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Hexabromocyclododecane (HBCD) in surface soils from coastal cities in north China: correlation between diastereoisomer profiles and industrial activities

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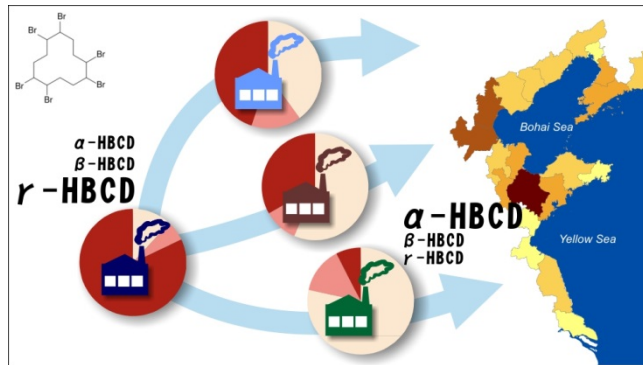
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Abstract art



1 **Abstract:**

2 Hexabromocyclododecane (HBCD) is a brominated flame retardant of extensive
3 applications which is mainly produced in the coastal area of China, but we know little
4 about its patterns of spatial distribution in soils in relation to industrial emissions. In
5 this study, we conducted a large-scale investigation in the most industrialized area in
6 China, exploring the concentrations, spatial distribution and diastereoisomer profiles
7 of HBCD in 188 surface soils from 21 coastal cities in north China. The detection
8 frequency was 100% and concentrations of total HBCD in the surface soils ranged
9 from 0.123 to 363 ng/g dw and averaged 7.20 ng/g, showing its ubiquitous existence
10 at low level. The spatial distribution of HBCD exhibited a correlation with
11 manufacture facilities in Weifang, suggesting the production of HBCD as major
12 emission source. Diastereoisomer profiles varied in different cities, and the average
13 ratio ranged from 10.6-74.4%, 3.3-26.9% and 10.6-82.3% for α -, β -, and γ -HBCD
14 respectively. Diastereoisomer compositions in soils were compared with the
15 emissions from HBCD industrial activities, and correlation was found between them,
16 which could be used for source identification. Although the current levels of HBCD in
17 soils are relatively low, HBCD-containing products (EPS/XPS insulation boards)
18 would be a potential source after its service life, and attention needs to be paid to
19 prioritizing large-scale management efforts.

20
21 **Keywords:** HBCD; brominated flame retardant; soil pollution; emission source;

22 Bohai Sea, Yellow Sea

1. Introduction

Hexabromocyclododecane (HBCD) is used as additive flame retardant mainly in expanded polystyrene (EPS) and extruded polystyrene (XPS) plastic foam for thermal insulation in buildings and transport vehicles, while used in polymer dispersion on cotton or mixed blends in the back-coating of textiles and used in high impact polystyrene (HIPS) in electric and electronic equipment with quite a smaller volume ¹. With common usage in some applications, HBCD has become alternative brominated flame retardant since the production and use of PBDEs were restricted. In 2001, the global market demand for HBCD was 16500 tons ², while the estimated global production of HBCD increased to 31000 tons in 2011 ³.

Due to its persistence, bioaccumulation, toxic effect, and long-range transport potential, listing HBCD in the Annex A of Stockholm Convention entered into force on 26 Nov 2014, and the production and use of HBCD would be eliminated in most countries, with specific exemptions for production and use in EPX and XPS in buildings in registered countries ⁴. HBCD can enter the environment through air and wastewater/surface water, during the production and micronising of HBCD, formulation of EPS, XPS and polymer dispersion, industrial use of EPS, XPS, HIPS and textile (back-coating), professional use of insulation boards, and service life of textiles (washing and wear), EPS and XPS. Furthermore, HBCD can directly enter the soil through landfill of worn-out articles and demolition materials ⁵. HBCD has been widely detected in air ^{6, 7}, soil ⁸, river sediment ^{9, 10}, water ¹¹, plant ¹² and biota samples, such as birds/eggs ¹³, fish ¹⁴, benthic invertebrates ¹⁵ and marine mammals ¹⁶,

in Europe, North America, Asia, Arctic and other parts of the world. In addition to natural environment, HBCD has also entered the indoor environment with application of insulation boards in residential building and usage of HBCD-containing products. High concentrations of HBCD have been detected in indoor air from offices and cars¹⁷ and in house dust and air^{18, 19}. Meanwhile, HBCD has been detected in human milk^{20, 21}, whose levels have been observed positively associated with the numbers of electronic appliances at home.

