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# EFFECTS OF SENSITIZERS AND INHIBITORS ON PHOTOTRANSFORMATION OF POLYCHLORINATED DIBENZO-P-DIOXINs (PCDDs)

Qi Yan[1], S. Kapila[1]*, L.D. Sivils[1], and A.A. Elseewi[2]

[1]Department of Chemistry and Center for Environmental Science and Technology, University of Missouri-Rolla, Rolla, MO 65401

[2]Environmental Affairs Division, Southern California Edison, Rosemead, CA

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## ABSTRACT

The present study was designed to obtain a measure of the change in phototransformation efficiency in the presence of other chemicals. The efficiency of the phototransformation was evaluated by determining quantum yield and photohalf-lives of polychlorinated dibenzo-p-dioxins (PCDDs) in presence and absence of cocontaminants and sensitizers. The results obtained showed that the presence of these cocontaminants can affect the efficiency of the photodegradation process. The experimental results also showed that the efficiency of phototransformation is depended on the solvent and PCDD congener itself. Photoproducts has been found in both absence and presence of inhibitors or sensitizers.

## INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) as a class are some of the most toxic xenobiotic chemicals. It is generally accepted that phototransfromation is one of the principle pathway for disapperance of the chemicals in the environment and phenonmenous has been the object of a number of studies. The 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 [1-8]. The majority of these studies have been devoted to phototransformation process in solution phase and solid surface. The process has generally been thought to proceed primarily through reductive dechlorination, especially in the case of congeners with four or more chlorines where as photoirradiation of congeners with three or less chorines results in cleavage of the carbon-oxygen bond. Evidence of photoproducts resulting cleavage of carbon-oxygen bond has been reported by Miller and Co-workers [9]. The efficiency of the phototransformation process is affected by environmental parameters such as the presence of proton or electron donor and light quenching species, e.g. phototransformation efficiency of 2,3,7,8-tetrachlorodibenzo-p-dioxin at 313 nm was found to be 20 times higher in hexane solution than in water:acetonitrile solution as reported by Dulin and coworkers [10]. The efficiency of the phototransformation is also affected by the light sensitizing species in the environmental condition. Faust et. al reported sensitized photooxidation of phenols by the presence of fulvic acid in natural waters [11].

The common measure of phototransformation efficiency are quantum yield and photo-halflife. So far, only a

*Corresponding Author

limited number of studies on quantum yield measurement of the dioxin have been reported in the literature. Quantum yields for photochemical transformation of 1,2,3,4,7, pentachlorodibenzo-p-dioxin ($P_5CDD$), 1,2,3,4,7,8, hexachlorodibenzo-p-dioxin ($H_6CDD$), 1,2,3,4,6,7,8 heptachlorodibenzo-p-dioxin ($H_7CDD$) and octachlorodibenzo-p-dioxin (OCDD) was determined by Choudhry et al in both the natural aquatic systems and acetonitrile water mixtures. The quantum yields for the direct phototransformation of the PCDD isomers in these solvent system are found 5.42x10-4 (1,2,3,4-TCDD), 2.1x10-3 (1,3,6,8-TCDD), 1.53x10-5 (1,2,3,4,6,7,8-H7CDD) and 2.26x10-5 (OCDD) [12]. The phototransformation of three different tetrachlorodibenzo-p-dioxin congeners in dioxane solution was studied by Koshioka and coworkers [13]. Their results showed that the efficiency of the process varied by a factor of 3, the quantum yield for 1,2,3,4-TCDD, 1,3,6,8-TCDD and 2,3,7,8-TCDD were found to be $1x10^{-3}$, $2.8x10^{-3}$ and $2.0x10^{-3}$ mol.einstein $^{-1}$ respectively. On the basis of studies reported in the literature one can conclude that efficiency of photoprocess is affected by the medium as well as the position of chlorine substitution. Higher quantum yield have been obtained in organic solvent than in aqueous mixtures. However, quantitative assessment other dissolved chemical species on the phototransformation of chlorinated dioxins has not been reported in the literature. This is important since dioxins are found in presence of much larger concentration of other chemicals. These other chemicals are defined as cocontaminants. The cocontaminants could be quenchers or sensitizers and change the effeciency of phototransformation. The present study was designed to fill the gap. In our previous paper [14], we have reported the effect of cocontaminants from soils at wood treatment site on the photodegradation of OCDD. Present studies were undertaken to assess the effect of selected cocontaminants and sensitizers on the quantum yield and halflives of PCDD. Since chlorinated dioxins rarely, if ever, occur by themselves in the environment. The studies are important for determining environmental impact and remedial measure points of views.

