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OZONE SPARGE TECHNOLOGY FOR GROUNDWATER REMEDIATION

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ABSTRACT

Ozone sparging is an oxidization remedial technology for groundwater remediation, which is rapidly gaining wide acceptance by the State Agencies as an effective method for remediating groundwater impacted by volatile organic compounds (VOCs). In general, ozone based processes for site remediation are similar to other chemical oxidation techniques in which the oxidant of choice is injected into the desired treatment area. However, the use of ozone is different from most oxidation processes as the ozone can be injected as a gas or liquid (as ozonated water). This approach provides the opportunity to deliver more continuous oxidation as opposed to batch applications typically associated with other techniques.

This discussion will focus on the basic application and design theory of the ozone sparging process, agency acceptance of the technology, and site applicability. An actual case study of one remedial project using ozone technology will be presented. The case study will cover site logistics, site geology, presentation of data before and during remedial activities, and conclusions on the effectiveness of the remedial action. The session will provide the attendee with a good overview of ozone sparging technology and its applicability to VOC remediation.

INTRODUCTION

Over the past few years there has been an emphasis by government agencies to develop new and innovative technologies for ground water remediation that are both efficient and cost effective. One of these new technologies, in situ ozone sparging, has emerged and is becoming a widely used technique. Ozone sparging involves injecting ozone into the groundwater through a microporous oxidation point that is placed below the water table. The injected ozone migrates outward and upward through the ground water. As the ozone moves through the saturated region, chemical oxidation of the contaminants takes place.

TECHNOLOGY OVERVIEW

Chemical Oxidation

Ozone (O_3) is an allotrope of oxygen, consisting of three oxygen atoms that are less stable than diatomic oxygen (O_2). Ozone is more soluble than oxygen in water and has been used for decades in municipal water treatment applications for disinfectant purposes. However, the use of ozone as an in situ chemical oxidization (ISCO) compound for soil and groundwater remediation projects has increased over the last several years as an alternative remedial method. There are two distinct forms of in situ ozone application: vadose zone injection of ozone gas and ozone sparging below the water table.

In general, ozone based processes for site remediation is similar to other chemical oxidation techniques in that the oxidant of choice is injected into the desired treatment area. However, the use of ozone is different from most oxidation processes as the ozone can be injected as a gas or liquid (as ozonated water). This approach provides the opportunity to deliver more continuous oxidation as opposed to batch applications typically associated with other techniques.

Ozone is extremely effective in treating many groundwater pollutants, including:

- Benzene, toluene, ethylbenzene and xylenes (BTEX)
- Methyl tert-butyl ether (MTBE)
- Tert-Butyl Alcohol (TBA)
- Total Petroleum Hydrocarbons (TPH)
- Chlorinated solvents (ethenes and ethanes)
- Polychlorinated biphenyls (PCB)
- Perchloroethylene (PCE)
- Trichloroethylene (TCE)
- Phenols
- Chlorinated benzenes (CBs)
- Organic pesticides

When an ozone molecule comes in contact with a VOC molecule the ozone reacts with the contaminant, producing innocuous substances such as carbon dioxide (CO_2), water (H_2O), and inorganic chloride, as shown in **Figure 1, Ozone Oxidation of Hydrocarbons**.

