FIELD TREATABILITY STUDY RESULTS: TRENCH INJECTION OF POTASSIUM PERMANGANATE

CROSSLEY FARM SITE
HUFFS CHURCH, PA
XDD PROJECT NO. 84423
TTNUS SUBCONTRACT NO. 1000591

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1.0 INTRODUCTION

Xpert Design & Diagnostics, LLC (XDD) appreciates this opportunity to conduct field testing of the efficacy of potassium permanganate as a chemical oxidant for source area treatment at the Crossley Farm site (Site) in Huffs Church, PA. In accordance with XDD's November 12, 2004 Technical Proposal (Work Plan), bench scale and field treatability studies were performed to evaluate the effectiveness of chemical oxidation of trichloroethene (TCE) and tetrachloroethene (PCE) in groundwater in the area of the former borrow pit. The results of bench scale testing and a field tracer study were presented in XDD's February 2, 2005 draft report "Groundwater Treatability, Oxidant Demand, and Percolation/Tracer Results". This report summarizes the test procedures and results of an initial field application of potassium permanganate.

This report is organized as follows:

Section 2 **Background.** This section provides a brief summary of the bench scale and tracer test findings.

Section 3 **Permanganate Oxidation.** This section describes the process of oxidation of site VOCs by permanganate.

Section 4 **Procedures.** Field procedures and the sequence of events during the permanganate field treatability study are described in this section.

Section 5 **Results and Discussion.** Monitoring results and assessment of the effectiveness of permanganate in oxidizing groundwater VOCs are discussed.

Section 6 **Conclusions and Recommendations.** This section summarizes the findings and conclusions from the treatability study, and recommendations regarding data collection for development of design parameters for full scale application.

2.0 BACKGROUND

In December 2004 and January 2005, the following activities were performed and results were presented in a February 2, 2005 draft report "Groundwater Treatability, Oxidant Demand, and Percolation/Tracer Results".

1. A bench scale groundwater treatability test was performed to evaluate destruction of TCE and PCE in groundwater collected at the site. Tests were performed at concentrations of 2 g/L and 20 g/L potassium permanganate.
    a. 18,000 µg/L TCE was reduced below 88 µg/L (>99.95% reduction) in 2 g/L and 20 g/L potassium permanganate solutions.

   b. 885 µg/L PCE was reduced below 88 µg/L (>90% reduction) in 2 g/L and 20 g/L potassium permanganate solutions.

2. A soil oxidant demand (SOD) test was performed to evaluate the amount of potassium permanganate consumed due to contact with the bedrock present at the Site.
   a. A potassium permanganate demand of approximately 1.2 g per Kg bedrock material was determined from SOD testing. This demand is approximately 15 to 25 times smaller than typical unconsolidated soils with significant organic content, and approximately six times smaller than the demand measured for Passaic Formation siltstone.

3. A field percolation and tracer test was performed to evaluate the recharge capacity of the trench to be used for the in situ treatability study, and to evaluate fluid transport in the test area under gravity flow and natural gradient conditions.
   a. Sodium chloride tracer solution was delivered to the trench at a flow rate of approximately 40 gallons per minute (GPM) with no observable head buildup in the trench.
   b. Tracer solution reached the upper 20 feet of open-rock interval at extraction well EW-1 [open rock from 30 feet to 150 feet below ground surface (bgs)], but did not reach the screen interval of monitoring well Tt25S (screen interval from 56 feet to 66 feet bgs).
   c. The appearance of tracer at the Tt25 cluster approximately 100 feet downgradient of the injection trench could not be determined because of elevated baseline specific conductivity and pH, possibly related to grout.

3.0 PERMANGANATE OXIDATION

Permanganate reacts with and oxidizes a wide range of common organic chemicals relatively quickly and completely (e.g., chlorinated ethenes, phenols, aromatic hydrocarbons, and simple polycyclic aromatic hydrocarbons). Permanganate reacts rapidly with the non-conjugated (i.e., non-aromatic) double bonds in chlorinated ethenes such as Trichloroethene (TCE), tetrachloroethene (PCE), dichloroethene (DCE) isomers, and vinyl chloride (VC).

At the Crossley Farm Site, greater than 99% of the VOCs in the borrow pit area (predominantly TCE and PCE) can be rapidly oxidized by permanganate. The balanced chemical equations for potassium permanganate oxidation of TCE and PCE are:

- TCE: $2KMnO_4 + C_2HCl_3 \text{--->} 2CO_2 + 2MnO_2 + 2K^+ + 3Cl^- + H^+$
- PCE: $4KMnO_4 + 3C_2Cl_4 + 4H_2O \text{--->} 6CO_2 + 4MnO_2 + 4K^+ + 12Cl^- + 8H^+$

The stoichiometric mass ratio of $KMnO_4$:PCE and $KMnO_4$:TCE needed for complete oxidation is approximately 1.3 and 2.4, respectively. Half-lives for PCE and TCE are approximately 4.3 hours and 18 minutes, respectively, in the presence of 1 mM MnO_4^- (Yan and Schwartz, 1999).

4.0 PROCEDURES

XDD prepared a sampling plan (please see Attachment A) for the initial pilot test injection, and met with TtNUS project management and staff on January 14, 2005 to review the plan. The sampling plan outlines responsibilities and procedures for groundwater monitoring at the borrow pit area wells before and after permanganate injection. In particular, the plan presented a strategy for determining appropriate times for laboratory sample collection. The objective of the first groundwater sampling event was to evaluate the extent and magnitude of treatment around the time oxidant concentrations begin to decrease from peak levels, or at a designated threshold concentration. Under these conditions, VOC concentrations should approach minimum levels. As permanganate becomes depleted, additional samples would be collected to evaluate rebound in VOC concentrations. Rebound occurs when significant residual phase VOCs remain in the formation after an initial treatment, therefore the initial sampling event represents a time zero point for analysis of rebound. This sampling strategy is depicted in Figure 1 of Attachment A.

Baseline groundwater sampling for the following parameters was conducted by TtNUS at a number of monitoring wells in the borrow pit area during the week of January 17, 2005. Sampling locations included Tt25S, EW-1, EW-2, Tt25I1, Tt25I2, Tt25D1, and Tt25D2. Analyses of baseline samples included the following relevant parameters:

- VOCs
- Chloride and bromide
- Total and dissolved (field filtered) manganese
- Total and dissolved (field filtered)
- Field parameters (i.e., pH, ORP, conductivity, temperature, and dissolved oxygen) using flow-through cell.

On January 21, 2005, XDD personnel mobilized and calibrated four down-hole data logging water quality monitors (YSI Model 600 XLM) and performed baseline vertical profiling of groundwater parameters at the following locations after they were sampled by TtNUS. Vertical profiling was performed to evaluate variations in groundwater parameters as a function of depth of instrument placement, and to evaluate which fracture zone(s) may be conducting permanganate into a well as evidenced by increases in specific conductivity and ORP after permanganate injection.

1. TT25S - vertical profile measurements at depths of 57, 63, and 65 feet;
2. EW-1 - vertical profile measurements every 10 feet from 30 feet to 150 feet;
3. TT25I2 - vertical profile measurements at 67, 70, and 72 feet; and
4. Tt25D2 - vertical profile measurements at 97, 102, and 105 feet.

After baseline vertical profiling was completed, XDD installed the instruments at the following depths for continuous data logging. The data logging instruments were configured to monitor and record pH, ORP, conductivity, temperature, and dissolved oxygen at intervals of 10 minutes.

1. TT25S at a depth of approximately 63 feet (lower portion of screen);
2. EW-1 at a depth of approximately 45 feet (highly fractured zone in upper portion of open hole);
3. TT25I2 at a depth of approximately 70 feet (lower portion of screen); and
4. Tt25D2 at a depth of approximately 102 feet (lower portion of screen).

During the week of January 17, 2005, XDD mobilized for injection of approximately 5,000 gallons of potassium permanganate stock material at a concentration of approximately 25 g/L in de-ionized water. In accordance with the Work Plan, the solution also contained sodium bromide salt at a concentration of approximately 10 g/L to be used as a tracer to show distribution of the oxidant solution. Colonial Chemical of Tabernacle, NJ began blending the required materials for the injection solution during the week of January 17, 2005 for delivery to the site on January 25, 2005.

On January 19, XDD was notified by TtNUS of EPA's concern about oxidation of bromide to bromate in the presence of permanganate. The stock solution was already blended, so TtNUS requested that analyses be performed to determine if bromate would be formed. XDD prepared mixtures of potassium permanganate and sodium bromide in unused site groundwater from the laboratory treatability study. The samples were shipped overnight to STL's Savannah, GA laboratory for analysis by EPA Method 300.1B. The potassium permanganate and sodium bromide were prepared at different ratios in case elution times for either of the anions overlapped with bromate. The following samples were prepared for analysis:

1. 20 g/L KMnO4 + 10 g/L NaBr in site groundwater
2. 20 g/L KMnO4 + 0.1 g/L NaBr in site groundwater
3. 0.2 g/L KMnO4 + 10 g/L NaBr in site groundwater

Laboratory runs of calibration standards showed that permanganate ion elutes at nearly the same time as bromate ion in the EPA method. Attempts by STL to resolve the two standard peaks by adjusting the eluent ramp rates were unsuccessful. A laboratory report summarizing sample analytical results for bromate, along with chromatograms, is provided in Attachment B.

While analyses were being performed, TtNUS asked XDD to conduct a literature search, and to provide information on any cases in EPA Region 3 (by XDD and/or other firms) where bromide was used as a tracer, and samples were specifically analyzed for bromate as a by-product.

- According to the Gmelin Handbook of Inorganic Chemistry (Part C2, Manganese, 1975 page 67), "permanganate can oxidize bromide at an acidic pH. At a pH of 4 or higher, oxidation will not take place."
- A project summary provided in XDD's November 12, 2004 proposal (Project Summary #1) included treatability testing that showed bromide (10 g/L) to be non-reactive with potassium permanganate (20 g/L). No measurable loss of permanganate was observed during the study. However, the detection limit for bromate in the treatability study (500 µg/L) exceeds the MCL of 10 µg/L.

On January 25, 2005, TtNUS directed XDD to prepare a new solution of potassium permanganate without bromide, and the batch with bromide tracer would be held in reserve and used for a second injection, if possible. Modifications were made to the sampling plan (please see Sampling Plan Addendum in Attachment C). The Addendum included the following plan modifications:

1. Analyses for potassium (EPA Method 200.7) were added for baseline samples (January 26, 2005).
2. Bromide was deleted and potassium (total and dissolved) was added to the list of parameters to be sampled for and monitored as part of the initial sampling at each well when the sampling criteria were met. Potassium data would be used to evaluate dilution of post-injection groundwater samples by the injected permanganate solution.

On February 1, 2005, Colonial Chemical delivered 5,000 gallons of potassium permanganate solution (20 g/L) to the site. A lot analysis report for the stock potassium permanganate is provided in Attachment D. The oxidant was delivered to the trench through the stand-pipe and header system by gravity flow. A sample of the injected potassium permanganate solution was collected and analyzed on site using a field colorimetric method for permanganate (Hach Method 8034 via the Hach Model DR820 colorimeter). This method is sensitive to concentrations of approximately 1 mg/L, but samples greater than ~30 mg/L MnO_4^- require dilution for analysis within the linear range of the colorimeter. The tanker solution produced a colorimeter reading of 7.6 mg/L as potassium permanganate with a dilution factor of 2500, which resulted in a total potassium permanganate concentration of 19,000 mg/L.

Approximately 2.5 hours after injection was completed, two additional YSI 600 XLM instruments were installed at EW-2 (200 foot depth) and Tt2511 (60 foot depth). Post injection monitoring was performed from February 1 through March 17, 2005, in accordance with the sampling plan. A sampling/monitoring matrix summarizing parameters, locations, and dates is provided in Table 1. Monitoring was conducted jointly by XDD and TtNUS and included the following:

1. Maintenance and downloading of data loggers – Data loggers were downloaded daily for the first week following permanganate injection, and approximately twice per week thereafter through March 17, 2005. Instrument calibration was checked every two to three weeks. With the exception of a malfunctioning specific conductivity sensor (EW-2 on February 8 and February 24), only two re-calibrations were needed for pH only (please see Table 1).
2. Sampling and field analysis for permanganate – samples were collected using bailers (single check-valve and double check-valve) and a sampling pump. Samples collected using double check-valve bailers or a sample pump yielded more consistent results than the single check-valve bailer. Sampling for permanganate at wells in the borrow pit area was performed daily for the first week following permanganate injection and approximately bi-weekly thereafter until March 15, 2005.
3. Vertical profiling of groundwater field parameters at EW-1 (10 foot intervals from 30 feet to

150 feet bgs) and EW-2 (10 foot intervals from 150 feet to 200 feet bgs) we performed on February 2, 2005, one day following permanganate injection.

XDD field notes from permanganate injection monitoring are provided in Attachment E.

5.0 RESULTS AND DISCUSSION

5.1 Permanganate Injection

The entire 5,000 gallon batch was transferred to the trench in approximately 45 minutes, at an average flow of approximately 110 GPM. A positive pressure head was measured in the trench standpipe, possibly a result of head losses through the distribution pipe perforations. The actual pressure head in the trench (if any) is unknown.

