Kinetics of sunlight photodegradation of 2,3,4,7,8-pentachlorodibenzofuran in natural water

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Abstract. The aquatic photodegradation of the environmental contaminant 2,3,4,7,8-pentachlorodibenzofuran (P₅CDF) was studied under midsummer sunlight conditions at 50°N latitude both in distilled water–acetonitrile solutions and in lake water. The observed net photodegradation rate of P₅CDF in natural water was 240-fold faster than the rate of direct photolysis in distilled water–acetonitrile solutions. The difference in rates of photodegradation is attributed to the action of sensitizers present in natural waters.

Keywords. Aquatic; photodegradation; polychlorinated dibenzofurans; sunlight.

1. Introduction

Polychlorinated dibenzofurans (PCDFs) are persistent environmental contaminants characterized by low water-solubilities (Friesen *et al* 1990b) and extreme hydrophobicity (Sijm *et al* 1990). 2,3,4,7,8-Pentachlorodibenzofuran is one of the most toxic PCDF isomers, with a toxic equivalency factor (TEF) of 0.5 (Safe 1990) and a single oral dose LD₅₀ value of < 10 µg/kg body weight for the guinea pig (Kociba and Cabey 1985).

Although these pollutants tend to resist chemical and microbial degradation, there is some evidence that they undergo aqueous photodegradation. The quantum yields for the direct photolysis of PCDFs in water–acetonitrile mixtures at 313 nm vary from 10⁻² to 10⁻⁵ for a series of PCDFs (Choudhry *et al* 1990; Foga 1991). Recent reports (Dung and O'Keefe 1992) indicate that several tetrachlorinated PCDFs are photolyzed in both distilled and natural waters under sunlight conditions, with degradation rates in natural water roughly 2 times faster than in distilled water.

The objective of this study was to determine the rate of sunlight photolysis of 2,3,4,7,8-pentachlorodibenzofuran under environmental conditions, and in particular to ascertain the importance of direct versus indirect photolysis.

2. Experimental

2.1 Chemicals

¹⁴C₆-dichlorophenyl-2,3,4,7,8-pentachlorodibenzofuran (¹⁴C-P₅CDF) with a specific activity of 1.25 × 10¹⁰ Bq/mmol, was purchased from Wellington Laboratories (Guelph,

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ON) and purified (to a radiopurity of 99.9%) by RP-HPLC with 85:15 CH₃OH/H₂O as the mobile phase and redissolved in acetonitrile.

Liquid scintillation fluors, Scintiverse II and Atomlight, were purchased from Fisher Scientific (Winnipeg, MB) and Biotechnical Systems (Boston, MA), respectively.

All solvents used in sample preparation or as HPLC mobile phases were Burdick & Jackson Brand (High Purity) from Baxter Diagnostics Corporation, Canlab, Winnipeg, MB.

2.2 Instrumentation

Quantitative analysis of ¹⁴C-P₅CDF was carried out with a Waters Associates HPLC system equipped with a Model 6000A pump, a Rheodyne Model 7125 injector, and a 25 cm × 3.2 mm μ Bondapak C₁₈ column (Waters Scientific, Mississauga, ON). Three-minute fractions of HPLC eluent were collected, mixed with 12 ml of Scintiverse II, and analysed for carbon-14 on a Beckman LS 7500 Liquid Scintillation System.

2.3 Kinetics of sunlight photolysis

All glassware was thoroughly cleaned and sterilized at 180°C for 4–5 hours.

Direct aqueous photolysis was studied by preparing solutions of ¹⁴C-2,3,4,7,8-P₅CDF (1.1 ng/ml) in 10:25 (v/v) filter-sterilized CH₃CN/HPLC water (Mill *et al* 1982) and exposing to sunlight in 50 ml Pyrex centrifuge tubes. Indirect aqueous photolysis was monitored under similar conditions but in filter-sterilized lake water obtained from Lake 375 of the Experimental Lakes Area (ELA) near Kenora, ON. Dark controls, in which P₅CDF solutions in lake water were wrapped with aluminium foil to prevent sunlight photolysis, were used to check for biological and chemical degradation. The tubes were placed in a rack near the surface of Lake 375 (ELA), with sunlight exposures carried out over a 3-day period in June 1989.

