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Abstract

Diet is considered a major route of human exposure to hexabromocyclododecane, a chiral environmental contaminant. A previous study reported on the occurrence of hexabromocyclododecane diastereoisomers in food items of animal origin collected in Belgium. The present study reports further results on corresponding enantiomeric fractions of the same samples. None of the samples could be considered as racemic for the α-isomer suggesting that foodstuff contamination occurred prior to death of the corresponding producing animal and was not the result of the food item being in contact with technical HBCDD. Non-racemic chiral signatures were also observed for β- and γ-isomers. We conclude that, depending on their dietary habits, different individuals might be overall exposed to non-racemic profiles. Considering that toxicological effects are enantiomer-dependent, this could modulate potential adverse effects.

Keywords

Environmental contaminant; HBCDD; Chiral compound; Enantiomer; Food.

1. Introduction

1,2,5,6,9,10-Hexabromocyclododecane (HBCDD) is a brominated flame retardant exhibiting developmental neurotoxicity (Maurice et al., 2015) listed in the Annex A of the Stockholm Convention (UNEP) since 2014. Although 16 stereoisomers are possible, technical HBCDD is a racemic mixture of mainly 3 enantiomer pairs: γ-HBCDD (~80%), β-HBCDD (~10%) and α-HBCDD (~10%) (Heeb et al., 2005). While HBCDD contaminating surface soils close to suspected emission sources (e-waste recycling areas) remains racemic (Gao et al., 2011; Zhu et al., 2017), α-HBCDD dominates in biota and most processed food due to differential biodegradation, bioisomerisation and biomagnification rates (Law et al., 2014; Barghi et al., 2016).

Further, due to stereospecific biological processes depending on species, enantiomeric enrichments have been reported in biota, including plant (Zhu et al., 2016), earthworm (Li et al., 2016), marine mollusc, crustacean and fish (Janák et al., 2005; Köppen et al., 2010; Ortiz et al., 2011; Du et al., 2012; Zhang et al., 2014; Zhu et al., 2017; Ruan et al., 2018a), bird (Janák et al., 2008; Esslinger et al., 2011; Sun et al., 2012; Jondreville et al., 2017; Omer et al., 2017), marine mammal (Vorkamp et al., 2012; Ruan et al., 2018b) and human (Roosens et al., 2009; Abdallah et al., 2011).

Diet is considered a major route of human exposure to HBCDD through foodstuffs of animal origin (EFSA, 2011). In addition to the diastereoisomeric profile, chiral signature appears as a valuable information to determine whether such food was contaminated ante- or post-mortem of the producing animal, thereby contributing to elucidation of the contamination source (Omer et al. 2017).

A previous study reported on the occurrence of HBCDD diastereoisomers among other halogenated flame retardants in food items available on the Belgian market (Poma et al., 2018). Edible parts of 1289 individual food samples collected in 2015–2016 were pooled, ground and homogenized to create 183 composite food samples (further referred to as “samples”) representative of 15 relevant sub-categories. Results revealed the presence of HBCDDs above limits of quantification (LOQs, 5–250 pg g^{-1} wet weight – ww) in 22 samples of food from animal origin belonging to 7 sub-categories, and up to

5.5 ng g^{-1} ww in eel. Those specific results are gathered in **Table S1**. Authors provided complete results and discussed diastereomeric patterns thoroughly.

The present study aims at complementing the study of Poma et al. (2018) with information on enantiomeric fractions of HBCDD isomers, to discuss chiral signatures.

2. Material and methods

2.1. Sample preparation and diastereoisomeric analysis

Since the original extracts from Poma et al. (2018) (assay A) were no longer available, twenty-one out of the 22 samples from this previous study exhibiting quantified levels of at least one HBCDD diastereoisomer (**Table S1**) were extracted again from stored (-20 °C) lyophilised matter and analysed according to the same procedure and using the chemicals (assay B) (Malysheva et al., 2018). Briefly, 2.5 g lyophilised sample (or 1 g oil) fortified with ^{13}C-labelled internal standards for quantification according to the isotopic dilution principle were extracted with a mixture of hexane/dichloromethane 1:1 (*v/v*), purified with acidic silica and reconstituted in 100 µL acetonitrile prior to analysis. Reversed phase liquid chromatography coupled to tandem mass spectrometry (Xevo TQ-S, Waters, Milford, MA, USA) fitted with an electrospray ionisation source operating in the negative mode was used for analysis. Only diastereoisomer occurrences previously quantified by assay A were considered for assay B.

