Water Treatment – Advanced Oxidation Processes

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Appendix 2.1

Task 2.1: Advanced Oxidation Processes and UV Photolysis for Treatment of Drinking Water

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LEGAL NOTICE

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GLOSSARY

Advanced Oxidation Process (AOP) – a process in which the oxidative capacity of a parent compound is modified to make oxidation-reduction reactions more rapid or complete.

Bromate (BrO_3^-) – a suspected human carcinogen which is a byproduct of ozonating bromide-containing waters.

Closed-loop stripping analysis (CLSA) – an extraction technique useful for the isolation of volatile organic compounds, such as geosmin and MIB.

Collimated beam (CB) – a beam in which the light rays travel parallel to each other, allowing for irradiation of samples under lab conditions without any hydraulic disturbance.

Colorado River water (CRW) – influent water source from Lake Mathews, California, the southern terminus for the Colorado River aqueduct system.

Continuously-mixed batch reactor (CMBR) – a closed-loop reactor whose contents are mixed completely.

Continuously-stirred tank reactor (CSTR) – a steady-state reactor whose contents are completely mixed.

Cryptosporidium – an intestinal protozoan parasite causing diarrhea.

Disinfection byproduct (DBP) – a chemical byproduct of the disinfection process.

Dissolved oxygen (DO) – the concentration of oxygen in aqueous solution.

Gas chromatography (GC) - a technique commonly used in the analysis of organic compounds in water based on their retention time a chromatography column.

Geosmin ($C_{12}H_{22}O$)- common name for *trans*-1,10-dimethyl-*trans*-9-decalol, an earthy smelling chemical produced by certain blue-green algae and *Actinomycetes*.

Giardia – the genus name for a group of single-celled, flagellated, pathogenic protozoans. *Giardia lamblia* is a common cause of diarrhea in humans.

Granular activated carbon (GAC) – a form of particulate carbon manufactured with increased surface area per unit mass to enhance adsorption of soluble contaminants.

Groundwater (GW) – the water contained in interconnected pores located in a confined aquifer or below the water table in an unconfined aquifer.

Haloaceto-nitrile (HAN) – ($CX_3{\equiv}N$, where X = Cl, Br, or H in various combinations) - a class of disinfection byproducts formed primarily during the chlorination of water containing natural organic matter.

Haloketone (HK) – (CX_3COCX_3, where X = Cl, Br, or H in various combinations) - a class of disinfection byproducts formed primarily during the chlorination of water containing natural organic matter.

Hydroxyl radical (OH) – a strong oxidizing agent that can destroy many organic and inorganic compounds in water.

Ion chromatography (IC) – a technique for separating substances based on ion exchange, which is commonly used for the analysis of anions and cations in water.

Mass spectrometry (MS) – a method of chemical analysis in which compounds emerging from a gas chromatograph are fragmented and ionized by bombardment with a beam of electrons.

Maximum contaminant level (MCL) – a value defined under the Safe Drinking Water Act Section 1401(3) as the maximum permissible concentration of a contaminant in water delivered to any user of a public water system.

Method detection level (MDL) – the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero.

2-methylisoborneol (MIB) - ($C_{11}H_{20}O$) common name for 2-exo-hydroxy-2-methylbornane, a musty-camphor-smelling chemical produced by blue-green algae and *Actinomycetes.*

Methyl *tert*-butyl ether (MTBE) – ($(CH_3)_3COCH_3$) an organic solvent, which is highly soluble in water and a common oxygenated gasoline additive.

Minimum reporting limit (MRL) – the lowest concentration of a given analyte that a laboratory feels confident reporting to data users.

MS-2 coliphage – a ribonucleic acid virus that can replicate only within its bacterial host, *Escherichia coli.*

N-nitrosodimethylamine (NDMA) – ($(CH_3)_2N_2O$) a by-product of rocket fuel but is also formed as by-product during various manufacturing processes. NDMA is a known animal carcinogen and is classified as a probable human carcinogen.

Not analyzed (NA) – a sample was not collected to be analyzed.

Not detected (ND) – compounds not detected in samples analyzed.

Ozone (O_3) – a strong oxidant and disinfectant in the purification of drinking water.

Perchlorate (ClO_4^-)– used in the manufacturing of solid rocket fuels, explosives, munitions, and fireworks and at high concentrations it can interfere with thyroid gland ability.

PEROXONE – a combination of ozone and hydrogen peroxide.

Photolysis – chemical decomposition that is driven by photons of sunlight or ultraviolet light.

Pulsed UV – ultraviolet light generated in a wave form at a specific frequency.

Simulated distribution system (SDS) test – a type of test in which a treated water is dosed with a typical treatment plant level of disinfectant normally applied and is incubated under conditions that simulate disinfection byproduct production in a distribution system.

State Project water (SPW) – influent water source from Northern California via the California State Water Project.

Taste and odor (T&O) – the combination of sensations perceived by the mouth and nose.

Total dissolved solids (TDS) – the weight per unit volume of solids remaining after a sample has been filtered to remove suspended and colloidal solids.

Total organic carbon (TOC) – a measure of the concentration of organic carbon (all the carbon atoms covalently bonded in organic molecules) in water, determined by oxidation of the organic matter into carbon dioxide

Trihalomethane (THM) – any of numerous organic compounds named as derivatives of methane (CH_4) in which three halogen atoms (Cl, Br or I, singly or in combination) are substituted for three of the hydrogen atoms, which are formed during the disinfection of water with free chlorine.

Ultraviolet (UV) light – radiation having a wavelength between 10 and 390 nanometers, which can be used as a disinfectant or to create hydroxyl radicals.

Volatile organic compound (VOC) – a class of organic compounds that that includes gases and volatile liquids.

ACRONYMS

AOP – advanced oxidation process

Br^- - bromide ion

BrO^- - hypobromate ion

BrO_2^- - bromite ion

BrO_3^- - bromate

^{o}C – degree Celsius

CARB – California Air Resources Board

CB – collimated beam

CDHS – State of California Department of Health Services

Cl_2 – chlorine

CLSA – closed-loop stripping analysis

ClO_3^- – chlorate ion

ClO_4^o – perchlorate radical

ClO_4^- - perchlorate

cm - centimeter

CMBR – continuously-mixed batch reactor

CRW – Colorado River water

CSTR – continuously-stirred tank reactor

DBP – disinfection byproduct

DNA – deoxyribonucleic acid

DO – dissolved oxygen

ESWTR – Enhanced Surface Water Treatment Rule

ft – foot

GAC – granular activated carbon

gal – gallon

GC – gas chromatograph(y)

gpm – gallons per minute

GW - groundwater

h – hour

H_2O_2 - hydrogen peroxide

HAN – haloaceto-nitrile

HK - haloketone

Hz – Hertz (second^{-1})

IC – ion chromatograph(y)

in - inch

$KBrO_3$ - potassium bromate

kW – kilowatt

kWh – kilowatt-hour

L - liter

lb - pound

μg/L – microgram per liter

μL – microliter

μm – micrometer

μmho/cm – micromho or microsiemen per centimeter

m^3 – cubic meter

MCL – maximum contaminant level

MDL – method detection level

mg/L – milligram per liter

mg/kg/day – milligram per kilogram per day

MIB – 2-methylisoborneol

min – minute(s)

mJ/cm^2 – millijoule per square centimeter

mL– milliliter

MRL – minimum reporting limit

MS – mass spectrometry

MS-2 – male specific (coliphage)

MTBE – methyl *tert*-butyl ether

mW – milliwatt

mW/cm^2 – milliwatt per square centimeter

NA – not analyzed

N/A – not applied

ND – not detected

N/D – not determined

NDMA – N-nitrosodimethylamine

ng/L – nanogram per liter

nm – nanometer

NO_3^- - nitrate

NTU – nephelometric turbidity unit

O_3 – ozone

OH – hydroxyl radical

PIER – Public Interest Energy Research

ppb – part per billion

RD&D - Research, Development and Demonstration

SDS – simulated distribution system

SPW – State Project water

SWTR – Surface Water Treatment Rule

T&O – taste and odor

TBA – *t*-butyl alcohol

TBF – *t*-butyl formate

TDS – total dissolved solids

THM – trihalomethane

TOC – total organic carbon

USEPA – U.S. Environmental Protection Agency

UV – ultraviolet

UV_{254} – UV light absorbance at 254 nm

VOC – volatile organic compound

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER program, managed by the Commission, annually awards up to $62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

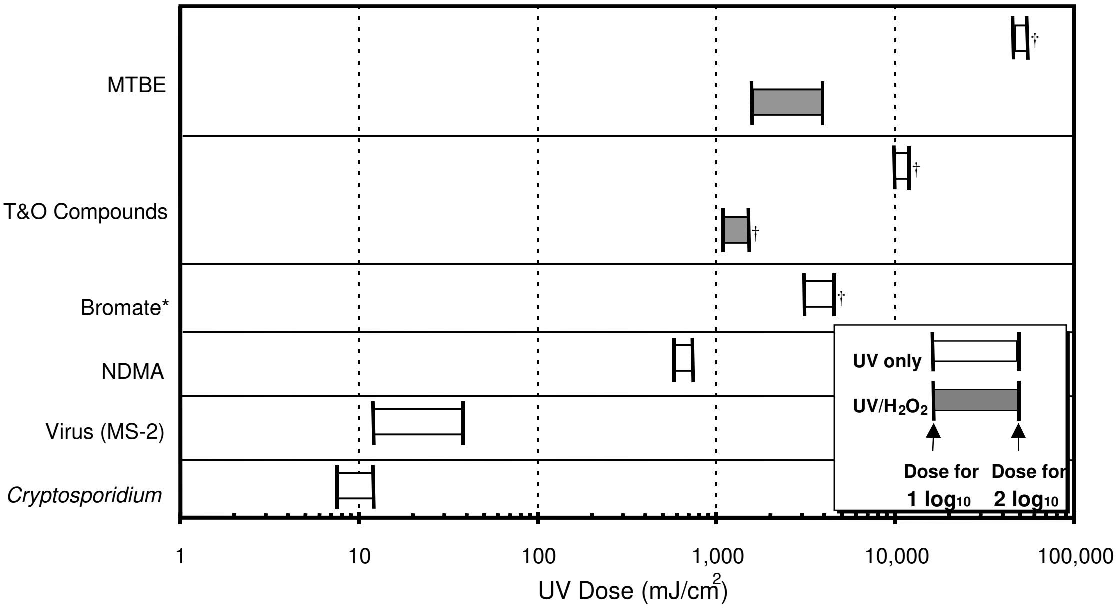
What follows is the final report for the Electrotechnology Applications for Potable Water Production and Protection of the Environment, contract No. 500-97-044 conducted by the Metropolitan Water District of Southern California (Metropolitan). The report is entitled Electrotechnology Applications for Potable Water Production and Protection of the Environment: "Task 5, Advanced Oxidation Processes and UV Photolysis for Treatment of Drinking Water". This project contributes to the Industrial/Agricultural/Water End-Use Energy Efficiency program.

For more information on the PIER Program, please visit the Commission's Web site at: http://www.energy.ca.gov/research/index.html or contact the Commission's Publications Unit at 916-654-5200.

EXECUTIVE SUMMARY

This project investigated the use of ultraviolet (UV) light and ozone for micropollutant control in drinking water. The micropollutants studied included methyl *tert*-butyl ether (MTBE), N-nitrosodimethylamine (NDMA), perchlorate, bromate, and the taste-and-odor (T&O) compounds 2-methylisoborneol (MIB) and geosmin. The work was conducted at the bench- and pilot-scale involving a pulsed-UV lamp (43-liter batch reactor) or an over-under ozone contactor system.

A summary of the UV data from this research is presented in Figure ES-1 (bars represent the range of UV dose required to achieve from 1 to 2 $\log_{10}$ reduction of contaminant). The results indicate that the required UV dose may differ by more than one-thousand-fold, depending on the target contaminant treated. For example, compared to the UV dose needed to achieve 1-$\log_{10}$ inactivation of *Cryptosporidium*, it takes almost a 10-fold greater UV dose for the same reduction of virus, a more than 100-fold greater UV dose for MTBE and T&O compounds (treatment combined with hydrogen peroxide, H_2O_2), and an approximately 1,000-fold greater UV dose for the same reduction of bromate. Based on these results, it is not feasible to achieve significant reduction in bromate or MTBE at UV doses less than 100 mJ/cm^2. Moderate reductions of NDMA (51 percent) and T&O compounds (up to 65 percent) may be accomplished at a disinfection-level UV dose of 100 mJ/cm^2. However, because of the raw-water levels of NDMA and T&O compounds in some California drinking waters, these moderate reductions may not satisfy regulatory or utility-imposed water quality objectives. Additional concerns arise from H_2O_2 residuals leaving the UV/H_2O_2 process. Because the H_2O_2 residual may be more than 85 percent of the H_2O_2 dose, effluents would need further treatment before transmission to the distribution system. When perchlorate was treated by UV light, no measurable reduction of the contaminant was recorded. Additional research is required to investigate compatibility issues that may arise when integrating UV and UV/H_2O_2 processes into conventional drinking water treatment plants.



* Bromate reduction in laboratory water, all other data for natural waters

† 2 $\log_{10}$ reduction estimated based on data from this study

Figure ES1. UV Dose Range for 1 to 2 $\log_{10}$ Reduction of Water Contaminants

In addition to the issues outlined above, large utilities must also consider unique technical and regulatory constraints when developing and implementing new technologies such as UV light. Technical constraints include hydraulic performance, reactor verification, reliability, and system redundancy. Regulatory considerations include (1) any potential compromise with other treatment objectives; (2) a reduced ability to monitor performance; and (3) the time required to deploy new treatment technologies. Lastly, without a well-documented and scientifically sound dose measurement method, it is nearly impossible for water utilities to implement UV technologies.

The ozone process was investigated for its ability to remove MTBE and NDMA in drinking water. Figure ES2 shows that high ozone dosages (>15 milligrams per liter [mg/L]) were needed to meet a secondary non-health based standard for MTBE of 5 micrograms/L (µg/L). PEROXONE (ozone combined with hydrogen peroxide [H_2O_2]) did not provide any significant improvements in treatment. During MTBE testing, several by-products were formed, including *t*-butyl alcohol, *t*-butyl formate, acetone, and various aldehydes.

NDMA was shown to be resistant to ozone treatment, as shown in Figure ES3. When ozone was combined with H_2O_2, 67 percent removal of NDMA could be achieved. Both micropollutants required an ozone and H_2O_2 dosage which was too large for practical application.

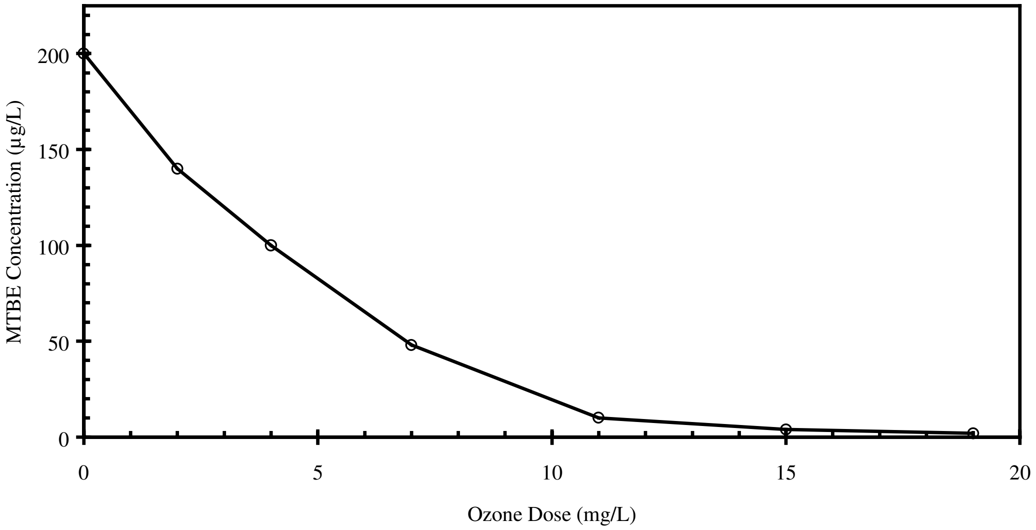


Figure ES2. Ozone Dosage Required to Control MTBE

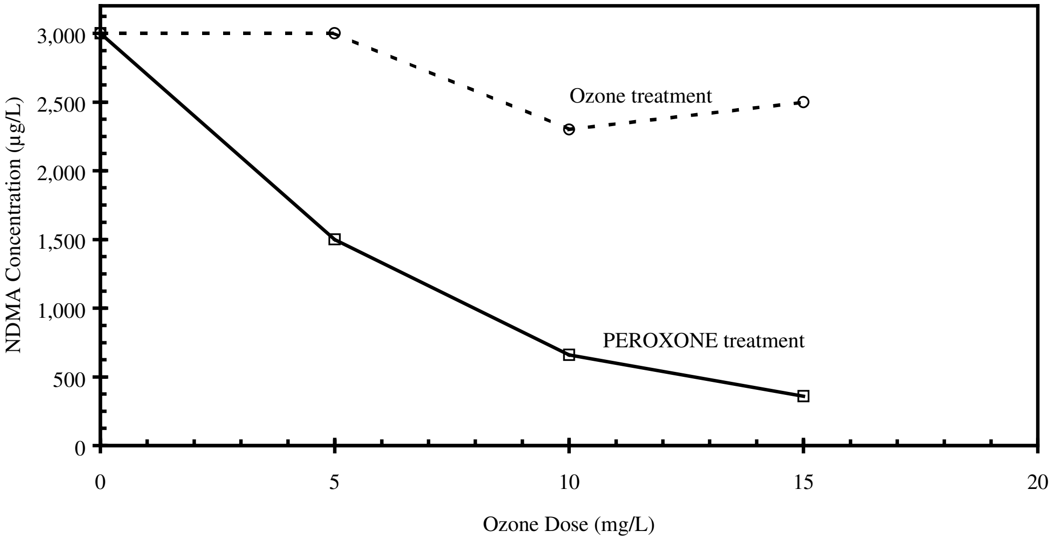


Figure ES3. Effects of Ozone and H_2O_2 Dose on NDMA Reduction in Laboratory Water

ABSTRACT

Ultraviolet (UV) disinfection is receiving increased attention in the drinking water industry as a method for utilities to comply with upcoming disinfection regulations. Because most disinfectants provide multiple benefits (e.g., both disinfection and oxidation), this study was conducted to learn whether UV light would provide the same multiple benefits as ozone/PEROXONE. This research investigated the ability of both UV light and ozone (both with the periodic addition of H_2O_2) to remove methyl *tert*-butyl ether (MTBE) and N-nitrosodimethylamine (NDMA), and the ability of UV light to remove bromate, perchlorate, and the taste-and-odor (T&O) compounds 2-methylisoborneol (MIB) and geosmin. In natural waters, the amenability of treating these compounds by UV (in order of increased UV dose) was NDMA (580 mJ/cm^2 for 90 percent reduction), T&O compounds (10,000 mJ/cm^2 for 90 percent reduction), MTBE (47,000 mJ/cm^2 for 90 percent reduction), bromate (18 percent reduction at 4,000 mJ/cm^2), and perchlorate (no reduction achieved with UV treatment).

The ozonation process also did not show favorable results for its ability to remove MTBE and NDMA in drinking water. High ozone dosages (>15 mg/L) combined with H_2O_2 (30-50 mg/L) were needed to reduce MTBE concentrations from 200 µg/L to the secondary standard of 5 µg/L. NDMA was shown to be resistant to ozone treatment, but when ozone was combined with H_2O_2, 67 percent removal could be achieved. Both micropollutants were seen to require too significant of an ozone and H_2O_2 dosage to be practical technologies to implement at the large scale. Based on these results it may be more cost effective to treat MTBE with ozone and NDMA with UV technologies.

Keywords: bromate, geosmin, MIB, micropollutants, MTBE, NDMA, oxidation, ozone, perchlorate, photolysis, UV

INTRODUCTION

Background and Overview

The objective of this task was to evaluate and compare ultraviolet (UV) irradiation and ozone (both with the addition of hydrogen peroxide [H_2O_2]) for the removal of micropollutants.