All solutions were adjusted to pH 9 and extracted with four 5 ml portions of hexane. The extracts were dried by passing through a Na₂SO₄ column and concentrated prior to analysis. Concentrations of parent ¹⁴C-P₅CDF were determined by HPLC-LSC using 85:15 CH₃OH/H₂O as the mobile phase. The extracted aqueous phase was tested for nonextractable ¹⁴C by adding 12 ml of Atomlight to 4 ml of water and counting by LSC. A standard ¹⁴C-P₅CDF was used to establish both the extraction efficiency (105%) and the overall recovery of P₅CDF at the analytical stage (90%).

3. Results and discussion

3.1 Direct photolysis

The absorption spectrum of P₅CDF shows a weak, tailing band above 290 nm (figure 1) producing the potential for direct photolytic degradation of this compound under environmental conditions. However, the aqueous photolysis of P₅CDF was extremely slow in water–acetonitrile solutions (figure 2), with a pseudo-first-order direct photolysis rate constant (k_{DE}) of $0.015 \pm 0.007 \text{ d}^{-1}$ ($t_{1/2} = 46 \text{ d}$). This rate constant has been corrected for tube geometry (Dulin and Mill 1982) to provide a value applicable to surface waters. Quantitative recoveries of P₅CDF from the dark controls

Figure 1. The absorption spectrum of a 1.2×10^{-5} M solution of 2,3,4,7,8-pentachlorodibenzofuran in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ determined with a Hewlett-Packard 8452A diode array spectrophotometer using a quartz cell with a 1 cm pathlength.

sampled over the entire exposure period indicated negligible losses due to biological degradation, volatilization, and/or analytical procedures. Therefore, the observed decreases are attributed to photolytic degradation of this congener under sunlight conditions.

No ^{14}C -labelled intermediates could be detected by HPLC-LSC analysis and no detectable levels of nonextractable ^{14}C appeared throughout the entire experiment. The results are consistent with recent reports which showed that polychlorinated dibenzofurans (Dung and O'Keefe 1992) and polychlorinated dibenzo-*p*-dioxins (Dulin *et al* 1986; Friesen *et al* 1990a) undergo very slow direct aqueous photolysis under environmental conditions.

3.2 Indirect sunlight photolysis

P_5CDF transformation in filter-sterilized lake water was much more rapid with essentially complete degradation after 6 hours of sunlight exposure. Although degradation rates are affected by solar flux and temperature changes, fitting the data to a first-order model (figure 2) and correcting for tube geometry provided a net pseudo-first-order photolytic degradation rate constant (k_{PE}) of $3.6 \pm 0.3 \text{ d}^{-1}$ ($t_{1/2} = 0.19 \text{ d}$). Dark controls showed no significant changes over the sampling period, hence biological and chemical degradation was again negligible.

The dramatic increase in the rate of photolysis of P_5CDF in lake water relative to distilled water (240-fold) is attributed to the action of photosensitizers present in natural waters. Indirect photolysis of organic contaminants in natural waters is known to be sensitized by dissolved humic material (Zafiriou *et al* 1984; Mill 1989). The dissolved organic carbon (DOC) content of the lake water used in this study ($440 \mu\text{M}$) is believed to contribute to the rapid photolytic destruction of P_5CDF . Photooxidation

Figure 2. Midsummer sunlight photolysis of 2,3,4,7,8-pentachlorodibenzofuran in lake water (○) and in distilled water-acetonitrile solutions (●) at 50°N latitude.

Figure 3. Reconstructed chromatogram for the HPLC-LSC analysis of the hexane extract of a solution of 2,3,4,7,8-pentachlorodibenzofuran exposed to sunlight for 6 h in filter-sterilized lake water. The major bands include unreacted parent P_5 CDF ($t_r = 45$ min) and a suspected T_4 CDF ($t_r = 33$ min).

by singlet oxygen (Zafiriou *et al* 1984; Haag and Hoigne 1986), reaction with photochemically generated peroxy and hydroxy radicals (Mill 1989), triplet energy transfers (Zepp *et al* 1985), and electron transfers (Zafiriou *et al* 1984) are possible routes of photodegradation of chlorinated dibenzofurans in natural waters.

