THE FATE OF TWO PRIORITY POLLUTANTS 2,4-DINITROPHENOL AND PHENANTHRENE, IN THE AQUATIC ENVIRONMENT WHEN EXPOSED TO ULTRAVIOLET RADIATION AT VARIOUS pH VALUES

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CHAPTER I

INTRODUCTION

A June 7, 1978 court settlement involving EPA and several environmentally concerned plaintiffs has become commonly known as the "EPA Consent Decree." These environmental groups brought suits against the EPA for failing to implement portions of the Federal Water Pollution Control Act. One result of this suit required EPA to publish a list of toxic pollutants for which technology-based effluent limitations and guidelines would be required (1). This list of toxic pollutants has become known as the priority pollutants' list and consists of 129 individual compounds.

The Office of Water Planning and Standards of the U.S. Environmental Protection Agency (EPA) is conducting a program to evaluate exposure and subsequent risk from the presence of toxic pollutants in this nation's environment (2). This program addresses the goals of the Clean Water Act of 1977. In this program, the most important component is the discussion of the environmental fate processes, especially, the environmental fate processes of the priority pollutants.

Today there is a world-wide shortage of clean safe water supplies. Contaminants are entering the receiving stream from domestic, industrial, and agricultural compounds including organic pesticides as well as aromatic, aliphatic and halogenated hydrocarbons. The presence of these refractory compounds in natural water presents a problem to those concerned with public health and the provision of safe drinking water. Because of the toxicity of many of these compounds and their tendency to accumulate in fish body fat, it is plausible that long term ingestion of these substances could lead to adverse effects in humans. Thus, the fate of these compounds in aquatic systems and the removal of these compounds from water supplies are of immediate interest.

The impact of these compounds on aquatic life and human health gives cause to study the water-related environmental fate and the removal of these compounds from water. There are a number of physical, chemical and biological processes that may be important in affecting the concentration of a chemical in an aquatic system. These processes include photolysis, hydrolysis, volatilization, biodegradation, bioaccumulation, and adsorption.

The purpose of this study is to investigate the potential for photochemical degradation of 2,4-dinitrophenol and phenanthrene in aquatic systems. The effect of pH upon photolyisis rate is also determined. These two compounds are refractory compounds and are listed as priority pollutants.

CHAPTER II

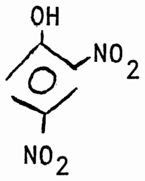
LITERATURE REVIEW

2,4-Dinitrophenol

Phenolic compounds have been noted to effect the taste of domestic water supplies and cause diseases (3). Current government standards for phenolic compounds in terms of phenol are limited to 0.0001 parts per million for public water supplies (4). 2,4-Dinitrophenol is a toxic phenolic compound, which causes skin irradiation (5), and symptoms of poisoning including fever, increased perspiration, and gastric distress.

2,4-Dinitrophenol also acts as an uncoupler of oxidative phosphorylation. Because of its ability to uncouple oxidation phosphorylation, 2,4-dinitrophenol can be used as a pesticide causing an increase in the rate of respiration resulting in death from metabolic exhaustion. 2,4-Dinitrophenol also is used in the organic synthesis of dyes and other organic compounds, such as amidol, and as a wood preservative (5).

The chemical structure of 2,4-dinitrophenol is shown below and its physical properties are listed in Table I (2), and its biological properties are listed in Table II.



2,4-Dinitrophenol

Alternate Name
Aldifen
2,4-DNP

TABLE I

PHYSICAL PROPERTIES OF 2,4-DINITROPHENOL

Property	Value
Molecular weight	184.11
Melting point	114
Boiling point	No data found
Vapor pressure	No data found
Solubility in water at 18°C	5,600 mg/L
Log octanol/water partition coefficient (4)	1.53
pKa	4.09

TABLE II

BIOLOGICAL PROPERTIES OF 2,4-DINITROPHENOL (6)

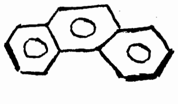
Property	Value
Biodegradable	99.9% treatment achieved

Phenanthrene

Polynuclear aromatic hydrocarbons are widespread contaminants of the environment, occurring primarily as a result of combustion (vehicle exhaust--especially diesel) and pyrolysis of organic materials (7). They may occur naturally in coal, graphite, and roots from forest fires or may be derived from man-made sources such as carbon blacks, fossil fuel derived soots, activated carbon (8). These compounds have been detected in animal and plant tissue, sediment, soil, air, and surface water (5). Rain fall may have the effect of returning these polymeric carbons to the aquatic system. Concern over the prevalence of polynuclear aromatic hydrocarbons results from the evidence that a significant number of these compounds are known to be carcinogenic (7).

Phenanthrene is a toxic chemical suspected of being a carcinogenic agent. The lowest published toxic concentration is 1350 mg/kg (9). In a study by Shachelford and Keith, this compound was identified 12 times (10) (four times in effluents from a chemical plant, five times in a river, two times in the effluent of wood preserving plants, and has also been identified in finished drinking water) (4). Phenanthrene is used in dye stuffs, explosives, and the synthesis of drugs (8).

The chemical structure for phenanthrene is shown below and its physical and biological properties are listed in Table III.



Phenanthrene

Alternate Name

Phenanthrin

TABLE III

PHYSICAL, CHEMICAL, AND BIOLOGICAL PROPERTIES OF PHENANTHRENE

Property	Value
mol. wt.	178.2
mp., ^{o}C	101
b.p. (760 torr)	340^{o}C
Vapor pressure	20^{o}C
Solubility in water (25^{o}C)	1.29 mg/L
Log octanol/water partition coefficient	4.46
Biodegradability	98.2% treatment achieved (6)

Ultra-Violet Light

Sun light between the wavelengths of 280 and 320 nm is termed UV-B radiation and is responsible for causing sunburn, fading fabric and the direct photolysis of many pollutants. The intensity of UV-B radiation, as with all solar radiation, decreases with decreasing angular height of the sun. In other words, intensity decreases from midday to sunset, summer to winter, and the tropics to higher latitudes. It should be noted, however, that the intensity reduction of UV-B radiation experienced as one moves away from the equator is more pronounced than for UV-A or visible (320-400 nm) solar radiation. The ozone layer of the upper atmosphere is the main reason for the sharp intensity decrease of the UV-B radiation. The ozone layer so effectively absorbs UV-8 radiation that virtually no radiation of a wavelength less than 295 nm penetrates it

(11). At the mean solar distance, solar energy emits about 0.14 W/cm^2. However, only about two-thirds of this energy reaches the earth's surface.

Fundamentals of Photochemical Process

Photochemical reactions are initiated by the absorbance of electromagnetic radiation energy by an atom or molecule which is then elevated to a higher energy level. The resulting species is unstable at this new level and by a deactivation process it reverts to a lower, less energetic, and more stable state. This deactivation is known as the primary photochemical process, and can be achieved by any of several mechanisms. Two possible mechanisms for deactivation are for the higher energy molecule to either rid itself of the energy by loss of an atom or radical, or to break energy bonds between elements (12).

A number of different photochemical processes may account for the transformation of pollutants in the aquatic environment. Two broad classes of photochemical reactions are direct and indirect (sensitized) photolysis. Direct photolysis involves direct absorption of light by the pollutant followed by chemical reaction. Indirect photolysis involves the presence of a carrier compound to capture light energy and transfer it to the compound undergoing photooxidation. For a chemical dissolved in pure water, direct photolysis is the only mechanism, for photochemical transformation (13).

Absorption of Light

Light incident upon a system can be transmitted, reflected, scattered, refracted, absorbed, or be subjected to any combination of these processes. In 1818 Grotthuss and Draper (14) pointed out that only light which is absorbed can be effective in producing a photochemical change. In order for light to be effective in producing photochemical transformation, not only must the photon be absorbed, it must possess sufficient energy to initiate the reaction. This is considered to be the first law of photochemistry (14).

Photolysis of 2,4-Dinitrophenol

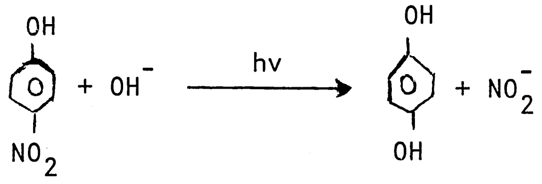
Investigations of the photolysis of dinitrophenols were described as early as 1935 (15) when the effect of ultraviolet light on dinitrophenol was examined. Dinitrophenols appear to be stable in acid solution, but are susceptible to decomposition by ultraviolet light in alkaline solution (16).

2,4-Dinitrophenol is a moderately acidic substance pKa = 4.09 (17), and will exist substantially as an anion in environmental surface waters (5). The ultraviolet absorption spectrum of 2,4-dinitrophenol in methanol exhibits a maximum at about 290 nm which extends out beyond 400 nm (18). All sunlight which reaches the surface of the earth falls within 2,4-dinitrophenol's absorption spectrum.

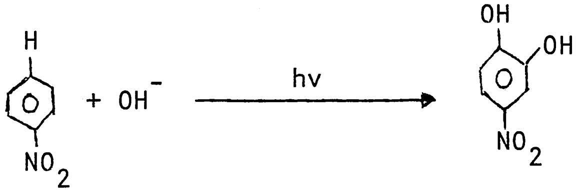
Nakawa and Grosby (19) reported that 4-nitrophenol, at a concentration of 200 mg/L, was degraded in aqueous solution within a period of 1-2 months when it was exposed to sunlight. The principle products were hydroquinone and 4-nitrocatechol. A dark, acidic intractable polymer was also produced (5).

The photoreaction mechanism proposed is as follows:

(1)

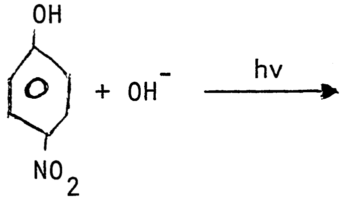


(2)



(4-nitrocatechol)

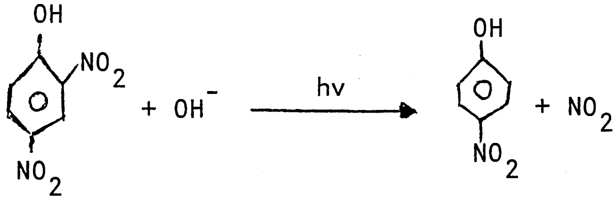
(3)



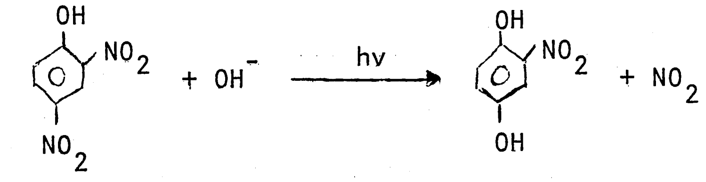
A dark, acidic intractable polymer

Although no specific information was found in the reviewed literature demonstrating that 2,4-dinitrophenol would also be photochemically hydroxylated, one could assume, based on the information gathered by Suarez and Güther (30) and Nakagawa and Grosby (19) that under similar conditions, 2,4-dinitrophenol could be degraded to a mixture of compounds which include 4-nitrophenol, 2-nitrohydroquinone, and 3,5-dinitrocatechol (5).

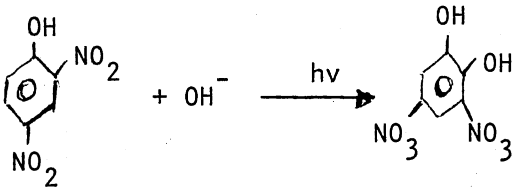
(1)



(4-nitrophenol)

(2) 

(2-nitrohydroquinone)

(3) 

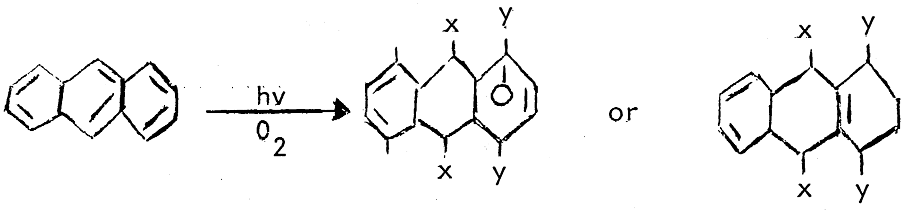
(3,5-dinitrocatechol)

Photolysis of Phenanthrene

Polycyclic aromatic hydrocarbons absorb solar radiation strongly at wavelengths above 300 nm, and may, therefore, undergo photochemical reaction (21). In general, the behavior of all unsaturated organic molecules in the presence of molecular oxygen and irradiated by sunlight or ultraviolet light may be represented by the reaction (22) $M \xrightarrow[O_2]{s(hv)} MO_2$. The sensitizer, s, absorbs the incident radiation but remains chemically unchanged. In addition, molecular oxygen is excited to a singlet state by the transfer of energy from the sensitizer. This singlet oxygen is the oxidant (22). However, the organic compounds like anthracene, naphthalene, phenanthrene and their derivatives are capable of acting as the sensitizer in a process of autoperioxidation. Expected reaction products in the photylysis of polycyclic aromatic hydrocarbons are peroxides, hyperoxides (22) and quinones (5).

Anthracene and its derivatives undergo photo-oxygenation involving singlet oxygen with the formation of 1,4- and/or 9, 10-cyclic peroxides

(23).



1,4 cyclic peroxides

9,10 cyclic peroxides

The position of attack by the oxygen is dependent on the nature of the substituents x and y.

Southworth (23) observed that anthracene in distilled water and rapidly degraded under exposure to natural light with a photolysis half-life of about 35 minutes under a midday sunlight in midsummer at 35°C.

No information specific of the photolysis of phenanthrene was found. However, it might be inferred from the behavior of other polycyclic aromatic hydrocarbons that undergo autoperoxidation using singlet oxygen as an oxidant that the resulting endproducts from the photolysis of phenanthrene could be quinones or cyclic peroxides.

CHAPTER III

MATERIALS AND METHODS

Solution Preparation

2,4-Dinitrophenol (powder) was dissolved in distilled water, and made up to a concentration of 100 mg/L. The pH of the solution was adjusted to 3.5, 7, 11 and 13 with HCl, $CaCO_3$ or NaOH.

One thousand milligrams of phenanthrene (powder) was dissolved in 100 ml of benzene. This was done because phenanthrene is very difficult to dissolve in distilled water and much of the benzene was probably stripped out during the mixing process. One ml of this solution was then dissolved in 1000 ml of distilled water. This produced a phenanthrene concentration of 1 mg/L. The pH of the solution was adjusted to 3.5, 7 and 12 with HCl, $CaCO_3$ or NaOH.

Photolysis Experiments

Several photolysis experiments were conducted on both compounds at various pH values using a U.V. lamp and sunlight as energy sources. The U.V. lamp utilized was a model UVL-56 long wave, 366 nm, 115 volt lamp produced by Ultra-Violet Products, Inc. Samples having U.V. light as an energy source were subjected to light 24 hours per day. Tables IV and V give the dates of the experimental periods, the frequency at which samples were taken within the experimental period, the pH of the sample

TABLE IV

THE DATES OF STUDYING ON 2,4-DINITROPHENOL

Date	pH	Energy Source	Frequency of Sampling
October to November, 1981	3.5, 7, 11	UV light	2 months
November to December, 1981	13	UV light	4,10,15, and 20 days
April to May, 1982	3.5, 7, 11 and 13	Sunlight	2,4,6, and 8 weeks

TABLE V

THE DATES OF STUDYING ON PHENANTHRENE

Date	pH	Energy Source	Frequency of Sampling
November, 1981	7	Sunlight	1,2,3,4 weeks
April, 1982	3.5, 7, 12	Sunlight	1,2,3 and 4 weeks
April, 1982	7	UV light	1,2,3,5,10,15 and 20 days
June, 1982	3.5, 7, 12	Sunlight	1,2,4, and 6 days

and the source of radiation used for the experiments for 2,4-dinitrophenol. The test conditions and sampling schedules for all of the experiments conducted for phenanthrene are presented in Table V.

For the photolysis experiments conducted over the period of October to December for both 2,4-dinitrophenol and phananthrene, 500 ml of a pH adjusted solution were placed in glass quart jars with a screw cap. The jars were then subjected to either UV light or sunlight. During the period of April to May for 2,4-dinitrophenol and for phenanthrene 1000 ml aliquots of pH adjusted sample were placed in 1000 ml pyrex borosilicate glass Erlenmeryer flasks. These flasks filter sunlight below 240 nm. Since the solar cutoff is approximately 300 nm the utilization of this material for reaction was appropriate.

Control samples were prepared in exactly the same manner as the test samples relative to compound concentrations, pH condition and type of sample container but were kept in the dark for the duration of the experiment.

Experimental Procedures

Test and control samples were extracted with methylene chloride using the procedure found in the Federal Register, Proposed Rules (1).

For phenanthrene, which is classified as a base extractable, the pH of the solution was adjusted to 11 or higher, prior to extraction. For 2,4-dinitrophenol, which belongs to the acid extractable group, the pH of the solution was adjusted to 2 or lower, prior to extraction.

