In Situ Remediation of Fractured Bedrock DNAPL Sites Using Chemical Oxidation
J.S. Konzuk, L.K MacKinnon, E.D. Hood, and E.E. Cox
GeoSyntec Consultants, Guelph, Ontario, Canada

Abstract

The remediation of dense non-aqueous phase liquids (DNAPLs) such as tetrachloroethene (PCE) and trichloroethene (TCE) has been recognized as a complex challenge, particularly in fractured rock environments. Groundwater remediation approaches for this type of sites have historically employed groundwater extraction and ex situ treatment (i.e., pump-and-treat). Unfortunately, pump-and-treat is typically unable to significantly improve groundwater quality, even after relatively long periods (i.e., decades) of operation (Doty and Travis, 1991; USEPA, 1992; NRC, 1994). The limited performance of most pump-and-treat systems stems largely from the inability to significantly accelerate the rate of mass transfer from the DNAPL into the aqueous phase (e.g., dissolution). Further, the effectiveness of remedial technologies at fractured bedrock sites can be limited by counter-diffusion of chlorinated solvents resident in stagnant fractures and/or the rock matrix into mobile groundwater.

In comparison to pump-and-treat approaches, technologies capable of enhancing DNAPL dissolution into the aqueous phase may shorten the time to achieve site restoration. One promising technology involves the injection of permanganate (MnO_4^-) to mineralize chlorinated ethenes (i.e., PCE and TCE) to non-toxic, inorganic products such as carbon dioxide and chloride. Permanganate offers significant advantages over other oxidants (e.g., Fenton’s reagent or ozone) used for in situ chemical oxidation (ISCO) because it is less reactive with aquifer solids (resulting in lower oxidant consumption), is typically more stable and safer to handle, requires no pH adjustment or catalyst addition, and produces less heat and insoluble gas in the treatment zone. At typical MnO_4^- application concentrations, the destruction half-lives of these contaminants are on the order of a few minutes. Provided that permanganate can be efficiently delivered to bedrock fractures containing source chemicals (the key uncertainty with in situ remediation technologies), the rapid destruction rates promote accelerated DNAPL dissolution, which translates into faster site restoration.

Bench-scale studies and field demonstrations were conducted for three fractured bedrock sites with a range of rock types, including shale, siltstone, metagabbro, and graphitic shist. The permanganate demand exerted by the fracture matrix, the potential for oxidant diffusion into the rock matrix, and the potential for mineral leaching from the rock to groundwater resulting in adverse groundwater impacts were evaluated through bench-scale testing. The results of these studies demonstrated that permanganate destroyed high PCE/TCE concentrations within very short time frames without adverse impacts to groundwater chemistry. Based on these results, field pilot tests have been completed at two of the three sites.

At the first site in Pennsylvania, where TCE concentrations in groundwater are as high as 18 mg/L, pilot testing was planned based on the results of treatability studies as well as pre-design site characterization. An eight-week pilot test using continuous recirculation of site groundwater amended with 1 to 5 g/L potassium permanganate (KMnO_4) was implemented with the objective of assessing the impact of oxidant injection on TCE. Field pilot results demonstrated that TCE was oxidized in situ and that the technology was implementable in the fractured bedrock media. At the second site in South Carolina, where PCE concentrations in groundwater are as high as 10 mg/L, sodium permanganate (NaK MnO_4) was injected to evaluate the efficacy of the technology. Permanganate was injected at concentrations up to 2 g/L for a period of 19 weeks followed by 4 weeks of groundwater recirculation without oxidant addition. Results, including chloride and PCE concentrations, indicated that significant VOC mass was destroyed during the pilot test. Based upon the results of these pilot tests, full scale ISCO remedies are currently being planned for both sites.

