite-difference method to simulate physical conditions and processes.

To use MODFLOW, the region to be simulated must be divided into cells with a rectilinear grid resulting in layers, rows and columns. Files containing hydraulic parameters (hydraulic conductivity, transmissivity, specific yield, etc.), boundary conditions (constant heads and concentrations), and stresses (pumping wells, recharge from precipitation, rivers, drains, etc.) must then be prepared.

## 3.1 Model Grid and Layers

The region simulated by Visual MODFLOW in this study is divided into 80 rows and 50 columns. This model size allowed good spatial resolution without making the model too large to run; there are 4000 equally-sized cells in total. To simulate Site conditions more accurately, two layers are presented in the model: a top layer of clay overlying a bottom

sand layer. Different hydraulic parameters were assigned to the two layers to simulate these different materials.

#### 3.2 Model Parameters

#### 3.2.1 Basic Model Parameters

Conductivity, specific storage, specific yield, and porosity values are needed to run groundwater flow simulations in Visual MODFLOW. A summary of these parameters is given in table C-1. Values of conductivities, porosities, first layer specific yield, and second layer specific storage were obtained from field measurements, while values of the first layer specific storage and second layer specific yield were obtained from literature (Fetter, 1988).

Table A-1. Basic Parameters for Visual MODFLOW

Parameters	Units	Layer 1 (clay)	Layer 2 (sand)
Conductivity - Kx, Ky	ft/day	0.1134	31.18
Vertical Conductivity - Kz	ft/day	0.01134	3.118
Specific Storage	1/ft	0.001	0.0008
Specific Yield	-	0.048	0.2
Effective Porosity	-	0.4	0.35
Total Porosity	-	0.45	0.4

# **3.2.2** Transport Model Parameters

In the transport model, the contaminant plume migration was simulated by MT3DMS, which is part of the Visual MODFLOW package. Several parameters are needed for the transport simulation, and are presented in Table A-2. Values for these parameters were determined either through literature review or by using the model default values. Of these parameters, the solid-liquid partitioning coefficient (Kd) has the most significant

influence on the COC plume migration rate because the retardation factor (R) is strongly dependant on Kd. The formula for the retardation factor is provided below:

$$R = 1 + \frac{Pb}{n}Kd$$

where R is the retardation factor (dimensionless); Pb is the bulk density (g/cm³); n is the effective porosity; and Kd (mL/g) is the soil-water partition coefficient.

Two retardation factors were developed for the Site in order to account for the differing redox conditions encountered at and down-gradient to the Site. Kd values of 1 mL/g and 29 mL/g were selected to conservatively represent two different redox conditions. A Kd value of 1 mL/g corresponds to a retardation factor of 5.86, while a Kd value of 29 mL/g corresponds to a retardation factor of 141.94. The two retardation factors were then used for two different scenarios of transport modeling. Specifically, the retardation factor of 5.86 was used for the one-source COC release simulation, and the retardation factor of 141.94 was used for the two-source COC release simulation. A detailed discussion on the two simulation scenarios is presented in section 4 of this appendix.

Table A-2. Transport Model Parameters for Visual MODFLOW

Parameters	Units	Value
Bulk Density	lb/ft <sup>3</sup>	106.1457
Distribution Coefficient, Kd*	mL/g	1, 29
Dispersion Coefficient, $\alpha_L$	1/ft	10
Dispersion Coefficient, α <sub>H</sub> **	1/ft	1
Dispersion Coefficient, $\alpha_V^{**}$	1/ft	0.1
Molecular Diffusion Coefficient		0

#### Notes:

<sup>\*</sup> There are two Kd values used in this simulation for two different scenarios.

<sup>\*\*</sup> For the model input,  $\alpha_H/\alpha_L=0.1$  and  $\alpha_V/\alpha_L=0.01$  are used instead of using  $\alpha_H$  and  $A_V$  values.

### 3.3 Extraction Wells and Pumping Rates

There are four city extraction wells (EX-01A, -03A, -02 and -04) located downgradient of the Site for groundwater recovery. Table A-3 gives detailed information about these extraction wells. Based on flow meter reading records from 2001, 2003, and 2004, none of the four extraction wells was running at its full capacity. Tables A-4 and A-5 compare designed pumping rates and actual pumping rates from the 2001 and 2003-2004 records, respectively. Flow meter reading records indicated that all extraction wells, including the abandoned EX-01 and EX-03, were operating at about 1% of their capacities.

