

**Phased Implementation of In Situ Chemical Oxidation  
for a Large TCE DNAPL Source Area at the Portsmouth Gaseous Diffusion Plant**

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**ABSTRACT**

This paper describes the In Situ Chemical Oxidation (ISCO) remediation being implemented for the the X-701B groundwater plume at the Department of Energy (DOE) Portsmouth Gaseous Diffusion Plant (PORTS). Modified Fenton's reagent is the principal oxidant for the remedy, and Direct Push Technology (DPT) is being used for delivery of the oxidant. Trichloroethene (TCE) is the primary contaminant of concern and is present within the unit as a dense non-aqueous phase liquid (DNAPL). A phased approach is being implemented to optimize the type, location, and mass of the oxidant injections. During Phase I, a unique near-real time monitoring approach was utilized to observe the transient effects of the oxidant injections on the formation. As a result of the positive results from Phase I, Ohio EPA has approved the final work plan for the remedy, and the approach is now being applied to the source area of the plume. The results from Phase I and the layout for the first series of Phase II injections are presented in this paper.

Previous testing at the site has shown that the shallow, water-bearing formation is primarily composed of silty gravel and clay, and is both heterogeneous and anisotropic. These factors have significantly compromised earlier attempts to remediate the unit. A patented ISCO process from In-Situ Oxidative Technologies, Inc. (ISOTEC) was selected for the remediation of the plume. Phase I results indicate that oxidant delivery via DPT is feasible for the unit. Contaminant reduction to date has been minimal due to the small quantity of oxidant injected during Phase I. Contaminant rebound in the aqueous phase remains a concern and will be monitored closely during the remedy.

**INTRODUCTION AND SITE BACKGROUND**

PORTS is located in a rural area of Pike County, Ohio. DOE activities at PORTS include environmental restoration, waste management, and operation of non-leased facilities. The principal groundwater flow system for PORTS is limited to four geologic and hydraulic units (Minford, Gallia, Sunbury Shale, and Berea Sandstone). The uppermost unconsolidated unit is the Minford, with an approximate thickness of 25 to 30 feet (ft). The Gallia and the silt of the lower Minford constitute the unconsolidated aquifer at PORTS. The Gallia unit underlies the Minford and is relatively thin (4 to 8 ft) in the area near the X-701B pond. The average hydraulic conductivity values for the Gallia and Minford are approximately 40 ft/day and 0.62 ft/day, respectively. The uppermost bedrock unit is the Sunbury Shale. This unit is typically encountered at a depth of approximately 30 ft below ground surface (bgs) and the Sunbury is considered to be an effective aquitard. The Berea Sandstone underlies the Sunbury Shale and is encountered at depths between 40 to 45 ft bgs. The primary source of water for the hydrogeologic flow system is natural recharge through precipitation. Natural groundwater flow beneath the X-701B pond is directed to the east and northeast. The flow direction is the same for both the Gallia and Berea units.

The X-701B groundwater plume primarily consists of TCE and its degradation products. Dissolved TCE concentrations up to 1,200,000 micrograms per liter (ug/L) have been measured in the source area of the plume and DNAPL has been pumped from one well within the unit. Several metals, radioactive inorganics, and other organic chemicals have also been identified as contaminants of concern (COCs) and are components of the plume. The primary release mechanisms are surmised to have been migration of separate-phase and dissolved contaminants from the bottom and sides of the X-701B pond and leakage from several chemical process pipelines (currently inactive) that cross the plume area in

proximity to the pond. The groundwater plume (Figure 1) is elongated west to east and extends from a point just west of the X-701B pond, downgradient to the Little Beaver Creek, and is approximately 2,200 ft in length. The plume is relatively narrow north to south, approximately 250 ft wide in the X-701B holding pond area, and expands to approximately 500 ft wide as it approaches Little Beaver Creek. A localized source area for the plume is believed to exist upgradient near the X-701B pond, and is identified in the X-701B Decision Document (Ohio EPA 2003) as the focus for the remedy.

Previous remedial activities at X-701B include a RCRA closure and a technology demonstration that recirculated permanganate solutions between two horizontal wells. Results showed that the permanganate effectively destroyed TCE in portions of the aquifer where adequate distribution was achieved, but that oxidant delivery using the recirculation approach was problematic. In addition, TCE concentration in the treatment area eventually rebounded to near the saturation point.