5.2 Baseline Vertical Profiling

On January 21, 2005, XDD personnel measured changes in groundwater parameters with depth at EW-1, Tt25S, Tt25I2, and Tt25D2, particularly to evaluate sensitivity of pH and conductivity to changes in depth. Baseline vertical profile data are summarized in Attachment F.

- Vertical profile data from Tt25S show relatively constant specific conductivity, dissolved oxygen, pH, and ORP with depth along an interval of eight feet within the screen interval.
- Vertical profile data from EW-1 show a significant increase in conductivity over a vertical distance of 120 feet. This may be explained by gravity separation and/or downward borehole flow of sodium chloride tracer water that entered this well during the tracer test.
- Data from Tt25I2 and Tt25D2 show significant increases in conductivity with depth along a vertical distance of only six to seven feet, in addition to elevated pH (up to ~12). Given the uncertainty of the source of high pH dissolved solids at these wells (possibly related to Portland cement in the grout seal), and the high degree of sensitivity to depth of measurement, the usefulness of these parameters in interpreting the results of the tracer study is limited.

5.3 Post-injection Vertical Profiling

The results of post-injection vertical profiling at EW-1 and EW-2 on February 2, 2005 are provided in Attachment F. These data are used to evaluate which fracture zone(s) were conducting permanganate into EW-1, as evidenced by increases in specific conductivity and ORP above baseline after permanganate injection. Profiling of the upper 50 feet of EW-2 was performed to determine if permanganate was entering this well.

- Post injection data from EW-1 showed the following:
  - Increases in specific conductivity and dissolved oxygen concentrations significantly above baseline occurred between 30 feet and 40 feet bgs, in the upper 10 feet of open borehole.
  - Post injection data at EW-1 also showed significant increases in ORP above baseline throughout the well. ORP ranged from 736 mV at a depth of 30 feet to a maximum of 995 mV at a depth of 120 feet.
  - Post injection pH levels decreased by approximately 0.5 to 1.0 units in the upper 70 feet of the well, with a maximum decrease of 1.5 to 2 units at a depth of 110 feet to 120 feet. A minimum pH of 3.7 was measured at a depth of 120 feet.
- ORP levels in the upper 50 feet of EW-2 on February 2, 2005 (one day following permanganate injection) ranged from -312 mV to -383 mV, indicating no oxidant was present.[1]

5.4 Groundwater Geochemical and Physical Parameters (Data Logger Results)

Graphical summaries of groundwater pressure head change, ORP, specific conductivity, pH, dissolved oxygen, and temperature are provided in Attachment G, Figures G.1 through G.6, respectively. Significant changes in geochemical parameters following permanganate injection were limited to two monitoring wells: EW-1, Tt25S, and Tt25D2 (pressure head only). Results are discussed below..

5.4.1 Pressure Head Changes

Transient increases in pressure head were observed during and immediately after the permanganate injection at each well containing a pressure transducer-equipped YSI instrument: EW-1, Tt25S, and Tt25D2 (please see Figure F.1). Similar increases in head were observed at EW-1 and Tt25S during the tracer study in December 2004. It is noteworthy that hydraulic response to the permanganate injection at all three wells was immediate, within 10 minutes of the start of injection (please see Figure F.1b). However, Tt25D2 is located approximately 100 feet farther from the trench than EW-1 and Tt25S. These data suggest these wells share a common and significant fracture zone.

5.4.2 Groundwater ORP

The results show a rapid increase in ORP at EW-1 immediately following the permanganate injection (please see Figure F.2). ORP increased from a baseline of approximately -20 mV to over 800 mV approximately one hour after the permanganate injection, and remained at a plateau greater than 800 mV for 18 days. Groundwater sampled approximately six hours after injection was dark purple, clearly indicating the presence of permanganate. Between day 18 and day 23 following permanganate injection, ORP decreased from approximately 800 mV to 450 mV.

No significant increases in ORP indicating the presence of free permanganate ion were observed at the other monitoring wells. Occasional spikes in ORP in Figure F.1 coincide with events where the YSI instrument was removed from the well for sampling and/or calibration while the instrument

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[1] Specific conductivity sensor was later determined to be malfunctioning; no conductivity data are reported.

remained in data logging mode. In some instances the ORP sensor required several hours to re-stabilize.

5.4.3 Groundwater Specific Conductivity

The results show a rapid increase in conductivity in EW-1 from a baseline of approximately 0.8 mS/cm to 3.0 mS/cm over a period of approximately 12 hours following permanganate injection (please see Figure F.3). Specific conductivity at EW-1 remained above baseline levels for a period of approximately 18 days, similar to the plateau period for ORP levels.

An increase in specific conductivity was also observed at Tt25S immediately after the permanganate injection. Specific conductivity increased from a baseline of approximately 0.13 mS/cm to 0.9 mS/cm in a period of approximately three hours following permanganate injection, and returned to baseline levels approximately 30 hours after injection.

No significant changes in conductivity were observed at the other monitoring wells.

5.4.4 Groundwater pH

pH levels decreased at EW-1 immediately following permanganate injection, from a baseline level of approximately 6.0 to a minimum of 3.9 approximately two hours after injection (please see Figure F.4). pH levels rebounded to above 5.0 approximately six hours after injection, and approached the baseline level of 6.0 for through March 21, 2005. A reduction in pH is consistent with production of an 'acid front' likely resulting from oxidation of TCE, PCE, and ferrous iron at the front of the permanganate flow. The front of the permanganate flow becomes concentrated in H^+ as it progresses. Vertical profiling in EW-1 one day after the permanganate injection revealed a depression in pH near the bottom of the well. While it appears that the majority of permanganate enters the well near the top of the well, between 30 and 40 feet bgs, the increased head of the injection and/or the natural downward gradient may have pushed some of the 'acid front' water down into the well.

5.4.5 Groundwater Dissolved Oxygen

A significant increase in dissolved oxygen was observed at EW-1, coincident with the period of elevated ORP and specific conductivity (please see Figure F.5).

Dissolved oxygen concentrations at Tt25S decreased slightly after permanganate injection, from 1.9 mg/L to 1.1 mg/L over a period of approximately 12 hours, then gradually returned to baseline levels in another 12 hours.

5.4.6 Groundwater Temperature

A slight and transient increase in groundwater temperature was observed at EW-1 during the permanganate injection, from 11.55 °C to 11.75 °C (0.2 °C increase). A smaller transient increase in temperature was observed at Tt25S (0.06 °C). These temperature increases are significant compared to baseline.

5.4.7 Summary – Geochemical and Physical Parameters

In summary, EW-1 showed significant, sustained, and concurrent increases in ORP, specific conductivity, and dissolved oxygen concentrations which were clearly a result of permanganate entering the well. A transient decrease in ph was observed, likely the result of acid production during oxidation of TCE and PCE. Transient increases in hydraulic head and temperature were also observed as a result of the injection. Increases in hydraulic head in response to the permanganate injection revealed significant hydraulic connection between EW-1 and TT25S (adjacent to the trench) and Tt25D2 (approximately 100 feet away from the trench).

Monitoring well Tt25S showed a transient increase in specific conductivity, and slight transient decreases in dissolved oxygen and pH. Transient increases in hydraulic head and temperature indicate movement of groundwater through the screened interval of this well during the injection process. However, no change in ORP was observed. The observed transient changes in some parameters with no evidence of permanganate were probably the result of displacement of groundwater in the vicinity of the well during permanganate injection.

5.5 Field Permanganate and Jar Headspace Measurements

Groundwater samples were collected at monitoring wells in the borrow pit area for analysis of permanganate as described above in Section 3.0. Groundwater permanganate results are summarized in Table 2. Permanganate was detected only at EW-1, at maximum concentrations up to approximately 3,000 to 4,000 mg/L, or approximately 15% to 20% of the injection concentration. Concentrations increased rapidly following injection, reaching maximum levels approximately seven to ten days after injection. Groundwater sampling for VOCs and other laboratory parameters at EW-1 and Tt25S bracketed the peak permanganate concentration period to provide data regarding treatment effectiveness, and to provide a measure of time-zero (i.e., lowest) TCE and PCE concentrations as a basis for evaluating rebound of these VOCs after consumption and dissipation of permanganate.

After permanganate concentrations decreased below ~100 mg/L, field analysis of groundwater samples included measurement of jar headspace VOCs to provide an indication of VOC rebound and support the selection of subsequent rebound sampling times and locations. Jar headspace data are summarized in Table 2.

5.6 Evaluation of Groundwater Analytical Results

Groundwater analytical results for selected parameters and samples collected in the borrow pit area from pre-design investigation (PDI) work in 2002 and 2003 through the final treatability sampling round in March 2004 are summarized in Table 3. Concentrations of several VOCs at EW-1 decreased immediately after permanganate injection, and concurrent with the presence of permanganate at EW-1. Accounting for dilution by the permanganate solution of approximately 15% to 20%, the greatest reductions were for TCE (99.9%) and PCE (90%); TCE and PCE together represent approximately 98% of the total VOC mass in groundwater at EW-1. Dilution-corrected reductions in concentrations of carbon tetrachloride (67%), toluene (58%), and trichlorofluoromethane (44%) were also observed during the two week period following permanganate injection. These compounds oxidize very slowly compared to TCE and PCE, and as expected were not considerably reduced in concentration.

Table 3 also shows rebound in concentrations of TCE and PCE at EW-1 after permanganate injection. Concentration rebound occurs as a result of mass transfer from a residual or matrix-adsorbed phase into the aqueous phase after treatment. Rebound can also be caused by advection and dispersion of contaminants into the treated zone from surrounding source material.

Changes in VOC concentrations from baseline and historical levels at other monitoring wells are assumed to be a result of site-related processes and are unrelated to the permanganate injection because:

1. permanganate was not detected;
2. there was no substantial change in ORP;
3. there was no substantial increase in total or dissolved manganese concentrations, and
4. there was no substantial increase in potassium concentrations.

Slight increases in total and dissolved manganese were observed at Tt25S after the permanganate injection, however these increases were small (100 to 200 µg/L). Elevated levels of potassium were detected at wells Tt25I2, Tt25D2, and Tt25D1 on march 22, 2005, in the range of 50,800 µg/L to 54,500 µg/L. Baseline potassium data are not available for these well locations, however baseline pH data suggest that water in these wells may be impacted by dissolution of hydroxides (typically calcium, sodium, and potassium) from the cement grout seals, which may explain the presence of ~50 mg/L potassium found in water from these wells.

Monitoring results from EW-1 (Table 3), where permanganate was clearly detected and where VOC concentrations clearly decrease, are discussed and analyzed in more detail below. Analysis focuses particularly on permanganate decay (half life) and VOC rebound.

5.6.1 Molar Concentration Analysis

Laboratory analytical results for total potassium, total and dissolved manganese, TCE, PCE are plotted together with field permanganate results in Figure H.1 (Attachment H). Results are plotted in molar concentrations for comparison. One mole of potassium permanganate contains one mole of potassium, and one mole of permanganate ion (measured as permanganate ion or dissolved manganese). Except for the first post-injection laboratory results for manganese, field permanganate and laboratory dissolved manganese results correlate reasonably well. Permanganate concentrations estimated from specific conductivity also correlate reasonably well with field and laboratory data. The reason for the discrepancy between field permanganate and laboratory manganese in the February 4, 2005 sample is unknown.

Data in Figure G.1 show that as permanganate concentrations declined at EW-1 between February 14 and March 4, 2005, potassium (tracer) concentrations remained relatively steady while TCE and PCE concentrations rebounded. After March 4, potassium concentrations fell by approximately 60%

(dilution), indicating movement of 'untreated' groundwater into the area of EW-1. During this period, TCE and PCE concentrations returned to levels at or near baseline.

The data from February 16 through March 4 (shaded area in Figure G.1) is of particular interest because potassium concentrations appear relatively steady (potassium is assumed to be a relatively inert tracer for the injection), indicating relatively static conditions in the vicinity of EW-1. During this period, permanganate concentrations (as field permanganate and as dissolved manganese) are relatively low and slowly decreasing, while PCE and TCE concentrations are rebounding. Provided that the decay of tracer (potassium) is negligible compared to the decay and rebound of other constituents, the effects of groundwater advection and dispersion may also be assumed negligible and a simple exponential decay/rebound analysis may be performed.

5.6.2 Permanganate Decay

The shaded region of Figure G.1 is presented in Figure G.2 with approximations of half lives for potassium and permanganate, assuming exponential decay in concentrations. The analysis is performed using the following equation for first-order decay:

$$C/C_o = e^{-(\ln 2/\lambda)t}$$

where;
C = concentration at time t,
C_o = concentration at time 0,
e = exponential function,
λ = half life, and
t = elapsed time.

The estimated half-life for potassium between February 16 and March 4 (Figure G.2) is approximately 116 days. Estimated half-life for permanganate during the same period is much shorter, approximately 3.6 to 7.0 days. This estimate is conservative, because the apparent rate of decrease in permanganate concentrations between February 10 and February 16 is significantly greater.

