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## A FIELD-SCALE TEST OF IN SITU CHEMICAL OXIDATION THROUGH RECIRCULATION

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## ABSTRACT

In situ chemical oxidation is a developing class of remediation technologies in which organic contaminants are degraded in place by powerful oxidants. Successful implementation of this technology requires an effective means for dispersing the oxidant to contaminated regions in the subsurface. An oxidant delivery technique has been developed wherein the treatment solution is made by adding an oxidant to extracted groundwater. The oxidant-laden groundwater is then injected and recirculated into a contaminated aquifer through multiple horizontal and/or vertical wells. This technique, referred to as "in situ chemical oxidation through recirculation" (ISCOR), can be applied to saturated and hydraulically conductive formations and used with relatively stable oxidants such as potassium permanganate ( $\text{KMnO}_4$ ). A field-scale test of ISCOR was conducted at a site where groundwater in a 5-ft thick silty gravel aquifer is contaminated with trichloroethylene (TCE) at levels that indicate the presence of residual dense non-aqueous phase liquids (DNAPLs). The field test was implemented using a pair of parallel horizontal wells with 200-ft screened sections. For approximately one month, groundwater was extracted from one horizontal well, dosed with crystalline  $\text{KMnO}_4$ , and re-injected into the other horizontal well 90 ft away. Post-treatment characterization showed that ISCOR was effective at removing TCE in the saturated region. Lateral and vertical heterogeneities within the treatment zone impacted the uniform delivery of the oxidant solution. However, TCE was not detected (at an approximate detection level of 5 ppb) in groundwater

samples collected from monitoring wells and soil samples from borings in locations where the oxidant had permeated.

## I. INTRODUCTION

In situ chemical oxidation is a developing class of remediation technologies in which oxidants are delivered to the subsurface to rapidly degrade chlorinated hydrocarbons such as trichloroethylene (TCE) and perchloroethylene (PCE) which are common contaminants at industrial sites.<sup>1,2</sup> The successful implementation of in situ chemical oxidation requires effective techniques for delivering and dispersing chemical oxidants to the subsurface. This paper describes the use of a recirculation approach to deliver oxidant solutions to relatively permeable aquifers (e.g., hydraulic conductivity  $>10^{-4}$  cm/s). This approach, referred to as in situ chemical oxidation through recirculation or ISCOR, involves the addition of an oxidant to extracted groundwater and re-injection of the oxidant-laden groundwater back into the subsurface, essentially setting up a recirculation cell between the injection and extraction wells.  $\text{KMnO}_4$  is especially amenable to ISCOR implementations because it is relatively stable (i.e., it can be circulated in the subsurface over long distances), readily available, and relatively easy to handle in solid or solution form. The approach is very similar to the chemical flushing technique described by Schnarr et al 1997<sup>2</sup>, the primary difference being the use of groundwater to make up the oxidant solution in the method described here. The advantages of ISCOR when compared to well injections alone include better control of

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oxidant and contaminant migration within the treatment zone, and the introduction of potentially higher volumes of oxidant solution because existing soil pore water is extracted prior to oxidant injection. ISCOR is a viable approach to chemical oxidation at remote sites where transport of pre-mixed oxidant solutions may be logistically difficult.

## II. SITE DESCRIPTION

The ISCOR field test was conducted at the X-701B Unit, an area within the U.S. Department of Energy's (DOE) Portsmouth Gaseous Diffusion Plant in Piketon, OH where TCE concentrations in some groundwater wells have been measured at or near saturation.<sup>3</sup> From 1954 through 1988, solvent-laden wastewater from degreasing and decontamination facilities was disposed of in unlined ponds at X-701B. Contamination of the underlying soil and sediments may have been from wastewater percolating from these ponds or leaking from pipelines. Use of the ponds has been discontinued, and sludge from the ponds has been dredged and disposed of as part of a RCRA closure in 1990.

