

Multiple Oxygen Injection “Curtain Walls” Treat Groundwater Impacted with MGP Contaminants

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ABSTRACT:

Multiple oxygen injection “curtain walls” are being used to stimulate and sustain an aerobic environment to bioremediate a groundwater plume containing Benzene, Toluene, Ethylbenzene, Xylene (BTEX) and polycyclic aromatic hydrocarbons (PAH). This groundwater plume stems from a former manufactured gas plant (MGP) site in Suffolk County, NY and migrates beneath a mixed commercial and residential community for approximately $\frac{3}{4}$ of a mile (1.2 kilometers) to its discharge point in a tidal bay. With the water table fluctuating at 3 and 7 feet (0.9 and 2.1 meters) below ground surface (bgs), the plume has expanded to approximately 500 feet (152.4 meters) wide and between 30 and 70 feet (9.1 and 21.3 meters) deep bgs. This paper will detail the methods used to design the oxygen injection “curtain walls;” and how they have significantly reduced contaminant concentrations in the groundwater plume within 2 years of system operation. The groundwater monitoring results indicate that this remedial technology has significantly reduced the extent and reach of the groundwater plume at all elevations, and decreased the BTEX and PAH concentrations by approximately 60 to 99%.

INTRODUCTION

Site Description. The former MGP operations began in the late 1880s and continued into the 1970s. Most of the MGP facilities were demolished in 1973. Various remedial investigations, interim remedial measures, and remedial actions have been completed or implemented at the Site. The Site is broken into 4 operable units (OU); however, this paper will focus on the remedial activities at OU-2 and their integration with the remedial strategy planned with OU-1. OU-1 represents the former MGP facility and is the location of the primary source area. OU-2 represents the dissolved phase contaminant plume emanating from OU-1 and ultimately discharges into a tidal creek.

OU-2 includes a mixture of residential and light commercial properties. The OU-2 dissolved-phase groundwater plume migrates south to southeast from OU-1 in the direction of local groundwater flow. The boundary of the plume as shown in Figure 1 is based on concentration isopleths of the contaminants of concern (COCs) or total BTEX and total PAHs

Figure 1 – Site Plan



greater than 100 micrograms per liter (ug/L) established during the remedial investigation. The plume extends approximately 3,400 feet (1036 m) from OU-1 to the discharge point at the tidal creek, and is approximately 500 feet (152.4 m) wide. To date, the groundwater plume in OU-2 has impacted the overburden aquifer from the water table to the aquitard and has not penetrated the deeper confined aquifer at approximately 60 to 70 feet (18.2 to 21.3 m).

MATERIALS AND METHODS

A series of pre-design groundwater and soil investigations were conducted between January and August 2008 to collect the required analytical data to design and install the oxygen injection curtain walls in OU-2. The investigations included the collection of groundwater samples from temporary groundwater probes, newly installed groundwater monitoring wells and existing groundwater monitoring wells. The results of the investigations were used to estimate the contaminant flux in the vicinity of the proposed curtain wall locations, determine the required depth of the injection, specify the injection system components, and determine the location of permanent monitoring well clusters for system performance monitoring.

This paper will utilize the curtain wall installed at the D-D' cross-section to illustrate the design process and data results (Figure 2).

