

# Electrical Monitoring of In Situ Chemical Oxidation by Permanganate

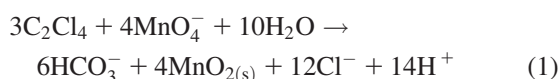
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## Abstract

An array of electrical monitoring probes was constructed to monitor a concentrated permanganate ( $\text{MnO}_4^-$ ) solution injected to treat perchloroethylene (PCE) contamination in a shallow sandy aquifer. The simple probes use pairs of stainless steel wires as electrodes for electrical conductivity (EC) and platinum wires as the working electrodes for oxidation-reduction potential (ORP) measurements. Combined EC/ORP probes were assembled into bundles with multilevel ground water samplers and installed in boreholes around the injection point. Copper/copper sulfate half-cells, inserted to the depth of the water table, acted as ORP reference electrodes. All electrodes were connected to a central data acquisition system, which collected data for a period of 25 d following the injection. Large contrasts in the EC and ORP characteristics of the ground water, compared with the  $\text{MnO}_4^-$  solution, allow the subsurface migration of  $\text{MnO}_4^-$  to be tracked using these relatively simple electrical measurements. The electrical data were used to track the arrival times of the  $\text{MnO}_4^-$  at discrete positions in the aquifer, to guide the timing and selection of locations for water sampling, and for three-dimensional visualization of the  $\text{MnO}_4^-$  distribution during destruction of PCE.

## Introduction

In situ chemical oxidation (ISCO) of chlorinated compounds by chemical oxidants, such as permanganate ( $\text{MnO}_4^-$ ), can be an effective means of treating dense non-aqueous phase liquid (DNAPL) contamination in ground water (Schnarr et al. 1998; Nelson et al. 2001; Schroth et al. 2001). Permanganate is a strong oxidizing agent that is injected into the subsurface as a concentrated solution or slurry. It oxidizes organic compounds, in particular those containing unsaturated carbon bonds, such as perchloroethylene (PCE,  $\text{C}_2\text{Cl}_4$ ), trichloroethylene ( $\text{C}_2\text{HCl}_3$ ), and dichloroethylene ( $\text{C}_2\text{H}_2\text{Cl}_2$ ), to produce manganese oxides ( $\text{MnO}_x$ ), carbon dioxide ( $\text{CO}_2$ ), proton acidity, and chloride ( $\text{Cl}^-$ ) ions, exemplified here by the overall reaction for PCE:



The reactions also cause changes in oxidation-reduction potential (ORP), electrical conductivity (EC), and chemical composition of the ground water (Nelson et al. 2001; Crimi and Siegrist 2003), which can be monitored to

determine the effectiveness of the treatment. Heterogeneity in the physical and chemical properties of an aquifer affects both the distribution of DNAPLs (Brewster et al. 1995; Allen-King et al. 1998) and the efficient delivery of the oxidant to the contaminated zones (Seol et al. 2003). With near-saturation concentrations of  $\text{KMnO}_4$  in saturated geologic systems, the situation is even more complex because of contrasts in fluid densities between the ground water and the concentrated  $\text{MnO}_4^-$  solution (Parker et al. 2002). Detailed monitoring at discrete depth intervals is necessary to improve our understanding of how  $\text{MnO}_4^-$  moves in the saturated zone and how to treat source zones efficiently. Traditional multilevel chemical sampling is expensive and time consuming because of the large number of sample analyses required for adequate spatial coverage and frequency. In addition, reaction processes and/or ground water velocity may be rapid and geochemical effects may be missed entirely by the sampling events. In such cases, it is useful to employ rapid measurements of aggregate properties of the ground water as indicators of geochemical processes to guide the selection of sampling points and frequency. Electrical measurements, such as EC and ORP, are relatively quick and provide good indicators of the presence of  $\text{MnO}_4^-$  and treatment products in a fresh water aquifer. High EC readings result from concentrated  $\text{MnO}_4^-$  solutions in the treatment zone and from the release of high concentrations of  $\text{Cl}^-$  during chlorinated ethene degradation (reaction 1), and the presence of

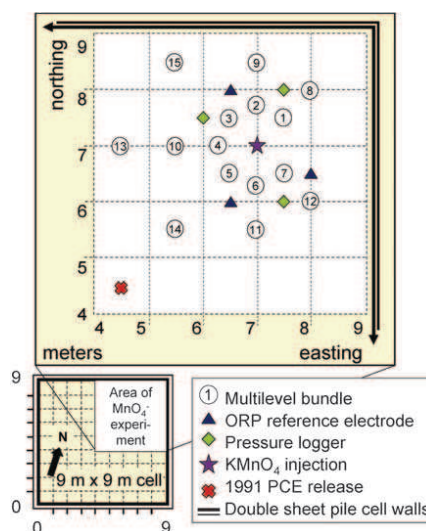
strongly oxidizing  $\text{MnO}_4^-$  generates high ORP readings above background levels.