HBCD has 16 stereoisomers in theory, but commercial technical HBCD mainly consists of three diastereoisomers, α -HBCD (10-13%), β -HBCD (1-12%) and γ -HBCD (75-89%), depending on the manufacture and production method. Another two stereoisomers, ϵ - and δ -HBCD, have been detected at low concentrations²². Structural dissimilarities of individual diastereoisomer lead to differences in polarity, water solubility, and octanol-water partitioning coefficient ($\log K_{ow}$), and further result in their different environmental behaviors²³. The composition of HBCD diastereoisomers can be affected by thermal isomeric rearrangement during product processing, and by abiotic/biotic transformation in the environment, leading to a different composition from the original technical HBCD. Diastereoisomer rearrangement occurred and γ -HBCD was enriched when HBCD-containing material was exposed at temperature above 140-160°C²⁴. In addition to thermal processing, natural light exposure could cause a photolytically mediated shift from γ -HBCD to α -HBCD in indoor dust²⁵. Besides transformation, degradation kinetics also affected the diastereoisomer profile that α -HBCD exhibited longer half-life compared to β - and

γ -HBCD under anaerobic conditions, with respect to the enrichment of α -HBCD in biota²⁶.

In China, 18000 tons of HBCD was 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 XPS³. Attention has been paid to HBCD 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 detected to be relatively high^{7, 8, 12, 27, 28}. A larger scale of investigation on HBCD level and spatial distribution is necessary in order to better understand the contamination status, identify sources, and reduce associated impacts.

Rapid industrialization and urbanization in China's coastal cities has brought in both economic growth and environmental pollution from various anthropogenic activities. The intensive industries have been reported to be the sources of heavy metals, legacy POPs and novel POPs²⁹⁻³². The north coast around the Bohai and Yellow Seas in China was investigated in this study, including 21 coastal cities in 5 provinces (3 cities in Jiangsu Province, 8 cities in Shandong Province, 3 cities in Hebei Province, 6 cities in Liaoning Province, and Tianjin municipality). 5.2% of the China's population living in this region, taking 2.2% land area of the whole country, contributes to 12.6% of the China's total GDP³³⁻³⁷. HBCD production facilities are mostly distributed in the coastal areas of Shandong, Hebei and Jiangsu Provinces. Except for raw HBCD production, brominated flame retardant manufacture, EPS and XPS board processing, flame retardant textile processing, electric and electronic

component production, e-waste recycling industries are located in this region, which are potential sources of HBCD release. It is also an important agricultural region where crop, vegetables and fruits are cultivated at large scale, while HBCD can be absorbed by these plants. Therefore, the monitoring of HBCD 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 HBCD in soils from the coastal cities in north China. Correlation of the HBCD contamination and industrial activities in the region was analyzed to identify potential sources.

2. Materials and Methods

2.1. Sample collection

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 with a stainless steel trowel that had been rinsed with methanol and placed in polypropylene bags. Each sample consisted of five sub-samples within a 100m×100m area. Sampling information including location, land use, and surrounding environmental conditions were summarized in Table S1. All samples were air-dried, homogenized and sieved through a 2 mm mesh, and stored in PP bags at room temperature before extraction.

2.2. Reagent and standards

Solvents used in extraction and analysis procedures were HPLC-grade and

purchased from Fisher. Silica gel 60 (63-100 μm) were purchased from Merck. Individual standard stock solutions (α -HBCD, β -HBCD, γ -HBCD, C13- γ -HBCD, d18- γ -HBCD) were obtained from Wellington Laboratories (Canada) with concentration of 50 $\mu\text{g mL}^{-1}$ in toluene with purity >98%.

2.3. Extraction and cleanup

Sample extraction followed the procedure described by Harrad, Abdallah, Rose, Turner and Davidson¹¹ 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 -HBCD 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 90s, flush volume 50%, static cycle 3). Extract was concentrated by a rotary evaporator to 1-2 mL. Then the extract was 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 (heated at 500°C for 6 hrs), 1 g activated silica gel (heated at 130°C for 16 hrs), 2 g of Florisil (130°C for 4 hrs), 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 N_2 , and reconstituted in 200 μL of methanol/water (8:2, v/v) containing 10 ng of d18- γ -HBCD as recovery determination standard.

2.4. Instrumental analysis

The analysis of HBCD 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 (2.1×100 mm, 1.8 μm) maintained at 30°C. The mobile phase consisted of water and methanol in a constant proportion of 20:80 (v/v) at a flow rate of 0.25 mL/min. The injection volume was 5 μL. The mass spectrometry operated with the electrospray ionization (ESI) interface in the negative mode. The parameters used for MS were as follows: gas temperature 300°C, gas flow 10 L/min, nebulizer 35 psi, capillary -4000 V. Multiple reaction monitoring (MRM) was used for analytes scanning: m/z 640.6 > 80.7 for native HBCD, m/z 652.6 > 81.0 for C13-γ-HBCD, m/z 657.6 > 80.6 for d18-γ-HBCD, respectively. Fragmentor is 80V and collision energy is 5 eV for native HBCD, 9 eV for C13-γ-HBCD and 7 eV for d18-γ-HBCD, respectively. The elution order was α-HBCD, β-HBCD and then γ-HBCD. However, in some high concentration samples, an unidentified peak with very low response was observed between α-HBCD and β-HBCD with the same transition as native HBCD, which was implied as another diastereoisomer (Fig. S2).

