Polybrominated Diphenyl Ethers (PBDEs) in a Large, Highly Polluted Freshwater Lake, China: Occurrence, Fate, and Risk Assessment

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Supplementary Information

Table S1. Optimized MS/MS parameters of the eight PBDEs.
Table S2. Recovery rates of the eight PBDEs in water samples.
Table S3. Recovery rates of the eight PBDEs in sediment/biota samples.
Table S4. Method detection limits (MDLs) for the eight PBDEs.
Table S5. Regression equations, correlation coefficients and retention time of the eight PBDEs.
Table S6. Contents of PBDEs in main rivers connected to Chaohu Lake (ng/L).
Table S7. Contents of PBDEs in the effluents of main sewage treatment plants surrounding Chaohu Lake (ng/L).
Table S8. Contents of PBDEs in water from Chaohu Lake (ng/L).
Table S9. Contents of PBDEs in sediments of rivers flowing into Chaohu Lake and the sludge of sewage treatment plants (ng/g).
Table S10. Contents of PBDEs in sediments from Chaohu Lake (ng/g).
Table S11. Concentrations of PBDEs in aquatic species from Chaohu Lake (ng/g).
Table S12. Estimated daily intake (EDI) and Hazard quotient (HQ) for BDE-47, BDE-99 and BDE-153.
Table S13. The values of PNEC for fish, daphnia and green algae.
Table S14. The base set of acute toxicity for the calculation of MRQ_{MEC/PNEC} and MRQ_{STU}.

Materials and Methods

Sample Extraction and Analyses

Water samples were filtered through 0.45 µm glass fiber filters (GF/F, Whatman, Clifton, NJ, USA) to remove particles. The water samples filtrate mixed with 0.1 volumes of methanol and sonicated for 5 min. Then the filtrate was extracted by solid phase extraction (SPE) on HLB cartridges (200 mg, Waters, Massachusetts, USA). The cartridges were preconditioned with 5 mL dichloromethane, 5 mL ethyl acetate, 5 mL methanol and 5 mL water. The samples were eluted from the cartridges using 3 mL dichloromethane and 3 mL ethyl acetate. The extracts were evaporated to dryness under a stream of nitrogen, reconstituted with 2 mL n-hexane.

Fish tissue (brain, liver, gills and muscle) samples were homogenized and weighed prior to extracting with an accelerated solvent extractor followed by an ASE 300 (Dionex Ltd., Sunnyvale, CA, USA). Weighed samples were mixed with 5 g of anhydrous sodium sulfate and
were loaded into 33 mL ASE cells on top of 10 g of activated Florisil, which was used as a clean-up. Cells were spiked with 10 µL of 1 ng/µL 13C12-labelled 2,2',4,4',5,5'-hexa-BDE (BDE-153) as a recovery internal standard (RIS) solution. The fish sample was then extracted at 100°C with a mixture of n-hexane/dichloromethane (DCM) (4:1, v/v) working at a constant pressure of 1500 psi, a flush volume of 60% and a purge time of 90 s. Two static extraction cycles of 5 min each were applied to achieve the maximum recovery of the analytes. After extraction, the solvents were evaporated down to 1.0 mL and analyzed by GC/MS/MS.

PBDEs and bromophenols were analyzed on a Bruker 450 GC-320 triple quadrupole mass spectrometer (Fremont, CA, USA) fitted with a DB-5HT capillary column (15 cm × 250 µm × 0.1 µm), combined with the multiple-reaction monitor (MRM) mode of tandem mass spectrometry. The mass spectrometer was operated in negative electrospray ionization mode (ESI-) using MRM. The quantification of PBDEs was conducted using 13C12-labelled BDE-153 as an internal standard.

A total of 39 PBDEs were analyzed by GC-MS/MS (EI, 70 eV). The GC-MS/MS was operated in pulsed splitless injection mode with an injector temperature of 340°C. The helium carrier gas flow rate was 1.3 mL/min, and the oven temperature program was as follows: 40°C, 230°C (20°C/min), 285°C (6°C/min), 340°C (25°C/min), held for 7 min. The interface, source and quadrupole temperature were set at 300, 300 and 40°C, respectively, and the MRM parameters are listed in Table S1.

Parameter Measurement and Statistical Analysis

Health Risk Assessment

The estimated daily intake (EDI, ng/kg-bw/day) of PBDEs by adult was calculated as follows:

\[
\text{EDI}_{\text{water}} = C \times V / BW \tag{1}
\]

where \(C\) is the concentration of a PBDE congener in water (ng/L); \(V\) (mL/day) is the consumption rate of water (L); and \(BW\) (kg) is the adult body weight.

\[
\text{EDI}_{\text{fish}} = C \times R / BW \tag{2}
\]

\[
\text{EDI}_{\text{fish}} = C \times R / BW \tag{3}
\]

where \(C\) is the concentration of a PBDE congener in fish (ng/g); \(R\) is the consumption rate of fish (g/day); and \(BW\) (kg) is the adult body weight.

