

# Case Histories

Resource Control Corporation  
PO Box 579, 103 Wills St.  
Rancocas, New Jersey  
08073-0579

## Introduction:

In the current political climate of environmental remediation, responsible parties and regulators have put a major focus on risk-based corrective action. Due to this trend, fewer contaminated sites are requiring active remediation. As a result, a larger number of the sites which do require remediation are characterized by high concentration of recalcitrant contaminants, free-product, and/or nearby sensitive receptors. These 'high-risk' sites require remedial technologies that are proven effective, and affect timely clean-ups.

Additionally, the responsible parties at contaminated sites are more educated consumers; and as such, demand economical approaches, efficient service, and rapid, quantifiable results. These factors put a large responsibility on the environmental remediation contractor. The environmental remediation firm must have an arsenal of proven, efficient, effective and economical technologies at their disposal, in order to mitigate difficult, 'high-risk' contaminated sites.

Oxidation has been utilized in the wastewater treatment industry for more than a century, and these technologies have been proven highly efficient and effective at remediating contaminants in the controlled environment of a wastewater treatment system. Over the last decade, there has been an increasing effort to bring these technologies to the realm of in-situ application. There has been much published on the use of hydrogen peroxide and/or potassium permanganate for applying in-situ oxidation.

**The result of using in-situ chemical oxidation with ozone is rapid remediation of even the most recalcitrant of site contaminants.**

**Faster remediation of contaminants, with a proven, efficient technology means a more economical remediation project.**

While these oxidizing compounds have been proven effective in field applications, the efficiency and economics of use have limited their application on a large scale. Delivery of these aqueous oxidizers to the subsurface and effective distribution in the subsurface may limit the efficiency; and expense of purchasing these commodities can prove high.

The use of ozone as the oxidizing agent to implement in-situ oxidation of soil and groundwater contaminants exhibits the effectiveness of the other oxidizers; but also has the advantages of being very economical and highly efficient. Ozone is a more powerful oxidizer than either hydrogen peroxide or potassium permanganate. Ozone is generated on-site from process equipment, so there is little recurring

expense for production, unlike the aqueous commodities. Being a gas, ozone is much easier to deliver to the subsurface, and exhibits better subsurface distribution. The result of using in-situ oxidation with ozone is rapid remediation of even the most recalcitrant of site contaminants.

Faster remediation of contaminants, with a proven, efficient technology means a more economical remediation project. Resource Control Corporation (RCC) has worked for several years to develop safe and effective processes and procedures to provide ozone based, in-situ oxidation to the subsurface remediation market. RCC is committed to regulatory site closure for our clients. In-situ oxidation with ozone has proven to be very effective in providing our customers with swift, efficient and comprehensive site closure.

## Technology Overview:

### Ozone - ***“What is it ?”***

Ozone is the tri-atomic form of oxygen. It is a molecule comprised of three oxygen atoms. The molecular weight is 48 g/mol. Ozone is formed by the bonding of three oxygen atoms under the influence of ultraviolet radiation or an electrical arc (corona discharge). In nature, ozone is formed in the atmosphere from ultraviolet rays of the sun, or from the electrical discharge of lightning. In a typical ozone generator, ozone is formed by passing an oxygen stream across an electrical corona discharge, within a reaction chamber. This process creates an ozone concentration of approximately 5% by weight in the process air stream.

Ozone is a relatively unstable molecule, with a very short half-life. The half-life of ozone in air is approximately 2 minutes, as it degrades back to oxygen. In the aqueous phase, dissolved ozone has a half-life of approximately 20 minutes, as it reacts with water to form hydroxyl-radicals or degrades back to oxygen. This short life-span makes ozone ideal for in-situ remediation of contaminants, as it reacts quickly in the subsurface and rapidly reverts to harmless oxygen.

### Chemical Oxidation - ***“How does it work ?”***

During its short life-span, ozone is very reactive. Ozone has an oxidation potential of 2.07 V; the third highest oxidizer in nature (behind fluorine and hydroxyl-radicals(**Table 1**)). The higher the oxidation potential of an oxidizer, the more powerful the oxidizer - allowing it to break down the more recalcitrant compounds.

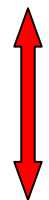
In the aqueous phase, dissolved ozone can directly oxidize contaminants, can degrade to hydroxyl-radicals (which in turn oxidize contaminants), or can degrade to dissolved oxygen which can enhance natural biodegradation of contaminants (biological oxidation). Ozone is 12.5 times more soluble in water than oxygen, which allows ozone to dissolve into water at more than 500 ppm and can saturate the water with dissolved oxygen following degradation.

### Application - ***“Where is it used ?”***

Ozone can be used to remediate contaminated groundwater and soil, in both the saturated and unsaturated (vadose) zones. Ozone has been proven an effective oxidizer against petroleum hydrocarbons and additives/oxygenates (such as MTBE), polynuclear aromatic hydrocarbons (PAHs), chlorinated hydrocarbons, phenols, and inorganic compounds.

COMPOUND	OXIDATION POTENTIAL (volts)	RELATIVE POWER OF CHLORINE
Fluorine	3.06	2.25
Hydroxyl radical *	2.80	2.05
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Permanganate	1.67	1.23
Hypochlorous Acid	1.49	1.10
Chlorine	1.36	1.00

\* This ion is formed when ozone decomposes



Ozone can be introduced to the subsurface as either a gas (ozone sparging) or a liquid (dissolved ozone injection). In gas phase, ozone is typically introduced to the subsurface (either alone or with air) through traditional air sparge wells. However, the gas sparge rate is typically lower than for air sparging, because the aim is to maximize mass transfer to the dissolved phase and/or maximize contact time with contaminants. In aqueous phase, ozone dissolved in water is typically injected to the subsurface through injection wells, trenches or infiltration galleries.

