Concentrations and Profiles of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Bank Soils Collected from Dongting Lake, China

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Abstract Twelve bank soil samples from the Dongting Lake area were determined to investigate the concentrations and distributions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). The result showed the PCDD/Fs contamination was not only confined to the surface soil, but extended into the subsoil. Total I-TEQ values for all surface soils averaged 30.3 pg/g dw (ranging from 5.53 to 75.6 pg/g dw). There were some differences in the congener profiles among soil, sediment samples and technical product of sodium pentachlorophenate, which could reflect the variety of PCDD/F sources to the environment over time.

Keywords PCDD/Fs · Sodium pentachlorophenate · Bank soil · Dongting Lake

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are a group of the most toxic persistent organic pollutants (POPs) listed in the Stockholm Convention (UNEP 2001). Even at very low exposure levels, they may produce carcinogenic, immunotoxic effects to host organism, as well as severe reproductive and developmental problems (USEPA 2010). The main PCDD/Fs sources are from various combustion processes and numerous chemical processes such as waste incineration, metallurgical processes, paper and pulp processing, and chemicals manufacturing (especially production of pentachlorophenol and

herbicides). Therefore, the areas with potential PCDD/F sources often raise great concerns and need to be evaluated for potential ecological risk (UNEP 1999).

Dongting Lake, located in the middle Yangtze River region, is the second largest freshwater lake of China. For centuries, the lake area was ravaged by Asian schistosomiasis. Since the 1960s, technical product of sodium pentachlorophenate (Na-PCP) has been extensively used as molluscicide to kill oncomelania-the intermediate host of Schistosoma (Cheng 1971). It has been estimated that at least 9,800 tons of Na-PCP were used over the 30 year period. Also, PCDD/Fs present as impurities of Na-PCP were released to the environment (Zheng et al. 1997). Despite the fact that restrictions have been officially placed on the use of Na-PCP since 1995, the contamination of the PCDD/F still remains. As Zheng et al. (1997) reported, the concentrations of PCDD/Fs in sediments in Dongting Lake were 128.3–890.5 pg I-TEQ/g dw in 1995. According to Holoubec et al. (Vartiainen et al. 1997) classification, the sediments in these areas were heavily polluted.

Actually, in order to reduce populations of the snail host, Na-PCP was sprayed on river banks by the local people. After treatment was completed, high levels of Na-PCP remained in the bank soil. Soil is considered as an important global reservoir for persistent organic pollutants (POPs) due to their high storage capacity (Meijer et al. 2002). According to a report by Cousins and Jones (1998), more than 90% of the total environmental burden of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and PCDD/Fs in the UK are contained in this environmental compartment. Since the half-life of PCDD/Fs in the soil has been estimated at least 10 years (Jackson and Eduljee 1994), these chemicals may remain in soils for a very long time, posing potential threats to human health and the environment.

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So even after Na-PCP has been banned from use for many years, it's still very important to know about PCDD/F remains and compositional characteristic in soil. The objectives of this research were to conduct initial investigation on the extent of PCDD/F pollution in bank soils and to identify possible factors affecting concentrations and distributions of PCDD/F. By making some sort of comparisons of PCDD/F contamination among soil, sediment and Na-PCP, the changes in concentrations and patterns of the PCDD/F source to the environment over time were also examined.

Materials and Methods

Soil sampling was performed in two sites located at Western Dongting Lake and Southern Dongting Lake, respectively. According to the information from the local environmental protection authorities, both sites were within the areas where Na-PCP has been intensively used.

To adequately assess the distribution of PCDD/Fs, the surface and depth soil sampling were conducted. In surface soil sampling, we laid out one transect with four sampling stations allocated along each transect at each site. Transects were located generally perpendicular to the lake along a general north–south compass bearing. Along the transect, samples were taken at regular intervals, with the first station located at a distance of 5 m from the lake bank's edge, and the other three sampling stations were 15, 25 and 35 m far away from the lake respectively. These stations were labeled as S1–S8. Four stations (S1–S4) were from the western Dongting Lake, and the others were from the southern Dongting Lake. Each station was sampled compositely in 0–10 cm below the surface. With respect to depth sampling, we excavated a pit and collected soil at various depths at the station S1 with a solvent-rinsed stainless steel spatula. The samples were divided into five categories with the depth interval of 10 cm. They were respectively labeled as S1, SD1–SD4.

The samples were collected separately with cleaned hand trowel, wrapped with clean aluminum foil, then sealed in the plastic bags, and placed in a cool box. After being transferred to the laboratory, the samples were stored at -5°C until further analysis.

The soils were freeze-dried, homogenized and sieved with a 2-mm mesh sieve. Then a mixture of $^{13}\text{C}_{12}$ -labelled PCDD/Fs internal standards (Wellington Laboratories, Canada) was spiked and Soxhlet extraction was employed with 250 ml toluene for 24 h. After extraction, the extracts were washed with concentrated H_2SO_4 until colorless. Then they were loaded to multilayer silica gel columns and basic alumina columns, respectively. Finally, the extracts were fractionated on a florisil column. The fraction was

concentrated and transferred to the GC vials. After being dried to 20 μl under a stream of nitrogen, the $^{13}\text{C}_{12}$ -labelled mixed PCDD/Fs recovery standards (Wellington Laboratories, Canada) were added.

