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Sunlight catalyzed ozone oxidation of volatile organic chemicals

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The University of Arizona, 1990

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SUNLIGHT CATALYZED OZONE
OXIDATION OF
VOLATILE ORGANIC CHEMICALS

by

Susan Marlene Scanlon

A Thesis Submitted to the Faculty of the
DEPARTMENT OF CIVIL ENGINEERING
AND ENGINEERING MECHANICS
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
WITH A MAJOR IN CIVIL ENGINEERING
In the Graduate College
THE UNIVERSITY OF ARIZONA

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ABSTRACT

The degree of oxidation of 3 VOCs; tetrachloroethylene (PCE), trichloroethylene (TCE), and 1,2 dichloroethane (DCA); was evaluated in the presence and absence of catalysts UV light and sunlight, at 3 nominally applied ozone concentrations; high (8.8 mg/L), medium (5.5 mg/L), and low (3.3 mg/L).

Decomposition of dissolved ozone was accelerated in the presence of sunlight over dissolved ozone in the dark, implying that solar catalyzed ozone decomposition would lead to a larger net free radical production over non-catalyzed reactions.

The degree of compound removal was found to be dependent on the type of compound, which was significant at the 99.8 percent confidence level. PCE degradation was mainly photolytic, TCE destruction was more dependent on ozone dose, and DCA was the most refractory of the 3 compounds tested. At a 95 percent confidence level, ozone dose and catalyst type and concentration were also significant, in terms of compound removal.

CHAPTER 1

INTRODUCTION

A potable water supply and environmentally acceptable disposal of pollutants are basic requirements for healthful living. However, past and present waste disposal practices have contributed to the contamination of the nation's water resources. In 1962, Rachel Carson, in her celebrated book, Silent Spring, alerted the nation to water pollution, pesticide contamination, and other environmental problems. Increased public awareness followed also as a result of the situation at Love Canal, which ranked as one of the largest man-made environmental disasters in decades (McDougall, Fusco, and O'Brien, 1980). Originally a 16-acre landfill extending through a large residential community just southeast of Niagara Falls, Love Canal was purchased in 1946 by Hooker Chemical Company and turned into a chemical dump site. Over 43 million pounds of industrial chemical wastes were deposited in the landfill from 1947 to 1952, resulting ultimately in the evacuation of 240 families in August of 1978.

The U.S. Environmental Protection Agency (EPA), from 1979 to 1982, estimated the amount of active and inactive hazardous waste sites to be between 30,000 and 50,000; with 2,000 of those labeled as extremely dangerous, thus receiving priority status for clean-up (Greenberg and Anderson, 1984). Usually the states having many high priority sites, such as New Jersey, California, and Ohio, are densely populated, urban-industrial states that depend on groundwater for a large portion of their drinking water requirements. These sites generally contain toxic organic and inorganic chemicals stored above ground, that have either contaminated water supplies or have the potential to do so. Regardless of population or industrial density, no area of the U.S. is now exempt from the hazards of previously improperly disposed of wastes. Many industries, when there is insufficient land for on-site disposal, have utilized rural areas to provide dump sites, because the land is inexpensive and usually not heavily populated. Illegal dumpings have been numerous and have created unsafe pits, ponds, lagoons, and landfills throughout the countryside. Examples of improper hazardous materials disposal in rural America include "Valley of the Drums", a farm outside of Louisville, Kentucky, where 17,000 to 100,000 drums of waste were illegally dumped and Hardeman County, Tennessee. Here the Velsicol Chemical Corporation dumped an estimated 16.5

million gallons of waste in over 250,000 55-gallon drums between 1964 and 1972 (Epstein, Brown, and Pope, 1982).

The major chemicals involved in these situations include heavy metals, acids and bases, asbestos, and a relatively new category of industrial products, synthetic organic chemicals (SOC). The advent of the use of petroleum virtually revolutionized the entire chemical industry and made possible the synthesis of enormous quantities of organic chemicals. Examples of such chemicals include the halogenated hydrocarbons, which now represent the most common drinking water contaminants. The addition of atoms of chlorine, bromine, or iodine to the basic hydrocarbon structure results in relatively simple chemicals, such as trichloro-ethylene (TCE) and tetrachloroethylene (PCE) or more complex chemicals, such as chlordane. Many of these compounds, such as TCE, are known carcinogens and, therefore, pose a serious threat to humans. They are classified as priority pollutants by the EPA (Pruden, 1983) and are released into the environment through the domestic and industrial discharge of solvents and the application of pesticides. Eventually, these pollutants migrate into the water supply.

In order to protect the nation's water resources, the EPA was granted by Congress the power to establish standards for permit programs to control discharges of active landfills, surface impoundments, and disposal wells; to develop plans for groundwater regulation; and to set water quality standards for public drinking water supplies. Two of the major federal statutes that apply are the Resource Conservation and Recovery Act (RCRA) and the Safe Drinking Water Act (SDWA). RCRA focuses directly on hazardous wastes and regulates the "cradle to grave" handling, transportation, storage, and disposal of hazardous wastes. The SDWA was legislated to provide the authority for the EPA to govern the amount of contaminants in the water supplies, both surface and groundwaters (Greenberg and Anderson, 1984). These Acts attempt to control further contamination and also establish levels to which contaminated supplies must be upgraded.

A contaminated water supply may be upgraded in quality for reuse in agricultural, manufacturing, industrial cooling water, and domestic and potable uses. Appropriate treatment is defined by the quality required for the level of intended use, the highest level being that of human consumption. Often there is no easy solution to the problem of treating

highly toxic wastes in a cost effective manner to meet regulatory and public demands. Natural biological degradation is often unacceptably slow for synthetic chemicals, while adsorption and air stripping processes transfer the pollution from one medium, water, to another medium, activated carbon or air. Oxidation processes such as ozone can be effective in producing innocuous end-products but do so at a high cost. The combination of ozone plus a catalyst, such as ultraviolet light, increases the kinetics of the reactions, thereby reducing processing costs. However, the current method of introducing UV light into the process via lamps is itself quite energy intensive. The ability to utilize solar radiation as a catalyst in place of synthetically produced UV light in the ozone oxidation process could effectively lower the cost of this treatment to an acceptable level, while providing high quality water virtually free of synthetic organic materials.

CHAPTER 2

SCOPE AND NATURE OF THE PROBLEM

Though water can be considered a renewable resource, its supply is not unlimited. Of the 40 million cubic miles of total water available on the planet earth, the oceans and seas contain 97 percent. Of the 3 percent useable water, in terms of acceptable salt content, only 0.5 percent is easily accessible for man's use (Chanlett, 1979). The demand for fresh water is increasing. Public water-supply use in the United States is now estimated at 570 liters per capita per day (Chanlett, 1979), yet the supply remains constant. Population increases and modern conveniences make domestic use high. Industrial and commercial operations obtain approximately 20 percent of their process and service water from public water supplies, the other 80 percent supplied by the users. In most cases the quality of water deteriorates with use, as approximately 60 to 80 percent of a community's total water supply becomes wastewater. Standards for water quality are increasing, while pollution is effecting an overall decrease in raw-water quality. This scenario has created enormous demands on water supply and wastewater disposal facilities, necessitating the development and use

of new combinations of treatment processes. Industrial activities such as pulp and paper mills, food processing, and chemical manufacturing create a wide variety of waste materials. Contaminants from such waste materials often find their way into the environment through unacceptable waste disposal practices. One of the least acknowledged results of such practices has been the gradual but cumulative degradation of groundwater quality. Since the mid 1970s, every state in the nation has reported groundwater contamination problems with increased frequency (WPCF Government Affairs Committee, 1988). Although abandoned hazardous waste disposal sites have been implicated for much of the contamination, there exists many other threats to groundwater supplies; including industrial ponds, pits, and lagoons; landfills, buried pipelines and storage tanks, pesticides, brine disposal, and agricultural runoff.

Impounded reservoirs for industrial wastewater are a serious and commonly reported source of groundwater contamination. U.S. industries treat roughly 5,000 billion gallons of wastewater per year prior to discharge to the environment, including 1700 billion gallons through lagoons or oxidation ponds (Geraghty and Miller, 1978). Basins, pits, and other

types of impoundments also store unknown quantities, resulting in approximately 100 billion gallons of industrial effluent entering the groundwater system per year.

Municipal landfills have been the receptical for countless tons of solid wastes, and this, too, poses a threat to groundwater. Of the 19,000 land-disposal sites accepting municipal wastes, only 20 percent are "authorized" (Geraghty and Miller, 1978). Most receive practically every kind of solid waste: hazardous industrial, hospital, and agricultural wastes, such as plasticizers, phenolic compounds, pesticides and solvents.

Enormous amounts of chlorinated organic solvents, greater than 2 million tons per year (Parsons and Lage, 1985), are used throughout the U.S. The most commonly encountered groundwater contaminants are trichloro-ethylene (TCE) and tetrachloroethylene (PCE), both of which are used as metal degreasing agents or dry-cleaning solvents. A recent survey by the EPA reported that 22 percent of 466 randomly sampled utilities using groundwater as their source have produced drinking water containing volatile organic chemicals (VOCs) at detectable levels (Clark, Fronk, and Lykins, 1988). Other chemicals that are found often are 1,1,1-tri-

chloroethylene; 1,1,1-trichloroethane; cis-1,2 dichloroethylene; 1,2-dichloroethane; and 1,1-dichloroethylene (Clark et al., 1988). Many of these organic compounds are only slowly degraded by bacteria and are relatively mobile in the groundwater environment, hence they remain stable in the water supply and can be transported to create extensive contamination areas.

In response to this growing problem, the EPA defined hazardous waste under the RCRA of 1976 as the following (Greenberg and Anderson, 1984):

- a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may
- (a) cause or significantly contribute to an increase in serious irreversible, or incapacitating reversible illness; or
 - (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

A manifest-system was initiated that allows the EPA to monitor wastes from generator to final treatment, storage, or disposal; a process referred to as "cradle-to-grave" monitoring. Included also was a compliance monitoring program, and currently of the 380 hazardous constituents included in this requirement, only 14 have set concentration limits, established as Maximum Contaminant Levels (MCLs) under the SDWA. Table 1 (Rice, 1988) lists the contaminants under regulation as required by the SDWA of 1986, and Table 2 (Thompson, 1986) lists established Recommended Maximum Contaminant Level Goals (RMCLGs) and MCLs for 8 volatile organic chemicals (VOCs). In addition, the RMCLG and MCL for PCE are anticipated to be established at 0 and 1-5 ug/L, respectively (Rice, 1988). In 1980, the EPA was given authority to clean up hazardous-waste sites when Congress enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and appropriated \$1.6 billion for a Superfund (Dowd, 1988). The program was extended for an additional 5 years in 1986, and \$8.6 billion was added to the fund. The number of such sites is huge, listed at 27,571 by the EPA at the end of fiscal year 1987 and increasing steadily by about 2500 per year.

Table 1. Contaminants Required to be Regulated Under the SDWA of 1986 (Rice, 1988).

Volatile Organic Chemicals

Trichloroethylene	Tetrachloroethylene	Benzene
Chlorobenzene	Carbon Tetrachloride	Dichlorobenzene
1,1,1-Trichloroethane	Trichlorobenzene	Vinyl Chloride
1,2-Dichloroethane	1,1-Dichloroethylene	
<u>trans</u> -1,2-	<u>cis</u> -1,2-	Methylene
Dichloroethylene	Dichloroethylene	Chloride

Microbiology and Turbidity

Total Coliforms	Viruses	Turbidity
Standard Plate Count	<u>Giardia lamblia</u>	<u>Legionella</u>

Inorganics

Arsenic	Barium	Cadmium	Chromium	Lead
Mercury	Nitrate	Selenium	Fluoride	*Silver
*Aluminum	Antimony	*Molybdenum	Asbestos	Sulfate
Copper	*Vanadium	Sodium	Nickel	*Zinc
Thallium	Beryllium	Cyanide		

Organics

Endrin	Lindane	Methoxychlor
2,4-D	2,4,5-TP	Aldicarb
Dalapon	Diquat	Endothall
Carbofuran	Alachlor	Epichlorohydrin
Adipates	Vydate	Simazine
PCBs	Atrazine	Phthalates
Picloram	1,2-Dichloropropane	Dinoseb
Ethylene dibromide (EDB)	2,3,7,8-TCDD (Dioxin)	Toluene
Xylene	Hexachlorocyclo-	Acrylamide
Dibromochloropropane	pentadiene	Glyphosate
(DBCP)	Chlordane	Toxaphene
1,1,2-trichloroethane	PAHs	**Styrene
Pentachlorophenol	*Dibromoethane	**Heptachlor
**Aldicarb sulfone	**Nitrite	**Aldicarb
**Ethylbenzene	**Heptachlor eposide	sulfoxide

Radionuclides

Radium 226 and 228	Gross a-particle activity
Uranium	Radon
B-particle and photon radioactivity	

*removed from list 1/22/88

**substituted onto list 1/22/88

Table 2. VOCs-Proposed RMCLGs (Thompson, 1986).

VOC	RMCLG (mcgm/L)	Proposed MCL (mcgm/L)
Benzene	0	5
Vinyl Chloride	0	1
Carbon Tetrachloride	0	5
1,2-Dichloroethane	0	5
Trichloroethylene	0	5
1,1-Dichloroethylene	7	7
1,1,1-Trichloroethane	200	200
p-Dichlorobenzene	750	750

An example of a currently monitored contamination site is the Motorola 52nd Street plant in Phoenix, Arizona. This site contains numerous organic contaminants in wells located in and around the plant, which were identified via well sampling, several of these compounds far exceeding MCLs for potable water (see Table 3) (Motorola, Inc., 1987). In November of 1982, a leak was discovered at this site in an underground storage tank containing virgin TCA. This initiated a sampling program that followed and quantified large amounts of other chlorinated organic contaminants in the soil and water supply, including TCE and PCE. Concentrations of VOCs as high as 1,000,000 ppb have been measured at the Motorola plant.

Many of these VOCs are a threat to human health, with both acute and chronic risks. Injection wells have been used extensively in the past as a means of disposing the waste, with an estimated 400,000 wells injecting fluids below the surface in 1982 (Epstein et al., 1982). However, the risk is high for contaminants to find their way into the groundwater through leaks in the well shaft or cracks and fissures in the strata. Rather than simply disposing of the waste, efforts are now focusing on treatment technology, and in most cases, clean-up costs for a contaminated aquifer are

Table 3. Organic Compounds Detected During Sampling of Motorola 52nd Street Plant Contamination Site (Motorola, Inc., 1988).

<u>Organic Compound</u>	<u>Highest Mean Concentration (ppb)</u>		<u>Frequency of Occurrence(%)</u>
	<u>On Site</u>	<u>Off Site</u>	
Trichloroethylene	896,000	25,200	92.3
1,1,1-Trichloroethane	870,000	1,810	88.1
Tetrachloroethylene	40,600	489	60.5
Trans-1,2-Dichloro-ethylene	5,220	22,400	51.0
1,1-Dichloroethylene	41,800	2,930	42.3
1,1,2-Trichloro-1,2,2-Trifluoroethane	3,800	11,500	32.4
Chloroform	928	498	27.3
1,1-Dichloroethane	4,370	167	20.5
Chlorobenzene	165	710	7.3
Methylene Chloride	39,300	81.7	7.3
Carbon Tetrachloride	4,770	475	5.7
1,2-Dichloroethane	60.8	2.6	2.0
1,2-Dichloropropane	0.4	1.4	0.6
Trans-1,3-Dichloropropane	65.0	0.7	0.3
1,1,2,2-Tetrachloroethane	66.0	0.02	0.2
Dichlorodifluoromethane	12.8	35	0.2
Trichlorofluoromethane	0.08	24.2	0.2
1,1,2-Trichloroethane	1.6	ND	0.2
Chloroethane	0.09	1.0	0.2
Vinyl Chloride	ND	8	0.1
Dichlorobromomethane	1.1	ND	0.1

prohibitive. Because conventional physical-chemical treatment processes, such as flocculation, sedimentation, and filtration, are often ineffective in removing many of these VOCs, current research is being focused on evaluating alternative processes, such as catalyzed ozone oxidation, to keep within the legislated MCLs for such VOCs in a cost effective manner.

CHAPTER 3

OBJECTIVES

The general objective of this investigation was to determine if sunlight was an influential catalyst in the ozone oxidation of three VOCs; trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,2 dichloroethane (1,2 DCA) in aqueous solutions. Specifically, the objectives were as follows:

- 1) To compare the effects of 2 catalysts (sunlight and synthetically produced ultraviolet (UV) light) and no catalyst (dark) on the ozone oxidation of VOCs in deionized, distilled water, over a reaction period of one hour.
- 2) To evaluate the degree of oxidation for the above named substrates in the presence and absence of catalysts UV light and sunlight, at 3 nominally applied ozone concentrations; high (8.8 mg/L), medium (5.5 mg/L), and low (3.3 mg/L).

CHAPTER 4

LITERATURE REVIEW

4.1 Physical and Chemical Properties of Ozone

Since 1906 when it was first used in Nice, France, ozone has been continually employed to aid in the production of potable water. Though initial use focused mainly on disinfection, modern treatment facilities utilize ozone's ability to function as an oxidant. Ozone has enjoyed widespread use in Europe, but it had not been extensively used in the U.S. until the late 1970s, basically due to its high generating costs. Water treatment experts are now beginning to realize the potential of ozone as a chemical oxidant. Examples of application include flocculation and microfloculation for turbidity removal, promotion of aerobic biological processes in filter and adsorption media, and oxidation of inorganic and organic materials (Rice, Robson, et al., 1985).

Ozone is an unstable gas that boils at -112°C at atmospheric pressure. Partially soluble in water, it is approximately 13 times more soluble than oxygen over the temperature range of 0°C to 30°C . Possessing a characteristically penetrating

odor, ozone is readily detectable by the human nose at concentrations of 0.01 to 0.05 ppm and toxic in concentrations greater than 0.1 ppm by volume (Rice, Robson, et al., 1985).

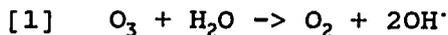
Ozone must be generated on site, usually by the silent-electric discharge process in a flowing air or oxygen stream. Ozone, along with heat, light, and sound, is produced when a high voltage alternating current (6 to 20 kV) is placed across a dielectric discharge gap containing either oxygen-bearing gas or pure oxygen (Rice and Miller, 1985). This process is highly energy intensive, requiring 6-8 kWh/lb of ozone produced when air is the feed gas, and 4-6 kWh/lb when oxygen is the feed. Concentrations of 1 to 3 percent by weight of ozone are obtained under the most economical circumstances when air is the feed gas, while concentrations of 3 to 5 percent may be obtained under the same circumstances when oxygen is the feed gas (Glaze, 1983).

