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Project Title: **Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes**

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Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes

Principal Investigators; Dr. F.W. Schwartz and Dr. Hubao Zhang

Introduction

The purpose of this brief report is to present the results of studies over the past year concerned with the oxidation of chlorinated solvents by potassium permanganate. The study is organized with a laboratory component that looks generally at the basic reaction processes and kinetics, and a theoretical component that is developing modeling tools appropriate for designing systems under field conditions. The following sections will examine new results in both of these research strands separately.

Laboratory Investigations

Early in the study, there was emphasis on establishing details of permanganate oxidation reactions involving DNAPLs like PCE and TCE. Yan and Schwartz (1999) provide preliminary information on the pathways and pseudo-first-order rate constants for various compounds. A second paper that is close to submission describes the intermediates and how they change as a function of solution pH.

With this work completed, attention has turned to ways of speeding up the oxidation reactions and the potential role of MnO_2 surfaces in catalyzing oxidation reactions. The oxidation reactions appear to be limited by the low solubilities of the contaminants in the aqueous phase. So far, the effort to increase the efficiency of permanganate oxidation has been mainly concentrated on ways to enhance the solubility of the chlorinated ethylenes. One approach has been to examine whether cosolvents (e.g., alcohol) could increase reaction rates through solubilization of the pure-phase liquid. A series of laboratory batch tests were undertaken with various alcohol and water mixtures. However, there are interactions, as yet poorly understood, which appear to reduce reaction rates in the cosolvent phase. In addition, there is competition between the cosolvent and the target contaminant reacting with permanganate ions. These two reasons explain why an increased efficiency with cosolvent enhanced permanganate oxidation is not observed.

Another approach taken in our laboratory has been to examine the possibilities of reaction speedups using *phase-transfer catalysis*, which is a popular technique in synthetic organic chemistry. With phase-transfer catalysis, we usually use two immiscible phases that are in contact -- an aqueous phase containing an ionic reactant and an organic phase containing the organic substrate. One might normally expect that the reaction of two substances in separate phases is inhibited because of the inability of the reagents to interact. Adding a phase-transfer catalyst (PTC) solves this problem by transferring the ionic reactant into the organic phase.

Phase-transfer catalysts are organic-soluble cations. Due to their amphiphilic nature, the catalysts are distributed between aqueous and organic phases, form ion pairs with the reactive anions, such as permanganate ions (MnO_4^-), to bring them into the organic phase in a form suitable for reaction. Presumably, the phase-transfer catalyst would not be consumed but perform the transport function repeatedly. The relative affinity of a catalyst-anion complex to organic phase versus aqueous phase (K_E), as well as the lipophilicity of the anions, would determine the efficiency of catalysts as a vehicle for anion transfers.

Kinetic batch experiments were conducted to verify the hypothesis that PTCs would initiate permanganate oxidation of TCE in the nonaqueous phase and that the overall rates of decomposition of TCE with permanganate oxidation would increase. Three catalysts were selected based on their extraction constants (K_E) and molecular structures. The selection of catalyst was also restricted by the solubility of catalyst-anion complex in aqueous phase. By measuring the chloride concentration (Figure 1) and UV-Vis absorbance for permanganate consumption (Figure 2) in aqueous phase, TCE decomposition rates were estimated for three catalysts and a blank as a control. The results of batch experiments showed that one of selected PTCs were able to increase oxidation rates of TCE.

In addition to the catalytic oxidation of TCE with permanganate, enhanced solubilization of TCE in aqueous phase with PTCs would also be a possible mechanism that can explain the accelerated TCE decomposition in the presence of the large molecules. In order to assure the catalytic mechanism for enhanced TCE decomposition, therefore, it is necessary to examine any increased TCE aqueous solubility with the PTCs and their contribution to overall TCE decomposition. Our future effort to develop the catalytic scheme to stimulate the permanganate oxidation will also include the studies on the mechanism of catalytic reaction in nonaqueous phase utilizing various PTCs and the impact of PTC addition on the modification of NAPL mobility. Evaluation of PTC in larger scale, i.e. column or tank experiments, will be conducted in an attempt to simulate a field situation.

