

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

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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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FATE OF POLYCHLORINATED DIBENZO-p-DIOXINS IN AQUATIC ECOSYSTEMS

BY

KENNETH J. FRIESEN

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

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 T<sub>4</sub>CDD at 41°C to as low as 0.9 ng/L for H<sub>7</sub>CDD 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·m<sup>3</sup>/mol for 1,2,3,7-T<sub>4</sub>CDD to 1.5 Pa·m<sup>3</sup>/mol for 1,2,3,4,7-P<sub>5</sub>CDD. Vapor pressures at ~25°C were predicted to be  $6 \times 10^{-6}$  and  $7 \times 10^{-7}$  Pa for T<sub>4</sub>CDD and P<sub>5</sub>CDD, 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-P<sub>5</sub>CDD and 1,2,3,4,6,7,8-H<sub>7</sub>CDD, were found to undergo rapid sunlight photolysis in natural waters, with observed first-order rate constants of 0.74 and 0.28 d<sup>-1</sup> 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-P<sub>5</sub>CDD 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 P<sub>5</sub>CDD 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 P<sub>5</sub>CDD 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 P<sub>5</sub>CDD 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.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	viii
LIST OF TABLES	xi
INTRODUCTION	1
CHAPTER 1. DETERMINATION OF AQUEOUS SOLUBILITIES AND HENRY'S CONSTANTS OF SELECTED POLYCHLORINATED DIBENZO- <i>p</i> -DIOXINS	8
I. INTRODUCTION	8
II. EXPERIMENTAL	11
A. Chemicals	11
B. Apparatus	11
C. Purification of dioxins	12
D. Water solubility determinations	14
E. Determination of Henry's law constants	16
III. RESULTS AND DISCUSSION	19
A. Aqueous solubilities	19
B. Thermodynamics of dissolution	21
C. Correlation of solubility with structure	27
D. Henry's law constants	31
E. Estimation of vapor pressures of PCDDs	36
IV. CONCLUSIONS	39
CHAPTER 2. SUNLIGHT PHOTOLYTIC DEGRADATION OF 1,2,3,4,7- PENTA- AND 1,2,3,4,6,7,8-HEPTACHLORODIBENZO- <i>p</i> -DIOXIN IN NATURAL WATERS	40
I. INTRODUCTION	40



II. EXPERIMENTAL	43
A. Chemicals	43
B. Preparation of solutions for photolysis	43
C. Sunlight photolysis	45
D. Sample workup and analysis	45
E. UV-visible spectrophotometry	47
III. RESULTS AND DISCUSSION	49
A. Sunlight photolysis of chlorinated dioxins in natural waters	49
B. Prediction of direct aqueous photolysis rates	54
C. Chemical actinometry	64
D. Products of photodegradation	71
IV. CONCLUSIONS	76
 CHAPTER 3. FATE OF 1,2,3,4,7-PENTACHLORODIBENZO- <i>p</i> -DIOXIN IN POND MESOCOSMS AS A FUNCTION OF THE ENVIRONMENTAL INPUT PATHWAY	 77
I. Introduction	77
II. Experimental	81
A. Chemicals	81
B. Site preparation	82
C. Sample application	83
D. Sampling	85
E. Sample workup and analysis	86
F. Environmental conditions	90
G. Water chemistry	90

III. RESULTS AND DISCUSSION	92
A. Fate of P <sub>5</sub> CDD as a function of the input method	92
1. Water column	92
2. Surface films	97
3. Air	97
4. Crayfish and fathead minnows	101
5. Sediment	106
6. Benthic biota	109
7. Interpretation of trends	111
B. Mass balance studies	117
C. Prediction of volatilization	121
D. Environmental fate modelling	125
1. Sediment slurry application of P <sub>5</sub> CDD	126
2. Sprayover application of P <sub>5</sub> CDD	134
IV. CONCLUSIONS	141
BIBLIOGRAPHY	144
APPENDICES	159
A. Water chemistry of all ponds used in the fate study, one day prior to sample input.	159
B. Calibration of wind anemometer	160
C. Parameters used to model the fate of P <sub>5</sub> CDD with QWASI after sample input as a sediment slurry	162
D. Parameters used to model the fate of P <sub>5</sub> CDD with QWASFI after sample input as a sprayover	165