The purpose of the UV research conducted was to determine if UV could offer multiple benefits (such as other disinfectants) for drinking water treatment. For example, chlorine may be used to disinfect pathogenic bacteria and viruses, oxidize reduced iron and manganese, improve particle removal by pre-oxidation, and control algae growth. Ozone offers the same advantages but may also inactivate *Cryptosporidium* oocysts and reduce taste and odor (T&O) compounds (e.g., 2-methylisoborneol [MIB] and geosmin produced by algae) and organic micropollutants (e.g., chlorinated solvents, gasoline additives, and pesticides). Typically, chlorine or ozone doses required to achieve these objectives do not differ by more than a factor of two or three. Thus, a single application of chlorine or ozone often achieves multiple disinfection/oxidation goals. If UV could offer multiple benefits, it would help reduce water utility electrical usage. This is because water utilities in California may have difficulty meeting pending U.S. Environmental Protection Agency (USEPA) regulations for disinfection by-products (DBPs) with traditional chlorine disinfection systems. The first response of a utility may be to switch to ozone to meet these regulations, which is more costly than UV and also may increase formation of ozonated DBPs (such as bromate).

UV disinfection—and its potential replacement of chlorine or ozone—is receiving increased attention in the drinking water industry because of its newfound ability to disinfect protozoa. This ability has been unveiled by the establishment of three fundamental features: (1) the mechanism through which UV photons react with intracellular DNA (Jagger 1967); (2) the significant reduction of *Cryptosporidium* when compared to experiment controls (Clancy et al. 1998, Bukhari et al. 1999); and (3) a UV dose-response relationship (Mofidi et al. 2000). It is now understood that potential benefits of UV technologies include a significant level of microbial disinfection, a low operating cost, and the minimal formation of DBPs. Though disinfection efficiency of UV light has been demonstrated, other issues must be addressed before a full-scale process can be appropriately implemented. These issues include the ability of UV to control emerging contaminants (N-nitrosodimethylamine [NDMA], methyl *tert*-butyl ether [MTBE]), manage longstanding issues (T&O oxidation), and remain complimentary with other treatment goals (reduce bromate and perchlorate) all at low UV doses (<100 mJ/cm^2). Thus, the use of UV may reduce the need for chlorine and ozone but not eliminate it.

The UV portion of the study was conducted to examine the potential of UV light to photolyze bromate and NDMA and initiate hydroxyl radical (OH) oxidation of MTBE and the T&O compounds MIB and geosmin was investigated. Treatment of perchlorate by pulsed-UV light was also investigated.

Bromate

Recently, drinking water treatment plants in the U.S. which historically used chlorine for disinfection have switched to ozonation. This switch has been primarily fueled by regulations which lower the acceptable amount of halogenated disinfection by-products (DBPs) formed by chlorination (USEPA 1998). Ozone can be implemented by utilities to accomplish a variety of treatment objectives, however, ozone doses will vary over a wide range, depending on water quality parameters such as the concentration of total organic carbon (TOC) and solution pH. A significant concern that utilities have with ozonating natural waters is the formation of the ozonation by-product bromate. Bromate forms through complex reactions between ozone, bromide, TOC, and hydroxyl radicals (Haag and Hoigne 1983, Haag and Hoigne 1984, Ozekin et al. 1998). These researchers have shown that the possible end products from ozonating brominated waters is both bromate and hypobromous acid. To combat bromate formation, the pH of ozonation can be reduced (Haag and Hoigne 1983). Unfortunately, pH adjustment typically increases total dissolved solids (TDS), decreasing the aesthetic quality of the treated water.

Bromate is a suspected human carcinogen and will be regulated by the USEPA at a maximum contaminant level (MCL) of 0.010 milligrams per liter (mg/L) (USEPA 1998). Tests using a variety of source waters demonstrated bromate formed above the MCL for a range of operating conditions and with and without the use of H_2O_2 (von Gunten and Hoigne 1993, Westerhoff et al.

1998). Metropolitan has also demonstrated that significant formation potential exists in both of its source waters, Colorado River water (CRW) and California State Project water (SPW) (Gramith et al. 1993, Krasner et al. 1993a, Krasner et al. 1993b, Coffey et al. 1998, Coffey et al. 1999, Williams et al. 2000). Water utilities would benefit from having a technique which could reduce bromate after ozonation of natural waters and not decrease the aesthetic quality (by increasing TDS) or increase the carcinogenic risk (by forming DBPs) of the treated water.

MTBE

The use of reformulated gasoline is mandated by the U.S. Environmental Protection Agency to reduce air pollution by vehicle emissions. The California Air Resources Board (CARB) mandated year-round, statewide use of reformulated gasoline beginning in March 1996 (Denton 1997). MTBE is the most common oxygenated fuel additive and is typically added at 11 percent MTBE by volume (Squillace et al. 1996).

The widespread use of MTBE in reformulated gasoline quickly resulted in its widespread presence in the environment. In southern California, MTBE has been detected in groundwater wells used for drinking water or irrigation in Los Angeles, Orange, and Riverside counties. The most serious case of groundwater MTBE contamination observed to date occurred in groundwater supplies for the City of Santa Monica, California (Rodriguez 1997). Seven of Santa Monica’s production wells have been closed because of MTBE contamination, with levels as high as 610 micrograms per liter (µg/L). In addition to groundwater, MTBE has also been detected in southern California surface water supplies (Dale et al. 1997a, b).

No maximum contaminant level in federal regulation has been established for MTBE in drinking water. The USEPA has issued a draft lifetime health advisory—which is currently being revised—of 20-200 µg/L for drinking water. (A lifetime health advisory describes a nonregulatory concentration at which a contaminant would not cause adverse health effects over a specific duration of exposure, within a margin of safety to protect sensitive populations.) The State of California Department of Health Services (CDHS) has established both a primary and a secondary standard of 13 and 5 µg/L, respectively.

Limited information is available for removing MTBE from drinking water. Some work has been done with air stripping and granular activated carbon (GAC) for the removal of MTBE from water, but because of the high solubility of MTBE, effective removal of MTBE is challenging. To remove MTBE from water, it typically requires tall stripping towers and high air-to-water ratios. Also, MTBE needs to be removed from the off-gas depending on the regulatory requirement for air emission. Although the application of GAC is a feasible option to treat low MTBE concentration, it is not an effective alternative for high concentrations of MTBE contamination. This approach requires frequent carbon regeneration, and thus involves high costs of operation. An alternative approach is the use of UV/peroxide or ozonation for MTBE oxidation.

Although UV has been commercially available for many years and has been very successful in wastewater disinfection applications, it is uncommon in drinking water applications due to lack of oxidant residual in treated water. Most of the published literature on UV applications in drinking water has been focused on the use of continuous wave UV light from low-pressure, mercury-vapor lamps.

Among the potential groundwater treatment technologies being investigated for MTBE removal, the use of ozone and PEROXONE (ozone combined with H_2O_2) would be of interest for utilities where ozone is currently being used or considered. Since the MTBE oxidation is primarily accomplished by the hydroxyl radical, any advanced oxidation process (AOP) which has capability to generate hydroxyl radicals can be potentially used for the treatment of MTBE.

Ozonation of MTBE can result from direct reaction with molecular ozone or indirect reaction with radical oxidant species (mainly the hydroxyl radical) which form when ozone decomposes in water. Direct oxidation occurs very slowly and oxidation by hydroxyl radicals is extremely rapid (Buxton et al. 1988).

NDMA

In February 1998, the presence of NDMA in drinking water was detected at an aerospace facility in northern California, and subsequently in drinking water wells throughout southern California (CDHS 2000). NDMA is a by-product of rocket fuel but is also formed as by-product during various manufacturing processes.

The USEPA identified NDMA as a probable human carcinogen. Because NDMA has not been historically considered as a common drinking water contaminant, no federal or state drinking water standards exist. In April 1998, the CDHS announced an action level of 0.002 µg/L for NDMA (CDHS 2000). In northern California, NDMA was found in one drinking water well in eastern Sacramento County at concentrations of approximately 0.14 µg/L (CDHS 2000). In southern California, NDMA was found in three drinking water wells in the San Gabriel Basin at concentrations of 0.07 to 3 µg/L (CDHS, 2000). Furthermore, recent results (Brennan and Robbins 2000, Davis et al. 2000) indicate that NDMA may be present in (1) sewage and reclaimed water after chlorination and (2) surface water treated through conventional drinking water treatment. Although the exact mechanisms of formation are unknown, they appear to be associated with the chlorination or chloramination process. In December 1999, the CDHS established a temporary action level of 0.020 µg/L for NDMA so that more utilities can participate in the NDMA screening effort.

NDMA is not removed from water using air-stripping, reverse-osmosis membranes, or granular activated carbon because of its high water-solubility and polar nature (Jobb et al 1992, 1994). The current widespread detection and changing regulatory status of NDMA demonstrate the need for an effective, alternative technology that can remediate drinking water sources contaminated by this compound. Ozone has not been investigated for removal of NDMA, however, it is well known that NDMA can be reduced by UV technologies (Calgon 1996). Jobb and co-workers (1992, 1994) demonstrated that low-pressure mercury UV lamp irradiation could reduce NDMA from 0.089 to 0.005 µg/L at an UV dosage of approximately 2.6 kilowatt-hours per cubic meter (kWh/m^3) or 10 kWh/1,000 gallons in the laboratory-scale tests. They further conducted pilot-scale studies and found that an UV dose of 1.26 kWh/m^3 or 4.85 kWh/1,000 gal was effective in reducing NDMA to less than 0.005 µg/L. Bircher and co-workers (1999) reported that NDMA was reduced from 0.053 to 0.002 µg/L in groundwater with an UV dose of 1.5 kWh/1,000 gal produced through medium-pressure lamps.

Perchlorate

Ammonium perchlorate is the commercial perchlorate compound used in the manufacturing of solid rocket fuels, explosives, munitions, and fireworks. This compound (with the molecular formula ClO_4^-) is stable in water and does not readily decompose. The primary health concern with perchlorate is that at high concentrations it can interfere with thyroid gland ability to utilize iodine to produce metabolic hormones, consequently affecting normal growth and development. Perchlorate was not detected in drinking water prior to the development of an improved analytical method. Therefore, no federal and state drinking water regulation has been established.

After analytical methods improved, perchlorate was found in drinking water wells in eastern Sacramento County (northern California) as a result of monitoring at a Superfund cleanup site. Based on this finding the CDHS extended its monitoring to southern California and targeted groundwater wells near aerospace, munitions, and fireworks manufacturing facilities. Perchlorate was detected in drinking water wells in San Bernardino, Riverside, and Los Angeles counties. Overall, between April and June 1997, the CDHS analyzed 232 wells, and 18 wells were closed (State of California 1997). In 1998, the CDHS has adopted requirements for public water systems to monitor for perchlorate as an unregulated chemical.

In June 1997, low levels of perchlorate (5-9 µg/L) were discovered in the Colorado River water system along Metropolitan's aqueduct and up to Lake Mead (165 µg/L) at the Hoover Dam outlet. With the assistance of the U.S. Bureau of Reclamation, an extensive investigation was conducted in July 1997 to identify the source of perchlorate in the Colorado River watershed. It was found that high concentrations of perchlorate were entering Lake Mead from the Las Vegas Wash. Probable sources of perchlorate in Lake Mead include areas near Henderson, Nevada, where ammonia perchlorate has been manufactured for several decades. In August 1997, sampling in Nevada detected perchlorate at up to 13 µg/L in certain drinking water samples, as high as 1,700 µg/L in the Las Vegas Wash, and as high as 3,700,000 µg/L in the monitoring well of a current perchlorate manufacturing site in Henderson (LVRJ 1997a, b). The Southern Nevada Water Authority, the Nevada Division of Environmental Protection, and Region 9 of the USEPA are currently working together to address this issue. Outside of California and Nevada, perchlorate in surface or groundwater was reported throughout the United States (Arkansas, Arizona, Iowa, Indiana, Kansas, Maryland, New Mexico, New York, Pennsylvania, Texas, Utah, and West Virginia) (USEPA 1999).

Because perchlorate ingestion has been shown to cause adverse health effects, CDHS has established a provisional action level of 18 µg/L for perchlorate in drinking water (CDHS 2000). In January 1999, the USEPA proposed the reference dose level of 0.0009 mg/kg/day (corresponding to MCLs between 12 and 32 µg/L, with the uncertainty factor between 100 and 300) (USEPA ORD 2000).

Currently, limited information is available on treatment options for removing perchlorate from drinking water sources. Physicochemical treatment processes such as ion-exchange and membrane processes have been identified as treatment technologies that are potentially applicable to the removal of perchlorate from drinking water (Najm et al. 1999, Liang et al. 1998). These techniques, however, will merely remove the chemical from drinking water and convert it to a waste concentrate, which may pose a disposal challenge. Biological reduction of perchlorate, on the other hand, has been demonstrated in wastewater treatment process to break down perchlorate to harmless chloride and oxygen, requiring no additional treatment. However, direct application of biological treatment is not a widely adopted treatment method for drinking water.

T&O Compounds

There are many utilities which experience T&O in their raw waters due to algal blooms in sourcewater reservoirs (Price et al. 1989, Ferguson et al. 1990, Morioka et al. 1993, Lang et al. 1996). To effectively reduce these high levels of T&O causing compounds, advanced oxidation processes (AOPs) can be implemented. AOPs are effective in the generation of hydroxyl radicals (Ozekin et al. 1998).

As summarized by Gramith, previous research has shown that UV radiation of H_2O_2 produces hydroxyl radicals (Gramith 1995). Gramith further states that research previous to 1990 indicated that UV/H_2O_2 was less cost effective than others (O_3/H_2O_2, O_3/UV and O_3 & high pH) due to the need for high doses of H_2O_2 to produce sufficient hydroxyl radicals (Gramith 1995).

Since this, work has been published by Jobb, Andrews, and co-workers which describes UV/H_2O_2 oxidation of geosmin (Andrews et al. 1995, Jobb et al. 1995). Jobb et al. indicated that a UV energy of 3.5 kWh/1,000 gal (from a 1 kW medium-pressure UV lamp) could reduce 25 to 28 percent of geosmin, while this UV dose with 20 mg/L H_2O_2 removed up to 95 percent. With a 0.5 kW medium-pressure UV lamp, Andrews and co-workers (1995) showed that 5 kWh/1,000 gal provided 21 percent removal while combined with 5 and 25 mg/L of H_2O_2 provided 56 and 92 percent removal of geosmin. The above kWh/1,000 gal energy requirements may translate to UV doses between 2,000 and 4,000 mJ/cm^2 (Bolton 1999).

PROJECT OBJECTIVES

Bromate Reduction by Pulsed UV

Bromate tests were conducted to study the effect of the following parameters:

- Water matrix (two were studied);
- Measurement of UV dose (two techniques were used);
- Bromate concentration (three were used); and,
- Application of H_2O_2.

MTBE Reduction by Pulsed UV and ozone/PEROXONE

The objectives of the MTBE tests with UV/H_2O_2 were to:

- Determine the optimum UV and H_2O_2 dose for MTBE reduction;
- Evaluate impacts of other compounds such as *t*-butyl alcohol (TBA) on MTBE destruction; and,
- Identify by-products such as bromate, aldehydes, and MTBE by-products (*t*-butyl formate [TBF], TBA, isopropyl alcohol, and acetone).

The subtask objectives for MTBE reduction by ozone/PEROXONE were to:

- Determine the optimum ozone and H_2O_2 dosages for MTBE removal;
- Evaluate the effects of MTBE influent concentration on process efficiency; and,
- Identify oxidation by-products, including bromate, aldehydes, TBF, TBA, isopropyl alcohol, and acetone.

NDMA Treatment by Pulsed UV and ozone/PEROXONE

This subtask evaluated the effectiveness of pulsed UV/H_2O_2 for NDMA removal. The objectives of this subtask were to:

- Investigate the effects of UV dose on NDMA destruction;
- Determine the effects of H_2O_2 doses on NDMA removal;

- Determine the effects of different source water on NDMA destruction;
- Evaluate the effects of other compounds such as nitrate on NDMA destruction;
- Determine the optimum conditions selected in a continuously-stirred tank reactor (CSTR) (flow through) mode; and,
- Investigate the possible reformation/regeneration of NDMA.

Ozone/PEROXONE test objectives were to:

- Investigate the effects of ozone dose on NDMA destruction;
- Determine the effects of H_2O_2 dose on NDMA removal;
- Evaluate the effects of NDMA influent concentration on process efficiency; and,
- Determine the optimum applied ozone and H_2O_2 doses for the ozone/H_2O_2 processes for NDMA removal for flow through tests.

Perchlorate Reduction by Pulsed UV

The main objective of applying the pulsed-UV technology for perchlorate reduction was to investigate whether perchlorate removal can be enhanced in the presence of pulsed-UV light. Perchlorate reduction by ozone/PEROXONE was not evaluated because perchlorate is already the most highly oxidized state of chlorite possible. Specifically, the subtask objectives were to:

- Determine whether perchlorate can be reduced by pulsed UV light;
- Investigate the effect of initial perchlorate concentration, H_2O_2 dose, and solution pH on perchlorate reduction by pulsed UV light;
- Select a catalyst which may enhance the reduction of perchlorate and determine the catalyst's feasibility; and,
- Investigate the effects of pH on perchlorate reduction with the catalyst in the presence of pulsed UV light.

PROJECT APPROACH

Bromate Reduction by Pulsed-UV Light

Preliminary research by Siddiqui and co-workers (1994, 1995, 1996) showed that the application of UV light to bromate-laden waters could significantly reduce bromate concentration. Siddiqui and co-workers described that UV radiation between the wavelengths of 180 to 300 nm provided energy to alter the molecular bond of bromate. Siddiqui also indicated that reactions generated by UV radiation which include the in-situ formation of H_2O_2 and hydroxyl radicals may also assist in bromate decomposition. This claim has been supported by research from von Gunten and Oliveras (1998) who demonstrated reduction of bromate in the presence of hydroxyl radicals. Solution pH was shown to have no effect on bromate destruction efficiency. Pulsed-UV lamps emit polychromatic light of the same wavelength which is described above as effective in bromate reduction (Haag 1992, Blystone et al. 1993, Haag 1996).

Bromate levels were varied to replicate three concentrations: (1) the amount of bromate that could possibly be formed if SPW (or CRW, depending on which is available at the time of conducting the experiments) was ozonated at normal levels to meet Surface Water Treatment Rule (SWTR) regulations (i.e., 1-$\log_{10}$ *Giardia* inactivation and 3-$\log_{10}$ virus inactivation) without pH control; (2) the amount of bromate that could possibly be formed if the natural water was ozonated at levels to meet future enhanced SWTR (ESWTR) regulations for disinfection (i.e., 1-$\log_{10}$ *Cryptosporidium* inactivation which equals approximately 10-$\log_{10}$ *Giardia* inactivation) without pH control; and, (3) a level above the preceding concentrations, as a worst case scenario. These targeted levels were 0.010 mg/L, 0.050 mg/L, and 0.100 mg/L, respectively.

Experiments were carried out in laboratory and natural waters. The difference between these cases were targeted to identify possible negative effects that natural water matrices (i.e., organic material and suspended particles) may have on the UV photolysis of bromate.

Th applied UV dose was carefully measured in this work, which should increase the understanding of bromate destruction by UV compared to previously reported research. Dose measurement was conducted with a biological actinometer, as described in the Materials and Methods section.

Experiments were also conducted with the application of H_2O_2 to process water prior to UV treatment to form a significant concentration of hydroxyl radicals. This was done to address claims in previous research that hydroxyl radicals may enhance the bromate destruction capabilities of UV.

MTBE

Reduction by Pulsed-UV Light

Several processes have been used to treat chemical contaminants (such as MTBE) in aqueous solution. These processes include ozonation, UV photolysis, and AOPs. UV photolysis of MTBE has been shown to occur directly and indirectly (Zepp 1988). Direct photolysis involves light absorption by MTBE followed by chemical reaction of MTBE in its electronically excited state. Indirect photoreactions of MTBE are mediated by hydroxyl radicals.