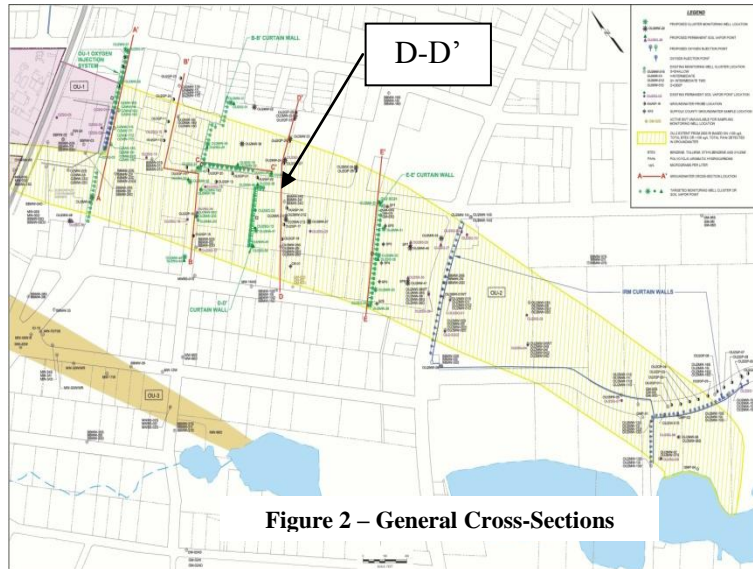
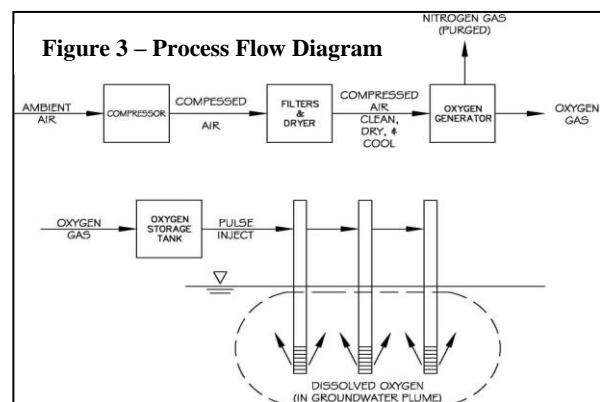


Figure 2 – General Cross-Sections

Oxygen Injection Technology. Oxygen injection technology involves the injection of a 90 to 95 percent pure oxygen gas into groundwater to increase the dissolved oxygen concentration and enhance aerobic biodegradation of COCs. The technology filters ambient air to generate a 90 to 95 percent pure oxygen gas, which is then injected in pulsed intervals into the subsurface through a series of injection wells at low flow rates. The low flow rates and pulsed injection intervals are cycled to allow for the maximum transfer of vapor-phase oxygen into dissolved-phase oxygen. A schematic of the process flow is provided in Figure 3.

The system is patented and built by Matrix Environmental Technologies, Inc. In general, it consists of a rotary screw air compressor, refrigerated air dryer, pressure-swing adsorption oxygen generator and automated oxygen delivery manifold. Ambient air is compressed to 110 pounds per square inch



(PSI) or 758 kilopascals and conditioned through a series of filters and the air dryer. The compressed air flows to an oxygen generator where the nitrogen is removed through a process called pressure swing adsorption. This process uses a molecular sieve (synthetic zeolite) which adsorbs nitrogen at high pressure and releases it at low pressure. The resulting gas stream has an oxygen purity of 90 to 95 percent and is stored in a receiver tank for injection into the aquifer. This process of generating oxygen gas produces no waste other than nitrogen which is inert and purged to the atmosphere. It is also a safe and reliable process that does not require special handling as with high pressure oxygen cylinders, liquid oxygen or hydrogen peroxide. The equipment is contained in an insulated cargo trailer and includes sound dampening, heating, ventilation and electrical controls.

The injection wells are installed in drilled boreholes and consist of Schedule 40 PVC risers with 1 foot slotted screen intervals. The annular space around the screen interval is filled with a sand filter pack. Hydrated bentonite creates a seal above the filter pack to prevent the injected gas from travelling upwards through the annular space. Each injection well is connected to the oxygen injection system with high density polyethylene tubing. The filter pack acts as a diffuser by creating small bubbles of oxygen gas which disperse into the surrounding formation.

