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Laboratory Evaluation of In Situ Chemical Oxidation for Groundwater Remediation, Test Area North, Operable Unit 1-07B, Idaho National Engineering and Environmental Laboratory

Volume One - Main Text and Appendices A and B

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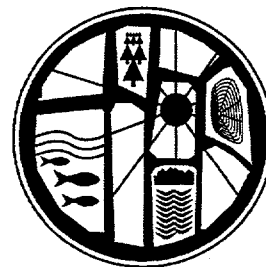
ENVIRONMENTAL SCIENCES DIVISION

LABORATORY EVALUATION OF IN SITU CHEMICAL OXIDATION FOR GROUNDWATER REMEDIATION, TEST AREA NORTH, OPERABLE UNIT 1-07B, IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY

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ABBREVIATIONS

1,1-DCE	1,1-Dichloroethylene
cis-1,2 DCE	cis-1,2 Dichloroethylene
DI	distilled, deionized
DF	Dilution Factor
DNAPL	dense, non-aqueous phase liquid
ECD	Electron Capture Detector
ESD	Environmental Sciences Division (ORNL)
GC	gas chromatograph
GW	groundwater
INEEL	Idaho National Environmental Engineering Laboratory
ISCO	In Situ Chemical Oxidation
$KMnO_4$	Potassium permanganate
L/S	liquid to solid ratio
MDL	method detection limit
MnO_4^-	permanganate anion
$\mu g/L$	parts per billion
ppm	parts per million
ORNL	Oak Ridge National Laboratory
RCRA	Resource Conservation and Recovery Act
RMAL	Radioactive Materials Analytical Laboratory (ORNL)
SOW	statement of work
spg	specific gravity
TAN	Test Area North
TC	total carbon
TCE	Trichloroethylene
TOC	total organic carbon
trans-1,2 DCE	trans-1,2 Dichloroethylene
VOA	volatile organic analysis
VOC	volatile organic compound
QA/QC	quality assurance and quality control
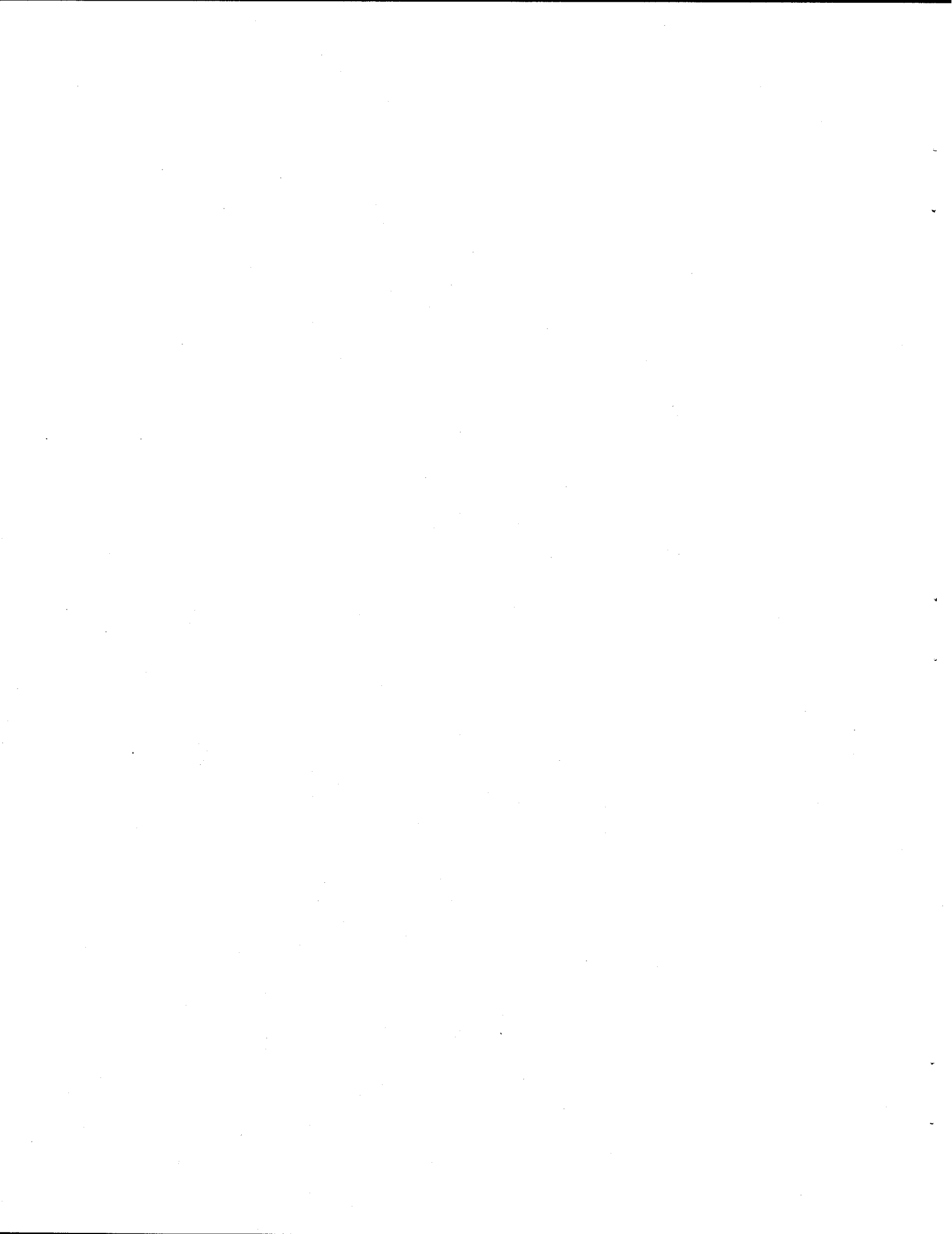
ABSTRACT

This laboratory investigation was performed to evaluate the feasibility of utilizing in situ chemical oxidation for remediating the secondary source of groundwater contaminants at the Idaho National Engineering and Environmental Laboratory (INEEL) Test Area North (TAN) Site. The study involved trichloroethene (TCE) contaminated media (groundwater, soil, and sludge) from TAN. The effectiveness of the selected oxidant, potassium permanganate (KMnO$_4$), was evaluated at multiple oxidant and contaminant concentrations. Experiments were performed to determine the oxidant demand of each medium and the rate of TCE oxidation. The experiments were performed under highly controlled conditions (gas-tight reactors, constant 12 °C temperature). Multiple parameters were monitored over time including MnO$_4^-$ and TCE concentrations and pH.

The organic sludge has a very large oxidant demand (70 mg MnO4$^-$/g) relative to the other media evaluated (0.05-0.2 mg MnO$_4^-$/g). TCE was rapidly oxidized under all conditions investigated in this study. In most cases, TCE concentrations declined to less than the method detection limit in less than 30 minutes. The oxidation rate appeared to increase with initial TCE concentration. Even the lowest TCE loss rates observed are sufficiently rapid to suggest that in situ chemical oxidation would be effective for remediating dissolved TCE at the INEEL TAN site.

1. IMPLEMENTATION APPROACH AND OBJECTIVES

1.1 BACKGROUND

A laboratory treatability study was recently conducted at the Oak Ridge National Laboratory (ORNL) to evaluate the feasibility of using in situ chemical oxidation (ISCO) for subsurface remediation at the Idaho National Engineering and Environmental Laboratory (INEEL). More specifically, this investigation focused upon using potassium permanganate ($KMnO_4$) to remediate a hot spot near the former injection well TSF-05 at INEEL's Test Area North (TAN). The ORNL research team has been involved in laboratory and field investigations of ISCO since 1994 and has the facilities and experience needed to perform the required experiments.

Wastes were disposed into TSF-05 during the period 1953 through 1972. The wastes consisted of organic sewage and industrial waste from manufacturing and maintenance operations. The aquifer beneath TAN is contaminated with chloroethenes and radionuclides. Presently, a plume of trichloroethylene (TCE) extends approximately 10,000 feet downgradient from TSF-05 at concentrations exceeding the regulatory MCL value of 5 μg/L. Plumes of tritium (^{3}H), strontium (^{90}Sr), and cesium (^{137}Cs) are much smaller than the TCE plume. Organic sludge in the vicinity of TSF-05, which is derived from sewage and other wastes disposed using TSF-05, is believed to act as a secondary source of dissolved contaminants. ISCO is being evaluated for possible use in destroying chloroethenes in the dissolved phase (both groundwater and matrix porewater), sorbed to geologic material (basalt and fracture-fill material), and associated with the organic sludge. Factors that affect the feasibility of ISCO for subsurface remediation at TAN include (1) the amount of oxidant that would be consumed by reactions with non-targeted materials, i.e. geologic materials, and (2) the effectiveness of ISCO for destroying dissolved chloroethenes and organic sludge. This laboratory investigation was designed and performed to evaluate these factors. Other factors that certainly ISCO feasibility include: mass transfer limitations, accurate delineation of source contamination, and effective oxidant delivery to the source area.

Equations for the typical oxidation of TCE and organic matter as presented below:

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2(s) + 2KCl + HCl \tag{1}$$
$$\{ORG\ Matter\} + MnO_4^- \rightarrow CO_2 + 2MnO_2(s) + H_2O \tag{2}$$
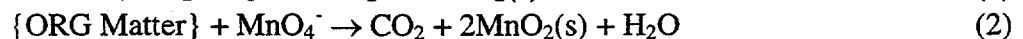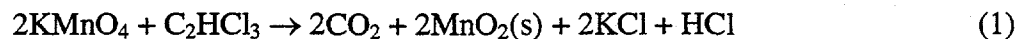
As depicted in the first equation, stoichiometric molar ratio of 2:1 exists for the reaction between MnO_4^- and TCE. A pH change would also be expected during ISCO due to the generation of H^+ ions. Please note that the second equation is a hypothesized reaction due to the complexity of organic matter like that present within the anthropogenic TSF-05 sludge.

1.2 OBJECTIVES

Following initial laboratory shakedown and development work, the laboratory studies performed at ORNL were designed to meet the following objectives:

1. Measure oxidant demand of "dissolved plume media"
2. Measure oxidant demand of "hot spot media"
3. Measure oxidation rate of chloroethenes in the "dissolved plume media"
4. Measure oxidation rate of chloroethenes in "hot spot media"

Actual media from the INEEL TAN site were used in these experiments. A summary of the TAN site materials received by ORNL is presented in Table 1. For the purposes of this treatability study, "dissolved plume media" is defined as any of the following TAN Site materials: TAN-40 groundwater (GW), aggregate basalt, crushed basalt, or sediment. Similarly, TSF-05 GW and organic sludge from the TSF-05 injection well are defined as "hot spot media" in these experiments. Furthermore, as a result of the work performed to meet objectives No. 2 and 4 above, the effectiveness of ISCO for destroying organic sludge was also obtained (see Section 2.4.5).

Table 1. TAN Site Materials Used in the Laboratory Treatability Studies.

Material	As Received Labeling/Description	Quantity Received
Dissolved Plume Groundwater	Received 2/11/98 TAN-40/GW/01 Collected at 275'.	60 liters
Hot Spot Groundwater	Received 2/11/98 TSF-05/GW/01	80 liters
Aggregate Basalt	Received 2/11/98 TAN-37/BSLT/01	6 kg
Crushed Basalt	Received 2/11/98 TAN-37/BSLT/02	9 kg
Sediment (SED1)	Received 2/11/98 TAN-37 Sed/01 Received 3/3/98 Q-R Interbed 322 TAN 33 Frac/Fill TAN-38 & TAN-40	100 g 500 g 50 g 775 g
Sediment (SED2)	Received 7/31/98 Sediment from TAN-33 Borehole (Interbed beneath and within the TAN aquifer) Sample 1 (213.5'-228') Sample 2 (348'-353') Sample 3 (366') Sample 4 (QR 441') Sample 5 (CI 144')	 149 g 85 g 10 g 190 g 113 g
TSF-05 Sludge	Received 2/27/98 & 3/2/98 Depth: 307.5'-310'	20 liters (36 kg)

1.3   APPROACH

Activities conducted during this study were guided by the scope of work (SOW) transmitted to ORNL. The SOW included preliminary activities to prepare for the laboratory experiments and a framework of parameters and variables to be evaluated in order to accomplish the objectives described in Section 1.2. Guidelines for disposing of the laboratory residuals and preparing monthly cost and technical progress reports were also included in the SOW. Specifically, the SOW consisted of the following eight (8) tasks:

Task 1. Preparation of Project Planning Documents
Task 2. Preliminary Laboratory Studies
Task 3. Measurement of the Oxidant Demand of TAN Subsurface Materials
Task 4. Measurement of Oxidation Rates of the TAN Subsurface Materials
Task 5. Waste Disposal
Task 6. Progress Reports
Task 7. Preparation of Final Report
Task 8. Presentation of the Laboratory Results

Several of these eight main tasks involved multiple subtasks. For additional details, the SOW can be found in this report as Appendix A. The majority of the laboratory activities were associated with Tasks 3 and 4 of the SOW, which were further divided into studies involving the dissolved plume media and the hot spot media. Due to the higher radionuclide activity of the TSF-05 sludge, most experiments involving the hot spot media were conducted at ORNL's Radioactive Materials Analytical Laboratory (RMAL). The RMAL is functionally a part of ORNL's Chemical and Analytical Sciences Division. ORNL's Environmental Sciences Division (ESD) performed all the experiments involving the dissolved plume media. Furthermore, ESD performed the all the VOC analyses for both ORNL research teams.

1.4   PROCEDURES

A detailed laboratory testplan with step by step instructions needed to execute the laboratory experiments was prepared by ORNL. This section describes the general procedure/approach used for each type of experiment and/or task. This section also describes many of the QA/QC elements that were written into the testplan. The laboratory testplan is included in this report as Appendix B if further details regarding the mechanics of each experiment are desired. Any significant deviations from the testplan and/or problems encountered during execution of the experiments are presented within the results and discussion section of this report (Section 2.0) for the affected experiment(s).

1.4.1. Summary Procedures for Preliminary Laboratory Experiments

The preliminary laboratory experiments (Task 2 SOW in Appendix A) were conducted to assess whether the equipment and/or approach planned for the experiments in Tasks 3 and 4 of the SOW were appropriate. The general methodology used for each Task 2 subtask is discussed here.

1.4.1.1. Reactor Development

The oxidation experiments utilizing TCE-spiked TAN media and $KMnO_4$ (SOW Task 4) must be performed under controlled conditions to minimize and quantify VOC losses from the reaction vessels due to volatilization. Zero headspace extraction vessels used by the ORNL research team in the past could not be used due to their small sample capacity (130 mL). Thus, alternative reactors had to be acquired and tested. These experiments were designed using the TCE mass balance as the main criterion to evaluate reactor acceptability. Most reactor acceptability experiments were conducted at room temperature using distilled water as the TCE spiked medium. This development task was an iterative process until the right combination of sampling ports, gaskets, etc. was achieved. Procedures used in the numerous shakedown experiments are not presented here. Instead, a summary of the procedure used to evaluate the final reactor configuration can be found in Section 2.2.1 along with a description of the selected reactor.

1.4.1.2. Determination of Hexane Extraction time of TCE from TAN Media

TCE was extracted from aqueous and solid media by hexane extraction, and the hexane was analyzed by gas chromatography. Before the experimental procedures for the oxidation experiments could be finalized, experiments were performed to determine the optimum extraction time for transferring TCE from the solid and aqueous phases of the TAN site media into the hexane phase. In these batch experiments, TAN site groundwater was spiked with TCE and allowed to equilibrate overnight at 12-15°C with each type of solid phase media at ≈4:1 liquid/soil (weight basis). (Extraction of TCE from the groundwater alone was also evaluated.) A summary of the hexane extraction time experiments is presented in Table 2. Each test condition was conducted in duplicate.

After equilibration of the spiked groundwater with the solid phase material (when applicable), the contents of each vessel (40 mL vials) were transferred to a larger container (125 mL glass jar) and extracted with an equal volume of hexane. The extraction portion of the experiment was conducted at room temperature. At various time points during the extraction step, samples from both the hexane and aqueous phases were collected and analyzed for TCE as discussed below in Section 1.4.4. For these experiments, the aqueous phase samples pulled from the second container were extracted for an additional 30 minutes prior to analysis. The detailed procedures used for these experiments can be found in the laboratory testplan (Appendix B) under the applicable Exp. ID listed in Table 2.

Table 2. Hexane Extraction Time Experiments for the TAN Site Media.

ORNL Exp. I.D.[a]	Media Used	Basalt Form	L/S Ratio	Initial TCE Conc. (µg/L)	Initial Organic Co-Contaminant Conc. (µg/L)	Initial MnO$_4^-$ Conc. (%)
	TAN-40 GW	NA	NA	1,000	0	0.0
	TAN-40 GW	NA	NA	1,000	0	0.0
	TAN-40 GW/basalt	Crushed	4:1	1,000	0	0.0
2b-1	TAN-40 GW/basalt	Crushed	4:1	1,000	0	0.0
	TAN-40 GW/SED1	NA	4:1	1,000	0	0.0
	TAN-40 GW/SED1	NA	4:1	1,000	0	0.0
	TAN-40 GW	NA	NA	1,000	0	0.0
	TAN-40 GW	NA	NA	1,000	0	0.0
2b-2	TAN-40 GW/basalt	Aggregate	4:1	1,000	0	0.0
	TAN-40 GW/basalt	Aggregate	4:1	1,000	0	0.0
	TSF-05 GW	NA	NA	100,000	0	0.0
2b-3	TSF-05 GW	NA	NA	100,000	0	0.0
	TSF-05 GW/Sludge	NA	4:1	100,000	0	0.0
	TSF-05 GW/Sludge	NA	4:1	100,000	0	0.0

[a] Experimental identifier used by ORNL in the collection and interpretation of the test data.

1.4.1.3. Determination of Equilibration Time of the Aggregate Basalt with TCE Solutions

The length of time needed to equilibrate TCE concentrations in matrix pore water of aggregate basalt pieces (i.e. 1/4 to 1 inch diameter) with TCE concentrations in the surrounding (bulk) water is unknown. Thus, there experiments were designed to assess the needed spiking time that would be required for spiking the aggregate basalt in the Task 4 experiments. The goal of this task was to determine the length of time required for equilibrium to be reached between TCE in the matrix pore water and the surrounding solution. Two different experimental approaches were attempted at ORNL for this task. Unfortunately, neither technique yielded definitive results.

In the first experimental approach, an initial TCE spike concentration of 1,000 µg/L was used (12-15°C). A study by Pavlostathis and Jaglal (1991) involving TCE sorption onto a silty sand indicated quasi-equilibrium within a period of three (3) days. However, other studies with PCE and course grain bulk material show equilibration to be on the order of 20 days, whereas equilibration using pulverized material was approximately 1 day (Ball, 1991). This experiment employed the use of several 40 mL volatile organic analysis (VOA) vials that were filled with either aggregate basalt or crushed basalt and TCE-spiked TAN-40 GW at a 4:1 Liquid to Soil (L/S) ratio. (The samples containing crushed basalt were used for comparison.) These vials were sacrificially sampled and analyzed for TCE at various times ranging from 2 hours to 21 days. The TCE analyses technique used in this experiment involved a hexane extraction of the aqueous samples prior to analysis (see Section 1.4.6 for additional information). Experimental controls (TCE-spiked TAN-40 groundwater with no solid phase) were also carried through the experiment to help account for losses via volatilization, biodegradation, or sorption of TCE onto

the test equipment, etc. There was no attempt to assess parameters such as ionic strength, pH, etc. The detailed procedure used in this experiment can be found in Appendix B.

In the second experimental attempt for this task, the general approach used was similar. However, many steps were slightly modified (See Appendix B) in order to measure for TCE via a purge and trap technique rather than performing a hexane extraction. Additional information regarding why these experiments were inconclusive is presented in Section 2.2.3.

1.4.2. Summary of Procedures for Oxidant Demand Experiments

The batch oxidant demand experiments (Task 3 in the SOW) were performed to determine the amount of oxidant consumed by each type of TAN site media received from INEEL. TCE was removed from all TAN site media used in the oxidant demand experiments prior to the start of each experiment. To remove TCE from the media as received from INEEL, groundwater was sparged with air and solid phase material was oven dried at 100°C for a minimum of 4 hours. It should be noted that experiments were not performed to determine whether this step affected the oxidant demand of the TAN media.

Tables 3 and 4 summarize the factors evaluated during each oxidant demand experiment performed for the dissolved plume media and hot spot media, respectively. The dissolved phase media were evaluated using initial oxidant solution concentrations of 0.01%, 0.1% and 1% MnO_4^-. The hot spot media were subjected to initial oxidant solution concentrations of 0.01%, 0.1%, 1%, and 3% MnO_4^-. Each TAN site medium was evaluated in duplicate

As presented in Tables 3 and 4, each solid phase medium was evaluated using a 4:1 L/S ratio. All oxidant demand experiments were performed under controlled temperature conditions. Each ORNL research team acquired an incubator/shaking chamber (Innova 4230), allowing all oxidant demand experiments to be conducted at a constant 12°C. All test samples were also agitated via a reciprocating shaker at 200-250 rpm. The groundwater ($\approx$400 mL) and solid phase material ($\approx$100 g, when applicable) were first added to 500 mL Erlenmeyer flasks and allowed to equilibrate overnight at 12°C. (The mass of each medium added was measured and recorded.) A sample aliquot ($\approx$ 6.5 mL) was then collected for pH and MnO_4^- analyses prior to the addition of oxidant to the flasks (reactors). (Further information regarding the pH and MnO_4^- analyses is presented in Sections 1.4.2 and 1.4.3, respectively.) Oxidant was then added to each reactor in accordance with Tables 3 and 4. Initial target MnO_4^- concentrations of 0.01% and 0.1% were obtained by spiking the reactors with a known volume of MnO_4^- stock solution ($\approx$4% MnO_4^-) prepared with distilled water. Use of a high concentration MnO_4^- stock solution to obtain the initial target MnO_4^- concentrations of 1% and 3% was not feasible since the maximum solubility of $KMnO_4$ is $\approx$5% at room temperature. Instead, the mass of crystalline $KMnO_4$ needed to achieve the desired starting MnO_4^- concentration was added to each reactor. An additional aliquot ($\approx$ 6.5 mL) was removed from each reactor for pH and MnO_4^- analyses at approximately 0.5 hr, 1 hr, 2 hrs, 4 hrs, 20 hrs, and 24 hrs after oxidant addition for the dissolved plume media. Suspecting that the oxidant consumption is more rapid for the hot spot media, the experiments in Table 4 were also sampled at $\approx$10 minutes after the reaction start time. In all cases, the sampling times were noted and recorded. After the final sampling period (typically 24 hrs for most experiments), the contents of the test reactors were discarded, and laboratory determined data

were used to compute the mass of oxidant consumed by each TAN site material. Sample calculations are presented in Appendix C. Results are presented in Section 2.3.

Table 3. Oxidant Demand Experiments for the Dissolved Plume Media. [a]

ORNL Exp. I.D.[b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (μg/L)	Initial Organic Co-Contaminant Conc. (μg/L)	Initial MnO_4^- Conc. (%)
	TAN-40 GW	NA	NA	0	0	0.01
	TAN-40 GW	NA	NA	0	0	0.01
	TAN-40 GW/basalt	Crushed	4:1	0	0	0.01
3a-R1	TAN-40 GW/basalt	Crushed	4:1	0	0	0.01
	TAN-40 GW/basalt	Aggregate	4:1	0	0	0.01
	TAN-40 GW/basalt	Aggregate	4:1	0	0	0.01
	TAN-40 GW/SED1	NA	4:1	0	0	0.01
	TAN-40 GW/SED1	NA	4:1	0	0	0.01
	TAN-40 GW	NA	NA	0	0	0.10
	TAN-40 GW	NA	NA	0	0	0.10
	TAN-40 GW/basalt	Crushed	4:1	0	0	0.10
3a-R2	TAN-40 GW/basalt	Crushed	4:1	0	0	0.10
	TAN-40 GW/basalt	Aggregate	4:1	0	0	0.10
	TAN-40 GW/basalt	Aggregate	4:1	0	0	0.10
	TAN-40 GW/SED1	NA	4:1	0	0	0.10
	TAN-40 GW/SED1	NA	4:1	0	0	0.10
	TAN-40 GW	NA	NA	0	0	1.00
	TAN-40 GW	NA	NA	0	0	1.00
	TAN-40 GW/basalt	Crushed	4:1	0	0	1.00
3a-R3	TAN-40 GW/basalt	Crushed	4:1	0	0	1.00
	TAN-40 GW/basalt	Aggregate	4:1	0	0	1.00
	TAN-40 GW/basalt	Aggregate	4:1	0	0	1.00
	TAN-40 GW/SED1	NA	4:1	0	0	1.00
	TAN-40 GW/SED1	NA	4:1	0	0	1.00

[a] Equivalent to Table 2.3 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.

Table 4. Oxidant Demand Experiments for the Hot Spot Media. [a]

ORNL Exp. I.D. [b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (μg/L)	Initial Organic Co-Contaminant Conc. (μg/L)	Initial MnO_4^- Conc. (%)
	TSF-05 GW	NA	NA	0	0	0.01
	TSF-05 GW	NA	NA	0	0	0.01
3b-R1	TSF-05 GW/sludge	NA	4:1	0	0	0.01
	TSF-05 GW/sludge	NA	4:1	0	0	0.01
	TSF-05 GW	NA	NA	0	0	0.10
	TSF-05 GW	NA	NA	0	0	0.10
3b-R2	TSF-05 GW/sludge	NA	4:1	0	0	0.10
	TSF-05 GW/sludge	NA	4:1	0	0	0.10
	TSF-05 GW	NA	NA	0	0	1.00
	TSF-05 GW	NA	NA	0	0	1.00
3b-R3	TSF-05 GW/sludge	NA	4:1	0	0	1.00
	TSF-05 GW/sludge	NA	4:1	0	0	1.00
	TSF-05 GW	NA	NA	0	0	3.00
	TSF-05 GW	NA	NA	0	0	3.00
3b-R4	TSF-05 GW/sludge	NA	4:1	0	0	3.00
	TSF-05 GW/sludge	NA	4:1	0	0	3.00

[a] Equivalent to Table 2.4 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.

1.4.3. Summary of Procedures for Oxidation Rate Experiments

The batch oxidation rate experiments (Task 4 in the SOW) were performed to determine the rate and extent of volatile organic compound (VOC) oxidation by $KMnO_4$ in the presence of the various INEEL TAN media under investigation.

To better control initial conditions, removal of residual VOCs was attempted for all TAN site media used in experimentation. Groundwater was sparged with air and solid phase material was oven dried at 100° for a minimum of 4 hours. The general approach for these experiments was similar to that described earlier for the oxidant demand studies in Section 1.4.2; however, the addition of the VOC spiking step and the subsequent VOC analyses increased the complexity of the test procedure.

Table 5 summarizes the oxidation experiments conducted using the dissolved plume media. Tables 6 and 7 summarize the factors evaluated during the oxidation experiment performed on the hot spot groundwater alone and for hot spot groundwater/sludge mixture, respectively. Since the actual contamination levels of the dissolved phase media are lower than those of the hot spot media, the dissolved plume media was only spiked with TCE at two levels: 100 μg/L and 1,000 μg/L. In addition, only initial target MnO_4^- concentrations of 0.01% and 0.1% were evaluated. The hot spot media were spiked at three different initial VOC levels, with one of them having a

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non-aqueous phase component. (The majority of the hot spot work involved TCE as the target VOC.) The hot spot treatment experiments were investigated using four (4) initial oxidant solution concentrations: 0.01%, 0.1%, 1%, and 3% MnO_4

Each initial test condition was conducted in duplicate. Duplicate controls (containing the VOC-spiked GW, but no MnO_4^- or solid phase medium) were included in each experimental run. As will be presented and discussed in Section 2, these controls provided a QA/QC check on the ability of the reactors to maintain gas-tight conditions and minimize VOC losses resulting from volatilization. Data collected from the control reactors were later used in the mass computations that were performed to evaluate oxidation effectiveness.

Each solid phase medium was evaluated using a 4:1 L/S ratio with the appropriate VOC-spiked TAN site groundwater. The procedure for the VOC spiking step varied depending upon the initial VOC concentration that was desired. The different approaches used are included in the laboratory testplan (Appendix B). With the exception of the DNAPL test conditions in Tables 6 and 7, a single spike solution was prepared within a 5 liter Tedlar bag (see Figure 1) for each experiment, then distributed among the test reactors. This approach allowed the initial VOC concentration to be relatively constant within a particular experimental run. In general, the solid phase material ($\approx$100 g, when applicable) was added to reaction vessel followed by distribution of the spiked groundwater ($\approx$400 mL). In all cases, the spiked groundwater or groundwater/solid phase slurry was allowed to equilibrate at least overnight at 12°C while being shaken. (The mass of each medium added was measured and recorded.)

Figure 1.   Tedlar Bags Used to Spike TAN Site Groundwater with Target VOCs.

As in the oxidant demand studies, a sample aliquot ($\approx$7-10 mL) was then collected for VOC, pH, and MnO_4^- analyses prior to the addition of oxidant to the reactors. (Further information regarding the pH, MnO_4^-, and VOC analyses is presented in Sections 1.4.4 through 1.4.6. Oxidant was then added to each reactor in accordance with Tables 5, 6, and 7. The initial target MnO_4^- concentrations of 0.01% and 0.1% were obtained by spiking the reactors with a known volume a MnO_4^- stock solution ($\approx$4% MnO_4^-) prepared with distilled water. Use of a highly concentrated MnO_4^- stock solution to obtain the initial target MnO_4^- concentrations of 1% and 3% was not feasible since the solubility of $KMnO_4$ is near 5% at room temperature. Instead, the mass of crystalline $KMnO_4$ needed to achieve the desired starting MnO_4^- concentration was added to each reactor. The reactors were immediately placed back onto the reciprocating shaker (200-250 rpm) inside of the 12°C incubator.

An additional aliquot ($\approx$ 7-10 mL) was removed from each reactor and subjected to VOC, pH, and MnO_4^- analyses approximately 0.5 hr, 1 hr, 2 hrs, 4 hrs, 20 hrs, and 24 hrs after oxidant injection in both the dissolved plume media and hot spot media studies. The actual sampling time was noted and recorded each time. To obtain an indication of sample variability, a duplicate sample was collected from one of the test reactors during each sampling interval. After the final sampling period (typically 24 hrs for most experiments), the entire contents of the "treatment" reactors (300+ mL) were extracted with hexane ($\approx$ 400 mL) for eventual VOC analyses (see Section 1.4.6). All laboratory data were then used to compute the mass of oxidant consumed by the VOC spiked media and the extent of VOC oxidation. Sample calculations are presented in Appendix C. Results are presented in Section 2.4.

Table 5. Oxidation Rate Experiments for the Dissolved Plume Media. [a]

ORNL Exp. I.D. [b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (µg/L)	Initial Organic Co-Contaminant Conc. (µg/L)	Initial MnO$_4^-$ Conc. (%)
	Control TAN-40 GW	NA	NA	100	0	0
	Control TAN-40 GW	NA	NA	100	0	0
	TAN-40 GW	NA	NA	100	0	0.01
4a-R1	TAN-40 GW	NA	NA	100	0	0.01
	TAN-40 GW	NA	NA	100	0	0.10
	TAN-40 GW	NA	NA	100	0	0.10
	Control TAN-40 GW	NA	NA	1,000	0	0
	Control TAN-40 GW	NA	NA	1,000	0	0
	TAN-40 GW	NA	NA	1,000	0	0.01
4a-R2	TAN-40 GW	NA	NA	1,000	0	0.01
	TAN-40 GW	NA	NA	1,000	0	0.10
	TAN-40 GW	NA	NA	1,000	0	0.10
	Control TAN-40 GW	NA	NA	100	0	0
	Control TAN-40 GW	NA	NA	100	0	0
	TAN-40 GW/basalt	Crushed	4:1	100	0	0.01
4a-R3	TAN-40 GW/basalt	Crushed	4:1	100	0	0.01
	TAN-40 GW/basalt	Crushed	4:1	100	0	0.10
	TAN-40 GW/basalt	Crushed	4:1	100	0	0.10
	Control TAN-40 GW	NA	NA	100	0	0
	Control TAN-40 GW	NA	NA	100	0	0
	TAN-40 GW/ basalt	Aggregate	4:1	100	0	0.01
4a-R4	TAN-40 GW/ basalt	Aggregate	4:1	100	0	0.01
	TAN-40 GW/basalt	Aggregate	4:1	100	0	0.10
	TAN-40 GW/basalt	Aggregate	4:1	100	0	0.10

[a] Equivalent to Table 2.5 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.

Table 5 Continued. Oxidation Rate Experiments for the Dissolved Plume Media. [a.]

ORNL Exp. I.D. [b.]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (μg/L)	Initial Organic Co-Contaminant Conc. (μg/L)	Initial MnO_4^- Conc. (%)
	Control TAN-40 GW	NA	NA	1,000	0	0
	Control TAN-40 GW	NA	NA	1,000	0	0
	TAN-40 GW/basalt	Crushed	4:1	1,000	0	0.01
4a-R5	TAN-40 GW/basalt	Crushed	4:1	1,000	0	0.01
	TAN-40 GW/basalt	Crushed	4:1	1,000	0	0.10
	TAN-40 GW/basalt	Crushed	4:1	1,000	0	0.10
	Control TAN-40 GW	NA	NA	1,000	0	0
	Control TAN-40 GW	NA	NA	1,000	0	0
	TAN-40 GW/basalt	Aggregate	4:1	1,000	0	0.01
4a-R6	TAN-40 GW/basalt	Aggregate	4:1	1,000	0	0.01
	TAN-40 GW/basalt	Aggregate	4:1	1,000	0	0.10
	TAN-40 GW/basalt	Aggregate	4:1	1,000	0	0.10
	Control TAN-40 GW	NA	NA	100	0	0
	Control TAN-40 GW	NA	NA	100	0	0
	TAN-40 GW/sediment	NA	4:1	100	0	0.01
4a-R7	TAN-40 GW/sediment	NA	4:1	100	0	0.01
	TAN-40 GW/sediment	NA	4:1	100	0	0.10
	TAN-40 GW/sediment	NA	4:1	100	0	0.10
	Control TAN-40 GW	NA	NA	1,000	0	0
	Control TAN-40 GW	NA	NA	1,000	0	0
	TAN-40 GW/sediment	NA	4:1	1,000	0	0.01
4a-R8	TAN-40 GW/sediment	NA	4:1	1,000	0	0.01
	TAN-40 GW/sediment	NA	4:1	1,000	0	0.10
	TAN-40 GW/sediment	NA	4:1	1,000	0	0.10

[a.] Equivalent to Table 2.5 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b.] Experimental identifier used by ORNL in the collection and interpretation of the test data.

Table 6. Oxidation Rate Experiments for Hot Spot Groundwater. [a]

ORNL Exp. I.D. [b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (μg/L)	Initial Organic Co-Contaminant Conc. (μg/L)	Initial MnO_4^- Conc. (%)
	Control-TSF-05 GW	NA	NA	10,000	0	0
	Control-TSF-05 GW	NA	NA	10,000	0	0
4b-R1	TSF-05 GW	NA	NA	10,000	0	0.01
	TSF-05 GW	NA	NA	10,000	0	0.01
	TSF-05 GW	NA	NA	10,000	0	0.10
	TSF-05 GW	NA	NA	10,000	0	0.10
	Control-TSF-05 GW	NA	NA	10,000	0	0
	Control-TSF-05 GW	NA	NA	10,000	0	0
4b-R2	TSF-05 GW	NA	NA	10,000	0	1.00
	TSF-05 GW	NA	NA	10,000	0	1.00
	TSF-05 GW	NA	NA	10,000	0	3.00
	TSF-05 GW	NA	NA	10,000	0	3.00
	Control-TSF-05 GW	NA	NA	100,000	0	0
	Control-TSF-05 GW	NA	NA	100,000	0	0
4b-R3	TSF-05 GW	NA	NA	100,000	0	0.01
	TSF-05 GW	NA	NA	100,000	0	0.01
	TSF-05 GW	NA	NA	100,000	0	0.10
	TSF-05 GW	NA	NA	100,000	0	0.10
	Control-TSF-05 GW	NA	NA	100,000	0	0
	Control-TSF-05 GW	NA	NA	100,000	0	0
4b-R4	TSF-05 GW	NA	NA	100,000	0	1.00
	TSF-05 GW	NA	NA	100,000	0	1.00
	TSF-05 GW	NA	NA	100,000	0	3.00
	TSF-05 GW	NA	NA	100,000	0	3.00

[a] Equivalent to Table 2.6 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.

Table 6 Continued. Oxidation Rate Experiments for Hot Spot Groundwater. [a]

Exp. I.D. [b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (µg/L)	Initial Organic Co-Contaminant Conc. (µg/L)	Initial MnO_4^- Conc. (%)
	Control-TSF-05 GW	NA	NA	100,000	10,000	0
	Control-TSF-05 GW	NA	NA	100,000	10,000	0
4b-R5	TSF-05 GW	NA	NA	100,000	10,000	0.01
	TSF-05 GW	NA	NA	100,000	10,000	0.01
	TSF-05 GW	NA	NA	100,000	10,000	0.10
	TSF-05 GW	NA	NA	100,000	10,000	0.10
	Control-TSF-05 GW	NA	NA	100,000	10,000	0
	Control-TSF-05 GW	NA	NA	100,000	10,000	0
4b-R6	TSF-05 GW	NA	NA	100,000	10,000	1.00
	TSF-05 GW	NA	NA	100,000	10,000	1.00
	TSF-05 GW	NA	NA	100,000	10,000	3.00
	TSF-05 GW	NA	NA	100,000	10,000	3.00
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
4b-R7	TSF-05 GW	NA	NA	2,000,000 [c]	0	0.01
	TSF-05 GW	NA	NA	2,000,000 [c]	0	0.01
	TSF-05 GW	NA	NA	2,000,000 [c]	0	0.10
	TSF-05 GW	NA	NA	2,000,000 [c]	0	0.10
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
4b-R8	TSF-05 GW	NA	NA	2,000,000 [c]	0	1.00
	TSF-05 GW	NA	NA	2,000,000 [c]	0	1.00
	TSF-05 GW	NA	NA	2,000,000 [c]	0	3.00
	TSF-05 GW	NA	NA	2,000,000 [c]	0	3.00

[a] Equivalent to Table 2.6 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.

[c] Indicates that TCE is present as a DNAPL.

Table 7. Oxidation Rate Experiments for Hot Spot Groundwater and Sludge. [a,c]

Exp. I.D. [b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (μg/L)	Initial Organic Co-Contaminant Conc. (μg/L)	Initial MnO$_4^-$ Conc. (%)
	TSF-05 GW/sludge	NA	4:1	0	0	0
	Control-TSF-05 GW	NA	NA	10,000	0	0
	Control-TSF-05 GW	NA	NA	10,000	0	0
4b-R9	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~0.01~~
	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~0.01~~
	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~0.10~~
	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~0.10~~
	~~Control-TSF-05 GW~~	~~NA~~	~~NA~~	~~10,000~~	~~0~~	~~0~~
	~~Control-TSF-05 GW~~	~~NA~~	~~NA~~	~~10,000~~	~~0~~	~~0~~
~~4b-R10~~	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~1.00~~
	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~1.00~~
	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~3.00~~
	~~TSF-05 GW/sludge~~	~~NA~~	~~4:1~~	~~10,000~~	~~0~~	~~3.00~~
	Control-TSF-05 GW	NA	NA	≈40,000 [d]	0	0
	Control-TSF-05 GW	NA	NA	≈40,000 [d]	0	0
4b-R11	TSF-05 GW/sludge	NA	4:1	≈40,000 [d]	0	0.01
Replaced	TSF-05 GW/sludge	NA	4:1	≈40,000 [d]	0	0.01
4b-R9	TSF-05 GW/sludge	NA	4:1	≈40,000 [d]	0	0.10
	TSF-05 GW/sludge	NA	4:1	≈40,000 [d]	0	0.10
	Control-TSF-05 GW	NA	NA	100,000	0	0
	Control-TSF-05 GW	NA	NA	100,000	0	0
4b-R12	TSF-05 GW/sludge	NA	4:1	100,000	0	1.00
	TSF-05 GW/sludge	NA	4:1	100,000	0	1.00
	TSF-05 GW/sludge	NA	4:1	100,000	0	3.00
	TSF-05 GW/sludge	NA	4:1	100,000	0	3.00

[a] Equivalent to Table 2.7 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.

[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.

[c] Strike-through text indicates an experiment that was not completed due to problems that developed. All such experiments were re-performed, but were assigned a different ORNL Exp. I.D.

[d] Although the target TCE concentration for this run was 100,000 μg/L, the actual TCE spike concentration was 40,000 μg/L. Thus, this experiment was used to replace experiment 4b-R9. (4b-R16 replaced 4b-R11)

Table 7 Continued. Oxidation Rate Experiments for Hot Spot Groundwater and Sludge. [a]

Exp. I.D. [b]	Media Used	Basalt Form	L/S Ratio (wt:wt)	Initial TCE Conc. (μg/L)	Initial Organic Co-Contaminant Conc. (μg/L)	Initial MnO_4^- Conc. (%)
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
4b-R13	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	0.01
	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	0.01
	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	0.10
	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	0.10
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
	Control-TSF-05 GW	NA	NA	2,000,000 [c]	0	0
4b-R14	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	1.00
	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	1.00
	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	3.00
	TSF-05 GW/sludge	NA	4:1	2,000,000 [c]	0	3.00
	Control-TSF-05 GW	NA	NA	10,000	0	0
	Control-TSF-05 GW	NA	NA	10,000	0	0
4b-R15	TSF-05 GW/sludge	NA	4:1	10,000	0	1.00
Replaced	TSF-05 GW/sludge	NA	4:1	10,000	0	1.00
4b-R10	TSF-05 GW/sludge	NA	4:1	10,000	0	3.00
	TSF-05 GW/sludge	NA	4:1	10,000	0	3.00
	Control-TSF-05 GW	NA	NA	100,000	0	0
	Control-TSF-05 GW	NA	NA	100,000	0	0
4b-R16	TSF-05 GW/sludge	NA	4:1	100,000	0	0.01
Replaced	TSF-05 GW/sludge	NA	4:1	100,000	0	0.01
4b-R11	TSF-05 GW/sludge	NA	4:1	100,000	0	0.10
	TSF-05 GW/sludge	NA	4:1	100,000	0	0.10

[a] Equivalent to Table 2.7 in the Implementation Plan, INEEL/EXT-97-01111, Rev 0.
[b] Experimental identifier used by ORNL in the collection and interpretation of the test data.
[c] Indicates that TCE is present as a DNAPL.

1.4.4. MnO_4^- Analyses

A portion of each sample aliquot collected from the reactors during both the oxidant demand and the oxidation rate studies was used for MnO_4^- analysis. This portion was first passed through a 0.45 μm membrane syringe filter (cellulose acetate) to remove particulates from the aqueous sample. (Tests for MnO_4^- sorption onto the filters were not performed, but is expected to be negligible given the concentrations being evaluated.) The sample was then analyzed colorimetrically using a Hach™ D/R 2000 spectrophotometer (wavelength= 525 nm). The spectrophotometer was calibrated using MnO_4^- standards (50 mg/L MnO_4^- maximum) prepared using the same technical grade $KMnO_4$ used in the oxidant demand and oxidation rate experiments. Most aliquot samples required dilution prior to analysis in order to obtain absorbance and/or concentration values in the linear calibration range of the instrument. The spectrophotometers were zeroed using DI (distilled, deionized) water blanks. The instrument

used by ORNL/ESD provided absorbance values, which were then manually converted to concentration values using the calibration curve (absorbance vs. concentration) obtained from the standards. The instrument used by ORNL/RMAL was programmed to provide output in units of concentration (mg/L MnO_4^-) using the absorbance data obtained from calibration standards. Calibration check samples (typically 10 mg/L and 50 mg/L MnO_4^-) were analyzed each time aliquot samples were analyzed. Results of the calibration checks were recorded in the laboratory research notebooks (Appendix F). Note that the MnO_4^- parameter was not defined as a decision making criterion in the SOW; therefore, formal data packages for these measurements were not required and/or prepared.

1.4.5. pH Analyses

A portion of each sample aliquot collected from the reactors during both the oxidant demand and the oxidation rate studies was used for pH analysis. This portion was not filtered prior to analysis, however, the small quantity of solids present with an aqueous aliquot was not expected to significantly affect the pH of the aqueous solution. The pH meters used by both ORNL research teams were calibrated with and/or checked against standard pH buffer solutions (typically pH 4 and 7). The instrument was recalibrated if the readings obtained for the buffer solutions drifted significantly (i.e., >15% or 1 pH unit max) during the time period that samples were being analyzed. Note that the pH parameter was not defined as a decision making criterion in the SOW; therefore, formal data packages for the pH measurements were not required and/or prepared.

1.4.6. VOC Analyses

VOC analyses were conducted on aliquot samples collected from the oxidation rate experiments listed in Tables 5, 6, and 7. An unfiltered portion ($\approx$3 mL) of each sample aliquot was added to a vial (12 mL, Teflon septum, glass) containing a known volume ($\approx$ 3 mL) of hexane. It is important to note that, to minimize volatilization of VOCs, this portion of the sample aliquot was immediately added to a hexane-filled vial before any other analyses (pH and MnO_4^-) were conducted. The glass vial was then weighed again to determine the mass of the aliquot added. It was assumed that the mass of solids present in this portion of the sample aliquot was negligible. Therefore the mass of sample added was equivalent to the volume of the aqueous sample (assumed spg=1.0). The assumption that the mass of particulates in the unfiltered aliquots was negligible was evaluated by determining the mass of solids retained on a 0.45 μm membrane after filtering supernatant from reactors that contained the same media used in this experiment. For a 10 mL sample of a groundwater slurry (4:1 L/S ratio), 0.017 g of crushed basalt, 0.00001 g of aggregate basalt, and 0.007 g of sediment were retained. Since the mass of solids retained was significantly less than the masses present in the slurries, it was assumed that this assumption was valid. The unfiltered samples were extracted for 2 hrs before the hexane extract was analyzed via gas chromatography.

All of the VOC analyses were conducted using a gas chromatograph (GC) equipped with an electron capture detector (ECD). All sample injections were performed using an autosampler (1 μL direct injection). Over 90% of the samples were analyzed using a Hewlett Packard (HP) 5890 Series II GC that was configured and optimized to resolve TCE as the target analyte. In fact, all VOC analyses were conducted on this instrument except those from experiments 4b-R5 and 4b-R6 in Table 6 (the co-contaminants experiments). For these optimized TCE analyses, a

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HP-5 capillary column (50 m length x 0.32 mm ID x 0.52 μm film thickness) was used. The oven temperature was held at 50°C for 2 minutes and was then ramped at 10°C/min until the maximum over temperature of 105°C was reached and then held for 2 additional minutes. Helium was the carrier gas for this setup, with a column flowrate of 2.2 mL/minute. The detector temperature was 275°C. The GC software also produced electronic files (Microsoft Excel format) of the chromatographic run results.

The samples from experiments 4b-R5 and 4b-R6 were analyzed using a second HP 5890 GC optimized to resolve both TCE and the co-contaminants used in experiments 4b-R5 and 4b-R6. For these analyses, a J&W Scientific DB-624 capillary column (30 m length x 0.53 mm ID x 3 μm film thickness) was used. Samples were introduced via 1 μL direct injections (autosampler). The oven temperature was held at 50°C for 0.3 minutes and was then ramped at 5°C/min until the maximum over temperature of 100°C was reached. The temperature was then immediately ramped at 50°C until a final temperature of 150°C was attained. The total run time was 11.3 minutes. Nitrogen was the carrier gas for this setup, with a column flowrate of 4.2 mL/minute. The injector temperature was 70°C, and the detector temperature was 300°C. The GC software also produced electronic files (Microsoft Excel format) of the chromatographic run results.

Information regarding the QA/QC attributes of the GC data are outlined in the SOW (Appendix A) for the oxidation rate experiments. In general, however, each sample analyzed was assigned a unique ORNL GC sample number for tracking purposes. Sample concentrations were determined using a 5 point calibration curve prepared following guidelines in EPA Method 8000B (USEPA, 1997). A calibration check standard (typically 100 μg/L) was analyzed at the beginning and end of each GC sequence. A sample blank was analyzed at the beginning and end of a GC sequence and after every 10 or 11 samples. Samples were re-analyzed with a different dilution factor if either (1) the concentration of the extract exceeded that of the largest calibration standard or (2) the concentration of a *diluted* extract was less than that of the lowest calibration standard. Any sample values that deviated from this approach or samples where the target analyte was not detected are clearly flagged and indicated in the results presented in Section 2.4. Finally, example calculations that illustrate how the GC values obtained for the hexane extracts were converted back to aqueous phase concentrations are presented in Appendix C.

1.4.7. Baseline Sludge Characterization and Carbon Analyses

A description of the procedures used to characterize the untreated TSF-05 sludge (moisture, bulk density, percent carbon, etc.) is included in Section 2.4.5 along with the results of the baseline characterization work. The approach and results used to assess the effect of oxidation on the TSF-05 sludge is also presented in Section 2.4.5.

2. RESULTS AND DISCUSSION

2.1   TASK 1. PREPARATION OF PROJECT PLANNING DOCUMENTS

2.1.1. Laboratory Testplan

Preparation of the laboratory testplan, which is presented in Appendix B, was initiated in January 1998. The testplan contains the standard procedures for the experimental tasks (Tasks 2-4 in the SOW) conducted during this treatability study. The first draft of the laboratory testplan was submitted to INEEL for concurrence. However, the testplan has undergone modifications throughout the course of the treatability study, primarily as a result of findings discovered in the Task 2 development work that necessitated changes in the way the oxidant demand and oxidation rate experiments were to be conducted. The most current version of the testplan is presented in Appendix B. It is against this version of the testplan that any experimental deviations that occurred will be discussed in the following sections.

2.1.2. Other Documents Required by ORNL

In addition the laboratory testplan, several other documents had to be in place before ORNL could begin the actual experimental work. The documentation that was obtained is listed below.

1. Documentation of PCB concentrations of TSF-05 sludge being less than TSCA action levels
   (Electronic mail correspondence from R.C. Starr-INEEL, dated: 2-12-98)

2. NEPA Project Review Summary, and Categorical Exclusion Assignment
   (ORNL memo from D.C. Parzyck-ORNL, dated: 1-28-98)

3. Project Environmental, Safety, Health, and Quality Evaluation
   (Approved by B.M. Ross-ORNL, ESH&Q Evaluation No. 9801-15, dated: 1-6-98)

4. Notification to ORNL of intent to perform a U.S. EPA Treatability Study
   (Submitted 12-17-98, Approved by J.H. Taylor-ORNL)

5. Determination that TAN Site Material is not subject to USDA quarantine regulations
   (Electronic mail correspondence from A.S. Dixon-ORNL, dated: 12-12-98)

2.2   TASK 2. PRELIMINARY LABORATORY STUDIES

2.2.1. Reactor Development

After several weeks of laboratory testing, equipment substitutions, and minor modifications, a relatively simple but effective reaction vessel was selected for use in the oxidation treatment experiments. A description of the selected test reactor and its QA/QC attributes are discussed here.

The final reactor design, which is illustrated in Figure 2, consisted of a glass, 500 mL Erlenmeyer flask equipped with a gas-tight adapter/closure. The flask has a ground glass, 29/42 standard taper opening. The adapter (Figure 3) is a non-stock item acquired from ACE Glass, Inc. The matching 29/42 standard taper fitting of the adapter was fitted with a 0.076 mm thick Teflon sleeve to provide a gas-tight connection. The adapter was also equipped with a gas-tight Teflon stopcock that remained closed except during aliquot sampling. (Note that tests to assess TCE sorption onto Teflon were not performed.) The stopcock opening is 2 mm in diameter. Aliquot sampling was performed using a long 25 cm (10 inch) stainless steel syringe having a 1.83 mm OD (also pictured in Figure 2). Thus, only 0.51 mm^2 of the sampling port opening was open to the atmosphere during aliquot sampling, further minimizing VOC losses. During aliquot sampling, the long syringe was attached to a 10 mL disposable, polyethylene syringe and lowered through the vertical sampling port, through the stopcock opening, and into the reactor. The upper 8 mm OD sampling port is closed off using a rubber septum after sampling is complete. (Attempts were originally made to inject the needle through this septum, but the thick wall of the syringe cored out the septum.) The aliquot sampling step of procedure easily takes less than 10 seconds to complete.

The second (horizontal) sampling port was equipped with a charcoal desorption tube (Supelco, ORBO brand). Such desorption tubes (See Figure 4) are typically used in industrial hygiene air sampling operations; however, it was used here to help quantify the amount of VOC that might be escaping from the Teflon stopcock. The desorption tubes contain two (2) separate charcoal beds. The first bed (positioned closest to the sampling port) contains 100 mg of charcoal, and the second bed contains 50 mg of charcoal. After the last aliquot sample is collected from the reactor, each charcoal bed is extracted into a known volume of hexane. As with the aqueous samples collect during the experiment, the mass of charcoal transferred into hexane is determined gravimetrically. These samples are then analyzed for VOCs similar to the aqueous aliquot samples.

During the overnight contaminant equilibration periods, a solid glass 29/42 stopper was used in place of the sampling port adapter discussed above. This prevented the potential contamination of the charcoal desorption tubes prior to the start of the oxidation reactions. The solid stoppers were replaced by the adapters (1) after the T=0 samples were collected for the GW control reactors or (2) immediately after oxidant was added to the treatment reactors.
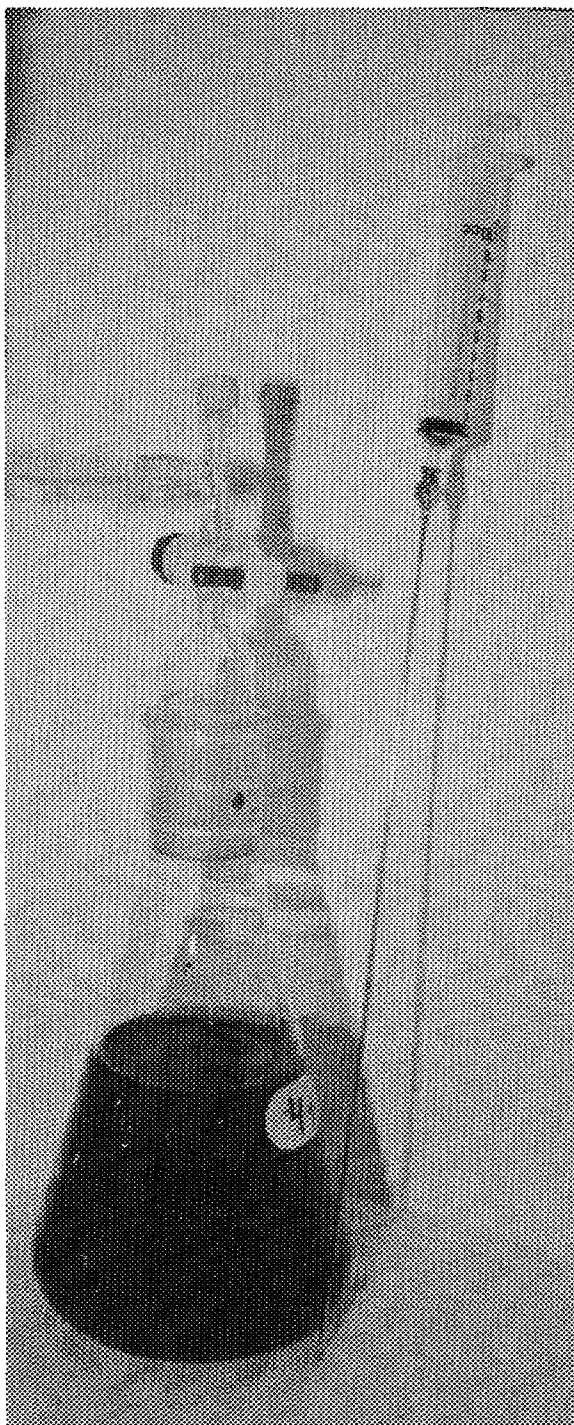
Figure 2. Photograph of the Reaction Vessel used in the Oxidation Experiments.

NOTES:
1. ALL DIMENSIONS ARE IN MILLIMETERS UNLESS OTHERWISE NOTED.
2. APPLY DECAL AS REQUIRED.
3. LATHE CUTTER:
   CUT 1 SEPTUM –
   SNAP 1 S/C ARM AT FLANGE
4. SUPPLY: (2) 9096-32 SEPTUMS FOR BOTH PORTS
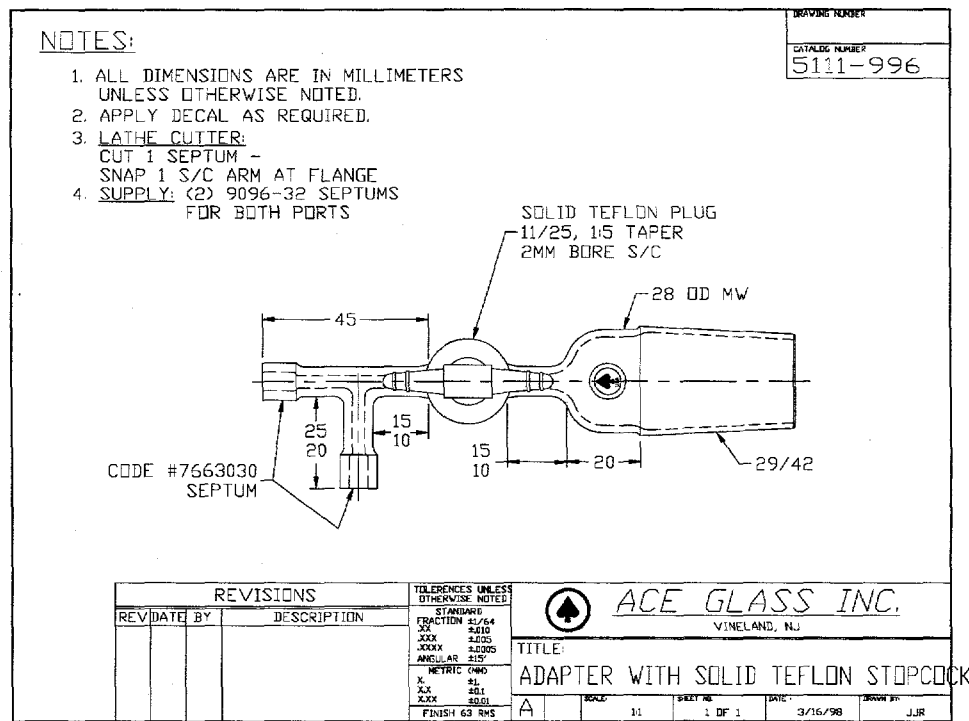
Figure 3. Illustration of the Adapter used in conjunction with the Reaction Vessels.

Figure 4. Photograph of the Charcoal Desorption Tubes used with the Reaction Vessels.

This final reactor configuration was experimentally evaluated by filling the flask with 500 mL of distilled water. This volume of water was spiked with TCE (target 100 µg/L TCE) and allowed to equilibrate at 12°C for 22 hours with the glass stopper in place. At time T=0, the solid stopper was replaced with the adapter and two initial aliquot samples were collected and processed for TCE analysis as discussed in Section 1.4.6. Similarly, duplicate aliquot samples were also collected at 1, 2, 4, 21, and 24 hrs after the initial sampling. The procedure for this final performance verification is included in the laboratory testplan as experiment 2a-3-B.

The resulting aqueous TCE concentration did not change with time. The average TCE value of all 12 aliquots collected was 106 µg/L with a standard deviation of 3 µg/L. No TCE was detected in either bed of the carbon desorption tube. A TCE mass balance was then performed. The cumulative quantity of TCE present in the aliquots was calculated, and the mass of TCE remaining in the flask was computed by multiplying the final aliquot TCE concentration by the volume of solution remaining in the flask. When compared to the TCE present at the initial sampling, 98.7 % of the TCE was accounted for. (The TCE mass potentially present in the headspace was not computed, but was expected to be small since no TCE was detected in the desorption tubes.) Thus, this reactor configuration was considered appropriate, particularly when considering that a given reactor will not be sampled in duplicate at every time interval as was done here.

The duplicate sampling at every interval was conducted to determine if plastic disposable syringes would adsorb a significant amount of TCE. Thus, at each time period, one sample was collected using a glass syringe, and the second sample was collected using a plastic syringe. Half of the six (6) sampling periods yielded higher aqueous TCE concentrations for samples collected using glass syringes (maximum 5.3% greater). Conversely, the other 3 sampling periods resulted in higher aqueous TCE concentrations for the samples from the plastic syringe (maximum 4% greater). The average difference between values obtained for the glass and plastic syringes was only 0.1%. Thus, it was concluded that the use of plastic disposable syringes did not bias the results, and therefore plastic syringes were used in the remaining experiments.

2.2.2. Hexane Extraction Time Determinations

ORNL Exp. 2b-1

All dissolved plume media were investigated in this experiment with the exception of aggregate basalt. Results of the hexane extraction experiments are presented in Figures 5, 6, and 7 for the TAN-40 GW only, crushed basalt and TAN-40 GW, and sediment and TAN-40 GW, respectively. The (#1) and (#2) notations included in the figure legends refer to the duplicate reactors evaluated for that test condition.

Per the testplan for experiment 2b-1, aliquots of both the aqueous and hexane phases were collected at each time period. Greater than 99.9% of the total TCE recovered at the 2 hr sampling point was found in the hexane phase. In addition, there was not a significant increase in the TCE concentration of the hexane phase between 2 hrs and 24 hrs for any of these materials. Thus, a 2 hr hexane extraction time was selected for use in the subsequent oxidation rate experiments.

TCE mass balances were also performed for each test condition. Average TCE recoveries of 91%, 95%, and 94% were obtained for the sediment and GW, crushed basalt and GW, and GW only reactors, respectively. The TCE mass unaccounted for is not expected to exist as residual contamination on the sediment or crushed basalt since the recoveries obtained for the groundwater only case were comparable to those obtained for the GW and solids reactors. These mass balance computations are strongly influenced by the value used for the initial TCE concentration of the spiked groundwater. Here, the duplicate analyses of the initial spike solution were in close agreement (average= 722 μg/L, σ= 3 μg/L). The potential for VOC losses, however, certainly existed between the time these initial samples were collected and the time the vials were equilibrated (overnight) and finally transferred to the extraction bottles for the start of the actual hexane extraction test. There was certainly some TCE lost as a result of the transfer step from the 40 mL VOA vial to the 125 mL extraction bottle. Laboratory gravimetric data indicated that an average of 98.5% of the initial GW or GW/soil slurry was successfully transferred to the extraction jar. (The procedure used for final extraction of the reactors in the oxidation rate studies was modified as a direct result of this finding.)

While factored out of the TCE mass recovery computations, a procedural problem did affect some of the data collected from this experiment. As written in the testplan, two samples were collected from the aqueous phase of the extraction at each time point. One of these aqueous samples was filtered (0.45 μm) in an attempt to determine the "true" aqueous concentration. Unfortunately, subsequent lab experiments provided evidence that the filters absorbed TCE, thereby making the data TCE obtained for these samples invalid. For the purpose of the mass balance, the volume of the filtered sample was used in the computations, but the TCE concentration of the filtered sample was assumed to be the same as the value obtained for the unfiltered aqueous sample. As direct result of this finding, the testplan was modified and aqueous samples for VOC analyses were not filtered during the oxidation rate experiments.
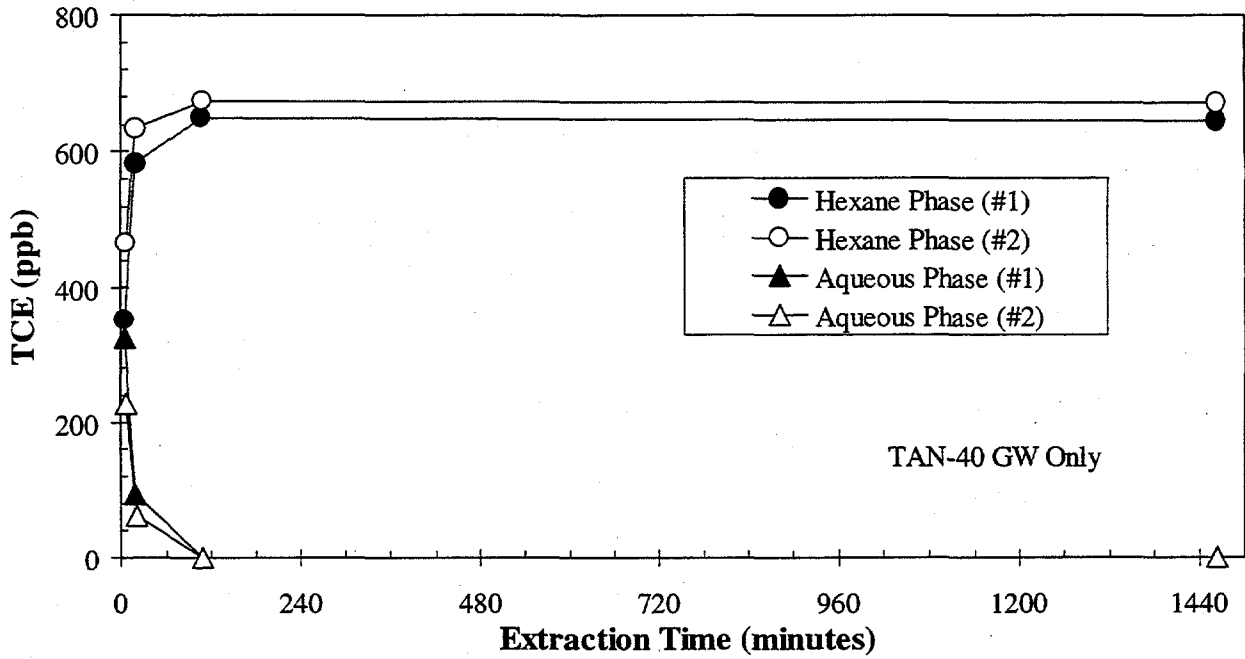
Figure 5. TCE Concentrations of the Hexane and Aqueous Phases from Extraction of TAN-40 GW Only. Initial TCE Conc.= 932 µg/L, ORNL Exp. 2b-1.
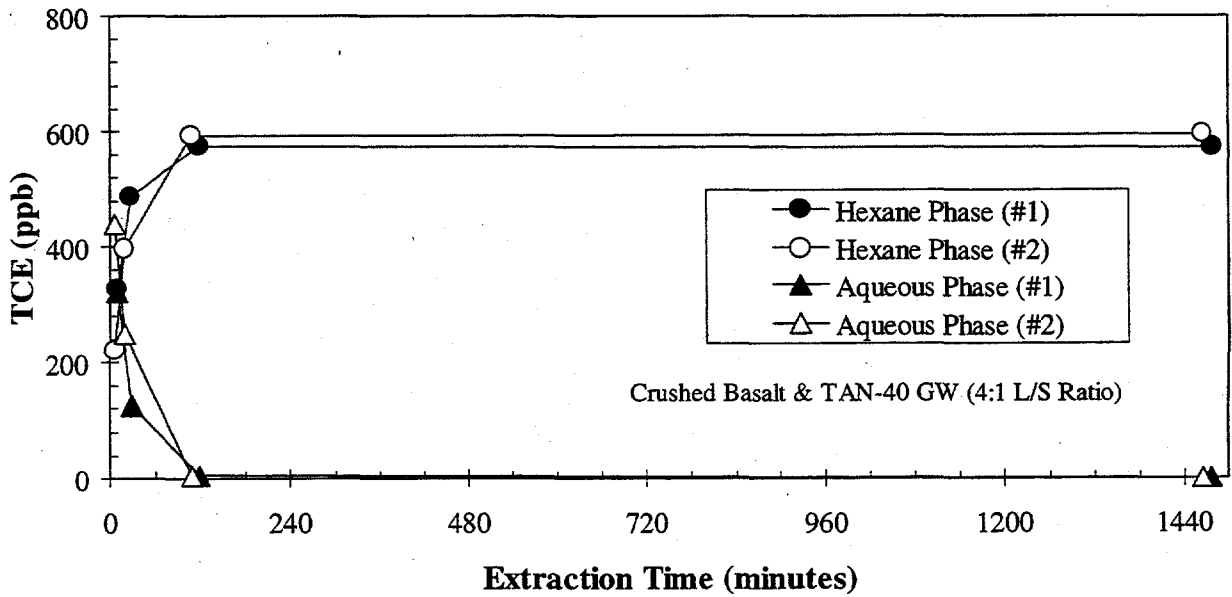
Figure 6. TCE Concentrations of the Hexane and Aqueous Phases from Extraction of Crushed Basalt in TAN-40 GW. Initial TCE Conc.= 932 µg/L, ORNL Exp. 2b-1.
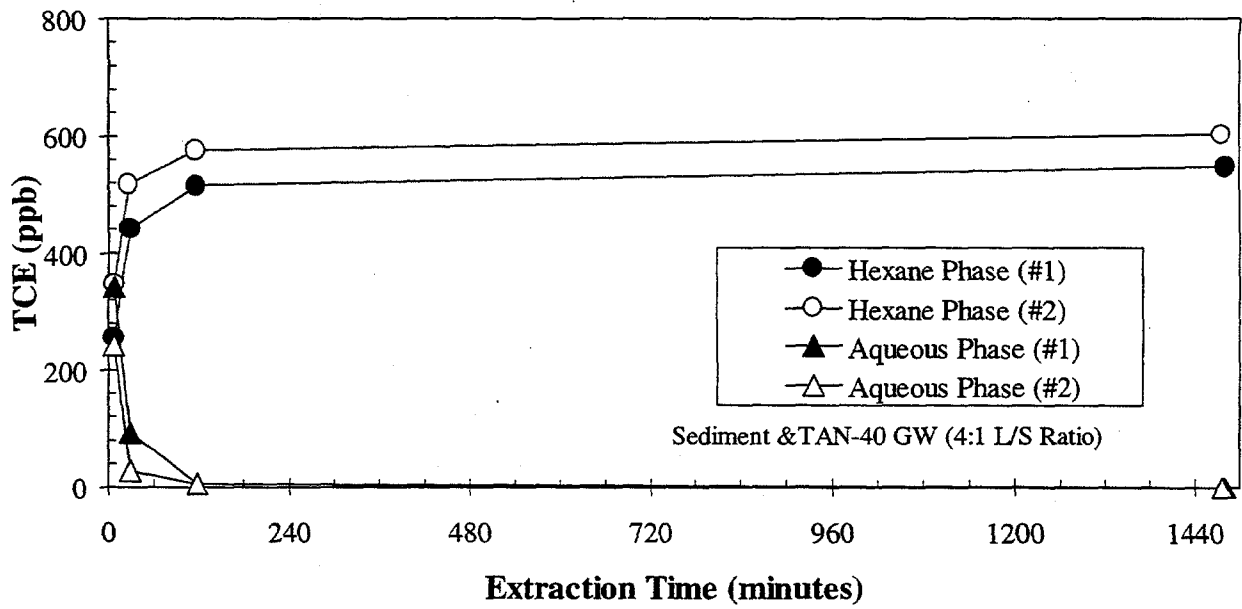
Figure 7. TCE Concentrations of the Hexane and Aqueous Phases from Extraction of Sediment in TAN-40 GW. Initial TCE Conc.= 932 µg/L, ORNL Exp. 2b-1.

ORNL Exp. 2b-2

This experiment was intended to investigate the optimum time needed to extract TCE from aggregate basalt. This experiment could not properly be performed until the results from the aggregate basalt equilibration study (ORNL Exps. 2c-1 and 2c-2) were obtained. Given difficulties encountered in performing the equilibration study and the resulting schedule slip, this experiment was not performed. Instead, it was assumed that a 2 hr extraction time would be appropriate for the aggregate basalt too. This deviation from the SOW was not expected to have a significant impact on the overall information gained from this treatability study. In fact, the majority of the hexane extractions performed during the oxidation experiments involving aggregate basalt were essentially groundwater extractions. The large, heavier aggregate basalt would not be present in the aqueous aliquots collected during the course of an experiment. However, the only exception is the extraction of the entire treatment reactor at the end of each experiment. Lower residual TCE values may be obtained if 2hrs of extraction is not adequate for nearly complete extraction into the hexane.

The hexane extraction time needed for the hot spot media was determined in this experiment. Results of the hot spot hexane extraction experiments are presented in Figures 8 and 9 for the TSF-05 GW only, and TSF-05 GW and sludge cases, respectively. The (#1) and (#2) notations included in the figure legends refer to the duplicate reactors evaluated for that test condition.

As observed for the dissolved plume media, hexane quickly extracted TCE from the aqueous and slurry phases. It should be noted that the concentrations of the hexane phases associated with the extractions of the TSF-05 GW only containers (Figure 8) were expected to be greater than those from the GW and Sludge extractions (Figure 9). This is because all the samples (GW and GW & Sludge) were extracted with approximately the same volume of hexane, but the GW only vials contained a larger volume of spiked GW (and therefore more TCE) than did the slurry containers.

The ultimate hexane concentration to be achieved for each type of extraction could not be explicitly determined. It is believed the value obtained for the initial spike solution was less than the true starting concentration. The first attempt to analyze the spike solution resulted in GC values that exceeded the maximum standard for the calibration curve. The second analysis of the TCE-spiked groundwater resulted in an initial TCE concentration of 77,400 μg/L (σ= 2,300 μg/L). However, this second analysis could not be performed until more than a week after the experiment had been completed. Thus, it is suspected that volatilization during storage caused the measured concentration to be less than the true initial concentration. As a result, all of the hexane TCE concentrations obtained at 2hrs and beyond exceeded that which theoretically could be present. The TSF-05 GW controls (Figure 8) appeared to reach a steady hexane TCE concentration. Thus, it was assumed that TCE was completely extracted from the groundwater. The average percentage of "initial" TCE mass extracted from the TSF-05 GW controls was computed to be 152%. (The >100% recovery is a result of the true concentration being greater than the measured initial concentration as discussed above.)

There is more variability in both the hexane and aqueous phase TCE concentrations for the TSF-05 slurries (Figure 9). Assuming 152% as the maximum amount of TCE to be extracted, 116% and 154% of the initial TCE was present in the hexane phase at T=2hrs. After 24 hrs, 155% and 176% of the initial TCE was present in the hexane phase. It is unknown why the TCE mass in the hexane phase of the duplicate (#2) increased beyond anticipated the expected quantity. There is the possibility that (1) "residual" TCE was present on the sludge used even after oven drying or (2) the hexane began to evaporate during the 20+ hrs of extraction, which in effect concentrated the TCE. The latter theory is supported by the fact that the vapor pressure of hexane (120 mm vs @ 20°C) is greater than that of TCE (60 mm @ 20°C) (Verschueren 1983). As observed in Figure 9, the aqueous TCE concentrations appeared to increase at 24 hrs. This phenomenon seems unlikely, unless re-adsorption of TCE were occurring. It is likely that at least some of these apparent increases in TCE concentrations (both hexane and aqueous phases) are a result of the analytical sample holding time. All samples were collected at the appropriate time period, but none were analyzed until after the 24 hr samples were collected. Hence, it is probable that all of the TCE concentrations reported (with the exception of the T=24 hrs samples) are underestimates of the actual TCE concentrations present at that time period.

Given the anomalies observed during this experiment, it was truly unknown which factor(s) affected the data most significantly (i.e., extraction time or sample holding time). Thus, a 2hr extraction time was chosen for the TSF-05 sludge Task 4 experiments. The use of a 2hr extraction was also beneficial in the conduct of the experiments and general laboratory operations. A matrix spike study not originally planned was also conducted after all the SOW Tasks 3 and 4 work was completed. This spike study (See Section 2.4.6) was conducted to help determine if the results observed here for the TSF-05 sludge were "real".
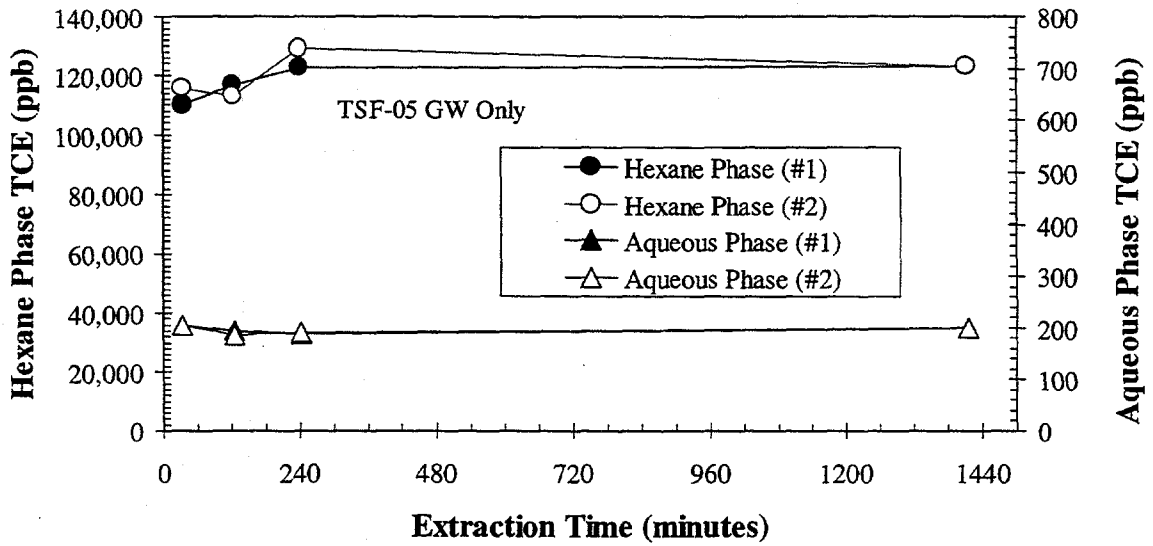
Figure 8.   TCE Concentrations of the Hexane and Aqueous Phases from Extraction of TSF-05
             GW Only. Initial TCE Conc.= 77,400 μg/L, ORNL Exp. 2b-3.
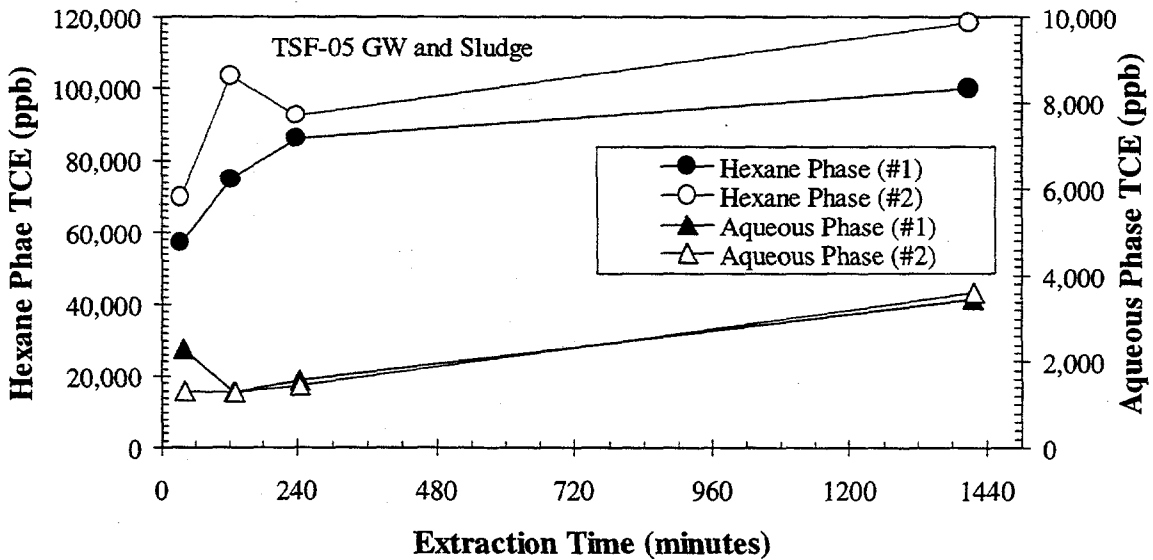
Figure 9.   TCE Concentrations of the Hexane and Aqueous Phases from Extraction of TSF-05
             GW and Sludge. Initial TCE Conc.= 77,400 μg/L, ORNL Exp. 2b-3.

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2.2.3. Aggregate Basalt Equilibration Time

As discussed in Section 1.4.1.3, the experimental results obtained for task 2c were inconclusive in terms of determining the appropriate spiking/equilibration time needed for the aggregate basalt medium. This experiment involved measuring the TCE concentration of the aqueous portion of a test sample after various equilibration periods. Individual vials, containing no headspace, were sacrificially subsampled at each sampling period as a means to minimize losses associated with volatilization. Aqueous TCE concentrations decreased during the 21 day test period. The average TCE decreases were 30%, 32%, and 29% for the groundwater control, crushed basalt, and aggregate basalt samples, respectively. With the highest TCE losses from the groundwater control samples, the observed TCE decreases could not explicitly be attributed to sorption or uptake by the TAN basalt media. Further investigation of these results lead to the conclusion that the procedure used for this experiment (2c-1) was not valid. The 0.45 µm membrane filters that were used prior to extraction with hexane at least contributed to the TCE losses observed. In an independent experiment, these filters were found to absorb approximately 10-20% of a 1,000 µg/L TCE solution (See Appendix E, March Monthly Report).

Upon realizing these procedural shortcomings, the testplan was modified, and a second equilibration experiment (Exp. 2c-2 in Appendix B) was conducted. In this experiment, the samples were not filtered before TCE analyses. The aqueous samples were also analyzed via purge and trap analyses rather than via a hexane extraction, for the additional transfer sample handling step required in transferring the aqueous aliquot into hexane was likely another source of TCE loss. The results of the second experiment, however, were similar to the first experiment in that the losses observed in the basalt samples correlated well with the TCE losses observed in the groundwater control samples. It is believed that a majority the TCE loss is associated with septa leakage during such long sample holding times (i.e., >> 7 day sample holding time criterion established by EPA for VOC analyses).

Since a specific equilibration time could not be determined, the aggregate basalt was equilibrated with TCE for the same amount of time as the other TAN Site media (i.e., overnight) in the Task 4 experiments. Furthermore, the fact that an equilibration time could not be determined for the aggregate basalt was not expected to impact the task 4 results since all experiments in Task 4 were performed in agitated, temperature controlled incubators. However, one should consider this effect when attempting to design and implement ISCO in the field, where pore water conditions will be much different.

Beyond the discussion that is presented above, the experimental data for the equilibration studies are not plotted or included elsewhere in this report (e.g, Appendix C) in order to avoid confusion and mis-interpretation of the data.

2.3   TASK 3. MEASUREMENT OF THE OXIDANT DEMAND OF TAN SUBSURFACE MATERIALS

2.3.1. Laboratory Controls and QA

Since the oxidant demand experiments did not involve the use of TCE or other volatile compounds, gas-tight conditions did not have to be maintained for these experiments. In addition to the QA/QC techniques already discussed for pH and MnO_4^- analyses (calibrations, filtering, etc.), all pipette and analytical balances used in these experiments were calibrated each day of use. The testplan procedure for these experiments involved the extensive use of gravimetric determinations to obtain accurate initial starting masses of $KMnO_4$ and TAN site media being used in the following experiments. A distilled water "control" sample was carried throughout each of the dissolved plume media experiments. Oxidant was added to this control to provide a baseline for evaluating the TAN site materials.

2.3.2. Oxidant Demand in Dissolved Plume Media

The dissolved plume media oxidant demand experiments were performed twice. The data values obtained from the initial attempt were difficult to interpret, requiring a refinement/modification of the test procedure. Problems were encountered in determining the true oxidant concentrations in the test reactors. Often the final, measured oxidant concentration was greater than the initial concentration that was computed using the laboratory gravimetric data. To alleviate this problem, a new calibration curve was prepared, and the use of stock MnO_4^- solutions was implemented as the means to add oxidant to test reactors with low target MnO_4^- doses rather than via addition of crystalline $KMnO_4$. (This procedural modification was also made to the oxidation rate procedures.)

The MnO_4^- concentration data obtained from the aliquot sampling is presented in Figure 10 for the 0.01% (100 mg/L) MnO_4^- initial oxidant experiment. The duplicate test reactors for each test condition are represented in the legend by the (#1) and (#2) notations. (This graphing scheme is used for most plots of the oxidant demand and oxidation rate data included in this report). The initial MnO_4^- value is a *calculated* value based on several pieces of laboratory data. Detailed explanations regarding such computations are included in Appendix C. The remaining data points are *measured* values obtained from the MnO_4^- analyses. Residual oxidant was still present after the 24 hr reaction time, indicating that the initial oxidant demand of the dissolved plume media is not extensive or rapid. As expected, the sediment and crushed basalt media consume more oxidant than the aggregate basalt.

Similar results are presented in Figure 11 for the 0.1% (1,000 mg/L) MnO_4^- initial oxidant experiment. The MnO_4^- values for a given reactor are more sporadic, and trends among the various media types, while similar to those in Figure 10, are less distinct. One particular anomaly is the marked drop in the MnO_4^- concentration of the distilled water and TAN-40 GW samples at the end of the reaction period. No additional laboratory observations were recorded that would explain this phenomenon.

Oxidant demand results of the 1% MnO_4^- experiments are presented in Figure 12. As expected there appears to be little oxidant consumption from any of the dissolved plume media.

Crystalline $KMnO_4$ was used in this experiment, while a concentrated MnO4- stock solution was used in the previous experiments. Thus, the apparent oxidant demand early in the reaction period (Figure 12) is likely attributed to the inability of the solid $KMnO_4$ to dissolve rapidly enough, even though the first aliquot sampling period in this experiment was increased to 1 hour to allow more time for $KMnO_4$ to solublize. The initial oxidant mass added was determined gravimetrically using an analytical balance with a ±0.0001 gram resolution, hence there is a great deal of confidence in the initial MnO_4^- concentrations. Preparation of the sample dilutions needed for the MnO_4^- analyses is certainly an area in which experimental/human error could have contributed to the variability of the oxidant values, particularly for the experiments involving the higher initial MnO_4^- concentrations. Dilutions, for example of 50 and 500 were required for aliquot samples from the 0.1% and 1% experiments. However, the value added of performing extremely accurate dilutions is not warranted when considering that the accuracy of the spectrophotometer itself is only ±0.2 mg/L. Because the MnO_4^- data was not intended to be a decision making criterion (see SOW, Appendix A), the standards prepared and used to calibrate the spectrophotometer were not titrated or measured against a known standard. Finally, it is unknown why the oxidant demand of the distilled water control is so much greater than that of the TAN Site materials in Figure 12. This effect was not observed in Figures 10 and 11 and is thought to be a laboratory artifact rather than a real effect.

The data from these experiments were further evaluated to obtain oxidant demand or consumption values for each discrete type of dissolve plume media. This value could be readily obtained for the TAN-40 GW. However, further computations were needed to obtain such consumption data for the solid phase media since the experiments were conducted using a GW and solids slurry. Both the measured and "derived" consumption values are presented in Table 8 for the dissolved plume media. To standardize the consumption data, the values in Table 8 represent the amount of MnO_4^- consumed per unit of TAN media or DI water after a 24 hour reaction time. To be more precise, the data in Table 8 represent the difference in overall oxidant mass at the two reaction points (T= 0 and 24 hrs), and does not depict any of the fluctuations observed in MnO_4^- concentrations between these two sample points. The oxidant mass consumed was determined by the difference in the beginning and ending aqueous MnO_4^- concentrations and multiplying that value by the initial liquid volume that was present in the reactor at T=0 hrs. This approach yields a conservative, maximum oxidant demand value (for the given time period), for it does not account for any MnO_4^- mass removed by aliquot sampling.

Note that a more refined oxidant consumption value can be determined by computing the cumulative mass of oxidant consumed during each sampling interval. This second approach, however, will yield a lower total consumption values since the mass of MnO_4^- associated with the aliquot samples must be accounted for since it is no longer available to be consumed within the test reactors. The degree of error between the two techniques does not become significant unless the bulk of the consumption occurs toward the end of the test period. The test data and the subsequent calculations discussed here are presented in Appendix C for each oxidant demand experiment.

These oxidant consumption values were then divided by the total mass of TAN site media (GW or GW & Solid) initially added to the each reactor. (The specific gravity of TAN-40 GW is

assumed to be 1.0.) To derive the oxidant demand for the basalt and sediment, the MnO_4^- mass predicted to be associated with the GW was subtracted from the total oxidant consumption value for the slurry according to the equation presented in Table 8.

The resulting oxidant demand values obtained for the crushed basalt, aggregate basalt, and sediment at the 0.01% and 0.1% loadings are in good agreement with each other. The negative values obtained for aggregate basalt and sediment for the 1% MnO_4^- experiment are because the measured MnO_4^- concentration of the TAN-40 GW at 24 hrs is less than that of the slurry reactors (See Figure 12).
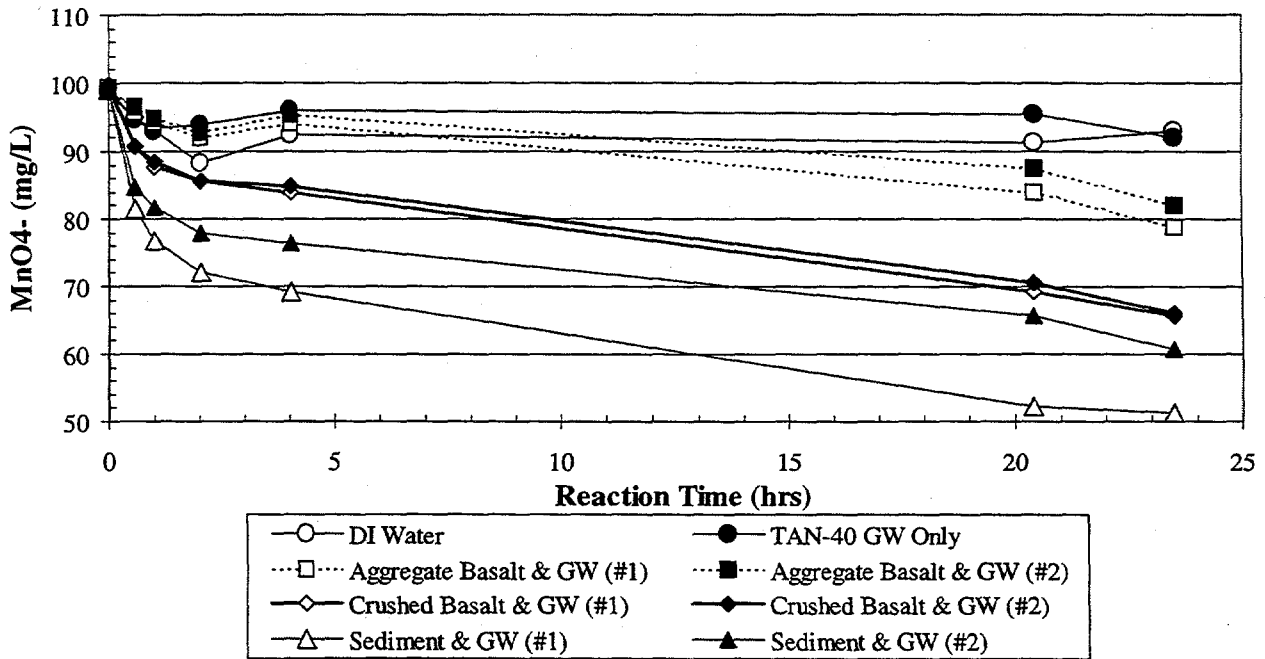
Figure 10. Oxidant Demand Results for Dissolved Plume Media, Initial $MnO_4^- = 0.01\%$ (ORNL Exp. 3a-R1b, Conducted at 12°C and 4:1 L/S ratio where applicable)
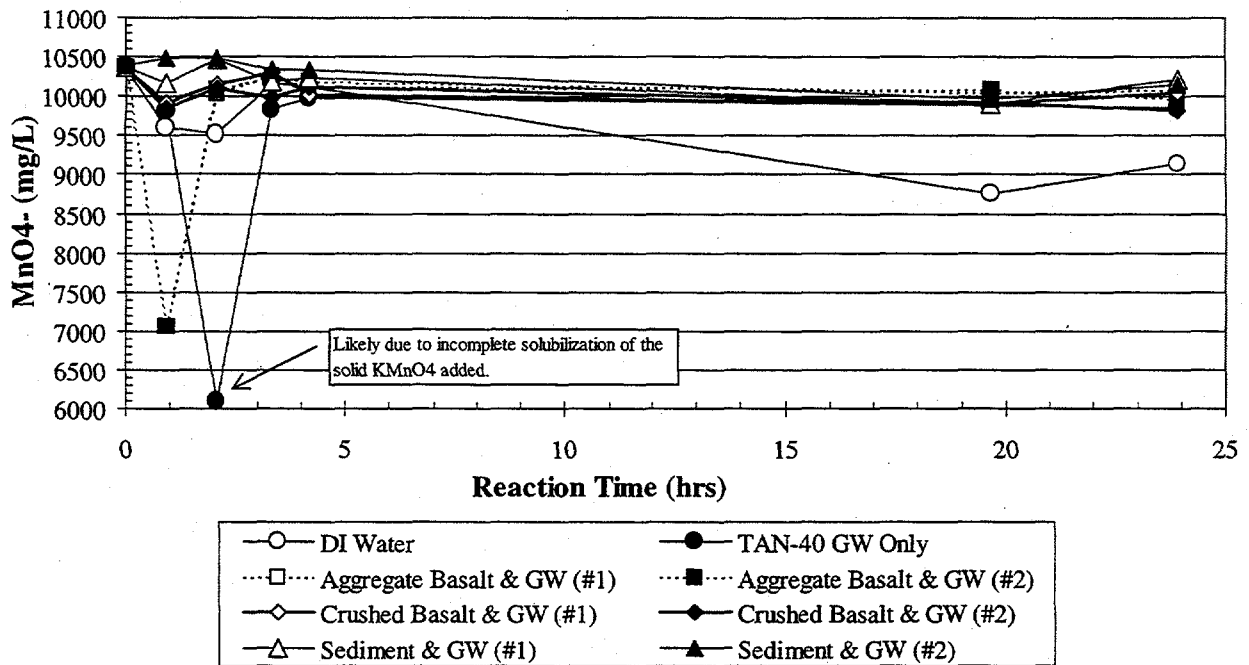
Figure 11. Oxidant Demand Results for Dissolved Plume Media, Initial $MnO_4^- = 0.1\%$ (ORNL Exp. 3a-R2b, Conducted at 12°C and 4:1 L/S ratio where applicable)
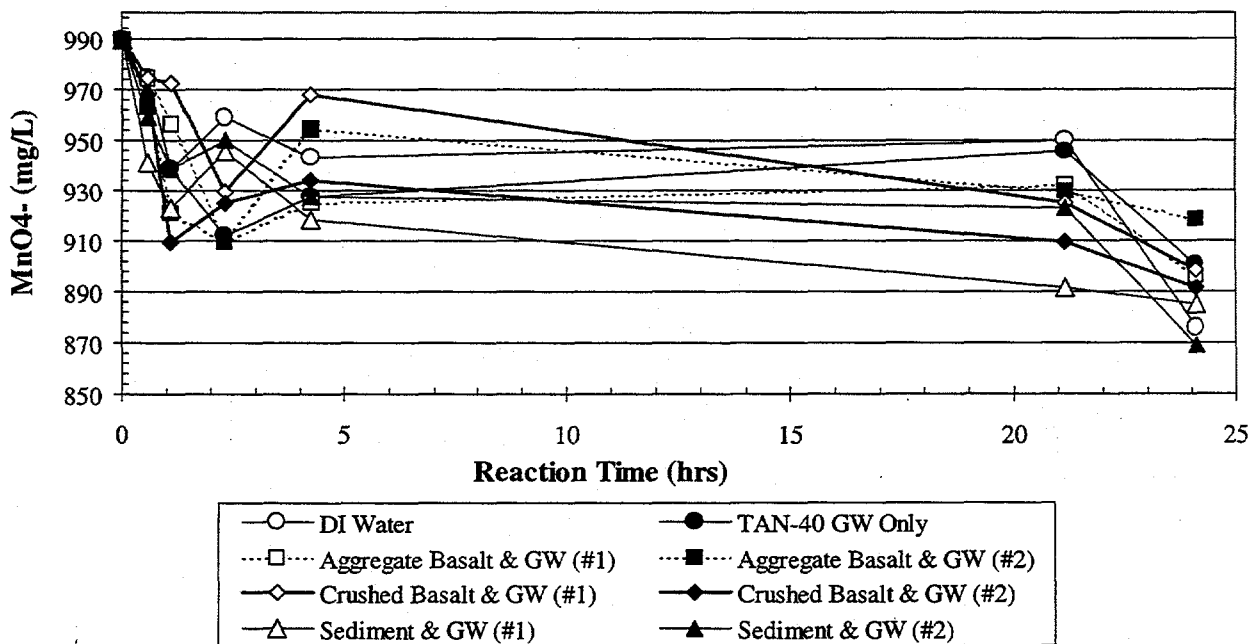
Figure 12. Oxidant Demand Results for Dissolved Plume Media, Initial $MnO_4^- = 1\%$ (ORNL Exp. 3a-R3b, Conducted at 12°C and 4:1 L/S ratio where applicable)

Table 8. Calculated Oxidant Demand Values for the Dissolved Plume Media. [a,b]

| Test Media | Initial MnO$_4^-$ Concentration | | | | | |
| | 0.01% | | 0.1% | | 1.0% | |
	Initial Loading	Consumed	Initial Loading	Consumed	Initial Loading	Consumed
Distilled Water	0.1	0.001	1.0	0.09	10.4	0.97
TAN-40 GW	0.1	0.005	1.0	0.07	10.4	0.41
GW & Crushed Basalt	0.08	0.03	0.8	0.08	8.2	0.33
GW & Aggregate Basalt	0.08	0.01	0.8	0.07	8.2	0.27
GW & Sediment	0.08	0.04	0.8	0.11	8.2	0.19
Crushed Basalt [c]	NA	0.11	NA	0.09	NA	0.05
Aggregate Basalt [c]	NA	0.05	NA	0.04	NA	-.233
Sediment [c]	NA	0.15	NA	0.18	NA	-.835

[a] All values in units of [mg MnO$_4^-$/g of TAN Site Media or DI Water]

[b] Consumption values represent a 24 hr reaction time. Values presented for the GW slurries are the averages of duplicate samples.

c. Derived by subtracting the GW consumption component from the total oxidant consumption of the slurry via the following equation:

Solid Phase Demand (mg/g)= [Total-(GW Demand x Wt$_{GW}$)]/(Wt$_{solid}$)

Where: Total= total mass of MnO$_4^-$ (mg) consumed by the slurry.

