

PHYSICAL PROPERTIES, SUNLIGHT PHOTOLYSIS, AND
ENVIRONMENTAL FATE OF POLYCHLORINATED DIBENZO-*p*-DIOXINS
IN AQUATIC ECOSYSTEMS

A Thesis
Presented to the
Faculty of Graduate Studies
The University of Manitoba

In Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

Kenneth J. Friesen
1988

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BY

KENNETH J. FRIESEN

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY

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To Jeri and Travis

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ABSTRACT

Several physical properties, water solubility (S_w) and Henry's law constant (H), which are important parameters influencing the behaviour of chemicals emitted into the environment, were determined for a homologous series of polychlorinated dibenzo-*p*-dioxins. Water solubilities for 1,2,3,7-tetra-, 1,2,3,4,7-penta-, 1,2,3,4,7,8-hexa-, and 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxins, determined by the generator column method over the environmentally significant temperature range of 7-41°C, increased gradually with temperature and ranged from as high as 1400 ng/L for T₄CDD at 41°C to as low as 0.9 ng/L for H₇CDD at 7°C. Thermodynamic analysis of dissolution yielded enthalpies of solution for these congeners ranging from 39.8-47.5 kJ/mol and indicated that entropy losses are important in limiting the solubilities of these hydrophobic compounds. Henry's law constants, determined at 23°C by the gas-sparging technique, decreased from 2.7 Pa·m³/mol for 1,2,3,7-T₄CDD to 1.5 Pa·m³/mol for 1,2,3,4,7-P₅CDD. Vapor pressures at ~25°C were predicted to be 6 x 10⁻⁶ and 7 x 10⁻⁷ Pa for T₄CDD and P₅CDD, respectively, from the experimentally determined S_w and H values. The Henry's law constants suggest that these PCDDs will experience both liquid and gas phase resistance in volatilizing from water.

Two PCDDs, 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD, were found to undergo rapid sunlight photolysis in natural waters, with observed first-order rate constants of 0.74 and 0.28 d⁻¹ for the two congeners, respectively. These rates were much higher than the rates predicted with Mill's model for the direct aqueous photolysis of these compounds under midsummer sunlight conditions at 50°N latitude. The results indicated that sensitized photolysis, likely by dissolved humic

materials in the water, contributed to the fast photolytic breakdown of these compounds. Although structures were not confirmed, small amounts of several compounds with HPLC retention characteristics of less chlorinated dioxins were detected along with a large amount of polar degradation product(s) which was nonextractable from the water.

The environmental fate of 1,2,3,4,7-P₅CDD was studied in pond mesocosms to determine whether the input pathway of the PCDD had any effect on the overall redistribution of the dioxin in the aquatic ecosystem. The dioxin was added to the ponds as either a sediment slurry or as a sprayover in a water miscible organic solvent, simulating environmental influx of PCDDs into lakes with the chemical either sorbed to particulate matter (as in runoff or atmospheric deposition) or in solution (spraydrift or rainfall). Air, surface microlayers, the water column, caged crayfish and fathead minnows held in the water column, bottom sediments, and benthic biota were monitored during the course of the experiment (105 d). When P₅CDD was sprayed onto the water surface, volatilization and bioavailability to fish in the water column were enhanced in comparison to these processes in ponds receiving a sediment slurry input of the dioxin. For the spray-over input, levels of P₅CDD in bottom sediments were approximately one-half of the levels observed for a sediment slurry input of the dioxin. Two fugacity-based models (QWASI and QWASFI) were used to generate transport parameters to fit the observed behaviour patterns for the two types of input. A rapid rate of sediment deposition dominated the movement of P₅CDD in ponds treated with a sediment slurry of the dioxin whereas, according to the model, volatilization was an important removal process when the PCDD entered the system as a surface spray.

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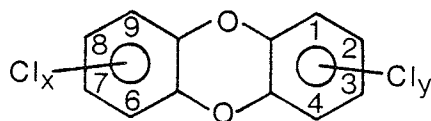
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INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are a group of hazardous chemicals which have received much attention since the discovery of the most toxic member, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (T₄CDD), in the herbicide Agent Orange used as a defoliant in Vietnam in the 1960s. Most of the early dioxin publicity resulted from incidents involving 2,3,7,8-T₄CDD. For example, the contamination of the town of Times Beach, MO by dioxin contaminated oil used to control street dust, the discovery of 2,3,7,8-T₄CDD in sewer sediments near a former chemical waste disposal site at Love Canal in Niagara Falls, NY, and the explosion of a 2,4,5-T plant in Seveso, Italy were all of concern because of the release of 2,3,7,8-T₄CDD into the environment. These incidents stimulated research into the toxicology, physico-chemical properties, and environmental behaviour of 2,3,7,8-T₄CDD. More recently a wide range of PCDD congeners have been detected in Great Lakes sediments and in municipal and industrial incinerator emissions resulting in increased interest in isomers other than 2,3,7,8-T₄CDD.

Polychlorinated dioxins are tricyclic, aromatic compounds which have essentially planar structures. Single-crystal X-ray diffraction



$x, y = 1-4$

measurements (1) showed that 2,3,7,8-T₄CDD is contained within a unit cell of dimensions 3.783 x 9.975 x 15.639 Å. There are 75 possible chlorinated dioxin isomers divided among the eight congener groups as summarized in Table 1.

Table 1. Distribution of the 75 Polychlorinated Dibenzo-*p*-dioxin Isomers into Congener Groupings.

No. Cl	Congener Group	No. Isomers
1	chloro	2
2	dichloro	10
3	trichloro	14
4	tetrachloro	22
5	pentachloro	14
6	hexachloro	10
7	heptachloro	2
8	octachloro	1

In general, PCDDs are characterized by water solubilities in the ng/L or ppt range (2) with vapor pressures of the order of 10^{-11} atm for T₄CDD and lower for more highly chlorinated congeners (3). As a result of their extreme hydrophobicity, PCDDs released into the environment tend to partition out of water into available organic phases. In aquatic ecosystems PCDDs bioconcentrate in fish and aquatic organisms and accumulate in bottom and suspended sediments, whereas in the terrestrial environment PCDDs sorb strongly to soil organic matter. Bioconcentration factors (28-day BCFs) for 2,3,7,8-T₄CDD in fathead minnows and rainbow trout of 5800 (4) and 29000 (5) have been reported. Muir, et al. (6,7) calculated equilibrium BCFs for a series of PCDDs from measured uptake and elimination rate constants and demonstrated that steric factors and true water solubility were important parameters affecting the uptake of PCDDs by fish. In spite of extremely low vapor pressures, PCDDs have a tendency to volatilize from both soil and water surfaces. For example, losses of 1,3,6,8-T₄CDD (8) and 2,3,7,8-T₄CDD

(9,10) from soils have been attributed to volatilization.

Chlorinated dioxins are persistent organic chemicals, resisting microbial and chemical degradation in soil, sediments, and water. PCDDs may, however, be quite rapidly photolyzed under sunlight conditions. Dulin, et al. (11) reported a half-life for sunlight photolysis of 2,3,7,8-T₄CDD in water-acetonitrile solutions of 1.15 d. The importance of this degradation pathway in the environment is decreased in aquatic and terrestrial ecosystems since partitioning of these compounds to organic phases decreases their accessibility to sunlight photolysis.

Concern with PCDDs resulted due to the general persistence of these compounds combined with the extreme toxicity of several members of this family. A single, oral dose LD₅₀ value of 2 µg/kg has been reported for guinea pigs exposed to 2,3,7,8-T₄CDD (12), with lethal doses for mice approximately 100 times greater. Kociba and Cabey (13) have reported the comparative toxicity and biological effects of PCDDs relative to the most toxic chlorinated dioxin, 2,3,7,8-T₄CDD. Barnes, et al. (14) report toxicities of other congeners relative to 2,3,7,8-T₄CDD with toxic equivalence factors (TEF). Data for several PCDDs, including the two most toxic isomers and the PCDDs used in this study are summarized in Table 2. Congeners with 4-6 chlorine atoms and all lateral positions (2,3,7, and 8) chlorinated are the most toxic PCDDs (15). The reproductive NOEL (no-observed-effect-level) for rats is as low as 30 ng/kg body weight/day for 2,3,7,8-T₄CDD and as high as 3 g/kg body weight/day for 1,3,6,8-T₄CDD demonstrating the extreme variations in toxicities and biological effects of different PCDDs.

Background PCDD levels of 1-600 ppt have been found in the general

Table 2. Toxicities and Biological Effects of Several Polychlorinated Dibenzo-*p*-dioxins.

Congener	LD ₅₀ (μg/kg) guinea pig	AHH Activity ^a in Rat Hepatoma Cells	TEF ^b	NOEL ^c
2,3,7,8-T ₄ CDD	0.6-2	1.0	1.0	0.03-0.125
1,2,3,7-T ₄ CDD	>2000 ^d	--	--	--
1,2,3,4,7-P ₅ CDD	>1000 ^d	0.048-0.0076	--	--
1,2,3,7,8-P ₅ CDD	3.1	0.2-0.019	0.2	--
1,2,3,4,7,8-H ₆ CDD	72.5	0.1-0.05	0.04	0.1 ^e
1,2,3,4,6,7,8-H ₇ CDD	>600	0.0035-0.0027	0.001	--
O ₈ CDD	--	0.000019	0	500,000

^aAryl hydrocarbon hydroxylase activity expressed relative to the enzyme activity in 2,3,7,8-T₄CDD (13).

^bToxic Equivalence Factor expressing the toxicity of PCDDs relative to 2,3,7,8-T₄CDD (14).

^cReproductive no-observed-effect-level for rats expressed in μg/kg body weight/day (13).

^dEstimated single dose oral LD₅₀ from data in Barnes, et al. (14) for non-2,3,7,8-substituted PCDDs.

^eUnspecified mixture of two hexachlorinated dioxins (13).

population using autopsy samples (16), with highest levels found in adipose tissue. Only 2,3,7,8-substituted PCDDs were detected, with O₈CDD being the most dominant isomer and concentrations decreasing for hepta-, hexa-, penta-, and tetrachlorinated dioxins. The major sources of PCDD emissions into the environment, particularly in Canada, are believed to be incineration of municipal and industrial wastes, the use of chlorophenols in wood treatment, and the use of a chlorine bleaching process by pulp and paper mills (121). A recent review (18) estimates that forest fires may also be a major source of combustion-generated PCDDs. Hutzinger et al. (19) suggest that chlorination of municipal drinking water may result in the chlorination of naturally occurring

phenolics in water, followed by condensation reactions to produce chlorinated dioxins. Several reports (20,21) implicate automobile exhausts as a nonpoint source of PCDD emissions, with dioxins produced during combustion of fuel in the presence of chlorinated additives. PCDDs have been found in fish and other aquatic organisms (22), in lake sediments in remote areas (23), in herring gull eggs (24), and in breast milk (25) leading to the belief that PCDDs may be ubiquitous in the environment.

The PCDD homologue pattern found in different environmental matrices may provide clues as to their likely sources. Czuczwa and Hites (26) suggest that the presence of T₄CDDs, P₅CDDs, H₆CDDs, H₇CDDs, and O₈CDD in sediments, human adipose tissue, and incinerator effluents indicate combustion as the major source of background contamination of PCDDs in the environment. Rappe and Kjeller (27) report that automobile emissions will produce the same isomer pattern as general combustion, with concentrations of O₈CDD > H₇CDDs > H₆CDDs > P₅CDDs > T₄CDDs. A concentration profile showing enrichment in other isomers may suggest a local point source emitting dioxins into the environment. For example, Norstrom (22) has found an isomer distribution enriched in 1,2,4,7,8-P₅CDD and 1,2,3,6,7,9/1,2,3,6,8,9-H₆CDDs in crab hepatopancreas in various sampling sites near wood treatment plants and sawmills in British Columbia. Typical levels of PCDDs in a variety of samples are summarized in Table 3. The enrichment of the higher chlorinated dioxins in surficial sediments relative to combustion sources may be due to faster rates of atmospheric photolytic degradation of the less chlorinated isomers along with greater sorption partition coefficients into sediment organic matter by the more highly chlorinated congeners.

Table 3. Polychlorinated Dioxin Levels in Various Environmental and Biological Samples.

Congener Group	Human Adipose Tissue (pg/g) ^a	Human Milk (ppt) ^b	Sediments (ppt) ^c	Air (ppb) ^d	Municipal Incinerator (ppb) ^e
T ₄ CDDs	7.4	0.6	26	0.5	90
P ₅ CDDs	10	6.5	12	6.4	220
H ₆ CDDs	61	27.8	10	1.6	370
H ₇ CDDs	110	59.5	70	21.2	280
O ₈ CDD	430	302	560	200	119

^a2,3,7,8-substituted PCDDs found in human autopsy abdominal fat sample reported in pg/g wet tissue weight (16).

^bLevels of PCDDs, all 2,3,7,8-substituted, reported on fat weight basis (22).

^cTotal PCDDs in surficial sediments in Siskiwit Lake (23).

^dTotal PCDDs in air particulate samples collected in Washington, DC (23).

^eEstimated total PCDDs in effluent from a municipal incinerator in the Netherlands (26).

However, any interpretation of the levels and patterns of PCDDs in any matrix must take into account all sources as well as the potential for accumulation of different PCDDs.

Due to the occurrence of a wide range of chlorinated dioxins in the environment, it is important to study isomers other than the most toxic 2,3,7,8-T₄CDD. In this thesis a set of experiments have been performed to determine physico-chemical properties of several PCDDs and then to determine the environmental fate of 1,2,3,4,7-P₅CDD as a function of its input mechanism into an aquatic ecosystem. The water solubilities and Henry's constants are important physical constants influencing the environmental behaviour of these hydrophobic contaminants. The rate of sunlight photolysis of several PCDD isomers in natural waters provides the major transformation rate constant which is expected to apply

during the environmental fate study. Finally, the environmental fate of one isomer, 1,2,3,4,7-P₅CDD, is determined in outdoor model aquatic ecosystems using two different input schemes simulating spraydrift and influx of contaminated particulate matter into an aquatic system. The physico-chemical parameters are used to predict the fate of the PCDD in the system with a quantitative water-air-sediment-film interaction model (118). The experimental results should be useful in validating the applicability of the model in predicting the environmental fate of extremely hydrophobic chemicals in aquatic ecosystems.

CHAPTER 1

DETERMINATION OF AQUEOUS SOLUBILITIES AND HENRY'S CONSTANTS OF SELECTED POLYCHLORINATED DIBENZO-*p*-DIOXINS

I. INTRODUCTION

With current increased awareness of the presence of polycyclic and polychlorinated aromatic hydrocarbon pollutants in the environment, efforts have increased to accurately determine the physical properties of these compounds. The aqueous solubility of these environmental contaminants is of particular importance since their fate and distribution in the environment, in particular, the availability for uptake by biota, is largely controlled by this parameter. The Henry's law constant (H), a parameter which represents the equilibrium partitioning of a sparingly soluble chemical between air and water, is important in describing the tendency of a chemical to volatilize from a body of water. Henry's constant is therefore useful in describing the environmental transfer of pollutants across the air-water interface.

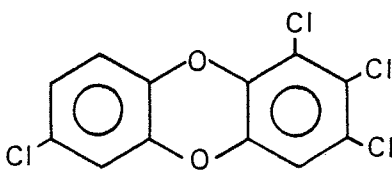
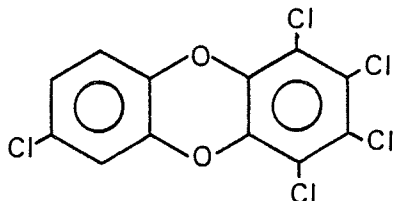
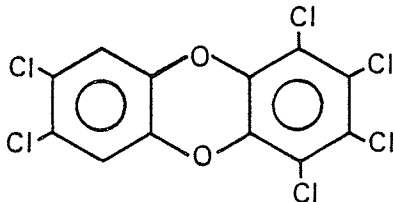
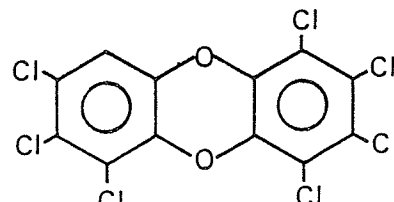
The HPLC-generator column method developed by May et al. (28,29) has become a widely accepted method for the accurate determination of aqueous solubilities of super lipophilic compounds. In their initial development of the technique, May et al. (29) reported the water solubilities of several polycyclic aromatic hydrocarbons (PAHs). More recently, Dickhut et al. (30) and Opperhuizen et al. (31) have reported aqueous solubilities of polychlorinated benzenes (PCBs), whereas Friesen et al. (2) determined the solubilities of a series of polychlorinated dibenzo-*p*-dioxins (PCDDs) at 20° and 40°C. Shiu et al. (32) have reported enthalpies of solution of several PCDDs using the generator column technique.

For hydrophobic compounds, where aqueous concentrations are very

small, the gas-sparging technique of Mackay et al. (33) is generally considered a convenient method for the experimental determination of Henry's constant. Mackay, et al. (33) showed that H could be measured for a number of aromatic hydrocarbons with an estimated accuracy of approximately 5%. Nicholson, et al. (34) have used a similar stripping technique to determine H of the trihalomethanes; whereas, Gossett (35) used the EPICS (Equilibrium Partitioning in Closed Systems) technique to measure Henry's constants of 13 C₁ and C₂ chlorinated hydrocarbons. Henry's law constants have recently been predicted for PCBs (36) from aqueous solubilities and vapor pressures of individual congeners. However, the calculations utilized predicted water solubilities and vapor pressures and hence the reported Henry's constants are based on theoretical predictions rather than on experimental measurements.

In this investigation the water solubilities of four PCDD congeners are reported at a series of environmentally significant temperatures. The congeners chosen for the study (see Table 4) are closely related structurally, having very similar chlorine substitution patterns. The results are used for a brief evaluation of the thermodynamics of dissolution of these compounds. Correlation of the water solubilities or aqueous activity coefficients of these congeners with two molecular descriptors, total surface area and total molecular volume, is also discussed. The Henry's law constants of two congeners, T₄CDD and P₅CDD, are determined at 23°C using the gas-sparging technique. The results are combined with aqueous solubility data to calculate vapor pressures of these congeners.

Table 4. Structures and Physical Constants of Polychlorinated Dibenzo-*p*-dioxins used in the Solubility Study.^a

	T ₄ CDD
	MW 321.96
	mp 172-175
1,2,3,7-tetrachlorodibenzo- <i>p</i> -dioxin	
	P ₅ CDD
	MW 356.40
	mp 187-188
1,2,3,4,7-pentachlorodibenzo- <i>p</i> -dioxin	
	H ₆ CDD
	MW 390.85
	mp 259-261
1,2,3,4,7,8-hexachlorodibenzo- <i>p</i> -dioxin	
	H ₇ CDD
	MW 425.29
	mp 264-265
1,2,3,4,6,7,8-heptachlorodibenzo- <i>p</i> -dioxin	

^aMelting points, reported in °C, determined by Pathfinder Laboratories Inc.

II. EXPERIMENTAL

A. CHEMICALS

The polychlorinated dibenzo-p-dioxins (PCDDs), purchased from Pathfinder Laboratories Inc. (St. Louis, MO) were each universally carbon-14 ring labelled with a specific activity of 24.16 mCi/mmol. Solvents used to purify the dioxins were distilled-in-glass quality purchased from Caledon Laboratories Inc. (Georgetown, ON). Water for the solubility and Henry's constant determinations was lab distilled water further distilled first from KMnO_4 and then from $\text{K}_2\text{Cr}_2\text{O}_7$ to destroy organic impurities and finally filtered through a $0.22\mu\text{m}$ Durapore filter (Waters Scientific, Mississauga, ON) prior to use. Liquid scintillation cocktail, Scintiverse I, was purchased from Fisher Scientific (Winnipeg, MB). Atomlight, supplied by New England Nuclear (Boston, MA) was used to dissolve and radioassay water samples in the Henry's constant determination.

B. APPARATUS

All high pressure liquid chromatography (hplc) was performed with a system consisting of a Waters model 6000A dual-piston reciprocating pump, a Waters model 440 UV detector operated at 254nm, and a 30cm x 3.9 mm i.d. Waters $\mu\text{Bondapak}$ octadecylsilane (C_{18}) analytical column. The system included a Rheodyne sample injection valve and a Valco 8-port switching valve to bring the generator column in or out of line with the C_{18} column. A Waters model III column oven and temperature control unit were used to maintain temperature of the generator column.

Liquid scintillation was conducted with a Beckman LS7500 Liquid Scintillation Counter. The H# method, with automatic quench compensation, was used for quench monitoring of all samples. A 10

min count time was preset with samples counted to a 2σ error of 2%. β -Emissions from carbon-14 were monitored in the 397-655 counting channel providing an energy window of 18-160 keV. A set of Amersham sealed quenched standards containing C-14 labelled toluene were used to prepare the quench curve for the analyses.

C. PURIFICATION OF DIOXINS

A purity check was made of all dioxin congeners by reverse phase hplc on a μ Bondapak C₁₈ column with 85% CH₃OH (15% H₂O) as the mobile phase. Fractions were collected and analyzed by liquid scintillation counting using 10 mL Scintiverse I as scintillation cocktail. The reconstructed chromatograms (Figure 1) showed that all congeners required further purification.

Initially, purification was attempted by thin-layer chromatography on silica gel (Sil G-25, Brinkman) with *n*-hexane as the mobile phase and autoradiographic detection using x-ray film (Kodak). Recovery of the "dioxin" band followed by hplc analysis showed that this band consisted of several fairly nonpolar products in each case. Therefore, subsequent purifications simply utilized preparative hplc on a C₁₈ column with 85% CH₃OH as the mobile phase at a flow rate of 1.0 mL/min, collecting each dioxin in a window centered at its retention time. In the purchased T₄CDD, hplc revealed the presence of two isomers with very similar retention times. Using hplc in the recycle mode, with 80% CH₃OH at a flow rate of 2.0 mL/min, 1,2,3,7-T₄CDD was separated from what was believed to be 1,2,3,8-T₄CDD formed during the synthesis of this dioxin. The more intense peak, having a slightly shorter retention time, was believed to be the major component and was collected as 1,2,3,7-T₄CDD.

