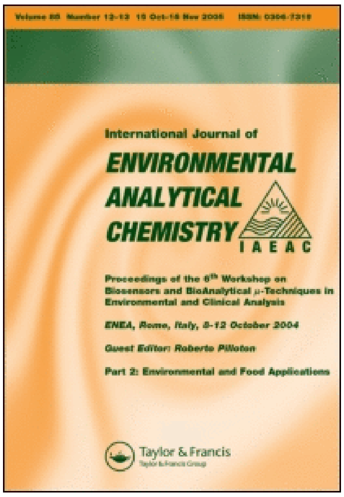

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Environmental Fate of 1,2,3,4,7-Pentachlorodibenzo-*p*-Dioxin in a Canadian Prairie Soil

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ENVIRONMENTAL FATE OF 1,2,3,4,7-PENTACHLORODIBENZO-*p*-DIOXIN IN A CANADIAN PRAIRIE SOIL

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The fate of 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin (P_5CDD) was studied in a Canadian prairie soil under field conditions by applying ^{14}C-labelled P_5CDD to a series of soil microplots and sampling the 0–2 and 2–5 cm depths over a period of 2 years. Analysis by HPLC-LSC revealed that, although P_5CDD dissipated from the plots with a half-life of approximately 1.1 y, leaching and biodegradation were unable to account for the observed losses. Only 1.3% of the applied ^{14}C-P_5CDD appeared in the 2–5 cm depth at 639 days indicating minimal leaching during the course of the experiment. Furthermore, since only 0.9% of the applied radiolabel appeared as extractable degradation products at day 639, biodegradation was not an important loss pathway for P_5CDD in soil. Nonextractable ^{14}C, representing an irreversibly bound fraction of P_5CDD, stabilized at approximately 10% leaving roughly 70% of the radiolabel unaccounted for at day 639. The observed losses are attributed to volatilization of parent P_5CDD from the soil plots.

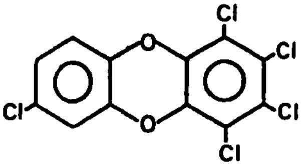
KEY WORDS: Chlorinated dioxins, PCDDs, soil, fate, volatilization.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are a group of highly persistent, toxic[1] environmental contaminants characterized by extreme hydrophibocity.[2] Chlorinated dioxins enter the environment through processes such as incineration of municipal and industrial wastes,[3] use of chlorophenol-based chemicals, and chlorine bleaching in the pulp and paper industry.[4] In this study we are concerned with the fate of PCDDs in the terrestrial environment, specifically in agricultural soils. Specific PCDDs enter agricultural soils as trace contaminants in phenoxy acid herbicides[5] sprayed over or incorporated into the soil, whereas atmospheric deposition may introduce a more complex mixture of congeners.[3] PCDDs in the soil are subject to the usual redistribution processes including photolytic, chemical, and microbial degradation, leaching, volatilization, and erosion in which chemicals sorbed to solids are transported from a localized site by wind or runoff water. The ultimate fate of PCDDs in soil will be determined by the relative importance of the individual redistribution processes.

The behavior of the most toxic PCDD congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (T_4CDD), in soil has been the subject of a number of studies. Kearney *et al.*[6] reported a half-life of approximately 1 year for 2,3,7,8-T_4CDD in several soils. Nash and Beall[7] detected volatilization of 2,3,7,8-T_4CDD from grass plots when applied as either an emulsifiable concentrate or a granular formulation. Freeman and Schroy[8] attributed the slow movement of T_4CDD in soil, approximately 1 cm/y, to vapor diffusion driven primarily by temperature gradients in the soil column. Cerlesi *et al.*[9] reported a $t_{1/2}$ of 8.6 y for 2,3,7,8-T_4CDD in Seveso soil in contrast to the 1 y reported in Kearney, illustrating the effect of depth of incorporation of PCDD on its persistence in soil. Muir *et al.*[10] recently studied the fate of 1,3,6,8-T_4CDD in soil microplots, citing volatilization as the most likely mechanism to explain the observed losses. Their data indicated a half-life in the 130–400 day range for this TCDD congener in a Canadian prairie soil and climate.

In this study the fate of 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin (P_5CDD), was investigated in a Canadian prairie soil in order to determine the relative importance of biodegradation, volatilization, and leaching in the dissipation of PCDDs from surface contaminated soils. This PCDD congener is of intermediate hydrophobicity within the dioxin family.