Unlike air sparging, the goal of oxygen injection is to transfer the injected vapor to the aqueous phase. The goal of air sparging is to maintain the injected air in the vapor phase where it can strip the VOCs, such as BTEX, from the groundwater for collection in the vadose zone and subsequent treatment. By slowly injecting oxygen at 90 to 95 percent purity, dissolved oxygen concentrations can increase to a maximum of approximately 40 mg/L. Whereas air injected under sparge processes will typically yield dissolved oxygen concentrations of approximately 9 mg/L.

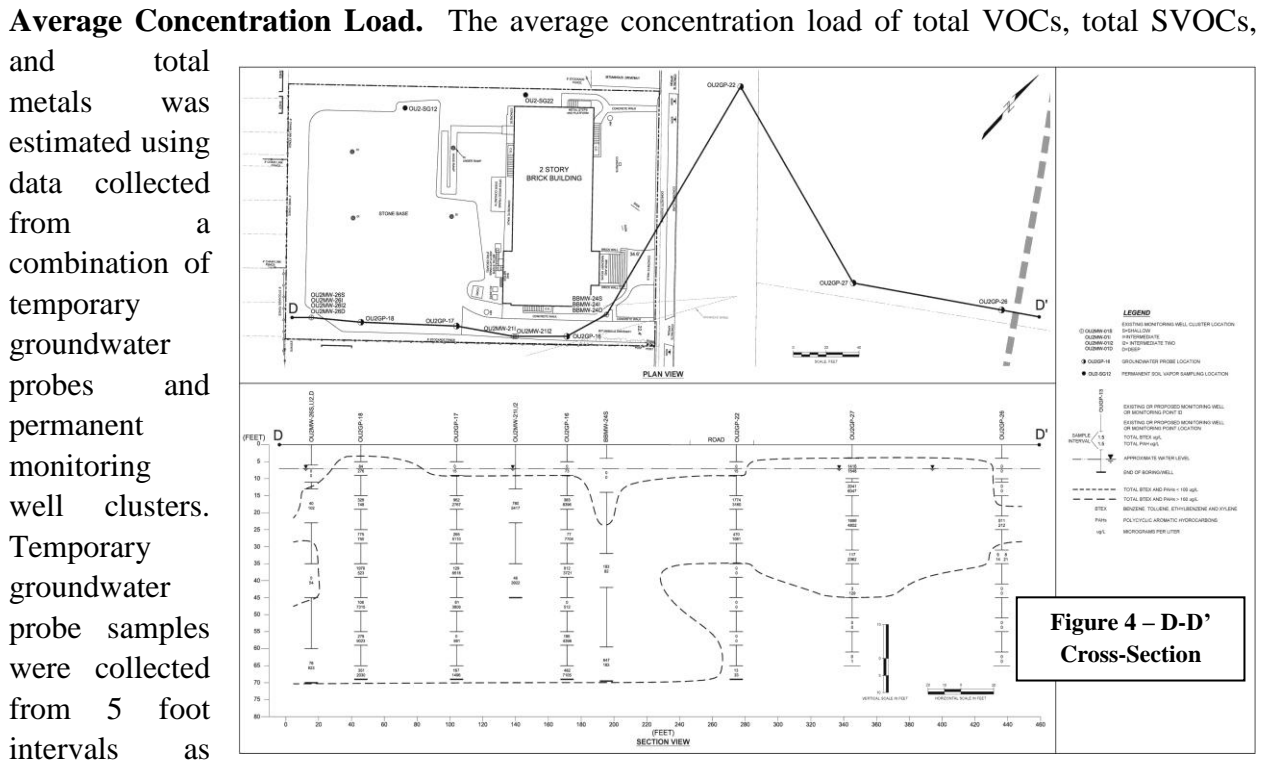
Furthermore, one operational advantage of this system is that larger amounts of oxygen mass can be routed to any particular section of the plume. Therefore, if monitoring activities during system operation indicates that a specific section of the approaching plume has a higher compound loading relative to the rest of the plume, then higher amounts of oxygen mass can be directed to this section without sacrificing the lower oxygen demand across the rest of the plume. This does require adherence to a comprehensive monitoring program; however, this makes the oxygen injection technology very versatile.