EC and ORP readings are typically made on ground water samples pumped to the surface by immersing a conductivity probe or combination ORP electrode in a flow-through cell (to limit contact with the atmosphere). In our study, an electrical monitoring system was devised to collect EC and ORP measurements using electrodes that were permanently installed in the subsurface. The concept of in situ electrical monitoring devices has been applied successfully by other workers. For instance, buried platinum rods or wires have been used as working electrodes in studies of redox conditions in soils (Cogger et al. 1992; Karathanasis et al. 2003). A limited number of commercially available platinum microelectrodes were installed by van Bochove et al. (2002) to test continuous in situ measurements of redox potential at depths up to 30 cm in soils, using a multiplexer and datalogger system similar to the one described in this article. The platinum wire ORP electrodes used in this study are modified from a design by Swerhone et al. (1999), which the authors tested in situ for more than 3 years under aerobic and anaerobic conditions. Murdoch et al. (2000) also describe a device that they used to embed both platinum wire electrodes and conductivity sensors in the sidewall of a borehole for in situ measurements.

Our electrical monitoring system was designed to aid hydrochemical sampling by tracking the migration of a single injection of  $\text{MnO}_4^-$  treatment solution in the subsurface and to support the modeling of density-driven advection, dispersion, and chemical reactions. The spatial and temporal density of the data is well suited to computer-aided visualization of the movement of  $\text{MnO}_4^-$  through the solvent-contaminated zone of the aquifer. In this article, we demonstrate the use of electrical monitoring to investigate an injection of  $\text{KMnO}_4$ , but this type of measurement system could be used or adapted for monitoring a variety of other remediation techniques where there is a significant contrast between the electrical properties of the ground water and the treatment medium.

## Site Description

The experimental site is located approximately 100 km north of Toronto, Canada, at the Canadian Forces Base Borden. Our experiment was conducted in a controlled aquifer cell, constructed by driving double walls of sealable joint steel sheet pile through approximately 3.3 m of aquifer sands to penetrate 0.6 m into an underlying silty clay layer. The sheet pile walls create a square cell 9 × 9 m in areal extent (Figure 1) that is isolated from the natural ground water flow system and was used for a large free-form PCE DNAPL release experiment in 1991 (Brewster et al. 1995). The aquifer sand at Borden is a fine- to medium-grained foreshore beach deposit with relatively homogeneous hydraulic conductivity. Thin horizontal to subhorizontal laminations, 0.01 to 0.1 m thick and typically 2 to 5 m long, introduce local heterogeneity to the aquifer (Thomson 2004). The silty clay layer that underlies the sand behaves as a leaky aquitard (Foley 1992). During our



**Figure 1. Plan of the 9- × 9-m cell, showing the monitoring network for the  $\text{MnO}_4^-$  injection experiment in the northern corner of the cell.**

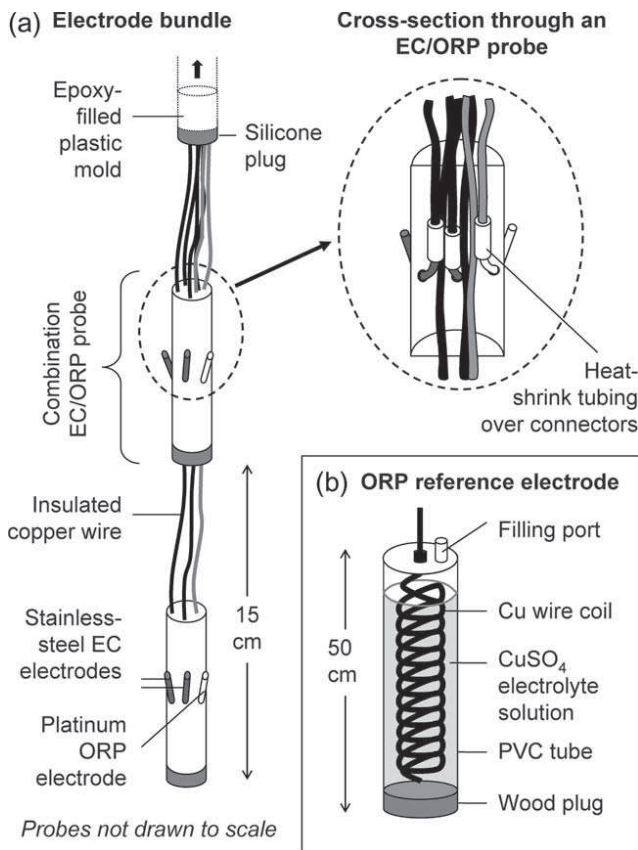
work at the 9- × 9-m cell, the water table inside the cell was typically less than 30 cm below surface.

In July 1991, industrial grade PCE was injected below the water table in the center of the cell at a depth of 0.6 m below ground surface (Brewster et al. 1995). Approximately 770 L of PCE were released and tracked through the subsurface by geophysical methods (Brewster et al. 1995). Several remediation techniques were tested after the geophysical experiments were completed, including pump and treat, air sparging, vacuum extraction (Thomson and Flynn 2000), and two previous  $\text{MnO}_4^-$  injection episodes in 1997 and 1998 (Nelson et al. 2001). Sediments have been disrupted at certain locations by sand coring, piezometer installation, previous  $\text{MnO}_4^-$  injections, and a soil mixing experiment. Our  $\text{MnO}_4^-$  injection experiment was sited in the northern corner of the 9- × 9-m cell (Figure 1), an area that was unaffected by previous experiments.

## Construction and Installation of Monitoring Network

The monitoring network for the  $\text{MnO}_4^-$  experiment in the 9- × 9-m cell consisted of three fully screened wells equipped with pressure/temperature loggers (LT Levelogger Model 3001, Solinst, Georgetown, Canada); 15 multilevel combined water sampling and electrode bundles (comprising a total of 128 EC/ORP and water sampling points), and 3 ORP reference electrodes (Figures 1 through 3). To prevent short circuiting of the  $\text{MnO}_4^-$  solution during injection, the screened wells were installed to a depth of only 1.5 m.