5.6.3 Rebound Analysis

Concentration rebound following treatment is a mass transfer process in which the contaminant sink (in this case oxidation by permanganate) becomes depleted, and the rate of reaction can no longer keep pace with the rate of mass transfer from the matrix (e.g., diffusion from residual phase and/or the matrix itself). Concentration rebound is also caused by movement of contaminant mass by advection and dispersion.

Rebound rates for TCE and PCE at EW-1 are approximated in Figure G.1 by zero-order rate constants (i.e., $\Delta C/\Delta t$). In reality, the observed rebound rate is a function of the aqueous VOC concentration and the concentration of available oxidant, and therefore can vary with time. This is evidenced in Figure G.2 by the apparent increase in observed rebound rates for both TCE (~10 fold increase) and PCE (~3-fold increase) as available permanganate concentrations decrease. Rebound rates during the period from February 14 and March 4, which is characterized by relatively low permanganate concentrations and relatively static tracer concentrations, provide the best indication of mass transfer rates of PCE and TCE from residual and/or adsorbed phases in the vicinity of EW-1.

The rebound rate for TCE during this period is approximately 29 µg/L/day, which is small relative to the baseline concentration. This suggests that a significant fraction of residual TCE mass in the area of EW-1 was treated. Between March 4 and March 21, the TCE rebound rate increased dramatically to 1,500 µg/L/day. Based on the amount of reduction (dilution) in potassium concentrations during this period, this rebound can be explained by migration of groundwater containing TCE into the area of EW-1. Potassium was diluted by a factor of approximately 2.5, so an increase in TCE concentration from 530 µg/L to 26,000 µg/L during the same period can be accounted for by proportional mixing with upgradient groundwater with a TCE concentration of approximately 65,000 µg/L, which is well within the range of historical concentrations at EW-1.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions from treatability testing are summarized below.

1. Approximately 98% of the groundwater VOC mass in the former borrow pit area is amenable to rapid oxidation by permanganate.
2. The oxidant demand of the native bedrock is very low. A maximum oxidant demand of 1.2 g potassium permanganate per Kg rock was determined from bench scale testing. However, oxidant demand by massive bedrock is likely dominated by surface reactions, and therefore is more a function of fracture surface area than bedrock mass. The actual oxidant demand per unit mass of bedrock at he Crossley Farm site is on average likely to be significantly less than 1.2 g/Kg.
3. Open bedrock trenches may allow rapid delivery of very large volumes of oxidant to the subsurface. Transport of 5,000 gallons of oxidant to the shallow, highly fractured bedrock was rapid. However, once the oxidant reaches this zone, subsequent transport is limited by natural gradients.
4. Evidence of potassium permanganate was observed at intermediate bedrock monitoring well EW-1 (approximately 10 feet from the trench, open rock from 30 feet to 150 feet below ground) within one hour of completing permanganate injection. This was the only monitoring well clearly indicating the presence of permanganate, and the only monitoring well showing significant reductions in VOC concentrations. Reductions in concentrations of TCE (99.9%) and PCE (90%) were observed at EW-1 three days after permanganate injection.
5. There was no evidence of permanganate transport to deep bedrock monitoring well EW-2, located approximately 20 feet from the trench with open rock from 158 feet to 338 feet below ground.
6. Evaluation of the lateral movement of permanganate in the subsurface was limited by the distance between the trench and surrounding monitoring locations. After EW-1, the next

closest intermediate bedrock monitoring well (Tt25 cluster) is approximately 100 feet from the trench. Nonetheless, sufficient data were collected to evaluate treatment effectiveness by permanganate, and potential application scenarios.

7. The relatively small rate of rebound in TCE concentrations of 29 μg/L/day under source-rebound conditions (i.e., not influenced by migration of TCE from upgradient) indicates significant removal of residual TCE mass in the vicinity of EW-1, where permanganate was effectively delivered.
8. Analysis of permanganate decay rates under source-rebound conditions indicated a half life in the range of 3.6 to 7 days. Half life data may be used to estimate time periods between larger scale permanganate injections under mass transfer limited conditions. Alternatively, permanganate half life and VOC rebound data may be used to evaluate scenarios for maintaining a stoichiometrically derived permanganate concentration within an induced gradient application scenario (e.g., during pumping).
9. Groundwater at the site has limited buffering capacity. As evidenced at EW-1, rapid oxidation of a large mass of VOCs can be expected to cause transient but significant reductions in pH. The effects of changes in groundwater pH on the mobility of metals and the design of future remedies should be considered.

Data from the initial trench application provide credible evidence that permanganate is capable of source VOC mass reduction at the Crossley Farm site. Because the borrow pit area lies near a hydraulic divide, and because a groundwater extraction and re-injection system is planned for the former borrow pit area as part of the remedy, options for delivery and distribution of permanganate to the subsurface should involve the use of pumping to control the distribution of permanganate. Applications emulating the initial treatability study injection, or even the proposed alternative injection at a vertical well, rely on natural gradients for permanganate distribution. Compared to induced gradients during pumping, natural gradients are typically small, and flow paths controlled by natural gradients may be limited. Furthermore, groundwater velocities under natural gradients may not be capable of taking full advantage of the relatively rapid kinetics of chemical oxidation during source treatment.

Injection of permanganate to the upper bedrock zone (<100 feet) may be accomplished using trenches cut into exposed bedrock and/or vertical injection wells. Trenches may afford the ability to quickly inject large volumes of oxidant to the shallow bedrock zone, while injection rates at wells are expected to be slower. Trench injection of permanganate would still rely on the use of pumping wells to directionally distribute permanganate once it reaches the saturated zone. To reach the deeper bedrock zones (>100 feet), injection will likely be required at vertical wells. Packer systems and/or specially constructed wells may be used to isolate permanganate flow to discrete fractures or fracture zones.

Distribution of permanganate after injection is likely to be best controlled by pumping and recirculation. Under this scenario, the concentration of permanganate and the zones of treatment can be controlled. Although the directional flow between wells (lateral and vertical) will be controlled by the orientation of significant fractures, extraction and injection locations and flow rates can be determined to take advantage of these flow paths.

Groundwater analytical data indicate TCE concentrations in excess of 10% aqueous solubility (and in some cases in excess of 50% of aqueous solubility) indicating non-aqueous TCE throughout the borrow pit area. To evaluate costs for various permanganate injection and/or recirculation scenarios, a better understanding of the total VOC mass in the former borrow pit area is needed, along with an understanding of the spatial distribution of that mass. Because oxidant demand by the bedrock is limited, oxidant costs for treating source VOCs in the borrow pit area will be determined largely by the mass of VOCs present.

The highest TCE concentrations are generally found in the deepest wells within and downgradient of the borrow pit area (i.e., EW-2, Tt25D1, EW-4). However, higher dissolved concentrations do not necessarily indicate greater VOC mass in the deep bedrock. The degree of fracturing and the transmissivity of the deeper rock are very low, suggesting limited available pore volume for residuals, and the potential for more intimate contact of residual TCE with groundwater. VOC concentrations in the deep bedrock zone are also less likely to be reduced by the diluting effects of recharge than in the shallow bedrock. The effects of low transmissivity, low pore volume, and low dilution by recharge may work together to create higher dissolved TCE concentrations in the deep bedrock than in the shallow bedrock, with less regard to the relative distribution of TCE mass.

An analysis of the potential range of VOC mass (as TCE) is provided in Attachment J. The intent of this analysis is to provide upper and lower range estimates of the potential mass of residual TCE in the borrow pit area, and the corresponding range of costs. The analysis approximates plume volumes based on the contour lines in Figures 4, 5, and 6 of the RFP. No site specific data are available for fracture porosity and residual DNAPL saturation, therefore upper and lower ranges of these parameters are estimated. Fracture porosity values are assumed for each rock type encountered in the borrow pit area (shallow weathered gneiss, shallow to intermediate moderately fractured gneiss, and deep poorly fractured gneiss). Upper and lower ranges of TCE residual retention within the plume areas greater than 100,000 μg/L TCE and 10,000 μg/L are also assumed.

The resulting range of TCE bulk retention values calculated from these assumptions, summarized in Table 4, span approximately three orders of magnitude within the 100,000 μg/L and 10,000 μg/L contours. Thus, the approximation of potential TCE mass spans three orders of magnitude, ranging from approximately 4,300 pounds to 430,000 pounds The corresponding upper and lower cost range for potassium permanganate (material only) is approximately $350K to $2,385K; a potential difference of up to $2,000K (likely a worst case scenario).

Given the large potential difference between the upper and lower cost range for oxidant, which stems from the broad range in potential TCE mass, site specific data should be collected to provide a better estimate of residual VOC mass. These site specific data will be used to evaluate scale and costs for chemical oxidation treatment in the borrow pit area. Measurement of VOC mass in situ may be evaluated using more controlled permanganate injection schemes that allow determination of the mass balance of both tracer and permanganate. In essence, the mass balance of injected/extracted conservative tracer is used to estimate the mass of permanganate consumed by reaction with TCE, which can be determined by stoichiometry, and by reaction with the bedrock fracture surfaces, which can be approximated based on rock oxidant demand.

Controlled permanganate injection/extraction testing may be performed at a single well (i.e., push-pull test) or at a series of wells by injecting and extracting at different locations (i.e., inter-well circulation test). A list of advantages and disadvantages in comparing each test approach as they may be applied at the Crossley Farm site is summarized below.

Single Well Push-Pull Test

Advantages:

- Minimal equipment
- Short duration (1 – 3 days)
- Relatively low cost
- Can use existing wells
- Estimate of VOC mass destruction and rock oxidant demand
- Low oxidant volume needed

Disadvantages:

- Area of evaluation limited to vicinity of test well
- Investigation derived waste (IDW) is generated, however the volume can be controlled by the parameters of the test

Inter-well Circulation Test

Advantages:

- Larger aquifer volume is evaluated
- May provide better estimate of VOC mass destruction and rock oxidant demand
- Provides evaluation of oxidant distribution
- Relatively simple equipment

Disadvantages:

- Will likely require the installation of at least one additional well
- Sufficient fracturing and interconnectivity between wells needs to be confirmed before testing
- Longer test durations (1 – 2 weeks)
- Larger volume of oxidant is needed, and larger volume of IDW is generated
- Cost is greater than a single well push-pull test

The advantages of each type of test are basically similar, except that the inter-well test can evaluate a larger volume of aquifer. The test volume limitation of the push-pull test may be overcome by performing tests at multiple locations. In doing so, the overall duration of testing will increase, however no additional wells will be needed, and the volume of IDW and testing costs can be controlled by test parameters and the scope of work.

In summary, the following steps are recommended for developing design criteria for the use of permanganate to reduce VOC mass in the borrow pit area:

1. Evaluation of the nature and extent of VOC source mass.
2. Evaluate location and orientation of dominant fracture zones and flow paths in relation to source VOC mass.

Alternatives for conducting these evaluations were discussed in our April 18, 2005 meeting with TtNUS and USEPA Region III. A FLUTe™ liner may be used by TtNUS at open bedrock wells to identify specific depths where residual VOCs may reside in fractures. In addition, down-hole and hydraulic testing may be performed to evaluate fracture zones, hydraulic interconnectivity between wells, and dominant flow paths. The performance of a series of single well push-pull tests using permanganate and a conservative tracer is recommended to quantitatively evaluate the mass and distribution of VOCs in the borrow pit area. Results of FLUTe™ testing and hydraulic analyses may be used to identify well locations and specific depth intervals for performing push-pull testing. In taking this approach, push-pull testing efforts may be focused on locations and zones of particular interest.

These data, along with data collected from previous phases of the treatability study, will provide a basis for describing and evaluating alternatives for implementing chemical oxidation for source treatment. This analysis will include conceptual design parameters for full scale application, and preliminary cost information as called for in the Contract Scope of Work. A conceptual scope of work for performing push-pull testing is outlined in Attachment K.

