

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

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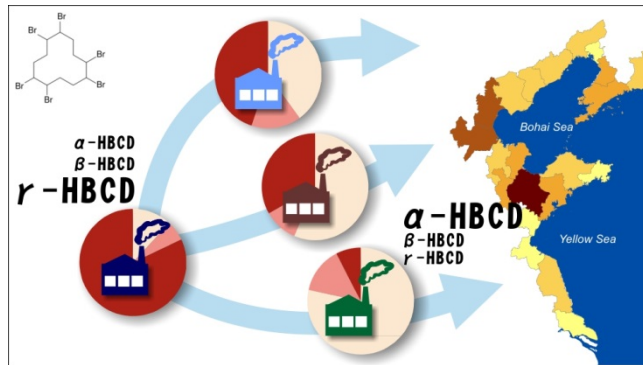
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Abstract art



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

23 **1. Introduction**

24 Hexabromocyclododecane (HBCD) is used as additive flame retardant mainly
25 in expanded polystyrene (EPS) and extruded polystyrene (XPS) plastic foam for
26 thermal insulation in buildings and transport vehicles, while used in polymer
27 dispersion on cotton or mixed blends in the back-coating of textiles and used in high
28 impact polystyrene (HIPS) in electric and electronic equipment with quite a smaller
29 volume ¹. With common usage in some applications, HBCD has become alternative
30 brominated flame retardant since the production and use of PBDEs were restricted. In
31 2001, the global market demand for HBCD was 16500 tons ², while the estimated
32 global production of HBCD increased to 31000 tons in 2011 ³.

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

45 in Europe, North America, Asia, Arctic and other parts of the world. In addition to
46 natural environment, HBCD has also entered the indoor environment with application
47 of insulation boards in residential building and usage of HBCD-containing products.
48 High concentrations of HBCD have been detected in indoor air from offices and cars
49 ¹⁷ and in house dust and air ^{18, 19}. Meanwhile, HBCD has been detected in human
50 milk^{20, 21}, whose levels have been observed positively associated with the numbers of
51 electronic appliances at home.

52 HBCD has 16 stereoisomers in theory, but commercial technical HBCD mainly
53 consists of three diastereoisomers, α -HBCD (10-13%), β -HBCD (1-12%) and
54 γ -HBCD (75-89%), depending on the manufacture and production method. Another
55 two stereoisomers, ϵ - and δ -HBCD, have been detected at low concentrations ²².
56 Structural dissimilarities of individual diastereoisomer lead to differences in polarity,
57 water solubility, and octanol-water partitioning coefficient ($\log K_{ow}$), and further
58 result in their different environmental behaviors ²³. The composition of HBCD
59 diastereoisomers can be affected by thermal isomeric rearrangement during product
60 processing, and by abiotic/biotic transformation in the environment, leading to a
61 different composition from the original technical HBCD. Diastereoisomer
62 rearrangement occurred and γ -HBCD was enriched when HBCD-containing material
63 was exposed at temperature above 140-160°C ²⁴. In addition to thermal processing,
64 natural light exposure could cause a photolytically mediated shift from γ -HBCD to
65 α -HBCD in indoor dust ²⁵. Besides transformation, degradation kinetics also affected
66 the diastereoisomer profile that α -HBCD exhibited longer half-life compared to β - and

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

69 In China, 18000 tons of HBCD was produced in 2011, more than half of the
70 global production, in which 5500-6000 tons was exported, 9000 tons was applied in
71 EPS and 3000 tons was applied in XPS³. Attention has been paid to HBCD
72 contamination in China, and investigations have been conducted near point-source
73 sites or in the most industrialized cities where concentrations in environmental media
74 have been detected to be relatively high^{7, 8, 12, 27, 28}. A larger scale of investigation on
75 HBCD level and spatial distribution is necessary in order to better understand the
76 contamination status, identify sources, and reduce associated impacts.

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

89 component production, e-waste recycling industries are located in this region, which
90 are potential sources of HBCD release. It is also an important agricultural region
91 where crop, vegetables and fruits are cultivated at large scale, while HBCD can be
92 absorbed by these plants. Therefore, the monitoring of HBCD contaminants in soils is
93 necessary to ensure food safety.