Wagler and Malley (1994) conducted bench-scale studies to determine the effectiveness of UV light absorbance, H_2O_2, and UV combined with H_2O_2 to remove MTBE from a contaminated groundwater in New Hampshire. Treatment of a simulated groundwater by UV alone or by H_2O_2 alone produced less than 10-percent removal of MTBE after 2 h of exposure at a pH between 6.5 and 8.0. UV/H_2O_2 produced more than 95-percent removal of MTBE after 40 min of exposure time within the pH range of 5.5–10. This study confirmed that hydroxyl radicals are the primary compounds responsible for MTBE oxidation. During these experiments, methanol, formaldehyde, TBA, and 1,1-dimethylethyl formate were identified as by-products generated from the UV/H_2O_2 process. Chang and Young (1998) studied the kinetics of UV/H_2O_2 treatment for MTBE with a recirculating batch reactor fitted with a low-pressure mercury lamp. With a spiked MTBE level of 10 mg/L, UV/H_2O_2 treatment resulted in 99.9-percent removal of MTBE in water with a major by-product identified as TBF. The yield for the formation of TBF from the treatment was 27 percent.

During the MTBE treatment by UV/H_2O_2, it is now known that many typical by-products are formed. These include TBF, TBA, isopropyl alcohol, acetone, formaldehyde (also a DBP of natural organics), and methyl acetate. Currently, these contaminants are not regulated for drinking water supplies but may pose public health concerns. CDHS has proposed an action level for TBA of 12 µg/L for its cancerous effect. When an action level is exceeded, certain requirements and recommendations apply such as notifying government agencies and consumers. By-product formation was evaluated during this study.

Pulsed-UV and pulsed-UV/H_2O_2 tests were conducted in two phases with a laboratory water and a southern California groundwater. Phase I was conducted in a completely mixed batch reactor (CMBR) to determine UV and H_2O_2 dosages for MTBE reduction. Two MTBE concentrations were evaluated (200 and 2,000 μg/L). Phase II was conducted in a continuously stirred tank reactor (CSTR) to validate CMBR testing and investigate impacts of other compounds (such as TBA) on MTBE destruction.

Reduction By Ozone and PEROXONE

MTBE can be oxidized directly by ozone (a very slow reaction) or indirectly by the hydroxyl radical (which is much more rapid). MTBE is typically not completely mineralized to carbon dioxide and water, however, and major by-products are formed, including TBA, TBF, aldehydes, isopropyl alcohol, and acetone.

Karpel Vel Leitner and co-workers (1994) studied the reaction of ozone/PEROXONE on MTBE in dilute aqueous solution. Experiments showed that PEROXONE was a more effective than ozone alone. TBF, formaldehyde, and TBA were identified as by-products. Dyksen and co-workers (1992) conducted pilot studies evaluating ozone/PEROXONE treatment of MTBE. Their results also showed PEROXONE to be more effective than ozone alone for its removal. This study produced nondetectable levels of MTBE after 8 mg/L of ozone and 4 mg/L of H_2O_2 at a contact time of 3–6 min. Liang and co-workers (1999) conducted a pilot-scale study to investigate the effectiveness of ozone and PEROXONE for MTBE removal. PEROXONE was seen as more effective than ozone alone. Results indicated that PEROXONE (4 mg/L ozone and 1.3 mg/L H_2O_2) achieved MTBE removals of 78 percent (on average) in two California waters. However PEROXONE testing produced more than 10 μg/L of bromate (0.1 mg/L initial bromide).

Ozone/PEROXONE tests were conducted in two phases using a southern California groundwater. Tests were performed in the CMBR to determine required ozone and H_2O_2 dosages. Effects of influent MTBE concentrations on MTBE removal were also tested with

MTBE spikes of 200 and 2,000 µg/L. Procedures for experiments were as follows: (1) the test water for the experiment was collected and spiked with MTBE (and other compounds if required); (2) water was pumped to the ozone treatment chamber; (3) initial water samples were taken from the test water; (4) ozone and H_2O_2 were continuously added; and, (5) treated water samples were collected at different time intervals.

NDMA

Reduction by Pulsed-UV Light

NDMA absorbs UV light in a strong band centered at 228 nm (Figure 1) and a weak band centered at 332 nm (not shown) resulting in breakdown of the nitrogen-nitrogen (N-N) bond. Because of this strong absorption, photolysis of NDMA by polychromatic UV technology is promising. Polychromatic, pulsed lamps may be effective in treating NDMA (compared to low-pressure mercury lamps which emit light primarily at 254 nm) because of light output across the 200 to 300 nm wavelength range.

Pulsed UV and pulsed UV/H_2O_2 tests for the reduction of NDMA were conducted in two different phases. A laboratory water (Millipore Corp., Bedford, Mass.), Colorado River water (CRW), and a southern California groundwater with varied levels of NDMA were treated. Phase I was performed in the CMBR to determine the required UV dosages and H_2O_2. The effects of NO_3^- and of influent NDMA concentrations on NDMA removal were also tested with a NO_3^- spike of 38 mg/L and NDMA spikes of 0.1 and 3 µg/L. Phase II was conducted in a CSTR to confirm the effects of other compounds on NDMA destruction and investigate possible reformation of NDMA. Procedures for experiments were similar to that shown previously for MTBE treatment.

Reduction by Ozone and PEROXONE

Hydroxyl radicals can react effectively with NDMA (Wink et al. 1991). Ozone/H_2O_2 utilizes the generation of hydroxyl radicals to oxidize NDMA and break down NDMA degradation by-products.

Ozone and PEROXONE tests were conducted in two different phases using a southern California groundwater. Phase I was performed in a CMBR to determine the required ozone and the H_2O_2 dosage. Effects of influent NDMA concentration were tested with NDMA spikes of 0.1 and 3 μg/L respectively. Phase II was conducted in a CSTR to investigate the effects of applied ozone dose and validate optimized conditions.

Procedures for experiments were as follows: (1) test water was collected and spiked with NDMA and other compounds (if required); (2) water was pumped to the bench scale ozone treatment chamber and the reactor mixer was turned on; (3) initial samples were taken; (4) ozone and H_2O_2 were continuously added to the process water; and, (6) ozonated water samples were collected.

Perchlorate Reduction by Pulsed-UV Light

The perchlorate ion does not absorb UV light. However, pulsed UV, due to its ability to deliver much higher UV light intensities than other continuous wave UV technologies, has potential to provide enough energy to excite or break up perchlorate while in combination with catalysts or reducing agents under anaerobic conditions. These conditions can potentially produce a perchlorate radical (ClO_4^o), or a perchlorate molecule in an excited state, capable of dissociating into a reduced chlorate ion (ClO_3^-) and oxygen.

Reduction processes of perchlorate are based upon the premise that perchlorate is thermodynamically unstable. High energy UV sources, such as pulsed UV, may produce a perchlorate radical or a perchlorate molecule at an excited state which—when in the presence of a reducing agent—may convert it to chloride and reduce the perchlorate concentration (Theis et al. 1999).

Pulsed UV tests with and without catalyst were conducted. Tests were performed in the CMBR to determine the required UV dose, develop perchlorate decay information, and investigate the evolution of perchlorate by-product formation. Perchlorate reduction by ozone/PEROXONE was not evaluated because perchlorate is already the most highly oxidized state of chlorite possible.

Taste-and-Odor Reduction by Pulsed-UV Light

This subtask spiked known amounts of 2-methylisoborneol (MIB) and geosmin into CRW. Target baseline levels for each compound were 50 nanograms/L (ng/L), an amount which Metropolitan has seen leaving its raw water reservoirs. UV dose and H_2O_2 dose were varied in order to determine the most cost efficient operation of the system.

Experiments were conducted in the following matrix:

- Effects of increasing UV-alone dose (no H_2O_2);
- Effects of increasing H_2O_2 dose (UV dose remaining constant); and,
- Effects of increasing UV dose (H_2O_2 dose remaining constant).

Procedures for experiments were similar to the bromate experiments.

Methods and Materials

Aldehydes

Formaldehyde and acetaldehyde were analyzed by a derivatization-extraction gas chromatography (GC) electron-capture detection method (Glaze et al. 1989). Other aldehydes, such as glyoxal and methyl glyoxal, were analyzed by a modification (heated derivatization) of this method (Sclimenti et al. 1990).

Bromate

Bromate tests were conducted by dissolving potassium bromate (99.8 percent $KBrO_3$; EM Science, Gibbstown, N.J.) into the subject waters to target concentrations of 100, 50, and 10 µg/L. Bromate analyses were performed by a modified ion-chromatographic (IC) method. This modification, use of an on-line silver cartridge sample preparation technique, is described by Kuo and co-workers (1990). A purging step was also incorporated into the method to shorten total analytical time. The IC system (DX 500; Dionex Corp., Sunnyvale, Calif.) included a pair of analytical and guard columns (AS9HC, AG9HC; Dionex), an anion self-regenerating suppressor, and a conductivity detector. The minimum reporting limit (MRL) for bromate was 3 µg/L.

Bromide

Bromide analyses were conducted on an IC (model 2010, Dionex Corp., Sunnyvale, Calif.) with a 20- or 50-µL sample loop. An IC analytical column (model AS4A, Dionex Corp.), an anion micromembrane suppresser, and a conductivity detector were used.

Hydrogen Peroxide

Two different methods were used for detection of residual H_2O_2. A fluorescence method developed by Kok and co-workers (1986) was used when residuals were less than 1 mg/L and an iodometric titration method (Salvage 1951, Schumb et al. 1955) was used for more concentrated residuals. The fluorescence method involved reaction of H_2O_2 with p-hydroxyphenylacetic acid and horseradish peroxidase, and subsequent detection of the fluorescent product by a fluorescence spectrophotometer (Lambda-3B model; Perkin-Elmer Corp., Norwalk, Conn.). Iodometry included a sodium thiosulfate titrant for the samples after acidification with sulfuric acid combined with ammonium molybdate.

MTBE and MTBE By-products

The method used was developed by Church and co-workers (1997a, b), a direct aqueous injection analytical technique for the routine analysis of MTBE and its likely degradation products. The technique features the direct aqueous injection of water containing the analytes onto a highly polar column via a split/splitless injector operated in splitless mode. This injection technique, when coupled with detection by mass spectrometry allows simultaneous qualification and quantification of MTBE and all of its expected degradation products. This method has a detection limit of 0.1, 0.1, 5.0, and 10 μg/L for MTBE, TBA, TBF, and acetone, respectively.

NDMA

Prior to June 1999, NDMA samples were analyzed by DataChem Labs, Inc. (Salt Lake City, Utah). DataChem extracted NDMA samples in a continuous liquid-liquid extractor and analyzed the extract by gas chromatography/mass spectrometry (GC/MS), with a selected ion-monitoring mode to determine NDMA. This method has a detection limit of 0.020 μg/L. The Canadian Ministry of the Environment (Etobicoke, Ontario, Canada) analyzed NDMA samples taken after June 1999. NDMA was analyzed by a solid-phase extraction method combined with low-resolution GC/MS as described by Taguchi et al. (1994). This method has a detection limit of 0.001 μg/L. Before the NDMA samples were submitted, catalase was used to quench the H_2O_2 (when H_2O_2 was used) to prevent any further reaction of NDMA.

Ozone Contactor Tests

MTBE treatment by ozone was conducted with a pilot-scale ozone contactor presented in Figure 2. This arrangement holds approximately 200-gal in a semi-batch reactor system consisting of an ozone contactor column, an ozone reactor column, a water recirculation pump, and a equalization tank. For each test, 99.5-percent pure MTBE (Burdick & Jackson, Inc., Muskegon, Mich.), in a predetermined amount, was well mixed in an equilibrium tank. Water was then pumped to the top of the ozone contactor from a 200-gal Nalgene® tank at 2.4 gallons per minute (gpm). In the first contactor column, ozone gas was applied countercurrently to the treated water flow. The second contactor column served as a reactor chamber (no gas applied). Each ozone column was operated at a residence time of 10 min. Water levels were maintained at 16 ft in the 6-in diameter columns. Ozone was bubbled through 4-in diameter ceramic diffusers to generate fine bubbles. Ozone transfer efficiencies were above 98 percent in all tests. The ozone generator was a tube-type, water-cooled unit operating on a low-frequency (60 pulses per second [Hz]), variable-voltage power supply (model Labo-76, Praxair/Trailigaz Ozone Co., Cincinnati, Ohio). The capacity of the ozone generator was 1 lb/day, with oxygen or compressed air as the feed gas. The target gas-phase concentration of ozone produced was 2 percent by weight. The ozone concentration in the feed gas was measured by a gaseous ozone monitor (model HC-12, PCI Ozone Corp., West Caldwell, N.J.). Off-gas from the contactor flowed through a thermocatalytic ozone destruction unit before being discharged to the atmosphere. When used, H_2O_2 (3 percent by weight, USP grade) was injected upstream of the ozone contactor, in predetermined amounts, by peristaltic pumps. A series of pilot-scale tests was conducted in which the total applied ozone dosage of 30 mg/L was added in increments of either 1, 2 or 3 mg/L. The tests were performed using PEROXONE ratios between 0 and 3.3 (defined as the weight ratio of H_2O_2 to ozone).

For NDMA tests, a bench-scale reactor was used as shown in Figure 3. The reactor consisted of a gas tight, 20-L glass shell, with inlet and outlet ports for applying ozone gas and diverting the off gas to the ozone destruction unit. Ozone was bubbled directly to a mixing blade to increase the transfer efficiency of ozone. The liquid volume was 16 L, and the H_2O_2 was injected to the water by a peristaltic pump. A pump, with stainless steel tubing, was attached to the reactor bottom for sampling purposes during batch experiments. The same ozone generator was used as described above.

For NDMA flow-through tests, the batch setup was modified slightly (illustrated in Figure 4). Two high-speed pumps were attached to the reactor. The influent water line was extended to the bottom of the reactor, and the stainless steel tubing was placed at the surface of the water for the effluent line. The flow rate to the reactor was controlled by the influent water line, and the effluent line flowrate was set at a higher speed to prevent any increase in the working volume of the water in the reactor. H_2O_2 was applied by a peristaltic pump to the system. Samples were taken from the influent and the effluent lines.

Perchlorate

Perchlorate samples were analyzed using an ion chromatograph (model DX300; Dionex Corp., Sunnyvale, Cal.) modified with a 200 µL-sample loop. An IC analytical column (model AG11; Dionex), an anion micromembrane suppressor, and a conductivity detector were used. The method detection limit was 1.4 µg/L, and the reporting limit was 4.0 µg/L.

Pulsed-UV Apparatus

Pulsed-UV experiments were conducted using a bench-scale, completely mixed batch reactor (CMBR) which housed a pulsed-UV lamp illustrated in Figure 5. The reactor was made of 316 stainless steel and operated in a 43.5-L batch configuration using a variable-speed mixer. The CMBR housed a 15-cm, xenon-filled, tungsten-electrode flashlamp (ILC Technology, Sunnyvale, Calif.) inside a 0.5-in diameter quartz jacket (a conduit for deionized cooling water) mounted through the center of the tank. The lamp emitted polychromatic light across the UV, infrared, and visible spectra and was powered by a 5-kilowatt (kW) source (Innovatech model PUV-04; PurePulse Technologies, San Diego, Calif.) that allowed pulse rates up to 30 Hz. Between pulses, a standby “simmer” mode consisting of a steady-state partial ionization of the xenon gas was maintained with a low current arc between the electrodes (Smith 1986). Experiments were conducted with the lamp pulsing at 2, 10, or 25 Hz.

To characterize applied UV doses in the traditional format seen in disinfection studies (i.e., millijoules per square centimeter [mJ/cm^2]), a biological dose measurement technique was used (Linden and Mofidi 1999) with results presented in Table 1. The bioassay (also termed biodosimetry) was conducted with male-specific (MS-2) coliphage. The $\log_{10}$ reduction of MS-2 was measured to quantify both the simmer mode UV irradiance and the UV dose applied per pulse. These results were correlated back to a low-pressure equivalent dose, i.e., collimated beam (CB) experiments with MS-2 coliphage disinfection by low-pressure UV light. CB experiments were conducted using equipment and procedures described elsewhere (Mofidi et al. 2000); the MS-2 assay procedures have been summarized by Mofidi and co-workers (1998). The resulting simmer irradiance and UV dose per pulse were quantified to be 0.03 ± 0.0 mW/cm^2 and 1.0 ± 0.2 mJ/cm^2, respectively. Limited petri-dish experiments were conducted with the pulsed-UV lamp in a CB configuration (shown in Figure 6) as described by Linden and co-workers (2000). For these limited experiments, dose measurement was accomplished by potassium iodide-iodate actinometry (Linden et al. 2000, Rahn et al. 2000).

Figure 7 illustrates the orientation of the pulsed-UV reactor when investigating pulsed-UV light effects on MTBE and NDMA. Water quality samples were taken from the pulsed-UV reactor while it was oriented in the CMBR and CSTR configurations at various time intervals. When H_2O_2 was added to the reactor, catalase was added to the samples to quench any further oxidation reactions from the H_2O_2.

The pulsed-UV reactor was modified for the perchlorate treatment experiments as shown in Figure 8. This setup allowed for nitrogen purging of dissolved oxygen (DO). Nitrogen purging consisted of introducing compressed nitrogen with a diffuser in the reactor to purge DO prior to tests. Once nitrogen purging was completed, DO was monitored during testing.

Residual Ozone

For residual ozone, method 4500-O_3 (APHA 1998) was slightly modified. The measurement was corrected for the absorbance of background organics at 800 nm.

Simulated Distribution System Tests

Water samples were dosed with chlorine at 1.5 mg/L to each bottle with a volume of 600 mL sample and incubated at 25°C for 1 day. The chlorine dosage of 1.5 mg/L was used because chlorine demand tests indicated that this dosage was needed to maintain a residual of at least 0.2 mg/L after 24 h. Analyses were conducted on SDS samples to evaluate the formation of pentane-extractable disinfection by-products—such as total THMs, haloaceto-nitriles (HANs), haloketones (HKs), and chloropicrin—that employed modified THM liquid-liquid extraction as described by Koch and co-workers (1988).

Miscellaneous

Grab samples were collected for alkalinity, TOC, conductivity, UV light absorbance at 254 nm (UV_{254}), and nitrate analyses, which were all measured by *Standard Methods* (APHA 1998). Grab samples for turbidity were quantified by a 2100N turbidimeter (Hach Co., Loveland, Colo.), and pH was measured by a 920A pH meter (Orion Research, Inc., Boston, Mass.) calibrated daily with pH 7.0 and 10.0 buffer solutions.

Taste-and-Odor Compounds

MIB and geosmin (99 percent MIB and 98.9 percent geosmin; Supelco, Bellefonte, Pa.) were dissolved in water and analyzed using salted closed-loop stripping analysis (CLSA) followed by GC/MS identification. During CLSA, VOCs were stripped from the water by a recirculating air stream and adsorbed onto an activated carbon filter. The compounds were eluted from the filter with carbon disulfide. The obtained extract was then injected onto a GC/MS for identification and quantification by selective ion monitoring. The method detection level (MDL) was 2 ng/L for both geosmin and MIB. A more detailed description of the CLSA method can be found in *Standard Methods* (APHA 1998) Method 6040B.

PROJECT OUTCOMES

The potential of UV light (with and without H_2O_2) was evaluated for photolysis and oxidation of micropollutants dissolved into different waters, including: an organic-free, particle-free, deionized laboratory water (Super-Q; Millipore Corp., Bedford, Mass.); a treated blend of SPW and CRW; and, two groundwaters from southern California. Water quality characteristics are presented in Table 2 and test parameters are summarized in Table 3.

Raw water quality parameters for ozone/MTBE tests are shown in Table 4. Water quality variations within each test group were insignificant. Water quality for the ozone/NDMA tests is included in the water quality summary for the UV/NDMA tests.

Bromate Reduction by Pulsed-UV Light

Ozonating natural waters containing bromide can result in the formation of bromate, which is regulated by the USEPA to a maximum contaminant level of 10 µg/L (USEPA 1998). Siddiqui and co-workers (Siddiqui et al. 1994, 1995, 1996) have described the premise that UV wavelengths near 195 nm provide sufficient energy to break bromate's molecular bonds. The resulting decomposition intermediates from bromate (BrO_3^-) include bromite ion (BrO_2^-), with a peak effective photolyzing wavelength of 260 nm, and hypobromite ion (BrO^-), which is reduced to Br^- after sufficient exposure to 330 nm irradiation.