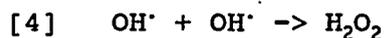
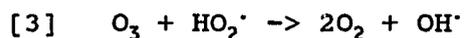
Ozone must then be mixed with water to ensure efficient transfer to the liquid phase; and since it is produced in dilute form in the gas phase (typically 1 to 5 percent weight per weight) solubilities in water greater than 20

mg/L are not often reached in water treatment practices (Glaze et al., 1980). In aqueous solution, ozone is relatively unstable with a half-life of up to 30 minutes, depending on temperature and pH (Rice and Miller, 1985). This half life is even shorter when oxidant-demanding materials are present; therefore, there is no long lasting ozone residual in treated water.

4.2 Ozone Chemistry

As an oxidant, ozone is the most powerful of those used in water treatment, with a potential of -2.07 volts at unit hydrogen activity in alkaline solution, compared to -1.91 V for chlorine dioxide, -1.77 V for hydrogen peroxide, and -1.36 V for chlorine. Second only to fluorine among the readily available water treatment chemicals, ozone is capable of oxidizing many of the organic and inorganic substances found in raw waters (Rice, Robson, et al., 1985). In aqueous solution, ozone is naturally unstable and readily decomposes to molecular oxygen. The following is a proposed mechanism for the decomposition of ozone in water (Glaze et al., 1980):





In this mechanism, O^\cdot , the oxide radical, has a lower reactivity than that of OH^\cdot , the hydroxyl free radical, in many reactions. The ozonide ion, O_3^\cdot , has a half-life of only several milliseconds at 25°C , and the hydroperoxyl radical, HO_2^\cdot , is practically unreactive toward organic substances. The most important intermediate in the decomposition of ozone is the hydroxyl radical, OH^\cdot . With an oxidation potential of -2.80 V , it is an even more powerful oxidizing agent than molecular ozone.

Both molecular ozone and OH^\cdot , an ozone decomposition by-product, are involved in the ozonation process. Thus ozone oxidation pathways are divided into 2 types (Hoigne and Bader, 1983): direct ozonation reactions by molecular O_3 and free radical decomposition reactions by the OH^\cdot species. The direct pathway, involving the ozone molecule, is highly selective and favors low pH conditions. The

presence of OH^\cdot , ultraviolet light, ultrasound, H_2O_2 (HO_2^\cdot) or other solutes in an ozonation process in water initiates a chain reaction decomposition of ozone into OH^\cdot radicals (Glaze, Kang, and Aieta, 1987), which then react in much faster, less selective reactions. Aieta et al. (1988) have summarized the chemistry of ozone decomposition and reaction (see Figure 1).

The hydroxyl radical, one of the main products of ozone decomposition, may react with organic solutes, bicarbonate ion, or molecular ozone. The reaction pathways and kinetics are complex, involving many parameters, including pH and temperature. Experimental observations of rate and reaction order involving ozone/radical reactions reported in the literature are often contradictory and make comparisons difficult (Staehelin and Hoigne, 1982). A summary of the results of various investigators concerned with the kinetics of ozone decomposition in water under a range of conditions and the reaction order relative to ozone is presented in Table 4 (Gurol and Singer, 1982).

As an oxidant ozone is able to react via two different pathways, direct and indirect through its decomposition products, primarily the hydroxyl radical. One factor which

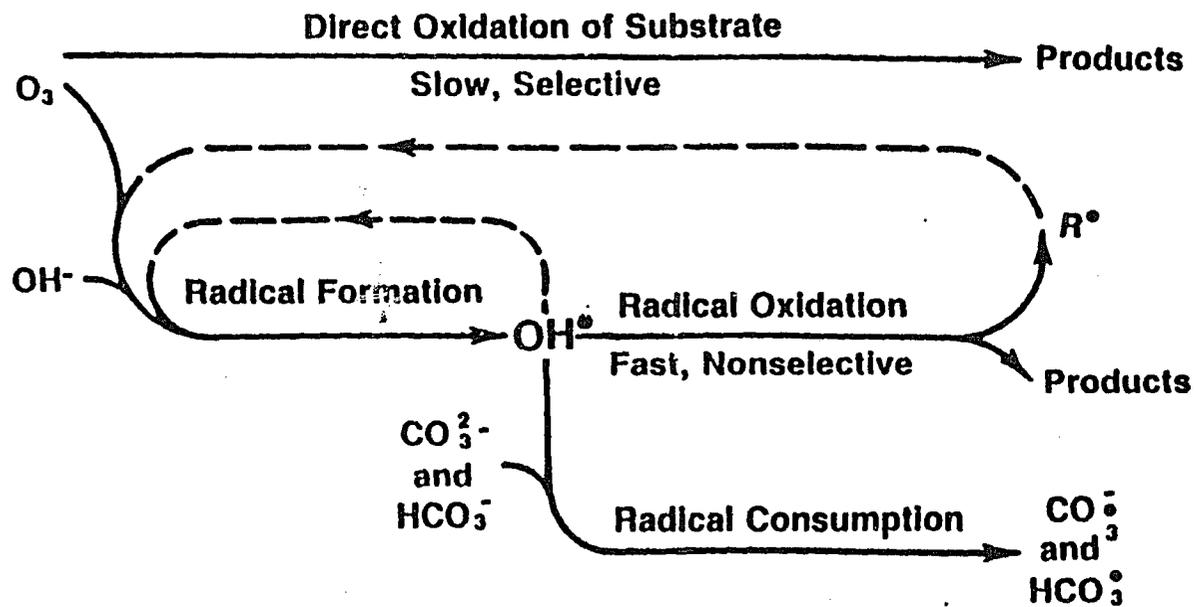


Figure 1. Reaction Pathways of Ozone (Aieta et al., 1988).

Table 4. Summary of the Kinetics of Ozone Decomposition in Water (Gurol and Singer, 1982).

Reference	pH	temp, °C	reaction order
Rothmund & Burgstaller	2-4	0	2
Sennewald	5.3-8	0	2
Weiss	acidic		3/2
	basic		1
Alder & Hill	1-2.8	0-27	1
Stumm	7.6-10.4	1.2-19.8	1
Kilpatrick et al.	0-6.8	25	3/2
Kilpatrick et al.	8-10	25	2
Raukas et al.	5.4-8.5	5-25	3/2
Czapski et al.	10-13	25	1
Rogozhkin	9.6-11.9	25	1
Hewes & Davidson	6	10-50	3/2-2
Hewes & Davidson	8	10-20	1
Hewes & Davidson	2-4	30-60	2
Merkulova et al.	0.22-1.9	5-40	1 or 2
Shambaugh & Melnyk	9	20	1
Rizzuti et al.	8.5-13.5	18-27	1
Sullivan & Roth	0.5-10.0	3.5-60	1
Li	2.1-10.2	25	3/2
Teramoto & Imamura	acidic	25	1-2
	basic	25	1

affects ozone decomposition is the hydroxide ion. The hydroxide ion catalyzes the decomposition of ozone; however, the degree of pH dependence on the reaction order and velocity constant differs among investigators.

Kilpatrick et al. (1956) studied ozone decomposition in both acidic and basic solutions and found the reaction order to be three halves, with second order reactions at high pH. Raukas et al. (1962) also determined a three-halves-order reaction for a pH range of 5.4 to 8.5. Sennewald (1933) reported a second order reaction for pH 5.3 to 8 and 0°C. Hewes and Davidson (1971) postulated that in the pH range of 6 to 8 the reaction order may change from second to first order. Possible reasons for these discrepancies include the different analytical techniques used in aqueous ozone determinations, the data analysis and interpretation, the influence of solution composition, such as the ionic strength, and the presence of impurities in the reagents employed (Gurol and Singer, 1982).

Alder and Hill (1950) measured ozone concentration by two different methods, iodometric and spectrophotometric, and produced different results. The iodometric method for ozone determination has been found to be unreliable and disavan-

tageous for aqueous ozone due to a lack of selectivity, as it measures collectively the total oxidants present, including ozone's decomposition products as well (Gordon et al., 1988). A problem associated with the use of the spectrophotometric method is the uncertainty of the molar absorptivity for aqueous ozone, reported values ranging from 2900 to 3600 L cm⁻¹ mol⁻¹. The recommended procedure for residual ozone determination is the indigo trisulfonate method, because it is based on a discoloration that is both rapid and stoichiometric and has few interferences (Gordon et al., 1988).

Other differences in the past were due to the use of batch reactors in the majority of the research efforts, and kinetic analyses consisted of only the integral method (Gurol and Singer, 1982). Gurol, using initial-rate, differential, and integral methods and independent verification under dynamic conditions, found ozone decomposition to be approximated by second-order kinetics in the pH range of 2-9.5.

Given ozone's high thermodynamic oxidation potential, in theory it is able to completely oxidize organics to CO₂ and water. In actual practice, however, ozone oxidation

reactions are highly selective and electrophilic in nature (Glaze, 1983). For water treatment purposes, it is most useful for the cleavage of multiple bonds and aromatic systems, and reacts slowly with unactivated aromatics like chlorinated benzenes (Glaze, Kang, and Chapin, 1987). Ozone can react with many groupings; C=C bonds, C≡C bonds, aromatic rings, various nucleophilic groupings (amines, phosphines, phosphites, sulfides, etc.), C=N and C=S bonds, carbonyl groups, C-H bonds, organometallics; some more rapidly than others, and some to the exclusion of others in multiple systems (Bailey, 1982). The following relationships have been observed, in general, for relative rates of reaction of various groups with ozone (Bailey, 1978):

alkenes > aromatics > alkanes

Generally, compounds should have unsaturated linkages, i.e. alkenes, acetylenes, aromatics, thiophosphates, amines, etc (Glaze, 1985). Ozone will, for example, react quickly with unsaturated aliphatics, such as TCE, amino groups and phenolic compounds; but does not, however, react with saturated aliphatics, like PCE, and benzene (Hoigne and Bader, 1987). Organics not amenable to ozone oxidation include chlorinated aromatics, chlorinated alkanes,

unsubstituted alkanes, and monocyclic aromatics. These compounds are all subject, however, to attack by radical producing systems (Glaze, 1985).

It is important to recognize that the ozonation of dissolved organic materials will rarely proceed through complete oxidation-that is, to CO_2 and water. As individual organic compounds are partially oxidized, new organic compounds are formed. In most cases, these oxidation products are smaller in molecular size and contain more O_2 atoms than the original compounds, making them less reactive with the oxidant than the original compound, and the reaction becomes kinetically limited. The oxidation products will require longer exposure to higher concentrations of oxidant in order to be converted to the ultimate oxidation products, CO_2 and water. Examples of such oxidation products are carbonyl compounds, alcohols, or stable organic acids like formic, acetic, and oxalic acids. This tendency of ozone to produce refractory compounds resistant to further degradation becomes increasingly costly and impractical (Prengle, 1983). The hydroxyl radical is capable of reacting with so-called refractory aliphatics such as alcohols, short chain acids, etc. (Glaze, 1985). While the reactions of ozone with dissolved solutes is often rather slow-on the order of

minutes-radical reactions can take microseconds. Rate constants for the reaction of OH[·] with organics are commonly in the range of 10⁷-10⁹ M⁻¹ s⁻¹ (Glaze, 1987). Table 5 (Francis, 1987) is a comparison of rate constants for reactions of O₃ and OH[·] with various organic compounds.

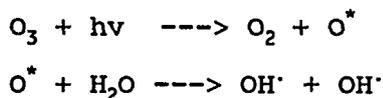
Since in general the hydroxyl radical, a decomposition product of ozone, is more reactive than molecular ozone, a more efficient use of ozone may be to maximize the generation of its decomposition products. One of the most effective ways of accomplishing this decomposition of ozone is with ultraviolet (UV) radiation (Glaze, Kang, and Chapin, 1987). Ozone in the gas and water phase absorbs UV radiation strongly within the band of 200 to 300 nm, exhibiting a maximum at 254 nm. When UV is present, the reactions involved are complex. If the wavelengths emitted include the absorption spectrum of the organic compound as well, the molecule may then either decompose or be excited to a higher energy state. Thus the overall oxidation process is likely to be a combination of photolysis, ozonation, and reactions with the hydroxyl radical produced from the photolysis of ozone (Francis, 1987). The relative importance of any of these processes depends on a large number of factors, including pH, intensity and wavelength of

Table 5. Comparison of Rate Constants for the Reactions of O_3 and OH^\cdot with Various Organic Compounds (Francis, 1987).

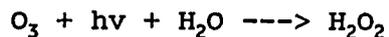
Compound	k_{OH} (L/mol-sec)	k_{O_3} (L/mol-sec)
$ClCH=CHCl$		5.7×10^3
$CH_2=CCl_2$		110
$CHCl=CCl_2$	10^8	17
$Cl_2C=CCl_2$		<0.1
$CHCl_3$	8.5×10^6	<0.1
CCl_4		<0.005
olefins	10^9 to 10^{11}	1 to 450×10^3
aromatics	10^8 to 10^{10}	1 to 10^2
aldehydes	10^9	10
alcohols	10^8 to 10^9	10^{-2} to 1
alkanes	10^6 to 10^9	10^{-2}
carboxylic acids	10^7 to 10^9	10^{-3} to 10^{-2}

UV radiation, substrate concentration, and the presence of radical scavengers.

The UV photolysis of ozone in moist air involves dissociation into an oxygen molecule and oxygen atom, which may then further react with a water molecule, giving two hydroxyl radicals according to the following equations (Glaze et al., 1980):

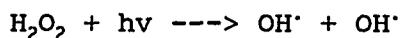


where O^* is in the ^1D excited state. It is the reaction of $\text{O}(^1\text{D})$ with H_2O that is the main OH^{\cdot} producing mechanism. It formerly was assumed that photolysis of ozone in water proceeded the same way; however, the greater number of water molecules quench the excited ozone molecule, resulting in a lower quantum yield in the liquid phase. The overall reaction for the photolysis of aqueous ozone is represented in the equation below, where the primary photolytic product is hydrogen peroxide (H_2O_2):



The H_2O_2 thus formed may then initiate further decomposition of ozone into hydroxyl radicals according to a series of reactions (see Figure 2), ultimately yielding 2 OH^\cdot per 3 O_3 (Glaze, Kang, and Aieta, 1987).

Hydrogen peroxide can also be a direct source of hydroxyl radicals:



However, hydrogen peroxide has an extremely low molar absorption coefficient, $19.6 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm, if it is to be the primary absorber in a photochemical process. On the other hand, the value for ozone is $3300 \text{ M}^{-1} \text{ cm}^{-1}$, resulting in a much higher radical yield in practice (Glaze, Kang, and Chapin, 1987).

The rate of decomposition of ozone is dependent on UV intensity, as well as pH. Hydrogen peroxide is the primary product of the UV photolysis of ozone; but at higher pH values, H_2O_2 will proceed to react with additional O_3 to form OH^\cdot before all the ozone has been photolyzed to H_2O_2 . At lower pH values, if the rate of photolysis of O_3 is decreased by lowering the UV light intensity, time is

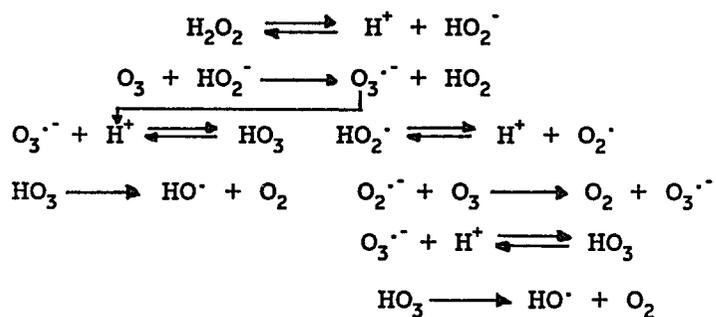


Figure 2. Expected Stoichiometry for Hydroxyl Radical Formation from Ozone and Hydrogen Peroxide (Glaze, Kang and Aieta, 1987).

allowed for residual O_3 to interact with the H_2O_2 formed from the photolysis of O_3 (Hoigne and Bader, 1987). In a study by Hoigne and Bader (1987), ozone irradiated with a 254 nm UV lamp had a half-life of 7 s ($[O_3] < 0.5$ mg/L, pH < 7). When the bulb was shielded with "Parafilm", the halflife increased by a factor of 10.

4.3 Sunlight

The intensity of the solar radiation outside the earth's atmosphere, at the earth's mean solar distance, is known as the solar constant and has the value of 1396 W/m². The energy distribution for this solar spectrum not influenced by the earth's atmosphere is shown in Figure 3. Approximately one half of the sun's energy is in the visible range (380 to 770nm), 40 percent infrared (>770nm), and 10 percent UV (180 to 380 nm). About two-thirds of this energy actually reaches the surface of the earth, the rest being reflected, scattered, or absorbed in the atmosphere (Koller, 1965).

Nearly all of the UV radiation less than 285 nm is absorbed in the atmosphere. The amount of solar UV intensity reaching the earth's surface depends on a number of factors including time of day, time of year, latitude, elevation

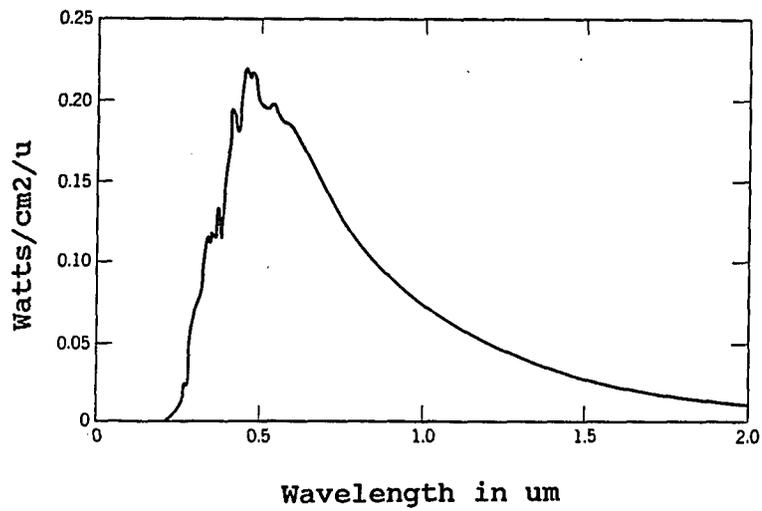


Figure 3. Energy Distribution in the Solar Spectrum Outside the Earth's Atmosphere (Koller, 1965).

above sea level, atmospheric turbidity, and thickness of the ozone layer (Koller, 1965). A term encompassing the first four terms is air mass.

