

## POLYCHLORINATED DIBENZO-*p*-DIOXINS (PCDDs): EFFECTS OF SENSITIZERS AND INHIBITORS ON PHOTOTRANSFORMATION

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### 1. Introduction

Photodechlorination is perhaps the most important transformation pathway for polychlorinated dibenzo-*p*-dioxins (PCDDs) in environmental compartments exposed to sunlight. As a result, a number of studies on this subject have been reported in the literature<sup>1-8</sup>). The majority of these studies have been devoted to phototransformation processes in the solution phase. A few studies have also been reported on dioxins in the solid surfaces. In the case of congeners with four or more chlorines, the process is generally thought to proceed either through reductive dechlorination or the cleavage of the carbon-oxygen bond. The evidence of photoproducts resulting in cleavage of the carbon-oxygen bond has been reported by Miller and co-workers<sup>9</sup>). It has also been demonstrated that the efficiency of phototransformation processes is affected by environmental parameters such as the presence of proton or electron donors. For example, phototransformation efficiency of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin at 313nm was found to be 20 times higher in hexane solution than in water:acetonitrile solution<sup>10</sup>). The efficiency of the phototransformation has also been shown to be affected by the presence of sensitizing species. The sensitized photo oxidation of phenols in the presence of fulvic acid has been observed by Faust *et al*<sup>11</sup>).

The quantum yield and the photo half-life are good semiquantitative measures of phototransformation efficiency. However, only a limited number of studies dealing with these measurements for phototransformation of chlorinated dioxins have been reported in the literature. Quantum yields for photo transformation of pentachlorodibenzo-*p*-

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dioxin (P<sub>5</sub>CDD), hexachlorodibenzo-*p*-dioxin (H<sub>6</sub>CDD), heptachlorodibenzo-*p*-dioxin (H<sub>7</sub>CDD) and octachlorodibenzo-*p*-dioxin (OCDD) were determined by Choudhary *et al* in natural aquatic systems and acetonitrile water mixtures. The quantum yields for these compounds were found to range from  $2.1 \times 10^{-3}$  to  $2.26 \times 10^{-5}$  mol. einstein<sup>-1</sup>. The phototransformation efficiency was also found to vary within congeners with the same number of chlorines. Quantum efficiencies for three tetrachloro dioxins were reported to range from  $1 \times 10^{-3}$  to  $2.8 \times 10^{-3}$  mol. einstein<sup>-1</sup> <sup>13</sup>). These results indicate that the efficiency of the photoprocess is affected by the medium as well as the position of chlorine substitutions<sup>14</sup>). There is some evidence that other dissolved species can affect phototransformations of chlorinated dioxins. However, there is no quantitative data on the subject, and the present studies were undertaken to obtain these data. Such data are important for both predicting environmental stability of dioxins and developing photodegradation-based remedial measures.

## 2. Experiments

The irradiation experiments were carried out with a modified spectrophotometer. A xenon arc lamp served as the light source. An alkane/alcohol mixture was used as the solvent, since such mixtures have been shown to be effective for removing chlorinated dioxins from soils<sup>15</sup>). The incident light intensity was normalized with *O*-nitrobenzaldehyde as the chemical actinometer. The molar yield of nitrobenzoic acid after irradiation of benzaldehyde was determined with reverse phase high pressure liquid chromatography (HPLC)<sup>16</sup>). The yield was used for determination of the system intensity.

PCDD irradiation experiments were carried out in the standardized radiation set-up. Irradiation experiments in the laboratory were carried out at 313nm. The irradiation period was varied from 2 to 200 hours. Experiments were carried out with pure PCDD solutions and PCDD solutions containing pentachlorophenol, naphthalene, phenanthrene and anthracene. These are the predominant contaminants at wood treatment sites. Irradiation experiments were also carried out in the presence of photosensitizers, such as hydrogen peroxides and azobis (isopropionitrile) (AIBN). For these experiments a small amount of methanol was added to the decane/butanol mixtures to enhance H<sub>2</sub>O<sub>2</sub> solubility in the alkane/alcohol mixture. After the set exposure period, an aliquot of the irradiated solution was removed, mixed with appropriate <sup>13</sup>C labeled chlorinated dioxin (internal standard) and analyzed by a gas chromatography-mass spectrometry system.

