Installation Restoration Research Program

A Laboratory Evaluation of the Feasibility of Chemical Oxidation Processes for Treatment of Contaminated Groundwaters

by   Mark E. Zappi, Fred Ragan, Danea Guimbellot,
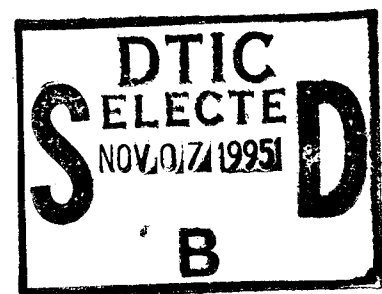Keith Martin, Norman R. Francingues, Steven D. Harvey, WES

James D. Smith, David Strang, Rocky Mountain Arsenal

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A Laboratory Evaluation of the Feasibility of Chemical Oxidation Processes for Treatment of Contaminated Groundwaters

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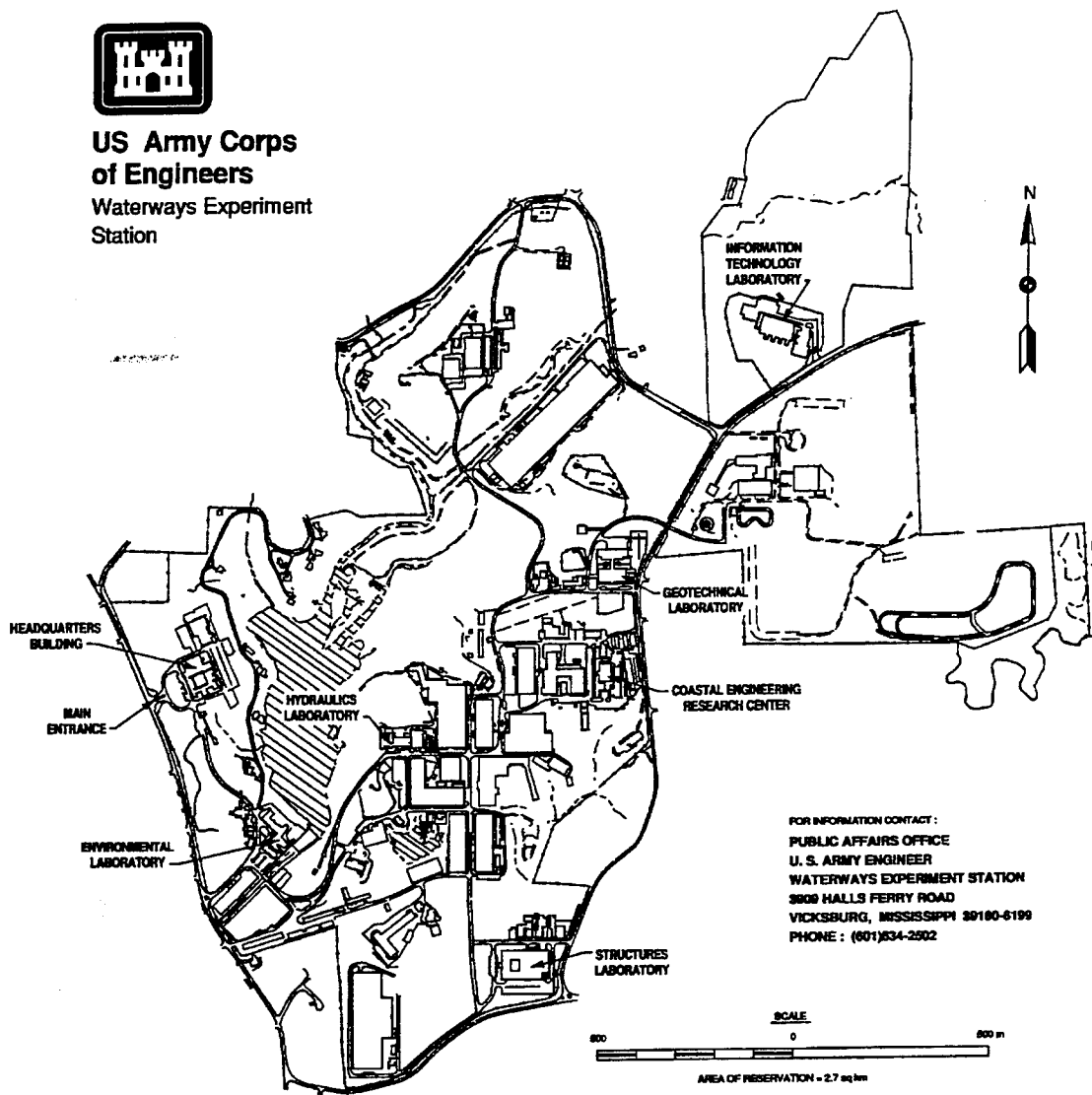   Ebasco Services, Inc.
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Final report

**US Army Corps
of Engineers**
Waterways Experiment
Station

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INFORMATION
TECHNOLOGY
LABORATORY

GEOTECHNICAL
LABORATORY

HEADQUARTERS
BUILDING

MAIN
ENTRANCE

HYDRAULICS
LABORATORY

COASTAL ENGINEERING
RESEARCH CENTER

ENVIRONMENTAL
LABORATORY

STRUCTURES
LABORATORY

SCALE

0

600 m

AREA OF RESERVATION = 2.7 sq km

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Preface

This report should be cited as follows:

x

1 Introduction

Background

The Rocky Mountain Arsenal (RMA) occupies more than 17,000 acres in Adams County, Colorado near Denver, Colorado. The property occupied by the RMA was obtained by the United States government in 1942. Throughout World War II, RMA manufactured and assembled chemical intermediate and toxic end-products and incendiary munitions. In addition to these military operations, portions of the arsenal have been leased by Shell Chemical Company for the manufacture of industrial chemicals including pesticides and herbicides. As a result of these production activities, the migration of contaminants into the environment, in particular, portions of the shallow alluvial aquifer, has occurred.

The Office of Program Manager of Rocky Mountain Arsenal (PMRMA) is currently performing a Feasibility Study (FS) on the management and treatment of contaminated groundwaters at RMA. Several groundwater management and treatment options are currently under evaluation.

Chemical oxidation processes are one of several candidate treatment technologies under consideration by the RMA FS Team. In support of the FS activities, the U.S. Army Engineer Waterways Experiment Station (WES) performed a bench scale study as a means of evaluating chemical oxidation processes for treatment of two RMA groundwaters. The results of this study will be used by the RMA FS Team to determine the technical and economical feasibility of oxidation processes for treatment of RMA groundwaters. This report presents the results of the WES study on chemical oxidation processes.

Chemical Oxidation

Chemical oxidation is a treatment technology that uses powerful chemical oxidizers to destroy organic contaminants. Typical oxidizers used in chemical oxidation processes include ozone, hydrogen peroxide, chlorine, and potassium permanganate. The chemical reaction products are usually simple organic compounds, such as carboxylic acids, and/or inorganic compounds,

such as carbon dioxide, water, and simple inorganic complexes (e.g., chloride salts, in the case of chemical oxidation treatment of chlorinated solvents).

This technology has historically been used as a treatment technology for municipal drinking water (Metcalf and Eddy Inc. 1991). Chlorination has been used almost extensively in the United States for disinfection of municipal drinking water (James Montgomery Engineers Inc. 1985). Ozone has been used quite extensively for municipal water treatment in several European communities (Messenchein 1982). Appendix A presents a description of a detailed literature review performed concerning application of chemical oxidation processes for treating contaminated waters.

Ozonation and peroxone (the combined use of ozone and hydrogen peroxide) have been used in drinking water treatment for removal of chemical compounds which impart taste or are of concern due to possible carcinogenic properties. Examples of such chemicals include geosmin (American Water Works Association (AWWA) 1991), pesticides (Dore et al. 1992), and trichloroethylene (Glaze et al. 1988).

For groundwater or industrial wastewater treatment, chemical oxidation has been used primarily in conjunction with ultraviolet (UV) photolysis. Hydrogen peroxide (H_2O_2) and ozone (O_3) have been used almost extensively in conjunction with UV photolysis with respect to groundwater remediation projects. Mayer et al. (1990) concluded that chemical oxidation processes are very cost competitive with both air stripping and activated carbon adsorption for treating volatile organic compound (VOCs) in contaminated groundwaters.

Chemical oxidation processes that result in the generation of the hydroxyl radical (OH·) have been referred to as advanced oxidation processes (AOPs) by the American Water Works Association (1991). Commercial application of AOPs for contaminated groundwater treatment in the United States has traditionally involved UV irradiation of hydrogen peroxide, ozone, or a combination of both.

The addition of UV light to an aqueous solution of hydrogen peroxide or ozone results in the generation of hydroxyl radicals. The hydroxyl radical is a much more powerful oxidizer than either hydrogen peroxide or ozone (Sundstrom et al. 1986). Figure 1 presents the absorbance of UV irradiation by both hydrogen peroxide and ozone. From Figure 1, ozone absorption of UV irradiation occurs primarily at 254 nm (2,540 angstrom units), while hydrogen peroxide absorbs UV irradiation at wavelengths of approximately 230 nm and lower. Low pressure mercury vapor UV lamps (LP-UV), commonly used in water treatment for disinfection, emit the vast majority of their radiation spectrum at the 253.9 nm wavelength (Figure 2). Medium pressure mercury vapor UV lamps (MP-UV) emit the majority of their radiation spectra over a wide band from approximately 190 to 600 nm, with a large portion of energy centered around the 200-300 nm range (Table 1 and Figure 3).
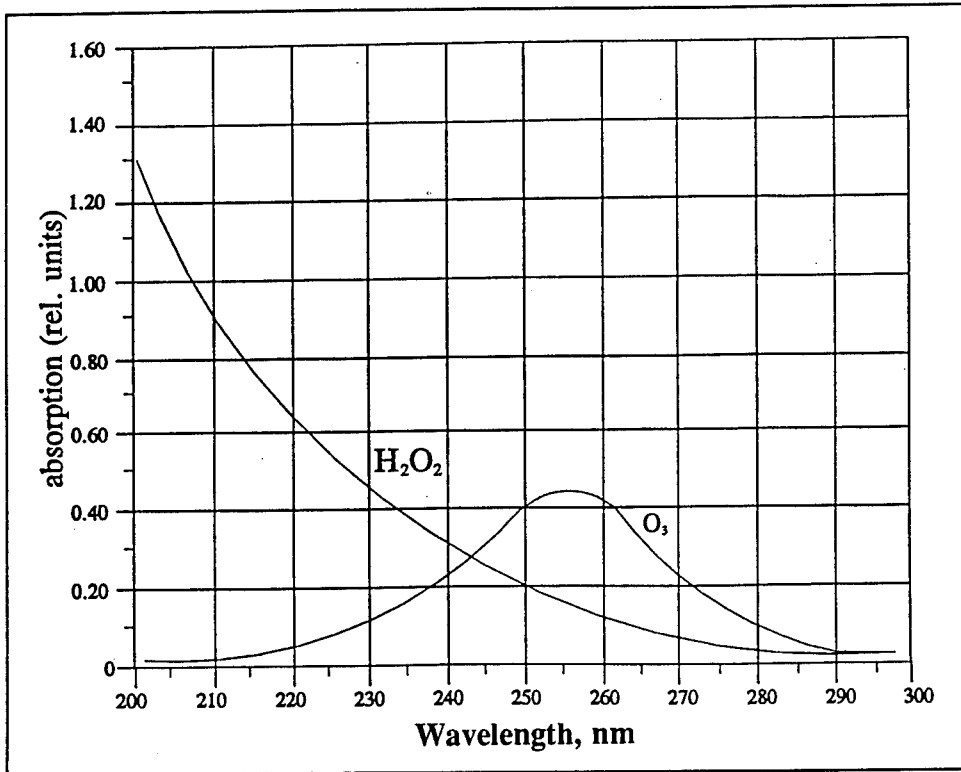
Figure 1.   Adsorption spectra of H_2O_2 and O_3
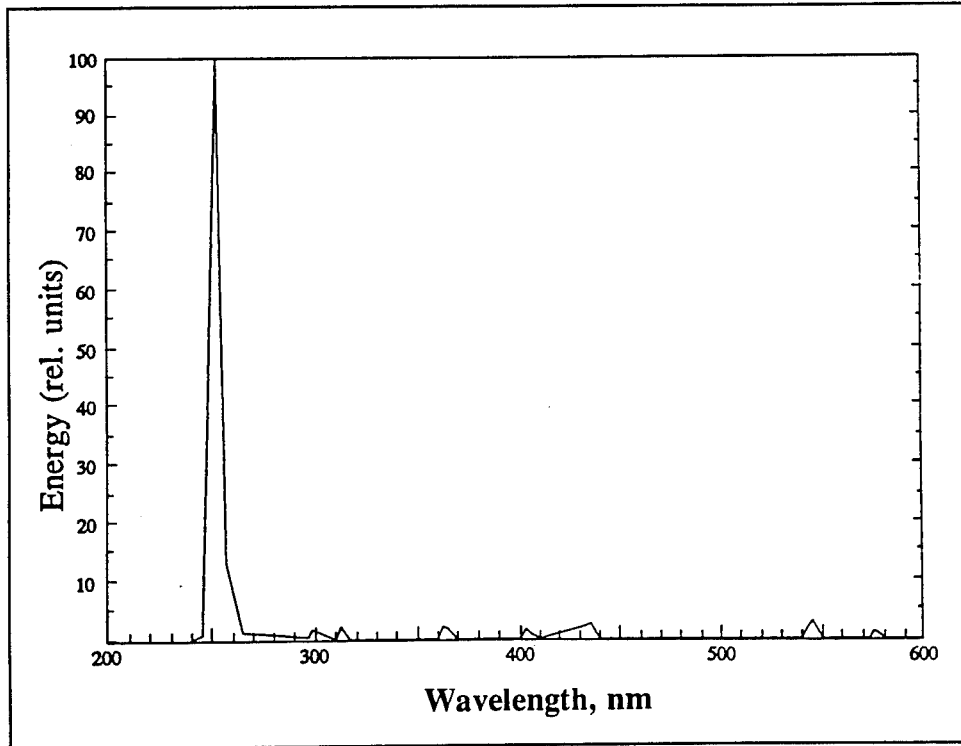
Figure 2.   Spectral energy distribution, Hg low pressure lamp

Table 1
Electrical Output of MP-UV Lamp Within the 222-302 nm Range

Electrical Output, W	Wavelength, nm
7.2	302.5
4.3	296.7
1.6	289.4
2.4	280.4
0.7	275.3
1.0	270.0
4.0	265.2
1.5	257.1
5.8	253.7
2.3	248.2
1.9	240.0
2.3	238.0
2.3	236.0
1.5	232.0
3.7	222.4

Note: Total energy emitted within this UV bandwidth = 42.5 W.
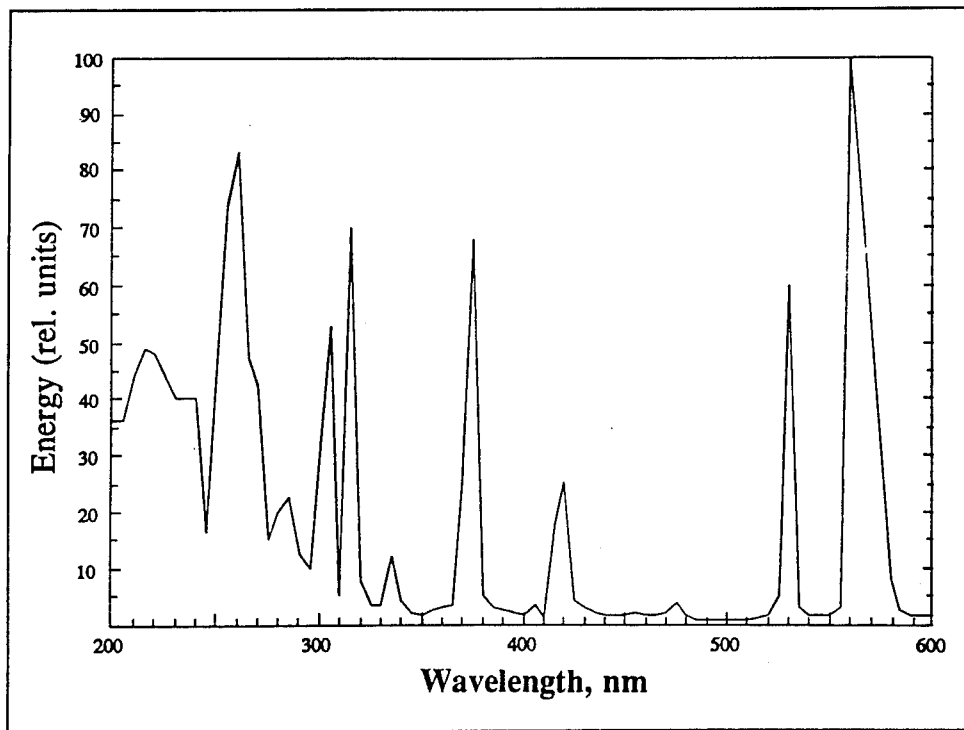
Figure 3.   Spectral energy distribution, Hg medium pressure lamp

Chemical oxidation systems utilizing ozone are better served using LP-UV lamps. These lamps are more energy efficient than MP-UV lamps and produce the exact UV spectrum that is readily utilizable by ozone for production of OH· radicals. These systems typically do not result in the destruction of the organic contaminants via UV photolysis (destruction of the compound due to absorbance of UV photons). Destruction of the organic contaminants in LP-UV/ozone based systems is due primarily to hydroxyl radical oxidation. Many organic compounds absorb at lower UV wavelengths (i.e., < 230 nm), making the direct absorbance of UV energy emitted from a LP-UV lamp of little benefit toward direct photolysis.

MP-UV lamps are much more energy intensive than LP-UV lamps. Much of the electrical energy utilized by MP-UV lamps is wasted as heat radiation. However, UV based chemical oxidation systems using hydrogen peroxide are better served with MP-UV lamps that emit more UV energy in the absorbance band of hydrogen peroxide, thereby resulting in optimum OH· radical production. Although MP-UV lamps are more energy intensive, some benefit may be derived by using a MP-UV lamp for treatment of some organic contaminants due to direct UV photolysis. However, in most UV based chemical oxidation systems, it is usually more advantageous to convert the parent chemical oxidizers (O_3 and H_2O_2) into hydroxyl radicals with the UV energy unless the rate of contaminant degradation under direct photolysis is rapid. An optimal UV/chemical oxidizer treatment system should be selected and designed on the basis of the photochemical properties of the contaminant(s) and the physical, chemical, and optical properties of the influent (these properties of water influents are often collectively referred to as water matrix).

The stoichiometric mechanism responsible for generation of hydroxyl radicals in UV/hydrogen peroxide systems as proposed by Sundstrom et al. (1986) is presented below:

$$H_2O_2 \xrightarrow{\ h\nu\ } 2OH$$
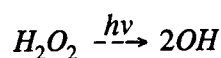
Oxidation of liquid phase contaminants using UV irradiation and hydrogen peroxide is commonly referred to as UV/peroxidation. This technology has been successfully used for treatment of several contaminated waters containing a variety of organic contaminants (Zappi et al. 1990a, Froelich 1992, Zappi, Fleming, and Cullinane 1992a).

Hager, Lovern, and Giggy (1987) present several case studies where a commercial UV/hydrogen peroxide based system successfully treated a variety of contaminants. They suggest the costs for treatment would range from $1.37 to $58.51 per 1,000 gal treated.

Peyton, Michelle, and Peyton (1987) presented a mechanism for $OH·$ generation during UV irradiation of ozone. This mechanism is presented below:

$$O_3 \;+\; H_2O \overset{h\nu}{\rightarrow} O_2 \;+\; H_2O_2$$

$$H_2O_2 \;+\; H_2O \longleftrightarrow H_3O^+ \;+\; HO_2^-$$

$$O_3 \;+\; HO_2 \longleftrightarrow O_2 \;+\; {}^{\cdot}O_2^- \;+\; {}^{\cdot}OH$$

$$O_3 \;+\; {}^{\cdot}O_2 \;+\; H_2O \rightarrow 2O_2 \;+\; {}^-OH \;+\; {}^{\cdot}OH$$
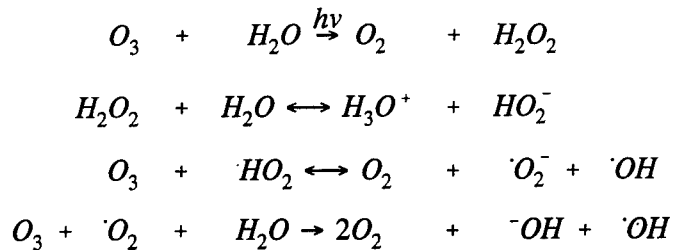
Barich and Zeff (1989) list a variety of contaminated groundwaters and wastewaters that were successfully treated using a commercially available UV/ozone system. They indicate that treatment costs range from \$0.15 to \$86.00 per 1,000 gal treated.

Peroxone is an AOP that utilizes the combination of hydrogen peroxide and ozone to form the hydroxyl radical without the addition of UV light. The results reported by Glaze and Kang (1988) indicate that peroxone could effectively remove chlorinated solvents from the groundwater. Since peroxone does not require the addition of high concentrations of chemical oxidizers and UV light, it is estimated that reductions in treatment costs of 50 percent or higher may be realized.

Langlais, Reckhow, and Brink (1991) proposed the following mechanism for the formation of hydroxyl radicals during peroxone treatment:

$$H_2O_2 \;+\; H_2O \longleftrightarrow HO_2^- \;+\; H_3O^+$$

$$O_3 \;+\; HO_2^- \rightarrow OH \;+\; O_2^- \;+\; O_2$$

$$O_2^- \;+\; H^+ \longleftrightarrow HO_2$$

$$O_3 \;+\; O_2^- \rightarrow O_3^- \;+\; O_2$$

$$O_3 \;+\; H^+ \longleftrightarrow HO_3$$

$$HO_3 \rightarrow OH^{\cdot} \;+\; O_2$$
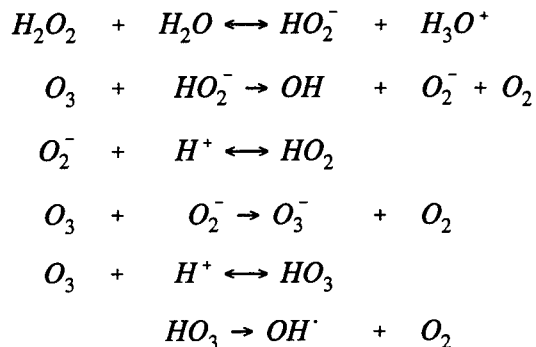
Some water utilities in France are currently using peroxone to treat millions of gallons per day of pesticide laced groundwater for use as drinking water (Dore et al. 1992). The French researchers claim that treatment costs are on the order of \$0.05 per 1,000 gal treated. Mayer et al. (1990) evaluated air stripping, activated carbon, and peroxone for treatment of chlorinated solvent contaminated groundwater. Cost estimates for each process were \$0.19, \$0.43, and \$0.25 per 1,000 gal treated for air stripping, carbon adsorption, and peroxone, respectively.

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Past Chemical Oxidation Research Efforts Using RMA Waters

A review of past research efforts oriented toward chemical oxidation treatment of contaminated RMA waters was made to determine the extent of knowledge obtainable without further bench study. A summary of each study is presented below. At the end of this section, a discussion of the identified knowledge gaps is presented.

Khan and Thompson (1978) evaluated treatment of diisopropylmethylphosphonate (DIMP) in Well 118 groundwater using UV/ozone bench scale reactors. The initial DIMP concentration in the groundwater was approximately 70 mg/ℓ. Khan and Thompson had to treat the influent samples with caustic and/or lime to remove soluble iron and manganese in order to prevent the precipitation of these cations in the reactor and onto the quartz sleeves housing the UV lamps. The higher intensity lamps proved more effective than the lower intensity lamps. An UV wavelength spectrum of 240.0 nm and 300.0 nm (NOTE: 10 A = 1 nm) proved to be most effective. The optimal ozonated air feed rate was approximately 2.5 ℓ/min. Batch treatment times of 4 hr were required to bring the DIMP concentration down to the study target level of 0.5 ppm.

Thompson et al. (1977) performed pilot scale evaluations for DIMP removal from groundwater collected from Well PW-3 using a 100 gpd LP-UV/ozone based chemical oxidation system. The average DIMP concentration in the test influent for this study was 3,000 ppb. DIMP removal down to 300 ppb was achieved using the pilot system. A decrease in TOC removal was achieved with increased UV dosage. The estimated treatment costs were $0.54/1,000 gal for an effluent containing less then 200 ppb DIMP and $0.70/1,000 gal for an effluent containing less than 150 ppb DIMP.

Buhts (1978) evaluated the intermediate products of incomplete oxidation of DIMP, P-chlorophenylmethylsulfone (CPMSO2), aldrin, dieldrin, and dicyclopentadiene. This work was done using gas chromatography (GC), GC/mass spectroscopy (MS), nuclear magnetic resonance, and inorganic ion specific probe techniques. Several organic intermediates for all of the contaminants were identified. Most of the intermediate products identified were organic acids and carbon dioxide. Conversion of the organic compounds into inorganic phosphates, sulfurs, and carbon dioxide was noted.

Zappi et al. (1990a) evaluated treatment of four RMA contaminated waters using a 60-gal UV/hydrogen peroxide based unit. The four waters evaluated were groundwater from Sump A of the North Boundary Treatment System, groundwater from the South Plants Area, wastewater from the Hydrazine Storage Facility, and influent to the former South Plants Treatment System. Water with low levels of contaminants (North Boundary and Existing Treatment System influent) could be treated using treatment times of 15 min or less. DIMP seemed to be very reactive toward the UV light and hydrogen

peroxide. The chlorinated aliphatics were much more difficult to oxidize. Treatment of the South Plants groundwater was not successful in terms of VOC removal. The VOCs concentration, especially benzene, was too high for effective treatment with the hydraulic retention times evaluated. Increased hydraulic rentention times would have been required for increased removal. Oxidized iron posed serious operational problems in terms of fouling of the UV lamps during treatment of the South Plants groundwater. Chloroform seemed to be UV sensitive with the aromatics being much more susceptible to attack by the oxidizer. The hydrazine fuels were treated effectively, but residual n-nitrosodimethylamine (NDMA) was detected in the effluent. This indicated that higher treatment times would be required for NDMA removal.

Jelinek, Riese, and Cain (1990) used a 300-gal UV/hydrogen peroxide chemical oxidation reactor operated in batch mode for treatment of wastewater from the hydrazine storage facility at the RMA. Selection of the UV/hydrogen peroxide process was based on treatability work performed by three candidate vendors. After design and construction, the UV/hydrogen peroxide system was used to perform 10 test runs in order to determine optimal treatment conditions. It was determined that the system could effectively remove the hydrazine fuels with the use of a tungsten catalyst within a treatment time of approximately 16 hr at a pH of less than 3.0. Unfortunately, NDMA removal proved much more difficult. Treatment times as high as 60 hr were required for removal of NDMA to target levels.

The early research activities using RMA waters were essentially treatability studies that investigated a single oxidizer with UV irradiation. No evaluation of catalysts were made nor attempts to treat the water without UV irradiation. Recent work by Glaze and Kang (1988) indicates the potential oxidation capability of peroxone for removing fairly recalcitrant compounds such as TCE at rates that are comparable to chemical oxidation with UV irradiation catalyzation. Also recent work by Kuo and Zappi (1993) and Jelinek, Riese, and Cain (1990) indicate that the addition of inorganic catalysts can significantly reduce required treatment times.

Table 2 presents summaries for past AOP studies using RMA waters discussed above. The past RMA studies were generally performed using water samples containing different contaminants than those considered by the RMA FS Team. Also, past studies did not have to treat the contaminants to the low levels required by the FS Team.

Recent advances in chemical oxidation indicated that it may be possible to treat the mildly contaminated aquifers at RMA using chemical oxidation alone without the need for UV irradiation. Without UV addition the cost of treating these waters, such as the North Boundary groundwater, would be substantially reduced compared to UV/chemical oxidation treatment. Many operational problems and costs associated with UV/chemical oxidation would be eliminated if UV irradiation were not required (i.e., peroxone).

Table 2		
Summary of Past RMA AOP Studies		
Performers (Year)	**Water(s) Studied**	**Conclusions**
Khan and Thompson (1978)	Well 118 Groundwater	Removed DIMP from 70 mg/ℓ to 0.5 mg/ℓ within four hours of batch treatment using UV/ozone.
Thompson et al. (1977)	Well PW-3	Removed DIMP from 3,000 mg/ℓ to 0.3 mg/ℓ using UV/ozone. Estimated costs were $0.70/ 1,000 gallons treated.
Buhts (1978)	Laboratory solutions of DIMP, CPMSO2, and selected organochloro-pesticides	Identified a variety of oxidation intermediates for each compound. In general, most compounds were oxidized to simple acids, carbon dioxide, salts, and water.
Zappi et al. (1990)	North Boundary and South Plants Ground-waters, Hydrazine wastewater, and influent to the South Plants Treatment System	A UV/hydrogen peroxide pilot system was used. The lower level contaminated groundwaters were easily treated. South Plants groundwater required excessively long HRTs. Hydra-zines were converted to NDMA.
Jelinek, Riese, and Cain (1991)	Hydrazine Wastewater	Total hydrazines were removed to target levels. NDMA proved to be quite refractory. A GAC polishing unit was used to achieve target NDMA levels.

Study Objectives

The overall objective of this study was to support the PMRMA in evaluating chemical oxidation as a groundwater treatment technology as part of the FS.

Specific study objectives were as listed below:

a. Evaluate the feasibility of chemical oxidation processes for treatment of two contaminated groundwaters from two different plume groups at RMA by utilization of various combinations of UV light, catalysts, and chemical oxidizers.

b. Determine optimal operating conditions required to degrade target contaminants in the two groundwaters.

c. Identify primary intermediates produced during the oxidation of the target contaminants.

d. Perform a mass balance on ozone based systems to determine the extent of contaminant removal attributable to air stripping.

e. To assess the impact of residual oxidizer concentrations on the performance of granular activated carbon (GAC) for adsorption of organic contaminants.

Scope of Study

The scope of this study was limited to the bench scale. Chemical oxidizers other than ozone and hydrogen peroxide were not assessed in this effort.

2 Materials and Methods

Study Influents

Two groundwater samples, Wells 36001 and 01062, were selected by personnel from PMRMA, Ebasco (a RMA contractor), and WES as test influents for this study. Figure 4 shows the general location of both wells. The chemical composition of both groundwaters is discussed in Chapter 3 of this report.

The groundwater samples were collected in April 1992 by Harding, Lawson, and Associates (HLA) while working under contract to the PMRMA. Three well volumes of groundwater were purged from the wells prior to sample collection. The samples were collected and transported to WES in Department of Transportation (DOT) approved steel, 5-gal pails under sample chain-of-custody initiated at RMA by HLA. While filling the pails, a constant nitrogen purge was maintained within the pails. This was done as an attempt to reduce the loss of solubilized iron from the groundwater samples due to oxidation of iron with the oxygen in the headspace air. The pails were filled to within 2-in. of pail tops, and the remaining headspace was filled with nitrogen to control iron oxidation during shipping and storage at WES. Upon receiving the samples at WES, the samples were stored at 4 °C in a walk-in cooler until needed for testing. Sample chain-of-custody was maintained throughout the course of the study.

Chemical Oxidation Runs

The chemical oxidation studies were performed by WES technicians within the Chemical Oxidation Technologies Laboratory of the WES Hazardous Waste Research Center (HWRC). The evaluation of chemical oxidation as a candidate treatment system for both groundwaters was accomplished through performance of a series of bench scale experiments (referred to as "runs").

Chemical oxidation runs were performed using 1-ℓ, all glass reactors available from Ace Glass, Inc., Vineland, New Jersey. Figure 5 is an illustration of the Ace Glass photochemical reactors used in this study. The quartz immersion wells housing the UV lamps were equipped with a cooling jacket
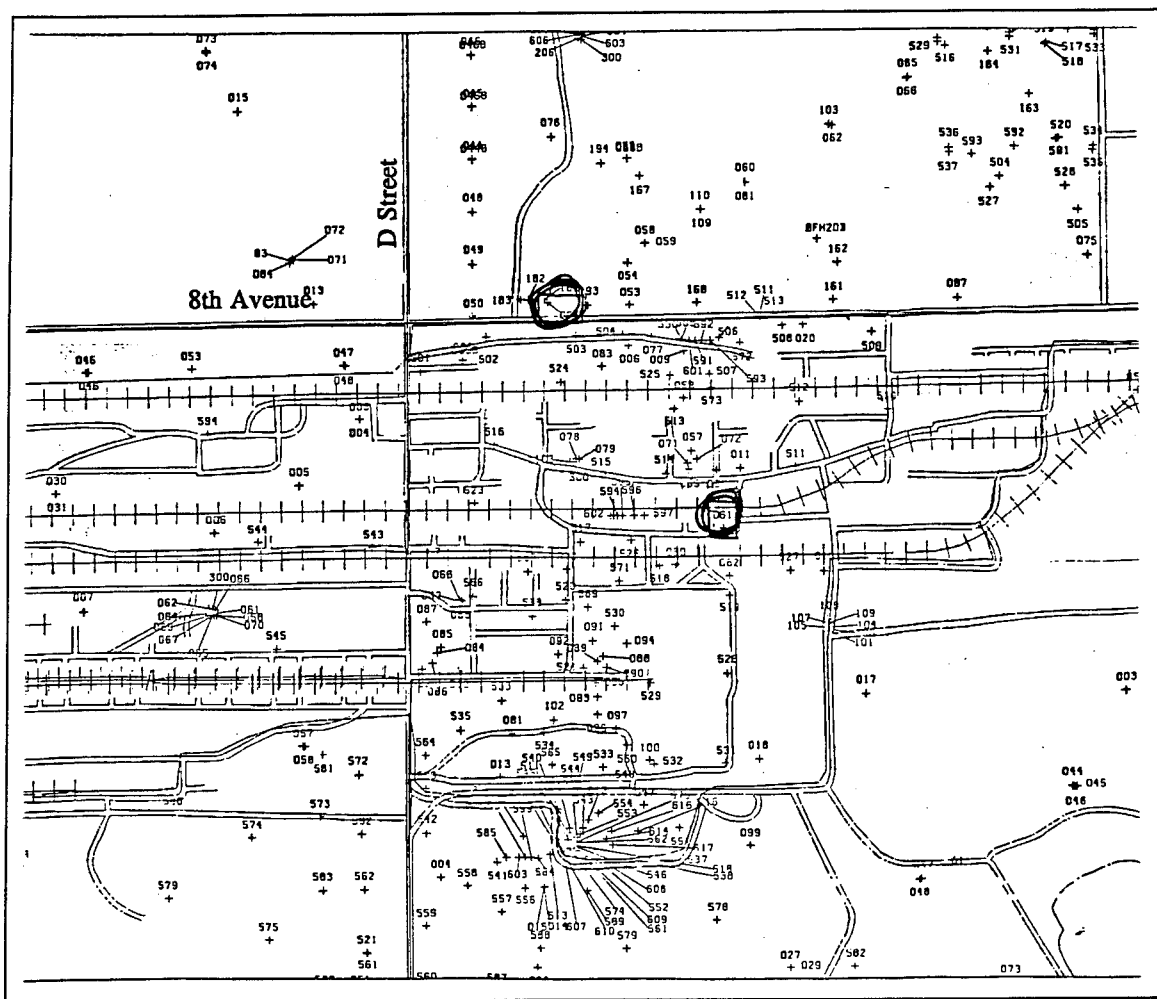
Figure 4.   RMA Site map

which allowed the reaction temperature to be controlled. Chilled, distilled, deionized water was recirculated through the cooling jackets using MasterFlex brand (Cole-Palmer, Inc.) peristaltic pumps. For this study, reactor temperatures were always maintained below 45 °C.

The reactors were operated in semi-batch mode during the experiments involving ozonation; batch with respect to test influents, hydrogen peroxide, and chemical catalysts and continuous flow in terms of ozone because ozonated air was continuously sparged throughout the runs. Ozonation was initiated at the start of each run (i.e., t = 0). During the non-ozone runs, the reactors were operated as true batch systems.

Hydrogen peroxide was added at the beginning of each run at the desired dosage using a 50 percent (vol/vol) stock solution (Fisher Chemical, Inc.). An air stream containing approximately one percent ozone (w/w) at a rate of 2.5 scfm was continuously introduced directly into the Ace Glass bench reactors through a ceramic sparging stone placed at the bottom of the reactor.

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OXIDIZER INPUT

COOLING JACKET — UV LAMP

QUARTZ
IMMERSION WELL —

AC POWER
TRANSFORMER

STIR BAR — SAMPLE TAP

MAGNETIC STIRRER
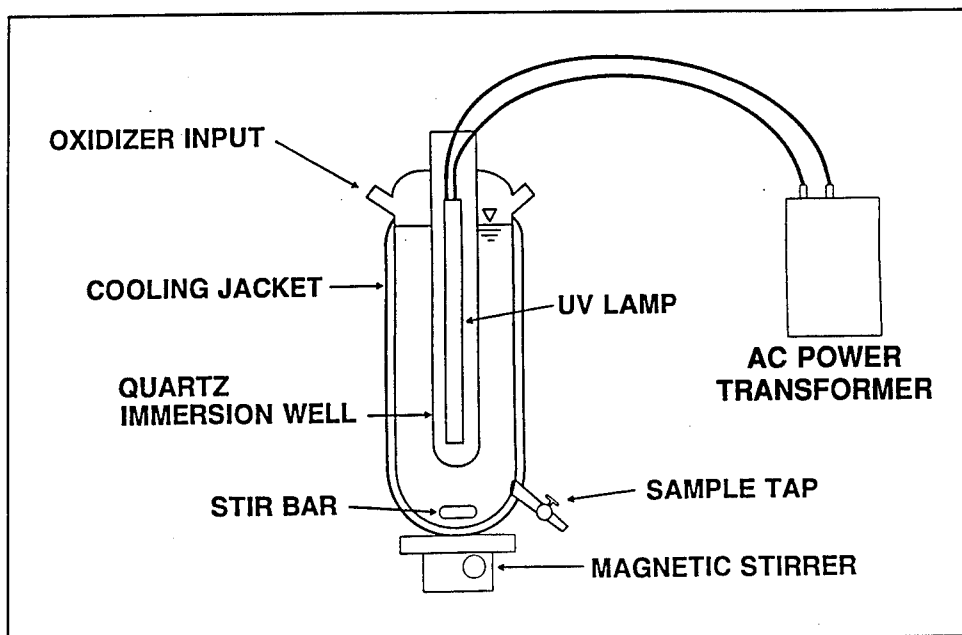
Figure 5.   Bench scale AOP reactor

The ozonated air was produced by a corona discharge ozone generator manu-
factured by Ozoteq, Inc. (Evansville, IL) which uses air as the source gas.
Low pressure 12 W and 450 W medium pressure UV mercury lamps (both
available from Hanovia/Ace Glass, Inc., Vineland, NJ) were used as UV light
sources. The UV spectra typically emitted by lamps of these types are illus-
trated in Figures 2 and 3. The energy output of the MP-UV lamp at various
wavelengths, in terms of percent of total lamp energy input (watts), is
presented in Table 1.