Plume Volumetric Flow Rate. The data sets generated from the pre-design investigations were used to create a snap shot in time of the plume and construct an approximate cross section for each proposed treatment area. The plume boundary and cross-section was estimated and defined by the 100 µg/L concentrations of the COCs. When available and relevant to the curtain wall, quarterly monitoring data was also used from adjacent monitoring well clusters.

The cross-sectional area of the groundwater plume at cross-section D-D' was estimated by using groundwater data collected from groundwater probes OU2GP-16 to OU2GP-18, OU2GP-22, OU2GP-26, OU2GP-27, and monitoring well clusters OU2MW-21, OU2MW-26, and BMW-24. The analytical data and the estimated plume cross section is illustrated on Figure 4 below. Due to access agreements and the location of the road, this curtain wall was designed to only treat the left portion of the cross-section. Therefore, the volumetric flow rate of this targeted portion was estimated using the following assumptions:

- The cross-sectional shape of the targeted portion of the plume is equivalent to a rectangle 235 feet (72 m) wide by 70 feet (21.3 m) deep.
- The formation porosity is 30%.
- The groundwater seepage velocity of approximately 1 foot per day (ft/day)(0.3m/day).

Using the data and these assumptions, the volumetric flow rate of the groundwater plume passing through the injection area was estimated at 4,935 cubic feet per day (CF/day) or 0.037 million gallons per day (MGD) (140 kiloliters/day (kl/d)).



**Figure 4 – D-D’
Cross-Section**

However, because a large portion of the oxygen demand is derived from the amount of oxygen consumed by the amount of carbon in a compound, this load is converted to a carbon load. Assuming that the estimated concentration load for oxygen consumption is comprised of 94% carbon, the average carbon load for this cross-section is 0.07 and 2.61 mg/L. Applying the average carbon concentration load to the estimated plume flow rate of 0.037 MGD (140 kl/d) as found above with a unit conversion factor of 8.34 (lbs)(L)/(MG)(mg), the average carbon mass load can be estimated using Equation 1 below:

EQUATION 1: $Mass\ Loading\ (lbs/DAY) = 2.61\text{mg} / L * 0.037\text{Mgal} / \text{Day} * 8.34\text{lbs} \cdot L / \text{Mgal} \cdot \text{mg} = 0.81\text{lbs} / \text{DAY}$

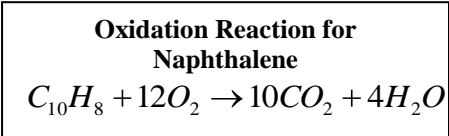
Using Equation 1, the total carbon mass load for this plume ranges from 0.02 to

0.81 lbs/day (0.009 to 0.37 kg/d) (Table 1). Assuming a percentage of dissolved metals will also consume oxygen as it passes through the curtain wall, the average compound mass load is then estimated by adding the carbon mass load to the mass load due to dissolved metals. For the D-D' curtain wall, 50% of the average dissolved total metals, or 40.5 mg/L, is assumed to be available for oxygen consumption. Using equation 1, the average metals mass load contributing to the compound mass load is 12.5 lbs/day (5.7kg/d). When added to the carbon mass load, this value yields a range of average compound mass loads of 12.52 to 13.30 lbs/day (5.7 to 6.0 kg/d) (Table 1).

