OZONATION OF SOILS CONTAMINATED WITH POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

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ABSTRACT

OZONATION OF SOILS CONTAMINATED WITH POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

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This research indicates the feasibility of using ozone as an oxidant in solutions containing with humic acid or in soils. The effect of ozone dosage on these reactions was considered.

The results obtained from experiments conducted in aqueous solutions suggest that the oxidation of polycyclic aromatic hydrocarbons (PAHs) involves the OH radical which is generated during the decomposition of ozone.

The results obtained from experiments conducted in soil using 581 mg/hr of gaseous ozone indicate that 95% removal of phenanthrene was achieved while only 83% removal of pyrene and 50% removal of chrysene were obtained. When soil contaminated with pyrene and chrysene together, no removal of chrysene, while 94% removal of pyrene, was obtained.

The results suggests that when PAH contaminated soils are treated with ozone, the removal efficiency appears to depend on the bond-localization energy of the individual PAH and its partition coefficient to the soil.

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CHAPTER I

INTRODUCTION

The polycyclic aromatic hydrocarbons (PAHs) are of significant environmental importance because they are not readily biodegradable [1], are persistent in soils [2], are bioaccumulated [3,4] and are either carcinogenic or potentially carcinogenic [5,6,7]. The PAHs are found in many petroleum products including crude oils, motor oils, gasoline and heating fuels. The release of these compounds to the environment can occur as a result of transportation spills, pipeline breakages, combustion of fossil fuels and release of emissions, the release of wastewater effluent from oil and gas works, manufactured gas plant sites, oil refineries and coding operations.

The concentration and relative percentages of PAHs varies significantly with the origin of the crude oil, the type of petroleum product and the refinement process. Nevertheless, several generalizations can be made: the lower molecular weight PAHs occur in crude oil in the greatest concentrations ranges (26 to 31,000 mg/L); and C4 to C6 PAHs are present but in lower concentrations ranging from 0.5 to 200 mg/L [8]. Griest et al. [5] found that the concentrations of C4 to C6 PAHs compounds ranged from 20 to 68 μg/g oil. Despite the variation in the concentrations of these compounds, it is clear from the data presented that the release of petroleum products to the environment can result in the significant contamination. Better methods by which these contamination incidents can be dealt with are crucial to the protection of our natural resources.

The purpose of this research is to study the use of chemical oxidation, using gaseous ozone, to treat soils contaminated with polycyclic aromatic hydrocarbons. Previous work with chlorinated compounds by Masten [9] has shown that in the presence of humic material, ozone degrades to form secondary oxidants. Hydroxyl radicals are most likely the oxidant of greatest interest. These hydroxyl radicals react more rapidly with many organic chemicals than would ozone itself. In these soil systems, the chlorinated compounds are able to effectively compete with the naturally occurring soil organic matter for the ozone, or free radicals produced during the decomposition of ozone. In this research, ozone degradation to form hydroxyl radicals was expected to occur. These hydroxyl radicals should be able to react with polycyclic aromatic hydrocarbons rapidly and compete with the soil organic matter.

A modified vacuum extraction system [10] in an actual field situation, such as that shown in Figure 1.1, might be used. The contamination of unsaturated subsoils could be treated by pumping gaseous ozone into the unsaturated zone through injection wells. This would require the use of an ozone generation system as shown in the figure. The cost of

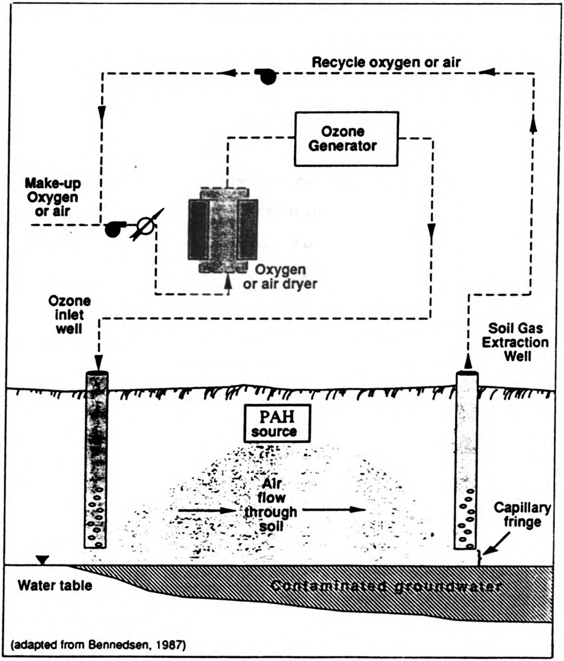


Figure 1.1 Schematic of a Modified Vacuum Extraction System

ozone treatment is high, therefore, complete oxidation of the PAHs using ozone may not be economically feasible. However, if ozone can be used to partially degrade the PAHs and form more bioavailable (or biodegradable) compounds, the cost of treatment could be significantly reduced. Further degradation of the reacted PAHs to innocuous chemicals could be accomplished by the indigenous microbial populations. After the desired level of treatment using ozone has been achieved, nutrients could be added to the soil to enhance biodegradation. Preliminary work (Dunbar, personal comm.) suggests that much of the microbial community survives ozone treatment. As such, reinoculation of the soil may not be necessary.

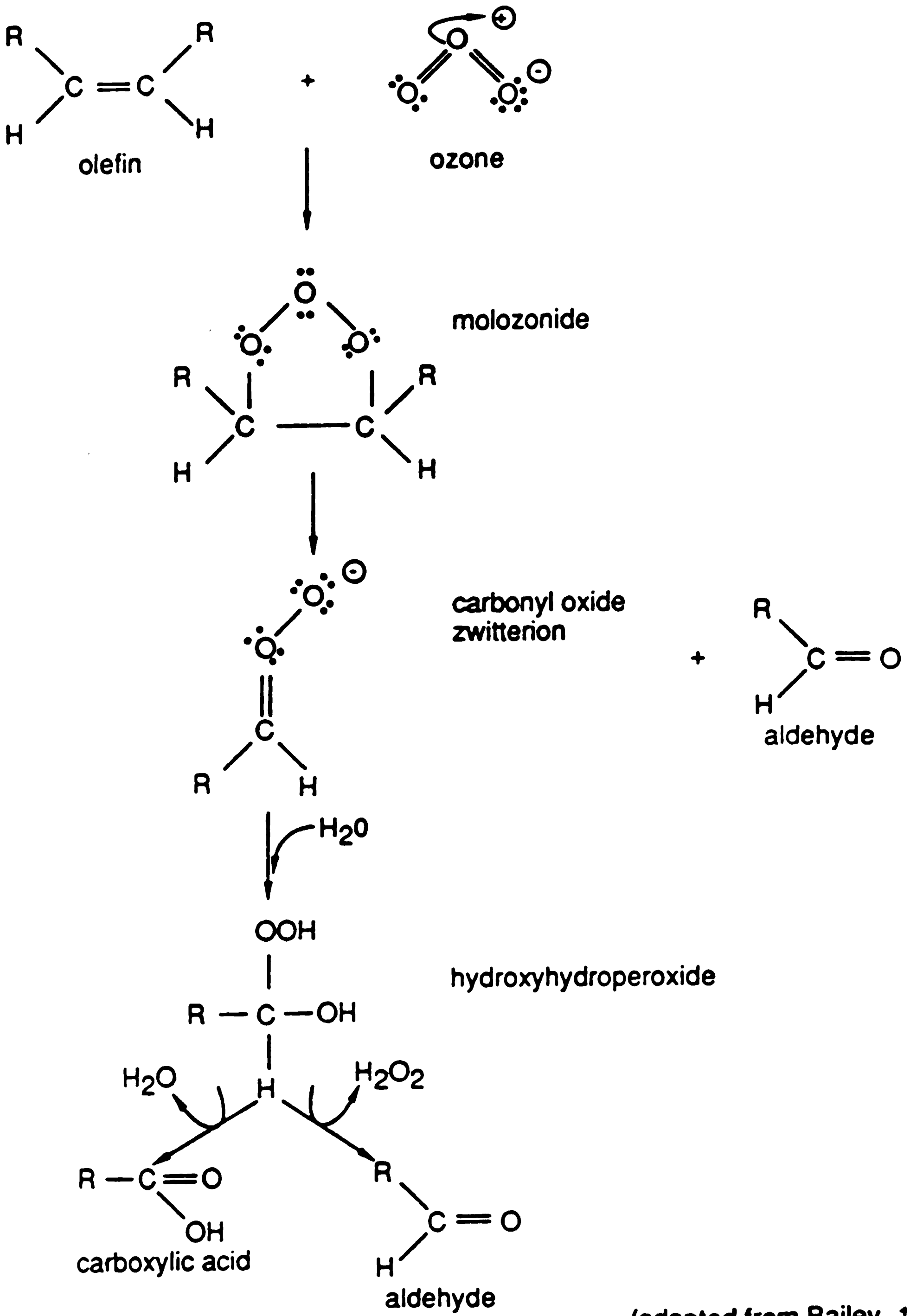
CHAPTER II

BACKGROUND

2.1 The Reaction of Ozone with Aromatic Compounds

Ozone is a very strong oxidant, more powerful than other oxidants commonly used in water and wastewater treatment. Ozone reacts with olefinic compounds by a 1,3-dipolar cyclic addition across the double bond to yield an unstable intermediate, known as a molozonide. These intermediates rapidly decompose to form aldehydes, ketones and/or organic acids [11]. Figure 2.1 illustrates this mechanism.

Early work [11] has shown that a unsubstituted benzene ring is much less reactive toward ozone than is an olefinic double bond. The reactivity of polycyclic aromatic compounds fall in between that of unsubstituted benzene and olefinic. The substitution of alkyl and other functional groups on the benzene ring activate the ring for electrophilic attack and facilitate ozone attack. As a result, substituted benzene compounds are more reactive than benzene itself. When ozone reacts with aromatic compounds, either substitution or ring cleavage results. Very little has been firmly established concerning the mechanism of ozonation of aromatic compounds. This is due to: (1) the slowness by which the first molecule of ozone can attack the aromatic molecule; after that, the reaction rate increases because the degradation compounds are



(adapted from Bailey, 1972)

Figure 2.1 Mechanism of The Ozonolysis Reaction

olefinic; (2) the peroxidic ozonolysis products are very unstable and probably polymeric; (3) there may be more than one mode of initial ozone attack; (4) subsequent to the initial ozone attack there are several different competing reaction pathways leading to both peroxidic and nonperoxidic ozonolysis products [12].

Three types of ozone attack can occur, depending on the system: (1) 1,3-dipolar cycloaddition (ozonolysis) at the bond or bonds having the most double bond character (the bond with the lowest bond-localization energy); (2) electrophilic ozone attack where there are atoms of low atom-localization energy; (3) conjugate addition where there is a reactive diene system (a system of low para-localization energy). When considering the ozonation of PAHs, the lowest bond-localization energy is the parameter of greatest interest. For the PAHs studied in this research, the order of rate of reaction is: pyrene > phenanthrene > chrysene > naphthalene. The example reactions are illustrated in Figures 2.2-2.4 [12].

Naphthalene was found to be much more reactive than benzene and reacted with ozone readily. Subsequent reactions with additional ozone occurred more slowly. Naphthalene appears to undergo ozonolysis, only at the reactive 1,2 and 3,4 bonds. As shown in Figure 2.2, when naphthalene was ozonated in methanol solution, hemiperacetal *(12)* was obtained at a 95% yield along with decomposition products of *(8)*. Compared to naphthalene, phenanthrene has a much lower bond-localization energy, which is at the 9,10-bond. Phenanthrene,

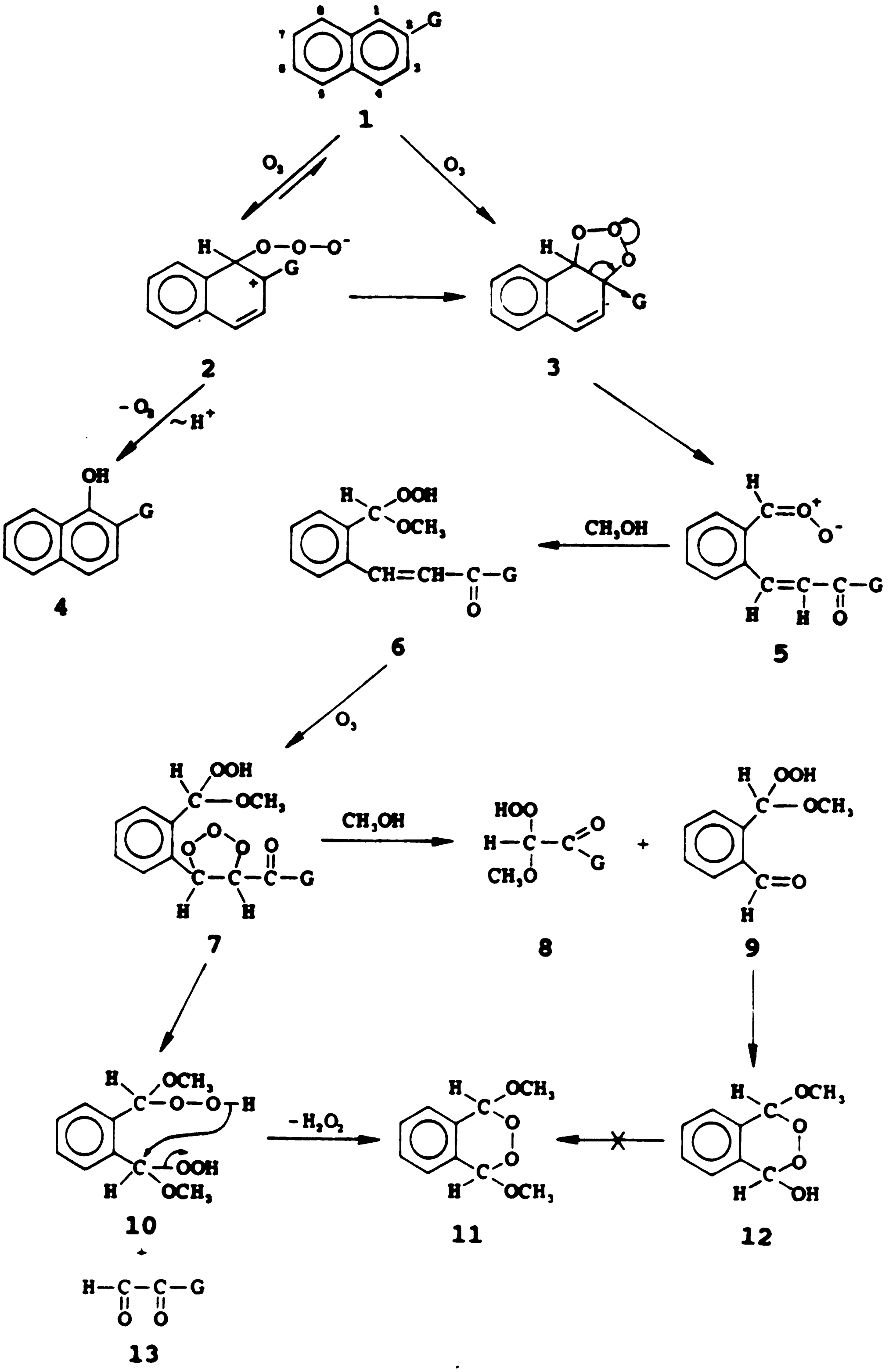


Figure 2.2 Ozonation of Naphthalene

therefore, is considerably more reactive than naphthalene toward ozone. The mechanism of phenanthrene in methanol is as shown in Figure 2.3. Chrysene includes a phenanthrene ring system and, two bonds with bond localization energy considerably lower than that of any bond encountered in naphthalene. Because of this, the behavior toward ozone should be similar to that of phenanthrene. Chrysene reacts readily with ozone at the 5,6-bond (or 11,12-bond, the bond of the lowest bond-localization energy). The ozonolysis product, which was probably a polymeric ozonide, decomposes oxidatively. The ozonation of pyrene is illustrated in Figure 2.4. Two unstable intermediates, which are similar to that obtained from ozonation of phenanthrene, are produced. The biphenyl structure of the carbonyl oxide produced from phenanthrene *(16)* has free rotation; however, the carbonyl oxide intermediates from pyrene *(21,23)* are rigid, and the carbonyl and carbonyl oxide portion consequently are held close together. Thus, intramolecular interaction predominates. If pyrene is treated with excess ozone, further products *(27)* will be produced.

