

## **The Use of Ozone Sparging to Remove MTBE from Groundwater in a Uniform Sand Aquifer**

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### **Abstract**

In February of 2002 it was discovered that a retail petroleum station had a chronic release of gasoline, including Methyl-Tertiary-Butyl-Ether (MTBE)-containing fuel. While the benzene plume from this Site extended a maximum of 400 feet downgradient from its source release area, the MTBE plume had traveled over 1,800 feet down gradient and impacted a public water supply. Concentrations of MTBE in the groundwater at the Site were as high as 6,900 ug/L near the source area.

Because of the impacted public water supply, there was significant community and regulatory pressure to remediate the source area as quickly as possible. After evaluating a variety of technologies, ozone sparging was selected as the most expedient and cost-effective groundwater remediation technology for this Site. The permeable sand aquifer and shallow depth to groundwater made this Site well suited to sparging in general and it was believed that the use of ozone would greatly enhance the degradation rate of MTBE and other gasoline hydrocarbons on the Site.

Ozone sparging was pilot tested at the Site in August of 2003 and construction of the full-scale ozone sparging remediation system began in March 2004 and was completed in July 2004 when the system became operational. The ozone sparging system utilizes two 120-gram/hour ozone generators with 16 injection wells. Preliminary groundwater analyses indicate the ozone system has been highly effective in reducing concentrations of MTBE and other hydrocarbons in groundwater at the Site.

## Site Operations and Release History

The Site is currently operating as a retail and bulk fuel facility with a convenience store and office on the property that was previously agricultural land. The Site is bordered by agricultural land to the south, and by residential property to the west, east, and by a state road to the north. There are currently 9 underground storage tanks (USTs) located at the Site. To date, no USTs have been removed from the property and no detectable releases have been reported. It is believed that the source of petroleum is due to numerous small surface spills over an extended period of time.

Verbal notification of a petroleum release at the Site was made by a county health department employee in February 2002 as a result of the bathroom water in the station exhibiting a petroleum odor. An *Initial Site Characterization Report* (ISC) was completed in August 2002. The results of soil and groundwater sampling and testing indicated areas of unsaturated soil and groundwater beneath the Site had been impacted by benzene, toluene, ethylbenzene, total xylenes (BTEX) and methyl tertiary butyl ether (MTBE). In addition, a dissolved hydrocarbon plume extended off-Site to the north-northwest. In December 2002, additional investigation was completed to further document the extent of impacts on and off the Site and to establish a permanent monitoring well network for future plume monitoring.

## Benzene and MTBE Plume

On-Site impacts are in isolated areas of unsaturated soil and groundwater in the central portion of the Site. The Benzene plume from this Site extends a maximum of 400 feet downgradient, while the MTBE plume has traveled over 1,800 feet downgradient. The release at this Site has impacted the public drinking water supply at the Site, based on the levels of BTEX and MTBE in the drinking water well, and made it necessary to treat the water prior to consumption. Off-Site impacts are restricted to a narrow plume of MTBE-impacted groundwater between approximately 25 and 50 feet below ground surface. Surface infiltration of water has forced the far downgradient plume down to the lower portion of the aquifer. This plume has impacted the drinking water supply at an elementary school and a private residence. Both of these drinking water supplies contained detectable levels of MTBE prior to treatment. Initially, the level of MTBE in the private residence was below the state drinking water advisory of 45 ug/L but has since risen to above 100 ug/L; the level of MTBE in the school well has varied between non-detectable amounts to greater than 350 ug/L. Drinking water treatment systems were designed and installed in the fall of 2002 to provide safe potable water supplies for the school, station and residence. The Site layout and groundwater plume are illustrated in Figure 1.