1,2,3,4,7-P_5CDD

EXPERIMENTAL

Chemicals

Universally ring ^{14}C-labelled 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin, with a specific activity of 24.16 mCi/mmol, was purchased from Pathfinder Laboratories Inc. (St. Louis, MO). P_5CDD was purified by preparative HPLC using a Waters Scientific μBondapak column as previously described[11] to a radiopurity of 99+%. Solvents used in HPLC and sample workup were Distilled-in-Glass grade purchased from Caledon Laboratories Inc. (Georgetown, ON). Fluor used in liquid scintillation counting of HPLC fractions, Scintiverse I, was provided by Fisher Scientific (Winnipeg, MB). The $^{14}CO_2$ trapping agent, 2-methoxyethylamine, and PCS fluor used in the oxidizer were supplied by Packard Instrument Co. Inc. (Downers Grove, IL).

Soil Microplot Applications

Fourteen 10 cm × 10 cm microplots at the Agriculture Canada Research Station, White City, SK were used for the fate study. The soil at this site was previously characterized[10] as a sandy loam (Dark Brown Chernozemic of the Asquith Association) consisting of 10% clay, 25% silt, and 65% sand and containing 4.6% organic matter with a pH of 7.6 (aqueous suspension). A stock solution containing 7.50 μg of the purified P_5CDD/mL was prepared in 2:3 THF-acetone. A 1.0 mL Mohr pipet was used to apply 0.90 mL (6.75 μg) of the P_5CDD solution to each of the microplots on the hot, dry, and windy afternoon of July 9, 1984. The pipet was moved back and forth during the application in an attempt to distribute the PCDD over the surface of the microplot but being careful to keep approximately 2 cm from the edges of each plot. A thin layer of soil was then sprinkled over each plot immediately after application and the plot was somewhat compacted to minimize losses due to wind erosion. The plots were kept free of weed growth by cutting weeds at the soil level periodically. Each microplot was marked with stakes for future sampling and the entire plot area was enclosed with barbed wire fence to minimize disturbance of the plot by wandering cattle and wildlife.

Sampling

Duplicate microplots were sampled immediately after application ($t = 0$) and subsequently at 29, 70, 276, 336, 389 and 639 days post-application. In each case the soil was sampled into 0–2 and 2–5 cm levels by excavating as precisely as possible with a trowel, scraping the appropriate depth of soil from the plot and transferring to a plastic bag. Samples were transported to the laboratory and stored at −32 °C until analysis.

Cleanup and Analysis

Individual samples, containing approximately 250–500 g of soil, were mixed and ground to a fine consistency in a glass jar using a paint spinner attached to a variable speed drill. Duplicate 30 g subsamples were soxhlet extracted for 16 h with 300 mL of 1:1 acetone-hexane. The extract was reduced to ~3 mL by rotary evaporation, dried by passing through a column of anhydrous Na_2SO_4, washing the column with 10 mL of hexane and 3 mL of dichloromethane (DCM). After evaporation to ~1 mL, the samples were washed into 10 mL graduated centrifuge tubes with hexane and ethyl acetate, reduced in volume with N_2, and finally made to exactly 5.0 mL with hexane.

A 2.00 mL aliquot was evaporated to dryness with N_2 and made up to 0.5 mL with CH_3OH for HPLC analysis. A Rheodyne injector was used to introduce 100 μL of this solution to a Waters Scientific HPLC system consisting of a 30 cm × 3.9 mm i.d. μBondapak column, a 6000A solvent delivery system, and a model 440 UV detector. The column eluent, using 85:15 methanol-water as the mobile phase, was fraction collected and analyzed by LSC on a Beckman 7500 Liquid Scintillation Counter after addition of 10 mL of Scintiverse I fluor to each fraction. All samples were counted for 10 min.

The nonextractable ^{14}C was determined by oxidation of duplicate 0.2–0.4 g subsamples of extracted soil with a Packard B306 Tri-Carb Sample Oxidizer. The CO_2 was collected in 2-methoxyethylamine (Carbo-Sorb), diluted with a 2:1 PCS-xylene fluor, and assayed for 10 min by LSC.

Parent P_5CDD identity was established with a Hewlett-Packard 5890 gas chromatograph equipped with a 5970 mass selective detector (MSD) with an HP-5 cross-linked fused silica column (25 m × 0.2 mm × 0.11 μm film thickness). The MSD was operated in the selected ion monitoring mode with the 355.9 to 357.9 amu ions monitored for P_5CDD.

Finally, soil moisture content was determined gravimetrically for both the 0–2 and 2–5 cm layers by heating duplicate 10 g subsamples of each soil fraction for 2 h at 120 °C.

