## ENVIRONMENTAL AQUATIC PHOTOCHEMISTRY OF 2,3,7,8-TETRACHLORODIBENZOFURAN AND 2,3,4,7,8-PENTACHLORODIBENZOFURAN

A Thesis

Submitted to the Faculty of Graduate Studies in partial fulfillment of the requirements for the degree of Master of Science

> University of Manitoba Department of Chemistry

> > Myrosia M. Foga 1991

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BY

MYROSIA M. FOGA

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

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The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission. To Mom, Dad, and Irene

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## ABSTRACT

The aquatic photochemistry of two ubiquitous, toxic, environmental contaminants, 2,3,7,8-tetrachlorodibenzofuran  $(2,3,7,8-T_4CDF)$  and 2,3,4,7,8-pentachlorodibenzofuran  $(2,3,4,7,8-P_5CDF)$ , was studied in the laboratory and under natural sunlight conditions.

direct photolysis Quantum yields for the of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF in 50:50 (v/v)  $H_2O/CH_3CN$ , measured in the laboratory at 313 nm with a Rayonet Photoreactor, were determined to be (2.9  $\pm$  0.5) x 10<sup>-4</sup> and  $(6.6 \pm 0.9) \times 10^{-4}$ , respectively. Pseudo-first-order sunlight photolysis rate constants for the direct photolysis of  ${}^{3}H-T_{4}CDF$  and  ${}^{14}C-P_{5}CDF$ ,  $k_{DE}$ , in 70:30 (V/V)  $H_{2}O/CH_{3}CN$ , were determined at 50°N latitude under midsummer conditions to be 0.10  $\pm$  0.007 and 0.014  $\pm$  0.007 d<sup>-1</sup>, respectively. The measured rates of direct aqueous photolysis were in reasonably good agreement with predicted rates (GCSOLAR, US-EPA). Accelerated degradation rates were observed in lake water under identical sunlight conditions, producing net degradation rate constants,  $k_{PE}$ , of 0.50 ± 0.05 and 3.6  $\pm$  0.3 d<sup>-1</sup> for <sup>3</sup>H-T<sub>4</sub>CDF and <sup>14</sup>C-P<sub>5</sub>CDF, respectively. The large differences observed between the direct and net photolytic degradation rate constants emphasize the importance of indirect photolysis in the aquatic environment.

GC-MS analyses of non-polar degradation products

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produced by photolysis of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF in lake water exposed to a xenon light source, identified dechlorination as a route of degradation. Several T<sub>4</sub>CDFs, in particular, 2,3,6,8-T<sub>4</sub>CDF; 2,3,4,8-T<sub>4</sub>CDF; and one or both  $2,3,7,8-T_4CDF$  and  $2,3,4,7-T_4CDF$ ; were confirmed of as non-polar degradation products of the photolysis of  $2, 3, 4, 7, 8 - P_5 CDF.$ Similarly, with  $2, 3, 7, 8-T_4 CDF$ , а trichlorodibenzofuran  $(T_3CDF)$  was identified, but the specific congener could not be confirmed. However, the major degradation product resulting from photolysis of  $2,3,4,7,8-P_5CDF$  in lake water, appeared to be polar in nature and was identified as a dihydroxybiphenyl. Although chlorinated products were detected not in the polar fraction, reductive dechlorination played an important role in the production of non-polar intermediates during aquatic photolysis of both 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF.

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## I. INTRODUCTION

Polychlorinated dibenzofurans (PCDFs) are a class of chloroaromatic, environmental contaminants that have been studied in greater detail in the past decade as a direct consequence of their persistent, ubiquitous, and toxic nature. These compounds have the general structure:



where x and y represent the number of chlorine atoms on the respective rings. PCDF nomenclature involves a numbering scheme such that the lowest numerical combination describes the chlorine substitution pattern.

PCDFs may be synthesized by the pyrolysis of the appropriate solid polychlorinated biphenyl (PCB) under high temperature (600°C) and anaerobic conditions (1). It is well-known that both PCDFs and PCDDs may be formed as by-products in the manufacturing of chlorophenols (2), which are used as fungicides, bactericides, and herbicides (3). Although 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-T<sub>4</sub>CDD) has not been identified as а contaminant in pentachlorophenol (PCP) manufacturing, it has been found in commercial trichlorophenols (2). For example,

in 2,4,5-1,2,4,5-tetrachlorobenzene, the precursor trichlorophenol preparation, undergoes hydrolysis at high temperatures and pressures, and may result in the formation of trace heterocyclic impurities such as  $2,3,7,8-T_4CDD$  (3). PCBs have excellent dielectric properties, are inert and stable, and have commonly been used as insulating fluids in Accidents involving the thermal transformers (4). combustion of PCBs have been responsible for the formation PCDDs (4, 5). Recently, accidents have of PCDFs and illustrated that PCDDs and PCDFs form as a result of thermal In the summer of 1976 an explosion in a reactions. trichlorophenol reactor in Seveso, Italy released of a cloud of trichlorophenol contaminated with  $2, 3, 7, 8 - T_4 CDD$ and 2,3,7,8 substituted PCDFs (6, 7). In 1982, an electrical transformer fire in a Binghamton, New York office building released several PCDDs (20 mg/g), PCDFs (700-2200 mg/g), and polychlorinated biphenylenes into the atmosphere (8). In the late 1950's, an epidemic in chickens, known as the chick edema factor, occurred in the midwestern U.S.A. as a result of the intake of a large dose of "toxic fat" (a combination of residues of distilled animal fats and a series of PCDDs in chicken feed) (9, 10). PCBs, which have been used as plasticizers in paints in the past, have also produced similar symptoms in chickens (9). An accident of a more drastic nature occurred in Japan when chlorobiphenylcontaminated rice bran oil used for cooking resulted in food poisoning in at least 600 people in Western Japan (9). The contamination was the result of PCBs leaking from a pipe

used in the heat exchange during the oil manufacturing process (7).

Since PCDFs are commonly synthesized in extremely small quantities for laboratory purposes, they tend not to be disposed of into the environment as direct wastes. The recent historic accidents cannot account for the levels of material known to exist in air, water, and sediments. Their increased levels in the environment with time, therefore, must be the result of other sources.

A well-known source of PCDFs and PCDDs is the use of chlorine in the bleaching process of pulp and paper mills. Used only for aesthetic purposes, this process could alternately be achieved by oxygenation  $(ClO_2)$  with minimal levels of chlorine. This type of contamination, along with the disposal of chlorinated household bleaches into sewage, may provide a Cl source for the formation of PCDFs and PCDDs natural waters in (11). Incineration of municipal, hospital, and chemical wastes remains as another major source of PCDF formation. It is estimated that 70-80% of PCDFs emitted from incinerator stacks is in the gaseous phase, with the remaining 20-30% bound to fly ash (2). The emissions are subject to long-range atmospheric transport with eventual deposition into waters and soils. The presence of PCDFs and PCDDs in Lake Siskiwit sediments, provided evidence of this phenomenon. This lake, located on an island in Lake Superior, is isolated from industry and is at a higher elevation than Lake Superior itself. Therefore, detectable PCDF levels cannot be due to run-off from Lake

Superior or from industrial waste and must thus be the result of atmospheric input (12). Other common sources include runoff of chlorinated pesticides and insecticides which provide precursors for PCDF formation, and the processes involved in the production of steel and iron (7).

The environmental fate of these pollutants is dependent upon the nature of environmental input; however, it has been established that the ultimate "sink" of PCDFs in water is the sediment (2). The adsorption to sediment minimizes desorption into solution, but the recirculation into the water column that does occur allows for photodegradation at the water surface. Unlike the accumulation of these pollutants in sediments, bioaccumulation in plants is significantly lower since neither leaves nor roots seem to absorb the PCDFs (2). Generally, PCDF levels have appeared higher in aquatic rather than terrestrial animals. Geographical trends indicate that animals from the northern parts of the world contain higher levels of PCDFs than those from the south. This is perhaps explained by the direction of prevailing winds over the northern hemisphere, and the fact that most of the developed countries producing these contaminants are geographically located in the northern hemisphere. PCDF levels in fish are further dependent on the species, organ, weight, fat content, and sex (13, 14). Due to the hydrophobic nature of these contaminants, the liver tends to be the major site of accumulation (13).

There are 135 possible PCDF isomers which may be divided into eight congener groups. Fortunately, only a few

of these isomers present in the environment are thought to be of toxicological significance (15). The 2,3,7,8 substituted congeners are of particular interest since these congeners are accumulated in mammalian lipid, show a higher toxic potency, and are more persistent in the environment. The non-2,3,7,8 substituted isomers are not persistent in mammals and do not bioaccumulate since they are metabolized and excreted rapidly (16). Two of the most toxic, hence environmentally significant PCDF congeners, 2,3,7,8-tetrachlorodibenzofuran and 2,3,4,7,8-pentachlorodibenzofuran, were chosen for the present study.



2,3,7,8-T<sub>4</sub>CDF

2,3,4,7,8-P<sub>5</sub>CDF

Both PCDF congeners have extremely low water solubilities, 419 and 235 ng/L (at 23°C) for the  $T_4CDF$  and  $P_5CDF$ , respectively (17).The octanol/water partition coefficients, log  $K_{ow}$ , have been established as 6.53 and 6.92  $T_4 CDF$ for and  $P_5CDF$ , respectively (18). These properties explain the favorable partitioning of PCDFs from organic phases. An air/water water into partition coefficient, Henry's Law Constant (H), for 2,3,7,8-T4CDF of 1.3 Pa.m<sup>3</sup>/mol (19) suggests slow volatilization of PCDFs

from contaminated water.

Very little information is available with respect to the exact toxic nature of these two PCDF congeners; however, a fair amount of work has been done on the corresponding PCDD congeners, and some comparisons may be made.

Toxicity of a compound is generally defined as the adverse effects experienced by an organism as a result of exposure to the toxin. The toxicity is then indicated by the observed signs of dysfunction or distress as а consequence of a dose or an extent of exposure. With compounds such as PCDFs, it is difficult to attribute any medical dysfunction in humans strictly to exposure, since there are а wide variety of contributing variables. Toxicity of PCDFs and PCDDs seems to be associated with the chlorine substitution pattern of the molecule. Congeners containing lateral chlorine atoms (ie. 2,3,7,8 substituted) exhibit toxic effects at lower doses than other congeners The PCDF binds to the Ah receptor, the complex is (15).transported to the nucleus, interferes with DNA sequencing and then induces biological effects (20). Certain enzymes such as hepatic monooxygenase increase in activity (at low levels of PCDF, but may decrease with higher levels) and may result in thymic atrophy and body weight loss (20, 21). In addition to these biochemical reactivities, toxic potential also seems to be affected by the bioavailability and metabolic fate of PCDFs.

Although no well-documented data is available on the malformations induced in man by PCDFs and PCDDs, data is

available from experimental studies with animals. This information, particularly data from the study of monkeys, is often applied with reasonable modifications to humans. Wacker and Poiger (22) identified a major difference between rats and humans with regards to the site of accumulation in the body, illustrating that rats experience severe liver disorders due the hepatic accumulation of PCDDs and PCDFs. From a mixture of PCDFs, 2,3,4,7,8-P5CDF was found to be the most highly accumulated PCDF congener in rats and monkey liver tissue (23). Alternately, in humans the storage site appeared to be adipose tissue. Relative toxicities between PCDDs and PCDFs may be determined from Toxic Equivalency Factors (TEFs) which compare the relative toxicity of different compounds to the most potent member of the PCDD family, namely,  $2,3,7,8-T_4$ CDD. The development of TEFs was the result of the excellent correlations observed between the structure-binding and structure-activity relationships for several classes of halogenated aromatic compounds (21). A variety of animals have been subjected to single oral doses of PCDDs and PCDFs to establish  $LD_{50}$  values which are useful in establishing relative toxicities (TEFs) (see Table 1). PCDDs and PCDFs, other than the tetrachlorinated congeners, appear to be less toxic within the same species. Toxicity is clearly dependent on species and weight. A variety of side effects have been observed in affected animals as a result of exposure to PCDDs and PCDFs, including thymic atrophy (the wasting away of tissue),

TABLE 1: SINGLE ORAL DOSE LD<sub>50</sub> VALUES<sup>2</sup> (24,25) AND TEFs<sup>b</sup> (21) FOR SELECTED PCDDs AND PCDFs.

Isomer	Oral LD <sub>50</sub> (µg/kg)		TEFs
	Guinea Pig	Monkey	
2378-T₄CDD	0.6-2.0	≈70	1.0
$2378 - T_4 CDF$	5-10	1000	0.1
23478-P <sub>5</sub> CDF	<10	34(25)	0.5
28-D <sub>2</sub> CDF			
234678-H <sub>6</sub> CDF	120		0.1
28-D <sub>2</sub> CDD	>300,000		
1368-T <sub>4</sub> CDD	1.5x10 <sup>7</sup>		
123789-H <sub>6</sub> CDD	60-100		0.1
0 <sub>8</sub> CDD			0.001

<sup>a</sup>LD<sub>50</sub>, the dose required to kill half of the experimental population, is reported in  $\mu$ g/kg body weight. <sup>b</sup>TEFs are toxic equivalency factors which compare the toxicity of a compound relative to 2,3,7,8-

 $T_4$ CDD.

body weight loss, teratogenicity (fetal malformations), immunotoxicity (disruption of bone and spleen activity), tumor promoting activity, and chloracne (24). The lowest-observed-effect- level, LOEL, (see Table 2) is the minimum required quantity of a compound to elicit a response and is frequently used to express toxicity.

The LOEL (for teratogenicity) for mice subjected to 2,3,7,8-T<sub>4</sub>CDF is 10-30  $\mu$ g/kg/day (24). If one assumes that a monkey is a relatively good model for humans, exposure of an average 70 kg human to a single dose of 35 mg would be considered hazardous.

Chloracne, a side effect resulting from exposure to these toxic contaminants, has been well-studied (9, 27). Chloracne is described by the formation of comedones with or without straw-colored cysts and pustules which may lead to scarring. Several symptoms following exposure include the loss of appetite, nausea, edema of the hands and feet, possibly abdominal pain, and skin discoloration. Affected areas are normally the upper extremities including temples, cheeks, ears, the chest, and back. Usually, the hands, feet, and nose are not affected. Acute chloracne can result in edema of the face. Neurological symptoms include headaches, fatique, and emotional instability. Chloracnegenic chemicals are identified by the rabbit ear test in which the chemical is dissolved in propylene glycol and applied to the rabbit's ear. If the result is positive, erythema occurs within two days and hyperkeratosis develops in several weeks. Chloracne can persist for as long as 15

Effect		LOEL	

TABLE 2: LOEL<sup>a, b</sup> FOR 2,3,7,8-T<sub>4</sub>CDF IN MONKEYS (26)

Weight loss<500</th>Biochemical effect<500</td>Pathological/Histological<500</td>TeratogenicNot AvailableCarcinogenicNot AvailableImmunotoxicNot Available

<sup>a</sup>LOEL is defined as the lowest amount of pollutant ingested ( $\mu$ g) per kg of body weight per day which produces the defined effect. <sup>b</sup>The data is the result of daily single doses of T<sub>4</sub>CDF by intraperitoneal injection.

years following exposure. The disease was first described in Europe by Von Bettman in 1897 in workers manufacturing hydrochloric acid. Toxic residues resulting from accidents of exploding chlorophenol plants in France, Germany, and Great Britain, buried underground, were recently the cause of a chloracne outbreak in pipe fitting workers (27). Treatments may include surgery, dermabrasion, and the use of Vitamin A acid (0.05%-0.3%) in different bases.

Rats exhibit tumor formation as a result of exposure to TCDFs; however, such effects have not yet been observed in humans. One major concern is the possible long-term adverse effects of these contaminants, particularly the ultimate reproductive consequences in humans.

It is the objective of this thesis to shed some light on the photolytic activity of these PCDFs in aqueous solutions. Direct photoreaction quantum yields have been determined in the laboratory at 313 nm and are used in predicting rates of direct aqueous photolysis (28). These predictions are then compared with the rates of direct and indirect aqueous photolysis determined experimentally under sunlight conditions at 50°N latitude in the Experimental Lakes Area (ELA), Ontario, Canada. Both non-polar and polar degradation products were isolated and identified by GC-MS in several of these studies.

It has become evident that 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8- $P_5$ CDF, two common environmental pollutants, are still mysterious compounds with respect to their toxicity and

the environment. tend to behaviour PCDFs resist in microbial degradation, but they do undergo slow photodegradation (2). Although some data is available on the photodegradation of PCDFs and PCDDs in organic solvents at environmentally insignificant wavelengths (3,29-41), no information is available on the aqueous photolysis of these two PCDFs under environmental conditions. Although the upper solar irradiance cutoff is approximately 290 nm as a result of ozone filtration (42), the sun emits sufficient energy to break C-O, C-C, and C-Cl bonds (44). Provided that the compound contains chromophoric groups whose absorption spectra overlap the sun's spectrum on the earth's surface, direct absorption and subsequent photodegradation may occur, as is the case for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8persistent nature contaminants  $P_5 CDF$ . The of these emphasizes the significance of the small degree of photodegration. Photolytic degradation may, in fact, be the major degradation pathway for PCDDs and PCDFs in the environment, especially in natural waters where sensitized photolysis is known to occur (45).

## II. EXPERIMENTAL

### A. CHEMICALS

Reagent grade potassium chromate  $(K_2CrO_4)$  and sodium carbonate  $(Na_2CO_3)$ , supplied by the Aldrich Chemical Company (Milwaukee, WI), were used to prepare a chemical filter solution.

Two chemical actinometers, *p*-nitroacetophenone (PNAP) and *p*-nitroanisole (PNA); pyridine (PYR) (spectrophotometric grade, Gold Label), used as a quantum yield adjuster; and 4-nitrotoluene (PNT), used as an internal standard, were all purchased from Aldrich Chemical Company.

A series of nonradiolabelled PCDF congeners (see Table 3) were supplied by Wellington Laboratories (Guelph, ON) as standard solutions and were used without further purification.

Radiolabelled dibenzofurans,  $4,6^{-3}H_2-2,3,7,8$ -tetrachlorodibenzofuran ( ${}^{3}H-T_4CDF$ ) and  ${}^{14}C_6$ -dichlorophenyl-2,3,4,7,8-pentachlorodibenzofuran ( ${}^{14}C-P_5CDF$ ) with specific activities of 4.47 x 10<sup>12</sup> Bq/mmol (May 1988) and 1.25 x 10<sup>10</sup> Bq/mmol, respectively (see Figure 1); were purchased from Wellington Laboratories and further purified by preparative HPLC prior to use.

With 85:15 CH<sub>3</sub>OH/H<sub>2</sub>O as the mobile phase, five 1 µg portions of each PCDF were chromatographed on a C<sub>18</sub> column, collecting in a six minute window centered at the retention time of the PCDF. After collecting the parent material,

## TABLE 3: STANDARD PCDF CONGENERS, AS SUPPLIED BY WELLINGTON LABORATORIES

Congener	Purity	(%)	Solution/Solid
238-T <sub>3</sub> CDF	98	50	µg/mL (toluene)
$2348 - T_4 CDF$	98	44	µg/mL (isooctane)
2347-T <sub>4</sub> CDF	98	42	µg/mL (isooctane)
$2367 - T_4 CDF$	95	40	µg/mL (isooctane)
$2368 - T_4 CDF$	98	48	µg/mL (isooctane)
$2378 - T_4 CDF$	98	50	$\mu$ g/mL (toluene)
23478-P <sub>5</sub> CDF	98	50	$\mu$ g/mL (toluene)
$2378 - T_4 CDF$		100	$\mu$ g (crystalline)
23478-P <sub>5</sub> CDF		100	$\mu$ g (crystalline)



 $(4, 6-{}^{3}H_{2})-2, 3, 7, 8-TETRACHLORODIBENZOFURAN$ 



(<sup>14</sup>C<sub>6</sub>)-DICHLOROPHENYL-2, 3, 4, 7, 8- PENTACHLORODIBENZOFURAN

## FIGURE 1: MOLECULAR STRUCTURES OF TWO RADIOLABELLED PCDF CONGENERS

most of the methanol was evaporated via rotary evaporator. The PCDF was extracted into hexane, passed through an anhydrous sodium sulfate column, evaporated to dryness, and redissolved in acetonitrile. Radiopurities, established by HPLC-LSC, were 99.6% for  ${}^{3}\text{H-T}_{4}\text{CDF}$  and 99.9% for  ${}^{14}\text{C-P}_{5}\text{CDF}$ .

