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1 **Seasonal and particle size-dependent variations of HBCDs in**
2 **settled dust: implications for sampling**

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21 **ABSTRACT**

22 Particle size is a significant parameter which determines the environmental fate, the behavior of
23 dust particles and, implicitly, the exposure risk of humans to particle-bound contaminants.
24 Currently, the influence of dust particle size on the occurrence and seasonal variation of
25 hexabromocyclododecanes (HBCDs) remains unclear. While HBCDs are now restricted by the
26 Stockholm Convention, information regarding HBCD contamination in indoor dust in China is
27 still limited. We analyzed composite dust samples from offices (n=22), hotels (n=3),
28 kindergartens (n=2), dormitories (n=40) and main roads (n=10). Each composite dust sample
29 (one per type of microenvironment) was fractionated into 9 fractions (F1–F9: 2000–900,
30 900–500, 500–400, 400–300, 300–200, 200–100, 100–74, 74–50, and <50 μm). Total HBCD
31 concentrations ranged from 5.3 (road dust, F4) to 2580 ng g^{-1} (dormitory dust, F4) in the 45
32 size-segregated samples. The seasonality of HBCDs in indoor dust was investigated in 40
33 samples from two offices. A consistent seasonal trend of HBCD levels was evident with dust
34 collected in the winter being more contaminated with HBCDs than dust from the summer.
35 Particle size-selection strategy for dust analysis has been found to be influential on the HBCD
36 concentrations, while overestimation or underestimation would occur with improper strategies.

37
38 **Keywords:** HBCDs; settled dust; particle size; temporal variation; indoor microenvironments;
39 China

40 **1. Introduction**

41 Hexabromocyclododecanes (HBCDs) are primarily incorporated in flame-retard-polystyrene
42 foams which are used for thermal insulation and back coating of fabrics for furniture, and in high
43 impact polystyrene (HIPS) which is commonly used in various household electronic
44 equipment^{1,2,3,4}. Due to the high lipophilicity and low vapor pressure, most airborne HBCDs tend
45 to be adsorbed onto particulate matter, such as dust^{1,3}. Ingestion of dust is considered to be a
46 significant exposure pathway for humans to flame retardants (FRs), including HBCDs^{5,6,7,8}.
47 HBCDs persist in the environment and may bioaccumulate via the food chain^{4,9}. In November
48 2014, an amendment of Stockholm Convention, which lists HBCDs in Annex A (Elimination)
49 with specific exemptions (decision SC-6/13), has entered into force for most parties⁸. Therefore,
50 concern has risen over their environmental occurrence and public health risk during their
51 progressive replacement.

52 Originating from a number of sources, settled dust, a sink for different organic contamination
53 and residues, is a heterogeneous material with substantially varying chemical and biological
54 composition¹⁰. The contribution of house dust to the total human exposure is associated with a
55 number of uncertainties, resulting from the different sampling methods, sample preparation
56 techniques, and the assessment models used for assessing dust ingestion^{11,12,13}. Recent research
57 focused on the impact factors (temporal, spatial, particle size, etc) of FR variations in dust and on
58 the influence of sampling strategies to FR analysis and human exposure assessment^{14,15,16,17,18}.

59 In 2001, the world market demands of decabromodiphenyl ether (Deca-BDE) and HBCDs
60 were 56,100¹⁹ and 16,700 tons²⁰, respectively. Though without any information on HBCD
61 applications in specific industries, the total production amounts of Deca-BDE and HBCDs in
62 China in 2006 were 36,000 and 7,500 tons, respectively²¹. These data indicate an important share
63 of China in the market demand and production of HBCDs. While information on BDE-209 in the

64 indoor environment is now rather substantial, the data needed to perform a full assessment of
65 potential risks from HBCDs are still missing^{22,23}. Studies on HBCD contamination in indoor dust
66 have been conducted specifically in Europe and North America^{11,20,22,24,25}. However, indoor
67 contamination of HBCDs in China remains poorly understood²⁶, causing an substantial
68 impediment in regulating such chemicals in China. While knowledge on HBCDs in China has
69 accumulated mostly from the aquatic environment^{27,28}, additional research is needed to
70 investigate the exposure to HBCDs in indoor microenvironments and the public health risks
71 associated with this exposure.

72 This study attempts to bridge the above-mentioned knowledge gaps by determining for the first
73 time the seasonality and particle size-dependent variations of HBCDs in settled dust from five
74 microenvironment categories (offices, hotels, kindergartens, dormitories and road) from Beijing,
75 China.

