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Aquatic Photodegradation of Polychlorinated Dibenzofurans: Rates and Photoproduct Analysis

KENNETH J. FRIESEN,*
MYROSIA M. FOGA, AND
MARK D. LOEWEN

Department of Chemistry, University of Winnipeg,
515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9

The aquatic photochemistry of 2,3,7,8-tetrachlorodibenzofuran (T$_4$CDF) and 2,3,4,7,8-pentachlorodibenzofuran (P$_5$CDF) was studied in the laboratory using a xenon light source and under sunlight conditions at 50° N latitude at the Experimental Lakes Area of northwestern Ontario, Canada. Under midsummer sunlight conditions ^{3}H-T$_4$4CDF and ^{14}C-P$_5$CDF photolyzed slowly in 25:10 (v/v) distilled water/acetonitrile solutions with rate constants of 0.11 ± 0.01 and 0.015 ± 0.007 d^{-1}, respectively. Both congeners experienced enhanced degradation rates in lake water, with rate constants of 0.58 ± 0.05 and 3.6 ± 0.3 d^{-1}. Photoproduct analysis confirmed reductive dechlorination as a degradative pathway for both PCDFs in lake water. Three T$_4$CDFs were detected as photoproducts of 23478-P$_5$CDF, with two of these products identified by GC/MS as 2368- and 2348-T$_4$CDF. Similarly, one T$_3$CDF was detected in the photolysis of 2378-T$_4$CDF, although the specific congener was not identified. One polar photoproduct was detected in the photolysis of 23478-P$_5$CDF in lake water. Although the identity of this product could not be confirmed, GC/MS analysis of the TMS derivative suggested a hydroxylated, completely dechlorinated compound with an apparent $M^+ = 330$ amu. Photolysis of nonchlorinated dibenzofuran in lake water yielded 2,2′-dihydroxybiphenyl as photoproduct, with this product producing a trihydroxybiphenyl, tentatively identified as 2,2′,3-trihydroxybiphenyl, under similar conditions. The results show that reductive dechlorination, C−O cleavage, and hydroxylation all play a role in the photolytic transformation of PCDFs and the dibenzofuran nucleus in natural water.

Introduction

Although polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) are persistent environmental contaminants, several studies have shown that these chemicals undergo aqueous photodegradation under environmental conditions. PCDFs have low quantum yields for direct aqueous photolysis at 313 nm (*1*, *2*) and low molar absorptivities above the solar cutoff (290 nm). Therefore, these compounds are expected to undergo relatively slow direct aqueous photolysis. However, several studies have shown that the photolysis rates of both PCDDs (*3*) and PCDFs (*4*, *5*) may be significantly enhanced in natural water, a fact usually attributed to the presence of naturally occurring sensitizers. Although reductive dechlorination of PCDDs and PCDFs has been reported in organic solvents (*6*−*9*), there have been few investigations of the photolytic reactions of these compounds in aquatic environments. The potential for C−O cleavage as a pathway in the aqueous photolysis of several PCDDs has been suggested (*3*, *10*) although this was not confirmed with photoproduct analysis. Similarly, the involvement of reductive dechlorination in the sunlight photolysis of several tetrachlorinated dibenzofurans (2378- and 1278-T$_4$CDF) was reported in natural water (*5*), but the identities of the photoproducts were not confirmed.

The objectives of this study were to determine the rates of aqueous photolysis of two toxic PCDF congeners, 2378-T$_4$CDF and 23478-P$_5$CDF, in water/acetonitrile solutions and in a natural water under midsummer sunlight conditions. The investigation furthermore sought to identify both polar and nonpolar organic photoproducts in the photolysis of PCDFs and dibenzofuran in order to provide information on an important transformation pathway affecting the behavior of these contaminants in the aquatic environment.

Experimental Section

Reagents. Radiolabeled PCDFs, ^{14}C$_6$-dichlorophenyl-2,3,4,7,8-pentachlorodibenzofuran (^{14}C-23478-P$_5$CDF) and 4,6-^{3}H$_2$-2,3,7,8-tetrachlorodibenzofuran (^{3}H-2378-T$_4$CDF) with specific activities of 1.25×10^{10} and 4.47×10^{12} Bq/mmol, respectively, were purchased from Wellington Laboratories (Guelph, ON). Radiolabeled PCDFs were purified by preparative reverse-phase HPLC, extracted into hexane, and redissolved in HPLC-grade acetonitrile (Fisher Scientific, Winnipeg, MB). Radiopurities, established by HPLC-LSC (liquid scintillation counting), were 99.6 and 99.9% for ^{3}H-T$_4$CDF and ^{14}C-P$_5$CDF, respectively. Nonlabeled 23478-penta-, 2348-tetra-, 2347-tetra-, 2367-tetra-, 2368-tetra-, 2378-tetra-, and 238-trichlorodibenzofuran were also supplied by Wellington Laboratories as stock solutions in either isooctane or toluene at concentrations of 40−50 μg/mL. Dibenzofuran (99+%), 2,2′-dihydroxybiphenyl (99%), and 2,5-dihydroxybiphenyl (97%) were provided by Aldrich Chemical Company (Milwaukee, WI), while 2,3-dihydroxybiphenyl (98%) was supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

p-Nitroacetophenone (PNAP) used as the chemical actinometer, spectrophotometric grade pyridine used as a quantum yield adjuster, and *p*-nitrotoluene used as an internal standard in PNAP analyses were purchased from Aldrich. Scintiverse II (Fisher) and Atomlight (Biotechnical Systems, Boston, MA) were used as scintillation fluors. Carbosorb (Packard Instrument Co., Downers Grove, IL) diluted 1:9 (v/v) with Scintiverse II was used as a trap for ^{14}CO$_2$ produced during photolysis. Reagent-grade anhydrous sodium sulfate, supplied by Mallinckrodt (Paris, NY), was Soxhlet extracted in acetone/hexane (1:1, v/v) for 24

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* Corresponding author fax: 204-786-1824; e-mail address: kfriesen@uwinnipeg.ca.

