

## The Role of Natural Organic Compounds in Photosensitized Degradation of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans

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### Introduction

It is well documented that certain xenobiotics photolyze more rapidly in natural water than in pure water. Enhancement of the degradation process can occur through reactions of pollutants with reactive oxygen species (ROS) produced by photolysis, such as hydroxyl radicals, peroxy radicals, singlet oxygen etc. or through electron/photon transfer from a photosensitized natural compound. Previous studies conducted in this laboratory showed that the sunlight photodegradation rates of 1,2,7,8-tetrachlorodibenzofuran (TCDF) and 2,3,7,8-TCDF were increased by factors of two in natural water relative to rates in distilled water (1). Other investigators have shown that <sup>14</sup>C-labeled 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin (PeCDD) and 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1,2,3,4,6,7,8-HpCDD) are photodegraded at rates 13 to 15 times faster in natural water than in acetonitrile/water (2).

In this study the effects of natural organic substances on the photodegradation of PCDDs and PCDFs were investigated as follows. First, the results from the earlier study were confirmed by photolyzing 1,2,7,8-TCDD (TCDD); TCDF; OCDD and OCDF in natural water from seven different locations. Secondly the PCDD/PCDF compounds were photolyzed in aqueous suspensions of algae and solutions of two chemicals prevalent in natural waters, humic acid and tryptophan.

### Materials and Methods

The natural water samples were obtained from marshes, ponds and lakes in New York State at the locations listed in Table 1. They were stored in amber borosilicate bottles in the dark at 4 °C until used. Aqueous solutions of PCDDs/PCDFs were prepared using generator columns (1). After filtering the natural water samples through a 2.7 µm glass fiber filter followed by a 0.2 µm membrane filter they were mixed with the pure aqueous PCDD/PCDF solutions, generally in a 50:50 v/v ratio and equilibrated for 16 hr before being used for photolysis experiments. Photolysis solutions containing L-tryptophan or algal suspensions were prepared in the same manner using stock solutions of L-tryptophan or stationary stage cultures of *Senedesmus* algae respectively. Humic acid (HA), from Aldrich Chemical Co., Inc., Milwaukee, USA was dissolved in 0.1% NaOH, centrifuged at 5000 rpm and diluted 50/50

with distilled water prior to mixing with the pure PCDD/PCDF solutions.

Photolysis was carried out in the laboratory with UV (300 nm) and halogen lamps or outdoors in sunlight (1). In each case the aqueous solutions were photolyzed in 150 ml Corex centrifuge bottles which transmit 10%, 30% and 50% light at 267, 280 and 288 nm respectively. Methylene chloride extracts were analyzed by selected ion monitoring GC/MS for parent and dechlorinated PCDDs/PCDFs. Total and dissolved organic carbon (DOC) concentrations were determined with a Beckman 915-B Total Organic Carbon Analyzer and UV/VIS spectra were obtained with a Beckman DU 640 Spectrophotometer. Light intensity was measured with a potassium ferrioxalate actinometer (1). All reported photolysis data were obtained from duplicate experiments, with less than 17% variability between individual results. Half-lives were calculated assuming first order kinetics.

### Results and Discussion

The half-lives of TCDD, TCDF, OCDD and OCDF after exposure to sunlight in either distilled water or in natural water samples are shown in Table 1:

Table 1. Photolysis of PCDDs and PCDFs in Natural Waters Exposed to Sunlight

Water Source	TCDD	Half-life ( $t_{1/2}$ , hr)		
		OCDD	TCDF	OCDF
Pure water	8.7	20	9.5	9.6
Ann Lee Pond	3.8	30	4.3	11
Beaver Pond	3.6	7.5	4.0	8.0
Pond in Delmar	3.5	19	3.6	16
Hudson River Marsh	4.0	5.6	5.0	11
Onondaga Lake	3.5	11	3.9	15
Pond in Schaghticoke	4.6	19	4.5	17
Saratoga Lake	5.9	17	4.7	23
Average $\pm$ S.D	4.1 $\pm$ 0.8	16 $\pm$ 7.7	4.3 $\pm$ 0.5	14 $\pm$ 4.6
Relative S.D. (%)	19	49	12	32

The half-lives of TCDD and TCDF were approximately two times shorter than their half-lives in distilled water. However the natural water half-lives of OCDD and OCDF showed considerable variation, in some cases the half-lives were shorter than the distilled water half-lives and in other cases longer. Since OCDD and OCDF are more strongly bound to organic molecules than TCDD or TCDF, in the water samples with longer half-lives the octa congeners could be bound to molecules which are not photosensitizers or to sites on a polymeric molecule such as HA which are remote from sensitizing sites. The DOC content ranged from 6.0 to 24 mg/L and it was found that there was no relationship between half-life and DOC data. This also supports the hypothesis that only selected natural compounds are acting as photosensitizers and these compounds could be making a minimal contribution to the DOC content.