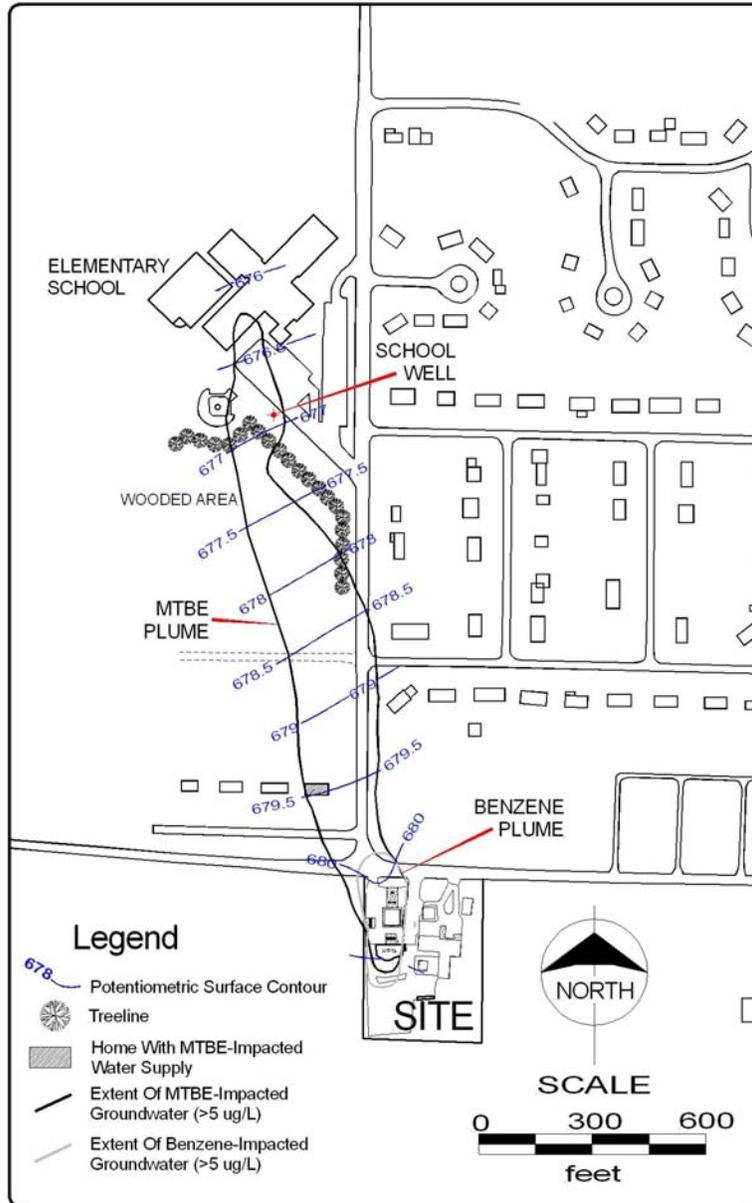
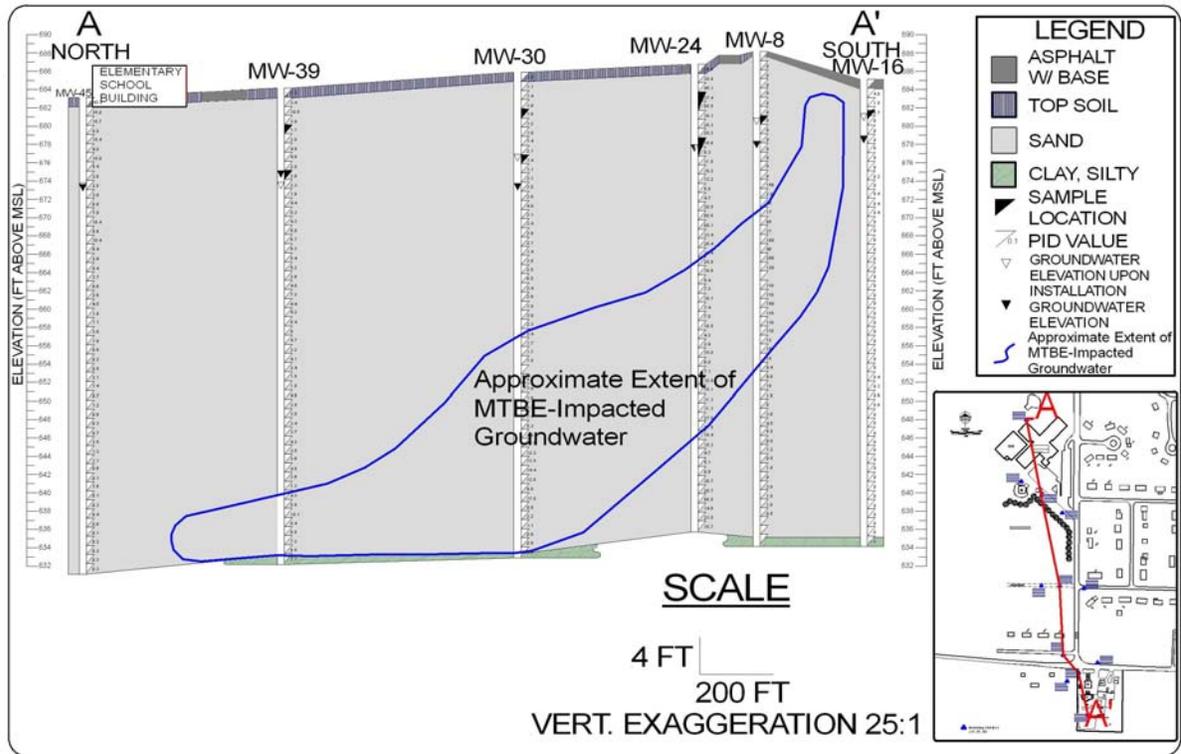