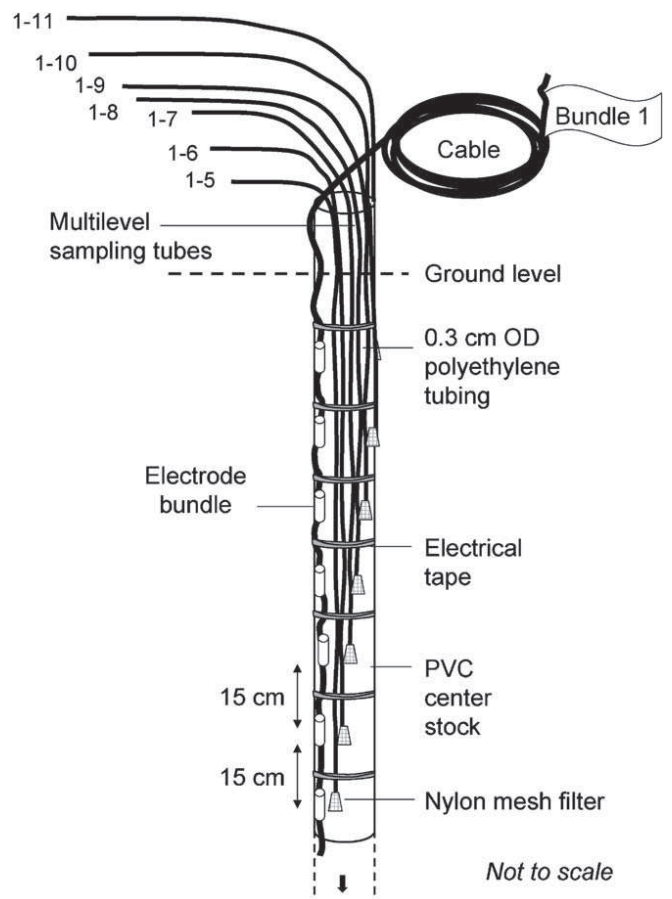
The electrode bundles (Figure 2a) comprise 11 combination EC/ORP probes connected together at approximately 15-cm intervals. For each EC/ORP probe, we used two short lengths (~1.5 cm each) of stainless steel wire as EC electrodes and a similar length of platinum wire (99.95%, 0.5-mm diameter) as the ORP working electrode. The stainless steel and platinum electrodes were connected



**Figure 2. Construction of (a) electrical monitoring probes and (b) copper/copper sulfate ORP reference electrode.**

to copper wires (individually insulated strands, each ~10 m long) using tin-plated crimp connectors. The connections were electrically isolated by fitting a small piece of heat shrink tubing over each connector. The three connections in each EC/ORP probe were then encased in a cylindrical plastic mold, which was filled with epoxy to form a water-tight seal, leaving only the tips of the wire electrodes protruding. The three copper wires joined to each EC/ORP probe were successively accumulated into a bundled cable when the EC/ORP probes were stacked together.

Measurements of ORP require that the platinum working electrodes be connected to a reference electrode immersed in the same solution. Instead of a single reference electrode, we used three large copper/copper sulfate ( $\text{Cu}/\text{CuSO}_4$ ) reference electrodes wired together and buried to just below the water table inside the 9- × 9-m cell. The reference electrodes (Figure 2b) were constructed from bare copper grounding wire coiled tightly inside 50 cm lengths of polyvinyl chloride (PVC) pipe (5-cm diameter). A wooden plug was secured in the base of each pipe to provide a porous junction between the reference electrode half-cell and the shallow ground water near the water table. Once installed in the ground, a small opening in the top cap of each pipe was used to fill the electrode with saturated  $\text{CuSO}_4$  electrolyte solution and excess  $\text{CuSO}_4$  crystals. The reference electrodes were wired together with insulated copper wire, creating a cable for connection to an electrical terminal, which provides a stable reference potential



**Figure 3. Bundled assembly of EC/ORP probes and multi-level sampler.**

(Pawel et al. 1998) for ORP measurements in the electrical monitoring system.

Electrode bundles were tested in the laboratory before installation at the site. They were connected to the data acquisition system and successively submerged in three solutions, tap water, 0.01 M KCl, and 0.1 M KCl, to test the response of the EC electrodes. Recorded values for each EC probe from the laboratory test solutions were later used to normalize readings from the field experiment to the response from one of the EC probes. This normalization procedure corrects for small differences in the readings due to inconsistencies in the electrode construction (e.g., different surface areas of metal tips exposed), allowing EC readings to be compared between probes.

Similar tests were conducted for the ORP electrodes using tap water and solutions of  $6 \times 10^{-4}$  and 0.03 M potassium permanganate ( $\text{KMnO}_4$ ), along with a  $\text{Cu}/\text{CuSO}_4$  reference electrode. ORP values from the test solutions were used to normalize readings relative to the response from one of the ORP probes. Although the readings were normalized to allow comparison between probes, the measurements for EC and ORP were not calibrated to the conventional measurement scales of  $\mu\text{mho}/\text{cm}$  for EC or mV (referenced to the standard hydrogen electrode) for ORP (or Eh). Electrical monitoring in this system relies on relative changes in the EC and ORP readings in space and time, rather than absolute measurements.



