

In-situ Chemical Oxidation via Ozone at a Multiple-Remedy UST Site - 9124

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ABSTRACT

URS Corporation (URS), under contract with the Pennsylvania Department of Environmental Protection (PADEP), has implemented a multiple remedy corrective action at a former leaking underground storage tank (LUST) Site contaminated with BTEX and MTBE. Aquifer impacts resulting from former leaking USTs at the Site, located in Sewickley, PA, potentially threaten the local water supply. Significant remedial challenges at the Site include challenging geology, constituent distribution and fate, public health, and land use. The Site has a large vadose zone and UST-related impacts have been investigated to extend to the deep portions of the Ohio River sand and gravel aquifer (approximately 90 feet). Further complicating remediation is land use issues, as the former gas station property is presently utilized as an integral part of an existing profitable retail business, thereby limiting potential remedial options. In-situ chemical oxidation via a patented combined ozone-hydrogen peroxide process was implemented in the former source area, replacing a formerly installed SVE system that proved ineffective. The remedial technology and design implemented have resulted in significant source area concentration reduction and the associated development of subsurface conditions conducive to bioremediation. Additional remedial measures undertaken at the Site include passive oxygen addition and plume cut-off for the off-site MTBE plume, which is threatening a local water supply. The application of these multiple remedies at the Site has provided for an effective, site-wide remedial strategy to achieve corrective action.

INTRODUCTION

Site Setting

The Site is located in Sewickley Borough, Allegheny County, Pennsylvania, within the Allegheny Plateau Physiographic Province of southwestern Pennsylvania. The Site is situated on the northern bank of the northwesterly flowing Ohio River (Figure 1). The Ohio River is located approximately 400 feet south of the Site.

The site is located in a mixed land use setting, surrounded by commercial and residential properties, as well as public lands including a middle school and the local Water Authority. The Water Authority, which operates water supply wells that withdraw approximately one million (1 MM) gallons of groundwater per day, is located approximately ½ mile upstream of the Site along the banks of the Ohio River, within the Well Head Protection Area (WHPA) of the Water Authority well field (Figure 2)

The property had been used for retail gasoline sales and auto repair since the 1940s. The USTs were in operation for an unknown number of years until operations ceased in December 1998, prior to the closure of the USTs in May 1999. The current use of the Site is high-end automobile retail sales and represents a significant revenue base for the local borough.

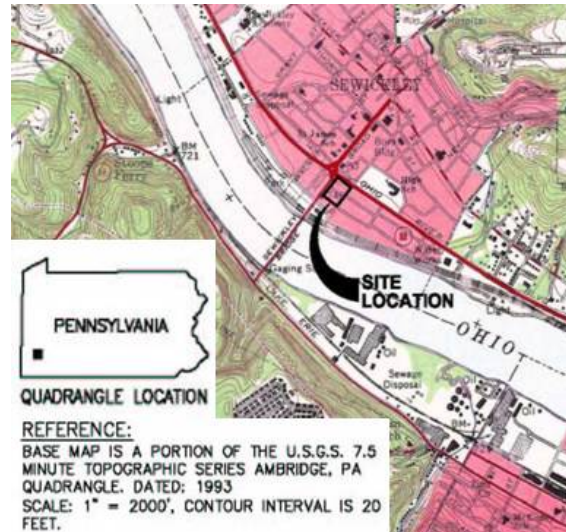


Figure 1. Modified Site Location Map (USGS, 1993).

Conceptual Site Model

The Site overlies unconsolidated materials that comprise the Ohio River Sand and Gravel Aquifer, a prolific aquifer with hydraulic conductivities estimated at 600 feet / day and determined to be approximately 100 feet thick in the vicinity of the Site. The water table is encountered at approximately 40 feet below ground at the Site, yielding a saturated thickness on the order of 60 feet in vicinity of the Site. The unconfined aquifer water table approximates the water elevations of the nearby Ohio River, suggesting hydraulic communication between the water table aquifer and the Ohio River.

A comprehensive monitoring well network was established during site investigative activities completed between 2000 and 2004, as illustrated in Figure 2. Groundwater flow direction at the Site was determined to be generally south, towards Ohio River at low gradients (0.0005 ft/ft). At distances removed from the Site, the groundwater flow direction is influenced by operation of the Water Authority supply wells, resulting in southeasterly groundwater flow directions, as portrayed in Figure 3.

The results of the investigative activities indicated significant source area impacts dominated by BTEX and MTBE. Preliminary investigative work completed by former site engineers defined impacts limited to the vadose zone and smear zone (e.g. shallow groundwater).