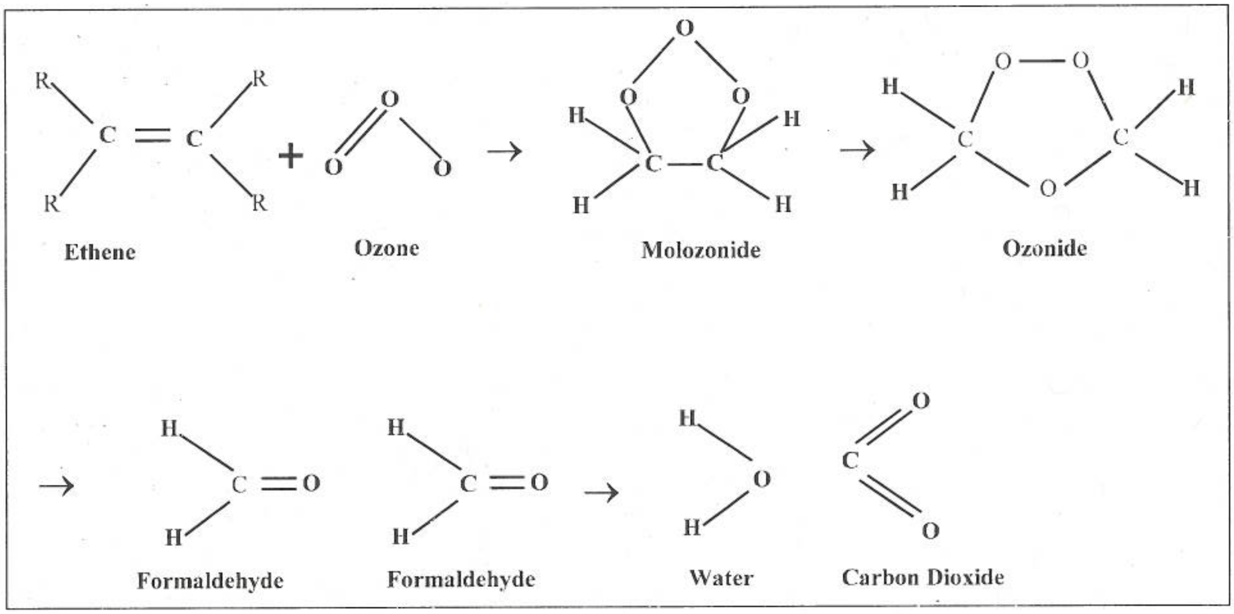

Figure 1: Ozone Oxidation of Hydrocarbons

Ozone Production

Ozone gas is formed when oxygen molecules (O_2) are exposed to a controlled high-voltage electrical field. As oxygen molecules pass through this field, a portion of the molecules are split, creating a pair of O_1 atoms. Seeking molecular stability, these atoms recombine with other O_2 molecules in the air stream to form ozone (O_3), as shown in **Figure 2, Ozone Production**.

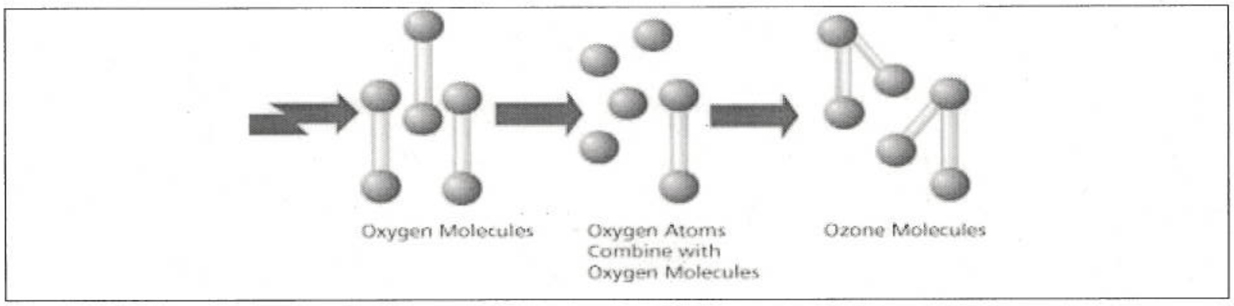

Figure 2: Ozone Production

Ozone Sparge Equipment

For soil and groundwater remediation applications, ozone is delivered to the subsurface below the groundwater table via specialized equipment designed specifically for each site. An air compressor draws in ambient air, which is passed through an oxygen concentrator. The oxygen concentrator removes nitrogen from the air stream, and delivers 90% pure oxygen to the ozone generator after drying the air stream. The ozone generator uses a high-voltage electrical current to convert oxygen to ozone at 6% concentration by weight of ozone. Another air compressor is then used to blend in ambient air with the produced ozone, allowing the ozone to be injected into the subsurface at typical flow rates of 1 to 4 cubic feet per minute (cfm) and up to 10 cfm at pressures up to 50 pounds per square inch (psi). The mixture of air and ozone is injected into the groundwater aquifer through microporous oxidation points via a 10, 20, 30, or 40 oxidation port manifold at rates up to 20.4 lbs/day at 1% concentration by weight of ozone delivered to the subsurface. A field programmable PLC-based controller with an interface panel viewer is used to control the manifold, allowing field personnel to enable and disable oxidation points, switch between ozone and oxygen injection, set lag time between sparge cycles, and set sparge duration.

It is imperative that all components on the ozone side of the system are ozone compatible. Compatible materials such as stainless steel, Teflon, Kynar, Viton, and schedule 80 PVC should always be used for ozone applications. High-density polyethylene (HDPE) and natural rubbers should not be utilized with ozone. **Figure 3, Ozone Sparge Equipment** shows a cabinet and trailer-mounted ozone sparge system that meets all the requirements described above.