The UV lamps were allowed to come to full energy output prior to adding
the reactants (i.e., groundwater and oxidizers). At desired test times, analyti-
cal samples from the reactor were collected from the reactor using a stainless
steel, positive displacement pump (Cole-Palmer, Inc.) fitted with 1/4-in. OD
teflon suction and discharge tubes. The suction tube was inserted into the
mid-point of the reactor through the reactor crown. Both teflon pump lines
were drained after each sampling event to prevent cross-contamination
between sampling events.

Sample containers of appropriate volume and cleaning preparation for the
respective chemical analysis were used to accommodate the sample until
chemical analysis. Approximately 0.05 g and 1.25 g of bovine catalase were
added to the VOA vials and 1-ℓ sample bottles, respectively. This was done
to reduce the residual oxidizers remaining in the test solutions so further
degradation of the analytes did not occur during storage prior to chemical
analysis. Catalase (Aldrich, Inc.) is an enzyme produced in the liver of warm
blooded mammals that breaks down chemical oxidizers. Catalase reduction of
the residual oxidizers in the test solutions prevented further oxidation of the
contaminant during transport and storage of the samples prior to chemical

analysis. Catalase has been successfully used in numerous WES chemical oxidation studies for destruction of residual oxidizer species in analytical samples (Zappi, Fleming, and Cullinane 1992a). Analysis of catalase-laced analytical controls demonstrated that there were no interferences associated with the analytical methods. Hydrogen peroxide indicator strips (Quant brand) were used to ensure all of the oxidizers were reduced prior to sealing the sample bottles.

In experiments of this type, it is important that the oxidation reactions are stopped at that exact time they are intended to represent. Since further oxidation of the contaminant after sample collection will skew the results toward better than actual contaminant oxidation.

The combinations of various oxidizer types, catalysts, additive concentrations, and UV lamps that could be evaluated in studies of this type are almost unlimited. A set combination of additives and reaction conditions are combined to form the treatment conditions for each run. Treatment conditions evaluated in this study were selected by WES based on past experience and from data collected from previous runs (as the data became available). Particular emphasis was placed on the selection of systems that are representative of those that can be provided using commercially available equipment. Sampling intervals for each run were also initially selected based on past experiences with chemical oxidation studies. After the results of the runs became available, treatment conditions and sampling increments were adjusted accordingly. Tables 3-6 list the treatment conditions for all experimental runs evaluated during this study.

The pH and temperature of the reactors during the chemical oxidation runs were recorded at each sampling interval. A detailed laboratory data sheet describing complete test parameters and selected comments was completed by the WES technicians prior to the initiation of each run. Figure 6 illustrates an example data sheet. Appendix B contains the data sheets for all of the runs performed during this study.

The impact of iron removal in terms of improved chemical oxidation treatment was evaluated using groundwater samples that had been dosed with 200 mg/ℓ of hydrogen peroxide (unless otherwise noted). After dosing with the hydrogen peroxide, the iron oxides were allowed to settle overnight. The supernatant was removed and used as influent to the chemical oxidation runs.

Since the chemical oxidation test runs were essentially performed as batch reactors, analytical samples were collected at various treatment times. The results of chemical analyses are listed and/or plotted against treatment time to generate kinetic data. These data will be extensively discussed in Chapter 3 of this report.

Table 3
VOC Chemical Oxidation Runs on Well 36001 Groundwater

Run	Oxidizer	Oxidizer Concentration mg/ℓ	UV Lamp W	Catalyst Type Concentration mg/ℓ-type	Iron Removal[1]
V41	--	--	450	--	No
V42	H[2]	50	450	--	No
V43	H	100	12	--	No
V44	H	100	450	--	No
V45	H	200	450	--	No
V46	H	200	12	--	No
V47	H	500	--	50-WO_3	No
V48	H	500	--	50-WO_3(pH = 3)	No
V49	--	--	12	--	No
V50	H	500	--	--	No
V51	H	500	--	10-WO_3	No
V52	O[3]	SP[4]	12	--	No
V53	H	100	450	--	No
V54	O/H	SP\10	--	--	No
V58	H	50	12	--	No
V59	H	100	12	--	No
V60	H	200	12	--	No
V67	O/H	SP/10	--	--	No
V68	O/H	SP/50	--	--	No
V69P	O/H	SP/500	--	--	No
V69	H	500	450	--	No
V70	H	1,000	450	--	No
V71	O	SP	12	--	No
V72	H	500	450	100-WO_3	No
V73	O/H	SP/200	12	--	No
V74	H	500	450	--	No
V75	AIR	--	12	--	No
					(Continued)

[1] Pretreated with 200 mg/ℓ H_2O_2 except as noted.
[2] H = Hydrogen peroxide.
[3] O = Ozone.
[4] SP = Ozone was sparged into the reactor.

Table 3 (Concluded)					
Run	Oxidizer	Oxidizer Concentration mg/ℓ	UV Lamp W	Catalyst Type Concentration mg/ℓ-type	Iron Removal[1]
V82	O	SP	--	--	No
V83	O/H	SP/0.25	--	--	No
V84	O/H	SP/5	--	--	No
V85	O/H	SP/1	--	--	No
V86	O/H	SP/10	--	--	No
V87	O/H	500	450	--	No
V93	O/H	SP/5	--	--	Yes
V97	O/H	SP/1	--	--	Yes
V104	H	50	450	--	No
V110	H	50	450	--	Yes
V111	O/H	SP/0.50	--	--	Yes
V112	O/H	SP/0.05	--	--	No
V113	O	SP	--	--	No
V114	O/H	SP/0.01	--	--	No

Evaluation of Chemical Oxidizer/Activated Carbon Compatibility

One potential implementation scenario of chemical oxidation systems is in conjunction with GAC polishing units. GAC polishing units may be used to remove residual levels of contaminants from chemical oxidation system effluents. This scenario may be used if the chemical oxidation systems do not remove a particular compound or compounds to acceptable levels or if oxidation of a particular compound is kinetically slow. If a compound is kinetically slow to oxidize, it may be economically more attractive to use GAC adsorption rather than to pay potentially higher treatment costs associated with prolonged chemical oxidation treatment. This scenario is valid only if the compound in question adsorbs strongly to GAC and oxidizes relatively slow. It is likely that chemical oxidation will be followed by GAC, as a polishing unit, if oxidation is implemented.

This series of experiments was performed because of concern that residual levels of oxidizers in the effluent from a chemical oxidation reactor may adversely impact the performance of GAC systems by either upsetting the

Table 4
Pesticides/DBCP Chemical Oxidation Runs on Well 36001 Groundwater

Run	Oxidizer	Oxidizer Concentration mg/ℓ	UV Lamp W	Catalyst Type Concentration mg/ℓ-type	Iron Removal
P6	--	--	450	--	No
P7	H[1]	50	450	--	No
P8	H	100	12	--	No
P9	H	100	450	--	No
P10	H	200	450	--	No
P11	H	200	12	--	No
P12	H	500	--	50-WO_3	No
P13	H	500	--	50-WO_3(pH = 3)	No
P14	--	--	12	--	No
P15	H	500	--	--	No
P16	H	500	--	10-WO_3	No
P26	H	500	--	10-WO_3	No
P27	H	500	--	50-WO_3	No
P28	H	50	12	--	No
P29	H	200	12	--	No
P30	O[2]	SP[3]	12	--	No
P35	O	SP	12	--	No
P36	O/H	200	450	--	No

[1] H = Hydrogen peroxide.
[2] O = Ozone.
[3] SP = Ozone was sparged into the reactor.

adsorption equilibria established between the contaminants and the carbon, or hindering the adsorption process during GAC treatment. Rice (1980) suggests that residual levels of oxidizers may increase the polarity of organic compounds thereby making them more soluble. Increased solubility tends to reduce adsorptivity.

The fate of residual chemical oxidizers within an activated carbon system was evaluated using laboratory batch systems. The fate of various levels of hydrogen peroxide within 200 ml of a 50-gal/ℓ GAC/distilled water slurry was evaluated. Hydrogen peroxide doses of 1, 5, 10, 20, 50, 100, 200, 500, and 1,000 mg/ℓ were added to the GAC slurries and agitated using a recipitating shaker table. Nalge brand 250 ml polyethylene sample bottles were used as

Table 5
VOC Chemical Oxidation Runs on Well 01061 Groundwater

Run	Oxidizer	Oxidizer Concentration mg/ℓ	UV Lamp W	Catalyst Type Concentration mg/ℓ-type	Iron Removal[1]
V55	O[2]	SP[3]	12	--	No
V56	H[4]	100	450	--	No
V57	O/H	SP/10	--	--	No
V61	H	100	12	--	No
V62	H	50	12	--	No
V63	H	200	12	--	No
V64	O/H	SP/10	--	--	No
V65	O/H	SP/500	--	--	No
V66	H	500	--	100 WO_3	No
V76	O/H	SP/1	--	--	No
V77	O/H	SP/0.25	--	--	No
V78	O	SP	12	--	No
V79	H	500	450	--	No
V80	O/H	SP/10	--	--	No
V81	O/H	SP/0.5	--	--	No
V88	H	500	450	--	No
V89	O	SP	12	--	Yes[5]
V90	H	500	450	--	Yes
V91	O	SP	12	--	No
V92	O	SP	12	--	Yes[6]
V94	O/H	SP/1	--	--	Yes[6]
V95	O/H	SP/5	--	--	Yes
V96	O	SP	12	--	Yes
V97b	AIR	--	--	--	HNU
V98	AIR	--	--	--	No
V99	AIR	--	--	--	Yes

(Continued)

[1] Pretreated with 500 mg/ℓ H_2O_2 except as noted.
[2] O = Ozone.
[3] SP = Ozone was sparged into the reactor.
[4] H = Hydrogen peroxide.
[5] Used a 25 mg/ℓ H_2O_2 dose.
[6] Used a 200 mg/ℓ H_2O_2 dose.

Table 5 (Concluded)					
Run	Oxidizer	Oxidizer Concentration mg/ℓ	UV Lamp W	Catalyst Type Concentration mg/ℓ-type	Iron Removal[1]
V100	H	200	450	--	No
V101	H	100	450	--	No
V102	H	100	450	--	Yes[6]
V103	H	50	12	--	Yes[6]
V105	H	50	450	--	Yes[6]
V1061	O/H	SP/0.5	--	--	Yes[6]
V107	O/H	SP/0.05	--	--	No
V108	O/H	SP	--	--	No
V109	O/H	SP/0.01	--	--	No
V115	AIR	--	--	--	No

system agitation vessels. Hydrogen peroxide concentrations within the slurries were analyzed using Quant brand test strips after 30, 60, 120, and 180 min of agitation.

The impact of hydrogen peroxide on contaminant/GAC adsorption equilibria was evaluated by generation of three adsorption isotherms. GAC doses evaluated in all three isotherm tests were 0 (a test control), 0.5, 1.0, 5.0, 10.0, 20.0, 40.0, and 100.0 g in 800 ml of distilled, deionized water. Type BL powdered activated carbon (Calgon Carbon, Inc., Pittsburgh, PA) was used as the GAC source. This carbon sample is a pulverized version of Calgon Filtrasorb 400 which is commonly used in water treatment. The slurries were agitated in 1-ℓ precleaned amber bottles in which agitation was achieved using an end-over-end laboratory tumbler. Agitation was further enhanced by adding six 6-mm diam glass beads to each bottle. A 50-mg/ℓ DIMP solution was used as the aqueous phase of this experiment. This solution was synthesized using 96 percent pure DIMP and distilled, deionized water.

The three test conditions used to generate the three isotherms are listed below:

a. 4-hr contact time without hydrogen peroxide addition. This condition is a standard isotherm condition which served as a test control.

b. 2-hr contact time without hydrogen peroxide addition, then 2 hr of tumbling with 10 mg/ℓ of hydrogen peroxide. This condition evaluates the scenario where adsorption equilibria is established; then chemical oxidizers are introduced into the adsorber.

Table 6
Pesticides/DBCP Chemical Oxidation Runs on Well 01061 Groundwater

Run	Oxidizer	Oxidizer Concentration mg/ℓ	UV Lamp W	Catalyst Type Concentration mg/ℓ-type	Iron Removal[1]
P17	--	--	12	--	No
P18	H[2]	200	--	--	No
P19	H	500	--	--	No
P20	H	500	--	10-WO$_3$	No
P21	H	500	--	50-WO$_3$	No
P22	H	200	--	50-WO$_3$ (pH=3)	No
P23	--	--	450		No
P24	H	500	450	--	No
P25	H	100	450	--	No
P31	H	200	12	--	No
P32	O[3]	SAT	12	--	No
P33	O	SAT	12	--	No
P34	O/H	SP[4]/200	450	--	No
P37	H	500	450	--	No
P38	H	500	450	--	Yes
P39	O	SP	12	--	Yes
P40	O	SP	12	--	No
P41	H	500	450	--	No
P42	H	500	450	--	Yes
P43	O	SP	12	--	No
P44	O	SP	12	--	Yes
P45	H	200	450	--	No
P46	H	200	450	--	Yes[5]

[1] Pretreated with 500 mg/ℓ H$_2$O$_2$ except as noted.
[2] H = Hydrogen peroxide.
[3] O = Ozone.
[4] SP = Ozone was sparged into the reactor.
[5] Used a 200 mg/ℓ H$_2$O$_2$ dose.

c. 4-hr contact time with 10 mg/ℓ of hydrogen peroxide present. This condition represents the case where the oxidizer is continuously present in the influent to the adsorber.

```
CHEMICAL OXIDATION TEST RUN
          DATA SHEETS
------------------------------------------------------------
DATE:_____    TECHNICIAN:_____

PROJECT:_____    RUN NUMBER:_____

SAMPLE:_____    TARGET ANALYTE:_____


1ST OXIDIZER:_____    1ST OX. CONCENTRATION:_____

2ND OXIDIZER:_____    2ND OX. CONCENTRATION:_____

STRENGTH OF H2O2 USED:_____    AMOUNT OF H2O2 STOCK ADDED:_____

O3 PRESS:_____  O3 FLOW:_____  TURNDOWN:_____  CELL USED:____


CATALYST:_____    CATALYST CONCENTRATION:_____

UV LIGHT WATTAGE:_____    UV WAVELENGTH:_____


REACTOR USED:_____    ANALYTICAL LAB:_____

TOTAL NUMBER OF SAMPLES COLLECTED:_____

TARGET PH:_____    TARGET TEMPERATURE:_____

TYPE OF OXIDIZER QUENCHER USED:_____  AMOUNT USED:_____

SAMPLE BOTTLES USED:_____
------------------------------------------------------------
SAMPLE ID  REACTION TIME  PH  OXIDIZER CONCENTRATION  TEMPERATURE
            (MIN)              (PPM)                    (°C)

_____   _____   ____   _____   _____

_____   _____   ____   _____   _____

_____   _____   ____   _____   _____

_____   _____   ____   _____   _____

_____   _____   ____   _____   _____

_____   _____   ____   _____   _____

COMMENTS (COLOR? BUBBLES? PRECIPITATION? ODORS?)
```

Figure 6.   Sample run data sheet

The isotherms were generated by methods described by James M.
Montgomery Engineers, Inc. (1985). All three isotherms were plotted on a
single semi-log graph for purposes of direct comparison. Aqueous samples
were filtered using a Whatman A/E filter prior to DIMP analysis. As stated
above, this approach will give RMA personnel an indication of how residual
oxidizer concentrations may impact adsorption equilibria. Compounds other
than DIMP may behave differently, but the results of this effort do provide
insight as to how organic compound adsorption equilibria may be impacted, if
at all, by the presence of oxidizing species in the GAC influent.

Iron Fouling Potential

The potential for excessive iron scumming (fouling) of UV quartz sleeves
was evaluated using the bench units on site at RMA by WES technicians. A
bench scale unit similar to the units used in the chemical oxidation runs was
transported to RMA in October 1992. The unit was operated under the fol-
lowing treatment conditions: 1,000 mg/ℓ hydrogen peroxide influent

concentration, a 10 min hydraulic retention time, and a 200 W MP-UV Hanovia/Ace Glass lamp.

Two portable 4.5 kw electrical generators were initially used to power the bench system. Unfortunately, the generators did not have enough surge power capacity to handle full operation of the bench system. However, the unit was operated for an 8-hr period at Well 01061. To operate the system for longer run times, the unit was setup within the former South Plants Treatment System Complex where electrical power was available. Groundwater from Well 01061 was transported to the unit from the well using two 35 gal drums.

Iron concentrations in the influent and effluent from the bench unit were determined in the field using a portable spectrophotometer (Hach, Inc.). The system temperature and pH were also measured using a portable pH meter (Fisher brand). Periodic visual observations were made to evaluate build-up of oxidized iron within the reactor.

Iron Removal

A limited evaluation of iron removal using chemical oxidizers was performed at WES. Iron oxidation was evaluated through bench-scale oxidation/precipitation studies by addition of hydrogen peroxide, ozone (ozonation), or air (aeration). These oxidation iron removal techniques were evaluated because iron removal may improve UV influent transmissivity and lead to subsequent improved treatment efficiency.

Jar tests were performed in all glass graduated 1-ℓ cylinders. Various hydrogen peroxide doses were investigated along with ozone and air sparging. Ozone and air were sparged into the cylinders for 30 min. After adding the hydrogen peroxide or sparging with ozone or air, the cylinders were sealed to prevent headspace air from contributing atmospheric oxygen to the test solutions. Periodically, visual observations of test solutions were used to determine optimum dose and oxidizer utility for iron removal.

Sample UV transmissivity as measured using a Milton-Roy scanning spectrophotometer (scanned from 200 nm to 400 nm) was used to evaluate the impact of iron removal on UV transmissivity. Hydrogen peroxide addition was used as a means of removing iron from the groundwater samples. The following hydrogen peroxide doses were evaluated: 5, 50, 100, 200, 500, and 1,000 mg/ℓ. Distilled water samples dosed with equal hydrogen peroxide amounts were used as spectrophotometric base controls. The UV absorbance data were plotted on absorbance versus wavelength charts for direct comparison of the various hydrogen peroxide doses toward improved UV transmissivity.

The potential for using filters for removal of the iron oxides from the water samples was evaluated using a sequential solids analysis. An aliquot of sample containing iron oxides was passed through a series of filter papers with sequentially reduced nominal pore size ratings. Total solids analyses were performed on the treated groundwaters to determine total solids concentrations. Filter testing was performed on both groundwater samples after iron oxidation had occurred using a hydrogen peroxide dose of 500 mg/ℓ. These tests were performed in triplicate. The weight percentages of iron oxides retained on each filter were recorded after passing 100 ml of the treated water through each filter followed by drying the wetted filter pads at 104 °C for at least 2 hr. The filter size that retained appreciable percentages of iron oxide mass was used to estimate iron oxide particle size and potential filter size.

Mass Balance Testing

Several techniques were used for evaluating the fate of VOCs during ozone based oxidation treatment of both groundwaters. These experiments were performed because ozone based chemical oxidation systems involved sparging of an air stream containing ozone into the oxidation reactor. Sparging of the ozonated air will result in the desorption (stripping) of VOCs from the system influent.

Techniques for estimating the fate of VOCs in the ozone sparged systems were as follows: (a) the use of air sparging controls, (b) VOC capture on Tenex traps followed by extraction/chemical analysis, and (c) analysis of the reactor off-gases using a photoionizing detection (PID) organic vapor analyzer (OVA). Each technique is described below.

Sparging runs

The sparging experiments involved comparing the rate of VOC removal in three sparged systems: air sparging, ozonated air sparging (ozonation), and ozonated air sparging with hydrogen peroxide addition (peroxone). These experiments were performed on both groundwater samples. The air system involved sparging of air into the reactor at the same flowrate (2.5 scfm) used in the ozone addition chemical oxidation runs. At test times of 0, 5, 10, 20, and 40 min of sparging, samples were collected using the same techniques used in the chemical oxidation runs. The ozone sparged runs involved ozonation of the reactors and collection of samples at the same test times as the air only runs. The peroxone experiments were performed similarily to the ozone runs, except 5.0 mg/ℓ of hydrogen peroxide was added to the reactors. Catalase was added to VOC samples collected during the ozonation and peroxone runs to remove the residual oxidizer species prior to MS/GC purge and trap analysis.

Tenex traps

This technique involves using Tenex traps for the capture of the VOCs from the gas streams exiting from an ozonation system, followed by the extraction of the adsorbed VOCs from the trap using freon, then subsequent VOC analysis of the extracts using a purge and trap concentrator in conjunction with a spectrophotometry/gas chromatography (MS/GC) unit. This method was successfully used by Zappi et al. (1992b) for performing mass balances around aerobic bioreactors treating contaminated groundwaters from two Superfund sites.

Figure 7 presents the experimental set-up used for performance of the tenex trap experiments. The full system gas flow exiting the reactor was passed through two gas washing bottles. Each gas washing bottle contained 500 ml of a 4 percent solution of potassium iodide (KI). Two gas washing bottles were plumbed in series to prevent escape of ozone into the Tenex traps (gas washing is rarely 100 percent efficient). The KI solution removed the ozone via liberation of the free iodide ion with the ozone so that the ozone does not interfere with VOC adsorption onto the Tenex. KI solutions turn a blood-red color when saturated with liberated iodine indicating that the KI solution does not have any more removal capacity for ozone. This allowed the gas washing bottles to be monitored for ozone washing potential to ensure that excessive carry over of ozone into the traps did not occur during testing. A small portion of the system gas flow was directed through the Tenex traps using an in-line rotameter with regulatory capability. A slight vacuum was maintained on the other side of the Tenex trap to overcome the headloss
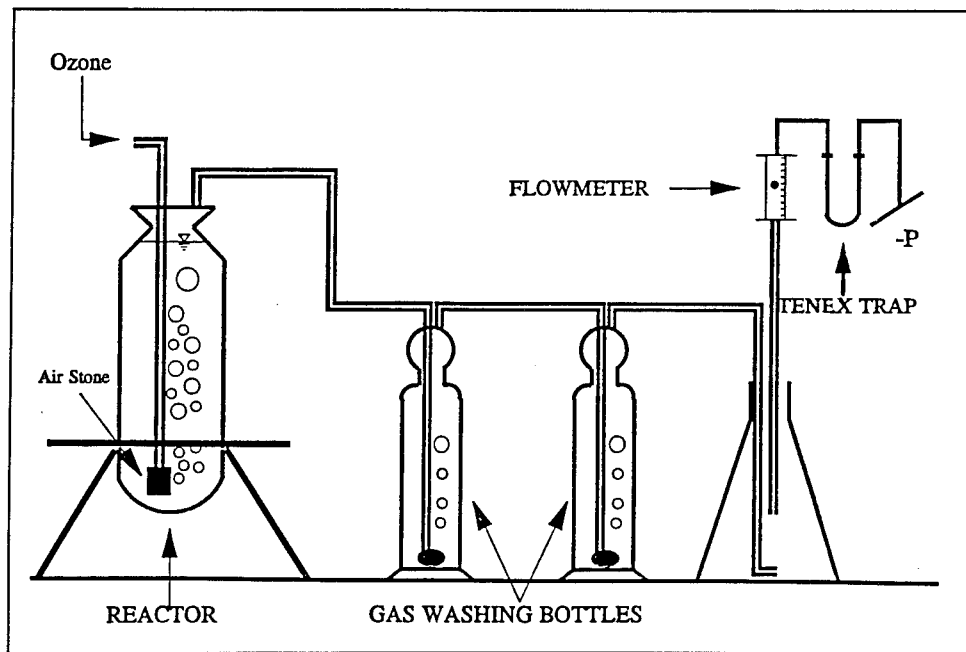
Figure 7. Ozone sampling system

across the traps. This allowed for target flows across the traps to be maintained.

Estimation of gas concentrations using Tenex traps is usually made by maintaining a constant gas flow through the traps and varying trap/gas contact time. Varying trap/gas contact allows for selection of data from a trap that is not saturated with VOCs. Typically, trap VOC mass loadings versus contact time are plotted. The maximum contact time that does show an increase from the previous time is selected. This technique is appropriate for systems having a constant gas phase concentration, but batch processes do not have a constant gas phase VOC concentration.

Batch processes with VOC releases via process air will initially contain relatively high levels of VOCs in the process gas with rapidly decreasing gas phase concentrations occurring over time as liquid phase concentrations are reduced. Estimating VOC releases using Tenex traps from batch systems should be made over the course of the complete run time. For this study, a 20 min run time was selected. Since trap/gas contact times need to be varied to select a trap system that contains the adsorbed VOCs, but is not saturated with the adsorbed VOCs; gas flowrates through the traps were varied. Flowrates evaluated were 5, 10, 20, 30, and 40 ml/min. For each VOC of interest, a trap gas flowrate was selected, and the mass analysis (presented in μg) associated with that VOC and flowrate is used for calculating system process gas phase concentration by:

$$C_{pg} = MASS_{at}/VOL_{tt}$$

where

C_{pg} = VOC concentration in process gas, μg/ℓ

$MASS_{at}$ = mass absorbed onto trap (analyzed by lab), μg

VOL_{tt} = total volume of gas passed through traps, ℓ

Once the VOC concentrations in the process gases exiting the reactor are calculated, then the total amount of VOC mass exiting the reactor is calculated by:

$$MASS_{ts} = (C_{pg} \times VOL_{ts}) + (C_{ki} \times VOL_{ki})$$

where

$MASS_{ts}$ = total amount of VOC mass exiting the reactor during run, μg

VOL_{ts} = total volume of process gases exiting the reactor, ℓ

C_{ki} = VOC concentration in aqueous KI trap, $\mu g/\ell$

VOL_{ki} = total liquid volume in both traps, ℓ

The percentage of VOC removal attributable to stripping from the reactor is calculated by:

$$\% \ REM_{st} = [MASS_{ts} \ / \ (C_{aq} \times VOL_r)] \times 100$$

where

$\% \ REM_{st}$ = percent VOC removed via stripping

C_{aq} = initial VOC concentration in reactor, $\mu g/\ell$

VOL_r = total volume of test influent in reactor, ℓ

PID analysis of reactor off-gases

The total concentration of VOCs in the off-gases from the sparged reactors were estimated using a HNU Model 101 PID OVA detector. The off-gases from the reactors were scrubbed free of ozone by passing the gases through two gas washing bottles, containing a 4-percent KI solution, that were plumbed in series. After ozone scrubbing in the KI solution, the off-gases were analyzed by the PID detector.

Batch oxidations studies

As an attempt to assess the ability of ozone and peroxone for oxidation of VOCs, true batch studies were performed in the 1-ℓ glass photochemical reactors under dark conditions. True batch systems involve presparging of the ozonated gas into the reactors followed by addition of the groundwater sample with hydrogen peroxide added for the peroxone evaluations and without hydrogen peroxide for the ozonation evaluations. The ozone was sparged into 500 ml of distilled, deionized water. After equilibrium was established, usually at approximately 7.5 mg/ℓ ozone, 500 ml of the groundwater (and hydrogen peroxide for the peroxone runs) was added. Over time samples were collected for tracking of the target VOC.

Tests of this type allow for complete evaluation of oxidation reactions without stripping of the VOCs because no gas is entering or exiting the reactor system. The major limitation of this technique is that peroxone reactions often become ozone limited to the limited amounts at the initiation of testing (approximately 3.5 mg/ℓ). Studies of this type determine the feasibility for oxidation of the contaminant to be evaluated.

Analytical Techniques

All chemical analyses were performed by the Environmental Chemistry Branch (ECB), Environmental Engineering Division (EED), and Environmental Laboratory (EL), WES.

Sample collection

Samples were collected during testing by WES laboratory personnel in 40-ml precleaned vials for VOC analyses and 1-ℓ precleaned bottles (Allpack, Inc.) for DIMP and pesticide/DBCP analyses. Due to the large sample volumes (1-ℓ) required for DIMP and pesticide/DBCP analyses, and the capacity of the reactors (1-ℓ), the reactor was fully drained into the sample bottles at each sampling event for the DIMP and pesticide/DBCP runs. After draining, the reactor was refilled, testing was restarted from t = 0, and treatment continued until the next sampling event (t = i).

As previously discussed, further oxidation of contaminants in the sample bottles is prevented by the addition of catalase to the samples.

VOCs

These samples were analyzed according to U.S. Environmental Protection Agency Method Number 8240 (USEPA SW846 1986) with a Hewlett-Packard Model 5995 gas chromatography/mass spectrophotometry unit outfitted with an OI International, Inc. purge-and-trap system.

DIMP

DIMP samples were analyzed using RMA Method No.33. A Hewlett-Packard Model 5890 Series II gas chromatography (GC) unit outfitted with a flame polarization detector (FPD) was used to perform these analyses. A 99.3 percent pure DIMP solution was used as the calibration standard.

(DBCP)/pesticides

DBCP and pesticide samples were analyzed using USEPA Method No. 8080. The GCs used in this study for pesticides and DBCP analyses were a Hewlett-Packard 5840A and a Hewlett-Packard 5890 Series II. Both units were equipped with Hewlett-Packard Chem Station set-ups which utilized electron capture detectors. A capillary column No. DB5 with a 30 m length and 0.25 mm ID were used. Film thickness on the column was 0.25 um. The confirmation column used was a SPB608 with a 30 m length and 0.25 mm ID. Both standards were purchased from USEPA.

Ozone and hydrogen peroxide

Quant-brand hydrogen peroxide test strips or iodometric titrations were used to measure residual oxidizer concentrations.

Temperature/pH

A Fisher brand pH meter with temperature measuring capability and probes were used to measure the temperature and pH of the test solutions.

3 Results

Characterization of Test Influents

Potential impact of water matrix on treatment

Chemical oxidation processes are very sensitive to water chemistry. The chemical composition of water is often referred to as "water matrix." Simple, naturally occurring compounds such as hardness (calcium complexes) and iron (iron oxides) can have a significant impact on oxidation rate (Yurteri and Gurol 1989; Zappi et al. 1990). Studies by Zappi, Fleming, and Cullinane (1992a) indicated that some form of influent pretreatment may be required to allow sufficient transmittance of the UV light through the influent.

Both groundwater samples used in this study, Wells 01061 and 36001, had very complex water matrices. These groundwater samples are characterized by relatively high concentrations of organic contaminants and the presence of both reduced (Fe^{2+}) and oxidized iron (Fe^{3+}). Oxidized iron has a low solubility in water and usually precipitates as a bright orange solid. The total iron concentrations measured during this study were 2.2 mg/ℓ and 9.7 mg/ℓ for Wells 36001 and 01061, respectively.

Impact of water matrix on chemical analysis

Water matrix can have a significant impact on the relative success of chemical analyses. Water matrix impacts both the minimum allowable analytical method detection limit (MAAMDL) and the minimum instrument detection limit (MIDL). Understanding the difference between both types of detection limits is important for interpretation of treatability results. The MAAMDL is a changing value that is determined through statistical evaluation of the chromatographs based on peak integration and elutriation time. If two compounds chromatograph at similar times and one of the two compounds is present at a much higher concentration, then the detection limit for the compound present at the lower concentration will be higher than if the other compound was not present. It is possible to estimate the respective concentrations of compounds elutriating out at similar times at much lower levels than are allowable by the analytical QA/QC guidance of the analytical method (i.e., MAAMDL). The

estimated concentration tends to approach the MIDL which is the lowest concentration value that can be analyzed with the particular analytical equipment and method being used.

Under the USEPA's Contract Laboratory Program (CLP), a concentration that is estimated below the MAAMDL is qualified on the data sheet as a "J" value. The lowest "J" value reportable under the best of sample matrices is the MIDL.

The analytical results from the oxidation runs presented in this report list both the minimum allowable analytical method detection limit values (MAAMDL) and "J" values. The "J" values will be indicated by the insertion of a "J" after the listed values. This will allow for full evaluation of reaction kinetics and potential concentrations obtainable by the various treatment systems. Representation of the data in this manner will allow for trending evaluations to be made based on removal kinetics and not on analytical limitations.

Evaluation of analytical blanks

The methylene chloride QA/QC analytical blanks indicated the presence of low levels of methylene chloride. Concentrations on the order of 1.0 $\mu g/\ell$ were generally detected in the analytical blanks. The level of methylene chloride contamination detected in the blanks were considered insignificant as compared to the initial concentrations detected in the groundwater samples which were typically an order of magnitude higher. The analytical results for the other analytes did not indicate the presence of any of the other compounds in the blanks. No blank corrections were performed on the chemical oxidation run data presented in this report.

Groundwater Analytical Results

Tables 7 and 8 present the results of the chemical analysis of Wells 36001 and 01061, respectively. The data listed in Tables 7 and 8 represent an average of all analytical data collected from the initial analyses (t = 0) of the chemical oxidation runs for each water. These samples are considered untreated samples. The tables also list the percent removals required to meet target levels for key RMA compounds based on the listed average concentrations. These levels were estimated by the RMA-FS Team based on a review of current regulatory guidelines.

The term "VOCs" will be used throughout this report to represent all volatile organic contaminants. This term is inclusive of both aromatic and chlorinated aliphatic organic compounds.

Table 7
Average Concentration of Key Contaminants Detected in
Well 36001 Groundwater Samples

| Analyte | Concentration in µg/ℓ | | Percent Removal Required |
	Average Concentration	Target Concentration	
Benzene	16,411.67	5	99.97
T-Xylenes	660.55	10,000	None
Toluenes	141.19	2,400	None
TCE	1,263.86	5	99.60
Chloroform	1,421.36	10	99.30
M. Chloride	899.13	5	99.44
Aldrin	0.0859	0.1	None
Dieldrin	1.20863	0.1	91.72
DBCP	9.9855	0.2	98.00
PPDDE	0.1115	0.1	10.31
DIMP	0.6	600	None

Table 8
Average Concentration of Key Contaminants Detected in
Well 01061 Groundwater Samples

| Analyte | Concentration in µg/ℓ | | Percent Removal Required |
	Average Concentration	Target Concentration	
Benzene	851.5	5	99.41
T-Xylenes	140	10,000	None
Toluenes	83	2,400	None
TCE	218.3	5	97.71
Chloroform	25,689.4	10	99.96
M. Chloride	2,117.3	5	99.76
Aldrin	0.0859	0.1	None
Dieldrin	.3624	0.1	72.41
DBCP	9.9855	0.2	98.00
PPDDE	0.1115	0.1	10.31
DIMP	0.839	600	None

Well 36001

From Table 7, Well 36001 groundwater had high concentrations of volatile organic contaminants. Benzene was by far the most prevalent contaminant detected in this groundwater sample. Total aromatic compounds were detected at approximately 17,200 $\mu g/\ell$. Total chlorinated solvents concentrations were found to be present at approximately 3,500 $\mu g/\ell$. Well 36001 also had detectable levels of pesticides and dibromochloropropane (DBCP). Approximately 0.6 $\mu g/\ell$ of DIMP was detected in this groundwater.

DIMP and OCPs, except dieldrin, were not present at levels requiring treatment based on review of the target treatment levels provided by the RMA FS Team. Dieldrin, DBCP, and PPDDE require percent removals of 92, 98, and 10 percent, respectively, to meet target treatment levels. The chlorinated solvents of prime concern are chloroform, methylene chloride, and trichloroethylene (TCE). All of these compounds will require at least 99 percent removal to meet the target treatment levels. Benzene was the only aromatic compound requiring removal based on study target levels. Approximately 99.9 percent removal of the benzene will be required to achieve target treatment levels.

Well 01061

The groundwater samples collected from Well 01061 also contained a variety of organic contaminants (Table 8). The majority of the contamination detected was chlorinated VOCs. By far, the most predominant chlorinated VOC detected in the groundwater was chloroform at 25,690 $\mu g/\ell$. Residual levels of pesticides and DBCP were also detected. Based on target treatment levels; chloroform, benzene, TCE, methylene chloride, and DBCP will have to undergo at least 97 percent removal to meet target treatment levels. Dieldrin and PPDDE will require percent removals of 72 and 10 percent, respectively, to meet target treatment levels.

Oxidized Iron Interference

Throughout the performance of chemical oxidation runs, oxidized iron was frequently present within the reactors in the form of both water discoloration and as a precipitant. In most cases, the extent of discoloration and iron oxidation increased as treatment time proceeded. The extent of water discoloration and iron oxide present in the reactors varied greatly between runs. Visual observations indicated that the amount of iron oxides present in the influents also varied from one run to another.

Well 36001 groundwater samples were much more susceptible to formation of oxidized iron when exposed to oxidizers, including air (oxygen), than the

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groundwater samples from Well 01061. Iron oxidation of RMA groundwaters is not unexpected since previous studies at RMA indicated that these groundwaters have a very sensitive reduction/oxidation (REDOX) potential (Zappi et al. 1990). As such, any exposure of the groundwaters to air resulted in the formation of a bright orange precipitant that was determined to be oxidized iron (Zappi et al. 1990).

The extent of iron oxidation in Well 36001 groundwater samples is surprising considering that the total iron concentration was found to be relatively low (2.2 mg/ℓ) during this study. This further strengthens past observations that RMA waters have a very sensitive REDOX equilibria in terms of iron oxidation.

Well 01061 groundwater samples tended to have less water discoloration due to iron oxidation than the samples from Well 36001, yet this groundwater had almost four times the amount of total iron present (9.5 mg/ℓ). However, some discoloration of the test influents did occur during the chemical oxidation runs.

After using the majority of the groundwater samples in the pails for testing (this period of time usually lasted for several days), the water samples collected near the bottom of the pails were consistently observed to have much more orange discolorization than the samples collected from the upper portion of a newly opened pail. Neither groundwater samples typically had oxidized iron present when the pails were first opened throughout the course of this study.

When hydrogen peroxide, regardless of the amount, was added at the initiation of the runs, oxidation of the reduced iron did proceed within the reactor. The rate of formation and extent of iron oxidation varied with hydrogen peroxide dosage; the higher the hydrogen peroxide dose, the higher the degree of water discoloration that occurred. Ozone also produced iron oxides within the bench reactors, but at a slower rate and amount.