Tables

Table 1. Field Activity Summary
Crossley Farm Super Fund Site
Huffs Church, PA
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Site Visit Date	Injection Event	Install Data Logger	Remove Data Logger	Download Data Logger	Discrete Paramater Readings	Vertical Profile Wells	New Instrument Calibration	Calibration Check	Instrument Recalibration Required	Sampling and Analysis			
										Field Permanganate	Field Chloride	Field Headspace	Laboratory Analytical
12/16/2004		EW-1s, EW-1d Tt25S					EW-1s, EW-1d Tt25S						
12/20/2004	NaCl Injection			EW-1s, EW-1d Tt25S									
12/21/2004		Tt25I2 Tt25D2	EW-1s, EW-1d	EW-1s, EW-1d Tt25S				Tt25I2 Tt25D2					
12/22/2004		Tt27S, Tt27I EW-3, EW-4	Tt25S, Tt25I2 Tt25D2	Tt25S, Tt25I2 Tt25D2			EW-4						
12/23/2004				Tt27S, Tt27I EW-3, EW-4									
12/28/2004				Tt27S, Tt27I EW-3				Tt27S, Tt27I EW-3	Tt27I				
12/30/2004				Tt27S, Tt27I EW-3									
1/4/2005				Tt27S, Tt27I EW-3, EW-4				EW-4					
1/5/2005			Tt27S, Tt27I EW-3, EW-4	Tt27S, Tt27I EW-3, EW-4	EW-1, EW-2, Tt25S, Tt25D2, Tt25I1, Tt25I2								
1/17/2005 through 1/21/2005					EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2								EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2
1/20/2005		EW-1, Tt25S					EW-1, Tt25S Tt25I2, Tt25D2						
1/21/2005		Tt25I2, Tt25D2				EW-1,, Tt25S Tt25I2, Tt25D2							
1/25/2005				EW-1, Tt25S, Tt25I2, Tt25D2									
1/31/2005				EW-1, Tt25S, Tt25I2, Tt25D2									
2/1/2005	Permanganate Injection	EW-2, Tt25I1					EW-2, Tt25I1			EW-1, Tt25S			
2/2/2005				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2		EW-1, EW-2				EW-1, Tt25S,			Tt25S
2/3/2005				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2			

Table 1. Field Activity Summary
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Site Visit Date	Injection Event	Install Data Logger	Remove Data Logger	Download Data Logger	Discrete Paramater Readings	Vertical Profile Wells	New Instrument Calibration	Calibration Check	Instrument Recalibration Required	Sampling and Analysis			
										Field Permanganate	Field Chloride	Field Headspace	Laboratory Analytical
2/4/2005				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2			EW-1
2/7/2005			EW-2	EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	Tt25I2 (pH only)	EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2			
2/8/2005		EW-2					EW-2						
2/10/2005				EW-1, Tt25S, Tt25D2, Tt25I1, Tt25I2						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2			
2/14/2005				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2			
2/16/2005													EW-1
2/18/2005				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2			Tt25S
2/22/2005				EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-2		
2/24/2005		EW-2 replaced with EW-1 Sonde	EW-1, Tt25S Tt25I2	EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2				EW-2, Tt25I1 EW-1, Tt25D2		EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-1, EW-2, Tt27I, Tt27S, EW-5		EW-2
3/1/2005				EW-2, Tt25D2, Tt25I1						EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-2	EW-1, EW-2, Tt25S	
3/4/2005					EW-1, Tt25S Tt25I2								EW-1
3/8/2005				EW-2, Tt25D2, Tt25I1	EW-1, Tt25S Tt25I2					EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-1, EW-2, Tt25S	
3/14/2005				EW-2, Tt25D2, Tt25I1								EW-1, EW-2, Tt25S	
3/15/2005				EW-2, Tt25D2, Tt25I1	EW-1, Tt25S Tt25I2			EW-2, Tt25D2, Tt25I1	Tt25D2 (pH only)	EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2	EW-1, EW-2, Tt25S	
3/17/2005			EW-2, Tt25D2, Tt25I1	EW-2, Tt25D2, Tt25I1									
3/18/2005					EW-1								EW-1
3/21/2005 through 3/25/2005					EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2								EW-1, Tt25S, EW-2, Tt25D2, Tt25I1, Tt25I2

Table 2. Field Measurements of Permanganate and Jar Headspace VOCs
Crossley Farm Superfund Site
Huffs Church, PA

Date Time	Field Permanganate Ion measurements (mg/L)									Head Space Analysis (PID ppm reading)		
M/D/Y	EW-1	EW-2	EW-5	Tt25S	Tt25I1	Tt25I2	Tt25D2	Tt27S	Tt27I	EW-1	EW-2	Tt25S
2/1/2005 11:00	0											
2/1/2005 16:00	742.5			<1								
2/2/2005 9:45	1260			<1								
2/2/2005 12:40	1035											
2/2/2005 14:25	1645											
2/3/2005 9:50	990											
2/3/2005 10:50	1610											
2/3/2005 14:00	1040	<1		<1	<1	**	<1					
2/3/2005 15:20	605											
2/3/2005 14:00	1300											
2/4/2005 10:30	1395	<1		<1	<1	**	<1					
2/4/2005 13:45	2045											
2/7/2005 11:50	2090	<1		<1	<1	**	<1	**	**			
2/7/2005 15:45	2070											
2/10/2005 10:15	4440	1.2		<1	**	**	<1	**	**			
2/10/2005 10:15	2750											
2/10/2005 15:30	3510											
2/14/2005 10:30	1010	<1		<1	**	**	<1					
2/14/2005 11:30	1090											
2/16/2005 14:10	126.5	<1		<1	<1	**	<1					
2/18/2005 13:45	121	<1		<1	<1	<1	**					
2/22/2005 13:45	15.4	<1		<1	<1	**	<1					
2/24/2005 14:30	13.4	**	<1	<1	**	**	<1	<1	**			
3/1/2005 13:30	16.9	<1		<1	<1	<1	<1			>2,000	>2,000	>2,000
3/4/2005 12:10	14.8	<1		<1	<1	<1	<1			194	>2,000	>2,000
3/8/2005 10:15	6	<1		<1	<1	<1	<1			1,609	>2,000	>2,000
3/15/2005 12:40	<1	<1		<1	<1	<1	<1			7,832 (D)	180,800 (D)	191,800 (D)

Sampled with single check-valve bailer

Sampled with double check-valve bailer

▨ Sampled with Grundfos redi-flo 2 pump

** - Sample cloudy and white, no purple tint indicating permanganate.

Blank cells = not sampled.

(D) - Groundwater samples diluted to obtain reading within range of PID.

Table 3. Analytical Results Summary
Crossley Farm Superfund Site
Huffs Church, PA
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EW-1		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI	1/16/2003	4000	120000	48	58	1400	130	15	110	ND	1010		256		165		1.85	ND
PDI	4/25/2003	4400	73900	31.4	77.8	1700	99	15.6	9906	–			–		–		–	–
Baseline	**1/17/2005**	**4000**	**42000**	**60**	**44**	**540**	**52**	**8**	**40**	**3.14**			**1390**	**1460**	**2310**	**1240**	**117**	**0.0981**
EW-1-01	2/4/2005	360	38	16	20	510	18	U (50)	U (50)		406000	421000	118000	83400	100 U	100 U	267	25.4
EW-1-02	2/16/2005	810	76	U (50)	12	250	22	U (50)	24		83200	75700	33500	24800	1630	77.3	175	6.15
EW-1-03	3/4/2005	2500	530	U (250)	29	420	47	U (250)	28		75800	74800	11300	5440	6020	46.7	171	7.3
EW-1-final	3/21/2005	4300	26000	71	17	350	43	13	60	–	30100	–	4570	4920	7150	–		3.33
Tt25S		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	10/29/2002	10000	500000	180	170	6200	110	41	250	–	–	–	–	–	–	–	–	–
Baseline	**1/17/2005**	**990**	**42000**	**160**	**140**	**450**	**840**	**86**	**560**	**5.45**			**188**	**215**	**85.7**	**55.5**	**17.1**	**0.0479**
Tt-25S-01	2/2/2005	7200	260000	U (5,000)	U (5,000)	4900	U (5,000)	U (5,000)	U (5,000)		3540	4450	421	449	1930	156	53.9	0.5 U
Tt-25S-02	2/18/2005	13000	600000	U (25,000)	U (25,000)	6300	U (25,000)	U (25,000)	U (25,000)		2580	2230	302	270	231	105		
Tt-25S-final	3/21/2005	18000	770000	260	710	12000	430	73	550	–	1920	–	198	202	74.1	–		
EW-2		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	1/17/2003	3600	690000	1500	110	6100	550	27	190	7.7	1960		7.2		175		14.5	–
PDI	4/25/2003	3200	814000	1400	47	7940	600	31.7	199.9	–	–		–		–		–	–
Baseline	**1/20/2005**	**1300**	**230000**	**1200**	**32**	**2200**	**410**	**24**	**51**	**8.69**			**103**	**50.2**	**5770**	**27.1**	**15.6**	**0.127**
EW-2-01	2/24/2005	5100	810000	U (50,000)	U (50,000)	8500	U (50,000)	U (50,000)	U (50,000)		8260	8330	119	93.3	3410	417	53.4	0.5 U
EW-2-final	3/21/2005	2700	370000	1100	U (200)	3500	280	U (200)	120	–	6320	–	126	116	2570	–		
Tt25I1		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	10/28/2002	3500	63000	18	16	600	94	3	10	–	–		–		–		–	–
Baseline	**1/18/2005**	**310**	**6100**	**U (50)**	**U (50)**	**44**	**U (50)**	**U (50)**	**U (50)**	**0.811**			**75**	**74.6**	**235**	**49.3**	**3.33**	**0.015 U**
Tt-25I1-final	3/21/2005	4800	76000	20	23	930	150	9	38	–	3850	–	109	113	33.3	–		
Tt25I2		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	10/30/2002	5600	110000	ND	ND	920	ND	ND	ND	–	–		–		–		–	–
Baseline	**1/17/2005**	**1300**	**33000**	**41**	**19**	**1100**	**240**	**11**	**55**	**6.62**			**17.7**	**11.8**	**261**	**78.2**	**2.62**	**0.0415**
Tt-25I2-final	3/22/2005	1500	31000	U (100)	U (100)	460	98	U (100)	U (100)	–	51400	–	71.3	4.9	992	–		
Tt25D2		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	10/30/2002	12000	510000	140	ND	5400	570	ND	ND	–	–		–		–		–	–
Baseline	**1/18/2005**	**2700**	**110000**	**140**	**46**	**3000**	**420**	**23**	**140**	**6.95**			**9.9**	**8.2**	**128**	**77.2**	**6.88**	**0.0686**
Tt-25D2-final	3/22/2005	5200	190000	120	U (200)	2200	320	U (200)	100	–	50800	–	5.7	0.63	172	–		
Tt25D1		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	10/30/2002	ND	1300000	ND	ND	16000	ND	ND	ND	–	–		–		–		–	–
Baseline	**1/18/2005**	**47**	**280000**	**11**	**0.86**	**3900**	**11**	**0.23**	**1.2**	**8.72**			**12.5**	**9.9**	**259**	**104**	**8.49**	**0.0676**
Tt-25D1-final	3/22/2005	2600	620000	1000	120	12000	850	U (200)	93	–	54500	–	21.7	1.2	456	–		
EW-3		**PCE**	**TCE**	**cDCE**	**CT**	**TCFM**	**T**	**E**	**X**	**TOC**	**K (T)**	**K (D)**	**Mn (T)**	**Mn (D)**	**Fe (T)**	**Fe (D)**	**Cl (mg/L)**	**Br (mg/L)**
PDI	1/20/2003	1800	33000	ND	ND	420	ND	ND	ND	ND	1480		68.3		ND		6.08	ND
Baseline	**1/19/2005**	**3700**	**93000**	**U (50)**	**37**	**1400**	**U (50)**	**U (50)**	**U (50)**	**2**			**66.5**	**71.5**	**1030**	**56.8**	**3.7**	**0.0345**
EW-3-final	3/22/2005	950	18000	U (100)	U (100)	200	U (100)	U (100)	U (100)	–	2020	–	24.9	24.6	635	–		

Table 3. Analytical Results Summary
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Huffs Church, PA
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EW-4		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI	1/22/2003	6100	420000	ND	ND	ND	ND	ND	ND	3.4	1840		69.8		784		7.7	ND
PDI	4/25/2003	4960	235000	377	5.6	2170	408	22.1	121.5	–	–		–		–		–	–
Baseline	**1/20/2005**	**3500**	**150000**	**120**	**21**	**1900**	**110**	**24**	**51**	**2.01**			**131**	**102**	**2880**	**67.2**	**3.34**	**0.0329**
EW-4-final	3/22/2005	6100	210000	140	U (200)	2600	140	U (200)	U (200)	–	1840	–	104	111	885	–		

Tt27S		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI	10/28/2002	1900	68000	8	5	180	ND	ND	ND	–	–		–		–		–	–
Baseline	**1/18/2005**	**92**	**870**	**U (2.5)**	**U (2.5)**	**6.6**	**1.1**	**U (2.5)**	**U (2.5)**	**1.05**			**13.7**	**15.3**	**23.4**	**87.8**	**5.1**	**0.0461**
Tt-27S-final	3/21/2005	83	1000	U (10)	U (10)	8	U (10)	U (10)	U (10)	–	1790	–	4.6	5.3		–		

Tt27I		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI	10/28/2002	210	15000	1	3	65	ND	ND	ND	–	–		–		–		–	–
Baseline	**1/19/2005**	**780**	**52000**	**33**	**21**	**730**	**U (25)**	**U (25)**	**U (25)**	**1.2**			**21.5**	**26.9**	**157**	**193**	**4.77**	**0.101**
Tt-27I-final	3/21/2005	1300	81000	45	U (200)	1100	U (200)	U (200)	U (200)	–	1960	–	15	14	94.4	–		

Tt24I		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI	10/28/2002	1700	64000	18	25	690	ND	ND	ND	–	–		–		–		–	–
Baseline	**1/19/2005**	**1600**	**45000**	**U (25)**	**U (25)**	**490**	**5**	**U (25)**	**U (25)**	**1.44**			**70.7**	**56.2**	**1660**	**90.5**	**6.58**	**0.0368**
Tt-24I-final	3/22/2005	1400	33000	U (200)	U (200)	500	U (200)	U (100)	U (100)	–	2180	–	64.2	64.6	234	–		