76

77 **2. Materials and methods**

78 *2.1. Sampling strategy and methods*

79 Individual dust samples were vacuumed from 22 offices, 3 hotels (conducted by the cleaners),
80 2 kindergartens, 40 dormitories and 10 sites on main roads (conducted by the researchers) in
81 Beijing, China in 2012, respectively. These offices and dormitories were located in five and two
82 buildings, respectively. Samples from same microenvironment were pooled and homogenized to
83 one composite sample and each of the resulting five composite samples were individually
84 fractionated into nine fractions (F1 (900–2000 μm), F2 (500–900 μm), F3 (400–500 μm), F4
85 (300–400 μm), F5 (200–300 μm), F6 (100–200 μm), F7 (74–100 μm), F8 (50–74 μm) and F9
86 (<50 μm)). The fractionation was done with stainless sieves and particles larger than 2 mm were
87 discarded. Total of 45 fractionated samples were obtained (Table SI-1 and Table SI-2).

88 Another two offices from the same building, located in Beijing, China, were selected to study
89 the seasonality of HBCDs in indoor dust. Based on the cleaning routines of each site, dust
90 sampling from Office A was conducted at weekly intervals between 4th March 2012 and 5th
91 August 2012 (about 5 consecutive months), while dust from Office B was sampled fortnightly
92 from 25th March 2012 to 23rd December 2012. In total, 40 dust samples were collected from these
93 two carpeted offices, of which 23 samples were from Office A and 17 were from Office B (Table
94 SI-3). Each sample was sieved through a stainless mesh to collect particles <2 mm in size and
95 through which all samples were homogenized. All 85 dust samples were stored in freezer at
96 -20 °C until analysis was performed. Further details in relation to the sampling and fractionation
97 are described in the Supporting Information (SI) and our previous work^{14,15}.

98

99 *2.2. Analytical methods*

100 Analysis of HBCDs in dust was performed at the Toxicological Centre of University of
101 Antwerp (Belgium). Three HBCD isomers (α -, β -, and γ -HBCD) were analyzed. The analysis
102 procedure developed by Dodson et al. was applied in this study and the information of chemicals,
103 reagents, instrument and detailed methodology are described in the SI²⁹. The organic content of
104 the dust fractions was determined by measuring the loss on ignition (LOI) at 550 °C for 5 h in a
105 muffle oven³⁰.

106

107 *2.3. QA/QC*

108 Dust samples (n=85) were analyzed in five batches. Limit of quantification (LOQ) was 0.5 ng
109 g⁻¹ for each HBCD stereoisomer. The HBCD concentrations measured in SRM 2585 dust (NIST,
110 Gaithersburg, MD, US) were in good agreement with the indicative values reported in literatures
111 (Table SI-4)^{20,31}.

112

113 **3. Results and discussion**

114 *3.1 HBCD levels in various microenvironments*

115 We conducted a preliminary assessment of differences in the HBCD contamination among five
116 types of microenvironment categories. HBCDs (α -, β -, and γ -HBCD) were detected in all
117 fractions of the five composite samples. Generally, kindergarten and office dust exhibited higher
118 HBCD levels than other types of dust in this study, while HBCD levels in road dust were much
119 lower than in indoor dust (Figure 1a). For the seasonal dust samples, the means of Σ HBCDs for
120 Office A (n=23) and Office B (n=17) were 1310 and 1210 ng g⁻¹, respectively (Figure 1b). These
121 values are within the reported range in dust from US, Canada, UK, Sweden, Belgium, Germany,
122 Czech Republic, and New Zealand (Table SI-5).

123 Data available on HBCD contamination in indoor dust mainly refer to homes and offices. In
124 most studies, HBCD contents were usually < 1000 ng g⁻¹, while much less information exists for
125 other microenvironments, such as daycare centers and cars (Table SI-5, Figure SI-1). Similar to
126 the results of this study, a previous study found that HBCD levels in dust from daycare centers
127 (n=10, median=340 ng g⁻¹) exceeded those from houses (n=10, median=100 ng g⁻¹), cars (n=4,
128 median=54 ng g⁻¹) and apartments (n=34, median=45 ng g⁻¹)²². This suggests that HBCDs might
129 have been used extensively in consumer products or construction materials in kindergarten or
130 daycare centers and the exposure risks for (young) children should be of concern.

131 Car dust appeared to contain low HBCD levels in Sweden (n=4, median=54 ng g⁻¹)²² and
132 Czech Republic (n=27, median=33 ng g⁻¹)³², but, in some cases/countries, samples contained
133 extremely high concentrations, e.g., UK car dust (n=20, median=12300 ng g⁻¹)²³ and US airplanes
134 dust (n=19, median=7110 ng g⁻¹)³³ (Figure SI-1). The regional and international variability of
135 HBCD contamination patterns is still unclear. Therefore, more data are needed to establish a

136 better international comparison, especially for the poorly characterized Asian microenvironments
137 (e.g., cars/vehicles, daycare centers and schools).