Iron Oxidation and Removal Studies

Upon visual observation of the color imparted within the groundwater samples due to the excessive amounts of oxidized iron present, a limited evaluation of potential iron oxidation and removal techniques prior to AOP treatment was conducted. It was postulated that UV transmissivity could be improved by complete oxidation and subsequent precipitation of the iron present in the groundwater. It was also theorized that any increase in influent UV transmissivity would improve treatment kinetics by increasing the achievable quantum yield toward contaminant degradation. Quantum yield is the amount of photons that is emitted by the UV lamps and is involved in a beneficial reaction over the total amount of photons emitted by the lamp. This ratio is rarely calculated but often considered when UV transmissivity is obviously impacted by water matrix. Quantum yield can be determined experimentally

through the use of chemical or optical actinometers. Unfortunately, the practical use of actinometers was outside the scope of this study because development of actinometric techniques as applied toward photochemical treatment reactors is extremely limited (WES is currently conducting research in this area). However, visual observation of oxidized iron solids in suspension within the test influents indicated hinderance to the transmission of UV light through the samples. Based on these observations, a limited iron removal study was initiated by WES.

Iron removal using chemical oxidizers followed by gravity settling

The applications concept of iron removal that was conceived and evaluated by WES was that hydrogen peroxide is added initially as a pretreatment technique to initiate formation of iron oxides. The iron oxides are then subsequently removed via settling or filtration. The residual hydrogen peroxide remaining in the groundwater after iron removal is utilized by the chemical oxidation system that follows. James Montgomery Engineers Inc. (1985) report that, under highly oxidized conditions, reduced iron (Fe^{2+}) is converted to an oxidized state (Fe^{3+}) which then precipitates out of solution as ferrous hydroxide, $Fe(OH)_3$. Their studies indicate that a 7:1 concentration ratio of iron to oxygen is typically required to oxidize inorganic iron.

Originally, it was theorized that the iron oxides could be removed using a clarifier, but the settling rate of the iron oxides seemed quite long based on visual observations made during performance of the jar tests. Table 9 presents visual observations made on iron oxidation formation and settling rates during the oxidizer evaluations for iron removal in groundwater samples from Wells 36001 and 01061. From Table 9, the removal rate of iron seemed dependent on hydrogen peroxide dosage. Hydrogen peroxide doses less than 200 mg/ℓ did not indicate iron oxide formation until after approximately 14 hr of exposure. The 200 mg/ℓ and greater hydrogen peroxide doses almost immediately formed iron oxides and subsequent settling within the test cylinders. As the hydrogen peroxide doses were increased, so did the apparent iron removal efficiencies. The settling rate of the iron oxide solids formed during all of the iron removal experiments seemed to be quite slow. At least 2 hr were required for appreciable iron oxidation and settling to occur during any of the jar tests. Knocke et al. (1991) determined that iron and manganese oxidation kinetics were extremely rapid (on the order of seconds); however, they concluded that cation-organic compound complexes can have a significantly adverse effect on the rate of iron oxidation. It is possible that a portion of the iron present in the groundwaters may be in the form of an iron-organic complex. Higher doses of hydrogen peroxide would tend to release the complexed iron through oxidation of the organic substrate. This would explain why doses of hydrogen peroxide, much higher than stoichiometrically required to oxidize the amount of iron detected in the groundwaters (15 mg/ℓ and 54 mg/ℓ for Wells 36001 and 01061, respectively), were required to remove the iron from the groundwater samples.

Table 9
Visual Observations Made During Iron Oxidation Studies on Groundwater Samples from Wells 36001 and 01061

Oxidizer and Dose	1 Hr	2 Hr	3 Hr	24 Hr
01061 Groundwater Sample				
Initial Condition - Sample was a yellow color with no oxides present				
HP[1]-50 ppm	No oxides	A few oxides	Orange color Oxides present	Clear sample
HP-200 ppm	No oxides	A few oxides	Orange color Oxides present	Clear sample
Hp-500 ppm	Iron oxides present	Visible oxides on bottom	Sample almost clear	Clear sample
HP-1000	Iron oxide forming	Iron oxides on bottom	Sample almost clear	Clear sample
Ozone-Sparged for one hour	No oxides present	Few oxides on bottom	Some oxides present	Murky-clear sample
Air-Sparged for one hour	No oxides present	Few oxides on bottom	Some oxides present	Murky-orange sample

Note: The initial condition was a yellow-colored sample with no oxides present.
[1] HP = Hydrogen peroxide.

Based on analysis of hydrogen peroxide present within the test solutions after performance of the jar tests, little hydrogen peroxide was used during iron removal. Using a 7:1 oxygen to iron concentration ratio as suggested by J.M.Montgomery Engineers, Inc. (1982) for conversion of reduced iron to iron oxides, approximately 10 mg/ℓ and 54 mg/ℓ of hydrogen peroxide is required in the complete oxidation of the iron from Well 36001 and 01061 groundwaters, respectively. The change in hydrogen peroxide concentration during iron oxidation experiments for both waters supports this estimate. However, it is surprising that so little hydrogen peroxide was reacted during iron oxidation when considering that iron is commonly used as a catalyst for producing hydroxyl radicals from hydrogen peroxide via Fenton's reactions (see Chapter 1, Part I).

Sparging the samples with ozone did result in the formation of iron oxides (Table 9), but the precipitant formed at a slower rate and did not settle as well as those formed by the hydrogen peroxide. Hydrogen peroxide seems much more efficient than ozone sparging, plus hydrogen peroxide does not result in stripping of the volatile contaminants. Air sparging resulted in far less iron removal than either hydrogen peroxide or ozone mediated iron removal. It is possible that hydrogen peroxide addition resulted in higher and more rapid establishment of oxidized conditions than the ozone and air mediated systems. This theory is further supported by the improved removal of the iron using ozone as compared to the air system.

Based on the rate of iron oxide settling observed during the jar tests, surface overflow rates (SOR) within a clarifier removing iron oxides will have to be fairly low to achieve appreciable iron oxide removal. The use of a lamella clarifier should improve settling efficiency and increase SOR. Polymer(s) may be added to increase clarifier surface overflow rate if desired. Care must be taken to ensure that the polymers added do not adversely impact the performance of a chemical oxidation system by dramatically increasing oxidizer requirements (i.e., oxidation of polymers).

Pre and post iron removal spectrophotometer scans

As discussed in Chapter 2 of this report, the untreated groundwater and distilled water samples were scanned initially for purposes of direct comparison (Figures 8 and 9). From these figures, it can be seen that both "untreated" groundwater samples did have significant UV absorbance of the photons emitted at the 200-300 nm wavelengths.

After oxidizer addition and filtration of the iron oxides from the water samples (using 0.45 μm filters), the UV absorbances of the treated groundwater samples were analyzed using a scanning spectrophotometer. Distilled water dosed with the same hydrogen peroxide doses served as system baselines for each groundwater sample containing the similar hydrogen peroxide doses. The improvement in UV transmissivity for groundwaters 36001 and 01061, as measured by a decrease in UV absorbance, is presented in Figures 8 and 9, respectively. Both figures show that increasing the hydrogen peroxide dose resulted in increased UV transmissivity, thereby indicating that the presence of iron oxides within a UV based treatment system probably does hinder treatment due to reduced UV transmissivity. The reduced UV absorbance produced by the 50 mg/ℓ hydrogen peroxide dose for the Well 36001 groundwater (Figure 8) is surprising compared to the other doses. The rationale for this dose to perform differently from the others is not known. The test was rerun to verify the results, with the same results obtained. It may be possible that an optimum dosage exists that optimizes both UV transmissivity as well as hydrogen peroxide. This was not noted with the Well 01061 groundwater (Figure 9). However, it is possible that the range of hydrogen peroxide doses tested in the Well 36001 experiments were not within the range of the optimum dose for that groundwater.

Use of filters to remove iron oxides

The use of filtration systems may be an alternative to clarifiers for removing oxidized iron from the groundwaters. An estimation of iron precipitant effective particle diameter was evaluated by performing a sequential solids mass balance using filter papers of varying pore sizes. Tables 10 and 11 present the results of these efforts for groundwater samples 36001 and 01061, respectively.
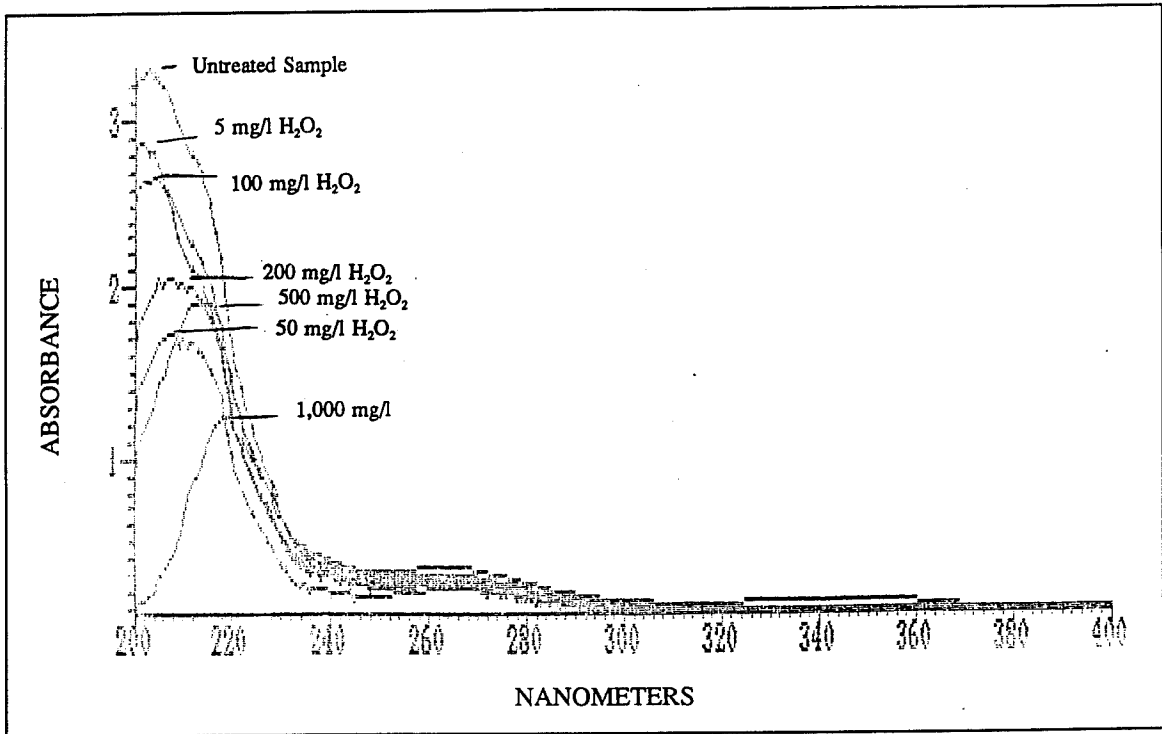
Figure 8.   UV transmissivity measurements for Well 36001

Figure 9.   UV tranmissivity measurements for Well 01061

Table 10	
Filter Size Evaluation for Well 36001 Groundwater Sample	
Filter Pore Size	**Percent Retained on Filter**
20-25 μm	2.2
2.5 μm	2.7
0.45 μm	0.4
Total retained on filters -> 5.3	

Table 11	
Filter Size Evaluation for Well 01061 Groundwater Sample	
Filter Pore Size	**Percent Retained on Filter**
20-25 μm	1.0
2.5 μm	1.0
0.45 μm	1.0
Total retained on filters -> 3.0	

As shown in Tables 10 and 11, the effective particle diameters indicate that iron removal using the filters does not appear successful. Even the 0.45 μm filter paper did not remove appreciable amounts of iron oxide from the groundwater samples. Pore sizes lower than 0.45 μm are not feasible for field systems treating contaminated groundwater.

Further investigation into iron oxide filtration was undertaken, yielding quite contradictory information. James Montgomery Engineers, Inc. (1985) report that sand filters were found to be quite successful in removing iron oxides from drinking water. They report that initially the iron oxides were poorly removed using the sand filters, but after a short period, as iron oxide solids began to build within the filter bed, interparticle charges associated with the trapped oxides tremendously enhanced removal by retaining increasingly greater amounts of iron oxides.

The filter pads used in this study had no prior build-up of iron oxides within the filter matrix; thus, enhanced removal was not established. Compared to the J.M. Montgomery Engineers, Inc. information, the results gained during this study may not reflect what can actually be achieved using filter systems. It is also realized that comparison of laboratory membrane filters to multimedia filters is difficult at best. The use of polymers may also enhance iron oxide filtration. More detailed studies on iron removal techniques should be performed if treatment of the groundwaters using any process that may be adversely hindered due to excessive build-up of iron oxides is proposed.

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Examples of such technologies include UV based chemical oxidation systems, air stripping units, aerobic bioreactors, and, possibly, activated carbon adsorbers. These studies should not be initiated unless pilot studies indicate that the actual groundwater influent entering the candidate treatment units will pose iron oxidation and subsequent operational problems.

Evaluation of Iron Fouling

The field evaluations on iron oxide formation proved quite interesting in that iron fouling was found not to be as prolific as originally thought based on the bench experiments. As discussed in Chapter 2, Well 01061 groundwater was used in this phase of the study because of ease of access with equipment and to electrical utilities. Although Well 36001 was found to have a greater potential for excessive iron oxidation, the bench studies at WES indicated that oxidation of the iron in the Well 01061 should also take place in the presence of an oxidizing agent.

Initially, a 1-ℓ chemical oxidation bench unit was set up at the old South Plants Treatment System Complex. Samples from Well 01061 were transported in 30 gal aliquots to the system using 35-gal drums. Approximately 48 ℓ of groundwater were treated using the bench system. Visual observations of the interior of the reactor during operation indicated that small amounts of iron oxide were present on the reactor bottom. Very little iron scumming was observed on the quartz tube (immersion well) housing the 200 W MP-UV lamp. The average total iron concentration measured using the HACH portable spectrophotometer in the Well 01061 groundwater influent to the reactor was 0.76 mg/ℓ. This value is significantly lower than the iron concentrations measured at WES. This indicates that much of the iron present in the groundwater was removed via air oxidation and subsequent settling within the drums during transport of the drums and MP-UV system operation. Measurement of the iron concentrations in the bench system effluents were not successful because the residual hydrogen peroxide present within the effluent interfered with the analyses.

At the end of the day, the untreated and treated Well 01061 groundwater was taken to the CERCLA Wastewater Treatment Plant for further treatment as required by RMA protocol. When the contents of the bench system influent drum were emptied, a large amount of iron oxides was found in the bottom portion of the drum. This indicates that much of the iron within the groundwater influent fed into the reactor was removed through oxidation with the air in the drum headspace. This observation is consistent with the observations made by WES technicians during collection of groundwater samples from the RMA North Boundary Treatment System over the past few years for a variety of system operations oriented activities.

The complete bench system was moved to the Well 01061 site to prevent loss of iron via contact with air during transport and storage. As mentioned in Chapter 2, the electrical generators used for the electrical supply at the well

site could not handle the electrical power surging of the peristaltic pumps. Approximately 25 ℓ of groundwater was treated in spite of electrical difficulties. No signs of iron oxidation within the reactor were noted. Since 25 ℓ are only 25 reactor volumes, little information could be derived from this effort.

Since the electrical system could not handle the reactor system load, the reactor system was moved back to the Old South Plants Treatment System Complex. Approximately 48 more liters were treated. Influent was supplied using 5-gal plastic pails that were kept covered to reduce air exposure. Few iron oxides were observed within the pail bottom during this effort. A small amount of iron oxide was observed within the reactor, but no signs of scumming could be found on the quartz tube.

The results of the field efforts are considered of limited value. Observations made during this effort are in agreement with the laboratory studies performed at WES which indicate that the iron REDOX equilibrium of RMA groundwater is indeed very sensitive. The field studies also indicated that iron oxide formation is possible within an oxidation reactor, but not as prevalent as originally thought. Pilot testing should be performed to assess the adverse impacts to system performance based on the results of this effort and past experiences concerning RMA groundwaters and their well-documented tendency for producing iron oxides. A key observation made during this study is that design of a system treating groundwaters similar to the ones tested in this study should include provisions for cleaning oxidized iron sludge from influent storage tanks.

Chemical Oxidation Runs

Contaminant removal due to stripping

Many of the contaminants present in both groundwater samples are volatile in nature. Chemical oxidation processes utilizing ozone require sparging of ozone enriched air into the reactors. The fate of VOCs present in both groundwaters was investigated through performance of several mass balance techniques.

Partitioning of a compound from the liquid phase to the gas phase due to the introduction of a gas stream into the liquid through vigorous and intimate air contact, is often referred to as "stripping." Sparging of a gas into liquid solutions containing volatile compounds, regardless of rate, will result in the partitioning of volatile compounds from the liquid phase into the gas phase (Thibodeaux 1979). However, the amount of contaminant that is stripped from solution during sparging is dependent on gas flowrate, bubble diameter, the Henry's Law Constant of the compound of interest, and the reactivity of the compound toward any chemical species present in the gas stream such as

ozone, hydroxyl radicals, or any other oxidizer species that are produced (Roth 1992).

Removal of any contaminant from an aqueous solution, within a treatment system that is comprised of ozonated air sparging and/or UV photolysis (*PHOTO*), may be described as presented below:

$$-dC/dt = ST + OX_p + OX_{so} + PHOTO$$

where

$-dC/dt$ = rate of net contaminant removal

ST = rate of contaminant removal attributable to stripping

OX_p = rate of contaminant removal attributable to oxidation by parent oxidizer (ozone)

OX_{so} = rate of contaminant removal attributable to secondary oxidizers (hydroxyl radicals)

$PHOTO$ = rate of contaminant removal attributable to direct UV photolysis

Sparging experiments

The first technique used in this study to estimate the amount of VOC removal achieved due to stripping in UV/ozone and peroxone systems was the sparging experiment. This method of evaluating mass balance is flawed in that it does not differentiate between stripping (*ST*), oxidation by the parent oxidizer (*OX$_p$*), oxidation by the secondary oxidizer species (*OX$_{so}$*), and direct photolysis (*PHOTO*), if UV irradiation is applied.

When sparging only air, all contaminant removals can be attributed to stripping. The sparging of the ozonated air, which was used in the ozone based chemical oxidation runs, involves contaminant removal via stripping (*ST*) and oxidation by ozone (*OX$_p$*). Unfortunately, in experiments of this type, it is impossible to differentiate between the two removal mechanisms. Removal of the VOCs during the ozonated air sparged runs can be due to either ST, OX$_p$, or both. The peroxone runs are even more complex. All of the peroxone runs serve as a means of collectively assessing contaminant removal via all pathway terms, except the direct photolysis term. Like the ozonated air sparged experiments, the peroxone sparging tests do not allow differentiation between the various removal terms.

Since it is impossible to differentiate between the various removal mechanisms, it is also impossible to estimate the amount of removal attributable to

stripping (ST) alone. For example, removal of a contaminant in the air sparging run is due to stripping only. Removal of the contaminant due to the sparging of ozonated air into the same water is due to both stripping and ozonation. The extent of removal attributable to either mechanism cannot be determined using sparging data. Therefore, data produced from this set of experiments serve as a strong "worst case" estimate of the extent of stripping occurring within ozone based AOPs.

Figures 10 through 13 present the results of sparging runs for the Well 36001 groundwater. Figure 10 presents the air, ozonated air, and ozone (in the presence of a 5.0 mg/ℓ hydrogen peroxide dose) sparging benzene removal runs for Well 36001. There is a distinct difference between the air sparged run and the two oxidizer based runs. This data tends to agree with the work of Kuo and Soong (1984) which indicated that benzene is very reactive toward ozone. The peroxone run seemed to have approximately the same benzene removal rate as the ozonated air sparged run. This is somewhat surprising since the peroxone system does produce hydroxyl radicals that are more powerful oxidizing agents than ozone.
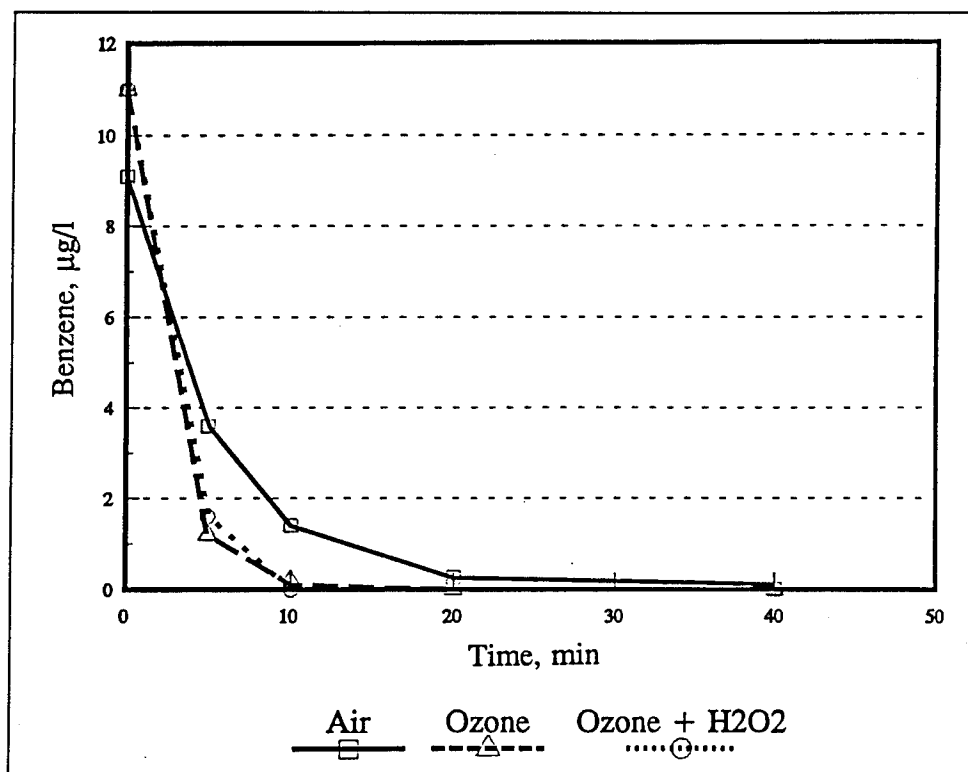
Figure 10. Benzene treatment comparisons for Well 36001

Figures 11, 12, and 13 present similar results for TCE, chloroform, and methylene chloride, respectively. All of the VOCs followed the same trend exhibited by benzene. Peroxone generally had the highest removal rate, followed closely by ozonation, with air sparging having the slowest removal rate.

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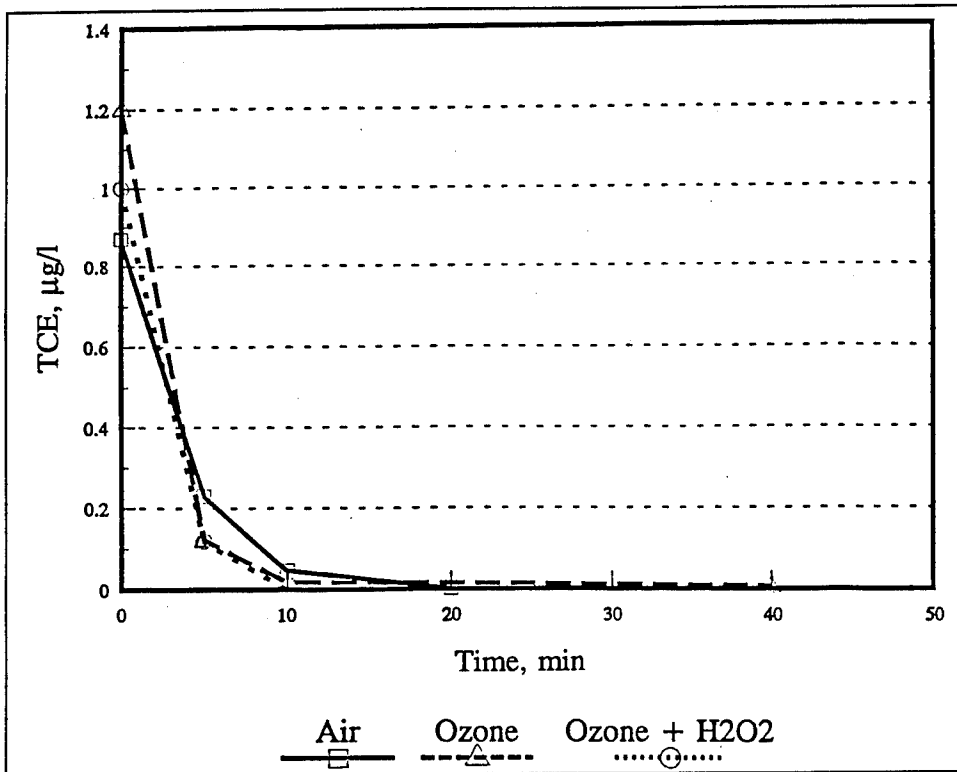
Figure 11. TCE treatment comparisons for Well 36001
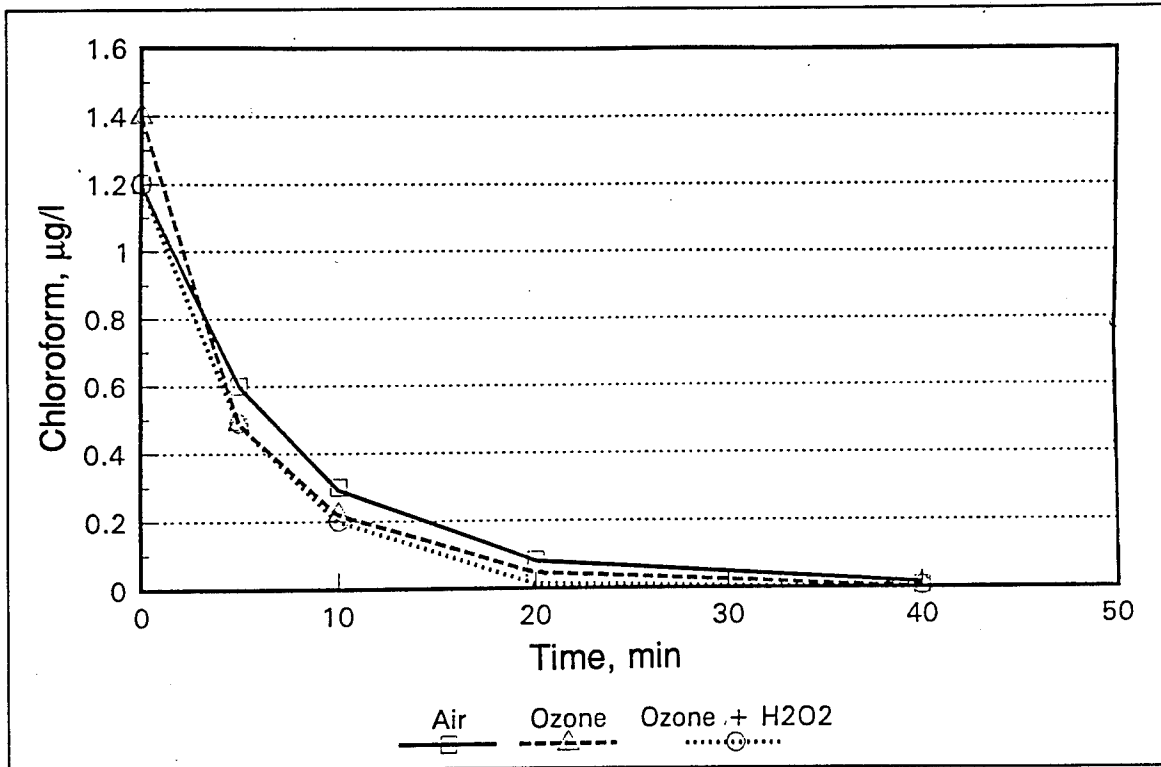
Figure 12. Chloroform treatment comparisons for Well 36001
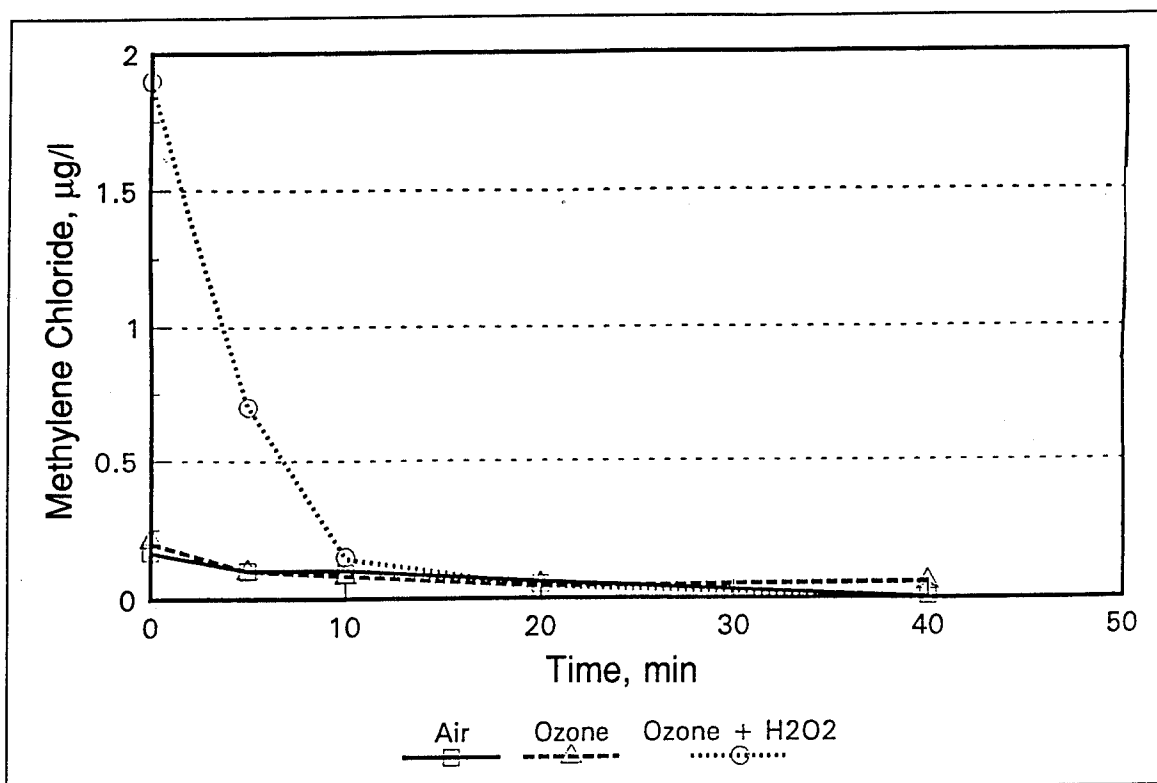
Figure 13. Methylene chloride treatment comparisons for Well 36001

Figures 14, 15, 16, and 17 present the sparging experiments for benzene, TCE, chloroform, and methylene chloride in groundwater samples from Well 01061, respectively. Figures 14 through 17 indicate that the VOC sparging data for Well 01061 groundwater were somewhat different from those obtained with the Well 36001 groundwater. The presence of oxidizing agents had a much more pronounced impact than the Well 36001 runs. The more oxidizing the system, the greater the removal rate.

Chloroform has been traditionally considered a difficult-to-oxidize compound. These data tend to contradict this theory. Oxidation is apparently occurring between chloroform and the oxidizers upon review of Figures 12 and 16, and chloroform seems to be more reactive toward the oxidizers than previously thought. This would tend to support the use of AOPs for removal of chloroform (UV based or not) from contaminated groundwaters.

In summary, this set of experiments yielded mostly qualitative results. It can be concluded that stripping within air sparged reactors does occur. The extent of stripping due to the presence of oxidizers cannot be assessed because of the lack of differentiation between removal mechanisms. The oxidizer sparged system did have higher removal rates as compared to the air sparged systems.
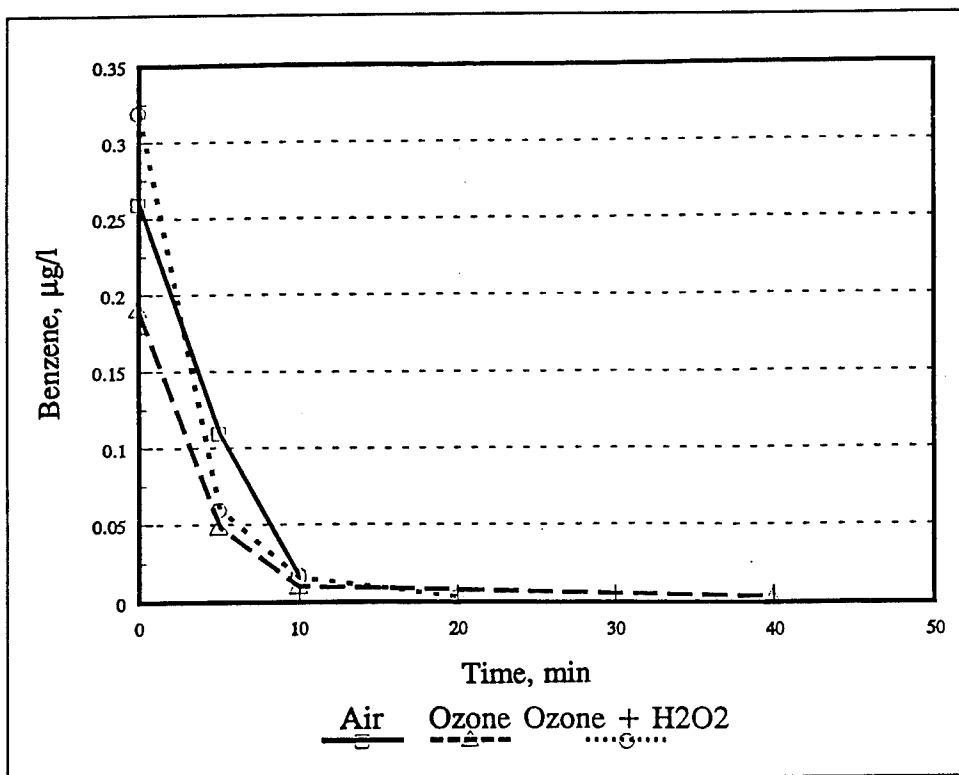
Figure 14. Benzene treatment comparisons for Well 01061
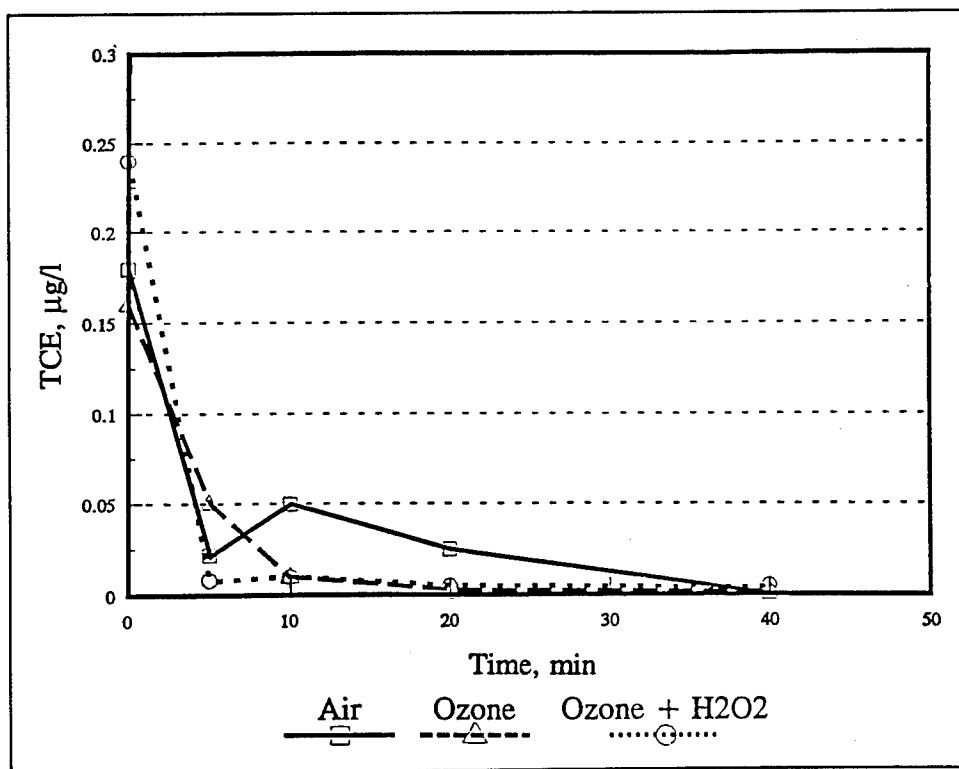
Figure 15. TCE treatment comparisons for Well 01061
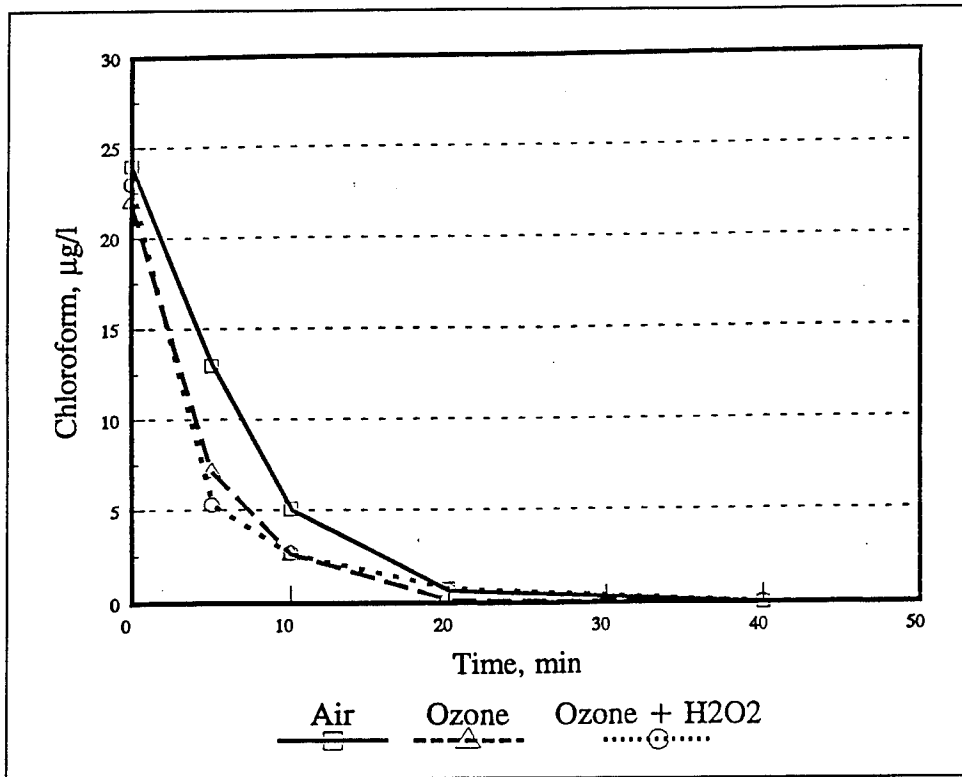
Figure 16. Chloroform treatment comparisons for Well 01061
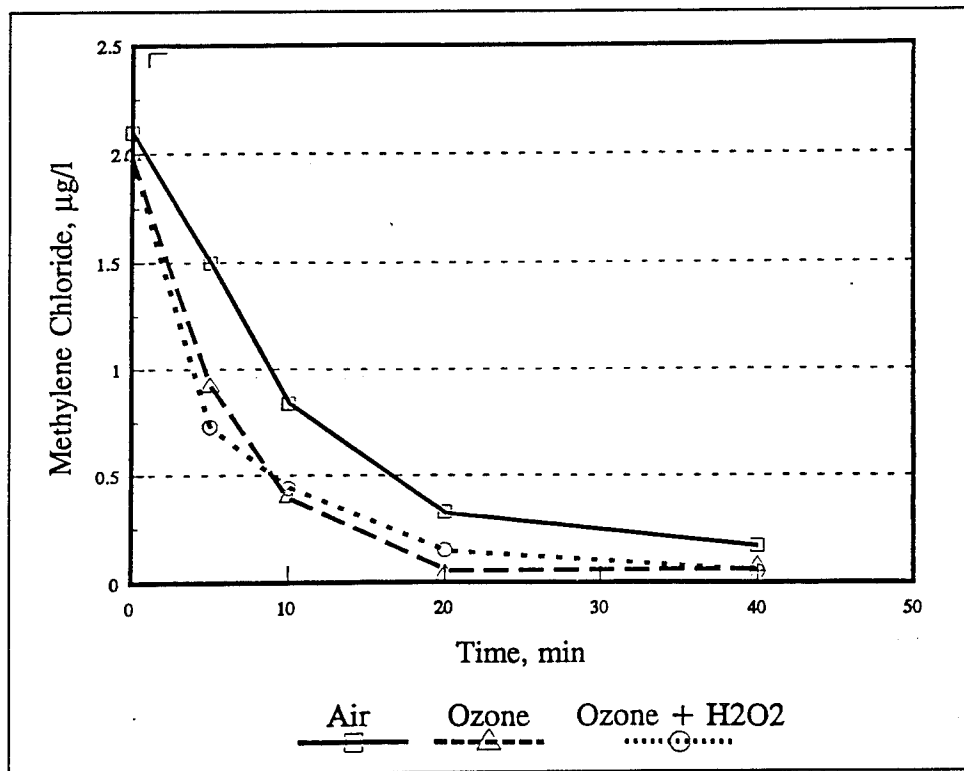
Figure 17. Methylene chloride treatment comparisons for Well 01061

Tenex traps

The use of Tenex traps was a second technique employed to estimate the fate of VOCs in the ozone based systems. This technique also did not result in data that could be used to assess the amount of contaminants stripped from the sparged systems. No trends in terms of mass accumulation and flowrate were noted upon review of the various mass amounts versus flowrate data. The lack of trending prevented selection of an appropriate retention time for the process gas within the traps. Since no clear-cut retention time could be determined, the percentage of contaminant removal attributable to stripping based on data from all five trap gas retention times was calculated. Since this technique did not provide reliable data, only the ozonated air sparged runs were performed.