Pre-purified nitrogen gas used in concentrating solutions was supplied by Union Carbide (Winnipeg, MB).

Scintillation fluors, Scintiverse II and Atomlite were purchased from Fisher Scientific (Winnipeg, MB) and Biotechnical Systems (Boston, MA), respectively.

Lake water used to study environmental photolysis of PCDFs was obtained from Lake 375, ELA. (See Appendix 1 for lake water chemistry.)

Reagent grade, anhydrous sodium sulfate supplied by Mallinckrodt (Paris, KY) and Pyrex fiber glass wool (Corning Glass Works, NY) were Soxhlet extracted in acetone:hexane (1:1, v/v) for 23-27 hours prior to use. Sodium sulfate was stored in a glass bottle at 120°C.

Distilled water was redistilled in the presence of "Baker Analyzed" reagent potassium permanganate, supplied by J.T. Baker Chemical Company (Phillipsburg, NJ).

A trimethylsilyl donor, BSTFA [Bis (trimethylsilyl)trifluoroacetamide], purchased from Chromatographic Specialties (Brockville, ON), was used to prepare volatile derivatives for GC-MS analyses.

2,2'-dihydroxybiphenyl (99%) and 2-phenylphenol (99+%), supplied by Aldrich Chemical Company, were used as standards in testing the derivatization procedure.

Carbosorb, supplied by the Packard Instrument Co. (Downers Grove, IL) diluted 1:9 (v/v) with Scintiverse II was used as a trap for  ${}^{14}CO_2$  produced during photolysis.

All solvents used in sample preparation or as HPLC mobile phases were B & J Brand High Purity (Baxter Diagnostics Corporation, Canlab, Winnipeg, MB), unless otherwise specified.

### **B. INSTRUMENTATION**

### 1. LABORATORY PHOTOLYSIS

Quantum yield determinations for the direct aqueous photolysis of the two PCDF congeners were conducted in a RPR-100 Rayonet photochemical RMA-440 Merry-go-round reactor, equipped with 16 RPR 3000 Å lamps (The Southern New England Ultraviolet Co.) with a maximum energy output between 290 and 320 nm (46). Photochemical reaction cells consisted of an internal Pyrex (borosilicate glass) tube (10 mm i.d.), with a 5 mL capacity, fused to an outer Pyrex cylindrical tube (34 mm o.d.) (See Figure 2) (30).

The outer compartment of the cell was filled with the  $Na_2CO_3/K_2CrO_4$  chemical filter solution (47) to isolate the 313 nm band from the light source. The inner tubes contained either 2 mL of the aqueous PCDF solution or the appropriate actinometer solutions.

A 150 watt xenon lamp powered by a Perkin Elmer 150



FIGURE 2: DIAGRAM OF A TYPICAL PHOTOCHEMICAL REACTION CELL USED IN RAYONET PHOTOREACTOR. Xenon Power Supply was used to simulate sunlight conditions for generation of degradation products in the laboratory. A Perkin Elmer MPF-44 Fluorescence Spectrophotometer was used to verify the spectral distrubution of the xenon lamp emissions.

### 2. UV-VISIBLE SPECTROSCOPY

All UV-Visible spectra were obtained with a Hewlett-Packard model 8452A diode array spectrophotometer at ambient temperature. Quartz cells with a 1.0 cm path length (supplied by Baxter Diagnostics Corporation, Canlab, Winnipeg, MB) were used to obtain background corrected spectra in the 190-800 nm wavelength region.

### 3. HPLC ANALYSES

For the quantum yield study, quantitative analyses of PCDFs and actinometer solutions were conducted on a Waters Associates HPLC system equipped with a Model 6000A pump, a Rheodyne Model 7125 injector (100  $\mu$ L sample loop), a 25 cm x 3.2 mm (i.d.) Waters  $\mu$ Bondapak C<sub>18</sub> column (Waters Scientific), and a M440 UV detector (set at 254 nm for PCDF analysis, and 280 nm for the PNAP/PNA analyses).

4. LSC ANALYSES

All radioactive samples were analyzed either by

HPLC-LSC, in which fractions of HPLC eluent were collected and then analyzed by LSC (liquid scintillation counting), or by LSC alone. LSC was performed on a Beckman LS 7500 Liquid Scintillation System. Samples containing both tritium and carbon-14 isotopes were counted for 10 minutes on a dual label program, using the H# method with automatic quench compensation. Calibration of the instrument was performed with sealed <sup>14</sup>C-toluene, provided by Amersham, or with <sup>3</sup>H-toluene standards, prepared in the laboratory.  $\beta$ -Emissions from tritium and carbon-14 were monitored in the 0-397 and 397-655 counting channels, providing energy windows of 0-18 and 18-160 keV, respectively. All samples were counted to a  $2\sigma$  error of 2% with calculated error based on the 95% confidence level.

### 5. HRGC-LRMS ANALYSES

All GC-MS analyses were performed with a Hewlett Packard 5890A gas chromatograph coupled to a Hewlett Packard 5970B Series quadrupole mass spectrometer via capillary direct interface. The electron impact mass spectrometer was operated at an electron energy of 70 eV. All injections were performed in the splitless mode with the column head pressure maintained at 10 psi. Helium served as the carrier gas and was maintained at a volumetric column flow rate of 0.92 mL/min (linear flow rate of 31.3 cm/s) on a DB-5 column (30 m x 0.25 mm x 0.1  $\mu$ m); and 0.54 mL/min (17.4 cm/s) on a DB-1701 column (60 m x 0.256 mm x 0.25  $\mu$ m); septum purge
remained consistent at ~2 mL/min. Both fused silica capillary columns were purchased from J & W Scientific; Folsom, CA.

6. HRGC-HRMS ANALYSES

Additional structural confirmation was obtained by analysis on a GC-MS system consisting of an HP5890 GC (25 m DB-5 capillary column) and a high resolution double focusing magnetic sector mass spectrometer (VG 7070E-HF) at electron energies of 75 and 15eV.

Positive chemical ionization mass spectrometry was also performed on this system with ammonia reagent gas.

#### C. QUANTUM YIELD DETERMINATIONS

Both PCDF congeners, originally in 1.2 mL of toluene, were quantitatively transferred to separate 2 mL volumetric test tubes. The solvent was then evaporated under a gentle stream of nitrogen, in a warm water bath before being brought up to the 2 mL mark with filtered spectrophotometric grade acetonitrile. The concentration of  $2,3,7,8-T_4CDF$ (6.30 x  $10^{-5}$  M) was established using previously determined response factors. Similarly, concentration of the  $2,3,4,7,8-P_5CDF$  was determined by HPLC to be  $8.00 \times 10^{-5}$  M.

Aqueous solutions (1:1,  $CH_3CN/H_2O$ , v/v) of both PCDFs were prepared by slowly adding 1.5 mL of the PCDF standard solution to 5 mL of HPLC grade water and 3 mL of  $CH_3CN$  in a

10 mL volumetric flask, with constant swirling, and diluting to the mark with  $CH_3CN$ . Concentrations of the aqueous 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF solutions were 9.45 x 10<sup>-6</sup> M and 1.20 x 10<sup>-5</sup> M, respectively.

The chemical filter solution was prepared with 0.290 g of  $K_2CrO_4$  and 1.06 g of  $Na_2CO_3$  in 1 L of HPLC grade water. UV-visible absorption spectra of both aqueous PCDF solutions and the chemical filter solution were obtained prior to the photolytic experiments.

Approximate half-lives were estimated by performing a trial photoreaction of each PCDF, allowing selection of the chemical appropriate actinometers. The PNAP/PYR actinometer, used for photolysis studies of 2,3,7,8-T<sub>4</sub>CDF, was prepared by dissolving 4.0 mg of PNAP in 10 mL of CH<sub>3</sub>CN, and diluting 1 mL of this solution and 0.0593 g of pyridine to 1 L with HPLC grade water. The resulting solution contained 4.8 x 10<sup>-6</sup> M PNAP and 1.50 x 10<sup>-3</sup> M PYR. The PNA/PYR actinometer, used for exposures of  $P_5CDF$ , was prepared in a similar manner with final concentrations of 7.9 x  $10^{-6}$  M PNA and 2.22 x  $10^{-3}$  M PYR.

The outer compartments of four photolytic cells (see Figure 2) were filled with the chemical filter solution; 1.5 mL of 9.45 x  $10^{-6}$  M aqueous 2,3,7,8-T<sub>4</sub>CDF was pipetted into the inner tube of one cell, and 1.5 mL of PNAP/PYR actinometer was pipetted into another three cells. All four cells were simultaneously exposed in the photoreactor. Microliter aliquots of the exposed PCDF solution were removed every 5 min for 30 min and analyzed immediately by

HPLC with 100% methanol as the mobile phase, a 1.0 mL/min flow rate, and the detector set to 254 nm. Cells containing the actinometer solutions were removed at approximately 4, 8, and 16 hours and analyzed by HPLC with a  $50:50 \text{ CH}_3\text{CN/H}_2\text{O}$ mobile phase, a 1.0 mL/min flow rate, and the detector set to 280 nm. Triplicate injections of the reacted PCDF solution were made for each subsample. Peak heights were used to monitor degradation of the PCDFs and the actinometers.

In the photolysis of the  $2,3,4,7,8-P_5CDF$ , eight cells were filled with chemical filter solution; one cell contained 1.0 mL of the aqueous  $P_5CDF$  (1.20 x  $10^{-5}$  M), and the other seven contained 1.0 mL of PNA/PYR actinometer. The exposed PCDF solution was sampled every 15 min for 105 min and analyzed immediately by HPLC as described above. Actinometer solutions were also removed at 15 min intervals for 105 min, spiked with 40  $\mu$ L of 2.08 x 10<sup>-4</sup> M PNT, as internal standard, and analyzed in triplicate by HPLC with  $65:35 \text{ CH}_{3}\text{OH}/\text{H}_{2}\text{O}$  (1.0 mL/min) at 280 nm. PNAP and PNA concentrations were determined from a previously prepared standard curve of the PNA/PNT peak height ratio as a function of the concentration of PNA. All photolytic experiments were replicated at least two times.

#### D. KINETICS OF SUNLIGHT PHOTOLYSIS

#### 1. PREPARATION OF SOLUTIONS

All glassware was thoroughly cleaned and sterilized at 180°C for 4-5 hours. Two actinometer solutions, PNAP/PYR and PNA/PYR, were prepared to monitor sunlight intensities for chemicals with kinetic half-lives greater than 12 hours and less than 12 hours, respectively (42). Stock solutions of PNAP (0.3315 mg/mL) and PNA (0.03222 g/mL) were prepared in  $CH_3CN$ . Actinometer solutions were prepared by diluting 10 mL of stock PNAP and 6.67 mL pyridine, or 10 mL of stock PNA and 0.27 mL pyridine, to 1 L with HPLC grade water, filter-sterilized through GV 0.22 μ**m** filters (Waters-Division of Millipore, Bedford, MA). The concentrations of the final aqueous solutions were 2.01 x 10<sup>-5</sup> M PNAP in 8.28 x  $10^{-2}$  M PYR, and 2.10 x  $10^{-5}$  M PNA in 3.35 x  $10^{-3}$  M PYR.

35 mL of the PNAP/PYR actinometer were pipetted into ten 50 mL Pyrex centrifuge tubes and 35 mL of the PNA/PYR actinometer were added to another ten tubes. All tubes were wrapped in foil immediately following preparation and stored in the dark until exposure at ELA.

Ten (10) mL of filter-sterilized  $CH_3CN$  (43) and 25 mL of filter-sterilized HPLC water (43) were added to 18-50 mL Pyrex centrifuge tubes, producing solutions of pH 6.45. 45 ng of purified  ${}^{3}H-2,3,7,8-T_4CDF$  and 40 ng of purified  ${}^{14}C-2,3,4,7,8-P_5CDF$  were spiked into each of the aqueous solutions. Although the water solubilities (17) are

exceeded by 3.5 and 5.1 fold for the respective congeners, the 28.6%  $CH_3CN$  (v/v) in each sample justified these concentrations. Each tube was tightly capped, inverted to ensure homogeneity, wrapped in foil, and stored in the dark until exposure to sunlight at ELA.

Another 18-50 mL Pyrex centrifuge tubes were filled with 35 mL of filter-sterilized lake water (43), spiked with the same amount of both PCDF congeners, tightly capped, and stored as above.

To monitor for biological or chemical degradation, six Pyrex tubes were prepared with the same amounts of PCDFs in filter-sterilized lake water (43). These samples were not exposed to sunlight, but remained wrapped in foil throughout the experiment.

#### 2. SUNLIGHT PHOTOLYSIS

All tubes were placed in a rack, spray-painted with a flat-black finish to minimize reflections, at a 45° angle to the horizontal. This rack was in turn placed on a black platform just above the surface of lake 375 (ELA) (see Appendix 2) to study photolysis at the lake surface. Samples were removed from sunlight over the sampling period 11:00 AM June 26, 1989 to 3:00 PM June 29, 1989 (see Table 4), and weather conditions were periodically recorded.

Five (5) mL of hexane were added to all PCDF solutions on site at each sampling time. Solutions were foil wrapped and transported to the laboratory for further work-up. The

#### TABLE 4: SAMPLING TIMES & FOR SUNLIGHT PHOTOLYSIS

Time PNAP/PYR Direct<sup>b</sup> PNA/PYR Indirect<sup>c</sup> Control (h)

0.00	x		x	x	
0.25				x	
0.50		х		x	
1.00		х	x	x	
2.00			x		
2.50		х		x	
3.00	х				
6.00		x	x	x	x
8.00	х				
10.00		x	x	х	
27.00		x		х	. <b>X</b>
34.25	х	x			
51.50		x		х	
76.00	x	x			х

"Samples were taken as indicated (x), with t=0 at 11:00 AM, June 26, 1989." "Direct refers to the photolysis of PCDFs in

distilled water/acetonitrile.

'Indirect refers to the photolysis of PCDFs in lake water.

preparation of PCDF/actinometer solutions and sunlight photolyses were performed by Dr. K. J. Friesen.

3. SAMPLE WORK-UP AND ANALYSIS

#### a) Actinometer Solutions

All PNAP/PYR solutions were spiked with 350  $\mu$ L of 2.62 x 10<sup>-3</sup> M PNT. Successive 30  $\mu$ L injections were analyzed by HPLC with a 55:45 CH<sub>3</sub>OH/H<sub>2</sub>O mobile phase at a flow rate of 1.0 mL/min and 280 nm detection. Adjusted retention times of PNAP and PNT were 6:30 min and 14:10 min, respectively. Duplicate actinometer solutions were removed at each sampling time, and each sample was analyzed in triplicate. Concentrations of PNAP were determined from a standard curve of PNAP/PNT peak height ratio vs amount of PNAP.

All PNA/PYR solutions were also spiked with PNT, as above, but were analyzed with 70:30 CH<sub>3</sub>OH/H<sub>2</sub>O at the same flow rate and wavelength of detection. PNA and PNT adjusted retention times were 8:00 min and 10:00 min, respectively. A standard curve was also used to establish concentrations of PNA.

b) PCDF Solutions

All aqueous solutions of PCDFs were quantitatively transferred to 60 mL separatory funnels, adjusted to a pH of  $\approx$ 9 with the addition of several drops of 0.1 M KOH, and extracted four times with 5 mL portions of hexane. The solutions were made basic to sustain possible hydroxylated products in the aqueous phase. The hexane was passed

through a small  $Na_2SO_4$  column and collected in a 100 mL roundbottom flask. Following extraction, glassware and drying columns were rinsed with 24 mL of hexane to remove residual radioactivity from the glass. Recoveries, established with standard  ${}^{3}H-T_{4}CDF$  and  ${}^{14}C-P_{5}CDF$ , were 96% and 105% for the two congeners, respectively. Immediately following extraction, 4 mL of the extracted aqueous phase was added to 12 mL of Atomlight and analyzed by liquid scintillation counting to monitor for nonextractable activity. Samples were reduced to a volume of approximately 2 mL by rotary evaporation, quantitatively transferred to 15 mL graduated centrifuge tubes, and concentrated to near dryness with a gentle stream of nitrogen. Final volumes were adjusted to 500  $\mu$ L with hexane. Solutions were mixed to ensure homogeneity and transferred to 1.5 mL amber, septum-sealed vials. After carefully marking the meniscus, each vial was stored at 7°C until analysis.

Concentrations of parent  ${}^{3}H-2,3,7,8-T_{4}CDF$  and  ${}^{14}C-2,3,4,7,8-P_{5}CDF$  were determined by HPLC-LSC using 85:15 CH<sub>3</sub>OH/H<sub>2</sub>O as mobile phase at 1.0 mL/min and 254 nm detection. Injections of the individual purified standards established an HPLC recovery of 80% for T<sub>4</sub>CDF and 90% for P<sub>5</sub>CDF.

Aliquots (25  $\mu$ L) of each hexane extract were analyzed by HPLC collecting three minute fractions into scintillation vials. A three minute fraction was collected prior to each injection to establish background activity. Scintiverse II (12 mL) was added to all fractions prior to LSC analysis.

Results were used to obtain reconstructed chromatograms and mass balance relationships.

#### E. IDENTIFICATION OF NON-POLAR DEGRADATION PRODUCTS

#### 1. GENERATION OF DEGRADATION PRODUCTS

#### a) Spectral Distribution Of Xenon Lamp

Although xenon lamps have a spectral distribution similar to sunlight (44), the actual emission spectrum of the xenon light source used in this experiment was verified with a fluorimeter (see Figure 3). Spectra were scanned from 190-800 nm with the slit width set to 3 nm and the attenuation set appropriately. The spectral distribution of the xenon lamp was determined without the presence of a filter, with Pyrex glass (~2 mm thickness), with a 290 nm filter, and a combination of the two. Although the lower limit of emission of the xenon lamp, used in subsequent photolyses, was approximately 250 nm, Pyrex glass filtered out 95% of the wavelengths below ~276 nm in close agreement with the 290 nm filter of the fluorimeter (see Figure 4).

A UV-visible absorption spectrum of the 2 L separatory funnel (wall thickness ~4 mm) used for laboratory photolysis, revealed that less than 1% of the wavelengths below 286 nm were transmitted. Solarization of glass, with aging, will shift the lower wavelength cutoff to even higher wavelengths (48). Since the solar cutoff for radiation reaching the earth's surface is approximately 290 nm (42),



FIGURE 3: SPECTRAL IRRADIANCE OF A XENON LAMP AS MEASURED BY A PERKIN ELMER FLUORIMETER, WITH SLIT WIDTHS SET TO 3 nm.



FIGURE 4: EFFECT OF VARIOUS FILTERS ON XENON LAMP EMISSIONS.

these Pyrex filtered (by 4 mm glass) xenon lamp emissions are appropriate simulations of sunlight for laboratory studies.

b) Preparation of PCDF Solutions

In order to study the fate of PCDFs in the environment, lake water was determined to be more suitable for photolysis than distilled water. Approximately 400  $\mu$ L of hexane were added to each vial containing the crystalline PCDFs, allowing solubilization overnight. Each solution was quantitatively transferred into a 10 mL volumetric flask using multiple hexane rinses, with final concentrations of both congeners at 10 ng/ $\mu$ L. Purities of the PCDFs were established by GC-MS (since they were not provided by the supplier, see Figure 5) as 96.0% and 98.5% for P<sub>5</sub>CDF and T<sub>4</sub>CDF, respectively.

c) Laboratory Photolysis of PCDFs

All glassware was cleaned and oven dried at 130°C. The xenon lamp was used as a simulated sunlight source to non-polar degradation intermediates (49). produce Α circular photoreaction chamber (approximately 55 CM in diameter) was constructed of cardboard and lined with aluminum foil to maximize reflections. The top and bottom covers of the chamber were also lined with foil. The 2 L separatory funnel, containing the aqueous PCDF solution, and the xenon lamp were placed in the chamber approximately 20 fans were used to maintain a water CM apart. Two temperature of ~50°C and an air temperature of 26°C in the chamber during photolysis.