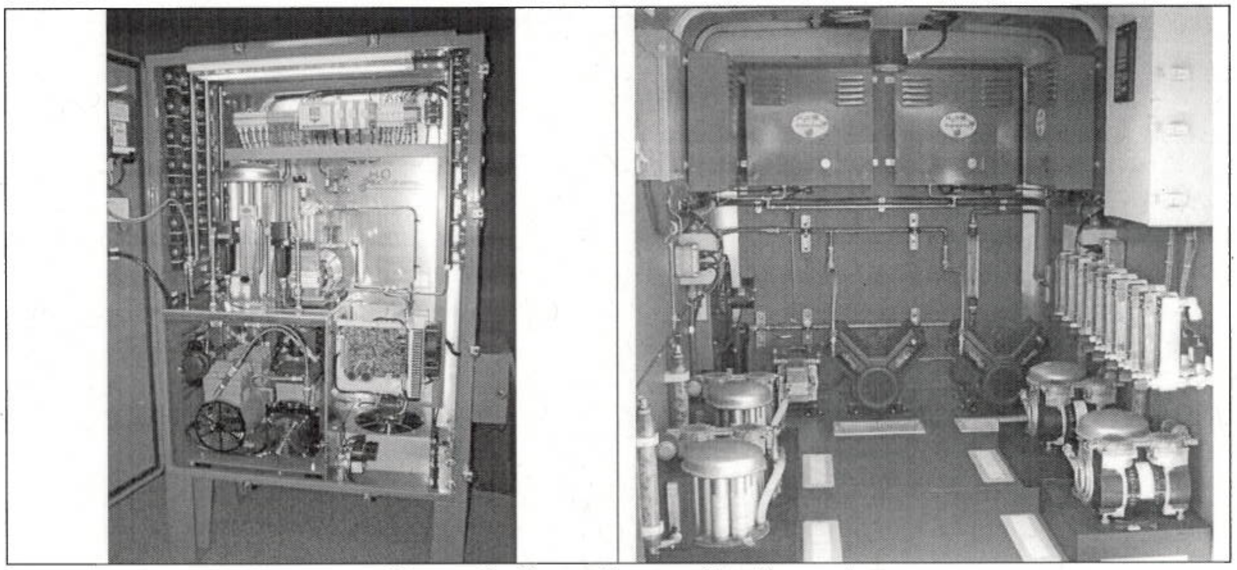

Figure 3: Ozone Sparge Equipment

Advantages of Ozone Sparge Technology

Compared to other treatment methods, Ozone Sparge technology offers many important advantages when used for the remediation of contaminated groundwater:

- Minimizes the amount of waste materials produced.
- Treatment is often accomplished in a shorter period of time.
- Ozone is generated on site, so storage and transportation of dangerous liquid chemicals is not required.
- Equipment is compact, minimizing site disruption.
- The by-product of oxidation with ozone is oxygen, so no additional compounds are added to site chemistry.
- Ozone can be used to enhance other ISCO compounds, creating the conditions for Advanced Oxidation Process (AOP).

DESIGN THEORY

The four most critical design considerations for ozone sparging are site-specific parameters that affect the ozone dosage rate, the distribution of ozone in the contaminated region, the reactivity of ozone with the contaminants of concern, and regulatory requirements, which vary from agency to agency.

Site-Specific Considerations

Oxidation is dependent on achieving adequate contact between oxidants and contaminants. Failure to account for subsurface heterogeneities or preferential flow paths can result in extensive pockets of untreated contaminants. Each system is sized based on site-specific conditions. The systems are not one size fits all. The total treatment time is dependent on the site-specific goals and characteristics and should be sized accordingly. Site-specific characteristics that should be considered during the design of ozone sparge systems, at a minimum, includes the following:

- Contaminants of concern (COC)
- Plume volume (determined from isoconcentration map)
- Contaminant mass
- Soil lithology or radius of influence data
- Hydrogeological data
- Groundwater quality (inorganic and organic oxygen receptors)