Prior to installation, each electrode bundle was attached along the outside of a PVC center stock (3.65 m long, 2.5-cm diameter) using electrical tape (Figure 3). Multilevel water samplers, consisting of 11 minipiezometers made from lengths of polyethylene tubing (0.3-cm diameter), were secured around the outside of the electrode bundles. The base of each minipiezometer tube was wrapped in a small piece of nylon mesh, secured with stainless steel wire, and bound with electrical tape to create a filter at the sampling port. Multilevel sampling ports were positioned just above the electrodes, also at 15-cm vertical spacing, so that each EC/ORP probe had a corresponding hydrochemistry sampling point. The combined electrical and hydrochemical multilevel samplers were installed in 15 vertical boreholes, located at radial distances of 0.7 to 2.5 m from the injection point (Figure 1). The boreholes were each approximately 5 cm in diameter and 3.65 m deep, penetrating between 0 and 40 cm into the underlying silty clay aquitard. They were used to collect continuous sand cores to characterize the PCE distribution prior to the experiment. Cores were collected in 5-cm-diameter aluminum tubing using a piston coring device (Starr and Ingleton 1992).

Bentonite grout was used to fill the bottom of the boreholes to the level corresponding to the top of the aquitard. Multilevel bundles were lowered into the boreholes with the electrodes oriented toward the injection point. The lowest EC/ORP probes and sampling ports were positioned at the aquifer-aquitard interface. The aquifer sand was then allowed to collapse around the bundles by withdrawing a supporting casing from the boreholes. All the water sample tubes were developed using a peristaltic pump, until clear ground water was observed. The ORP reference electrodes were installed in shallow soil auger holes, about 50 cm deep, and the sediments were backfilled around them. Finally, all copper cables from the electrode bundles and ORP reference electrodes were connected to the data acquisition system.

A custom-built data acquisition system was assembled to collect the electrical data. Each electrode in the bundles was wired into a terminal on a multiplexer rack, with the data acquisition system controlling the multiplexer switching of the electrodes. The data acquisition system could then select, measure, and log EC and ORP for each individual probe. Direct readings of ORP were made by measuring the potential between the ORP reference electrodes and each platinum electrode in turn. EC readings for each probe were recorded via a single digital conductivity meter (Traceable<sup>®</sup> 92-075-00, Control Company, Friendswood, TX) and modified conductivity probe. Software was written in Visual Basic to control the data acquisition system and to display the data in real time as it was collected.

## Injection Experiment, Sampling, and Analysis

During a single 3-h injection episode in June 2004, 10 kg of  $\text{KMnO}_4$  were released into the 9- × 9-m cell. A total of 250 L of  $\text{KMnO}_4$  solution (43 g/L) were introduced at a depth of 2.1 m below surface, approximately 1.2 m above the aquifer-aquitard interface, using a drive point delivery system (Nelson et al. 2001) with an injection pressure of 480 kPa. The injection screen was a 15 cm long, 3.2 cm

diameter continuous spiral wrap screen flush threaded to an AW drill rod.

The collection of electrical data began 1 h after the injection was completed. For this experiment, the data acquisition system was set to record the average of 10 readings collected over a period of 100 ms for each EC/ORP probe. In this manner, 128 EC and 128 ORP probes were monitored at 4-min intervals over 25 d.

The continuous sand cores collected from the boreholes were subsampled for PCE at 5-cm spacing. Each core was cut longitudinally and a minicoring device was used to take sediment samples for chemical analysis. Samples were extracted with methanol following the procedure described by Nelson et al. (2001). Over the first 8 d of the experiment, ground water samples were withdrawn from selected multilevel sampling tubes using 60-mL plastic syringes and filtered with disposable 0.2- $\mu\text{m}$  membrane filters (Acrodisc<sup>®</sup> Pall Corporation, East Hills, NY). Alkalinity measurements were made in the field (digital titrator kit, Hach Company, Loveland, CO). Colorless samples were titrated using methyl-red/bromocresol green indicator, and samples containing  $\text{KMnO}_4$  were titrated potentiometrically to an end point of pH 4.5. Potassium permanganate concentrations were determined colorimetrically (525 nm, Genesys 20 spectrophotometer, Geneq Inc., Montreal, Canada). Samples with high  $\text{KMnO}_4$  concentrations were diluted to less than 150 mg/L using deionized water. Filtered, unpreserved samples were collected in 20-mL plastic vials for analysis of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  by ion chromatography (DX-120, Dionex Corporation, Sunnyvale, CA). Samples containing  $\text{MnO}_4^-$  were first reduced by adding excess glucose, centrifuged, and refiltered to remove  $\text{MnO}_x$  precipitates.

## Results and Discussion

The water level measurements indicate that the radial propagation of injection pressure caused a 0.15- to 0.21-m rise in ground water level, which was recorded at the screened wells 4 h after the start of the injection, and then dissipated to background levels over 24 h following the injection.

Monitoring of EC and ORP over 25 d produced a large volume of electrical data. Only selected examples will be discussed to illustrate some of the potential applications of this monitoring method, such as tracking the arrival times of the  $\text{MnO}_4^-$  at discrete positions in the aquifer, guiding the timing and selection of locations for water sampling to improve the efficiency of water quality monitoring, and three-dimensional (3D) visualization of the  $\text{MnO}_4^-$  distribution during destruction of PCE.

