PILOT STUDY REPORT
BUILDING 40 IN SITU CHEMICAL OXIDATION
Watervliet Arsenal, Watervliet, New York

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1.0 Introduction

A Pilot Study was conducted to evaluate the effectiveness of in-situ chemical oxidation using potassium permanganate for reducing the concentration of CVOCs in the bedrock groundwater in the Building 40 area. This Pilot Study was conducted in accordance with the *Work Plan for Building 25 and Building 40 Pilot Studies, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York* (Pilot Work Plan) (Malcolm Pirnie, 2001a). The goals of the Pilot Study were as follows:

- Assess the degree to which CVOCs were present in the shale bedrock matrix through rock core sampling;
- Evaluate whether potassium permanganate could be effectively delivered and distributed through the bedrock treatment area;
- Confirm that CVOCs in the bedrock groundwater could be oxidized by the permanganate;
- Assess the persistence of the permanganate in the subsurface; and
- Estimate the degree and rate of diffusion of permanganate into the shale bedrock matrix.

2.0 In Situ Chemical Oxidation Treatment Concept

2.1 Selection of In Situ Chemical Oxidation using Permanganate

In-situ chemical oxidation (ISCO) involves the delivery and distribution of oxidants and other amendments into the subsurface to transform contaminants of concern into innocuous end products such as carbon dioxide (CO_2), water, and inorganic compounds. The primary advantages of ISCO technologies are their relatively low cost and short treatment times. Since the reaction is near immediate, treatment is far more rapid than biological techniques and can be faster than thermal or vapor recovery technologies. Also, the technology does not generate large volumes of waste material that must be disposed of and/or treated. ISCO generally provides the greatest benefit for localized source areas since it is capable of treating very high concentrations of contaminants rapidly. ISCO typically becomes prohibitively expensive over large treatment areas. The appropriateness of ISCO technology at a site depends on matching the oxidant and delivery system to the site contaminants and site conditions.

The most common oxidants utilized for ISCO are hydrogen peroxide (Fenton's reagent), potassium and sodium permanganate, sodium persulfate, and ozone. Potassium permanganate was selected as an oxidant for the Building 40 Pilot Study for several reasons:

- The other common oxidants are stronger than permanganate; therefore, they degrade more rapidly in the environment. Other oxidants' short active lives are not conducive to the longer diffusive time scales required to treat the rock matrix. Permanganate is more stable and is expected to remain active in the subsurface for weeks or months.
- There is a higher risk of excess pressure building in the subsurface by using other oxidants (e.g., Fenton's reagent) rather than permanganate
- Permanganate is effective over a wider range of pH than Fenton's reagent, which is most effective in acidic conditions

The main reason for the selection of potassium permanganate was that unreacted potassium permanganate in solution is relatively stable, it can diffuse into media with low permeabilities (e.g., silt, clay, porous rock) over time, further enhancing oxidant delivery to hard-to-treat contaminated zones. This is particularly advantageous at Building 40, since it is believed that a significant portion of the contaminant mass has diffused into the rock matrix. As contaminant concentrations decrease in the fractures following permanganate injections, the concentration gradient will lead matrix contamination to diffuse out of the rock matrix into the fractures. Application of excess potassium permanganate will allow for diffusion of permanganate into the matrix at the same time as contamination is diffusing out of the matrix (i.e., the reactants will be moving towards each other), speeding the treatment of contamination sorbed to the rock matrix.

2.2 Mechanics of ISCO using Potassium Permanganate

The oxidation of PCE (C_2Cl_4) and TCE (C_2Cl_3H) by potassium permanganate ($KMnO_4$) is governed by the following reactions:

$$C_2Cl_4 + 2KMnO_4 \rightarrow 2\,CO_2\,(aq) + 2MnO_2\,(s) + 2KCl + Cl_2 \qquad (1)$$

$$C_2Cl_3H + 2KMnO_4 \rightarrow 2\,CO_2\,(aq) + 2MnO_2\,(s) + 2KCl + HCl \qquad (2)$$

Chemical oxidation occurs at both the soil interface and free-phase interface (for NAPL situations) and within the interstitial pore spaces in the saturated subsurface (for dissolved compounds).

Potassium permanganate can oxidize a wide range of inorganic and organic compounds including:

- Chlorinated solvents (CVOCs)
- Polycyclic aromatic hydrocarbons (PAHs)
- Phenolics (including creosols)

Cyanides

Organic compounds that contain carbon-carbon double bonds (alkenes) are more readily oxidized by permanganate than compounds having single carbon-carbon bonds (alkanes). Thus, permanganate is more effective at remediating chlorinated CVOCs consisting of TCE or PCE rather than 1,1,1-trichloroethane (TCA).

Environmental parameters that influence the rate and degree of potassium permanganate oxidations include:

- pH (effective over a range of 3 to 12 with an optimum near 7)
- Temperature
- Contact (or reaction) time
- Oxidant concentration

2.3 Potential Limitations

Some potential limitations to the use of potassium permanganate include the following:

- The potential to alter subsurface biogeochemistry and locally mobilize co-contaminants (e.g., redox sensitive metals such as Cr). This issue is not of concern at Building 40.
- The potential for manganate (Mn^{4+}) to be reduced to dissolved divalent manganese (Mn^{2+}) under low-pH or redox conditions.

Hazardous intermediate compounds may be formed due to incomplete oxidation caused by insufficient quantity of the oxidant, the presence of interfering compounds (natural organic-rich media, iron and/or manganese) that consume the reagents, and/or inadequate mixing or contact time between contaminant and oxidizing agent.

The by-products (HCl, Cl_2, etc.) released into the subsurface are generally not considered harmful in the environment. However, it is important to understand the fate of the primary by-products in order to minimize adverse impacts to the treatment zone.