60 ml of methylene chloride was transferred into a separatory funnel containing 1000 ml of sample. The sample was extracted by shaking the funnel for two minutes with periodic venting to release excess vapor

pressure. The methylene chloride layer was then collected in a 250-ml Erlenmeyer flask. The sample was extracted two additional times with 60 ml aliquots of methylene chloride. The methylene chloride extracts were combined and dried over sodium sulfate. This extract was then concentrated using a 500 ml Kuderna Danish flask equipped with a 10 ml concentration tube. The apparatus was placed over a warm water bath (60°C to 65°C) so that the concentrator tube was partially immersed in the water, and the entire lower rounded surface of the flask was bathed with water vapor. After concentrating the extract, the concentrator tube was removed from the Kuderna Danish apparatus. The volume of extract was adjusted to 5 ml (2,4-dinitrophenol) or 1 ml (phenanthrene) and was transferred to sample tubes.

Gas Chromatography Analysis

For the first test, a Hewlett Packard 76000A Chromatography System, utilizing a flame ionization detector was used to analyze samples. For 2,4-dinitrophenol, an acid column (SP-1240) was used. The oven temperature was 90°C and the final temperature was 200°C. The temperature of the detector was 250°C, while the temperature of the injection port was 170°C. For the phenanthrene, a base column (SP-2250) was utilized. An oven temperature program having an initial temperature of 90°C and final temperature 260°C were used. The temperature of the detector was 250°C, while the temperature of injection part was 170°C.

Near the end of the study, a SIGMA 15 Chromatography Chromatogram System from PERKIN-ELMER was used to analyze samples. The operational conditions were similar to those used with the Hewlett-Packard GC.

CHAPTER IV

RESULTS AND DISCUSSIONS

2,4-Dinitrophenol

Control

Control samples were treated exactly as the test samples (relative to the condition of pH and time) except with respect to irradiation by light.

From the results of Gas Chromatography analysis, it was found that all the control samples had almost the same percentage of recovery regardless of the pH or duration of the test. Therefore, the percentage of recovery of 2,4-dinitrophenol was not effected by pH or test duration.

The percentage of recovery was in the range of 90 to 95.

2,4-Dinitrophenol, C_o = 100 mg/L, pH = 13, UV Lamp as Light Source

In this study, the pH of the solution of 2,4-dinitrophenol was adjusted to 13 with NaOH. The data showing remainig 2,4-dinitrophenol concentration and percentage reduction vs. irradiation time are presented in Table VI, Figure 1 and Figure 2. It was found that 2,4-dinitrophenol was reduced from a concentration of 100 mg/L to 96 mg/L, after 4 days of irradiation. After irradiation for 10 days, the Gas Chromatography

TABLE VI

2,4-DINITROPHENOL, C_o = 100 MG/L, pH = 13, UV LAMP AS LIGHT SOURCE

Irradiation Time Day	Remaining Concentration mg/L	% Reduction
4	96	4
10	88	12
15	66	34
20	0	100

Figure 1. Photolysis of 2,4-Dinitrophenol; Concentration Versus Time; pH = 13; UV Lamp as Light Source

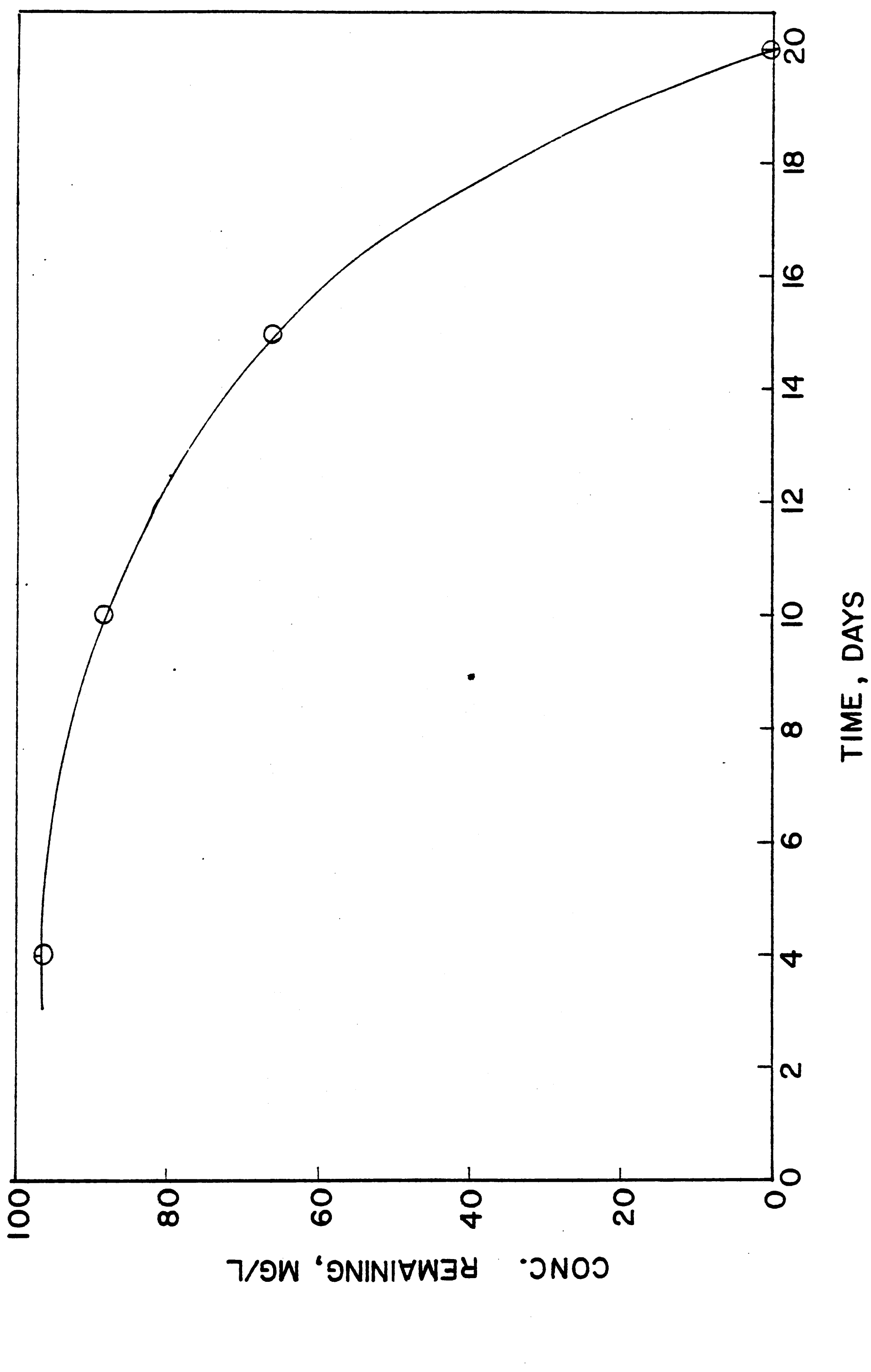
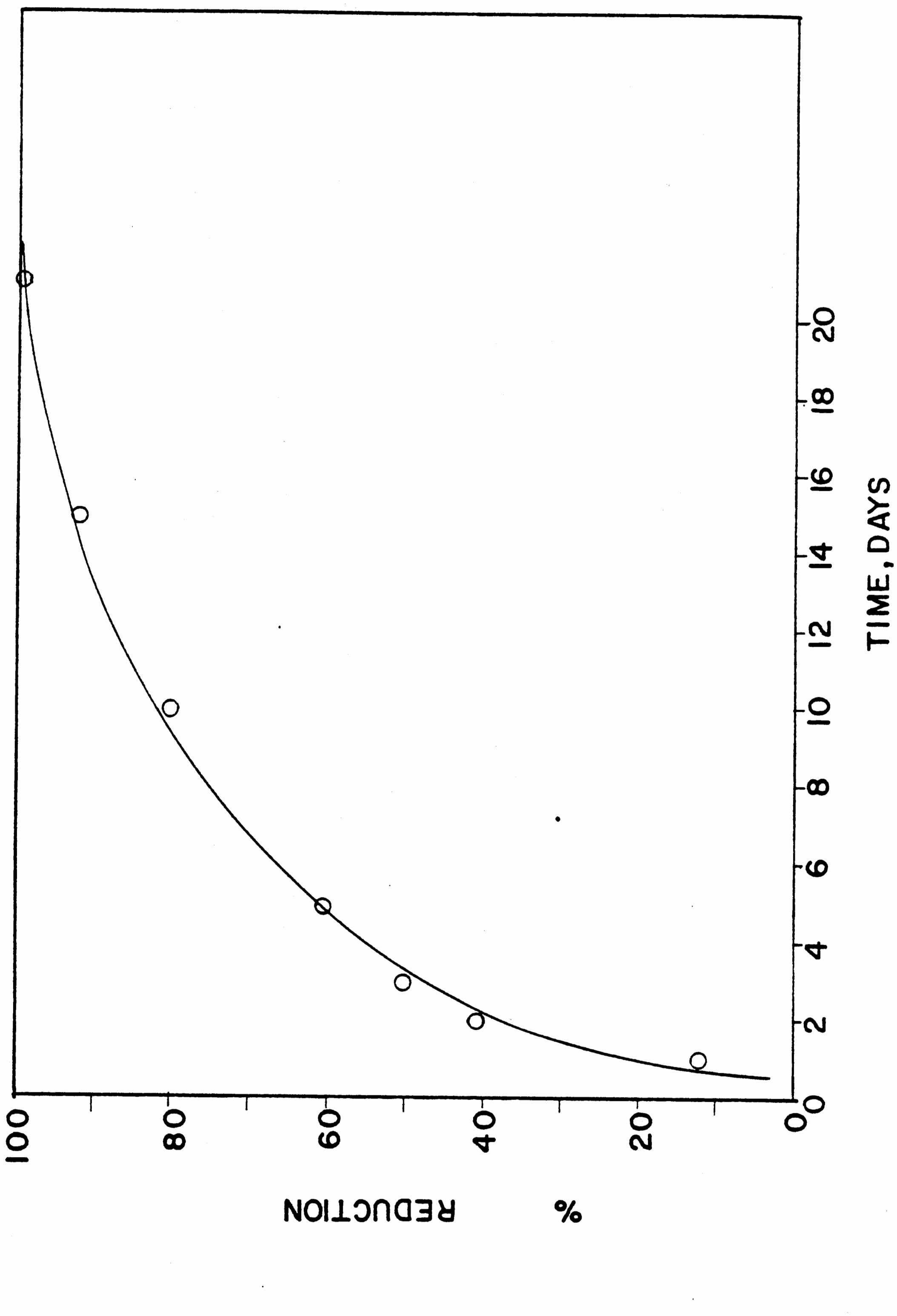

CONC. REMAINING, MG/L
100
80
60
40
20
0
TIME, DAYS
0
2
4
6
8
10
12
14
16
18
20

Figure 2. Photolysis of 2,4-Dinitrophenol; % Reduction Versus Time; pH = 13; UV Lamp as Light Source


% REDUCTION
0
20
40
60
80
100
TIME, DAYS
0
2
4
6
8
10
12
14
16
18
20

Chromatogram showed two small peaks: (one at retention time 1.6 minutes and another at retention time 6.3 minutes), while 88% of the 2,4-Dinitrophenol remained (retention time 13.7 minutes) (Figure 3). After 20 days of irradiation, the Gas Chromatography Chromatogram showed no peak for 2,4-Dinitrophenol (retention time 13.7 minutes), but one small peak at retention time 3.7 minutes, Figure 4. It can be seen that after 20 days of irradiation, 2,4-Dinitrophenol was reduced from 100 mg/L to less than 0.1 mg/L.

The presence of unknown peaks on the GC Chromatogram for the ten and twenty day samples indicated that 2,4-Dinitrophenol was converted to other methylene chloride extractable compounds probably of lower molecular weight. It should be noted that these unknown peaks did not appear for the control samples.

In the literature reviewed, 2,4-Dinitrophenol in the presence UV irradiation and at high pH was suspected to be converted to 4-nitrophenol or 2-nitrohydroquinone (30). Since both of these compounds have lower molecular weight than 2,4-Dinitrophenol they might have resulted in the additional peaks found on the 10 day and 20 day GC Chromatogram.

The rate of reduction of many chemicals $(-\frac{dc}{dt})$ by direct photochemical processes may be expressed by simple first order kinetic expressions. An equation for direct photolysis is $-\frac{dc}{dt} = K[c] = Ka\ \phi\ [c]$. Where K is a first order rate constant, ϕ is the reaction quantum yield, and Ka is a rate constant for absorption of light by the chemical.

The equation $-\frac{dc}{dt} = K[c]$ can be derived to give $\ln C/C_o = -Kt$. Curves were plotted for $-\ln C/C_o$ vs. Kt. Slopes of these curves indicated a rate of reduction constant, K. Half-life was represented as $T_{\frac{1}{2}} = \frac{0.093}{K}$.

Figure 3. Gas Chromatogram for Analyses of 2,4-Dinitrophenol After Exposure to 10 Days of Irradiation

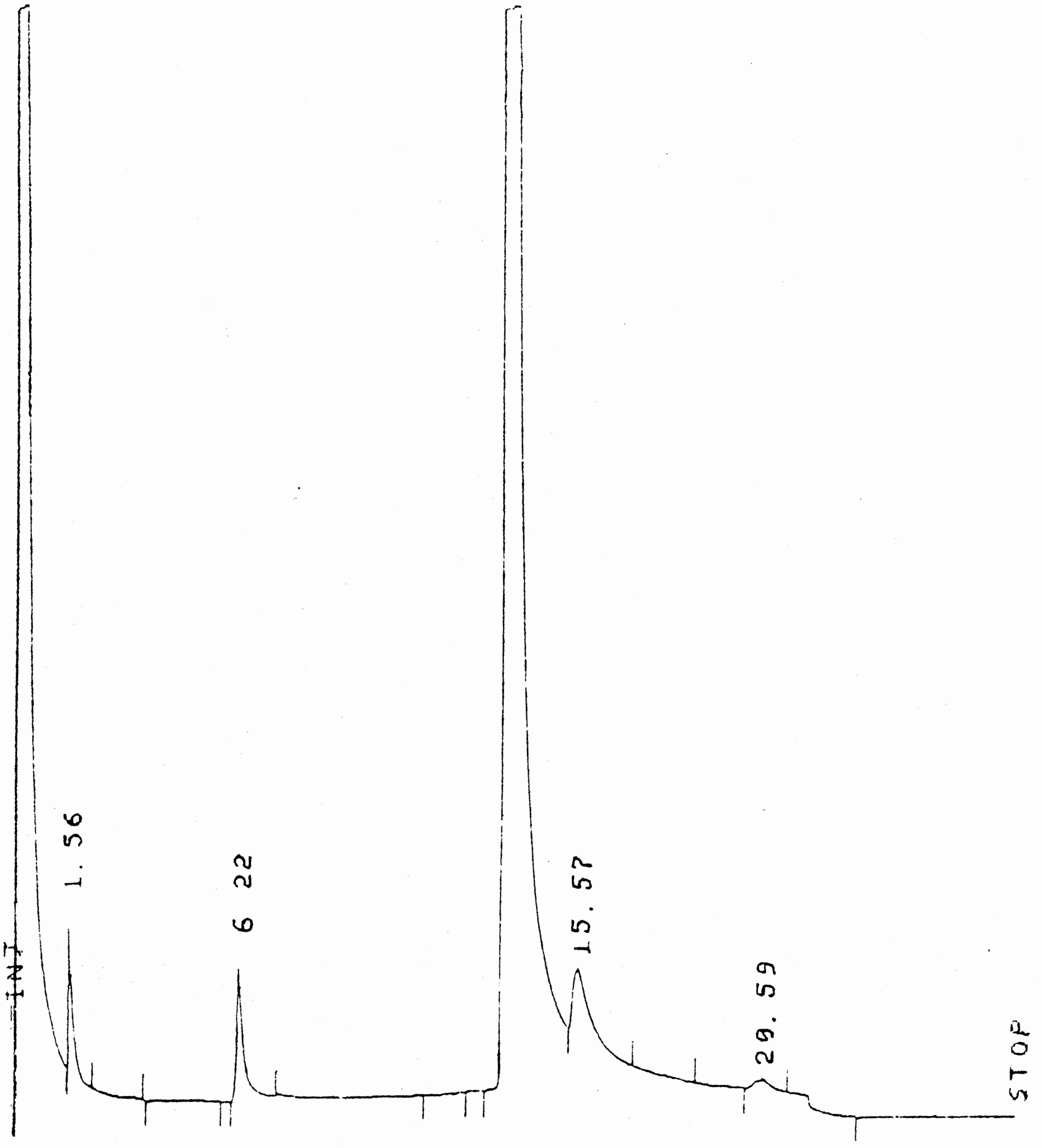
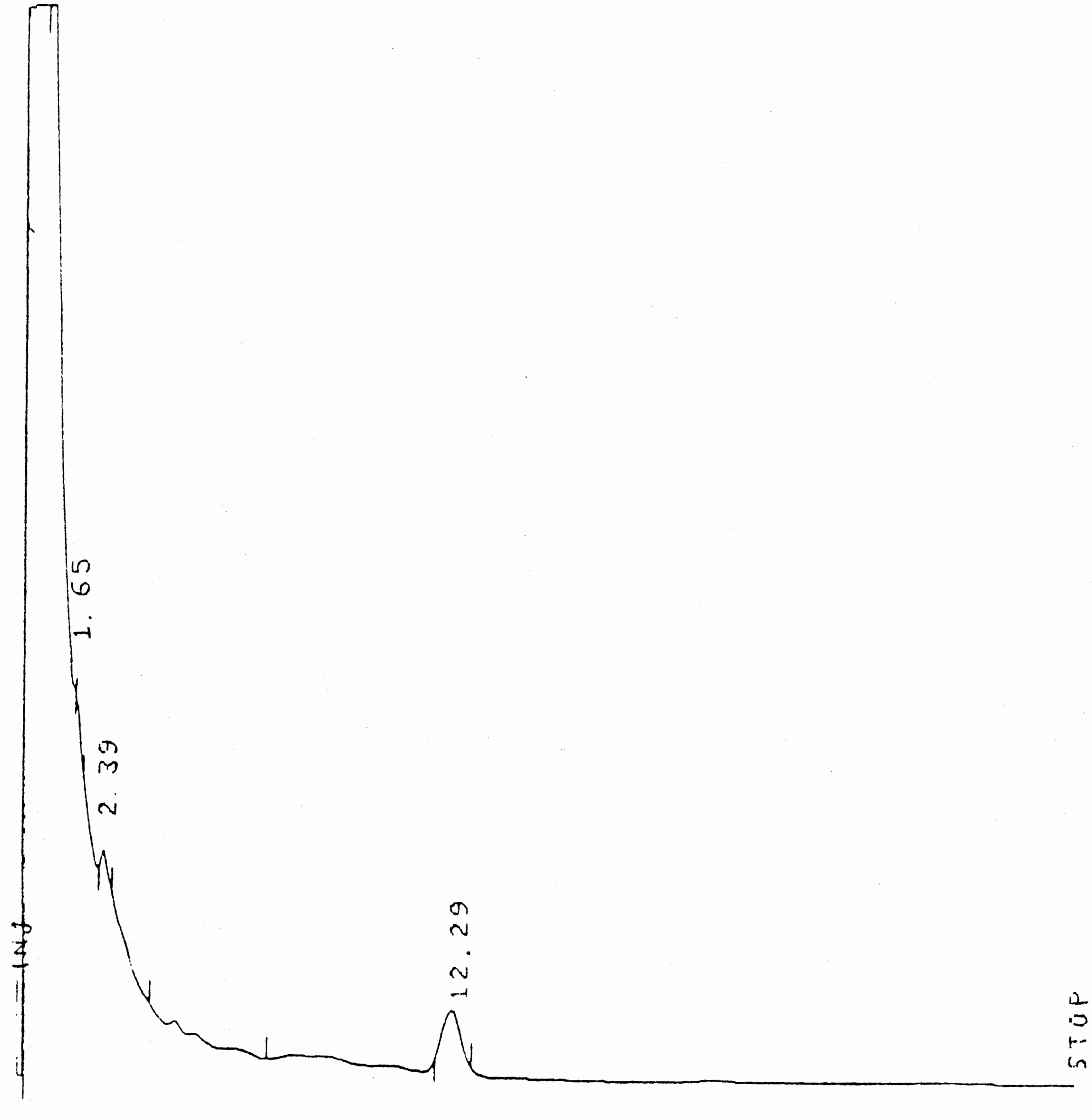

