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HBCDs and TBBPA are widely used BFRs, and their globe production and environmental concentrations has increased over the past decades. Tris(2,3-dibromopropyl) isocyanurate (TBC) is another BFR which has been receiving attention recently. The present study reported the concentration levels of these three BFRs in surface soils in Ningbo, East China. Although the information about BFRs in different environmental and biota matrices is extensive in literature, there is little data about the HBCDs, TBBPA and TBC BFRs in soils. The paper reports concentration levels of HBCD, TBBPA and TBC BFRs in surface soils in Ningbo, which could reflect the usage of BFRs and the total burden of contaminants of BFRs in this area.

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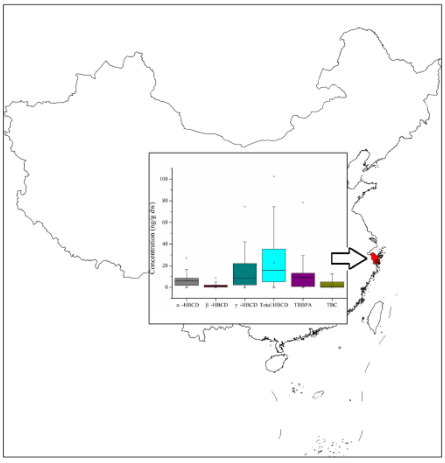
HBCD, TBBPA and TBC BFRs are ubiquitous contaminants in surface soils of industrialized region of East China.



Levels of the flame retards HBCD, TBBPA and TBC in surface soils from an industrialized region of East China

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Abstract:

Hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA) are raising concern because of their potential persistence, bioaccumulation and toxicity. Tris- (2, 3-dibromopropyl) isocyanurate (TBC) is another brominated flame retardant (BFR) which has recently been found in environment and began to attract attention. The objective of this study is to determine concentrations of these three BFRs in surface soil samples collected from a heavily industrialized and urbanized region in East China. Levels of ∑HBCDs ranged from below detection limits (0.020 ng/g) to 102.6 ng/g on a dry weight basis (dw) with a median level of 15.8 ng/g dw. Whereas for TBBPA, the concentration ranged from below detection limits (0.025 ng/g) to 78.6 ng/g dw with the median level of 9.17 ng/g dw. TBC has relative lower concentrations ranging from below detection limits (0.024 ng/g) to 16.4 ng/g dw with a median level of 0.95 ng/g dw. The concentrations of these three BFRs are significantly positively correlated, indicating a common source. Variable BFRs levels were found in different types of soils, with significant higher concentrations were observed at the waste dumping sites and industrial areas. The diastereoisomer profiles of HBCD in most of the soil samples differed from those of the commercial products. The mass inventories of HBCDs, TBBPA and TBC in this region gave preliminarily estimates of 6.68, 2.67 and 0.85 kg， respectively. Therefore, the ubiquitous contamination for these BFRs in soils may well reflect the widespread usage of these BFRs in study area.

1. Introduction

Brominated flame retards (BFRs) are a diverse group of compounds which are used to prevent or minimize fire hazards. Environmental concerns relating to BFRs are growing due to their environmental persistence, bioaccumulative properties and potential toxicity [1, 2]. Some BFRs such as polybrominated diphenyl ethers (PBDEs) have faced increasing regulations by governments and agencies worldwide [3]. Tetrabromobisphenol A (TBBPA), hexabromocyclododecanes (HBCDs) and other BFRs have been used as alternatives for the discontinued PBDEs in some application [3]. Over the past decade globe production and environmental concentrations of these BFRs has increased [1 2].

TBBPA is employed in manufacturing epoxy and polycarbonate resins, as well as it is also the primary flame retardant used in electronic circuits[4]. It can also be used as an additive, for instance in high-impact polystyrene. In additive applications, there is potential for TBBPA to escape from the product and enter the environment. The annual global market of TBBPA was over 170,000 t in 2004 [5]. TBBPA has been found in lower concentrations than those found for PBDEs and HBCDs in air, soils, sediments and biota [6]. TBBPA is toxic to primary hepatocytes and has weak estrogen-like properties [7], and it is toxic to aquatic life [8].