- **CO_2 – carbon dioxide** will combine with water to form the carbonate series and lower the pH of the ground water.
- **Cl_2 – chlorine gas** is highly reactive, and it will readily combine with water to form hypochlorous acid (HOCl) and hypochlorite (OCl^-). These two compounds are also very strong oxidants.
- **HCl – hydrochloric acid** will be neutralized in carbonate environments.
- **MnO_2 – manganese dioxide** will precipitate out, coating the subsurface. The buildup of manganese dioxide, and other manganese oxides that may be formed, may reduce matrix permeability over time.

3.0 Rock Core Testing

In conjunction with the field elements of the Pilot Study, representative rock core samples collected from monitoring wells drilled during the CMS Data Gap Study were sent to Golder Associates Ltd. (Golder) of Mississauga, Ontario, Canada for analysis of physical and hydrogeologic parameters. Matrix diffusion tests were also performed on the rock cores to evaluate the rock matrix diffusion coefficient for the bedrock in the Building 40 area. The results of the rock core testing are summarized in Table 1. Detailed results of the testing are presented in the Golder report contained in Attachment 1. As shown in Table 1, the average hydraulic conductivity of the shale bedrock matrix is approximately $3x10^{-6}$ feet per day (ft/d) indicating that, as expected, advective groundwater transport in the bedrock is entirely controlled by fractures. The average porosity of the Watervliet shale is approximately 2.3 percent, as compared to a typical range of five percent to 25 percent for sedimentary rocks (shale and sandstone). This low porosity is likely a result of the low-grade metamorphism to which the rock has been exposed. The average matrix diffusion coefficient (D) of the shale was $7.5x10^{-7}$ cm^2/second.

3.1 Bedrock Coring and Monitoring Well Installation

As discussed in Section 2.3, five additional bedrock groundwater monitoring wells, designated MW-74 through MW-78, were installed in the Building 40 area as part of the chemical oxidation Pilot Study. Each monitoring well was installed in accordance with the *Work Plan – Additional Monitoring and Pilot Test Injection Well Point Installations, Corrective*

Measures Study, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York (Drilling Work Plan) (Malcolm Pirnie, 2001b).

3.1.1 Coring

During drilling, continuous HQ-size bedrock cores were collected in five foot intervals from the competent bedrock surface to the final depth the well from each monitoring well borehole with the exception of monitoring well MW-76. Monitoring well MW-76 was drilled without coring since it was determined that sufficient information on the characteristics of the bedrock had been collected previously in the area of this monitoring well. Each core sample was visually inspected and logged by the on-site geologist upon retrieval from the borehole. In accordance with the Pilot Work Plan, rock core samples from monitoring wells MW-74 and MW-75 were collected, crushed, specially preserved, and then sent to the University of Waterloo (UW) for analysis of CVOCs in the rock matrix (see Section 3.3 below for further discussion). Several of the rock core samples were also preserved for a bench-scale diffusivity study to evaluate that rate of potassium permanganate diffusion into the rock matrix.

Discrete interval groundwater samples were collected at 20 foot intervals during drilling of each monitoring well boreole using a packer system to isolate the lower portion of the boring. Where possible, a minimum of three interval volumes was purged from each sampling interval prior to sampling using a submersible pump. Sampling intervals that were purged to dryness were allowed to recover before the collection of a groundwater sample. In accordance with the Drilling Work Plan, monitoring for hydraulic connection was performed during purging of each borehole interval to ensure that the new monitoring wells were hydraulically connected to the planned potassium permanganate injection points. Hydraulic monitoring was performed by measuring changes in water levels in the bedrock monitoring wells surrounding the drilled borehole during purging of the discrete interval packer zones.

Upon reaching the final depth, each well was developed to remove drilling water lost to the formation and any sediment resulting from coring. Drilling logs for the monitoring wells installed during the Pilot Study are presented in Attachment 2.

3.1.2 Well Completion

In accordance with the Pilot Work Plan, each new monitoring well was completed with a multi-level monitoring system. Monitoring wells MW-74 and MW-75 were completed using the

Solinst Continuous Multi-Channel Tubing (CMT®) System. Monitoring wells MW-76, MW-77, and MW-78 were completed using the Westbay MP38 Multi-Level Sampling System (Westbay). Monitoring wells MW-65, MW-68, MW-71, and MW-72, which were installed during the CMS Data Gap Study, were also completed with Westbay multi-level monitoring systems prior to the Pilot Study. Pilot Study monitoring well construction is summarized in Table 2. Multi-level monitoring well construction diagrams are presented in Attachment 3.

3.2 Rock Core CVOC Profiles

3.2.1 Field Procedures

During coring at MW-74 and MW-75, a three-person field crew from the University of Waterloo (UW) collected samples from the rock cores for quantitative CVOC analysis and physical property measurements. Rock coring at these locations was conducted from December 5 to 13, 2001. Coring was started at 20 ft and 17.5 ft bgs, extending to 150 ft and 150.5 ft bgs, for a total cored interval of 130 ft and 133 ft at MW-74 and MW-75, respectively.

Collection of samples was performed according to the protocol outlined in the Pilot Work Plan. Three types of samples were collected: (1) CVOC samples, which were crushed and preserved in the field by placing in jars with methanol for extraction and later laboratory analysis, (2) intact adjacent sections of core for physical property measurements (moisture content/porosity and fraction organic carbon), and (3) intact sections of core for laboratory diffusion tests. Duplicates, field blanks and equipment blanks were retained during sampling, and trip blanks were included with the CVOC samples shipped to UW. Table 3 contains a summary of samples collected by UW during the coring episode. Rock samples were collected during coring by breaking specific sections of the core, placed in aluminum foil lined PVC trays, with a hammer and chisel. CVOC samples were collected at fractures (i.e. one of the fracture faces) and bedding planes, at lithologic changes, and from matrix blocks between fractures. Sample lengths typically ranged from 0.1 to 0.4 ft of core, and averaged 0.2 ft. CVOC samples were immediately wrapped in aluminum foil to minimize volatile losses, and were taken to an on-site field lab for crushing/processing. Prior to crushing, the outer rind of the core samples was chipped off to eliminate potential error from contact with the drilling fluids. Samples were then crushed with the an hydraulic rock crusher provided by UW using five stainless steel rock crushing cells, which typically allowed samples from one core run to be processed. Between samples, the cells were decontaminated using a four-part wash and rinse sequence (soapy water, clean water, methanol, DI water). The crushed rock samples were placed into 125-mL wide-mouth jars with Teflon-lined screw caps, containing a known amount (~60 mL) of HPLC grade methanol (MeOH), which acts to extract and preserve the CVOC mass. On average, five samples were collected for each core run, with a total of 118 and 115 CVOC samples (including duplicates) collected from MW-74 and MW-75, respectively. Excluding duplicates, and using the total cored interval, the average sample spacing was about 1.2 ft.