GW Demand= demand determined from experiments (mg/g) involving GW only

Wt$_{GW}$ = mass of GW in the slurry

Wt$_{solid}$ = mass of solid in the slurry

In summary, as indicated in Table 8, for both the .01% and 0.1% MnO$_4^-$ experiments the oxidant demand of the aggregate basalt is ≈ 0.05 mg/g and approximately double that for the crushed basalt (≈ 0.1 mg/g). Similarly, the oxidant demand of the sediment is approximately 0.2 mg/g for both initial oxidant loadings. Due to the low oxidant demand of distilled water and the dissolved plume media, the variation observed in the 1% data is likely due to (1) the very small differences in concentration being measured being less than the precision of the analytical technique employed and/or (2) common laboratory errors in the handling of and the gravimetric determination of the initial KMnO$_4$ mass added to each reactor.

As mentioned previously, the oxidant demand experiments had to be repeated due to problems associated with the MnO$_4^-$ analyses. (The MnO$_4^-$ results of the repeated experiments plotted in Figures 10-12). In order to expedite completion of the repeated experiments, pH values were not measured for the repeated experiments. However, the pH data from the initial experiments are presented in Figures 13, 14, and 15. There was no indication why the pH results from the first experiments would not be acceptable to determining pH trends related to the different types of dissolved plumed media.

The initial pH of the sediment slurries before oxidant addition are consistently less (≈ 0.5 pH units) than that of the basalt or TAN-40 groundwater. Changes in pH, however, that result from

oxidant addition and subsequent consumption appear to be small. Although small in magnitude, the most evident pH changes were observed in the experiment involving 1% MnO_4^-. Oxidant addition appears to initially increase the system pH for the groundwater and basalt samples. In contrast, the pH of the sediment material decreases further as a result of oxidant addition. Thus, pH changes due to oxidant addition are at least in part affected by the chemical characteristics of the TAN site media. Additional discussion and presentation of pH data will be presented in the Task 4 work.
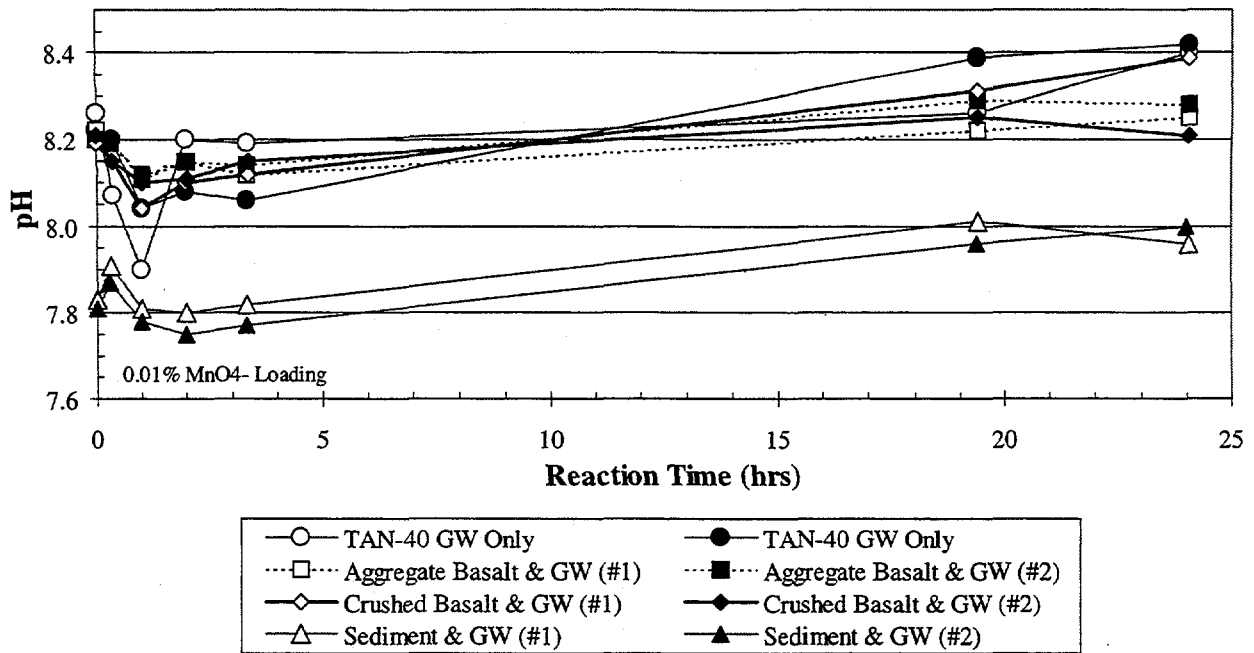
Figure 13. pH Results Obtained During Consumption of Dissolved Plume Media, Initial MnO_4^- = 0.01% (ORNL Exp. 3a-R1, Conducted at 12°C and 4:1 L/S ratio where applicable)
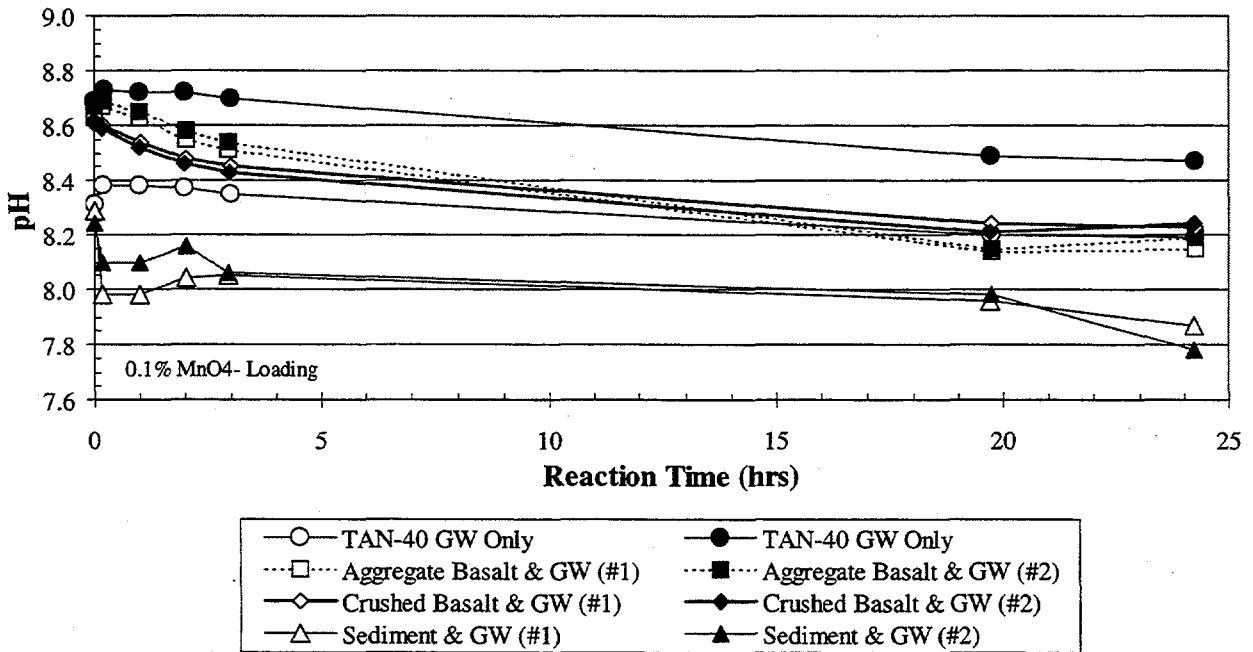
Figure 14. pH Results Obtained During Consumption of Dissolved Plume Media, Initial MnO_4^- = 0.10% (ORNL Exp. 3a-R2, Conducted at 12°C and 4:1 L/S ratio where applicable)
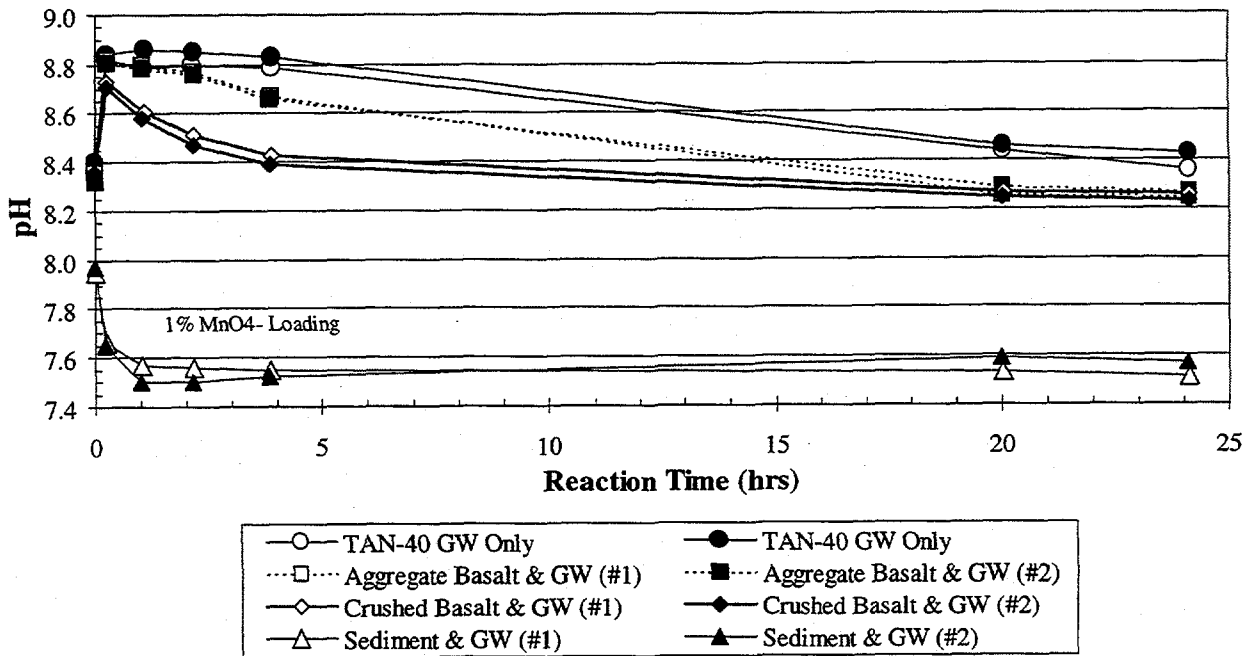
Figure 15. pH Results Obtained During Consumption of Dissolved Plume Media, Initial MnO_4^- = 1% (ORNL Exp. 3a-R3, Conducted at 12°C and 4:1 L/S ratio where applicable)

2.3.3. Oxidant Demand in Hot Spot Media

The oxidant demand of the hot spot media was determined in a similar fashion as that of the dissolved media with a few notable differences presented here. A distilled water control sample was not used in these experiments; instead, two (2) TSF-05 GW samples were used. A stock MnO_4^- solution was not used for the initial MnO_4^- addition into the 0.01% and 0.1% MnO_4^- test reactors. An equivalent mass of solid $KMnO_4$ was added instead. As discussed in Section 1.4.2, the first sampling time was set at 10 minutes in hopes of being able to more accurately quantify the initial oxidant consumption rate. Unfortunately, as the plots reflect, the slow solubization time of the crystalline $KMnO_4$ impeded those efforts. Some variability in the MnO_4^- measured concentrations was also observed in these experiments but is not as readily apparent due to the large scale needed for the vertical axes. Preparation of the sample dilutions needed for the MnO_4^- analyses is certainly an area in which experimental/human error could have contributed to some of this variability of the oxidant values

The MnO_4^- concentration data obtained from the aliquot sampling is presented in Figure 16 for the 0.01% (100 mg/L) MnO_4^- initial oxidant concentration experiment. As in the dissolved plume experiments, the initial MnO_4^- values presented in Figure 16 are *calculated* values based on several pieces of laboratory data. Detailed explanations regarding such computations are included in Appendix C. The remaining data points are *measured* values obtained from the MnO_4^- analyses. It is readily apparent that the TSF-05 sludge exerts a sufficiently high oxidant demand to completely consume all added oxidant within the first 10 minutes of interaction. As noted on Figure 16, the apparent consumption of MnO_4^- in the TSF-05 GW only reactors is likely due to the lack of equilibration time. Nearly identical results were obtained for 0.1% (1,000 mg/L) MnO_4^- initial oxidant concentration experiment and are presented in Figure 17.

Oxidant demand results of the 1% MnO_4^- experiments are presented in Figure 18. Here, the initial loading appears to be great enough to allow the consumption reactions to be observed and quantified. Averaging the MnO_4^- concentrations of the duplicate TSF-05 GW and sludge slurries, results in a consumption rate of 250-900 mg MnO_4^-/hour between the 0.5 hr and 4 hr sampling periods. The actual time at which the oxidant was consumed was not captured temporally, thus a consumption rate cannot be computed for the period after T= 4 hours.

Oxidant demand results of the 3% MnO_4^- experiments are presented in Figure 19. For this oxidant loading, the TSF-05 GW and sludge slurry did not completely consume the available MnO_4^- within the 24 hr reaction time. Averaging the MnO_4^- concentrations of the duplicate TSF-05 GW and sludge slurries results in a consumption rate of 615-700 mg MnO_4^-/hour between 1hr and 4 hr sampling periods. The rate of consumption then appears to slow to an average of 132 mg MnO_4^-/hr between 4 and 24 hrs. Because residual oxidant was still present in the slurry samples at 24 hrs, these reactors were allowed to continue reacting for an additional three days. Residual MnO_4^- was still present after 95 total hours. The average consumption rate between 24 and 95 hrs declined to 34 mg MnO_4^-/hr.

The raw data for these experiments were further evaluated to obtain an oxidant demand or consumption value for TSF-05 sludge itself. Both the measured and "derived" consumption values are presented in Table 9 for the hot spot plume media. To standardize the consumption

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data, the values in Table 9 represent the amount of MnO_4^- consumed per unit of hot spot media after a 24 hour reaction time. The approach used to obtain the oxidant demand of the TSF-05 is the same as that used for the dissolved plume media discussed above in Section 2.3.2. Since the 0.01%, 0.1%, and 1% experiments resulted in complete oxidation consumption within 24 hrs, only the value obtained for the 3% initial oxidant concentration experiment is meaningful. The oxidant demand of the TSF-05 sludge is about 70 mg MnO_4^-/mg sludge. A semi-log plot of the consumption data was also prepared to ascertain whether the consumption rate was first order with respect to the MnO_4^- concentration; however, a linear trend was not observed throughout the reaction interval.
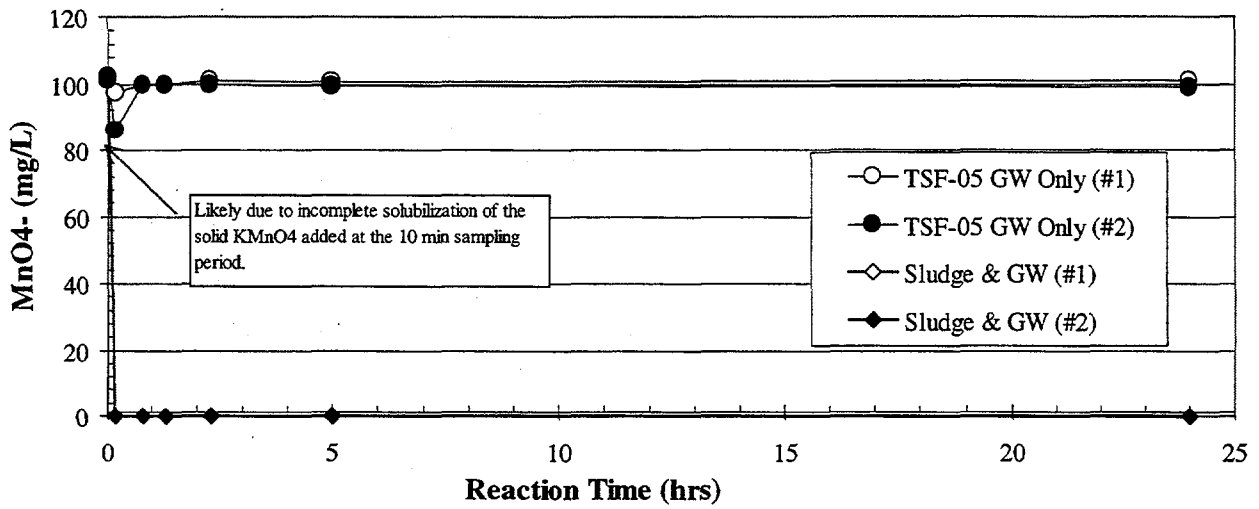
Figure 16. Oxidant Demand Results for Hot Spot Media, Initial $MnO_4^- = 0.01\%$ (ORNL Exp. 3b-R1, Conducted at 12°C and 4:1 L/S ratio where applicable)

Figure 17. Oxidant Demand Results for Hot Spot Media, Initial $MnO_4^- = 0.10\%$ (ORNL Exp. 3b-R2, Conducted at 12°C and 4:1 L/S ratio where applicable)

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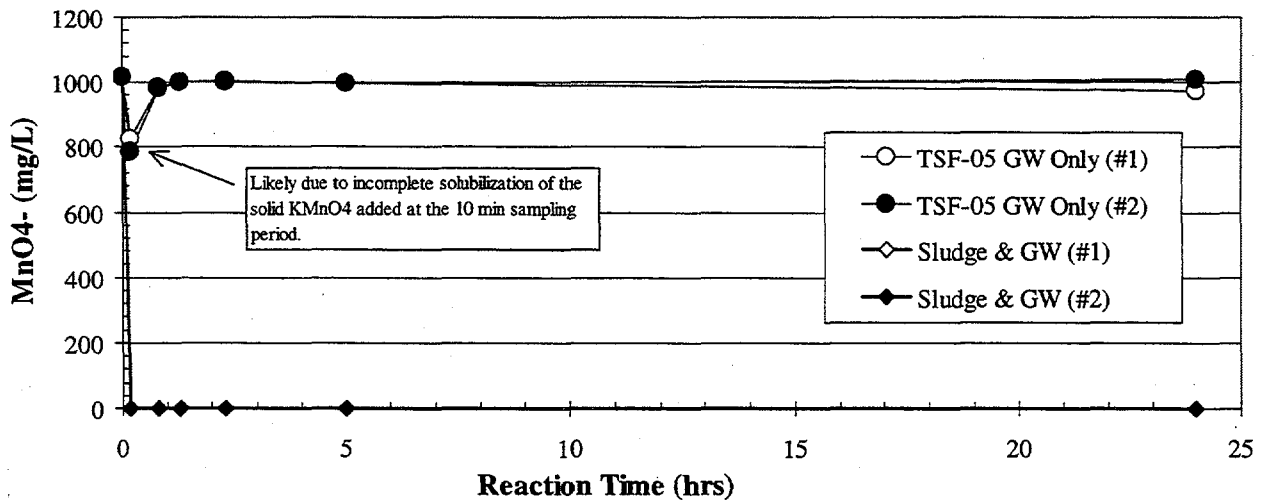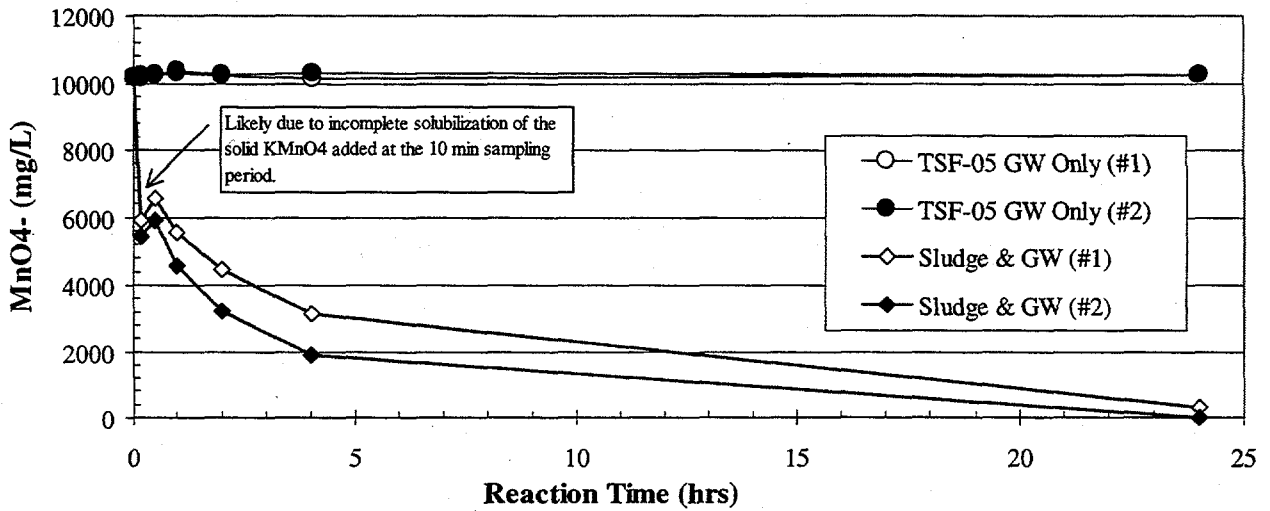
Figure 18. Oxidant Demand Results for Hot Spot Media, Initial $MnO_4^- = 1\%$ (ORNL Exp. 3b-R3, Conducted at 12°C and 4:1 L/S ratio where applicable)
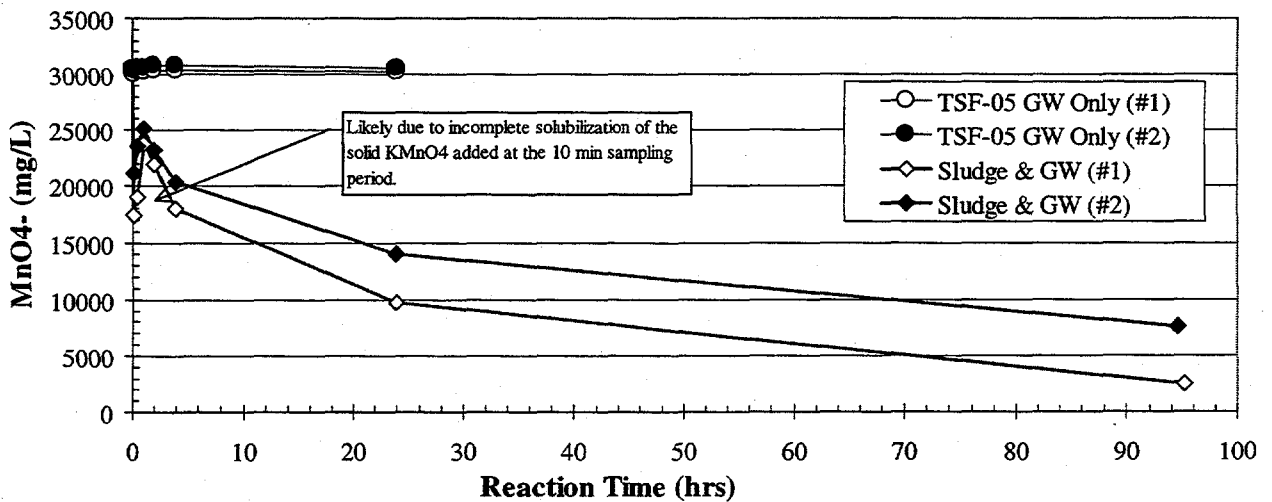
Figure 19. Oxidant Demand Results for Hot Spot Media, Initial $MnO_4^- = 3\%$ (ORNL Exp. 3b-R4, Conducted at 12°C and 4:1 L/S ratio where applicable)

Table 9. Calculated Oxidant Demand Values for the Hot Spot Media. [a,b]

| | Initial MnO$_4^-$ Concentration | | | | | | | |
| | 0.01% | | 0.1% | | 1% | | 3% | |
Test Media	Initial Loading	Consumed	Initial Loading	Consumed	Initial Loading	Consumed	Initial Loading	Consumed
TSF-05 GW Only	0.1	0.002	1.0	0.02	10.2	-0.08	30.5	0.10
TSF-05 GW & Sludge	0.08	0.08 [d]	0.8	0.8 [d]	8.1	7.9 [d]	24.1	14.7
TSF-05 Sludge [c]	NA	0.36 [d]	NA	3.5 [d]	NA	38.2 [d]	NA	69.5

[a.] All values in units of [mg MnO$_4^-$/g of TAN Site Media]

[b.] Consumption values represent a 24 hr reaction time. Values presented for the GW slurries are the averages of duplicate samples.

[c.] Derived by subtracting the GW consumption component from the total oxidant consumption of the slurry via the following equation:

Solid Phase Demand (mg/g)= [Total-(GW Demand x Wt$_{GW}$)]/(Wt$_{solid}$)

Where: Total= total mass of MnO$_4^-$ (mg) consumed by the slurry.
GW Demand= demand determined from experiments (mg/g) involving GW only
Wt$_{GW}$ = mass of GW in the slurry
Wt$_{solid}$ = mass of solid in the slurry

[d.] All of available oxidant was consumed before the oxidant demand was satisfied.

The pH values were also tracked during the hot spot oxidant demand studies. The results are presented in Figures 20-23 for the 0.01%, 0.1%, 1% and 3% MnO$_4^-$ experiments. A few observations can be made from these figures: The pH of the TSF-05 GW (at 12°C) was around 8 for all four (4) of the oxidant loadings investigated. (Some variation in the initial TSF-05 GW chemistry, e.g. pH values, was expected since the containers of TSF-05 GW received from INEEL were not combined/mixed prior to experimentation). The pH's of the slurries, on the other hand, were lower at an average of 7.6 after an overnight equilibration period with the TSF-05 GW at 12°C. (Note: the pH values plotted at T=0 were measured immediately prior to oxidant addition.) Upon oxidant addition, the pH values of the TSF-05 GW only reactors increased from ≈7.9 to 8.3 for both the 0.01% and 0.1% MnO$_4^-$ treatments. Similarly, reactor pH's increased to ≈8.6 and ≈9 for the 1% and 3% MnO$_4^-$ treatments. These pH increases in the GW reactors is likely due to the change in the ionic strength of the reactors following oxidant addition. The pH's of the slurry reactors, on the other hand, all decreased with addition of the oxidant. This was expected as a result of oxidation of organic matter (See equation 2). For the 0.1% and 0.1% MnO$_4^-$ reactors (Figures 20 and 21), the pH dropped to ≈0.5 pH units at the beginning of the reaction period. This decrease occurs immediately and persists until all of the MnO$_4^-$ is consumed. The reactor pH values remained steady for the rest of the reaction period. The pH values of the 1% and 3% MnO$_4^-$ reactors also initially decrease by approximately the same magnitude. For these two oxidant loadings, however, the reactor pH increased after this initial oxidation reaction occurred. In fact, the final pH values for these latter slurry reactors

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rebounded to at least the starting (T=0 hrs) values. Note from Figures 22 and 23 that a residual oxidant concentration existed beyond the 4 hr sampling period. As observed for TSF-05 GW only reactors, this excess MnO_4^- was likely the cause of the pH increases after sludge consumption slowed and/or ceased. The preceding discussion suggests that the overall (net) pH change experienced in a TSF-05 slurry reactor are a combination of pH increases due to the ionic strength of the oxidant and pH decreases as a result of H^+ generation during oxidation. Thus, the final pH of such a slurry system is dependent upon the relative amounts of oxidant and oxidizible material present.
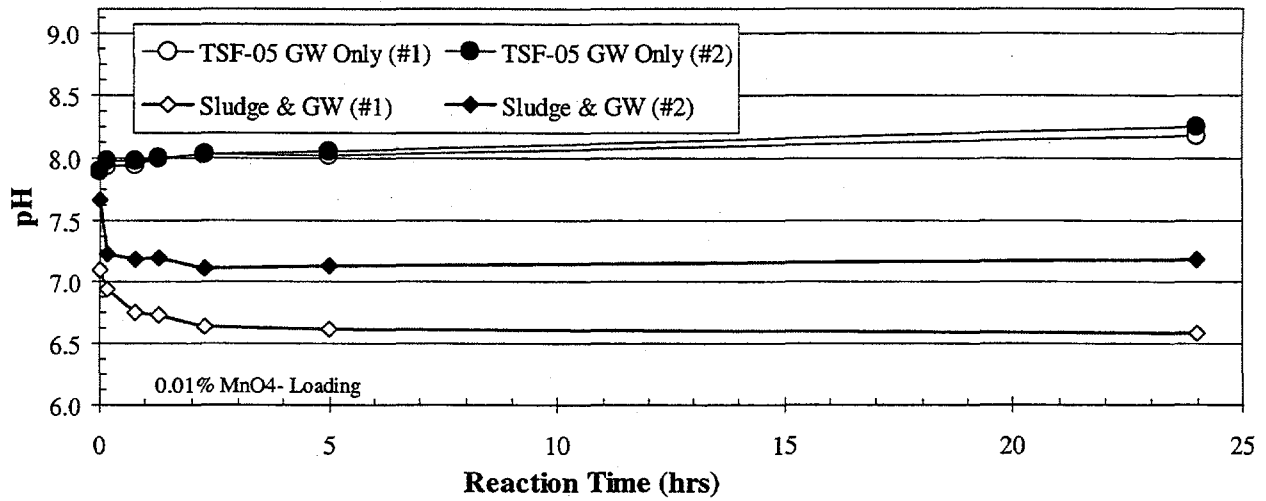
Figure 20. pH Results Obtained During Consumption of Hot Spot Media, Initial $MnO_4^- = 0.01\%$ (ORNL Exp. 3b-R1, Conducted at 12°C and 4:1 L/S ratio where applicable)
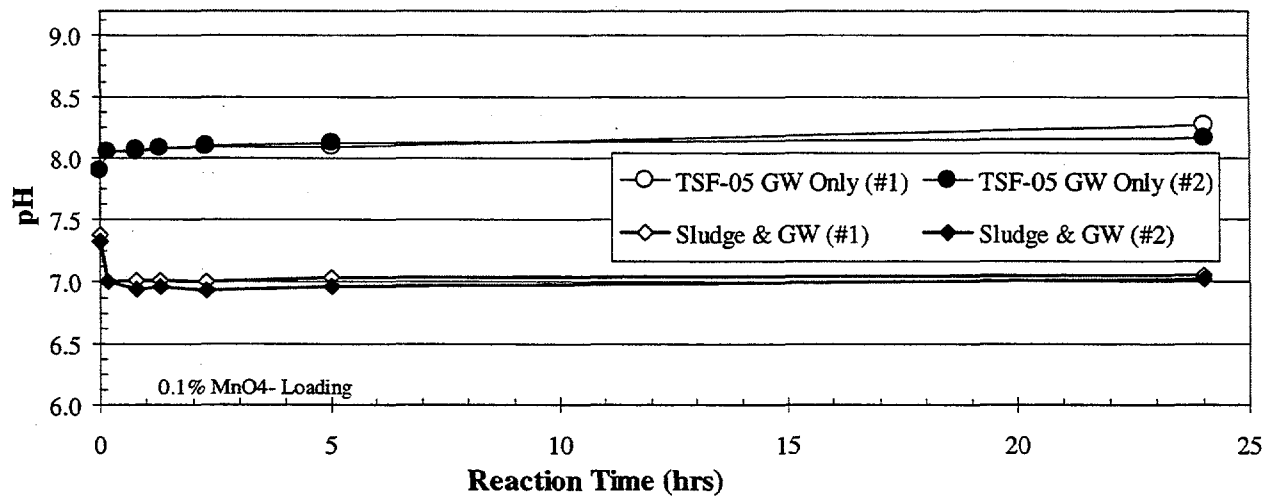
Figure 21. pH Results Obtained During Consumption of Hot Spot Media, Initial $MnO_4^- = 0.10\%$ (ORNL Exp. 3b-R2, Conducted at 12°C and 4:1 L/S ratio where applicable)
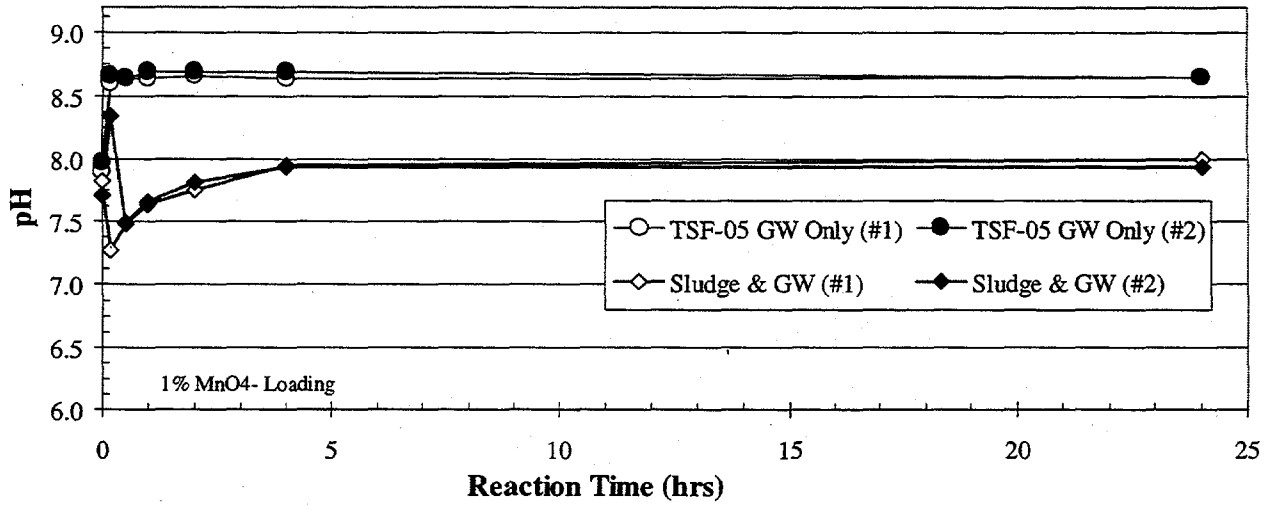
Figure 22. pH Results Obtained During Consumption of Hot Spot Media, Initial $MnO_4^- = 1\%$ (ORNL Exp. 3b-R3, Conducted at 12°C and 4:1 L/S ratio where applicable)
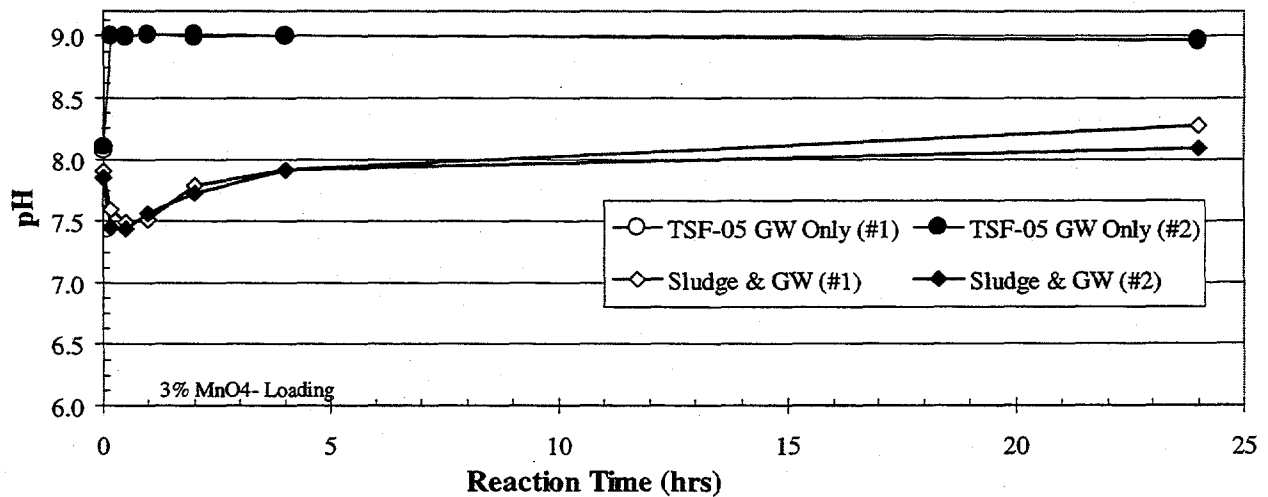
Figure 23. pH Results Obtained During Consumption of Hot Spot Media, Initial $MnO_4^- = 3\%$ (ORNL Exp. 3b-R4, Conducted at 12°C and 4:1 L/S ratio where applicable)

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2.3.4 Summary - Oxidant Demand of TAN Subsurface Materials

This set of experiments measured the oxidant demand exerted by materials from the subsurface beneath TAN, including both natural geologic materials (groundwater, basalt, and fracture-fill material) and anthropogenic organic sludge. The MnO_4^- concentrations investigated range from 0.01% to 3%, which is the same range investigated in the oxidation rate experiments described in Section 2.4

The experimental identification for this series of experiments is presented in Table 10.

Table 10. Experimental Identification for the 'Oxidant Demand' (Task 3) Studies.

MnO4- Concentration (%)	Dissolve Plume Media Experiments	Hot Spot Media Experiments
0.01	3aR1b	3b-R1
0.1	3aR2b	3b-R2
1	3aR3b	3b-R3
3	Not Evaluated	3b-R4

Representative values of the oxidant demand of subsurface materials from TAN, including media from both the dissolved plume and the hot spot, are given in Table 11. For comparison, the oxidant demand determined in a previous study (Istok, personal communication) of surficial basalt from Hell's Half Acre was approximately 1 mg MnO_4^-/g basalt. The oxidant demand determined in this study for geologic materials (i.e. not organic sludge) are at least on half order of magnitude less than that value, while the oxidant demand of organic sludge is approximately two orders of magnitude larger.

Table 11. Representative Oxidant Demand for TAN Subsurface Media.

TAN Site Medium	Oxidant Demand (mg MnO_4^- /g Medium)
TAN-40 GW	0.01
TSF-05 GW	0.02
Crushed Basalt	0.05
Aggregate Basalt	0.1
Sediment	0.2
TSF-05 Sludge	70

2.4 TASK 4. MEASUREMENT OF OXIDATION RATES OF TAN SUBSURFACE MATERIALS

2.4.1. Laboratory Controls and QA

During the oxidation rate studies, between 800-900 aliquot samples were collected and analyzed for VOCs (primarily TCE), pH, and MnO_4^-. Over 550 additional QA/QC samples directly related to QA/QC were also analyzed for VOCs (160 duplicate aliquot samples, $\approx$300 desorption tube extractions, and $\approx$100 "final reactor" extractions.)

During each experiment presented in Section 2.4, duplicate aliquot samples were collected from one of the test reactors at each sampling period. A comparison (% difference basis) was made between the two TCE values obtained for a given time point. In all, 160 duplicate aliquot samples were collected. A histogram of the percent difference between duplicate samples is presented in Figure 24. The average % difference between duplicate samples was 3%. Greater than 90% of the duplicates evaluated had a % difference of less than 20%. In addition, 67% of the duplicates evaluated had a % difference of less than 1%. When the % difference values of duplicate samples are compared to the average aqueous TCE concentration of the duplicates (Figure 25) the degree of variability between duplicates appears the greatest at the lower TCE concentrations. This is expected. In fact, most of the larger %difference values observed in this entire treatability here were associated with samples where at least one of the duplicates yielded TCE concentrations less than the minimum detection limit.

TCE mass balances were performed at the end of each oxidation experiment discussed in this section. Since good agreement exists between duplicate samples, the mass balances were computed assuming that the concentrations of any duplicate samples were the same. More specifically, the TCE concentration was assumed to be the same as the first (sample "a") of the two duplicate samples collected. Finally, to better facilitate the discussion of the individual experiments, the results of the remaining QA/QC samples for (collected primarily for the mass balance calculations) are presented and discussed in concert with the actual test data.
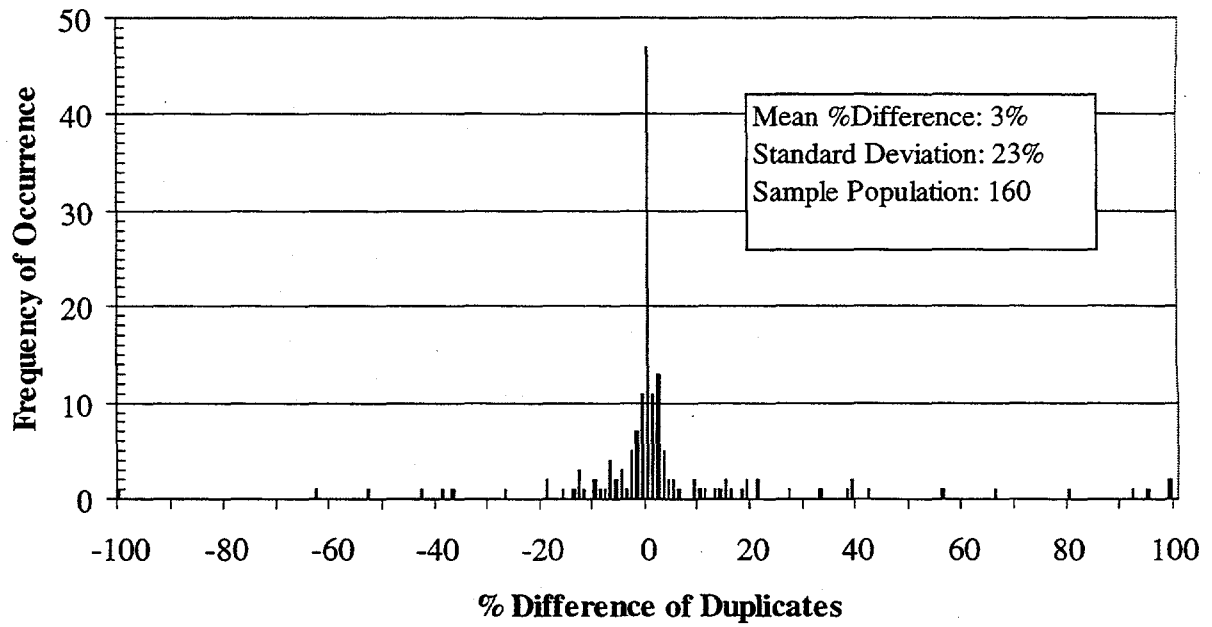
Figure 24. Histogram Illustrating Results of QA/QC Duplicate Sampling.
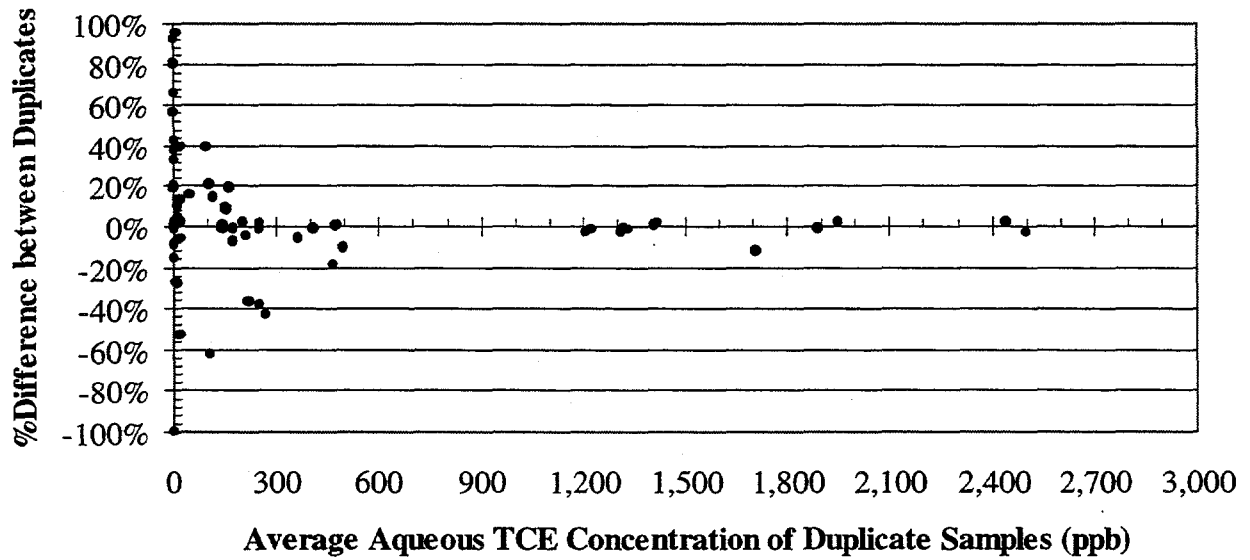
Figure 25. % Difference of QA/QC Duplicates vs. the Average Duplicate Concentration.

2.4.2. Oxidation Rate of Organic Contaminants in Dissolved Plume Media

Eight (8) separate oxidation rate experiments were performed using the dissolved plume media. Each experimental discussion is identified in this section by the ORNL Exp. ID that is presented in Table 5. In general, plots of "TCE vs. Time", "MnO_4^- vs. Time", and "pH vs. Time" are presented for each experiment. For all plots of TCE vs. Reaction time: values resulting from analyses in which the sample extract concentration was out of the calibration range are clearly labeled.

In addition to the plots, summary tables for the TCE and MnO_4^- data are also presented for each experiment. Several parameters are included in the TCE mass balance tables (e.g., Table 12). The approach and/or calculations made to obtain each of the values presented in the mass balance tables are presented below.

As will be observed in the following experimental discussions, most of the actual TCE spike concentrations for this series of experiments were approximately doubled that of the target TCE spike concentrations presented in Table 5.

TCE MASS BALANCE TABLE DESCRIPTION
- Column 1, "Test Conditions" refers the experimental condition. In this column "Control" refers to reactors containing only TAN GW and no oxidant. The (#1) and (#2) notations included in parentheses refer to the duplicate reactors evaluated. The number followed by the percentage sign is the nominal initial MnO_4^- concentration added to the treatment reactors.

- Column 2, "Total Initial Mass" refers to the TCE mass added to each reactor. For the GW control reactors and treatment reactors containing TAN-40 GW only (Exps. 4a-R1 & 4a-R2) this value is determined by the following equation: (Aqueous TCE Conc. at T=0) x (GW Volume in the Non-Slurry Reactor) Note: T=0 sampling occurred after overnight equilibration and immediately before oxidant addition to the treatment reactors. For reactors containing both TAN-40 GW and a solid phase media, the initial total TCE mass is computed by the following equation: (Average Aqueous TCE Conc. at T=0 of the 2 GW Controls) x (GW volume in the Slurry Reactor). It is computed in this way, as opposed to using the measured aqueous concentration in the slurry reactor at T=0, in the event that some TCE is sorbed to the solid phase at T=0.

- Column 3, "Initial Aqueous Mass". For all cases, this value is computed by multiplying the Aqueous TCE Conc. at T=0 for a given reactor by the volume of GW added to that reactor. Note: The aqueous concentration at T=0 for each reactor is used here rather than the concentration of the spiked GW before it is distributed to the individual reactors and equilibrated. (This approach effectively accounts for the any TCE lost during equilibration from the mass balance calculations performed for the actual oxidation reactions.) For the reactors containing both TAN-40 GW and a solid phase medium, another value is also presented in Column 3 of the mass balance tables. This "% Sorbed" value represents the fraction of TCE at T=0 partitioned to the solid phase. It is computed for each GW/solid phase slurry via the following equation:

$\%$Sorbed=100 x [1-(Initial Aqueous Mass/Total Initial Mass)] or 100 x [1-(Col. 3/Col. 2)]

- Column 4, "Mass Sorbed on Orbo Tubes" represents the summed TCE mass found on each charcoal bed of the reactor's desorption tube at the end of the reaction period (T=24 hrs). The TCE mass was obtained by extraction of charcoal beds with hexane. If TCE is detected on the desorption tubes, it is realized that the value obtained represents a *minimum* that was volatilized since the entire reactor headspace volume would not pass through the desorption tube. The values in percent (%) for this column represent the percentage of the Total Initial Mass (column 1 of the Table) found within the Orbo Tube.

- Column 5, "Mass Remaining in Reactor" represents the TCE mass still present in each reactor following the reaction period (T=24 hrs). For the Control reactors and test reactors containing TAN-40 GW only (Exps. 4a-R1 and 4a-R2), this value was computed by the following equation: (Aqueous TCE concentration at T=24 hrs) x (Init. GW volume –Cum. Vol. of Aliquot Samples). For treatment reactors containing a slurry of GW and solid-phase media, the remaining TCE mass in the reactor was obtained by extracting the entire contents remaining in the reactor after T=24 hrs with hexane ($\approx$1:1 v/v extraction). For both cases, the values in % for this column represent the percentage of the Total Initial Mass (column 1 of the Table) still present in the reactor.

- Column 6, "Cum. Mass Removed in Aliquots" represents the mass of TCE removed from the reactor as a result of the aliquot sampling. In all cases, this column is computed by summing the masses of TCE that were found in each aliquot interval for a given reactor, i.e., Σ(Aqueous TCE Conc. x Aliquot Volume). The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) removed from the reactor (and thereby not subjected to oxidation) during the course of the experiment.

- Column 7, "Cum. Aqueous Mass Oxidized" represents the TCE mass initially in the aqueous phase that was considered to have been oxidized during the reaction period. The oxidized TCE masses presented in this column were computed by summing the change in aqueous TCE mass obtained for each sampling period, i.e., $\Sigma[($Aq. TCE Conc. $_{T=x}$ – Aq. TCE Conc.$_{T=x+1})$ x GW Vol. $_{T=x}]$. Thus, this approach corrects for TCE removed via previous aliquot samplings. Again, the % values in this column represent the percentage of the Total Initial Mass (Column 1 of the Table) believed to have been oxidized. It is important to note that this component of the mass balance does not take into account any TCE initially sorbed to a solid phase media.

- Column 8, "Total Mass Recovered" is the sum of the TCE masses found in four (4) different "compartments" at the end of the reaction period (T=24 hrs), i.e., Col. 4+Col. 5 + Col. 6 + Col. 7. The % values for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) that was accounted for during the course of the experiment.

For each TCE oxidation experiment presented in this section, a oxidant consumption summary table is presented (e.g. Table 13). The approach and/or calculations made to obtain each of the values presented in the oxidant consumption tables are presented below.

MnO₄⁻ CONSUMPTION TABLE DESCRIPTION

- Column 1, "Test Conditions" refers the experimental condition. The (#1) and (#2) notations included in parentheses refer to the duplicate reactors evaluated. The number followed by the percentage sign is the nominal initial MnO_4^- concentration added to the treatment reactors (0.01%, 0.1%, 1%, or 3% MnO_4^-).

- Column 2, "Initial Oxidant" represents the oxidant (MnO_4^-) mass added to each reactor. For the oxidant loadings of 0.01% and 0.1% MnO_4^- this value was computed by multiplying the concentration of the stock MnO_4^- spiking solution used by the volume of stock solution used. For oxidant loadings of 1% and 3% MnO_4^-, this value was computed by multiplying the mass of crystalline $KMnO_4$ added to each reactor (gravimetrically determined) by the MnO_4^- /$KMnO_4$ mole fraction (0.753).

- Column3, "Initial Loading". For all cases, this value is computed dividing the value presented in Column 1 by the total mass of TAN site media (groundwater and solid phase) added to each slurry reactor. These masses were determined gravimetrically.

- Column 4, "Cum. Consumed" represents the MnO_4^- mass that was consumed at the end of the reaction period. This value was obtained by difference between the initial MnO_4^- concentration between the final aliquot MnO_4^- concentration. The exact equations used to compute the initial aqueous oxidant concentration varied based up the oxidant spiking method employed. (The exact equations used are presented in Appendix C, Calculations.) The final aqueous MnO_4^- concentrations of each aliquot were determined via spectrophotometry. These values are also presented in Appendix C.

- Column 5, "Cum Consumed" represents the same value determined in Column 3 but is expressed in units of consumption per gram of TAN site media. The mass of TAN site media used (groundwater and solid phase mass) is the same as the value used in Column3.

Also note that variation in the initial TAN-40 GW chemistry, e.g. pH values, is expected since each dissolved plume media experiment was conducted using a different batch of TAN-40 GW that had been sparged for varying amounts of time. (The containers of TAN-40 GW received from INEEL were not combined/mixed prior to experimentation).

ORNL Exp. 4a-R1
(TAN-40, No Solids, 100 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

Only TAN-40 GW was evaluated in this experiment. The TCE, MnO_4^- and pH values with time are presented in Figures 26, 27, and 28, respectively. Tables 12 and 13 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No significant deviations from the testplan procedures were made in this experiment.

After equilibration, the initial aqueous TCE concentration of the spike solution was 190 µg/L. After transfer to the test reactors, the spiked groundwater TCE concentration ranged between 169 and 182 µg/L TCE (T=0 aliquots) prior to the start of the oxidation reaction. Excellent TCE mass balances were obtained from the control reactors. The lowest TCE recovery of 93% was obtained for the second control sample (see drop in TCE concentration for that reactor in Figure 26).

It is believed that the observed reductions in TCE concentrations for the treatment reactors were primarily due to oxidation since (1) the recoveries of the GW controls were high and (2) TCE was not detected in the extracts from the charcoal desorption tubes from either the control or the treatment reactors. Complete TCE oxidation occurred within 3 hrs for the 0.01% MnO_4^- treatments and within the first 0.5 hrs for the 0.1% MnO_4^- reactors. The three aqueous TCE data points between T=0 and T=1.6 hrs were used to compute the reaction rate for the initial, rapid step of the oxidation reaction in the 0.01% reactors. The data were plotted as $\ln(C/C_o)$ vs. Time in Figures 29 and 30 for the first and second 0.01% reactors in order to approximate a first order reaction rate constant, k. The linear regression resulted in an average first order rate constant of k=1.78 hr^{-1}. While the fit of the data to a first order rate constant may not be optimal, attempts to evaluate other rate models were not made since the mechanisms occurring in such a complex system are not known. Enough data points were not available to compute a rate constant for the 0.1% MnO_4^- reactors; however, the observed oxidation rate is greater than 0.2 mg TCE/hr.

While all of the TCE was consumed, little of the initial MnO_4^- added was consumed by the TCE spiked TAN-40 GW mixture (Table 13). The pH of the reactors was affected by both the addition of the oxidant and the subsequent oxidation reaction that occurred. The pH of the test reactors loaded with the 0.01% MnO_4^- did not begin to effectively increase until after the TCE had been oxidized. For the 0.1% MnO_4^- oxidant loading, there was not an initial pH decrease, although TCE was completely oxidized. Instead, the overall reactor pHs quickly increased. It is likely that any pH reductions that did occur as a result of TCE oxidation were very small in comparison to the pH effect imparted by addition of the 0.1% MnO_4^- oxidant solution.
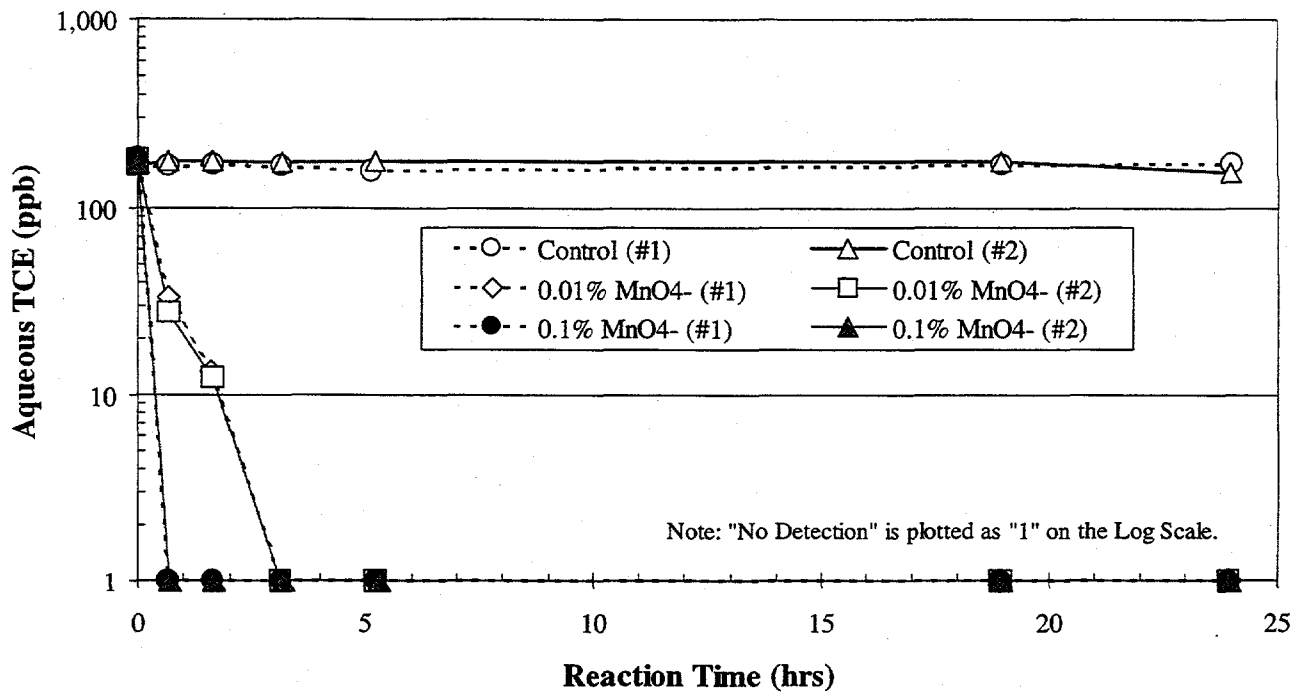
Figure 26. TCE vs. Time, TAN-40 GW Only, (ORNL Exp. 4a-R1, Initial TCE= 100 μg/L, Conducted at 12°C)
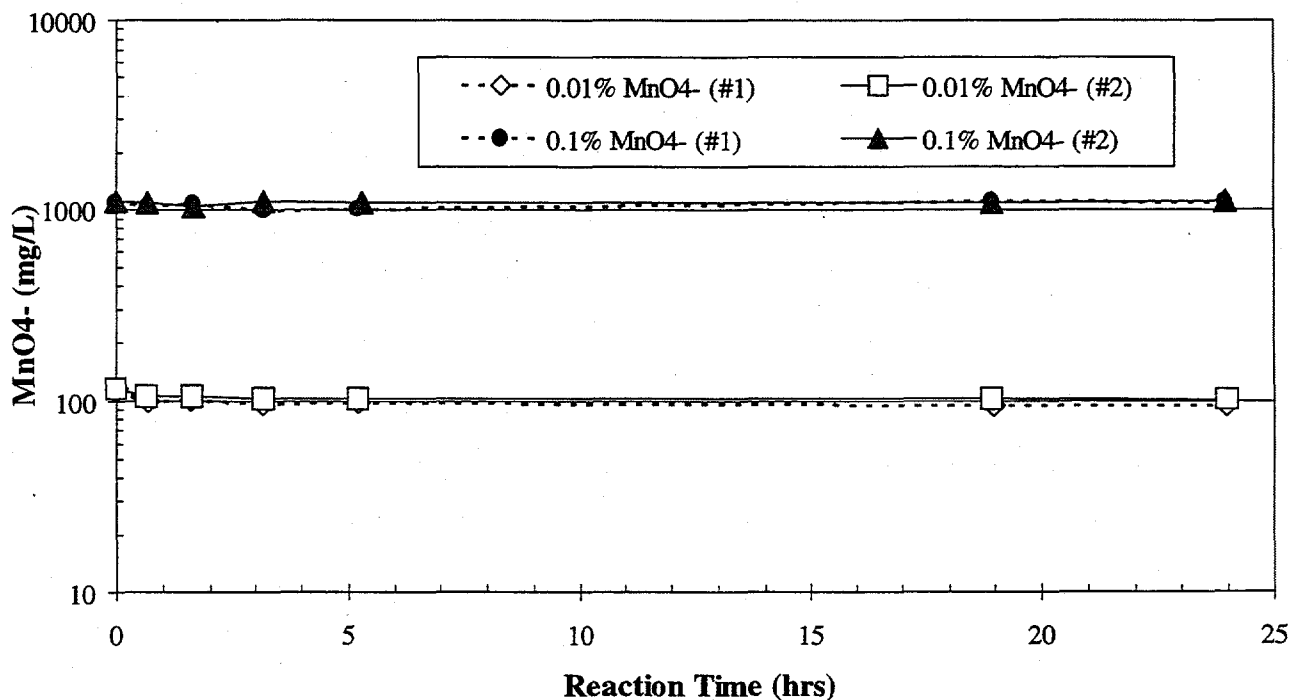
Figure 27. MnO$_4^-$ vs. Time, TAN-40 GW Only, (ORNL Exp. 4a-R1, Initial TCE= 100 μg/L, Conducted at 12°C)
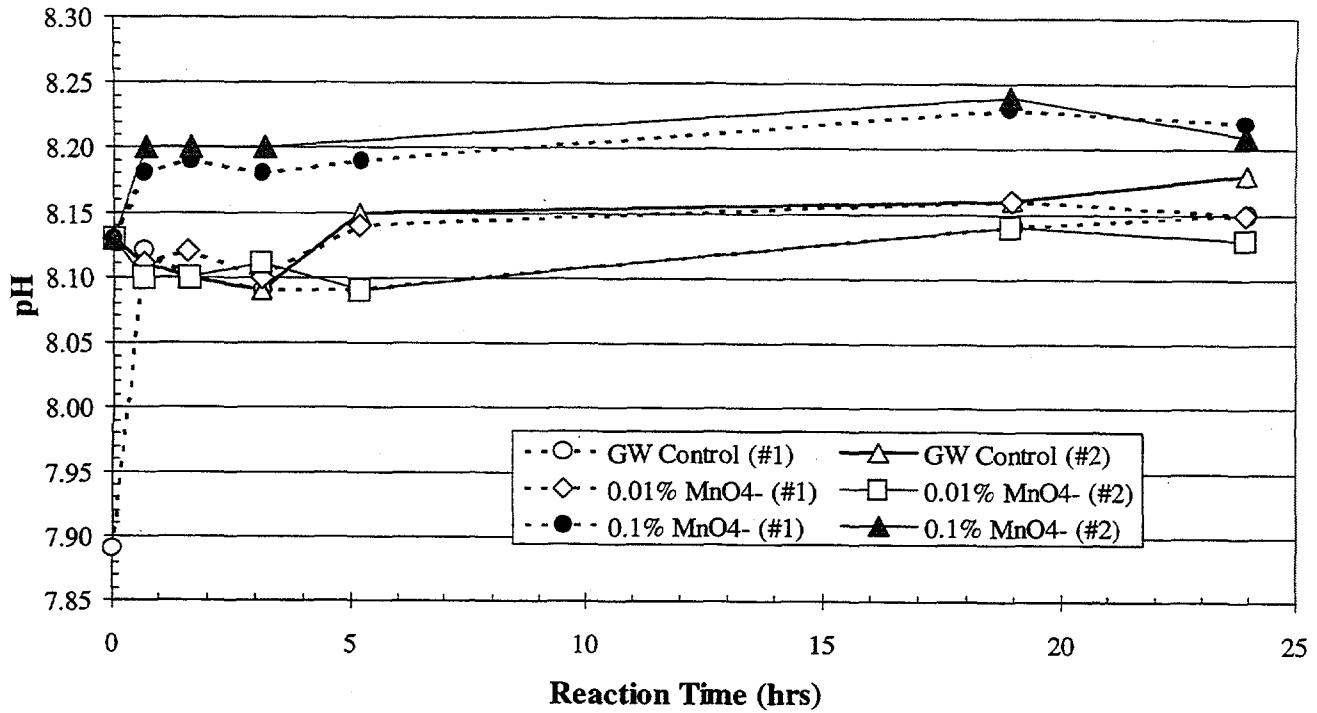
Figure 28. pH vs. Time, TAN-40 GW Only, (ORNL Exp. 4a-R1, Initial TCE= 100 µg/L, Conducted at 12°C)

Figure 29   First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW Only, (ORNL Exp. 4a-R1, Initial TCE= 100 µg/L, Conducted at 12°C,)

Figure 30   First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#2) Reactor, TAN-40 GW Only, (ORNL Exp. 4a-R1, Initial TCE= 100 µg/L, Conducted at 12°C)

Table 12. TCE Mass Balance for ORNL Exp. 4a-R1 (TAN-40 GW Only).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.09	0.09	0.000 0%	0.08 90%	0.01 12%	NA NA	0.1 102%
Control (#2)	0.09	0.09	0.000 0%	0.07 82%	0.01 11%	NA NA	0.1 93%
0.01% (#1)	0.09	0.09	0.000 0%	0.00 0%	0.002 2%	0.09 98%	0.1 100%
0.01% (#2)	0.10	0.10	0.000 0%	0.00 0%	0.002 2%	0.09 98%	0.1 100%
0.1% (#1)	0.10	0.10	0.000 0%	0.00 0%	0.001 1%	0.10 100%	0.1 102%
0.1% (#2)	0.09	0.09	0.000 0%	0.00 0%	0.001 1%	0.09 100%	0.1 102%

Table 13. MnO_4^- Consumption Data for ORNL Exp. 4a-R1 (TAN-40 GW Only). [a]

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	59.7	0.11	10.39	0.02
0.01% (#2)	59.7	0.11	6.68	0.01
0.1% (#1)	596.8	1.09	0.78	0.00
0.1% (#2)	596.8	1.11	0.26	0.00

[a.] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R2
(TAN-40, No Solids, 1000 TCE, 0 Other, 0.01% and 0.1% MnO$_4^-$)

Only TAN-40 GW was evaluated in this experiment. The TCE, MnO$_4^-$ and pH values with time are presented in Figures 31, 32, and 33, respectively. Tables 14 and 15 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

Known Testplan Deviations:
The only significant deviation from the testplan procedure was the method used to prepare the spiked groundwater. Here, the air-sparged GW was temperature equilibrated first, then it was spiked via a saturated TCE solution for 2-3 hrs prior to distribution into the test reactors. (Testplan procedures state that the air-sparged GW should be spiked at room temperature and then equilibrated overnight at 12°C).

Following temperature equilibration, the average initial aqueous TCE concentration of the spike solution was 1440 µg/L (σ= 39 µg/L). After transfer to the test reactors, the spiked groundwater TCE concentration ranged between 1414 and 1497 µg/L TCE (T=0 aliquots for the test reactors) prior to the start of the oxidation reaction. TCE recoveries of 91% and 98% were obtained for the control reactors. From the aliquot TCE concentrations of the control samples, it appears that the first control reactor was losing TCE via volatilization. Its TCE concentration steadily decreased from 1,430 µg/L at T=0 hrs to 1,296 µg/L at T=24 hrs. The second control reactor, on the other hand, started with an initial TCE concentration of 1,351 µg/L and an ending concentration of 1,323 µg/L (average of 6 aliquots= 1,360 µg/L).

It is believed that the observed reductions in TCE concentrations for the treatment reactors were primarily due to oxidation since recoveries of the GW controls were high and TCE was not observed in the extracts from the charcoal desorption tubes. The data suggests that complete TCE oxidation occurred within 5 hrs for the second 0.01% MnO$_4^-$ reactor and within the first 2 hrs for both of the 0.1% MnO$_4^-$ reactors (Figure 31). The residual TCE present in the first 0.01% MnO$_4^-$ reactor ($\approx$10 µg/L) was not expected. Evidence of any analytical problems (e.g., solvent blank contamination) does not exist to dispute the reported TCE concentrations.

The four aqueous TCE data points between T=0 and T=3.2 hrs were used to compute the reaction rate for the initial, rapid step of the oxidation reaction in the 0.01% reactors. The data were plotted as ln(C/C$_o$) vs. Time in Figures 34 and 35 for the first and second 0.01% reactors in order to approximate a first order reaction rate constant, k. The linear regression resulted in an average first order rate constant of k=1.51 hr^{-1}. While the fit of the data to a first order rate constant may not be optimal, attempts to evaluate other rate models were not made since the mechanisms occurring in such a complex system are not known. Enough data points were not available to compute a rate constant for the 0.1% MnO$_4^-$ reactors; however, the observed oxidation rate is greater than 0.34 mg TCE/hr.

While all the TCE was consumed, little of the initial MnO$_4^-$ added was consumed by the TCE spiked TAN-40 GW mixture. While it is unknown why a residual TCE concentration existed in

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the first 0.01% reactor, there is a correlation between the slowed TCE oxidation rate and an observed decrease in MnO_4^- between 6 hrs and 24 hours. The oxidation reactions appear to have produced an overall net decrease in the pH of the systems. The pH decrease was more pronounced in the 0.01% MnO_4^- reactors. As discussed in Exp. 4a-R1, the higher final pHs for the 0.1% MnO_4^- reactors is likely due to the fact that the ionic strength of 0.1% oxidant is considerably greater than that of the 0.01% oxidant solution. All of these observed pH changes however are small; in fact, the pH values for the control reactors (no oxidant added) also decreased by approximately the same amount as the 0.01% MnO_4^- reactors.
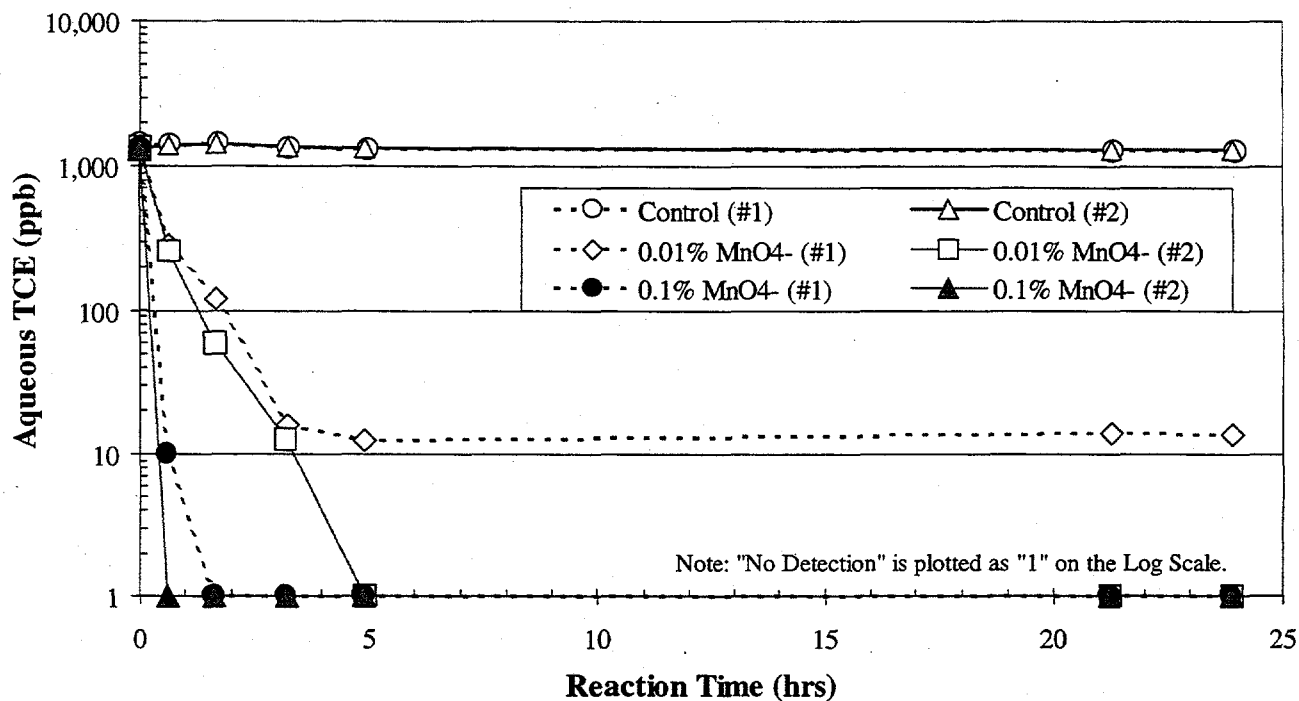
Figure 31. TCE vs. Time, TAN-40 GW Only, (ORNL Exp. 4a-R2, Initial TCE= 1000 µg/L, Conducted at 12°C)
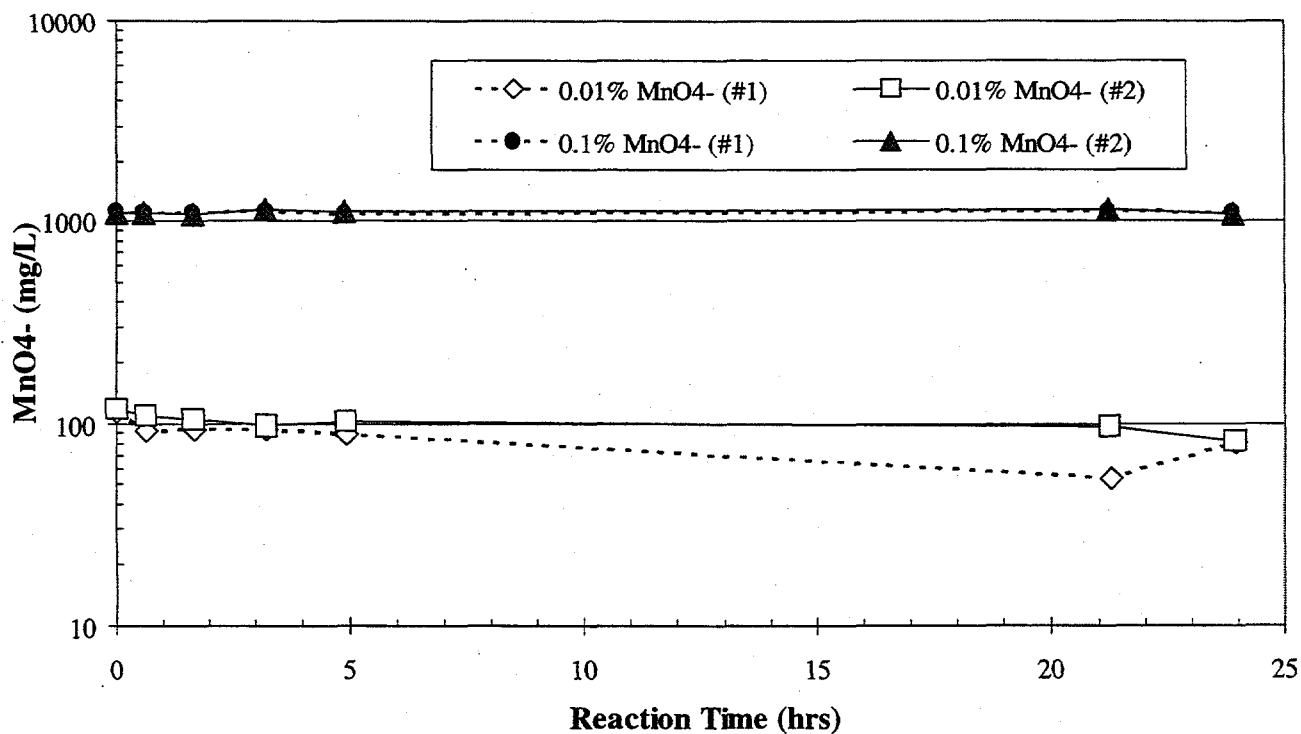
Figure 32. MnO$_4^-$ vs. Time, TAN-40 GW Only, (ORNL Exp. 4a-R2, Initial TCE= 1000 µg/L, Conducted at 12°C)
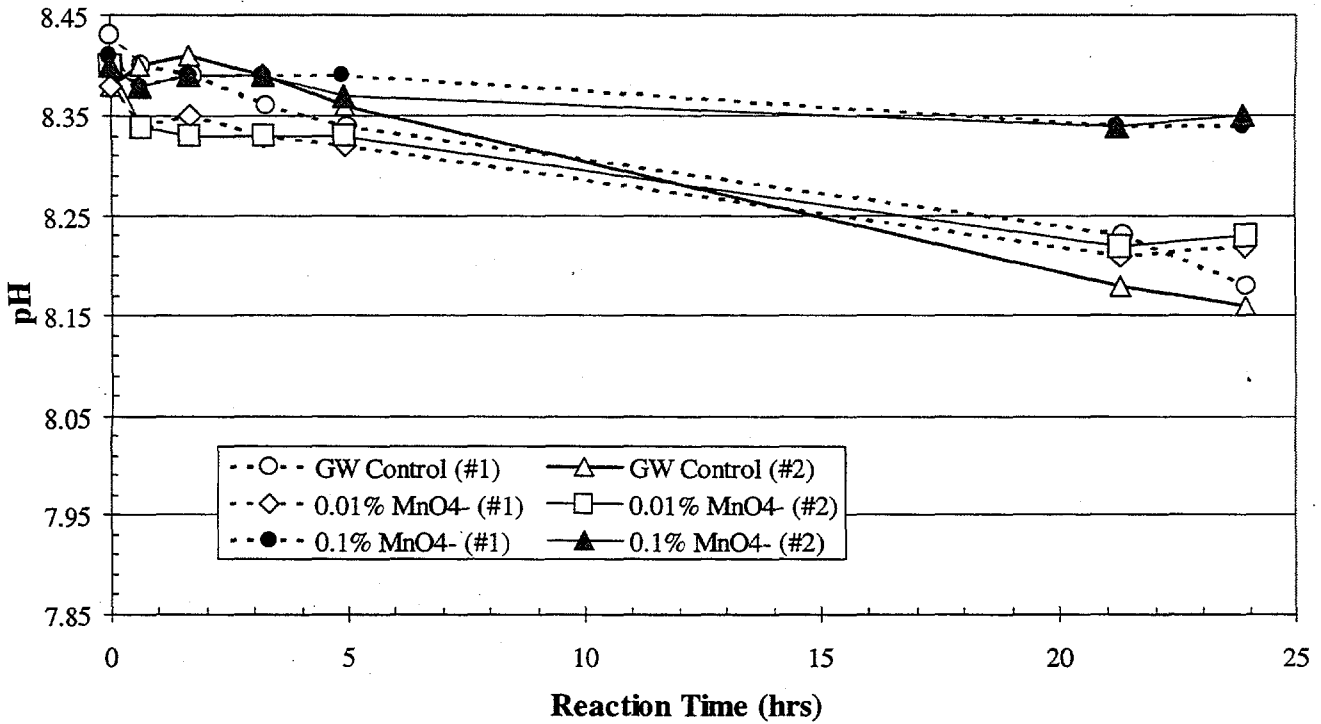
Figure 33. pH vs. Time, TAN-40 GW Only, (ORNL Exp. 4a-R2, Initial TCE= 1000 µg/L, Conducted at 12°C)

$y = -1.4305x$

$R^2 = 0.9552$

Figure 34 First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW Only, (ORNL Exp. 4a-R2, Initial TCE= 1,000 µg/L, Conducted at 12°C)

Figure 35   First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW Only, (ORNL Exp. 4a-R2, Initial TCE= 1,000 µg/L, Conducted at 12°C)

Table 14. TCE Mass Balance for ORNL Exp. 4a-R2 (TAN-40 GW Only).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.73	0.73	0.000	0.58	0.09	NA	0.7
			0%	79%	12%	NA	91%
Control (#2)	0.68	0.68	0.000	0.59	0.08	NA	0.7
			0%	87%	11%	NA	98%
0.01% (#1)	0.70	0.70	0.000	0.00	0.014	0.68	0.7
			0%	0%	2%	97%	99%
0.01% (#2)	0.68	0.68	0.000	0.00	0.012	0.67	0.7
			0%	0%	2%	98%	100%
0.1% (#1)	0.69	0.69	0.000	0.00	0.009	0.70	0.7
			0%	0%	1%	101%	102%
0.1% (#2)	0.67	0.67	0.000	0.00	0.009	0.68	0.7
			0%	0%	1%	101%	102%

Table 15. MnO_4^- Consumption Data for ORNL Exp. 4a-R2 (TAN-40 GW Only).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	58.0	0.11	17.72	0.04
0.01% (#2)	58.0	0.12	18.44	0.04
0.1% (#1)	580.4	1.11	7.80	0.01
0.1% (#2)	580.4	1.11	8.97	0.02

[a.] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R3
(TAN-40, Crushed Basalt, 100 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

Slurries of TAN-40 GW and crushed basalt were evaluated in this experiment. The TCE, MnO_4^- and pH values with time are presented in Figures 36, 37, and 38, respectively. Tables 16 and 17 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No deviations from the procedures described in the testplan were made.
As explained at the beginning of this section, the total initial mass of TCE in a reactor that contained both GW and a solid phase media was computed differently than for a reactor that contained only GW. Here, the initial masses of TCE in the reactors containing a slurry of crushed basalt were computed by averaging the TCE concentration in the aqueous controls (at T=0 hrs) and multiplying that by the aqueous volume present in the slurry reactor. The rationale for using this approach is the fact that the TAN site solid phase media may adsorb or retain a significant quantity of the initial TCE added. Because of the solid phase present in these reactors, the "Total Mass Recovered" column values in Table 16 are based on an *assumed* total initial TCE mass, rather than the *measured* initial aqueous TCE mass. (This technique for determining the total initial TCE mass was performed on all experiments like this only involving a solid phase medium.)

After overnight equilibration, the average initial aqueous TCE concentration of the spike solution was 180 µg/L (σ= 8 µg/L). After transfer to the test reactors and equilibration with the crushed basalt, the groundwater TCE concentration ranged between 144 and 164 µg/L TCE (T=0 aliquots) prior to the start of the oxidation reaction. TCE recoveries of 94% and 97% were obtained for the control reactors. No TCE was observed in the extracts from the charcoal desorption tubes from either the control or the treatment reactors. Note that the total recoveries presented in Table 16 for treatment reactors are all greater than 100% because of the mass balance approach used for this experiment (see above). Since the resulting %Sorbed values presented in Table 16 are negative, it is believed that the crushed basalt media was not initially adsorbing TCE. The %Sorbed values are negative because the initial aqueous concentration of the slurries were greater than the average initial concentration of the groundwater controls. (Refer to the beginning of Section of 2.4.2 for a more detailed description of how the %Sorbed values are computed.) If the "% Sorbed" values were added to the "Total Mass Recovered" values in Table 16, it is evident that the true recovery for the treatment would be nearly 100%.

TCE oxidation was complete within 3 hrs for the 0.01% MnO_4^- reactors and within 0.5 hrs for the 0.1% MnO_4^- reactors. This trend is similar to that observed in Exp. 4a-R1 involving TAN-40 GW only spiked at 100 µg/L. The three aqueous TCE data points between T=0 and T=1.6 hrs were used to compute the reaction rate for the initial, rapid step of the oxidation reaction of the 0.01% MnO_4^- reactors. The data were plotted as $\ln(C/C_o)$ vs. Time in Figure 39 for the first 0.01% reactor in order to approximate a first order reaction rate constant, k. The linear regression resulted in a first order rate constant of $k=2.32$ hr^{-1}. (Enough data points were not available to obtain a rate constant for the second 0.01% MnO_4^- reactor.) While the fit of the data to a first order rate constant may not be optimal, attempts to evaluate other rate models were not

made since the mechanisms occurring in such a complex system are not known. Enough data points were not available to compute a rate constant for the 0.1% MnO_4^- reactors; however, the observed oxidation rate is greater than 0.14 mg TCE/hr.

More MnO_4^- was consumed (Table 17) here than in the TAN-40 GW only case (Table 13). Hence, the additional MnO_4^- consumption observed here is likely attributed to oxidation/destruction of crushed basalt. When compared to the pH values of the control reactors, oxidant addition resulted in a small, net pH increases for both the 0.01% and 0.1% MnO_4^- reactors. As expected, the magnitude of this pH increase was the greatest for the 0.1% MnO_4^- reactors. Note: the increases in pH at the very end of the reaction period appear to result from a change in instrument performance (i.e., new calibration, etc) since nearly all reactors behave similarly.

Figure 36. TCE vs. Time, TAN-40 GW & Crushed Basalt, (ORNL Exp. 4a-R3, Initial TCE= 100 μg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 37. MnO_4^- vs. Time, TAN-40 GW & Crushed Basalt, (ORNL Exp. 4a-R3, Initial TCE= 100 μg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 38. pH vs. Time, TAN-40 GW & Crushed Basalt, (ORNL Exp. 4a-R3, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
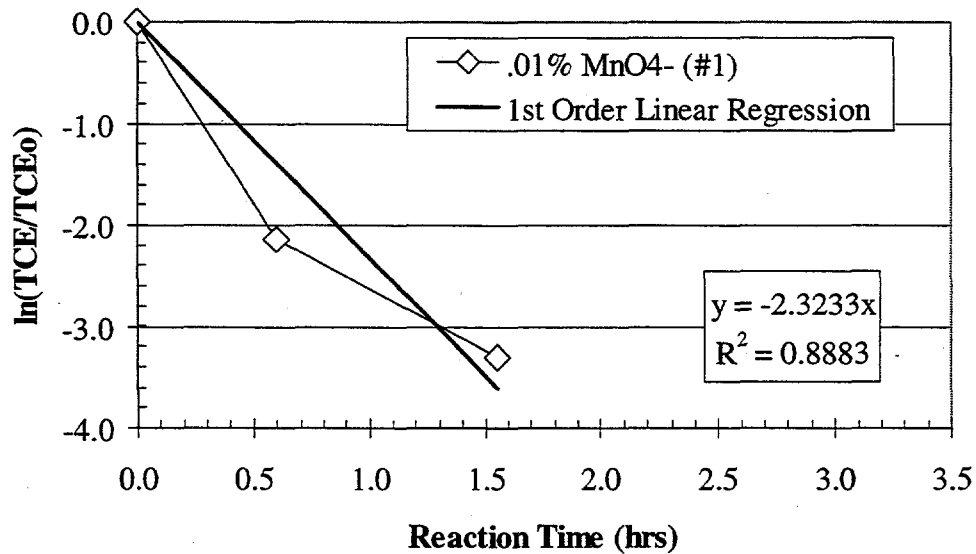
Figure 39 First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW and Crushed Basalt, (ORNL Exp. 4a-R3, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 16. TCE Mass Balance for ORNL Exp. 4a-R3 (TAN-40 GW & Crushed Basalt).

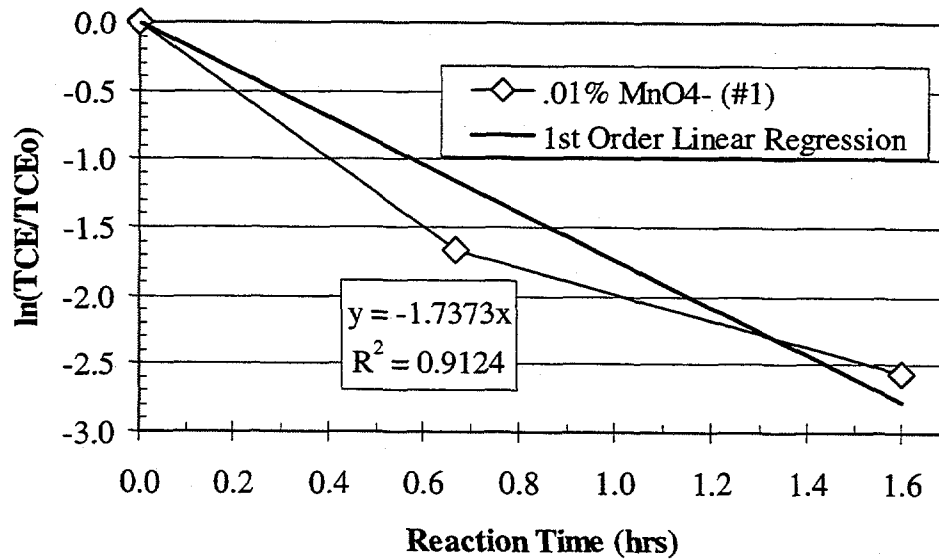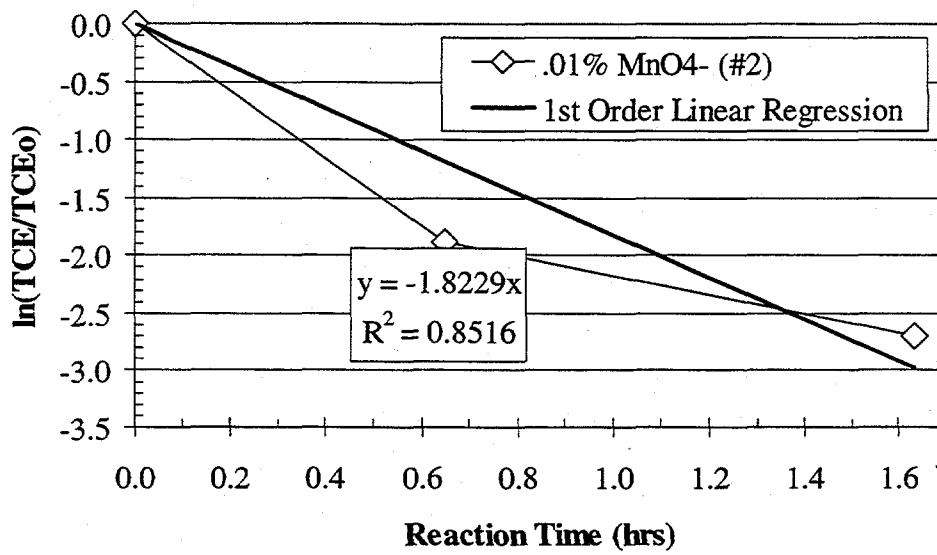| Test Condition	Total Initial Mass (mg) [a].	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.08	0.08	0.000	0.07	0.01	NA	0.1
			0%	83%	11%	NA	94%
Control (#2)	0.08	0.08	0.000	0.06	0.01	NA	0.1
			0%	86%	11%	NA	97%
0.01% (#1)	0.07	0.07	0.000	0.00	0.001	0.07	0.1
	%Sorbed:	-8%	0%	0%	2%	106%	108%
0.01% (#2)	0.07	0.07	0.000	0.00	0.001	0.07	0.1
	%Sorbed:	-5%	0%	0%	2%	103%	105%
0.1% (#1)	0.07	0.07	0.000	0.00	0.001	0.07	0.1
	%Sorbed:	-2%	0%	0%	2%	102%	104%
0.1% (#2)	0.07	0.07	0.000	0.00	0.001	0.07	0.1
	%Sorbed:	-2%	0%	0%	2%	102%	104%

[a.] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg=151 µg/L, σ=11 µg/L). For GW controls, Total Initial = Initial Aqueous.

Table 17. MnO_4^- Consumption Data for ORNL Exp. 4a-R3 (TAN-40 GW & Crushed Basalt).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	60.5	0.11	24.57	0.04
0.01% (#2)	60.5	0.11	10.39	0.02
0.1% (#1)	605.0	1.09	61.42	0.11
0.1% (#2)	605.0	1.08	30.36	0.05

[a.] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R4
(TAN-40, Aggregate Basalt, 100 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

Slurries of TAN-40 GW and aggregate basalt were evaluated in this experiment. The TCE, MnO_4^- and pH values with time are presented in Figures 40, 41, and 42, respectively. Tables 18 and 19 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No deviations from the testplan procedure were made in this experiment.

After overnight equilibration, the average initial aqueous TCE concentration of the spike solution was 164 µg/L ($\sigma= 30$ µg/L). After transfer to the test reactors and equilibration with the aggregate basalt, the groundwater TCE concentration ranged between 128 and 144 µg/L TCE (T=0 aliquots) prior to the start of the oxidation reaction. TCE recoveries of 94% and 102% were obtained for the control reactors. No TCE was observed in the extracts from the charcoal desorption tubes from either the control or the treatment reactors.

In this experiment, the total recovered TCE was less than 100% for 3 of the 4 treatment reactors. The initial aqueous TCE values for these 3 reactors were slightly lower than those observed for the TAN-40 GW controls. This suggests that TCE was initially (1) adsorbed by the aggregate basalt and/or (2) trapped within the intra-particle porewater spaces. Differences in the *predicted* total TCE mass and the initial *measured* aqueous TCE mass for these three treatment reactors results in predicted adsorption values of 2%, 4%, and 8% (see Table 18). These predicted adsorption values are maximum values; i.e., assuming no volatilization occurred, etc. Unfortunately, the TCE equilibration experiments attempted for the aggregate basalt (SOW Task 2c) did not provide meaningful results to further verify this potential retention mechanism.

Although less than 100% recoveries were obtained, it is believed that complete oxidation of both sorbed and aqueous TCE did occur. If adsorption mechanisms were to preclude the sorbed TCE from being oxidized, one would have expected TCE to be detected in the extraction of the entire reactor following the 24 hrs reaction period. However, No TCE was found in that component of the mass balance. If the "% Sorbed" values in Table 18 are added to the "%Cumulative Aqueous Mass Oxidized", a total TCE oxidized value at or near 100% is obtained.

The TCE data presented in Figure 40 indicate that complete TCE oxidation occurred within 2 hrs and within 0.5 hrs for the 0.01% and 0.1% MnO_4^- reactors, respectively. This trend is similar to that observed in Exp. 4a-R1 involving TAN-40 GW spiked at 100 µg/L. For the 0.01% MnO_4^- reactors, the two aqueous TCE data points (T=0 and T=0.5 hrs) were used to compute the reaction rate for the initial, rapid step of the oxidation reaction. The data were plotted in Figures 43 and 44 as $\ln(C/C_o)$ vs. Time in order to approximate a first order reaction rate constant, k. The linear regressions resulted in an average first order rate constant of $k=4.28$ hr^{-1}. Note that each of these rate constants were computed using only 2 points, and thus the resulting R^2 values of 1.00 should be viewed with skepticism. Enough data points are not available to compute a rate constant for the 0.1% reactors; however, the observed oxidation rate is greater than 0.12 mg TCE/hr for these reactors.

The plots of the MnO_4^- and pH vs. reaction time follow similar trends to those that have already been discussed. As expected, the amount of oxidant consumed falls between that consumed by TCE-spiked TAN-40 GW only (Exp. 4a-R1) and TCE-spike Crushed Basalt (Exp. 4a-R3). There was a net pH increase of approximately 0.3 pH units at 24 hrs as a result of the oxidant addition and subsequent oxidation reactions that took place.

Figure 40. TCE vs. Time, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R4, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 41. MnO$_4$⁻ vs. Time, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R4, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

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Figure 42. pH vs. Time, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R4, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 43. First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R4, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
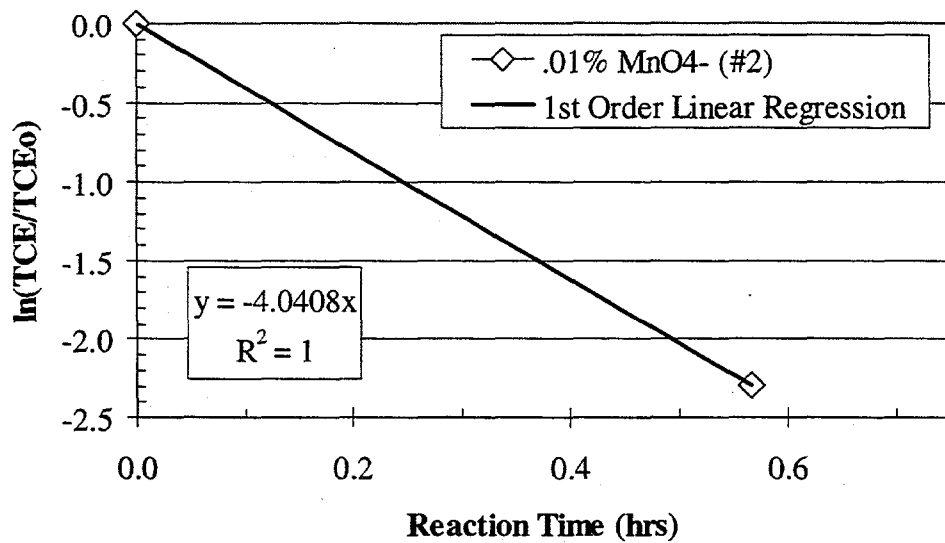
Figure 44. First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#2) Reactor, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R4, Initial TCE= 100 μg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 18. TCE Mass Balance for ORNL Exp. 4a-R4 (TAN-40 GW & Aggregate Basalt).

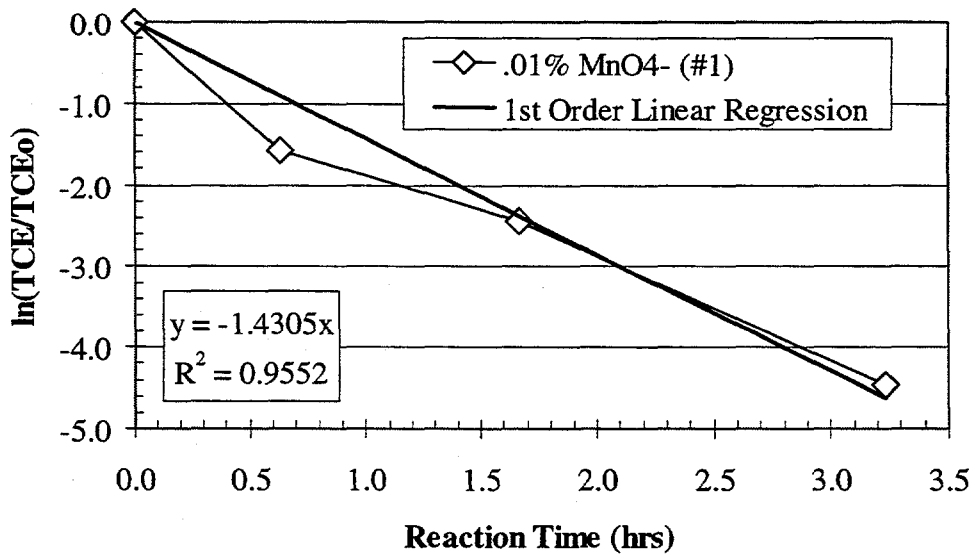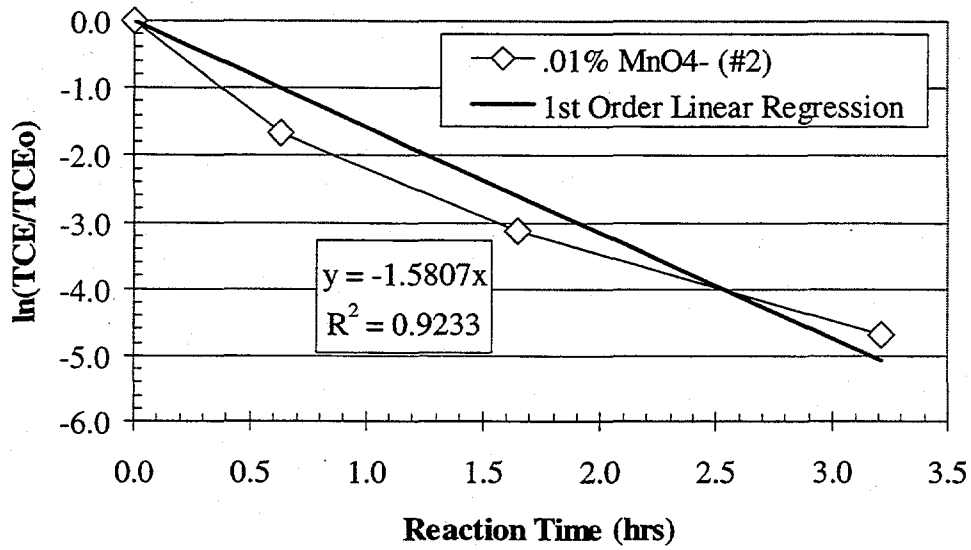| Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.07	0.07	0.000	0.06	0.01	NA	0.1
			0%	82%	11%	NA	94%
Control (#2)	0.07	0.07	0.000	0.06	0.01	NA	0.1
			0%	90%	12%	NA	102%
0.01% (#1)	0.06	0.06	0.000	0.00	0.001	0.05	0.1
	%Sorbed: 2%		0%	0%	2%	96%	98%
0.01% (#2)	0.06	0.05	0.000	0.00	0.001	0.05	0.1
	%Sorbed: 4%		0%	0%	2%	93%	95%
0.1% (#1)	0.06	0.05	0.000	0.00	0.001	0.05	0.1
	%Sorbed: 8%		0%	0%	2%	92%	94%
0.1% (#2)	0.06	0.06	0.000	0.00	0.001	0.06	0.1
	%Sorbed: -3%		0%	0%	2%	103%	105%

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg=140 µg/L, σ=1 µg/L). For GW controls, Total Initial = Initial Aqueous.