This paper will present the results of the bench-scale studies and field pilot tests, and will discuss the ability of the ISCO technology to accelerate source remediation in fractured bedrock environments.
Introduction

The remediation of chlorinated solvent DNAPLs such as PCE and TCE in fractured bedrock environments has been recognized as a complex challenge. Pump and treat, often chosen as the remedial remedy for fractured rock sites, has been shown to be ineffective in significantly improving groundwater quality, even after relatively long periods (i.e., decades) of operation (Doty and Travis, 1991; USEPA, 1992; Bartow and Davenport, 1992; NRC, 1994). The limitations of the pump and treat approach relates largely to its inability to significantly accelerate the mass transfer of a DNAPL to the aqueous phase. Technologies that enhance DNAPL dissolution into the aqueous phase through in situ destruction of the contaminant have more potential to shorten the time to achieve site restoration. Emerging research is showing that ISCO can accelerate DNAPL dissolution by order(s) of magnitude, with the promise of reducing the time for source remediation by a comparable factor. However, the effective implementation of remedial technologies such as ISCO in fractured bedrock environments can be challenging due to the difficulty in effectively delivering amendments to areas containing contamination because of complex hydrogeology that is governed by the geometrically complex secondary porosity (i.e., fractures) and/or the need to rely on counter-diffusion of chlorinated solvents resident in stagnant fractures and/or the rock matrix into mobile groundwater.

Laboratory treatability and field pilot studies were conducted to evaluate the technical feasibility of using ISCO for aggressive remediation of chlorinated volatile organic compound (CVOC) source zones for two fractured bedrock Sites, herein referred to as Site 1 and Site 2. The treatability studies were designed to identify performance factors that may influence design and scale-up of the remediation technology for field pilot studies. The pilot testing further evaluated these design parameters for Site conditions, and also the impact of fractured bedrock hydraulics on remedial performance. Presented below are the results of the bench-scale studies and field pilot tests for both Sites 1 and 2.

Site Descriptions

Site 1

The geology at Site 1 consists of a low permeability silty clay overburden, overlying dark gray shaley siltstone and/or reddish-brown siltstone sequences. The mineralogy of both the siltstones is dominated by plagioclase feldspar and quartz, with minor amounts of calcite, clinopyroxene, and pumpellyite. The bedrock has low primary porosity, and contains discrete fractures to greater than 500 ft bgs that are oriented both vertically and horizontally. There are indications of isolated regions of bedrock with poor connectivity to surrounding areas.

TCE and related breakdown products are the primary chemicals of concern at this Site, with elevated TCE concentrations detected in several wells that are indicative of DNAPL presence within the bedrock. The rate and extent of intrinsic biodegradation of TCE in the groundwater at Site 1 appears to be limited by the absence of key nutrients (electron donors) required to mediate the intrinsic biodegradation reactions and/or redox conditions that favor reductive dechlorination.

Site 2

The geology at Site 2 consists of residual soil underlain by a saprolite containing fine-grained to medium-grained dense sand with traces of clay and silt. The saprolite is underlain by a weathered rock formation, which forms a transition zone separating the saprolite from the underlying competent metamorphic crystalline bedrock (primarily metagabbro with some granite). The bedrock mineralogy is dominated by quartz and plagioclase feldspar with minor to trace amounts of talc, microcline, chlorite, mica, and goethite. The bedrock has negligible primary porosity and unknown effective porosity, with discrete vertical fractures to 110 ft bgs. Less distinct sub-horizontal fractures also exist on Site.

Groundwater data from Site 2 indicate that the redox environment is primarily aerobic and oxidizing. The PCE concentrations detected near the facility are indicative of the presence of DNAPL within the saprolite and bedrock materials, with a PCE plume extending from the suspected source area. PCE and related degradation
products have been detected in groundwater samples collected from both saprolite and bedrock monitoring wells; however, intrinsic degradation of PCE is limited by insufficient availability of electron donors, oxidizing redox conditions, and/or a low concentration of biomass of PCE-dechlorinating microorganisms. There is a strong upward component of flow from the crystalline bedrock into the saprolite.

**Treatability Studies**

*Methodology*

While ISCO has been successfully tested in the laboratory and field for porous media applications, the application of this technology in fractured bedrock has not been extensively studied. Thus, careful consideration was given to the approach and methods of the treatability studies for both Sites to ensure that critical performance factors for design and scale-up were identified. These performance factors include:

1. the oxidant demand of the groundwater and geologic materials;
2. the potential impacts of oxidation on the inorganic chemistry of groundwater, including mobilization of metals from the geologic materials;
3. the potential for precipitate formation which may decrease the transmissivity of the fractured bedrock;
4. the loss of permanganate through diffusion into the bedrock matrix that would represent an additional oxidant demand of the matrix, but that may also oxidize CVOC mass in the rock matrix; and
5. the impact of oxidant treatment on both fracture face and bulk bedrock matrix geochemistry.

