Estimation of OCDD degradation rate in soil

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Abstract The current concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were determined in soils contaminated with Chinese technical product sodium pentachlorophenate(Na-PCP). The estimated half-life of octachlorodioxin(OCDD) was about 14 years in contaminated soils based on the local historical record and mass balance calculation during the past 43 years(1960—2003). The isomer profiles remained the same regardless of paddy field soil or riverbank soil. The results indicated that the congener-specific information was efficient in estimating the PCDD/Fs fate in contaminated soils.

Keywords: OCDD; degradation rate; Na-PCP

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are well-known as toxic environmental contaminants that were never manufactured intentionally. These contaminants originate from human activities, such as combustion related to energy production, industrial processes and agriculture, and accumulate in various environmental compartments, e.g., soils, vegetation, animals, and humans (Joseph, 1998). Because being resistant to degradation, they can persist for years. A number of extensive investigations have been conducted in some developed nations to elucidate the transport behavior, global fate, and emission/deposition of PCDD/Fs using soils as a suitable sampling matrix in recent years (Brzuzy, 1995; Duarte-Davidson, 1997; Wagrowski, 2000). However, most of the selected sampling sites were untouched by human being (Wagrowski, 2000). Some researchers have studied the environmental profile transformation and fate of PCDD/Fs using the fugacity-based multimedia environmental fate model (Suzuki, 2000), but the half-life estimates for PCDD/Fs in soils are highly variable due to many processes which could have a complex contribution in the environment. On the other hand, some studies reported that congener-specific data well reflect the mixture of PCDD/Fs input from various origins and are potentially useful in understanding the environmental fate of these compounds(Masunaga, 2003). Hagenmaier *et al.* showed that PCDD/Fs were 9 years at least in contaminated soils, and Masunaga *et al.*(Masunaga, 2003) estimated the half life of PCDD/Fs as impurity contained in PCP in Tokyo Bay basin soil were about 7—14 years based on the congener-specific information.

In China, schistosomiasis prevailed in some areas for a long time, and technical sodium pentachlorophenate (Na-PCP) had been used to control the spread of snailborne schistosomiasis since the 1960s. Thus, PCDD/Fs as impurities contained in Na-PCP accumulated in soil. In this study, the selected region was the most serious area of the schistosomiasis prevailed in the 1960s, and the local farmer used Na-PCP many times more than the restriction dose to kill the snailborne in paddy field and reaches of the rivers. Since the schistosomiasis had been gradually extinct since the 1970s in different areas in this region, the residue levels of PCDD/Fs in soil compartments in the region were different due to the

amount of Na-PCP used. In this paper, the current concentrations of the seventeen 2, 3, 7, 8-chlorine-substituted congeners in the collected soil samples were determined. Based on the determinated data and mass balance calculation, the degradation rate of octachlorodioxin (OCDD) in the agriculture field was estimated.

1 Materials and methods

1.1 Sample collection

The samples were collected from the areas where schistosomiasis prevailed in the 1960s in southern China in October, 2003. Samples were collected to a depth of 0—20 cm. One field soil with no record of using Na-PCP were selected as control group. Three samples collected from paddy field and two samples collected from the riverbank. The detailed description is shown in Table 1. Each sample was placed onto a piece of foil. Once the samples were collected, they were stored in a cool box until delivered to laboratory. In the laboratory, they were stored at – 20℃ until analyzed.

Table 1 Description of the soil samples

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Soil	Riverbank	Riverbank	Paddy field	Paddy field	Paddy field
Beginning of spraying Na-PCP	1960	1960	–	1960	1960
End of spraying Na-PCP	1983	1976	–	1985	1973

1.2 Chemical analysis

PCDD/Fs were analyzed with the method of EPA1613B modification. Briefly, the soil samples were spiked with known amounts of a $^{13}C_{12}$-PCDD/Fs mixture(EPA 1613-LCS mixture, Cambridge Isotope Laboratories(CIL), USA), and mixed with anhydrous sodium sulfate. Allowing the samples to equilibrate for 1 to 2 h, and Soxhlet extracted with toluene for 18—24 h. The extracts were purified with a multi-layer silica gel column. The column was prepared by packing a glass column(15 mm i.d.) with a series of layers of silica gel, according the following order from bottom to top: 1 g silica gel, 1.5 g AgNO₃ silica gel, 1 g silica gel, 3 g basic silica gel, 1 g silica gel, 8 g acid silica gel, 1 g silica gel, and 2 g granular anhydrous sodium sulfate. Afterwards, each extract was fractionated by the basic alumina column, which was prepared by packing a glass column(10 mm i.d.) in the following order from bottom to top: 8 g basic alumina and 2 g

granular anhydrous sodium sulfate. The first fraction eluted with 130 ml methylene chloride∶hexane 5∶95(v/v) contained PCBs, the second fraction eluted with 50 ml methylene chloride∶hexane 50∶50(v/v) comprised PCDD/Fs. Then concentrated the second fraction, and added $^{13}C_{12}$-PCDD/Fs internal standards mixture(EPA 1613-IS mixture, Cambridge Isotope Laboratories (CIL), USA) prior to injection into HRGC/HRMS. Identification and quantification of individual PCDD/F congeners were accomplished with a gas chromatograph (HP6890, Agilent, USA) coupled to an autospec ultima mass spectrometer(Waters, USA), at 10000 resolving power (10% valley definition). Chromatographic separation was achieved with a DB-5 (J&W, USA) fused-silica capillary column(60 m × 0.25 mm × 0.25 μm). The temperature program was 160℃ for 3 min, 5 ℃/min to 220℃ for 16 min, 5 ℃/min to 235℃ for 7 min, then 5 ℃/min to 330℃. Injector and transfer line temperatures were held at 290℃ and 330℃, respectively.

1.3 Quality assurance

Analytical quality control was applied to ensure the analysis PCDD/Fs, such as a continuous monitoring of laboratory contamination based on the determination of a blank sample covering the whole analytical procedure, including extraction, cleanup and quantification. Recoveries of spiked soil with the calibration mixture were in the range of 60%—95%. CIL standard reference material (EDF-5183: soil) was analyzed for selected PCDD/Fs congeners, and the reliable results were obtained by comparison of the data from our laboratory with those from material reference values(*RSD* < 20% on results).

2   Results and discussion

PCDD/Fs concentrations in soil samples from the schistosomiasis areas were summarized in Table 2. The results indicated that OCDD was the predominant congener of PCDD/Fs. The total concentrations of PCDDs in soils were more than those of PCDFs, the pattern consisted with the PCDD/Fs profile in Chinese technical product of Na-PCP (Bao, 1995), except sample 3 in which Na-PCP was not used. In order to facilitate comparison, the concentrations of the 2, 3, 7, 8-substituted PCDD/Fs in Chinese products of Na-PCP are shown in Table 3(Bao, 1995). The ratios of the PCDF/PCDD in soils were relatively lower than those of PCDF/PCDD in the products of Na-PCP. It may be because that PCDD and PCDF had different degradation rate, and PCDFs were photochemically less stable than PCDDs(Suzuki, 2000; Wagenaar, 1995).

The results also indicated that the isomer profiles remained the same regardless of paddy field soil or riverbank soil. It was also observed that the amount of PCDD/Fs in agriculture fields was proportional to the years of Na-PCP used. In the field(sample 3) where had never been sprayed Na-PCP, the levels of PCDD/Fs were trivial. So the simple mass balance calculation was based on the steady-state condition, in which the technical product Na-PCP was assumed as the only source of PCDD/Fs in the region.

Loss of PCDD/Fs in soils may be due to several processes such as biodegradation, volatilization, leaching, photochemical transformation, plant uptake, removal by grazing animals, irreversible binding and alteration(humification)

Table 2   Concentrations of PCDD/Fs in soil samples (pg/g dry weight)

PCDD/Fs	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
2378-TCDF	5.8	1.4	< 0.08	3.2	3.4
12378-PeCDF	1.9	1.0	0.9	1.2	1.6
23478-PeCDF	2.4	0.7	0.8	1.1	1.3
123478-HxCDF	7.1	1.6	0.7	1.9	2.6
123678-HxCDF	1.8	0.7	0.6	1.0	1.0
234678-HxCDF	4.8	1.3	1.1	1.3	1.1
123789-HxCDF	0.9	0.3	0.2	0.3	0.5
1234678-HpCDF	35	9.0	3.8	10.9	7.3
1234789-HpCDF	1.4	0.6	0.3	1.3	0.5
OCDF	19	7.1	2.3	6.9	2.8
2378-TCDD	1.5	0.2	< 0.1	0.4	0.4
12378-PeCDD	9.4	0.8	0.6	1.6	1.2
123478-HxCDD	87	7.4	0.4	6.2	12
123678-HxCDD	8.7	1.3	1.4	3.9	1.7
123789-HxCDD	15	2.4	1.1	6.0	2.9
1234678-HpCDD	250	61	5.9	113	62
OCDD	13894	7595	63.7	14924	6407

Table 3   PCDD/Fs in Chinese Na-PCP(ng/g) (Bao, 1995)

PCDDs	Concentration	PCDFs	Concentration
2378-TCDD	4.0	2378-TCDF	3.1
12378-PCDD	2.1	12378-PCDF	40.9
		23478-PCDF	2.4
123478-HxCDD	244	123478-HxDF	76.1
123678-HxCDD	13.8	123678-HxDF	9.4
123789-HxCDD	2.1	123789-HxDF	0.3
		234678-HxCDF	0.9
1234678-HpCDD	1702	1234678-HpDF	135
		1234789-HpDF	18.3
OCDD	12514	OCDF	1647
Total PCDDs	15760	Total PCDFs	2260

and erosion. These loss processes are slow(Duarte-Davidson, 1997). According to the local historical record, the estimated annual amount of Na-PCP used, the estimated annual amount of OCDD input and the total amount of OCDD at the time of spraying Na-PCP was stopped in soils are shown in Table 4. Considering the above PCDD/Fs loss processes, and using the dominant OCDD congener information, we suggest the annual loss rate of OCDD from field were constant over the past 43 years, and simulated trends at different annual loss rates 4%, 5%, and 6% per year assumed on previous studies(Masunaga, 2003; Suzuki, 2000). Although the fitting was not so well, an annual loss rate of 5% per year best fits the trend of OCDD resident in soils contaminated with Chinese technical product Na-PCP.

The following is the simple mass balance equation for estimating the current concentration of OCDD in the contaminated soils:

$$C_1 = C_0(1 - 0.95_n)/(1 - 0.95), \tag{1}$$
$$C_2 = C_1 0.95_m - 1, \tag{2}$$

where C_0 is the annual concentration of OCDD in the soil of input, C_1 is the concentration of OCDD in the soil at the year of spraying Na-PCP stopped, n is the years of Na-PCP used, m is the years from the year of spraying Na-PCP was stopped to 2003 and C_2 is the current concentration of OCDD in the soil.

Table 4 OCDD mass balance in soils of the schistosomiasis area during the past 43 years (1960—2003)

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Estimation level of OCDD in 1960, 10^{-6} g/m²	743	743	0.0	743	743
Estimation total input PCP-Na, g/m²	1366	950	No	1485	772
Estimation total input OCDD, 10^{-6} g/m²	17089	11888	No	18575	9659
Estimation level of OCDD at sparying Na-PCP stopped, pg/g	34314	27736	0.0	35798	24109
Estimation level of OCDD(2003), pg/g	12948	7309	0.0	14968	5447
Determination level of OCDD(2003), pg/g	13894	7595	64	14924	6407

The estimated current concentrations of OCDD in soils based on the record information were comparable to the measured environmental concentration. This indicates that the PCDD/Fs in this area were mainly from Na-PCP, the estimated half-life of OCDD in agriculture field was about 14 years. Table 4 also shows the OCDD mass balance in the Schistosomiasis area soils during the past 43 years (1960—2003). Masunaga et al. (Masunaga, 2003) reported that the annual loss rates estimated based on the decrease in PCDD/Fs concentration in sediment and soil were 5% per year for PCP in terms of PCDD/Fs. So the simple mass balance calculation based on congener-specific information was efficient in estimating the PCDD/Fs fate in contaminated soils.

3 Conclusions

The estimated fate of OCDD was about 14 years in soils contaminated with Na-PCP based on the record information. The results indicated that the congener-specific information was efficient in estimating the PCDD/Fs fate in contaminated soils. OCDD was persistent and resistant to degradation in soil, so it may accumulate in soils and can under some conditions enter the agricultural food chain.

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