



Hexabromocyclododecanes (HBCDDs) in surface soils from coastal cities in North China: Correlation between diastereoisomer profiles and industrial activities



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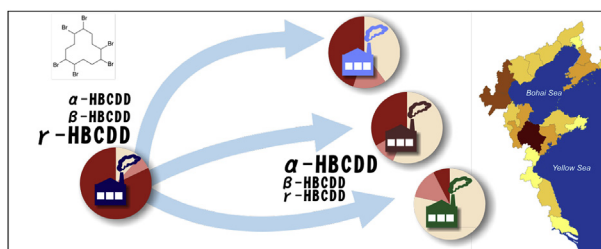
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HIGHLIGHTS

- Large scale investigation of HBCDD in soils from 21 cities of China.
- Correlation between diastereoisomer composition in soils and industrial activities.
- Highest concentration was detected in HBCDD production area in Weifang City.
- α -HBCDD as predominant diastereoisomer in soil was found in Cangzhou City.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexabromocyclododecane (HBCDD) is a brominated flame retardant with a wide range of industrial applications, although little is known about its patterns of spatial distribution in soils in relation to industrial emissions. This study has undertaken a large-scale investigation around an industrialized coastal area of China, exploring the concentrations, spatial distribution and diastereoisomer profiles of HBCDD in 188 surface soils from 21 coastal cities in North China. The detection frequency was 100% and concentrations of total HBCDD in the surface soils ranged from 0.123 to 363 ng g⁻¹ and averaged 7.20 ng g⁻¹, showing its ubiquitous existence at low levels. The spatial distribution of HBCDD exhibited a correlation with the location of known manufacturing facilities in Weifang, suggesting the production of HBCDD as major emission source. Diastereoisomer profiles varied in different cities. Diastereoisomer compositions in soils were compared with emissions from HBCDD industrial activities, and correlations were found between them, which has the potential for source identification. Although the contemporary concentrations of HBCDD in soils from the study were relatively low, HBCDD-containing products (expanded/extruded polystyrene insulation boards) would be a potential source after its service life, and attention needs to be paid to prioritizing large-scale waste management efforts.

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1. Introduction

Hexabromocyclododecane (HBCDD) is used as an additive flame retardant mainly in expanded polystyrene (EPS) and extruded

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polystyrene (XPS) foam for thermal insulation in buildings and transport vehicles. It is also used on cotton or mixed blend textiles as a back-coating and in high impact polystyrene (HIPS) applications for use in electric and electronic equipment, albeit at lower volumes (POPRC, 2010). As a result of its widespread usage, HBCDD has become an important alternative brominated flame retardant after the production and use of PBDEs were restricted. In 2001, the global market demand for HBCDD was 16,500 tons (POPRC, 2011), while the estimated global production of HBCDD increased to 31,000 tons in 2011 (POPRC, 2012).

HBCDD can enter the environment via releases to air and wastewater/surface water, during the production and micronising of HBCDD, formulation of EPS, XPS and polymer dispersion, industrial use of EPS, XPS, HIPS and textiles (back-coating), professional use of insulation boards, and service life of textiles (washing and wear), EPS and XPS. Furthermore, HBCDD can directly enter the soil through landfill of end of life articles and demolition materials (European Commission, 2008). HBCDD has been widely detected in the environment (Covaci et al., 2006).

HBCDD has 16 stereoisomers in theory, but commercial technical HBCDD mainly consists of three diastereoisomers, α -HBCDD (10–13%), β -HBCDD (1–12%) and γ -HBCDD (75–89%), depending on the manufacture and production method. Another two stereoisomers, ϵ - and δ -HBCDD, have been detected at low concentrations (Heeb et al., 2005). The composition of HBCDD diastereoisomers could be affected by thermal isomeric rearrangement during product processing and by abiotic/biotic transformation in the environment, which may lead to a different composition from the original technical HBCDD (Covaci et al., 2006; Gerecke et al., 2006; Harrad et al., 2009a; Heeb et al., 2010).

In China, 18000 tons of HBCDD were produced in 2011, more than half of the global production, in which 5500–6000 tons was exported, 9000 tons was applied in EPS and 3000 tons was applied in XPS (POPRC, 2012). Attention has been paid to HBCDD contamination in China, and investigations have been conducted near point-source sites or in the most industrialized cities where concentrations in environmental media have been shown to be relatively high (Yu et al., 2008a; Gao et al., 2011; Li et al., 2012; Zhang et al., 2013; Zhu et al., 2014). A larger scale investigation into HBCDD concentrations and spatial distribution is necessary in order to better understand the contamination status, identify sources, and ultimately reduce associated impacts.