2.5. QA/QC

Quantification was carried out by an isotopic dilution technique. C13-γ-HBCD was used as surrogate standard for HBCD quantification, and d18-γ-HBCD was used for C13-γ-HBCD recovery evaluation for each sample. The calibration curve was derived with a series of standards ranging from 2 to 500 ng/mL and fixed concentrations (50 ng/mL) of the internal standards ($r^2 > 0.999$). A procedural blank

(anhydrous Na₂SO₄) was added within each batch of 12 samples to assess introduction of contaminants. These were below LOD. Spiking tests were conducted that matrix soil (preheated at 550°C for 12 hrs) was spiked with 10 ng each of native HBCD before extraction and analysis. The mean recoveries (n=7) of individual HBCD isomers were 69±8% for α-HBCD, 67±6% for β-HBCD and 66±12% for γ-HBCD. The surrogate standard recoveries were in average 78±18% for C13-γ-HBCD. LODs, defined as 3 times of signal to noise, were 0.006, 0.006, 0.005 ng/g for α-, β-, γ-HBCD. LOQs, defined as 10 times of signal to noise, were 0.015, 0.018, 0.022 ng/g for α-, β-, γ-HBCD. Values of concentrations less than the LOQ were set to one-half of the LOQ, and those less than the LOD were assigned values of LOD/√2.

3. Result and discussion

3.1. HBCD levels in soils

For individual diastereoisomer, detection frequencies were 97.3%, 97.9% and 100% for α-, β- and γ-HBCD, respectively. Concentration ranges were ND-49.3 ng/g (averaged 2.02 ng/g) for α-HBCD, ND-30.0 ng/g (averaged 0.800 ng/g) for β-HBCD, and 0.052-284 ng/g (averaged 4.38 ng/g) for γ-HBCD. ΣHBCD was detected in all 188 soil samples (α-HBCD in 183 samples, β-HBCD in 184 samples and γ-HBCD in all samples, respectively) and ranged from 0.123 to 363 ng/g dw with a mean value of 7.20 ng/g, suggesting HBCD's ubiquitous existence along the north coast of Bohai and Yellow seas in China. Among the 188 samples, in terms of HBCD concentration, 2 samples are higher than 100 ng/g, 17 samples ranged 10-100 ng/g, 93 samples ranged 1-10 ng/g, and the rest 76 samples were all below 1 ng/g, showing an overall

low level of contamination (Fig. 1).

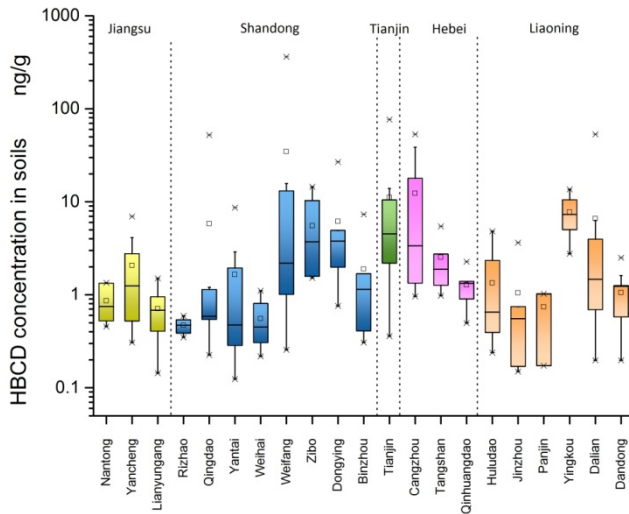


Fig. 1 HBCD concentrations in soils from 21 coastal cities. In this box char, “-” in each box is for median value; “□” is for average value; “*” is for max and min value.

Reports of HBCD in surface soils were scarce in the globe, especially at such a large scale. Early investigations of HBCD in soils were focused on point-sources like HBCD manufacturing and processing sites. In point source areas, HBCD concentrations detected exceeded thousands of ng/g, like soils from HBCD manufacturing plants in China ranging 0.88-6901 ng/g²⁷, and XPS producing plant in Sweden ranging from 140-1300 ng/g⁶. Levels in these areas were one magnitude higher than that of this study, which was similar to those from e-waste recycling areas (0.01-284 ng/g) in Guangzhou City⁸ and BFR-manufacturing region (0.30-280 ng/g) in Shouguang²⁸ (a county of Weifang City). HBCD levels in soils in non-point source areas were only reported in China, 0.17-34.5 ng/g in farm soils in rural areas of Beijing³⁸, Nd-0.094 ng/g in rural areas of Shanghai³⁹, 1.7-5.6 ng/g in urban area of Guangzhou⁴⁰, and 0.03-29.9 ng/g in industrial soils from 5 cities of Guangdong

Province ⁸, and were one magnitude lower than those of point source areas. In this study, more than 90% of the samples detected were within this range as non- point source area., while in Rizhao, Weihai and Panjin cities, HBCD exhibited overall low concentrations below 1 ng/g.