In the course of sampling, we found that there was very good agreement between the onset of high EC and ORP values and elevated concentrations of  $\text{KMnO}_4$  in the ground water withdrawn from the corresponding sampling ports (Figure 4). The ORP measurements display background values between -1.2 and 0, and these are readily distinguished from the positive ORP values of samples containing  $\text{MnO}_4^-$ , thereby allowing this parameter to be used as an indicator for the presence or absence of  $\text{MnO}_4^-$ . The low slope of the ORP response to  $\text{KMnO}_4$  concentrations

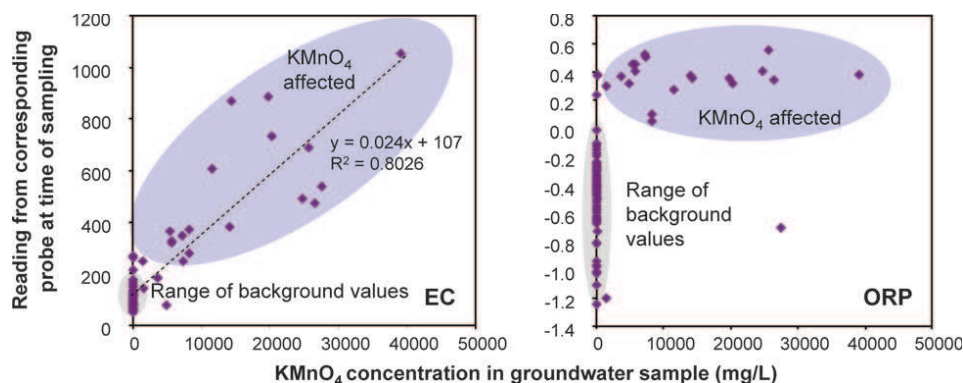


Figure 4. Comparison between measured EC and ORP readings and  $\text{KMnO}_4$  concentrations of ground water samples taken at the same time for EC/ORP probes and their corresponding sampling ports.

does not allow for quantification of  $\text{MnO}_4^-$  using ORP measurements. On the other hand, elevated EC measurements not only indicate the presence of  $\text{MnO}_4^-$  but also show a linear relationship between EC and  $\text{KMnO}_4$  concentration ( $R^2 = 0.80$ ).

#### Tracking Arrival Time

Data from the EC/ORP electrodes provide an effective means of tracking the arrival of the oxidant because of the large EC and ORP contrast between mildly reducing

ground water and the strongly oxidizing, concentrated  $\text{MnO}_4^-$  solution. Figure 5 shows 25-d time-series plots of normalized ORP and EC readings at two electrode bundles, 1 and 5, each 0.7 m away from, but on opposite sides, of the injection point (Figure 1).

The contrast in EC between the concentrated  $\text{MnO}_4^-$  solution and the ground water is large enough to indicate the arrival of peak  $\text{MnO}_4^-$  concentrations at each monitoring point (indicated by peaks in the EC data). However, the initial EC was higher in the lower part of the aquifer, leading to an interference with the detection of low  $\text{MnO}_4^-$  concentrations at depth. Advection and dispersion of the  $\text{MnO}_4^-$  and reaction products may contribute to the decrease in EC response at all probes with increasing time.

The graphs show a decrease in ORP and EC with time at the upper probes in each bundle, and an increase in both ORP and EC with time at the deeper probes. These changes indicate the movement of  $\text{MnO}_4^-$  away from the shallow probes toward the deeper ones, which is likely due to the relatively high density (1.03 g/mL) of the injection solution. An abrupt shift from negative to positive ORP, highlighted by the dots on Figure 5, marks the  $\text{MnO}_4^-$  arrival times at each ORP probe. The ORP and EC graphs indicate that  $\text{MnO}_4^-$  affected the upper four monitoring points at bundle 1 on the first day of the experiment and then gradually moved downward through the aquifer. There is no indication that the  $\text{MnO}_4^-$  contacted the aquifer sand above 2.5-m depth at bundle 5; however, changes in EC/ORP demonstrate the arrival of  $\text{MnO}_4^-$  at the lower probes from day 3 onward. Changes in EC/ORP at bundles 1 and 5 show the  $\text{MnO}_4^-$  solution traveling a vertical distance of 1.2 m and reaching the aquitard at a depth of approximately 3.3 m below surface 8 d after injection. Because there is no ground water flow within the sheet pile cell, the downward movement of the oxidant is a result of density-driven advection and influenced by dispersion and reaction processes, as described by Nelson et al. (2001).

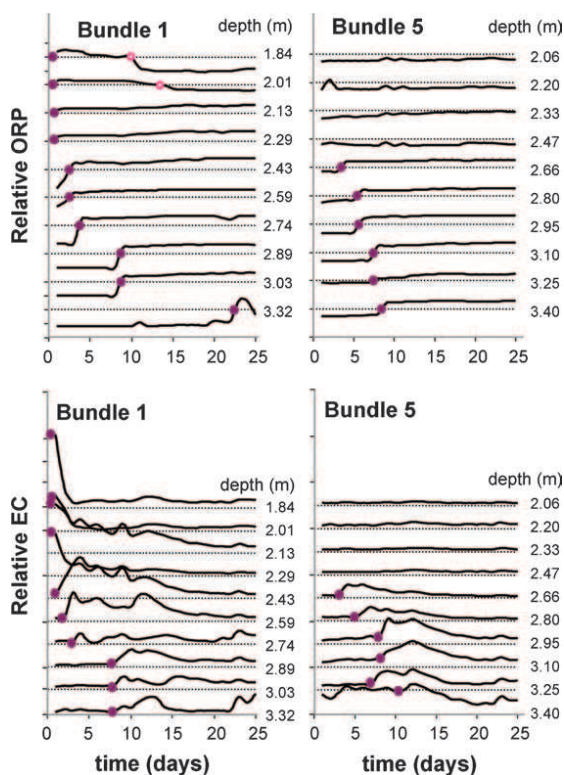


Figure 5. Time-series plots of ORP and EC for bundles 1 and 5, either side of the injection point. Filled dots mark the approximate time when the  $\text{MnO}_4^-$  solution reached each EC/ORP probe. Open circles on the ORP graph for bundle 1 show that ground water ORP at the two shallowest probes returned to negative values after injection.

