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## Environmental Photochemistry of PCDDs. 2.<sup>1</sup> Quantum Yields of the Direct Phototransformation of 1,2,3,7-Tetra-, 1,3,6,8-Tetra-, 1,2,3,4,6,7,8-Hepta-, and 1,2,3,4,6,7,8,9-Octachlorodibenzo-*p*-dioxin in Aqueous Acetonitrile and Their Sunlight Half-Lives<sup>2</sup>

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Photochemistry of four polychlorodibenzo-*p*-dioxins (PCDDs), namely 1,2,3,7-tetrachlorodibenzo-*p*-dioxin (1,2,3,7-T<sub>4</sub>CDD), 1,3,6,8-T<sub>4</sub>CDD, 1,2,3,4,6,7,8-H<sub>7</sub>CDD, and 1,2,3,4,6,7,8,9-O<sub>8</sub>CDD, in water-acetonitrile (2:3, v/v) was investigated at 313 nm; the quantum yields for the direct phototransformation of the candidate PCDD isomers in these solvent systems were  $(5.42 \pm 0.42) \times 10^{-4}$ ,  $(2.17 \pm 0.14) \times 10^{-3}$ ,  $(1.53 \pm 0.17) \times 10^{-5}$ , and  $(2.26 \pm 0.33) \times 10^{-5}$ , respectively. These quantum yields and the measured absorption spectra together with solar intensity data available in the literature were utilized to estimate the direct sunlight (environmental) phototransformation first-order rate constants of these PCDD congeners in water under conditions of variable sunlight intensity during various seasons; the corresponding half-lives were also determined. In summer, typical midday, midseason half-lives for the direct phototransformation of 1,2,3,7-T<sub>4</sub>CDD, 1,3,6,8-T<sub>4</sub>CDD, 1,2,3,4,6,7,8-H<sub>7</sub>CDD, and O<sub>8</sub>CDD near the surface of water bodies at 40° north latitude would be  $1.8 \pm 0.1$ ,  $0.31 \pm 0.02$ ,  $47 \pm 5$ , and  $18 \pm 3$  days, respectively, time being expressed in terms of 24-h day. Furthermore, the experimentally determined sunlight photolysis half-life of <sup>14</sup>C-labeled 1,3,6,8-T<sub>4</sub>CDD in pond water was 3.5 days.

The contamination of our environment by polychlorinated dibenzo-*p*-dioxins (PCDDs) is well-known. There are 75 isomers of PCDDs; some of these tricyclic aromatic pollutants have remarkably high toxicity, teratogenicity, mutagenicity, and acnegenicity (Buser, 1976; Dobbs and Grant, 1979). For example, the LD<sub>50</sub> for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-T<sub>4</sub>CDD) (3) (structures of this dioxin along with others are described in Figure 1) in female rats is 45 μg/kg, while that of the octachloro isomer, viz., 1,2,3,4,6,7,8,9-O<sub>8</sub>CDD (7), is >10<sup>6</sup> μg/kg.

In addition to a large number of other organics, several isomers of PCDDs have recently been detected in the flue

gas and fly ash emitted by some municipal and industrial incinerators located in Canada, Japan, Switzerland, and The Netherlands (references cited in Choudhry and Hutzinger (1982, 1983) and Choudhry et al. (1982)). Furthermore, commercial 2,3,5-tri-, 2,4,6-tri-, and pentachlorophenol have been shown to contain 2,7-dichlorodibenzo-*p*-dioxin (2,7-D<sub>2</sub>CDD) and 1,3,6,8-T<sub>4</sub>CDD (2) together with H<sub>6</sub>CDDs, H<sub>7</sub>CDDs, and O<sub>8</sub>CDD (7) (ppm) in spite of improved manufacturing techniques (Jones, 1981). Technical (2,4-dichlorophenoxy)acetic acid (2,4-D) herbicide products have been reported to contain 2,7-D<sub>2</sub>CDD and 1,3,6,8-T<sub>4</sub>CDD (2) amounting to 1.8-8.7 ppm (Cochrane et al., 1982). Likewise, a mean of more than 1.9 and a maximum of 47 ppm of 2,3,7,8-T<sub>4</sub>CDD (3) were identified in the military defoliant Agent Orange (butyl esters of 2,4-D and (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) in equal amounts) (Choudhry and Hutzinger, 1982).

Webster and co-workers (1985) published that the solubilities of 1,3,6,8-T<sub>4</sub>CDD (1) in triple-distilled water were  $3.2 \times 10^{-7}$  and  $3.9 \times 10^{-7}$  g/L at 20.0 and 40.0 °C, respectively, whereas such data in the case of O<sub>8</sub>CDD (7)

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<sup>1</sup> Part 1: Choudhry and Webster (1985b).

<sup>2</sup> Partly presented at the Fourth International Symposium on Chlorinated Dioxins and Related Compounds, Ottawa, Canada, Oct 16-18, 1984.

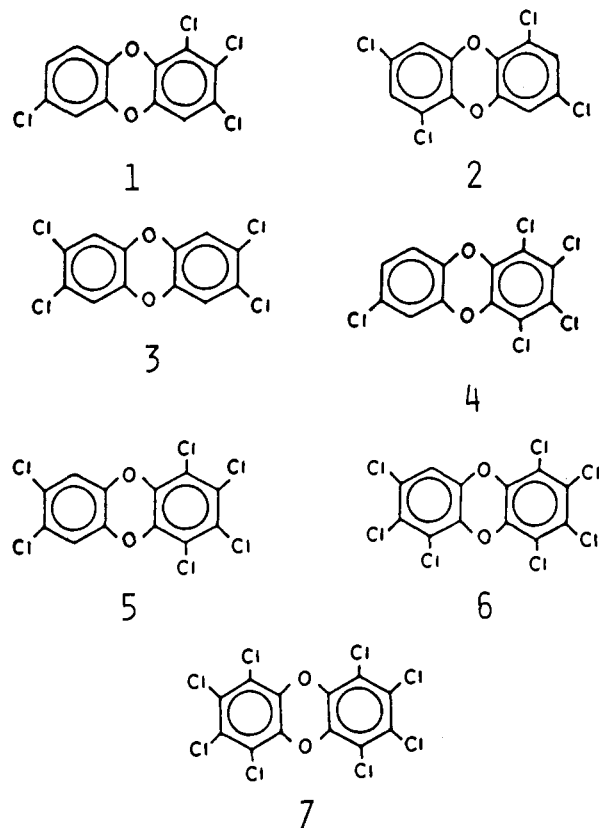


Figure 1. Structures of some tetra- through octachlorodibenzo-*p*-dioxins.

amounted to  $0.4 \times 10^{-9}$  and  $2.0 \times 10^{-9}$  g/L at 20.0 and 40.0 °C, respectively. Very recently, Doucette and Andren (1988) have also reported the solubility of dibenzo-*p*-dioxin, 2-chlorodibenzo-*p*-dioxin, and 1,2,3,4-*T*<sub>4</sub>CDD in Milli Q water amounting to  $(4.89 \pm 0.0151) \times 10^{-6}$ ,  $(1.46 \pm 0.052) \times 10^{-6}$ , and  $(1.46 \pm 0.065) \times 10^{-9}$  mol·L<sup>-1</sup> at 25 °C, respectively, whereas such solubility of O<sub>8</sub>CDD (7) at 40 °C is  $(6.75 \pm 2.61) \times 10^{-13}$  mol·L<sup>-1</sup>. These data apparently suggest that it is unlikely that in the environment PCDD congeners really exist as aqueous solutions. However, it should be pointed out that widespread occurrence of dissolved humic substances (HSs) in the natural water bodies is well-known, and these HSs have ability to solubilize the chlorinated aromatic pollutants (CAPs) present in the aquatic systems (Choudhry 1984, 1982). Furthermore, experience in our own laboratory (Servos, 1988; Friesen, 1988) gained during the determination of environmental fate of some isomers of PCDDs in the outdoor ponds as well as those of Boddington et al. (1983) and Swackhamer and Armstrong (1986) concerning Great Lakes in Canada clearly reflects that CAPs occur in polluted water bodies to some extent in dissolved form, thereby demanding that the determination of the photochemical fate of CAPs, viz., PCDDs, as aqueous solution is of utmost importance.