Ozone Distribution Considerations

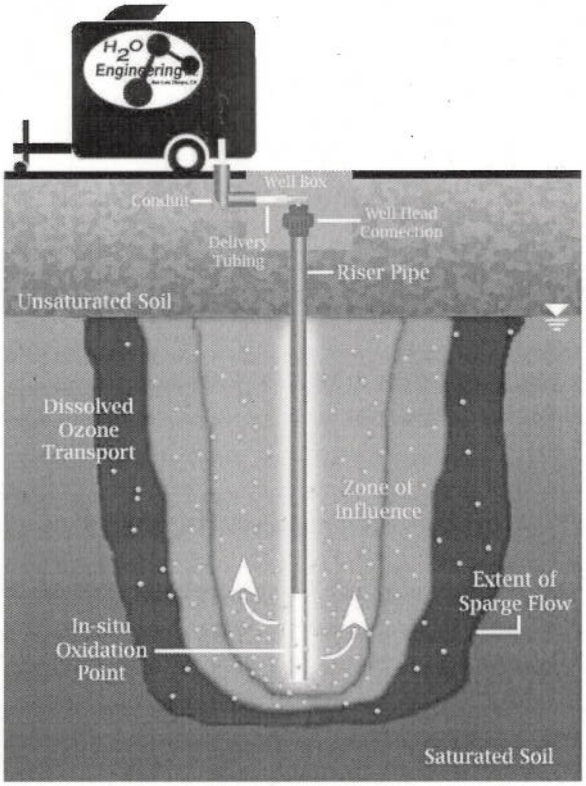

Figure 4: Ozone Distribution

One of the most important aspects of any chemical oxidation program is providing adequate contact with the contaminants to be oxidized. Typically, most applications deliver the oxidant throughout the area of impact in an effort to provide a greater amount of destruction. Injection points are strategically placed across the area of impact to provide over lap of the oxidant injections. Placement of each oxidation point is determined based on the radius of influence (ROI), which is dependent on the site lithology. For sandy sites the ROI can be as much as 40 feet, but is usually around 25 feet, and 10 feet or less in silty clay. The ROI can be determined for each site by conducting a typical air sparge pilot test using an air compressor and a few monitoring points. **Figure 4, Ozone Distributions**, illustrates a typical distribution of ozone around an oxidation point.

Another consideration is the half-life of ozone. Spacing of oxidation points should also consider how fast the ozone will move through the saturated region. The half-life of ozone in the presence of water is typically 30 minutes at standard temperatures and pressures, but it can be longer in subsurface environments because of natural deviation from standard temperatures and pressures with the absence of ozone demand. Since the mass transfer of ozone to groundwater is limited, ozonation is typically sustained over a longer period of time than with other oxidants. To maximize mass transfer to groundwater, ozone is commonly delivered via a microporous diffuser screen that creates very fine bubbles; thereby, increasing the surface area necessary for improving the efficiency of the oxidization process. **Figure 5, Oxidation Point** is a typical oxidation point that is utilized for sparging ozone into the subsurface.

Ozone Reactivity Considerations

The type of contaminants is important when designing an ozone sparge system. Ozone oxidizes different contaminants at different rates. By rule of thumb it takes about 4 pounds of ozone to oxidize 1 pound of petroleum hydrocarbons, and about 6 pounds to oxidize 1 pound of chlorinated solvents. Ozone will target all organic contaminants present in the subsurface; therefore, it is important to delineate all COCs present.

The contaminant mass is determined empirically from measured COC concentrations. The estimation of contaminant mass (in pounds) should include a full lateral and vertical assessment of the saturated zone (including any free-phase product) and the smear zone. Both the dissolved and adsorbed phases of contamination should be included in the mass estimation because ozone will attack the adsorbed phase as well as the dissolved phase. A spike in the dissolved concentrations has been noted in previous remediation projects involving ISCO technology because of the release of adsorbed-phase contaminants into the dissolved phase.

Figure 5: Oxidation Point

Another factor of ozone reactivity to consider is the presence of inorganic compounds in soil and groundwater. Inorganic compounds are oxygen receptors that, if present, will create an additional demand on ozone. Knowing the mass of these inorganic compounds will aid in determining the amount of ozone needed to remediate the site. In the absence of groundwater quality data, a rule-of-thumb is to add an additional 25% of ozone mass.

The initial investigation should include, at a minimum, an analysis of the following metals: arsenic, barium, cadmium, chromium, copper, iron, lead, and selenium. In addition, hexavalent chromium should be tested using EPA method 7199, since CR^{+3} can be converted to CR^{+6} when oxidized using ozone.

Other groundwater quality tests such as chemical oxidant demand (COD), total organic carbon (TOC), and total inorganic carbon (TIC) should be conducted to determine what will be the oxidant demand from naturally occurring organic and inorganic compounds in soil and groundwater.