Tables 12 and 13 present the Tenex trap based estimates of VOC removals for the groundwater samples for Well 36001 and 01061, respectively, using ozonated air as the sparged gas. The data presented in Tables 12 and 13 are considered of little value because of the lack of closure of the mass balance. No conclusions can be drawn from these data.

PID off-gas analyses

The PID off-gas analyses for the air sparged, ozonated air sparged, peroxone, and UV/ozone runs for Wells 36001 and 01061 at no time produced readings greater than 2.0 ppm during any of the experiments. This observation is important because it indicates that air pollution may not be of concern when considering the low concentrations of VOCs (and water vapor and ozone) detected in the off-gases using the PID.

Batch studies

Figure 18 presented the results of the batch oxidation runs for benzene using peroxone with a 1.0 mg/ℓ hydrogen peroxide dose and a sparged ozone peroxone with a 10 mg/ℓ hydrogen peroxide dose (semi-batch). Well 36001 was used as the test influent for this run. The averaged sparged ozone run is the numerical average of all the peroxone runs using 10 mg/ℓ hydrogen peroxide while ozone was continuously sparged into the reactor. From Figure 18, the true batch system apparently became ozone limited very quickly into the reaction. However, distinct oxidation of some of the benzene did occur, thereby indicating that benzene is indeed susceptable to oxidation by parent oxidizers and secondary radical species.

Figure 19 presents comparisons of batch to semi-batch TCE runs for both groundwaters. As with the benzene data (Figure 18), the sparged data represent averaged run data. From Figure 19, TCE did indicate susceptibility to oxidation. The rate of oxidation in the Well 36001 groundwater seems to be

Table 12
Well 36001 Groundwater VOC Stripping Estimates Using Tenex Traps

Analyte	Flow, ml/min	Percent Removal
Methylene Chloride	5	261.7
	10	192.3
	20	174.8
	30	99.8
	40	9.7
Chloroform	5	1,299.6
	10	1,050.5
	20	1,025.1
	30	782.9
	40	20.7
TCE	5	0.63
	10	0.89
	520	0.98
	30	0.63
	40	2.6
Benzene	5	0.93
	10	1.1
	20	1.6
	30	1.3
	40	3.6
T-Xylenes	5	427.5
	10	39.1
	20	201.9
	30	174.0
	40	139.0

dependent on the presence of ozone in the solution. The Well 01061 data indicate that sufficient solubilized ozone must have been present to generally follow the trends exhibited by the semi-batch data.

Figure 20 presents the batch versus semibatch data for chloroform in Well 01061 groundwater samples. This figure indicates some oxidation of chloroform in the batch system. Quite surprisingly, when averaged, the

Table 13		
Well 01061 Groundwater VOC Stripping Estimates Using Tenex Traps		
Analyte	Flow, ml/min	Percent Removal
Methylene Chloride	5	8.5
	10	14.2
	20	30.7
	30	168.9
	40	736.6
Chloroform	5	2.8
	10	4.3
	20	4.6
	30	9.4
	40	77.4
TCE	5	7.1
	10	0
	520	1.0
	30	1.5
	40	1.0
Benzene	5	65.4
	10	5.1
	20	22.3
	30	10.6
	40	6.5
T-Xylenes	5	5,510.8
	10	85.9
	20	1,861.7
	30	668.3
	40	529.9

semi-batch data indicate little or no chloroform removal. The rationale for the overall poorer performance of the semi-batch system to the batch system is not known. It is possible that the semi-batch runs did have problems with poor sample matrix which adversely impacted hydroxyl radical chemistry.

Figure 21 presents the methylene chloride batch data in which peroxone was compared to ozonation. From this figure, the benefits of hydrogen peroxide addition to ozone (i.e., peroxone) is highlighted by an increase in
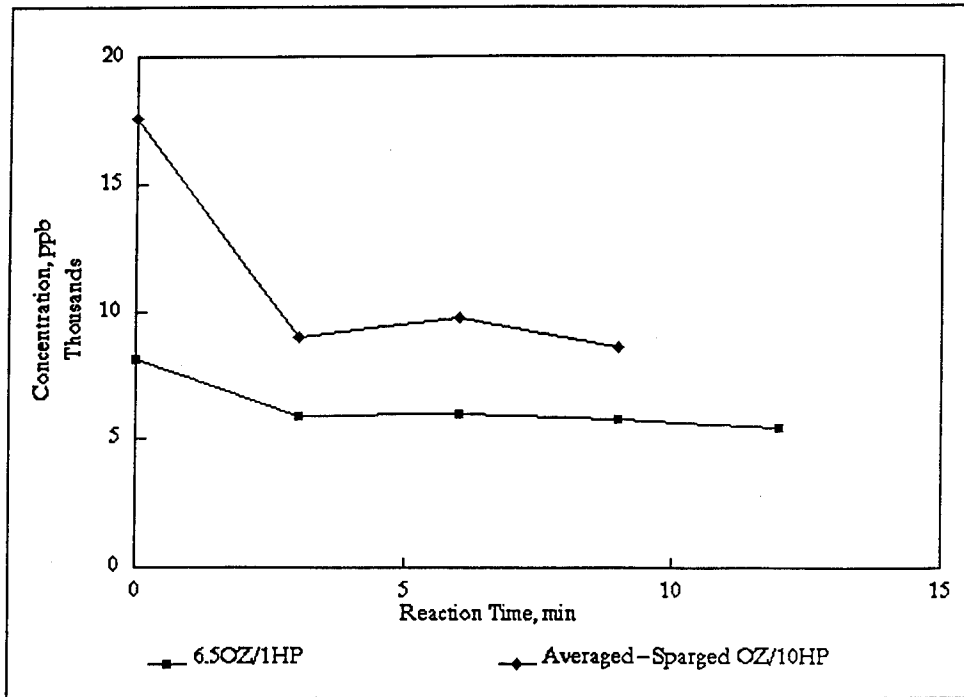
Figure 18. Benzene batch oxidation kinetic studies for Well 36001
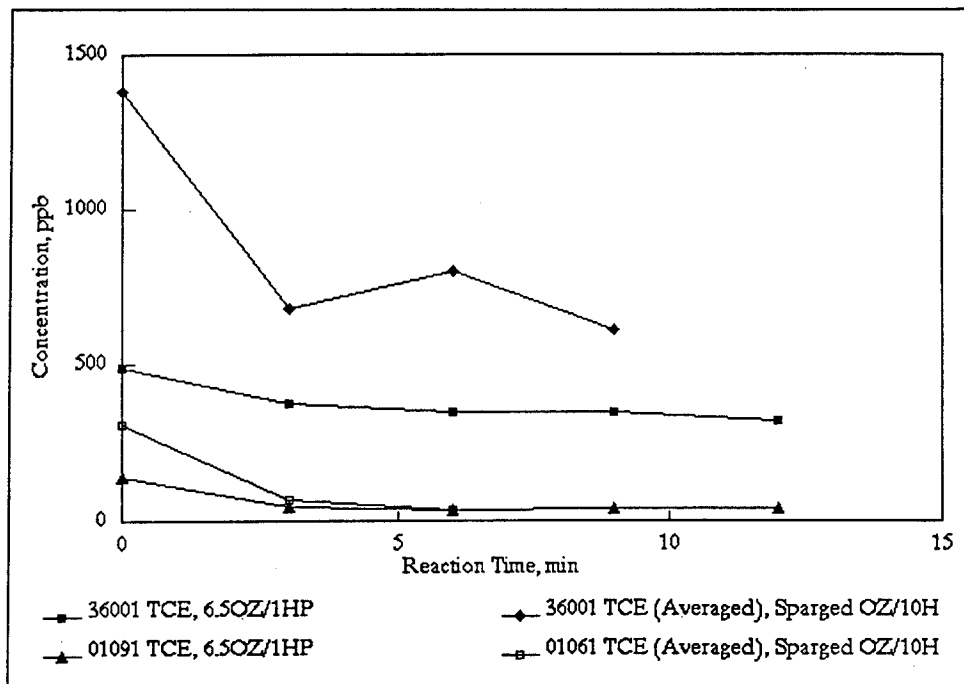
Figure 19. TCE batch oxidation kinetic studies
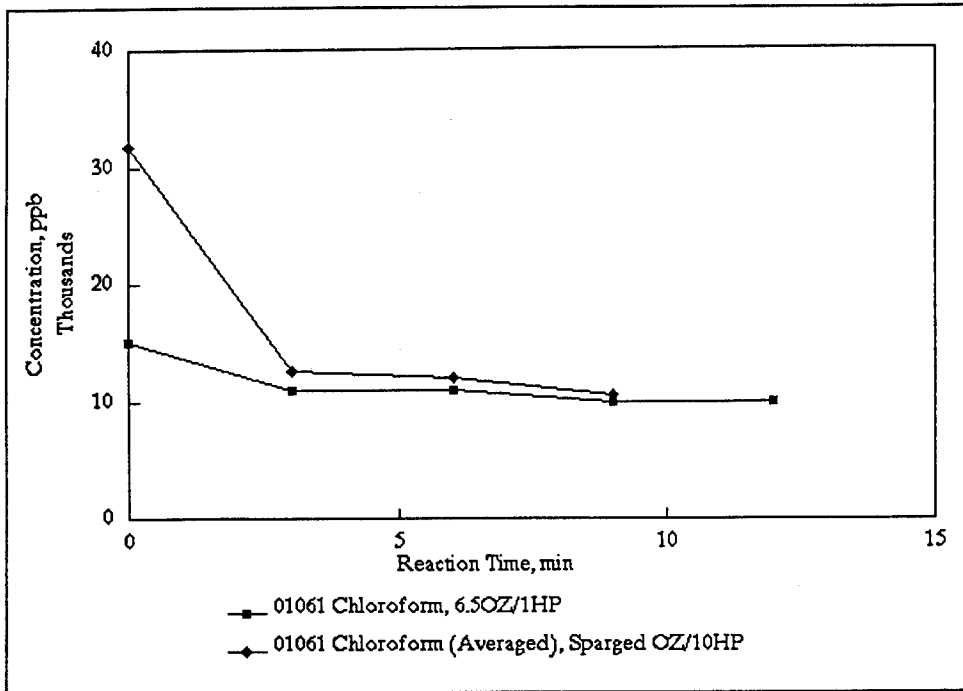
Figure 20. Chloroform batch oxidation kinetic studies
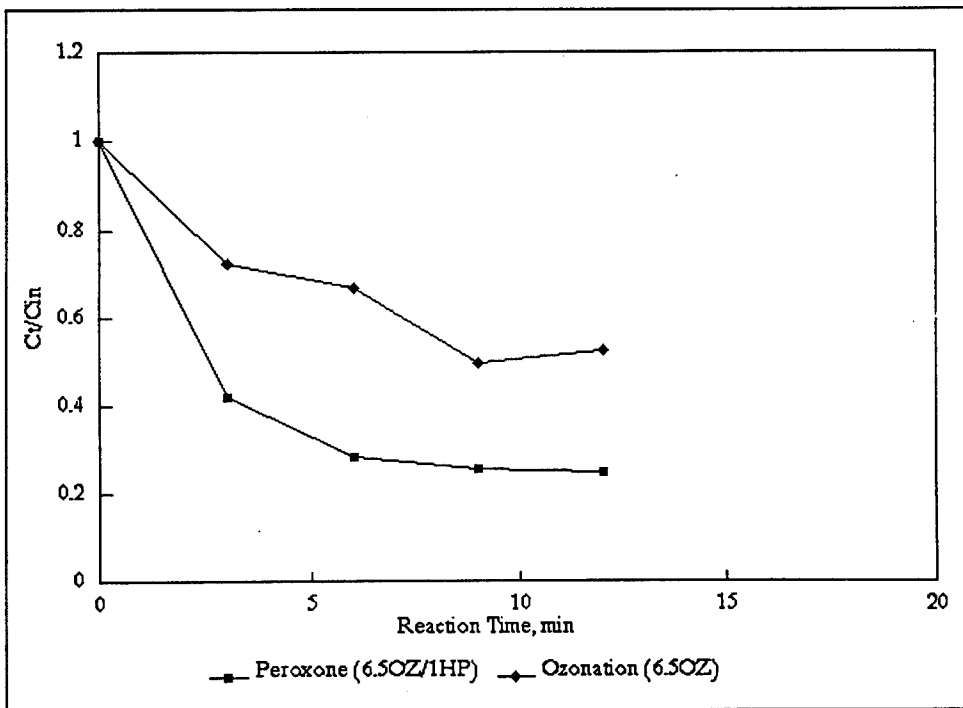
Figure 21. Comparison of peroxone to ozonation - Methylene chloride

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degradation rate. This figure also indicates that methylene chloride is reactive to oxidizer species. Figure 22 presents the methylene chloride batch versus semi-batch data for both groundwaters. These data indicate that a significant portion of methylene chloride removal may be attributable to oxidation and not volatilization during ozonated air sparging. The Well 01061 initial data point has a poor fit, but otherwise these data follow the same trend as the semi-sparged data.
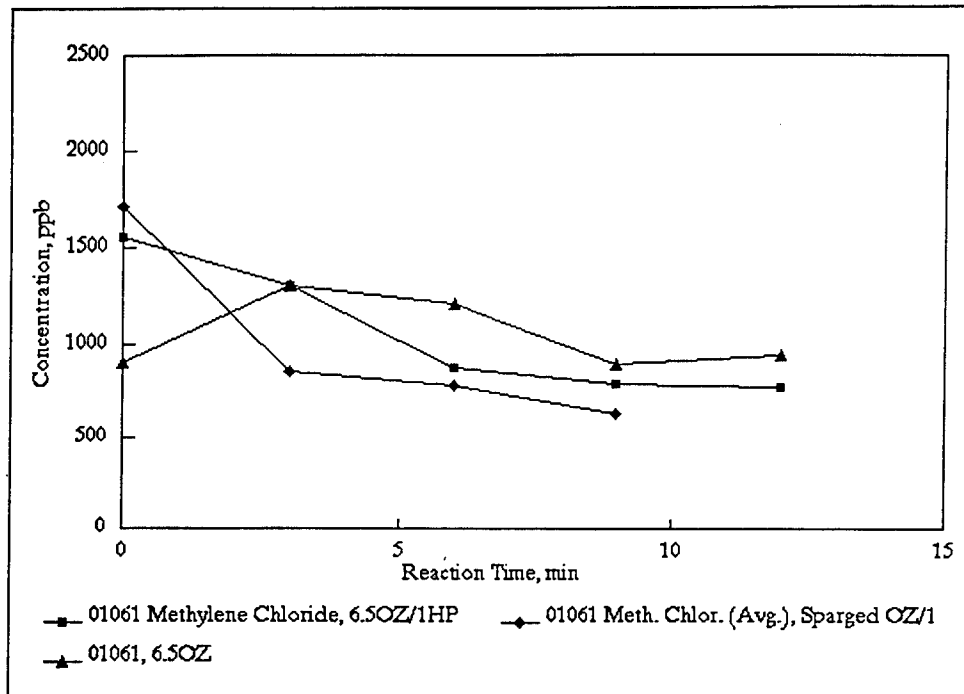
Figure 22. Methylene chloride batch oxidation kinetic studies

Summary

The results from the mass balance experiments are somewhat ambiguous in that an exact estimate on the extent of stripping occurring in the ozone based system cannot be made. A very conservative estimate (worst case) of VOC stripping can be made using the data obtained from the sparging tests. The PID tests indicate that the highest VOC concentration in the reactor off-gases is only 2.0 ppm.

The stripping estimates presented in the preceeding discussions are valid only for the Well 36001 and 01061 groundwater samples. Other groundwater samples will be affected by different mixtures of organics (impacting the cosolvency effects of VOC desorption from the water phase into the gas phase) or different levels of benzene (the rate of benzene desorption from an

aqueous solution is dependent on the concentration gradient of the contaminant [Thibodeaux 1979]).

The batch data indicate that all of the VOCs indicate some degree of reactivity toward the chemical oxidizers present in the reactors. These data, although circumstantial in nature, do present some evidence that oxidation is a major pathway for VOC removal.

Results of Chemical Oxidation Runs

The results of the various chemical oxidation runs for both groundwater samples are presented below. Tables 3 through 6 present descriptions of each chemical oxidation run performed during this study using Wells 36001 and 01061, respectively.

None of the runs utilizing hydrogen peroxide as a stand-alone oxidizer (i.e., hydrogen peroxide added without benefit of UV irradiation or ozone addition) resulted in removal of any contaminants. The addition of inorganic catalysts to the hydrogen peroxide alone system did not improve contaminant removal. In light of the poor results achieved using hydrogen peroxide as a stand-alone oxidation technology, these runs will not be further discussed. The addition of UV or ozone is required to make hydrogen peroxide an effective oxidizer for treatment of the RMA groundwaters evaluated in this study.

Interpretation of run analytical results

Interpreting the results from the chemical oxidation runs proved to be somewhat difficult due to the heterogeneity of the samples in terms of analytical detection limits, variable test influent concentrations, and iron oxides present in the test influents (these difficulties will be discussed later). In some cases, runs with identical treatment conditions had very differing results. The main cause of variability in treatment performance between similar runs is believed to have been caused by interference from iron oxides present in the influent samples. As stated earlier, the amount of iron oxides present varied greatly between runs. As the 5-gal pails containing the samples were opened for removal of samples, oxygen was introduced into the pails. Once a pail was opened, the presence of oxidized iron in the samples tended to increase over time. Careful inspection of several pails indicated that the source of the oxidized iron was not from the steel pails. No indication of corrosion within the pails was observed upon visual inspection. Therefore, it is believed that the source of oxidized iron in the groundwater samples was the groundwater.

Varying analytical detection limits at the various sample times during the same run also made evaluation of the results difficult. Reportable detection limits for a particular sample become lower as the sample matrix is cleaned due to a variety of reasons which include reduction of contaminant levels. As

the AOPs reduced the organics in the samples, lower detection limits were achievable.

In order to analyze the primary contaminants in groundwater samples from Wells 36001 and 01061, which were benzene and chloroform, respectively, sample dilutions were necessary. Dilution of samples tends to reduce secondary contaminant concentrations below those that can be analyzed. Examples of secondary contaminants include toluene, T-xylenes, TCE, and methylene chloride. Once the primary contaminant levels were reduced during treatment, the extent of dilution was also reduced, thereby allowing for improved analysis of the secondary contaminants.

Reductions in detection limits are indicative of organic contaminant treatment. For purposes of data evaluation, reductions in detection limits were construed as increased treatment.

Another factor in evaluation of the results was variable influent (t = 0) contaminant levels. Variability in influent levels was attributable to the loss of VOCs after the pails were opened. Every time samples were removed from a pail, VOCs were released and the headspace within the pail increased. Increased headspace within a sample container increases the total capacity of air available for VOC transfer (i.e., volatilization). Every time a pail was opened, more VOCs were released. Also, since high volumes of sample were collected from each well, variances in sample strength could also have occurred within the well. Varying sample strengths during well pumping would cause variability between sample pails.

The impact of the individual test influent matrix on the test reproducibility cannot be overstated. The high detection limits associated with both groundwater samples are inherit to testing very complex samples. Variable amounts of oxidized iron from one run to another make evaluation and drawing of firm conclusions difficult. However, based on replication of testing and close evaluation of trending in terms of contaminant degradation rates and reduction in analytical detection limits, conclusions as to the suitability of AOPs for treating these groundwater samples were made.

Well 36001 chemical oxidation runs

Benzene. Table 14 presents the MP-UV photolysis based chemical oxidation runs performed on Well 36001 groundwater samples. Run V41 evaluated direct MP-UV photolysis (i.e., no oxidizer present). Although approximately 4g of benzene was degraded during Run V41, the overall benzene removal rate achieved was relatively slow compared to some of the other runs. The addition of 50 mg/ℓ hydrogen peroxide (Run V42) did little to improve benzene degradation in the MP-UV photolysis system.

Runs V44, V45, V53, and V74 indicated that hydrogen peroxide doses between 100 mg/ℓ and 500 mg/ℓ added to the MP-UV photolysis system

Table 14
Well 36001 Groundwater Chemical Oxidation Runs-Benzene Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V70	V74	V87	V72	V69	V45
UV Lamp	MP[1]	MP	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO	NO	NO
$[H_2O_2]$	1,000	500	500	500	500	200
[Catalyst]	NO	NO	NO	$100WO_3$	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time, min	Benzene Concentration , $\mu g/\ell$					
0	6,640	7,140	20,300	13,680	5,360	19,100
3	--	--	--	--	--	15,440
5	1,320	4,390	--	3,270	2,750	15,085
10	4,220	--	2	1,380	1,140	8,650
20	--	--	<1	--	--	--
30	6,700	362	<1	4,880	10,270	--
40	--	--	<1	--	--	--

Run No.	V110	V53	V44	V104	V42	V41
UV Lamp	MP	MP	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO	NO	NO
$[H_2O_2]$	250	100	100	50	50	NO
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO	NO	NO

Reaction Time, min	Benzene Concentration , $\mu g/\ell$					
0	15,000	22,750	25,000	--	24,540	22,100
3	--	334	4,910	--	17,000	19,620
5	790	80	1,260	1.2	17,250	18,900
10	100	3	5,000	<1	15,400	17,620
20	--	1	--	<1	--	--
30	1.7	--	--	--	--	--
40	--	--	--	<1	--	--

[1] MP = Medium pressure UV lamp used.

dramatically improved benzene degradation rates. The 100 mg/ℓ hydrogen peroxide dosed runs (V44 and V53) had differing degradation kinetics in that the Run V53 degradation rate was much more rapid than Run V44. The

target benzene treatment goal of 5.0 $\mu g/\ell$ was reached within 10 min of treatment in Run V53. Run V45 (200 mg/ℓ hydrogen peroxide dose) showed relatively lower degradation rates and only removed approximately 55 percent of the benzene within 10 min of treatment. A review of the run data sheet for Run V45 indicates that comparatively more iron oxides were present within the reactor than in Run V53, thereby explaining the poorer removal.

The two 500 mg/ℓ hydrogen peroxide dosed MP-UV photolysis runs (V74 and V87) showed differing results. Run V87, with an initial concentration of 20,300 $\mu g/\ell$, resulted in an excellent degradation rate by reaching target levels within 10 min of treatment. Run V74 which had a much lower initial benzene concentration (7,140 $\mu g/\ell$) only reached a benzene concentration of 362 mg/ℓ within 30 min of treatment.

Based on review of the Run V70 results, the addition of a 1,000 mg/ℓ hydrogen peroxide dose to the MP-UV photolysis system seemed to hinder treatment. This is probably due to the increased rate of iron oxide formation within the reactor during treatment. The iron removal studies indicated that a hydrogen peroxide dose of 1,000 mg/ℓ resulted in increased iron oxidation as compared to the lower hydrogen peroxide doses (i.e., 500 mg/ℓ or less). Increased iron oxide formation during UV treatment has an adverse effect on treatment due to reduced water UV transmissivity.

The difference in performance of 100 mg/ℓ to 1,000 mg/ℓ hydrogen peroxide dosed MP-UV photolysis runs indicate just how sensitive UV based systems can be to water matrix. In the case of both the 100 mg/ℓ and 500 mg/ℓ runs, one of the two replicates of each dose had poorer water quality hindering treatment due to excessive UV absorption within the water matrix, while the other two replicates had excellent degradation kinetics.

Run V110 was designed to evaluate the benefits of iron removal prior to oxidation treatment using a 210 mg/ℓ hydrogen peroxide dose in the MP-UV system. This experiment indicated that removal of the iron oxide significantly improved degradation rates by meeting the target treatment levels within 15 min of treatment. Comparing this run to Run V45, which utilized a similar hydrogen peroxide dose (200 mg/ℓ), but only achieved 55 percent removal within 10 min of treatment, indicates the benefits of iron removal prior to oxidation treatment.

The addition of tungsten trioxide catalyst to the 500 mg/ℓ hydrogen peroxide/MP-UV photolysis system was evaluated in Run V72. These results indicate that tungsten trioxide does not improve benzene degradation rates for Well 36001 groundwater, thereby indicating little benefit in adding this catalyst.

Based on review of the data presented in Table 14, it is believed that a MP-UV reactor containing hydrogen peroxide initially dosed in the 100-500 mg/ℓ range should be able to reach target benzene treatment goals within

10 to 20 min of treatment. Control of iron oxide formation and/or removal could potentially improve benzene degradation kinetics.

Table 15 presents the LP-UV photolysis based benzene chemical oxidation runs for the Well 36001 groundwater samples. As with the direct MP-UV photolysis run presented in Table 15, direct LP-UV photolysis of Well 36001 groundwater (Run V49) resulted in little or no benzene degradation. Direct LP-UV photolysis of Well 36001 groundwater while sparging air (i.e., no ozone) into the reactor (Run V75) resulted in little or no benzene removal. This indicates that little or no benzene removal could be attributed to stripping or photolysis in the LP-UV irradiated and/or ozonated air sparged runs. This observation is in agreement with the results of the tenex trap mass balance experiments but not with the sparging studies. The air sparged experiment performed during the sparging studies did have better removal of the benzene than exhibited in Run V75.

The benefits of sparging ozone into the LP-UV photolysis system was evaluated in Runs V52 and V71. The initial benzene concentration in Run V52 was three times higher than in Run V71. Run V71 also was noted as having substantially more yellow/orange tint than what was typically observed in other runs (Appendix B). Both runs achieved at least 90 percent removal, but only Run V52 reached target levels. Run V52 was able to reach target treatment levels within 20 min, while Run V71 did not reach target levels even after 30 min of treatment. In spite of the complex water matrix and subsequent poorer benzene removal achieved in Run V71, the results achieved in Run V52 indicate promise that a LP-UV photolysis chamber with ozone sparging should result in meeting benzene treatment goals within approximately 30 min of treatment. The water quality observed in the majority of Well 36001 runs indicated that Run V52 is probably much more indicative of the degree of treatment expected using a LP-UV/ozone system.

Run V73 evaluated the benefits of adding a 200 mg/ℓ hydrogen peroxide dose to the LP-UV/ozone system. This experiment showed insignificant improvement in the degradation rate as compared to the LP-UV/ozone runs (V52 and V71). The addition of the hydrogen peroxide probably initiated the formation of iron oxides which reduced the water UV transmissivity within the reactor. The LP-UV is a low power lamp that is more sensitive to water UV transmissivity than the MP-UV because of limited photon production per volume of reactor.

In runs V43, V46, V58, V59, and V60 the feasibility of using hydrogen peroxide as an alternative oxidizer in the LP-UV photolysis system was investigated. Hydrogen peroxide doses in these runs ranged from 50 mg/ℓ to 200 mg/ℓ. These runs indicate little promise for benzene removal using the LP-UV/hydrogen peroxide combination. These data highlight the limited quantum yield achieved toward hydroxyl radical formation and subsequent benzene oxidation due to the limited hydrogen peroxide absorbance of photons emitted by LP-UV lamps (Figure 2).

Table 15
Well 36001 Groundwater Chemical Oxidation Runs-Benzene Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V60	V46	V73	V59	V43
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	NO	SAT[2]	NO	NO
[H_2O_2]	200	200	200	100	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$				
0	22,980	12,810	6,960	23,800	10,220
3	14,680	10,340	--	16,300	9,660
5	16,060	9,680	563	16,700	9,060
10	12,730	5,670	2,010	15,280	2,040
20	11,900	--	--	15,220	2,040
30	--	--	24J	--	--
40	--	--	--	--	--

Run No.	V71	V52	V75	V49	V58
UV Lamp	LP	LP	LP	LP	LP
[O_3]	SAT	SAT	AIR[3]	NO	NO
[H_2O_2]	NO	NO	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$				
0	7,080	23,970	6,950	13,160	21,950
3	--	2,590	--	5,750	17,801
5	4,570	981	5,830	11,640	18,000
10	1,820	7<20	5,500	10,770	18,600
20	--	<20	--	--	17,600
30	483	--	7,870	--	--
40	--	--	--	--	--

[1] LP = Low pressure UV Lamp used.
[2] SAT = Ozone used as an oxidizer.
[3] AIR = Air sparged.

Table 16 presents the results from the benzene peroxone runs for the Well 36001 groundwater samples. As suggested in literature (Glaze and Kang 1988) and contradictory to what one would expect based on typical chemical kinetics (Espension 1981), increased hydrogen peroxide to ozone (H:O) ratios (i.e., > > 10:1 based on concentration) did not significantly improve treatment. This is exemplified by Run V68 which consisted of a 50 mg/ℓ hydrogen peroxide dose which equates to an approximate 12:1 H:O concentration ratio (Note: this ratio is based on a residual ozone concentration of 4.0 mg/ℓ which is typically achieved within 10 min of non-reactive ozonated air [1.5 percent ozone by weight air feed] sparging). In Run V68 (50 ppm hydrogen peroxide), 25 percent benzene degradation was obtained within 20 min, while Run V54, which was a 10 mg/ℓ hydrogen peroxide dosed peroxone run, degraded over 99 percent of the benzene and met target levels within 20 min.

Peroxone experiments with hydrogen peroxide doses ranging from 1.0 to 10.0 mg/ℓ generally reached treatment goals within 40 min of treatment. Run V112 which had a 0.25 mg/ℓ hydrogen peroxide dose achieved the most rapid benzene removal rates of all of the AOP processes evaluated. The other lower hydrogen peroxide doses (< 1.0 mg/ℓ) also had impressive degradation rates. Hydrogen peroxide doses lower than 10 mg/ℓ had reaction rates which indicated that target benzene levels may be reached within 10 min of treatment. The peroxone benzene experiments indicate much promise for the peroxone process to meet target benzene treatment levels within at least 20 min of treatment.

Total Xylenes. T-xylenes were detected in the Well 36001 groundwater at levels (approximately 800 μg/ℓ) much lower than the target treatment levels (10,000 μg/ℓ). Since removal of T-xylenes is not required, these data are presented simply to provide an estimate of the extent of T-xylene removal that will likely occur with the Well 36001 groundwater while being treated for other target contaminants that are present at levels requiring treatment.

Table 17 presents the MP-UV photolysis based T-xylene chemical oxidation runs for Well 36001 groundwater. Direct MP-UV photolysis (Run V41) did result in limited T-xylene degradation by reducing T-xylene from 852 mg/ℓ to 390 mg/ℓ within 10 min of treatment. The addition of 50 mg/ℓ of hydrogen peroxide to the MP-UV system (Run V42) did not improve the T-xylene degradation over direct photolysis.

Hydrogen peroxide doses between 100 mg/ℓ and 500 mg/ℓ added to the MP-UV photolysis system generally seemed to improve the T-xylene degradation rate (Runs V44, V53, V74, and V87). Runs V45 and V69 had the poorest T-xylene removal of all the runs using hydrogen peroxide doses in the 100-500 mg/ℓ range. This lends some confusion to the results in that it is expected that these runs should have performed as well as the 100 mg/ℓ and 500 mg/ℓ runs. The 100 mg/ℓ and 500 mg/ℓ hydrogen peroxide dosed MP-UV photolysis runs indicate that within 10 min of treatment at least 90 percent removal of T-xylenes will occur.

Table 16
Well 36001 Groundwater Chemical Oxidation Runs-Benzene Peroxone Based Systems

Run No.	V69P	V68	V67	V54	V86	V84
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT[1]	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	500	50	10	10	10	5
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$					
0	<200	25,070	14,500	20,700	19,000	20,500
3	<200	21,200	17,600	534	--	--
5	<200	19,600	19,400	237	--	--
10	<200	18,900	17,300	19	6,220	11,100
20	<200	19,100	10,400	5	435	1,260
30	--	--	--	--	26	3,450
40	--	--	--	--	1	52

Run No.	V111	V97	V85	V112	V114	V83
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	200.5	201	1	0.05	0.01	0.25
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	NO	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$					
0	13,000	2,000	16,200	15,000	14,000	20,800
3	--	--	--	--	--	--
5	250	--	--	200	270	--
10	7.9	39	4,330	<1	7.2	9,270
20	1	--	--	1.6	<1	--
30	--	0.76J	1,000	--	--	3,550
40	--	<1	<2	--	--	33J

[1] SAT = Ozone used as an oxidizer.

Review of the Run V45 test data sheets (Appendix B) indicate that the groundwater sample used in this run had a darker orange/yellow tint than

Table 17
Well 36001 Groundwater Chemical Oxidation Runs - T-Xylene Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V70	V74	V87	V72	V69	V45
UV Lamp	MP	MP	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO	NO	NO
$[H_2O_2]$	1,000	500	500	500	500	500
[Catalyst]	NO	NO	NO	$100WO^3$	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	T-Xylene Concentration , $\mu g/\ell$					
0	285	270	590	292	227J	1,100
3	--	--	--	--	--	894
5	59	193	--	117	<400	788
10	154	24	<2	127	<200	498
20	--	--	<2	--	--	--
30	219	--	<2	189	217	--
40	--	--	<2	--	--	--

Run No.	V110	V53	V44	V104	V41	V42
UV Lamp	MP	MP	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO	NO	NO
$[H_2O_2]$	250	100	100	50	NO	50
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO	NO	NO

Reaction Time min	T-Xylene Concentration , $\mu g/\ell$					
0	<520	1,100	896	--	852	708
3	--	100	175J	--	1,040	730
5	27J	3J	43J	<2	593	658
10	<10	<2	164	<2	390	587
20	<10	--	--	--	--	--
30	--	<2	--	<2	--	--
40	--	--	--	<2	--	--

[1] SAT = Ozone used as an oxidizer.

usual for this sample. The sample also contained some small solid particles
that looked like oxidized iron which made the sample appear very cloudy.
The cloudiness may explain the difference in performance of the 200 mg/ℓ
hydrogen peroxide run as compared to the 100 mg/ℓ and 500 mg/ℓ hydrogen

peroxide dosed runs. Review of the Run V69 data sheet does not indicate anything extraordinary about the influent used in this study.

As was the case with the benzene experiments, the addition of 1,000 mg/ℓ hydrogen peroxide to the MP-UV photolysis system (Run V70) resulted in relatively poor contaminant removal. Also, the addition of tungsten trioxide catalyst (Run V72) resulted in slow degradation and low removal efficiency.

The benefits of iron removal using the 210 mg/ℓ hydrogen peroxide dose was evaluated in Run V110. High detection limits reported for this initial sample (t = 0) run make assessment of the results from this run difficult. However, these data indicate significant improvement in treatment after iron removal. This observation is based on the 5-min sample (t = 5 min) which had a value of 27 μg/ℓ and the reduced detection limits which indicate an improvement in sample matrix during the subsequent sample increments.

Table 18 presents the LP-UV photolysis based T-xylenes chemical oxidation runs for the Well 36001 groundwater. Direct LP-UV photolysis (Run V49) did not degrade the T-xylenes. Run V75 evaluated the amount of stripping via gas sparging by sparging air into the LP-UV reactor. Like the similar benzene run, no T-xylenes were removed in the LP-UV/air sparged system indicating that volatilization probably accounts for a small percentage of T-xylenes removal in the UV/ozone and peroxone systems.