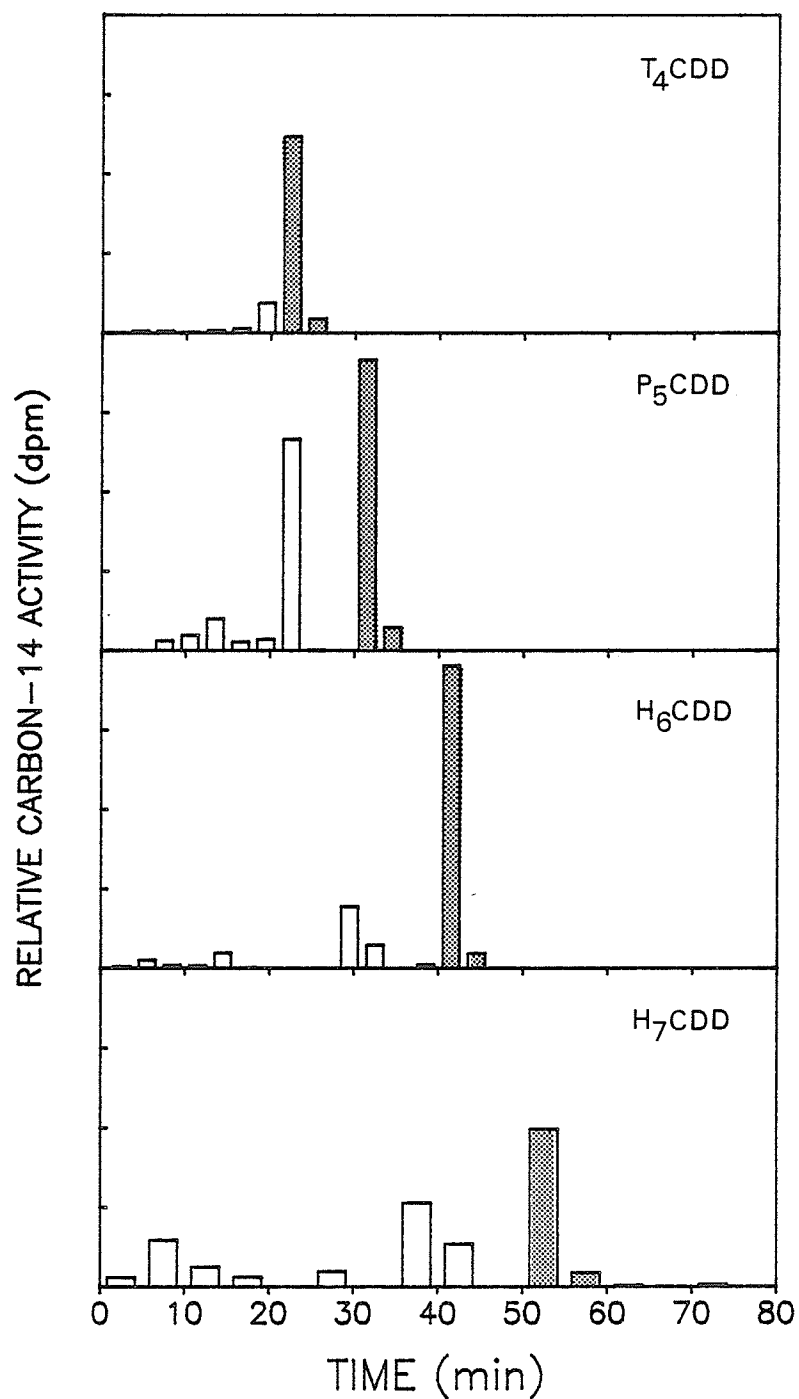


Figure 1. Reconstructed chromatograms of the PCDDs prior to purification with 85% CH₃OH as the mobile phase. Continuous 3 min samples (5 min for H₇CDD) were collected and analyzed by hplc-lsc with parent PCDD indicated (■) in each case.

The water in each of these fractions was then removed by formation of a low boiling ternary azeotrope (81% CHCl₃-15% CH₃OH-4% H₂O; bp 52.6°C) followed by careful rotary evaporation. This procedure was repeated until addition of CHCl₃ no longer caused formation of either a second layer or cloudiness, indicating that all of the water had been removed. CHCl₃ was then removed as a binary azeotrope (87% CHCl₃-13% CH₃OH; bp 53.5°C). Finally, CH₃OH was also removed as a binary azeotrope (88% acetone-12% CH₃OH; bp 55.7°C) leaving the dioxin in a relatively volatile solvent.

After purification, radiopurity was again checked by the hplc-lsc combination with all isomers having >99% radiopurity.

D. WATER SOLUBILITY DETERMINATIONS

Glass beads, sieved to 60/80 mesh and cleaned by soxhlet extraction with 1:1 acetone-hexane for 6 h, were used as the solid support. The solute, dissolved in acetone or tetrahydrofuran (THF), was coated onto the beads by swirling on a rotary evaporator for 1 h. Excess solvent was carefully removed under reduced pressure and the beads were allowed to air dry overnight. The coated beads, carrying a dioxin load of 0.0002-0.0003% (~20-30 µg/10 g beads), were dry-packed into a 30 cm x 3.9 mm i.d. stainless steel hplc column fitted with 2 µm end frits, to form the generator column for the solubility determinations.

The generator column was placed into the column oven which was then set into a styrofoam cooling chamber containing a layer of bagged crushed ice. Frozen Fridgpaks were placed on top of the column oven to cool the oven to below 5°C for the low temperature determinations. The generator column was plumbed into the hplc system (Figure 2) forming a loop on the 8-port Valco switching valve. The column was conditioned

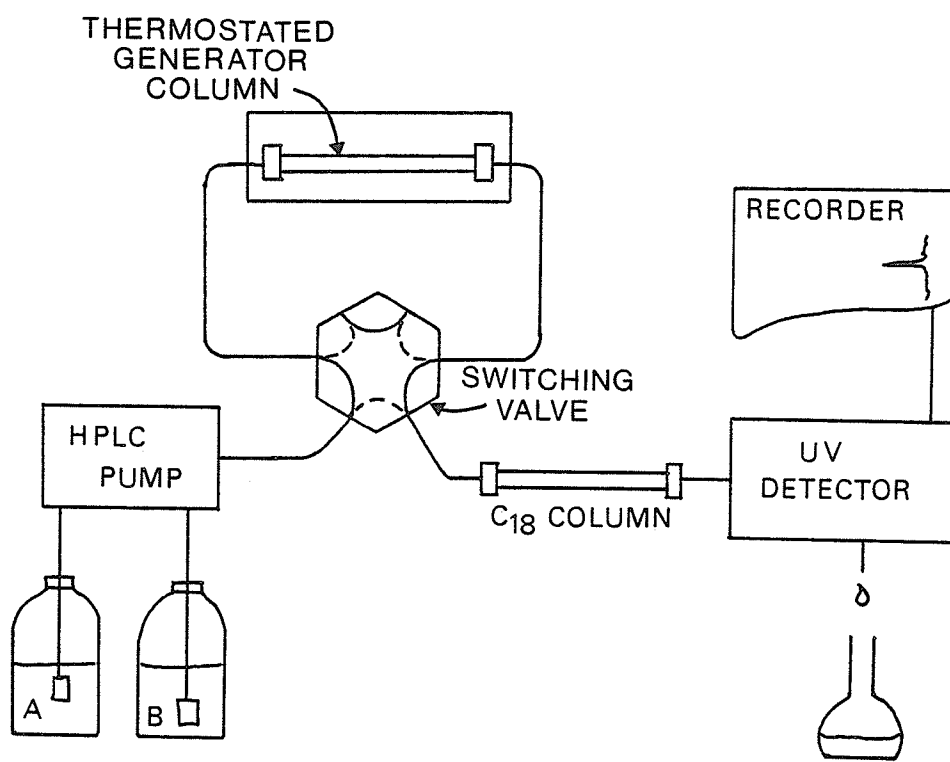


Figure 2. Hplc system configuration for water solubility determination, with A = water and B = 85% CH₃OH.

with 300 mL of water at 1.0 mL/min prior to connecting it at the switching valve. This procedure was assumed to have coated the inner surface of the tubing from the generator column to the switching valve with solute with the result that adsorptive losses were minimized during the actual solubility determination. This line, essentially an extension of the generator column, was kept as short as possible and was wrapped with polyurethane foam to insulate it for low temperature studies. The rest of the hplc system, including the C₁₈ column and all connecting tubing, was pre-eluted with CH₃OH and thoroughly equilibrated with water.

The generator column was then connected to the switching valve and the solubility determination was carried out by pumping the purified water through the system at 1.0 or 2.0 mL/min. The solute dissolved in the water was carried to the analytical column where it partitioned onto the C₁₈ stationary phase. After a measured volume of water had been collected, the generator column was taken out of line with a turn of the switching valve. The analytical column was then eluted with 85% CH₃OH at a flow rate of 1.0 mL/min. Fractions were collected at regular intervals, 10 mL of Scintiverse I was added to each, and analyses were carried out by liquid scintillation counting. Water solubilities were calculated after correcting for background activity.

E. DETERMINATION OF HENRY'S LAW CONSTANTS

Initially 900 mL of prepurified water was carefully pipetted into the gas-sparging apparatus (Figure 3). The dioxin (dissolved in THF) was then spiked directly into the water column and an additional 100 mL of water was added to bring the water volume up to exactly 1 L. The solution was stirred rapidly for 10 h to ensure proper dissolution of

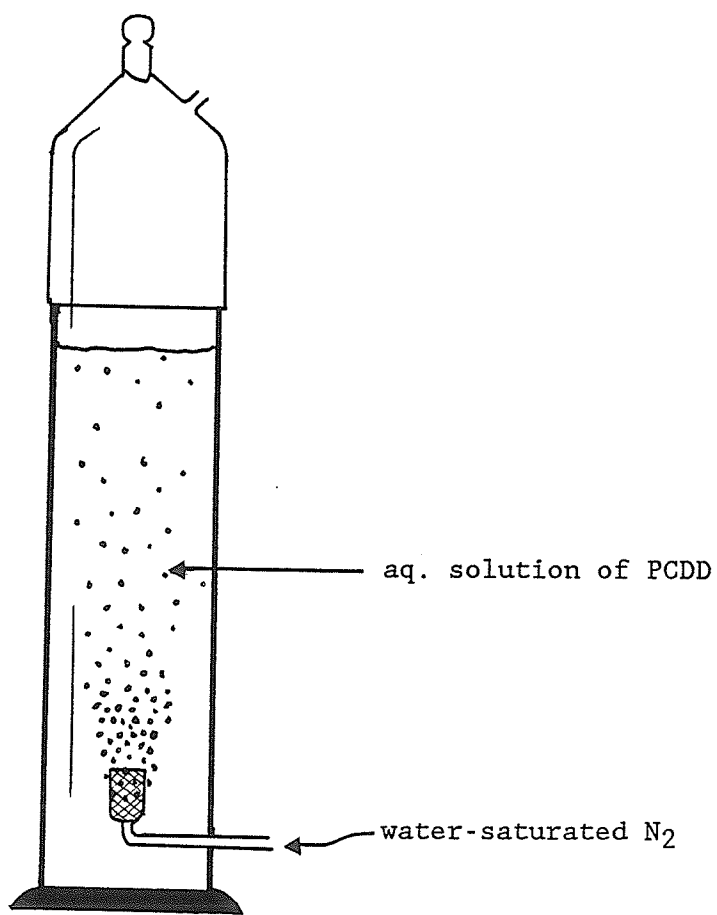


Figure 3. Gas-sparging apparatus used in the determination of Henry's law constants.

the dioxin. This procedure allowed the small amount of organic solvent carrier to evaporate and provided time for dioxin losses to the glass walls of the apparatus to stabilize. A slow flow of zero-grade nitrogen, presaturated with water to prevent evaporation of water in the sparging cylinder, was used to prevent backup of water into the N₂ line.

The stirrer was then turned off and the N₂ flow rate, controlled by a rotameter, was set to ~100 mL/min. The sparging was allowed to continue for 2 h prior to commencing sampling in order to allow the dioxin in the water to equilibrate with dioxin in the gas at the head of the water column. Triplicate 4.00 mL water samples were removed at each sampling time and analyzed by adding 15 mL of Atomlight for liquid scintillation counting. A 20 min counting time was used due to the low levels of activity in all of these samples.

Henry's law constants for both PCDDs were determined in duplicate, using two gas-sparging cylinders for simultaneous replication. In order to minimize temperature fluctuations, the experiment was performed in an environment room maintained at 23°C. Accurate N₂ flow rates were measured with a soap-bubble flow meter throughout the duration of the experiment.

III. RESULTS AND DISCUSSION

A. AQUEOUS SOLUBILITIES

Solubilities of four congeners, 1,2,3,7-tetrachlorodibenzo-*p*-dioxin (T₄CDD), 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin (P₅CDD), 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (H₆CDD), and 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (H₇CDD), were each measured at six temperatures as summarized in Table 5. Duplicate measurements were generally sufficient to obtain excellent precision, with variations ranging from 0.2% to 4.4%. In certain cases, for example the 21°C measurements, the entire procedure including dioxin purification and generator column preparation was repeated in order to check the overall reproducibility of the method. Variations ranged from 2.3% for P₅CDD to 9.6, 14.3, and 14.1% for H₆CDD, H₇CDD, and T₄CDD, respectively. The variations for H₆CDD and H₇CDD may indicate the difficulty in determination of solubility of the more hydrophobic congeners. The lack of precision for determinations of the T₄CDD congener, however, is attributed to difficulties in purification of the parent dioxin from a closely related isomer.

Solubilities were generally determined at several flow rates, usually 1.0 and 2.0 mL/min, to verify that equilibrium was in fact established between dioxin coated to the glass beads and dioxin in the water flowing through the column. Except for H₇CDD at 40°C, no significant differences in solubility, as determined by the null hypothesis test at the 95% confidence level, could be attributed to flow rate changes. Solubilities at 1.0 mL/min varied within 95.3 to 106.3% of the values at 2.0 mL/min for all other determinations. These variations fell within the range of all the determinations at 1.0

Table 5. Water Solubilities of Four PCDD Congeners at Different Temperatures.

Congener	Temp(°C) ^a	n	S _w (mol/L)
T ₄ CDD	7	2	(7.56 ± 0.20) x 10 ⁻¹⁰
	11.5	2	(8.12 ± 0.11) x 10 ⁻¹⁰
	17	4	(1.25 ± 0.36) x 10 ⁻⁹
	21	6	(1.49 ± 0.21) x 10 ⁻⁹
	26	2	(2.26 ± 0.10) x 10 ⁻⁹
	41	6	(4.33 ± 0.54) x 10 ⁻⁹
P ₅ CDD	7	3	(1.42 ± 0.01) x 10 ⁻¹⁰
	11.5	2	(1.88 ± 0.01) x 10 ⁻¹⁰
	17	2	(2.44 ± 0.01) x 10 ⁻¹⁰
	21	7	(3.45 ± 0.08) x 10 ⁻¹⁰
	26	2	(4.63 ± 0.03) x 10 ⁻¹⁰
	41	6	(1.28 ± 0.01) x 10 ⁻⁹
H ₆ CDD	7	2	(5.91 ± 0.05) x 10 ⁻¹²
	11.5	2	(7.98 ± 0.15) x 10 ⁻¹²
	17	2	(1.07 ± 0.04) x 10 ⁻¹¹
	21	6	(1.25 ± 0.12) x 10 ⁻¹¹
	26	2	(2.02 ± 0.04) x 10 ⁻¹¹
	41	3	(4.86 ± 0.14) x 10 ⁻¹¹
H ₇ CDD	7	2	(2.20 ± 0.09) x 10 ⁻¹²
	11.5	2	(2.69 ± 0.01) x 10 ⁻¹²
	17	2	(3.04 ± 0.06) x 10 ⁻¹²
	21	4	(5.40 ± 0.77) x 10 ⁻¹²
	26	2	(6.03 ± 0.18) x 10 ⁻¹²
	41	2	(1.49 ± 0.05) x 10 ⁻¹¹

^aGenerator column oven temperatures calibrated with an iron-constantan thermocouple (Omega Engineering Model 199 J).

mL/min indicating that saturation conditions were established even at 2.0 mL/min. For H₇CDD at 40°C, solubilities at 1.0 mL/min were 25% greater than those measured at 2.0 mL/min. Since this suggests that saturation was not achieved at 2.0 mL/min, only the data at 1.0 mL/min was considered valid. In several experiments the volume of water used in the determination was varied in order to ensure that a systematic error was not left undetected. For T₄CDD and P₅CDD, water volumes ranging from 50 to 200 mL provided sufficient dioxin to produce signals of 600 to 23700 dpm. Doubling the volume of water collected resulted in solubility increases of less than 6% in all cases. For H₆CDD, 500 mL of water were used in the majority of trials, producing signals of 160-1360 dpm. At 5°C, one trial in which 1 L was used produced a 1.7% decrease in solubility, again well within the precision of the method. For H₇CDD, 1 L of water dissolved sufficient dioxin to produce signals of 115-820 dpm, depending upon the temperature. The data suggests that changes in the volume of water collected do not produce significant differences in the measured aqueous solubilities of the chlorinated dioxins under investigation. The relative error in the analysis, however, was expected to increase as smaller amounts of material were collected.

B. THERMODYNAMICS OF DISSOLUTION

According to the van't Hoff equation (37), the dependence of the aqueous solubility on temperature for solids below their melting point is given by

$$d(\ln X)/d(1/T) = -\Delta H_{s_s}/R$$

where X is the mole fraction aqueous solubility, T the absolute temperature, R the gas constant, and ΔH_{s_s} the enthalpy of solution of

the solid solute. Assuming that $\Delta H_{s,s}$ is constant over the fairly small temperature range used in this study (7 - 41°C), the integrated form of the equation

$$\ln X = -\Delta H_{s,s}/RT + C$$

may be used to obtain enthalpies of solutions of the dioxins studied. Therefore, plotting $\ln X$ vs. $1/T \times 10^3$ (Figure 4) will provide $\Delta H_{s,s}$ from the slope of a linear regression of each set of data, as summarized in Table 6.

Table 6. Enthalpies of Solution of PCDD Congeners

Congener	$\Delta H_{s,s}$ (kJ/mol)	r^2
1,2,3,7-T ₄ CDD	39.8 ± 2.4	0.985
1,2,3,4,7-P ₅ CDD	47.5 ± 1.9	0.993
1,2,3,4,7,8-H ₆ CDD	45.5 ± 2.2	0.991
1,2,3,4,6,7,8-H ₇ CDD	42.2 ± 3.6	0.971

The enthalpies of solution for the PCDDs studied fall within a fairly narrow range of 39.8 to 47.5 kJ/mol. Previous studies have reported a range in the heats of solution for PCBs from 28.5 to 66.6 kJ/mol (30) and for PAHs from 28.7 to 56.9 kJ/mol (29). The variations are, however, likely due to structural features of the congeners studied. For the PCDDs studied here, the four compounds form a homologous series with each successive member containing an additional chlorine atom. If the PCB and PAH data are broken down into structurally similar compounds the variation is not nearly as severe. For example, $\Delta H_{s,s}$ for the three members of the anthracene group range from 42.3 to 44.8 kJ/mol whereas $\Delta H_{s,s}$ for hexa-, octa-, nona-, and decachlorobiphenyl, with similar Cl substitution patterns, range from

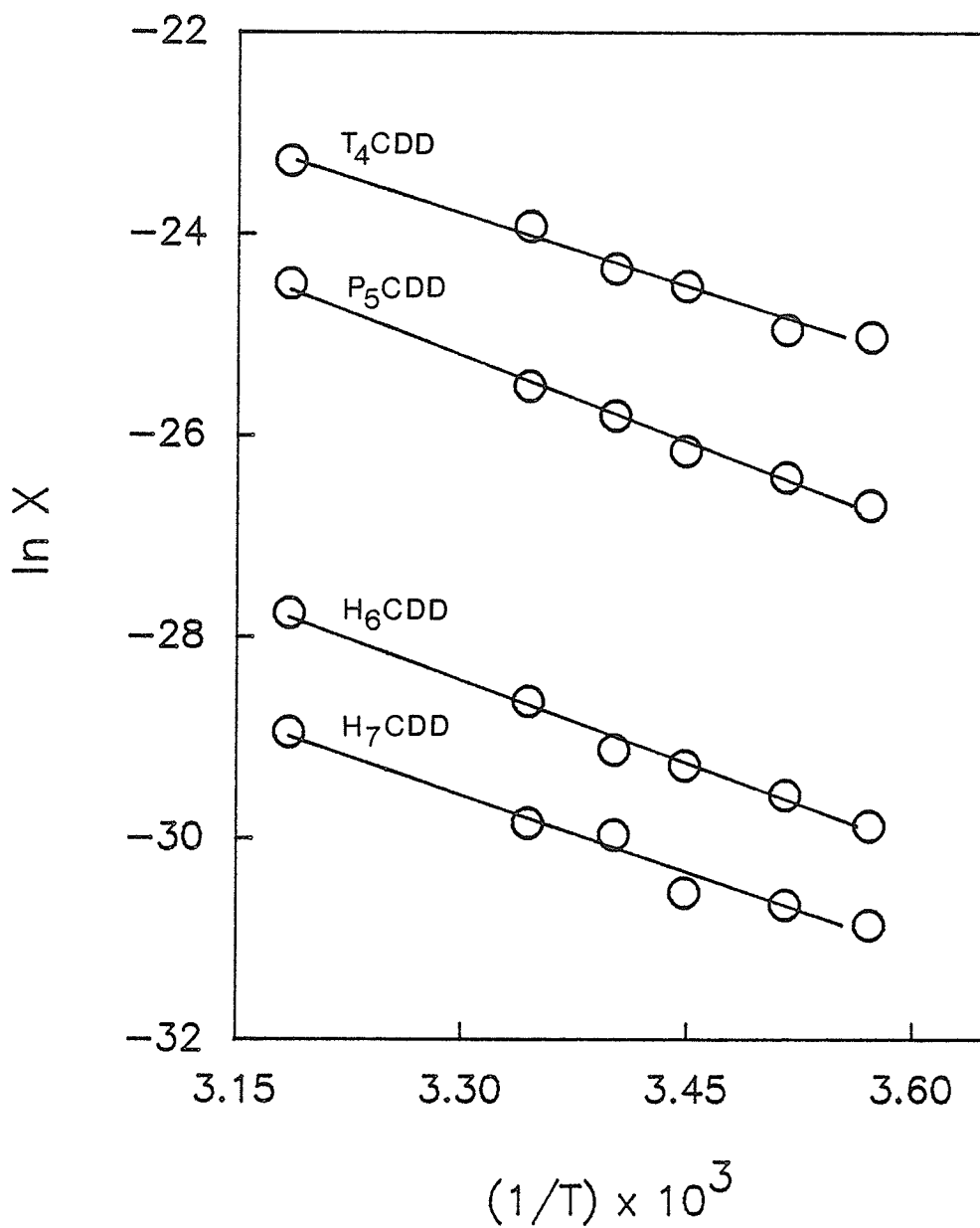


Figure 4. Plots showing the temperature dependence of the aqueous solubility of four polychlorinated dioxins.

45.6 to 66.6 kJ/mol. The smaller variation in $\Delta H_{s,s}$ for the PCDDs and PAHs above may reflect the greater degree of rigidity of these compounds since they are not subject to rotation about a C-C bond as are most PCBs (38). However, recent data reported by Shiu, et al. (32) show that enthalpies of solution range from 33.4 to 53.6 kJ/mol for a series of chlorinated dioxins, ranging from the parent nonchlorinated dioxin to 1,2,3,4-T₄CDD. The range is narrowed to 40.9-53.6 kJ/mol without the low value for 1,2,3,4-T₄CDD. Possibly the particular symmetry of this structure changes the orientation of the molecules in the crystal lattice affecting the fusion energy.

For solids, the validity of the assumption that $\Delta H_{s,s}$ is constant with temperature has been questioned (39). Nonlinearity in the van't Hoff plots would support this premise. Such a conclusion could be reached after careful examination of the plots for P₅CDD and H₆CDD. For T₄CDD and H₇CDD, scatter in the data makes such a conclusion tenuous. However, a more thorough analysis of the thermodynamics of the dissolution process of these hydrophobic dioxins is possible.