Chromatography separations were carried out with a 15m x 0.25mm (i.d.) fused silica column (DB-5, J&W Scientific, Folsom, CA). The gas chromatographic inlet and transfer line temperatures were maintained at 275°C. The column oven temperature was varied from 120°–290°C at 10°C/min. Helium was used as the carrier gas. The quadrupole mass spectrometer was operated in selected ion monitoring mode, and two ions for each congener group (dichloro through octachlorodibenzo-*p*-dioxin) were monitored.

The non-labeled PCDD standards were purchased from Ultra-Scientific Inc., North Kingstown, RI. The <sup>13</sup>C labeled PCDD standards were purchased from Cambridge Isotope Lab Inc., Andover, MA. Naphthalene, phenanthrene, anthracene and penta-

chlorophenol were purchased from Sigma Inc., St. Louis, MO. The analytical grade solvents were obtained from Fisher Scientific, Pittsburgh, PA. The standard chemicals and solvents were used without further purification.

### 3. Results and Discussion

The results of irradiation experiments revealed that the phototransformation of PCDDs followed a first order kinetics under all experimental scenarios. The first order plots for polychlorodibenzo-*p*-dioxin (PCDD) in the absence of sensitizers and inhibitors are presented in Figure 1. The rate constant for phototransformation under each condition was determined through the first order expressions, which are presented below:

$$\ln \frac{C_0}{C_t} = K_{sp} \cdot t \quad [1]$$

where

$C_0$  = initial concentration of PCDDs  
 $C_t$  = concentration of PCDDs at time  $t$   
 $t$  = irradiation time (hours)

The quantum yield was determined through the following expression

$$f = \frac{K_{sp}}{I_0} e l \quad [2]$$

where

$f$  = quantum yield (mole.einstein<sup>-1</sup>)  
 $K_{sp}$  = first order rate constant  
 $I_0$  = intensity of incident light  
 $e$  = molar extinction coefficient  
 $l$  = pathlength of light

The intensity of incident light was determined from phototransformation of the chemical actinomer (*o*-nitrobenzaldehyde) by the expression:

$$I_0 = \frac{C_t}{\phi_A} t \quad [3]$$

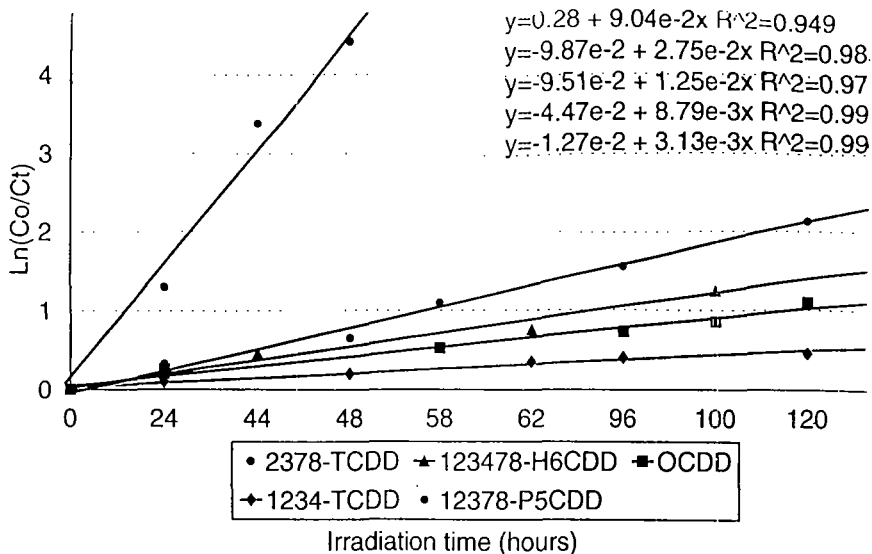
where

$\phi_A$  = quantum yield of *o*-nitrobenzaldehyde  
 $C_t$  = the concentration of photoproduct from chemical actinomer  
 $t$  = exposure time

The intensity of incident light in the photocell used for the present study was found to be  $2.3 \times 10^{-7}$  einstein/second. The molar extinction coefficients were determined from absorption data obtained with a UV spectrophotometer. The values for 2,3,7,8-TCDD, 1,2,3,4,7,8-H<sub>6</sub>CDD, OCDD and 1,2,3,4-TCDD were calculated to be 2930, 4150, 3980 and 2210 [M<sup>-1</sup>cm<sup>-1</sup>], respectively.

