

10. PHOTOCHEMICAL SOURCES OF CDDs/CDFs

10.1. PHOTOTRANSFORMATION OF CHLOROPHENOLS

Several researchers have demonstrated that CDDs/CDFs can be formed via photolysis of PCP under laboratory conditions. These studies are described below. However, the extent to which CDDs/CDFs are formed in the environment via this mechanism cannot be estimated at this time.

Lamparski et al. (1980) conducted laboratory studies to determine the effect of simulated summer sunlight on the formation of OCDD, HpCDDs, and HxCDDs in wood that was pressure-treated in the laboratory with PCP. In the first set of experiments, wood veneers (southern pine) treated with purified PCP or with Dowicide EC-7, using methylene chloride as the PCP carrier, were exposed to light for 70 days. The PCP concentration in the treated wood was 5% by weight, which approximates the concentration in the outer layer of PCP-treated wood utility poles. Photolytic condensation of PCP to form OCDD was observed, with the OCDD concentration increasing by a maximum factor of 3,000 for the purified PCP and by a factor of 20 for EC-7 at about day 20 before leveling off. HpCDD and HxCDD were also formed, apparently by photolytic degradation of OCDD rather than by condensation of PCP and tetrachlorophenols. The HxCDD concentration increased by a factor of 760 for the purified PCP and by a factor of 50 for EC-7 over the 70-day exposure period. The predominant HpCDD congener formed was 1,2,3,4,6,7,8-HpCDD as a result of an apparently preferential loss of chlorine at the peri position (i.e., positions 1, 4, 6, and 9).

In a second set of experiments conducted by Lamparski et al. (1980), a hydrocarbon oil (P-9 oil) was used as the carrier to treat the wood. The increases observed in the OCDD, HpCDD, and HxCDD were reported to be much lower relative to the increases observed in the first set of experiments, which used methylene chloride as the carrier. Results were reported only for OCDD. The OCDD concentration increased by a maximum factor of 1.5 for both EC-7 and technical PCP and by a factor of 88 for purified PCP. The authors concluded that the oil either reduced condensation of PCP to OCDD or accelerated degradation to other species by providing a hydrocarbon trap for free-radical species.

Vollmuth et al. (1994) studied the effect of irradiating laboratory water and landfill seepage water that contained PCP under conditions simulating those used to purify water with

1 ultraviolet (UV) radiation (5-hr exposure to 254 nm radiation from low-pressure mercury lamps).
2 Before irradiation, the three solutions tested contained approximately 1 mg/L of PCP or PCP-Na,
3 but the CDD/CDF content of one solution varied dramatically from those of the other two (1.5
4 vs. 2,066 and 2,071 pg I-TEQ_{DF}/L). Irradiation resulted in nearly total destruction of PCP
5 (greater than 99% loss) in all three experiments. An overall net increase in I-TEQ_{DF}-content was
6 observed in the initially low I-TEQ_{DF}-content water, but a net decrease was observed for the two
7 initially high I-TEQ_{DF}-content waters.

8 Irradiation of laboratory water containing purified PCP showed an increase in I-TEQ_{DF}
9 concentration from 1.5 pg/L to 214.5 pg/L. The increase was due entirely to the formation of
10 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,4,6,7,8-HpCDF. Formation of non-2,3,7,8-substituted
11 HpCDDs and HpCDFs was also observed. The ratios of the concentrations of these non-2,3,7,8-
12 congeners to the concentrations of the 2,3,7,8-congeners were 0.6 for HpCDDs and 5 for
13 HpCDFs. The HpCDD and HpCDF congeners formed indicated that the operative mechanism
14 was photoinduced dechlorination of OCDD at a peri position and dechlorination of OCDF at
15 only the 1- and 9-peri positions.

16 Irradiation of water containing technical PCP-Na (Dowicide-G) resulted in a net loss in I-
17 TEQ_{DF} content, from 2,065.5 pg/L to 112.7 pg/L. The only 2,3,7,8-substituted congener showing
18 an increased concentration was 1,2,3,6,7,8-HxCDD. The other congeners originally present in
19 the technical PCP-Na showed reductions of 80.6 to 100%.

20 The I-TEQ_{DF} content of seepage water from a landfill (2,071 pg I-TEQ_{DF}/L) was reduced
21 by a factor of 2 to 1,088 pg I-TEQ_{DF}/L. However, several 2,3,7,8-substituted congeners did
22 increase in concentration (1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and
23 OCDF).