If sufficient physico-chemical data are available, then the dissolution process may be treated as a series of steps within an overall thermodynamic cycle (40) as summarized in Figure 5. In the following treatment a thermodynamic analysis of the solid→subcooled liquid→aqueous solution process will be considered. In the absence of fusion data the Walden rule (41), which states that for rigid organic solids the entropy of fusion (ΔS_{fus}) may be approximated by the value 56.5 J/mol K, seems appropriate for the rigid PCDDs and is used in subsequent calculations. The free energy change ($\Delta G_{s,s}$) for the dissolution of the solid may be broken down into contributions for the

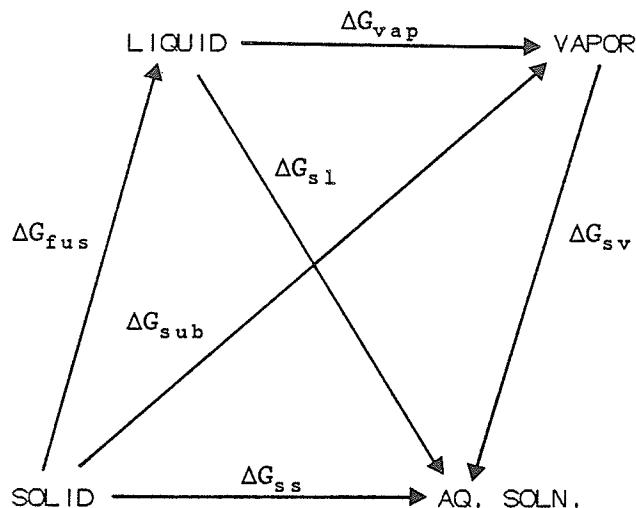


Figure 5. Thermodynamic cycle for the dissolution process, involving solid, subcooled liquid, vapor, and aqueous solution.

solid→subcooled liquid process (ΔG_{fus}) and the subcooled liquid→aqueous solution process (ΔG_{sl}).

For the overall solid→aqueous solution process, ΔH_{ss} is determined from the van't Hoff plots as indicated in Table 7. The free energy change for the process (ΔG_{ss}) is calculated from the mole fraction solubility at 26°C (299 K) according to

$$\Delta G_{ss} = -RT \ln X$$

The entropy contribution is then calculated from the relation between these three thermodynamic parameters, which breaks the free energy change into an enthalpy and an entropy contribution, namely

$$\Delta G_{ss} = \Delta H_{ss} - T\Delta S_{ss}$$

For the solid→liquid step, assuming $\Delta S_{fus} = 56.5 \text{ J/mol K}$, then the enthalpy of fusion may be calculated as

$$\Delta H_{fus} = T_m \Delta S_{fus}$$

This calculation further assumes that ΔH_{fus} at the system temperature

of 299 K is the same as that at the melting point (T_m). The free energy change associated with this process is calculated from

$$\Delta G_{fus} = \Delta S_{fus} (T_m - T)$$

The entropy term is then calculated from the familiar relationship

$$\Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus}$$

The thermodynamics of the subcooled liquid→aqueous solution stage are simply determined from a summation, since the overall dissolution is viewed as a two-step process, hence

$$\Delta G_{s1} = \Delta G_{ss} - \Delta G_{fus}$$

$$\Delta H_{s1} = \Delta H_{ss} - \Delta H_{fus}$$

$$\text{and } -T\Delta S_{s1} = \Delta G_{s1} - \Delta H_{s1}$$

The thermodynamic parameters for each of these steps calculated for each PCDD congener are summarized in Table 7. Differences in the melting points of the congeners studied have a noticeable correlation with the observed solubilities. For example, T₄CDD and P₅CDD have similar melting points (175 and 188°C respectively) with P₅CDD having a 4.3-fold decrease in S_w at 26°C. A large melting point change occurs for the H₆CDD (261°C) with a corresponding 27-fold decrease in solubility. The melting point of H₇CDD (265°C) is virtually identical

Table 7. Importance of Free Energy, Enthalpy, and Entropy in the Dissolution of PCDDs at 299 K (all values in kJ/mol).

Congener	ΔG_{ss}	ΔG_{fus}	ΔG_{s1}	ΔH_{ss}	ΔH_{fus}	ΔH_{s1}	$-T\Delta S_{ss}$	$-T\Delta S_{fus}$	$-T\Delta S_{s1}$
T ₄ CDD	59.5	8.4	51.1	39.8	25.3	14.5	19.7	-16.9	36.6
P ₅ CDD	63.4	9.2	54.2	47.5	26.0	21.5	15.9	-16.8	32.7
H ₆ CDD	71.2	13.3	57.9	45.5	30.2	15.3	25.7	-16.9	42.6
H ₇ CDD	74.2	13.5	60.7	42.2	30.4	11.8	32.0	-16.9	48.9

with that of H₆CDD, yet a 2.3-fold decrease in S_w is observed at 26°C. The fact that ΔG_{s1} >> ΔG_{fus} suggests that the subcooled liquid → aqueous solution step is a critical step in determining the solubilities of these solutes. A similar observation has recently been reported for PCBs (30,31,42). The relatively large negative entropy which accompanies the dissolution of the liquid molecules may be more important than the corresponding enthalpy of solution in controlling the solubility of these solutes in water. It appears that greater order is established in this process, hence this step is thermodynamically unfavorable. This is consistent with the observations recently discussed regarding the solubility process for PCBs (42). The solute-solvent interactions which accompany the formation of a cavity in the solvent (43) followed by placement of the hydrophobic solute into the cavity are thus important interactions determining the solubilities of these compounds as they are for PCBs (40,42).

C. CORRELATION OF SOLUBILITY WITH STRUCTURE

Two structural parameters describing the size of the solute, total surface area (TSA) and total molecular volume (TMV), are frequently used to provide correlations with aqueous solubility, or more generally the aqueous activity coefficient of the solute, γ_w (44). For solutes which are solids at the system temperature, γ_w may be calculated according to the equation (44)

$$-\ln X = \ln \gamma_w + \frac{\Delta S_{fus}}{R} \left(\frac{T_m - T}{T} \right)$$

This calculation assumes that the differential heat capacity between the solid and subcooled liquid, ΔC_p = 0 (31). Using ΔS_{fus} = 56.5 J/mol K, the activity coefficients are calculated for the system

temperature, $T = 26^{\circ}\text{C}$ or 299 K .

Total surface areas were calculated by Gobas (45) using a previously described method (31) whereas total molecular volumes were calculated by the method proposed by Edward (46) using volume increments for each type of atom or group in the molecule. The results, along with γ_w values calculated above, are summarized in Table 8.

Plots showing the correlation of γ_w with TSA and TMV are presented in Figures 6 and 7 respectively. The relationship of these structural

Table 8. Aqueous Solubility and Structural Parameters of Several PCDD Congeners at 299 K .

Congener	$T_m (^{\circ}\text{C})$	$-\ln X$	$\ln \gamma_w$	TSA(\AA^2)	TMV(\AA^3)
T ₄ CDD	175	23.93	20.54	297.2	210.0
P ₅ CDD	188	25.51	21.83	309.4	224.5
H ₆ CDD	261	28.64	23.30	321.3	239.0
H ₇ CDD	265	29.85	24.42	338.0	253.5

parameters to the aqueous activity coefficient is described by the following equations

$$\ln \gamma_w = 0.0966(\text{TSA}) - 8.041 \quad r^2 = 0.984$$

$$\text{and } \ln \gamma_w = 0.0904(\text{TMV}) + 1.569 \quad r^2 = 0.998$$

The fact that TMV provides a somewhat better correlation with solubility than TSA lends support to the thermodynamic data which highlighted the importance of entropy in the dissolution process. During the dissolution of the solute, a cavity of a particular volume must be created in the aqueous medium to accommodate placement of the solute. This structuring process in the solvent becomes more unfavorable as the volume of the solute molecule increases. Hence, the increased order or

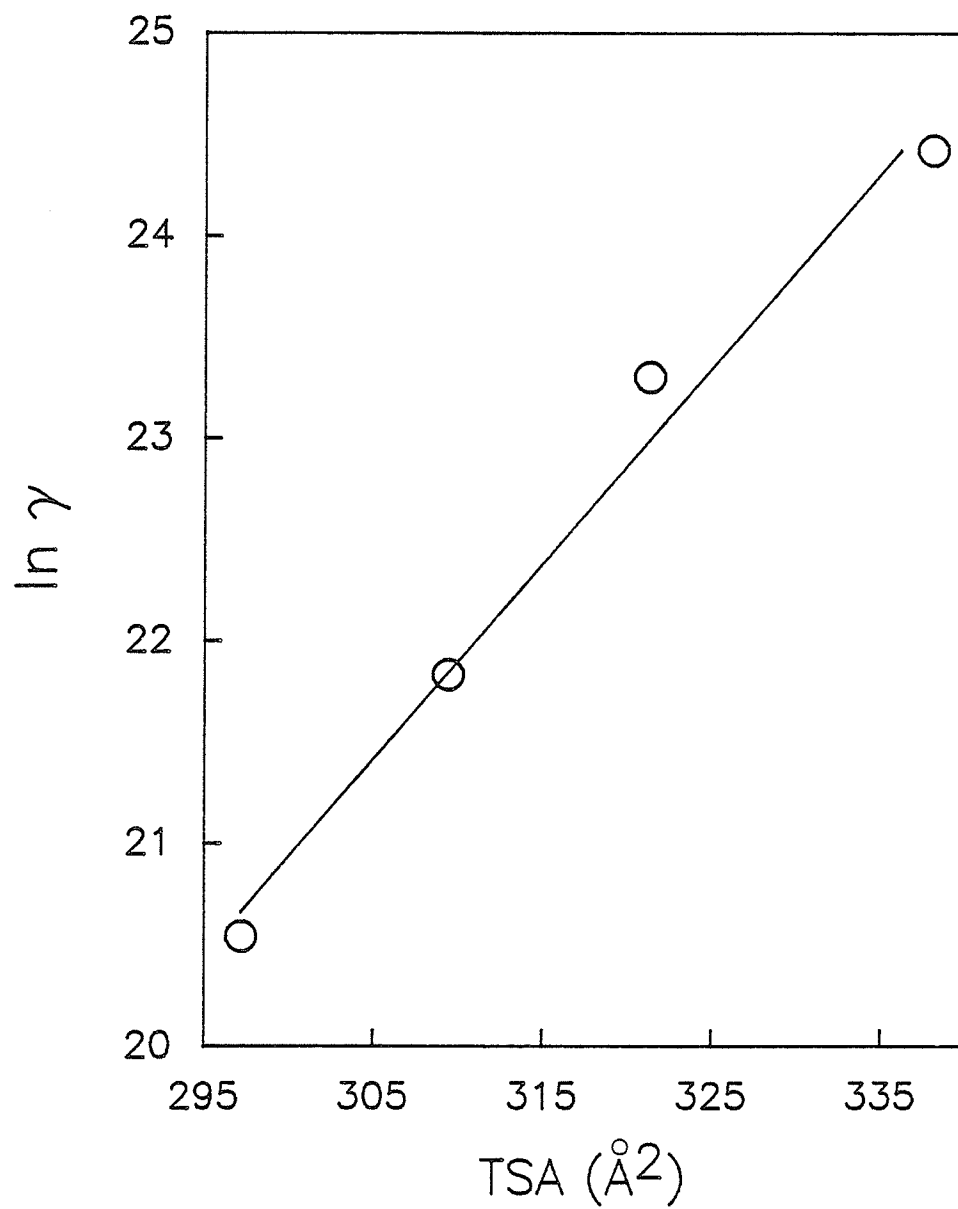


Figure 6. Correlation of total surface area of the four PCDDs with the aqueous activity coefficient.

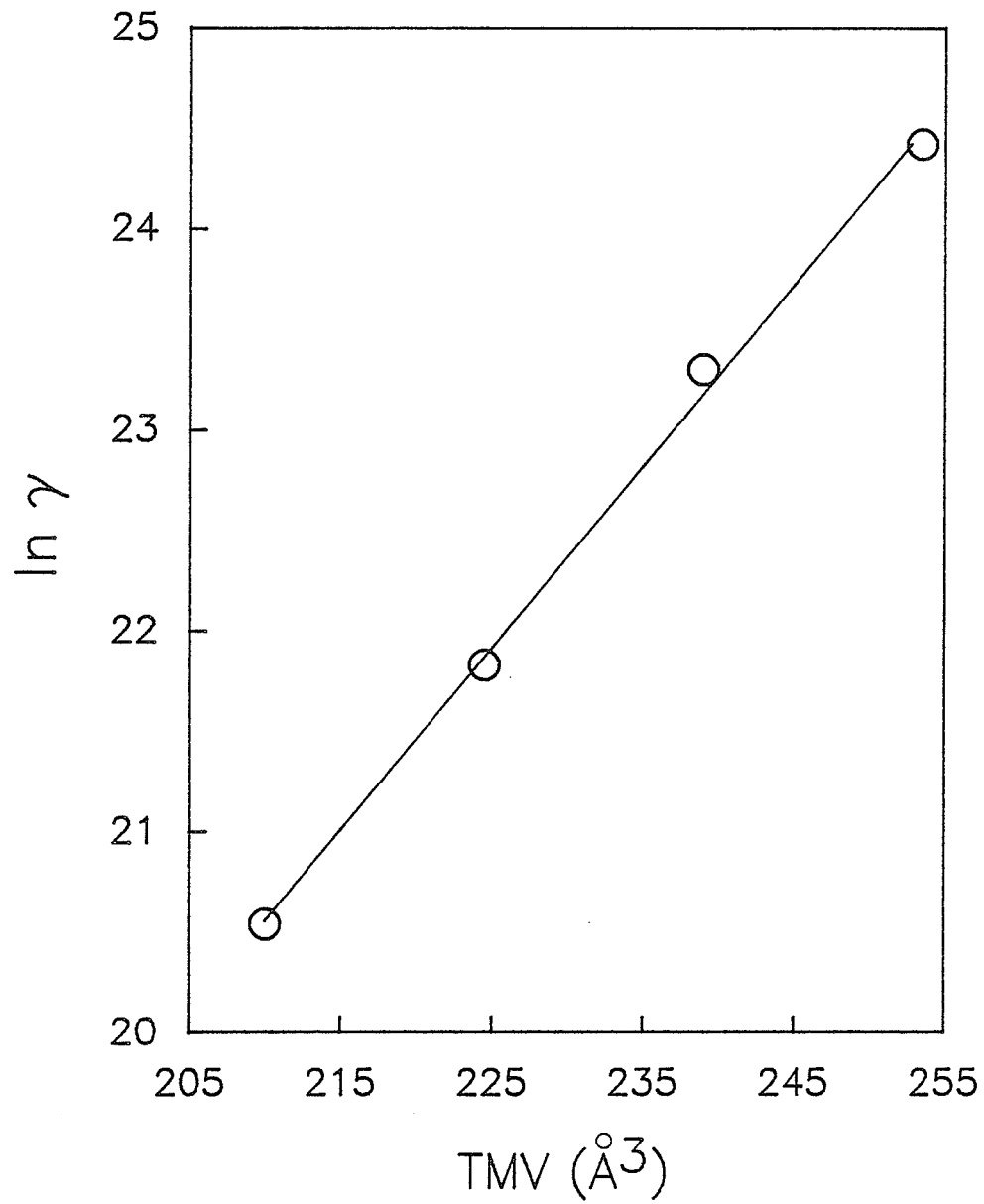


Figure 7. Correlation of total molecular volume of the four PCDDs with the aqueous activity coefficient.

unfavorable entropy plays a significant role in limiting the solubility of these highly hydrophobic PCDDs.

D. HENRY'S LAW CONSTANTS

Several preliminary experiments were necessary to establish proper conditions for Henry's constant determinations of these extremely lipophilic compounds. First, it was found that the method of preparing the aqueous solution of the dioxin was important to the success of the experiment, at least for P₅CDD, the least soluble of the congeners studied. It was necessary to spike this dioxin directly into the water column. When the stock solution of P₅CDD was spiked onto the glass walls of the stripping apparatus, desorption from the glass was so slow that levels were at or below the detection limit for up to 36 h of sparging. Furthermore, after adding dioxin to the water, it was necessary to stir the aqueous solution for 10-12 h in order to attain equilibrium aqueous concentrations of the dioxin. If such a period did not precede sampling, concentrations of P₅CDD increased up to the 12 h mark before beginning to decrease due to stripping by the gas. Finally, losses of dioxin to the glass were estimated to be close to the aqueous solubilities of both congeners studied. In both cases, when dioxin additions were made at the solubility level of the congener under investigation, initial activities were approximately half of that expected based on knowledge of the solubility of the compound. This was acceptable for T₄CDD where, due to the higher aqueous solubility of this congener, activities well above the detection limit were still attained. However, for P₅CDD, an amount of dioxin equal to twice the aqueous solubility level was added to the water. When sampling was initiated, activities were still below the saturation levels expected

from solubility considerations.

Gas-sparging of the dioxins from the aqueous solutions continued for approximately 3 days for both congeners. Triplicate 4.00 mL samples were removed periodically for analysis by liquid scintillation. The activities were corrected for background and PCDD concentrations were calculated. As derived by Mackay et al. (33), the stripping process may be described mathematically by the equation

$$\ln(C/C_0) = -(HG/VRT)t$$

where C is the aqueous concentration of the solute at time t , C_0 is the initial concentration, R is the gas constant, G is the gas flow rate (m^3/h), V is the volume of the solution (m^3), T is the system temperature (K), and H is the Henry's law constant. In their method, the concentrations of solute in the sparging vessel were determined by using a micropump to circulate solution through a flow cell where absorbances were monitored. Therefore, the above equation applied to a stripping procedure in which the water volume in the apparatus remained essentially constant throughout the experiment. Here, where samples were removed for analysis, an equation (34) which corrected for volume changes was required,

$$\ln(C/C_0) = -(HG/RT)\sum_{j=1}^i (\Delta t_j/V_j)$$

where Δt_j is the duration of the j^{th} interval and V_j is the volume of the solution during the j^{th} interval.

A plot of $\ln C$ against $\sum_{j=1}^i (\Delta t_j/V_j)$ followed by linear regression analysis yields a slope of $-(HG/RT)$ from which the Henry's law constant may be calculated. In the calculations the unit of H is either $\text{Pa} \cdot m^3/\text{mol}$ or $\text{atm} \cdot m^3/\text{mol}$ depending on the units for R , $8.205 \times 10^{-5} \text{ atm} \cdot m^3/\text{mol} \cdot \text{K}$ or $8.314 \text{ Pa} \cdot m^3/\text{mol} \cdot \text{K}$. Henry's constants for the two chlorinated

dioxins, determined in duplicate at a temperature of 23°C, are summarized along with several experimental parameters in Table 9.

Table 9. Henry's law constants for two chlorinated dioxins at 23°C

Congener	H (atm·m ³ /mol)	G (m ³ /h)	T (K)	r ²
T ₄ CDD	(2.25 ± 0.44) x 10 ⁻⁵	0.00625	296.2	0.814
	(3.05 ± 0.34) x 10 ⁻⁵	0.00622	296.2	0.933
P ₅ CDD	(1.40 ± 0.47) x 10 ⁻⁵	0.00612	296.0	0.561
	(1.54 ± 0.26) x 10 ⁻⁵	0.00621	296.0	0.837

Although the correlations are not very good, it was difficult to rationalize the deletion of any points on a scientific basis, especially for T₄CDD. For the first trial with P₅CDD, three points appeared at unreasonably high concentrations. Deletion of these points, at t = 0, 38, and 49 h, improved the precision significantly (r² = 0.971) yet only changed the Henry's constant by 8%, to 1.29 x 10⁻⁵ atm·m³/mol. Therefore, all of the data points were used to determine H. Plots of one trial for each congener are presented in Figure 8, for illustration.

In order to determine Henry's law accurately with the gas-sparging technique, equilibration of the vapor and liquid at the head of the water column is necessary. Mackay reported that with his apparatus each 10 cm depth of water provided sufficient contact time for an 80% approach to equilibrium for benzene, a compound with a Henry's constant of 5.55 x 10⁻³ atm·m³/mol. The water column of 25 cm used in this experiment would then suggest that the approach to equilibrium was approximately 97%. If one considers that chlorinated dioxins, with

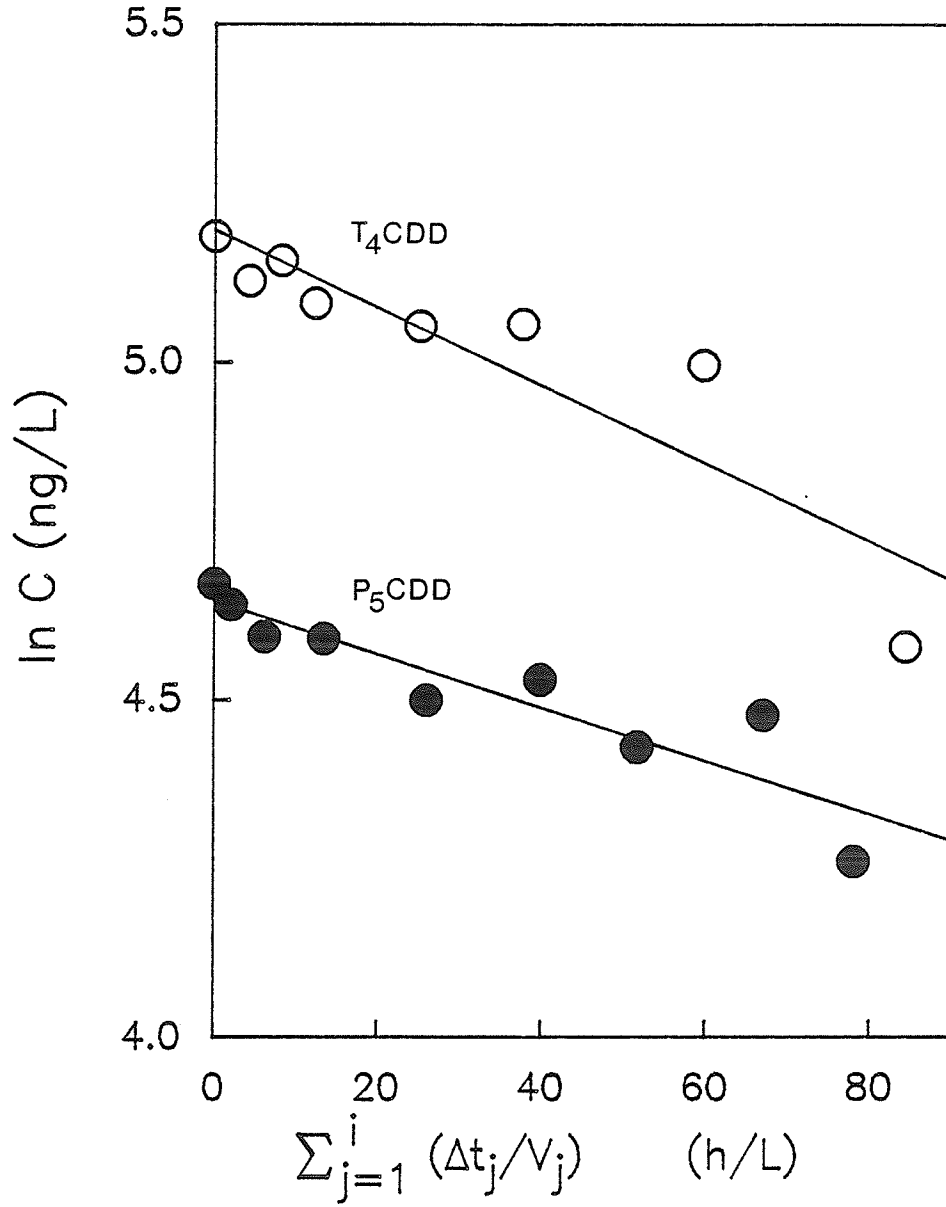


Figure 8. Plots showing the stripping of chlorinated dioxins from water by gas-sparging at 23°C.

considerably lower Henry's constants than benzene, should approach equilibrium more quickly (33), then it is reasonable to assume that equilibrium was in fact established in these measurements.