The phototransformation efficiencies for individual PCDD congeners in the alkane/alcohol mixture are shown in Figure 1. The half-life and quantum yield data are pre-

sented in Table 1. The data revealed that position of chlorine substitution (either peri or lateral) plays an important role in determining the role of PCDD phototransformation, and similar results have been reported earlier.



Irradiation wavelength: 313nm; Solvent: 20% butanol in decane; Initial OCDD concentration  $6.7 \times 10^{-6}M$ ; Ct=concentration of OCDD at given sampling period;

The introduction of co-contaminants to PCDD solutions led to a significant decrease in the quantum yield. The decrease was found to be dependent upon both the concentration and the extinction coefficient of the co-contaminants. The largest decrease

Table 1. Quantum yield, half-life and rate constants of various dioxin congeners

PCDDs	Rate Constant (hr <sup>-1</sup> )	Half-life (hr)	Quantum Yield (mol/E)
2,3,7,8-TCDD	$9.04 \times 10^{-2}$	7.7	$1.62 \times 10^{-2}$
1,2,3,4,7,8-H <sub>6</sub> CDD	$1.25 \times 10^{-2}$	55.4	$1.58 \times 10^{-3}$
OCDD	$9.54 \times 10^{-3}$	72.6	$1.25 \times 10^{-3}$
1,2,3,4-TCDD	$3.14 \times 10^{-3}$	220.7	$7.4 \times 10^{-4}$

occurred in the presence of anthracene, the compound with the highest extinction coefficient. The results of the OCDD experiments are tabulated in Table 2.

Table 2. Effects of co-contaminants on quantum yield, half-lives and phototransformation rate constant of OCDD

Contaminants	rate constant (hr <sup>-1</sup> )	Half-life (hr)	quantum yield (mol/E)
OCDD:Naph (1:50)	$6.63 \times 10^{-3}$	104.5	$8.74 \times 10^{-4}$
OCDD:Phen (1:50)	$6.48 \times 10^{-3}$	107.1	$8.55 \times 10^{-4}$
OCDD:PCP (1:50)	$5.92 \times 10^{-3}$	117.1	$7.81 \times 10^{-4}$
OCDD:Anth (1:50)	$4.71 \times 10^{-3}$	147.1	$6.23 \times 10^{-4}$

A similar decrease of photodegradation was also observed for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). These results are given in Table 3.

Table 3. Effects of co-contaminants on quantum yield, and half-life and rate constant of TCDD

Contaminants	Rate Constant (hr <sup>-1</sup> )	Half-life (hr)	Quantum Yield (mol/E)
2,3,7,8-TCDD only	$9.04 \times 10$	7.8	$1.62 \times 10$
TCDD:Mixed(1.50 each, w/w)	$2.26 \times 10$	30.7	$4.05 \times 10$

Mixed: a mixture of the pentachlorophenol, naphthalene, phenanthrene and anthracene

Chromatographic profiles of timed irradiation experiments for OCDD are shown in Figure 2. The results show that the irradiation of OCDD results in the formation of two heptachlorodibenzo-*p*-dioxins as the photoproducts through hydrodechlorination. The

Table 4. Effects of sensitizers on quantum yield, half-life and rate constants of OCDD

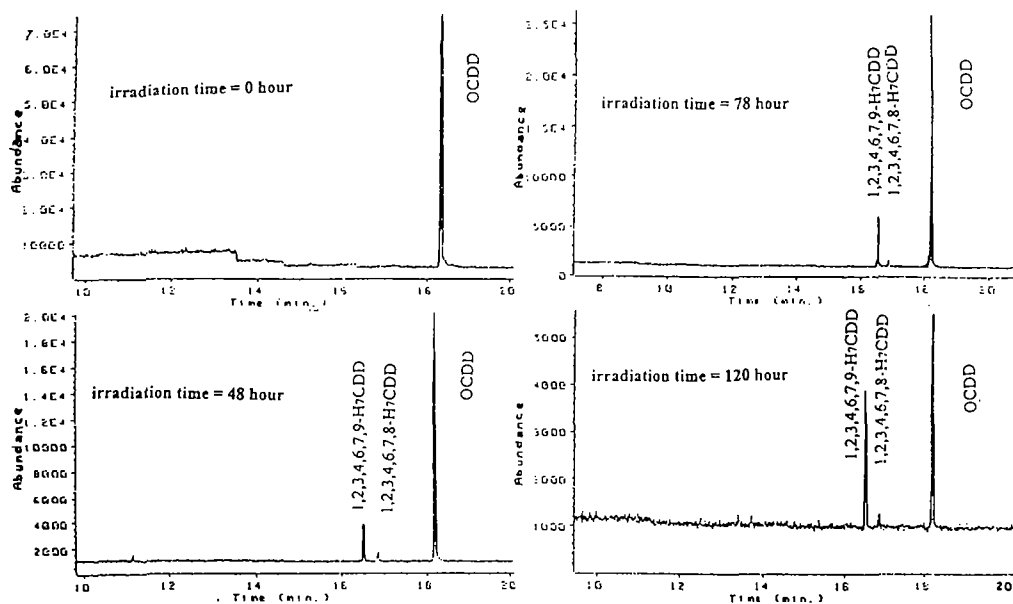
Contaminants	Rate Constant (hr <sup>-1</sup> )	Half-life (hr)	Quantum Yield (mol/E)
OCDD only	$9.54 \times 10^{-3}$	72.6	$1.25 \times 10^{-3}$
OCDD:AIBN (1:1000 w/w)	$1.74 \times 10^{-2}$	39.8	$2.30 \times 10^{-3}$
OCDD:H <sub>2</sub> O <sub>2</sub> (1:1000 w/w)	$3.75 \times 10^{-2}$	18.4	$4.95 \times 10^{-3}$