94 The objectives of this study were to investigate the occurrence, spatial
95 distribution, and diastereoisomer profiles of HBCD in soils from the coastal cities in
96 north China. Correlation of the HBCD contamination and industrial activities in the
97 region was analyzed to identify potential sources.

98 **2. Materials and Methods**

99 **2.1. Sample collection**

100 Sampling campaign was conducted in 21 cities from 5 provinces (Liaoning,
101 Hebei, Tianjin, Shandong, Jiangsu) covering a total area of 213,000 km² along the
102 China's coast of Bohai and Yellow Seas in September 2013 (Fig. S1). A total of 188
103 surface (top 0-10 cm) soil samples were collected with a stainless steel trowel that had
104 been rinsed with methanol and placed in polypropylene bags. Each sample consisted
105 of five sub-samples within a 100m×100m area. Sampling information including
106 location, land use, and surrounding environmental conditions were summarized in
107 Table S1. All samples were air-dried, homogenized and sieved through a 2 mm mesh,
108 and stored in PP bags at room temperature before extraction.

109 **2.2. Reagent and standards**

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

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

115 **2.3. Extraction and cleanup**

116 Sample extraction followed the procedure described by Harrad, Abdallah, Rose,
117 Turner and Davidson¹¹ with some modifications. 10 g accurately weighed soil (mixed
118 with 15 g pre-heated anhydrous sodium sulfate) were spiked with 10 ng of
119 C13- γ -HBCD as surrogate standard and were extracted using ASE 350 with
120 hexane/dichloromethane (1:9, v/v) at 90°C and 1500 psi (heating time 5 min, static
121 time 4 min, purge time 90s, flush volume 50%, static cycle 3). Extract was
122 concentrated by a rotary evaporator to 1-2 mL. Then the extract was loaded onto a
123 multi-layer silica gel column (15 mm I.D.) for purification, filled from bottom to top
124 with 1 g of anhydrous sodium sulfate (heated at 500°C for 6 hrs), 1 g activated silica
125 gel (heated at 130°C for 16 hrs), 2 g of Florisil (130°C for 4 hrs), 1 g activated silica
126 gel, 3 g of basic silica gel (2%, w/w), 1 g activated silica gel, 8 g of acid silica gel
127 (44%, w/w), 1 g activated silica gel, 1 g of anhydrous sodium sulfate. The column
128 was wet-filled with hexane. Analytes were eluted with 120 mL
129 hexane/dichloromethane (1:1, v/v). The eluate was concentrated by a rotary
130 evaporator to 1-2 mL and further evaporated to incipient dryness under N₂, and
131 reconstituted in 200 μL of methanol/water (8:2, v/v) containing 10 ng of d18- γ -HBCD
132 as recovery determination standard.

133 2.4. Instrumental analysis

134 The analysis of HBCD was performed on Agilent 1290 UPLC system coupled to
135 Agilent 6460 triple quadrupole tandem mass spectrometry. Separation was performed
136 on an Agilent Eclipse Plus C18 column (2.1×100 mm, 1.8 μm) maintained at 30°C.
137 The mobile phase consisted of water and methanol in a constant proportion of 20:80
138 (v/v) at a flow rate of 0.25 mL/min. The injection volume was 5 μL. The mass
139 spectrometry operated with the electrospray ionization (ESI) interface in the negative
140 mode. The parameters used for MS were as follows: gas temperature 300°C, gas flow
141 10 L/min, nebulizer 35 psi, capillary -4000 V. Multiple reaction monitoring (MRM)
142 was used for analytes scanning: m/z 640.6 > 80.7 for native HBCD, m/z 652.6 > 81.0
143 for C13-γ-HBCD, m/z 657.6 > 80.6 for d18-γ-HBCD, respectively. Fragmentor is
144 80V and collision energy is 5 eV for native HBCD, 9 eV for C13-γ-HBCD and 7 eV
145 for d18-γ-HBCD, respectively. The elution order was α-HBCD, β-HBCD and then
146 γ-HBCD. However, in some high concentration samples, an unidentified peak with
147 very low response was observed between α-HBCD and β-HBCD with the same
148 transition as native HBCD, which was implied as another diastereoisomer (Fig. S2).

