Supporting Information

Tetrabromobisphenol-A and Hexabromocyclododecane in Birds: from an E-waste Region in China: Influence of Diet on Diastereoisomer- and Enantiomer- specific distribution and Trophodynamics

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Sample Extraction and Clean-UP. Water sample extraction was according to Streets et al. (1) with minor modification. In brief, water samples were filtered using ashed glass fiber filters (Whatman, 293-mm GF/F) and the filtered water was passed through a column containing XAD-2 and XAD-4 mix resins (Supelco, Bellefonte, PA, precleaned by successive Soxhlet extraction with methanol and dichloromethane) to retain the organic matter. Each XAD column was spiked with internal standards ($^{13}\text{C}_{12}$ - α -, β -, γ -HBCD), and eluted with 25 mL of methanol followed by 50 mL of dichloromethane. The resins were then transferred into a flask and extracted with methanol (3×50 mL) followed by dichloromethane (3×25 mL) in an ultrasonic bath. Upon addition of 175 mL of saturated NaCl solution, all of the methanol fractions were back-extracted three times each with 50 mL of dichloromethane. The combined dichloromethane fraction was then further extracted with 10 mL of organic free water to remove residual MeOH. The extract was concentrated and solvent exchanged to hexane, and further reduced to approximately 1 mL. The extracts of water samples were further purified by passing through a multilayer silica/alumina column. The extracts were concentrated, solvent exchanged to methanol, and finally concentrated to 200 μL under a gentle stream of nitrogen. A known amount of recovery standard (d_{18} - α -, β -, and γ -HBCD) was added to all extracts prior to instrumental analysis.

The procedure for the grain and soil samples extraction was in detailed in our previous study (2) with some modification. About 35g sample was Soxhlet extracted with 50% acetone in hexane for 24 h. The extract was concentrated and solvent-exchanged to hexane using a rotary evaporator. The hexane extract was

subject to a multilayer silica column for cleanup and fractionation. The fraction containing targets was eluted using 30 mL of 50% dichloromethane in n-hexane (volume fraction). Elute was concentrated to near dryness under gentle nitrogen and redissolved in 200 μ L of methanol and spiked with known amounts of recovery standards prior to instrument analysis.

The plant samples about 20g, were Soxhlet extracted with 50% acetone in hexane for 48 h. The extracts were rotary-evaporated at 30°C to 30-40ml and then treated with concentrated sulfuric acid (60ml) for a overnight. The extract was rinsed and shaken with about 40ml n-hexane each time (3×40 ml). The extract was filtered through a nylon syringe filter. Organic phase was gathered each time and then concentrated to 2ml before passing through a multiple silica column. The target compounds were eluted with 30ml 50% dichloromethane in n-hexane (volume fraction). Extracts were solvent exchanged into methanol and reduced to 200 μ L for analysis.

Instrumental Analysis TBBPA, HBCD diastereoisomers and HBCD enantiomers were analyzed by a LC-ESI-MS/MS. An Agilent 1200 series liquid chromatography system coupled with an Agilent 6410 electrospray triple quadrupole mass spectrometer was used. TBBPA and HBCD diastereoisomers were separated through a C₁₈ column (XDB- C₁₈ 1.8 μ m 4.6 $\times$ 50mm Agilent Made in USA). The mobile phase was 100% methanol throughout the process, holding for 5 min. The flow rate was 0.25 ml/min with a injection volume of 5 μ L. The ESI ion source and an electrospray negative ion mode were preferred for determination of TBBPA and

HBCD isomers. The optimized parameters were as follows: Gas temperature, 350°C, capillary voltage, -4000V, nebulizer, 40psi; Gas flow 10 L/min; dwell time, 200 ms for TBBPA and HBCD; the collision energy, -15 eV for HBCD and -60 eV for TBBPA. MS analysis of TBBPA and HBCD diastereoisomers was done on an Agilent 6410 triple quadrupled based on the multiple reaction monitoring (MRM) conditions. The ions were selected at the $([M-H]^-)$ transition of m/z 640.7 $[M-H]^- \rightarrow 79(Br)^-$ and m/z 640.7 $[M-H]^- \rightarrow 81(Br)^-$ for native HBCDs, 652.7 $[M-H]^- \rightarrow 79 (Br)^-$ and 652.7 $[M-H]^- \rightarrow 81(Br)^-$ for $^{13}C_{12}$ -HBCDs, and 658.7 $[M-H]^- \rightarrow 79(Br)^-$ and 658.7 $[M-H]^- \rightarrow 81(Br)^-$ for d_{18} -labeled HBCD, respectively. The ions m/z 540.7 $\rightarrow 79$ and 552.7 $\rightarrow 79$ were monitored for TBBPA and $^{13}C_{12}$ -labeled TBBPA. Quantification of α -, β -, and γ -HBCDs were done based on the relative response factors for the corresponding ^{13}C -labeled internal standard.