2.2 The Formation of OH Radicals in Aqueous Solutions

In water, ozone degrades to form OH radicals; the rate of degradation depends on pH, and on the concentration, and types of chemicals and ions present. Staehelin and Hoigné [13] have shown that the most important reactive species present in "pure" water are ozone, OH radicals and superoxide (see Figure

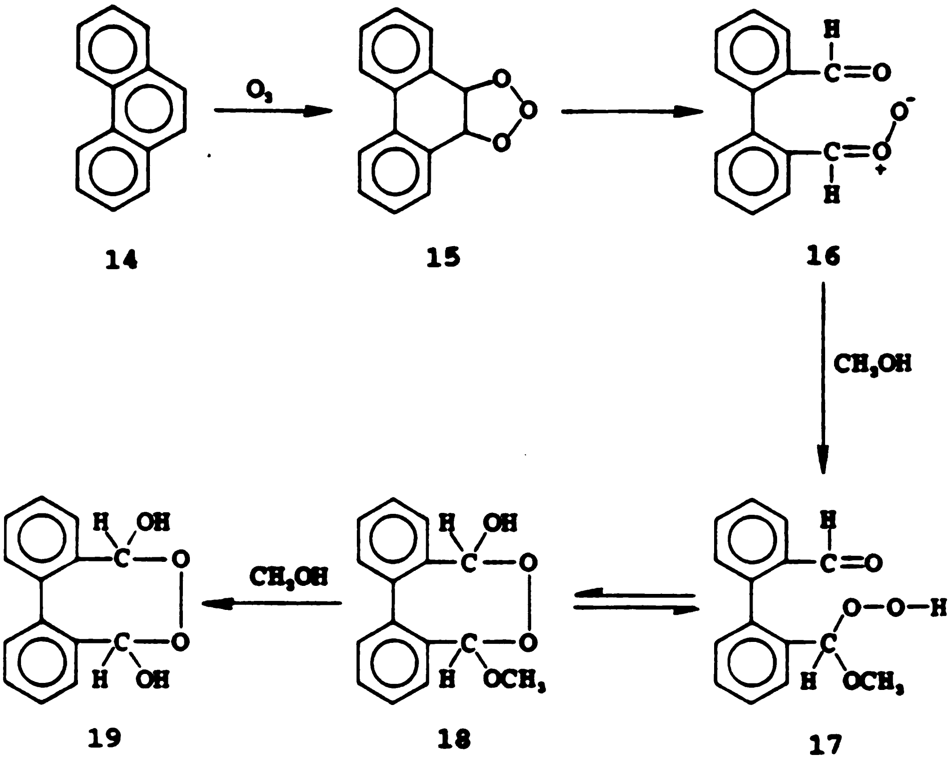
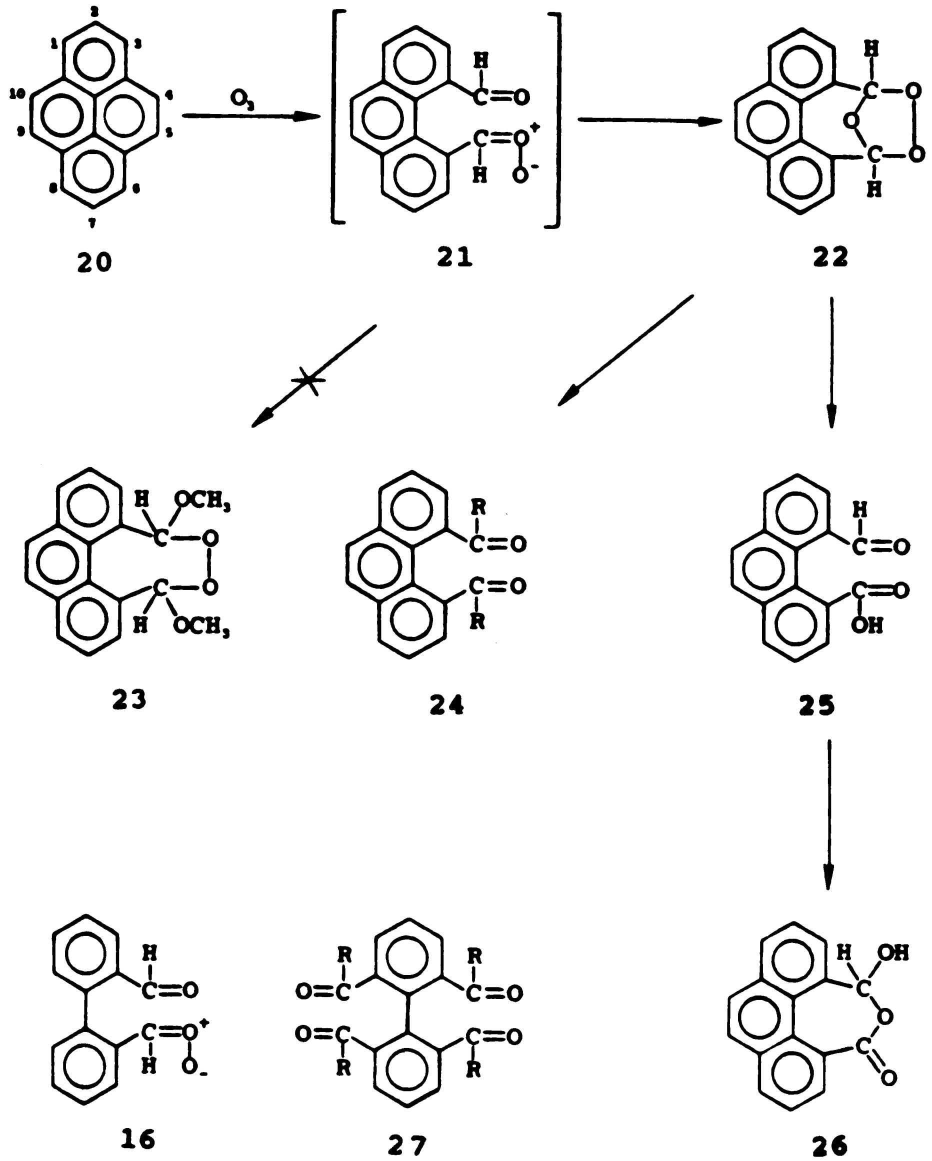


Figure 2.3 Ozonation of Phenanthrene



a: R = H
b: R = OH

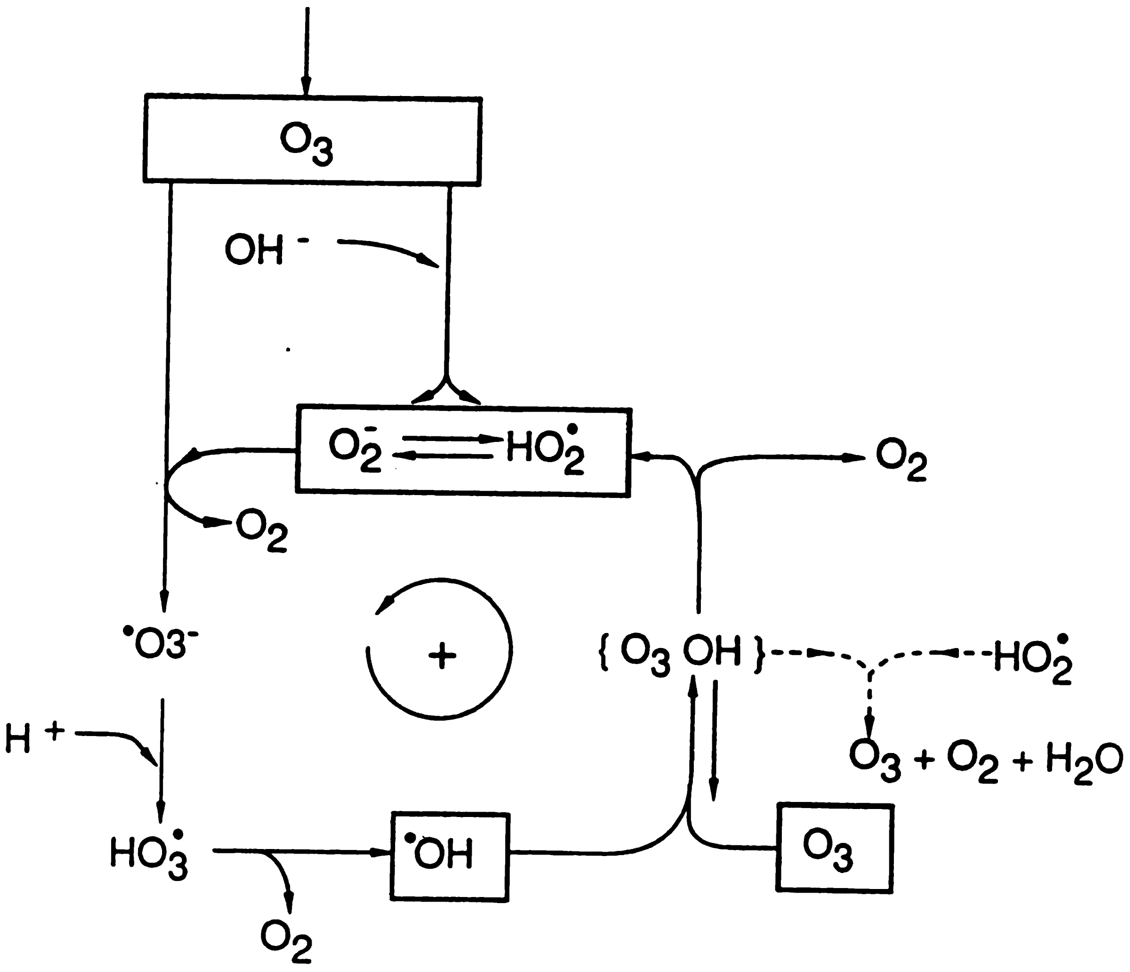
Figure 2.4 Ozonation of Pyrene

2.5). Both superoxide and OH radicals enter into the cyclic reaction which enhance the decomposition of ozone. Additionally, hydroxide will react with ozone to form superoxide and, thus, will result in an enhancement of the rate of ozone decomposition.

Figure 2.6 illustrates the complexity of the ozone system when a reactive compound, M, is present. As in the previous system, ozone, superoxide and OH radicals are present as three of the oxidizing species. In addition, organoperoxides may be present. The mechanisms of these free radical reactions are complex and the oxidations may occur by three pathways: hydrogen abstraction from a -CH group, radical addition, and electron transfer. The secondary radicals formed during these reactions can react with additional ozone, with one another, or with the target compound(s). Organoperoxides can be formed by the reaction of the carbonyl (C·) radical with any oxygen present. These compounds can enter into a chain reaction involving ozone and the hydroxyl radicals resulting in the formation of new radicals or superoxide. Other compounds can react with the free radicals produced to terminate the chain reaction.

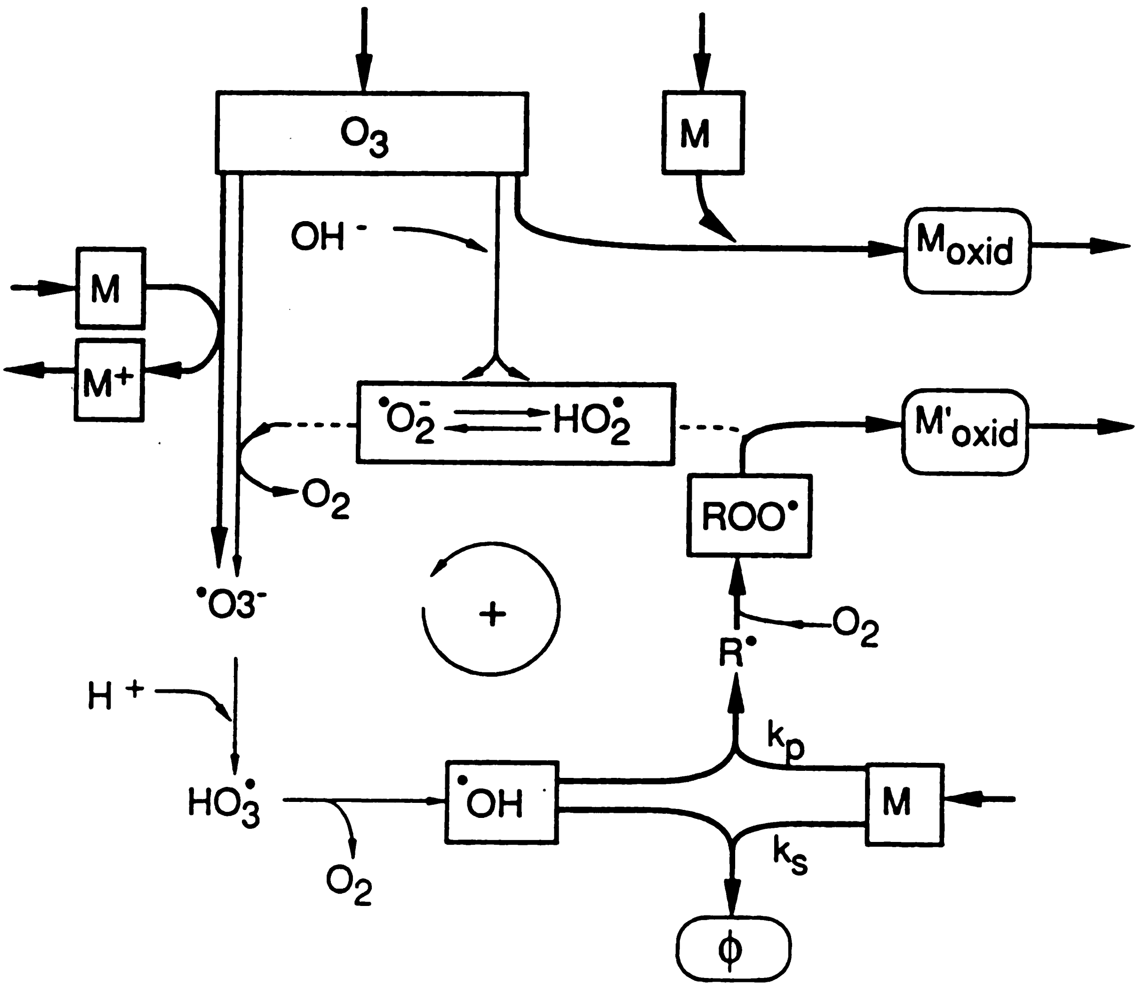
2.3 The Effect of Organic Matter on Ozonation Processes

Only a limited amount of research has been conducted on the effect of natural organic matter on the ozonation of organic compounds. Work done in aqueous systems by Staehelin and Hoigné [13] showed that naturally occurring organic matter



(adapted from Staehelin and Hoigné, 1985)

Figure 2.5 Reactions of Aqueous Ozone in "Pure Water"
(the most important oxidants present in aqueous systems are O_3, O_2^- and •OH)



(adapted from Staehelin and Hoigné, 1985)

Figure 2.6 Reactions of Aqueous Ozone in The Presence of Target Compounds M Which React With O_3 or Which Interact With •OH Radicals By Scavenging and/or Converting •OH into HO_2•
(the most important oxidants present in aqueous systems are O_3, O_2^- and •OH)

acted as chain promoters of the decomposition of ozone. Peyton et al. [14] studied the reaction of diethyl malonate with ozone in the presence of soil. High molecular weight compounds present in the soil, such as humic materials, produce secondary species that catalyzed the conversion of ozone to hydroxyl radical. The hydroxyl radical reacted with diethyl malonate.

Only a limited number of studies of the reaction of ozone in soils have been conducted. Work done by Masten [9] indicated that the presence of the soil ozone decomposes to form hydroxyl radicals which then oxidize the target compounds. Willms et al. [15] showed that aqueous phase oxidation of m-xylene was inhibited by the presence of a Louisiana silt loam (a fine-silty, mixed, non-acid, thermic Aeric Fluvaquent) when the soil was present at a concentration of 5 g/L and at temperatures of 523°K and pressures of 10.3 MPa. Under the same conditions, however, PCE oxidation was not inhibited. They interpret their results as indicating that free radicals must play a role in the oxidation of m-xylene, but not in the oxidation of PCE and that the soils scavenge the OH radicals formed. Additionally, Wu et al. [16] studied the gas phase reaction of ozone with perylene and benzo[a]pyrene adsorbed on fused silica plates. It was found that PAHs when dispersed reacted much faster than when they were in their aggregated states.

CHAPTER III

MATERIALS AND METHODS

In this study, we considered the efficiency by which PAHs can be oxidized by ozone in a soil system. Soil systems are extremely complex since the target organic compound may react by one or more of several possible mechanisms. In an attempt to simplify the systems, some of the work conducted was performed in homogeneous aqueous systems containing humic acid as a model of naturally occurring organic matter. A schematic of the reactions involved when soils contaminated with PAHs are ozonated is shown as Figure 3.1. The PAHs are shown with methanol, since in the empirical work conducted the PAHs had to be first dissolved in methanol then added to water in order to get the compounds to dissolve. Aldrich humic acid was chosen as a model of organic matter because of its terrestrial origin. Most of the experiments were conducted in heterogeneous systems using a sandy soil containing approximately 0.5% organic matter.