2.2. Enantiomeric fraction

Extracts were further reconstituted in a mixture of acetonitrile/water 4:1 (*v/v*, 50 µL) and HBCDD enantiomers analysed according to Omer et al. (2017) with minor modifications (assay C). Briefly, enantiomers were separated on a cellulose tris-(3,5-dimethylphenylcarbamate) chiral column (ACQUITY UPC² Trefoil CEL1, 2.1 mm × 150 mm, 2.5 µm of granulometry, Waters) and analysed using an Orbitrap Q-Exactive mass spectrometer fitted with an electrospray ionisation source (Thermo Scientific, San Jose, CA, USA). Data were acquired in negative mode over the *m/z* range [620–680] at a

93 resolving power of about 78,000 full width at half-maximum for the $[M-H]^-$ monitored ions. Peak
94 areas from extracted ion chromatograms (± 5 ppm) were used to calculate enantiomer concentrations.
95 **Figure S1** illustrates the typically obtained chromatographic separation for a selected sample (fresh
96 oysters MC-01). Further analytical and QA/QC details are available in the Supplementary Data.
97 Enantiomeric fraction (EF) of each considered enantiomeric pair was determined according to the
98 following equation:

99 $$EF = \frac{\frac{(+)A}{(+)A_{IS}}}{\frac{(+)A}{(+)A_{IS}} + \frac{(-)A}{(-)A_{IS}}}$$

100 where (+)A and (–)A represent the peak areas for the native pair, $(+)A_{IS}$ and $(-)A_{IS}$ the peak areas for
101 the corresponding internal standards, assuming that internal standards are racemic mixtures and that
102 relative response factors are equal within each pair of enantiomers, as described in the literature
103 (Marvin et al., 2007; Gao et al., 2011). Four standard calibration curves (25 injections) including 2
104 independent preparations (assays B and C, different manufacturers and different operators in distinct
105 laboratories) were used to determine racemic ranges as mean ± 3 standard deviations (Table S2).
106
107 **3. Results and discussion**
108 *3.1. Consistency between assays for diastereoisomers*
109 Assay B confirmatory results of diastereoisomer concentrations were generally consistent with
110 assay A original results. Indeed, mean absolute deviation was 21% and the linear regression curve slope
111 was 0.91 (R^2 = 0.997), excluding four cases. The first case was an increase from 3.8 to 10.5 ng g^{-1} ww
112 of α-HBCDD in organic chicken eggs (EGC-02), making it the most contaminated sample, instead of the
113 fresh eel sample as initially reported. This divergence could originate from heterogeneity of lyophilised
114 sample or varying amounts of extracted fat which was not checked, according to the procedure.
115 However, no influence on the EF was expected. The three other cases showed results below LOQs
116 (β-HBCDD in fresh low fat milk LC-07 and chorizo MEC-03, and α-HBCDD in duck rillettes MEC-12
117 samples), likely due to slightly higher LOQs. Detailed results are available in **Table S3** and **Figure S2**.

Results for assays B and C, obtained from the same sample extracts but with different instrumental set-ups, were generally consistent. Indeed, mean absolute deviation was 14% and the linear regression curve slope was 0.99 (R^2 = 0.999). Moreover, while confirmatory assay B failed to provide values above LOQs for 3 diastereoisomer values quantified with original assay A, assay C provided 2 consistent values above LOQs. Thus, assays B and C did not confirm the presence of β-HBCDD in fresh low fat milk which was the only sample with β-HBCDD as only isomer. Detailed results are presented in **Table S3** and **Figure S3**.

3.2. Enantiomeric fractions

Enantiomeric fractions observed are provided in **Table S4** and displayed in Figure 1.

α-HBCDD. Diastereoisomer profiles of the 19 considered samples were all dominated by α-isomer (70–100%), suggesting a preferential accumulation through the food chain rather than migration from food contact material. It appears that none of the samples could be considered as racemic for the α-isomer (**Figure 1a**), suggesting that foodstuff contamination occurred prior to death of the corresponding producing animal and was not the result of the food item being in contact with technical HBCDD. No trend was observed between EF_α and α-HBCDD concentration, suggesting that enrichment processes do not depend on the contamination levels. Interestingly, the samples from terrestrial bird or mammal (n = 6) were enriched in (–)α-isomer while most samples from aquatic mollusc, crustacean or fish (n = 11) were enriched in (+)α-isomer; sole and anchovies were enriched in (–)α-isomer.