Regulatory Considerations

As with any remediation technology, regulatory and legislative barriers should be considered. **Appendix A, Regulatory Permitting Requirements for Oxidant Injection by State** provides information on permitting requirements for injection of ISCO compounds.

OZONE SPARGE CASE STUDY

One of the challenges that many environmental professionals face today is the cleanup of contaminants in a tight formation. The following case study is presented to show the effectiveness of ozone sparge technology at reducing contaminant concentrations in a silty clay unit in a relatively short period. The case study will cover site logistics, site geology and hydrogeology, presentation of data before and during remedial activities, and conclusions on the effectiveness of the remedial action.

Background

This case study involves a site in northern Alabama. The area of investigation is an open, unpaved area at a farm. A barn and underground storage tank (UST) system were formerly located at the site. During the UST closure assessment in July 1995, one gasoline and two diesel USTs were removed. Soil samples collected during tank closure revealed the presence of petroleum hydrocarbon impact, and Alabama Department of Environmental Management (ADEM) required that investigative and corrective action be implemented at the site.

In August 1995, seven groundwater monitoring wells (MW-1 through MW-7) were installed, and soil and groundwater was sampled and analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX), Total Petroleum Hydrocarbons (TPH) and Polynuclear Aromatic Hydrocarbons (PAH) concentrations as part of the Preliminary Investigation. A risk assessment was also conducted to establish Site-Specific Corrective Action Level (SSCALs).

Geology and Hydrogeology

In general, the upper 25 feet of soil consists of moist, reddish-brown clay (CH) and silty or sandy clay (CL). In most of the borings, saturated soil conditions were encountered at depths ranging from 19 to 25 feet BGS. The static water levels generally rose slightly above the initial saturation level. Groundwater levels in the wells measured on June 14, 2006, ranged from 16.30 feet below top of casing (BTOC) in monitoring well MW-1 to 26.65 feet BTOC in MW-7. Based on available data, the direction of groundwater flow is in a south-southwest direction, which is consistent with previous data. The hydraulic gradient measured between MW-3 and MW-7 was estimated to be 0.096 feet/foot (ft/ft). The average hydraulic conductivity value was estimated from slug test to be 3.8 x 10^{-5} cm/sec.

Contaminant Concentrations

All BTEX concentrations in soil were below the Groundwater Resource Protection values at the source and all Site-Specific Corrective Action Levels (SSCALs) as determined during the Alabama Risk-Based Corrective Action (ARBCA) Evaluation. Elevated BTEX concentrations were present in groundwater in one well (MW-4) near the former tank pit. This area was excavated and the well replaced and renamed MW-8. BTEX concentrations rebounded to above pre-excavated concentrations, and ADEM requested that additional action be taken to reduce concentrations. Additional excavation was considered, but was abandoned in lieu of a lower cost alternative.

Free product has never been encountered at the site. Dissolved benzene at MW-8 is the only COC concentration that exceeds its GRP SSCALs. On November 28, 2006, monitoring well MW-8 exhibited a dissolved benzene concentration of 27.1 ppm (SSCAL = 0.465 ppm), as shown in **Figure 6, Dissolved Benzene/BTEX Concentrations (Baseline)**.