The experiments were designed to be a continuation of an earlier feasibility study [9] to assess the effect of naturally occurring organic matter on the ozonolysis of hydrocarbons. In order to determine the feasibility of using ozone to treat contaminated soils, the effect of natural organic matter on the ozonation process must be considered.

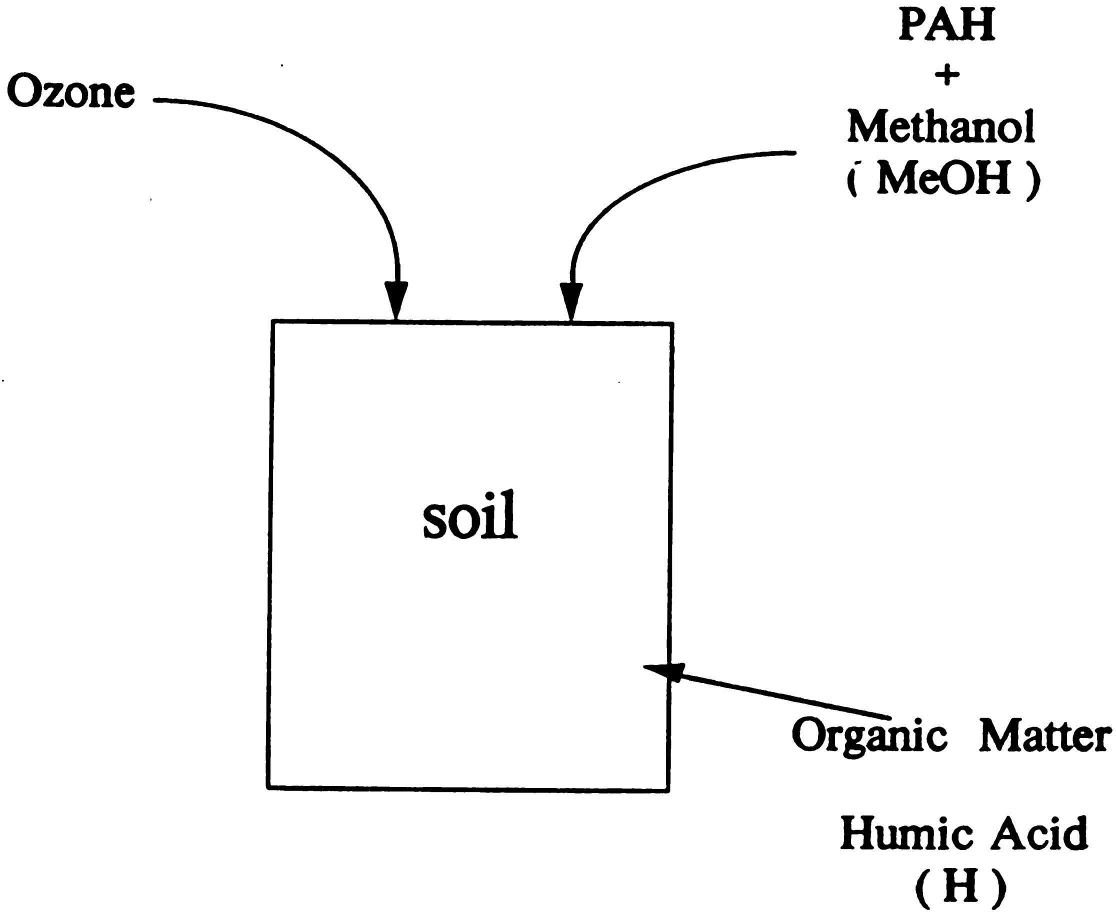


Figure 3.1 Modeling of PAH Reactions in Soil

(contaminated soil is prepared by mixing soil and PAH which is dissolved in methanol; humic acid is used to simulate the natural organic matter in the soil; the soil-organic mixture is treated using ozone)

Doing this will assist in determining the reaction kinetics for the oxidation of the target compounds in soil systems and, therefore, in choosing the conditions under which ozone-modified soil venting is applicable. The target compounds have been chosen so as to investiqate a range of chemical reactivities and hydrophobicities. PAHs having two to four rings are considered. The compounds were chosen to cover a range of mutagenic activities but to avoid those compounds which are strongly carcinogenic. The target compounds are listed in Table 3.1. The selected properties of these compounds are given in Table 3.2.

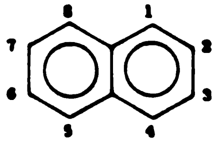
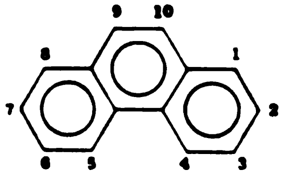
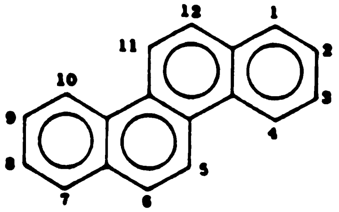
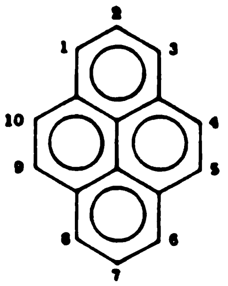
Table 3.2

Target Compounds Studied

Compound	Number of Rings	Relative Carcino-genicity	[12] Most Reactive Bond	[12] Bond-localization Energy
Naphthalene	2	negative[18]	1,2	1.26
Phenanthrene	3	negative[18]	9,10	1.07
Chrysene	4	weakly[19]	5,6	1.12
Pyrene	4	negative[18]	4,5	1.06

Table 3.1

Structure of PAHs to be Studied

COMPOUND	STRUCTURE	ABBREVIATION
Naphthalene		NA
Phenanthrene		PH
Chrysene		C
Pyrene		PY

3.1 Materials

Ozone Generation

Ozone was produced using a Polymetrics Model T - 408 ozone generator (San Jose, CA). According to procedures given in Masten's previous work [9], all ozonated solutions were maintained at a pH of 3 to decrease the extent to which ozone would "autocatalytically" degrade.

To prepare aqueous ozone solutions, gaseous ozone (approximately 3.5% ozone in oxygen) was bubbled into distilled water at a flow rate of approximately 1 ml/min. The distilled water had been previously acidified to a pH of 3 with phosphoric acid, and was kept on ice. During the bubbling of the gas, the ozone solution was kept chilled on ice. After one hour, the system was shut down and the ozone solution (approximately 25 mg/L) was ready for use.

Preparation of Naphthalene Stock Solution

Naphthalene is insoluble in water, but soluble in alcohols. Naphthalene (Aldrich Chem. Co. 99+% purity) was, therefore, first dissolved in methanol before case. The maximum concentration of naphthalene in methanol we were able to obtain was 0.65 mg/ml methanol. Naphthalene solutions were diluted in pH 3 distilled water to 10^{-4} M.

Preparation of Humic Acid Solution

A stock solution of Aldrich humic acid (sodium salt) was prepared by dissolving the humic acid in pH 3 distilled water followed by filtration through a 0.45 μM filter. Stock solutions was stored in the dark.

Preparation of Contaminated Soils

The soils used were obtained from the south end of the Michigan State University campus near an old orchard adjacent to the research farms and Engineering Research Complex Building. Soils were taken from the B horizon and analyzed for physical and chemical properties (percentage organic matter (O.M.), pH, particle size analysis, PAH concentration, and specific gravity (Gs) [17]). The results are presented in Table 3.3.

Because of the difficulty of mixing PAHs and soils, we developed a method to contaminate the soils. The soils were air-dried, then sieved through a series of sieves, (minimum diameter of 0.5 mm). Fifty (50.0) mg of each of the PAHs to be studied were dissolved in an organic solvent. Naphthalene was dissolved in of methanol (35 ml) while phenanthrene and pyrene

Table 3.3

Soil Testing Result

Soil Analysis		Results
Soils Tested by Soil Testing Lab (MSU)	% O.M.	0.5
	pH	6.6
	lime index	71.0
	sand	82.3 %
	silt	10.0 %
	clay	7.7 %
CEE research lab	[PAH]	negligible
	*Gs	2.55

* Gs: Specific gravity

were dissolved in 35 ml pentane, chrysene was dissolved in <50 ml acetonitrile. Five hundred grams of soil was weighted out. A quantity of the soil was then added to a glass jar, followed by a few drops of the PAH solution. The soil was then shaken by hand. More soil and PAH solution were added repeatedly until all the PAH solution and soil had seen mixed. The soil-organic solvent mixture was then rotated at 30 rev/min for 1 hour. The soil was poured out into a pan and air-dried for 15 to 30 minutes. The treated soil, which contained $\sim$ 100 μg/g of PAHs, was then kept in a beaker, covered with parafilm, in the refrigerator until it was to be treated in the experiments.

3.2 Analysis Method

Ozone Analysis

The concentration of the ozone in the aqueous solutions was determined either spectrophotometrically at 258 nm, or using the indigo method (Bader and Hoigné, 1982) [20]. Absorbance was measureded using a diode array spectrophotometer (Model No. 8452A, Hewlett Packard, Palo Alto, CA). An extinction coefficient of 2950 M^{-1} cm^{-1} [9] was used to convert the absorbance units to concentration. The degradation of ozone in pH 3 distilled water was measured using UV spectrophotometry at a wavelength of 258 nm [9], the peak maximum for ozone. The concentration of ozone generated during soil treatment was monitored by potassium iodide traps [21]. The potassium iodide solution was then titrated using 0.05N $Na_2S_2O_3$ to determine the I_2 formed.

Headspace Analysis of Naphthalene

Naphthalene concentrations were determined using a gas chromatograph (Model No. 8700, Perkin-Elmer, Norwalk, CT) equipped with a PID detector. A headspace sampler (Model No. SH 101, Perkin-Elmer, Norwalk, CT) was used. A megabore column (DB-624, J & W Scientific) was used with helium as the carrier gas. Quantification of the peak areas was performed using an integrator (series 1600, PE Nelson, Cupertino, CA). The conditions for the headspace sampler and the GC are shown in Table 3.4. A calibration curve was prepared daily using five standards ranging in concentration from $3x10^{-8}$ to $2x10^{-5}$ M.

Analysis of PAHs: Direct Injection onto GC

PAHs concentrations were determined using a gas chromatograph (Model No. 8700 or AutoSystem, Perkin-Elmer, Norwalk, CT) equipped with a FID detector. The PAHs in solution were injected using a direct injection autosampler (Model No. AS 8300 or AutoSystem, Perkin-Elmer, Norwalk, CT). A megabore column (SPB-5, Supelco, Bellefonte, PA) was used with helium as the carrier gas. Quantification of the peak areas was performed using an integrator (series 1600, PE Nelson, Cupertino, CA or Omega AutoSystem Control, Perkin-Elmer, Norwalk, CT). Conditions for the headspace sampler and the GC were showed as Table 3.5. Fluorene (100 mg/L) was used an internal standard. Calibration standards were prepared daily and run prior to analyzing the samples. For each set of analyses, additional internal standards were run every five samples.

Table 3.4

Headspace Sampler and GC Operation Condition

Photo Ionization Detector(PID)	
Temperature	200°C
Injector	
Temperature	250°C
Pressure	18 psi
Column	DB-624, 30 m x 0.53 mm ID
GC Conditions	
Oven	
Equil. Time	0.5 min
Initial Temp.	50°C
Hold Time	0 min
Program Rate	15°C/min
Final Temp.	200°C
Hold Time	2 min
Carrier Gas	Helium (high purity)
Pressure	7 psi
Headspace Conditions	
Bath Temperature	80°C
Transfer Line and Needle Temp.	100°C
Carrier Gas	Helium (high purity)
Pressure	7 psi
Equilibration Time	1 hour

Table 3.5

GC Direct Injection Operation Condition

	Instrument I No. 8700	Instrument II AutoSystem
Flame Ionization Detector(FID)		
Temperature	250°C	275°C
Hydrogen Pressure	10 psi	40 ml/min
Air Pressure	20 psi	400-480 ml/min
Injector		
Temperature	220°C	250°C
Volume	3 μl	1 μl
Column	SPB-5, 30 m x 0.53 mm ID	
GC Conditions		
Oven		
Equil. Time	1 min	1 min
Initial Temp.	60 °C	175°C
Hold Time	10 min	3 min
Program A:		
Ramp Rate	10°C/min	25°C/min
Final Temp.	120°C	250°C
Hold Time	0 min	10 min
Program B:		
Ramp Rate	30°C/min	
Final Temp.	240°C	
Hold Time	6 min	
Carrier Gas	Helium (high purity)	
Flow Rate	5 ml/min	5 ml/min
Autosampler Air Pressure	60 psi	

Extraction Techniques

Conventional soxhlet extraction techniques as developed by EPA [22,23] were used. A simplified version of this procedure could be used because the soil had a low organic carbon content and extensive clean-up of the extracts was unnecessary.

Five grams of sample soil was added to a soxhlet extraction thimble. The samples were freeze-dried (at a pressure < 10 psi) for approximately two hours, after which the thimble was inserted into the upper section of the soxhlet extraction unit.

Approximately 180 ml of methylene chloride and 20 ml of methanol were added into the 250 ml soxhlet extraction flask. Methanol was added 10% because PAHs are hydrophobic and readily adsorbed onto mineral surfaces, they are not easily extracted from soils using only a non-polar solvent such as methylene chloride. Methanol is a polar solvent which can coat the mineral surface. Thus, when a small percentage of methanol is present in the methylene chloride, better recoveries of the PAHs can be obtained. Samples were extracted for approximately 18 hours (overnight).

The extract was concentrated by collecting the solvent in the thimble section of the soxhlet extractor until it is concentrated to a volume of approximately 20 ml. After that, the methylene chloride in the concentrated solution was evaporated using Kuderna-Danish concentrator. If the sample was not completely dry, the remaining solvent was evaporated using filtered air. Five ml of internal standard solution (100 mg/L fluorene in methylene chloride) was then added to the concentrator. The sample was ready for GC direct injection analysis.

3.3 Experimental Work

Kinetic Measurements

Prior to determining the kinetics for the oxidation of naphthalene in methanol/water solutions using ozone, the rate of reaction of ozone with methanol was determined. Samples were prepared by adding a known volume of methanol in acidified distilled water, then adding a known volume of ozone. The initial time value (t=0) is taken as the time when the ozone solution was added in sample. After a certain time, a sample was withdrawn and placed into a quartz cuvette and determined the concentration of ozone using a UV spectrophotometer at a wavelength 258 nm [9].

For the reaction of naphthalene with ozone, quenching techniques were applied to determine the rate constant since naphthalene also absorbs light in the mid-UV range. Samples were prepared by combining 50.0 ml of acidified water with 50.0 ml of 10^{-4} M naphthalene solution. Timing was begun as soon as 50.0 ml of ozone solution was added. After a certain time, a 10.0 ml aliquot was withdrawn and placed in a 20 ml headspace vial containing 1.0 ml of 0.25M $NaNO_2$, and, at the same time, a 5.0 ml aliquot was pipetted into a 50 ml flask containing 25.0 ml indigo blue solution. As both the sodium nitrite and indigo blue reagents react, essentially, instantaneously with the ozone, the reaction is stopped at the time which the reagents are mixed. After mixing the reagents, the ozone concentration was determined using the indigo method [9]. The naphthalene concentration was determined by headspace GC using the solution quenched by $NaNO_2$.

Effect of Organic Matter

As a comparison to the soil experiments, the effect of humic acid on the rate of chemical oxidation in aqueous systems was studied. Aldrich humic acid was used because it is representative of terrestrial derived organic matter.

Samples were prepared by adding a known volume of acidified water, humic acid solution (200 mg/L), and, if necessary, phosphate buffer (85%) to a 20 ml headspace vial. Five ml of the 10^{-4} M naphthalene solution was added to the vial. Immediately, 5.0 ml of the ozone solution was pipetted into the headspace vial. The final volume of the sample was 15.0 ml. The vial was capped with a Teflon®-lined silicone septum and crimped with an aluminum ring. The sample was then mixed well and stored in the dark. The samples were allowed to react until all the ozone present had reacted (usually 24 hours). Then the sample were analyzed for naphthalene by headspace GC.