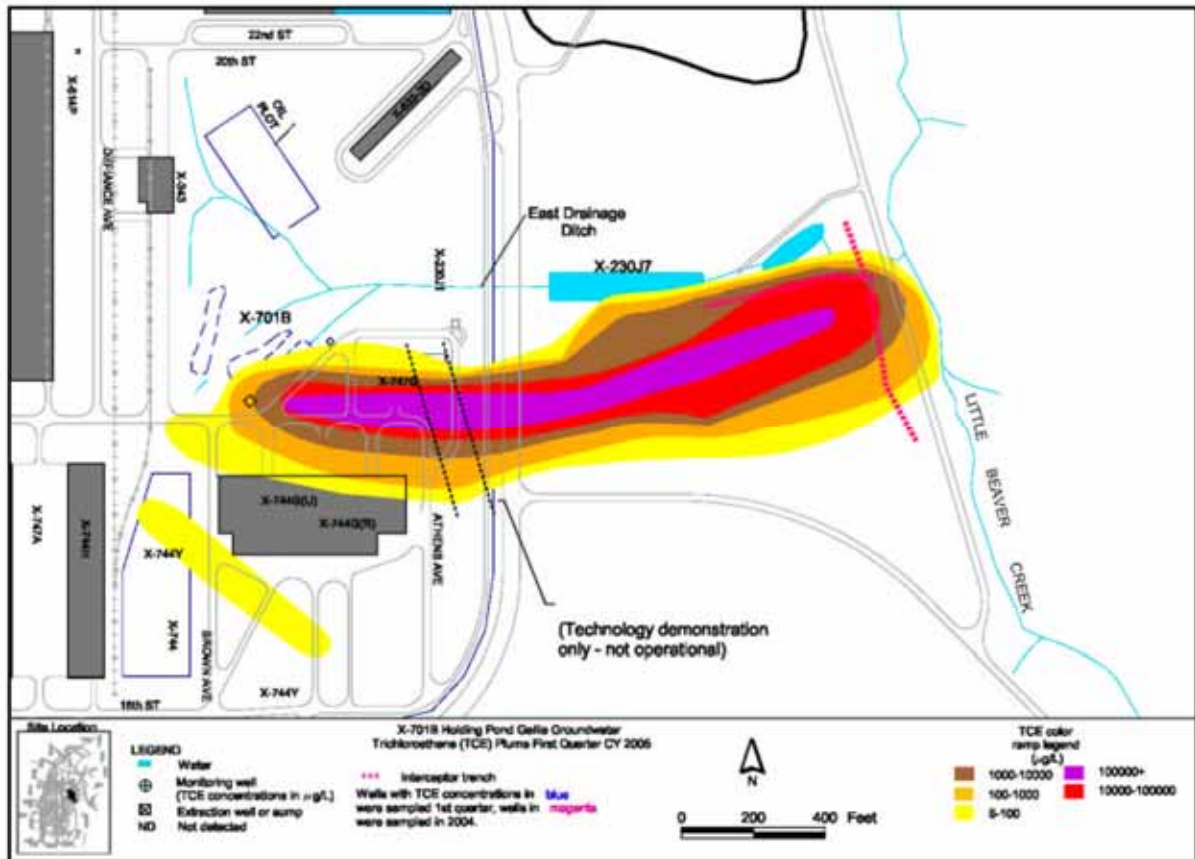


Figure 1. X-701B groundwater plume

In order to overcome oxidant delivery issues and to more aggressively remediate the source, a new remediation approach is being implemented. The new approach involves the injection of Modified Fenton's Reagent directly into the source area using temporary DPT injection points. The primary advantage of this approach (as compared to injection wells) is that the oxidant can be targeted directly to multiple contamination zones at a reasonable cost. This targeting reduces limitations imposed by heterogeneities in the subsurface and is achieved by injecting a relatively small volume of reagent into each of the injection points that are distributed over a large area.

## REMEDICATION APPROACH

The remediation of groundwater contamination using ISCO involves injecting oxidant(s) directly into the source and downgradient areas of the plume. The oxidant(s) react with contaminants to produce innocuous substances such as carbon dioxide, water, and, in the case of chlorinated compounds, inorganic chloride. It is important to consider the natural oxidant demand (the consumption of oxidant due to reactions unrelated to contaminant destruction) of an aquifer

when designing and implementing ISCO. Because oxidants are non-selective and will react with other constituents in the aquifer and the soil, sufficient oxidant must be added both to satisfy the natural oxidant demand and to destroy the target contaminant. Natural oxidant demand will normally remain relatively high during early injections, and will diminish for subsequent injection events in the same area.

During ISCO, the destruction of contaminants occurs in the aqueous phase. Yet ISCO can stimulate much faster dissolution of contaminants from the DNAPL phase and desorption of contaminants from aquifer solids. In addition, contaminants bound to organic soil matter are liberated when oxidant reacts with organic matter. Because of these factors, oxidant injections may result in significant increases in contaminant concentrations within groundwater if the subsurface has significant DNAPL and/or sorbed phase contaminant mass. Such cases, however, are an indication of successful remediation because the overall mass of contaminant (dissolved, adsorbed, and DNAPL) in the aquifer system decreases. Subsequent injections of oxidant then address any temporary increases in groundwater concentrations.