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h prior to use and stored in a glass bottle at 120 °C. *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA), supplied by Chromatographic Specialties (Brockville, ON), and *n*-butaneboronic acid and 2,2-dimethoxypropane (Aldrich) were used for derivatization of polar photoproducts prior to GC/MS analyses. All solvents were Burdick & Jackson Brand High Purity (Baxter Diagnostics Corporation, Canlab, Winnipeg, MB) unless otherwise specified.

Lake water used in photolysis studies was collected from Lake 375 of the Experimental Lakes Area in northwestern Ontario, Canada (93°47'30''W and 49°44'30''N). The water, with a pH of 7.45 and dissolved organic carbon (DOC) of 4.2 mg/L, was filter-sterilized with a 0.22 μm GV filter (Millipore Canada Ltd., Mississauga, ON) for use in photolytic studies.

Kinetics of Sunlight Photolysis. Photodegradation rates of $^{14}C_6$-23478-P_5CDF and $^3H_2$−2378-T_4CDF were determined at approximately 50° N latitude in filter-sterilized natural water and in distilled water/acetonitrile (25:10, v/v) at the Experimental Lakes Area under midsummer sunlight conditions. All glassware was cleaned and sterilized at 180 °C for 5 h prior to use. A 2.01×10^{-5} M PNAP solution containing 0.0828 M pyridine was used to monitor sunlight intensities during the photolysis period (*11*). Photolysis of actinometer solutions and of PCDFs in natural water and in distilled water/acetonitrile was carried out in tightly capped 50-mL Pyrex centrifuge tubes. Additional solutions of PCDFs in natural water were wrapped in aluminum foil and served as controls during the photolysis period. All PCDF solutions contained 45 ng of ^3H-2378-T_4CDF and 40 ng of ^{14}C-23478-P_5CDF in 35 mL of solvent. Photolyses were carried out over the period from 11:00 A.M. June 26, 1989, to 3:00 P.M. June 29, 1989, as previously described (*3*). At each sampling time, 5 mL of hexane was added to duplicate PCDF solutions, and the tubes were then wrapped with aluminum foil and transported to the lab for analysis.

PNAP/pyridine solutions ($n = 2$ at each sampling time) were spiked with 350 μL of 2.62×10^{-3} M PNT and analyzed in triplicate by HPLC with 55:45 methanol/water as mobile phase and detection at 280 nm. Analyses were carried out on a Beckman HPLC system equipped with a 25 cm × 3.2 mm (i.d.) μBondapak C_{18} column (Waters Scientific, Mississauga, ON).

PCDF solutions were adjusted to pH 9 with several drops of 0.1 M KOH and extracted four times with 5-mL portions of hexane. Extracts were passed through a sodium sulfate drying column, concentrated to a volume of 500 μL, and stored at 7 °C until analyses. Extraction efficiencies, established with standard ^3H-2378-T_4CDF and ^{14}C-23478-P_5CDF, were 96 and 105% for the two congeners, respectively. Nonextractable activity was determined by assaying 4 mL of extracted water by LSC in 12 mL of Atomlight.

Hexane extracts were analyzed by HPLC-LSC with 85:15 methanol/water as the mobile phase at a flow rate of 1.0 mL/min. Three-minute fractions were collected and assayed on a Beckman LS 7500 counter (Beckman Instruments, Irvine, CA) after the addition of 12 mL of Scintiverse II. Samples containing both tritium and carbon-14 isotopes were assayed with a 10-min preset count time on a dual-label program, using the H# method with automatic quench compensation. Calibration was performed with sealed [^{14}C]-toluene standards supplied by Amersham Canada Ltd. (Oakville, ON) or with standards prepared in the laboratory using [^{3}H]-toluene provided by Du Pont Canada, Inc. (Montreal, PQ). β-Emissions from tritium and carbon-14 were monitored in the 0−397 and 397−655 counting channels, providing energy windows of 0−18 and 18−160 keV, respectively. All samples were counted to a 2σ error of 2%. A 3-min fraction was collected prior to each injection to establish background activity. Results were used to obtain reconstructed chromatograms, with resolution of unreacted parent PCDF from extractable degradation products.