The general lack of precision in these determinations may be due to losses of solute to the pipet during sampling and general difficulty associated with the accurate measurement of extremely small amounts of solute. The standard deviation (SD) in the Henry's constants are 21% and 7% for T₄CDD and P₅CDD respectively. For T₄CDD, flow rate and temperature fluctuations produce SDs of 2.6 and 2.2%, respectively. Somewhat better precision was attained during the P₅CDD determination, with SDs of 1.4% in the flow rates and 0.3% in the temperatures over the 3 days of the experiment. The method of direct counting of an aliquot of the water was convenient since additional steps of solvent extraction with further potential for losses of dioxin to glassware was avoided. A 4.00 mL aliquot was used since this amount of water could be dissolved in 15.0 mL of the scintillation fluor. This method was then limited by the aqueous solubility of the solute, since the solute must be sufficiently soluble to provide detectable levels of material in the 4.00 mL aliquot. The aqueous solubilities of the chlorinated dioxins indicate that the method is, therefore, limited to determination of H up to the pentachlorinated congener. Based on the precisions reported above, it is believed that the accuracy of the Henry's constant is in the range of 15-25%.

In certain instances it may be more convenient to report Henry's law constant as a dimensionless air-water partition coefficient,

$$K_{aw} = H/(RT)$$

The results, summarized in Table 10, indicate that for the air-water

two phase system, the dioxins partition predominantly into the aqueous phase. The environmental implications of these Henry's constants is that with favorable mass transfer coefficients, dioxins emitted into the atmosphere, for example in the incineration process, will effectively partition into lakes and rivers. Favorable water partitioning provides a route into aquatic food chains for these toxic compounds. However, due to the persistence of dioxins, volatilization after emission into a body of water may be an important removal process leading to the potential for long-range environmental transport.

Few data are available in the literature for Henry's law constants of extremely hydrophobic compounds. Mackay et al. (33) have reported H for a series of aromatic hydrocarbons at 25.0°C, with values ranging from 4.83×10^{-4} to 3.93×10^{-5} atm·m³/mol for the series: naphthalene, biphenyl, acenaphthalene, phenanthrene. Burkhard et al. (36) have predicted H for a series of polychlorinated biphenyls with an average value of 4.0×10^{-4} atm·m³/mol at 25.0°C. More recently, Shiu, et al. (32) estimated Henry's constants of chlorinated dioxins from available literature values of vapor pressure and aqueous solubility, with H falling in the 1-15 Pa·m³/mol ($1-15 \times 10^{-5}$ atm·m³/mol) range for PCDDs. The values reported here for two polychlorinated dioxins at 23°C, 1.5 and 2.7×10^{-5} atm·m³/mol (1.5 and 2.7 Pa·m³/mol) are in reasonable agreement with the values of Shiu, et al.

E. ESTIMATION OF VAPOR PRESSURES OF PCDDs

The air-water partition coefficient, $K_{aw} = C_a/C_w$, where C_a and C_w are the concentrations of the solute in the air and water compartments, respectively, may be used to derive an expression relating Henry's constant to the vapor pressure and aqueous solubility of the solute.

If the gaseous solute is treated as an ideal gas and if the water phase is saturated with the hydrophobic solute, then under standard temperature and pressure conditions (25°C and 101 kPa) the equation

$$H = K_{aw}RT$$

may be simplified to

$$H \approx V_p/S_w$$

Since both the Henry's constants and the water solubilities of these two dioxins have been determined experimentally, the vapor pressures may be calculated with the above relationship. The results, with the average H determined at 23°C and S_w at 26°C, are presented in Table 10.

Table 10. Physical constants of 1,2,3,7-T₄CDD and 1,2,3,4,7-P₅CDD related to air-water partitioning.

Congener	H (atm·m ³ /mol)	K _{aw}	S _w (mol/m ³)	V _p ^{calc} (atm)
T ₄ CDD	2.7 x 10 ⁻⁵	1.1 x 10 ⁻³	2.26 x 10 ⁻⁶	6.1 x 10 ⁻¹¹
P ₅ CDD	1.5 x 10 ⁻⁵	6.2 x 10 ⁻⁴	4.63 x 10 ⁻⁷	6.9 x 10 ⁻¹²

Rordorf (3) has recently predicted the vapor pressures of a series of chlorinated dioxins at various temperatures. At 25°C, the vapor pressures of the solid solutes, 1,2,3,7-T₄CDD and 1,2,3,4,7-P₅CDD, are predicted to be 1.0 x 10⁻⁶ and 8.8 x 10⁻⁸ Pa, respectively. The vapor pressures calculated here from experimentally determined Henry's constants and aqueous solubilities of the solid solutes, 6.1 x 10⁻⁶ and 6.9 x 10⁻⁷ Pa (6.1 x 10⁻¹¹ and 6.9 x 10⁻¹² atm) for these two dioxins, respectively, are somewhat higher than the predicted values. The disparity is likely due to a combination of uncertainties in the predicted values as well as errors in the experimental determinations of H, V_p, and S_w. Both sets of data show a strong dependence of vapor

pressure on the degree of chlorine substitution. The predicted vapor pressures show that the V_p of P₅CDD is 8.8% that of the T₄CDD congener, whereas data derived in this study have the V_p of the pentachlorinated congener at 11.3% that of the tetrachlorinated compound.

IV. CONCLUSIONS

The generator column method has been used to determine aqueous solubilities of polychlorinated dibenzo-*p*-dioxins in the range of 0.9 to 1400 ng/L (parts-per-trillion).

The enthalpies of solution of these solid solutes, ranging from 39.8 to 47.5 kJ/mol, are comparable to those reported in the literature for PCBs, PAHs, and PCDDs. The importance of losses in entropy appear to be critical in limiting the solubility of PCDDs in water as has been reported for PCBs. Excellent correlation of total molecular volumes with the aqueous activity coefficient supports this conclusion.

Henry's law constants have been determined for two of the congeners using the gas-sparging technique, with values of 1.5×10^{-5} and 2.7×10^{-5} atm·m³/mol for 1,2,3,7-tetrachlorodibenzo-*p*-dioxin and 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin respectively at 23°C. These values compare favorably with literature values for other PCDDs as well as hydrophobic compounds such as PAHs and PCBs.

Chemicals, such as the chlorinated dioxins, with extremely low aqueous solubilities will approach the behaviour of ideal dilute solutions (in a Henry's Law sense) in the environment. Henry's law will therefore be a reasonable approximation describing the behaviour of these chemicals between air and water phases which are in contact.

CHAPTER 2

SUNLIGHT PHOTOLYTIC DEGRADATION OF 1,2,3,4,7-PENTA- AND 1,2,3,4,6,7,8-HEPTACHLORODIBENZO-P-DIOXIN IN NATURAL WATERS

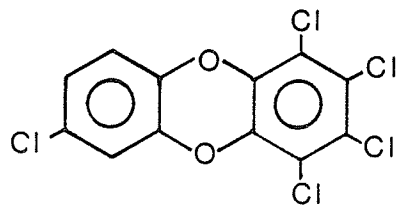
I. INTRODUCTION

Polychlorinated dioxins (PCDDs) are anthropogenic compounds which are now widely distributed in the environment, particularly in aquatic systems. These compounds are extremely persistent, resisting both chemical and biological degradation. However, since the absorption spectra of many of the PCDD congeners overlap the solar spectrum incident on the earth's surface, these chemicals have the potential for photolytic degradation. Chlorinated dioxins present in lakes and streams, particularly in shallow or surface waters, may undergo direct as well as indirect aqueous photolysis. Similarly, dioxins in the atmosphere, whether in the vapor state or sorbed to air-borne particulate matter, are exposed to sunlight and may consequently photodegrade (47). Sunlight photolysis may, in fact, be the major degradative mechanism for removal of chlorinated dioxins from the total environment.

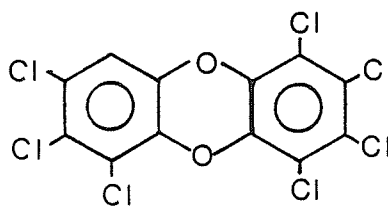
Several studies have shown that chlorinated dioxins undergo fairly efficient photodegradation in a variety of organic solvents. Crosby et al. (48,49) reported the reductive dechlorination of 2,3,7,8-T₄CDD in organic media including methanol and leaf surfaces which can act as hydrogen donors. Buser (50,51) demonstrated that O₈CDD and several H₆CDDs undergo reductive dechlorination in hexane when exposed to 254 nm light, detecting lower chlorinated dioxins among the degradation products. Dobbs and Grant (52) noted a similar mechanism for the photolysis of O₈CDD by sunlight. Massé and Pelletier (53) reported that the parent dibenzo-p-dioxin was ultimately photolyzed to 2-hydroxy-

benzoic acid in several organic solvents at 253.7 nm. Although the mechanism of photolytic degradation in water has not been reported, Dulin et al. (11) have determined first-order rate constants and quantum yields for the photolysis of 2,3,7,8-T₄CDD in aqueous acetonitrile (1:1) solutions exposed to both 313 nm light and sunlight. These authors also showed that the photolysis of 2,3,7,8-T₄CDD was much more efficient in hexane than in aqueous solutions at 313 nm. Quantum yields and first-order rate constants for the direct photolysis of 1,2,3,4,7-P₅CDD, 1,2,3,4,7,8-H₆CDD, 1,2,3,4,6,7,8-H₇CDD, and O₈CDD in aqueous acetonitrile solutions exposed to 313 nm light were reported by Choudhry and Webster (54-56). Corbet et al. (57) also demonstrated that 1,3,6,8-T₄CDD photodegraded in filter-sterilized pond water exposed to sunlight.

There are currently no known reports providing photolysis rate constants of chlorinated dioxins in natural waters. Therefore, in this study the sunlight photodegradation of two PCDD congeners, 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD, were investigated in filter-sterilized



1,2,3,4,7-P₅CDD



1,2,3,4,6,7,8-H₇CDD

natural waters. The kinetics of degradation of the two congeners were then compared with literature data available for the photolysis of these compounds at 313 nm in distilled water-acetonitrile solutions.

Quantum yields determined for these congeners in the lab (54) at 313 nm are combined with solar irradiance data available in the literature to predict the half-lives for direct aqueous photolysis of these compounds in midsummer sunlight conditions. The results are used for a brief discussion of the relative importance of direct versus indirect photolysis of these solutes in natural waters.

Environmental quantum yields are estimated for the chlorinated dioxins by assuming that direct aqueous photolysis is the sole means of photolysis of these chemicals in natural waters. These quantum yields are calculated by combining measured molar absorptivities of the PCDDs with solar intensity data collected by sunlight chemical actinometry during the course of the sunlight exposures.

The probable nature of the photodegradation products, based on retention behaviour during reverse-phase HPLC, is briefly discussed.

Exposure of the solutions to sunlight coincided with a field study to determine the fate of these congeners in an aquatic ecosystem (Chapter 3). The results, since obtained under environmental field conditions which prevailed during the first two weeks of the fate study, provide reliable constants, such as the photolysis rate constants, environmental quantum yields, and sunlight half-lives, which may be used to model the behaviour of these solutes in the field.

II. EXPERIMENTAL

A. CHEMICALS

The polychlorinated dibenzo-*p*-dioxins, purchased from Pathfinder Laboratories Inc. (St. Louis, MO), were each universally carbon-14 ring labelled with a specific activity of 24.16 mCi/mmol. All solvents were distilled-in-glass quality (Caledon Laboratories Inc., Georgetown, ON) unless otherwise specified. *p*-Nitroacetophenone, the sunlight chemical actinometer, and *p*-nitrotoluene, an internal standard, were used as purchased (Aldrich Chemicals, St. Paul, MN.). Pyridine, a quantum yield adjuster, was supplied by Aldrich Chemicals, St. Paul, MN. (Gold Label). Prepurified nitrogen (Welders Supply, Winnipeg, MB) was used to concentrate samples.

B. PREPARATION OF SOLUTIONS FOR PHOTOLYSIS

All glassware used in preparing solutions for photolysis was sterilized by either steam autoclaving for ~40 min or by heating at 180°C for 2-4 h.

A 2.018×10^{-2} M stock solution of *p*-nitroacetophenone (PNAP) was prepared in 100 mL of CH₃CN. A 10 mL aliquot was then diluted to 1.0 L with filter-sterilized (0.22 μm) triple-distilled water under laminar flow conditions to minimize introduction of microorganisms to the system. Water, with a pH of 6.55, was added in small portions with proper mixing to prevent the PNAP from precipitating. Prior to diluting to the mark, 1.778 mL of pyridine was added to adjust the quantum yield for sunlight exposure. 25.0 mL of the chemical actinometer solution, consisting of 2.018×10^{-4} M PNAP in 1% CH₃CN containing 0.02214 M pyridine, was transferred by pipet into twenty 50 mL cylindrical Pyrex centrifuge tubes. A strip of Teflon tape was

wrapped around the glass screw threads and the tubes tightly closed with Teflon-lined screw caps. All tubes were wrapped in aluminum foil to prevent any photodegradation prior to the start of the experiment.

The chlorinated dioxins, 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD, were purified by preparative HPLC on a C₁₈ column with 85% CH₃OH as the mobile phase. The dioxin band was collected from prior knowledge of its retention time in this chromatographic system. The PCDDs were then partitioned into hexane, the extracts evaporated to ~3 mL on a rotary evaporator, and dried by passing through a microcolumn containing anhydrous Na₂SO₄ (Fisher Scientific, Winnipeg, MB). The samples were then carefully evaporated to dryness with a stream of N₂ and taken up in 5 mL of CH₃CN. The concentrations of the solutions, 1.16 µg P₅CDD/mL and 0.227 µg H₇CDD/mL, were determined by liquid scintillation counting. The radiochemical purities, determined to be 99+% and 98+% for P₅CDD and H₇CDD respectively, were checked by LSC of fractions collected during HPLC. 50 µL of the P₅CDD solution were spiked into twenty cylindrical Pyrex centrifuge tubes containing 25.0 mL of pond water previously sterilized by filtration through a 0.22 µm Durapore filter (Waters Scientific, Mississauga, ON). The solutions, containing 2.3 ng P₅CDD/mL water (0.2% CH₃CN) were sealed and wrapped in aluminum foil as described for the actinometer solutions. 200 µL of the H₇CDD solution were spiked into ten centrifuge tubes containing 25.0 mL of sterilized pond water, resulting in concentrations of 1.8 ng H₇CDD/mL water (0.8% CH₃CN). The solutions were sealed and foil wrapped for transport to the field. All preparations were carried out in a laminar flow hood to maintain the sterile conditions of the solutions.

C. SUNLIGHT PHOTOLYSIS

All samples were placed in a rack at an angle of 45° to the horizon (Figure 9) on site at the University of Manitoba Agriculture Field Station, Glenlea, MB before sunrise on July 18, 1986. The rack, painted with a flat black finish to minimize reflections, was situated with its long axis pointing in an east-west direction. The site was relatively free of shadows until late in the evening. The aluminum foil was removed from all tubes except for eight P₅CDD samples which served as controls to determine the extent of degradation of this congener in the absence of sunlight. Two actinometer and two H₇CDD samples were also left unexposed, serving as t=0 samples. Six actinometer tubes were also set into one of the ponds to a depth of ~4 cm of water to determine the extent of attenuation by pond water. At each sampling time, duplicate tubes were wrapped in aluminum foil on site and transported back to the laboratory. Here, samples were acidified by addition of ~1 mL of conc. H₂SO₄ and 1.5 mL of dichloromethane (DCM) were added to begin the extraction. The samples were carefully mixed and refrigerated until analysis. Samples were taken at appropriate intervals for a period of 18.25 days.

D. SAMPLE WORKUP AND ANALYSIS

Actinometer solutions were analyzed for PNAP by HPLC with a C₁₈ column and 70% CH₃OH as the mobile phase at a flow rate of 1.0 mL/min, with UV detection at 280 nm and a detector sensitivity of 0.1 AUFS. PNAP was quantified by spiking all samples with 500 μL of freshly prepared 1.082 x 10⁻² M p-nitrotoluene (PNT) as an internal standard. Calibration standards were prepared by pipetting, by syringe, 500 μL of the PNT and varying amounts (10-250 μL) of 2.018 x 10⁻² M PNAP into 25

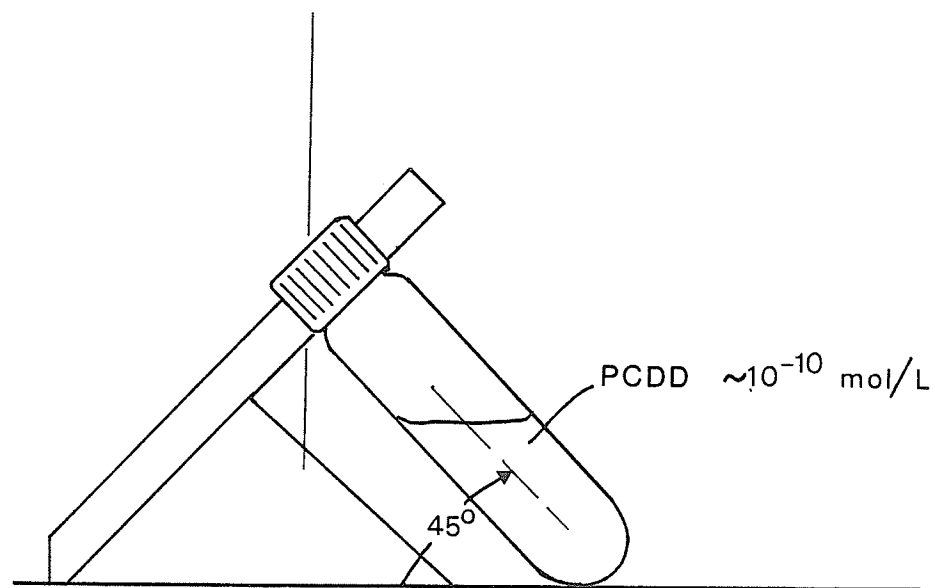


Figure 9. Arrangement of samples for sunlight photolysis.

mL volumetric flasks and diluting to the mark with water. For all HPLC determinations 12 μ L injections were used. Peak height measurements, representing absorbances, were used to quantify PNAP.

The acidified water samples were extracted five times with 5 mL of DCM and once with hexane. 4 mL of extracted water was occasionally checked for C-14 activity by LSC using 14 mL of Atomlight as the scintillation cocktail. The combined extracts were dried by passing through a column of anhydrous Na_2SO_4 and then reduced to a volume of ~2 mL by rotary evaporation. The samples were quantitatively washed into 15 mL graduated centrifuge tubes and concentrated to <0.2 mL over dried prepurified N_2 . Samples were made up to exactly 0.50 mL with hexane, carefully vortex mixed, and then transferred into 2 mL amber vials fitted with PTFE rubber septa. After standing for several minutes the meniscus was carefully marked so that evaporative losses could later be replaced thus maintaining sample integrity. The vials were then placed into storage at -6°C . Analyses were performed by reverse phase HPLC with an octadecylsilane bonded phase column and 85% CH_3OH as the mobile phase. A 50 to 100 μ L aliquot was first analyzed by LSC to determine appropriate volumes for HPLC analysis. Aliquots were then injected into HPLC to separate the parent PCDD from degradation products which coextracted in the above procedure. For P_5CDD , 3 min fractions were collected for 48 min, whereas for H_7CDD 5 min fractions were collected for 85 min. 10 mL of Scintiverse I was added to each fraction and C-14 activity was assayed by liquid scintillation counting.

E. UV-VISIBLE SPECTROPHOTOMETRY

UV-visible spectra were determined on a HP 8452 single-beam diode array spectrophotometer using quartz cells with a pathlength of 1.00

cm. A blank scan, providing a baseline spectrum which was subtracted from the sample scan, was performed prior to each analysis. The instrument then provided background corrected absorbances for all samples at 2 nm intervals in the 270-800 nm region. Cell temperatures ranged from 20.5-22.4°C for all samples and were recorded with each analysis.

III. RESULTS AND DISCUSSION

A. SUNLIGHT PHOTOLYSIS OF CHLORINATED DIOXINS IN NATURAL WATERS

Choudhry and Webster (54) reported approximately 70% and 40% disappearance of 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD when distilled water-acetonitrile solutions of these PCDDs were exposed to 313 nm light in a merry-go-round photolyzer (58) for 72 h. Dulin et al. (11) further reported that in distilled water-acetonitrile solutions, 2,3,7,8-T₄CDD photolyzed more efficiently at 313 nm compared to sunlight, with 62% disappearance after 24 h of exposure at 313 nm and 49% disappearance with 26.3 h of sunlight exposure. Using this data as a rough guide, it was decided to expose the dioxin solutions in this experiment to sunlight for at least 10 days. Considering an average of 14 h of direct sunlight daily this would provide 140 h of exposure time. A final sample was left in the field for 18.25 d in case photolysis was slower than expected.

