Sinking behavior of micro-nano particulate matter for bisphenol analogues in the surface water of an ecological demonstration zone, China

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2.4 Quality assurance and quality control

The extraction efficiency of BPs from the water samples was examined by a strict QA/QC protocol. With each set of samples to be analyzed, a solvent blank, a membrane and a procedure blank were run in sequence to check for background BPs, peak identification and quantification. The performance of analytical methods was evaluated in terms of linearity, Limits of detection (LOD) and quantification (LOQ) and recoveries. LOD and LOQ were determined as the minimum detectable amount of an analyte with a signal-to-noise (S/N) of 3 and 10, respectively. The linearity of the target compounds was also studied by injecting different concentrations (seven-point calibration curves) of standard solutions in the 1.0-200 ng/mL range ($R^2 > 0.998$). To evaluate the recoveries of water and SPM, spiked samples were prepared using surface water and sediment of Yangtze River. Before use, the surface water sample and sediment used for recovery test was analyzed for the presence of BPs. The recovery data for BPs were corrected to account for this fact, i.e. average blank peak area of BPs was subtracted from average peak areas of other recovery points. Six independent chromatographic runs were carried out for each of two concentration levels. Obtained recoveries were presented in Table S4. Analysis of reagent blanks (n = 3) demonstrated that the analytical system and glassware were free of BPs.

2.5 Parameter measurement and statistical analysis

The risk assessment of target compounds in the surface water was evaluated using the risk quotient (RQ) estimation. The RQ_{Total} was calculated as Eq (1).

$$RQ_{Total} = \Sigma\frac{MEC}{PNEC} = \Sigma\frac{MEC}{EC50\ or\ LC50/f} \quad (1)$$

where MEC and PNEC are the measured environmental concentration and the predicted no effect concentration. To estimate a PNEC on the basis of toxicity data when only the short-term/acute toxicity data EC_{50} or LC_{50} are available, the calculation of PNEC is obtained from the EC_{50} or LC_{50} divided by a security factor (*f*) of 1000. Once the long-term/chronic NOEC values for one, two or three trophic levels are available, a *f* of 100, 50 or 10 is used (ECHA, 2008). The PNEC is derived from the chronic and acute toxicity data in literature by a *f* of 100 or 1000 in our study. The values of PNEC calculation for fish, daphnia and green algae were provided in the Table S6.

Calculation of the oestrogen equivalent concentration (EEQ) of a chemically determined mixture is based on all measured xenoestrogens with a known oestrogen equivalency factor (EEF; Table S6), as shown in the following equation (Eq (2)). Contaminants are thought to affect the endocrine systems of organisms in the water bodies when EEQ >1.0 ng E_2/L.

$$EEQ_{Total} = \Sigma EEQ_i = \Sigma(C_i \times EEF_i) \quad (2)$$

Where C_i refers to the compound *i* with concentration C in the truly dissolved phase, EEQ_{Total} is the total estradiol equivalent quantity and EEF_i is the estradiol equivalency factor.