Tests investigating the bromate reduction potential of UV were conducted with up to 100 µg/L of bromate. The results from this study are summarized in Figure 9. Data were collected from both CB screening tests (in laboratory water) and CSTR tests. The CB tests demonstrated 6 percent bromate reduction after applying a UV dose of 110 mJ/cm^2. Subsequent laboratory water tests in the CSTR, with a starting bromate concentration of 50 µg/L or more, showed up to 89 percent bromate reduction after an applied dose of about 3,100 mJ/cm^2. With a starting concentration of 10 µg/L, bromate was reduced below detectable limits. Polychromatic UV experiments by Siddiqui and co-workers (1996) in similar water showed 46 percent reduction with 550 mJ/cm^2. In CMBR tests treating natural water, a significant drop in performance was realized. Although light transmission decreased (e.g., at 254 nm, transmittance dropped from 100 percent for laboratory water to between 75 and 91 percent for the blend), the magnitude of this change could not adequately explain the significant difference in experiment results. In the natural water, only 18 percent reduction was measured at doses as high as 4,000 mJ/cm^2. UV/H_2O_2 experiments were conducted in treated natural water to determine the effects of hydroxyl radical presence in bromate reduction. However, H_2O_2 addition (4.1 mg/L) did not improve process performance.

MTBE

Reduction by Pulsed UV

MTBE removal was investigated under various test conditions. UV dose is expressed both as kilowatt-hours per 1,000 gallons (kWh/1,000 gallons) and mJ/cm^2. No loss of MTBE by volatilization was observed.

MTBE spiked in groundwater was treated at a UV pulse rate of 25 Hz. Min and co-workers (2001) established that this groundwater may contain significant amounts of hydroxyl radical initiators, therefore, MTBE removal was likely to be enhanced because of this. Figure 10 shows MTBE reduction increased with increasing UV dose. MTBE removals of 11, 25, 38, and 87 percent were achieved with applied UV doses of 4, 11, 22, and 131 kWh/1,000 gallons, respectively, at 25 Hz. Compared to pulsed UV alone, the addition of H_2O_2 significantly improved MTBE reduction.

Figure 11 shows results of investigating the effects of 2 pulse rates (10 and 25 Hz) and two H_2O_2:MTBE molar ratios (99.5 and 135). It is difficult to determine if there were significant effects due to either the different pulse rates H_2O_2 doses.

Because TBA might already be present in waters contaminated with MTBE, tests were conducted to examine the effect of increased TBA concentration on MTBE removal efficiency. Figure 12 shows that while spiking 181 μg/L TBA, MTBE removals of 37, 56, 77, and 99.2 percent were achieved with applied UV doses 4, 11, 22, and 131 KWh/1,000 gallons (19 mg/L H_2O_2 dose). Without spiking TBA, MTBE concentrations were reduced by 36, 89, 98, and 100 percent under similar conditions. This indicates that the added TBA may slow the rate of MTBE reduction.

The USEPA has proposed a bromate maximum contaminant level of 10 µg/L, based on a 10^{-5} risk level of 0.5 µg/L. Exposing bromide-laden groundwater to pulsed-UV irradiation (with H_2O_2) did not result in the formation of bromate in all conditions tested; this result agrees with the results of Symmons and co-workers (1997).

UV treatment of MTBE (with and without the addition of H_2O_2) forms several by-products as shown in Figure 13. (data presented as carbon equivalents). When pulsed UV was applied to the ~2,000 µg/L (~900 µg/L as carbon) MTBE spiked groundwater, the concentrations of TBA, and formaldehyde increased with increasing UV (25 Hz). However, TBF and acetaldehyde increased first, then decreased. Acetone gradually increased throughout testing. These data indicate that the addition of H_2O_2, compared to UV alone, more fully mineralized the MTBE.

To allow for a comparison of this data to the disinfection efficiency of UV light, UV dosages from the experiments described above are presented in units of mJ/cm^2. A summary of MTBE treatment plotted against this unit of UV dose measure is presented in Figure 14. These data indicate the amount of UV energy required to reduce MTBE, with and without H_2O_2. Without H_2O_2, a UV dose of 47,000 mJ/cm^2 reduced MTBE by 87 percent (more than 1,000-fold greater UV dose than required for disinfection). With 19 mg/L H_2O_2, a UV dose of 3,900 mJ/cm^2 provided 89 percent reduction. Adding 69 mg/L H_2O_2 lowered this required dose to 1,600 mJ/cm^2. These UV and H_2O_2 doses may be prohibitive in drinking water applications, and certainly could not be attained by a UV system designed primarily for disinfection.

Reduction by Ozone and PEROXONE

Ozone and H_2O_2 residuals at the ozone contactor column effluent were analyzed throughout the study. The addition of H_2O_2 effectively eliminated the ozone residuals which ranged from not detected to 0.04 mg/L. In contrast, significant ozone residuals were detected for ozone alone for all tests. Low levels of H_2O_2 residuals were also detected in ozone-alone tests. This finding is consistent with reports that H_2O_2 is a by-product of ozone decomposition (AWWA 1991 a,b).

Figures 15 and 16 show the effects of ozone dose, PEROXONE dose (at a constant H_2O_2 to ozone ratio of 1.0) and initial MTBE concentration on MTBE removal. When MTBE concentrations were high (~2,000 µg/L, Figure 15), PEROXONE removed substantially more MTBE than ozone alone. However, when the MTBE concentrations were lower (~200 µg/L, Figure 16), ozone and PEROXONE performed similarly, particularly at ozone dosages above 4 mg/L. This difference in performance may result from the production of MTBE by-products, which—particularly at high MTBE levels—consume additional ozone and hydroxyl radicals which slow the degradation of MTBE.

To further investigate the effect of MTBE by-products on MTBE removal by PEROXONE, tests were conducted at the high (~2,000 µg/L) and low (~200 µg/L) MTBE levels with the addition of ~200 µg/L of TBA. Figures 17 and 18 show the effect of adding TBA. These tests confirmed that the presence of TBA could reduce MTBE removal, particularly when MTBE concentrations were high.

If water containing bromide is ozonated, bromide is oxidized through both a molecular ozone pathway and a hydroxyl-radical-initiated pathway to form bromate (Song et al. 1997, Von Gunten et al. 1993, Krasner et al. 1993a, Siddiqui et al. 1993, Daniel et al. 1993, Von Gunten et al. 1996). Effects of ozone dose on bromate formation for MTBE tests are shown in Figures 19 and 20. Bromate formation increased with increasing ozone dosage and decreasing MTBE concentrations. This groundwater contained extremely high levels of bromide (1.1 – 1.3 mg/L), which would be expected to form problematic levels of bromate. The highest bromate levels produced were 422 and 216 µg/L for the 200 and 2,000 µg/L MTBE tests, respectively. The higher MTBE concentrations may have acted as an ozone scavenger thereby minimizing the formation of bromate. In virtually all tests, however, bromate was formed at or above the MCL of 10 µg/L.

NDMA

Reduction by Pulsed-UV Light

The following discussion of NDMA removal highlights the effects of UV dosage, source water, UV/H_2O_2, and nitrate, as well as the effects of initial NDMA concentration on NDMA removal.

Figure 21 shows that the addition of H_2O_2 did not measurably improve the removal of NDMA in any of the waters tested. Because NDMA strongly absorbs UV light near 200 nm, it is removed primarily by photolysis. The additional production of hydroxyl radicals by the absorption of UV light by H_2O_2 was not beneficial to treatment.

However, water quality differences my affect NDMA removal. The data from Figure 21 indicate that NDMA was more readily removed in laboratory water, followed by groundwater and CRW. Competitive absorption of UV light by water quality constituents such as TOC and may result in reduced photolysis of NDMA. In addition, because NDMA concentrations are very low, there is little competitive absorption of UV light by NDMA or its by-products at concentrations typically encountered in water treatment. Figure 22 shows the effect of nitrate has on NDMA removal in laboratory water. This data indicates that nitrate, which is present in many waters contaminated with NDMA, may reduce the efficiency of UV treatment.

UV absorption of nitrate is in the range of 230–240 and 300–310 nm (Calgon 1996). This is close to the absorption bands of NDMA. For photolysis, competition for UV light between nitrate and NDMA might reduce the effectiveness of NDMA removal. In addition to nitrate, the exposure of nitrate to UV produces nitrite which also absorbs UV (Zepp et al. 1987, Warneck and Würzinger 1988).

Once removed, NDMA regeneration may occur because the degradation products from the photolytic destruction of NDMA could reform NDMA after chlorination. Samples taken for an NDMA reformation study were dosed with 1 mg/L Cl_2 for 5 days at 4 to 8°C. Chlorination more than doubled the final NDMA concentration in the waters tested. The addition of H_2O_2 reduced the reformation, probably by quenching the chlorine residual.

The effects of UV treatment (UV dose measured as mJ/cm^2) on NDMA in two waters are presented in Figure 23. In laboratory water, doses of 120 and 310 mJ/cm^2 achieved 69 and 90 percent NDMA reduction, respectively. With the addition of 1 mg/L of H_2O_2, as stated earlier, there was no significant performance improvement. When conducting similar experiments in groundwater, process performance declined slightly (as discussed earlier). This was probably caused by UV absorption (due to nitrate) or scattering (due to turbidity). Interpolated data indicates that a UV dose of 580 mJ/cm^2 would provide 90 percent reduction of NDMA in groundwater. At a dose of 100 mJ/cm^2, 51 percent reduction may be achieved.

Reduction by Ozone and PEROXONE

Minimal reduction of NDMA was observed by ozone as shown in Figure 24. NDMA removal was much greater with PEROXONE (ratio of 1:1). At a starting NDMA level of 3 µg/L, 90 percent was removed after 15 mg/L of ozone. With 5 mg/L of ozone, no NDMA reduction was observed. However, about 50 percent reduction of NDMA was observed with PEROXONE at a dose of 5 mg/L (H_2O_2:ozone ratio of 1:1).

Groundwater, spiked at two NDMA concentrations, was treated in the CMBR. As shown in Figure 25, NDMA removal was found to be independent of initial NDMA concentration. Similar removal efficiencies were observed at 5 mg/L applied ozone for both low and high initial NDMA concentrations.

Perchlorate Reduction by Pulsed-UV Light

Tests exposed samples at a pulse rate 25 Hz and results are presented in Figure 26. No perchlorate reduction was observed, as expected, because perchlorate does not absorb UV light. Changing solution pH or adding H_2O_2 did not affect perchlorate reduction by UV.

Catalysts that generate hydrated electrons were considered for use with the pulsed UV reduction of perchlorate. Among these catalysts considered, elemental iron was chosen because it was the most compatible chemical to be used in the drinking water treatment process. The UV energy applied was hypothesized to work two-fold: (1) to initiate catalyst to generate hydrated electrons and (2) to provide energy to assist perchlorate molecules to become excited and further break down to a more reduced chlorate species that would require less energy to destroy.

During the UV experiments, there were clear indications that the elemental iron was being oxidized effectively. Each sample was filtered with a 0.45-µm filter before perchlorate analysis. The filters retained elemental iron particles which had clearly changed from metallic gray powder before the test to a reddish brown color after treatment. The color change was more apparent as UV dose increased. Without exposure to UV light, the metallic powder did not oxidize in the water under similar hydraulic conditions. Test results shown in Figure 27 indicate, however, that only slight reduction of perchlorate was achieved when adding the catalyst. Samples were analyzed for DO which showed that the DO level gradually increased to as much as 2 mg/L. Since the hypothesis for perchlorate reduction assumes results can be achieved only under anaerobic conditions, adjustments to testing were made. Figure 28 shows that reduced pH also provided no effect on improving perchlorate reduction.

To help keep DO levels sequestered, chemicals (sodium thiosulfate and ascorbic acid) and nitrogen DO stripping were considered as adjustments to testing. However, since sodium thiosulfate would absorb UV light, it was not used. Because of similar concerns, ascorbic acid was also not used. A nitrogen purging system was evaluated during a control experiment and the DO level was maintained at zero for up to one hour after the purging stopped (no UV light was applied). During perchlorate testing, however, Figure 29 shows that the DO level increased up to 2.3 mg/L. The increase in the DO level may have interfered with the reduction of perchlorate.

Since the continuous bubbling of nitrogen in solution during UV irradiation will also cause problems with reduced UV penetration due to light scattering by the bubbles, alternative approach might be applying the nitrogen gas in the headspace during the UV irradiation to minimize the intrusion of atmospheric oxygen to the water. The other alternative is to find a reducing agent which will not interfere with the perchlorate reduction process. In fact, certain reducing agents may be able to reduce DO level prior to UV application and generate hydrated electrons during the UV irradiation, serving the dual role. These background tests however, would have required the following assessments of a specific compound:

- Its ability to remove DO effectively;
- Its ability to absorb UV light;
- Its ability to generate hydrated electrons;
- Whether the DO level can be maintained at zero throughout the experiment;
- Whether there is any effect of the compound on perchlorate reduction with and without UV in the absence of elemental iron; and,
- Whether the compound is safe to add to drinking water.

Since the full characterization of DO controlling compound is beyond the scope of this project, more detailed work was not conducted.

Perchlorate removal data is also presented in Figure 30 according to UV dose expressed as mJ/cm^2. This indicates that UV dosages attempted to control perchlorate were in exceedance of 40,000 mJ/cm^2. This UV dose of 40,000 mJ/cm^2 is equal to or less than the dosages used during the previously reported catalyst experiments.

Taste-and-Odor Reduction by Pulsed-UV Light

Many utilities experience T&O problems in their raw waters as a result of algal blooms in reservoirs (Morioka et al. 1993, Lang et al. 1996). MIB and geosmin, by-products of algae and bacteria that may grow in surface water reservoirs, contribute to T&O problems by imparting earthy and/or musty odors to drinking water. Ozone has been established as the most effective treatment process for oxidizing T&O compounds (McGuire and Gaston 1998).

Experimental results from this study are presented in Figures 31 and 32. MIB and geosmin were dissolved in pretreated natural water (light transmission at 254 nm ranging from 91 to 95 percent) and irradiated with UV alone and UV/H_2O_2. Data are presented as the average and standard deviation of three replicate experiments. As with the MTBE results, very high doses of

UV alone are required for MIB and geosmin reduction. Without H_2O_2, an applied UV dose of 10,100 mJ/cm^2 reduced MIB and geosmin by 92 and 97 percent, respectively. A lower dose of 2,600 mJ/cm^2 (still significantly greater than would be needed for disinfection purposes) only reduced MIB and geosmin by 9 and 28 percent, respectively. However, after adding 5.5 mg/L of H_2O_2, hydroxyl radical generation significantly improved treatment efficiency. With H_2O_2, a UV dose of 1,100 mJ/cm^2 reduced MIB and geosmin by 91 and 93 percent, respectively. At 27 mJ/cm^2, a dose comparable to that recommended by the Surface Water Treatment Rule for virus disinfection (Parotta 1998), H_2O_2 assisted in providing 57 percent reduction of MIB and 46 percent reduction of geosmin. Interpolating between data points presented in Figure 32, a UV dose of 100 mJ/cm^2 (reasonable for drinking water disinfection) combined with 5 mg/L H_2O_2 may reduce MIB and geosmin by 65 and 55 percent, respectively. In these experiments, between 86 to 96 percent of the initial dose of H_2O_2 remained as residual after treatment. This H_2O_2 residual would need to be oxidized before a chlorine residual could be established.

Results from previous studies are difficult to compare to the work presented here. This difficulty arises from inconsistencies in reported UV dose measurement. Glaze and co-workers (1990) found that UV/H_2O_2 treatment of SPW (0.56 watts UV applied per liter, 5 mg/L H_2O_2) provided 29 and 40 percent reduction of MIB and geosmin, respectively. Two polychromatic UV studies showed up to 95 percent geosmin reduction when 40 mg/L H_2O_2 was combined with UV doses significantly greater than needed for disinfection (Andrews et al. 1995, Jobb et al. 1995).

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on the work completed here, the following conclusions are offered.

Bromate

Bromate reduction was more efficient in laboratory waters than natural waters, and the difference in treatment could not be explained fully by the change in water qualities. Specifically, results showed:

- 3,100 mJ/cm^2 was needed to reduce bromate by 89 percent in laboratory water;
- At dosages up to 4,000 mJ/cm^2, only 18 percent bromate reduction was seen; and,
- The addition of H_2O_2 did not improve performance.

MTBE

Reduction by Pulsed UV

The purpose of this research was to explore the use of photochemical processes for the removal of MTBE from contaminated groundwater and determine the key variables that affect the processes. Based on this testing, the following conclusions were drawn about the effectiveness of pulsed UV alone and pulsed UV/H_2O_2 for MTBE removal:

- UV alone cannot effectively reduce MTBE;
- UV/H_2O_2 is effective in reducing MTBE;
- H_2O_2 dose strongly affects reduction efficiency of MTBE;
- UV/ H_2O_2 did not result in the formation of bromate with 0.2 mg/L bromide;
- MTBE by-products reduced the effectiveness of pulsed UV/H_2O_2 treatment for MTBE;
- A UV dose of 47,000 mJ/cm^2 was needed to reduce MTBE by 90 percent; and,
- A UV dose of 1,600 mJ/cm^2 combined with 69 mg/L H_2O_2 reduced MTBE by 90 percent.

Reduction by Ozone and PEROXONE

Experiments conducted in a large-scale, semi-batch reactor demonstrated that PEROXONE (ratios up to 3.3, ozone dosages up to 30 mg/L) was consistently more effective in oxidizing MTBE than ozone alone. Although chemical dosages were high, PEROXONE may prove to be a suitable alternative in removing MTBE. The following is a summary of outcomes:

- PEROXONE was more effective in oxidizing MTBE than ozone, particularly when water contained higher MTBE concentrations;
- Ozone doses of 19 mg/L (with 47 mg/L H_2O_2) and 24 mg/L (with 30 mg/L H_2O_2) were needed to meet the secondary standard of 5 μg/L for 200 and 2,000 μg/L of MTBE, respectively;
- MTBE by-products such as TBF, TBA, acetone, and aldehydes were identified and may have hindered MTBE removal efficiency;
- TBF was produced immediately, followed by TBA, acetone, and formaldehyde;
- Treatment of groundwater by ozone and PEROXONE produced bromate; and,
- The addition of H_2O_2 prior to ozonation produced lower levels (< 13 μg/L) of bromate than ozone.

NDMA

Reduction by Pulsed UV

The following summary can be drawn regarding the effectiveness of pulsed-UV irradiation and pulsed-UV/H_2O_2 treatment for the destruction of NDMA:

- UV alone is effective in removing NDMA;
- Less NDMA reformation was seen after chlorination of H_2O_2 treated water, possibly because H_2O_2 reduced the chlorine residual;
- Characteristics of water type played an important role for NDMA reduction due to the differences in transmittance and background constituents;

- A strong competition for UV light absorption between NDMA and background organics (e.g., TOC and UV_{254}-absorbing organics) affected NDMA removal;
- Nitrate competed with NDMA for absorbing UV light and consequently limited UV effectiveness;
- Treatment is independent of initial NDMA concentration (at very low levels tested);
- A UV dose of 580 mJ/cm^2 reduced NDMA in groundwater by 90 percent; and,
- A UV dose of 100 mJ/cm^2 reduced NDMA in groundwater by 51 percent.

Reduction by Ozone and PEROXONE

The following summaries can be drawn regarding the effectiveness of ozone and PEROXONE treatment for the destruction of NDMA:

- Ozone alone is ineffective in NDMA reduction in drinking water;
- PEROXONE improved NDMA removal efficiency compared to ozone alone; and,
- NDMA (< 3ppb) destruction by PEROXONE depended on ozone dosage, but not on the initial NDMA concentrations.

Taste-and-Odor Compounds

Reduction of taste-and-odor causing compounds MIB and geosmin was investigated in a natural water matrix. Specifically, results showed:

- A UV dose of 10,100 mJ/cm^2 reduced MIB and geosmin by 92 and 97 percent, respectively; and,
- 100 mJ/cm^2 (a disinfection-level UV dose) and 5 mg/L H_2O_2 provided 86 and 96 percent reduction of MIB and geosmin, respectively.