Analyses, by LSC of fractions collected during HPLC, show 98.0% conversion of P₅CDD in 5.25 days and 94.4% conversion of H₇CDD in 10.21 days as summarized in Table 11. Although several solutions of the PCDDs were subjected to longer exposures, these were not used in determining first-order photolysis rate constants. Typical reconstructed chromatograms for P₅CDD and H₇CDD are shown in Figures 10 and 11 respectively. The disappearance of the PCDDs, plotted according to first-order kinetics (59),

$$\ln(C_0/C_t) = k_p E t$$

or

$$\ln C_t = -k_p E t + \ln C_0$$

are provided in Figure 12. The first-order sunlight environmental photolysis rate constants, k_{pE} , for the PCDDs in natural waters are

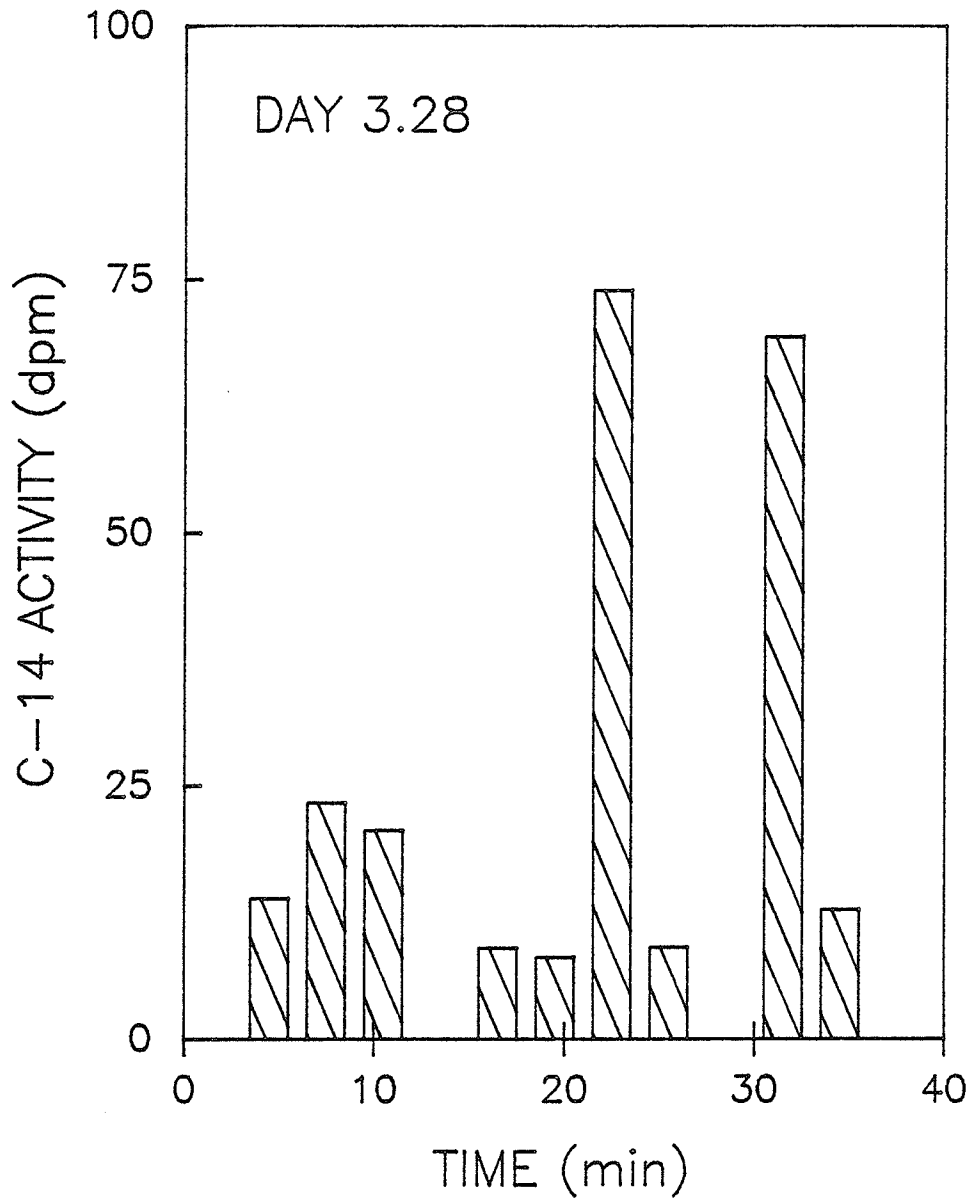


Figure 10. Reconstructed chromatogram for the analysis of a photolyzed P₅CDD solution by HPLC-LSC, with continuous collection of 3 min samples. (P₅CDD, τ_r = 30-35 min)

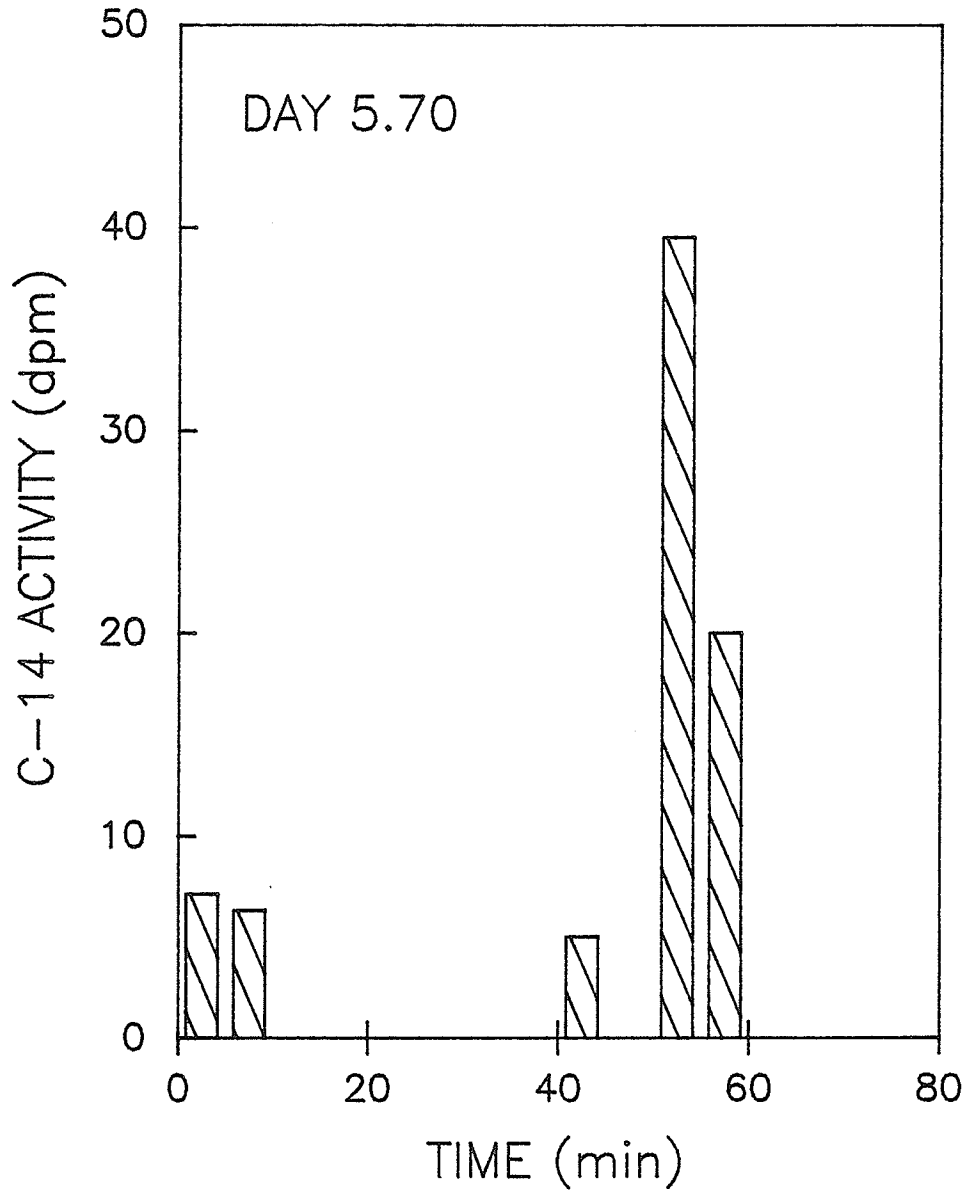


Figure 11. Reconstructed chromatogram for the analysis of a photolyzed H₇CDD solution by HPLC-LSC, with continuous collection of 5 min samples. (H₇CDD, t_r = 50-60 min)

simply the negative slopes of these plots. The k_{pE} values for P₅CDD and H₇CDD are 0.74 ± 0.06 and 0.28 ± 0.04 d⁻¹ respectively, with r² of 0.986 and 0.958 respectively. In this calculation the t₀ point is used since the number of points is otherwise limited to three sampling

Table 11. Photodegradation of Two PCDD Congeners During Sunlight Exposure in Natural Waters at 50°N Latitude in Midsummer.

Congener	Time (d) ^a	C (M) ^b	% Conversion
P ₅ CDD	0.0	6.66 x 10 ⁻⁹	-
	1.29	1.78 x 10 ⁻⁹	73.3
	3.28	0.417 x 10 ⁻⁹	93.8
	5.25	0.133 x 10 ⁻⁹	98.0
H ₇ CDD	0.0	4.44 x 10 ⁻⁹	-
	2.29	1.57 x 10 ⁻⁹	64.7
	5.70	0.543 x 10 ⁻⁹	87.8
	10.21	0.247 x 10 ⁻⁹	94.4

^aTime in 24 h days rather than sunlight hours.

^bP₅CDD and H₇CDD solutions contain 0.2% and 0.8% acetonitrile respectively.

times. The rate constants without the t₀ points are slightly smaller, 0.65 and 0.23 d⁻¹ for P₅CDD and H₇CDD respectively. The corresponding first-order half-lives for the photolytic degradation of these PCDDs, using all four data points, calculated according to

$$t_{1/2} = \ln 2/k_{pE}$$

are 0.94 and 2.5 days for P₅CDD and H₇CDD respectively. Since the initial concentrations were 6.6 x 10⁻⁹M and 4.2 x 10⁻⁹M for P₅CDD and H₇CDD, losses to glassware or the HPLC column were negligible as

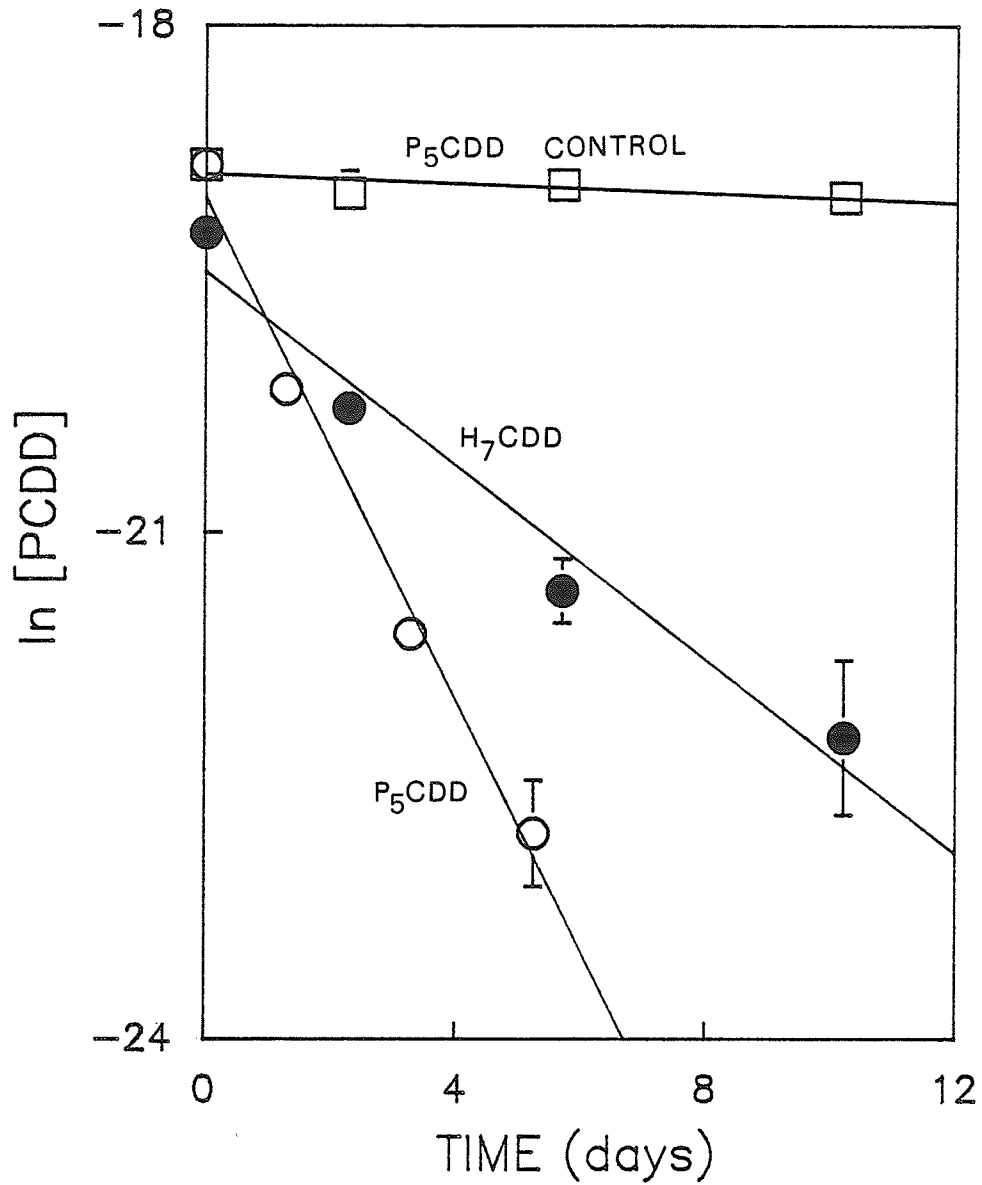


Figure 12. Midsummer sunlight photolysis of P₅CDD and H₇CDD in filter-sterilized natural waters at 50°N latitude. A P₅CDD dark control is included.

indicated by the excellent recoveries for the t_0 samples. A series of P₅CDD solutions were placed in the field but were kept wrapped in aluminum foil. These solutions serve as a dark control, monitoring the degradation of P₅CDD in natural waters in the absence of any influence of sunlight. This control, also plotted in Figure 12, shows negligible degradation of P₅CDD without the influence of sunlight. It is therefore assumed that H₇CDD will also not degrade in the absence of sunlight.

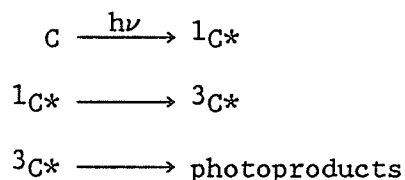
Choudhry and Webster (54) reported $t_{1/2}$ values of 1.86 and 7.87 d for direct aqueous photolysis of 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD, respectively, at 313 nm. The fact that these congeners photodegrade faster in natural water when exposed to sunlight indicates either that 313 nm light is less efficient in photolyzing these dioxins than is the full sunlight spectrum or that these PCDDs undergo indirect photodegradation in natural waters. Dulin et al. (11) demonstrated that 2,3,7,8-T₄CDD experienced faster aqueous photolysis in distilled water when exposed to 313 nm light compared to sunlight, with half-lives of 0.549 and 1.15 days, respectively. These results, although for a different PCDD congener, suggest that sunlight is less effective in degrading chlorinated dioxins by direct absorption of light than is monochromatic light of wavelength 313 nm. Therefore, sensitized photolysis involving dissolved organic compounds in the natural water may be leading to enhanced rates of photolysis.

B. PREDICTION OF DIRECT AQUEOUS PHOTOLYSIS RATES

To examine the possibility that direct aqueous photolysis alone may not account for the observed photodegradation rates, a theoretical treatment may be used. The rates of direct aqueous photolysis of these

chlorinated dioxins under sunlight conditions may be predicted from knowledge of the absorption spectra of the PCDDs, solar irradiance data for the particular time, season, and latitude, and the quantum yields for the direct aqueous photolysis of the particular congener.

In direct aqueous photolysis the chemical, here PCDD, is excited to a singlet electronic energy state by the direct absorption of solar energy. After intersystem crossing to the triplet state, excitation energy is dissipated (60) through photodegradation to form degradation products. This mechanism (depicted below) will compete with other



processes, such as nonradiative energy losses or losses via emission of fluorescent radiation (61). The efficiency of a particular mechanism is described by a quantum yield for that process. For direct aqueous photolysis a reaction quantum yield, ϕ , may be defined as the relative rate of photodegradation to the rate of sunlight absorption, i.e.

$$\phi = k_p/k_a$$

Zepp and Cline (62) have developed a method for calculating rates of direct photolysis of chemicals in aquatic environments. These authors have compiled a set of Z_λ values which represent underwater solar irradiance available to chemicals in shallow water under clear weather conditions. Published Z_λ values are available for midday, midseason sunlight conditions at 40°N latitude and hence represent the underwater solar irradiance spectrum for shallow waters under these conditions. These values are generally applicable to systems in which the water column absorbs very little of the incident sunlight. Using

the published Z_λ values the rate of sunlight absorption, k_a , is calculated as

$$k_a = \frac{2.303}{j} \sum_\lambda Z_\lambda \epsilon_\lambda$$

where ϵ_λ is the molar absorptivity of the PCDD congener ($M^{-1}cm^{-1}$), Z_λ is in photons $cm^{-2} s^{-1}$, and j is a conversion factor (6.02×10^{20}) changing solar flux to mol $cm^{-2}s^{-1}$ and cm^3 to L. The predicted sunlight photolysis rate constant is then calculated by multiplying the rate of sunlight absorption by the quantum yield which represents the efficiency with which absorption of photons leads to photodegradation,

$$k_{pE} = \phi k_a$$

In order to calculate photolysis rate constants, accurate molar absorptivity values must be available for the chemical above 290 nm, the wavelength generally considered to be the solar cutoff for light reaching the earth's surface (63). The ϵ_λ values centered at the appropriate wavelengths to be used with published Z_λ data were determined for $4.97 \times 10^{-6}M$ and $2.61 \times 10^{-6}M$ aqueous solutions of P₅CDD and H₇CDD. Due to the extremely low solubilities of these chemicals in water (Chapter 1) a cosolvent is required. Acetonitrile is recommended as an appropriate cosolvent in these studies (64) since the refractive index of this solvent closely matches that of water. Therefore, the absorption spectra of the dioxins in 1:1 water-acetonitrile are good approximations of those expected in water alone. Replicate spectral determinations were performed for each PCDD congener and average molar absorptivities were calculated at required wavelengths. The P₅CDD solution was prepared and analyzed without difficulty, however the H₇CDD solution was difficult to prepare due to solubility limitations of this congener, even with the use of the cosolvent. The precision in

the determination of ϵ_λ values for H₇CDD is of the order of 10-15% whereas P₅CDD data replicate to within 1% except in the region of very low absorbance. The absorption spectra at $\lambda > 290$ nm show that P₅CDD has a reasonably strong absorption with λ_{\max} of 296 nm ($\epsilon_{\max} \sim 3300 \text{ M}^{-1} \text{ cm}^{-1}$) and a much weaker band centered at 472 nm ($\epsilon_{\max} \sim 290 \text{ M}^{-1} \text{ cm}^{-1}$). The higher energy, lower λ , band is likely a $\pi \rightarrow \pi^*$ electronic transition, with a $\epsilon_\lambda > 1000$ (61). The lower energy (high λ) band may be the forbidden, hence much weaker, $n \rightarrow \pi^*$ transition (61). H₇CDD shows only a $\pi \rightarrow \pi^*$ transition with λ_{\max} of 314 nm ($\epsilon_{\max} \sim 2000 \text{ M}^{-1} \text{ cm}^{-1}$). Average molar absorptivities are calculated for each λ center for which a Z_λ value is available. For example, since Z_λ data are reported at 2.5 nm intervals in the 295-320 nm region, ϵ_λ is calculated as an average for this interval, i.e., for 297.5 nm

$$\epsilon_{297.5} = (\epsilon_{295} + \epsilon_{300})/2$$

The results along with literature Z_λ values are summarized in Table 12.

Mill et al. (60,65) have calculated solar intensity data, L_λ , by averaging sunlight conditions over a 24 h day. Their values, in units of millieinsteins $\text{cm}^{-2} \text{ d}^{-1}$, centered at the same wavelengths as the Zepp data, are also included in Table 12 for both 40°N and 50°N latitudes. Their data for midsummer, taken on July 21, are appropriate for this experiment which was begun on July 18. The rate of sunlight absorption is then calculated as

$$k_a = \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}$$

from which the sunlight photolysis rate constant is calculated as

$$k_{pE} = \phi k_a = \phi \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}$$

The quantum yields reported for these congeners at 313 nm (54), 9.8×10^{-5} and 1.5×10^{-5} for P₅CDD and H₇CDD respectively, are used to

Table 12. Solar energy distribution (Z_λ and L_λ) and molar absorptivities of P₅CDD and H₇CDD in the solar region.

λ (nm) ^a	ϵ_λ P ₅ CDD ^b	ϵ_λ H ₇ CDD ^b	Z_λ ^c	L_λ ^d	L_λ ^e
297.5	3284	1598	7.16 (11)	6.17 (-5)	2.86 (-5)
300.0	3287	1686	2.40 (12)	2.69 (-4)	1.50 (-4)
302.5	3277	1770	7.23 (12)	8.30 (-4)	5.33 (-4)
305.0	3248	1843	1.81 (13)	1.95 (-3)	1.39 (-3)
307.5	3202	1900	3.05 (13)	3.74 (-3)	2.89 (-3)
310.0	3154	1956	4.95 (13)	6.17 (-3)	5.05 (-3)
312.5	3087	1994	7.17 (13)	9.07 (-3)	7.75 (-3)
315.0	2980	1990	9.33 (13)	1.22 (-2)	1.08 (-2)
317.5	2780	1895	1.15 (14)	1.55 (-2)	1.40 (-2)
320.0	2461	1697	1.35 (14)	1.87 (-2)	1.71 (-2)
323.1	1942	1398	2.52 (14)	3.35 (-2)	3.12 (-2)
330.0	1434	1207	8.46 (14)	1.16 (-1)	1.10 (-1)
340.0	567	711	9.63 (14)	1.46 (-1)	1.40 (-1)
350.0	301	609	1.03 (15)	1.62 (-1)	1.57 (-1)
360.0	254	569	1.10 (15)	1.79 (-1)	1.74 (-1)
370.0	246	540	1.22 (15)	1.91 (-1)	1.86 (-1)
380.0	229	540	1.35 (15)	2.04 (-1)	1.99 (-1)
390.0	217	-	1.61 (15)	1.93 (-1)	1.87 (-1)
400.0	206	-	2.31 (15)	2.76 (-1)	2.69 (-1)
410.0	200	-	3.02 (15)	3.64 (-1)	3.55 (-1)
420.0	199	-	3.10 (15)	3.74 (-1)	3.65 (-1)
430.0	217	-	2.98 (15)	3.61 (-1)	3.52 (-1)
440.0	233	-	3.51 (15)	4.26 (-1)	4.17 (-1)
450.0	265	-	3.94 (15)	4.80 (-1)	4.69 (-1)
460.0	298	-	3.98 (15)	4.85 (-1)	4.75 (-1)
470.0	286	-	4.11 (15)	5.02 (-1)	4.91 (-1)
480.0	298	-	4.20 (15)	5.14 (-1)	5.03 (-1)
490.0	245	-	3.96 (15)	4.86 (-1)	4.76 (-1)
500.0	218	-	4.04 (15)	4.96 (-1)	4.85 (-1)
525.0	132	-	4.26 (15)	1.31	1.28

^aWavelength centered at tabulated values.

^bAverage ϵ_λ values centered at the indicated λ .

^cMidday, midsummer Z_λ values (photons $\text{cm}^{-2} \text{s}^{-1}$) reported by Zepp and Cline (62) at 40°N latitude.

^d L_λ values (milliEinsteins $\text{cm}^{-2} \text{d}^{-1}$) reported by Mill (65) at 40°N latitude. Numbers in parentheses are exponents.

^e L_λ values (65) at 50°N latitude.

calculate expected k_{pE} values for direct aqueous photolysis. Predicted k_{pE} values and those determined experimentally in this study are summarized in Table 13 and plotted in Figure 13. In this calculation

Table 13. Comparison of Observed and Predicted Rates of Aqueous Photolysis of 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD.

Congener	λ range (nm) ^a	k_{pE} (d ⁻¹)		
		Exptl	Zepp ^b	Mill ^c
P ₅ CDD	295-525	0.74 ± 0.06	0.50	0.20
	295-400		0.19	0.078
H ₇ CDD	295-380	0.28 ± 0.04	0.028	0.012
	295-360		0.021	0.0093

^aRange of ϵ_{λ} values used in the calculations.

^bCalculated using midday, midsummer Z_{λ} values for 40°N latitude.

^cCalculated using L_{λ} values for 40°N latitude.

it is assumed that the quantum yield is wavelength independent, an assumption which is generally valid for complex molecules in solution (61,66).