Table 19. MnO_4^- Consumption Data for ORNL Exp. 4a-R4 (TAN-40 GW & Aggregate Basalt).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	48.3	0.10	5.16	0.01
0.01% (#2)	48.3	0.10	3.81	0.01
0.1% (#1)	482.6	0.95	29.67	0.06
0.1% (#2)	482.6	0.95	6.79	0.01

[a] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R5
(TAN-40, Crushed Basalt, 1000 TCE, 0 Other, 0.01% and 0.1% MnO$_4^-$)

Slurries of TAN-40 GW and Crushed basalt were evaluated in this experiment. The TCE, MnO$_4^-$ and pH values with time are presented in Figures 45, 46, and 47, respectively. Tables 20 and 21 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No deviations from the testplan procedure were made in this experiment.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 1350 μg/L (σ= 5 μg/L). After transfer to the test reactors and equilibration with the crushed basalt, the groundwater TCE concentration ranged between 1259and 1319 μg/L TCE (T=0 aliquots) prior to the start of the oxidation reaction. Comparison of the total initial TCE masses with the initial aqueous TCE masses (Table 20), leads to predicted TCE adsorption values between −2 and 3% for the crushed basalt used in this experiment.

TCE contamination (8-12 μg/L) was observed in the GC QA/QC checks blanks for this experiment. The TCE values obtained from the experimental samples further suggest that the hexane used to extract the aqueous samples and the carbon desorption tubes may have been contaminated with a small, unknown amount of TCE. Presence of TCE on the charcoal beds of the desorption tubes could be attributed to volatilization. It is suspected, however, that it is largely a result of the solvent contamination problem, particularly since the second charcoal bed sample, in several instances, contained detectable amounts of TCE while the first charcoal bed did not. The experiment was not repeated. The overall results from this experiment were very similar to those obtained in the previous dissolved plume tests that had been conducted. Thus, it did not appear prudent or cost effective to repeat the experiment in light of the benefits that would be gained.

TCE recoveries for the control samples were 94% and 95%, suggesting that some TCE may have been lost to volatilization. The degree of potential volatilization, however, cannot be completely estimated due to the potential contamination of the charcoal desorption tubes discussed above.

Again, complete oxidation of the added TCE was not observed in this experiment. With the exception of the first 0.1% MnO$_4^-$ reactor, extracts from all the other treatment reactors contained approximately a 10-20 μg/L residual TCE concentration. The residual TCE is likely to be a result of sample/solvent contamination problem. While the presence of the additional TCE complicates the interpretation of the mass balance, the amount of solvent contamination is small and does not completely invalidate general trends observed in the TCE oxidation reactions. The general trend of rapid TCE oxidation was still observed. If one were to assume that the residual TCE concentration are due to contamination, complete TCE oxidation likely occurred within 5 hrs and within 0.5 hrs for the 0.01% and 0.1% MnO$_4^-$ reactors, respectively. Although there are greater than three TCE data points present, a rate constant was not computed for this experiment since it is likely that the accuracy of the some of the data points is questionable. However,

observed rates of TCE oxidation are *estimated* to be greater than and 1.0 mg TCE/hr for the 0.01% and 0.1% MnO_4^- reactors, respectively.

Little oxidant was consumed by the treatment reactors. In fact, the MnO_4^- consumption values from this experiment (Table 21) are similar to those obtained in Experiment 4a-R2, the TAN-40 GW only case (Table 15). It is not known what phenomenon lead to the negative oxidant value for the second 0.1% MnO_4^- reactor. From the pH plot (Figure 47), the treatment reactors appear to experience a slight pH drop before ultimately reaching a net pH increase during the course of the 24 hr reaction period. It is interesting to note that the trend in pH for second 0.1% MnO_4^- reactor, which resulted in a negative oxidant value, did not follow that of the other treatment reactors evaluated in this experiment.
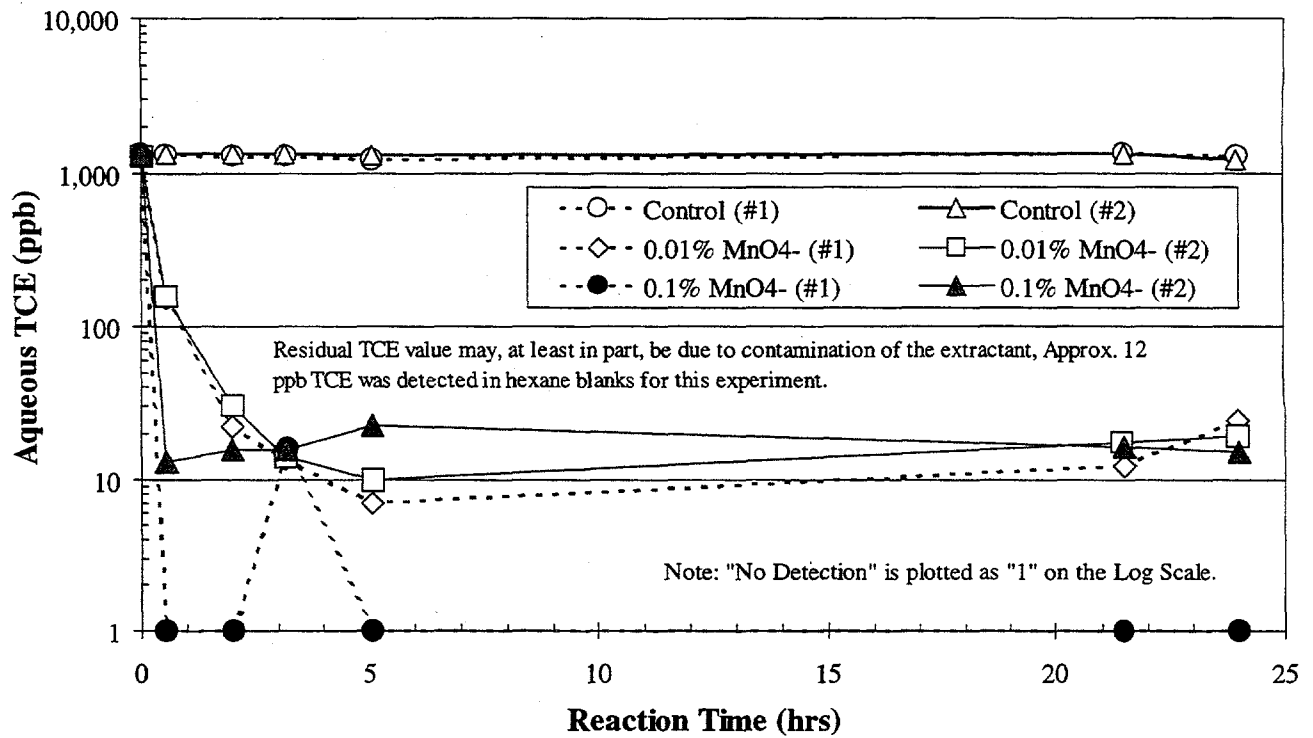
Figure 45. TCE vs. Time, TAN-40 GW & Crushed Basalt, (ORNL Exp. 4a-R5, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
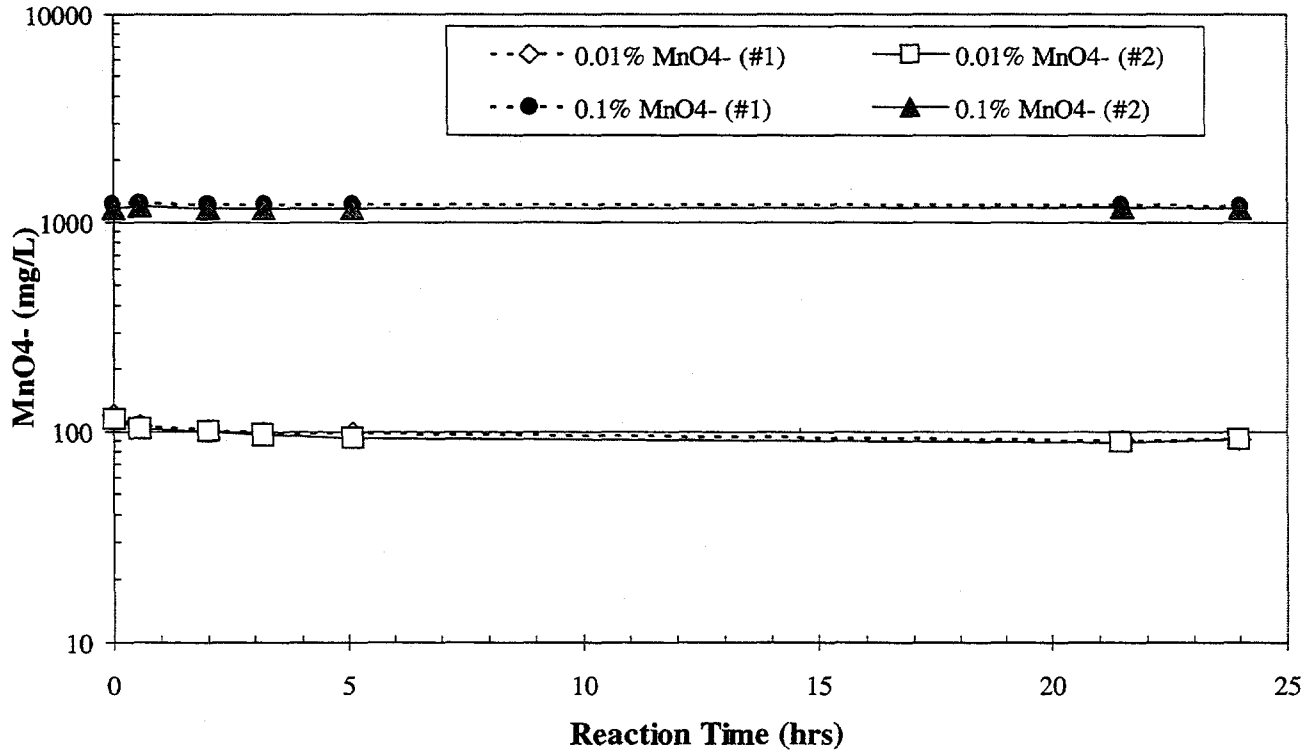
Figure 46. MnO$_4^-$ vs. Time, TAN-40 GW & Crushed Basalt, (ORNL Exp. 4a-R5, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
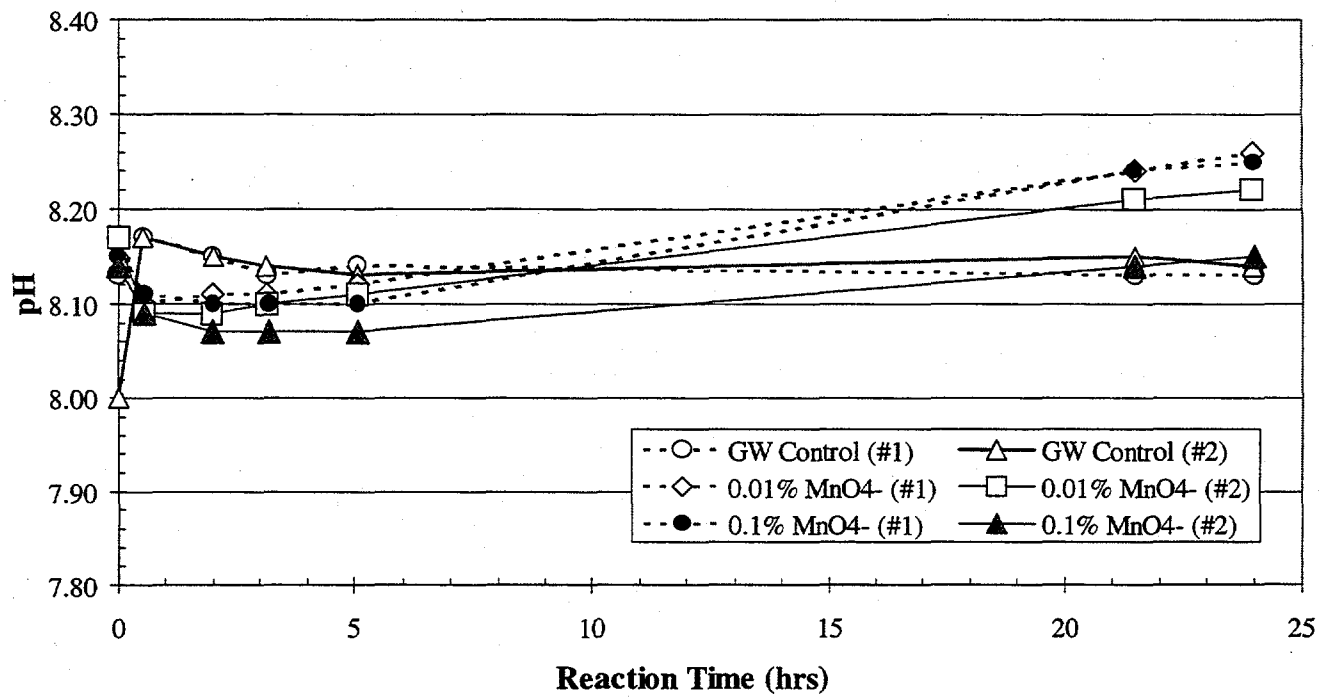
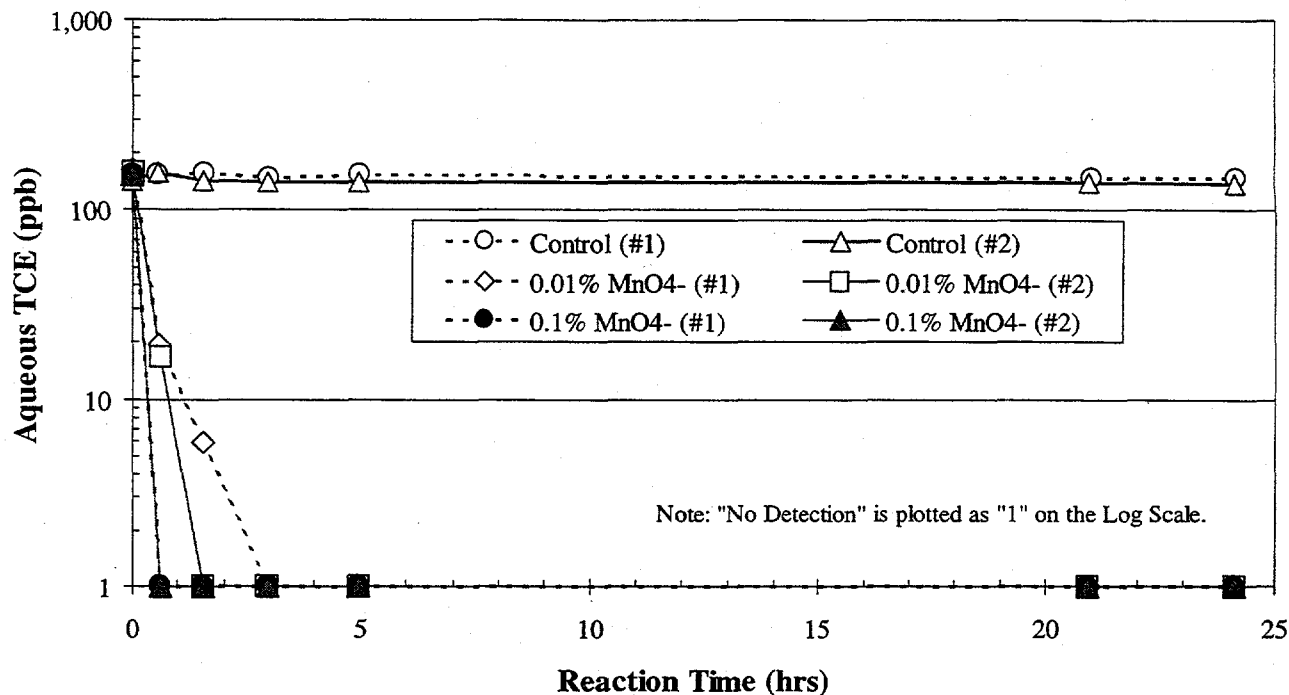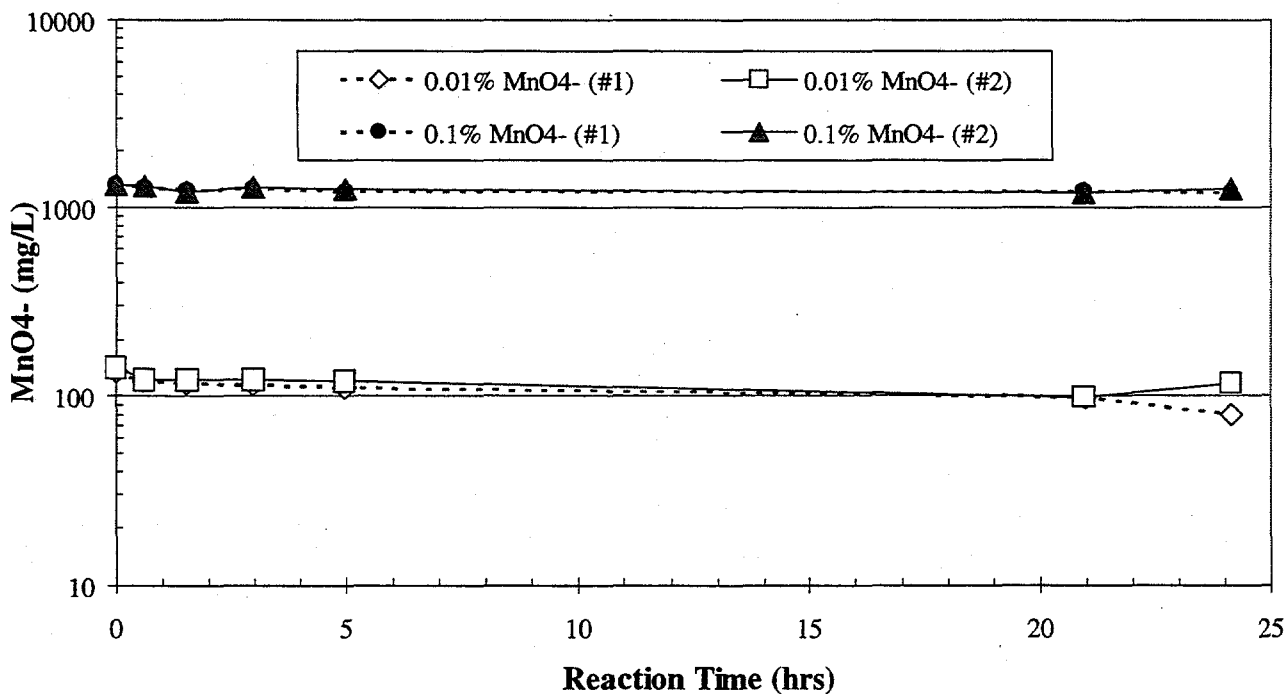Figure 47. pH vs. Time, TAN-40 GW & Crushed Basalt, (ORNL Exp. 4a-R5, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

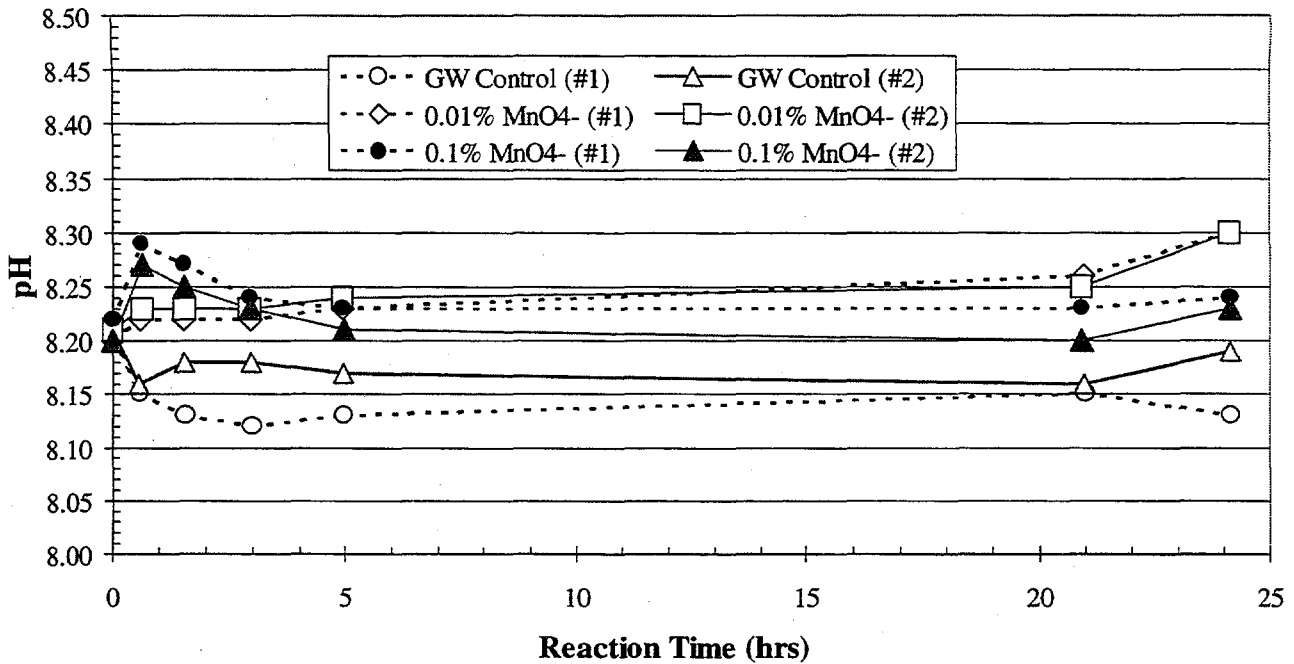Table 20. TCE Mass Balance for ORNL Exp. 4a-R5 (TAN-40 GW & Crushed Basalt).

Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.65	0.65	4.05E-05	0.55	0.08	NA	0.6
			0%	85%	11%	NA	96%
Control (#2)	0.64	0.64	3.79E-05	0.54	0.08	NA	0.6
			0%	85%	12%	NA	97%
0.01% (#1)	0.53	0.51	3.94E-05	0.01	0.011	0.49	0.5
	%Sorbed: 3%		0%	1%	2%	94%	97%
0.01% (#2)	0.54	0.53	2.71E-05	0.00	0.011	0.52	0.5
	%Sorbed: 2%		0%	0%	2%	95%	97%
0.1% (#1)	0.50	0.48	0.00E+00	0.00	0.009	0.49	0.5
	%Sorbed: 3%		0%	0%	2%	98%	100%
0.1% (#2)	0.53	0.53	3.64E-05	0.01	0.010	0.54	0.6
	%Sorbed: -2%		0%	2%	2%	102%	105%

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg=1,297 µg/L, σ=30 µg/L). For GW controls, Total Initial = Initial Aqueous.

Table 21. MnO_4^- Consumption Data for ORNL Exp. 4a-R5 (TAN-40 GW & Crushed Basalt).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	47.7	0.10	11.14	0.02
0.01% (#2)	47.7	0.09	10.01	0.02
0.1% (#1)	477.0	0.97	8.47	0.02
0.1% (#2)	477.0	0.93	-4.39	-0.01

[a] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R6
(TAN-40, Aggregate Basalt, 1000 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

Slurries of TAN-40 GW and aggregate basalt were evaluated in this experiment. The TCE, MnO_4^- and pH values with time are presented in Figures 48, 49, and 50, respectively. Tables 22 and 23 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

A procedural change was made to the testplan for this experiment. The TCE-spiked TAN-40 GW was only mixed/equilibrated for 3 hrs (instead of overnight) prior to being added to the reactors and equilibrated with the aggregate basalt. The change was made due to a leak observed in the Tedlar spiking bag. The control and 0.01% MnO_4^- reactors were quickly filled using the spike solution still within the Tedlar bag. The two 0.1% MnO_4^- test reactors were filled using an approximate 50/50 mixture of remaining groundwater in the Tedlar bag with that which had leaked out onto the spill containment tray. Hence, it was expected that the initial TCE mass for these 0.1% MnO_4^- test reactors would be low.

After the shortened equilibration period, the average initial aqueous TCE concentration of the spike solution was 2,440 µg/L (σ= 140 µg/L). After transfer to the test reactors and equilibration with the aggregate basalt, the groundwater TCE concentration ranged between 2,304 and 2,574 µg/L TCE (T=0 aliquots) for the control and 0.01% MnO_4^- reactors. The initial aqueous TCE concentration within the 0.1% MnO_4^- reactors was 635 µg/L (σ= 16 µg/L) prior to the start of the oxidation reaction. The control reactors yielded total TCE recoveries of 99% and 97% after the 24 hr reaction period. Thus, it was again believed that the reactors minimized the amount of TCE lost via volatilization. TCE was not found on the charcoal desorption tubes or in the final treatment reactor extractions. Total TCE recoveries for the 0.01% MnO_4^- reactors were only 91% and 93%. A closer look at the data reveals that initial aqueous TCE concentrations of in both of these slurry reactors were 8% lower than that of the groundwater controls. (A very similar adsorption/retention value was observed for the aggregate basalt in Exp.4a-R4). Since TCE was not present when the remaining basalt and GW was extracted at the end of the test period, it is expected that all of the total initial TCE present was oxidized. Even if this assumption is correct, the TCE fraction initially associated with the aggregate basalt would still not appear in the "Cumulative Aqueous Mass Oxidized" column of Table 22. (This part of the mass balance only takes beginning and ending *aqueous* concentrations into account.) However, if one assumes that the aggregate bound TCE is oxidized, effective total TCE recoveries of 99% and 101% are obtained for the 0.01% MnO_4^- test reactors. This assumption appears valid since the control reactors for this experiment yielded high TCE recovery values.

Since the total initial TCE in the 0.1% MnO_4^- reactors is computed using the average concentration of the GW controls at T=0, the resulting total TCE recoveries are only $\approx$ 26%. Unfortunately, there are no QA/QC samples to ascertain the total initial TCE mass in the 0.1% MnO_4^- reactors (due to the leak in the Tedlar bag). However, if one were to assume that the aggregate basalt in these reactors initially adsorbed 8% of the total initial TCE (as in the case of the 0.01% MnO_4^- reactors), total initial TCE masses of 0.29 mg and 0.26 mg would result for the first and second 0.1% MnO_4^- reactors, respectively. Recalculation of the Cumulative Aqueous

Mass Oxidized component of the mass balance would then yield a value of 94% being oxidized for both 0.1% MnO_4^- reactors. Similarly, total effective recoveries for these reactors would then be in the range of 96% and 97% for the first and second 0.1% MnO_4^- reactor, respectively.

The rate of TCE oxidation by the 0.01% MnO_4^- reactors appeared were slower for this experiment than that observed in other dissolved plume media experiments. From the TCE data in Figure 48, a TCE residual was present in the first 0.01% MnO_4^- reactor until the final aliquot samples were collected. There is no information to suggest that this residual TCE is not "real". TCE oxidation appeared to follow a 2-step process, with the first step ($\approx$0-5 hrs) being rapid. The aqueous TCE data between T=0 and T=3 hrs was used to compute the reaction rate for the initial, rapid step of the oxidation reaction. The data were plotted in Figure 51 as $\ln(C/C_o)$ vs. Time in order to approximate a first order reaction rate constant, k. The linear regression resulted in a first order rate constant of k=1.83 hr^{-1}. While the fit of the data to a first order rate constant may not be optimal, attempts to evaluate other rate models were not made since the mechanisms occurring in such a complex system are not known.

Complete oxidation was observed for the second 0.01% MnO_4^- reactor within 5 hrs. If calculated as in previous experiments, an observed oxidation rate of 0.2 mg TCE/hr is obtained for the second 0.01% MnO_4^- reactor. An attempt was also made to compute the first order reaction rate constant(s) for the TCE data (T=0-3 hrs) from the second 0.01% MnO_4^- reactor. The plot of the first order relationship is presented in Figure 52, and a first order rate constant of 2.12 hr^{-1} was obtained. Thus, the rate constants obtained for both of the 0.01% MnO_4^- reactors are similar.

Complete TCE oxidation occurred within 2 hrs in the 0.1% MnO_4^- reactors. Enough data points are not available to compute a rate constant; however, the observed oxidation rate is greater than 0.14 mg TCE/hr for the 0.1% MnO_4^- reactors. Note, however, that the initial TCE mass was significantly less than expected to the leak in the Tedlar bag and was assumed to be $\approx$0.28 mg TCE (see above).

Finally, as with all the dissolved plume media experiments conducted, little oxidant consumption was observed. The lower MnO_4^- consumption for the second 0.01% MnO_4^- reactor (Table 23) is likely related to accuracy and precision of the spectrophotometry. The MnO_4^- values for this reactor (Figure 49) change little during the reaction period until the last sample aliquot is collected.

Only small changes in pH were observed (< 0.2 pH units). However, in this experiment, the final pH values of the slurries were less than the values before oxidant addition (Figure 50). This is easily explained by the fact that the initial starting pH of the TAN-40 GW for this experiment was $\approx$8.4, which was slightly highly than that observed in most other dissolved plume experiments. (Note: A similar trend was also observed in Exp. 4a-R2.)
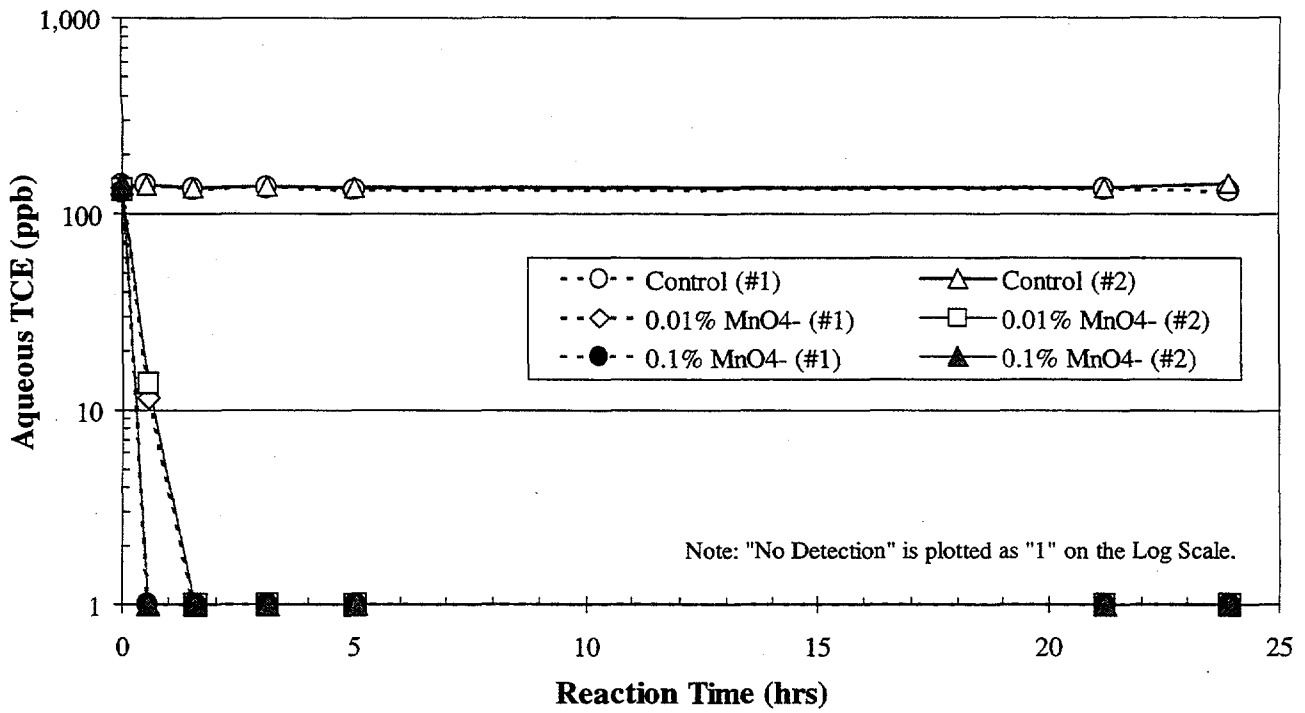
Figure 48. TCE vs. Time, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R6, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
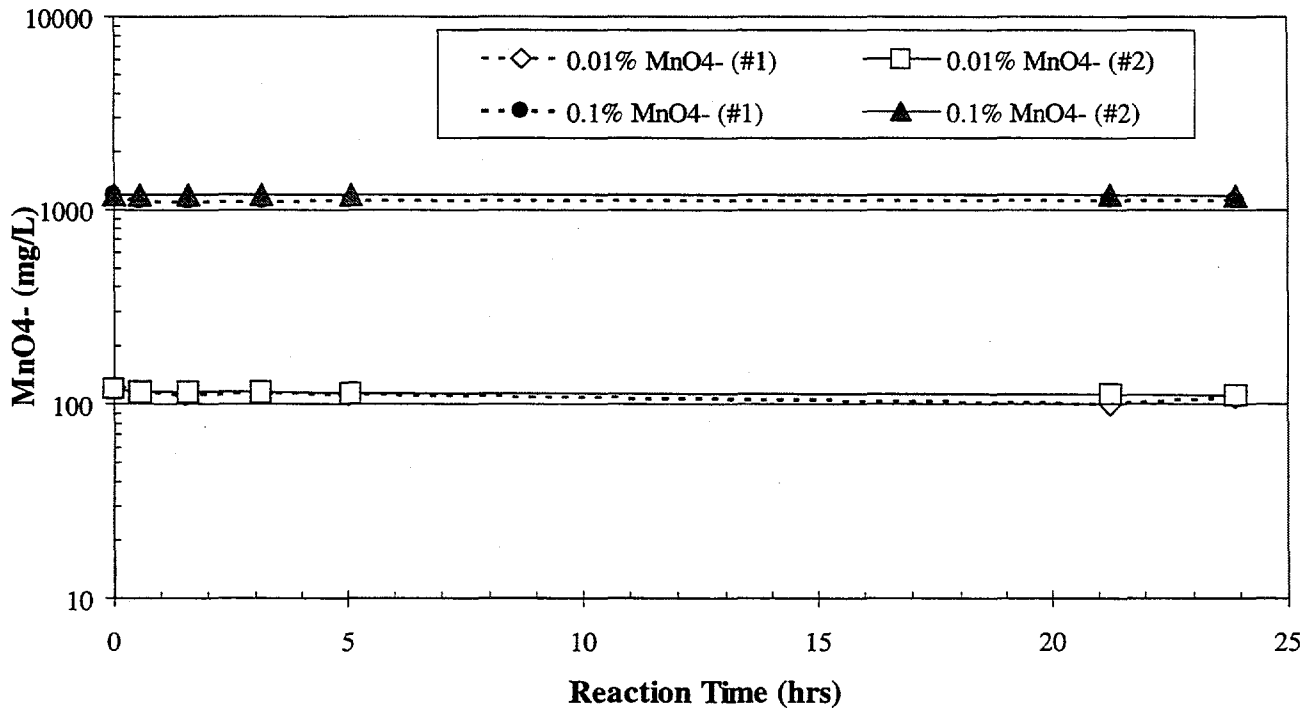

Figure 49. MnO$_4^-$ vs. Time, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R6, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
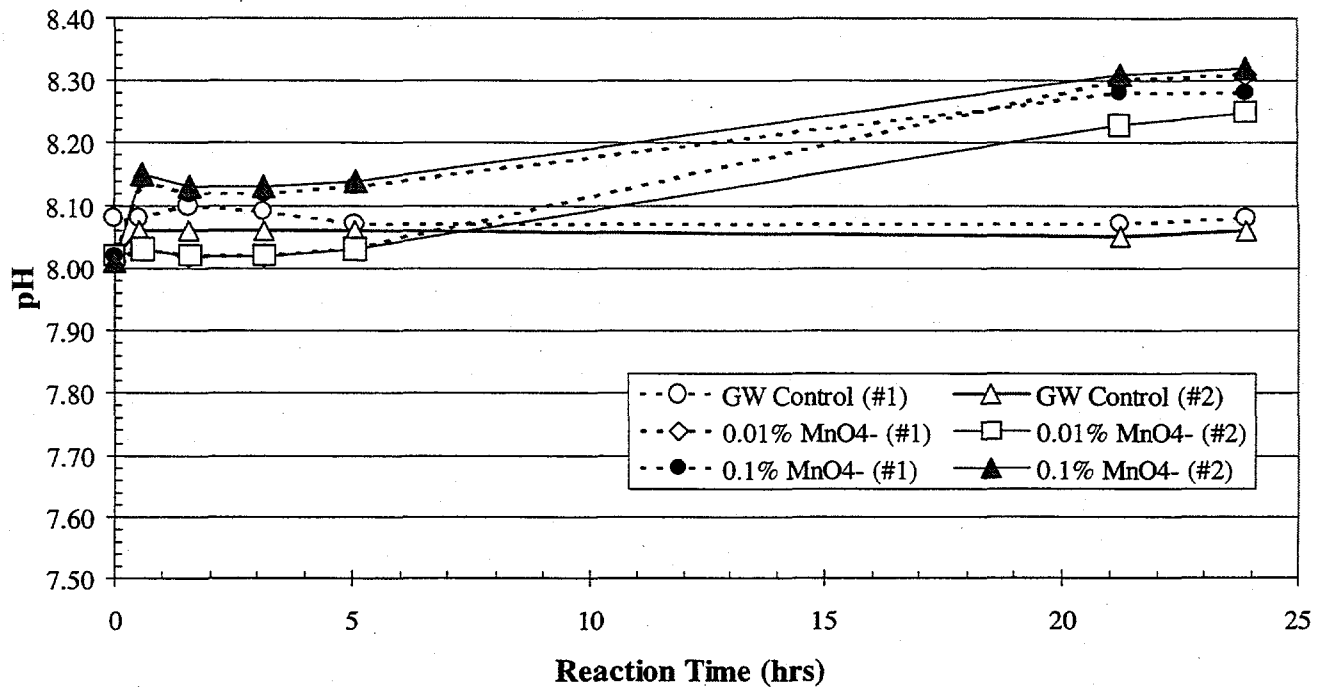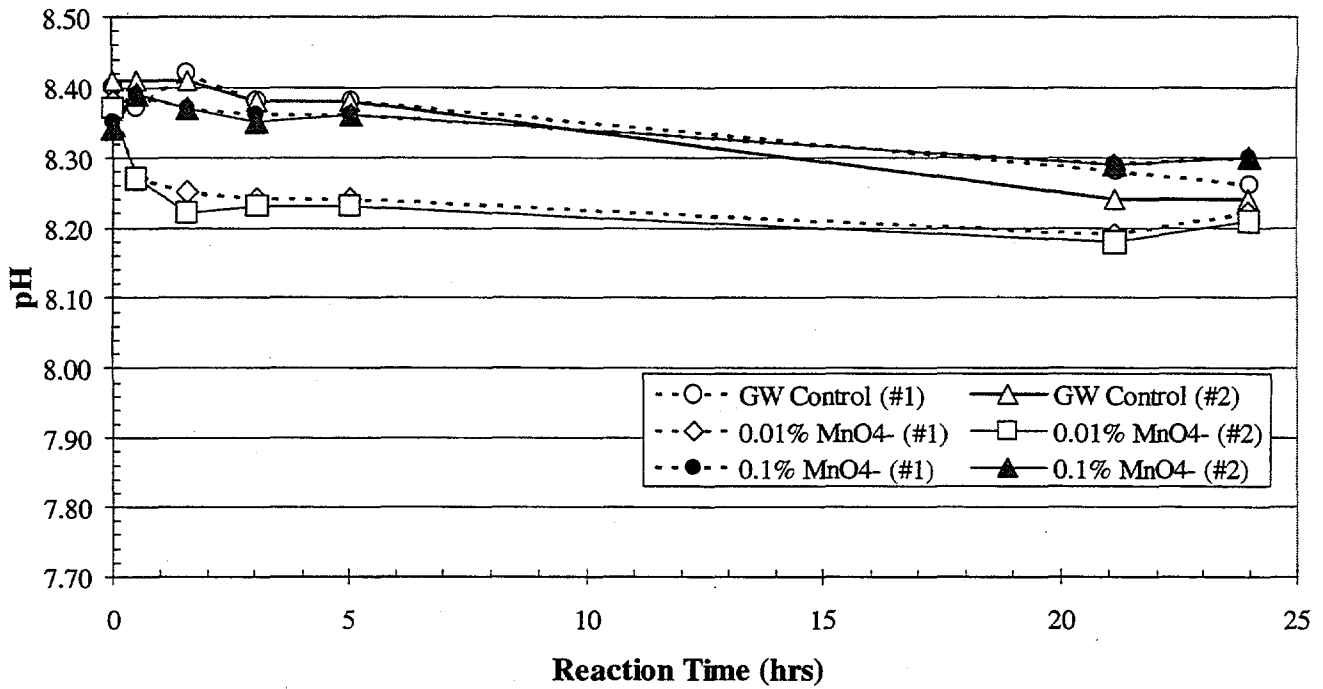
Figure 50. pH vs. Time, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R6, Initial TCE=
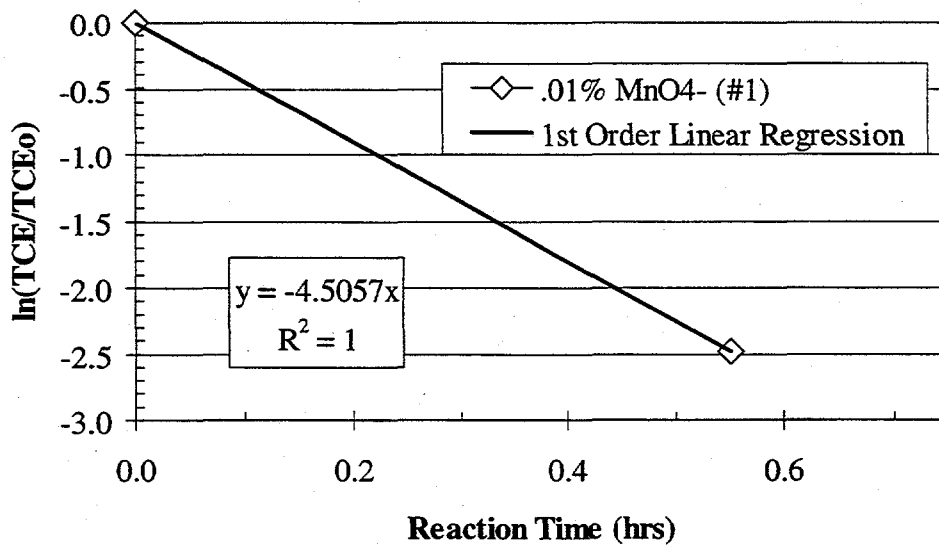1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 51. First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-
40 GW & Aggregate Basalt, (ORNL Exp. 4a-R6, Initial TCE= 1000 µg/L,
Conducted at 12°C, 4:1 L/S Ratio)

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Figure 52. First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#2) Reactor, TAN-40 GW & Aggregate Basalt, (ORNL Exp. 4a-R6, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 22. TCE Mass Balance for ORNL Exp. 4a-R6 (TAN-40 GW & Aggregate Basalt).

Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	1.25	1.25	0.000	1.10	0.15	NA	1.2
			0%	87%	12%	NA	99%
Control (#2)	1.22	1.22	0.000	1.03	0.15	NA	1.2
			0%	85%	12%	NA	97%
0.01% (#1)	0.98	0.89	0.000	0.00	0.022	0.87	0.9
	%Sorbed: 8%		0%	0%	2%	89%	91%
0.01% (#2)	1.02	0.94	0.000	0.00	0.019	0.93	0.9
	%Sorbed: 8%		0%	0%	2%	91%	93%
0.1% (#1)	1.05[†]	0.27	0.000	0.00	0.005	0.27	0.3
	%Sorbed: 74%[†]		0%[†]	0%[†]	0%[†]	26%[†]	26%[†]
0.1% (#2)	0.96[†]	0.24	0.000	0.00	0.004	0.24	0.2
	%Sorbed: 75%[†]		0%[†]	0%[†]	0%[†]	25%[†]	26%[†]

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg=2,516 µg/L, σ=81 µg/L). For GW controls, Total Initial = Initial Aqueous.

[†] Total Initial TCE mass is unknown due to leak in spiking solution container prior to distribution of TAN-40 GW to this reactor.

Table 23. MnO₄⁻ Consumption Data for ORNL Exp. 4a-R6 (TAN-40 GW & Aggregate Basalt).

Test Condition	Initial Oxidant (mg MnO$_4^-$)	Initial Loading (mg MnO$_4^-$/g)	Cum. Consumed (mg MnO$_4^-$)	Cum. Consumed (mg MnO$_4^-$/g)
0.01% (#1)	50.3	0.10	9.08	0.02
0.01% (#2)	50.3	0.10	0.81	0.00
0.1% (#1)	503.1	0.96	22.91	0.04
0.1% (#2)	503.1	1.03	13.46	0.03

[a] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R7
(TAN-40, SED1, 100 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

Slurries of TAN-40 GW and sediment were evaluated in this experiment. The TCE, MnO_4^- and pH values with time are presented in Figures 53, 54, and 55, respectively. Tables 24 and 25 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No deviations were made to the testplan during the conduct of this experiment. However, this experiment was performed using the first sediment sample received by ORNL (SED1 in Table 1)

After equilibration, the average initial aqueous TCE concentration of the spike solution was 274 $\mu g/L$ ($\sigma = 6$ $\mu g/L$). After transfer to the test reactors and equilibration with the sediment, the groundwater TCE concentrations ranged between 206 and 255 $\mu g/L$ TCE (T=0 aliquots). This apparent reduction may be a result of either (1) loss via volatilization during the transfer or (2) adsorption onto the TAN sediment. The control reactors yielded total TCE recoveries of 92% and 96% after the 24 hr reaction period, indicating that some loss or volatilization may have occurred. However, no TCE was not found on the charcoal desorption tubes from any of the control or treatment reactors. Recall, however, that not all of the headspace volume of each reactor is passed through the desorption tubes.

Initial TCE adsorption by the sediment of 7-19% is indicated by the data in Table 24. Since TCE was not found in the last few aqueous aliquots (see Figure 53) or in the final reactor extractions after 24 hrs, it is again suspected that any TCE sorbed by the sediment was oxidized during the reaction period. Assuming that the sorbed TCE mass oxidized yields effective total TCE recoveries of 100% for both 0.01% MnO_4^- reactors and 103% for both 0.1% MnO_4^- reactors.

Complete TCE oxidation occurred within 3 hrs for the 0.01% MnO_4^- reactors and within 0.5 hrs for the 0.1% MnO_4^- reactors. For the 0.01% MnO_4^- reactors, the aqueous TCE data between T=0 and T=2 hrs was used to compute the reaction rate for the initial, rapid step of the oxidation reaction. The data were plotted in Figures 56 and 57 as $\ln(C/C_o)$ vs. Time in order to approximate a first order reaction rate constant, k. The linear regressions resulted in an average first order rate constant of $k=2.16$ hr^{-1}. While the fit of the data to a first order rate constant may not be optimal, attempts to evaluate other rate models were not made since the mechanisms occurring in such a complex system are not known. There were not enough available data points to accurately compute a rate constant for the 0.1% MnO_4^- reactors, the observed oxidation rates was greater than 0.19 mg TCE/hr for those reactors.

As with all dissolved plume media evaluated, significant oxidant consumption was not observed in this experiment. The oxidation consumption masses observed were on the order of those observed for slurries of crushed and aggregate basalt that were nominally spiked with 100 $\mu g/L$ TCE (Experiments. 4a-R3 and 4a-R4).

The pH values obtained here for the sediment and TAN-40 GW slurries were distinctly different than those obtained for the TAN site basalt (crushed or aggregate). First, the initial pH values of

the treatment reactors (before oxidant was added) were about 0.2 pH units less than those observed for the two TAN-40 GW control reactors. The pH values in the treatment reactors clearly decrease as the oxidation reactions go to completion. Unlike the TAN basalt material, an overall net increase in pH at the end of the reaction period was not observed in any of the treatment reactors. In fact, a net decrease was observed for the 0.1% MnO_4^- reactors. The same trend was also observed in the oxidant consumption work (See Figures 14 and 15). This phenomenon may be due to the buffer capacity of the sediment being lower than that of basalt. Thus, the sediment may not be able to buffer the H^+ ions created as a result of the oxidation reactions. The pH decrease may also be due to chemistry effects caused by the destruction (via oxidation) of some of the organic matter present in the TAN sediment. Regardless of the mechanisms at work, the pH changes that were observed after oxidant addition were small (<0.2 pH units).
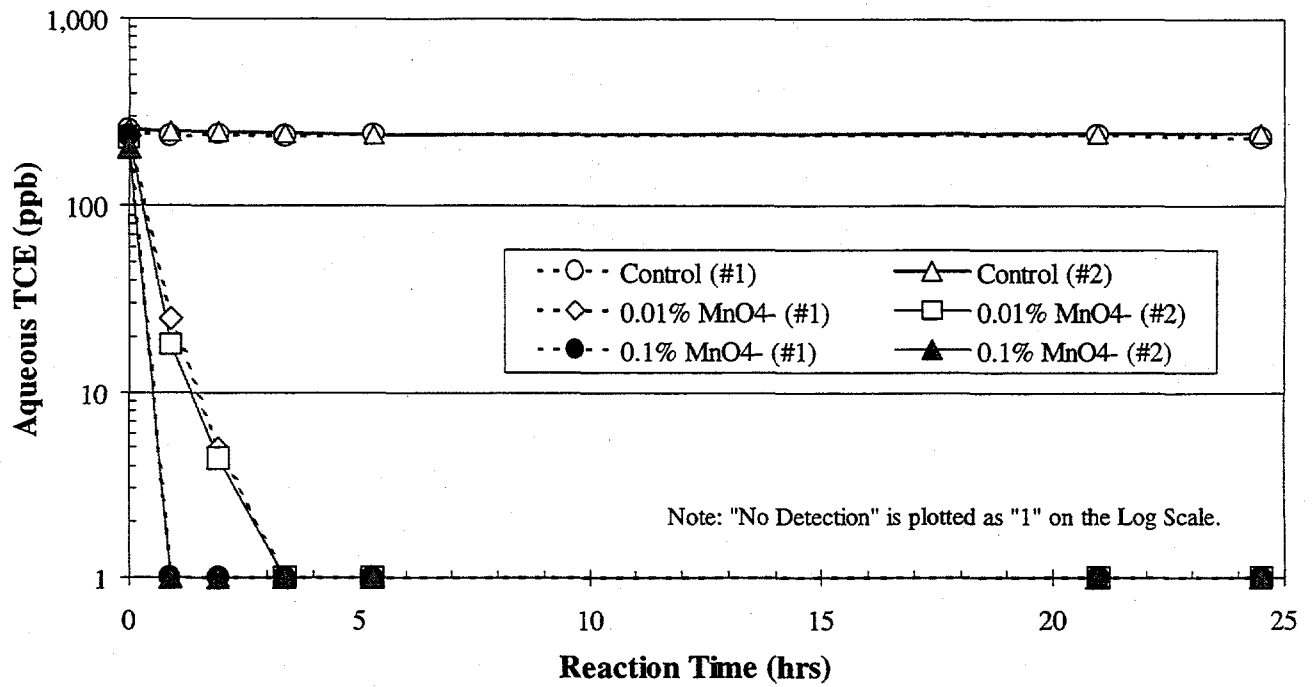
Figure 53. TCE vs. Time, TAN-40 GW & Sediment, (ORNL Exp. 4a-R7, Initial TCE= 100 μg/L, Conducted at 12°C, 4:1 L/S Ratio)
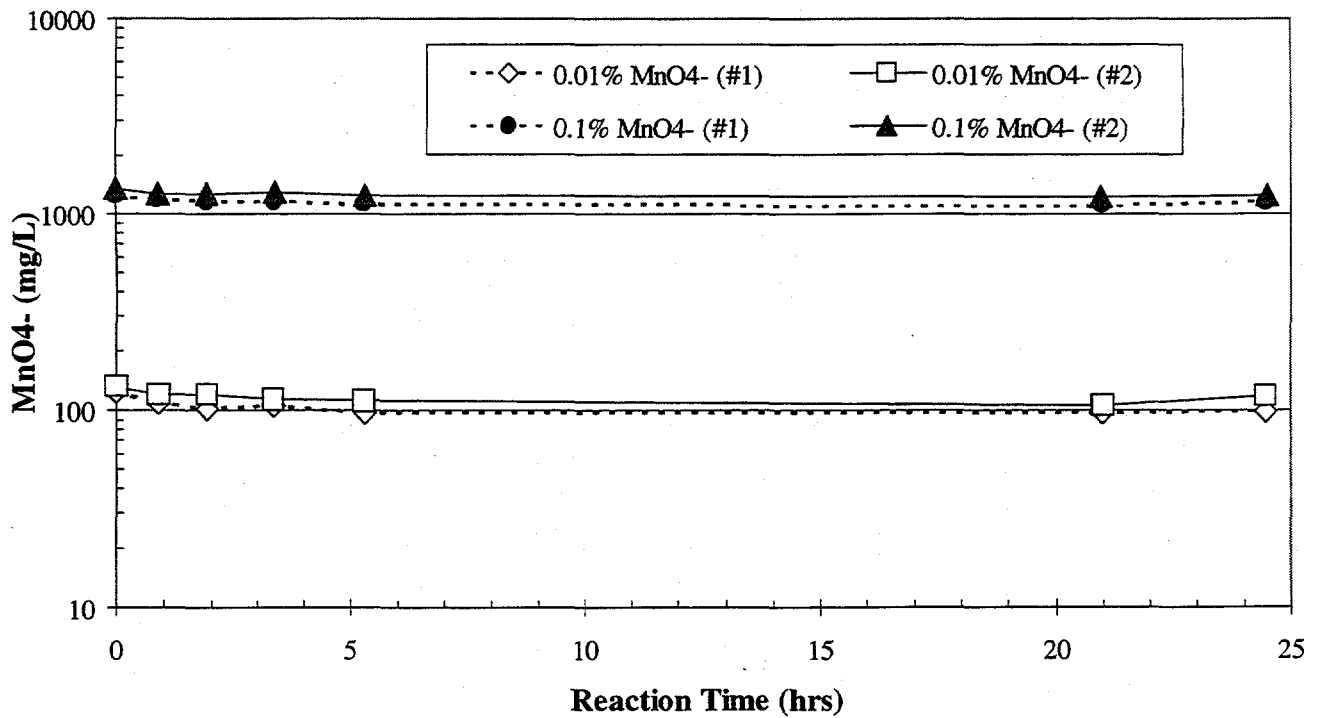
Figure 54. MnO₄⁻ vs. Time, TAN-40 GW & Sediment, (ORNL Exp. 4a-R7, Initial TCE= 100 μg/L, Conducted at 12°C, 4:1 L/S Ratio)
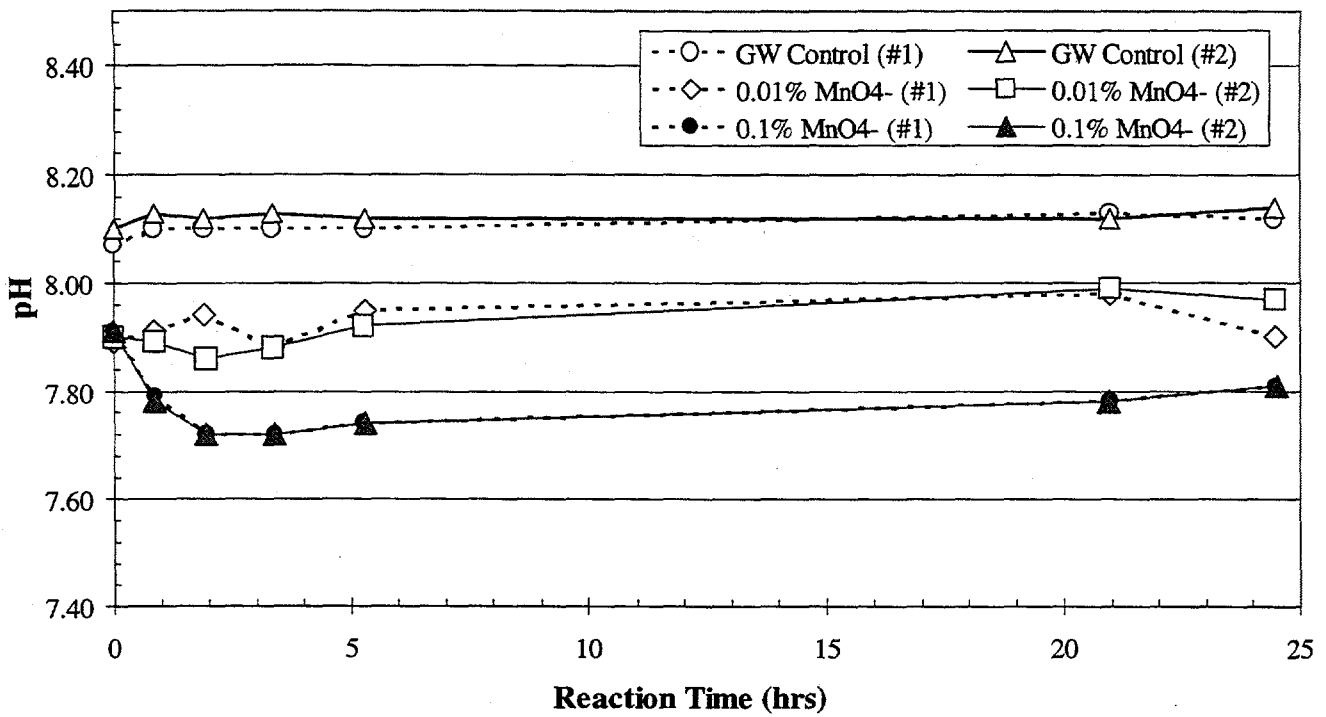
Figure 55. pH vs. Time, TAN-40 GW & Sediment, (ORNL Exp. 4a-R7, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
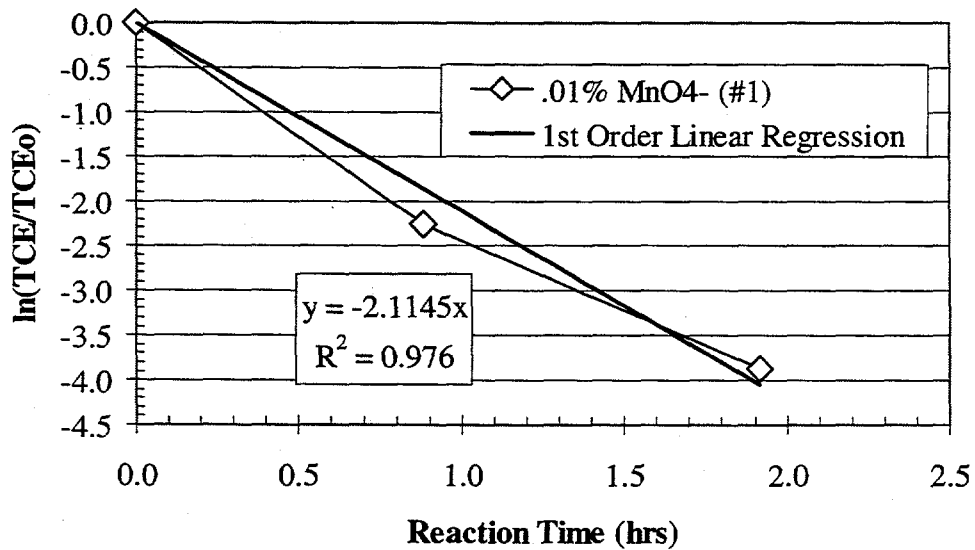
Figure 56 First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW & Sediment, (ORNL Exp. 4a-R7, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
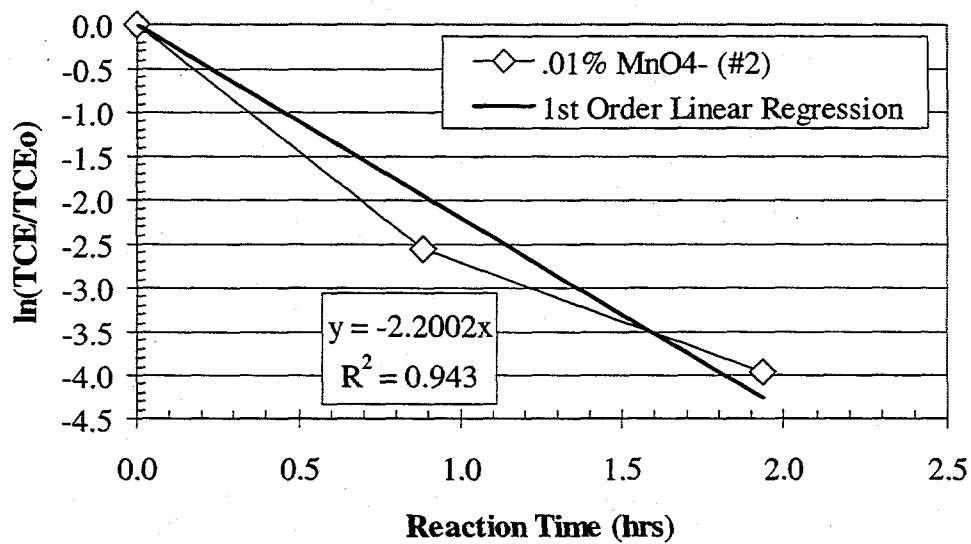
Figure 57   First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#2) Reactor, TAN-40 GW & Sediment, (ORNL Exp. 4a-R7, Initial TCE= 100 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 24. TCE Mass Balance for ORNL Exp. 4a-R7 (TAN-40 GW & Sediment).

Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.12	0.12	0.000	0.10	0.01	NA	0.1
			0%	82%	11%	NA	92%
Control (#2)	0.12	0.12	0.000	0.10	0.01	NA	0.1
			0%	84%	12%	NA	96%
0.01% (#1)	0.11	0.10	0.000	0.00	0.002	0.10	0.1
	%Sorbed: 7%		0%	0%	2%	92%	93%
0.01% (#2)	0.10	0.09	0.000	0.00	0.002	0.09	0.1
	%Sorbed: 8%		0%	0%	2%	90%	92%
0.1% (#1)	0.10	0.10	0.000	0.00	0.002	0.10	0.1
	%Sorbed: 7%		0%	0%	2%	94%	96%
0.1% (#2)	0.09	0.08	0.000	0.00	0.001	0.08	0.1
	%Sorbed: 19%		0%	0%	1%	82%	84%

[a]. Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg=253 µg/L, σ=2 µg/L). For GW controls, Total Initial = Initial Aqueous.

Table 25. MnO_4^- Consumption Data for ORNL Exp. 4a-R7 (TAN-40 GW & Sediment).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	50.4	0.10	9.98	0.02
0.01% (#2)	50.4	0.10	5.28	0.01
0.1% (#1)	504.1	0.99	28.28	0.06
0.1% (#2)	504.1	1.08	37.44	0.08

[a]. Consumption is computed after 24 hr reaction time.

ORNL Exp. 4a-R8
(TAN-40, SED2, 1000 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

Slurries of TAN-40 GW and sediment were evaluated in this experiment. The TCE, MnO_4^- and pH values with time are presented in Figures 58, 59, and 60, respectively. Tables 26 and 27 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No deviations were made to the testplan during the conduct of this experiment. However, this experiment was performed using the second batch of sediment material received by ORNL (SED2 in Table 1).

After equilibration, the average initial aqueous TCE concentration of the spike solution was 1,892 μg/L (σ= 69 μg/L). After transfer to the test reactors and equilibration with the sediment, the aqueous TCE concentrations in the slurries were lower than those observed in the groundwater controls. In fact, the TAN sediment (SED2) adsorbed an average of 11% of the total initial TCE added (Table 26). A decrease in the aqueous TCE concentrations of the control reactors with time was observed and culminated in final TCE recovery values of only 88% and 90% for the first and second control reactors, respectively. Closer examination of the aliquot TCE data for the control reactors revealed that most of the loss occurred immediately following the T=0 hrs sampling period. The TCE concentrations then held relatively constant throughout the remainder of the reaction period. The loss of TCE from the control reactors was likely via volatilization. However, no TCE was found on the charcoal desorption tubes from any of the control or treatment reactors. (Recall that not all of the headspace volume of each reactor is passed through the desorption tubes.)

For the treatment reactors, TCE was not detected at 24 hrs either in the aqueous aliquot sample or in the extraction of the reactor contents following collection of the last aliquot sample. If the initial adsorbed fraction is assumed to be oxidized along with the aqueous TCE, which is supported by the lack of TCE detection in the final reactor extractions, effective total TCE recoveries for the treatment reactors would range between 100-103%. While complete oxidation TCE present is likely, it should be understood that some of the initial TCE may have been lost to volatilization in this experiment since both control reactors experienced a significant loss of TCE between the T=0 hrs and T= 0.5 hrs sampling periods.

From Figure 58, the aqueous TCE concentrations were readily reduced to no detection within hours for each treatment reactors (with the exception of the first 0.01% MnO_4^- reactor). While the oxidation rate within the first 0.01% MnO_4^- reactors appeared to slow after T= 5hrs, TCE was ultimately not detected at 24 hrs. An attempt to calculate a rate constant for both 0.01% MnO_4^- reactors was performed using the TCE data between T=0 and T=3 hrs. The aqueous TCE data were plotted in Figure 61 and Figure 62 as $\ln(C/C_o)$ vs. Time for the first and second 0.01% reactor, respectively. These linear regression resulted in first order rate constants of k=1.57 hr^{-1} and 1.70 hr^{-1}. While the fit of the data to a first order rate constant may not be optimal, attempts to evaluate other rate models were not made since the mechanisms occurring in such a complex system are not known. These first order rate constants are lower than those obtained in Exp. 4a-

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R6 for the aggregate basalt. As will be presented in a summary table for the dissolved plume experiments, the initial TCE mass was ≈25% greater for the aggregate basalt experiment. Thus, the TCE oxidation rate may be dependent upon the initial TCE concentration.

As observed previously for the dissolved plume media, complete TCE oxidation occurred within 0.5 hrs for the 0.1% MnO_4^- reactors. Enough data points are not available to compute a rate constant; however, the observed oxidation rate is greater than 1.6 mg TCE/hr for the 0.1% MnO_4^- reactors.

As with all dissolved plume media evaluated, little oxidant consumption was observed. In fact, negative oxidant consumption values were obtained for the 0.1% MnO_4^- reactors. As discussed previously, this result likely stems from the inability to accurately quantify very small changes in MnO_4^- concentrations with the spectrophotometer used.

The pH values initially decreased as the oxidation reactions went to completion. The final pH values for this sediment experiment, however, were distinctly different than those obtained for the TAN site basalt. The results are similar to those obtained from the other sediment experiment (Exp. 4a-R7). After the initial pH decrease associated with active oxidation, the pH values for the 0.01% MnO_4^- reactors nearly increased back to their initial values. The pH values of the 0.1% MnO_4^- reactors, on the other hand, did not rebound after the initial oxidation reactions. Instead, the slurry pH values remained ≈0.2-0.3 pH units below their initial values (before oxidant addition). This phenomenon again may have resulted from the lack of sediment buffering capacity to counteract the formation of the H^+ ions released during either TCE or sediment oxidation.
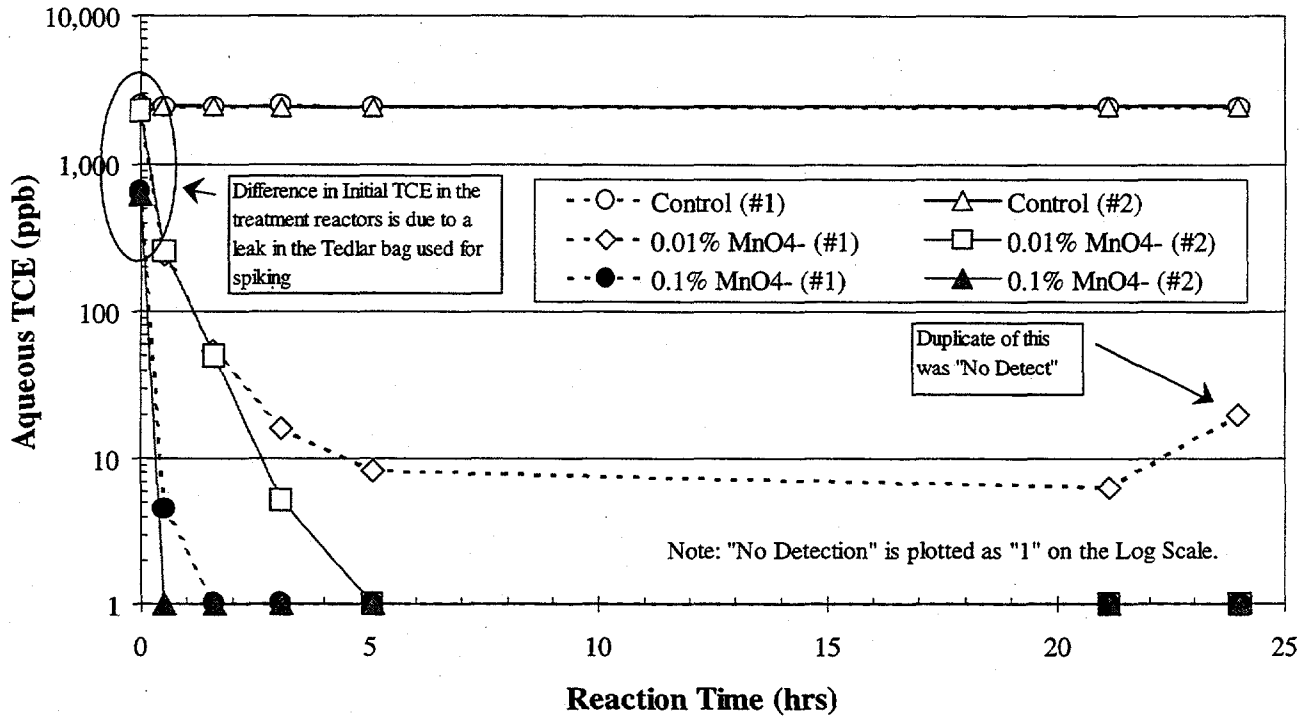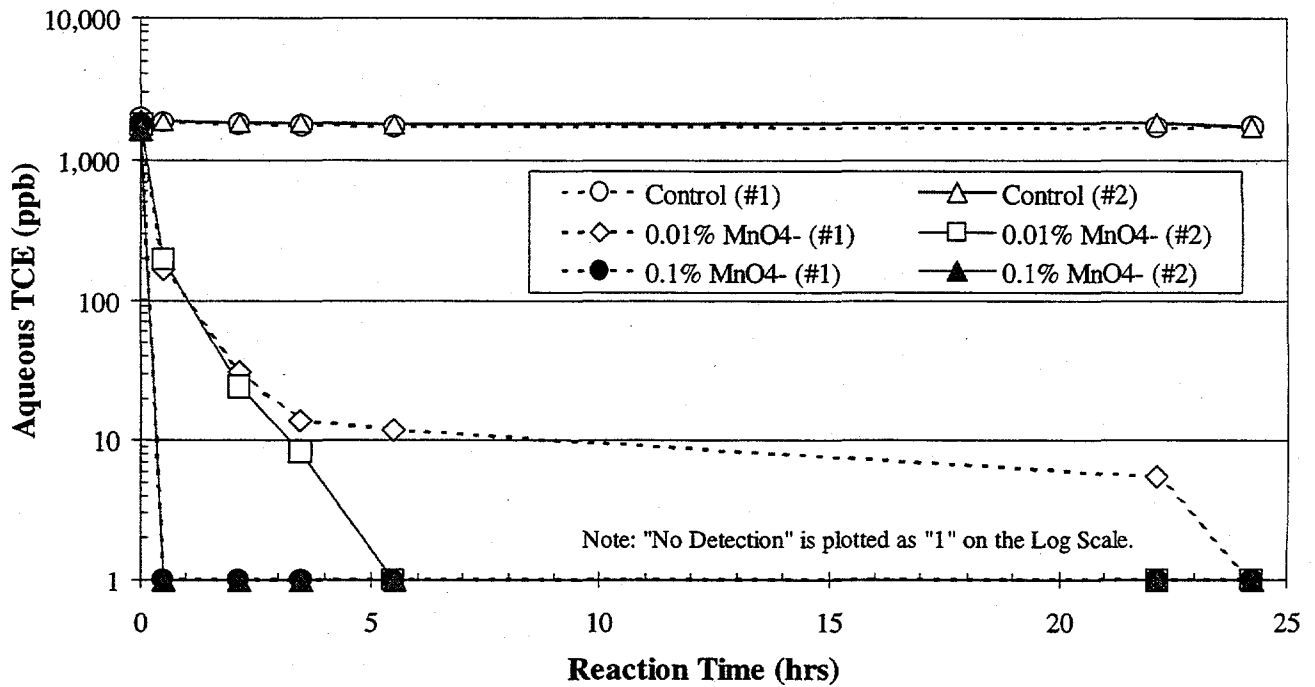
Figure 58. TCE vs. Time, TAN-40 GW & Sediment, (ORNL Exp. 4a-R8, Initial TCE= 1000 μg/L, Conducted at 12°C, 4:1 L/S Ratio)
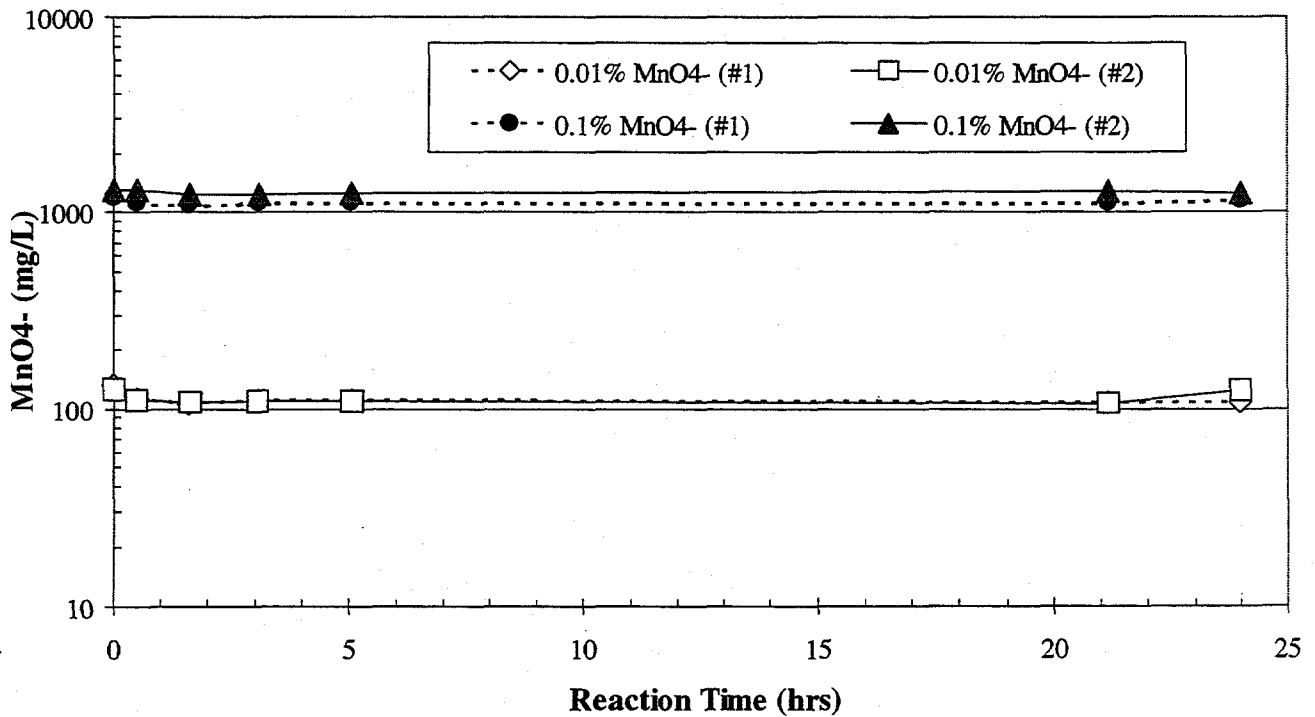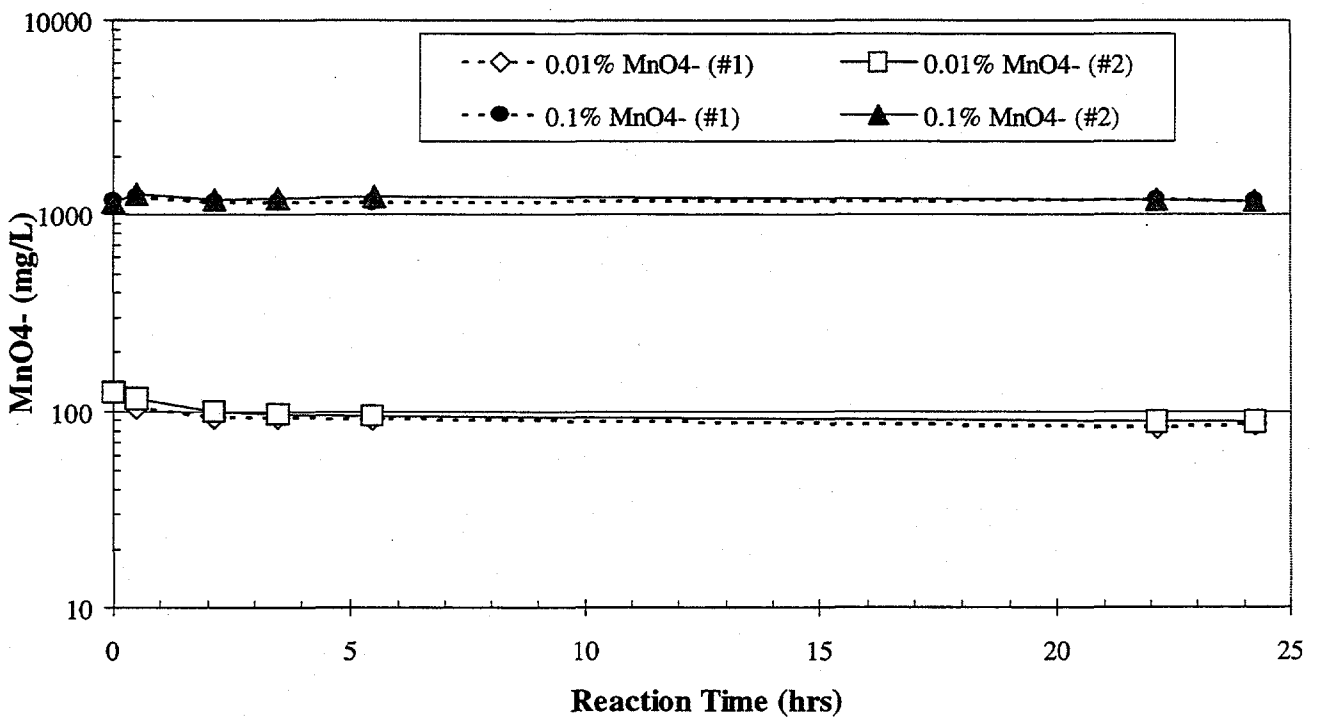

Figure 59. MnO_4^- vs. Time, TAN-40 GW & Sediment, (ORNL Exp. 4a-R8, Initial TCE= 1000 μg/L, Conducted at 12°C, 4:1 L/S Ratio)
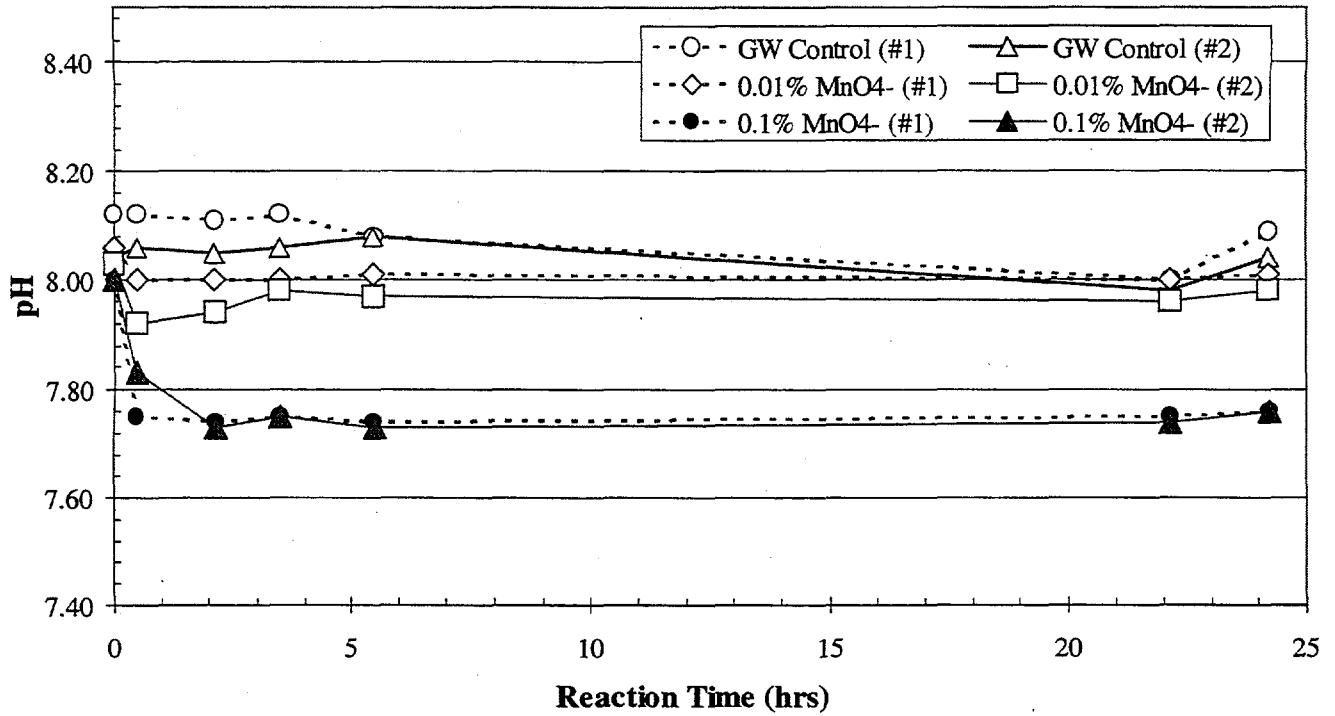
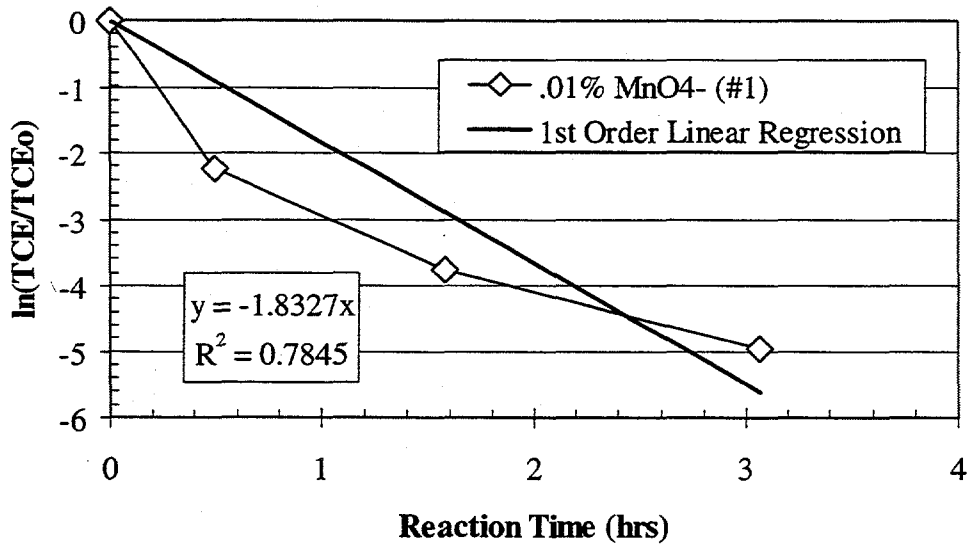Figure 60. pH vs. Time, TAN-40 GW & Sediment, (ORNL Exp. 4a-R8, Initial TCE= 1000 μg/L, Conducted at 12°C, 4:1 L/S Ratio)

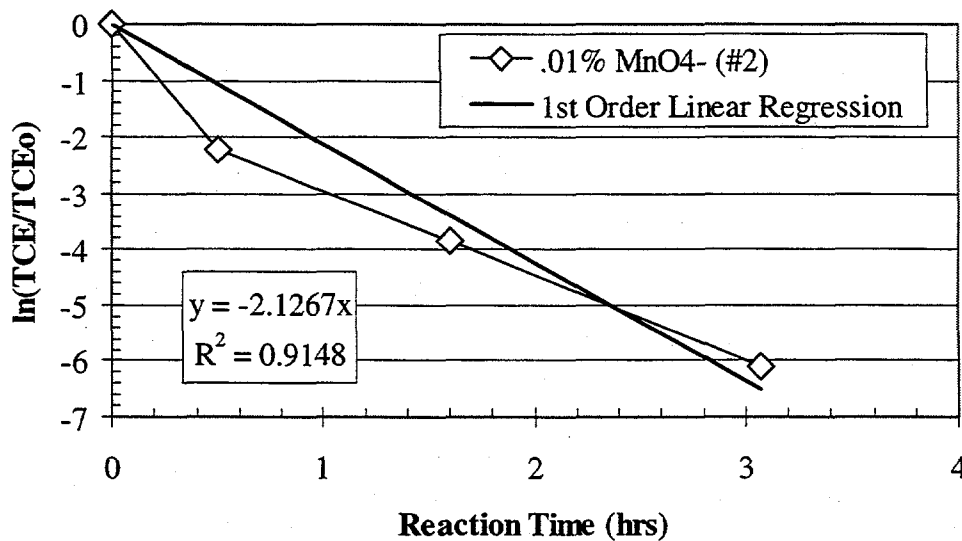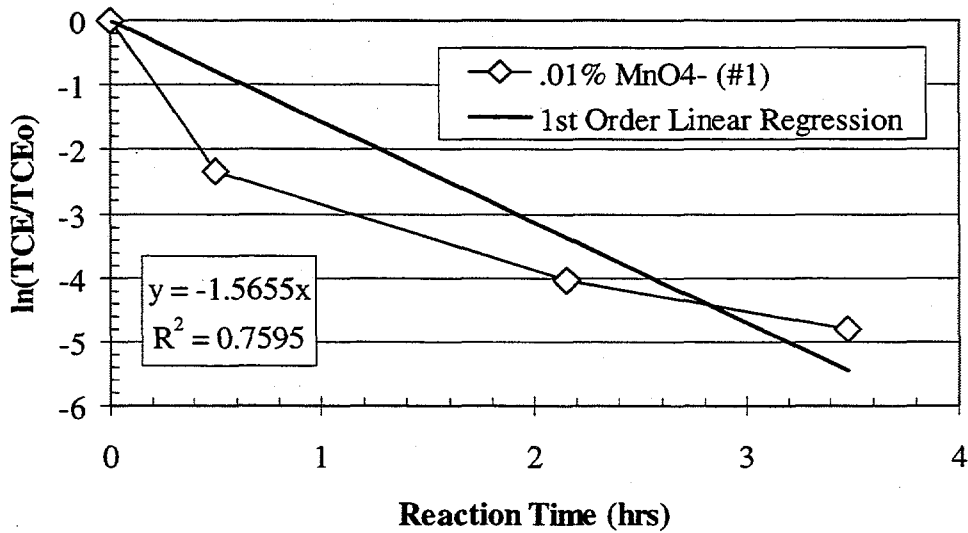
Figure 61. First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#1) Reactor, TAN-40 GW & Sediment, (ORNL Exp. 4a-R8, Initial TCE= 1000 μg/L, Conducted at 12°C, 4:1 L/S Ratio)
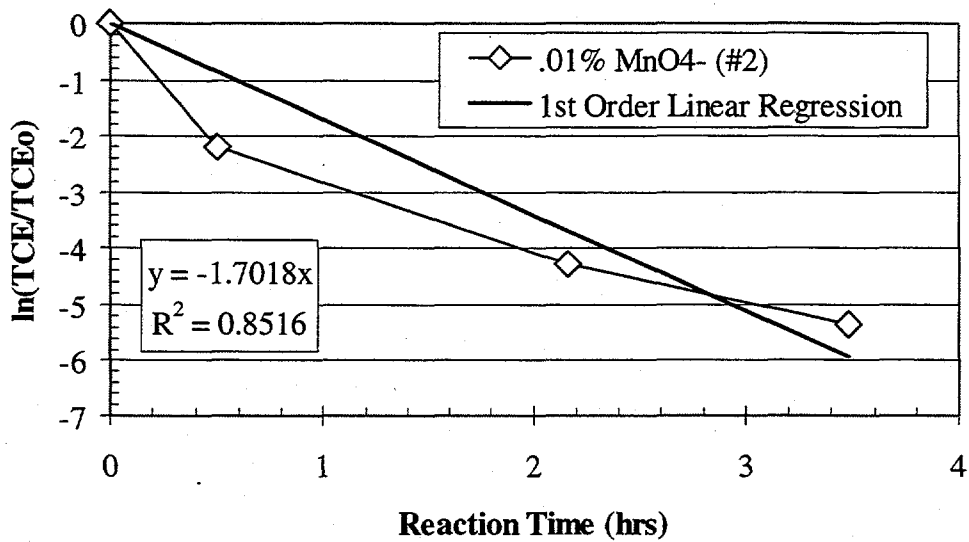
Figure 62. First Order TCE Oxidation Rate Constant for the 0.01% MnO_4^- (#2) Reactor, TAN-40 GW & Sediment, (ORNL Exp. 4a-R8, Initial TCE= 1000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 26. TCE Mass Balance for ORNL Exp. 4a-R8 (TAN-40 GW & Sediment).

Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	0.98	0.98	0.000	0.75	0.11	NA	0.9
			0%	77%	11%	NA	87%
Control (#2)	0.97	0.97	0.000	0.76	0.11	NA	0.9
			0%	79%	11%	NA	90%
0.01% (#1)	0.74	0.65	0.000	0.00	0.014	0.64	0.7
	%Sorbed:	12%	0%	0%	2%	87%	89%
0.01% (#2)	0.75	0.68	0.000	0.00	0.014	0.67	0.7
	%Sorbed:	9%	0%	0%	2%	90%	91%
0.1% (#1)	0.77	0.71	0.000	0.00	0.013	0.72	0.7
	%Sorbed:	8%	0%	0%	2%	93%	95%
0.1% (#2)	0.79	0.67	0.000	0.00	0.011	0.68	0.7
	%Sorbed:	15%	0%	0%	1%	86%	87%

[a] Total Initial computed using the average initial aqueous TCE concentration of the GW control samples (Avg=1,954 µg/L, σ=28 µg/L).

Table 27. MnO_4^- Consumption Data for ORNL Exp. 4a-R8 (TAN-40 GW & Sediment).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	47.4	0.10	15.33	0.03
0.01% (#2)	47.4	0.10	13.50	0.03
0.1% (#1)	474.2	0.95	-0.81	0.00
0.1% (#2)	474.2	0.92	-12.58	-0.02

[a] Consumption is computed after 24 hr reaction time.

Summary – TCE Oxidation Rate Measurements, Dissolved Plume Media

This set of experiments measured the rate of TCE oxidation in the presence of geologic media (groundwater, basalt, and fracture fill material [sediment]) from the 'dissolved plume' at TAN, i.e. down gradient of the hot spot. The concentrations of MnO_4^- used in this experiment (0.01% and 0.1% MnO_4^-) are lower than the concentrations used in the parallel experiments using media from the hot spot because the oxidant demands of dissolved plume media are less than those of hot spot media. Summary Data from this series of experiments are presented in Tables 28 through 38. (Table 38 is a complete summarization of these experiments and the data presented in Tables 28 through 37.)

Table 28 lists the experimental identification used by ORNL for this series of experiments.

Table 28   Experimental Identification for Dissolved Plume Media Experiments.

Nominal	Nominal TCE Concentration	
MnO_4^- Concentration	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	4aR1	4aR2
0.1%	4aR1	4aR2
Groundwater and Crushed Basalt		
0.01 %	4aR3	4aR5
0.1%	4aR3	4aR5
Groundwater and Aggregate Basalt		
0.01%	4aR4	4aR6
0.1%	4aR4	4aR6
Groundwater and Sediment		
0.01%	4a4R7	4aR8
0.1%	4a4R7	4aR8

The initial and final MnO_4^- concentrations in this series of experiments are presented in Tables 29 and 30, respectively. The MnO_4^- concentrations used in these experiments were high enough that MnO_4^- was present at the end of each experiment, and thus TCE oxidation was not limited by low MnO_4^- concentrations. This is in contrast to the 'hot spot media' experiments described in following sections (2.4.3 and 2.4.4).

Table 29.   Initial Aqueous MnO$_4^-$ Concentrations for Dissolved Plume Media Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	115	117
0.1%	1,100	1,112
Groundwater and Crushed Basalt		
0.01 %	138	117
0.1%	1,322	1,191
Groundwater and Aggregate Basalt		
0.01%	120	129
0.1%	1,186	1,244
Groundwater and Sediment		
0.01%	127	126
0.1%	1,287	1,170

[a]   Average Concentration of 2 test reactors (mg/L MnO$_4^-$). All samples filtered (0.45 µm) prior to analysis.

Table 30.   Final MnO$_4^-$ Concentrations for Dissolved Plume Media Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	99	80
0.1%	1,100	1,095
Groundwater and Crushed Basalt		
0.01 %	99	91
0.1%	1,221	1,185
Groundwater and Aggregate Basalt		
0.01%	109	116
0.1%	1,141	1,200
Groundwater and Sediment		
0.01%	108	88
0.1%	1,202	1,186

[a]   Average Concentration of 2 test reactors (mg/L MnO$_4^-$). All samples filtered (0.45 µm) prior to analysis.

Tables 31 and 32 show the initial and final aqueous TCE concentrations in the MnO$_4^-$- spiked reactors. Note that the TCE concentrations included in these tables do not include TCE that was originally bound to the TAN solid phases that might have been present in the test reactors. As observed in Table 31, the actual TCE spike concentrations for the dissolved plume media experiments were typically greater than the target (nominal) TCE concentrations. In fact, the average TAN-40 GW spike concentrations were 200 and 1,780 µg/L for experiments having target TCE spike concentrations of 100 and 1,000 µg/L TCE, respectively. This anomaly is

believed to have resulted from the use of a saturated TCE solution to prepare the spiked groundwater solution (see Appendix B, Testplan). Volumes of saturated TCE needed for spiking were made with the assumption that the maximum aqueous TCE solubility was near 1,000 mg/L. It is suspected that its actual concentration was somewhat greater since DNAPL was also present in the bottom of the saturated solution container. While nearly double the desired values, the actual TCE spike concentrations are all within the same order of magnitude of the nominal, target values.

Table 33 shows the percentage of TCE oxidized and removed during sampling. (These values were obtained from the mass balance tables presented previously in this section.) TCE concentrations in control reactors remained approximately constant, while TCE concentrations declined to less than method detection limits (MDLs) in reactors that contained MnO_4^-. This demonstrates that oxidation of TCE by MnO_4^- is the predominant mechanism whereby TCE was destroyed.

Table 31.   Initial TCE Concentrations for Dissolved Plume Media Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	178	1,368
0.1%	179	1,319
Groundwater and Crushed Basalt		
0.01 %	162	1,266
0.1%	154	1,288
Groundwater and Aggregate Basalt		
0.01%	136	2,314
0.1%	136	636[b]
Groundwater and Sediment		
0.01%	235	1,753
0.1%	221	1,724

[a]   Average Concentration of 2 test reactors (µg/L TCE).

[b]   Initial TCE concentration is unknown due to a leak in the spiking solution container prior to filling these reactors.

Table 32.   Final TCE Concentrations for Dissolved Plume Media Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	ND	ND,14
0.1%	ND	ND
Groundwater and Crushed Basalt		
0.01 %	ND	22[b]
0.1%	ND	ND,15[b]
Groundwater and Aggregate Basalt		
0.01%	ND	ND, 20
0.1%	ND	ND[c]
Groundwater and Sediment		
0.01%	ND	ND
0.1%	ND	ND

[a]   Average Concentration of 2 test reactors (µg/L TCE).

[b]   TCE Contamination detected in hexane GC blanks.

[c]   Initial TCE concentration is unknown due to a leak in the spiking solution container prior to filling these reactors.

Table 33. Percentage of Initial TCE Mass Oxidized and Removed by Sampling. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	100	100
0.1%	101	102
Groundwater and Crushed Basalt		
0.01 %	106	97
0.1%	104	100
Groundwater and Aggregate Basalt		
0.01%	97	92
0.1%	100	26[b]
Groundwater and Sediment		
0.01%	93	90
0.1%	89	91

[a] Average Value determined from 2 test reactors (wt%)
[b] Initial TCE concentration is unknown due to a leak in the spiking solution container prior to filling these reactors.

The rate of TCE oxidation on 'per reactor' and 'per unit volume' bases are presented in Tables 34 and 35, respectively. These are lower bound estimates of the zero order reaction rate.

Table 34. Observed Minimum Zero Order TCE Destruction Rates - Per Reactor Basis, Dissolved Plume Media. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 µg/L	1000 µg/L
Groundwater Only		
0.01 %	0.03	0.14
0.1%	0.2	0.34
Groundwater and Crushed Basalt		
0.01 %	0.02	0.11
0.1%	0.14	1.0
Groundwater and Aggregate Basalt		
0.01%	0.03	0.2
0.1%	0.12	0.14
Groundwater and Sediment		
0.01%	0.04	0.15
0.1%	0.19	1.6

[a] Values are the average of 2 test reactors (mg TCE / hr per reactor). Computed by dividing the Average Initial TCE Mass present in each reactor by the earliest aliquot sampling time at which TCE was not detected. Each reactor contained nominally 400 mL water and, if a solid phase was present, 100 g of solid media. See Appendix C for actual GW and solid phase masses in each reactor.

Table 35. Observed Minimum Zero Order TCE Destruction Rates -Per Unit Volume Basis, Dissolved Plume Media. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration	
	100 μg/L	1000 μg/L
Groundwater Only		
0.01 %	0.06[†]	0.28[†]
0.1%	0.36	0.64
Groundwater and Crushed Basalt		
0.01 %	0.04[†]	0.27
0.1%	0.30	2.5
Groundwater and Aggregate Basalt		
0.01%	0.07[†]	0.50[†]
0.1%	0.29	0.33
Groundwater and Sediment		
0.01%	0.10[†]	0.4[†]
0.1%	0.48	4

[a] Values are the average of 2 test reactors (mg TCE/L per hour). Values were computed by dividing the Average Initial TCE Mass present in each reactor by both (1) the earliest aliquot sampling time (hrs) at which TCE was not detected and (2) the average initial liquid volume in the reactor (GW and MnO$_4^-$ stock solution).