The stratigraphy underlying the X701-B site consists of the following layers proceeding downward from the surface: (1) Minford silt and clay with a thickness of 25 to 30 ft, (2) Gallia silty gravel which has a thickness varying from 2 to 10 ft, (3) Sunbury shale which is the first bedrock layer and consists of a 10 to 15-ft thick, moderately hard shale that often exhibits an upper weathered zone of gray, highly plastic clay, and (4) Berea sandstone which is present at an approximate depth of 47 ft in this area.<sup>3</sup> The Minford silt and Sunbury shale layers have very low conductivities, while the Gallia and Berea layers are the main water-bearing units. Past characterization has shown TCE contamination to be mainly in the Minford, Gallia and weathered region of the Sunbury shale. The highest risk for offsite contaminant migration is associated with the relatively permeable Gallia layer. Hence, the ISCOR field test was targeted at treating contamination in the Gallia.

The ISCOR field test was implemented at X-701B using a pair of previously installed parallel horizontal wells. The wells are 90 ft apart and have 200-ft screened sections consisting of 5-in. diameter, high-density polyethylene porous filters (500  $\mu$ m pore size). The horizontal wells were drilled such that screened sections were on top of the Sunbury shale and within the Gallia water-bearing unit. Details regarding installation of the wells can be found in Korte et al., 1997.<sup>4</sup>

The goal of the field test was to determine the efficacy of introducing  $\text{KMnO}_4$  into the Gallia using an ISCOR approach. The field test duration was preset at 4 weeks. As such, clean up of the entire zone between the

horizontal wells was not a test objective. ISCOR performance was evaluated by comparing pre- and post-treatment soil and groundwater contamination in areas that were permeated by the oxidant.

## III. PRE-TREATMENT CHARACTERIZATION

Immediately prior to the ISCOR field test, 22 boreholes were drilled between the horizontal wells down to bedrock to confirm the underlying lithology and collect samples for volatile organic compound (VOC) and other physical/chemical analyses. Continuous core samples were obtained from the boreholes starting from a depth of 18 ft down to the weathered zone of the Sunbury shale. Within the horizontal well area, the thickness of the Gallia layer ranged from 5 to 6 ft. Soil samples were collected from every 1.0-ft interval from 20 to 30 ft below ground surface for VOC analysis through hexane extraction followed by analysis of the extracts on a Hewlett Packard® Model 5890 gas chromatograph equipped with an electron capture detector (GC/ECD). The GC/ECD was calibrated for TCE with an approximate detection limit of 5 ppb.

Three-quarter inch diameter PVC wells with 5-ft screens within the Gallia layer were installed at 14 of the 22 boreholes (see Fig. 1 for monitoring well locations). A higher number of monitoring wells was installed around the central region between the horizontal wells where the highest TCE concentrations had previously been measured.<sup>4</sup>

Soil samples from the Minford, Gallia and Sunbury shale layers exhibited a wide range of TCE concentrations (Table 1). There is a significant amount of TCE contamination in both the Gallia and Sunbury and in the Minford layer below 20-ft (contamination at shallower depths can not be confirmed since samples were not collected at depths < 20 ft).

Table 1. Trichloroethylene concentrations in soil samples from ISCOR pretreatment characterization.

Layer	No. of samples	Trichloroethylene concentration ( $\mu\text{g}/\text{kg}$ )**				
		Average	Std. Dev.	Median	Min.	Max.
Minford *	90	19,493	21,770	10,002	nd	80,471
Gallia	163	53,596	52,713	43,320	nd	302,237
Sunbury*	13	132,405	269,791	46,932	32	1,048,174

\* Minford: based on samples collected at depths > 20 ft. Sunbury: based on samples from the top weathered region.

\*\* Based on wet soil weights, nd = not detected at an approximate detection limit of 5  $\mu\text{g}/\text{kg}$ . Avg. moisture content = 16%.