In all cases, the predicted k_{pE} values are smaller than the rate of photolysis measured experimentally. The predicted rate constants are, furthermore, extremely dependent on the availability of accurate ϵ_{λ} data. Since the absorption spectrum of P₅CDD showed a discernible, albeit weak, absorption between 400 and 525 nm, the calculations are performed both with and without this data. The predicted rate of photolysis of this congener is 2.6 times faster if the weak tailing absorption at longer wavelengths is included in the calculation. The calculations for H₇CDD are also carried out by using the λ range 295-

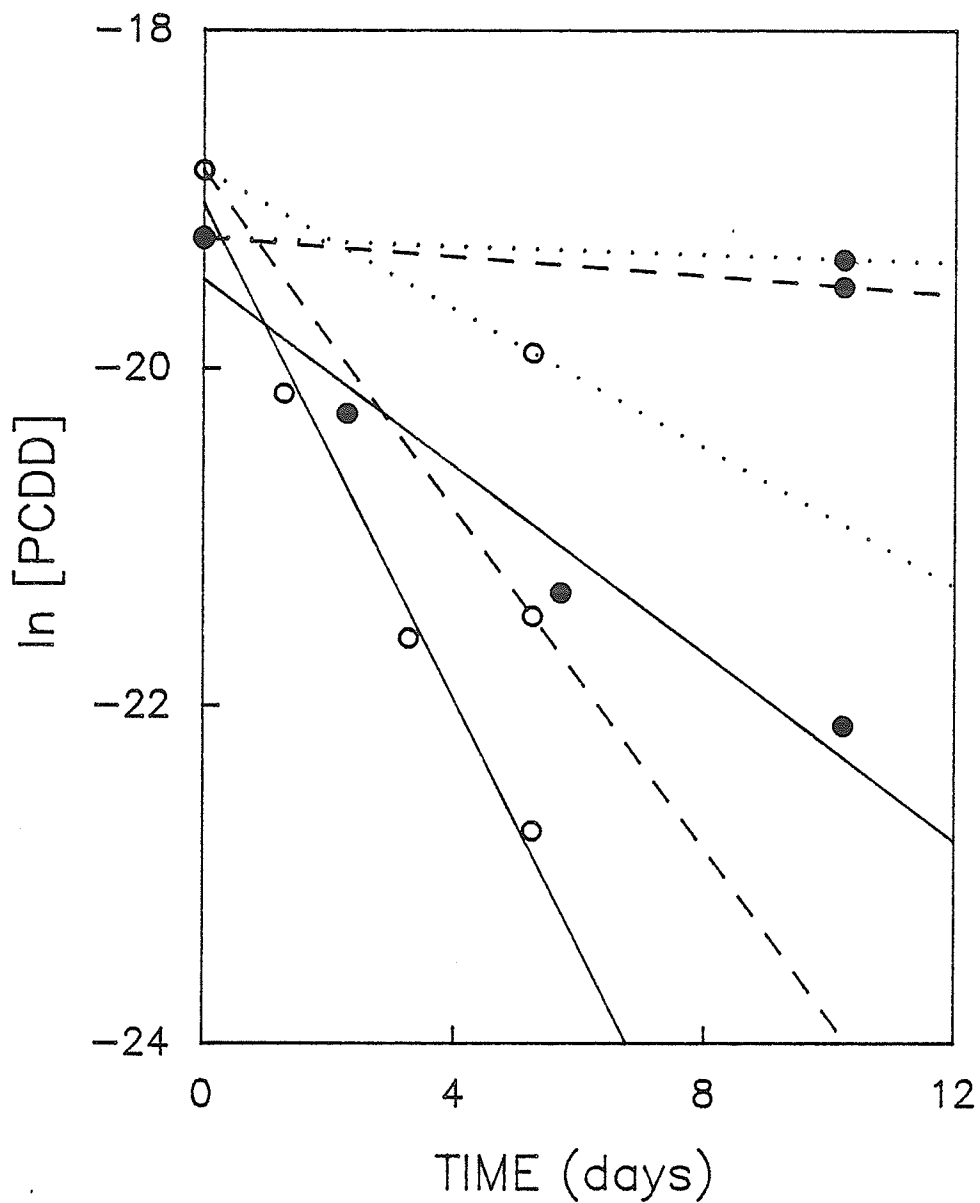


Figure 13. Comparison of the observed rates (—) of sunlight photolysis of P_5CDD (○) and H_7CDD (●) in natural waters at $50^{\circ}N$ latitude with rates predicted by the methods of Mill (.....) and Zepp (---) for the direct aqueous photolysis of these congeners.

380 nm and then repeated by assuming that the last few ϵ_λ values are not significant. Truncating the absorption spectrum for H₇CDD at 360 nm results in a 20% decrease in the calculated rate. It is believed that the ϵ_λ data for the full spectra, i.e., 295-525 and 295-380 nm for P₅CDD and H₇CDD, respectively, should be included in the calculations.

The predictions using the method of Mill, et al. appear to be more realistic than those of Zepp and Cline for comparison with actual observed rate constants for the chlorinated dioxins. This is the case because the L_λ values used in the Mill method represent sunlight intensity data which have been averaged over 24 h days. Zepp used Z_λ values which are midday, midseason sunlight intensities in shallow water. Therefore, for compounds which photolyze in several minutes or perhaps a few hours, the predictions based on Z_λ or midday sunlight conditions would be acceptable provided the experiments are also carried out during midday. For chlorinated dioxins, the experimental exposure continues for several days. The use of sunlight data which has been averaged over 24 h days will then be a realistic representation of actual conditions. With midday sunlight intensities (Z_λ) the predicted rates will be greater since nights are not averaged into the model. Therefore the predictions utilizing L_λ values are preferred for these compounds. It should be noted that both methods have no way of correcting for cloud cover, which will decrease observed rates in the field.

The calculations were also carried out with L_λ values provided for 50°N latitude since the experiments were carried out at approximately this latitude. The calculated rates are only slightly smaller (by approximately 6%) and then only if the shorter wavelength ranges are

used for both congeners. Previous calculations by Zepp and Cline (62) showed that a 10° change in latitude has a minimal effect on the predicted rates of photolysis in midsummer. In any event, had the experiment been performed at 40°N latitude the result would be an even greater difference between predicted and observed rates since the observed rates would increase as one moves toward the equator.

The observed rates of photolysis for P₅CDD and H₇CDD are 3.7 and 230 times greater, respectively, than predicted by the method of Mill. If the dioxins had been exposed to midday, midsummer sunlight conditions continuously, as in the Zepp method, the experimental rates would still be 1.5 and 10 times greater than predicted. The observed t_{1/2} values are compared to those calculated by the above two methods in Table 14 to highlight the differences in terms of actual days for degradation.

Table 14. Comparison of Observed and Predicted First-order Half-lives (days) for the Aqueous Photolysis of P₅CDD and H₇CDD^a.

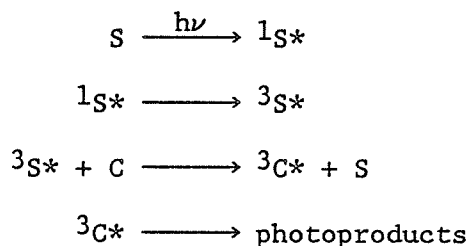
	P ₅ CDD	H ₇ CDD
t _{1/2} exptl	0.94	2.5
Zepp method	1.4	24.6
Mill method	3.4 (3.5) ^b	55.5 (58.5) ^b

^aObserved t_{1/2} in natural water and calculated values assuming direct aqueous photolysis.

^bValues in brackets calculated for 50°N with all other values calculated for 40°N latitude.

The observations strongly suggest that another mechanism is involved in the photolytic breakdown of the chlorinated dioxins. Energy transfers and free radical reactions involving dissolved humic

materials have been reported for organic chemicals in natural waters (67-69). In sensitized photolysis, a sensitizer molecule becomes electronically excited by absorption of sunlight. After intersystem crossing to the longer-lived excited triplet state, an intermolecular energy transfer from the sensitizer to the ground singlet state of the chemical of interest may occur. The chemical, in an excited triplet state, then releases its excitation energy by degrading to photoproducts. The scheme may be represented (60) as follows:



Natural waters contain many chemicals which are known to cause indirect photoreactions (70). Dissolved humic substances have been shown to sensitize the photodegradation of organic compounds in natural waters (71-73) through electronic energy transfer to dissolved oxygen. Photochemically generated singlet oxygen (74), which can oxidize many compounds quite rapidly, may also be involved in the indirect photolysis of chlorinated dioxins in natural waters. Hydrogen peroxide (H_2O_2), photochemically generated from humic material serves as a source of hydroxide radicals ($OH\cdot$) which are known to oxidize certain pesticides (75). Acetone, a triplet sensitizer present in most natural waters, is known to sensitize the photodegradation of several organochlorine xenobiotics (76). It is therefore quite possible that the large rates of photolysis of several chlorinated dioxins observed in natural waters in this study may be explained by indirect photolysis.

It should also be noted that sunlight intensity will increase with

increasing altitudes (62) although this effect is expected to be minimal. However, cloud cover experienced in the outdoor study would tend to reduce rates somewhat. This means that under clear weather conditions, the rates would have been even greater than observed. On the other hand, errors in molar absorptivities, particularly for H₇CDD due to solubility problems, will lead to longer predicted $t_{1/2}$ values. This would tend to narrow the gap between predictions and observations somewhat. Screening due to strong absorption of sunlight by dissolved organics in the water (61) would further reduce the amount of light available to the PCDD and also reduce direct photolysis rates.

C. CHEMICAL ACTINOMETRY

The sunlight photolysis of these chlorinated dioxins has not been studied in distilled water, a medium in which only direct aqueous photolysis could occur. However, it is known that these compounds experience direct aqueous photolysis in distilled water-acetonitrile solutions at 313 nm (54). Hence, these compounds should also experience direct photolysis in natural aquatic systems. What isn't known is the extent of direct photolysis versus other competing mechanisms of photodegradation. Without a study of sunlight photolysis in distilled water or without controlled studies clearly demonstrating the effects of suspected sensitizers, such as dissolved humic or fulvic acids, one may assume that a combination of direct and indirect photolysis accounts for the results and that the measured rate constant is a weighted average of the rates of direct and indirect photolysis (59). Since the extent of the competition between direct and indirect photolysis is not known, an assumption that direct photolysis is the sole mechanism for degradation allows for a calculation of an

environmental or sunlight quantum yield for this process. This value may be viewed as an upper limit to the efficiency with which direct absorption of solar photons leads to degradation of these PCDD congeners. Further studies currently underway in distilled water alone will allow for an estimation of the rate of sensitized photolysis and a better value for the environmental quantum yield for direct photolysis.

The rate of photolysis of the PCDDs will be dependent on the prevailing sunlight intensity, with all of its variations due to cloud cover, diurnal cycling, and weather conditions. In order to determine the quantum yield, or the efficiency with which direct absorption of sunlight leads to photodegradation, it is necessary to monitor the sunlight intensity during the entire photolysis period.

The *p*-nitroacetophenone (PNAP)/pyridine sunlight actinometer (63) was used to monitor the variable solar irradiance during this experiment. This actinometer, operating on the basis of photonucleophilic substitution, has the advantage of having an adjustable quantum yield, ϕ_A , given by

$$\phi_A = 0.0169 \text{ [pyr]}$$

With the aid of the data in Dulin and Mill (63), the quantum yield of the actinometer was adjusted with the addition of 0.02214 M pyridine, to provide a half-life similar to the half-lives of the dioxins being studied. This approach ensured that the actinometer integrated sunlight intensities during the entire period of sunlight photolysis of the chlorinated dioxins. Since ϕ_A for the actinometer is known, the rate at which PNAP photodegrades will provide a record of the prevailing sunlight intensity during the experiment.

The PNAP solutions were easily analyzed by reverse phase HPLC. It

was necessary to use 70% methanol as the mobile phase to separate PNAP from both pyridine and *p*-nitrotoluene (PNT), the internal standard (see Figure 14). The calibration plot used to quantitate PNAP showed excellent linearity with $r^2 = 0.9999$.

The photolysis of PNAP was monitored over a period of 18.25 days, up to the last sampling time for the chlorinated dioxins. The disappearance of PNAP (Table 15) indicated that the conditions were chosen properly with 54.8% conversion during the time of exposure. A set of PNAP solutions immersed under 4 cm of water in a nearby pond were used to determine the extent of attenuation of sunlight by pond water at the Glenlea site. Semi-log plots showing the disappearance of PNAP in both experiments are presented in Figure 15. The negative slope of the plot for solutions not immersed in water represents the rate constant for sunlight photolysis of the actinometer, $k_{pA} = 0.044 \pm 0.003 \text{ d}^{-1}$. Approximately 4 cm below the surface of the ponds the rate drops by 65% to $0.015 \pm 0.002 \text{ d}^{-1}$.

Table 15. Sunlight Photolysis of the PNAP Sunlight Actinometer at 50°N Latitude in Midsummer.

Time (days)	C (M)	% Conversion
0.0	1.97×10^{-4}	-
1.29	1.83×10^{-4}	7.0
3.28	1.62×10^{-4}	17.8
5.69	1.38×10^{-4}	29.6
9.29	1.21×10^{-4}	38.5
13.33	1.02×10^{-4}	48.0
18.25	0.89×10^{-4}	54.8

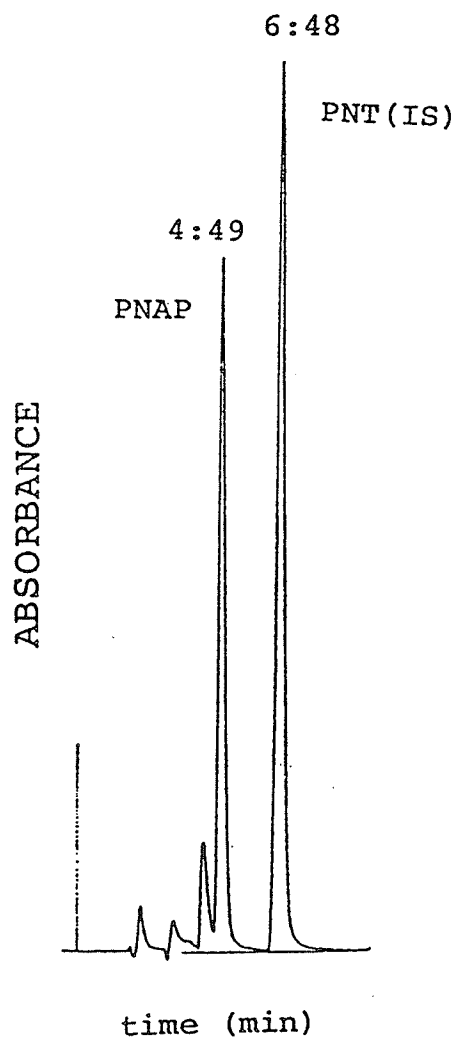


Figure 14. HPLC analysis of *p*-nitroacetophenone (PNAP) with 70% CH₃OH as the mobile phase and *p*-nitrotoluene (PNT) as the internal standard.

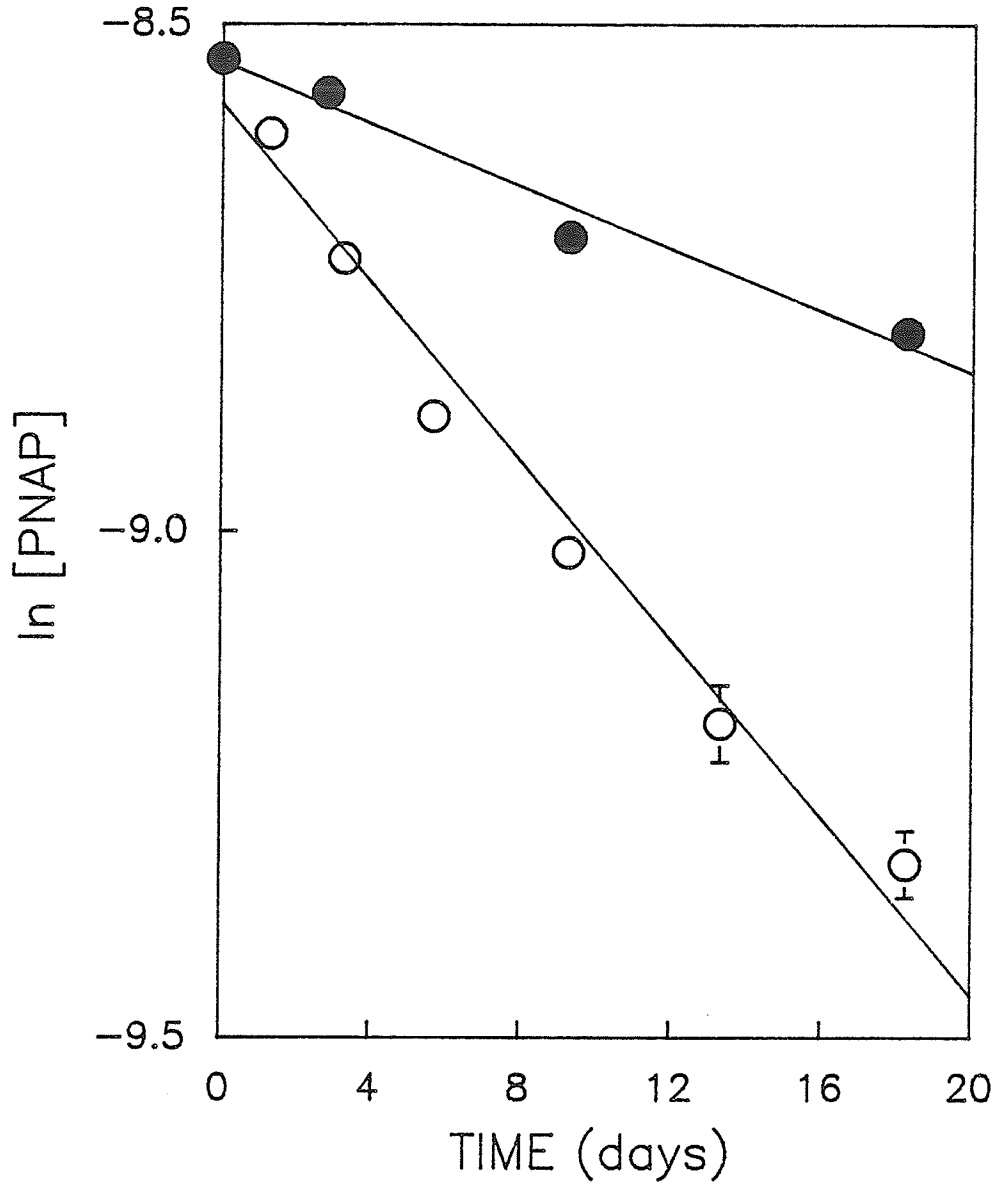


Figure 15. Rates of sunlight photolysis of the chemical actinometer, PNAP, in 50 mL centrifuge tubes at the experimental site (O) and under 4 cm. of pond water on site (●).

To determine environmental quantum yields (ϕ_{cE}) for direct aqueous photolysis of PCDDs, i.e., quantum yields averaged over all wavelengths absorbed by the chemical, the data for the chemical actinometer were utilized. Assuming the solution did not absorb strongly, the rate of aqueous photolysis of the chlorinated dioxins is given by (63)

$$\begin{aligned} \text{rate} &= -(dC/dt) = 2.303r\phi_{cE} \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^c [C] \\ &= (k_{pE})_C [C] \end{aligned}$$

where r represents a reaction parameter characteristic of the system (i.e., optical properties of the solvent and glass walls of the cell used), L_{λ} is the solar irradiance at wavelength λ , ϵ_{λ}^c is the molar absorptivity of the chemical at wavelength λ , ϕ_{cE} is the quantum yield for direct aqueous photolysis of the chemical, and $(k_{pE})_C$ is the first-order environmental sunlight photolysis rate constant. Sunlight irradiance and molar absorptivities are integrated or summed over all wavelengths of environmental significance, i.e., >290 nm, to account for photolysis over all incident wavelengths which are absorbed by the chemical. The equation may be rearranged to

$$- dC/[C] = (k_{pE})_C dt$$

which, on integration, yields

$$\ln\{[C_0]/[C_t]\} = (k_{pE})_C t$$

A similar set of expressions may be written for the actinometer giving

$$\begin{aligned} \text{rate} &= -(dA/dt) = 2.303r\phi_A \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^A [A] \\ &= (k_{pE})_A [A] \end{aligned}$$

which, on integration, yields

$$\ln\{[A_0]/[A_t]\} = (k_{pE})_A t$$

where ϕ_A is the quantum yield for direct aqueous photolysis of the actinometer, ϵ_{λ}^A is the molar absorptivity of the actinometer at

wavelength λ , and $(k_{pE})_A$ is the first-order photolysis rate constant for the actinometer.

The ratio of the measured rate constants for the PCDD and PNAP is determined experimentally and is given by

$$\frac{(k_{pE})_C}{(k_{pE})_A} = \frac{2.303r\phi_{cE} \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^c}{2.303r\phi_A \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^a}$$

The sunlight intensity information is incorporated into the rate of photolysis of the actinometer, $(k_{pE})_A$. The environmental quantum yield for the dioxin may then be calculated since rearrangement of the above equation gives

$$\phi_{cE} = \phi_A \frac{(k_{pE})_C \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^a}{(k_{pE})_A \sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^c}$$

The ϵ_{λ}^a data for PNAP, summarized in Table 16, are combined with L_{λ} values (Table 12) to calculate $\sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^a$. Together with previously

Table 16. Molar Absorptivities Determined for $2.09 \times 10^{-5}M$ PNAP in Water (1% Acetonitrile).

λ center (nm)	ϵ_{λ} PNAP
297.5	4053
300.0	3620
302.5	3287
305.0	3010
307.5	2768
310.0	2546
312.5	2330
315.0	2122
317.5	1919
320.0	1725
323.1	1495
330.0	1046
340.0	629
350.0	421
360.0	296
370.0	203
380.0	144

calculated values of $\sum_{\lambda} L_{\lambda} \epsilon_{\lambda}^C$ for the chlorinated dioxins, this allows for a calculation of the environmental quantum yields for the PCDDs. The values of ϕ_{cE} for P₅CDD and H₇CDD calculated by this method are very sensitive to the wavelength ranges used in the calculation of the $\sum_{\lambda} L_{\lambda} \epsilon_{\lambda}$ terms. By considering two λ ranges for each PCDD and also for PNAP, one which extends over what is felt to be the range of readable absorbances and a second which truncates the range to avoid using readings with higher uncertainty, different values for ϕ_{cE} will result. If the calculations are performed with different combinations of λ ranges, one obtains an estimate of the range within which ϕ_{cE} likely falls. The results show that at 50°N latitude, ϕ_{cE} values are of the order of 0.006 ± 0.003 for P₅CDD and 0.004 ± 0.001 for H₇CDD, respectively. Literature values (54) for ϕ at 313nm in distilled water are 0.000098 and 0.000015 for P₅CDD and H₇CDD, respectively. For 2,3,7,8-TCDD in distilled water ϕ is reported (11) to be 0.0022 at 313 nm and 0.0007 in sunlight experiments. The literature results represent quantum yields for direct aqueous photolysis. The values reported in this study are upper limits for direct aqueous photolysis of these two PCDDs in sunlight since the $(k_{pE})_C$ values used in their calculation appear to be affected, to a large degree, by indirect or sensitized photolysis.

D. PRODUCTS OF PHOTODEGRADATION

Earlier studies have shown that reductive dechlorination of chlorinated dioxins takes place in organic solvents, especially H-donors. Dulin et al. (11) studied the photodegradation of 2,3,7,8-T₄CDD in aqueous solutions and were unable to detect any lower chlorinated congeners. Another route, possibly involving C-O bond

cleavage, was postulated as this appeared to be a mode of degradation of parent dibenzodioxin (77).

In the sunlight photodegradation of P₅CDD, analysis of extracts by HPLC-LSC shows bands of ¹⁴C activity with retention characteristics similar to T₄CDD and T₃CDD standards. These bands are transient, appearing during the first sampling time, after 1.29 d of sunlight exposure, and then disappearing to base line during further exposure. This suggests that reductive dechlorination to lower congeners may be one route or that the breakdown proceeds through these intermediates. However, since these peaks disappear quickly it is likely that any intermediate PCDDs also photolyze efficiently. The distribution of ¹⁴C activity among the various fractions is summarized in the plot in Figure 16. A major fraction of ¹⁴C is not accounted for as shown in the figure. Increases in this fraction mirror the disappearance of the parent P₅CDD and hence represent a product(s) formed during the photolysis. For the 5.25 d sample approximately 43% of the unaccountable portion of the activity was found in the water, drying agent, and glassware combined. This indicates that some extremely polar product(s) were formed which were not easily extracted and which sorb strongly to the drying agent and glassware. These products could be phenolics formed via C-O bond cleavage. Work is continuing to determine the nature of the extractable products by GC/MS.