Identification of Photoproducts. For photoproduct analysis, nonlabeled 2378-T_4CDF (98.5%) and 23478-P_5-CDF (96.0%) were photolyzed in the laboratory in filter-sterilized lake water using a 150-W xenon lamp powered by a Perkin Elmer 150 Xenon Power Supply to simulate sunlight conditions. Solutions containing 1 ng/mL of the PCDF in lake water were photolyzed for 4−6 h in 2-L Pyrex (4 mm) separatory funnels. Nonpolar photoproducts were isolated by solid-phase extraction using three preconditioned C_{18} SepPaks (Millipore) in series. The SepPaks were dried with a gentle stream of nitrogen for 20 min and eluted with 12 mL of hexane. Extracts from four photolyses were combined and concentrated to 50 μL. A blank, consisting of nonspiked filter-sterilized lake water was photolyzed and worked up as above to determine background levels of PCDF contaminants that could be detected in lake water after photolysis. A control consisting of lake water spiked with PCDF remained in the dark for the same period of time as the photolyzed samples to determine recoverable PCDF impurities from the starting material.

Standard solutions (concentrations of 5−12 ng/μL) of 2348-, 2347-, 2367-, 2368-, and 2378-T_4CDF and of 238-T_3CDF were prepared in isooctane for GC retention time confirmation. Extracts were analyzed by GC-MSD using a Hewlett Packard 5890A gas chromatograph coupled with a 5970B mass selective detector with electron impact ionization at 70 eV. Samples were chromatographed on a 60 m × 0.256 mm × 0.25 μm DB-1701 fused silica capillary column (J&W Scientific, Folsom, CA), with a helium carrier gas linear flow rate of 17.4 cm/s. Injections were in the splitless mode with a column head pressure of 10 psi and an injection port temperature of 250 °C. Column temperature was maintained at 100 °C for 2.70 min, followed by a 5 °C/min ramp to 180 °C and a 0.5 °C/min ramp to 270 °C. Degradation products were detected using the selected-ion monitoring (SIM) mode, monitoring the most intense ions of potential dechlorinated PCDFs, with dwell times of 100 ms.

To probe for polar photoproducts, 1.7 L of filter-sterilized lake water was spiked with P_5CDF in acetonitrile to produce a nominal concentration of 2 ng/mL. Aqueous solutions were photolyzed for 12 h and extracted with six C_{18} SepPaks to remove nonpolar photoproducts along with unreacted, parent P_5CDF. The aqueous phase was evaporated to dryness using very low heat. The residue was treated with 15 mL of tetrahydrofuran (THF) for 12 h, transferred to a 15-mL centrifuge tube, and evaporated to dryness under nitrogen. The sample was derivatized with the addition of 100 μL of 3:2 (v/v) THF/BSTFA and 10 mL of THF in a water bath at 70 °C for 20 min. Solvents were evaporated, the solutions were adjusted to 50 μL with hexane, and a total ion chromatogram (TIC) was obtained by GC-MSD. A similar volume of filter-sterilized lake water without added PCDF was photolyzed, extracted, and derivatized as above to check for possible derivatization of naturally occurring polar components in the lake water.

TABLE 1

Rates of Aqueous Photolysis of PCDFs and Chemical Actinometer PNAP at 50° N Latitude under Midsummer Sunlight Conditions[a]

	k_p (d^{-1})	$t_{1/2}$ (d)	conditions
2378-T$_4$CDF	0.11[b]	6.3	water/acetonitrile
	0.58[c]	1.2	lake water
23478-P$_5$CDF	0.015[b]	46.2	water/acetonitrile
	3.6[c]	0.19	lake water
PNAP	0.15[d]	4.6	

[a] All photolysis rates have been corrected for tube geometry to provide rates of photolysis in surface waters (*11*). [b] Pseudo-first-order photolysis rate constants (k_{dE}) and corresponding half-lives, $t_{1/2} = 0.693/k$ determined in 25:10 (v/v) distilled water/acetonitrile. [c] Pseudo-first-order photolysis rate constants (k_{pE}) and half-lives determined in filter-sterilized natural water from lake 375 of the Experimental Lakes Area. [d] Degradation rates of the chemical actinometer, *p*-nitroacetophenone (PNAP), were measured during the photoperiod for PCDF degradation.

Photochemistry of Dibenzofuran and its Photoproducts. Dibenzofuran was dissolved in filter-sterilized lake water to produce a nominal concentration of 1 mg/L and stirred overnight. Samples were photolyzed in the laboratory for up to 18 h, acidified with 3 mL of glacial acetic acid, and extracted by passing through a Cyanopropyl SepPak at a flow rate of 2 mL/min. SepPaks were eluted with 5 mL of acetonitrile, and the extract evaporated to near dryness and spiked with 30 μL of BSTFA. The solution was heated for 20 min at 70 °C to yield TMS derivatives of potential phenolic photoproducts. The solution was evaporated to dryness, redissolved in 50 μL of acetonitrile, and analyzed by GC/MS with full-scan detection.

The photolysis of 2,2′-dihydroxybiphenyl (DHB) was studied with the same technique except that a 20 mg/L solution of DHB in lake water was photolyzed for 1.5 h. After extraction and evaporation of the solvent, BSTFA derivatives were prepared for GC/MS analysis. In order to test for ortho-dihydroxy substitution, another extract was treated with 100 μg of *n*-butaneboronic acid in 100 μL of 2,2′-dimethoxypropane for 15 min. The sample and an additional 0.2 μL of BSTFA were drawn into a syringe and injected into the GC injection port at 250 °C.