Photochemical degradation may be an important process affecting atmospheric contaminants and chemicals that reside on surfaces (pesticides on leaves and vegetation) or in water bodies. A chemical present in our environment can undergo direct phototransformation and/or indirect phototransformation. The latter environmental fate may include processes such as photosensitized degradation and oxygenation as well as photoinduced degradation (Choudhry and Webster, 1985a). Although a good deal of research work on the photochemical fate of PCDDs, both in solution and in solid phase has appeared (Choudhry and Hutzinger, 1982; Corbet et al., 1983); to the best of our

Table I. Light Absorption Spectra<sup>a</sup> of Polychlorinated Dibenz-*p*-dioxins (PCDDs)<sup>b</sup>

λ, nm	ε <sub>λ</sub> , L·mol <sup>-1</sup> ·cm <sup>-1</sup>			
	1,2,3,7- T <sub>4</sub> CDD (1) <sup>c</sup>	1,3,6,8- T <sub>4</sub> CDD (2) <sup>d</sup>	1,2,3,4,6,7,8- H <sub>7</sub> CDD (6) <sup>e</sup>	O <sub>8</sub> CDD (7) <sup>f</sup>
254.0	2089	2288	23020	44068
297.5	2900	3747	3597	5307
300.0	3027	3880	3597	4986
302.5	3115	3913	3957	4825
305.0	3125	3880	3957	4664
307.5	3066	3781	3957	4342
310.0	2920	3250	4316	4182
312.5	2753	2520	4316	4182
313.0	2714	2255	4316	4182
315.0	2519	1658	4316	4021
317.5	2128	1194	4316	4021
320.0	1621	796	3237	3860
323.1	1035	663	2158	3217
330.0	332	531	360	965
340.0	127	464	0	483
350.0	97	332	0	322
360.0	78	299	0	322
370.0	58	265	0	161
380.0	19	66	0	161
390.0	19	33	0	0
400.0	0	0	0	0

<sup>a</sup>Data for PCDD (6) were recorded on the solutions of the pollutant in H<sub>2</sub>O-CH<sub>3</sub>CN (2:3, v/v), while in the case of 1, 2, and 7 the solvent was neat CH<sub>3</sub>CN. <sup>b</sup>Structures of the dioxins are given in Figure 1. <sup>c</sup>Concentration of dioxin 1 was  $2.560 \times 10^{-4}$  M. <sup>d</sup>Concentration of dioxin 2 was  $7.539 \times 10^{-6}$  M. <sup>e</sup>Concentration of dioxin 6 was 2.780 μM. <sup>f</sup>Concentration of dioxin 7 was 6.218 μM.

knowledge no investigator has reported the quantum yield ( $\phi$ ) for the photolysis of these environmental pollutants. However, we have recently reported the kinetics and quantum yields for the direct phototransformation ( $\phi_{tr,\lambda}$ ) of two individual dioxin isomers, namely 1,2,3,4,7-*P*<sub>5</sub>CDD (4) and 1,2,3,4,7,8-*H*<sub>6</sub>CDD (5) in water-acetonitrile (2:3, v/v) at wavelength (λ) 313 nm determined (Choudhry and Webster, 1985b) through the utilization of the photolytic test methods and protocol guidelines applicable for the investigation of photochemical fate of pesticides occurring in water, air, and soils proposed by Choudhry and Webster (1985a) for Environment Canada, Ottawa. Furthermore, very recently, Dulin and his associates (1986) have published  $\phi_{tr,\lambda}$  values of 2,3,7,8-*T*<sub>4</sub>CDD (3) dissolved in aqueous acetonitrile (1:1) at 313 nm.

In view of our continuing interest in the photochemical fate of chlorinated aromatic pollutants present in the environment (see Choudhry et al. (1987) and preceding publications), we decided to further investigate the environmental solution-phase photochemistry of some model isomers of PCDDs, viz., 1,2,3,7-*T*<sub>4</sub>CDD (1), 1,3,6,8-*T*<sub>4</sub>CDD (2), 1,2,3,4,6,7,8-*H*<sub>7</sub>CDD (6), and O<sub>8</sub>CDD (7) using our previously reported methodology (Choudhry and Webster 1985b). This paper presents the values of laboratory  $\phi_{tr,\lambda}$  at 313 nm and the estimated sunlight photolysis half-lives ( $(t_{1/2})_{sp}$ ) of nonlabeled PCDDs 1, 2, 6, and 7 along with experimentally determined absolute natural sunlight photolysis first-order rate constant and the corresponding half-life of the <sup>14</sup>C-labeled *T*<sub>4</sub>CDD (2) (<sup>14</sup>C]-2) in auto-claved pond water.

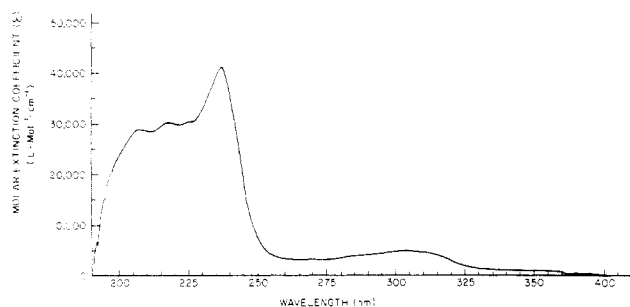
#### EXPERIMENTAL SECTION

**Substrates and Solvents.** In the cases of indoor photolytic experiments, sources of the substrates, viz., nonlabeled PCDDs 1, 2, 6, and 7 in crystalline form (see Figure 1 and Table I), *o*-nitrobenzaldehyde, *o*-nitrosobenzoic acid, *p*-nitrotoluene, and 1,2,3,4-tetrachlorobenzene, and solvents were the same as previously reported (Choudhry and

**Table II. Photolysis of Nonlabeled Polychlorinated Dibenzo-*p*-dioxins (PCDDs)<sup>a</sup> in Water-Acetonitrile (2:3, v/v)<sup>b</sup> at 313 nm**

no.	substrate	init concn, starting dioxin ( $P_0$ ), $10^{-6}$ M	$t_{\max}$ , h	disappearance of starting dioxin after $t_{\max}$ , %	$k_{p,\lambda}$ , $10^{-6}$ s $^{-1}$	$t_{1/2}$ , <sup>c</sup> h	$\phi_{tr,\lambda}$ <sup>d</sup>
1	1,2,3,7-T <sub>4</sub> CDD <sup>e</sup>	6.40	8	39.5	18.13 ± 1.40	10.69 ± 0.83	(5.42 ± 0.42) × 10 <sup>-4</sup>
2	1,3,6,8-T <sub>4</sub> CDD <sup>e</sup>	10.55	4	57.1	59.57 ± 2.81	3.24 ± 0.15	(2.17 ± 0.14) × 10 <sup>-3</sup>
3	2,3,7,8-T <sub>4</sub> CDD <sup>f</sup>	0.361	24	62.0			2.2 × 10 <sup>-3</sup>
4	1,2,3,4,7-P <sub>5</sub> CDD <sup>g</sup>	2.81	72	71.2	4.31 ± 0.70	45.86 ± 7.42	(9.78 ± 2.38) × 10 <sup>-5</sup>
5	1,2,3,4,7,8-H <sub>6</sub> CDD <sup>g</sup>	3.33	72	87.2	7.86 ± 0.03	24.50 ± 0.10	(1.10 ± 0.02) × 10 <sup>-4</sup>
6	1,2,3,4,6,7,8-H <sub>7</sub> CDD <sup>e</sup>	2.78	72	39.1	1.02 ± 0.11	190.97 ± 20.25	(1.53 ± 0.17) × 10 <sup>-5</sup>
7	O <sub>8</sub> CDD <sup>e</sup>	0.31	112	52.9	1.06 ± 0.14	183.95 ± 23.85	(2.26 ± 0.33) × 10 <sup>-5</sup>