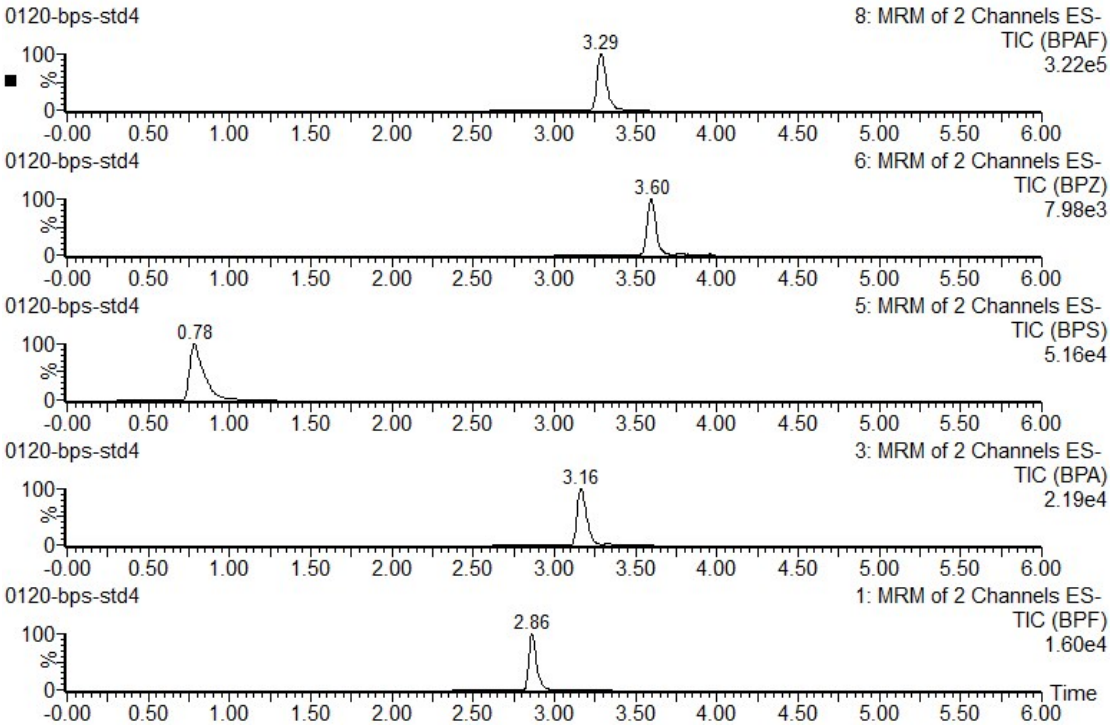

Figure S1. Representative chromatogram of BPs at concentration of 10 μg/L.

Table S1

Sampling sites	Study area	Longitude (°E)	Latitude (°N)
S1	Luting River	119.89222	32.664112
S2	Longxi Port	119.942764	32.57825
S3	Qinhu Lake	120.080025	32.638935
S4	Qinhu Lake	120.07943	32.61762
S5	Qinhu Lake	120.10093	32.624752
S6	Jiangqin River	119.91262	32.593544
S7	Tuanjie River-YanjingRiver	120.10329	32.68101
S8	Fengshou River-Hongmiao River	120.17716	32.586494
S9	East Jiangqin River	120.13501	32.60366
S10	West Jianghuang River	120.12988	32.375004
S11	Tongyang Canal	119.997055	32.586216
S12	Huangcun River	120.08544	32.588924
S13	Siheng River	120.09579	32.61161
S14	New Tongyang Canal	120.073	32.481976
S15	West Jianghuang River	120.176384	32.456966
S16	New Shengchan River	120.164474	32.41596
S17	East Jianghuang River	120.26685	32.467136
S18	Nangan River	120.0292202	32.43897906
S19	Yuejin River	120.252495	32.411575
S20	Maoshan River	119.985085	32.648396
S21	Taidong River	120.07154	32.566017
S22	Taidong River	120.071915	32.645847
S23	Zhoubian River	120.072716	32.663445
S24	Qindong River-Yanjingkang River	120.096596	32.6514
S25	Shedong River	119.86438	32.60696
S26	Jiangqin River	120.131744	32.570312
S27	New Tongyang Canal	120.22337	32.53705
S28	Tongyang Canal	120.223	32.509064
S29	Zhoushan River	120.016785	32.52461
S30	New Tongyang Canal	120.135864	32.53172
S31	Zhonggan River- West Jianghuang River	120.12737	32.4802
S32	Tongyang Canal	120.15739	32.51356
S33	Nangan River	120.04503	32.36462

Table S2

Time (min)	Composition of the mobile phase (%)	
Negative mode	Eluent A1 (0.01% Ammonium hydroxide)	Eluent B1 (Acetonitrile)
0	90	10
0.25	90	10
3.00	10	90
4.00	10	90
4.01	90	10
5.00	90	10

Table S3

Compound	Retention time (min)	Parent ion (m/z)	Daughter ions (m/z)	Dwell time (s)	Cone voltage (v)	Collision energy (v)
BPA	3.16	227.10	133.00	0.042	31	25
			212.00*			17
BPF	2.86	199.10	93.10	0.042	30	20
			105.10*			20
BPS	0.78	249.13	92.05	0.161	42	30
			108.07*			24
BPZ	3.60	267.22	93.02	0.042	56	32
			173.17*			30
BPAF	3.29	335.23	197.10	0.042	32	25
			265.16*			22

* represents quantification ion.

