

## PCDD/PCDF Formation by UV Photolysis of Pentachlorophenol With and Without the Addition of Hydrogen Peroxide

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### Introduction

The use of ultraviolet (UV) light to degrade and destroy organic pollutants in contaminated waters is now a well-developed commercial process. The most common technology involves addition of hydrogen peroxide to the contaminated water and irradiation with powerful (up to 30 kW) UV lamps. Highly reactive hydroxyl radicals are generated from hydrogen peroxide under UV conditions. These radicals initiate oxidation and eventually mineralize the organic pollutants to CO<sub>2</sub>, H<sub>2</sub>O and mineral acids (e.g. HCl from any organic chlorine present). Such processes are known as advanced oxidation processes (AOPs) since the rate of oxidation is greatly enhanced relative to direct photolysis.

Pentachlorophenol (PCP) is widely used as a wood preservative. Consequently, many groundwaters in the vicinity of wood preserving plants have been contaminated. Other previous uses included applications as a fungicide, bactericide, herbicide, molluscicide, algicide and insecticide. The photochemical degradation of PCP has been extensively studied<sup>1-5)</sup> as has the behaviour of PCP in artificial freshwater streams<sup>6)</sup> and the fate and biological effects of PCP in natural outdoor ponds<sup>7)</sup>. Other contaminated matrices, such as soils, have also been investigated<sup>8,9)</sup>.

In consideration of the time required for biodegradation and natural (solar) photodecomposition processes to occur, the development of AOPs that can be readily applied to the treatment of PCP-contaminated waters is of prime importance. The use of AOPs for the treatment of PCP-contaminated waters has come under scrutiny owing to the possibility of producing intermediates which are far more toxic than is PCP. Lamparski and co-workers reported the formation of chlorinated dibenzo-p-dioxins from the photolysis of PCP-treated wood as early as 1980<sup>10)</sup>. More recently, the generation of PCDDs and PCDFs from the direct photolysis of a 1 ppm solution of PCP was reported<sup>11)</sup>. Clearly, photolytic destruction of PCP is not a viable remediation technology if it is accompanied by the formation of more toxic compounds such as PCDD/Fs. The authors<sup>11)</sup> recommended the use of proposed AOPs as a potential solution to this problem. In the present work, we examine the formation of PCDDs and PCDFs by the UV photolysis of PCP using such oxidative conditions, namely the addition of hydrogen peroxide.

## Experimental

*Pentachlorophenol.* Analytical grade pentachlorophenol was obtained from the Aldrich Chemical Company and used without further purification.

*UV Reactor.* A Solarchem UV reactor was used for the photolysis experiments. The apparatus consists of a medium pressure 1 kW Hg lamp which is surrounded by a quartz sleeve and placed centrally into a 6 L stainless steel vessel with a path length of 6 cm. The emission of the lamp is optimized in the range of 200 to 300 nm and a lamp efficiency of approximately 30% is achieved. A photon flux of  $3.6 \times 10^{-4}$  einsteins/s was measured by ferrioxalate actinometry. The reactor was filled to a volume of 30 litres for all experiments and the contents were circulated at 110 L/min.

*Preparation of the UV Reactor.* The reactor surfaces were cleaned thoroughly with distilled water and Decon soap. An overnight soaking period was followed by several rinses with distilled water. The reactor was then rinsed with 12 L of analytical grade toluene (BDH Labs), followed by 4 L of distilled-in-glass grade toluene (Caloden Labs). An aliquot of this rinse was then analyzed for PCDD/Fs. Finally, the reactor was rinsed with 2 L of technical grade acetone and several times with distilled water.

*Reactor Blank.* Following the above preparation, the reactor was filled with 30 L of distilled water and the UV lamp was turned on for 30 min. Samples were then taken for GC/MS analysis.

*Direct photolysis of PCP.* Distilled water (30 L) was spiked with PCP (10 ppm) at pH 7.0 and irradiated in the UV reactor. Samples (1 L) were taken for GC/MS analysis at time=0 (prior to the lamp being turned on), and after 4, 8 and 12 min. of irradiation.