Although ISCOR implementation at X-701B was aimed at removal of TCE from the Gallia water-bearing unit, TCE concentrations were also of interest in the Minford and Sunbury to determine whether ISCOR will affect TCE levels in these layers. TCE concentrations in

the Gallia were highest in the central region of the treatment zone between the horizontal wells, consistent with past characterization results.<sup>4</sup>

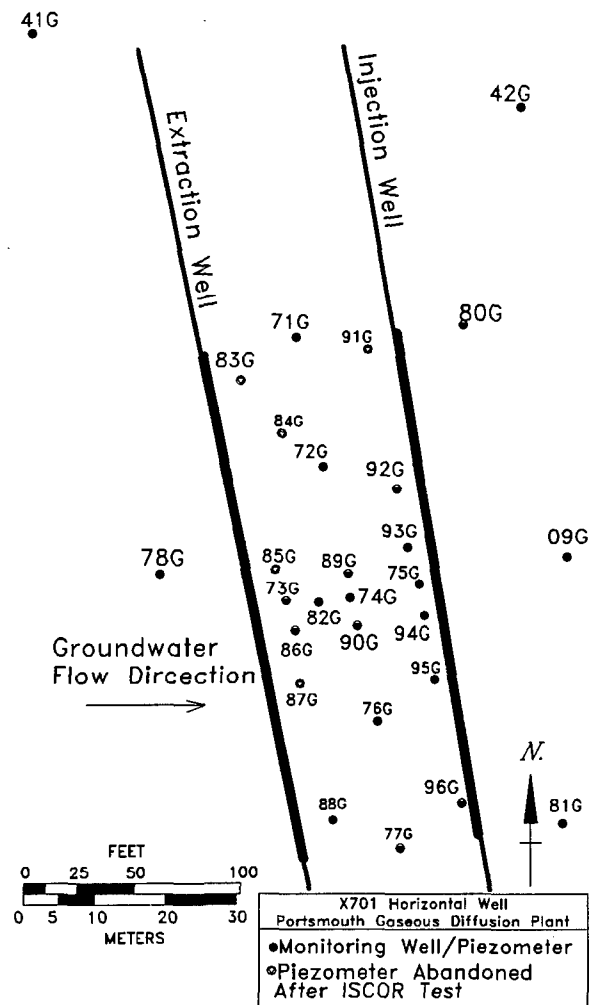


Figure 1. Location of monitoring wells in the vicinity of the ISCOR field test site.

#### IV. FIELD TEST OPERATIONS

A conceptual schematic for the flow system used during the ISCOR field test is shown in Fig. 2; a more detailed flow diagram can be found in West et al 1998.<sup>5</sup> During the implementation of ISCOR at the X-701B site, water extracted from the west horizontal well was sent through a nearby groundwater treatment facility before the addition of  $\text{KMnO}_4$ . This modification to the original ISCOR concept was made to comply with a regulatory requirement for TCE in the re-injected groundwater to be less than 5 ppb. A screening test of TCE degradation in water from one of the monitoring wells showed that 1.5%

$\text{KMnO}_4$  can reduce the initial TCE concentration from 1000 ppm (close to saturation) to 10 ppm in 90 minutes. Although this is a significant reduction in concentration (99%),  $\text{KMnO}_4$  amendments coupled with a 90-minute residence time were not adequate to ensure compliance with the 5-ppb injection limit. Longer residence times were not considered due to limited space for additional holding tanks. In the state of Ohio as well as in most other states, it is possible to obtain a permit to re-inject groundwater that does not satisfy drinking water standards. However, an application for this injection permit was not pursued due to time and scheduling constraints.

Groundwater extracted from the west horizontal well was delivered to the nearby X-623 Groundwater Treatment Facility (X-623 GTF) where the water was treated using air strippers and activated carbon. Water for the oxidant injection solution was taken from a portion of the X-623 GTF effluent, and mixed with crystalline  $\text{KMnO}_4$  using a solids feeder. The oxidant-laden water was then injected without pressurization into the east horizontal well. As such, flow between the horizontal wells was opposite the direction of ambient groundwater flow, following previous recirculation tests at the site.<sup>4</sup> Extraction from the west horizontal well was set to ~10 gpm by flow regulators. The target injection flow rate at the east horizontal well was 10 gpm. However, this well could only take in a maximum of 6 gpm; water backed up to the ground surface when higher oxidant injection flow rates were attempted. Previous hydraulic tests have shown the east horizontal well to be less efficient than the west horizontal well.<sup>4</sup>