predominant product was found to be 1,2,3,4,6,7,9-H<sub>7</sub>CDD, which resulted from the loss of a chlorine from one of the four lateral positions. The other photoproduct was 1,2,3,4,6,7,8 H<sub>7</sub>CDD. This resulted from the loss of the peri chlorine. The relative ratio of the lateral loss vs. peri loss product was found to be approximately 10:1, indicating a clear preference for removal of lateral (2,3,7,8) chlorines.

#### 4. Conclusion

The quantum yield and photo half-life of various dioxin congeners was determined under varied experimental conditions. The results demonstrate that the photodegradation efficiency of co-contaminants is curtailed by chemicals associated with dioxins at

wood treatment sites. On the other hand, photodegradation rate can be enhanced significantly with photosensitizers such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).



## 5. References

- 1) Plimmer, J.R., M.I. Klingebiel, D.G. Crosby and A.S. Wong, *Adv Chem. Sc.*, No. 120, 144 (1971).
- 2) Crosby, D.G., A.S. Wong, J.R. Plimmer and E.A. Woolson, *Science*, 173, 748-749 (1971).
- 3) Crosby, D.G., A.S. Wang, *Science*, 195, 1337-1338 (1977).
- 4) Choudhry, G.G. and G.R. Webster, *Toxicol. Environ. Chem.*, 14, 43-61 (1987).
- 5) Koester, C.J. and R.A. Hites; *Environmental Sci. and Technol.* 26, 502-507 (1992).
- 6) Tysklind M., K. Lundgren, C. Rappe, L. Erickson and M. Sjostrom, *Organohalogen Compounds*, 8, 173 (1992).
- 7) Crosby, D.G., A.S. Wong, J.R. Plimmer and E.A. Woolson, *Science*, 173, 748-749 (1971).
- 8) Sivils, L.D., S. Kapila, Q. Yan and A.A. Elseewi, *J of Chromotography A*. 688. 1221-1230 (1994).
- 9) Kietiwong, S., L.V. Nguyen, V.R. Herbert, M. Hackett, G.C. Miller, M.J. Miller and R. Hitzel, *Environ. Sci. Technology*, 1575-1580 (1990).
- 10) Dulin, D. and T. Mill, *Environ. Sci. Technol.* 16, 815 (1982).
- 11) Faust, B.C. and J. Hoigne, *Environ. Sci. Technol.* Vol 21, No. 10, 957-963 (1987).
- 12) Choudhry, G.G. and G.R.B. Webster, *Toxicol. Environ. Chem* 14, 43-61 (1987).
- 13) Koshika, M., M. Ishizaka, T. Yamada and T. Murai, *J. Pesticide Sci.* 15, 39-45 (1990).
- 14) Yan, Q., L.D. Sivils, S. Kapila and A.A. Elseewi, *Chemosphere*, Vol. 29, Nos. 9-11, 2183-2192 (1994).
- 15) Yanders, A. F., C.E. Orazio, R.K. Puri and S. Kapila, *Chemosphere*, 18, 841 (1989).
- 16) Choudhry, G.G. and G.R.B. Webster, *ACS Symposium Series* 327, 61-74 (1987).