Hexabromocyclododecanes (HBCDs) are used primarily in extruded and expanded polystyrene for thermal insulation in the building industry, and to a minor extent to incorporation into textiles, furniture, car interiors, electric appliance and electronics[9]. HBCDs mainly consist of three diastereoisomers: α-, β- and γ-HBCD, with the

gamma-isomer predominating in the mixture[10]. The demand of HBCDs has increased with implementation of mandatory (EU) or voluntary (Japen) restrictions of other BFRs, such as penta- and octabrominated diphenylether (PBDE) formulations[11]. During the last decades, HBCDs was the third most used BFRs worldwide with a globe production volume of totaled 16 700 tonnes in 2001 [12]. With the widespread application, HBCDs has become the subject of scientific concern about its environmental fate and toxicity [12]. Evidences have been support HBCDs' classification as persistence, bio-accumulative and toxic (PBT) substance and a substance prone to long distance transportation[12].

Tris- (2,3-dibromopropyl) isocyanurate (TBC) is one of the "novel" additive brominated flame retardant, which has been recently detected in the environment near a point source and in fish [13]. The current globe production volume of TBC is unclear but the production amount for China is probably higher than 500 t per year [13]. TBC could cause some adverse effects to environment and biota, such as it could impair the gas bladder function of zebrafish, and disrupt its reproduction and endocrine [14]. TBC might also be the causative compound of neuronal cell toxicity [15]. Although no restrictive regulations have been imposed on TBC, the environmental release of TBC has also been of a concern to many countries. It has been identified as a high priority chemical for further investigation by the UK Environment Agency and added into the OSPAR list of substances of possible concern and the Environment Canada screening list of substances of lower ecological concern [16]. A rapid increasing temporal level of TBC was found in farm soils in North, China[17], the results indicated that the

environmental release of TBC should be problematic and more information is needed on its production volume, environmental distribution and potential health effects [17].

Most studies on BFRs levels in environmental matrix have been performed in Europe and North American, with few reports in Asia[18]. China is expected to become a large BFRs manufactures and consumers for its rapid urbanization and economic development[19]. TBBPA and HBCDs are the two widely used BFRs in China, with estimated domestic production volumes of 38,000 and 12,000 tons in 2006 [19]. HBCDs and TBBPA have been investigated previously in air (34-1300 pg/m^3 for HBCDs and 0.7-33 ng/m^3 for TBBPA) and dust (140-140 000 ng/g dw for HBCDs and nd-382 ng/g dw for TBBPA) [3], sewage (nd-97.5 ng/g dw for HBCDs and nd-472 ng/g dw for TBBPA) [4], sediment (0.2-1680 ng/g dw) [20], as well as biota (0.0026-2.14 ng/g lipid for HBCDs and 0.0033-0.464 ng/g lipid for TBBPA in human adipose tissues, respectively) [21]. However, very little is known about concentrations of HBCDs and TBBPA in soils, information on the presence of TBC is also scarce.

The aim of the present study was to investigate the concentrations of HBCDs, TBBPA and TBC in surface soils in Ningbo, one heavily industrialized and urbanized region of East China, and the diastereoisomer profiles of HBCDs were further discussed in order to better understand their source and fate in the soil.

2. Materials and methods

2.1 Materials

All solvents used in extraction and analysis procedures were HPLC grade. Technical grade TBC (97%) was purchased from Sigma-Aldrich (St. Louis, MO). The native α-,

β-, γ-HBCD were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The d_{18} labeled α-, β-, γ-HBCD, TBBPA and ^{13}C-TBBPA were purchased from Wellington Laboratories (Guelph, ON, Canada). Individual stock solutions were prepared on a weight basis in methanol and stored at -20℃. A mixture of all selected analyzing standards was prepared by appropriate dilution of individual stock solutions.

2.2 Sampling procedure and sample pretreatment

The sampling campaign was conducted in the Ningbo region located to the South of the Yangtze River Delta in September, 2012. Ningbo belongs to Zhejiang province, with a total area of about 9695 km^2, which is one of the most industrialized and urbanized region in China. Moreover, it is also a major production centre for textiles, electronic appliance and chemical industry. There are also numerous small scale workshops and medium sized industries spread around the region. A large amount of polymer raw materials, textile, electronic appliances and fine petrochemicals are being produced which could bring BFRs pollution to this region.

A total of 90 surface soils (0-20 cm depth) were collected in Ningbo region (Figure 1). In order to contextualize the pollution impacts from various human activities, land use was further classified into six functional types, namely: waste dumping sites, industrial areas, residential areas, traffic areas, vegetable soils and farmland soils. Soil samples were obtained by mixing 5 subsamples from each site. The samples were wrapped in two-layers of aluminum foil, sealed in plastic bags, and stored in a cool box. In pretreatment procedure, the samples were freeze-dried, sieved through a 2-mm

sieve, transferred to amber glass, and stored at -20℃ until chemical analysis.