Perchlorate

Pulsed UV in combination with a catalyst was tested for its ability to remove perchlorate. The following is a summary of results:

- Perchlorate was not reduced by UV;
- Perchlorate concentration, H_2O_2 dose and pH had no effect on perchlorate reduction;
- Elemental iron, an attempted catalyst for perchlorate reduction, had no effect, possibly because of interferences from dissolved oxygen;
- pH had no effect on perchlorate reduction by UV in the presence of catalyst;
- Elemental iron oxidation (probably by oxygen) was observed during the experiment, indicating hydrated electron generation by UV and iron particles; and,
- An improved DO control strategy is needed to further evaluate catalytic UV/perchlorate treatment.

General

A summary of the UV data from this research (except for perchlorate data in which no removal was measured) is presented in Figure 33. Bars represent the range of UV dose required to achieve from 1 to 2 $\log_{10}$ reduction of contaminant. Results indicate that the required UV dose may differ by one-thousand-fold, depending on the target contaminant treated. For example, based on the UV dose needed to achieve 1-$\log_{10}$ inactivation of *Cryptosporidium*, it takes almost a 10-fold greater UV dose for the same reduction of virus, a more than 100-fold greater UV dose for MTBE and T&O compounds (treatment combined with H_2O_2), and an approximately 1,000-fold greater UV dose for the same reduction of bromate (bromate reduction in laboratory water). Based on these results, it is not feasible to achieve significant reduction in bromate or MTBE at sub-100 mJ/cm^2 UV doses. Moderate reductions of NDMA (51 percent) and T&O compounds (up to 65 percent) may be accomplished at a disinfection-level UV dose of 100 mJ/cm^2 with the addition of H_2O_2. However, because of the raw-water levels of NDMA and T&O compounds in some California drinking waters, these moderate reductions may not satisfy regulatory or utility-imposed water quality objectives. Additional concerns arise from H_2O_2 residuals leaving the UV/H_2O_2 process. Because the H_2O_2 residual may be more than 85 percent of the H_2O_2 dose, effluents would need further treatment before transmission to the distribution system. Additional research is required to investigate compatibility issues that may arise when integrating UV and UV/H_2O_2 processes into conventional drinking water treatment plants.

In addition to the issues outlined above, large utilities must also consider unique technical and regulatory constraints when developing and implementing new technologies such as UV light. Technical constraints include hydraulic performance, reactor verification, reliability, and system redundancy. Regulatory considerations include (1) any potential compromise with other treatment objectives; (2) a reduced ability to monitor performance; and (3) the time required to deploy new treatment technologies. Lastly, without a well-documented and scientifically sound dose measurement method, it is nearly impossible for water utilities to implement UV technologies.

Commercialization Potential

To understand the commercialization potential of ozone or UV to treat the contaminants studied, Table 5 presents a summary of the energy requirements for these technologies to provide treatment. Cost estimates for ozone were determined based on an energy requirement of 10 kWh/pound of ozone generated. Based on the energy requirements shown in Table 5, ozone treatment requires much less energy when compared to UV for treatment of MTBE, NDMA, and T&O compounds. To reduce NDMA, MTBE, and T&O compounds (with H_2O_2), UV required approximately 1.5-fold, 20-fold, and 25-fold more energy than ozone, respectively. For ozone, reduction of T&O compounds required the least amount of energy with MTBE and NDMA reqiuring 2.5-fold and 6.5-fold more energy, respectively. For UV treatment, NDMA required the least amount of energy with T&O compounds, MTBE, and bromate requiring 2.5-fold, 5-fold, and 10-fold more energy, respectively. However, the energy required for UV treatment of NDMA was still twice that of ozone treatment. Based on these results, ozone (already commercially feasible for treatment of T&O compounds) may be commercially feasible for MTBE treatment, but the increased costs to treat NDMA may be prohibitive. Although UV costs seem prohibitive, it still may be feasible on a water quality basis due to its tendency to not form as many DBPs as the ozone process.

Recommendations

Based on water quality issues and cost requirements, one of the technologies evaluated here could be applied for reduction of water contaminants. Although ozone may be significantly less energy-intensive when compared to UV for several of the micropollutants studied, UV may be a more appropriate option based on DBP formation potential. In considering these technologies, utilities must weigh energy and DBP costs prior to implementation.

Benefits to California

It is beneficial for California utilities to understand the limitations of advanced treatment techniques before implementation. As UV light may provide excellent disinfection efficiency and low DBP formation at disinfection-level dosages, the high energy requirements for treatment of micropollutants may cause utilities to consider ozone. Utilities must, however, also consider the level of DBPs that high ozone dosages may produce.

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TABLES AND FIGURES

Table 1. Biodosimetry characterization of UV dose distributed throughout the pulsed-UV reactor

Simmer Mode Experiments	Time (min)	Sample Exposure Reduction	Log$_{10}$ MS-2 per CB* (mJ/cm^2)	UV Dose Irradiance† (mW/cm^2)	Calculated UV
Simmer		0	0.2	N/D	**
Experiment		20	1.0	11.5	0.01**
1	30	2.4	46.5	0.03	1
	45	3.1	65.8	0.02	
	60	3.6	78.9	0.02	
Simmer		0	0.0	N/D	**
Experiment		20	2.0	35.7	0.03
2	30	3.1	64.3	0.04	2
40	3.8	82.8	0.03		25
	50	4.3	95.9	0.03	
	60	4.7	106.4	0.03	
Simmer		0	0.0	N/D	**
Experiment		20	2.1	38.8	0.03
3	30	3.3	69.4	0.04	3
40	3.8	83.0	0.04		25
	50	4.1	91.8	0.03	
	60	4.6	102.6	0.03	
	60	4.6	102.6	0.03	

Pulsing Experiments (no.)	Number of Pulses Reduction (min)	Log$_{10}$ Sample MS-2 Exposure Time per CB* (mJ/cm^2)	Total UV Dose Per Pulse‡ (mJ/cm^2)	Calculated UV Dose
Pulsing	1....0.2	0.0	N/D	**
Experiment	10...1.2	4.3	16.9	0.9
15	1.5..5.4	23.6	0.9	
20	1.8..6.3	32.1	1.0	
25	2.2..7.3	41.4	1.1	
30	2.4..8.5	47.5	1.1	
Pulsing	1....0.3	0.0	N/D	**
Experiment	15...1.1	3.3	14.6	0.6
20	1.4..4.0	21.6	0.7	
1.9	4.7 32.9	1.0		
30	2.2..5.5	41.1	1.0	
40	2.7..6.4	54.5	1.1	
50	3.2..7.3	68.1	1.1	
Pulsing	1....0.0	0.0	N/D	**
Experiment	15...1.2	3.3	16.9	0.7
20	1.7..4.0	29.5	1.1	
2.2	4.7 42.4	1.4		
30	2.7..5.5	53.5	1.5	
40	3.0..6.4	63.5	1.3	
50	3.6..7.3	76.9	1.3	

Simmer Irradiance (avg. ± st. dev.):0.03 ± 0.00UV Dose per pulse (avg. ± st. dev.):1.04 ± 0.2

N/D = Not determined

* UV dose based on low-pressure UV CB results which showed that log$_{10}$ MS-2 Inactivation = 0.039 (UV dose, mJ/cm^2) + 0.57

† Irradiance = (CB based UV dose) / (time sample was exposed to simmer)

‡ UV dose per pulse = (total CB UV dose) – (dose from simmer irradiance)

** Not used in calculation of average

Table 2. Water quality characteristics for UV tests

Parameter	Laboratory Water	22 ± 3 Percent SPW*	44 ± 3 Percent SPW*	CRW for UV Tests	GW1†	GW2†
UV absorbance at 254 nm (1/cm)	ND‡	0.02 – 0.04	0.04 – 0.13	0.1	ND‡	0.022
Alkalinity (mg/L as CaCO3)	NA	111 - 114	87 - 102	131	166	298 - 331
Conductivity (µmho/cm)	1.1	NA	NA	919	389	1,193 - 1,337
Nitrate (mg/L)	ND	NA	NA	1.1	1.98	0.42 - 22.2
pH	5.4	7.9 - 8.0	8.0 – 8.3	8.29	7.76	7.03 - 8.18
Total organic carbon (mg/L)	0.1	NA	NA	3.04	0.17	0.42 - 2.02
Turbidity (ntu)	N/A	0.07 – 0.10	0.06 – 0.17	0.88	0.07	0.04 - 7.66
Bromide (mg/L)	ND	NA	NA	NA	NA	0.16 - 0.23
Hardness (mg/L as CaCO3)	ND	NA	NA	NA	NA	520 - 545
Iron (mg/L)	ND	NA	NA	NA	NA	0.006 - 1.47
Manganese (mg/L)	ND	NA	NA	NA	NA	0.007 - 0.052
MTBE	ND	NA	NA	NA	NA	<0.5 - 2.0

Range of water quality given if more than one grab sample was used in experiments
NA = not analyzed
ND = not detected

Super-Q©
* A pretreated blend of SPW and CRW. The 22 percent blend pretreated by ozone/biofiltration and the 44 percent blend pretreated by microfiltration, described by Mofidi et al.7
† From groundwater wells in Southern California
‡ below detection of 0.004/cm

Table 3. Test parameters for UV tests

Experiment SetStarting Contaminant Concentration	Approximate Matrix (type)	Water UV Dose Range* (mJ/cm^2)	Applied H_2O_2 Dose (mg/L)	Applied
Bromate	980, 45, and 9 µg/L	Lab. Water	0 to 550†	N/A
108 ± 16, 54 ± 2, 13 ± 1 µg/L		Lab. Water	0 to 3,100	N/A
87 and 11 µg/L	44% blend	0 to 3,100	N/A	
88 ± 1 µg/L	44% blend	0 to 4,000	4.1 ± 1.1	
NDMA	2,675 ± 300 ng/L	GW1	0 to 700	N/A
	Lab. Water	0 to 700	N/A	
	Lab. Water	0 to 700	1.0‡	
MTBE	1,269 ± 84 µg/L	GW2	0 to 47,000	N/A
	GW2	0 to 4,000	19‡	
	GW2	0 to 4,000	70‡	
MIB and	59 ± 13 ng/L	22% blend	0 to 10,000	N/A
Geosmin		22% blend	0 to 1,000	5.5 ± 0.5

N/A = not applied

* For actual UV doses, see data presented in figures

† Petri-dish experiments

‡ Single experiments

Table 4. Raw groundwater quality for ozone tests with MTBE

Parameter	High-MTBE Spiking Tests		Low-MTBE Spiking Tests	
	Ozone	PEROXONE	Ozone	PEROXONE
Temperature (°C)	17	17	17	17
Turbidity (ntu)	6.5	6.7	NA	NA
pH (unit)	7.73	7.96	NA	NA
Total hardness (mg/L as calcium carbonate)	521	513	487	526
Alkalinity (mg/L)	338	332	286	321
Conductivity (μmhos/cm)	1,208	1,200	1,157	1,183
Bromide (mg/L)	0.25	0.289	0.292	0.269
Iron (mg/L)	0.167	0.346	0.479	1.160
Manganese (mg/L)	0.042	0.107	0.015	0.063
Nitrate (mg/L) as Nitrogen *	0.02	0.016	0.047	0.044
UV light absorbance (1/cm)	0.010	0.016	0.016	0.014
TOC (mg/L)	0.639	0.977	1.33	1.18

NA—Not analyzed.
*Typical level of nitrate for this groundwater source is 0.42 to 22.2 mg/L of nitrate (for the tests with TBA spike)

Table 5. Energy requirements to provide 1-$\log_{10}$ reduction of water contaminants with ozone or UV light

Contaminant	Energy Requirement (kWh/1,000 gal)			
Ozone*	UV Light			
With H_2O_2	Without H_2O_2	With H_2O_2	Without H_2O_2	
Bromate	NA	NA	20	20
MTBE	0.5	1.0	10	130........
NDMA	1.3	--[†]	2	4
T&O Compounds	0.2[‡]	0.4[‡]	5	50.........
Perchlorate	NA	NA	--[†]	--[†].........

[*] 10 kWh/pound estimated energy usage for ozone generated by air-fed ozone generator

[†] 1-$\log_{10}$ reduction was not achieved with this treatment option

[‡] Results not from this study (Koch et al. 1992)

NA = not analyzed

N/F = technology not feasible

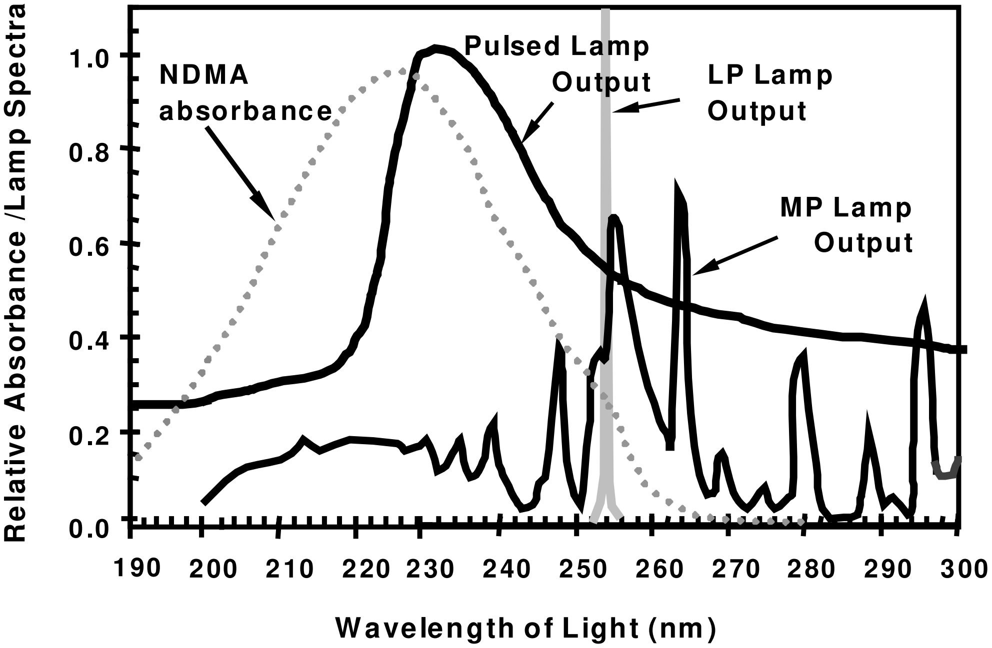


Figure 1. UV lamp output characteristics compared with NDMA light absorbance

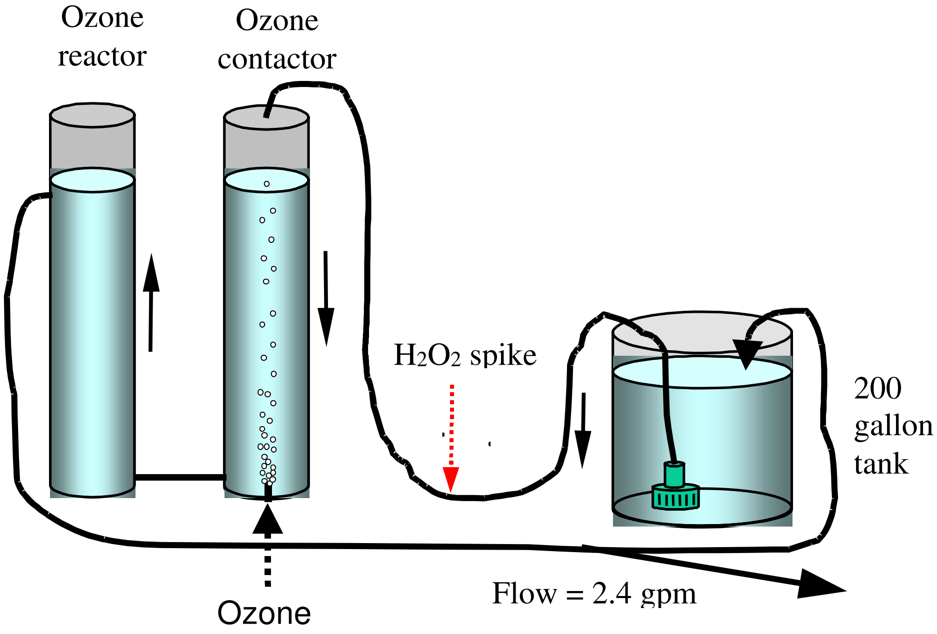


Figure 2. Schematic of ozonation setup for MTBE tests

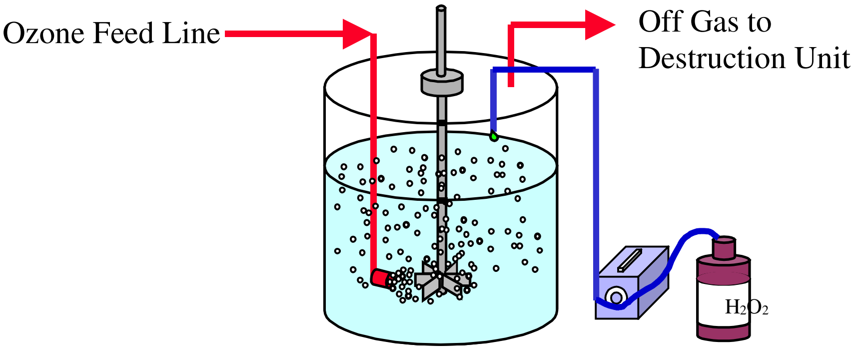


Figure 3. Schematic of the ozone and PEROXONE batch reactor

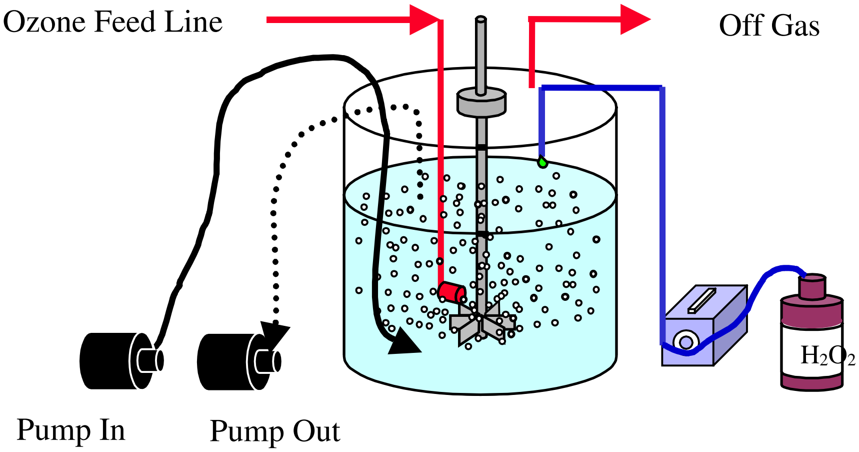


Figure 4. Schematic of the PEROXONE batch reactor (flow through setup)