RESULTS AND DISCUSSION

Dissipation of P_5CDD from 0–2 cm

The concentrations of extractable parent P_5CDD, extractable degradation products, and nonextractable ^{14}C were determined over the 639 days of the experiment for both the 0–2 and 2–5 cm layers of the soil column. HPLC-LSC analysis was used to determine both parent P_5CDD and extractable degradation products. The concentration of degradation products represents total ^{14}C eluting outside of the parent P_5CDD band and is calculated in terms of P_5CDD equivalents. Since the nature of nonextractable residues are not known, these concentrations are also expressed in terms of P_5CDD equivalents, using the specific activity of the parent P_5CDD in the calculations. All concentrations are reported on a dry weight soil basis.

Initial rapid volatile losses are believed to account for the less than expected recovery (81 %) of applied ^{14}C at $t=0$. This is consistent with the fact that the application was carried out on a hot, windy afternoon. Losses of parent ^{14}C-P_5CDD from the 0–2 cm soil layer are summarized in Table 1 and plotted in Figure 1. Fifty percent of the applied radiolabel had disappeared by day 276, corresponding to a half-life of approximately 0.8 y. However, because of the initial rapid losses, a first-order treatment provides a better quantitative description of the rate of dissipation of P_5CDD from this soil. Linear regression analysis (ln C vs time) yields a pseudo first-order loss rate constant of $0.0017\,d^{-1}$ and a corresponding half-life of 1.1 y, with a correlation coefficient, r, of 0.87. A number of factors including soil compaction and physical cutting of the soil layers contribute to uncertainties in calculated concentrations in each layer.

The observed half-life for P_5CDD is consistent with previous data in the literature where dioxin congeners have been applied to surface soils. For example,

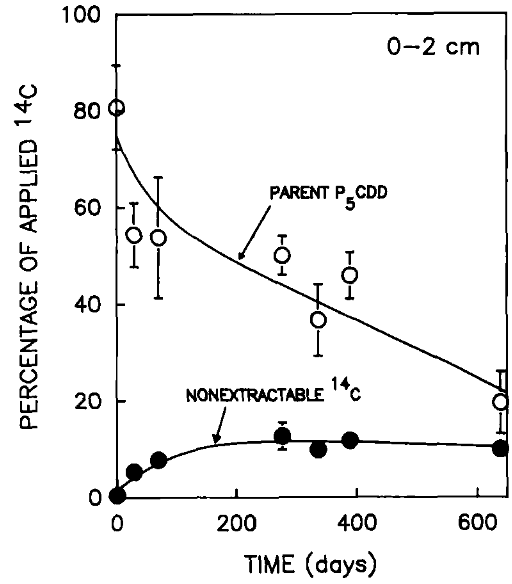


Figure 1 Loss of parent ^{14}C-1,2,3,4,7-P$_5$CDD and corresponding levels of nonextractable ^{14}C in the 0–2 cm soil layer over 2 years under field conditions, expressed in terms of the percent of ^{14}C-P$_5$CDD initially applied to each plot. Error bars represent the standard deviation of 4 trials.

Muir *et al.*[10] reported 50% disappearance of 1,3,6,8-T$_4$CDD in 130–400 days in a similar study whereas Kearney *et al.*[6] reported 54% recovery of 2,3,7,8-T$_4$CDD in 350 days when incorporated into several soils at concentrations of 1 ppm.

Leaching

The amount of ^{14}C-P$_5$CDD leaching into the 2–5 cm layer appears to be insignificant in the two years of the study as indicated in Table 1. In total only 0.9 to 2.2% of the ^{14}C-P$_5$CDD originally applied to the microplots appears in the lower soil layer with the majority present as intact parent compound. Since there is no pattern to indicate increased leaching with time, the ^{14}C detected in the 2–5 cm layer is believed to be largely the result of cross contamination occurring during sampling of the microplots. Furthermore, HPLC-LSC analysis revealed that the ^{14}C in the 2–5 cm layer is predominantly parent P$_5$CDD and not a more mobile degradation product.

The results agree qualitatively with the literature. Muir *et al.*[10] sampled 0–5 and 5–10 cm soil depths and found negligible ^{14}C in the 5–10 cm depth over a period of 495 days. It is apparent that leaching of P$_5$CDD beyond the 2 cm depth during the 639 days of this study is not a major route of removal of this dioxin congener from surface soils. Freeman and Schroy[8] reported a 10 cm migration of 2,3,7,8-T$_4$CDD in soil over a period of 12 years. P$_5$CDD, a somewhat more hydrophobic congener, would be expected to be even less mobile than T$_4$CDD.