Four tests were designed for the treatability studies for both Sites to evaluate these factors including batch tests with Site groundwater and bedrock, extended leach tests, and matrix penetration and diffusion tests. The batch tests with Site groundwater were conducted by adding enough concentrated potassium permanganate solution to each reactor containing Site groundwater to attain a concentration of 1 and 10 g/L potassium permanganate (KMnO$_4$). A reaction period of 24 hours was used for all reactors. At the end of this period, the concentrations of MnO$_4^-$, VOCs, total organic carbon, and anions were measured. As well the mass of precipitate formed by oxidation reactions was determined.

The batch tests with Site bedrock utilized both the natural fracture faces and bulk bedrock. These materials were separately crushed and particles passing a No.10 standard sieve and retained on a No. 200 standard sieve were selected for the batch tests. A 10 g/L KMnO$_4$ solution was added to each batch reactor and mixed for seven days. The oxidant demand of the bedrock was calculated from the decrease in KMnO$_4$ concentration and the mass of geologic material in each reactor.

For the extended leach tests, bedrock samples were prepared with an exposed natural fracture face and the remainder of the sample coated with an impermeable metal-based epoxy polymer. Each sample was immersed in separate containers of concentrated KMnO$_4$ and stored for up to eight weeks. At the end of the reaction period, aqueous samples were collected for dissolved metals analysis.

Natural fracture faces of the bedrock were selected for the matrix penetration and diffusion tests and prepared in a similar manner as for the extended leach tests, immersed in a solution of KMnO$_4$ and stored for up to 8 weeks. Bedrock samples were sacrificed at two-week intervals and evaluated for the extent of oxidant penetration through diffusion into the matrix.

*Results of the Treatability Studies*

The results of batch tests with groundwater from Sites 1 and 2 indicated that the groundwater matrix did not exert a significant oxidant demand, and that minimal precipitate was formed. Groundwater quality with respect
to metals and anions was largely unaffected by the addition of KMnO$_4$. Concentrations of metals decreased, with the exceptions of potassium and manganese; suggesting that ISCO would not adversely impact the groundwater chemistry in a field application at these Sites, with the exception of transient increases in the concentration of these metals.

The oxidant demand of the materials from Site 1 was low, with a maximum demand of 5.8 g/kg exerted by the shale; the demand exerted by the siltstone was negligible. The oxidant demand of the bedrock from Site 2 was negligible. The saprolite exerted a slightly higher demand (3.1 g/kg). Although these results indicate that there may be some demand for the oxidant in a field application, they represent the worst case scenario as pulverization of the bedrock samples prior to testing significantly increases the surface area available for reaction relative to that expected during field application. Oxidant demands on the order of the maximum observed during the treatability studies (i.e., 3.1 and 5.8 g/kg) are small in comparison to typical oxidant demands exerted by many porous media soils with relatively low organic carbon contents (Hood, 2000).

Results from the extended leach tests indicate that oxidation did not result in adverse mobilization of dissolved metals from the geologic materials from either Site. For the Site 1 samples, slight increases in barium, calcium, and magnesium concentrations were observed in the siltstone sample, while no increases in metals concentration was observed for the shale sample. For Site 2, the concentration of calcium increased for the crystalline bedrock, to a level similar to that observed in the Site groundwater.

No evidence of oxidant diffusion into the shale and siltstone from Site 1 was observed after eight weeks of immersion in the oxidant solution. The diffusion into the bedrock materials was small in comparison to the average background manganese concentration (~1,200 mg/kg) in both the shale and siltstone materials. The minimal penetration of the oxidant into the rock matrix was likely a result of the low porosity of the bedrock materials. The oxidant demand resulting from diffusive loss of KMnO$_4$ into the bedrock matrix is unlikely to have a significant impact during an extended treatment using ISCO.

**Pilot Testing**

*Site 1*

Pilot test objectives for field application of ISCO at Site 1 included:

1. demonstrating the ability of ISCO to aggressively destroy TCE *in situ* and reduce mass flux from the source zone;
2. evaluating the impacts of ISCO on groundwater chemistry, including the mobilization of redox-sensitive metals;
3. evaluating the oxidant demand exerted by the bedrock matrix; and
4. identifying design and operational factors that influence the performance of a field-scale system, and optimize, to the extent possible, potential operating conditions for a full-scale ISCO system.