Table 1 – Calculation Summary

Sample Depth Interval (ft bgs) (m bgs)	Ave. Contaminant Concentration Load (mg/L)	Ave. Carbon Concentration Load (mg/L)	Ave. Carbon Mass Load (lbs/day)(kg/day)	Ave. Total Metals Concentration (mg/L)	Percent of Total Metals Consuming Oxygen (mg/L)	Ave. Total Metals Concentration Load (mg/L)	Ave. Total Metals Mass Load (lbs/day)(kg/day)	Total Compound Mass Load (lbs/day)(kg/day)
6 to 10(1.8 to 3)	0.08	0.07	0.02(0.01)	81	50	40.5	12.5(5.63)	12.52(5.7)
15 to 19(4.5 to 5.7)	2.78	2.61	0.81(0.36)	81	50	40.5	12.5(5.63)	13.30(6.0)
25 to 29(7.5 to 8.7)	2.22	2.09	0.64(0.28)	81	50	40.5	12.5(5.63)	13.14(5.9)
35 to 39(10.5 to 11.7)	2.15	2.02	0.62(0.27)	81	50	40.5	12.5(5.63)	13.12(5.9)
45 to 49(13.5 to 14.7)	1.62	1.53	0.47(0.21)	81	50	40.5	12.5(5.63)	12.97(5.8)
55 to 59(16.5 to 17.7)	2.18	2.05	0.63(0.28)	81	50	40.5	12.5(5.63)	13.13(5.9)
65 to 69(19.5 to 20.7)	1.60	1.50	0.46(0.21)	81	50	40.5	12.5(5.63)	12.96(5.8)

Estimated Oxygen Demand. For the purpose of design, the ratio of oxygen to contaminant mass is estimated from the reaction of oxygen with a carbon source producing entirely carbon dioxide and water. Naphthalene was chosen based on its dominating presence within the plume and its higher recalcitrance to attenuation when compared to the BTEX molecules. As noted in this reaction, 12 gmol of oxygen are required for the oxidation of 1 gmol of naphthalene. Expressed in molecular weights, this calculates a ratio of approximately 3.0 grams of oxygen per gram of naphthalene. This oxygen to carbon ratio was used to estimate the required oxygen demand.



A small percentage of injected oxygen will either not get dissolved or be consumed by cations or other organic matter. A factor of safety of 2.0 was applied to oxygen in the 3:1 oxygen to carbon ratio in order to ensure that the required amount of oxygen is available. Therefore, a minimum 6.0 pounds of oxygen per pound of carbon must be injected into the treatment zone to accommodate the compound mass in the plume. Using the highest average compound load of 13.30 lbs/day (6.0 kg/d), approximately 80 pounds (36.3 kg) of oxygen is required for daily injections.

System Capacity and Design. Based on pilot testing performed during Interim Remedial Measure (IRM) activities, typical well spacing within each curtain wall is approximately 20-25 ft. However, 18-20 ft spacing was selected for the D-D' curtain wall based on the distribution of contaminated groundwater. Therefore, this curtain wall was designed using 40 injection points (Figure 5).

Using a flow rate of 120 SCFH (3.4 cubic meter per hour (cmh)) per the manufacturer's specifications and the ideal gas law, the corresponding mass flow rate of oxygen into the aquifer was estimated at approximately 10.68 lbs (4.8