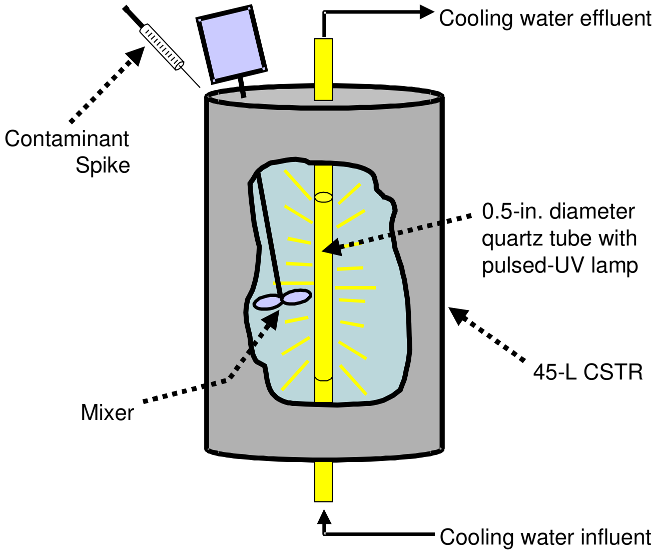


Figure 5. Bench-scale pulsed-UV reactor completely mixed batch reactor setup

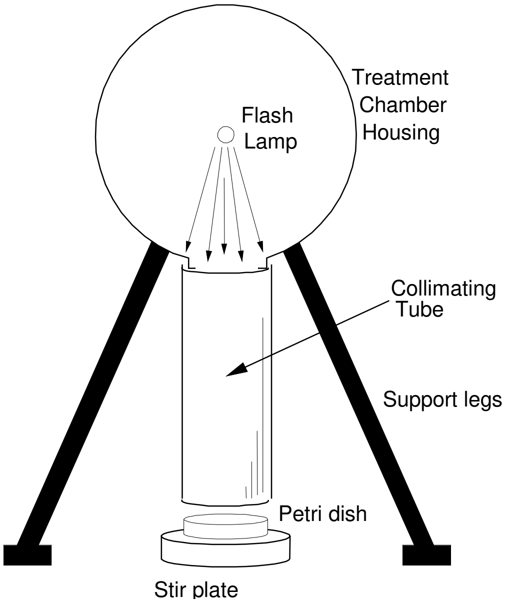


Figure 6. Pulsed-UV, collimated-beam setup for preliminary bromate experiments

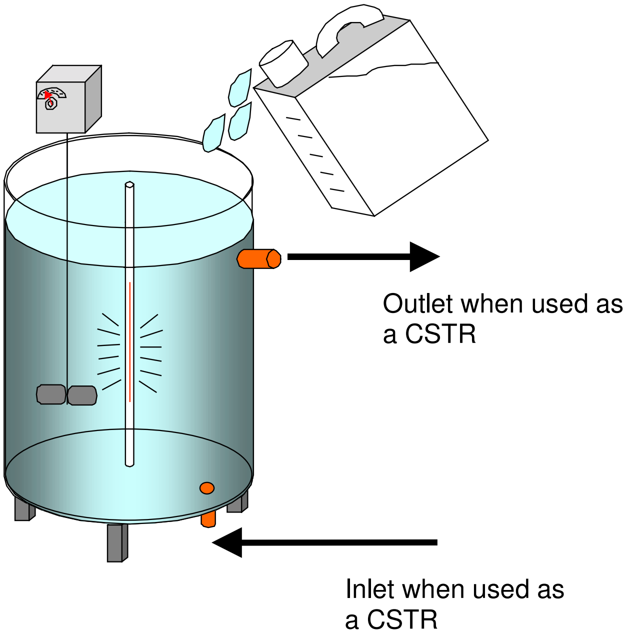


Figure 7. Schematic of the pulsed-UV, continuously stirred tank reactor setup

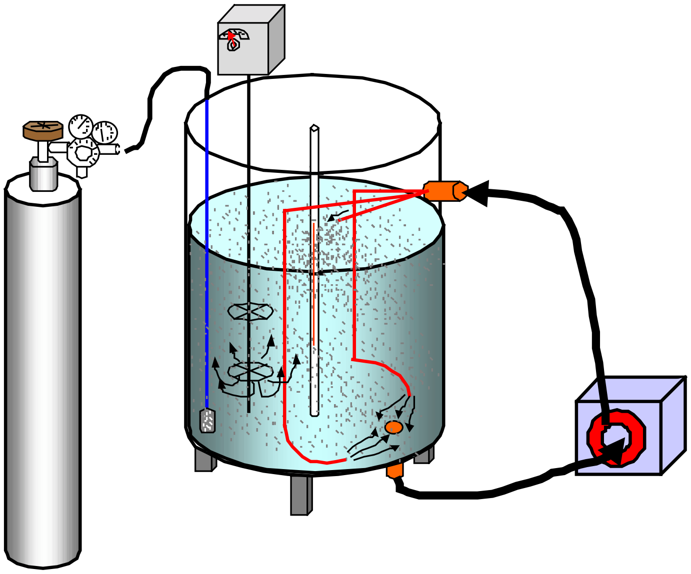


Figure 8. Schematic of the batch pulsed-UV reactor with modified settings

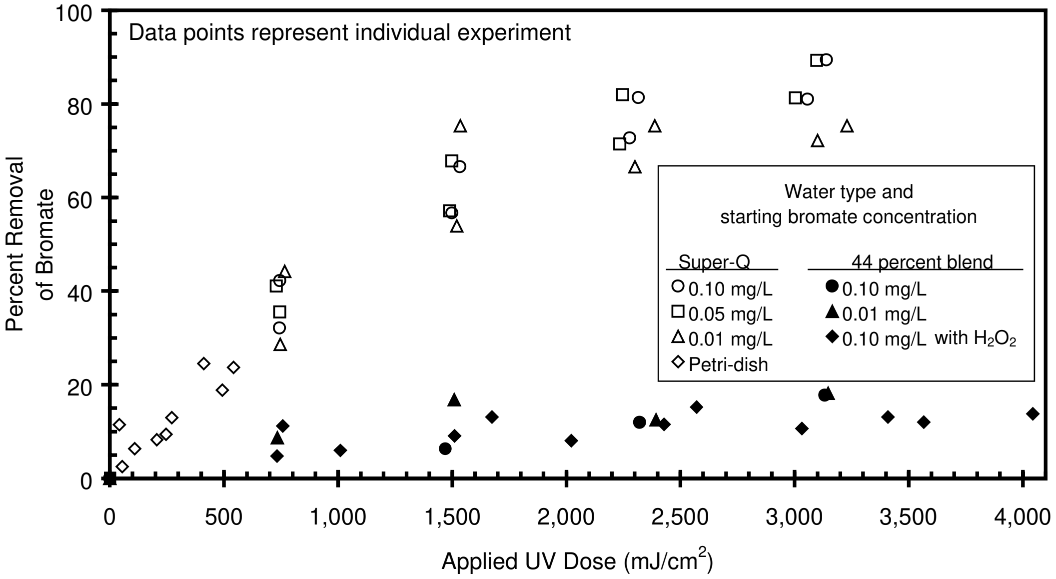


Figure 9. Effect of UV and UV/H_2O_2 treatment on two waters containing bromate (4.1 mg/L H_2O_2 dose)

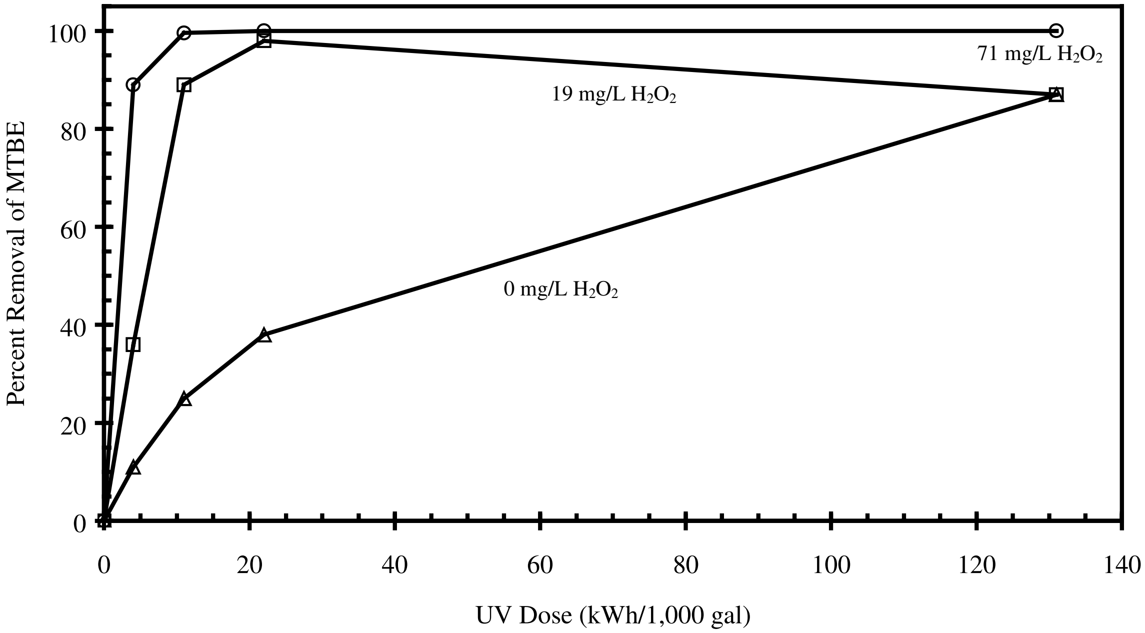


Figure 10. Effect of H_2O_2 on MTBE percent removal

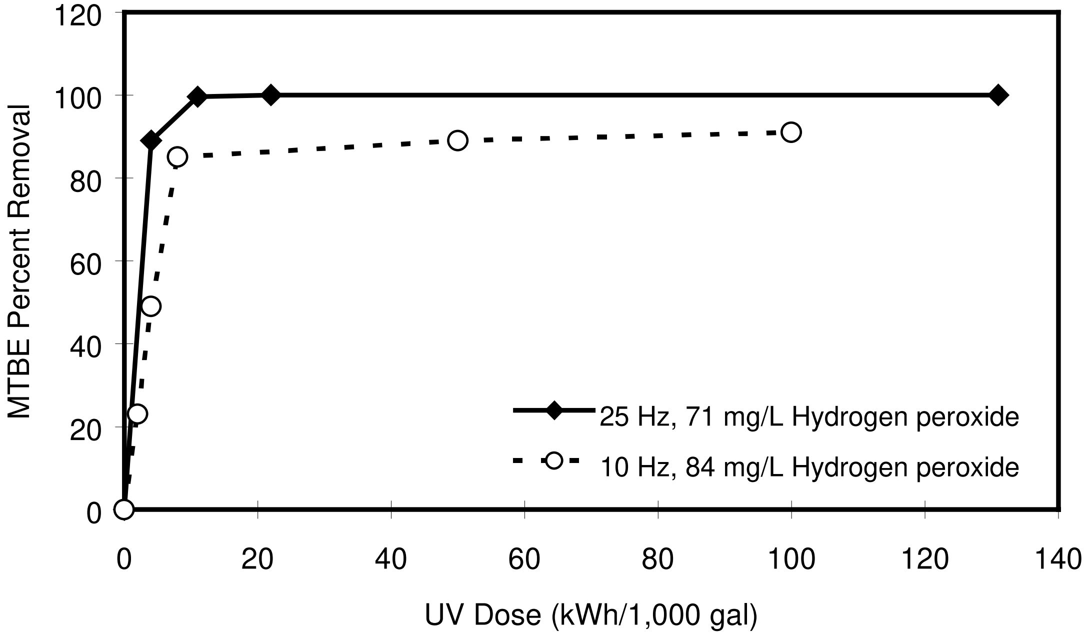


Figure 11. Effect of UV dose (UV frequency) on MTBE percent removal

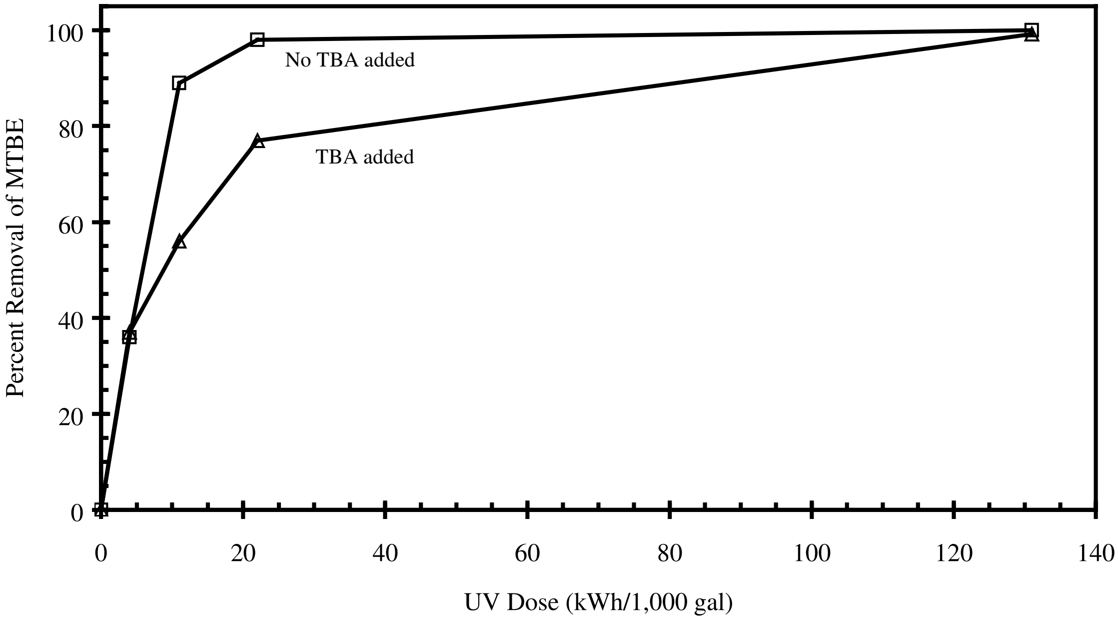
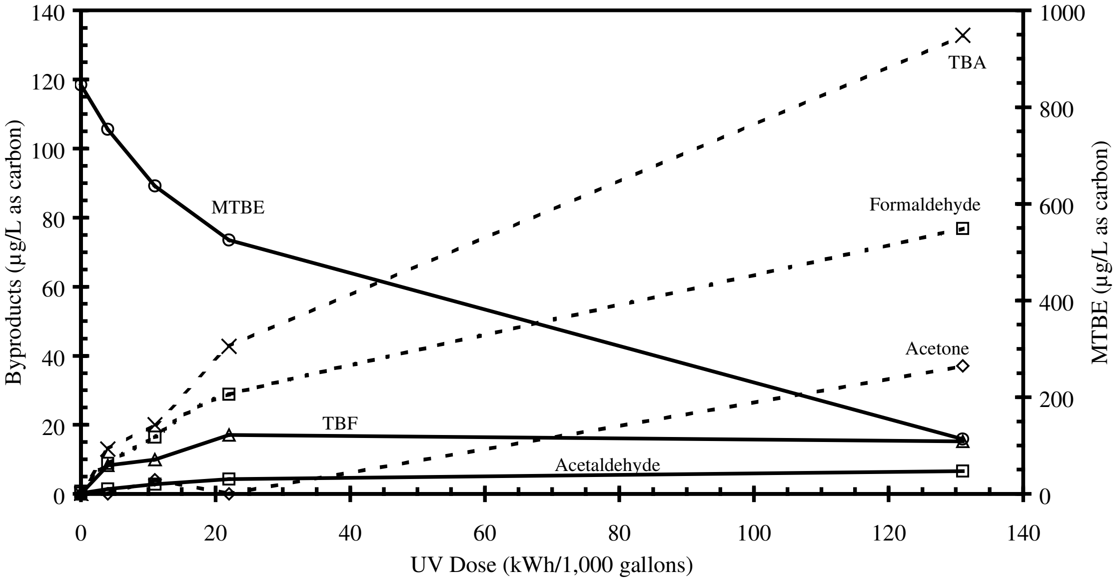
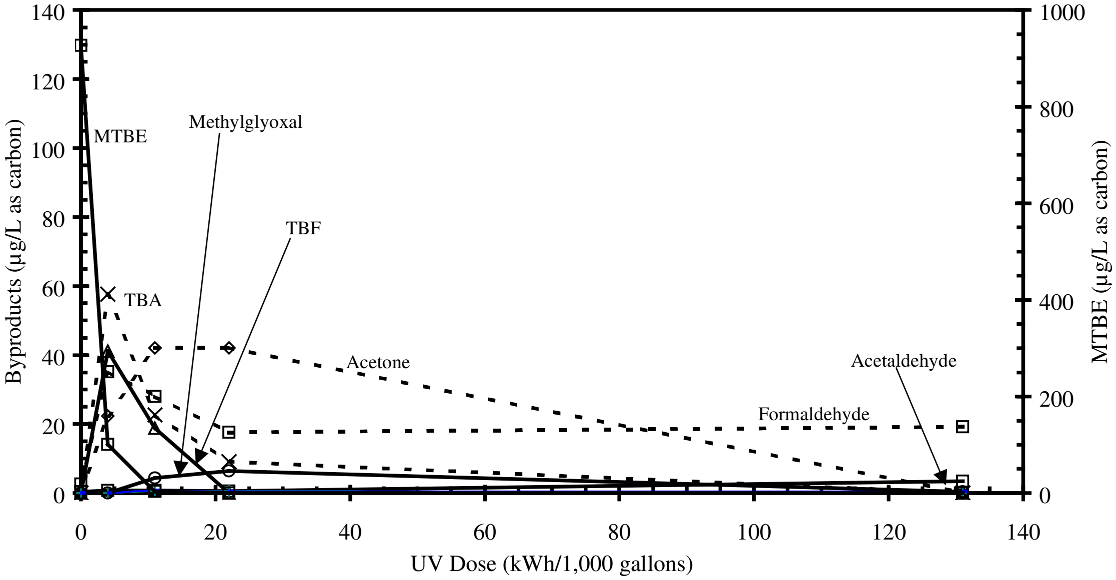


Figure 12. Effect of initial TBA spike on MTBE reduction
(25 Hz)

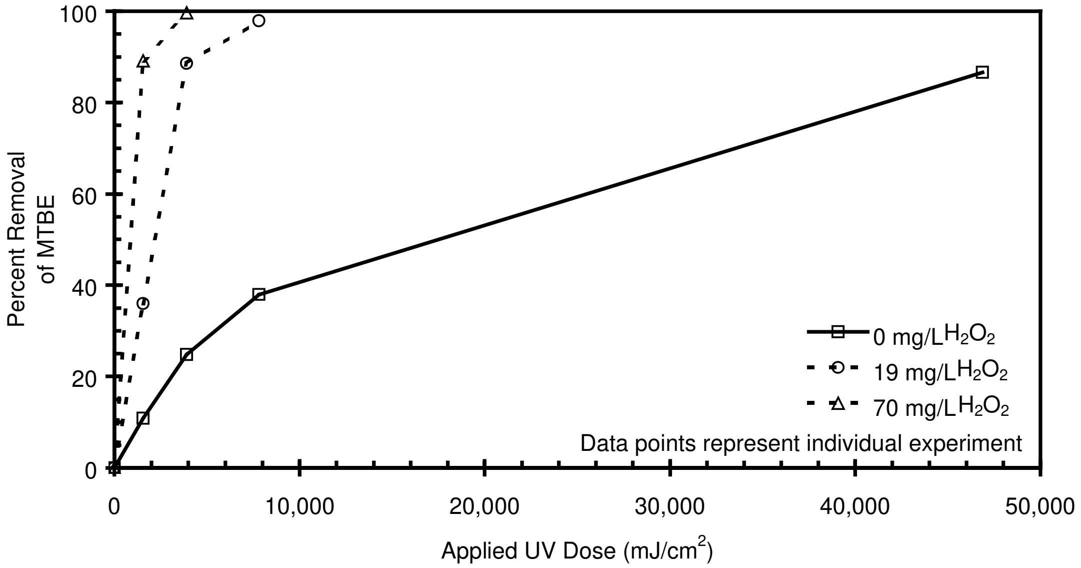


(a) UV only



(b) UV and 71 mg/L H_2O_2

Figure 13. Effect of H_2O_2 addition on MTBE reduction and by-product



formation

Figure 14. Effect of UV and UV/H_2O_2 on MTBE

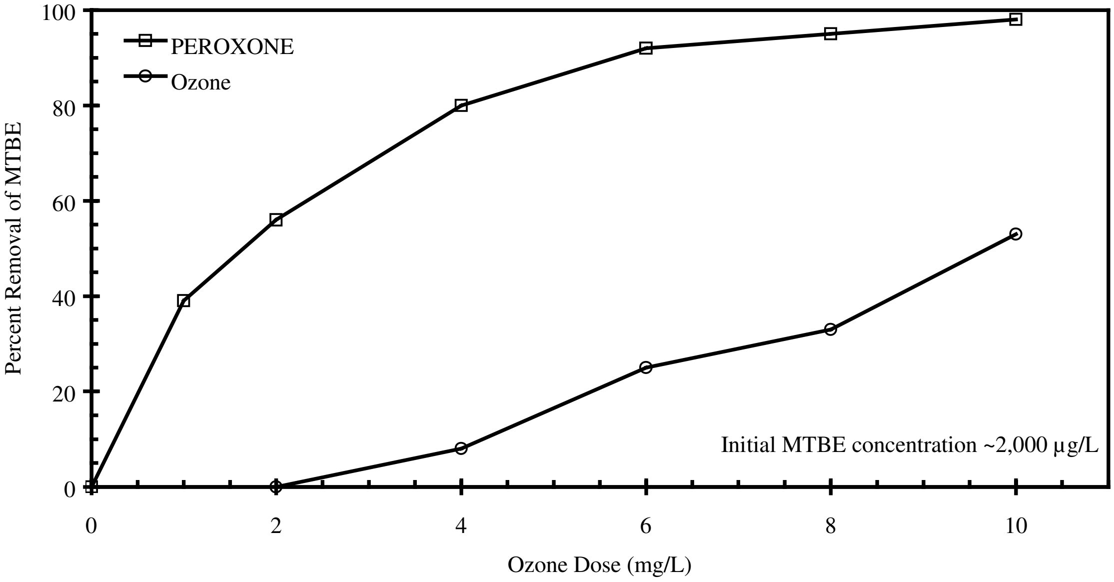


Figure 15. Effect of ozone and PEROXONE on MTBE removal (initial MTBE concentration = 2,000 µg/L)