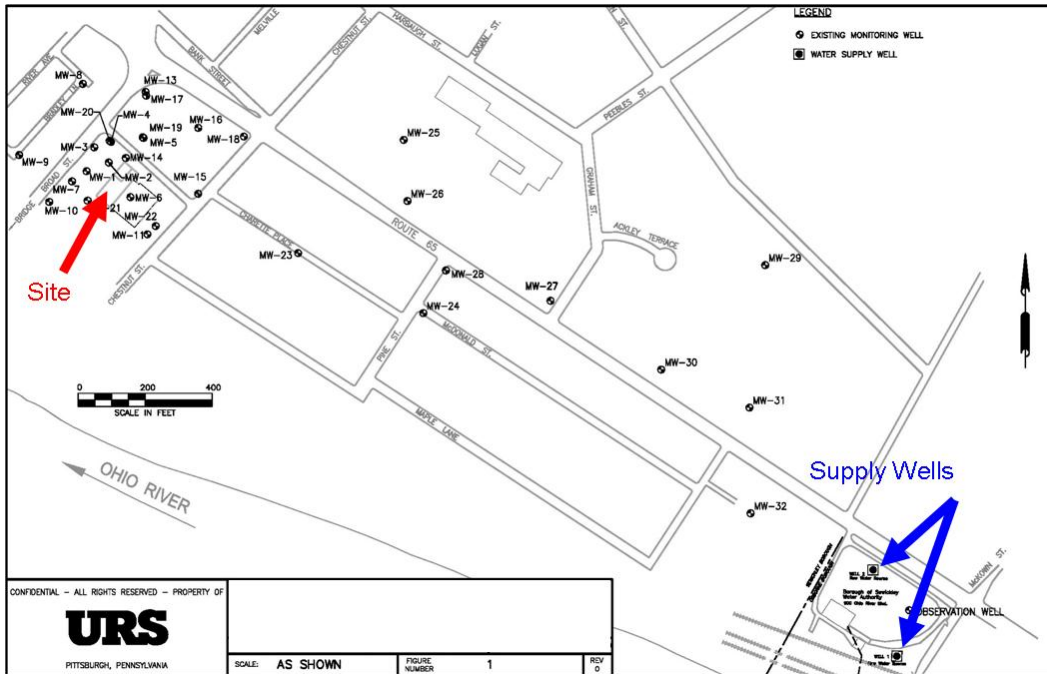


Figure 2. Site Plan Depicting Monitoring Well Network and Supply Wells.

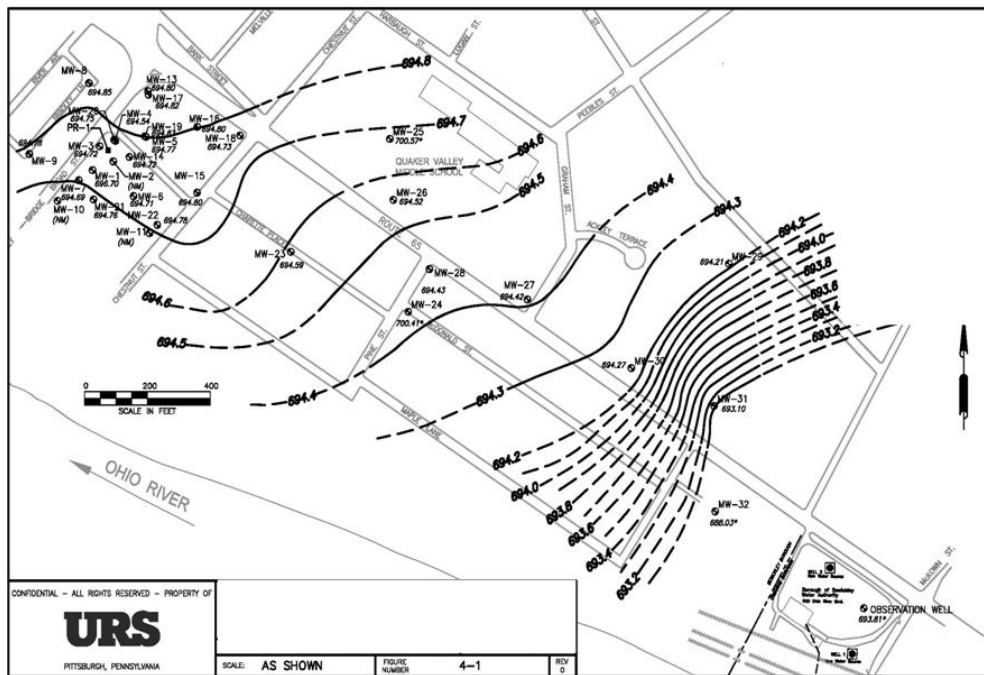


Figure 3. Site Plan Depicting Monitoring Well Network and Potentiometric Surface.

