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

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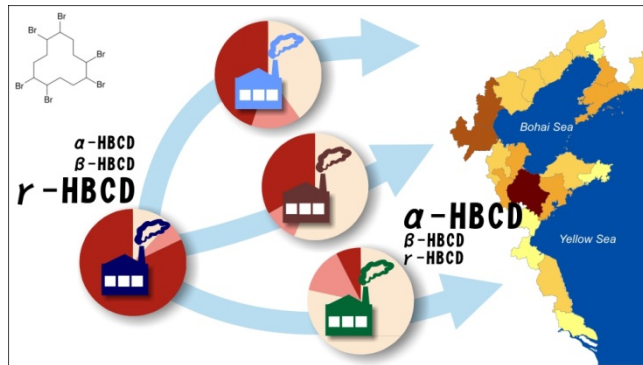[∥] Centre for Ecology & Hydrology, Wallingford, OX10 8BB, UK

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Abstract art

Abstract:

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

Keywords: HBCD; brominated flame retardant; soil pollution; emission source; Bohai Sea, Yellow Sea

1.   Introduction

Hexabromocyclododecane (HBCD) is used as addictive 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],

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 diastereosiomer lead to differences in polarity,

57   water solubility, and octanal-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℃ [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 biota [26].

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 XPS [3]. 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 POPs [29-32]. 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 GDP [33-37]. 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 km^2 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 μg mL^{-1} in toluene with purity >98%.

2.3.   Extraction and cleanup

116   Sample extraction followed the procedure described by Harrad, Abdallah, Rose,

117   Turner and Davidson [11] 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℃ 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℃ for 6 hrs), 1 g activated silica

125   gel (heated at 130℃ for 16 hrs), 2 g of Florisil (130℃ 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 N_2, 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.

2.4. Instrumental analysis

The analysis of HBCD was performed on Agilent 1290 UPLC system coupled to Agilent 6460 triple quadruple tandem mass spectrometry. Separation was performed on an Aglient Eclipse Plus C18 column (2.1×100 mm, 1.8 μm) maintained at 30℃. 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℃, 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

155 (anhydrous Na$_2$SO$_4$) 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℃ 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/$\sqrt{2}$.

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).
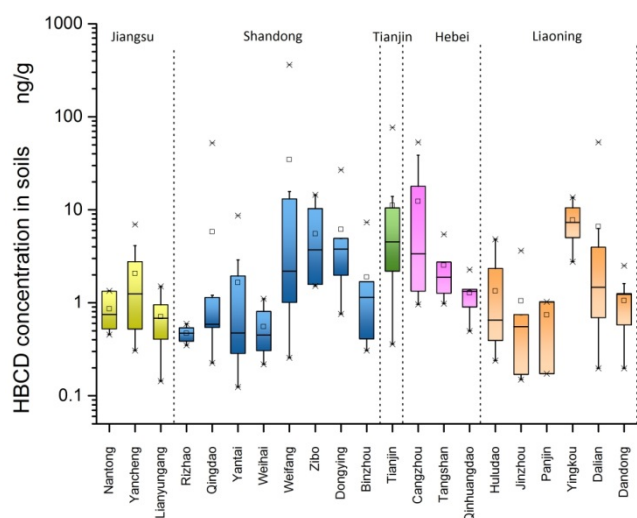
178

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/g [27], and XPS producing plant in

187   Sweden ranging from 140-1300 ng/g [6]. 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 City [8] and BFR-manufacturing region (0.30-280 ng/g)

190   in Shouguang [28] (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   Beijing [38], Nd-0.094 ng/g in rural areas of Shanghai [39], 1.7-5.6 ng/g in urban area of

193   Guangzhou [40], 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 concentrention 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

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.

