

# **Advanced Oxidation Process Technology (Ultraviolet Radiation /Ozone Treatment) for Removal of Methyl Tertiary Butyl Ether (MTBE) in Groundwater Supplies.**

Craig L. Patterson<sup>1</sup>, Roy C. Haught<sup>1</sup>, James A. Goodrich<sup>1</sup>, Kim Ngo Kidd<sup>2</sup>, Fernando Cadena<sup>3</sup>,  
and Rajib Sinha<sup>4</sup>

1. Craig L. Patterson, P.E., U.S. EPA (M.S. T&E), 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268, patterson.craig@epg.gov.

1. Roy C. Haught, U.S. EPA (M.S. 690), 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268, haught.roy@epa.gov.

1. James A. Goodrich, Ph.D., U.S. EPA (M.S. 689), 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268, goodrich.james@epa.gov.

2. Kim Ngo Kidd, USEPA REGION VI (6WQ-SD), 1445 Ross Avenue, Suite 1200, Dallas, TX 75202-2733, ngo.kim@epa.gov.

3. Fernando Cadena, Ph.D., P.E., Visiting Faculty Researcher, P.O. Box 30001, MSC WERC, New Mexico State University, Las Cruces, NM 88003-8001, fcadena@nmsu.edu.

4. Rajib Sinha, P.E., Shaw Environmental, Inc., 5050 Section Avenue, Cincinnati, OH 45212, rajib.sinha@shawgrp.com.

## **Abstract**

U.S. Environmental Protection Agency's (EPA) Office of Research and Development in Cincinnati, Ohio has been testing and evaluating MTBE and MTBE byproduct destruction using three oxidant combinations: hydrogen peroxide/ozone, ultraviolet irradiation (UV)/ozone, and UV/ozone/hydrogen peroxide. Pilot-scale studies (3 gallons/minute flow at 20 degrees C) conducted on dechlorinated Cincinnati tap water spiked with 300 µg/L MTBE showed that UV/ozone treatment removed 98% of the MTBE from tap water (at 254 nm UV, 5.8 mg/L dissolved ozone).

EPA's Water Quality Management Branch, EPA Region VI (Dallas, TX) and New Mexico State University, conducted a field study on oxidation of MTBE and MTBE byproducts at a groundwater well in Roswell, New Mexico. EPA also compared the costs of UV/ozone treatment with GAC adsorption. Results from the pilot-scale and field-scale MTBE studies are summarized and presented to highlight alternative treatment options for small drinking water systems.

## **Background**

MTBE was first used in the United States in the late 1970s to enhance octane levels when the use of lead in gasoline was discontinued. MTBE helps gasoline burn more cleanly and reduces emissions of carbon monoxide and organic compounds into the air. Because it mixes readily with gasoline, has low production costs, and a high octane rating, MTBE became the oxygenate of choice for most gasoline producers facing State and Federal mandates (Clean Air Act 1990) to produce less-polluting gasoline (1).

The widespread use of MTBE in gasoline led to the contamination of both surface and ground waters in the U.S.. MTBE contamination is found in soils and groundwater wells near leaking underground storage tanks (UST), and in reservoirs used for public water supplies. MTBE is classified as a possible human carcinogen and has a pungent taste and smell. MTBE is on the U.S. EPA's Contaminant Candidate List (CCL) of contaminants to be regulated (2). The EPA has issued a drinking water advisory of 20 to 40 µg/L (3), however, some States have established State levels that are lower. For instance, Texas established 15 µg/L MTBE as a target level used for cleanup after a fuel spill occurred in Lake Tawakoni (March 2000), a drinking water supply for North Texas (4). MTBE is currently listed on the CCL as a contaminant in need of both occurrence and research priorities (including health research, treatment research, and analytical methods research).

### **Occurrence of MTBE in Drinking Water Supplies**

According to a 2001 United States Geological Survey (USGS) study (5), of 954 community water systems (CWS) sampled in the U.S., 0.5% of the systems contained MTBE levels at  $\geq 5$  µg/L. If we extrapolate this percentage to the 160,000 public water systems (PWS) in the United States, then roughly 800 PWS are likely to have MTBE contamination at levels  $\geq 5$  µg/L. The number of affected water systems may increase with time, as plumes from leaking gasoline-underground storage tanks begin to reach more groundwater systems (6). Private wells are also affected, although they are not currently regulated under the Safe Drinking Water Act.

