

1 **SUPPORTING INFORMATION**

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4 **Trophodynamics of Polybrominated Diphenyl Ethers in the Marine Food Web of Bohai**
5 **Bay, North China**

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1 **Sample collection.** Aquatic food web samples were collected in May, June and September of
2 2002 in Bohai Bay (39°12'N, 117°59'E). Seabirds were collected in November of 2002 on the
3 coast of Bohai Bay (39°07'N, 117°44'E). Zooplankton samples were obtained from vertical
4 tows (bottom to surface) using a zooplankton net (37 cm mouth diameter, 140 m in length,
5 160 µm mesh) from six locations (39°00'N, 117°53'E; 39°00'N, 118°00'E; 38°45'N,
6 117°53'E; 38°45'N, 118°00'E; 38°30'N, 117°53'E and 38°30'N, 118°00'E) (SUPPORTING
7 INFORMATION Figure S1). The samples of zooplankton mainly consisted of small copepods
8 (*Acartia bifilosa*, *Paracalanus parvus*, *Labidocera euchaeta* and *Oithona similis*).
9 Invertebrates and fish were caught with a bottom trawl, and seabirds were captured before
10 their winter migration commenced. All samples were stored at –20°C prior to analysis.

11 **Chemicals.** Thirteen PBDEs (BDE-11, BDE-25, BDE-28, BDE-71, BDE-47, BDE-66,
12 BDE-100, BDE-119, BDE-99, BDE-154, BDE-153, BDE-138 and BDE-183) were selected
13 as target compounds due to their reported abundance on a worldwide scale. PBDE standards
14 and surrogate standards (PCB 198, PCB 204 and PCB 209) were obtained from AccuStandard
15 (New Haven, Connecticut, USA). All solvents (dichloromethane, acetonitrile and hexane)
16 were pesticide grade purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). Sodium
17 sulfate and silica gel (100-200 mesh size) were purchased from Beijing Chemical Reagent
18 Company (Beijing, China).

19 **GC-MS condition.** A DB-5MS capillary column (30m × 0.25 mm × 0.1 µm film thickness;
20 J&W Scientific, USA) was used to separate the PBDE congeners. A splitless injector was
21 used and the injector was maintained at 250°C. The temperature program was from 110°C (1
22 min) to 180°C at the rate of 10°C/min, then increased to 220°C (5 min) at the rate of 5°C/min,

1 and then to 310°C (5 min) at a rate of 20°C/min. The interface and ion temperatures were
2 320°C and 280°C, respectively. The carrier gas was helium at a constant flow rate of 2 ml/min.
3 Data acquisition was conducted in selected ion monitoring mode.

4 **Quantitation and Quality Assurance Quality Control (QA/QC).** All equipment rinses were
5 done with acetone and hexane, and the sample preparations were conducted in a super clean
6 lab to avoid background contamination. A procedural blank was analyzed with every set of
7 seven samples, and concentrations of PBDEs in blank samples were low compared with those
8 in samples and all results were blank corrected. The procedure described above was validated
9 for the recovery experiment by analyzing spiked biota samples. Analyte addition was made
10 with the criterion of at least three times the original concentrations. The six replicate spiked
11 samples and one matrix blank sample were analyzed to determine the general recovery rate.
12 The recoveries for spiked samples ranged from 73±4.6 to 84±5.6 % for all targeted
13 compounds. The method detection limits (MDL) were set to be the three times the average
14 concentrations in the blank samples. In blank samples, BDE-28, BDE-47, BDE-99, BDE-153
15 and BDE-183 were detected, and the average concentrations were 0.3, 0.4, 0.2, 0.4 and 1 pg/g
16 ww (wet weight), respectively. And MDLs for the other compounds, which were not detected
17 in blank samples, were set to the instrumental minimum detectable amounts. The detection
18 limits were 0.4 pg/g ww for BDE-25, BDE-75, BDE-71, BDE-66, BDE-77, BDE-100 and
19 BDE-119; 0.7 pg/g ww for BDE-28; 0.6 pg/g ww for BDE-99; 0.8 pg/g ww for BDE-154; 1
20 pg/g ww for BDE-47, BDE-153 and BDE-138; and 2 pg/g ww for BDE-183.

21 **Lipid Content Analysis.** To determine the lipid content of the analyzed samples, about 1 g
22 dry samples were ground with anhydrous sodium sulfate and Soxhlet extracted for 24 h using

1 200 ml dichloromethane / methanol (7:3 v/v) mixture solution. The extracts were then rotated
2 to dry and heated at 65°C for about 30 min, and lipid amounts were determined
3 gravimetrically.