## EXPERIMENTS

The irradiation experiments were carried out with a modified spectrophotometer. A xenon arc lamp served as the light source. Alkane/alcohol mixture was used as the solvent, such mixtures have been shown to be effective for removing chlorinated dioxins from OCDD contaminated soil in Vasilia pole yard [15]. Normalization of incident intensity was obtained with a chemical actinometer. O-nitrobenzaldehyde has been found to be a satisfactory chemical actinometer for radiation in the 290-330 nm region. O-nitrobenzaldehyde was used as the chemical actinometer in the present study to ascertain the intensity of 313 nm incident light used for PCDD irradiation. A known concentration (0.03M) was irradiated under light for varied time periods. The degree of phototransfromation of o-nitrobenzaldehyde to nitrosobenzoic acid was determined by reverse phase high pressure liquid chromatography (HPLC) (Model series 4, Perkin-Elmer Corp. Norwalk, CT). The analysis procedure analogous to the one by Choudhry and Webster [16].

PCDD irradiation experiments were carried out in the standardized radiation set-up. A xenon arc lamp was used as the light source. Irradiation experiments in the laboratory were carried out at 313 nm. The irradiation period was varied from 2 to 200 hours. Three sets of experiments were conducted. In the first set only pure solution of selected PCDDs was irradiated. The second set of irradiation experiments were carried out in presents of co-contaminants which are predominant at wood treatment sites. There were pentachlorophenol, naphthalene, phenanthrene and anthracene. The concentration of cocontaminants was 50 times higher than the PCDD concentration. The third set of PCDD irradiation experiments were carried out in the presence of hydrogen peroxides and azobis(isopropionitrile) (AIBN) as the photosensitizers. The initial concentration of sensitizers was 1000 times higher than the PCDD concentration. Small amount of methanol was added to the decane/butanol mixtures to enhance $H_2O_2$ solubility in this mixture. After the set exposure period an aliquot of the irradiated solution was removed,

mixed with appropriate $^{13}C$ labelled internal standard and analyzed by gas chromatography-mass spectrometry (GCMS) system. Chromatography separations were carried out with a 15m x 0.25mm (i.d.) fused silica column (DB-5, J&W Scientific, Folson, 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. Quadruple mass spectrometer was operated in selected ion monitoring mode, and two ions for each congener group (di-octachlorodibenzo-p-dioxin) were monitored.

The non-labeled PCDD standards were purchased from Ultra-Scientific Inc., North Kingstown, RI. The $^{13}C$-PCDD standards were purchased from Cambridge Isotope Lab Inc., Andover, MA. Naphthalene, phenanthrene, anthracene, pentachlorophenol were purchased from Sigma Inc., St. Louis, MO. Analytical grade solvents were obtained from Fisher Scientific, Pittsburgh, PA. The standard chemicals and solvents were used without further purification.

## RESULTS AND DISCUSSION

The results of irradiation experiments revealed that the phototransformation of PCDDs followed a first order kinetics in all three experimental scenarios. The first order plots for polychlorodibenzo-p-dioxin (PCDD) in absence or presence of sensitizers and inhibitors are presented in Figure 1-4. Figure 1 depicts the results of PCDD photolysis in absence of inhibitors and sensitizers where as Figure 2 and 3 shown the OCDD and 2,3,7,8-TCDD degradation results obtained in the presence of inhibitors. Figure 4 shows the sensitizer effects on the OCDD photodegradation.