Table S4

Compound	Recovery [%] (n = 6)				Detection and quantitation limits (n = 3)	
	Surface water		SPM		LOD (ng/L)	LOQ (ng/L)
	10 ng/L	100 ng/L	10 ng/g	100 ng/g		
BPA	92.1±10.1	93.1±11.2	119.2±17.1	122.7±10.4	2.42	8.60
BPF	90.0±10.5	93.8±9.4	82.4±10.5	93.1±14.7	6.63	20.74
BPS	85.3±7.0	82.4±12.3	75.2±5.3	82.7±3.5	1.46	5.37
BPZ	79.2±6.6	84.6±11.0	70.5±8.1	80.2±6.9	3.32	10.67
BPAF	94.3±13.3	92.3±6.3	85.2±13.6	92.3±17.7	0.50	1.70

Table S5

Compound	Non-target organism	Test Endpoint	Toxicity data (mg/L)	PNEC (ng/L)	Reference	EEF Ref. (Ruan et al., 2015)
BPA	Pseudokirchneriella	72h-EC50	2.2 (Growth)	2200	Debenest et al., 2010	1.07×10^{-4}
	Daphnia magna	48h-EC50	3.9 (Immobility)	3900	Staples et al., 1998	
	Danio rerio	48h-EC50	3.6 (Pigmentation)	3600	Tišler et al., 2016	
	Algae	96h-EC50	6.9	6900	US EPA, 2011[a]	
BPS	Daphnia magna	48h-EC50	55 (Immobility)	55000	Chen et al., 2002	1.06×10^{-6}
	Zebrafish Larvae	72hpf-EC50	155 (Hatching success)	155000	Moreman et al., 2017	
BPF	Desmodesmus subspicatus	72h-IC50	22.1 (Growth)	22100	Tišler et al., 2016	1.08×10^{-4}
	Daphnia magna	21d-NOEC	0.84 (Reproduction)	8400	Tišler et al., 2016	
	Danio rerio	48h-EC50	1.1 (Pigmentation)	1100	Tišler et al., 2016	
BPAF	Desmodesmus subspicatus	72h-IC50	3.0 (Growth)	3000	Tišler et al., 2016	7.23×10^{-4}
	Daphnia magna	21d-NOEC	0.23 (Reproduction)	2300	Tišler et al., 2016	
	Zebrafish Larvae	72hpf-EC50	0.92 (Mortality)	920	Moreman et al., 2017	

[a] The toxicity data was calculated from the ecological structure activity relationships (ECOSAR) model.