Results and Discussion

Photodegradation Rates of 23478-P$_5$CDF and 2378-T$_4$CDF. The rates of photolysis of both PCDF congeners in distilled water/acetonitrile were slow as expected (see Table 1), with pseudo-first-order degradation rate constants (k_{dE}) of 0.11 ± 0.01 ($r^2 = 0.98$) and 0.015 ± 0.007 ($r^2 = 0.37$) d^{-1}, corresponding to half-lives of 6.3 and 46.2 d for 2378-T$_4$CDF and 23478-P$_5$CDF, respectively. T$_4$CDF degraded 7 times more rapidly than P$_5$CDF, with 54% disappearance of T$_4$CDF after 76 h compared to 27% disappearance of P$_5$CDF over the same period. Although the sunlight photolysis rate of 2378-T$_4$CDF was approximately 13 times slower than recently reported in distilled water alone (*5*), the differences are rationalized by consideration of diurnal cycling, geometry corrections, differing sunlight intensities, and the presence of acetonitrile in the solutions. Geometry corrections applied in this study provide degradation rates applicable to surface waters but decrease photolysis rates by a factor of approximately 2.2 compared to photolysis in tubes (*11*). In previous reports (*5*), the 8-h photoperiod from 9 A.M. to 5 P.M. was used in calculating rate constants, producing degradation rates under daylight conditions. In the present study, real 24-h days were used in the calculations. By including the effects of diurnal cycling, reported photolysis rates will be substantially slower; however, this will also provide more realistic environmental transformation rates. Finally, the photolysis of several T$_4$CDFs at 300 nm have been reported to be 2−4 times greater in water than in 60% acetonitrile/water (*5*). Although somewhat less acetonitrile (28%, v/v) was used in the present study, photolysis rates will undoubtedly be reduced by its presence; however, the magnitude of the effect has not been assessed.

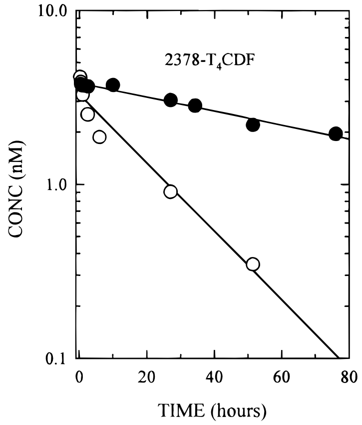


FIGURE 1. Midsummer sunlight photodegradation of 2,3,7,8-T$_4$CDF in 25:10 (v/v) distilled water/acetonitrile (●) and in natural water (○) at 50° N latitude at the Experimental Lakes Area in northwestern Ontario, Canada. The data, representing the disappearance of extractable parent TCDF (with $n = 2$ at each sampling time), are fitted to a first-order kinetic model.

Photodegradation of PCDFs in natural water was significantly enhanced, with 89% disappearance of P$_5$CDF and 56% disappearance of T$_4$CDF after 6 h of sunlight exposure. Using data in the 10−70% disappearance range, the net photolysis degradation rate constants (k_{pE}) for 2378-T$_4$CDF (see Figure 1) and 23478-P$_5$CDF were 0.58 ± 0.05 ($r^2 = 0.96$) and 3.6 ± 0.3 ($r^2 = 0.98$) d^{-1}, corresponding to half-lives of 1.2 and 0.19 d for the two congeners, respectively. Quantitative recoveries of both PCDFs from dark controls, in both water/acetonitrile solutions and in natural water, sampled over the entire exposure period confirmed that the observed decreases in the concentrations of PCDFs were due to photodegradation. The kinetics represent homogeneous photodegradation of the PCDFs since the concentrations of both congeners were within the maximum solubility enhancement factors attributable to 4.2 mg/L DOC in the lake water as summarized in Table 2. This rapid photolysis, resembling the behavior of chlorinated dioxins in natural water (*3*), is attributed to the presence of naturally occurring photosensitizers in lake water. Reactive chromophores in natural water absorb sunlight energy and are known to initiate indirect photoreactions with organic contaminants (*12*). Energy, electron, and hydrogen atom transfer reactions as well as reactions with photochemically generated free radicals may be very significant in the environmental photodegradation of compounds like PCDDs and PCDFs, which do not absorb strongly above 290 nm (*10, 12*). Although the identity of the sensitizers is unknown, dissolved fulvic and humic acids and proteins have been shown to sensitize the photodegradation of organic contaminants in aqueous solutions (*13−15*). The 5-fold rate enhancement observed for 2378-T$_4$CDF is comparable to the 2-fold enhancement previously

TABLE 2

Solubility Enhancement of PCDFs and Dibenzofuran in Lake Water[a] and the Concentration/Solubility Ratios used in Photodegradation Studies

	log K_{ow}[b]	S_w (ng/L)[b]	(S_w^*/S_w)[c]	(C_w/S_w)[d]
2378-T_4CDF	6.53 ± 0.5 (*26*)	419 (*28*)	5.5	2.4−3.1
23478-P_5CDF	6.92 ± 0.5 (*26*)	211 (*28*)	12.0	4.7−11.1
dibenzofuran	3.92 ± 0.5 (*27*)	4 200 000 (*29*)	1.004	0.24

[a] Water from lake 375 of the Experimental Lakes Area with a dissolved organic carbon (DOC) concentration of 4.2 mg/L. [b] Octanol−water partition coefficients (K_{ow}) and water solubilities (S_w) of the dibenzofurans. [c] Solubility enhancement (S_w^*/S_w) calculated from $1 + XK_{DOC}$ (*30*) where X is the DOC in g/mL and K_{DOC} is estimated as 0.1 K_{ow} (*31*). [d] Concentrations of dibenzofurans used in experimental work relative to reported water solubilities of each chemical.