[†] A corresponding first order rate constant is included in Table 38 for this test case.

- TCE oxidation was rapid at the MnO$_4^-$ concentrations utilized (0.01% and 0.1%) in these tests. TCE concentrations typically declined to less than MDLs within 0.5 – 5 hours. Cases in which TCE concentrations did not decline to less than MDLs are attributed to low level contamination of the hexane used for extracting the samples prior to GC analysis.

- TCE oxidation was so rapid that the data resolution is insufficient to calculate reliable reaction rate parameters.

- TCE oxidation was often complete before the first sample was collected (typically approximately 0.5 hours after the start of oxidation). Therefore, neither a zero order reaction rate nor a first order reaction rate constant can be calculated for these cases. Instead, a lower bound of the zero order reaction rate was calculated by assuming that the TCE concentration reached zero at the time that the first sample was collected.

- In other cases, TCE concentrations declined to less than the MDL between the first and second samples. In these cases, lower bound of the a zero order reaction rate was calculated by assuming that the TCE concentration reached zero at the time that the second sample was collected.

- In cases where TCE concentrations were greater than the MDL in both the first and second samples, a first order reaction rate constant was calculated.

- The TCE oxidation rate increased with MnO$_4^-$ concentration.

- The calculated TCE oxidation rate also increased with TCE concentration. However, this may be an artifact of estimating a lower bound of the reaction rate (see items items above) instead of having sufficient data resolution to calculate an actual reaction rate. Higher initial TCE concentrations cause the estimated lower bound of the reaction rate to be greater.

- The TCE oxidation rate does not appear to be sensitive to the type of geologic medium tested (groundwater only, aggregate basalt, crushed basalt, and sediment). Although the rates calculated for sediment and crushed basalt at high TCE and permanganate concentrations are much higher than for other materials, closer inspection of the results shows that the differences between materials can be attributed to variations in initial TCE concentration and the lack of data resolution (i.e., the time at which concentrations declined to less than MDL was not determined more closely than less than ≈ 0.5 or ≈ 2 hours).

Observed zero order reaction rates (mg TCE / L / hour), averaged for all four materials are shown in Table 36.

Table 36.   Representative Zero Order TCE Oxidation Rates. [a]

MnO_4^- Concentration	TCE Concentration	
	100 (μg/L)	1000 (μg/L)
0.01(%)	0.1	0.4
0.1 (%)	0.4	2

[a] Rate value presented in mg TCE / L per hour

Observed pH trends for these experiments are presented in Table 37.

Table 37. pH Trends for Dissolved Plume Experiments. [a]

Nominal MnO_4^- Concentration	Nominal TCE Concentration	
	100 μg/L	1000 μg/L
Groundwater Only		
0.01 %	+0.05	-0.2
0.1%	+0.2	-0.1
Groundwater and Crushed Basalt		
0.01 %	+0.1	+0.1
0.1%	+0.1	+0.1
Groundwater and Aggregate Basalt		
0.01%	+0.3	-0.2
0.1%	+0.3	-0.1
Groundwater and Sediment		
0.01%	0	-0.1
0.1%	-0.1	-0.2

[a]   Values represent net pH changes.

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- Changes in pH were small in all experiments, typically only a few tenths of a pH unit. No patterns are apparent, indicating that pH would <u>not</u> be a useful parameter for monitoring ISCO at these MnO_4^- and TCE concentrations for the dissolved plume media.

A complete summary of the preceding tables is presented in Table 38 for all the oxidation rate experiments conducted on the dissolved plume media.

Table 38. Summary of the Dissolved Plume Media Oxidation Rate Experiments.

ORNL Exp. No.	Dissolved Plume Media	Nominal Initial TCE (µg/L)	Avg. Initial TCE Mass (mg)	TCE Oxidation Observed Rates (mg TCE/hr·Reactor Contents)[†]	Initial MnO_4^- (wt%)	Max. MnO_4^- Consumed (mg MnO_4^-/g)	pH Trends (After 24 hrs)
4a-R1	TAN-40 GW	100	0.10	Complete (<3 hrs) Obs. Rate ≥0.03 **Avg k=1.78 hr^{-1}**	0.01%	0.02	<0.05 Net Increase
			0.10	Complete (<0.5 hr) Obs. Rate ≥0.2	0.1%	0.00	<0.2 Net Increase
4a-R2	TAN-40 GW	1000	0.69	Complete[1] (<5 hrs) Obs. Rate ≥ 0.14 **Avg k=1.51 hr^{-1}**	0.01%	0.04	<0.2 Net Decrease
			0.68	Complete (<2 hrs) Obs. Rate ≥0.34	0.1%	0.02	<0.1 Net Decrease
4a-R3	Crushed Basalt & TAN-40 GW	100	0.07	Complete (<3 hrs) Obs. Rate ≥0.02 **Avg k=2.32 hr^{-1}**	0.01%	0.04	<0.1 Net Increase
			0.07	Complete (< 0.5 hr) Obs. Rate ≥0.14	0.1%	0.11	<0.1 Net Increase
4a-R5	Crushed Basalt & TAN-40 GW	1000	0.54	Complete[2] (≈5 hrs) Obs. Rate ≥0.11	0.01%	0.02	<0.1 Net Increase
			0.52	Complete[2] (≈0.5 hr) Obs. Rate ≥1.0	0.1%	0.02	<0.1 Net Increase
4a-R4	Aggregate Basalt & TAN-40 GW	100	0.06	Complete (<2 hrs) Obs. Rate ≥0.03 **Avg k=4.28 hr^{-1}**	0.01%	0.01	<0.3 Net Increase
			0.06	Complete (< 0.5 hr) **Obs. Rate ≥0.12**	0.1%	0.06	<0.3 Net Increase
4a-R6	Aggregate Basalt & TAN-40 GW	1000	1.0	Complete (<5hrs)[1] Obs. Rate ≥0.2 **Avg k=1.98 hr^{-1}**	0.01%	0.02[3]	<0.2 Net Decrease
			0.28[4]	Complete (<2 hrs) Obs. Rate ≥0.14[4]	0.1%	0.04	<0.1 Net Decrease

Table 38 (continued)

ORNL Exp. No.	Dissolved Plume Media	Nominal Initial TCE (μg/L)	Avg. Initial TCE Mass (mg)	TCE Oxidation Observed Rates (mg TCE/hr·Reactor Contents)[†]	Initial MnO_4^- (wt%)	Max. MnO_4^- Consumed (mg MnO_4^-/g)	pH Trends (After 24 hrs)
4a-R7	Sediment (SED1) & TAN-40 GW	100	0.11	Complete (< 3hrs) Obs. Rate ≥0.04 **Avg k=2.16 hr^{-1}**	0.01%	0.02	No Net Change
			0.10	Complete (< 0.5 hr) Obs. Rate ≥0.19	0.1%	0.08	<0.1 Net Decrease
4a-R8	Sediment (SED2) & TAN-40 GW	1000	0.75	Complete (<5 hrs)[1] Obs. Rate ≥0.15 **Avg k=1.64 hr^{-1}**	0.01%	0.03	<0.05 Net Decrease
			0.78	Complete (< 0.5 hr) Obs. Rate ≥1.6	0.1%	0.00	0.2-0.3 Net Decrease

†   Observed Oxidation Rate= (Total Initial mg TCE)/(X hrs·Reactor Contents); Where X represents the earliest sampling time at which TCE was not detected in the aqueous aliquot. Where available, the predicted first order reaction rate constant, k, is presented. "Reactor Contents" are nominally 400 mL TCE-spiked GW and 100 g Solid Phase (if applicable). See Appendix C for actual GW and solid phase masses in each reactor.

1   One of the duplicate samples contained a 10 μg/L TCE residual.

2   It is assumed that the reactions were completed. Residual TCE was present due to a solvent contamination problem. The reported values are estimates.

3   maximum based on the first 0.01% MnO_4^- reactor only.

4   Low due to the fact that the initial TCE was less for these reactors (0.28 mg TCE rather than 1 mg TCE as in the case of 0.01% reactors)

2.4.3. Oxidation Rate of Organic Contaminants in Hot Spot Groundwater

Eight (8) separate oxidation rate experiments were performed for the hot spot groundwater (TSF=05 GW). Each experiment is discussed below and identified by the ORNL Experiment IDs presented earlier in Table 6. In general, plots of "TCE vs. Time", "MnO$_4^-$ vs. Time", and "pH vs. Time" are presented for each experiment. For all plots of TCE vs. Reaction time: any values resulting from analyses in which the sample extract concentration was out of the GC calibration range are clearly labeled. Note that some experiments were continued after 24 hrs. Such a modification is clearly noted in the experimental discussions.

In addition to the plots, summary tables for the TCE and MnO$_4^-$ data are presented for each experiment. Several parameters are included in the TCE mass balance tables (e.g., Table 39). The approach and/or calculations made to obtain each of the values presented in the TCE mass balance tables are presented below. (Descriptions of the MnO$_4^-$ consumption tables are presented at the beginning of Section 2.4.2.)

TCE MASS BALANCE TABLE DESCRIPTION

- Column 1, "Test Conditions" refers the experimental condition. In this column "Control" refers to reactors containing only TSF-05 GW and no oxidant. The (#1) and (#2) notations included in parentheses refer to the duplicate reactors evaluated. The number followed by the percentage sign is the nominal initial MnO$_4^-$ concentration added to the treatment reactors.

- Column 2, "Total Initial Mass" refers to the TCE mass added to each reactor. For the control reactors and treatment reactors containing TSF-05 GW this value is determined by the following equation: (Aqueous TCE Conc. at T=0) x (GW Volume in the Reactor) Note: T=0 sampling occurred after overnight equilibration and immediately before oxidant addition to the treatment reactors.

- Column3, "Initial Aqueous Mass" For all cases, this value is computed by multiplying the Aqueous TCE Conc. at T=0 for a given reactor by the volume of GW added to that reactor. Note: The aqueous concentration at T=0 for each reactor is used here rather than the concentration of the spiked GW before it is distributed to the individual reactors and equilibrated. (This approach effectively "removes" or accounts for the any TCE lost during equilibration from the mass balance calculations performed for the actual oxidation reactions.)

- Column 4, "Mass Sorbed on Orbo Tubes" represents the summed TCE mass found on each charcoal bed of the reactor's desorption tube at the end of the reaction period. The TCE mass was obtained by extraction of charcoal beds with hexane. If TCE is detected on the desorption tubes, it is realized that the value obtained represents a *minimum* that was volatilized since the entire reactor headspace volume would not pass through the desorption tube. The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) found within the Orbo Tube.

- Column 5, "Mass Remaining in Reactor" represents the TCE mass still present in each reactor following the reaction period. For the control reactors and treatment reactors, this value was computed by the following equation: (Aqueous TCE concentration at T=24 hrs) x (Init. GW volume –Cum. Vol. of Aliquot Samples). The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) still present in the reactor.

- Column 6, "Cum. Mass Removed in Aliquots" represents the mass of TCE removed from the reactor via aliquot sampling. In all cases, this column is computed by summing the masses of TCE that were found in each aliquot interval for a given reactor, i.e., Σ(Aqueous TCE Conc. x Aliquot Volume). The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) removed from the reactor (and thereby not subjected to oxidation) during the course of the experiment.

- Column 7, "Cum. Aqueous Mass Oxidized" represents the TCE mass initially in the aqueous phase that was considered to have been oxidized during the reaction period. The oxidized TCE masses presented in this column were computed by summing the change in aqueous TCE mass obtained for each sampling period, i.e., $\Sigma[(\text{Aq. TCE Conc.}_{T=x} - \text{Aq. TCE Conc.}_{T=x+1}) \times \text{GW Vol.}_{T=x}]$. Thus, this approach corrects for TCE removed via previous aliquot samplings. This component of the mass balance can be difficult to interpret, particularly when the final TCE concentration for a given sampling interval is greater than the initial TCE concentration. Such an occurrence will be noted in the following discussions of the hot spot groundwater experiments. Again, the values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) believed to have been oxidized.

- Column 8, "Total Mass Recovered" is the sum of the TCE masses found in four (4) different "compartments" at the end of the reaction period (T=24 hrs), i.e., Col. 4+Col. 5 + Col. 6 + Col. 7. The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) that was accounted for during the course of the experiment.

Also note that variation in the initial TSF-05 GW chemistry, e.g. pH values, is expected since each hot spot groundwater experiment was conducted using a different batch of TSF-05 GW that had been sparged for varying amounts of time. (The containers of TSF-05 GW received from INEEL were not combined/mixed prior to experimentation).

NOTE: A different mass balance approach was required for the experiments involving DNAPL phase TCE. Deviations and/or variations of the above approach are presented in the individual results and discussion sections for those experiments.

ORNL Exp. 4b-R1
(TSF-05 GW, No Sludge, 10000 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

This experiment investigated the oxidation of TSF-05 GW spiked at 10,000 µg/L TCE. The TCE, MnO_4^- and pH values with time are presented in Figures 63, 64, and 65, respectively. Tables 39 and 40 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

This experiment was performed without significant deviations from the testplan procedure.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 15,545 µg/L (σ= 612 µg/L). After transfer to the test reactors, the groundwater TCE concentration ranged between 13,100 and 14,700 µg/L (T=0 aliquots) prior to the start of the oxidation reactions.

TCE contamination (4-5 µg/L) was observed in the GC QA/QC blanks for this experiment. The TCE values obtained from the experimental samples further suggest that the hexane used to extract the aqueous samples and the carbon desorption tubes may have been contaminated with a small, unknown amount of TCE. The presence of TCE on the charcoal beds of the desorption tubes could be attributed to volatilization. It is suspected, however, that it is largely a result of the solvent contamination problem. In several cases, more TCE was found on the second charcoal bed of the desorption tubes (Figure 4) than on the first charcoal bed which was closer to the sampling port opening. (Note: Clean desorption tubes were also placed in the incubator in a subsequent experiment to verify that the headspace of the incubator was not the source of this TCE "contamination", and TCE was not detected in these later extractions.) Although solvent contamination was suspected, the experiment was not repeated. The amount of contamination was small, and the overall results from this experiment were very similar to those obtained in the other TSF-05 GW experiments that were conducted. Thus, it did not appear prudent or cost effective to repeat the experiment in light of the benefits that would be gained.

TCE recoveries for the control samples were 102% and 95%, suggesting that little TCE was lost to volatilization. (The >100% recovery may be a result of the solvent contamination problem.) Accurate estimates of the TCE volatilized from the control samples, however, cannot be made due to the potential contamination of the charcoal desorption tubes discussed above.

Although the TCE oxidation of greater than an order of magnitude was initially observed, all treatment reactors contained a $\approx$200 µg/L TCE residual at the end of the reaction period (regardless of initial oxidant loading). Since a residual oxidant was present following the reaction period, the TCE residual is likely to be a result of the solvent contamination during sample extraction. The presence of the additional TCE complicates the interpretation of the mass balance. Fortunately, the amount of solvent contamination ($\approx$200 µg/L TCE) is relatively small compared to the initial spike level (nominal 10,000 µg/L TCE) and does not completely invalidate general trends observed in the TCE oxidation reactions. In fact, TCE recovery calculations for this experiment indicate TCE oxidation values of 96-100% in spite of the fact that an aqueous TCE residual was present.

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The general trend of rapid TCE oxidation was still observed. If one were to assume that the residual TCE concentrations (≈ 200 μg/L) are due to contamination, complete TCE oxidation likely occurred within 15 hrs and within 0.5 hrs for the 0.01% and 0.1% MnO_4^- reactors, respectively. (These values were determined by extrapolating the initially rapid portion of the curves in Figure 63 to a concentration of 10 μg/L TCE.) Although there are more than three TCE data points present, a rate constant was not computed for this experiment since it is likely that the accuracy of the T=5 hrs data points is questionable. However, observed rates of TCE oxidation are *estimated* to be greater than 0.5 and 13.8 mg TCE/hr for the 0.01% and 0.1% MnO_4^- reactors, respectively.

A significant amount of oxidant was consumed by the treatment reactors. Approximately 73% and 58% of the initial oxidant mass was consumed in the 0.01% and 0.1% MnO_4^- reactors, respectively. However, the MnO_4^- consumption values from this experiment (Table 40) indicate that a much greater MnO_4^- mass was consumed in the 0.1% MnO_4^- reactors than observed for the 0.01% MnO_4^- reactors. This trend was not observed in the dissolved plume media experiments spiked at much lower TCE concentrations. Since the oxidant demand of the TSF-05 GW was not significantly high (Task 3 work), the oxidant demand observed here was attributed to the large TCE spike concentrations.

The pH values within the treatment reactors decreased rapidly during the oxidation the TCE spiked GW (Figure 65). The pH of the 0.01% MnO_4^- reactors reached a final pH value of ≈ 7.8, a net decrease of >0.8 pH units. Similarly, the 0.1% MnO_4^- loading resulted in final pH values of ≈ 7.7, a net decrease of >0.9 pH units. The rate at which the pH dropped, however, was greatest for the 0.1% MnO_4^- reactors. The general trend of these pH changes corresponds with the TCE decreases observed (Figure 63). Thus, the pH decreases appear to be directly related to the oxidation of the TCE in the reactors.

Figure 63. TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R1, Initial TCE= 10,000 µg/L, Conducted at 12°C)

Figure 64. MnO₄⁻ vs. Time, TSF-05 GW, (ORNL Exp. 4b-R1, Initial TCE= 10,000 µg/L, Conducted at 12°C)

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Figure 65. pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R1, Initial TCE= 10,000 µg/L, Conducted at 12°C)

Table 39. TCE Mass Balance for ORNL Exp. 4b-R1 (TSF-05 GW).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	6.4	6.4	0.000	5.5	0.9	NA	6.4
			0%	87%	14%	NA	101%
Control (#2)	7.1	7.1	0.000	5.9	0.8	NA	6.7
			0%	83%	12%	NA	95%
0.01% (#1)	7.2	7.2	0.000	0.00	0.2	6.9	7.0
			0%	0%	2%	96%	98%
0.01% (#2)	7.5	7.5	0.000	0.00	0.2	7.3	7.4
			0%	0%	2%	97%	99%
0.1% (#1)	6.9	6.9	0.000	0.00	0.1	6.9	7.0
			0%	0%	2%	100%	101%
0.1% (#2)	6.9	6.9	0.000	0.00	0.1	6.9	7.0
			0%	0%	2%	99%	101%

Table 40. MnO_4^- Consumption Data for ORNL Exp. 4b-R1 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	51.2	0.10	37.37	0.08
0.01% (#2)	51.2	0.10	37.63	0.07
0.1% (#1)	511.5	1.01	303.72	0.60
0.1% (#2)	511.5	1.00	293.90	0.57

a. Consumption is computed after 24 hr reaction time.

ORNL Exp. 4b-R2
(TSF-05 GW, No Sludge, 10,000 TCE, 0 Other, 1% and 3% MnO$_4^-$)

This experiment investigated the oxidation of TSF-05 GW spiked at 10,000 µg/L TCE. The TCE, MnO$_4^-$ and pH values with time are presented in Figures 66, 67, and 68, respectively. Tables 41 and 42 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

This experiment was performed without significant deviations from the testplan procedure.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 12,426 µg/L (σ= 1,470 µg/L). After transfer to the test reactors the groundwater TCE concentration ranged between 8,900 and 12,200 µg/L (T=0 aliquots) prior to the start of the oxidation reactions. While a part of this wide variability may be due to human error in performing sample dilutions, some TCE was likely lost during transfer of the spiked GW to the test reactors.

TCE was not detected in the desorption tube extracts. TCE recoveries for the control samples were only 82% and 92%. The majority of this TCE loss occurred between the T=0 hrs and T=0.5 hrs sampling periods, when the TCE concentrations dropped from $\approx$12,000 µg/L to $\approx$10,000 µg/L.

From Figure 66, the rate of disappearance of TCE from the treatment reactors significantly exceeded the rate of TCE loss from the control reactors. Thus, oxidation is the controlling TCE removal mechanism for this experiment, although a small fraction of the TCE disappearance may be due to volatilization. TCE was not detected in any of the four treatment reactors at the end of the 24 hr reaction period. TCE recovery calculations for this experiment indicate TCE oxidation values of 99% and total TCE recoveries of 100%. Since control reactor recoveries were low (89-92%), one could be conservative and report the maximum TCE oxidation as 82-92%.

It is unknown why the oxidation reaction slowed for the first 1% MnO$_4^-$ reactor, but complete TCE oxidation appears to have occurred within 2 hrs for the second 1% MnO$_4^-$ reactor. Enough data points are not available to compute a rate constant; however, the observed oxidation rate is greater than 2.65 mg TCE/hr for the second 1% MnO$_4^-$ reactor. Complete TCE oxidation for both 3% MnO$_4^-$ reactors occurred within 0.5 hrs, yielding an observed oxidation rate greater than 10 mg TCE/hr for the 3% MnO$_4^-$ reactors.

As observed in the Task 3 oxidant demand experiments, not all of the initial MnO$_4^-$ mass added to each reactor was solubilized at the 0.5 hr sampling point. A maximum of 10% of the initial oxidant was consumed in the 3% MnO$_4^-$ reactors. Oxidant consumption in the 1% MnO$_4^-$ reactors varied between –5% and +5% (see Table 42). The occurrence of negative consumption value is likely due to difficulties in performing accurate dilutions (DF$\approx$ 1600) for the MnO$_4^-$ analyses. These low consumption values were not unexpected since there was even a residual MnO$_4^-$ concentration in the 0.01% MnO$_4^-$ reactors of experiment 4b-R1 (Figure 64).

In this experiment, the pH values within the treatment reactors rapidly and significantly changed during the oxidation the TCE spiked GW. The 1% MnO_4^- reactors experienced an initial pH decrease of ≈ 0.4 pH, but the pH values then rebounded until a final net pH decrease of <0.1 pH units was obtained. (Recall that the 0.01% and 0.1% MnO_4^- reactors in Exp. 4b-R1 also experienced overall pH decreases as a result of the oxidation reactions.) In contrast, an initial pH decrease was not observed for the 3% MnO_4^- reactors. Moreover, the 3% MnO_4^- reactors experienced a pH increase of ≈ 0.4 pH units during the course of the reaction period. This phenomenon may be due to the initially higher pH of the 3% MnO_4^- solution.
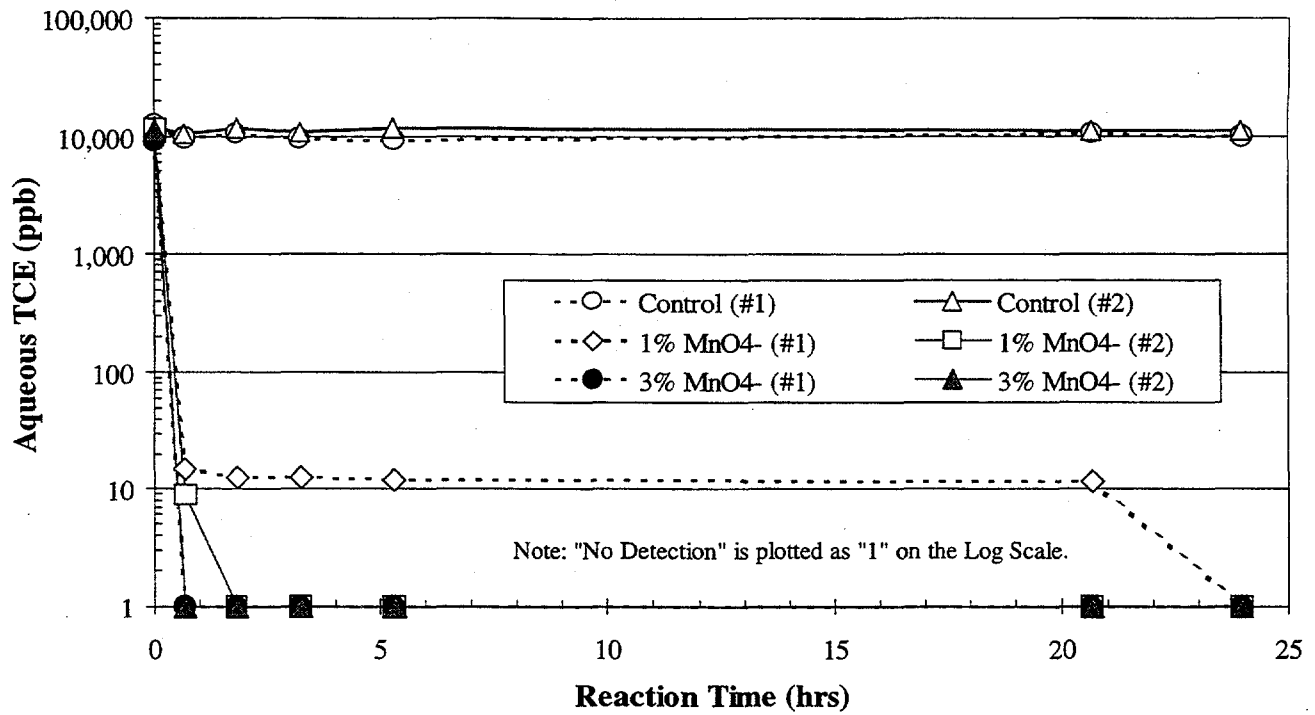
Figure 66.   TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R2, Initial TCE= 10,000 µg/L, Conducted at 12°C)

Note: "No Detection" is plotted as "1" on the Log Scale.

Legend (Figure 66):
- - -O- - Control (#1)
- —△— Control (#2)
- - -◇- - 1% MnO4- (#1)
- —□— 1% MnO4- (#2)
- - -●- - 3% MnO4- (#1)
- —▲— 3% MnO4- (#2)

Y-axis: Aqueous TCE (ppb)
X-axis: Reaction Time (hrs)

Legend (Figure 67):
- - -◇- - 1% MnO4- (#1)
- —□— 1% MnO4- (#2)
- - -●- - 3% MnO4- (#1)
- —▲— 3% MnO4- (#2)

Added MnO4 was likely not completely dissolved at 0.5 hrs

Y-axis: MnO4- (mg/L)
X-axis: Reaction Time (hrs)
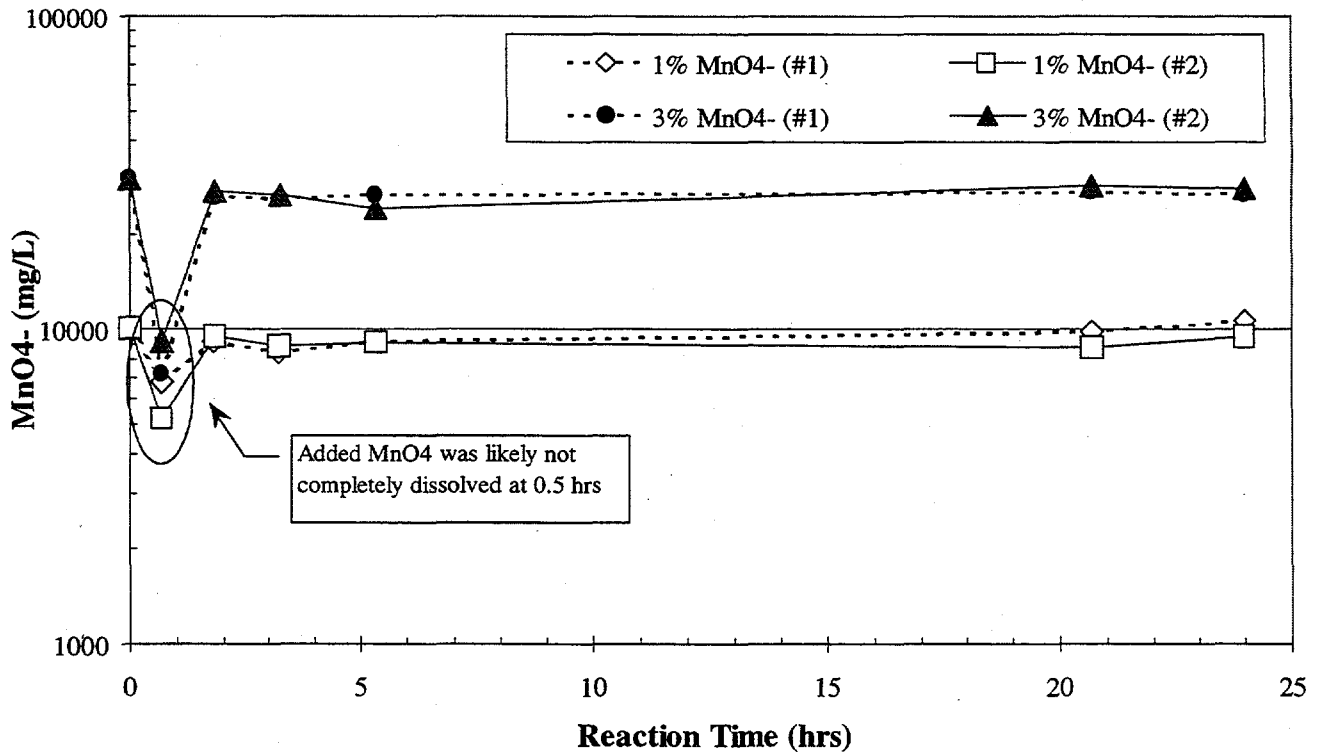
Figure 67.   MnO4- vs. Time, TSF-05 GW, (ORNL Exp. 4b-R2, Initial TCE= 10,000 µg/L, Conducted at 12°C)

Figure 68.   pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R2 Initial TCE= 10,000 µg/L, Conducted at 12°C)

Table 41. TCE Mass Balance for ORNL Exp. 4b-R2 (TSF-05 GW).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	6.3	6.3	0.000	4.6	0.6	NA	5.2
			0%	73%	10%	NA	82%
Control (#2)	6.0	6.0	0.000	4.8	0.6	NA	5.5
			0%	81%	11%	NA	92%
1% (#1)	4.9	4.9	0.000	0.00	0.1	4.8	4.9
			0%	0%	1%	99%	100%
1% (#2)	5.7	5.7	0.000	0.00	0.1	5.6	5.7
			0%	0%	1%	99%	100%
3% (#1)	4.4	4.4	0.000	0.00	0.1	4.4	4.4
			0%	0%	1%	99%	100%
3% (#2)	5.6	5.6	0.000	0.00	0.1	5.5	5.6
			0%	0%	1%	99%	100%

Table 42. MnO_4^- Consumption Data for ORNL Exp. 4b-R2 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
1% (#1)	4975	10.1	-241	-0.5
1% (#2)	4967	10.1	291	0.6
3% (#1)	15065	30.6	1728	3.5
3% (#2)	15075	30.3	1066	2.1

a. Consumption is computed after 24 hr reaction time.

ORNL Exp. 4b-R3
(TSF-05 GW, No Sludge, 100,000 TCE, 0 Other, 0.01% and 0.1% MnO$_4^-$)

This experiment investigated the oxidation of TSF-05 GW spiked at 100,000 µg/L TCE. The TCE, MnO$_4^-$ and pH values with time are presented in Figures 69, 70, and 71, respectively. Tables 43 and 44 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

In this experiment, the method used to prepare the TSF-05 spike solution differed from the approach set forth in the testplan. Here, a small quantity of pure phase TCE ($\approx$280 µL) was added to the Tedlar bag filled with sparged GW. The approach described in the testplan involved the use of a saturated aqueous TCE solution rather than pure phase TCE in the spiking step. A 96 hr reaction time was also evaluated in this experiment, while the tests were terminated at 24 hrs in the procedure described in the testplan.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 148,400 µg/L (σ= 1,020 µg/L). After transfer to the test reactors the groundwater TCE concentration ranged between 97,500 and 107,800 µg/L (T=0 aliquots) prior to the start of the oxidation reactions. While a part of this wide variability may be due to human error in performing sample dilutions, some TCE was likely lost during transfer of the spiked GW to the test reactors.

TCE was detected in the first charcoal bed of the desorption tubes. TCE recoveries for the control samples were 115% and 116%. A closer examination of the experimental data provides explanation to this apparent net increase in TCE. This experiment was continued past 24 hrs and the last aliquot samples were collected at T=96 hrs. All aqueous aliquots collected between T=0 hrs and T=24 hrs were extracted and analyzed on the day the 24 hr samples were collected. The final 96 hr aliquot sample was immediately extracted and analyzed on the day it was collected. GC performance was well within defined limits on both analysis days (max 5% drift of calibration check standard). The TCE values obtained for the 24 hr and 96 hr samples were both greater than any obtained from TCE aliquots collected between 0 and 20 hrs. Thus, it is believed that TCE was lost from the diluted 0-20 hrs GC extracts during the time elapsed between sample collection/extraction and sample analysis. Computing the % recovery of control reactors using the data for the 0-20 hrs timeframe results in recoveries of near 95%. Total TCE recoveries for all four (4) treatment reactors are between 100-103%.

This discrepancy resulting from sample holding times should not affect the validity of this experiment. In fact, the discrepancy should theoretically result in conservative TCE oxidation rates since a shorter holding time for the 24 hrs aliquots would be expected to produce a larger TCE residual at the end of the reaction period. Hence, the calculated reaction rates are less than the true reaction rates. It should be noted that this sample holding time problem likely affected other experiments. The effect was heightened here because of the very high TCE spike concentrations being evaluated. Thus, this problem is not believed to have adversely affected the results of the other experiments.

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From Figure 69, TCE concentrations initially decreased for the 0.01% MnO_4^- reactors, but a residual TCE concentration was still present following the 96 hr reaction period. The slowed TCE oxidation rate observed for the 0.01% MnO_4^- reactors at $\approx$ 4 hrs coincides well with the nearly total depletion of available oxidant for these reactors (Figure 70). Thus, a shortage of available oxidant existed for the 0.01% MnO_4^- reactors. This behavior is different than that seen in previous experiments, where the MnO_4^- masses have always been in excess of that required for TCE oxidation. While not called for in the testplan, the final treatment reactors were also extracted and analyzed in this experiment. The final TCE masses remaining in the reactors (Table 43) were obtained from these extractions. An average of 68% of the initial TCE was oxidized in the 0.01% MnO_4^- reactors. Enough data points are not available to compute a rate constant; however, the observed oxidation rate during the 4 hr period is greater than 7.25 mg TCE/hr.

Complete TCE oxidation occurred in the 0.1% MnO_4^- reactors within 0.5 hrs. While the reaction proceeded too rapidly to determine a rate constant, an observed oxidation rate of 82 mg TCE/hr was determined for the 0.1% MnO_4^- reactors.

Essentially all of the initial 0.01% MnO_4^- was consumed during the oxidation reaction. A MnO_4^- residual of approximately 1 mg/L was measured (Figure 70), but the lowest MnO_4^- calibration standard was 5 mg/L. Excess MnO_4^- was present in the 0.1% MnO_4^- treatment reactors. An average of 18% of initial 0.1% MnO_4^- was consumed during the oxidation of the 100,000 µg/L spiked TSF-05 GW.

The pH values within the treatment reactors decreased to a much greater extent than observed for the TSF-05 GW experiments spiked at only 10,000 µg/L (Exp. 4b-R1). Here too, the greatest pH decreases occurred in the 0.1% MnO_4^- reactors. Net pH decreases of 1.5 and 1.8 pH units were observed for the 0.01% and 0.1% MnO_4^- reactors. Since all conditions other than the initial TCE are the same between this experiment and Exp. 4b-R1, the significant pH reductions must be a result of the TCE oxidation reactions.

Finally, it is interesting to note from Figures 69 and 70 that nearly the same TCE and final MnO_4^- consumption values would have been obtained for these particular oxidant loadings even if a 24 hr reaction period had been evaluated instead of a 96 hr reaction period. This observation provides confidence in the use of a 24 hr reaction time in other experiments to assess TCE oxidation.
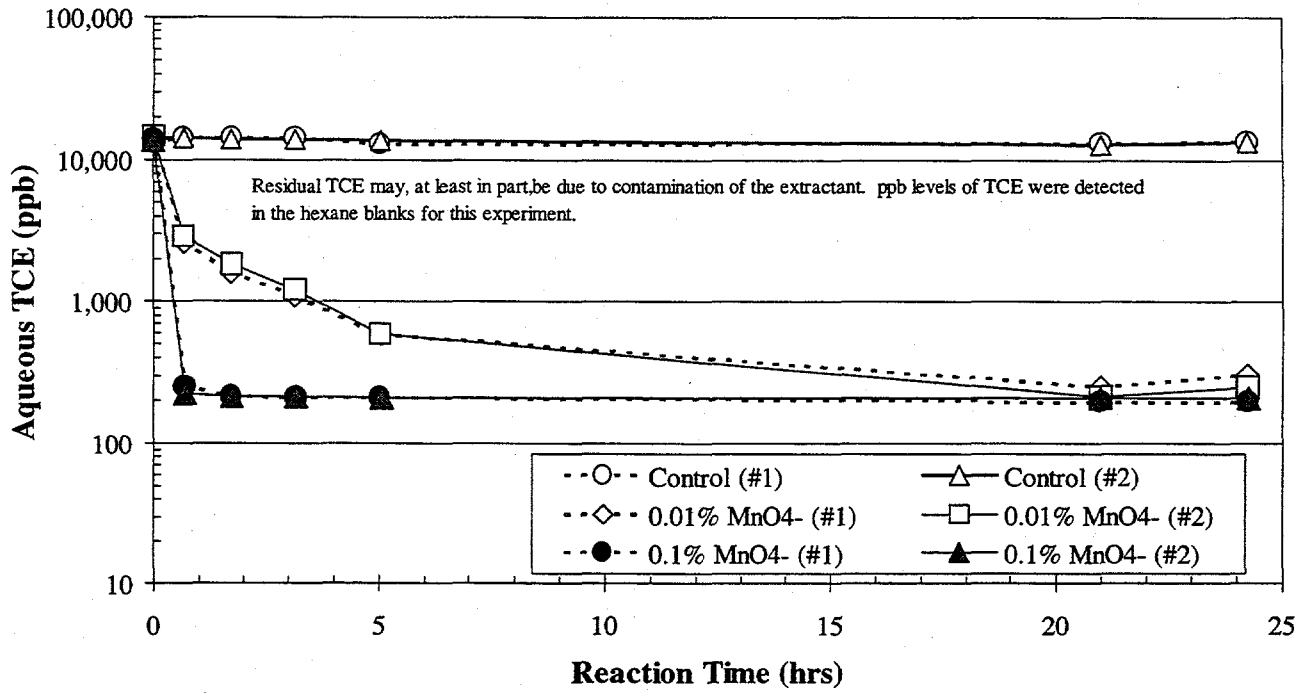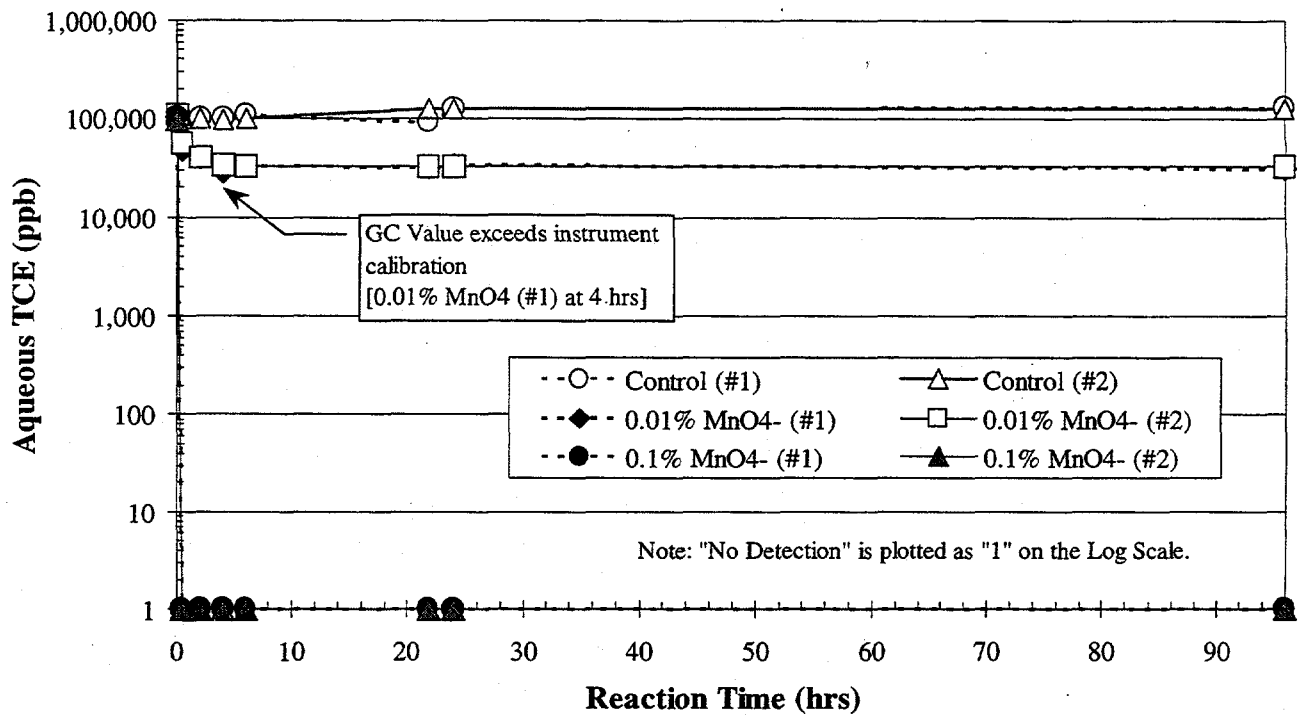
Figure 69. TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R3, Initial TCE= 100,000 µg/L, Conducted at 12°C)
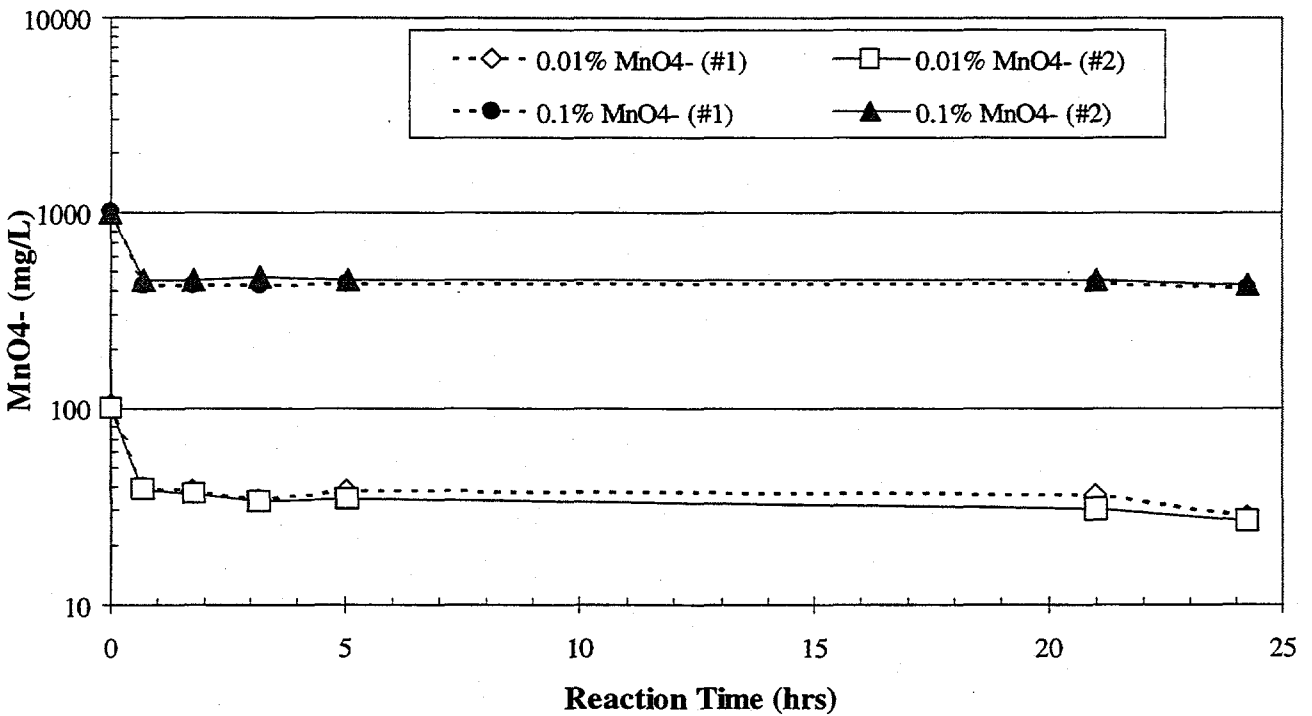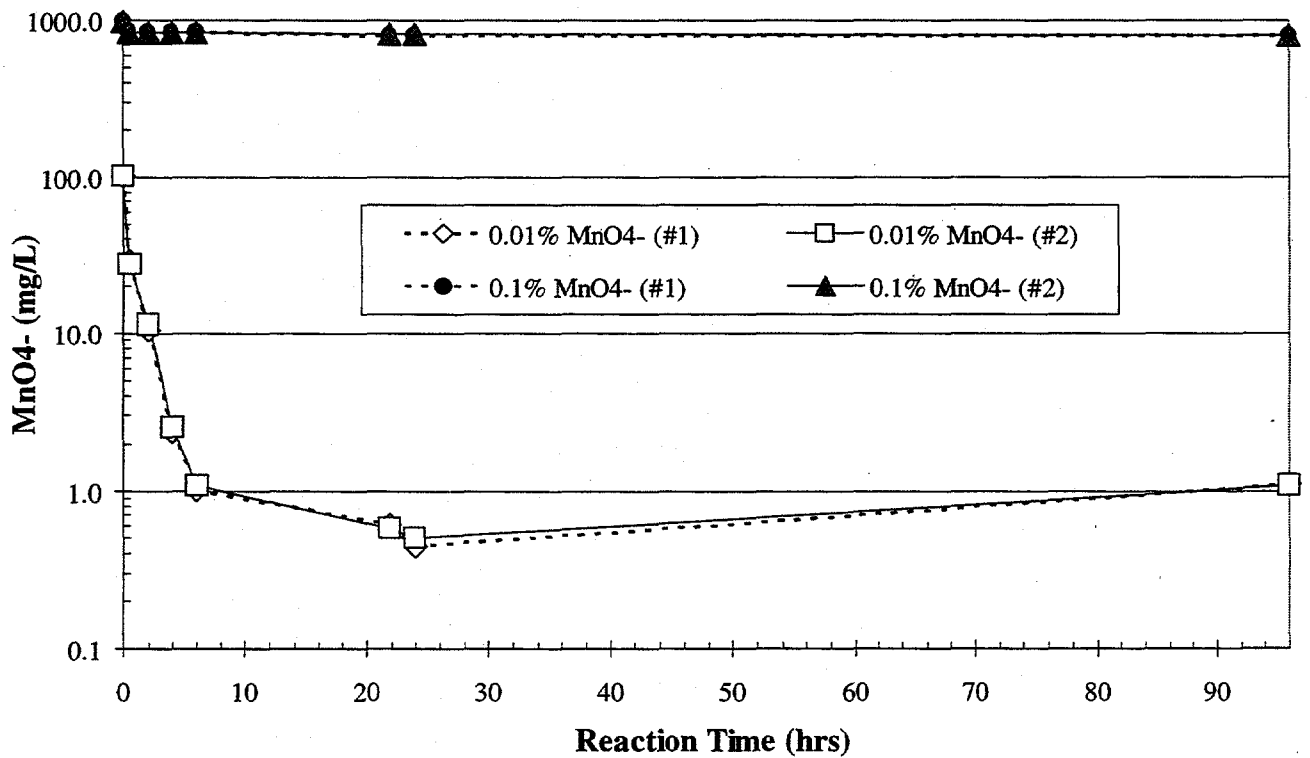

Figure 70. MnO4- vs. Time, TSF-05 GW, (ORNL Exp. 4b-R3, Initial TCE= 100,000 µg/L, Conducted at 12°C)
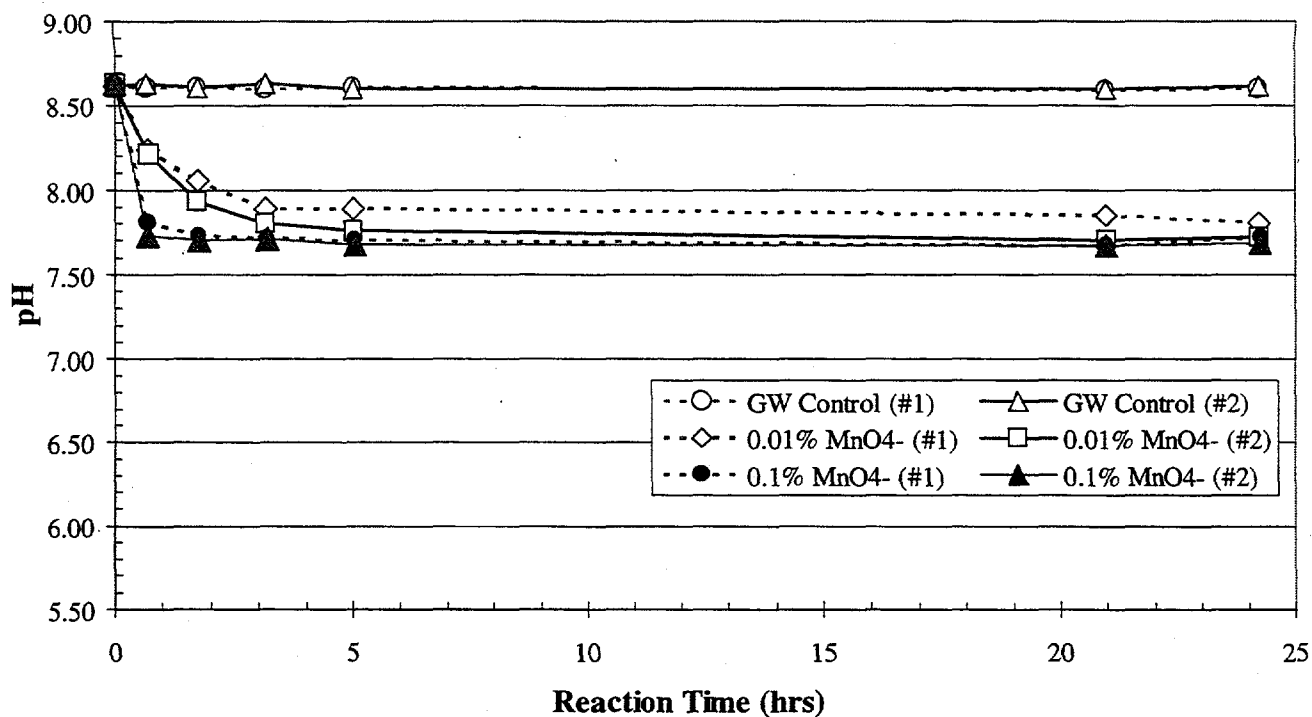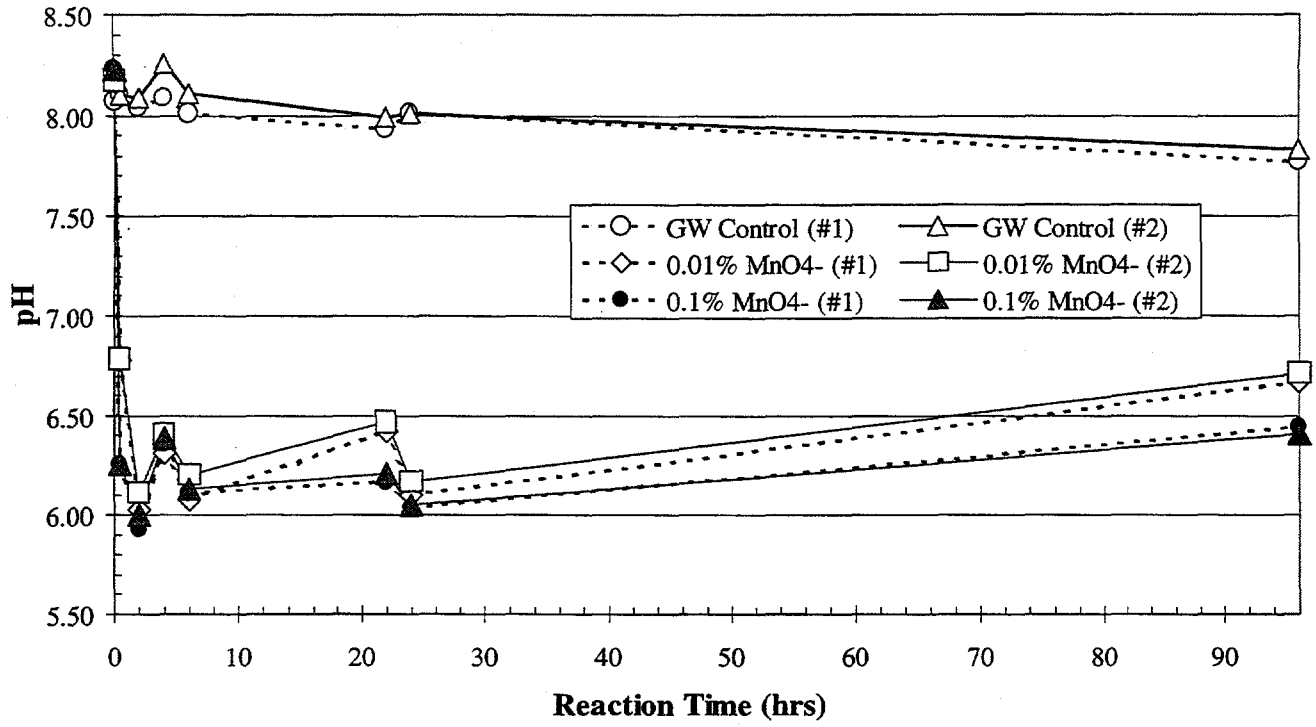
Figure 71. pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R3, Initial TCE= 100,000 µg/L,
Conducted at 12°C)

Table 43. TCE Mass Balance for ORNL Exp. 4b-R3 (TSF-05 GW).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	43	43	0.012	39	11	NA	50
			0%	90%	26%	NA	115%
Control (#2)	43	43	0.007	39	11	NA	50
			0%	90%	26%	NA	116%
0.01% (#1)	43	43	0.006	10†	4	29	43
			0%	23%†	9%	69%	101%
0.01% (#2)	43	43	0.034	10†	4	29	43
			0%	23%†	9%	67%	100%
0.1% (#1)	42	42	0.015	0†	1	42	43
			0%	0%†	3%	100%	103%
0.1% (#2)	39	39	0.012	0†	1	39	40
			0%	0%†	2%	100%	103%

† These values were obtained from extractions of the post-treatment reactors.

Table 44. MnO$_4^-$ Consumption Data for ORNL Exp. 4b-R3 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO$_4^-$)	Initial Loading (mg MnO$_4^-$/g)	Cum. Consumed (mg MnO$_4^-$)	Cum. Consumed (mg MnO$_4^-$/g)
0.01% (#1)	39.6	0.10	39.42	0.10
0.01% (#2)	39.6	0.10	39.40	0.10
0.1% (#1)	396.0	0.99	73.00	0.18
0.1% (#2)	396.0	0.99	68.10	0.17

[a.] Consumption is computed after 96 hr reaction time.

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ORNL Exp. 4b-R4
(TSF-05 GW, No Sludge, 100,000 TCE, 0 Other, 1% and 3% MnO4⁻)

This experiment investigated the oxidation of TSF-05 GW spiked at 100,000 µg/L TCE. The TCE, MnO_4^- and pH values with time are presented in Figures 72, 73, and 74, respectively. Tables 45 and 46 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

In this experiment, the method used to prepare the TSF-05 spike solution differed from the approach set forth in the testplan. Here, a small quantity of pure phase TCE (≈280 µL) was added to the Tedlar bag filled with sparged GW. The approach described in the testplan involved the use of a saturated aqueous TCE solution rather than pure phase TCE in the spiking step. A 96 hr reaction time was also evaluated in this experiment, while the tests were terminated at 24 hrs in the procedure described in the testplan.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 147,03µg/L (σ= 428 µg/L). After transfer to the test reactors the groundwater TCE concentration ranged between 102,900 and 110,600 µg/L (T=0 aliquots) prior to the start of the oxidation reactions. While a part of this wide variability may be due to human error in performing sample dilutions, some TCE was likely lost during transfer of the spiked GW to the test reactors.

As in the previous experiment involving 100,000 µg/L TCE (Exp. 4b-R3), the extractions of the first charcoal bed of the desorption tubes contained measurable quantities of TCE. Like Experiment 4b-R3, TCE recoveries for the control samples were greater than 100% (110% and 114%). These two experimental runs were conducted concurrently. Hence, these samples also experienced the same discrepancy between initial and final measured TCE concentrations of the control samples.

This discrepancy resulting from sample holding times should not affect the validity of this experiment. In fact, the discrepancy should theoretically result in conservative TCE oxidation rates since a shorter holding time for the 24 hrs aliquots would be expected to produce a larger TCE residual at the end of the reaction period. Hence, the calculated reaction rates are less than the true reaction rates. It should be noted that this sample holding time problem likely affected other experiments. The effect was heightened here because of the very high TCE spike concentrations being evaluated. This problem is not believed to have adversely affected the results of the other experiments.

From Figure 72, the complete oxidation of TCE is observed in both the 1% and 3% MnO4⁻ reactors. Total TCE recoveries for all four (4) treatment reactors were 100%. While not called for in the testplan, the final treatment reactors were also extracted and analyzed in this experiment. These extractions also verified the absence of TCE after 96 hrs. Enough TCE data points are not available to compute rate constants; however, the observed oxidation rates are greater than 88 and 84 mg TCE/hr for the 1% and 3% MnO4⁻ reactors, respectively.

While all of the initial 100,000 μg/L TCE was oxidized in this experiment, very little oxidant was consumed in the process (Figure 73). Less than 2% of the initial MnO_4^- mass was consumed for either initial oxidant loading.

The pH values within the treatment reactors decreased significantly during the reaction period. The greatest pH decreases occurred in the 1% MnO_4^- reactors. Net pH decreases of 1.6 and 1.0 pH units were observed for the 1% and 3% MnO_4^- reactors, respectively. The pH decreases were less in magnitude than those observed in Exp. 4b-R3 where 0.01% and 0.1% MnO_4^- loadings were evaluated at the same nominal TCE concentration. This effect is likely a result of the greater ionic strength of the 1% and 3% residual oxidant solutions when compared to the 0.01% and 0.1% MnO_4^- solutions. This also explains why the net pH decrease observed for the 3% MnO_4^- reactors was less than that for the 1% MnO_4^- reactors.

Finally, it is interesting to note from Figures 72 and 73 that nearly the same TCE and final MnO_4^- consumption values would have been obtained for these particular oxidant loadings even if a 24 hr, rather than a 96 hr, reaction period had been evaluated.
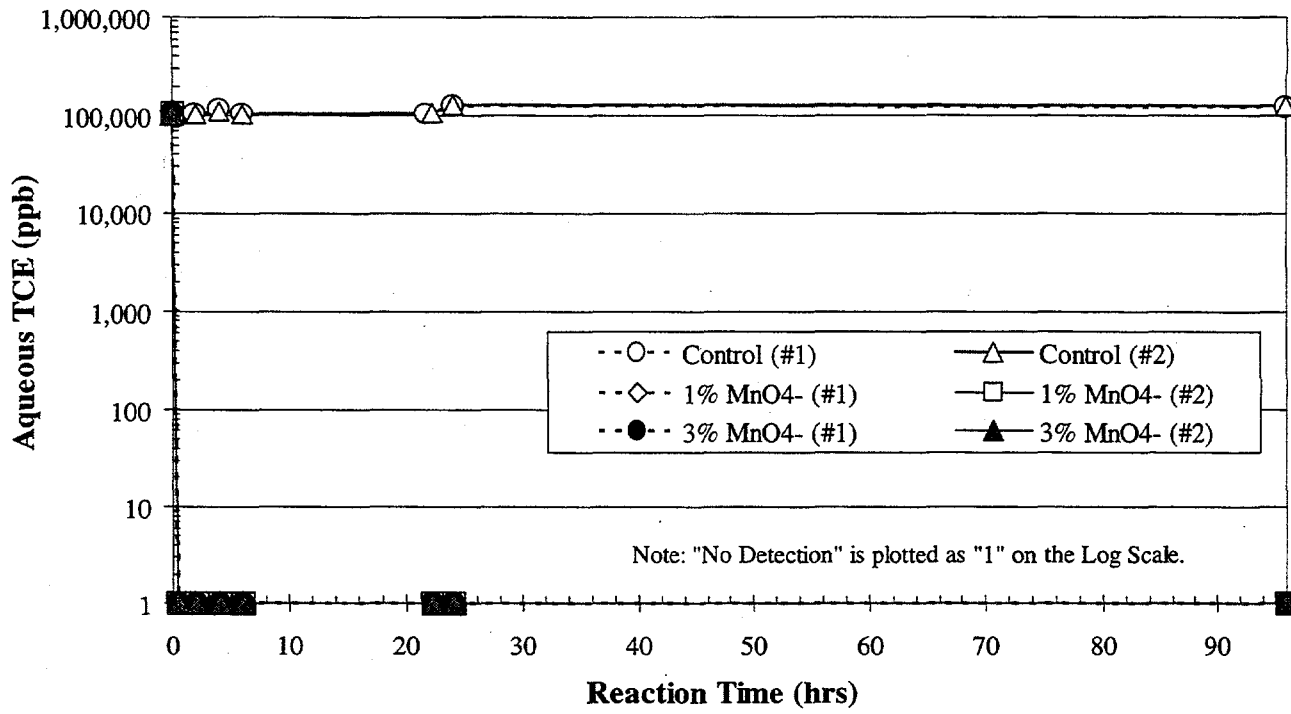
Figure 72. TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R4, Initial TCE= 100,000 µg/L,
Conducted at 12°C)
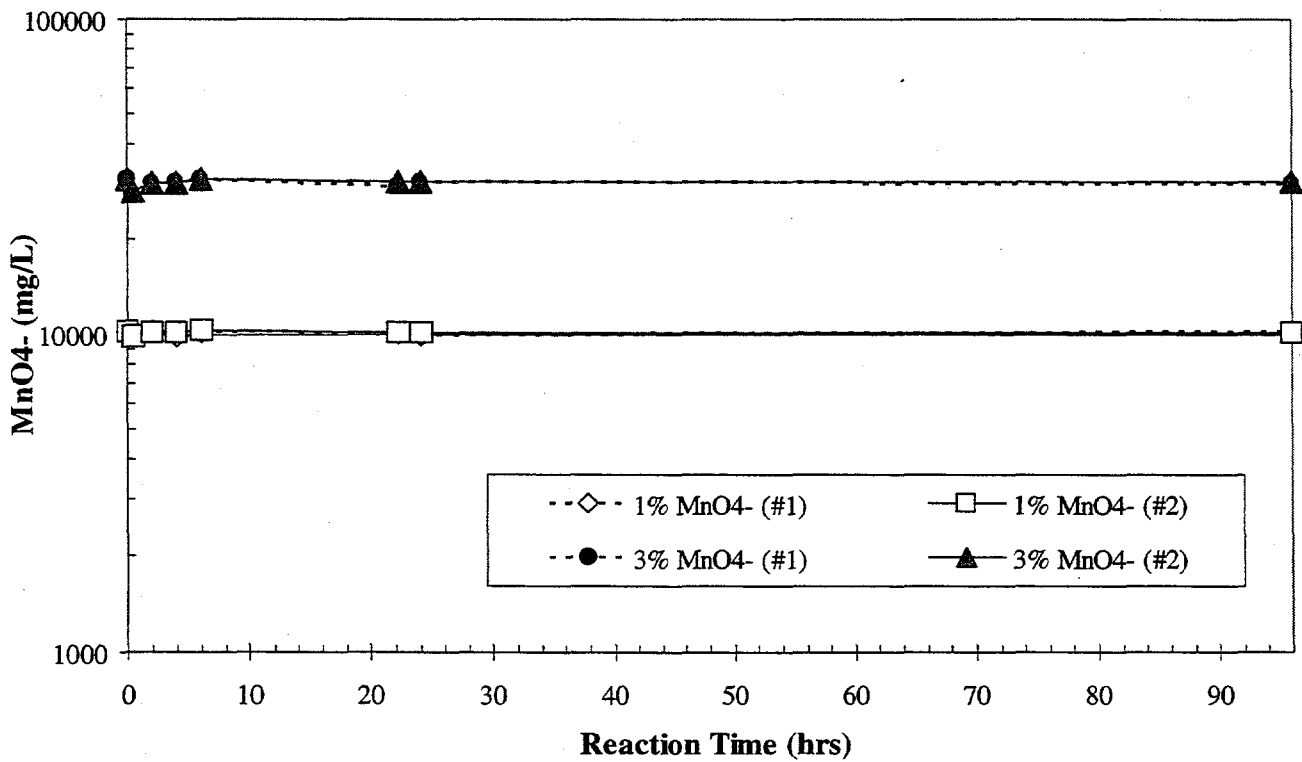
Figure 73. MnO$_4^-$ vs. Time, TSF-05 GW, (ORNL Exp. 4b-R4, Initial TCE= 100,000 µg/L,
Conducted at 12°C)
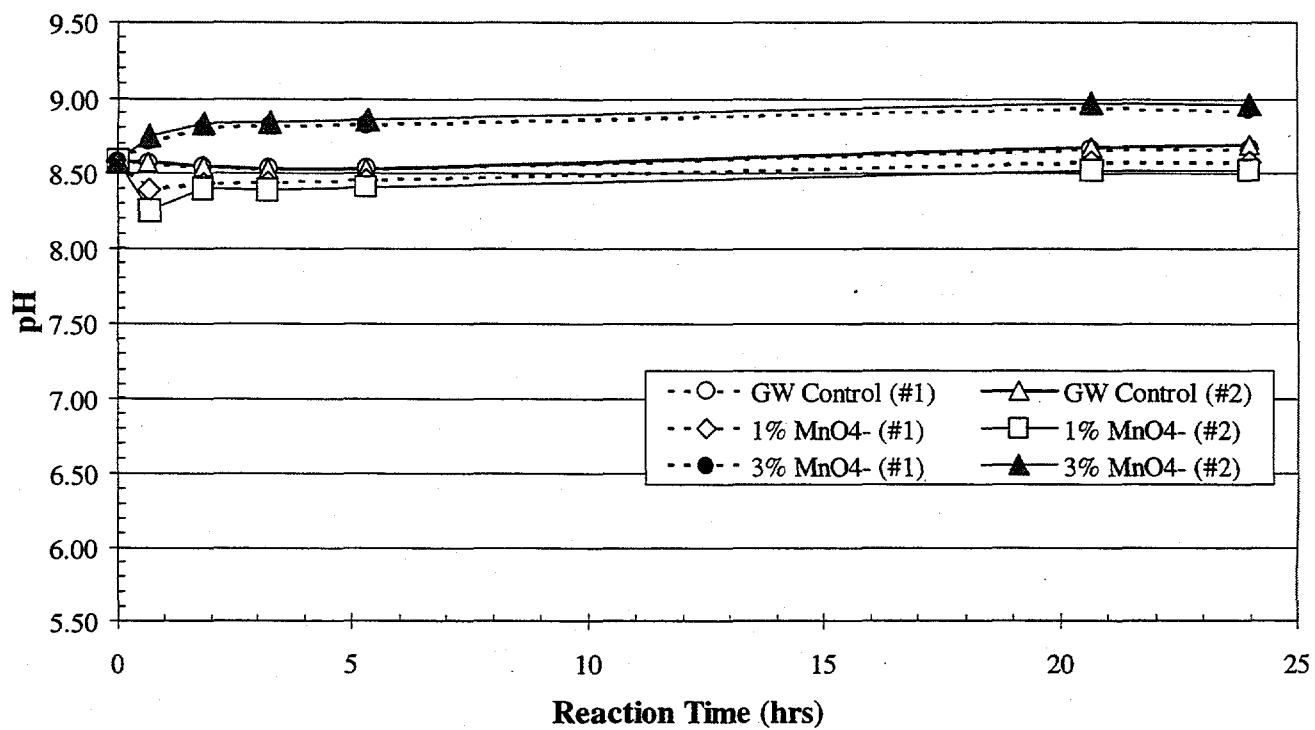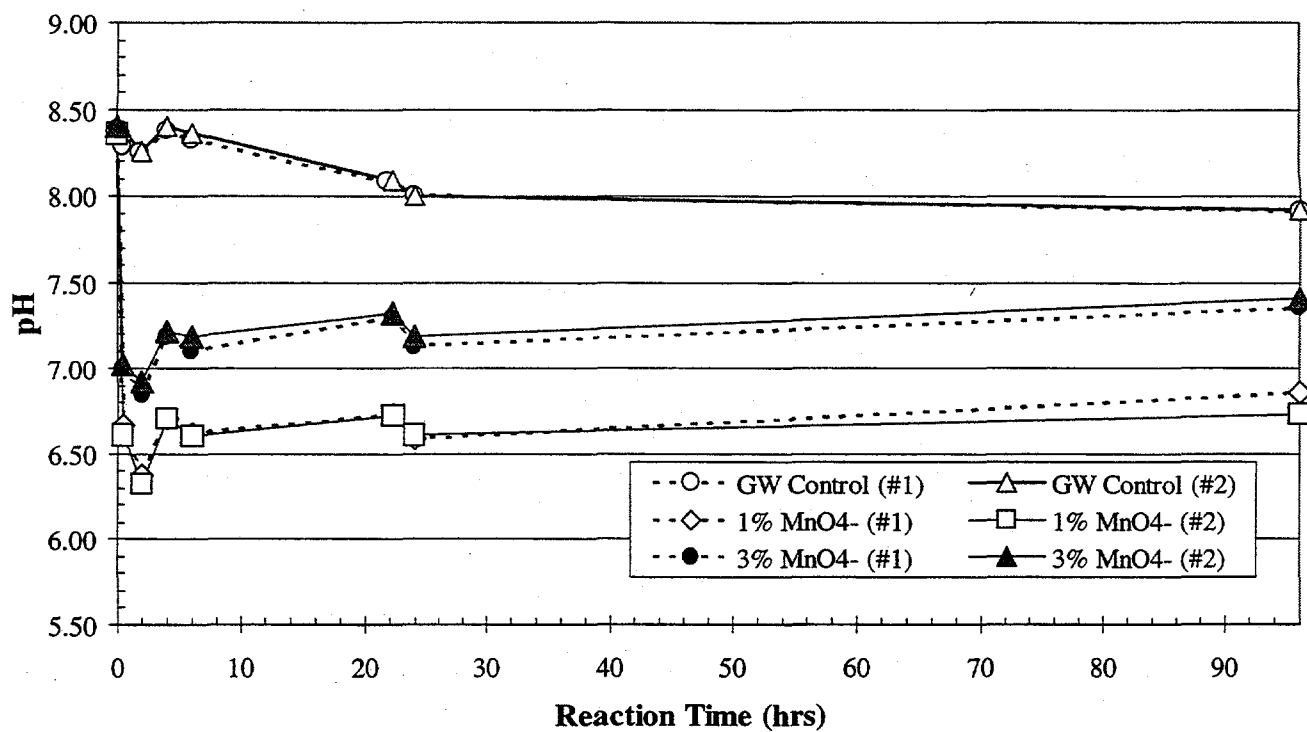
Figure 74. pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R4 Initial TCE= 100,000 µg/L, Conducted at 12°C)

Table 45. TCE Mass Balance for ORNL Exp. 4b-R4 (TSF-05 GW).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	43	43	0.027	36	11	NA	47
			0%	84%	26%	NA	110%
Control (#2)	43	43	0.005	38	11	NA	49
			0%	88%	26%	NA	114%
1% (#1)	44	44	0.008	0	1	43	44
			0%	0%	3%	97%	100%
1% (#2)	43	43	0.001	0	1	42	43
			0%	0%	3%	97%	100%
3% (#1)	43	43	0.004	0	1	42	43
			0%	0%	3%	97%	100%
3% (#2)	41	41	0.008	0	1	40	41
			0%	0%	3%	97%	100%

† These values were obtained from extractions of the post-treatment reactors.

Table 46. MnO_4^- Consumption Data for ORNL Exp. 4b-R4 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
1% (#1)	3977	10.2	83	0.2
1% (#2)	3977	10.2	51	0.1
3% (#1)	12051	30.9	149	0.4
3% (#2)	12051	30.9	149	0.4

a. Consumption is computed after 96 hr reaction time.

ORNL Exp. 4b-R5
(TSF-05 GW, No Sludge, 100,000 TCE, 10,000 Other, 0.01% and 0.1% MnO_4^-)

This experiment investigated the oxidation of TSF-05 GW spiked at 100,000 μg/L TCE. In this experiment, TSF-05 GW was also spiked with other VOCs (co-contaminants). In addition to TCE, the groundwater was also spiked with 1,1-DCE; trans-1,2 DCE; and cis-1,2 DCE at a nominal concentration of 10,000 μg/L of each compound. Otherwise, the test conditions evaluated in this experiment were to be the same as those studied in Experiment 4b-R3.

Plots of TCE; 1,1-DCE; trans-1,2 DCE; and cis-1,2 DCE with time are presented in Figures 75, 76, 77, and 78, respectively. Plots of MnO_4^- and pH values with time are presented in Figures 79 and 80, respectively. Tables 47 and 48 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition. Mass balance tables were not prepared for the co-contaminants since the intent of the experiment was to determine whether the presence of these compounds affected the overall TCE oxidation characteristics.

In this experiment, the method used to prepare the TSF-05 spike solution differed from the approach set forth in the testplan. Here, a small quantity of pure phase TCE ($\approx$200 μL) was added to the Tedlar bag filled with sparged GW. The approach described in the testplan involved the use of a saturated aqueous TCE solution rather than pure phase TCE in the spiking step. The co-contaminants were also added to the Tedlar bag in the same manner.

The GC used in the TCE analyses for this co-contaminants experiment was different than the one used for all other treatment experiments. The instrument was properly calibrated, but the MDL was 10 μg/L rather than the 5 μg/L obtained using the other instrument. A very small amount of TCE was detected in the analysis of the QA/QC solvent blank, which was ran between every 10 or 11 samples. The TCE concentrations determined for the QA/QC blank ranged between 0.2 to 6 μg/L. The peak area counts for these analyses were much less than that of the lowest calibration standard (10 μg/L). While these small TCE quantities in the blank sample may be a result of sample carryover, it its not expected to affect the validity of the data. The sequence for the analyses was such that all T=0 samples were analyzed before T=0.5 samples were analyzed, and so forth.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 18,800 μg/L (σ= 1,580 μg/L). After transfer to the test reactors, the groundwater TCE concentration ranged between 19,340 and 30,580 μg/L (T=0 aliquots) prior to the start of the oxidation reactions. Although an overnight equilibration (at 12°C) of the spike solution was performed, it is apparent that the pure phase TCE added to the Tedlar bag was not equilibrated long enough before distribution into the test reactors. The initial TCE concentrations of the 0.1% MnO_4^- reactors were greater than those of the control and 0.01% MnO_4^- reactors. This result makes sense if the water in the Tedlar bag was not well mixed before distribution into the reactors. Being the last reactors to be filled, the 0.1% MnO_4^- reactors may have received a higher amount of TCE than the other reactors. This problem was not considered detrimental

since the aqueous T=0 hrs TCE concentrations, which are used in the mass balance computations, were determined for each reactor.

TCE recoveries for the control samples were 110% and 105%, suggesting that little TCE was lost to volatilization. The >100% TCE recoveries in the control were computed because the aqueous TCE concentrations at T=24 hrs were greater than those at T=0 hrs. This phenomenon is either due to (1) the sample holding time effect as noted in Exps. 4b-R3 and 4b-R4 or (2) the occurrence of further TCE spike equilibration (i.e., solubilization of pure phase TCE) during the course of the reaction period. A very small quantity of TCE was detected in the charcoal desorption tubes for the control reactors and the first 0.01% MnO_4^- reactor. (The concentrations were significantly less than the MDL and perhaps a result of sample carryover between analyses as discussed above.) TCE recoveries for the four treatment reactors ranged between 100-102%.

As in other experiments, TCE oxidation of greater than an order of magnitude was initially observed. From Figure 75, however, it appears that all of the TCE was not completely oxidized from the 0.01% MnO_4^- reactors, even though a residual MnO_4^- concentration existed (Figure 79). This is the first experiment in which both a residual TCE and MnO_4^- concentration existed at the end of the reaction period. These residual TCE concentrations ($\approx$20-110 µg/L at 24 hrs) are believed to be "real" and not a result of instrument performance or solvent contamination since the residual concentrations observed here are much greater than the 10 µg/L MDL. Hence, it is possible that the presence of the co-contaminants slowed and/or halted the TCE oxidation reaction.

The aqueous TCE data between T=0 and T=3 hrs was used to compute the reaction rate for the initial, rapid step of the oxidation reaction in the 0.01% MnO_4^- reactors. The aqueous TCE data were plotted in Figure 81 and Figure 82 as $\ln(C/C_o)$ vs. Time for the first and second 0.01% reactors, respectively. These linear regressions resulted in first order rate constants of k= 1.66 hr^{-1} and 1.55 hr^{-1}. While the fit of the data to a first order rate model may not be optimal, attempts to evaluate other rate models were not made since the mechanisms occurring in such a complex system are not known.

While a residual TCE concentration was measured for the 0.1% MnO_4^- reactors, the values obtained are less than that of the lowest calibration standard. Hence, it is very possible that the observed TCE concentrations are not "real". It appears that nearly complete TCE oxidation occurred in the 0.1% MnO_4^- reactors at T= 2 hrs. (This value was determined by extrapolating the initially rapid portion of the curve in Figure 75 to a concentration of 1.0 µg/L TCE.) Enough data points are not available to compute a rate constant. However, if one assumes nearly complete TCE oxidation within 2 hrs, an oxidation rate greater than 7.7 mg TCE/hr is obtained for the 0.1% MnO_4^- reactors. Note that complete oxidation occurred within 0.5 hrs for all the other TSF-05 GW experiments having a 0.1% MnO_4^- loading (Exps. 4b-R1 and 4b-R3). Hence, as noted above for the 0.01% MnO_4^- reactors, the TCE oxidation rate observed for the 0.1% MnO_4^- loading may also be affected by the presence of the VOC co-contaminants.

As suggested in the above paragraphs, the TCE oxidation rate may be affected by the presence of the co-contaminants. The initial aqueous concentrations (T=0 hrs) of the co-contaminants were approximately 3,300 µg/L 1,1-DCE; 3,530 µg/L trans-1,2 DCE; and 7,400 µg/L cis-1,2 DCE.

From Figures 76, 77, and 78, it appears that the control reactors performed effectively in minimizing the volatilization of the co-contaminants. Thus, the rapid decreases in the co-contaminant concentrations within the treatment reactors are due to oxidation mechanisms. (Recall that mass balance computations were not performed on the co-contaminants) Oxidation of 1,1-DCE occurred within 2 hrs for the 0.01% MnO_4^- reactors and within 0.5 hrs for the 0.1% MnO_4^- reactors. Similarly, complete trans-1,2 DCE oxidation occurred within the first 0.5 hrs after oxidant addition for both initial oxidant loadings. Finally, cis-1,2 DCE oxidation was completed within 3 hrs and within 0.5 hrs for the 0.01% and 0.1% MnO_4^- reactors, respectively.

Approximately 62% of the oxidant added to the 0.01% MnO_4^- reactors was consumed. The rate of oxidant consumption (Figure 79) was gradual for these treatment reactors. This trend correlates well with the slow TCE oxidation rate observed in Figure 75. Only about 12% of the initial MnO_4^- mass was consumed in the 0.1% MnO_4^- reactors.

The pH values within the treatment reactors decreased rapidly during the oxidation of TCE and the co-contaminants (Figure 80). The pH of the 0.01% MnO_4^- reactors reached a final pH value of ≈ 7.4, a net decrease of >1 pH unit. Similarly, the 0.1% MnO_4^- loading resulted in final pH values of ≈ 7.2, a net decrease of >1.3 pH units. The total concentration of VOCs in this experiment (TCE + co-contaminants) is on the order of 35,000 µg/L VOCs. Furthermore, the magnitude of the net pH decreases observed here falls in between that measured in Experiments 4B-R1 and 4B-R3, in which the initial TCE concentrations are nominally 10,000 and 100,000 µg/L, respectively.
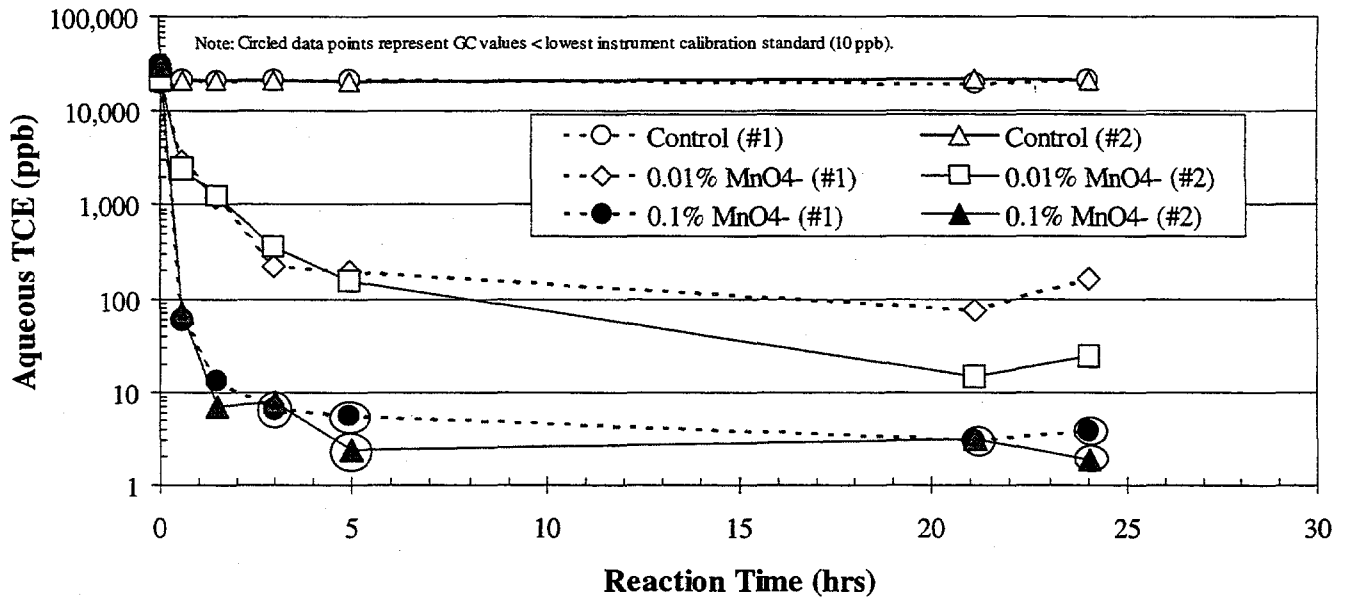
Figure 75. TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R5, Initial Target TCE= 100,000 μg/L, Co-Contaminants = 10,000 μg/L, Conducted at 12°C)
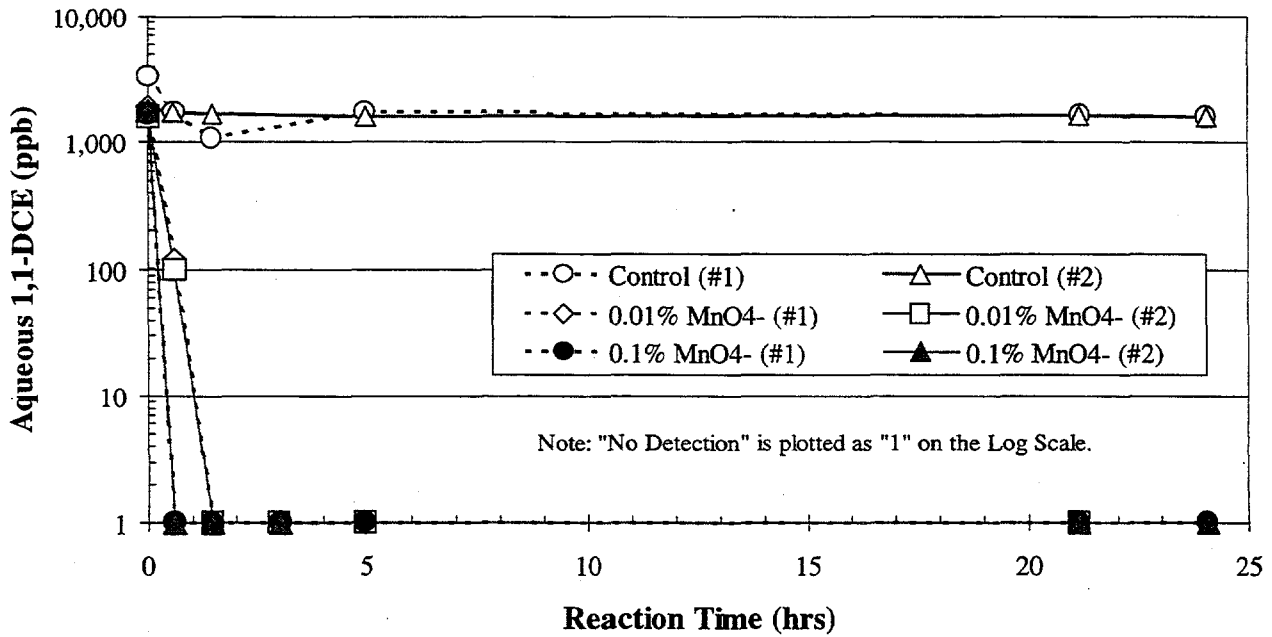
Figure 76. 1,1-DCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R5, Initial Target TCE= 100,000 μg/L, Co-Contaminants = 10,000 μg/L, Conducted at 12°C)
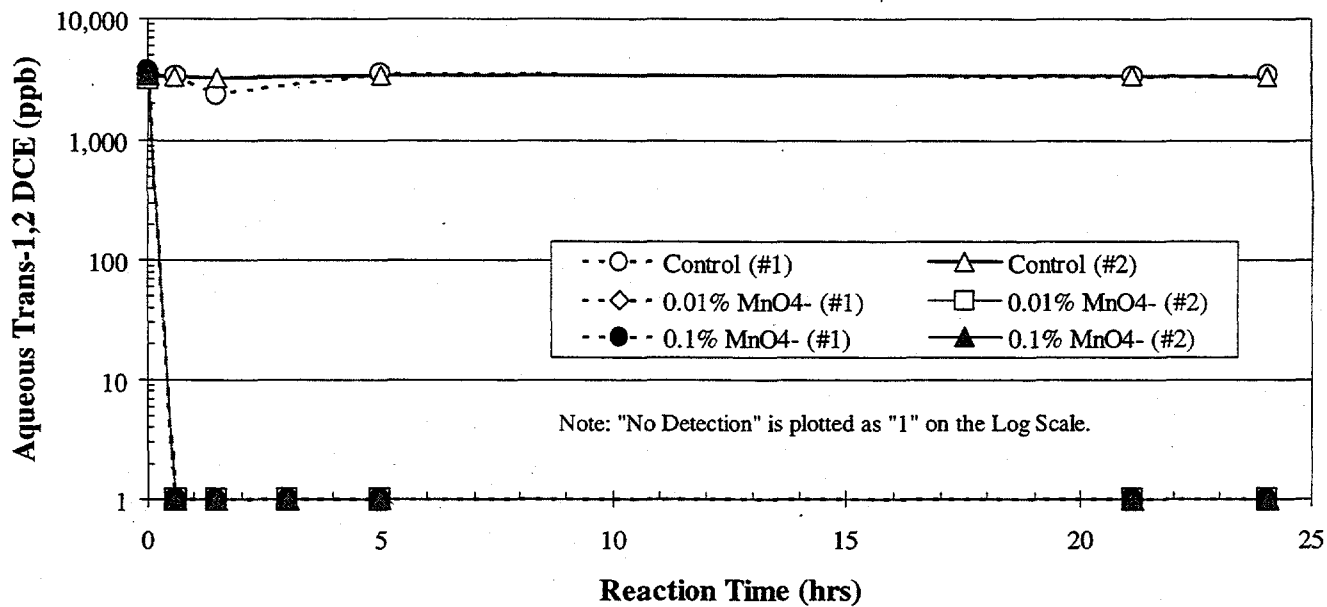
Figure 77. Trans-1,2 DCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R5, Initial Target TCE= 100,000 µg/L, Co-Contaminants = 10,000 µg/L, Conducted at 12°C)
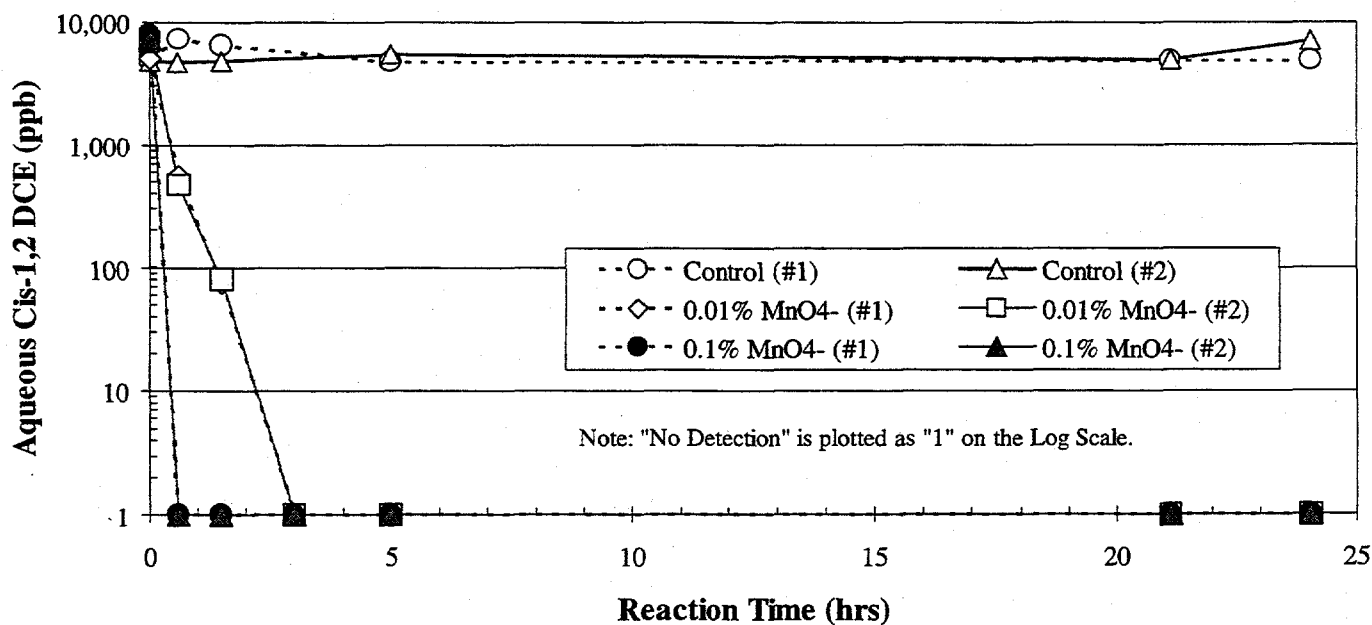
Figure 78. Cis-1,2 DCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R5, Initial Target TCE= 100,000 µg/L, Co-Contaminants = 10,000 µg/L, Conducted at 12°C)
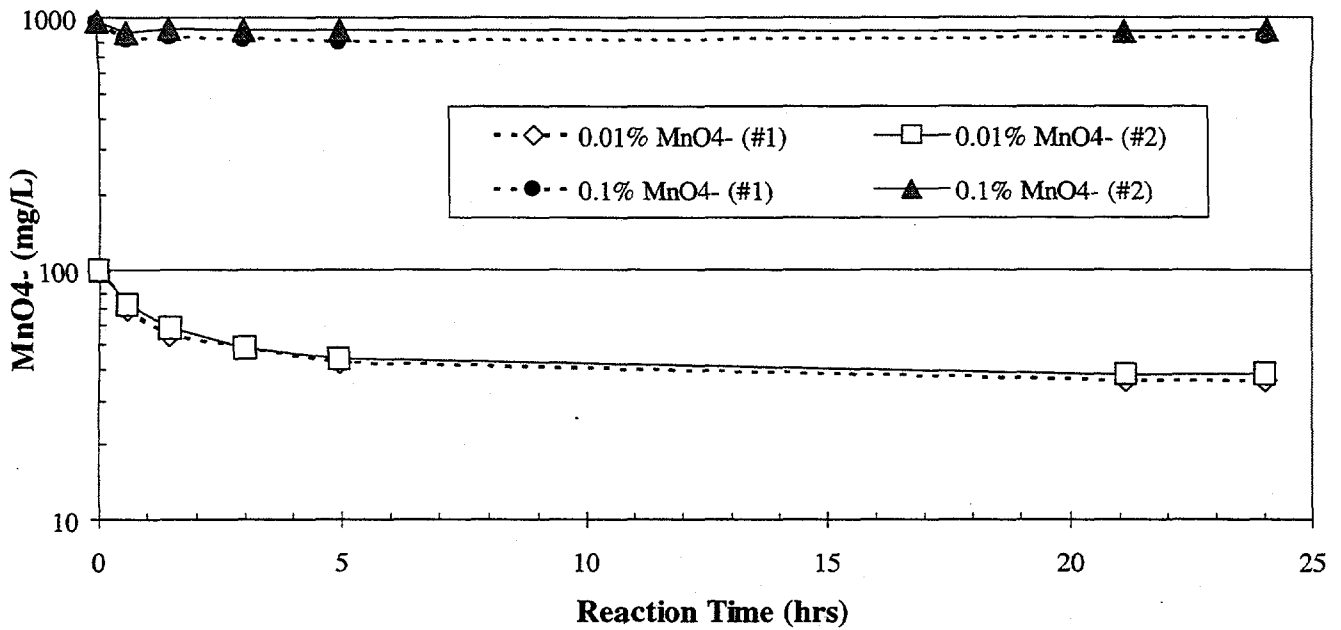
Figure 79. MnO$_4$⁻ vs. Time, TSF-05 GW, (ORNL Exp. 4b-R5, Initial Target TCE= 100,000 µg/L, Co-Contaminants = 10,000 µg/L Conducted at 12°C)
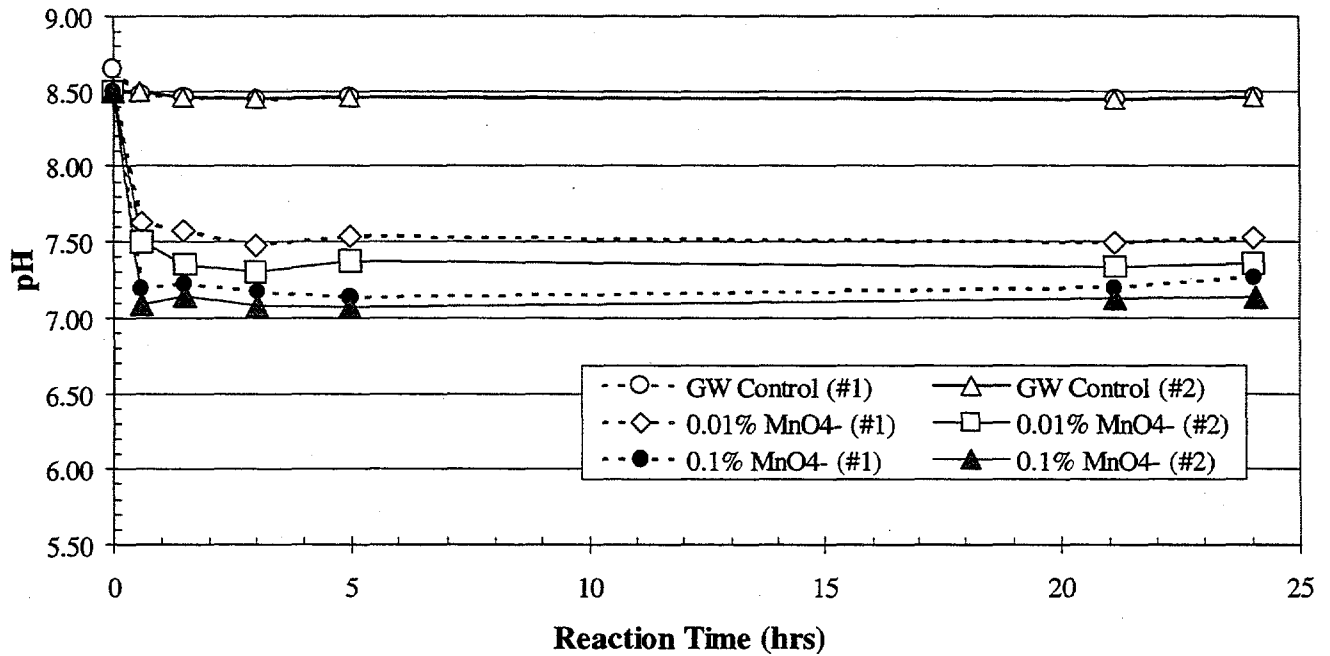
Figure 80. pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R5 Initial Target TCE= 100,000 µg/L, Co-Contaminants = 10,000 µg/L Conducted at 12°C)
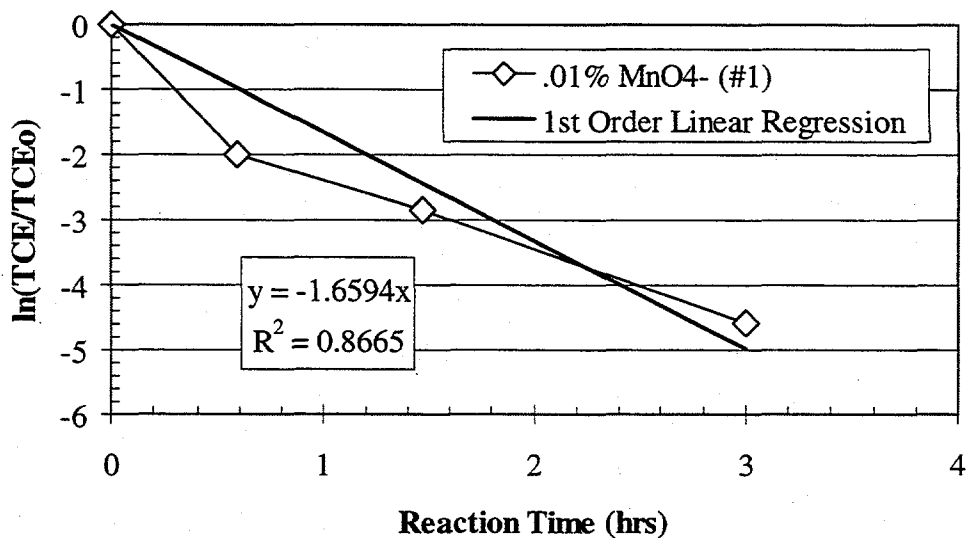
Figure 81. First Order TCE Oxidation Rate Constant for the 0.01% MnO$_4^-$ (#1) Reactor, TSF-05 GW, (ORNL Exp. 4b-R5, Initial TCE= 100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
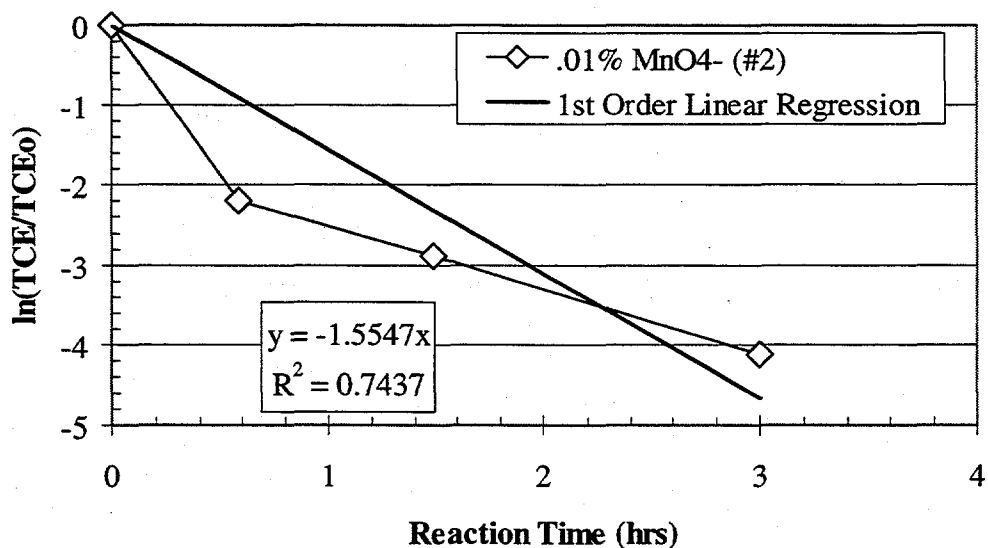
Figure 82. First Order TCE Oxidation Rate Constant for the 0.01% MnO$_4^-$ (#2) Reactor, TSF-05 GW, (ORNL Exp. 4b-R5, Initial TCE= 100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 47. TCE Mass Balance for ORNL Exp. 4b-R5 (TSF-05 GW).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	9.5	9.5	7.2E-06	9.4	1.1	NA	10.4
			0%	99%	11%	NA	110%
Control (#2)	10.1	10.1	4.6E-06	9.6	1.1	NA	10.6
			0%	94%	11%	NA	105%
0.01% (#1)	10.6	10.6	4.9E-06	0.00	0.2	10.4	10.6
			0%	0%	2%	98%	100%
0.01% (#2)	11.0	11.0	0.0E+00	0.00	0.2	10.8	11.0
			0%	0%	2%	98%	100%
0.1% (#1)	15.4	15.4	0.0E+00	0.00	0.2	15.6	15.8
			0%	0%	1%	101%	102%
0.1% (#2)	15.3	15.3	0.0E+00	0.00	0.2	15.5	15.7
			0%	0%	1%	101%	102%

Table 48. MnO_4^- Consumption Data for ORNL Exp. 4b-R5 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	48.7	0.10	30.7	0.06
0.01% (#2)	48.7	0.10	29.7	0.06
0.1% (#1)	487.3	0.95	60.3	0.12
0.1% (#2)	487.3	0.96	36.7	0.07

a. Consumption is computed after 24 hr reaction time.