Another nationwide USGS study (7) conducted in 1995 found concentrations of MTBE in urban and agricultural wells to be in the range of 0.2 to 23,000 µg/L. In Dallas/Fort Worth, Texas, 5 of 17 wells tested positive for MTBE and in Albuquerque, New Mexico 1 of 24 wells tested positive. The study also looked at the frequency of occurrence of MTBE in groundwater wells and found that MTBE was the second most commonly detected volatile organic compound (VOC) after chloroform. Of the wells tested, 28% had chloroform contamination followed by 27% with MTBE contamination. Additional VOCs found that were harmful to public health included, tetrachloroethene 18%; trichloroethene 10%; cis-1,2 dichloroethene 7%; 1,1-dichloroethane 5%; and benzene 5%). These harmful VOCs can also be removed by AOP technologies.

### **Treatment Technologies and Cost**

For large groundwater systems, air stripping, granular activated carbon (GAC), and resin adsorbents are all capable of removing MTBE from the water supply (8). Small water systems typically choose GAC because it is the more affordable treatment technology. It would not be cost effective for a small system producing only 10,000 gallons of water per day to purchase an air stripper intended for a million gallon per day producer. It makes more sense for a small water

system to purchase a small tank of activated carbon (GAC) and pay for the replenishing and processing of the carbon.

According to two new studies by the American Water Works Association and the Association of Metropolitan Water Agencies (9), the estimated cost to remove MTBE from public drinking water systems is in the range of \$25-\$85 billion. The California MTBE Partnership of 2000 determined that it would cost between \$1 to \$11 million dollars per well. These clean-up costs (capital and operation and maintenance costs), were determined using GAC adsorption over 30 years with influent MTBE levels of 200 µg/L and non-detect effluent levels.

This project investigated a low cost alternative for MTBE treatment and utilizes an advanced oxidation process (AOP) technology that combines ultraviolet radiation (UV) with ozonation for oxidation of MTBE and MTBE byproducts from water. One of the benefits of UV/ozone treatment is the low operating cost for small drinking water systems. Both the UV light and ozone generation require minimal use of electricity. Because UV/ozone treatment destroys MTBE through oxidation, it does not require hazardous transport for processing. Additional benefits are the elimination of the need for chemical additives and processing of adsorbed contaminants. The net result is cost savings for the water system.

## **Introduction**

The EPA Water Quality Management Branch in Cincinnati, Ohio began evaluating pilot-scale studies by testing and evaluating MTBE and MTBE byproduct destruction using three oxidant combinations: hydrogen peroxide/ozone, ultraviolet irradiation (UV)/ozone, and UV/ozone/hydrogen peroxide. Pilot-scale studies conducted on dechlorinated Cincinnati tap water spiked with 300 µg/L MTBE showed that UV/ozone treatment removed 98% of the MTBE from tap water (at 254 nm UV, 5.8 mg/L dissolved ozone). The studies were setup to simulate real-world conditions at small groundwater systems (3 gallons/minute flow at 20 degrees C).

In July 2004, EPA, in partnership with New Mexico State University (NMSU), customized a research trailer with a groundwater well pump, a 110-gallon feed tank, a pretreatment system (water softener with iron reduction), and a UV/ozone treatment system (See Figures 1 and 2). EPA worked with Shaw Environmental, Inc. (an ORD Contractor), NMSU, and Souder, Miller and Associates (a consulting firm with remediation sites in New Mexico) to locate potential field sites with drinking water levels of MTBE exceeding the recommended standards. To compare field study results with Cincinnati pilot-scale results, several well sites in Artesia and Roswell, New Mexico were selected with groundwater containing around 300 µg/L MTBE.

## **Field Study**

A field study was designed to assess the performance and reliability of UV/ozone treatment under real-world conditions. From field study results, EPA was able to estimate and compare the costs of UV/ozone treatment with GAC adsorption.

EPA worked with the ORD contractor to provide a Quality Assurance Project Plan (QAPP) and a Health and Safety Project Plan (HSPP) for the field study. The ORD contractor subcontracted with NMSU and Souder, Miller and Associates to work with the local community of Roswell to establish the field study location at an existing MTBE contaminated groundwater well. The

ORD contractor coordinated the setup of the research trailer with electrical connections, plumbing lines, and GAC post-treatment at the field site. The ORD contractor also coordinated the upgrade and operation of the treatment system to ensure optimum MTBE removal.