INJ
1.56
6 22
15.57
29.59
STOP

Figure 4. Gas Chromatogram for 2,4-Dinitrophenol After Exposure to 20 Days of Irradiation


INJ
1.65
2.39
12.29
STOP

After the data were plotted using equation $\ln C/C_o = -Kt$ a reasonable fit to a straight line could not be made (Figure 5). However, the same data were plotted for reduction rate $(\frac{C_o - C}{C_o})$ vs irradiation time on semilog graph paper, Figure 6. The data fit a straight line plot quite well indicating that the first order decreasing equation $dc/dt = -K(C_o - C)$, which is the differentiated form of $\ln \frac{C_o - C}{C_o} = Kt$, describes this photolytic reaction. From Figure 6, it can be seen that $K = 0.2$ Day^{-1}. The half-life is 3.5 days.

A possible reason for 2,4-Dinitrophenol being degraded in such a way might be that some endproducts from 2,4-Dinitrophenol decomposition absorbed much more energy from light and was able to transfer this energy to 2,4-Dinitrophenol. In other words, the breakdown products may act as sensitizers which have the effect of increasing, further, the photolysis of 2,4-Dinitrophenol.

2,4-Dinitrophenol C_o = 100 mg/L, pH 3.5, pH 7, pH 11 and pH 13. Sunlight as Light Source, Exposure Period During April to May, 1982

In this study, pH of solutions of 2,4-Dinitrophenol were adjusted to 3.5, 7, 11 and 13. Irradiation times were from 2 weeks to 2 months. After two months of irradiation and at pH 13, the 2,4-Dinitrophenol concentration was reduced by 14 or 15 percent. This result may, at first, seem inconsistent, when compared to the study using the UV lamp as light source (20 days of continuous irradiation) where the 2,4-Dinitrophenol concentration was reduced to less than 0.1 mg/L (about 99 percent reduction). A possible reason for this discrepancy might be that the intensity of the UV lamp for this study is much higher than the intensity of

Figure 5. Determination of a Kinetic Expression to Describe the Photolysis of 2,4-Dinitrophenol; ln C/C_O Versus Time; pH = 13; UV Lamp as Light Source

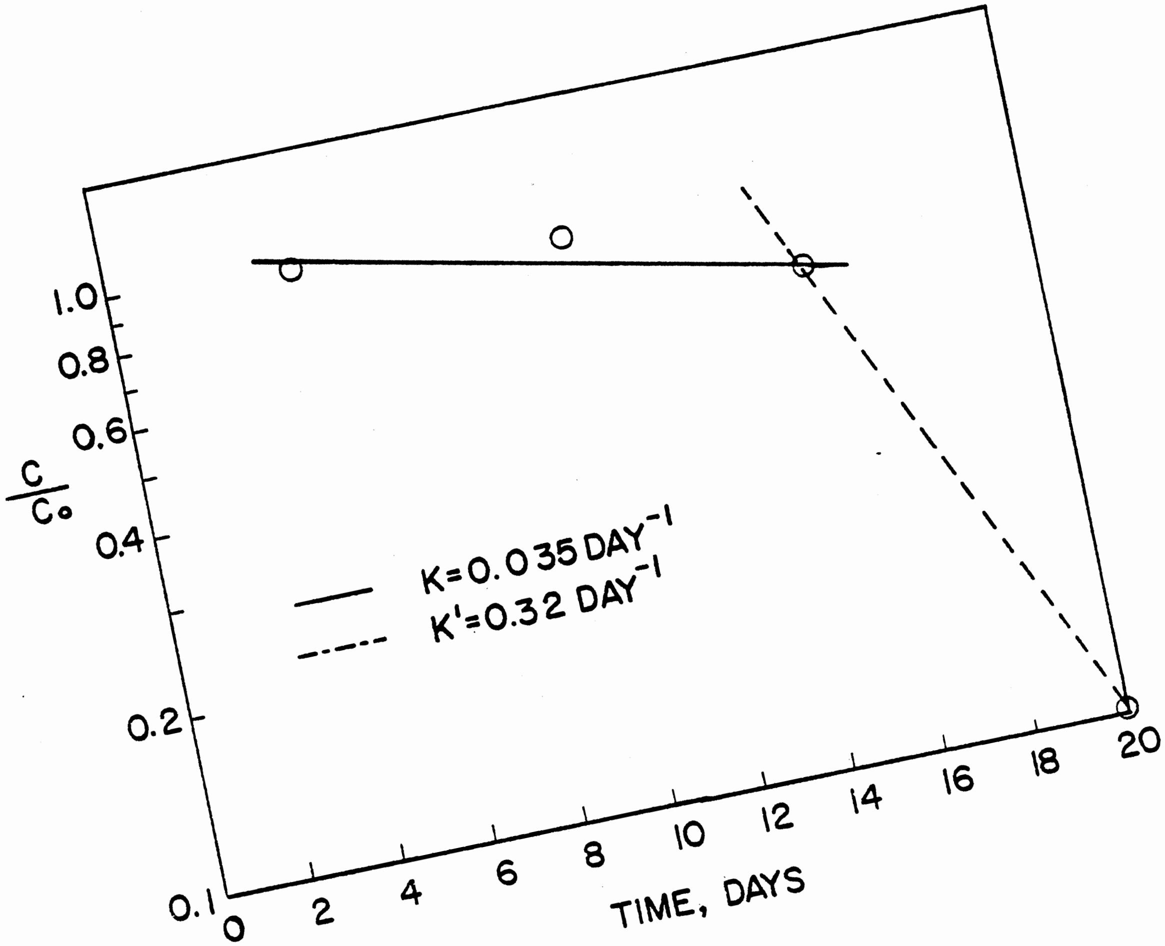
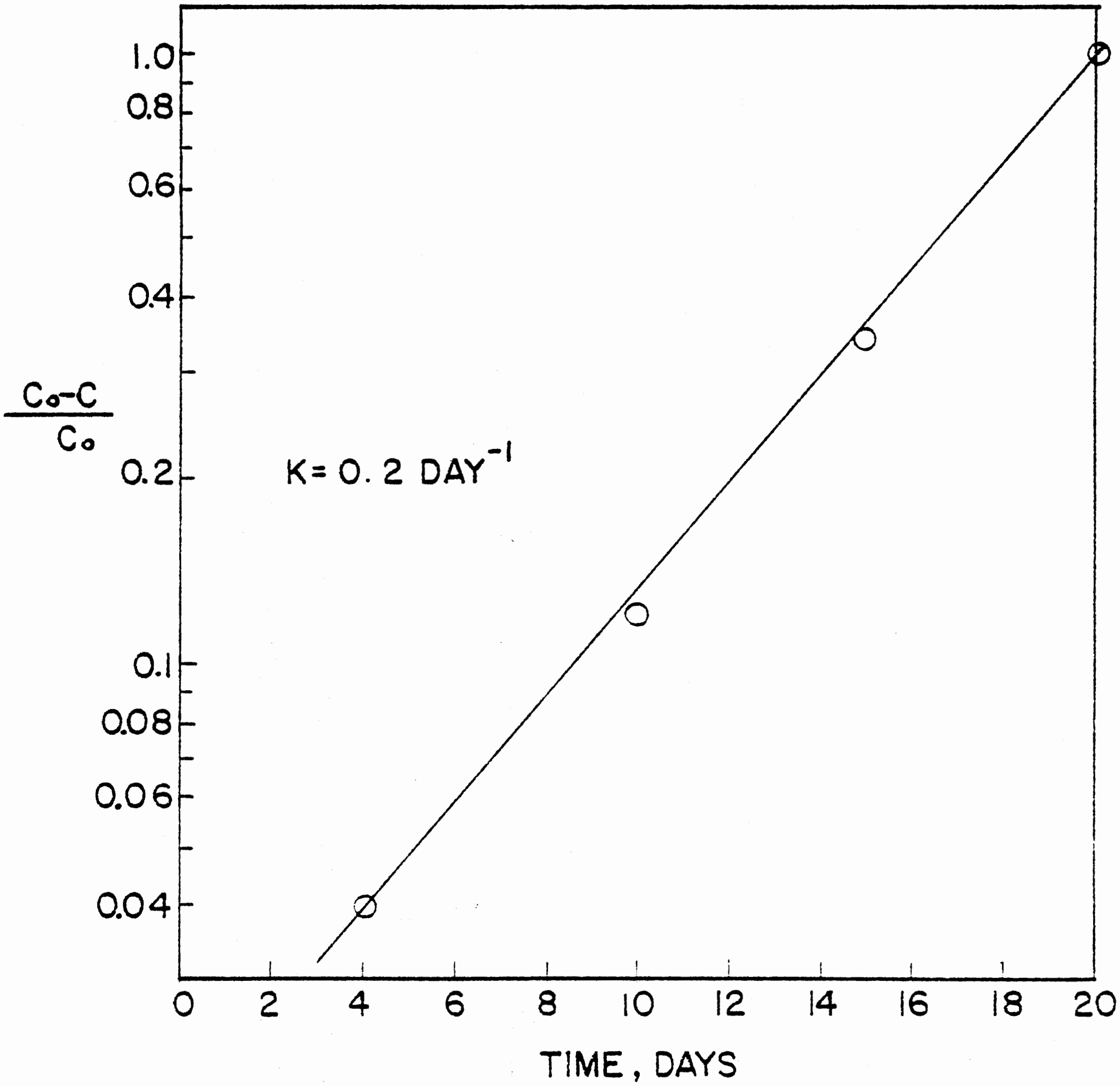

C/Co
1.0
0.8
0.6
0.4
0.2
0.1
0
2
4
6
8
10
12
14
16
18
20
TIME, DAYS
K=0.035 DAY^{-1}
K'=0.32 DAY^{-1}

Figure 6. Determination of a Kinetic Expression to Describe the Photolysis of 2,4-Dinitrophenol; $\ln \frac{C_o - C}{C_o}$ Versus Time; pH = 13; UV Lamp as Light Source


1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
$\frac{C_o - C}{C_o}$
$K = 0.2\ DAY^{-1}$
0
2
4
6
8
10
12
14
16
18
20
TIME, DAYS

sunlight in the spring season.

For all other conditions of pH, 2,4-DNP concentrations were not reduced at all by sunlight even after 2 months of irradiation.

The data showing remaining 2,4-DNP concentration and percentage reduction vs irradiation time are presented in Table VII. Plots of remaining 2,4-DNP concentration vs irradiation time are shown in Figure 7 while the curve of percentage reduction vs irradiation time is shown in Figure 8. The curve ln C/C_o vs time is shown in Figure 9. From that curve, the slope is presented as a reduction rate constant. The reduction rate constant was 0.023 day^{-1}, and the half-life ($T_{\frac{1}{2}}$) was 35 days. When ln $\frac{C_o - C}{C_o}$ was plotted vs time, as shown in Figure 10, the reduction rate constant was found to be 0.023 day^{-1}, which happens to be the same reduction rate constant calculated when ln C/C_o was plotted vs time.

For all the conditions of pH tested and for both the UV lamp and sunlight, 2,4-DNP photolysis was only found to occur at pH 13. One possible explanation might be that for photodegradation of 2,4-DNP to occur, there must be a displacement of the nitro group by a hydroxy group (16). Therefore, the hydroxyl radicals play an important role in this photolysis and the concentration of OH is a critical factor. From these results, it appears that only at a pH of 13 is the hydroxyl concentration sufficient to permit the photolysis of 2,4-Dinitrophenol.

Phenanthrene

Control

Control samples were treated exactly as the test samples (relative to the condition of pH and time) except with respect to irradiation by light.

TABLE VII

2,4-DINITROPHENOL pH 3.5, 7, 11 and 13 SUNLIGHT AS ENERGY, EXPOSURE PERIOD DURING APRIL AND MAY, 1982

Irradiation Time Week	Final Conc. mg/L pH 3.5	pH 7	pH 11	pH 13
2	100	100	100	97.5
3	100	100	100	94, 92*
4	100	100	100	90.5
6	100	100	100	90
8	100	100	100	86, 85*

Irradiation Time Week	% of Reduction pH 3.5	pH 7	pH 11	pH 13
2	0	0	0	2.5
3	0	0	0	6, 8*
4	0	0	0	9.5
6	0	0	0	10
8	0	0	0	14, 15*

*The second test.