In summary, there have positive results in the development of approaches to increase the rate of oxidation. We believe that there is significant potential for testing these approaches under field conditions.

Modeling Experiments

There has also been good progress on the development of numerical approaches to simulate the behavior of source zone floods. An initial paper has been submitted to Water Resources Research. To date, there is no published work on efficient numerical tools to assist in the design and the prediction of oxidization processes in field. We see this need as important because the optimization of the remediation process will reduce the cost of the operation, and potential complications of the process. Preliminary modeling of permanganate oxidization of TCE was presented by Zhang *et al*. (1997).

The conceptual model assumes that there exists a zone of residual NAPL or a dissolved plume of chlorinated compounds in the saturated zone. As permanganate is injected into an aquifer as a dissolved oxidant and transported along a flow path, the permanganate reacts with not only carbon and other reactive species (Fe^{+2}, Mn^{+2} and S^{-2}) but also dissolved chlorinated compounds in the aqueous phase. With the injection of permanganate into a NAPL zone, the increased concentration gradient between the solubility and the aqueous concentration near the NAPL zone accelerates the pure-phase dissolution.

Illustrative Results

Here, we present some illustrative results. A field-scale experiment of permanganate oxidation of TCE was performed at the Department of Energy Portsmouth Gaseous Diffusion Plant by researchers at Oak Ridge National Laboratory (West *et al.*, 1997). The field test was implemented by injecting permanganate in one horizontal well and extracting fluid in other horizontal well about 27 m up-gradient of the injection well (Figure 3). Extracted fluid with residual permanganate was regenerated by adding additional $KMnO_4$ crystals and re-injected into the aquifer. There are four major geological layers underlying the study site. The test was conducted in the Gallia sand and gravel with an average thickness of 1.5 m.

A total of 10,740 kg of Permanganate was injected through the horizontal well between July 26 and August 27, 1997. In addition, a total of 1960 kg of permanganate was delivered by a vertical well (74G injected at 2 gpm) located at the center of the treatment zone between August 20, 1997 and August 28, 1997. The injected permanganate front shows a pattern of preferential flow near two ends of the wells (Figure 3).

A two-dimensional model of 51x51 nodes was constructed to represent the treatment zone and vicinity (Figure 4). The simulation grid was designed with a fine discretization inside the test region (Δx = 1m, and Δy= 2 m) and a coarse discretization outside of the region (maximum Δx = 6 m, and maximum Δy= 7.5 m). The thickness of the simulation domain is that of the Gallia formation (Δz = 1.5 m). To simplify the model setup, flow rates along the well were adjusted to approximately reflect the migration front of $KMnO_4$, while keeping the hydraulic conductivity of the simulation domain the same.

An average hydraulic conductivity of 35 m/day is assumed for the entire simulation domain. Values of longitudinal and transverse dispersivity are selected as 5 and 0.5 m, respectively, to ensure that Peclet number is less than 2. The average porosity of the Gallia is 0.2 as reported by Beard and Anderson (1996). A small regional horizontal gradient of $1.43\text{x}10^{-6}$ was imposed in the simulation region to account for regional flow.

Figure 5 displays the permanganate distribution at 7 days, 32 days, and 120 days, starting from the initial injection of permanganate. Initial concentration (Figure 5a) was assigned as reported by West *et al*. (1997). At time = 7 days, permanganate was located at the two ends of the horizontal wells (Figure 5b). At time = 32 days, the transport front of permanganate originated from the horizontal injection well expanded and the permanganate injected through well 74G covered an area near the center of the test region (Figure 5c). These characteristics were observed by the field experiment (Figure 3). It may be expected that unused permanganate will remain in the aquifer for a period of time (Figure 5d) after the injection of permanganate has been completed. The residual permanganate may be useful in oxidizing TCE in the aqueous phase from the continuous dissolution of TCE located in the aquifer above and below.

The simulation indicates TCE concentration was significantly reduced where the permanganate was delivered as compared with the initial TCE distribution in the aquifer (Figure 6b). At time = 7 days, the contour line of 0.005 mg/L TCE (drinking water standard) is located near the horizontal injection well (Figure 6c). The 0.005 mg/L TCE contour line expands outward significantly at time = 32 days (Figure 6d). The 0.005 mg/L TCE contour line doesn’t expands much at time = 120 days because the permanganate front doesn’t change from that at time = 32 days.