FIGURE 5: TOTAL ION CHROMATOGRAMS OF PCDF SOLUTIONS, DETERMINED BY GC-MS ANALYSIS ON A DB-5 CAPILLARY COLUMN (PROGRAM #1).

A polar solvent was used to introduce PCDFs into the lake water to prevent significant losses to glass (50). Therefore, the hexane (containing 1550 ng of PCDF) was evaporated to dryness under a gentle stream of nitrogen and the final volume was brought up to 155  $\mu$ L with CH<sub>3</sub>CN. A 2 L cylindrical separatory funnel, containing 1.5 L of filter-sterilized lake water, was spiked with 1550 ng of non-labelled  $2, 3, 4, 7, 8 - P_5 CDF$ in  $CH_3CN.$ То avoid cross-contamination between congeners, a second 2  $\mathbf{L}$ cylindrical separatory funnel was used for T<sub>4</sub>CDF exposures. Separatory funnels were wiped free of fingerprints and mixed well prior to exposures. Four exposures, each of 4-6 hours duration, were performed. The solutions were pooled in an attempt to isolate significant amounts of degradation products for identification.

#### 2. SAMPLE WORK-UP

Following exposures, the lake water was extracted through three  $C_{18}$  Sep-Pak Cartridges in series (each pre-wet with 2 mL of methanol and 10 mL of HPLC grade water) into a 2 L flask, with flow rates of approximately 5-10 mL/min, using in-house vacuum. Sep-Paks were dried under a gentle stream of  $N_2(g)$  for 20 min and eluted with 12 mL of hexane. This method yielded recoveries of >98% for 2,3,4,7,8-P<sub>5</sub>CDF, therefore, similar recoveries were expected for other PCDFs which may be produced by photolysis. Any water present, was removed with a pipetting syringe. All extracts from the

four exposures were combined, and concentrated to 50  $\mu L$  in hexane.

A blank, consisting of filter-sterilized lake water (43) without PCDF, was photolyzed and worked up as above to check for background levels of contaminants in lake water. A control, consisting of lake water spiked with PCDF, remained in the dark for the same period of time as the photolyzed samples. This sample established levels of key non-polar contaminants in the original starting PCDF.

3. GC-MS ANALYSES

Standard solutions (5-12 ng/ $\mu$ L) of T<sub>4</sub>CDFs and T<sub>3</sub>CDF were prepared for GC retention time confirmation by evaporating toluene, if present, under N<sub>2</sub>(g), quantitatively transferring solutions to 5 mL volumetric flasks, and adjusting the volumes with iso-octane.

Three temperature programs (see Appendix 3) and two capillary columns were used in identifying and confirming the degradation products produced by photolysis of both  $P_5$ CDF and  $T_4$ CDF.

Controls, blanks, and photolyzed samples were analyzed using the appropriate programs.

## F. ISOLATION AND IDENTIFICATION OF POLAR DEGRADATION PRODUCTS

1. GENERATION OF POLAR PRODUCT(S)

Filter-sterilized lake water (1.7 L) (43) was spiked with either 4  $\mu$ g of purified <sup>14</sup>C-2,3,4,7,8-P<sub>5</sub>CDF in CH<sub>3</sub>CN or stock non-radiolabelled P<sub>5</sub>CDF in CH<sub>3</sub>CN. The aqueous solutions were photolyzed for approximately 12 hours and extracted with six C<sub>18</sub> Sep-Paks to remove non-polar degradation products along with unreacted, parent P<sub>5</sub>CDF. The aqueous phase was evaporated in the fumehood under low continuous heat, with the last 5 mL volatilized without heating.

2. DERIVATIZATION OF POLAR PRODUCT(S)

Derivatization was required to increase the volatility of the polar degradation products(s) for GC analysis. BSTFA was selected since it forms stable trimethylsilyl (TMS) derivatives of potential degradation products, including alcohols, carboxylic acids, and phenols. Α standard, 2-phenylphenol µg), was (420 spiked into the beaker containing the polar material to verify the effectiveness of the derivatization procedure. Most of the yellow/brown residue, caked to the walls of the beaker, was dislodged using a metal scoopula. The residue was soaked in 15 mL of THF for 12 hours, and then transferred to a 15 mL graduated

centrifuge tube. THF was evaporated to dryness under  $N_2(g)$ in a warm water bath. THF/BSTFA (3:2;v/v) (50-100 µL) and 10 mL of THF were added to the dry tube. The tubes were capped, shaken, and placed in a water bath at 70°C for 20 min (41). After evaporating all solvents and rinsing down the walls of each tube with THF, volumes of solutions were adjusted to 50 µL with hexane.

1.7 L of filter-sterilized lake water was photolyzed, extracted, and derivatized as described above to check for possible derivatization of naturally occuring polar components present in lake water. The final solution was concentrated to 5  $\mu$ L prior to GC-MS analysis.

3. ANALYSES

Each solution (1.4  $\mu$ L) was analyzed by HRGC-LRMS using program #4 (see Appendix 3). A derivatized product detected by this technique was further analyzed by HRGC-HRMS, with both EI and CI techniques, using similar conditions (program #4), with the exception of a change in injection port temperature to 255°C.

#### G. ADDITIONAL EXPERIMENTS

1. EVOLUTION OF <sup>14</sup>CO<sub>2</sub> DURING PHOTOLYSIS OF PCDFs

An attempt to trap  ${}^{14}CO_2(g)$  evolving during the exposure of  ${}^{14}C-2,3,4,7,8-P_5CDF$  in lake water was made over

a period of 76 hours. The headspace above the solution being photolyzed was swept out via  $N_2(g)$ , and into scintillation vials containing 1 mL Carbosorb and 9 mL Scintiverse II (51). LSC analyses yielded low <sup>14</sup>C activity over the 76 hour period; hence, this study was not pursued further.

#### 2. ISOLATION OF PRODUCTS FROM DIRECT PHOTOLYSIS

Three attempts were made to generate non-polar degradation intermediates from the photolysis of 2,3,7,8- $T_4CDF$  in pure, distilled water. Filter-sterilized distilled water (43) was spiked with 600 ng of 2,3,7,8-T<sub>4</sub>CDF in  $CH_3CN$ , allowed to equilibrate for several hours, then exposed to the xenon lamp for three different periods of time, including 29, 31, and 63 hours. Another attempt was made to isolate degradation intermediates by photolyzing T<sub>4</sub>CDF in 30:70  $CH_3CN/H_2O$  for 46 hours. Liquid-liquid extraction with hexane, sample work-up, and analysis yielded non-detectable levels of products. Therefore, no attempts were made to study  $P_5CDF$  degradation in distilled water, since  $P_5CDF$ degraded approximately 7 times slower than  $T_4CDF$ .

## III. <u>RESULTS AND DISCUSSION</u>

### A. DIRECT PHOTOLYSIS OF 2,3,7,8-T4CDF AND 2,3,4,7,8-P5CDF

#### 1. LABORATORY QUANTUM YIELD DETERMINATIONS

Despite their hydrophobic nature, detectable amounts of PCDFs have been found in natural water bodies (52, 53) and therefore could potentially undergo both direct and indirect photolytic transformations in the aquatic environment. Computer programs have been developed to predict the rate of direct phototransformation  $(k_{DE})$  of organic compounds in surface waters provided that the quantum yields for direct aqueous photolysis  $(\phi_{dc})$  are available.

During photolysis, the intensity of the light source (artificial or natural) plays an important role in determining the degradation rate of the chemical and must be carefully monitored. Although there are several ways of measuring solar/lamp irradiances (radiometry, photometry, and actinometry), actinometry has powerful advantages over other instrumental procedures and is frequently the method of choice (44). Actinometer solutions, subjected to exactly the same light conditions as the PCDF solutions, adequately monitor the solar/lamp flux experienced by the analyte. For sunlight studies, these variations in light intensity are also affected by weather conditions, ozone layer thicknesses, time, season, latitude, and elevation. Two actinometers, *p*-nitroacetophenone (PNAP) and *p*-nitroanisole

(PNA), have been well characterized for use in sunlight kinetic experiments. PNAP is the actinometer of choice for experiments where greater than 12 hours of exposure are required; whereas, PNA is used for experiments of less than 12 hours duration (42). Both of these actinometers behave well kinetically, are wavelength independent, and absorb radiation moderately in the 290-400 nm (sunlight) region (42, 54, 55). The quantum yields ( $\phi$ ) of these actinometers may be adjusted by careful control of pyridine concentrations according to:

$$\phi_{\text{PNAP/PYR}} = 0.0169[\text{PYR}] \qquad [1]$$

$$\phi_{PNA/PYR} = 0.44[PYR] + 0.00028$$
[2]

The quantum yield, which describes the efficiency with which light absorption leads to degradation, is defined as the number of molecules that react per number of photons absorbed by the analyte. The  $\phi$  adjustment ensures that the rate of photodegradation of the actinometer is similar to that of the test chemical (PCDF, in this study), thus ensuring careful monitoring of light during the entire exposure period. Upon exposure to a light source, PNA undergoes a photonucleophilic substitution reaction with pyridine (56):



PNAP reacts by a similar mechanism (42), however, its photoproducts have not been successfully identified. UV-visible spectra of both PCDFs (Figure 6 and 7) illustrate that these compounds exhibit weak absorptions in the same wavelength region as the actinometers (57).

Quantum yield determinations and direct aqueous photolysis for PCDFs are limited by their low water solubilities. Acetonitrile, with refractive а index (1.3441) similar to that of water (1.3330), should not affect molar absorptivities of strong absorption bands of non-polar compounds (58, 59). Therefore, acetonitrile was used as a cosolvent (50:50, v/v,  $CH_3CN/H_2O$ ) in determining UV-visible spectra of  $T_4CDF$  and  $P_5CDF$ . Although absorption maxima exist for both congeners at 303 and 313 nm, the tailing absorptions to higher wavelengths (Table 5) are responsible direct photolytic for degradation under environmental conditions.

For quantum yield determinations, 313 nm was used since



WAVELENGTH (nm)

FIGURE 6: UV-VISIBLE ABSORPTION SPECTRUM OF 9.45 x  $10^{-6}$  M 2,3,7,8-T<sub>4</sub>CDF IN 50:50 (v/v) CH<sub>3</sub>CN/H<sub>2</sub>O.



NAVELLINGIN (IIII)

# FIGURE 7: UV-VISIBLE ABSORPTION SPECTRUM OF 1.20 x $10^{-5}$ M 2,3,4,7,8-P<sub>5</sub>CDF IN 50:50 (v/v) CH<sub>3</sub>CN/H<sub>2</sub>O.

1ABLE 5 : MOLAR 2,3,7,	ABSORPTIVITIES, $\in$ (M <sup>*</sup> 8-T <sub>4</sub> CDF AND 2,3,4,7	<sup>-</sup> 'cm <sup>-</sup> '), OF <sup>a</sup> <sup>7</sup> ,8-P <sub>5</sub> CDF.
Wavelength (nm)	2,3,7,8-T <sub>4</sub> CDF	2,3,4,7,8-P <sub>5</sub> CDF
297.5 300.0 302.5 305.0 307.5 310.0 312.5 313.0 315.0 317.5 320.0	28290 30480 32370 31950 27790 24410 25470 25470 25790 24930 17990 9310	24060 25210 25540 23790 20270 17430 16810 16810 16770 15820 12740 9410
323.1 330.0	3730 620	6390 3180

<sup>a</sup>Concentrations of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF were 9.45 x  $10^{-6}$  M and 1.20 x  $10^{-5}$  M, respectively; in 1:1 (v/v), CH<sub>3</sub>CN/H<sub>2</sub>O

the chemical filter solution allowed isolation of this wavelength (Figure 8).

Analyses of the degradation of simultaneously exposed PCDF and actinometer solutions in the Rayonet photoreactor are summarized in Tables 6 and 7. Analyses were performed by HPLC, with concentrations determined by peak height measurements according to:

$$C_{t} = C_{o} \frac{(PEAK HEIGHT)_{t}}{(PEAK HEIGHT)_{o}}$$
[3]

where  $C_t$  = concentration of PCDF at time,t and  $C_{\circ}$  = concentration at t = 0. Concentrations of the PCDFs were monitored from approximately 10-70% transformation which is within the range in which first-order kinetics is expected (44). In studying the photolytic degradation of  $T_4CDF$ , the PNAP solutions were sampled over a longer time period than solutions since rates of  $T_4CDF$  and actinometer T₄CDF photodegradation were not well matched. However, the excellent correlation coefficient describing the first-order kinetics of PNAP degradation (r = 0.994) provided a reliable time-averaged intensity of the light incident on the From simple observation, it is evident that solutions. there is a difference in the rates of degradation between the two PCDF congeners; however, light intensity must be accounted for before any meaningful comparison between the two congeners can be made.





FIGURE 8: UV-VISIBLE ABSORPTION SPECTRUM OF THE CHEMICAL FILTER SOLUTION (0.29031 g  $K_2CrO_4$  AND 1.05980 g  $Na_2CO_3$  IN 1 L OF WATER).

X Degradation 1.4 5.8 4.5 2.9 8.1 8.8 8 11.8 15.0 TABLE 6: PHOTODEGRADATION OF 2,3,7,8-T,CDF<sup>a</sup> AND PNAP ln(A<sub>t</sub>/A<sub>o</sub>) -0.125 -0.163 -0.014 -0.019 -0.059 -0.046 -0.029 -0.085 -0.092 Experiment 313 nm. Number - C @ n N m - N 0 Time (h) Exposure SOLUTIONS AT 4.0 8.0 8 7.5 16.0 16.0 16.0 4.1 7.0 X Degradation 36.1 39.5 38.2 45.9 42.1 44.7 15.7 16.3 19.3 23.9 24.6 38.2 29.6 32.8 33.8 9.9 9.3 10.6 ACTINOMETER ln(ct/c°) -0.615 -0.548 -0.592 -0.097 -0.171 -0.178 -0.340 -0.413 -0.502 -0.104 -0.215 -0.274 -0.282 -0.300 -0.448 -0.481 -0.351 Experiment Number - C - E - C E NΘ 2 0 **N** m ----- N m Time (min) Exposure ഗ 2 15 20 25 30

r

<sup>a</sup> Aqueous T<sub>4</sub>CDF solution, [C]<sub>o</sub> = 9.45 x 10<sup>-6</sup> M, in 1:1 (v/v) CH<sub>3</sub>CN/H<sub>2</sub>O.

 $C_t$  is the concentration of the  $T_4\,\text{CDF}$  at time, t.

For PNAP, [A]<sub>o</sub> = 4.84 x 10<sup>-6</sup>M with [PYR] = 1.5 x 10<sup>-3</sup>M.  $A_t$  is the concentration of the actinometer at time, t. q

AND PNA		% Degradation	17.5 20.3 21.9	27.1 28.7 31.9	27.5 40.3 32.8	37.1 50.1 42.7	58.5 58.9 58.7	66.3 63.5 57.8	69.6 72.4 65.2
3,4,7,8-P <sub>5</sub> CDF <sup>a</sup>	AT 313 nm.	ln(At/A°)	-0.192 -0.226 -0.245	-0.316 -0.339 -0.384	-0.321 -0.515 -0.397	-0.463 -0.696 -0.556	-0.879 -0.888 -0.885	-1.090 -1.010 -0.864	-1.190 -1.290 -1.056
10N OF 2,3	SOLUTIONS	% Degradation	11.7 33.8 13.1	27.7 45.6 22.4	34.3 54.3 25.0	39.2 60.3 26.2	52.8  45.0	54.8  48.7	  56.0
DEGRADAT	METER <sup>b</sup> S	ln(c,/c。)	-0.125 -0.412 -0.140	-0.324 -0.609 -0.253	-0.421 -0.783 -0.288	-0.497 -0.924 -0.304	-0.750  -0.597	-0.79 <b>4</b>  -0.668	  -0.916
PHOTOI	ACTINO	Experiment Number	N M	- ~ %	- ~ ~ ~	- 0 m	- 0 m	~ m	1 7 B
7:				<del>, 19 allait - ar <sup>19</sup> de 'un Tras-ur</del> us					
TABLE		Exposure Time (min)	15	30	ۍ: ۲:	60	75	06	105

<sup>a</sup> Aqueous  $P_sCDF$  solution, [C]<sub>o</sub> = 1.20 x 10<sup>-5</sup> M, in 1:1 (v/v)  $CH_3CN/H_2O$ 

 $C_{t}$  is the concentration of the  $P_{5}\text{CDF}$  at time, t.

<sup>b</sup> For PNA,  $[A]_{o} = 7.90 \times 10^{-6} \text{M}$  with [PYR] = 1.5 x 10^{-3} \text{M}. A<sub>t</sub> is the concentration of the actinometer at time, t.

The quantum yields for direct photolysis of a chemical in weakly absorbing, dilute, aqueous solutions, may be calculated according to (60):

$$\Phi = \frac{-k_p}{2.303 I_{Q\lambda}(A/V) \epsilon_{\lambda} l}$$
[4]

where  $I_{O\lambda}$  is the incident light intensity at wavelength,  $\lambda$ (nm);  $\epsilon_{\lambda}$  the molar absorptivity of the compound (M<sup>-1</sup>cm<sup>-1</sup>), 1 the pathlength, A the exposed area of the solution, V the volume of solution in the vessel, and  $k_P$  the first-order photodegradation rate constant. Since equation [4] requires the exact intensity of light incident on the solutions, actinometer solutions with well-known quantum yields are required to calibrate Inl. Since both the PCDF and actinometer solutions were exposed in the reactor simultaneously, equation [4] is applicable not only to the PCDF solutions, but also to the actinometer solutions. Writing simultaneous equations for PCDF and actinometer, a simple expression may be derived for use in calculating quantum yields for the direct photolysis of the PCDFs at a particular wavelength,  $(\phi_{dc,\lambda})$ , under laboratory conditions (43):

$$\Phi = \frac{(k_{dc,\lambda})(\epsilon_{A,\lambda})}{(k_{dA,\lambda})(\epsilon_{c,\lambda})} \cdot \Phi_{A}$$
[5]

where  $k_{dc,\lambda}$  and  $k_{dA,\lambda}$  are first-order photodegradation rate

constants and  $\epsilon_{c,\lambda}$  and  $\epsilon_{A,\lambda}$  are wavelength specific molar absorptivities for the PCDF congener and actinometer, respectively. Since quantum yields were determined at 313 nm,  $\epsilon_{313}$  of PNAP and PNA, 2056 M<sup>-1</sup>cm<sup>-1</sup> and 10300 M<sup>-1</sup>cm<sup>-1</sup>, respectively (44) were required. These rate constants are obtained from slopes of a first-order treatment of photodegradation:

$$\ln (C_t/C_o) = -k_{dc}t$$
 [6]

where  $C_t$  and  $C_o$  have been previously defined, and  $k_{d\,c}$  is the negative slope. A similar equation may be used for the actinometer, providing  $k_{dA}$  as the negative slope. Figures 9 and 10 are typical first-order plots illustrating the kinetics of photodegradation of  $T_4CDF$  and  $P_5CDF$  exposed along with the appropriate actinometers. A good linear relationship was observed for both PCDF congeners and their respective actinometers. First-order degradation rate constants and quantum yields for the two PCDF congeners are summarized in Table 8. The quantum yields for direct aqueous photolysis at 313 nm ( $\phi_{dc}^{313}$ ) of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CF were calculated by equation [5] to be (2.9  $\pm$ 0.5) x  $10^{-4}$  and (6.6 ± 0.9) x  $10^{-4}$ , respectively with approximate deviations within triplicate results of ±15%. Although both values are of the same order of magnitude, the quantum yield for direct aqueous photolysis of P<sub>5</sub>CDF is approximately 2.3 times larger than that of  $T_4CDF$ . The higher quantum yield for  $P_5CDF$  indicates that this congener



FIGURE 9: PLOT OF PHOTOLYTIC DEGRADATION OF 2,3,7,8-T<sub>4</sub>CDF AND PNAP ACTINOMETER AT 313 nm. CORRELATION COEFFICIENTS FOR T<sub>4</sub>CDF AND PNAP DEGRADATION WERE 0.998 AND 0.993, RESPECTIVELY. PRECISION OF EACH DATUM POINT WAS WITHIN  $\pm 3\%$ .