<sup>a</sup> For structures of PCDDs, see Figure 1. <sup>b</sup> In the case of T<sub>4</sub>CDD (3), the H<sub>2</sub>O to CH<sub>3</sub>CN ratio used was 1:1. <sup>c</sup> Calculated from the following relationship:  $t_{1/2} = \ln 2/k_{p,\lambda}$ . <sup>d</sup> Equation 2 was used. <sup>e</sup> Data from present work. <sup>f</sup> Data from Dulin et al. (1986). In this case, the CH<sub>3</sub>CN to H<sub>2</sub>O ratio was 1:1. <sup>g</sup> Data from Choudhry and Webster (1985b).



**Figure 2.** Plot of the light absorption spectrum of a  $3.200 \times 10^{-5}$  M solution of 1,2,3,7-T<sub>4</sub>CDD (1) in CH<sub>3</sub>CN. (Quartz cell path length was 1.0 cm.)

Webster, 1985b). No impurity was observable, when solutions of PCDDs were injected onto the HPLC instrumentation (see below).

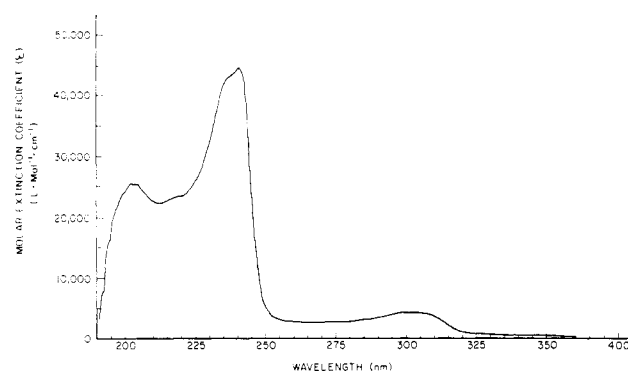
For outdoor photolyses, universally labeled [<sup>14</sup>C]-1,3,6,8-tetrachlorodibenzo-*p*-dioxin ([<sup>14</sup>C]-1,3,6,8-T<sub>4</sub>CDD) ([<sup>14</sup>C]-2) was purchased from New England Nuclear Ltd. (sp act. 14.8 mCi/mM). The purity of [<sup>14</sup>C]-2 claimed by the manufacturer was 97%. Two contaminants accounting for 3.8% of the label were seen on HPLC. The water used for these sunlight photolyses was obtained from the experimental ponds present at the University of Manitoba agriculture field station at Glenlea, Manitoba, located 20 km south of Winnipeg on Highway 75. The pond water was drawn through a preextracted glass fiber (0.45 μm) Whatman filter and was then autoclaved.

**Reagents.** Reagents such as sodium sulfate (anhydrous, granular) was purchased from Fischer Scientific Co., whereas both scintillation fluors, namely PCS cocktail and Atomlight, were obtained from Amersham Radiochemical and New England Nuclear, respectively.

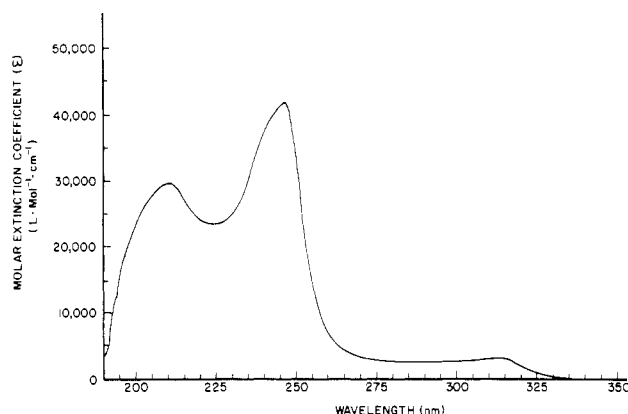
**Preparation of Solutions of PCDDs in Water-Acetonitrile (2:3, v/v).** Techniques for the preparation of the solution of 1,2,3,4,7,8-H<sub>6</sub>CDD (5) in water-acetonitrile (2:3, v/v) reported by Choudhry and Webster (1985b) were followed to prepare similar solutions of dioxins 1, 2, 6, and 7. For these investigations, the concentration of T<sub>4</sub>CDD (1), T<sub>4</sub>CDD (2), H<sub>7</sub>CDD (6), and O<sub>8</sub>CDD (7) were 6.40, 10.55, 2.78, and 0.31 μM, respectively (Table II).

**Preparation of Samples of [<sup>14</sup>C]-1,3,6,8-T<sub>4</sub>CDD ([<sup>14</sup>C]-2) in Pond Water.** A 1-L portion of autoclaved pond water (described above) was added to each of a series of 13 Pyrex glass 1-L Erlenmeyer flasks. One milliliter of [<sup>14</sup>C]-2 dissolved in benzene-acetone (1:1, v/v) was then injected into each flask, the application level of [<sup>14</sup>C]-2 being 4.992 nM (164, 255 dpm) for each sample.

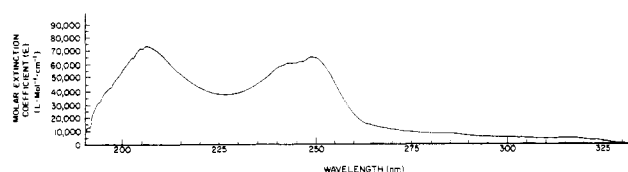
**UV Absorption Spectroscopy.** UV absorption spectral data for PCDDs 1 and 2 as well as those of PCDDs 6 and 7 were obtained with a Unicam spectrophotometer and single-beam Bausch and Lomb Spectronic 710 spec-



**Figure 3.** Plot of the light absorption spectrum of  $3.770 \times 10^{-5}$  M solution of 1,3,6,8-T<sub>4</sub>CDD (2) in CH<sub>3</sub>CN. (Quartz cell path length was 1.0 cm.)



**Figure 4.** Plot of the light absorption spectrum of  $3.627 \times 10^{-5}$  M solution of 1,2,3,4,6,7,8-H<sub>7</sub>CDD (6) in CH<sub>3</sub>CN. (Quartz cell path length was 1.0 cm.)



**Figure 5.** Plot of the light absorption spectrum of  $6.218 \times 10^{-6}$  M solution of O<sub>8</sub>CDD (7) in CH<sub>3</sub>CN. (Quartz cell path length was 1.0 cm.)

trometer, respectively. The spectra of 1, 2, 6, and 7 shown in Figures 2–5, respectively, were recorded on the former instrument.