Table. 1 Comparison of HBCD concentration in soils

Location description	Range/ng g ⁻¹
Point source area	
XPS producing plant, Sweden ⁶	140-1300
E-waste areas, Guangzhou, China ⁸	0.01-284
Manufacturing plants, Laizhou bay, China ²⁷	0.88-6901
BFR-manufacturing region, Shouguang, China ²⁸	0.30-280
Non-point source area	
Urban area, Guangzhou, China ⁴⁰	1.7-5.6
Rural area, Chongming Island, Shanghai, China ³⁹	Nd-0.094
Farm soil, Beijing, China ³⁸	0.17-34.5
Industrial soil, Guangdong, China ⁸	0.03-29.9
Open waste dumping site, south Asian countries ⁴¹	ND-2.5

3.2. Spatial distribution

Average HBCD concentrations of 21 cities varied in spatial distribution and the highest values of 34.6, 12.3, 11.1 ng/g were detected in Weifang, Cangzhou, Tianjin

respectively (Fig. 2). 18 other cities showed lower concentrations than 10 ng/g and among them 5 cities have concentrations lower than 1 ng/g. All manufacture facilities of HBCD we could find were presented in Fig. 2, and they were mainly located in 3 cities, Weifang, Cangzhou and Lianyungang. However, HBCD levels in these three cities varied significantly, which may result from different emission intensities due to their different production volume and history. The first HBCD production facility was built in 1999 in Weifang. At present, several facilities claimed annual production capacity higher than 2000 tons. In Liangyungang, HBCD production started in 2004 with a relatively small capacity, while in Cangzhou the production was even smaller. HBCD in most of the other cities exhibited low levels and evenly distributed in space, which may come from diffuse sources of widely used HBCD-containing products or transport via atmosphere.