In order to determine the extent to which naphthalene reacts via a OH radical mechanism, a scavenger of OH radicals was added. In similar experiments as that described above, 3.0 ml of each solution (ozone, naphthalene and humic acid) was pipetted into a headspace vial. 3.0 ml of a 100 mg/L solution of *tert*-butyl alcohol was added to bring the final volume of the sample to 12.0 ml. AS before, the vials were capped, mixed and allowed to react until no ozone was present. The residual naphthalene concentrations were determined using headspace GC.

Soil Column Studies

Glass columns (21.2 mm I.D., 25 cm length) were packed with the dried contaminated soil. The treatment system is shown in Figure 3.2. Gaseous ozone (produced at a concentration of approximately 3.5% ozone in oxygen) was passed through the soil column. Flows were measured using a rotameter calibrated using a bubble flow meter.

The concentration of ozone generated was monitored by trapping the ozone into potassium iodide traps [21]. After ozone flowed through the column for a period of time at a certain rate (depending on experimental design), the soil was removed from the column and mixed well. The concentration of PAHs remaining in the soil was tested by conventional soxhlet extraction techniques. Controls to determine losses due to volatilization were performed by passing air through a contaminated soil.

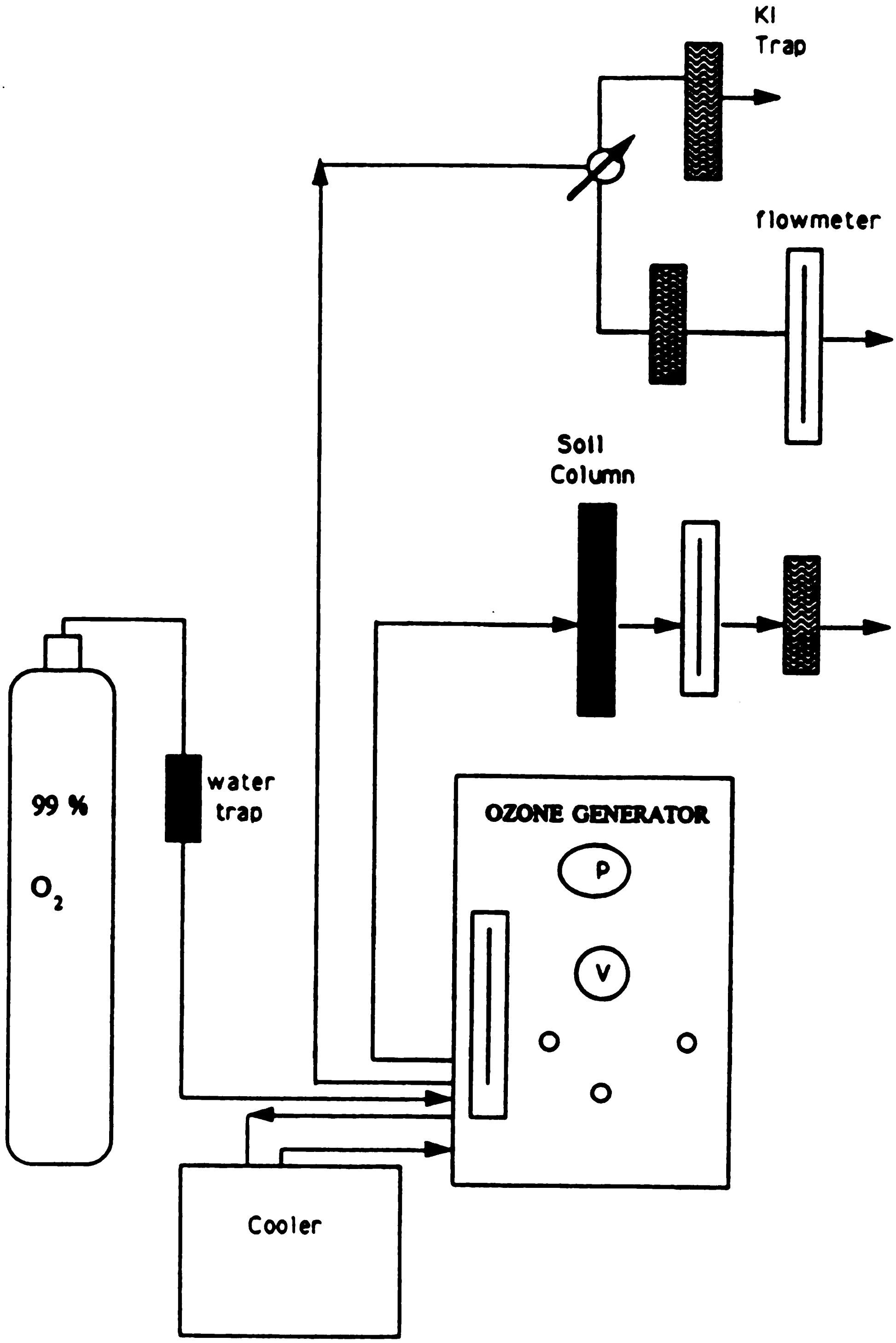


Figure 3.2 Soil Treatment System Connection

CHAPTER IV

REACTION KINETICS

4.1 Ozone Auto-degradation in The Presence of pH 3 Water

In water, the degradation of ozone will affect the reaction rate of any target organic chemical. The ozone degradation rate in water having a pH of 3 has been determined. The rate of degradation can be expressed using the following equation:

$$-\frac{d[O_3]}{dt} = k_{O_3,1}[O_3]^{a}$$

where $k_{03,1}$ is the auto-catalytic degradation rate constant for ozone in acidic water (pH 3). Using this rate expression and the data shown in Appendix Table A.1, we perform a kinetics simulation (using MINSQ computer package to obtain the best curve fitting), the results of which are given in Table 4.1. The reaction order for the degradation rate is either 1.0 to 2. This is consistent with the findings of Gurol & Singer [24].

4.2 Ozone Degradation in The Presence of Methanol

Several experiments were conducted to determine the ozone degradation rate in methanol solutions. Based upon the work of Staehelin and Hoigné [13], the direct reaction of methanol

TABLE 4.1

Ozone Degradation Rate in pH 3 Water
Simulation Results

a		1.0	1.5	2.0
K_{03}		2.36E-4	2.73E-2	3.153
standard deviation		3.16E-6	3.11E-6	3.09E-6
r - squared		0.99872	0.99876	0.99877
residual analysis significant	serial corr.	NO	NO	NO
	skewness	YES	NO	NO
	kurtosis	NO	NO	NO

with ozone is rather slow; thus, we have assumed that methanol acts to stabilize ozone. In these experiments, the methanol concentrations ranged from 0.035% to 0.66% ($8.75\text{x}10^{-3}$ to $1.65\text{x}10^{-1}$ M). The ozone concentration was $<5\text{x}10^{-4}$ M. Because methanol concentrations were 10 - 300 times higher than ozone concentration, the assumption that the methanol concentrations were constant during the experiments is valid; therefore, the reaction between ozone and methanol will be pseudo-first order. When methanol is equal to $1.65\text{x}10^{-1}$ M, the data (shown in Appendix Table A.2-1) could be modelled using a pseudo-first order kinetics simulation (using MINSQ computer software package to obtain the best curve fitting), as illustrated in Figure 4.1. If the assumption that the reaction is first order in methanol concentrations is correct, then the plot of the first order rate constant vs. methanol concentration should be linear, and the kinetics rate equation will be:

$$-\frac{d[O_3]}{dt} = k_{MeOH}[O_3]^{b}[MeOH]$$
$$= k_{O_{3,2}}[O_3]^{b}$$

where $k_{03,2}$ is the pseudo-first order ozone reaction rate constant in methanol, i.e.:

$$k_{O_{3,2}} = k_{MeOH}[MeOH]$$

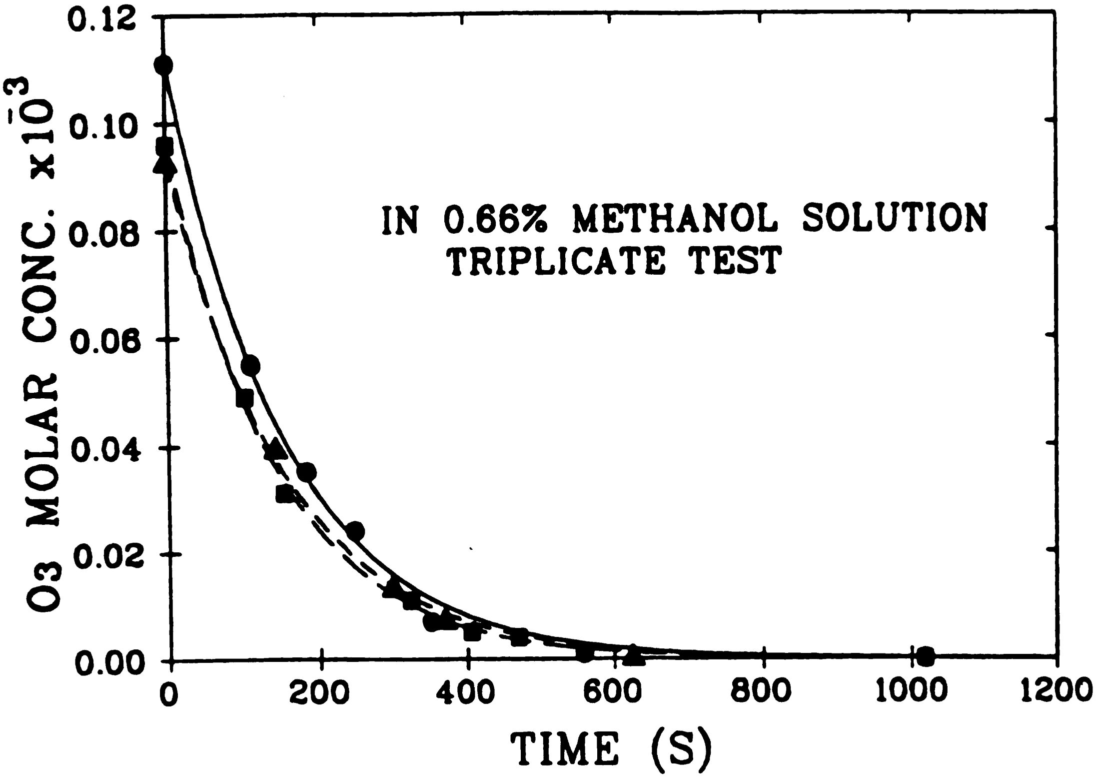


Figure 4.1 Ozone Degradation Kinetics in Methanol Solution

From the simulation results, $k_{O3,2}$ is equal to $6.66\times10^{-3}s^{-1}$; therefore, the rate constant of ozone degradation in methanol, k_{MeOH}, is equal to 4.03×10^{-2} $M^{-1}s^{-1}$. In Figure 4.2, it was found the reaction rate constant increases linearly with increasing methanol concentration. This relationship confirms our assumption that the reaction is first order in methanol concentration.

4.3 Oxidation of Naphthalene By Ozone

The results for the experiments conducted on the oxidation of naphthalene by ozone can be observed in Figure 4.3. Naphthalene is completely degraded in <120 sec, when present at an initial concentration of 3.33×10^{-5} M, and in the presence of 1.65×10^{-1} M methanol and 1.46×10^{-4} M ozone.

Using the assumption that the ozone concentrations are constant, the data obtained for naphthalene (shown in Appendix Table A.3) fits a first order reaction. The kinetics rate equation obtained was as:

$$\begin{aligned} -\frac{d[NA]}{dt} &= k_{NA}[O_3]\,[NA] \\ &= k_1[NA] \end{aligned}$$

where k_1 is pseudo-first order naphthalene reaction rate constant with a constant ozone concentration.

From the results, naphthalene is degraded in 114 sec (approximately eight half-lifes) and the time-averaged ozone concentration is equal to 9.34×10^{-5} M. Therefore, the pseudo-

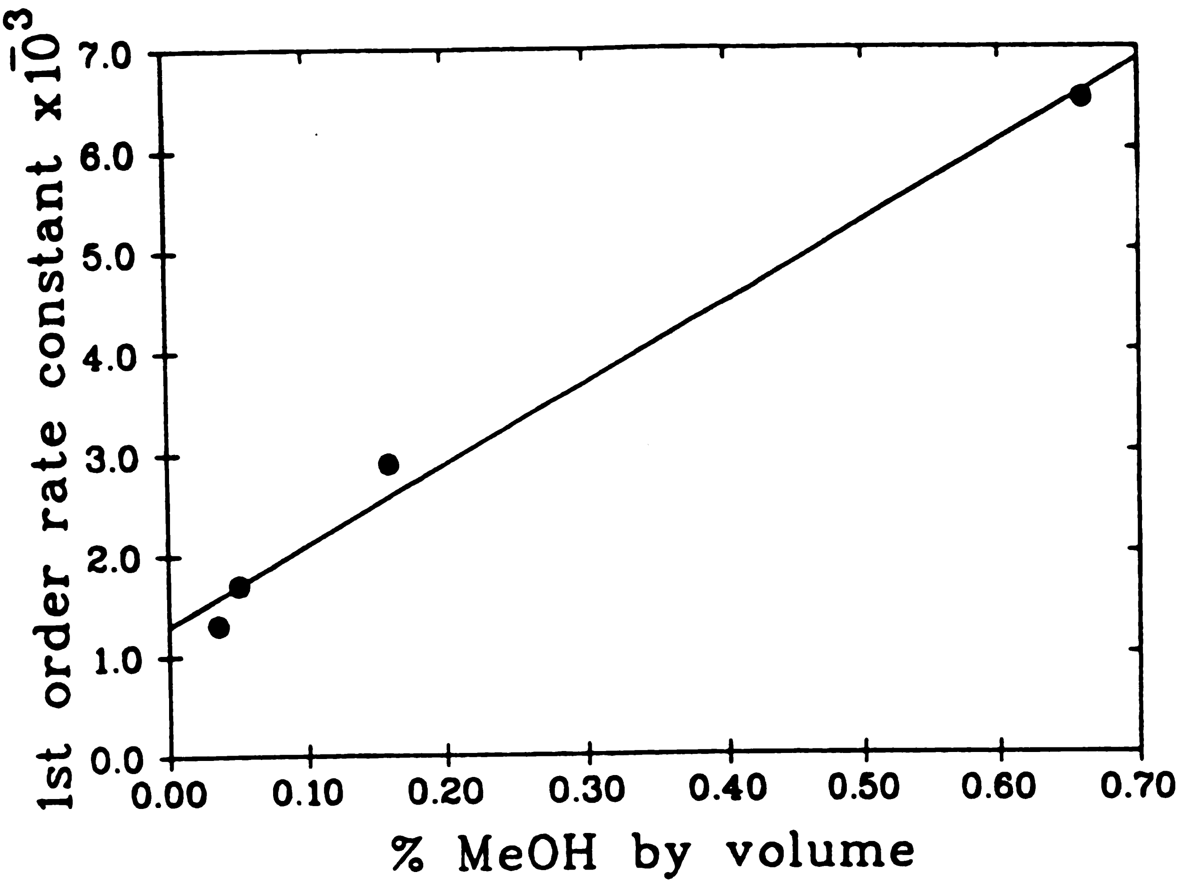


Figure 4.2 Effect of Methanol Concentration on The Ozone Degradation Rate

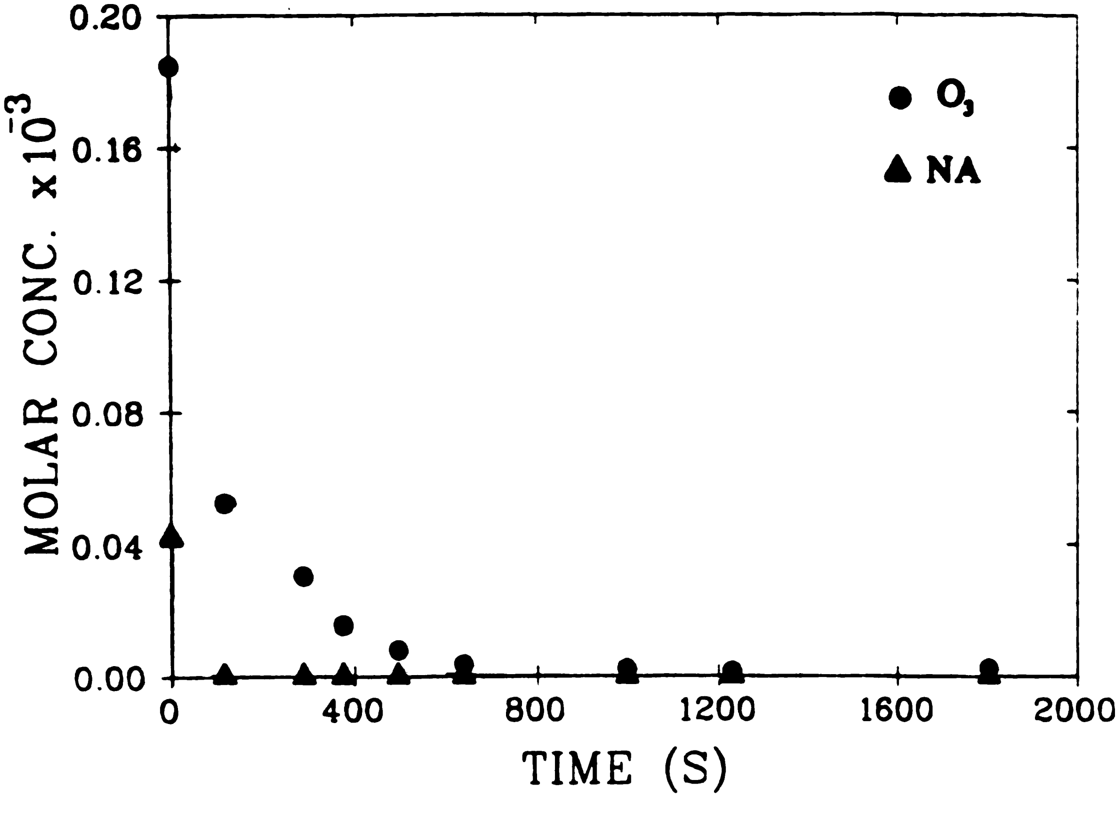


Figure 4.3 Ozonolysis of Naphthalene in pH 3 Water

first order rate constant, k_1, and the reaction rate constant for naphthalene, k_{NA}, can be derived, shown as Appendix B. This results in a value for k_1 pseudo-first order rate constant of 4.86×10^{-2} s^{-1} and a value for k_{NA} of 520 M^{-1} s^{-1} (20°C, pH 3). Compared with the work done by Legube at al. [25], from the linear relationship for pH and temperature that they derived, we calculated a the reaction rate constant for naphthalene of 925 M^{-1} s^{-1} (20°C, pH 3) for their system.