Detailed analytical was given elsewhere [22]. Briefly, after adding surrogate standards ($^{13}C_{12}$-labled α-, β- and γ-HBCD), about 10 g soil sample were mixed with 15 g anhydrous Na_2SO_4. The sample was then loaded into an accelerated solvent extraction cell (ASE 300, Dionex, Canada) using dichloromethane (DCM) as extraction solvent. The extract was concentrated and purified further onto an activated silica gel column, and then was washed with 38 mL hexane followed by elution with 60 mL DCM. The eluate was concentrated under a gentle stream of N_2, and the solvent was exchanged into methanol for instrumental analysis.

2.3 Instrumentation and analysis

Samples were analyzed using an Alliance 2695 HPLC system (Waters, Milford, MA) with a ZORBAX C_{18} column (3 mm × 150 mm, 5 μm, Aginent, USA) coupled to a Quattro Premier XE triple quadrupole MS spectrometer (Micromass, Manchester, UK). Instrumental analysis of TBC and three HBCD diastereoisomers was performed with the methods described by Feng *et al* (2010)[22]. The gradient mobile phase consisted of methanol (A)/acetonitrile (B)/water (C). The flow rate was set at 0.4 ml/min. The gradient program started at an intial composition of 30:30:40 A/B/C (v/v) and was ramped to 70:30:0 A/B/C in 10 min, held for 4.9 min and then returned to 30:30:40 A/B/C in 0.1 min. The column was then allowed to be equilibrated for 5 min. The quadrupole MS used in this study was triple-quadrupole mass spectrometer (Quattro Premier XE, Micromass, Manchester, UK). The mass spectromer was operated in ESI mode, the ions were selected at the ($[M-H]^-$) transition of *m/z* 640.6→

79, 652.7→79, 657.7→79 and 640.6→81 for HBCD isomers , $^{13}C_{12}$-labled HBCD isomers , d_{18}-labled HBCD isomers and TBC, respectively. The ions *m/z* 542.7→79 for TBBPA and 554.7→79 for $^{13}C_{12}$-labled TBBPA were monitored.

2.4 Quality assurance / quality control (QA/QC) and data analysis

Since labeled TBC standars are not currently available, so the labeled HBCD standars was used as surrogate because these two compounds have similar physical and chemical properties. For each batch of 12 soil samples, a procedural blank sample, a standard-spiked blank sample, a standard-spiked matrix sample and a standard-spiked matrix sample duplicate were analyzed for quality control. No analytes was detected in procedual blanks. The recoveries of surrogates were 82.4%-96.3%. Reported concentrations were not surrogate recovery corrected. Limits of detections (LODs) were defined as a signal to noise ratio of 3:1, were 0.028、0.020、0.020, 0.024 and 0.025 ng/g for α-, β-, γ-HBCD, TBC and TBBPA, respectively.

Data analysis was performed using SPSS 16.0 (SPSS Inc., Illinois). Concentrations were log transformed before statistical analysis. The levels of statistical significance was set at $p<0.05$.

3 Results and discussion

3.1 Levels and composition of HBCDs, TBBPA and TBC in surface soils

The three BFRs were detected in most of the surface soil samples, the detection frequency of HBCDs, TBBPA and TBC were 92.2%, 80.0% and 57.8%, respectively. This implies that HBCDs and TBBPA were ubiquitous contaminants in the study areas. The summarized information are depicted in Figure 2.

We detected α-, β-, and γ-HBCD in 79, 75 and 83 samples of the 90 analyzed samples, respectively. γ-HBCD was the dominant diastereomer comprising an average of 61.0% (range:7.73-100%) of ∑HBCDs, whereas α-, β-HBCD comprised 32.1% (range:0-64.1%) and 6.90% (range:0-28.2%) of ∑HBCDs, respectively. Levels of ∑HBCDs ranged from below detection limits to 102.6 ng/g on a dry weight basis (dw) with a median level of 15.8 ng/g dw. Whereas the concentration of TBBPA ranged from below detection limits to 78.6 ng/g dw with the median level of 9.17 ng/g dw. Compared to HBCDs and TBBPA, TBC has a relative lower concentration with a median level of 0.95 ng/g dw (ranged between below detection limits to 16.4 ng/g dw).

We observed previously that despite the far greater production and use of TBBPA compared to HBCDs, concentrations of TBBPA in most soil samples (except 3 samples of vagetable soil) were lower than those of HBCDs, this may atribute to the widespread use of TBBPA as a reactive flame retard, this makes its release from treated goods less facile than for additive flame retards like HBCDs. Similar trends were also found in both indoor air and dust[3].