Previous Source Area Remediation

A soil vapor extraction (SVE) system was installed and operated within the source area in 2000 by former site engineers. Free product recovery from the water table was initiated 1999 and a soil vapor extraction (SVE) system was selected as a source area remedial action in 2000. Consistent with the preliminary investigative findings, these on-site interim remedial measures served to address only the impacted, shallow source area. The SVE System targeted the vadose zone (up to 40 feet below ground). Asymptotic volatile organic compound (VOC) recoveries were realized by late 2005, with persistently high source area concentrations remaining. Figure 4 presents a plan depicting Site details as well as the vapor extraction points.

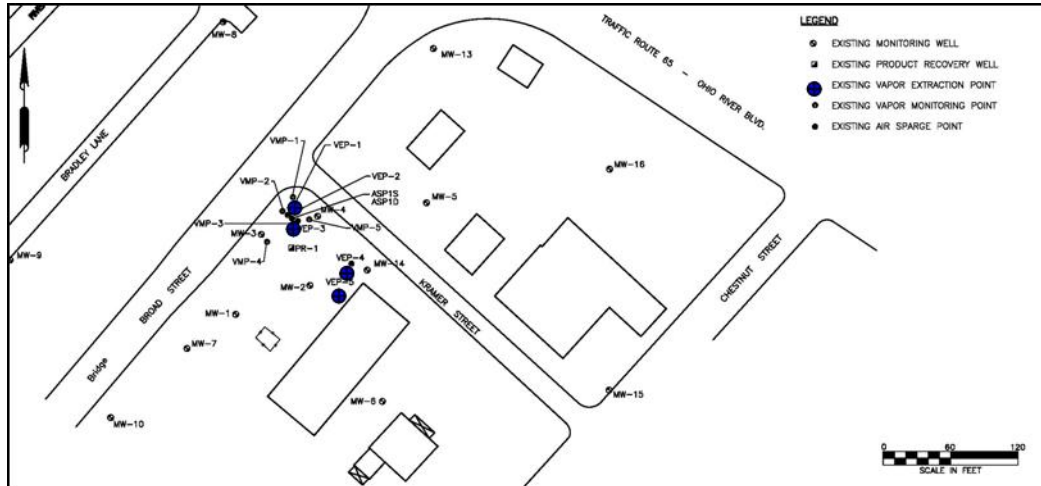


Figure 4. Site Plan Depicting SVE Locations Within Former Source Area.

Figure 5 presents the persistent BTEX impacts, portrayed in parts per billion (ppb), within the former source area between 2004 and 2006, supporting the need for the development of an alternate remedial strategy.

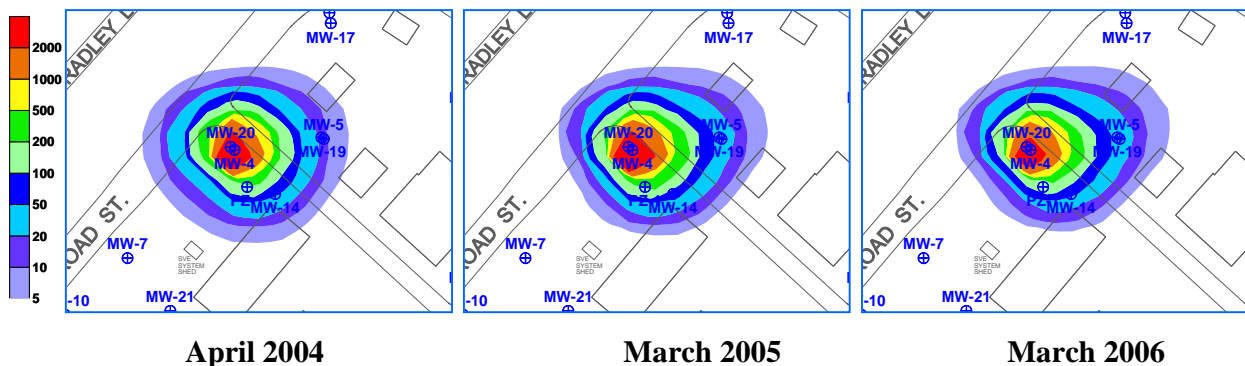


Figure 5. Persistent Dissolved Phase BTEX Impacts in Former Source Area (ppb).