ORNL Exp. 4b-R6
(TSF-05 GW, No Sludge, 100,000 TCE, 10,000 Other, 1% and 3% MnO$_4$⁻)

This experiment investigated the oxidation of TSF-05 GW spiked at 100,000 µg/L TCE. In this experiment, TSF-05 GW was also spiked with other VOCs (co-contaminants). In addition to TCE, the groundwater was also spiked with 1,1-DCE; trans-1,2 DCE; and cis-1,2 DCE at a nominal concentration of 10,000 µg/L each compound. Otherwise, the test conditions evaluated in this experiment were to be the same as those studied in Experiment 4b-R4.

Plots of TCE; 1,1-DCE; trans-1,2 DCE; and cis-1,2 DCE with time are presented in Figures 83, 84, 85, and 86, respectively. Plots of MnO$_4$⁻ and pH values with time are presented in Figures 87 and 88, respectively. Tables 49 and 50 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition. Note that mass balance tables were not prepared for the co-contaminants since the intent of the experiment was to determine whether the presence of these compounds affected the overall TCE oxidation characteristics.

In this experiment, the method used to prepare the TSF-05 spike solution differed from the approach set forth in the testplan. Here, a small quantity of pure phase TCE (≈200 µL) was added to the Tedlar bag filled with sparged GW. The approach described in the testplan involved the use of a saturated aqueous TCE solution rather than pure phase TCE in the spiking step. The co-contaminants were also added to the Tedlar bag in the same manner.

The GC used in the TCE analyses for this co-contaminants experiment was different than the one used for all other treatment experiments. The instrument was properly calibrated, but the minimum detection limit was 10 µg/L rather than the 5 µg/L obtained using the other instrument. A very small amount of TCE was detected in the analysis of the QA/QC solvent blank, which was ran between every 10 or 11 samples. This solvent blank was analyzed nine (9) times during the course of the analytical sequence. TCE was not detected in 5 of these analyses. The remaining 4 analyses of the blank resulted in TCE concentrations between <1 µg/L and 11 µg/L. (The peak area counts for these blanks were less than that of the lowest calibration standard of 10 µg/L.) While these small TCE quantities in the blank sample may be a result of sample carryover, it its not expected to affect the validity of the data. The sequence for the analyses was such that all T=0 samples were analyzed before T=0.5 samples were analyzed, and so forth.

After equilibration, the average initial aqueous TCE concentration of the spike solution was 11,300 µg/L (σ= 183 µg/L). After transfer to the test reactors, the groundwater TCE concentration ranged between 11,150 and 40,840 µg/L (T=0 aliquots) prior to the start of the oxidation reactions. Although an overnight equilibration (at 12°C) of the spike solution was performed, it is apparent that the pure phase TCE added to the Tedlar bag was not equilibrated long enough before distribution into the test reactors. The initial TCE concentrations of the 3% MnO$_4$⁻ reactors were greater than those of the control and 1% MnO$_4$⁻ reactors. This result makes sense if the water in the Tedlar bag was not well mixed before distribution into the reactors. Being the last reactors to be filled, the 3% MnO$_4$⁻ reactors may have received a higher amount of

TCE than the other reactors. This problem was not considered detrimental since the aqueous T=0 hrs TCE concentrations, which are used in the mass balance computations, were determined for each reactor.

TCE recoveries for the control samples were 97% and 104%, suggesting that little TCE was lost to volatilization. The >100% TCE recovery for the first control reactor was obtained because the aqueous TCE concentration at T=24 hrs was greater than that at T=0 hrs. This phenomenon is either due to (1) the sample holding time effect as noted in Exps. 4b-R3 and 4b-R4 or (2) the occurrence of further TCE spike equilibration (i.e., solubilization of pure phase TCE) during the course of the reaction period. A very small quantity of TCE was detected in the charcoal desorption tubes for most of the test reactors in this experiment. (The concentrations were significantly less than the minimum TCE detection limit and perhaps a result of sample carryover between analyses as discussed above.) TCE recoveries for the four treatment reactors were essentially 100%.

As in other experiments, TCE oxidation of greater than an order of magnitude was initially observed. From Figure 83, however, it appears that all of the TCE was not completely oxidized from the 1% and 3% MnO_4^- reactors, even though a residual MnO_4^- concentration existed for both oxidant loadings (Figure 87). Note however that all of the values obtained after T=0.5 hrs were less than that of the lowest calibration standard. Hence, it is very possible that these residual TCE concentrations are not "real". In fact, It appears that TCE was effectively oxidized in both the 1% and 3% MnO_4^- reactors within the first 1 hr. (This value was determined by extrapolating the initially rapid portion of the curves in Figure 83 to a concentration of 0.1 $\mu g/L$ TCE.) Thus, these are not enough data points available to compute a rate constant. However, if one assumes nearly complete TCE oxidation within 1 hr, oxidation rates greater than 6.9 and 17.4 mg TCE/hr are obtained for the 1% and 3% MnO_4^- reactors, respectively. Note that complete oxidation occurred within 0.5 hrs for all the other TSF-05 GW experiments with a 3% MnO_4^- loading (Exps. 4b-R1 and 4b-R3). Hence, the TCE oxidation rates observed here (at least for the 3% MnO_4^- loading) may be affected by the presence of the VOC co-contaminants.

As suggested in the above paragraphs, the TCE oxidation rate may be affected by the presence of the co-contaminants. The initial aqueous concentrations (T=0 hrs) of the co-contaminants were approximately 15,600 $\mu g/L$ 1,1-DCE; 16,750 $\mu g/L$ trans-1,2 DCE; and 11,150 $\mu g/L$ cis-1,2 DCE. From Figures 84, 85, and 86 it appears that the control reactors performed effectively in minimizing the volatilization of the co-contaminants. Thus, the rapid decreases in the co-contaminant concentrations within the treatment reactors are due to oxidation mechanisms. (Recall that mass balance computations were not performed on the co-contaminants) Oxidation of all the co-contaminants occurred within 0.5 hrs for both the 1% and 3% MnO_4^- reactors.

As observed elsewhere for the nominal 1% and 3% oxidant loadings, the MnO_4^- added (as crystalline $KMnO_4$) to the treatment reactors did not readily dissolve (Figure 87). However, an overall 2-4% net decrease in amount of oxidant present at the end of the reaction period was observed for the 1% MnO_4^- reactors. About 23% of the initial MnO_4^- mass was consumed in the 3% MnO_4^- reactors.

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The pH values within the treatment reactors decreased rapidly during the oxidation of TCE and the co-contaminants (Figure 88). The greatest pH decreases occurred in the 1% MnO_4^- reactors. As discussed previously, this effect is likely a result of the greater ionic strength of the 3% oxidant solutions. The pH of the 1% MnO_4^- reactors reached a final pH value of ≈ 7.3, a net decrease of >1.2 pH units. The 3% MnO_4^- loading resulted in an average final pH values of ≈ 7.5, a net decrease of >1 pH unit. The total concentration of VOCs in this experiment (TCE + co-contaminants) is on the order of 54,000 µg/L VOCs. The magnitude of the net pH decreases observed here are similar to those observed in Experiment 4B-R4, where the initial TCE concentrations were also nominally 100,000 µg/L (but with no co-contaminants).
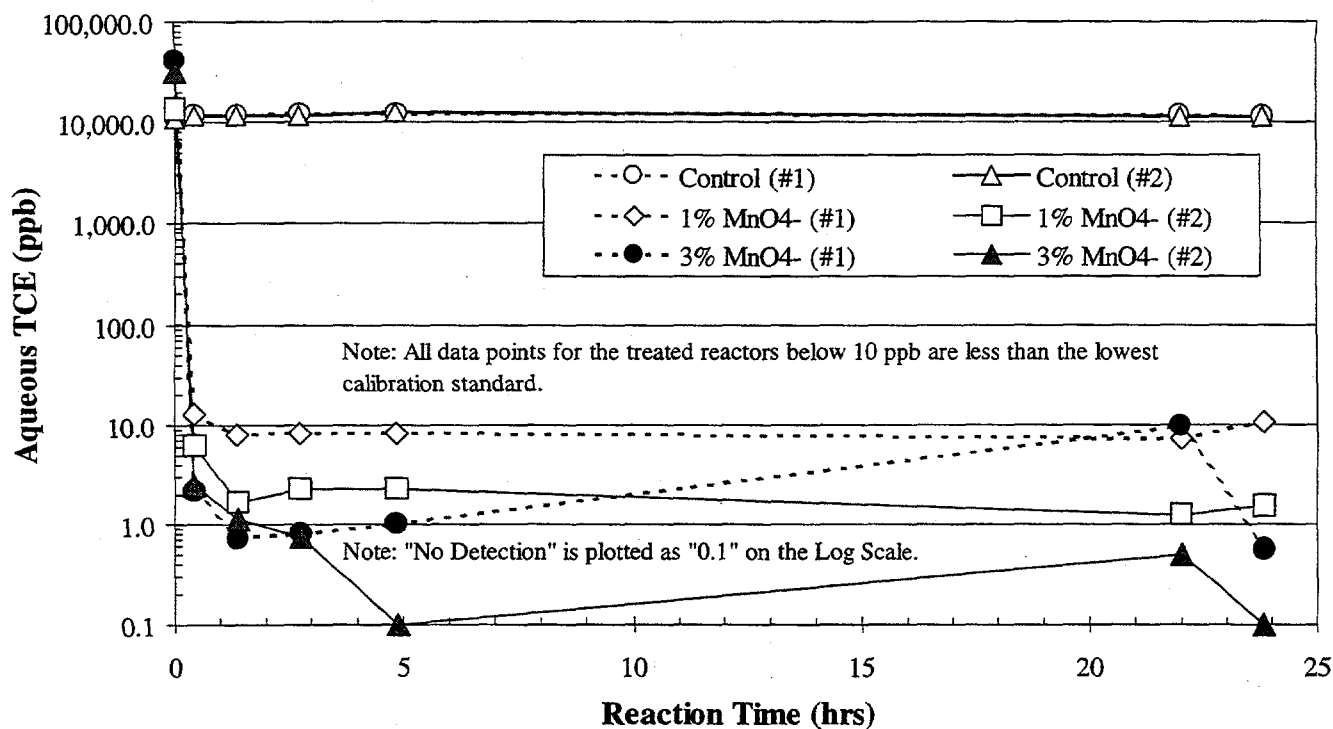
Figure 83. TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R6, Initial Target TCE= 100,000 μg/L, Co-Contaminants = 10,000 μg/L, Conducted at 12°C)
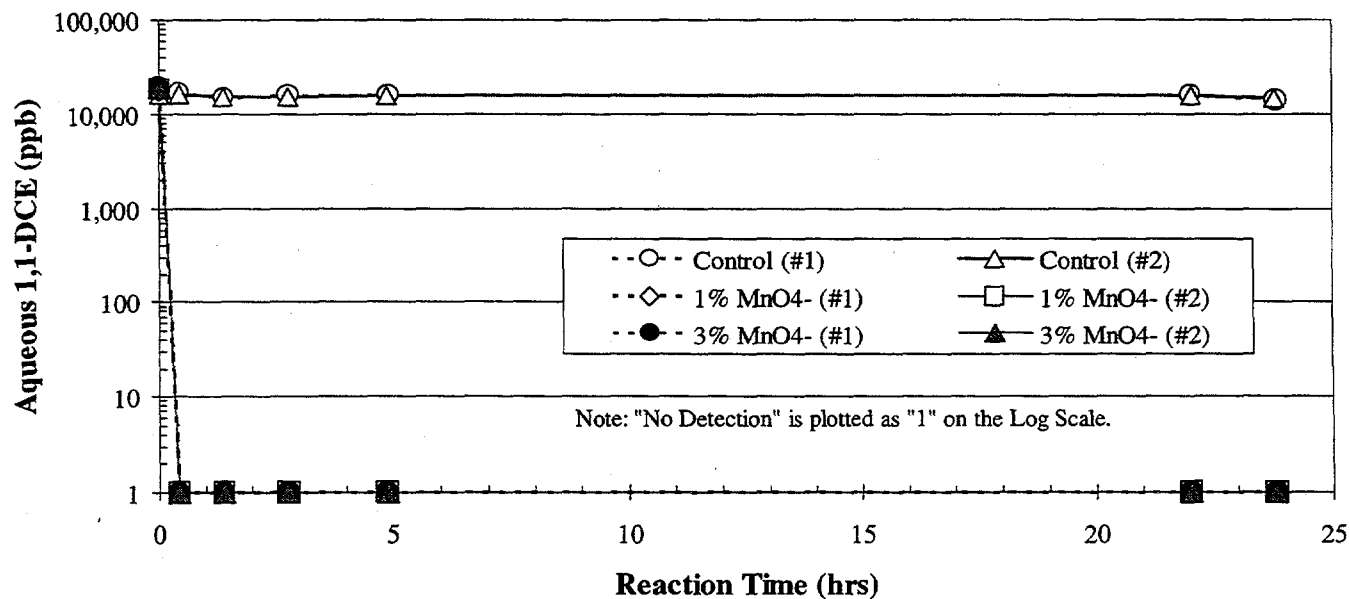
Figure 84. 1,1-DCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R6, Initial Target TCE= 100,000 μg/L, Co-Contaminants = 10,000 μg/L, Conducted at 12°C)
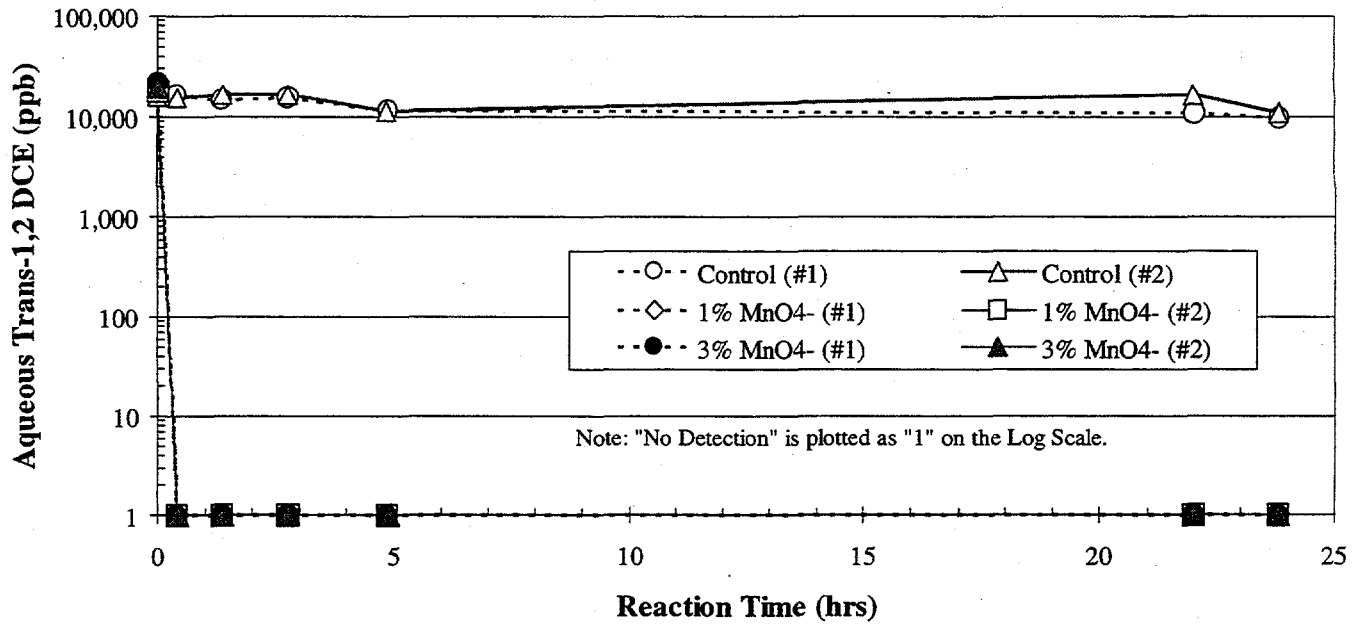
Figure 85. Trans-1,2 DCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R6, Initial Target TCE=
100,000 µg/L, Co-Contaminants = 10,000 µg/L, Conducted at 12°C)
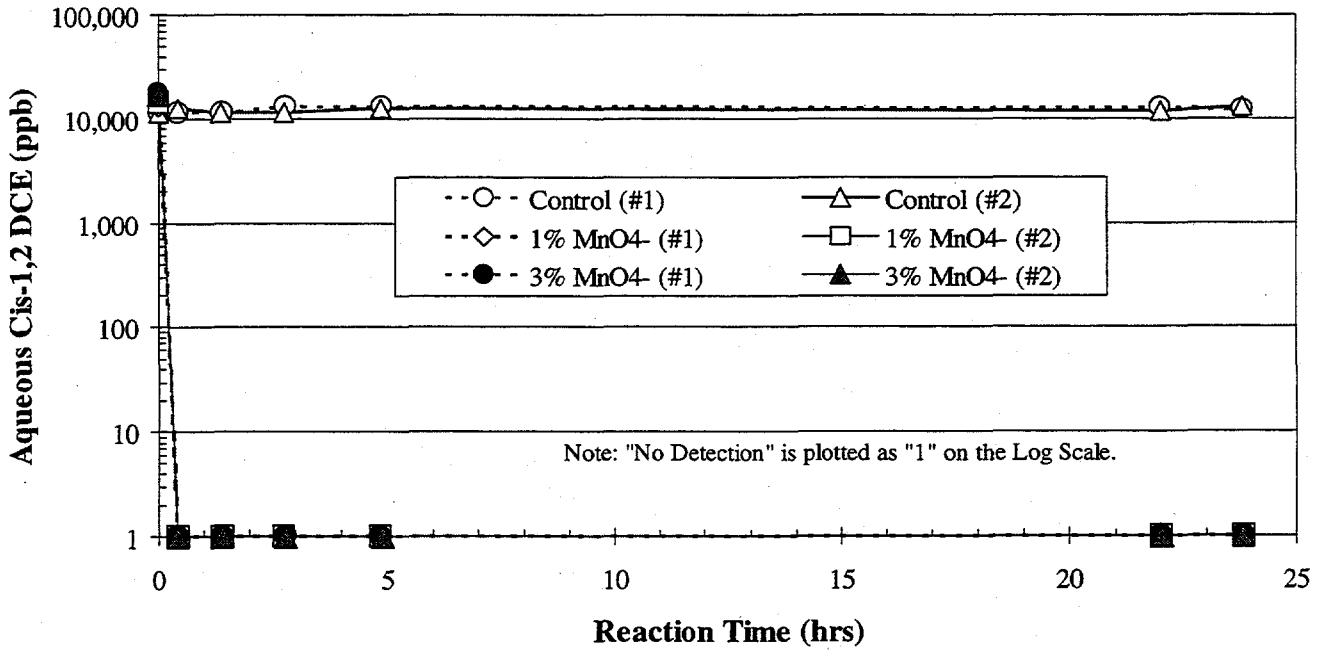
Figure 86. Cis-1,2 DCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R6, Initial Target TCE=
100,000 µg/L, Co-Contaminants = 10,000 µg/L, Conducted at 12°C)
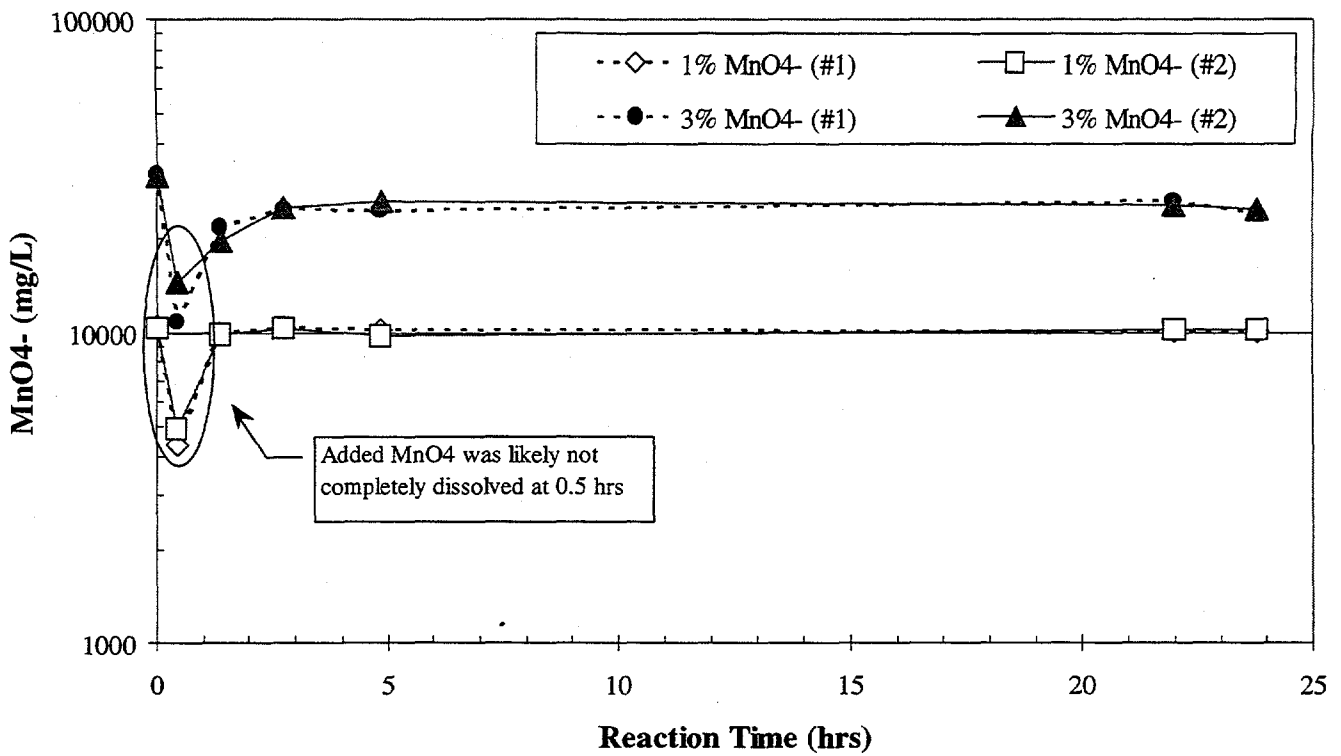
Figure 87.   MnO₄⁻ vs. Time, TSF-05 GW, (ORNL Exp. 4b-R6, Initial Target TCE= 100,000 μg/L, Co-Contaminants = 10,000 μg/L Conducted at 12°C)
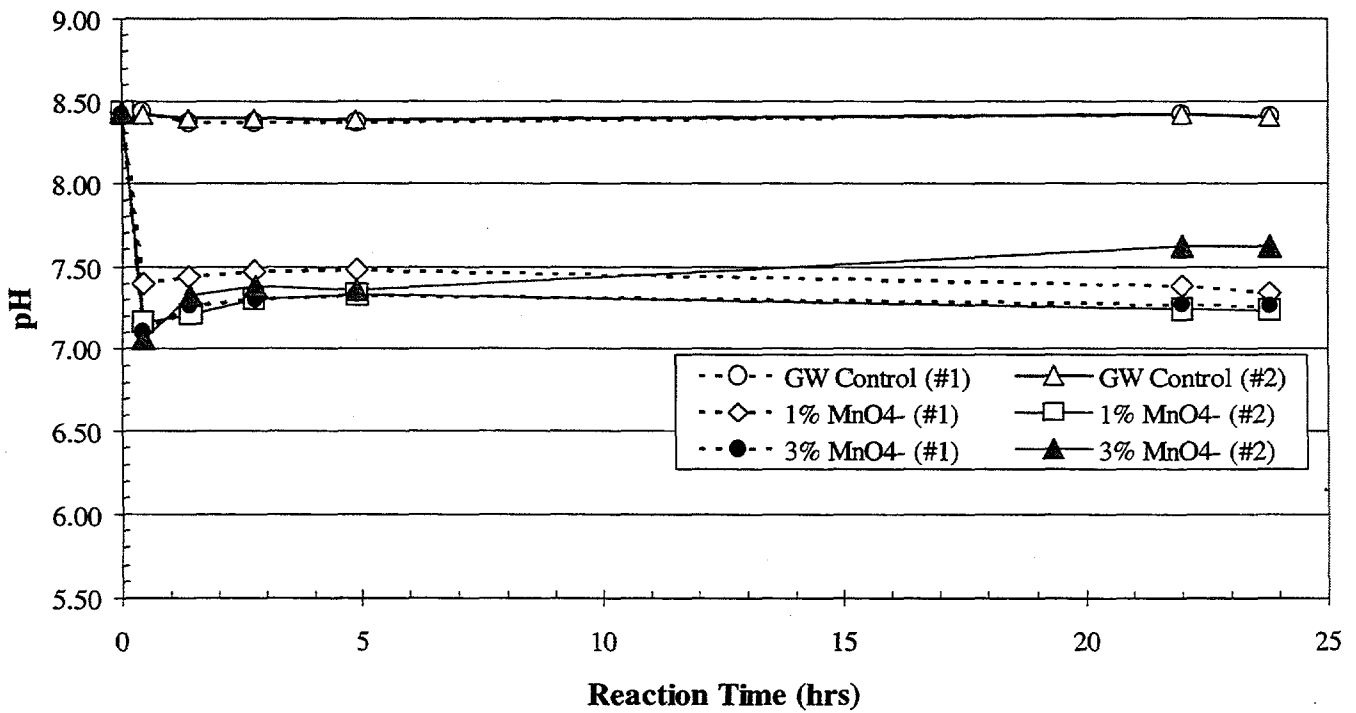
Figure 88.   pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R6 Initial Target TCE= 100,000 μg/L, Co-Contaminants = 10,000 μg/L Conducted at 12°C)

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Table 49. TCE Mass Balance for ORNL Exp. 4b-R6 (TSF-05 GW).

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	5.8	5.8	2.8E-06	5.1	0.6	NA	5.6
			0%	87%	10%	NA	97%
Control (#2)	5.4	5.4	3.2E-06	5.0	0.6	NA	5.6
			0%	93%	11%	NA	104%
1% (#1)	6.8	6.8	3.8E-06	0.00	0.1	6.7	6.8
			0%	0%	1%	98%	100%
1% (#2)	6.9	6.9	2.6E-05	0.00	0.1	6.8	6.9
			0%	0%	1%	99%	100%
3% (#1)	19.5	19.5	1.3E-04	0.00	0.3	19.2	19.5
			0%	0%	1%	99%	100%
3% (#2)	15.3	15.3	0.0E+00	0.00	0.2	15.1	15.3
			0%	0%	1%	99%	100%

Table 50. MnO_4^- Consumption Data for ORNL Exp. 4b-R6 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
1% (#1)	4974	10.5	213	0.4
1% (#2)	4978	10.3	90	0.2
3% (#1)	15065	32.1	3693	7.9
3% (#2)	15066	31.8	3226	6.8

[a.] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4b-R7
(TSF-05 GW, No Sludge, DNAPL TCE, 0 Other, 0.01% and 0.1% MnO₄⁻)

This experiment investigated the oxidation of TSF-05 GW spiked at DNAPL TCE Levels; i.e., the groundwater was spiked at $\approx 2 \times 10^6$ µg/L TCE so that a saturated aqueous solution was created.

The TCE, MnO_4^- and pH values with time are presented in Figures 89, 90, and 91, respectively. Tables 51 and 52 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition. Note that some of the columns in the mass balance table were computed differently than the method described at the beginning of Section 2.4.3. The deviations to this computational approach are clearly defined in the upcoming discussion of this experiment.

As presented in the testplan, a single TCE spiking solution could not be made and then subsequently distributed among the test reactors for the DNAPL experiments. Instead, a known mass (gravimetric determination) of pure TCE was added directly to each reactor and allowed to equilibrate at 12°C. Since the initial target TCE concentration (2×10^6 µg/L) was approximately twice the aqueous solubility of TCE ($1, \times 10^6$ µg/L @ 20°C), a non-aqueous TCE phase (i.e., DNAPL) was expected to exist within each reactor. At the T=0 hr time period, the aqueous TCE concentrations were indeed indicative of TCE saturation (average= 1,065,000 µg/L, σ= 24, 700 µg/L). Due to the spiking approach used, the reactors could potentially have very different initial TCE masses. There was no means of obtaining the *total* TCE mass in each reactor following equilibration (ie, at the T=0 hrs sampling period). Thus, the gravimetric spiking data was used to compute the total initial TCE mass present in each reactor with the gross assumption that no TCE was volatilized during equilibration (Table 51, Column 2).

A reaction period of 96 hrs was evaluated for this experiment rather than the 24 hr period called for in the testplan procedure.

To accurately compute the TCE recoveries for the control and treatment reactors, each reactor should have been extracted at the end of the reaction period. The step was unfortunately not included in the testplan procedure developed for this particular experiment, and the "Mass Remaining in Reactor" column of Table 51 only represents the TCE mass present in the aqueous phase at T=96 hrs. As a result, total TCE recoveries presented in the mass balance table also do not account for the non-aqueous phase TCE that might be present. (Note that the step to extract each reactor following treatment was properly incorporated into the test procedure prepared for the two DNAPL experiments involving the TSF-05 GW and sludge that are discussed later.)

Although total TCE recoveries were not determined for the reactors, trends observed in the aqueous TCE values of the control reactors suggest that, like Experiments 4b-R3 and 4b-R4, at least some of the variation in the aqueous TCE values is a function of the sample holding time. As observed in Figure 89, aliquot TCE values at T=24 hrs and 96 hrs, for example, are generally greater than those obtained at T=0 hrs for the control reactors. For this experiment, laboratory notebook records indicate that all 0-24 hr sample extracts were stored at 4°C for $\approx$ 2-3 days

before GC analysis. (This delay is the longest that was ever experienced during the entire INEEL treatability study and is due to an analysis backlog created by the simultaneous collection of samples from two experiments on the same day.)

Despite the time lag between sample collection and sample analysis, TCE oxidation is evident in Figure 89. There was an initial reduction in TCE concentrations for all four of the treatment reactors in the first 0.5 hrs of the reaction period. The magnitude of this overall reduction was the greatest for the 0.1% MnO_4^- reactors. As evidenced in Figure 90 and in Table 52, complete consumption of MnO_4^- occurred within the first 0.5 hrs for both reactors. Thus, as in Experiment 4b-R3 for the 0.01% MnO_4^- reactors, all four treatment reactors lacked available MnO_4^- to allow the oxidation reactions to continue. With all available oxidant depleted at T=0.5 hrs, it is suspected that the observed increase in aqueous TCE is a result dissolution of additional DNAPL into the aqueous phase.

Since all MnO_4^- was consumed and a surplus of TCE existed, the oxidized TCE masses obtained in this DNAPL experiment likely represent the upper limit of oxidation that can be achieved by MnO_4^-. The TCE oxidized mass (Table 51, Column 7) was approximated by computing the change in the aqueous TCE mass observed between 0-0.5 hrs. Using this approach, an average of 40 mg TCE (0.30 mMoles) and 193 mg TCE (1.47 mMoles) were oxidized in the 0.01% and 0.1% MnO_4^- reactors, respectively. From the theoretical equation for TCE oxidation by MnO_4^- given below, 2 moles of MnO_4^- are stochiometrically required for complete oxidation of each mole of TCE:

$$2 \ MnO_4^- + C_2HCl_3 \rightarrow 2 \ CO_2 + 2 \ MnO_2 + 2 \ Cl^- + HCl$$

After converting the initial oxidant masses for this experiment (in Table 52) to units of mMoles, experimentally determined molar ratios of MnO_4^- consumed/TCE oxidized was 1.10 and 2.26 for the 0.01% and 0.1% MnO_4^- reactors, respectively. These molar ratios were computed assuming that any MnO_4^- consumed by the TSF-05 GW was minimal as observed in the oxidant demand studies (Table 9). Since it is highly unlikely that the reactions proceeded at less than stochiometric ratio (2 moles MnO_4^-:1 mole TCE) conditions, the approximate mass of TCE mass oxidized was likely overestimated at least for the 0.01% MnO_4^- reactors.

Although the oxidation estimates for the non-aqueous TCE cannot be computed, observed *aqueous* oxidation rates are at least 80 and 386 mg TCE/hr for the 0.01% and 0.1% MnO_4^- reactors, respectively. Note that these values are minimum oxidation rates since TCE oxidized masses used in the calculations only represent TCE oxidized from the aqueous phase.

Essentially all of the initial 0.01% and 0.1% MnO_4^- was consumed during the oxidation reactions. A MnO_4^- residual of less than 1 mg/L was measured (Figure 90) for both cases, but it should be noted that the lowest MnO_4^- calibration standard was 5 mg/L.

Trends in pH values for these reactors were similar to those observed in Experiments 4b-R1 and 4b-R3 (Figures 65 and 71) in which all experimental variables except for the initial TCE concentration were the same. The magnitude of the pH drop observed in these experiments, however, is greatest for this DNAPL experiment. In fact, net pH decreases of greater than 2.1 and 5.4 pH units were observed here for the 0.01% and 0.1% MnO_4^- reactors. Thus, the degree

of pH change appears to be dependent upon the initial TCE concentration present. These significant pH changes are likely due to the large amount of H^+ ions released during the oxidation of TCE. These test reactors were also void of any solid phase to help buffer these changes.
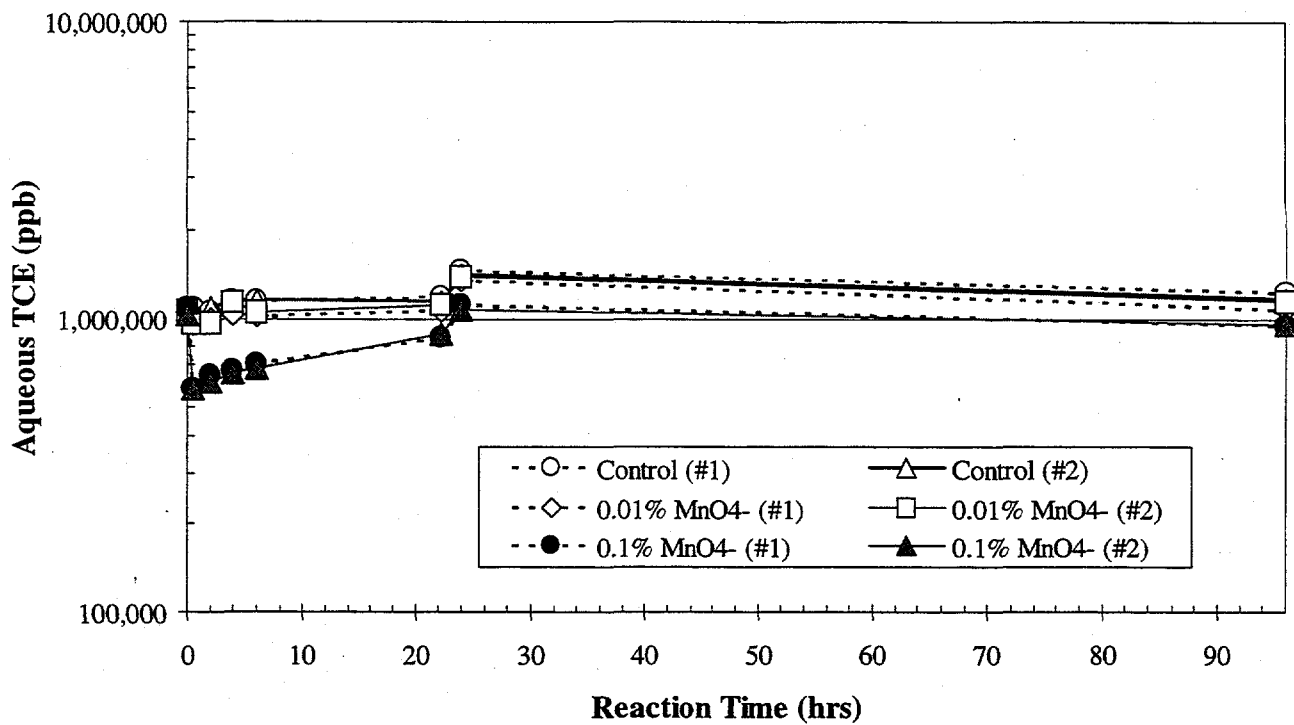
Figure 89.   TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R7, Initial TCE=DNAPL, Conducted at 12°C)
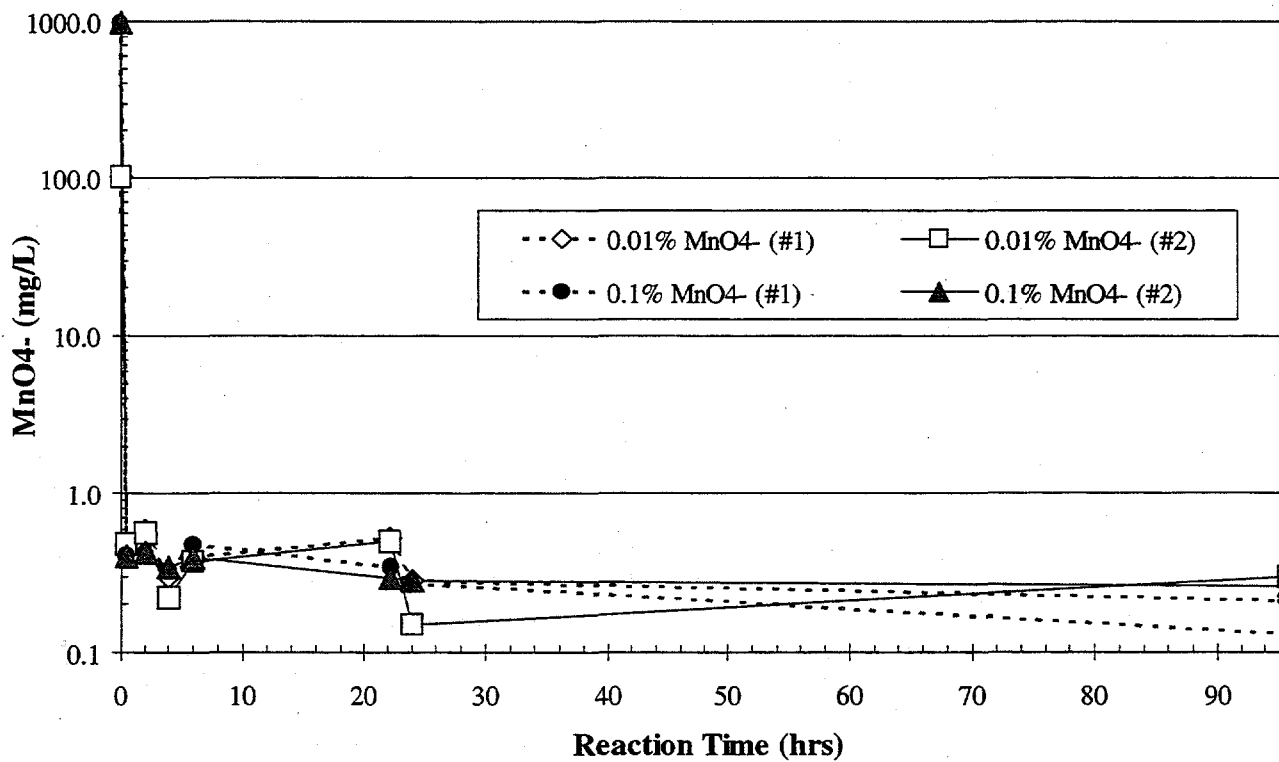
Figure 90.   MnO$_4^-$ vs. Time, TSF-05 GW, (ORNL Exp. 4b-R7, Initial TCE= DNAPL, Conducted at 12°C)

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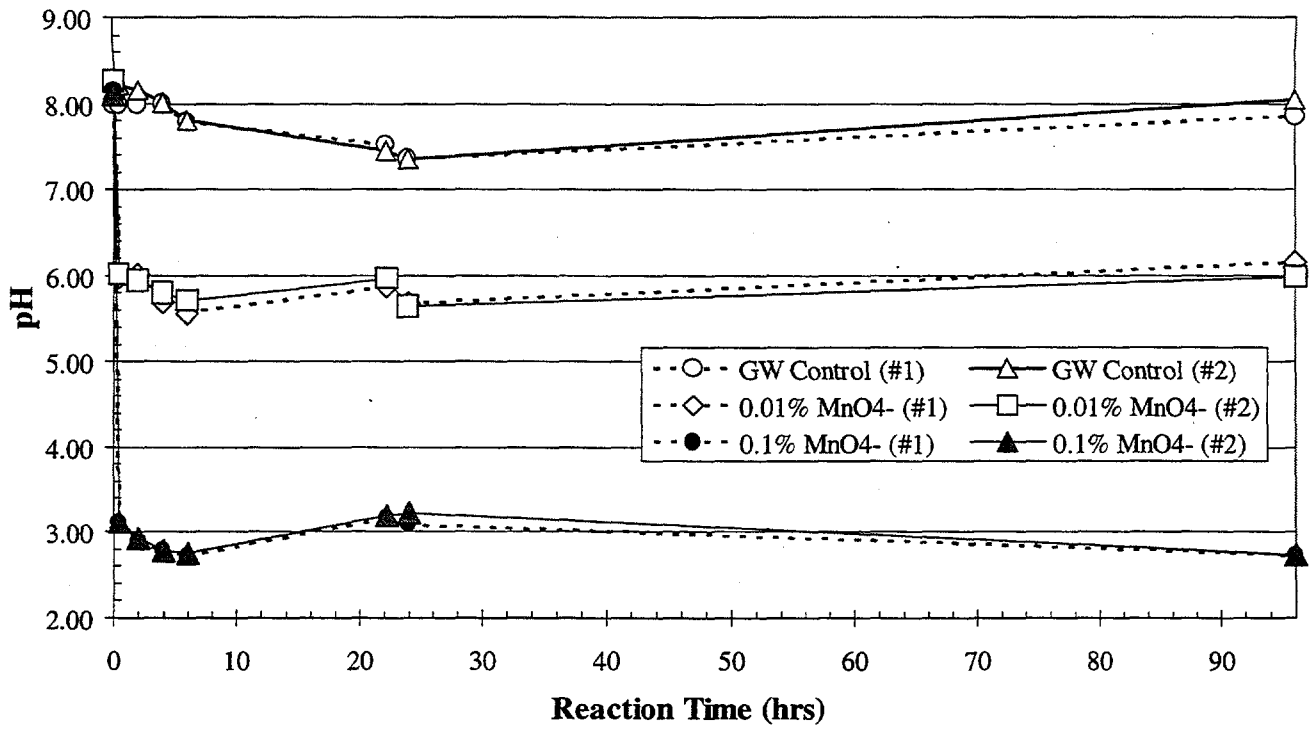
Figure 91. pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R7, Initial TCE= DNAPL, Conducted at 12°C)

Table 51. TCE Mass Balance for ORNL Exp. 4b-R7 (TSF-05 GW). [a]

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg) (Aqueous)	Cum. Mass Removed in Aliquots (mg)	TCE Oxidized	Total Mass Recovered (mg)
Control (#1)	798	433	0.59	366	119	NA	485
			0%	46%	15%	NA	61%
Control (#2)	815	434	0.22	349	115	NA	465
			0%	43%	14%	NA	57%
0.01% (#1)	807	418	0.25	333	95	35	462
			0%	41%	12%	4%	57%
0.01% (#2)	795	426	2.89	357	99	46	505
			0%	45%	12%	6%	64%
0.1% (#1)	806	435	2.12	302	73	206	582
			0%	37%	9%	26%	72%
0.1% (#2)	808	410	4.44	305	73	180	563
			1%	38%	9%	22%	70%

[a] Total Initial is assumed to be the actual DNAPL TCE mass added to each reactor.
Final Remaining TCE only represents the final TCE in the aqueous phase.
TCE oxidized only includes mass associated with the difference in the aqueous TCE concentrations between 0-0.5 hrs.
Total Recovered values do not include remaining non-aqueous phase TCE

Table 52. MnO_4^- Consumption Data for ORNL Exp. 4b-R7 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	39.6	0.10	39.5	0.10
0.01% (#2)	39.6	0.10	39.5	0.10
0.1% (#1)	396.0	0.99	395.9	0.99
0.1% (#2)	396.0	0.99	395.9	0.99

[a] Consumption is computed after 96 hr reaction time.

ORNL Exp. 4b-R8
(TSF-05 GW, No Sludge, DNAPL TCE, 0 Other, 1% and 3% MnO$_4^-$)

This experiment investigated the oxidation of TSF-05 GW spiked at DNAPL TCE Levels; i.e., the groundwater was spiked at $\approx 2 \times 10^6$ µg/L TCE so that a saturated aqueous solution was created.

The TCE, MnO$_4^-$ and pH values with time are presented in Figures 92, 93, and 94, respectively. Tables 53 and 54 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition. Note that some of the columns in the mass balance table were computed differently than the method described at the beginning of Section 2.4.3. The deviations to this computational approach are clearly defined in the upcoming discussion of this experiment.

As presented in the testplan, a single TCE spiking solution could not be made and then subsequently distributed among the test reactors for the DNAPL experiments. Instead, a known mass (gravimetric determination) of pure TCE was added directly to each reactor and allowed to equilibrate at 12°C. Since the initial target TCE concentration (2×10^6 µg/L) was $\approx$twice the aqueous solubility of TCE, a non-aqueous TCE phase (i.e., DNAPL) was expected to exist within each reactor. At the T=0 time period, the aqueous TCE concentrations were indeed indicative of TCE saturation (average= 1,031,000 µg/L, σ= 40,600 µg/L). Due to the spiking approach used, the reactors could potentially have very different initial TCE masses. There was no means of obtaining the total TCE mass in each reactor following equilibration (i.e., at the T=0 hrs sampling period). Thus, the gravimetric spiking data was used to compute the total initial TCE mass present in each reactor with the gross assumption that no TCE was volatilized during equilibration (Table 53, Column 2).

A reaction period of 96 hrs was evaluated for this experiment rather than the 24 hr period called for in the testplan procedure.

To accurately compute the TCE recoveries for the control and treatment reactors, each reactor should have been extracted at the end of the reaction period. The step was unfortunately not included in the testplan procedure developed for this particular experiment, and the "Final Remaining" column in Table 53 only represents the TCE mass present in the aqueous phase at T=96 hrs. As a result, total TCE recoveries for the reactors also do not account for any non-aqueous phase TCE that may be present. (Note that the step to extract each reactor following treatment was properly incorporated into the test procedure prepared for the two DNAPL experiments involving the TSF-05 GW and sludge that are to be discussed later.)

Although total TCE recoveries were not determined for the reactors, TCE oxidation is quite evident in Figure 92. Here, the overall reductions in TCE concentrations for the treatment reactors are significant and by far exceed the reductions observed for the control reactors. The oxidation reactions occurring were robust. Laboratory observations indicated significant pressure build up and release at the 0.5 hr aliquot sampling time for the 3% reactors. As noted in Figure 92, the first 1% MnO$_4^-$ reactor was cracked and replaced after t= 4hrs. The contents of

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the cracked reactor were transferred into an intact reactor. Some TCE may have volatilized during this transfer, but oxidation was likely still the primary removal mechanism since the oxidant consumption values presented in Table 54 are the same for both of the 1% MnO_4^- reactors. Given the fact that residual oxidant was present and TCE was not detected in the 96 hr aqueous aliquots, complete oxidation of both the aqueous and non-aqueous TCE phase is suspected. The TCE oxidized masses presented in Table 53, Column 7 represent the maximum TCE that could have been oxidized within a given reactor. The values were calculated by subtracting the TCE mass present in the desorption tubes and sample aliquots from the total initial TCE.

Furthermore, the oxidation for both oxidant loadings appears to be a 2-step process, where the bulk of the TCE is oxidized rapidly, followed by a slower oxidation step. Due to the presence of the non-aqueous phase in these reactors, oxidation rate constants cannot be accurately computed. The mechanism controlling the oxidation of the DNAPL is not well understood. It is not known how or when the non-aqueous phase TCE is being oxidized (e.g., is it solubilized first?). If it is assumed that all TCE is oxidized by T=0.5 hrs, a maximum oxidation rate of 1,620 mg TCE/hr would be obtained for both the 1% and 3% MnO_4^- reactors in this experiment.

As evidenced in Figure 93 and in Table 54, residual oxidant was still present in all the treatment reactors after the 96 hr reaction time. In fact, only 35% and 14% of the initial oxidant mass was consumed in the 1% and 3% reactors, respectively. Nearly all of this consumption occurred within the first 0.5 hrs.

Trends in pH values for these reactors as similar to those observed in Experiments 4b-R2 and 4b-R4 (Figures 68 and 74) in which all experimental variables except for the initial TCE concentration were the same. The magnitude of the pH decrease, however, is greatest for this DNAPL experiment (>6.3 pH units). Thus, the degree of pH change again appears to be dependent upon the initial TCE concentration present.

In TSF-05 GW experiments not involving a non-aqueous phase, the 1% and 3% MnO_4^- reactors typically resulted in net pH decreases smaller is magnitude than those observed for the 0.01% and 0.1% MnO_4^- reactors. This was attributed to the greater ionic strength of the more concentrated oxidant solution. This trend was not observed for the DNAPL experiments, for the pH decreases observed in this experiment were greater than those observed in Experiment 4b-R7. For the high TCE concentrations evaluated in this experiment, the release of H^+ ions during TCE oxidation likely had a greater effect on the system pH than did the ionic strength of the oxidant solution.
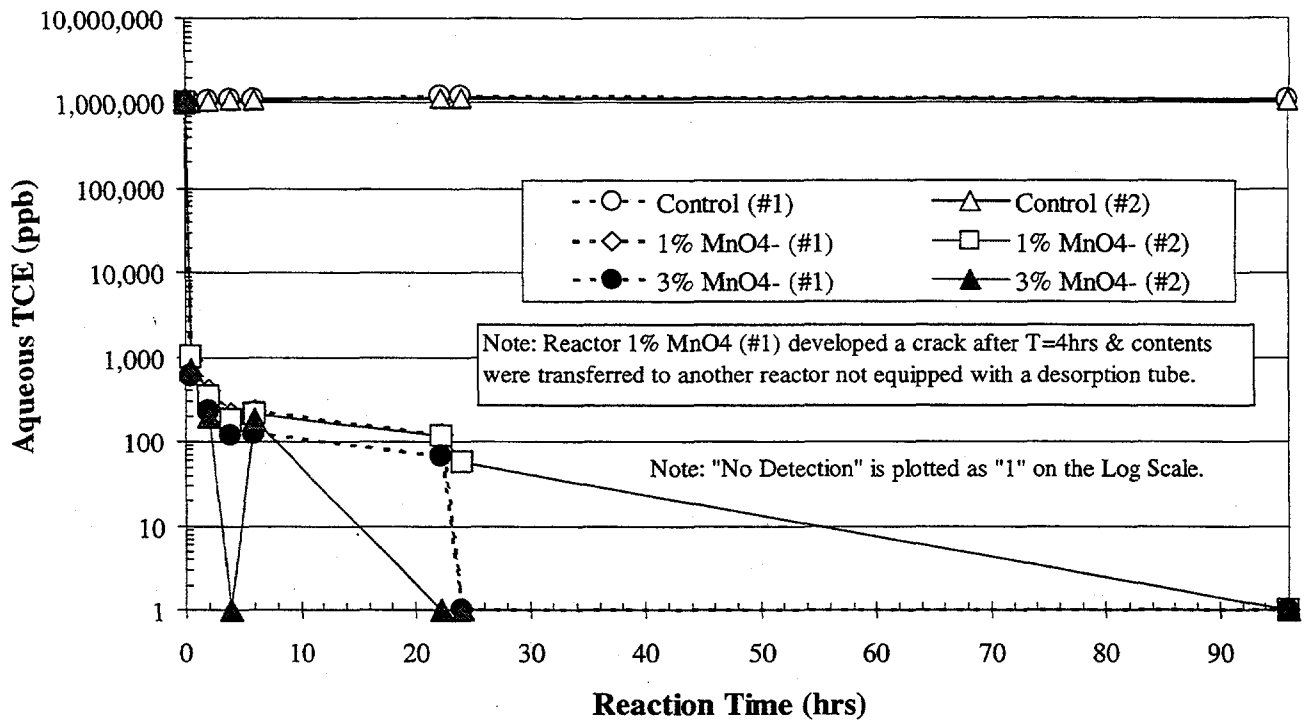
Figure 92. TCE vs. Time, TSF-05 GW, (ORNL Exp. 4b-R8, Initial TCE= DNAPL, Conducted at 12°C)
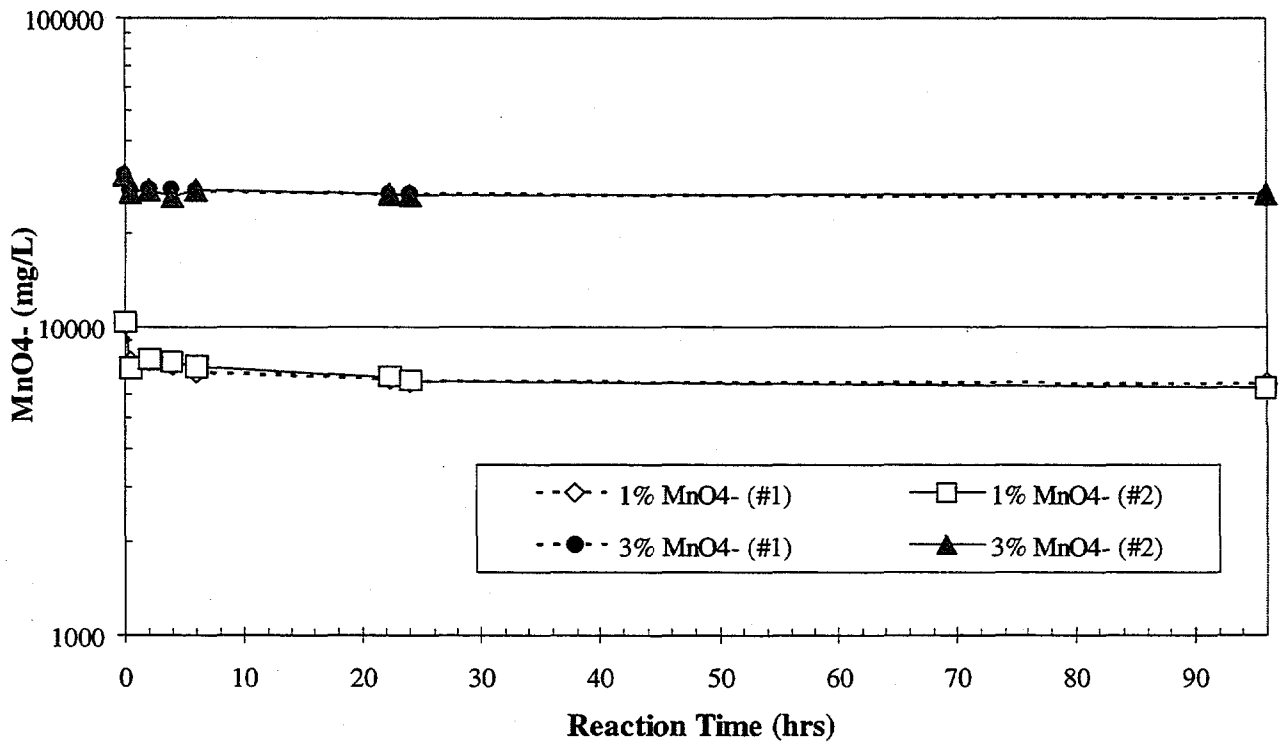
Figure 93. MnO$_4$⁻ vs. Time, TSF-05 GW, (ORNL Exp. 4b-R8, Initial TCE= DNAPL, Conducted at 12°C)

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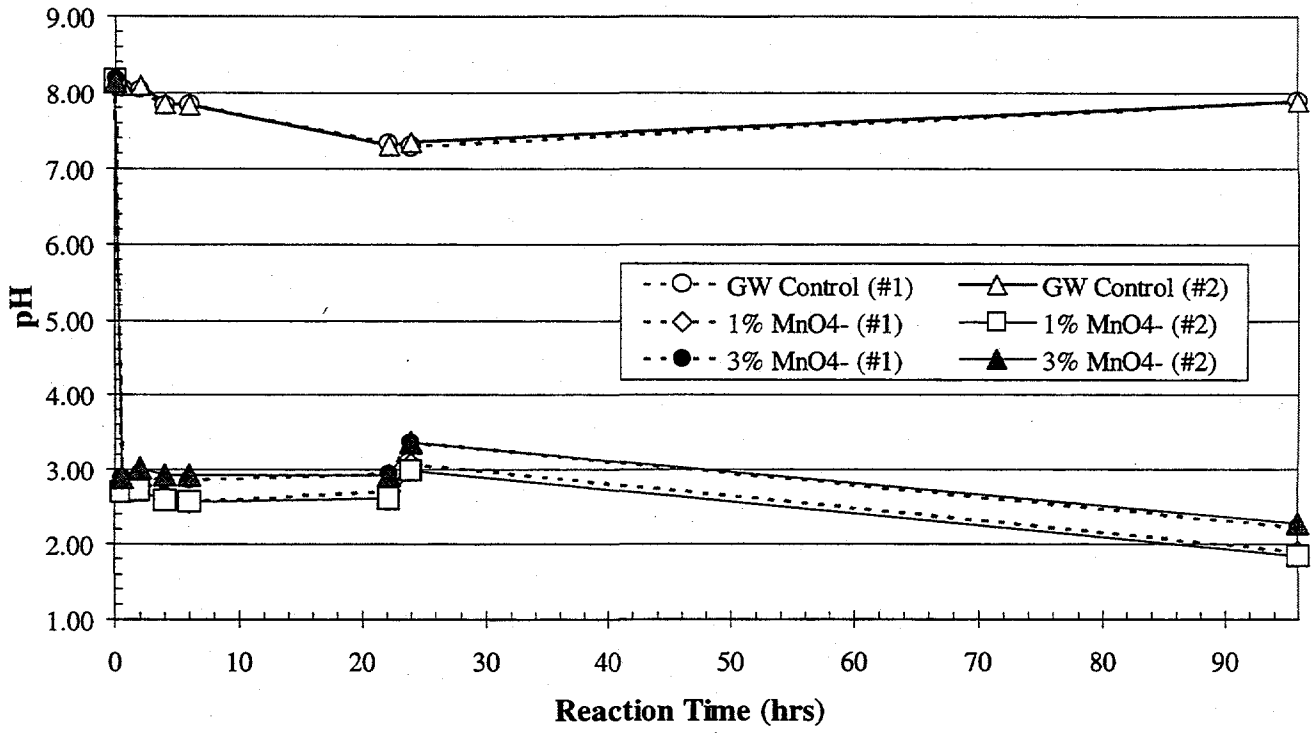
Figure 94.   pH vs. Time, TSF-05 GW, (ORNL Exp. 4b-R8, Initial TCE= DNAPL, Conducted at 12°C)

Table 53. TCE Mass Balance for ORNL Exp. 4b-R8 (TSF-05 GW) [a]

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg) (Aqueous)	Cum. Mass Removed in Aliquots (mg)	Max.TCE Oxidized[†]	Total Mass Recovered (mg)
Control (#1)	812	396	0.841	326	109	NA	436
			0%	40%	13%	NA	54%
Control (#2)	806	417	0.142	332	108	NA	440
			0%	41%	13%	NA	55%
1% (#1)	810	404	0.000	0	10	799[†]	Not computed
			0%	0%	1%	99%	Not computed
1% (#2)	817	411	0.032	0	10	807[†]	Not computed
			0%	0%	1%	99%	Not computed
3% (#1)	806	404	0.013	0	10	796[†]	Not computed
			0%	0%	1%	99%	Not computed
3% (#2)	809	442	0.033	0	11	798[†]	Not computed
			0%	0%	1%	99%	Not computed

[a] Total Initial is assumed to be the actual DNAPL TCE mass added to each reactor. Final Remaining TCE only represents the final TCE in the aqueous phase.

[†] Max. TCE Oxidized= Total Initial-Orbo Tube-Cum. Aliquot.

Table 54. MnO_4^- Consumption Data for ORNL Exp. 4b-R8 (TSF-05 GW).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
1% (#1)	4017	10.3	1421	3.6
1% (#2)	4017	10.3	1421	3.6
3% (#1)	12051	30.9	1649	4.2
3% (#2)	12051	30.9	1680	4.3

[a] Consumption is computed after 96 hr reaction time.

Summary – VOC Oxidation Rate Measurements, Hot Spot Groundwater

This set of experiments measured the rate of TCE oxidation in groundwater from the hot spot. The concentrations of TCE used in these experiments are higher than those used in the 'dissolved plume' experiments, reflecting the higher in situ TCE concentrations in the hot spot. The MnO_4^- concentrations used were also higher in the 'hot spot' experiments due to the greater oxidant demand of hot spot media and the potentially higher oxidant concentrations needed to achieve rapid and complete oxidation of the higher TCE concentrations.

- Permanganate concentrations ranged from 0.01% (100 mg/L) to 3% (30 g/L), which is close to the solubility limit for potassium permanganate at groundwater temperature. TCE concentrations ranged from approximately 10,000 µg/L to approximately 1,000,000 µg/L; TCE was present as a non-aqueous phase liquid at the highest concentrations. The nominal TCE and oxidant concentrations and the associated experiment identification number are tabulated below in Table 55.

Table 55.   Experimental Identification for Hot Spot Groundwater Experiments.

Nominal MnO_4^- Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[†] (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	4bR1	4bR5	4bR3	4bR7
0.1 %	4bR1	4bR5	4bR3	4bR7
1 %	4bR2	4bR6	4bR4	4bR8
3 %	4bR2	4bR6	4bR4	4bR8

[†]   With DCE isomers as co-contaminants

- Most experiments were performed with TCE as the only VOC, but a few included DCE isomers as well to evaluate the effect of co-contaminants on the rate of TCE oxidation.

- Similar to the observations from the dissolved plume media experiments, concentrations of TCE and DCE isomers remained constant in reactors without permanganate, and generally declined rapidly to less than MDLs if a sufficient mass of permanganate was present. This again demonstrates that oxidation of TCE and DCE isomers by MnO_4^- is the predominant mechanism whereby these VOCs were destroyed.

- Cases in which TCE concentrations did not decline to less than MDLs can be attributed to insufficient MnO_4^- to oxidize the mass of TCE present; to the presence TCE as a non-aqueous phase liquid in the reactor; and to analytical problems caused by contamination of the hexane used for extracting samples prior to analysis. Even in reactors in which there was insufficient MnO_4^- for all of the TCE to be oxidized, oxidation was rapid until the MnO4- was depleted.

- In several cases, insufficient MnO_4^- was added and TCE concentrations remained high. Initial and final MnO_4^- concentrations for this experimental series is presented in Tables 56 and 57, respectively.

Table 56. Initial MnO$_4^-$ Concentrations for the Hot Spot Groundwater Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (μg/L)	100,000[†] (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	102	99	101	101
0.1 %	1008	956	989	990
1 %	10,120	10,380	10,200	10,300
3 %	30,475	31,900	30,900	30,900

[a] Values are the average of 2 test reactors (mg/L MnO$_4^-$). All samples filtered (0.45 μm) prior to analysis

[†] With DCE isomers as co-contaminants

Table 57. Final MnO$_4^-$ Concentrations for the Hot Spot Groundwater Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (μg/L)	100,000[†] (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	27	38	1.1 U	0.3 U
0.1 %	419	861	804	0.2 U
1 %	10,070	10,105	10,145	6,420
3 %	27,650	24,580	30,160	26,400

[a] Values are the average of 2 test reactors (mg/L MnO$_4^-$). All samples filtered (0.45 μm) prior to analysis.

[†] With DCE isomers as co-contaminants

A value followed by "U" represents cases where the measured concentration is less than the MDL.

- The initial concentration of TCE varied between different experiments that were intended to have the same initial concentration. In most cases, the actual initial concentrations were close to the intended concentrations. However, in the experiments with DCE isomers as co-contaminants, the initial TCE concentrations (Table 58) were only 11 - 41 percent of the intended concentration.

Table 58. Initial Aqueous TCE Concentrations for the Hot Spot Groundwater Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[†] (µg/L)	100,000 (µg/L)	1,000,000[††] (µg/L)
0.01%	14,525	21,680	106,540	1,054,500
0.1 %	13,775	30,500	100,810	1,056,500
1 %	10,590	14,020	109,395	1,017,500
3 %	9,990	36,300	104,970	1,057,600

[a] Values are the average of 2 test reactors (µg/L TCE).
[†] With DCE isomers as co-contaminants
[††] Estimated Concentration

TCE oxidation generally proceeded rapidly. In many cases, oxidation was essentially complete when the first or second sample was collected, and thus there is insufficient data resolution to determine reaction rate parameter values, such as first order rate constants. In this case, a zero order reaction rate was estimated by assuming that the TCE concentration declined to zero when the first or second sample was collected. If there were two or more values greater than the MDL, a first order rate constant was determined. The final TCE concentrations are tabulated in Table 59, and the percentage of the initial mass of TCE oxidized and removed by sampling is shown in Table 60.

Table 59. Final Aqueous TCE Concentrations for the Hot Spot Groundwater Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[†] (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	277	165,25	37,440	952,400[††]
0.1 %	204	3 U	ND	573,820[††]
1 %	ND	2 U, 11 U	ND	ND
3 %	ND	1 U	ND	ND

[a] Values are the average of 2 test reactors (µg/L TCE).
ND= Not Detected.
A value followed by "U" represents cases where the measured concentration is less than the MDL.
[†] With DCE isomers as co-contaminants
[††] Final Value at T= 0.5 hrs rather than T= 24 hrs.

Table 60. Percentage of Initial TCE Mass Oxidized and Removed via Sampling. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[†] (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	98	100	77	17[††]
0.1 %	101	102	102	33[††]
1 %	100	100	100	100
3 %	100	100	100	100

[a] Values are the average of 2 test reactors (wt%).
[†] With DCE isomers as co-contaminants
[††] Final Value at T= 0.5 hrs rather thanT= 24 hrs.

Observed zero order reaction rates for TCE destruction are presented below in Table 61 on the basis of mass of TCE per unit time per reactor and in Table 62 on the basis of mass of TCE per unit time per liter. Trends in the pH values of the test reactors are presented in Table 63. Finally, the entire series of hot spot groundwater experiments (Tables 55 through 63) are summarized in Table 64.

Table 61. Observed Minimum Zero Order TCE Destruction Rates - Per Reactor Basis, Hot Spot Groundwater. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[†] (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	0.5[1]	5.0[1]	7.3[2]	80[2]
0.1 %	13.8[1]	7.7	82	386[2]
1 %	2.7	6.9	88	1,628
3 %	10.0	17.4	84	1,616

[a] Values are the average of 2 test reactors (mg TCE/hr per reactor). Computed by dividing the Average Initial TCE Mass present in each reactor by the earliest aliquot sampling time at which TCE was not detected. Each reactor contained nominally 400 mL. See Appendix C for actual GW masses in each reactor.
[†] With DCE isomers as co-contaminants
[1] Possibly affected by contamination of hexane used for extracting samples.
[2] MnO$_4^-$ depleted before TCE oxidized. Rate Estimated from period while MnO$_4^-$ was present.

Table 62. Observed Minimum Zero Order TCE Destruction Rates –Per Unit Volume Basis, Hot Spot Groundwater. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[††] (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	1[1]	10[1,†]	18[2]	200[2]
0.1 %	27[1]	15	200	940[2]
1 %	5	14	220	4,100
3 %	20	36	210	4,040

[a] Values are the average of 2 test reactors (mg TCE/L/hour). Values were computed by dividing the Average Initial TCE Mass present in each reactor by both (1) the earliest aliquot sampling time (hrs) at which TCE was not detected and (2) the average initial liquid volume in the reactor (GW and MnO$_4^-$ stock solution, when applicable).

[†] A corresponding first order rate constant is included in Table 64 for this test case.

[††] With DCE isomers as co-contaminants

[1] Possibly affected by contamination of hexane used for extracting samples.

[2] MnO$_4^-$ depleted before TCE oxidized. Rate Estimated from period while MnO$_4^-$ was present.

Table 63. Observed pH Trends in the Hot Spot Groundwater Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration			
	10,000 (µg/L)	100,000[†] (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	-0.8	-1.0	-1.5	-2.1
0.1 %	-0.9	-0.3	-1.8	-5.4
1 %	-0.1	-1.2	-1.6	-6.3
3 %	+0.4	-1.0	-1.0	-6.3

[a] pH Trends are the average of 2 test reactors

Table 64. Summary of the Hot Spot Groundwater Oxidation Rate Experiments.

ORNL Exp. No.	Nominal Initial TCE (μg/L)	Avg. Initial TCE Mass (mg)	TCE Oxidation Observed Rates (mg TCE/hr·Reactor Contents)[†]	Initial MnO_4^- (wt%)	Max. MnO_4^- Consumed (mg MnO_4^-/g)	pH Trends
4b-R1	10,000	7.4	Complete[1] (≈15 hrs) Obs. Rate ≥0.5	0.01%	0.08	>0.8 Net Decrease
		6.9	Complete[1] (≈0.5 hrs) Obs. Rate ≥ 13.8	0.1%	0.6	>0.9 Net Decrease
4b-R2	10,000	5.3	Complete (<2 hrs) Obs. Rate ≥ 2.65	1%	0.6	<0.1 Net Decrease
		5.0	Complete (<0.5 hrs) Obs. Rate ≥ 10.0	3%	3.5	≈ 0.4 Net Increase
4b-R3	100,000	43	Incomplete (68% oxidized)[4] **Obs. Rate ≥ 7.25**	0.01%	0.1	>1.5 Net Decrease
		41	**Complete (<0.5 hrs)** Obs. Rate ≥ 82	0.1%	0.2	>1.8 Net Decrease
4b-R4	100,000	44	**Complete (0.5 hrs)** Obs. Rate ≥ 88	1%	0.2	>1.6 Net Decrease
		42	**Complete (0.5 hrs)** Obs. Rate ≥ 84	3%	0.4	>1.0 Net Decrease
4b-R5	100,000 & Other VOCs[2]	10.8	Complete[1] (≈5 hrs) **Avg k= 1.66 hr^{-1}**	0.01%	0.06	**>1.0 Net Decrease**
		15.4	Complete <2 hrs)[1] **Obs. Rate ≥ 7.7**	0.1%	0.12	>1.3 Net Decrease
4b-R6	100,000 & Other VOCs[2]	6.9	**Complete (<1 hr)1** **Obs. Rate ≥ 6.9**	1%	0.4	>1.2 Net Decrease
		17.4	**Complete (<1 hr)1** Obs. Rate ≥ 17.4	3%	7.9	> 1.0 Net Decrease
4b-R7	DNAPL[3]	800	Incomplete (≈5% Oxidized)[4] Obs. Rate ≥ 80[5]	0.01%	0.1	> 2.1 Net Decrease
		807	Incomplete (≈24% Oxidized)[4] Obs. Rate ≥ 386[5]	0.1%	1.0	>5.4 Net Decrease
4b-R8	DNAPL[3]	814	**Complete (0.5 hrs)1** **Obs. Rate ≥ 1628**	1%	3.6	> 6.3 Net Decrease
		808	Complete (0.5 hrs)[1] Obs. Rate ≥ 1616	3%	4.3	> 6.3 Net Decrease

For footnotes, see next page.

† Observed Oxidation Rate= (Total Initial mg TCE)/(X hrs·Reactor Contents); Where X represents the earliest sampling time at which TCE was not detected in the aqueous aliquot. Where available, the predicted first order reaction rate constant, k, is presented. "Reactor Contents" are nominally 400 mL TCE-spiked GW. See Appendix C for actual GW mass in each reactor.

[1] It is assumed that the reactions were essentially completed at this time point, even though a low residual TCE concentration was present. The reported values are estimates.

[2] Co-contaminants also present at approximately 10,000 ppb each.

[3] "DNAPL" equates to an aqueous concentration of 2×10^6 µg/L TCE.

[4] Oxidant depleted before all TCE could be oxidized.

[5] A conservative value which does take account for any non-aqueous TCE which was oxidized.

- There is a general trend of increasing TCE oxidation rate with increasing MnO_4^- concentration and a general trend of increasing TCE oxidation rate with increasing TCE concentration, as observed in the dissolved plume media experiments. The observed zero order rates ranged from >0.5 mg/hr to >1600 mg/hr on per reactor basis, and from >1 mg/L/hr to >4000 mg/L/hr on a unit volume basis.

- DCE isomers were rapidly oxidized by MnO_4^-, but rates were not determined.

- Evaluation of the effect of co-contaminants on the rate of TCE oxidation is confounded by inconsistent TCE concentrations between oxidation rate measurements with and without co-contaminants present. Co-contaminants are an additional sink for MnO_4^-, and therefore MnO_4^- concentrations would be lower if co-contaminants were present than if they were not. The data show that the TCE oxidation rate increases with MnO_4^- loading, and thus it is likely that the presence of co-contaminants does slow the rate of TCE oxidation. In these experiments, TCE was rapidly oxidized with co-contaminants present, but the degree that the presence of co-contaminants affects the rate of TCE oxidation cannot be determined from this data set.

- In general, if sufficient MnO_4^- was present, TCE concentrations rapidly declined to approximately the MDL.

- Production of H^+ during oxidation of TCE causes the pH to decline. However, pH increased by 0.4 units in one experiment; this observation is problematic. In other experiments, the pH decline is generally greater with larger initial concentrations of TCE, presumably due to a greater mass of oxidant consumed and H^+ produced as more TCE is available to reduce MnO_4^-. In the absence of a TCE non-aqueous phase, the pH shifts were on the order of 0.1 - 2 pH units. With a non-aqueous phase present, much larger pH shifts occurred (2-6 pH units). Trends as a function of MnO_4^- concentration are less distinct, except where a non-aqueous phase was present. Note that there was not a solid phase present to buffer the pH change; pH changes might be smaller if buffered by a solid phase.

2.4.4. Oxidation Rate of Organic Contaminants in Hot Spot Sludge

Six (6) separate oxidation rate experiments were performed for the hot spot sludge (TSF-05 Sludge). Each experiment is discussed below and identified by the ORNL Experiment IDs presented earlier in Table 7. In general, plots of "TCE vs. Time", "MnO_4^- vs. Time", and "pH vs. Time" are presented for each experiment. For all plots of TCE vs. Reaction time: any values resulting from analyses in which the sample extract concentration was out of the GC calibration range are clearly labeled. Note that some experiments were continued after 24 hrs. Such a modification is clearly noted in the experimental discussions.

In addition to the plots, summary tables for the TCE and MnO_4^- data are also presented for each experiment. Several parameters are included in the TCE mass balance tables (e.g., Table 65). The approach and/or calculations made to obtain each of the values presented in the mass balance tables are presented below. (Descriptions of the MnO_4^- consumption tables are presented at the beginning of Section 2.4.2.)

- Column 1, "Test Conditions" refers the experimental condition. In this column "Control" refers to reactors containing only TSF-05 GW and no oxidant. The (#1) and (#2) notations included in parentheses refer to the duplicate reactors evaluated. The number followed by the percentage sign is the nominal initial MnO_4^- concentration added to the treatment reactors.

- Column 2, "Total Initial Mass" refers to the TCE mass added to each reactor. For the GW control reactors, this value is determined by the following equation: (Aqueous TCE Conc. at T=0) x (GW Volume in the Control Reactor) Note: T=0 sampling occurred after overnight equilibration and immediately before oxidant addition to the treatment reactors. For reactors containing both TSF-05 GW and Sludge, the initial total TCE mass is computed by the following equation: (Average Aqueous TCE Conc. at T=0 of the 2 GW Controls) x (GW volume in the Slurry Reactor). It is computed in this way in the event that some TCE is sorbed to the TSF-05 sludge at T=0.

- Column3, "Initial Aqueous Mass" For all cases (with exception of DNAPL case), this value is computed by multiplying the Aqueous TCE Conc. at T=0 for a given reactor by the volume of GW added to that reactor. Note: The aqueous concentration at T=0 for each reactor is used here rather than the concentration of the spiked GW before it is distributed to the individual reactors and equilibrated. (This approach effectively "removes" or accounts for the any TCE lost during equilibration from the mass balance calculations performed for the actual oxidation reactions.) For the treatment reactors containing both GW and sludge, another value is also presented in Columns 2 and 3 of the mass balance tables. This "% Sorbed" value represents the fraction of TCE at T=0 partitioned to the sludge. It is computed for each GW/sludge slurry via the following equation:
  %Sorbed=100 x [1-(Initial Aqueous Mass/Total Initial Mass)] or 100 x [1-(Col. 3/Col. 2)]

- Column 4, "Mass Sorbed on Orbo Tubes" represents the summed TCE mass found on each charcoal bed of the reactor's desorption tube at the end of the reaction period. The TCE mass

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was obtained by extraction of charcoal beds with hexane. If TCE is detected on the desorption tubes, it is realized that the value obtained represents a *minimum* that was volatilized since the entire reactor headspace volume would not pass through the desorption tube. The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) found within the Orbo Tube.

- Column 5, "Mass Remaining in Reactor" represents the TCE mass still present in each reactor following the reaction period. For the control reactors, this value was computed by the following equation: (Aqueous TCE concentration at T=24 hrs) x (Init. GW volume – Cum. Vol. of Aliquot Samples). For treatment reactors containing a slurry of GW and sludge, the remaining TCE mass in the reactor was obtained by extracting the entire contents remaining in the reactor after T=24 hrs with hexane ($\approx 1:1$ v/v extraction). For both cases, the values in parentheses for this column represent the percentage of the Total Initial Mass (column 1 of the Table) still present in the reactor.

- Column 6, "Cum. Mass Removed in Aliquots" represents the mass of TCE removed from the reactor as a result of the aliquot sampling. In all cases, this column is computed by summing the masses of TCE that were found in each aliquot interval for a given reactor, i.e., Σ(Aqueous TCE Conc. x Aliquot Volume). The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) removed from the reactor (and thereby not subjected to oxidation) during the course of the experiment.

- Column 7, "Cum. Aqueous Mass Oxidized" represents the TCE mass initially in the aqueous phase that was considered to have been oxidized during the reaction period. The oxidized TCE masses presented in this column were computed by summing the change in aqueous TCE mass obtained for each sampling period, i.e., $\Sigma[($Aq. TCE Conc. $_{T=x}$ – Aq. TCE Conc.$_{T=x+1}$) x GW Vol. $_{T=x}$]. Thus, this approach corrects for TCE removed via previous aliquot samplings. Again, the values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) believed to have been oxidized. It is important to note that this component of the mass balance does not take into account any TCE initially sorbed to the sludge, i.e., TCE that desorbed and was oxidized would <u>not</u> be included in this column. Hence, this column represents the minimum mass oxidized.

- Column 8, "Total Mass Recovered" is the sum of the TCE masses found in four (4) different "compartments" at the end of the reaction period, i.e., Col. 4+Col. 5 + Col. 6 + Col. 7. The values in parentheses for this column represent the percentage of the Total Initial Mass (Column 1 of the Table) that was accounted for during the course of the experiment.

Also note that variation in the initial TSF-05 GW and sludge chemistry, e.g. pH values, is expected since each hot spot media experiment was conducted using a different batch of hot spot material. (The various containers of TAN site materials received from INEEL were not combined/mixed prior to experimentation).

NOTE: A different mass balance approach was required for the experiments involving DNAPL phase TCE. Deviations and/or variations of the above approach are presented in the individual results and discussion sections for those experiments.

ORNL Exp. 4b-R11
(TSF-05, Sludge, 10,000 TCE, 0 Other, 0.01% and 0.1% MnO$_4^-$)
(Replaced Exp. 4b-R9)

This experiment investigated the oxidation of TSF-05 GW and sludge spiked at 10,000 µg/L TCE. The TCE, MnO$_4^-$ and pH values with time are presented in Figures 95, 96, and 97, respectively. Tables 65 and 66 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

No deviations were made to the testplan during the conduct of this experiment.

After equilibration, the average initial aqueous TCE concentration of the spike solution (TSF-05 GW) was 42,756 µg/L (σ= 721 µg/L). After transfer to the test reactors and equilibration with the TSF-05 sludge, the aqueous TCE concentrations in the slurries were lower than those observed in the groundwater controls. In fact, the sludge adsorbed an average of 56% of the total initial TCE added to each treatment reactor. Final TCE recovery values of 100% and 110% were obtained for the first and second control reactors, respectively. The first groundwater control yielded initial and final TCE concentrations of 30,900 µg/L and 32,000 µg/L, respectively. Similarly, the initial aqueous TCE concentration for the second control reactor was 30,078 µg/L, and the final concentration was 33,544 µg/L. The larger final TCE values are likely not a result of a sample holding time effect since there is no observed trend between TCE conc. and sample collection time. Instead, the higher recovery of the second control appears to result from sample to sample variability (See data in Appendix C).

From Figure 95, the aqueous TCE concentrations of the treatment reactors are quickly reduced as oxidation occurs. In Figure 96, MnO$_4^-$ is quickly consumed. The MnO$_4^-$ variability between 0 and 6 hrs is small when compared to the initial MnO$_4^-$ concentrations that existed for each reactor (note use of log scale). When Figures 95 and 96 are examined in concert, the observed rise in aqueous coincides with the time the oxidant is depleted. This increase in aqueous TCE may be due to (1) the release of TCE from the organic sludge that was initially oxidized and/or (2) the transfer of sludge bound TCE into the aqueous phase in order to establish equilibrium conditions within each test reactor.

TCE was still present in the reactors following the reaction period. The TCE mass extracted from the final reactors are presented in Table 65. Likewise, a small amount of TCE was found on the first charcoal bed of each desorption tube, indicating that some TCE was lost to volatilization. (Although small, the amount of TCE on the charcoal beds of the 0.1% MnO$_4^-$ reactors was approximately three times that found on the control and 0.01% MnO$_4^-$ reactors.) Since oxidant consumption occurred within the first 0.5 hrs of reaction, it is plausible to assume that TCE oxidization only occurred during the same time interval. Therefore, the mass of TCE oxidized in Table 65, Column 7 includes only the TCE associated with the difference in *aqueous* TCE concentrations between 0-0.5 hrs. Basing the oxidized TCE mass on this experimentally determined difference yields oxidation percentages of 10-12% for the 0.01% MnO$_4^-$ reactors and 20-35% for the 0.1% MnO$_4^-$ reactors. The computed total TCE recoveries presented in 44, certainly do not equate to 100%. As discussed in previous sections, some of the unrecovered

TCE may have escaped from the reactors since the desorption tubes were not configured to capture 100% of the vapor phase when the port was in the open position (See Section 2.2.1). It is also possible that complete extraction of the remaining GW & sludge slurry did not occur (Exp. 2b-3 in Section 2.2.2). However, the preliminary data presented in Figure 9 indicated that at least 90% of the starting TCE mass can be extracted from the TSF-05 slurry within 2 hrs.

As discussed in the experiments for the dissolved plume media, the TCE oxidation component of the mass balance does not take into account any TCE initially bound to solid phase. If the highly organic sludge was being oxidized, it would seem plausible that TCE originally sorbed onto the sludge could have been partitioned into the aqueous phase and subsequently oxidized. Furthermore, it is possible, particularly for the 0.1% MnO_4^- reactors, that the chosen aliquot sampling times did not temporally capture the exact point in time that oxidant depletion occurred. At the point of oxidant depletion, the reactors would have reached their lowest initial aqueous TCE concentration before the subsequent rise in aqueous TCE concentrations due to TCE DNAPL dissolution. (In the earlier experiments with TSF-05 GW, complete oxidation of all initial TCE often occurred prior to T=0.5 hrs.) Thus, the low total TCE recoveries reported in Table 65 may actually be due to the inability to quantify additional TCE oxidation that was occurring. The computation of reaction rates was not attempted for this experiment since the use of 0.01% and 0.1% MnO_4^- loadings do not adequately satisfy the oxidant demand of the TCE contaminated sludge.

As mentioned above oxidant depletion occurred rapidly for both the 0.01% and 0.1% MnO_4^- reactors. It should be noted that in Figure 96 all of the measured MnO_4^- concentrations after the T=0 hrs are below that of the lowest MnO_4^- calibration standard (5 mg/L). Thus, any MnO_4^- trends presented in Figure 96 are of little significance.

From Figure 97, there is a marked difference in the initial pH of the reactors due to the presence of the sludge itself. In fact, the initial pH value of the treatment reactors (before oxidant addition) was approximately 1 pH unit less than that of the GW controls. (Slurries of the dissolved plume media had pH values similar to that of TSF-05 GW) The overall pH values of the test reactors increased slightly after the oxidant mass was depleted. Since the presence of the sludge resulted in initial pH decreases, the observed pH increases may have been caused by the oxidation of the organic sludge itself.
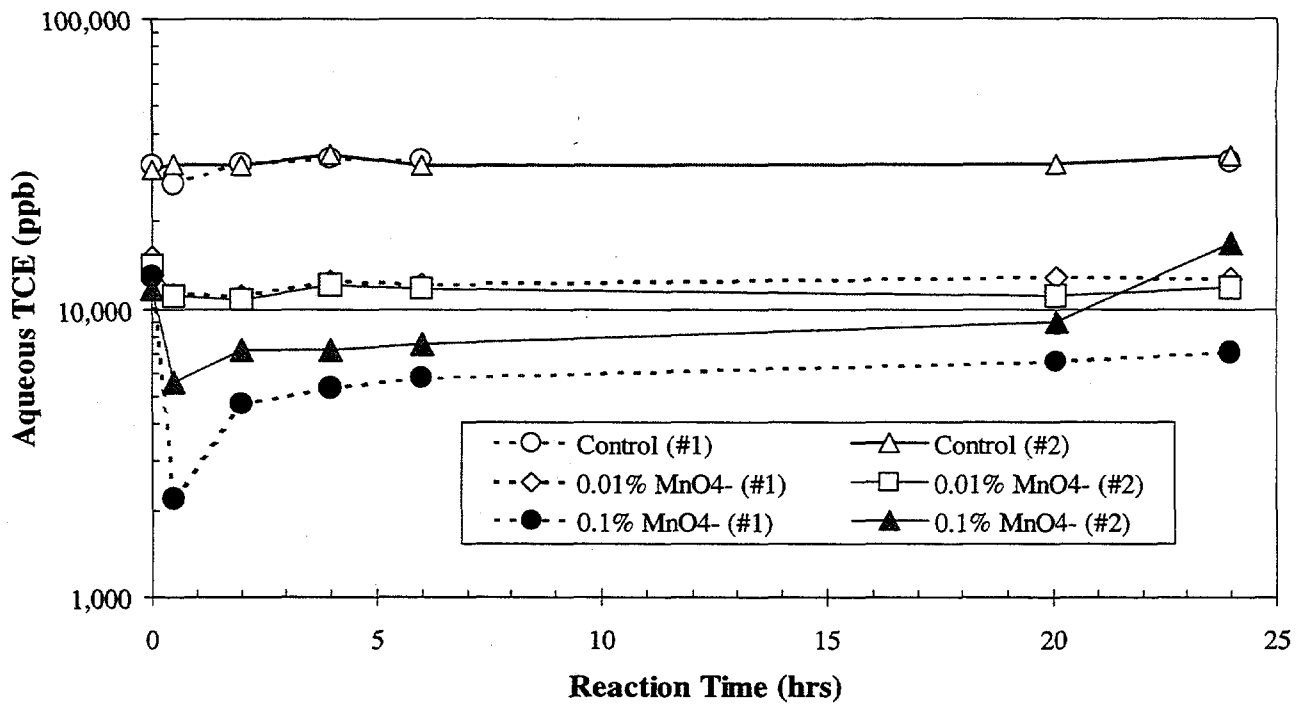
Figure 95. TCE vs. Time, TSF-05 GW& Sludge, (ORNL Exp. 4b-R11, Initial TCE=10,000
μg/L, Conducted at 12°C, 4:1 L/S Ratio)
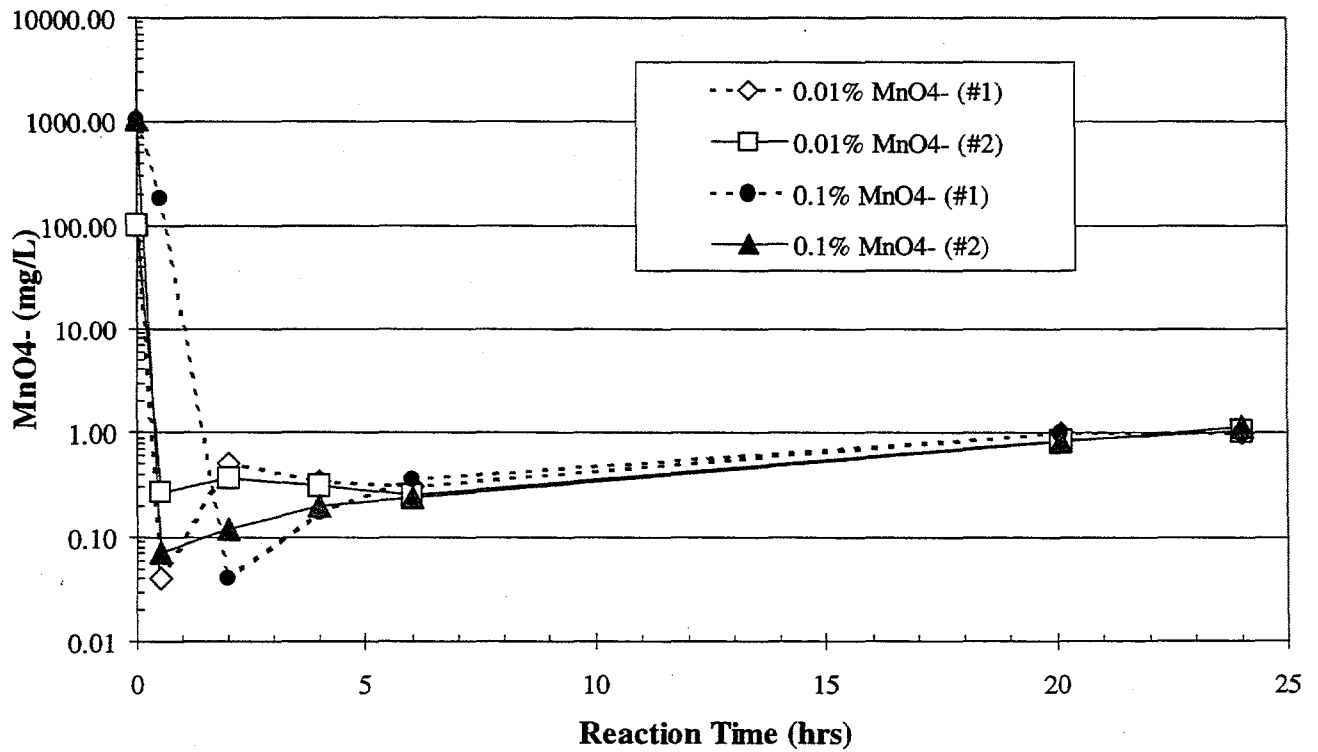
Figure 96. MnO$_4$⁻ vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R11, Initial TCE=10,000
μg/L, Conducted at 12°C, 4:1 L/S Ratio)

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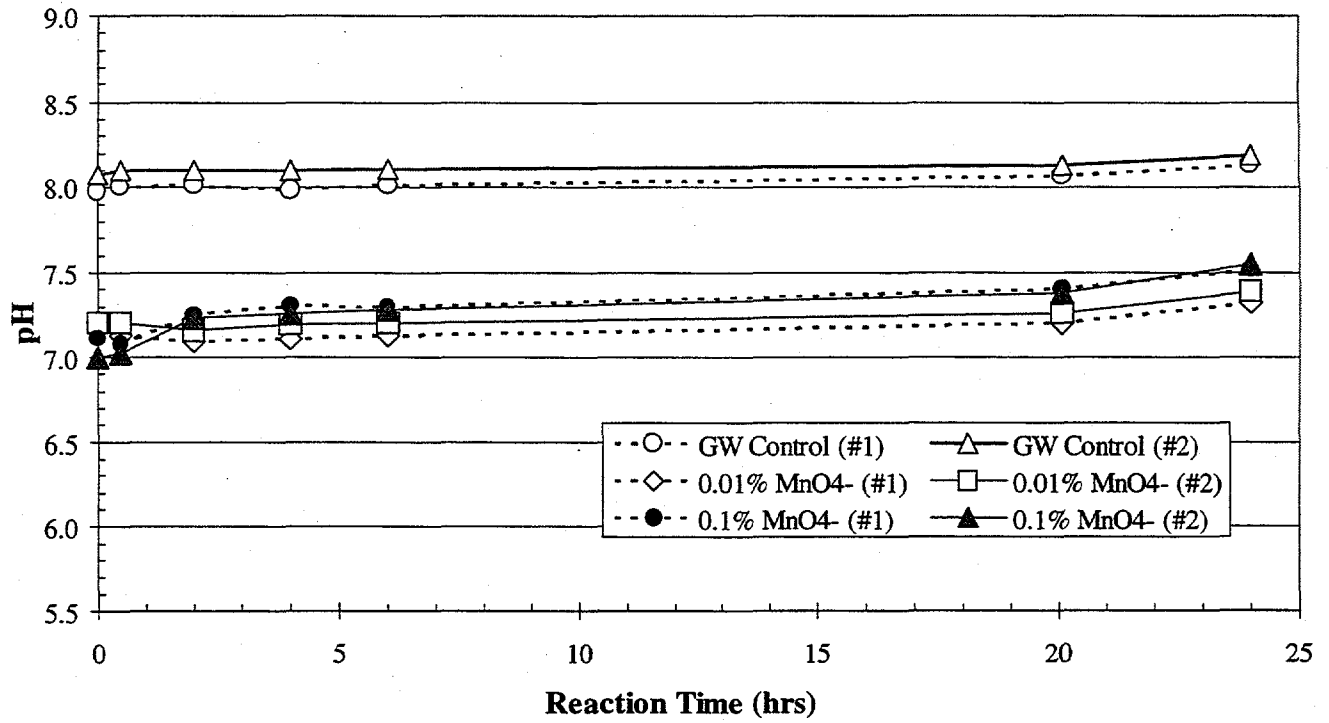
Figure 97. pH vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R11, Initial TCE= 10,000 μg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 65. TCE Mass Balance for ORNL Exp. 4b-R11 (TSF-05 GW & Sludge). [a]

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	TCE Oxidized	Total Mass Recovered (mg)
Control (#1)	11.1	11.1	0.00	8.6	2.5	NA	11.1
			0%	78%	22%	NA	100%
Control (#2)	10.9	10.9	0.00	9.5	2.5	NA	12.0
			0%	87%	23%	NA	110%
0.01% (#1)	11.6	5.7	0.00	8.6	1.0	1.4	11.1
	%Sorbed:	50%	0%	75%	9%	12%	96%
0.01% (#2)	11.62	5.38	0.00	7.2	0.9	1.1	9.3
	%Sorbed:	54%	0%	62%	8%	10%	80%
0.1% (#1)	11.46	4.84	0.00	4.3	0.5	4.0	8.8
	%Sorbed:	58%	0%	38%	4%	35%	77%
0.1% (#2)	11.13	4.28	0.00	5.4	0.7	2.2	8.4
	%Sorbed:	61%	0%	48%	7%	20%	75%

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg= 30,491 µg/L, σ=584 µg/L). For GW controls, Total Initial =Initial Aqueous.
TCE Oxidized only includes mass associated with the difference in the aqueous TCE concentrations between 0-0.5 hrs.