When ozone is dissolved in groundwater, the groundwater itself becomes a remediating agent, which can destroy contaminants. Dissolved ozone distribution in the saturated zone is typically better than gas distribution, as it is less affected by preferential flow pathways, upward migration, and has the benefit of aqueous diffusion and dispersion.

### **Effectiveness - “What are the results?”**

The use of ozone remediation by RCC has proven to be an economical and efficient means of rapidly remediating petroleum hydrocarbon contamination. The use of ozone sparging at remediation sites has resulted in mitigation of sites impacted with free product to below regulatory cleanup standards within a period of months, as opposed to the years required by conventional methods. Significant and rapid reductions in contaminant concentrations are not only realized with the volatile petroleum hydrocarbons (benzene, toluene, ethylbenzene, xylenes and cumene), but also with PAHs (naphthalenes) and MTBE. These non-volatile and/or recalcitrant compounds are effectively destroyed by ozone. RCC has documented that ozone rapidly oxidizes petroleum contaminants to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O), leaving no harmful residual by-products.

Presented below are real-world, field studies and case histories performed by RCC that demonstrate the effectiveness of ozone remediation.

## **Field Studies:**

### **Case History 1: Ozone Sparge Pilot Test - Former Bulk Storage Terminal**

The subject site is a decommissioned bulk fuel oil storage facility, located in southeastern Pennsylvania. The property was undergoing divestiture, and is planned for residential housing development. One portion of the former facility exhibits groundwater impacts in excess of the Pennsylvania Department of Environmental Protection's (PADEP) groundwater standards for benzene and naphthalene. Remediation of these dissolved compounds and their sources is required prior to development of the property.

#### **Study Objectives**

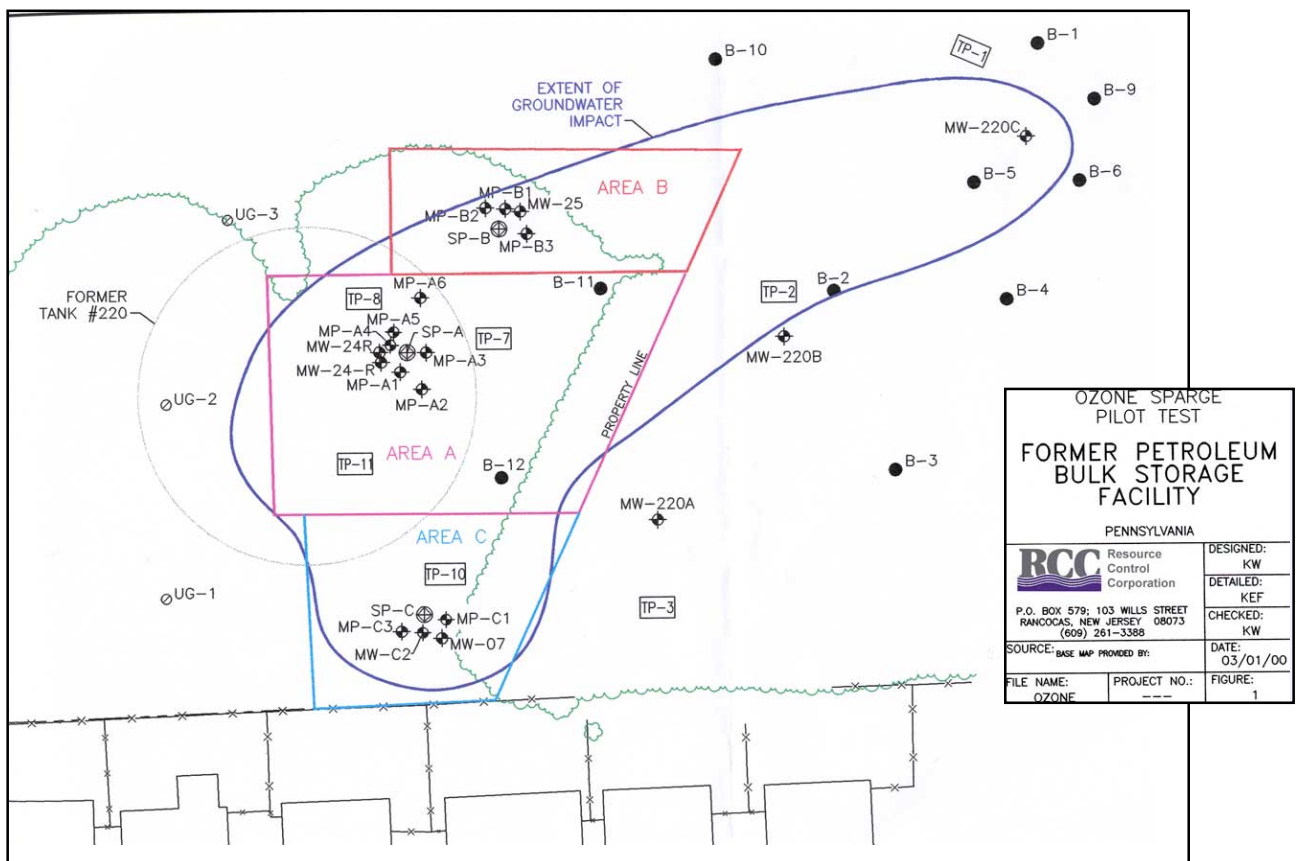
A week-long (5-day) pilot test was designed for implementation at this site, to determine if ozone sparging would be an appropriate remedial technology for this property. The test was conducted in order to determine the effects of ozone sparging on the subsurface environment in three areas of the site (see **Figure 1** below), and to develop the design basis and criteria for a full-scale system, if appropriate.