3.2 Comparison with published levels

The concentration levels of BFRs have been reported during last decade, resulting in a large amount of environmental data. Although there are several studies about the contamination levels of HBCDs and TBBPA in differnet environmental and biota matrices [5], this is not the case of soils. Futhermore, only a few studies have reported the levels TBC in soils.

The HBCDs levels detected in this study were significantly higher than those reported from rural soils in Chongming Island (the Yangtze River Delta, YRD) (range from not detected to 93.8 pg/g dw with average 23.3 pg/g) [23] and those from urban soils from Guangzhou (1.7-5.6 ng/g dw)[24], as well as the soils from dumping sites in Indian, Vietnam, Malaysia, Indonesia, and Cambodia (from not detected to 2.4 ng/g dw)[25]. The results of this study were comparable with those soils collected near a Chinese HBCDs manufacturing facility ranged from 2.8 to 144.5 ng/g dw [24]. In this study the levels of HBCDs were lower than the levels reported by Gao *et al*[18] of which soil samples collected from e-waste recycling areas (ranging from 0.38 to 284 ng/g dw). The studies carried out nearby an expanded polystyrene manufacturing plant in Sweden (ranged 140-1300 ng/g dw) [26] or near HBCD-processing factories also contained higher concentrations [27], which ranging from 140 to1 300 ng/g dw and 111 to 23 200 ng/g dw, respectively. Overall, the levels of HBCDs in soils collected from Ningbo were at moderate concentrations compared with the reported concentrations worldwide.

To date, few studies focused on TBBPA in soil. The levels detected in this study were significantly lower than those reported from an e-waste recycling site in Beijing, China (26-104 ng/g dw)[28], and a contaminant soil sample collected from Isreal (more than 50 ng/g dw)[29], but compatable with those collected from industrial soils in Spain (3.4-32.2 ng/g)[30]. Because of limited data, TBBPA levels in sediments were also included for comparison. Most studies on sediment TBBPA have been performed in Europe, different concentrations were reported. The studies carried out close to a site

of BFRs manufacture in England estuarine and riverine sediments found significant higher levels, ranging from 2.4-9 750 ng/g [8]. Relatively higher concentrations have also been found in PRD, south China (0.06-304 ng/g). Lower sediment concentrations were found in sediments from the English lake (0.3-3.8 ng/g dw)[6] and Duch rivers (0.1-6.9 ng/g dw) [8].

TBC is of environmental concern recently and was recently detected in the water, sediment, and biota near a manufacturing factory in Southern China [13]. Although the oveall production volume of TBC is currently not clear, increased production volume are expected due to the enormous demand for electronic products. To date, there are quite few reports on TBC in environment. The leveles detected in this study were lower than those reported from agriculture soils near a TBC manufacturing plant (19.6-672 ng/g dw) [13] but higher than those in the farm soil samples collected at a peri-urban region in Southeast Beijing (below detection limits to 1.62 ng/g dw) [17]. The frequent detection and relative higher level of TBC in the study area should be an environmental concern regarding its bioaccumulation potential. The physical-chemical properties of TBC is similar to those of PBDEs, which are known to be highly bioaccumulative [13].

3.3 Source attribution

Examination of relationships between the concentrations of individual disstereoisomer , total of HBCD, TBBPA and TBC at each site, was summarized in Table 1. The results reveals a significant positive correlation between each diastereoisomers and total HBCD ($p<0.01$), which suggested these compounds have

similar sources. Interestingly, significant correalitions between the concentration of TBBPA, HBCDs and TBC were also found. While this requries continued monitoring to be confirmed, it indicates a common source or sources, and may reflect widespread use of these BFRs in commercial application. Similar positive correlation has also been found between the TBBPA and HBCDs concentrations in English lake sediments[6]. The study area is a major production centre for BFRs, textiles, electronic appliances and chemical industril which could bring HBCDs, TBBPA and TBC pollution to this region.