138

139 *3.2 HBCD distribution on size-segregated dust fractions*

140 Knowledge on FR distribution on size-segregated dust fractions is needed to understand the
141 comparability of results from different studies. It also assists in the interpretation of migration
142 pathways and also the calculation of exposure estimates. However, information on size-specific
143 particle distribution for FRs is limited and data on HBCDs is not even available. In this study,
144 dust samples were fractionated according to particle size for the investigation of size-specific
145 distribution of HBCDs.

146 Among the 45 size-segregated samples, concentrations of \sum HBCDs ranged from 5.3 (road dust,
147 F4) to 2580 ng g⁻¹ (dormitory dust, F4) (Figure 2). For HBCD distributions among these dust
148 fractions, no constant increasing or decreasing trends were found and no common distribution
149 patterns could be observed in dust among the five microenvironments. For road dust, it is
150 apparent that HBCDs were more concentrated in the finest fraction in a similar way to
151 BDE-209¹⁵. The maximum HBCD concentration (F9) exceeded the minimum (F4) by a factor of
152 25. On the contrary, dormitory dust had the highest HBCD concentration in the coarse particles
153 (F2–F4), with a peak value at F4 (Figure 2). Fractions F1–F5 of the hotel dust showed very low
154 HBCD values compared to F6–F9, presenting an apparent peak at F6. Office and kindergarten
155 dust did not show any remarkable peak values, but a relatively steady distribution, especially for
156 kindergarten dust.

157 LOI values were higher for indoor dust fractions (around 50%) than for road dust fractions
158 (<10%) (Table SI-6). After normalizing the HBCD levels on the LOI, the HBCD levels in road
159 dust (3320 ng g⁻¹ in F9) were comparable to those in other indoor microenvironments (Figure 2),

160 implicating that the lower concentrations of HBCDs in road dust resulted from its lower organic
161 content (>90%). The HBCD distribution patterns did not change with LOI normalization.

162 HBCDs can be released into the environment throughout the lifetime of commercial products.
163 Two dominant pathways for FRs migrating from FR-treated materials into dust have been
164 suggested, e.g. “evaporation-adsorption” and “abrasion”^{15,34}. Recent studies have demonstrated
165 that abrasion processes might be the dominating route of less-volatile FRs migrating from
166 products to indoor dust^{6,35}. Concentrations of FRs resulting from evaporation processes might
167 increase with the decrease in dust particle size, while FRs released from abrasion processes might
168 show peak values in specific diameter ranges³⁴. For HBCDs present in the four types of indoor
169 dust, the elevated (e.g. F3-F6 of kindergarten dust) and accidental peak values (e.g. F2 and F4 of
170 dormitory dust) in coarse fractions suggests that coarse particle-bound HBCDs in indoor dust
171 probably originate from abrasion process. For road dust, HBCD levels increased constantly with
172 the decrease in the particle size, implying that evaporation was the major migration pathway and
173 that gaseous HBCDs might ventilate from car interiors. Specifically, these opposite HBCD
174 patterns for indoor and road dust and the variation of particle-specific distribution for HBCDs
175 among the four types of indoor dust implied that, in these microenvironments, HBCDs originated
176 mainly from various HBCD-treated materials with different resistance to tear¹⁵.

177

178 *3.3 Seasonal variations of HBCDs in office dust*

179 Temporal variation of FRs is of great concern for indoor environments¹⁸. HBCDs in dust
180 samples from two offices in the same building were investigated in this study. Overall mean of
181 HBCDs and their isomer-profiles were similar between dusts from these two offices (Figure 1b).
182 However, our previous study on seasonal variation of PBDEs, novel brominated flame retardants
183 (NBFRs) and phosphorus flame retardants (PFRs) in dust from Office A and Office B presented

184 different concentrations and profiles¹⁴. HBCDs originate probably from similar sources present in
185 these two offices, such as the extruded polystyrene foam used for building insulation which was
186 already suggested as the major emission source of particle-bound HBCDs^{36,37}, while other FRs
187 present in dust from these two offices should derive from different sources.

188 The seasonal trends of HBCDs in dust of these two offices were consistent. Generally, HBCDs
189 showed roughly three times higher concentrations in cold seasons than warm seasons (Figure 3).
190 Interestingly, HBCDs showed different seasonality from PBDEs and NBFs, but similar to PFRs
191 in these dust samples¹⁴. Like PFRs, HBCDs exhibit higher volatility (vapor pressure: 3.03×10^{-5}
192 Pa) than other important BFRs in dust, such as BDE 209, decabromodiphenyl ethane (DBDPE),
193 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) and bis(2-ethylhexyl) tetrabromophthalate
194 (BEH-TBEP)¹⁵. Seasonality in evaporation from indoors to outdoors through ventilation, which
195 would be stronger in warm seasons than cold seasons, may govern the temporal variations of
196 HBCDs in dust, resulting in lower HBCD and PFR levels¹⁴ in these dust samples during warm
197 seasons. The fitted curves for HBCD concentrations to sampling time using quadratic polynomial
198 regression analysis are given in Figure 3. The R-values of the two curves are 0.94 and 0.85 for
199 Office A and B, suggesting strong associations between HBCD concentrations and sampling
200 time.