The samples were analyzed by HRGC/HRMS with Agilent 6890 GC (Agilent, USA) and Autospec Ultima mass spectrometer (Waters, UK). Chromatographic separation was achieved with a DB-5MS fused-silica capillary column (J&W Scientific, CA, USA, 60 m, 0.25 mm ID, 0.25 μm film thickness). Exactly 1 μl sample solution was injected with a CTC PAL autosampler in splitless mode. The MS was operated at $\geq 10,000$ resolution with an electron impact (EI) ion source (38 eV electron energy) and in the selected ion monitoring (SIM) mode. Ion source and interface temperatures are 250°C . Organic matter content was determined using the Walkley–Black method (Sahrawat 1982).

Results and Discussion

The recovery of labeled compound of PCDD/Fs ranged from 58.7 to 110%, which met the limits of US EPA methods. Properties of surface soils, results of PCDD/Fs analysis expressed as individual congener concentration and I-TEQ of the samples were presented in Table 1. The overall concentrations in the surface soil ranged from 5.53 to 75.6 pg I-TEQ/g dw, with an average value of 30.3 pg I-TEQ/g dw. The average PCDD/Fs concentrations between the western of the lake and the southern of the lake were very similar, 30.0 and 30.6 pg I-TEQ/g dw respectively. The total PCDD/Fs concentration decreased gradually with increasing distance from the maximum concentration station at both sites. According to the previous reports (Gao et al. 2008), PCDD/Fs concentrations in sediments from the western of the lake and the southern of the lake were 3.6 and 5.5 pg I-TEQ/g dw, respectively. They were far less than those found in most contaminated bank soils.

In order to classify contaminated soils and perform environmental risk assessment, the German guidelines referring to PCDD/Fs in soil (Im et al. 2002) was adopted. The result showed that the PCDD/Fs concentrations in almost all samples (92%) were notably above the German guideline for grazing land use of 5 pg I-TEQ/g dw. Seven of 12 soil samples contained TEQs between 5 and 40 pg I-TEQ/g dw. Four of 12 soil samples were greater than the German guideline for agricultural land use of 40 pg I-TEQ/g dw. The maximum concentration was 75.6 pg I-TEQ/g dw in S1, which exceeds the guideline value of 5 pg I-TEQ/g dw by more than a factor of 15. According to the guidelines, critical land uses, e.g. grazing as well as animal feedstuff cultivation should be

Table 1 Concentrations of PCDD/Fs (pg/g dw) in bank soil samples from the Dongting Lake area

Congeners	S1	S2	S3	S4	S5	S6	S7	S8
2378-TCDF	0.78	<0.65	<0.28	<0.13	<0.06	<0.1	<0.26	0.79
12378-PeCDF	<0.17	0.17	0.2	0.04	<0.06	0.05	<0.18	1.83
23478-PeCDF	1.84	0.06	0.35	0.02	<0.06	0.05	<0.18	3.85
123478-HxCDF	6.49	0.59	0.37	0.05	1.08	0.29	<0.34	5.58
123678-HxCDF	3.1	0.18	0.35	<0.01	<0.07	<0.02	1.56	9.14
234678-HxCDF	2.58	0.19	0.34	0.06	0.76	<0.01	2.96	10.8
123789-HxCDF	<0.12	0.13	0.14	0.05	<0.09	0.09	<0.31	1.87
1234678-HpCDF	17.8	4.05	2.58	0.85	4.65	3.48	17	40.8
1234789-HpCDF	0.78	1.26	0.48	0.31	<0.2	1.39	<0.64	4.78
OCDF	179	115	48.1	29.8	87	212	103	49.6
2378-TCDD	<0.24	0.88	<0.11	<0.1	<0.04	<0.59	<0.14	0.04
12378-PeCDD	3.1	0.54	0.11	0.05	<0.1	0.14	<0.35	0.4
123478-HxCDD	10	3.64	0.67	0.37	0.29	0.69	<0.33	0.51
123678-HxCDD	14.1	1.57	0.93	0.54	0.87	1.2	<0.35	0.89
123789-HxCDD	16.5	1.79	1.26	0.6	0.71	1.38	<0.33	1.03
1234678-HpCDD	738	372	119	95.7	66	316	81.7	21.2
OCDD	59,999	24,952	6,236	4,323	20,908	40,391	47,376	1,301
Total PCDFs	212	121	53	31.2	93.5	218	125	129
Total PCDDs	60,780	25,332	6,359	4,420	20,976	40,710	47,457	1,325
Total PCDD/Fs	60,993	25,454	6,412	4,451	21,070	40,927	47,582	1,454
I-TEQ	75.6	30.8	8.15	5.53	22.1	44.3	48.9	7.33
R(PCDDs/PCDFs)	287	209	120	142	224	187	380	10.3
R(I-TEQ PCDDs/I-TEQ PCDFs)	28.3	96.8	20.3	78.6	68.5	135	66.3	0.37
SOM(%)	0.69	1.69	1.83	1.47	3.66	3.78	3.19	2.34

avoided if increased dioxin levels were found in food-stuffs grown on such soils.