3.4 Variation of HBCDs, TBBPA and TBC with land use

Significant differences for the three BFRs were observed in six types of soils. The summarized data are listed in Table 2. The total HBCDs, TBBPA and TBC concentrations in soils varied substantially between different types of land use. On the other hand, as shown in table 2, two special areas demonstrated significantly higher concentrations: waste dumping sites and industrial areas. The mean concentration of total HBCDs in waste dumping sites was about 2.0 times higher than that in industrial areas (1.8 times) and traffic areas (2.1 times), and was 4.8 times, 6.1 times and 8.7 times higher than that in residential area, vegetable soils and farmland soils, respectively. It could be expected that higher HBCDs concentrations could occur in the waste dumping sites and industirl area, which could be derived from the local sources in those areas. The mean concentrations of total HBCDs in traffic areas was 31.8 ng/g dw, which showed higher trend than those in residential areas and vegetable soils and farmland soils. Finally, those samples from vegetable soils and farmland

soils had a mean total HBCDs level of 11.0 and 7.75 ng/g, respectively, the lowest level among all the samples. Similar trends were also found for TBBPA and TBC. The BFRs concentrations in soils in Ningbo varied substantially between different land use, indicating that the BFRs contamination was propably derived from local discharges. Higher BFRs levels in both e-waste dumping sites and industrial areas may suggest that e-waste recycling activities and industrial activities were important source of BFRs in this areas.

3.5 Diastereoisomer profiles of HBCDs

The diastereoisomer profiles in surface soils with different types of land use are shown in Figure 3. The HBCD diastereoisomer profiles were similar in six types of soils, where the predominant diastereoisomer was γ-HBCD, followed by α-HBCD and β-HBCD. As shown in Figure 3, the diastereoisomer profiles of HBCDs in this study were different from those of commercial HBCDs. The mean percentages in all soil samples were 32.1%, 6.9% and 61.0%, respectively. γ-HBCD was the dominant isomer of Chinese commercial technical products (71%-87%), howerever, among all the soil samples, only 23 of 90 soil samples(70%-100%) showed the similar profiles to the commercial technical products. Most of the samples exhibited variable diastereoisomeric profiles, the mean percentage of α-HBCD (32.1%) in the soil samples was significantly higher than that in commercial mixtures[31], and α-HBCD was the dominant isomer in 15 of 90 samples. Variations in isomer profiles have frequently been reported in soil and sediment samples in other studies [18, 23]. Marvin *et al* [32] reported that two-thirds of the suspended sediment samples were dominated by

γ-HBCD, while one-third exbited relatively higher concentrations of α-HBCD. Morris *et al* [8] also reported that a higher percentage of α-HBCD was frequently found in sediments of rivers around the North Sea. Meng *et al* [23] and Yu *et al* [33] have found that in some soil samples only α-HBCD was detected. Furthermore, a predominant of α-HBCD or γ-HBCD has also reported in various biotic and air samples[12]. However, the mechanism responsible for the significant variation of HBCDs diastereoisomer profiles are currently unclear.

Briefly, the ratio of soil HBCD diastereoisomers could be affected by their thermal isomerization during the processing of HBCDs, and by abiotic/biotic transformation in the environmental media. Barotini *et al* [34] indicated that γ-HBCD might be converted to α-HBCD above 160℃, while incorporating HBCDs into plastic sometimes requires this temperature. Therefore, the dominant isomer can be transferred from γ-HBCD to α-HBCD during this process. Based on the results of their previous study, Heeb *et al* [35] also suggested that isomeric interconvention rather than selective degradation processes were responsible for the observed diastereoisomers changes of HBCDs exposed to expanded and extruded polystyrenes at temperature of 140-160℃. In addition to thermal interconversion, variations in diastereoisomers profiles can also be caused by their difference of transport/partitioning in envrionmental media [36]. Futhermore, α-HBCD has relatively longer environmetal half time than that of γ-HBCD in anaerobic soils [37, 38]. Many other factors can still affect HBCDs diastereoisomer profiles. Therefore, the mechanisms responsible for the variable diasteroisomer profiles should be further

309 investigated.

310 **3.6 Preliminary estimation of HBCDs, TBBPA and TBC inventory**

311 The levels of contaminants in soils can, to some extent, reflect the total burden of
312 contaminants during a certain period. To assess the influence of HBCDs, TBBPA and
313 TBC on the terrestrial environment in Ningbo, the mass inventories of the BFRs were
314 estimated using the following equation[39]:

315 $$I = \sum kC_i A_i \, d\rho \qquad (1)$$

316

317 Where C_i (ng/g dw) is the mean concentration of BFRs in soils for each sampling area;
318 A_i is the land area (km^2), d is the thickness of the soil sampled (cm); ρ is the average
319 density of dry soil particles (g/cm^3); k is the unit conversion factor.