#### **Implementation**

The pilot test was implemented over a one-week (5-day) duration. The first day included two rounds of baseline monitoring, to document pre-test conditions, and the implementation of an Air Sparge (AS) only (no SVE or ozone) pilot test within the central portion of the site (Area A). The purpose of this test was to determine the effects of traditional air sparging, or biosparging, and document the need for Soil Vapor Extraction (SVE) to control sparge off-gas. AS was conducted at flow rates of 2.5, 5, 10 and 20 SCFM. Following the conclusion of sparging on the first day, respirometry monitoring (O<sub>2</sub> and CO<sub>2</sub>) of soil gas was conducted to assess the effects and rate of

biodegradation in the subsurface.

**FIGURE 1**



The second day of testing included one round of pre-test monitoring, followed by the implementation of a traditional AS/SVE pilot test (without ozone) in Area A. The purpose of this test was to determine the effectiveness of SVE at capturing off-gas and volatilizing adsorbed phase organics. This test was followed by respirometry measurements.

The third day of testing included one round of pre-test monitoring, followed by AS with the addition of ozone to the injected air in Area A. SVE was also implemented. Following the completion of ozone sparging, respirometry measurements were recorded.

The final two days of testing included post-operational monitoring of site conditions in Area A to measure the long-term residual effects and respirometry results. Additionally, an ozone sparge/SVE test was conducted each of these days, in Area C and Area B, respectively. These tests were run to determine the effects of horizontal subsurface heterogeneity on remedial operating conditions, to aid in the design of a full-scale system.

Site monitoring, during pilot test activities included DO, pH, ORP and dissolved ozone in groundwater monitoring wells; and VOC, O<sub>2</sub>, CO<sub>2</sub>, ozone concentrations, and induced vacuum/pressures in vapor monitoring points.

### **Significant Findings**

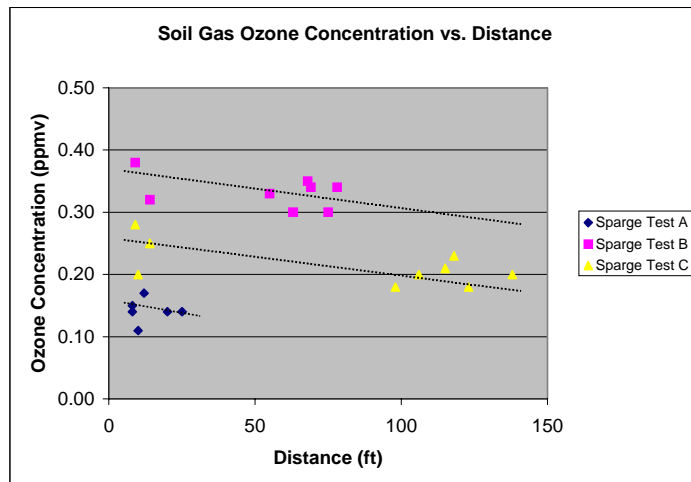
The first two days of pilot testing at the site provided physical data on the radii of influence from applied sparge pressures and SVE vacuums. Additionally, it provided a baseline measure of tradi-

tional remediation technology effects, from which to assess the effects of ozone sparging. Based on the results of this small scale, short duration, pilot test, several significant findings were noted:

**Radius of Influence** - Measurement of induced pressure differential in the subsurface during AS or SVE testing can determine an effective radius of influence (ROI) for gas flow in the subsurface. Field screening of soil gas VOC changes during remedial testing can help verify this effective radius. However, monitoring of groundwater quality indicator parameters (DO, pH, ORP, dissolved ozone) can indicate a ROI for groundwater changes resultant from remedial activities.

The induced pressure/vacuum ROI from AS/SVE calculated for the site ranged from 8 to 14 feet. This range was consistent with the changes in monitored soil gas VOC concentrations. In comparison, however, during ozone sparging at the site groundwater quality changes to pH and ORP were observed from as far away as 25 to 90 feet. In fact, dissolved ozone concentrations in Area A were detected 25 feet from the applied sparge point. Low level ozone gas concentrations were also detected in soil gas over 100 feet away from the active sparge point. This indicates that chemical oxidation of contaminants can occur well beyond the physical extent of the soil gas flow ROI (see **Table 2**).

Sparge Test Area	Monitoring Point ID	Distance From Sparge Well (ft)	Soil Gas Ozone Concentration (ppmv)
A	MP-A1	12	0.17
	MP-A2	20	0.14
	MP-A3	8	0.15
	MP-A4	8	0.14
	MP-A5	10	0.11
	MP-A6	25	0.14
B	MP-B1	75	0.30
	MP-B2	78	0.34
	MP-B3	69	0.34
	MP-B4	68	0.35
	MP-B5	63	0.30
	MP-B6	55	0.33
	MP-B7	9	0.38
	MP-B8	10	2.00
	MP-B9	14	0.32
C	MP-C1	106	0.20
	MP-C2	98	0.18
	MP-C3	115	0.21
	MP-C4	118	0.23
	MP-C5	123	0.18
	MP-C6	138	0.20
	MP-C7	10	0.20
	MP-C8	9	0.28
	MP-C9	14	0.25



**TABLE 2**

**Ozone Dispersion** - The reaction kinetics for ozone slow down at lower pH ranges, and the half-life increases. As a result of this effect, dissolved ozone concentrations persisted in the vicinity of the sparge points for more than 48 hours following cessation of sparging. Additionally, dispersion of the high dissolved ozone concentrations near the sparge point resulted in increasing dissolved ozone concentrations over a 48 hour period following cessation of sparging in Area A, at a monitoring point 25 feet away. This persistence of dissolved ozone and aqueous dispersion driven by the high concentration gradient results in a significant enhancement in saturated zone distribution (see **Table 3**).