Five common oxidants used for soil and groundwater remediation of chlorinated organic solvents are permanganate, persulfate, Fenton's reagent, Modified Fenton's Reagent, and ozone. Several oxidant molecules are typically required for the complete mineralization of the solvent to CO<sub>2</sub>. The oxidant first attacks the carbon double bonds of an alkene, and then subsequent oxidant molecules proceed to break down the solvent into esters, organic acids, and ultimately CO<sub>2</sub>. The pathway leading to mineralization is a function of pH<sup>1</sup>.

Because of the presence of a significant DNAPL mass in the subsurface at X-701B, ISOTEC's Modified Fenton's Reagent process was chosen for remediation of the source area. Fenton's chemistry is characterized by the combination of soluble iron with low concentrations of hydrogen peroxide to produce hydroxyl radicals (OH•). These hydroxyl radicals are very powerful, short-lived oxidizers, typically reacting within minutes or hours. Iron with a valence of +2 is used to catalyze the reaction; maintaining the iron ion in solution is important for the process to be successful. To eliminate the necessity of performing the reaction under low-pH conditions, as is the case with traditional Fenton's chemistry, ISOTEC's process utilizes complexed iron during the treatment process. In addition, a proprietary agent is added to stabilize the hydrogen peroxide and to reduce its reaction rate with the subsurface. This reduction in reaction rate can increase the radius of effect for the treatment. The degree of stabilization is adjustable and can be tailored to a specific site's geologic setting. Overall, ISOTEC's proprietary Modified Fenton's treatment process is very fast compared to persulfate and permanganate treatment systems. The oxidant is typically consumed within a few days. Hydrogen peroxide breaks down either into water and oxygen or into water and carbon dioxide if it reacts with an organic solvent. The iron catalyst is reduced and ultimately precipitates out of solution.

In the ISOTEC process, an aqueous catalyst solution and an aqueous stabilized hydrogen peroxide solution are prepared immediately prior to an injection event. The catalyst solution is prepared from two ISOTEC solid products. Catalyst A provides the source of iron and Catalyst B provides a chelating agent for the iron. The stabilized hydrogen peroxide solution is prepared by mixing water, industrial-grade hydrogen peroxide, and a proprietary ISOTEC stabilizing agent. The mixing of catalyst and oxidant solutions occurs in the subsurface.

Injections are typically conducted in one of two sequences. Under the preferred sequence, injections proceed in the following order: water, oxidant solution, water, catalyst solution, water. If the aquifer is pore space limited, or if there is an unusually large contaminant mass present, an alternative sequence can be utilized. Under the alternative sequence, injections proceed in the following order: water, catalyst solution, water, oxidant solution, water. Under both approaches, the quantity of reagent injected and the rate of injection for each component are adjusted in accordance with field conditions. The preferred sequence is thought to result in a greater radius of influence, but may also sometimes result in excessive production of O<sub>2</sub> and CO<sub>2</sub> near the injection point. These gases may fill the available pore space and stall the injection.

ISOTEC has noticed that, for their Modified Fenton's process, there is a difference between the subsurface radius that is "physically" affected by an injection event and the subsurface radius where remediation occurs at a significant rate. For this reason, the radius of "physical" effect is commonly referred to as "the radius of effect" (ROE) and the radius for effective remediation is referred to as "the radius of influence" (ROI). The ROE is typically much larger than the ROI; however, it is much easier and less expensive to measure the ROE for an injection event.

Groundwater remediation for X-701B is currently proceeding under four separate phases.

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<sup>1</sup> F.W. Schwartz, H. Zhang, "Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes", U.S. DOE Final Report for Project Number 54585, (2000).

**Phase I** – Phase I was completed during the fall of 2005. The goals for Phase I were: (1) to initiate treatment of contaminated groundwater and soils in the smaller source area and (2) to develop system efficiency and remediation effectiveness data that could be used for the design of the remaining injections over the full treatment zone. System efficiency refers to the optimization of time, energy, and cost toward the achievement of remediation goals. Examples of efficiency parameters include achievable injection rates, subsurface pressures, reagent concentrations and volumes, ROE, and ROI.

Phase I injections were conducted in a 5,000-square foot area (Figure 2). Modified Fenton's Reagent was injected into eight temporary direct-push injection points during each of three injection events (total of 24 injection points). The injection events were separated in time by approximately one month. The number and spacing of the injection points for each event were based upon an anticipated 15-ft ROI. The injections targeted the Gallia formation and the top of the Sunbury formation.

Prior to the start of Phase I, four new monitoring wells were installed in the Phase I treatment area: X701-145G, -146G, -147G, and -148G (Figure 2). Baseline soil and groundwater samples were obtained from the new monitoring wells and baseline groundwater samples were also collected from down gradient well X701-78G. All samples were analyzed for pre-selected volatile organic compounds (VOCs), metals, and radionuclides.