Air mass is unity when the sun is at its zenith (directly overhead) and the path length through the atmosphere is at a minimum. The air mass is greater than 1 for any other position of the sun. Figure 4 (Koller, 1965) shows that as air mass increases, the energy reaching the earth's surface decreases, due to attenuation of the radiation. Attenuation involves absorption and scattering which is influenced by dust, water droplets, and gas molecules of the atmosphere. This effect is not uniform throughout the spectrum, however, and is most prominent at shorter wavelengths. Attenuation of visible wavelengths in clear air is minor. Table 6 (Koller, 1965) compares the solar energy distribution at Tucson, Arizona to corresponding values that would be seen if there were no atmospheric absorption. At 500nm, approximately 90 percent of the energy reaches the earth's surface. The short wavelengths in blue and UV exhibit the most pronounced scattering, hence the sky's blue color.

Ozone is formed from oxygen in the upper atmosphere by a photochemical process. Ozone is a very strong UV absorber in

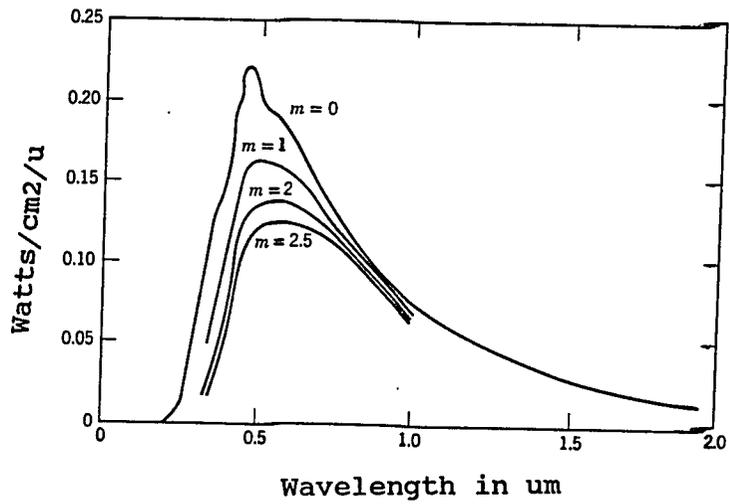


Figure 4. Energy Distribution in the Solar Spectrum in Space and at the Earth's Surface for Various Values of Air Mass, m (Koller, 1965).

Table 6. Solar Energy Distribution at Tucson, Arizona
(Koller, 1965).

Wavelength in Millimicrons	Microwatts per cm ² per 100 A Band	
	Sun in Zenith	No Atmosphere
700	8.3 x 10 ²	10.5 x 10 ²
600	12.4	15.7
550	14.2	18.2
500	15.2	19.9
450	14.7	20
420	11.7	16.4
400	10.9	16
390	7.3	11.1
380	5.9	9.2
370	5.9	9.7
360	5.5	9.6
350	4.6	8.5
340	4.2	8.6
330	3.8	8.7
325	3.5	8.9
320	2.4	6.8
315	1.8	6.1
310	1.1	4.5
305	0.71	4.1
300	0.29	4.1
295	0.08	2.4
292	0.03	1.1

the 200 to 300nm range, exhibiting a maximum at 254 nm, resulting in the screening out of practically all the radiation in this region. Ozone exhibits two other weaker absorption bands from 300 to 350 nm, and stronger bands again in the visible region from 450 to 770 nm (see Figure 5) (Inn & Tanaka, 1959).

The energy in sunlight can be used to produce quantum effects such as photochemical reactions. The energy and absorption of that energy in light is dependent on the wavelengths available. Shorter wavelengths contain more energy per photon than longer wavelengths. The basic law of photochemistry is that a chemical or physical change can occur only when light is absorbed. Atoms and molecules absorb only those wavelengths that provide the amount of energy required to change their state. Most photochemical reactions respond only to UV and visible light, since light of longer wavelength in infrared does not have energy of sufficient intensity to give chemical activity. Table 7 (Legan) gives dissociation energies for various chemical bonds. It can be seen that the higher dissociation energies require the shorter wavelengths not available in sunlight; for example the maximum wavelength to break the C=C bond is 196.1 nm. However, there remain many bonds with lower

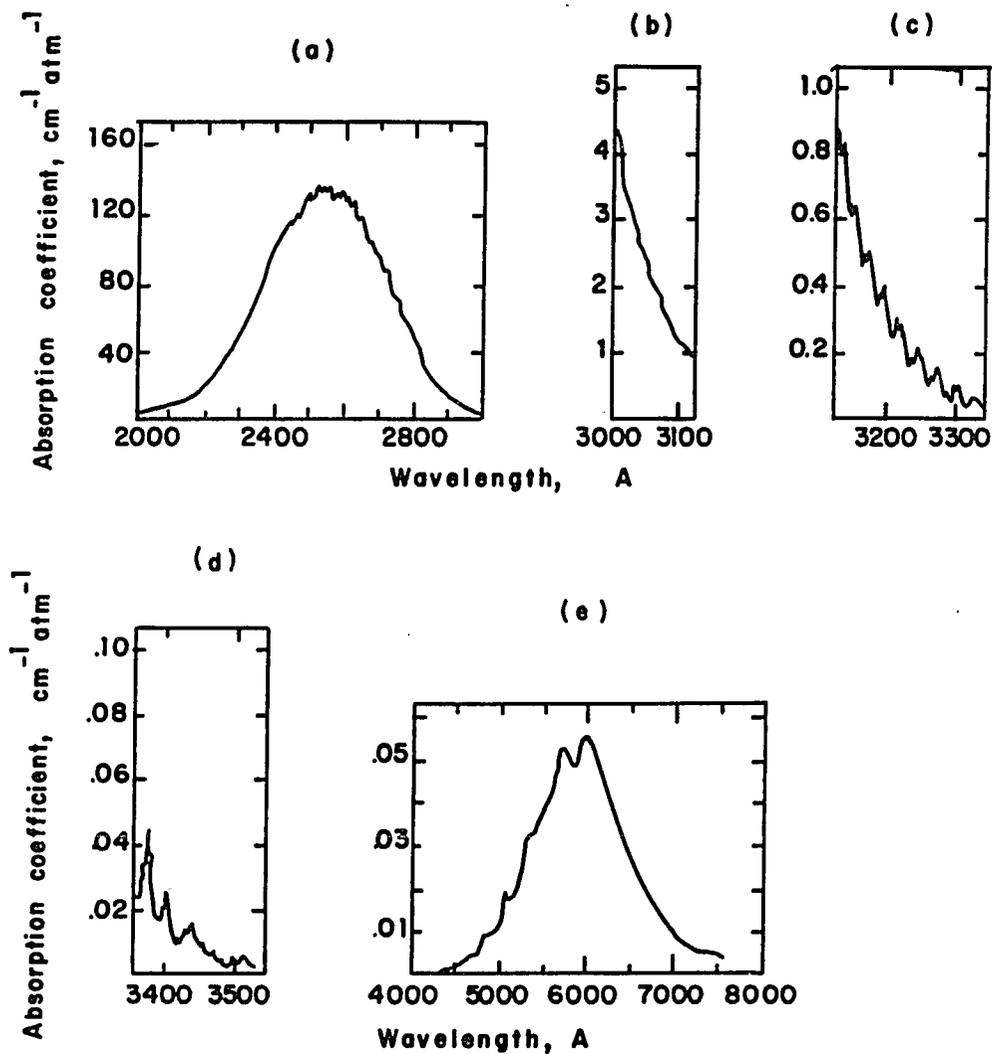


Figure 5. Absorption Spectrum of O_3 (Inn and Tanaka, 1959).

Table 7. Dissociation Energies for Chemical Bonds

<u>Bond</u>	<u>Dissociation energy, kcal/gmol</u>	<u>Maximum wavelength to break bond, nm</u>
Carbon		
C-C	82.6	346.1
C=C	145.8	196.1
C≡C	199.6	143.2
C-Cl	81.0	353.0
C-F	116.0	246.5
C-H	98.7	289.7
C-N	72.8	392.7
C=N	147.0	194.5
C≡N	212.6	134.5
C-O	85.5	334.4
C=O	176.0	162.4
C-S	65.0	439.9
C=S	166.0	172.2
Hydrogen		
H-H	104.2	274.4
Nitrogen		
N-N	52.0	549.8
N=N	60.0	476.5
N≡N	226.0	126.6
N-H (NH)	85.0	336.4
N-H (NH ₃)	102.0	280.3
N-O	48.0	595.6
N=O	162.0	176.5
Oxygen		
O-O (O ₂)	119.1	240.1
-O-O-	47.0	608.3
O-H (water)	117.5	243.3
Sulfur		
S-H	83.0	344.5
S-N	115.0	248.6
S-O	119.0	240.3

dissociation energies that the wavelengths of sunlight can satisfy, such as the C-C bond, which can be broken with wavelengths up to 346.1 nm. These reactions are governed by thermodynamics, kinetics, and photochemistry.

Absorption of energy from UV or visible light is accomplished by displacement of an electron (e^-) from its normal position in the molecule. This e^- displacement involves enough energy to provide sufficient activation energy for bringing about ordinary chemical reactions. For sunlight, this extends from red at about 800 nm to UV at about 300 nm, 36 kcal/mole and 95 kcal/mole, respectively. One photon can activate only one molecule, and the primary photo process is nearly independent of temperature (Daniels, 1964).

It is currently recognized that sunlight is capable of inducing photochemical processes in surface waters and has a strong effect on the redox chemistry of these waters. Generally, absorption by the dissolved organic matter decreases with increasing wavelength, the most solar energy absorbed between 300 and 500 nm. This corresponds to 95 and 58 kcal/mol, respectively, for the primary excitation step,

which is energy sufficient to initiate a variety of different photochemical processes (Cooper et al., 1989).

A few natural molecules are capable of undergoing direct photolysis, but most possess only weak absorbances of the solar spectrum available at the surface. Secondary reactive species resulting from photochemical formation that have been identified and studied include the aqueous electron, singlet oxygen, organo-peroxy radicals, hydroxyl radicals, superoxide, hydrogen peroxide, and other phototransients (Cooper et al., 1989). One of the most studied has been the formation of singlet oxygen, which has been found effective in oxidizing chlorinated phenols (Haag and Hoigne, 1984). Chlorine dioxide exhibits high absorption in the near-UV and visible range of the spectrum, with the result that both ClO_2 and ClO_2^- readily decompose in sunlight (Zika et al., 1984). Thus, sunlight-induced photochemistry has demonstrated its importance in the transformation of natural and anthropogenic chemicals in surface waters, and its potential for use in water treatment.

4.4 Catalyzed Ozone Reactions

Hoigne and Bader (1983), in their work on ozone oxidation, determined rate constants for TCE and PCE to be 17 and <0.1

$M^{-1}s^{-1}$, respectively, at a pH of 2. They found very low reactivity for the saturated alkyl groups, similar to a rate constant of 0.014 reported for n-octane.

Fronk (1987), in her studies of ozone oxidation, found TCE and PCE, at initial concentrations of 10 mg/L, were not removed well at low ozone applied doses and that destruction improved at higher ozone doses. Applied ozone doses of 2 and 6 mg/L gave average percent removals of 39 and 76 for TCE and 40 and 60 for PCE. An applied dose of 20 mg O_3 /L gave an average percent removal of 95 for TCE and 72 for PCE. Alkanes were found to be unreactive, even over extended periods of time, at neutral pH. At pH greater than 9, however, 1,2 DCA, at an initial concentration of 10 mg/L, had an average percent removal of 43 and 69 at 2 mg/L and 20 mg/L applied ozone, respectively.

Francis (1987) reported rate constants for various organics with ozone and the hydroxyl radical. The rate constant for the reaction of TCE with the hydroxyl radical is $10^8 M^{-1}s^{-1}$ and with ozone is $17 M^{-1}s^{-1}$. For PCE, the rate constant with ozone is $<0.1 M^{-1}s^{-1}$. Alkanes have a range of reactivity with the hydroxyl radical from 10^6 to $10^9 M^{-1}s^{-1}$ and with ozone a rate constant of $10^{-2} M^{-1}s^{-1}$. He also evaluated the

ozone and UV oxidation of organic contaminants in deionized water in continuous flow recycle experiments. There was a fast reaction between ozone and TCE attributed to its double bond; and the reaction rate was observed to slow significantly with time, due to organic acid formation. TOC was reduced by 80 percent in approximately 60 minutes, then the decay rate plateaued. The addition of UV with the ozone reduced TOC levels to the sensitivity limit of the TOC analyzer.

Masten and Butler (1986) studied the UV-enhanced ozonation of TCE and 1,2 DCA and found it oxidized both compounds in batch systems at a pH of 2. The reaction was found to be first order in substrate and ozone at ozone concentrations of 1 to 5 mg/L. Rate constants of $25 \text{ M}^{-1}\text{s}^{-1}$ for DCA and $130 \text{ M}^{-1}\text{s}^{-1}$ for TCE were seen for UV-ozone oxidation at a pH of 2 and an initial ozone concentration of 2.2-2.6 mg/L. Ozone oxidation alone gave rate constants of 4.3 and $47 \text{ M}^{-1}\text{s}^{-1}$ for DCA and TCE, respectively.

Koster and Asmus (1971) found that the reaction of OH^\cdot with TCE and PCE produced chloride ions. They reported a reaction rate constant of $2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for TCE with OH^\cdot , $1.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for PCE.

Glaze et al. (1980) studied the ozone/UV oxidation of several refractory species, including PCE, and found the ozone/UV system to be 4 to 50 times faster than ozone or UV alone. Of the 3 reactions to consider in the ozone/UV process, ozonolysis, photolysis, and ozone/UV, the effect due to the O_3/UV process on PCE destruction was 65-98 percent of the reaction rate. The O_3/UV reaction with PCE was found to be first order in substrate and in ozone dose rate. PCE is a UV absorber and it was determined that the photolysis contribution to the reaction rate of 10 percent was more significant than that of ozonolysis, which contributed negligibly. Elimination times were examined for PCE by O_3 and O_3/UV at various pH levels. The reaction rate for ozone increased with increasing pH, requiring 5000 and 450 seconds for 95 percent removal at pHs 4 and 10, respectively. On the other hand, the rate for the combined O_3/UV process decreased with increasing pH, requiring 53 and 395 seconds for 95 percent removal at pHs 4 and 10.

Peyton (1982), in studying the O_3/UV oxidation of PCE, found the process to be overall first order in substrate. Using a continuously sparged stirred tank reactor, times for 63 percent substrate removal were 100, 26, 20, and 7 minutes

for purging, ozonolysis, photolysis, and O_3/UV , respectively.

Glaze et al. (1987) summarized the chemistry of the ozone/UV treatment process for PCE and TCE. PCE, a stronger UV absorber than TCE, was sufficiently dependent on UV flux that it was a significant contributor. Holding the ozone dose rate constant at 8.5 mg/min, the pseudo-first-order rate constant increased from $11 \times 10^4 s^{-1}$ to $27 \times 10^4 s^{-1}$ when UV dose was increased from 13.2 to 39.6 W/L. With UV held constant at 13.2 W/L, the rate constant increased from $9 \times 10^4 s^{-1}$ to $11 \times 10^4 s^{-1}$ when ozone was increased from 4.5 mg/L to 8.5 mg/L. TCE, on the other hand, was influenced more by the ozone dose rate and only weakly dependent on UV flux. At a constant applied ozone dose of 4.5 mg/L, rate constants were $8 \times 10^4 s^{-1}$ and $11 \times 10^4 s^{-1}$ for 13.2 and 39.6 W/L UV, respectively. A constant UV dose of 13.2 W/L gave rate constants of $8 \times 10^4 s^{-1}$ and $14 \times 10^4 s^{-1}$ for ozone dose rates of 4.5 and 8.5 mg/L, respectively.

CHAPTER 5

EXPERIMENTAL METHODS

A statistically designed set of experiments was performed according to the matrix presented in Table 8. A total of 54 experiments were run to evaluate the effectiveness of uncatalyzed, sunlight catalyzed, and UV catalyzed oxidation by varying concentrations of ozone on 3 pure compounds, PCE, TCE, and 1,2-DCA. Reactions were followed by measuring the change in substrate concentrations over time with gas chromatography.

Table 8. Experimental Matrix

Substrate	PCE/TCE/ 1,2 DCA	Catalyst		
		Dark	Sun	UV Lamp
	Zero O ₃	2x	2x	2x
Oxidant Concentrations	Low O ₃	1x	2x	1x
	Med O ₃	2x	1x	1x
	High O ₃	1x	1x	2x

1x, 2x = replications

Total number of experiments = 54

5.1 Ozonation

Ozone was generated from pure oxygen by a Griffen air-cooled generator, Griffen Technics Corporation Inc., New Jersey 07644, Model GR-1B. Oxygen supply pressure in the reactor was set manually at 12 psig on the ozone generator. A variable range of 0 to 2.25 amps DC was used to vary the concentration of ozone in the output gas to obtain average low, medium and high concentrations of aqueous ozone; 3.3, 5.5, and 8.8 mg/L, respectively.

Total gas flow rate out of the reactor was kept a constant 0.4 L/min and measured with a Gilmont #13 glass in-line flow meter fitted with teflon inlet and outlet. Flow rate was controlled with a Whitney stainless steel Model 1MR4 in-line needle valve with stainless steel or Tygon tubing connections.

Ozone carrier gas was passed through a gas washing trap filled with Milli-Q water and fitted with medium glass frits for a reaction time that varied from 15 min to 1 hour, depending on concentration of ozone required and ambient temperature.

Spectrophotometric aqueous ozone determinations were made according to the indigo method as described by Hoigné and Bader (1982) for the anticipated range of over 0.3 mg/L O₃. Since much higher concentrations of O₃ were required, a correspondingly lower volume of sample was added to the flask. 10.0 ml of indigo reagent II was added to two 100 ml volume flasks, A and B. Flask A, the blank, was filled to the 100 ml mark with Milli-Q water. Flask B was dosed with 1 ml of ozone-containing water by use of a glass pipet that was pre-rinsed with the sample water, keeping the pipet tip below the surface of the liquid. Absorbance measurements of both solutions, A and B, was at 600 nm in 1 cm cuvettes using a Perkin-Elmer UV-VIS Hitachi 200 model double-beam grating spectrophotometer with variable wavelength and 2.0 nm bandwidth. Solutions were measured within 1 hour, with a maximum time delay of 4 hours.