ISCOR between the horizontal wells began operation on July 26, 1997 and continued through August 21, 1997. Simultaneous injections in the east horizontal well and well 74G were initiated on August 20, 1997. Well 74G was selected because it is centrally located (see Fig. 1) and had high levels of TCE (734 ppm in groundwater) prior to the beginning of the ISCOR field test. Injection and extraction from the horizontal wells were halted on August 21, 1997, while oxidant injection into well 74G was continued through August 28, 1997, approximately 4 weeks after the ISCOR field test was initiated. As mentioned previously, the field test duration was preset at 4 weeks. The oxidant flow rate into 74G was 2 gpm. Thus, injection into well 74G, which had a screened section of 5 ft, was significantly more efficient than injection into the 200-ft horizontal well which could only be sustained at a maximum of 6 gpm.

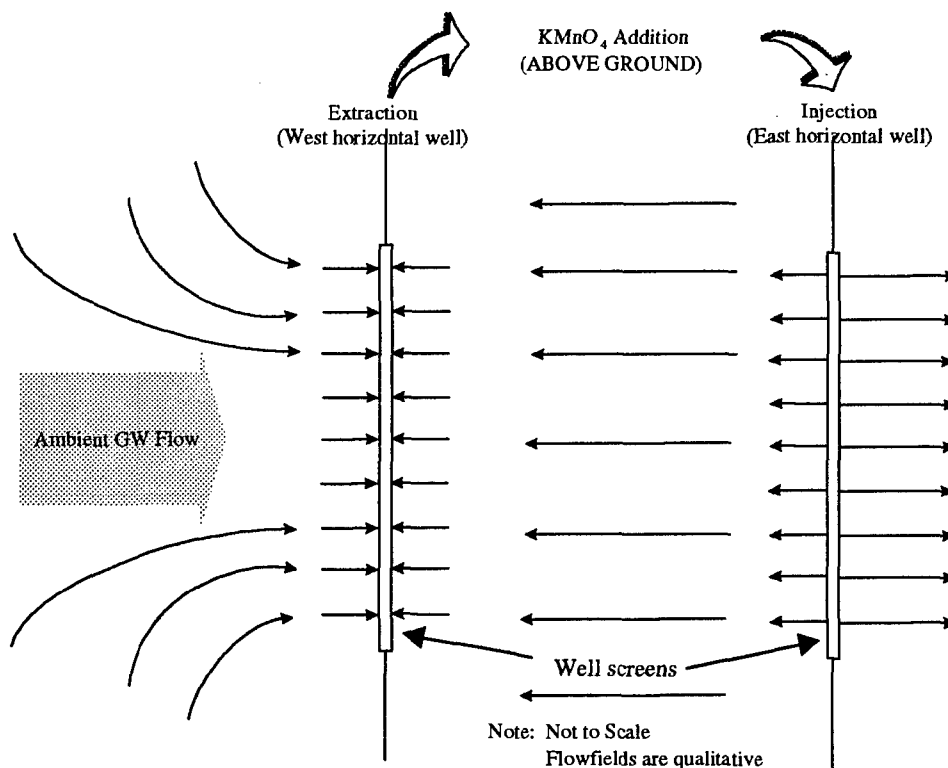


Figure 2. Conceptual schematic of ISCOR flow system at X-701B.