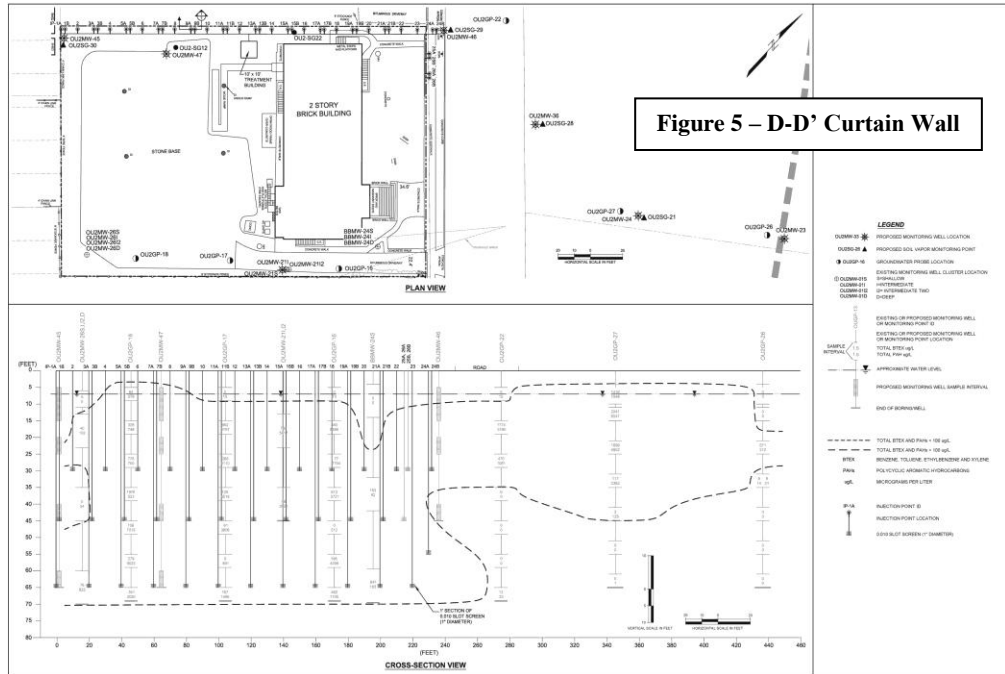


Figure 5 – D-D' Curtain Wall

kg) of oxygen per hour or 256.3 lbs/day (115.3 kg/d) across all injection points. However, the oxygen transfer efficiency to groundwater is not 100%. It is very difficult to estimate this variable. It is dependent on both the oxygen solubility and the depth of injection, although oxygen solubility does not have as significant an effect on the transfer efficiency as depth of injection. The deeper the point of injection is installed below the water table, the higher the transfer efficiency due to a longer contact time between the oxygen gas molecule and the groundwater. For injection points at depths of 25 to 70 feet (7.5 to 21 m) bgs, a transfer efficiency of between 75-95%, respectively, is assumed. Therefore, approximately 8.0 to 9.6 lbs (3.6 to 4.3 kg) of oxygen per hour is available. This equates to a supply rate of approximately 192 to 230.4 lbs (86.4 to 103.7 kg) of oxygen or 0.16 lbs/min (0.07 kg/min) across all injection points. At this rate, approximately 6.4 lbs (2.9 kg) of oxygen per minute is injected by the 40 injection points installed at this location [0.16 lbs/min (0.07 kg/min) x 40 injection points = 6.4 lbs/min (2.9 kg/min)]. To achieve the 80 pounds (36.3 kg) of oxygen as estimated above to treat the highest average compound load of 13.30 lbs/day (6.0 kg/d), the system pulses oxygen into the plume for approximately 12.5 minutes every hour.

Performance Monitoring. Each curtain wall is monitored by a series of soil vapor points and groundwater monitoring well clusters. These monitoring points are located up-gradient, side-gradient and down-gradient of the curtain wall. Vapor points were sampled prior to start-up, each day after startup for 1 week, weekly, then monthly for 1 year. Vapor samples are analyzed for VOCs and Naphthalene via Modified EPA TO-15. Monitoring well clusters were sampled

under low-flow conditions prior to startup, monthly for 3 months after startup, then quarterly. Prior to startup and quarterly after startup, groundwater samples are analyzed for VOCs via EPA Method 8260, PAHs via EPA Method 8270, Sulfate and Total Sulfide via EPA Method 375.4, Nitrogen via EPA Method 351.2, Nitrate/Nitrite via EPA Method 353.3, Ammonia via EPA Method 350.1, TAL (23) Metals, Phosphate via EPA Method 3651, and Heterotrophic Plate count (HPC). Monthly samples collected after startup for 3 months are only analyzed for VOCs via EPA Method 8260, PAHs via EPA Method 8270, and HPC. Low-flow parameters include Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), pH, and specific conductance.

RESULTS AND DISCUSSION

In general, any successful remediation campaign for an extensive groundwater plume requires a source area remediation strategy that will ultimately augment and facilitate a full-scale plume remediation and vice-versa. Conceptually, the success of the remedial strategy to eliminate the plume in OU-2 is directly contingent with the success of the remedial actions implemented at its source area (OU-1). Both strategies were designed and implemented to integrate and complement each other.