Revised Conceptual Site Model

URS revisited the preliminary conceptual site model and completed additional investigative activities during 2004 and 2005. The findings of these additional investigations included the following:

- Benzene, toluene, ethylbenzene and xylenes (BTEX) impacts were predominantly confined to the area immediately surround the former source area.
- BTEX impacts were observed throughout aquifer to depths of 90 feet below ground.
- Methyl tert butyl ether (MTBE) impacts were identified to be present throughout the saturated thickness of the aquifer and extending to significant downgradient distance from the Site, migrating under influence of the Water Authority supply wells.
- The MTBE dissolved phase plume was determined to dive to greater depths along the off-site migration pathway, due to density and hydraulic conductivity effects.
- The SVE System was ineffective for source area contaminant reduction.
- The aquifer contained sufficient biological capacity to support in-situ bioremediation, however, depressed availability of dissolved oxygen (DO) in groundwater was determined to be the main limiting factor.

REMEDIAL TECHNOLOGY IMPLEMENTATION

Source Area Remedial Action - In-situ Chemical Oxidation

Following a technical evaluation, it was determined that the application of in-situ chemical oxidation technology best suited remediation of the former source area. Additionally, the remedial strategy for the Site included the delivery of DO to the downgradient aquifer to provide this necessary electron acceptor to stimulate the in-situ bioremediation of the MTBE dissolved phase plume.

In order to properly remediate the entire thickness of the unconsolidated aquifer, including the 40-foot thick vadose zone, a gaseous-based chemical oxidation technology was selected. A Perozone™ Remediation System, manufactured by Kerfoot Technologies, Inc. was designed and installed in the former source area. The Perozone™ oxidation process represents an enhanced ozone oxidation and includes patented technology in which the generated ozone bubbles are coated with liquid hydrogen peroxide. The Perozone™ System utilizes an ozone sparging process termed C-Sparger™, which employs the generation of nano- to micro-sized bubbles of air-encapsulated ozone, created by forcing an air/ozone mixture through specialized delivery points termed Spargepoints®, to treat subsurface impacts in soil or groundwater.

The oxidation technology was installed to target persistent source area impacts and included the installation of ten Spargepoints®, designated as SP-1 through SP-10. Each Spargepoint® was installed at a depth of 55 to 60 feet below grade using standard hollow-stem auger drilling techniques. Two (2) Spargepoints®, SP-8 and SP-10, were installed at a depth of approximately 80 feet below grade, to treat deep aquifer impacts.

The existing SVE remediation shed was refurbished to house the Perozone™ System. The Perozone™ System construction included the installation of underground conduit to convey the individual ozone and peroxide delivery lines to each Spargepoint® location. Figure 6 presents the layout of the source area

Perozone™ System at the Site. Figure 7 presents the typical vault installation with the underground conduits and the individual Spargepoint® locations.

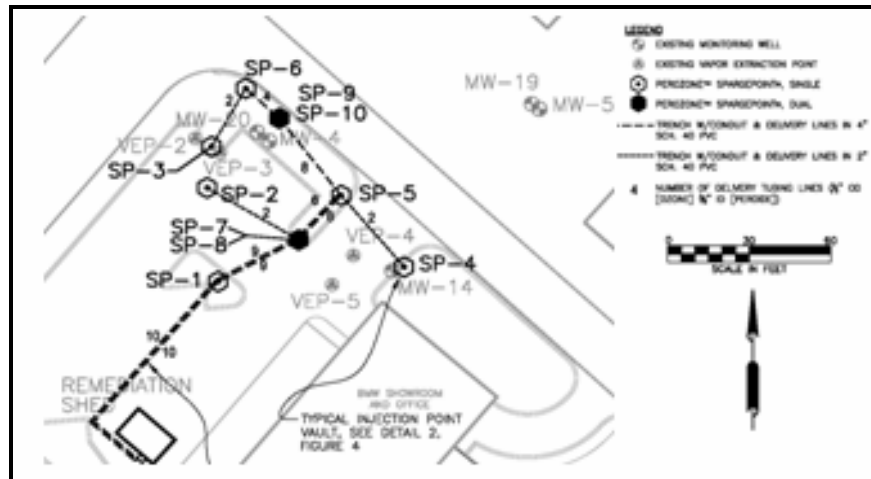


Figure 6. Perozone™ System Layout.