#### Electrical Monitoring as a Guide to Sampling

Real-time monitoring of electrical readings provides a useful guide for selecting sampling ports to monitor the

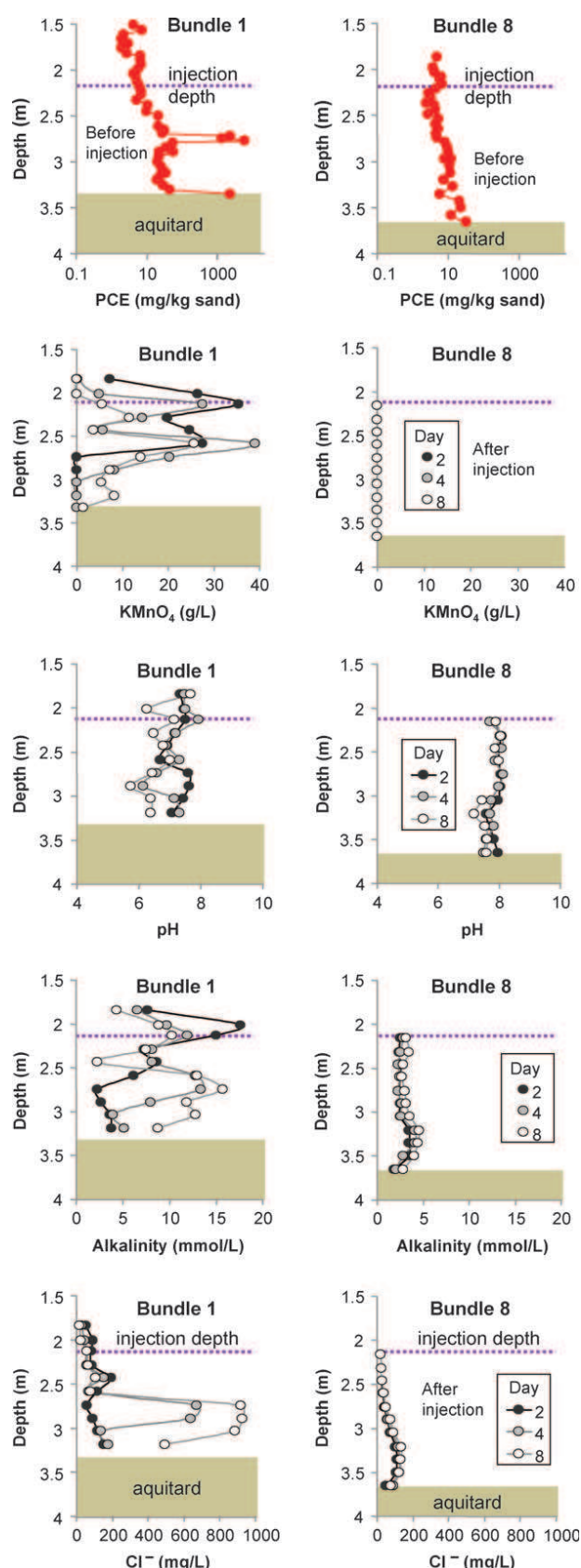
effects of the  $\text{MnO}_4^-$ -PCE reaction, while saving time and effort by excluding unaffected regions of the aquifer. In a relatively homogeneous system with horizontal to sub-horizontal stratification, such as the Borden aquifer, it is anticipated that injection pressure would cause  $\text{MnO}_4^-$  to migrate radially away from the injection point. We had planned to conduct water sampling along a vertical cross section at two distances along a radial spoke through bundles 3 and 15, but early in the experiment, the EC/ORP data indicated that the distribution of  $\text{MnO}_4^-$  solution was not symmetrical and was preferentially orientated toward the north corner of the sheet pile, causing us to change plans and sample bundles 1 and 8 instead.

Prior to the  $\text{MnO}_4^-$  injection, the greatest accumulation of PCE in core 1 (5730  $\mu\text{g/g}$  sediment) was found at a depth of 2.77 m and at the base of the aquifer (Figure 6). A decrease in pH and increased  $\text{Cl}^-$  concentrations at depths below 2.7 m in bundle 1 are a good indication of the rapid reaction of  $\text{MnO}_4^-$  with PCE (Figure 6). This hydrochemical evidence of PCE degradation would not have been detected if sampling had not been triggered by the electrical indications of  $\text{MnO}_4^-$  arrival at bundle 1. The hydrochemistry at bundle 8 is unaffected by the  $\text{MnO}_4^-$  solution by day 8 and shows relatively uniform water chemistry with depth on all three sampling days. Figure 6 shows marked variations in alkalinity and  $\text{KMnO}_4$  concentrations with depth in bundle 1 after injection, probably controlled by local heterogeneities in the aquifer.