Rock cores were obtained on average every 20 to 30 minutes. A break of at least one hour was usually necessary after every 20 ft of coring to allow crushing activities to keep pace with coring. On average, about 40 ft of core per day could be collected and processed, including logging, sampling, crushing/processing, packaging, QA/QC, documentation and shipping. CVOC samples were packed and shipped to UW for analysis in one of three ways (bubble wrap and zip-lock bags, plastic containers filled with DI water or plastic containers containing no water). Samples for porosity determination were double wrapped in aluminum foil and plastic wrap, then duct taped and coated in a wax mixture. All physical property samples were shipped back to UW in a separate cooler. Chain of custody forms were filled out prior to sample shipping and signed upon arrival at UW. All samples were shipped in coolers containing ice both on top and below the samples.

3.2.2 Analytical and Calculation Procedures

Laboratory rock matrix CVOC analyses were conducted after allowing sufficient time for the CVOCs to completely extract into the methanol (approximately six weeks). An aliquot of methanol was injected directly into a gas chromatograph (GC) for separation and quantification using a microelectron capture detector (μ−ECD). The list of analytes quantified included TCE, PCE and the DCE isomers. The direct, on-column injection of methanol onto the gas chromatograph was tailored by UW for analysis of PCE, TCE and relevant breakdown products so that the resulting detection limits were very low (<0.1 ug/L in MeOH for TCE and PCE, and <10 ug/L in MeOH for the DCE isomers). These were converted to equivalent pore water concentrations using bulk density, porosity and sorption estimates, and rock sample and MeOH masses, as discussed later.

The laboratory analysis provided the total mass of each CVOC per unit mass of wet crushed rock sample (c_t) (e.g., μg PCE per g wet rock) and included CVOC mass present in the aqueous, sorbed and DNAPL (if present) phases. Equivalent pore water concentrations (c_w) were estimated using:

$$c_W = c_t \frac{\rho_{bwet}}{R\phi} \qquad [1]$$

where ρ_{bwet} is the rock wet bulk density (g/cm^3), ϕ is the porosity and R is the retardation factor, accounting for CVOC mass sorbed to organic carbon present in the rock. Retardation factors (R) were estimated using the relation:

$$R = 1 + \left[\frac{\rho_b}{\phi}\right] K_d \qquad [2]$$

where K_d is the distribution coefficient (mL/g) and ρ_b is the dry rock bulk density (g/cm^3). It was assumed that sorption is rapid, linear and reversible.

In converting total CVOC concentrations to equivalent porewater concentrations, average values for porosity (ϕ =0.023) and bulk density (ρ_b=2.66 g/cm^3) were used based on the five samples analyzed by Golder Associates. Distribution coefficients were estimated using the correlation $K_d = K_{oc}\ f_{oc}$, where literature values were used for the organic carbon partitioning coefficients (K_{oc}) of 380, 92 and 86 mL/g for PCE, TCE and cDCE, respectively (Table 12.1, Pankow and Cherry, 1996). Fraction organic carbon (f_{oc}) was measured by the Organic Geochemistry Lab at UW, according to the procedure outlined by Churcher and Dickhout (1987). Based on the fifteen samples collected from MW-74 and MW-75, f_{oc} ranged from 0.31% to 0.68%, with an average of 0.40%. The average f_{oc} was used in the retardation factor estimates. Using these parameters, average retardation factors of 177, 44 and 41 were estimated for PCE, TCE and cDCE, respectively. For samples where the estimated pore water concentration exceeded the aqueous solubility (~240 mg/L for PCE and 1,400 mg/L for TCE), it is likely that DNAPL was present. However, such inferences must be made with caution, considering uncertainty in parameters used to estimate the pore water concentrations, particularly the estimated retardation factors. Pore water detection limits were approximately 0.16 μg/L, 0.04 μg/L and 6 μg/L for TCE, PCE and cDCE, respectively, using Equation 1 and the above parameter values, assuming MeOH detection limits of 0.1 μg/L for PCE and TCE and 5.5 μg/L for cDCE, and 60 mL of MeOH and 100 g of rock sample placed in each jar.

3.2.3 Results

Figures 1a and 1b show plots of total PCE, TCE and cDCE concentrations in MW-74 (Figure 1a) and MW-75 (Figure 1b), obtained directly from the laboratory analyses. Estimated equivalent pore water concentrations are shown in Figures 2a and 2b for MW-74 and MW-75 respectively. As indicated on the equivalent pore water plots, several samples from MW-74 and MW-75 have estimated equivalent pore water PCE concentrations within an order of magnitude of solubility; however, only one sample from MW-75 (from ~73 ft bgs) actually exceeds the solubility value. Therefore, this provides evidence that PCE DNAPL is likely absent at most depths with the possible exception of the one sample from MW-75. However, as discussed above, uncertainty in parameter estimates, particularly retardation factors, complicate such an assessment. Analysis of f_{oc} before and after batch permanganate consumption tests has indicated the organic carbon to be quite recalcitrant to oxidation by permanganate, which might also indicate that it is not as sorptive. If this is the case, by examination of Equation 1, lower R values would result in higher estimated pore water concentrations and possibly more samples where the estimated pore water concentration exceeds PCE aqueous solubility.