The computer simulations together with column, test cell, and field experiments also suggest that the proper determination of NAPL saturation, aqueous concentration of chlorinated compounds, and the reactive properties of aquifer material with permanganate are very important to a successful chemical oxidization design and field operation. This study and previous work also indicate that permanganate oxidization of chlorinated compounds may only work well for contamination with a low NAPL saturation or in the dissolved phase, because the chemical reaction between the chlorinated compounds and permanganate occurs in dissolved phase and the dissolution of NAPLs is a rate-limited, although the chemical reaction accelerates the dissolution process.

Selected References

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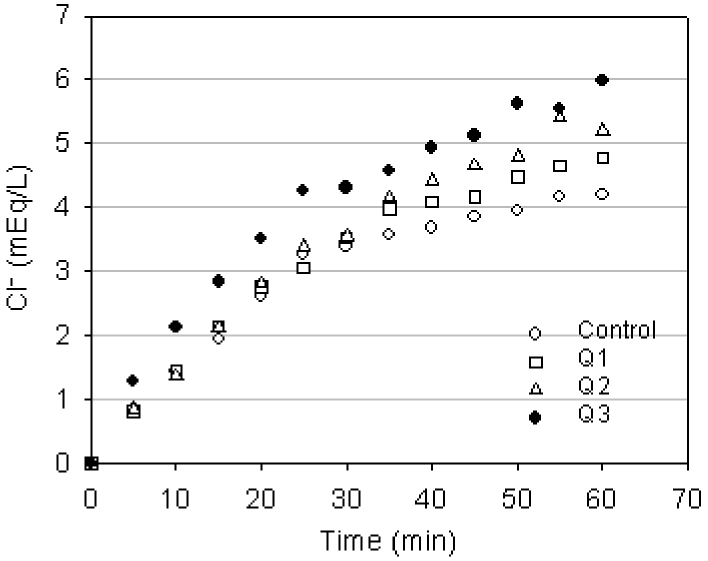


Figure 1. Concentration of chloride ion released from permanganate oxidation of TCE with different PTCs

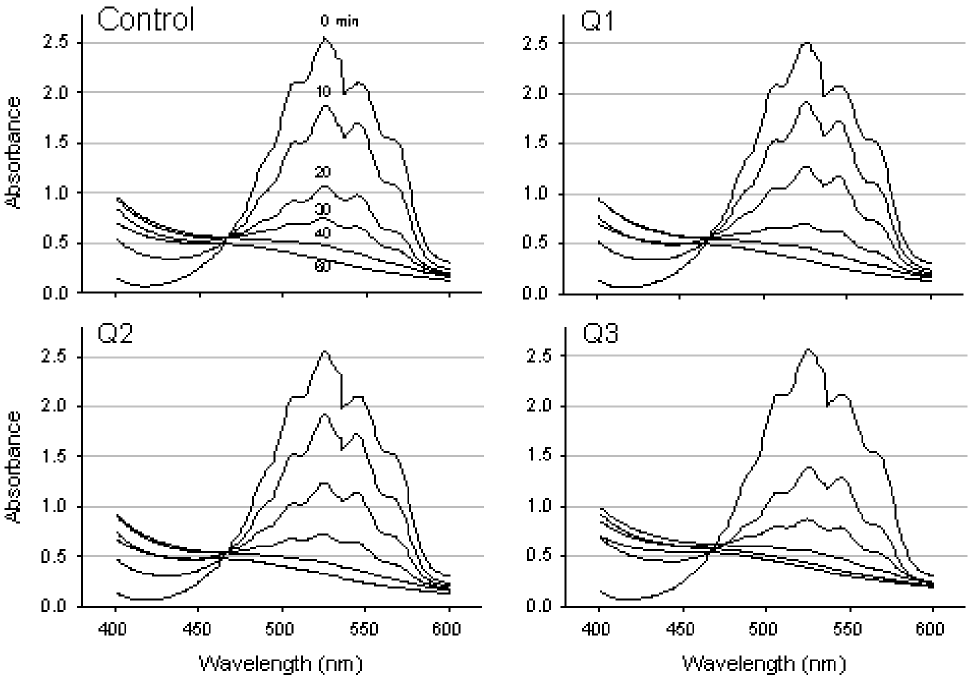


Figure 2. UV-Vis spectra of aqueous phase in permanganate oxidation of TCE facilitated with different PTCs. Numbers on graphs indicate the reaction time (min).