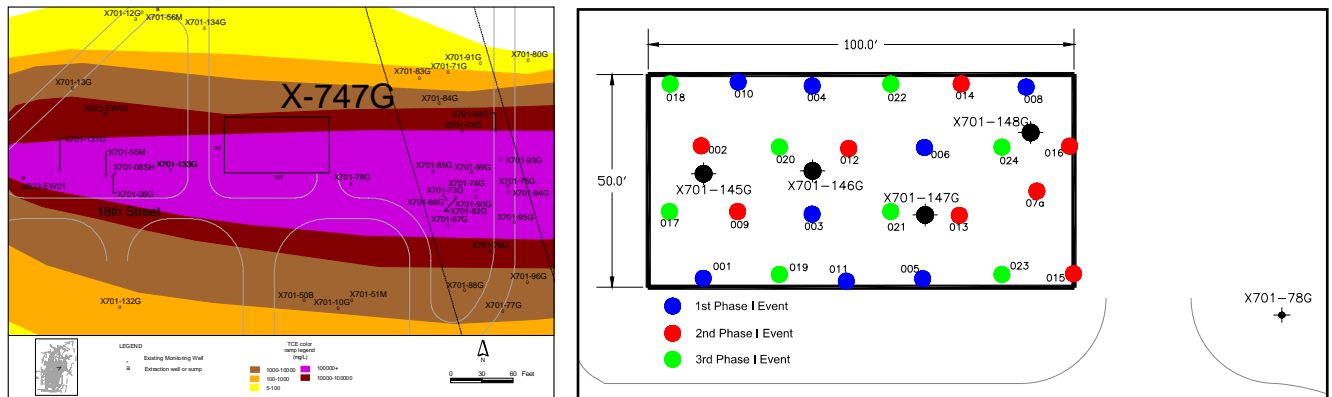


Figure 2. Phase I location of injections within the Plume and Phase I area

Before, during and after each Phase I injection event, near-real time groundwater quality data was collected from each of the four new monitoring wells in the treatment area. This data collection was accomplished by installing multi-parameter water quality instruments in the wells. The data from these instruments provided an indication of the ROE. The instruments measured and recorded pH, temperature, specific conductivity, oxidation/reduction potential (ORP), dissolved oxygen concentration (DO), and pressure. Internal data loggers within the instruments recorded each of the data channels at pre-determined time intervals as small as 1 minute. The instruments were installed using a sanitary seal at the top of each well to minimize the potential for surfacing of treated groundwater.

After each Phase I injection event, groundwater samples were collected from the four new monitoring wells and a downgradient well (X701-78G) and were analyzed for the same analyte list as the baseline samples.

After completion of all Phase I injection events, soil samples were collected at the same locations and for the same analytes as the baseline soil samples.

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**Phase II** - Initiated during the Fall of 2006, Phase II is applying the Phase I technology to the entire source area for the plume. Phase II will be complete when groundwater remediation goals are achieved or when mass destruction between successive injections becomes negligible.

**Phase III** - Phase III, planned to start during the Spring of 2008, will monitor TCE groundwater concentrations to ensure that significant rebound does not occur following Phase II.

**Phase IV** - Phase IV will provide limited treatment for the downgradient portion of the plume and will continue groundwater monitoring for the unit until remediation goals are achieved.

## CURRENT STATUS

To date, all Phase I activities have been completed and the Phase I report has been issued. A summary of all Phase I injection events is presented in Table I.

Near-real time groundwater quality measurements for selected Phase I events are presented in Figures 3 and 4. To facilitate interpretation of the near-real time groundwater quality data, Table II contains the nominal straight-line distance between the injection locations and each monitoring point.

The Final Remediation Work Plan for the unit was approved by Ohio EPA in October, 2006, and the initial set of Phase II injections was completed during the Fall of 2006. A layout for the initial set of Phase II injections is provided in Figure 5.

## CONCLUSIONS

The goals for Phase I of the remedy were successfully achieved. The data collected thus far indicates:

1. Reagent delivery via DPT is feasible for the unit at less than 75 psig without significant surfacing of treated groundwater.
2. On average, a single work crew can complete approximately 8 injection locations per work day.
3. On average each injection location is capable of receiving approximately 75 gallons of stabilized hydrogen peroxide (12%<sub>w</sub>), plus 75 gallons of catalyst solution (~3,000 mg Fe/L).
4. Near-real time water quality data indicates that the radius of influence for the injections is affected by heterogeneities within the formation. However, on average, a 15-foot radius of influence is achievable in the east-west direction.

The extent of contaminant destruction during Phase I is currently unknown and will be evaluated after a review of all analytical results. The magnitude of the side reactions between oxidant and non-targeted soil and groundwater components is also an unknown at this time. Further monitoring will be required during the remedy to determine the rate of contaminant destruction and whether the oxidant demand from side reactions is a significant factor.