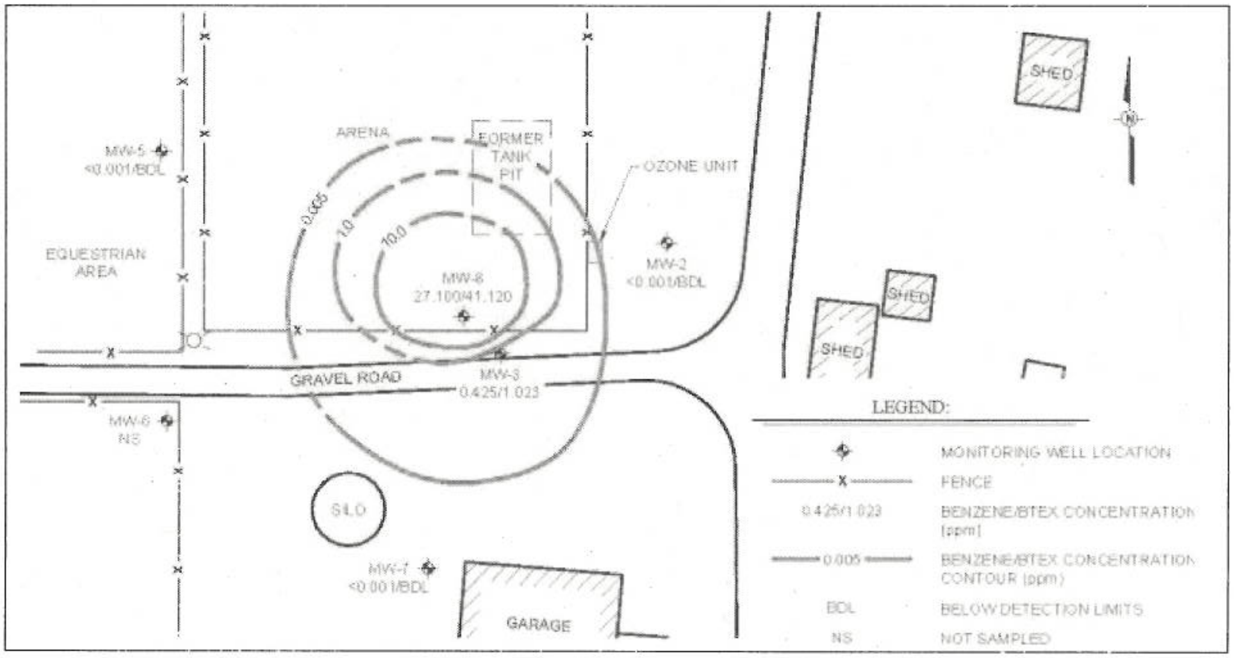

Figure 6: Dissolved Benzene/BTEX Concentrations (Baseline)

Corrective Action

A corrective action plan (CAP) was developed and submitted to ADEM for approval. The CAP recommended that ozone sparge technology be utilized to remediate the site concentrations below the SSCALs.

An H_2O Engineering, Inc. Model OSU20-52 ozone unit was selected as the equipment to be used to remediate the site. The Model OSU20-52 is capable of producing up to 2.72 lbs/day of ozone. The ozone delivery pump can deliver ozone at a maximum rate of 3.8 cfm at 50 psi for up to 20 ozone injection points, sequentially. The unit has a field programmable controller with an interface panel viewer. Independent time duration control for each injection point is available ranging from 1 to 99 minutes per oxidation point. A programmable cycle lag time is used to control the time duration between each injection cycle. System components that are in contact with ozone are manufactured of ozone resistant material to maintain acceptable run time during the project. Components can be easily replaced during maintenance intervals recommended by the equipment manufacturer.

On November 13, 2006, installation of the ten, 1-inch diameter oxidation points designated in the corrective action plan was initiated. A hollow-stem auger rig was used to advance each boring and facilitate construction of the oxidation points. Oxidation points were installed to an approximate depth of 38 feet below ground surface (BGS). **Figure 7, Oxidation Point Locations** shows the location of each oxidation point and injection tubing run. See **Appendix B, System Installation Photographs**, which depicts the installation of the ozone sparge system components.