Flow meter records indicate that extraction well EX-02 has been removed from service since December 2003. Therefore, only three extraction wells, EX-01A, EX-03A, and EX-04, were simulated for groundwater flow and contaminant transportation with different pumping rates. Table A-6 summarizes the extraction well pumping rates used in the simulation.

Extraction Well ID\* Location (Coodinates) Screen Interval (ft) Pumping Rate(GPD) Actual\*\* X Y **Bottom** Top Design -4910 EX-01A 1888 1935.2 1945.2 63360 843 N/A\*\*\* EX-02 -4685 2300.89 1935.9 1945.9 57600 EX-03A -4665.92 2234.3 1936.1 1946.1 57600 727 EX-04 -5046.8 2405.16 1936.9 1946.9 74880 968

Table A-3. Extraction Well Information

Notes:

<sup>\*</sup> EX-01A and EX-03A were installed in 2001 after EX-01 and EX-03 were permanently abandoned. EX-02 and EX-04 were installed in 1993 alone with EX-01 and EX-03.

<sup>\*\*</sup> Actual pumping rates were calculated from flow meter readings recorded in 2003 and 2004.

<sup>\*\*\*</sup> Not in operation since December 2003.

Table A-4. Designed and Actual Pumping Rates from 2001 Records

Well ID	Designed Flow Rate (GPD)	Flowmeter Reading 1 (Gal)	Flowmeter Reading 2 (Gal)	Period (days)	Actual Flow Rate (GPD)	Operating Capacity (%)
EX-01	77760	831393	841604	20	510.55	0.6566
		841604	867078	35	727.83	0.9360
EX-02	48960	54910	62458	20	377.4	0.7708
		62458	78986	35	472.23	0.9645
EX-03	51840	625799	632168	20	318.45	0.6143
		632168	653408	35	606.86	1.1706
EX-04	72000	355074	365953	20	543.95	0.7555
		365953	390834	35	710.89	0.9873

Table A-5. Designed and Actual Pumping Rates from 2003-2004 Records

Well ID	Designed Flow Rate (GPD)	Flowmeter Reading 1 (Gal)	Flowmeter Reading 2 (Gal)	Period (days)	Actual Flow Rate (GPD)	Operating Capacity (%)
EX-01A	92160	23789.81	43262.85	34	572.74	0.6215
	63360	43262.85	65183.96	26	843.12	1.3307
EX-03A	57600	39646.03	54671.32	34	441.92	0.7672
	57600	54671.32	73580.22	26	727.27	1.2626
EX-04	74880	890889.63	909894.35	34	558.96	0.7465
	74880	909894.35	935058.36	26	967.85	1.2925

Table A-6. Pumping Rate Used in Visual MODFLOW Simulation

Well ID	Design Rate (GPD)	Pumping Rate (GPD)	Percentage of the Design Rate (%)
EX-01A	63360	843	1.3305
		2500	3.9457
		5000	7.8914
		5500	8.6806
		6000	9.4697
		7000	11.0480
		10000	15.7828
EX-03A	57600	727	1.2622
		2500	4.3403
		5000	8.6806
		5500	9.5486
		6000	10.4167
		7000	12.1528
		10000	17.3611
EX-04	74880	968	1.2927
		2500	3.3387
		5000	6.67734
		5500	7.3451
		6000	8.0128
		7000	9.3483
		10000	13.3547

# 3.4 Boundary Conditions

## 3.4.1 Constant Head

Constant heads along the northern and southern borders of the simulated region were proposed based on historical groundwater levels measured at and near the Site. A constant head of 1970 ft above mean sea level (MSL) was assumed at the northern border, while a constant head of 1962 ft MSL was assumed at the southern border.

# 3.4.2 Recharge

A recharge value of 100 mm/year was assigned for the area southeast of the Site, which encompasses approximately 80,000 ft<sup>2</sup>. This area was selected based on a review of historical groundwater levels measured at the Site, and based on surface conditions of that area (boring logs indicate that the aquifer is overlain by silt rather than silty clay there). All other areas of the simulated region assume a recharge value of zero. In order to simulate conditions encountered at the Site, recharge areas and recharge values were varied until the simulation matched measured conditions at the Site. The selected recharge area and recharge value produced a contour map that closely matched the contour maps produced from groundwater field measurements.