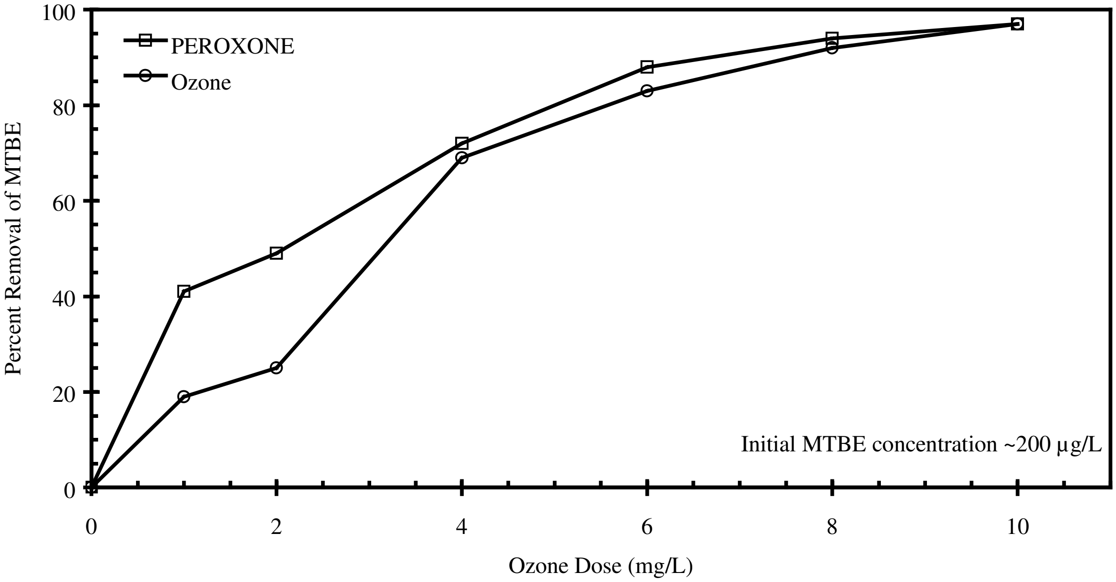


Figure 16. Effect of ozone and PEROXONE on MTBE removal (initial MTBE concentration = 200 µg/L)

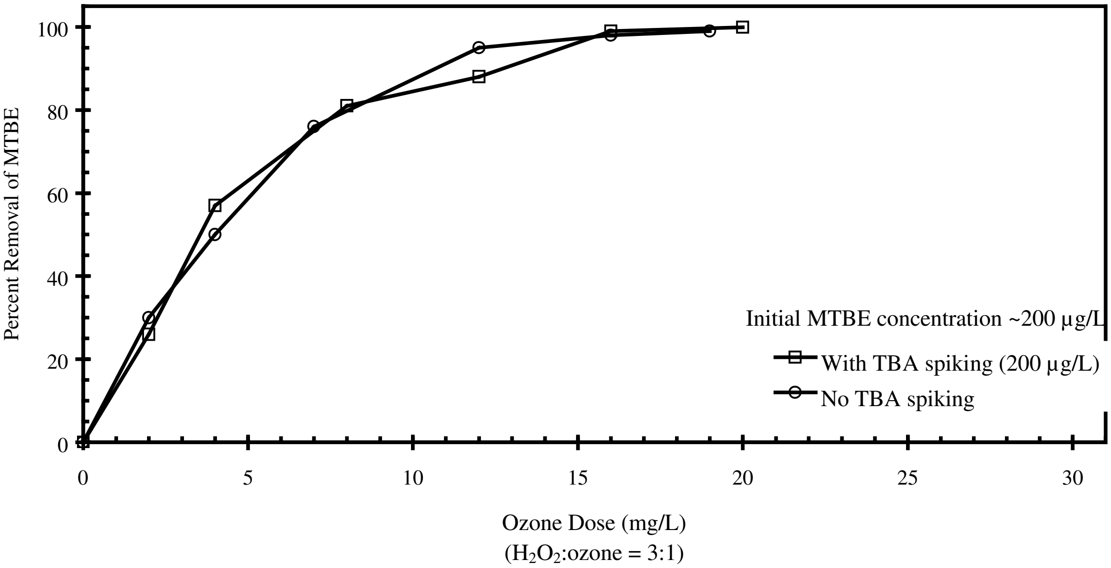


Figure 17. Effect of TBA spiking on MTBE removal (initial MTBE concentration = 200 µg/L)

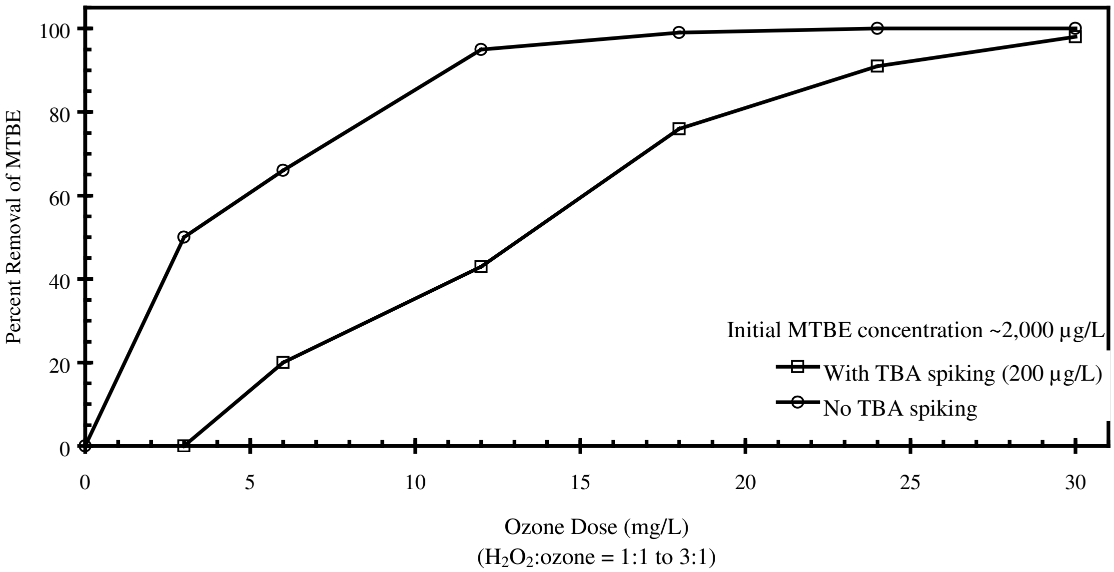


Figure 18. Effect of TBA spiking on MTBE removal (initial MTBE concentration = 2,000 µg/L)

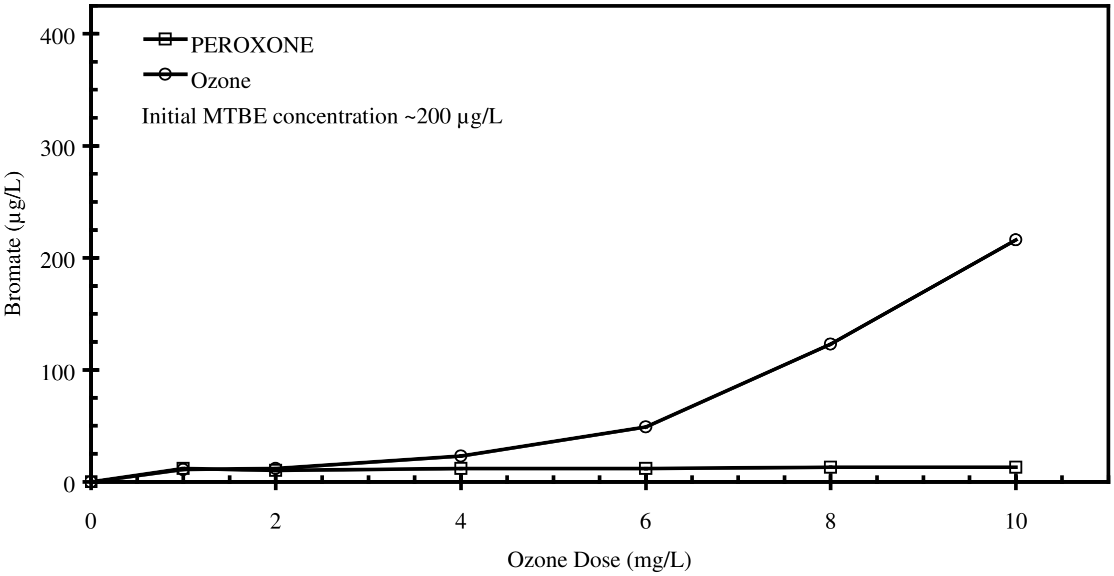


Figure 19. Effect of ozone and PEROXONE on bromate formation (initial MTBE concentration = 200 µg/L)

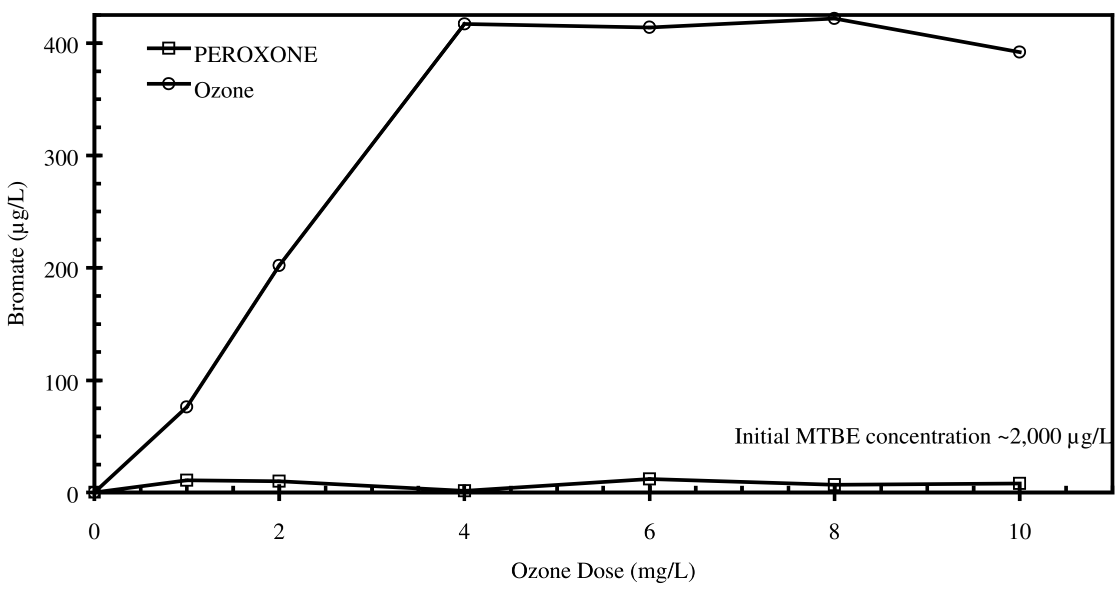


Figure 20. Effect of ozone and PEROXONE on bromate formation (initial MTBE concentration = 2,000 µg/L)