4.0 Pilot Study $KMnO_4$ Injections

The Pilot Study consisted of two phases of $KMnO_4$ solution application. The purpose of the first phase was to test delivery of $KMnO_4$ solution in a major transmissive zone (identified by hydro-geophysical testing) and monitor horizontal and vertical distribution in the contaminated area. The second phase was a longer-term permanganate delivery designed to flood certain areas with sufficient permanganate to allow for diffusion into the rock matrix. The methods followed and results obtained for each phase are described in detail in the following sections. Table 4 summarizes injection pressures, volumes, and average flow rates for each injection event performed during Phases 1 and 2.

4.1 Permanganate Injection Methodology

Malcolm Pirnie contracted with Environmental Business Solutions, Inc. (EBSI) to perform the $KMnO_4$ injections throughout the course of the Pilot Study. EBSI purchased potassium permanganate from Carus Chemical Company and arranged to have it delivered to the Arsenal in 5-gallon (25-kilogram) pails. Potassium permanganate exists as a fine powder that is dissolved in water prior to injection. EBSI used a recirculating mixer assembly to mix the permanganate with potable water obtained from a nearby fire hydrant. Although the Pilot Work Plan specified use of a 5% potassium permanganate solution (approximate solubility of potassium permanganate at 20°C), it was not possible to maintain that concentration due to low ambient air and water temperatures. The highest achievable permanganate solution concentration was approximately 2.5%.

4.2 Phase 1 Injection

During Phase 1 of the Pilot Study, approximately 8,000 gallons of a 2.5% solution of $KMnO_4$ were injected at MW-59 from March 5 to March 11, 2002. MW-59 has its open interval between 76-96 feet bgs and its static water level is typically 11 feet bgs. MW-59 was chosen for the Phase 1 injection because it intersects a highly transmissive zone that was expected (based on the hydro-geophysical tests) to be extensive and well-connected over a large lateral and vertical area. During the injections, samples were collected from several wells and analyzed for field parameters (i.e., chloride, specific conductivity and permanganate), as well as for CVOC concentrations. The data collected during Phase 1 injection are included in Attachment 4. The results of field parameter monitoring are discussed below.

4.2.1 Injection Rates

Phase 1 injection of $KMnO_4$ commenced on March 5, 2002. Initially, the $KMnO_4$ solution was delivered via gravity flow at MW-59. On the second day of injection (March 6, 2002), the PVC casing at MW-59 was extended approximately five feet above ground surface to enhance injection pressure. Pressurized injections were performed on March 7, 8, and 11 to increase $KMnO_4$ injection rates and consequently, travel times. Applied injection pressures ranged from approximately 5 to 22 pounds per square inch (psi) including water column pressure. Flow rates ranged from three gallons per minute (gpm) to eight gpm.

4.2.2 Water Level Fluctuations

Three transducer arrays were set up during Phase 1 injection to monitor water level, pressure, and temperature shifts. The transducers were transferred between monitoring wells to obtain data from multiple locations. Figure 3 shows the effect of varying injection rates at MW-59 on water levels at MW-59, MW-62, MW-65, and MW-71 during injection on March 6, 2002. All of the Westbay sampling ports were open at MW-65 and MW-71 during injection at MW-59. As expected, there was an immediate response at MW-59, where water levels rose up to 16 feet above the baseline measurement (i.e., ground level) when the injection rate peaked at 6 gpm for the day. The response at MW-71 (located between MW-59 and MW-65) was more muted, with peak water levels rising up to three feet above the baseline measurement. Peak water levels at MW-65 rose approximately one foot above the baseline measurement and as high as two feet on March 7th when the injection was pressurized. There was no response at MW-62. The transducer arrays were installed up-gradient of MW-59 on March 11th in MW-68, MW-77, and MW-78. There was a slight response of approximately 0.1 feet at MW-78, 0.35 feet at MW-77, and 0.15 feet at MW-68 during injection on March 11th.

4.2.3 Field Parameters

Field parameters including specific conductivity, chloride concentrations, and permanganate concentrations were measured frequently at several locations throughout the Phase 1 injection period. Specific conductivities were measured using a standard probe; chloride concentrations were determined using a digital titrator; and permanganate concentrations were measured using a spectrophotometer. Graphs showing results of field parameter monitoring are included in Attachment 4.

Specific Conductivity

Specific conductivity was monitored as an indicator to impending arrival of $KMnO_4$ because a rise in specific conductivity can be measured prior to visually identifiable $KMnO_4$ due to dissolution of the potassium cation and the permanganate anion. As expected, at the locations where permanganate was later detected, increasing specific conductivities were measured prior to detection of permanganate. The higher the concentration of permanganate, the higher the specific conductivity of the sample. Specific conductivities rose even at locations where $KMnO_4$ was not detected, reflecting the temporary increased ionic strength of groundwater in the vicinity of MW-59.

Chloride

Chloride (Cl^-) was also monitored as an indicator to impending arrival of $KMnO_4$. The oxidation of chlorinated solvents produces Cl^-. It was expected that Cl^- would arrive at monitoring points before the $KMnO_4$ front if it were pushed forward in advance of the reaction front. Contrary to expectations, Cl^- concentrations decreased at most locations where permanganate was detected. At locations where permanganate was not detected, Cl^- concentrations were generally stable. One possibility for why increased Cl^- concentrations were not detected is that the increased ionic strength of the samples containing permanganate may have interfered with the chloride titration. Also, production of Cl^- may have not have been detectable because initial concentrations of Cl^- were quite high, ranging from 200 to 350 milligrams per liter (mg/L).