FIGURE 1. Site map with groundwater plume

## Geology and Hydrogeology

The Site is located within a previously glaciated region of northern Indiana, approximately 30 miles south of Lake Michigan. The unconsolidated deposits beneath the Site are dune and outwash deposits. The lithology encountered during drilling at this Site and on adjacent properties was exceptionally uniform. Depending on the use of the property where the boring was located, the upper foot of soil consisted of gravel, fill or native topsoil. Below one foot, the soil lithology consisted of uniform, poorly-graded fine to medium sand (SP, according to the Unified Soil Classification System). Over the majority of the Site and in the

off-Site borings, groundwater was typically encountered between 3 and 10 feet below ground surface (bgs). The sand aquifer ended at a depth of approximately 54 feet bgs where borings encountered a dense silty clay layer. A geologic cross section is included as Figure 2.



**FIGURE 2. Geologic cross section and MTBE plume**

To provide Site-specific values of hydraulic conductivity, single-well aquifer response (i.e., slug) tests were performed at eight monitoring wells to determine the hydraulic properties of the upper, middle and lower portions of the sand aquifer in the vicinity of the Site. The Bouwer and Rice (1976, 1989) method was used for analyzing the single well response test data. The data collected during these tests confirmed that the uppermost aquifer in this area is unconfined and relatively isotropic. The results of the analysis indicate the hydraulic conductivity of the aquifer ranges from about 18 to 77 feet per day in the upper to middle part of the aquifer, while the lower portion ranged from 49 to 92 feet per day. Assuming a hydraulic conductivity of 50 feet per day and an aquifer thickness of 40 feet, the transmissivity of this aquifer is about 2,000 feet<sup>2</sup> per day. A linear groundwater flow velocity in this aquifer of approximately 0.4 feet per day was calculated based on the aquifer horizontal gradient of 0.0025 ft/ft. and assuming an average porosity of 30%.

## Ozone Sparging

Because of the impacted public water supply there was significant community and regulatory pressure to remediate the source area as quickly as possible. After evaluating a variety of technologies, ozone sparging was selected as the most expedient and cost-effective groundwater remediation technology for this Site. The permeable sand aquifer and shallow depth to groundwater made this Site well suited to sparging in general and it was believed that the use of ozone would greatly enhance the degradation rate of MTBE and other gasoline hydrocarbons on the Site.

Ozone-air sparging provides enhanced stripping of VOCs from groundwater while introducing ozone as a highly reactive oxidant to destroy the target compounds. Ozone is a highly reactive chemical that has proven to be effective in destroying a wide variety of organic chemicals, including MTBE and chlorinated VOCs. Ozone destroys organic chemicals through the process of chemical oxidation, which breaks the targeted organic chemical down into carbon dioxide and water. Ozone is commonly used in aboveground treatment systems for treatment of wastewater and is widely used to treat extracted groundwater generated from pump-and-treat remediation systems. A much more cost-effective way to utilize ozone remediation is with an in-situ ozone-air sparging system.

Ozone-air sparging destroys dissolved BTEX and MTBE by three key processes. First, when air is bubbled through ground water in soil pores, dissolved VOCs transfer from liquid to gas phase in accordance with Henry's law. Second, ozone in the sparge bubbles reacts extremely rapidly with VOCs, destroying them in the process. Thirdly, residual oxygen from the reaction encourages bioremediation, which consumes the breakdown products and converts them to carbon dioxide and water.

Typical air sparging systems have traditionally been ill-suited to MTBE remediation due to its low Henry's Law Constant (approximately one-tenth that of benzene), which tends to keep MTBE in solution with the groundwater. The advantages of ozone-air sparging as a remediation method for this Site are that it combines aggressive stripping and treatment of BTEX and MTBE *in situ*, no vapor extraction is necessary since target compounds are destroyed through oxidation, and Site disturbance is minimal. The disadvantages of ozone-air microsparging center on the lack of hydraulic control. Because there is no pumping of groundwater, the ozone injection points were positioned in such a way as to intercept the groundwater as it moves naturally downgradient. (Kerfoot and LeCheminant, 2002)