Figure 7. Photolysis of 2,4-Dinitrophenol; Concentration Versus Time; Sunlight as Light Source; Exposure Period During April to May, 1982

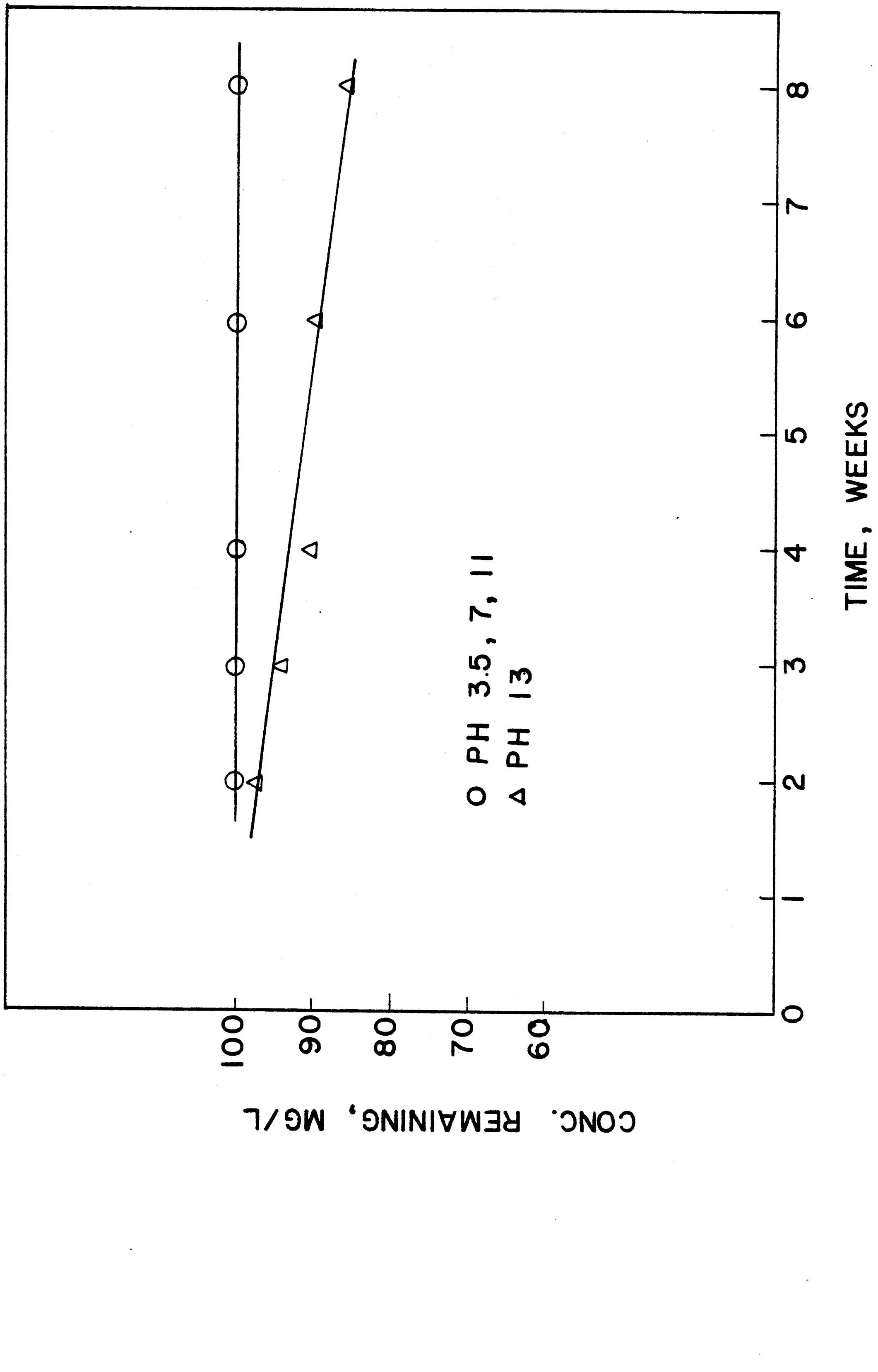

CONC. REMAINING, MG/L
100
90
80
70
60
TIME, WEEKS
0
1
2
3
4
5
6
7
8
O PH 3.5, 7, 11
Δ PH 13

Figure 8. Photolysis of 2,4-Dinitrophenol; % Reduction Versus Time; Sunlight as Light Source; Exposure Period During April to May, 1982

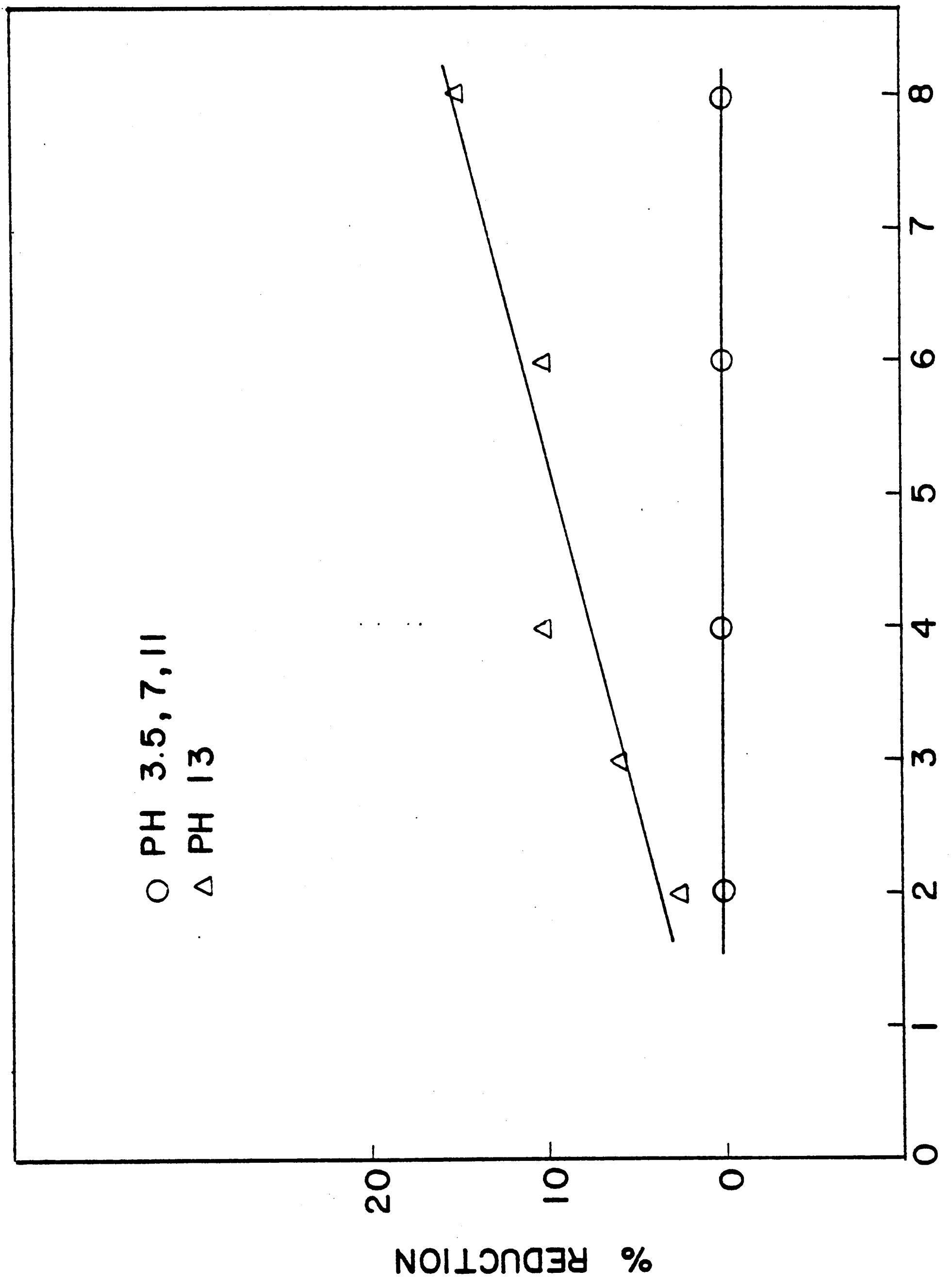

○ PH 3.5, 7, 11
△ PH 13
% REDUCTION
20
10
0
TIME, WEEKS
0
1
2
3
4
5
6
7
8

Figure 9. Determination of a Kinetic Expression to Describe the Photolysis of 2,4-Dinitrophenol; ln C/C_0 Versus Time; Sunlight as Light Source; Exposure Period During April to May, 1982

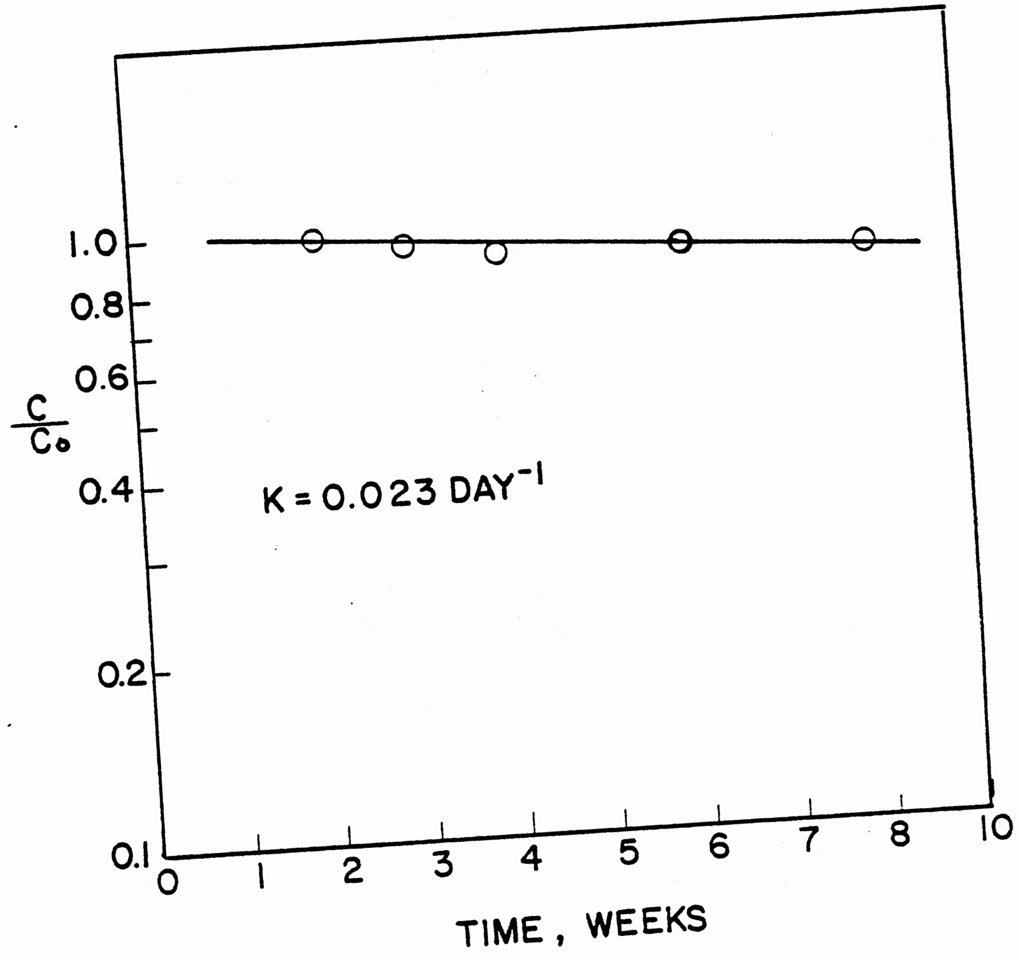
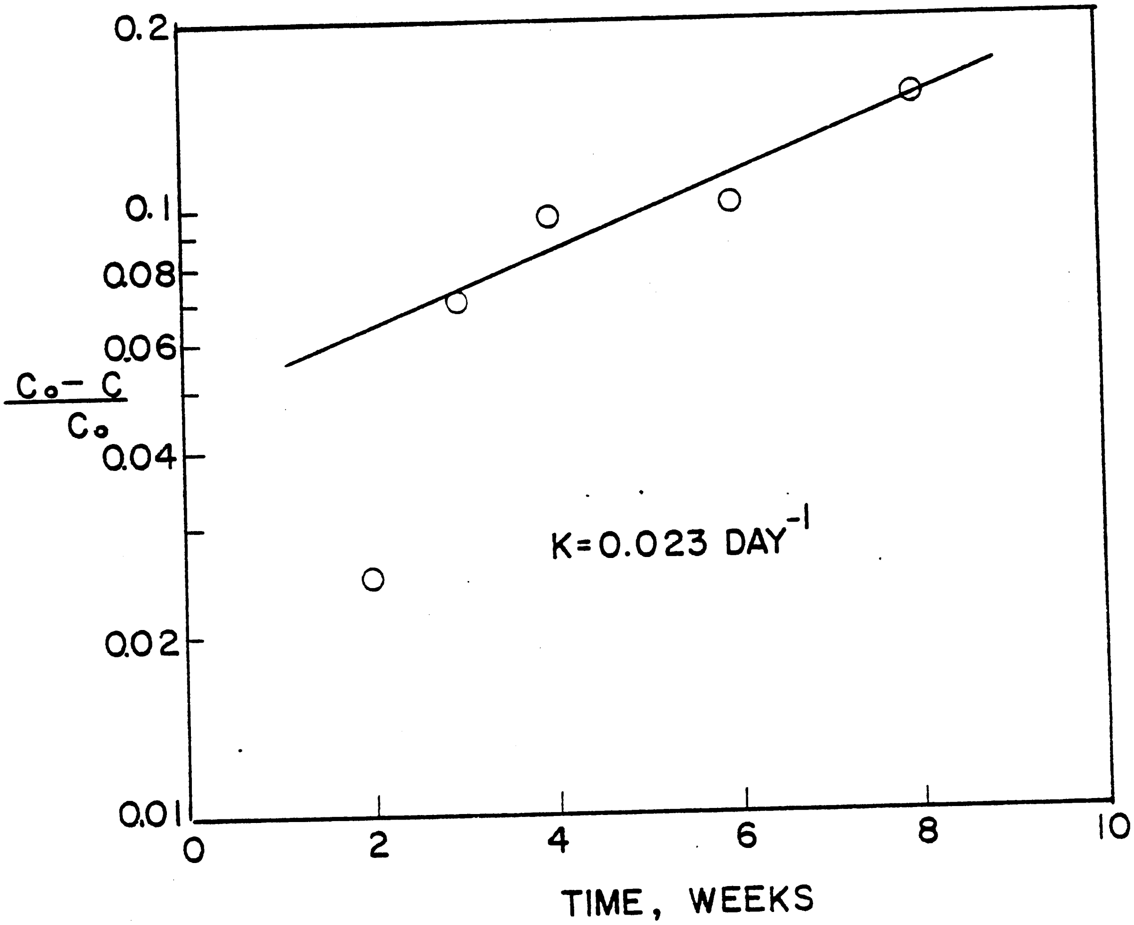

1.0
0.8
0.6
0.4
0.2
0.1
$\frac{C}{C_o}$
K = 0.023 DAY^{-1}
0
1
2
3
4
5
6
7
8
10
TIME , WEEKS

Figure 10. Determination of a Kinetic Expression to Describe the Photolysis of 2,4-Dinitrophenol; $\ln \frac{C_o - C}{C_o}$ Versus Time; Sunlight as Light Source; Exposure Period During April to May, 1982


0.2
0.1
0.08
0.06
0.04
0.02
0.01
$\frac{C_o - C}{C_o}$
0
2
4
6
8
10
TIME, WEEKS
K=0.023 DAY^{-1}

From the results of Gas Chromatography analysis, it was found that all the control samples had almost the same percentage of recovery regardless of the pH or duration of the test. Therefore, the percentage of recovery of phenanthrene is not effected by pH or test duration.

The percentage of recovery was in the range 85 to 90.

Phenanthrene, C_o = 1 mg/L, pH = 7, UV Lamp as Light Source

In this study, 1 mg/L solutions of phenanthrene were prepared and their pH found to be 7.0. Samples were irradiated by UV lamp continuously for 24 hours per day.

The data showing remaining phenanthrene concentration and percentage reduction vs irradiation time are presented in Table VIII, Figure 11 and Figure 12. From the data, it can be seen that the reduction of phenanthrene by UV irradiation was 50% after three days and 99.9% at 20 days of irradiation. After irradiation by UV lamp and extraction, the color of the methylene chloride extract was yellow, while the extract of the control was colorless. However, the phenanthrene concentration was so low (1 mg/L) that the aqueous solution seemed colorless and only after the solution was extracted and condensed to 1 ml, was the yellow color obvious. To insure that the yellow color of the extract was not due to the photolysis of benzene in the solution or some reaction of the benzene with the phenanthrene, one solution containing only benzene and another solution containing only phenanthrene were irradiated. The solution of benzene exhibited no yellow color after several days of irradiation while the phenanthrene solution produced a yellow color, even though much of the phenanthrene did not go into solution. This change of color might

TABLE VIII

DATA COLLECTED FROM THE CONTINUOUS IRRADIATION OF A 1 Mg/L SOLUTION OF PHENANTHRENE AT A pH OF 7 U.V. LAMP LIGHT SOURCE

Irradiated Time, Day	Final Conc. mg/L	% Remaining	% Reduction
1	0.88	88	12
2	0.59	59	41
3	0.50	50	50
5	0.40	40	60
10	0.20	20	80
15	0.08	8	92
20	0.00	0	100

Figure 11. Photolysis of Phenanthrene; Concentration Versus Time; a pH - 7; U.V. Lamp as Light Source