Permanganate

Permanganate was measured throughout the Phase 1 injection period to estimate the time of arrival of $KMnO_4$ in order to gain insight into the nature (i.e., permeability and connectivity) of the fracture network. It was predicted, based upon geophysical testing results, that the large volume injection of $KMnO_4$ into the highly transmissive zone in MW-59 would cause rapid transmission of $KMnO_4$ to the MW-71/MW-74 and MW-65/MW-75 monitoring clusters, and somewhat slower transmission to other monitoring locations such as MW-34, MW-58 and MW-68 and perhaps MW-72. The resulting distribution of $KMnO_4$ solution was similar to what was expected. The $KMnO_4$ solution was first detected at the MW-71/MW-74 monitoring well cluster on March 7th (third day of Phase 1 injection). Approximately one hour later, it was detected at the MW-65/MW-75 monitoring cluster. A very low concentration of $KMnO_4$ was detected at MW-34 at about the same time as the detections at the other wells. Due to the close timing of the $KMnO_4$ arrival at monitoring points, the variations in injection pressures and flow-rates, and changing permanganate concentrations due to on-going reactions, it was not possible to discern travel time between the monitoring points. The times of initial detection of $KMnO_4$, and the concentrations initially detected are summarized in the table below. Note that the detection times are presented for comparison only, since injections were not continuous.

Location (Well-Monitoring zone)	**Time of KMnO4 Detection After Start of Injection (minutes)**	**$KMnO_4$ Concentration (mg/L)**
MW-65-1	3170	207
MW-74-3	2984	399

MW-34	3130	25
MW-71-2	3105	811
MW-75-1	3195	462

The first arrival of $KMnO_4$ at each location occurred at very low concentrations and increased throughout the injection period. For instance, the initial detected concentration of $KMnO_4$ at MW-74-3 was 399 mg/L; the $KMnO_4$ concentration rose to 2,860 mg/L after 1.5 hours, to 4,400 mg/L after another 1.5 hours, and then to 6,070 mg/L after another hour. For comparison, the injected $KMnO_4$ solution concentration was approximately 25,000 mg/L.

4.3 Phase 2 Injection

Phase 2 consisted of $KMnO_4$ injections into MW-65 and MW-71 in April, May and June 2002, with the purpose of flooding these areas and achieving $KMnO_4$ diffusion into the rock matrix. MW-65 and MW-71 were selected for the Phase 2 injections because they are both completed with Westbay systems, which allow for the injection of $KMnO_4$ into several different depth intervals in each well, either simultaneously or individually. Also, it was expected that the materials from which the Westbay system is constructed should not be damaged by the strong oxidation capacity of $KMnO_4$ (this was not the case – see further discussion in Section 3.??). The Pilot Study Work Plan specified an injection frequency of between 2 weeks and 4 weeks, depending on field observations of $KMnO_4$ persistence. The goal was to maintain a $KMnO_4$ concentration of at least 1% throughout the duration of Phase 2 to encourage diffusion of MnO_4^- into the rock matrix in the vicinity of the injection points (MW-65 and MW-71). After the first Phase 2 injection, all of the sample intervals at MW-74 and MW-75 (located directly adjacent to MW-71 and MW-65) were tested daily for $KMnO_4$ until $KMnO_4$ concentrations fell to less than 1% in any of the sample ports. Since $KMnO_4$ concentrations fell below 1% in at least one sampling point within the first two weeks of monitoring, the Phase 2 injection frequency was set at two weeks.

A total of 8,320 gallons of 2.5% $KMnO_4$ solution were injected into MW-65 and MW-71 over a series of five injection events. Injection was accomplished by gravity feed of the $KMnO_4$ solution into the inside of the Westbay casing, with the exception of the final injections in June 2002. Injection flow rates decreased markedly in both wells after the second injection. Injection volumes, pressures, and flow rates for each well are summarized in Table 4.

All of the Westbay ports in both MW-65 and MW-71 were kept open during the injection period. Theoretically, when the $KMnO_4$ was fed into the casings and more than one port was open, the $KMnO_4$ entered each port at a relative rate in proportion to the transmissivity of each port interval. Thus, if one interval was much more transmissive than the others, it received nearly all of the injected volume. Both MW-65 and MW-71 have Westbay pumping ports situated at depth intervals with highly transmissive zones. Therefore, it is expected that the majority of the $KMnO_4$ solution left the Westbay systems through the ports associated with the high transmissivity zones. After completion of each Phase 2 injection, the high transmissivity Westbay ports were closed, and additional $KMnO_4$ solution was poured into the Westbay casings to bring the fluid level up to the ground surface with only the low transmissivity ports (i.e., port 3 in MW-71 and ports 4 and 6 in MW-65) open. This port configuration allowed for slow $KMnO_4$ distribution to the lower transmissivity zones in the rock matrix. The $KMnO_4$ solution depth was monitored and adjusted as required to maintain at least five feet of head as compared to the highest open port. The permanganate solution levels in MW-65 dropped gradually; however, the MW-71 permanganate levels did not change.

The Pilot Study Work Plan called for the injection of $KMnO_4$ solution into MW-58 at the end of Phase 2 to treat any CVOC contamination that may have been displaced from up-gradient fractures during previous injection events. Monitoring at MW-58 did not indicate any change in CVOC concentrations throughout the course of the Pilot Study, so permanganate was not added to MW-58.

5.0 Pilot Study Monitoring

The main purpose of the pilot study monitoring program was to confirm that the $KMnO_4$ being distributed in the fractured rock was in fact destroying chlorinated solvents, and to assess the geochemical impacts on the system. During the pilot study, three synoptic sampling rounds were performed during which samples from all monitoring locations and depths in the pilot study area were collected and analyzed for CVOCs, inorganic parameters, and C12/C13 isotopes. Monitoring wells MW-62, MW-68, MW-77, and MW-78 were selected to monitor up-gradient aquifer conditions. Monitoring wells MW-51, -58, -59, -65,–71, -74, and -75 are located in the source zone and were sampled to monitor the effectiveness of the potassium permanganate injections. Monitoring wells MW-72 and MW-76 were selected to monitor down-gradient aquifer conditions.