The addition of ozone to the LP-UV photolysis system resulted in significant degradation of T-xylenes (Runs V52). Run V71 evaluated the same conditions, but unfortunately it had high detection limits associated with it; however, this data does indicate promise for T-xylene removal using this oxidation system. Run V52 was the most successful LP-UV/ozone run, in that, approximately 100 percent removal was obtained within 10 min of treatment. This run also had the highest initial T-xylene concentration evaluated in this set of experiments. These data indicate a high potential for LP-UV/ozone processes to remove T-xylenes from this groundwater. The other LP-UV/ozone run (V71) was not as successful as Run V52, yet it did degrade at least half of the T-xylenes present within 10 min of treatment. Unfortunately, the high detection limits reported for Run V71 (200 μg/ℓ) do not allow for a thorough evaluation of T-xylene degradation kinetics.

Run V73 investigated the impact of dosing the LP-UV/ozone system with 200 mg/ℓ of hydrogen peroxide. The addition of hydrogen peroxide at the level investigated did not seem to significantly improve the T-xylene degradation rate over LP-UV photolysis and ozone addition (Runs V51 and V71). It is possible that hydrogen peroxide doses comparable to those used in peroxone systems (i.e., > 10 mg/ℓ) may be of more benefit utilizing both the UV light and ozone/hydrogen peroxide reactions as sources of hydroxyl radical formation. Unfortunately, hydrogen peroxide doses below 200 mg/ℓ were not investigated during this study. It may be warranted to investigate the benefits of adding hydrogen peroxide doses less than 10 mg/ℓ to LP-UV/ozone

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Table 18
Well 36001 Groundwater Chemical Oxidation Runs - T-Xylene
Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V60	V46	V73	V59	V43
UV Lamp	LP[3]	LP	LP	LP	LP
[O_3]	NO	NO	SAT[1]	NO	NO
[H_2O_2]	200	200	200	100	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	T-Xylene Concentration , $\mu g/\ell$				
0	918	640	275	1,038	583
3	581	424	--	617	188J
5	568	442	17J	778	253J
10	488	292J	31J	554	80J
20	432	--	--	422	--
30	--	--	<100	--	--

Run No.	V71	V52	V75	V49	V58
UV Lamp	LP	LP	LP	LP	LP
[O_3]	SAT	SAT	AIR[2]	NO	NO
[H_2O_2]	NO	NO	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	T-Xylene Concentration , $\mu g/\ell$				
0	288	1,160	287	620	1,083
3	--	142J	--	604	980
5	126	25	258	596	961
10	<200	<2	230	513	879
20	--	<40	--	--	849
30	<200	--	287	--	--

[1] SAT = Ozone used as an oxidizer.
[2] AIR = Air sparged.
[3] LP = Low pressure UV Lamp used.

systems in future studies involving potential treatment of contaminated groundwaters.

Runs V43, V46, V58, V59, and V60 evaluated the effect of adding hydrogen peroxide (50 mg/ℓ - 200 mg/ℓ) to the LP-UV photolysis system. Apparently, there is some benefit derived from adding hydrogen peroxide to the LP-UV/ozone system. This was also observed during evaluation of the benzene runs. The 100 mg/ℓ hydrogen peroxide dosed LP-UV runs (V43 and V59) showed improved T-xylene removal as compared to the 50 mg/ℓ (V58) and 200 mg/ℓ hydrogen peroxide dosed runs (V46 and V60). For groundwaters containing lower levels of organics than the two samples evaluated in this study, this system may be worthy of further investigation.

Table 19 presents the T-xylene peroxone runs for Well 36001 groundwater. The T-xylene peroxone runs generally followed the same trends as those observed in the benzene runs. The 50 mg/ℓ hydrogen peroxide dosed run (V68) generally had slower degradation than those exhibited by the lower H:O ratio runs.

Run V114 which utilized 0.01 mg/ℓ hydrogen peroxide had the best degradation rate of all the peroxone runs. A 0.01 mg/ℓ hydrogen peroxide dose yields an approximate H:O ratio of 0.0025 which is much lower than what Glaze and Kang (1990) suggest will yield appreciable oxidation rates. The 1.0 mg/ℓ to 10.0 mg/ℓ hydrogen peroxide dosed peroxone runs (except Run V67), which performed well in benzene degradation, seem capable of degrading at least 90 percent of the T-xylenes within 30 min of treatment. The lower range of hydrogen peroxide doses (< 1.0 mg/ℓ) indicated a higher removal rate than the higher doses. The lower H:O ratios may afford superior conditions for aromatic degradation than the higher ratios (i.e., > 10 mg/ℓ hydrogen peroxide doses).

Toluene. Toluene was detected in the Well 36001 groundwater at levels (approximately 150 μg/ℓ) much lower than the target treatment levels (2,400 μg/ℓ). Since removal of toluene is not required, these data are presented simply to provide an estimate of the extent of toluene removal that will likely occur when the Well 36001 groundwater is treated for the other target contaminants that are present at levels requiring treatment.

Table 20 presents the MP-UV photolysis based toluene chemical oxidation runs for Well 36001 groundwater samples. Direct MP-UV photolysis (Run V41) resulted in approximately 50 percent degradation within 10 mins of treatment.

Much like the benzene and T-xylene runs, the addition of hydrogen peroxide doses of 100 mg/ℓ hydrogen peroxide (Runs V44 and V53) resulted in significantly improved removal. The 200 mg/ℓ hydrogen peroxide dosed run (V45), although it had high detection limits associated with it, seemed to perform much poorer than the 100 mg/ℓ hydrogen peroxide dosed runs. As stated with the other aromatics, Run V45 did have a poorer sample matrix than the other runs. All of the 500 mg/ℓ hydrogen peroxide dosed runs (V69, V74, and V87) resulted in data of limited value due to high detection limits during these runs. These runs did show improvements in sample matrices

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Table 19
Well 36001 Groundwater Chemical Oxidation Runs - T-Xylene Peroxone Based Systems

Run No.	V69P	V68	V67	V54	V86	V84
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT[1]	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	500	50	10	10	10	5
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	T-Xylene Concentration , $\mu g/\ell$					
0	<400	702	493	958	530	568
3	<400	527	391J	37J	--	--
5	<400	546	597	24	--	--
10	<400	641	525	3J	186J	385
20	<400	455	<400	<2	40J	151
30	--	--	--	--	<20	194
40	--	--	--	--	<2	6J

Run No.	V111	V97	V85	V112	V114	V83
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	200.5	201	1	0.05	0.01	0.25
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	NO	NO	NO

Reaction Time min	T-Xylene Concentration , $\mu g/\ell$					
0	530	<85	664	570	530	626
3	--	--	--	--	--	--
5	6J	--	--	<20	2.8J	--
10	<2	<10	349J	<2	<2	340
15	<2	--	--	<2	<2	--
20	--	<2	237J	--	--	120
30	<2	<4	5J	<2	<	116
40	--	<2	<2	--	--	1

[1] SAT = Ozone used as an oxidizer.

Table 20
Well 36001 Groundwater Chemical Oxidation Runs-Toluene Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V70	V74	V87	V72	V69	V45
UV Lamp	MP[1]	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO	NO
[H_2O_2]	1,000	500	500	500	500	200
[Catalyst]	NO	NO	NO	100 WO_3	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO
Reaction Time min	**Toluene Concentration , μg/ℓ**					
0	46J	52	<200	105	<200	115J
3	--	--	--	<250	--	<250
5	<50	38J	--	--	12	143
10	<50	--	<100	28J	<100	<200
20	--	--	<100	<50	--	--
30	42J	<50	<100	<50	47J	--
40	--	--	<100	--	--	--

Run No.	V110	V53	V44	V104	V42	V41
UV Lamp	MP	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	SAT	NO
[H_2O_2] pH	250	100	100	50	50	NO
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO	NO	NO
Reaction Time min	**Toluene Concentration , μg/ℓ**					
0	100	225	126J	--	205J	455
3	--	11J	85J	--	<205	168J
5	1.4J	24	<50	<1	<205	193J
10	<5	--	--	--	--	--
15	<5	--	--	--	--	--
20	--	<1	--	<1	--	--
30	--	--	--	<1	--	--
40	--	--	<1	--	--	--

[1] MP = Medium pressure UV lamp used.

(which usually indicates removal of contaminants from the samples) and reductions in toluene concentrations when concentrations were reported. Also similar to the other two aromatics, the addition of 1,000 mg/ℓ of hydrogen peroxide (V70) did not result in the degradation of toluene.

Unlike the benzene and T-xylenes experiments, the addition of 50 mg/ℓ of hydrogen peroxide (Run V42) to the MP-UV photolysis system did result in significant toluene removal. In general, toluene seems to be much more susceptible to oxidation within the Well 36001 water matrix than the other two aromatic compounds, studied benzene and T-xylene. This is consistent with the results presented by Rice and Browning (1980) who found toluene to be much more reactive to chemical oxidizers than benzene.

Run V110 investigated the effect of iron removal on toluene degradation. This run indicates that removal of the iron had a dramatic positive impact on toluene removal.

Table 21 presents the LP-UV based toluene chemical oxidation runs for Well 36001. Direct LP-UV photolysis (Run V49) resulted in approximately 25 percent toluene degradation. The sparging of air into the LP-UV photolysis system (Run V75) resulted in minimum toluene removal, thereby indicating that stripping of toluene during ozonation did not contribute significantly to the removal of toluene during these runs.

As with the other aromatics, the addition of ozone into the LP-UV system (Run V52) resulted in rapid toluene degradation by removing toluene to below the target treatment goal within 10 min. Although data assessment is hindered by high detection limits, the dosing of 200 mg/ℓ hydrogen peroxide to the LP-UV/ozone system (V73) did indicate promise for similar toluene degradation kinetics to the LP-UV/ozone runs. However, there does not seem to be an obvious advantage to hydrogen peroxide addition to the LP-UV/ozone system based on comparison of the 200 mg/ℓ hydrogen peroxide dosed LP-UV/ozone run (V73) to the LP-UV/ozone runs (V52 and V71).

The addition of hydrogen peroxide to the LP-UV system (Runs V43, V46, V59 and V60) did not achieve the level of toluene removal as did the LP-UV/ozone runs based on review of toluene removal and improvements in sample matrix (marked by improved detection limits). These runs indicated that increasing the hydrogen peroxide dose from 50 mg/ℓ to 100 mg/ℓ to 200 mg/ℓ does result in improved toluene degradation. This trend was not observed during the benzene and T-xylenes runs.

Table 22 presents the toluene peroxone chemical oxidation runs for Well 36001 groundwater samples. Unlike the case for the other two aromatics studied thus far, Run V68, the 50 mg/ℓ hydrogen peroxide dose run, did achieve some toluene removal and improvements to sample matrix. Unfortunately, due to the high levels of benzene and T-xylenes remaining in the samples, the toluene detection limits for Run V68 were quite high making

Table 21
Well 36001 Groundwater Chemical Oxidation Runs-Toluene Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V43	V46	V49	V52	V58
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	NO	NO	NO	SAT[2]	NO
$[H_2O_2]$	100	200	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Toluene Concentration , $\mu g/\ell$				
0	102J	<200	132J	200	199J
3	<205	77J	61J	36J	144
5	<205	<200	<200	8J	150
10	<205	22J	111J	<1	155
20	--	--	--	<20	145

Run No.	V71	V73	V59	V60	V75
UV Lamp	LP	LP	LP	LP	LP
$[O_3]$	SAT	SAT	NO	NO	AIR[3]
$[H_2O_2]$	NO	200	100	200	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Toluene Concentration , $\mu g/\ell$				
0	55	27J	212	179J	38J
3	--	--	128J	137J	--
5	<50	<50	129	87J	<50
10	<100	9J	108J	66J	43J
20	--	--	118J	79J	--
30	<100	<50	--	--	<50

[1] LP = Low pressure UV Lamp used.
[2] SAT = Ozone used as an oxidizer.
[3] AIR = Air sparged.

direct comparison to the lower hydrogen peroxide dosed peroxone runs difficult. The lower hydrogen peroxide dosed (<10 mg/ℓ) peroxone runs (V54, V67, V68, V83, V84, V85, V86, V97, V111, V112, and V114), although plagued by high detection limits, appeared to perform as well or better in

Table 22
Well 36001 Groundwater Chemical Oxidation Runs-Toluene Peroxone Based Systems

Run No.	V69	V68	V84	V67	V86	V54
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT[1]	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	500	50	5	10	10	10
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	Toluene Concentration , $\mu g/\ell$					
0	<200	145	150J	<100	<200	169J
3	<200	27J	--	149J	--	11J
5	<200	<200	--	130J	--	4
10	<200	100	100J	<100	<100	1J
20	<200	<200	<200	<200	<100	<1
30	--	<200	<200	<10	<10	--
40	--	<5	<5	<1	<1	--

Run No.	V85	V97	V111	V112	V114	V83
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$ pH	1	1	0.50	0.05	0.01	0.25
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	NO	NO

Reaction Time min	Toluene Concentration , $\mu g/\ell$					
0	171J	<100	93J	97J	78J	185J
5	--	--	<20	<10	<10	--
10	96J	<5	0.13J	<1	<1	27J
15	--	--	<1	<1	<1	--
20	83J	<1	--	--	--	28J
30	3J	<2	<1	<1	<1	<200
40	<2	<1	--	--	--	<1

[1] SAT = Ozone used as an oxidizer.

terms of toluene degradation and sample matrix improvement compared with the 50 mg/ℓ hydrogen peroxide dosed run (V68). The 1.0 to 10.0 mg/ℓ hydrogen peroxide doses (V54, V67, V85, V86, and V97) seem to provide

optimum conditions for toluene removal in a peroxone system. Although plagued by high detection limits in some cases, almost complete removal of toluene was obtained within 20 min of treatment using the peroxone systems containing hydrogen peroxide doses ranging from 1.0 to 10 mg/ℓ.

Trichloroethene. Table 23 presents the MP-UV based TCE chemical oxidation runs for Well 36001 groundwater samples. Direct MP-UV photolysis (Run V41) yielded data of limited value due to no TCE being detected in the initial sample. However, the t = 3 min and t = 5 min TCE concentrations were reported as 1,480 μg/ℓ and 920 μg/ℓ, respectively. No limitation of TCE in the initial sample was probably caused by the high sample dilution required for analyzing the high benzene levels. Therefore, if one assumes that the actual initial TCE concentration (t = 0) for this run was at least 1,480 μg/ℓ, then removal of TCE via photolysis seems possible. The addition of 50 mg/ℓ of hydrogen peroxide to the MP-UV photolysis system (V42) did not result in appreciable TCE degradation.

Runs V74, V44, V45, V53, V69, and V87 evaluated the benefits of adding hydrogen peroxide doses ranging from 100 mg/ℓ to 500 mg/ℓ to the MP-UV system. These runs indicated much improved TCE degradation when hydrogen peroxide doses in excess of 100 mg/ℓ were added as compared to the 50 mg/ℓ dosed run (V42). There was not an appreciable difference between the 100 mg/ℓ and 500 mg/ℓ hydrogen peroxide doses in terms of TCE degradation. The 200 mg/ℓ hydrogen peroxide dose (Run V45) did not perform as well as the 100 and 500 mg/ℓ doses. Based on review of the Run Data Sheet for this run (Appendix B), the water sample used in this run was much more tinted and contained higher amounts of solids, which appeared to be iron oxides, than the other runs. This reduced quality in water matrix probably caused the poorer performance observed in Run V45. The results indicate that target TCE levels (5 mg/ℓ) could probably be reached within 20 min of treatment.

Run V70 evaluated a 1,000 mg/ℓ hydrogen peroxide dose in the MP-UV photolysis system. This run resulted in no TCE removal. The 1,000 mg/ℓ hydrogen peroxide dose probably oxidized much higher amounts of iron than the <500 mg/ℓ runs, thereby reducing UV transmissivity throughout the test solution. This result is consistent with the results from the other VOC runs.

Run V72 evaluated the benefits of adding tungsten trioxide catalyst to a 500 mg/ℓ hydrogen peroxide dosed MP-UV photolysis system. The TCE degradation achieved in this run was less than the other 500 mg/ℓ hydrogen peroxide dosed runs, except Run V69 which achieved similar results. The addition of tungsten trioxide to improve contaminant degradation does not appear promising.

The removal of iron prior to treatment was evaluated in Run V110 which used a 210 mg/ℓ hydrogen peroxide dose. Except for Run V87, this run achieved the most rapid of all the TCE MP-UV photolysis runs for Well 36001. As was observed with the other VOCs, the benefits of iron

Table 23
Well 36001 Groundwater Chemical Oxidation Runs-TCE Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V70	V74	V87	V72	V69	V45
UV Lamp	MP[1]	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO	NO
[H_2O_2]	1,000	500	500	500	500	200
[Catalyst]	NO	NO	NO	100WO$_3$	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	TCE Concentration , $\mu g/\ell$					
0	418	409	1,460	783	294	1,520
3	--	--	--	--	--	<250
5	<50	288	--	295	235	1,410
10	419	--	<1	309	<100	<200
20	--	--	<1	--	--	--
30	443	36J	<1	366	392	--
40	--	--	<1	--	--	--

Run No.	V110	V53	V44	V104	V42	V41
UV Lamp	MP	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO	NO
[H_2O_2] pH	250	100	100	50	50	NO
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO	NO	NO

Reaction Time min	TCE Concentration , $\mu g/\ell$					
0	1,200	1,840	1,780	--	2,160	<250
3	--	9J	<500	--	1,460	1,480
5	26	1J	153	0.59	1,460	1,480
10	<5	<1	<50	<1	<250	<250
15	<5	--	--	--	--	--
20	--	<1	--	<1	--	--
30	<1	--	--	--	--	--
40	--	--	--	<1	--	--

[1] MP = Medium pressure UV lamp used.

removal and subsequent improved UV transmissivity is quite significant as evident by the results from this run.

Based on review of the results of the TCE MP-UV based runs, a MP-UV system with a 100 mg/ℓ-500 mg/ℓ hydrogen peroxide dose should achieve target TCE levels within 10-20 min of treatment.

Table 24 presents selected LP-UV TCE chemical oxidation runs on Well 36001 groundwater. Direct LP-UV photolysis (Run V49) did result in approximately 60 percent removal of TCE. This percentage of TCE removal is similar to that achieved by the direct MP-UV photolysis run. This result is surprising since MP-UV lamps produce higher amounts of photons at a broader spectra than the LP-UV lamp.

Runs V52 and V71 evaluated the impact of ozone addition on TCE degradation within the LP-UV system. Run V52 was successful in meeting the TCE treatment goals within approximately 20 min of treatment. The high detection limits associated with Run V71 made it difficult to determine if target goals were met; however, it did indicate potential for meeting treatment goals. Run V75 evaluated air sparging in conjunction with LP-UV photolysis. This run indicated that the amount of TCE removal attributable to stripping is minimal. This result supports the conclusions derived during the tenex trap mass balance experiments.

Run V73 evaluated the benefits of hydrogen peroxide addition (200 mg/ℓ) to the LP-UV/ozone system. This run resulted in similar TCE degradation rates to the LP-UV/ozone runs (V71 and V52). There does not seem to be much benefit in hydrogen peroxide addition since the extent of kinetic improvement over the LP-UV/ozone is not apparent.

Runs V43, V46, V58, V59, and V60 were LP-UV photolysis runs with hydrogen peroxide dosing. Hydrogen peroxide doses evaluated ranged from 50 mg/ℓ to 200 mg/ℓ. In general, the LP-UV runs with hydrogen peroxide addition did not result in appreciable removal of TCE from the Well 36001 groundwater.

Table 25 presents the TCE peroxone chemical oxidation runs for Well 36001 groundwater samples. Run V69 evaluated a hydrogen peroxide dose of 50 mg/ℓ with the peroxone system. The results of this run had similar results as the benzene and T-xylenes runs in that no contaminant removal was achieved.

Most of the hydrogen peroxide doses less than 10 mg/ℓ (0.01 mg/ℓ to 10 mg/ℓ) resulted in appreciable TCE degradation. All of these runs, except the 0.25 mg/ℓ hydrogen peroxide dosed (Run V83), were able to meet TCE target levels (5.0 μg/ℓ) within approximately 40 min of treatment.

Table 24
Well 36001 Groundwater Chemical Oxidation Runs-TCE Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V60	V46	V73	V59	V43
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	NO	SAT[2]	NO	NO
[H_2O_2]	200	200	200	100	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	TCE Concentration , $\mu g/\ell$				
0	1,754	<200	384	1,950	1,650
3	1,160	<200	--	1,235	1,020
5	1,325	<200	35	1,360	1,000
10	1,070	<200	<50	1,200	<250
20	1,090	--	--	1,270	--
30	--	--	<50	--	--
40	--	--	--	--	--

Run No.	V71	V52	V75	V49	V58
UV Lamp	LP	LP	LP	LP	LP
[O_3]	SAT	SAT	AIR[3]	NO	NO
[H_2O_2]	NO	NO	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	TCE Concentration , $\mu g/\ell$				
0	436	<200	417	938	1,815
3	--	110	--	25	1,390
5	272	41	348	<200	1,510
10	81J	1	293	<200	1,566
20	--	<20	--	--	1,422
30	<100	--	364	--	--
40	--	--	--	--	--

[1] LP = Low pressure UV Lamp used.
[2] SAT = Ozone used as an oxidizer.
[3] AIR = Air sparged.

Table 25
Well 36001 Groundwater Chemical Oxidation Runs-TCE Peroxone Based Systems

Run No.	V69P	V68	V67	V54	V86	V84
UV Lamp	NO	NO	NO	NO	NO	NO
[O_3]	SAT[1]	SAT	SAT	SAT	SAT	SAT
[H_2O_2]	500	50	10	10	10	5
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO
Reaction Time min	**TCE Concentration , µg/ℓ**					
0	190J	2,030	1,020	1,750	1,510	1,670
3	<200	1,720	1,330	25J	--	--
5	<200	1,690	1,570	24	--	--
10	193J	1,530	1,220	3J	352	836
20	180J	1,550	<200	1	21J	143J
30	--	--	--	--	4J	309
40	--	--	--	--	<1	6

Run No.	V111	V97	V85	V112	V114	V83
UV Lamp	NO	NO	NO	NO	NO	NO
[O_3]	SAT	SAT	SAT	SAT	SAT	SAT
[H_2O_2] pH	200.5	201	1	0.05	0.01	0.25
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	NO	NO	NO
Reaction Time min	**TCE Concentration , µg/ℓ**					
0	930	<100	1,570	1,100	1,000	1,600
5	16J	--	--	16	21	--
10	1.1	<5	388	1.2	0.87J	621
15	<1	--	--	<1	<1	--
20	--	<1	184	--	--	289
30	<1	<2	5	<1	<1	129
40	--	<1	<2	--	--	2

[1] SAT = Ozone used as an oxidizer.

Chloroform. Table 26 presents the MP-UV based chloroform chemical oxidation runs for Well 36001 groundwater samples. Direct MP-UV photolysis (Run V41) resulted in appreciable chloroform degradation via photolysis alone. These results are similar to those observed by Sundstrom et al. (1986) who determined that LP-UV photolysis alone was almost as effective as the LP-UV runs with hydrogen peroxide present in terms of chloroform removal.

The 1,000 mg/ℓ hydrogen peroxide dosed Run (V70) had similar results to those of the other VOC experiments in that no chloroform degradation was observed. The 500 mg/ℓ hydrogen peroxide dosed MP-UV photolysis runs (V69, V74 and V87) had mixed results. No chloroform was removed during Run V69. Run V74 only achieved 60 percent removal within 30 min of treatment, while Run V87 achieved 99 percent removal within 20 min. Run V87 initially had twice the amount of chloroform compared to the other Well 36001 chloroform runs, yet it achieved a higher chloroform removal.

Differing results were also noted for the 100 mg/ℓ hydrogen peroxide dosed MP-UV runs (V44 and V53). Run V44 had poor removal, yet Run V53, which evaluated the same system, resulted in excellent chloroform removal. Run V45, the 200 mg/ℓ hydrogen peroxide dosed run, exhibited very poor chloroform removal. This trend was also observed for the other VOCs. As discussed previously, this run had a very complex water matrix which obviously effected VOC removal.

Much like the results of the majority of VOC runs, the 50 mg/ℓ hydrogen peroxide dosed run did not have appreciable chloroform removal. The 1,000 mg/ℓ hydrogen peroxide dosed run (V70) also did not indicate any chloroform removal.

Removal of the iron prior to treatment using a 210 mg/ℓ hydrogen peroxide dose in the MP-UV photolysis system (Run V110) proved to be quite successful. This run resulted in the most rapid removal rates of all the MP-UV runs performed. Scientific literature suggests that chloroform removal is dependent on the UV irradiation dose. This run indicates that if appropriate UV transmissivity can be achieved, then rapid chloroform removals are obtainable.

Assuming appropriate influent UV transmissivity can be obtained, MP-UV/ hydrogen peroxide systems should achieve target chloroform treatment levels within 10-20 min of treatment. As indicated by comparing the results of Run V110 to Run V45, in order to achieve significant chloroform removal, it is imperative that significant reductions in UV transmissivity inside the UV reactor are prevented or minimized.

Table 27 presents the LP-UV photolysis based chloroform chemical oxidation runs for Well 36001 groundwater samples. Direct LP-UV photolysis for chloroform degradation was evaluated in Run V49. Direct LP-UV photolysis achieved minimal chloroform degradation as compared to direct MP-UV

Table 26
Well 36001 Groundwater Chemical Oxidation Runs-Chloroform Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V70	V74	V87	V72	V69	V45
UV Lamp	MP[1]	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO	NO
[H_2O_2]	1,000	500	500	500	500	200
[Catalyst]	NO	NO	NO	100WO$_3$	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	Chloroform Concentration , $\mu g/\ell$					
0	732	760	1,720	807	639	1,540
3	--	--	--	--	--	1,410
5	943	638	--	1,240	649	1,421
10	960	--	160	1,160	616	1,324
20	--	--	18	--	--	--
30	846	218	1	749	879	--
40	--	--	<1	--	--	--

Run No.	V110	V53	V44	V104	V42	V41
UV Lamp	MP	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO	NO
[H_2O_2] pH	250	100	100	100	50	NO
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO	NO	NO

Reaction Time min	Chloroform Concentration , $\mu g/\ell$					
0	1,300	1,690	1,700	--	1,750	5,540
3	--	224	895	--	1,500	1,270
5	140	148	806	33	1,340	1,250
10	31	13	1,290	18	1,480	832
15	1.9	--	--	--	--	--
20	--	1	--	8.5	--	--
30	1.9	--	--	--	--	--
40	--	--	--	4.7	--	--

[1] MP = Medium pressure UV lamp used.

Table 27
Well 36001 Groundwater Chemical Oxidation Runs-Chloroform
Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V60	V46	V73	V59	V43
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	NO	NO	SAT[2]	NO	NO
$[H_2O_2]$	200	200	200	100	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Chloroform Concentration , $\mu g/\ell$				
0	1,820	1,120	737	1,830	1,460
3	1,350	1,100	--	1,290	1,160
5	1,370	1,100	480	1,290	1,100
10	1,349	1,060	671	1,360	955
20	1,500	--	--	1,432	--
30	--	--	45	--	--
40	--	--	--	--	--

Run No.	V71	V52	V75	V49	V58
UV Lamp	LP	LP	LP	LP	LP
$[O_3]$	SAT	SAT	AIR[3]	NO	NO
$[H_2O_2]$	NO	NO	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Chloroform Concentration , $\mu g/\ell$				
0	733	1,800	756	1,070	1,840
3	--	470	--	1,128	1,540
5	680	354	673	1,090	1,510
10	565	82	663	966	1,700
20	--	<20	--	--	1,510
30	438	--	839	--	--
40	--	--	--	--	--

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.
[3] AIR = Air sparged.

photolysis run (V41, Table 26). This is not surprising when taking into account the greater amount of photons and overall greater UV band emitted by the MP-UV lamps as compared to the LP-UV lamps.

Air sparging in the LP-UV photolysis system (Run V75) did not result in any removal of chloroform. This result is surprising because of the volatility of chloroform. All of the mass balance experiments indicated that some degree of chloroform volatilization will occur within a gas sparged reactor. Upon further review of the Run V75 data, if the t = 30 min value is ignored, then some volatilization of chloroform is noted. The rate of chloroform vola-tilization observed at the t = 10 min falls in line with the rate that is observed in the mass balance experiments.

The addition of ozone to the LP-UV system was evaluated in Runs V52 and V71 which yielded mixed results. At t = 20, Run V52 degraded the chloroform to less than 20 $\mu g/\ell$ (the sample detection limit) indicating promise for achieving target goals. Run V71 only removed 50 percent of the chloro-form (resulting in a concentration that is an order of magnitude higher concen-tration than the target treatment level) within 30 min. Over the course of reviewing the results of the VOC chemical oxidation runs performed on Well 36001 groundwater, it is obvious that water matrix is one of the most significant factors impacting treatment. Run V71 consistently performed poorly compared to Run V52 for almost all of the VOCs evaluated. The dependence of system performance on water matrix cannot be overemphasized.

The benefits of hydrogen peroxide addition (200 mg/ℓ) to the LP-UV/ ozone system was evaluated in Run V73 with no improvement in chloroform degradation as compared to the results of Run V52. In fact, a slight adverse impact was observed, possibly due to increased production of iron oxides within the reactor during testing. However, Run V73 did have much better chloroform removal than Run V71.

Runs V43, V46, V58, and V59 evaluated the possibility of using hydrogen peroxide in conjunction with LP-UV photolysis at doses ranging from 50 mg/ℓ to 200 mg/ℓ. Not surprisingly, these runs did not result in signifi-cant chloroform degradation because of the poor absorbance of hydrogen peroxide at the 254 nm wavelength. There was no significant difference in performance noted between any of the LP-UV/hydrogen peroxide runs.

The data presented in Table 27 indicate that a LP-UV system with ozone addition should meet target chloroform treatment goals within 30 min of treat-ment assuming proper iron management is obtained.

Table 28 presents the chloroform peroxone chemical oxidation runs for Well 36001 groundwater samples. As was the case for the majority of the other VOC experiments, the 50 mg/ℓ hydrogen peroxide peroxone run (V68) did not achieve appreciable contaminant degradation. The 10.0 mg/ℓ hydro-gen peroxide dosed peroxone runs (V54, V67, and V86) were not as effective

Table 28
Well 36001 Groundwater Chemical Oxidation Runs-Chloroform Peroxone Based Systems

Run No.	V69P	V68	V67	V54	V86	V84
UV Lamp	NO	NO	NO	NO	NO	NO
[O_3]	SAT[1]	SAT	SAT	SAT	SAT	SAT
[H_2O_2]	500	50	10	10	10	5
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO
Reaction Time min	Chloroform Concentration , $\mu g/\ell$					
0	25,400	1,608	1,480	1,440	1,530	1,670
3	28,500	1,340	1,590	191	--	--
5	26,500	1,310	1,624	292	--	--
10	32,200	1,320	1,580	87	885	1,160
20	34,200	1,400	560	17	317	529
30	--	--	--	--	116	786
40	--	--	--	--	.25	64

Run No.	V111	V97	V85	V112	V114	V83
UV Lamp	NO	NO	NO	NO	NO	NO
[O_3]	SAT	SAT	SAT	SAT	SAT	SAT
[H_2O_2] pH	200.5	201	1	0.05	0.01	0.25
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	NO	NO	NO
Reaction Time min	Chloroform Concentration , $\mu g/\ell$					
0	950	270	1,700	1,100	1,100	1,660
5	120	--	--	75	83	--
10	12	16	964	4	24	1,090
20	1.6	1	583	0.88J	24	634
30	0.26J	<2	157	0.98J	2.3	347
40	--	<1	9	--	0.35J	116

[1] SAT = Ozone used as an oxidizer.

for chloroform as they were for the other VOCs. However, Runs V54 and V86 did achieve approximately 99 percent removal within 20 and 40 min of treatment, respectively. None of these runs met chloroform target levels

(10 $\mu g/\ell$), but Runs V54 and V86 did indicate potential for reaching this value with continued treatment.

In terms of chloroform removal, Runs V85 and V111, provided the best chloroform degradation of all the peroxone systems tested. The 0.25 mg/ℓ hydrogen peroxide dose (V83) did not perform as well as the other sub-10 mg/ℓ hydrogen peroxide dosed runs. In summary, based on the results of the peroxone experiments, hydrogen peroxide doses less than 50 mg/ℓ in a peroxone system should reach target chloroform levels within 40 min of treatment.

Methylene chloride. The methylene chloride QA/QC analytical blanks indicated the presence of small amounts of methylene chloride. Concentration on the order of 1.0 $\mu g/\ell$ were detected in most of the analytical blanks. No blank corrections were performed on the chemical oxidation run data represented in this report. The levels of contamination detected in the blanks were considered insignificant as compared with the initial concentrations detected in the Well 36001 groundwater samples.

Table 29 presents the methylene chloride MP-UV photolysis based chemical oxidation runs for Well 36001 groundwater samples. Direct MP-UV photolysis of Well 36001 groundwater (Run V41) did result in approximately 90 percent removal demonstrating that methylene chloride is photoreactive. The addition of 50 mg/ℓ of hydrogen peroxide to the MP-UV photolysis based system (V42) did not result in improved methylene chloride removal as compared to direct MP-UV photolysis alone (approximately 75 percent versus 90 percent).

Runs V44, V45, V53, V69, V74, and V87 evaluated the addition of hydrogen peroxide to the MP-UV photolysis system at doses ranging from 100 mg/ℓ to 500 mg/ℓ. This series of runs indicate that this range of hydrogen peroxide doses have a low potential for reaching target treatment goals (5 $\mu g/\ell$) within 20 min of treatment. The same runs that performed poorly in the other VOC experiments also performed poorly for methylene chloride removal (i.e., V45 and V69).

Removal of iron prior to MP-UV photolysis/hydrogen peroxide treatment was evaluated in Run V110. This run was not as successful in terms of methylene chloride removal as it was for removal of other VOCs. However, this run did indicate promise, but some of the 100-mg/ℓ and 500-mg/ℓ dosed runs produced better methylene chloride removal. In essence, the methylene chloride data indicate that if proper sample UV transmissivities are maintained, then target treatment goals may be met using MP-UV systems.

The addition of 1,000 mg/ℓ of hydrogen peroxide to the MP-UV photolysis system (V70) once again seemed to have a negative impact on treatment compared to the lower dosed runs. As was the case with the other VOCs, the 1,000 mg/ℓ dose probably induced excessive amounts of iron oxides within

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Table 29
Well 36001 Groundwater Chemical Oxidation Runs-Methylene Chloride Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V70	V74	V87	V72	V69	V45
UV Lamp	MP[1]	MP	MP	MP	MP	MP
[O$_3$]	NO	NO	NO	NO	NO	NO
[H$_2$O$_2$]	1,000	500	500	500	500	200
[Catalyst]	NO	NO	NO	100WO$_3$	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO
Reaction Time min	Methylene Chloride Concentration , $\mu g/\ell$					
0	305	109	580	322	1,700	1,400
3	--	--	--	--	--	1,500
5	302	121	--	253	2,240	623
10	420	--	20	245	1,100	1,170
20	--	--	5	--	--	--
30	308	93	1	225	302	--
40	--	--	1	--	--	--
Run No.	V110	V53	V44	V104	V42	V41
UV Lamp	MP	MP	MP	MP	MP	MP
[O$_3$]	NO	NO	NO	NO	NO	NO
[H$_2$O$_2$] pH	250	100	100	50	50	NO
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO	NO	NO
Reaction Time min	Methylene Chloride Concentration , $\mu g/\ell$					
0	520	699	1,580	--	2,240	17,230
3	--	74	2,090	--	1,480	1,460
5	130	9	197	5.8	620	1,000
10	25	5	212	3.7	533	1,130
15	1.4	--	--	--	--	--
20	--	2	--	2	--	--
30	14	--	--	--	--	--
40	--	--	--	<1	--	--

[1] MP = Medium pressure UV lamp used.

the MP-UV photolysis reactor. The addition of the tungsten catalyst
(Run V72) also did not improve methylene chloride removal.

Table 30 presents the methylene chloride LP-UV photolysis based chemical
oxidation runs for Well 36001 groundwater samples. Direct LP-UV photoly-
sis treatment (V49) did not result in any methylene chloride removal. Sparg-
ing of air into the LP-UV photolysis system (V75) did not result in the
volatilization of methylene chloride.

The addition of ozone into the LP-UV photolysis system was evaluated in
Runs V52 and V71. As was observed in the other VOC experiments,
Run V71 achieved no methylene chloride removal. Run V52 exhibited excel-
lent methylene chloride degradation kinetics by achieving approximately
99 percent removal, but did not meet the target treatment goals for methylene
chloride.

The addition of hydrogen peroxide to the LP-UV photolysis system was
evaluated in Runs V43, V46, V58, V59, and V60. These runs evaluated
hydrogen peroxide doses ranging from 50 mg/ℓ to 200 mg/ℓ. The addition of
hydrogen peroxide to the LP-UV photolysis system resulted in some degrada-
tion of the methylene chloride present in Well 36001 groundwater. No con-
clusions with regard to methylene chloride removal could be made upon
review of these data. The 200 mg/ℓ hydrogen peroxide dose (V60) achieved
approximately 75 percent removal within 20 min of treatment. The 50 and
100 mg/ℓ doses (V46, V43, and V59) did not result in any methylene chloride
removal.

The addition of 200 mg/ℓ of hydrogen peroxide to the LP-UV photolysis/
ozone system was investigated in Run V73. This run achieved approximately
80 percent removal within 30 min of treatment.

In summary, the LP-UV photolysis system with ozone addition may have
potential for meeting target methylene chloride levels within extended periods
of treatment (i.e., treatment times in excess of 30 min). There is no strong
evidence to support this assessment, but the data indicate some potential.
None of the LP-UV based runs were successful at fully meeting target treat-
ment goals of 5.0 μg/ℓ of methylene chloride.

Table 31 presents the methylene chloride peroxone runs for Well 36001
groundwater samples. The higher hydrogen peroxide dosed (5 mg/ℓ to
50 mg/ℓ) peroxone runs (Runs V67, V68, V69, V84, and V86) generally
resulted in relatively poor methylene chloride removal than the sub-5 mg/ℓ
hydrogen peroxide dosed runs. However, Run V54, a 10 mg/ℓ hydrogen
peroxide dosed run, met the target treatment goal of 5 μg/ℓ methylene
chloride within 20 min of treatment. The reasons for the overall poorer per-
formance of the higher doses is not known. It is difficult to speculate on a
sound rationale for this due to the overall complexity of this water.