The initial stages of the pilot testing activities consisted of the following Site characterization activities:

1. **Electromagnetic borehole flow meter (EBF) survey of the extraction well**: Used to delineate the vertical profile of hydraulic conductivity within the extraction well and thus identify any conductive fracture zones. The survey showed a small number of conductive zones (~3) over the 500 ft depth, with the majority of the extraction well intersecting non-conductive fractures;

2. **Baseline depth-discrete groundwater sampling**: Used for VOC and tracer sampling to delineate vertical contaminant distribution within the targeted subsurface zone, and assess possible intervals of
TCE migration into the extraction well. Depth discrete sampling of VOCs showed elevated TCE presence coinciding with the transmissive fracture zones;

iii) **Tracer testing:** Used to delineate the degree of lateral and vertical hydraulic connection between the pilot test injection and extraction wells and other surrounding monitoring wells, and to demonstrate the ability to contain amendments and degradation products. Depth-discrete sampling in the extraction well indicated that the majority of bromide was transported in the shallow portions of the bedrock, with some at depth. Bromide breakthrough coincided with transmissive fracture zones indicated by the EBF survey. Approximately 40% of the bromide mass was recaptured. Dye tracer testing indicated that lateral connection between monitoring wells was good, although some wells may have been hydraulically isolated from the others.

The pilot test was designed as a two-well recirculation cell, where groundwater was extracted from the downgradient well (FTW) at 2 gpm, amended with potassium permanganate, passed through a sedimentation tank containing an air sparging system used to remove unoxidized VOCs and settle out particles (i.e., manganese dioxide) from the groundwater stream prior to reinjection upgradient into BCM-1. KMnO₄ was amended at a rate of 1 g/L for 41 days, and then increased to 5 g/L for seven days. Following termination of KMnO₄ amendment, groundwater was recirculated for 16 more days. Extracted groundwater was analyzed for VOCs, permanganate, field parameters, dissolved metals and anions such as chloride.

Initial breakthrough of MnO₄⁻ in the extraction well occurred 13 days after the start of injection; in comparison, bromide breakthrough occurred eight times faster. The retardation is attributed to reaction of the MnO₄⁻ with TCE and, to a lesser extent, reaction with the bedrock material. The concentration of permanganate breaking through to the extraction well increased to a maximum of 324 mg/L during amendment, and rapidly decreased once MnO₄⁻ addition ceased (Figure 1). TCE concentrations in the extraction well decreased to near detection limits concurrently with the breakthrough of MnO₄⁻ (Figure 1). Effluent chloride concentration rapidly increased from 50 mg/L to 70 mg/L and increased gradually thereafter (Figure 2).

Operational challenges were minimal. The settling tank proved to be an effective means of minimizing precipitated manganese dioxide impacts to well capacities and piping.

On- and off-site monitoring for bromide, permanganate, VOCs and metals indicated that off-site water quality was not impacted and effects of the pilot testing were localized to the immediate area surrounding the injection and extraction wells. Increases in total and hexavalent chromium, a known trace constituent of commercial grades of potassium permanganate, were localized to the injection and extraction wells. While the chromium impacts are expected to be limited and transient, the potential for chromium contamination will be closely monitored during full-scale application. ISCO treatment was stated as the preferred source zone remedial remedy in the Record of Decision (ROD) at Site 1, and full-scale implementation is currently undergoing regulatory approval.

**Site 2**

Pilot test objectives for field application of ISCO at Site 2 included:

i) demonstrating the ability of ISCO to aggressively destroy PCE *in situ* and reduce mass flux from the source zone;

ii) evaluating the impacts of ISCO on groundwater chemistry, including the mobilization of redox-sensitive metals; and

iii) identifying design and operational factors that influence the performance of a field-scale system, and optimize, to the extent possible, potential operating conditions for a full-scale ISCO system.
**Figure 1:** TCE and Permanganate Concentrations in the Extracted Groundwater

![Graph showing TCE and Permanganate Concentrations over time.](image)

**Figure 2:** Chloride Concentrations in the Extracted Groundwater

![Graph showing Chloride Concentrations over time.](image)
The pilot test was designed as a two- to three-well recirculation cell \([i.e.,\text{ one extraction well (MW-12C) and two injection wells (MW-37A and MW-39)}]\) using existing monitoring wells. Groundwater was extracted from MW-12C, amended with permanganate, passed through in-line filters to remove manganese dioxide particles, and then the flow was split prior to reinjection into one or two injection wells. Tracer was amended to extracted groundwater at the injection well head. A number of constraints impacted the pilot test design, including: \((i)\) the requirement to use existing wells; \((ii)\) the Site is an active manufacturing facility, and thus access constraints were significant, including a large building overlying the targeted PCE source area; and \((iii)\) limited locations were available to situate pilot testing infrastructure, which dictated the location of the extraction well, thus resulting in groundwater recirculation cross-gradient to the natural flow direction.