A 30 day pilot test was scheduled to determine if ozone-air sparge technology would be effective in treating the plume, and to help determine an appropriate system design. The pilot test involved injecting air and ozone at one injection point and monitoring groundwater at 5 adjacent monitoring wells. Ozone and air was injected at 0.25 feet<sup>3</sup> per minute. The ozone source was an ozone generator capable of producing 14 g/hr of ozone. (Superior Environmental, 2003)

## Remediation System Specifications

Sixteen (16) ozone sparge wells were installed at the Site. The locations of the ozone sparge wells are shown on Figure 2. The wells are two inches in diameter with a five feet stainless steel wire wrapped screen installed at a depth of 36 to 41 feet below grade level with a stainless steel riser. The annular space is grouted from above the screen to the ground surface. Wells are spaced approximately 15 to 20 feet apart. Four vapor monitoring points were installed. These vapor monitoring points, along with the three existing points have been monitored by PID for VOC levels during routine operation and maintenance Site visits to monitor for the presence of vapors in the vadose zone.

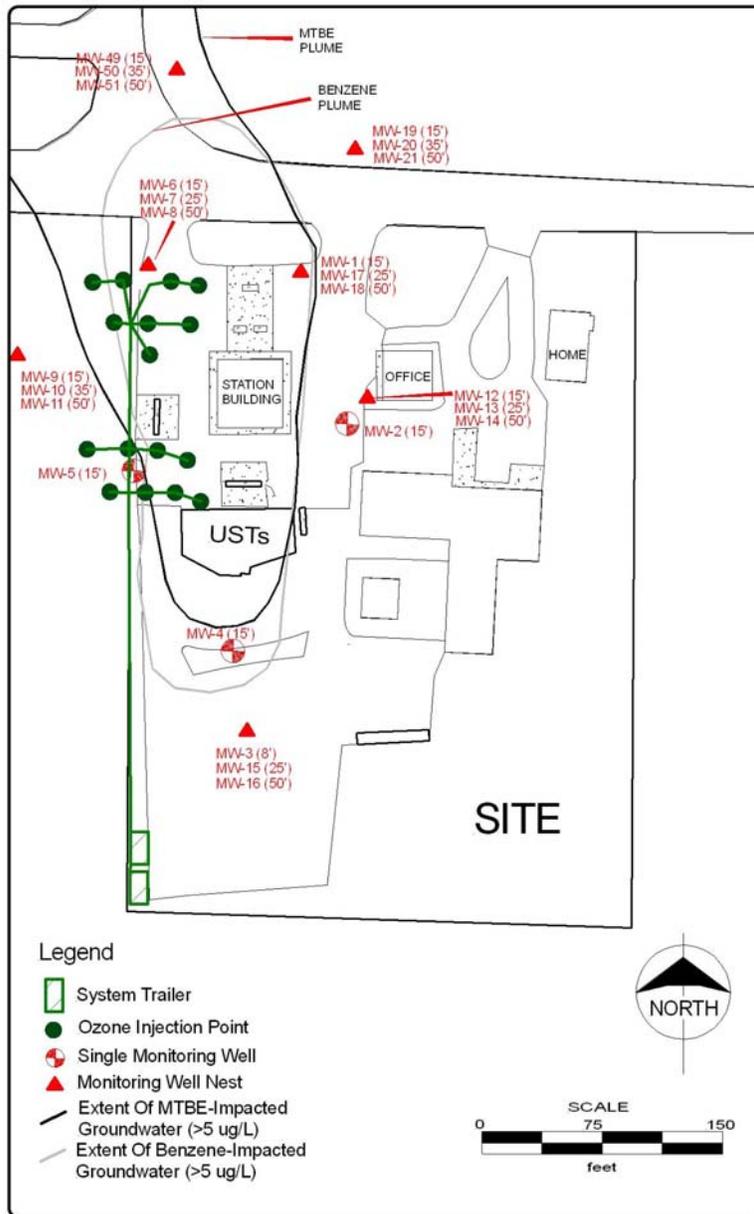


FIGURE 3. Ozone injection system layout

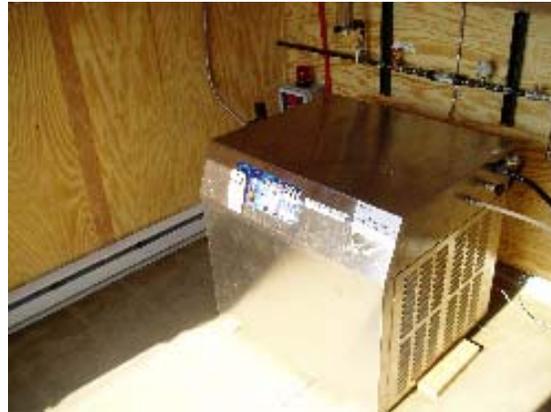
Remediation equipment was installed in two identical trailer units consisting of a compressor supplying air directly to sparge points and to an ozone generator capable of generating 120 g/hour of ozone with a built in oxygen concentrator. A booster compressor capable of delivering ozone at 40 psig pressure supplies ozone back into the compressed air line to the sparge points after it has gone through the oxygen concentration and ozone generation process. The trailer units include safety controls to shut down the system in case of ozone leak and auto dialers to call out in an alarm condition.