24 Waddell et al. (1995) also studied the effect of irradiating distilled laboratory water
25 containing PCP under conditions simulating those used to purify water with UV radiation. The
26 results obtained were similar to those of Vollmuth et al. (1994). Analytical-grade PCP at a
27 concentration of 10 mg/L was exposed for 12 min to 200 to 300 nm radiation from a medium-
28 pressure mercury lamp. All CDD/CDF congener groups increased in concentration over the
29 12-min exposure period, with the greatest increases observed for OCDD (75-fold increase) and
30 HpCDDs (34-fold increase). The I-TEQ_{DF} content of the solution increased from 4.2 pg I-
31 TEQ_{DF}/L to 137 pg I-TEQ_{DF}/L over the 12-min period. The dominant congeners formed, in terms

1 of both concentration and contribution to I-TEQ_{DF}, were 1,2,3,4,6,7,8-HpCDD, OCDD, and
2 1,2,3,7,8,9-HxCDD.

3 4 **10.2. PHOTOLYSIS OF HIGHER CDDs/CDFs**

5 Photolysis appears to be one of the few environmentally significant degradation
6 mechanisms for CDDs/CDFs in water, air, and soil. Although, in most studies, good mass
7 balances were not obtained and the photolytic pathways for CDDs/CDFs were not fully
8 identified, a major photolysis pathway appears to be photodechlorination, resulting in formation
9 of less-chlorinated CDDs/CDFs. A preferential loss of chlorines from the peri positions (1, 4, 6,
10 and 9) rather than from the lateral positions (2, 3, 7, and 8) was reported for some congener
11 groups when irradiated as dry films and sorbed to soil and in gas-phase CDDs/CDFs (Choudhry
12 and Webster, 1989; Kieatiwong et al., 1990; Sivils et al., 1994, 1995; Tysklind et al., 1992).
13 Several researchers reported that carbon-oxygen cleavage and other mechanisms may be
14 similarly or more important pathways for CDDs/CDFs containing four or fewer chlorines.

15 Because of the difficulties inherent in controlling experimental variables for nonvolatile
16 and highly lipophilic compounds such as CDDs/CDFs, few photolysis studies have been
17 performed on natural waters, soils, atmospheric particulates, and atmospheric gases to examine
18 the rates and products of photolysis under environmentally relevant conditions. Thus, it is not
19 possible at this time to quantitatively estimate the mass of various CDD/CDF congeners formed
20 in the environment annually via photolytic mechanisms. Sections 10.2.1 through 10.2.4
21 summarize the key findings of recent environmentally significant studies for the water, soil, and
22 air media.

23 24 **10.2.1. Photolysis in Water**

25 Numerous studies have demonstrated that CDDs/CDFs will undergo photodechlorination
26 following first-order kinetics in organic solution, with preferential loss of chlorine from the
27 lateral positions. Photolysis is slow in pure water, but it increases dramatically when solvents
28 serving as hydrogen donors such as hexane, benzene, methanol, acetonitrile, hexadecane, ethyl
29 oleate, dioxane, and isooctane are present. However, only a few studies have examined the
30 photolysis of CDDs/CDFs using natural waters and sunlight.

1 Choudhry and Webster (1989) experimentally determined the sunlight photolysis half-life
2 of 1,3,6,8-TCDD in pond water to be 3.5 days (more than 10 times greater than the half-life
3 predicted by laboratory experiments using a water/acetonitrile solution). The authors attributed
4 this significant difference in photolysis rates to the light screening/quenching effects of dissolved
5 organic matter.

6 Friesen et al. (1990) examined the photolytic behavior of 1,2,3,4,7-PeCDD and
7 1,2,3,4,6,7,8-HpCDD in water:acetonitrile (2:3, v/v) and in pond water under sunlight at 50
8 degrees north latitude. The observed half-lives of these two compounds in the water:acetonitrile
9 solution were 12 and 37 days, respectively, but were much shorter in pond water, 0.94 and 2.5
10 days, respectively. Similarly, Friesen et al. (1993) studied the photodegradation of 2,3,7,8-TCDF
11 and 2,3,4,7,8-PeCDF by sunlight using water:acetonitrile (2:3, v/v) and lake water. The observed
12 half-lives were 6.5 and 46 days, respectively, in the water:acetonitrile solution and 1.2 and 0.19
13 days, respectively, in lake water. The significant differences between the natural water and
14 water:acetonitrile solution results were attributed to indirect or sensitized photolysis due to the
15 presence of naturally occurring components in the lake and pond water.