Tracer testing was conducted concurrently with the injection of permanganate to evaluate residence time between the injection/extraction wells, quantify the mass capture efficiency of the extraction well from each injection well, and to confirm the connectivity between the injection/extraction wells under pilot test conditions. During the early stages of the tracer testing, bromide was injected at a concentration of 60 mg/L into the more conductive injection well (MW-37A) during recirculation of the groundwater at a rate of 15 gpm for three days. Injection into the second injection well (MW-39) did not occur during this period. Extracted bromide concentrations were monitored on a minimum daily basis for a further 14 days during recirculation of groundwater at 8 to 12.5 gpm. After the two week period, the second, less-conductive injection well was brought on-line, and bromide injection into this well commenced at a rate of 2,740 mg/L amended to 0.6 gpm of groundwater for three days. Captured bromide concentrations were continually monitored in the extraction well for a further 7 days, at which point, groundwater recirculation was terminated. Bromide samples were periodically collected from surrounding monitoring wells to evaluate potential vertical and lateral tracer impacts throughout the pilot test area.

During the pilot test, bromide concentrations continued to rise in the extraction well (MW-12C) from 1.7 days post-startup and reached a maximum concentration of 8.3 mg/L \((i.e.,\text{ 14\% of the injected concentration into MW-37A})\) after 9 days (Figure 3). The bromide concentration remained stable for 4 days, and then gradually decreased through to the termination of the groundwater recirculation 49 days later. No increase in bromide concentrations was observed related to the injection of bromide into MW-39 mid-way through the pilot test. However, tracer injected into MW-39 during previous tracer testing activities was observed to break through to MW-12C immediately upon restarting recirculation after a four day shutdown period. Bromide concentrations above background levels were also detected in monitoring wells immediately surrounding the pilot test area.

This tracer behavior indicates the following:

\(i)\) Injection wells MW-37A and MW-39 were hydraulically connected to the extraction well MW-12C; however, under recirculating conditions, groundwater injected into MW-37A is predominantly captured by MW-12C causing significant dilutions to any amendments injected into MW-39;

\(ii)\) Significant dispersion and/or dilution of the tracer within the pilot test area occurred due to one or more of the following reasons:

- A number of fractures of varying sizes and flowpath lengths between MW-12C and MW-37A may have been participating in flow between these wells, creating substantial delay and tailing of tracer breakthrough;
- Tracer may have been diffusing from the groundwater into the bedrock matrix or poorly connected and low transmissivity fractures, resulting in mass loss;
- The majority of groundwater extracted from MW-12C was not coming from fractures that are hydraulically connected to either MW-37A or MW-39, causing dilution of the tracer in extracted groundwater; and
- Some tracer mass was likely being lost downgradient due to the cross-gradient configuration of the pilot test.

\(iii)\) Increases in chloride related to PCE degradation during permanganate amendment and/or permanganate breakthrough to the extraction well was likely significantly impacted by dilution and thus small changes will represent much larger changes within the pilot test area.
Permanganate amendment occurred concurrently with tracer testing. Continuous oxidant addition occurred over a period of 19 days, with 0.5 g/L amended for the first 11 days, then 2.3 g/L for the remaining 8 days. At the end of the 19 days, a high concentration, small duration pulse of permanganate was injected into each injection well (50 gallons of ~140 g/L permanganate solution into MW-39 and 40 gallons into MW-37A) to see whether we could achieve breakthrough of the permanganate to the extraction well. Total sodium permanganate mass injected into each well is estimated to be 900 kg into MW-37A and 30 kg into MW-39 throughout the entire pilot test. Upon termination of permanganate amendment, groundwater was recirculated for a further 29 days to provide additional distribution of the injected oxidant throughout the pilot test area. Extracted groundwater was monitored for field parameters, VOCs, dissolved metals, anions such as chloride, and permanganate.