4 **Calculations of Trophic Magnification Factor.** The trophic magnification factor (TMF)
5 represents the average rate of increase per trophic level, and was used to describe the
6 food-web biomagnification of chemicals in the present study. The continuous integrative
7 measures of trophic position were obtained according to stable nitrogen isotope ratios
8 reported previously (1-4). The factors are based on the relationships between the trophic
9 levels and the PBDE concentrations using simple linear regression:

$$10 \quad \log \text{PBDE concentration (lipid equivalent)} = a + b \times \text{TL}. \quad (1)$$

11 The concentrations below the detection limit were treated as half of the detection limit (Table
12 1). The b in Eq. 1 was used to calculate TMF by the following equation:

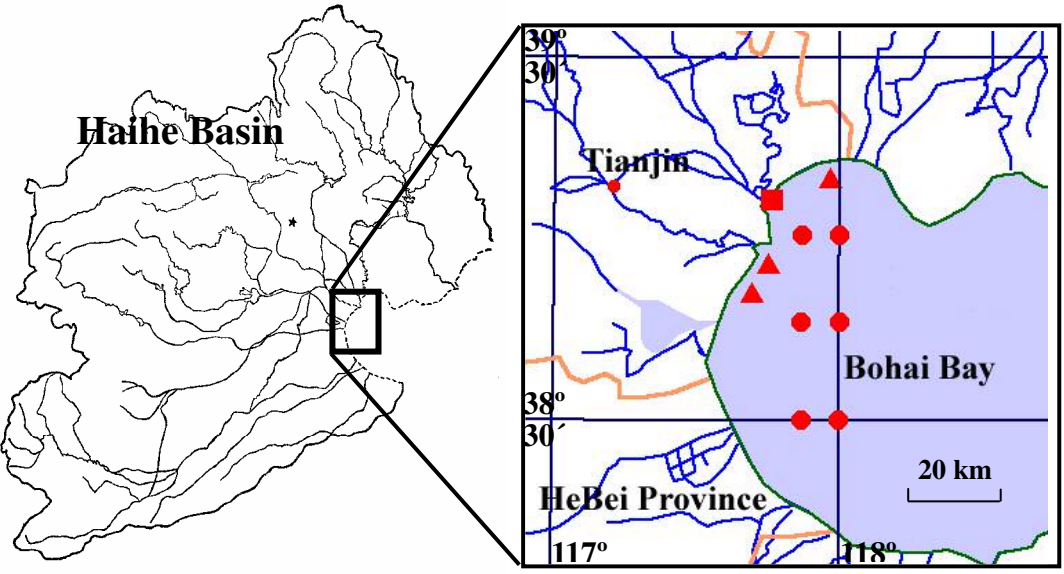
$$13 \quad \text{TMF} = 10^b. \quad (2)$$

14 **Statistical Analysis.** Correlations between PBDE concentrations and trophic levels were
15 examined by Pearson's rank correlation test, and when the *p* value was below 0.05, the linear
16 regression between the PBDE concentrations and trophic level was regarded as significant.

17 The software used was SPSS 11.0 (SPSS Inc., Chicago, IL, USA).

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SUPPORTING INFORMATION Figure 1. Location of sampling sites, ●: sampling locations of plankton; ▲: sampling locations of fishes and invertebrates; ■: sampling locations of seabirds.

1 SUPPORTING INFORMATION TABLE 1. Comparison of PBDEs levels (ng/g lw) in various organisms from Bohai Bay with those reported
 2 in previous investigations.

| Location | Zooplankton | | Invertebrates | | Fish | | Birds | | ref |
|--|-------------|------------|---------------|-------------|--------------|------------|--------------|------------|-----|
| | Sum PBDEs | BDE-47 | Sum PBDEs | BDE-47 | Sum PBDEs | BDE-47 | Sum PBDEs | BDE-47 | |
| Bohai Bay | 1.00 | 0.03 | 0.15-1.09 | 0.03-0.41 | 0.56-6.31 | 0.21-3.78 | 32.78±5.09 | 16.13±2.37 | |
| Various organisms from other locations worldwide | | | | | | | | | |
| Svalbard | 0.16 | 0.08 | - | - | 1.99±1.19 | 0.81±0.53 | - | - | 5 |
| Baltic Sea | - | 1.8-3.4 | - | - | - | 0.92-37 | - | - | 6 |
| <u>Lake Winnipeg</u> | 36.42-90.42 | 6.38-15.94 | 110.48-160.58 | 11.87-33.12 | 11.10-381.26 | 1.82-83.84 | - | - | 7 |
| <u>Arctic lakes</u> | - | <5-39.3 | - | - | - | <16-595 | - | - | 8 |
| northern Atlantic Ocean | - | - | - | - | - | 0.75-4.8 | - | - | 6 |
| southern Greenland | - | - | 5.5 | 5 | 7.74-43.39 | 7.87-41.32 | - | - | 9 |
| coastal British Columbia | - | - | 4.2-480 | 2.8-210 | 12-340 | 6.1-160 | - | - | 10 |
| Belgian North Sea | - | - | 3.33-73.68 | - | 7.50-190 | - | - | - | 11 |
| Belgium | - | - | - | - | - | - | 95-900 | 81-430 | 12 |
| Great Lakes | - | - | - | - | - | - | 1,800-16,500 | 667-6,100 | 13 |

3 Location underlined was freshwater ecosystem.

4 a: ng/g dry weight.

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