Ozone concentration was then calculated from the difference between the absorbance of sample A and sample B (ΔA), as shown in equation (1):

$$\text{O}_3 \text{ concentration in mg O}_3/\text{L} = \frac{\Delta A \cdot 100}{f \cdot b \cdot v}$$

where

ΔA = Difference in absorbance between sample and blank

b = Pathlength of the cuvette in cm

v = Volume of the sample added in ml

f = 0.42

Initial and final aqueous ozone concentrations were determined for all experiments involving ozone.

5.2 Sunlight Enhanced Ozone Decomposition

The decomposition rate of ozone dissolved in distilled, de-ionized water was measured at a pH of 5.1 and a temperature of 32⁰C in the presence and absence of sunlight. A known concentration of aqueous ozone, measured by the method described above, was placed in each of 2 quartz test tubes. One of the tubes was covered by aluminum foil. Both tubes were placed in direct sunlight to keep their contents at the same temperatures, and the changes in concentration were monitored over time.

5.3 Sample Preparation

A concentrated stock solution for each of the 3 chemicals was prepared in an acid washed 15-ml test tube filled with methanol and sealed with a teflon screw cap equipped with a two-way valve which permitted sampling. The concentration was such that a 250 ul injection into a 50 ml test tube of the type described above, containing a 50-50 solution of

methanol and water, gave a final concentration of 1100 mg/L. Stock solutions were stored in an inverted position at 10°C for use in sample and standard preparation. Pure chemicals and stocks were given a warm-up time of at least an hour before preparing samples.

5.4 Uncatalyzed and Sunlight Catalyzed Experiments

Quartz crystal test tubes of 11mm I.D., 14mm O.D., and 240mm length were used for the uncatalyzed and sunlight catalyzed experiments. One test tube was designated for each compound, to eliminate the effect of volumetric variation among test tubes. The test tube was filled to capacity with Milli-Q or ozonated water and sealed with a rubber stopper with open ended needle inserted into it to allow ejection of excess water, thus eliminating any head space within the tube. The needle was left in the stopper for the the injection of 100 ul of the 1100 mg/L stock solution, giving nominal concentrations of 9.02 mg/L for TCE, 8.66 mg/L for PCE, and 9.09 mg/L for 1,2 DCA, then removed. The filled test tube was then inverted and shaken for 10 seconds.

For the uncatalyzed experiments, the quartz tube was shielded with aluminum foil, and a time zero sample was withdrawn through the rubber stopper. Similarly, samples

were withdrawn through the stopper at designated time intervals for a period of 66 minutes. For experiments involving sunlight, the quartz tube was placed in direct sunlight, inverted and placed at a 45° angle, together with a LI-1000 pyranometer/data logger. The pyranometer was placed at the same inclination as the test tube to measure the incident solar radiation, which was recorded in the data logger at 10 minute intervals in W/m^2 . A time zero sample was withdrawn before placing the test tube in direct sunlight, then samples were withdrawn through the stopper at the same designated intervals for a period of 66 minutes. All tests were run at a pH of 5.1 and ambient temperature.

5.5 UV Lamp Catalyzed Experiments

A 500 ml stainless steel Port StarTM Ultra-violet Water Purifier reactor, model PW-1, manufactured by Port Star Industries, was used for the ultraviolet catalyzed experiments. The electrical power to the UV lamp housed within the quartz tube was previously measured to produce a minimum UV lamp intensity of $320 \text{ W}/\text{m}^2$ at the predominant wavelength of 254 nm. The reactor was fitted with a stainless steel inlet tube at the top of the column and a sampling port at the bottom. The UV lamp had an initial warm-up period of half an hour prior to the start of each

experiment. A 400 ml portion of Milli-Q or ozonated water was injected with enough of the 1100 mg/L stock solution to give the same concentration as that in the previous two experiments. The solution was placed on a magnetic stirrer for a few seconds, then poured into the reactor. An initial sample was taken from the port at the bottom of the reactor and the lamp was turned on. At each sampling interval, the port was opened and allowed to flow for 5 seconds before taking a representative sample. Irradiation was continuous during the entire experiment. The reactor was flushed with Milli-Q water between runs. An experimental flow chart is shown in Figure 6.

5.6 Hydrogen Peroxide

After completion of all experiments involving ozone, the final dissolved ozone concentration was determined and the hydrogen peroxide concentration in the sample was measured using a Chemetrics Inc., Calverton, Virginia 22016, test kit model HP-10 colorimetric comparator. The sample was mixed with reagent in a vacuum-sealed vial and the color compared with standards provided.

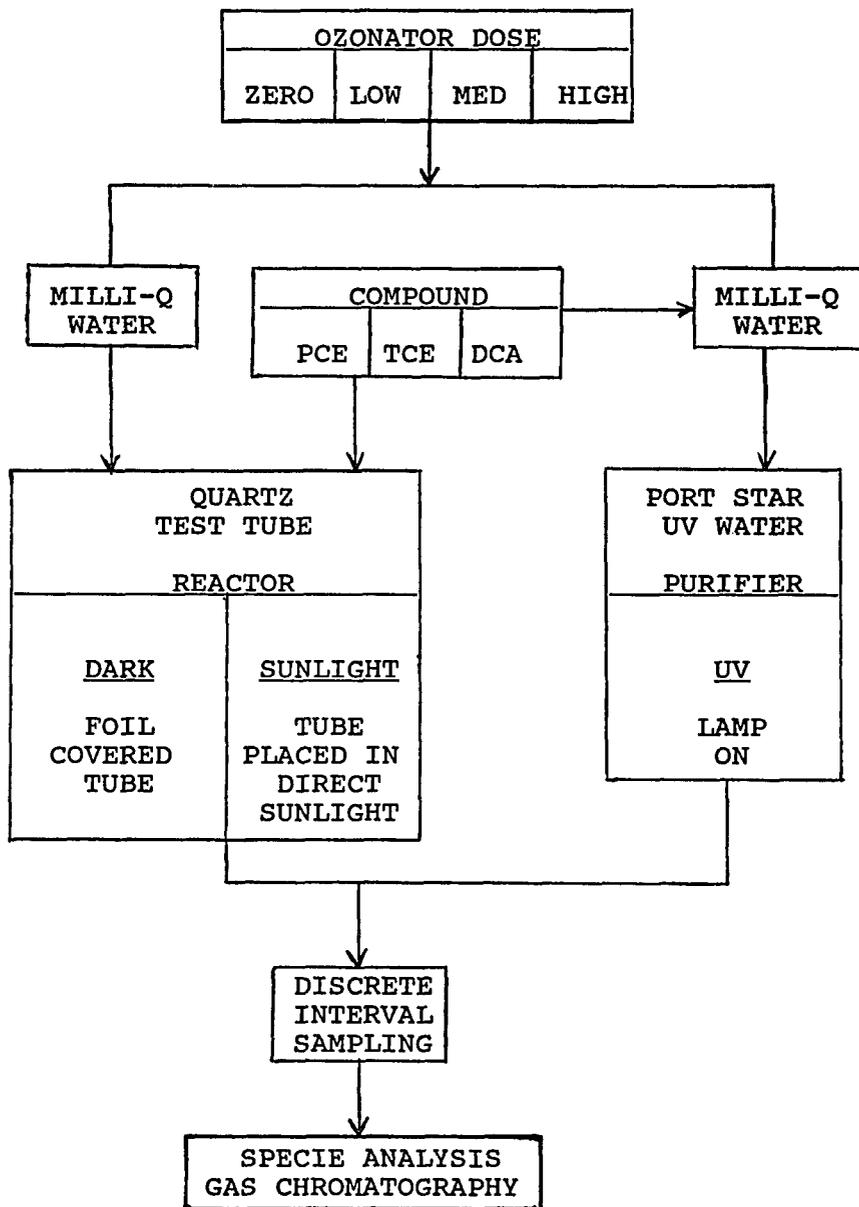


Figure 6. Experimental Flow Diagram

5.7 Gas Chromatographic Procedure

Gas chromatography was used to quantify the organic compounds. Data were obtained from a Hewlett Packard 5890A Gas Chromatograph, equipped with a flame-ionization detector (FID) and a 30 meter DB-WAX Megabore column. The organic compounds of interest are combusted when passed through the detector's burning hydrogen flame forming ion fragments and electrons. The resulting electrical current is monitored and sent to a HP 3392A integrator.

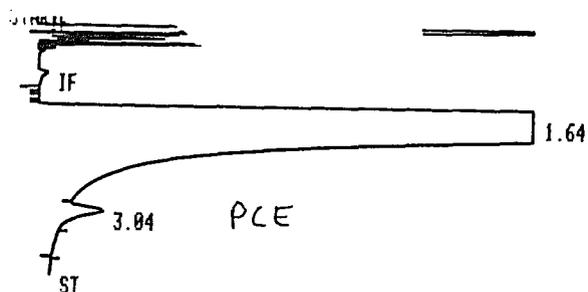
Samples injections were made using the more accurate double bubble technique. This involves the sandwiching of 1 ul aqueous volume of sample between two bubbles of air. Operation conditions for the GC are listed in Table 9. An example of the chromatograph is shown in Figure 7.

5.8 Wavelength Scan

A wavelength scan was run on all three compounds using a Shimadzu UV-VIS Spectrophotometer UV-160A (P/N 204-04550), a micro-computer controlled double-beam recording spectrophotometer with variable wavelength and 2.0nm band width. Absorbance measurements were recorded from 200nm to 500nm in 1 cm cuvettes, using 2.5 times the concentration of

Table 9. GC/FID Operating Conditions

Inlet Temperature.....110°C
 Detector Temperature.....200°C
 Oven Temperature.....35°C
 Column Type.....DBWAX Megabore
 Carrier Gas.....Helium



RUN # 14 MAY/24/88 12:07:05
 WORKFILE ID: B
 WORKFILE NAME:

RT	AREA	TYPE	AR/HT	AREA%
1.64	1.0822E+08	↑SPH	0.227	99.923
3.04	83112	TBB	0.152	0.077

TOTAL AREA 1.0822E+08
 MUL FACTOR

Figure 7. PCE Chromatograph

stock solution as was injected into the test tubes for the above described experiments.

5.9 Statistical Analysis

Results obtained from the experimental matrix were statistically analyzed using a one-way analysis of variance (ANOVA), as presented by Iman and Conover (1983), applied to each component of the experiments; ozoned dosage, type of catalyst, and compound. Analysis was performed for three different sampling times in the experiments; 11, 33, and 66 minutes. The data for DCA was taken at slightly different times, 13, 39, and 65 minutes, and was considered acceptable for comparison purposes. Calculation methods used for the ANOVA are presented in Table 10.

Duncan's Multiple Range Test (Duncan, 1955) was also used to determine whether the differences among the treatment means were significant. To use the test, the treatment means were arranged in ascending order, and the standard error of each mean was calculated as follows:

$$S_m = (MSE/n)^{0.5}$$

where MSE = mean standard error

n = average replication

Table 10. Analysis of Variance Calculations

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square	F-calc.
Treatment A	(a-1)	SS_A	$MS_A = SS_A / (a-1)$	MS_A / MSE
Treatment B	(b-1)	SS_B	$MS_B = SS_B / (b-1)$	MS_B / MSE
Treatment C	(c-1)	SS_C	$MS_C = SS_C / (c-1)$	MS_C / MSE
Experimental Error (Replication)	q	SSE	$MSE = SSE / q$	
Residual Error	$(EU-1) - (a-1) - (b-1) - (c-1) - q$	SS_R		
TOTAL	(EU-1)	SST		

The values $r(p, f)$ were obtained from Duncan's table of significant ranges for α equal to 0.05, f equal to the degrees of freedom on which the standard error is based, and $p = 2, 3, \dots, a$. A set of shortest significant ranges, R_p , was calculated as

$$R_p = r(p, f)S_m, \text{ for } p = 2, 3, \dots, a$$

To compare means, the difference between the largest and the smallest was compared against the shortest significant range R_a . The largest vs. the second smallest was then compared with the shortest significant range R_{a-1} , and so on until all means were compared to the largest. The difference between the second largest and the smallest was then compared against R_{a-1} , and the process continued until all possible combinations of means had been compared. The means were significantly different if their difference was greater than the corresponding shortest significant range.

An analysis of covariance (Dowdy, 1983), which combines a regression analysis with an analysis of variance, was used to determine if the response variable, compound removal, was affected not just by the treatment, i.e. ozone dose, but also linearly related to another variable, the ratio of

ozone dose to initial substrate concentration. An analysis of covariance reduced the within-treatment variability by combining a regression of ozone dose on the ratio of ozone dose to initial substrate concentration with the analysis of variance on ozone dose, making it more likely to see a difference between ozone doses. The data for a one-way analysis of covariance for $a = 3$ treatments and $n_1 = n_2 = n_3 = 12$ observations per treatment group can be arranged as in Figure 8. The general procedure for an analysis of covariance is summarized in Figure 9.

The Lilliefors test (Iman and Conover, 1983) was applied to each sample within the catalyst group, dark, sunlight, and UV lamp, to determine if the populations were normally distributed. The equality of variances was then tested for each catalyst type. The two-sample t-test (Iman and Conover, 1983) was applied to the dark and sunlight data to evaluate any difference in means, and the procedure for small samples with unequal variances was used for comparing dark and UV lamp means and for comparing sunlight and UV lamp means.

Treatment							
I		II		III			
x	y	x	y	x	y		
x_{11}	y_{11}	x_{21}	y_{21}	x_{31}	y_{31}		
x_{12}	y_{12}	x_{22}	y_{22}	x_{32}	y_{32}		
...		
x_{1n}	y_{1n}	x_{2n}	y_{2n}	x_{3n}	y_{3n}	Totals	
$T_{1.(x)}$	$T_{1.(y)}$	$T_{2.(x)}$	$T_{2.(y)}$	$T_{3.(x)}$	$T_{3.(y)}$	$T_{..(x)}$	$T_{..(y)}$

Figure 8. Data Arrangement for Analysis of Covariance

Uncorrected Sums of Squares and Products

x	xy	y
$T_{(x)} = \sum_i \sum_j x_{ij}^2$	$T_{(xy)} = \sum_i \sum_j x_{ij} y_{ij}$	$T_{(y)} = \sum_i \sum_j y_{ij}^2$
$A_{(x)} = \sum_i T_{i.(x)}^2 / n_i$	$A_{(xy)} = \sum_i T_{i.(x)} T_{i.(y)} / n_i$	$A_{(y)} = \sum_i T_{i.(y)}^2 / n_i$
$CF_{(x)} = T_{..(x)}^2 / N$	$CF_{(xy)} = T_{..(x)} T_{..(y)} / N$	$CF_{(y)} = T_{..(y)}^2 / N$

Corrected Sums of Squares and Products

Source	df	$SS_{(x)}$	SP	$SS_{(y)}$
Treat- ment	a-1	$SS_{a(x)} = A_{(x)} - CF_{(x)}$	$SP_a = A_{(xy)} - CF_{(xy)}$	$SS_{a(y)} = A_{(y)} - CF_{(y)}$
Error	N-a	$SS_{e(x)} = T_{(x)} - A_{(x)}$	$SP_e = T_{(xy)} - A_{(xy)}$	$SS_{e(y)} = T_{(y)} - A_{(y)}$
Total	N-1	$SS_{t(x)} = T_{(x)} - CF_{(x)}$	$SP_t = T_{(xy)} - CF_{(xy)}$	$SS_{t(y)} = T_{(y)} - CF_{(y)}$

Adjusted Sums of Squares

Source	df	$SS_{(y)}'$	$MS_{(y)}'$
Treat- ment	a-1	$SS_{a(y)}' = SS_{t(y)}' - SS_{e(y)}$	$MS_{a(y)}' = SS_{a(y)}' / (a-1)$
Error	N-a-1	$SS_{e(y)}' = SS_{e(y)} - SP_e^2 / SS_{e(x)}$	$MS_{e(y)}' = SS_{e(y)}' / (N-a-1)$
Total	N-2	$SS_{t(y)}' = SS_{t(y)} - SP_t^2 / SS_{t(x)}$	

Reject H_0 if $F = MS_{a(y)}' / MS_{e(y)}' > F_{\alpha, a-1, N-a-1}$ at the level of significance.

Figure 9. Analysis of Covariance Calculations

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Solar Enhanced Ozone Decomposition

Ozone decomposition rates were determined for ozone dissolved in Milli-Q water at a pH of 5.1 and 36⁰C, both in the dark and in the presence of sunlight. A stock solution of aqueous ozone was prepared using Milli-Q water and added to two stoppered quartz test tube reactors, one encased with aluminum foil. Both reactors were then placed in the open atmosphere (i.e. sun), and the change in dissolved ozone concentration with respect to time was monitored. Results are presented in Figure 10.

The experimental data was modeled by integrating standard kinetic equations for first, three halves, and second order reactions. The statistical parameter to determine the reaction order was the correlation coefficient for the linear regression lines of the above mentioned plots. The correlation coefficient had the highest value for a first order model in both cases of dark and sunlight, 0.981 and 0.991, respectively, yielding reaction rates of 0.924 hr⁻¹ in the dark and 2.136 hr⁻¹ in sunlight.