In contrast to field demonstrations at most other sites, permanganate breakthrough did not occur at the extraction well, even as a result of the high concentration permanganate pulse at the end of injection. The lack of any permanganate breakthrough suggests that the oxidant was reacting with the target VOCs \textit{in situ}, and potentially, to a lesser extent, with natural dissolved constituents in the groundwater and/or the fractured bedrock material. Concentrations of chloride, a breakdown product of chlorinated solvents and permanganate, increased in the MW-12C effluent by a maximum of 17 mg/L (baseline concentrations were 32 mg/L, see Figure 4). Given the extent of dilution/dispersion of the tracer, and assuming that capture efficiency of the chloride at MW-12C is a corresponding 14% of the \textit{in situ} concentrations, an increase of 17 mg/L would represent an estimated resulting chloride concentration increase of 121 mg/L within the pilot test area impacted by permanganate. This represents significant destruction of VOCs along the flow path between MW-37A and MW-12C, as permanganate reaction with recirculated VOCs would only cause an increase in chloride of $<1$ mg/L. VOC concentrations in MW-12C did not show a decrease in relation to the increase in chloride (see Figure 5); however, this was likely impacted by background water also being captured, and potentially from desorption from bedrock and/or dissolution of VOCs from suspected DNAPL mass present \textit{in situ}. Evaluation of the post-ISOC changes to groundwater chemistry demonstrated increases to the oxidation-reduction potential (ORP), no permanganate detected at any monitoring wells outside of one situated in close proximity to the injection well MW-37A, and no changes to the concentrations of dissolved metals.
Figure 4: Chloride Concentration in the Extracted Groundwater

Figure 5: VOC Concentrations in the Extracted Groundwater
Operational challenges included: (i) frequent fouling of the in-line filters with manganese dioxide precipitates, requiring daily changes; (ii) reduction in capacity of MW-39, potentially due to fouling with manganese dioxide that may have been inadvertently injected to the well during initial system testing; and (iii) a need to occasionally flush the piping and clean the injection wells. Frequent fouling of the in-line filters created significant back pressure in the piping, which impacted the effectiveness of dosing pumps and other instrumentation not designed to withstand the elevated pressures.

A Feasibility Study was developed based upon the results of the ISCO and enhanced in situ bioremediation field testing, with ISCO chosen as the preferred full-scale remedy. Full-scale implementation is currently in the initial approval stages.

**Discussion of Findings**

The results of the treatability studies and pilot tests demonstrated the following:

1. **Oxidant demands from the groundwater and bedrock were low for the siltstone, saprolite and metagabbro bedrock environments tested.** Oxidant demands were small in comparison to typical oxidant demands exerted by many porous media soils with relatively low organic carbon contents. Oxidant diffusion into the bedrock matrix was also negligible, likely as a result of the low primary porosity of the bedrocks tested. Diffusion into the rock matrix may, however, become a significant factor in the loss of oxidant mass in bedrock environments where the primary porosity of the bedrock is significant (e.g., sandstone).

2. **There is a need for characterization of both vertical and lateral hydraulic flow paths and contaminant distribution within the pilot test area, as well as an evaluation of the impacts of dilution and dispersion on the groundwater chemistry at the monitoring locations.** We found that a combination of tracer testing, depth-discrete sampling and vertical profiling of conductive fracture zones was an effective method for delineating expected flow paths and expected capture efficiency. A minimum capture efficiency is needed prior to using the geochemistry of the sampled groundwater as an effective measure of system performance. Data collected from a monitoring well downgradient of the injection well would provide a more effective measure, as it is not impacted by dilution caused by
extraction of background groundwater. An understanding of the chemical profile and flow path distribution is also essential in designing an appropriate oxidant delivery approach to achieve maximum effectiveness while minimizing impacts to groundwater geochemistry.

**iii)** Monitoring of chloride concentration increases provides a more accurate indication of oxidation effectiveness than either breakthrough of permanganate or reductions in VOC concentrations. Permanganate may react with other non-VOC organic material in the subsurface, and thus its consumption is not a reliable indicator of the destruction of VOCs. VOCs may also be released to the groundwater *in situ* through enhanced dissolution of DNAPLs, desorption from aquifer material or diffusion from hydraulically isolated fractures or the rock matrix; therefore, once the permanganate is consumed, the VOC concentrations may increase to background concentrations prior to capture with the extraction well. Chloride, however, is a conservative compound that does not react with or sorb to aquifer material.