Per an Interim Remedial Measure (IRM), two oxygen injection systems were installed within the path of the plume prior to its discharge into the tidal creek in order to mitigate the impacts to the tidal creek. These systems were able and continue to reduce COC concentrations by approximately 95% at the discharge point. Meanwhile, a subsurface containment barrier with a perforated window was installed at OU-1 to prevent the migration of DNAPL and gain control of the source material while an ozone injection system could be designed. The perforated window of the barrier was designed to maintain a controlled release of the groundwater out of OU-1 to maintain hydraulic equilibrium within the aquifer. To address this controlled release, an oxygen injection curtain wall was installed immediately down-gradient of the barrier wall. Within one year of operation while subsequent curtain walls were being designed, concentrations of total BTEX were reduced by up to 90%, and total PAH by 68% in a well cluster approximately 220 ft (67 m) down-gradient.

Based on the success of the IRM systems, three more oxygen curtain walls were designed and installed in OU-2. These curtain walls were spaced as evenly as possible throughout the middle of the plume extent to accelerate the cleanup of the plume. Installed in this fashion, the curtain walls will create and maintain multiple aerobic environments along the flow path of the plume. As a result, each curtain wall will supplement one another by reducing the dissolved contaminant mass as the groundwater flows through each curtain wall towards its discharge point. A remedial strategy schematic is illustrated in

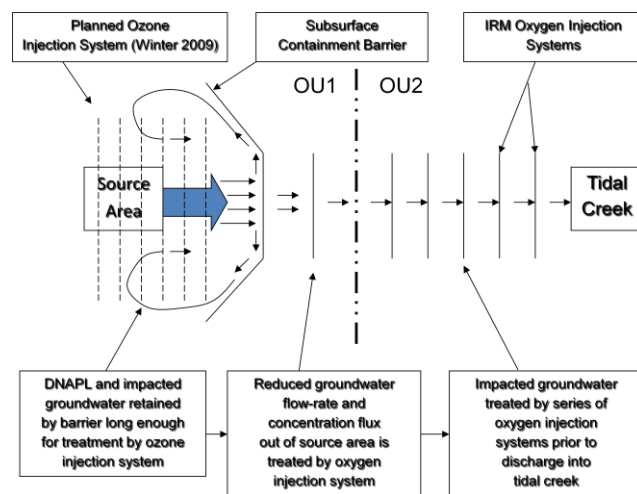


Figure 6.

Figure 6 –Remedial Strategy Schematic

After the D-D' curtain wall operated for approximately 2 months, reductions in total BTEX and total PAH concentrations ranged between 75-99% and 21-99%, respectively. Within the same timeframe, standard plate counts of bacteria populations increased between 1 to 3 orders of magnitude. Within one week of operation, dissolved oxygen (DO) concentrations ranged between 20 and 40 mg/L; and have since remained above 20 mg/L. In conclusion, these curtain walls are proving very effective at reducing the COC concentrations within the groundwater plume.

The following figures present a comparison of the plume between Q1 2009 and Q2 2011 [Figure 7 presents a simplified color legend for the isoconcentration lines; Figures 8 to 10 illustrate Total BTEX concentrations within the three aquifer zones; and Figures 11 to 13 – Total PAH]. As illustrated by the figures, there has been significant reductions in the footprint of the groundwater plume within 2 years of full operation of the oxygen injection curtain walls.