HBCD enantiomer-specific separations were performed on a Phenomenex Nucleosil β -PM chiral LC column (20 cm $\times$ 4 mm i.d., 5 μ m particle size) containing permethylated β -cyclodextrin on silica (Macherey-Nagel, GmbH&Co, Duren, Germany). The parameters optimized were the same with diastereomers separation described before. The solvent was constituted of 30 % methanol and 70% acetonitrile for A, 30% methanol and 70% water for B. The injection volume was 20 μ L. The initial solvent composition was 30% A and 70% B, and then changed linearly over 14 min to a final solvent composition of 70% A and 30% B. The final condition was held for 31 min before returning back to the initial solvent composition. The post time was 7 min. Mass monitored using selected ion monitoring, m/z 640.7, 652.7, 658.7 were

for HBCDs, $^{13}\text{C}_{12}$ -HBCDs and d^{18} -HBCDs, respectively.

Enantiomeric Fractions Correction. Enantiomeric composition was expressed as enantiomeric fraction (EF), which is normally calculated from the peak areas of the enantiomeric pairs by $\text{EF} = A_{\text{first}} / (A_{\text{first}} + A_{\text{second}})$. Due to sample matrix effects, the target analyte signal can be enhanced or suppressed thus affect their quantification. In order to avoid this effect, which can affect EF calculations, Marvin et al. (3) introduced the corrected EF values, calculated by following:

$$\text{EF}_{\text{correct}} = \frac{A_{\text{first}} / A_{\text{first}}^{13}\text{C-labeled} \times C_{\text{first}}^{13}\text{C-labeled}}{[A_{\text{first}} / A_{\text{first}}^{13}\text{C-labeled} \times C_{\text{first}}^{13}\text{C-labeled} + A_{\text{second}} / A_{\text{second}}^{13}\text{C-labeled} \times C_{\text{second}}^{13}\text{C-labeled}]}$$

TABLE S1. The Habitat And Diet Type of Collected Bird Species.

Species		habitat	diet type
Chinese Pond heron	<i>Ardeola bacchus</i>	Live near water bodies such as ponds, rivers, marshes and swamps	Piscivorous bird feeding primarily on fish (95%) and aquatic insects
White-breasted waterhen	<i>Amaurornis phoenicurus</i>	Moist ground overgrow with bushes; also seen in waterlogged low lying areas	insectivores/garnivores bird feeding on insects, worms, and march plant shoots, paddy grainsand fish
Common snipe	<i>Gallinago gallinago</i>	reshwater marshes, ponds, flooded meadows,	larval insects, aquatic invertebrates also some plant material.
Slaty-breasted rail	<i>Gallirallus striatus</i>	Paddy fields, wetland	Shrimp, crab, and insect
Spotted Dove	<i>Streptopelia chinensis</i>	around human habitation can easily be seen in parks, gardens and agricultural areas	terrestrial phytophagous bird feeding on seeds and grains.
Chinese Francolin	<i>Francolinus pintadeanus</i>	Forests, grassland and scrub	terrestrial phytophagous bird feeding on berries, grains, small reptiles, grasshoppers, and insects.

TABLE S2. The Comparison of Total HBCD Concentration in Bird Eggs or Muscles from Different Areas. (ng/g lipid weight)

Species	tissues	Total HBCD(ng/g)	Site	Reference
Guillemot	egg	140	Baltic Sea	(4)
Peregrine falcon	egg	34–2400	Sweden	(5)
Sparrowhawk	muscle	84–19,000	United Kingdom	(6)
Cormorant	liver	796-1200	United Kingdom	(7)
Common tern	egg	1501	Western Scheldt	(7)
Common tern	egg	210	Western Scheldt	(8)
Peregrine falcon	egg	17	S. Greenland	(9)
Little owl	egg	20–50	Belgium	(10)
Glaucous gull	egg	22	Bjørnøya,	(11)
four species sea bird	egg	45-140	Bjørnøyay	(12)
Shag	Yolk sac	420	Mid-Norway	(13)
guillemot	egg	138	Baltic Sea	(14)
guillemot	muscle	65	Baltic Sea	(14)
Northern fulmars	Liver	3.8 -62	Bjørnøya	(15)
Northern fulmars	Egg yolk	7.23-63.9 ng/g wt	Norwegian Arctic	(15)
Herring gulls	egg	<0.01-20.7 ng/g wt	Laurentian Great Lakes	(16)
Africal darter	egg	<LOD-11	South Africa	(17)
Sacred ibis	egg	4.8-71	South Africa	(17)
Little grebe	egg	1.6	South Africa	(17)
Predatory birds	egg	7.5-3100	Sweden	(18)
glaucous gulls	Liver	200-15000	Bjørnøya	(19)
glaucous gulls	brain	5-500	Bjørnøya	(19)

FIGURES1. Chromatographic separation of HBCD enantiomers in a standard mixture and collected bird samples.

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