#### 3.4.3 Constant Concentration

To simulate a worst-case scenario—that of the metal in continuous use at the Site—constant concentration boundary conditions were used for the COC plume transport simulation under both metal release scenarios. Concentrations at each source area were assigned based on an initial concentration that would theoretically yield results matching those observed in field sampling.

The constant concentration boundary condition for the one-source scenario is presented in Table A-7

Table A-7. Constant Concentration Boundary Condition
- One-source Release Scenario

Start Time (days)	Stop Time (days)	Concentration (mg/L)
0	3650	0.4
3650	14600	0
14600	18250	1

For the two-source release scenario, the constant concentration boundary condition is presented in Table A-8.

Table A-8. Constant Concentration Boundary Condition
- Two-source Release Scenario

Source Area	Start Time (days)	Stop Time (days)	Concentration (mg/L)
1	0	18250	0.6
2	0	18250	0.04

#### 3.5 Particles

Six hypothetical particles were used to evaluate the effects of different pumping rates and time frame on the capture of COCs by the city extraction wells. Although the time frame of the simulation determines how far these particles can travel, the extraction wells' pumping rates influence the capability of these wells to capture particles. The effective area of influence of these extraction wells is termed the radius of influence. Particle travel was simulated by MODPATH, which is part of the Visual MODFLOW package. In the MODPATH simulation, particles travel with groundwater and retardation effects are ignored. Note that MODPATH is used only for determining capture radii; COC transport was modeled using MT3DMS, which allows retardation to be taken into account.

#### 4.0 Model Calibration

Model calibration involved statistical comparisons of observed groundwater head distribution with model-generated groundwater elevations, followed by comparison of

observed COC concentrations with model-generated ones for both single- and two-source scenarios.

## 4.1 Head Calibration

Table A-9 is a summary of gauged and model-generated heads of 22 monitoring wells in the model-simulated area. It can be seen from the table that the model-generated heads closely fit the field measurement data, with an average model error of 0.018%. Figure A-1 is a scatter plot of gauged and model-generated heads. For statistical analysis, a linear regression line is drawn in the figure. The linear regression equation generated from the two data sets is:

Y = 0.9999X (assuming intercept=0)

The correlation coefficient for this linear regression is R=0.9569 ( $R^2=0.9156$ ), implying a good fit between the two data sets.

#### 4.2 Concentration Calibration

Four groundwater sampling events were conducted in 2003. Nine monitoring wells had indications of the metal concentrations above the detection limit of 0.01 mg/L for at least once out of the four groundwater sampling events. Table A-10 is a summary of field-observed COC concentrations from 2003 groundwater sampling events. The average COC concentrations of the nine monitoring wells were calculated from the field data and are presented in Table A-10. For model calibration, model-generated COC concentration data from both one-source and two-source release scenarios are given in Table A-11, and model errors are calculated for both scenarios. Compared with head calibration, model errors for concentration calibration are much higher: 46.08% for one-source COC release model and 33.72% for two-source release model. However, given

the relatively high standard deviation of the observed COC concentration data, the model errors for both scenarios are within acceptable limits.

Table A-9. Gauged and Model-Generated Heads

Well ID*	Gauged Head** (ft. msl)	Model Head (ft. msl)	Head Difference (ft.)	Model Error*** (%)
1	1969.29	1969.7	0.41	0.02082
2	1969.29	1969.7	0.41	0.02082
3	1968.75	1968.9	0.15	0.00762
4	1969.58	1969.6	0.02	0.00102
5	1969.12	1969.2	0.08	0.00406
6	1969.28	1969.3	0.02	0.00102
7	1968.9	1968.9	0	0.00000
8	1969.13	1969	-0.13	-0.00660
9	1969.4	1969.7	0.3	0.01523
10	1968.98	1968.7	-0.28	-0.01422
11	1966.55	1966.5	-0.05	-0.00254
12	1967.13	1966.4	-0.73	-0.03711
13	1966.27	1966	-0.27	-0.01373
14	1967.07	1966.5	-0.57	-0.02898
15	1966.99	1966.1	-0.89	-0.04525
16	1967.37	1967	-0.37	-0.01881
17	1965.65	1966.7	1.05	0.05342
18	1967.47	1967.2	-0.27	-0.01372
19	1965.46	1965.5	0.04	0.00204
20	1965.4	1965.3	-0.1	-0.00509
21	1967.58	1966.2	-1.38	-0.07014
22	1964.56	1964.3	-0.26	-0.01323
Average				0.01798****