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Table 30
Well 36001 Groundwater Chemical Oxidation Runs-Methylene Chloride Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V60	V46	V73	V59	V43
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	NO	SAT[2]	NO	NO
[H_2O_2]	200	200	200	100	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Methylene Chloride Concentration , $\mu g/\ell$				
0	2,400	1,110	268	998	362
3	2,960	796	--	1,499	665
5	376	834	256	655	678
10	823	1.330	296	1,090	608
20	839	--	--	1,620	--
30	--	--	57	--	--

Run No.	V71	V52	V75	V49	V58
UV Lamp	LP	LP	LP	LP	LP
[O_3]	SAT	SAT	AIR[3]	NO	NO
[H_2O_2]	NO	NO	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Methylene Chloride Concentration , $\mu g/\ell$				
0	362	320	286	1,024	1,040
3	--	252	--	1,160	368
5	362	55	312	1,110	874
10	417	9	461	1,000	259
20	--	44	--	--	265
30	538	--	373	--	--

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.
[3] AIR = Air sparged.

The lower hydrogen peroxide dosed (< 1.0 mg/ℓ) peroxone runs (Runs V83, V85, V97, V112, and V114) were all successful in meeting target treatment levels. As was the case with the other VOC experiments, Run V83, the 0.25 mg/ℓ hydrogen peroxide dosed run, did not achieve nearly the

Table 31
Well 36001 Groundwater Chemical Oxidation Runs-Methylene Chloride Peroxone Based Systems

Run No.	V69P	V68	V67	V54	V86	V84
UV Lamp	NO	NO	NO	NO	NO	NO
[O$_3$]	SAT[1]	SAT	SAT	SAT	SAT	SAT
[H$_2$O$_2$]	500	50	10	10	10	5
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	Methylene Chloride Concentration , μg/ℓ					
0	2,800	1,070	521	313	22	1,220
3	4,620	1,570	1,380	86	--	--
5	3,880	1,380	2,050	19	--	--
10	1,950	1,190	1,450	25	15	1,040
20	2,610	1,450	1,300	3	46	1,120
30	--	--	--	--	34	1,200
40	--	--	--	--	6	5,280

Run No.	V111	V97	V85	V112	V114	V83
UV Lamp	NO	NO	NO	NO	NO	NO
[O$_3$]	SAT	SAT	SAT	SAT	SAT	SAT
[H$_2$O$_2$] pH	200.5	201	1	0.05	0.01	0.25
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	NO	NO	NO

Reaction Time min	Methylene Chloride Concentration , μg/ℓ					
0	220	200	965	230	92	986
5	37	--	--	33	11	--
10	2.4	12	864	1.20	49	830
15	0.54	--	--	0.31	13	--
20	--	2.7	912	--	--	794
30	<2	5.5	39	0.26	0.50	800
40	--	2.5	2	--	--	15

[1] SAT = Ozone used as an oxidizer.

percent removal that was achieved in runs containing slightly higher and lower hydrogen peroxide doses. The 0.05 mg/ℓ and 0.01 mg/ℓ hydrogen peroxide

dosed peroxone runs (V112 and V114) look particularly encouraging by reaching the target levels within 15 min of treatment. These peroxone runs indicate that peroxone systems exhibit much more promise for methylene chloride removal than the UV based systems.

Runs V97 and V111 were runs in which the iron was removed using a 205 mg/ℓ hydrogen peroxide dose prior to the sparging of the ozonated air into the reactor. After removing the iron, the degradation rate achieved by these indicate promise for methylene chloride removal. The degradation rates were very similar to the sub-1 mg/ℓ dosed runs. Comparing these runs to the greater than 1 mg/ℓ dosed runs without iron removal indicated that the iron may be interfering with the peroxone chemistry at higher hydrogen peroxide levels. This conclusion is speculative, but iron removal prior to peroxone treatment may be worthy of further evaluation at a later date.

Aldrin. Aldrin was measured in two of the Well 36001 groundwater samples at levels below the target treatment level of 0.05 μg/ℓ. Table 32 presents the aldrin MP-UV photolysis based chemical oxidation runs for Well 36001 groundwater samples. The results of these runs indicate that direct MP-UV photolysis alone (Run P6) degrades approximately 99 percent of the aldrin within 10 min of treatment. The addition of any amount of hydrogen peroxide generally reduced the time needed to degrade 99 percent of the aldrin to only 5.0 min of treatment.

Table 32
Well 36001 Groundwater Chemical Oxidation Runs-Aldrin Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P6	P7	P9	P36
UV Lamp	MP[1]	MP	MP	MP
[O_3]	NO	NO	NO	SAT[2]
[H_2O_2]	NO	50	100	200
[Catalyst]	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO
Reaction Time min	Aldrin Concentration, μg/ℓ			
0	0.27	0.031	0.027	0.033J
3	0.024	0.022	0.056	<0.041
5	0.023	<0.043	<0.043	<0.043
10	<0.043	<0.043	<0.043	<0.042
20	--	--	--	<0.042

[1] MP = Medium pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 33 presents the aldrin LP-UV photolysis based chemical oxidation runs for Well 36001 groundwater samples. The results of these runs indicate

Table 33
Well 36001 Groundwater Chemical Oxidation Runs-Aldrin Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P8	P29	P30	P35	P28
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	NO	NO	SAT	SAT[2]	NO
$[H_2O_2]$	100	200	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO
Reaction Time min	Aldrin Concentration, $\mu g/\ell$				
0	0.023	0.15	0.071	<0.042	<0.042
3	0.10	0.050	0.050	<0.042	<0.042
5	0.15	0.053	<0.042	<0.041	<0.052
10	0.11	0.008J	<0.042	<0.041	<0.042
20	--	<0.042	0.030J	<0.041	<0.042

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

that aldrin will be reduced by 99 percent within 20 min of treatment regardless of oxidizer type added (ozone or hydrogen peroxide). The LP-UV photolysis/ozone system (P30) did have removal rates approximately twice as rapid as the hydrogen peroxide dosed runs. Run P30 degraded over 40 percent of the aldrin present in the groundwater within 5 min of treatment.

Dieldrin. Table 34 presents the MP-UV based dieldrin chemical oxidation runs from Well 36001 groundwater samples. Run P23 evaluated direct MP-UV photolysis which yielded excellent dieldrin degradation with at least 90 percent degradation within 3.0 min of treatment. The target dieldrin treatment goal of 0.05 $\mu g/\ell$ was not met within 10 min of direct photolysis; however, based on review of the degradation rate achieved by this run, target treatment levels may be met with increased treatment time (i.e., HRT).

Runs P7, P9, and P36 evaluated the addition of hydrogen peroxide to the MP-UV photolysis system. Dosing the MP-UV photolysis system with less than 200 mg/ℓ hydrogen peroxide (Runs P7 and P9) does not result in appreciable degradation of dieldrin. Increasing the hydrogen peroxide dose from 50 mg/ℓ (P7) to 100 mg/ℓ (P9) resulted in a 60 percent increase in degradation. However, the 100 mg/ℓ dose did not meet the target dieldrin level. Run P36, a 200 mg/ℓ hydrogen peroxide dosed run, achieved 90 percent removal of dieldrin within 20 min of treatment.

Table 35 presents the LP-UV based dieldrin chemical oxidation runs for Well 36001 groundwater. None of the LP-UV based runs were successful in treating dieldrin. The data indicate an increase in dieldrin concentration after 5 min of treatment. Dieldrin is an intermediate of incomplete chemical

Table 34
Well 36001 Groundwater Chemical Oxidation-Dieldrin Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P6	P7	P9	P36
UV Lamp	MP[1]	MP	MP	MP
[O_3]	NO	NO	NO	SAT[2]
[H_2O_2]	NO	50	100	200
[Catalyst]	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO

Reaction Time min	Dieldrin Concentration, $\mu g/\ell$			
0	1.1	1.2	0.95	1.6
3	1.4	1.4	0.57	0.89
5	0.7	1.4	0.30	0.50
10	0.6	1.3	0.37	0.16
20	--	--	--	0.11

[1] MP = Medium pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 35
Well 36001 Groundwater Chemical Oxidation Runs-Dieldrin Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P8	P29	P30	P35	P28
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	NO	SAT	SAT	NO
[H_2O_2] pH	100	200	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	Dieldrin Concentration, $\mu g/\ell$				
0	1.2	0.22	0.16	1.4	1.2
3	1.1	0.26	0.28	1.0	1.3
5	1.3	0.33	0.29	1.0	1.1
10	0.78	0.27	0.25	1.3	1.1
20	--	0.28	0.21	1.1	1.0

[1] LP = Low pressure UV lamp used.

oxidation and/or LP-UV photolysis of other organochloro-pesticides that are present in Well 36001 groundwater. The LP-UV based systems evaluated seem ineffective in treating the dieldrin present within the Well 36001 water matrix.

PPDDE. Table 36 presents the MP-UV based PPDDE chemical oxidation runs for Well 36001 groundwater samples. There is little noticeable difference between the MP-UV runs. In all of the runs, except Run P9, PPDDE concentrations were reduced by approximately 50 percent. The 100 mg/ℓ hydrogen peroxide dosed MP-UV photolysis run (P9) was the only exception in that no degradation of PPDDE was noted. Unfortunately, the PPDDE runs were only carried out through 10 min of treatment. A 100 mg/ℓ hydrogen peroxide dose (Run P9) indicates some potential for reaching target PPDDE levels with increased HRTs.

Table 37 presents the LP-UV based PPDDE chemical oxidation runs for Well 36001 groundwater samples. Only two runs, the 50 mg/ℓ and 100 mg/ℓ hydrogen peroxide dosed runs (P8 and P28), had any measurable amounts of PPDDE. The 100 mg/ℓ dosed run basically achieved the same degree of PPDDE removal as did the MP-UV runs by removing approximately 50 percent within 10 min. The 50 mg/ℓ dosed run did not degrade any of the PPDDE. Unfortunately the LP-UV photolysis/ozone systems could not be evaluated for PPDDE removal because no PPDDE was detected during any of these runs.

DBCP. Table 38 presents the DBCP MP-UV photolysis based chemical oxidation runs for Well 36001 groundwater samples. None of the treatment conditions evaluated reduced DBCP to below target treatment levels (0.2 μg/ℓ). Unfortunately, only one of these runs was operated beyond 10 min of treatment.

The direct MP-UV photolysis run (P6) achieved approximately 87 percent removal within the 10 min of treatment. The addition of hydrogen peroxide to the MP-UV photolysis system which was evaluated in Runs P7 (50 mg/ℓ) and P9 (100 mg/ℓ) yielded different results in that approximately 75 percent of the DBCP was removed within 10 min in Run P9 and no removal in Run P7. This indicates that hydrogen peroxide doses greater than 50 mg/ℓ are required. Run P36 evaluated the combined effect of both hydrogen peroxide and ozone presence within a MP-UV reactor; unfortunately DBCP was not detected in any of the water samples collected during this run.

Table 39 presents the DBCP LP-UV photolysis based chemical oxidation runs for Well 36001 groundwater samples. This series of experiments indicated significant variability between initial DBCP (t = 0) concentrations. Much like the MP-UV data, no trends were observed. The data generally indicate that DBCP is reactive in the LP-UV photolysis based systems, but sample variability and the lack of trends make prediction of system performance difficult. However, the data do indicate that increased treatment times would probably reduce DBCP concentrations to within acceptable levels based on improved sample matrix (lower detection limits) and review of the data from Runs P30 and P28.

Table 36
Well 36001 Groundwater Chemical Oxidation Runs-PPDDE Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P6	P7	P9	P36
UV Lamp	MP[1]	MP	MP	MP
$[O_3]$	NO	NO	NO	SAT[2]
$[H_2O_2]$	NO	50	100	200
[Catalyst]	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO
Reaction Time min	PPDDE Concentration, $\mu g/\ell$			
0	1.1	1.2	0.94	<0.043
3	1.3	1.4	0.57	<0.041
5	0.69	1.4	0.30	<0.043
10	0.6	1.2	0.36	<0.042
20	--	--	--	<0.042

[1] MP = Medium pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 37
Well 36001 Groundwater Chemical Oxidation Runs-PPDDE Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P28	P8	P29	P30	P35
UV Lamp	LP[1]	12	12	12	12
$[O_3]$	NO	NO	NO	SAT[2]	SAT
$[H_2O_2]$ pH	50	100	200	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO
Reaction Time min	PPDDE Concentration, $\mu g/\ell$				
0	1.2	1.2	<0.042	<0.041	<0.042
3	1.3	1.1	<0.042	<0.041	<0.042
5	1.1	<0.043	<0.041	<0.041	<0.041
10	1.1	0.77	<0.041	<0.041	<0.041
20	1.0	--	<0.041	<0.041	<0.041

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 38
Well 36001 Groundwater Chemical Oxidation Runs-DBCP Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P6	P7	P9	P36
UV Lamp	MP[1]	MP	MP	MP
[O_3]	NO	NO	NO	SAT[2]
[H_2O_2]	NO	50	100	200
[Catalyst]	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO

Reaction Time min	DBCP Concentration, $\mu g/\ell$			
0	16	15	13	0.058
3	5.4	5.0	5.9	0.20
5	1.6	4.0	3.3	0.25
10	2.1	1.3	4.1	0.09
20	--	--	--	<0.053

[1] MP = Medium pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 39
Well 36001 Groundwater Chemical Oxidation Runs-DBCP Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P8	P29	P30	P35	P28
UV Lamp	12	12	12	12	12
[O_3]	NO	NO	SAT	SAT[1]	NO
[H_2O_2] pH	100	200	NO	NO	50
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time min	DBCP Concentration, $\mu g/\ell$				
0	12	2.6	2.9	0.25	0.17
3	9.7	<0.052	<0.052	0.43	0.14
5	9.7	<0.051	<0.052	0.25	<0.65
10	9.2	<0.051	<0.052	0.20	<0.052
20	--	<0.051	<0.052	0.24	<0.052

[1] SAT = Ozone used as an oxidizer.

Well 01061 chemical oxidation runs

Benzene. Table 40 presents the benzene MP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. No benzene was detected in the samples used for Runs V100, V101, V102, and V105 based on the detection limits associated with these runs.

The runs performed on Well 01061 groundwater samples focused on the MP-UV photolysis system dosed with hydrogen peroxide doses ranging from 50 mg/ℓ to 500 mg/ℓ. These experiments were selected based on the results obtained from Well 36001 experiments.

The addition of hydrogen peroxide to the MP-UV photolysis system at doses of 100 mg/ℓ and 500 mg/ℓ were evaluated in Runs V56, V79, and V88. Although over 80 percent reduction in benzene was achieved, target benzene treatment levels (5 μg/ℓ) were not reached during these runs. Iron pretreatment and a 1,000 mg/ℓ hydrogen peroxide dose in the MP-UV photolysis system (V90) resulted in meeting target benzene treatment levels within 10 min of treatment. This run further substantiates the theory that the formation of oxidized iron interferes with UV/oxidation systems.

Table 41 presents the benzene LP-UV photolysis chemical oxidation runs for Well 01061 groundwater samples. Run V103 did not have any benzene detected at any time during the experiment.

Runs V55, V78, and V91 evaluated the LP-UV photolysis system with ozone addition. These runs indicated promise for reaching target benzene treatment levels using this treatment system. Run V55 performed better than the other two runs by reaching target levels within 10 min of treatment. Run V78 took at least 30 min to achieve the same goal (whether the goal was reached cannot be assessed due to the high detection limits reported for this run). Run V91 had an initial benzene concentration (t = 0) that was approximately six times higher than the initial concentrations detected in the other two runs. Run V91 reached target treatment levels within 40 min of treatment.

Runs V89, V92, V96, and V103 evaluated the benefits of iron removal and, since little hydrogen peroxide was removed during iron removal, the benefits of hydrogen peroxide dosing to the LP-UV photolysis system. Runs V89 and V96 involved the addition of ozone to pretreated groundwater samples. Run V89 used a 25 mg/ℓ hydrogen peroxide dose while Runs V92 used a 500 mg/ℓ dose. These runs yielded removal rates that were superior to the other runs. The difference between Runs V89 and V96 indicates that once UV transmissivity is improved through iron removal, then increasing the hydrogen peroxide dose also increases the benzene degradation rate.

The data generated from Run V92 indicate that after iron removal, hydrogen peroxide addition to the LP-UV photolytic system without ozone introduction results in appreciable benzene degradation. The results obtained from

Table 40				
Well 01061 Groundwater Chemical Oxidation Runs-Benzene				
Medium Pressure Mercury Vapor UV Lamp Based Systems				

Run No.	V90	V88	V79	V102
UV Lamp	MP[1]	MP	MP	MP
[O_3]	NO	NO	NO	NO
[H_2O_2]	1,000	500	500	300
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	YES

Reaction Time, min	Benzene Concentration , $\mu g/\ell$			
0	1,500	1,500	270	<100
3	--	--	--	--
5	--	--	--	<50
10	<5	<200	<200	<50
20	<5	<200	37J	<50
30	<5	<100	35J	--
40	<5	<100	51J	<50

Run No.	V105	V100	V56	V101
UV Lamp	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO
[H_2O_2]	250	200	100	100
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO

Reaction Time, min	Benzene Concentration , $\mu g/\ell$			
0	<100	<100	106J	<100
3	--	--	29J	--
5	<100	<50	26	<20
10	<100	<20	27	<20
20	--	<10	9J	<50
30	<100	--	--	--
40	--	<5	--	<50

[1] MP = Medium pressure UV lamp used.

Table 41
Well 01061 Groundwater Chemical Oxidation Runs-Benzene Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V62	V89	V91	V78	V55
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	NO	SAT[2]	SAT	SAT	SAT
$[H_2O_2]$	50	25	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$				
0	75J	1,500	1,500	266	141J
3	40J	--	--	--	30J
5	60J	--	--	--	<1
10	39J	<200	<200	142J	5J
20	31J	<100	<100	24J	4J
30	--	<50	12	<200	--
40	--	10	<5	<200	--

Run No.	V96	V103	V63	V92	V61
UV Lamp	LP	LP	LP	LP	LP
$[O_3]$	SAT	NO	NO	NO	NO
$[H_2O_2]$	500	250	200	200	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	YES	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$				
0	1,200	<100	56	1,600	54J
3	--	--	<200	--	117J
5	--	<50	19	--	63J
10	3.4J	<50	<200	<200	30J
20	0.25J	--	--	<50	--
30	<1	<20	--	<50	--

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Run V92 indicate that post-iron removal LP-UV photolysis of hydrogen peroxide may be capable of reaching target levels within lower HRTs than the systems where iron is not removed. It must be pointed out that the data

generated in Run V92 is made of primarily less than detection values; however, an obvious improvement in sample matrix and significant treatment based on review of the initial concentration is noted.

Runs V62, V61, and V63 evaluated the benefits of hydrogen peroxide addition to the LP-UV photolysis system using hydrogen peroxide doses of 50 mg/ℓ, 100 mg/ℓ, and 200 mg/ℓ, respectively. The results from these runs varied from approximately 50 percent removal in Run V62 (50 mg/ℓ) to 85 percent removal in Run V61 (100 mg/ℓ). The removal rates achieved in Runs V61, V62, and V63 were as rapid as those achieved in the iron removal run (V92). In terms of benzene removal, hydrogen peroxide addition to the LP-UV system indicates promise. These runs are the first set of experiments that yielded promising results for contaminant oxidation using a hydrogen peroxide/LP-UV photolysis system.

Table 42 presents the benzene peroxone runs for Well 01061 groundwater samples that evaluated hydrogen peroxide doses ranging from 0.01 mg/ℓ to 10.0 mg/ℓ. All of these runs, with the exception of Runs V64 and V65 indicate a high potential for benzene degradation using the peroxone system. Based on review of the peroxone data, target benzene treatment levels are achievable after 10-40 min of treatment (depending on the run). The degradation rates achieved in the peroxone experiments were slightly more rapid than those obtained using the two UV based systems. This is surprising since peroxone is traditionally not considered as aggressive as the UV based AOPs. However, the formation of iron oxides in the UV based systems evaluated for treatment of the RMA groundwaters tended to reduce the effectiveness of the UV based systems making peroxone systems seem particularly attractive.

Iron removal (Runs V94, V95, and V106) prior to peroxone treatment yielded similar degradation rates to the other peroxone runs. It is surprising that such high hydrogen peroxide doses (200-500 mg/ℓ) did not hinder hydroxyl radical formation and subsequent benzene oxidation.

Total Xylenes

T-xylenes were detected in Well 01061 groundwater at levels much lower than the target treatment level. Many of these values are reported as less than detection limit values due to sample dilution for measuring chloroform concentrations. The diluting of the samples reduces the T-xylene concentrations to values too low to accurately measure or quantify. Although those concentrations measured were lower than the target levels, these data are presented to give the reader an estimate of the extent of T-xylene removal that will occur with Well 01061 groundwater while being treated for the other target contaminants that are present at levels requiring treatment.

Table 42
Well 01061 Groundwater Chemical Oxidation Runs-Benzene Peroxone Based Systems

Run No.	V65	V95	V94	V106	V57	V64
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT[1]	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	500	505	201	200.5	10	10
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	YES	YES	YES	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$					
0	<200	730	880	<100	124J	8J
3	<200	--	--	--	18J	81J
5	<200	--	--	<10	10	41J
10	<200	14	11	<1	3J	<200
15	--	--	--	<1	--	--
20	<100	<5	<5	--	2J	<200
30	--	<1	<5	<1	--	--
40	--	<1	<1	--	--	--

Run No.	V81	V76	V81	V77	V107	V109
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$ pH	0.5	1	0.5	0.25	0.05	0.01
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	Benzene Concentration , $\mu g/\ell$					
0	245	233	245	247	<100	<100
3	--	--	--	--	--	--
5	--	--	--	--	<20	<20
10	34J	29J	34J	76J	<5	<5
15	--	--	--	--	<5	<5
20	11J	8J	11J	37J	--	--
30	9J	<20	9J	22J	<5	<5
40	<50	<1	<50	<1	--	--

[1] SAT = Ozone used as an oxidizer.

Table 43 presents the MP-UV photolysis based T-xylenes chemical oxidation runs for Well 01061 groundwater samples. All but two of the runs listed in Table 43 did not detect any T-xylenes present in the groundwater samples. Run V56 achieved at least 87 percent removal with a hydrogen peroxide dose

Table 43
Well 01061 Groundwater Chemical Oxidation Runs - T-Xylene
Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V90	V88	V79	V102
UV Lamp	MP[1]	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	1000	500	500	300
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	YES
Reaction Time, min	**VOA Concentration, $\mu g/\ell$**			
0	<400	<400	129	<200
3	---	---	---	---
5	---	---	---	<100
10	<10	<400	<400	<100
20	<10	<400	<400	<100
30	<10	<2	<400	---
40	<10	<2	<400	<100

Run No.	V105	V100	V56	V101
UV Lamp	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	250	200	100	100
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO
Reaction Time, min	**VOA Concentration, $\mu g/\ell$**			
0	<200	<200	143J	<200
3	---	---	6J	---
5	<200	<100	52	<40
10	<200	<40	53	<40
20	---	<20	18J	<100
30	<200	---	---	---
40	---	<10	---	<100

[1] MP = Medium pressure UV lamp used.

of 100 mg/ℓ in MP-UV systems. Run V79 also indicated potential for T-xylene removal, but unfortunately high detection limits prevent quantification of the T-xylene removal.

Table 44 presents the LP-UV based total xylenes chemical oxidation runs for Well 01061 groundwater samples. Once again, dilution of the samples for chloroform analysis produced difficult data to interpret. Several of these runs did not detect any T-xylenes present in the test influents. The results of these experiments indicate that any of the LP-UV photolysis based systems were effective at removing at least 90 percent of the T-xylenes within 10 min of treatment. Ozonated LP-UV photolysis based systems (Runs V78 and V55) provided the best T-xylenes removal of all the LP-UV photolysis systems evaluated.

Table 45 presents the T-xylenes peroxone chemical oxidation runs for Well 01061 groundwater samples. Only one of the peroxone runs (V57) listed in Table 45 had detectable amounts of T-xylenes. This run did achieve 95 percent removal within 5 min of treatment. The other runs did show reduced analytical detection limits as the treatments proceeded indicating that the complexity of the water matrix improved as oxidation proceeded. Improvements in water matrices over time indicate that organic contamination was also reduced over time.

Toluene. Toluene was also detected in Well 01061 groundwater at levels much higher than target treatment levels. These data are presented to give the reader an estimate of the extent of toluene removal that will occur with Well 01061 groundwater while being treated for the other target contaminants that are present at levels requiring treatment.

Table 46 presents the MP-UV photolysis based toluene chemical oxidation runs for Well 01061 groundwater samples. Only one run (V56) in this set of experiments had detectable amounts of toluene present. Run V56 evaluated a 100 mg/ℓ hydrogen peroxide dose in the MP-UV photolysis system. This experiment resulted in over 80-percent reduction of toluene within 10 min of treatment. The other runs indicated increasingly lower detection limits as the runs proceeded.

Table 47 presents the LP-UV photolysis based toluene chemical oxidation runs for Well 01061 groundwater samples. Only two LP-UV photolysis based toluene runs (Runs V55 and V62) had detectable amounts of toluene present due to the extent of sample dilution required for chloroform analysis. The only run that was really useful was Run V55, which evaluated ozone addition to the LP-UV photolysis system, and resulted in almost complete removal within 5 min of treatment. The other runs had high detection limits beyond the initial (t = 0) value. In spite of the high detection limits, no toluene was detected beyond the initial samples of these runs. Based on reducing detection limits, indicating improved samples matrices, no toluene was detected as the detection limits were reduced with continual oxidation.

Table 44
Well 01061 Groundwater Chemical Oxidation Runs - T-Xylene
Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V62	V89	V91	V78	V55
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	NO	NO	NO	SAT[2]	SAT
$[H_2O_2]$	50	25	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	NO

Reaction Time, min	T-Xylene Concentration, $\mu g/\ell$				
0	33J	140	<400	35J	175J
3	<400	---	---	---	28J
5	<400	---	---	---	1
10	<400	<400	<400	<400	6J
20	<400	31J	<200	<400	5J
30	---	10J	<10	<400	---
40	---	<100	<10	<400	--

Run No.	V96	V103	V63	V92	V61
UV Lamp	LP	LP	LP	LP	LP
$[O_3]$	SAT	NO	NO	SAT	NO
$[H_2O_2]$	500	250	200	200	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	YES	NO

Reaction Time, min	T-Xylene Concentration, $\mu g/\ell$				
0	<200	<200	10	<400	<2
3	---	---	<400	---	<2
5	---	<100	<400	---	<2
10	<20	<100	<400	<400	<400
20	<4	<40	<400	<100	<400
30	<2	---	---	<100	---
40	<2	<40	---	16J	---

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 45
Well 01061 Groundwater Chemical Oxidation Runs - T-Xylene
Peroxone Based Systems

Run No.	V65	V95	V94	V106	V57	V64
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT[1]	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	500	505	201	200.5	10	10
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	YES	YES	YES	NO	NO

Reaction Time, min	T-Xylene Concentration, $\mu g/\ell$					
0	<400	<200	<200	<200	167J	<400
3	<400	---	---	---	49J	<400
5	<400	---	---	<20	8J	<400
10	<400	<20	<10	<2	10J	<400
15	---	---	---	<2	---	---
20	<200	<10	<10	---	4J	<400
30	---	<2	<10	<2	---	---
40	---	<2	<2	---	---	---

Run No.	V80	V76	V81	V77	V107	V109
UV Lamp	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	10	1	0.5	0.25	0.05	0.01
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time, min	T-Xylene Concentration, $\mu g/\ell$					
0	<400	<400	<400	<400	<200	<200
3	---	---	---	---	<40	<40
5	<400	<400	<400	<400	<10	<10
10	<400	<400	<400	<400	<10	<10
15	---	---	---	---	<10	<10
20	33J	<400	<200	<400	---	---
30	<2	<40	<200	<39J	<10	<10
40	<2	<2	<100	<2	---	---

[1] SAT = Ozone used as an oxidizer.

Table 46
Well 01061 Groundwater Chemical Oxidation Runs - Toluene
Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V56	V88	V100	V101
UV Lamp	MP[1]	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	100	500	200	100
[Catalyst]	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO

Reaction Time, min	VOA Concentration, $\mu g/\ell$			
0	81J	<200	<100	<100
3	<50	---	---	---
5	17J	---	<50	<20
10	14J	---	<20	<20
20	7J	---	<10	<50
30	---	<1	---	---
40	---	<1	<5	<50

Run No.	V79	V90	V102	V105
UV Lamp	MP	MP	MP	MP
$[O_3]$	SAT	NO	NO	NO
$[H_2O_2]$	500	500	100	50
[Catalyst]	NO	NO	NO	NO
Fe Removal	NO	YES	YES	YES

Reaction Time, min	VOA Concentration, $\mu g/\ell$			
0	<200	<200	<100	<100
5	---	---	<50	<100
10	<200	<5	<50	<100
20	<200	<5	<50	---
30	35J	<5	---	<100
40	15J	<5	<50	---

[1] MP = Medium pressure UV lamp used.

Table 48 presents the toluene peroxone chemical oxidation runs for
Well 01061 groundwater samples. These runs also suffered from high detection limits. Only three peroxone runs (V57, V76, and V77) had

Table 47
Well 01061 Groundwater Chemical Oxidation Runs - Toluene Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V55	V61	V62	V63	V78
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	SAT[2]	NO	NO	NO	SAT
$[H_2O_2]$	NO	100	50	200	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO
Reaction Time, min	**Toluene Concentration, $\mu g/\ell$**				
0	51	<200	22J	<200	<200
3	16	<200	<200	<200	---
5	<1	<200	<200	<200	---
10	<10	9J	<200	<200	<200
20	<5	13J	<200	<200	<200
30	---	---	---	---	<200
40	---	---	---	---	<200

Run No.	V96	V92	V91	V89	V103
UV Lamp	LP	LP	LP	LP	LP
$[O_3]$	SAT	SAT	SAT	SAT	NO
$[H_2O_2]$	NO	NO	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	YES	YES
Reaction Time, min	**Toluene Concentration, $\mu g/\ell$**				
0	<100	<200	<200	<200	<100
5	---	---	---	---	<50
10	<10	<200	<200	<200	<50
20	<2	<50	<100	<10	<20
30	<1	<50	<5	6.3J	---
40	<1	<50	<5	<50	<20

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

detectable amounts of toluene present in the run influents. Runs V57, V76, and V77 evaluated hydrogen peroxide doses of 10.0 mg/ℓ, 1.0 mg/ℓ, and 0.25 mg/ℓ, respectively. The higher hydrogen peroxide doses (10.0 and

Table 48
Well 01061 Groundwater Chemical Oxidation Runs - Toluene Peroxone Based Systems

Run No.	V57	V64	V65	V77	V81	V94	V95
UV Lamp	NO	NO	NO	NO	NO	NO	NO
$[O_3]$	SAT[1]	SAT	SAT	SAT	SAT	SAT	SAT
$[H_2O_2]$	10	10	500	0.25	0.50	1.0	5.0
[Catalyst]	NO	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	YES	YES

Reaction Time min	Toluene Concentration, $\mu g/\ell$						
0	85J	<200	<200	26J	<200	<200	<200
3	<50	<200	<200	---	---	---	---
5	<20	<200	<200	---	---	---	---
10	4J	16J	<200	<200	<200	<5	10
20	2J	<200	<100	<200	<100	<5	5
30	---	---	---	<200	<100	<5	1
40	---	---	---	<1	<50	<1	1

Run No.	V76	V80	V106	V109	V107		
UV Lamp	NO	NO	NO	NO	NO		
$[O_3]$	SAT	SAT	SAT	SAT	SAT		
$[H_2O_2]$	1	10	0.05	0.01	0.5		
[Catalyst]	NO	NO	NO	NO	NO		
Fe Removal	NO	NO	YES	NO	NO		

Reaction Time min	Toluene Concentration, $\mu g/\ell$						
0	31J	<200	<100	<100	<100		
5	---	---	<20	<20	<20		
10	<200	<200	<1	<5	<5		
15	---	---	<1	<5	<5		
20	<200	<200	---	---	---		
30	<20	<1	<1	<5	<5		
40	<1	<1	---	---	---		

[1] SAT = Ozone used as an oxidizer.

1.0 mg/ℓ) tended to indicate improved sample matrices over time as compared to the 0.25 mg/ℓ hydrogen peroxide dose, possibly indicating quicker reductions in organic compounds over time (as proven upon review of Well 01061 peroxone chloroform data). However, the high detection limits associated with the 0.25 mg/ℓ hydrogen peroxide dosed run (V77) make direct comparison of degradation kinetics difficult. Run V57 (10 mg/ℓ dose) resulted in over 90 percent removal of toluene within 10 min of treatment.

Trichloroethylene. Table 49 presents the MP-UV photolysis based TCE chemical oxidation runs for Well 01061 groundwater samples. All of the runs presented in Table 49 with hydrogen peroxide at doses ranging from 50 to 500 mg/ℓ resulted in removal efficiencies ranging from 70 to 90 percent within 10 min of treatment. The 200 mg/ℓ hydrogen peroxide dosed run (V100) had the highest degradation rate. This run met the target TCE treatment goal (5 μg/ℓ) within 20 min of treatment and was the only run where the target treatment goal was met. Based on the review of the kinetics associated with the other MP-UV photolysis based runs (without iron removal), there is potential for meeting target TCE treatment goals with increased HRTs.

Removal of the iron prior to MP-UV photolysis/hydrogen peroxide treatment seemed to improve TCE degradation kinetics (Runs V90, V102, and V105). The degree of improvement toward TCE degradation seems to be only slight. The numerous less than detection limits associated with this set of runs values makes proper comparison difficult.

Table 50 presents the TCE LP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. The addition of ozone to the LP-UV photolysis system was evaluated in Runs V55, V63, and V91. These runs indicate that systems of this type have a high potential for reducing TCE to target treatment levels (5.0 μg/ℓ) within approximately 30 min of treatment.

Runs V62, V61, and V63 evaluated the impact of hydrogen peroxide addition to the LP-UV photolysis system at concentrations of 50 mg/ℓ, 100 mg/ℓ, and 200 mg/ℓ, respectively. All of the hydrogen peroxide dosed LP-UV photolysis runs had appreciable TCE degradation rates; however, none of these runs reached target TCE treatment levels. The 50 mg/ℓ hydrogen peroxide dosed run (V62) had a slower degradation rate than the other two hydrogen peroxide dosed runs by removing only approximately 50 percent of the TCE after 20 min of treatment. The 100 mg/ℓ dosed run (V61) removed 60 percent of the TCE within 20 min, while the 200 mg/ℓ dosed run (V63) removed 90 percent of the TCE within 20 min of treatment. These data indicate that increased TCE removals can be realized with increased hydrogen peroxide dosage. This trend agrees with the work of Sundstrom et al. (1986) who found that increasing hydrogen peroxide concentrations within LP-UV photolysis systems also increased TCE degradation.

Table 49
Well 01061 Groundwater Chemical Oxidation Runs - TCE Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V90	V88	V79	V102
UV Lamp	MP[1]	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	1000	500	500	300
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	YES

Reaction Time, min	TCE Concentration, $\mu g/\ell$			
0	<200	<200	289	110
3	---	---	---	---
5	---	---	---	22J
10	<5	<200	<200	12J
20	<5	<200	74J	<50
30	<5	<1	57J	---
40	<5	<1	64J	<50

Run No.	V105	V100	V56	V101
UV Lamp	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	250	200	100	100
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO

Reaction Time, min	TCE Concentration, $\mu g/\ell$			
0	<160	<110	353	130
3	---	---	53	---
5	31J	43J	40	60
10	<100	24	35	36
20	---	5.8J	15J	18J
30	<100	---	---	---
40	---	1.7J	---	6.4J

[1] MP = Medium pressure UV lamp used.

Table 51 presents TCE peroxone chemical oxidation runs for Well 01061 groundwater samples. All of the peroxone runs that had detectable amounts

Table 50
Well 01061 Groundwater Chemical Oxidation Runs - TCE Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V62	V89	V91	V78	V55
UV Lamp	LP[1]	LP	LP	LP	LP
[O$_3$]	NO	SAT[2]	SAT	SAT	SAT
[H$_2$O$_2$]	50	25	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	NO

Reaction Time, min	TCE Concentration, $\mu g/\ell$				
0	297	170J	<200	294	265
3	208	---	---	---	31J
5	187	---	---	---	1
10	169	41J	<200	50J	<10
20	120J	14J	<100	<200	3J
30	---	<50	<5	<200	---
40	---	<50	<5	<200	---

Run No.	V96	V103	V63	V92	V61
UV Lamp	LP	LP	LP	LP	LP
[O$_3$]	SAT	NO	NO	SAT	NO
[H$_2$O$_2$]	500	250	200	200	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	YES	NO

Reaction Time, min	TCE Concentration, $\mu g/\ell$				
0	<200	<100	261	230	169J
3	---	---	143J	---	265
5	---	71	127J	---	169J
10	<10	21J	105J	<200	125J
20	<2	51	27J	<50	68J
30	<1	---	---	<50	---
40	<1	48	---	<50	---

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

of TCE in the test influents had appreciable degradation rates. The data were not consistent enough to select an optimum hydrogen peroxide dose for

Table 51
Well 01061 Groundwater Chemical Oxidation Runs - TCE Peroxone Based Systems

Run No.	V65	V95	V94	V106	V57	V64
UV Lamp	NO	NO	NO	NO	NO	NO
[O₃]	SAT[1]	SAT	SAT	SAT	SAT	SAT
[H₂O₂]	500	505	201	200.5	10	10
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	YES	YES	YES	NO	NO

Reaction Time, min	TCE Concentration, $\mu g/\ell$					
0	<200	145	140	160	391	230
3	<200	---	---	---	38J	<200
5	<200	---	---	<10	11J	56J
10	<200	<10	<5	<1	5J	<200
15	---	---	---	<1	---	---
20	<100	<5	<5	---	3J	<200
30	---	<1	<5	<1	---	---
40	---	<1	<1	---	---	---

Run No.	V80	V76	V81	V77	V107	V109
UV Lamp	NO	NO	NO	NO	NO	NO
[O₃]	SAT	SAT	SAT	SAT	SAT	SAT
[H₂O₂]	10	1	0.5	0.25	0.05	0.01
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time, min	TCE Concentration, $\mu g/\ell$					
0	195J	269	228	260	140	160
3	---	---	---	---	---	---
5	---	---	---	---	<20	<20
10	<200	<200	<200	40J	<5	<5
15	---	---	---	---	<5	<5
20	<200	<200	3J	<200	---	---
30	<1	<20	<100	<200	<5	<5
40	<1	<1	<50	<1	---	---

[1] SAT = Ozone used as an oxidizer.