*Photolysis of PCP in the Presence of Hydrogen Peroxide.* Distilled water (30 L) was spiked with PCP (10 ppm) and 300 ppm of hydrogen peroxide at pH 7.0 and irradiated in the UV reactor. Samples were taken for GC/MS analysis at time=0 (prior to the lamp being turned on), and after 2, 4 and 6 min. of irradiation.

*PCDD/F Analysis.* Samples were extracted using liquid/liquid techniques. The resultant extracts were cleaned up using a dual stage open column chromatography procedure consisting of modified silica and alumina stationary phases. The PCP sample was analyzed by GC/MS/MS (Varian 3400 GC, Finnigan MAT TSQ 70 triple quadrupole mass spectrometer, and an ICIS II data system). All samples from the photolysis experiments were 1 L in size and analyzed by GC/HRMS (Hewlett-Packard 5890 Series II GC, VG Autospec at 10,000 resolution, and an OPUS data system). Samples were chromatographed using a 60m x 0.25 mm i.d. x 0.25  $\mu$ m film thickness J&W DB-5 fused silica capillary column. Complete details of the analytical procedure are available elsewhere.<sup>(12)</sup>

## Results and Discussion

*PCP Analysis.* Prior to beginning the UV treatment experiments, a sample of the PCP was analyzed by GC/MS for PCDD/Fs. These data are presented in Table 1. The International Toxicity Equivalence Factors are included in column 3 of Table 1 for completeness. A mean value of 3.25 ppb of TEQ was obtained for the duplicate analyses. This value compares favourably with the 1.524  $\mu$ g/L of TEQ detected by Vollmuth *et al* in a sample of purified PCP.<sup>(11)</sup>

*PCP Isomer Profiles.* Since the PCDD/F profiles of various grades of PCP and its sodium salts are readily available<sup>(13-16)</sup>, some preliminary attempts were made at identifying the PCDD/F isomers found in the analytical grade PCP. Efforts at identifying the PCDD/F isomers were directed toward tracking the formation and/or destruction of PCDD/Fs during the subsequent

Table 1 - PCDD/F Content (ppb) of Analytical Grade Pentachlorophenol

	Sample A	Sample B	I-TEF
T4CDD	ND(0.4)	ND(0.5)	
P5CDD	ND(0.2)	0.36 <sup>1</sup>	
H6CDD	27 <sup>5</sup>	28 <sup>4</sup>	
H7CDD	79 <sup>2</sup>	92 <sup>2</sup>	
O8CDD	39	42	0.001
T4CDF	ND(0.7)	ND(0.5)	
P5CDF	ND(0.3)	0.31	
H6CDF	8.0 <sup>3</sup>	0.47	
H7CDF	11 <sup>3</sup>	3.9	
O8CDF	3.5	0.25	0.001
2,3,7,8-Substituted Isomers			
2,3,7,8-T4CDD	ND(0.4)	ND(0.5)	1
1,2,3,7,8-P5CDD	ND(0.2)	0.36	0.5
1,2,3,4,7,8-H6CDD	0.47	0.59	0.1
1,2,3,6,7,8-H6CDD	17	19	0.1
1,2,3,7,8,9-H6CDD	0.73	ND(0.9)	0.1
1,2,3,4,6,7,8-H7CDD	71	83	0.01
2,3,7,8-T4CDF	ND(0.7)	ND(0.5)	0.1
1,2,3,7,8-P5CDF	ND(0.3)	0.31	0.5
2,3,4,7,8-P5CDF	ND(0.3)	0.47	0.05
1,2,3,4,7,8-H6CDF	3.3	3.9	0.1
1,2,3,6,7,8-H6CDF	ND(0.2)	0.25	0.1
2,3,4,6,7,8-H6CDF	ND(0.2)	ND(0.2)	0.1
1,2,3,7,8,9-H6CDF	ND(0.2)	ND(0.1)	0.1
1,2,3,4,6,7,8-H7CDF	3.2	3.7	0.01
1,2,3,4,7,8,9-H7CDF	ND(0.3)	0.39	0.01
TEQ	2.9	3.6	

All concentrations expressed in ppb (parts-per-billion; nanograms ( $10^9$  grams) of PCDD/PCDF per gram of sample).