## REFERENCES

1. DOE, 2001, *Quadrant II Cleanup Alternative Study/Corrective Measures Study Final Report*, DOE/OR/12-1223&D5.
2. Ohio EPA, 2003, *Ohio EPA's Decision Document for the X-701B SWMU in Quadrant II of the US DOE Portsmouth Facility Piketon, Ohio*.
3. DOE, 2005, *Work Plan for the Groundwater Remediation of the X-701B Solid Waste Management Unit at the Portsmouth Diffusion Plant, Piketon, Ohio*, DOE/OR/11-3177&D1.
4. DOE, 2005, *Work Plan Addendum for the Groundwater Remediation of the X-701B Solid Waste Management Unit at the Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*, DOE/OR/11-3177&D1/A1/R1

**Table I.** Summary of Phase I Volume Injected & Average Rate of Injection

Table I. Phase I Injection Event Summary of Volume Injected & Average Rate Of Injection								
Temporary Injection Point	Date Injected	Water (gallons)	ISOTEC Reagent		Water (gpm)	ISOTEC Reagent		Notes
			12% H <sub>2</sub> O <sub>2</sub> Solution (gallons)	Catalyst Solution (gallons)		12% H <sub>2</sub> O <sub>2</sub> Solution (gpm)	Catalyst Solution (gpm)	
004	9-12-05	55	85	75	1.3	0.8	1.4	An 8-ft screen was used at this location. Injection order-WCWOWCW
005	9-12-05	60	30	50	0.5	0.6	1.5	An 8-ft screen was used at this location, Location failed to take additional oxidant. Injection order-WOWCW
008	9-12-05	55	75	75	1.8	3.0	3.0	An 8-ft screen was used at this location, but only 3 ft were exposed during the injections. Injection order-WCWOW
001	9-13-05	45	78	100	1.5	2.9	2.3	An 8-ft screen was used at this location. Injection stopped-surfacing noted at X701B-145G. Injection order-WCWOW
003	9-13-05	60	75	75	2.1	2.1	2.4	Injection order-WCWOW
006	9-13-05	60	75	75	1.5	1.2	2.4	An 8 ft screen was used at this location. Injection order-WCWOW
010	9-13-05	65	75	75	2.2	1.8	2.1	Injection order-WCWOW
011	9-13-05	45	25	75	1.3	0.3	3.0	The location failed to take additional oxidant. Injection order-WCWOW
002	10-19-05	60	75	75	2.1	1.2	2.9	Injection order-WCWOW
009	10-19-05	65	75	75	2.2	2.7	3.4	Injection order-WCWOW
012	10-19-05	78	75	75	2.3	1.3	3.4	Injection order-WCWOW
013	10-19-05	65	75	75	2.1	2.7	3.4	Injection order-WCWOW
015	10-19-05	60	75	75	2.1	1.2	2.9	Injection order-WCWOW
016	10-19-05	78	75	75	2.2	1.3	3.4	Injection order-WCWOW
07A	10-20-05	60	100	75	1.6	1.1	2.9	Injection order-WCWOW
014	10-20-05	65	50	75	1.4	0.6	2.9	Injection order-WCWOW
017	11-15-05	45	75	75	2.7	2.5	3.1	Injection order-WCWOW
020	11-15-05	45	75	75	2.3	1.6	4.4	Injection order-WCWOW
022	11-15-05	45	75	75	2.0	2.1	3.3	Injection order-WCWOW
024	11-15-05	45	75	75	2.5	1.6	4.4	Injection order-WCWOW
018	11-16-05	45	75	75	2.1	1.9	3.8	Injection order-WCWOW
019	11-16-05	45	100	75	4.1	3.9	5.8	Injection order-WCWOW
21a	11-16-05	30	26	75	1.9	2.0	3.1	Injection order-WCWOW
023	11-16-05	50	100	75	1.7	1.9	3.3	Injection order-WCWOW

**Notes:**

All temporary injection points were advanced to 33 feet bgs.  
 Unless otherwise noted, a 5-ft temporary screen was exposed at each location.  
 For injection order: W=Water, C=Catalyst Solution, O=Oxidant Solution

Table II. Straight Line Distance between Injection Points and Monitoring Wells (ft)

Mon. Well	Injection Point																							
	001	003	004	005	006	008	010	011	002	07a	009	012	013	014	015	016	017	018	019	020	021	022	023	024
X701-145G	24.6	27.2	32.8	57.1	52.2	78.5	23.0	42.0	6.6	78.4	12.0	34.6	60.8	64.1	90.0	86.2	12.0	22.5	29.6	18.9	44.8	48.8	73.9	70.3
X701-146G	36.0	10.2	20.0	36.2	26.9	53.9	27.2	27.1	26.8	52.9	20.0	10.0	36.0	40.5	65.9	60.7	34.9	39.2	25.6	9.6	20.7	27.5	50.7	44.8
X701-147G	54.2	26.6	40.3	15.0	15.9	38.3	53.9	24.2	55.0	26.8	44.0	23.8	8.0	32.0	37.5	37.6	60.1	67.3	37.0	37.8	8.1	31.8	22.8	24.1
X701-148G	84.2	54.8	52.5	42.7	25.2	10.8	69.7	55.7	77.5	13.8	71.3	42.9	25.7	19.9	34.7	9.7	86.8	85.5	67.8	59.1	37.7	34.8	34.0	7.6