## LIST OF FIGURES

Figure		Page
1.	Reconstructed chromatograms of the PCDDs prior to purification with 85% CH <sub>3</sub> OH as the mobile phase.	13
2.	HPLC system configuration for water solubility determination.	15
3.	Gas-sparging apparatus used in the determination of Henry's law constants.	17
4.	Plots showing the temperature dependence of the aqueous solubility of four PCDDs.	23
5.	Thermodynamic cycle for the dissolution process, involving solid, subcooled liquid, vapor, and aqueous solution.	25
6.	Correlation of total surface areas of the four PCDDs with the aqueous activity coefficient.	29
7.	Correlation of total molecular volume of the four PCDDs with the aqueous activity coefficient.	30
8.	Plots showing the stripping of chlorinated dioxins from water by gas-sparging at 23°C.	34
9.	Arrangement of samples for sunlight photolysis.	46
10.	Reconstructed chromatogram for the analysis of a photolyzed P <sub>5</sub> CDD solution by HPLC-LSC.	50
11.	Reconstructed chromatogram for the analysis of a photolyzed H <sub>7</sub> CDD solution by HPLC-LSC.	51
12.	Midsummer sunlight photolysis of P <sub>5</sub> CDD and H <sub>7</sub> CDD in filter-sterilized natural waters at 50°N latitude.	53
13.	Comparison of the observed rates of sunlight photolysis of P <sub>5</sub> CDD and H <sub>7</sub> CDD in natural waters at 50°N latitude with the predictions of Mill and Zepp.	60
14.	HPLC analysis of PNAP with 70% CH <sub>3</sub> OH as the mobile phase and PNT as the internal standard.	67
15.	Rates of sunlight photolysis of PNAP in 50 mL centrifuge tubes at the experimental site and under 4 cm of pond water.	68

16.	Distribution of carbon-14 activity as determined by HPLC-LSC for extracts of the photolyzed P <sub>5</sub> CDD solutions.	73
17.	Distribution of carbon-14 activity as determined by HPLC-LSC for extracts of the photolyzed H <sub>7</sub> CDD solutions.	74
18.	Clearance of P <sub>5</sub> CDD from the water column after application as a sediment slurry and a sprayover.	96
19.	Levels of P <sub>5</sub> CDD in surface films, of 100 $\mu$ m thickness, after application as a sediment slurry and a sprayover.	98
20.	P <sub>5</sub> CDD concentrations in air above ponds receiving a sediment slurry and a sprayover treatment, at both 5 and 10 cm above the water surface.	100
21.	Uptake of P <sub>5</sub> CDD by caged crayfish in the water column of ponds receiving a sediment slurry and a sprayover application of the dioxin.	102
22.	Uptake of P <sub>5</sub> CDD by caged fathead minnows in the water column for sediment slurry and sprayover applications.	105
23.	Accumulation of extractable P <sub>5</sub> CDD in bottom sediments of ponds receiving dioxin input as a sediment slurry stirred into the water column and as a sprayover in a water miscible organic solvent.	108
24.	Levels of P <sub>5</sub> CDD in benthic biota in ponds receiving the dioxin as a sediment slurry and a sprayover.	110
25.	QWASI model predictions fitted to observed levels of P <sub>5</sub> CDD in the water column, with model input entirely into the water compartment.	129
26.	QWASI model predictions fitted to observed levels of P <sub>5</sub> CDD in the sediment compartment with dioxin emission entirely into the water compartment.	130
27.	QWASI model predictions fitted to observed levels of P <sub>5</sub> CDD in the water column with initial input of dioxin evenly divided between the water and sediment compartments.	132
28.	QWASI model predictions fitted to observed levels of P <sub>5</sub> CDD in bottom sediments with half of the dioxin emitted into the water and half into the sediment compartments initially.	133

