ANALYSIS OF POLYCHLORINATED AND POLYBROMINATED DIBENZO-*p*-DIOXINS, DIBENZOFURANS IN EARTHWORM AND SOIL SAMPLES

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Abstract

PCDD/Fs and PBDD/Fs were analyzed in the earthworm and soil samples collected from an electronic waste dismantling area in China. The results showed that the concentrations in the earthworms were in the range of 72.8-407 pg.g^{-1}dw (1.2-8.0 pg WHO-TEQ.g^{-1}dw) for PCDD/Fs and 6-56 pg.g^{-1}dw for PBDD/Fs. Higher concentrations were found in the soil samples, which were 1374-6608 pg.g^{-1}dw (26-71 pg WHO-TEQ.g^{-1}.dw) for PCDD/Fs and 191-442 pg.g^{-1}dw for PBDD/Fs. Additionally, differences in the congener profiles could be seen for PCDD/Fs and PBDD/Fs, in all samples were PXDFs detected in higher concentrations compared to PXDDs, indicating that incineration or combustion is the main pollution source in this local area. The low biota-to-soil accumulation factors suggest that the chlorinated and brominated dioxins and furans do not bioaccumulate in earthworms.

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are mainly formed as by-products during chemical and combustion process involving the use, production or disposal of chlorine or chlorine-derived chemicals. They are ubiquitous environmental contaminants, which persist and bioaccumulate through the food chain and finally constitute a threat to human health. Many studies on PCDD/Fs have been carried out during last two decades. In recent years, polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) have received increased attention due to its toxicological effects and distribution in the environment similar to PCDD/Fs. PBDD/Fs are also unintentionally formed in the process of manufacturing brominated flame retardants (BFRs) and from photolytic and thermal degradation of BFRs. They exhibit somewhat different physical-chemical properties compared to PCDD/Fs, including less persistence in the environment and higher sensitivity towards UV degradation, which make a big challenge to accurately determine PBDD/Fs in different matrices. On the other hand, it seems that the elimination half-life of tetra-brominated dibenzo-*p*-dioxin (TBDD) is similar to tetra-chlorinated dibenzo-*p*-dioxin (TCDD), but some congeners, such as tetra-brominated dibenzo-*p*-furan (TBDF), are more persistent towards mammalian metabolism in the animal body, and the level of toxicity could be altered because of the larger size of the bromine atom comparing with PCDD/Fs[1].

Earthworms were considered as an important bioindicator for the transport of contaminants from the soil to organisms. Many studies[2,3] were conducted to show the bioaccumulation of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and PCDD/Fs in earthworms, but no report about PBDD/Fs was found as far as we know.

In the present study, an existing analytical method was adapted for the analysis of tetra- to

octa-brominated and chlorinated dioxins and furans and applied to environmental samples to evaluate the contamination levels and bioaccumulation in earthworms.

Materials and methods

The earthworm and soil samples were collected from an electronic-waste dismantling area in Taizhou, Zhejiang Province, southeast of China. Each earthworm sample was formed by collecting about 30 earthworms from the same farmland where the soil was sampled simultaneously. The samples were freeze-dried and homogenized, and stored at -20ºC before analysis. The extraction and cleanup procedure followed our previous reports[4,5]. In brief, open column was employed to extract the earthworms with dichloromethane/n-hexane (1:1, v/v). After lipid determination, the extracts went through the multilayer silica column, alumina column and carbon column, respectively. The final extracts were concentrated into 25μl tetradecane in GC vials. The soils were extracted using pressurized liquid extraction (PLE) with toluene, and then cleaned up using an automated Powerprep system from FMS (using a series of acidic silica, aluminum oxide and carbon columns all obtained from FMS). Before the extraction and GC analysis, ^{13}C surrogated standards were added prior to extraction and before injection a recovery standard was added. Labeled standards of all bromination and chlorination levels were used in this study, including ^{13}C-2,3,7,8-TeBDD, ^{13}C-1,2,3,7,8-PeBDD, ^{13}C-1,2,3,4,7,8-HxBDD, ^{13}C-1,2,3,6,7,8-HxBDD, ^{13}C-1,2,3,4,6,7,8-HpBDD, ^{13}C-OBDD, ^{13}C-2,3,7,8-TeBDF, ^{13}C-2,3,4,7,8-PeBDF, ^{13}C-1,2,3,4,7,8-HxBDF, ^{13}C-1,2,3,4,6,7,8-HpBDF, ^{13}C-OBDF (as surrogated standards), and ^{13}C-1,2,3,7,8,9-HxBDD, ^{13}C-1,2,3,7,8-PeBDF (as recovery standards).

The PCDD/Fs and PBDD/Fs were analyzed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), which is Agilent 6890N coupled to an Autospec-Ultima HRMS system with an electron impact (EI) ion source. For PCDD/Fs, a 30m BPX5 fused silica capillary column (SGE, 0.25μm×0.25mm i.d.) was used in splitless mode; for PBDD/Fs, ramped on-column injection and 15m capillary column (SGE, 0.1μm×0.25mm i.d.) was employed to avoid thermal degradation and discrimination.

Results and discussion

Generally, it seems difficult to get good recovery yields for PBDD/Fs compared to PCDD/Fs[4], which also occurred in this present work. For PCDD/Fs, the recoveries were in the range of 50-103% for both the earthworm and soil samples. In contrast, PBDD/Fs showed larger range between 68-152% for earthworms and 54-104% for the soil samples (except for ^{13}C-OBDD/F).

The average concentration of PCDD/Fs in the four earthworm samples was 195 pg.g^{-1}dw (dry weight) (range 72.8-407 pg.g^{-1}dw), and the TEQ concentrations were between 1.2-8.0 pg WHO-TEQ.g^{-1}dw. The congener profiles showed that OCDD was the most abundant PCDD/F in all samples, which accounted for more than 40% of the sum concentration (Fig. 1). In the soils, the concentrations were in the range of 1374-6608 pg.g^{-1}dw (or 26-71 pg WHO-TEQ.g^{-1}.dw), which are consistent with the report by Ma et al.[6], but higher than the results from Zhao et al.[7]. Comparing the results from the earthworms, it was obvious that PCDFs were higher than PCDDs, which indicates that incineration or combustion is the main pollution source in this local area. However, OCDF and 1,2,3,4,6,7,8-HpCDF were the dominant congeners besides OCDD in the soil samples, which is also different from the report of Zhao et al.[7].

For PBDD/Fs, the average concentration was only 29 pg.g^{-1}dw (6-56 pg.g^{-1}dw) in the earthworm

samples and 319 pg.g^{-1}dw (191-442 pg.g^{-1}dw) in the soils. Interestingly, PBDDs were not found in any samples except for low-levels of 1,2,3,4,6,7,8-HpBDD in the soil samples. In contrast, 1,2,3,4,6,7,8-HpBDF was significantly detected in all samples, which was comparable to the PCDD/Fs results (Fig. 2). This congener is considered to be a marker for incomplete combustion and the dominant PBDD/F-congener measured after fires and back-yard burning of electronic equipment that have been treated with brominated flame retardants[8]. Furthermore, all the furans could be determined in the soils, but only a few of them, such as 2,3,7,8-TeBDF and 1,2,3,4,6,7,8-HpBDF, could be detected in the earthworms. Special attention was paid to the analysis of OBDD/Fs in the samples. However, no satisfactory results were obtained due to the degradation on the column and low intensity during the analysis.

Biota-to-soil accumulation factors (BSAFs) were calculated based on the congener concentrations in the earthworms and soils: BSAF= C_{worm}/C_{soil}, assuming steady-state conditions. As shown in figure 3, the BSAFs of PXDD/Fs were in the range of 0.03-0.33, which were much lower than that of PCBs (0.71-70)[3]. This implicates that both the chlorinated and brominated dioxins and furans do not bioaccumulate in earthworm, which is in agreement with data from Nakamura et al.[9]. Moreover, the heavier congeners showed smaller BSAFs, which is in agreement with the study by Krauss et al.[3] and Hallgren et al.[10]. This phenomenon is closely related to the K_{ow} value of each congener. As illustrated by Krauss et al.[3], BSAFs of PCBs decreased with increasing K_{ow}, and the decreasing uptake with increasing degree of chlorination points towards a limited membrane permeability of highly chlorinated compounds. In this case, the brominated dioxins and furans showed the same tendency.

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Figure 1. Distribution of PCDD/Fs concentrations (pg.g^{-1}dw) in the earthworm and soil samples. OCDD in S4 soil was 5715 pg.g^{-1}dw, of which the column was truncated in order to obtain a clear comparison between each sample profile.

