

ENVIRONMENTAL AQUATIC PHOTODEGRADATION OF CHLORINATED DIBENZOFURANS AND THEIR PHOTOPRODUCTS

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Although polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are persistent organic contaminants, several studies have presented evidence that these chemicals are subject to photolytic degradation under environmental conditions. Quantum yields for the direct aqueous photolysis of PCDFs at 313 nm, determined in water/acetonitrile solutions due to the limited solubilities of these chemicals in water^{1,2}, range from 10^{-2} to 10^{-5} . Combined with the low molar absorptivities of these compounds above 290 nm, relatively slow direct photolysis rates are expected for PCDFs in the aquatic environment. However, several reports have shown that both PCDDs³ and PCDFs⁴ experience enhanced photodegradation rates in natural water compared to their rates in distilled water.

The objectives of this study were to investigate the photolytic behaviour of two toxic PCDF congeners, 2,3,7,8-tetrachlorodibenzofuran (TCDF) and 2,3,4,7,8-pentachlorodibenzofuran (PCDF), under environmental conditions. The study was designed to investigate the rates of both direct and indirect aqueous photolysis of these congeners under midsummer sunlight conditions, to identify photoproducts of these reactions, and to study the photochemistry of the photoproducts.

1. Kinetics

Kinetic studies were performed with ¹⁴C₆-dichlorophenyl-2,3,4,7,8-pentachlorodibenzofuran (¹⁴C-P₅CDF) and 4,6-³H₂-2,3,7,8-tetrachlorodibenzofuran (³H₄-CDF) in both distilled water/acetonitrile (10:25 v/v) and in filter-sterilized lake water from Lake 375 of the Experimental Lakes Area (ELA) near Kenora, Ontario, Canada. Sunlight exposure was carried out over a 3 day period at 50°N latitude (at ELA) in June, 1989, with 1 ng/mL solutions of the PCDFs in 50 mL Pyrex centrifuge tubes.

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Solutions were extracted with hexane and analyzed by HPLC with liquid scintillation detection to determine the radiolabel distribution.

The results showed relatively slow direct aqueous photolysis in distilled water, with pseudo-first-order rate constants (k_{DE}) of 0.106 and 0.015 d^{-1} for T_4 CDF and P_5 CDF, respectively, as summarized in Table 1. These values have been corrected for tube geometry in order to be applicable to surface waters. Photolysis rates were significantly faster in lake water, with net photolytic degradation rate constants of 0.58 and 3.59 d^{-1} for T_4 CDF and P_5 CDF, respectively (see Table 1). Dark controls showed no significant changes over the sampling period, hence volatilization and biological or chemical degradation cannot account for the loss of parent PCDF during these experiments. The 5.5 and 240-fold enhancement in photolysis rates for T_4 CDF and P_5 CDF in natural water indicates the importance of indirect or sensitized photolysis of PCDFs due to the presence of naturally occurring components in lake water.

TABLE 1. Rates of aqueous photolytic degradation of PCDFs under midsummer sunlight conditions at 50°N latitude.

CONGENER	$k_{DE}(d^{-1})^a$	$t_{1/2}(d)$	$k_{PE}(d^{-1})^b$	$t_{1/2}(d)$
2378-TCDF	0.106	6.5	0.58	1.2
23478-PCDF	0.015	46.2	3.59	0.19

^a k_{DE} is the pseudo-first-order direct aqueous photolysis rate constant determined in distilled water/acetonitrile solutions.

^b k_{PE} is the pseudo-first-order net aqueous photolysis rate constant determined in natural water.

2. Photoproduct Analysis

Direct aqueous photolysis of both PCDF congeners (in distilled water/acetonitrile solutions) was too slow for detectable amounts of degradation products to be produced. However, for the photolysis of both T_4 CDF and P_5 CDF in natural water, HPLC-LSC analysis revealed the presence of radiolabelled degradation products with retention times characteristic of lower chlorinated PCDF congeners. GC/MS analysis of nonpolar photoproducts produced during the photolysis of 23478- P_5 CDF confirmed the presence of at least three tetrachlorinated dibenzofurans. Similarly, a lone trichlorinated dibenzofuran was identified as a nonpolar product formed on photolysis of 2378- T_4 CDF. However, these

photoproducts were relatively short-lived intermediates which were further photolyzed during sunlight exposure. Previous studies have shown similar behaviour for several PCDDs in natural water.³

During photolysis of 23478-P₅CDF in natural water, the nonextractable ¹⁴C activity increased with photolysis time, suggesting the formation of a polar degradation product. Isolation of the polar fraction and derivatization with BSTFA followed by GC/MS analysis revealed a completely dechlorinated product with mass spectral features of a dihydroxybiphenyl. Although the GC retention time did not match those of several dihydroxybiphenyl standards, lack of additional standards precluded positive identification of the photoproduct.

3. Photoproduct Photochemistry

In order to determine a possible photodegradative pathway for PCDFs, the photolytic behaviour of several photoproducts or suspected photoproducts were examined in lake water, beginning with the nonchlorinated dibenzofuran. Photoproducts were generated in the laboratory using a 150-watt xenon lamp. Solid phase extraction using Waters cyanopropyl Sep-Paks isolated polar degradation products. After derivatization with BSTFA, HRGC/LRMS analysis confirmed 2,2'-dihydroxybiphenyl (DHB) as a major photoproduct in the photolysis of dibenzofuran.

Using 2,2'-DHB as starting material, 2,2',3-trihydroxybiphenyl (THB) was identified as a photoproduct by HRGC/LRMS after derivatization with butane boronic acid/BSTFA. The results suggest a possible route for the overall degradative pathway for the environmental photodegradation of PCDFs, involving dechlorination, ring opening, and hydroxylation.

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