29. QWASFI model predictions fitted to observed levels of P<sub>5</sub>CDD in surface microlayers after sprayover application of the dioxin. 137
30. QWASFI model predictions fitted to observed levels of P<sub>5</sub>CDD in the water column after a sprayover sample application. 138
31. QWASFI model predictions fitted to observed levels of P<sub>5</sub>CDD in bottom sediments in ponds receiving a sprayover treatment of the dioxin in a water miscible organic solvent. 139

## LIST OF TABLES

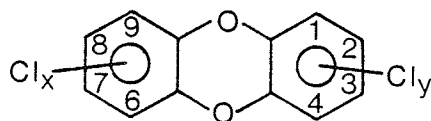
Table		Page
1.	Distribution of 75 polychlorinated dibenzo- <i>p</i> -dioxin isomers into congener groupings	2
2.	Toxicities and biological effects of several polychlorinated dibenzo- <i>p</i> -dioxins.	4
3.	Polychlorinated dioxin levels in various environmental and biological samples.	6
4.	Structures and physical constants of polychlorinated dibenzo- <i>p</i> -dioxins used in the solubility study.	10
5.	Water solubilities of four PCDD congeners at different temperatures.	20
6.	Enthalpies of solution of PCDD congeners.	22
7.	Importance of free energy, enthalpy, and entropy in the dissolution of PCDDs at 299 K.	26
8.	Aqueous solubility and structural parameters of several PCDD congeners at 299 K.	28
9.	Henry's law constants for two chlorinated dioxins at 23°C.	33
10.	Physical constants of 1,2,3,7-T <sub>4</sub> CDD and 1,2,3,4,7-P <sub>5</sub> CDD related to air-water partitioning.	37
11.	Photodegradation of two PCDD congeners during sunlight exposure in natural waters at 50°N latitude in mid-summer.	52
12.	Solar energy distribution and molar absorptivities of P <sub>5</sub> CDD and H <sub>7</sub> CDD in the solar region.	58
13.	Comparison of observed and predicted rates of aqueous photolysis of 1,2,3,4,7-P <sub>5</sub> CDD and 1,2,3,4,6,7,8-H <sub>7</sub> CDD.	59
14.	Comparison of observed and predicted first-order half-lives for the aqueous photolysis of P <sub>5</sub> CDD and H <sub>7</sub> CDD.	62
15.	Sunlight photolysis of the PNAP sunlight actinometer at 50°N latitude in midsummer.	66
16.	Molar absorptivities determined for 2.09 x 10 <sup>-5</sup> M PNAP in water (1% acetonitrile).	70

17.	Concentrations of P <sub>5</sub> CDD in the water column as a function of the method of introduction to the ecosystem.	92
18.	Cummulative 12 h air concentrations sampled at two heights above the water surface as a function of the method of P <sub>5</sub> CDD input.	99
19.	Determination of advective movement of P <sub>5</sub> CDD from air sampled near two ponds receiving different modes of chemical input.	101
20.	Total <sup>14</sup> C expressed as P <sub>5</sub> CDD concentrations in fathead minnows and crayfish as a function of the chemical input method.	106
21.	Fraction of nonextractable P <sub>5</sub> CDD and extent of polar degradation products in bottom sediments.	109
22.	Concentrations of P <sub>5</sub> CDD in surface microlayers relative to concentrations in the water column.	113
23.	Average sizes of the various compartments of the aquatic ecosystems.	118
24.	Recoveries of 1,2,3,4,7-P <sub>5</sub> CDD from the matrices used in the fate study.	119
25.	Mass balance for P <sub>5</sub> CDD distribution in the aquatic ecosystems as a function of the input mechanism.	120

## 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 (T<sub>4</sub>CDD), 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-T<sub>4</sub>CDD. 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-T<sub>4</sub>CDD 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-T<sub>4</sub>CDD into the environment. These incidents stimulated research into the toxicology, physico-chemical properties, and environmental behaviour of 2,3,7,8-T<sub>4</sub>CDD. 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-T<sub>4</sub>CDD.