The rate constant for phototransformation under each condition was determined through the fist order expression.

$$\mathrm{Ln}\,(Co/Ct) = Ksp \cdot t$$

where

Co = initial concentration of PCDDs

Ct = concentration of PCDDs at time t

t = irradiation time (hours)

The quantum yield was determined through the following expression

$$\phi = Ksp/Io\ \varepsilon\ l$$

where

$\phi$ = quantum yield (mole.einstein-1)

Ksp = first order rate constant

Io = intensity of incident light

$\varepsilon$ = molar extinction coefficient

l = pathlength of light

The intensity of incident light was estimated from phototransformation of the chemical actinomer (o-nitrobenzaldehyde).

$$Io = Ct/\ \phi_A \cdot t$$

$\phi_A$ = quantum yield of o-nitrobenzaldehyde = 0.505 mole · einstein-1

Ct = the concentration of photoproduct from chemical actinomer

t = exposure time

The intensity of incident light was determined to be 2.3 x $10^{-7}$ einstein/second for our photocell. The molar extinction coefficients can be determined from the Beer-Lambert law ($A=c\varepsilon l$) using UV spectrophotometer. These values obtained in our laboratory are 2930, 4150, 3980 and 2210 [$M^{-1}cm^{-1}$] for 2,3,7,8,-TCDD, 1,2,3,4,7,8-$H_6$CDD, OCDD and 1,2,3,4-TCDD, respectively.

The efficiency of phototransformation of various PCDD congeners in alkane/alcohol solvent can be arranged in this order: 2,3,7,8,-TCDD > 1,2,3,4,7,8-$H_6$CDD > OCDD > 1,2,3,4-TCDD. The results were shown in the table 1 and figure 1. The position of chlorine in either peri- or lateral- substitution was important in PCDD phototransformation. The dissociation of chlorine on the lateral position has been found as a dominant pathway in phototransformation of solution phase.

Table 1 quantum yield, half-lives and rate constants of various dioxin congeners

| PCDDs | rate constant($hr^{-1}$) | half-life (hr) | quantum yield (mol/E) |
|---|---|---|---|
| 2,3,7,8-TCDD | 9.04x10-2 | 7.7 | 1.62x10-2 |
| 1,2,3,4,7,8-H6CDD | 1.25x10-2 | 55.4 | 1.58x10-3 |
| OCDD | 9.54x10-3 | 72.6 | 1.25x10-3 |
| 1,2,3,4-TCDD | 3.14x10-3 | 220.7 | 7.4x10-4 |

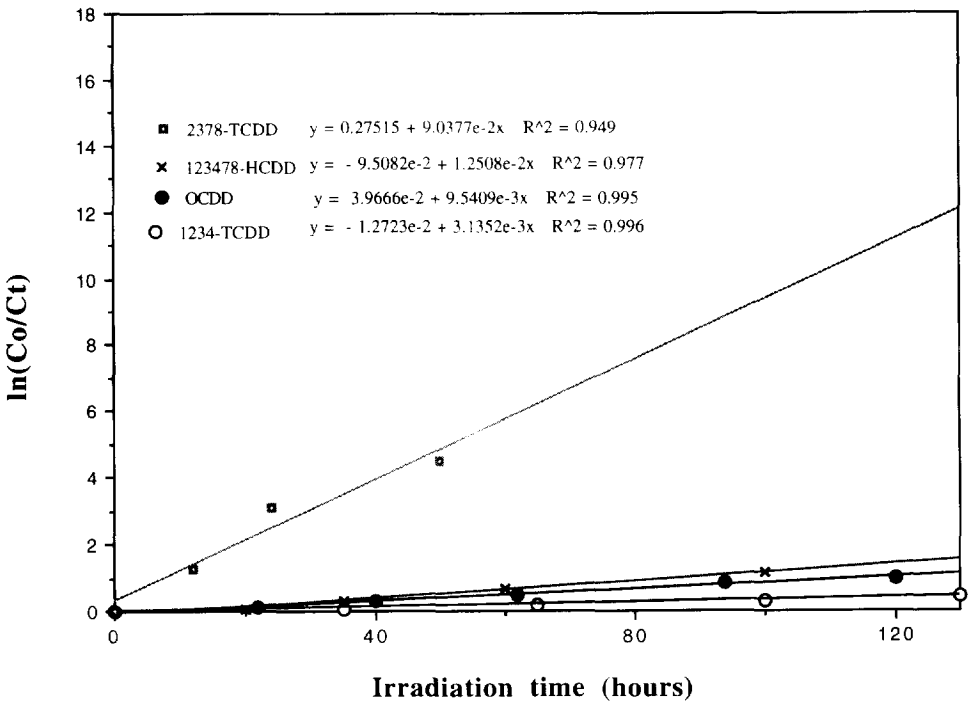



**Figure 1. First Order Treatment of Photodegradation of Various Dioxin Congeners**

The quantum yield decreased measurably with the introduction of the cocontaminants. The decrease was related to concentration and extinction coefficient of the cocontaminants. The largest decrease occurred in presence of anthracene, which has the highest extinction coefficient of the compounds used in the present study. The results were shown in Table 2,3 and Figure 2.