The H₇CDD shows a similar pattern as plotted in Figure 17. Transient amounts of ¹⁴C activity eluting with retention times characteristic of H₆CDD and P₅CDD, as determined by comparison with standards, were each detected at one sampling time, suggesting that these peaks may simply be artifacts of the method. The major portion

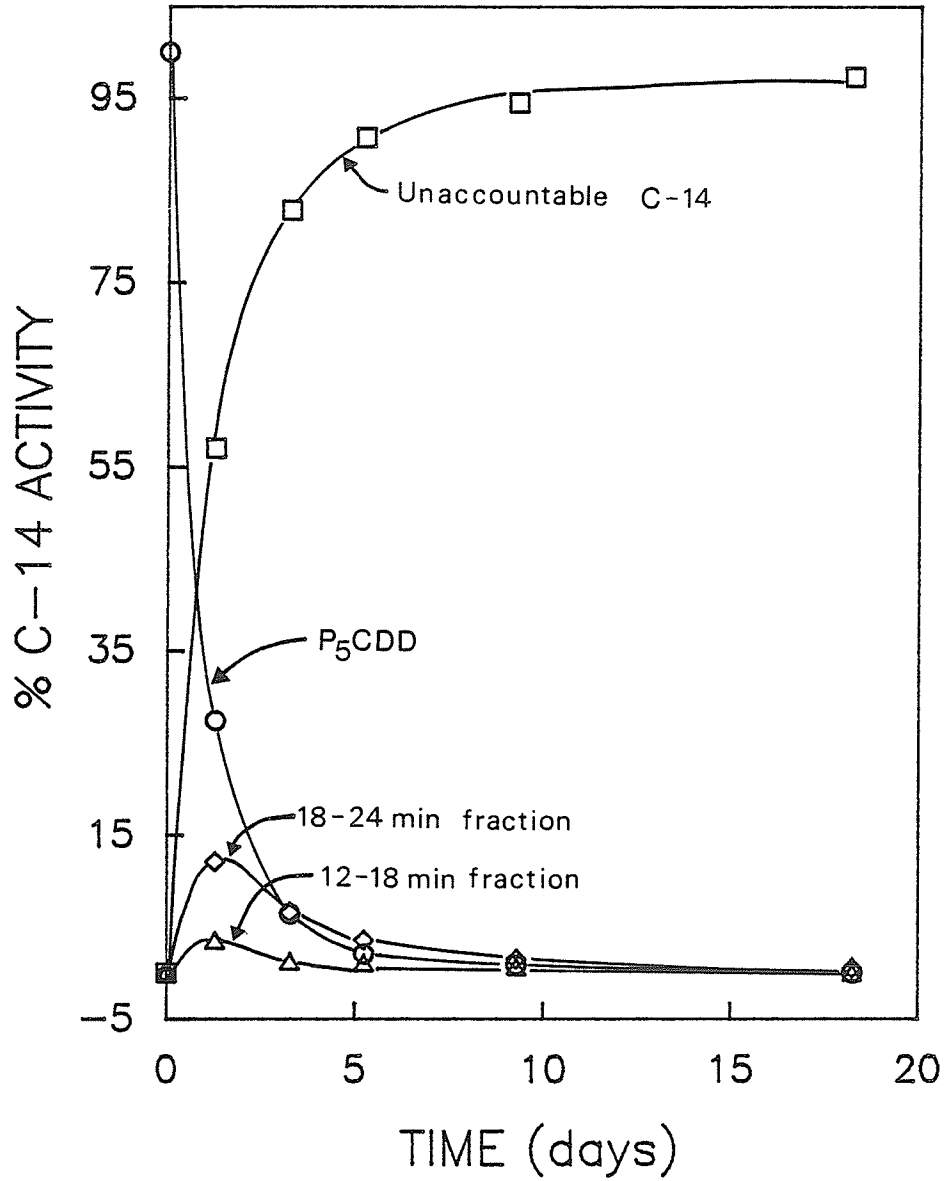


Figure 16. Distribution of carbon-14 activity as determined by HPLC-LSC for extracts of the photolyzed P₅CDD solutions.

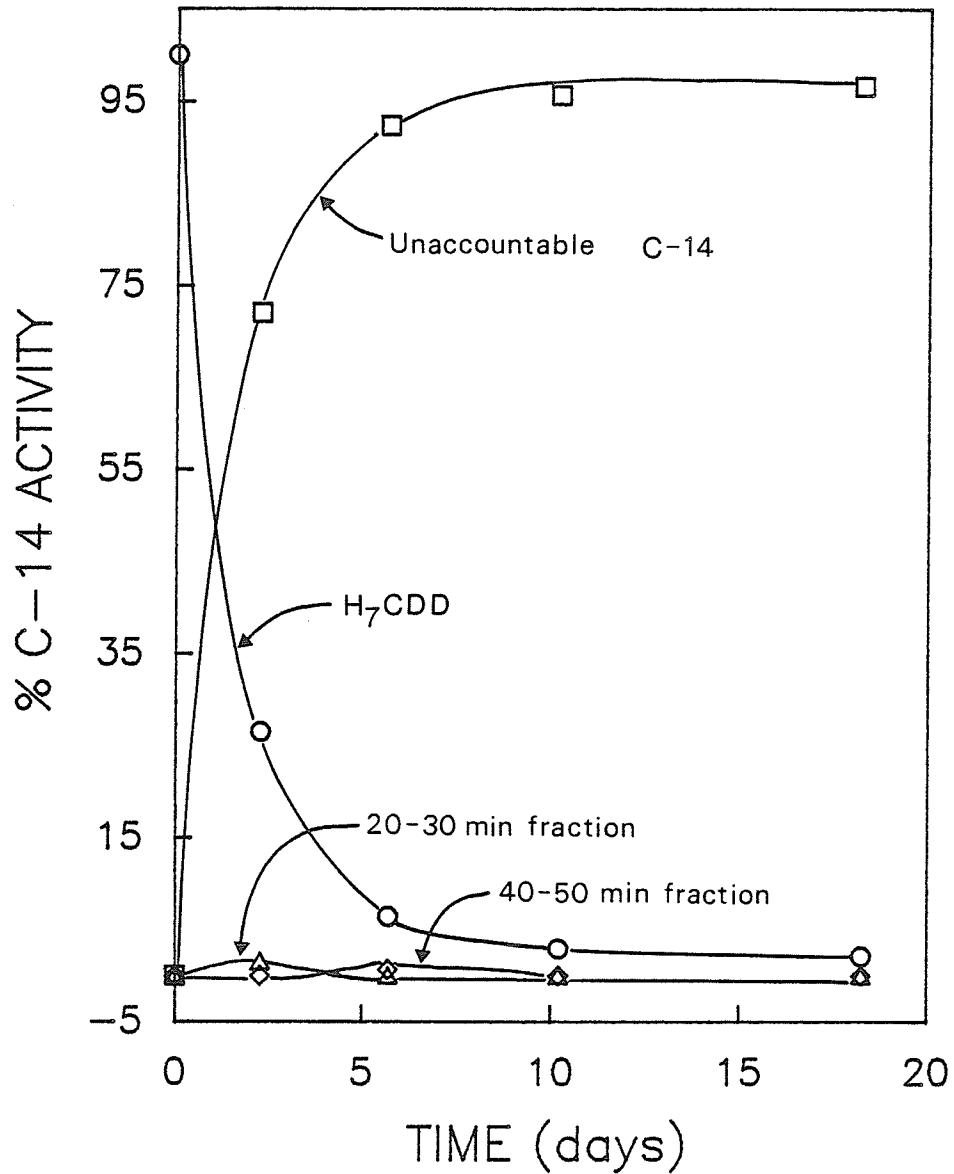


Figure 17. Distribution of carbon-14 activity as determined by HPLC-LSC for extracts of the photolyzed H₇CDD solutions.

of activity, up to 92% by day 5.7, is not extractable. The appearance of this fraction mirrors the disappearance of the parent H₇CDD. For the 5.7 d sample, 33% of this activity is found in extracted water and glassware. The formation of highly polar, nonextractable product(s) suggest degradation to very polar, possibly phenolic products.

It is interesting to note that although a slight amount of degradation of P₅CDD was observed in the dark control, especially beyond 10 days of exposure, the polar product was not prevalent. Several bands of activity, with retentions characteristic of T₄CDD and T₃CDD appeared in the HPLC analysis. The concentrations of these compounds increased with time such that at day 18.25 the bands with T₄CDD- and T₃CDD-like behaviour account for 21 and 5% of the total activity, respectively. Therefore, in the absence of sunlight, chemical degradation proceeding through a different mechanism and at a much slower rate is postulated. In this set of samples, no polar product eluting at the HPLC solvent front was detected. This is again not in agreement with the photolyzed samples and supports degradation via a different mechanism. Attempts are being made to analyze the intermediates by GC/MS to confirm the presence of lower chlorinated dioxins and hence a reductive dechlorination mechanism.

IV. CONCLUSIONS

Two chlorinated dioxins, 1,2,3,4,7-P₅CDD and 1,2,3,4,6,7,8-H₇CDD, were rapidly photolyzed in natural waters exposed to midsummer sunlight at 50°N latitude, with half-lives of 0.94 and 2.5 d, respectively. The rates of photolysis were considerably higher than those predicted with Mill's model for direct aqueous photolysis. The results implicate involvement of indirect or sensitized photolysis in the overall sunlight breakdown of these congeners in natural waters.

Using the assumption of direct aqueous photolysis, upper limits for the environmental quantum yields for this process were calculated to be 0.006 and 0.004 for P₅CDD and H₇CDD, respectively. Until further studies reveal the extent of direct versus indirect photolysis, these values may be used as upper limits for the direct aqueous photolysis of these congeners in sunlight. This assumption should be valid in modelling where actual field data allow the model to incorporate actual rates of photolysis.

The degradation process resulted in primarily polar photoproducts which were difficult to extract from aqueous solution. In addition, trace amounts of what appeared to be lower chlorinated congeners have been isolated. However, further studies are required to confirm the structure of these products and thus to unravel the mechanism of the degradation reaction.

CHAPTER 3

FATE OF 1,2,3,4,7-PENTACHLORODIBENZO-*p*-DIOXIN IN POND MESOCOSMS AS A FUNCTION OF THE ENVIRONMENTAL INPUT PATHWAY

I. INTRODUCTION

Early concerns about polychlorinated dioxins generally involved specific isomers or a limited group of isomers produced during the synthesis of chlorophenol-based chemicals. For example, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin were the major PCDD contaminants produced in the synthesis of the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) (78) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (79), respectively. Currently, combustion (80) is believed to rival the use of chlorophenol-based chemicals as the major sources of PCDD emissions into the Canadian environment (17). Combustion, in the presence of dioxin precursors such as chloroaromatic compounds, is a potential source of a complex mixture of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) which may subsequently be emitted into the atmosphere. Czuczwa and Hites (26), for example, reported the presence of T₄CDDs, P₅CDDs, H₆CDDs, H₇CDDs, and O₈CDD as well as the corresponding PCDF congener groups in effluents from municipal and industrial incinerators. Their work with air particulates and lake sediments indicated the importance of long-range atmospheric transport of these chemicals with subsequent deposition into aquatic ecosystems.

Model aquatic ecosystems and pond or lake mesocosms have been used to study the environmental fate of several PCDDs. Although the relative sizes of the sediment and water compartments in the model systems do not necessarily replicate real lakes, the behaviour of chemicals in these small scale ecosystems provide valuable insights into their over-

all fate in the environment. Early research with PCDDs focused primarily on 2,3,7,8-T₄CDD due to its extreme toxicity (13) and its presence in Agent Orange, a military herbicide used as a defoliant in Vietnam (81). Isensee and Jones (82) and Yockim et al. (83) used soil pretreated with 2,3,7,8-T₄CDD to prepare the sediment bed in glass aquaria, with subsequent examination of the distribution and bioaccumulation potential of 2,3,7,8-T₄CDD in the model ecosystem. Ward and Matsumura (84) conducted similar experiments in glass culture tubes containing lake sediment and water. However, in their investigations, 2,3,7,8-T₄CDD was applied into the water as a benzene solution. Tsushimoto et al. (85) compared the fate of 2,3,7,8-T₄CDD in outdoor ponds with that in aquatic ecosystems prepared in glass bottles in the lab. The T₄CDD was applied to the surface of the pond in a mixture of anisole, Triton-X 100, and pond water. More recently, Corbet et al. (57,86) and Marcheterre et al. (87) examined the distribution of 1,3,6,8-T₄CDD and O₈CDD, respectively, in outdoor aquatic ecosystems. Corbet applied 1,3,6,8-T₄CDD subsurface to the water column as an acetone-benzene solution whereas Marcheterre coated NaCl crystals with O₈CDD and then sprinkled the crystals onto the water surface. Finally, Servos (88) determined the relative bioavailability and fate of 1,3,6,8-T₄CDD and O₈CDD in limnocorrals with PCDDs applied as a sediment slurry stirred into the water column.

In this study, the fate of ¹⁴C-1,2,3,4,7-pentachlorodibenzo-p-dioxin was determined in pond mesocosms using two different methods of chemical input into the aquatic ecosystem. Although different methods of PCDD input have been reported in the literature, as reviewed above, no previous investigations have focused on the effect of the mode of

input on the relative distribution of PCDDs in an aquatic ecosystem. In the environment, hydrophobic pollutants such as PCDDs enter aquatic ecosystems by a variety of pathways. PCDD contamination produced through the use of agricultural chemicals could be carried into a lake or stream with soil runoff or in spraydrift. Dioxins released into the atmosphere from combustion sources may be introduced to a water body through washout during a rainfall event, atmospheric deposition with particulate matter, or diffusion from air into water. The physical state of the pollutant as it enters a lake or stream, whether sorbed to particulate matter or in solution in spraydrift or rainfall, may have a significant effect on the overall fate of the chemical in the system. Redistribution processes, such as volatilization, photolytic degradation, and sedimentation rates, as well as the availability of the PCDDs to aquatic biota and hence the potential for food chain transfer may all be affected by the input pathway. It is, therefore, extremely important to determine the effect of the mode of input on the overall environmental fate of PCDDs in aquatic ecosystems. Therefore, replicate ponds were treated with a surface spray of the P₅CDD in a water-miscible organic solvent, simulating environmental influx of PCDDs into lakes via rainfall or spray drift. Two additional ponds were treated by stirring a sediment slurry of the dioxin into the water column, simulating environmental input into lakes by particulate matter contaminated with PCDDs, either as runoff or as atmospheric deposition. The redistribution dynamics of ¹⁴C-P₅CDD were investigated by frequent monitoring of the water column, surface films, air, caged fish, bottom sediment, and benthic biota. Particular emphasis was placed on determining relative differences in bioavailability and volatilization

of ^{14}C -P₅CDD as a function of the method of introduction of P₅CDD into the ecosystem.

Finally, several mathematical models are now available to predict the environmental fate of organic chemicals in aquatic ecosystems (89-92). Using the water solubility and Henry's constant reported earlier (Chapter 1) and the rate of photolysis of 1,2,3,4,7-P₅CDD determined on site (Chapter 2) during this fate study, a version of the quantitative water-air-sediment interaction model (90) facilitating a single pulse input of chemical into an aquatic system was used to predict the behaviour of P₅CDD in this study. Various transport coefficients, physical properties, and transformation rates were adjusted until the model predictions agreed with the observed concentration profiles. After fitting to the experimental data, the model indicated the important processes dominating the fate of P₅CDD in the pond mesocosms.

II. EXPERIMENTAL

A. CHEMICALS

Universally ring-labelled ^{14}C -1,2,3,4,7-pentachlorodibenzo-*p*-dioxin, purchased from Pathfinder Laboratories Inc. (St. Louis, MO) with a specific activity of 24.16 mCi/mmol, was purified by preparative HPLC as previously described (see Chapter 1). Repeated injections were made until ~2.2 mg of the purified P₅CDD were isolated from ^{14}C -labelled impurities. The aqueous solution of the dioxin was extracted into hexane and the extracts were reduced to a volume of <5 mL by rotary evaporation and dried by passage through a microcolumn of anhydrous Na₂SO₄ (Fisher Scientific, Winnipeg, MB). The solution was transferred to a 15 mL graduated centrifuge tube, reduced to a volume of ~1.5 mL with a stream of prepurified N₂ and made up to 10.0 mL with THF.

Reagent grade concentrated H₂SO₄, used in pH adjustments and fat degradation procedures was supplied by Allied Chemical Canada Ltd. (Pointe Claire, PQ). All solvents used in the purification of 1,2,3,4,7-P₅CDD and in workup of samples, including dichloromethane, acetone, hexane, toluene, methanol, and tetrahydrofuran were distilled-in-glass quality (Caledon Laboratories Inc., Georgetown, ON).

Manganous sulfate (MnSO₄·H₂O), sodium hydroxide, sodium azide (NaN₃), sodium thiosulfate (Na₂S₂O₃·5H₂O), and soluble starch, certified ACS grade chemicals (Fisher Scientific, Winnipeg, MB), were used in dissolved oxygen determinations. Sodium iodide (NaI), also required in this procedure, was supplied by BDH (Canada) Ltd.

Combustion of samples to determine levels of nonextractable ^{14}C in various matrices including sediment and fish, were carried out with a

Packard Model B306 Tri-Carb Sample Oxidizer. Carbo-Sorb (Packard Instrument Co. Inc., Downers Grove, IL) was used to trap $^{14}\text{CO}_2$, which was then analyzed by liquid scintillation counting with PCS fluor (Amersham Corp., Arlington Heights, IL) diluted 2:1 with xylene. Other LSC analyses utilized Scintiverse I (Fisher Scientific, Winnipeg, MB) as the scintillation fluor except for samples containing >15% water in which case Atomlight (New England Nuclear, Boston, MA) was used.

B. SITE PREPARATION

Five ponds, constructed approximately 30 months earlier at the University of Manitoba Agriculture Field Station at Glenlea, MB were used for the field study. The ponds had been constructed by excavating an area measuring approximately 4.5 x 5.5 m to a depth of ~0.9 m. The excavations were lined with polyethylene, the sloping sides were covered with a clay-based sod, and 10 cm of earth was added to the bottom as previously described (57). Approximately two months prior to the current study, the ponds were groomed by pumping out the water and removing all macrophytes which had been established in the ponds. Approximately 10 cm of fresh soil was added to each pond to create a good bed of sediment for the study. The ponds were then filled with water and left to acclimate for ~8 weeks. Two ponds were used for sediment slurry applications of PCDDs, two for sprayover applications, and one served as a control.

Air sampling stations were set up by plumbing CPVC pipe from a pumping station to the center of each pond. Inverted glass tulip funnels, used to hold polyurethane foam (PU) traps, were added to the system with tygon tubing and positioned so that the PU foams sampled air at distances of 5 and 10 cm above the surface of each pond. Two

stations were set ~25 cm above ground level at the edge of two ponds to monitor for advective movement of PCDDs from the pond area. The PU foams, cleaned by soxhlet extraction for 12 h with hexane, were set into each sampling station just prior to addition of PCDDs to the ponds. Flow rates, set by adjustment of a screw clamp on the tygon tubing in-line, were measured with a rotameter flowmeter.

Two cages were suspended approximately 10 cm from the bottom sediment in each pool and stocked with 65 fathead minnows (*Pimephales promelas*) and 20 crayfish (*Procambarus spp.*), respectively, 11 days prior to sample treatment. Fathead minnows did not survive the transfer to the field well. Therefore, just prior to spike time the survivors were evenly distributed among the minnow cages in the five ponds so that each cage now contained approximately 10 fish.

One week prior to spike day eight 250 mL glass jars were set onto the bottom of each pond. Four of these contained ~2 cm of soil to be used as sediment samples early in the sampling period at a time when core sampling would too severely disturb the water column. The other four were empty and served as sedimentation traps to be removed monthly to freezeup.

C. SAMPLE APPLICATION

The purified ^{14}C -1,2,3,4,7-P₅CDD was quantitatively transferred from the 15 mL graduated centrifuge tube into a 110 mL volumetric flask and made to volume with THF. Analysis of an aliquot by liquid scintillation counting established the concentration as 18.7 $\mu\text{g/mL}$.

Two days before application of PCDDs to the pond mesocosms, water-sediment slurries were prepared by weighing 458 g of soil into each of two 4 L glass bottles and adding 500 mL of pond water. The slurry was

shaken occasionally and allowed to sit overnight to properly saturate the soil with water. The soil used to prepare these slurries, a clay textural designation (65% clay, 30% silt, 5% sand), was the same soil used to form the bottom sediments in the ponds. Aliquots (25.0 mL) of the standard ^{14}C -1,2,3,4,7- P_5CDD solution were then pipetted into the bottles. The contents were thoroughly mixed and allowed to stand overnight to ensure equilibrium partitioning of P_5CDD to the sediment. The cap was left open overnight to allow THF to evaporate from the mixture.

For the sprayover application, replicate samples were prepared at the site just prior to application. After 250 mL of THF was added to each of two plastic sprayer containers (purchased from a local garden supply center), 25.0 mL of the ^{14}C - P_5CDD standard was pipetted into each sprayer. Another 250 mL of THF was added to each container and the solution was well mixed.

The P_5CDD was applied to the ponds under calm conditions at 11:30 PM on July 18, 1986. The THF solutions were sprayed over replicate ponds through a gravity-feed spout attached to the sprayer containers in which the samples were prepared. A sweeping motion was used to distribute the sample evenly onto the water surface. In order to minimize edge effects, the sprayover was kept ~0.5 m from the edges of the ponds. Another 250 mL of THF was added to the containers and also sprayed over to rinse most of the P_5CDD out of the sprayer. For the application of P_5CDD sorbed to suspended sediment, the bottles containing the sediment slurries were shaken and the contents poured into the ponds subsurface. The water was continually stirred during addition of the slurry in order to distribute the sample evenly in the

water column. However, to again minimize edge effects, application was not made within an area of ~ 0.5 m from the pond edges. The last portions of sediment were rinsed out of the bottles using 300 mL of pond water. Considering the estimated volumes of the ponds and assuming an even distribution of dioxins in the water column, concentrations of P₅CDD were 72 and 81 ng/L in ponds receiving sediment slurry and sprayover treatments, respectively.

D. SAMPLING

Air was continuously drawn through PU foams at a rate of 10-12 L/min. Cumulative 12 h air samples were taken for a period of 3 d above all ponds at both 5 and 10 cm heights. Two 12 h and two 24 h samples were taken at the advection stations. Flow rates were measured just prior to sample application and again at the completion of air sampling 3 d later. Foams removed from sampling stations were placed into cold storage (-32°C) in clean glass jars.

Sampling of surface films was begun immediately after application of P₅CDD to each pond, using a modification of the method of Harvey and Burzell (93). A 20x20 cm glass plate was touched to the water surface and the water collected was washed into glass jars with a stream of DCM from a wash bottle. Duplicate samples, each the result of three subsamples taken as described above, were obtained from each pool and stored at 6°C .

The water column was also sampled immediately after application of P₅CDD to each pond and continued until day 105. Samples were taken by immersing a 4 L bottle to a depth of approximately 30 cm in the center of the water column. A long glass tube, extending from the sampler to the surface was used to bleed air from the sampling bottle, minimizing

the amount of turbulent mixing of the surface water. Samples were extracted on site after completion of all sampling procedures.

Crayfish and fathead minnows were withdrawn from their cages with a small net and placed into cold storage (-32°C) in Whirl-Pak bags (Fisher Scientific, Winnipeg, MB). Crayfish survived well and were sampled to day 59. However, in most of the ponds fathead minnows could only be sampled to day 3.