Table S6

Sampling sites	RQ for algae				RQ for Daphnias				RQ for fish			
	BPA	BPF	BPS	BPAF	BPA	BPF	BPS	BPAF	BPA	BPF	BPS	BPAF
S1	0.2219	0.0000	0.0048	0.0028	0.1252	0.0000	0.0006	0.0037	0.1356	0.0000	0.0002	0.0092
S2	0.1406	0.0005	0.0081	0.0043	0.0793	0.0014	0.0010	0.0055	0.0859	0.0109	0.0004	0.0139
S3	0.1743	0.0032	0.0067	0.0045	0.0983	0.0084	0.0008	0.0059	0.1065	0.0643	0.0003	0.0147
S4	0.0718	0.0000	0.0062	0.0091	0.0405	0.0000	0.0008	0.0118	0.0439	0.0000	0.0003	0.0296
S5	0.0343	0.0015	0.0024	0.0010	0.0194	0.0040	0.0003	0.0013	0.0210	0.0309	0.0001	0.0033
S6	0.0698	0.0000	0.0026	0.0008	0.0394	0.0000	0.0003	0.0011	0.0426	0.0000	0.0001	0.0027
S7	0.0274	0.0002	0.0005	0.0010	0.0155	0.0005	0.0001	0.0013	0.0168	0.0038	0.0000	0.0032
S8	0.0271	0.0003	0.0005	0.0007	0.0153	0.0007	0.0001	0.0009	0.0166	0.0055	0.0000	0.0023
S9	0.0089	0.0000	0.0034	0.0033	0.0050	0.0000	0.0004	0.0043	0.0054	0.0000	0.0002	0.0109
S10	0.0105	0.0000	0.0038	0.0083	0.0059	0.0000	0.0005	0.0109	0.0064	0.0000	0.0002	0.0272
S11	0.0856	0.0000	0.0067	0.0028	0.0483	0.0000	0.0008	0.0037	0.0523	0.0000	0.0003	0.0092
S12	0.2502	0.0011	0.0025	0.0010	0.1412	0.0030	0.0003	0.0013	0.1529	0.0227	0.0001	0.0033
S13	0.2314	0.0016	0.0047	0.0059	0.1305	0.0042	0.0006	0.0077	0.1414	0.0323	0.0002	0.0193
S14	0.0625	0.0000	0.0020	0.0025	0.0353	0.0000	0.0003	0.0033	0.0382	0.0000	0.0001	0.0082
S15	0.2820	0.0011	0.0099	0.0049	0.1591	0.0028	0.0012	0.0064	0.1724	0.0214	0.0004	0.0160
S16	0.1723	0.0006	0.0050	0.0073	0.0972	0.0017	0.0006	0.0095	0.1053	0.0127	0.0002	0.0236
S17	0.2798	0.0006	0.0088	0.0022	0.1578	0.0017	0.0011	0.0028	0.1710	0.0127	0.0004	0.0071
S18	0.2461	0.0014	0.0071	0.0040	0.1388	0.0037	0.0009	0.0052	0.1504	0.0282	0.0003	0.0130
S19	0.1778	0.0079	0.0071	0.0031	0.1003	0.0208	0.0009	0.0040	0.1087	0.1585	0.0003	0.0101
S20	0.1581	0.0003	0.0050	0.0062	0.0892	0.0008	0.0006	0.0080	0.0966	0.0059	0.0002	0.0201
S21	0.3191	0.0009	0.0073	0.0057	0.1800	0.0023	0.0009	0.0074	0.1950	0.0177	0.0003	0.0185
S22	0.2925	0.0052	0.0046	0.0057	0.1650	0.0137	0.0006	0.0074	0.1788	0.1045	0.0002	0.0185
S23	0.3105	0.0005	0.0121	0.0090	0.1751	0.0014	0.0015	0.0117	0.1897	0.0109	0.0005	0.0293
S24	0.1616	0.0030	0.0064	0.0043	0.0912	0.0078	0.0008	0.0055	0.0988	0.0595	0.0003	0.0139
S25	0.0480	0.0002	0.0011	0.0011	0.0271	0.0004	0.0001	0.0014	0.0293	0.0032	0.0000	0.0035
S26	0.1693	0.0053	0.0044	0.0048	0.0955	0.0140	0.0006	0.0063	0.1035	0.1068	0.0002	0.0158
S27	0.2259	0.0076	0.0086	0.0035	0.1274	0.0201	0.0011	0.0046	0.1381	0.1532	0.0004	0.0114
S28	0.3114	0.0006	0.0053	0.0042	0.1756	0.0015	0.0007	0.0054	0.1903	0.0114	0.0002	0.0136
S29	0.1500	0.0014	0.0107	0.0034	0.0846	0.0036	0.0013	0.0044	0.0917	0.0277	0.0005	0.0110
S30	0.1050	0.0004	0.0023	0.0041	0.0592	0.0009	0.0003	0.0053	0.0642	0.0070	0.0001	0.0133
S31	0.2143	0.0019	0.0025	0.0030	0.1209	0.0050	0.0003	0.0039	0.1310	0.0382	0.0001	0.0098
S32	0.2584	0.0046	0.0051	0.0160	0.1458	0.0121	0.0006	0.0209	0.1579	0.0923	0.0002	0.0522
S33	0.2735	0.0122	0.0088	0.0050	0.1543	0.0322	0.0011	0.0065	0.1671	0.2460	0.0004	0.0162

Yellow area represents $0.01 < RQ < 0.1$,

Red area represents $0.1 < RQ < 1$.

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