In aqueous solutions which contained methanol, the expression for rate of ozone decomposition in the presence of naphthalene can be written as:

$$-\frac{d[O_3]}{dt} = k_M[O_3]\,[NA] + k_{MeOH}[O_3]\,[MeOH]$$

Based on the work done by Hoigné [26], for every one mole of naphthalene that reacts, two moles of ozone react. Therefore, the above rate expression can be derived using the method developed by Hill [27]. The competitive parallel rate equation was derived as:

$$\frac{dX}{dt} = k_M(\,[O_3]_o - 0.5X - [MeOH]_o(1 - (\frac{[NA]_o - X}{[NA]_o})^{\frac{k_{MeOH}}{k_M}}))\,(\,[NA]_o - X)$$

Where X is naphthalene concentration to be consumed during the reaction, i.e.:

$$X = [NA]_o - [NA]$$

In general, this equation must be solved using numerical methods. When using this rate expression and the data shown in Appendix Table A.3 to determine the rate constant (using MINSQ computer package), the simulated rate constant, k_M, is equal to 95 $M^{-1}s^{-1}$. If using Tayler series expression to integrate this equation, the result for k_M is equal to 110 $M^{-1}s^{-1}$.

4.4 Effect of Humic Acid on Ozone and Target Compounds Reaction

The effect of humic acid dosing on the decomposition rate of naphthalene by ozone is showed on Figure 4.4. The initial ozone and naphthalene concentrations were 1.5×10^{-4} M and 3.33×10^{-5} M, respectively. Both solutions were prepared in pH 3 distilled water. Up to 25 mg/L of humic acid did not effect the decomposition of naphthalene. At humic acid concentrations greater than 25 mg/L, an increase in the humic acid resulted in a decrease the reaction rate between ozone and naphthalene or an increase in the naphthalene concentration remaining after all the ozone was reacted. Nevertheless, even in solutions containing 70 mg/L humic acid, 75% of the naphthalene was degraded by ozone. This is consistent with the hypothesis that not only does ozone directly attack naphthalene but also free radicals play an important role in the decomposition of the target compound when humic acid is present.

In experiments conducted to determine the extent to which naphthalene reacted via a free radical mechanism, *tert*-butyl

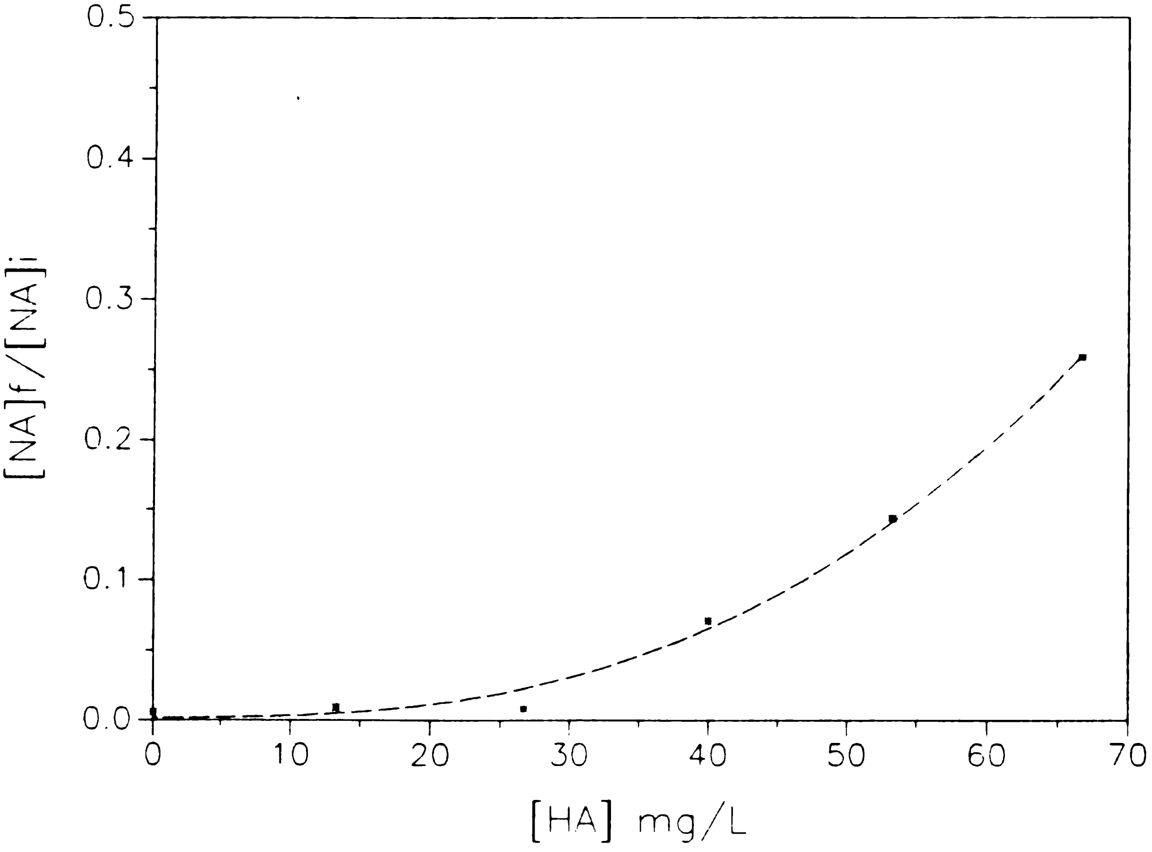


Figure 4.4 Ozonolysis of Naphthalene in Solutions Containing Aldrich Humic Acid

alcohol (0.34 mM) was added as a scavenger of OH radicals. As shown in Figure 4.5, the addition of *tert*-butyl alcohol reduced the extent to which naphthalene reacted with ozone. When the difference in the ratios of naphthalene which reacted ($[NA]_f/[NA]_i$) in the presence and absence of *tert*-butyl alcohol are plotted against humic acid concentration, we observed that the difference in reaction efficiencies increased as the initial humic acid concentration was also increased. This suggests that the extent to which the naphthalene reacted via the OH radicals mechanism (as compared to the direct reaction with ozone) increases as humic acid concentration is increased. The observation that even in the presence of 0.34 mM *tert*-butyl alcohol, a significant fraction of the naphthalene reacted, suggests that some of the naphthalene which reacted, did so by the direct reaction with ozone; or that *tert*-butyl alcohol did not completely scavenge the OH or other radicals.

4.5 Competitive Kinetic Model

In the systems described here, the ozone concentration present at any time will affect the decomposition reaction. If the oxidation of the organic chemical occurs by a direct mechanism, then an increase in the ozone decomposition rate will result in a decrease in the extent to which the target compounds react. However, if the target compound does not or only very slowly reacts with ozone directly, but reacts with other oxidants such as OH radicals, the decomposition of ozone

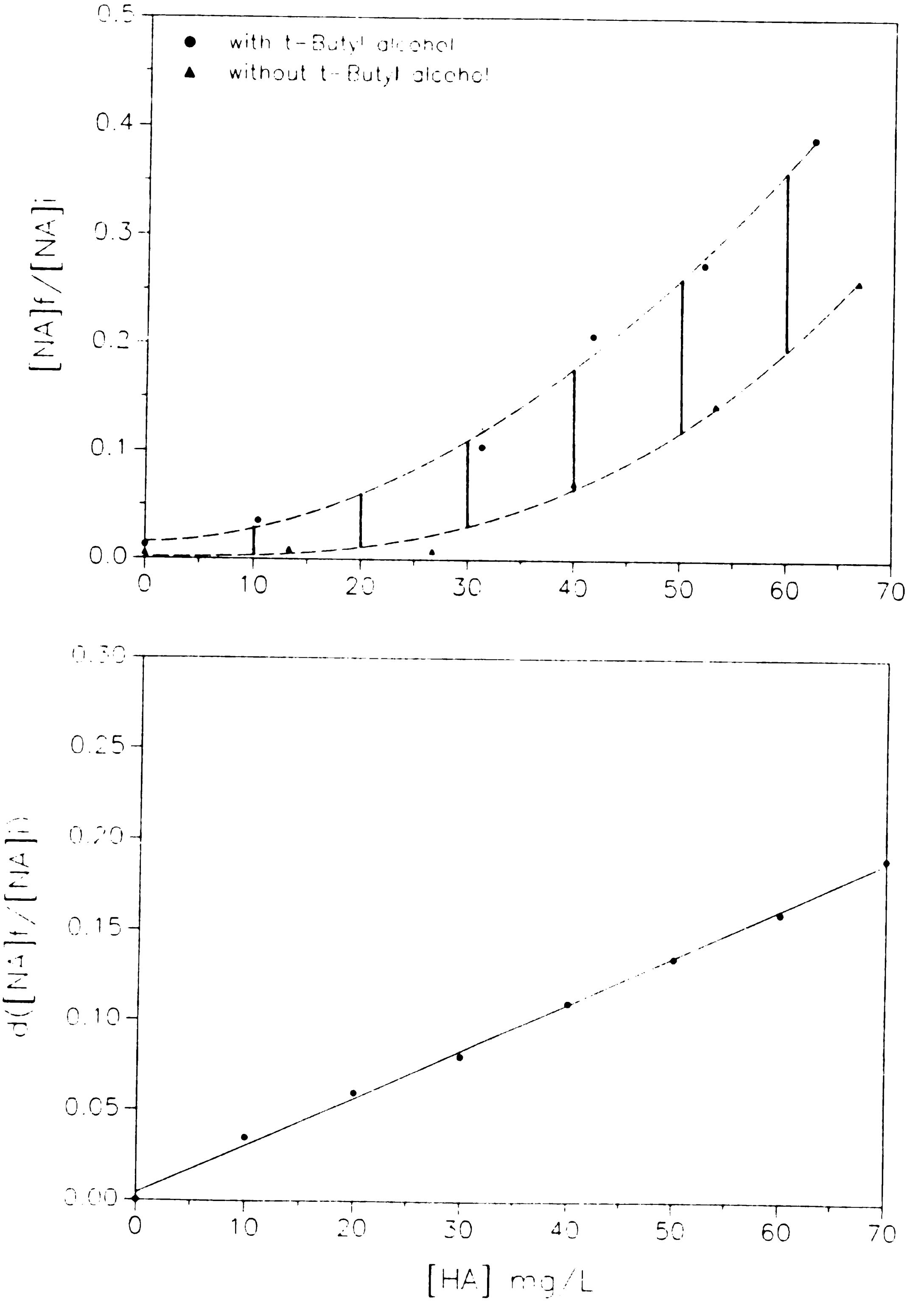


Figure 4.5 Effect of OH Radical Scavengers on The Ozonolysis of Naphthalene in Solutions Containing Aldrich Humic Acid

and the resulting formation of OH radicals may increase the removal efficiencies of these compounds.

The competitive parallel reaction model can be used to describe the kinetics of ozone decomposition reaction. In aqueous solutions the four reactions which would contribute to the decomposition of ozone are:

(1) the direct reaction of ozone with methanol:

$$MeOH + O_3 \xrightarrow{k_{MeOH}} 2H_2O + CO_2$$

(2) the direct reaction involving ozone and the target compound, designated as M for micropollutant:

$$M + O_3 \xrightarrow{k_M} M_{oxid}$$

(3) the direct reaction of ozone with humic acid (H):

$$H + O_3 \xrightarrow{k_H} H_{oxid}$$

and (4) the direct reaction involving ozone and hydroxide ions:

$$OH^- + O_3 \xrightarrow{k_{OH}} HO_2\bullet + O_2$$

On the other hand, if PAHs were present in aqueous solution, the two reactions which would contribute to the decomposition of target compound, M (or the PAH) are:

(1) the direct reaction involving the target compound (designated as M for micropollutant) and ozone:

$$M + O_3 \xrightarrow{K_1} M_{oxid}$$

and (2) the decomposition which results from the reaction of the target compound with hydroxyl radicals:

$$M + \bullet OH \xrightarrow{K_2} M_{rxn}$$

If one assumes that the decomposition of the target compounds in aqueous solution is due solely to the direct reaction of the compounds with ozone, (i.e. only the first four reactions which would contribute to the composition of ozone are important), the rate of ozone decomposition can be expressed by the following equation:

$$-\frac{d[O_3]}{dt} = k_{MeOH}[O_3]^{b}[MeOH]^{c} + k_{M}[O_3]^{d}[M]^{e} + k_{H}[O_3]^{f}[H]^{g} + k_{OH}[O_3]^{h}[OH^-]^{i}$$

Previous work on the ozonation of organic compounds ([28,29], Hoigné (1982) [26], Gilles and Kuczkowski (1983) [30], Williamson and Cvetanovic (1968) [31]) has revealed that one mole of the individual target compound reacts with one mole of ozone (1:1 stoichiometry). Work done by Masten [9] has shown that 1 mg of ozone reacts with 1 mg of humic acid, which is consistent with the findings of Gilbert [32]. The fourth term in the kinetic expression was derived by Gurol at al.

[21]. They derived the rate constant of hydroxyl ion with ozone in different pH range. When pH ranging in 2 - 4, they shown that the ozone decomposition rate is second-order and independent of pH, i.e.:

$$\begin{aligned} k_d &= k_{OH}\,[OH^-]^{0.49} \\ &= 0.24\sim0.27\ M^{-1}s^{-1} \end{aligned}$$

If it is assumes that both f and g are 1.0 which is consistent with the findings of Staehelin and Hoigné [13], the ozone decomposition expression becomes:

$$\begin{aligned} -\frac{d[O_3]}{dt} = {} & 4.03x10^{-2}[O_3]\,[MeOH] + k_M[O_3]\,[M] \\ & + k_H[O_3]\,[H] + k_d[O_3]^2 \end{aligned}$$

CHAPTER V

OXIDATION OF PAHs IN SOILS

The oxidation of PAHs in soils was studied by passing gaseous ozone through a soil column which had been packed with a dry sandy soil contaminated with 100 μg/g of the target PAHs. During each experiment, ozone flux was measured and calculated by two different methods: (1) based on ozone being 3.5% in oxygen, and (2) based on empirical results using KI traps. The sample calculation for ozone flux and for the determination of the percentage ozone in the gas are shown in Appendix D. The residual ozone concentration was found to be very sensitive to the pH of the sample. When measuring the samples, they have to be kept at a pH of less than 3, otherwise, the results will be lower than expected due to testability of the iodine solutions. As a result, the ozone fluxes which were calculated based on the empirical results were less than the ozone fluxes which were calculated based on the ozone being 3.5% in oxygen. Therefore, the following discussion is based on the ozone flux as calculated from the assumption that the ozone gas was 3.5% in oxygen.