149 2.5. QA/QC

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

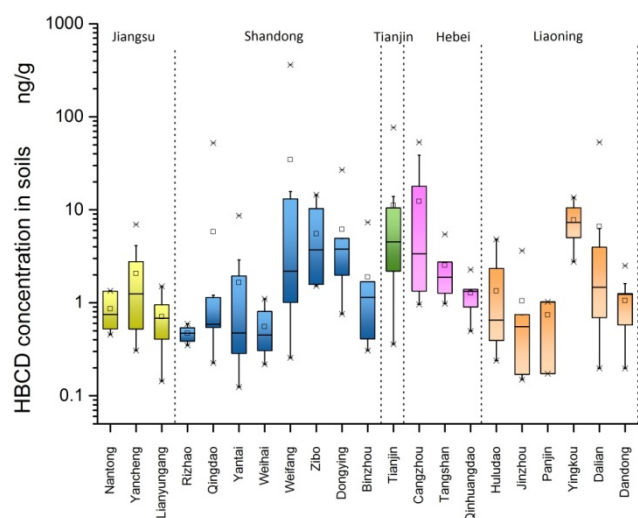
155 (anhydrous Na₂SO₄) was added within each batch of 12 samples to assess introduction
156 of contaminants. These were below LOD. Spiking tests were conducted that matrix
157 soil (preheated at 550°C for 12 hrs) was spiked with 10 ng each of native HBCD
158 before extraction and analysis. The mean recoveries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

165 **3. Result and discussion**

166 **3.1. HBCD levels in soils**

167 For individual diastereoisomer, detection frequencies were 97.3%, 97.9% and
168 100% for α-, β- and γ-HBCD, respectively. Concentration ranges were ND-49.3 ng/g
169 (averaged 2.02 ng/g) for α-HBCD, ND-30.0 ng/g (averaged 0.800 ng/g) for β-HBCD,
170 and 0.052-284 ng/g (averaged 4.38 ng/g) for γ-HBCD. ΣHBCD was detected in all
171 188 soil samples (α-HBCD in 183 samples, β-HBCD in 184 samples and γ-HBCD in
172 all samples, respectively) and ranged from 0.123 to 363 ng/g dw with a mean value of
173 7.20 ng/g, suggesting HBCD's ubiquitous existence along the north coast of Bohai
174 and Yellow seas in China. Among the 188 samples, in terms of HBCD concentration,
175 2 samples are higher than 100 ng/g, 17 samples ranged 10-100 ng/g, 93 samples
176 ranged 1-10 ng/g, and the rest 76 samples were all below 1 ng/g, showing an overall

177 low level of contamination (Fig. 1).



178

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

181

182 Reports of HBCD in surface soils were scarce in the globe, especially at such a
183 large scale. Early investigations of HBCD in soils were focused on point-sources like
184 HBCD manufacturing and processing sites. In point source areas, HBCD
185 concentrations detected exceeded thousands of ng/g, like soils from HBCD
186 manufacturing plants in China ranging 0.88-6901 ng/g²⁷, and XPS producing plant in
187 Sweden ranging from 140-1300 ng/g⁶. Levels in these areas were one magnitude
188 higher than that of this study, which was similar to those from e-waste recycling areas
189 (0.01-284 ng/g) in Guangzhou City⁸ and BFR-manufacturing region (0.30-280 ng/g)
190 in Shouguang²⁸ (a county of Weifang City). HBCD levels in soils in non-point source
191 areas were only reported in China, 0.17-34.5 ng/g in farm soils in rural areas of
192 Beijing³⁸, Nd-0.094 ng/g in rural areas of Shanghai³⁹, 1.7-5.6 ng/g in urban area of
193 Guangzhou⁴⁰, and 0.03-29.9 ng/g in industrial soils from 5 cities of Guangdong