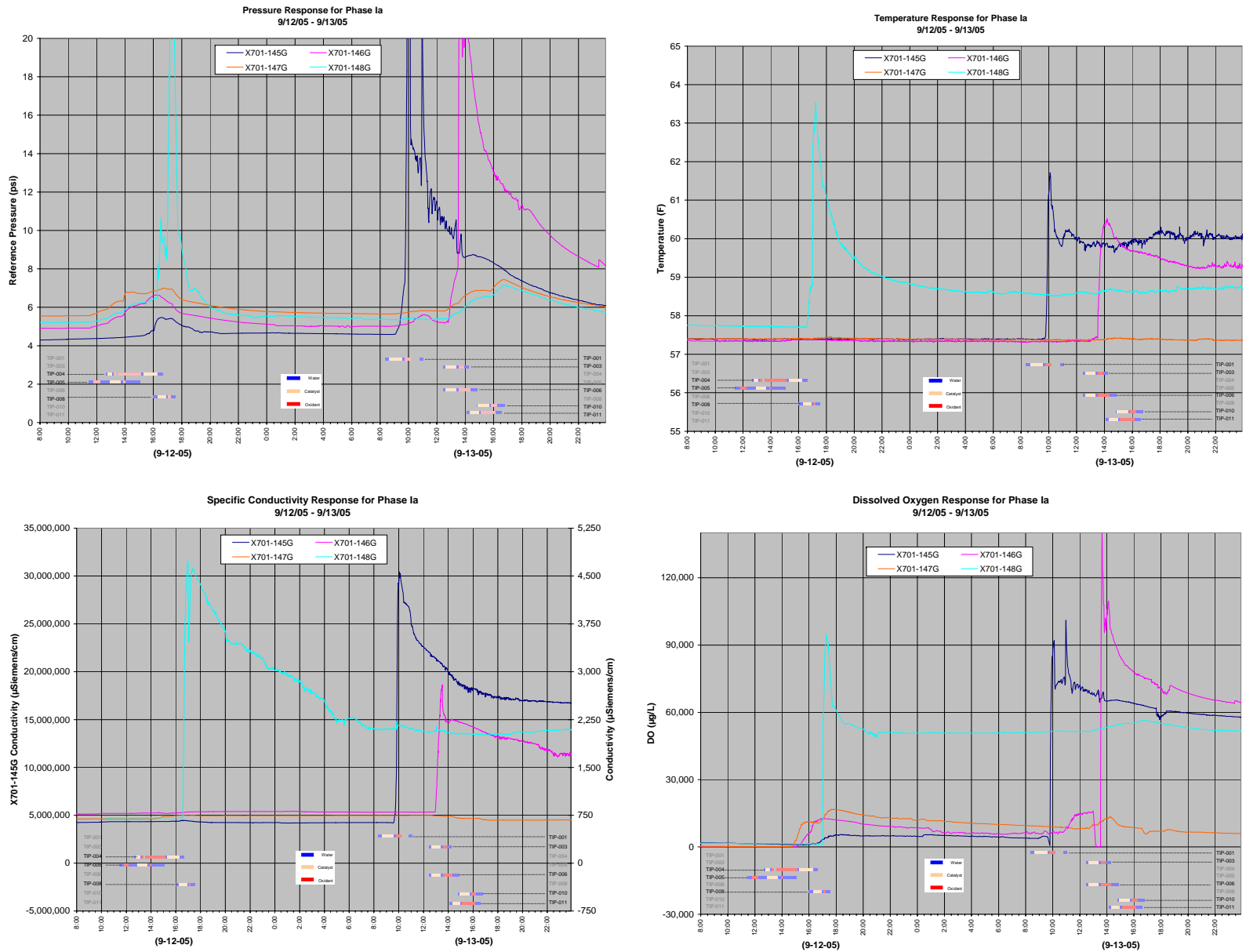


Figure 3. Typical near-real time groundwater quality measurements for September 2005 injections