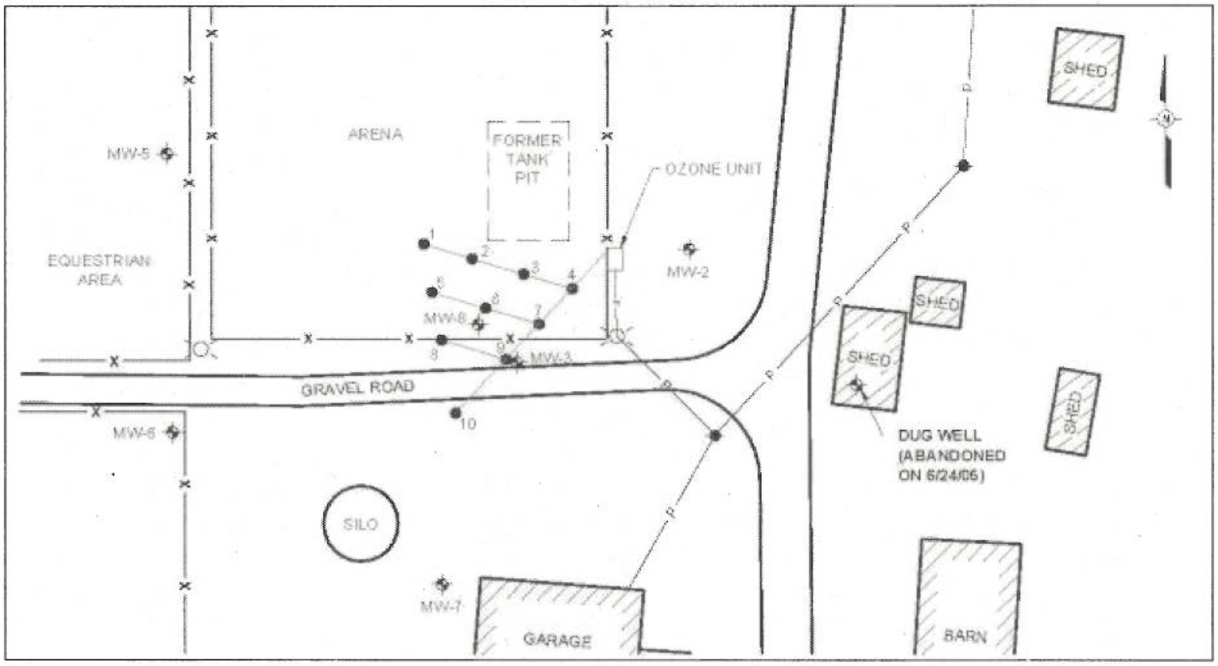

Figure 7: Oxidation Point Locations

Baseline samples were collected on November 28, 2006, and submitted for laboratory analysis. System startup and optimization began and was completed on November 29, 2006. The system ran continuously, with approximately 100 percent runtime, until December 21, 2006. Due to a minor ozone leak within the system housing, the system's ozone sensor safety feature would shut the system down periodically. There was an approximate 14-day period (from December 21, 2006 to January 4, 2007) where the system was sparging oxygen continuously and ozone only intermittently. This was followed by an approximate 13-day period where the system was sparging oxygen only. The leak was eventually isolated and repaired. The system has maintained 100 percent continuous operation since January 17, 2007.

The system was programmed to sparge ozone alternating between each oxidation point for 20 to 30 minutes each and then shutting down for system cool down for 30 minutes before restarting the next cycle.

Results

After 7 months of ozone sparge operation, remediation efforts have reduced benzene concentrations from 27.1 mg/L on November 28, 2006, to 0.366 mg/L on July 17, 2007, a 98.6 percent reduction. Additionally, all BTEX concentrations were reduced by 98.7 percent, while MTBE was reduced by 47.5 percent. The SSCAL for benzene at the site is 0.465 mg/L. **Table 1, Contaminant Concentrations in Monitoring Well MW-8** and **Figure 8, Benzene and BTEX Concentrations versus Time in MW-8** provide concentrations over time of monitoring well MW-8.

Table 1: Contaminant Concentrations in Monitoring Well MW-8

Well I.D.	Date	Benzene (mg/L)	Toluene (mg/L)	Ethyl-benzene (mg/L)	Xylenes (mg/L)	Total BTEX (ppm)	MTBE (ppm)
MW-4/MW-8 [1]	1/27/1997	**14.000**	13.000	0.370	6.200	33.570	NS
	11/5/1997	**13.000**	6.800	0.400	3.000	23.200	<1
	8/21/1998	**14.000**	8.700	0.380	3.100	26.180	<1
	7/25/2002	**9.770**	6.020	0.330	2.820	18.940	0.850
	10/9/2002	**7.100**	2.890	0.190	1.350	11.530	0.060
	1/15/2003	**12.100**	7.260	0.350	2.460	22.170	0.870
MW-8	9/15/2004	**9.830**	1.350	0.106	1.020	12.306	<0.005
	6/28/2005	**31.600**	13.500	0.610	5.600	51.310	0.016
	9/6/2005	**19.700**	5.200	0.548	4.440	29.888	<0.0050
	6/14/2006	**14.800**	22.300	2.110	12.400	51.610	0.090
	11/28/2006	**27.100**	8.200	0.720	5.100	41.120	0.040
	12/11/2006	**13.000**	2.100	0.200	2.500	17.800	<0.005
	1/2/2007	**6.800**	2.320	0.307	2.270	11.697	<0.005
	3/5/2007	**4.650**	2.510	0.182	1.330	8.672	0.400
	7/17/2007	0.366	0.094	0.006	0.086	0.552	0.021
SSCALs	--	0.465	93	65.1	198	--	1.86

Notes: [1]*- MW-4 was destroyed during excavation and replaced as MW-8*
November 28, 2006, represents baseline sampling results
SSCALs - Site Specific Corrective Action Levels
Bold *- indicates concentration that exceeds the SSCALs*

