

## **Analytical and Bioanalytical Chemistry**

### **Electronic Supplementary Material**

#### **Simultaneous analysis of 45 pharmaceuticals and personal care products in sludge by matrix solid-phase dispersion and liquid chromatography tandem mass spectrometry**

Mingyue Li, Qian Sun, Yan Li, Min Lv, Lifeng Lin, Yang Wu, Muhammad Ashfaq,  
Chang-ping Yu

**Table S1** Commercial use, physicochemical properties and MS parameters of the target PPCPs

PPCPs	Commercial use	LogK <sub>ow</sub>	pK <sub>a</sub>	RT1 (min)	RT2 (min)	MS parameters						
						Mode	DP	EP	CEP	CX P	CE (P1/P2)	Precursor ions/ Quantification ions, confirmation ions
Sulfamerazine	Antibiotics		2.17; 6.77 <sup>a</sup>	7.53	7.48	Positive	41	6.0	16	2	35/24	265/108, 156
Sulfameter	Antibiotics			8.34	8.34	Positive	56	3.5	16	4	35/27	281/ 92, 156
Sulfamethoxazole	Antibiotics	0.89 <sup>c</sup>	1.83; 5.57 <sup>a</sup>	9.51	9.46	Positive	51	4.5	16	5	30/24	254/ 92, 156
Sulfadimethoxine	Antibiotics		1.87; 5.86 <sup>a</sup>	11.93	11.91	Positive	56	10.5	14	4	27/25	311/ 156, 218
Ofloxacin	Antibiotics	-0.39 <sup>f</sup>	5.20; 6.20; 8.20 <sup>a</sup>	8.65	8.65	Positive	65	7.0	20	8	40/40	358/ 340, 280
Sarafloxacin	Antibiotics		5.62; 8.18 <sup>a</sup>	10.49	10.55	Positive	67	3.0	20	8	35/35	386/ 268, 299
Oxytetracycline	Antibiotics	-0.90 <sup>d</sup>	3.04; 8.00 <sup>a</sup>	8.80	8.73	Positive	45	8.0	23	17	25/25	461/426, 444
Tetracycline	Antibiotics		3.32; 7.78; 9.58 <sup>a</sup>	8.52	8.53	Positive	20	10.0	22	5	25/30	445/427, 410
Ketoprofen	NSAIDs	3.12 <sup>f</sup>	4.36 <sup>a</sup>	4.33	4.36	Negative	-25	-8.0	-16	-4	-10/-14	253/ 209, 197
Naproxen	NSAIDs	3.18 <sup>f</sup>	4.16 <sup>a</sup>	4.31	4.36	Negative	-30	-7.5	-12	-2	-38/-15	229/ 169, 185
Fenoprofen	NSAIDs			4.86	4.91	Negative	-20	-3.0	-16	-2	-12/-27	241/ 197, 93
Diclofenac	NSAIDs	4.51 <sup>f</sup>	4.21 <sup>a</sup>	5.22	5.25	Negative	-30	-4.5	-18	-2	-18/-36	294/ 250, 214
Ibuprofen	NSAIDs	3.97 <sup>f</sup>	4.51 <sup>a</sup>	5.55	5.61	Negative	-30	-10.0	-14	-2	-10/-10	205/ 161, 159
Codeine	NSAIDs		8.21 <sup>b</sup>	5.94	5.91	Positive	91	4.5	24	4	85/48	300/ 152, 165
Acetaminophen	NSAIDs	0.46 <sup>d</sup>	9.78 <sup>c</sup>	5.93	5.94	Positive	61	4.5	12	4	21/29	152/ 110, 93
Antipyrine	NSAIDs			9.81	9.76	Positive	61	3.0	10	8	45/38	189/ 55, 76
Propyphenazone	NSAIDs			12.86	12.85	Positive	86	11.0	14	4	49/38	31/189,201
Ethenzamide	NSAIDs	1.40 <sup>h</sup>	8.79, 6.30 <sup>h</sup>	11.96	11.91	Positive	31	9.0	10	4	25/15	166/ 121, 149
Indomethacine	NSAIDs			14.21	14.23	Positive	61	4.5	16	4	27/19	358/ 139, 174
Crotamiton	NSAIDs			13.52	13.55	Positive	61	7.0	12	6	33/29	204/ 69, 136
Clofibrac acid	Lipid regulator	2.72 <sup>h</sup>	3.37 <sup>h</sup>	4.13	4.11	Negative	-25	-10.0	18	-2	-22/-22	213/ 126, 84