**FIGURE 4. System trailers**



**FIGURE 5. Air compressor**



**FIGURE 6. Oxygen concentrator and ozone generator**

Approximately 2.6 to 2.8 scfm of air and ozone is delivered to each sparge point at a pressure of 11 to 14 psi. Ozone is produced at 89 scfh (standard cubic feet per hour) at a concentration of approximately 8% by weight (of the ozone sparge stream) totaling approximately 6.4 lbs per day of ozone produced by each of the two trailer units.

## Results and Conclusions

An evaluation of the impact of the ozone sparging system on groundwater quality was performed to determine the extent of the ozone sparge system influence on the groundwater geochemical environment, and potential rates of BTEX and MTBE reductions resulting from system operation. After approximately three months of operation by the ozone system, two (2) on-Site monitoring wells exhibited detectable BTEX/MTBE concentrations, as compared to five (5) monitoring wells prior to system startup. Significant benzene and MTBE reductions since system start-up demonstrate effective treatment of the groundwater plume by the ozone injection system. Results of selected monitoring wells are summarized in Table 1. Monitoring well locations are shown in Figure 2.

**TABLE 1. MTBE and benzene concentrations in select monitoring wells**

Sample Event Date	Sample Locations and Concentrations									
	MW-1		MW-4		MW-5		MW-7		MW-50	
	MTBE (ug/L)	Benzene (ug/L)	MTBE (ug/L)	Benzene (ug/L)	MTBE (ug/L)	Benzene (ug/L)	MTBE (ug/L)	Benzene (ug/L)	MTBE (ug/L)	Benzene (ug/L)
04/23/02	<5	<b>192</b>	<5	<b>1,110</b>	<5	<b>92</b>	<b>1,190</b>	<b>24,700</b>	NA	NA
08/01/02	<5	<5	< <b>500</b>	<b>140</b>	<5	<b>710</b>	<b>350</b>	<b>5,100</b>	NA	NA
10/15/02	<5	<b>46</b>	< <b>500</b>	<b>780</b>	<5	<b>9,400</b>	<b>260</b>	<b>3,300</b>	NA	NA
08/01/03	< 5.0	< 5.0	<b>21</b>	< <b>1200</b>	< 5.0	< 5.0	<b>140</b>	<b>26,000</b>	NA	NA
11/07/03	<5.0	<5.0	< <b>500</b>	<b>3,800</b>	< <b>250</b>	<b>2,000</b>	<b>110</b>	<b>14,000</b>	NA	NA
03/03/04	<5.0	<b>8.5</b>	< <b>2,500</b>	<b>2,800</b>	< <b>250</b>	<b>3,200</b>	<b>270</b>	<b>19,000</b>	NA	NA
04/22/04	<5.0	<5.0	< <b>250</b>	<b>3,000</b>	< <b>120</b>	<b>1,600</b>	< <b>500</b>	<b>31,000</b>	NA	NA
7/2/04	Initial Ozone Injection System Startup									
09/01/04	<b>19</b>	<b>11</b>	<5.0	<b>210</b>	<5.0	<5.0	<b>140</b>	<b>5,700</b>	<b>26</b>	<5.0
12/23/04	<5.0	<5.0	<5.0	<b>390</b>	<5.0	<5.0	<5.0	<b>720</b>	<b>13</b>	<5.0
03/03/05	<5.0	<5.0	<5.0	<b>24</b>	<5.0	<5.0	<5.0	<b>140</b>	<b>15</b>	<5.0

VOC analysis via US EPA SW846 Method 8260

As listed in Table 1, significant reductions in concentrations of benzene and MTBE have occurred near the source area of the plume. The selected remediation technology appears to be effectively treating the source area. However, a drop in downgradient MTBE concentrations in immediately off-Site monitoring wells has not been observed. Continued operation of the on-Site ozone injection system and treatment of the downgradient plume will be necessary to completely remediate impacted groundwater in a timely manner. Treatment of the downgradient plume will need to occur in order to reduce MTBE concentrations faster than can be accomplished with source removal and natural attenuation alone

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