To assess health risks associated with exposure to PBDEs concerning non-carcinogenic endpoints, hazard quotient (HQ) values were estimated and used. It can be calculated simply by dividing the estimated daily intake by the reference dose (RfD) of PBDEs reported by the Integrated Risk Information System (IRIS) of the USEPA as follows:

\[
HQ = f \times \text{EDI} / RfD \tag{4}
\]

where \(f\) is the transfer factor of unit (which is 0.001 in this case)

According to the risk addition method, the total HQs of all PBDE congeners can be treated as the mathematical sum of the HQ values of single PBDE congener:

\[
\text{THQ} = \Sigma HQ \tag{5}
\]

Eco-toxicity assessment
Eco-toxicity of target compounds in water was assessed using the risk quotient (RQ) on nontarget organisms. At three trophic levels, LC50 or EC50 for fish, daphnia and green algae associated with PBDEs were used for RQ calculation as Eq (6).

\[
RQ = \frac{\text{MEC}}{\text{PNEC}} = \frac{\text{MEC}}{\text{EC50 or LC50}/f}
\]  

where PNEC is the predicted no effect concentration (mg/L), estimated as a quotient of toxicological relevant concentration (EC50 or LC50) with a security factor (\( f = 1000 \)). The values of EC50 or LC50 for fish, daphnia and green algae for PNEC calculation were provided in the Table S13.

Two approaches for calculating the mixture risk quotient (MRQ) are outlined by Eq. (7): the calculation of MRQ, based on the sum of MEC/PNEC values (MRQ_{MEC/PNEC}); and Eq. (8): the calculation of MRQ, based on the sum of toxic units (STUs) for the most sensitive trophic level (MRQ_{STU}). The acute toxicity data EC50 and LC50 are represented by EC50 in Eqs. (7) and (8).

\[
\text{MRQ}_{\text{MEC/PNEC}} = \sum_{i=1}^{n} \frac{\text{MEC}_{ij}}{\text{PNEC}_{ij}} = \sum_{i=1}^{n} \frac{\text{MEC}_{ij}}{\text{min}(\text{EC50}_{\text{aglue}}, \text{EC50}_{\text{daphnids}}, \text{EC50}_{\text{fish}})} \times (1/\text{AF}_i)
\]

\[
\text{MRQ}_{\text{STU}} = \max (\text{STU}_{\text{aglue}}, \text{STU}_{\text{daphnids}}, \text{STU}_{\text{fish}}) \times \text{AF} = \max \left( \sum_{i=1}^{n} \frac{\text{MEC}_{ij}}{\text{EC50}_{\text{aglue}}} \right) \times \sum_{i=1}^{n} \frac{\text{MEC}_{ij}}{\text{EC50}_{\text{daphnids}}} \times \sum_{i=1}^{n} \frac{\text{MEC}_{ij}}{\text{EC50}_{\text{fish}}} \times (1/\text{AF}_i)
\]

where TU and STU are the “toxic unit (MEC/EC50)” and the “sum of toxic unit”, respectively.

Table S1. Optimized MS/MS parameters of the eight PBDEs.

| Compounds | Retention time (min) | Precursor ion (m/z) | Product ion (m/z) | Collision energy (eV) |
|-----------|----------------------|---------------------|-------------------|----------------------|
| BDE-28    | 7.5-9.0              | 407.8(M+2)          | 247.9             | 25                   |
| BDE-47    | 9.0-10.0             | 485.7(M)            | 325.9             | 25                   |
| BDE-99    | 10.0-11.1            | 565.7(M+2)          | 405.9             | 25                   |
| BDE-100   |                      |                     |                   |                      |
| BDE-153   | 11.1-12.3            | 483.9(M-Br)         | 376.9             | 25                   |
| BDE-154   | 11.1-12.3            | 643.6(M)            | 483.9             | 30                   |
| 13C12-BDE-153 | 11.1-12.3     | 495.6               | 388.9             | 25                   |
| BDE-183   | 12.3-14.2            | 721.6(M-Br)         | 561.6             | 35                   |
| BDE-209   | 14.2-20              | 800(M-Br)           | 642               | 40                   |

Table S2. Recovery rates of the eight PBDEs in water samples.