Grey fresh shrimp exhibited the highest EF_α value (0.606), which is consistent with enrichment in (+)α-HBCDD reported by Zhu et al. (2017) and Zhang et al. (2013) in mantis shrimp (EF_α = 0.545 and 0.588, respectively). EF_α values of the three herring-based foodstuffs (matjes, herring in "roll mops" process and prepared herring) were consistently within the 0.543-0.562 range. Although less pronounced, enrichment in (+)α-HBCDD observed in eel (0.518) was also consistent with EF_α reported by Janák et al. (2005) (0.54), Bester and Vorkamp (2013) in sand eel oil (0.554) and Zhang et al. (2013) in ricefield eel (0.516).

144 The general trend of most samples from aquatic mollusc, crustacean and fish toward relative
145 enrichment in (+)α-HBCDD was consistent with some previous studies on distinct species: bib and
146 whiting liver (Janák et al., 2005), zebrafish (Du et al., 2012), mirror carp (Zhang et al., 2014) and bartial
147 flathead (Zhu et al., 2017). Opposite EF_{α} tendencies of sole was also in line with Janák et al. (2005)
148 findings for the same species and Köppen et al. (2010) results in mackerel, codfish, thorny skate,
149 pollack and flounder. Actually, Ruan et al. (2018a) reported a small but significant decrease in the EF_{α}
150 with the trophic level in a Hong Kong waters (5 mollusc species, 6 crustacean species, and 19 fish
151 species) but the species-specific enrichments remained diverse. Intrinsic (species) and extrinsic (diet)
152 factor contributions to the observed enrichments remain undetermined.

153 The lowest EF_{α} value (0.404) was observed in organic chicken eggs, this pronounced enrichment in
154 (+)α-enantiomer being consistent with findings of Omer et al. (2017), Jondreville et al. (2017) and
155 Zheng et al. (2017) on chicken egg and various tissues. In the literature, reported EF_{α} in eggs of other
156 bird species were dominated by either the (–)α-enantiomer in peregrine falcon, common tern and
157 herring gull or the (+)α-enantiomer in white-tailed sea eagle and guillemot (Janák et al., 2008; Esslinger
158 et al., 2011).

159 **β-HBCDD**. Among the 6 considered samples of animal source, 4 were of aquatic origin and 2 of
160 terrestrial origin (**Figure 1b**). Only chicken eggs and eel seemed to be enriched in (+) or (–)β-
161 enantiomer, respectively, likely due to a higher uncertainty as regards the racemic range but also due
162 to concentration levels relatively close to LOQs. Jondreville et al. (2017) previously reported
163 enrichment in (+)β-enantiomer in eggs of hens after ingestion of HBCDD-containing extruded
164 polystyrene.

165 Interestingly, enrichment was more pronounced for (–)β-isomer than (+)α-enantiomer in eel. At the
166 opposite, enrichment was more pronounced for (–)α- than for (+)β-enantiomer in eggs. For these two
167 relatively highly contaminated samples, β-isomer contributed to less than 1% of the diastereoisomer
168 contamination profile. Pronouncement of enantiomer enrichment also appeared to vary from one
169 isomer to another.

γ-HBCDD. The 4 considered samples were from animals of aquatic origin (**Figure 1c**). For oysters, trout and eel, enrichments were significant but also appeared to be possibly opposite depending on the animal species. Also, enriched enantiomer was independent from other diastereoisomers behaviours.

The most pronounced enrichment was observed for (–)γ-enantiomer in fresh oysters (EF_γ = 0.293). In eel, the slight enrichment observed for (+)γ-enantiomer was consistent with findings of Bester and Vorkamp (2013). In scampi, the only sample with γ-HBCDD as only isomer according to original assay A, the diastereoisomer profile suggests food contamination by direct contact; but the significant enrichment in (–)γ-isomer suggests the opposite. However, the EFγ value was very close to the decision limit. Eventually, assays revealed the presence of α- and β-isomers in a way that the diastereoisomeric profile was 42-4-54% for α-β-γ-isomers, suggesting that, in that case, contamination arose from cumulated sources.

4. Concluding remarks

The present study corroborates preferential accumulations of selected HBCDD enantiomers in food from animal origin intended for human consumption. Enantiomer enrichments suggest contamination of the human food chain through biological processes related to feedstock of animal origin rather than food contact contamination. Observed extent and opposite enrichments (depending on species) might lead to average dietary exposure to racemic mixtures, as observed by Roosens et al. (2009) in most duplicate diet samples from their sampling plan (except those containing fish, meat or cheese). However, in this particular study, most samples were dominated by γ-HBCDD, which was not consistent with Poma et al. findings. Thus, depending on their dietary habits, probabilistic total diet study considering consumption habits could reveal that Belgian sub-populations might be overall exposed to non-racemic mixtures. This could exacerbate (or mitigate) enantiomer enrichments occurring in the human body by enantioselective metabolism after consumption. Considering that enantiomeric pairs mostly display different toxicological activities (Müller and Kohler, 2004; Zhang et

al., 2008), risk assessors should consider chiral profiles of HBCD diastereomers. Consequently, it is advised, on the one hand, to also include EF values in reporting the HBCDD occurrence levels, and on the other hand, to put focus of toxicological studies on investigating enantiomer-specific adverse effects.