**TABLE 3**

Monitoring Point ID	Distance From Sparge Point (ft)	Dissolved Ozone Concentration (ug/l)			
		Baseline Pre-test	Cessation of Sparging	19 Hrs After Test	43 Hrs After Test
Sparge Well	0	0	>2000	>2000	>2000
MP-A5	10	0	100	300	500
MP-A6	25	0	0	0	50

**Dissolved Ozone vs. Distance**

Distance (ft)	Cessation of Sparging (ug/l)	19 Hrs After Sparging (ug/l)	43 Hrs After Sparging (ug/l)
0	2000	2000	2000
10	100	300	500
25	0	0	50

Based on the successful results of the pilot test, a 21-well, full-scale, ozone sparge remediation system was designed and installed at the site, to remediate a five-acre area of the property. The system is currently in operation, for an anticipated 9-month period.

**Case History 2: Ozone Sparge Remediation - Former Service Station**

The subject site is the location of an out-of-service, former, retail petroleum service station. Environmental assessment activities at the site, following gasoline, underground storage tank removal activities revealed the presence of separate phase hydrocarbons on the water table beneath the site, and high residual concentrations of petroleum hydrocarbons in soil and groundwater. Targeted compounds, exceeding the PADEP cleanup standards included benzene, toluene, ethylbenzene, xylenes, naphthalene, and MTBE.

**Objective**

To facilitate sale of the property, the client required that the site be remediated within a nine-month period. The remedial goal for the site was to remove separate phase hydrocarbons (SPH) from the subsurface, and reduce adsorbed and dissolved phase hydrocarbons to levels that would allow natural attenuation of remaining contaminants to achieve site cleanup.

**Approach**

To ensure that the aggressive timeline would be met for the remediation project, RCC selected in-situ advanced oxidation as the primary remedial technology to be employed at this site. Ozone sparging was conducted through a series of nested, sparge points to oxidize the hydrocarbon compounds in both the saturated and unsaturated soils. The ozone sparge system was augmented with soil vapor and groundwater extraction using total phase extraction technology and traditional groundwater pumping. Extracted and treated groundwater was re-injected to the subsurface,

upgradient of the impacted area to further enhance remedial effectiveness by flushing the contaminated area with clean water.

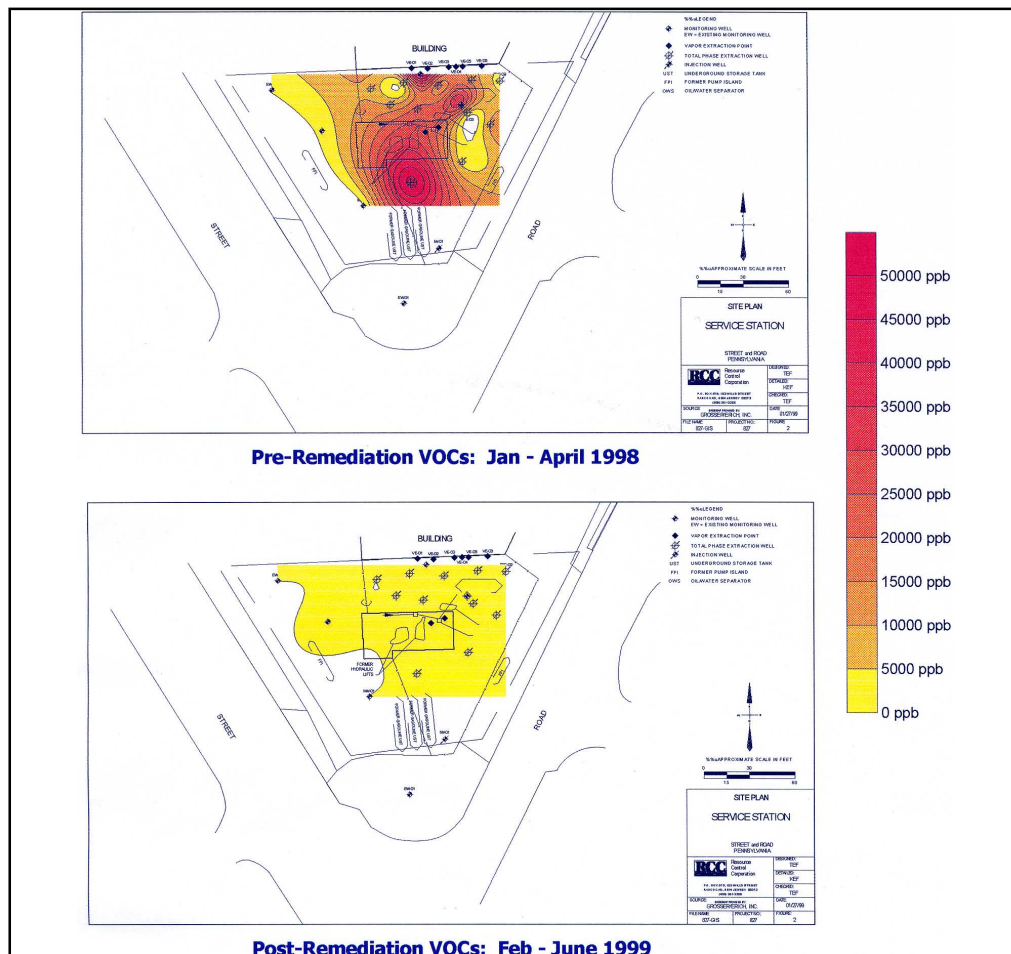
RCC's remedial approach employed a high density network of remedial wells which first utilized Total Phase Extraction (TPE) to remove the separate phase product in approximately one month. Residual dissolved hydrocarbons were then addressed via a combination of TPE, groundwater extraction, dual zone air and ozone sparging, soil venting and re-injection of treated groundwater. After approximately four months of these activities, the remedial system was shut off.

### Results

The remedial effort at this project site vastly exceeded the design goals. The objective for the remediation system was to remove SPH, reduce soil concentrations to an acceptable risk level, and to reduce dissolved phase concentrations to the low parts-per-million (ppm) range to allow natural attenuation to further remediate the site. One week prior to turning on the remedial system, slightly more than 100 gallons of separate phase product was present in an area of approximately 600 square feet. In addition, dissolved hydrocarbons were present over Statewide Health Standards in an area encompassing over 11,000 square feet with BTEX as high as 58,000 ug/L and dissolved MTBE as high as 17,000 ug/L (see **Figure 2**).