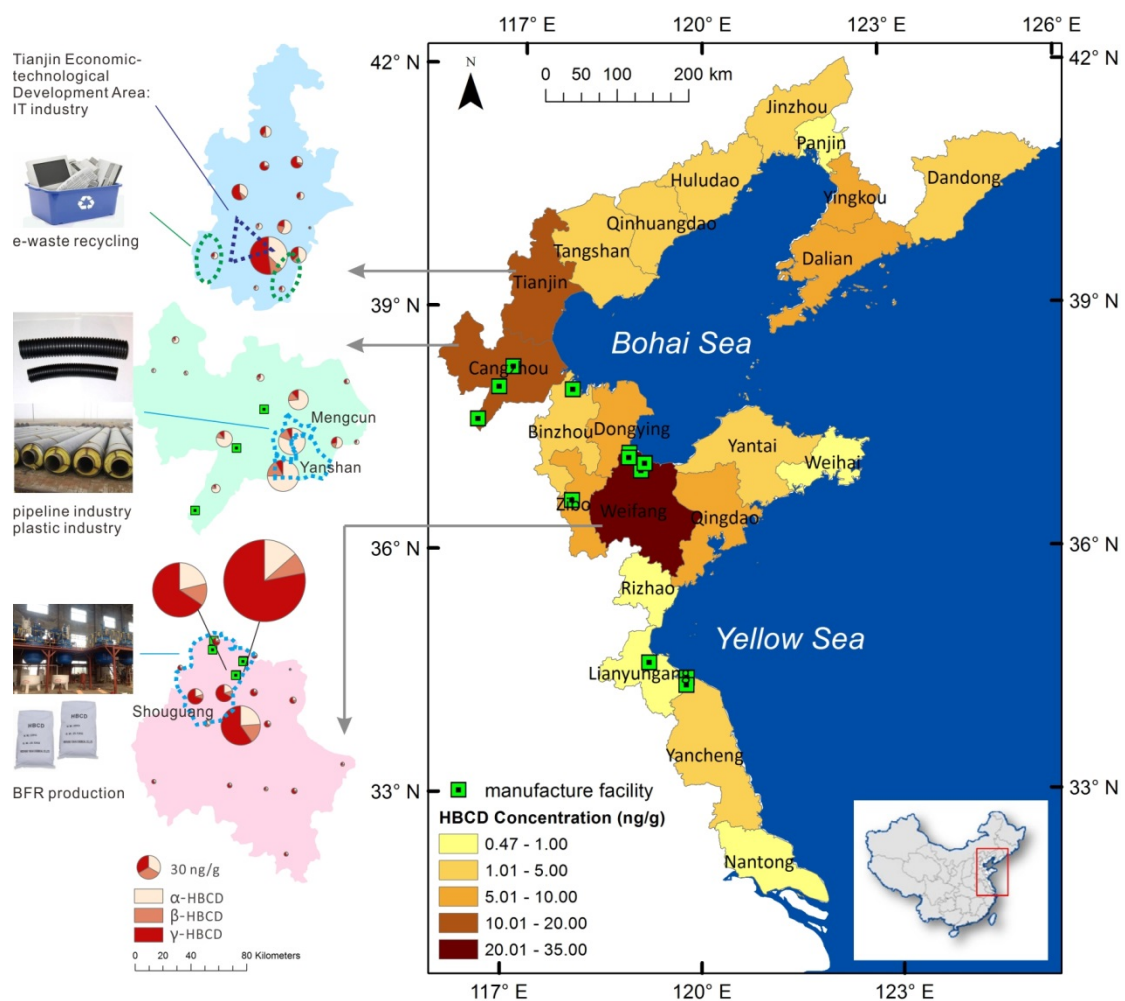


Fig. 2 Spatial distribution of mean HBCD concentrations in soils from 21 cities.

Green squares stand for HBCD manufacture facilities in China.

The spatial distribution of HBCD in Weifang significantly varied with sampling location. The highest concentrations of 3 sampling sites were all detected in Weifang and elevated the mean value of this city, while the concentrations of the other sites (except two sites) were lower than 3 ng/g (Fig. 2). The level of the nearest site from WF-19 (with the highest concentration of 363 ng/g), 11 km away, is only 1.71 ng/g, suggesting that the contamination was mostly caused by local discharge rather than

regional transport, and the distance of HBCD transport from point source to soil is very short. Li, Zhang, Wang, Li, Lv, Chen, Geng, Wang, Thanh and Jiang²⁷ investigated a HBCD manufacturing site in Weifang and reported the decreasing concentration of HBCD in soil with increasing distance from the center to 8 km away. In this investigation, even though we sampled evenly in space and did not aim at any facility or source, higher concentrations were detected if sample sites got closer to the manufacturing facilities or other sources.

High concentrations were detected in the northern coast of Weifang, where the Coastal Economic and Technological Development Zone (known as the biggest flame retardant production base in China) is located. The occurrence of HBCD in soils showed a spatial correlation with HBCD manufacturing facility, inferred to be the source. These facilities were intensively located in 3 towns, Yangkou, Houzhen and Dajiawa in the northern coast of the city (Fig. 2). WF-19 (363 ng/g) was sampled in a crop land in the east of Dajiawa Town, 2.6 km away from a manufacturing facility with a production capacity of 3000 ton/a in the northeast⁴², which should be the direct emission source in this area. WF-03 (159 ng/g) is sampled in an industrial land in the west of Dajiawa Town, but there is no manufacturing facility found as direct source. The nearest potential source is Houzhen Industrial Zone, 10 km away in the southeast, where more than 3 manufacturing facilities are located.

In Cangzhou, the highest level was detected in its southeast part with a concentration of 53.1 ng/g. However, manufacturing facilities in Cangzhou are located more than 40 km away from this sampling site, which may not be the source

for this site. In Tianjin, another city with relative high HBCD concentration, no HBCD manufacturing has been reported. So HBCD may be discharged and transported from other sources in Cangzhou and Tianjin.

3.3. Diastereoisomer profiles

Diastereoisomer profiles of HBCD in different cities were shown in Fig. 3. α -HBCD ranged from 10.6% to 74.4%, β -HBCD from 3.3% to 26.9%, and γ -HBCD from 10.6% to 82.3% and were predominated in all cities except Cangzhou. There was a trend that β -HBCD showed less change than α -HBCD and γ -HBCD, and α -HBCD's proportion increased while γ -HBCD's decreased. Among the 21 cities, 12 cities exhibited similar composition of commercial technical products, which were composed of 70-89% γ -HBCD and 11-30% α - and β -HBCD^{23,43}, while 8 cities had γ -HBCD ranging from 40-60% and only 1 city (Cangzhou) had γ -HBCD below 40%.