Supporting Information

The following file is available free of charge (PDF file): overview of the analysed samples, including quantification and EF results; extracted ion chromatogram illustrating achieved chromatographic separation; Comparisons between assay results.

Funding

The food samples were acquired under project RT 14/12 FLAREFOOD financed by the Belgian Federal Public Service Health, Food Chain Safety and Environment.

Conflict of interest

The authors declare no financial competing interest.

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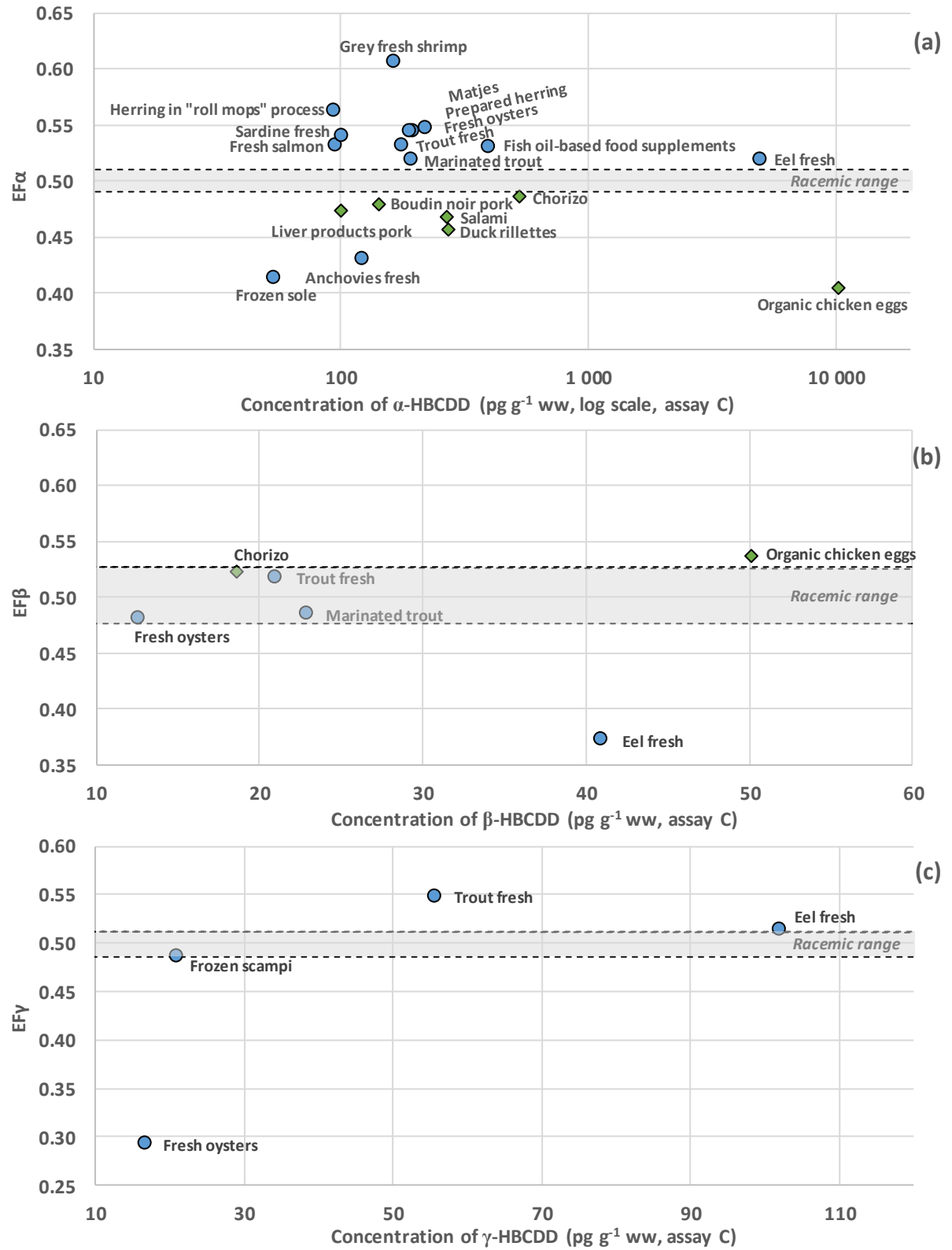
322