FIGURE 10: PLOT OF PHOTOLYTIC DEGRADATION OF 2,3,4,7,8- $P_5$ CDF AND PNA ACTINOMETER AT 313 nm. CORRELATION COEFFICIENTS FOR  $P_5$ CDF AND PNA DEGRADATION WERE 0.984 AND 0.971, RESPECTIVELY. PRECISION FOR EACH DATUM POINT WAS WITHIN ±3%.

TABLE 8:	: DIREC DETEI	CT PHOTORE. RMINED AT	ACTION QL 313 NM	JANTUM YIELDS
Congener	Trial	k dc <sup>a</sup> (h <sup>-1</sup> )	k dA b (h <sup>-1</sup> )	φ <sup>313</sup> c dc ( x 10 <sup>-4</sup> )
2,3,7,8-T <sub>4</sub> CDF	- N M	1.19 1.13 1.13	0.0064 0.0092 0.0087	3.56 2.46 2.64
	Average:	(1.2 ± 0.03)	(0.008 ± 0.001)	(2.9 ± 0.5)
2,3,4,7,8-P <sub>5</sub> CDF		0.536 0.684	0.727 0.702	5.65 7.47
	Average:	(0.61 ± 0.07)	(0.72 ± 0.01)	(6.6 ± 0.9)
<sup>a</sup> k <sub>de</sub> represents	the direct <sub>I</sub>	photoreaction first c	order rate constant	for the PCDF solution,

calculated by equation (6).

- $^{
  m b}\,k_{
  m dA}$  represents the direct photoreaction first order rate constant for the actinometer, calculated by equation (6).
- $^{\rm c}$   $\phi_{\rm d_c}{}^{313}$  represents the direct photoreaction quantum yield for the PCDF congener; calculated by equation [5]. Molar absorptivities ( $\epsilon_c^{313}$ ,  $\epsilon_A^{313}$ ) for the  $T_4$ CDF congener and PNAP were  $P_{s}CDF$  and PNA were 16770 M<sup>-1</sup>cm<sup>-1</sup> and 10300 M<sup>-1</sup>cm<sup>-1</sup>, respectively.  $\phi_{A}$  for the PNAP and PNA 25790 M<sup>-1</sup>cm<sup>-1</sup> and 2056 M<sup>-1</sup>cm<sup>-1</sup>, respectively. Molar absorptivities ( $\epsilon_{c}^{313}$ ,  $\epsilon_{A}^{313}$ ) for the 2.54 x  $10^{-5}$  and 1.25 x  $10^{-3}$ , respectively, were calculated by equations [1] and [2].

utilizes absorbed light for phototransformation more efficiently than does the  $T_4$ CDF congener, despite a smaller molar absorptivity at 313 nm. Since  $k_p$  depends on the quantum yield and  $\epsilon_{\lambda}$  according to (55):

$$k_{p} = \phi \Sigma L_{\lambda \epsilon \lambda}$$
 [7]

the more rapid degradation of T4CDF is likely due to more favorable absorption ( $\epsilon_{313}$ ), since its lower  $\phi^{313}$  would suggest a slower degradation rate. The resistance of  $T_4CDF$ degradation may be the result of its molecular structural aspects such as its symmetry, bond strengths, and atomic features (61). spatial Chemicals with weak absorption spectra and thus significant absorption tailing into the higher wavelength region may result in extremely efficient quantum yields, but slow rates of degradation (34). The quantum yield for  $2,3,7,8-T_4CDF$ , is approximately 7.6 fold smaller than that for 2,3,7,8-T<sub>4</sub>CDD (2.2 x  $10^{-3}$ ) determined by Dulin et al. (42) under similar conditions. Quantum yields do not reveal any information about the rate of reaction since the value is dimensionless; but they do represent the efficiency with which absorbed radiation leads to phototransformations in reactions.

2. PREDICTED DIRECT AQUEOUS PHOTOLYSIS RATES

The study of PCDF degradation under sunlight conditions was planned in conjunction with a PCDF fate study at ELA

(Kenora, ON). Preliminary sunlight exposure times (*ie.* length of time required for the entire exposure experiment) are required for an adequate kinetics study and may be determined based upon predicted first-order photodegradation rate constants, established with the aid of laboratory determined quantum yields.

The computer program, GCSOLAR, has been developed by R. Zepp and D. Cline of the US-EPA (28) to predict direct aqueous photolysis rates  $(k_{dE})$ , and corresponding half-lives  $(t_{\frac{1}{2}})$  of pollutants under sunlight conditions in surface waters. Radiation reaching the earth's surface includes both direct sunlight and reflected sky light. The program requires the input of a number of parameters, including laboratory determined quantum yields and  $\epsilon_{\lambda}$  of the chemical, refractive index of the medium, time of year, geographical location (latitude and longitude), depth of the water body, type of atmosphere, and appropriate ozone layer thicknesses. Parameters used to predict  $k_{dE}$  values for both  $T_4CDF$  and  $P_5$ CDF are summarized in Appendix 4. The default attenuation coefficients for distilled water were utilized in the calculations, although absorption values could be entered to account for light attenuation due to the presence of dissolved organics in a particular body of water. The attenuation of light with depth in the water column is adjusted by a subroutine in the program. The terrestrial atmosphere was selected for this study since it utilizes solar UV irradiances characteristic of atmospheres over the earth's land masses (including lakes, streams, forests, or

The marine atmosphere, on the other hand, uses farmland). solar irradiances which are typical of the atmosphere over Since the two default atmospheres differ in the ocean. light attenuation in the 280-380 nm region (55), this selection will have an important effect in the present The quantum yields determined in the laboratory at study. 313 nm (see Table 8) were assumed to be adequate for this Although the program is able to predict calculation. photolytic degradation rates at various water depths, only surface rates are of interest in this study; consequently, the 10 cm default increment value was selected. Although field experiments were planned for ELA (at 49° 47'N latitude, and a 0.39 km elevation), 50°N was used since the program accepts latitudes only in 10° increments.

In order to formulate a general picture of the photolytic behaviour of PCDFs in the aquatic environment as a function of the time of year, calculations were performed with light intensity data available for January 21, April 16, July 21, and October 20. Since data on ozone layer thickness was not available for ELA, the default ozone and ephemeride values were selected. Degradation rates were calculated hourly throughout the day, and then integrated to produce a day-averaged rate. For both PCDF congeners, molar absorptivities from 297.5 to 330 nm were used in predicting the direct environmental photolytic degradation rate constant,  $k_{\text{DE}}$ . The 330 nm cutoff of the tailing absorption band (see Figures 6 and 7) was established by assuming that absorbances were real only if the measured signal:noise
(S/N) ratio exceeded 5:1; baseline noise was established by averaging all signals over the 330-800 nm range. Several small "peaks" above 330 nm did not meet the 5:1 (S/N) criterion and were thus not considered real absorbances. Furthermore, instrument errors ranging from 3-5% (62) introduce uncertainties in molar absorptivity data.

Using the above parameters, the program calculated the direct aqueous photolytic degradation rate constants according to (34):

$$k_{DE} = \phi_{dc} \Sigma L_{\lambda \epsilon_{\lambda}}$$
[8]

where  $L_{\lambda}$  values are 24-hour, day-averaged, midseason, solar irradiances for surface waters under clear sky conditions (in millieinsteins cm<sup>-2</sup>d<sup>-1</sup>), and summation of  $L_{\lambda} \in_{\lambda}$  over a wavelength region represents the sunlight absorption rate constant,  $k_{a}$ ; *ie*.

$$k_a = \Sigma L_{\lambda \in \lambda}$$
 [9]

Since real solar irradiances may differ from  $L_{\lambda}$  values available in the program by ±15% (42), further uncertainty is introduced into the predictions.

Changes in the 24-hour, day-averaged  $k_{DE}$ , as a function of the time of day are plotted in Figure 11 for both PCDFs. As solar altitudes vary from sunrise to sunset (Figure 12), the rate of photodegradation increased from zero to a



FIGURE 11: DIRECT AQUEOUS PHOTOLYSIS RATE CONSTANTS  $(k_{DE})$  OF 2,3,7,8-T4CDF AND 2,3,4,7,8-P5CDF, PREDICTED BY GCSOLAR, AS A FUNCTION OF THE TIME OF DAY AT 50 °N LATITUDE IN MIDSUMMER.



FIGURE 12: DIAGRAM ILLUSTRATING THE CHANGE IN SOLAR ZENITH ANGLE ( $\beta$ ) AND SOLAR ALTITUDE ( $\alpha$ ) DURING A 24-HOUR DAY.

maximum at midday, and then decreased in a similar manner as the sun set (Appendix 5).

The program predicts that 2,3,4,7,8-P<sub>5</sub>CDF degrades more rapidly than 2,3,7,8-T<sub>4</sub>CDF. For example, at the midpoint of a typical midsummer day at 50°N, 2,3,4,7,8-P<sub>5</sub>CDF is predicted to degrade approximately 2.3 times faster than 2,3,7,8-T<sub>4</sub>CDF.

The changes in predicted  $k_{DE}$  of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF as a function of season (Appendix 5) and at 50°N latitude are plotted in Figure 13. Radiation intensities decrease from summer to winter and thus in midsummer  $P_{5}CDF$ T₄CDF and degradation rates appear approximately 1.5 faster than those observed in winter.

Table 9 summarizes the pseudo-first-order direct aqueous photolysis rate constants and half-lives for both PCDF congeners as predicted by the GCSOLAR program. Due to the fluctuations in sunlight intensity during the year, it is not surprising that the rate constants for a given chemical vary dramatically with the changing seasons. As the number sunlight hours decreased, the rate of of photodegradation tended to decrease, *ie.* the corresponding half-life increased. The rate of photodegradation of both PCDF congeners is greatest in the summer months, suggesting greater persistence in cold climates. According to the computer prediction, 2,3,4,7,8-P<sub>5</sub>CDF should degrade more rapidly than 2,3,7,8-T<sub>4</sub>CDF in any season, the differences being most significant during the summer months. In midsummer,  $k_{DE}$  for  $P_5CDF$  is  $\approx 2x k_{DE}$  for  $T_4CDF$ .



Season

FIGURE 13: DIRECT AQUEOUS PHOTOLYSIS RATE CONSTANTS FOR 2,3,7,8-T<sub>4</sub>CDF AND 2,3,4,7,8-P<sub>5</sub>CDF AS A FUNCTION OF TIME OF YEAR AT 50°N LATITUDE, PREDICTED BY GCSOLAR. PSEUDO-FIRST-ORDER RATE CONSTANTS ARE PREDICTED FOR TYPICAL MIDSEASON DAYS: APRIL 16, JULY 21, OCTOBER 20, AND JANUARY 21 (63).

ODEGRADATION HALF- LIVES. ITH GCSOLAR <sup>a</sup> , <sup>b</sup>	t <sub>X</sub> (d) <sup>d</sup>		2.6	1.6	6.7	25		1.1	0.71	2.8	8.7	
UEOUS PHOT STANTS AND PREDICTED W	k <sub>DE</sub> (d <sup>-1</sup> ) <sup>c</sup>		0.27	0.44	0.10	0.028		0.64	0.98	0.25	0.080	e from US-EPA (28)
DIRECT AC RATE CON: OF PCDFs H	Season		Spring	Summer	Fall	Winter		Spring	Summer	Fall	Winter	rogram (55) available
TABLE 9:	Congener	2,3,7,8-T <sub>4</sub> CDF				:	2,3,4,7,8-P <sub>5</sub> CDF					<sup>a</sup> GCSOLAR computer p

 $^{\rm D}$  Calculated results are for 50°N latitude and a 390 m elevation (ELA, Kenora, ON).

 $^{\rm C}\,{\rm k}_{\rm DE}$  represent pseudo-first order direct photoreaction rate constants under sunlight d conditions , calculated by equation [8]. Half-lives calculated from  $t_{y_{e}}^{-} \ln 2/h_{DE}$ .

## 3. DIRECT AQUEOUS SUNLIGHT PHOTOLYSIS

Direct aqueous photolysis of <sup>3</sup>H-2,3,7,8-T<sub>4</sub>CDF and <sup>14</sup>C-2,3,4,7,8-P<sub>5</sub>CDF, monitored under sunlight conditions, produced results of environmental significance. First-order plots of the photolytic degradation are presented in Figure 14. Concentrations at t=0 were not plotted to avoid forcing the slope through zero (42). Quantitative recoveries of both PCDFs from the dark controls sampled over the entire exposure period indicated negligible losses due to biological degradation, volatilization, and/or analytical procedures. Therefore, any significant decreases in concentrations could be attributed to photolytic degradation. Both congeners exhibited a slow degradation rate, with pseudo-first-order rate constants,  $k_{\text{DE}}$ , of 0.22 and 0.031 d<sup>-1</sup> (not geometry corrected) corresponding to half-lives of 3 and 23 d for  $T_4CDF$  and  $P_5CDF$ , respectively. Both congeners resist direct aqueous photolysis; P<sub>5</sub>CDF degradation is approximately 7 times slower than that for  $T_4$ CDF, with 46% and 73% of the parent 2,3,7,8- $T_4$ CDF and  $2,3,4,7,8-P_5CDF$ , respectively, unreacted for the two congeners after 76 hours (Table 10).

Reconstructed chromatograms, obtained by LSC analysis of HPLC fractions (Figure 15), provided an illustration of the changes in elution profiles of the samples as a result of direct photolysis. Analysis of the extracts with tritium detection revealed two degradation products, originating from  ${}^{3}\text{H-T}_{4}\text{CDF}$ , with retention times of approximately 9 and



FIGURE 14: MIDSUMMER DEGRADATION OF  ${}^{3}H-2,3,7,8-T_{4}CDF$  AND  ${}^{14}C-2,3,4,7,8-P_{5}CDF$  BY DIRECT AQUEOUS PHOTOLYSIS UNDER SUNLIGHT CONDITIONS. CORRELATION COEFFICIENTS FOR  ${}^{3}H-T_{4}CDF$  CONTROL,  ${}^{14}C-P_{5}CDF$ CONTROL,  ${}^{3}H-T_{4}CDF$ , AND  ${}^{14}C-P_{5}CDF$  WERE 0.934, 0.913, 0.985, AND 0.900, RESPECTIVELY.

CDF AND JGHT R SOLUTIONS <sup>a</sup>	<pre>% Disappearance % C-P<sub>5</sub>CDF</pre>	20.5 24.5 23.5 15.7 20.7 28.2 28.2 27.5
DF <sup>3</sup> H-2,3,7,8-T, DURING SUNI STILLED WATEI	Mass of Parent 14 <sub>C-Ps</sub> CDF <sup>b</sup> (ng)	31.8 ± 0.8 30.2 ± 2.0 30.6 c 33.7 ± 1.3 31.7 ± 1.8 29.7 ± 0.3 28.7 ± 0.8 28.7 ± 0.8
APPEARANCE ( 2,3,4,7,8-P5CDF OSURE IN DIS	<pre>% Disappearance % of Parent 3 H-T_CDF</pre>	10.4 12.2 13.3 11.6 27.6 32.7 47.8 53.6
BLE 10: DISA 14C-: EXP(	Mass of Parent <sup>3</sup> H-T <sub>4</sub> CDF <sup>b</sup> (ng)	40.3 ± 1.3 39.5 ± 2.6 39.8 ± 1.7 32.6 ± 2.5 30.3 ± 0.6 23.5 ± 1.0 23.5 ± 1.0
TA	Exposure Time (h)	0.5 1.0 2.5 2.5 27.0 34.25 51.5 76.0

<sup>a</sup> Experiment was performed at ELA, ON; June 26-29,**1989.**Sunlight intensity was monitored with two actinometers, PNAP and PNA, which provided pseudo-first-order degradation rate constants of 0.33 and 2.0 d<sup>-1</sup>, respectively.

data reduction program on the LSC. Background corrected activities which were 30 above baseline mobile phase at 1.0 mL/minute. Three minute fractions collected and counted on the dual label HPLC was performed on a C<sub>13</sub> Maters µBondapak column (25cm x 3.2 mm) with an 85:15 CH<sub>3</sub>OH/H<sub>2</sub>O <sup>b</sup> Starting masses of 2,3,7,8-T<sub>3</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF were 45 and 40 ng. respectively. were considered significant.

<sup>c</sup> n=1 for these sampling times; n=2 for all other sampling times.



FIGURE 15: RECONSTRUCTED HPLC CHROMATOGRAMS OF: a) STANDARD  ${}^{14}C-P_5CDF$ ; b) STANDARD  ${}^{3}H-T_4CDF$ ; AND c)  ${}^{3}H$  SAMPLE EXPOSED TO SUNLIGHT FOR 76 HOURS IN DISTILLED WATER. HPLC ANALYSES WERE PERFORMED ON A WATERS C<sub>18</sub> µBONDAPAK COLUMN WITH A MOBILE PHASE OF 85:15 CH<sub>3</sub>OH/H<sub>2</sub>O AT 1.0 mL/min. THREE MINUTE FRACTIONS WERE COLLECTED AND SUBSEQUENTLY ANALYZED ON THE DUAL LABEL REDUCTION PROGRAM BY LSC.

18 minutes (see Figure 15c). This chromatographic behaviour on a C<sub>18</sub> column suggests the presence of a more polar product than the starting PCDF, which partitions into hexane during sample work-up. Although the activities in these bands were small, they were in excess of  $3\sigma$  in background activities and were therefore considered statistically significant. There were no <sup>14</sup>C intermediates detected, consistent with the slow rate of degradation of  ${\rm ^{14}C-P_5CDF}.$ Since both PCDFs were present in the same sample and the tritiated congener was of considerably greater specific activity than the <sup>14</sup>C congener, tritium overflow into the <sup>14</sup>C channel led to significant statistical errors in actual counts produced by the dual label data reduction program. The excessive tritium activity causes large uncertainties in counts when simultaneous equations are solved, producing extreme negative results. Furthermore, an instrument error of ±4% may be expected. The counts from any potential <sup>14</sup>C-T<sub>4</sub>CDF products formed from parent <sup>14</sup>C-P<sub>5</sub>CDF will appear in the <sup>3</sup>H channel and will, therefore, be of large uncertainty due to the overflow from parent <sup>3</sup>H-T<sub>4</sub>CDF. Since possible  ${}^{14}C-T_4CDFs$  will co-elute with  ${}^{3}H-2,3,7,8-T_4CDF$ under any HPLC conditions, the dual label data reduction program is necessary to differentiate between the two radionuclides. Statistical errors in dual-label samples could be minimized by using two radionuclides of comparable activity.

Non-extractable <sup>3</sup>H activity in the water phase increased consistently over the entire exposure period (see

Table 11). However, no detectable levels of non-extractable <sup>14</sup>C appeared throughout the entire experiment. Since PCDFs partitioned into hexane with extraction efficiencies of >96%, the increase in tritium activity in the aqueous phase cannot be due to non-extractable parent PCDF, suggesting formation of a more polar product as a result of sunlight exposure. It is interesting to note that after 76 hours, the amount of extracted <sup>3</sup>H activity is identical to the non-extractable <sup>3</sup>H-activity. A complete mass-balance of <sup>3</sup>H during direct sunlight photolysis of  ${}^{3}H-T_{4}CDF$  is summarized in Table 11 and plotted in Figure 16. The non-polar intermediates comprise a small fraction of the total activity. The rate of degradation of parent compound and the appearance of a polar product mirror one another. The parent PCDF and non-extractable activity accounted for >87% of the original activity at all sampling times. The remaining activity was attributed to non-polar products (<8%) and to losses during sample work-up and analysis.