| Compounds | Low concentration (ng/L) | Recovery rates (%) | Median concentration (ng/L) | Recovery rates (%) | High concentration (ng/L) | Recovery rates (%) |
|-----------|--------------------------|--------------------|-----------------------------|--------------------|--------------------------|--------------------|
| BDE-28    | 5.0                      | 90–110             | 90–110                      | 90–110             | 90–110                   | 90–110             |
| BDE-47    | 5.0                      | 90–110             | 90–110                      | 90–110             | 90–110                   | 90–110             |
| BDE-99    | 5.0                      | 90–110             | 90–110                      | 90–110             | 90–110                   | 90–110             |
| BDE-100   | 1.0                      | 75–95              | 75–95                       | 75–95              | 75–95                    | 75–95              |
| BDE-153   | 1.0                      | 75–95              | 75–95                       | 75–95              | 75–95                    | 75–95              |
| BDE-154   | 1.0                      | 75–95              | 75–95                       | 75–95              | 75–95                    | 75–95              |
| BDE-183   | 4.0                      | 75–95              | 75–95                       | 75–95              | 75–95                    | 75–95              |
| BDE-209   | 4.0                      | 65–70              | 65–70                       | 65–70              | 65–70                    | 65–70              |

Table S3. Recovery rates of the eight PBDEs in sediment/biota samples.
### Table S4. Method detection limits (MDLs) for the eight PBDEs.

| Compounds | Instrument Detection Limit (IDL, pg) | Water samples (ng/L) | Sediment/biota (pg/g) |
|-----------|--------------------------------------|----------------------|----------------------|
|           | Low concentration (ng/g) Recovery rates (%) | Median concentration (ng/g) Recovery rates (%) | High concentration (ng/g) Recovery rates (%) |
| BDE-28    | 0.03                                 | 0.014                | 0.009                | 5                   |
| BDE-47    | 0.02                                 | 0.025                | 0.048                | 4                   |
| BDE-99    | 0.015                                | 0.024                | 0.033                | 4                   |
| BDE-100   | 0.03                                 | 0.018                | 0.007                | 4                   |
| BDE-153   | 0.03                                 | 0.027                | 0.011                | 5                   |
| BDE-154   | 0.04                                 | 0.036                | 0.005                | 6                   |
| BDE-183   | 0.02                                 | 0.02                 | 0.018                | 4                   |
| BDE-209   | 0.15                                 | 0.06                 | 1.5                  | 20                  |

### Table S5. Regression equations, correlation coefficients and retention time of the eight PBDEs.

| Compounds | Regression equation | Correlation coefficient | Retention time (min) |
|-----------|---------------------|-------------------------|----------------------|
| BDE-28    | y = 0.611x - 0.921  | 0.997                   | 8.100                |
| BDE-47    | y = 0.626x - 0.648  | 0.997                   | 9.426                |
| BDE-99    | y = 0.597x - 0.033  | 0.997                   | 10.392               |
| BDE-153   | y = 0.346x - 0.501  | 0.998                   | 10.676               |
|           | y = 0.185x + 0.081  | 0.9991                  | 11.424               |
| BDE-154   | y = 0.105x - 0.057  | 0.9994                  | 11.767               |
| BDE-183   | y = 0.232x - 0.143  | 0.998                   | 12.674               |
| BDE-209   | y = 0.010x - 0.343  | 0.9996                  | 17.030               |

### Table S6. Contents of PBDEs in main rivers connected to Chaohu Lake (ng/L).

| Compounds | Time     | P1  | P2  | P3  | P4  | P5  | P6  | P7  | P8  | P9  |
|-----------|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| BDE-28    | June     | 0.16| 0.23| ND  | ND  | ND  | 0.34| ND  | 0.15| ND  |
|           | October  | 0.20| 0.24| ND  | ND  | ND  | 1.36| ND  | 0.26| 0.09|
| BDE-47    | June     | 0.38| 0.13| 0.16| 0.25| 0.19| 0.34| ND  | 0.05| ND  |
|           | October  | 0.45| 0.21| 0.17| 0.25| 0.27| 1.31| 0.05| 0.22| 0.12|
| BDE-99    | June     | 0.15| 0.24| 0.16| 0.20| 0.21| 1.03| ND  | 0.05| ND  |
|           | October  | 0.30| 0.14| 0.13| 0.06| 1.05| 0.06| ND  | 0.05| 0.11|
| BDE-100   | June     | 0.17| 0.11| 0.06| 0.34| ND  | ND  | ND  | ND  | ND  |
|           | October  | 0.12| 0.17| 0.09| 0.17| 1.06| ND  | 0.22| ND  | ND  |
| BDE-153   | June     | 0.06| 0.21| 0.05| 0.16| ND  | ND  | ND  | ND  | ND  |
|           | October  | 0.16| 0.07| 0.06| 1.01| 0.12| ND  | 0.11| ND  | ND  |
| BDE-154   | June     | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  |
|           | October  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  |
| BDE-183   | June     | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  |
|           | October  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  | ND  |
| ΣPBDEs    | June     | 0.75| 0.98| 0.43| 0.45| 0.65| 1.70| 0.15| 0.64| 0.40|
| Compounds | W1 | W2 | W3 | W4 | W5 |
|-----------|----|----|----|----|----|
| BDE-28    | ND | ND | ND | ND | ND |
| BDE-47    | 0.31 | 0.26 | 0.21 | 0.38 | ND |
| BDE-99    | 0.22 | 0.32 | 0.23 | 0.26 | 0.20 |
| BDE-100   | 0.16 | ND | ND | ND | ND |
| BDE-153   | ND | 0.23 | ND | ND | ND |
| BDE-154   | ND | ND | ND | ND | ND |
| BDE-183   | ND | ND | ND | ND | ND |
| BDE-209   | ND | ND | ND | ND | ND |
| ΣPBDEs    | 0.69 | 0.71 | 0.44 | 0.64 | 0.20 |

ND: below the Method detection limit.