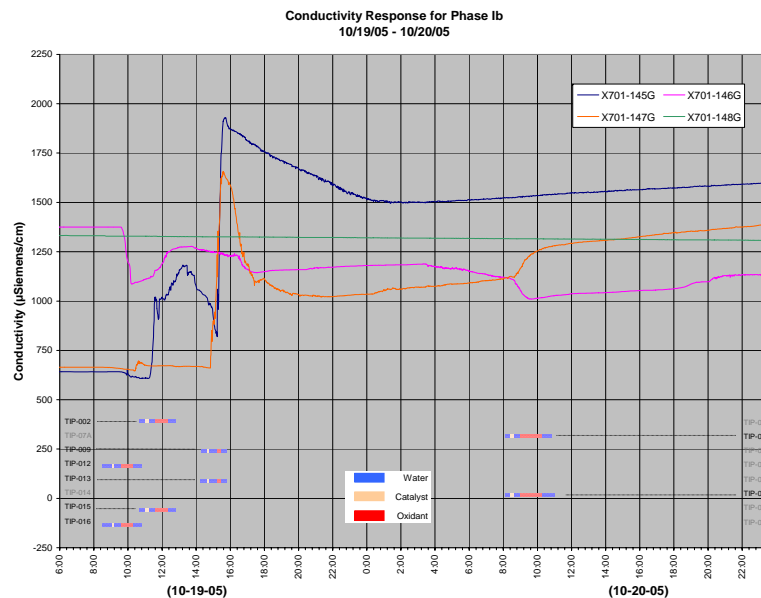
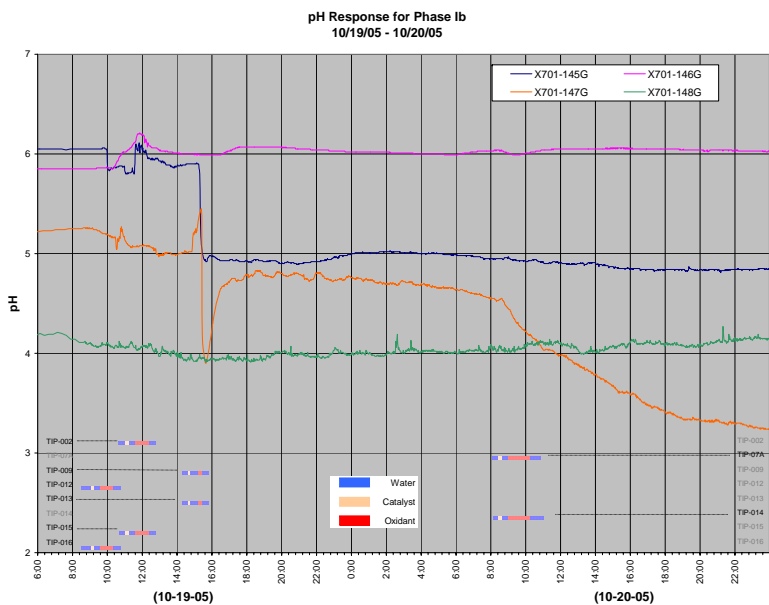
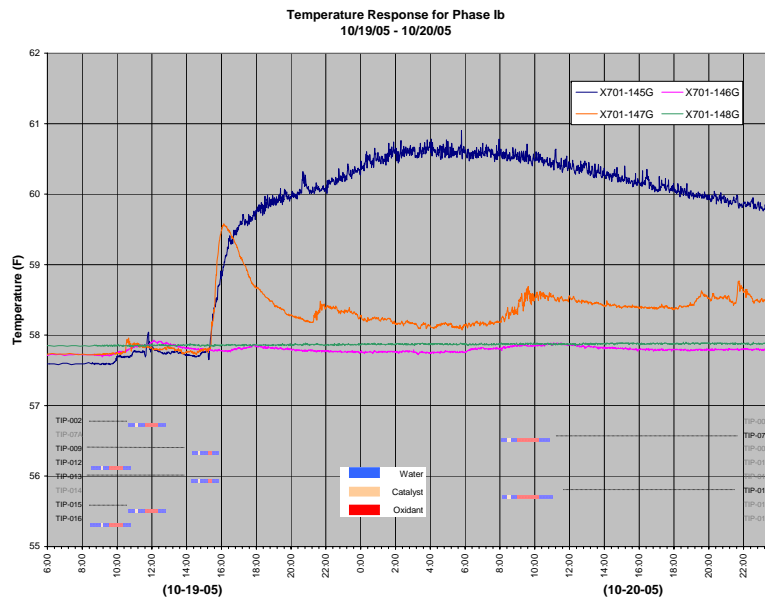
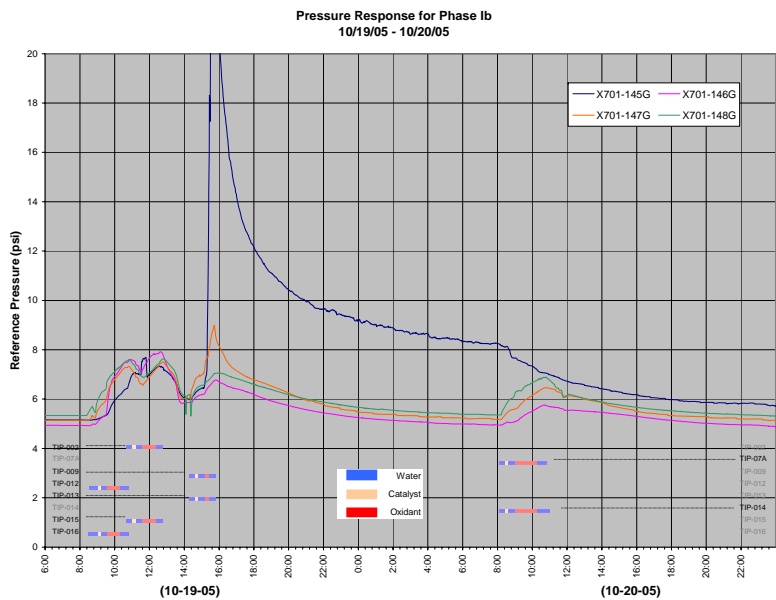