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-T<sub>4</sub>CDD 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 T<sub>4</sub>CDD 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-T<sub>4</sub>CDD 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-T<sub>4</sub>CDD (8) and 2,3,7,8-T<sub>4</sub>CDD

(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-T<sub>4</sub>CDD 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 LD<sub>50</sub> value of 2 µg/kg has been reported for guinea pigs exposed to 2,3,7,8-T<sub>4</sub>CDD (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-T<sub>4</sub>CDD. Barnes, et al. (14) report toxicities of other congeners relative to 2,3,7,8-T<sub>4</sub>CDD 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-T<sub>4</sub>CDD and as high as 3 g/kg body weight/day for 1,3,6,8-T<sub>4</sub>CDD 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 <sub>50</sub> (μg/kg) guinea pig	AHH Activity <sup>a</sup> in Rat Hepatoma Cells	TEF <sup>b</sup>	NOEL <sup>c</sup>
2,3,7,8-T <sub>4</sub> CDD	0.6-2	1.0	1.0	0.03-0.125
1,2,3,7-T <sub>4</sub> CDD	>2000 <sup>d</sup>	--	--	--
1,2,3,4,7-P <sub>5</sub> CDD	>1000 <sup>d</sup>	0.048-0.0076	--	--
1,2,3,7,8-P <sub>5</sub> CDD	3.1	0.2-0.019	0.2	--
1,2,3,4,7,8-H <sub>6</sub> CDD	72.5	0.1-0.05	0.04	0.1 <sup>e</sup>
1,2,3,4,6,7,8-H <sub>7</sub> CDD	>600	0.0035-0.0027	0.001	--
O <sub>8</sub> CDD	--	0.000019	0	500,000

<sup>a</sup>Aryl hydrocarbon hydroxylase activity expressed relative to the enzyme activity in 2,3,7,8-T<sub>4</sub>CDD (13).

<sup>b</sup>Toxic Equivalence Factor expressing the toxicity of PCDDs relative to 2,3,7,8-T<sub>4</sub>CDD (14).

<sup>c</sup>Reproductive no-observed-effect-level for rats expressed in μg/kg body weight/day (13).

<sup>d</sup>Estimated single dose oral LD<sub>50</sub> from data in Barnes, et al. (14) for non-2,3,7,8-substituted PCDDs.

<sup>e</sup>Unspecified 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 O<sub>8</sub>CDD 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 T<sub>4</sub>CDDs, P<sub>5</sub>CDDs, H<sub>6</sub>CDDs, H<sub>7</sub>CDDs, and O<sub>8</sub>CDD 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 O<sub>8</sub>CDD > H<sub>7</sub>CDDs > H<sub>6</sub>CDDs > P<sub>5</sub>CDDs > T<sub>4</sub>CDDs. 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-P<sub>5</sub>CDD and 1,2,3,6,7,9/1,2,3,6,8,9-H<sub>6</sub>CDDs 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) <sup>a</sup>	Human Milk (ppt) <sup>b</sup>	Sediments (ppt) <sup>c</sup>	Air (ppb) <sup>d</sup>	Municipal Incinerator (ppb) <sup>e</sup>
T <sub>4</sub> CDDs	7.4	0.6	26	0.5	90
P <sub>5</sub> CDDs	10	6.5	12	6.4	220
H <sub>6</sub> CDDs	61	27.8	10	1.6	370
H <sub>7</sub> CDDs	110	59.5	70	21.2	280
O <sub>8</sub> CDD	430	302	560	200	119

<sup>a</sup>2,3,7,8-substituted PCDDs found in human autopsy abdominal fat sample reported in pg/g wet tissue weight (16).

<sup>b</sup>Levels of PCDDs, all 2,3,7,8-substituted, reported on fat weight basis (22).

<sup>c</sup>Total PCDDs in surficial sediments in Siskiwit Lake (23).

<sup>d</sup>Total PCDDs in air particulate samples collected in Washington, DC (23).

<sup>e</sup>Estimated 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-T<sub>4</sub>CDD. 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-P<sub>5</sub>CDD 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-P<sub>5</sub>CDD, 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