5.1 Soil Contaminated With Phenanthrene

The experimental results for phenanthrene are presented in Table 5.1. Before treating the soil using ozone, a control experiment was performed by passing oxygen through a phenanthrene contaminated soil at a flow rate of 2.64 L/hr for 7 hours. It showed that no phenanthrene had been removed by the air. After passing ozone through the soil at a flux of 253 mg O_3/hr for 2.3 hours, greater than 95% of the phenanthrene had disappeared. The final concentration of phenanthrene in the soil was below detection limits. The gas chromatographic scans showed that no degradation products were found. When the ozone dosage was reduced to a flux of 151 mg O_3/hr and the soil was treated for one hour, 60-84% removal was still obtained.

Table 5.1 Treatment of Phenanthrene In Soil Columns (Initial Concentration = 100 μg PH/g soil)

# Ozone Flux (mg/hr) (1)	# Ozone Flux (mg/hr) (2)	Gas Flow Rate (L/hr)	Run Time (hr)	% Removal
0.00	0.00	2.64	7.0	[-]
940	879	13.6	8.0	>95%
882	1010	12.8	6.0	>95%
253	111	3.66	2.3	>95%
170	73.0	2.46	2.5	87%
151	78.4	2.35	1.0	* 60% ** 84%

Phenanthrene Recovery Rate From Soil: 78.8%

* 12 extracts analyzed

** 6 extracts analyzed

Ozone Flux (1): flux based on 3.5% ozone in oxygen

(2): flux based on KI trap measurements

5.2 Soil Contaminated With Chrysene and Pyrene

The oxidation results of the soil contaminated with chrysene and pyrene are presented in Table 5.2. In this case, less than 20% removal of chrysene and pyrene occurred with an ozone dosage of 177 mg O_3/hr for one hour. It appears that when the target compounds are present together, as they were in these studies with pyrene and chrysene, the ozone dosage must be increased in order to achieve the same levels of removal as that obtained when phenanthrene was the contaminant present in the soil. When the ozone dosage was increased to a flux of 217 mg O_3/hr and the soil was treated for one hour, 34% removal of pyrene was obtained while no removal of chrysene was found. Increasing the ozone dosage to 549 mg O_3/hr for one hour, resulted in no removal of chrysene while 94% removal of pyrene was obtained.

Table 5.2 Treatment of Chrysene And Pyrene In Soil Columns (Initial Concentration = 100 μg PY+100 μg C/g soil)

# Ozone Flux (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal	
(1)	(2)			PY	C
549	78.4	8.53	1.0	94%	[-]
217	121	3.25	1.0	34%	[-]
177	107	2.56	1.0	3%	18%

PY Recovery Rate From Soil: 63.3%
C Recovery Rate From Soil: 80.1%

Ozone Flux (1): flux based on 3.5% ozone in oxygen

(2): flux based on KI trap measurements

These findings seem to suggest the importance of the direct ozone reaction in the dry soil, since the results follow the order of reactivity for ozone with chrysene and pyrene [12].

5.3 Soil Contaminated With Chrysene

The experimental results for chrysene oxidation are presented in Table 5.3. After passing ozone through the soil at a flux of 500 mg O_3/hr for one hours, the total ozone dosage was closed to the dosage using when the phenanthrene contaminated soil had been treated with a flow rate of 253 mg O_3/hr for 2.3 hours. Only 40% removal of chrysene can be achieved as compared to greater than 95% removal of the phenanthrene.

When the ozone dosage was increased to a flux of 594 mg O_3/hr and the soil was treated for four hours, only 50% removal of chrysene was achieved. Thus, chrysene needs more than eight times the ozone dosage requirement of phenanthrene. These results follow the order of reactivity for ozone with chrysene and phenanthrene [12]. The gas chromatographic scans showed peaks for what appears to be two major degradation products.

5.4 Soil Contaminated With Pyrene

The results of soil contaminated with pyrene are presented in Table 5.4. The passage of ozone through the soil at a flux of 26.3 mg O_3/hr for one hour, resulted in 53%

Table 5.3 Treatment of Chrysene In Soil Columns

(Initial Concentration = 100 μg C/g soil)

# Ozone Flux (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal
(1)	(2)			
594	48.4	8.65	4.0	50%
558	250	8.68	2.0	43%
611	278	8.97	1.0	33%
501	27.1	7.45	1.0	40%
412	32.9	6.00	1.0	39%
339	166	4.94	1.0	* 39% ** 65%
C Recovery Rate From Soil: 82.7%				

* 12 extracts analyzed

** 6 extracts analyzed

Ozone Flux (1): flux based on 3.5% ozone in oxygen

(2): flux based on KI trap measurements

removal of pyrene. When the results are compared to that for chrysene, it can be shown that pyrene can be more efficiently oxidized. When the ozone dosage is increased to a flux of 581 mg O_3/hr and the soil was treated for one hour, 83% removal of pyrene was achieved. Moreover, increasing the ozone dosage to a flux of 598 mg O_3/hr and treating the soil for four hours, resulted in 91% removal of pyrene. When scanning by the gas chromatographic, no degradation products were found.

Table 5.4 Treatment of Pyrene In Soil Columns

(Initial Concentration = 100 μg PY/g soil)

# Ozone Flux (mg/hr)		Gas Flow Rate (L/hr)	Run Time (hr)	% Removal
(1)	(2)			
598	238	8.65	4.0	91%
581	266	8.40	1.0	83%
315	20.7	4.55	1.0	79%
218	8.91	3.22	1.0	>95%
119	8.79	1.72	1.0	71%
26.3	1.40	0.38	1.0	53%
PY Recovery Rate From Soil: 105%				

Ozone Flux (1): flux based on 3.5% ozone in oxygen

(2): flux based on KI trap measurements

5.5 Effect of Bond Localization Energy and Soil Partitioning of PAHs

When considering the reactivity of PAHs with ozone, the bond-localization energy is the parameter of greatest interest. If one compound has lower bond-localization energy than the other, it is more easily attacked by ozone. Thus, the reaction rate with ozone will be highest for the compound of lowest bond-localization energy. Based upon bond-localization energies, the order of reactivity for the compounds studied should be pyrene > phenanthrene > chrysene > naphthalene [12].

The treatment of the soil contaminated with both chrysene and pyrene by ozone with a dosage of 549 mg O_3/hr for one hour, resulted in no removal of chrysene while 94% removal of pyrene was obtained. If the results for the ozonation of phenanthrene and pyrene are compared, when the ozone dosage was 581 mg O_3/hr and the soil was treated for one hour, it is observed that 83% removal of pyrene was achieved while greater than 95% removal of phenanthrene had been obtained. Based upon theses results, order of reactivity observed was phenanthrene > pyrene > chrysene.

Comparing the results for phenanthrene and chrysene or for pyrene and chrysene are consistent with the order of reactivity for the results obtained the direct ozone reaction in the dry soil. Since the lowest bond-localization energy for chrysene, phenanthrene and pyrene are 1.12, 1.07 and 1.06 respectively, these results can be explained by bond-localization energies. However, the reactivity of pyrene and phenanthrene are not consistent with bond-localization energies.

A possible explanation for this inconsistency may be the sorption of the hydrophobic PAHs onto the soils which protect the PAHs from being oxidized by ozone. The logarithmic partition coefficients of the PAHs studied, together with octanol-to-water and aqueous solubility, are presented in Table 5.5 [33]. The partition coefficients (log K_{oc}) for phenanthrene and pyrene are 6.12 and 6.51 respectively. Thus, the soil could be expected to absorb pyrene much more strongly than it absorbed phenanthrene. As a result, a higher ozone dosage is required for the treatment of pyrene contaminated soils. This suggests that soil adsorption may play a important role in determining the reactivity of compounds which have higher partition coefficients.

Table 5.5

Partition Coefficient for Target Compound

PAH	Log K_{ow}	Log K_{oc}	Log S_w
NA	3.36	5.00	- 5.35
PH	4.57	6.12	- 6.89
C	5.61	6.27	- 9.80
PY	5.18	6.51	- 7.92

5.6 Efficiency of Ozone Reactions In Soils

From the treatment results, an ozonation dosage for phenanthrene (PH) was obtained of 25 mg O_3/mg PH, with greater than 95% of removal of the phenanthrene. When the ozonation dosage was reduced to 21 mg O_3/mg PH, 87% removal rate was obtained. When a further reduction to 11 mg O_3/mg PH was made, 60% removal rate was obtained. The results show a nonlinear requirement for ozonolysis.

Compared to phenanthrene, pyrene (PY) needs higher ozonation dosage to degrade it. When the ozonation dosage was 30 mg O_3/mg PY, 83 - 90% removal rate was obtained. However, reducing ozonation dosage to 8 mg O_3/mg PY, 71% removal rate was obtained. It may suggest that pyrene reaction rate with ozone is greater than phenanthrene because pyrene has a lower bond-localization energy than phenanthrene. Sorption of the pyrene to the soil may be the reason that a higher ozonation dosage is required for completely removing pyrene from soil.

When considering chrysene, only 50% removal was obtained when ozonation dosage was 216 mg O_3/mg C. A higher dosage is required because both the bond-localization energy and partition coefficient are higher than for phenanthrene and pyrene.

CHAPTER VI

CONCLUSIONS

6.1 Conclusions

This research indicates the feasibility of using ozone as an oxidant in solutions containing humic acid or in soils. In solution, the oxidation reactions appear to occur not only by ozone directly but also by the indirect reaction involving some oxidant other than ozone. The effects of the addition of *tert*-butyl alcohol support this hypothesis.

The importance of developing a competitive kinetic models to predict the reactivity of target compounds with ozone in the presence of methanol have been shown by this work. When the solution contained humic acid, there is very strong evidence that the indirect reaction involving some free radical, such as the OH radical, plays a significant role in the oxidation of these compounds. This finding is extremely significant since it suggests that *in-situ* treatment of contaminated soils may be feasible.

From the results of the soil column experiments, it appears that the removal efficiency of the PAH of interest depends on the bond-localization energy and partition coefficient (K_{oc}) of the PAH. Based upon the results presented here, it appears that for phenanthrene-type compounds, the reactivity decreases as functional group are added on to the phenanthrene structure. When increasing the number of benzene ring, the reactivity decreases. This finding is significant since it suggests that hydrophobicity of target compounds may affect the adsorption of the compound to soil, resulting in the bond localization energy becoming less important. From the experimental results, by-products produced were noted only when chrysene was oxidized. These findings substantiate early work suggestive that the *in-situ* treatment of contaminated soils may be technically feasible.

6.2 Further Research

Based on the conclusion drawn in this research, several areas should be researched:

1) Evidence suggests that the OH radical is involved in indirect reactions in aqueous solutions. Therefore, further experiments showed be conducted to better predict the reactivities of the PAHs in soils and to understand the effect of soil moisture content on their reactivity.

2) In order to model the competitive kinetics, the rate constant for reaction of humic acid with ozone must be determined.

3) It is important to identify the degradation products formed and assess biodegradability of these products.

LIST OF REFERENCES

[1]. R.C. Sims and M.R. Overcash, "Fate Of Polynuclear Aromatic Compounds (PAHs) In Soil-Plant Systems", Residue Reviews 88: 2-68 (1983).

[2]. D.K. Stevens, W.J. Grenney, and Z. Yan, "Sensitive Parameter Evaluation For A Vadose Zone Fate And Transport Model - Project Summary", U.S. Environmental Protection Agency Report No. EPA/600/S2-89/0393 (1989).

[3]. J.D. Smith, J. Bagg, and B.N. Bycroft, "Polycyclic Aromatic Hydrocarbons In The Clam Tridacna Maxima From The Great Barrier Reef, Australia", Environ. Sci. Technol. 18(5): 352-358 (1984).

[4]. J.E. Solbakken, A.H. Knap, C.E. Searle, and K.H. Palmork, "Uptake And Elimination Of [9-^{14}C]-Phenanthrene In The Turkey Wing Mussel (Arcazebra)", Bull. Environ. Contam. Toxicol. 30: 420-423 (1983).

[5]. W.H. Griest, B.A. Tomkins, M.V. Buchanan, A.R. Jones, and R.R. Reagan, " Level Of Polycyclic Aromatic Hydrocarbon Dermal Tumorigens In Various Liquid Fuel", Fuel 66: 1046-1049 (1987).

[6]. E.L. Calvalieri, E.G. Rogan, and W.G. Thilly, "Carcinogenicity, Mutagenicity And Binding Studies Of The Environmental Contaminant Cyclopenteno[c,d]pyrene And Some Of Its Derivatives", In: Chemical Analysis and

Biological Fate: Polynuclear Aromatic Hydrocarbons, M. Cooke and A.J. Dennis Eds., Battelle Press, Columbus, Ohio, pp. 199-208 (1981).

[7]. S.C. Thorton, L. Diamond, M. Hite, and W.M. Baird, "Mutation Induction, Metabolism And DNA Adduct Formation By Polycyclic Aromatic Hydrocarbon In L5178Y Mouse Lymphoma Cells: Effects Of S-20 Concentration", In: Cemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons, M. Cooke and A.J. Dennis Eds., Battelle Press, Columbus, Ohio, pp. 199-208 (1981).

[8]. J.M. Neff, "Polynuclear Aromatic Hydrocarbons In The Aquatic Environment: Sources, Fates And Biological Effects", London: Applied Science Publishers, Ltd. (1979).

[9]. S.J. Masten, "Ozonation of VOC's in The Presence of Humic Acid", Ozone: Sci. and Eng. In press. (1991).

[10].M.B. Bennedsen, "Vacuum VOC's From Soil", Pollution Engineering, February, pp. 66-68 (1987).

[11].P.S. Bailey, "Organic Groupings Reactive Towards Ozone - Mechanisms In Aqueous Media", In: Ozone In Water And Wastewater Treatment, F.L. Evans Ed., Ann Arbor, MI: Ann Arbor Science, pp. 29-59 (1972).

[12].P.S. Bailey, "Ozonation Of Aromatic Compounds: Bond Attack On Benz-Fused Carbocyclics", In: Ozonation In Organic Chemistry, H.H. Wasserman Ed., Academic Press, New York, New York, 39(2): 43-76 (1982).

[13].J. Staehelin and J. Hoigné, "Decomposition Of Ozone In Water In The Presence Of Organic Solutes Acting As Promoters And Inhibitors Of Radical Chain Reactions", Env. Sci. Technol. 19: 1206-1213 (1985).

[14].G.R. Peyton, C.S. Gee, J. Bandy, and S.W. Maloney, "Influence On Fate And Treatment Of Pollutants", In: Aquatic Humic Substances, I.H. Suffet and P. MacCarthy Eds., ACS Adv. in Chem. Ser., American Chemical Society: Washington, D.C. 219: 639-661 (1989).

[15].R.S. Willms, D.M. Wetzel, D.D. Reible and D.P. Harrison, "Aqueous Phase Oxidation: The Effect Of Soil On Oxidation Kinetics", Hazardous Waste and hazardous Materials 5(1): 65-71 (1988).

[16].C.H. Wu, I. Saleem, and H. Niki, "Fluorescence Spectroscopic Study Of Reactions Between Gaseous Ozone And Surface - Adsorbed Polycyclic Aromatic Hydrocarbons", Environ. Sci. Technol. 18(8): 603-607 (1984).

[17].J.E. Bowles, "Engineering Properties of Soil and Their Measurement - Specific Gravity of Soil Solids", McGraw - Hill Book Company, 3rd ed., No.7 (1986).

[18].National Academy of Sciences, "Particulate Polycyclic Organic Matter", Washington, D.C., NAS: pp. 361 (1972).

[19].K. Verschueren, "Handbook Of Environmental Data On Organic Chemicals - Chrysene", 2nd Ed., pp. 393-394 (1977).

[20].H. Bader and J. Hoigné, "Determination of Ozone in Water By The Indigo Method - A Submitted Standard Method", Sci. and Eng. 4: 169-176 (1982).

[21]."Ozone (Residual)", In: <u>Standard Method for The Examination of Water And Wastewater</u>, APHA, AWWA, WPCF, 16th ed. (422): 426-429 (1985).

[22]."Method 8100 - Polynuclear Aromatic Hydrocarbons", EPA method report, Rev. 0, Sep. (1986).

[23]."Method 3540 - Soxhlet Extraction", EPA method report, Rev.1, Dec. (1987).

[24].M.D. Gurol and P.C. Singer, "Kinetics Of Ozone Decomposition: A Dynamic Approach", Environ. Sci. Technol. 16(7): 377-383 (1982).

[25].B. Legube, H. Sugimitsu, S. Guyon, and M. Dore, "Ozonation Of Naphthalene In Aqueous Solution - Kinetic Studies Of The Initial Reaction Step", Wat. Res. 20(2): 209-214 (1986).