Figure 4. Typical near-real time groundwater quality measurements for October 2005 injections

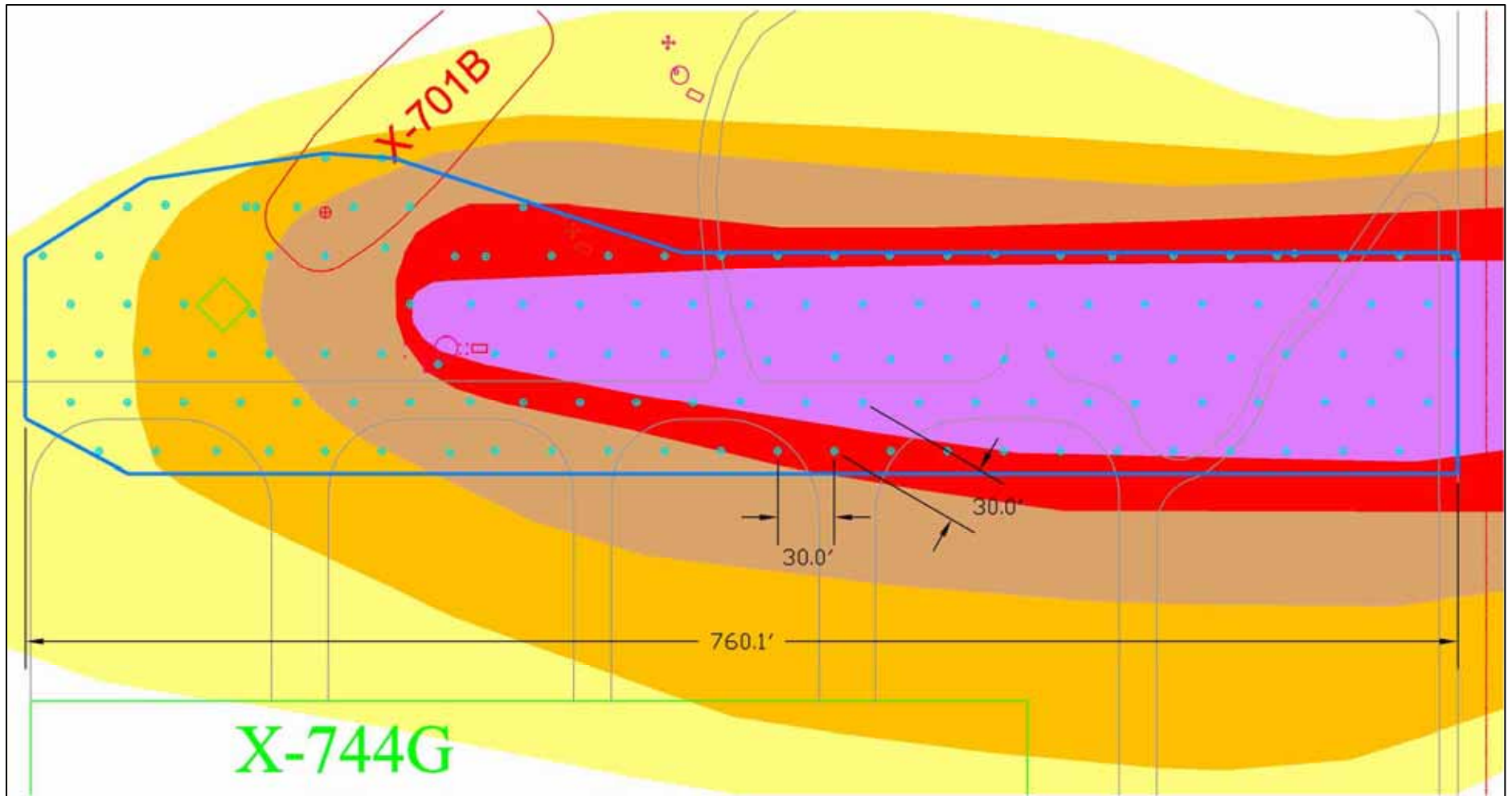


Figure 5. Layout for initial phase II injections