**Table S7.** Contents of PBDEs in the effluents of main sewage treatment plants surrounding Chaohu Lake (ng/L).

| Compounds | Time   | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 |
|-----------|--------|----|----|----|----|----|----|----|----|----|
| BDE-28    | June   | 0.10 | ND | ND | ND | ND | ND | ND | ND | ND |
|           | October | 0.16 | ND | ND | ND | ND | ND | ND | ND | ND |
| BDE-47    | June   | 0.35 | 0.30 | 0.12 | 0.10 | ND | 0.24 | ND | ND | 0.19 |
|           | October | 0.54 | 0.36 | 0.20 | 0.28 | ND | 0.44 | ND | ND | 0.46 |
| BDE-99    | June   | 0.43 | 0.24 | 0.21 | 0.17 | 0.16 | 0.23 | 0.20 | 0.23 | 0.40 |
|           | October | 0.48 | 0.32 | 0.43 | 0.36 | 0.28 | 0.39 | 0.27 | 0.28 | 0.45 |
| BDE-100   | June   | ND | ND | ND | ND | ND | ND | ND | ND | ND |
|           | October | 0.15 | ND | ND | ND | ND | ND | ND | ND | ND |
| BDE-153   | June   | 0.14 | 0.10 | 0.12 | ND | ND | 0.11 | ND | ND | ND |
|           | October | 0.23 | ND | 0.31 | ND | ND | 0.26 | ND | ND | ND |
| BDE-183   | June   | ND | ND | ND | ND | ND | ND | ND | ND | ND |
|           | October | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| BDE-209   | June   | ND | ND | ND | ND | ND | ND | ND | ND | ND |
|           | October | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| ΣPBDEs    | June   | 1.02 | 0.64 | 0.45 | 0.27 | 0.16 | 0.58 | 0.20 | 0.23 | 0.59 |
|           | October | 1.56 | 0.68 | 0.94 | 0.64 | 0.28 | 1.09 | 0.27 | 0.28 | 0.91 |

ND: below the Method detection limit.

**Table S8.** Contents of PBDEs in water from Chaohu Lake (ng/L).

| Compounds | P1 | P2 | P3 | P3-1 | P4 | P5 | W1 |
|-----------|----|----|----|------|----|----|----|
| BDE-28    | ND | ND | ND | ND   | ND | ND | ND |
| BDE-47    | 0.017 | 0.022 | 0.023 | 0.025 | 0.023 | 0.022 | 0.324 |
| BDE-99    | 0.023 | ND | ND | ND   | ND | ND | 0.251 |
| BDE-100   | ND | ND | ND | ND   | ND | ND | 0.014 |
| BDE-153   | 0.012 | ND | ND | 0.014 | 0.013 | 0.013 | 0.014 | 0.294 |
| BDE-154   | ND | ND | ND | 0.021 | 0.025 | ND | 0.021 | 0.047 |
| BDE-183   | 0.056 | 0.020 | 0.024 | 0.022 | 0.020 | 0.021 | 0.081 |
| BDE-209   | 1.27 | 0.27 | 1.45 | 3.96 | 0.20 | 1.34 | 10.5 |
| ΣPBDEs    | 1.38 | 0.312 | 1.53 | 4.05 | 0.256 | 1.42 | 11.5 |

ND: below the Method detection limit.

**Table S9.** Contents of PBDEs in sediments of rivers flowing into Chaohu Lake and the sludge of sewage treatment plants (ng/g).