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

198

199 Table. 1 Comparison of HBCD concentration in soils

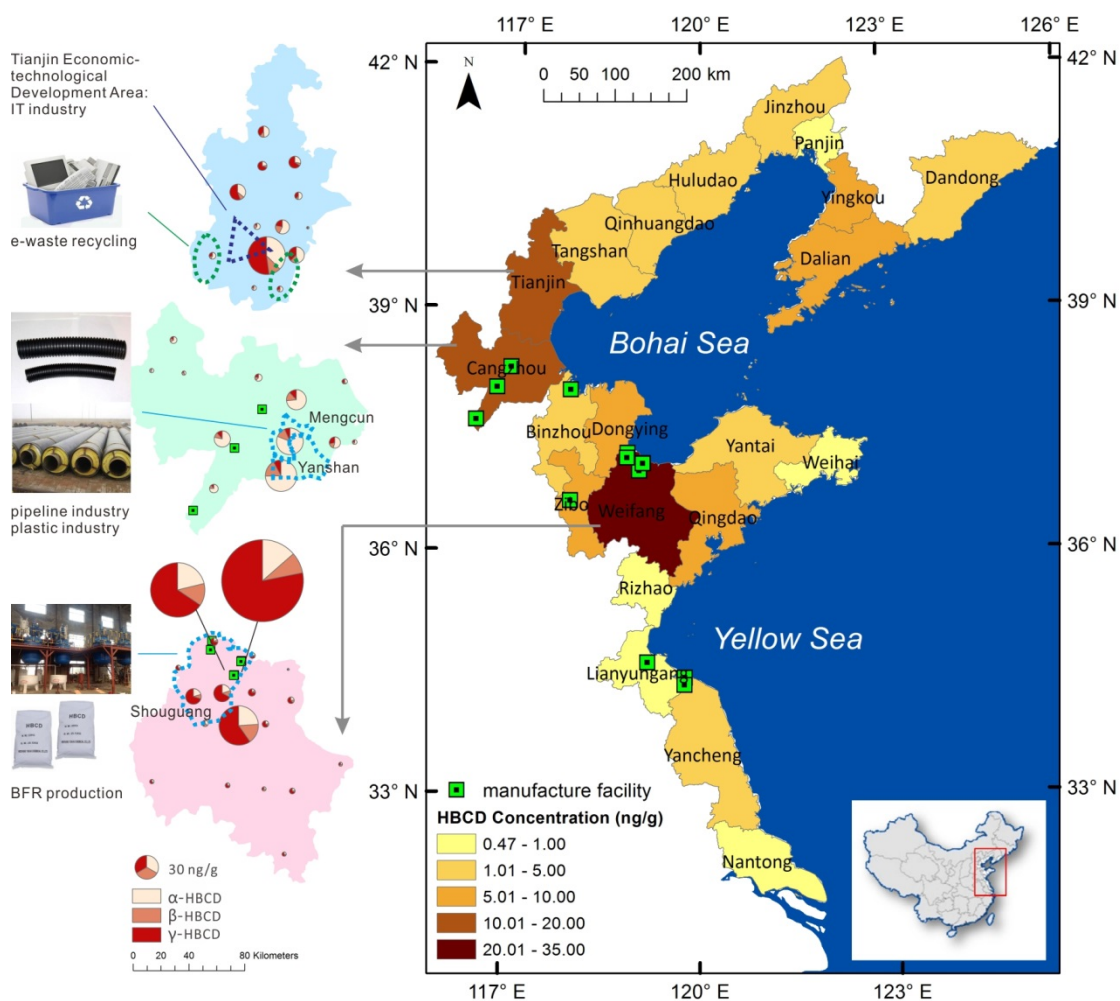
Location description	Range/ng g⁻¹
Point source area	
XPS producing plant, Sweden ⁶	140-1300
E-waste areas, Guangzhou, China ⁸	0.01-284
Manufacturing plants, Laizhou bay, China ²⁷	0.88-6901
BFR-manufacturing region, Shouguang, China ²⁸	0.30-280
Non-point source area	
Urban area, Guangzhou, China ⁴⁰	1.7-5.6
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

200

201 3.2. Spatial distribution

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

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



216

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

218 Green squares stand for HBCD manufacture facilities in China.

219

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

226 regional transport, and the distance of HBCD transport from point source to soil is
227 very short. Li, Zhang, Wang, Li, Lv, Chen, Geng, Wang, Thanh and Jiang ²⁷
228 investigated a HBCD manufacturing site in Weifang and reported the decreasing
229 concentration of HBCD in soil with increasing distance from the center to 8 km away.
230 In this investigation, even though we sampled evenly in space and did not aim at any
231 facility or source, higher concentrations were detected if sample sites got closer to the
232 manufacturing facilities or other sources.

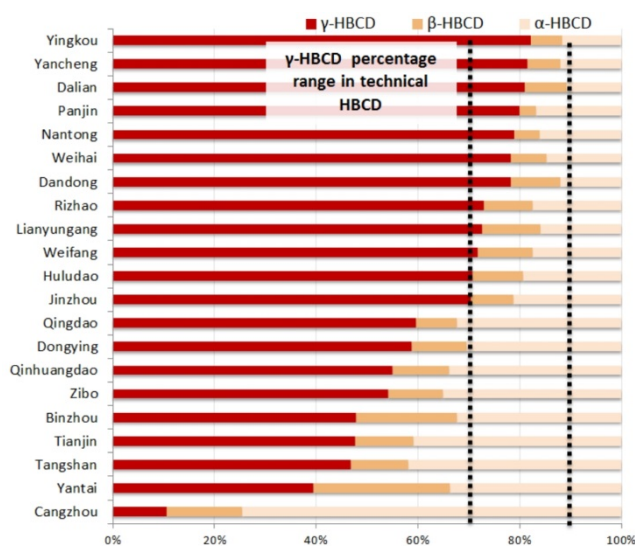
233 High concentrations were detected in the northern coast of Weifang, where the
234 Coastal Economic and Technological Development Zone (known as the biggest flame
235 retardant production base in China) is located. The occurrence of HBCD in soils
236 showed a spatial correlation with HBCD manufacturing facility, inferred to be the
237 source. These facilities were intensively located in 3 towns, Yangkou, Houzhen and
238 Dajiawa in the northern coast of the city (Fig. 2). WF-19 (363 ng/g) was sampled in a
239 crop land in the east of Dajiawa Town, 2.6 km away from a manufacturing facility
240 with a production capacity of 3000 ton/a in the northeast ⁴², which should be the direct
241 emission source in this area. WF-03 (159 ng/g) is sampled in an industrial land in the
242 west of Dajiawa Town, but there is no manufacturing facility found as direct source.
243 The nearest potential source is Houzhen Industrial Zone, 10 km away in the southeast,
244 where more than 3 manufacturing facilities are located.

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

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

251 3.3. Diastereoisomer profiles

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



260
261 **Fig. 3** Diastereoisomer composition of HBCD in 21 cities. The dotted line represents
262 the γ -HBCD percentage range (70-89%) in commercial technical HBCD
263

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

265 conducted in China. In some early investigations of HBCD in environmental media,
266 GC was used for instrumental analysis, which could only give the total amount of
267 HBCD isomers, so the results were reported in total concentrations of HBCD isomers
268 without concentrations or percentages of individual diastereoisomers. In soils from
269 the manufacturing area in China, γ -HBCD (67.3%) was the most abundant
270 diastereoisomer followed by α - and β -HBCD with proportions of 20.4%, 12.3%
271 respectively, which was very close to the composition of commercial HBCD product
272 ²⁷. Diastereoisomer composition in point-source sites (12.0% α -HBCD, 18.5%
273 β -HBCD, 67.5% γ -HBCD) were different from those in non-point-source sites (23.8%
274 α -HBCD, 19.7% β -HBCD, 56.4% γ -HBCD) from BER manufacturing area in China
275 ²⁸. In surface soils from 2 e-waste recycling sites in south China, γ -HBCD proportion
276 ranged from 40-50%, which was similar to α -HBCD (50-40%) (industrial area in the
277 article was not included here)⁸. γ -HBCD's predominance was reported in rural area in
278 Beijing ³⁸ and Shanghai ³⁹, but the ratio of γ -HBCD in Beijing (59%) was relatively
279 lower than that in Shanghai (70%). The variation of diastereoisomer profiles in soils
280 was also reported in South Asian countries ⁴¹.