Values are corrected for recovery of isotopically labelled surrogate standards.

"ND" Not detected. Detection limit in ppb given in brackets ( ).

Superscripts indicate the number of isomers detected.

I-TEF International Toxicity Factor

TEQ Toxic Equivalents

photolysis experiments. It should be noted that only 2,3,7,8-substituted isomers were unambiguously assigned. All other identifications were based upon comparisons of patterns with published data and reference mixtures such as fly ash extracts.

The H6CDD profile was dominated by the 1,2,3,6,7,8-substituted isomer and the H7CDD by the 1,2,3,4,6,7,8 isomer. These data are in general agreement with the patterns observed by Buser<sup>13)</sup> and Hagenmaier<sup>15)</sup> but disagree with earlier findings<sup>14)</sup> which reported a co-eluting pair of H6CDD isomers (1,2,3,6,7,9/1,2,3,6,8,9) to be dominant. The H7CDF data are dominated by the 1,2,3,4,6,8,9 isomer, which is typically observed in PCP samples<sup>13,15,16)</sup>. The greatest discrepancy was observed with the H6CDF data for which the traces were dominated by the 1,2,3,4,7,8 isomers and another non-2378-substituted isomer at the same concentration. This is in marked contrast with the data reported by Hagenmaier<sup>15)</sup> and Harrad<sup>16)</sup> who observed a

total dominance of the H6CDF chromatogram by a single isomer, the 1,2,4,6,8,9, which is considered a signature of PCP.

*Photolysis Experiments.* Data for the PCDD/F analyses of the photolysis runs are presented in Table 2. The predicted concentrations of PCDD/Fs in the 30 L reactor vessel at a 10 ppm spike level of PCP are listed in column 1. These data should be directly comparable to the data for t=0 (lamp off) sampling points. At t=0, however, a significant decrease in total TEQs was observed for both the direct photolysis (4.2 pg TEQ/L) and the photolysis with H<sub>2</sub>O<sub>2</sub> (9.5 pg TEQ/L) as compared to the predicted level of 36.5 pg TEQ/L. Several of the predicted concentrations in Table 2 for the 2,3,7,8-substituted PCDFs are approaching instrument detection limits. If the values for 1,2,3,4,7,8-H6CDF and 1,2,3,4,6,7,8-H7CDF are retained in column 1, and the remaining low level 2,3,7,8-substituted PCDFs are excluded, a revised TEQ value for the PCP spike of 34 pg TEQ/L is calculated. Detection limits arising from the different scaling of the experiments (i.e. PCP analysis at ppb levels vs. photolysis experiments at ppq) cannot account for the differences in columns 1,2, and 6.

A closer examination of the data at t=0 reveals a substantial decrease in the contributions from the 1,2,3,6,7,8-H6CDD and 1,2,3,4,6,7,8-H7CDD isomers. It is difficult to accept isomer specific adsorption to the reactor vessel as an explanation for these differences. The homologue profiles for the H6CDD and H7CDD congener groups are also substantially different from that of the PCP starting material. We currently do not have any explanation for this anomaly.

For both the direct photolysis conditions and the photolysis with H<sub>2</sub>O<sub>2</sub>, gradually increasing levels of PCDD/Fs were observed with increasing time. Vollmuth<sup>11)</sup> observed a 150-fold increase in TEQs following the irradiation of pure PCP and detected Cl<sub>6</sub>- Cl<sub>8</sub> PCDD/Fs. We also observe an increase in the TEQs, although to a lesser degree, and further report on the formation of T4CDFs, P5CDFs, P5CDDs and trace amounts of T4CDDs. The 2,3,7,8-substituted T4CDD was not observed under any of the experimental conditions. The contributions of the 2,3,7,8-substituted PCDFs to the total TEQs were found to be minor, with the exception of the two 2,3,7,8-substituted H7CDFs. The levels of O8CDF were found to increase under both sets of conditions, possibly arising from photolysis of polychlorinated diphenyl ethers (PCDPE) impurities in the PCP.<sup>17)</sup> High levels of PCDPEs were observed in both the PCP starting material and some of the initial reactor rinsings. No efforts were made to quantitate the level of PCDPEs, which appeared as false positives in the PCDF selected ion recording channels. The PCDPEs were selectively removed from all of the photolysate samples using a carbon column clean-up.