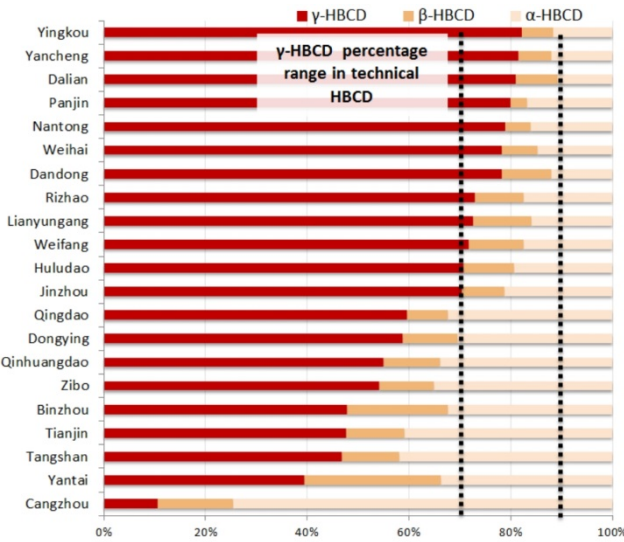


Fig. 3 Diastereoisomer composition of HBCD in 21 cities. The dotted line represents the γ -HBCD percentage range (70-89%) in commercial technical HBCD

There are a few investigations on diastereoisomer profiles in soils and mainly

conducted in China. In some early investigations of HBCD in environmental media, GC was used for instrumental analysis, which could only give the total amount of HBCD isomers, so the results were reported in total concentrations of HBCD isomers without concentrations or percentages of individual diastereoisomers. In soils from the manufacturing area in China, γ -HBCD (67.3%) was the most abundant diastereoisomer followed by α - and β -HBCD with proportions of 20.4%, 12.3% respectively, which was very close to the composition of commercial HBCD product²⁷. Diastereoisomer composition in point-source sites (12.0% α -HBCD, 18.5% β -HBCD, 67.5% γ -HBCD) were different from those in non-point-source sites (23.8% α -HBCD, 19.7% β -HBCD, 56.4% γ -HBCD) from BER manufacturing area in China²⁸. In surface soils from 2 e-waste recycling sites in south China, γ -HBCD proportion ranged from 40-50%, which was similar to α -HBCD (50-40%) (industrial area in the article was not included here)⁸. γ -HBCD's predominance was reported in rural area in Beijing³⁸ and Shanghai³⁹, but the ratio of γ -HBCD in Beijing (59%) was relatively lower than that in Shanghai (70%). The variation of diastereoisomer profiles in soils was also reported in South Asian countries⁴¹.

In contrast, HBCD diastereoisomer profiles showed an α -HBCD predominance in birds' tissues/eggs⁴⁴, fish^{45, 46}, mollusks¹⁵, ringed seals⁴⁷ and other biota, suggesting the impact of environmental processes on the change of diastereoisomer contribution.

3.4. Relations with industrial activities

Relatively high concentrations occurred in Weifang, Cangzhou and Tianjin, and the significant different diastereoisomer contributions indicated the existence of

different emission sources. As discussed before, distribution of HBCD in soils and its spatial correlation with manufacture facilities were found and used to identify HBCD manufacture as the major emission source in Weifang. Furthermore, diastereoisomer profiles and their relations with industrial activities were also observed. Besides the formulation of raw HBCD product, HBCD could enter the environment via air deposition, wastewater discharge, and landfill of waste in the life cycle of EPS/XPS insulation boards, electric and electronic appliances(plastic shell, wire and cable), and textile back-coatings.

In Weifang, the diastereoisomer ranged from 13.6% to 37.6% for α -HBCD, from 8.3% to 31.4% for β -HBCD, and from 32.9% to 78.1% for γ -HBCD, and averaged 17.4%, 10.8%, 71.8% respectively. The composition, especially in the BFR production area in Shouguang (16.2%, 9.9%, 73.9% for α -, β - and γ -HBCD respectively), was consistent with the commercial technical HBCD product. This was an evidence that the contamination of HBCD in soil was released from adjacent BFR production facilities, and HBCD composition was not changed by natural processes in the environment.

In Cangzhou, α -HBCD was predominant in the whole city ranging from 42.8% to 81.1% (averaged 63.9%) while γ -HBCD ranged from 6.6% to 41.1% (averaged 18.0%). It was noted that relatively high concentrations (53.1 ng/g at CZ-07, 38.7 ng/g at CZ-08) were found in Yanshan, and that the lowest γ -HBCD proportions (6.6% and 8.0%) were also detected in Yanshan, known as the Pipeline Equipment Manufacturing Base of China in the southeast of Cangzhou. In this area, metal and

plastic pipelines were produced including flame retardant pipe, pipe shell and board. Additionally, a plastics industrial park was also located in this area, and the industrial chain included flame retardant production, plastic pipe and board (mainly XPS) forming and cutting. In 2013, the production of plastic products reached 520,000 tons in Cangzhou⁴⁸, implying a large market demand for HBCD.