Table 66. MnO₄⁻ Consumption Data for ORNL Exp. 4b-R11 (TSF-05 GW & Sludge).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	38.0	0.08	37.64	0.08
0.01% (#2)	38.2	0.08	37.81	0.08
0.1% (#1)	386.8	0.82	386.40	0.82
0.1% (#2)	376.8	0.83	376.34	0.83

[a] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4b-R15
(TSF-05, Sludge, 10,000 TCE, 0 Other, 1% and 3% MnO_4^-)
(Repeat of Exp. 4b-R10)

This experiment investigated the oxidation of TSF-05 GW and sludge spiked at 10,000 µg/L TCE. The TCE, MnO_4^- and pH values with time are presented in Figures 98, 99, and 100, respectively. Tables 67 and 68 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

This experiment was primarily conducted according the testplan. However, a crack was observed in the second 1% MnO_4^- reactor immediately following the overnight equilibrium and before collection of the T=0 aliquots. The contents of this reactor were quickly transferred to a spare reactor flask but a spare stopcock adapter (Figure 3) was not available. Instead, a solid glass stopper was used, and its removal was required each time an aliquot sample was collected. Therefore, losses of TCE due to volatilization may have been greater for this reactor than for the other reactors.

After equilibration, the average initial aqueous TCE concentration of the spike solution prepared (TSF-05 GW) was 9,180 µg/L (σ= 93 µg/L). After transfer to the test reactors and equilibration with the TSF-05 sludge, the aqueous TCE concentrations in the slurries were lower than those observed in the groundwater controls. In fact, the sludge adsorbed an average of 45% of the total initial TCE added to each reactor. Final TCE recovery values of 93% and 94% were obtained for the first and second control reactors, respectively. Closer examination of the aqueous TCE values obtained with time for the control samples suggest that the <100% recovery is likely a result of volatilization. In fact, the control reactors were the only reactors in this experiment that had any detectable amount of TCE present on their charcoal desorption tube beds.

From Figure 98, the aqueous TCE concentrations of the treatment reactors are quickly reduced as oxidation occurs. A low residual TCE concentration is present in the first 1% MnO_4^- reactor throughout the remainder of the reaction period. This residual is likely not associated with any solvent contamination problems during analysis since TCE was not detected in other samples collected and analyzed at the same time. The corresponding oxidant consumption curve for this reactor (Figure 99) indicates that ≈100 mg/L MnO_4^- residual also exists. Thus, it is unknown why both TCE and MnO_4^- co-existed in this reactor. While there is no evidence to the effect, the residual oxidant concentration may not have been great enough to drive the oxidation reaction to completion. Examination of the mass balance components for this reactor (Table 67) revealed that at least 58% of the initial TCE was oxidized and that 32% (0.92 mg TCE) of the initial TCE mass was still present in the reactor after 24 hrs. Of this remaining TCE mass, a maximum of 0.002 mg was associated with the ≈300 mL of TSF-05 GW present following the last aliquot sampling. Hence, essentially all of remaining TCE was associated with the sludge. Since 41% of the initial TCE was originally adsorbed by the sludge and 32% remains, the fate of the "missing" 9% is unknown. It may have been (1) oxidized, (2) volatilized, or (3) present in the sludge but not measured due to the hexane extraction efficiency being <100%. The volatilization option is supported by the comparable total recoveries obtained for the control reactors.

It appears from figure 89, that complete oxidation also occurred for the second 1% MnO_4^- reactor. Recall, however, that this reactor developed a crack during contaminant equilibration. While the TCE mass actually present in the reactor at T=0 was likely oxidized, a good mass balance cannot be made for this reactor since the initial total TCE in the reactor is unknown. Very little TCE was present in the final extraction of the reactor.

The experimental data collected suggest that complete oxidation did occur for the 3% MnO_4^- reactors. TCE was not detected in the aqueous aliquot samples after 0.5 hrs, and little, if any, TCE was present in the extraction of the remaining slurry. TCE was not detected on these sample extracts which were diluted 20 fold. Thus, the 0.04 mg TCE value presented in Table 67 is an assumed maximum (Assumed Conc.= Min. Detection Limit X 20). As discussed previously, the TCE oxidation component of the mass balance does not take into account any TCE initially bound to the sludge. Since TCE was not detected in the final extraction of these test reactors and a large MnO_4^- residual existed, it is suspected that the unaccounted for TCE was likely oxidized. Thus, the low total TCE recoveries reported in Table 67 for the 3% MnO_4^- reactors may actually be due to the inability to quantify the additional TCE oxidation that was occurring. Although enough data points are not available to compute a reaction rate constant, an observed oxidation rate of approximately 5.8 mg/hr was computed for both the 1% the 3% MnO_4^- reactors.

During this experiment, greater than 90% of the oxidant mass in the 1% MnO_4^- reactors was consumed. Consumption of MnO_4^- throughout the reaction period was also observed. Since there was little TCE oxidation beyond T=3 hrs, it is suspected that the TSF-05 sludge was the source of the continued oxidant demand. Approximately 50% of the initial MnO_4^- added to the 3% MnO_4^- reactors was consumed during this experiment.

As observed in the other sludge experiments, there is a marked difference in the initial pH of the treatment reactors due to the presence of the sludge itself. Following an initial drop associated with the oxidation reaction, the pH values eventually increased by approximately 0.7 and 0.1 pH units for the 1% and 3% MnO_4^- reactors, respectively. Other experiments involving the 1% and 3% MnO_4^- loadings have also resulted in similar net increases in overall system pH, which is likely due to destruction of the organic sludge and /or the increased ionic strength imparted by the residual oxidant solution.

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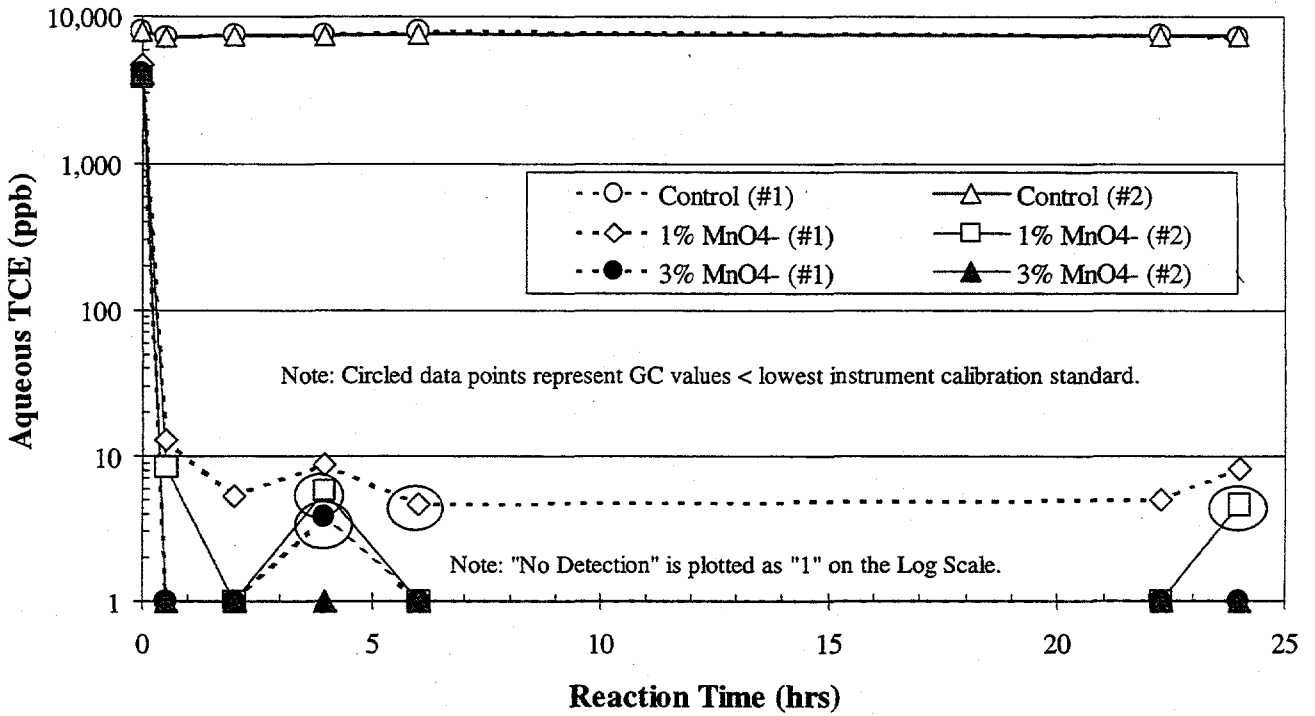
Figure 98. TCE vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R15, Initial TCE=10,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
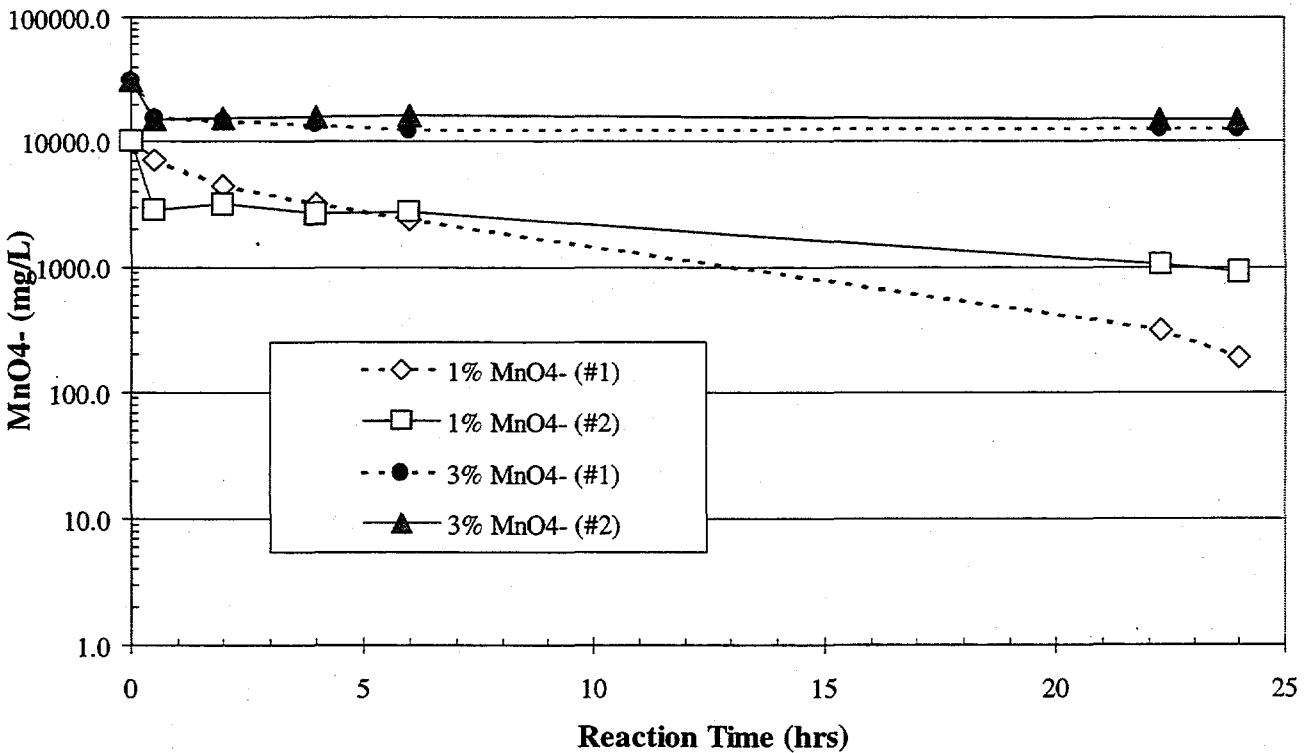
Figure 99. MnO_4^- vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R15, Initial TCE=10,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
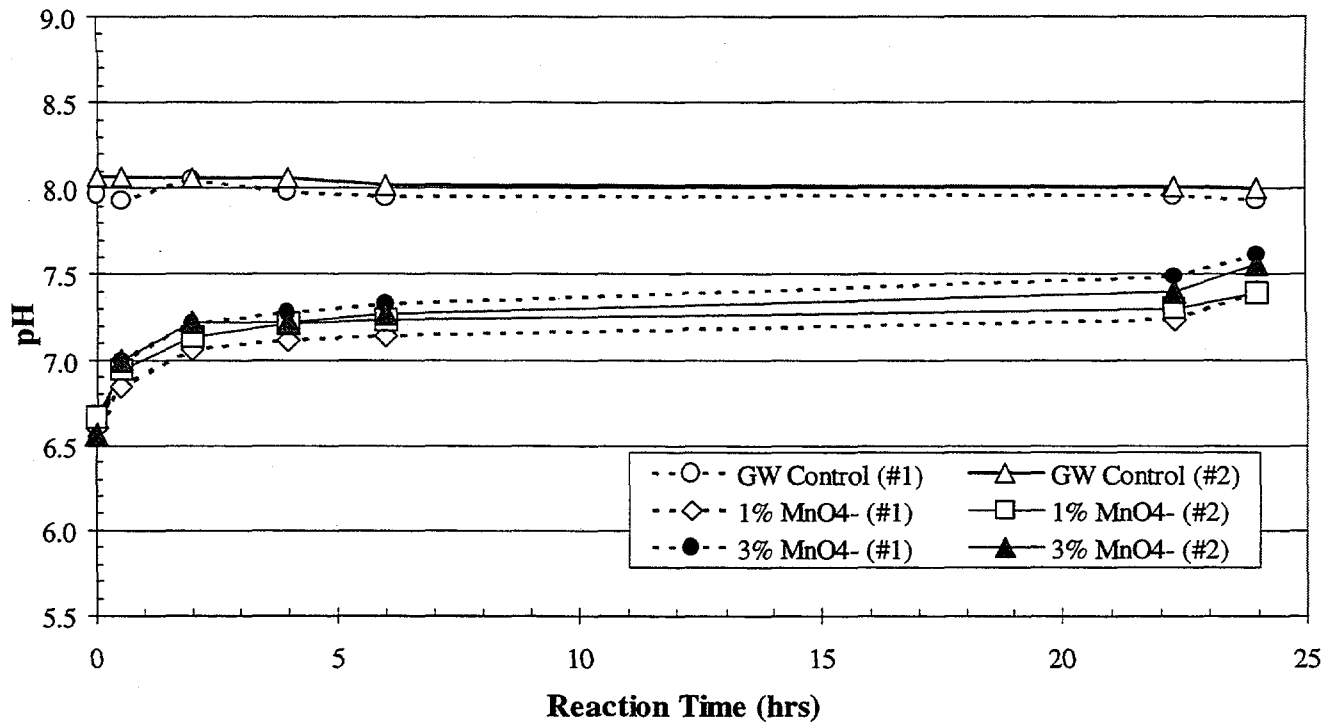
Figure 100. pH vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R15, Initial TCE= 10,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 67. TCE Mass Balance for ORNL Exp. 4b-R15 (TSF-05 GW & Sludge). [a]

Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	2.9	2.9	0.000	2.0	0.7	NA	2.7
			0%	69%	24%	NA	93%
Control (#2)	2.8	2.8	0.000	2.1	0.6	NA	2.6
			0%	73%	21%	NA	94%
1% (#1)	2.9	1.7	0.000	0.92	0.05	1.7	2.6
	%Sorbed: 41%		0%	32%	2%	58%	91%
1% (#2)	2.9[†]	1.4	No Sample	0.16	0.04	1.4	1.6
	%Sorbed: 51%[†]		No Sample	6%[†]	1%[†]	48%[†]	55%[†]
3% (#1)	2.9	1.5	0.000	0.04	0.04	1.5	1.5
	%Sorbed: 48%		0%	1%	1%	51%	54%
3% (#2)	2.9	1.5	0.000	0.04	0.04	1.5	1.6
	%Sorbed: 47%		0%	1%	1%	51%	54%

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg= 7,841 µg/L, σ=66 µg/L). For GW controls, Total Initial =Initial Aqueous.

[†] There is uncertainty in the Initial Total value due to a leak in this reactor prior to T=0 hrs.

Table 68. MnO_4^- Consumption Data for ORNL Exp. 4b-R15 (TSF-05 GW & Sludge).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^- /g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
1% (#1)	3683	8.1	3614	8.0
1% (#2)	3630	8.1	3301	7.4
3% (#1)	11026	24.6	6574	14.7
3% (#2)	11147	24.7	5761	12.7

[a] Consumption is computed after 24 hr reaction time.

ORNL Exp. 4b-R16
(TSF-05, Sludge, 100,000 TCE, 0 Other, 0.01% and 0.1% MnO_4^-)
(Repeat of 4b-R11)

This experiment investigated the oxidation of TSF-05 GW and sludge spiked at 100,000 µg/L TCE. The TCE, MnO_4^- and pH values with time are presented in Figures 101, 102, and 103, respectively. Tables 69 and 70 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

This experiment was conducted in accordance to the appropriate testplan procedure.

After equilibration, the average initial aqueous TCE concentration of the spike solution (TSF-05 GW) was 90,483 µg/L (σ= 2,123 µg/L). After transfer to the test reactors and equilibration with the TSF-05 sludge, the aqueous TCE concentrations in the slurries were lower than those observed in the groundwater controls. In fact, the sludge adsorbed an average of 34% of the total initial TCE added to each reactor. Final TCE recovery values of only 80% and 83% were obtained for the first and second control reactors, respectively. Closer examination of the aqueous TCE values revealed that most of this TCE loss was experienced between the T=0 hrs and T=0.5 hrs sampling periods. Detectable amounts of TCE were present on the first charcoal bed extracts for both control samples.

All of the experimental results lead to the conclusion that little of the initial TCE mass was oxidized during the experiment. This was not unexpected due to the (1) high TCE spike levels (2) the presence of the highly organic sludge and (3) the use of the lower 0.01% and 01% MnO_4^- loadings. Table 69 and Figure 101 do indicate that the higher initial oxidant loadings resulted in the greatest amount of TCE oxidation (16% max). It should also be noted that the apparent decrease in TCE for the second 0.01% MnO_4^- reactor is likely because the TCE concentration determined for the hexane extract exceeded that of the maximum calibration standard (Figure 101).

As observed in Exp. 4b-R11, aqueous TCE concentrations appeared to gradually increase following MnO_4^- depletion, suggesting that TCE might have been released into the aqueous phase as a result of sludge oxidation. Total TCE recoveries for the treatment reactors (88%-97%) are much higher than those obtained for the GW control reactors (see Table 69). TCE was present on most of the desorption tubes used for the treatment reactors. The largest percentage of the initial TCE mass recovered was found in the slurry that remained following completion of the test. To determine how much of the remaining TCE was partitioned to the sludge, the TCE mass expected to be associated with the aqueous portion of the slurry was computed using the concentration of the final aliquot sample. For the 0.01% and 0.1% MnO_4^- reactors, an average of 32% and 37% of the remaining TCE was present on the solid phase. These values are comparable to the initial sorption values reported in Table 69.

The computation of reaction rates was not attempted for this experiment since the use of 0.01% and 0.1% MnO_4^- loadings do not adequately satisfy the oxidant demand of the TCE contaminated sludge.

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As mentioned above, oxidant depletion occurred rapidly for both the 0.01% and 0.1% MnO_4^- reactors. It should be noted that in Figure 102 all of the measured MnO_4^- concentrations after the T=0 hrs are below that of the lowest MnO_4^- calibration standard (5 mg/L). Thus, any MnO_4^- trends presented in Figure 102 are of little significance.

From Figure 103, there is again a marked difference in the initial pH of the reactors due to the presence of the sludge itself. As observed in other hot spot sludge experiments, the overall pH values of the treatment reactors increases of less than 0.2 and 0.4 pH units for the 0.01% and 0.1% MnO_4^- reactors, respectively.
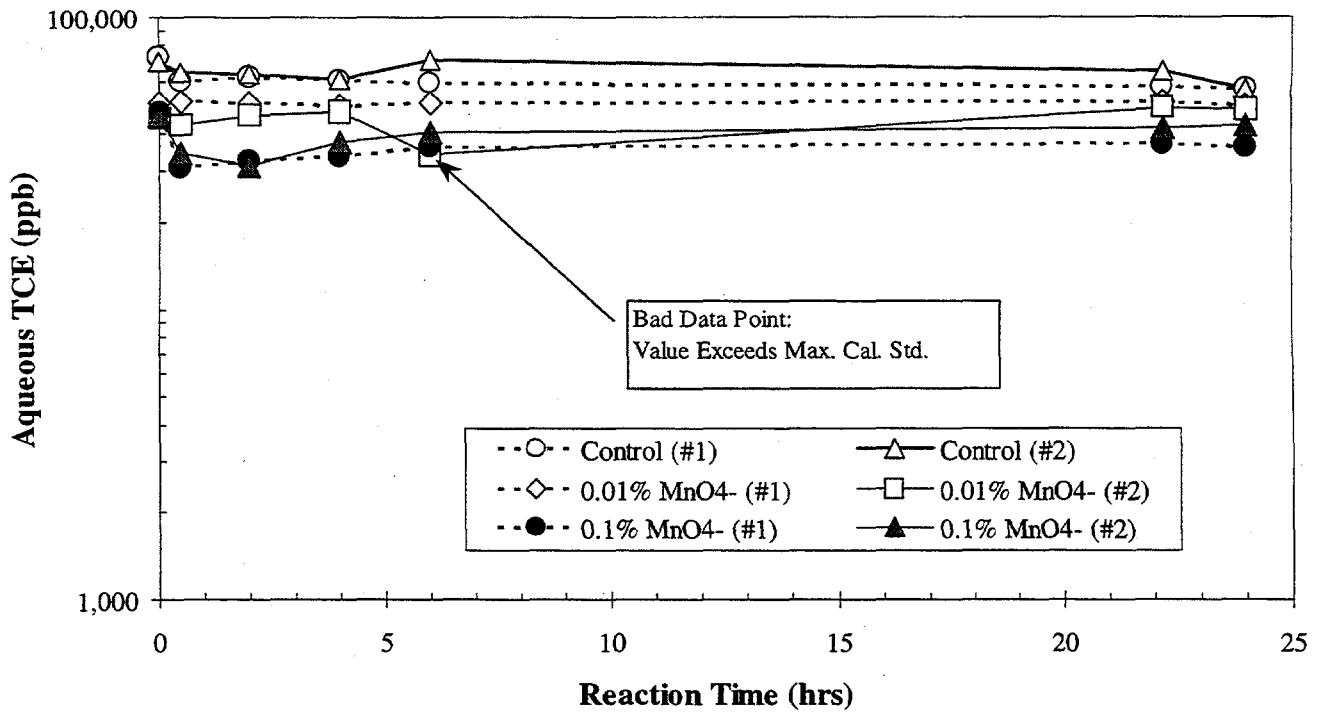
Figure 101. TCE vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R16, Initial TCE=100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
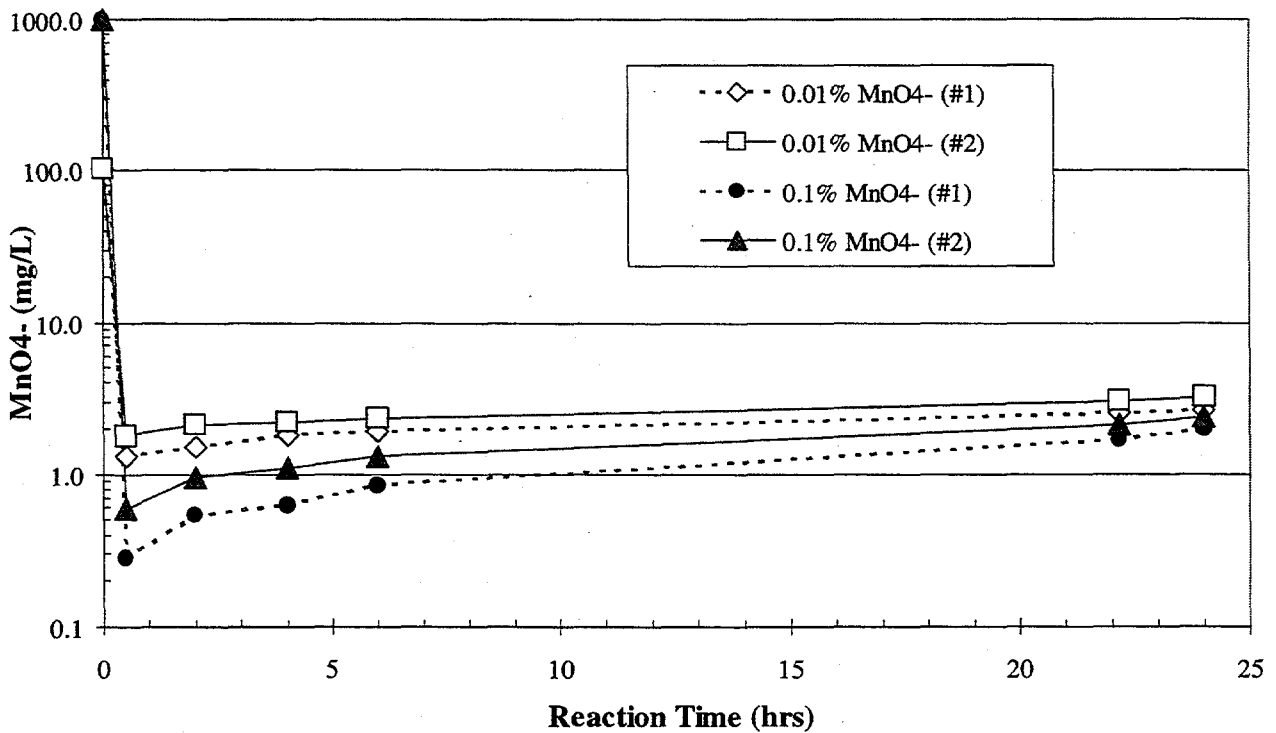
Figure 102. MnO_4^- vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R16, Initial TCE=100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)
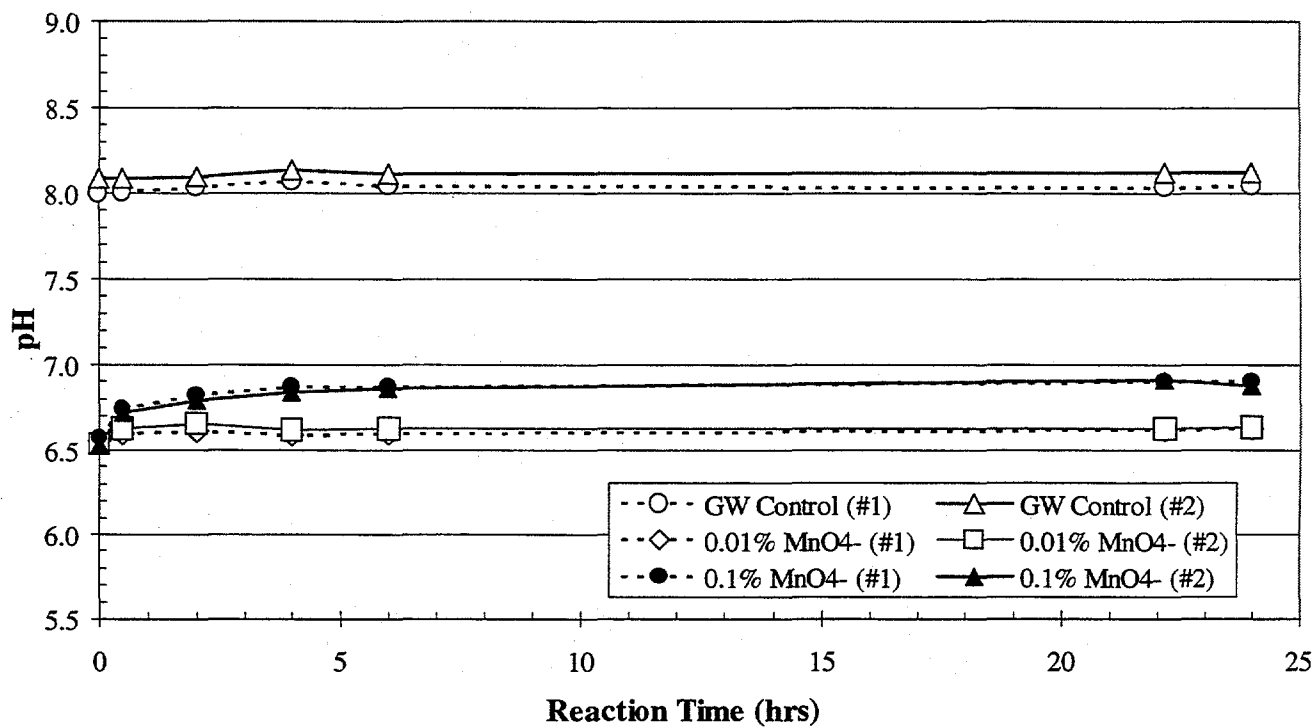
Figure 103. pH vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R16, Initial TCE= 100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 69. TCE Mass Balance for ORNL Exp. 4b-R16 (TSF-05 GW & Sludge).

Test Condition	Total Initial Mass (mg) [a]	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	Cum. Aqueous Mass Oxidized (mg)	Total Mass Recovered (mg)
Control (#1)	26.5	26.5	0.001	15.6	5.6	NA	21.2
			0%	59%	21%	NA	80%
Control (#2)	25.4	25.4	0.001	16.0	5.2	NA	21.2
			0%	63%	20%	NA	83%
0.01% (#1)	26.1	18.7	0.000	20.88	4.07	0.5	25.4
	%Sorbed: 28%		0%	80%	16%	2%	97%
0.01% (#2)	26.2	16.6	0.001	20.28	3.62	-1.0	22.9
	%Sorbed: 37%		0%	78%	14%	-4%	88%
0.1% (#1)	26.2	17.2	0.004	17.08	2.89	4.1	24.1
	%Sorbed: 34%		0%	65%	11%	16%	92%
0.1% (#2)	25.7	16.7	0.002	19.34	3.16	1.6	24.1
	%Sorbed: 35%		0%	75%	12%	6%	94%

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg= 71,490 μg/L, σ=1.805 μg/L). For GW controls, Total Initial =Initial Aqueous.

Table 70. MnO₄⁻ Consumption Data for ORNL Exp. 4b-R16 (TSF-05 GW % Sludge).

Test Condition	Initial Oxidant (mg MnO₄⁻)	Initial Loading (mg MnO₄⁻/g)	Cum. Consumed (mg MnO₄⁻)	Cum. Consumed (mg MnO₄⁻/g)
0.01% (#1)	36.2	0.08	35.3	0.08
0.01% (#2)	36.3	0.08	35.1	0.08
0.1% (#1)	363.1	0.80	362.4	0.79
0.1% (#2)	357.1	0.80	356.3	0.79

[a] Consumption is computed after 24 hr reaction time.

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ORNL Exp. 4b-R12
(TSF-05, Sludge, 100,000 TCE, 0 Other, 1% and 3% MnO$_4^-$)

This experiment investigated the oxidation of TSF-05 GW and sludge spiked at 100,000 µg/L TCE. The TCE, MnO$_4^-$ and pH values with time are presented in Figures 104, 105, and 106, respectively. Tables 71 and 72 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition.

Significant deviations from the procedure were not noted for this experiment.

After equilibration, the average initial aqueous TCE concentration of the spike solution prepared (TSF-05 GW) was 100,290 µg/L (σ= 1,422 µg/L). After transfer to the test reactors and equilibration with the TSF-05 sludge, the aqueous TCE concentrations in the slurries were lower than those observed in the groundwater controls. In fact, the sludge adsorbed an average of 35% of the total initial TCE added to each reactor. Despite the presence of TCE on the desorption tubes, final TCE recovery values of 103% and 97% were obtained for the first and second control reactors, respectively. Closer examination of the aqueous TCE values for the first control indicate that that final aqueous TCE concentration is slightly greater than what was obtained at the T=0 hrs. Both samples were analyzed on the same day, and the variation may have been a result of the sample holding times for these samples. At any rate, the control reactors indicate that the experiment was conducted under well-controlled conditions.

From Figure 104, the control reactors exhibited steady TCE values, and the aqueous TCE concentrations of the treatment reactors were quickly reduced several orders of magnitude as oxidation occurred. Some problems were experienced in analyzing the aliquots collected between T=6 hrs and T=24 hrs. A TCE residual definitely existed, but it could not be properly quantified. The samples in questions were over diluted on the first round of analysis, resulting in GC values less than that of the lowest calibration standard (5 µg/L TCE). When the samples were prepared with a smaller dilution factor ($\approx$24-30 hrs after the initial analysis) TCE was no longer detected in the samples.

A small amount of TCE was also present in the final extractions of the slurry reactors. There is a strong possibility that all of these residual TCE values are the result of a solvent contamination problem. TCE was not detected in the GC hexane blanks, however, the actual test samples were collected and prepped (extracted with hexane) at RMAL, and the GC hexane blank used in the analytical sequence originated within ESD. Based upon observations made from other experiments already conducted, it seems improbable that a residual TCE concentration would exist in the presence of a large MnO$_4^-$ residual (3% MnO$_4^-$ reactors in Figure 105).

To be conservative in the computation of the oxidized TCE component of the mass balance (Table 71, Column 7), it was assumed that the residual TCE values observed were real. Since excellent mass balances were obtained for the control reactors, the amount of TCE oxidized was computed as follows: Mass TCE oxidized= (Total Initial- Orbo Tube -Final Remaining- Cum. Aliquot). Based on this conservative approach, TCE oxidation values of 98% were obtained for all four of the treatment reactors.

Since the TCE concentrations for the aliquots are likely a result of solvent contamination, reaction rate constants were not computed. Instead, it was assumed that oxidant essentially occurs in the first 0.5 hrs, and observed oxidation rates of 59.6 mg TCE/hr was computed for both the 1% and 3% MnO_4^- reactors.

After the initial oxidant demand, the mass of MnO_4^- present in the 1% reactors gradually decreased during the reaction period. It is assumed that the continued decrease in oxidant was a result of continued oxidation and breakdown of the TSF-05 sludge. Laboratory comments indicate a "yellowing" of the aqueous samples and hexane extracts after a 24 hr period of contact/agitation. Final MnO_4^- consumption was 94% and 100% of the initial MnO_4^- mass added to the first and second 1% MnO_4^- reactors. Note that the apparent large discrepancy between the MnO_4^- data for the 1% reactor at 24 hrs (see Figure 105) is accentuated by the use of a semi-log plot. Approximately 60% of the initial oxidant mass was consumed within the 3% reactors.

For these higher 1% and 3% MnO_4^- loadings, the overall pH (Figure 106) eventually increased following an initial drop associated with the oxidation reaction. These net increases were less than 0.8 and 1.1 pH units for the 1% and 3% MnO_4^- reactors, respectively. Other experiments involving the 1% and 3% loadings for the hot spot sludge have also resulted in similar trend in overall increase in system pH.

Figure 104. TCE vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R12, Initial TCE=100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 105. MnO₄⁻ vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R12, Initial TCE=100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Figure 106. pH vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R12, Initial TCE= 100,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio)

Table 71. TCE Mass Balance for ORNL Exp. 4b-R12 (TSF-05 GW & Sludge). [a]

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	TCE Oxidized	Total Mass Recovered (mg)
Control (#1)	29.3	29.3	0.002	22.9	7.2	NA	30.1
			0%	78%	24%	NA	103%
Control (#2)	28.7	28.7	0.001	21.4	6.3	NA	27.8
			0%	75%	22%	NA	97%
1% (#1)	29.6	20.3	0.000	0.15	0.57	28.9	Not Computed
	%Sorbed:	31%	0%	1%	2%	98%	Not Computed
1% (#2)	29.9	20.2	0.000	0.09	0.56	29.2	Not Computed
	%Sorbed:	32%	0%	0%	2%	98%	Not Computed
3% (#1)	29.7	17.7	0.000	0.06	0.49	29.2	Not Computed
	%Sorbed:	41%	0%	0%	2%	98%	Not Computed
3% (#2)	30.0	19.1	0.000	0.06	0.52	29.4	Not Computed
	%Sorbed:	36%	0%	0%	2%	98%	Not Computed

[a] Total Initial for slurries computed using the average initial aqueous TCE concentration of the GW control samples (Avg= 80,565 µg/L, σ=1,330 µg/L). For GW controls, Total Initial =Initial Aqueous.

TCE oxidized= Total Initial- Orbo Tube -Final Remaining- Cum. Aliquot.

Table 72. MnO$_4^-$ Consumption Data for ORNL Exp. 4b-R12 (TSF-05 GW & Sludge).

Test Condition	Initial Oxidant (mg MnO$_4^-$)	Initial Loading (mg MnO$_4^-$/g)	Cum. Consumed (mg MnO$_4^-$)	Cum. Consumed (mg MnO$_4^-$/g)
1% (#1)	3660	8.1	3660	8.1
1% (#2)	3691	8.1	3461	7.6
3% (#1)	11124	24.7	7021	15.6
3% (#2)	11200	24.7	6351	14.0

[a] Consumption is computed after 24 hr reaction time.

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ORNL Exp. 4b-R13
(TSF-05, Sludge, DNAPL TCE, 0 Other, 0.01% and 0.1% MnO_4^-)

This experiment investigated the oxidation of TSF-05 GW and sludge spiked at DNAPL TCE levels; i.e., the groundwater was spiked at $\approx 2 \times 10^6$ µg/L TCE so that a saturated aqueous solution was created.

The TCE, MnO_4^- and pH values with time are presented in Figures 107, 108, and 109, respectively. Tables 73 and 74 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition. Note that some of the columns in the mass balance table were computed differently than the method described at the beginning of Section 2.4.4. The deviations to this computational approach are clearly defined in the upcoming discussion of this experiment.

As presented in the testplan, a single TCE spiking solution could not be made and then subsequently distributed among the test reactors for the DNAPL experiments. Instead, a known mass (gravimetric determination) of pure TCE was added directly to each reactor and allowed to equilibrate at 12°C with the TSF-05 sludge. Since the initial target TCE concentration (2×10^6 µg/L) was ≈twice the aqueous solubility of TCE, a non-aqueous TCE phase (i.e., DNAPL) was expected to exist within each reactor.

The experiment was conducted according to the testplan procedure, with the exception that the reaction period was extended from 24 hrs to 120 hrs.

At the T=0 time period, the aqueous TCE concentrations within the six reactors were indeed indicative of TCE saturation. The TSF-05 GW controls exhibited an average initial aqueous TCE concentration of 1,312,000 µg/L (σ= 32,060 µg/L). The four treatment reactors containing the TSF-05 sludge slurries experienced TCE concentrations on the order of 665,000 µg/L (σ= 61,400µg/L) after the overnight equilibration period. Due to the spiking approach used, the reactors could potentially have very different total initial TCE masses. There was no means of obtaining the total initial TCE mass in each reactor following equilibration (i.e., at the T=0 hrs sampling period). Thus, the gravimetric spiking data was used to compute the total initial TCE mass present in each reactor with the gross assumption that no TCE was volatilized during equilibration (Table 73, Column 2).

Using this approach, the data suggests that approximately 36% of the TCE initially present in the GW controls existed as DNAPL. Similarly, 65-70% of the initial TCE within the treatment reactors would have either been adsorbed to the sludge and/or present in the reactors as DNAPL.

Little variation in the aqueous concentration of the GW control reactors was observed during the experiment. In fact, the average aqueous TCE concentration for all of the control reactor aliquots during the 120 hr reaction time was 1,250,000 µg/L (σ= 57, 200 µg/L). This was expected since the presence of a DNAPL phase in the reactors enables continuous TCE saturation of the aqueous phase. Thus, TCE losses from the control reactors could not be obtained via simple evaluation of the aqueous TCE concentrations with time. To accurately

compute the TCE recoveries for the control reactors, each was extracted at the end of the reaction period with a known volume of hexane (1:1 v/v extraction). Adding the TCE quantities of each mass balance component listed in Table 73 yielded total TCE recoveries of 74% and 76% for the first and second TSF-05 GW control reactors. It is expected that the majority of this 25% loss occurred during the overnight equilibration period when the reactors were sealed with the glass stoppers. (Recall that all recoveries for this DNAPL experiment are based on the initial TCE mass added to each reactor *before* equilibration and rather than a value obtained *after* equilibration; i.e., the T=0 hrs sampling point) This estimated 25% loss during equilibration is comparable to that observed during equilibration of all the experiments performed during this treatability study.

Apparent TCE oxidation during at least the early portion of the reaction period is observed in Figure 107. As evidenced in Figure 108 and in Table 74, complete consumption of MnO_4^- occurred within the first 0.5 hrs. It is interesting to note that aqueous TCE in the treatment reactors was initially less than aqueous saturation due to the large sorption capacity of highly organic TSF-05 sludge. However, there was a gradual increase in aqueous TCE for the treatment reactors to aqueous saturation levels following the rapid oxidation reaction that occurred. This increase is attributed to (1) pure phase TCE (not sorbed to the sludge) remaining in the reactors being solubilized and/or (2) the dissolution of TCE originally sorbed onto the sludge once the sludge as a result of the sludge itself being oxidized.

Since all oxidant was consumed quickly, the TCE oxidized mass presented in Table 73, Column 7 for each reactor represents the change in TCE mass associated with the difference in aqueous TCE concentration between 0-0.5 hrs. Using this approach, essentially no TCE is removed from the 0.01% MnO_4^- reactors, and approximately 50-100 mg of TCE were oxidized from the 0.1% MnO_4^- reactors. In contrast, averages of 40 mg TCE and 193 mg TCE were oxidized from the 0.01% and 0.1% MnO_4^- reactors of Exp. 4b-R7, where TSF-05 GW was evaluated in the absence of TSF-05 sludge. Via comparison of these two experiments, the reduced TCE oxidation values may be a direct result of competition by the TSF-05 sludge for the available oxidant.

Since oxidation depletion likely occurred before the 0.5 hr sampling point, the true aqueous TCE mass oxidized cannot be determined. (At the point of oxidant depletion, the reactors would have reached their lowest initial aqueous TCE concentration before the subsequent rise in aqueous TCE concentrations due to TCE DNAPL dissolution.) Thus, the low values obtained for the total aqueous TCE mass oxidized (Table 73, Column 7) may be due to the inability to quantify all of the TCE oxidation that was occurring.

The computation of reaction rates was not attempted for this experiment since the use of 0.01% and 0.1% MnO_4^- loadings do not adequately satisfy the oxidant demand of the TCE contaminated sludge.

Finally, the total TCE recoveries determined for the treatment reactors were in the range of 75%-80% and were very comparable to that obtained by the GW control reactors. Again, it is assumed that the majority of this unaccounted for TCE ($\approx$25%) was lost during contaminant equilibration and cannot be explicitly determined or verified with the approach used to spike these reactors.

As mentioned above, the MnO$_4^-$ was quickly consumed in all treatment reactors within 0.5 hrs. The apparent rise in MnO$_4^-$ concentrations at the 120 hr sampling period is likely caused by the breakdown of the sludge after such a long agitation period. As observed in other TSF-05 sludge experiments, the aqueous samples and hexane extracts collected after more than 6 hrs were yellow in color. This "yellowing" likely biased the colorimetric MnO$_4^-$ analyses.

Figure 109 indicates some initial pH reductions as the oxidation of the sludge and/or TCE occurs. However, following oxidant depletion, the pH values of the treatment reactors begin to increase. Net pH increases of approximately 0.5 and 1.2 pH units were observed for the 0.01% and 0.1% MnO$_4^-$ reactors, respectively. Higher pH's for 0.1% MnO$_4^-$ reactors is likely due to the fact that more of the sludge was oxidized in these reactors. Because less sludge is present after oxidation, the contribution of the GW in the pH of the slurry may now be more significant.
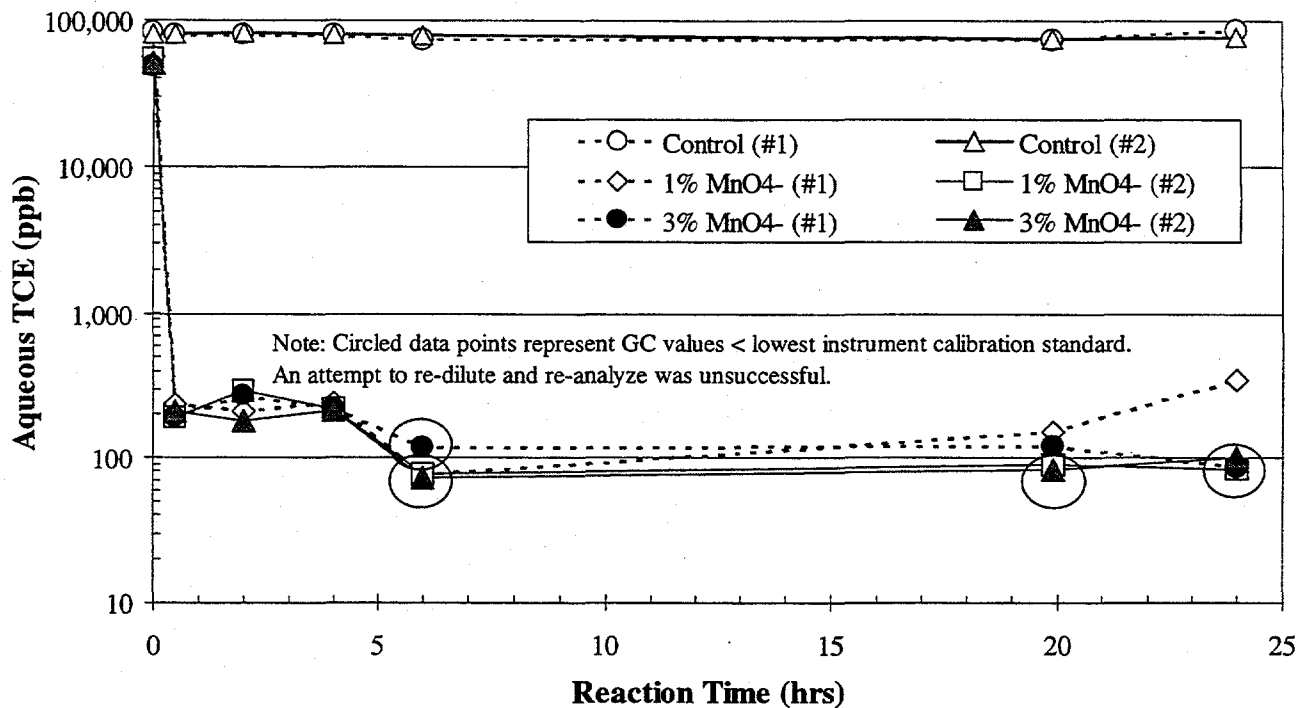
Figure 107. TCE vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R13, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)

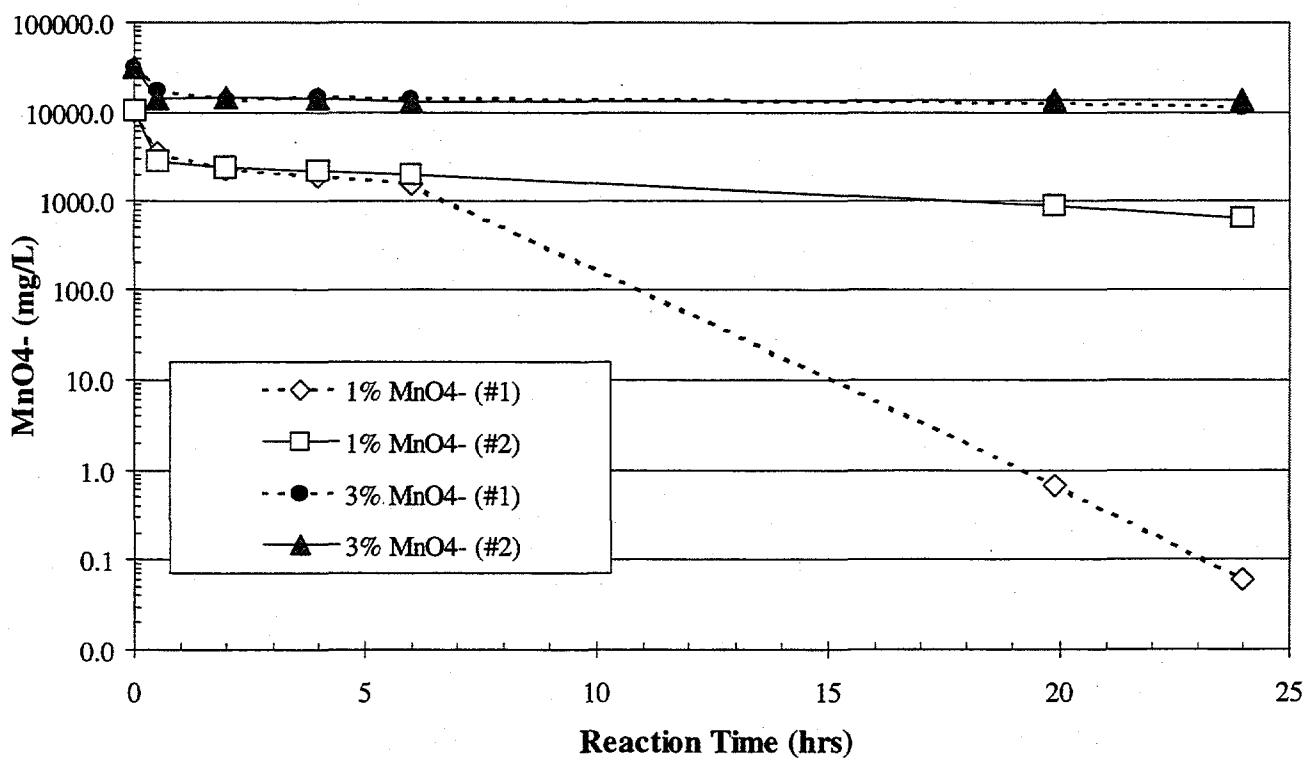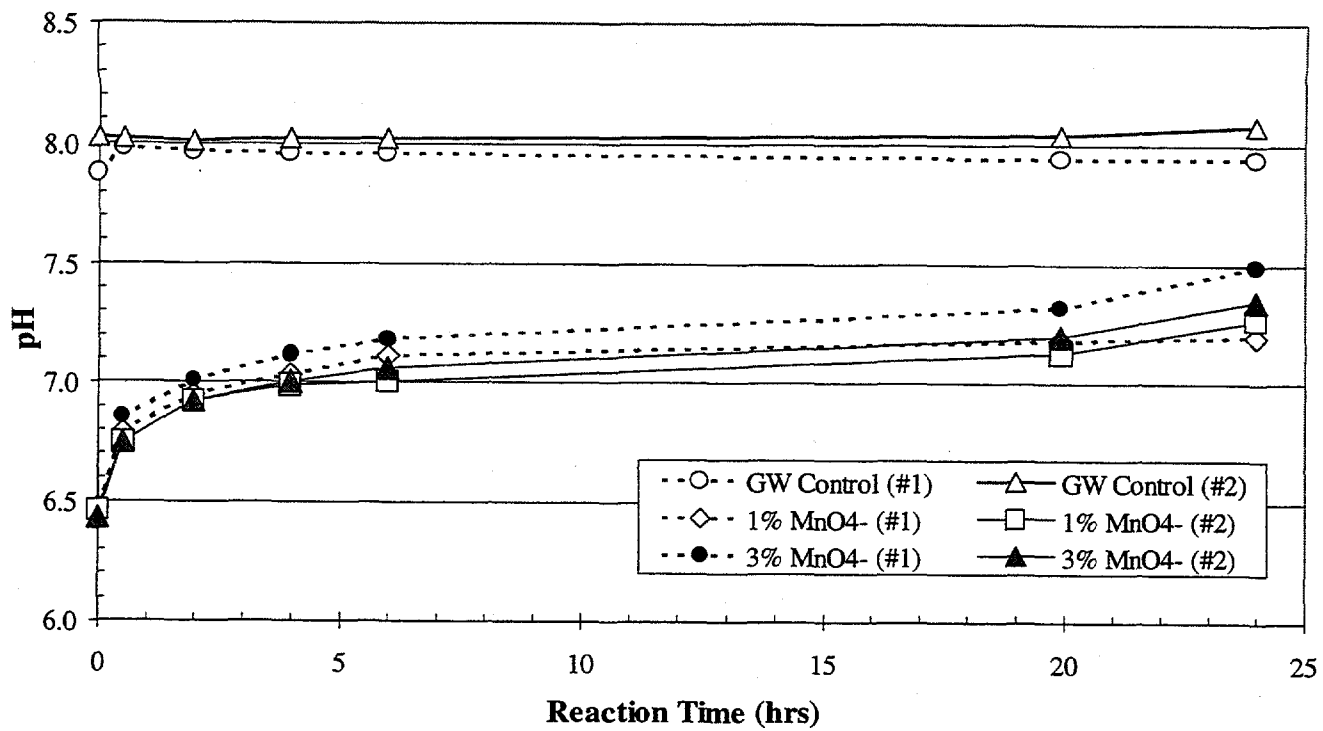Figure 108. MnO$_4^-$ vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R13, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)

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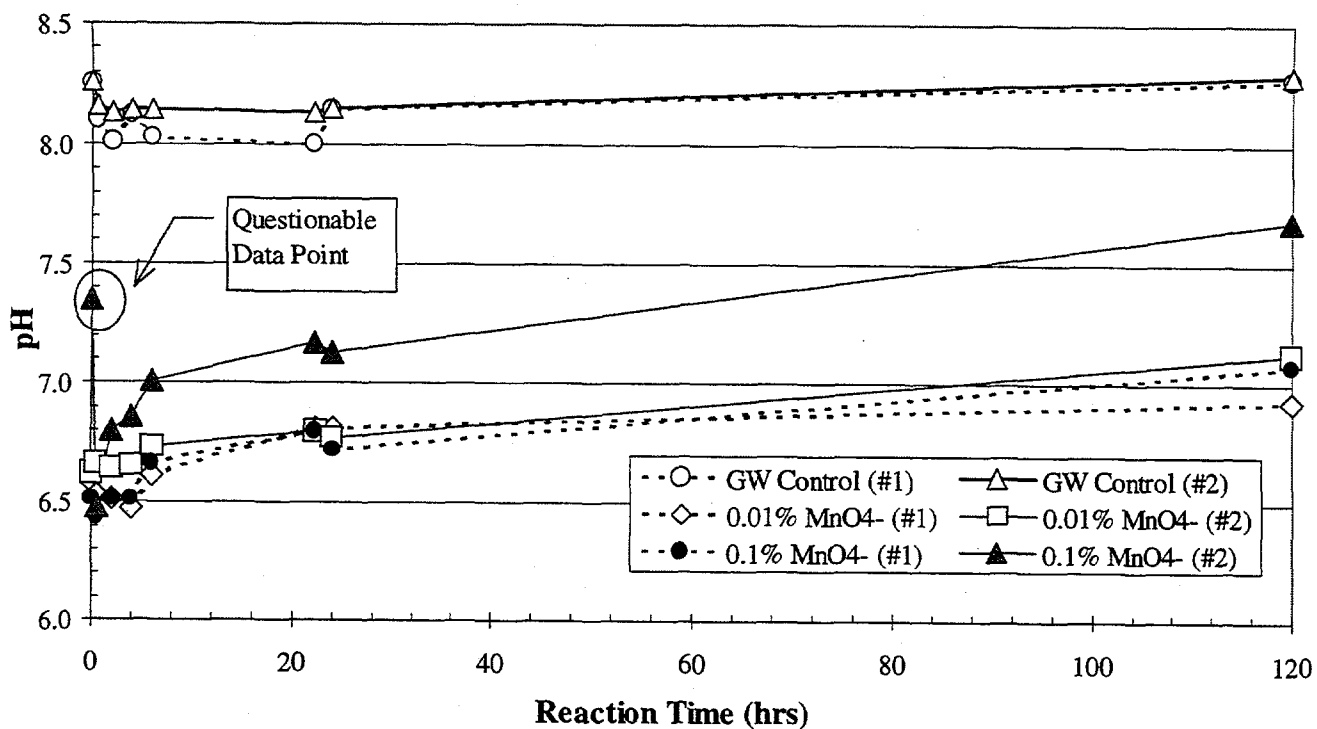
Figure 109. pH vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R13, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)

Table 73. TCE Mass Balance for ORNL Exp. 4b-R13 (TSF-05 GW & Sludge). [a.]

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	TCE Oxidized	Total Mass Recovered (mg)
Control (#1)	751	480	2.20	425	127	NA	555
			0%	57%	17%	NA	74%
Control (#2)	727	467	0.43	424	124	NA	549
			0%	58%	17%	NA	76%
0.01% (#1)	736	256	0.42	475	81	-2	556
	%Non-Aq: 65%		0%	65%	11%	0%	75%
0.01% (#2)	721	266	0.48	485	82	8	576
	%Non-Aq: 63%		0%	67%	11%	1%	80%
0.1% (#1)	728	225	0.74	438	59	55	553
	%Non-Aq: 69%		0%	60%	8%	8%	76%
0.1% (#2)	725	221	0.04	408	53	95	556
	%Non-Aq: 70%		0%	56%	7%	13%	77%

[a.] Total Initial is assumed to be the actual DNAPL TCE mass added to each reactor. TCE oxidized only includes mass associated with the difference in the aqueous TCE concentrations between 0-0.5 hrs (Does not take non-aqueous phase TCE into account)

Table 74. MnO_4^- Consumption Data for ORNL Exp. 4b-R13 (TSF-05 GW & Sludge).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
0.01% (#1)	36.6	0.08	35.6	0.08
0.01% (#2)	36.1	0.08	35.2	0.08
0.1% (#1)	366.5	0.80	365.8	0.80
0.1% (#2)	358.6	0.80	358.3	0.80

[a.] Consumption is computed after a 120 hr reaction time.

ORNL Exp. 4b-R14
(TSF-05, Sludge, DNAPL TCE, 0 Other, 1% and 3% MnO$_4$⁻)

This experiment investigated the oxidation of TSF-05 GW and sludge spiked at DNAPL TCE levels; i.e., the groundwater was spiked at $\approx 2 \times 10^6$ µg/L TCE so that a saturated aqueous solution was created.

The TCE, MnO$_4$⁻ and pH values with time are presented in Figures 110, 111, and 112, respectively. Tables 75 and 76 provide additional TCE mass balance and oxidant consumption information. The (#1) and (#2) notations included in both the figure legends and the first column of these tables refer to the duplicate reactors evaluated for that test condition. Note that some of the columns in the mass balance table were computed differently than the method described at the beginning of Section 2.4.4. The deviations to this computational approach are clearly defined in the upcoming discussion of this experiment.

As presented in the testplan, a single TCE spiking solution could not be made and then subsequently distributed among the test reactors for the DNAPL experiments. Instead, a known mass (gravimetric determination) of pure TCE was added directly to each reactor and allowed to equilibrate at 12°C with the TSF-05 sludge. Since the initial target TCE concentration (2×10^6 µg/L) was $\approx$ twice the aqueous solubility of TCE, a non-aqueous TCE phase (i.e., DNAPL) was expected to exist within each reactor.

The experiment was conducted according to the testplan procedure, with the exception that the reaction period was extended from 24 hrs to 120 hrs.

At the T=0 time period, the aqueous TCE concentrations within the six reactors were indeed indicative of TCE saturation. The TSF-05 GW controls exhibited an average initial aqueous TCE concentration of 1,274,000 µg/L (σ= 45,060 µg/L). The four treatment reactors containing the TSF-05 sludge slurries experienced TCE concentrations on the order of 757,000 µg/L (σ= 24,430 µg/L) after the overnight equilibration period. Due to the spiking approach used, the reactors could potentially have very different initial TCE masses. There was no means of obtaining the total TCE mass in each reactor following equilibration (i.e., at the T=0 hrs sampling period). Thus, the gravimetric spiking data was used to compute the total initial TCE mass present in each reactor with the gross assumption that no TCE was volatilized during equilibration (Table 75, Column 2).

Using this approach, the data suggests that approximately 40% of the TCE initially present in the GW controls existed as DNAPL. Similarly, $\approx$ 62% of the initial TCE within the treatment reactors would have either been adsorbed to the sludge and/or present in the reactors as DNAPL.

Little variation in the aqueous concentration of the GW control reactors was observed during the experiment. In fact, the average aqueous TCE concentration for all of the control reactor aliquots during the 120 hr reaction time was 1,252,000 µg/L (σ= 57, 280 µg/L). This was expected since the presence of a DNAPL phase in the reactors enables continuous TCE saturation of the aqueous phase. Thus, TCE losses from the control reactors could not be obtained via simple evaluation of the aqueous TCE concentrations with time. To accurately

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compute the TCE recoveries for the control reactors, each was extracted at the end of the reaction period with a known volume of hexane (1:1 v/v extraction). Adding the TCE quantities of each mass balance component listed in Table 75 yielded total TCE recoveries of 79% and 72% for the first and second TSF-05 GW control reactors. It is expected that the majority of this 20-25% loss occurred during the overnight equilibration period when the reactors were sealed with the glass stoppers. (Recall that all recoveries for this DNAPL experiment are based on the initial TCE mass added to each reactor *before* equilibration and rather than a value obtained *after* equilibration; i.e., the T=0 hrs sampling point) This estimated 25% loss during equilibration is comparable to that observed during equilibration of all the experiments performed during this treatability study.

Reductions in aqueous TCE concentrations were observed for all treatment reactors. The aqueous TCE concentration data was more variable for the 1% MnO_4^- reactors. Complete oxidation was not observed for the 1% MnO_4^- reactors. (TCE was observed in both the aqueous aliquot at T=120 hrs and in the final reactor extractions.) However, there was a gradual increase in aqueous TCE for the 1% MnO_4^- treatment reactors which ultimately approached aqueous saturation levels following the rapid oxidation reaction that occurred. This increase is attributed to (1) pure phase TCE (not sorbed to the sludge) remaining in the reactors being solubilized and/or (2) the dissolution of TCE originally sorbed onto the sludge once the sludge itself is oxidized. The computation of a reaction rate was not attempted for the 1% MnO_4^- reactors since this loading does not adequately satisfy the oxidant demand of the TCE contaminated sludge.

Due to the fluctuations observed in the 1% MnO_4^- aqueous TCE concentrations, the "oxidized" component of the TCE mass balance in Table 75, Column 7 was computed differently in this experiment. This value represents the maximum observed aqueous TCE mass oxidized during the course of aliquot sampling. Using this approach, an average of 265 mg of TCE is oxidized 36%) from the aqueous phase from the 1% MnO_4^- reactors. These values are similar to the initial mass predicted to be in the aqueous phase at T=0 (Table 75, Column 3). It is expected that oxidation of some TCE originally present as non-aqueous phase TCE also occurred for the 1% reactors. (Unlike treatment reactors in Exp. 4b-R13, the final aqueous concentrations at T=120 hrs for the 1% MnO_4^- reactors were *less* than the aqueous TCE saturation value of ≈1,100,000 μg/L.) Unfortunately, better estimates of the amount of non-aqueous phase TCE that was oxidized in the 1% MnO_4^- reactors cannot be obtained since it is unknown how much of the initial total TCE was loss to volatilization during equilibration (20-25% for the GW control reactors).

Complete TCE is indicated for the 3% MnO_4^- reactors, in which no detectable TCE was observed in the post-treatment extractions of these reactors. For the 3% reactors, an average of 270 mg of TCE is oxidized from the aqueous phase (Table 75, Column 7). These values are similar to the initial mass predicted to be in the aqueous phase at T=0 (Table 75, Column 3). Of course, this value does not take into account the non-aqueous TCE mass that was oxidized.

It is plausible to assume that complete TCE oxidation of the total initial TCE mass for the 3% MnO_4^- reactors occurred within 2 hrs. (The 2 hrs estimate was determined by extrapolating the initially rapid portion of the curves in Figure 110 to a concentration of 1 μg/L TCE.) Hence, an observed zero order oxidation rate of approximately 730 mg TCE/hr is obtained for the 3%

MnO_4^- reactors. The actual rate may be less since some ($\approx$20-25%) of the initial TCE mass (Table 75, Column 2) added to the reactors was likely volatilized during the equilibration step. Although the TCE sample data from T=0.5 through T=24 hrs are questionable due to samples dilution problems, a first order reaction rate constant of k= 4.1 hr^{-1} was computed for the second 3% MnO_4^- reactor and is presented in Figure 113.

The TCE observations correspond well with the MnO_4^- data. As evidenced in Figure 111 and in Table 76, complete consumption of MnO_4^- occurred within the first 6-10 hrs for the 1% MnO_4^- reactors, and a residual oxidant was still present in the 3% MnO_4^- reactors at T=120 hrs. For the two 3% MnO_4^- reactors, an average oxidant consumption value of 64% was observed (see Table 76). The apparent rise in MnO_4^- concentrations at the 120 hr sampling period is likely caused by the breakdown of the sludge after such a long agitation period. As observed in other TSF-05 sludge experiments, the aqueous samples and hexane extracts collected after more than 6 hrs were yellow in color. This "yellowing" likely biased the colorimetric MnO_4^- analyses.

Figure 112, indicates initial pH reductions on the order of 1 pH unit or less as oxidation of the sludge and/or TCE occurs. The pH values of the treatment reactors begin to increase after the initial reaction. In fact, net pH increases of less than 0.5 pH units were observed for both the 1% and 3% reactors. It is interesting that these net increases are smaller in magnitude than those observed in the DNAPL sludge experiment evaluating 0.01% and 0.1% MnO_4^- (Exp. 4b-R13). The difference is likely because significantly more TCE was oxidized in this experiment, thereby producing more H^+ as a reaction product. Thus, the net pH increases expected (and observed in Exp. 4b-R13) due to oxidation of the sludge were offset by the destruction of TCE.
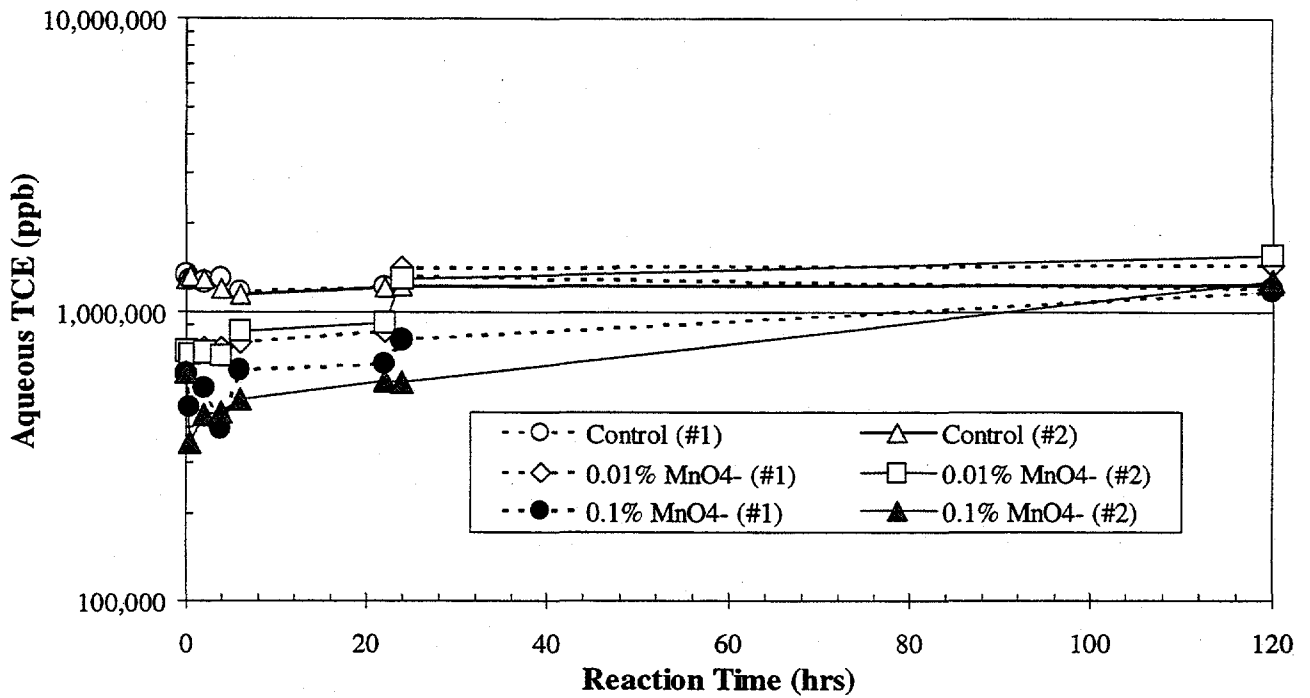
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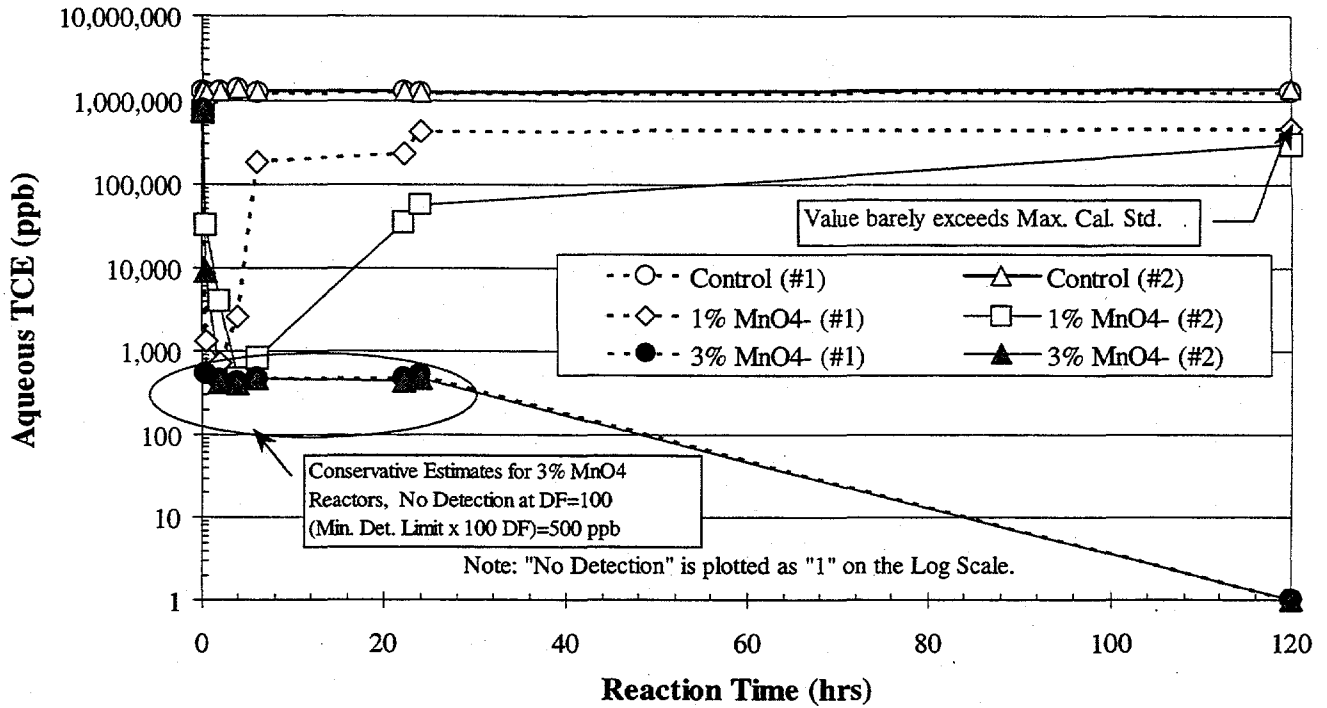
Figure 110. TCE vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R14, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)
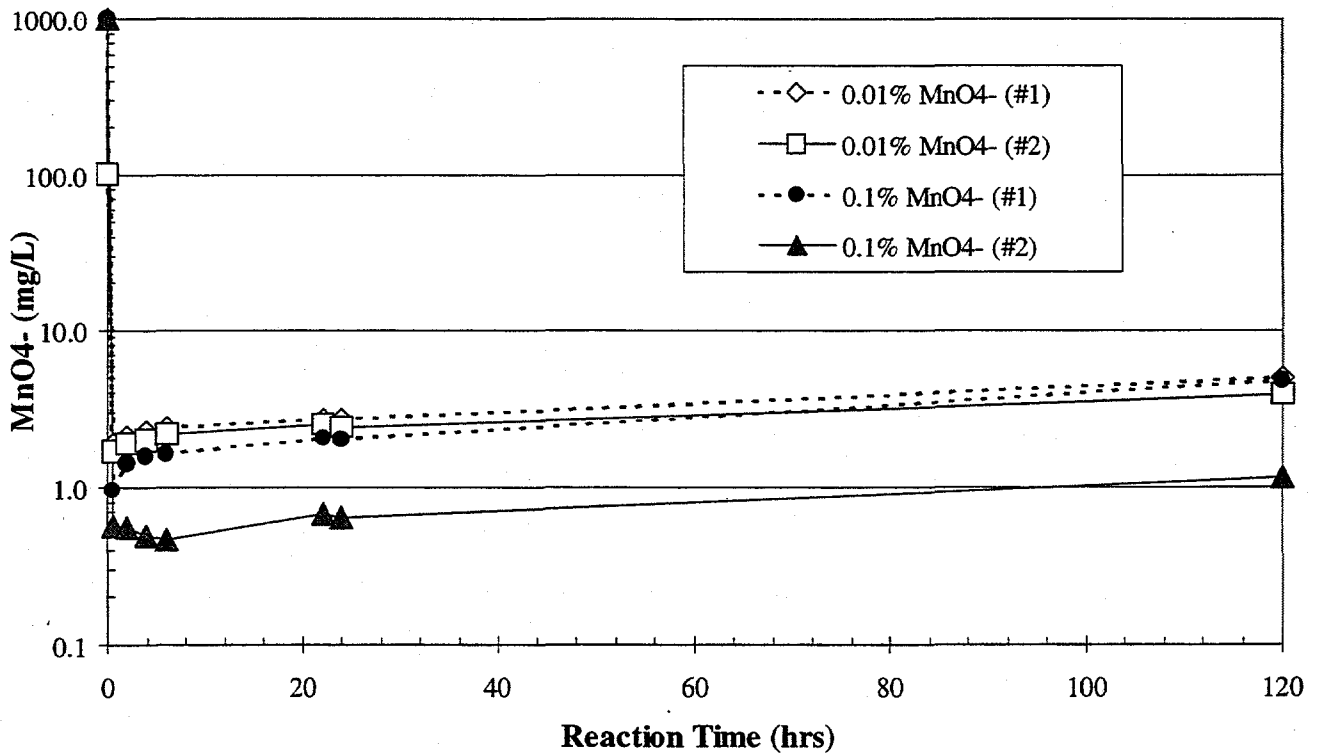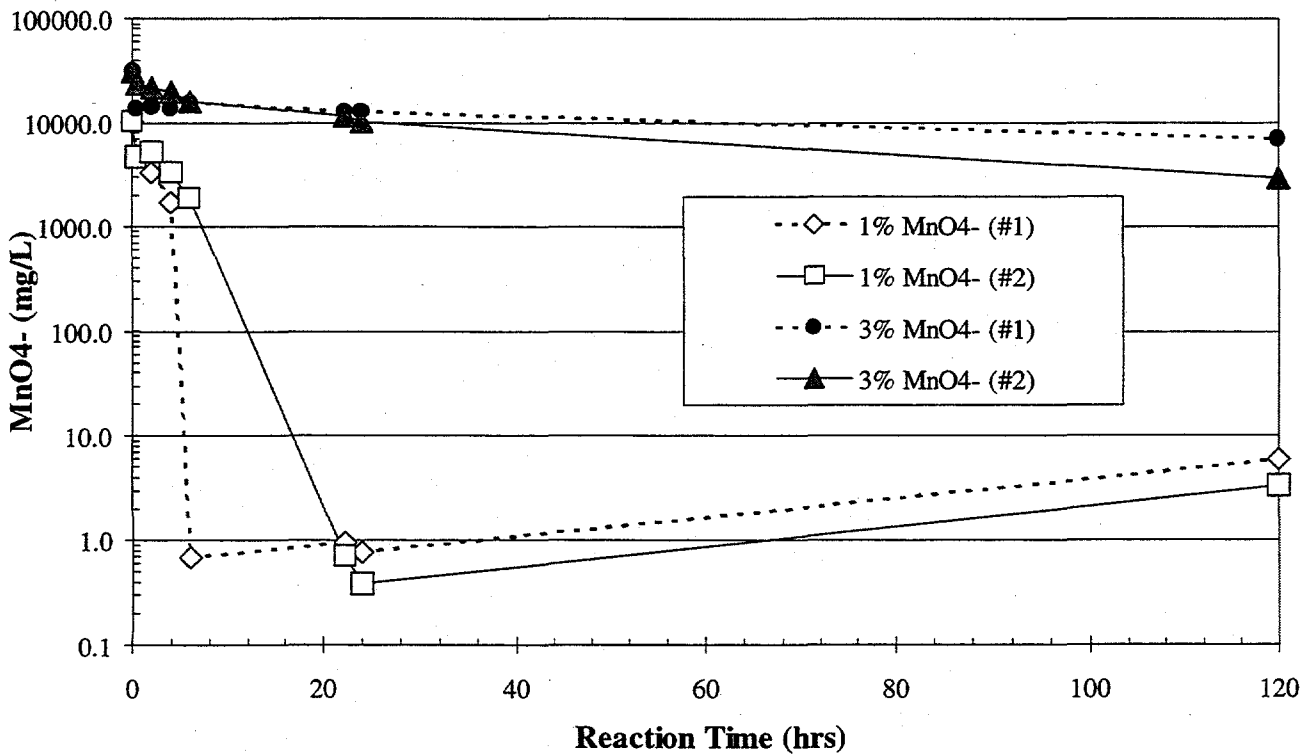

Figure 111. MnO$_4^-$ vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R14, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)

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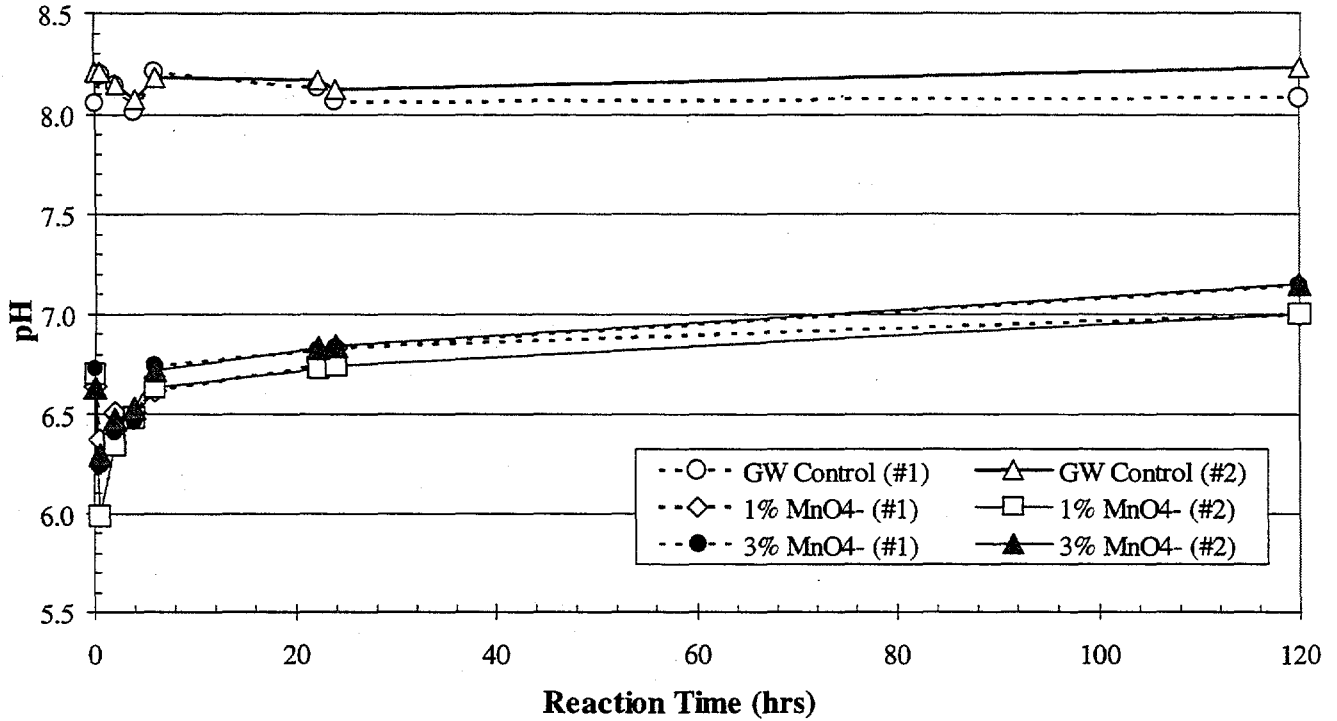
Figure 112. pH vs. Time, TSF-05 GW & Sludge, (ORNL Exp. 4b-R14, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)
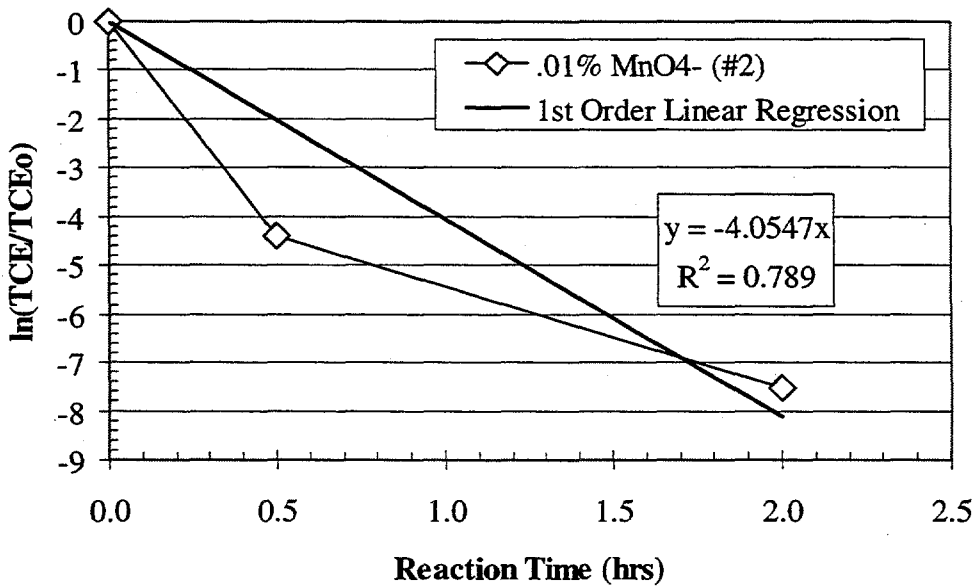
Figure 113. First Order TCE Oxidation Rate Constant for the 3% MnO_4^- (#2) Reactor, TSF-05 GW & Sludge, (ORNL Exp. 4b-R14, Initial TCE= DNAPL, Conducted at 12°C, 4:1 L/S Ratio)

Table 75. TCE Mass Balance for ORNL Exp. 4b-R14 (TSF-05 GW & Sludge). [a]

Test Condition	Total Initial Mass (mg)	Initial Aqueous Mass (mg)	Mass Sorbed on Orbo Tubes (mg)	Mass Remaining in Reactor (mg)	Cum. Mass Removed in Aliquots (mg)	MAX. Cum Aq. Oxidized	Total Mass Recovered (mg)
Control (#1)	734	447	1.19	458	123	NA	581
			0%	62%	17%	NA	79%
Control (#2)	791	470	0.16	437	129	NA	566
			0%	55%	16%	NA	72%
1% (#1)	736	286	0.72	152	23	278	453[†]
%Non-Aq:		61%	0%	21%	3%	38%	62%[†]
1% (#2)	718	269	0.01	104	12	251	367[†]
%Non-Aq:		62%	0%	15%	2%	35%	51%[†]
3% (#1)	720	271	0.18	0	7	264	271[†]
%Non-Aq:		62%	0%	0%	1%	37%	38%[†]
3% (#2)	734	279	0.10	0	8	268	276[†]
%Non-Aq:		62%	0%	0%	1%	37%	38%[†]

[a] Total Initial is assumed to be the actual DNAPL TCE mass added to each reactor. TCE oxidized is the maximum observed aqueous TCE mass oxidized during the course of aliquot sampling (Does not account for oxidation of TCE in non-aqueous phase)

[†] The un-recovered TCE is that which was oxidized from the non-aqueous phase and/or volatilized during equilibration.

Table 76. MnO_4^- Consumption Data for ORNL Exp. 4b-R14 (TSF-05 GW & Sludge).

Test Condition	Initial Oxidant (mg MnO_4^-)	Initial Loading (mg MnO_4^-/g)	Cum. Consumed (mg MnO_4^-)	Cum. Consumed (mg MnO_4^-/g)
1% (#1)	3610	8.1	3610	8.1
1% (#2)	3649	8.1	3649	8.1
3% (#1)	11028	24.6	6588	14.7
3% (#2)	10998	24.6	7353	16.5

[a] Consumption is computed after a 120 hr reaction time.

Summary – VOC Oxidation Rate Measurements, Hot Spot Sludge

Organic sludge from TSF-05 was included in reaction vessels in this suite of experiments. Thus, this set of experiments measured the rate of TCE oxidation in the presence of both groundwater and organic sludge from the hot spot. The experiments were designed to evaluate the effect of the presence of sludge on TCE oxidation and the effect of oxidation on organic sludge. Nominal TCE and permanganate concentrations were the same as those used in the 'Hot Spot Groundwater' series of experiments. The nominal TCE and permanganate concentrations and the associated experiment identification number are below in Table 77.

Table 77.   Experimental Identification for Hot Spot Sludge Experiments.

Nominal MnO₄⁻ Concentration	Nominal TCE Concentration		
	10,000 (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	4bR11	4bR16	4bR13
0.1 %	4bR11	4bR16	4bR13
1 %	4bR15	4bR12	4bR14
3 %	4bR15	4bR12	4bR14

- TCE concentrations in 'control' reactors, which did not contain permanganate, remained constant, while concentrations declined in reactors that contained permanganate. This demonstrates that oxidation is the major removal mechanism in these experiments.

The results of these experiments fall into two general categories, depending on whether the mass of permanganate was sufficient or insufficient to oxidize the mass of TCE present. Nominal permanganate concentrations ranged from 0.01% (100 mg/L) to 3% (30 g/L). The average initial permanganate concentration for each experiment is tabulated below (Table 78).

Table 78. Initial MnO$_4^-$ Concentrations for the Hot Spot Sludge Experiments. [a.]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	103	102	102
0.1 %	1,032	995	999
1 %	10,220	10,225	10,225
3 %	30,970	30,965	30,980

[a.] Values are the average of 2 test reactors (mg/L MnO$_4^-$). All samples filtered (0.45 μm) before analysis.

The permanganate concentrations at the end of each experiment are presented below in Table 79. All experiments were performed in duplicate, and replicate reactors generally exhibited similar behavior. In contrast, the reactors for experiment 4bR12 had very different final permanganate concentrations; both values are tabulated. There was excess permanganate (i.e. sufficient permanganate to react with all of the oxidizable material) only for initial concentrations of 1% and 3%. This is attributed to complete consumption of oxidant by reaction with organic sludge and TCE in the cases with lower initial permanganate concentrations. The ≈4-5 mg/L residual MnO$_4^-$ concentrations presented in Table 79 for the nominal 1,000,000 μg/L TCE case, it likely due to interferences during the colorimetric MnO$_4^-$ analyses. As noted earlier, these experiments were conducted using a 120 hr reaction time, and yellowing of the slurry was observed during the course of the reaction.

Table 79. Final MnO$_4^-$ Concentrations for the Hot Spot Sludge Experiments. [a.]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	1	3	4[2]
0.1 %	1	2	5[2]
1 %	190/930[1]	0.1/636[1]	5[2]
3 %	13,740	12,410	7,000/2,950[1]

[a.] Values are the average of 2 test reactors (mg/L MnO$_4^-$). All samples filtered (0.45μm) before analysis.

[1] Values for replicates that exhibited substantially different behavior.

[2] Value likely resulted from yellow of slurry due to sludge breakdown with 120 hr reaction period.

Initial TCE concentrations ranged from 10,000 µg/L to 1,000,000 µg/L. TCE was present as a non-aqueous phase at the highest concentration. The actual (as opposed to nominal) concentrations initially present are presented below in Table 80. TCE concentrations in experiment 4bR11 were substantially higher than the target concentrations, but other concentrations were fairly close to the intended concentrations. These values are the initial concentrations in the 'groundwater control' reactors. Although a similar mass of TCE was present in reactors that contained organic sludge, sorption of TCE by sludge (on the order of 50%) would cause the aqueous concentrations to be less than those in the aqueous controls.

Table 80. Initial Aqueous TCE Concentrations for the Hot Spot Sludge Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	30,500	71,500	1,311,950
0.1 %	30,500	71,500	1,311,950
1 %	7,840	80,560	1,273,650
3 %	7,840	80,560	1,273,650

[a] Values are the average of the 2 "Groundwater Control" reactors (µg/L TCE) used in each experiment.

The aqueous TCE concentrations at the end of the reaction period are presented below in Table 81. (Note that direct comparison with Table 80 is not appropriate in all cases since the values presented here are from reactors containing a slurry of sludge and groundwater) Two types of behavior were observed: either TCE concentrations declined orders of magnitude from the initial concentration, or they declined only slightly. If there was sufficient permanganate present for there to be a permanganate residual at the end of the experiment, than TCE concentrations declined to low concentrations (≈100 µg/L or less). If permanganate was exhausted before the end of the experiment, then TCE concentrations remained high.

Table 81. Final Aqueous TCE Concentrations for the Hot Spot Sludge Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	12,300	49,125	1,502,350
0.1 %	11,930	39,360	1,220,900
1 %	6[2]	83/350[1,2]	380,850[3]
3 %	ND	95[2]	ND

[a] Values are the average of 2 test reactors (µg/L TCE).
[1] Values for replicates that exhibited substantially different behavior.
[2] One replicate value <MDL.
[3] One replicate exceeded instrument calibration.

The percentage of TCE initially present that was oxidized in each experiment is presented below in Table 82. The cases in which ~100% of the TCE was oxidized correspond with the cases in which there was a permanganate residual at the end of the experiment.

Table 82. Percentage of TCE Oxidized for the Hot Spot Sludge Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (µg/L)	100,000 (µg/L)	1,000,000 (µg/L)
0.01%	11	2[1]	1
0.1 %	28	16[1]	10
1 %	58[1]	100	36
3 %	100	100	100

[a] Values are the average of 2 test reactors (wt%).
[1] Value from only a single reactor.

Zero order TCE oxidation rates were estimated for the cases in which there was a permanganate residual. The estimated rates are presented in Table 83 and 84 on a 'per reactor' basis and on a 'unit volume' basis, respectively. Although the data set is limited, the TCE oxidation rate increases with initial TCE concentration. A trend as a function of initial permanganate concentration cannot be determined from this data set, although experiments described previously indicate that the TCE oxidation rate is proportional to the permanganate concentration.

Table 83. Observed Minimum Zero Order TCE Destruction Rates - Per Reactor Basis, Hot Spot Sludge. [a.]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	NC[†]	NC[†]	NC[†]
0.1 %	NC[†]	NC[†]	NC[†]
1 %	5.8	59.6	NC[†]
3 %	5.8	59.6	730

[a.] Values are the average of 2 test reactors (mg TCE/hr per reactor). Computed by dividing the Average Initial TCE Mass present in each reactor by the earliest aliquot sampling time at which TCE was not detected. Each reactor contained nominally 400 mL. See Appendix C for actual GW masses in each reactor.

[†] Value not calculated, oxidant was depleted rapidly before all TCE was oxidized.

Table 84. Observed Minimum Zero Order TCE Destruction Rates - Per Unit Volume Basis, Hot Spot Sludge. [a.]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	NC[††]	NC[††]	NC[††]
0.1 %	NC[††]	NC[††]	NC[††]
1 %	16	162	NC[††]
3 %	16	162	2000[†]

[a.] Values are the average of 2 test reactors (mg TCE/L/hour). Values were computed by dividing the Average Initial TCE Mass present in each reactor by both (1) the earliest aliquot sampling time (hrs) at which TCE was not detected and (2) the average initial liquid volume in the reactor (GW and MnO$_4^-$ stock solution, when applicable).

[†] A corresponding first order rate constant is included in Table 86 for this test case.

[††] Value not calculated, oxidant was depleted rapidly before all TCE was oxidized.

• The results of this experiment differ from those of the parallel experiment with groundwater from the same source but no sludge (Section 2.4.3). In the 'sludge' experiments, there were fewer cases in which there was a permanganate residual than in the 'groundwater' experiments. This can be attributed to consumption of oxidant by reaction with the organic sludge. Oxidation of sludge would cause lower permanganate concentrations. Previous experiments indicate that the TCE oxidation rate is proportional to the permanganate concentration, and hence lower permanganate concentrations in the 'sludge' experiments would be expected to cause lower TCE oxidation rates. TCE oxidation rates in the 'sludge' experiments were less than the TCE oxidation rates in the corresponding 'groundwater' experiments. This indicates that the presence of organic sludge would have two effects on

TCE oxidation: (1) Sludge will exert an additional oxidant demand, which may exhaust the supply of oxidant before all of the TCE has been oxidized. (2) Oxidation of sludge will lower permanganate concentrations and thus lead to slower TCE oxidation rates. However, it should be noted that the rate of TCE oxidation is very rapid, even in the presence of organic sludge.

Trends in pH are presented in Table 85 below. pH values increased by approximately 0.1 - 1 pH units. This behavior is in marked contrast to that observed in the 'groundwater' experiments, in which pH decreased, and the changes were much larger. The smaller pH changes observed in the 'sludge' experiments are attributed to the buffering capacity of the organic sludge. The reason for the difference in the sign of the pH change between the 'sludge' and 'groundwater' experiments is unknown. However, the effect may be associated with oxidation of the organic sludge since the initial pHs of the slurry reactors (containing TSF-05 GW and sludge) were significantly lower than the pHs of control reactors containing only TSF-05 GW.

- Changes in pH were so small that pH would not useful for monitoring the progress of ISCO at the field scale

Table 85.   Observed pH Trends in the Hot Spot Groundwater Experiments. [a]

Nominal MnO$_4^-$ Concentration	Nominal TCE Concentration		
	10,000 (μg/L)	100,000 (μg/L)	1,000,000 (μg/L)
0.01%	+0.2	+0.2	+0.5
0.1 %	+0.6	+0.4	+1.2
1 %	+0.7	+0.8	+0.5
3 %	+0.1	+1.1	+0.5

[a] pH Values are the average of 2 test reactors.

A summary of the TSF-05 Slurry experiments (GW and sludge) is presented in Table 86. This table in essence is a summary of the preceding Tables 77 through 85.

It was determined that available oxidant was depleted when it was attempted to use an initial loading of 0.01% MnO$_4^-$ to treat any TCE contaminated sludge (regardless of TCE spike level). Similarly, complete treatment of TSF-05 GW and sludge spiked with ≈2x10^6 μg/L (DNAPL) could only be achieved using an oxidant loading of 3% MnO$_4^-$.

For the 3% MnO$_4^-$ cases, in which MnO$_4^-$ was in excess, it is interesting to note from Table 86 that the amount of oxidant consumed does not increase significantly although the initial TCE masses are orders of magnitude different. In fact, 56%, 60%, and 64% of the initial oxidant mass added was consumed in experiments having initial nominal TCE concentrations of 10,000 μg/L; 100,000 μg/L; and 2x106 μg/L (DNAPL), respectively.

As observed for the TSF-05 GW, the higher the oxidant loading, the higher the oxidant consumption (mg MnO$_4^-$/g media) for oxidizing the same mass of TCE. It is not known precisely what causes this phenomenon. However, from a cost effectiveness standpoint, this

result points to the need to closely tailor the oxidant loading to the field observed VOC contamination levels.

Table 86. Summary of the Hot Spot Sludge Oxidation Rate Experiments.

ORNL Exp. No.	Nominal Initial TCE (μg/L)	Avg. Initial TCE Mass (mg)	TCE Oxidation Observed Rates (mg TCE/hr·Reactor Contents)[†]	Initial MnO_4^- (wt%)	Max. MnO_4^- Consumed (mg MnO_4^-/g)	pH Trends
4b-R11	10,000	11.6	Incomplete (Min 12 % oxidized)[1]	0.01%	0.08	<0.2Net Increase
		11.3	Incomplete (Min 38% oxidized)[1]	0.1%	0.8	< 0.6 Net Increase
4b-R15	10,000	2.9	Residual Present (Min 58% oxidized)[2] Obs. Rate: 5.8[2]	1%	7.7	< 0.7 Net Increase
		2.9	Complete (< 0.5 hrs) Obs. Rate$\geq$ 5.8	3%	13.7	< 1.0 Net Increase
4b-R16	100,000	26.2	Incomplete ($\approx$2% oxidized)[1]	0.01%	0.08	< 0.2 Net Increase
		26.4	Incomplete ($\approx$16% oxidized)[1]	0.1%	0.8	< 0.4 Net Increase
4b-R12	100,000	29.8	Complete (< 0.5 hrs) Obs.Rate $\geq$59.6	1%	8.1	< 0.8 Net Increase
		29.8	Complete (< 0.5 hrs) Obs.Rate $\geq$59.6	3%	15.6	< 1.1 Net Increase
4b-R13	DNAPL[3]	729	Incomplete (Min 1% oxidized)[1,4]	0.01%	0.08	$\approx$0.5 Net Increase
		727	Incomplete (Min 10% oxidized)[1,4]	0.1%	0.8	$\approx$1.2 Net Increase
4b-R14	DNAPL[3]	727	Incomplete (Min 36% oxidized)[1,4]	1%	8.1	<0.5 Net Increase
		727	Complete (< 2 hrs) $k= 4.1\ hr^{-1}$ Obs. Rate $\approx$ 730	3%	16.5	<0.5 Net Increase

[†] Observed Oxidation Rate= (Total Initial mg TCE)/(X hrs·Reactor Contents); Where X represents the earliest sampling time at which TCE was not detected in the aqueous aliquot. Where available, the predicted first order reaction rate constant, k, is presented.
"Reactor Contents" are nominally 400 mL TCE-spiked GW and 100 g TSF-05 Sludge. See Appendix C for actual masses added to each reactor.
[1] Oxidant depleted before all TCE could be oxidized.
[2] It is assumed that the reactions were essentially completed at this time point, even though a low residual TCE concentration was present. The reported values are estimates.
[3] "DNAPL" equates to an aqueous concentration of 2×10^6 μg/L TCE.
[4] A conservative value which does take into account for any non-aqueous TCE which was oxidized.

2.4.5. TSF-05 Sludge Baseline Characteristics and Effect of Oxidation

Various baseline measurements were performed on the TSF-05 sludge prior to the start of the consumption and oxidation experiments. These measurements consisted of bulk density, percent moisture, radiochemical analysis (gross alpha, gross beta, and gamma scan), and total carbon content (see Appendix B). Carbon content was measured on portions of the TSF-05 sludge prior to the oxidant demand and oxidation rate studies and after reaction to determine sludge oxidation trends for each experiment.