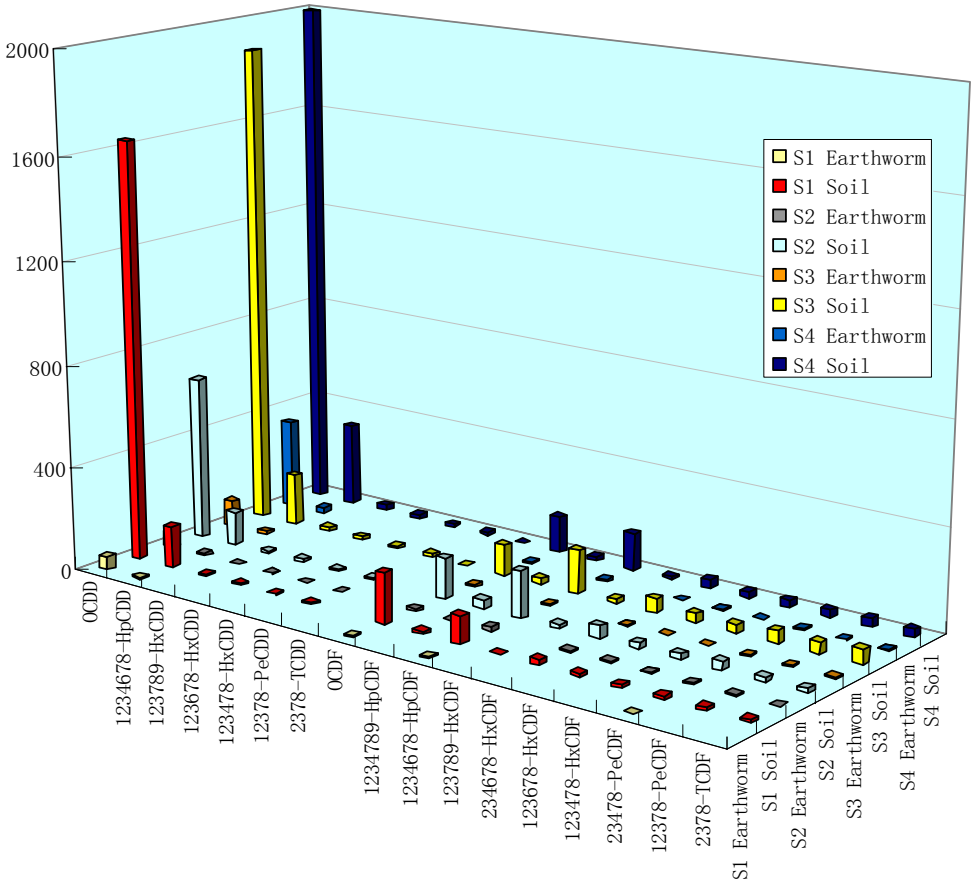

Figure 2. Distribution of PBDD/Fs concentrations (pg.g^{-1}dw) in the earthworm and soil samples

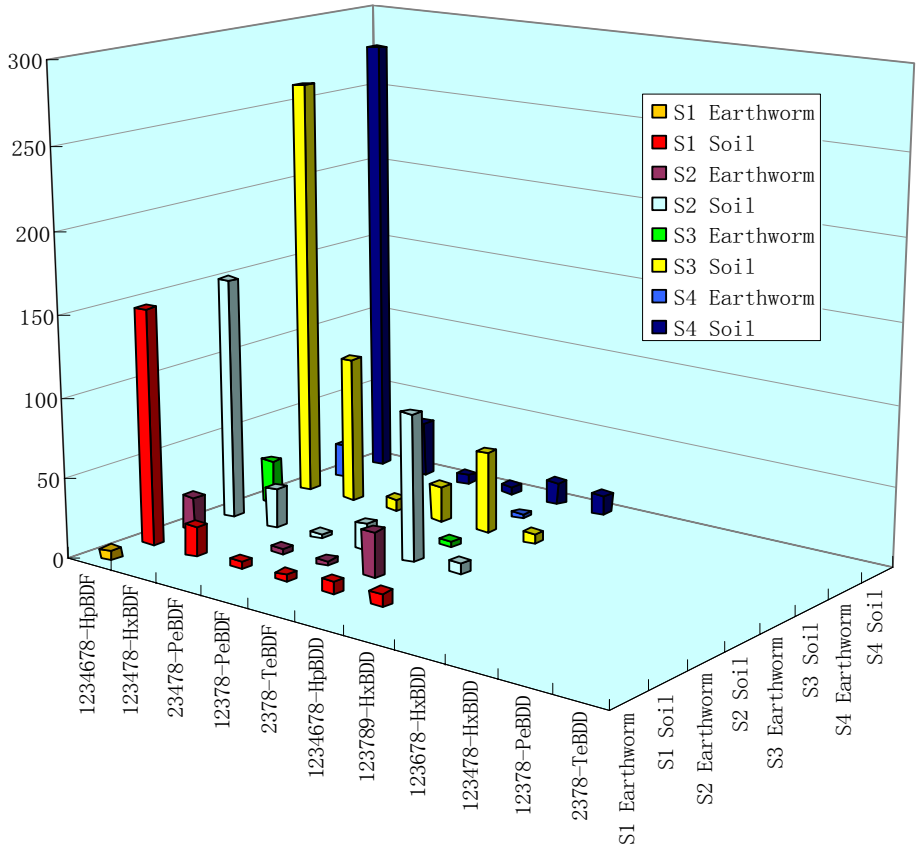

Figure 3. Biota-to-soil accumulation factors (BSAFs) for each detected congener of PCDD/Fs and PBDD/Fs