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

284 **3.4. Relations with industrial activities**

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

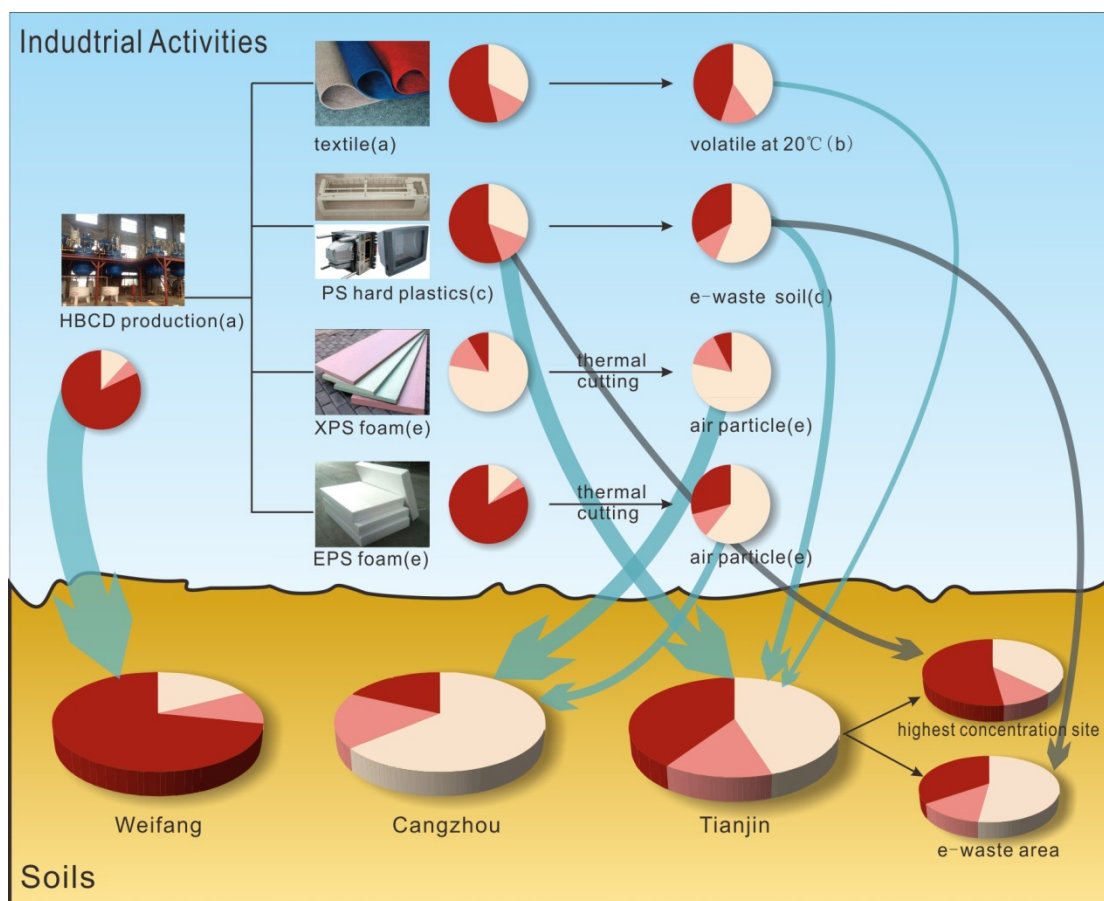
287 different emission sources. As discussed before, distribution of HBCD in soils and its
288 spatial correlation with manufacture facilities were found and used to identify HBCD
289 manufacture as the major emission source in Weifang. Furthermore, diastereoisomer
290 profiles and thier relations with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

295 In Weifang, the diastereoisomer ranged from 13.6% to 37.6% for α -HBCD, from
296 8.3% to 31.4% for β -HBCD, and from 32.9% to 78.1% for γ -HBCD, and averaged
297 17.4%, 10.8%, 71.8% respectively. The composition, especially in the BFR
298 production area in Shouguang (16.2%, 9.9%, 73.9% for α -, β - and γ -HBCD
299 respectively), was consistent with the commercial technical HBCD product. This was
300 an evidence that the contamination of HBCD in soil was released from adjacent BFR
301 production facilities, and HBCD composition was not changed by natural processes in
302 the environment.