Initial sediment samples, at days 2 and 5, were simply taken by lifting appropriate sediment jars from the pond bottom. Thereafter, sediment cores were taken by pushing a 5.1 cm inside diameter plexiglass tube into the bottom sediment. A rubber stopper was placed into the top opening of the 70 cm long tube and the excised sediment was brought to the surface by slowly lifting the sampler. The bottom of the tube was then closed with a rubber stopper while still subsurface. The sampler was removed from the pond and mounted vertically for recovery of the upper layer of sediment. After the water was siphoned off, the sediment column was forced up the tube. A short piece of plexiglass tubing was used as an extension of the sampler to receive the sediment as it was forced out of the sampler. The 0-2 cm layer was cut with a thin sheet of stainless steel and washed into a 250 mL glass jar. Duplicate samples were taken from each pond at each sampling time up to day 105 and placed into cold storage (-32°C).

E. SAMPLE WORKUP AND ANALYSIS

PU foams, dried in a dessicator overnight, were soxhlet extracted for 5 h with hexane. Extracts were reduced to ~2 mL by rotary evaporation and transferred to 15 mL graduated centrifuge tubes. After evaporation with a stream of prepurified N₂, the volume was adjusted to

0.60 mL with hexane, mixed, and transferred to 2 mL amber vials. A 300 μ L aliquot was analyzed for ^{14}C -1,2,3,4,7-P₅CDD by LSC.

Surface film samples were extracted twice with 5 mL of DCM. The water was then acidified (pH 0.9-1.2) with 0.5 mL of conc. H_2SO_4 and extracted two more times with 5 mL of DCM. The DCM extracts were passed through an anhydrous Na_2SO_4 drying column and reduced in volume as described above, finally being made to a volume of 0.60 mL with hexane. During extractions, water volumes were occasionally measured and 4 mL aliquots of extracted water were counted in the presence of 12 mL of Atomlight fluor to determine levels of nonextractable ^{14}C . Aliquots (100 μ L) of all sample extracts were counted to determine total ^{14}C . HPLC analysis was carried out on samples with >100 dpm to check for extractable degradation products.

Water column samples were extracted on site with two 50 mL portions of DCM. The water was then acidified with 1.5 mL conc. H_2SO_4 and again extracted twice with 50 mL DCM. In the lab, extracts were passed through a Na_2SO_4 drying column, reduced in volume and made to 1.00 mL with DCM:hexane. LSC was used to determine the total ^{14}C in 400 μ L aliquots of the extracts. A 200 μ L aliquot was then evaporated to dryness, redissolved in 50 μ L of CH_3OH , and analyzed by HPLC-LSC collecting 3 min fractions for 42 min. In most of the water column extractions 1 L portions of water were extracted except for later in the study when levels of ^{14}C were expected to be very low. Therefore, 3.5 and 8.0 L of water were extracted on days 59 and 105, respectively. In order to determine the relative amounts of P₅CDD associated with dissolved organic matter (DOM), sorbed to suspended particulate matter (POM), and in true solution in the water column, the Sep-Pak technique

of Landrum et al. (98) was used. A 4.00 mL aliquot of water was analyzed by LSC to determine ^{14}C in the total water column. After centrifuging 21.0 mL of the water at 20,000 g for 30 min, another 5.0 mL aliquot was assayed by LSC. The differences in the two assays represented the ^{14}C associated with POM. To determine ^{14}C associated with DOM a 10.0 mL aliquot of the centrifuged water was passed through a preconditioned C_{18} Sep-Pak (Waters Scientific, Mississauga, ON). P_5CDD complexed to DOM passed through the Sep-Pak (98) and was evaporated to dryness, taken up in 5 mL of CH_3OH and assayed in the presence of 10 mL of Scintiverse I fluor. P_5CDD free in the water column sorbed to the C_{18} phase and was eluted with 5 mL of CH_3OH and was also assayed by LSC with Scintiverse I.

In order to determine total suspended solids at each sampling time, another 100 mL of pond water were filtered through Whatman GF/C glass microfibre filters (Whatman, Maidstone, England) with a 1.2 μm cutoff, previously brought to constant weight, tared, and dessicated. The filters were washed with distilled water, placed in Petri dishes, and dessicated. Weighing was continued until the filters attained constant weight. The ^{14}C associated with the suspended solids was determined by combustion of the filters as described above.

The wet weight of biota, both fathead minnows and crayfish, was determined by removing samples from cold storage, rinsing with distilled water, and weighing. After freezing overnight the fish were freeze-dried for 72 h at -68°C and pressures of 1-2 torr. Whole fish were ball-mill extracted with 20 mL of toluene for 1 h on a wrist-action shaker. Samples were washed into 50 mL Corex centrifuge tubes with 10-20 mL of toluene and centrifuged for 40 min at 3000 rpm. A

2.00 mL aliquot of the supernatant was pipetted into a tared LSC vial and evaporated to dryness, dessicated, and weighed to constant weight to determine the fat content (94). The rest of the supernatant was removed and the insoluble fraction was washed twice with toluene. Each time the sample was centrifuged and the wash was added to previous toluene extracts. Finally, solids were washed into aluminum dishes and evaporated to dryness for combustion to determine nonextractable ^{14}C . The toluene fractions were reduced in volume by rotary evaporation and then washed into 60 mL separatory funnels with hexane. In order to degrade the fat in these samples, the hexane solutions were partitioned with three 3 mL portions of conc. H_2SO_4 (95). The mixtures were well shaken and 30-60 min allowed for phase separation. The hexane layer was then washed with 4 mL of water and dried by passage through a Na_2SO_4 column. Volumes were reduced by the methods described above, made to exactly 0.60 mL with hexane, mixed, and transferred to 2 mL amber vials. Analysis of 50 μL of crayfish and 350 μL of fathead minnow extracts was conducted by LSC. Sufficient sample remained of the crayfish extracts to check for degradation products by HPLC with 85% CH_3OH as mobile phase. Replicate 0.2-0.3 g samples of solid material remaining after extraction of all fish samples were oxidized to determine nonextractable ^{14}C .

Sediments were freeze-dried for 72 h at -68°C and pressures of 1-2 torr. Benthic biota were removed from the dried sediments with forceps, thoroughly rinsed with distilled water, and oxidized to determine ^{14}C content. Dried sediments were thoroughly ground in a mortar and pestle and weighed into 500 mL round-bottom flasks. After refluxing for 24 h with 200 mL of 1:1 acetone-hexane, all samples were

filtered through prewashed Whatman GF/A filters (Whatman, Maidstone, England) with a cutoff of 1.6 μm . The sediments were washed twice with 30 mL of acetone and twice with 30 mL of hexane. The volume was then reduced by the methods described above and made to 3.00 mL with hexane. A 250 μL aliquot was applied to a Si Sep-Pak (Waters Scientific, Mississauga, ON) and eluted with 5 mL of hexane to cleanup and recover P₅CDD. The extracted ¹⁴C was assayed by LSC to determine P₅CDD concentrations in sediment. The Sep-Pak was then eluted with 5 mL of CH₃OH, which was also assayed by LSC, to determine polar degradation products. Nonextractable ¹⁴C in sediment samples was determined by oxidizing 0.15-0.30 g samples as described above.

E. ENVIRONMENTAL CONDITIONS

Wind speed was continuously monitored at both 28 and 80 cm above the water surface near one of the ponds with the use of a Rimcoe wind anemometer. Wind direction was also frequently noted, particularly during the first 72 h of the fate study.

Water temperatures at depths of 1-2 cm and 30 cm were recorded with a thermocouple probe connected to a digital thermometer (Fluke 52 K/J thermometer, John Fluke Mfg. Co. Inc., Everett, WA).

G. WATER CHEMISTRY

A 1 L polyethylene bottle was used to obtain a water sample from each pond prior to the spike date and then monthly thereafter. Samples were submitted to the Freshwater Institute Water Chemistry Lab for determination of water chemistry including chlorophyll-*a*, total suspended solids, total dissolved N, P, and organic C, conductivity, pH, alkalinity, suspended C and N, and % organic C in suspended matter.

The pH of the water was measured on site (Fisher Accumet pH Meter

Model 600) using a combination pH electrode precalibrated to pH 7.40 with a standard buffer (Fisher Scientific, Winnipeg, MB). Dissolved oxygen was determined on site in duplicate for each pond using the azide modification of the Winkler method (96,97) Samples were taken at a depth of ~40 cm in BOD bottles which had been thoroughly flushed with N₂ and tightly stoppered for transport to the field.

Results of water parameter measurements one day before sample application are summarized in Appendix A.

III. RESULTS AND DISCUSSION

A. FATE OF P₅CDD AS A FUNCTION OF THE INPUT METHOD

1. WATER COLUMN

The total concentration of P₅CDD in the water column, sampled at a depth of ~30 cm, declined very rapidly, regardless of the method of introduction of the dioxin as summarized in Table 17. Initial concentrations, within 10 min of sample application, were approximately twice as high in ponds treated with a sediment slurry of P₅CDD reflecting the nature of the input. In the sprayover treatment, P₅CDD entered the water column by diffusion whereas in the sediment-slurry treatment, the P₅CDD was mixed directly into the water column.

The results of the Sep-Pak studies used to determine the amounts of

TABLE 17. Concentrations of P₅CDD (pg/L) in the Water Column as a Function of the Method of Introduction to the Ecosystem.

Time (d)	Slurry ^a	Spray ^b
0.01	29900 ± 3600	13500 ± 7000
0.33	7000 ± 1900	7800 ± 640
1	4050 ± 950	3910 ± 690
3	1610 ± 690	2030 ± 20
8	860 ± 630	770 ± 100
15	240 ± 70	120 ± 30
29	220 ± 30	120 ± 4
59	23 ± 15	15 ± 4
105	16 ± 1	22 ± 0.4

^aAverage of two samples, one from each pond, for ponds treated with a sediment slurry of P₅CDD.

^bAverage of two samples for ponds treated with a sprayover of P₅CDD.

P₅CDD associated with DOM as opposed to the fraction truly dissolved in the water column were difficult to interpret due to the large variability of the data. Statistical analysis using the null hypothesis at the 95% confidence level was applied to all data to determine whether observed results were significantly different compared to the control. According to the tests, levels of P₅CDD extracted by C₁₈ Sep-Paks (the fraction in true solution) were not statistically significant in any of the samples. However, using the method suggested by Landrum et al. (98), levels of P₅CDD in true solution could be calculated from levels eluting through the Sep-Pak (DOM bound) and from the total P₅CDD determined prior to centrifugation.

After centrifugation, counts in the sediment slurry treatments dropped to such an extent that any differences between samples and controls proved to be due to indeterminate error. In the sprayover treatments, significant counts were monitored up to the day 3 samples. The results established that a significant difference existed between levels of P₅CDD sorbed to POM in the two types of treatment, with 40-60% of P₅CDD sorbed to POM at t₀ in the sprayover treated ponds.

Levels of P₅CDD which eluted through the Sep-Paks (associated with DOM) were also statistically valid for the sprayover treatments to day 3 but only to day 1 for the sediment slurry samples. Averaging the data for replicate ponds showed that approximately 5-20% of P₅CDD was associated with DOM in both treatments. These results suggested that 80-95% of P₅CDD in the sediment treated ponds was sorbed to POM. Results for the sediment slurry treatment compare favorably with data reported by Servos (88), which showed 75-90% of both 1,3,6,8-T₄CDD and O₈CDD sorbed to POM and 10-30% of both congeners associated with DOM in

limnocorrals treated with a sediment slurry of these two congeners. Although DOC levels in the ponds were approximately four times greater than in limnocorrals, effects on the fraction of PCDD complexed to DOM did not reflect this difference.

Levels of P₅CDD in true solution were below the detection limits for the slurry treated ponds and could not be estimated from data for POM and DOM associated P₅CDD. However, approximately 30-45% was estimated to be free in solution at t₀ for the sprayover treatments. In the limnocorral study Servos (88) reported 10-15% of T₄CDD and <1% of O₈CDD extractable by the C₁₈ Sep-Pak and hence free in solution.

Although the data are semi-quantitative at best, the results demonstrate that the method of environmental input of PCDDs into aquatic systems affects the relative distribution of the chemical between water and organic phases in the water at the time of input. When PCDDs enter lakes in solution form, as in spraydrift or in rainfall, availability of the dioxin for volatilization, photolysis, and uptake by biota is greater than with influx of dioxins sorbed to particulate matter.

Losses of ¹⁴C to the centrifuge tubes and pipets may account for much of the observed variability. The levels of P₅CDD sorbed to POM may be low due to fine POM not centrifuged out of the water. Since the samples were not centrifuged and analyzed on site, further partitioning could have occurred to reduce the levels of P₅CDD in true solution.

The GF/C filters, used in the determination of total suspended solids (TSS) in the water column, were oxidized to determine the concentrations of P₅CDD sorbed to POM. Data for samples from ponds treated with a sprayover technique are in good agreement with results presented above using the centrifuge technique. Using the direct assay

prior to centrifugation as an indication of total P₅CDD, the combustion results show 40-50% of P₅CDD sorbed to POM compared to 40-60% calculated above. However, results for slurry treated ponds do not compare favorably with the 80-95% P₅CDD sorbed to POM estimated above. Oxidation of filters for these samples show an extremely low level (20-40%) sorbed to POM in the first day after sample input. These results are unreasonable in view of the fact that the P₅CDD is essentially quantitatively sorbed to POM at the time of input. A possible explanation could be that oxidation of these samples was less efficient since most of the solids in these samples would be sediment (clay) added to the ponds with the sample input. In sprayover treated ponds, the natural suspended solids would be richer in organic matter producing a more efficient oxidation and release of sorbed ¹⁴C.

Analysis of aliquots of extracted water by reverse-phase HPLC did not reveal any obvious degradation products. Although several peaks of activity, with retention times of ~5 and 22 min, may be extractable degradation products, the signals were too small to be considered significant. A better check of degradation might be made by combining a large number of samples and isolating bands with different retention characteristics.

The time-concentration profiles, plotted in Figure 18, represent extractable P₅CDD in the total water column, including P₅CDD sorbed to POM and complexed to DOC. The rapid clearance from the water column was not unexpected due to the extremely hydrophobic nature of chlorinated dioxins. Although initial levels were of the order of 13-30 ng/L in the two treatments, P₅CDD levels decrease to ~2 ng/L by day 3 and ~0.2 ng/L by day 15 in all ponds, with pseudo first-order

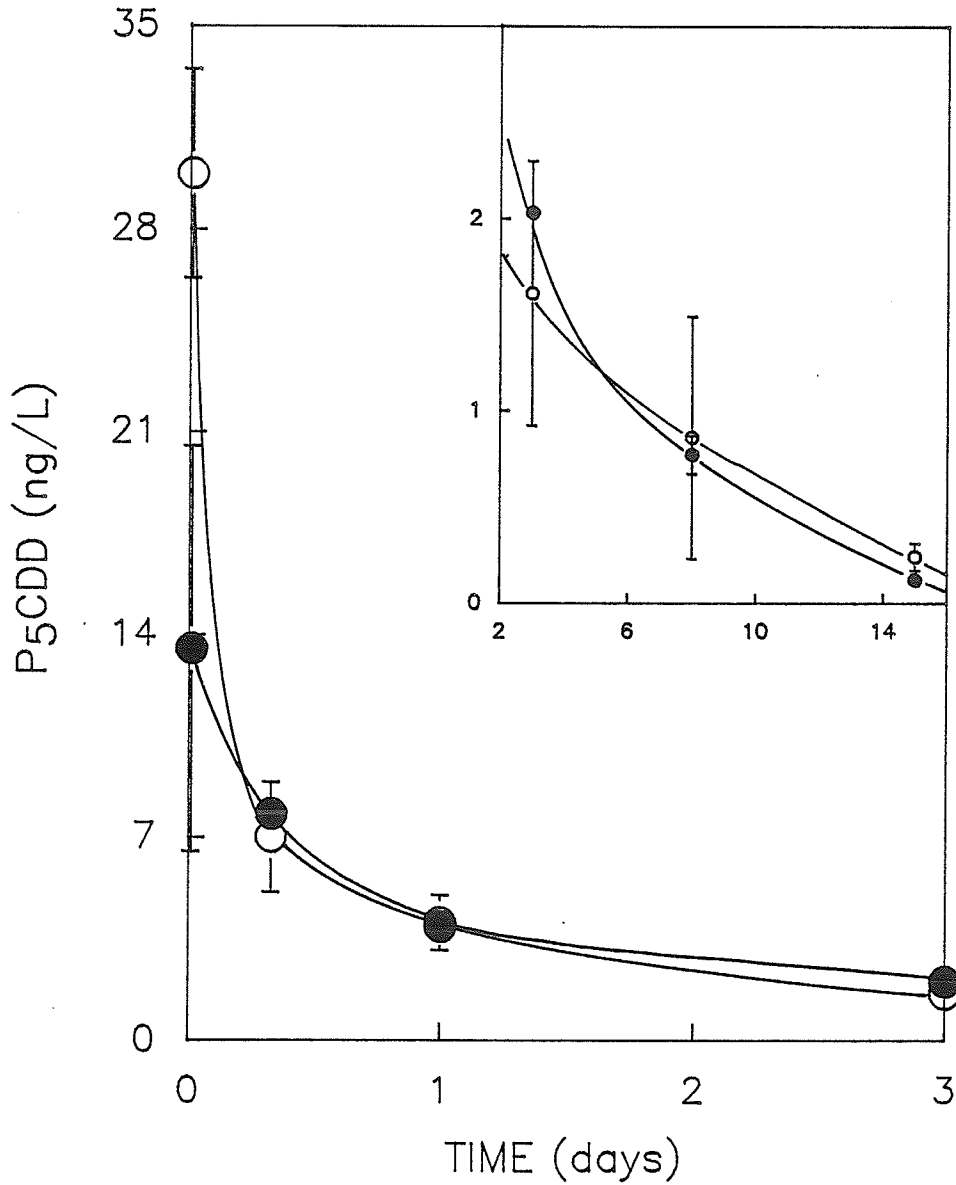


Figure 18. Clearance of P₅CDD from the water column after application as a sediment slurry (O) and a sprayover (●). The concentrations represent extractable P₅CDD in the total water column.

half-lives of 2.7 ± 0.5 d and 2.4 ± 0.2 d for the slurry and sprayover treated ponds, respectively. These $t_{1/2}$ values were not significantly different on a statistical basis. Therefore, rates of clearance of P₅CDD showed no dependence on the type of influx of the chemical into the water. Servos (88) reported similar half-lives for clearance of 1,3,6,8-T₄CDD (2.6 ± 0.2 d) and O₈CDD (4.0 ± 0.3 d) from the water column in limnocorrals treated with a sediment slurry of dioxins. However, Corbet (57) noted a much faster clearance of 1,3,6,8-T₄CDD (0.6 ± 0.3 d) in ponds treated subsurface with an acetone-benzene solution of the dioxin.

2. SURFACE FILMS

Initial concentrations of P₅CDD in surface microlayers were much greater for ponds receiving a sprayover of the dioxin, reflecting the differences in the two types of sample input. The data, plotted in Figure 19, show a very rapid dissipation of P₅CDD from surface microlayers, irrespective of the input method. Since the input pathway produces a large difference in concentrations in surface microlayers, a direct comparison of P₅CDD behaviour in this compartment is not as important as are the implications on the effect these differences have on the overall environmental redistribution of the dioxin.

3. AIR

Wind anemometers, set up approximately 1 m from the edge of one of the ponds which received a sprayover treatment, monitored wind speeds at two levels, estimated to be approximately 28 and 80 cm above the water level in the nearest pond. The data, summarized in Appendix B, indicated that wind speeds were less than 1 m/s during the first 12 h after sample input. During the second 12 h collection period winds

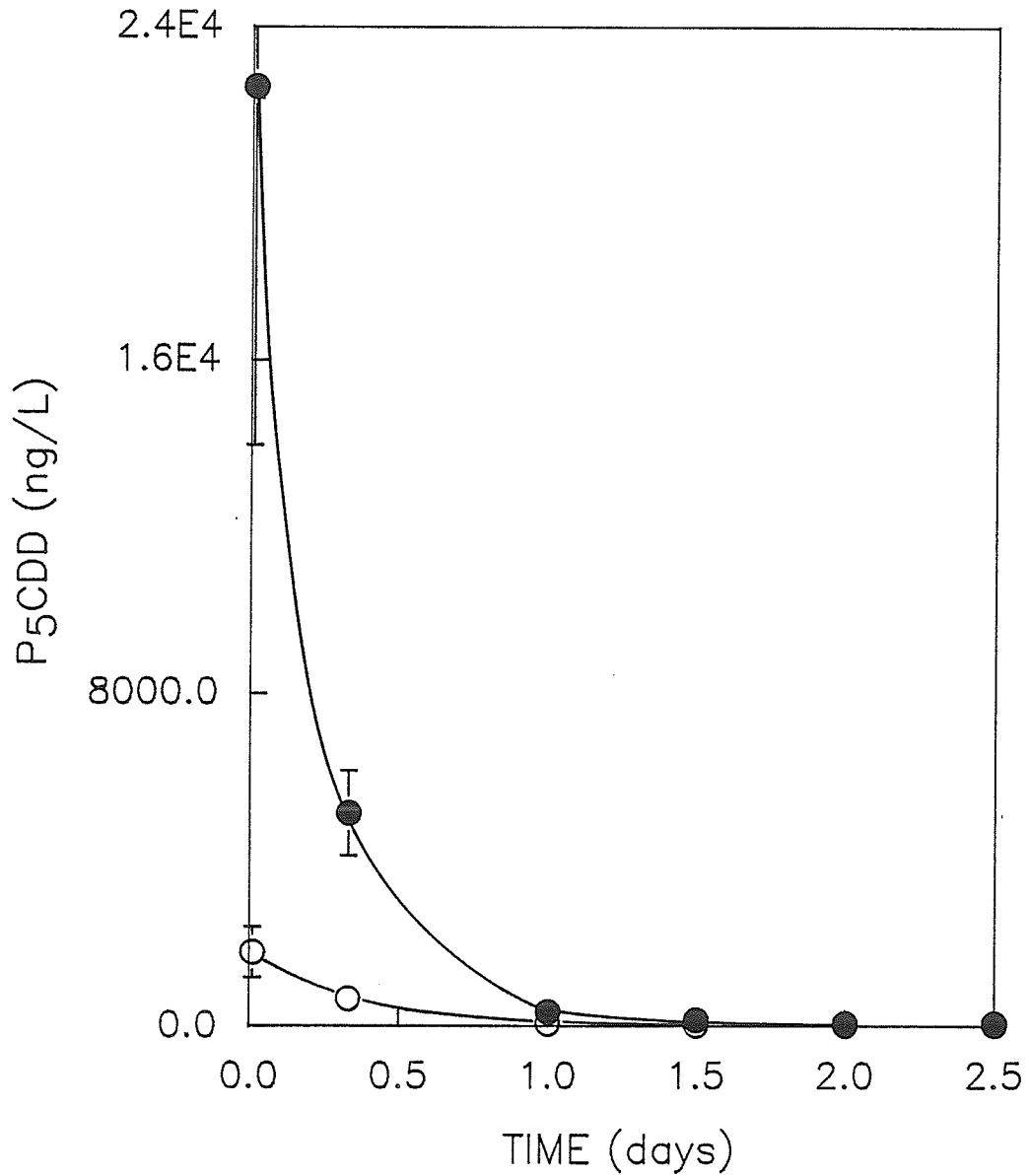


Figure 19. Levels of P₅CDD in surface films, of ~100 μm thickness, after application as a sediment slurry (O) and a spray-over (●).