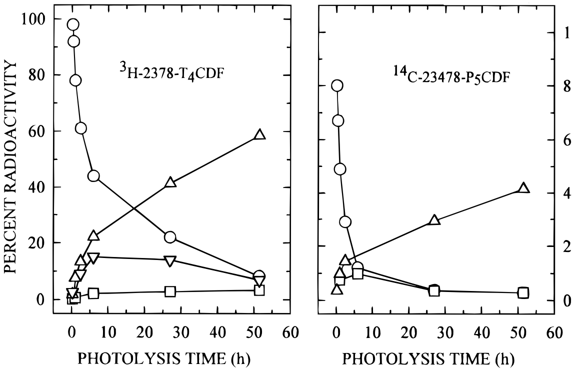


FIGURE 2. Radiodistribution diagrams showing the disappearance of parent PCDF (○), the increase in nonextractable activity (△), and the appearance of several intermediates (▽) and (□), during the midsummer sunlight photodegradation of ^{3}H-2,3,7,8-T_4CDF and ^{14}C-2,3,4,7,8-P_5CDF in natural water.

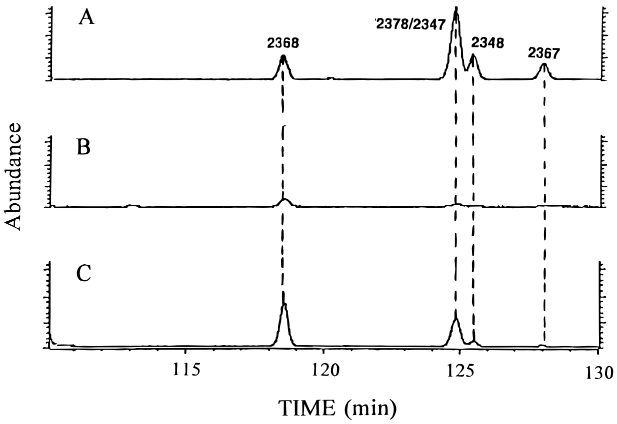


FIGURE 3. Chromatograms obtained by GC-MS-SIM on a 60-m DB-1701 fused silica capillary column of (A) a standard mixture of 2,3,6,8-tetra-, 2,3,7,8-tetra-, 2,3,4,8-tetra-, 2,3,6,7-tetra-, and 2,3,4,7-tetra-chlorodibenzofuran; (B) a lake water control; and (C) the hexane extract obtained in the sunlight photodegradation of 2,3,4,7,8-pentachlorodibenzofuran in natural water.

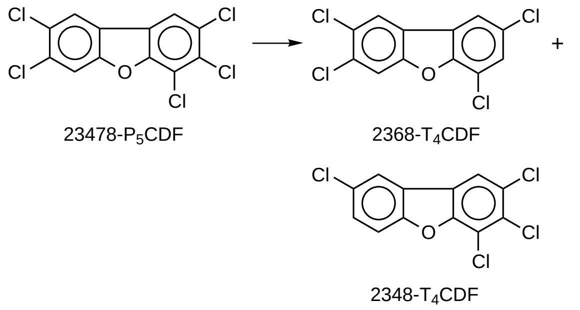
reported for 2378- and 1278-T_4CDFs in natural water (*5*). The more rapid photodegradation of 23478-P_5CDF compared to 2378-T_4CDF (by 6.2-fold) indicates that the chlorine substitution pattern on the dibenzofuran nucleus affects the selectivity of photolytic reactions in the environment. However, the effect of natural sensitizers may be considerably less than the 240-fold observed rate enhancement for 23478-P_5CDF, since the effect of 28% acetonitrile in the experiments with distilled water was not quantified.

Photoproduct Analysis. *Radiolabel Distribution.* In the sunlight photolysis of ^{3}H-2378-T_4CDF in water/acetonitrile solutions, two peaks were resolvable from parent T_4CDF by HPLC-LSC, although <8% of the total activity at each sampling time was attributed to these photoproducts. Nonextractable activity increased steadily over the entire exposure period, reaching 46% of total activity in 76 h, suggesting the formation of a more polar degradation product(s). Since the rate of aqueous photolysis was very slow, insufficient amounts of photoproducts were formed over the photolysis period for GC/MS analysis. With ^{14}C-23478-P_5CDF, no ^{14}C-labeled degradation products were detected in hexane extracts or in the extracted water, since P_5CDF was essentially nondegradable ($t_2 = 46.2$ d) in water/acetonitrile solutions.