320 The area of Ningbo city is 9695 km^2, with a soil depth of 20 cm and assummed soil
321 bulk density of 1.5 g/cm^3. The mass inventory of HBCDs, TBBPA and TBC in soils in
322 the study region were estimated to be 6.68, 2.67 and 0.85 kg, respectively. The
323 occurrence of relatively higher concentrations of these BFRs suggested that these
324 BFRs have been widely used in this region. Further inveatigations into the use of
325 BFRs in this area are needed.

326 **4.Conclusions**

327 The study reported the concentration levels of HBCDs, TBBPA and TBC in Ningbo
328 region, East China, one of the most developed regions in China. The widespread
329 distribution and relative higher concentrations of HBCDs, TBBPA and TBC in
330 surface soils suggest that emissions of these BFRs were huge in this region. This
331 might be due to general increasing production volumes and usage of these compounds,

replacing other BFRs that are banned or being phase out. There are currently few reports on the soil levels of TBBPA and TBC. This study revealed that TBBPA and TBC are ubiquitous environmental contaminants and occur at relatively higher end of level in the region. The contamination of these BFRs is expected to increasing usage in the future. Therefore, more research should be conducted on the potential transfer of these BFRs from soils to food chain and investigate the potential risks by consumption of contaminated food.

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Figure captions

Fig.1. Map of the study area and sampling sites.

Fig.2. BFRs concentrations from soil samples collected in Ningbo, East China. The number of samples is 90. The box represents data between 25th and 75th percentile, the middle band represent the median value whereas mean values are symbolized by □. The whiskers extending from the box show the lowest and highest non-outlier values. "×" represents the lowest and highest values for each compound among all samples.

Fig.3. HBCD diastereoisomer profiles in soil samples with different land use.

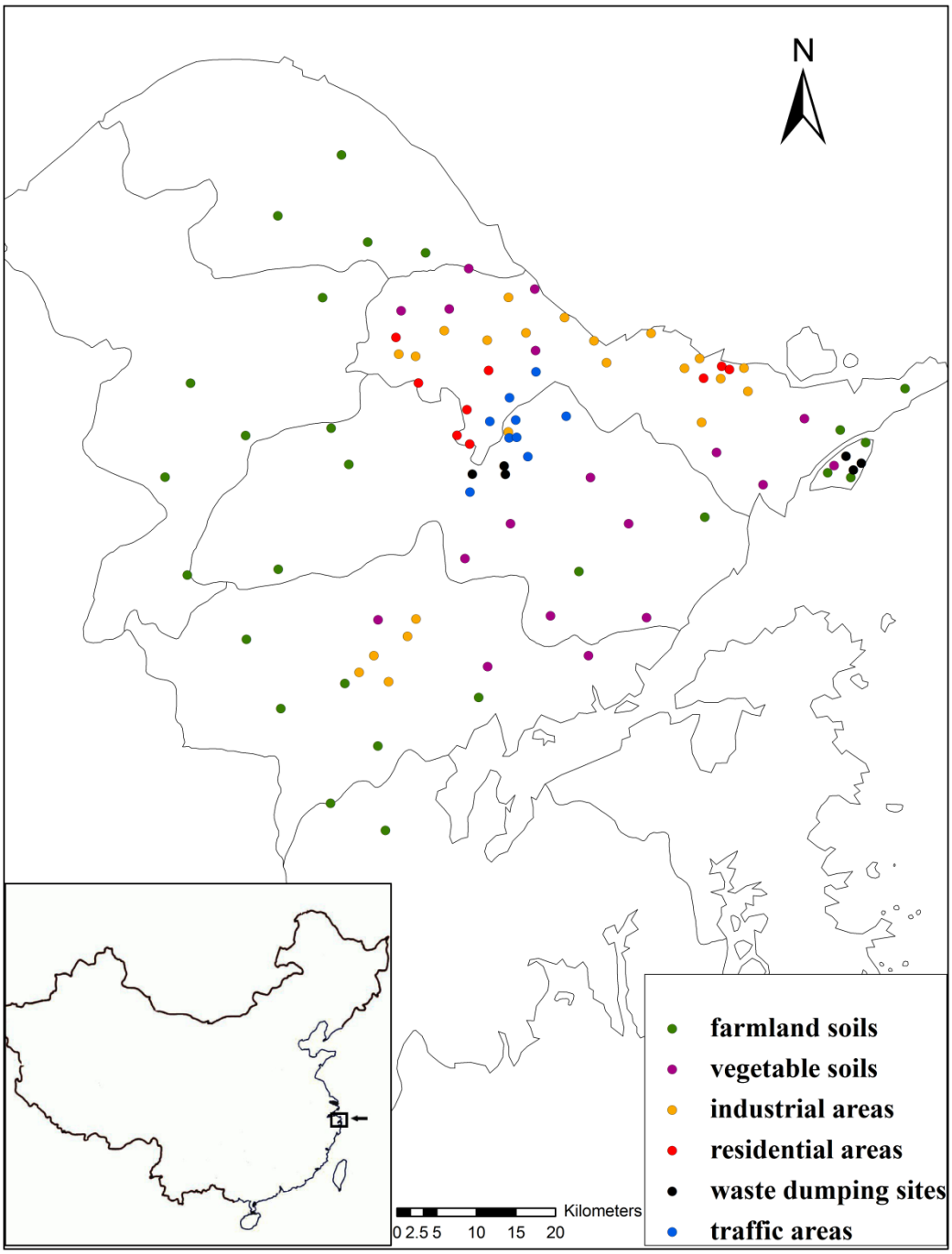
Table 1 Spearman's correlation matrix of each contaminant in all soil samples