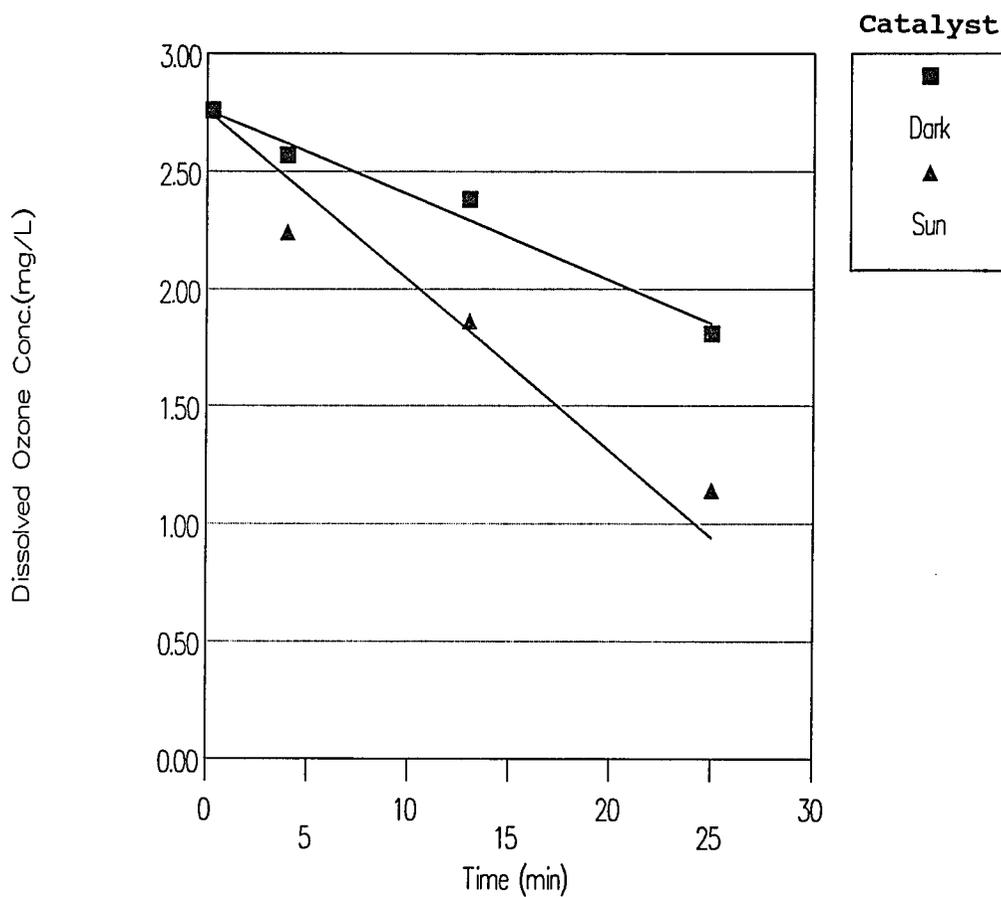


Figure 10. Dissolved Ozone Concentration as a Function of Reaction Time and Catalyst.

Since both samples originated from the same batch of ozonated water at the same pH and temperature, the enhanced decomposition of the dissolved ozone in sunlight must be due to absorption of energy from the sun's rays. The efficiency of the reaction depends on the overlap between the absorption spectrum of ozone and the emissions from the sun. The UV portion of the spectrum ranges from 180 to 380 nm; however, the UV range of sunlight is almost entirely absorbed by the ozone layer in the upper atmosphere at wavelengths below 285 nm. Ozone exhibits the strongest absorption band from 200 to 300 nm, with a maximum at 254 nm, and it possesses weaker bands from 300 to 350 nm and stronger bands again in the visible region, beginning around 400 nm, from 450 to 770 nm (Inn and Tanaka, 1959). Therefore, all other factors held constant, the accelerated decomposition of dissolved ozone in sunlight over dissolved ozone in the dark must be due to the absorption of energy from a portion of the sun's rays.

The results of first order kinetics agree with those of several other researchers (Alder and Hill, 1950; Hewes and Davidson, 1971). Hewes and Davidson determined the first order rate constant to be 12.1520 hr^{-1} at 20°C . This value differs from that determined in this research due to pH

differences (pH 8 vs. pH 5), and the method employed for measuring dissolved ozone (iodometric vs. indigo trisulfonate).

First order kinetics is not in agreement with many other researchers (Sennewald, 1933; Kilpatrick et al., 1956). Gurol (1982) concluded that the decomposition kinetics were second order over the pH range of 2 to 9.5, using a more detailed method of analysis by initial-rate, differential, and integral methods.

The experimental results imply that solar catalyzed ozone decomposition would lead to a larger net free radical production over the non-catalyzed reaction.

6.2 Oxidation Reactions

The major experimental matrix was devised to compare the effect of 4 oxidant dosages; zero, low, medium, and high; and 3 catalyst conditions; dark, sunlight, and UV lamp; on the removal of three 3 substrates; PCE, TCE, and 1,2 DCA. All data derived from these experiments can be found in the Appendix. Percent removals as a function of reaction conditions for the three compounds are presented in Table 11.

Due to the high volatility and low concentration of the substrates employed in this research, experimental difficulties were encountered. For example, in the control experiments, defined as zero ozone dose and no catalyst (dark), some compound removal occurred. Since no treatment was being applied, other mechanisms must be responsible for the disappearance of the compounds. Possibilities for this occurrence include volatilization of the compound, sorption onto the surface of the reactor, inefficient mixing and analytical error. Though the compounds tested have a high volatility, Henry's Law constants of 0.05, 0.48, and 1.1 (unitless dimensions), at 25⁰C for DCA, TCE, and PCE, respectively, reactions were conducted in batch systems to minimize gas stripping of the compound. The quartz test

Table 11. Percent Compound Removal After 1 Hour Reaction

Compound	Ozone Dose	Catalyst		
		Dark	Sun	UV Lamp
PCE	Zero	18.9, 8.7	24.7, 27.8	100, 100
	Low	23.9	26.7, 40.6	100
	Med	19.6, 34.6	20.5	100
	High	3.0	36.3	87.3, 70.8
TCE	Zero	15.1, 29.7	9.3, 54.1	42.5, 50.8
	Low	43.6	39.3, 45.1	42.9
	Med	49.7, 23.5	28.3	32.5
	High	43.5	54.4	35.7, 38.2
DCA	Zero	5.4, 51.2	20.4, 79.7	-1.0, 3.0
	Low	29.5	17.6, 19.4	8.2
	Med	13.1, 26.9	12.8	-4.0
	High	12.0	19.2	-28, 3.4

tubes were filled to be head-space free and turned upside down for the duration of the experiment, minimizing the possibility of any volatilization occurring through the injection hole in the rubber stopper. The act of filling the UV Portstar reactor, however, produced volatilization. This occurred when the organic was mixed with the ozonated water by a magnetic stirrer, then admitted to the reactor. For example, the experiment involving PCE and zero ozone dose had an initial PCE concentration of 12.9 mg/L for the reaction carried out in the quartz test tube reactor and an initial PCE concentration of 4.16 mg/L for the reaction in the UV Portstar reactor (see Appendix). Volatilization could be occurring in the Portstar reactor itself in the headspace above the injection port in the top of the reactor. Since the reactor was not cooled, heat generation from the UV lamp raised the temperature of the reactor fluid. Due to a lack of external mixing, concentration variations could also have existed throughout the length of the reactor. This can be seen by examining the data; for example, the reaction involving a medium ozone dose and the UV lamp yielded normalized DCA concentrations of 1.10, 0.973, and 1.10 at reaction times of 26, 39, and 52 minutes, respectively (see Appendix).

6.3 PCE Treatment

PCE is an alkane and thus has a double bond, however, it is totally halogen substituted, making it less reactive towards oxidants such as ozone. PCE is, however, the most photolytic of the three compounds tested in this research and, therefore, the choice of catalyst should have influenced compound destruction rate and extent. Results of the wavelength scan from 200 nm to 400 nm for PCE are shown in Table 12. This compound exhibited peak absorption of UV radiation at 200 nm. With light frequency increase, PCE declined in absorption, but continued to absorb minimally through 400 nm, well within the UV range of sunlight which extends from 285 nm to 380 nm. Though it absorbs only weakly at 254 nm, nevertheless, it is sufficient for direct photolysis via UV light bulbs (Glaze et al., 1987).

Table 12. Wavelength Absorbance Data for PCE

<u>Wavelength</u>	<u>ABS</u>	<u>Wavelength</u>	<u>ABS</u>
400	0.090	290	0.073
390	0.089	280	0.075
380	0.088	270	0.077
370	0.085	260	0.083
360	0.085	250	0.125
350	0.073	240	0.264
340	0.068	230	0.456
330	0.069	220	0.764
320	0.068	210	1.154
310	0.068	200	1.300
300	0.070		

Shown in Figures 11 and 12 are PCE oxidation data with zero and low applied ozone dose, respectively, for three catalyst conditions: (1) in the dark, (2) in the presence of sunlight, and (3) in the presence of synthetically generated UV light at the predominant wavelength of 254 nm. The data indicate that the sunlight experiments yielded an oxidation rate intermediate between the dark and synthetic UV catalyzed reactions. That sunlight itself has potential to photolytically degrade PCE is evident in Figure 11. Figure 12 demonstrates sunlight's ability to enhance the ozone oxidation of PCE. Though UV light at 254 nm was considerably more effective in decomposing molecular ozone than energy rays from the sun, sunlight did impact positively on the oxidation process.

Additional kinetic analysis of the ozone experiments was made by plotting the negative value of the natural log of the substrate concentration at time t divided by the substrate concentration at time zero vs. t , (i.e. $-\ln S/S_0$ vs. t). The following procedure was used to determine first-order reaction rate constants.

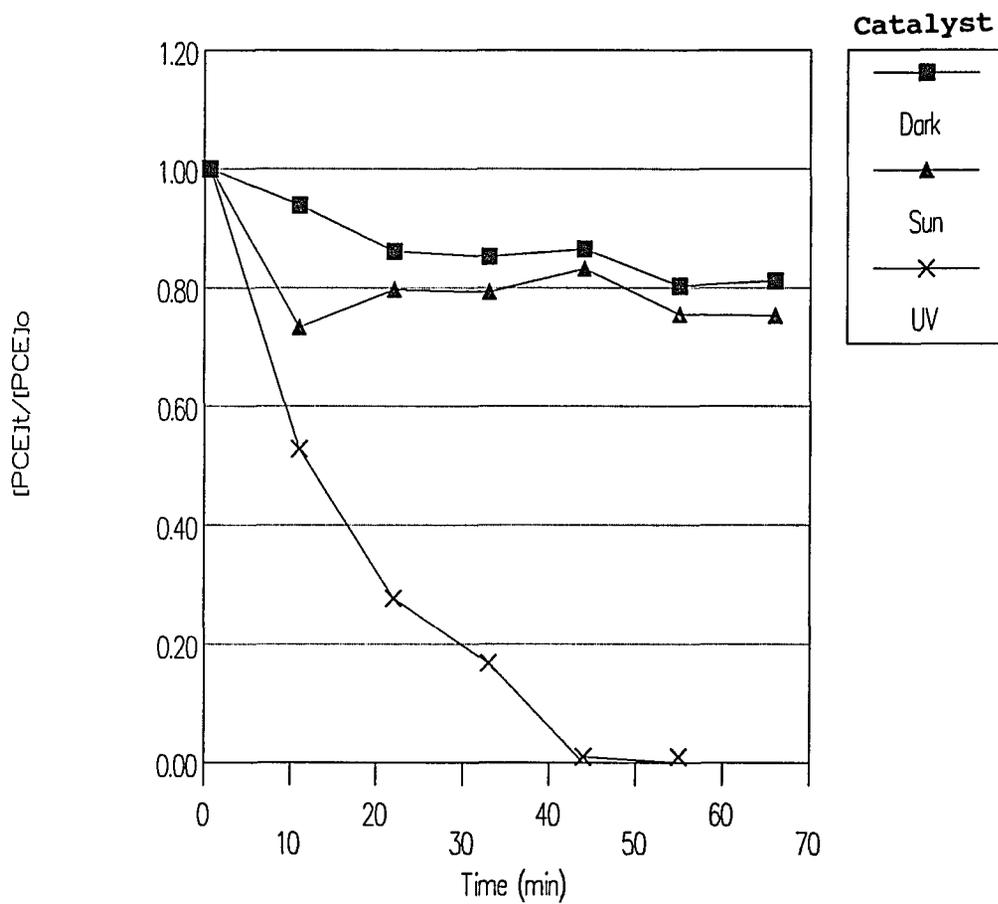


Figure 11. Normalized PCE Destruction as a Function of Reaction Time and Catalyst.

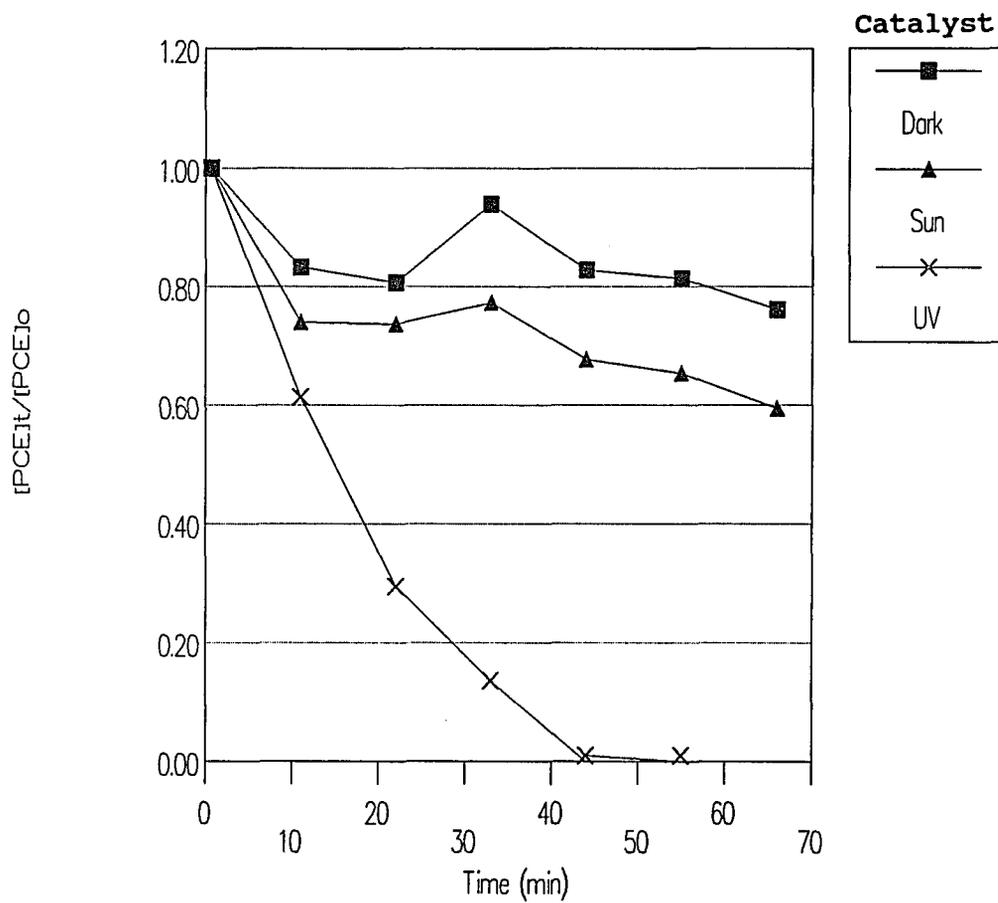


Figure 12. Normalized PCE Destruction with Low Ozone Dose as a Function of Reaction Time and Catalyst.

For each experimental point, $-\ln(S/S_0)/t$ was calculated and tabulated as follows for the condition of low ozone dose and sunlight:

t, sec:	660	1320	1980	2640	3300	3960
$10^5 \times (-\ln S/S_0)/t, \text{ sec}^{-1}$:	45.8	23.3	13.1	14.8	12.9	13.2

After the first few points, it can be seen that the reaction settles into first order format. The 4 standard deviation (4d) rule (Blaedel, Meloche, and Ramsay, 1951) was applied to determine which points were outliers. Starting with the last experimentally generated point and working towards the initial point, mean and standard deviations were calculated until the value did not fall within 4 standard deviations of the previously calculated mean. In the above example, the first two values were eliminated. The remaining values were averaged to give the resultant rate constant.

It appears that with the addition of ozone (Figure 12), the majority of the reaction takes place within the first 11 minutes. The rate constants for the first 11 minutes were 27.7, 45.8, and $73.9 \times 10^{-5} \text{ s}^{-1}$ for dark, sun and UV lamp, respectively. The reaction in sunlight proceeds 1.65 times

faster than in the dark, and the reaction with the UV lamp proceeds 1.61 times faster than in sunlight.

Based on the visual examination of the data in Figure 12 for the dark and sunlight catalyzed cases, it appears that after approximately 20 minutes, all the dissolved ozone should have been exhausted, leaving the remaining reaction due to photolysis. The rate for this second part of the reaction, from 11 to 66 minutes, was calculated next employing the 4d method. The resulting rate constants were 6.77, 13.1, and $89.1 \times 10^{-5} \text{s}^{-1}$ for dark, sun, and lamp, respectively. The high kinetic reaction velocity constant together with its high correlation coefficient (0.995) for the UV lamp catalyzed experiment gives support to the proposition that PCE degradation is mainly photolytic in nature.

The moles of H_2O_2 formed per ozone molecule decomposed were experimentally measured to be 0.42, 0.24, and 0.20 for dark, sun, and UV lamp, respectively. That nearly half of the ozone was converted into H_2O_2 when left in the dark supports PCE's low reactivity to molecular ozone. For the sunlight and lamp experiments, H_2O_2 yields were approximately half that of the dark, indicating that more ozone could have been

converted to OH^\cdot , thus contributing to the increased reaction rates in the first 11 minutes of the experiments.

Fronk (1987) found that PCE was not removed well at low and medium applied ozone doses of 2 and 6 mg/L but achieved a 72 percent removal with a 20 mg/l applied ozone dose. A high pH, greater than 9, doubled the destruction of PCE, indicating it is more amenable to hydroxyl radical destruction. Fronk concluded that the reactions were mainly mass transfer controlled, since increasing ozone dose increased destruction over a wide pH range.

It was noted that the incident solar radiation during the conduct of the sunlight catalyzed experiments was quite variable. The experiments were conducted during the summer months of June and July. Table 13 gives the incident solar radiation to the inclined surface of the quartz test tube reactor for the days the sunlight experiments were conducted. Average incident solar radiation values over the duration of the experiments were measured as 329 and 887 W/m^2 for zero and high ozone doses, respectively, due to the time of day the experiments were run and the amount of cloud cover. First-order rate constants for zero and high ozone doses and sunlight were determined to be 10.3 and 10.7 x

Table 13. Incident Solar Radiation (W/m²)

Time	06/14	06/19	06/21	07/14	07/21	07/22	07/23
07:45	893		797				
07:55	920		848				
08:05	943		880				
08:15	973		902				
08:25	990		924				
08:35	1005		930			984	
08:45	1014		947			1006	
08:55	1024		970			1020	
09:05	1023		986			1034	
09:15	1027		1007			1045	934
09:25	1034		1012			1058	963
09:35	1039		1016			1065	977
09:45	1044		1014			1074	985
09:55	1044		1011			1083	988
10:05	1048		1011			1085	990
10:15	1045		1010			1085	977
10:25	1032		999			1082	993
10:35	1028		994		671	1084	993
10:45	1011		989		752	1078	981
10:55	987		978		895	1070	977
11:05	970		959		805	1053	970
11:15	948		943		783	1037	961
11:25	930		924		964	1016	942
11:35	907		897		940	999	926
11:45	889		872		924	979	902
11:55	861		613		904	701	873
12:05	829				879	723	846
12:15	759				850	755	820
12:25	718				730	784	752
12:35	741				759	809	
12:45	768				787	835	
12:55	793				812	859	
13:05				935			
13:15				959	854		
13:25				979	636		
13:35				986	697		
13:45				987			
13:55				995			
14:05		676		996			
14:15		814		1004			
14:25		170		997			
14:35		257		990			
14:45		119		981			
14:55		176					
15:05		217					

10^{-5}s^{-1} . No apparent difference in PCE destruction rate can be detected from the variations in one sun exposure.