In the sunlight photolysis of the PCDFs in lake water, two tritium and one ^{14}C-labeled bands were resolved from parent PCDFs by HPLC-LSC analysis of hexane extracts. Retention times of these nonpolar photoproducts were similar to those of lower chlorinated PCDFs, suggesting that reductive dechlorination was occurring. However, these photoproducts appeared to be intermediates in the overall photolytic degradation since their amounts increased in the early stages of photolysis and then decreased with longer sunlight exposure. For both congeners, the level of nonextractable radioactivity increased as exposure time increased, accounting for 59% and 42% of total activity for T_4CDF and P_5CDF, respectively, after 52 h of exposure indicating the formation of a polar photoproduct(s) and possibly C−O bond cleavage. Very low levels of $^{14}CO_2$ evolved during the photolysis of ^{14}C-P_5CDF in lake water over a 76-h photoperiod. The radiolabel distribution diagrams (Figure 2) are similar to those previously reported for the sunlight photolysis of several PCDDs in natural water (*3*).

Extractable Photoproducts. Co-extractable material from lake water produced a very complex total ion chromatogram of the hexane extract in the photolysis of 23478-P_5CDF. However, extracted ion chromatograms, using the most intense ions in the M^+ region for T_4CDF (m/z of 304 and 306 amu), indicated the presence of several T_4CDFs. Mass spectra confirmed that these were tetrachlorinated dibenzofurans, with an intense 4-chlorine M^+ isotope pattern and a low abundance 3-chlorine pattern corresponding to the $[M - COCl]^+$ fragment with m/z of 241 amu. The presence of 2368-T_4CDF, 2348-T_4CDF, and one or both of 2378-T_4CDF and 2347-T_4CDF as well as the absence of 2367-T_4CDF were confirmed by GC-MSD-SIM (see Figure 3). Controls produced considerably lower levels of T_4CDFs (Figure 3B), confirming that the T_4CDFs were not simply background levels in the lake water or trace impurities in the starting P_5CDF. Although further dechlorination is feasible, trichlorinated dibenzofurans were not detected, perhaps because T_3CDFs degraded more rapidly than T_4-CDFs.

The confirmed intermediates, 2368- and 2348-T_4CDF both form by the loss of a lateral chlorine nearest the oxygen atom. The dominant product, 2368-T_4CDF, is formed by reductive dechlorination involving the loss of a lateral Cl atom (from position 3) which is flanked by Cl atoms (in positions 2 and 4). This preferential loss of lateral chlorine atoms has previously been observed in the photolysis of several chlorinated dioxins, including O_8CDD, 123789- and 123678-H_6CDD, and a series of P_5CDDs in benzene/hexane (5:95, v/v) solutions (*16, 17*). Although a third chromatographic peak was detected, the lack of resolution prevented the confirmation of 2378-T_4CDF and/or 2347-T_4CDF as photoproducts in this reaction.



Analysis of the hexane extracts of the photolysate of 2378-T_4CDF in lake water revealed the presence of only one T_3CDF using GC-MS-SIM. Although a mass spectrum confirmed the structure of the product as a trichlorodibenzofuran, the identity of this congener could not be confirmed due to the lack of T_3CDF standards. However, the one standard available (238-T_3CDF) did not match the retention time of the photoproduct, hence the product is believed to be 237-T_3CDF. No T_3CDFs were detected in lake water extracts or in a dark control, eliminating the possibility that the T_3CDF was present prior to the photolysis of 2378-T_4CDF. Dichloro-, monochloro-, and nonchlorinated dibenzofuran could not be detected, likely due to the low concentrations of these photoproducts. While supporting previous studies that PCDFs are photoreduced in natural water (*5*), these are the first results confirming the identities of several photoproducts of such a reaction, thereby providing conclusive evidence that reductive dechlorination is one mechanism responsible for the aqueous photolysis of PCDFs under environmental conditions.

$$\mathrm{P_5CDF} \rightarrow \mathrm{T_4CDF} \rightarrow \mathrm{T_3CDF}$$

However, reductive dechlorination appears to be a minor pathway in the overall aqueous photodegradation of PCDDs and PCDFs. It has previously been reported (*5*) that reductive dechlorination was minimal for 2378-T_4CDF in pure water and contributed only 7–12% to its overall sunlight photodegradation in natural water. The relative ineffectiveness of reductive dechlorination has also been reported in the photolysis of 2378-T_4CDD in isooctane (*6*) and in acetonitrile/water solutions (*10*).

Nonextractable Photoproduct(s). Since the photolysis of both 2378-T_4CDF and 23478-P_5CDF in lake water produced significant amounts of nonextractable radioactivity, the identification of possible polar organic photoproducts was investigated. Although the total ion chromatogram of this fraction after derivatization with BSTFA showed a large number of peaks, most were confirmed as components in the original lake water. However, one distinct peak was present only in samples in which P_5CDF was photolyzed. The mass spectrum of the polar photoproduct included a base peak with m/z of 73 amu, the absence of recognizable chlorine isotope patterns in any fragment ions, and an apparent molecular ion (M^+) of 330 amu. The ion of mass 73 amu confirmed successful trimethylsilylation of the photoproduct. Although $M^+ = 330$ amu suggested a dihyroxybiphenyl (DHB), the M:M + 1:M + 2 isotope ratios for the TMS derivative of the photoproduct (100:23.4:10.3) did not compare favorably with the calculated ratios for TMS-derivatized DHB, $C_{18}H_{26}Si_2O_2$ (100:30.9:11.5), or the experimental ratios for the TMS derivative of 2,2′-DHB (100:30.0:11.3). Furthermore, the photoproduct did not coelute with available dihydroxybiphenyl standards including 2,2′-DHB, 2,3-DHB, and 2,5-DHB. Although the photoproduct could not be positively identified, it appears that another pathway involving C–O cleavage may be more important than reductive dechlorination in the photolytic degradation of PCDFs as has been suggested for PCDDs (*3*, *6*, *10*). No chlorinated hydroxybiphenyls could be detected as has been reported in the photolysis of 2378-T_4CDD and 2,7-D_2CDD in toluene (*6*) and of PCBs in water (*18*).