303 In Cangzhou, α -HBCD was predominant in the whole city ranging from 42.8%
304 to 81.1% (averaged 63.9%) while γ -HBCD ranged from 6.6% to 41.1% (averaged
305 18.0%). It was noted that relatively high concentrations (53.1 ng/g at CZ-07, 38.7
306 ng/g at CZ-08) were found in Yanshan, and that the lowest γ -HBCD proportions (6.6%
307 and 8.0%) were also detected in Yanshan, known as the Pipeline Equipment
308 Manufacturing Base of China in the southeast of Cangzhou. In this area, metal and

309 plastic pipelines were produced including flame retardant pipe, pipe shell and board.
310 Additionally, a plastics industrial park was also located in this area, and the industrial
311 chain included flame retardant production, plastic pipe and board (mainly XPS)
312 forming and cutting. In 2013, the production of plastic products reached 520,000 tons
313 in Cangzhou ⁴⁸, implying a large market demand for HBCD.

314 During the manufacturing process of these plastic products, intense thermal
315 processing could be the reason for changing HBCD diastereoisomer percentage. In
316 Polystyrene (PS) consumer products (food container, packing support, etc.) collected
317 in Korea, γ -HBCD was the dominant isomer with an average percentage of 56%,
318 which was lower than the original percentage of technical HBCD. PS hard plastics
319 (general purpose polystyrene, GPPS; high impact polystyrene, HIPS; etc.), which
320 received more processing in industry than EPS, contained lower γ -HBCD proportion
321 than other materials ⁴⁹. In insulation board, γ -HBCD was the predominant component
322 with a similar composition to commercial technical HBCD product in EPS raw foam,
323 while α -HBCD was predominant in XPS raw foam. However, in particles emitted
324 from thermal cutting of both EPS and XPS, α -HBCD was predominant and γ -HBCD
325 was only 29% from EPS and 8% from XPS ⁵⁰. This proportion of γ -HBCD was close
326 to that of Yanshan. Considering the spatial distribution and diastereoisomer profiles of
327 HBCD in soils, and the local industrial activity, XPS and EPS foam processing could
328 be identified as the major source of HBCD in Cangzhou.



329

330 Fig. 4 Correlation between industrial activities and HBCD in soils for the
 331 diastereoisomer contribution. Pie charts here were only for percentages, not for
 332 concentrations. Compiled from (a, Kajiwara et al. 2009; b, Kajiwara and Takigami
 333 2013; c, Rani et al. 2014; d, Gao et al. 2011; e, Zhang et al. 2012.)

334

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

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

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

357 Since high concentrations of HBCD had been reported in e-waste recycling sites
358 in south China, in this paper, high level was also assumed to be in the biggest e-waste
359 recycling area in north China, which was located in Tianjin. Unexpectedly, the
360 concentrations of HBCD were only 2.96 ng/g (51.7% α -HBCD, 9.9% β -HBCD and
361 38.4% γ -HBCD) and 1.79 ng/g (52.6% α -HBCD, 16.4% β -HBCD and 31.0%
362 γ -HBCD) respectively in Jinghai County and Dagang District, where the e-waste

363 recycling area is located. In e-waste recycling sites in South China, γ -HBCD was the
364 predominant isomer (36.3% α -HBCD, 4.8% β -HBCD and 58.9% γ -HBCD) in
365 Qingyuan with a total concentration of 106 ng/g, while α -HBCD was the predominant
366 (56.4% α -HBCD, 10.3% β -HBCD and 33.3% γ -HBCD) in Guiyu with a total
367 concentration of only 2.34 ng/g⁸. The diastereoisomer profiles in Tianjin in this study
368 were very close to that of Guiyu, suggesting the impact of e-waste recycling as the
369 common source in both areas. Compared to that in South China, there may be a major
370 reason for the low levels in Tianjin, that is, the recycling facilities were under strict
371 and formal (closed) operation, different from the informal (open) recycling process in
372 Guangzhou, so the emission were under control. Differently, in the investigation in
373 informal e-waste recycling sites in Vietnam, α -HBCD was predominant in both dust
374 and air samples collected in the backyard of e-waste recycling houses, and 6 and 10
375 times more abundant than γ -HBCD respectively⁵³. This variation may result from the
376 difference in e-products category and recycling method in the two countries.

377 **4. Conclusions**

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

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

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

407

408 **Acknowledgements**

409 This study was supported by the Chinese Academy of Sciences under Grant no.
410 KZZD-EW-TZ-12, the International Scientific Cooperation Program with Grant no.
411 2012DFA91150, and the National Natural Science Foundation of China under Grant
412 no. 414201040045 and 41371488. We would like to thank the editors and reviewers
413 for their valuable comments and suggestions.

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