Table 2 effects of various cocontaminants on quantum yield, half-lives and rate constant of OCDD

| Contaminants | rate constant(hr-1) | half-life (hr) | quantum yield (mol/E) |
|---|---|---|---|
| OCDD only | 9.54x10-3 | 72.6 | 1.25x10-3 |
| OCDD:Naph (1:50) | 6.63x10-3 | 104.5 | 8.74x10-4 |
| OCDD:Phen (1:50) | 6.48x10-3 | 107.1 | 8.55x10-4 |
| OCDD:PCP (1:50) | 5.92x10-3 | 117.1 | 7.81x10-4 |
| OCDD:Anth (1:50) | 4.71x10-3 | 147.1 | 6.23x10-4 |

Table 3 effects of cocontaminant concentration on quantum yield, half-lives and rate constant of OCDD

| Contaminants | rate constant(hr-1) | half-life (hr) | quantum yield (mol/E) |
|---|---|---|---|
| OCDD only | 9.54x10-3 | 72.6 | 1.25x10-3 |
| OCDD:Anth (1:5w/w) | 6.51x10-3 | 106.5 | 8.59x10-4 |
| OCDD:Anth (1:50w/w) | 4.64x10-3 | 149.4 | 6.12x10-4 |

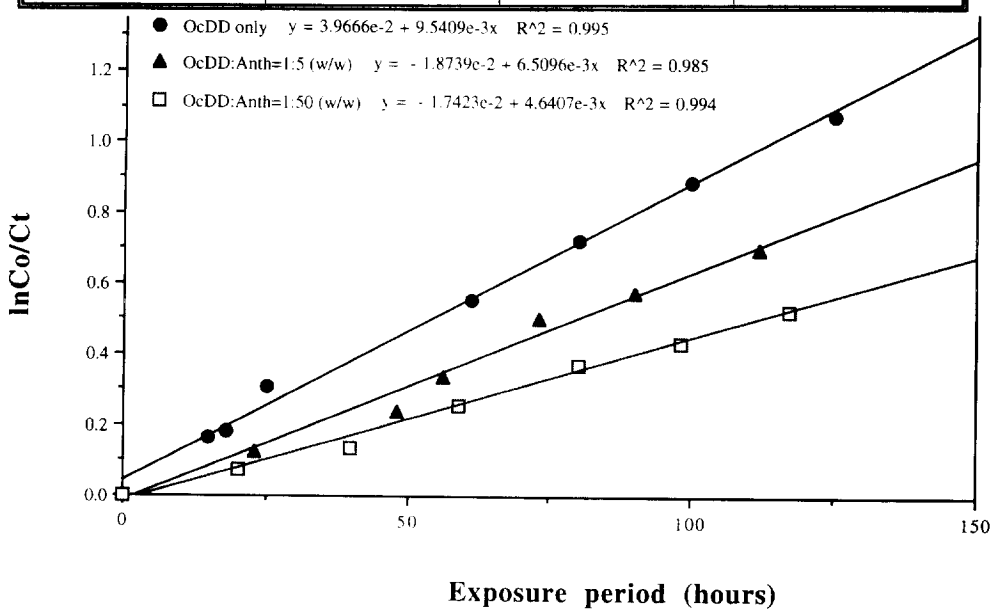



**Figure 2. First Order Treatment of OCDD Photodegradation in Presence of Anthracene**

A similar decrease of photodegradation caused by the presence of cocontaminants was also observed for

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The results were shown in Table 4 and Figure 3.