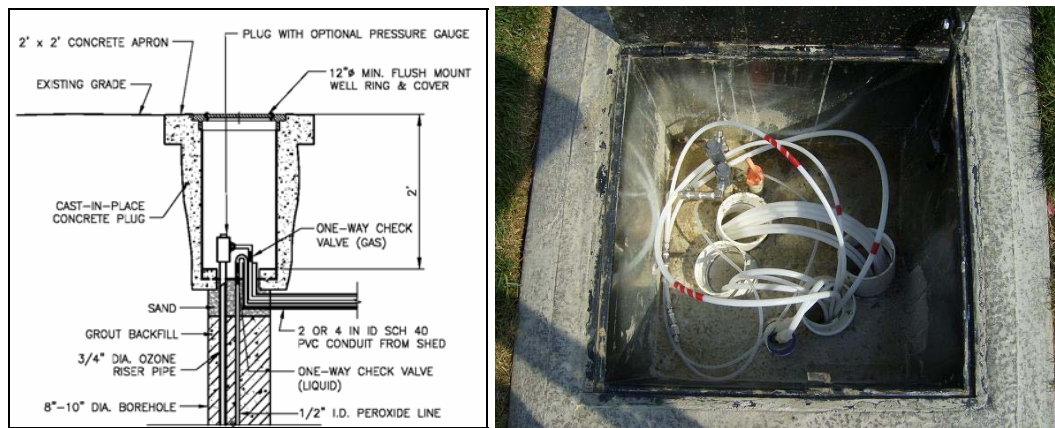


Figure 7. Typical Perozone™ System Well-Head Detail and As-Built Vault.

The start-up of the Perozone™ System was initiated in May 2007 following system component installations and included a shakedown period in which system optimization related to delivery was completed. Figure 8 presents the final installation surface completions with minimal impact to the current property operations.



Figure 8. Final Construction Photos of Installed Perozone™ System.

The Perozone™ System components within the remediation shed include two wall-mounted panels that control the peroxide and ozone injections. The Perozone™ System components were installed within a climate-controlled room within the existing SVE remediation shed. Figure 10 depicts the system panels and other components.



Liquid Peroxide Pump Panel

Gas Delivery
Compressor

Ozone Generator Panel

Figure 9. Main Components of the Perozone™ System – Control Shed Photos.

The ozone-hydrogen peroxide chemical oxidation system operation is fully automated and only requires the periodic re-supply of hydrogen peroxide to the work tank. The Perozone™ System operation was initiated in May 2007 and since that time, a total of 985 gallons of 10% by weight hydrogen peroxide has been delivered to the subsurface distribution network with an accompanied average ozone gas concentration of 800 parts per million (ppmv).

The in-situ chemical oxidation results have provided for significant contaminant concentration reductions in the source area including BTEX constituents and MTBE. Tert butyl alcohol (TBA), an aerobic degradation byproduct of MTBE, was not previously detected at the Site, therefore, its presence suggests active MTBE degradation processes at the Site. The successfulness of the Perozone™ System is evidenced by the benzene reductions, portrayed in Figure 10 as iso-concentration contours.

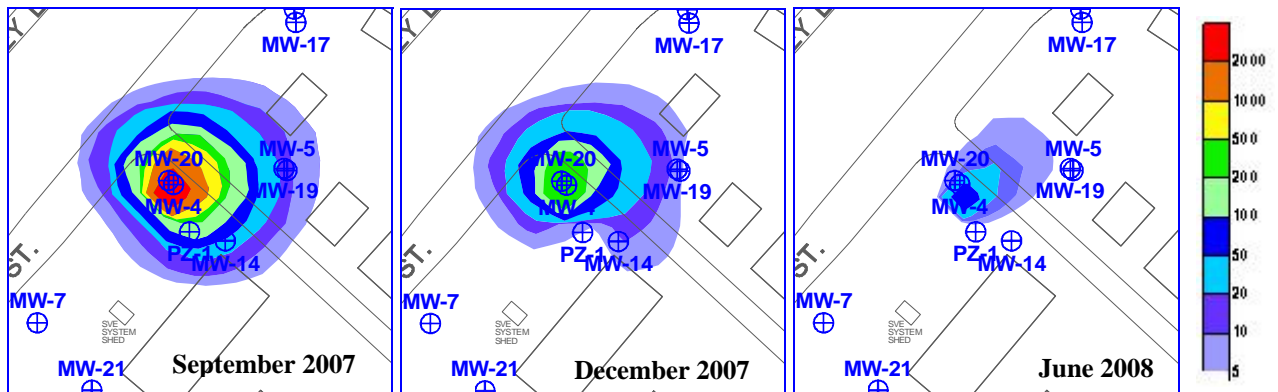


Figure 10: Source Area Benzene Reductions (ppb).

Additionally, Figure 11 presents the time-series results for source area monitoring wells MW-4, MW-14, MW-20 and PZ-1 depicting the remedial effectiveness of the source area in-situ chemical oxidation remediation to date. As evidenced in Figure 11, TBA generation and subsequent reduction is indicative of the conditioning of the aquifer for downgradient biodegradation processes.