The site wells were sampled one month after shut down. Only one of the 17 wells slightly exceeded the Statewide Standards indicating results which were substantially cleaner than the remedial goals. These site wells were sampled again two months after shut down and all were found to comply with Statewide Health Standards with a decreasing trend evident between the two rounds.

Three months after system shut down, sampling of soil and groundwater from 10 temporary wells installed between the permanent monitoring points indicated further reduction in hydrocarbon compounds. During the installation of these wells, the test borings indicated that the previously



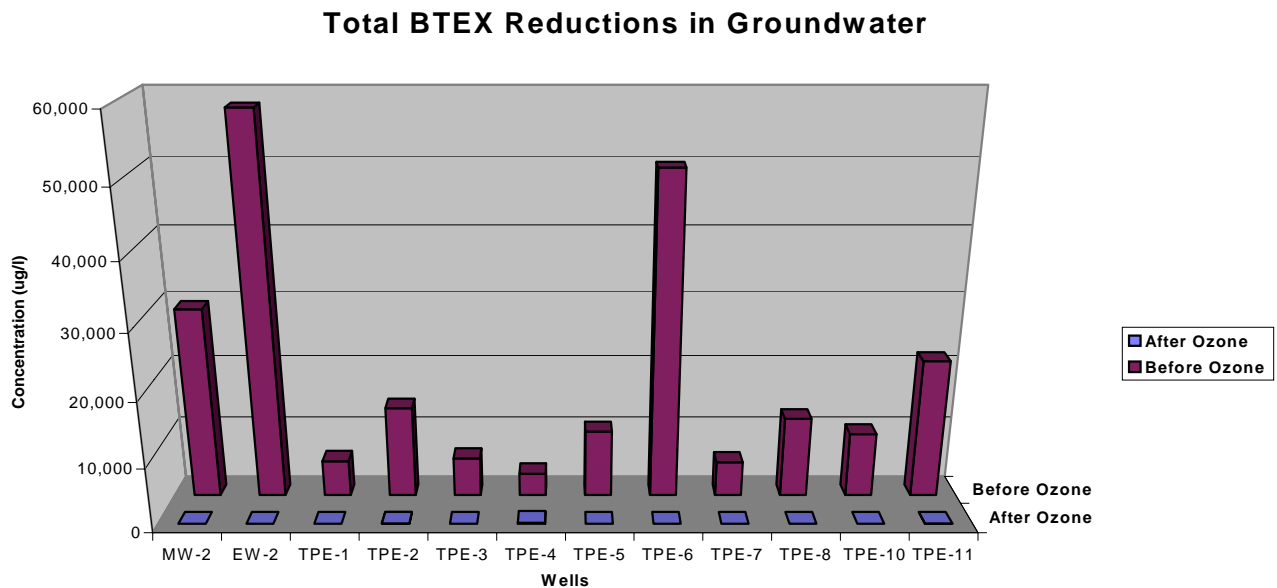
**FIGURE 2**



dark brown to black clay layers were oxidized to a whitish-grey color, indicative of the reaction of ozone with the organics in the clay materials and documenting a widespread distribution of the sparge gas.

Finally, six months after system shut down, groundwater monitoring of source area wells indicated a continued decreasing trend. For this final monitoring event, analysis was expanded from unleaded gasoline to incorporate priority pollutant volatile organic and base neutral compounds. This analysis indicated that none of these compounds were generated as by-products from the ozone application. Statewide Health Standards for both soils and groundwater were met with decreasing trends in dissolved hydrocarbons continuing.

The remedial approach removed approximately 3,500 pounds of hydrocarbons from the subsurface via active remediation while stimulating subsequent bioremediation through increased dissolved oxygen concentrations. BTEX and MTBE concentrations were reduced by 99.75% and 98.21%, respectively, and naphthalene was reduced between 52% and 97% site-wide (see **Charts 1, 2 and 3**).



**CHART 1**

Based on post-remedial site monitoring and sampling, the PADEP issued a 'No Further Action' letter with an Act 2 Release of Liability.