**Table S10.** Contents of PBDEs in sediments from Chaohu Lake (ng/g).
| Compounds | BDE-28 | BDE-47 | BDE-99 | BDE-100 | BDE-153 | BDE-154 | BDE-183 | BDE-209 | ΣPBDEs |
|-----------|--------|--------|--------|---------|---------|---------|---------|---------|--------|
| H1        | 0.032  | 0.043  | 0.036  | 0.16    | 0.033   | 0.071   | 0.086   | 4.95    | 5.41   |
| H2        | ND     | 0.032  | ND     | ND      | 0.023   | 0.039   | ND      | 2.48    | 2.57   |
| H3        | ND     | 0.021  | 0.026  | ND      | 0.014   | ND      | ND      | 1.21    | 1.27   |
| H4        | ND     | ND     | 0.01   | 0.06    | ND      | ND      | 0.04    | 1.80    | 1.91   |
| H5        | ND     | 0.025  | 0.030  | ND      | 0.013   | 0.019   | 0.019   | 0.54    | 0.605  |
| H6        | ND     | 0.025  | ND     | ND      | 0.023   | 0.039   | ND      | 2.48    | 2.57   |
| H7        | ND     | 0.021  | 0.030  | ND      | 0.013   | 0.019   | ND      | 0.45    | 0.533  |
| H8        | ND     | 0.026  | 0.032  | ND      | ND      | ND      | ND      | ND      | ND     |
| H9        | ND     | 0.027  | 0.035  | ND      | 0.013   | ND      | ND      | 0.075   |        |
| H10       | ND     | 0.042  | ND     | ND      | 0.018   | 0.022   | 0.022   | 4.56    | 4.66   |
| H11       | ND     | 0.015  | 0.014  | 0.051   | 0.024   | 0.030   | 0.047   | 2.71    | 2.89   |
| H12       | ND     | 0.026  | 0.015  | 0.067   | 0.017   | 0.019   | 0.033   | 1.54    | 1.72   |
| H13       | ND     | 0.021  | 0.013  | ND      | 0.012   | 0.019   | ND      | ND      | 0.065  |
| H14       | ND     | 0.022  | 0.024  | ND      | 0.012   | ND      | ND      | ND      | 0.058  |

ND: below the Method detection limit.

Table S11. Concentrations of PBDEs in aquatic species from Chaohu Lake (ng/g).

| Species | BDE-28 | BDE-47 | BDE-99 | BDE-100 | BDE-153 | BDE-154 | BDE-183 | BDE-209 | ΣPBDEs |
|---------|--------|--------|--------|---------|---------|---------|---------|---------|--------|
| River shrimpa | ND | ND | 0.05 | ND | ND | ND | ND | ND | 0.05 |
| Chinese hooksnout carp | ND | 0.115 | 0.079 | 0.056 | 0.113 | 0.126 | 0.035 | ND | 0.524 |
| Crucian carp | ND | 0.021 | ND | ND | ND | ND | ND | ND | 0.021 |
| Topmouth culter | 0.008 | 0.013 | ND | ND | ND | ND | ND | ND | 0.021 |
| Silver fish | ND | 0.026 | 0.012 | ND | ND | ND | 0.012 | ND | 0.05 |
| Chinese hooksnout carp b | ND | ND | 0.014 | ND | ND | ND | ND | ND | 0.043 |
| Silver fish b | ND | ND | 0.0009 | ND | ND | ND | ND | ND | 0.049 |
| Topmouth culter b | ND | 0.018 | ND | ND | ND | 0.026 | 0.011 | 0.009 | ND | 0.064 |
| Common carp b | ND | 0.024 | ND | ND | ND | 0.013 | 0.018 | ND | 0.275 |
| Crucian carp (Brain) b | ND | 0.549 | ND | ND | 1.25 | 0.028 | ND | ND | 1.876 |
| Crucian carp (Gill) b | ND | 0.066 | ND | ND | ND | 0.047 | ND | ND | 0.205 |
| Crucian carp (Liver) b | ND | 0.025 | 0.034 | ND | ND | 0.032 | ND | ND | 0.091 |
| Crucian carp (Intestines) b | ND | 0.018 | 0.022 | ND | ND | ND | ND | ND | 0.04 |

a: Biota samples were collected from S1 site; b: Biota samples were collected from S2 site; ND: below the Method detection limit.

Table S12. Estimated daily intake (EDI) and Hazard quotient (HQ) for BDE-47, BDE-99 and BDE-153.