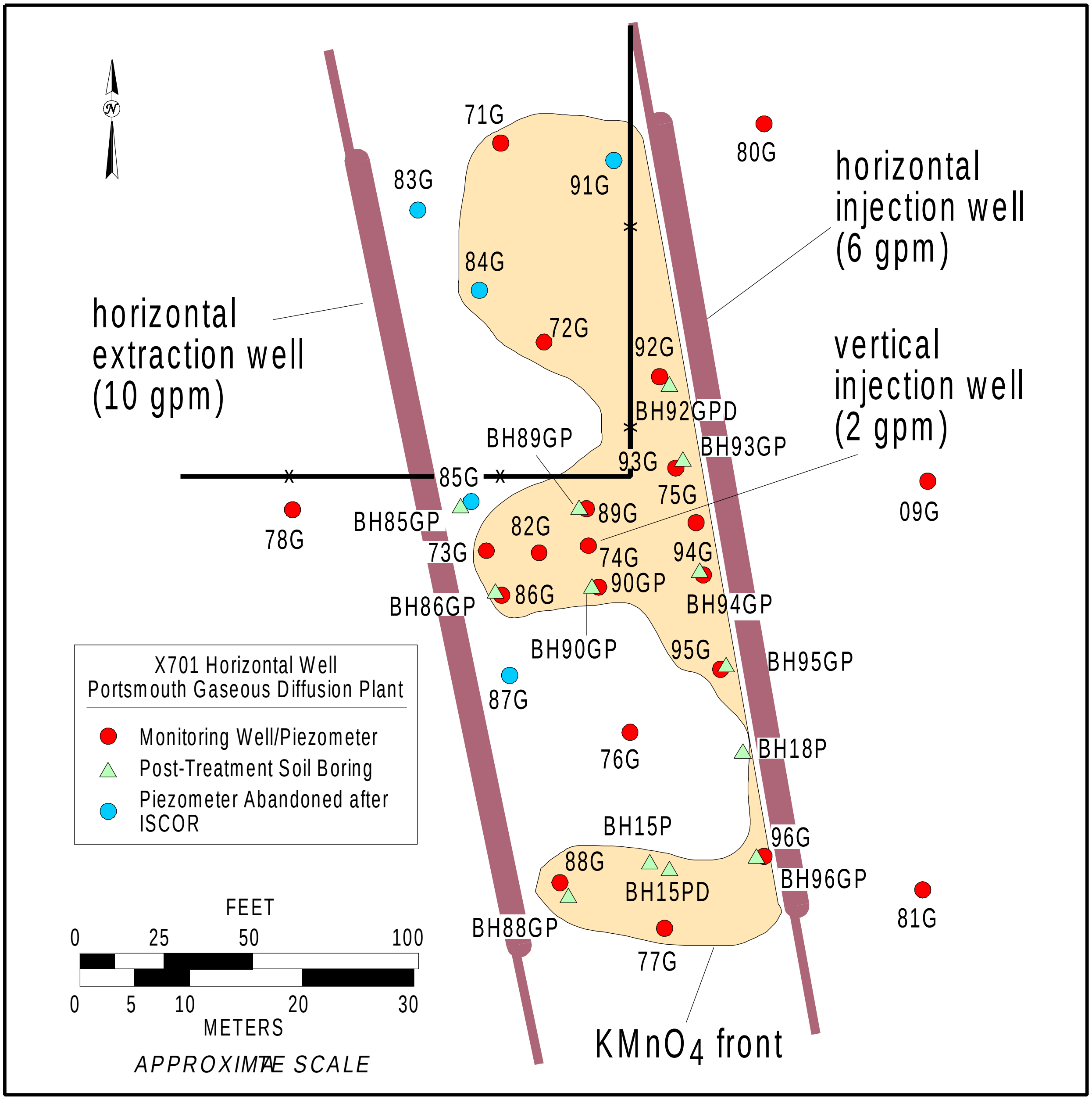


Figure 3. A field-scale experiment of permanganate oxidation of TCE at the Department of Energy Portsmouth Gaseous Diffusion Plant (PORTS) (West et al., 1997).