#### **Notes:**

<sup>\*</sup> Not represent the real well name on the site map

<sup>\*\*</sup> Gauged head data from April 1995 sampling event

<sup>\*\*\*</sup> Model error = (head difference)/(gauged head)

<sup>\*\*\*\*</sup> Average model error is the mean of absolute values of 22 model error data

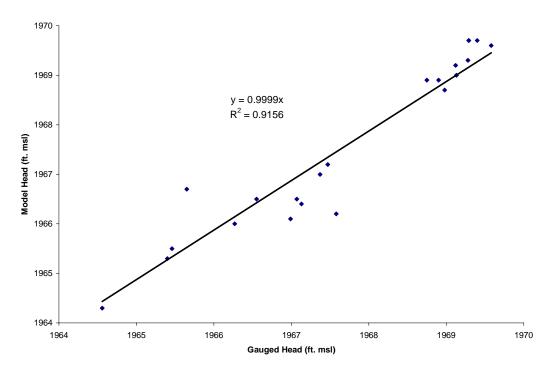


Figure A-1. Correlation of Gauged and Model Heads

	Observed COC Concentration (mg/L)				Standard	
Well ID*	2/12/2003	5/14/2003	8/27/2003	11/12/2003	Average**	Deviation**
1	0.014	0.014	0.014	0.025	0.0168	0.0055
2	ND (0.01)	0.014	ND (0.01)	ND (0.01)	0.0110	0.0020
3	0.204	0.143	0.146	0.503	0.2490	0.1716
4	0.234	0.228	0.213	0.192	0.2168	0.0187
5	0.019	0.013	ND (0.01)	ND (0.01)	0.0130	0.0042
6	0.016	0.016	ND (0.01)	0.011	0.0133	0.0032
7	0.021	ND (0.01)	0.01	ND (0.01)	0.0128	0.0055
8	0.031	0.025	0.02	0.022	0.0245	0.0048
9	0.026	ND (0.01)	ND (0.01)	ND (0.01)	0.0140	0.0080

#### Note:

- \* Not represent the real well name on the site map
- \* When calculating average concentration and standard deviation, ND = 0.01 mg/L

Table A-11. Model Calibration for Concentrations

	Model COC Concentration (mg/L)		Model Err	or** (%)
Well ID*	One-source	Two-source	One-source	Two-source
1	0.013	0.013	-22.3881	-22.3881
2	0.019	0.019	72.7273	72.7273
3	0.52	0.32	108.8353	28.5141
4	0.2	0.2	-7.7278	-7.7278
5	0.019	0.01	46.1538	-23.0769
6	0.01	0.01	-24.5283	-24.5283
7	0.02	0.019	56.8627	49.0196
8	0.013	0.013	-46.9388	-46.9388
9	0.01	0.01	-28.5714	-28.5714
Average***			46.0815	33.7214

#### **Notes:**

- \* Not represent the real well name on the site map
- \*\* Model error = (model COC concentration average observed COC concentration)/average observed COC concentration
- \*\*\* Average model error is the mean of absolute values of 9 model error data.

Figure A-2 is a scatter plot of observed and model-generated concentrations. For statistical analysis, two linear regression lines are shown in figure A-2. The linear equations generated are:

Y = 1.5752X (one-source release model and assuming intercept=0); and

Y = 1.1241X (two-source release model and assuming intercept=0).

The correlation coefficients for one-source and two-source release models are  $R_1$ =0.9175 ( $R_1^2$ =0.8418) and  $R_2$ =0.9807 ( $R_2^2$ =0.9617), respectively. Statistically speaking, the two-source model more closely fits the observed data than does the one-source model.