201

202 *3.4 Stereoisomeric profiles of HBCDs*

203 According to literature data on HBCDs in indoor dust (Figure 4), stereoisomeric patterns of
204 HBCDs significantly varied among samples, for which α -HBCD, β -HBCD and γ -HBCD isomer
205 contributed 4–69%, 0.4–16% and 23–95% to Σ HBCDs, respectively. Isomer patterns of HBCDs
206 in dust were different among studies, even if data was reported from the same country. Results
207 from North Carolina (α -HBCD contributed 69% to Σ HBCDs)²⁴ were significantly different from

208 those from Texas (α -HBCD contributed 20% to Σ HBCDs)²⁰. No clear correlation was observed
209 between HBCD isomer patterns and types of microenvironment or geographical location.

210 In this study, the dominance of α -HBCD was consistent in the five types of dust samples,
211 contributing 71%, 74%, 76%, 83% and 86% to total HBCDs in F9 of dormitory, office, road,
212 kindergarten and hotel dust, respectively (Figure 4). Stereoisomeric profiles of HBCDs in
213 different fractions of the same type of dust were also similar (Figure SI-2). Nevertheless,
214 temporal variations were found different for the three HBCD isomers. The proportion of
215 β -HBCD ($13\pm 1\%$ and $12\pm 2\%$ for Office A and B) was apparently more seasonally stable than
216 that of α -HBCD ($72\pm 4\%$ and $73\pm 2\%$ for Office A and B) and γ -isomer ($15\pm 4\%$ and $15\pm 3\%$ for
217 Office A and B) (Figure SI-3).

218 In these samples, deviations from the profiles in technical mixture were observed in varying
219 degrees and the influencing factors could include sample collection strategy, indoor lighting
220 conditions, and differences in the HBCD sources. A previous study had discovered a significant
221 shift (~ 10 – 30% of the Σ HBCDs) from γ - to α -HBCD in dust samples influenced by the sampling
222 distance from HBCD sources and the exposure time of dust to natural light¹⁶. Therefore, sample
223 collection techniques and photochemical reactions may contribute to the profile variability
224 between the studies (Figure 4). Although the commercial HBCD mixtures are dominated by the
225 γ -HBCD isomer (75–89%), thermal isomerization (from the γ -HBCD to the α -HBCD isomer) can
226 occur during the manufacturing or processing of materials (e.g. textiles) with HBCDs introduced
227 to temperatures above 160 °C, leading to a change in the profile of HBCD stereoisomers^{3,38}. Thus,
228 distinctive HBCD isomer patterns (Figure 4) are conceivably resulting from different conditions
229 of microenvironments.

230 To discuss the international or spatial variations of isomer patterns of HBCDs in dust, more
231 data in a variety of microenvironment categories and locations, particularly in Asia, are needed

232 before this issue can be fully assessed. Factors influencing the predominance of α -HBCD in dust
233 should be further explored.

234

235 *3.5 Implications for dust sampling and size-selection strategies for dust analysis*

236 Most studies on FRs do not distinguish between dust fractions, nor the selection of dust size
237 has been consistent in the literature¹². Since FR concentrations changed with the particle size, we
238 performed the following estimations to assess if any discrepancy exists among dust sizes that
239 commonly employed. Four dust fractions were proposed to represent commonly employed dust
240 fractions for FR analysis: <2000 (0–2000, including F1–9), <500 (0–500, including F3–9), <200
241 (0–200, including F6–9) and <50 μm (F9). The weighted averages of HBCDs in different sizes of
242 dust were calculated using the data in this study. Concentrations of other FRs in the chosen
243 fractions were taken from our previous study¹⁵, in which a broad range of FRs was determined to
244 explore the influence of selection of size fraction on estimation of FR concentrations in dust. The
245 FR concentrations (c , ng g^{-1}) in fraction <2000, <500 and <200 μm are calculated as follows:

$$246 \quad c = \frac{\sum c_i \times m_i}{M}$$

247 in which c_i stands for FR concentration in certain size fraction (F_i , F1–9 which are included in
248 fraction <2000, <500 or <200 μm); m_i stands for dust mass of F_i ; and M stands for total dust mass
249 of the fraction <2000, <500 and <200 μm . Data on mass of the fractionated dust samples are
250 represented in Table SI-2.