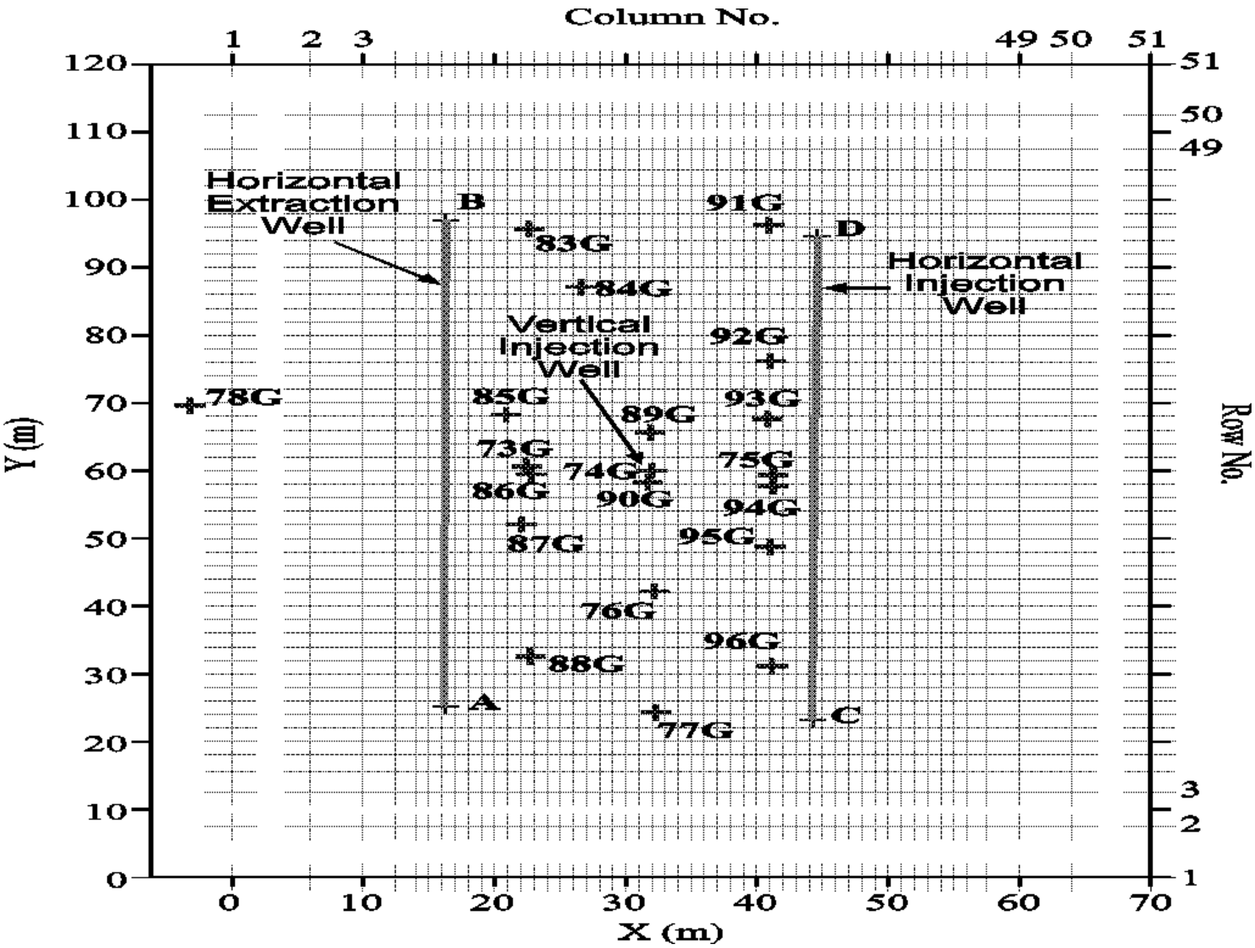