### MTBE Reductions in Groundwater

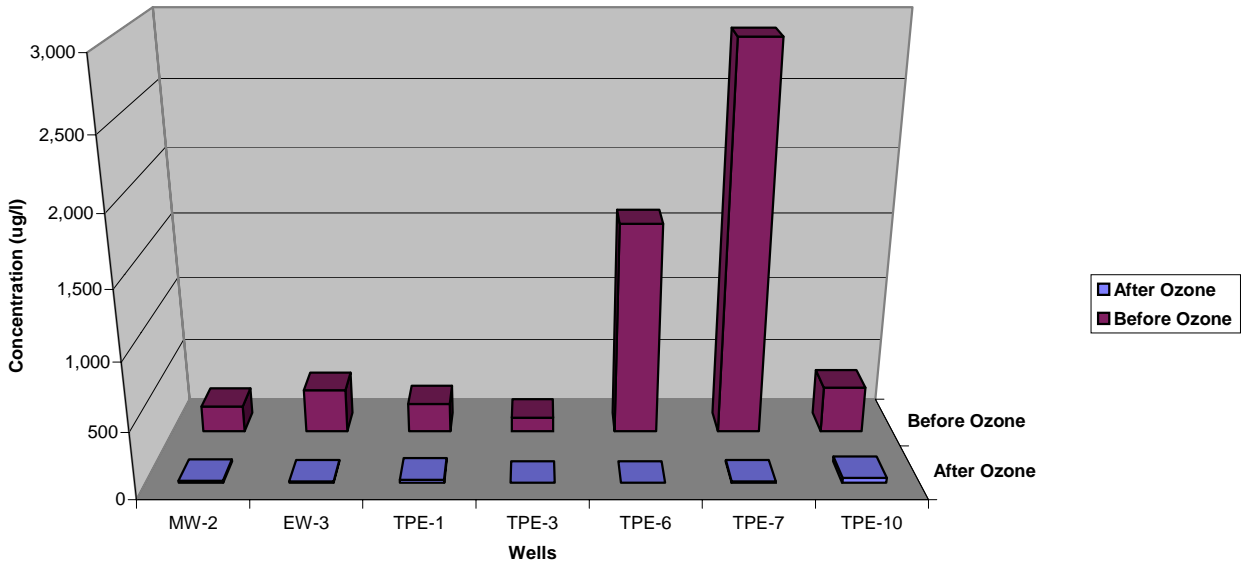


CHART 2

### Naphthalene Reductions in Groundwater

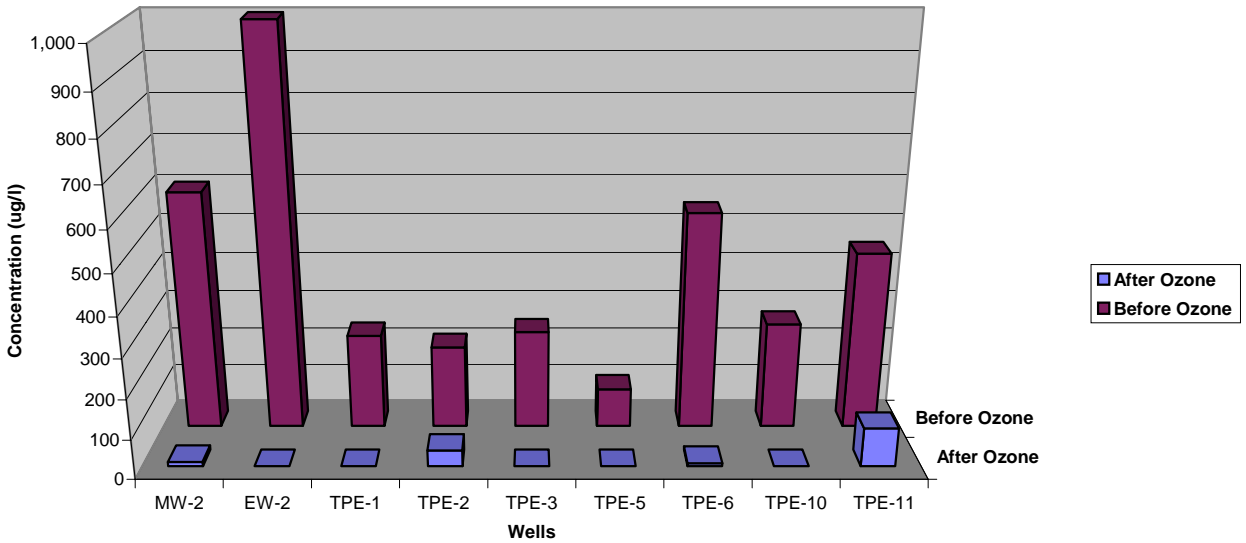


CHART 3

### **Case History 3: Ozone Sparge Remediation - Former Bulk Storage Terminal**

The subject site is a decommissioned bulk gasoline and fuel oil storage and distribution facility, which had been in operation for over 50 years. Previous environmental assessment activities at the site revealed the presence of separate phase hydrocarbons and high residual concentrations of petroleum hydrocarbons in soil and groundwater. Targeted compounds, exceeding NYSDEC-STARS cleanup standards included benzene, toluene, ethylbenzene, xylenes, naphthalene, and MTBE. Another consulting firm was already operating several dual-phase extraction systems in the impacted area upon RCC's arrival to the project in November 1998.

#### **Objective**

The subject property was under contract for a real estate transaction. As such, the client required that the site be rapidly remediated. The initial goal for the site was to remove separate phase hydrocarbons; however, subsequently the NYSDEC required that soil and groundwater contamination be reduced to levels that would allow for natural attenuation of remaining contaminants to represent a viable long-term approach to site cleanup. Based on the more stringent cleanup goals, RCC was contracted to test the remedial effectiveness of ozone sparging at this site.

#### **Approach**

Air sparge testing was initially performed to forecast an effective sparge area and to select operational flow rates for the pilot system. Ozone sparging commenced in February 1999 using an existing 380-foot horizontal well to affect in-situ oxidation of the hydrocarbon compounds in groundwater and both saturated and unsaturated soils. Air was combined with the discharge from two ozone generators, and was used to deliver compressed air and ozone simultaneously to both ends of the horizontal well. The ozone sparge system was operated in conjunction with dual-phase extraction from two adjacent horizontal wells to control any potential fugitive emissions. Daily field screening of groundwater, in-situ soil gas and extracted vapors was conducted to evaluate the subsurface ozone distribution and monitor other indicator parameters (DO, ORP, pH, temp, O<sub>2</sub>, CO<sub>2</sub>, etc.).