251 After screening and conducting the above calculation to all BFRs and PFRs detected in the five
252 types of dust, we found that, in some cases, the selection of size fractions showed significant
253 influence on analytical results of FRs. Typical estimation results for HBCDs, BDE 209,
254 BEH-TEBP, tris n-butyl phosphate (TNBP) and triphenyl phosphate (TPHP) are displayed in

255 Figure 5, in which remarkable variability exists among different size-selection strategies.

256 HBCD concentrations estimated for the four typical dust fractions varied in road and dormitory
257 dust (Figure 5, Figure SI-4). In general, a clear trend in the contamination levels could be seen
258 along with the selected dust size decrease. HBCD concentration was over five times higher in the
259 fraction <50 μm in road dust than in the fraction <2000 μm , while in the fraction <500 μm in
260 dormitory dust it was about two times higher than in fraction <50 μm . Particularly, estimated
261 BDE 209 level of fraction <50 μm exceeded that of <2000 μm by eight times in road dust, and
262 twice for BEH-TEBP in dormitory dust. However, for TNBP and TPHP, concentration of
263 HBCDs in fractions <2000 μm and <500 μm exceeded that of <50 μm by six and three times in
264 office dust, respectively.

265 To assess human exposure, the selection of dust size would be more crucial, since it could lead
266 to significant differences in the estimated results. For example, when choosing the fraction <2000
267 μm for assessment, HBCD level in dormitory dust would be about over thirty times higher than
268 that in road dust, however, the difference would be only three times if fractions <50 μm were
269 selected for analysis (Figure 5). These estimation differences arising from the selection of dust
270 with specific particle size are due to the segregation of FRs in dust (Figure 2), with some FRs
271 being more bound to finer particles. Since finer particles are considered to have a higher potential
272 risk to human health³⁹, it can be concluded that FR exposure assessment based on dust samples
273 with too large particle size would lead to pronounced overestimation (e.g. HBCD in dormitory
274 dust) or underestimation (e.g. HBCD in road dust) (Figure 5). Furthermore, the strategy for size
275 selection of dust may obstruct the comparability of results from different studies^{18,40}. It is
276 recommended that only the adherent fraction⁴¹ (finer particles, e.g. <200 μm) is suitable to
277 estimate the human exposure to toxicants from (indoor) dust. Differences might exist among
278 populations regarding the particle size of the adherent dust fractions.

279 In this study, we reported for the first time the particle size and seasonal variations of HBCDs
280 in indoor and outdoor settled dust. With some interesting findings, this paper has also a few
281 limitations. During dust collection for the studying of particle size distribution, we aimed to
282 collect more samples and have a large sample size in order to reach more generalizable results.
283 However, we had a small sample size for kindergarten and hotel dust (n=3 and 2, respectively).
284 Since data on these microenvironments are rather limited in the literature, this paper shows a
285 combination of novelty and opportunism. It is clear that a larger number of samples will help
286 overcome this drawback and will lead to more robust conclusions.

287

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299

300 **Supporting Information Available**

301 Further details of the sampling information, analytical methodology and quality assurance are
302 available free of charge via the Internet at <http://pubs.acs.org/>.

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422

423 **Figure Captions**

424
425 **Fig. 1.** HBCD concentrations in fractions $< 50 \mu\text{m}$ (F9) of the five types of dust (a) and HBCD
426 mean concentrations and profiles of the two offices (b).

427
428 **Fig. 2.** Concentration variations of HBCDs with dust particle size.

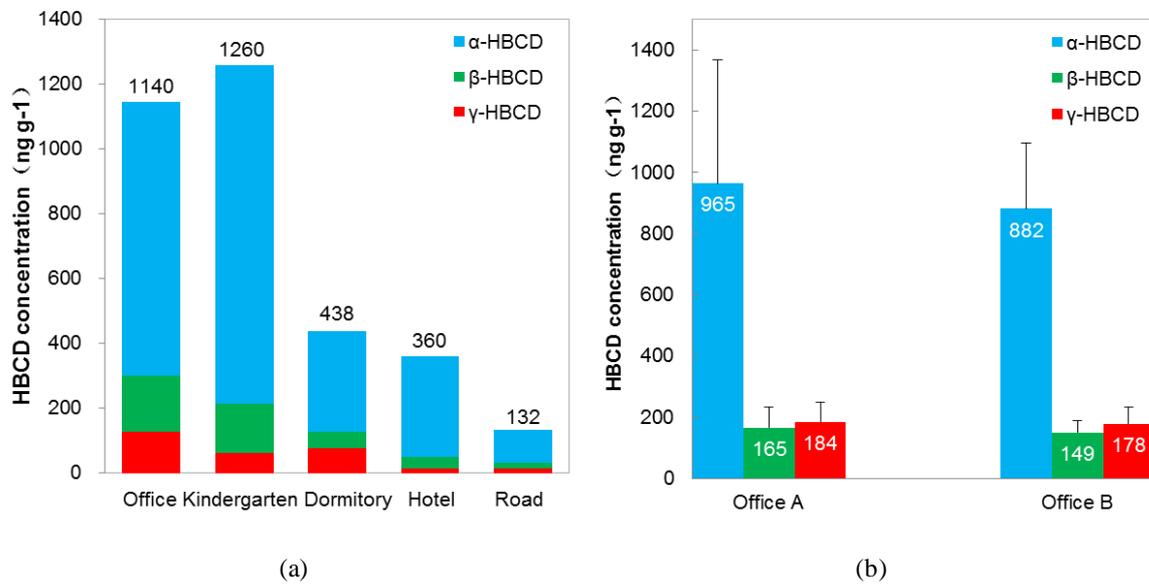
429
430 **Fig. 3.** Seasonal variation of HBCD concentrations.