[26].J. Hoigné, "Mechanisms, Rates And Selectivities Of Oxidations Of Organic Compounds Initiated By Ozonation Of Water", In: <u>Handbook of Ozone Technology and Applications</u>, Vol.1, R.G. Rice and A. Netzer, Eds. (Ann Arbor, MI: Ann Arbor Science), pp. 341-479 (1982).

[27].C.G. Hill Jr., Chemical System Involving Multiple Reactions - Competitive Parallel Reactions", In: <u>An Introduction To Chemical Engineering Kinetics And Reactor Design</u>, John Wiley & Sons, New York, pp. 144-146 (1977).

[28].S.J. Masten and J.N. Butler, "Ultraviolet-Enhanced Ozonation Of Organic Compounds: 1,2-Dichloroethane And Trichloroethylene And Model Substrates", Ozone: Sci. and Eng. 8: 339-353 (1986).

[29].S.J. Masten, "Mechanisms And Kinetics Of Ozone And Hydroxyl Radical Reactions With Model Aliphatic And Olefinic Compounds", PhD. Thesis, (Cambridge, MA: Harvard University) (1986).

[30].C.W. Gilles and R.L. Kuczkowski, "The Ozonolysis Of Haloalkenes In Solution", Israel J. Chem. 23: 446-450 (1983).

[31].D.G. Williamson and R.J. Cvetanovic, "Rates Of Reaction Of Ozone With Chlorinated And Conjugated Olefins", J. Am. Chem. Soc. 90(16): 4248-4252 (1968).

[32].E. Gilbert, "Einwirkung Von Ozon Auf Huminsauren In Wässerigen Lösungen", Vom Wasser, 55: 1-14 (1980).

[33].S.I. Kayal and D.W. Connell, "Partitioning of Unsubstituted Polycyclic Aromatic Hydrocarbons Between Surface Sediments And The Water Column In The Brisbane River Estuary", Aust. J. Mar. Freshwater Res., 41: 443-456 (1990).

APPENDICES

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APPENDIX A

Kinetics Measurements Data

Table A.1

Ozone Auto-catalytic Degradation

Time (s)	* ABS	$[O_3]$ ($\times 10^5$ M)
0	0.2691	9.1
73	0.2638	8.9
137	0.2617	8.8
267	0.2511	8.5
370	0.2548	8.6
445	0.2265	7.6
920	0.2016	6.8
1154	0.2176	7.3
1250	0.2011	6.8
1869	0.1724	5.8

* ABS: absorbance of ozone by UV spectrophotometer

Table A.2-1

Ozone Degradation In Methanol

A.2-1 Ozone Degradation In Methanol

Trial 1		Trial 2		Trial 3	
Time (s)	$[O_3]$ (x10^{-5}M)	Time (s)	$[O_3]$ (x10^{-5}M)	Time (s)	$[O_3]$ (x10^{-5}M)
0	11.	0	9.6	0	9.2
110	5.5	102	4.9	142	3.9
182	3.5	153	3.1	298	1.3
246	2.4	322	1.1	370	0.7
350	0.7	405	0.5	625	0.0
558	0.1	470	0.4	937	0.0
1018	0.0	1018	0.0	2121	0.0
K_{O3}= 6.54x10^{-3} s^{-1}		K_{O3}= 6.98x10^{-3} s^{-1}		K_{O3}= 6.45x10^{-3} s^{-1}	

A.2-2 Pseudo-First Order Rate Constant OF Ozone Degradation In Methanol

MeOH % by volume	Pseudo-first order const. $k_{O3,2}$
0.035	0.0013
0.05	0.0017
0.16	0.0029
0.66	0.0065

Table A.3

Oxidation Of Naphthalene By Ozone

Time (s)	$[O_3]$	[NA]
0	14.6E-5	3.33E-5
114	5.26E-5	1.38E-7
288	3.05E-5	2.32E-8
374	1.56E-5	2.32E-8
494	0.81E-5	1.49E-8
638	0.37E-5	1.78E-8
996	0.22E-5	2.91E-8
1229	0.13E-5	8.43E-8
1807	0.23E-5	8.68E-8

Table A.4

Effect Of Humic Acid On Ozonation Of Naphthalene

Sample No.	$[NA]_f$ M	* [HA] mg/L	$[NA]_f/[NA]_i$
0	1.87E-7	0.0	5.60E-3
1	3.04E-7	13.3	9.14E-3
2	2.70E-7	26.7	8.10E-3
3	2.36E-6	40.0	7.10E-2
4	4.79E-6	53.3	1.44E-1
5	8.64E-6	66.7	2.59E-1

Initial concentration: $[NA] = 3.33 \times 10^{-5}$ M
$[O_3] = 1.5 \times 10^{-4}$ M

* [HA] = humic acid concentration

Table A.5

Effect Of *tert*-butyl alcohol On Ozonation Of Naphthalene In Humic Acid

Initial concentration: $[NA]_i = 2.5\mathrm{x}10^{-5}$ M
$[O_3] = 1.37\mathrm{x}10^{-4}$ M
$[t\text{-BuOH}] = 3.4\mathrm{x}10^{-4}$ M

A.5-1

Sample No.	$[NA]_f$ M	[HA] mg/L	$[NA]_f/[NA]_i$
0	3.16E-7	0.0	1.27E-2
1	8.85E-7	10.4	3.54E-2
2	2.61E-6	31.3	1.05E-1
3	5.19E-6	41.7	2.08E-1
4	6.86E-6	52.1	2.74E-1
5	9.74E-6	62.5	3.90E-1

A.5-2

[HA] mg/L	$\Delta([NA]_f/[NA]_i)$
0.0	0.00
10.0	0.04
20.0	0.06
30.0	0.08
40.0	0.11
50.0	0.14
60.0	0.16
70.0	0.19

APPENDIX B

Rate Constant Analysis

The kinetics rate equation for naphthalene was as below:

$$-\frac{d[NA]}{dt} = k_{NA}[O_3]\,[NA]$$
$$= k_1\,[NA]$$

where: k_1 = pseudo-first order naphthalene reaction rate constant with ozone

Assume that naphthalene was degraded in 114 sec, the concentration was reduced from $3.33\text{x}10^{-5}$ to $1.38\text{x}10^{-7}$, it is equal to 8 half lives. So, naphthalene half life and k_1 can be derived as follow:

$$t_{1/2} = \frac{114}{8} = 14.25\ s$$
$$= \frac{0.693}{k_1}$$
$$\text{->}\ k_1 \approx 4.86x10^{-2}\ s^{-1}$$

Ozone concentration was changes from $1.464\text{x}10^{-4}$ M to $5.26\text{x}10^{-5}$ M. So, the average ozone concentration used, $[\bar{O}_3]$, during this time was $9.34\text{x}10^{-5}$ M.

$$\therefore \qquad k_{NA} = \frac{k_1}{[\overline{O_3}]} = \frac{4.86x10^{-2}}{9.34x10^{-5}} \approx 520\ M^{-1}\ s^{-1}$$

APPENDIX C

Soil Treatment Data

C - 1.1

Untreated Soil Recovery Rate
Soil Contaminant : 100 ppm PH

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	78.81	10	77.11
2	77.56	11	75.99
3	75.90	12	73.97
4	76.55	13	85.68
5	76.89	14	83.12
6	76.71	15	84.27
7	74.75	16	83.59
8	75.59	17	83.14
9	74.60	18	83.98
		Average	78.79

C .1- 2

Soil Contaminant : 100 ppm PH

Oxygen Treatment Flow Rate : 44 ml/min = 2.64 L/hr
Oxygen Treatment Time : 7 hours
Volume of KI Titrant : 0 ml

Soil Recovery Rate : 78.79 %

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	92.96	10	75.61
2	91.79	11	76.79
3	93.02	12	75.48
4	86.44	13	70.71
5	96.58	14	74.37
6	95.47	15	69.26
7	75.58	16	70.92
8	79.86	17	69.31
9	81.12	18	69.94
		Average	80.29
		Ture Value	101.89

C .1 - 3

Soil Contaminant :	100 ppm PH
Titrant :	0.00515 N-Na2S2O3

Ozone Treatment Flow Rate :	227 ml/min	= 13.6 L/hr
Ozone Treatment Time :	8 hours	
Volume of KI Titrant :	0 ml	

Flow Rate of Ozone into KI Trap :	144 ml/min	
Ozone Collection Time :	60 min	
Titration-1st KI solution :	11.34 ml	(1:50 dilution)
Titration-2nd KI solution :	2.47 ml	

Ozone Flux :	*(1) =	940.03 mg/hr
	**(2) =	879.35 mg/hr

*(1) based on ozone being 3.5 % in oxygen

**(2) based on empirical results

Soil Recovery Rate : 78.79 %

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	< DL	10	< DL
3	< DL	12	< DL
4	< DL	13	< DL
5	< DL	14	< DL
6	< DL	15	< DL
7	< DL	16	< DL
8	< DL	17	< DL
9	< DL	18	< DL
		Average	< DL
		Ture Value	< 5 %

*** DL : Detection Limits

C .1 - 4

Soil Contaminant : 100 ppm PH
Titrant : 0.00515 N-Na2S2O3

Ozone Treatment Flow Rate : 212.6 ml/min = 12.76 L/hr
Ozone Treatment Time : 6 hours
Volume of KI Titrant : 0 ml

Flow Rate of Ozone into KI Trap : 144 ml/min
Ozone Collection Time : 61.33 min
Titration-1st KI solution : 14.23 ml (1:50 dilution)
Titration-2nd KI solution : 5.6 ml

Ozone Flux : *(1) = 881.97 mg/hr
**(2) = 1014.45 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : 78.79 %

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	< DL	10	< DL
2	< DL	11	< DL
3	< DL	12	< DL
4	< DL	13	< DL
5	< DL	14	< DL
6	< DL	15	< DL
7	< DL	16	< DL
8	< DL	17	< DL
9	< DL	18	< DL
		Average	< DL
		Ture Value	< 5 %

*** DL : Detection Limits

C .1- 5

Soil Contaminant : 100 ppm PH
Titrant : 0.00447 N-Na2S2O3

Ozone Treatment Flow Rate : 61.05 ml/min = 3.66 L/hr
Ozone Treatment Time : 2.3 hours
Volume of KI Titrant : 0 ml

Flow Rate of Ozone into KI Trap : 144 ml/min
Ozone Collection Time : 60 min
Titration-1st KI solution : 6.08 ml (1:50 dilution)
Titration-2nd KI solution : 1.66 ml

Ozone Flux : *(1) = 252.98 mg/hr
**(2) = 110.65 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : 78.79 %

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	< DL	10	< DL
2	< DL	11	< DL
3	< DL	12	< DL
4	< DL	13	< DL
5	< DL	14	< DL
6	< DL	15	< DL
7	< DL	16	< DL
8	< DL	17	< DL
9	< DL	18	< DL
		Average	< DL
		Ture Value	< 5 %

*** DL : Detection Limits

C .1 - 6

Soil Contaminant : 100 ppm PH
Titrant : 0.00447 N-Na2S2O3

Ozone Treatment Flow Rate : 41 ml/min = 2.46 L/hr
Ozone Treatment Time : 2.5 hours
Volume of KI Titrant : 0 ml

Flow Rate of Ozone into KI Trap : 144 ml/min
Ozone Collection Time : 62.5 min
Titration-1st KI solution : 6.21 ml (1:50 dilution)
Titration-2nd KI solution : 2.41 ml

Ozone Flux : *(1) = 170.04 mg/hr
**(2) = 73.00 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : 78.79 %

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	10.26	10	9.98
2	11.22	11	10.65
3	11.48	12	10.65
4	10.80	13	9.15
5	10.45	14	9.16
6	10.25	15	9.25
7	10.46	16	9.29
8	10.47	17	9.11
9	9.75	18	9.41
		Average	10.10
		Ture Value	12.82

C .1 - 7

Soil Contaminant : 100 ppm PH
Titrant : 0.00447 N-Na2S2O3

Ozone Treatment Flow Rate : 39.21 ml/min = 2.35 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 1 ml (1:25 dilution)

Flow Rate of Ozone into KI Trap : 144 ml/min
Ozone Collection Time : 55 min
Titration-1st KI solution : 7.00 ml (1:50 dilution)
Titration-2nd KI solution : 1.30 ml

Ozone Flux : *(1) = 151.15 mg/hr
**(2) = 78.43 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : 78.79 %

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	31.78	13	12.66
2	30.14	14	12.32
3	32.16	15	12.62
4	30.61	16	12.18
5	30.68	17	12.09
6	30.62	18	12.22
7	31.22	Average	12.35
8	31.25	** Ture Value	15.67
9	31.09		
10	31.63		
11	31.03		
12	32.52		
Average	31.23		
* Ture Value	39.63		

* 39.63% removal based on analysis of extracts from two thimbles (12 samples)
** 15.67% removal based on analysis of extracts from the 3rd thimble (6 samples)

C.2 - 1

Untreated Soil Recovery Rate
Soil Contaminant : 100 ppm PY +100 ppm C

Sample Number	Conc. (ppm) PY	C
1	63.20	73.97
2	64.10	75.22
3	63.10	77.75
4	64.35	75.48
5	63.75	75.00
6	57.47	75.01
7	64.88	85.19
8	62.92	82.16
9	64.12	86.38
10	64.40	86.82
11	63.32	83.06
12	63.50	85.38
Average	63.26	80.12

C.2 - 2

Soil Contaminant : 100 ppm C + 100 ppm PY
Titrant : 0.00447 N-$Na_2S_2O_3$

Ozone Treatment Flow Rate : 142 ml/min = 8.53 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 1 ml [1:10 dilution]

Flow Rate of Ozone into KI Trap : 144 ml/min
Ozone Collection Time : 55 min
Titration-1st KI solution : 7.00 ml [1:50 dilution]
Titration-2nd KI solution : 1.30 ml

Ozone Flux : *(1) = 548.65 mg/hr
**(2) = 78.43 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 63.26%
C - 80.12%

Sample Number	Conc. (ppm)	
	PY	C
1	2.24	66.27
2	2.26	66.24
3	2.29	64.83
4	2.55	69.27
5	2.52	65.33
6	2.61	67.56
7	3.83	77.92
8	2.12	75.54
9	2.56	72.63
10	2.85	72.80
11	1.05	73.69
12	3.38	79.11
13	2.10	62.38
14	1.73	71.36
15	2.02	60.02
16	2.11	58.33
17	2.18	65.89
18	2.33	67.99
Average	3.77	85.92
Ture Value	5.96	107.23

C.2 - 3

Soil Contaminant : 100 ppm C + 100 ppm PY
Titrant : 0.00447 N-Na2S2O3

Ozone Treatment Flow Rate : 54 ml/min = 3.25 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 0.67 ml [1:25 dilution]

Flow Rate of Ozone into KI Trap : 139 ml/min
Ozone Collection Time : 54 min
Titration-1st KI solution : 6.72 ml [1:50 dilution]
Titration-2nd KI solution : 2.00 ml

Ozone Flux : *(1) = 216.84 mg/hr
**(2) = 120.58 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 63.26%
C - 80.12%

Sample Number	Conc. (ppm) PY	C
1	45.87	104.97
2	38.19	105.04
3	38.36	109.51
4	45.58	111.96
5	38.98	112.05
6	44.71	112.19
7	38.57	156.33
8	42.63	114.74
9	42.79	116.73
10	44.09	116.06
11	40.45	117.30
12	39.96	117.69
13	44.99	116.98
14	42.35	118.64
15	43.41	121.73
16	41.41	119.35
17	39.52	119.14
18	39.11	121.21
Average	41.72	117.31
Ture Value	65.95	146.42

C.2 - 4

Soil Contaminant : 100 ppm C + 100 ppm PY
Titrant : 0.00447 N-Na2S2O3

Ozone Treatment Flow Rate : 43 ml/min = 2.56 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 0 ml

Flow Rate of Ozone into KI Trap : 137 ml/min
Ozone Collection Time : 54.3 min
Titration-1st KI solution : 7.20 ml [1:50 dilution]
Titration-2nd KI solution : 2.23 ml

Ozone Flux : *(1) = 176.95 mg/hr
**(2) = 106.68 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 63.26%
C - 80.12%

Sample Number	Conc. (ppm) PY	C	Sample Number	Conc. (ppm) PY	C
1	50.39	54.95	10	73.85	79.51
2	51.12	55.96	11	80.60	83.67
3	51.31	56.30	12	80.08	85.35
4	51.17	55.85	13	52.50	58.41
5	51.89	57.35	14	54.03	58.02
6	48.84	56.53	15	53.94	57.90
7	79.44	81.15	16	53.93	59.98
8	79.52	81.85	17	53.80	59.63
9	80.96	83.30	18	53.51	59.20
			Average	61.16	65.83
			Ture Value	96.68	82.16