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treating the TCE in the Well 01061 groundwater. The results of this set of experiments do indicate that peroxone treatment systems should reach target TCE treatment goals (5.0 $\mu g/\ell$) within 20 to 40 min of treatment depending on water matrix and peroxone system.

Chloroform. Table 52 presents the chloroform MP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. Only one of the MP-UV photolysis based runs indicated any real potential for treating the Well 01061 groundwater to target chloroform levels (10 $\mu g/\ell$). Run V88, a 500 mg/ℓ hydrogen peroxide dosed MP-UV photolysis run, did reach target levels after 30 min of treatment. Removal of the iron from Well 01061 groundwater did not improve chloroform removal.

In general, removal of chloroform from this groundwater sample to target treatment levels using MP-UV based systems seems kinetically slow. With the exception of Run V88, there does not seem to be much potential for reaching the target treatment goal using these systems.

Chloroform is an organic compound that is very photoreactive. Photoreactive compounds can compete with chemical oxidizers for the photons emitted by UV lamps. In some chemical systems, UV photon competition between absorbing species can prevent organic compound photolysis or hydroxyl radical forming reactions from occurring due to limited quantum yields achieved by either reaction. Since Well 01061 groundwater contained high levels of chloroform, it is possible that photon competition did hinder degradation of chloroform in UV based systems that traditionally have been successful in treating this compound. In summary, the poor UV transmissivities associated with the samples used in these studies may have adversely impacted system performance.

Table 53 presents the chloroform LP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. Of all the LP-UV photolysis treatment systems evaluated, the iron removal runs showed the highest potential for meeting the target goal. Three of the four iron removal runs (V89, V92, and V96) indicated potential for meeting target chloroform treatment goals within 40 min of treatment. Run V103, the fourth iron removal run, did not indicate much promise. Run V96 basically met target treatment goals within 20 min of treatment. This run was dosed with the highest amount of hydrogen peroxide evaluated in the iron removal set of experiments. This result agrees with the removal rates achieved for the benzene in Well 01061 groundwater.

Only one of the three ozonated LP-UV photolysis runs performed (Run V91) met the target chloroform treatment goal. This was accomplished after 40 min of treatment. Although the other two ozonated LP-UV photolysis runs (V78 and V55) did not meet target treatment goals, they did achieve at least 95-percent removal within 40 min of treatment.

Table 52
Well 01061 Groundwater Chemical Oxidation Runs - Chloroform
Medium Pressure Mercury Vapor UV Based Systems

Run No.	V.90	V88	V79	V102
UV Lamp	MP[1]	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	1,000	500	500	300
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	YES

Reaction Time, min	Chloroform Concentration, $\mu g/\ell$			
0	<3,000	<3,000	41,700	16,000
5	---	---	---	9,600
10	150	13,000	26,800	9,600
20	58	18,000	20,600	7,000
30	930	8.6	9,350	---
40	450	3.8	3,140	4,900

Run No.	V105	V100	V56	V101
UV Lamp	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO
$[H_2O_2]$	250	200	100	100
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO

Reaction Time, min	Chloroform Concentration, $\mu g/\ell$			
0	18,000	16,000	29,000	15,300
3	---	---	17,400	---
5	18,000	12,000	13,550	12,300
10	15,000	11,000	13,820	12,200
20	---	8,900	10,180	10,300
30	11,000	---	---	---
40	---	6,000	---	10,600

[1] MP = Medium pressure UV lamp used.

Table 54 presents the chloroform peroxone chemical oxidation runs for Well 01061 groundwater samples. With higher hydrogen peroxide doses (10 - 500 mg/ℓ), peroxone achieved slower chloroform removal rates than the lower

Table 53
Well 01061 Groundwater Chemical Oxidation Runs - Chloroform
Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V62	V89	V91	V78	V55
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	SAT[2]	SAT	SAT	SAT
[H_2O_2]	50	25	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	NO
Reaction Time, min	**Chloroform Concentration, $\mu g/\ell$**				
0	33,500	29,000	27,000	33,600	30,200
3	33,020	---	---	---	6,880
5	29,040	---	---	---	243
10	30,450	2,800	880	22,144	2,700
20	32,420	330	35	11,350	755
30	---	13J	280	3,980	---
40	---	87	7.5	1,770	---

Run No.	V96	V103	V63	V92	V61
UV Lamp	LP	LP	LP	LP	LP
[O_3]	SAT	NO	NO	SAT	NO
[H_2O_2]	500	250	200	200	200
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	YES	NO
Reaction Time, min	**Chloroform Concentration, $\mu g/\ell$**				
0	26,000	16,000	32,600	29,000	30,750
3	---	---	27,700	---	35,300
5	---	14,000	26,900	---	31,800
10	770	6,000	25,200	84	28,690
20	17	12,000	25,520	<50	27,810
30	3.3	---	---	<50	---
40	2.6	12,000	---	<50	---

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Table 54
Well 01061 Groundwater Chemical Oxidation Runs - Chloroform Peroxone Based Systems

Run No.	V65	V95	V94	V106	V57	V64
UV Lamp	NO	NO	NO	NO	NO	NO
[H₂O₂]	500	505	201	200.5	10	10
[O₃]	SAT[1]	SAT	SAT	SAT	SAT	SAT
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	YES	YES	YES	NO	NO

Reaction Time min	Chloroform Concentration, µg/ℓ					
0	35,640	19,000	20,000	19,000	35,600	27,800
3	16,600	---	---	---	5,540	19,620
5	14,080	---	---	1,000	3,642	20,600
10	13,720	890	550	99	1,560	19,600
15	---	---	---	10	---	---
20	5,400	24	7.7	---	75	10,050
30	---	2.7	1.8J	3.6	---	---
40	---	1.3	0.77J	---	---	---

Run No.	V80	V76	V81	V77	V107	V109
UV Lamp	NO	NO	NO	NO	NO	NO
[O₃]	SAT	SAT	SAT	SAT	SAT	SAT
[H₂O₂]	10	0.5	0.5	0.25	0.05	0.01
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO

Reaction Time min	Chloroform Concentration, µg/ℓ					
0	29,800	29,900	32,400	34,270	18,000	16,000
3	---	---	---	---	---	---
5	---	---	---	---	2,200	1,700
10	8,400	10,600	5,430	12,500	94	230
15	---	---	---	10	11	24
20	2,330	2,900	4,820	4,930	---	---
30	298	504	2,210	1,040	3.30J	4.70J
40	26	44	946	77	---	---

[1] SAT= Ozone used as an oxidizer.

hydrogen peroxide doses. The peroxone runs with iron removal (V94, V95, and V106) had much better degradation rates. Run V65 and V95 both used a 500 mg/ℓ hydrogen peroxide dose, yet Run V95 achieved target levels in 30 min while Run V65 did not. The difference in run performance may be attributable to the pretreatment step which removes the iron, a critical hydroxyl radical sink, and the possible breakdown of refractory organic complexes.

The 0.01 mg/ℓ and 0.05 mg/ℓ hydrogen peroxide dosed peroxone runs (V107 and V109) achieved the most rapid degradation rates of all of the peroxone systems evaluated. These runs met target treatment goals within 30 min of treatment.

The difference in chloroform removal obtained during performance of all the peroxone runs as compared to the other peroxone runs, except Runs V107 and V109, indicates that volatilization of chloroform did not account for all of the removal achieved. If volatilization accounted for all of the chloroform removal obtained, then all of the ozonated runs would have resulted in similar removal kinetics.

Methylene chloride. Table 55 presents the methylene chloride MP-UV photolysis based chemical oxidation runs for Well 101061 groundwater samples. Only two of the runs listed in Table 55 (Runs V88 and V90) indicated any potential for meeting the target methylene chloride treatment goal of 5 μg/ℓ. Some skepticism is felt about the extremely rapid removal of methylene chloride occurring in Run V88 between test times of 20 to 40 min of treatment. Difficulty with sample matrix and respective analytical dilution may have skewed the analytical results to indicate more promise for treatment than there may actually be. Run V90 is another run that indicated potential for effective methylene chloride removal. This run evaluates a MP-UV photolysis system that contained an extremely high dose of hydrogen peroxide (1,000 mg/ℓ) with iron removal. It is possible that the addition of extremely high doses of hydrogen peroxide may outcompete the chloroform for photons; thereby, resulting in increased production of hydroxyl radicals that can attack the organic compounds, such as methylene chloride, in Well 01061 groundwater. Also, the removal of iron from the water improved UV transmissivity. The combination of both factors probably resulted in increased quantum yield toward hydroxyl radical formation.

The above results indicate that the MP-UV photolysis based systems evaluated will not be able to reach the target methylene chloride treatment goal. Increased hydrogen peroxide doses (i.e., >500 mg/ℓ) and iron removal may improve degradational kinetics, thereby potentially improving the potential of this process for treating Well 01061 groundwater. This concept should be evaluated on the bench scale prior to any form of pilot and/or field evaluation. However, as discussed with the chloroform data, the MP-UV systems are very sensitive to UV transmissivity and photon competition. An improved influent matrix may dramatically improve the degradation rate.

Table 55
Well 01061 Groundwater Chemical Oxidation Runs - Methylene Chloride Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	V90	V88	V79	V102
UV Lamp	MP[1]	MP	MP	MP
[O_3]	NO	NO	NO	NO
[H_2O_2]	1,000	500	500	300
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	YES

Reaction Time, min	Methylene Chloride Concentration, $\mu g/\ell$			
0	1,800	1,600	2,010	2,200
5	---	---	---	1,400
10	48	590	1,930	1,500
20	33	1,100	1,990	1,300
30	130	7.9	1,190	---
40	72	3.9	1,180	940

Run No.	V105	V100	V56	V101
UV Lamp	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO
[H_2O_2]	250	200	100	100
[Catalyst]	NO	NO	NO	NO
Fe Removal	YES	NO	NO	NO

Reaction Time, min	Methylene Chloride Concentration, $\mu g/\ell$			
0	4,000	2,100	2,490	2,200
3	---	---	1,290	---
5	3,800	1,700	855	2,000
10	3,400	1,700	875	1,900
20	---	1,500	724	1,600
30	2,900	---	---	---
40	---	1,100	---	1,600

[1] MP = Medium pressure UV lamp used.

Table 56 presents the methylene chloride LP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. None of the hydrogen

Table 56 Well 01061 Groundwater Chemical Oxidation Runs - Benzene Low Pressure Mercury Vapor UV Lamp Based Systems					
Run No.	V62	V89	V91	V78	V55
UV Lamp	LP[1]	LP	LP	LP	LP
$[O_3]$	NO	SAT[2]	SAT	SAT	SAT
$[H_2O_2]$	50	25	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	NO
Reaction Time, min	Benzene Concentration, $\mu g/\ell$				
0	75J	1,500	1,500	266	141J
3	40J	---	---	---	30J
5	60J	---	---	---	<1
10	39J	<200	<200	142J	5J
20	31J	<100	<100	24J	4J
30	---	<50	12	<200	---
40	---	10	<5	<200	--
Run No.	V96	V103	V63	V92	V61
UV Lamp	LP	LP	LP	LP	LP
$[O_3]$	SAT	NO	NO	NO	NO
$[H_2O_2]$	500	250	200	200	100
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	YES	NO	YES	NO
Reaction Time, min	Benzene Concentration, $\mu g/\ell$				
0	1,200	100	56	1,600	54J
3	---	---	<200	---	117J
5	---	<50	19	---	63J
10	3.4J	<50	<200	<200	30J
20	<2	<20	<200	<50	8J
30	0.25J	---	---	<50	---
40	<1	<20	---	<50	---

[1] LP = Low pressure UV lamp used.
[2] SAT= Ozone used as an oxidizer.

peroxide dosed LP-UV photolysis runs (V62, V61, and V63) resulted in the removal of methylene chloride from this groundwater.

The results from the ozonated LP-UV photolysis runs (Runs V55, V78, and V91) were somewhat variable. Runs V78, V55, and V91 achieved approximately 50, 95, and 99-percent removal efficiencies, respectively, yet none of these runs reached the target methylene chloride treatment goal of 5.0 $\mu g/\ell$.

The iron removal runs (V89 and V96) indicated promise for treating methylene chloride. Run V89 did not indicate potential for meeting treatment levels within the 40-min time span evaluated, while Run V96 met the 5.0 $\mu g/\ell$ treatment goal after 30 min of treatment. The methylene chloride removal achieved in Run V103, an iron removal run which used a 250 mg/ℓ hydrogen peroxide dose, was minimal. This run performed much poorer than the other two iron removal runs.

Table 57 presents the methylene chloride peroxone based chemical oxidation runs for Well 01061 groundwater samples. All of the peroxone runs that included iron removal resulted in meeting the target methylene chloride treatment goals within at least 40 min of treatment. The other runs (except V81) generally succeeded in removing approximately 99 percent of the methylene chloride within 30 min of treatment; but unfortunately, that was not enough to meet the target treatment goal.

Aldrin. Table 58 presents the aldrin MP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. The results of this set of experiments indicate that no removal of aldrin occurs in a MP-UV photolysis/hydrogen peroxide system. In fact, a slight increase of aldrin was noted as the runs proceeded.

Table 59 presents the aldrin LP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. Two of the ozonated LP-UV photolysis runs (P40 and P43) had detectable amounts of aldrin present in the test influent. These experiments indicated that ozonated LP-UV photolysis treatment removed aldrin to below the detection limit within 20 min of treatment. Runs P39 and P44 which were iron removal runs with ozonated LP-UV photolysis treatment also had similar results. The hydrogen peroxide dosed LP-UV photolysis systems (Runs P18 and P31) did not achieve any aldrin removal.

Dieldrin. Table 60 presents the MP-UV photolysis based dieldrin chemical oxidation runs from Well 01061 groundwater. All of the MP-UV photolysis based runs resulted in at least 60 percent removal (0.05 $\mu g/\ell$) within 30 min of treatment. Target dieldrin treatment goals were generally reached within 10 min of treatment. The greater the hydrogen peroxide dose, the more rapid the removal rate achieved.

Table 61 presents the dieldrin LP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. None of the LP-UV photolysis runs achieved appreciable dieldrin removal. None of the LP-UV photolysis based runs met the target treatment goal. The data show no significant trends

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Table 57
Well 01061 Groundwater Chemical Oxidation Runs-Methylene Chloride Peroxone Based Systems

Run No.	V65	V95	V94	V106	V57	V64
UV Lamp	NO	NO	NO	NO	NO	NO
[O_3]	SAT	SAT	SAT	SAT	SAT	SAT
[H_2O_2]	500	505	201	200.5	10	10
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO
Reaction Time min	**Methylene Chloride Concentration , $\mu g/\ell$**					
0	1,400	910	1,000	4,000	2,160	1,320
3	1,060	--	--	--	636	1,080
5	1,660	--	--	500	364	1,200
10	1,380	100	67	91	200	1,060
15	--	--	--	16	--	--
20	792	14	<5	--	44	1,000
30	--	1.5	18	2.1	--	--
40	--	1.9	1.7	--	--	--

Run No.	V80	V76	V81	V77	V107	V109
UV Lamp	NO	NO	NO	NO	NO	NO
[O_3]	SAT	SAT	SAT	SAT	SAT	SAT
[H_2O_2]	10	1	0.50	0.25	0.05	0.01
[Catalyst]	NO	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO	NO
Reaction Time min	**Methylene Chloride Concentration , $\mu g/\ell$**					
0	1,390	1,640	1,790	2,200	4,100	3,600
3	--	--	--	--	950	760
5	802	774	1,010	1,580	99	190
10	--	--	--	--	1.7	57
20	810	426	562	1,300	--	--
30	54	106	572	2,070	15	15
40	12	19	292	20	--	--

[1] SAT = Ozone used as an oxidizer.

Table 58
Well 01061 Groundwater Chemical Oxidation Runs-Aldrin Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P23	P25	P45	P34	P46
UV Lamp	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	SAT	NO
[H_2O_2]	NO	100	200	200	400
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	NO

Reaction Time, min	Aldrin Concentration , $\mu g/\ell$				
0	<0.041	<0.042	<0.045	<0.040J	<0.044
3	<0.043	<0.042	--	<0.042	--
5	<0.043	<0.042	<0.045	<0.042	<0.061
10	<0.043	<0.042	<0.043	<0.042	<0.043
20	<0.043	<0.042	--	<0.042	--
30	--	--	<0.043	--	<0.044

Run No.	P37	P41	P42	P24	P38
UV Lamp	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO
[H_2O_2]	500	500	1,000	500	1,000
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	YES	NO	YES

Reaction Time, min	Aldrin Concentration , $\mu g/\ell$				
0	0.027	0.21	0.13	<0.043	<0.047
3	--	--	--	<0.042	--
5	--	--	--	<0.042	--
10	<0.055	0.18	0.28	<0.042	0.078
15	<0.049	--	--	--	--
20	<0.049	0.028	0.19	<0.042	0.033
30	<0.042	0.053	0.15	--	0.024
40	--	0.072	0.034	--	<0.044

[1] MP = Medium pressure UV lamp used.

Table 59
Well 01061 Groundwater Chemical Oxidation Runs-Aldrin Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P17	P18	P31	P39	P32
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	NO	NO	SAT[2]	SAT
[H_2O_2]	NO	200	200	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	YES	NO
Reaction Time, min	**Aldrin Concentration , $\mu g/\ell$**				
0	<0.041	0.006	0.058	0.12	<0.042
3	0.009J	0.008	0.042	--	<0.040
5	0.013J	<0.031	0.23	--	<0.040
10	0.071	0.032J	0.39	<0.044	<0.041
20	--	--	0.17	<0.044	<0.041
30	--	--	--	>0.044	--
40	--	--	--	<0.044	--

Run No.	P33	P40	P43	P44	
UV Lamp	LP	LP	LP	LP	
[O_3]	SAT	SAT	SAT	SAT	
[H_2O_2]	NO	NO	NO	NO	
[Catalyst]	NO	NO	NO	NO	
Fe Removal	NO	NO	NO	YES	
Reaction Time, min	**Aldrin Concentration , $\mu g/\ell$**				
0	<0.042	0.10	0.088	0.080	
3	<0.042	--	--	--	
5	<0.042	--	--	--	
10	<0.042	<0.042	0.021J	<0.049	
20	<0.053	<0.041	<0.044	<0.042	
30	--	<0.041	<0.045	<0.041	
40	--	<0.042	<0.043	<0.043	

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

in terms of treatment. Treatment of the dieldrin in this groundwater using LP-UV based systems does not look encouraging.

Table 60
Well 01061 Groundwater Chemical Oxidation Runs-Dieldrin Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P23	P25	P45	P34	P46
UV Lamp	MP[1]	MP	MP	MP	MP
[O$_3$]	NO	NO	NO	SAT	NO
[H$_2$O$_2$]	NO	100	200	200	200
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	YES
Reaction Time, min	Dieldrin Concentration , μg/ℓ				
0	0.23	0.22	0.14	0.27	0.14
3	<0.021	<0.021	--	0.11	--
5	<0.021	<0.021	<0.022	<0.021	0.090
10	<0.021	<0.021	<0.022	0.058	0.081
20	<0.021	0.034	--	0.059	--
30	--	--	<0.022	--	<0.022
40	--	--	--	--	--

Run No.	P37	P41	P42	P24	P38
UV Lamp	MP	MP	MP	MP	MP
[O$_3$]	NO	NO	NO	NO	NO
[H$_2$O$_2$]	500	500	500	500	200
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	YES	NO	YES	NO	YES
Reaction Time, min	Dieldrin Concentration , μg/ℓ				
0	0.31	0.38	0.23	0.23	0.26
3	0.14	--	--	0.073	--
5	0.14	--	--	<0.021	--
10	0.27	0.032	0.21	<0.044	0.010
20	0.099	0.052	0.13	<0.022	0.023
30	--	0.009	0.089	--	0.012
40	--	0.010	0.039	--	0.013

[1] MP = Medium pressure UV lamp used.

PPDDE. Table 62 presents the PPDDE MP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. Direct MP-UV photolysis (Run P23) resulted in removal of the PPDDE to below the detection limit within 3 min of treatment.

Table 61
Well 01061 Groundwater Chemical Oxidation Runs-Dieldrin Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P17	P18	P31	P39	P32
UV Lamp	LP[1]	LP	LP	LP	LP
[O_3]	NO	NO	NO	SAT[2]	SAT
[H_2O_2]	NO	200	200	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	YES	NO
Reaction Time, min	Dieldrin Concentration , $\mu g/\ell$				
0	0.24	0.30	1.3	0.31	1.3
3	0.25	0.27	1.2	--	1.4
5	0.26	0.21	1.3	--	1.2
10	0.27	0.21	1.5	0.36	1.2
20	--	--	0.98	0.61	1.1
30	--	--	--	0.20	--
40	--	--	--	0.41	--
Run No.	P33	P40	P43	P44	
UV Lamp	LP	LP	LP	LP	
[O_3]	SAT	SAT	SAT	SAT	
[H_2O_2]	NO	NO	NO	NO	
[Catalyst]	NO	NO	NO	NO	
Fe Removal	NO	NO	NO	YES	
Reaction Time, min	Dieldrin Concentration , $\mu g/\ell$				
0	0.24	0.32	0.23	0.31	
3	0.25	--	--	--	
5	0.22	--	--	--	
10	0.21	0.27	0.30	0.61	
20	0.12	0.32	0.48	0.51	
30	--	0.39	0.37	0.18	
40	--	0.48	0.33	0.18	

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

The hydrogen peroxide dosed runs had variable results. All of the runs, except Run P42 and P46, met the target treatment level of 0.054 $\mu g/\ell$ within

Table 62
Well 01061 Groundwater Chemical Oxidation Runs-PPDDE Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P23	P25	P45	P34	P46
UV Lamp	MP[1]	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	SAT	NO
$[H_2O_2]$	NO	100	200	200	200
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	YES

Reaction Time, min	PPDDE Concentration , $\mu g/\ell$				
0	0.23	0.22	<0.045	<0.042	<0.044
3	<0.043	<0.042	--	<0.042	--
5	<0.043	<0.042	<0.045	<0.042	0.18
10	<0.043	<0.042	<0.043	<0.042	0.19
20	<0.043	<0.34J	--	<0.04	--
30	--	--	<0.043	--	<0.044

Run No.	P37	P41	P42	P24	P38
UV Lamp	MP	MP	MP	MP	MP
$[O_3]$	NO	NO	NO	NO	NO
$[H_2O_2]$	500	500	500	500	500
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	YES	NO	YES

Reaction Time, min	PPDDE Concentration , $\mu g/\ell$				
0	0.095	0.083	0.06	0.23	0.064
3	--	--	--	0.075	--
5	--	--	--	<0.043	--
10	0.049	0.034J	0.06	0.045	0.009
20	0.075	0.046	0.00	<0.043	0.009
30	0.13	0.0060J	0.19	--	0.005
40	0.081	0.0090J	0.033J	--	0.024

[1] MP = Medium pressure UV lamp used.

at least 10 to 20 min of treatment. Runs P42 and P46 met the target treatment level within 40 and 30 min of treatment, respectively.

Runs P37 and P41 evaluated identical conditions (500 mg/ℓ hydrogen peroxide and MP-UV photolysis) with very different results. Run P37 resulted in

only 10 percent removal of PPDDE within 40 min of treatment. It must be pointed out that the water treated in Run P37 was below the target treatment levels at the initiation of the experiment. Run P41 achieved approximately 90 percent removal (0.009 $\mu g/\ell$) within the same timespan.

Iron removal did not result in an improvement in system performance. The iron removal runs generally performed the same as the runs using the same hydrogen peroxide dose.

Table 63 presents the PPDDE LP-UV based chemical oxidation runs for Well 01061 groundwater samples. The levels of PPDDE detected in the test influent ranged from 0.046 $\mu g/\ell$ to 0.16 $\mu g/\ell$; therefore, treatment of this groundwater for PPDDE may not be required. However, based on the results of the experiments listed in Table 63, LP-UV based systems do not seem capable of significant removal of PPDDE from Well 01061 groundwater samples tested.

DBCP. Table 64 presents the DBCP MP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. Only two of the MP-UV photolysis based runs, Runs P38 and P41, were able to reach the target DBCP treatment goal of 0.2 $\mu g/\ell$. Both were 500 mg/ℓ hydrogen peroxide dosed runs, while Run P38 also included iron removal. Both runs met the target treatment goal within 10 min of treatment. Runs P34 and P46 had no DBCP detected in the groundwater samples used in these experiments. The reason for such variability in initial DBCP concentrations is not known.

In general, the various MP-UV photolysis based systems resulted in at least an 85 percent reduction of DBCP. Run P41 met the target DBCP treatment goal of 0.2 $\mu g/\ell$ within 10 min of treatment. The results from this set of runs are somewhat inconclusive. Based on the results of this set of experiments, meeting the target treatment goal for DBCP using MP-UV photolysis based systems would likely require treatment times in excess of 40 min.

Table 65 presents the DBCP LP-UV photolysis based chemical oxidation runs for Well 01061 groundwater samples. Much like the MP-UV based runs, the results of the LP-UV based runs varied. The DBCP concentrations in the test influent were also varied (0.066 $\mu g/\ell$ to 17.7 $\mu g/\ell$). Direct LP-UV photolysis (P17) did not result in the removal of the DBCP from Well 01061 groundwater.

Most of the LP-UV/oxidizer based photolysis runs resulted in some degree of DBCP removal. There were no trends in DBCP degradation detected from the results of the LP-UV/oxidizer runs. The results of these experiments indicate some potential for reaching target treatment goals with increased treatment times (possibly 30 to 40 min) if the initial DBCP concentration is in the 2.0 $\mu g/\ell$ to 3.0 $\mu g/\ell$ range. If the influent contains DBCP in the 15 $\mu g/\ell$ to 18 $\mu g/\ell$ range, then degradation of DBCP in Well 01061 groundwater to target treatment levels will require much longer treatment times using LP-UV photolysis.

Table 63
Well 01061 Groundwater Chemical Oxidation Runs-PPDDE Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P17	P18	P31	P32	
UV Lamp	LP[1]	LP	LP	LP	
[O_3]	NO	NO	NO	SAT[2]	
[H_2O_2]	NO	200	200	NO	
[Catalyst]	NO	NO	NO	NO	
Fe Removal	NO	NO	NO	NO	
Reaction Time, min	**PPDDE Concentration , $\mu g/\ell$**				
0	0.046	0.057	<0.041	<0.041	
3	0.051	0.053	<0.041	<0.041	
5	0.23	0.048	<0.041	<0.041	
10	0.070	0.048	<0.041	<0.041	
20	--	0.13	<0.041	<0.041	
Run No.	P33	P39	P40	P43	P44
UV Lamp	LP	LP	LP	LP	LP
[O_3]	SAT	SAT	SAT	SAT	SAT
[H_2O_2]	NO	NO	NO	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	YES	NO	NO	YES
Reaction Time, min	**PPDDE Concentration , $\mu g/\ell$**				
0	<0.041	0.16	0.11	0.048	<0.044
3	<0.041	--	--	--	--
5	<0.042	--	--	--	--
10	<0.042	0.15	0.14	0.027	0.038
20	<0.042	0.16	0.17	0.078	0.050
30	--	0.11	0.19	0.034	0.027
40	--	0.15	0.20	0.040	0.047

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

Evaluation of selected reaction kinetics

The data from various selected chemical oxidation runs performed during this study were used to calculate the kinetic coefficient (*k*). The runs that

Table 64
Well 01061 Groundwater Chemical Oxidation Runs-DBCP Medium Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P23	P25	P45	P34	P46
UV Lamp	MP[1]	MP	MP	MP	MP
[O_3]	NO	NO	NO	SAT	NO
[H_2O_2]	NO	100	200	200	200
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	NO	YES

Reaction Time, min	DBCP Concentration , $\mu g/\ell$				
0	18.40	11.30	<0.056	<0.053	<0.056
3	4.81	7.41	--	<0.052	--
5	2.45	2.51	<0.056	8.2	<0.062
10	1.51	0.86	<0.054	3.8	<0.054
20	0.82	2.05	--	1.8	--
30	--	--	<0.054	--	<0.055
40	--	--	--	--	--

Run No.	P37	P41	P42	P24	P38
UV Lamp	MP	MP	MP	MP	MP
[O_3]	NO	NO	NO	NO	NO
[H_2O_2]	500	500	500	500	500
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	YES	NO	YES

Reaction Time, min	DBCP Concentration , $\mu g/\ell$				
0	15	22	22	17	0.015
3	--	--	--	6.68	--
5	--	--	--	0.37	--
10	5.6	<0.053	13	4.80	<0.063
20	4.3	<0.053	8.1	<0.54	<0.064
30	7.5	<0.053	6.6	--	<0.056
40	2	<0.053	2.7	--	<0.055

[1] MP = Medium pressure UV lamp used.

were used to generate these data were selected because they had the best treatment achieved while having good support data (i.e., little or no less than detection limit values). As expected, these experiments resulted in appreciable

Table 65
Well 01061 Groundwater Chemical Oxidation Runs-DBCP Low Pressure Mercury Vapor UV Lamp Based Systems

Run No.	P17	P18	P31	P39	P32
UV Lamp	LP[1]	LP	LP	LP	LP
[O$_3$]	NO	NO	NO	SAT[2]	SAT
[H$_2$O$_2$]	NO	200	200	NO	NO
[Catalyst]	NO	NO	NO	NO	NO
Fe Removal	NO	NO	NO	YES	NO
Reaction Time, min	**DBCP Concentration , μg/ℓ**				
0	15.4	17.7	1.2	18	1.1
3	13.3	19.9	1.0	--	0.79
5	15.1	17.6	0.52	--	0.78
10	15.4	14.7	0.37	10	0.73
20	--	--	0.48	12	0.69
30	--	--	--	12	--
40	--	--	--	13	--
Run No.	P33	P40	P43	P44	
UV Lamp	LP	LP	LP	LP	
[O$_3$]	SAT	SAT	SAT	SAT	
[H$_2$O$_2$]	NO	NO	NO	NO	
[Catalyst]	NO	NO	NO	NO	
Fe Removal	NO	NO	NO	YES	
Reaction Time, min	**DBCP Concentration , μg/ℓ**				
0	0.24	0.28	0.066	0.067	
3	--	--	--	--	
5	--	--	--	--	
10	<0.11	0.37	0.25	0.027	
20	<0.12	0.39	0.10	<0.093	
30	0.019	0.41	0.077	0.018	
40	<0.099	0.41	0.075	--	

[1] LP = Low pressure UV lamp used.
[2] SAT = Ozone used as an oxidizer.

contaminant degradation and yet were considered realistic in terms of field application.

Most chemical oxidation reactions are usually second order with respect to both contaminant and chemical oxidizer. In most treatment systems, chemical oxidizer concentrations are not limiting; therefore, pseudo-first order degradation kinetics with respect to the contaminant may be assumed. A first order reaction with respect to the contaminant may be described by

$$\frac{dC}{dt} = -kC$$

where

C = contaminant concentration, mg/ℓ

t = reaction time, min

k = first order reaction coefficient, 1/min

The equation may be rearranged as presented below,

$$1/C \ dC = -k \ dt$$

By integrating and using the separation of the variables method, the above equation may be integrated as presented below,

$$C_i = C_o \times e^{-kt}$$

where

C_i = Contaminant concentration at time, i, mg/ℓ

This equation is referred to as a first order contaminant degradation model. The two unknowns in this model at this point are C_i, which is transient with respect to time, and k which is a constant. The degradation model may be linearized as follows,

$$\ell n \ (C_i \ / \ C_o) = -k \times t$$

The k term is the slope of the line and may be estimated using the above linearized equation. The k term is calculated using linear regression analysis of the data presented using the linearized form of the first order model.

The first order contaminant degradation model can be used to estimate hydraulic retention time within a plug flow chemical oxidation reactor required to achieve a given fractional removal (C/C_o). The chemical oxidation system that is modeled is the same system (treatment conditions) as the run

used to generate the kinetic data. With this information, an estimate of the hydraulic retention time (HRT) required to meet target concentrations for a given influent contaminant concentration can be made. The model can also be used to estimate HRT changes if target effluent contaminant levels are changed or under consideration for change.

It is important that the theory and assumptions made in model development are understood prior to utilization of the kinetic data to be presented. In research, kinetic information between an oxidizer and contaminant are typically performed using a system that contains only the two target reactants. During this work effort, actual groundwater samples were used. As mentioned earlier, these samples were extremely complex, making the kinetic data generated only representative of the specific groundwater matrix and respective treatment system under evaluation. Extrapolation of these kinetic data toward other waters must be performed with extreme caution because only those conditions very similiar to those used in the model development can be properly modeled. The intent of this effort is not to present general kinetic data for universal application, but to sample specific data that can be used with extreme care as another means of evaluating treatability data.

Table 66 presents the k values for selected contaminants for both groundwaters. The table lists the run that was used to calculate the k term, the correlation of fit (r^2) of the regression analysis, and the respective k terms. Table 66 compares the k terms for Well 36001 versus Well 01061 for each contaminant. For Table 67, Well 36001 UV based runs had higher k terms than Well 01061 UV based runs. The peroxone runs were very similar. Although, Well 36001 groundwater had a much greater tendency for iron oxide formation, Well 01061 UV based systems still had slower kinetics. It may be possible that the high concentrations of chloroform present in Well 01061 served as UV photon sinks to such an extent that little conversion of the oxidizers to hydroxyl radicals could occur. However, if this were true then it would intuitively seem that the MP-UV based system would have a higher chloroform k than the LP-UV, which is not the case. Therefore, a rational explanation for the difference in Well 36001 versus Well 01061 k terms cannot be made. Complex chemical matrices often challenge current knowledge of chemical oxidation degradation kinetics by not performing as expected.

The correlation of fit for some of the runs are considered poor in terms of engineering acceptance. Typically r^2 values less than 0.5 are not used for engineering applications. To estimate HRT for the various conditions, less than ideal data had to be utilized due to difficulties associated with the complexity of the groundwater samples.

Table 66 presents several example runs for various contaminants using the first order kinetic model. The first four entries in Table 67, which were benzene runs, illustrate the impact of influent and effluent concentrations on reaction kinetics. As one would expect, as the fractional removal term is decreased so is HRT (Table 67). The value of the HRT cannot be over

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Table 66
Kinetic Data for Selected Runs

Analyte	<---MP-UV--->			<---LP-UV--->			<---PEROX--->		
	Run No.	r^2	k	Run No.	r^2	k	Run No.	r^2	k
Well 36001									
Benzene	V53	0.797	-0.797	ND	ND	ND	V54	0.820	-0.374
T-xylenes	V53	0.622	-0.315	V52	0.340	-0.194	V86	0.981	-0.155
Toluene	V53	0.795	-0.282	V52	0.300	-0.137	V54	0.823	-0.178
TCE	V53	0.762	-0.772	V71	0.791	-0.069	V54	0.744	-0.315
Chloroform	V53	0.970	-0.360	V52	0.983	-0.250	V54	0.894	-0.196
Meth. Chl.	V53	0.726	-0.256	V52	0.366	-0.112	V54	0.858	-0.206
Aldrin	ID[1]	ID	ID	P30	0.250	-0.036	ND[2]	ND	ND
Dieldrin	P9	0.604	-0.094	P35	0.024	-0.003	ND	ND	ND
Well 01061									
Benzene	V56	0.782	-0.099	V55	0.205	-0.124	V57	0.761	-0.182
T-xylenes	V56	0.082	-0.044	V55	0.246	-0.124	V57	0.691	-0.161
Toluene	V56	0.788	-0.102	V55	0.893	-0.141	V57	0.883	-0.188
TCE	V56	0.690	-0.124	V55	0.355	-0.176	V57	0.698	-0.207
Chloroform	V56	0.724	-0.043	V91	0.755	-0.175	V57	0.967	-0.283
Meth. Chl.	V56	0.600	-0.049	V91	0.982	-0.120	V76	0.953	-0.109
Aldrin	P41	0.877	+0.035	P43	0.533	-0.053	ND	ND	ND
Dieldrin	P34	0.068	-0.040	P33	0.905	-0.036	ND	ND	ND
PPDDE	P24	0.502	-0.091	P43	0.003	-0.001	ND	ND	ND
DBCP	P25	0.724	-0.056	P32	0.584	-0.018	ND	ND	ND

[1] ID = Inappropriate data.
[2] ND = No data for comparison.

emphasized in that it correlates directly to treatment costs. The longer a treatment system takes to treat an aliquot of water, the more costly the system will be per aliquot treated.

Using Well 36001 kinetic data (Table 67), HRT estimates for treatment of selected VOCs and pesticides at concentrations of 1,000 $\mu g/\ell$ and 0.5 $\mu g/\ell$, respectively, using a MP-UV/hydrogen peroxide system indicates that methylene chloride and dieldrin are the controlling consitutents. A 20 min HRT is estimated to remove all of the selected contaminants to target treatment levels. Using the same example influent in a peroxone system with Well 36001

Table 67			
Comparison of Kinetic Data			
Systems Well No.	MP-UV/ Hydrogen Peroxide 36001/01061	LP-UV/ozone 36001/01061	Peroxone 36001/01061
Benzene	-0.456/-0.099	NA/-0.124	-0.374/-0.182
T-xylenes	-0.315/-0.044	-0.194/-0.124	-0.155/-0.161
Toluene	-0.282/-0.102	-0.137/-0.141	-0.178/-0.188
TCE	-0.772/-0.124	-0.069/-0.176	-0.315/-0.207
Chloroform	-0.360/-0.043	-0.250/-0.175	-0.196/-0.283
Meth. Chl.	-0.256/-0.049	-0.112/-0.120	-0.206/-0.109
Aldrin	NA/+0.035	-0.036/-0.532	NA
Dieldrin	-0.094/-0.040	-0.003/-0.036	NA
PPDDE	NA/-0.091	NA/-0.001	NA
DBCP	NA/-0.056	NA/-0.017	NA
[1] NA = No data for comparison.			

kinetics, the HRT required to meet target levels is 25 min. Methylene chloride and chloroform are the controlling constituents in this system. Finally, evaluating the same example influent using a LP-UV/ozone system, the estimated HRT is 530 min to meet all treatment levels. In this example, dieldrin is by far the controlling constituent. Ignoring dieldrin, the HRT is estimated at 64 min. Using a combination of this system and GAC to remove the dieldrin may reduce treatment costs because the required HRT is reduced to 64 min (of course, the cost of GAC has to be included in the overall treatment cost estimates).