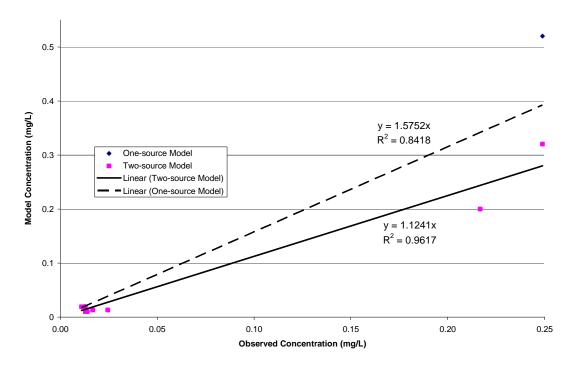


Figure A-2. Correlation of Observed and Model Concentrations

## 5.0 Simulation Scenarios

After analyzing COC concentration data over time, two possible COC release scenarios were proposed for the transport simulation. Both scenarios closely match measured COC concentrations in groundwater. The first scenario assumes that the COC was released from one source area on the property over a 50-year time frame. The second scenario assumes that the COC was released from two different source areas over a 50-year time frame. For the two-source scenario, one source area is located at the Site, and the other hypothetical source area is located downgradient of the Site. See Tables A-12 and A-13 for the one- and two-source area COC release schedules, respectively (in these tables, "T," for "transport," refers to a theoretical pumping schedule of the three extraction wells, as shown).

For the one-source COC release, a Kd value of 1 mL/g was used for the MT3DMS simulation. For the two-source COC release, a Kd value of 29 mL/g was used.

Different pumping rates of the extraction wells were used in the MT3DMS simulation to evaluate their impacts on the plume migration.

Table A-12. One-source COC Release Simulation Test Schedule

<b>Pumping Schedule</b>	Start Time (days)	Stop Time (days)	Pumping Rate (GPD)
T-1	0	14600	0
	14600	18250	Actual
	18250	73000	0
T-2	0	14600	0
	14600	73000	Actual
T-3	0	14600	0
	14600	18250	Actual
	18250	73000	5500
T-4	0	14600	0
	14600	18250	Actual
	18250	73000	10000
T-5	0	14600	0
	14600	18250	Actual
	18250	73000	7000

Table A-13. Two-source COC Release Simulation Test Schedule

<b>Pumping Schedule</b>	Start Time (days)	Stop Time (days)	<b>Pumping Rate (GPD)</b>
T2S-1	0	14600	0
	14600	18250	Actual
	18250	73000	0
T2S-2	0	14600	0
	14600	73000	Actual
T2S-3	0	14600	0
	14600	18250	Actual
	18250	73000	5500

#### **6.0** Simulation Results

Three simulation programs in the Visual MODFLOW package, MODFLOW 2000, MODPATH, and MT3DMS, were run for the Site simulation. MODFLOW 2000 and MODPATH simulated groundwater flow and particle travel patterns under various site conditions such as different extraction well pumping rates, while MT3DMS simulated the COC plume migration and control.

A 3-D physical model of the site created by Visual MODFLOW is presented in Figure A-3. Two layers in the model with different colors represent clay and sand materials existed at the Site. Figure A-4 is a semi-transparent view of the 3-D physical model.

For all six particles to be captured by the city extraction wells, each extraction well must maintain a minimum pumping rate of 5,500 gallons per day (GPD), and operate continually for at least 15 years. A pumping rate of 5,500 GPD corresponds to 7-10% of the designed pumping rates of the three extraction wells. A higher pumping rate reduces the time needed for extraction wells to capture all particles. For instance, at pumping rate of 10,000 GPD, all particles can be captured by extraction wells within 12 years. Note that retardation is not considered for contaminant migration in the MODPATH simulation. Figures A-5 and A-6 showed the particle travel pathlines without pumping and with a pumping rate of 5,500 GPD for every city extraction well, respectively.

In the MT3DMS simulation, extraction well pumping rates were varied in order to investigate the effects of differing pumping rates on the plume migration. Two scenarios were simulated based on different Kd values: a one-source COC release and a two-source COC release. For the one-source COC release simulation, pumping rates had an influence on both the COC plume migration rate and the shape of the plume. A minimum pumping rate of 7,000 GPD (about 9-13% of the designed pumping rates for the three extraction wells) for each extraction well is needed to control the COC plume.