431
432 **Fig. 4.** Stereoisomer distribution, given as percentage of total HBCDs (values of the F9 ($<50 \mu\text{m}$)
433 were represented for this study; median values were adopted for the literature data) in indoor
434 settled dust (Table SI-5 in the Supporting Information). Isomer pattern of commercial HBCD
435 products is configured as 12:8:80 (%) (α -HBCD: β -HBCD: γ -HBCD). Different symbols are used
436 to differentiate the types of microenvironment (\clubsuit for houses, \square for offices and \odot for other types of
437 microenvironment)^{3, 5, 7, 11, 20, 23, 24, 26, 29, 32, 33, 42, 43}.

438
439 **Fig. 5.** Influence of selection of dust fraction on HBCD estimation.

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441

442 **Figure 1**



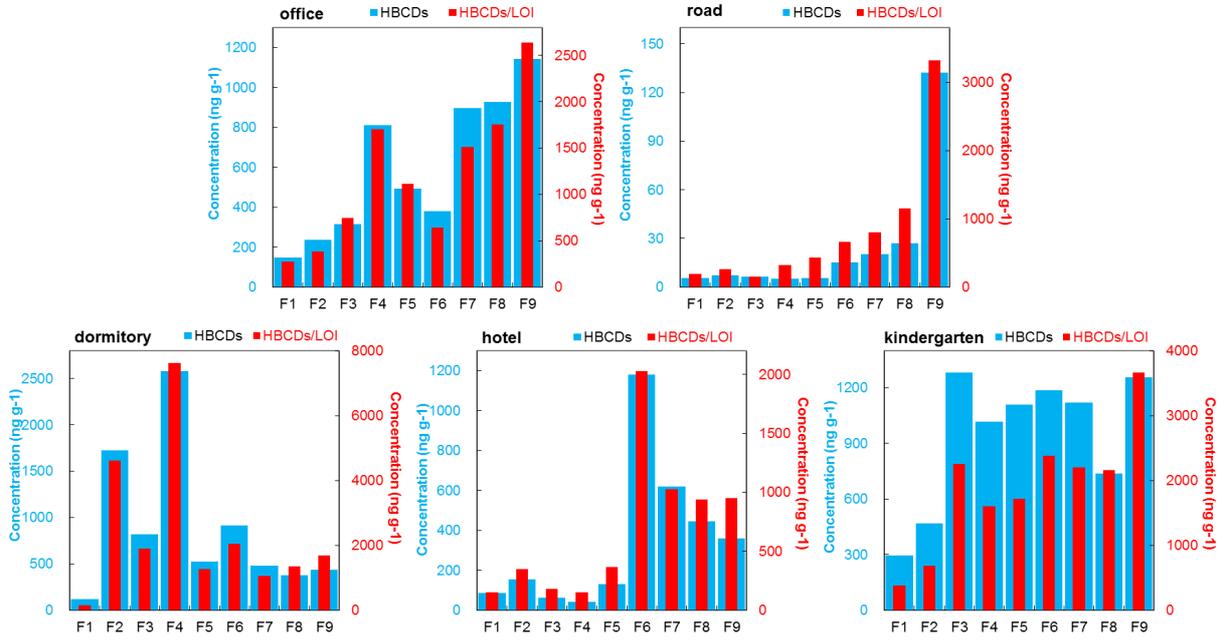
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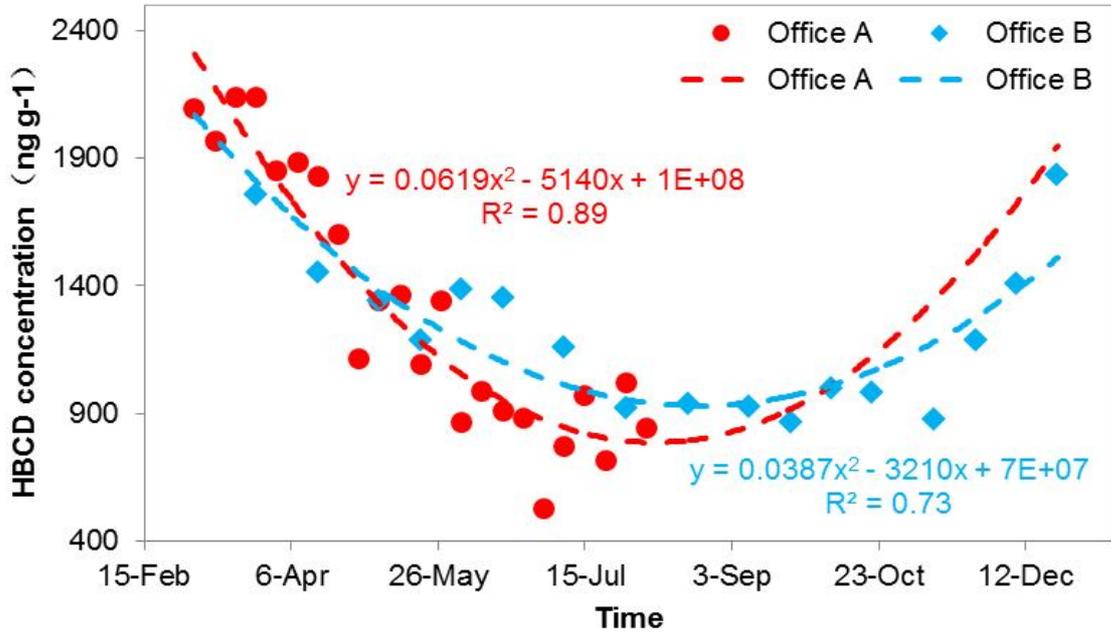
446 **Figure 2**