Since Well 01061 had slower kinetics, the estimated HRTs for the MP-UV/hydrogen peroxide system are much longer as compared to those estimated using Well 36001 data (Table 67). The estimated peroxone HRTs using Well 01061 data are approximately twice as long as the Well 36001 estimates. Quite surprisingly, treatment of these same compounds using Well 01061 data and a LP-UV/ozone system estimated lower HRTs. The HRT estimated for removing PPDDE to target treatment levels is 1,200 min. Once again, a combination of LP-UV/ozone and GAC will improve the competitiveness of this option. Unfortunately, kinetic data for removing PPDDE from Well 36001 was not available because no PPDDE was detected in this water.

In summary, the treatment of both groundwaters using chemical oxidation systems seems to be controlled by the pesticides. Unfortunately, pesticide data were not available for the peroxone systems and Well 36001 LP-UV/ozone (just PPDDE in this case), due to the test influents used in these studies

are deficit of these compounds. Based on current data, if all of the oxidation technologies were combined with GAC for pesticide removal, then HRT estimates for MP-UV/hydrogen peroxide, peroxone, and LP-UV/ozone systems (based on the best of the two groundwater kinetic data) would be 20, 48, and 76 min, respectively, to meet target levels. If not, then the estimated HRTs are 20, 48, and 1,200 min for MP-UV/hydrogen peroxide, peroxone, and LP-UV/ozone, respectively.

Oxidation Pathways of Selected Compounds

Evaluation of potential oxidation pathways is of concern when release of treated media into the environment is likely to occur. This effort was performed to identify through literature review any potential intermediates that may be of concern during chemical oxidation treatment of RMA groundwaters.

Rice and Browning (1980) discuss the three major mechanisms responsible for destruction of organic compounds via chemical oxidation, addition, substitution, and true oxidation. Addition occurs when organic compounds containing aliphatic unsaturation, such as olefins, react with ozone to form an ozonide. The ozonide is formed by crosslinkage across the double bond. These reactions usually result in the formation of aldehydes and ketones as transitory intermediates. Substitution involves replacement of a single atom or functional group with another. This reaction is not a primary mechanism of ozonation, but it is common with chlorination reactions. True oxidation involves introduction of oxygen into the chemical structure of the compound. For example, oxidation of phenol with ozone can produce catechol as a first product via introduction of a hydroxy group onto the second carbon of the aromatic ring. Ring cleavage occurs during prolonged oxidation which results in the formation of several organic acids. Carbon dioxide is suggested as the ultimate product. However, some simple organic acids can be quite refractory to further oxidation (Prengle, Hewes, and Mauk 1975) and are likely endpoint products.

Benzene. It is clear from the work of Symons, Prengle, and Belhateche (1989) that conversion of benzene to oxalic acid and subsequently to carbon dioxide will occur only after extended exposure to UV radiation in the presence of hydrogen peroxide. Stable and semi-stable by-products and intermediates to be expected are phenol, ortho- and para-hydroquinone, ortho- and para-quinone, hydroxylated quinones (such as tetraquinone), more highly oxidized ringed products, and finally, ring cleavage products (i.e., simple organic acids).

Kuo and Soong (1984) determined that benzoquinone and hydroquinone were intermediates of benzene ozonation under neutral pH conditions. They did not detect the presence of phenol as an oxidation intermediate of benzene ozonation as implied by others. They further concluded that only

benzoquinone was produced under acidic conditions. Kuo and Soong did not attempt to further oxidize the quinones via continued ozonation.
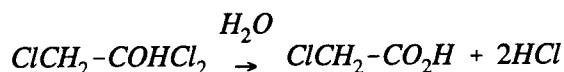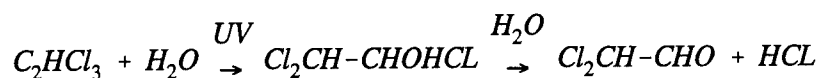
Jurs (1966), as discussed in Rice and Browning (1980), concluded that benzene during ozonolysis initially forms a triozonide (a three-pronged ozonide). After ozonide formation, the reaction quickly proceeds through glyoxal, glyoxylic acid, and finally, oxalic acid.

In summary, oxidation of benzene should result in the degradation of the compound into environmentally safe compounds. Expected intermediates of oxidation are simple carboxylic acids and carbon dioxide.

TCE. Sundstrom et al. (1986) report quantative conversion of TCE to the chloride ion at the completion of a series of runs performed using bench scale, batch reactors. They did not detect any chlorinated organic intermediates appearing in GC traces. On the contrary, Symons, Prengle, and Belhateche (1989) detected numerous unidentified intermediates, most of which eventually disappeared. Neither research group pursued intermediates rigorously; Sundstrom et al. used a flame ionization GC detector, although an electron capture detector is more suitable for halogenated organic compounds. Symons, Prengle, and Belhateche (1989) did not describe their GC detector; they claim to have mass spectra of the intermediates, but present none of these data.

Intermediates of the diverse stability of TCE could be dichloroacetaldehyde (and its oxidation product, dichloroacetic acid) and chloroacetic acid, according to Scheme 1 (presented below). Glyoxylic acid (Scheme 2) would oxidize rapidly to oxalic acid, which could be indefinitely stable and not be readily detected.
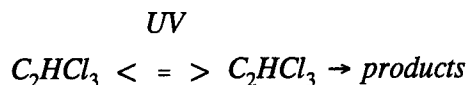
Scheme 1:

$$C_2HCl_3 + H_2O \xrightarrow{UV} Cl_2CH\text{-}CHOHCL \xrightarrow{H_2O} Cl_2CH\text{-}CHO + HCL$$

$$ClCH_2\text{-}COHCl_2 \xrightarrow{H_2O} ClCH_2\text{-}CO_2H + 2HCl$$

Scheme 2:

$$C_2HCl_3 + H_2O_2 \xrightarrow{UV} Cl_2COH\text{-}COHHCl \xrightarrow{H_2O} HO_2C\text{-}CHO + 3HCl$$
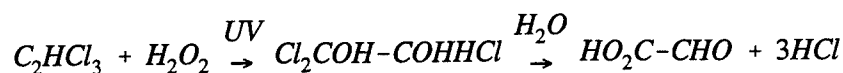
There are two distinct, logical pathways to explain the photooxidation of TCE. In the first (Scheme 3), TCE is photoactivated (presumably to the

diradical), and then it reacts with hydrogen peroxide. This would explain the occurrence of pure photolysis products.

Scheme 3:

$$C_2HCl_3 \xrightarrow{UV} \;<\;=\;>\; C_2HCl_3 \rightarrow products$$

$$\xrightarrow[\rightarrow]{H_2O_2} products$$
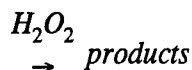
In the second pathway (Scheme 4), hydrogen peroxide is photodisassociated to hydroxyl radicals (see Chapter 1), which then react with TCE. Scheme 4 seems to be better supported based on review of the degradation information gathered during this study.
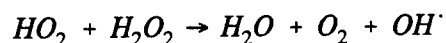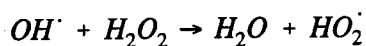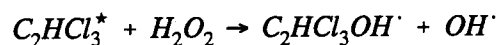
Scheme 4:

$$H_2O_2 \xrightarrow{UV} \;<\;=\;>\; 2HO^{\cdot}$$

$$C_2HCl_3 + HO^{\cdot} \rightarrow C_2HCl_3OH^{\cdot} \rightarrow products$$
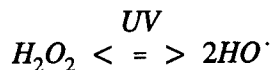
There are two additional observations that must be accommodated by any mechanism or combination of mechanisms:

a. Hydrogen peroxide is not significantly degraded by UV photolysis in the absence of an oxidizable substrate (Symons, Prengle, and Belhateche 1989). This observation also favors Scheme 3.

b. Consumption of peroxide during photooxidation of TCE substantially exceeds the stoichiometric prediction (16:1 m/m versus 3:1 m/m; Symons, Prengle, and Belhateche (1989)), assuming that products are carbon dioxide and chloride. Some of the excess could be attributed to oxidation to other chlorine species, but the major portion probably results from breakdown of peroxide by a pathway such as Scheme 5.
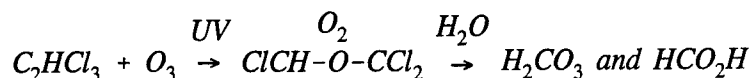
Scheme 5:

$$C_2HCl_3^{\star} + H_2O_2 \rightarrow C_2HCl_3OH^{\cdot} + OH^{\cdot}$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow H_2O + O_2 + OH^{\cdot}$$

Ultraviolet irradiation promoted photooxidation of TCE with hydrogen peroxide has been successfully demonstrated in batch studies and in continuous treatment of contaminated groundwater (Yost 1989). Probable intermediates are essentially organic acids that are of little or no environmental concern. Organic acids produced are usually simple carboxylic acids, such as oxylic acid, that will likely be degraded by natural microbial populations in receiving natural ecosystems.

Ozonation of TCE in the presence and absence of UV irradiation would be expected to produce primarily carbonic and formic acids with only transitory appearance of chlorinated carbon compounds (Scheme 6).

Scheme 6:

$$C_2HCl_3 + O_3 \xrightarrow{UV} ClCH-O-CCl_2 \xrightarrow{O_2 \quad H_2O} H_2CO_3 \text{ and } HCO_2H$$

Formic acid, in turn, would probably be oxidized to carbonate. Insofar as ozone is converted to hydrogen peroxide (see Chapter 1), the same photooxidation products can be anticipated during ozonation as with hydrogen peroxide (Schemes 1 and 2). However, in the only reported study found that documented the use of electron capture detectors for TCE analysis (specific for halogenated organic compounds), no residual chlorinated compounds were noted (Paillard, Brunet, and Dore 1987). Glaze and Kang (1988) found at least 97 percent of the TCE degraded could be accounted for by chloride ions; thus mineralization is essentially complete (i.e., no intermediates).

Rice (1981) suggests that organic compounds containing double bonds (olefins) are oxidized by ozone via conversion to an ozonide, then subsequent oxidation to aldehydes and ketones. Rice suggests that if the original olefin contains at least one hydrogen substituent, then the ozonized fragment is an aldehyde, otherwise both fragments are ketones.

Glaze, Kennake, and Ferry (1993) determined that trichloroacetaldehyde was an intermediate of TCE oxidation. In addition, three other chlorinated compounds were identified: dichloroacetic acid, trichloroacetaldehyde, and trichloroacetic acid. The overall yield of the TCE into the chlorinated organic acids was less than ten percent. Glaze, Kennake, and Ferry further conclude that the chlorinated organic acids are hydrolized by oxygen into simpler non-chlorinated acids as the reactions proceed. They also state that the chlorinated organic acids may not degrade into the non-chlorinated species using Titanium dioxide mediated oxidation. They conclude by stating that they are currently investigating the refractory nature of the chlorinated organic acids in UV based and peroxone oxidation systems for groundwater treatment due to concern for their suspected carcinogenic nature.

In summary, oxidation of TCE does not seem to be of concern with respect to intermediate formation. Simple organic acids, chlorides, and carbon dioxide are the primary suspected products of TCE oxidation. The recent work of Glaze, Kennake, and Ferry (1993) does indicate some concern for intermediate formation.

Chloroform. Due to its simple chemical composition, oxidation of chloroform is of little concern in terms of intermediate formation. Little information is available within the literature specifically on chloroform oxidation, but simple saturated aliphatic compounds such as chloroform have stoichiometrically few pathway options, outside of direct conversion to simple organic acids.

Peyton and Glaze (1988) have proposed a general pathway for photolytic ozonation involving proton abstraction in the absence of radical scavengers. No indication of chemical intermediates are proposed; however, conversion to primarily carbonate, and chlorides, carbon dioxide should be expected.

Kormann, Bahnemann, and Hoffman (1991) propose a degradation pathway for chloroform using titanium dioxide/UV and zinc oxide/UV systems. They propose that chloroform is ultimately reduced to carbon dioxide and chloride ions. Kondo and Jardin (1991) observed similar results using silver loaded titanium dioxide. Kondo and Jardin were able to show high conversion of chloroform to carbon dioxide and chlorides using laboratory scale experiments.

Much like the other contaminants (or even more so), chemical oxidation of chloroform, whether photolytically or not, should not result in the formation of any products of concern. Products to be expected are carbonates, chlorides, and carbon dioxide.

DBCP. Milano, Bernat-Escallon, and Vernet (1990) have identified the products of UV photolysis of DBCP (400 mg/ℓ) in the presence and absence of hydrogen peroxide (concentration unknown). Figure 23 lists products detected after 50 percent disappearance of DBCP. A higher proportion of ketone products is present in the hydrogen peroxide system, as expected, it is also likely that the presence of molecular oxygen affects the ratio of products in the absence of hydrogen peroxide. The authors propose detailed pathways involving both direct photolysis of DBCP and initial attack on DBCP by the hydroxyl radical; however, in consideration of the data presented, these pathways are highly speculative.

DIMP. Buhts (1978) investigated the oxidation pathways of selected organic contaminants using a 10-ℓ UV/ozone bench unit. Various analytical techniques were used to identify key intermediate compounds. Key intermediates of DIMP oxidation identified were (in order of appearance): organo-phosphoric acids (methylated), phosphoric acid, formic acid, acetic acid, inorganic phosphate, and carbon dioxide.

UV		Hydrogen Absent	Peroxide Present
$BrCH_2CHBrCH_2Cl$ ---> $HOCH_2CHBrCH_2Cl$ (DBCP)		+	+
$BrCH_2CHOHCH_2Cl$		+	+
$BrCH_2COCHCH_2Cl$		+	+
$BrCH_2COCH_2Cl$		+	+
$BrCH_2CH=CHCl$ (c/t)		+	tr
$CH_2=CBrCH_2Cl$		+	tr
$BrCH_2CH_2CH_2Cl$		+	tr
CH_2CHCH_2Cl		+	-
CH_3COCH_2Cl		+	+
CH_3COCH_3		+	+
CH_3OH		+	+
$BrCH_2COCH_2Br$		tr	-
$BrCH_2COCH_3$		tr	-
$HOCH_2CHOHCH_2Cl$		tr	tr
CH_3CO_2H		tr	tr

Note: tr = trace amounts.

Figure 23. Proposed oxidation pathway for DBCP (Milano, Bernat-Escallon, and Vernet 1990)

Aldrin and dieldrin. Buhts (1978) determined that dieldrin and endrin were the first level intermediates of aldrin oxidation. The reaction does proceed into formation of the following compounds (in order of expected formation): aldehydes, alcohols, carbonic acid, acetate, and carbon dioxide. The extent of conversion of total aldrin was not specified.

Summary

All of the organic contaminants studied, when submitted to advanced oxidation process treatment, should produce simple organic acids, carbon dioxide, water, inorganic salts (Liang et al. 1991). These compounds are relatively benign and therefore should not pose an environmental threat. A very small percentage of the organic carbon present in the groundwaters may be converted to simple aldehydes and ketones, but literature suggests that these compounds will be transient in nature.

Activated Carbon Compatibility With Residual Oxidizers

The fate of the residual hydrogen peroxide levels in activated carbon systems using the batch agitation experiments indicated that rapid reaction of hydrogen peroxide with the carbon quickly removes hydrogen peroxide from solution. The hydrogen peroxide is broken down into oxygen and water via carbon oxidation. None of the hydrogen peroxide levels tested (even the 1,000 mg/ℓ dose) indicated the presence of the oxidizer within the agitated systems after adding the hydrogen peroxide. This indicates that residual hydrogen peroxide levels entering a GAC column would be very quickly reduced within the first few inches of the carbon bed.

Figure 24 presents isotherms for DIMP, preadsorbed DIMP with oxidizer added, and DIMP/oxidizer systems. From Figure 24, there were no significant differences noted between the three isotherms. The DIMP only activated carbon loading appears to be the lowest of the three. However, the difference between the three isotherms is not considered significant. The two oxidizer present isotherms probably have slightly higher apparent loadings due to oxidation of DIMP by the hydrogen peroxide. Any oxidation of DIMP within the agitated system would appear as increased carbon loading. In summary, residual oxidizer levels within the influent to a GAC column should not have an adverse impact on column performance.
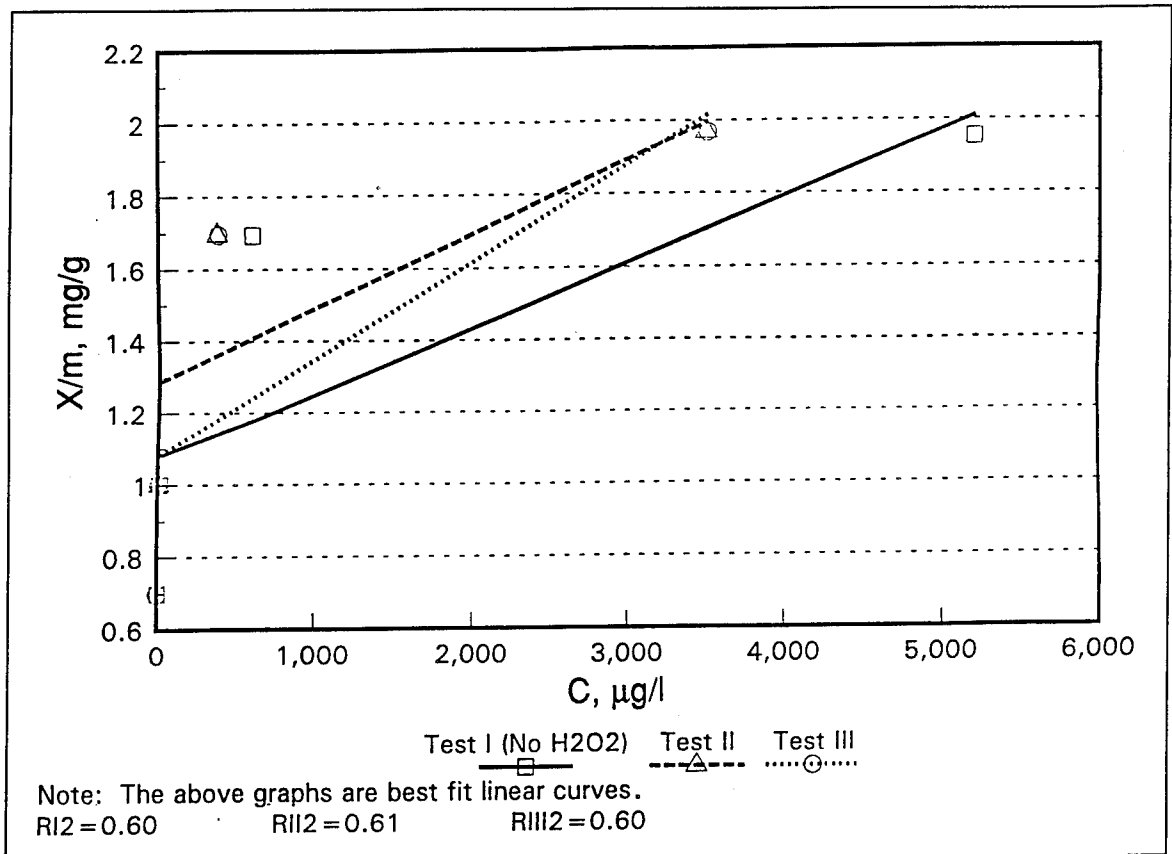
Figure 24. GAC/DIMP study

4 Ongoing WES Activities

The RMA-FS Team and WES are currently planning to perform a pilot scale evaluation of peroxone treatment at RMA. The groundwater that will be used as the influent to this system has not been determined to date. The system flowrate will be in the 2- to 10-gpm range. The estimated schedule for performance of the pilot study is September 1993.

5 Conclusions and Recommendations

Conclusions

The major conclusions derived from this study are listed below:

a. Well 36001 groundwater is composed primarily of benzene at approximate levels in excess of 16,000 $\mu g/\ell$.

b. Well 01061 groundwater is composed primarily of chloroform at approximate levels in excess of 25,000 $\mu g/\ell$.

c. Iron oxidation was considered to adversely impact the performance of the UV based processes due to reduced UV transmissivity.

d. Well 36001 groundwater samples were much more prone to form iron oxides than the Well 01061 groundwater.

e. Hydrogen peroxide was considered the superior means for removing iron from the groundwater as compared to ozonation and aeration. Relatively low amounts of hydrogen peroxide (<50 mg/ℓ) were required to effectively remove the iron.

f. Increasing the amount of hydrogen peroxide to remove the iron increased the UV transmissivity of both groundwaters. However, an optimum dosage below those doses evaluated (<50 mg/ℓ) may exist.

g. The use of filter paper did not indicate promise for removing iron oxide by simple particle straining due to the small size of the iron oxides. However, the use of filters for removing iron oxides is commonly used and is believed feasible since literature suggests that a build-up of oxides is required before appreciable removal can occur.

h. The iron fouling experiments indicated that the groundwaters have a very sensitive REDOX and that prolonged exposure to air will initiate oxidation and subsequent removal of the soluble iron.

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i. The degree of VOC removal attributable to stripping could not be definitely quantified. The series of experiments used to estimate percent stripping did indicate that the majority of benzene and TCE removal was due to oxidation. Chloroform and methylene chloride removal was probably achieved through an equal combination of both stripping and oxidation; however, methylene chloride did seem much more susceptable to oxidation than chloroform.

j. Concentration measured by PID analysis of the off-gases did not exceed 2.0 ppm at any time during the batch experiments indicating a low potential for air pollution due to contaminant stripping during ozonation.

k. Removal of the VOCs from Well 36001 groundwater to target treatment levels using a MP-UV/hydrogen peroxide system would require approximately 20 min of treatment.

l. Removal of the VOCs from Well 36001 groundwater to target treatment levels using a LP-UV/ozone system would require approximately 30 min of treatment.

m. Removal of the VOCs from Well 36001 groundwater to target treatment levels using a peroxone system would require approximately 40 min of treatment.

n. Removal of dieldrin from Well 36001 groundwater to target treatment levels using a MP-UV/hydrogen peroxide system would require approximately 20 min of treatment.

o. Removal of dieldrin from Well 36001 groundwater to target treatment levels using a LP-UV/ozone system does not seem feasible within the treatment times evaluated.

p. PPDDE could be removed by an MP-UV/hydrogen peroxide system within 20 min of treatment.

q. The ability of LP-UV/ozone to remove DBCP from Well 36001 groundwater could not be evaluated because PPDDE was not detected in the test influents used in this series of experiments.

r. No pesticides were detected in the test influents for the peroxone experiments.

s. The DBCP MP-UV/hydrogen peroxide runs were not carried out beyond 10 min of treatment. These runs indicated approximately 88 percent removal within a 10 min HRT.

t. The ability of LP-UV/ozone to remove DBCP from Well 36001 looks promising. Although, the data was extremely variable, LP-UV/ozone systems should remove DBCP to target levels within 30 min.

u. Removal of the VOCs from Well 36001 groundwater to target treatment levels using a peroxone system would require approximately 40 min of treatment.

v. Removal of the VOCs, except methylene chloride, from Well 01061 groundwater to target treatment levels using a MP-UV/hydrogen peroxide system would require approximately 30 min of treatment. The MP-UV/ hydrogen peroxide system did not indicate a high potential for removing methylene chloride from Well 36001 groundwater to target levels.

w. Removal of VOCs, except methylene chloride, from Well 01061 groundwater to target treatment levels using a LP-UV/ozone system would require approximately 30 min of treatment. This set of experiments did not indicate a high potential for removing methylene chloride from this groundwater.

x. Removal of VOCs from Well 01061 groundwater to target treatment levels using a peroxone system would require approximately 30 min of treatment.

y. Removal of dieldrin from Well 01061 groundwater to target levels was obtained within 10 min of treatment using the MP-UV/hydrogen peroxide system.

z. None of Well 01061 LP-UV photolysis based runs were able to reach target dieldrin levels. The use of LP-UV based systems for removing dieldrin from Well 01061 groundwater does not look promising.

aa. None of the pesticide peroxone runs had detectable levels present in the test influents.

ab. The MP-UV/hydrogen peroxide system treating Well 01061 groundwater seems capable of meeting target PPDDE levels within 10 min of treatment.

ac. The LP-UV based system did not achieve significant removal of PPDDE from Well 01061 groundwater.

ad. Variability in terms of DBCP test concentrations was observed in Well 01061 experiments.

ae. MP-UV based systems were capable of meeting DBCP levels with the Well 01061 groundwater at the lower initial concentrations. Treatment

kinetics indicate that the higher range of influents will require longer treatment times than those evaluated.

af. Well 01061 LP-UV DBCP runs also indicated promise for treating DBCP to target levels during treatment of the lower strength influents. As was the case with the MP-UV systems, treatment of the higher strength influents would be difficult and will require longer treatment times.

ag. Iron pretreatment significantly improved VOC degradation rates for both groundwaters. Iron removal prior to oxidation treatment of Well 01061 groundwater did improve removal of methylene chloride to such an extent that target levels were met with all three oxidation systems. Control of iron scavenging and oxide formation could significantly reduce treatment times.

ah. Simple kinetic models were developed using the degradation data from both groundwater samples. The pesticides were determined to be the controlling factor in treatment of both groundwaters. Well 36001 groundwater samples indicate that all three systems have potential for successful treatment. The Well 01061 groundwater was much more difficult to treat. The LP-UV based systems do not indicate a high potential for treating Well 01061 groundwater due to poor pesticides removal. Both the MP-UV based systems and peroxone indicate promise for treating Well 01061 groundwater; however, degradation kinetics achieved in both systems (MP-UV and peroxone) are slow compared to Well 36001 data.

ai. The review of oxidation pathways indicate that all of the compounds evaluated during chemical oxidation treatment would be oxidized to at least simple carboxylic acids. Evidence exists that these compounds during chemical oxidation treatment could yield high conversions to carbon dioxide. In summary, there does not seem to be much potential for the formation of compounds of environmental concern.

aj. The presence of oxidizers in the influent to GAC columns should not have an impact on adsorber performance.

Recommendations

The results of this study indicate that iron oxide formation has a significant impact on treatment performance. The issue of iron oxidation will have to be addressed if any treatment process that increases the REDOX of the water is selected. Examples of these technologies include aerobic biotreatment, air stripping, and chemical oxidation.

Processes considered as strong candidates for design should be pilot tested prior to full scale implementation due to the complexity of these

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groundwaters. Peroxone treatment seems to be an attractive alternative in terms of chemical oxidation. A peroxone pilot study is recommended to further evaluate the potential of this technology for application at RMA. Pilot testing of the other two oxidation processes should also be considered if these processes look promising from an economic standpoint.

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Appendix A
Detailed Literature Review on AOPs

Hydrogen Peroxide Based AOPs

Sundstrom et al. (1986) evaluated the feasibility of using UV/hydrogen peroxide based systems for treatment of a variety of chlorinated, aliphatic VOCs. They concluded that the rate of TCE degradation increases with increasing hydrogen peroxide dose. Increased rate with increasing oxidizer dose observed by Sundstrom et al. was probably due to increased radical production rates per volume of water treated. Sundstrom et al. also concluded that photolysis alone was responsible for removal of chloroform and tetrachloroethane. Direct photolysis of chloroform and tetrachloroethane was nearly as effective as the UV/peroxidation process.

Sundstrom et al. (1989) also used LP-UV lamps with hydrogen peroxide to treat a variety of aromatic VOCs. They concluded that increasing the hydrogen peroxide concentration also increased contaminant degradation rate.

Sims (1981) evaluated using hydrogen peroxide with an iron catalyst (commonly referred to as Fenton's reagent) to oxidize phenol in an industrial wastewater. The Fenton's reagent promotes degradation of hydrogen peroxide into hydroxyl radicals. Sims concluded that chemical oxidation using hydrogen peroxide without the use of Fenton's reagent was impractical due to the slow resulting reaction rate. Sims recommends an iron to phenol ratio of 10:1 and discusses other studies which recommend a ratio of 100:1.

The Sims study introduces a topic of great importance. Several inorganic catalysts are capable of causing the formation of hydroxyl radicals from hydrogen peroxide. If inorganic catalysts are capable of producing enough oxidative radicals without the addition of UV, then treatment of contaminated groundwater using chemical oxidation may even be more cost effective than GAC and air stripping.

Fenton's reagents are a type of catalyst discovered in the late 1800's by Fenton. Fenton's reagent only refers to inorganic iron complexes that serve as a catalyst for a variety of chemical reactions (which can include the formation of radical species from hydrogen peroxide). Another group of inorganic catalysts that have merit are the complexes of other non-ferrous inorganic elements such as tungsten and nickel. These catalysts will be referred to as Milas' reagents; Milas investigated catalysts of this type during the early 1900's. Both Fenton's and Milas' reagents are capable of producing hydroxyl radicals from hydrogen peroxide. Although the hydroxyl radical production rate is slower than the UV based systems, in some cases, it is significant enough for degrading the contaminant.

Wier, Sundstrom, and Klei (1987) evaluated the use of UV/hydrogen peroxide for destruction of benzene in aqueous solutions. They used a modified glucose oxidase titration method for detection of the residual hydrogen peroxide. They concluded that UV addition is required for degradation of benzene. Also, they concluded that decreasing pH increases the degradation rate. Further conclusions are that increasing UV intensity and stoichiometric ratio of oxidizer to benzene increased benzene degradation rate. Intermediates detected were phenol, catechol, hydroquinone, and resorcinol; however, they concluded that further treatment resulted in the complete oxidation of benzene to carbon dioxide and water.

Simovic and Jones (1987) also found that Fenton's reagent serves as a good catalyst for the oxidation of a contaminated groundwater containing various VOCs including trichloroethane and chloroform. They evaluated the ability of four chemical oxidizers to oxidize the VOCs in the groundwater. Oxidizers evaluated include ozone, chlorine dioxide, hydrogen peroxide, and sodium hypochlorite. They concluded that the oxidizers performed in the following sequence of effectiveness: ozone, chlorine dioxide, hydrogen peroxide, and sodium hypochlorite. One shortcoming of their work is that they did not account for off-gasing of the VOCs in the ozone streams exiting the reactor. Combinations of the various chemical oxidizers were not evaluated. Their work indicates promise, but an incomplete evaluative approach prevents any real conclusions from being drawn from their data.

Tatsumi, Murayama, and Terashima (1987) present the results of their work with removal of lignin using hydrogen peroxide with UV irradiation. Fenton's reagent at a 100:1 concentration ratio was used to successfully destroy the lignin. They suggest that the following reaction occurs:

$$Fe^{++} + H_2O_2 \rightarrow Fe^{+++} \ OH^{\cdot} + OH^{-}$$
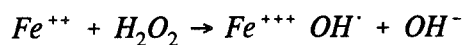
where

$OH^{\cdot}$ is the hydroxyl radical. The source of the iron was a 0.5 mm solution of ferrous ammonium sulfate.

Ozone Based AOPs

Jody, Klein, and Judeikis (1989) used UV/ozone to treat wastewater contaminated with hydrazine compounds. They concluded that UV/ozonation with the addition of tungsten catalyst was the most optimal system evaluated. The UV/ozone/ tungsten system had a slightly slower kinetic rate than other systems evaluated; however, this system produced an effluent with fewer intermediates (e.g., NDMA which is a proven animal carcinogen).

Hoigne and Bader (1975) evaluated the effect of carbonate and bicarbonate on the degradation rate of ozone. They concluded that carbonate species can act as oxidizer sinks resulting in the loss of oxidizer species available for reaction with the contaminants. They further concluded that more efficient oxidation reactions occur in lower pH's favoring carbonate species over those occurring in high pH's which favor the bicarbonate ion. Their results imply that groundwaters that naturally contain carbonates may have increased oxidation efficiency if performed at lower pHs in order to reduce the protective effect of the carbonates. This research gives light to one of many inorganic water constituents that can potentially interfere with oxidation reactions by serving as a sink for the chemical oxidizer species.

Other potential oxidizer sinks commonly found in groundwaters are iron and manganese. Oxidation of these cations resulting in the scumming of the UV quartz tubes were experienced by Zappi et al. (1990) during UV/chemical oxidation treatment of groundwater from the South Plants Area of RMA. The oxidation of iron and manganese caused fouling of the quartz tubes housing the UV lamps resulting in severe reduction of UV irradiation.

Li, Kuo, and Weeks (1979) evaluated the reaction mechanisms of phenol and ozone. They present a method for determination of the reaction order of the oxidation reactions using stopped-flow UV light spectrophotometry. They concluded that increasing pH results in an increase in the degradation rate of the phenol into various chemical intermediates. They further conclude that complete chemical oxidation of the phenol may not be attainable due to the presence of oxidizer-refractory intermediates. The intermediates were determined to be simple organic acids such as oxylic acid. The significance of this work is how both pH and the potential production of intermediates may inhibit the successful implementation of oxidation processes for the treatment of groundwater contaminated with organic compounds.

Kuo (1982) evaluated the mass transfer of ozone from the gas phase into the liquid phase. Kuo presents mathematical equations that can be used to model the kinetics of ozone absorption into an influent during chemical oxidation treatment. These equations are of importance when evaluating contact time (treatment time) of waters containing various levels of a contaminant.

Kuo and Soong (1984) evaluated the oxidation of benzene by ozone in aqueous solutions. They concluded that the half life of benzene decreases from about 20 sec to approximately 0.2 sec with an increase in pH from

3.0 to 7.0. Using gas chromatography, they further concluded that benzoquinone and hydroquinone were detected as intermediates of incomplete chemical oxidation. This work has importance in that a shift from slightly acidic conditions to neutral can result in a two log reduction in the half life of benzene.

Peroxone Based AOPs

Glaze and Kang (1988) performed laboratory scale studies to evaluate the ability of peroxone to remove TCE and tetrachloroethylene (PCE) from a contaminated groundwater. The results proved positive enough to warrant subsequent pilot-scale evaluations by Aieta et al. (1988). Both the bench and pilot studies concluded that the reaction rate of TCE and PCE was increased by factors of 1.8 to 2.8 and 2.0 to 6.5, respectively, using peroxone as opposed to those achieved by ozonation alone. Apparently, TCE was reactive toward ozone alone as well as the hydroxyl radicals formed during peroxone treatment; PCE was only reactive toward the radical species formed during peroxone treatment. Both studies indicated that a hydrogen peroxide-to-ozone ratio between 0.25 and 0.5 was optimal for removing TCE and PCE from the groundwater.

The Metropolitan Water District of Southern California (1991) evaluated peroxone using pilot-scale systems for treatment of 2-methylisoborneal (MIB) and trans-1,10-dimethyl-trans-9-decanol (geosmin). The District concluded that optimum hydrogen peroxide-to-ozone ratios for removal of MIB and geosmin was 0.1 to 0.2. They further conclude that peroxone was better for removal of MIB and geosmin than ozone alone due to hydroxyl radical production.

Mayer et al. (1990) evaluated the feasibility of using peroxone for treatment of a contaminated groundwater containing 75 $\mu g/\ell$ tetrachloroethene, 15 $\mu g/\ell$ TCE, and 1.1 carbon tetrachloride. Their results indicated that the peroxone process could meet their treatment goals within 6 min of treatment. They determined that less than 10 percent of TCE, PCE, and DCE removals could be attributable to air stripping; however, stripping did account for the majority of carbon tetrachloride removal. The optimal molar ratio of hydrogen peroxide to ozone was found to be approximately 0.5. Cost estimates for three treatment options were evaluated: air stripping with off-gas treatment using GAC, liquid phase GAC treatment, and peroxone treatment. Costs estimates for each process were $0.19, $0.43, and $0.25 per 1,000 gal treated for air stripping, carbon adsorption, and peroxone, respectively.

Appendix B
Chemical Oxidation Run Data Sheets

Table B1
Summary of Past RMA AOP Studies

Performers (Year)	Water(s) Studied	Conclusions
Khan and Thompson (1978)	Well 118 Groundwater	Removed DIMP from 70 mg/ℓ to 0.5 mg/ℓ within 4 hr of batch treatment using UV/ozone.
Thompson et al. (1977)	Well PW-3	Removed DIMP from 3,000 mg/ℓ to 0.3 mg/ℓ using UV/ozone. Estimated costs were $0.70/1,000 gal treated.
Buhts (1978)	Laboratory solutions of DIMP, CPMSO2, and selected organochloro-pesticides	Identified a variety of oxidation intermediates for each compound. In general, most compounds were oxidized to simple acids, carbon dioxide, salts, and water.
Zappi et al. (1990)	North Boundary and South Plants Groundwaters, Hydrazine wastewater, and influent to the South Plants Treatment System	A UV/hydrogen peroxide pilot system was used. The lower level contaminated groundwaters were easily treated. South Plants groundwater required excessively long HRTs. Hydrazines were converted to NDMA.
Jelinek et al. (1991)	Hydrazine Wastewater	Total hydrazines were removed to target levels. NDMA proved to be quite refractory. A GAC polishing unit was used as a polishing unit to achieve target NDMA levels.

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE September 1995	3. REPORT TYPE AND DATES COVERED Final report

4. TITLE AND SUBTITLE
A Laboratory Evaluation of the Feasibility of Chemical Oxidation Processes for Treatment of Contaminated Groundwaters

5. FUNDING NUMBERS

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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3909 Halls Ferry Road, Vicksburg, MS 39180-6199;
Rocky Mountain Arsenal, Commerce City, CO 80022;
Ebasco Services, Inc., Lakewood, CO 80022;
U.S. Army Biomedical Research Laboratory, Fort Detrick, MD 21701

8. PERFORMING ORGANIZATION REPORT NUMBER
Miscellaneous Paper IRRP-95-1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers
Washington, DC 20314-1000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The Rocky Mountain Arsenal (RMA) occupies more than 17,000 acres near Denver, Colorado. During World War II, RMA manufactured weapons with resulting chemical and toxic waste products being produced. Additionally, the site was used by Shell Chemical Company to manufacture pesticides and herbicides. As a result of these activities, contaminants have migrated into the groundwater aquifer.

U.S. Army Engineer Waterways Experiment Station performed a bench scale study to evaluate chemical oxidation processes for treatment of two RMA groundwaters. The bench scale study evaluated combinations of ultraviolet light (UV), UV with ozone, and hydrogen peroxide with ozone (peroxone) to determine the feasibility of using chemical oxidation processes to treat the groundwater.

Peroxone treatment of the groundwater was recommended as the best treatment option based on degradation rates and cost. A peroxone pilot study was recommended to further evaluate this technology for RMA application.

14. SUBJECT TERMS
Advanced oxidation processes
Hydrogen peroxide
Ozone
Peroxone
Ultraviolet light

15. NUMBER OF PAGES
163

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT