Photolysis of OCDF and OCDD on soil.

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ABSTRACT

Photodechlorination of OCDF and OCDD is observed on sunlight irradiated soil samples. The dechlorination of OCDF occurs preferentially at the lateral positions resulting in a decreasing proportion of 2,3,7,8-substituted products. The proportion of lower chlorinated 2,3,7,8-substituted PCDDs is increasing during irradiation, indicating peri rather than lateral dechlorination.

INTRODUCTION

The environmental transport and fate of the polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) has been extensively studied during recent years. The deviation found between source patterns and patterns found in different environmental samples is difficult to interpret, but may indicate that transformation reactions are occurring. Photolysis of halogenated aromatic compounds, such as the PCDDs and PCDFs, has been suggested to be one of the main processes for transformation and removal from the environment. The major fraction of these semi-volatile compounds will be adsorbed onto the surface of particles, e.g. soil and fly ash, and the properties of these carrier matrices will to a large extent determine the rate and direction of the transformation reaction.

Several studies have found photodechlorination to be an important pathway, that occurs at fairly rapid rates[1]. Miller et al.[2] and Kieatiwong et al.[3] report on the photolytic dechlorination of OCDD on soil. They found a production of lower chlorinated congeners with the 2,3,7,8-substituted TCDD and PeCDD congeners in greater yields than could be expected on the basis of the number of potential congeners.

The aim of this work is to study the photodechlorination of OCDF and OCDD on soil and to determine the specific congener distribution within the dechlorination products.

EXPERIMENTAL

Soil Samples. The soil used in the experiments was a northeastern Montana soil (2.2% organic matter; 50% sand, 28% silt, 22% clay). The soil was air-dried and sieved through 425 μm sieve.

Pretreatment of Soil samples. Portions of 50 g soil were placed into two round bottom flasks and covered with methylene chloride to a depth of 0.5 cm. 12C-OCDF and 12C-OCDD were spiked (Cambridge Isotope Lab.) into the two flasks and the solvent removed by rotary evaporation for 30 minutes. Two gram portions with the final concentration of 1 μg/g OCDF and OCDD respectively, were weighed and placed into 100 mm glass petri dishes. The dishes were covered with polyethylene film. Three samples were prepared for each sampling time.

Sunlight exposure. The sunlight exposure started on 9 October 1990 (Reno, Nevada, USA). Samples were taken after 0, 1, 2, 4, 8 and 16 days. Dark controls covered with aluminum foil were taken after 8 and 16 days. All samples were shaken gently on each of the sampling days to redistribute the soil. After sampling, the soil was immediately transferred into a screw test tube and placed in the dark. The ultraviolet (UV-B) irradiance at midday was 49 - 50 μW/m2, as measured using a Spectronics Model DM-300N UVB Ultraviolet Meter. Bright sun existed throughout the experiment until day 9. Day 9 was overcast with some rain late in the day. No sun on day 10 (~1μW/m2). Sun returned on day 11, with sunlight intensity (47 μW/m2) similar to the previous period. The experiment was terminated on 25 October 1990 (Day 16).

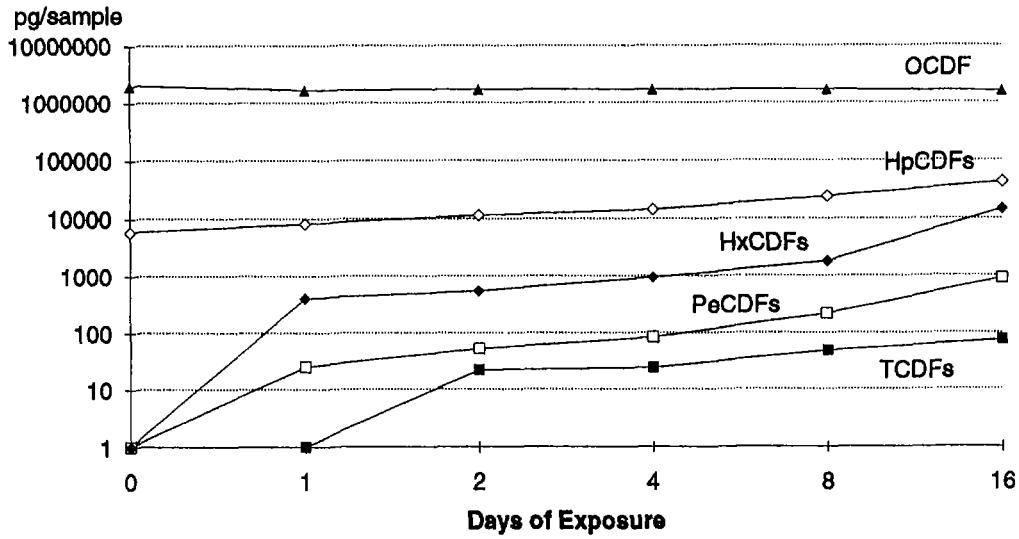
Analysis. The soil samples were Soxhlet extracted for 12 hours in toluene. Prior to the extraction the samples were spiked with 2,3,7,8-substituted 13C-labeled PCDD/Fs, covering all the different congener groups. The clean-up of the extracts was performed by silica, aluminum oxide and carbon columns. The samples were also spiked with additional 13C-labeled PCDD/Fs prior to the clean-up. The extraction and clean-up procedure has been described elsewhere (Marklund S, et al. 1986 [4] and Marklund S. 1990 [5]). The isomer specific analysis was performed with high resolution mass spectrometer (VG 70E) running in EI^+ - mode. The GC-column used was a 50m Chrompack CP-Sil88.