Aromatic amino acids are certainly a potential group of photosensitizing compounds in natural waters. Results from the exposure of PCDD/PCDF solutions containing L-tryptophan

to either 300 nm light or sunlight are shown in Table 2:

Table 2. Effect of Tryptophan on the Photolysis of PCDDs and PCDFs in Aqueous Solution

300 nm

Solution	Half-life ( $t_{1/2}$ , min)	
	TCDD	TCDF
Pure water	29	50
Tryptophan (mg/L)		
0.1	5.8	9.9
1.0	5.3	9.2
10	2.9	6.3

Sunlight

Solution	Half-life ( $t_{1/2}$ , hr)			
	TCDD	OCDD	TCDF	OCDF
Pure water	7.5	24	15	12
Tryptophan (10 mg/L)	3.9	25	6.0	17

At 300 nm the half-lives of TCDD and TCDF were decreased by almost an order of magnitude in the presence of 10 mg/L tryptophan. The increased photodegradation rates probably occurred by either excitation or electron transfer. In sunlight the half-lives were only decreased by a factor two, reflecting the lower sunlight intensity in the 300 nm region compared to the UV lamp. The lack of a photosensitizing effect on either OCDD or OCDF degradation can be explained by the fact that the  $\lambda_{max}$  of tryptophan at 280 nm is closer to the  $\lambda_{max}$  values of TCDD and TCDF (298 and 296 nm respectively) than the  $\lambda_{max}$  values of OCDD and OCDF (318 and 305 nm respectively).

Filtered and unfiltered algal solutions containing TCDD and TCDF were exposed to light from a halogen lamp. In the filtered solutions the half-lives of the two compounds did not differ from the control values whereas the unfiltered solutions had half-lives which were decreased by a factor of two (Table 3). These results showed that pigments in the algal cells were responsible for the photosensitizing effect and not any DOC which may have been released into the water. When chloroplasts were isolated from spinach leaves they were also found to decrease the half-life of TCDF solutions exposed to sunlight, providing confirmatory evidence for the role of chlorophyll pigments in the sensitization of PCDD/PCDF degradation by sunlight.

Table 3. Effect of Algae on the Photolysis of TCDD and TCDF in Aqueous Solutions

Medium	Half-life ( $t_{1/2}$ , hr)	
	TCDD	TCDF
Pure water	3.7	3.8
Filtered algal solution	3.5	3.7
Unfiltered algal solution	2.0	2.7

Humic acids are the most ubiquitous organic compounds in natural waters and the effect of Aldrich HA on PCDD/PCDF photodegradation is shown in Table 4. At 300 nm the minimum half-life for TCDF was found at a HA concentration of 1.1 mg/L. However the minimum half-life for TCDD may have been at a HA concentration below 0.03 mg/L, the lowest concentration used in the experiment.

Table 4. Effect of Humic Acid on the Photolysis Half-lives of PCDDs and PCDFs

<u>300 nm</u>				
Solution	TCDD	Half-life ( $t_{1/2}$ , min)		
		OCDD	TCDF	OCDF
Pure water	29	440	50	260
Humic acid (mg/L)				
11	35		53	
5.4	22		29	
1.1	8.7		12	
0.3	5.0		15	
0.1	5.9	270	15	100
0.03	4.1		14	

<u>Sunlight</u>				
Solution	TCDD	Half-life ( $t_{1/2}$ , hr)		
		OCDD	TCDF	OCDF
Pure water	7.5	24	15	12
Humic acid				
1.1 mg/L	9.1	11	15	7.1

The photosensitizing effect of HA at 300 nm was stronger for the tetra congeners than the octa congeners. However the reverse was found in sunlight. Differences in the emission spectra of sunlight and the medium pressure mercury lamps may explain the photoreactivity differences between the two light sources. Humic acid has a relatively high molar absorptivity near 300 nm. However since sunlight intensity is minimal at this wavelength only a small fraction of the HA molecules will be energized. These excited molecules will probably undergo radiationless transitions or quenching before sensitizing PCDD/PCDF photolysis. Sunlight intensity increases at wavelengths above 300 nm, leading to an increased number of excited HA molecules which could sensitize OCDD/OCDF photolysis. On the other hand the maximum emission from the mercury lamp was around 300 nm, close to the  $\lambda_{max}$  values of TCDD and TCDF.

#### References

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