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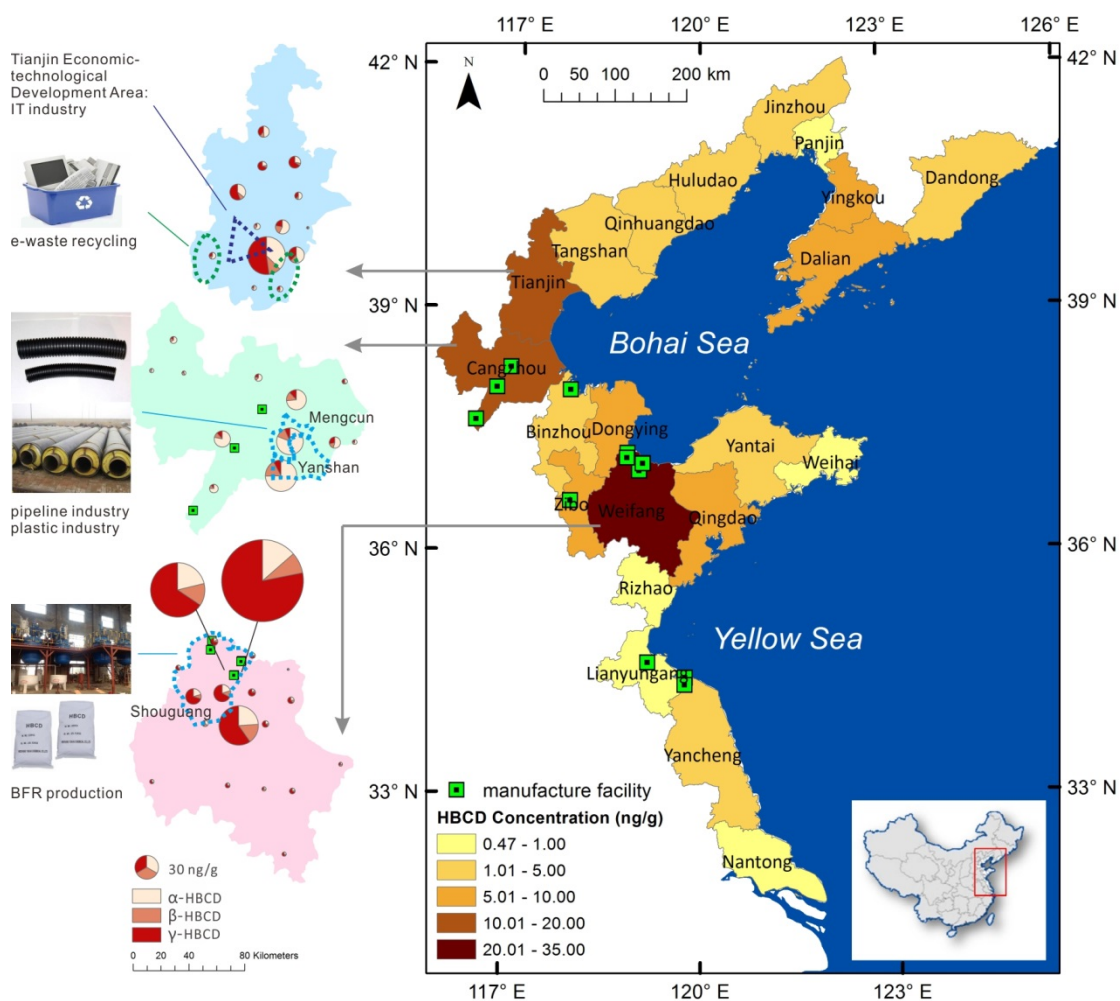
Fig. 2 Spatial distribution of mean HBCD concentrations in soils from 21 cities.

Green squares stand for HBCD manufacture facilities in China.

219

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

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.

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%.
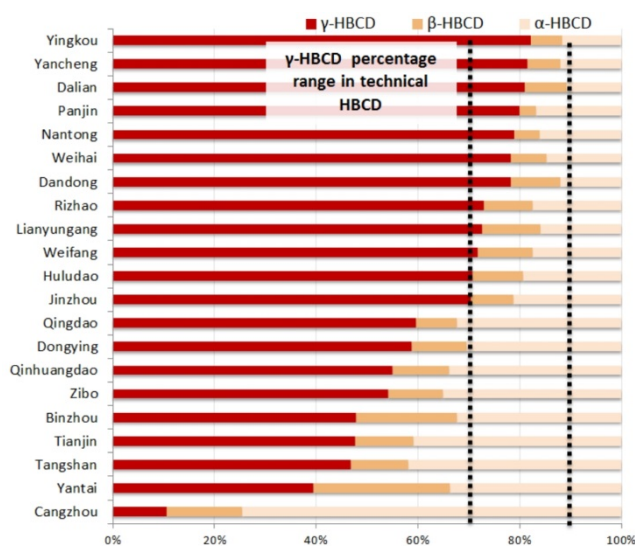
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261 **Fig. 3** Diastereoisomer compostion of HBCD in 21 cities. The dotted line represents