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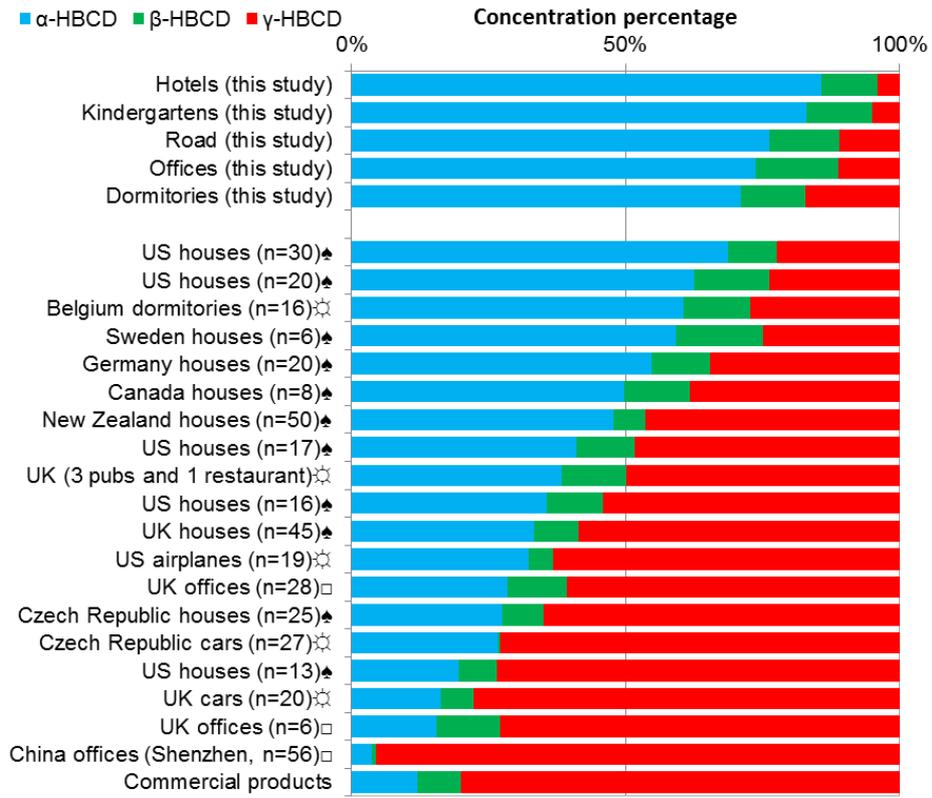
450 **Figure 3**