16 Dung and O'Keefe (1992), in an investigation of aqueous photolysis of 2,3,7,8-TCDF and
17 1,2,7,8-TCDF, reported findings similar to those of Friesen et al. (1993). The photolysis rates of
18 the two TCDF congeners observed in river and lake water (half-lives of about 4 to 6 hr) were
19 double those observed in pure water (half-lives of about 8 to 11 hr). The authors attributed the
20 difference in rates to the presence of natural organics in the river and lake water that may act as
21 sensitizers.

22 23 **10.2.2. Photolysis on Soil**

24 Photolysis of CDDs/CDFs on soil has not been well characterized. According to the data
25 generated to date, however, photolysis is an operative degradation process only in the near-
26 surface soil where UV light penetrates (the top few millimeters or less of soil), and
27 dechlorination of peri-substituted chlorines appears to occur preferentially.

28 Miller et al. (1989) studied the CDD degradation products resulting from irradiation of
29 ¹³C-labeled OCDD on two soil types using sunlamps. Approximately 38 to 42% of the OCDD
30 was degraded by day 5 of the experiment; no significant further loss of OCDD was observed over
31 the following 10 days. Although the authors determined that photodechlorination was not the

1 dominant photolysis pathway, it was observed in both soils; approximately 10 to 30% of the less-
2 chlorinated congeners were produced from the immediate more-highly chlorinated congeners.
3 The HpCDD and HxCDD congeners observed as degradation products were present in
4 proportions similar to the number of congeners in each congener group. However, the
5 investigators observed greater yields of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD than would be
6 expected on the basis of the number of potential TCDD and PeCDD congeners. One-fifth to
7 one-third of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the total yield of
8 TCDDs was 2,3,7,8-TCDD.

9 Kieatiwong et al. (1990) performed experiments similar to those of Miller et al. (1989)
10 using natural sunlight rather than sunlamps for irradiation of ¹³C-labeled OCDD on soils.
11 Photodechlorination was estimated to account for approximately 10% of the loss of OCDD.
12 One-third to one-half of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the
13 total yield of TCDDs was 2,3,7,8-TCDD. These findings, along with those of Miller et al.
14 (1989), indicate that the 2,3,7,8-substituted TCDD and PeCDD congeners were either
15 preferentially formed or were photochemically less reactive than the other congeners that were
16 formed.

17 Tysklind et al. (1992) studied the sunlight photolysis of OCDD on soil and reported
18 results similar to those of Miller et al. (1989) and Kieatiwong et al. (1990). Photodechlorination
19 was observed with production of HpCDDs, HxCDDs, PeCDDs, and TCDDs over the 16-day
20 irradiation period. Photodechlorination at the peri-substituted positions was the preferred
21 photodechlorination mechanism; the proportions of 2,3,7,8-substituted congeners present in the
22 soils after 16 days for each congener group were as follows: HxCDD, 65%; PeCDD, 40%; and
23 TCDD, 75%. Tysklind et al. (1992) also studied the sunlight photolysis of OCDF on soil.
24 Photodechlorination was observed; however, unlike the case with OCDD, photodechlorination of
25 the lateral-substituted positions was found to be the dominant photodechlorination mechanism,
26 resulting in a relative decreasing proportion of 2,3,7,8-substituted congeners during the
27 irradiation period. 2,3,7,8-TCDF was not observed in any of the irradiated samples.

28 29 **10.2.3. Photolysis on Vegetation**

30 Photolysis of CDDs/CDFs sorbed on the surface of vegetation has not been well
31 characterized, and the findings to date are somewhat contradictory. McCrady and Maggard

1 (1993) reported that 2,3,7,8-TCDD sorbed on the surface of reed canary grass (*Phalaris*
2 *arundinacea L.*) undergoes photolytic degradation with a half-life of 44 hr in natural sunlight. In
3 contrast, Welsch-Pausch et al. (1995) found little difference in the CDD/CDF congener patterns
4 between grass (*Lolium multiflorum*) grown on an outdoor plot and grass grown in a greenhouse
5 (i.e., UV light transmission blocked).