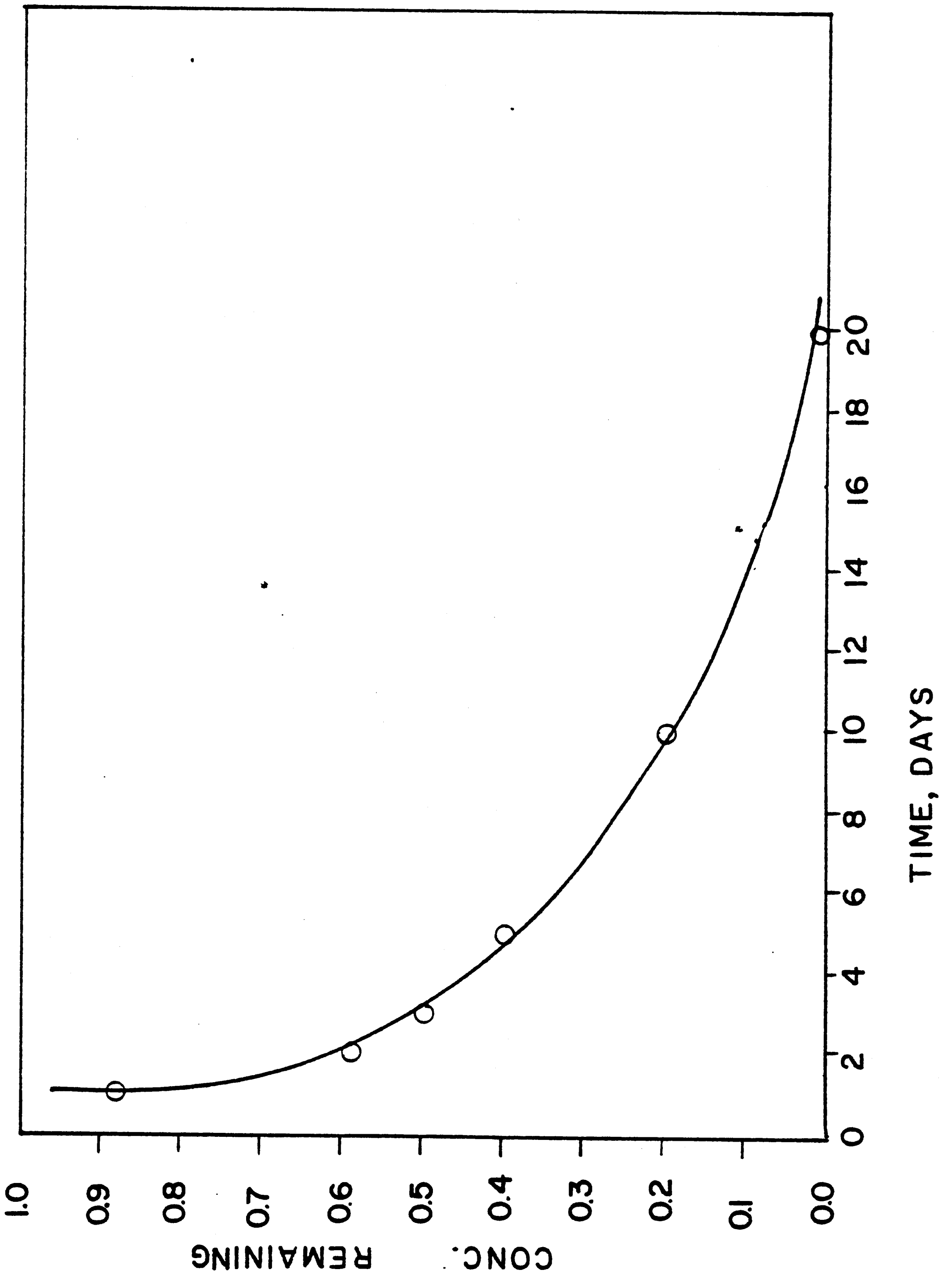
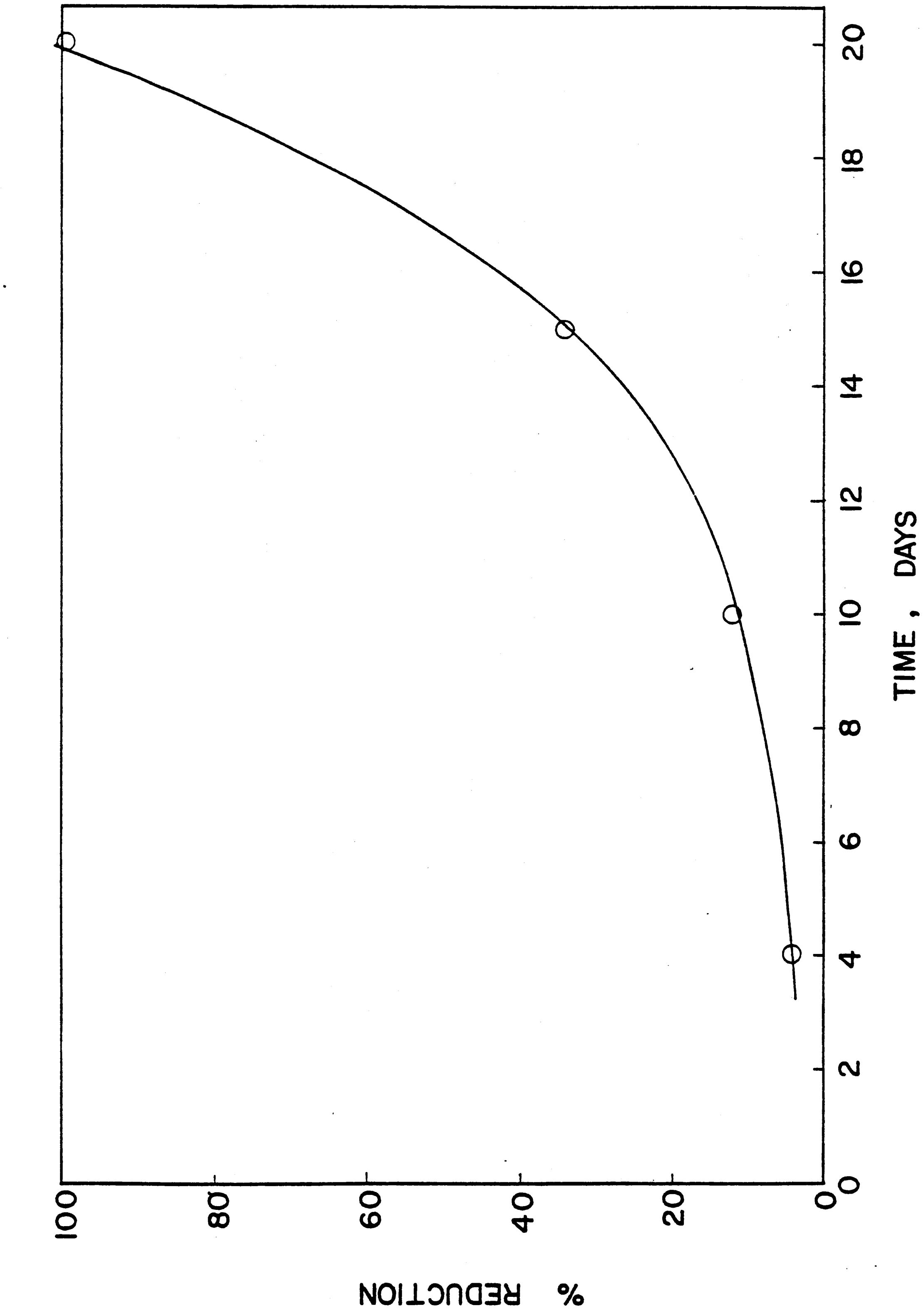

CONC. REMAINING
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
12
14
16
18
20
TIME, DAYS

Figure 12. Photolysis of Phenanthrene; % Reduction Versus Time; pH = 7; U.V. Lamp as Light Source


% REDUCTION
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
18
20
TIME , DAYS

be evidence to prove that quinones, which are yellow in color, were among the endproducts formed during the photooxidation of phenanthrene.

Figure 13 shows the curve of ln C/C_o vs. irradiation time for phenanthrene irradiated by a U.V. lamp at a pH of 7. It can be seen that the rate constant, K is 0.16 day^{-1}, and that the half-life ($T_{\frac{1}{2}}$) is 4.33 days.

Phenanthrene, C_o = 1 mg/L, pH Was Not Adjusted (pH = 7), Sunlight as Light Source, Exposure Period During November, 1981

In this study, the pH of the solution of phenanthrene was not adjusted and was 7. Samples were irradiated by sunlight. The data showing remaining phenanthrene concentration and percent reduction vs. irradiation time are presented in Table IX, Figure 14 and Figure 15. From the curve, plotted with ln C/C_o vs. irradiation time, a reduction rate constant of K = 0.04 day^{-1} was found (Figure 16). The half-time, ($T_{\frac{1}{2}}$) was 17.3 days. In this test, also, the concentrated methylene chloride extract had a yellow color. This color might indicate that some of the phenanthrene was converted to quinones by irradiation.

It should also be pointed out that the reduction rate constant for this test was significantly less (about four times) than for the experiment using the U.V. lamp. This can be explained by differences in the intensity and duration of the U.V. light sources. The U.V. lamp irradiation continuously 24 hours per day, but sunlight irradiation is diurnal.

Figure 13. Determination of a Kinetic Expression to Describe the Photolysis of 2,4-Dinitrophenol; pH = 7; U.V. Lamp as Light Source.

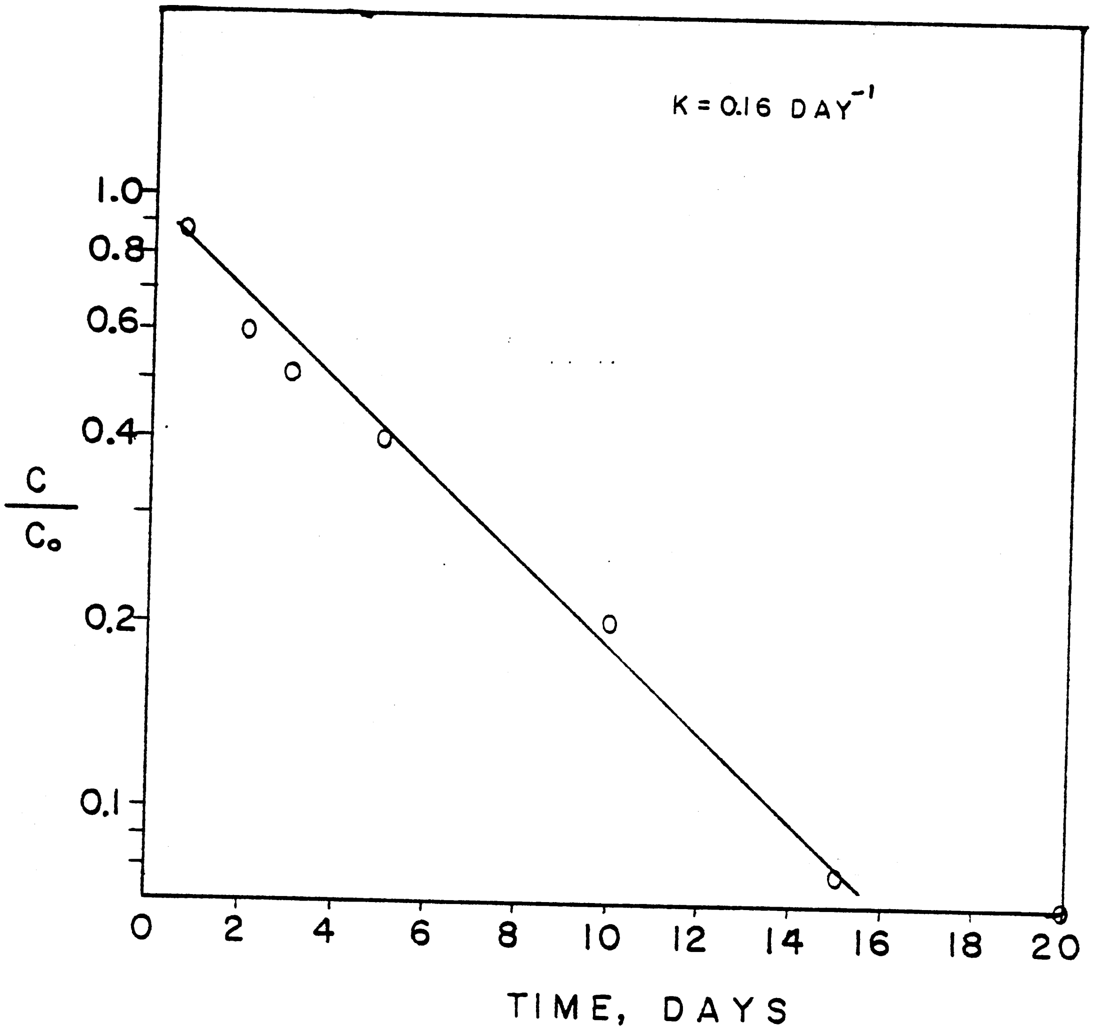

K = 0.16 DAY^{-1}
1.0
0.8
0.6
0.4
0.2
0.1
$\frac{C}{C_o}$
0
2
4
6
8
10
12
14
16
18
20
TIME, DAYS

TABLE IX

PHENANTHRENE, USING SUNLIGHT AS ENERGY, EXPOSURE PERIOD DURING NOVEMBER, 1981

Irradiated Time Day	Final Concentration Mg/L	% of Remaining	% of Reduction
7	0.50	50	50
14	0.30	30	70
21	0.23	23	77
28	0.20	20	80

Figure 14. Photolysis of Phenanthrene; Concentration Versus Time; pH = 7; Sunlight as Light Source; Exposure Period During November, 1981

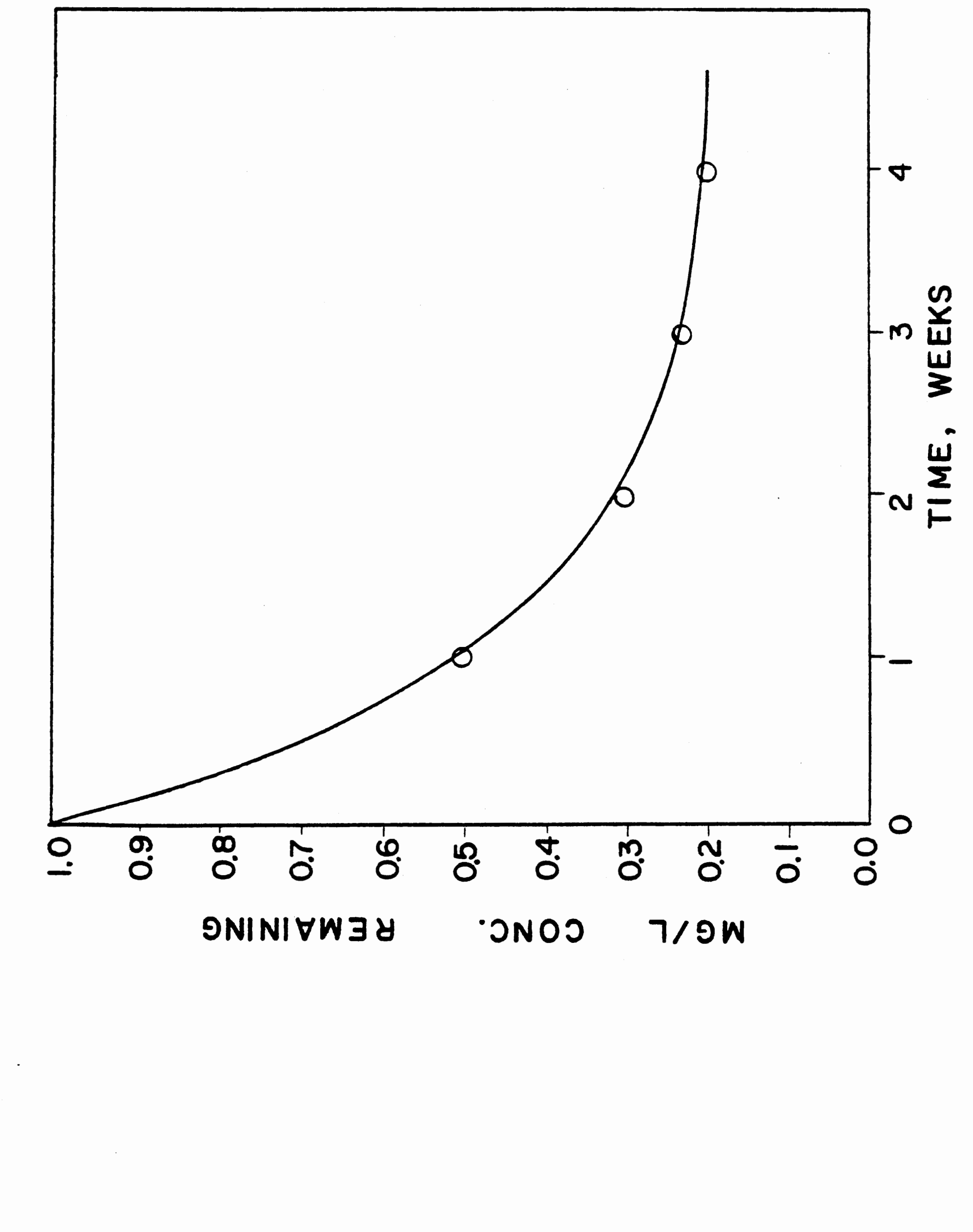

MG/L CONC. REMAINING
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
TIME, WEEKS

Figure 15. Photolysis of Phenanthrene: % Reduction Versus Time; pH = 7; Sunlight as Light Source; Exposure Period During November, 1981