Direct photolysis of PCDFs involves the absorption of light which leads to photodegradation, usually from the triplet excited state (see Figure 17). The degradation pathway for the direct photolysis of PCDFs may involve excitation to the first excited singlet state, homolytic cleavage of the C-Cl bond or intersystem crossing to the triplet state (which would also lead to homolytic C-Cl bond cleavage), and subsequent formation of ionic species (34) in aqueous media. Recently, Dulin et al. demonstrated that monochlorobiphenyls photodegrade to hydroxybiphenyls in

<sup>14</sup>C-2,3,4,7,8-P<sub>5</sub>CDF IN DISTILLED WATER SOLUTIONS. <sup>3</sup>H-2,3,7,8-T,CDF AND % Parent 14 C-P<sub>5</sub>CDF Remaining b 75.5 74.3 72.5 79.5 76.5 84.3 79.3 71.8 <sup>3</sup>H AND <sup>14</sup>C MASS BALANCE FOLLOWING % Non-extractable <sup>3</sup> H Activity 1.72.5 5.4 9.8 19.1 24.4 35.4 46.2 SUNLIGHT EXPOSURE OF <sup>3</sup> H- Activity at t<sub>r</sub> = 18 min 0.38 0.80 0.20 1.2 2.2 2.4 4.7 3.1 ઝર <sup>3</sup>H- Activity at t<sub>r</sub> = 9 min 0.42 0.22 0.82 2.2 2.4 3.6 2.0 1.2 94 <sup>3</sup>H-T<sub>4</sub>CDF Remaining % Parent TABLE 11: 89.6 87.8 86.7 88.4 72.4 67.3 52.2 46.4 Exposure Time (h) 34.25 1.0 2.5 27.0 0.5 10.0 51.5 76.0

of non-extractable material was performed by analyzing 4 mL of extracted aqueous phase on the LSC. 2,3,4,7,8-P<sub>5</sub>CDF were 45 and 40 ng, respectively. HPLC was performed on a  $C_{18}$  Waters µBondapak  $^{a}$ Experiment was performed at ELA, ON; June 26-29, **1989.** Starting masses of 2,3,7,8- $T_{4}^{cDF}$  and column (25 cm x 3.2 mm) with an 85:15  $CH_3OH/H_2O$  mobile phase at 1.0 mL/min. Analysis  $^{
m b}$  No detectable levels of non-extractable  $^{
m 14C}$  were observed.



FIGURE 16: MASS BALANCE OF TRITIUM LABELLED PRODUCTS DURING DIRECT PHOTOLYSIS OF  ${}^{3}H-2,3,7,8-T_{4}CDF$  UNDER SUNLIGHT CONDITIONS AT ELA (SEE TABLE 11).



FIGURE 17: PROPOSED JABLONSKI ENERGY DIAGRAM FOR THE ABSORPTION OF LIGHT AND PRODUCT FORMATION PROCESS IN DIRECT PHOTOLYSIS, SHOWING RADIATIVE ( $\longrightarrow$ ) AND NON-RADIATIVE (///) TRANSITIONS. S<sub>o</sub>, S<sub>1</sub>, AND T<sub>1</sub> ARE THE GROUND SINGLET STATE, EXCITED SINGLET STATE, AND TRIPLET STATE, RESPECTIVELY. ISC (INTERSYSTEM CROSSING) INVOLVES THE CHANGING OF ELECTRON SPIN STATES IN A MOLECULE. k<sub>p</sub> AND k<sub>DE</sub> ARE THE RATE CONSTANTS OF PHOSPHORESCENCE AND OF PHOTOLYTIC DEGRADATION, RESPECTIVELY.

water at 254 nm. Reductive dechlorination was also not observed in photolysis of 2,3,7,8-T<sub>4</sub>CDD in  $H_2O/CH_3CN$ . Since T<sub>4</sub>CDD degradation was observed, the authors suggest that the mechanism may involve C-O bond cleavage (34).

Α comparison of the data obtained from sunlight experiments, with the predicted rates of direct aqueous photolysis, is summarized in Table 12. Since GCSOLAR predictions apply to surface waters, the rate constants determined experimentally in cylindrical tubes must be corrected for geometry before valid comparisons can be made. The rate constants determined in tubes are approximately 2.2 times faster than rates on flat surfaces (42) since tubes receive radiation from all directions as well as scattered light off the walls; whereas, surface water receives light from only one direction. Geometry-corrected direct photolysis half-lives for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF at 50°N latitude were 6.9 and 50 d, respectively. These half-lives are 4 and 70 times longer than predicted for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF, respectively, by GCSOLAR calculations. The unfortunate consequence of this trend is that the computer program appears to overestimate the rate of direct photolytic degradation of these toxic pollutants in the environment. Experimental data suggest less favorable degradation rates for PCDFs via direct photolysis. Recently, a correlation between toxicity of PCDDs and photolytic half-lives has been suggested (64). Half-lives of the more toxic PCDDs were shorter than those of the less

LY DETERMINED DATION RATES -P <sub>5</sub> CDF <sup>ª</sup>	7,8-P <sub>5</sub> CDF	EXPERIMENTAL DATA <sup>b</sup>	0.014	ũ
XPERIMENTAL PHOTODEGRA AND 2,3,4,7,8	2,3,4,7	GCSOLAR PREDICTIONS	0.98	0.71
DICTED AND E CT AQUEOUS 2,3,7,8-T,CDF	, 8-T₄CDF	EXPERIMENTAL DATA <sup>b</sup>	0.10	¢.ý
LE 12: PRED DIRE FOR	2,3,7	GCSOLAR PREDICTIONS	0.41	1.7
TAB			k <sub>DE</sub> (d <sup>-1</sup> )	t <sub>1</sub> (d)

 $^{a}$  The values presented in this table apply to 50°N latitude, and midsummer sunlight conditions  $^{b}$  All experimental  $k_{DE}$  values were divided by 2.2 to correct for geometry of the tubes (42). toxic congeners. The observed half-lives for PCDFs in this experiment followed this trend, with  $T_4CDF$  degrading approximately seven-fold faster than  $P_5CDF$ .

According to the GCSOLAR predictions, 2,3,4,7,8-P5CDF degrades more rapidly in sunlight than  $2,3,7,8-T_4CDF$  (Table There are a variety of variables that could explain 12). the discrepancy between these two sets of results. Large errors may be introduced into calculated rate constants, if the quantum yields measured at 313 nm, used in the predictions, are wavelength dependent. The chemical filter solution is susceptible to degradation upon exposure to light and must be replaced frequently in order to provide a narrow band of the proper wavelength of light. Uncertainties in  $k_{dc}$  and  $k_{dA}$  from first-order plots of ln  $(C_t/C_o)$  vs time will also affect  $k_{DE}$  values. Since the first-order rate constant for photolytic degradation is directly proportional to the quantum yield (equation [5]), errors in rate constants will produce corresponding errors in the laboratory determined quantum yields, and hence also in the predicted direct first-order rate constants. Errors in molar absorptivities as a result of overestimated solution concentrations do not significantly affect the predicted first-order rate constants, since negative errors in  $\epsilon_{\lambda}$  lead to positive errors in quantum yields (see equation [7]). The net result is that these errors tend to offset variations in  $k_{DE}$ . Truncation of the tailing absorption band used to calculate k<sub>DE</sub> introduces error since the GCSOLAR program is extremely sensitive to this

parameter, producing smaller first-order degradation rate constants, and therefore larger half-lives. As an example, it was observed that truncation of the molar absorptivity at 500 as opposed to 330 nm, (ie. including many small  $\epsilon_{\lambda}$ values previously judged statistically insignificant) produced a 43% increase in the predicted  $k_{DE}$ . Although predicted  $k_{DE}$  values are also affected by the elevation chosen for the calculation, with fluctuations of ±10% per km of elevation above sea level, a reliable value for the elevation of ELA was available. The half-life generally decreased with increasing elevation as a result of increased solar fluxes (65).

Errors in determining  $k_{DE}$  could also have been of experimental nature. Losses due to volatilization may not have been detectable in the controls, but may have been more significant in exposed samples containing the PCDFs. The GCSOLAR program predicts rate constants under clear sky conditions. During the exposure, however, cloud cover persisted for approximately 20% of the entire exposure Cloud cover has been known to reduce the UV-B time. radiation (290-320 nm) by as much as 50% (55). Since UV-B radiation will transform any chemical with an absorption in this region by direct photolysis, cloud cover could explain the slower experimental degradation rates observed for both congeners. Rain droplets on the tubes could feasibly distort or absorb sunlight and alter the intensity of light reaching the samples (43). Ozone is known to filter out radiation above 286 nm at the earth's surface (55, 66).

Ozone thicknesses can vary as much as 30% at midlatitudes during one day affecting experimentally determined degradation rates (67, 68). Despite these explanations, it is difficult to rationalize the discrepancy between the predicted and experimental rate constants.

Direct aqueous photolytic degradation under environmental conditions is a slow process for polychlorinated dibenzofurans, with half-lives of 6.9 and 50 d for 2,3,7,8- $T_4$ CDF and 2,3,4,7,8-P<sub>5</sub>CDF, respectively. The P<sub>5</sub>CDF may be considered essentially non-degradable by direct aqueous photolysis.

## B. INDIRECT SUNLIGHT PHOTOLYSIS OF 2,3,7,8-T<sub>4</sub>CDF AND 2,3,4,7,8-P<sub>5</sub>CDF

Photolytic transformation can only occur when energy is absorbed by a compound. However, the chemical does not necessarily need to absorb sunlight energy directly to undergo photolysis. There are many naturally occurring compounds in the aqueous environment which behave as sensitizers (69-79). These sensitizers have a more favorable absorption spectrum and therefore absorb sunlight more efficiently, transferring energy from their excited states to other compounds. The resulting reaction is defined as indirect photolysis. Various sensitizers are known to a variety induce of different types of indirect photoreactions (80), including photosensitized oxygenations and photosensitization involving energy transfer. The

latter may involve photoisomerization or simply the breaking of bonds as a result of the energy transfer. In natural waters such as the lake water used in this experiment, direct and indirect photolysis of a chemical may occur simultaneously. A fraction of the degradation rate is attributed to the direct absorption of light by the chemical, and the other fraction is a result of energy transfers from excited sensitizer molecules. By studying degradation of the PCDFs in lake water under sunlight conditions, the *net* photolytic degradation rate is measured. The rate constant for indirect photolysis may then be determined from the following relationship:

$$k_{PE} = k_{DE} + k_{SE}$$
 [10]

where  $k_{PE}$  is the *net* first-order photolytic degradation rate constant,  $k_{DE}$  is the direct photolysis rate constant, and  $k_{SE}$  is the rate constant describing strictly indirect photolysis. Of these three rate constants,  $k_{DE}$  was measured in distilled water (see Direct Photolysis section) and  $k_{PE}$  was obtained from the study performed in lake water. Since both types of photolyses are occurring simultaneously in natural water, the difference (equation [10]) represents the rate of indirect photolysis,  $k_{SE}$ .

First-order plots of the indirect photodegradation for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF are illustrated in Figure 18. Although the P<sub>5</sub>CDF transformation was essentially complete after 6 hours of sunlight exposure, sampling was



FIGURE 18: MIDSUMMER DEGRADATION OF  ${}^{3}H-2,3,7,8-T_{4}CDF$ AND  ${}^{14}C-2,3,4,7,8-P_{5}CDF$  BY INDIRECT PHOTOLYSIS UNDER SUNLIGHT CONDITIONS AT 50 °N LATITUDE AT ELA. CORRELATION COEFFICIENTS FOR  ${}^{3}H-T_{4}CDF$  CONTROL,  ${}^{14}C-P_{5}CDF$  CONTROL,  ${}^{3}H-T_{4}CDF$ , AND  ${}^{14}C-P_{5}CDF$  WERE 0.934, 0.913, 0.989, AND 0.989, RESPECTIVELY.

continued for 3 days (see Table 13). If the rates of degradation are again described by first-order kinetics,  $k_{PE}$ is obtained from the negative slope of the plot of  $ln(C_t/C_o)$ vs time. Concentrations at t=0 were again not used in the first-order treatment of the data. Only data in the 10-70% transformation range were used in determining the net photolytic degradation rate constants,  $k_{PE}$  (see Figure 18). The slight curvature exhibited for 2,3,7,8-T<sub>4</sub>CDF in Figure 18, may be the result of diurnal cycling; however, since data is not available between 7:00 PM and 2:00 PM the following day, no conclusive statement may be made regarding this observation. Dark controls, containing PCDFs in sterilized lake water, were used to monitor for biological and/or chemical degradation. No significant decrease in the concentration of PCDFs in the controls was evident over the exposure period. Therefore, all observable decreases in concentrations over the 52 hour exposure period are attributed to photolytic degradation. Net pseudo-firstorder degradation rate constants were determined to be 1.1 and 7.8 d<sup>-1</sup> for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF, with corresponding half-lives of 0.64 and 0.089 d, for the two congeners, respectively. In lake water,  $2,3,4,7,8-P_5CDF$ degraded seven-fold faster than 2,3,7,8-T4CDF. However, the rates of degradation of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF in lake water were approximately 5 and 250 times larger than in distilled water, respectively. those The dramatic increase in degradation rates in lake water is attributed to the presence of sensitizers.

% Disappearance EXPOSURE IN LAKE WATER SOLUTIONS.<sup>a</sup> AND 14 c-P<sub>5</sub>cDF cf Parent 20.5 33.0 50.8 71.0 88.5 96.3 97.3 14 C-2,3,4,7,8-P<sub>s</sub>CDF DURING SUNLIGHT DISAPPEARANCE OF <sup>3</sup>H-2,3,7,8-T,CDF Mass of Parent ф. ± 0.4 ± 0.5 ± 0.8 <sup>14</sup> c-P<sub>s</sub>CDF ' 0.9 ± 0.2 1.1 ± 0.0 (gu) H H 31.8 26.8 4.6 1.5 11.6 20 % Disappearance of Parent <sup>3</sup>H-T<sub>4</sub>CDF 2.0 8.0 22.2 55.8 78.4 91.8 39.1 Mass of Parent <sup>3</sup> H-T<sub>4</sub>CDF <sup>b</sup> ± 0.6 0.3 0.7 1.9 TABLE 13: ო 2  $\sim$ (gu) H 44.1 41.4 3.7 9.7 35 27 30 Exposure 0.25 0.50 Time (h) 1.0 2.5 6.0 27.0 51.5

Sunlight intensity was monitored with two actinometers, PNAP and PNA, which provided pseudo-first-order degradation rate constants of 0.33 <sup>a</sup>Experiment was performed at ELA, ON; June 26-29, **1989.** and 2.0 d<sup>-1</sup>, respectively.

HPLC was performed on a  $C_{18}$  Maters µBondapak column (25 cm x 3.2 mm) with an 85:15 CH<sub>3</sub>OH/H<sub>2</sub>O mobile phase at 1.0 mL/min. Three minute fractions were collected and counted on the dual label <sup>b</sup>Starting masses of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF were 45 and 40 ng, respectively. data reduction program on LSC.

Many substances have recently been identified as naturally occurring sensitizers including: acetone (31), humic and fulvic acids (77), singlet oxygen (81, 70), peroxy radicals, and hydroxy radicals (82). The absorption spectrum of the lake water (Figure 19) and its slight yellow discoloration both reveal the presence naturally of occurring dissolved material in the water. Although natural waters contain sensitizers which accelerate rates of reaction, other organics such as dissolved humic and fulvic acids (in particular, high concentrations) may inhibit degradation rates by screening the light intensity (73, 82). Degradation rates of other pollutants may be increased as a result of the presence of humic/fulvic acids (83). Singlet oxygen (102), peroxy, and hydroxy radicals have been shown to be small, but significant contributors to photolytic degradation rate enhancements (82). Singlet oxygen is present in low steady-state concentrations (<10<sup>-12</sup> M) since it absorbs energy from excited states of dissolved organics and rapidly quenches back to ground state oxygen in the absence of light. The rate constant for total removal of singlet oxygen from water, 2 x 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup>, reveals the efficiency with which it is depleted. Therefore, it is unlikely  ${}^{1}O_{2}$  is the sole contributor to the rate enhancement observed. Perhaps the dissolved organic carbon (DOC) (Appendix 1) and hydroxy radicals, which are the most reactive and least selective of natural oxidants, play a more significant role in sensitizing the degradation rates of both PCDFs in lake water (Lake 375, ELA); however,



WAVELENGTH (nm)

FIGURE 19: UV-VISIBLE ABSORPTION SPECTRUM OF LAKE WATER (LAKE 375, ELA, ON) USED IN INDIRECT PHOTOLYTIC STUDIES (SEE APPENDIX 1 AND 2 FOR DETAILS).

further studies are required to identify the exact identity of these sensitizers.

Reconstructed chromatograms from HPLC analyses with LSC detection of  ${}^{3}H-2,3,7,8-T_{4}CDF$  and  ${}^{14}C-2,3,4,7,8-P_{5}CDF$ , shown in Figures 20b and 21b, demonstrated the changes in elution profiles of the samples as a result of exposure to sunlight in lake water. Two <sup>3</sup>H non-polar degradation products appear at retention times of approximately 12 and 21 min. The of the зH intermediate of  $t_r=21$  minutes amount is significantly larger, after only 6 hours of exposure, than was observed as a result of the direct photolysis of  ${}^{3}\text{H-T}_{4}\text{CDF}$  following 76 hours of exposure to sunlight (see Figures 20a and 20b). As is evident from Table 14, a significant amount of <sup>3</sup>H activity appears in the extracted lake water, suggesting the formation of a polar degradation product. The <sup>14</sup>C-2,3,4,7,8-P<sub>5</sub>CDF, producing a much more dramatic elution profile following only 6 hours of exposure in lake water (Figure 21b), formed only one significant <sup>14</sup>Clabelled degradation product  $(t_r=33 \text{ minutes})$ . The rapid rate of degradation of parent  ${}^{3}H-T_{4}CDF$  decreased the overflow of <sup>3</sup>H activity into the <sup>14</sup>C window during liquid scintillation counting; hence, a statistically significant <sup>14</sup>C-labelled product was detectable. The concentration of the <sup>14</sup>C degradation product was at a maximum after 6 hours of sunlight exposure, with a retention time similar to that of the  ${}^{3}H-T_{4}CDF$ . However, in distilled water, most of the parent <sup>14</sup>C-P<sub>5</sub>CDF remained unreacted (see Table 11) after 76 hours of sunlight exposure.



FIGURE 20: RECONSTRUCTED HPLC CHROMATOGRAMS OF EXTRACTABLE <sup>3</sup>H ACTIVITY FROM: a) DISTILLED WATER FOLLOWING 76 HOURS OF EXPOSURE, b) LAKE WATER FOLLOWING 6 HOURS OF EXPOSURE. DETECTABLE INTERMEDIATES ARE LABELLED AS "1" AND "2". (SEE EXPERIMENTAL SECTION FOR ANALYTICAL DETAILS).



FIGURE 21: RECONSTRUCTED HPLC CHROMATOGRAMS OF EXTRACTABLE <sup>14</sup>C ACTIVITY FROM: a) DISTILLED WATER FOLLOWING 52 HOURS OF EXPOSURE, b) LAKE WATER FOLLOWING 6 HOURS OF EXPOSURE. THE ONLY DETECTABLE <sup>14</sup>C INTERMEDIATE IS LABELLED "1". (SEE EXPERIMENTAL SECTION FOR ANALYTICAL DETAILS).

TAB	LE 14:	<sup>3</sup> H AND	<sup>14</sup> C M.	ASS BAL.	ANCE FC	DLLOWING	לז	
		SUNLIGH	T EXPOS	URE OF	<sup>3</sup> H-2,3,7	8-T,CDF	AND	
		<sup>14</sup> C-2,3,4,7	,8-P <sub>s</sub> CDF	IN LAKE	WATEH	s solut	IONS. <sup>a</sup>	
Exposure Time (h)	<pre>% Parent % Parent 3H-T_4CDF Remaining</pre>	χ <sup>3</sup> H- Activity at t <sub>r</sub> =12 min	z <sup>3</sup> H- Activity at t <sub>r</sub> =21 min	<b>%</b> Non- extractable <sup>3</sup> H Activity	% Parent 14C-P <sub>S</sub> CDF Remaining	x <sup>14</sup> C - Activity at t <sub>r</sub> =33 min	% Non- extractable <sup>14</sup> C Activity	Y
0.25	86	0.17	2.7	1.8	80	6.0	3.6	
0.50	92	0.40	4.4	3.6	67	N.D.	6.2	
1.0	78	0.67	6.4	7.6	49	7.5	9.8	
2.5	61	1.0	9.1	13.4	29	4.5	14.4	·
6.0	44	2.1	15	22.1	12	9.8	13.4	_
27.0	22	2.8	14	41.4	3.8	3.5	29.4	
51.5	8.2	3.3	6.9	58.6	2.8	2.8	41.5	
<sup>a</sup> Experime	nt was perfo	ormed at ELA, ON;	June 26-29, <b>1</b> .	989. Starting 1	nasses of 2,3,	7,8-T <sub>4</sub> CDF and		-

2,3,4,7,8-P<sub>5</sub>CDF were 45 and 40 ng, respectively. HPLC was performed on a C<sub>18</sub> Waters µBondapak column (25 cm x 3.2 mm) with an 85:15  $CH_3OH/H_2O$  mobile phase at 1.0 mL/min. Analysis of non-extractable material was performed by analyzing 4 mL of extracted aqueous phase by LSC.