EW-5		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI	1/21/2003	1400	22000	ND	ND	ND	ND	ND	ND	ND	1310		14.9		ND		3.64	ND
Baseline	**1/20/2005**	**280**	**5400**	**1.8**	**1.2**	**57**	**U (2.5)**	**U (2.5)**	**U (2.5)**	**0.599**			**13.2**	**17.7**	**103**	**48.7**	**2.73**	**0.0203**
EW-5-final	3/24/2005	620	10000	4	3	140	U (10)	U (10)	U (10)	–	1350	–	9.4	9.1	63.8	–		

Tt20I		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI/RI	10/24/2002	860	22000	4	3	190	ND	ND	ND	–	–		–		–		–	–
Baseline	**1/20/2005**	**310**	**6500**	**U (50)**	**U (50)**	**43**	**12**	**U (50)**	**U (50)**	**0.761**			**12.6**	**11.2**	**239**	**34.4**	**2.66**	**0.0299**
Tt-20I-final	3/24/2005	330	5800	U (10)	U (10)	64	U (10)	U (10)	U (10)	–	1260	–	4.4	3.3	117	–		

Tt-26I		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI/RI		2100	69000	20	21	760	U	U	U									
Tt-26I-final	3/24/2005	1600	34000	U (200)	U (200)	470	U (200)	U (200)	U (200)	–	1240	–	10.7	10.1	95.9	–	–	–

Tt-26D1		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI/RI		4200	420000	U	U	4200	U	U	U									
Tt-26D1-final	3/24/2005	4900	230000	500	44	3400	440	U (200)	92	–	2110	–	26.8	20.7	365	–	–	–

Tt-26D2		PCE	TCE	cDCE	CT	TCFM	T	E	X	TOC	K (T)	K (D)	Mn (T)	Mn (D)	Fe (T)	Fe (D)	Cl (mg/L)	Br (mg/L)
PDI/RI		3300	140000	U	U	1500	U	U	U									
Tt-26D2-final	3/24/2005	3300	130000	93	47	1900	U (200)	U (200)	U (200)	–	2120	–	47.1	15.8	1640	–	–	–

NOTES

All concentrations are in ug/L unless otherwise noted.

PCE = Tetrachloroethene
TCE = Trichloroethene
cDCE = cis 1,2-Dichloroethene
CT = Carbon Tetrachloride
TCFM = Trichlorofluoromethane
T = Toluene
E = Ethylbenzene
X = Total Xylenes
TOC = Total Organic Carbon
(T) = Total
(D) = Dissolved

Table 4. Range of TCE Bulk Retention Values - Mass Estimate

Crossley Farm Superfund Site
Huffs Church, PA

		Fracture porosity						
		2.00%	**0.20%**	**0.50%**	**0.05%**	**0.10%**	**0.01%**	**Plume Area**
DNAPL retention as % of porosity	**0.03%**	6.00E-06	6.00E-07	1.50E-06	1.50E-07	3.00E-07	3.00E-08	>10,000 ug/L - LOW
	0.3%	6.00E-05	6.00E-06	1.50E-05	1.50E-06	3.00E-06	3.00E-07	>10,000 ug/L HIGH
	0.8%	1.50E-04	1.50E-05	3.75E-05	3.75E-06	7.50E-06	7.50E-07	>100,000 ug/L LOW
	7.5%	1.50E-03	1.50E-04	3.75E-04	3.75E-05	7.50E-05	7.50E-06	>100,000 ug/L HIGH
		WEATHERED GNEISS - HIGH	**WEATHERED GNEISS - LOW**	MODERATELY FRACTURED ZONE - HIGH	MODERATELY FRACTURED ZONE - LOW	**DEEP ZONE - HIGH**	**DEEP ZONE - LOW**	

Bulk retention values expressed as TCE volume divided by total rock volume (dimensionless).

Attachment A
Initial Pilot Sampling Plan, January 13, 2005

XPERT
DESIGN
AND
DIAGNOSTICS, LLC
1275 GLENLIVET DR., SUITE 100, ALLENTOWN, PA 18106 TEL: (484) 224-3031 FAX: (484) 224-2999

MEMORANDUM

To: Vincent Ou

From: Matthew Walsh

Re: DRAFT Sampling Plan, Crossley Farm Treatability Study

Date: January 13, 2005

cc: Aaron Norton, XDD
Ken Sperry, XDD

Groundwater samples will be obtained from key wells within and surrounding the treatability study area before and after charging the aquifer with potassium permanganate to characterize the effectiveness, extent, and magnitude of treatment.

Baseline groundwater sampling will be conducted by TtNUS during the week of January 17, 2004 at monitoring wells TT25S, EW-1, EW-2, Tt25I1, Tt25I2, Tt25D1, and Tt25D2 (among others) for the following parameters:

- VOCs - EPA Method 8260B
- Chloride and bromide – EPA Method 300
- Total and dissolved (field filtered) manganese – EPA Method 200.7
- Total and dissolved (field filtered) iron – EPA Method 200.7
- Total Organic Carbon
- SVOCs – EPA Method 8270C (Tt25S and EW-1)

Field parameters (i.e., pH, ORP, conductivity, temperature, and dissolved oxygen) using flow-through cell.

Field analysis of chloride.

Table 1 summarizes typical analytical methods, preservation procedures, and sample container requirements for the above analyses. Sodium thiosulfate quenching of permanganate in VOC samples will only be necessary in post-treatment samples with visual evidence of permanganate (purple in color and visible to the naked eye at a concentration of approximately 1 mg/L). Quenching prevents further VOC oxidation in the sample prior to analysis.

Field chloride data will be evaluated by XDD to confirm NaCl tracer testing results, which are the basis for selecting groundwater monitoring locations and estimating sampling time frames discussed in this plan.

During the week of January 17, 2005, XDD personnel will install four down-hole data logging water quality monitors (YSI Model 600 XLM or equivalent) at the following locations (after they are sampled by TtNUS):

1. TT25S at a depth of approximately 63 feet (lower portion of screen);
2. EW-1 at a depth of approximately 45 feet (highly fractured zone in upper portion of open hole);
3. TT25I2 at a depth of approximately 70 feet (lower portion of screen); and
4. Tt25D2 at a depth of approximately 102 feet (lower portion of screen).

The instruments will monitor and record pH, ORP, conductivity, temperature, and dissolved oxygen. Each meter will be calibrated before installation. Calibration checks and re-calibrations (if necessary) will be performed weekly. Well EW-1 is an open rock hole extending from 30 feet to 150 feet below ground surface. Although the instrument will be positioned at a depth of 45 feet, vertical profiling of field parameters will be performed at approximately 10 foot intervals in the well before and after permanganate injection. The objective of vertical profiling is to evaluate which fracture zone(s) conduct permanganate into the well after the injection.

Potassium permanganate solution for the trench test will be delivered to the site by Colonial Chemicals, Inc. (Colonial) of Tabernacle, NJ under subcontract to XDD. Approximately 5,000 gallons at of solution will be delivered at a concentration of 25 g/L potassium permanganate. Colonial will also add sodium bromide salt to a concentration of approximately 10 g/L to the oxidant solution. Bromide will be used as a tracer to show distribution of the oxidant liquid. A batch analysis sample will be collected by Colonial prior to shipment, and the results of the analysis will be provided to XDD.

The solution will be delivered to the site on the morning of January 25, 2005 at approximately 8:00 AM in a 5,000 gallon tank trailer. Delivery of the oxidant to the trench will be by gravity flow over a period of approximately two to three hours immediately after the tank is delivered. (During the tracer study, 5,000 gallons of NaCl tracer solution infiltrated the trench in a period of approximately two hours). Permanganate solution flow into the trench will be controlled manually such that a positive head is maintained within the trench distribution piping. This will be monitored visually through the manholes. During oxidant delivery, a sample of the permanganate solution will be obtained and analyzed for permanganate using a field colorimeter to document the mass of oxidant delivered to the subsurface.

After the oxidant is injected, monitoring will be performed as follows over a period of up to four weeks:

1. The down-hole water quality instruments will be maintained by XDD to monitor and record pH, ORP, conductivity, temperature, and dissolved oxygen.
2. XDD will monitor for evidence of oxidant breakthrough to the down gradient wells. Groundwater ORP and conductivity are the primary parameters that will provide evidence of oxidant breakthrough.
    a. If an increase in ORP and/or conductivity are observed, the presence of oxidant will be confirmed and measured using a field colorimetric method for permanganate (Hach Method 8034 via the Hach Model DR820 colorimeter), which is sensitive to concentrations of approximately 1 mg/L. the readout will be set to provide concentrations of permanganate ion.
    b. Grab samples of groundwater will be collected for permanganate analysis using battery-powered centrifugal pumps and/or bottom filling dedicated polyethylene bailers. The grab samples will be obtained by lowering the pump or bailer to the approximate depth of the YSI instrument to obtain a sample of groundwater for analysis.
    c. **Based on the results of tracer testing, it is anticipated that permanganate breakthrough will start immediately at EW-1, and *may* be observed within the first 24 hours after injection at wells Tt25S and Tt25D2. Breakthrough at Tt25I2 *may* occur sometime between day 2 and day 10.**
    d. XDD will monitor breakthrough of permanganate in order to determine the appropriate time for initial post-treatment groundwater sampling using the criteria described below.
3. **Groundwater quality sampling and analyses will be conducted by TtNUS.** The objective of the first groundwater sampling event is to evaluate the extent and magnitude of treatment around the time oxidant concentrations begin to decrease from peak levels, or at a designated threshold concentration (i.e., permanganate concentration below the stoichiometric level required to treat the assumed baseline VOC concentration). Under these conditions, VOC concentrations should approach minimum levels. As permanganate becomes depleted, VOC concentrations may begin to rebound if significant residual phase VOCs remain in the formation, thereforethis sampling event represents a time zero point for analysis of rebound. This sampling strategy is depicted in Figure 1.

   a. The criteria for conducting the initial round of groundwater sampling at a monitoring well are as follows:
      i. If the peak permanganate ion concentration exceeds the value in Column A of Table 2, sample groundwater when permanganate concentrations approach the threshold values in Column B of Table 2, or approximately 48 hours after the peak (whichever occurs first);
      ii. Otherwise, sample groundwater when permanganate concentrations have decreased by approximately 20% from peak levels, or approximately 48 hours after the peak (whichever occurs first).

4. The following parameters will be sampled for and monitored as part of the initial sampling at each well when the sampling criteria are met (specifications are summarized in Table 1):
   a. VOCs - EPA Method 8260B (quenched if permanganate is visible)
   b. Chloride and bromide – EPA Method 300
   c. Total and dissolved (field filtered) manganese – EPA Method 200.7
   d. Total and dissolved (field filtered) iron – EPA Method 200.7
   e. Field parameters (i.e., pH, ORP, conductivity, temperature, and dissolved oxygen) using flow-through cell.
5. XDD will continue to maintain and download data from the water quality monitoring instruments, and collect grab samples of groundwater for permanganate analysis for the remainder of the four week monitoring period. Sampling for permanganate analysis will be conducted at a frequency that allows evaluation of the criteria for initial sampling. XDD anticipates monitoring daily for the first week after injection, and then bi-weekly (on average) during the remaining three weeks.
6. To evaluate the extent of rebound in VOCs after the initial sampling event, additional groundwater sampling is recommended at monitoring wells affected by permanganate. The time frames for subsequent groundwater sampling wil be determined from the results of NaCl tracer monitoring (including data collected during the week of January 17, 2005) and the persistence of permanganate during the post-treatment monitoring period.