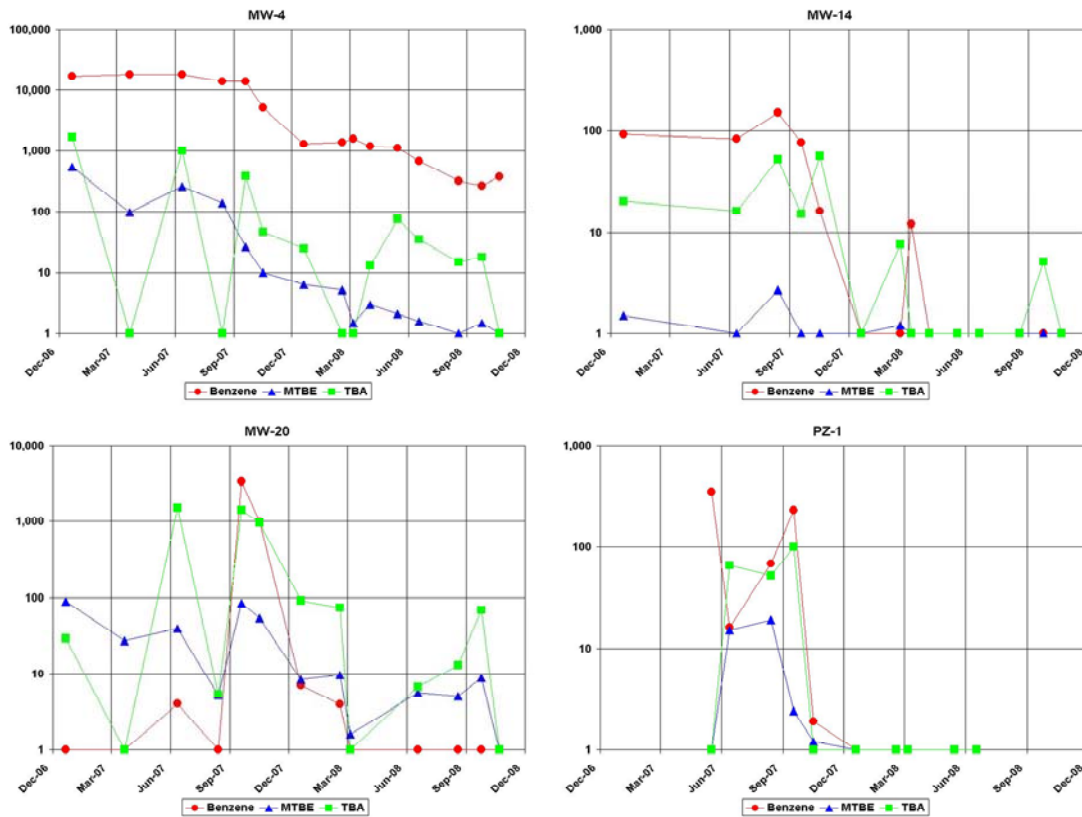


Figure 11. Source Area Monitoring Well Time Series Trends (ppb).

Downgradient Remedial Actions

As noted, the dissolved phase MTBE plume was determined to be threatening the local Water Authority supply wells, with observed MTBE plume diving. MTBE impacts were detected up to 1,500 feet east-southeast of the Site, migrating under influence of the operating water supply wells. Figure 12 presents

the 2004 MTBE iso-concentrations of the shallow aquifer, mid-aquifer, and deep aquifer zones, demonstrating the off-site impacts and the MTBE plume diving, as the core of the plume is observed to shift in an easterly direction with depth.

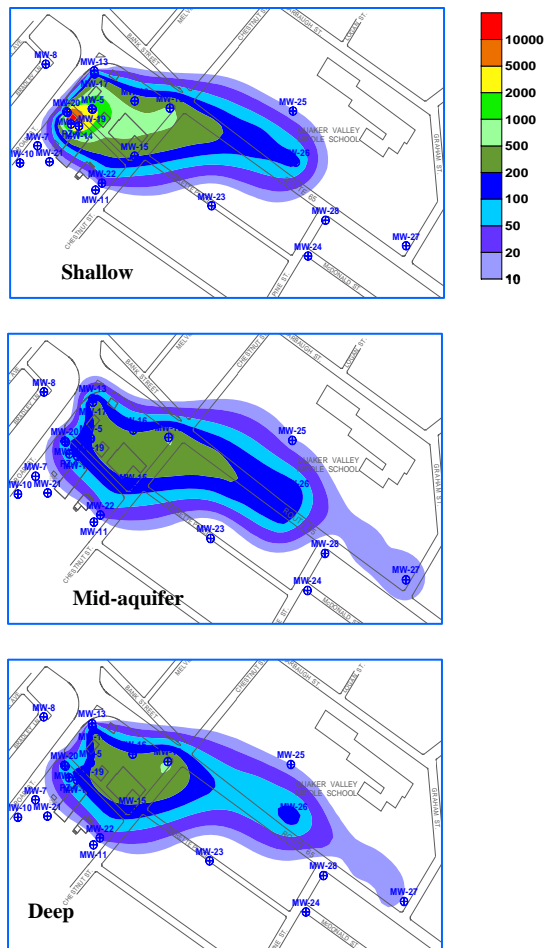


Figure 12. Downgradient MTBE Impacts (ppb) and Plume Diving.