Table 4 The effects of cocontamiants on quantum yield, half-lives and rate constants of TCDD

| contaminants | rate constant($hr^{-1}$) | half-life (hr) | quantum yield (mol/E) |
|---|---|---|---|
| 2,3,7,8-TCDD only | 9.04x10-2 | 7.8 | 1.62x10-2 |
| TCDD:Mixed(1:50each,w/w) | 2.26x10-2 | 30.7 | 4.05x10-3 |

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

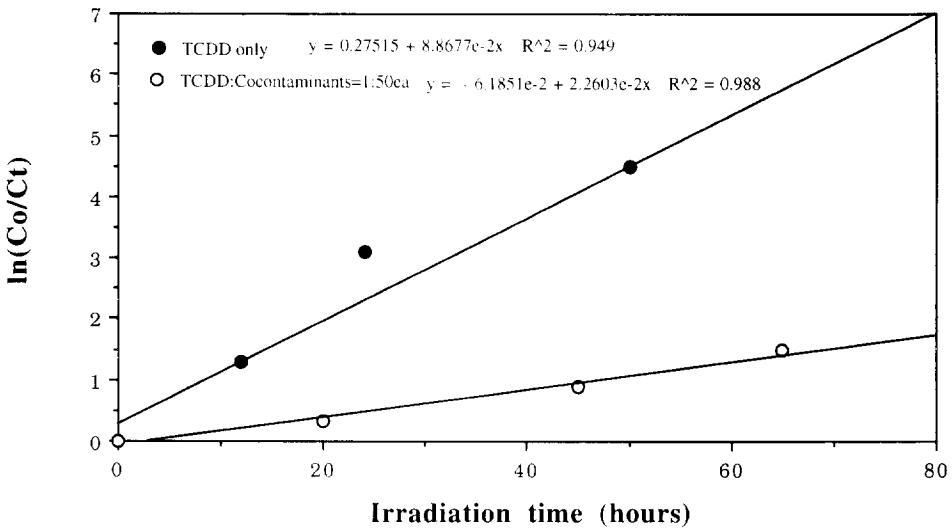



**Figure 3. First Order Treatment of TCDD Photodegration in Presence of Cocontaminants**

solvent: 20% butanol in decane. Irradiation wavelength: 313nm.

The sensitizer effect on the OCDD photodegradation are shown in Table 5 and Figure 4. Introduction of photosensitizers to the OCDD solution resulted in an enhance of phototransformation rate. The sensitizing effects of both hydrogen peroxide and azobis(isopropionitrile) (AIBN) are evident in OCDD solution. Hydrogen peroxide shows better sensitizing effects on OCDD photodegradation due to its high oxidation potential. The quantum yield of OCDD photodegradation are increased about four fold when 0.3% hydrogen peroxide has been incorporated into the solution.

Table 5 effects of sensitizers on quantum yield, half-lives and rate constants of OCDD

| contaminants | rate constant($hr^{-1}$) | half-life (hr) | quantum yield (mol/E) |
|---|---|---|---|
| OCDD only | 9.54x10-3 | 72.6 | 1.25x10-3 |
| OCDD:AIBN (1:1000 w/w) | 1.74x10-2 | 39.8 | 2.30x10-3 |
| OCDD:H2O2 (1:1000 w/w) | 3.75x10-2 | 18.4 | 4.95x10-3 |

Two photoproducts are evident from OCDD photodegradation. The results are shown in Figure 5. These

photoproducts are 1,2,3,4,6,7,9-heptachlorodibenzo-p-dioxin ($H_7CDD$) with chlorine loss at lateral position and 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin ($H_7CDD$) with chlorine loss at peri position. The ratio of both products is about 10 to 1. The results are shown that in solution phase photodegradation the chlorine is preferred loss on lateral position. Photoproducts are undergo a competitive formation and degradation process. The peak time of the product formation is about 70 hrs. At this peak time, a total of 12% 1,2,3,4,6,7,9-$H_7CDD$ are formed.