Recirculation between the horizontal wells was halted 3 weeks into the field test because of increasing amounts of colloidal particles coming from the extraction well which X-623 GTF was not prepared to handle. These particles, which were on the order of 1  $\mu\text{m}$  in size, were identified using a scanning electron microscope and energy dispersive x-ray as amorphous manganese oxides. In future applications of this technology, the flow system must be modified to include a means for removing manganese oxide particles from extracted groundwater. Such techniques have been developed for wastewater treatment where manganese oxides are a by-product of dissolved iron removal using  $\text{KMnO}_4$ .<sup>6,7</sup>

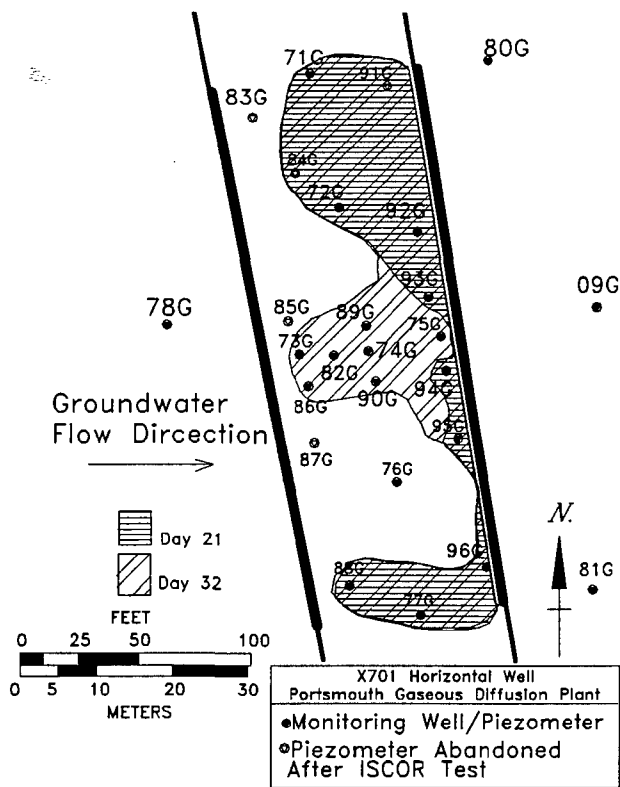
A total of ~12,700 kg of  $\text{KMnO}_4$  was delivered to the treatment region during the ISCOR field test, 1960 kg of which was introduced through vertical well 74G. Of the 206,000 gallons of oxidant solution, 14,000 gallons were delivered through well 74G.

## V. PERFORMANCE MONITORING

The performance of the ISCOR system was monitored through collection of water samples from the influent and effluent streams (daily), and from monitoring wells (daily to every three days) in the vicinity of the treatment region. The  $\text{MnO}_4^-$  concentration in these water samples was quantified in the field by measuring absorbance of filtered

samples using a Hach DR2000 spectrophotometer at 525 nm. TCE concentrations were quantified by hexane extraction followed by GC/ECD analysis of the extracts. TCE analyses were done within 7 days of groundwater sample collection.

The delivery of oxidant solution through the east horizontal well was not uniform through the length of the treatment region. After 21 days, the oxidant had been detected in all the monitoring wells that were ~15-ft from the injection wells, except for well 75G (Fig. 3). The oxidant was only detected in the central area of the treatment zone after oxidant injection in vertical well 74G was initiated. The non-uniform distribution of  $\text{MnO}_4^-$  was probably due to spatially variable hydraulic conductivities which ranged from 24 to 411 ft/day as measured in monitoring wells within the treatment zone.<sup>4</sup> The highest conductivity (411 ft/day) was measured in well 77G which is in the southern end of the treatment zone. Pressure drop along the 200-ft well screen could have also caused more oxidant solution to flow out near the well head. Additionally, the injection well screen may have had a variable efficiency along its length.