| Sites/Biology | EDI(ng/kg/day) | Sum of EDI | HQ | Sum of HQ |
|---------------|---------------|------------|----|-----------|
|               | BDE-47 | BDE-99 | BDE-153 | BDE-47 | BDE-99 | BDE-153 | BDE-47 | BDE-99 | BDE-153 |
| P1            | 1.6E-02 | 1.0E-02 | 5.6E-03 | 3.2E-02 | 1.6E-06 | 1.0E-06 | 2.8E-07 | 2.9E-06 |
| P2            | 7.3E-03 | 4.9E-03 | 2.4E-03 | 1.5E-02 | 7.3E-07 | 4.9E-07 | 1.2E-07 | 1.3E-06 |
| P3            | 8.7E-03 | 4.5E-03 | 4.5E-04 | 1.4E-02 | 8.7E-07 | 4.5E-07 | 2.3E-08 | 1.3E-06 |
| P4            | 5.9E-03 | 2.1E-03 | 2.8E-03 | 1.1E-02 | 5.9E-07 | 2.1E-07 | 1.4E-07 | 9.4E-07 |
| P5            | 9.4E-03 | 5.2E-03 | 3.5E-03 | 1.8E-02 | 9.4E-07 | 5.2E-07 | 1.7E-07 | 1.6E-06 |
| P6            | 4.6E-02 | 2.3E-02 | 7.3E-03 | 7.6E-02 | 4.6E-06 | 2.3E-06 | 3.7E-07 | 7.2E-06 |
| P7            | 2.1E-03 | 1.7E-03 | 4.5E-04 | 4.3E-03 | 2.1E-07 | 1.7E-07 | 2.3E-08 | 4.1E-07 |
| P8            | 1.1E-02 | 7.3E-03 | 3.8E-03 | 2.2E-02 | 1.1E-06 | 7.3E-07 | 1.9E-07 | 2.0E-06 |
| P9            | 6.3E-03 | 2.8E-03 | 4.5E-04 | 9.5E-03 | 6.3E-07 | 2.8E-07 | 2.3E-08 | 9.3E-07 |
| H1            | 1.9E-02 | 1.7E-02 | 8.0E-03 | 4.4E-02 | 1.9E-06 | 1.7E-06 | 4.0E-07 | 4.0E-06 |
| H2            | 1.3E-02 | 1.1E-02 | 4.5E-04 | 2.4E-02 | 1.3E-06 | 1.1E-06 | 2.3E-08 | 2.4E-06 |
| H3            | 7.0E-03 | 1.5E-02 | 1.1E-02 | 3.3E-02 | 7.0E-07 | 1.5E-06 | 5.4E-07 | 2.7E-06 |
| H4            | 9.8E-03 | 1.3E-02 | 4.5E-04 | 2.3E-02 | 9.8E-07 | 1.3E-06 | 2.3E-08 | 2.3E-06 |
| H5            | 4.2E-04 | 9.8E-03 | 4.5E-04 | 1.1E-02 | 4.2E-08 | 9.8E-07 | 2.3E-08 | 1.0E-06 |
| H6            | 1.5E-02 | 1.4E-02 | 9.1E-03 | 3.8E-02 | 1.5E-06 | 1.4E-06 | 4.5E-07 | 3.8E-06 |
| Sites          | Toxic Units | BDE-28 (ng/L) | BDE-47 (ng/L) | BDE-99 (ng/L) | BDE-100 (ng/L) | BDE-153 (ng/L) | BDE-154 (ng/L) | BDE-183 (ng/L) |
|---------------|-------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| P1            | Tijalg × 10^{-5} | 0.68 | 5.36 | 12.50 | 5.00 | 22.86 | 2.57 | 5.62 | 0.05 |
|               | Tijaphy × 10^{-3} | 2.25 | 25.00 | 75.00 | 30.00 | 221.91 | 24.97 | 71.94 | 0.45 |
|               | Tijlas × 10^{-3} | 1.82 | 21.43 | 75.00 | 30.00 | 230.88 | 25.97 | 80.65 | 0.47 |
|               | MEC/min(EC50) × 10^{-3} | 2.25 | 25.00 | 75.00 | 30.00 | 230.88 | 25.97 | 80.65 | 0.47 |
| P2            | Tijalg × 10^{-5} | 0.02 | 2.50 | 5.83 | 0.38 | 10.00 | 2.57 | 5.62 | 0.03 |
|               | Tijaphy × 10^{-3} | 0.08 | 11.67 | 35.00 | 2.25 | 97.09 | 24.97 | 71.94 | 0.24 |
|               | Tijlas × 10^{-3} | 0.06 | 10.00 | 35.00 | 2.25 | 101.01 | 25.97 | 80.65 | 0.25 |
|               | MEC/min(EC50) × 10^{-3} | 0.08 | 11.67 | 35.00 | 2.25 | 101.01 | 25.97 | 80.65 | 0.26 |
| P3            | Tijalg × 10^{-5} | 0.82 | 2.98 | 5.42 | 5.00 | 1.86 | 2.57 | 5.62 | 0.02 |