It should also be noted that the energy flux from the UV light reactor was considerably greater than that experienced with sunlight. The UV lamp used in these experiments had a minimum UV intensity of 320 W/m^2 at a wavelength of 254 nm. The intensity from one sun is approximately 70 W/m^2 maximum for the UV range, giving the lamp the equivalency of 5 to 6 suns. No attempt was made to measure with chemical actinometry the actual output of the UV lamp or any deterioration of the lamp output with usage throughout the duration of this research.

Glaze et al. (1987) demonstrated that when a compound absorbs strongly in the UV region, as is the case for PCE, increases in UV flux promote an increase in oxidation rates. A doubling of the UV flux while holding the ozone dose constant approximately doubled the value of the reaction velocity constant, and tripling the UV flux gave approximately a three times increase.

6.4 TCE Treatment

TCE is a tri-chlorinated ethene. It would be expected, therefore, that TCE would be reactive to simple ozone oxidation. However, having only 3 chlorine additions, it not as difficult to be oxidized by molecular ozone as PCE, which has 4 chlorine additions. Fronk (1987) found that for alkenes, destruction by ozone decreased with increasing halogen substitution consistently for all ozone doses applied. Cvetanovec (1960) stated that the rate of ozone attack decreased rapidly as the number of chlorine atoms in olefin molecules increased. This is due to steric factors and more importantly, to polarity effects contributed by halogen substitutions.

With respect to photolysis, an examination of the absorbance data for TCE in the UV range shows it has some ability to absorb around 200 nm, but TCE exhibits little absorbance capabilities above 240 nm. PCE absorbance at 254 nm is 5.6 times that for TCE, suggesting TCE is less susceptible to photolytic decomposition. Results of the wavelength scan from 200 nm to 400 nm for TCE are shown in Table 14.

Table 14. Wavelength Absorbance Data for TCE

<u>Wavelength</u>	<u>ABS</u>	<u>Wavelength</u>	<u>ABS</u>
400	0.004	290	0.010
390	0.005	280	0.011
380	0.005	270	0.013
370	0.005	260	0.015
360	0.005	250	0.021
350	0.005	240	0.069
340	0.005	230	0.293
330	0.007	220	0.721
320	0.006	210	1.359
310	0.008	200	1.928
300	0.009		

Figures 13, 14, and 15 show TCE oxidation in the dark, in sunlight, and with the UV lamp, respectively, for low, medium, and high ozone doses. Ozone appeared to be the predominant factor in the destruction of TCE, and the addition of either sunlight or UV 254 nm rays offered little destruction enhancement. The major portion of the reaction occurred in approximately the first 10 minutes, then little to no further reduction occurred, indicating the reaction is stoichiometrically limited. The ozone dose was insufficient to meet the ultimate oxidation demand of such a large substrate concentration, thus the reaction stopped when the ozone supply was exhausted.

Stoichiometrically, 8 mg of ozone are required to completely oxidize 1 mg of organic carbon to CO₂, if oxidations proceed by radicals, which corresponds to 1.46 mg of ozone per mg of

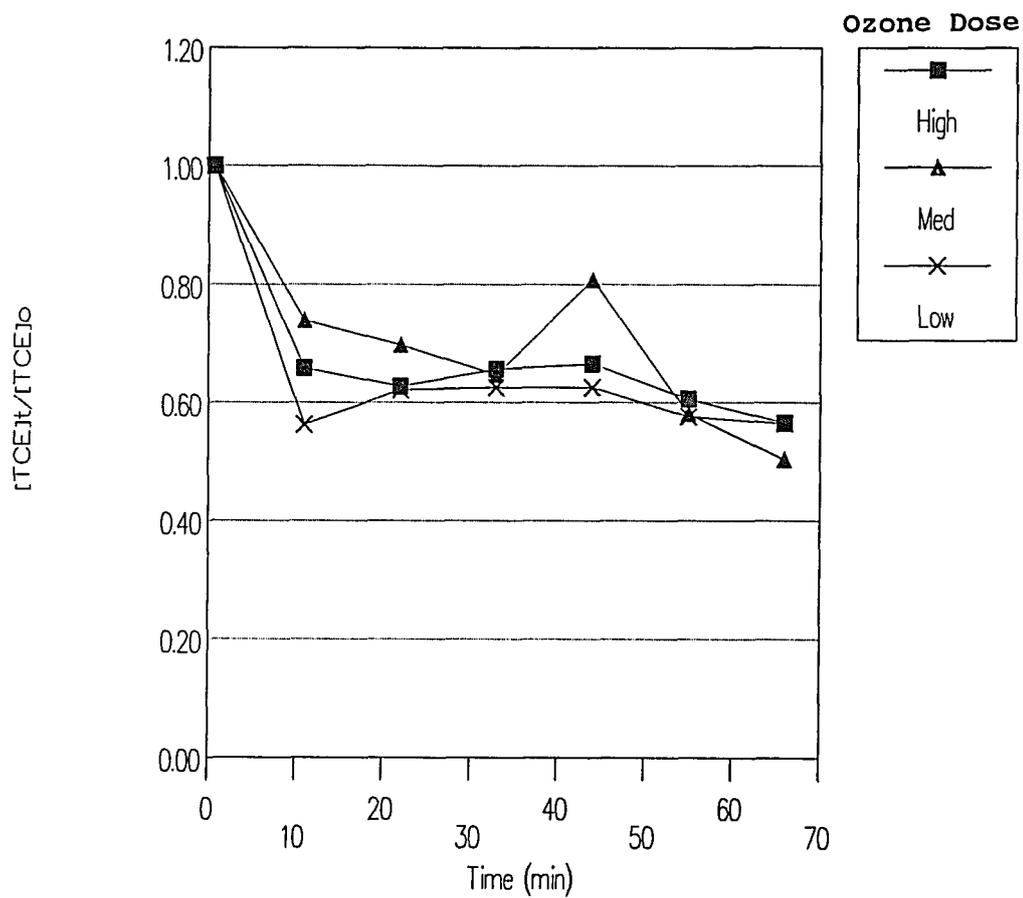


Figure 13. Normalized TCE Destruction as a Function of Reaction Time and Ozone Dose.

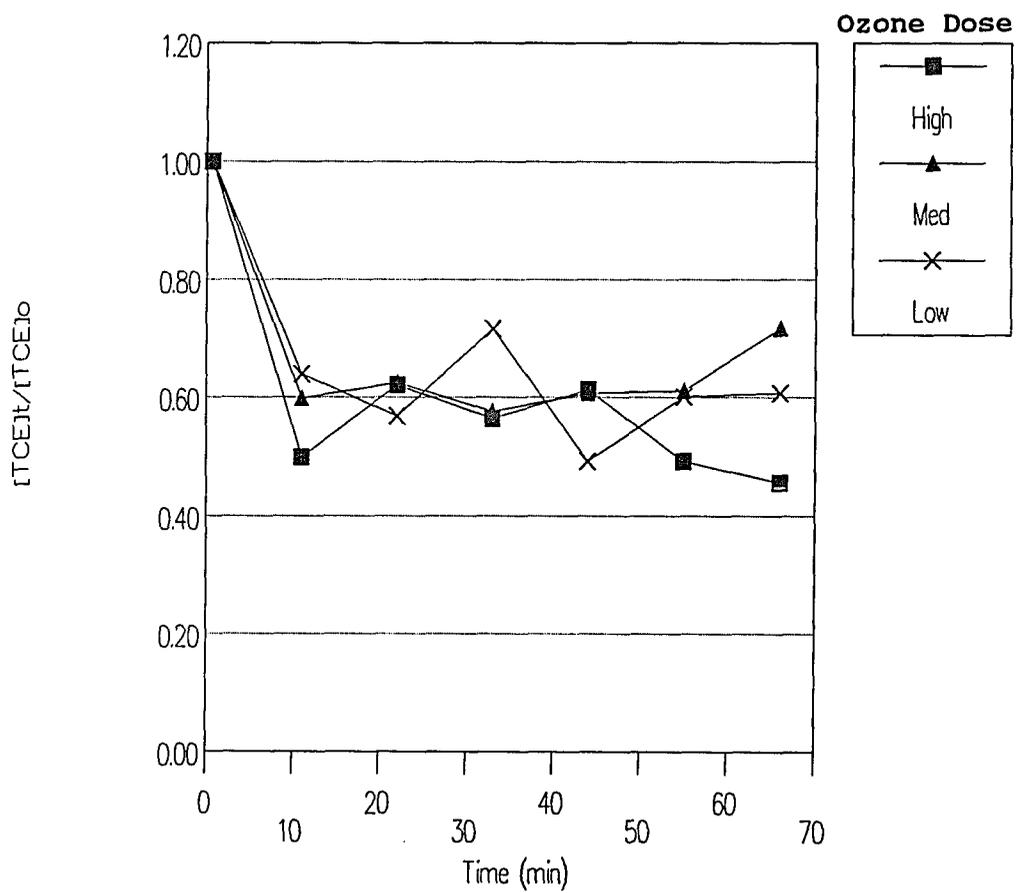


Figure 14. Normalized Sunlight Catalyzed TCE Destruction as a Function of Reaction Time and Ozone Dose.

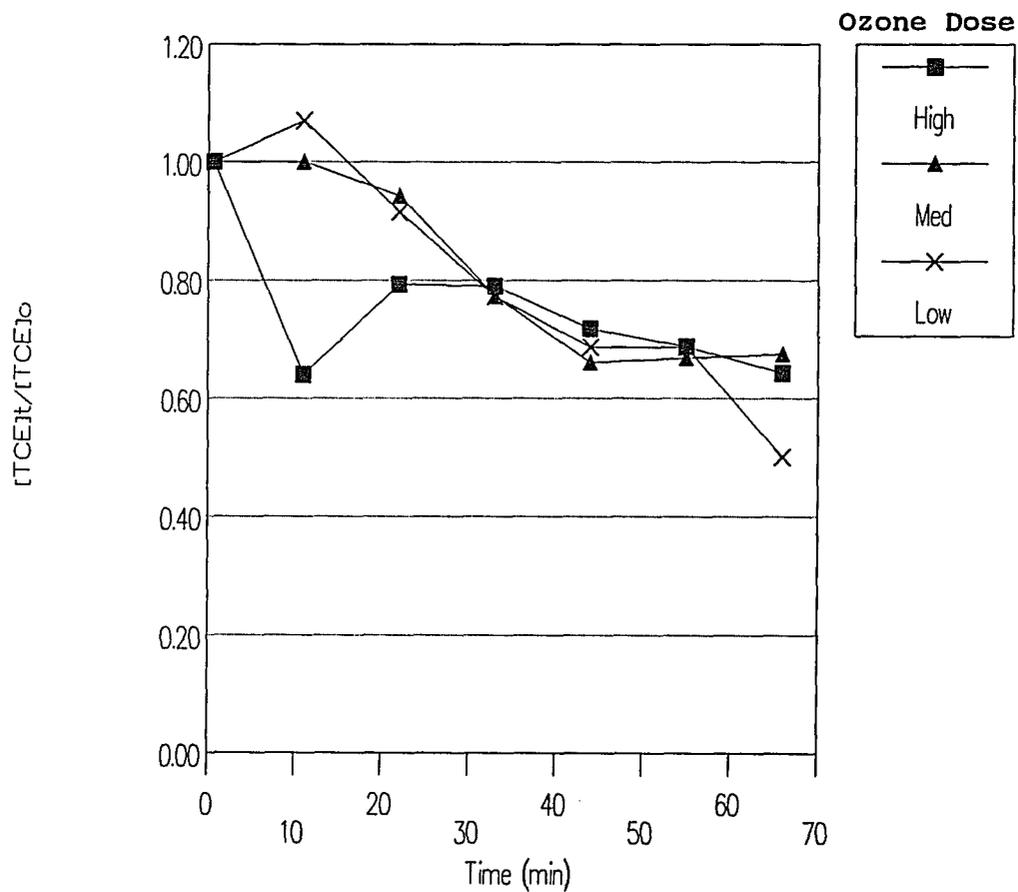


Figure 15. Normalized UV Light Catalyzed TCE Destruction as a Function of Reaction Time and Ozone Dose.

TCE. Thus the low applied ozone dose of 3.3 mg/L would theoretically be able to completely oxidize 2.28 mg/L of TCE. Kinetically, the reaction of TCE with molecular ozone proceeds slowly. Glaze et al. reported a rate constant of $10.7 \times 10^{-4} \text{s}^{-1}$ for TCE removal from well water at ambient pH and an ozone dose rate of 14.9 mg/min. Assuming then that the dissolved ozone is used up in the first 10 minutes, the total system reaction was broken up into two first order reactions. Examining the first portion of the reaction in Figure 13 for oxidation in the dark, first order rate constants were determined to be 87.3, 45.8, and $63.2 \times 10^{-5} \text{s}^{-1}$ for low, medium, and high ozone doses, respectively. This rapid reaction indicates that radical reactions must be taking place in addition to possible molecular ozone oxidation. Examination of the second portion of the reaction shows little further degradation, supporting the conclusion that the dissolved ozone concentration was exhausted. Final aqueous ozone concentrations were virtually zero for all TCE experiments involving ozone (see Appendix). For the first 10 minutes of the reaction with the addition of sunlight (Figure 14), an increase in reaction rate over the dark experiments occurred, giving first order rate constants of 67.9, 77.9, and $105.3 \times 10^{-5} \text{s}^{-1}$ for low, medium, and high ozone doses, respectively. This

agrees with the previous findings (see Figure 10) in the ozone decomposition study where sunlight was able to accelerate the decomposition of ozone, thus enhancing radical formation. Reaction rate also increased with increasing ozone dose. The second portion of the reaction again showed little further reduction in TCE concentration, indicating that the ozone supply was depleted and photolysis reactivity was minimal.

The moles of H_2O_2 formed per ozone molecule decomposed in the dark experiments with low and high ozone doses was 0.48 and 0.56, respectively; in sunlight, 0.25 and 0.26, respectively; and with the UV lamp, 0.06 and 0.35, respectively. Though molecular ozone is reactive with TCE, the rate is slow according to Hoigne and Bader (1983), at $17 M^{-1}s^{-1}$; therefore, a larger amount of H_2O_2 was able to form in the dark. Though H_2O_2 acts as an initiator with ozone in the formation of OH^\cdot (see Figure 2), it is also a potential OH^\cdot scavenger (Glaze et al., 1987); thus, a larger H_2O_2 yield could correspond to a lower OH^\cdot yield and less oxidation potential. In the experiments involving sunlight and the UV lamp, less H_2O_2 formation indicates the possibility of more radical formation, thus causing the enhanced reaction rate for TCE removal.

Figure 15 shows the UV lamp catalyzed experiments with TCE and the three ozone conditions. These experiments do not follow the same pattern as the dark and sunlight catalyzed experiments, most probably due to the different reactor (UV Portstar) employed. It appears to be an overall first-order reaction, as in the PCE experiments, with rate constants of 12.6, 9.15, and $15.4 \times 10^{-5} \text{s}^{-1}$ for low, medium, and high ozone doses, respectively. Though the predominant wavelength emitted by the UV reactor is 254 nm, which provides enough energy to break C-Cl and C-H bonds, there is also a lesser output at 185 nm that may have been sufficient to break the C=C bond (see Table 7). Other possibilities for this difference in reaction characteristics include the volatility of the compound, the higher effective oxidant to substrate ratio, and that there was not a true zero reading due to the required mixing time before the solution was admitted to the reactor.

In ozone only studies, Fronk (1987) found removals improved with increasing ozone dose. At applied ozone doses of 2, 6, and 20 mg/l, average percent removals were 39, 76, and 95, respectively. These were conducted at neutral pH. When the pH was adjusted to > 9, this offered only slight improvement over neutral pH. Fronk concluded, however, that reactions

with TCE were mainly mass transfer controlled, because increasing ozone concentrations gave greater destruction over a wide pH range. Glaze et al. (1987) also reported that TCE removal was influenced more by ozone dose rate and only weakly dependent on UV flux, which agrees with the interpretations in this research. Rate constants for removal of TCE were $8 \times 10^4 \text{s}^{-1}$ and $11 \times 10^4 \text{s}^{-1}$ at a constant applied ozone dose of 4.5 mg/L for 13.2 and 39.6 W/L UV, respectively, while a constant UV dose of 13.2 W/L gave rate constants of $8 \times 10^4 \text{s}^{-1}$ and $14 \times 10^4 \text{s}^{-1}$ for ozone dose rates of 4.5 and 8.5 mg/L, respectively. Masten and Butler reported a reaction rate constant of 47 and $130 \text{M}^{-1} \text{s}^{-1}$ for reactions of TCE and ozone only and TCE and ozone/UV, respectively, in a batch system at pH 2.

6.5 DCA Treatment

DCA is an alkane, specifically a saturated chlorinated ethane. Ozone is not particularly reactive to carbon-hydrogen bonds, and the probability of oxidation was expected to be low. DCA, the most refractory of the three compounds tested, has little to no absorptivity in the UV range, thus also no photodecomposition was expected to occur. Results of a wavelength scan from 200nm to 400 nm is presented in Table 15. DCA should, however, to be reactive

with the hydroxyl radical (Glaze, 1985).

Table 15. Wavelength Absorbance Scan for DCA

<u>Wavelength</u>	<u>ABS</u>	<u>Wavelength</u>	<u>ABS</u>
400	0.002	290	0.100
390	0.002	280	0.012
380	0.005	270	0.010
370	0.005	260	0.015
360	0.005	250	0.016
350	0.004	240	0.018
340	0.004	230	0.024
330	0.005	220	0.030
320	0.006	210	0.033
310	0.007	200	0.052
300	0.008		

Figures 16 and 17 show DCA removal in the dark and in sunlight, respectively, for the three ozone conditions. Removal appears to be occurring, however, the scatter in the data makes the determination of rate constants difficult. Given DCA's low reactivity with molecular ozone and low absorptivity in the UV range, the disappearance could be due to radical type reactions.