In order to address the immediate threat to the Water Authority supply wells, an MTBE plume cut-off action was initiated in February 2005. The groundwater extraction cut-off remedy was implemented within residential area monitoring well MW-28. The pumping system operates at the designed pumping rate of 35 gallons per minute (gpm) with discharge to the local authority. The cut-off pumping well provides for an additional level of protectiveness for the downgradient water supply wells. Figure 13 presents photographs of the completed installation and Figure 14 demonstrates the operational effectiveness of the MTBE plume cut-off remedial action.



Figure 13. MW-28 MTBE Cut-off Pumping Well Photographs.

Following installation, hydraulic testing was performed to determine the aquifer conditions during operating conditions of the Cut-off pumping system. The apparent capture zone was determined to be approximately 500 feet at 35 gpm. Figure 6 presents the March 2005 dynamic groundwater contours.

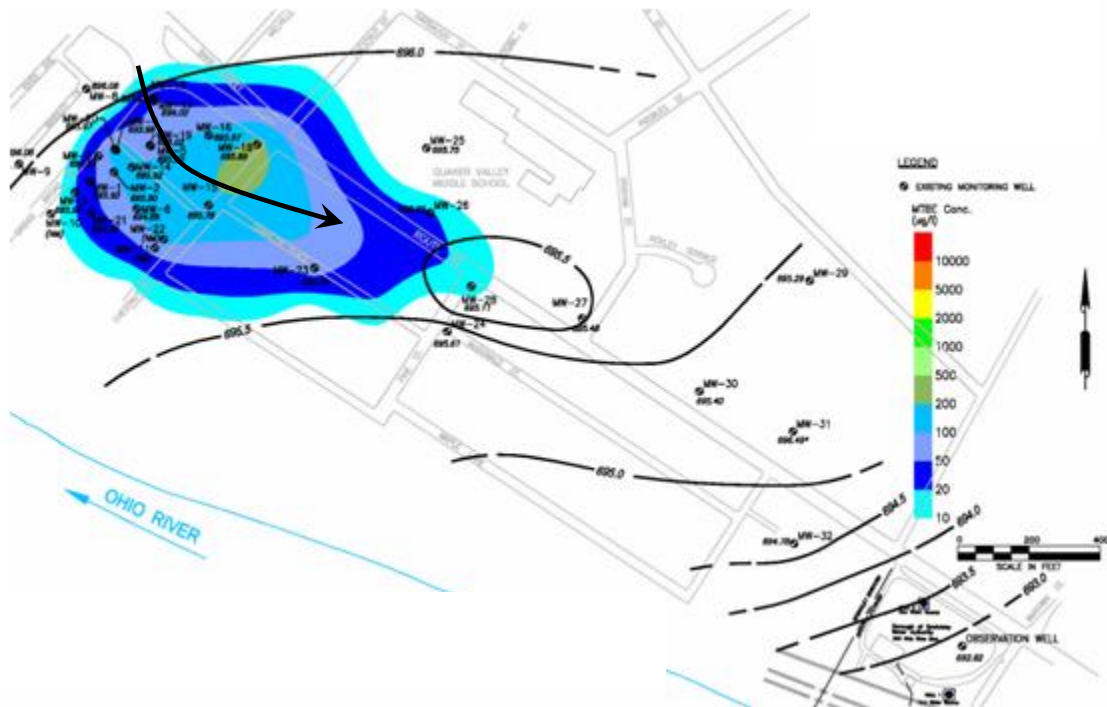


Figure 14: MTBE Iso-concentration Plume Distribution and Apparent Capture Zone of Groundwater Cut-off Remedy.

Additionally, in order to further address off-site MTBE impacts to groundwater, a passive oxygen infusion technology was applied at downgradient monitoring well MW-18, located mid-way between the source area at the Site and downgradient plume cut-off well MW-28. The passive oxygen addition via diffusion was initiated in January 2007 and included the installation of an oxygen concentrator that supplies oxygen to specially developed micro-porous delivery devices that generate miniscule oxygen gas, which diffuses directly into groundwater, providing the limiting DO source to groundwater to support biodegradation of MTBE. The overall system design limited impacts to the surrounding properties, as evidence in Figure 15. The results have proved highly beneficial at reducing MTBE

concentrations within the downgradient plume, as evidenced in Figure 16. Performance monitoring of this remedial action will continue and is envisioned to permit the termination of the MTBE plume cut-off remedy, based on the observed downgradient MTBE concentration reductions to date.