Figure captions

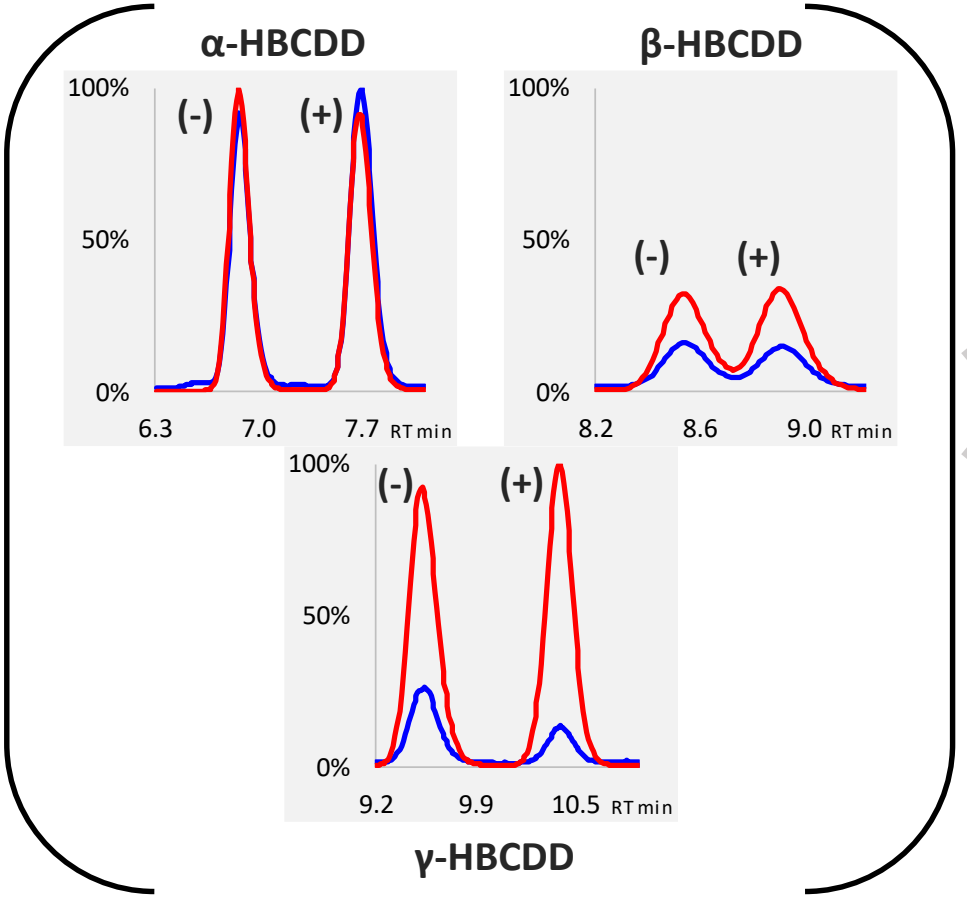
Figure 1. Enantiomeric fractions of α- (a), β- (b) and γ- (c) HBCDDs according to diastereoisomer concentration (log scale for α-) resulting from assay C. Sample from aquatic mollusc, crustacean or fish (●) or terrestrial bird or mammal (◆) food producing animal; racemic ranges delimited by dashed line.


(a)
EFα
Grey fresh shrimp
Herring in "roll mops" process
Matjes
Prepared herring
Fresh oysters
Sardine fresh
Fresh salmon
Trout fresh
Fish oil-based food supplements
Marinated trout
Eel fresh
Racemic range
Boudin noir pork
Chorizo
Salami
Liver products pork
Duck rillettes
Anchovies fresh
Frozen sole
Organic chicken eggs
Concentration of α-HBCDD (pg g-1 ww, log scale, assay C)
(b)
EFβ
Chorizo
Organic chicken eggs
Trout fresh
Racemic range
Marinated trout
Fresh oysters
Eel fresh
Concentration of β-HBCDD (pg g-1 ww, assay C)
(c)
EFγ
Trout fresh
Eel fresh
Racemic range
Frozen scampi
Fresh oysters
Concentration of γ-HBCDD (pg g-1 ww, assay C)

FOOD

of animal origin

ENANTIOMERIC FRACTION



ante-mortem

CONTAMINATION SOURCE

post-mortem