A baseline sampling round was performed in February 2002, prior to Phase 1 injection. The two other full sampling rounds were performed in March 2002 and July 2002, immediately after the end of Phase 1 and Phase 2 injections, respectively. An additional full sampling event was performed in January 2003 (CVOCs and C12/C13 isotopes only). The data collected in January will represent the baseline conditions for the full-scale remedy implementation (see Section 4.0).

5.1 Chlorinated Volatile Organic Compounds

Samples for CVOC analysis were collected in accordance with the methods specified in the Pilot Study Work Plan. The University of Waterloo performed the CVOC analyses. The results of CVOC analyses from samples collected throughout the pilot study are tabulated on Table 5. The March and July 2002 CVOC results remained stable compared to the baseline (February 2002) results, with the exception of the sampling locations where permanganate was detected during Phase 1 and Phase 2. At the sampling locations where permanganate was detected, CVOC concentrations diminished significantly, often to non-detectable concentrations.

In several instances, permanganate was present in a sample (i.e., the sample was purple), but CVOCs were still detected in that sample. This is because the CVOCs and permanganate were not in contact for a sufficient period of time for all of the CVOC mass to be oxidized. In order to accurately represent sub-surface conditions at the time of sample collection, a small quantity of sodium bisulfite was added to quench any permanganate present in sample vials, effectively halting CVOC oxidation reactions.

The January 2003 CVOC analyses showed that CVOC concentrations had rebounded to pre-injection concentrations. The January 2003 results are discussed in greater detail in Section ??.

5.2 Carbon Isotopes

5.2.1 Rationale

Carbon isotope analyses were performed to verify that decreases in CVOC concentrations were the result of chemical oxidation, not displacement or other mechanisms. The method is based on the observation that $KMnO_4$ oxidation is preferential for the lighter isotope (i.e., destroys ^{12}C more rapidly than ^{13}C). This preference causes the remaining CVOC carbon to become enriched in the heavier isotope (i.e., ^{13}C). The ^{13}C analyses were done by mass spectrometry, in which the ratio of ^{13}C to ^{12}C relative to a universal standard is determined. The University of Waterloo group has developed a method that enables the ^{13}C analyses to be performed on samples containing very low CVOC concentrations. This is important because successful remediation causes the CVOC concentrations to decline to very low levels and then to absence in many places.

During and after $KMnO_4$ injection, there were three types of water in the system, classified based on chlorinated solvents status:

Type 1 - water with no chlorinated solvents (fully treated by $KMnO_4$ - this water was purple for a period of time).

Type 2 – water with remnant chlorinated solvent concentrations – some or much of the solvent mass at this location was destroyed by $KMnO_4$ oxidation.

Type 3 – water that has not had any of its chlorinated solvent mass oxidized by $KMnO_4$

^{13}C analyses were conducted on samples of Type 2 and Type 3 waters. Type 1 waters cannot be analyzed for ^{13}C because no chlorinated solvent mass exists in these waters. The optimal sample type for ^{13}C analyses is Type 2 samples, where the solvent concentrations have declined but not disappeared completely. At the time of sampling in the field (after injections), chlorinated solvent concentrations were unknown; therefore, samples were collected for ^{13}C analyses along with separate samples for CVOC analyses. The University of Waterloo analyzed the CVOC samples first, and based on those results selected the samples for ^{13}C analysis. CVOC samples have a much shorter holding time than the ^{13}C samples, and therefore ^{13}C samples were always performed after the CVOC results were available.

5.2.2 Carbon Isotope Results

Table 6 summarizes the results from all of the ^{13}C analyses. Average, minimum, and maximum initial $\delta^{13}C$ from samples collected in February 2002 are shown in the table below:

Initial Carbon Isotope Values ($\delta^{13}C$), February 2002 (per mil)

	PCE	TCE	cis-DCE
Minimum (‰)	-26.82	-27.79	-26.79

Maximum (‰)	-33.97	-40.53	-35.71
Average (‰)	-30.58	-32.07	-32.45

There is approximately a 30% difference between the initial minimum and maximum isotope values for each compound. Therefore, only isotopic shifts of greater than 30% were considered to be indicative of a permanganate effect for purposes of this analysis. Enrichment in the ^{13}C isotope results in a positive shift in the $\delta^{13}C$ value. The most significant isotopic shifts were observed at MW-65-1, MW-65-7, MW-72-1, MW-72-2, MW-74-3, MW-74-4, MW-74-6, MW-75-3, and MW-76-1 (see Table 6). In addition, although only one ^{13}C isotope result was obtained from MW-71-3, the result (-6.67‰) is sufficiently higher than the average initial value for cis-DCE to suggest a permanganate effect. For the most part, the locations where isotopic shifts were noted correlate to detections of permanganate. The exception is MW-72, which is the farthest down-gradient monitoring point. The detection of permanganate-impacted CVOCs at MW-72 provides evidence that MW-72 is hydraulically connected to the Building 40 injection/monitoring network. It should be noted that although permanganate was detected at MW-34, no significant isotopic shift was detected. This is likely because the concentration of permanganate that reached MW-34 was too low to oxidize a significant portion of the CVOC mass.

In general, the extent of the isotopic shift effect increased as the number of substituted chlorines decreased. For instance, at MW-74-6, the January 2003 isotopic shifts for PCE, TCE, and cis-DCE were 11%, 54%, and 74% respectively, compared to the March 2002 results. At MW-65-7, the July 2002 isotopic shifts for PCE, and cDCE were 55%, and 306% respectively, compared to baseline results. The greater isotopic shifts in cDCE compared to TCE and PCE are likely related to the oxidation rates. The oxidation rate of cDCE is faster than TCE, which is faster than PCE. For instance, it was demonstrated that 95% oxidation was achieved in approximately 15 minutes for cDCE, 40 to 80 minutes for TCE, and 200 to 1200 minutes for PCE in a study performed using an excess of potassium permanganate (Poulson and Naraoka, 2002).