Table 1 Distribution of ^{14}C radiolabel as a percentage of the ^{14}C-1,2,3,4,7-pentachlorodibenzo-*p*-dioxin applied to soil microplots

Time (days)	*0–2 cm*			*2–5 cm*
	P_5CDD[a]	*Deg*[a]	*Nonextr*[c]	*Total*[d]
0	80.7	5.6	0.5	—
29	54.3	3.1	5.3	1.9
70	53.8	2.4	7.8	1.0
276	50.0	2.7	12.8	0.9
336	36.7	1.9	9.9	1.0
389	45.9	2.4	11.8	1.2
639	19.6	0.9	10.0	2.2

[a] Parent P_5CDD recovered in the 0–2 cm depth.

[b] Total extractable degradation products in the 0–2 cm depth.

[c] Nonextractable ^{14}C in the 0–2 cm depth.

[d] Total ^{14}C (parent P_5CDD + extractable degradation products + nonextractable ^{14}C) found in the 2–5 cm depth.

Biodegradation

Total extractable degradation products, determined by LSC of fractions collected during HPLC of soil extracts, show a somewhat unexpected trend (see Table 1 and Figure 2). With the organic carbon fraction (4.6%) of this soil potentially supporting a reasonably large microbial population, it was anticipated that slow degradation of P_5CDD might have been detectable, with the concentration of degradation products gradually increasing with time. However, the largest fraction of extractable degradation product, 5.6%, was present in the $t = 0$ sample. The majority of this activity eluted with a retention time (t_r) characteristic of a tetrachlorinated dioxin congener (see reconstructed chromatogram in Figure 3) although this has yet to be confirmed by GC-MS. Since P_5CDD was extensively purified by preparative HPLC prior to application, with a radiopurity greater than 99%, the appearance of the degradation product(s) is not simply a reflection of the purity of the starting material.

Photolytic degradation of PCDDs by reductive dechlorination has previously been observed in organic solvents[12,13] and may have occurred during sample handling at the time of application. The degradation product, believed to be a tetrachlorinated dioxin, then disappeared in a manner analogous to that of the parent P_5CDD applied to the soil microplots.

Nonextractable Residues

Nonextractable ^{14}C in the 0–2 cm soil depth increased gradually during the first summer (see Table 1), reaching 7.8% of the applied ^{14}C label by day 70, and then stabilized at 11–12% throughout the remaining sampling times, as indicated in Figure 1.

The results are consistent with those of Muir *et al.*[10] for 1,3,6,8-T_4CDD. Using the same soil type as in this experiment, nonextractable ^{14}C was reported to vary between 2 and 15% of the amount applied over a period of 495 days, with no

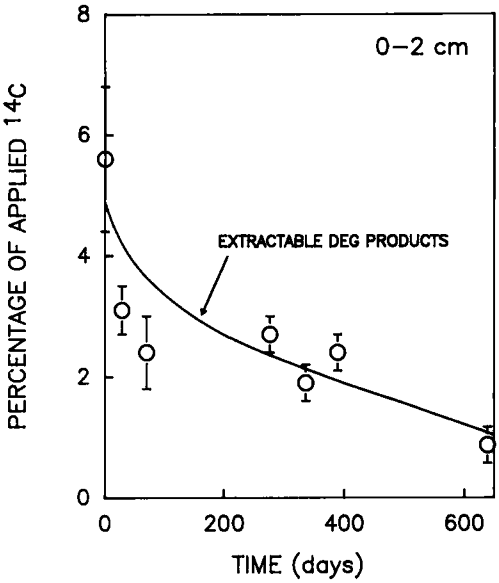


Figure 2 Recovery of extractable degradation products in the 0–2 cm soil layer reported as a percent of the ^{14}C-P$_5$CDD applied to each microplot.