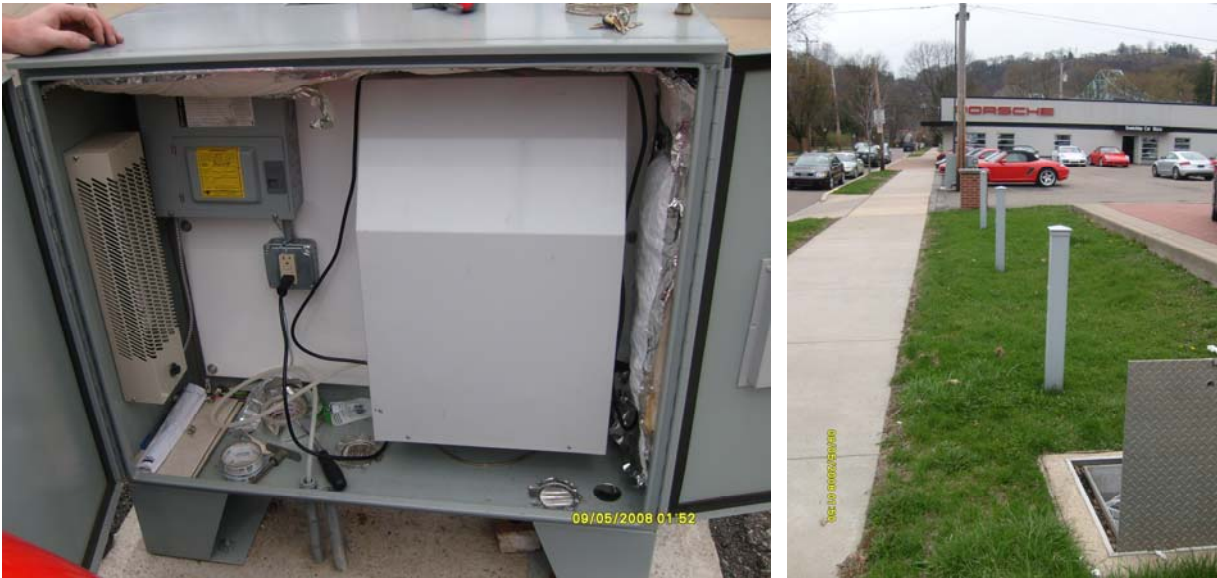


Figure 15: Passive Dissolved Oxygen Generator and MW-18 Vault - As-Built Photographs.

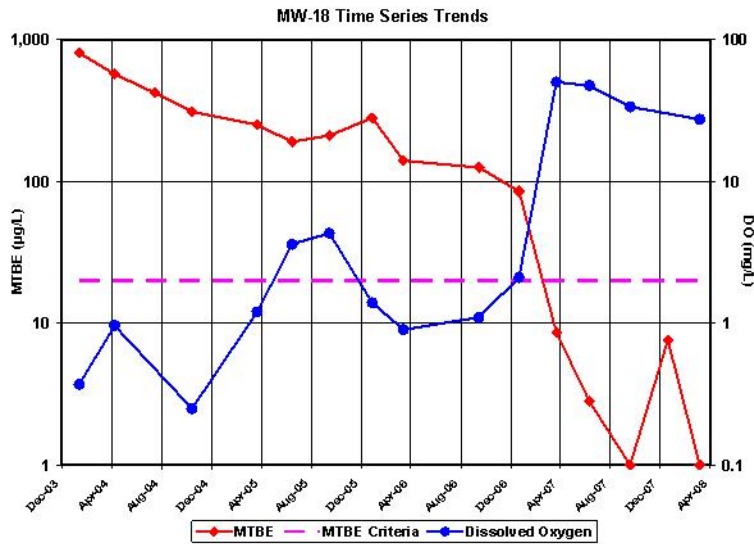


Figure 16: MTBE and Dissolved Oxygen Time-Series Results for Passive Oxygen Delivery Well MW-18.

CLOSING

Significant source area concentration reductions have been realized since initiation of the innovative in-situ chemical oxidation remedy. The management of the downgradient MTBE plume, which serves as the main environmental impact to receptors for the Site, has been successfully address through the application of both active and passive remedial measures. The incorporation of a multiple remedy strategy to address Site impacts has provided a cost-effective corrective action strategy for the Site and defined a clear path to site closure for the PADEP.