**Indoor Irradiation Equipment and Experiments.** The previously described Rayonet photochemical reactor equipped with a merry-go-round apparatus was used for the laboratory photolyses of solutions of nonlabeled PCDD candidates and the chemical actinometer (Choudhry et al., 1982, 1983, 1985, 1986a). The Pyrex photoreaction cell

**Table III. Sunlight Photodegradation of [<sup>14</sup>C]-1,3,6,8-Tetrachlorodibenzo-*p*-dioxin (3) in Autoclaved Pond Water<sup>a</sup>**

termination <sup>b</sup> of photolytic expt	photolysis time in terms of duration of bright sunshine <sup>c</sup> (t), h	P <sub>t</sub> (3), nM	ln (P <sub>0</sub> /P <sub>t</sub> ) <sup>d</sup>
25 h	7.6	4.957	0.0070
48 h	15.1	3.949	0.2344
60 h	20.0	3.734	0.2904
72 h	23.0	3.760	0.2834
84 h	25.8	2.570	0.6639
97 h	30.4	3.777	0.2789
5 days	41.4	3.562	0.3375
7 days	66.0	2.704	0.6131
10 days	94.4	1.504	1.1997
14 days	125.9	1.941	0.9446
28 days	266.0	1.732	1.0586

<sup>a</sup> Water filtered through a preextracted glass fiber (0.45 μm) Whatman filter was used. <sup>b</sup> Experiments were started on 14th of July, 1982, at 9 a.m. at the University of Manitoba Agriculture field station at Glenlea, Manitoba. <sup>c</sup> Data obtained through Dr. R. Parker (Director of the Glenlea Research Station) from Environment Canada. <sup>d</sup> P<sub>0</sub> = 4.992 nM.

(path length  $l = 1$  cm) and chemical filter solution (consisting of K<sub>2</sub>CrO<sub>4</sub> (0.270 g/L) and Na<sub>2</sub>CO<sub>3</sub> (1.000 g/L) in water) used for filtering out radiations around 313 nm from the Rayonet RPR 3000-Å lamps have been described elsewhere (Choudhry and Webster, 1985b). The chemical filter solution transmitted 47% of the incidental light (cell path length being 1 cm) at 313 nm, while the light transmissions at various wavelengths around 313 nm, e.g., at 296, 300, 305, 310, 320, 325, 330, 335, and 339 nm, were 3.4, 16.4, 57.4, 91.5, 97.9, 78.7, 51.1, 22.3, 8.1, and 3.4% relative to that at 313 nm, respectively. Optically thick solutions of *o*-nitrobenzaldehyde (10 mM) in acetonitrile were utilized as a chemical actinometer for the determination of the intensity ( $I_\lambda$ ) of the filtered incident light (Choudhry and Webster 1985a,b; Dulin and Mill, 1982). For this purpose, the concentration of the photoproduct *o*-nitrosobenzoic acid arising from the actinometer was monitored (Choudhry and Webster, 1985b). In the case of laboratory photochemical experiments on PCDDs 1, 2, 6, and 7 in solution phase, the measured values of  $I_\lambda$  were  $5.35 \pm 0.10$ ,  $5.29 \pm 0.13$ ,  $6.72 \pm 0.10$ , and  $4.92 \pm 0.33$  μeinstein·L<sup>-1</sup>·s<sup>-1</sup>, respectively.

**Outdoor Sunlight Exposures.** Eleven Pyrex Erlenmeyer flasks containing each 1.00 L of 4.99 nM dioxin [<sup>14</sup>C]-2 in autoclaved pond water were exposed to natural sunlight at Glenlea Research Station (described above). Two such sample flasks coated with a double layer of reflective aluminum foil were also placed in the sunlight in order to account for any reaction of the candidate substrate in dark. Individual photoreaction flasks were then sampled over at 28-day period at times recorded in the first column of Table III. The flasks were preserved in the field with 40 mL of dichloromethane (DCM) and were returned to the laboratory for immediate extraction (described below).

**Extraction Procedures.** The laboratory photolysates of the nonlabeled dioxins were not subjected to any extraction procedures. In the case of candidate [<sup>14</sup>C]-2, both photolyzed and unphotolyzed samples in pond water were extracted three times with 200, 100, and 100 mL of DCM, the range of pH of the samples prior to extraction being 8.9–9.6. The DCM extracts of [<sup>14</sup>C]-2 were passed through 20 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> and were subsequently concentrated by rotoevaporation to 5 mL in chloroform.

**Analyses.** In the case of nonlabeled PCDDs 1, 2, 6, and 7, all analyses were carried out by HPLC on a Waters Scientific liquid chromatograph (Model 6000A pump, U6K

injector, and an M440 UV absorbance detector). Separations were made with a 30 cm × 3.9 mm μBondapak C<sub>18</sub> column (reversed phase, RP) (Choudhry and Webster, 1985b). The analyses of the sample solution of T<sub>4</sub>CDDs 1 and 2 together with those of O<sub>8</sub>CDD 7 were carried out by this RP-HPLC using methanol as eluant, whereas in the case of H<sub>7</sub>CDD 6, the eluant was CH<sub>3</sub>OH–H<sub>2</sub>O (19:1, v/v). The flow rate of the eluants was 1.0 mL min<sup>-1</sup> for the analysis of each dioxin. Forty microlitres of 1,2,3,4,6,7,8-H<sub>7</sub>CDD (6) ( $7.255 \times 10^{-5}$  M) in CH<sub>3</sub>CN was added to each sample (2 mL) solution of the candidate dioxins 1 and 2 as an internal standard prior to analysis, while in the cases of 6 and 7, 20 μL of *p*-nitrotoluene (2.055 mM) and 90 μL of 1,2,3,4-tetrachlorobenzene (0.757 mM), both in CH<sub>3</sub>CN, were added, respectively, to each 2.0-mL sample solution as internal standard. Analytical procedures for actinometry have been described elsewhere (Choudhry and Webster, 1985b).

When a 60-μL aliquot of the DCM extracts (subsequently rotoevaporated to 5 mL of CHCl<sub>3</sub>) (see above) of the sunlight photolysates of [<sup>14</sup>C]-2 were injected onto the above-mentioned HPLC instrumentation (eluant being CHCl<sub>3</sub>–CH<sub>3</sub>OH, 7:93, v/v), no compound other than the starting dioxin was seen. The quantification of the photolyzed [<sup>14</sup>C]-2 was therefore done with LSC (liquid scintillation counting) technique; 100-μL aliquots of the concentrated DCM extracts of the <sup>14</sup>C-labeled dioxin 2 were utilized. The DCM extracts of the flasks stored in the dark were also analyzed by this LSC technique for the quantification of [<sup>14</sup>C]-2.