Only one apparent nonpolar ^{14}C -labelled degradation product was isolated by HPLC-LSC. This band (figure 3), with a chromatographic retention time corresponding to that of a tetrachlorinated dibenzofuran (T_4 CDF) standard ($t_r = 33$ min), reached a maximum concentration after 6 hours of sunlight exposure. However, chromatographic resolution was not adequate to determine the identity of the product or to verify the number of products formed. The disappearance of the product on longer sunlight exposures supported the formation of lower chlorinated dibenzofurans which would then undergo further photolytic degradation. Significant amounts (42%) of ^{14}C were non-extractable following 52 hours of exposure to sunlight, suggesting formation of polar degradation products. Previous studies have shown similar behaviour for photolysis of several polychlorinated dibenzo-*p*-dioxins in natural water (Friesen *et al* 1990a).

Although sunlight emits energy of 35.8–98.6 kcal/mol in the 290–800 nm region (Leifer 1988), sufficient to break typical Ar-O and C-Cl bonds (Lyman *et al* 1982), 2,3,4,7,8-pentachlorodibenzofuran was essentially nonreactive via direct aqueous photolysis. The large enhancement in the rate of photolytic degradation of P₅CDF in natural water relative to distilled water at 50°N latitude in midsummer indicates the important effect that naturally occurring components in lake water have on environmental photodegradation. Further work is underway to identify the degradation products and to determine the role of various sensitizers in the photolytic reaction.

Acknowledgements

Financial support by the Natural Sciences and Engineering Research Council of Canada and by the University of Winnipeg is gratefully acknowledged.

References

- Choudhry G G, Foga M M, Webster G R B, Muir D C G and Friesen K J 1990 *Toxicol. Environ. Chem.* **26** 181
- Dulin D, Drossman H and Mill T 1986 *Environ. Sci. Technol.* **20** 72
- Dulin D and Mill T 1982 *Environ. Sci. Technol.* **16** 815
- Dung M and O'Keefe P W 1992 Organohalogen compounds. *Proceedings of the 12th International Symposium on Dioxins and Related Compounds* (Helsinki: Finnish Institute of Occupational Health) vol. 8
- Foga M M 1991 *Environmental aquatic photochemistry of 2,3,7,8-tetrachlorodibenzofuran and 2,3,4,7,8-pentachlorodibenzofuran*, M Sc thesis, University of Manitoba
- Friesen K J, Muir D C G and Webster G R B 1990a *Environ. Sci. Technol.* **24** 1739
- Friesen K J, Vilk J and Muir D C G 1990b *Chemosphere* **20** 27
- Haag W R and Hoigné J 1986 *Environ. Sci. Technol.* **20** 341
- Dulin D, Drossman H and Mill T 1986 *Environ. Sci. Technol.* **20** 72
- Leifer A 1988 *The kinetics of environmental aquatic photochemistry – theory and practice* (Washington, DC: Am. Chem. Soc.) pp. 7, 100
- Lyman W J, Reehl W F and Rosenblatt D H 1982 *Handbook of chemical property estimation methods – environmental behaviour of organic compounds* (New York: McGraw-Hill)
- Mill T 1989 *Environ. Toxicol. Chem.* **8** 31
- Mill T, Mabey W R, Bomberger D C, Chou T W, Hendry D G and Smith J H 1982 In Laboratory protocols for evaluating the fate of organic chemicals in air and water, EPA Final Report EPA-600/3-82-022, 50–99
- Safe S 1990 *Crit. Rev. Toxicol.* **21** 51
- Sijm D T H M, Wever H, de Vries P J and Opperhuizen A 1990 *Chemosphere* **19** 263
- Zafiriou O C, Jousset-Dubien J, Zepp R G and Zika R G 1984 *Environ. Sci. Technol.* **18** 358A
- Zepp R G, Schlotzhauer P F and Sink R M 1985 *Environ. Sci. Technol.* **19** 74