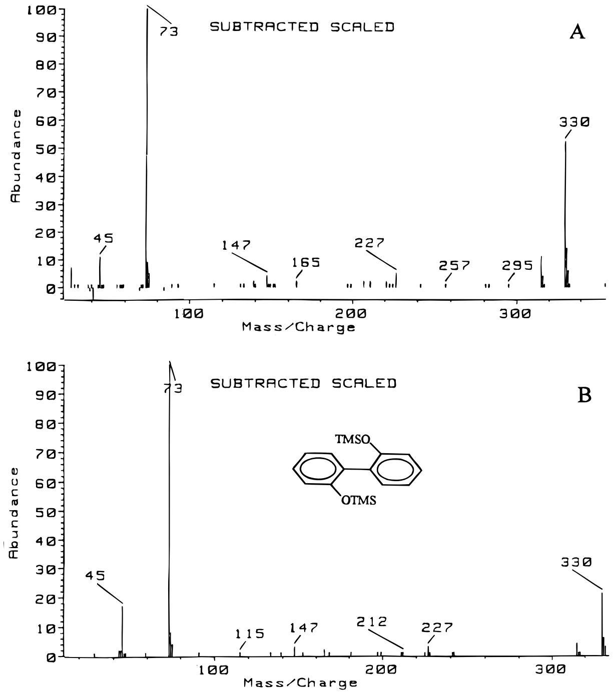


FIGURE 4. Electron impact mass spectra of (A) TMS-derivatized polar photoproduct formed in the laboratory photodegradation of dibenzofuran in natural water and (B) TMS-derivatized 2,2′-dihydroxybiphenyl.

Photodegradation of Dibenzofuran in Lake Water. The photolysis of dibenzofuran in lake water was studied to provide information on the potential degradation of the dibenzofuran nucleus. Ion chromatograms ($m/z = 73$ amu) of the derivatized polar fraction isolated by Cyanopropyl SepPaks were complex. Analysis of a lake water control using the same photolysis times and sample treatment procedures confirmed that most of the peaks were due to naturally occurring organic materials in lake water. However, one significant peak appeared in the sample that was not detected in the control. The mass spectrum (Figure 4A) indicated a derivatized phenolic compound, with a base peak of 73 amu, an apparent M^+ of 330 amu, and a small $[M - 15]^+$ peak. This spectrum was very similar to the mass spectrum of derivatized 2,2′-DHB (Figure 4B).

The isotope abundances of the molecular ion cluster (M:M + 1:M + 2) of 100:30.5:11.5 supported the structure of this product as a dihydroxybiphenyl. The identity of the photoproduct was confirmed as 2,2′-DHB by comparison of GC retention times of the photoproduct with retention times of derivatized 2,2′-, 2,3-, and 2,5-dihydroxybiphenyl congeners on a 30-m DB-5 capillary column. Therefore, the photolytic degradation of the dibenzofuran (DF) nucleus

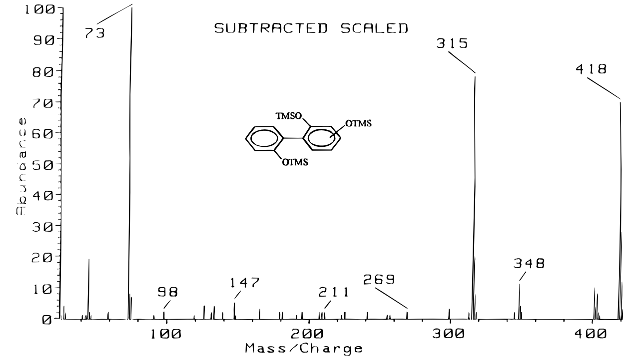


FIGURE 5. Electron impact mass spectrum of the TMS-derivatized photoproduct formed in the laboratory photolysis of 2,2′-dihydroxybiphenyl in natural water.

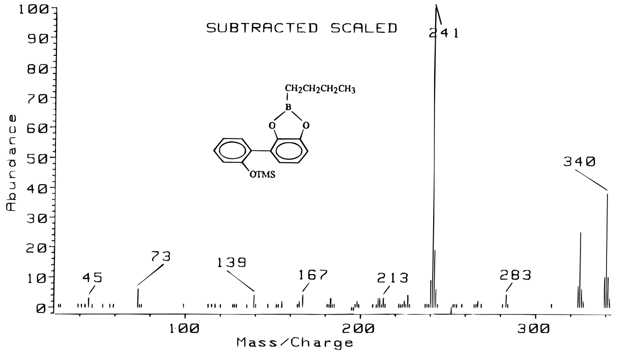
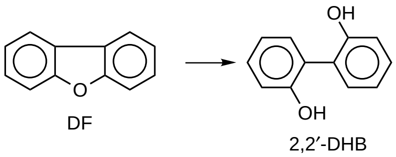


FIGURE 6. Electron impact mass spectrum of the *n*-butaneboronic acid/TMS-derivatized photoproduct formed in the laboratory photolysis of 2,2′-dihydroxybiphenyl in natural water.

