

On the basis of former reports¹, 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 solids²⁻⁵. 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

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

Chemicals	Mass Fractions (ng/g Dry Mass Basis, d.w.)	
	SRM 1944	SRM 2585
BDE-28	—	46.9±4.4
BDE-47	1.72±0.28	497±46
BDE-99	1.98±0.26	892±52
BDE-100	0.447±0.027	145±11
BDE-153	6.44±0.37	119±1.0
BDE-154	1.06±0.08	83.5±2.0

Table S2 The optimized MRM parameters for tandem mass spectrometry.

Compoun ds	MRM transitions(m/z)	Dwell time(s)	Collision(V)	Ion source (°C)	Electron energy (eV)
BDE-28	287>121	0.1	35	280	-70
	287>135		35		
BDE-47	483>325	0.1	20		
	325>217		35		
BDE-99	405>297	0.1	35		
	403>297		35		
BDE-100	405>297	0.1	35		
	403>297		35		
BDE-153	483>376	0.1	35		
	643>483		20		
BDE-154	483>376	0.1	35		
	643>483		20		

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).

Chemicals	Sample 1		Sample 2		Sample 3	
	UA-Q	SPLE	UA-Q	SPLE	UA-Q	SPLE
BDE-28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-47	11.4±0.50	13.6±0.45	N.D.	N.D.	21.1±0.38	24.4±0.31
BDE-99	34.2±0.76	33.7±0.49	1.15±0.05	0.95±0.03	27.7±0.36	28.7±0.53
BDE-100	1.56±0.22	1.47±0.04	N.D.	N.D.	0.99±0.08	0.86±0.02
BDE-153	0.77±0.04	0.99±0.03	N.D.	N.D.	2.02±0.08	2.14±0.31
BDE-154	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

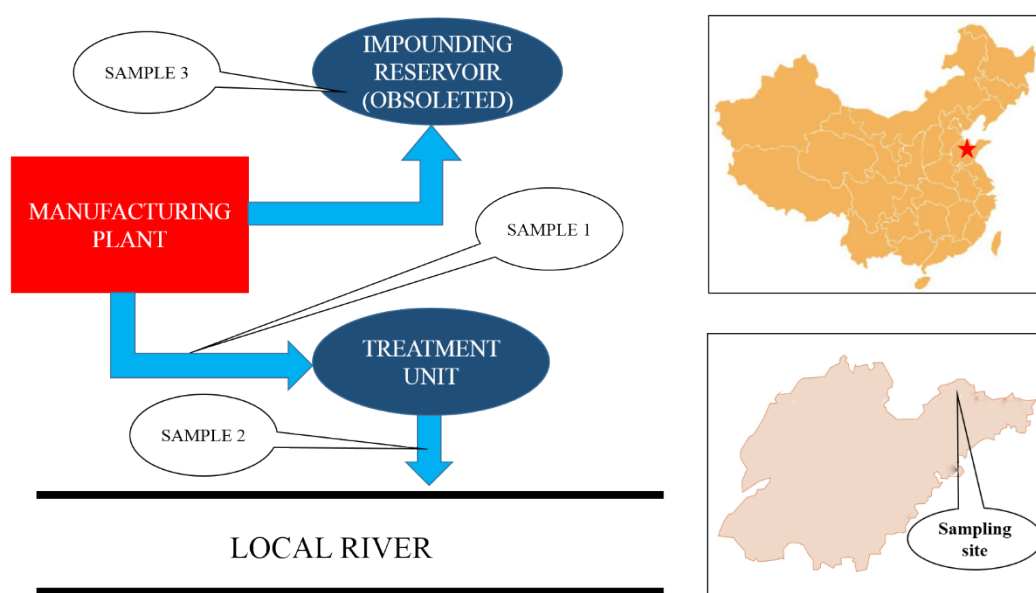


Figure S1 The sampling positions and detailed information. (Sample 1&2 were collected from canals in use; Sample 3 were collected from an impounding reservoir which was abandoned several years ago).