Rapid industrialization and urbanization in China's coastal cities has resulted in both economic growth and environmental pollution from a range of anthropogenic activities. Such intensive industries have been reported to be sources of heavy metals, legacy POPs and novel POPs to regional environments (Hu et al., 2010; Wang et al., 2012; Luo et al., 2013; Meng et al., 2015). The north coast around the Bohai Sea and Yellow Sea in China was investigated in this study, including 21 coastal cities in 5 provinces (Jiangsu Province, Shandong Province, Hebei Province, Liaoning Province, and Tianjin Municipality). HBCDD production facilities are mostly distributed in the coastal areas of Shandong, Hebei and Jiangsu Provinces. Except for raw HBCDD production, brominated flame retardant manufacture, EPS and XPS board processing, flame retardant textile processing, electric and electronic component production, e-waste recycling industries are all located in this region, which are potential sources of HBCDD release. It is also an important agricultural region where arable crops, vegetables and fruits are produced/cultivated at large scale, while HBCDD can be absorbed by plants (Wu et al., 2012; Zhang et al., 2013). Therefore, the monitoring of HBCDD contaminants in soils is necessary to ensure food safety.

The objectives of this study were to investigate the occurrence, spatial distribution, and diastereoisomer profiles of HBCDD in soils from the coastal cities in North China. Correlations between HBCDD

contamination and industrial activities in the region were analyzed to identify potential sources.

2. Materials and methods

2.1. Sample collection

The sampling campaign was conducted in 21 cities from 5 provinces (Liaoning, Hebei, Tianjin, Shandong, Jiangsu) covering a total area of 213,000 km² along the China's coast of Bohai and Yellow Seas in September 2013 (Fig. S1). A total of 188 surface (top 0–10 cm) soil samples were collected (detailed information in SI).

2.2. Reagent and standards

Solvents used in extraction and analysis procedures were HPLC-grade and purchased from Fisher. Silica gel 60 (63–100 μ m) were purchased from Merck. Individual standard stock solutions (α -HBCDD, β -HBCDD, γ -HBCDD, C13- γ -HBCDD, d18- γ -HBCDD) were obtained from Wellington Laboratories (Canada) with concentration of 50 μ g mL⁻¹ in toluene with purity >98%.

2.3. Extraction and cleanup

Sample extraction followed the procedure described in Harrad et al., 2009b with some modifications. 10 g accurately weighed soil (mixed with 15 g pre-heated anhydrous sodium sulfate) were spiked with 10 ng of C13- γ -HBCDD as surrogate standard and were extracted using ASE 350 with hexane/dichloromethane (1:9, v/v) at 90 °C and 1500 psi (heating time 5 min, static time 4 min, purge time 90 s, flush volume 50%, static cycle 3). The concentrated extract was then loaded onto a multi-layer silica gel column (15 mm I.D.) for purification, filled from bottom to top with 1 g of anhydrous sodium sulfate (500 °C for 6 h), 1 g activated silica gel (130 °C for 16 h), 2 g of Florisil (130 °C for 4 h), 1 g activated silica gel, 3 g of basic silica gel (2%, w/w), 1 g activated silica gel, 8 g of acid silica gel (44%, w/w), 1 g activated silica gel, 1 g of anhydrous sodium sulfate. The column was wet-filled with hexane. Analytes were eluted with 120 mL hexane/dichloromethane (1:1, v/v). The eluate was concentrated by a rotary evaporator to 1–2 mL and further evaporated to incipient dryness under N₂, and reconstituted in 200 μ L of methanol/water (8:2, v/v) containing 10 ng of d18- γ -HBCDD as recovery determination standard.

2.4. Instrumental analysis

The analysis of HBCDD was performed on Agilent 1290 UPLC system coupled to Agilent 6460 triple quadrupole tandem mass spectrometry. Separation was performed on an Agilent Eclipse Plus C18 column (2.1 \times 100 mm, 1.8 μ m) (detailed description in SI).

2.5. QA/QC

Quantification was carried out by an isotopic dilution technique. C13- γ -HBCDD was used as a surrogate standard for HBCDD quantification, and d18- γ -HBCDD was used for C13- γ -HBCDD recovery evaluation for each sample. The calibration curve was derived using a series of standards ranging from 2 to 500 ng mL⁻¹ and fixed concentrations (50 ng mL⁻¹) of the internal standards ($r^2 > 0.999$). A procedural blank (anhydrous Na₂SO₄) was added within each batch of 12 samples to assess possible contamination. These were all below LOD. Spiking-recovery tests were conducted using soil (preheated at 550 °C for 12 h) spiked with 10 ng each of native HBCDD before extraction and analysis. The mean recoveries ($n = 7$) of individual HBCDD isomers were 69 \pm 8% for α -HBCDD, 67 \pm 6%

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