In addition, the vertical distribution of PCDD/Fs concentrations was also investigated. The results presented an unsymmetric, skewed W-shaped distribution profile (Fig. 1). It can be seen that contamination is not only confined to the top 0–10 cm layer of soil, but extended into the subsoil. According to historical records (Cheng 1971), snail-infested area would be buried with uninfested soil after treatment with Na-PCP. This might result in the cover of contaminated soil with uncontaminated soil and then the distribution as shown in this study. However, these soil samples were only collected to a depth of 50 cm, which seemed to be not enough. In order to obtain more accurate information on the vertical distribution of PCDD/Fs in the soils, more samples and further depth distribution studies are necessary.

Although some previous studies have showed that the level and distribution of POPs in soils had a close correlation with organic matter content (Meijer et al. 2002), no such clear correlations were observed in both horizontal and vertical distribution in this study ($R^2 < 0.5$, $p > 0.05$). This may be due to PCDD/Fs concentrations can be

Fig. 1 Total PCDD/F concentrations versus depth profile in soils from the station S1

affected by factors other than SOM such as proximity to sources, usage trends (Sweetman et al. 2005).

From Table 1, it was also observed that concentrations of PCDDs were greater than those of PCDFs in all bank soil samples. The profile was overwhelmingly dominated by highly chlorinated congeners (hepta-, octa-CDD/Fs). In general, PCDDs concentrations increased with increasing

chlorination. The contribution of OCDD to $\sum$ PCDD/Fs was the highest and averaged 98%, ranging from 89.5 to 99.6% in all samples, followed by 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDF. But those less chlorinated, highly toxic congeners were present in very low concentrations. The present congener profile matched very closely with each other and with Na-PCP. No other clear pollution sources have been identified within the study site, suggesting that contaminated soil samples should had the same single major “Na-PCP” source (Zheng et al. 1997).

However, there were some differences in the PCDD/Fs congener profiles of soil, sediment samples and technical product of Na-PCP. We can find that the concentration ratio of total PCDDs to total PCDFs in all soil samples averaged 229, ranging from 10.3 to 457, and thus much higher than that in Chinese technical Na-PCP (with a ratio about 7.5). In addition, the contribution of OCDD to $\sum$ PCDD/Fs was observed to have elevated level in all soil samples in comparison with that of Na-PCP, in which the value was 76%. Further, the OCDD was the major contributor to TEQs in almost all soil samples (except S8), accounting for more than 75% of the TEQs. But in Na-PCP, OCDD accounted for only about 16.5% to the I-TEQ and 1,2,3,4,7,8-HxCDD was the major contributor (about 32%). These changes were likely due to degradation and volatilization processes. Generally, for the same level of chlorination, the vapour pressure of PCDFs were relatively higher than those of PCDDs and the degradation half-life times of PCDFs were relatively shorter than those of PCDDs (Sinkkonen and Paasivirta 2000; Srogi 2008). Therefore, PCDFs were more readily volatilized or degraded than PCDDs. In addition, according to Gaus et al. (2002), the natural PCDD formation such as the conversion of PCP or Na-PCP to PCDD (in particular OCDD) in the environment may lead to the presence of elevated levels of higher chlorinated PCDDs in some sediments and soil samples.

Furthermore, this study showed that the concentration of 1,2,3,7,8-PeCDF were 20 times higher than that of 1,2,3,7,8-PeCDD in technical Na-PCP, while the levels of 1,2,3,7,8-PeCDF were almost as much as those of 1,2,3,7,8-PeCDD in soil samples. Penta-chlorinated congeners of PCDD/Fs in most samples were below or near the detection limit. Among the 2,3,7,8-substituted HxCDDs, 1,2,3,4,7,8-HxCDD were 116 times higher than that of 1,2,3,7,8,9-HxCDD and 18 times higher than that of 1,2,3,6,7,8-HxCDD in commercial Na-PCP, while in seven soil samples, concentrations of 1,2,3,7,8,9-HxCDD were a little higher compared to 1,2,3,4,7,8- and 1,2,3,6,7,8-substituted HxCDDs. The concentrations of these three congeners are almost of the same magnitude. These differences might be attributed to the fact that although

PCDD/Fs are highly persistent, their level and profile are susceptible to be altered by physical/chemical and biological mechanisms such as volatilization, biodegradation and abiotic breakdown (Wenning et al. 1992). To a certain degree, less chlorinated congeners underwent these processes more easily and more pronounced than highly chlorinated ones for their low vapour pressure and relatively shorter half-lives.

After the use of Na-PCP was banned in the 1990s, the further PCDD/Fs contamination of soils should not occur and would decrease gradually. In order to draw up details of the changes in PCDD and PCDF contamination in this environment over time, further study would be necessary.

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