|               | Tijaphy × 10^{-3} | 2.70 | 13.89 | 32.50 | 30.00 | 18.03 | 24.97 | 71.94 | 0.19 |
|               | Tijlas × 10^{-3} | 2.18 | 11.90 | 32.50 | 30.00 | 18.76 | 25.97 | 80.65 | 0.20 |
|               | MEC/min(EC50) × 10^{-3} | 2.70 | 13.89 | 32.50 | 30.00 | 18.76 | 25.97 | 80.65 | 0.20 |
| P4            | Tijalg × 10^{-5} | 0.02 | 2.02 | 2.50 | 3.75 | 11.43 | 2.57 | 5.62 | 0.03 |
|               | Tijaphy × 10^{-3} | 0.08 | 9.44 | 15.00 | 22.50 | 110.96 | 24.97 | 71.94 | 0.24 |
|               | Tijlas × 10^{-3} | 0.06 | 8.10 | 15.00 | 22.50 | 115.44 | 25.97 | 80.65 | 0.27 |
|               | MEC/min(EC50) × 10^{-3} | 0.08 | 9.44 | 15.00 | 22.50 | 115.44 | 25.97 | 80.65 | 0.27 |
| P5            | Tijalg × 10^{-5} | 0.79 | 3.21 | 6.25 | 7.08 | 14.29 | 14.29 | 56.18 | 0.10 |
|               | Tijaphy × 10^{-3} | 2.58 | 15.00 | 37.50 | 42.50 | 138.70 | 138.70 | 719.42 | 1.09 |
|               | Tijlas × 10^{-3} | 2.09 | 12.86 | 37.50 | 42.50 | 144.30 | 144.30 | 806.45 | 1.19 |
|               | MEC/min(EC50) × 10^{-3} | 2.58 | 15.00 | 37.50 | 42.50 | 144.30 | 144.30 | 806.45 | 1.19 |
| P6            | Tijalg × 10^{-5} | 4.66 | 15.60 | 27.08 | 27.50 | 30.00 | 25.71 | 61.80 | 0.19 |
|               | Tijaphy × 10^{-3} | 15.28 | 72.78 | 162.50 | 165.00 | 291.26 | 249.65 | 791.37 | 1.75 |
|               | Tijlas × 10^{-3} | 12.36 | 62.38 | 162.50 | 165.00 | 303.03 | 259.74 | 887.10 | 1.85 |
|               | MEC/min(EC50) × 10^{-3} | 15.28 | 72.78 | 162.50 | 165.00 | 303.03 | 259.74 | 887.10 | 1.87 |
| P7            | Tijalg × 10^{-5} | 0.02 | 0.71 | 2.08 | 0.38 | 1.86 | 2.57 | 5.62 | 0.01 |
|               | Tijaphy × 10^{-3} | 0.08 | 3.33 | 12.50 | 2.25 | 18.03 | 24.97 | 71.94 | 0.13 |
|               | Tijlas × 10^{-3} | 0.06 | 2.86 | 12.50 | 2.25 | 18.76 | 25.97 | 80.65 | 0.14 |
|               | MEC/min(EC50) × 10^{-3} | 0.08 | 3.33 | 12.50 | 2.25 | 18.76 | 25.97 | 80.65 | 0.14 |
| P8            | Tijalg × 10^{-5} | 0.89 | 3.81 | 8.75 | 9.17 | 15.71 | 15.71 | 50.56 | 0.10 |
|               | Tijaphy × 10^{-3} | 2.92 | 17.78 | 52.50 | 55.00 | 152.57 | 152.57 | 647.48 | 1.08 |
|               | Tijlas × 10^{-3} | 2.36 | 15.24 | 52.50 | 55.00 | 158.73 | 158.73 | 725.81 | 1.17 |
|               | MEC/min(EC50) × 10^{-3} | 2.92 | 17.78 | 52.50 | 55.00 | 158.73 | 158.73 | 725.81 | 1.17 |
| P9            | Tijalg × 10^{-5} | 0.48 | 2.14 | 3.33 | 5.00 | 1.86 | 2.57 | 5.62 | 0.02 |
|               | Tijaphy × 10^{-3} | 1.57 | 10.00 | 20.00 | 30.00 | 18.03 | 24.97 | 71.94 | 0.18 |
|               | Tijlas × 10^{-3} | 1.27 | 8.57 | 20.00 | 30.00 | 18.76 | 25.97 | 80.65 | 0.19 |
|               | MEC/min(EC50) × 10^{-3} | 1.57 | 10.00 | 20.00 | 30.00 | 18.76 | 25.97 | 80.65 | 0.19 |