Table 1. Analytical Parameters, Methods, and Specifications

	Analytical Parameter	**Method**	**Holding Time**	**Preservation Method**	**Container Type(s)**
Lab Analyses (Note 6)	VOCs (Samples with no visible permanganate)	8260B	14 days	HCl, pH<2 cool to 4C	(3) 40-mL glass vials
	VOCs (Samples with visible permanganate)	8260B	7 days	Quench with sodium thiosulfate, cool to 4C **NO HCl**	(3) 40-mL glass vials
	Cl$^-$ and Br$^-$	300.1	28 days	cool to 4C	1-L plastic
	total Mn and Fe	200.7	180 days	HNO3, pH<2	250-mL plastic
	dissolved Mn and Fe	200.7	180 days	field filter, HNO3, pH<2	250-mL plastic
Field Analyses (Note 6)	MnO4$^-$ (XDD)	(Note 1)	NA	NA	NA
	temp.	(Note 2)	NA	NA	NA
	pH		NA	NA	NA
	spec. cond.		NA	NA	NA
	D.O.		NA	NA	NA
	ORP		NA	NA	NA
	water level		NA	NA	NA

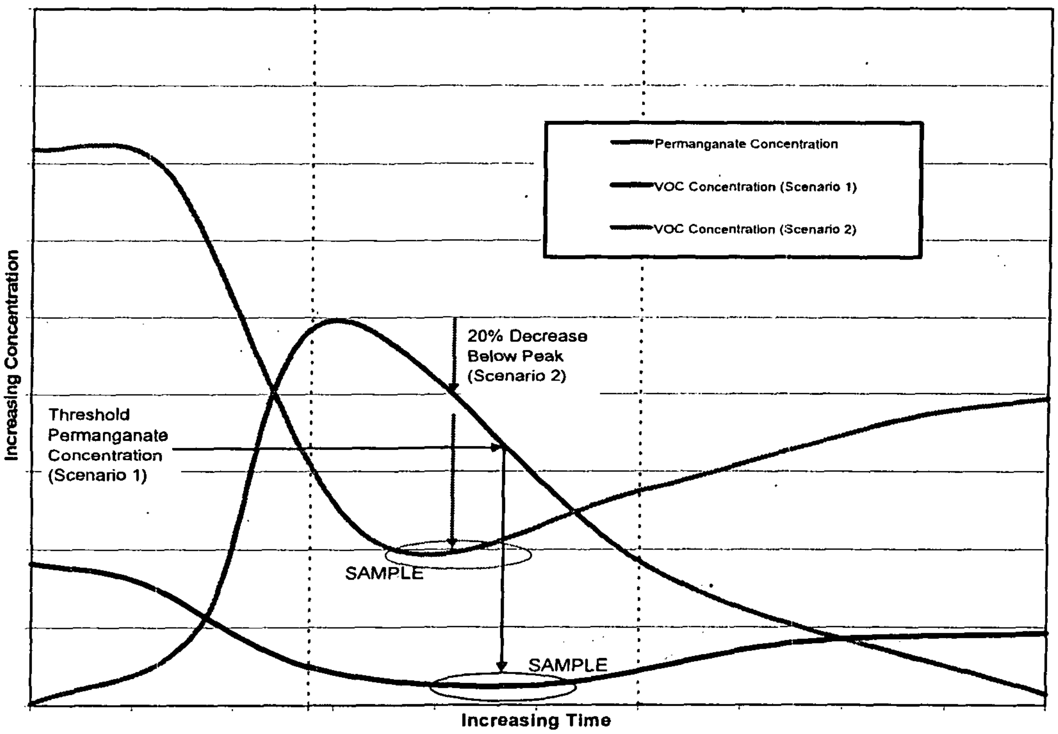
Note 1. Field analysis for permanganate will be performed by XDD using Hach Method 8034 using a hand-held colorimeter (Hach Model DR820).

Note 2. Field parameters will be measured using flow-through cell. Water levels will be measured using an electronic water level indicator.

Table 2. Sampling Criteria for Permanganate Threshold Scenario (Scenario 1, Figure 1)

Monitoring Well	Baseline TCE Concentration (mg/L)	**Column A** If Peak Permanganate Ion Concentration Exceeds: (mg/L)	**Column B** Sample at Theoretical Threshold Permanganate Ion Concentration (mg/L)
EW-1	120	280	220
EW-2	700	1,600	1,260
Tt25S	500	1,100	900
Tt25I1	63	140	110
Tt25I2	100	230	180
Tt25D2	510	1,150	920

FIGURE 1. Sampling Strategy Illustration



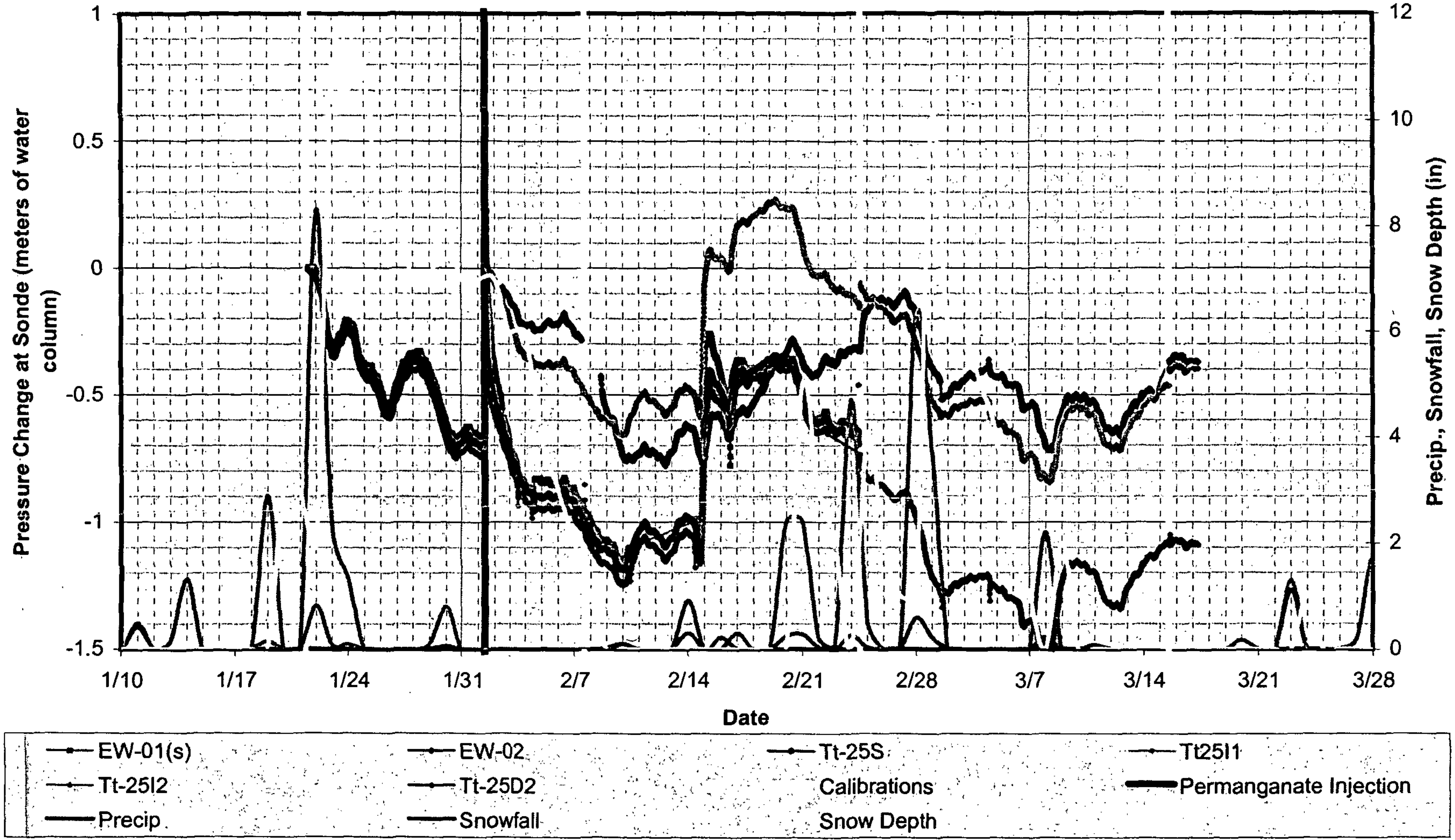
Summary of Evaluations

Site: Arrowhead
WA NO.: 015ROBE03Q9

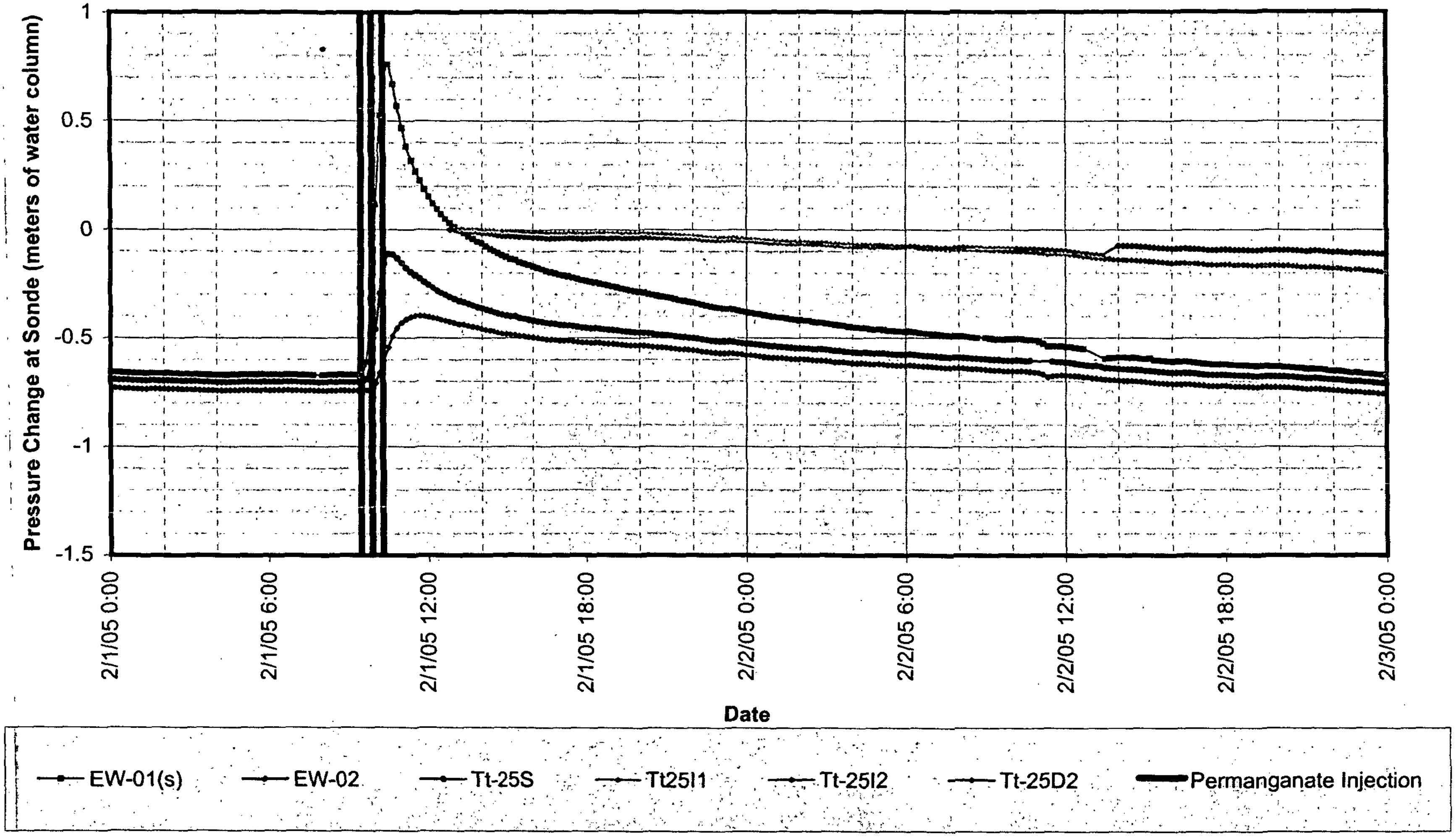
RACs PEB No.	LOE Expended	Overall Score	Weighed LOE
4	148	2	74
5	338.5	3	253.9
6	248.5	4	248.5
7	292	4	292
8	219	3	164.3
9	220	4	220
10	110.5	2	55.3
11	249	3	186.8
12	283	4	283
13	66	3	49.5
14	37	3	27.8
15	31	3	23.3
16	26	3	19.5
17	1.5	3	1.1
TOTALS:	2270	3.3	1899