It is interesting to note that carbon isotope compositions have not returned to original values in some of the samples collected in January 2003 (approximately six months after the last Phase 2 injection), although CVOC concentrations have rebounded. This implies that a portion of the CVOC mass in these samples was partially oxidized by $KMnO_4$.

5.3 Inorganic Parameters

Samples for inorganic parameter analysis were collected during the February 2002, March 2002 and June 2002 sampling events. Samples were sent to PSC Analytical in Bedford, Nova Scotia for analysis. Inorganic analysis results for all samples are summarized on Table 7. Table 8 compares the inorganic analysis results for monitoring points impacted by permanganate during Phase 1, versus monitoring locations where permanganate was not detected. As expected, at wells impacted by $KMnO_4$, concentrations of potassium rose from an average of 8 mg/L to 591 mg/L, while manganese concentrations increased from an average of 0.5 mg/L to 179 mg/L. Sulfate concentrations rose significantly from an average of 38 mg/L to 868 mg/L. This is likely due to a high concentration of pyritic minerals in the rock matrix and the presence of hydrogen sulfide in groundwater at greater depths. Several water quality parameters changed significantly in the presence of $KMnO_4$. For instance, alkalinity increased sharply, total dissolved solids (TDS) increased, and total organic carbon increased. In addition, concentrations of several metals seemed to fluctuate in response to the presence of permanganate. The only consistent trends seem to be decreasing barium concentrations and increasing zinc concentrations. Lead was not detected in any of the samples, and arsenic was detected only at very low concentrations.

6.0 Rebound Monitoring

It was anticipated that after the Phase 2 injections ceased, $KMnO_4$ concentrations would gradually diminish to below detection and CVOC concentrations would gradually rise from below detection to detectable values. This rebound in CVOC concentrations is due to reverse diffusion from the rock matrix and cross flow that can transport CVOCs into the treated zone from any untreated zones. Rebound monitoring was conducted to monitor the rate of $KMnO_4$ dissipation and subsequent CVOC concentration rebound.

Rebound monitoring was started immediately after the end of Phase 2 injections in June 2002. Monitoring wells 34, 74, 75, and 76 were selected for the rebound monitoring program because these wells all contained permanganate in at least one monitoring zone at the end of Phase 2 injections. Nine rebound monitoring events were performed at two week intervals, with the exception of the last two events, which were performed approximately one month apart from each other. During rebound monitoring, samples were analyzed for field parameters including permanganate and chloride. Samples were analyzed for CVOCs only if there was little or no permanganate in the sample.

Rebound monitoring results are summarized in Table 9. Graphs depicting the rebound results for each monitoring zone are included in Attachment 5. Rebound monitoring showed that permanganate persisted in the majority of the monitoring zones throughout the monitoring period (i.e., from June to December 2002). At many monitoring zones, there was a sharp decline in the permanganate concentration within the first one to three months of monitoring, followed by a slower decline as monitoring continued.

Analysis of the rebound monitoring results raised some doubt about the accuracy of the rebound samples because the persistence of permanganate during rebound monitoring was incompatible with the high rock oxidant demand (ROD) measured for the Watervliet shale in a UW laboratory study (see Section 3.?). Given the high ROD, it would be expected that permanganate concentrations would dissipate at a faster rate than what was measured. One hypothesis for the continued persistence of permanganate was that the sampling techniques being used were not yielding samples that accurately depicted sub-surface conditions. Throughout the pilot study, standard low-flow purge protocols were used for sample collection at all wells, with the exception of the wells completed with the Westbay system, which is a ‘no-purge’ system. Those techniques were used so that significant amounts of permanganate would not be withdrawn from the subsurface during sampling. It was hypothesized that the permanganate being detected in the rebound samples was an artifact of a borehole storage effect, where permanganate in the borehole annulus might accumulate because it is not in contact with the rock matrix and thus not being consumed by ROD. To test this hypothesis, the sampling protocol was modified for the January 2003 sampling event. Monitoring wells were purged of up to three well or zone volumes prior to collecting a sample. The results of the January 2003 sampling event are discussed in the following section.

7.0 January 2003 Monitoring Event

In January 2003, a full sampling event was performed during which samples were collected from all accessible wells/zones in the vicinity of Building 40. Samples were analyzed for field parameters including permanganate, chloride and conductivity, as well as for laboratory parameters including CVOCs and carbon isotopes. The purpose of this monitoring event was to obtain a synoptic snap-shot of CVOC and permanganate concentrations in the vicinity of Building 40, as well as to test the integrity of the sampling techniques used during previous events (see discussion in Section 3.7). Monitoring points were purged of up to three well or zone volumes prior to collecting a sample for CVOC analysis. Samples were collected for field parameter analysis prior to purging, and also after purging each well/zone volume. Up to four samples were analyzed for field parameters for each well/zone, depending on whether the well/zone recharged sufficiently.

Field parameter measurements collected during purging are summarized in graphs attached in Attachment 6. In most cases, permanganate concentrations dropped significantly after purging one well/zone volume, compared to the no-purge result, and then stabilized after purging the second and third well/zone volumes. This indicates that the borehole storage hypothesis for permanganate may be correct, and that future sampling efforts should include purging of at least one well or zone volume prior to collecting a sample. However, it should be noted that a high concentration of permanganate was detected at MW-59 in May 2003, even though during the January 2003 sampling event permanganate concentrations at MW-59 dropped to almost zero after purging of one well volume.

The CVOC results from the January sample event are summarized on Table 5, and carbon isotope results are shown on Table 6. CVOC results showed that CVOC concentrations had rebounded to the baseline (February 2002) conditions at many locations.