## RESULTS

### UV Light Absorbing Characteristics of PCDDs.

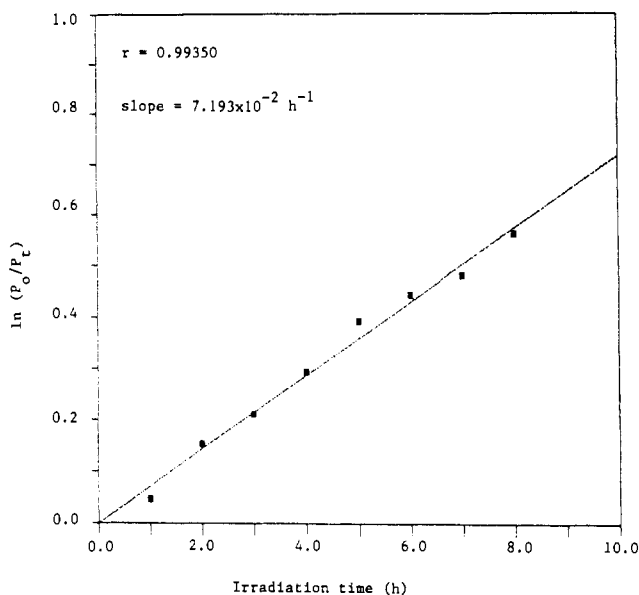
Figures 2–5 indicate UV spectra of the acetonitrile solutions of 1,2,3,7-T<sub>4</sub>CDD (1), 1,3,6,8-T<sub>4</sub>CDD (2), 1,2,3,4,6,7,8-H<sub>7</sub>CDD (6), and O<sub>8</sub>CDD (7). Table I records the molar extinction coefficient ( $\epsilon_\lambda$ ) at various wavelengths ( $\lambda$ ), of solutions of PCDDs 1, 2, 6, and 7. Water–acetonitrile (2:3, v/v) was used as a solvent of 6, whereas, in the case of dioxins 1, 2, and 7, the solvent was neat acetonitrile. These spectral data were used in the prediction of the direct sunlight photolysis rates, i.e.,  $k_{sp}$  and corresponding half-lives, ( $t_{1/2}$ )<sub>sp</sub>, of PCDDs 1, 2, 6, and 7 in aquatic environments (see below).

**Laboratory Photolysis First-Order Kinetics of Nonlabeled PCDDs at 313 nm.** Typical first-order plots (eq 1) of the photolysis data for dilute solutions (absorbance being <0.02 at 313 nm) of two individual congeners of nonlabeled PCDDs, namely 1,2,3,7-T<sub>4</sub>CDD (1) (6.40 μM) and 1,3,6,8-T<sub>4</sub>CDD (2) (10.55 μM) are shown in Figures 6 and 7. In eq 1, P<sub>0</sub> and P<sub>t</sub> are the concentrations of a

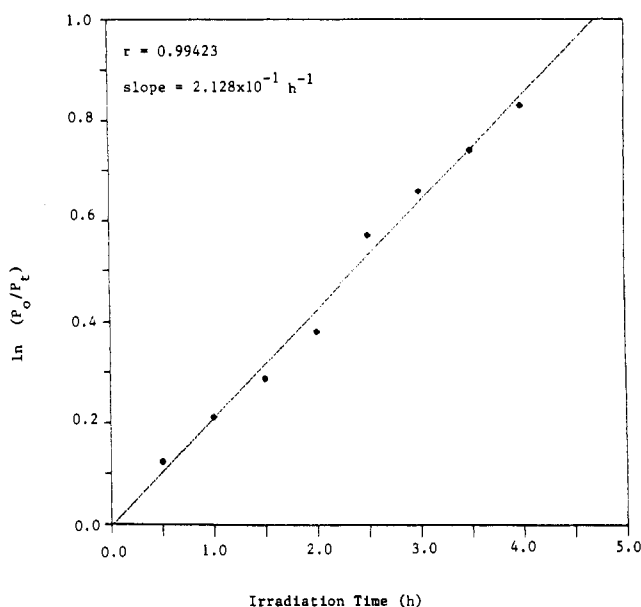
$$\ln (P_0/P_t) = k_{p,\lambda}t \quad (1)$$

PCDD congener at times zero and  $t$ , while  $k_{p,\lambda}$  is the photolysis first-order rate constant of the pollutant at a wavelength  $\lambda$ , e.g. 313 nm. The plots in Figures 6 and 7 were drawn by standard linear regression (Energraphics). The slopes of these plots provided the values of  $k_{p,\lambda}$  (expressed in reciprocal hours). Similar treatments of the additional photolyses data for all the investigated PCDDs 1, 2, 6, and 7 were carried out. Table II includes  $k_{p,\lambda}$  values expressed in reciprocal seconds for dioxins 1, 2, 6, and 7 determined in this fashion. This table also includes the  $k_{p,\lambda}$  data and other corresponding photolytic data for 1,2,3,4,7-P<sub>5</sub>CDD (4) and 1,2,3,4,7,8-H<sub>6</sub>CDD (5) for comparison purposes, which were previously reported by Choudhry and Webster (1985b).

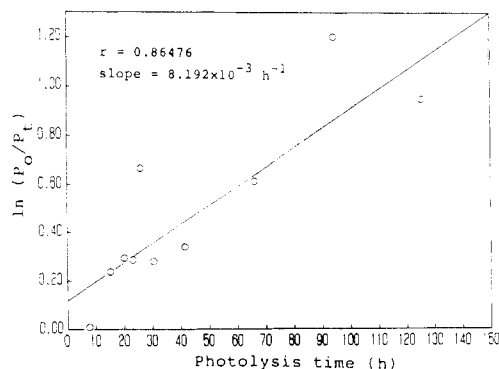
**Sunlight Photolysis First-Order Kinetics of [<sup>14</sup>C]-1,3,6,8-T<sub>4</sub>CDD ([<sup>14</sup>C]-2) in Pond Water.** Concen-



**Figure 6.** First-order plot (eq 1) of the photolysis data for 1,2,3,7-T<sub>4</sub>CDD (1) in water-acetonitrile (2:3, v/v) at 313 nm.



**Figure 7.** First-order plot (eq 1) of the photolysis data for 1,3,6,8-T<sub>4</sub>CDD (2) in water-acetonitrile (2:3, v/v) at 313 nm.



**Figure 8.** First-order plot (eq 1) of the sunlight photolysis data for [<sup>14</sup>C]-1,3,6,8-T<sub>4</sub>CDD (2) in autoclaved pond water (see the Experimental Section).

trations of the remaining starting material are recorded in column 3 of Table III, when the sunlight exposures of 4.99 μM <sup>14</sup>C-labeled PCDD 2 in autoclaved pond water

during the summer are terminated after 25, 48, 60, 72, 84, 97, 120, 168, 240, 336, and 672 h (shown in column 1). In Table III, columns 2 and 4 indicate the corresponding photolytic data concerning duration of bright sunshine (see also the pertaining footnote c) and  $\ln(P_0/P_t)$ , respectively. When photolysis times ( $t$ ) expressed in terms of bright sunshine hours versus  $\ln(P_0/P_t)$  (cf. eq 1) are plotted in the fashion described above in the case of dioxins 1, 2, 6, and 7, a straight line is obtained (Figure 1). The slope of this plot provides the sunlight photolysis first-order rate constant,  $k_p$ , amounting to  $8.19 \times 10^{-3} \text{ h}^{-1}$  for the candidate pollutant, [<sup>14</sup>C]-2. The absolute half-life ( $t_{1/2}$ ) for the sunlight phototransformation of dioxin [<sup>14</sup>C]-2 determined utilizing this value of  $k_p$  (see also footnote c, Table II) is 3.5 days.