#### Visualization of $\text{MnO}_4^-$ Migration

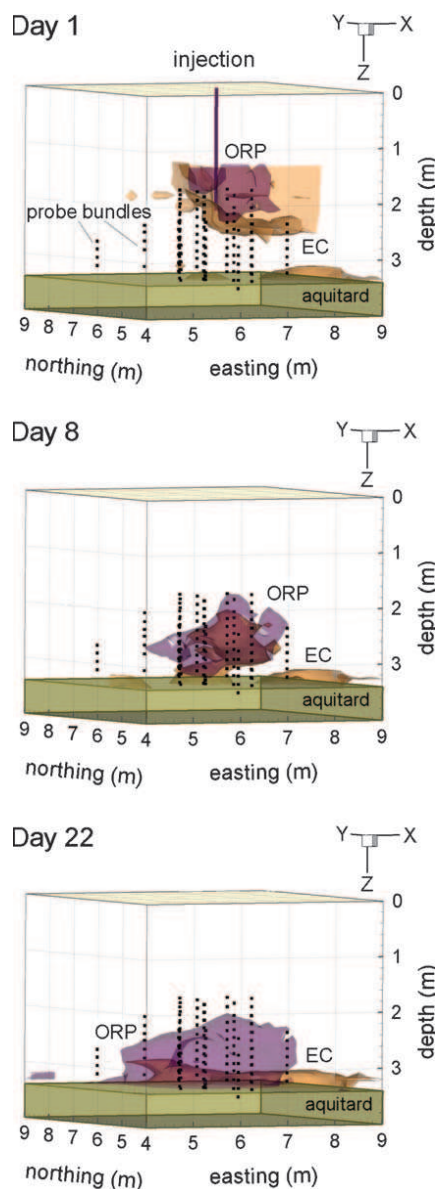
A 3D animation sequence was prepared from the data using Tecplot v. 9.0 software (Tecplot Inc., Bellevue, WA). This type of visualization tool can be used to illustrate the migration of  $\text{MnO}_4^-$  in the subsurface. Figure 7 provides three snapshots from the animation sequence, looking toward the northern corner of the cell. The distribution of the  $\text{MnO}_4^-$  is defined by a 3D contour surface plotted around all ORP values greater than the relative value of 0. A similar contour surface is plotted at a relative EC value of 200. These threshold values were chosen from the observed relationships between EC/ORP and  $\text{KMnO}_4$  shown in Figure 4. The time-series snapshots from the animation sequence clearly demonstrate the spatially variable, density-driven downward migration and the lateral spreading of the injection solution. Local heterogeneities in the hydraulic properties of the aquifer and PCE distribution are responsible for the complexity and asymmetrical shape of the  $\text{MnO}_4^-$  plume in the subsurface. Due to a lack of characterization of the aquifer heterogeneities, this complexity could not be predicted by numerical reactive-transport modeling, even with the inclusion of density-driven advection (T.H. Henderson, personal communication, 2005).

One of the concerns with in situ monitoring equipment is long-term performance in an environment where maintenance opportunities are limited. Poisoning of platinum electrode surfaces is a common problem preventing accurate ORP measurements, although various workers have found that in situ platinum electrodes can be viable for extended periods of several months (van Bochove et al. 2002 and references therein) or even years (Swerhone et al.



**Figure 6.** Geochemical changes with depth at multilevel samplers 1 and 8. The upper two graphs show variations in the concentration of PCE in sediment cores prior to injection (note the logarithmic scale). The remaining graphs display dissolved  $\text{KMnO}_4$ , pH, alkalinity, and  $\text{Cl}^-$  at three specific times after injection when hydrochemical samples were collected. The depth of injection is indicated by the dashed line.





**Figure 7.** 3D representation of the  $\text{MnO}_4^-$  solution in the subsurface, taken from snapshots of the EC/ORP data on day 1, day 8, and day 22 of the experiment. The purple colored contour surface encloses all probes with normalized ORP greater than 0, and the partially overlapping orange contour surface shows normalized EC values greater than 200 units.

1999), particularly under mildly reducing conditions. Our electrodes have not been tested for repeat injections over extended periods but gave reliable normalized EC and ORP readings over the month during which they were in operation. We expect that the electrodes may become fouled over the long term, particularly because of the precipitation of  $\text{MnO}_x$  and the chemical conditions induced by ISCO, which are harsh compared to conditions in the natural systems under which most in situ electrode systems have been tested and operated. Nevertheless, we were encouraged by the performance of the electrodes and particularly by the evidence that ORP and EC readings return to lower values after  $\text{MnO}_4^-$  disperses and is consumed by reactions. For example, ORP probes at 1.84 and 2.01 m in bundle 1 decrease on days 10 and 14 of the experiment, respectively (Figure 5).

## Summary and Conclusions

Inexpensive electrical probes constructed in our laboratory proved to be an effective means of:

- continually tracking the migration of a  $\text{MnO}_4^-$  solution and  $\text{Cl}^-$  generation over a 3-week monitoring period following injection
- efficiently selecting locations for meaningful hydrochemical sampling
- providing a detailed 3D data set to assist with visualization of the complex migration and heterogeneous treatment process.

The electrical monitoring system also provides a good opportunity to acquire detailed data sets for use in design and calibration of numerical models for simulation of the remediation process. The measurements allow inferences to be made about the presence of low permeability zones and their effect on the hydraulic behavior in response to injections, which often poses a major limitation on the success of a remediation system. Although the EC/ORP probe system does not allow quantitative measurements of EC or Eh, the normalized readings provide a good indication of spatial variations and time-series changes in the properties of the ground water during the experiment.