6 In an attempt to clarify this contradiction, Welsch-Pausch and McLachlan (1995) studied
7 the photodegradation of CDDs/CDFs on pasture grass (*Arrhenatherion elatioris*) during two
8 growing cycles (summer and autumn) using two greenhouses. One greenhouse was constructed
9 of glass that blocks UV transmission, and the other was constructed of plexiglass (4 mm) with a
10 UV light transmission of greater than 50% in the 280 to 320 nm range. In both the summer and
11 autumn exposure periods, the concentrations of CDDs/CDFs (on a congener-group basis) were
12 similar in the grass exposed to UV light and the grass that was not exposed. The authors
13 concluded that if photodegradation was occurring, it was a relatively insignificant factor in the
14 accumulation of CDDs/CDFs in pasture grass.

15 16 **10.2.4. Photolysis in Air**

17 Photolysis of CDDs/CDFs in the atmosphere has not been well characterized. On the
18 basis of data generated to date, however, photolysis appears to be a significant mechanism for
19 degradation (principally, dechlorination of the peri-substituted chlorines) of those CDDs/CDFs
20 present in the atmosphere in the gas phase. For airborne CDDs/CDFs sorbed to particulates,
21 photolysis appears to proceed very slowly, if at all. Because of the low volatility of CDDs/CDFs,
22 few studies have been attempted to measure actual rates of photodegradation of gas-phase
23 CDD/CDF, and only recently have studies examined the relative importance of photolysis to
24 particulate-bound CDDs/CDFs.

25 Sivils et al. (1994, 1995) studied the gas-phase photolysis of several CDDs (2,3,7-
26 TrCDD; 2,3,7,8-TCDD; 1,2,3,4-TCDD; 1,2,3,7,8-PeCDD, and 1,2,4,7,8-PeCDD) by irradiating
27 the effluent from a gas chromatograph with broadband radiation in the UV/visible region for
28 periods of up to 20 min. The irradiated sample was then introduced into a second gas
29 chromatograph to measure the extent of dechlorination. The results showed that degradation
30 followed first-order kinetics and that an inverse relationship existed between the degree of
31 chlorination and the rate of disappearance. Although the lack of photoproducts prevented an

1 independent confirmation of the preferential loss mechanism, the results indicate that laterally
2 substituted congeners (chlorines at the 2, 3, 7, and 8 positions) degrade at a slower rate than do
3 the peri-substituted congeners (chlorines at the 1, 4, 6, and 9 positions). Although Sivils et al.
4 (1994) did not present the rate constants, the degradation rate for 2,3,7,8-TCDD (30% loss in
5 20 min) was reported to be slower than the rates for all other tested CDDs. Also, 1,2,4,7,8-
6 PeCDD (with two perichlorines) degraded significantly faster than did 1,2,3,7,8-PeCDD (with
7 only one perichlorine).

8 Mill et al. (1987) studied the photolysis of 2,3,7,8-TCDD sorbed onto small-diameter fly
9 ash particulates suspended in air. The results indicated that fly ash confers photostability on
10 2,3,7,8-TCDD. Little (8%) to no loss was observed on the two fly ash samples after 40 hr of
11 illumination. Tysklind and Rappe (1991) and Koester and Hites (1992) reported similar results
12 of photolysis studies with fly ash. Tysklind and Rappe (1991) subjected fly ash from two
13 German incinerators to various simulated environmental conditions. The fraction of
14 photolytically degradable CDD/CDF after 288 hr of exposure was in the range of 20 to 40% of
15 the extractable CDD/CDF. However, a 10 to 20% reduction was also observed in the darkened
16 control samples. With the exception of HpCDD and HpCDF, the concentration of all other
17 congener groups either increased or stayed the same during the exposure period from hour 144 to
18 hour 288.

19 Koester and Hites (1992) studied the photodegradation of CDDs/CDFs naturally adsorbed
20 to fly ash collected from five electrostatic precipitators. They observed no significant
21 degradation in 11 photodegradation experiments performed on the ash for periods ranging from 2
22 to 6 days. The authors concluded that (a) the absence of photodegradation was not due to the
23 absence of a hydrogen-donor organic substance; (b) other molecules on the ash, as determined by
24 a photolysis experiment with an ash extract, inhibited photodegradation, either by absorbing light
25 and dissipating energy or by quenching the excited states of the CDDs/CDFs; and (c) the surface
26 of the ash itself may have hindered photolysis by shielding the CDDs/CDFs from light.