During the manufacturing process of these plastic products, intense thermal processing could be the reason for changing HBCD diastereoisomer percentage. In Polystyrene (PS) consumer products (food container, packing support, etc.) collected in Korea, γ -HBCD was the dominant isomer with an average percentage of 56%, which was lower than the original percentage of technical HBCD. PS hard plastics (general purpose polystyrene, GPPS; high impact polystyrene, HIPS; etc.), which received more processing in industry than EPS, contained lower γ -HBCD proportion than other materials⁴⁹. In insulation board, γ -HBCD was the predominant component with a similar composition to commercial technical HBCD product in EPS raw foam, while α -HBCD was predominant in XPS raw foam. However, in particles emitted from thermal cutting of both EPS and XPS, α -HBCD was predominant and γ -HBCD was only 29% from EPS and 8% from XPS⁵⁰. This proportion of γ -HBCD was close to that of Yanshan. Considering the spatial distribution and diastereoisomer profiles of HBCD in soils, and the local industrial activity, XPS and EPS foam processing could be identified as the major source of HBCD in Cangzhou.

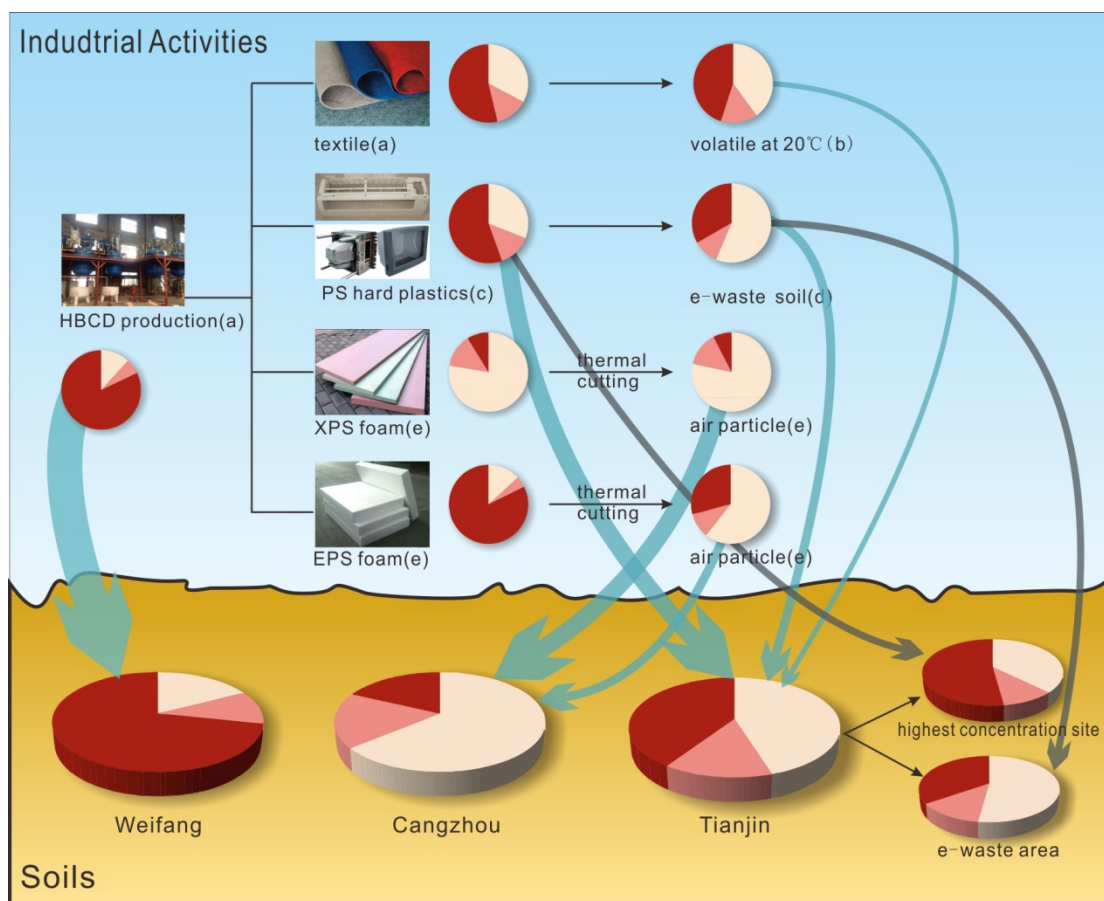


Fig. 4 Correlation between industrial activities and HBCD in soils for the diastereoisomer contribution. Pie charts here were only for percentages, not for concentrations. Compiled from (a, Kajiwara et al. 2009; b, Kajiwara and Takigami 2013; c, Rani et al. 2014; d, Gao et al. 2011; e, Zhang et al. 2012.)