Attachment F
Data Logger Results

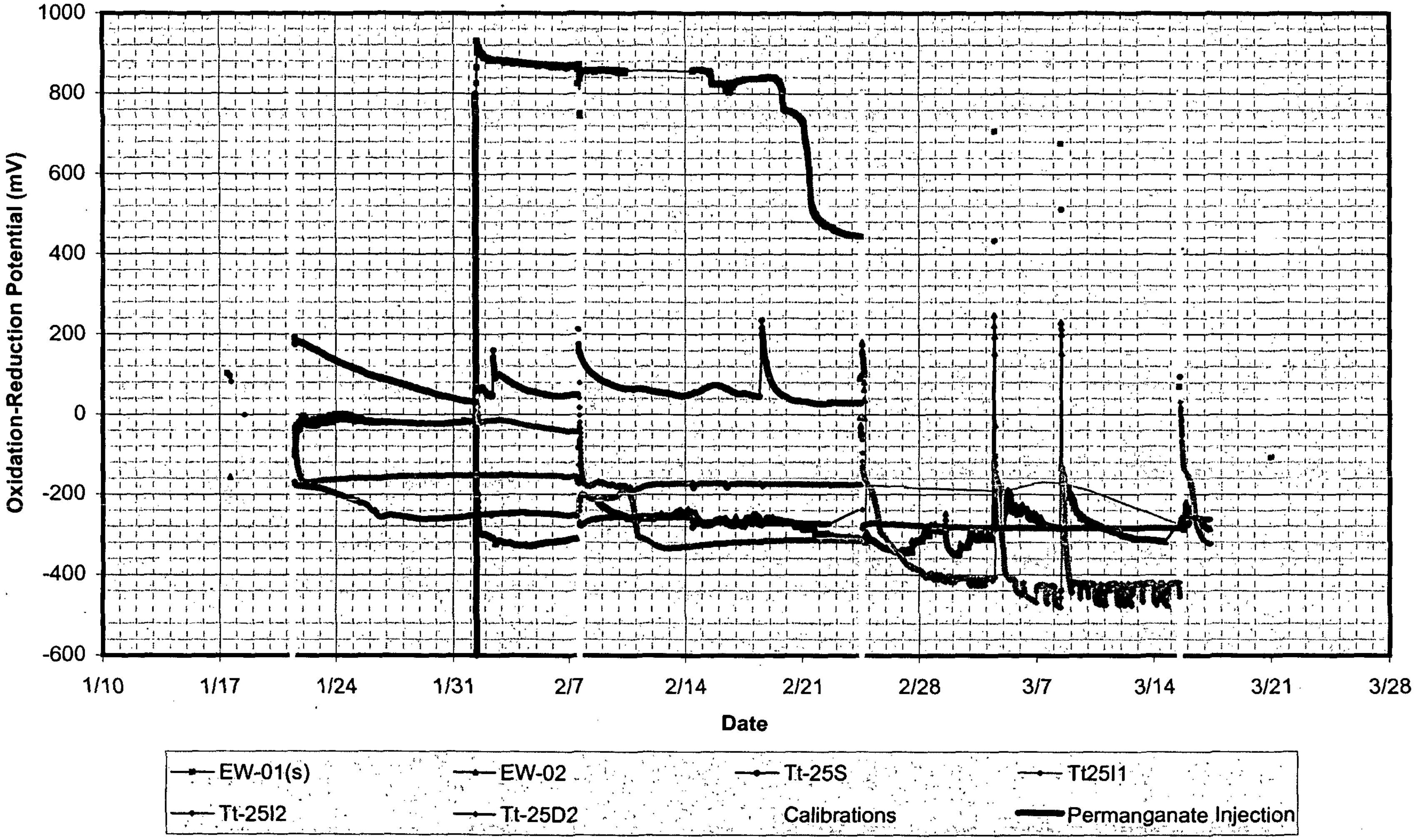
F.1. Pressure Head Changes
Crossley Farm Site, Huffs Church, PA



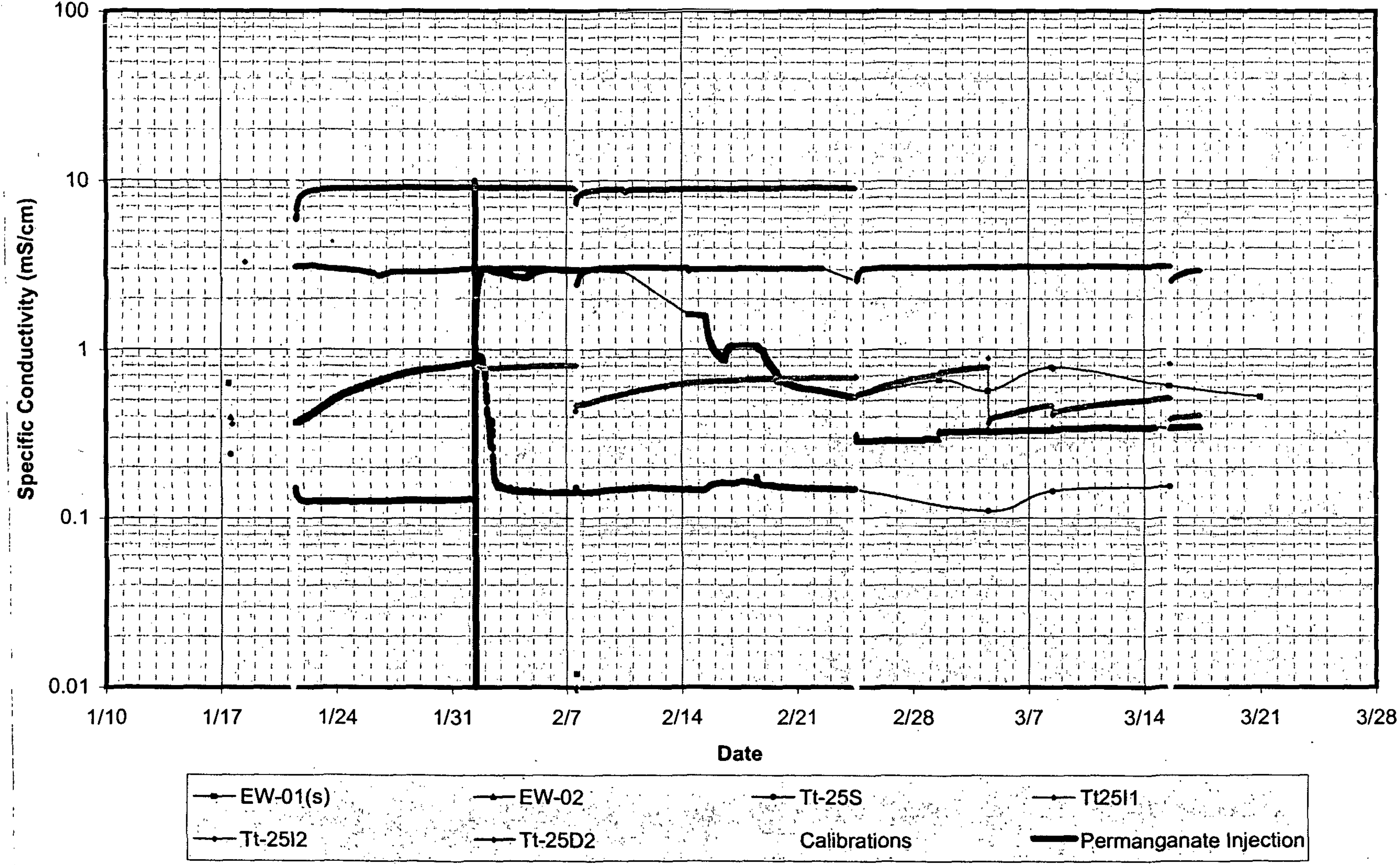
F.1b. Pressure Head Changes
Crossley Farm Site, Huffs Church, PA



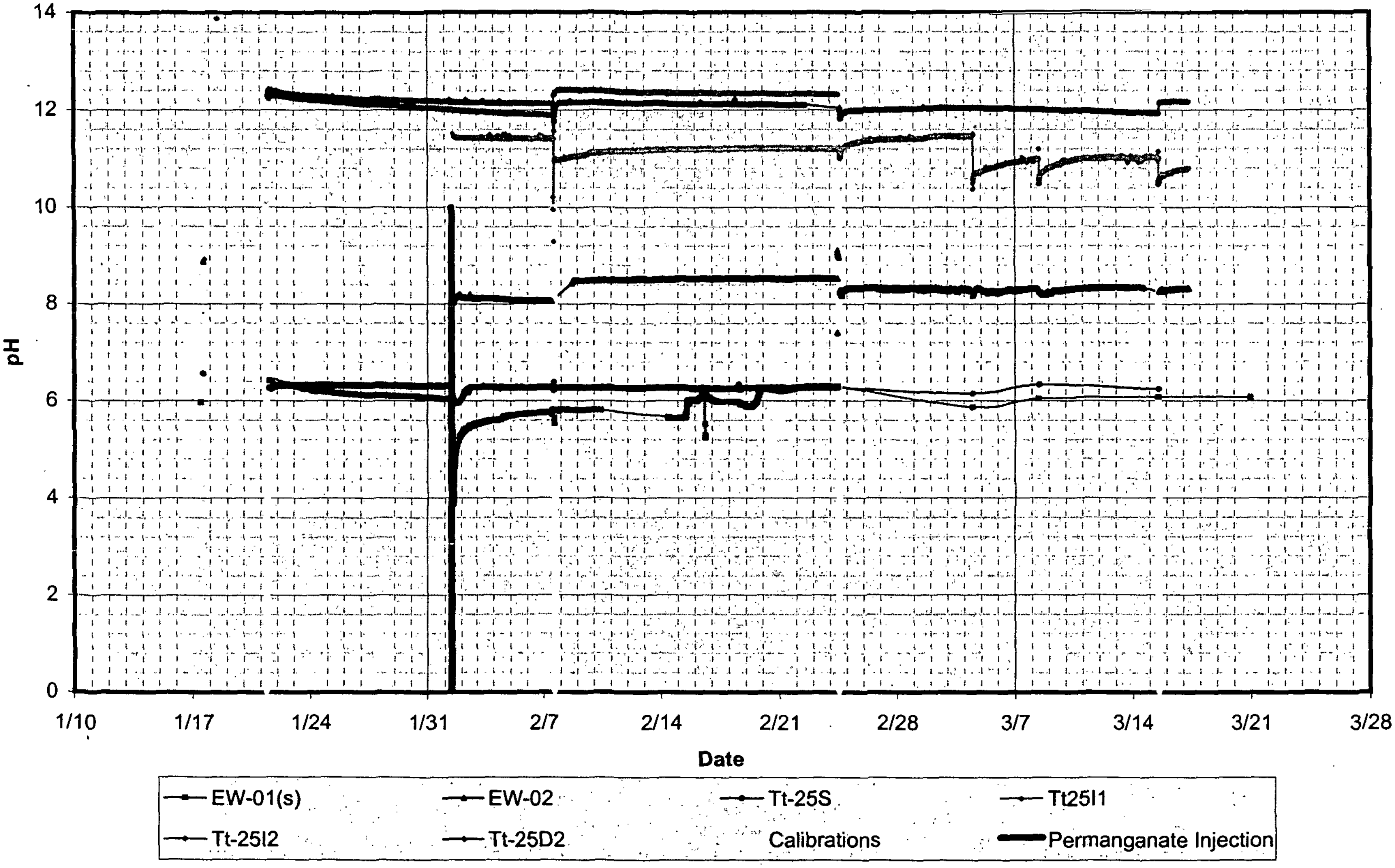
F.2. Groundwater Oxidation-Reduction Potential Readings
Crossley Farm Site, Huffs Church, PA



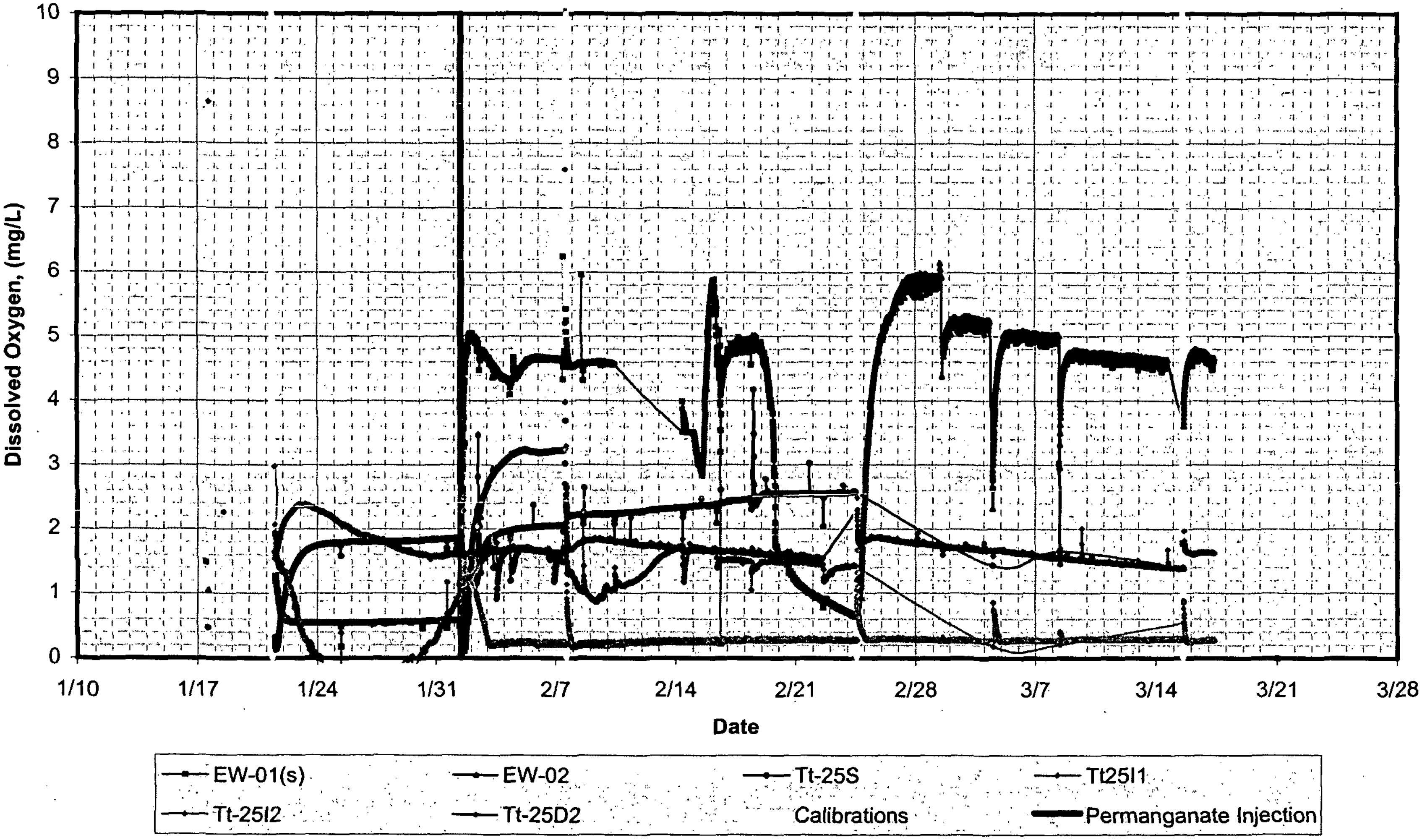
F.3. Groundwater Specific Conductivity Readings
Crossley Farm Site, Huffs Church, PA



