On the basis of former reports\(^1\), modifications of QuEChERS method on mobile phase system and extraction procedures were as follows:

The mobile phase system used in QuEChERS was a mixture of hexane and dichloromethane which has been approved practicable for PBDEs extraction and elution from various solids\(^2-5\). The mobile phase system was optimized at three gradients: hexane: dichloromethane=25:75, 50:50, and 75:25. To achieve the purpose of raising recoveries and elimination co-elutes, 50:50 was applied for the extraction solvent composition. For extraction procedure, labelled standards were spiked for each parameter optimization. Extraction time was optimized at 3, 5 and 7 min each cycle for total 3 cycles. Results showed extension of extraction time could not improve extraction efficiency. Five min/cycle for 3 cycles provided satisfying method performances.

References

Table S1 Reference Mass Fraction Values for Selected PBDEs in SRM 1944 & 2585.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Mass Fractions (ng/g Dry Mass Basis, d.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRM 1944</td>
</tr>
<tr>
<td>BDE-28</td>
<td>—</td>
</tr>
<tr>
<td>BDE-47</td>
<td>1.72±0.28</td>
</tr>
<tr>
<td>BDE-99</td>
<td>1.98±0.26</td>
</tr>
<tr>
<td>BDE-100</td>
<td>0.447±0.027</td>
</tr>
<tr>
<td>BDE-153</td>
<td>6.44±0.37</td>
</tr>
<tr>
<td>BDE-154</td>
<td>1.06±0.08</td>
</tr>
<tr>
<td>Compounds</td>
<td>MRM transitions (m/z)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>BDE-28</td>
<td>287 &gt; 121</td>
</tr>
<tr>
<td></td>
<td>287 &gt; 135</td>
</tr>
<tr>
<td>BDE-47</td>
<td>483 &gt; 325</td>
</tr>
<tr>
<td></td>
<td>325 &gt; 217</td>
</tr>
<tr>
<td>BDE-99</td>
<td>405 &gt; 297</td>
</tr>
<tr>
<td></td>
<td>403 &gt; 297</td>
</tr>
<tr>
<td>BDE-100</td>
<td>405 &gt; 297</td>
</tr>
<tr>
<td></td>
<td>403 &gt; 297</td>
</tr>
<tr>
<td>BDE-153</td>
<td>483 &gt; 376</td>
</tr>
<tr>
<td></td>
<td>643 &gt; 483</td>
</tr>
<tr>
<td>BDE-154</td>
<td>483 &gt; 376</td>
</tr>
<tr>
<td></td>
<td>643 &gt; 483</td>
</tr>
</tbody>
</table>
Table S3 The concentrations of detected PBDEs in 3 sampling locations using ultrasonication-assisted QuEChERS and SPLE. (UA-Q: ultrasonication-assisted QuEChERS; N.D.: Non-detected means a signal-to-noise ratio <10).

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UA-Q</td>
<td>SPLE</td>
<td>UA-Q</td>
</tr>
<tr>
<td>BDE-28</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>BDE-47</td>
<td>11.4±0.50</td>
<td>13.6±0.45</td>
<td>N.D.</td>
</tr>
<tr>
<td>BDE-99</td>
<td>34.2±0.76</td>
<td>33.7±0.49</td>
<td>1.15±0.05</td>
</tr>
<tr>
<td>BDE-100</td>
<td>1.56±0.22</td>
<td>1.47±0.04</td>
<td>N.D.</td>
</tr>
<tr>
<td>BDE-153</td>
<td>0.77±0.04</td>
<td>0.99±0.03</td>
<td>N.D.</td>
</tr>
<tr>
<td>BDE-154</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
</tbody>
</table>
**Figure S1** The sampling positions and detailed information. (Sample 1&2 were collected from canals in use; Sample 3 were collected from an impounding reservoir which was abandoned several years ago).