The distribution of зH and <sup>14</sup>C activity was dramatically different from the distribution observed in distilled water (Table 14 and 11). Mass balance of activities for both congeners over the entire exposure period are presented in Figures 22 and 23. The amount of tritiated intermediate with  $t_r=21$  min increased during the first 6 hours of sunlight exposure, and then slowly decreased. A similar trend was exhibited by the 14C intermediate (Figure 23). If both degradation intermediates are lower chlorinated PCDFs, they could potentially undergo photolytic degradation. Significant amounts of <sup>3</sup>H and <sup>14</sup>C (59% and 42%, respectively) were non-extractable following 52 hours of exposure to sunlight. Similarly, it has been observed that  $1, 2, 3, 4, 7 - P_5 CDD$ and 1,2,3,4,6,7,8-H<sub>7</sub>CDD produced significant levels of non-extractable activity following 5 days of sunlight exposure in pond water (45). In distilled water, however, non-extractable <sup>14</sup>C activity could not be detected following 76 hours of sunlight exposure.

The degradation intermediates resulting from the photolysis of both PCDFs in lake water revealed some similarities to the results obtained from photolysis of these congeners in distilled water. Formation of non-polar intermediates, possibly by dechlorination, appears to be a less significant pathway than the formation of polar products. It is unclear whether the non-polar products are intermediates in the production of the predominant



FIGURE 22: MASS BALANCE OF <sup>3</sup>H ACTIVITY FOLLOWING 52 HOURS OF SUNLIGHT EXPOSURE OF <sup>3</sup>H-2,3,7,8-T<sub>4</sub>CDF IN LAKE WATER. DATA IS SUMMARIZED IN TABLE 14.



FIGURE 23: MASS BALANCE OF <sup>14</sup>C ACTIVITY FOLLOWING 52 HOURS OF SUNLIGHT EXPOSURE OF <sup>14</sup>C-2,3,4,7,8- $P_5$ CDF IN LAKE WATER. DATA IS SUMMARIZED IN TABLE 14. degradation product(s).

The kinetics of photodegradation of  $2,3,7,8-T_4CDF$  and 2,3,4,7,8-P<sub>5</sub>CDF at 50°N latitude in midsummer are summarized in Table 15. All experimental rate constants  $(k_{PE})$  are corrected for tube geometry to allow comparison with the  $k_{DE}$ predicted by GCSOLAR. Both PCDFs degraded more rapidly than expected in natural water as a result of the significant contribution of indirect photolysis to the net photolytic rate. The half-lives of the  $2, 3, 7, 8-T_4 CDF$ and 2,3,4,7,8-P<sub>5</sub>CDF were 1.4 and 0.2 d, respectively. Although hydrophobic chemicals tend to accumulate in lake sediments, the rapid degradation in surface waters suggests that large portions of PCDFs entering lakes through atmospheric (vapor) deposition in daytime hours could be photolytically degraded. However, once the PCDFs are partitioned into sediments, their degradation bottom is minimal (2). Generally, **net** first-order photolytic degradation rate constants,  $k_{PE}$ , were larger than the corresponding direct aqueous first-order photolytic degradation rate constants,  $k_{\text{DE}}.$  Normalization of both PCDF  $k_{\text{PE}}$  values to their respective direct photolytic degradation rates,  $k_{\text{DE}}$  revealed that 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF degraded 5 and 250 times faster in natural water than in distilled water, respectively. This enhancement in degradation rate must be the result of a reaction with naturally occurring components in lake A comparison of predicted direct aqueous photolysis water. rates and experimentally determined, direct and indirect, photolytic degradation rates is shown in Figures 24 and 25.

EXPERIMENTAL DATA <sup>b</sup> 0.014 0.20 RATE CONSTANTS AND HALF-LIVES<sup>a</sup> 0.20 3.6 3.5 TABLE 15: COMPARISON OF ALL PHOTOREACTION 20 2, 3, 4, 7, 8-P<sub>s</sub>CDF PREDICTIONS GCSOLAR 0.98 0.71 EXPERIMENTAL DATA<sup>b</sup> 0.10 6.9 0.50 0.40 1.4 1.8 2,3,7,8-T<sub>2</sub>CDF PREDICTIONS GCSOLAR 0.41 1.7  $k_{PE} (d^{1})^d$  $k_{sE} (d^{-1})^{e}$ k<sub>DE</sub> (d<sup>-1</sup>)<sup>C</sup> t<sub>k</sub> (d) t<sub>¥</sub> (d) t<sub>k</sub> (d)

50°N latitude. <sup>a</sup> All data are for midsummer photolysis at

<sup>b</sup> All experimental  $k_{DE}$ ,  $k_{PE}$ , and  $k_{sE}$  values were divided by 2.2 to correct for the geometry of the tubes to allow comparison with GCSOLAR predictions (4.2).

 $c_{\rm k_{\rm bE}}$  is the direct aqueous photolytic degradation rate constant.

 $d_{k_{pE}}^{\nu_{E}}$  is the *net* aqueous photolytic degradation rate constant.  $e_{k_{sE}}$  is the indirect aqueous photolytic degradation rate constant.



FIGURE 24: COMPARISON OF EXPERIMENTAL AND PREDICTED RATES OF PHOTOLYSIS OF 2,3,7,8-T<sub>4</sub>CDF UNDER ENVIRONMENTAL CONDITIONS. DATA USED FOR THIS COMPARISON IS SUMMARIZED IN TABLE 15. EXPERIMENTAL VALUES WERE GEOMETRY CORRECTED.


FIGURE 25: COMPARISON OF EXPERIMENTAL AND PREDICTED RATES OF PHOTOLYSIS OF 2,3,4,7,8-P<sub>5</sub>CDF UNDER ENVIRONMENTAL CONDITIONS. DATA USED FOR THIS COMPARISON IS SUMMARIZED IN TABLE 15. EXPERIMENTAL VALUES WERE GEOMETRY CORRECTED.

## C. IDENTIFICATION OF NON-POLAR PRODUCTS FROM INDIRECT PHOTOLYTIC DEGRADATION OF 2,3,7,8-T<sub>4</sub>CDF AND 2,3,4,7,8-P<sub>5</sub>CDF.

Kinetic data, provided in the previous section, for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF clearly demonstrated that indirect photolysis was responsible for the generation of significantly greater amounts of non-polar intermediates than direct photolysis. As mentioned earlier, HPLC retention times suggested that the intermediates could be lower chlorinated PCDFs. Since both PCDFs exhibited very slow degradation rates in the distilled water medium, insufficient amounts of non-polar degradation products were produced allow structural to confirmation by mass spectrometry. However, accelerated rates of PCDF photodegradation in lake water resulted in the production of more significant amounts of non-polar products (see Figure 20 and 21); therefore, further studies were conducted with 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF in lake water only.

#### 1. GC-MS ANALYSES OF NON-POLAR DEGRADATION PRODUCTS

FORMED ON PHOTOLYSIS OF 2,3,4,7,8-P5CDF IN LAKE WATER.

A TIC (total ion chromatogram) produced from the analysis of the hexane extracts on a 30 m DB-5 stationary phase (see Appendix 3 for GC-MS conditions) revealed a large number of peaks attributed to the co-extractable non-polar materials from lake water (Figure 26). Despite rigorous



FIGURE 26: TIC (SCAN MODE) OF HEXANE EXTRACT ON A DB-5 CAPILLARY COLUMN (PROGRAM #1) FOLLOWING PHOTOLYSIS OF 2,3,4,7,8- $P_5$ CDF IN LAKE WATER (FOUR HOUR EXPOSURE TO XENON LAMP).

;

clean-up attempts of the lake water, persistent high levels of co-extractable material interfered with identification of the low levels of non-polar degradation products.

Since HPLC data suggested the possibility of reductive dechlorination as a degradation pathway, a search for possible  $T_4$ CDFs was performed by obtaining reconstructed chromatograms of carefully selected ions. To establish the chromatographic behaviour of typical  $P_5CDFs$  and  $T_4CDFs$ , the retention times  $2, 3, 7, 8 - T_4 CDF$ of 2,3,4,7,8-P<sub>5</sub>CDF and standards (12.5 and 13.7 min, respectively) were determined on a 30 m DB-5 capillary column (Figures 27a and 28a). Mass spectra of the standard PCDFs (Figures 27b and 28b) were then used to select appropriate ions for the reconstruction of chromatograms from TICs, where the identification of new peaks was not possible. The most prominent features of the mass spectra of PCDFs include the Cl isotope clusters of the intense molecular ion. and the absence of complex fragmentation patterns. The number of chlorine atoms on an ion provides a characteristic isotope cluster useful in identifying the degree of chlorination on a molecule. For  $T_4$ CDFs, the four Cl atoms produce a characteristic M, M+2, M+4, M+6, and M+8 pattern. The most intense ions of this cluster, m/z=304 (M<sup>+</sup>), 306, and 308 amu were used to reconstruct chromatograms in order to confirm the presence of  $T_4CDFs$ . A reconstructed chromatogram (from the TIC shown in Figure 26) using ion 306 revealed two peaks of  $t_r = 12.4$ and 12.6 min (Figure 29), suggesting the presence of two  $T_4$ CDFs as non-polar degradation products from the photolysis



FIGURE 27: TOTAL ION CHROMATOGRAM (a) AND MASS SPECTRUM (b) OF STANDARD 2,3,7,8-T<sub>4</sub>CDF (10 ng) ON A 30 m DB-5 CAPILLARY COLUMN.



FIGURE 28: TOTAL ION CHROMATOGRAM (a) AND MASS SPECTRUM (b) OF STANDARD 2,3,4,7,8- $P_5$ CDF (10 ng) ON A 30 m DB-5 CAPILLARY COLUMN



FIGURE 29: RECONSTRUCTED ION CHROMATOGRAM (ION 306) FROM TIC IN FIGURE 26.

of 2,3,4,7,8-P<sub>5</sub>CDF in lake water. Similar reconstructed chromatograms were obtained with both ions 304 and 308 amu. The small peak with  $t_r$  of 13.7 min, is due to unreacted parent  $P_5CDF$  which produces a weak fragment of m/z=306 amu through the loss of a chlorine (see Figure 28b). A check for the parent  $P_5CDF$  (m/z values of 338, 340, and 342) confirmed the presence of significant amounts of unreacted starting  $P_5CDF$  (t<sub>r</sub>=13.7 min). Having established the retention times of the suspected  $T_4CDF$  products, a mass spectrum of the components eluting at the appropriate  $t_r$  (Figure 30), revealed the presence of three characteristic fragment clusters for  ${\rm T_4CDFs},$  including 171, 242/243, and 304/306/308 Although this mass spectrum also contains fragments amu. produced by co-eluting material, general features of  $T_4CDF$ fragmentation were evident. Therefore, based on the match in retention times and the similarity in mass spectra with the standard 2,3,7,8-T<sub>4</sub>CDF, it was suspected that at least two  $T_4CDF$  isomers were produced by indirect photolysis of  $2, 3, 4, 7, 8 - P_5 CDF$ .

The only disadvantage of mass spectral data is that it alone cannot differentiate between the different  $T_4CDF$ isomers. It was therefore necessary to confirm the presence of  $T_4CDF$  degradation products by matching their retention times with retention times established for standard  $T_4CDFs$ . Increased sensitivity and lower detection limits are achieved by selected ion monitoring (SIM) since only the ions chosen are monitored. Since no ions with a m/z of 304, 306, or 308 amu were observed in non-photolyzed lake





water taken through the same extraction procedure as the PCDF solution, the  $T_4$ CDFs were not simply background levels of contaminants in the lake water. Similarly, lake water which was photolyzed for the same period of time as the  $P_5$ CDF "spiked" lake water, did not generate detectable levels of  $T_4$ CDFs. Therefore, the  $T_4$ CDFs are clearly not the result of merely a lake water component, but are formed on photolysis of  $P_5$ CDF.

Identification of the  $T_4$ CDFs was attempted by matching retention times of the products with those of  $T_4$ CDF standards. Reductive dechlorination of 2,3,4,7,8-P<sub>5</sub>CDF, assuming no Cl migrations, may potentially produce five  $T_4$ CDFs with Cl substitution patterns of: 2,3,4,7; 2,3,4,8; 2,3,6,7; 2,3,6,8; and 2,3,7,8. A 30 m DB-5 capillary column could only resolve three of the five  $T_4$ CDFs in a standard mixture of these isomers (see Figure 31a). Even with a very slow temperature ramp, the DB-5 capillary column was unable to resolve 2,3,7,8- $T_4$ CDF and 2,3,4,7- $T_4$ CDF, consistent with the work of Kuroki et al. (85).

The chromatogram of the photolyzed extract, analyzed under the same conditions as the  $T_4CDF$  standards, is shown in Figure 31b. Except for a slight shift to longer retention times, probably the result of a matrix effect, the chromatogram is similar to that of the standard  $T_4CDFs$ (Figure 31a and 31b). The small peak at  $t_r \approx 63.2$  min is believed to be an impurity, since only ions 241 and 243 amu were responsible for the appearance of this peak. The remaining peaks tentatively confirm the presence of



FIGURE 31: SIM CHROMATOGRAM OF (a) A MIXTURE OF STANDARD  $T_4$ CDFs AND (b) HEXANE EXTRACT OF PHOTOLYZED  $P_5$ CDF DETERMINED ON A 30 m DB-5 CAPILLARY COLUMN (PROGRAM #2, APPENDIX 3)

2,3,6,8-T<sub>4</sub>CDF, and the absence of 2,3,6,7-T<sub>4</sub>CDF. The moderately intense peak at  $t_r \approx 66$  min may be one or both of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7-T<sub>4</sub>CDF. The small shoulder observed on the tail end of the peak at  $t_r \approx 66$  min may be indicative of 2,3,4,8-T<sub>4</sub>CDF, although resolution of this isomer was not as good as in the standard mixture of the T<sub>4</sub>CDFs (Figure 31a). A standard addition of 2,3,6,7-T<sub>4</sub>CDF, introduced a new peak with  $t_r \approx 68.5$  min, confirming the absence of this congener in the original extract.

In an attempt to improve the resolution of all  $T_4CDF$ congeners, the extracts were re-analyzed on a 60 m DB-1701 capillary column, the stationary phase consisting of 86% methyl, and 14% cyanopropylphenyl silicone on a polysiloxane backbone. Although the overall resolution has somewhat improved, this column could also not resolve  $2,3,7,8-T_4CDF$ and 2,3,4,7-T<sub>4</sub>CDF (Figure 32a). Analysis of the lake water extract (without the 2,3,6,7-T<sub>4</sub>CDF addition), confirmed the presence of 2,3,6,8-T<sub>4</sub>CDF and one or both of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7-T<sub>4</sub>CDF. However, this analysis produced improved resolution of 2,3,4,8-T<sub>4</sub>CDF, confirming it as a non-polar product in the photolysis of  $2,3,4,7,8-P_5$ CDF. Although a small peak appeared at approximately 128 min, the presence of 2,3,6,7-T<sub>4</sub>CDF is ruled out for a number of reasons. First, there was clearly no detectable  $2,3,6,7-T_4CDF$ observed with the DB-5 capillary column. Secondly, of the five ions monitored in SIM mode, only ions 241 and 243 amu were responsible for the peak at 128 min. Absence of ions of 304, 306, and 308 amu, eliminates  $2,3,6,7-T_4CDF$  as a



FIGURE 32: SIM CHROMATOGRAMS OF (a) MIXTURE OF FIVE STANDARD  $T_4$ CDFs; (b) DARK CONTROL OF 2,3,4,7,8-P<sub>5</sub>CDF IN LAKE WATER, AND; (c) HEXANE EXTRACT OF PHOTOLYZED P<sub>5</sub>CDF DETERMINED ON A 60 m DB-1701 CAPILLARY COLUMN (PROGRAM #3, APPENDIX 3).

possible non-polar product.

Since the non-labelled 2,3,4,7,8-P<sub>5</sub>CDF was not purified prior to use in photolysis, the possibility that the observed T<sub>4</sub>CDFs were merely impurities in the starting 2,3,4,7,8-P<sub>5</sub>CDF was investigated. A dark control containing  $2,3,4,7,8-P_5CDF$  was subjected to the same analytical procedures used for the photolytic experiments. The chromatogram (SIM) of the extract of the control, is shown in Figure 32b. Although small amounts of T₄CDFs, particularly 2,3,6,8-T<sub>4</sub>CDF, were detected, the low levels of  $T_4$ CDFs present as impurities in the parent 2,3,4,7,8-P<sub>5</sub>CDF cannot possibly account for the significant amounts of  $T_4$ CDFs observed after photolysis. It can, therefore, be concluded that the non-polar intermediates formed as a result of the exposure of  $2,3,4,7,8-P_5CDF$  to light for four hours in lake water included 2,3,6,8-T<sub>4</sub>CDF; 2,3,4,8-T<sub>4</sub>CDF; and one or both of  $2,3,7,8-T_4CDF$  and  $2,3,4,7-T_4CDF$ .

Although further dechlorination is feasible, no  $T_3CDFs$  could be detected. It is possible the exposure time was not adequate, since  $k_{PE}$  for 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8-P<sub>5</sub>CDF were 1.4 and 0.2 d, respectively. Alternately, it is also possible that the  $k_{PE}$  of  $T_3CDF$  is much larger (*ie.* they degrade more rapidly than the parent PCDF), and hence, they are not detectable. Recently, Dulin et al. (34) similarly reported that no detectable levels of trichlorodibenzop-dioxin formed on photolysis of 2,3,7,8-T<sub>4</sub>CDD in hexane at 313 nm, since the rate of photolysis of  $T_3CDD$  was three times faster than that for  $T_4CDD$ .

The confirmed intermediates,  $2,3,6,8-T_4CDF$  and  $2,3,4,8-T_4CDF$ , have both been formed by the loss of a lateral chlorine atom, and more specifically, with loss of the lateral chlorine atom nearest to the oxygen atom:





2,3,4,8-T\_CDF



Dechlorination, with preferential loss of lateral chlorine atoms, has been reported by Buser (37) for octachlorodibenzo-p-dioxin ( $O_8CDD$ ), 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin ( $H_6CDD$ ), and 1,2,3,7,8,9-H\_6CDD in hexane; and by Nestrick and Lamparski (61) for the tetrachlorodibenzo-p-dioxins in isooctane. This would account for the formation of all the observed T<sub>4</sub>CDFs, with the exception of 2,3,7,8-T<sub>4</sub>CDF. However, 2,3,7,8-T<sub>4</sub>CDF formation cannot be confirmed, therefore, it may in fact not be a product of this photodegradation. Lateral chlorines flanked on both sides by chlorine atoms appear to be preferential sites of dechlorination for PCDDs (37). This appears to apply to PCDFs as well since, based on peak heights, 2,3,6,8-T<sub>4</sub>CDF is the predominant T<sub>4</sub>CDF produced by photolysis of 2,3,4,7,8-

P<sub>5</sub>CDF in lake water. Reductive dechlorination of PCDFs may involve dissociation into a Cl radical and a phenyl type The radicals could then potentially abstract radical. hydrogens from hydrogen donors present in the lake water (see Figure 33). This type of mechanism has been postulated for chlorobenzene (34), PCDDs (38, 86-87), and PCBs (88) in organic, hydrogen donor solvents. Natural waters contain many potential hydrogen donors (73), and could, therefore, follow a similar type of reductive dechlorination. A newly developed capillary column, DB-Dioxin, now available from Chromatographic Specialties (Brockville, ON), can resolve 2,3,7,8-T<sub>4</sub>CDF and 2,3,7,8-T<sub>4</sub>CDD from all other T<sub>4</sub>CDFs and T₄CDDs and would be useful in confirming whether 2,3,7,8-T<sub>4</sub>CDF contributes to the peak at 125 min.