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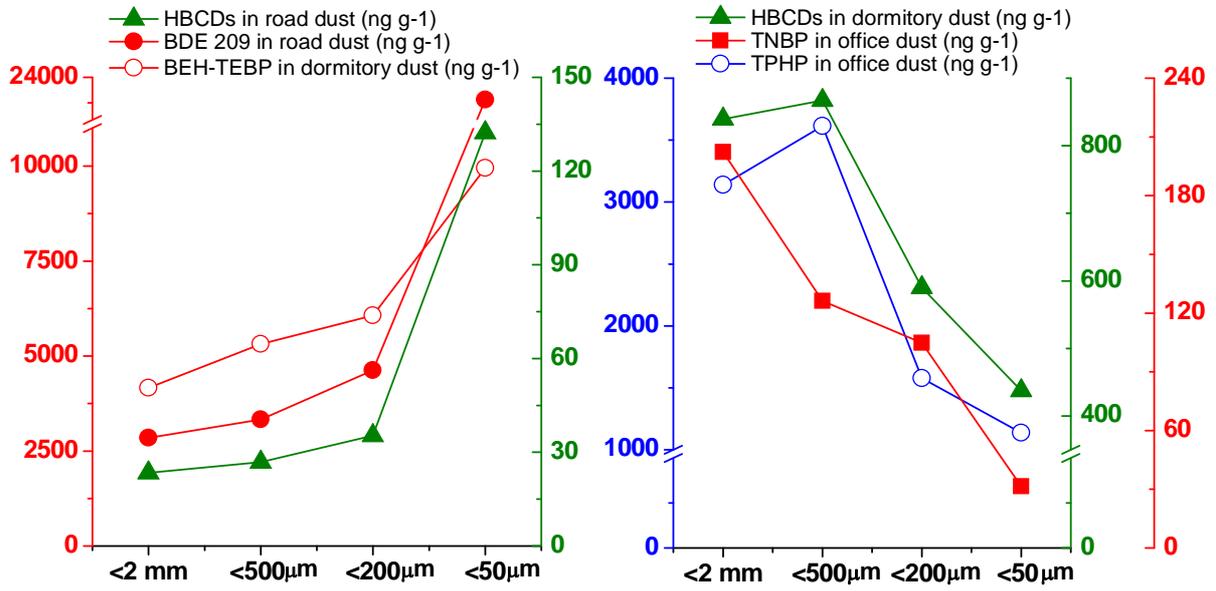
453 **Figure 4**



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456 **Figure 5**
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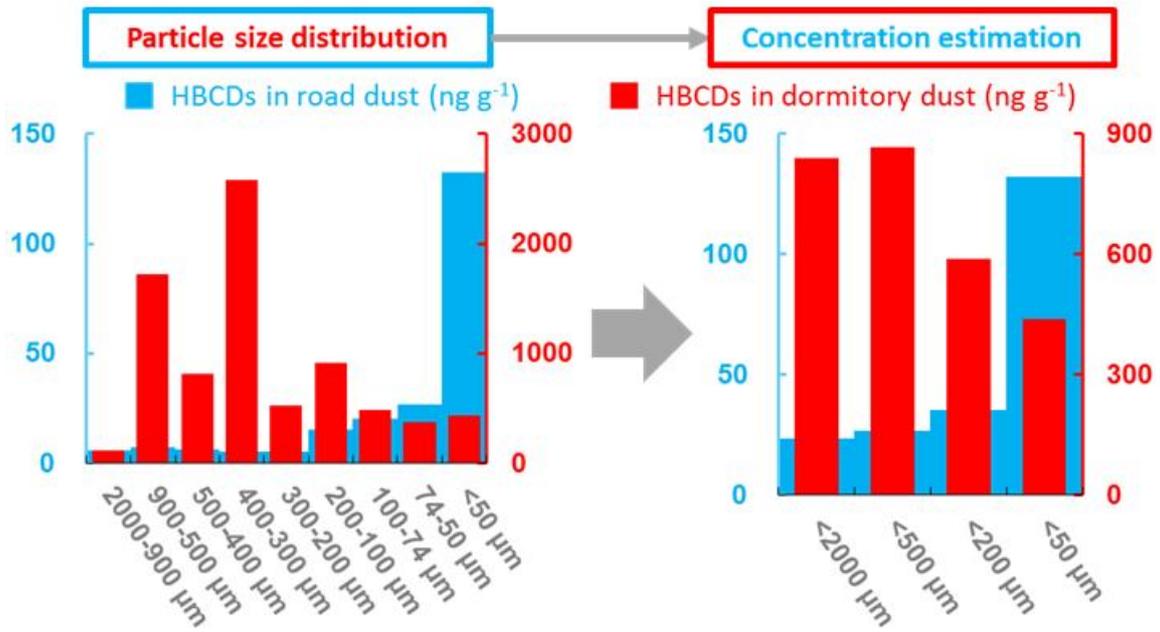
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TOC Art

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