**Photochemical Quantum Yields of Nonlabeled PCDDs at 313 nm.** The values of  $\epsilon_{313}$  (Table I),  $k_{p,\lambda}$  (Table II), and intensity of incident light at  $\lambda = 313 \text{ nm}$  ( $I_\lambda$ ) measured with the aid of simultaneous photolysis of the actinometer solution (Choudhry and Webster, 1985b) enabled the quantum yields ( $\phi_{tr,\lambda}$ ) to be determined at 313 nm for the phototransformation reactions of nonlabeled PCDDs from eq 2 (Choudhry and Webster, 1985a,b;

$$\phi_{tr,\lambda} = k_{p,\lambda} / 2.303 I_\lambda \epsilon_\lambda l \quad (2)$$

Choudhry, 1984, 1983; Zepp, 1982; Mill et al., 1981), where  $l$  (cell path length) = 1.00 cm. Table II indicates that the values of  $\phi_{tr,\lambda}$  for T<sub>4</sub>CDD (1), T<sub>4</sub>CDD (2), H<sub>7</sub>CDD (6), and O<sub>8</sub>CDD (7) determined in this manner are  $(5.42 \pm 0.42) \times 10^{-4}$ ,  $(2.17 \pm 0.14) \times 10^{-3}$ ,  $(1.53 \pm 0.17) \times 10^{-5}$ , and  $(2.26 \pm 0.33) \times 10^{-5}$ , respectively. Values of  $\phi_{tr,\lambda}$  amounting to  $(9.78 \pm 2.38) \times 10^{-5}$  and  $(1.10 \pm 0.02) \times 10^{-4}$  for 1,2,3,4,7-P<sub>5</sub>CDD (4) and 1,2,3,4,7,8-H<sub>6</sub>CDD (5) in H<sub>2</sub>O-C-H<sub>3</sub>CN (2:3, v/v) reproduced from Choudhry and Webster (1985b) and the value of  $2.2 \times 10^{-3}$  for 2,3,7,8-T<sub>4</sub>CDD (3) in H<sub>2</sub>O-CH<sub>3</sub>CN (1:1) (Dulin et al., 1986) are also documented in Table II. It should be noted that, in order to eliminate the introduction of a possible systematic error due to the probability of  $l$  being >1 cm, and to avoid the reflection and refraction errors at the front and back of the photoreaction cells during the determination of the  $\phi_{tr,\lambda}$  (recorded in Table II), the observed values of  $P_t$  (see eq 1) and those of the concentrations of the photoproduct *o*-nitrosobenzoic acid of the actinometer (which were subsequently utilized for the determination of  $I_\lambda$ ) were corrected with the aid of correction factors for each photochemical cell [for further details, see Choudhry and Webster (1985a,b)].

**Computation of Sunlight Photolysis Rate Constants and Half-Lives of PCDDs.** In estimating the first-order sunlight (environmental) photoconversion rate constants ( $k_{sp}$ ) of these environmental contaminants, the following relationship can be utilized (eq 3) (Choudhry and Webster, 1985a,b; Choudhry, 1982-1984; Mill et al., 1981; Zepp, 1982; Zepp and Cline, 1977; Wolf et al., 1976). In eq 3,  $k_a$  ( $=\sum k_{a,\lambda}$ ) is the sunlight absorption rate summed

$$k_{sp} = \phi_{tr,\lambda} k_a = \phi_{tr,\lambda} \sum k_{a,\lambda} = \phi_{tr,\lambda} \frac{2.303}{j} \sum \epsilon_\lambda Z_\lambda \quad (3)$$

over all the  $\lambda$  of the sunlight absorbed by the pollutant;  $Z_\lambda$  is the sunlight intensity for a specified wavelength interval ( $N$ ) centered at wavelength  $\lambda$  (units: photons  $\text{cm}^{-2} \text{ s}^{-1} \text{ N nm}^{-1}$ );  $j = 6.023 \times 10^{20}$  is a conversion constant that makes the units of  $Z$  and  $\epsilon$  compatible; and  $\phi_{tr,\lambda}$  and  $\epsilon_\lambda$  have been defined above (eq 2). The latter two variables are measured in the laboratory (cf. Tables I and II), while the solar intensity ( $Z_\lambda$ ) data as functions of time of day, season, and latitude for the range  $\lambda = 297.5\text{--}800 \text{ nm}$  are available in the literature (Choudhry and Webster, 1985a; Zepp,

**Table IV. Computation of Midday, Midseason Specific Sunlight Adsorption Rates,<sup>a</sup>  $k_a = \sum k_{a,\lambda} = 2.303/j \sum \epsilon_{\lambda} Z_{\lambda}$  (Where  $j = 6.023 \times 10^{20}$ ), of Some Dibenzop-dioxins (PCDDs)<sup>b</sup> at 40° N Latitude on the Surface of Water Bodies**

season	1,2,3,7-T <sub>4</sub> CDD (1)		1,3,6,8-T <sub>4</sub> CDD (2)		1,2,3,4,6,7,8-H <sub>7</sub> CDD (6)		O <sub>8</sub> CDD (7)	
	$\sum \epsilon_{\lambda} Z_{\lambda}, 10^{18} \text{ s}^{-1}$	$k_a, \text{ days}^{-1}$	$\sum \epsilon_{\lambda} Z_{\lambda}, 10^{18} \text{ s}^{-1}$	$k_a, \text{ days}^{-1}$	$\sum \epsilon_{\lambda} Z_{\lambda}, 10^{18} \text{ s}^{-1}$	$k_a, \text{ days}^{-1}$	$\sum \epsilon_{\lambda} Z_{\lambda}, 10^{18} \text{ s}^{-1}$	$k_a, \text{ days}^{-1}$
spring	1.870	618	2.764	913	2.465	814	4.624	1528
summer	2.199	727	3.166	1046	2.940	971	5.325	1759
fall	1.215	401	1.826	603	1.583	523	3.039	1004
winter	0.717	237	1.156	382	0.893	295	1.884	622

<sup>a</sup> Solar radiation data ( $Z_{\lambda}$ ) for latitude 40° N, near the surface of water bodies for the calculation of  $k_a$  for all the seasons was used from Roof (1982), whereas the corresponding molar extinction coefficients ( $\epsilon_{\lambda}$ ) for dioxins 1, 2, 6, and 7 were from Table I. <sup>b</sup> Structures of the PCDDs are described in Figure 1. <sup>c</sup> Time expressed in terms of a 24-h day.

1982; Zepp and Cline, 1977; Roof, 1982). For the calculation of  $k_{sp}$  using eq 3, it is assumed that the quantum yield for a chemical determined at a wavelength, e.g., 313 nm, is wavelength independent for the region of sunlight absorption of the substrate.

Table IV records the computed midday, midseason specific sunlight adsorption rates ( $k_a$ ) at 40° N latitude for nonlabeled T<sub>4</sub>CDD (1), T<sub>4</sub>CDD (2), H<sub>7</sub>CDD (6), and O<sub>8</sub>CDD (7) present at the surface of water bodies during various seasons. These estimations of  $k_a$  in the case of spring, summer, fall, and winter were carried out by utilizing eq 3 together with the UV absorption spectral data (Table I, except  $\epsilon_{254}$  and  $\epsilon_{313}$ ) of the pollutants and the corresponding solar radiation data ( $Z_{\lambda}$  values) from Roof (1982), these data being expressed in units of reciprocal of 24-h day. We have also calculated the first-order rate constants ( $k_{sp}$ ) for the direct phototransformation of each dioxin, 1, 2, 6, and 7 occurring near the surface of the water bodies anticipated to be caused by natural sunlight at 40° N latitude during midday, midseason for various seasons (Table V). These values of  $k_{sp}$  were estimated by eq 3 along with  $\phi_{tr,\lambda}$  (at  $\lambda = 313 \text{ nm}$ ) (Table II) and  $k_a$  (Table IV) values with the assumption that the former data are independent of wavelength of the incident light. Likewise, Table V also includes midday, midseason sunlight direct photolysis half-lives ( $(t_{1/2})_{sp}$ ) (expressed in terms of 24-h day) calculated from  $k_{sp}$  values. Furthermore, similar  $k_{sp}$  and  $(t_{1/2})_{sp}$  data for nonlabeled 1,2,3,4,7-P<sub>5</sub>CDD (4) and 1,2,3,4,7,8-H<sub>6</sub>CDD (5), reproduced from Choudhry and Webster (1985b), are also recorded in Table IV.