Table S13. The values of PNEC for fish, daphnia and green algae.

| PNEC fish (ng/L) | daphnia (ng/L) | green algae (ng/L) |
|-----------------|----------------|-------------------|
| BDE-28          | 110            | 89                |
| BDE-47          | 21             | 18                |
| BDE-100         | 4              | 4                 |
| BDE-99          | 4              | 4                 |
| BDE-154         | 0.693          | 0.721             |
| BDE-153         | 0.693          | 0.721             |
| BDE-183         | 0.124          | 0.139             |
| BDE-209         | 0.000656       | 0.000947          |

Table S14. The base set of acute toxicity for the calculation of MRQ_{MEC/PNEC} and MRQ_{STU}.
|   | TU algae × 10^{-3} | TU daphnids × 10^{-3} | TU fish × 10^{-3} | MEC/min(EC50) × 10^{-3} |
|---|---------------------|------------------------|------------------|-------------------------|
| H1 | 0.55 6.43 20.00 6.25 32.86 2.57 5.62 0.07 | 1.80 30.00 120.00 37.50 319.00 24.97 71.94 0.61 | 1.45 25.71 120.00 37.50 331.89 25.97 80.65 0.62 | 1.80 30.00 120.00 37.50 331.89 25.97 80.65 0.63 |
| H2 | 0.02 4.29 13.33 0.38 1.86 2.57 5.62 0.03 | 0.08 20.00 80.00 2.25 18.03 24.97 71.94 0.22 | 0.06 17.14 80.00 2.25 18.76 25.97 80.65 0.22 | 0.08 20.00 80.00 2.25 18.76 25.97 80.65 0.23 |
| H3 | 0.02 2.38 17.92 0.38 44.29 2.57 5.62 0.07 | 0.08 11.11 107.50 2.25 429.96 24.97 71.94 0.65 | 0.06 9.52 107.50 2.25 447.33 25.97 80.65 0.67 | 0.08 11.11 107.50 2.25 447.33 25.97 80.65 0.67 |
| H4 | 0.02 5.24 16.25 0.38 13.33 2.57 5.62 0.07 | 0.08 24.44 97.50 2.25 360.61 24.97 71.94 0.58 | 0.06 13.33 90.00 2.25 18.76 25.97 80.65 0.60 | 0.08 24.44 97.50 2.25 360.61 24.97 71.94 0.58 |
| H5 | 0.02 0.14 11.25 0.38 1.86 2.57 5.62 0.02 | 0.08 0.67 70.00 2.25 18.03 24.97 71.94 0.19 | 0.06 0.57 70.00 2.25 18.76 25.97 80.65 0.20 | 0.08 0.67 70.00 2.25 18.76 25.97 80.65 0.20 |
| H6 | 0.02 3.33 15.00 0.38 1.86 2.57 5.62 0.07 | 0.08 15.56 90.00 2.25 18.03 24.97 71.94 0.22 | 0.06 13.33 90.00 2.25 18.76 25.97 80.65 0.22 | 0.08 15.56 90.00 2.25 18.76 25.97 80.65 0.23 |
| H7 | 0.02 0.14 11.25 0.38 1.86 2.57 5.62 0.07 | 0.08 0.67 67.50 2.25 18.03 24.97 71.94 0.19 | 0.06 0.57 67.50 2.25 18.76 25.97 80.65 0.20 | 0.08 0.67 67.50 2.25 18.76 25.97 80.65 0.20 |
| H8 | 0.02 0.14 11.25 0.38 1.86 2.57 5.62 0.02 | 0.08 0.67 70.00 2.25 18.03 24.97 71.94 0.19 | 0.06 0.57 70.00 2.25 18.76 25.97 80.65 0.20 | 0.08 0.67 70.00 2.25 18.76 25.97 80.65 0.20 |
| H9 | 0.02 5.48 18.75 0.38 1.86 2.57 5.62 0.07 | 0.08 25.56 112.50 2.25 18.03 24.97 71.94 0.26 | 0.06 21.90 112.50 2.25 18.76 25.97 80.65 0.26 | 0.08 25.56 112.50 2.25 18.76 25.97 80.65 0.27 |
| W1 | 0.02 3.69 9.17 6.67 1.86 2.57 5.62 0.03 | 0.08 17.22 55.00 40.00 18.03 24.97 71.94 0.23 | 0.06 14.76 55.00 40.00 18.76 25.97 80.65 0.24 | 0.08 17.22 55.00 40.00 18.76 25.97 80.65 0.24 |
| W2 | 0.02 3.10 13.33 0.38 32.86 2.57 5.62 0.06 | 0.08 14.44 80.00 2.25 319.00 24.97 71.94 0.51 | 0.06 12.38 80.00 2.25 331.89 25.97 80.65 0.53 | 0.08 14.44 80.00 2.25 331.89 25.97 80.65 0.54 |
| W3 | 0.02 2.50 9.58 0.38 1.86 2.57 5.62 0.02 | 0.08 11.67 57.50 2.25 18.03 24.97 71.94 0.19 | 0.06 10.00 57.50 2.25 18.76 25.97 80.65 0.20 | 0.08 11.67 57.50 2.25 18.76 25.97 80.65 0.20 |
| W4 | 0.02 4.52 10.83 0.38 1.86 2.57 5.62 0.03 | 0.08 21.11 65.00 2.25 18.03 24.97 71.94 0.20 | 0.06 18.10 65.00 2.25 18.76 25.97 80.65 0.21 | 0.08 21.11 65.00 2.25 18.76 25.97 80.65 0.21 |
| W5 | 0.02 0.14 8.33 0.38 1.86 2.57 5.62 0.02 | 0.08 0.67 50.00 2.25 18.03 24.97 71.94 0.17 | 0.06 0.57 50.00 2.25 18.76 25.97 80.65 0.18 | 0.08 0.67 50.00 2.25 18.76 25.97 80.65 0.18 |