The photolytic condensation of PCP has been widely studied as has the photolytic destruction of O8CDD. The current data are in agreement with those reported by Lamparski<sup>10)</sup>, who observed these two processes occurring concurrently during the photolysis of PCP-treated wood. The data are interpretable, in part, by examination of the contributions of the various 2,3,7,8-substituted PCDD/F isomers. For example, the O8CDD concentration increased to 25,000 ppq within 6 minutes using H<sub>2</sub>O<sub>2</sub>, while a similar concentration (22,000 ppq) was reached after 12 minutes using direct photolysis. The formation of O8CDD by the photolysis of PCP has been accelerated by the addition of the H<sub>2</sub>O<sub>2</sub> relative to direct photolysis. Buser<sup>13)</sup> observed that photolysis of O8CDD yielded a variety of PCDDs of decreasing chlorine content. Amongst the H7CDDs, the 1,2,3,4,6,7,9-substituted isomer was found to predominate. This result was later confirmed by Dobbs<sup>17)</sup>, who further reported the 1,2,4,6,7,9-H6CDD isomer as

Table 2 - PCDD/F Content (ppq) of Photolysate Samples

	10 ppm PCP*	DIRECT PHOTOLYSIS				PHOTOLYSIS WITH H <sub>2</sub> O <sub>2</sub>			
		t=0	t=4	t=8	t=12	t=0	t=2	t=4	t=6
T4CDD	ND(5)	ND(2)	9.1 <sup>1</sup>	19 <sup>5</sup>	15 <sup>2</sup>	ND(3)	ND(1)	4.5 <sup>2</sup>	2.2 <sup>2</sup>
P5CDD	3.6 <sup>1</sup>	5.6 <sup>3</sup>	96 <sup>11</sup>	140 <sup>11</sup>	170 <sup>9</sup>	14 <sup>6</sup>	7.3 <sup>4</sup>	17 <sup>7</sup>	37 <sup>8</sup>
H6CDD	280 <sup>4</sup>	43 <sup>4</sup>	450 <sup>7</sup>	840 <sup>7</sup>	1100 <sup>7</sup>	91 <sup>6</sup>	110 <sup>7</sup>	210 <sup>6</sup>	420 <sup>6</sup>
H7CDD	920 <sup>2</sup>	180 <sup>2</sup>	2500 <sup>2</sup>	4700 <sup>2</sup>	6200 <sup>2</sup>	380 <sup>2</sup>	930 <sup>2</sup>	2200 <sup>2</sup>	4400 <sup>2</sup>
O8CDD	420	290	8800	17000	22000	960	4000	12000	25000
T4CDF	ND(5)	ND(1)	29 <sup>5</sup>	25 <sup>5</sup>	18 <sup>4</sup>	ND(1)	ND(1)	ND(1)	ND(1)
P5CDF	7.9 <sup>2</sup>	3.5 <sup>2</sup>	27 <sup>4</sup>	31 <sup>5</sup>	40 <sup>8</sup>	4.8 <sup>2</sup>	1.9 <sup>1</sup>	5.5 <sup>2</sup>	8.4 <sup>2</sup>
H6CDF	82 <sup>3</sup>	8.9 <sup>3</sup>	34 <sup>4</sup>	75 <sup>7</sup>	92 <sup>8</sup>	21 <sup>5</sup>	15 <sup>3</sup>	17 <sup>4</sup>	24 <sup>4</sup>
H7CDF	120 <sup>3</sup>	14 <sup>1</sup>	100 <sup>4</sup>	150 <sup>4</sup>	190 <sup>4</sup>	34 <sup>2</sup>	36 <sup>4</sup>	48 <sup>3</sup>	72 <sup>4</sup>
O8CDF	37	15	100	170	220	23	40	75	140
2,3,7,8-Substituted Isomers									