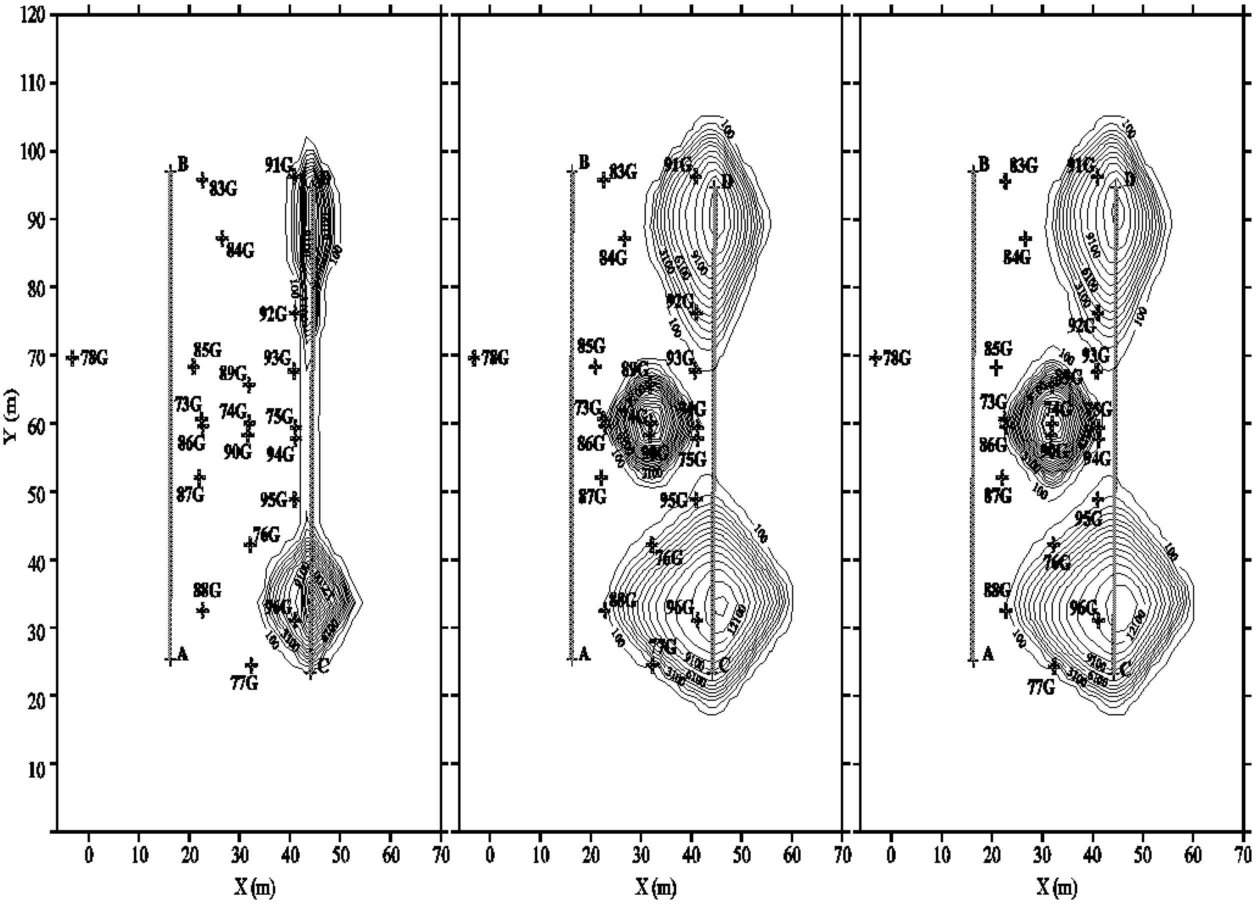