#### **Results**

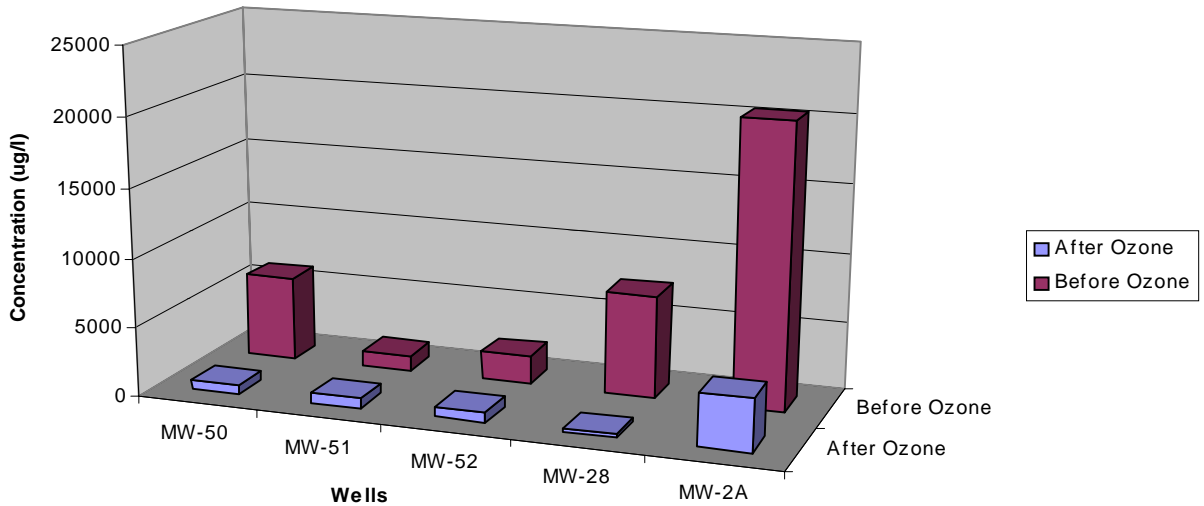
Prior to starting the ozone system, several dual-phase extraction systems had been in operation in the area of concern for a period of six months (August 1998 - February 1999). Remedial effectiveness soil and groundwater sampling was performed in February 1999, prior to full-scale operation of the ozone system, for comparison to pre-remediation conditions. Although the dual-phase extraction systems had recovered significant SPH, the sample results indicated insufficient improvement to site soil or groundwater quality had occurred relative to NYSDEC standards.

The ozone sparge system was installed and operated for a pilot period of seven months, concurrent with the dual-phase extraction systems. Routine field screening results indicated that dissolved phase ozone was being rapidly depleted; however, the distribution and concentration of gas-phase ozone in soil gas increased over time. Low concentrations of ozone began to be detected in extracted soil gas after four months of operation, indicating good distribution of ozone and a decrease in ozone demand. Groundwater quality trends, based on daily field screening, indicated increasing ORP and groundwater temperatures; however, post-operational soil and groundwater sampling was required to definitively measure the effects of remediation.

Effectiveness of the ozone system was evaluated after seven months of operation. Effectiveness was measured by performing soil and groundwater sampling at locations coincident with pre-remedial sampling locations and locations from the February 1999 event. The results of the effectiveness evaluation exceeded expectations, for samples collected both in soil and groundwater. Gauging and sampling indicated that SPH was effectively removed from the site. Average soil and groundwater concentrations at the site were found to be greatly reduced. Groundwater VOC concentrations showed average reductions of 64%. Soil VOC levels showed even more impressive reductions, with an average of 97%. Of special note is the 45% reduction of

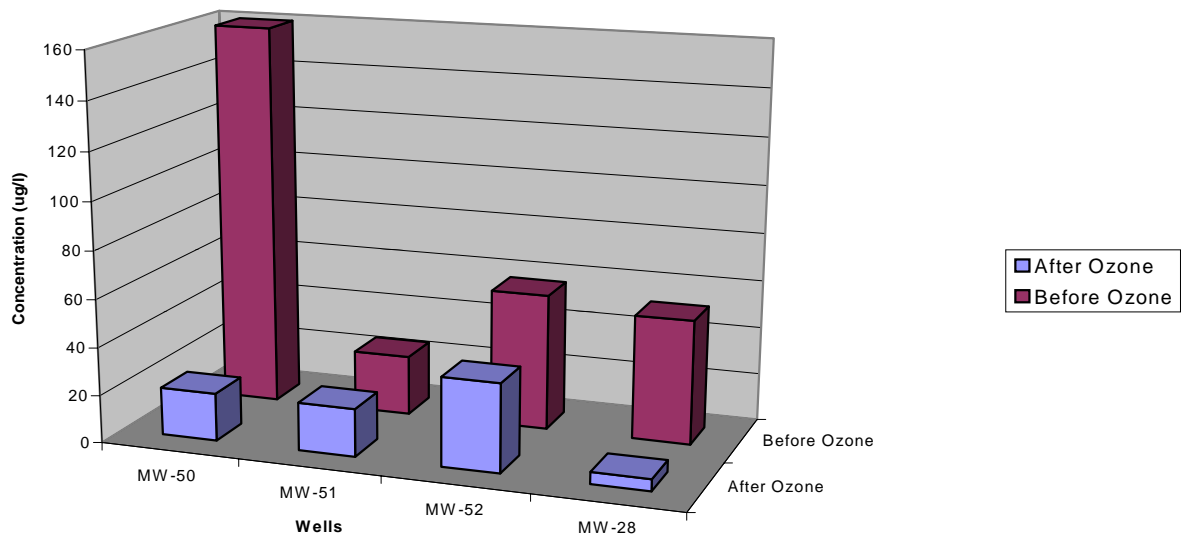
MTBE in groundwater and 90% in soil, as this result can be more directly attributed to the operation of the ozone system. The dual-phase extraction system may not be effective at remediating this contaminant from soil and groundwater, whereas ozone is capable of directly oxidizing MTBE. **Charts 4 and 5**(groundwater), and **Charts 6 and 7**(soil) summarize the results of the referenced sampling events.