## DISCUSSION

Comparison of light absorption spectra as well as spectral data of 1,2,3,7-T<sub>4</sub>CDD (1), 1,3,6,8-T<sub>4</sub>CDD (2), and O<sub>8</sub>CDD (7) with those of 1,2,3,4,6,7,8-H<sub>7</sub>CDD (6) indicates that contrary to the case of dioxin 6, pollutants 1, 2, and 7 possess absorption tail extending into the visible region (see Figures 2–5 and Table I). In the case of compounds 1 and 2, these tails were more intense, when the spectra were run with 8 and 2 times, respectively, more concentrated solutions of the dioxins, thereby revealing that the observed absorptions tails are real. Similarly, H<sub>7</sub>CDD (6) dissolved both in CH<sub>3</sub>CN and CH<sub>3</sub>CN–H<sub>2</sub>O (3:2, v/v) does not show an absorption tail even on two different spectrophotometers (see the Experimental Section).

It is well-known that during the solution-phase photolysis of PCDDs in organic solvents, substrates with chlorine atoms in the 2-, 3-, 7- and 8-position(s) (i.e., with lateral chlorine atoms) photolyze more rapidly than those with chlorine atoms in the 1-, 4-, 6-, and 9-positions (i.e., with peri chlorine atoms) [see references cited in Choudhry and Hutzinger (1982)]. Thus, if this theory is operative, one may predict that the quantum yields for the direct photolytic transformation ( $\phi_{tr,\lambda}$ ) of the tetrachlorodibenzo-*p*-dioxins 1 and 2 to increase in the following order: 1,3,6,8-T<sub>4</sub>CDD (2) < 1,2,3,7-T<sub>4</sub>CDD (1). However, Table II containing the experimental values of the  $\phi_{tr,\lambda}$  of these

PCDDs in aqueous acetonitrile indicates the opposite trend.

Moreover, reductive dechlorination is the usual process involved in the photodegradation of PCDDs containing four or more Cl contents (Choudhry and Hutzinger, 1982). However, in the case of the irradiation of PCDDs with three or fewer chlorine atoms, fission of the ether bond in the dioxin ring is the most likely route (Choudhry and Hutzinger, 1982). Such a possible route has also been proposed in the photolysis of 2,3,7,8-T<sub>4</sub>CDD (3) by Dulin et al. (1986). Furthermore, cleavage of one C–O bond is a well-known pathway involved in the photolytic degradation of the parent dibenzo-*p*-dioxin without any chlorine substituents (Plimmer et al., 1973). In the case of our studies, the RP-HPLC chromatograms of the photolysates of dioxins 4 and 5 (Choudhry and Webster, 1985b) as well as those of 1 and 2, 6, and 7 did not show any photoproduct derived from the reductive dechlorination of the starting dioxin as well as through secondary photodecomposition.

Absolute half-life times ( $t_{1/2}$ ) for 1,2,3,4,6,7,8-H<sub>7</sub>CDD (6) and O<sub>8</sub>CDD (7) in *n*-hexadecane reported by Nestrick and co-workers (1980) are 30 and 24 h, respectively, whereas Dobbs and Grant (1979) reported  $t_{1/2}$  of 11 and 16 h for dioxins 6 and 7 in *n*-hexane, respectively. However, Table II shows that  $t_{1/2}$  values for the photolysis of compounds 6 and 7 in H<sub>2</sub>O–CH<sub>3</sub>CN (2:3, v/v) at 313 nm are, respectively, 191 and 184 h, thereby indicating that absolute half-life time for pollutant 6 is larger than that of 7. This trend agrees with the former investigators (Nestrick et al., 1980) and disagrees with the latter one (Dobbs and Grant, 1979).

It is apparent from Table II that the absolute first-order rate constants ( $k_{p,\lambda}$ ) for the photolysis of the PCDDs at 313 nm decrease in the following order: T<sub>4</sub>CDD (2) > T<sub>4</sub>CDD (1) > H<sub>6</sub>CDD (5) > P<sub>5</sub>CDD (4) > O<sub>8</sub>CDD (7) > H<sub>7</sub>CDD (6).

A similar trend is observable in the case of quantum yields ( $\phi_{tr,\lambda}$ ) (see Table II) and estimated sunlight midday, midseason photolysis rate constants ( $k_{sp}$ ) (Table V). Similarly, absolute half-lives ( $t_{1/2}$ ) around 313 nm (Table II) and calculated midday, midseason sunlight photolysis half-lives ( $(t_{1/2})_{sp}$ ) (Table V) of these pollutants in a season increase in the following sequence: 2 < 1 < 5 < 4 < 7 < 6. For instance, the trend 1 > 5 > 4 > 7 > 6 for the  $k_{p,\lambda}$  and  $k_{sp}$  shows that additional Cl in the peri 4-position of dibenzo-*p*-dioxin 1 reduces the photoreactivity of the substrate 1. Moreover, it is evident from this trend that the presence of chlorine substituent in the lateral 8-position of dioxin 4 renders the substrate more photolabile (see above), whereas the additional substitution of the peri 6-position as well as the peri 6- and 9-positions of pollutant 5 with Cl atom(s) renders the substrate less photoreactive. The lower photolytic stability of O<sub>8</sub>CDD (7) compared to H<sub>7</sub>CDD (6) cannot apparently be ascribed to the steric interactions anticipated between the Cl substituents at 1-4- and 6-9-positions at the dioxin skeleton due to several reasons. For example, if there is steric hindrance among

Table V. Calculated Midday, Midseason Sunlight Photolysis First-Order Rate Constants<sup>a,b</sup> ( $k_{sp}$ ) and Half-Lives<sup>c</sup> ( $t_{1/2,sp}$ ) of PCDDs<sup>d</sup> in Aquatic Bodies for Various Seasons

season	1,2,3,7-T <sub>4</sub> CDD (1)		1,3,6,8-T <sub>4</sub> CDD (2)		1,2,3,4,7-P <sub>5</sub> CDD (4) <sup>e</sup>		1,2,3,4,7,8-H <sub>6</sub> CDD (5) <sup>e</sup>		1,2,3,4,6,7,8-H <sub>7</sub> CDD (6)		O <sub>8</sub> CDD (7)	
	$k_{sp} \times 10^2$ , days <sup>-1</sup>	$(t_{1/2})_{sp}$ , days	$k_{sp} \times 10^2$ , days <sup>-1</sup>	$(t_{1/2})_{sp}$ , days	$k_{sp} \times 10^2$ , days <sup>-1</sup>	$(t_{1/2})_{sp}$ , days	$k_{sp} \times 10^2$ , days <sup>-1</sup>	$(t_{1/2})_{sp}$ , days	$k_{sp} \times 10^2$ , days <sup>-1</sup>	$(t_{1/2})_{sp}$ , days	$k_{sp} \times 10^2$ , days <sup>-1</sup>	$(t_{1/2})_{sp}$ , days
spring	33.52 ± 2.61	2.1 ± 0.2	198.13 ± 12.28	0.35 ± 0.02	4.03 ± 0.98	18 ± 4	9.16 ± 0.16	7.6 ± 0.1	1.24 ± 0.14	57 ± 6	3.45 ± 0.51	21 ± 3
summer	39.41 ± 3.06	1.8 ± 0.1	226.99 ± 14.07	0.31 ± 0.02	4.86 ± 1.18	15 ± 4	11.06 ± 0.20	6.3 ± 0.1	1.48 ± 0.16	47 ± 5	3.97 ± 0.58	18 ± 3
fall	21.77 ± 1.69	3.2 ± 0.3	130.91 ± 8.12	0.53 ± 0.03	2.58 ± 0.62	29 ± 7	5.84 ± 0.10	12.0 ± 0.0	0.80 ± 0.09	88 ± 10	2.27 ± 0.33	31 ± 5
winter	12.86 ± 1.00	5.4 ± 0.4	82.85 ± 5.14	0.84 ± 0.05	1.41 ± 0.35	52 ± 13	3.21 ± 0.06	22.0 ± 0.0	0.45 ± 0.05	156 ± 17	1.40 ± 0.21	50 ± 7