Figure 4. A two-dimensional model of 51x51 nodes representing the treatment zone and vicinity at the PORTS experiment site.

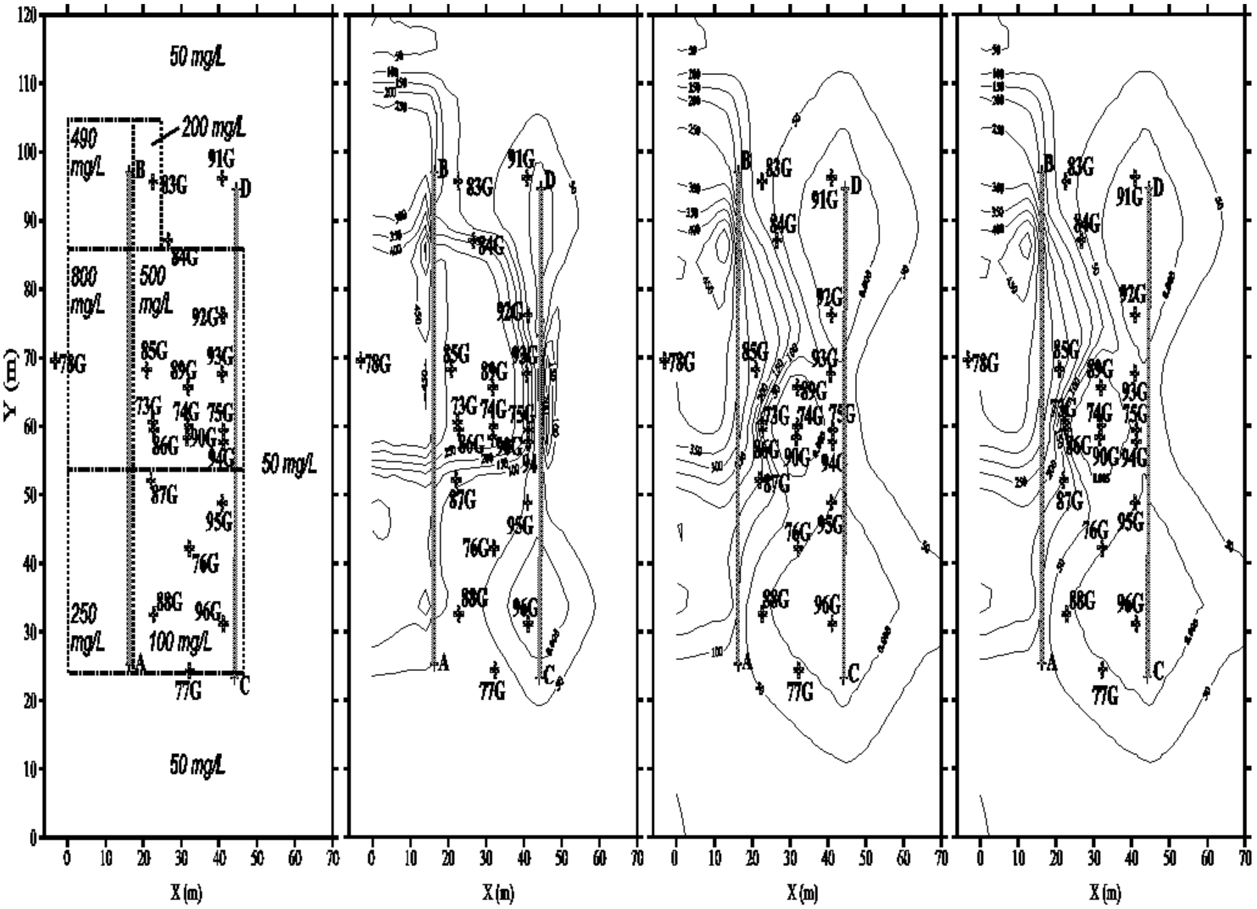


(a) 168 hours (7 days)

(b) 768 hours (32 days)

(c) 2880 hours (120 days)

Figure 5. Simulated permanganate distribution. (a) Time = 7 days; (b) Time = 32 days; (c) Time = 120 days.



(a) Initial TCE concentration (b) 168 hours (7 days) (c) 768 hours (32 days) (d) 2880 hours (120 days)

Figure 6. Simulated TCE distribution. (a) Time = 7 days; (b) Time = 32 days; (c) Time = 120 days.