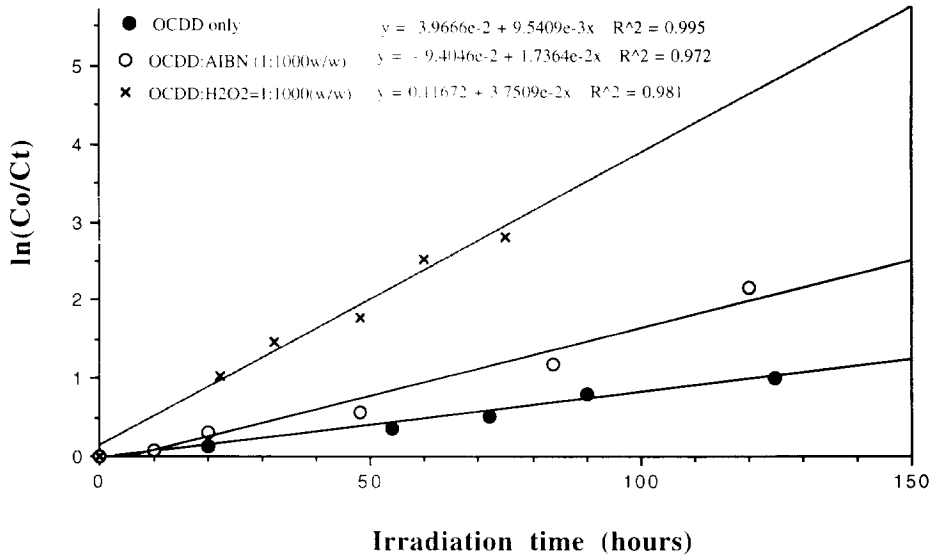
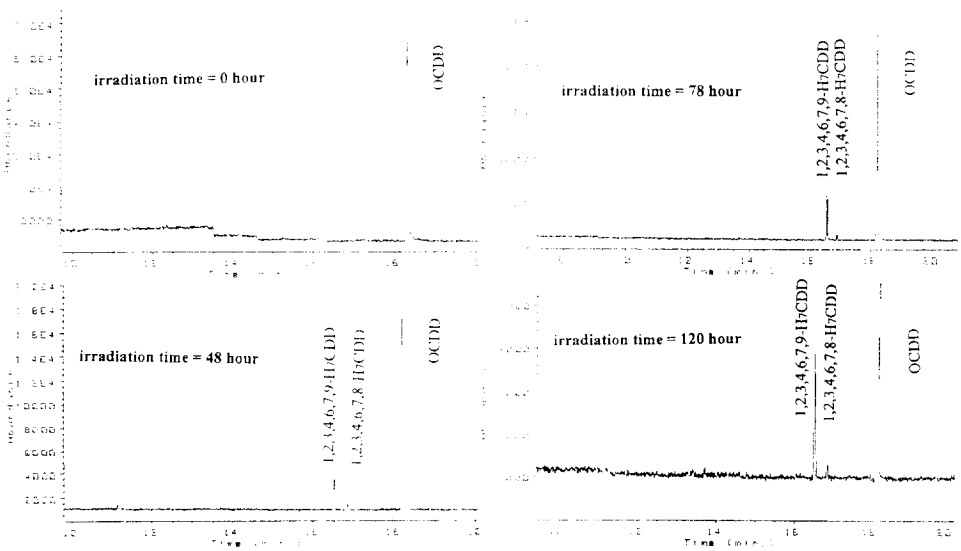



**Figure 4. Sensitizing effect on OCDD photodegradation**




GC/MS conditions for dioxins: initial 120°C , final 290°C, heating rate: 10°C/min. injector 280°C, detector 280°C. Mass window: 460/462 (OCDD), 472/474 (13C-OCDD), 424/426 (H7CDD), 388/390 (H6CDD), 354/356 (P5CDD), 322/320 (TCDD), 288/286 (TrCDD), 254/252 (DCDD); 220/218 (MCDD).

**Figure 5. Photoproduct formation from OCDD photodegradation**

## Conclusion

The quantum yields and photo-halflives of various dioxin congeners in absence and presence of sensitizers and inhibitors are calculated in this paper. The cocontaminants presented at wood treatment sites can curtail the photodegradation efficiency of OCDD. Photodegradation efficiency can be enhanced using photosensitizers such as hydrogen peroxides and azobis(isopropionitrile). Photoproducts are also evident. 12% 1,2,3,4,6,7,9-$H_7$CDD and 1.2% 1,2,3,4,6,7,8-$H_7$CDD are evident from the OCDD photodegradation.

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