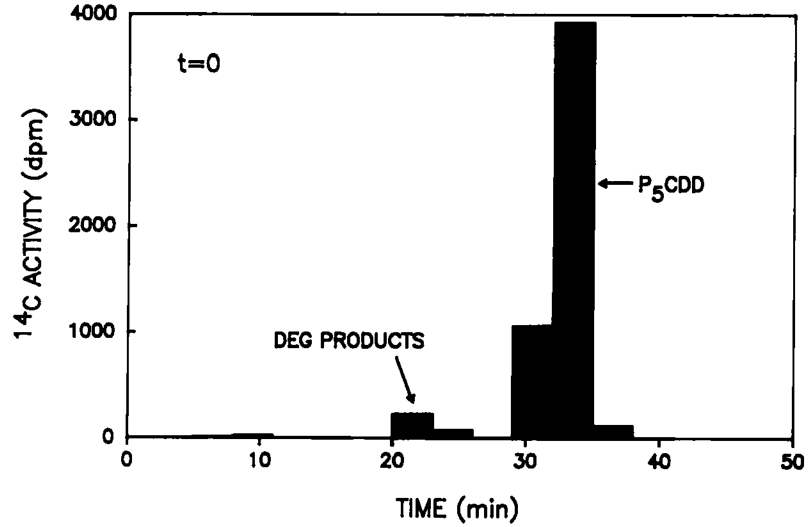


Figure 3 Reconstructed chromatogram for the HPLC-LSC analysis of extractable radioactivity at $t = 0$ days. HPLC conditions: 85% CH_3OH mobile phase, flow rate 1.0 mL/min, C_{18} stationary phase, with continuous 3 min fractions collected for liquid scintillation counting.

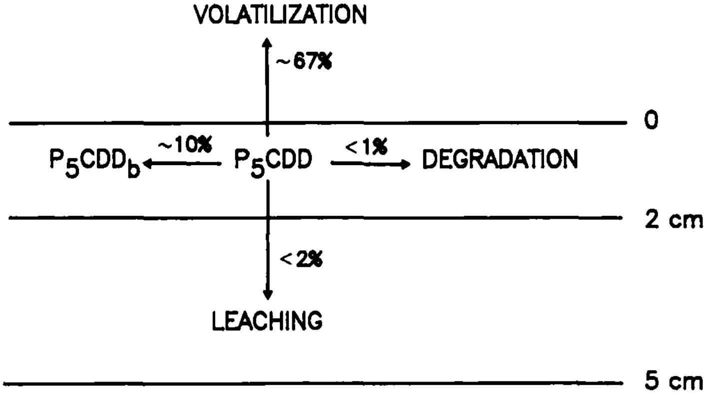


Figure 4 Fate processes describing the redistribution of P_5CDD in surface soils over a period of approximately 2 y. At $t = 639$ days, ~20% of the initially applied radioactivity is recovered as parent P_5CDD in the 0–2 cm layer, with another 10% being irreversibly bound to the soil. Since leaching (<2%) and biodegradation (<1%) are found to be negligible, loss of the remaining ~67% of the radiolabel is attributed to volatilization. (Note: P_5CDD_b and P_5CDD refer to bound and available forms of P_5CDD in the soil).

obvious increase in nonextractable ^{14}C with time. The nonextractable ^{14}C is believed to represent an irreversibly bound fraction of P_5CDD. If this were a nonextractable degradation product one would have expected an increase with time as degradation proceeds.

Mass balance calculations indicate that the largest portion of ^{14}C dissipated from the soil microplots has not been accounted for by the above fate processes as summarized in Figure 4. At day 639 only 19.6% of the applied ^{14}C was recovered as P_5CDD in the 0–2 cm depth. Leaching of 1,2,3,4,7-P_5CDD to depths greater than 2 cm of soil was insignificant over a period of 2 years under environmental conditions typical of the Canadian prairies. Furthermore, P_5CDD is a persistent chemical and was not observed to biodegrade in the soil after application. Since losses due to erosion were not believed to be significant during the course of this study, volatilization from the soil surface is believed to have been the major route explaining the observed losses of P_5CDD from the soil microplots. Volatilization of 2,3,7,8-T_4CDD[6] and 1,3,6,8-T_4CDD[10] from soil has previously been reported as a major loss pathway for chlorinated dioxins from soil. Eduljee,[14] using the fate model of Jury *et al.*,[15] modelled the fate of 2,3,7,8-T_4CDD in soil, concluding that T_4CDD movement in soils could occur by vapor-phase and liquid-phase diffusion as well as by convection during evaporation of water from surface soils. The model predicted a volatilization half-life of 104 days for 2,3,7,8-T_4CDD from thin dust films without water evaporation. Therefore, it is reasonable to conclude that volatilization was the dominant mode of dissipation of P_5CDD from soil microplots in the current investigation. Hence, the kinetic treatment essentially provides a volatilization rate constant, k_v, of 0.0017 d^{-1} and a volatilization half-life, $t^v_{1/2}$, of 1.1 y for the volatilization of P_5CDD from the soil microplots.

Although a volatilization half-life of 1.1 y would make this an insignificant loss pathway for many chemicals, for compounds with the hydrophobicity and persistence of the chlorinated dioxins, this volatilization rate becomes a dominant loss pathway. As illustrated in this study, the normal modes of disappearance, namely leaching and biodegradation, are essentially negligible for PCDDs in soil, resulting in increased importance of volatilization in determining the overall fate of these chemicals in the environment.

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