

HEXABROMOCYCLODODECANES (HBCDs) IN SURFACE SOILS AT A TYPICAL ELECTRONIC-WASTE RECYCLING SITE IN SOUTH CHINA

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Introduction

Hexabromocyclododecanes (HBCDs) are a class of additive brominated flame retardants (BFRs), and have been widely used in various commercial products, especially in electronic equipment for flame protection purposes. HBCDs have become the third most used BFR worldwide as an alternative for polybrominated diphenyl ethers (PBDEs). Lack of the official data on the production output and market demand, it was hard to estimate exactly the HBCDs consumption in China.

Over the past decade, e-waste is largely recycled by the informal sector in China. Out of the several informal e-waste processing domains, Guiyu, Taizhou and Qingyuan are the most prominent ones where crude recycling and extensive manual dismantling methods were applied for separation of reusable components and quick recovery of contained metals. Investigations have raised concerns about the serious contamination of brominated flame retardants, especially PBDEs and dioxins/furans (PCDD/Fs) in the environment derived from these recycling activities. Now, more and more recycling industrial parks were established with purpose of environmental-friendly recovery instead of the illegal and non-registered sites. But the reports of residues of HBCDs in soil around e-waste recycling sites were seldom.

Materials and methods

Surface Soil (less than 10 cm in depth) were sampled at 38 sites from informal e-waste dismantling sites, new extensive recycling plants, and agriculture soils in one county, South of China, where the e-waste was recycled from more than ten years. Soil samples were air dried, sieved by a 2 mm sieve, homogenized and packed in brown glass bottles in room temperature.

After water content was determined, 5.00g soil was extracted by accelerated solvent extraction (ASE 300, DIONEX Inc.) using a mixture of dichloromethane (DCM) and acetone (1:1 v/v) at 1500 psi and 100 °C for 5 min with two cycles. Extracts were concentrated to 2 mL with a rotary evaporator and then purified by elution with dichloromethane and hexane mixture (1:4 v/v) through cleanup column packed with 10g acid silica gel and 6g activated silica gel. The fraction was further concentrated to 1.0 mL prior to LC/MS/MS analysis.

An Agilent 1200 HPLC and a model 6410 mass spectrometer were used to the determinations of HBCD. A ZORBAX Eclipse plus C18 column (100 mm, 2.1 mm, 3.5 μm) was used to separate three native HBCD isomers. The mobile phase was consisted of methanol–acetonitrile (50:50, v/v). At a flow rate of 0.3 mL/min, the mobile phase gradient was begin from 10% of methanol–acetonitrile (50:50, v/v) and maintained for 4 min, the gradient was increased to 60% in 4 min, and then increased to 100% in 7 min and maintained for 5 min, at last ramped down again to 10% for another 2 min. The capillary temperature and gas were kept at 250 °C and 10 L/min. The MS/MS analysis was performed using electrospray ionization (ESI) with multiple reactions monitoring mode (MRM). α -, β -, and γ -HBCD isomers were quantified from the mean value of the response at two MRM transitions (m/z 640.6 > 81 and 640.6 > 79) corrected against the response of $^{13}\text{C}_{12}$ -labeled HBCDs (m/z 652.6 > 81 and 652.6 > 79).

PCDD/Fs analysis procedures were according to *Soil and sediment Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) Isotope dilution HRGC-HRMS (HJ77.4-2008)*.

Results and discussion:

HBCDs were detected in 38 surface soils, 21 from the farming land around the e-waste recycling sites, 12 from the original informal dismantling sites, and 5 from the new and registered industrial zone. The mean value of

total HBCDs in surface soil was 24.7ng/g, approximately 2-3 orders of magnitude greater than the control points. Generally, higher concentrations were measured in soils collected near original informal recycling sites, while lower concentrations were recorded in samples from locations far from the sites. Comparing the average values of different sites showed that the highest concentrations (7.4-121ng/g) were in the original informal sites, followed by these (1.3-22.4ng/g) in the formal sites. HBCDs in 3 samples from farming lands as the reference sites were not detected, others values were quite similar to those in the formal sites. HBCDs concentration in this study was the same level as the results obtained early from Qingyuan informal e-waste recycling sites. The results of these studies suggested that informal e-waste recycling activities could be a significant source of HBCDs to the soils.

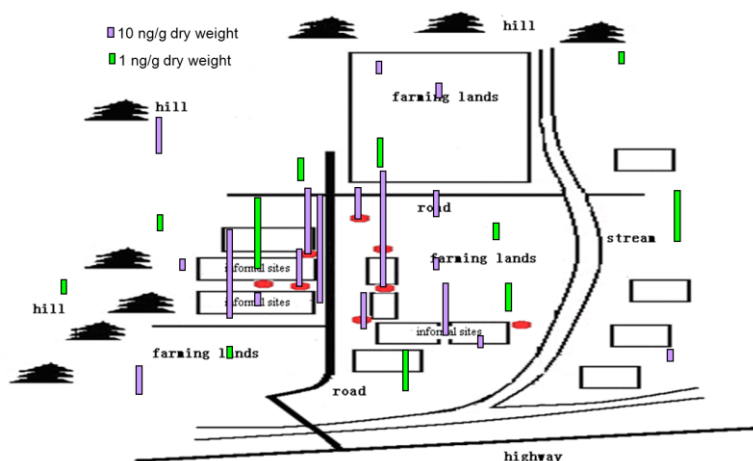


Fig. 1 Sampling locations in the informal e-waste recycling sites and mean total HBCDs concentrations in surface soils

Although γ -HBCD was the dominant isomers (75–89%) in the commercial HBCD mixtures, concentration of α -HBCD in soils was higher than that of the γ -HBCD. Very little aerobic degradation was observed in soil, meanwhile anaerobic degradation rates of α -, β -, γ -HBCDs were not significantly different. The pattern of HBCDs isomers were not changed greatly in soil for many years. In the informal recycling sector, crude heating and burning techniques were used in the history to remove components from printed circuit boards and recover copper and other metals. γ -HBCD started converting to α -HBCD at temperatures above 160 °C during the open burning and autogenous ignition. Depending on the temperature of the treatment processes, the proportions of the isomers in the ash may also vary. That was the true reason why there were quite different between HBCDs isomers pattern in soil and in technique products.

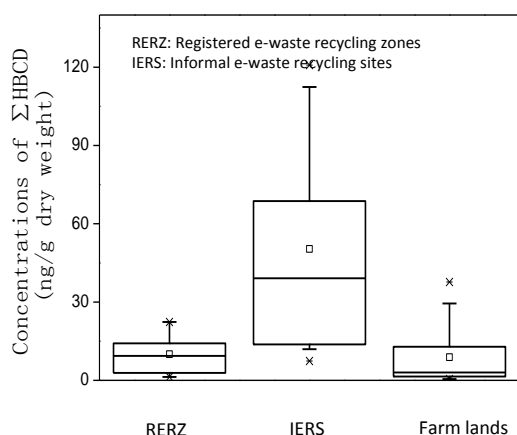
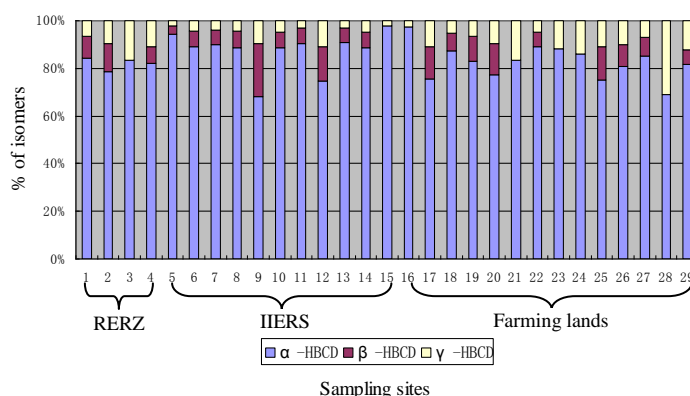


Fig. 2 Concentrations of total HBCDs in different sites



*: concentrations below 10ng/g were not listed.

Fig. 3 HBCDs profiles in soil samples

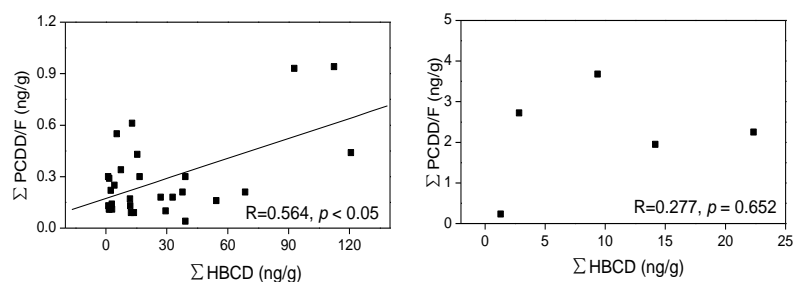


Fig.4 Relationship of total HBCDs and PCDD/Fs concentration in informal and legal recycling sites

The dioxins/furans were detected in higher levels at several e-waste processing domains, especially the illegal individual workshops. PCDD/Fs were released into ambient air and soils as un-potential persistent organic pollutants from combustion of printed circuit boards and cables in open air. HBCDs were released into environment as the same way. There was relatively good relationship ($R=0.564$, $p<0.05$) between HBCD and PCDD/Fs concentration in the surface soil from original informal e-waste recycling sites, whereas no significant relationships ($R=0.277$, $p<0.652$) were found between HBCD and PCDD/Fs concentrations in the e-waste industrial recycling parks where physical dismantling and heating under control were applied instead of open burning activities.

Recommendations for further work include research on how about the concentration of HBCDs in air and how the HBCDs transferred from soils into the other environment media, such as groundwater, sediment. Time trends need to be analyzed more in detail, including HBCD stereoisomers, and more data on terrestrial organisms are needed, especially for humans.

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