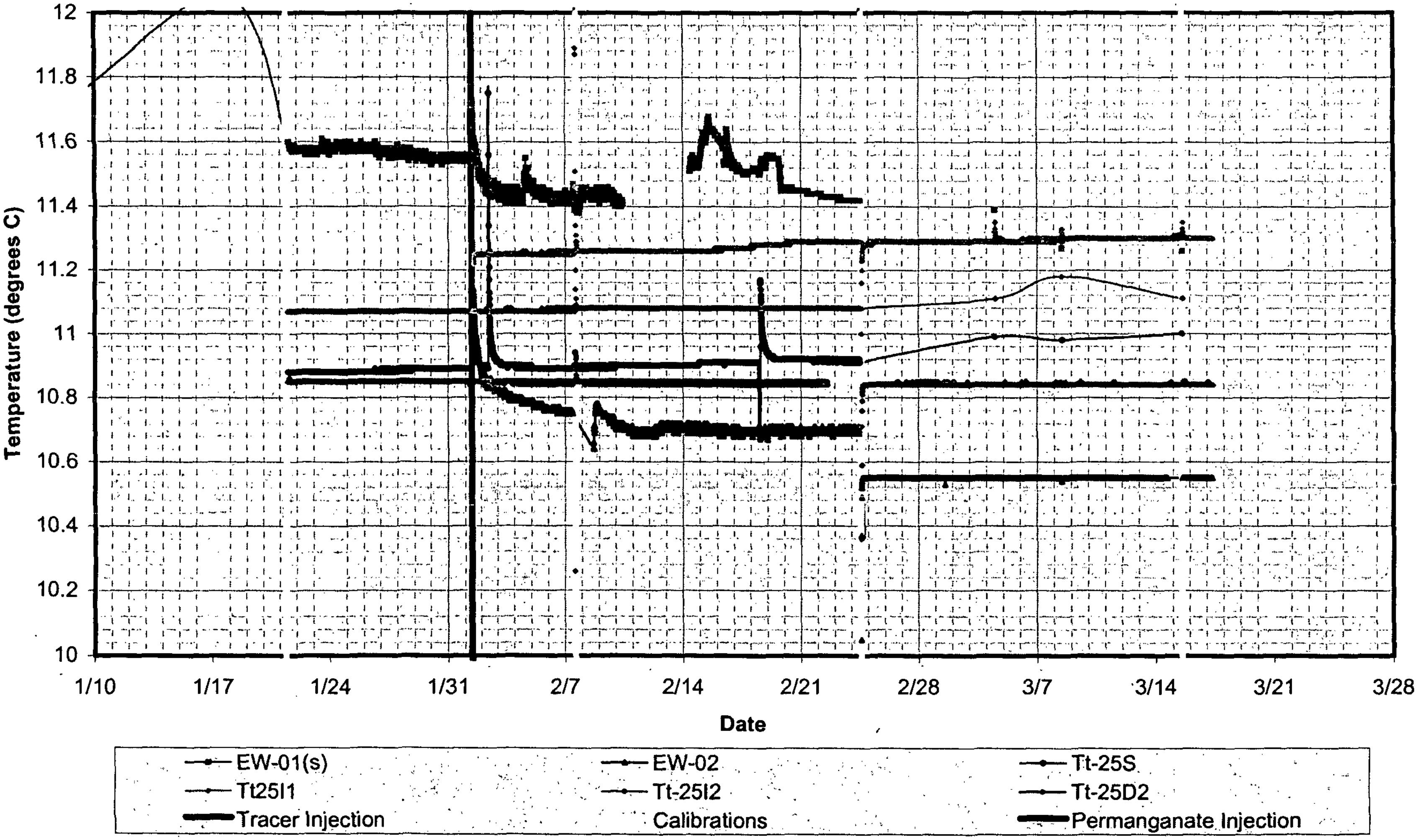
F.4. Groundwater pH Readings
Crossley Farm Site, Huffs Church, PA



F.5. Groundwater Dissolved Oxygen Readings
Crossley Farm Site, Huffs Church, PA



F.6. Groundwater Temperature Readings
Crossley Farm Site, Huffs Church, PA



Attachment G
Evaluation of groundwater Analytical Results

Figure G.1. Groundwater Constituents at EW-1 During Permanganate Injection Treatability Study Crossley Farm Site, Huffs Church, PA

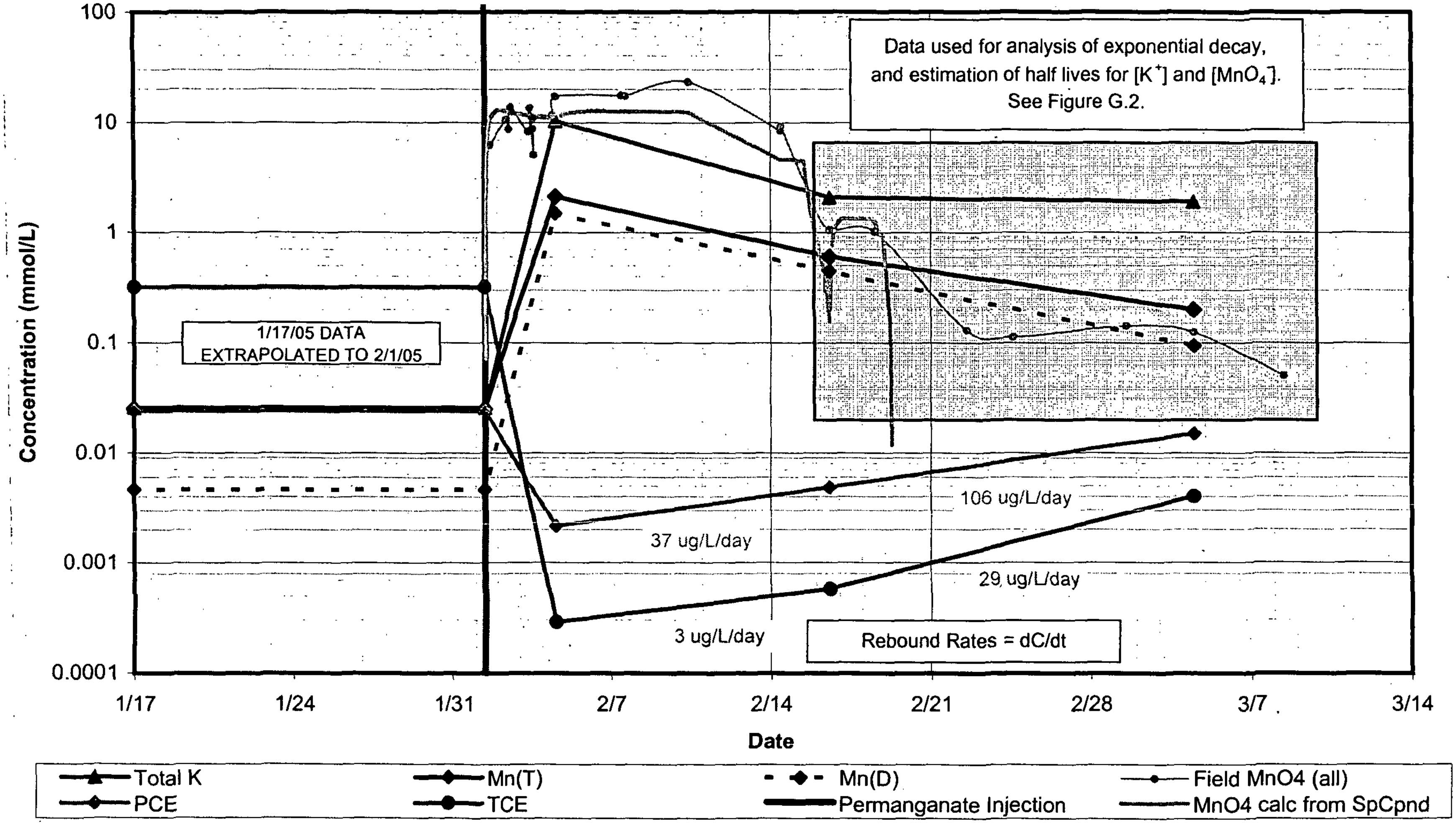
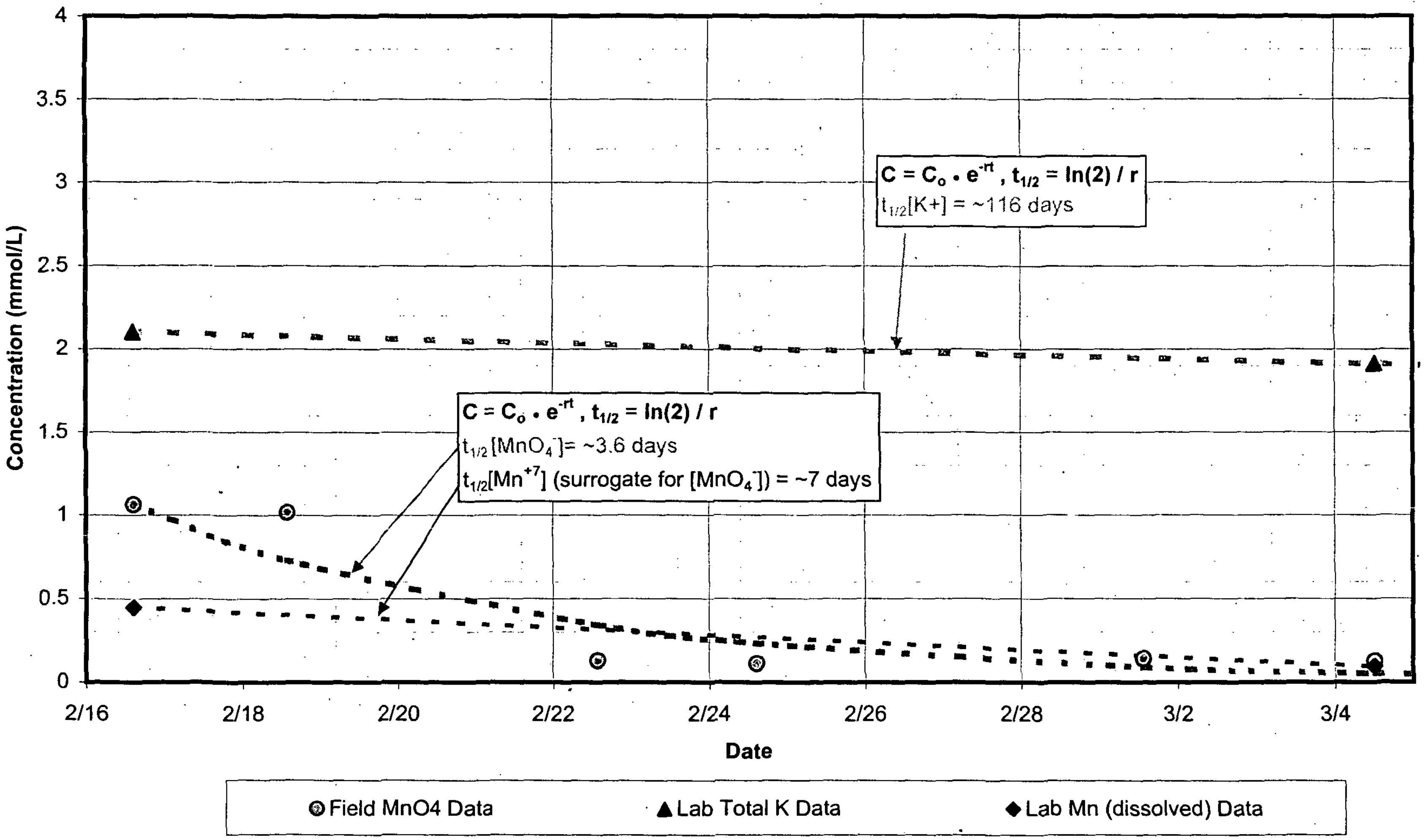


Figure G.2. Analysis of Exponential Decay and half Lives for $[K^+]$ and $[MnO_4^-]$
Crossley Farm Site, Huffs Church, PA



$C = C_o \cdot e^{-rt}$, $t_{1/2} = \ln(2) / r$
$t_{1/2}[K+]$ = ~116 days

$C = C_o \cdot e^{-rt}$, $t_{1/2} = \ln(2) / r$
$t_{1/2}[MnO_4^-]$= ~3.6 days
$t_{1/2}[Mn^{+7}]$ (surrogate for $[MnO_4^-]$) = ~7 days