Correlation	α-HBCD	β-HBCD	γ-HBCD	∑HBCDs	TBBPA	TBC
α-HBCD	1.000					
β-HBCD	0.788**	1.000				
γ-HBCD	0.875**	0.766**	1.000			
∑HBCDs	0.931**	0.822**	0.982**	1.000		
TBBPA	0.821**	0.735**	0.776**	0.815**	1.000	
TBC	0.685**	0.658**	0.665	0.701**	0.814**	1.000

** Correlation is significantly at the 0.01 level.

Table 2 HBCDs, TBBPA and TBC concentrations in surface soil samples collected in Ningbo region, East China

			Concentration (ng/g dw)					
sampling area			α-HBCD	β-HBCD	γ-HBCD	∑HBCDs	TBBPA	TBC
waste dumping sites	n=6	mean±SE	21.9±1.90	4.86±1.27	40.6±6.20	67.4±7.54	22.8±5.77	8.10±1.71
		Range	16.1-27.4	1.56-8.56	23.8-68.6	49.6-99.9	9.91-43.1	2.43-13.3
industrial areas	n=22	mean±SE	9.03±0.92	2.02±0.21	26.8±3.76	37.9±4.63	16.7±3.64	4.51±0.99
		Range	1.54-23.7	nd-4.31	0.87-74.5	6.27-103	1.11-78.6	nd-16.4
residential areas	n=9	mean±SE	4.47±1.28	1.02±0.34	8.59±3.04	14.1±4.39	5.50±2.07	1.39±0.99
		Range	1.35-13.4	Nd-2.80	2.86-30.2	5.12-45.8	1.12-19.7	nd-8.55
traffic areas	n=9	mean±SE	9.84±1.87	2.18±0.47	19.8±2.75	31.8±4.63	8.24±1.92	3.30±0.83
		Range	2.04-20.4	0.54-4.97	10.6-37.6	15.4-63.0	1.33-15.5	nd-7.40
vegetable soils	n=18	mean±SE	4.06±0.94	0.85±0.20	6.10±1.40	11.0±2.34	6.64±1.31	2.74±0.80
		Range	nd-13.1	nd-3.16	nd-21.6	nd-35.7	nd-14.9	nd-10.9
farmland soils	n=26	mean±SE	2.46±0.52	0.58±0.19	4.71±1.57	7.75±2.15	2.68±1.01	0.83±0.35
		Range	nd-8.65	nd-3.16	nd-37.8	nd-47.4	nd-15.6	nd-5.10