The bulk density measurement was used to calculate the total weight of sludge received for sample tracking purposes. The percent moisture was used to convert the raw (as received) sample carbon results to a dry weight basis so that the values could be compared to the dried sample carbon measurements. This was done to ascertain if any loss of sample carbon occurred during the drying process. The radiochemical measurements were conducted to confirm INEEL isotopic data and to establish the radioactive hazards associated with the sludge. Total carbon measurements were performed (1) to establish a baseline carbon value, (2) to determine post-treatment carbon values in the sludge following the oxidant demand and oxidation rate studies, and (3) to determine the effect (if any) that the presence of varying concentrations of TCE would have on the oxidation of the sludge. The average baseline carbon value obtained on the dried sample portions prior to the oxidation studies was compared with the post-treatment values to determine oxidation trends for each experiment. It should be noted that the TSF-05 sludge samples were highly heterogeneous containing such material as fine silt particles, small rocks, thin "shale-like" chips, and other debris that was not specifically identified. Overall, the sludges had a dark reddish brown color, and all containers had a liquid phase, making up half of the sample's weight, separated from the solid material. The sludge samples were homogenized as much as possible by hand stirring prior to subsampling for the baseline characterization work and for the project experiments. However, the sludges could never be described as completely homogeneous. This fact affects the precision of the baseline measurements. Thus, these values should not be interpreted as absolute. The post reaction carbon analyses were less affected by sample non-homogeneity because the sludge would breakdown into a more homogeneous slurry after undergoing 24 hrs or more of shaking during the reaction studies. The color of the sludge slurry remained a dark reddish brown.

2.4.5.1 Baseline Characterization
Bulk Density and Percent Moisture
The bulk density was determined on two 5 gram portions of the raw sludge which were randomly sampled from the one liter containers after hand stirring to homogenize. A Grabner Instruments MiniDens analyzer was used for the measurements. The MiniDens analyzer measures sample density by first obtaining a weight for the sample aliquot using a microbalance. Once the weight is obtained, the instrument then seals the sample in an air-tight chamber, filled only with air and the sludge sample, for volume determination. The volume determination is accomplished by using a piston to increase the pressure in the sealed chamber in 2 KPa increments. The amount of movement required for the piston to obtain a 2 KPa pressure change is directly proportional to the volume of the sample. Once the weight and the volume is known, the instrument's software computes and reports a density value.

The percent moisture determination, defined as $[M_{water}/(M_{water} + M_{solids})] \times 100$, was performed using a 250 gram sample portion which was randomly sampled from a one liter container after hand stirring to homogenize. The sample portion was weighed then dried in an oven (105 °C), cooled in a desiccator, and weighed again. This process was repeated until a stable dry weight was achieved. The density and the percent moisture results are summarized in Table 87.

Table 87. Baseline TSF-05 Sludge Density and Percent Moisture.

Sample	Moisture (wt%)	Wet Bulk density (g/mL)
1	58.4	1.878
2	NA	1.855
Average:	58.4	1.867

Radiochemical Measurements

After similar subsampling, radiochemical measurements were also performed. The aliquot was acid digested using the protocol set forth in SW846 method 3051 then analyzed for gross alpha, gross beta, and gamm using the procedures listed in Table 88. The results, which are corrected back to the original wet weight of the sludge, are reported as Bq/g and are presented in Table 89. The RMAL's radiochemical analytical results have good agreement with those values supplied by INEEL's radiochemical laboratory (Rowley, 1997).

Table 88. Radiochemical Methods used for TSF-05 Sludge Determinations.

Method	Analysis
Gross Alpha and Gross Beta Radioactivity in Drinking Water (CASD-AM-EPA-900.0)	Gross alpha and beta radioactivity sample preparation
Gamma-emitting Radionuclides in Drinking Water (CASD-AM-EPA-901.1)	Gamma emitting radionuclides sample preparation
Operation of Packard MO 2500TR Liquid Scintillation Counter (CASD-AM-RML-RA12)	1. Total activity by liquid scintillation 2. Sum of alpha- and beta-emitting radionuclides analysis
Operation and Calibration of the Tennelec LB4000 (CASD-AM-RML-RA02)	Gross alpha and gross beta analysis
Operation and Calibration of the Canberra, Nuclear Data Genie - ESP Data Acquisition and Processing (CASD-AM-RML-RA04)	Alpha and gamma spectroscopy data acquisition and processing system

Table 89. Baseline TSF-05 Sludge Radiochemical Analytical Results.

Analysis	Results (Bq/g)
Gross Beta	4400
Gross Alpha	3.3
Cs-137	460
Co-60	100

Throughout the project the hexane extractions performed for TCE analyses on the sludge/groundwater slurries were monitored for total activity at random intervals prior to transfer to ESD. No activity was detected in any of these extractions.

Total Carbon Data

For the carbon determinations, a Shimadzu TOC 5000 carbon analyzer interfaced with a solid sample module (SSM 5000) was used. The analyses were performed following the guidance set forth in EPA's SW846 method 9060 and the manufacturer's operation instructions provided with the instrument.

Initial carbon baseline results were obtained prior to the start of the project experiments involving the TSF-05 sludge. Carbon content was measured in both raw (as received) and dried portions of the sludge. The baseline values obtained are presented in Table 90.

Table 90. Baseline Total Carbon Values for Raw and Dried TSF-05 Sludges.

Sample	Total Carbon (%)	
Pre-treatment:	None (as received)	Dried at 105 °C
1	2.7	9.2
2	3.1	8.1
Average:	2.9	8.6

The raw sample result corrected for moisture is 6.9% total carbon. The average, measured dried sample result was 8.6%. The calculated dry value is 20% lower than the measured value with a relative percent difference of 22%. Given the highly heterogeneous matrix of the sludge samples these deviations are considered acceptable. Any loss of carbon as a result of drying the sludge is assumed to be within this percent error. Therefore, it was also assumed that the post reaction sludges could be dried to remove the hexane extraction medium without significant loss of sludge carbon.

2.4.5.2 Effect of Oxidation

As discussed above, a baseline total carbon value of 8.6% was used to determine (1) how much carbon was oxidized in the sludge following the oxidant demand and oxidation rate studies and (2) the effect that the presence of varying concentrations of TCE would have on the oxidation of the sludge.

At the completion of the oxidant demand (Task 3b) and the degradation rate (Task 4b) experiments, portions of all sludges were dried at a temperature of 105 °C to a constant weight to remove water and hexane (Task 4b only) from the samples. Total carbon analyses were then performed on each sample. The oxidant demand (Task 3b) results are presented in Table 91, and the oxidation rate studies (Task 4b) are presented in Table 92. The total carbon values presented in these tables for the #1 and #2 treatment reactors represent the values obtained for each duplicate sample for a given test condition.

Table 91. Post Oxidant Demand Results (Task 3b), TSF-05 Sludge Total Carbon.

ORNL Exp. No.	Oxidant Loading	Total Carbon (%)		
		Treatment Reactor #1	Treatment Reactor #2	Average Value
3b-R1	0.01% MnO_4^-	4.9	3.8	4.4
3b-R2	0.1% MnO_4^-	3.0	2.4	2.7
3b-R3	1% MnO_4^-	1.8	2.3	2.1
3b-R4	3% MnO_4^-	1.4	1.5	1.5

Table 92. Post-Treatment Degradation Rate Results (Task 4b) TSF-05 Sludge Total Carbon.

Nominal Aq. TCE (μg/L)	ORNL Exp. No.	Oxidant Loading	Total Carbon (%)		
			Treatment Reactor #1	Treatment Reactor #2	Average Value
40,000	4b-R11	0.01 % MnO_4^-	7.1	6.1	6.6
		0.1 % MnO_4^-	5.5	5.4	5.5
10,000	4b-R15	1 % MnO_4^-	2.7	2.1	2.4
		3 % MnO_4^-	1.4	1.9	1.7
100,000	4b-R12	0.01 % MnO_4^-	4.4	6.7	5.6
		0.1 % MnO_4^-	4.8	5.9	5.4
	4b-R16	1 % MnO_4^-	1.7	3.0	2.4
		3 % MnO_4^-	2.6	2.6	2.6
DNAPL	4b-R13	0.01 % MnO_4^-	2.0	3.8	2.9
		0.1 % MnO_4^-	3.5	2.5	3.0
	4b-R14	1 % MnO_4^-	5.5[†]	2.5	2.5[††]
		3 % MnO_4^-	2.4	3.4	2.9

[†]   Outlier (biased high)
[††]   Did not average/use the outlier value.

The average post-treatment total carbon values from the oxidant demand data in Table 91 was plotted in Figure 114 verses the initial oxidant loading. The data suggests a logarithmic decrease of the TSF-05 sludges; total carbon content with increasing permanganate concentration during the twenty-four hour reaction period. The trendline is a best fit only and does not exactly describe the data trend. Figure 115 depicts another view of the same carbon data. Here, the total carbon oxidized (calculated by subtracting the baseline value of 8.6% from the averaged measured post reaction values) is plotted versus initial oxidant loading. Here, the plot illustrates a logarithmic increase (essentially a mirror image of Figure 114) of the carbon oxidized with increasing permanganate concentration. As in Figure 114, a trendline is fitted to the data with its equation displayed.
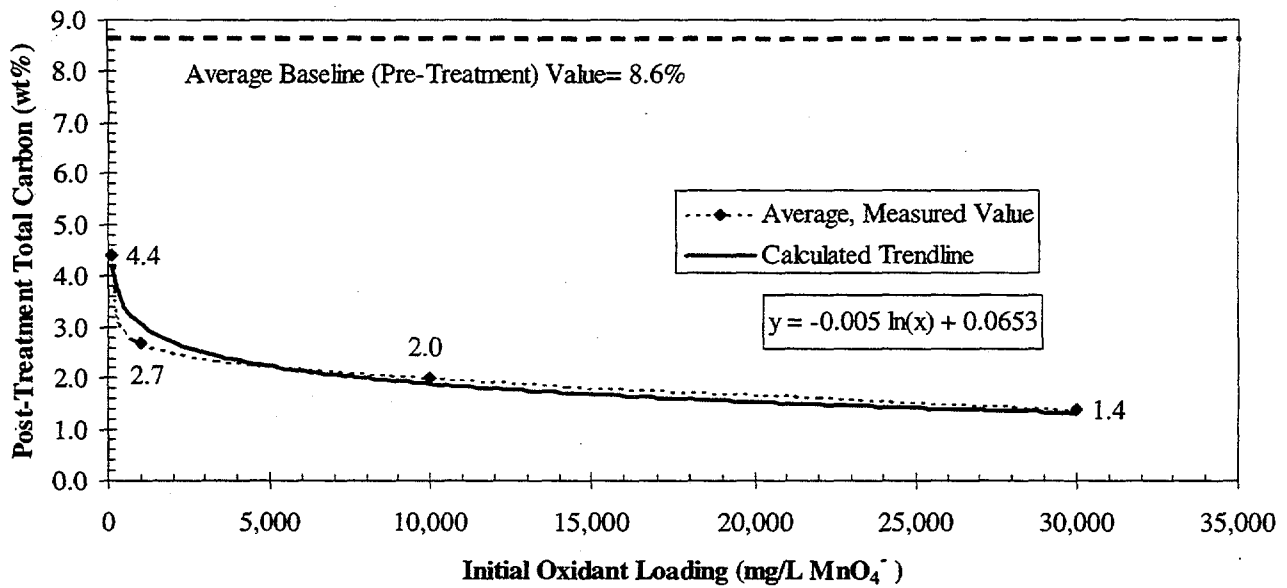
Figure 114. Post-Treatment %Carbon Value vs. Oxidant Loading for the Task 3b, Oxidant
Demand Experiments. (TSF-05 Sludge, 0 µg/L TCE, 4:1 L/S Ratio, 12°C).
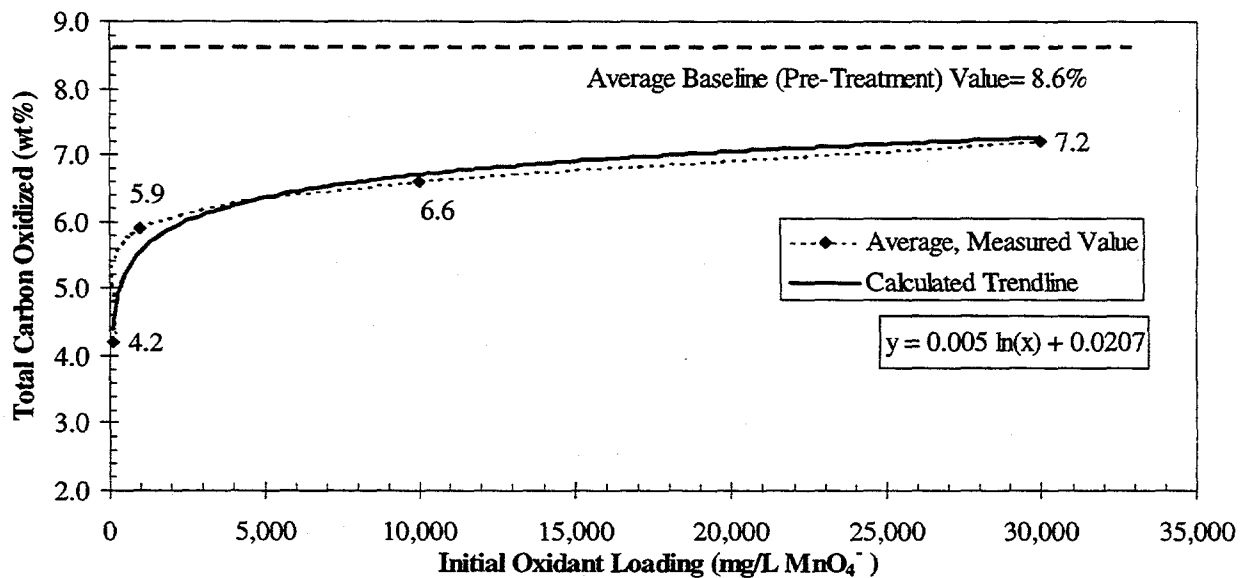
Figure 115. Post-Treatment %Carbon Oxidized vs. Oxidant Loading for the Task 3b, Oxidant
Demand Experiments. (TSF-05 Sludge, 0 µg/L TCE, 4:1 L/S Ratio, 12°C).

The average post-treatment total carbon values for the oxidation rate studies in Table 92 are plotted in Figure 116 versus the initial TCE spike concentration. The same data is also presented in Figure 117 but expressed as the percent of initial sludge total carbon that was oxidized. The carbon measurement obtained for the first 1% MnO_4^- reactor in experiment 4b-R14, (TCE present as DNAPL) is believed to be biased high when compared to the other carbon values measured in the DNAPL experiments. Instead of averaging the two 1% MnO_4^- samples, the second MnO_4^- sample from experiment 4b-R14 was used. The bar graphs in Figures 116 and 117 are grouped according to TCE concentrations to illustrate the effect that varying concentrations of TCE have on the oxidation of the carbon in the TSF-05 sludge. The first group of data (0 $\mu g/L$ TCE) is from the oxidant demand study (Table 91).

Several conclusions can be drawn from the oxidation rate carbon data. First, when TCE is present, there is generally a decrease in the amount of carbon oxidized in the sludge. (This trend is most obvious for the initial oxidant loadings of 0.01% and 0.1% MnO_4^-). It is believed that the permanganate is preferentially oxidizing the TCE in solution over the sludge carbon before it is completely consumed (i.e., there is competition for the oxidant). Although some carbon is oxidized when the sludge is spiked with TCE, the amount oxidized is less than what was observed when no TCE was present (oxidant demand studies).

For all TCE concentrations observed, the amount of carbon oxidized with the 1% and 3% permanganate solutions appears to be fairly similar, suggesting that sludge oxidation is less dependent on initial TCE concentration at higher oxidant loadings. With the 1% and 3% MnO_4^- loadings, there is sufficient oxidant available to destroy the TCE as well as the sludge carbon to approximately the same levels as were observed when no TCE was present.

Finally, when the TCE is present as DNAPL the post reaction sludge carbon concentrations are essentially equivalent regardless of the initial oxidant loading. This last conclusion is more difficult to explain. The data indicates that approximately 3% of the carbon remains in the sludges after the reaction period regardless of the initial permanganate concentrations (Note: All studies using TCE present as DNAPL had reaction periods of 120 hours verses 24 hours). After 24 hrs, only the 3% permanganate reaction flasks had any measurable permanganate still present (approx. 1.1%). After 120 hours, this permanganate concentration was approximately 0.5%. Regardless, all sludges were oxidized to the same carbon levels. A possible explanation may be that, at higher concentrations, the TCE is enhancing, or possibly adding to, the oxidation reaction between the TSF-05 sludge and the permanganate. For the DNAPL case, conditions may be present that are preventing the oxidation reaction from achieving a final carbon level significantly less than 3% (as observed in the oxidant demand study). For example, the TCE mass present may be competing for available oxidant and/or reaction products formed via TCE oxidation may have altered the degradation kinetics within the reactors. Without a detailed look at the oxidation/reductions (redox) reactions occurring among the sludge, TCE, and MnO_4^- a completely satisfactory explanation cannot be given for these observations.
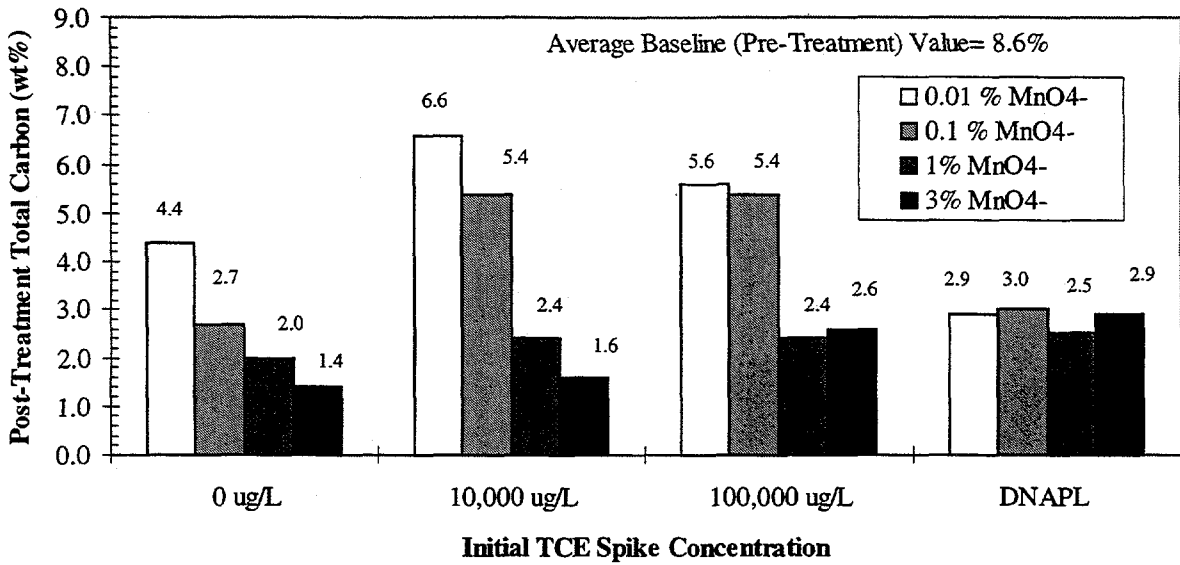
Figure 116. Post-Treatment Carbon Values vs TCE Spike Concentration for the Task 4b, TCE
Degradation Experiments. (TSF-05 Sludge, 4:1 L/S Ratio, 12°C).
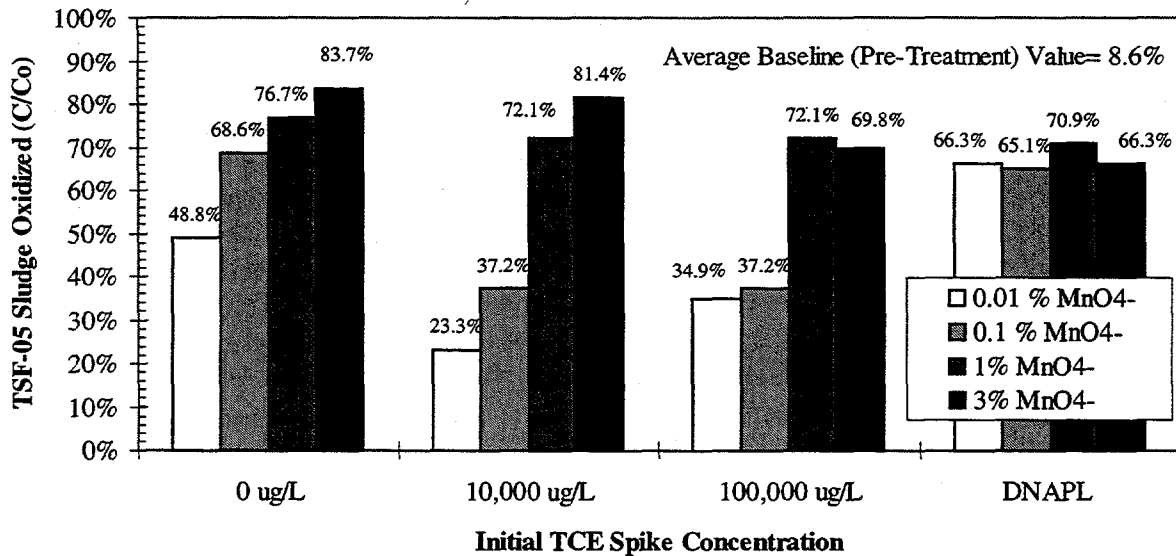
Figure 117. Percent of Initial Sludge Carbon Oxidized vs TCE Spike Concentration for the Task
4b, TCE Degradation Experiments. (TSF-05 Sludge, 4:1 L/S Ratio, 12°C).

2.4.6. Matrix Spike Experiments

Following completion of Tasks 2-4, INEEL requested that a matrix spike experiment be performed for each TAN Site media (dissolve plume and hot spot media) being evaluated at ORNL. The results of these additional experiments are presented below.

ORNL Exp. 2b-1b, Matrix Spike Experiment for the Dissolved Plume Media
(TAN-40 GW, Basalt, Sediment, TCE=275 μg/L, 0% MnO_4^-)

The matrix spike experiment involving the dissolved plume media was conducted without incident. (The detailed procedure used is included in Appendix B, page 16). Unfortunately, problems arose during GC analysis. The matrix spike TCE samples were analyzed using the GC that had been used for nearly all of the Task 4 work (with the exception of the co-contaminants experiments). This instrument had performed remarkably well throughout the entire project, requiring only two (2) calibrations between January and August 1998. This matrix spike experiment, however, was conducted several weeks after the completion of the task 4 work. All QA blanks, calibration checks, and test sample results contained numerous unidentified peaks, likely from capillary column and/or detector "bleeding". TCE could not be adequately resolved from the other eluting compounds. It is believed that the more than 2,000 hexane extracts that had been analyzed during the preceding months contaminated the detector, which had not been periodically baked out during the course of the project. The detrimental consequence of this activity did not surface until after the instrument had been placed in stand-by mode after completion of the Task 4 work. As a result, the ECD was removed from the instrument and returned to the manufacturing for refurbishing. The detector has just recently been returned, but it has not yet been re-installed.

With the current project funding, the experiment will not be re-performed. However, it is believed that the hexane extraction technique used for this project produced reliable results, particularly for the dissolved plume media. TCE recoveries from the control reactors (in Task 2 and Task 4) were high and little TCE sorption (<8%) by the basalt or sediment was observed during the project. (TCE sorption by the hot spot sludge was on the order of 50%.)

ORNL Exp. 2b-3b, Matrix Spike Experiment for the Hot Spot Media
(TSF-05 Sludge and GW, TCE= 1,000 µg/L, 0% MnO$_4^-$)

Nearly identical to the Task 4 TCE spiking procedure, samples for this matrix spike experiment (TSF-05 slurries and TSF-05 groundwater only) were spiked with 1,000 µg/L TCE at a 4:1 L/S ratio and equilibrated overnight at 12°C. The main difference between the two experimental setups was the use of 40 mL VOA vials here instead of the 500 mL reactors used in Task 4. (The detailed procedure used is included in Appendix B, page 21). As in Task 4, these samples were then extracted with hexane at a 1:1 v/v ratio for various time periods. The hexane aliquots hexane were then analyzed (1) to determine the extent of recovery and (2) to determine if the amount recovered is significantly affected by the extraction time. Since the results of experiment 2b-3 (Section 2.2.2) suggested that some TCE may still be bound to the sludge after 24 hrs, a 48 hr extraction period was also evaluated in this experiment. Since sample holding time effect had been observed in a few of the Task 4 experiments, samples collected between T=0 and 24 hrs were analyzed immediately after the T=24 hr samples were collected. Due to the instrument problem discussed above in the dissolved plume media experiment, these samples were analyzed using the GC that had been used for the co-contaminants experiments. The MDL for this instrument calibration was 10 µg/L rather than 5 µg/L TCE.

One of the three vials containing TSF-05 sludge and groundwater was broken soon after TCE equilibration has been initiated. Thus, only the results of 2 slurries samples and 1 groundwater only sample are presented here. Gravimetric analyses indicated that >98wt% of the contents from each of the 40 mL VOA vials was successfully transferred into each reactor of hexane. The TCE concentrations measured for each hexane aliquot are presented in Figure 118. Note that many of the TCE values presented in Figure118 just barely exceeded that of the largest calibration standard (1,169 µg/L). As was observed in the first hexane extraction time experiment (Exp. 2b-3), hexane rapidly extracts TCE from both the sludge and groundwater samples. The measured TCE concentrations for the groundwater only sample are lower than those of the slurries because a larger volume of groundwater was present in that vial (i.e., lower initial aqueous concentration).

From Figure 118, it also appears that the amount of TCE being extracted is increasing with time for each sample. However, the concentrations presented in Figure 118 only represent the concentrations of TCE in the 1 mL hexane aliquot and does not take into account any TCE that was removed from the extracting slurry by previous aliquot sampling event(s). Thus, the same TCE sample data is expressed in % TCE mass recovered in Figures 119, 120, and 121 for the first, second, and third test reactors, respectively. The percentage of the TCE removed from each reactor via previous aliquot samplings is also presented in Figures 119-121. Upon adding the sample TCE recovery and the aliquot recoveries in these figures, one can observe that there is little variation in the total TCE recovery (sum of the two fractions) with extraction time. This result further substantiates the use of a 24 hr hexane extraction time for the hot spot media.

Because of the spiking technique employed (use of a saturated TCE solution), the initial amount of TCE present in each reactor was not directly measured. However, each reactor should have initially contained ≈44 µg TCE at the start of equilibration, if one assumes that the saturated TCE solution used to spike the test reactors was 1,100 mg/L. It is realized that a matrix spike

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experiment will yield results that are more definitive if the initial spiking concentration is known. Measurement of the saturated TCE solution concentration was an oversight. This is likely why the total TCE recoveries presented in Figures 119-121 are all greater than 100% (Average 106%, $\sigma=1.4\%$). However, it is believed that all of the initial TCE has been extracted from both the slurry and groundwater only matrices. In addition, the total TCE masses represented by Figures 119-121 do not vary by more than 2.2 μg TCE for any sample matrix or extraction time examined. Hence, the use of hexane to extract TCE from the TAN site matrices is believed to be valid. (Additional information and calculations are presented in Appendix C for this experiment.)
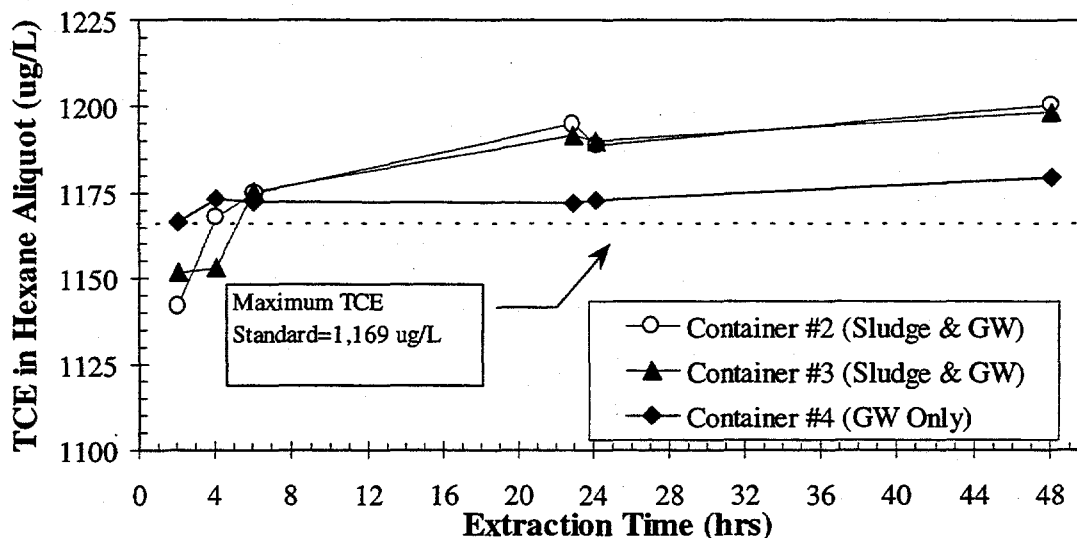
Figure 118. Hexane Aliquot TCE vs. Extraction Time, TSF-05 Sludge & Groundwater, (ORNL Exp. 2b-3b, Initial TCE= 1,000 μg/L, Conducted at 12°C, 4:1 L/S Ratio where applicable, 0% MnO$_4$)
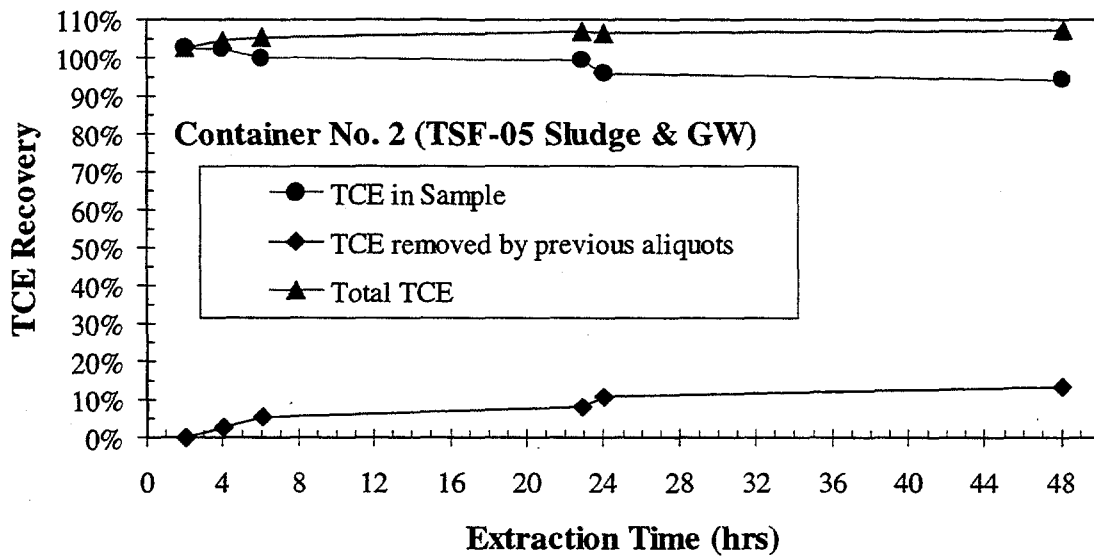
Figure 119. , TCE Recovery vs. Hexane Extraction Time, TSF-05 Sludge & Groundwater (#1), (ORNL Exp. 2b-3b, Initial TCE= 1,000 μg/L, Conducted at 12°C, 4:1 L/S Ratio, 0% MnO$_4^-$)
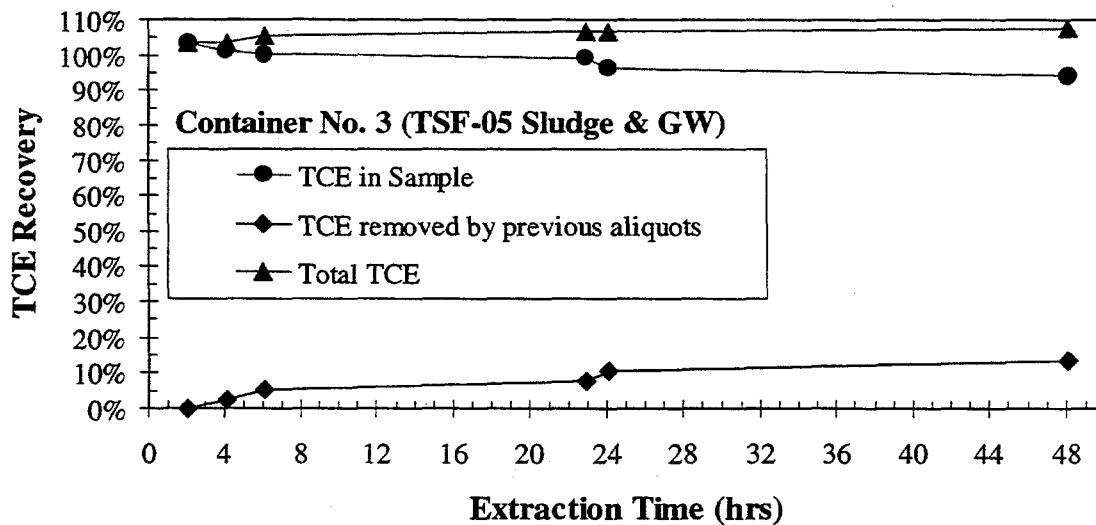
Figure 120. TCE Recovery vs. Hexane Extraction Time, TSF-05 Sludge & Groundwater (#2), (ORNL Exp. 2b-3b, Initial TCE= 1,000 μg/L, Conducted at 12°C, 4:1 L/S Ratio, 0% MnO$_4^-$)
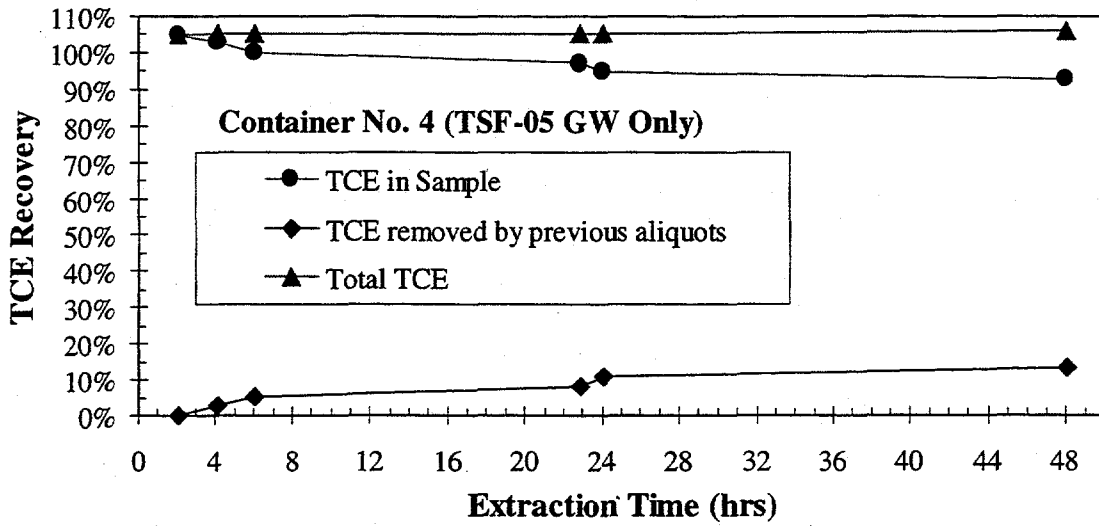
Figure 121. TCE Recovery vs. Hexane Extraction Time, TSF-05 Groundwater Only, (ORNL
Exp. 2b-3b, Initial TCE= 1,000 µg/L, Conducted at 12°C, 4:1 L/S Ratio, 0% MnO₄⁻)

2.5.7   TASK 5. WASTE DISPOSAL

All VOC-spiked TAN Site media used in this project have been declared as solid level waste and RCRA hazardous waste. The material is currently being handled and will ultimately be treated and/or stored according to both RCRA regulations and ORNL guidelines. Per the SOW, all un-used TAN media is currently being prepared for shipment back to INEEL as the original generator of the RCRA material used in this US EPA treatability study.

3. CONCLUSIONS AND RECOMMENDATIONS

In general, the oxidant demand of the geologic media (groundwater, basalt, and fracture-fill material) was low, while the oxidant demand of organic sludge from TSF-05 was very high. The rate of TCE oxidation was rapid, and when sufficient permanganate was available for oxidation to proceed to completion, TCE concentrations declined to less than the MDL. Permanganate oxidation was effective for destroying (1) TCE in the dissolved phase, (2) TCE initially present as a non-aqueous phase, (3) DCE isomers, and (4) organic sludge.

These observations indicate that ISCO is well suited for remediating both dissolved phase contamination and secondary sources of contamination in the hot spot, if oxidant can be delivered to the in situ contaminants.

A field evaluation at the hot spot should be performed to evaluate the performance of ISCO under field conditions.

Conclusions and recommendations are presented below for each task. Additional details are available for each task in Section 2.0

3.1.   TASK 1 - PREPARATION OF PROJECT PLANNING DOCUMENTS

Conclusions:
All project planning documents needed to execute this study were obtained.

Recommendations: None.

3.2.   TASK 2 - PRELIMINARY LABORATORY STUDIES

3.2.1. Reactor Development

Conclusion:

- A reactor suitable for executing this study was developed. In general, it performed well.

Recommendation:

- Procedures should be modified to allow quantification of the mass of individual VOCs in the headspace in order to determine better mass balance estimates.

3.2.2. Hexane Extraction Time

Conclusions:

- The 2-hour extraction time was adequate for groundwater, crushed basalt, sediment, and sludge.

- A 2-hour extraction time was assumed to be adequate for extraction of VOCs from aggregate basalt, but this assumption has not been rigorously evaluated.

Recommendation:

- The adequacy of the hexane extraction time for aggregate basalt should be further evaluated before performing additional laboratory studies of ISCO using these materials.

3.2.3. Determination of Equilibration Time for Aggregate Basalt with TCE

Conclusion:

- This activity was attempted twice without success. These equilibration experiments are conducted for time periods on the order of days to weeks. Due to the delays that would have been encountered in beginning the Task 3 and Task 4 experiments, a third attempt at this task was not performed. Instead, an overnight equilibration period was selected for the aggregate basalt medium in the Task 4 experiments.

Recommendation:

- The adequacy of the overnight equilibration period should be further evaluated before performing additional laboratory studies of ISCO using this material. This will require the preparation of new test methods and equipment to better minimize TCE losses.

3.3. TASK 3 - MEASUREMENT OF OXIDANT DEMAND OF TAN SUBSURFACE MATERIALS

3.3.1. Laboratory Controls and QA

Conclusion:

- Due to the low oxidant demand observed for most of the TAN site media, the spectrophotometric method used for MnO_4^- analyses was not capable of quantifying the very small changes in MnO_4^- concentrations that appeared to be occurring for groundwater and the dissolved plume media. However, it was determined prior to the start of the ORNL studies that the use of the spectrophotometric technique would be suitable for the level of QA desired for this parameter.

Recommendation:

- If extremely precise determinations of small MnO_4^- concentration changes are needed in the future, a more time-consuming standard titration method should be considered for the MnO_4^- analyses.

3.3.2. Oxidant Demand in Dissolved Plume Media

Conclusions:

- The oxidant demand of groundwater, aggregate basalt, crushed basalt, and sediment were all low, approximately 0.01 to 0.2 mg MnO_4^- / g medium. These values are less than the value determined in a preliminary study conducted elsewhere, on the order of 1 mg MnO_4^- / g basalt.

- Fracture fill material, i.e. sediment, had the highest oxidant demand of the geologic materials examined.

Recommendation:

- Field scale measurement of oxidant demand in the dissolved plume is not needed.

3.3.3. Oxidant Demand in Hot Spot Media

Conclusions:

- The oxidant demand of groundwater from TSF-05 is small and comparable to the demand measured on groundwater from the dissolved plume (TAN-40).

- The oxidant demand of organic sludge from TSF-05 is approximately three orders of magnitude greater than the oxidant demand of basalt and sediment, on the order of 70 mg MnO_4^- / g sludge. This sludge has the highest oxidant demand of any material examined in this study.

- Consumption of oxidant by reactions with sludge would be a substantial sink of oxidant in a field scale application of ISCO.

- Oxidation by MnO_4^- is an effective means of destroying organic sludge.

Recommendation:

- Evaluation of ISCO via a field test at the hot spot is warranted.

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3.4. TASK 4 - MEASUREMENT OF OXIDATION RATES OF TAN SUBSURFACE MATERIALS

3.4.1. Laboratory Controls and QA

Conclusions:

- Over 2,200 samples were uniquely labeled, tracked, and analyzed for VOCs via gas chromatography. Proper instrument performance was validated via calibration checks for over 95% of the samples analyzed. In addition, there is no information available to suggest that the instrument(s) was not performing properly for the remaining 5% of the samples.

- Analyses of duplicate aliquots for 160 test samples resulted in an average percent difference of 3% between duplicates.

- TCE was found in the sample blanks from some of the TCE degradation experiments. Such occurrences are clearly noted in the experimental discussions. Contamination of these blanks, however, did not severely affect the results/interpretation of the experiments. The amount of TCE found is such blanks (typically <10 μg/L TCE) was several orders of magnitude less than the amount of TCE that was oxidized by MnO_4^-.

Recommendation:

- Given the large number of samples managed and analyzed in this study, the level of QA/QC imposed upon these VOC analyses should be considered acceptable for evaluating the results of this ISCO treatability study. If a higher level of QA is needed in future ISCO studies, enough funds should be allocated to have the VOC analyses subcontracted out to a certified analytical laboratory.

3.4.2. Oxidation Rate of Organic Contaminants in Dissolved Plume Media

Conclusions:

- TCE was readily oxidized at the MnO_4^- concentrations used, 0.01 % and 0.1 % (100 mg/L and 1 g/L).

- TCE oxidation was so fast that the data resolution was generally not sufficient to determine reliable reaction rate parameter values because TCE concentrations generally declined to < MDL concentrations before the first or second samples were collected. The lower bound of the zero order reaction rates was estimated by assuming that the TCE concentration reached zero when the first or second sample, as appropriate, was collected.

- The estimated zero order reaction rates increased with both initial MnO_4^- and TCE concentrations, and ranged from 0.1 to 4 mg TCE /L /hour.

- Sufficient data were available in a few cases to determine first order reaction rate constants. These range from 1.64 hr^{-1} to 4.28 hr^{-1} (average= 22.2 hr^{-1}, σ= 1 hr^{-1}). All of the first order reaction rate constants correspond to experiments involving 0.01% MnO_4^-. There appears to be no trend with initial TCE concentration for these rate constants. Reaction rates were too rapid for the 0.1% MnO_4^- case to allow for their computation.

- There were no differences in reaction rate that could be attributed to different media (groundwater only, crushed basalt, aggregate basalt, and sediment).

- Changes in pH are too small to be of practical use for monitoring the progress of a field application of ISCO.

Recommendation:

- Oxidation of TCE by MnO_4^- is sufficiently rapid that field scale evaluation of ISCO is warranted.

3.4.3. Oxidation Rate of Organic Contaminants in Hot Spot Media

3.4.3.1. Hot Spot Groundwater
Conclusions:

- Higher concentrations of both MnO_4^- and TCE were used in this set of experiments than in the 'dissolved plume' experiments. Initial MnO_4^- concentrations ranged from 0.01% to 3% (100 mg/L to 30 g/L). Initial TCE concentrations ranged from 10,000 to 1,000,000 µg/L (10 to 1,000 mg/L). TCE was present as a non-aqueous phase liquid at the highest concentration.

- These experiments suggest that approximately 50% of the initial aqueous TCE added to the test reactors is immediately sorbed to the sludge during the equilibration period.

- In some cases, the mass of MnO_4^- was insufficient to oxidize all of the TCE present, and TCE concentrations remained high.

- If the concentration of MnO_4^- was sufficient, TCE was rapidly oxidized to less than MDLs.

- TCE oxidation was so fast that the data resolution is generally not sufficient to determine reliable reaction rate parameter values because TCE concentrations generally declined to < MDL concentrations before the first or second samples were collected. The lower bound of the zero order reaction rates was estimated by assuming that the TCE concentration reached zero when the first or second sample, as appropriate, was collected.

- The zero order reaction rate estimates increased with both initial MnO_4^- and TCE concentrations, and ranged from 1 to 4,100 mg TCE /L /hour. The rates observed in this set of experiments are faster than those observed in the 'dissolved plume' experiments largely because of the higher TCE concentrations used in the 'hot spot' experiments

- Sufficient data were available in only one case to determine first order reaction rate constant. (1.7 hr^{-1} for the 0.01% MnO_4^- reactors in Exp. 4b-R5) Again, the overall faster degradation rates observed for this series of experiments were likely influenced by the higher TCE concentrations in these 'hot spot' experiments.

- Permanganate rapidly oxidized TCE that was initially present as a non-aqueous phase liquid.

- Changes in pH were very large compared to the changes observed in the 'dissolved plume' experiments. The magnitude of the pH changes increased with both initial MnO_4^- and TCE concentrations. However, the reaction vessels used in these experiments did not contain a solid phase, which could buffer pH changes. Therefore, it cannot be concluded that pH changes of this magnitude would be observed in a field application of ISCO.

Recommendation:

- Oxidation of high concentrations of TCE, including TCE initially present as a non-aqueous phase, is sufficiently rapid that field evaluation of ISCO in the hot spot is warranted.

3.4.3.2. Hot Spot Sludge

Conclusions:

- The concentrations of MnO_4^- and TCE used in this set of experiments was the same as that used in the 'hot spot - groundwater' experiments.

- In some cases, the mass of MnO_4^- was insufficient to oxidize all of the TCE present, and TCE concentrations remained high.

- TCE was rapidly oxidized to less than MDLs if the concentration of MnO_4^- was sufficient.

- TCE oxidation was so fast that the data resolution is generally not sufficient to determine reliable reaction rate parameter values because TCE concentrations generally declined to < MDL concentrations before the first or second samples were collected. The lower bound of the zero order reaction rates was estimated by assuming that the TCE concentration reached zero when the first or second sample, as appropriate, was collected.

- The zero order reaction rate estimates increased with both initial MnO_4^- and TCE concentrations, and ranged from 16 to 2,000 mg TCE /L /hour. The rates observed in this set of experiments are faster than those observed in the 'dissolved plume' experiments largely because of the higher TCE concentrations used in the 'hot spot' experiments, but lower than those observed in the 'hot spot - groundwater' experiments because of reduced MnO_4^- concentrations resulting from sludge oxidation.

- Sufficient data were available in most cases to determine first order reaction rate constants due to (1) very rapid TCE degradation or (2) insufficient initial oxidant loading. However, the case in which the TCE-spiked (DNAPL) sludge was treated with 3% MnO_4^-, a first order reaction rate constant of 4 hr^{-1} was computed.

- Permanganate rapidly oxidized TCE that was initially present as a non-aqueous phase liquid.

- Consumption of MnO_4^- during oxidation of sludge reduced oxidant concentrations and slowed the rate of TCE oxidation compared to the rates observed at similar concentrations in the 'hot spot - groundwater' experiment. However, even the slower rates observed in these experiments are extremely rapid relative to the time scale needed for field application of ISCO.

- In some cases, oxidation of sludge consumed the available MnO_4^- before all of the TCE was oxidized, while at similar concentrations without sludge present TCE was oxidized to <MDL concentrations. This illustrates that the oxidant demand of sludge must be satisfied in order to achieve complete oxidation of TCE.

- Baseline characterization work on the TSF-05 revealed an initial dried total carbon value of ≈ 8.6%. After oxidation by MnO_4^- in the Task 4 experiments, post-treatment carbon values ranged between 1.6% and 6.6%. The degree to which the sludge is oxidized during ISCO appears to be dependent on both the initial TCE and initial oxidant loading.

- pH changes were much smaller than those observed in the 'hot spot - groundwater' experiments, presumably due to buffering of pH by organic sludge. The pH changes are so small that pH would not be suitable for monitoring the progress of a field application of ISCO.

Recommendations

- The rate of TCE and sludge oxidation are fast enough, and the TCE concentrations that remain after oxidation are low enough, that further field scale evaluation of ISCO at the hot spot is warranted.

3.5. TASK 5 - WASTE DISPOSAL

- This task is currently being conducted. ORNL personnel will ensure that all treatment residuals are properly stored and/or disposed of. Unused TAN material currently present at ORNL will be returned. INEEL officials will handle its ultimate disposition.
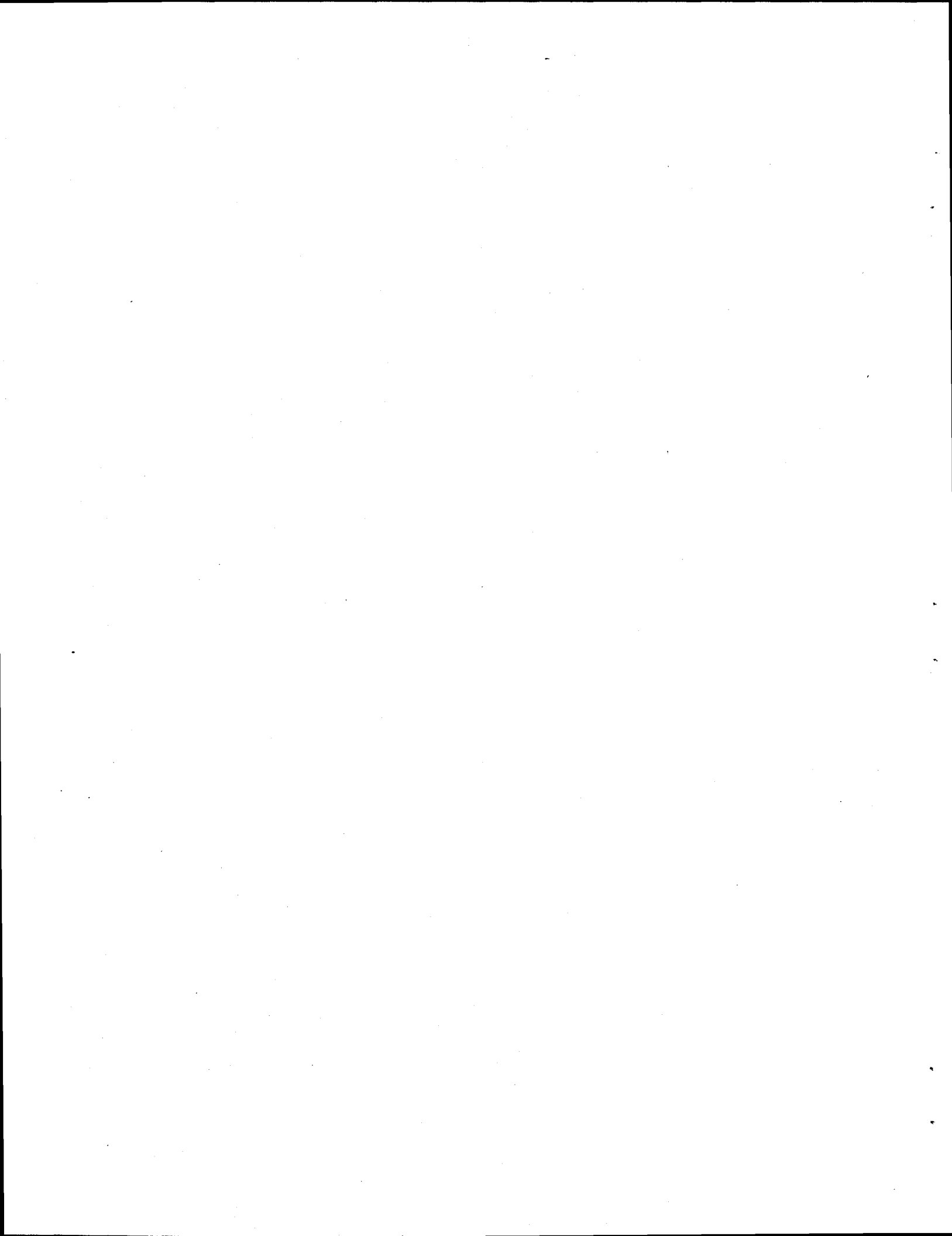
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Appendix A- Scope of Work
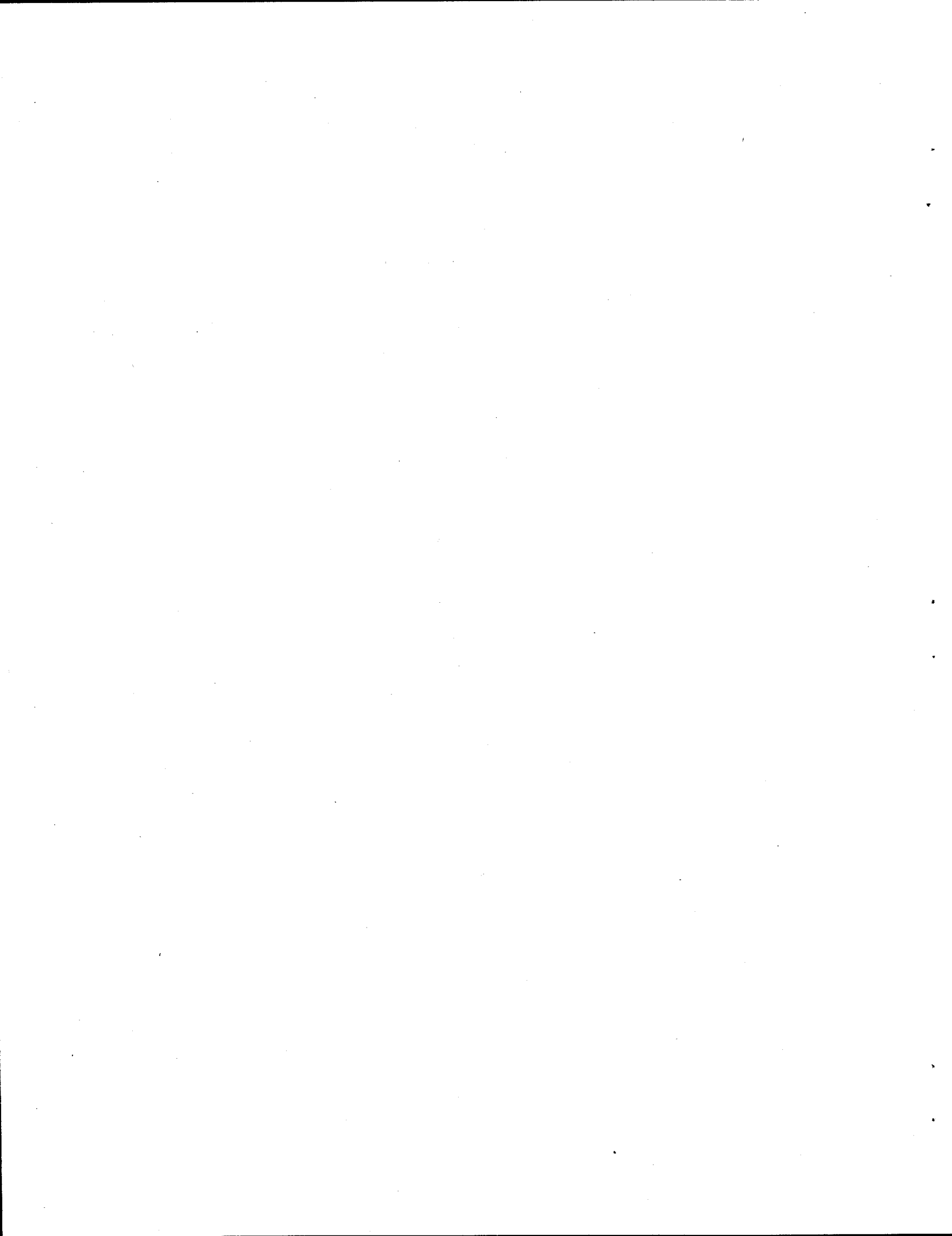
Scope of Work for
Laboratory Evaluation of In Situ Chemical Oxidation as a Technology for Groundwater Restoration at the INEEL TAN Site

December 10, 1997

Subcontractor: Oak Ridge National Laboratory
Environmental Sciences Division
P.O. Box 2008
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Technical Contact: Dr. Olivia R. West
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Background

The use of in situ chemical oxidation (ISCO) as a technology for remediating the secondary source of groundwater contamination at the INEEL near injection well TSF-05 is being evaluated. Oxidant demand and reaction rates will be measured in laboratory studies, which will be followed by field evaluations if the results from the laboratory investigation are promising.

Laboratory studies will be performed by researchers at the Oak Ridge National Laboratory, Environmental Sciences Division. The ORNL research team has been performing laboratory and field investigations on ISCO for subsurface remediation for approximately four years, and has the laboratory facilities and experience needed to perform the required experiments.

Assumptions

The following assumptions were made to prepare this scope of work.

1. Organic sludge from TSF-05 contains radionuclides at sufficiently high activities that experiments in which organic sludge is used must be conducted in the Radioactive Materials Analytical Laboratory at ORNL, but cannot be conducted in the Environmental Sciences Division laboratories.

2. Groundwater, basalt, and sediment from fractures in basalt do not contain radionuclides at activities that would preclude their use in experiments conducted in the Environmental Sciences Division laboratories.

3. Groundwater, basalt, and sediment will be delivered to ORNL by January 6, 1998.

4. Organic sludge from TSF-05 does not contain PCBs at concentrations greater than 50 ppm, and therefore is not regulated by the Toxic Substances Control Act.

5. Organic sludge will be delivered to ORNL by January 26, 1998.

6. Temperature control equipment will be delivered by a vendor to ORNL by January 30, 1998.

If information generated during this investigation invalidates the assumptions made to prepare this Scope of Work, then ORNL should notify the INEEL Technical Point of Contact, Dr. Robert Starr, and request any changes in scope, schedule, and budget required because the actual conditions differ from the assumed conditions.

Scope of Work

The majority of the work to be performed by the subcontractor is described in *Draft In Situ Chemical Oxidation Implementation Plan Test Area North Final Groundwater Remediation Operable Unit 1-07B*, INEEL/EXT/97-01111, Revision 0, which will be referred to as the 'Implementation Plan'. Chapter 2 *Laboratory Studies* has been substantially revised in accordance with agency review comments. References to Chapter 2 of the Implementation Plan are intended to refer to the revised Chapter 2 that is presented in Appendix A of this Scope of Work.

Task 1 Prepare Project Planning Documents

Project planning documents include:

- A Laboratory Test Plan that describes the technical aspects of the research, including quality assurance, in greater detail than presented in the Draft Implementation Plan;

- Environmental, safety, and health (ES&H) planning documentation;

- RCRA treatability study notification;

- Any other documentation required for conducting laboratory studies at ORNL.

Task 1a Prepare Laboratory Test Plan

Prepare a Laboratory Test Plan that describes the laboratory experiments in detail, and refers to or includes quality assurance procedures. The activities to be addressed are described in Tasks 2 through 4 of this scope of work. Submit a draft to INEEL for review and a final version that has been modified in response to INEEL review comments.

Task 1b Prepare Other Planning Documents and Obtain Permits

Prepare the ES&H documentation required by ORNL. Submit RCRA treatability study notification. Prepare any other planning documents required by ORNL.

The ES&H documentation will be prepared under the assumption that the material to be shipped from INEEL will be below TSCA action limits of 50 ppm. PCB analyses of the material will be conducted PRIOR to shipment to ORNL. If the material is found to have PCB concentrations near or greater than 50 ppm, the material will not be shipped to ORNL until additional arrangements and changes in both ESH&Q documentation and work scope are made.

Task 2 Preliminary Laboratory Studies

Preliminary studies are needed to refine laboratory procedures that will be used to measure oxidation demand (Task 3) and oxidation rates (Task 4).

Task 2a Reactor Development

Purchase and test reaction vessels that will be used for the oxidant consumption and oxidation rate studies.

Task 2b Determine Time Required for Hexane Extraction of TCE from Aqueous Samples, Organic Sludge, Sediment, and Basalt

Samples for analysis of organic analytes (TCE, DCE, etc.) are prepared by extracting organic solutes from solution into an organic solvent, hexane, and then determining the concentration of the solutes in hexane. The transfer of organic solutes into hexane is not instantaneous, particularly if the organic solute is associated with solid phase material such as basalt or organic sludge. The goal of this task is to determine the length of time necessary for the transfer of organic solutes from aqueous samples, sludge, sediment, and both crushed and aggregate basalt into hexane.

Perform a study to determine the length of time required for hexane extraction to transfer essentially all of the mass of TCE from either aqueous samples, organic sludge, sediment, or basalt into the organic (i.e. hexane) phase. Select extraction times to be used in subsequent experiments.

Submit a preliminary report that presents the principal results of this task, followed by more detailed information in the final report. The analytical and final reporting procedures shall comply with sections 2.4 and 9.1 of the Draft Implementation Plan.

Task 2c Determine Time Required to Equilibrate Basalt Aggregate with TCE Solutions

Basalt aggregate, i.e. 1/2 to 1 inch diameter pieces of vesicular basalt, will be used in the laboratory experiments described in the Implementation Plan. One step in the experiments is to equilibrate TCE concentrations in matrix pore water of the basalt pieces with TCE concentrations in the surrounding water. The length of time needed for this equilibration process to occur is unknown. The goal of this task is to determine the length of time required for equilibrium to be reached between TCE in the matrix pore water and the surrounding solution.

Perform a study to determine the relationship between equilibration time, i.e. the length of time that aggregate is immersed in a TCE solution, and the mass of TCE that can be extracted per unit mass of aggregate basalt.

Submit a preliminary report that presents the principal results of this task, followed by more detailed information in the final report. The analytical and final reporting procedures shall comply with sections 2.4 and 9.1 of the Draft Implementation Plan.

Task 3 Measure Oxidant Demand of TAN Subsurface Materials

The oxidant demand exerted by materials present in the subsurface at TAN will influence the mass and concentration of oxidant that must be injected during field evaluations and full scale implementation of ISCO.

Task 3a Measure the Oxidant Demand of Reactive Zone Media

Measure the oxidant demand of groundwater from TAN-29, crushed and aggregate basalt, and sediment (fracture fill material). Use the approach described in Section 2.2 of the Implementation Plan, and the experimental treatments described in Table 2-3.

Submit a preliminary report that presents the principal results of this task, followed by more detailed information in the final report. The analytical and final reporting procedures shall comply with sections 2.4 and 9.1 of the Draft Implementation Plan.

Task 3b Measure the Oxidant Demand of Hot Spot Media

Measure the oxidant demand of groundwater and organic sludge from TSF-05. Use the approach described in Section 2.2 of the Implementation Plan, and the experimental treatments described in Table 2-4.

Submit a preliminary report that presents the principal results of this task, followed by more detailed information in the final report. The analytical and final reporting procedures shall comply with Sections 2.4 and 9.1 of the Draft Implementation Plan.

Task 4 Measure Oxidation Rates

Oxidation rates as a function of oxidant and contaminant concentration must be determined in order to evaluate the feasibility of ISCO and to design field evaluations and full scale implementations of ISCO.

Task 4a Measure the Oxidation Rate of Organic Contaminants in Reactive Zone Media

Measure the rate of TCE oxidation in groundwater from TAN-29, crushed and aggregate basalt, and sediment (fracture fill material). Use the approach described in Section 2.2 of the Implementation Plan, and the experimental treatments described in Table 2-5.

Submit a preliminary report that presents the principal results of this task, followed by more detailed information in the final report. The analytical and final reporting procedures shall comply with sections 2.4 and 9.1 of the Draft Implementation Plan.

Task 4b Measure the Oxidation Rate of Organic Contaminants in Hot Spot Media

Measure the rate of TCE oxidation in groundwater and organic sludge from TSF-05. Use the approach described in Section 2.2 of the Implementation Plan, and the experimental treatments described in Tables 2-6 and 2-7.

Submit a preliminary report that presents the principal results of this task, followed by more detailed information in the final report. The analytical and final reporting procedures shall comply with sections 2.4 and 9.1 of the Draft Implementation Plan.

Task 5 Waste Disposal

The laboratory residuals generated in this investigation must be disposed in accordance with applicable regulations. Dispose of wastes and unaltered samples according to the procedures described in Section 7.3 of the Implementation Plan. All laboratory residuals generated in this study will be disposed by ORNL, with the following exceptions:

1. Unused, unaltered samples may be returned to INEEL for disposal;

2. If sludge from TSF-05 is determined to be regulated under the Toxic Substances Control Act, then samples and apparatus that contacted the sludge shall be returned to INEEL for disposal. Lab residuals that did not contact sludge will be disposed by ORNL.

Task 6 Progress Reports

Submit monthly reports that summarize the budget status and technical progress during the last month and for the project to date. An example of a monthly report is attached.

Task 7 Final Report

Submit a final report as described in Section 9.1 of the Implementation Plan, and data packages.

Task 8 Present Results of the Laboratory Study

Present the results of the laboratory study in a one-day meeting to be held in either Idaho Falls, Idaho, Boise, Idaho, or Seattle, Washington. The location and date will be determined approximately one month in advance of the meeting.

Schedule and Deliverables

Table A1. Schedule and deliverables

TASK	DELIVERABLE	SUBMITTAL DATE
1. Prepare project planning documents	1a Laboratory Test Plan – draft for review - final version	December 19, 1997 January 7, 1998
	1b Letter confirming that all permits, permissions, and documents needed to perform Tasks 2 – 5 are in place.	December 23, 1997
2. Refine laboratory procedures	2a–c Preliminary report	January 30, 1998
3. Measure oxidant demands	3a Preliminary report.	February 23, 1998
	3b Preliminary report	March 20, 1998
4. Measure oxidation rates	4a Preliminary report	April 14, 1998
	4b Preliminary report	May 29, 1998
5. Waste disposal	Letter confirming that all laboratory residuals and unaltered samples have been disposed in compliance with applicable regulations	June 19, 1998
6. Progress Reports	Monthly reports of costs and technical progress.	Ten days after the end of each accounting month
7. Final Report	Final report	June 12, 1998
8 Present Results	Presentation of results.	To be determined.

Sample Monthly Report

Month _____

Budget

Labor Hours
Labor Cost
Non-Labor Cost
Total Monthly Cost
Cumulative Project Cost
Total Budget

Technical Progress

Technical Problems and Proposed Resolutions

A2. LABORATORY STUDIES

Excerpted from *Draft In Situ Chemical Oxidation Implementation Plan Test Area North Final Groundwater Remediation Operable Unit 1-07B*, INEEL/EXT-97-01111, Rev 1.

This section describes laboratory studies that will be used to evaluate the feasibility of implementing ISCO to remove TCE contamination from the TAN site, and to provide data that will be used to design field evaluations, including both short term single well tests and longer term, larger scale evaluations in a reactive zone and at the hot spot. Lab studies will focus on quantifying oxidant consumption by groundwater, basalt, sludge, and sediment that fills basalt fractures, as well as reaction kinetics between potassium permanganate and TCE. Bench-scale experiments using materials taken from the TAN site will be conducted to establish the effectiveness of ISCO for removing TCE from the hot spot and the reactive zone. Furthermore, the optimum range of oxidant loadings for the hot spot and reactive zone will be determined based on TCE degradation kinetics and the amount of oxidant consumed by the natural (basalt and sediment) and anthropogenic (organic sludge) materials underlying the TAN site.

The effect of chemical oxidation on the migration of radionuclides and metals will not be investigated in the laboratory, but instead will be assessed via a transport modeling study.

A2.1 Objectives and Data Gaps

Results of laboratory studies will be used to evaluate the feasibility of ISCO for aquifer remediation, and for designing field evaluations of ISCO. The major questions addressed by laboratory studies are:

1. What are suitable concentrations of oxidant for use in single well tests, a field evaluation at the hot spot, and full scale implementation at the hot spot ?

2. How much oxidant will be needed for single well tests, field evaluations, and full scale implementation at the hot spot ?

Suitable concentrations can be determined based on the organic contaminant destruction rate as a function of oxidant concentration and on the amount of oxidant consumed by other reactions. The amount of oxidant needed can be determined from measurements of oxidant demand by materials present in the subsurface at TAN.

The objectives of this task are:

1. To determine potassium permanganate consumption rate and amount as a function of medium type (groundwater, basalt, sediment, sludge), potassium permanganate loading, and initial TCE concentration; and,

2. To determine the destruction rate and extent of TCE oxidation as a function of medium type, potassium permanganate loading, and initial contaminant concentration (including the presence of a non-aqueous phase).

The objectives, data gaps, and test methods developed through agency consensus are summarized in Table A2.1.

Table A2.1. Laboratory reaction studies objectives.

Objective	Data Gap	Test Method
Determine the effectiveness of chemical oxidation for destroying TCE in TAN media under ideal conditions	Oxidant demand of TAN groundwater, basalt, sludge, and sediment that fills fractures	Lab batch experiments
	TCE destruction rate and extent, and formation of chlorinated daughter products as a function of oxidant concentration and contaminant concentration	Lab batch experiments
	Rate of DNAPL depletion by chemical oxidation	Lab batch experiments

A2.2 Experimental Approach

Bench-scale batch reaction experiments will be conducted wherein residual TCE and MnO_4^- is measured in mixtures of TAN groundwater and solid material spiked with TCE and subsequently treated with potassium permanganate. Groundwater for the experiments will be taken from TAN-29 (representative of the reactive zone) and TSF-05 (representative of the hot spot). Organic sludge will be collected from TSF-05. Basalt will be collected from TAN-37 core, and sediment will be collected from fractures in TAN-48 core or archived core.

Experimental variables to be considered in the batch experiments include the following:

- Solid Medium - Within the hot spot, a majority of the TCE is believed to be associated with the organic sludge. Degradation of aqueous TCE in the presence of basalt and sediment present as fracture-fill material is relevant for both the hot spot and reactive zones.

- Basalt Form - Comparison of TCE degradation kinetics between systems with crushed and aggregate basalt may indicate diffusion-limitations that will impact the effectiveness of ISCO for removing TCE from the fractured basalt.

- Liquid-to-Solid Ratio - TCE degradation and potassium permanganate consumption will be measured in systems with groundwater alone (from the reactive zone and hot spot) and groundwater + solid at a 4:1 mass ratio.

- TCE Concentration - TCE concentrations range from low levels (1 ppm) representative of contamination in the reactive zone to DNAPL levels that are potentially present in the hot spot.

- Organic Co-Contaminants - Other chlorinated alkenes (cis-1,2- dichloroethene (DCE), trans-1,2-DCE, and vinyl chloride (VC)) will be included in a subset of the reaction experiments; these compounds have been detected at elevated levels within the TAN site.

- Potassium Permanganate Concentration - Previous studies have indicated that TCE degradation kinetics increase with permanganate concentration. A wide range of potassium permanganate concentrations will be evaluated, with lower and higher oxidant concentrations anticipated for the reactive zone and hot spot respectively.

- Temperature – Oxidant consumption and oxidation rate will be measured at 12 Celsius.

Table A2.2 summarizes the conditions/levels to be tested for each experimental variable while Tables A2.3 to A2.7 contain specific combinations of experimental conditions to be investigated in this laboratory study. The following general procedure will be followed for the reaction experiments:

1. Measured amounts of matrix material (groundwater + air-dried sludge, basalt, or sediment) are placed into multiple reaction vessels. Glass flasks or beakers will be used as reaction vessels for the oxidant consumption studies (Tables A2.3 and A2.4). Reaction vessels for the TCE degradation studies (Tables 2-5 through 2-7) will consist either of stainless steel zero-headspace extractors (ZHE's) or glass vessels equipped with Tedlar bags to capture generated gases (e.g., CO_2). In the oxidant demand studies (Tables A2.3 and A2.4) and the degradation studies (Tables A2.5 to A2.7) each experimental condition will be conducted in duplicate (i.e., two different reactor setups). In addition, duplicate control reactors will also be prepared for the degradation experiments in Tables A2.5 to A2.7. These control reactors will be spiked with TCE (and other co-contaminants when applicable) and aliquots will be collected at time zero and periodically thereafter to quantify changes in concentration due to processes other than oxidation. The actual number of control samples needed will be controlled by the approach in which the test series are conducted. For example, one set of control reactors could serve as the control for two experimental test conditions if the reactors had the same test medium and initial target TCE concentration. Residual volatile contaminants in the groundwater and solid materials will be removed by purging with N_2 and air-drying, respectively, before being placed into the reaction vessels. This will enable experiments to be conducted on materials with consistent and controlled initial levels of TCE contamination.

2. For the TCE degradation experiments, pre-determined amounts of TCE (either as a methanolic stock solution or as a pure-phase) will be added to the reaction vessels. After spiking, all the reaction vessels will be sealed and allowed to equilibrate for at least 24 hours (equilibration times will be longer for the tests on aggregate basalt). A preliminary study will be conducted to determine the necessary equilibration time. During equilibration, the reaction vessels will be gently agitated. Immediately prior to potassium permanganate additions (Step 3), duplicate reaction vessels will be sacrificially analyzed to obtain the initial TCE concentration (or mass).

1. Predetermined amounts of solid industrial-grade potassium permanganate will be added to the reaction vessels (except for a few which will serve as controls). Reaction vessels will be shaken immediately after potassium permanganate additions to ensure rapid dissolution of the crystalline oxidant. The reaction vessels will be gently agitated until extraction.

2. At predetermined reaction time intervals, liquid aliquots from the duplicate control and duplicate potassium permanganate-treated reaction vessels will be withdrawn for analysis. TCE will be measured through hexane extraction of the aliquot and analysis of the extract on a gas chromatograph (GC) equipped with an electron capture detector (ECD). The gas chromatograph/electron capture detector (GC/ECD) will also be calibrated for less chlorinated alkenes. Analysis of vinyl chloride may require a different analytical technique, as described in Section A2.4.2. Vinyl chloride concentrations will be measured in experimental treatments in which vinyl chloride is added as a co-contaminant, but will be measured in other experimental treatments only if it can be analyzed using the GC/ECD technique. For the experiments conducted in glass vessels equipped with Tedlar bags, TCE will also be measured in the gas collected by the Tedlar bag. Residual MnO_4^- will be

quantified using a spectrophotometric technique. pH will also be measured in the aqueous aliquots.

3. After aliquot sampling for the final predetermined reaction time interval, the entire contents of the reaction vessels will be extracted with hexane. The extracts will then be analyzed for TCE and potential oxidation by-products on the GC/ECD. The total organic carbon content of organic sludge will be measured. Mn speciation in the treated media at the final reaction interval will also be attempted.

4. The total organic carbon content of organic sludge will be determined once before the oxidant demand and oxidation rate studies, and will be measured again at the end of the experiments described in Tables A2.4 and A2.7.

Table A2.2. Experimental variables in reaction studies.

Parameter	Number of Values	Values
Media	3	Groundwater from TAN-29 + Basalt from TAN-37 (representing the reactive zone)
		Groundwater from TAN-29 + sediment from fractures (representing the reactive zone)
		Groundwater from TSF-05 + organic sludge from TSF-05 (representing the hot spot)
Liquid (groundwater) to solid (basalt, sludge, or sediment) ratios	2	1:0 (groundwater alone) 4:1 (groundwater : basalt, sludge, or fracture fill material)
Basalt form	2	Crushed (< 3 mm) Aggregate (1.3 to 2.5 cm)
TCE concentrations (in the aqueous phase)	5	0 mg/L[a] 1 mg/L 10 mg/L 100 mg/L DNAPL
Organic co-contaminants (cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and vinyl chloride)	2	0 mg/L 10 mg/L
Potassium permanganate concentrations	4	0.01% 0.1% 1.0% 3.0%
Temperature	1	12 C

a. This will provide matrix oxidant consumption.

Table A2.3. Oxidant consumption by reactive zone media.

Media	Basalt Form	Liquid : Solid Ratio	Initial TCE Concentration (mg/L)	Initial Organic Co-Contaminant Concentration (mg/L)	Initial Potassium Permanganate Concentration (%)
Groundwater	NA	NA	0	0	0.01
Groundwater/basalt	Crushed	4:1	0	0	0.01
Groundwater/basalt	Aggregate	4:1	0	0	0.01
Groundwater/sediment	NA	4:1	0	0	0.01
Groundwater	NA	NA	0	0	0.10
Groundwater/basalt	Crushed	4:1	0	0	0.10
Groundwater/basalt	Aggregate	4:1	0	0	0.10
Groundwater/sediment	NA	4:1	0	0	0.10
Groundwater	NA	NA	0	0	1.00
Groundwater/ basalt	Crushed	4:1	0	0	1.00
Groundwater/ basalt	Aggregate	4:1	0	0	1.00
Groundwater/sediment	NA	4:1	0	0	1.00

Table A2.4. Oxidant consumption by hot spot media.

Media	Basalt Form	Liquid : Solid Ratio	Initial TCE Concentration (mg/L)	Initial Organic Co-Contaminant Concentration (mg/L)	Initial Potassium Permanganate Concentration (%)
Groundwater	NA	NA	0	0	0.01
Groundwater/sludge	NA	4:1	0	0	0.01
Groundwater	NA	NA	0	0	0.10
Groundwater/sludge	NA	4:1	0	0	0.10
Groundwater	NA	NA	0	0	1.00
Groundwater/sludge	NA	4:1	0	0	1.00
Groundwater	NA	NA	0	0	3.00
Groundwater/sludge	NA	4:1	0	0	3.00

Table A2.5. TCE degradation rate in reactive zone groundwater and basalt

Media	Basalt Form	Liquid : Solid Ratio	Initial TCE Concentration (mg/L)	Initial Organic Co-Contaminant Concentration (mg/L)	Initial Potassium Permanganate Concentration (%)
Groundwater	NA	NA	0.1	0	0.01
Groundwater	NA	NA	0.1	0	0.10
Groundwater	NA	NA	1	0	0.01
Groundwater	NA	NA	1	0	0.10
Groundwater/basalt	Crushed	4:1	0.1	0	0.01
Groundwater/basalt	Crushed	4:1	0.1	0	0.10
Groundwater/ basalt	Aggregate	4:1	0.1	0	0.01
Groundwater/basalt	Aggregate	4:1	0.1	0	0.10
Groundwater/basalt	Crushed	4:1	1	0	0.01
Groundwater/basalt	Crushed	4:1	1	0	0.10
Groundwater/basalt	Aggregate	4:1	1	0	0.01
Groundwater/basalt	Aggregate	4:1	1	0	0.10
Groundwater/sediment	NA	4:1	0.1	0	0.01
Groundwater/sediment	NA	4:1	0.1	0	0.10
Groundwater/sediment	NA	4:1	1.0	0	0.01
Groundwater/sediment	NA	4:1	1.0	0	0.10

Table A2.6. TCE degradation rate in hot spot groundwater.

Media	Basalt Form	Liquid:Solid Ratio	Initial TCE Concentration (mg/L)	Initial Organic Co-Contaminant Concentration (mg/L)	Initial Potassium Permanganate Concentration (%)
Groundwater	NA	NA	10	0	0.01
Groundwater	NA	NA	10	0	0.10
Groundwater	NA	NA	10	0	1.00
Groundwater	NA	NA	10	0	3.00
Groundwater	NA	NA	100	0	0.01
Groundwater	NA	NA	100	0	0.10
Groundwater	NA	NA	100	0	1.00
Groundwater	NA	NA	100	0	3.00
Groundwater	NA	NA	100	10	0.01
Groundwater	NA	NA	100	10	0.10
Groundwater	NA	NA	100	10	1.00
Groundwater	NA	NA	100	10	3.00
Groundwater	NA	NA	2,000*	0	0.01
Groundwater	NA	NA	2,000*	0	0.10
Groundwater	NA	NA	2,000*	0	1.00
Groundwater	NA	NA	2,000*	0	3.00

* Indicates that TCE is present as a DNAPL.

Table A2.7. TCE degradation rate in hot spot groundwater and sludge.

Media	Basalt Form	Liquid : Solid Ratio	Initial TCE Concentration (mg/L)	Initial Organic Co-Contaminant Concentration (mg/L)	Initial Potassium Permanganate Concentration (%)
Groundwater/sludge	NA	4:1	0	0	0
Groundwater/sludge	NA	4:1	10	0	0.01
Groundwater/sludge	NA	4:1	10	0	0.10
Groundwater/sludge	NA	4:1	10	0	1.00
Groundwater/sludge	NA	4:1	10	0	3.00
Groundwater/sludge	NA	4:1	100	0	0.01
Groundwater/sludge	NA	4:1	100	0	0.10
Groundwater/sludge	NA	4:1	100	0	1.00
Groundwater/sludge	NA	4:1	100	0	3.00
Groundwater/sludge	NA	4:1	2,000*	0	0.01
Groundwater/sludge	NA	4:1	2,000*	0	0.10
Groundwater/sludge	NA	4:1	2,000*	0	1.00
Groundwater/sludge	NA	4:1	2,000*	0	3.00

* Indicates that TCE is present as a DNAPL.

Sacrificial sampling (i.e., extraction of reaction vessel contents) at reaction intervals will be conducted for one test series on TAN sludge (Table A2.7). The TCE level and potassium permanganate loading for this test series will be determined from results of the TCE degradation experiments where aliquot sampling was used.

The experimental procedures and conditions described above may be modified during the course of the laboratory study. Possible changes include the following:

- Modification of procedures to satisfy laboratory ES&H requirements. An ES&H evaluation of the planned laboratory experiments will be conducted before any work is initiated.

- Deletion of experiments from the test matrix deemed unnecessary based on completed tests. For example, 0.01% permanganate experiments will not be included in the TCE degradation and contaminant immobilization tests on TAN sludge if the sludge consumes significant amounts of potassium permanganate.

- Revision of reaction times to better capture temporal trends in TCE based on observations in completed experiments.

A2.3 Data Analysis and Interpretation

The first and second test series (Table A2.3 and A2.4) will provide oxidant consumption by TAN basalt, sediment from fractures, and organic sludge. The tests will be the first indicators of whether ISCO is feasible at the TAN reactive zone and hot spot. Excessive oxidant consumption will result in large amounts of oxidant required for the full-scale process. If this were the case, ISCO may be cost-prohibitive. Results of the oxidant consumption measurements series will serve as a basis for deciding whether to continue the laboratory studies and ISCO field evaluations at the hot spot or reactive zone. Oxidant consumption may be high for the organic sludge; it is not expected to be significant for the fractured basalt or sediment.

The reaction test matrix (Table A2.5 to A2.7) has been designed to provide TCE degradation rate as a function of potassium permanganate loading for each matrix type (groundwater from the hot spot with and without organic sludge, groundwater from the reactive zone with and without basalt). The relationship between degradation rate and potassium permanganate concentration will be used to select optimum potassium permanganate loading for each matrix.

Significant differences between TCE degradation trends in the crushed and aggregate basalt (Tables A2.3 and A2.5) will indicate diffusion limitation effects of TCE chemical oxidation in TAN basalt. The results of these experiments combined with results of the modeling described in Section A3.2 will determine whether matrix diffusion can impact the effectiveness of ISCO for remediating the hot spot and reactive zone at TAN.

A2.4 Analytical Methods and Quality Assurance

A2.4.1 Summary of Analytical Data from Laboratory Studies

The laboratory treatability studies described in the previous subsections will provide quantitative information regarding the technical feasibility and environmental impact of performing ISCO at the TAN site. This quantitative information can be categorized into the following groups of parameters:

- Parameter Group 1 - Consumption rate and extent of potassium permanganate by the contaminated matrix as a function of oxidant concentration and matrix type (Tables

A2.3 – A2.4). These will be used to assess the practicality of ISCO at the TAN site, as well as to determine optimum oxidant loadings.

- Parameter Group 2 - Degradation rate and extent of chlorinated organics by potassium permanganate as a function of initial organic contaminant level, oxidant concentration, and matrix type (Tables A2.5 – A2.7). These will be used to assess the effectiveness of ISCO for reducing organic contamination at the TAN site.

The following chemical measurements will be conducted to generate the parameter groups given above:

1. MnO_4^- in an aqueous matrix
2. Chlorinated organics in aqueous and solid matrices

Other physical and chemical measurements will be made during the laboratory experiments (e.g., pH, total organic content); however, use of these other parameters in any decision making process related to the evaluation of ISCO for the TAN site is not anticipated. This subsection focuses on the primary analyses mentioned above and associated quality assurance/quality control requirements deemed appropriate for the use of the analytical data.

Formal data packages will only be provided for the chlorinated organics analyses. The components of the data packages are also described in the following subsections. The data will be reported in sample data groups for the organic analyses. This will simplify preparation of the data packages without sacrificing the quality of information provided.

A2.4.2 Permanganate Analysis of Aqueous Samples

A2.4.2.1 Method Description. MnO_4^- concentrations in aqueous samples will be quantified using a spectrophotometric technique developed by researchers at ORNL who have been conducting R&D work related to chemical oxidation by potassium permanganate. Five MnO_4^- standard solutions will prepared in distilled water (concentration ranging from 5 to 50 ppm) using reagent grade potassium permanganate, and their respective absorbances will be measured at a wavelength of 525 nm using a Hach 2000 spectrophotometer. A calibration curve is then prepared from the absorbance vs standard concentration data. The MnO_4^- concentration of an aqueous sample will be quantified by measuring its absorbance at 525 nm, and calculating the corresponding concentration from the previously generated five-point calibration curve. Samples with concentrations greater than the calibrated range will be diluted to bring the concentration within the calibration range. Samples will be filtered with a 0.45 μm membrane prior to analysis via spectrophotometry to remove particulate matter that could interfere with the analysis.

This spectrophotometric method is substantially less time consuming than a more standard titration method for measuring MnO_4^-. The quality of the data generated by the spectrophotometric method is deemed suitable for its use in defining optimum oxidant loadings for ISCO implementations at the TAN site.

A2.4.2.2 Quality Assurance/Quality Control. Calibration will be verified on each analysis day by analyzing check standard solutions (10 and 50 ppm) prepared on the same day using distilled water and reagent-grade potassium permanganate. If the absorbance varies by 15% from the predicted absorbance based on the calibration curve, than a new calibration curve will be constructed.

A2.4.2.3 Data Package Components. A formal data package is deemed unnecessary for these analyses since the MnO_4^- measurements will only be used for establishing oxidant loadings.

A2.4.3 Analysis of Aqueous and Solid Samples for TCE and DCE

A2.4.3.1 Method Description. Target chlorinated organic contaminants (TCE, cis- and trans-1,2-DCE) in aqueous and solid samples from the ISCO reaction rate studies will be measured through hexane extraction followed by gas chromatographic analysis of the hexane extracts. Chlorinated organics in the hexane extract will be quantified using an HP5890 II GC/ECD and HP ChemStation Software. Wherever possible, procedural and quality control guidelines from SW846/Method 8000A (Gas Chromatography) will be followed to ensure the quality of the GC analyses of the hexane extracts. Previous experience at ORNL has demonstrated that TCE concentrations in aqueous and solid matrices as low as 10 ppb can be reliably measured with this method.

Aqueous Extraction - Five mL aliquots of liquid from the reaction study vessels will be placed in 5-mL of hexane and shaken on a reciprocal shaker for at least 30 minutes prior to analysis. Aqueous samples from the reactive experiments must be extracted with hexane immediately in order to quench any oxidative reactions.

Solids Extraction - After pouring out any excess fluid from the reaction vessel, 100 mL of hexane will be added to the reaction vessel to extract residual chlorinated organics from the solid (~100 g). The reaction vessel with the hexane and solid matrix will be shaken for at least 30 minutes prior to analysis.

Analysis of Hexane Extract

Calibration: The procedure for external calibration found in Section 7.4.2 of SW846/Method 8000A will be followed. Calibration standards in hexane will be prepared from certified calibration methanolic solutions and will include the following levels: 10, 50, 100, 500, 1000 ppb. One mL aliquots of these standards will be injected into the GC/ECD using an autosampler; area count vs standard concentration data will be used to construct calibration curves. The working calibration curve will be verified through the injection of a QC check standard (100 ppb) at least once every analysis day. If the response for any analyte varies from the predicted response by more than ±15%, a new calibration curve will be prepared.

Retention Time Windows: These will be established following Section 7.5 in SW846/Method 8000A.

GC Analysis: One μL aliquots of the extracts will be injected directly into the GC/ECD using an auto sampler. If the response for any of the target analytes exceeds the response for the 1000 ppb standard, the hexane extract is diluted and reanalyzed.

A2.4.3.2 Quality Control/Quality Assurance.

Calibration Checks - A QC check sample (100 ppb) will be analyzed on each analysis day. If the response for any of the target analytes varies from the predicted response by more than 15%, a new calibration curve will be prepared before any more samples are analyzed.

Method Blanks - A blank hexane sample will be analyzed between every 10 samples.

Precision and Accuracy - The precision and accuracy of the hexane extract analysis will be established by four replicate analysis of a QC check standard prepared independently from the calibration standards. The recovery (in ppb) and standard deviation (in ppb) of the recovery for each target chlorinated organic will be tabulated and included in the QC data for the organics analyses. This precision/accuracy check will be done once before initiating the laboratory studies.

Duplicate aliquots will be collected, extracted, and analyzed for at least every tenth test sample.

Matrix Interference - Matrix spike and matrix spike duplicate analyses will not be conducted because the water and solid materials will be artificially spiked with the target VOCs. Thus,

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extraction efficiency will be measured by comparing the analysis of the control samples (no treatment) with the theoretical spiking levels.

Calculations -Equation 3 calculates the concentration of target organic contaminants in the aqueous and solid samples.

$$C_{sample} = C_{extract} \times V_{extract} / M_{sample} \tag{3}$$

where

C_{sample}	=	the concentrations in the sample
$C_{extract}$	=	the concentrations in the hexane extracts
$V_{extract}$	=	the volume of hexane used to extract the sample
M_{sample}	=	the mass of sample extracted.

A2.4.3.3 Data Package Components. An organics data package will be prepared based on requirements for a Tier 2 sample data package outlined in Part II of the "Statement of work for organics analyses performed for the Idaho National Engineering Laboratory Sample Management Office" INEL-95/006 ER-SOW-169. Some components deemed inapplicable for this laboratory treatability study have been eliminated.

The data package will include the following:

1. Narrative:
    a. Laboratory name
    b. Table of samples including sample number (assigned by ORNL), date prepared/collected, date analyzed, calibration curve used (identified by date), and description of when/where samples were collected
    c. Summary of QC and analytical problems.

2. Chain of Custody forms:
    a. Chain of custody forms will only be used for treatability study materials (groundwater, sludge and basalt) that will be sent by INEEL to ORNL. These will be included in the data package. Chain of custody forms are unnecessary for the samples that will be generated during the laboratory experiments.

3. GC QC Data:
    a. Method Blank Summary (Form IV VOA)
    b. QC check sample summary (Form XI VOA including only target organics).

4. GC Sample Data:
    a. Target analyte results (Form I VOA including only target organics).

5. Standards Data:
    Initial (FORM VI including only target organics) and continuing calibration (FORM VII including only target organics).

A2.4.4 Analysis of Aqueous and Solid Samples for Vinyl Chloride

A2.4.4.1 Method Description

It is suspected that the analysis of vinyl chloride will require a different analytical approach. In gas chromatography analysis, the elution of vinyl chloride is often masked by the presence of the extraction solvent (i.e., hexane). In order to effectively quantify vinyl chloride, purge and trap analysis is preferred over solvent extraction. Upon purging, the aqueous samples will be will be quantified using an HP5890 II GC/FID and HP ChemStation Software. Wherever possible, procedural and quality control guidelines from SW846/Method 8000A (Gas Chromatography) will be followed to ensure the quality of the GC

analyses of the hexane extracts. Previous experience at ORNL has demonstrated that vinyl chloride in aqueous systems as low as 10 ppb can be reliably measured with this method. Analysis of vinyl chloride will only be performed on the test series defined in Table A2.6 where co-contaminants are added to the test reactors. For the vinyl chloride analysis, a separate 5 mL aliquot will have to be collected (in addition to the 5 mL extract for hexane extraction) for the purge and trap analysis. It may not possible to determine the remaining mass of vinyl chloride in the test reactors following sampling of the last time interval. Calibration and Retention Time Windows, etc. will be conducted similar to the approach outlined in 2.4.3.

A2.4.4.2 Quality Control/Quality Assurance

Calibration checks, method blanks, precision and accuracy, matrix interference, and calculations will be conducted and reported in a fashion similar to that described in Section A2.4.3.2

A2.4.4.3 Data Package Components

The vinyl chloride data package will be generated following the format discussed in 2.4.3.3 for the TCE and DCE analyses.

A2.4.5 Analysis of Aqueous Samples for pH

A2.4.5.1 Method Description

pH analyses will be conducted on aqueous aliquots collected from the test reactors. The analyses will be conducted using conventional pH meter/electrode procedures. Previous experience at ORNL does not indicate that matrix interferences are created by the presence of $KMnO_4$ in the test samples

A2.4.5.2 Quality Assurance/Quality Control

The instrument will be calibrated each day of use via standard buffer solutions of pH 4, 7, and 10. A calibration check will also be conducted following the final pH sample to be analyzed at the end of each day. Values obtained for the samples will be corrected via linear interpolation if a significant drift occurred in the calibration check.

A2.4.5.3 Data Package Components

    a.   As discussed in 2.4.1, pH measurements will most likely not be used in any decision making process regarding ISCO implementation. Hence, a formal data package is deemed unnecessary for pH analyses.

A2.5 INEEL Activities to Support Off-Site Laboratory Studies

A2.5.1 General

Laboratory studies will be performed in laboratories at the Oak Ridge National Laboratory (ORNL). INEEL will perform a variety of activities such as the following to support the laboratory studies:

- Audit by the INEEL Sample Management Office of ORNL laboratories confirm that the experimental results are technically sound

- Audit by the INEEL Environmental Affairs Department of ORNL laboratories to confirm that the permits and procedures needed to comply with environmental regulations are in place

- Collection, packaging, and shipping of samples of groundwater, sludge, sediment, and basalt to ORNL

- Disposal of the excess, unaltered samples

- Disposal of lab residuals that contacted organic sludge from TSF-05 if the sludge is found to contain greater than 50 ppm PCB.

Laboratory audits and waste disposal are described in Section 7. Sample collection and shipment are described in Section A2.5.2 through A2.5.6.

A2.5.2 Collection of Groundwater Samples

Groundwater will be collected from TSF-05 and TAN 29 to support the laboratory studies described in Sections A2.1 and A2.2. There will be 80 L (21 gal) of water collected from TSF-05 and 30 L (8 gal) collected from TAN-29.

Groundwater will be collected following procedures described in *Environmental Restoration SOP-11.8, Groundwater Sampling,* April 1994. Sampling equipment will be decontaminated between wells following procedures described in *Environmental Restoration SOP-11.5, Field Decontamination of Sampling Equipment,* July 1994. The exceptions to SOP-11.5 are that either deionized water or a detergent solution will be used instead of isopropanol as the decontaminating solution, and that decontamination will be performed by wiping equipment with a terry cloth towel soaked in the decontaminating solution instead of spraying the equipment with the decontaminating solution.

A2.5.3 Sampling and Analysis Plan Tables for Groundwater and Sludge

The sampling and analysis plan (SAP) for collecting groundwater and sludge samples is included in a document action request (DAR) for the *Surge and Stress Plan Test Area North Groundwater Remediation Operable Unit 1-07B* (Tomlinson et al. 1996).

A2.5.4 Collection of Sludge Samples

Sludge samples will be collected from TSF-05 to support the laboratory studies described in Sections A2.1 and A2.2. There will be 20 L (5 gal) of sludge collected.

Sludge samples will be collected in accordance with procedures described in *TSF-05 Sludge Sampling Procedure,* September 3, 1997.

A2.5.5 Collection of Basalt Samples

Two samples of basalt will be collected to support the lab studies described in Sections A2.1 and A2.2. Both samples will be collected by subsampling core from TAN-37, which will then be processed to generate two grain-size ranges. The core was surveyed for radiological contamination as it was collected, and was found to be free of radiological contamination above background levels.

Core from TAN 37 is presently stored at the temporary accumulation area (TAA) at the TAN Groundwater Treatment Facility (GWTF).

The procedure for subsampling the core and sizing the material is described below.

1. Collect samples from the interflow zones between depths of 61 and 122 m (200 and 400 ft) below ground surface. Collect material from the uppermost interflow first, and then from successively deeper interflow zones until sufficient material has been

collected. Collect samples from the vesicular portions of flows, but not from the massive flow interiors.

2. Air dry the samples.

3. Two grain-size fractions are required for laboratory studies: (1) a coarse fraction with pieces falling between 1.8- to 2.5-cm (1/2- to 1-in.), and (2) a fine fraction with pieces smaller than 0.3-cm (1/8-in.) in diameter.

    a. Generate the coarse fraction by manually selecting pieces in this size range and larger than this size range. Using the hammer and chisel and rock crusher in custody of the Subsurface Science Program and located in building TAN-607, reduce the size of larger pieces. Sieve the crushed rock using 2.5-cm (1-in.) and 1.8-cm (1/2-in.) sieve. Keep the fraction that passes the 2.5-cm (1-in.) sieve but is retained on the 1.8-cm (1/2-in.) sieve. There are 5 kg (11 lb) of this size fraction required.

    Contact Rick Colwell at 526-0097 to coordinate use of the rock crusher. Remove the rock crusher from the glove bag prior to use.

    b. Generate the fine fraction by using the rock crusher to reduce the size of larger pieces of basalt until they are in the desired size range. Sieve the crushed rock using a 0.4-cm (1/8-in.) sieve and a pan. Keep the fraction that passes through the 0.4-cm (1/8-in.) sieve. There are 7.5 kg (16.5 lb) of this size fraction required.

4. Store processed basalt samples in two liter wide mouth plastic bottles, such as Fisher Scientific Catalog number 11-815-11A or similar. Samples can be stored at room temperature.

5. After collection of the samples, they will be assayed for radiological contamination and shipped to the ORNL laboratory.

Basalt that is crushed but does not fall into the required size fractions will be disposed in the existing OU 1-07B drill cutting waste streams.

Equipment used for preparing the basalt samples will be decontaminated by wiping it with terry cloth towels soaked in a detergent solution and then with a terry cloth towel soaked in deionized water. The used towels will be disposed in the Waste Stream 1935.

    A job safety analysis will be prepared prior to commencing this activity.

A2.5.6 Collection of Sediment from Fractures in Basalt

Sediment will be collected from fractures in basalt core samples from TAN. Sediment will be collected from core from TAN-48 below the PQ interbed. If more sediment than can be collected from this core is needed, then additional sediment will be collected from archived core samples.

Approximately 2 kg of sediment will be placed into a 2L plastic bottle for storage and shipment.

A2.5.7 Sample Storage and Shipment

Groundwater and sludge samples will be stored at 4°C between collection and shipment. Groundwater and sludge samples will be shipped in insulated containers with reusable cold packs.

Basalt and sediment samples will be stored at room temperature between processing and shipment, and will be shipped at room temperature.

Groundwater, basalt, and sediment samples will be shipped to:

Dr. Olivia West
Oak Ridge National Laboratory
Building 1505, Room 224
Bethel Valley Road
Oak Ridge, TN 37831
(423) 576-0505

Sludge samples will be shipped to :

Joe Giaquinto
Oak Ridge National Laboratory
Bethel Valley Road
Building 2026
Oak Ridge, TN 37831
(423)574-4887

Appendix B- Test Procedures

Appendix B

Laboratory Test Plan for the
Laboratory Evaluation of In Situ Chemical Oxidation as a
Technology for Groundwater Restoration at the INEEL TAN Site.