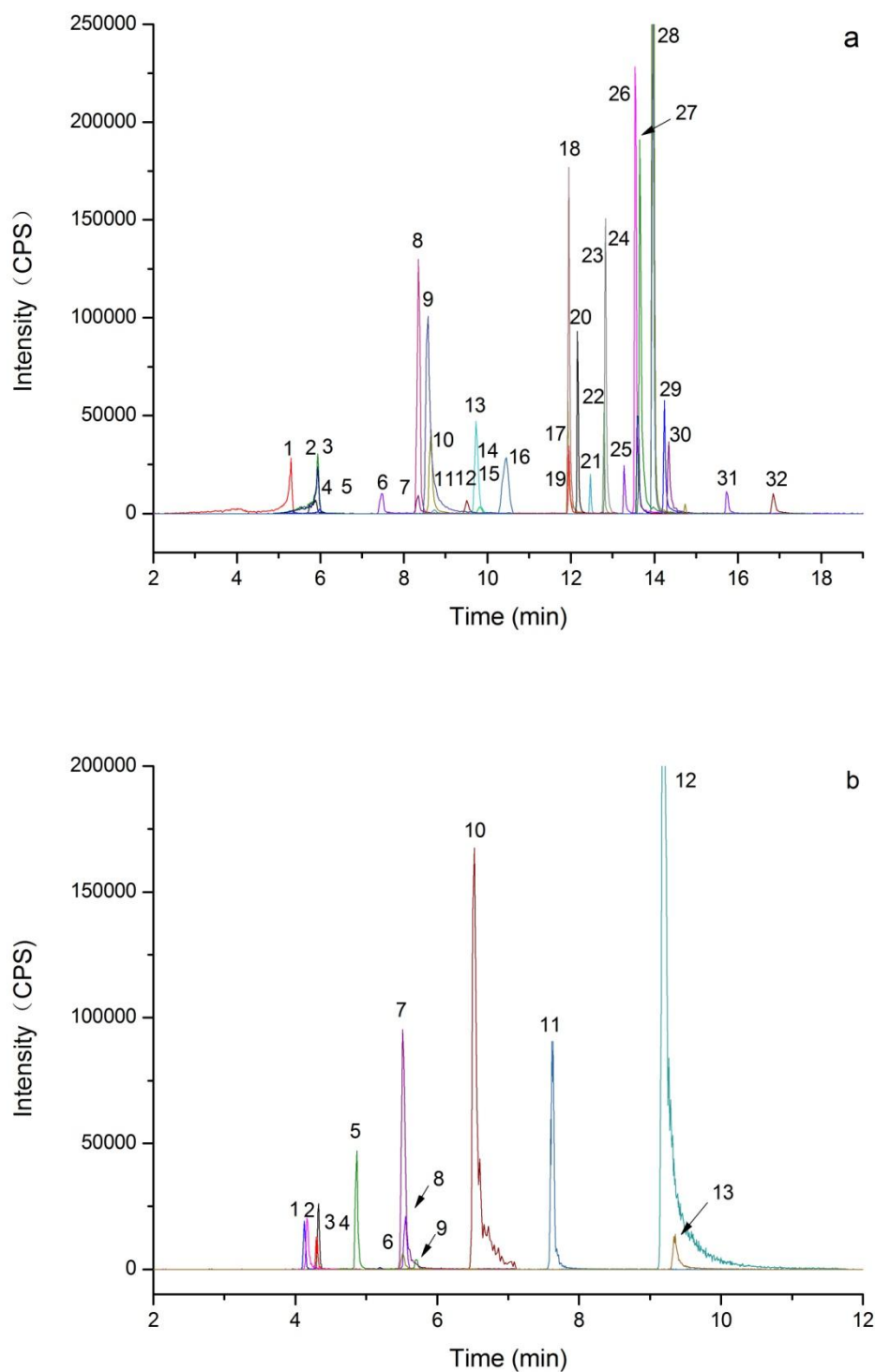
Gemfibrozil	Lipid regulator	3.40 <sup>g</sup>		7.63	7.65	Negative	-35	-7.5	-14	-2	-20/-20	249/121, 126
Pirenzepine	Ulcer drug			8.38	8.31	Positive	51	9.0	16	4	27/34	352/ 113, 69
Miconazole	Anti-fungal	6.20 <sup>i</sup>		13.71	13.66	Positive	91	10.5	22	4	41/28	427/ 159, 329
Carbamazepine	Anticonvulsant	2.45 <sup>f</sup>	13.9 <sup>d</sup>	12.91	12.84	Positive	56	6.0	14	4	27/38	237/ 194, 192
Sildenafil	Sexual function agent			12.58	12.56	Positive	106	8.0	23	4	48/49	475/ 283, 100
Fluoxetine	Antidepressant			12.73	12.76	Positive	101	3.5	18	4	31/16	310/ 43, 148
Loratadine	Antiallergic agent			14.12	14.15	Positive	60.5	11.0	19	6	33/40	383/ 337, 267
Diazepam	Anxiolytic			13.62	13.63	Positive	81	3.4	14	3	40/40	285/ 154, 193
Clenbuterol	$\beta$ -sympathomimetic			9.73	9.76	Positive	71	4.5	18	4	21/33	277/ 203, 168
Sotalol	$\beta$ -blocks	0.24 <sup>f</sup>	11.2 <sup>a</sup>	5.31	5.31	Positive	36	4.0	14	4	35/16	273/ 133, 255
Metoprolol	$\beta$ -blocks	1.69 <sup>f</sup>	9.44 <sup>a</sup>	6.01	6.08	Positive	41	9.5	18	4	35/27	268/ 145, 191
Atenolol	$\beta$ -blocks	0.16 <sup>f</sup>	9.42 <sup>a</sup>	6.03	6.06	Positive	51	1.5	12	4	35/39	267/145, 133
Propranolol	$\beta$ -blocks	3.48 <sup>g</sup>	11.2 <sup>a</sup>	12.20	12.24	Positive	51	4.0	18	4	39/30	260/ 55, 116
Methyl paraben	Preservative	1.91 <sup>g</sup>	8.30 <sup>i</sup>	4.16	4.22	Negative	-49	-10.0	-9	-10	-28/-22	151/ 92, 136
Propyl paraben	Preservative	2.94 <sup>g</sup>		5.51	5.55	Negative	-60	-7.5	-12	0	-30/-30	179/ 92, 136
Benzyl paraben	Preservative			6.56	6.59	Negative	-45	-10.0	-16	0	-34/-30	227/ 92, 136
Camphor	UV filters			13.34	13.38	Positive	61	10.5	14	4	41/38	255/ 105, 97
Benzophenone-3	UV filters	3.80 <sup>i</sup>		14.32	14.35	Positive	61	4.5	14	4	23/28	229/ 151, 105
Octocrylene	UV filters			16.83	16.82	Positive	61	9.0	24	6	27/27	363/ 232, 251
Triclocarban	Antimicrobials	3.50 <sup>g</sup>		9.18	9.12	Negative	-40	-12.0	-24	-3	-18/-18	313/160, 126
Triclosan	Antimicrobials	4.98 <sup>g</sup>		9.33	9.31	Negative	-45	-6.5	-18	-8	-22/-22	288/ 35, 37
Bisphenol A	Plasticizer	3.32 <sup>g</sup>		5.53	5.52	Negative	-20	-10.0	-21	-5	-30/-32	227/ 211, 133
Acetophenone	Fragrance			11.94	11.94	Positive	71	12.0	10	4	25/26	121/ 77, 91
Thiabendazole	Fungicide			8.61	8.56	Positive	66	4.5	12	4	35/44	202/ 175, 131