Below that pumping rate, the COC plume will pass the city extraction wells and continue to travel downgradient. At a pumping rate of 7,000 GPD, all three city extraction wells need to operate continually for approximately 85 to 100 years to control the COC plume and reduce the COC concentration below 10 ppb throughout the region simulated.

For the two-source release simulation, the city extraction wells have limited use for the COC plume control. Even if each extraction well pumps at a rate of 5,500 GPD and operates continually for 150 years, the COC plume will not migrate to the city extraction wells due to the higher Kd value (and the higher retardation factor R). The COC plume migrates very slowly, even under very high pumping rates.

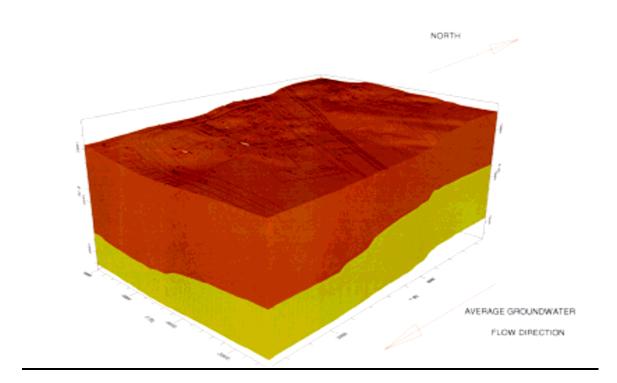


Figure A-3. Site Physical Model

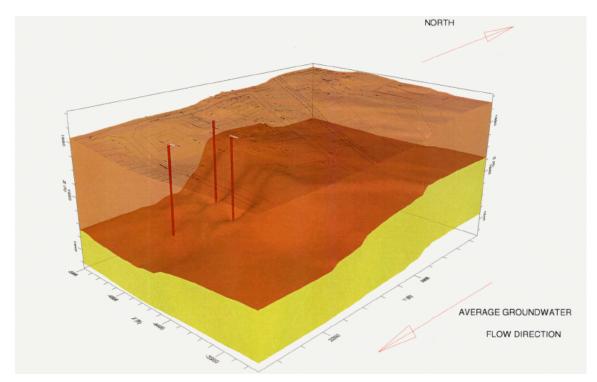


Figure A-4. Semi-transparent View of the Site Physical Model

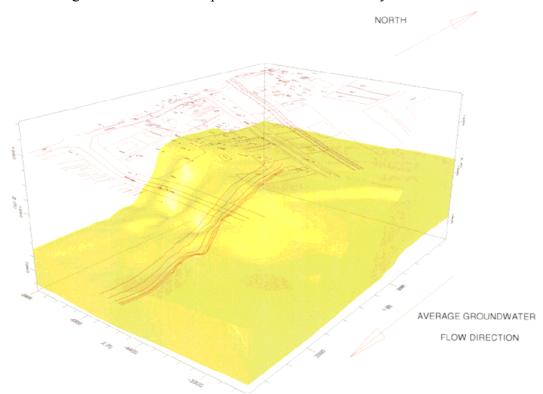


Figure A-5. Baseline Site Conditions without Pumping

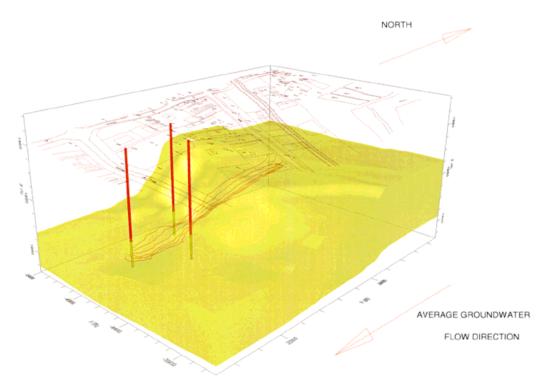


Figure A-6. Site Conditions with Appropriate Pumping

# 7.0 Reference

Fetter, C.W., 1999. Applied Hydrogeology (2nd ed.). Macmillan Publishing Company: Don Mills, Ontario.

# **VITA**

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