### 2. GC-MS ANALYSES OF NON-POLAR DEGRADATION PRODUCTS FORMED ON PHOTOLYSIS OF 2,3,7,8-T₄CDF IN LAKE WATER

Reductive dechlorination of 2,3,7,8-T<sub>4</sub>CDF in lake water was verified by analysis of the hexane extracts by GC-MS (SIM) on a 60 m DB-1701 capillary column (Figure 34c). Standard 2,3,8-T<sub>3</sub>CDF, analyzed under identical conditions (Figure 34a), had a retention time of 96.9 min. Only one peak is evident at this retention time (Figure 34c), suggesting the presence of one  $T_3CDF$ . However, since only the 2,3,8-T<sub>3</sub>CDF congener was available, confirmation of the identity of the T<sub>3</sub>CDF was not possible. However, degradation of the 2,3,7,8-T<sub>4</sub>CDF does produce a lower

### FIGURE 33: POSSIBLE MECHANISM FOR REDUCTIVE PHOTODECHLORINATION OF PCDFS IN LAKE WATER.









FIGURE 34: SIM CHROMATOGRAMS OF (a) STANDARD 2,3,8-T<sub>3</sub>CDF; (b) DARK CONTROL OF 2,3,7,8-T<sub>4</sub>CDF IN LAKE WATER, AND; (c) HEXANE EXTRACT OF PHOTOLYZED T<sub>4</sub>CDF DETERMINED ON A 60 m DB-1701 CAPILLARY COLUMN (PROGRAM #3, APPENDIX 3). chlorinated  $T_3CDF$ , likely 2,3,8- $T_3CDF$  and/or 2,3,7- $T_3CDF$ . A dark control provided evidence that the  $T_3CDF$  was not simply an impurity in the starting 2,3,7,8- $T_4CDF$  (Figure 34b). Lake water extracts, also checked for possible presence of  $T_3CDFs$ , proved to be negative.

If larger amounts of degradation products (such as  $\mu g$  or mg quantities) could be generated, additional spectroscopic analyses such as NMR could provide useful information about specific proton positions and thus confirm the sites of dechlorination.

## D. IDENTIFICATION OF POLAR PRODUCT(S) FROM INDIRECT PHOTOLYTIC DEGRADATION OF 2,3,4,7,8-P<sub>5</sub>CDF

According to results obtained from the indirect photolysis of  $2,3,4,7,8-P_5CDF$ , a significant fraction of nonextractable <sup>14</sup>C-activity accumulated in the lake water (Figure 23, Table 14). Although a similar trend was noticed for 2,3,7,8-T<sub>4</sub>CDF (Figure 22), the degradation was slower.  $(t_{\mbox{$\frac{1}{2}$T4CDF}}=1.4$  d and  $t_{\mbox{$\frac{1}{2}$P5CDF}}=0.2$  d) Therefore, efforts were made to examine the structural identity of the polar degradation product(s) of  $2,3,4,7,8-P_5CDF$  in lake water. In order generate significant amounts of degradation to product(s), lake water was spiked with as much as 4000 ng of 2,3,4,7,8- $P_5$ CDF, which exceeded its water solubility (235 ng/L, (17)) by a factor of ten. The apparent solubility of a solute in water containing coexisting solutes, however, is susceptible to modifications by interactions with cosolutes

(89). It appears that high-molecular-weight species, such as dissolved organic matter/carbon (DOC), in natural waters may significantly enhance the solubility of hydrophobic solutes through a partition-like interaction between the solute and the DOC (89). The solubility enhancement tends to increase with a decrease in solute solubility. An estimate of the amount by which a solute's solubility may be safely exceeded without introducing the possibility of precipitation, may be calculated by the relationship established by Chiou et al.(89):

$$S_{w}^{*}/S_{w} = (1 + XK_{DOC})$$
 [11]

where the solubility enhancement factor is defined by the ratio  $S_w^{\cdot}/S_w$ , X defines the concentration of DOC present in a specific water body and  $K_{D \circ C}$  the solute partition coefficient between DOC and pure water. Generally,  $K_{DOC}$ values, in natural waters, are estimated to be one order of magnitude smaller than  $K_{ow}$  values (90). Using DOC concentrations of 4.2 mg/L (specific for Lake 375, ELA), and the log  $K_{ow}$  for 2,3,4,7,8-P<sub>5</sub>CDF as 6.92 (18), it was predicted that a maximum solubility enhancement of 14 could be justified for the  $P_5CDF$  congener. Servos and Muir (91) have observed 5-fold solubility enhancements for 1,3,6,8-T<sub>4</sub>CDD as a result of the presence of 1.8 mg/L of Aldrich humic acid (DOC). It was, therefore, assumed that the levels of  $P_5CDF$  used in the lake water were in solution and did not precipitate. Figure 35 summarizes the

analytical steps used in the isolation and analysis of degradation products formed from the photolysis of  $2,3,4,7,8-P_5CDF$  in lake water.

Although relatively little information is available about the nature of polar degradation products from PCDFs, PCBs and PCDDs have been shown to produce carboxy- and hydroxy- type products in various media (92). In particular, production of singlet oxygen, with hydrogen donation from a hydrogen donor in the lake water, and possibly free OH radicals by sunlight may allow the displacement of chlorines with hydroxy groups (93-94). Degradation of PCBs, in particular 2,2',5,5'tetrachlorobiphenyl in hexane under sunlight and "blacklight" conditions, have resulted in the formation of hydroxylated and carboxylated polar products (86). These hydroxylated products are the result of a loss of one Cl and the addition of an OH to form a phenolic product. A recent study of dibenzo-p-dioxin degradation in methanol, hexane, and acetonitrile at 253.7 nm, revealed a variety of polar aromatic degradation products, including 2-hydroxybenzoic acid, 2,2'-dihydroxybiphenyl, and 2-phenoxyphenol (41). It was also suggested that these polar aromatic degradation products may further degrade to aliphatic molecules, but no conclusive evidence was presented. Recently, Kuroki et al. (95) demonstrated that rats produced dihydroxy-chlorinated metabolites after being fed a mixture of T<sub>4</sub>CDFs, indicating that PCDFs can be hydroxylated by different processes. Due to the structural similarities of PCDFs with PCBs and PCDDs,



FIGURE 35: PROCEDURE USED FOR ISOLATION AND ANALYSIS OF DEGRADATION PRODUCTS FROM THE PHOTOLYSIS OF 2,3,4,7,8-P<sub>5</sub>CDF IN LAKE WATER.

there is a strong suggestion that the same **types** of polar products could be generated from the photolysis of PCDFs.

Bis(trimethylsilyl)trifluoroacetamide (BSTFA), used as the derivatizing agent in this study, produces extremely volatile reaction by-products, monotrimethylsilyl trifluoroacetamide and trifluoroacetamide, which are eluted with the solvent front during GC-MS analyses on a DB-1701 capillary column. The following reaction represents a typical phenolic derivatization:



BSTFA

PHENOL

VOLATILE BY-PRODUCTS

Small scale derivatizations (50  $\mu$ L of 3:2, CH<sub>3</sub>CN/BSTFA) have been previously used in the derivatization of polar photoproducts of dibenzo-*p*-dioxin (41). This procedure successfully derivatized 2-phenylphenol, but did not produce any obvious derivatives (as determined by GC-MS analysis) of suspected polar product in the lake water residue. This may have been the result of the low solubility of the suspected polar product in small volumes of CH<sub>3</sub>CN. Use of 500:1 (v/v) THF/BSTFA in the procedure resulted in a major peak from the

analysis of the BSTFA-treated lake water residue by HRGC-LRMS on a 60 m DB-1701 capillary column (Figure 36). The success of this procedure was possibly due to increased solubility of the polar material in larger volumes of solvent.

Analysis of BSTFA-treated "non-spiked" lake water residue verified that most of the peaks in the chromatogram were due to compounds present in the lake water. The peak with  $t_r=23.9$  min was the derivative of TMS standard 2-phenylphenol, added to the residue to monitor the success of the derivatization procedure. The major component,  $t_r$ =20.6 min, was the result of the derivatization of a polar product formed on photolysis of 2,3,4,7,8-P<sub>5</sub>CDF in lake The major features of the mass spectrum of the water. derivatized product ( $t_r$ =20.6 min, Figure 36a) included a base peak of 73 amu, the absence of recognizable chlorine isotope patterns in any fragment ions, and a possible molecular ion (M<sup>+</sup>) of mass 330 amu. The fragment of m/z 73 amu corresponds to the trimethylsilyl (TMS) fragment, confirming successful derivatization of a polar product. Although this is a difficult product to isolate and derivatize, the procedure was reproduced with non-radiolabelled and  ${}^{14}C-P_5CDF$  on four occasions. Based on this evidence, it was suspected that the identified polar product was non-chlorinated, and dihydroxylated with a possible molecular ion  $(M^+)$  of 330 amu. A variety of lower injection port temperatures were attempted (see Appendix 3, program #4) and confirmed that the derivative (M\*=330) could





FIGURE 36: a) GC TOTAL ION CHROMATOGRAM OF BSTFA-TREATED POLAR DEGRADATION PRODUCT(S) AND STANDARD 2-PHENYLPHENOL ON A 60 m DB-1701 CAPILLARY COLUMN (SEE APPENDIX 3, PROGRAM #4). b) ELECTRON IMPACT (70eV) MASS SPECTRUM OF DERIVATIZED DEGRADATION PRODUCT OF  $t_r=20.6$  min.

not simply be the result of a high temperature reaction occurring in the injection port.

Derivatives of standards, 2-phenylphenol two and 2,2'-dihydroxybiphenyl, were analyzed under similar GC-MS conditions and used as a comparison with the derivative of the polar product in lake water residue. The retention times of these standards, 23.9 and 25.3 min respectively, eliminated these as possible degradation products of the photolysis of 2,3,4,7,8-P<sub>5</sub>CDF. However, analysis of the mass spectra of these compounds (Figure 37) revealed similarities with the mass spectrum of the derivatized polar product formed on the photolysis of  $P_5CDF$ . The molecular ion of the TMS derivative of 2-phenylphenol is more prominent than the M<sup>+</sup> of di-TMS 2,2'-dihydroxybiphenyl (330 amu). In addition to the number of substituents, their positions on the aromatic ring may also affect the stability of the molecular ion. This may explain the relatively low abundance of the  $M^+$  of the TMS derivative of the polar TMS derivatives of monohydroxybiphenyls fragment product. to form significant amounts of [M-15] + ions through the loss of a methyl radical (96). For 2-phenylphenol, the abundance of the  $[M-15]^+$  ion was second only to the abundance of the [M-31]<sup>+</sup> ion. However, for the 2,2'-dihydroxybiphenyl, this fragment was of extremely low abundance, consistent with previous observations (41). The 2,2'-dihydroxybiphenyl derivative, therefore, does not tend to undergo significant methyl cleavage to yield the [M-15]<sup>+</sup> fragment. No [M-15]<sup>+</sup>



FIGURE 37: COMPARISON OF THE EI MASS SPECTRA OF TMS DERIVATIZED: (a) 2-PHENYLPHENOL; (b) 2,2'-DI-HYDROXYBIPHENYL; AND (c) POLAR DEGRADATION PRODUCT. (SEE APPENDIX 3, PROGRAM #4).

ion was detected in the derivatized polar product, possibly due to a steric interaction of bulky TMS substituents in close proximity to each other. For similar reasons, dihydroxybiphenyls with ortho or 2,2'- disubstitution, may [-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> cation more eliminate the readily than monohydroxybiphenyls. In fact, the loss of the  $[-Si(CH_3)_3]^+$ ion is the preferred route of fragmentation producing the base peak for 2,2'-dihydroxybiphenyl; whereas, this ion is of very low abundance for 2-phenylphenol. Extraction of the ion of m/z 73 amu from the TIC of the derivatized product, produced a reconstructed chromatogram with one peak of  $t_r =$ 20.6 min, indicating that only one compound was successfully derivatized. The presence of a base peak at 73 amu further supports the proposed structure of a dihydroxybiphenyl. The peak of m/z 103 amu (Figure 37c) is likely attributed to the  $[CH_2OSi(CH_3)_3]^+$  fragment, which has previously been observed for TMS ethers and esters with an aromatic moiety (96). The ion of mass 240 amu could result from a loss of  $[HOSi(CH_3)_3]$ involving a hydrogen migration. Loss of a methyl radical from this fragment (240 amu) would result in the fragment of m/z of 225 amu. In addition, the significant abundance of the fragment with m/z 147 amu usually indicates the presence of di-TMS compounds (97). Although this fragment is found 2,2'-dihydroxybiphenyl standard in both the and the derivative of the polar degradation product, it appeared more prominent in the latter.

HRGC-HRMS analysis of the derivatized polar product on a 25 m DB-5 capillary column (Figure 38 and 39) produced a



RETENTION TIME (min)

FIGURE 38: HRGC TIC OF THE DERIVATIZED POLAR PRODUCT AND 2-PHENYLPHENOL ANALYZED ON A 25 m DB-5 CAPILLARY COLUMN. GC CONDITIONS WERE SIMILAR TO PROGRAM #4 (APPENDIX 3).



FIGURE 39: HRMS (EI, 75 eV) OF TMS DERIVATIVE OF POLAR PRODUCT (t<sub>r</sub>=8.5 min). (SEE APPENDIX 3, PROGRAM #4 FOR MS CONDITIONS).

mass spectrum similar to the one obtained with LRMS (Figure 36). These results further support formation of а dihydroxybiphenyl from the photolysis of 2,3,4,7,8-P<sub>5</sub>CDF. Accurate isotope ratios, characteristic of the elemental composition of the molecular ion, can provide the molecular formula for an unknown compound. Experimentally determined relative abundances of the isotope cluster in the molecular ion region,  $(M^+=330 \text{ amu})$ , for the TMS derivative of both the standard 2,2'-dihydroxybiphenyl and the derivatized product, the calculated isotope and ratios for the proposed structure, C<sub>18</sub>H<sub>25</sub>Si<sub>2</sub>O<sub>2</sub>, are summarized in Table 16. The predicted isotope ratios are in reasonably good agreement with the ratios observed for the unknown product. Although the data for 2,2 -dihydroxybiphenyl was in good agreement with the predicted ratios, the isotope ratios for the unknown may not be as accurate due to a 25-fold lesser abundance of the M<sup>+</sup> ion. Furthermore, the isotope ratios could be affected by fragmentation of co-eluting impurities. Therefore, the isotope ratio data supports a dihydroxybiphenyl as the proposed structure of the polar product.

Additional analysis of the derivatized product by positive chemical ionization (PCI) with NH<sub>3</sub>(g) yielded inconclusive results. The derivatized polar product did not produce a significant increase in the [M+1] fragment (*ie*. 331 amu); however, it is possible that this molecule is not susceptible to proton transfer from the ammonium ion. Although, in principle, the proton affinities of molecules may be calculated and used to predict its susceptibility to

# TABLE 16: ISOTOPE ABUNDANCE RATIOS<sup>2</sup> FOR TMS DERIVATIVES OF 2,2'-DIHYDROXYBIPHENYL AND THE POLAR PHOTODEGRADATION PRODUCT.

	М	M+1	M+2	
2,2 -DHB <sup>b</sup>				
Calc.	100	30.9	11.5	
Expt.	100	30.0	11.3	
Polar Product	100	23.4	10.3	

<sup>a</sup>M=330, M+1=331, M+2=332 amu.

<sup>b</sup>2,2'-DHB represents 2,2'-dihydroxybiphenyl.

undergo reaction with ammonia gas, experimental deviations from the predicted are not uncommon (98). For example, toluene and 1,2,3-trimethylbenzene both have proton affinities greater than that of  $NH_3(g)$ , 787 kJ/mol, but do not undergo ammonium ion attachment under CI conditions It has also been suggested that the (98). TMS from derivatized molecules can inhibit the formation of an [M+1]<sup>+</sup> ion (99). Reactivity, therefore, appears to be molecule specific and is difficult to predict.

In summary, the mass spectral data, therefore, provided supporting a dihydroxybiphenyl evidence as the polar degradation product of  $2,3,4,7,8-P_5CDF$  in lake water. It appears that during the photolysis of 2,3,4,7,8-P5CDF, ring opening via C-O bond cleavage leads to the formation of a 2-hydroxybiphenyl. Although the exact position of the second hydroxy group was not confirmed, 2,2'-dihydroxybiphenyl was ruled out as the polar degradation product on the basis of GC retention times. The possibility of o-dihydroxy substitution could be confirmed by preparation of *n*-butylboronate derivatives of the polar product (92). Absolute confirmation of the structure of the product would require GC-MS analysis of all other possible dihydroxybiphenyl isomers. Since many of these are not commercially available, their synthesis would be required. Consequently, the only conclusion which may be reached with the existing data is that the polar degradation product is а dihydroxybiphenyl:



These results clearly demonstrate that reductive dechlorination, ring opening, and hydroxylation result in at least one non-chlorinated polar product following the photolysis of  $2,3,4,7,8-P_5CDF$  in lake water.

### IV. CONCLUSIONS

It is evident that photolytic degradation plays an important role in determining the fate of the persistent polychlorinated dibenzofurans. Since the sun emits energy between 98.6 and 35.8 kcal/mol in the 290-800 nm region (44), it provides enough energy to break typical  $C_6H_5$ -OCH<sub>3</sub> and C-Cl bonds which have bond strengths of 92 (100) and 78-82 kcal/mol (101), respectively. Quantum yields for the direct aqueous photolysis of 2,3,7,8-T<sub>4</sub>CDF and 2,3,4,7,8- $P_5CDF$  in 50:50 CH<sub>3</sub>CN/H<sub>2</sub>O, at 313 nm, were determined to be  $(2.9 \pm 0.5) \times 10^{-4}$  and  $(6.6 \pm 0.9) \times 10^{-4}$ , respectively. The magnitude of these quantum yields implies slow photolytic degradation rates as a result of the direct absorption of light by the PCDF. However, under sunlight conditions in distilled water,  $2, 3, 7, 8 - T_4 CDF$ and 2,3,4,7,8-P<sub>5</sub>CDF degraded by direct photolysis with pseudo-first-order rate constants of 0.10 ± 0.007 and 0.014  $\pm$  0.002 d<sup>-1</sup>, respectively. These rates, corresponding to half-lives of approximately 7  $\pm$  0.5 and 50  $\pm$  15 d for  $T_4CDF$ and  $P_5 CDF$ , respectively, support the slow rates of photolysis of these compounds initially indicated by the small quantum yields. Predictions of direct aqueous photolysis rates, using the GCSOLAR program available from US-EPA (28), were consistent with the slow rates of degradation observed in sunlight. Although these predictions serve as reasonable estimations of environmental

degradation rates of organic contaminants, computer programs cannot simulate natural environments and, thus, may only provide approximations of real phenomena. Pseudo-firstorder rate constants for the net degradation of 2,3,7,8- $T_4CDF$  and 2,3,4,7,8-P<sub>5</sub>CDF, measured in midsummer at 50°N latitude in water from Lake 375, ELA, Kenora, ON; were determined to be 0.50  $\pm$  0.05 and 3.6  $\pm$  0.5 d<sup>-1</sup>, respectively (see Appendix 6 for statistical analysis). The significant enhancement in the photolytic degradation rate is attributed to the presence of naturally occurring sensitizers in lake water. Of the many photooxidants identified in natural waters, it has been suggested that the HO radical concentrations may be too low to contribute significantly to oxidation processes, but that the combination of oxyradicals and singlet oxygen could play significant roles (93). Although photodegradation, particularly direct photolysis, appears to be a relatively slow process, this may be the only possible, and therefore significant, degradation pathway for molecules as persistent as PCDFs.

