10. PHOTOCHEMICAL SOURCES OF CDD/CDF

10.1. PHOTOTRANSFORMATION OF CHLOROPHENOLS

Several researchers demonstrated that CDD/CDFs can be formed via photolysis of pentachlorophenol (PCP) under laboratory conditions. These studies are described below. However, the extent to which CDD/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 percent 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 apparent 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 ultraviolet (UV) radiation (i.e., 5-hour exposure to 254 nm radiation from low-pressure mercury lamps). Before irradiation, the three solutions tested contained approximately 1 mg/L of PCP or PCP-Na but the CDD/CDF content varied dramatically (1.5, 2,066, and 2,071 pg I-TEQ$_{DF}$/L). Irradiation resulted in nearly total destruction of PCP (greater than 99 percent loss) in all three experiments. An overall net increase in I-TEQ$_{DF}$ content was observed in the initially low I-TEQ$_{DF}$ content water, but a net decrease was observed for the two initially high I-TEQ$_{DF}$ content waters.

- Irradiation of laboratory water containing purified PCP showed an increase in I-TEQ$_{DF}$ concentration from 1.5 pg/L to 214.5 pg/L. The increase in I-TEQ$_{DF}$ was due entirely to the formation of 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 HpCDDs and HpCDFs was also observed. The ratios of the concentrations of these non-2,3,7,8-congeners to the concentrations of the 2,3,7,8-congeners were 0.6 for HpCDDs and 5.0 for HpCDFs. The HpCDD and HpCDF congeners formed indicated that the operative mechanism is photoinduced dechlorination of OCDD at a peri position and dechlorination of OCDF at only the 1- and 9-peri positions.

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

- The I-TEQ$_{DF}$ content of seepage water from a landfill (2,071 pg I-TEQ$_{DF}$/L) was reduced by a factor of two to 1,088 pg I-TEQ$_{DF}$/L. However, several 2,3,7,8-substituted congeners did 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 OCDF).

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

The dominant congeners formed, in terms of both concentration and contribution to I-TEQ$_{DF}$, were 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,7,8,9-HxCDD.

10.2. PHOTOLYSIS OF HIGHER CDD/CDFS

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

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

10.2.1   Photolysis in Water

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

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

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

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

10.2.2   Photolysis on Soil

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

Miller et al. (1989) studied the CDD degradation products resulting from irradiation of ^{13}C-labeled OCDD on two soil types using sunlamps. Approximately 38 to 42 percent of the OCDD was degraded by day 5 of the experiment; no significant further loss of

OCDD was observed over the following 10 days. Although the authors determined that photodechlorination was not the dominant photolysis pathway, it was observed in both soils; approximately 10 to 30 percent of the lower chlorinated congeners were produced from the immediate higher chlorinated congeners. The HpCDD and HxCDD congeners observed as degradation products were present in proportions similar to the number of congeners in each congener group. However, Miller et al. (1989) observed greater yields of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD than would be expected on the basis of the number of potential TCDD and PeCDD congeners.   One-fifth to one-third of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the total yield of TCDDs was 2,3,7,8-TCDD.

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

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

10.2.3 Photolysis on Vegetation

Photolysis of CDD/CDFs sorbed on the surface of vegetation has not been well characterized, and the findings to date are somewhat contradictory. McCrady and Maggard (1993) reported that 2,3,7,8-TCDD sorbed on the surface of reed canary grass (*Phalaris arundinacea L.*) undergoes photolytic degradation with a half-life of 44 hours in natural sunlight. In contrast, Welsch-Pausch et al. (1995) found little difference in the CDD/CDF congener patterns between grass (*Lolium multiflorum*) grown on an outdoor plot and grass grown in a greenhouse (i.e., UV light transmission blocked). In an attempt to clarify this contradiction, Welsch-Pausch and McLachlan (1995) studied the photodegradation of CDD/CDFs on pasture grass (*Arrhenatherion elatioris*) during two growing cycles (summer and autumn) using two greenhouses. One greenhouse was constructed of glass that blocks UV transmission, and the other was constructed of plexiglass (4 mm) with a UV-light transmission of greater than 50 percent in the 280-320 mm range. In both the summer and autumn exposure periods, the concentrations of CDD/CDFs (on a congener group basis) were similar in the grass exposed to UV light and the grass that was not exposed. Welsch-Pausch and McLachlan (1995) concluded that if photodegradation was occurring, it was a relatively insignificant factor in the accumulation of CDD/CDF in pasture grass.

10.2.4 Photolysis in Air

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

Sivils et al. (1994; 1995) studied the gas-phase photolysis of several CDDs (2,3,7-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 the effluent from a gas chromatograph with broadband radiation in the UV/visible region for periods up to 20 minutes. The irradiated sample was then introduced

into a second gas chromatograph to measure the extent of dechlorination. The results showed that degradation followed first order kinetics and that an inverse relationship exists between the degree of chlorination and the rate of disappearance. Although the lack of photoproducts prevented an independent confirmation of the preferential loss mechanism, the results indicated that laterally substituted congeners (i.e., chlorines at the 2, 3, 7, and 8 positions) degrade at a slower rate than the peri-substituted congeners (i.e., chlorines at the 1, 4, 6, and 9 positions). Although Sivils et al. (1994) did not present the rate constants, the degradation rate for 2,3,7,8-TCDD (30 percent loss in 20 minutes) was reported to be slower than the rates for all other tested CDDs. Also, 1,2,4,7,8-PeCDD (with two perichlorines) degraded significantly faster than 1,2,3,7,8-PeCDD (with only one perichlorine).

Mill et al. (1987) studied the photolysis of 2,3,7,8-TCDD sorbed onto small diameter fly ash particulates suspended in air. The results indicated that fly ash confers photostability on 2,3,7,8-TCDD. Little (8 percent) to no loss was observed on the two fly ash samples after 40 hours of illumination. Tysklind and Rappe (1991) and Koester and Hites (1992) reported similar results of photolysis studies with fly ash. Tysklind and Rappe (1991) subjected fly ash from two German incinerators to various simulated environmental conditions. The fraction of photolytically degradable CDD/CDF after 288 hours of exposure was in the range of 20 to 40 percent of the extractable CDD/CDF. However, a 10 to 20 percent reduction was also observed in the darkened control samples. With the exception of HpCDD and HpCDF, the concentration of all other congener groups either increased or stayed the same during the exposure period from hour 144 to hour 288. Koester and Hites (1992) studied the photodegradation of CDD/CDFs naturally adsorbed to fly ash collected from five electrostatic precipitators. They observed no significant degradation in 11 photodegradation experiments performed on the ash for periods ranging from 2 to 6 days. Koester and Hites (1992) concluded that (1) the absence of photodegradation is not due to the absence of a hydrogen-donor organic substance; (2) other molecules on the ash, as determined by a photolysis experiment with an ash extract, inhibit photodegradation, either by absorbing light and dissipating energy or by quenching the excited states of the CDD/CDFs; and (3) the surface of the ash itself may hinder photolysis by shielding the CDD/CDFs from light.