RESULTS AND DISCUSSION

Photodechlorination was observed in all samples, producing lower chlorinated congeners. The total loss of OCDF and OCDD after 16 days irradiation was approximately 25 -30%.
Photolysis of OCDF. Figure 1 shows the dechlorination of OCDF and the dechlorination products formed after 1,2,4,8, and 16 days of sunlight irradiation. After day one the levels of hepta-, hexa- and pentachloro congeners increased and after day two tetrachlorocongeners were also observed. The photodechlorination of OCDF to HpCDFs occurs preferentially at the lateral positions resulting in a relative decreasing proportion of 2,3,7,8-substituted HpCDFs during the irradiation period. This is even more significant for the HxCDFs. Here, the proportion of lateral substituted congeners decreases from 38% (day 1) down to 9% (day

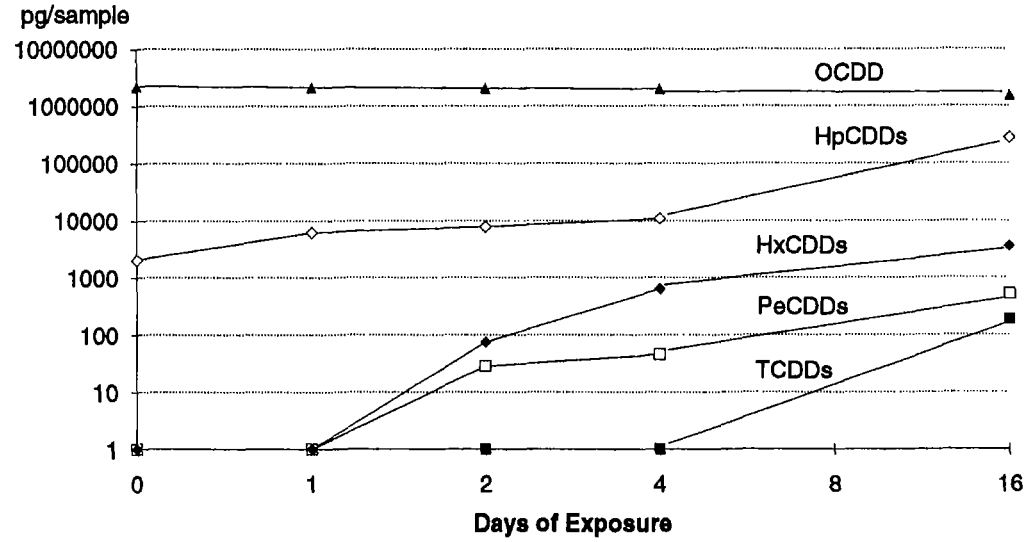
16). 2,3,7,8-TCDF was not observed in any of the irradiated samples even though other TCDFs were identified. These results indicate that a lateral rather than peri photo-dechlorination of PCDFs is predominating on soil.

Figure 1. Photolysis of OCDF on soil



Photolysis of OCDD. The reduction of OCDD and the dechlorination products formed after 1,2,4 and 16 days of sunlight irradiation is shown in Figure 2. HxCDD and PeCDD congeners can be observed after two days of irradiation and TCDD congeners after four days. The proportion of lateral substituted congeners within the different congener groups differs from the PCDFs. Here, the proportion of 1,2,3,4,6,7,8-HpCDD increased from 30% (day 0) to 46% (day 16). This striking tendency is even more pronounced for the lower

Figure 2. Photolysis of OCDD on soil



chlorinated groups. The proportion of 2,3,7,8-substituted congeners for the HxCDDs and PeCDDs increased from 54% to 65% and 24% to 40%, respectively. The 2,3,7,8-TCDD observed after 16 days of irradiation constituted as much as 75% of the total TCDDs. As 22 TCDD congeners exist, this is a substantial enhancement, indicating that peri rather than lateral dechlorination is predominating. These results are in good agreement with previous observations reported by Miller et al [2].

CONCLUSIONS

The results described above show a difference in the photochemistry of PCDFs and PCDDs on soil irradiated with sunlight. Dechlorination of OCDF and OCDD results in production of hepta-, hexa-, penta- and tetrachlorinated congeners. However, the proportion of 2,3,7,8-substituted congeners formed, is significantly different. The photodechlorination is favoured on the lateral (2,3,7,8) positions for the PCDFs and in the peri (1,4,6,9) positions for the PCDDs. 2,3,7,8-TCDF as well as other 2,3,7,8-substituted PCDFs have been found in archived soil samples collected during the period 1846 - 1986 [6]. Our study shows that these congeners are source related and not formed via photodecomposition. Sewage sludge is normally dominated by OCDD. The data presented here and earlier shows that the photochemical degradation of OCDD in sewage sludge should be studied.

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