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/eggs[44], fish[45, 46], mollusks[15], ringed seals[47] 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 precentage. 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.
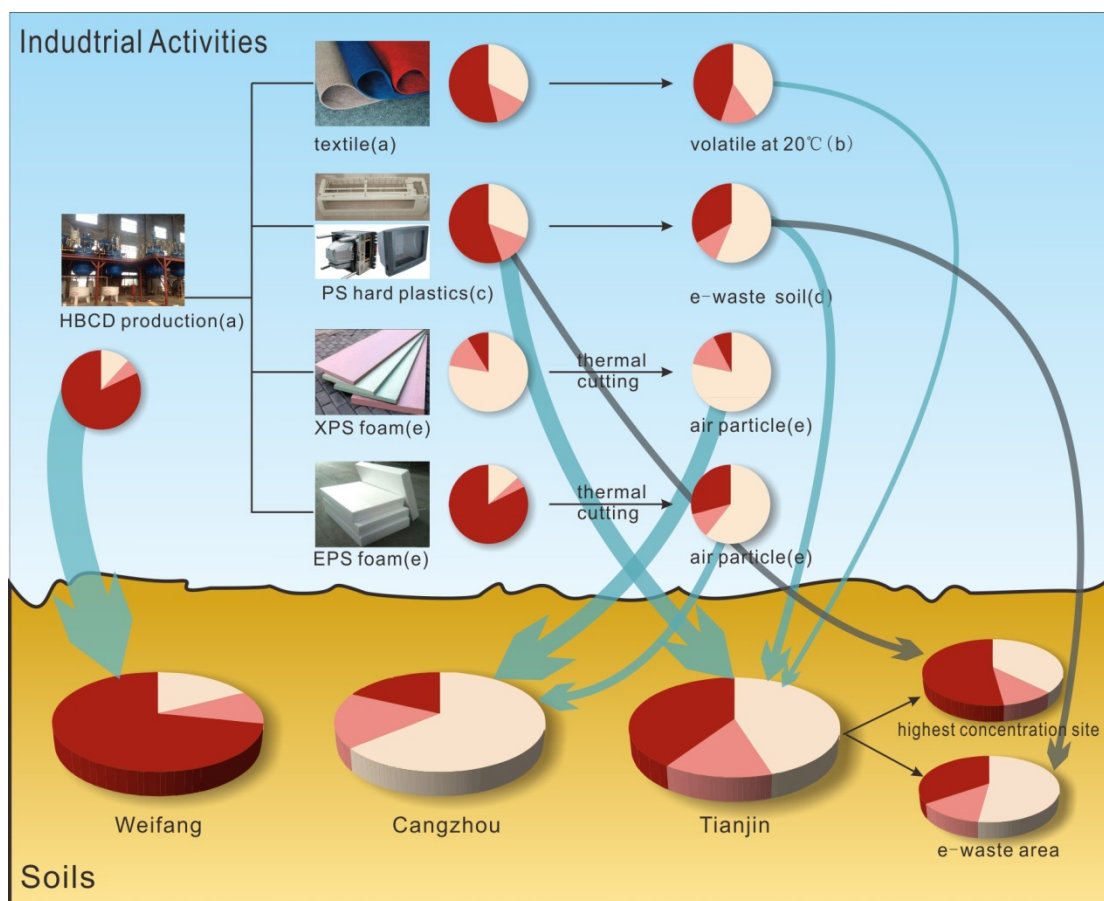
Fig. 4 Correlation between industrial activities and HBCD in soils for the diastereosiomer contribution. Pie charts here were only for percentages, not for concentrations. Compiled from (a, Kajiwara et al. 2009; b, Kajiwara and Takigami 2013; c, Rani et al. 2014; d, Gao et al. 2011; e, Zhang et al. 2012.)

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

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-HBCD [49]. 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℃), the proportion of α-HBCD increased when

353 the temperature increased [52]. 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/g [8]. 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 respectively [53]. 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

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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