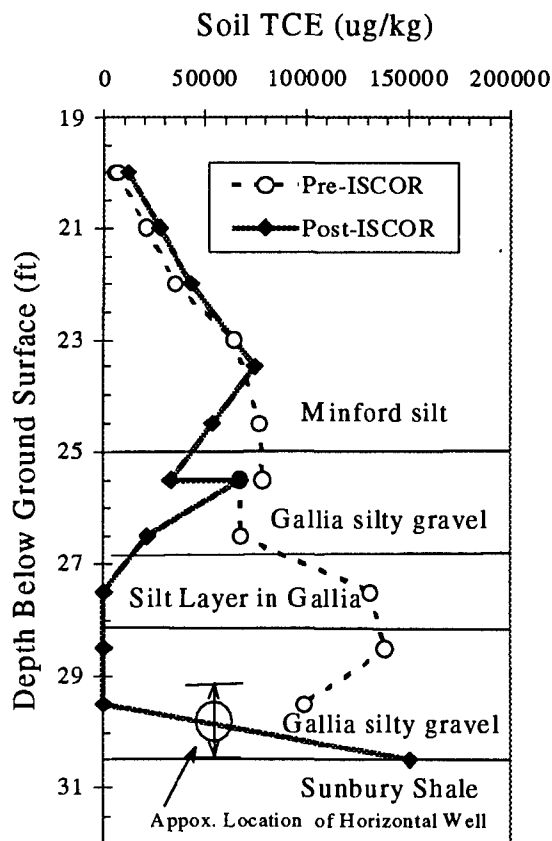


**Figure 3. Approximate permanganate front 21 and 32 days after the ISCOR field test was initiated. Wells within the shaded regions had detectable levels of permanganate. No  $MnO_4^-$  was detected in wells outside of the region between the horizontal wells (09G, 80G, 81G, 78G).**

Overall, whenever permanganate was detected in groundwater samples from the monitoring wells, TCE concentrations dropped to non-detectable or low ppb levels. This reduction in groundwater TCE concentration may be due to the degradation or removal of TCE from associated sediments, or displacement of contaminated groundwater from the pore space and non-equilibrium between the pore water and residual TCE in the sediments. Approximately two weeks after the ISCOR field test ended, boreholes were drilled in locations where  $MnO_4^-$  was detected during treatment operations. This post-treatment sampling showed that TCE soil concentrations were significantly reduced in the Gallia layer wherever  $MnO_4^-$  was able to permeate. This is illustrated in Figs. 4 and 5 where pre- and post-treatment TCE soil concentrations are compared in boreholes drilled near monitoring wells 90 and 95G. In borehole 90G, soil TCE levels remained elevated in the upper layer of the Gallia probably due to the presence of the silt layer which interfered with oxidant dispersion (Fig. 4). The presence of the silt layer was noted at this location from lithologic examination of cores during pretreatment sampling. All the post-treatment boreholes drilled 2 weeks after the field test showed that TCE levels in the Minford silt and

Sunbury shale did not significantly change with treatment. However, because  $MnO_4^-$  was still detected in some of the monitoring wells 5 months after the ISCOR field test, subsequent diffusion of the oxidant into the Minford and Sunbury layers is possible. Soil sampling planned for summer 1998 will help establish whether  $MnO_4^-$  delivered to the more permeable Gallia can address contamination in the Minford and Sunbury layers through oxidant diffusion.

Concentrations of TCE and  $MnO_4^-$  (as  $KMnO_4$ ) vs time in groundwater from monitoring wells 90G and 95G are shown in Figs. 6 and 7.  $MnO_4^-$  was detected in both of these wells 4 months after the field test, and TCE was not detected at an approximate 5-ppb detection limit. Five months after the field test (January 1998),  $MnO_4^-$  was no longer present in well 95G and corresponding TCE levels have increased. Because TCE was not detected in post-treatment soil samples (Fig. 5), the recent increase in TCE concentration in well 95G indicates that recontamination from groundwater upstream and/or from the adjacent Minford silt and Sunbury shale layers may be occurring in this well.