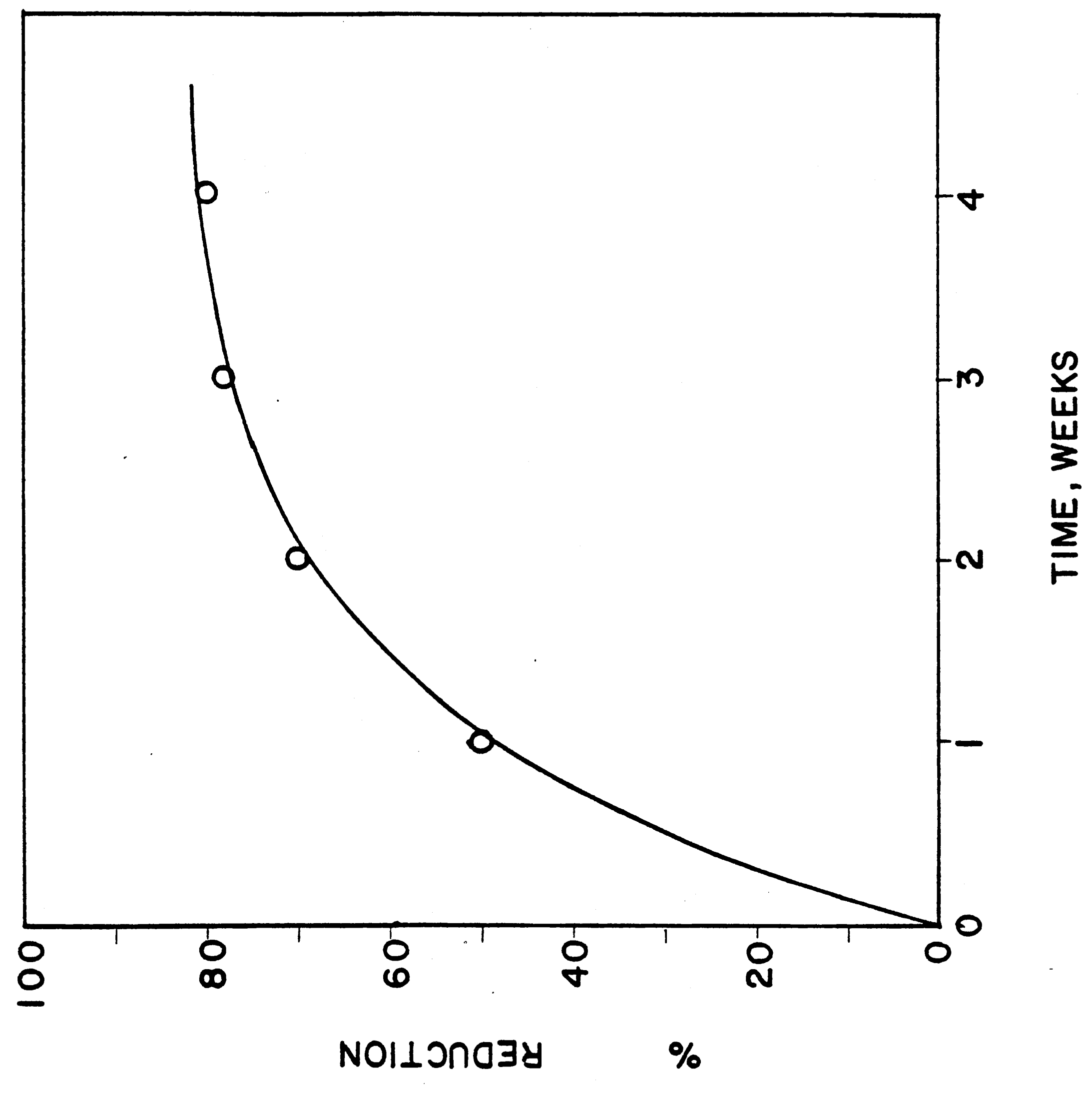
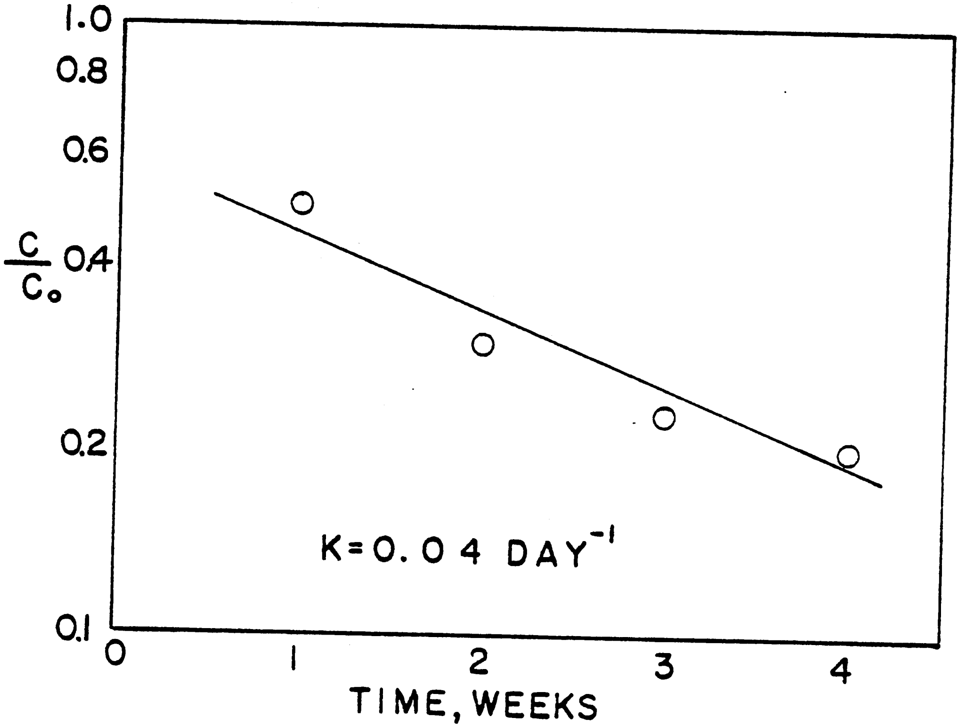

% REDUCTION
100
80
60
40
20
0
0
1
2
3
4
TIME, WEEKS

Figure 16. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 7; Sunlight as Light Source; Exposure Period During November, 1981


1.0
0.8
0.6
C/Co 0.4
0.2
0.1
0
1
2
3
4
TIME, WEEKS
K=0.04 DAY⁻¹

Phenanthrene, C_o = 1 Mg/L, pH = 3.5, 7 and 12. Sunlight as Light Source, Exposure Period During April, 1982

In this study, the pH of solutions of phenanthrene were adjusted to 3.5, 7 and 12 and irradiated by sunlight. The data showing remaining phenanthrene concentration and percentage reduction vs. irradiation time are presented in Table X, Figures 17 and 18. The reduction rate constants (K) were 1.02×10^{-1} day^{-1}, 9.4×10^{-2} day^{-1}, 9.8×10^{-2} day^{-1} for pH = 3.5, 7 and 12, and half-life $T_{\frac{1}{2}}$ was 6.8 day, 7.3 day, 7 day for pH 3.5, 7, and 12 respectively. It can be seen that the lower the pH value, the higher the reduction rate. However, pH is not a significant factor, and reduction rate constants are almost the same for three different pH values.

For pH conditions 3.5 and 7, the methylene chloride extracts of the irradiated samples were yellow, which could again indicate the presence of quinones. However, at pH 12, the color of the concentrated extracts of irradiated samples was not yellow. A possible reason might be that the endproducts of the photolysis of phenanthrene at pH 12 do not include quinones (yellow). Other colorless photolytic endproducts (as polyclic peroxides) (colorless) may have been produced at this condition.

Phenanthrene, C_o = 1 Mg/L, pH = 3.5, 7 and 12. Sunlight as Light Source Exposure Period During June, 1982

In this study, the pH of solutions of phenanthrene were adjusted

TABLE X

DATA COLLECTED FROM THE SUNLIGHT IRRADIATION OF 1 Mg/L SOLUTIONS OF PHENANTHRENE AT pH VALUES of 3.5, 7, AND 12, APRIL, 1982

Time Week	Final Conc. Mg/L pH = 3.5	pH = 7	pH = 12
1	0.12	0.16	0.440
2	0.06	0.09	0.150
3	0.03	0.045	0.060
4	0.014	0.022	0.035

Time Week	% Reduction pH = 3.5	pH = 7	pH = 12
1	88	84	36
2	94	91	85
3	96	94	94
4	98.6	97.8	96.5

Figure 17. Photolysis of Phenanthrene; Concentration Versus Time; pH = 3.5; pH = 7 and pH = 12; Sunlight as Light Source, Exposure Period During April, 1982

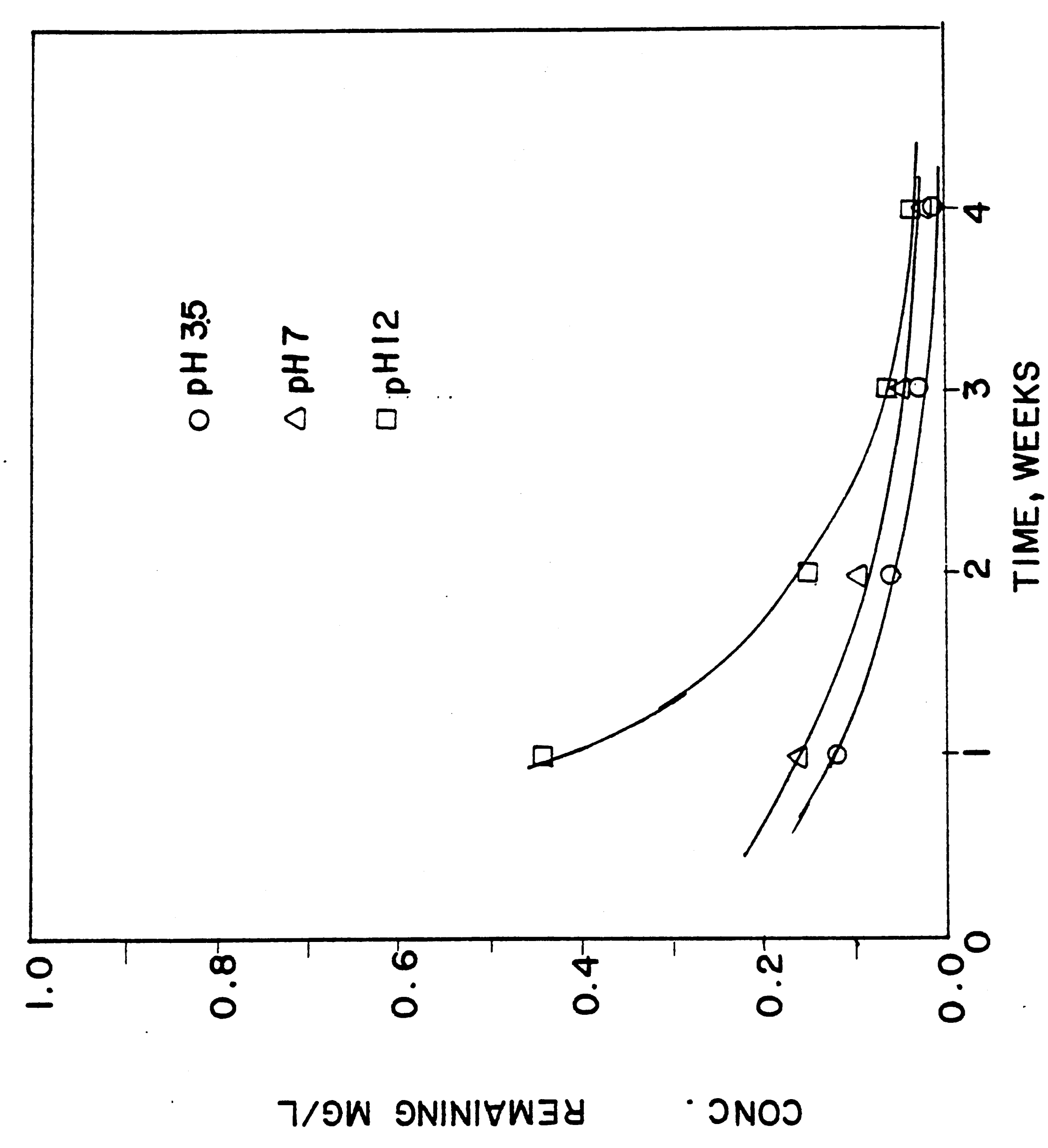

CONC . REMAINING MG/L
1.0
0.8
0.6
0.4
0.2
0.0
TIME, WEEKS
0
1
2
3
4
○ pH 3.5
△ pH 7
□ pH 12

Figure 18. Photolysis of Phenanthrene; % Reduction Versus Time; pH 3.5; 7 and 12; Sunlight as Light Source, Exposure Period During April, 1982

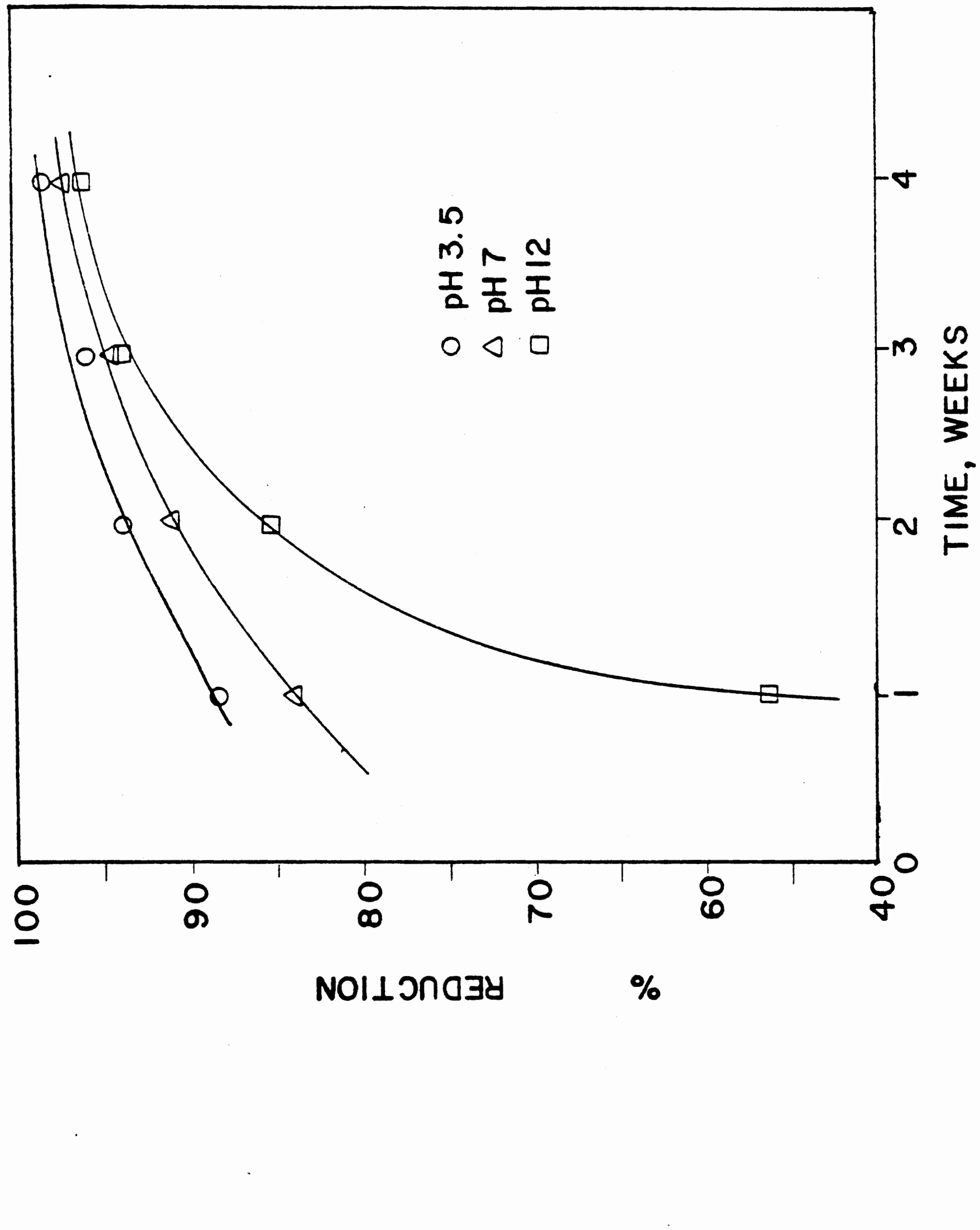
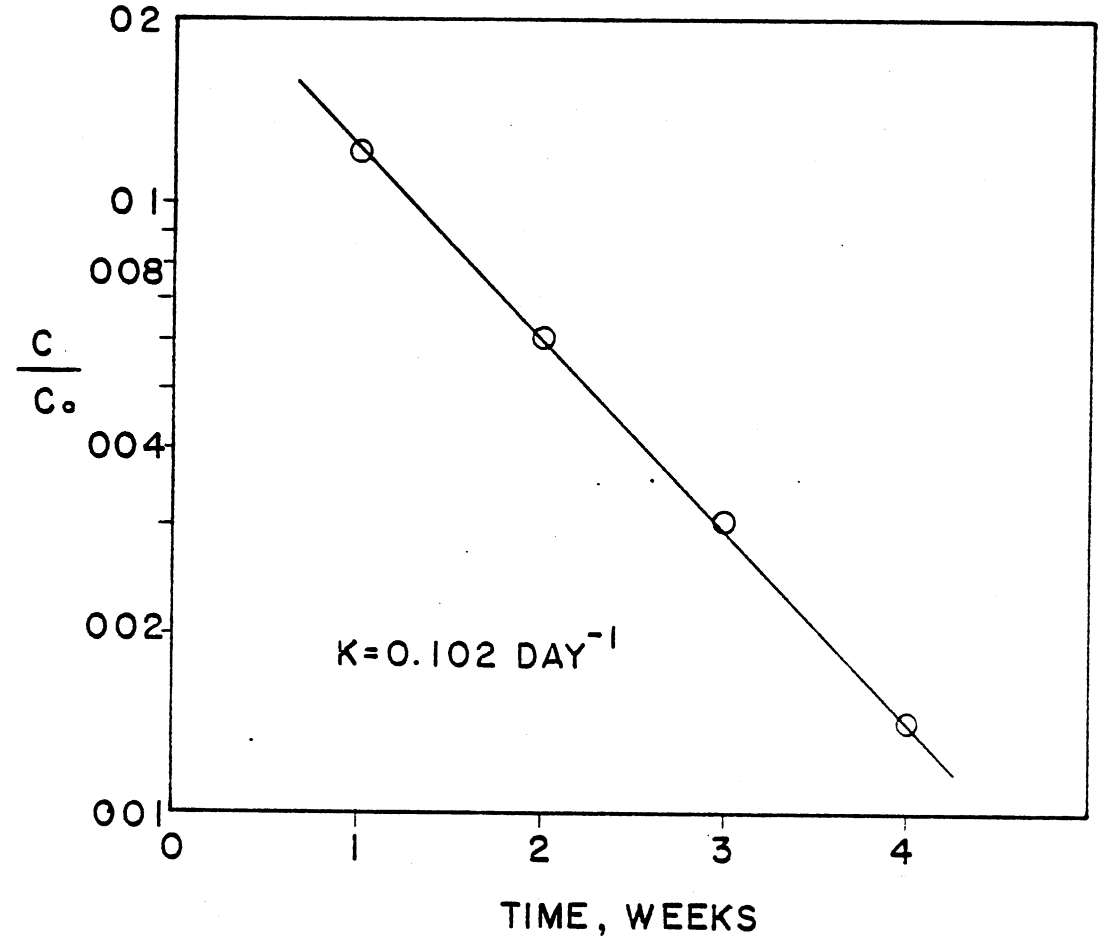