In Tianjin, α -HBCD ranged from 22.9% to 62.4% with an average of 45.1% while γ -HBCD ranged from 13.6% to 69.8% with an average of 40.6%. A significantly high level of HBCD, 76.5 ng/g at TJ-08, was detected in its south with the other 12 sites lower than 15 ng/g. It consisted of 37.5% α -HBCD, 10.4% β -HBCD and 52.1% γ -HBCD. This site was located among a group of small factories including a flame-retardant electric wire plant of 3 km away. To the west of this site was a

state-level economic and technology development zone, where integrated circuit, mobile communication, and electronic components were produced, including flame retardant electric wires and cables. Flame retardant EXP, XPS and textile were also produced in the neighboring area.

As shown in Fig. 4, PS hard plastics could be used to make various consumer products like mobile phone holders and computer shells, and it was composed of 31.0% α -HBCD, 13.5% β -HBCD and 55.5% γ -HBCD⁴⁹. The diastereoisomer contribution of Tianjin was similar to the flame-retardant upholstery textiles, which were mainly used for curtain manufacturing. The percentage of α -, β - and γ -diastereoisomers to total HBCDs were found to be 26-46%, 12-18%, 38-61% (except one sample with an extremely low concentration)⁵¹. In volatile substances emitted from textiles at different temperatures (20, 40, 60, 80°C), the proportion of α -HBCD increased when the temperature increased⁵². However, the consumption of HBCD in textile back-coating was negligible, so its impact on isomer profiles was less than PS plastics production. The contamination in Tianjin may be caused by mixed sources, and more investigation is needed to confirm that.

Since high concentrations of HBCD had been reported in e-waste recycling sites in south China, in this paper, high level was also assumed to be in the biggest e-waste recycling area in north China, which was located in Tianjin. Unexpectedly, the concentrations of HBCD were only 2.96 ng/g (51.7% α -HBCD, 9.9% β -HBCD and 38.4% γ -HBCD) and 1.79 ng/g (52.6% α -HBCD, 16.4% β -HBCD and 31.0% γ -HBCD) respectively in Jinghai County and Dagang District, where the e-waste

recycling area is located. In e-waste recycling sites in South China, γ -HBCD was the predominant isomer (36.3% α -HBCD, 4.8% β -HBCD and 58.9% γ -HBCD) in Qingyuan with a total concentration of 106 ng/g, while α -HBCD was the predominant (56.4% α -HBCD, 10.3% β -HBCD and 33.3% γ -HBCD) in Guiyu with a total concentration of only 2.34 ng/g⁸. The diastereoisomer profiles in Tianjin in this study were very close to that of Guiyu, suggesting the impact of e-waste recycling as the common source in both areas. Compared to that in South China, there may be a major reason for the low levels in Tianjin, that is, the recycling facilities were under strict and formal (closed) operation, different from the informal (open) recycling process in Guangzhou, so the emission were under control. Differently, in the investigation in informal e-waste recycling sites in Vietnam, α -HBCD was predominant in both dust and air samples collected in the backyard of e-waste recycling houses, and 6 and 10 times more abundant than γ -HBCD respectively⁵³. This variation may result from the difference in e-products category and recycling method in the two countries.

4. Conclusions

This study reported the occurrence, spatial distribution and diastereoisomer profiles of HBCD in surface soils from the coastal cities in North China, and investigated local industrial layout relevant to HBCD manufacture of technical HBCD and waste recycling. HBCD was detected in all the soil samples but the overall level was low, with relatively higher levels founded in Weifang, Cangzhou and Tianjin. The highest concentration was found in a cropland, and the risks on local food safety need to be further assessed. Industrial activities, especially extrusion molding and

thermal cutting, could change the diastereoisomer composition in HBCD-containing products and the composition in the environmental media through industrial emission. Correlation between diastereoisomer composition in soils and emission from local industrial activities was found and used to identify the emission sources. Commercial technical HBCD manufacture was identified as the main source in Weifang, while XPS and EPS foam processing could be the main source in Cangzhou, and PS hard plastics production, e-waste recycling and textile processing could be the the major source in Tianjin. Concentrated production of technical HBCD was the strongest source that caused the highest level of HBCD in soils. The processing of HBCD-containing products was relatively scattered and conducted in small plants, so HBCD release to environment was less. In the e-waste recycling area, the concentration was low, suggesting the closed-loop disposal of e-waste was effective to control flame retardant release.

Although the current level of HBCD in soils was relatively low, the majority of the produced HBCD was added into products, such as EPS and XPS insulation boards in buildings. After decades of services, these buildings would be demolished and filled in land, and these flame retardant insulation boards would become a potential source to discharge HBCD into the soil. HBCD could enter the indoor environment through air transportation, and indoor dust could adsorb very high concentration of HBCD and become the major source of human exposure. Further attention needs to be paid to waste management, and continuous investigations need to be conducted into HBCD emission and contamination after HBCD related products are put into use.

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