**Figure 4. Pre- and posttreatment trichloroethylene concentrations in soil samples collected from boreholes near well 90G.**

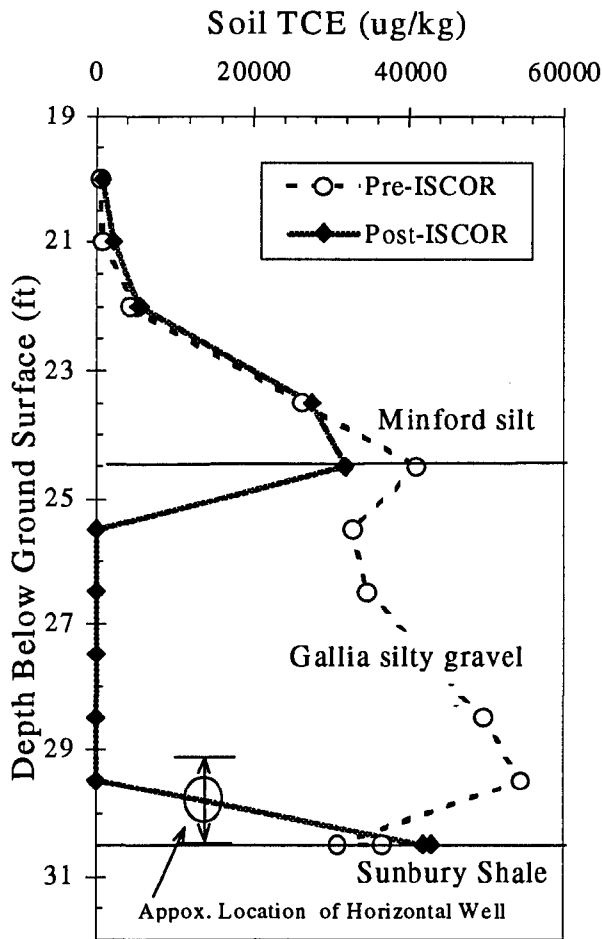


Figure 5. Pre- and posttreatment trichloroethylene concentrations in soil samples collected from boreholes near well 95G.

## VI. CONCLUSIONS

The field test described above showed that ISCOR is a viable remediation technique for saturated subsurface media. Lateral and vertical heterogeneity impacted the delivery of oxidants through the horizontal wells. Where the oxidant was able to permeate the Gallia, significant reductions in TCE were measured in both groundwater and soil samples. Oxidant injection through the vertical well was significantly more efficient than injection through the horizontal well. For the X-701B site, ISCOR implementation using a network of vertical wells can be more effective than horizontal wells at uniformly dispersing the oxidant through the Gallia.

Contamination in the Minford and Sunbury layers adjacent to the Gallia water-bearing unit did not change based on TCE measurements in soil samples collected 2 weeks after the field test. However, diffusion of the oxidant into the less conductive layers is possible, given that  $\text{MnO}_4^-$  was still present in some monitoring wells 5 months after the ISCOR field test. Soil sampling planned for the summer of 1998 will establish the extent to which ISCOR in the Gallia can address contamination in the adjacent Minford and Sunbury layers. Results of the latter would help determine the feasibility of using ISCOR in relatively conductive aquifers that are interspersed with lenses of low-conductivity materials.

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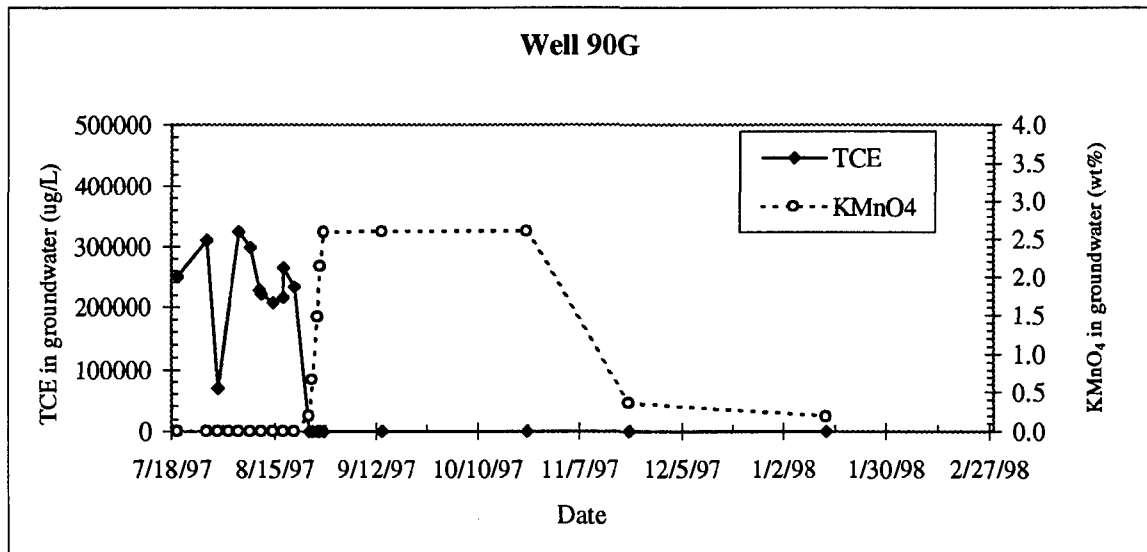