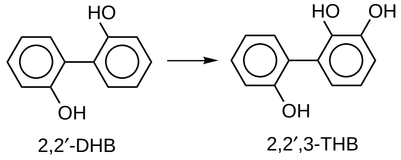
in natural water involves C−O cleavage and hydroxylation.



Previous studies have identified 2,2′-dihydroxybiphenyl as a photoproduct in the photolysis of nonchlorinated dibenzo-*p*-dioxin in organic solvents including toluene (*6*) and methanol (*7, 19*). With PCDDs, however, C−O cleavage is followed by reductive rearrangement to produce the photoproduct. Therefore, both the dibenzofuran and the dibenzo-*p*-dioxin structures appear to be photolytically unstable.

Photodegradation of 2,2′-Dihydroxybiphenyl in Lake Water. In photolytic studies of dibenzofuran with various exposure times, the concentration of the photoproduct (2,2′-DHB) increased initially but then slowly decreased with longer photolysis times. This suggested that 2,2′-DHB was an intermediate in the photolytic degradation of dibenzofuran. Since it is known that hydroxybiphenyls are photolabile (*10*), the photolytic fate of 2,2′-DHB was further investigated. In the photolysis of 2,2′-DHB in lake water, one significant photoproduct was evident in the TIC of the TMS-derivatized polar fraction when compared to a lake water control. The mass spectrum of the derivative (Figure 5) showed a base peak with m/z of 73 amu attributable to the $[Si(CH_3)_3]^+$ fragment, a strong apparent M^+ of 418 amu, and an $[M - 15]^+$ ion representing the loss of a CH_3 radical from the molecular ion. A strong peak at 315 amu is attributed to the $[M - Si(CH_3)_4(CH_3)]^+$ ion, a fragment previously reported in the EI mass spectra of 2,2′,3-trihydroxybiphenyl (*19*) and 2,3,4′-trihydroxybiphenyl (*20*). The isotope abundance ratio (M:M + 1:M + 2:M + 3) of 100:40.0:17.6:4.8 was in good agreement with that calculated for a TMS-trihydroxybiphenyl (THB), $C_{21}H_{34}O_3Si_3$, of 100: 39.6:18.0:4.6. Although the positions of the hydroxyl groups are not confirmed by this spectrum, the abundance of the 315 amu ion, attributed to the loss of $Si(CH_3)_4(CH_3)$ by interaction of two adjacent trimethylsilyl groups (*19*), suggested ortho-dihydroxy substitution.

In order to test for ortho-dihydroxy substitution, the *n*-butaneboronic acid derivatization procedure (*21, 22*) was utilized. A reconstructed chromatogram using the expected M^+ of 268 amu did not confirm the presence of a THB. Although the cyclic *n*-butylboronate may have formed, the volatility of the derivative may have been reduced by the other underivatized hydroxyl group in the molecule. By derivatizing the product with *n*-butaneboronic acid followed by derivatization in the injection port with BSTFA (*23*), a product with the expected M^+ of 340 amu was obtained (see Figure 6). This ion clearly contained the boron isotope pattern ($^{10}B/^{11}B$ in a 1:4 ratio). The isotope abundance ratio of the molecular ion cluster (18.6:100:26.3) compared favorably with the calculated ratios of the expected structure $C_{19}H_{25}O_3BSi$ (23.2:100:27.0). Fragmentation produced an $[M - 15]^+$ ion with the loss of a CH_3 radical from the TMS moiety. The $[M - CH_3]^+$ ion also exhibited the characteristic isotope pattern suggesting the presence of both Si and B. The base peak at M − 99 amu lacked the boron isotope pattern and may be formed by loss of $CH_3(CH_2)_3BO_2$ accompanied by H migration to the phenyl ring. A low abundance peak at M − 56 is the result of cleavage of the butyl group with H migration to boron. Although analytical standards were not available to confirm the structure of the photoproduct, the results indicate a trihydroxybiphenyl with two hydroxyls on adjacent carbons. Therefore, we tentatively conclude that the photoproduct is formed by hydroxyl attack ortho to one of the hydroxyl groups of 2,2′-dihydroxybiphenyl producing 2,2′,3- trihydroxybiphenyl in the process.



The low yield of this photoproduct suggested that THB is also an intermediate in the overall photodegradation of dibenzofuran. Although phenolic compounds are known to be readily oxidized by photolytically generated photooxidants (*24, 25*), additional photoproducts were either not isolated or derivatized by the procedures used in our experiments and hence were not detected.

Although several new photoproducts have been identified in the sunlight photolysis of PCDFs and dibenzofuran in natural water, the overall photolysis pathway remains unknown. The polar photoproducts detected in this study cannot account for the levels of nonextractable activity (Figure 2) that appear during the photolysis of PCDFs in natural water. However, considering the persistent nature of PCDFs, photodegradation of these compounds in surface waters is likely the most significant transformation reaction for these compounds in the aquatic environment.

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