2,3,7,8-T4CDD	ND(5)	ND(2)	ND(5)	ND(1)	ND(3)	ND(1)	ND(1)	ND(1)	ND(1)
1,2,3,7,8-P5CDD	3.6	1.6	9.8	19	31	ND(3)	2.1	3.7	7.2
1,2,3,4,7,8-H6CDD	5.9	ND(2)	59	110	133	7.2	9.7	22	47
1,2,3,6,7,8-H6CDD	190	16	55	100	150	32	27	41	71
1,2,3,7,8,9-H6CDD	ND(9)	4.3	86	170	230	11	27	64	130
1,2,3,4,6,7,8-H7CDD	830	110	1900	3500	4500	290	740	1800	3600
2,3,7,8-T4CDF	ND(5)	ND(1)	1.9	ND(2)	2.0	ND(1)	ND(1)	ND(1)	ND(1)
1,2,3,7,8-P5CDF	3.1	ND(1)	ND(1)	ND(4)	2.2	ND(1)	ND(1)	ND(1)	ND(1)
2,3,4,7,8-P5CDF	4.7	ND(1)	ND(2)	ND(2)	2.7	ND(1)	ND(1)	ND(1)	ND(1)
1,2,3,4,7,8-H6CDF	39	ND(3)	ND(5)	7.3	8.0	4.8	ND(3)	ND(3)	ND(4)
1,2,3,6,7,8-H6CDF	2.5	ND(7)	ND(2)	ND(4)	ND(4)	ND(1)	ND(1)	ND(1)	ND(2)
2,3,4,6,7,8-H6CDF	ND(2)	ND(4)	ND(7)	ND(9)	ND(10)	ND(4)	ND(4)	ND(5)	ND(6)
1,2,3,7,8,9-H6CDF	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)
1,2,3,4,6,7,8-H7CDF	37	ND(6)	26	45	59	10	12	16	24
1,2,3,4,7,8,9-H7CDF	3.9	ND(1)	8.6	14	18	ND(2)	2.7	ND(4)	6.8
TEQ	36.5	4.2	53.3	101.0	137.0	9.5	19.0	44.8	89.8
PCP (ppm)	10	10	1.47	0.20	0.04	10	1.88	0.03	0

\*Predicted PCDD/F levels based on 10 ppm spike of PCP (replicate b) into 30 L reactor vessel

All concentrations expressed in ppq (parts-per-quadrillion; picograms (10<sup>-12</sup> grams) of PCDD/PCDF per litre of effluent).

Values are corrected for recovery of isotopically labelled surrogate standards.

"ND" Not detected. Detection limit in ppq given in brackets ( ).

Superscripts indicate the number of isomers detected.

\*\* Maximum possible concentration due to potential chromatographic overlap.

dominant amongst the H6CDDs. We observe the dominance of the 1,2,3,6,7,8-H6CDD and the 1,2,3,4,6,7,8-H7CDD isomers in their respective congener groups. These isomers, which are distinctive of the PCP starting material, suggest that the PCP destruction has not proceeded to completion. However, this conclusion is not supported by the PCP analyses, which is almost completely destroyed under both sets of photolysis conditions. Future experiments will extend the time scale of the current studies in an effort to completely destroy all the PCP starting material and PCDD/F photolysis products.

## Conclusions

The UV photolysis of PCP was found to be accelerated by the addition of 300 ppm of H<sub>2</sub>O<sub>2</sub> when monitored by the formation of O8CDD. The progress of the reactions could not be monitored by the relative proportions of fingerprint isomers unique to the PCP starting material and photolysis of the OCDD.

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