**iv)** The generation of manganese dioxide precipitates *ex situ* can be a significant operational concern and should be considered in system design. This can be minimized through either stripping the VOCs from the effluent prior to amending with permanganate, or through the use of an in-line settling tank. We found that in-line filters did not have enough capacity to remove the precipitates efficiently, and as a result, frequent maintenance was required and significant system back pressure developed, which impacted other instrumentation.

**v)** Impacts to groundwater geochemistry were generally minimal. The only significant impact was a slight increase in chromium (hexavalent and total) at Site 1, and increases in ORP to reflect oxidizing conditions.

**References**


**Biographical Sketches**

**Dr. Eric Hood**, P.Eng. is a Remediation Scientist with GeoSyntec Consultants. Dr. Hood received his doctoral degree in Civil Engineering from the University of Waterloo, at Waterloo, Ontario. Dr. Hood has 11 years of specialized experience in the development of conceptual models for DNAPL transport, fate, and remediation in both porous and fractured media, and the implementation of in situ DNAPL remediation using chemical oxidation. With articles published in both peer-reviewed journals and conference proceedings, his expertise includes reactive transport modeling for evaluating chemical oxidation remediation processes, design approaches for chemical oxidation treatment systems, and the evaluation of treatment system performance.

Contact Information: Eric Hood, Ph.D., P.Eng., Remediation Scientist, GeoSyntec Consultants, 130 Research Lane, Suite 2, Guelph, Ontario, Canada, N1G 5G3, (phone) 519/822-2230 ext. 225, (fax) 519/822-3151, (email) ehood@geosyntec.com.
Ms. Leah MacKinnon is a Remediation Scientist with GeoSyntec Consultants. Ms. MacKinnon received her bachelor’s degree in Chemical Engineering and master’s degrees in Civil Engineering from the University of Waterloo, at Waterloo, Ontario, Canada in 1996 and 1999, respectively. Ms. MacKinnon has 8 years of specialized experience in design, implementation and interpretation of innovative in situ remediation technologies for chlorinated solvents, including chemical oxidation using permanganate, passive treatment using zero-valent iron barriers, and accelerated bioremediation.

Contact Information: Leah MacKinnon, M.A.Sc., GeoSyntec Consultants, 130 Research Lane, Suite 2, Guelph, Ontario, Canada, N1G 5G3, (phone) 519/822-2230 ext. 246, (fax) 519/822-3151, (email) lmackinnon@geosyntec.com.

Dr. Julie Konzuk, P.Eng. is an Environmental Engineer with GeoSyntec Consultants. Dr. Konzuk received both her bachelor’s and Ph.D. degrees in Civil Engineering from Queen’s University at Kingston, Ontario, Canada in 1993 and 2001 respectively. Dr. Konzuk has 10 years of specialized experience in the behavior and simulation of DNAPL and water flow through fractured rock, and 3 years experience in the design, implementation and interpretation of chemical oxidation and bioremediation remedial technologies applied in both fractured rock and porous media settings.

Contact Information: Julie S. Konzuk, Ph.D., P.Eng., Environmental Engineer, GeoSyntec Consultants, 130 Research Lane, Suite 2, Guelph, Ontario, Canada, N1G 5G3, (phone) 519/822-2230 ext. 241, (fax) 519/822-3151, (email) jkonzuk@geosyntec.com.

Mr. Cox, M.Sc. is a Principal Microbiologist with GeoSyntec Consultants. He specializes in the evaluation of natural attenuation and bioremediation for chlorinated solvents and recalcitrant chemicals in soil and groundwater environments. Mr. Cox holds a Masters degree in Environmental Microbiology from the University of Waterloo, with graduate studies focusing on the biodegradation of chlorinated solvents. Mr. Cox has published more than twenty papers regarding the biodegradation of chlorinated solvents.

Contact Information: Evan E. Cox, Principal, GeoSyntec Consultants, 130 Research Lane, Suite 2, Guelph, Ontario, Canada, N1G 5G3, (phone) 519/822-2230 ext. 237, (fax) 519/822-3151, (email) ecox@geosyntec.com.