8.0 Laboratory Studies and Modeling

Laboratory studies and numerical modeling were conducted by UW at the same time as field activities were being performed to enhance understanding of field observations. The following sections summarize the results of the laboratory studies to date. Detailed procedures and results are included in Attachment 7 to this document.

8.1 Rock Oxidant Demand Tests

Batch tests were conducted on three representative rock core samples obtained from MW-74 and MW-75 to evaluate the permanganate rock oxidant demand (ROD) exerted by the shale, and to perform a preliminary assessment of the main contributors to the ROD. For the batch tests, subsamples of the sections of rock core were first manually broken into small fragments, and then crushed to a fine powder using a ring mill. The batch tests were initiated by placing approximately 10 grams (g) of crushed rock from each of the three samples into 125-millileter (mL) Erlenmeyer flasks and then adding ~100 mL of $KMnO_4$ solution. The tests were set up with three different initial concentrations of $KMnO_4$ solution: 1, 5, and 20 g/L (0.1, 0.5, and 2.0 percent by weight, respectively). Aliquots of the solution were removed from the flasks at several times during the tests for $KMnO_4$ determination and estimation of the variation of ROD exerted over time. A second set of batch tests were conducted using sodium permanganate ($NaMnO_4$) on two of the three samples for which the $KMnO_4$ batch tests were performed. The purpose of these tests was to investigate the dependence of the ROD on permanganate concentration using higher concentrations achievable with $NaMnO_4$. As with the $KMnO_4$ tests, three different initial concentrations of $NaMnO_4$ were used: 20, 50, and 100 g/L (2.0, 5.0, and 10.0 percent by weight, respectively). For comparison at the lower end, a parallel test was also performed using $KMnO_4$ at 20g/L (2 percent by weight). Pre- and post-oxidation samples of the batch test solids from both tests were analyzed for fraction organic carbon. Post-oxidation samples from both batch tests were analyzed for sulfate concentrations ion chromatography (IC) following reduction of any remaining permanganate with glucose. Sulfate concentrations determined from the IC analyses were used to evaluate the contribution of pyrite oxidation to the measured ROD.

The results of the $KMnO_4$ batch tests indicated a maximum ROD after 21 days ranging from 19 to 32 mg $KMnO_4$ per g of rock, with about 83% to 91% of the 21-day ROD reached within the first seven days. The ROD values measured from the $NaMnO_4$ tests were a factor of two or three higher than those measured in the $KMnO_4$ tests. Therefore, there appears to be a concentration dependence on ROD – the higher the permanganate concentration, the higher the ROD exerted by the shale. Results of the sulfate analyses indicated that pyrite oxidation accounted for about 30% to 75% of the 21-day ROD values observed. The higher the permanganate concentration, the lower the percentage of ROD accounted for by pyrite. The fraction organic carbon analyses indicated some contribution to the ROD from organic carbon oxidation, particularly for higher permanganate concentrations. The batch test results on crushed samples must be evaluated with caution when applied to interpretation of anticipated ROD under field conditions with intact rock. Rates of reaction are much different between batch tests on crushed samples and intact rock, due to available surface area for reaction, and diffusion-limited permanganate transport to reactive minerals. Reaction rates in intact rock also may be hindered by deposition of MnO_2 coatings on reactive surfaces.

8.2 Permanganate Invasion Testing

Laboratory testing was conducted to measure the rate of permanganate invasion into the Watervliet shale. The goal of the testing was to have rock core samples in contact with $KMnO_4$ solution for a period of time during which diffusion into the core would take place. The initial scope called for the cores to be examined at various time intervals to determine the distance of $KMnO_4$ invasion. This would be done by splitting the core to observe the invasion distance from the $KMnO_4$ contact surface visually based on color change and also by chemical analyses of small samples obtained from the core by saw cutting or miniature core drilling. Several of these core diffusion experiments were to be set up to run concurrently so that the invasion distances after different invasion period could be determined.

The invasion tests were initiated on September 6, 2002. Six samples from intact rock (approximately 1 cm x 2 cm x 3 cm each) were immersed in a 2% potassium permanganate solution. Three of the six invasion test samples have been removed to date: on October 30, 2002 (~7.5 weeks), December 3, 2002 (~12.5 weeks) and March 6, 2003 (~26 weeks). Initially, it was thought that diffusion zones would be visible (i.e., would turn from black to dark brown) and could be chipped from the cores for analysis. However, given the very low permeability of the Watervliet shale, diffusion rates are very slow and not visible over the span of the invasion tests to date. Therefore, following removal of each sample, thin-sections were prepared at the University of New Brunswick (UNB) by cutting along the longitudinal axis and mounting so that the resulting section was about 3 cm by 1 cm with a thickness of about 200 microns. The thin sections were then analyzed for various elements using Laser Ablation Microprobe (LAM) ICP-MS analyses. Preliminary analysis indicates that invasion distances into the shale are very small (10 to 100 microns after 12.5 weeks), which is expected given the very large oxidant demand imposed by the shale.

8.3 Diffusion Rate Modeling

One-dimensional simulations of PCE and TCE diffusion into the shale matrix were conducted using an analytical solution to Fick's Second Law of Diffusion. The purpose of these simulations was to gauge the extent of contaminant diffusion into the rock matrix in the vicinity of Building 40. Diffusion profiles were generated for PCE and TCE at times of 10, 20, 30, and 40 years. These simulations indicate maximum invasion distances after 40 years of approximately 7 cm and 15 cm for PCE and TCE, respectively. The equations and parameters that were used for the model are described in detail in Attachment 7.

9.0 Pilot Study Conclusions

The following conclusions were reached based on the data presented in this report:

- The vast majority of the CVOC mass in the bedrock aquifer in the Building 40 area is entrained in the shale bedrock matrix pore spaces.
- Permanganate can be distributed both vertically and horizontally throughout the treatment area using a small number of injection points.
- Permanganate reduced the concentration of CVOCs in the bedrock groundwater and was able to diffuse into the bedrock matrix.