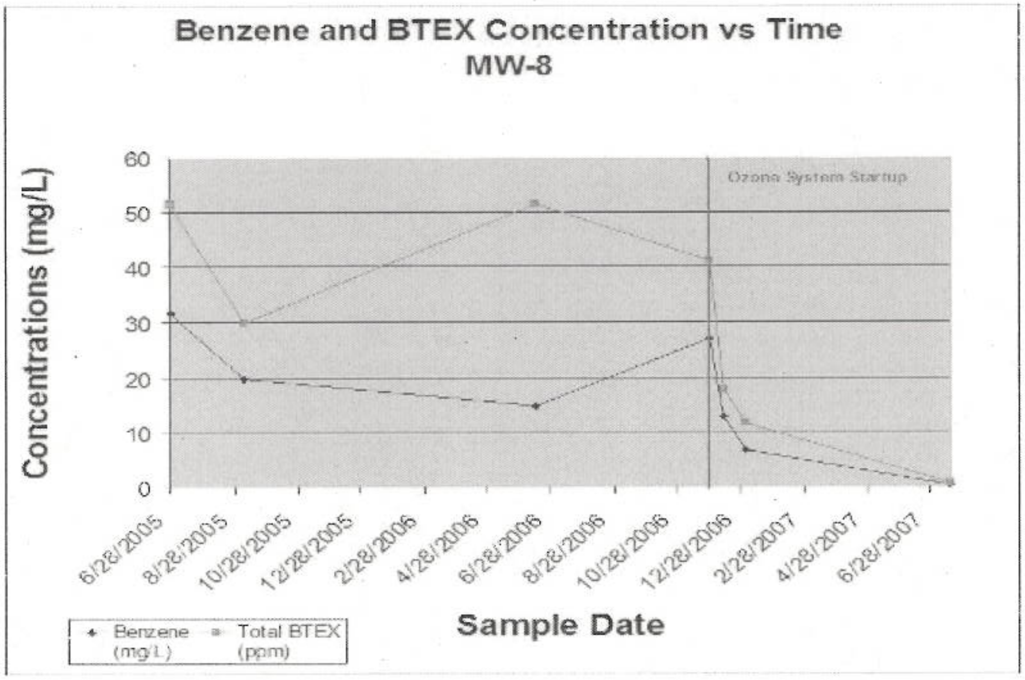

Figure 8: Benzene and BTEX Concentrations versus Time in MW-8

Cost

Total costs for installation of the ozone sparge system and 7 months of operation were approximately $106,000, as shown in **Table 2, Remediation Cost**. Equipment, installation, and startup costs were approximately $81,500. Seven months of operation and maintenance, including utilities of $200 per month, cost approximately $24,800 or $3,550 per month. These costs do not include report preparation. Three months of operation and maintenance and monitoring remain before the system can be shut down for post remediation monitoring.

Table 2: Remediation Cost

Item Description	Quantity	Unit Cost	Unit	Total Cost
Equipment Cost	1	$47,000.00	Each	$ 47,000.00
Ancillary Material Cost	1	$ 6,661.00	Each	$ 6,661.00
Installation Cost	1	$23,193.62	Each	$ 23,193.62
Startup Cost and Shipping	1	$ 4,613.00	Each	$ 4,613.00
Operations (Utilities) Cost	7	$ 200.00	Monthly	$ 1,400.00
Maintenance, Monitoring, and Sampling of MW-8 Cost	7	$ 3,342.67	Monthly	$ 23,398.69
			TOTAL COST:	**$106,266.31**

NOTE: Cost shown above does not include report preparation or demobilization cost.

Conclusions

Based on the sampling results, concentrations in monitoring well MW-8 have been reduced below the SSCALs. The ozone system will operate through one more sampling event, which will occur in October 2007. If concentrations remain below the SSCALs, then the ozone sparge system will be shutdown and the site monitored for one year. At the end of the one year sampling event, if concentrations remain below the SSCALs, then a recommendation to demobilize the system and plug and abandon site monitoring wells will be submitted to ADEM for approval.

These results indicate that ozone sparge technology was effective in reducing COC concentrations below the SSCALs in a silty clay lithology in a relatively short period.

APPENDIX A - REGULATORY PERMITTING REQUIREMENTS FOR OXIDANT INJECTION BY STATE

APPENDIX B - SYSTEM INSTALLATION PHOTOGRAPHS