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457 Fig.1

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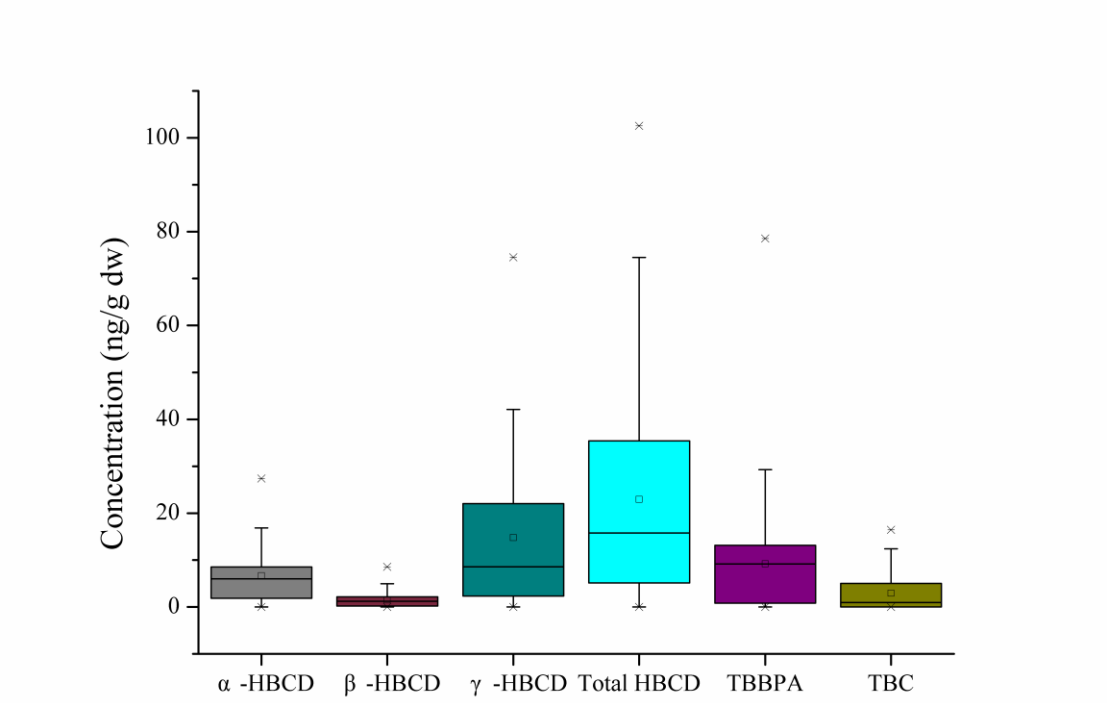

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463 Fig.2

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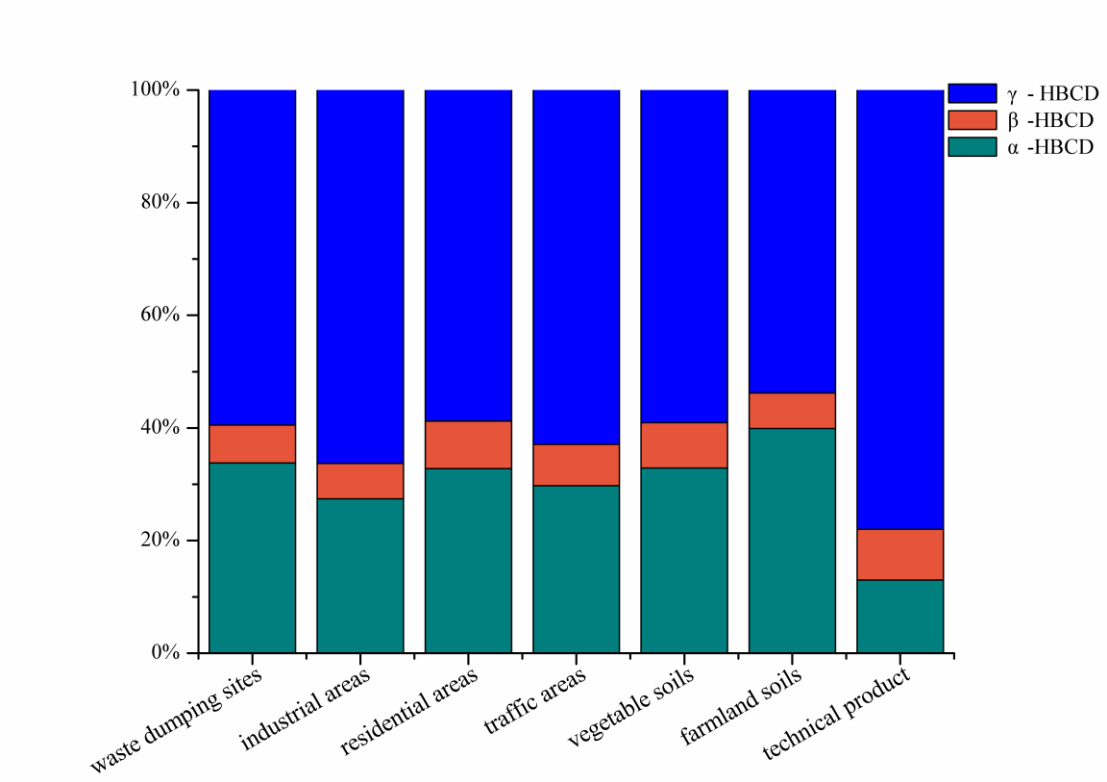

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466 Fig.3

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