Figure 6. Trichloroethylene and permanganate concentration vs time in well 90G.

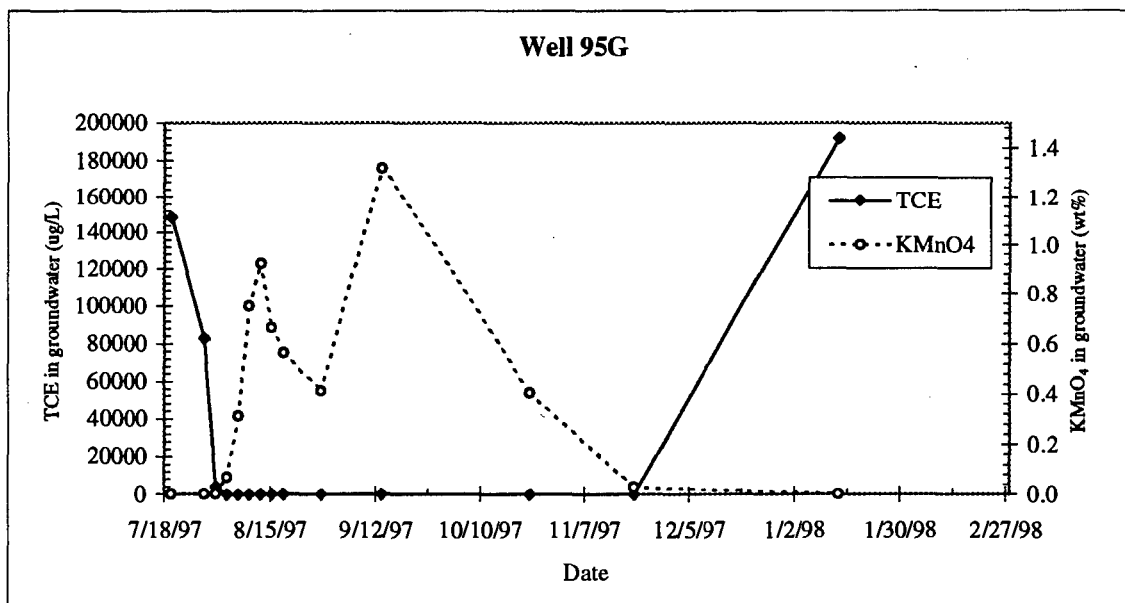


Figure 7. Trichloroethylene and permanganate concentration vs time in well 95G.

Gaseous Diffusion Plant. The planning and execution of a full-scale field demonstration requires the efforts of many individuals. Contributions of the following are greatly appreciated: J. Sheppard, L. Kantner, E. Phillips, T. Early, B. Abke, J. Callan, J. Ervin, H. Sydnor, S. Winters, M. Pelfrey, B. Carr, K. Davis, S. Hall, P. Kearl, N. Korte, G. Mahinthakumar, M. Morrissey, S. Y. Lee, K. McCracken, M. Mumby, J. Nyquist, C. Rightmire, Y. Roh, and J. Zutman. Oak Ridge National Laboratory is managed by the Lockheed Martin Energy Research Corporation for the U. S. DOE under contract DEAC05-96OR22464.

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