% REDUCTION
100
90
80
70
60
40
0
1
2
3
4
TIME, WEEKS
○ pH 3.5
△ pH 7
□ pH12

Figure 19. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 3.5; Sunlight as Light Source; Exposure Period During April, 1982



0.2
0.1
0.08
0.04
0.02
0.01
C/Co
K=0.102 DAY^{-1}
0
1
2
3
4
TIME, WEEKS

Figure 20. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 7; Sunlight as Light Source; Exposure Period During April, 1982

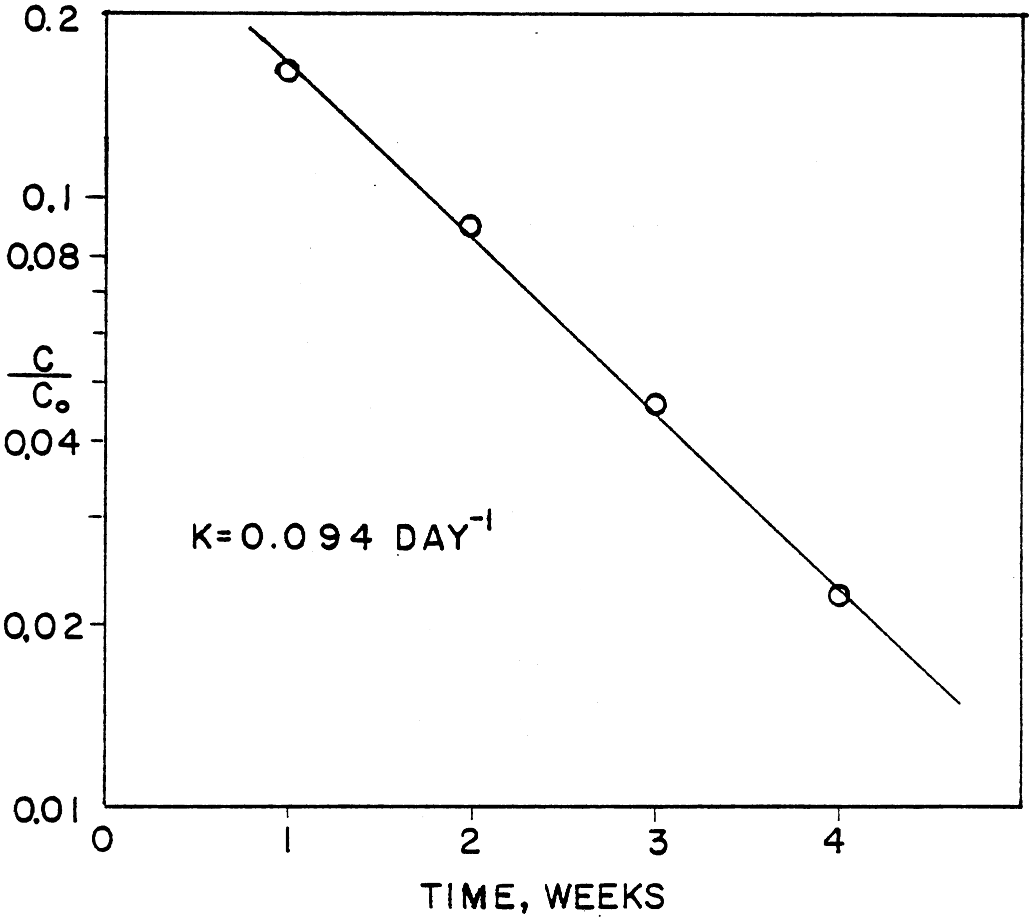
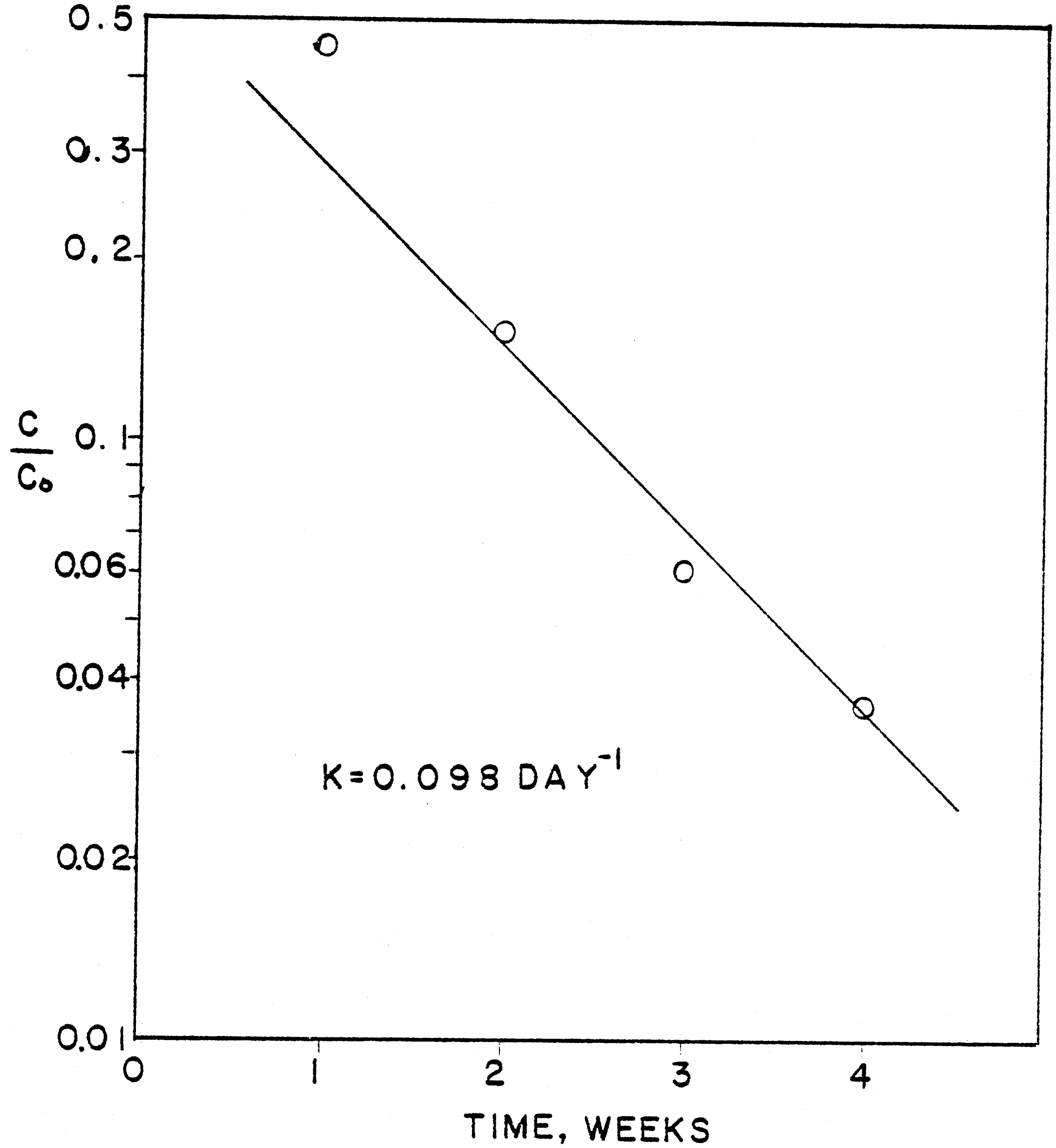

0.2
0.1
0.08
$\frac{C}{C_o}$
0.04
0.02
0.01
K=0.094 DAY^{-1}
0
1
2
3
4
TIME, WEEKS

Figure 21. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 12; Sunlight as Light Source; Exposure Period During April, 1982


0.5
0.3
0.2
C/C₀
0.1
0.06
0.04
0.02
0.01
0
1
2
3
4
TIME, WEEKS
K=0.098 DAY⁻¹

to 3.5, 7 and 12. The data showing remaining phenanthrene concentration and percentage reduction vs. irradiation time are presented in Table XI. Figure 22, and Figure 23. The plot of $\ln C/C_o$ vs. irradiation time is shown in Figure 24, Figure 25 and Figure 26. From those slopes, reduction constants were found, $K_1 = 0.365$ day^{-1}, $K_2 = 0.270$ day^{-1} and $K_3 = 0.220$ day^{-1}, respective to pH = 3.5, pH = 7, pH = 12. It can be seen that the higher the pH, the lower the reduction rate. Again, as in the November 1981 study, pH is not a significant factor, and reduction rate constants are almost the same for three different values. As in the November study, a yellow color was observed in the concentrated extracts of the samples irradiated at pH 3.5 and 7.

From the above studies, it was found that seasonal variations in UV light intensity had the most impact on the phenanthrene reduction rate constant. The phenanthrene reduction rates determined in June range between 2.2 and 3.6 times greater than those found in April. The pH of thephenanthrene solutions had substantially less impact on the rate of phenanthrene photolysis. During the April study, test solutions of 3.5, 7 and 12 yielded very similar reduction rate constants. For the June study, pH may have played a more significant role in the photolysis of phenanthrene. Here, the test solutions of phenanthrene irradiated at pH 7 and 12 showed comparable reduction rate constants, but at pH = 3.5, the reduction rate constant was found to be 1.4 to 1.7 times greater than those determined for the higher pH solutions. The effects of pH and season on the rate of phenanthrene photolysis are presented in Tables XII and XIII, respectively.

TABLE XI

PHENANTHRENE, C_o = 1 Mg/L, pH = 3.5, 9 AND 12 SUNLIGHT AS LIGHT SOURCE, EXPOSURE PERIOD DURING JUNE, 1982

Time	Final Conc. Mg/L		
Day	pH = 3.5	pH = 7	pH = 12
1	0.56	0.39	0.72
2	0.38	0.54	0.56
4	0.156	0.18	0.30
6	0.09	0.15	0.23

Time	% Reduction		
Day	pH = 3.5	pH = 7	pH = 12
1	44	41	28
2	62	46	44
4	84.4	81.8	70.6
6	91	84.5	77

Figure 22. Photolysis of Phenanthrene; Concentration Versus Time; pH = 3.5; 7 and 12; Sunlight as Light Source; Exposure Period During June, 1982

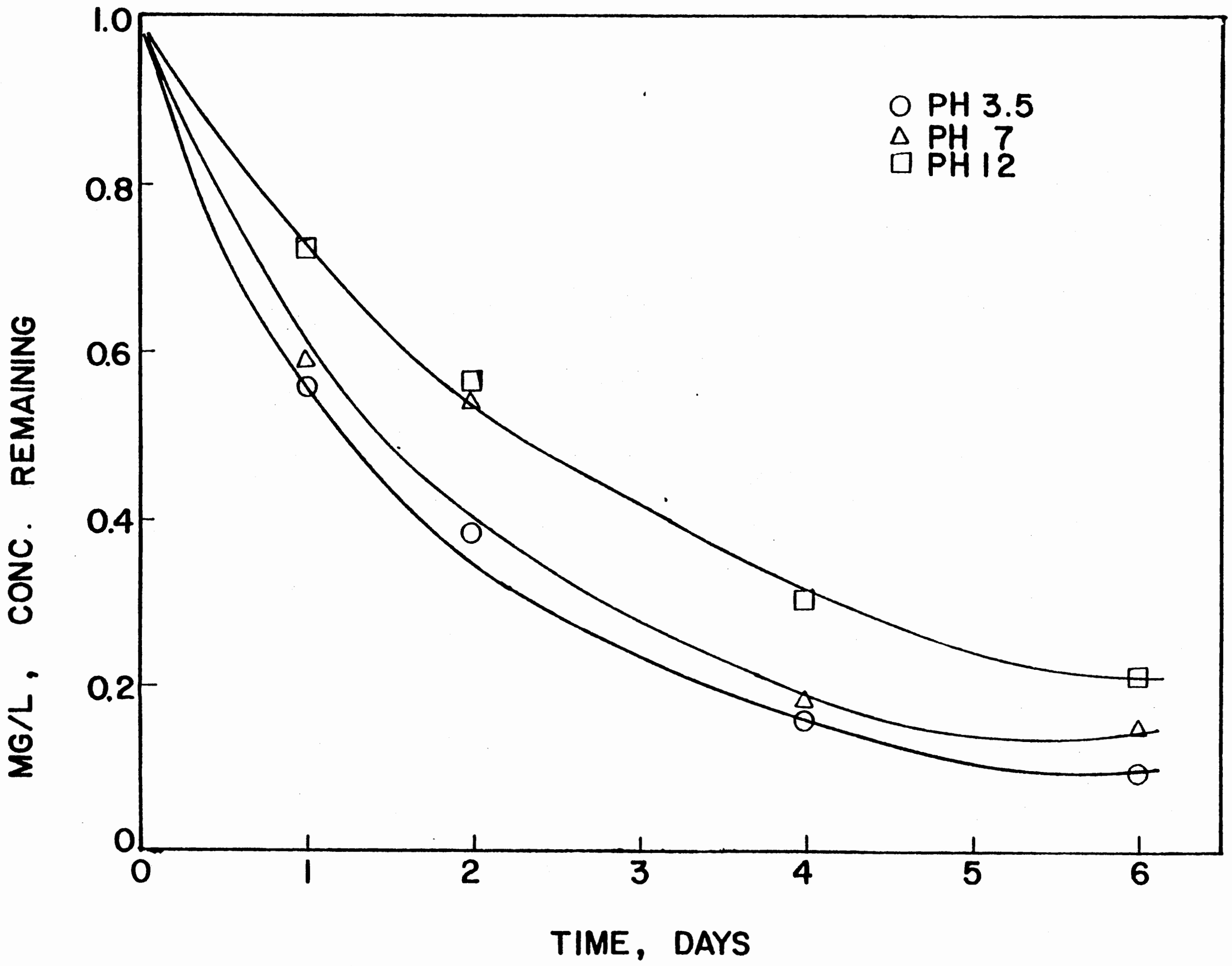

○ PH 3.5
△ PH 7
□ PH 12
1.0
0.8
0.6
0.4
0.2
0
MG/L , CONC. REMAINING
0
1
2
3
4
5
6
TIME, DAYS

Figure 23. Photolysis of Phenanthrene; % Reduction Versus Time; pH = 3.5, 7 and 12, Sunlight as Light Source; Exposure Period During June, 1982