<sup>a</sup>Equation 3 was utilized. <sup>b</sup>Time expressed in terms of a 24-h day. <sup>c</sup>Calculated from  $k_{sp}$  data. <sup>d</sup>Structures described in Figure 1. <sup>e</sup>Data reproduced from Choudhry and Webster (1985b).

the Cl atoms, then in the case of 1,2,3,4,7-P<sub>5</sub>CDD (5), 1,2,3,7-T<sub>4</sub>CDD (1), and 1,3,6,8-T<sub>4</sub>CDD (2), the former dioxin should be the most photodegradable. However, Tables II and V clearly indicate that, among these three dioxins, compound 2 (which is expected to have the least steric interactions) is the most photolabile. Likewise, in *n*-hexadecane, 1,2,3,4-T<sub>4</sub>CDD photodissipates 22.8 times more slowly than 2,3,7,8-T<sub>4</sub>CDD (3) (Nestrick et al., 1980), and in the case of tetrachlorobenzenes (Cl<sub>4</sub>Bz) in aqueous acetonitrile rates of the photodegradation increased in the order (Choudhry and Hutzinger 1984) 1,2,3,4-Cl<sub>4</sub>Bz < 1,2,3,5-Cl<sub>4</sub>Bz < 1,2,4,5-Cl<sub>4</sub>Bz, again indicating that the steric interactions between the chlorine substituents do not play a role in the photolytic instability of the chlorinated aromatic pollutants. Why the rate constants for O<sub>8</sub>CDD (7) are greater than those for H<sub>7</sub>CDD (6) remains unanswered.

As expected, the rates of the midday, midseason sunlight phototransformation ( $k_{sp}$ ) and the corresponding half-lives ( $(t_{1/2})_{sp}$ ) of the PCDDs 1, 2, and 4-7 are greatest and smallest, respectively, in the summer season (see Table V). Moreover, the greater difference between the estimated sunlight rate constants (and half-lives) for dioxins 7 and 6 in comparison with the difference between the  $k_{p,\lambda}$  (and  $t_{1/2}$ ) for 7 and 6 may be ascribable to the fact that the former pollutant absorbs more strongly in the region of wavelengths >295 nm (see Table I).

Finally, during midday, midsummer, the predicted sunlight half-life of 1,3,6,8-T<sub>4</sub>CDD (2) present near the surface of water bodies is 0.31 day (see Table V), while the experimentally determined sunlight summer half-life of 2 in autoclaved pond water is 3.5 days. This observation can be attributed to the fact that, in the latter case, the water contained dissolved organic matter, viz., humic acids, fulvic acids, etc. Furthermore, fulvic and humic acids present in natural aquatic environments are well-known to exert light screening and/or quenching effects on the photodegradation of environmental chemicals (Choudhry et al., 1986b; Choudhry, 1984; Kochany et al., 1988). In water-acetonitrile (1:1, v/v), for example, after 24-h exposure to UV light of  $\lambda \geq 285$  nm, the percentage disappearance of the starting 1,3,5-trichlorobenzene (1.16 mM) in the presence of fulvic acids (0.05%, w/v) was 14%, whereas in the absence of fulvic acids 64% of the starting pollutant disappeared (Choudhry et al., 1986b). Likewise, the quantum yields for the solution-phase photodegradation of 3,5-dibromo-4-hydroxybenzotrile (bromoxynil, a herbicide) in distilled water containing 0.3, 0.5, and 0.8% (w/v) of dissolved soil fulvic acids were lowered by 1.40-, 1.75-, and 2.02-fold as compared to the photoreaction of bromoxynil in the absence of fulvic acids (Kochany et al., 1988). Thus, the observed increasing of half-life of dioxin 2 in pond water compared to that in pure water is ascribable to the light screening/quenching, effects of the dissolved organic matter.

Further research work concerning the environmental photochemistry of PCDDs is in progress.

## CONCLUSIONS

Our photochemical investigations at 313 nm conducted on dilute solutions of nonlabeled 1,2,3,7-tetrachlorodibenzo-*p*-dioxin (1,2,3,7-T<sub>4</sub>CDD) (1) (6.40  $\mu$ M), 1,3,6,8-T<sub>4</sub>CDD (2) (10.55  $\mu$ M), 1,2,3,4,6,7,8-H<sub>7</sub>CDD (6) (2.78  $\mu$ M), and O<sub>8</sub>CDD (7) (0.31  $\mu$ M) (present work) and our previously reported work (Choudhry and Webster 1985b) on 1,2,3,4,7-P<sub>5</sub>CDD (4) (2.81  $\mu$ M) and 1,2,3,4,7,8-H<sub>6</sub>CDD (5) (3.33  $\mu$ M) in H<sub>2</sub>O-CH<sub>3</sub>CN (2:3, v/v) as well as those of 2,3,7,8-T<sub>4</sub>CDD (3) (0.361  $\mu$ M) in aqueous acetonitrile (1:1) published by Dulin et al. (1986) lead us to draw several

environmentally significant conclusions. The quantum yields for the PCDD congeners 1-7 amounting to  $(5.42 \pm 0.42) \times 10^{-4}$ ,  $(2.17 \pm 0.14) \times 10^{-3}$ ,  $2.2 \times 10^{-3}$ ,  $(9.78 \pm 2.38) \times 10^{-5}$ ,  $(1.10 \pm 0.02) \times 10^{-4}$ ,  $(1.53 \pm 0.17) \times 10^{-5}$ , and  $(2.26 \pm 0.33) \times 10^{-5}$ , respectively, are rather low, thereby reflecting that pollutants such as polychlorodibenzo-*p*-dioxins (PCDDs) present in the aquatic environments can be expected to photodegrade rather slowly. Similar conclusions can be drawn from both absolute ( $t_{1/2}$ ) and predicted sunlight phototransformation half-lives ( $(t_{1/2})_{sp}$ ) documented in Tables II and V, respectively. Contrary to the previous reports on the photodegradation of PCDDs in organic solvents (Dobbs and Grant, 1979; Choudhry and Hutzinger, 1982; Nestruck et al., 1980), our photolytic studies using H<sub>2</sub>O-CH<sub>3</sub>CN systems stress that, in the environment, PCDD contaminants are not likely to photodissipate as rapidly as was concluded by other researchers. Furthermore, comparison of the estimated midday, mid-summer sunlight half-life (0.31 day, time being described in terms of 24-h day) with experimentally determined sunlight half-life (3.5 days) of 1,3,6,8-T<sub>4</sub>CDD (2) present in neat water and pond water, respectively, again reflects that the rates of the phototransformation of PCDDs in water bodies containing dissolved organic materials such as fulvic and humic acids are likely to be lowered due to the light screening and quenching effects of the organics on these pollutants. However, enhancement of rates of the phototransformation of pollutants anticipated by the presence of natural photosensitizers needs also to be considered. Similarly, individual isomers of chlorinated dioxins possessing a greater number of lateral Cl substituents are not expected to always photoconvert faster than those with predominantly peri Cl groups, when such PCDD isomers are present in water bodies. Finally, the results of our studies presented herein may be altered in the case of PCDD congeners sorbed onto the surfaces of the suspended matter present in the natural water bodies.

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