Hoigne and Bader (1983) found the saturated alkyl group to have a low reactivity with molecular ozone. Francis (1987) reported the rate constant of ozone with alkanes to be $10^{-2} \text{ M}^{-1}\text{s}^{-1}$. Fronk (1987) reported that in general alkanes are not reactive to ozone. Fronk, using a countercurrent flow

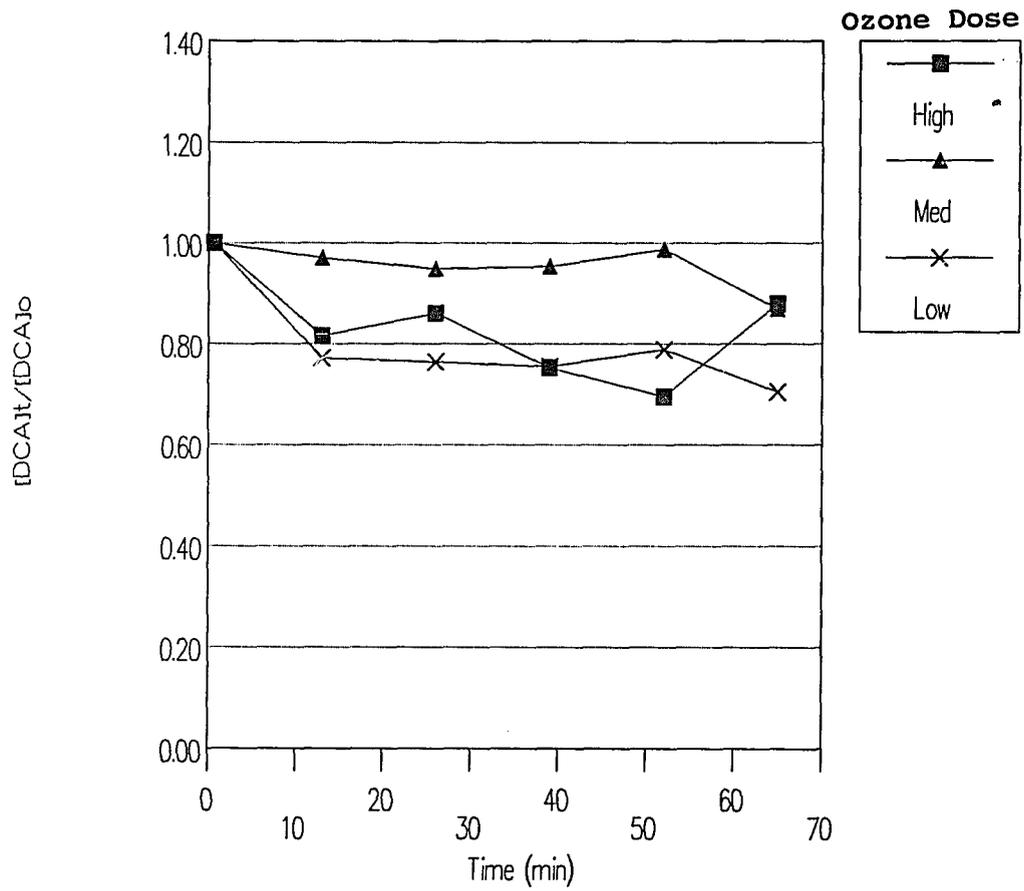


Figure 16. Normalized DCA Destruction as a Function of Time and Ozone Dose.

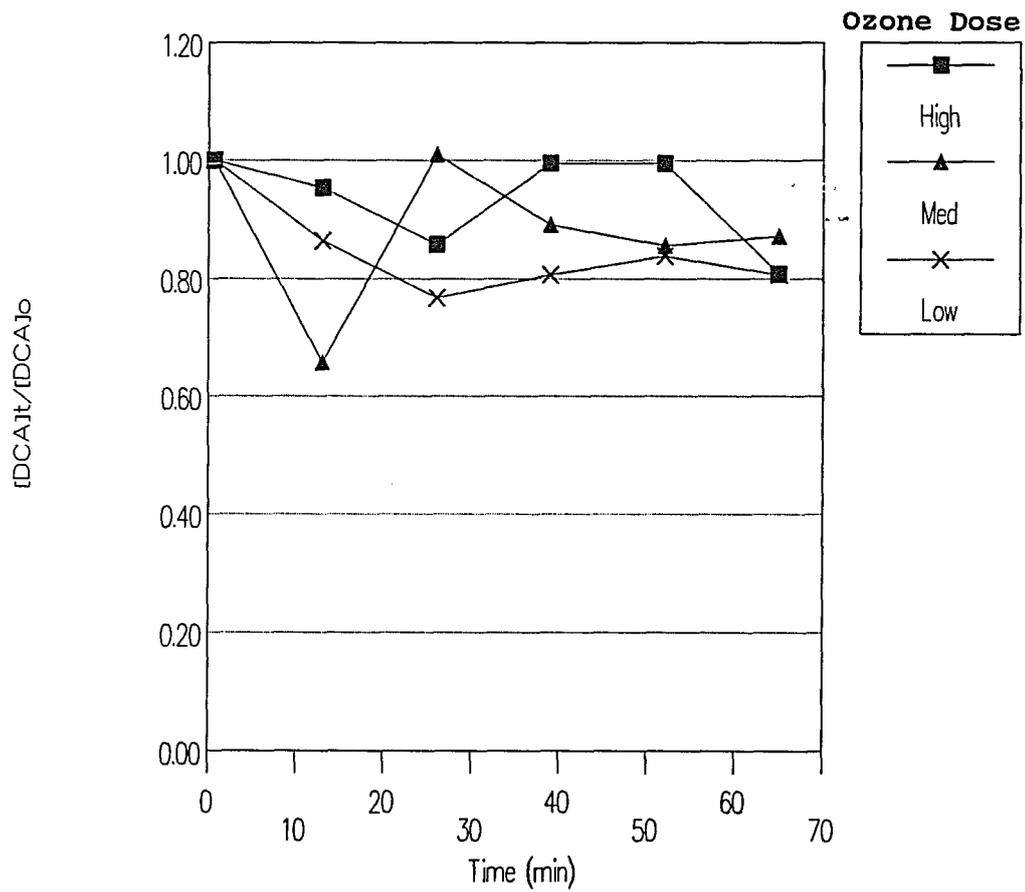


Figure 17. Normalized Sunlight Catalyzed DCA Destruction as a Function of Reaction Time and Ozone Dose.

scheme and accounting for air stripping, studied three ozone doses; a low of 2 mg O₃/l, medium of 6 mg O₃/l and high of 12-20 mg O₃/l, for destruction of various VOCs. Neither the low nor the medium ozone dose provided any removal of DCA. Even at the extreme dose of 20 mg O₃/l, only 9 percent removal of DCA was found. These experiments were conducted at neutral pH. The experiments conducted in this research were at a pH of 5, where the molecular ozone would be even more stable in aqueous solution than at pH 7. Therefore, DCA should not have been appreciably reduced in concentration. That there is reduction in DCA could be indicative of one or more of the following: adsorption onto the glass or the rubber stopper and/or experimental error in the sampling or GC techniques. Masten and Butler (1986) found ozone alone gave a rate constant of 4.3 M⁻¹s⁻¹ at an initial ozone concentration of 2.2-2.6 mg/l in a batch system at pH of 2. These data further substantiate DCA's low reactivity to molecular ozone.

The three levels of ozone offered no change in the destruction of DCA. These findings agree with previous aqueous studies that the reaction of DCA with molecular ozone is kinetically limited. Since DCA is so unreactive to ozone oxidation, one would expect ozone loss under direct

treatment to be minimal. However, final ozone concentrations in all cases were minimal to zero, due to a more rapid autodecomposition at 5.1 pH. Ozone concentrations were not monitored throughout the experiments, but a rapid exhaustion of ozone has been suggested to be a limiting factor in the cases for PCE and TCE. H_2O_2 formation in the DCA experiments, in general, followed the same pattern as the PCE and TCE experiments, with twice as much H_2O_2 formed per ozone molecule decomposed in the dark (0.52) as in sunlight (0.27) or the presence of the UV lamp (0.25). However, DCA's low reactivity could have allowed for more self extinguishment of radicals, effectively lowering the oxidation capacity.

With the addition of a catalyst, either sunlight or pure UV light, there still appeared to be no enhanced removal. Figure 18, DCA removal with the UV lamp and 3 ozone doses, again shows difficulty with the type of reactor.

Francis (1987) reported a k of 10^6 - $10^9 \text{ M}^{-1}\text{s}^{-1}$ for reactions of alkanes with OH^\cdot . Fronk found at high pH (>9) destruction began to improve. This improved destruction was accounted for by the presence of OH^\cdot at high pH. Fronk (1987) also found the reaction became mass transfer limited. Though at

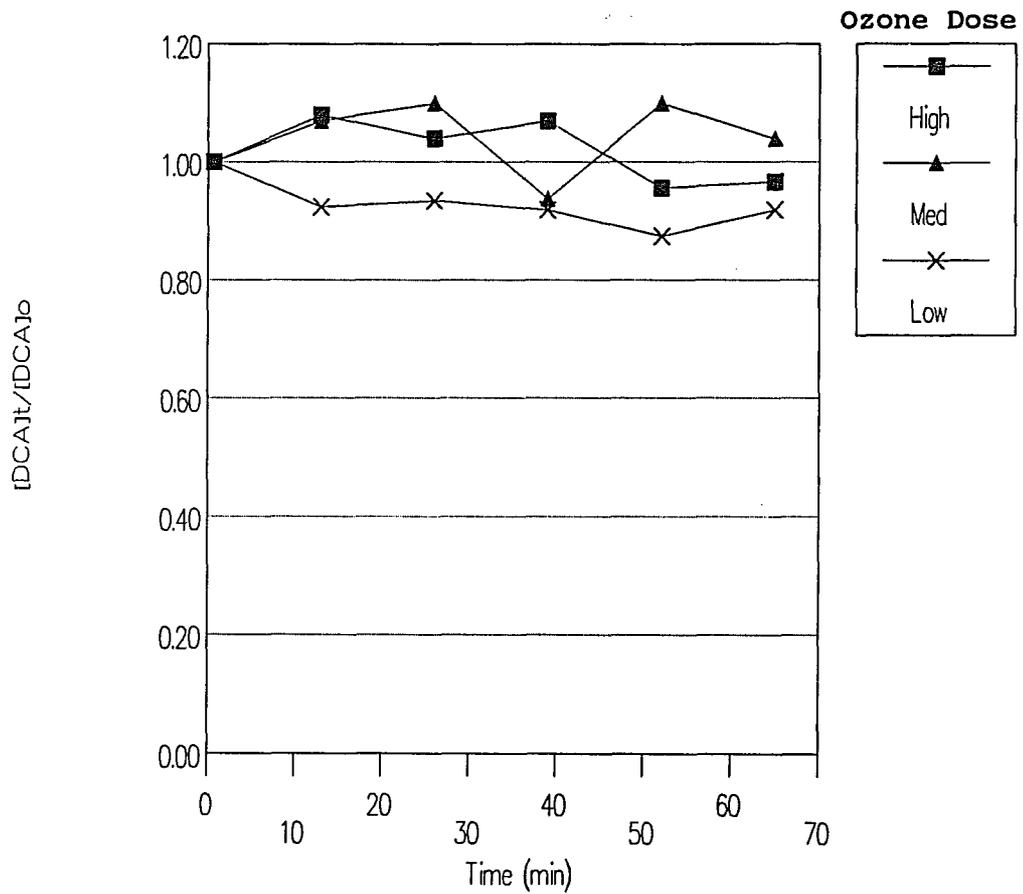


Figure 18. Normalized UV Light Catalyzed DCA Destruction as a Function of Reaction Time and Ozone Dose.

neutral pH, DCA was not well removed regardless of ozone dose; at pH > 9, destruction greatly improved with increasing ozone doses. Masten and Butler (1986) found the ozone/UV system capable of oxidizing DCA in a batch system at pH of 2 with ozone concentration of 1-5 mg/L at the rate of $25 \text{ M}^{-1}\text{s}^{-1}$ observed at an initial O_3 concentration of 2.2-2.6 mg/L.

6.6 Statistics

The experimental data was statistically analyzed as described in Chapter 3. An analysis of variance (ANOVA) was performed to determine if the independent variables, ozone dose, type of catalyst, and type of compound had a significant effect on the measured variable, removal of substrate. The sum of squares for experimental error was calculated from the results of the 18 replicate experiments. The effect of uncontrolled factors in the experiment, such as water quality, laboratory temperature, experimental procedure, etc., was estimated in the residual sum of squares. Results of the ANOVA are presented in Tables 16, 17 and 18 for sampling times of 11, 33, and 66 minutes, respectively.

Table 16. ANOVA for Percent Compound Remaining After 11 Minutes.

Source	DF	SS	MS	F-calc	F-tabular	
					a=.025	a=.01
Ozone Dose	3	0.096	0.032	0.669	3.954	5.092
Catalyst	2	0.594	0.297	6.213	4.560	6.013
Compound	2	0.072	0.036	0.753	4.560	6.013
Experimental Error	18	0.861	0.0478			
Residual	28	1.282	0.0459	0.960		
Total	54	2.905				

Table 17. ANOVA for Percent Compound Remaining After 33 Minutes.

Source	DF	SS	MS	F-calc	F-tabular	
					a=.025	a=.01
Ozone Dose	3	0.042	0.014	0.343	3.954	5.092
Catalyst	2	0.504	0.252	6.176	4.560	6.013
Compound	2	0.054	0.027	0.662	4.560	6.013
Experimental Error	18	0.734	0.0408			
Residual	28	2.288	0.0817	2.002		
Total	54	3.622				

Table 18. ANOVA for Percent Compound Remaining After 66 Minutes.

Source	DF	SS	MS	F-calc	F-tabular	
					a=.01	a=.001
Ozone Dose	3	0.077	0.0257	0.871	5.092	8.487
Catalyst	2	0.365	0.1825	6.186	6.013	10.39
Compound	2	0.941	0.471	15.97	6.013	10.39
Experimental Error	18	0.531	0.0295		F-tabular a=.025 a=.01	
Residual	28	2.310	0.0825	2.797	2.445	2.919
Total	54	4.224				

At 11 and 33 minutes sampling time, catalyst was determined to be significant at the 98 percent confidence level. Neither compound, ozone dose, nor residual were significant. Analysis of the final measurements, however, showed that compound was significant at the 99.8 percent confidence level and both catalyst and residual were significant at the 95 percent confidence level. In all cases, the residual was high compared to the rest of the total sum of squares, indicating a high amount of experimental error. The fact that catalyst and compound are statistically significant agrees with the interpretations of the data previously presented.

The conclusion that ozone dose is a significant factor in the outcome of the experiment is not, however, supported in the ANOVA. In order to determine whether the effect of ozone dose was co-dependent on the ratio of ozone dose to initial substrate concentration, an analysis of covariance was performed. It was found that after accounting for the relationship of measured initial ozone dose to initial substrate concentration, the within-treatment variability of ozone dose was reduced, and ozone dose was found to be significant at the 95 percent confidence level.

Though the ANOVA showed compound and catalyst to be significant treatment effects, the results of Duncan's Multiple Range Test (DMRT) (see Figures 19, 20 and 21) indicated that no mean was significantly different than any other for any of the treatment categories; catalyst, compound, or ozone dose. The DMRT assumes that the error in the experiment is evenly dispersed and that the data are not normally distributed. The graph in Figure 19 of the ratio of ozone dose to initial substrate concentration vs. final substrate concentration for dark, sunlight, and UV lamp catalyzed experiments shows that the data are more normally distributed, and the highest amount of variability is found in the UV lamp experiments. The data for all three catalyst conditions fit a normal distribution. When testing the equality of variances among the three catalyst conditions, dark and sunlight variances were found to be equal, but the variances for dark and UV lamp and for sunlight and UV lamp were found to be unequal, further emphasizing the higher degree of error associated with the UV lamp catalyzed experiments. For this reason, a two-sample t-test (Iman and Conover, 1983) was performed on the dark and sunlight data to determine any difference among the means, and the procedure for inferences about the difference in means of 2 normal populations with unequal variances was used for dark

Table 19. Duncan's Multiple Range Test to Examine Ozone Dosage at 66 Minutes

Experiment		Zero O ₃	High O ₃	Med O ₃	R _p
	S/S ⁰	0.644	0.687	0.702	
Low O ₃	0.630	0.014	0.057	0.072	0.449
Zero O ₃	0.644		0.043	0.058	0.437
High O ₃	0.687			0.015	0.416

Table 20. Duncan's Multiple Range Test to Examine Catalyst at 66 Minutes

Experiment		Sun	Dark	R _p
	S/S ⁰	0.680	0.749	
Lamp	0.562	0.118	0.187	0.437
Sun	0.680		0.069	0.416

Table 21. Duncan's Multiple Range Test to Examine Compound at 66 Minutes

Experiment		TCE	DCA	R _p
	S/S ⁰	0.619	0.840	
PCE	0.531	0.088	0.309	0.437
TCE	0.619		0.221	0.416

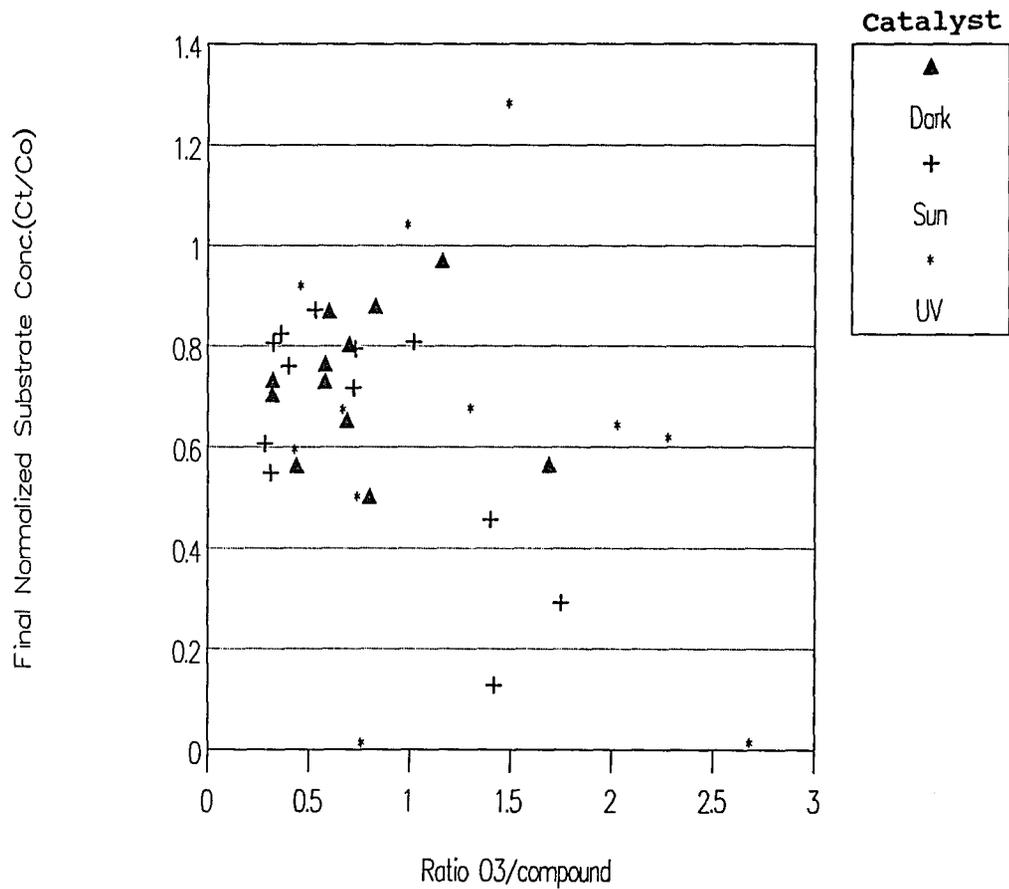


Figure 19. Normalized Concentration at 66 Minutes as a Function of the Ratio of Ozone Dose to Initial Substrate Concentration and Catalyst.

and UV lamp and for sunlight and UV lamp. Results indicate that there is no significant difference between means for dark and sunlight catalyzed experiments and between sunlight and UV lamp catalyzed experiments, however the dark and UV lamp means were found to be significantly different at the 90 percent confidence level. The unevenly distributed error in the experiments could be the reason that the DMRT, which should be more sensitive than the t-test, was not able to detect any difference among treatment means.