In situ monitoring devices offer several advantages over conventional extraction-based sampling techniques. Subsurface probes have time to equilibrate with the soil and ground water, which may give more representative measurements of aquifer conditions than EC/ORP readings taken on samples brought to surface. In situ measurements represent a very specific, small volume of the aquifer rather than a bulk, blended sample and are less disruptive to flow conditions and subsurface geochemistry than extracting a soil or water sample by coring or pumping. There is also no need to worry about heating or cooling of the samples at surface or rapid reequilibration due to contact with the atmosphere. There are, however, disadvantages to installing probes in the subsurface, which may affect the accuracy of the measurements over the long term. These include a lack of access for cleaning and maintenance of electrodes over time, and the use of long electrical cables to carry the signal to surface, which may introduce electrical impedance errors. Our approach to installing a subsurface network of probes is most suitable for shallow ground water systems with unconsolidated geological materials, where the collapse of sediments around the probes allows good contact between the electrodes and the system under study.

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**Editor's Note:** The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the National Ground Water Association.

## References

- Allen-King, R.M., R.M. Halket, D.R. Gaylord, and M.J. Robin. 1998. Characterizing the heterogeneity and correlation of perchloroethene sorption and hydraulic conductivity using a facies-based approach. *Water Resources Research* 34, no. 3: 385–396.
- Brewster, M.L., A.P. Annan, J.P. Greenhouse, B.H. Kueper, G.R. Olhoft, J.D. Redman, and K.A. Sander. 1995. Observed migration of a controlled DNAPL release by geophysical methods. *Ground Water* 33, no. 6: 977–987.
- Cogger, C.G., P.E. Kennedy, and D. Carlson. 1992. Seasonally saturated soils in the Puget Lowland. II. Measuring and interpreting redox potentials. *Soil Science* 154, no. 1: 50–58.
- Crimi, M.L., and R.L. Siegrist. 2003. Geochemical effects on metals following permanganate oxidation of DNAPLs. *Ground Water* 41, no. 4: 458–469.
- Foley, S.L. 1992. Influence of sand microbeds on hydraulic response of an unweathered clay aquitard. M.Sc. thesis, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada.
- Henderson, T.H. 2005. Electronic mail, September 28, Helena, Montana.
- Karathanasis, A.D., Y.L. Thompson, and C.D. Barton. 2003. Long-term evaluations of seasonally saturated “wetlands” in western Kentucky. *Soil Science Society of America Journal* 67, no. 2: 662–673.
- Murdoch, L.C., W.W. Slack, W. Harrar, and R.L. Siegrist. 2000. Embedded sidewall samplers and sensors to monitor the subsurface. *Ground Water* 38, no. 5: 657–664.
- Nelson, M.D., B.L. Parker, T.A. Al, J.A. Cherry, and D. Loomer. 2001. Geochemical reactions resulting from in situ oxidation of PCE-DNAPL by  $\text{KMnO}_4$  in a sandy aquifer. *Environmental Science and Technology* 35, no. 6: 1266–1275.
- Parker, B.L., J.A. Cherry, and T.A. Al. 2002. Passive permanganate remediation of a solvent DNAPL source zone. In *Proceedings for Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, California, ed. A.R. Gavaskar and A.S.C. Chen. Columbus, Ohio: Battelle Press Online.
- Pawel, S.J., R.J. Lopez, and E. Ondak. 1998. Chemical and environmental influences on copper/copper sulfate reference electrode half cell potential. *Materials Performance* 37, no. 5: 24–29.
- Schnarr, M., C. Truax, G. Farquhar, E. Hood, T. Gonullu, and B. Stickney. 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. *Journal of Contaminant Hydrology* 29, no. 3: 205–224.
- Schroth, M.H., M. Oostrom, T.W. Wietsma, and J.D. Istok. 2001. In-situ oxidation of trichloroethylene by permanganate: effects on porous medium hydraulic properties. *Journal of Contaminant Hydrology* 50, no. 1–2: 79–98.
- Seol, Y., H. Zhang, and F.W. Schwartz. 2003. A review of in situ chemical oxidation and heterogeneity. *Environmental and Engineering Geoscience* 9, no. 1: 37–49.
- Starr, R.C., and R.A. Ingleton. 1992. A new method for collecting core samples without a drilling rig. *Ground Water Monitoring and Remediation* 12, no. 1: 91–95.
- Swerhone, G.D.W., J.R. Lawrence, J.G. Richards, and M.J. Hendry. 1999. Construction and testing of a durable platinum wire Eh electrode for *in situ* redox measurements in the subsurface. *Ground Water Monitoring and Remediation* 19, no. 2: 132–136.
- Thomson, D.A. 2004. Influence of grain size variability and sedimentology on solvent DNAPL distribution in the Borden aquifer. M.Sc. thesis, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada.
- Thomson, N.R., and D.J. Flynn. 2000. Soil vacuum extraction of perchloroethylene from the Borden aquifer. *Ground Water* 38, no. 5: 673–688.
- van Bochove, E., S. Beauchemin, and G. Thériault. 2002. Continuous multiple measurement of soil redox potential using platinum microelectrodes. *Soil Science Society of America Journal* 66, no. 6: 1813–1820.

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