**Figure 1. Research Trailer**



**Figure 2. UV/Ozone Treatment System**

EPA coordinated and oversaw a two-week long study of the effectiveness of the UV/ozone treatment system for MTBE removal. The UV/ozone treatment system operated continuously to process ten 110-gallon batches of MTBE-contaminated groundwater. Daily operation and maintenance requirements were recorded and influent/effluent samples were analyzed as defined in the QAPP. The UV/ozone system and GAC adsorbent cost, reliability, and ease of operation were documented during the two-week study. Treatability study results were evaluated, compared and compiled into a final summary report.

EPA was able to compare the cost of UV/ozone treatment versus GAC adsorption. The primary cost of UV/ozone utilization comes from the electricity needed to generate ozone and to power the UV lamp. Electrical costs were determined by monitoring electrical output in kilowatts per hour. A cost comparison was calculated between the UV/ozone treatment (e.g., cost of electricity and UV lamp replacement) and the GAC treatment (e.g., cost of electricity for the feed pump, changing out the carbon tank and processing of used carbon).

### **Project Impacts**

VOC contamination of ground and surface waters is an on-going concern for environmental regulators. The project demonstrated the effectiveness of UV/ozone treatment for small groundwater systems. The project verified that AOP technologies, such as UV/ozone, are simple, affordable, readily available treatment alternatives for small groundwater systems affected by MTBE contamination. Effective treatment technologies for VOCs in groundwater

benefit the State primacy agencies and the Public. For instance, New Mexico drinking water supply is comprised of 95% groundwater systems that serve 85% of the population (1.8 million people). Texas drinking water supply is comprised of 80% groundwater systems that serve 6.4 million people daily (10). In both States, a majority of the groundwater wells are small drinking water systems that need affordable treatment technologies. Removing VOC contamination in groundwater will increase the availability of clean water supplies in dry and arid locations. Alternative treatment processes are vital for arid States such as New Mexico, which have on-going drought issues and desperately need clean water sources.

## References

1. United States Environmental Protection Agency (US EPA) Office of Water. *MTBE Fact Sheet 1 Overview*, EPA 510-F-97-014, January 1998.
2. United States Environmental Protection Agency (US EPA) Office of Water. *The Drinking Water Contaminant Candidate List – The Source of Priority Contaminants for the Drinking Water Program*, EPA 815-F-05-001, February 2005.
3. United States Environmental Protection Agency (US EPA) Office of Water. *Drinking Water Advisory - Health Effects Analysis on Methyl tertiary-Butyl Ether*, EPA 822-F-97-008, December 1997.
4. Freese and Nichols, Inc. for the Sabine River Authority (SRA) of Texas. *Summary Report of MTBE Contamination in Lake Tawakoni From Gasoline Pipeline Rupture*, SRA00230, December 4, 2000: 14-21.
5. Clawges, R., Rowe, B., and Zogorski, J. *National Survey of MTBE and Other VOCs in Community Drinking Water Sources*, United States Geological Survey (USGS) National Water Quality Assessment Program. FS-064-01, October 2001.
6. Thomson, J.A., and McKinley, J.W. "MTBE Occurrence in Surface and Groundwater", Contaminated Soil Sediment and Water, July-August 2002: 16-19.
7. United States Geological Survey (USGS) National Water Quality Assessment Program. *Occurrence of Gasoline Additive MTBE in Shallow Groundwater in Urban and Agricultural Areas*, FS-114-95, March 1995.
8. United States Environmental Protection Agency (US EPA) Office of Water, *MTBE in Drinking Water*, Retrieved August 31, 2005, from <http://www.epa.gov/safewater/mtbe.html>.
9. American Water Works Association (AWWA) Water Utility Council. *Two Updated MTBE Contamination Cost Analyses Pin MTBE Clean Up Costs*, June 21, 2005. Retrieved September 2, 2005, from <http://www.awwa.org/Communications/news/index.cfm?ArticleID=459>
10. Safe Drinking Water Information System Federal Database, FY2005 Quarter 2, March 2005.

**KEYWORDS:** Ozone, UV, Treatment, MTBE, Groundwater