Figure 7 – Isoconcentration Color Legend



Figure 8 – Total BTEX Shallow Zone Isoconcentration Lines



Figure 9 – Total BTEX Intermediate Zone Isoconcentration Lines



Figure 12 – Total PAH Intermediate Zone Isoconcentration Lines

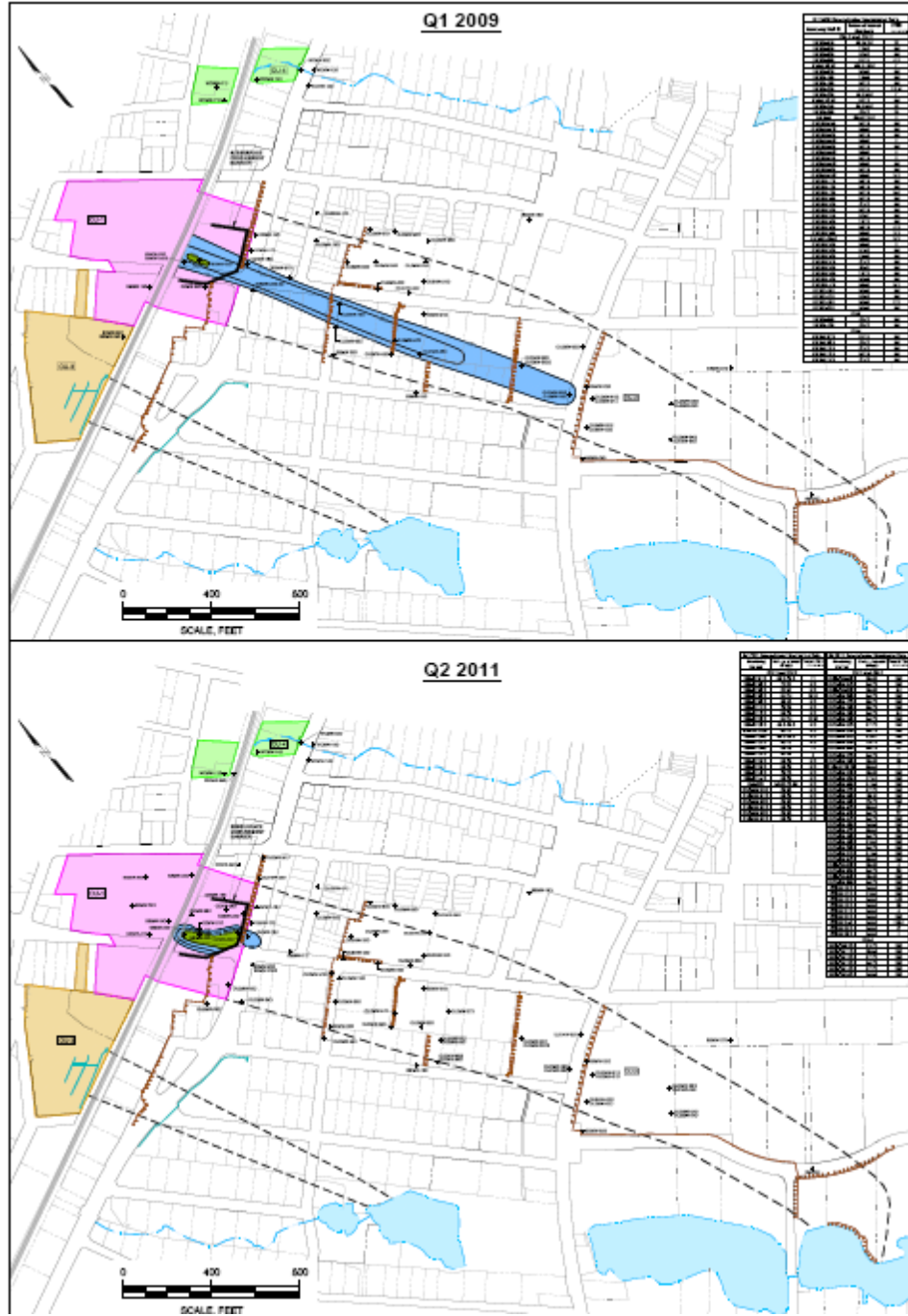


Figure 13 – Total PAH Deep Zone Isoconcentration Lines



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