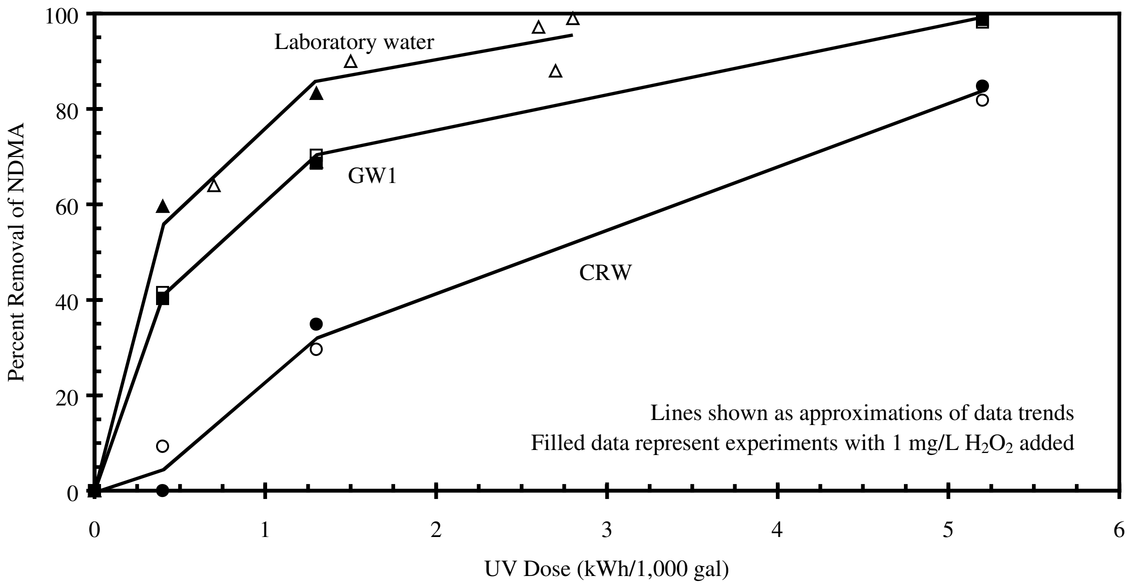


Figure 21. Effect of water type on UV treatment of NDMA

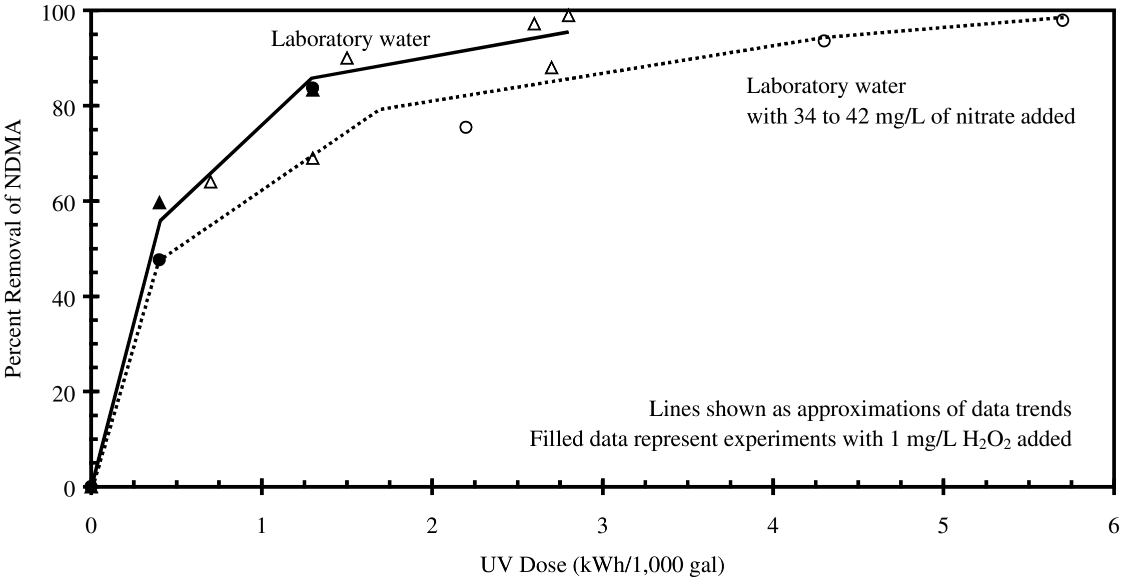


Figure 22. Effect of nitrate on UV treatment of NDMA

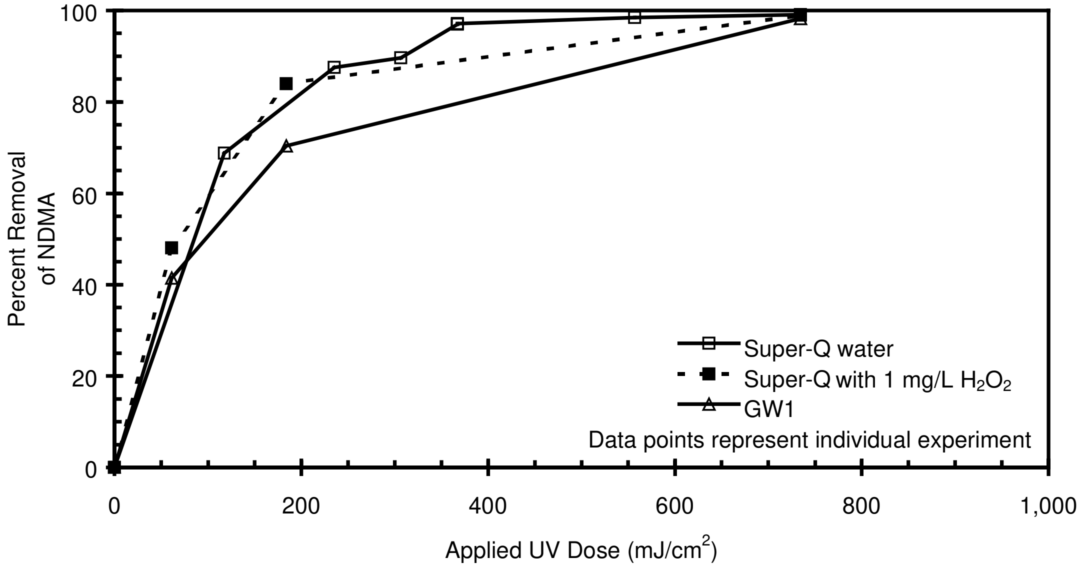


Figure 23. Effect of nitrate on NDMA reduction by UV light in laboratory water

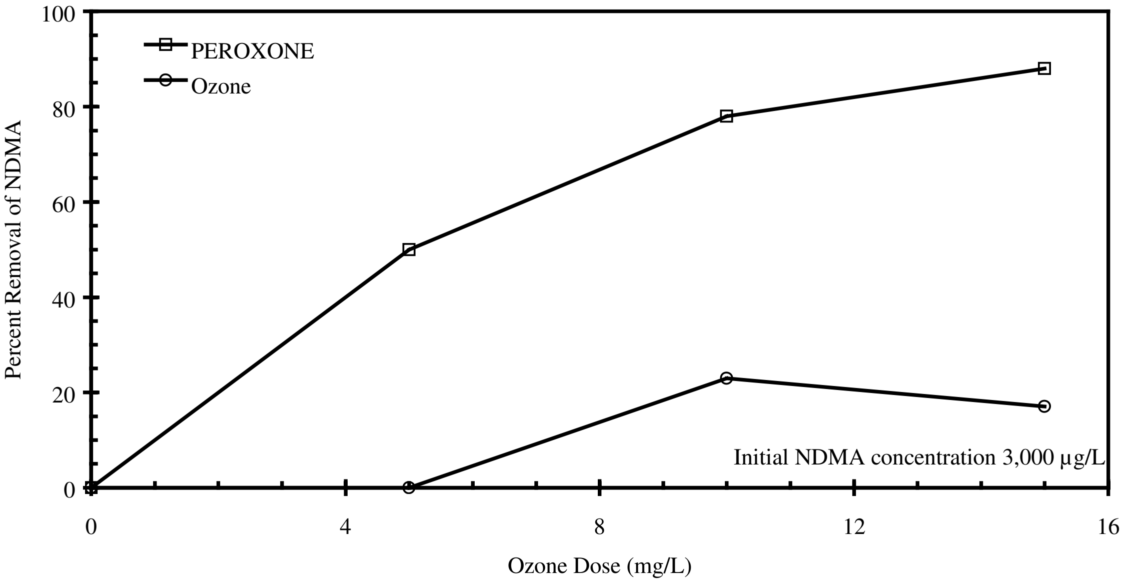


Figure 24. Effect of Ozone and PEROXONE on NDMA reduction

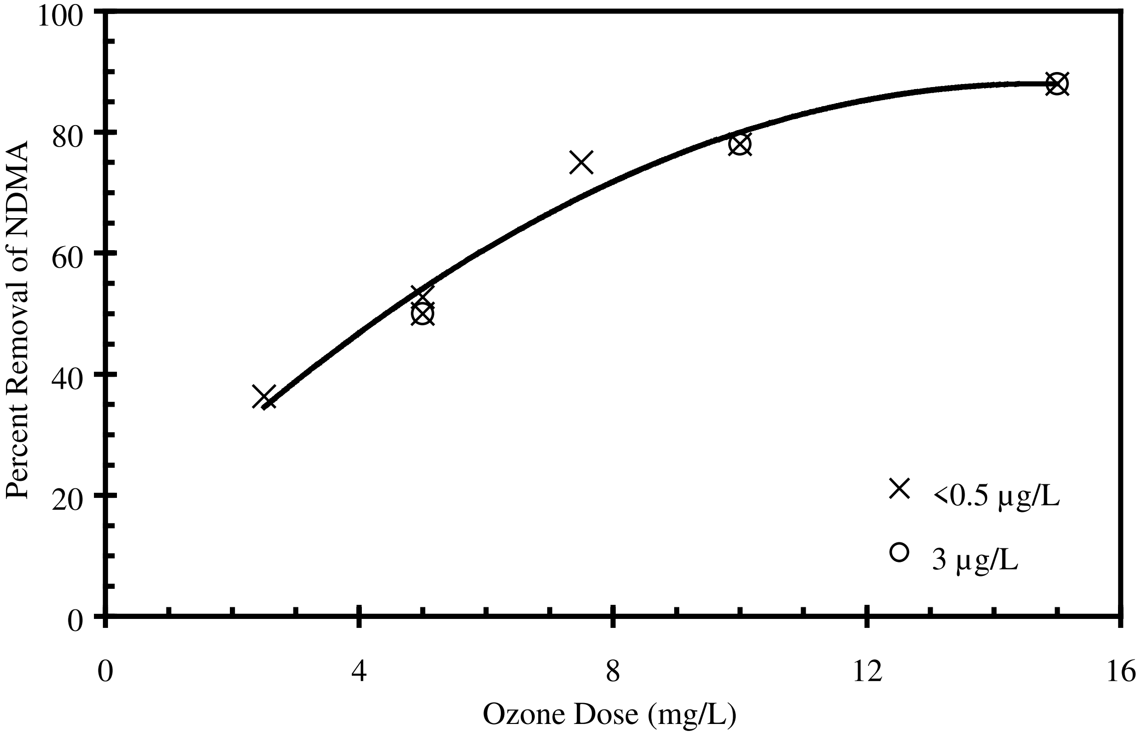


Figure 25. Effect of initial NDMA concentration on treatment by ozone

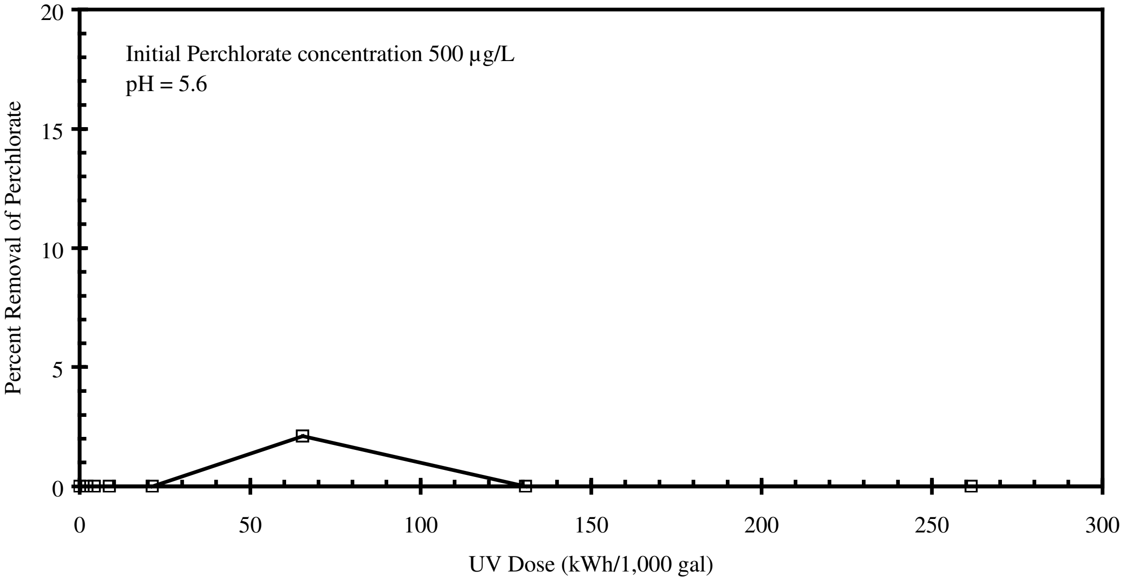


Figure 26. Reduction of perchlorate in laboratory water (25 Hz)

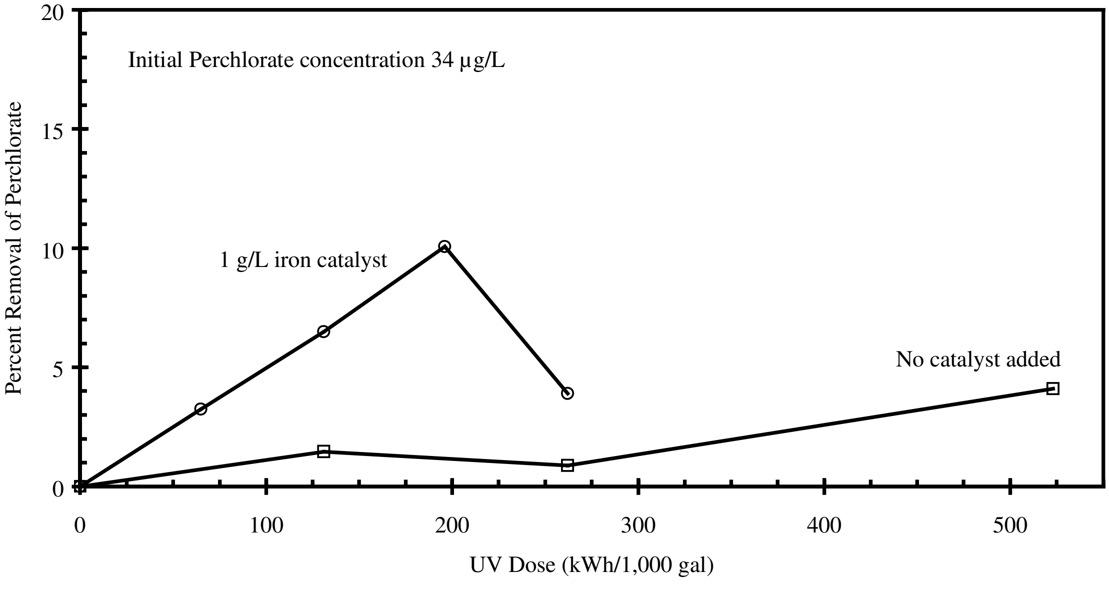


Figure 27. Effect of catalyst addition on perchlorate reduction
(laboratory water, ambient pH)

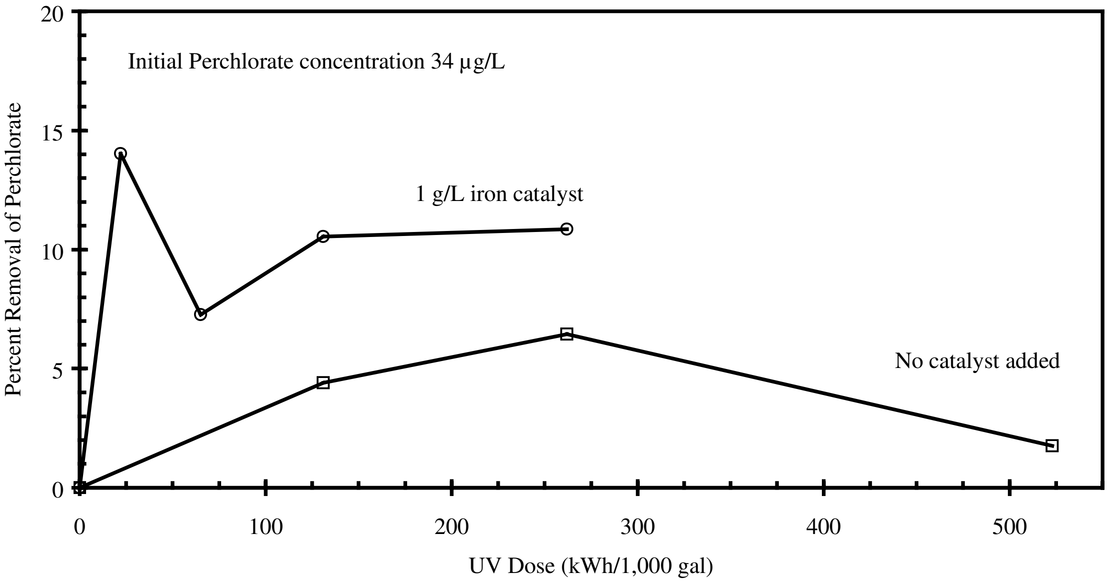


Figure 28. Effect of catalyst addition on perchlorate reduction (laboratory water, pH = 3)

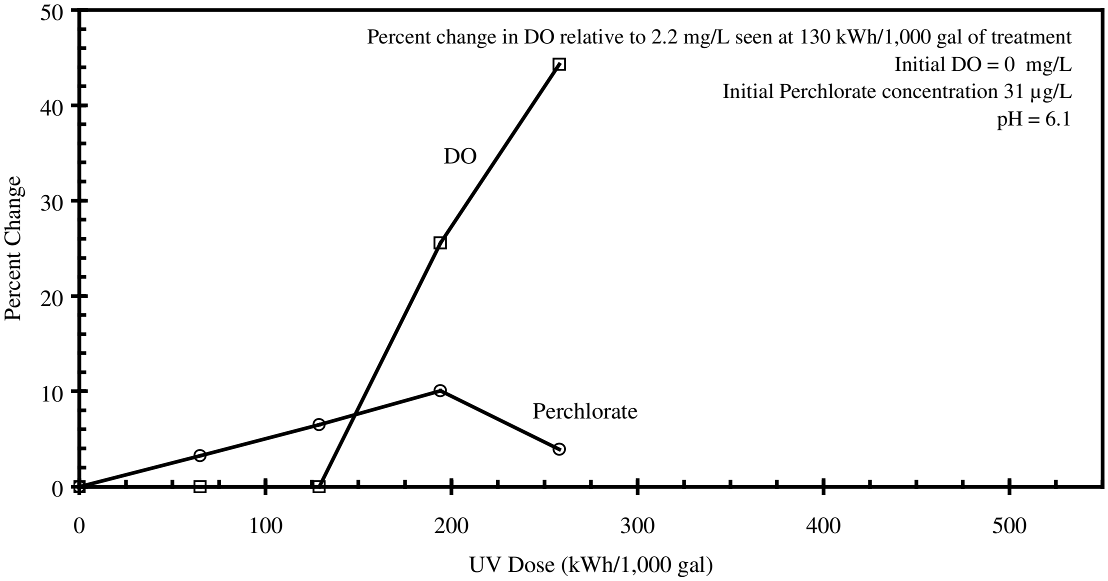


Figure 29. Perchlorate and dissolved oxygen levels during anaerobic treatment

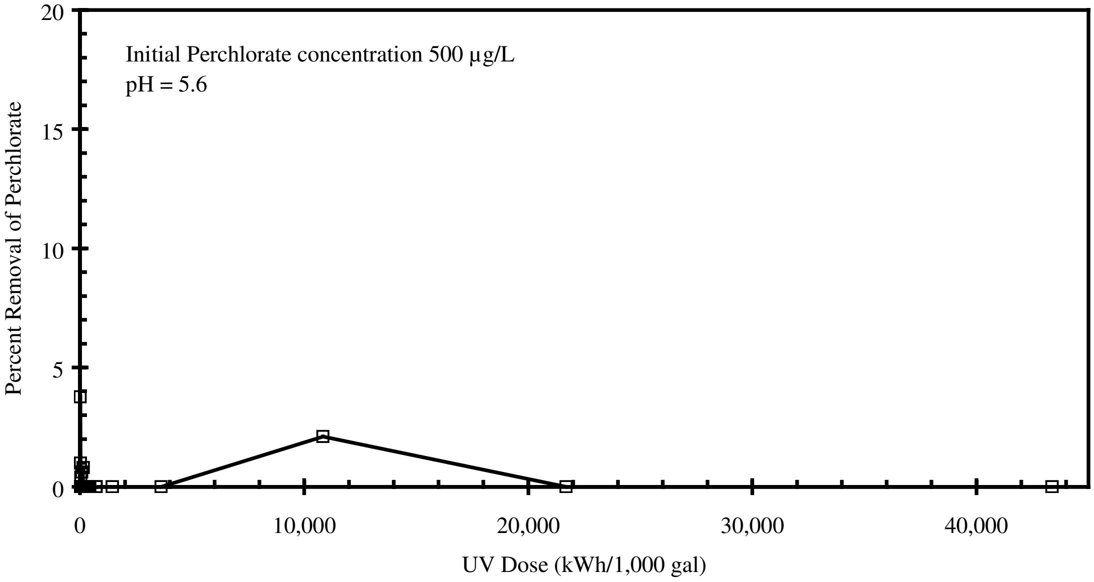


Figure 30. Reduction of perchlorate in laboratory water

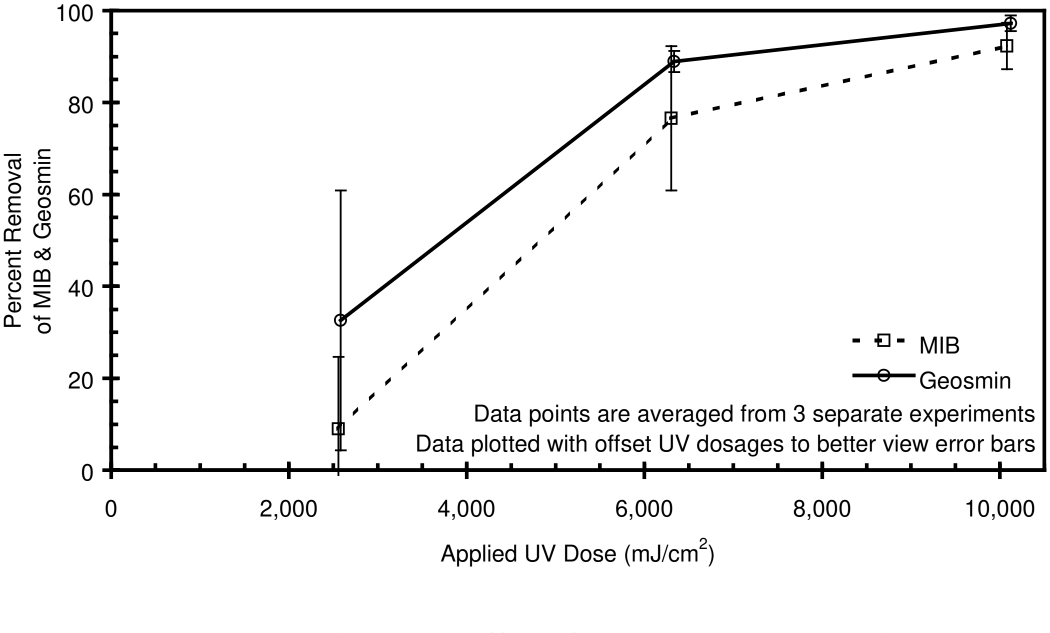


Figure 31. Effect of UV on MIB and geosmin

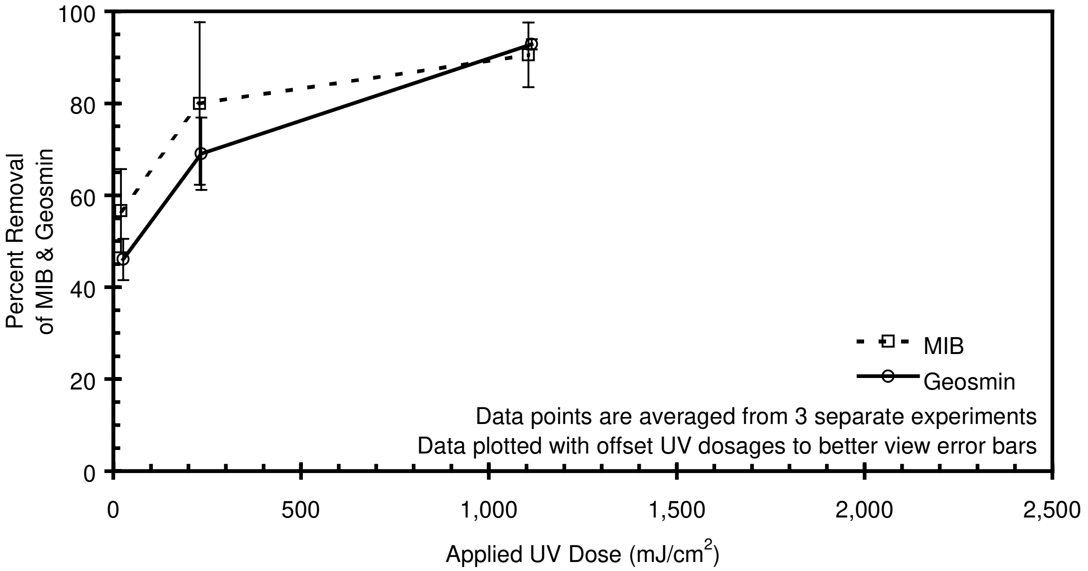
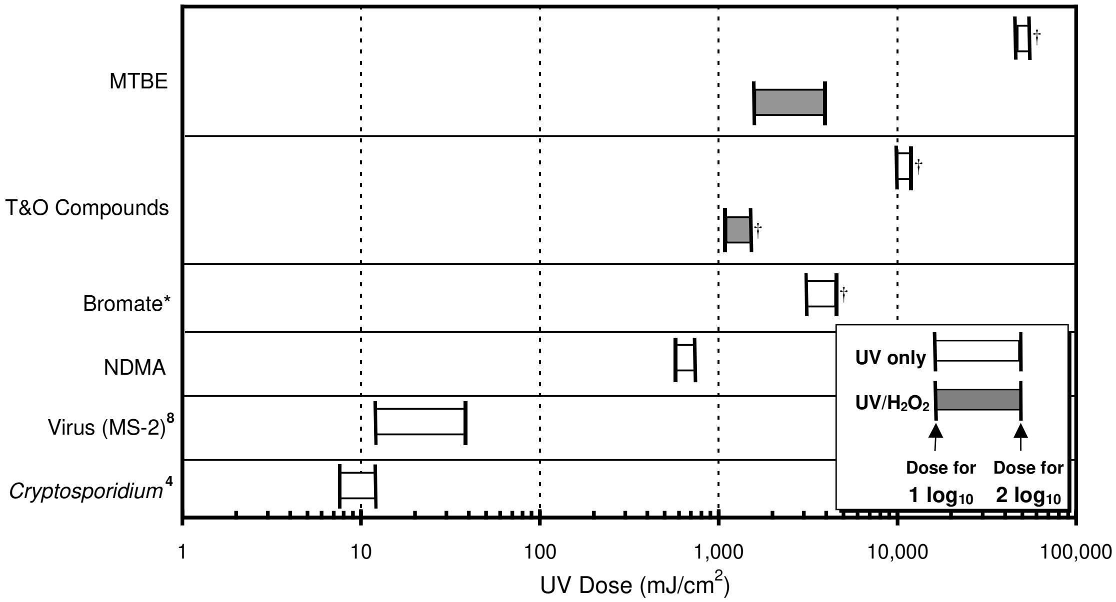


Figure 32. Effect of UV/H_2O_2 on MIB and geosmin (5.5 mg/L H_2O_2)



* Bromate reduction in laboratory water, all other data for natural waters

† 2 $\log_{10}$ reduction estimated based on data from this study

Figure 33. UV dose range for 1 to 2 $\log_{10}$ reduction of water contaminants (perchlorate not included)