### Total BTEX Reductions in Groundwater



**CHART 4**

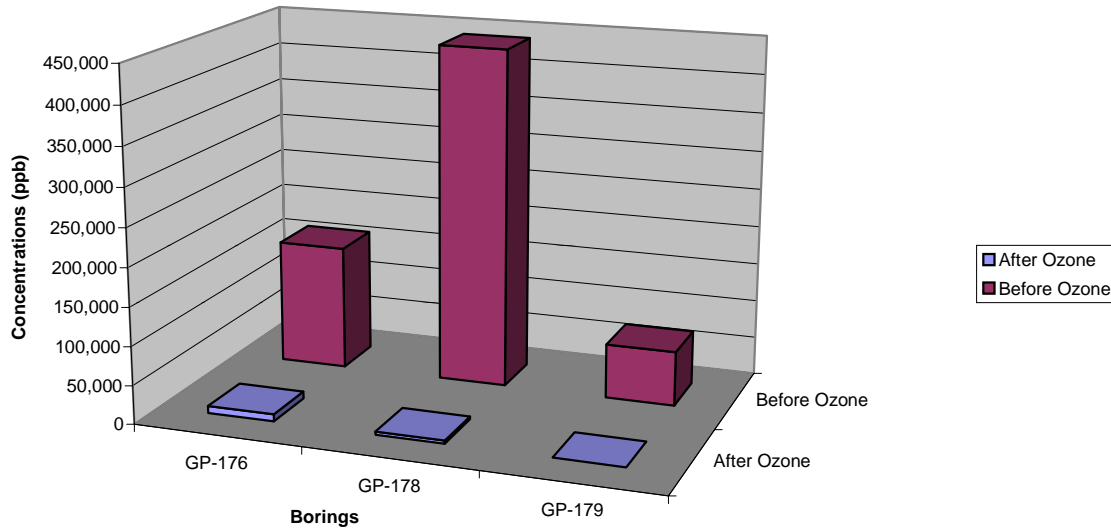
### MTBE Reductions in Groundwater



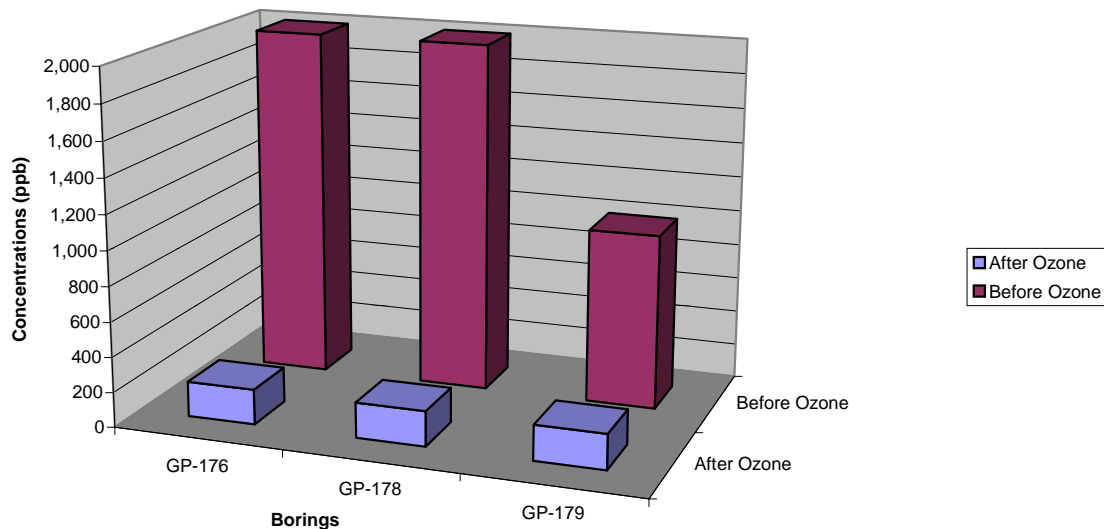
**CHART 5**

The positive results of the ozone sparging efforts have been used to scale-up ozone sparging remedial implementation at the site. A larger, mobile ozone sparging system has been constructed, and was deployed at the site in March 2000. This new system will address other areas of concern at the site, and the client has chosen to cease operation of the dual-phase extraction systems, eliminating their costly operating and maintenance due to groundwater processing. The mobile ozone sparging system will be used systematically, one well at a time, on a series of horizontal wells, without vapor extraction. The mobile system is projected to remediate the entire site, encompassing over 20 acres, over a period of three years.

**Total BTEX Reductions in Soil**



**MTBE Reductions in Soil**



**CHARTS 6 and 7**

## **Regulatory Acceptance:**

In addition to the two above referenced Pennsylvania projects, RCC is currently implementing an ozone sparge remediation project at a former gasoline service station located in southeastern Pennsylvania; and RCC has PADEP approved Cleanup Plans calling for ozone remediation of two other petroleum contaminated sites in the region. Regulatory acceptance in the PADEP's South-eastern Region is very good.

In New Jersey, RCC has a New Jersey Department of Environmental Protection (NJDEP) approved Remedial Action Workplan for a currently active ozone sparge remediation system located in the Pinelands Protected Area. Dissolved phase MTBE concentrations detected in groundwater at this site, in excess of 100,000 ppb, must be reduced to the analytical detection limit (ND). The use of ozone to remediate this site was accepted by both the NJDEP and the NJ Pinelands Commission.

As discussed above, the New York State Department of Environmental Correction (NYSDEC) approved the use of ozone sparging to remediate a former petroleum bulk storage and distribution facility located in upstate New York. Based on the success of the remedial actions, the ozone sparge system is being scaled-up for use site-wide.

## **Summary:**

The most apparent benefits of utilizing ozone remediation at petroleum hydrocarbon contaminated sites are the rapid remediation of a wide range of sites (in months as opposed to years), and the ability to oxidize recalcitrant compounds (ie. MTBE, PAHs). A rapid and effective remediation project results in a more economical cleanup.

During the 1990s RCC has developed and tested various processes and methods to deliver ozone in-situ oxidation on subsurface remediation projects. These case histories demonstrate the effectiveness of the technology in three different geologic settings on various types of petroleum hydrocarbon constituents of concern. When combined with an effective regulatory strategy, RCC can provide fixed cost and guaranteed remedial actions for you or your clients. RCC will use this chemical and biological remedial approach, along with other chemical, biological and physical remedial technologies, as needed to continue to provide our customers with world class customer service.