After 4-6 hours of irradiation in lake water, non-polar degradation products were detected by HPLC-LSC and GC-MS for both  $2,3,7,8-T_4CDF$  and  $2,3,4,7,8-P_5CDF$ . It was concluded that 2,3,6,8-T<sub>4</sub>CDF; 2,3,4,8-T<sub>4</sub>CDF; and one or both of 2,3,4,7-T<sub>4</sub>CDF and 2,3,7,8-T<sub>4</sub>CDF were the result of the photolytic degradation of 2,3,4,7,8-P<sub>5</sub>CDF. On the other hand, 2,3,7,8-T4CDF produced significant levels of either  $2, 3, 8 - T_3 CDF$ and/or  $2, 3, 7 - T_3 CDF$ . However, exact identification was not possible due to the lack of
analytical standards. However, the non-polar degradation products were not the major degradation products for either PCDF. It appeared that dechlorinated PCDFs were intermediates in the formation of a more abundant polar degradation product.

photolysis of 2,3,4,7,8-P<sub>5</sub>CDF The in lake water produced one polar degradation product which was identified by GC-MS analyses as a dihydroxybiphenyl. No chlorinated polar degradation products could be detected, demonstrating that the degradation pathway included reductive dechlorination, ring opening and hydroxylation. Although analysis of polar degradation products resulting from the photolysis of 2,3,7,8-T<sub>4</sub>CDF was not performed, it is possible that a similar degradation pathway also explains the increase in radioactivity in the polar phase. Figure 40 summarizes the degradation pathways of 2,3,4,7,8-P5CDF as a consequence of photolysis in lake water. To date, no data is available in the literature which identifies the non-polar and polar degradation products following the exposure of 2,3,4,7,8-P<sub>5</sub>CDF under environmental conditions.

No attempt was made to study possible aliphatic degradation products; however, this type of study could be important in completing the overall degradation scheme of PCDFs in the aquatic environment.

Additional analytical spectroscopic methods, such as FTIR, GC-IR, LC-MS, and NMR may provide useful structural information about the photolytic degradation products of PCDFs and PCDDs.



NON-POLAR DEGRADATION INTERMEDIATES



DIHYDROXYBIPHENYL

POLAR DEGRADATION PRODUCT

FIGURE 40: SUMMARY OF THE DEGRADATION PATHWAYS

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PHYSICAL AND CHEMICAL MEASUREMENTS OF LAKE 375, ELA.<sup>a</sup>

DAY	159	187	215	243	271	292	
Cond (µS/cm)	47	47	51	47	49	51	
pH	7.44	7.52	7.74	7.58	7.58	7.35	
Alkal (µEq/L)	341	333	336	342	347	383	
NH₃-N (µg/L)	1	2	8	7	3	13	
NO₃-N (µg/L)	1	1	<1	2	2	12.	
TDN (µg/L)	190	190	220	290	200	260	
Susp N (µg/L)	33	42	29	35	45	49	
TDP (µg/L)	2	2	2	2	2	5	
Susp P (µg/L)	3	3	2	-	4	4	
DIC (µM/L)	351	339	335	340	350	389	
DOC (µM/L)	430	430	470	440	440	530	
Susp C (µg/L)	380	560	440	420	580	830	
Cl (mg/L)	0.32	0.32	0.30	0.27	0.27	0.80	
$SO_4$ (mg/L)	3.42	3.38	3.35	3.35	3.35	3.92	
Na (mg/L)	1.36	1.35	1.35	1.32	1.42	1.47	
K (mg/L)	0.60	0.60	0.59	0.57	0.60	0.65	
Ca (mg/L)	5.38	5.10	5.14	5.33	5.73	6.07	
Mg (mg/L)	1.35	1.33	1.35	1.33	1.40	1.50	
Mn (mg/L)	<0.01	0.01	<0.01	0.01	<0.01	<0.01	
Fe (mg/L)	<0.01	<0.01	0.01	0.04	<0.01	0.02	
SRSi (mg/L)	2.440	2.380	2.350	2.310	2.310	2.430	
Chl-a (µg/L)	1.40	1.50	2.00	2.30	2.60	2.40	

<sup>a</sup>Data provided by Water Chemistry Laboratory, Department of Fisheries and Oceans; Winnipeg, Manitoba. Samples were taken in 1989 at a 1 m depth.

CONTOUR MAP OF LAKE 375 AT EXPERIMENTAL LAKES AREA (ELA), KENORA, ONTARIO. x = THE SITE OF ALL EXPERIMENTAL WORK.



# SUMMARY OF ALL CONDITIONS USED FOR GC-MS ANALYSES

### PROGRAM #1:

Column	:	DB-5 (30 m)
Acquisition Mode	:	Scan/SIM
Temperature Ramp	:	90-270°C at 20° min
Solvent Delay	:	2.70 min
Injection Port	:	250°C
Transfer Line	:	280°C
Dwell Time	:	100 ms
Ions Monitored	:	308, 306, 304, 241, 243, 171 -
		T₄CDFs
		272, 270, 171, 137 - $T_3$ CDF

### PROGRAM #2:

Column	:	DB-5 (30 m)
Acquisition MOde	2:	SIM
Femperature Ramp	:	100°C for 2.70 min
		100-140°C at 20°C/min
		140-200°C at 0.5°C/min
Solvent Delay	:	8.00 min
Injection Port	:	250°C
Fransfer Line	:	280°C
Dwell Time	:	100 ms
Ions Monitored	:	308, 306, 304, 243, 241, 171 -
		T₄CDFs
		272, 270, 171, 137 - $T_3$ CDFs

# PROGRAM #3:

Column :	DB-1701 (60 m)
Acquisition Mode:	SIM
Temperature Ramp:	100°C for 2.70 min
	100-180°C at 5°C/min
	180-270°C at 0.5°C/min
Solvent Delay :	7.00 min
Injection Port :	250°C
Dwell Time :	100 ms
Ions Monitored :	308, 306, 304, 206, $171 - T_4$ CDFs
	272, 270, 171, 137 - T <sub>3</sub> CDFs

# PROGRAM #4:

DB-1701 (60 m)
Scan
60°C for 2.00 min
60-240°C at 10°C/min
240-270°C at 5°C/min
13.00 min
280°C
290, 255, 250, and 180°C

#### **APPENDIX 4A**

SUMMARY OF THE PARAMETERS USED TO PREDICT  $k_{DE}$  FOR 2,3,7,8-T<sub>4</sub>CDF<sup>a</sup> WITH GCSOLAR.

XENOBIOTIC NAME:  $2, 3, 7, 8 - T_4 CDF$ WATER IDENTIFICATION: PURE WATER TYPE OF ATMOSPHERE: TERRESTRIAL QUANTUM YIELD: 0.00029 INITIAL DEPTH: 0.00100° DEPTH INCREMENT: 10.00000° FINAL DEPTH: 5.00000° **REFRACTIVE INDEX:** 1.34000<sup>d</sup> WAVE LENGTH \* WATER ABSORPTION<sup>e</sup> \* EPSILON<sup>f</sup> (nm) 297.50 \* 0.8200E-03 \* 0.2829E+05 300.00 \* 0.7800E-03 \* 0.3047E+05 302.50 \* 0.7400E-03 \* 0.3237E+05 305.00 \* 0.6900E-03 \* 0.3195E+05 307.50 \* 0.6900E-03 \* 0.2778E+05 \* 0.6500E-03 310.00 \* 0.2441E+05 \* 0.6300E-03 312.50 \* 0.2547E+05 315.00 \* 0.6100E-03 \* 0.2493E+05 \* 317.50 0.5600E-03 \* 0.1799E+05 320.00 \* 0.5200E-03 \* 0.9312E+04 323.10 \* 0.5000E-03 \* 0.3725E+04 330.00 \* 0.4300E-03 \* 0.6180E+03 LATITUDE 50 N WAS SELECTED. ALL SEASONS WERE SELECTED. LONDITUDE SELECTED: 94.22 TIME-OF-DAY COMPUTATIONS ARE REQUESTED. TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.

 $^{a}[2,3,7,8-T_{4}CDF] = 9.45 \times 10^{-6}M.$ 

<sup>b</sup>Quantum yields were determined using equation [5]. <sup>c</sup>Initial depth, depth increment, and final depth are in units of cm, and correspond to depths in the water body from the surface. A depth increment of 10 cm is irrelevant in this calculation since the final depth is only 5 cm. <sup>d</sup>Refractive index is applicable to water/acetonitrile solutions used in experimental work, since the refractive indices of the two solvents are 1.3330 and 1.3441, respectively.

"Water absorption refers to the absorbances of pure, distilled water over the wavelength region studied. Default values were used for calculations.

<sup>f</sup>Epsilon values are molar absorptivities , $\epsilon$ , of the PCDF.

#### **APPENDIX 4B**

SUMMARY OF THE PARAMETERS USED TO PREDICT  $k_{DE}$ FOR 2,3,4,7,8-P<sub>5</sub>CDF<sup>a</sup> WITH GCSOLAR.

XENOBIOTIC NAME: 2,3,4,7,8-P5CDF WATER IDENTIFICATION: PURE WATER TYPE OF ATMOSPHERE: TERRESTRIAL QUANTUM YIELD: 0.00066<sup>b</sup> INITIAL DEPTH: 0.00100° DEPTH INCREMENT: 10.00000° FINAL DEPTH: 5.00000° **REFRACTIVE INDEX:** 1.34000<sup>d</sup> WAVE LENGTH \* WATER ABSORPTION<sup>e</sup> \* EPSILON<sup>f</sup> (nm) 297.50 0.8200E-03 \* \* 0.2406E+05 300.00 \* 0.7800E-03 \* 0.2521E+05 302.50 \* 0.7400E-03 \* 0.2554E+05 305.00 \* 0.6900E-03 \* 0.2378E+05 307.50 \* \* 0.2027E+05 0.6900E-03 310.00 \* 0.6500E-03 \* 0.1743E+05 \* 312.50 0.6300E-03 \* 0.1681E+05 \* 0.6100E-03 315.00 \* 0.1582E+05. 317.50 \* \* 0.1274E+05 0.5600E-03 0.5200E-03 320.00 \* \* 0.9410E+04 323.10 \* 0.5000E-03 \* 0.6392E+04 330.00 \* 0.4300E-03 \* 0.3179E+04 LATITUDE 50 N WAS SELECTED. ALL SEASONS WERE SELECTED. LONDITUDE SELECTED: 94.22 TIME-OF-DAY COMPUTATIONS ARE REQUESTED. TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.

 $a[2,3,4,7,8-P5CDF] = 1.20 \times 10^{-5}M.$ 

<sup>b</sup>Quantum yields were determined by equation [5]. <sup>c</sup>Initial depth, depth increment, and final depth are in units of cm, and correspond to depths in the water body from the surface. A depth increment of 10 cm is irrelevant in this calculation since the final depth is only 5 cm.

<sup>d</sup>Refractive index is applicable to water/acetonitrile solutions used in experimental work, since the refractive indices of the two solvents are 1.3330 and 1.3441, respectively.

"Water absorption refers to the absorbances of pure, distilled water over the wavelength region studied. Default values were used for calculations.

<sup>f</sup>Epsilon values are molar absorptivities,  $\epsilon$ , of the PCDF.

GCSOLAR PREDICTIONS OF PHOTOLYTIC DEGRADATION CONSTANTS AND HALF-LIVES OF 2,3,7,8-T<sub>4</sub>CDF AND 2,3,4,7,8-P<sub>5</sub>CDF

XENOBIOTIC HAME: 2378-T400F WATER IDENTIFICATION: PURE WATER TYPE OF ATMOSPHERE: TERRESTRIAL ELEVATION: 0.39 (Km.) LONGITUDE: 94.22

LAT.	SEASON	SULAR	MORN	EVEN	RATE	HALF LIFE
		ALLI.	TIME	f HHE	ZSEC	HOURS
50.00	SPRING	0.00	ರ. ತಟ	19.09	0.0008+00	0.0008400
		5.00	5.94	18.47	0.108E-06	0.179E+04
		10.00	6.46	17.95	0.337E-06	0.572E+03
		20.00	7.50	16.91	0.169E-05	0.114E+03
		30.00	8.57	15.84	0.4326-05	0.446E+02
		40.00	4./8	14.63	0.767E-05	0.251E+02
		50.00	11.99	12.42	0.111E-04	0.174E+02
MII	DAY	50.09	12.20	12.20	0.111E-04	0.174E+02

AV5 RATE DURING DALITE(SEC\*\*-1) 0.516E-05 RATE INTEGRATED OVER FULL DAY(DAY\*\*-1) 0.256E+00 HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.271E+01 MEAR SURFACE

SO.OO SUMMER	0.00	4.47	20.07	0,000E+00	0.000E+00
	5.00	5.16	19.38	0.127E-06	0.152E+04
	10.00	5.72	18.6.	0.4008-06	0.4B1E403
	20.00	6.19	17.75	0.199E-05	0.967E+02
	30.00	7.82	16.72	0,501E-05	0.384E+02
	40.00	6.88	15.66	0.8796-05	0.219E+02
	50.00	10.04	14.50	0.126E-04	0,153E+02
	60.00	12.07	12.47	0.1586-04	0.1226402
MIDDAY	60.09	12.27	12.27	0.158E-04	0.122E+02

AVE RATE DURING DALITE(SEC\*\*-1) 0.736E-05 RATE INTEGRATED OVER FULL DAY(DAY\*\*-1) 0.414E+00 HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.168E+01 NEAR SURFACE

50.00	FALL	0.00	6.70	17.24	0.000E+00	0.000E+00
		5.00	7.34	16.61	0.140E-06	0.137E+04
		10.00	7.91	16.03	0.444E-06	0.434E+03
		20.00	9.21	14.73	0.2196-05	0.8788402
		30,00	11.77	12.17	0.5478-05	0.352E+02
1111	DAY	30.06	11.97	11.47	0.5496-05	0.351E+02

AVE RALE DURING DALITE(SEC\*\*-1) 0.255E-05 RATE THIEGRATED UVER FULL DAY(DAY\*\*-1) 0.96BE-01 HALF ALTE INTEGRATED UVER FULL DAY(DAYS) 0.715E+01 TH 5F SURFACE

SO.OO WHNERS	0.00	<b>U.</b> 00	16.72	0.000E400	0,000E+00
	5 (14)	8.74	15.90	0.119h=05	0.162E+04
	10,00	9.47	15.26	0.3Z3F 06	0.51 det $03$
PHDDA7	17.665	1	12.36	0.1641:-05	0.104E+0 <b>3</b>

AVE RATE DURING DALITE(SEC\*\*+1) 0.830E-04 BERT HIH:GRAFED OVER FULL DAY(DAY\*\*+1) 0.261E-01 HED FITT HIFFGRAFED OVER FULL DAY(DAYE) 0.266E402 HEAR SURFACE XFHUDIOLIC NAME: 23470-P5CDF WAIER IDENTIFICATION: FURE WATER TYPE OF ATMOSFIERE: TERRESTRIAL ELEVATION: 0.39 (Km.) LONGITUDE: 94.22

ALE OF MILION	THEFT A	EPU (GLD UN	1 / 11			
	COL 013	d MOUNT	ین ۲۵۱۰ ۲۱۵ ادا	GATE		
LAT. SEASON		FIGEN FILME				
STATISTICS AND AND A DAMAGE	F3L. I •	1 1 1 1 C. E. 270		7 000 0 0005±00	0.0013400	
50.00 SPRING	0.00	0.02 6 D.0	10 /17		0.4036403	
	10.00	4. /14.	17 05	0.1036-05	0.1546403	
	20.00	0.40 7 50	16 01	O SOSELOS	0.3918402	
	20.00		16.04		0.1678402	
	40.00	(3 76)	14 43		0.1016402	
	50.00	11 00	12 42	0 2646-04	0.7286+01	
MUDWAY	50.00 En 19	12 20	12.72	0.2458-04	0.7276+01	
1111111111	0.0.	1.1.1.1.1.1.1.1	a an		0.7274.001	
	AVG RA	TE DURT	NG DALT	TE (SEC++-1)	0.129E-04	ŧ
	BALE I	NTEGRAT	ED UVER	FULL DAY (	DAY**-1) 0.	641E+00
	HALE L	TEE INT	EGRATED	OVER FULL	DAY (DAYS)	0.108E+01
	NEAR S	URFACE				
50.00 SUMM-R	0.00	4.47	20.07	0.0008+00	0.000E+00	
	5.00	5.16	19.38	0.5018-06	0.384E+03	
	10.00	5.72	18.82	0.1376-05	0.141E+03	
	20,00	6.79	17.75	0.5628-05	0.343E+02	
	30.00	7.82	16.72	0.128E-04	0.151E+02	
	40.00	8.88	15.66	0.211E-04	0.913E+01	
	50.00	10,04	14.50	0.2918-04	0.463E+01	
	60.00	122. O Z	12.47	0.3586-04	0.538E+01	
MEDDAY	60.09	12.27	12.27	0.358E-04	0.5386+01	
	ALB: 157			107700000000000000000000000000000000000	) <u>0 1735-0</u>	a
	1.0 112 1	TTEL ROTA	THE FULLE		) () () () () () () ()	' 975E400
			10000000000000000000000000000000000000	LAVER FILL		0 711E+00
	FIFILLT L		1 C. OKA 1 C. D	UVERV PULL	DELIGENDY	
	PR. 2013 - 34					
50.00 FALL	0.00	6.70	17.24	0,000E+00	0.000E+00	
	5.00	7.34	16.61	0.531E-06	0.3638+03	
	10.00	7.91	16.03	0.146E-05	0.132E+03	
	20.00	9.21	14.73	0.5998-05	0.322E+02	
	30.00	11.77	12.17	0.136E-04	0.142E+02	
MIDDAY	30.06	11.97	11.97	0.136E-04	0.141E+02	
	AL10 107	ALC INCO		TET / CPU (Processing f	) () 64115-0)	43
		1 ELE ARUTA	LEA DUEL		$100 \times 100 $	251E+00
		TER NAV			- <u>ηαν (ηαν</u> αι	0.2765+01
	NEAR (	SURFACE	1 62 ( 31 Y P1 1 ) 62 L		DHIYDHIG	
		(1. <i>č</i>	1 / 20	65 - 65656577 + 6565	en encodate e com	
20.00 MILLER	0,00	13.UO 0 74	10.72	- 0.000000000 - 0.000000000		
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RELEVIN/WZ	10.00	112 11	10.20		- 0-1470400 - 0-3616400	
コーレントリート	17.00	C)	1	and the second secon	<ul> <li>An all statutes at the initial state</li> </ul>	

AVG RATE DURING DALITE(SEC\*\*-1) 0.254E-05 RATE INTEGRATED OVER FULL DAY(DAY\*\*-1) 0.797E-01 HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.869E+01 NEAK SURFACE

STATISTICAL ANALYSIS (SPSS) " OF THE PHOTOLYTIC DEGRADATION RATE CONSTANTS FOR 2,3,7,8-T4CDF AND  $2, 3, 4, 7, 8 - P_5 CDF$ .

> $2, 3, 7, 8 - T_4 CDF$ 2,3,4,7,8-P<sub>5</sub>CDF

k <sub>DE</sub> (d <sup>-1</sup> ) <sup>b</sup>	0.10	0.014
Std Err in k <sub>DE</sub> (d <sup>-1</sup> ) <sup>c</sup>	±0.007	±0.007
95% Confdnce Intrvl B <sup>d</sup>	0.083-0.12	0.0029-0.031
k <sub>PE</sub> (d <sup>-1</sup> ) <sup>e</sup>	0.50	3.6
Std Err in k <sub>PE</sub> (d <sup>-1</sup> ) <sup>e</sup>	±0.05	±0.3
95% Confdnce Intrvl B <sup>d</sup>	0.38-0.61	2.7-4.6

"SPSS computer program used for statistical analysis (102). <sup>b</sup>All  $k_{DE}$  values are summarized in Table 15. <sup>c</sup>Std Err represent the error in the slope of the line used

to calculate  $k_{DE}$  or  $k_{PE}$ .

<sup>d</sup>95% Confdnce Intrvl B represents the range within which there is a 95% probability of finding the true  $k_{\text{DE}}$  or  $k_{\text{PE}}$ value.