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Oak Ridge National Laboratory, Oak Ridge, TN

Prepared: September 1998
Revision 2

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Acronyms

CASD	Chemical and Analytical Sciences Division
ECD	Electron capture detector
ESD	Environmental Sciences Division
FID	Flame ionization detector
GC	Gas Chromatography
INEEL	Idaho National Environmental Engineering Laboratory
$KMnO_4$	Potassium permanganate
L/S	Liquid/Soil
ORNL	Oak Ridge National Laboratory
QA/QC	Quality Assurance and Quality Control
RMAL	Radioactive Material Analytical Laboratory
SOW	Statement of Work
TAN	Test Area North
TCE	Trichloroethylene
TOC	Total Organic Carbon
VC	Vinyl chloride
VOA	Volatile Organic Analysis
cis-1,2 DCE	cis-1,2 dichloroethylene
trans-1,2 DCE	trans-1,2 dichloroethylene
ZHE	Zero headspace extraction vessel
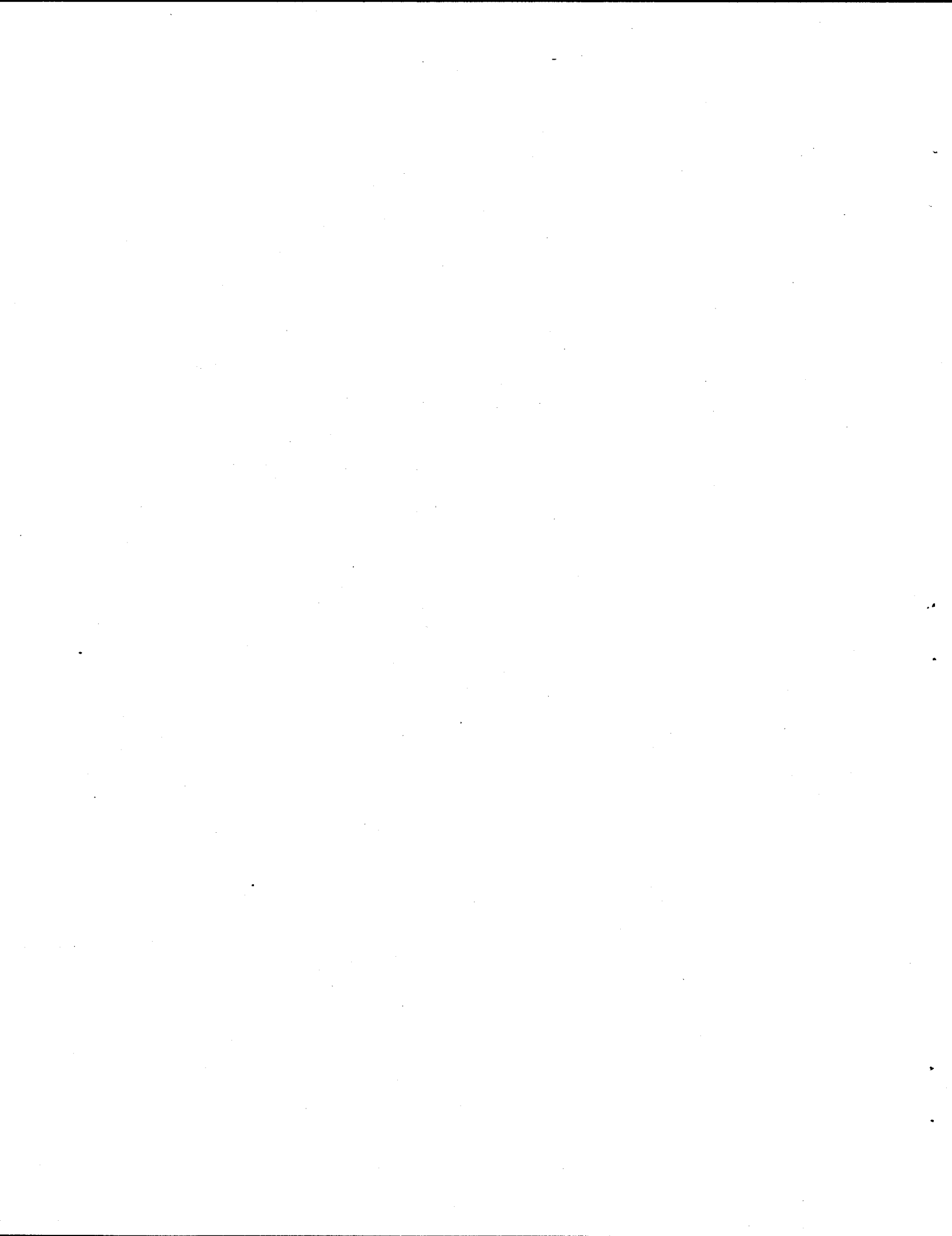
Laboratory Test Plan
Laboratory Evaluation of In Situ Chemical Oxidation as a Technology for Groundwater Restoration at the INEEL TAN Site
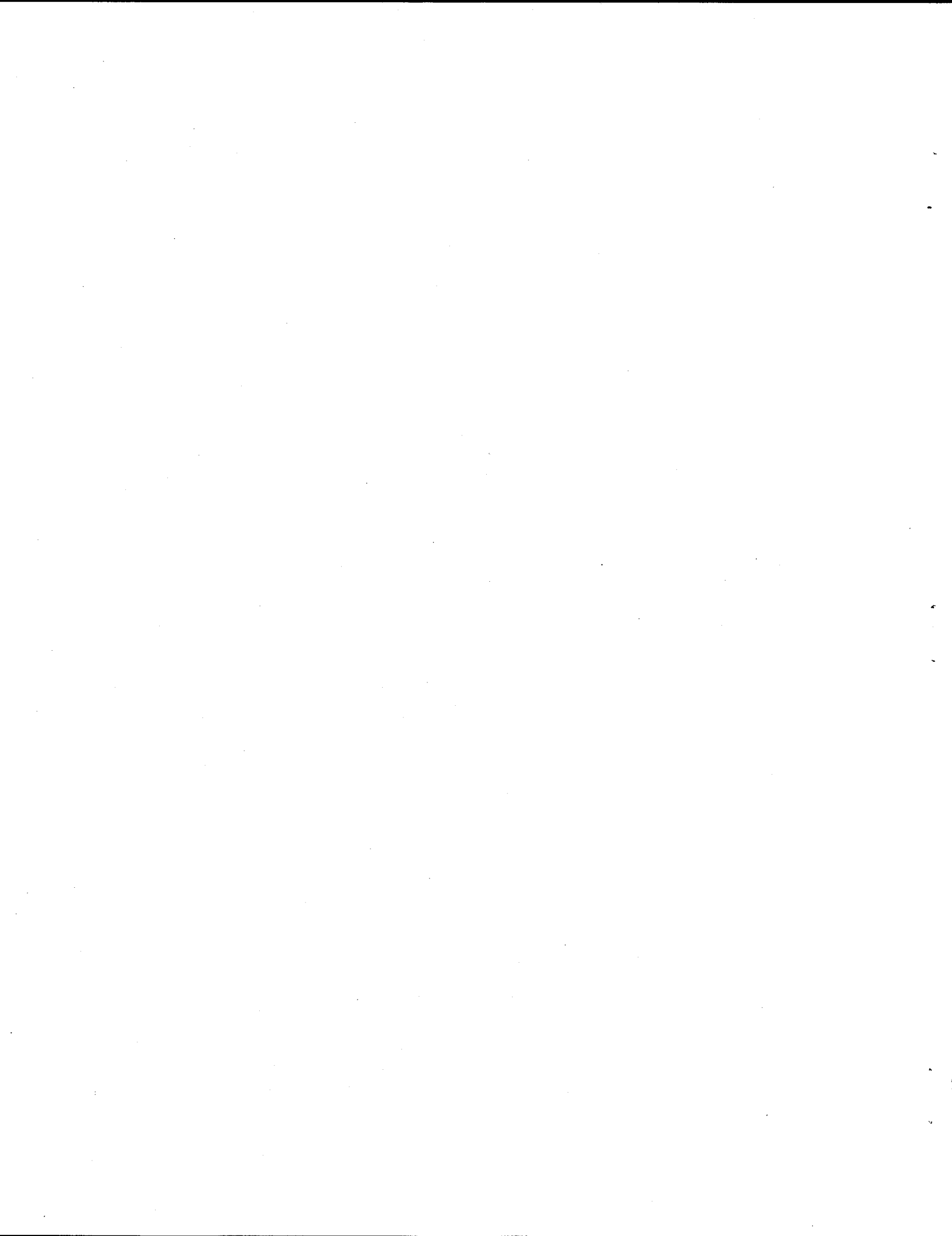
B1. Introduction

This laboratory test plan, completed to fulfill the requirements of SOW Task 1a, describes, in detail, the laboratory experiments to be performed during SOW Tasks 2-4. The discussion of these tasks also includes information about the quality assurance and control (QA/QC) elements that will be used during performance of the treatability study. The experiments described in this test plan serve as the current approach expected to be conducted; however, the materials and/or methodology may be modified if actual conditions in the laboratory warrant. Any modifications will be clearly noted and documented.

B2 Preliminary Laboratory Studies

These studies will be conducted to assess whether the equipment and/or approach planned for the experiments in Tasks 3 and 4 is appropriate. In particular, Task 2 studies include: (a) development and assessment of a reaction vessel (reactor) to be used in the Task 4 experiments, (b) determination of the optimum hexane extraction time for each media being evaluated in Task 4, and (c) the optimal equilibration time to use for TCE spiking of the aggregate basalt for Task 4.

B2.1 Reactor Development (Task 2a)

The reaction studies with TCE and $KMnO_4$ (Task 4) will be performed under controlled conditions. VOC losses from the reaction vessels due to volatilization mechanisms need to be minimized and quantified. Zero headspace extraction vessels (ZHEs) often used by ORNL researchers cannot be used due to their small sample capacity (130 mL). Thus, alternative reactors will be needed. Upon acquisition of new reactor vessels, this laboratory task will evaluate the performance of these vessels. In particular, the amount of TCE expected to be lost from the reactors will be quantified via a mass balance approach. The Task 4 reaction studies will be conducted using approximately 500 mL of INEEL TAN groundwater or a 500 mL slurry (4:1 L/S weight ratio) of TAN groundwater and solid phase media at a temperature of 12° C. This evaluation task, however, will be conducted using distilled water at room temperature spiked with TCE.

Currently, a glass reaction kettle will be evaluated. This reactor has a total gross volume near 500 mL, and consists of a glass reactor body and adapter top. A Teflon™ sleeve will be used as a seal to maintain liquid and gas-tight conditions. This port will be used for sampling, introducing $KMnO_4$, etc.

Due to the high organic content of the TAN site media, particularly the TSF-05 sludge, the reactor(s) may pressurize while the oxidation reaction(s) occurs. To reduce the health and safety risk, the reactors may need to be vented. For this situation, the bottom opening of a sampling port adapter will be covered with a thin LDPE film such as Parafilm M™ or aluminum foil to serve as a "pressure relief valve," with the assumption that the pressure buildup to rupture this thin film is much less than that required to force the ground glass adapter from the top of the reactor. Any emissions escaping through this film via either rupture or natural diffusion will be passed through

a desorption tube for quantification prior to its release to the atmosphere. (The quantity of TCE that may diffuse across this thin film under non-pressurized conditions is expected to be minimal but will be evaluated). Such desorption tubes contain two (2) successive activated charcoal filter beds and are typically used in industrial hygiene air sampling devices. Any TCE that is volatilized from the reactor should be retained via adsorption onto the charcoal media and can later be extracted with hexane for quantification. The overall performance of this reactor configuration will be evaluated to complete this task.

Experiment 2a-1. Evaluation of the rubber septum to reduce TCE losses.
(To be conducted at ORNL/ESD)
The reactor sampling port may be fitted with a thick rubber septum for the purpose of sample collection via a wide bore needle. Thus, this experiment will assess how well the fitting between the septum and the ground glass port opening minimizes TCE losses. The effect of performing repeated aliquot sampling through the septum will also be evaluated.

A 250 mL flask or equivalent having only a single 24/40 std taper opening will be used. This experiment will be conducted at room temperature.

1. A 100 mg/L aqueous TCE solution ($\approx$650 mL) will be prepared and allowed to equilibrate for at least 30 minutes. The solution will be prepared in a Tedlar Bag using DI water and pure TCE. Measure the mass of the spiking syringe when filled and then after spiking to record the total TCE mass added to the reactor (a QC check on the initial TCE analysis). Information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

2. Dispense the solution into 2 tared test containers, re-weigh and record the mass of TCE spike solution added to each. Duplicate 0.5 mL samples of the spike solution will be collected immediately before the septa is added to the test containers in order to determine the initial TCE concentration.

3. The aliquot samples will be added to pre-weighed vials holding a known volume of hexane. Each sample container will be weighed again after sample addition to determine the actual weight of sample added. (A calibration check of the gravimetric scale will be performed each day of use.) All such extracts will be placed on a horizontal shaker for 30 minutes. Store the extracts at 4°C until G.C. analysis.

4. Record the time that these duplicate samples are collected and the septum is placed onto each container. (Complete zero headspace conditions cannot be achieved here since excess water cannot be expelled from the containers as the septa are applied.)

5. After 2 hours, collect duplicate aqueous samples from one of the containers by puncturing the septum with the sampling syringe (wide bore needle desired since later experiments will be soil/sludge slurries). The septum will have to be punctured by a second needle in order to pull the samples into the syringe body. Do nothing to the other test container.

6. Extract and dilute the samples as needed (described above).

7. Repeat this sampling technique at least 5 more times over a period of 24 hours for the 1st test container.

8. Collect duplicate aqueous samples from the second test container after 24 hours. (This will be the first time that the septum of the 2nd test container is punctured.)

9. Analyze the extracts via GC/ECD for TCE quantification. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment.

10. Prepare a TCE mass balance to determine total mass of TCE not accounted for in either the remaining spike solution in the vial or in the sample aliquots for each test container. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

Experiment 2a-2. Evaluation of the pressure relief fitting to minimize and quantify TCE losses
(To be conducted at ORNL/ESD)
A shakedown experiment already conducted has shown that a thin layer of Parafilm-M material (wax based) is easily ruptured when placed on an otherwise sealed container in less time than is required to remove a rubber septum when a constant volume and rate of air is added to the container. However, a high degree of TCE diffusion is suspected through this type of material. A similar test was performed using aluminum foil as the thin film covering the bottom of the adapter. While desirable in the fact that TCE diffusion is likely minimal, the aluminum foil possessed a great deal of tensile strength in this configuration and could not be easily ruptured by pressurization of an erlenmeyer flask with air. For the purpose of this experiment four (4) different conditions will be evaluated: (a) no thin film, (b) Parafilm M, (c) aluminum foil punctured with a single pinhole (to reduce tensile strength), and (d) DuraSeal™, a solvent resistant LDPE film. Erlenmeyer flasks (125 mL) or equivalent containers having a 24/40 std. taper opening will be used in this experiment. There will not be an attempt to pressurize these containers. The "no thin film" set-up will represent the ruptured film case. This experiment will be conducted at room temperature.

1. Prepare the 24/40 std. Taper adapters as described above (a-d), securing the edges of each thin film by addition of a Teflon sleeve onto the ground glass fitting.

2. Assemble the ORBO-32 Tubes. Two ORBO-32 tubes will be used in series for each container in the event that the TCE adsorption capacity of the first tube is exceeded. Using Pliers, break the ends of two ORBO tubes. Smooth the broken ends with a file and connect them in series using tygon tubing. Orient them such that the "A" charcoal bed of each tube is first in line.
["A" is the larger of the two (100 mg charcoal), "B" contains 50 mg charcoal.]
NOTE: STORE THE OPENED ORBO TUBES OUTSIDE OF THE LABORATORY FUME HOODS. THE HOODS LIKELY HAVE THE GREATEST POTENTIAL FOR "CONTAMINATING" THE TUBES WITH TCE AND OTHER VOCs.

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3. A 100 mg/L aqueous TCE solution (≈1200 mL) will be prepared in a Tedlar bag and allowed to equilibrate overnight prior to being distributed into each container. (Preparing only one spiking solution, allows for each test set-up to have the same initial conditions). Measure the mass of the spiking syringe when filled and then after spiking to record the total TCE mass added to the reactor (a QC check on the initial TCE analysis). Information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

4. Fill each test container and collect duplicate 0.5 mL samples of the spike solution immediately before the containers are sealed in order to determine the initial TCE concentration in each.

5. The duplicate aliquot samples will be added to pre-weighed vials holding a known volume of hexane. Each sample container will be weighed again after sample addition to determine the actual weight of sample added. (A calibration check of the gravimetric scale will be performed each day of use.) All such extracts will be placed on a horizontal shaker for 30 minutes. Store the extracts at 4°C until G.C. analysis.

6. Record the time at which each sample is collected and the container is closed.

7. After 4 hours, remove the adapter from each container and collect an aqueous sample (0.5 mL) Extract and dilute the samples as needed for G.C. analysis for eventual analysis of the remaining TCE concentration in the solution. Store the extracts at 4°C until G.C. analysis.

8. For each container, separate the contents of each charcoal bed into separate vials pre-weighed with a known volume of hexane then reweigh the vials to determine the mass of charcoal present.

9. Extract these samples for 30 minutes and dilute as needed for G.C. analysis as done for the aqueous aliquots.

10. Analyze the extracts via GC/ECD for TCE quantification. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment.

11. Prepare a TCE mass balance on each container to determine which thin film configuration best minimized the mass of TCE that escaped from the reaction chamber. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

Experiment 2a-3-A. Overall performance of the test reactor
(To be conducted at ORNL/ESD)
In this experiment a complete reactor will be set up using the most optimal component(s) from the previous Task 2a experiments described above. To be consistent, a 100 mg/L TCE spike solution will be used here as well; however, this experiment will be conducted at approximately 12-15°C.

1. Set up a reactor, ensuring that a Teflon sleeve is fitted onto the glass adapter to be used. The top of the adapter will be sealed (Teflon stopper) during spiking and equilibration to minimize the mass of TCE lost.

2. Fill the reactor with distilled water, minimizing the headspace volume inside of the reactor. A record of the DI water volume added will be maintained.

3. Spike the reactor with TCE, Desired Concentration: 100 mg/L
Add a mass of pure phase TCE (density of 1.456 g/mL) to the liquid volume inside of the reactor that will yield a TCE solution of 100 mg/L. Measure the mass of the spiking syringe when filled and then after spiking to record the total TCE mass added to the reactor (a QC check on the initial TCE analysis). Information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

4. Replace the removed stopper back onto the adapter and allow the solution to equilibrate *at least* overnight in an incubator maintained at 12-15°C. (Record the equilibration period and temperature).

5. During the equilibration period, prepare an ORBO-32 assembly in the standard taper adapter and cover the bottom end of the adapter with the selected thin film [parafilm].
STORE UN-SEALED ORBO TUBES OUTSIDE OF THE LABORATORY FUME HOODS. THE HOODS LIKELY HAVE THE GREATEST POTENTIAL FOR "CONTAMINATING" THE TUBES WITH TCE AND OTHER VOCs.

6. After equilibration, collect duplicate ($\approx$0.5 mL) aqueous samples from the reactor (from the glass adapter that is sealed with a stopper) The aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane ($\approx$5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. (A calibration check of the gravimetric scale will be performed each day of use.) All such extracts will be placed on a horizontal shaker for 30 minutes. Store the extracts at 4°C until G.C. analysis.

7. Replace the adapter sealed with the stopper with one fitted with the charcoal desorption tube assembly from Step 5. Record the time the samples in the step above are collected and the desorption tube is added as Start Time=0.

8. Collect at the following time intervals in the same manner as performed in step 6: 30 min, 60 min, 2 hrs, 4 hrs, 24 hrs *(duplicate)*, 30 hrs, 48 hrs. The exact time at which each aliquot is collected will be recorded.

9. Breakdown the reactor after the last sample is collected. The charcoal desorption tube will then be removed from the reactor. Each charcoal bed contained in the tube will be placed into a pre-filled and pre-weighed vial containing a known volume of hexane ($\approx$5 mL). These extracts will be processed and analyzed in the same manner as the aqueous aliquots.

NOTE: The contents of such a test reactor will be extracted at the end of the experiments in Task 4 but is not necessary here since a solid phase is not present.

10. Analyze the sample and charcoal extracts via GC/ECD for TCE. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment.

11. Perform a mass balance for the reactor, taking sample aliquot volumes, initial concentrations, etc. into account to determine the overall reactor performance in maintaining gas-tight conditions. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

Experiment 2a-3-B. Overall performance of the test reactor
(To be conducted at ORNL/ESD)
In this experiment a complete reactor will be set up using the most optimal component(s) from the previous Task 2a experiments. A 100 ppb TCE spike solution will be used here as well; however, this experiment will be conducted at approximately 12-15°C.

1. Set up a 500 mL Flask (29/42 S.T.), ensuring that a Teflon sleeve is fitted onto a Standard Taper Stopper. (Will used during spiking and equilibration to minimize the mass of TCE lost)

2. Fill the reactor with 500 mLled water. A record of the DI water volume added will be maintained.

3. Spike the reactor with TCE, Desired Concentration: 100 ppb
Add approximately 50 microliters of SATURATED TCE solution to the flask. Information regarding the preparation of spiking solution will be recorded in the laboratory research notebook.

4. Replace the stopper back and allow the solution to equilibrate *at least* overnight in an incubator maintained at 12-15°C. (Record the equilibration period and temperature).

5. During the equilibration period, prepare an ORBO-32 assembly and connect it to the stopcock adapter.
STORE UN-SEALED ORBO TUBES OUTSIDE OF THE LABORATORY FUME HOODS. THE HOODS LIKELY HAVE THE GREATEST POTENTIAL FOR "CONTAMINATING" THE TUBES WITH TCE AND OTHER VOCs.

6. After equilibration, replace the stopper with the stopcock assembly.
7. Collect duplicate (≈5 mL) aqueous samples from the reactor by opening the stopcock and inserting the long sampling needle. *(collect one using a glass syringe and one using a plastic disposable syringe)* The aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane (≈5 mL). Each sample container will be

weighed again after sample addition to determine the actual weight of sample added. (A calibration check of the gravimetric scale will be performed each day of use.) All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

8. Record the time the last sample in the step above is collected and record as Time=0.

9. Collect at the following time intervals in the same manner as performed in step 7: 1 hour, 2 hrs, 4 hrs, 18 hours , and 24 hrs *(in duplicate-collect one using a glass syringe and one using a plastic disposable syringe)*. The exact time at which each aliquot is collected will be recorded.

10. Breakdown the reactor after the last sample is collected. The charcoal desorption tube will then be removed from the reactor. Each charcoal bed contained in the tube will be placed into a pre-filled and pre-weighed vial containing a known volume of hexane ($\approx$5 mL). These extracts will be processed and analyzed in the same manner as the aqueous aliquots.

11. Analyze the sample and charcoal extracts via GC/ECD for TCE. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment.

12. Perform a mass balance for the reactor, taking sample aliquot volumes, initial concentrations, etc. into account to determine the overall reactor performance in maintaining gas-tight conditions. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

B2.2 Determine Time Required for Hexane Extraction of TCE from Organic Sludge, Sediment, and Basalt (Task 2b)

A 30 minute extraction time period was used for the Task 2a Reactor Development experiments involving only aqueous TCE solutions; however, this task will help determine what the most effective extraction period is for each medium being evaluated: groundwater or groundwater with crushed basalt, aggregate basalt (following experiment 2c-1), sludge, or sediment at a 4:1 Liquid/Solid ratio. (Note that the hexane extraction period for aggregate basalt cannot be evaluated until after Task 2c, "TCE equilibration with aggregate basalt" is completed.) In this batch experiment, several aliquot samples will be taken with time as a TCE spiked mixture is being extracted with hexane. Samples will be taken of both the solvent and aqueous phases. The aqueous phase will be further evaluated by determining the fraction of TCE present in both the liquid and solid phases at each time interval. All media to be used in this experiment will be oven-dried, and the groundwater will be sparged to remove any initial TCE in order to conduct this test under controlled laboratory conditions. Each media type will be evaluated in duplicate. For these experiments, only a single initial TCE concentration will evaluated: 1 mg/L TCE for the reactive zone media and 100 mg/L TCE for the hot spot media. The contaminant equilibration period will be conducted at 12-15°C; however, the hexane extraction portion of the experiment will be conducted at room temperature.

Experiment 2b-1. Hexane Extraction Test for the Reactive Zone Media

(To be conducted at ORNL/ESD)

1. Prepare a STOCK (Saturated) TCE solution (2000 mg/L) by adding 100 µL of Pure TCE into a 12 mL VOA vial filled to volume with DI Water and allow to equilibrate overnight at room temperature. (Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.)

2. Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag, flask, or equivalent). Fill with approximately 300 mL of groundwater from TAN-40 previously sparged of any residual TCE or other VOCs that may have been present. (Properly indicate usage of this media in the treatability study tracking logbook.). By gravimetric methods, determine the amount of groundwater added to the container, and then place in an environmental chamber at 12-15 °C overnight. (A calibration check of the gravimetric scale will be performed each day of use.)

3. After temperature equilibration of the groundwater, remove the container from the incubator and add the appropriate quantity of the Saturated STOCK TCE solution to produce a TCE spike concentration of 1.0 mg/L. (Reactive zone media will only be spiked at 0.1 and 1 mg/L TCE during the Task 4 degradation studies.) This solution can be mixed and equilibrated within a few minutes.

4. After mixing, obtain duplicate aqueous samples ($\approx$ 5 mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. The duplicate aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane ($\approx$ 5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. These extracts will be placed on a horizontal shaker for 30 minutes. Store the extracts at 4°C until G.C. analysis.

5. Obtain the tare weight of six (6) 40 mL VOA vials. Add approximately 10 g of crushed (< 1/8" size fraction) basalt to two of these vials, and approximately 10 g of sediment to two more of the vials. These materials should be previously dried to remove any residual TCE that might have been present. Re-weigh the vials to determine the exact masses added. (Properly indicate usage of this media in the treatability study tracking logbook.)

6. Completely fill the remaining volume of all of the 40 mL vials with the spiked groundwater, and reweigh each vial to determine the total volume of spike solution added. Record the time each vial is filled and capped. Place the vials on an orbital shaker maintained at 12-15°C and allow the spike solution and media (if applicable) to equilibrate overnight.

7. Obtain a tare weight on six empty containers to be used for the hexane extractions (125 mL VOA bottles with Teflon lined caps). Add 40 mL of hexane to each of these and reweigh.

8. Remove the 40 mL vials from the shaker/incubator. Pour the entire contents of each 40 mL vial into a separate 125 mL extraction bottle. Reweigh each extraction bottle and record the time as "extraction time=0". (The amount of TCE that may have been lost during contaminant

equilibration will not be directly determined, but would be expected to be approximately the same for each 40 mL vial.)

9. Place each extraction jar on a horizontal reciprocating shaker at room temperature. Collect a 1 mL aliquot of the hexane layer from each extraction bottle at the following approximate time periods: 5 minutes, 30 minutes, 2 hours, and 24 hrs. Place these samples directly into a GC Vial (2 mL). (Calibrate the pipette used to collect the aliquot) Record the time the sample was collected. Store at 4°C until analyzed (no dilution will be necessary).

10. Also collect (using a disposable syringe with a luer-lok tip) a 6 mL aliquot of the aqueous layer from the extraction bottle at the same time periods used in Step 9: 5 minutes, 30 minutes, 1 hour, 3 hours, and 24 hrs. Dispense ½ of the aliquot ($\approx$3 mL) directly into 12 mL VOA vial that is pre-weighed and pre-filled with hexane ($\approx$3 mL). Using a 0.45μm syringe filter, filter the remaining aliquot volume in the syringe ($\approx$ 3 mL) into another 12 mL VOA vial that is pre-weighed and pre-filled with hexane ($\approx$3 mL).

11. Re-weigh each of these 12 mL VOA vials in the above step to determine the total sample volume added to each. Place these samples on a reciprocating shaker for at least 30 minutes. Store these extractions at 4°C if not analyzed immediately.

12. Analyze via GC/ECD for TCE, diluting if necessary. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment.

13. Using the analytical results (TCE in the hexane phase, aqueous phase, and solid phases), select the extraction time period that is most effective and efficient for each media type evaluated. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

Experiment 2b-1b Matrix Spike Study (September 1998)
(To be Conducted by ESD)
Make sure all scales and pipettes used are properly calibrated.
All TAN material is to be sparged or dried prior to use in the experiment.

Obtain Tare Weights of twelve (12) 40 mL VOA Vials

Fill Vials 1&2 almost to volume with DI Water
Fill Vials 3&4 almost to volume with TAN-40 GW
Fill Vials 5&6 almost to volume with TSF-05 GW
Fill Vials 7&8 with 10 g Aggregate Basalt
Fill Vials 9&10 with 10 g Crushed Basalt
Fill Vials 11&12 with 10 g Sediment (2nd shipment)

Re-weigh Vials 7-12.

Now add DI water to vials 7-12, almost filling to volume.

Using a SATURATED TCE solution, add 10 uL (.01 mL) into each vial and quickly fill to volume using DI water, cap.
THIS IS THE PIPETTE THAT REALLY NEEDS CALIBRATED PRIOR!!!!
NOTE: DO THE ABOVE STEP ONE AT A TIME!!-Record time of spiking

Re-weigh all vials to obtain final masses of material added.
Allow the vials to equilibrate at 12C overnight.

NEXT MORNING:
Obtain tare weights of twelve 125 mL jars (provided)
Add approx 40 mL of hexane to each jar
Reweigh to obtain the amount of hexane added

Remove the 12-40 mL vials from the incubator.
Transfer contents of each 40 mL vial into each 125 mL jar- Record Time
Re-weigh both the jar and the "emptied" VOA vial.

Extract the jars on a shaker for 2 hrs and then collect a 1 mL sample from each for GC analysis
(no dilutions will be needed)

Run Samples on GC, lab 211 method: ineelecd.mth

Experiment 2b-2. Hexane Extraction Test for Aggregate Basalt.
(To be conducted at ORNL/ESD)
NOTE: This experiment cannot be completed until Exp. 2c-1, Aggregate Basalt Equilibration is completed.

1. Sparge any residual TCE or other VOCs from the TAN-40 groundwater to be used. Also oven-dry the TAN-37 aggregate basalt sample to be used. (Properly indicate usage of this media in the treatability study tracking logbook.)

2. Prepare a STOCK (Saturated) TCE solution (2000 mg/L) by adding 100 μL of Pure TCE into a 12 mL VOA vial filled to volume with DI Water and allow to equilibrate overnight at room temperature. (Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.)

3. Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag, flask, or equivalent). Fill with approximately 200 mL of groundwater from TAN-40 previously sparged of any residual TCE or other VOCs that may have been present. By gravimetric methods, determine the amount of groundwater added to the container, and then place in an

environmental chamber at 12-15 °C overnight. (A calibration check of the gravimetric scale will be performed each day of use.)

4. After temperature equilibration of the groundwater, remove the container from the incubator and add the appropriate quantity of the Saturated STOCK TCE solution to produce a TCE spike concentration of 1.0 mg/L. (*SHOULD BE APPROX. 0.2 mL for 200 mL of gw*) Record the actual weight used. (Reactive zone media will only be spiked at 0.1 and 1 mg/L TCE during the Task 4 degradation studies.) This solution can be mixed and equilibrated within a few minutes.

5. After mixing, obtain duplicate aqueous samples (≈ 5 mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. The duplicate aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane (≈ 5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. These extracts will be placed on a horizontal shaker for 2 hrs. Store the extracts at 4°C until G.C. analysis.

6. Obtain the tare weight of four (4) 40 mL VOA vials. Add approximately 10 g of aggregate basalt to two of these vials. Re-weigh these vials to determine the exact masses added.

7. Completely fill the remaining volume of all of the 40 mL vials with the spiked groundwater, and reweigh each vial to determine the total volume of spike solution added. Record the time each vial is filled and capped. Place the vials on an orbital shaker maintained at 12-15°C and allow the spike solution and media (if applicable) to equilibrate for the length of time determined in Exp. 2c-1.

8. Obtain a tare weight on four empty containers to be used for the hexane extractions (125 mL VOA bottles with Teflon lined caps). Add 40 mL of hexane to each of these and reweigh.

9. Remove the 40 mL vials from the shaker/incubator. Pour the entire contents of each 40 mL vial into a separate 125 mL extraction bottle. Reweigh each extraction bottle to obtain the mass of material actually transferred and record the time as "extraction time=0". (The amount of TCE that may have been lost during contaminant equilibration will not be directly determined, but would be expected to be approximately the same for each 40 mL vial.)

10. Place each extraction jar on a horizontal reciprocating shaker at room temperature. Collect a 1 mL aliquot of the hexane layer from each extraction bottle at the following approximate time periods: 2 hours, 4 hours, 6 hrs, and 24 hrs. Place these samples directly into a 2 mL GC Vial. Record the time the sample was collected. Store at 4°C until analyzed (no dilution will be necessary).

11. Also collect (using a disposable syringe with a luer-lok tip) a 6 mL aliquot of the aqueous layer from the extraction bottle at the same time periods used in Step 10: 2 hours, 4 hours, 6 hrs, and 24 hrs. Dispense ½ of the aliquot (≈3 mL) directly into 12 mL VOA vial that is pre-weighed and pre-filled with hexane (≈3 mL). Using a 0.45μm syringe filter, filter the remaining aliquot

volume in the syringe ($\approx$ 3 mL) into another 12 mL VOA vial that is pre-weighed and pre-filled with hexane ($\approx$3 mL).

12. Re-weigh each of these 12 mL VOA vials in the above step to determine the total sample volume added to each. Place these samples on a reciprocating shaker for at least 30 minutes. Store these extractions at 4°C if not analyzed immediately. No dilutions should be necessary.

13. Analyze via GC/ECD for TCE, diluting if necessary. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment.

14. Using the analytical results (TCE in the hexane phase, aqueous phase, and solid phases), select the extraction time period that is most effective and efficient for each media type evaluated. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

Experiment 2b-3. Hexane Extraction Test for the Hot Spot Media
(To be conducted at RMAL)

In conjunction with the hexane extraction time studies, a baseline characterization of the hot spot media will be performed. This characterization will involve a total organic carbon analysis, a gross alpha and beta determination, and finally a gamma scan of the material.

The total organic carbon analysis will be performed on the TSF-05 sludge (wet and dry) following the guidance in SW846 method 9060 and the manufacturer's operating instructions provided with the instrument. Since a dried aliquot of the sludge will be used in the tests, moisture content of the sludge will also be obtained.

The radiochemical analysis will be performed on an acid digested portion of the dried sludge. The digestion will be performed following CASD-AM-SW846-3051 *Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils*. The digestates will then be analyzed for gross alpha and beta and a gamma scan will be performed using the appropriate procedures in Table B2.1.

Table B2.1. Analytical Methods for Hot Spot Media Sludges

Methods	Analysis
Gross Alpha and Gross Beta Radioactivity in Drinking Water (CASD-AM-EPA-900.0)	Gross alpha and beta radioactivity sample preparation
Gamma-emitting Radionuclides in Drinking Water (CASD-AM-EPA-901.1)	Gamma emitting radionuclides sample preparation
Operation of Packard MO 2500TR Liquid Scintillation Counter (CASD-AM-RML-RA12)	1. Total activity by liquid scintillation 2. Sum of alpha- and beta-emitting radionuclides analysis
Operation and Calibration of the Tennelec LB4000 (CASD-AM-RML-RA02)	Gross alpha and gross beta analysis
Operation and Calibration of the Canberra, Nuclear Data Genie - ESP Data Acquisition and Processing (CASD-AM-RML-RA04)	Alpha and gamma spectroscopy data acquisition and processing system

The hexane extraction time experiment will be performed according to the following steps:

1. Sparge any residual TCE or other VOCs from the TSF-05 groundwater to be used. Also oven-dry the sludge sample to be used. (Properly indicate usage of this media in the treatability study tracking logbook.)

2. Prepare approximately 200 mL of TCE spiking solution in a Tedlar™ bag, which allows for effective mixing under zero headspace conditions. Record the tare weight of the Tedlar bag. Fill the bag using groundwater from TSF-05. By gravimetric methods, determine the amount of groundwater actually added to the Tedlar bag. Next, add the appropriate quantity of pure phase TCE to produce a TCE spike concentration of 100 mg/L. *SHOULD BE APPROXIMATELY 14 μL NOTE: TCE spg= 1.456 mg/uL Please record the actual mass added by determining the weight of the spiking syringe when it is "full" and after the TCE has been delivered.* (The hot spot media will actually be evaluated using initial concentrations of 10, 100, and > 1,000 mg/L TCE in the Task 4 degradation studies.) This solution will be equilibrated overnight in an incubator or refrigeration unit at 12-15°C.

3. After equilibration, obtain duplicate aqueous samples (≈5 mL) from the Tedlar bag to obtain the initial TCE concentration of the spiked groundwater. The duplicate aliquot samples will be added to pre-weighed 12 mL VOA vials holding a known volume of hexane (≈5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. (A calibration check of the gravimetric scale will be performed each day of use.) These extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

4. Obtain the tare weight of four (4) 40 mL VOA vials. Add approximately 10 g of TSF-05 sludge to two of these vials, (This material should be previously dried to remove any residual

TCE or moisture that might have been present.) Re-weigh these two vials to determine the exact masses added.

5. Completely fill the remaining volume of all four of the 40 mL vials with the spiked groundwater from the Tedlar bag. Record the time each vial is filled and capped. Reweigh each vial to determine the total volume of spike solution added. Place the vials on an orbital shaker maintained at 12-15°C and allow the spike solution and sludge (if applicable) to equilibrate overnight.

6. Obtain a tare weight on four extraction bottles to be used for the hexane extractions (125 mL VOA bottles with Teflon lined caps). Add approximately 40 mL of hexane to each of these and reweigh to determine the actual hexane volume added (specific gravity= 0.66).

7. Remove the 40 mL vials from the shaker/incubator. Pour the entire contents of each 40 mL vial into a separate 125 mL extraction bottle. Reweigh each 125 mL extraction bottle to obtain the actual quantity transferred and record the time as "extraction time=0". (Any TCE that may have been lost during contaminant equilibration will not be directly determined, but would be expected to be approximately the same for each 40 mL vial.)

8. Place each extraction jar on a horizontal reciprocating shaker at room temperature. Collect a 0.1 mL (100 μL) aliquot of the hexane layer from each extraction bottle at the following approximate time periods: 30 minutes, 2 hours, 4 hours, and 24 hrs. Place these samples into 12 mL VOA vials already tared and containing a known volume of hexane (≈10 mL). Record the time each sample is collected. Store at 4°C until analyzed.

9. Collect (using a disposable syringe with a luer-lok tip) a 6 mL aliquot of the aqueous layer from each extraction bottle at roughly the same time periods used in Step 8: 30 minutes, 2 hours, 4 hours, and 24 hrs. Dispense ½ of the aliquot (≈3 mL) directly into a 12 mL VOA vial that is pre-weighed and pre-filled with hexane (≈ 3 mL). Add a 0.45μm syringe filter onto the disposable syringe, filter the remaining aliquot volume (≈ 3 mL) into another 12 mL VOA vial that is pre-weighed and pre-filled with hexane (≈3 mL).

10. Re-weigh each of these 12 mL VOA vials in the above step to determine the total sample volume added to each. Place these samples on a reciprocating shaker for at least 30 minutes. Store these extractions at 4°C if not analyzed immediately. Dilutions will have to be performed before being submitted to ESD. *For the hexane layer, no additional dilution should be expected, simply transfer 1 mL of the sample into a 2 mL G.C. vial. The dilutions for the aqueous samples are not as predictable. Please provide a sample not diluted (ie, the top layer of hexane in the vials from step 9). If required, a sample with a DF of 11. (0.1 mL of the hexane layer into 1 mL of clean hexane in a 2 mL G.G. Vial may be needed.)*

11. *NOTE: This step to be conducted at ESD.* Analyze via GC/ECD for TCE. G.C. analyses will be conducted closely following EPA Method 8000B, ensuring that a daily calibration check, blanks, etc. are also analyzed on each analysis day. Formal data packages, as outlined in Section 2.4.3.3 of the Chapter 2 Implementation Plan will not be prepared for this experiment. Using the

analytical results, select the extraction time period that is most effective and efficient for each media type evaluated.

12. Place any waste materials generated from the experiment in the appropriate satellite accumulation area.

Experiment 2b-4. (Exp 2b-3b) Matrix Spike Experiment (September 1998)
(To be conducted at RMAL)

1. Sparge any residual TCE or other VOCs from the TSF-05 groundwater to be used. Also oven-dry the sludge sample to be used. (Properly indicate usage of this media in the treatability study tracking logbook.)

2. Obtain the tare weight of four (4) 40 mL VOA vials.
3. Add approximately 10 g of TSF-05 sludge to THREE of these vials.
4. Re-weigh these THREE vials to determine the exact masses added.

5. Fill each of the 4 VOA vials (ALMOST TO VOLUME) with TSF-05 groundwater

6. Add 0.04 mL of a *SATURATED TCE* solution to each vial. Quickly fill the remaining volume with DI water of gw (whichever is easiest) and cap. Record the time each vial is filled.
THIS TCE VOLUME NEEDS TO BE VERY ACCURATE. MAKE SURE PIPETTE IS CALIBRATED.

7. Reweigh each vial to determine the total quantities of material added. Place the vials on an orbital shaker maintained at 12-15°C and allow to equilibrate overnight.

NEXT DAY:
8. Obtain tare weight on four extraction bottles to be used for the hexane extractions (125 mL VOA bottles with Teflon lined caps). Add approximately 40 mL of hexane to each of these and reweigh to determine the actual hexane volume added.

9. Remove the 40 mL vials from the shaker/incubator. Pour the entire contents of each 40 mL vial into a separate 125 mL extraction bottle. Reweigh each 125 mL extraction bottle to obtain the actual quantity transferred and record the time as "extraction time=0". Also re-weigh the "empty" VOA vials to determine mass that was NOT transferred.

10. Place each extraction jar on a horizontal reciprocating shaker at room temperature. Collect a 1 mL aliquot of the hexane layer from each extraction bottle at the following approximate time periods: 2 hours, 4 hours, 6hrs, 20 hrs, 24 hrs, and ≈48 hrs. PLACE DIRECTLY INTO GC VIALS FOR ESD ANALYSIS-NO dilutions should be needed.

B2.3 Determine Time Required to Equilibrate Basalt Aggregate with TCE (Task 2c)

Background and Experimental Approach

Aggregate basalt (¼" -1" size fraction) will also be investigated as a reactive zone medium from the TAN site. The needed length of time to spike or contaminant the aggregate basalt is currently unknown. The ultimate goal of this task is to determine the time required for the TCE concentration of the basalt's pore water to be in equilibrium with the TCE concentration in the bulk solution (TAN Site groundwater) via a sorption kinetics experiment.. The equilibration experiment will be conducted with an initial TCE concentration of 1 mg/L and at 12-15°C. A study by Pavlostathis and Jaglal (1991) involving TCE sorption onto a silty sand indicated quasi-equilibrium within a period of three (3) days. However, other studies with PCE and course grain bulk material show equilibration to be on the order of 20 days, whereas equilibration using pulverized material was approximately 1 day (Ball, 1991). Thus, a couple of the batch sorption test samples will be examined after a long time period (i.e., 14 days) to determine if such is the case of aggregate basalt.

Experimental controls (groundwater with no solid phase) will also be carried through the experiment to help account for losses via volatilization, biodegradation, or sorption of TCE onto the test equipment, etc. There will be no attempt to assess other factors commonly evaluated during laboratory sorption kinetics work such as ionic strength, pH, etc.

The preferred hexane extraction time (Exp. 2b-2) for the aggregate basalt will also be evaluated once the desired equilibration time is determined. As in Section 2.2, the hexane extraction will be performed at room temperature.

Experiment 2c-1. Sorption Kinetics Test for Crushed and Aggregate Basalt.
(To be conducted at ORNL/ESD)
1. All soil and groundwater to be used in these experiments (TAN-40 groundwater, TAN-37 crushed and aggregate basalt) will be prepped by sparging and/or drying to remove any residual TCE present on the media. (Properly indicate usage of this media in the treatability study tracking logbook.) Doing so will allow this experiment to be conducted with consistent and controlled initial TCE concentrations via contaminant spiking.

2. Prepare a STOCK (Saturated) TCE solution (2000 mg/L) by adding 100 µL of Pure TCE into a 12 mL VOA vial filled to volume with DI Water and allow to equilibrate overnight at room temperature. (Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.)

3. Sparge approximately 3100 mL of groundwater from TAN-40 of any residual TCE or other VOCs that may have been present and then place the groundwater into an incubator at 12-15°C. After temperature equilibration of the groundwater (*likely overnight*), remove the container from the incubator.

4. Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag). Fill with the Tedlar bag with the chilled TAN-40 GW. By gravimetric methods, determine the amount of groundwater added to the container. (A calibration check of the gravimetric scale will be performed each day of use.) All information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

5. Add the appropriate quantity of the Saturated STOCK TCE solution into the Tedlar bag to produce a TCE spike concentration of 1.0 mg/L. *SHOULD BE APPROXIMATELY 3 ML* Record volume and/or weight added. (Reactive zone media will only be spiked at 0.1 and 1 mg/L TCE during the Task 4 degradation studies.) This solution can be mixed and equilibrated within a few minutes.

6. After mixing, obtain duplicate aqueous samples ($\approx$ 5 mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. The duplicate aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane ($\approx$ 5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. These extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

7. Obtain the tare weights of seventy two (72) 40 mL VOA vials. Add approximately 10 g of aggregate basalt to 24 of the vials and 10 g of the crushed basalt to another 24 of the these vials. Gravimetrically determine the actual amount of solid media added.

8. Dispense the spiked groundwater from the Tedlar bag into each of the 72 VOA vials that have been prepared, filling them completely with no headspace and cap them. Record the time that each vial is filled as "T=0" for that vial.

9. Re-weigh each vial after it is completely filled to determine the actual weight of spiked groundwater added to it. Place the vials back into the environmental chamber at 12-15°C Slowly agitate the vials during this step.

The remaining steps will be performed at the time intervals of approximately 2 h, 4 h, 6 h, 18 h, 24h, 4d, 5d, 6d, 7d, 12 d, 14d, and 21d. The latter times may be changed depending upon results of the samples obtained for the earlier time periods.

10. Remove six (6) 40 mL vials from the incubator (two with groundwater only, two with crushed basalt, and two containing aggregate basalt.) Collect an aqueous sample ($\approx$ 5mL) from each vial using a disposable syringe with luer lok needle. Record the time the sample is collected.

11. Filter (0.45µm membrane) and dispense the sample into to a pre-weighed vial holding a known volume of hexane ($\approx$5 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. *A new syringe and filter will be used for each*

sample. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

12. Randomly collect and process (steps 10 and 11) a duplicate VOC sample from one of the six VOA vials during every other sampling period.

13. **FOR THE LAST SAMPLING PERIOD STUDIED ONLY:** Extract he remaining contents of each vial with hexane. (The mass of any remaining TCE on the solid phase can be determined with this extraction when a mass balance is performed using data from the aqueous aliquot sample) To accomplish this, transfer the remaining sample in the six 40 mL VOA vials (including basalt material) into a 125 mL extraction jar that has been pre-weighed and holding a known volume of hexane ($\approx$ 35 mL). The extraction jar will be weighed again after sample addition to determine the actual mass of sample (solid +Liquid) added.

14. **FOR THE LAST SAMPLING PERIOD STUDIED ONLY:** The extracts in the above step will be placed on a horizontal or reciprocating shaker for 2 hours. A 1 mL aliquot of the hexane phase will be placed into a 2 mL G.C. vial and stored at 4°C until analysis.

GC ANALYSIS of VOCs
All VOC analyses for this experiment will be conducted using a G.C./ECD detector. The instrument will calibrated for TCE using a 5 point calibration curve with standard concentrations ranging from 10-1000 µg/L (ppb)

The VOC analyses of the hexane extracts will closely follow EPA Method 8000B. Significant deviations from this method will be clearly documented.

REPEAT EXPERIMENT:

Experiment 2c-1B. Sorption Kinetics Test for Crushed and Aggregate Basalt.
(To be conducted at ORNL/ESD)
1. All soil and groundwater to be used in these experiments (TAN-40 groundwater, TAN-37 crushed and aggregate basalt) will be prepped by sparging and/or drying to remove any residual TCE present on the media. (Properly indicate usage of this media in the treatability study tracking logbook.) Doing so will allow this experiment to be conducted with consistent and controlled initial TCE concentrations via contaminant spiking.

2. Prepare a STOCK (Saturated) TCE solution (2000 mg/L) by adding 100 µL of Pure TCE into a 12 mL VOA vial filled to volume with DI Water and allow to equilibrate overnight at room temperature. (Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.)

3. Sparge approximately 1600 mL of groundwater from TAN-40 of any residual TCE or other VOCs that may have been present.

4. Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag). Fill with the Tedlar bag with the sparged TAN-40 GW. By gravimetric methods, determine the amount of groundwater added to the container. (A calibration check of the gravimetric scale will be performed each day of use.) All information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

5. (TUESDAY AFTERNOON) Add the appropriate quantity of the Saturated STOCK TCE solution into the Tedlar bag to produce a TCE spike concentration of 1.0 mg/L. *SHOULD BE APPROXIMATELY 1.6 ML* Record volume and/or weight added. (Reactive zone media will only be spiked at 0.1 and 1 mg/L TCE during the Task 4 degradation studies.) This solution can be mixed and equilibrated at least overnite at 12°C in the incubator.

6. After mixing, obtain duplicate aqueous samples using a glass syringe with a valve stopcock and luer needle (5mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. Weigh the syringe when filled and then again after the sample is dispensed to the P&T. The duplicate aliquot samples will be analyzed immediately using the Lab 211 P&T (30 minutes each).

7. Obtain the tare weights of thirty six (36) 40 mL VOA vials. Add approximately 10 g of aggregate basalt to 12 of the vials and 10 g of the crushed basalt to another 12 of these vials. Gravimetrically determine the actual amount of solid media added.

8. Dispense the spiked groundwater from the Tedlar bag into each of the 36 VOA vials that have been prepared, filling them completely with no headspace and cap them. Record the time that each vial is filled as "T=0" for that vial.

9. Re-weigh each vial after it is completely filled to determine the actual weight of spiked groundwater added to it. Place the vials back into the environmental chamber at 12°C Agitate the vials during this step (200 rpm or greater)

The remaining steps will be performed at the time intervals of approximately 4 hrs, 24h, 2d, 5d, 7d, and TBD. The latter times may be changed depending upon results of the samples obtained for the earlier time periods.

10. Remove six (6) 40 mL vials from the incubator (two with groundwater only, two with crushed basalt, and two containing aggregate basalt.) Collect an aqueous sample ($\approx$ 5mL) [allow the crushed basalt to settle a little before sampling) from each vial using a glass with valve stopcock and luer needle.

11. Weigh the full syringe and Record the time the sample is collected. Reweigh the syringe after the sample is dispensed into the P&T.

12. Randomly collect and process (steps 10 and 11) a duplicate VOC sample from one of the six VOA vials during each sampling period.

13. **FOR THE LAST SAMPLING PERIOD STUDIED ONLY:** Extract the remaining contents of each vial with hexane. (The mass of any remaining TCE on the solid phase can be determined with this extraction when a mass balance is performed using data from the aqueous aliquot sample) To accomplish this, transfer the remaining sample in the six 40 mL VOA vials (including basalt material) into a 125 mL extraction jar that has been pre-weighed and holding a known volume of hexane ($\approx$ 35 mL). The extraction jar will be weighed again after sample addition to determine the actual mass of sample (solid +Liquid) added.

14. **FOR THE LAST SAMPLING PERIOD STUDIED ONLY:** The extracts in the above step will be placed on a horizontal or reciprocating shaker for 2 hours. A 1 mL aliquot of the hexane phase will be placed into a 2 mL G.C. vial and stored at 4°C until analysis.

B3 Measure Oxidant Demand of TAN Subsurface Materials

The oxidant demand experiments planned for Task 3 of the project will assess, for selected oxidant loadings, the effect of the TAN site media (soil and groundwater) upon the amount of oxidant remaining or available for TCE degradation. All Task 3 experiments will be conducted in duplicate at 12°C using non-contaminated media; hence, there are no contaminant equilibration or TCE analysis steps in the following Task 3 experiments.

B3.1 Measure the Oxidant Demand of Reactive Zone Media (Task 3a)

General Procedure for Task 3a Experiments - Oxidant Demand of Reactive Zone Media
(To be conducted at ORNL/ESD)
1. All soil and groundwater to be used in these experiments (TAN-40 groundwater, TAN-37 crushed and aggregate basalt, and sediment) will be prepped by sparging and/or drying to remove any residual TCE present on the media. Doing so will allow this experiment to be conducted with a consistent and controlled initial TCE concentration ($\approx$ 0 mg/L). Properly indicate usage of this media in the treatability study tracking logbook.

2. Follow Table 2-3 in Chapter 2 of the Implementation Plan to obtain which test conditions to evaluate (soil type, oxidant concentration, etc.) The use of glass, wide-mouth erlenmeyer flasks, beakers, or equivalent will be used. It is currently planned to run four (4) test conditions from Table 2-3 each time this procedure is used. Thus, 8 reactors will be used during each run of this procedure.

3. Obtain the tare weight of each reactor. Add approximately 100g of solid media to the reactors in Table 2-3 that require it Re-weigh the reactors to determine the actual mass added. To each reactor, add 400 mL of TAN-40). Re-weigh each reactor to determine the actual weight of solution added. (A calibration check of the gravimetric scale will be performed each day of use.)

4. Place the reactors in the incubator at 12°C and allow to equilibrate to that temperature. Slowly agitate the reactors during this step.

5. Once temperature equilibrium is reached, remove the reactors from the incubator and collect a 5 mL aliquot (using a disposable syringe) of the water and/or slurry from each for pH analysis.

6. The pH analyses will be conducted using conventional pH meters/electrodes, calibrated each day of use via a minimum of two standard buffer solutions (4, 7, and 10). Values obtained for each sample will be recorded. A calibration check will also be conducted following the last sample to be measured each day. Values obtained for the samples will be corrected if a significant drift (i.e., > 15%) occurred.

7. Add the appropriate mass of crystalline $KMnO_4$ (Carus™ Free Flowing Technical Grade) into each reactor according to which test condition in Table 2-3 is being evaluated. The exact mass of $KMnO_4$ added to each reactor will be determined gravimetrically and recorded. The time that $KMnO_4$ is added to each individual reactor shall also be recorded (reaction start time).

8. Place each reactor back into the 12°C incubator as the oxidant consumption reaction proceeds. For each reactor, remove the reactor from the incubator at approximately 5-10 minutes from the reaction start time, and collect a 5-10 mL aliquot (using a disposable plastic syringe with a Luer Tip). Record the time the sample was collected and replace the reactor back into the incubator.

9. Add a 0.45 μm syringe filter onto the end of the syringe and filter approximately 1-2 mL into a beaker. Remove the syringe filter and dispense the remaining (unfiltered) portion of the sample into another beaker for pH analysis. Measure and record the pH of each sample as done in Step 6.

10. Perform a MnO_4^- analysis on the filtered sample from the previous step. (The sample is filtered to remove particulate matter that could interfere with the analysis.) The filtered sample will likely have to be diluted with DI water so that its spectrophotometric absorbance (at $\lambda = 525$ nm) is less than that of the highest standard to be prepared (50 mg/L MnO4-). Check standards (10 and 50 mg/L MnO4-) will be prepared with reagent grade $KMnO_4$ and measured each analysis day. A new 5 point calibration curve will be prepared if the absorbance of these check standards differs from the expected value by >15%.

11. Collect and analyze aliquots from each reactor for pH and $KMnO_4$ (Steps 8-10) at the following ADDITIONAL time periods: 1hr, 2 hrs, 4 hrs, 18 hrs, and 24 hrs.

12. Interpret results and clean up the reactors for re-use in the next run of the experiment. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

3.2 Measure the Oxidant Demand of Hot Spot Media (Task 3b)

General Procedure for Task 3b Experiments - Oxidant Demand of Hot Spot Zone Media
(To be conducted at RMAL)
1. All soil and groundwater to be used in these experiments (TSF-05 groundwater, TSF-05 sludge) will be prepped by sparging and/or drying to remove any residual TCE present on the

media. Doing so will allow this experiment to be conducted with a consistent and controlled initial TCE concentration (≈ 0 mg/L). Properly indicate usage of this media in the treatability study tracking logbook.

2. Follow Table 2-4 in Chapter 2 of the Implementation Plan to obtain which test conditions to evaluate (soil type, oxidant concentration, etc.) The use of glass, wide-mouth erlenmeyer flasks or equivalent will be used. It is currently planned to run two (2) test conditions from Table 2-4 each time this procedure is used. Thus, 4 reactors will be used during each run of this procedure.

3. Obtain the tare weight of each reactor. Add approximately 100g of solid media to the reactors in Table 2-4 that require it Re-weigh the reactors to determine the actual mass added. To each reactor, add 400 mL of TSF-05 groundwater. Re-weigh each reactor to determine the actual weight of solution added. (A calibration check of the gravimetric scale will be performed each day of use.)

4. Place the reactors in the incubator at 12°C and allow to equilibrate to that temperature. Slowly agitate the reactors during this step.

5. Once temperature equilibrium is reached, remove the reactors from the incubator and collect a 5 mL aliquot (using a disposable plastic syringe) of the water and/or slurry from each for pH analysis.

6. The pH analyses will be conducted using conventional pH meters/electrodes, calibrated each day of use via standard buffer solutions of pH 7, and 10. Values obtained for each sample will be recorded. A calibration check will also be conducted following the last sample to be measured each day. Values obtained for the samples will be corrected if a significant drift (i.e., > 15%) occurred.

7. Add the appropriate mass of crystalline $KMnO_4$ (Carus™ Free Flowing Technical Grade) into each reactor according to which test condition in Table 2-4 is being evaluated. The exact mass of $KMnO_4$ added to each reactor will be determined gravimetrically and recorded. The time that $KMnO_4$ is added to each individual reactor shall also be recorded (reaction start time).

8. Place each reactor back into the 12°C incubator as the oxidant consumption reaction proceeds. For each reactor, remove the reactor from the incubator at approximately 5-10 minutes from the reaction start time, and collect a 5-10 mL aliquot (using a disposable plastic syringe with a Luer Tip). Record the time the sample was collected and replace the reactor back into the incubator.

9. Add a 0.45 µm syringe filter onto the end of the syringe and filter approximately 1-2 mL into a beaker. Remove the syringe filter and dispense the remaining (unfiltered) portion of the sample into another beaker for pH analysis. Measure and record the pH of the sample as done in Step 6.

10. Perform a MnO_4^- analysis on the filtered sample from the previous step. (The sample is filtered to remove particulate matter that could interfere with the analysis.) The filtered sample will likely have to be diluted with DI water so that its spectrophotometric absorbance (at $\lambda = 525$

nm) is less than that of the highest standard to be prepared (50 mg/L MnO4-). Check standards (10 and 50 mg/L MnO4-) will be prepared with reagent grade $KMnO_4$ and measured each analysis day. A new 5 point calibration curve will be prepared if the absorbance of these check standards differs from the expected value by >15%.

11. Collect and analyze aliquots from each reactor for pH and $KMnO_4$ (Steps 8-10) at the following ADDITIONAL time periods: 30 minutes, 1 hour, 2 hrs, 4 hrs, and 24 hrs.

12. Upon completion of the test period, the post-treatment sludges will be analyzed for total organic carbon content following the guidance in SW846 method 9060 and the manufacturer's operating instructions provided with the instrument. The carbon results will be corrected back to the original dried starting weight of the sludge used in the test.

13. Interpret the results and clean up the reactors for re-use in the next run of the experiment. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

B4 Measure Oxidation Rates

The TCE degradation experiments will be conducted in Task 4 to determine the oxidation rate of TCE as a function of oxidant concentration and initial contaminant concentrations. All Task 4 experiments will be conducted in duplicate. The procedures presented below will be used to guide the experiments presented in Tables 2-5 through 2-7 in the Implementation Plan. Both the contaminant equilibration and oxidant reaction phases of these experiments will be conducted at 12°C.

B4.1 Measure the Oxidation Rate of Organic Contaminants in Reactive Zone Media (Task 4a)

General Procedure for Task 4a Experiments - Measure the oxidation rate of organic contaminants in the Reactive Zone Media

(To be conducted at ORNL/ESD)

NOTE: This experiment will be used to conduct the various test conditions presented in **Table 2-5** in Chapter 2 of the Implementation Plan. Control samples will be prepared and sampled throughout the reaction period to quantify changes in concentration due to mechanisms other than oxidation. In addition to the duplicate control samples, it is currently planned to run two (2) test conditions (in duplicate) from **Table 2-5** each time this procedure is used. Thus, 6 reactors will be used during each run of this procedure, and this procedure will be conducted 8 times. The controls and the treatment reactors will all contain the same media type and initial contaminant concentrations (i.e., all conditions will be the same for each run of this procedure with the exception of the MnO4- concentration used).

1. Soil Prepping
All soil and groundwater to be used in these experiments (**TAN-40 groundwater, TAN-37 crushed and aggregate basalt, and sediment**) will be prepped by sparging and/or drying to remove any residual TCE present on the media. Doing so will allow this experiment to be

conducted with consistent and controlled initial TCE concentrations via contaminant spiking. (Properly indicate usage of this media in the treatability study tracking logbook.) **TAN-40 GW** will also be temperature equilibrated to 12°C in this experiment.

2. TCE Stock Solution Preparation

Prepare a STOCK (Saturated) TCE solution ($\approx$1100 mg/L) by adding greater than 100 μL of Pure TCE into a 12 mL VOA vial filled to volume with DI Water and keep refrigerated. (Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.) This can easily be stored and used again in subsequent experiments.

3. TCE Spike Solution Preparation, PART 1

Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag, flask, or equivalent). Fill with approximately 3100 mL of 12°C **TAN-40 groundwater**. By gravimetric methods, determine the amount of groundwater added to the container. (A calibration check of the gravimetric scale will be performed each day of use.)

4. TCE Spike Solution Preparation, PART II

Add the appropriate quantity of the Saturated STOCK TCE solution to produce a TCE spike solution with the concentration prescribed in Table 2-5 for the particular test series being ran. The **reactive zone media** will only be spiked at **0.1 and 1 mg/L TCE** during this experiment, thus the volume of saturated STOCK TCE needed should be on the order of **0.3 mL and 3.0 mL**, respectively. This solution can be mixed and equilibrated within a few minutes. All Information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook. Place the spike solution in the incubator overnight at 12C for temperature equilibration.

5. Obtain Tare Weights of Reactors

Prepare the test reactors to be used. (The gas-tight reaction vessels acquired and tested in Task 2a will be used as the reactors in this experiment.) Obtain the tare weight of each, including the weight of a ground glass standard taper stopper fitted with a Teflon sleeve.

6. Fill with Solid Phase Media

Add approximately 100-110 g of the solid phase material desired for this particular test series (See **Table 2-5** in the Implementation Plan). Re-weigh each reactor to determine the actual amount of solid media added (when applicable).

7. Collection of Initial Spike Solution Samples

Remove the spike solution from the incubator, and obtain duplicate aqueous samples ($\approx$ 5 mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. Record the time the sample is collected. The duplicate aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane ($\approx$ 5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. These extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

8. Distribution of Spike Solution to Reactors

Quickly dispense the spike solution into each of the reactors to be used. Add ≈500 mL to each reactor. Immediately replace the ground glass stopper and re-weigh each to determine the actual weight of spiked groundwater.

9. Soil/Spike Equilibration

Place the reactors in the incubator at 12°C and allow the spike solution to equilibrate for 24 hours. (For aggregate basalt, equilibrate for the length of time determined in Exp. 2c-1., unless shorter than 24 hours) Agitate the reactors at ≈200 rpm during this step.

10. Preparation of Stock MnO_4^- Solution (**4 wt%**)

Add **2.66 g** of crystalline KMnO4 (Carus™ Free Flowing Technical Grade) into a **50 mL** Flask and fill to volume with DI water, and allow to mix for at least 2 hours.

11. Prepare Reactor Closure/Carbon Tube

During equilibration period, prepare the standard taper adapters/stopcock valve. (**Only one ORBO tube will be used for each reactor.**) The vertical sampling port will be fitted with a small septum) STORE UN-SEALED ORBO TUBES OUTSIDE OF THE LABORATORY FUME HOODS. THE HOODS LIKELY HAVE THE GREATEST POTENTIAL FOR "CONTAMINATING" THE TUBES WITH TCE AND OTHER VOCs.

12. Collection of Pre-Reaction Sample from Each Reactor

After equilibration, collect a ≈10 mL aqueous sample using a long need and disposable syringe from each of the reactors and quickly reseal. Record the time the sample is collected and note whether solids were present in the aqueous sample (particularly the groundwater/sediment reactors). If significant solids are present, a portion of this aliquot volume may be used for a total solids analysis.

13. Preparation of Pre Reaction TCE Sample

Dispense (unfiltered) ≈3 mL of this aliquot sample into to a pre-weighed vial holding a known volume of hexane (≈3 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis. Record the time this sample is taken.

14. Measurement of Pre Reaction pH Value

Tare a small beaker for pH analysis. Add a 0.45 micron filter to the sample syringe and dispense (filtered) the remaining portion of the sample in the syringe (≈7 mL) into the tared beaker. Reweigh the beaker to determine the volume of the sample (assuming that the solids fraction is negligible). The pH analyses will be conducted using conventional pH meters/electrodes, calibrated each day of use via a minimum of two standard buffer solutions. Values obtained for each sample will be recorded. A calibration check will also be conducted following the last sample to be measured each day. Values obtained for the samples will be corrected if a significant drift (i.e., > 15%) occurred.

15. Addition of Stock MnO4- Solution into Reactors

Quickly remove the ground glass stopper and add the needed volume of stock $KMnO_4$ to obtain the MnO_4^- concentrations in **Table 2-5** (approximately **1.25 mL and 12.5 mL for the 0.01 and .01% MnO4** concentrations respectively). Replace the glass ground stoppers with the adapters fitted with the stopcock and charcoal desorption tubes and quickly hand shake each reactor to ensure rapid dissolution of the oxidant. (No oxidant will be added to the control reactors). The time that the stock $KMnO_4$ is added to each individual reactor shall also be recorded (reaction start time). Place each reactor back into the 12°C incubator.

16. 30 Minute Sampling

At approximately 30 minutes from the reaction start time, remove the reactors from the incubator and collect a 10 mL aliquot (using a long needle and syringe with a Luer Tip). Record the time the sample is collected. Replace the reactor(s) back into the incubator.

17. Preparation of 30 Minute TCE Sample

Dispense (unfiltered) ≈3 mL of the collected aliquot into a pre-weighed vial holding a known volume of hexane (≈3 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

18. pH Analysis of 30 Minute Sample

Tare a small beaker. Add a 0.45 μm syringe filter unto the end of the syringe and dispense (filtered) the remaining portion of the sample in the syringe (≈7 mL) into a tared beaker for pH analysis. Reweigh the beaker to determine the volume of the sample (assuming that the solids fraction is negligible). Measure and record the pH of the sample as done in Step 13

19. MnO_4^- Analysis of the 30 Minute Sample

Use a portion of the filtered pH sample to perform a MnO_4^- analysis. The sample may have to be diluted (**likely DF3 and DF30 for the .01 and 0.1% MnO4- loadings, respectively**) so that its spectrophotometric absorbance (at λ =525 nm) is less than that of the highest standard to be prepared (50 mg/L MnO4-). Check standards (10 and 50 mg/L MnO4-) will be prepared with reagent grade $KMnO_4$ and measured each analysis day. A new 5 point calibration curve will be prepared if the absorbance of these check standards differs from the expected value by >15%.

20. Collection and Analysis of Additional Aliquot Samples

Collect and analyze aliquots from each reactor for TCE, pH, and $KMnO_4$ (Steps 16-19) at the following ADDITIONAL time periods: 2 hrs, 4 hrs, 6 hrs, 20 hrs, and 24 hrs.
IMPORTANT—For each reactor collect and extract a duplicate sample (Steps 16-19) from one of the 6 time intervals being evaluated.

21. Extraction of Residual TCE in Reactor

The entire contents of each reactor will be extracted with hexane. First, obtain a tare weight on six (6) empty containers to be used for the hexane extraction (1 liter VOA bottles). Measure out 400 mL of hexane into two (2) 200 mL volumetric flasks. Add 200 mL of the hexane directly into the 1 L extraction bottle. Quickly pour the contents of each test reactor into a separate extraction bottle. Use the remaining 200 mL flask of hexane to rinse any residual slurry from the test reactor into the extraction bottle. Weigh and record the mass of the filled extraction bottle to

determine the mass of the slurry and hexane added (taking into account the fact that hexane has a specific gravity of 0.66).

(The mass of any remaining TCE on the solid phase can be determined with this extraction when a mass balance is performed using data from the aqueous aliquot sampling that was conducted throughout the test.)

22. Reactor Extraction Continued

Place each extraction bottle on a horizontal reciprocating shaker for a minimum of 2 hours (May be longer for aggregate basalt samples, depending upon the results of Exp. 2b-2.) then collect duplicate **1 mL hexane aliquots from each extraction bottle and place into 2 mL G.C. vials (dilution is not expected to be necessary).**

23. Extraction of Charcoal Desorption Tubes

Remove the charcoal desorption tube(s) from each reactor. Each charcoal bed contained in the tube(s) will be placed into pre-filled and pre-weighed vials containing a known volume of hexane (≈ 5 mL). These extracts will be processed and analyzed in the same manner as the aqueous aliquots for TCE.

24. Clean up

Clean up the reactors for re-use in the next run of the experiment. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

25. GC ANALYSIS of VOCs

All VOC analyses for this experiment will be conducted using a **G.C./ECD** detector. The instrument will calibrated for TCE using a 5 point calibration curve with standard concentrations ranging from 5-1000 µg/L (ppb)

The VOC analyses of the hexane extracts will closely follow EPA Method 8000B. Significant deviations from this method will be clearly documented.

Formal data packages will be prepared for the analyses performed for all Task 3 and 4 samples will be prepared as discussed in Sections 2.4.3 and 2.4.4 in Chapter 2 of the Implementation Plan. The major QA/QC items pertaining to the VOC analyses include:

Calibration standards will be prepared from a certified, custom VOC mix stock solution containing each analyte of interest. The lot number of this custom mix will be included on each initial calibration data form.

The working calibration curve will be verified through injection of a QC check standard (100 µg/L) at least once each analysis day. If the response for any analyte varies from the predicted response by more than ± 15%, a new calibration curve will be prepared.

A blank hexane sample will be analyzed between every 10 test samples.

A sample will be diluted and reanalyzed if its GC peak area response is greater than that of the highest calibration standard being used that analysis day.

B4.2 Measure the Oxidation Rate of Organic Contaminants in Hot Spot Media (Task 4b)

General Procedure for Task 4b Experiments - Measure the oxidation rate of organic contaminants in the hot spot groundwater

(To be conducted by both ORNL/ESD and RMAL)
NOTE: This experiment will be used to conduct the various test conditions presented in **Table 2-6** in Chapter 2 of the Implementation Plan.

Control samples (no $KMnO_4$) will be prepared and sampled throughout the reaction period to quantify changes in concentration due to mechanisms other than oxidation. In addition to the duplicate control samples, it is currently planned to run two (2) test conditions (in duplicate) from **Table 2-6** each time this procedure is used. Thus, 6 reactors will be used during each run of this procedure, and this procedure will be conducted a total of 8 times (4 times at each facility). The controls and the treatment reactors will all contain the same initial contaminant concentrations (i.e., all conditions will be the same for each run of this procedure with the exception of the $KMnO_4$ concentration used).

Note: The 2,000 mg/L TCE spike solution in Table 2-6 experiments cannot be prepared in the same manner as the spike solution for the 10 and 100 mg/L spike levels. Both spiking methods are included in this procedure.

1. Soil Prepping
All groundwater to be used in these experiments (**TSF-05 groundwater**) will be prepped by sparging to remove any residual TCE present on the media. Doing so will allow this experiment to be conducted with consistent and controlled initial TCE concentrations via contaminant spiking. (Properly indicate usage of this media in the treatability study tracking logbook.)

For the 10 and 100 mg/L Spike concentrations ONLY.
--Proceed to step 9 if spiking at DNAPL levels (2,000 mg/L TCE) in Table 2-6

---

2. TCE Stock Solution Preparation
Prepare a STOCK (Saturated) TCE solution ($\approx$1100 mg/L). (Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.) This can easily be stored and used again in subsequent experiments

For 10 ppm TCE spiking (Runs 1 & 2): Add > 0.1 **mL** of Pure TCE into 65-70 mL of **TSF-05 groundwater** and keep refrigerated.

For 100 ppm TCE spiking (Runs 5&6): Add > 0.6 mL of Pure TCE into 625 mL of TSF=05 GW & keep refrigerated.

3. TCE Spike Solution Preparation, PART 1
Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag, flask, or equivalent). Fill with unspiked 12°C **TSF-05 groundwater** ($\approx$**3070 mL or $\approx$2800 mL for the 10 and 100 mg/L spike condition, respectively**). By gravimetric methods, determine the

amount of unspiked groundwater added to the container. (A calibration check of the gravimetric scale will be performed each day of use.)

4. TCE Spike Solution Preparation, PART II

Add the appropriate quantity of the Saturated STOCK TCE solution to produce a TCE spike solution with the concentration prescribed in **Table 2-6** for the particular test series being ran. The **hot spot groundwater** will only be spiked at **10 and 100 mg/L TCE via this method**, thus the volume of saturated STOCK TCE needed should be on the order of **30 mL and 300 mL**, respectively. Please record the volume of STOCK TCE added **(NOTE: will also added any contaminants required during this step.)** Place the spike solution in the incubator overnight at 12C for temperature equilibration. Ensure that all Information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

5. Obtain Tare Weights of Reactors

Prepare the test reactors to be used. (The gas-tight reaction vessels acquired and tested in Task 2a will be used as the reactors in this experiment.) Obtain the tare weight of each, including the weight of a ground glass standard taper stopper fitted with a Teflon sleeve.

6. Collection of Initial Spike Solution Samples

Remove the spike solution from the incubator, and obtain duplicate aqueous samples ($\approx$ 5 mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. Record the time the sample is collected. The duplicate aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane ($\approx$ 5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. These extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

7. Distribution of Spike Solution to Reactors

Quickly dispense the spike solution into each of the reactors to be used. Add $\approx$500 mL to each reactor. Immediately replace the ground glass stopper and re-weigh each to determine the actual weight of spiked groundwater added.

8. Keep Cool until Experiment is initiated.

Place the reactors in the incubator at 12°C until the experiment is initiated. Agitate the reactors at $\approx$200 rpm during this step.

For the DNAPL Spiking Level (2,000 mg/L TCE) in Table 2-6 ONLY
--Proceed to Step 13 if spiking at 10 or 100 mg/L

---

9. >2,000 mg/L Spiking: Obtain Tare Weights of Reactors

Prepare the test reactors to be used. (The gas-tight reaction vessels acquired and tested in Task 2a will be used as the reactors in this experiment.) Obtain the tare weight of each, including the weight of a ground glass standard taper stopper fitted with a Teflon sleeve.

10. >2,000 mg/L Spiking: Reactor Filling
Dispense ≈**500 mL un-spiked TSF-05 groundwater** into each of the reactors to be used. Immediately replace the ground glass stopper/sleeve and re-weigh each to determine the actual weight of groundwater added.

11. Reactor Spiking (>2,000 mg/L TCE)
To each of the six reactors, add enough pure phase TCE to achieve a TCE concentration of 2,000 mg/L (**should be around 700 µL pure TCE for 500 mL of groundwater**). Measure the mass of the spiking syringe when filled and then after spiking to determine the actual contaminant mass added (a QC check on the initial TCE analysis). Information regarding the preparation of each spiking solution will be recorded in the laboratory research notebook.

12. Spike Solution Equilibration (>2,000 mg/L Spike Condition)
Place the reactors into the incubator at 200 rpm or greater and allow the spike solutions to equilibrate at 12°C (likely overnight)

13. **For Loadings of .01 and 0.1 wt% MnO$_4^-$ in Table 2-6 ONLY.**
Preparation of Stock MnO$_4^-$ Solution (4 **wt%**)
Add **2.66 g** of crystalline KMnO4 (Carus™ Free Flowing Technical Grade) into a **50 mL** Flask and fill to volume with DI water, and allow to mix for at least 2 hours.

14. Prepare Reactor Closure/Carbon Tube
During equilibration period, prepare the standard taper adapters/stopcock valve. (**One Orbo tubes will be used.**) The vertical sampling port will be fitted with a small septum) STORE UN-SEALED ORBO TUBES OUTSIDE OF THE LABORATORY FUME HOODS. THE HOODS LIKELY HAVE THE GREATEST POTENTIAL FOR "CONTAMINATING" THE TUBES WITH TCE AND OTHER VOCs.

15. Collection of Pre-Reaction Sample from Each Reactor
After equilibration, collect a ≈10 mL aqueous sample using a long need and disposable syringe from each of the reactors and quickly reseal. Record the time the sample is collected and note whether solids were present in the aqueous sample. If significant solids are present, a portion of this aliquot volume may be used for a total solids analysis.

16. Preparation of Pre Reaction TCE Sample
Dispense (unfiltered) ≈3 mL of this aliquot sample into to a pre-weighed vial holding a known volume of hexane (≈3 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis. Record the time this sample is taken.

17. Measurement of Pre Reaction pH Value
Tare a small beaker for pH analysis. Add a 0.45 micron filter to the sample syringe and dispense (filtered) the remaining portion of the sample in the syringe (≈7 mL) into the tared beaker. Reweigh the beaker to determine the volume of the sample (assuming that the solids fraction is negligible). The pH analyses will be conducted using conventional pH meters/electrodes, calibrated each day of use via a minimum of two standard buffer solutions. Values obtained for

each sample will be recorded. A calibration check will also be conducted following the last sample to be measured each day. Values obtained for the samples will be corrected if a significant drift (i.e., > 15%) occurred.

18. **For Loadings of .01 and 0.1 wt% MnO$_4^-$ in Table 2-6 ONLY.**
Addition of Stock MnO4- Solution into Reactors
Quickly remove the ground glass stopper and add the needed volume of stock KMnO$_4$ to obtain the MnO$_4^-$ concentrations in **Table 2-6** (approximately **1.25 mL and 12.5 mL for the 0.01 and .01% MnO$_4^-$** concentrations respectively). Replace the glass ground stoppers with the adapters fitted with the stopcock and charcoal desorption tubes and quickly hand shake each reactor to ensure rapid dissolution of the oxidant. (No oxidant will be added to the control reactors). The time that the stock KMnO$_4$ is added to each individual reactor shall also be recorded (reaction start time). Place each reactor back into the 12°C incubator and 200 rpm or greater.

19. **For the Oxidant Loadings of 1 and 3wt% MnO$_4^-$ in Table 2-6 ONLY**
Addition of Crystalline KMnO4 to Reactors, Part I
Pre-weigh out (into disposable tare boats) the needed quantities of crystalline KMnO$_4$ (Carus™ Free Flowing Technical Grade) that is needed for each reactor according to which test condition in Table 2-6 is being evaluated. **For the 1 and 3 wt% MnO$_4^-$ loadings, ≈ 6.6 g and ≈20 g of KMnO4 will be needed for each reactor, respectively.** Record the actual mass of KMnO$_4$ weighed out for each reactor.

20. **For the Oxidant Loadings of 1 and 3wt% MnO$_4^-$ in Table 2-6 ONLY**
Addition of Crystalline KMnO4 to Reactors, Part II
Quickly remove the ground glass stopper and add these pre-weighed quantities of KMnO$_4$ into the applicable reactors. Replace the glass ground stoppers with the adapters fitted with the charcoal desorption tube assemblies and quickly hand shake each reactor to ensure rapid dissolution of the oxidant. (No KMnO$_4$ will be added to the control reactors). The time that KMnO$_4$ is added to each individual reactor shall also be recorded (reaction start time). Place each reactor back into the 12°C incubator and at 200 rpm of greater.

21. 30 Minute Sampling
At approximately 30 minutes from the reaction start time, remove the reactors from the incubator and collect a 10 mL aliquot (using a long needle and syringe with a Luer Tip). Record the time the sample is collected. Replace the reactor(s) back into the incubator.

22. Preparation of 30 Minute TCE Sample
Dispense (unfiltered) ≈3 mL of the collected aliquot into a pre-weighed vial holding a known volume of hexane (≈3 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

23. pH Analysis of 30 Minute Sample
Tare a small beaker. Add a 0.45 μm syringe filter unto the end of the syringe and dispense (filtered) the remaining portion of the sample in the syringe (≈7 mL) into a tared beaker for pH

analysis. Reweigh the beaker to determine the volume of the sample (assuming that the solids fraction is negligible). Measure and record the pH of the sample as done in Step **

24. MnO$_4^-$ Analysis of the 30 Minute Sample
Use a portion of the filtered pH sample to perform a MnO$_4^-$ analysis. The sample may have to be diluted so that its spectrophotometric absorbance (at λ =525 nm) is less than that of the highest standard to be prepared (50 mg/L MnO4-). Check standards (10 and 50 mg/L MnO4-) will be prepared with reagent grade KMnO$_4$ and measured each analysis day. A new 5 point calibration curve will be prepared if the absorbance of these check standards differs from the expected value by >15%.

25. Collection and Analysis of Additional Aliquot Samples
Collect and analyze aliquots from each reactor for TCE, pH, and KMnO$_4$ (Steps 21-24) at the following ADDITIONAL time periods: 2 hrs, 4 hrs, 6 hrs, 20 hrs, and 24 hrs.
IMPORTANT—For each reactor collect and extract a duplicate sample (Steps 21-24) from one of the 6 time intervals being evaluated.

26. Extraction of Charcoal Desorption Tubes
After the final aliquot samples are collected, remove the charcoal desorption tube(s) from each reactor. Each charcoal bed contained in the tube(s) will be placed into pre-filled and pre-weighed vials containing a known volume of hexane ($\approx$5 mL). These extracts will be processed and analyzed in the same manner as the aqueous aliquots for TCE.

27. Clean up
Clean up the reactors for re-use in the next run of the experiment. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

28. GC ANALYSIS of VOCs
All VOC analyses for this experiment will be conducted using a **G.C./ECD** detector. The instrument will calibrated for TCE (and also for cis-1,2 DCE, trans-1,2 DCE, and vinyl chloride for the co-contaminants experiment), using a 5 point calibration curve with standard concentrations ranging from 5-1000 µg/L (ppb)

The VOC analyses of the hexane extracts will closely follow EPA Method 8000B. Significant deviations from this method will be clearly documented.

Formal data packages will be prepared for the analyses performed for all Task 3 and 4 samples will be prepared as discussed in Sections 2.4.3 and 2.4.4 in Chapter 2 of the Implementation Plan. The major QA/QC items pertaining to the VOC analyses include:

Calibration standards will be prepared from a certified, custom VOC mix stock solution containing each analyte of interest. The lot number of this custom mix will be included on each initial calibration data form.

The working calibration curve will be verified through injection of a QC check standard (100 µg/L) at least once each analysis day. If the response for any analyte varies from the predicted response by more than ± 15%, a new calibration curve will be prepared.

A blank hexane sample will be analyzed between every 10 test samples.

A sample will be diluted and reanalyzed if its GC peak area response is greater than that of the highest calibration standard being used that analysis day.

General Procedure for Task 4b Experiments - Measure the oxidation rate of organic contaminants in the hot spot groundwater and sludge
(To be conducted at RMAL)

IMPORTANT: *Per the SOW, page 2-11, one of the duplicates for a single test condition listed in Table 2-7 of the plan will be sacrificially extracted with hexane at reaction intervasl. Selection of the test series for this task to be performed will be determined at a later date.*

NOTE: This experiment will be used to conduct the various test conditions presented in **Table 2-7** in Chapter 2 of the Implementation Plan. Control samples will be prepared and sampled throughout the reaction time interval to quantify changes in concentration due to processes other than oxidation. In addition to the duplicate control samples, it is currently planned to run two (2) test conditions (in duplicate) from **Table 2-7** each time this procedure is used. Thus, 6 reactors will be used during each run of this procedure, and this procedure will be conducted 6-7 times, depending upon how/when the "blank" test series (NO TCE) is performed. The controls and the treatment reactors will all contain the same media type and initial contaminant concentrations (i.e., all conditions will be the same for each run of this procedure with the exception of the $KMnO_4$ concentration used.

Note: The 2,000 mg/L TCE spike solution in Table 2-7 experiments cannot be prepared in the same manner as the spike solution for the 10 and100 mg/L spike levels. Both spiking methods are included in this procedure.

1. Soil Prepping
All groundwater and media to be used in these experiments (**TSF-05 groundwater and sludge**) will be prepped by sparging to remove any residual TCE present on the media. Doing so will allow this experiment to be conducted with consistent and controlled initial TCE concentrations via contaminant spiking. (Properly indicate usage of this media in the treatability study tracking logbook.)

For the 10 and 100 mg/L Spike concentrations ONLY.
--Proceed to step 10 if spiking at DNAPL levels (2,000 mg/L TCE) in Table 2-7.

---

2. TCE Stock Solution Preparation
Prepare a STOCK (Saturated) TCE solution ($\approx$1100 mg/L) by adding greater than **0.5 mL** of Pure TCE into a 500 mL flask filled to volume with **TSF-05 groundwater** and keep refrigerated.

(Use of a STOCK solution rather than pure phase TCE to prepare the spiking solution affords better accuracy in obtaining the target concentration.) This can easily be stored and used again in subsequent experiments.

3. TCE Spike Solution Preparation, PART 1
Obtain the tare weight of the container to be used to prepare the spike solution (Tedlar bag, flask, or equivalent). Fill with unspiked 12°C **TSF-05 groundwater (≈3070 mL or ≈2800 mL for the 10 and 100 mg/L spike condition, respectively)**. By gravimetric methods, determine the amount of unspiked groundwater added to the container. (A calibration check of the gravimetric scale will be performed each day of use.)

4. TCE Spike Solution Preparation, PART II
Add the appropriate quantity of the Saturated STOCK TCE solution to produce a TCE spike solution with the concentration prescribed in **Table 2-7** for the particular test series being ran. The **hot spot groundwater** will only be spiked at **10 and 100 mg/L TCE via this method**, thus the volume of saturated STOCK TCE needed should be on the order of **30 mL and 300 mL**, respectively. Please record the volume of STOCK TCE added (**NOTE: will also added any contaminants required during this step.**) Place the spike solution in the incubator overnight at 12C for temperature equilibration. Ensure that all Information regarding the preparation of the spiking solution will be recorded in the laboratory research notebook.

5. Obtain Tare Weights of Reactors
Prepare the test reactors to be used. (The gas-tight reaction vessels acquired and tested in Task 2a will be used as the reactors in this experiment.) Obtain the tare weight of each, including the weight of a ground glass standard taper stopper fitted with a Teflon sleeve.

6. Fill with Solid Phase Media
Add approximately 100-110 g of the **TSF-05 sludge** desired for this particular test series (See **Table 2-7** in the Implementation Plan). Re-weigh each reactor to determine the actual amount added (when applicable).

7. Collection of Initial Spike Solution Samples
Remove the spike solution from the incubator, and obtain duplicate aqueous samples (≈ 5 mL) of the spike solution to obtain the initial TCE concentration of the spiked groundwater. Record the time the sample is collected. The duplicate aliquot samples will be added to pre-weighed sample containers holding a known volume of hexane (≈ 5 mL). Each sample container will be weighed again after sample addition to determine the actual weight of sample added. These extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis.

8. Distribution of Spike Solution to Reactors
Quickly dispense the spike solution into each of the reactors to be used. Add ≈**500 mL** to each reactor. Immediately replace the ground glass stopper and re-weigh each to determine the actual weight of spiked groundwater added.

9. Soil/Spike Equilibration
Place the reactors in the incubator at 12°C and allow the spike solution to equilibrate for 24 hours with the sludge. Agitate the reactors at ≈200 rpm during this step.

For the DNAPL Spiking Level (2,000 mg/L TCE) in Table 2-7 ONLY
--Proceed to Step 15 if the samples were spiked at 10 or 100 mg/L

10. >2,000 mg/L Spiking: Obtain Tare Weights of Reactors
Prepare the test reactors to be used. (The gas-tight reaction vessels acquired and tested in Task 2a will be used as the reactors in this experiment.) Obtain the tare weight of each, including the weight of a ground glass standard taper stopper fitted with a Teflon sleeve.

11. Sludge Addition (>2,000 mg/L Spiking Condition)
Add approximately 100-110 g of the TSF-05 sludge to each reactor. Re-weigh each reactor (with stopper/sleeve) to determine the actual amount of sludge added

12. >2,000 mg/L Spiking: Reactor Filling
Dispense ≈500 mL un-spiked TSF-05 groundwater into each of the reactors to be used. Immediately replace the ground glass stopper/sleeve and re-weigh each to determine the actual weight of groundwater added.

13. Reactor Spiking (>2,000 mg/L TCE)
To each of the six reactors, add enough pure phase TCE to achieve a TCE concentration of 2,000 mg/L (**should be around 700 μL pure TCE for 500 mL of groundwater**). Measure the mass of the spiking syringe when filled and then after spiking to determine the actual contaminant mass added (a QC check on the initial TCE analysis). Information regarding the preparation of each spiking solution will be recorded in the laboratory research notebook.

14. Spike Solution Equilibration (>2,000 mg/L Spike Condition)
Place the reactors into the incubator at 200 rpm or greater and allow the spike solutions to equilibrate at 12°C (likely overnight).

15. **For the Oxidant Loadings of .01 and 0.1 wt% MnO₄⁻ in Table 2-7 ONLY**
Preparation of Stock MnO₄⁻ Solution (4 wt%)
Add **2.66 g** of crystalline KMnO4 (Carus™ Free Flowing Technical Grade) into a **50 mL** Flask and fill to volume with DI water, and allow to mix for at least 2 hours.

16. Prepare Reactor Closure/Carbon Tubes
During equilibration period, prepare the standard taper adapters/stopcock valve. (**One Orbo tubes will be used for each reactor**). The vertical sampling port will be fitted with a small septum. STORE UN-SEALED ORBO TUBES OUTSIDE OF THE LABORATORY FUME HOODS. THE HOODS LIKELY HAVE THE GREATEST POTENTIAL FOR "CONTAMINATING" THE TUBES WITH TCE AND OTHER VOCs.

17. Collection of Pre-Reaction Sample from Each Reactor
After equilibration, collect a ≈10 mL aqueous sample using a long need and disposable syringe from each of the reactors and quickly reseal. Record the time the sample is collected and note whether solids were present in the aqueous sample. If significant solids are present, a portion of this aliquot volume may be used for a total solids analysis.

18. Preparation of Pre Reaction TCE Sample
Dispense (unfiltered) $\approx$3 mL of this aliquot sample into to a pre-weighed vial holding a known volume of hexane ($\approx$3 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis. Record the time this sample is taken. (These samples will require Beta/Gamma Screenings before submittal to ESD.)

19. Measurement of Pre Reaction pH Value
Tare a small beaker for pH analysis. Add a 0.45 micron filter to the sample syringe and dispense (filtered) the remaining portion of the sample in the syringe ($\approx$7 mL) into the tared beaker. Reweigh the beaker to determine the volume of the sample (assuming that the solids fraction is negligible). The pH analyses will be conducted using conventional pH meters/electrodes, calibrated each day of use via a minimum of two standard buffer solutions. Values obtained for each sample will be recorded. A calibration check will also be conducted following the last sample to be measured each day. Values obtained for the samples will be corrected if a significant drift (i.e., > 15%) occurred.

20. **For the Oxidant Loadings of .01 and 0.1 wt% MnO_4^- in Table 2-7 ONLY**
Addition of Stock MnO4- Solution into Reactors
Quickly remove the ground glass stopper and add the needed volume of stock $KMnO_4$ to obtain the MnO_4^- concentrations in **Table 2-7** (approximately **1.25 mL and 12.5 mL** for the **0.01 and .01% MnO_4^-** concentrations respectively). Replace the glass ground stoppers with the adapters fitted with the stopcock and charcoal desorption tubes and quickly hand shake each reactor to ensure rapid dissolution of the oxidant. (No oxidant will be added to the control reactors). The time that the stock $KMnO_4$ is added to each individual reactor shall also be recorded (reaction start time). Place each reactor back into the 12°C incubator and 200 rpm or greater.

21. For the Oxidant Loadings of 1 and 3 wt% MnO_4^- in Table 2-7 ONLY
Addition of Crystalline KMnO4 to Reactors, Part I
Pre-weigh out (into disposable tare boats) the needed quantities of crystalline $KMnO_4$ (Carus™ Free Flowing Technical Grade) that is needed for each reactor according to which test condition in Table 2-6 is being evaluated. **For the 1 and 3 wt% MnO_4^- loadings, $\approx$ 6.6 g and $\approx$20 g of $KMnO_4$ will be needed for each reactor, respectively.** Record the actual mass of $KMnO_4$ weighed out for each reactor.

22. **For the Oxidant Loadings of 1 and 3 wt% MnO_4^- in Table 2-7 ONLY**
Addition of Crystalline $KMnO_4$ to Reactors, Part II
Quickly remove the ground glass stopper and add these pre-weighed quantities of $KMnO_4$ into the applicable reactors. Replace the glass ground stoppers with the adapters fitted with the charcoal desorption tube assemblies and quickly hand shake each reactor to ensure rapid dissolution of the oxidant. (No $KMnO_4$ will be added to the control reactors). The time that $KMnO_4$ is added to each individual reactor shall also be recorded (reaction start time). Place each reactor back into the 12°C incubator and at 200 rpm of greater.

23. 30 Minute Sampling

At approximately 30 minutes from the reaction start time, remove the reactors from the incubator and collect a 10 mL aliquot (using a long needle and syringe with a Luer Tip). Record the time the sample is collected. Replace the reactor(s) back into the incubator.

24. Preparation of 30 Minute TCE Sample

Dispense (unfiltered) $\approx$3 mL of the collected aliquot into a pre-weighed vial holding a known volume of hexane ($\approx$3 mL). This sample vial will be weighed again after sample addition to determine the actual weight of sample added. All such extracts will be placed on a horizontal shaker for 2 hours. Store the extracts at 4°C until G.C. analysis. (These samples will require Beta/Gamma Screenings before submittal to ESD.)

25. pH Analysis of 30 Minute Sample

Tare a small beaker. Add a 0.45 µm syringe filter unto the end of the syringe and dispense (filtered) the remaining portion of the sample in the syringe ($\approx$7 mL) into a tared beaker for pH analysis. Reweigh the beaker to determine the volume of the sample (assuming that the solids fraction is negligible). Measure and record the pH of the sample as done in Step **

26. MnO_4^- Analysis of the 30 Minute Sample

Use a portion of the filtered pH sample to perform a MnO_4^- analysis. The sample may have to be diluted so that its spectrophotometric absorbance (at λ =525 nm) is less than that of the highest standard to be prepared (50 mg/L MnO4-). Check standards (10 and 50 mg/L MnO4-) will be prepared with reagent grade $KMnO_4$ and measured each analysis day. A new 5 point calibration curve will be prepared if the absorbance of these check standards differs from the expected value by >15%.

27. Collection and Analysis of Additional Aliquot Samples

Collect and analyze aliquots from each reactor for TCE, pH, and $KMnO_4$ (Steps 23-26) at the following ADDITIONAL time periods: 2 hrs, 4 hrs, 6 hrs, 20 hrs, and 24 hrs.
IMPORTANT—For each reactor collect and extract a duplicate sample (Steps 23-26) from one of the 6 time intervals being evaluated.

28. Extraction of Residual TCE in Reactor

The entire contents of each reactor will be extracted with hexane. First, obtain a tare weight on six (6) empty containers to be used for the hexane extraction (1 liter VOA bottles). Measure out 400 mL of hexane into two (2) 200 mL volumetric flasks. Add 200 mL of the hexane directly into the 1 L extraction bottle. Quickly pour the contents of each test reactor into a separate extraction bottle. Use the remaining 200 mL flask of hexane to rinse any residual slurry from the test reactor into the extraction bottle. Weigh and record the mass of the filled extraction bottle to determine the mass of the slurry and hexane added (taking into account the fact that hexane has a specific gravity of 0.66).
(The mass of any remaining TCE on the solid phase can be determined with this extraction when a mass balance is performed using data from the aqueous aliquot sampling that was conducted throughout the test.)

29. Reactor Extraction Continued

Place each extraction bottle on a horizontal reciprocating shaker for a minimum of 2 hours then collect duplicate hexane aliquots from each extraction bottle for G.C. analysis (dilutions may be necessary).

30. Extraction of Charcoal Desorption Tubes

After the final aliquot samples are collected, remove the charcoal desorption tube(s) from each reactor. Each charcoal bed contained in the tube(s) will be placed into pre-filled and pre-weighed vials containing a known volume of hexane ($\approx$5 mL). These extracts will be processed and analyzed in the same manner as the aqueous aliquots for TCE.

31. VOC Sample Submittal

Submit 1 mL aliquots of the hexane extracts collected during the experiment to ESD personnel (diluted to <1000 ppb, if necessary). These aliquots will be surveyed by health physics before release to ESD.

32. Clean up

Clean up the reactors for re-use in the next run of the experiment. Also place any waste materials generated from the experiment in the appropriate satellite accumulation area.

33. GC ANALYSIS of VOCs

All VOC analyses for this experiment will be conducted using a **G.C./ECD** detector. The instrument will calibrated for TCE, using a 5 point calibration curve with standard concentrations ranging from 5-1000 µg/L (ppb)

The VOC analyses of the hexane extracts will closely follow EPA Method 8000B. Significant deviations from this method will be clearly documented.

Formal data packages will be prepared for the analyses performed for all Task 3 and 4 samples will be prepared as discussed in Sections 2.4.3 and 2.4.4 in Chapter 2 of the Implementation Plan. The major QA/QC items pertaining to the VOC analyses include:

Calibration standards will be prepared from a certified, custom VOC mix stock solution containing each analyte of interest. The lot number of this custom mix will be included on each initial calibration data form.

The working calibration curve will be verified through injection of a QC check standard (100 µg/L) at least once each analysis day. If the response for any analyte varies from the predicted response by more than $\pm$ 15%, a new calibration curve will be prepared.

A blank hexane sample will be analyzed between every 10 test samples.

A sample will be diluted and reanalyzed if its GC peak area response is greater than that of the highest calibration standard being used that analysis day.

34. Post Treatment TSF-05 Sludge TOC Analysis

Upon completion of the test period, the post-treatment sludges will be analyzed for total organic carbon content following the guidance in SW846 method 9060 and the manufacturer's operating instructions provided with the instrument. The carbon results will be corrected back to the original dried starting weight of the sludge used in the test.

B5. References

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Pavlostathis, S. G., and K. Jaglal. 1991. "Desorptive Behavior of Trichloroethylene in Contaminated Soil," *Environmental Science and Technology* 25(2):274-279.

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