C.3 - 1

Untreated Soil Recovery Rate
Soil Contaminant : 100 ppm C

Sample Number	Conc. ppm
1	82.90
2	81.97
3	82.85
4	83.81
5	83.22
6	81.98
7	82.79
8	82.62
9	82.89
10	82.20
11	82.00
Average	82.66

C.3 - 2

Soil Contaminant : 100 ppm C
Titrant : 0.00477 N-Na2S2O3

Ozone Treatment Flow Rate : 144.21 ml/min = 8.65 L/hr
Ozone Treatment Time : 4 hours
Volume of KI Titrant : 2.8 ml [1:5 dilution]

Flow Rate of Ozone into KI Trap : 136.84 ml/min
Ozone Collection Time : 66 min
Titration-1st KI solution : 1.13 ml [1:50 dilution]
Titration-2nd KI solution : 3.58 ml

Ozone Flux : *(1) = 593.74 mg/hr
**(2) = 48.41 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : C - 82.66%

Sample Number	Conc. ppm
1	46.73
2	46.32
3	36.07
4	38.14
5	40.79
6	40.91
Average	41.49
Ture Value	50.20

C.3 - 3

Soil Contaminant :	100 ppm C		
Titrant :	0.00477 N-Na2S2O3		
Ozone Treatment Flow Rate :	144.74 ml/min	=	8.68 L/hr
Ozone Treatment Time :	2 hours		
Volume of KI Titrant :	3.82 ml		[1:25 dilution]
Flow Rate of Ozone into KI Trap :	142.11 ml/min		
Ozone Collection Time :	60 min		
Titration-1st KI solution :	6.28 ml		[1:50 dilution]
Titration-2nd KI solution :	1.93 ml		

Ozone Flux : *(1) = 558.30 mg/hr

**(2) = 250.12 mg/hr

*(1) based on ozone being 3.5 % in oxygen

**(2) based on empirical results

Soil Recovery Rate : C - 82.66%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	60.30	10	54.25
2	34.95	11	45.33
3	37.84	12	48.16
4	53.32	13	47.70
5	46.86	14	42.39
6	49.25	15	51.17
7	53.80	16	49.30
8	34.12	17	49.61
9	52.30	18	36.30
		Average	47.05
		Ture Value	56.92

C.3 - 4

Soil Contaminant : 100 ppm C
Titrant : 0.00477 N-Na2S2O3

Ozone Treatment Flow Rate : 149.47 ml/min = 8.97 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 0.48 ml [1:50 dilution]

Flow Rate of Ozone into KI Trap : 142.11 ml/min
Ozone Collection Time : 60 min
Titration-1st KI solution : 5.97 ml [1:50 dilution]
Titration-2nd KI solution : 2.15 ml

Ozone Flux : *(1) = 611.40 mg/hr
**(2) = 278.44 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : C - 82.66%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	52.99	10	53.47
2	54.09	11	58.01
3	53.58	12	57.55
4	53.27	13	54.61
5	65.53	14	54.01
6	52.46	15	56.99
7	62.22	16	53.50
8	55.06	17	52.32
9	57.93	18	53.53
		Average	55.62
		Ture Value	67.34

C.3 - 5

Soil Contaminant :	100 ppm C		
Titrant :	0.00477 N-Na2S2O3		
Ozone Treatment Flow Rate :	124.21 ml/min	=	7.45 L/hr
Ozone Treatment Time :	1 hours		
Volume of KI Titrant :	1.3 ml		[1:25 dilution]
Flow Rate of Ozone into KI Trap :	147.37 ml/min		
Ozone Collection Time :	56 min		
Titration-1st KI solution :	1.00 ml		[1:50 dilution]
Titration-2nd KI solution :	1.40 ml		

Ozone Flux : *(1) = 500.64 mg/hr
**(2) = 27.06 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : C - 82.66%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	64.73	10	48.70
2	64.96	11	48.14
3	65.04	12	43.66
4	65.05	13	38.89
5	65.56	14	39.58
6	65.35	15	38.14
7	48.41	16	39.28
8	45.52	17	37.82
9	37.81	18	40.51
		Average	49.84
		Ture Value	60.30

C.3 - 6

Soil Contaminant : 100 ppm C
Titrant : 0.00477 N-Na2S2O3

Ozone Treatment Flow Rate : 100 ml/min = 6.00 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 0.86 ml [1:10 dilution]

Flow Rate of Ozone into KI Trap : 140 ml/min
Ozone Collection Time : 63 min
Titration-1st KI solution : 1.15 ml [1:50 dilution]
Titration-2nd KI solution : 1.85 ml

Ozone Flux : *(1) = 411.84 mg/hr
**(2) = 32.88 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : C - 82.66%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	39.61	10	47.59
2	40.24	11	45.22
3	42.90	12	45.63
4	41.57	13	65.49
5	41.61	14	65.46
6	44.06	15	65.57
7	44.59	16	65.48
8	42.55	17	65.48
9	45.18	18	64.47
		Average	50.71
		Ture Value	61.34

C.3 - 7

Soil Contaminant : 100 ppm C
Titrant : 0.00477 N-Na2S2O3

Ozone Treatment Flow Rate : 82.37 ml/min = 4.94 L/hr
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 3.07 ml [1:1 dilution]

Flow Rate of Ozone into KI Trap : 142 ml/min
Ozone Collection Time : 60 min
Titration-1st KI solution : 6.27 ml [1:50 dilution]
Titration-2nd KI solution : 1.97 ml

Ozone Flux : *(1) = 339.08 mg/hr
**(2) = 165.76 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : C - 82.66%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	58.87	13	25.41
2	57.88	14	27.22
3	59.10	15	28.81
4	58.44	16	30.74
5	58.72	17	30.21
6	58.48	18	32.16
7	44.33	Average	29.09
8	42.57	**Ture Value	35.20
9	42.18		
10	42.07		
11	41.71		
12	42.36		
Average	50.56		
* Ture Value	61.16		

* 61.16% removal based on analysis of extracts from two thimbles (12 samples)
** 35.20% removal based on analysis of extracts from the 3rd thimble (6 samples)

C.4 - 1

Untreated Soil Recovery Rate
Soil Contaminant : 100 ppm PY

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	97.04	10	107.00
2	95.46	11	111.99
3	96.39	12	112.35
4	92.59	13	114.84
5	94.80	14	121.44
6	96.23	15	117.03
7	109.11	16	97.94
8	112.04	17	103.03
9	103.69	18	117.09
		Average	105.56

C.4 - 2

Soil Contaminant :	100 ppm PY		
Titrant :	0.00477 N-Na2S2O3		
Ozone Treatment Flow Rate :	142.11 ml/min	=	8.65 L/hr
Ozone Treatment Time :	4 hours		
Volume of KI Titrant :	1.03 ml		[1:1 dilution]
Flow Rate of Ozone into KI Trap :	142.11 ml/min		
Ozone Collection Time :	60 min		
Titration-1st KI solution :	5.10 ml		[1:50 dilution]
Titration-2nd KI solution :	1.94 ml		

Ozone Flux : *(1) = 597.89 mg/hr
**(2) = 237.84 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 105.56%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	10.26	10	9.57
2	10.38	11	9.61
3	10.12	12	9.60
4	9.90	13	10.43
5	10.50	14	10.22
6	9.97	15	9.77
7	9.43	16	9.75
8	9.21	17	9.72
9	9.79	18	9.66
		Average	9.88
		Ture Value	9.36

C.4 - 3

Soil Contaminant :	100 ppm PY		
Titrant :	0.00477 N-Na2S2O3		
Ozone Treatment Flow Rate :	140 ml/min	=	8.40 L/hr
Ozone Treatment Time :	1 hours		
Volume of KI Titrant :	0 ml		
Flow Rate of Ozone into KI Trap :	142.11 ml/min		
Ozone Collection Time :	60 min		
Titration-1st KI solution :	5.88 ml		[1:50 dilution]
Titration-2nd KI solution :	1.92 ml		

Ozone Flux : *(1) = 580.61 mg/hr
**(2) = 266.19 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 105.56%

Sample Number	Conc. ppm	Sample Number	Conc. ppm
1	13.53	10	19.20
2	7.41	11	18.37
3	13.48	12	22.05
4	10.36	13	23.73
5	13.70	14	24.34
6	11.78	15	23.45
7	14.53	16	24.51
8	17.08	17	23.38
9	18.50	18	24.97
		Average	18.02
		Ture Value	17.07

C.4 - 4

Soil Contaminant :	100 ppm PY		
Titrant :	0.00477 N-Na2S2O3		
Ozone Treatment Flow Rate :	75.97 ml/min	=	4.55 L/hr
Ozone Treatment Time :	1 hours		
Volume of KI Titrant :	0 ml		
Flow Rate of Ozone into KI Trap :	142.11 ml/min		
Ozone Collection Time :	60 min		
Titration-1st KI solution :	0.83 ml		[1:50 dilution]
Titration-2nd KI solution :	1.92 ml		

Ozone Flux : *(1) = 314.50 mg/hr
**(2) = 20.74 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 105.56%

Sample Number	Conc. ppm
1	23.33
2	23.08
3	23.24
4	20.61
5	20.76
6	20.32
7	22.65
8	23.26
9	22.97
Average	22.25
Ture Value	21.08

C.4 - 5

L/hr

Soil Contaminant : 100 ppm PY
Titrant : 0.00477 N-Na2S2O3

Ozone Treatment Flow Rate : 53.68 ml/min = 3.22
Ozone Treatment Time : 1 hours
Volume of KI Titrant : 0.38 ml [1:25 dilution]

Flow Rate of Ozone into KI Trap : 142.11 ml/min
Ozone Collection Time : 60 min
Titration-1st KI solution : 0.73 ml [1:50 dilution]
Titration-2nd KI solution : 1.60 ml

Ozone Flux : *(1) = 217.93 mg/hr
**(2) = 8.91 mg/hr
*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 105.56%

Sample Number	Conc. ppm
1	< DL
2	< DL
3	< DL
4	< DL
5	< DL
6	< DL
7	< DL
8	< DL
9	< DL
Average	< DL
Ture Value	< 5%

*** DL : Detection Limits

C.4 - 6

Soil Contaminant :	100	ppm PY	
Titrant :	0.00477	N-Na2S2O3	
Ozone Treatment Flow Rate :	28.68	ml/min =	1.72 L/hr
Ozone Treatment Time :	1	hours	
Volume of KI Titrant :	0	ml	
Flow Rate of Ozone into KI Trap :	142.11	ml/min	
Ozone Collection Time :	60	min	
Titration-1st KI solution :	0.93	ml	[1:50 dilution]
Titration-2nd KI solution :	1.77	ml	

Ozone Flux : *(1) = 118.89 mg/hr
**(2) = 8.79 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 105.56%

Sample Number	Conc. ppm
1	30.78
2	30.33
3	30.32
4	31.71
5	26.78
6	27.00
7	30.68
8	31.00
9	32.56
Average	30.13
Ture Value	28.54

C.4 - 7

Soil Contaminant :	100 ppm PY		
Titrant :	0.00477 N-Na2S2O3		
Ozone Treatment Flow Rate :	6.32 ml/min	=	0.38 L/hr
Ozone Treatment Time :	1 hours		
Volume of KI Titrant :	0 ml		
Flow Rate of Ozone into KI Trap :	142.11 ml/min		
Ozone Collection Time :	60 min		
Titration-1st KI solution :	0.67 ml		[1:50 dilution]
Titration-2nd KI solution :	2.02 ml		

Ozone Flux : *(1) = 26.27 mg/hr
**(2) = 1.40 mg/hr

*(1) based on ozone being 3.5 % in oxygen
**(2) based on empirical results

Soil Recovery Rate : PY - 105.56%

Sample Number	Conc. ppm
1	51.03
2	51.11
3	51.21
4	41.25
5	41.53
6	40.99
7	57.36
8	57.47
9	57.48
Average	49.94
Ture Value	47.31

APPENDIX D

Sample Calculation

D.1 Ozone Generated Percentage

Operation parameters:

Ozone generator pressure: 7.5 Psi

Ozone generator voltage : 80 volts

Ozone flow rate, Q: 140.5 ml/min

Run time: 60 min

Titrant: 0.00485N of $Na_2S_2O_3$

All titrations are performed using 50.0 ml of solutions.

In this experiment, two bottles of KI solution have been used in series. The first bottle had 400.0 ml KI solution, the contents of which were diluted 50 times for the titrations. The titrant volume was 12.47 ml. The second bottle had 200.0 ml KI solution; no dilution was required. The titrant volume was 1.95 ml.

$$\because \quad N_{Na_2S_2O_3} V_{Na_2S_2O_3} = N_{KI} V_{KI}$$

$$\Rightarrow \quad N_{KI,1} = 1.21 \times 10^{-3} \text{ meq/L}$$

$$N_{KI,2} = 1.89 \times 10^{-4} \text{ meq/L}$$

for 1N O_3 = 2N KI

$$\therefore \quad \text{number of moles}:$$

$$\frac{N_{KI,1} \text{ x dilution factor}}{2} \text{ x } V_1 + \frac{N_{KI,2} \text{ x dilution factor}}{2} \text{ x } V_2$$

$$= 12.12 \; m \; mole$$

and

$$M = \frac{mole}{Q \text{ x run time}}$$

$$= 1.44 \; m \; mole/L$$

Total gas (oxygen/ozone) moles:

$\because$ PV = nRT

where P = 1 atm

V = Q x Run Time = 8.43 L

R = 0.082 atm·L/mole·°K

T = 22°C = 295°K

$\therefore$ n = 348.59 m mole

Ozone percentage in oxygen (by mole):

$$\frac{\text{number of moles for ozone}}{\text{number of moles for total gas}} = 3.5\%$$

D.2 Ozone Flux Calculation For Data C.1-3

All titrations are conducted using 50 ml solution.

Titrant: 0.00485N of $Na_2S_2O_3$

Ozone being 3.5% in oxygen = 12.12 m mole/L

(a). Ozone Pass Through Impinger Line

Ozone flow rate, Q_1: 38.95 ml/min = 2.34 L/hr

Run time: 61 min

KI solution: 200 ml

Dilution factor: 25

Titrant volume: 0.63 ml

$$\because \quad N_{Na_2S_2O_3} V_{Na_2S_2O_3} = N_{KI} V_{KI}$$

$$\Rightarrow N_{KI} = 6.3 \times 10^{-5}$$

for 1N O_3 = 2N KI

$$\therefore \quad mole = \frac{N_{KI} \ x \ dilution \ factor}{2} \ x \ V$$

$$= 0.14 \ m \ mole$$

and

$$M_{imp} = \frac{mole}{Q_1 \ x \ run \ time}$$

$$= 0.06 \ m \ mole/L$$

(b). Ozone Pass Through Collecting Line

In all experiments, two gas wash bottles of KI solution have been used in series.

Ozone flow rate, Q_2: 156.67 ml/min

Run time: 59 min

First gas wash bottle:

KI solution: 400 ml

Dilution factor: 50

Titrant volume: 7.93 ml

Second gas wash bottle:

KI solution: 200 ml

Dilution fold: 1

Titrant volume: 1.47 ml

$$\because \quad N_{Na_2S_2O_3} V_{Na_2S_2O_3} = N_{KI} V_{KI}$$

$$\Rightarrow N_{KI,1} = 6.3\text{x}10^{-5} \text{ meq/L}$$

$$N_{KI,2} = 1.89\text{x}10^{-4} \text{ meq/L}$$

for 1N O_3 = 2N KI

$$\therefore \quad number\ of\ moles:$$

$$\frac{N_{KI,1}\ x\ dilution\ factor}{2}\ x\ V_1 + \frac{N_{KI,2}\ x\ dilution\ factor}{2}\ x\ V_2$$

$$= 7.11\ m\ mole$$

and

$$M_{col} = \frac{mole}{Q_2\ x\ run\ time}$$

$$= 0.77\ m\ mole/L$$

(c). Ozone Flux

(1). based on ozone being 3.5% in oxygen

$$F = (M_{3.5\%} - M_{imp}) \frac{m\ mole}{L} \times Q_1 \frac{L}{hr} \times 48 \frac{mg}{m\ mole}$$

$$= 155 \frac{mg}{hr}$$

(2). based on empirical result

$$F = (M_{col} - M_{imp}) \frac{m\ mole}{L} \times Q_1 \frac{L}{hr} \times 48 \frac{mg}{m\ mole}$$

$$= 80 \frac{mg}{hr}$$