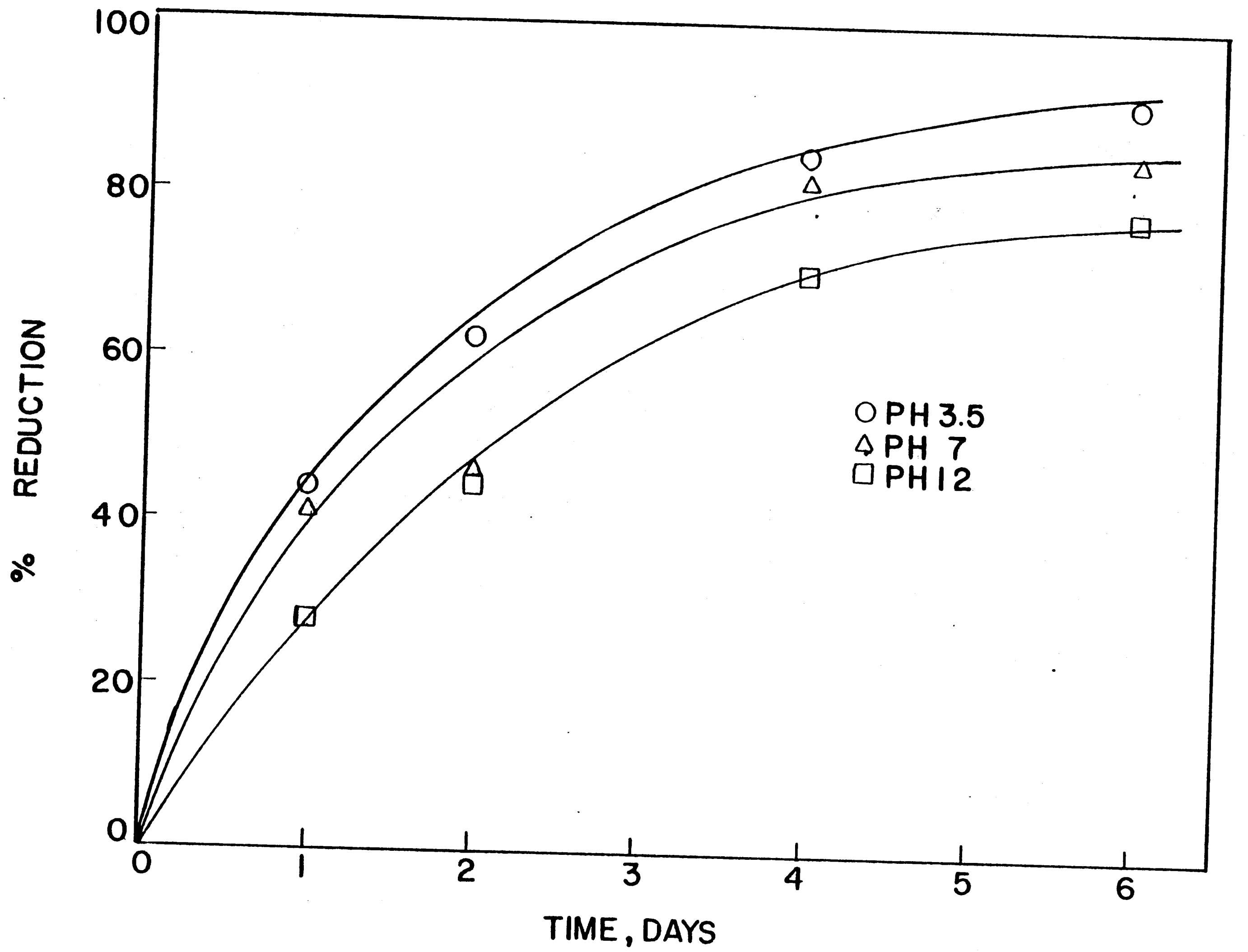

100
80
60
40
20
0
% REDUCTION
0
1
2
3
4
5
6
TIME, DAYS
○ PH 3.5
△ PH 7
□ PH 12

Figure 24. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 3.5; Sunlight as Light Source; Exposure Period During June, 1982

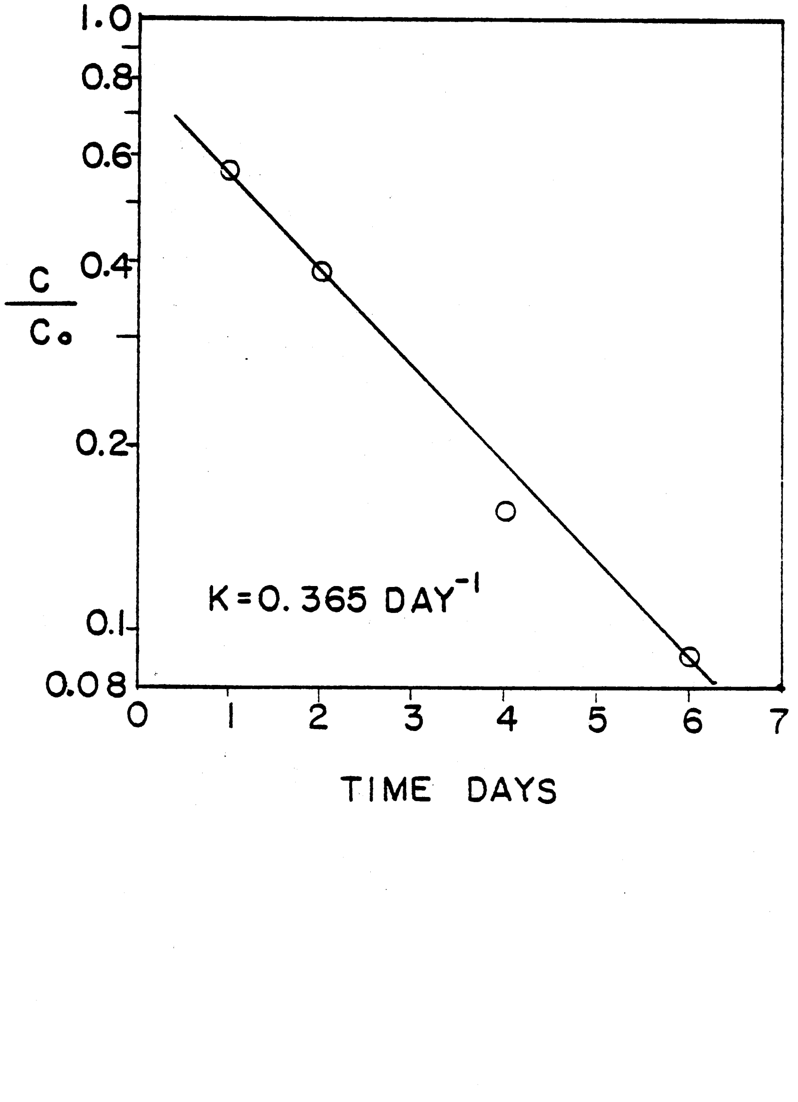

1.0
0.8
0.6
0.4
0.2
0.1
0.08
C/Co
K=0.365 DAY^{-1}
0
1
2
3
4
5
6
7
TIME DAYS

Figure 25. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 7; Sunlight as Light Source; Exposure Period During June, 1982

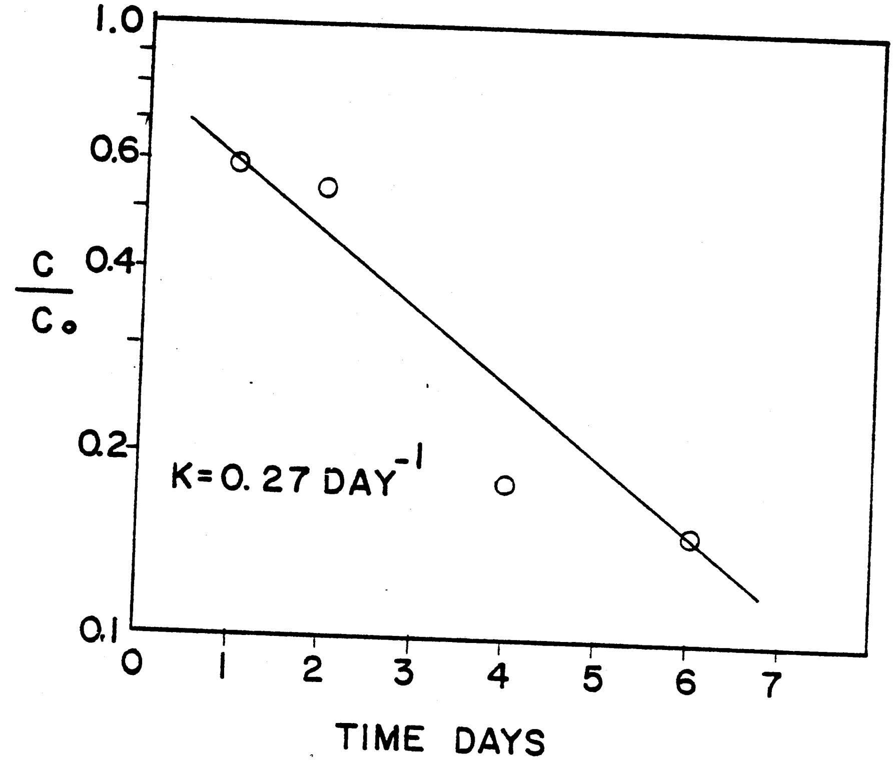

1.0
0.6
0.4
0.2
0.1
C/Co
0
1
2
3
4
5
6
7
TIME DAYS
K=0.27 DAY^{-1}

Figure 26. Determination of a Kinetic Expression to Describe the Photolysis of Phenanthrene; pH = 12; Sunlight as Light Source; Exposure Period During June, 1982

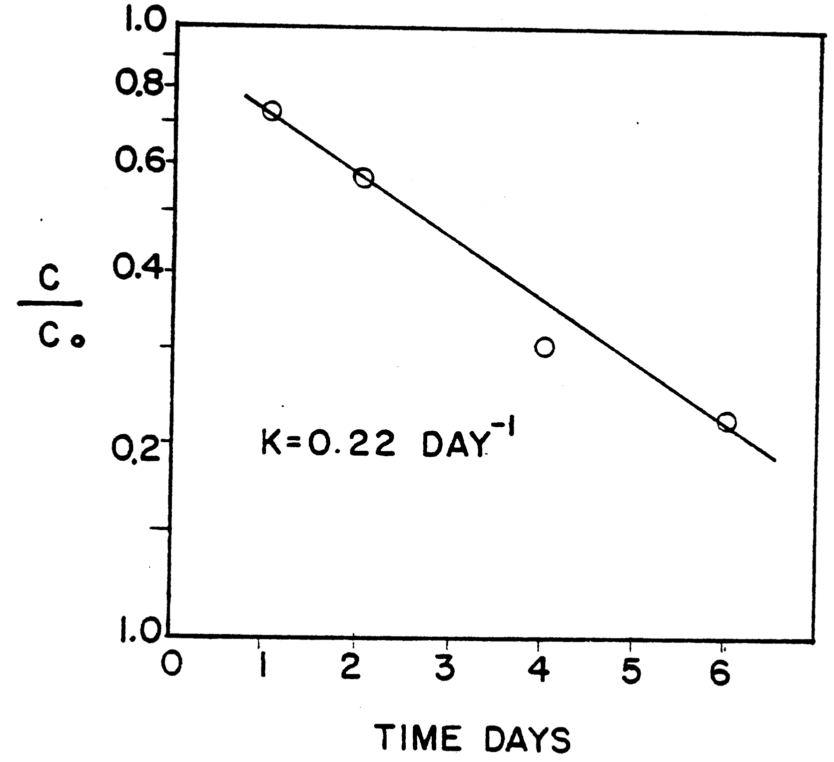

1.0
0.8
0.6
0.4
0.2
1.0
C/Co
K=0.22 DAY⁻¹
0
1
2
3
4
5
6
TIME DAYS

TABLE II

EFFECT OF pH ON RATE CONSTANT FOR PHOTOLYSIS OF PHENANTHRENE

Condition of Test C_o = 1 Mg/L, Sunlight as Light Source, During April, 1982	Ratio
$\frac{Ka(pH\ 3.5)}{Kb(pH\ 7)}$	1.08
$\frac{Ka(pH\ 3.5)}{Kc(pH\ 12)}$	1.04
$\frac{Kb(pH\ 7)}{Kc(pH\ 12)}$	0.96

TABLE XIII

EFFECT OF SEASON ON RATE CONSTANT FOR PHOTOLYSIS OF PHENANTHRENE

Condition of Test C_o = 1 Mg/L, Sunlight as Light Source, pH 3.5, 1982	Ratio
$\frac{K(\text{June, } 3.5)}{K(\text{April, } 3.5)}$	3.57
$\frac{K(\text{June, } 7)}{K(\text{April, } 7)}$	2.87
$\frac{K(\text{June, } 12)}{K(\text{April, } 12)}$	2.24

CHAPTER V

CONCLUSIONS

From previous experimental data, the following conclusions may be drawn.

2,4-Dinitrophenol

In aquatic systems (pH 6 to pH 8), 2,4-Dinitrophenol is not significantly photodegradable. However, it was found that in the photolysis of 2,4-Dinitrophenol, the hydroxyl ion concentration is a critical factor. Although at conditions of pH = 3.5, pH = 7 and pH = 12, 2,4-Dinitrophenol did not undergo photodegradation, when the test solution pH was adjusted to 13 and irradiated by sunlight for a period of 2 months, an initial 2,4-Dinitrophenol concentration of 100 mg/L was reduced to 85 mg/L. Another test was performed at pH 13 using a high intensity UV lamp. After continuous, 24 hours per day irradiation for a period of 20 days, the 2,4-Dinitrophenol concentration was reduced from 100 mg/L to less than 0.1 mg/L.

It was determined that the most appropriate kinetic expression for the data collected using sunlight as an energy source was a first order relationship which considered percent reduction of the initial 2,4-Dinitrophenol concentration. It was found that percent reduction of 2,4-Dinitrophenol $\frac{C_o - C}{C_o}$ increased with time until the 2,4-Dinitrophenol fell to non-detectable levels. This reduction rate constant for sunlight was found to be 0.023 day^{-1} yielding a half-life of 30 days. The reduction rate constant using a UV lamp continuously for 20 days was found to be 0.2 day^{-1} with a half-life of 3.5 days. The reduction rate constants and the half-lives of 2,4-Dinitrophenol for different conditions are presented in Table XIV. Since at pH 3.5, 7 and 12, 2,4-Dinitrophenol was not significantly photodegradable, just the pH = 13 tests are presented here.

TABLE XIV

REDUCTION RATE CONSTANTS AND THEIR HALF-LIFE OF 2,4-DINITROPHENOL FOR DIFFERENT CONDITIONS

Condition	Reduction Rate Constant, Day^{-1}	Half-Life, Day
UV Lamp, pH = 13	0.2	3.5
Sunlight, pH = 13	0.023	30

The comparison of reductions rate constants between light source and UV lamp for 2,4-Dinitrophenol is as follows:

$$\frac{K\ (\text{UV Lamp, pH} = 13)}{K\ (\text{Sunlight, pH} = 13)} = 8.7$$

Phenanthrene

In aqueous solutions, photodegradation of phenanthrene was found to be significant. The reduction rate was found to be a first order relationship dependent on the concentration of phenanthrene remaining in solution. Unlike 2,4-Dinitrophenol, the hydroxyl ion concentration does not play a critical role in the photolysis of phenanthrene. It should be noted that phenanthrene solutions irradiated at pH = 7 and pH = 12 showed similar rates of photodegradation. Even though phenanthrene solutions irradiated at pH 3.5 demonstrated slightly higher rates of photolysis the amount of increase was not significant. However, seasonal variations significantly affected the rate of photolysis. Photolytic rates were 2.2 to 3.5 times greater during the June 1982 test period when compared to the April 1982 test period. The results of all the phenanthrene testing can be found in Table XV.

Also it was found that for the pH conditions 3.5 and 7, the methylene chloride extracts of the irradiated samples were yellow, which could possibly indicate the presence of quinones.

Summary

In summary, from all previous studies, conducted in this investigation, these conclusions can be cited: In aquatic systems (pH 6 to pH 8), 2,4-Dinitrophenol is not significantly photodegradable, but it undergoes photolysis in the pH 13 test. In aqueous solution systems, phenanthrene is significantly photodegradable, and the degree of photodegradation is subject to seasonal variations.

TABLE XV

THE REDUCTION RATE CONSTANTS AND HALF-LIFE OF PHENANTHRENE, FOR DIFFERENT CONDITION

Condition	Reduction Rate Constant K Day^{-1}	Half-Life Day
UV lamp irradiated continuously 24 hours per day pH 7.	0.16	4.33
Sunlight irradiated diurnal during November pH 7.	0.04	17.32
Sunlight irradiated diurnal during April pH 3.5.	0.102	6.8
Sunlight irradiated diurnal during April pH 7.	0.094	7.4
Sunlight irradiated diurnal during April pH 12.	0.098	7.1
Sunlight irradiated diurnal during June pH 3.5.	0.365	1.9
Sunlight irradiated diurnal during June pH 7.	0.270	2.5
Sunlight irradiated diurnal during June pH 12.	0.220	3.1

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

1. For certain compounds which are photodegradable but not biodegradable, UV irradiation pretreatment might prove to be effective in either enhancing their biodegradation or reducing their concentration to acceptable levels.

2. The dissolved oxygen concentration may have some impact upon the photolysis of phenanthrene according to the literature concerning the proposed mechanism of phenanthrene photolysis. Similar studies involving exposure of phenanthrene solutions to UV irradiation under aerobic and anerobic conditions are recommended.

3. Pilot studies involving the optimization of operating conditions to remove phenanthrene from waste water discharges by UV irradiation are recommended.

4. Photodegradation studies of phenanthrene should be conducted in simulated natural aquatic systems to investigate the effect of water chemistry and suspended solids on the rate of photolysis.

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