CHAPTER 7

CONCLUSIONS

Based on the experimental conditions employed in this work, the following conclusions may be drawn:

1) Decomposition of dissolved ozone was accelerated in the presence of sunlight compared to a no light condition, implying that solar catalyzed ozone decomposition would lead to a larger net free radical production over the non-catalyzed reaction. Since both samples originated from the same batch of ozonated water, pH and temperature were identical; thus, the enhanced decomposition of molecular ozone in sunlight must be due to the absorption of energy from a portion of the sun's rays.

2) The chemical structure of the substrate has an effect on the degree of destruction. The type of compound tested was found to be significant at the 99.8 percent confidence level. PCE exhibited the most photolytic capabilities, while TCE destruction was most influenced by ozone dose. DCA was the most refractory of the 3 compounds tested.

3) After accounting for the relationship of measured initial ozone dose to initial substrate concentration, substrate removal was found by analysis of covariance to be dependent upon ozone dose at the 95 percent confidence level.

4) At the 95 percent confidence level, both catalyst type (sunlight, synthetically generated UV light) and uncontrolled variables, such as mixing conditions, were significant in terms of substrate removal.

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APPENDIX

TETRACHLOROETHYLENE DATA

DATE:	JUNE 17, 1988	JULY 13, 1988	JUNE 19, 1988
TIME OF DAY:	NA	NA	14:00
CAT TYPE:	DARK	DARK	SUNLIGHT
APPLIED O ₃ :	ZERO	ZERO	ZERO
RESIDUAL O ₃ :	NA	NA	NA
H ₂ O ₂ :	NA	NA	NA
INITIAL PCE CONC. (mg/L):	7.10	10.01	7.52

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.939	11	1.14	11	0.734
22	0.861	22	0.815	22	0.797
33	0.852	33	0.851	33	0.793
44	0.865	44	0.908	44	0.832
55	0.803	55	1.15	55	0.755
66	0.811	66	0.913	66	0.753

DATE:	JUNE 3, 1988	JULY 18, 1988	JUNE 18, 1988
TIME OF DAY:	09:20	NA	NA
CAT TYPE:	SUNLIGHT	LAMP	LAMP
APPLIED O ₃ :	ZERO	ZERO	ZERO
RESIDUAL O ₃ :	NA	NA	NA
H ₂ O ₂ :	NA	NA	NA
INITIAL PCE CONC. (mg/L):	12.9	4.16	5.32

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.822	11	0.724	11	0.528
22	0.829	22	0.308	22	0.276
33	0.930	33	0.228	33	0.168
44	0.768	44	0.103	44	0
55	0.783	55	0	55	0
66	0.722	66	0	66	0

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and unavailable from author or university.
Filmed as received.**

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TETRACHLOROETHYLENE DATA

DATE:	JULY 25, 1988	JUNE 14, 1988	JULY 28, 1988
TIME OF DAY:	NA	10:35	10:25
CAT TYPE:	DARK	SUNLIGHT	SUNLIGHT
APPLIED O ₃ :	3.33 mg/L	3.1 mg/L	3.57 mg/L
RESIDUAL O ₃ :	0 mg/L	0.24 mg/L	----
H ₂ O ₂ :	1 mg/L	0.4 mg/L	0.6 mg/L
INITIAL PCE CONC. (MG/L):	8.32	9.54	8.33

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.833	11	0.621	11	0.739
22	0.806	22	0.671	22	0.736
33	0.940	33	0.761	33	0.772
44	0.828	44	0.832	44	0.677
55	0.813	55	---	55	0.654
66	0.761	66	0.733	66	0.594

DATE:	JUNE 20, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	3.1 mg/L
RESIDUAL O ₃ :	0.24 mg/L
H ₂ O ₂ :	0.4 mg/L
INITIAL PCE CONC. (MG/L):	4.07

<u>TIME</u> <u>(MIN)</u>	<u>& REACTANT</u> <u>REMAINING</u>
00	1
11	0.614
22	0.295
33	0.135
44	0
55	0
66	0

TETRACHLOROETHYLENE DATA

DATE:	JUNE 19, 1988	JUNE 19, 1988	JULY 22, 1988
TIME OF DAY:	NA	NA	9:08
CAT TYPE:	DARK	DARK	SUNLIGHT
APPLIED O ₃ :	5.24 mg/L	5.7 mg/L	5.5 mg/L
RESIDUAL O ₃ :	0.12 mg/L	0.12 mg/L	0 mg/L
H ₂ O ₂ :	1 mg/L	1 mg/L	1 mg/L
INITIAL PCE CONC. (MG/L):	7.51	8.30	7.51

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.719	11	0.698	11	0.675
22	0.819	22	0.687	22	0.838
33	0.692	33	0.718	33	0.896
44	0.634	44	0.589	44	0.827
55	0.844	55	0.676	55	0.808
66	0.804	66	0.654	66	0.795

DATE:	JULY 4, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	5.7 mg/L
RESIDUAL O ₃ :	0 mg/L
H ₂ O ₂ :	1 mg/L
INITIAL PCE CONC. (MG/L):	2.13

<u>TIME</u> <u>(MIN)</u>	<u>& REACTANT</u> <u>REMAINING</u>
00	1
11	0.606
22	0.408
33	0
44	0
55	0
66	0

TETRACHLOROETHYLENE DATA

DATE:	JULY 23, 1988	JULY 21, 1988	JULY 21, 1988
TIME OF DAY:	NA	10:55	NA
CAT TYPE:	DARK	SUNLIGHT	LAMP
APPLIED O ₃ :	8.57 mg/L	8.1 mg/L	8.57 mg/L
RESIDUAL O ₃ :	0.24 mg/L	0 mg/L	---
H ₂ O ₂ :	3 mg/L	2 mg/L	---
INITIAL PCE CONC. (MG/L):	7.36	12.1	6.03

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.946	11	0.819	11	0.708
22	0.894	22	0.712	22	0.459
33	0.861	33	0.623	33	0.343
44	0.868	44	0.768	44	0.186
55	1.01	55	0.701	55	0.153
66	0.97	66	0.637	66	0.127

DATE:	JULY 20, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	8.1 mg/L
RESIDUAL O ₃ :	0 mg/L
H ₂ O ₂ :	3 mg/L
INITIAL PCE CONC. (MG/L):	4.62

<u>TIME</u> <u>(MIN)</u>	<u>& REACTANT</u> <u>REMAINING</u>
00	1
11	1.35
22	0.848
33	0.716
44	0.439
55	0.403
66	0.292

TRICHLOROETHYLENE DATA

DATE:	JUNE 17, 1988	JULY 13, 1988	JUNE 1, 1988
TIME OF DAY:	NA	NA	13:47
CAT TYPE:	DARK	DARK	SUNLIGHT
APPLIED O ₃ :	ZERO	ZERO	ZERO
RESIDUAL O ₃ :	NA	NA	NA
H ₂ O ₂ :	NA	NA	NA
INITIAL TCE CONC. (MG/L):	9.07	11.63	17.95

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.863	11	0.989	11	0.221
22	0.914	22	1.020	22	---
33	0.835	33	1.010	33	0.398
44	0.870	44	1.010	44	0.384
55	0.762	55	0.835	55	---
66	0.849	66	0.703	66	0.459

DATE:	JULY 22, 1988	JUNE 18, 1988	JUNE 18, 1988
TIME OF DAY:	11:51	NA	NA
CAT TYPE:	SUNLIGHT	LAMP	LAMP
APPLIED O ₃ :	ZERO	ZERO	ZERO
RESIDUAL O ₃ :	NA	NA	NA
H ₂ O ₂ :	NA	NA	NA
INITIAL TCE CONC. (MG/L):	6.97	4.89	5.57

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.935	11	1.07	11	1.03
22	0.805	22	1.03	22	0.817
33	1.010	33	0.869	33	0.725
44	0.917	44	0.818	44	0.688
55	0.696	55	0.755	55	0.619
66	0.907	66	0.575	66	0.492

TRICHLOROETHYLENE DATA

DATE:	JULY 25, 1988	JUNE 14, 1988	JUNE 14, 1988
TIME OF DAY:	NA	11:49	8:00
CAT TYPE:	DARK	SUNLIGHT	SUNLIGHT
APPLIED O ₃ :	3.33 mg/L	3.33 mg/L	3.1 mg/L
RESIDUAL O ₃ :	0.36 mg/L	0 mg/L	0.24 mg/L
H ₂ O ₂ :	1 mg/L	0.6 mg/L	0.4 mg/L
INITIAL TCE CONC. (MG/L):	7.60	11.69	10.16

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.562	11	0.639	11	0.833
22	0.622	22	0.568	22	---
33	0.626	33	0.716	33	0.721
44	0.626	44	0.492	44	0.795
55	0.576	55	0.601	55	0.764
66	0.564	66	0.607	66	0.549

DATE: JUNE 20, 1988
 TIME OF DAY: NA
 CAT TYPE: LAMP
 APPLIED O₃: 3.33 mg/L
 RESIDUAL O₃: 0.6 mg/L
 H₂O₂: 0.1 mg/L
 INITIAL TCE
 CONC. (MG/L): 4.47

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1
11	1.070
22	0.915
33	0.772
44	0.687
55	0.687
66	0.501

TRICHLOROETHYLENE DATA

DATE:	JULY 25, 1988	JUNE 16, 1988	JULY 22, 1988
TIME OF DAY:	NA	NA	10:36
CAT TYPE:	DARK	DARK	SUNLIGHT
APPLIED O ₃ :	5.24 mg/L	5.5 mg/L	5.24 mg/L
RESIDUAL O ₃ :	0 mg/L	0.36 mg/L	---
H ₂ O ₂ :	---	1 mg/L	---
INITIAL TCE CONC. (MG/L):	6.52	9.52	7.28

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.739	11	0.604	11	0.598
22	0.698	22	0.564	22	0.625
33	0.647	33	0.697	33	0.576
44	0.807	44	0.758	44	0.607
55	0.581	55	0.778	55	0.611
66	0.503	66	0.765	66	0.717

DATE:	JULY 15, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	5.48 mg/L
RESIDUAL O ₃ :	0 mg/L
H ₂ O ₂ :	---
INITIAL TCE CONC. (MG/L):	4.22

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1
11	1.00
22	0.943
33	0.773
44	0.668
55	0.668
66	0.675

TRICHLOROETHYLENE DATA

DATE:	JULY 23, 1988	JULY 23, 1988	JULY 20, 1988
TIME OF DAY:	NA	9:33	NA
CAT TYPE:	DARK	SUNLIGHT	LAMP
APPLIED O ₃ :	8.33 mg/L	8.33 mg/L	8.1 mg/L
RESIDUAL O ₃ :	0.71 mg/L	---	0 mg/L
H ₂ O ₂ :	3 mg/L	---	2 mg/L
INITIAL TCE CONC. (MG/L):	4.92	5.97	4.00

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
11	0.659	11	0.499	11	0.640
22	0.628	22	0.621	22	0.793
33	0.657	33	0.564	33	0.790
44	0.665	44	0.613	44	0.718
55	0.606	55	0.492	55	0.688
66	0.565	66	0.456	66	0.643

DATE: JULY 20, 1988
 TIME OF DAY: NA
 CAT TYPE: LAMP
 APPLIED O₃: 8.1 mg/L
 RESIDUAL O₃: ---
 H₂O₂: ---
 INITIAL TCE
 CONC. (MG/L): 3.56

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1
11	0.787
22	0.947
33	0.921
44	0.826
55	0.761
66	0.618

1,2-DICHLOROETHANE DATA

DATE:	JULY 13, 1988	JUNE 1, 1988	JULY 23, 1988
TIME OF DAY:	NA	NA	10:47
CAT TYPE:	DARK	DARK	SUNLIGHT
APPLIED O ₃ :	ZERO	ZERO	ZERO
RESIDUAL O ₃ :	NA	NA	NA
H ₂ O ₂ :	NA	NA	NA
INITIAL DCA CONC. (MG/L):	10.28	14.3	9.86

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
13	0.977	13	0.460	13	0.604
26	0.843	26	0.415	26	0.668
39	1.030	39	0.398	39	0.801
52	0.855	52	---	52	0.792
65	0.946	65	0.488	65	0.796

DATE:	JUNE 1, 1988	JUNE 18, 1988	JUNE 18, 1988
TIME OF DAY:	12:19	NA	NA
CAT TYPE:	SUNLIGHT	LAMP	LAMP
APPLIED O ₃ :	ZERO	ZERO	ZERO
RESIDUAL O ₃ :	NA	NA	NA
H ₂ O ₂ :	NA	NA	NA
INITIAL DCA CONC. (MG/L):	19.3	6.86	6.66

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
13	0.097	13	1.03	13	1.13
26	0.126	26	1.05	26	1.04
39	0.160	39	1.08	39	1.07
52	0.204	52	1.0	52	1.01
65	0.203	65	1.01	65	0.970

1,2-DICHLOROETHANE DATA

DATE:	JUNE 20, 1988	JUNE 21, 1988	JUNE 21, 1988
TIME OF DAY:	NA	7:58	9:38
CAT TYPE:	DARK	SUNLIGHT	SUNLIGHT
APPLIED O ₃ :	3.1 mg/L	3.1 mg/L	3.1 mg/L
RESIDUAL O ₃ :	0 mg/L	0.36 mg/L	0.24 mg/L
H ₂ O ₂ :	0.4 mg/L	0.4 mg/L	0.2 mg/L
INITIAL DCA CONC. (MG/L):	9.56	8.71	9.76

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
13	0.772	13	0.834	13	0.864
26	0.764	26	0.977	26	0.768
39	0.755	39	0.811	39	0.806
52	0.789	52	0.982	52	0.839
65	0.705	65	0.824	65	0.806

DATE:	JUNE 20, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	3.33 mg/L
RESIDUAL O ₃ :	0 mg/L
H ₂ O ₂ :	0.4 mg/L
INITIAL DCA CONC. (MG/L):	7.30

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1
13	0.923
26	0.934
39	0.918
52	0.874
65	0.918

1,2-DICHLOROETHANE DATA

DATE:	JULY 25, 1988	JUNE 19, 1988	JULY 14, 1988
TIME OF DAY:	NA	NA	13:21
CAT TYPE:	DARK	DARK	SUNLIGHT
APPLIED O ₃ :	5.7 mg/L	5.95 mg/L	5.48 mg/L
RESIDUAL O ₃ :	---	0.24 mg/L	0 mg/L
H ₂ O ₂ :	---	1 mg/L	1 mg/L
INITIAL DCA CONC. (MG/L):	9.52	10.20	10.36

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
13	0.970	13	0.743	13	0.658
26	0.949	26	0.720	26	1.01
39	0.953	39	0.819	39	0.891
52	0.987	52	0.775	52	0.856
65	0.869	65	0.731	65	0.872

DATE:	JULY 5, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	5.7 mg/L
RESIDUAL O ₃ :	0 mg/L
H ₂ O ₂ :	1 mg/L
INITIAL DCA CONC. (MG/L):	5.73

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1
13	1.07
26	1.10
39	0.937
52	1.10
65	1.04

1,2-DICHLOROETHANE DATA

DATE:	JULY 23, 1988	JULY 21, 1988	JULY 26, 1988
TIME OF DAY:	NA	12:16	NA
CAT TYPE:	DARK	SUNLIGHT	LAMP
APPLIED O ₃ :	8.33 mg/L	8.1 mg/L	8.1 mg/L
RESIDUAL O ₃ :	0.12 mg/L	---	---
H ₂ O ₂ :	3 mg/L	---	---
INITIAL DCA CONC. (MG/L):	10.08	7.95	5.45

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>	<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1	00	1	00	1
13	0.816	13	0.953	13	1.21
26	0.860	26	0.858	26	1.39
39	0.752	39	0.995	39	1.30
52	0.696	52	0.995	52	1.38
65	0.880	65	0.808	65	1.28

DATE:	JULY 26, 1988
TIME OF DAY:	NA
CAT TYPE:	LAMP
APPLIED O ₃ :	8.33 mg/L
RESIDUAL O ₃ :	---
H ₂ O ₂ :	---
INITIAL DCA CONC. (MG/L):	7.14

<u>TIME</u> <u>(MIN)</u>	<u>% REACTANT</u> <u>REMAINING</u>
00	1
13	1.08
26	1.04
39	1.07
52	0.955
65	0.966

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