a: Babić S, Horvat AJM, Pavlović DM, Kaštelan-Macan M. Determination of pKa values of active pharmaceutical ingredients. Trends Anal. Chem., 2007, 26:1043-1061.

- b:** Buckenmaier SMC, McCalley DV, Euerby MR. Determination of ionisation constants of organic bases in aqueous methanol solutions using capillary electrophoresis. *J. Chromatogr. A*, 2004, 1026:251-259.
- c:** Meloun M, Syrový T, Vrána A. The thermodynamic dissociation constants of losartan, paracetamol, phenylephrine and quinine by the regression analysis of spectrophotometric data. *Analytica chimica acta*, 2005, 533:97-110.
- d:** Jones OAH, Voulvoulis N, Lester JN. Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. *Water Res.*, 2002, 36:5013-5022.
- e:** Pavlovic DM, Perisa TPM, Babic S. Optimization of matrix solid-phase dispersion for liquid chromatography tandem mass spectrometry analysis of 12 pharmaceuticals in sediments. *J. Chromatogr. A*, 2012, 1258: 1-15.
- f:** Vieno NM, Härkki H, Tuhkanen T, Kronberg L. Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. *Environ. Sci. Technol.*, 2007, 41:5077-5084.
- g:** Caldas SS, Rombaldi C, de Oliveira Arias JL, Marube LC, Primel EG. Multi-residue method for determination of 58 pesticides, pharmaceuticals and personal care products in water using solvent demulsification dispersive liquid-liquid microextraction combined with liquid chromatography-tandem mass spectrometry. *Talanta*, 2016, 146:676-688.
- h:** Tanoue Rumi, Nomiyama K, Nakamura H, Hayashi T, Kim J, Isobe T, Shinohara R, Tanabe S. Simultaneous determination of polar pharmaceuticals and personal care products in biological organs and tissues. *J. Chromatogr. A*, 2014, 1355:193-205.
- i:** Cerqueira MBR, Guilherme JR, Caldas SS, Martins ML, Zanella R, Primel EG. Evaluation of the QuEChERS method for the extraction of pharmaceuticals and personal care products from drinking-water treatment sludge with determination by UPLC-ESI-MS/MS. *Chemosphere*, 107:74-82.

**Table S2** Gradient elution programs of LC in both positive and negative mode

Positive mode		Negative mode	
Time (min)	B (%)	Time (min)	B%
0.00	5	0.00	25
3.00	10	1.00	25
6.00	28	5.00	80
10.00	80	10.00	80
15.00	80	10.20	25
15.20	5	13.00	25
18.00	5		

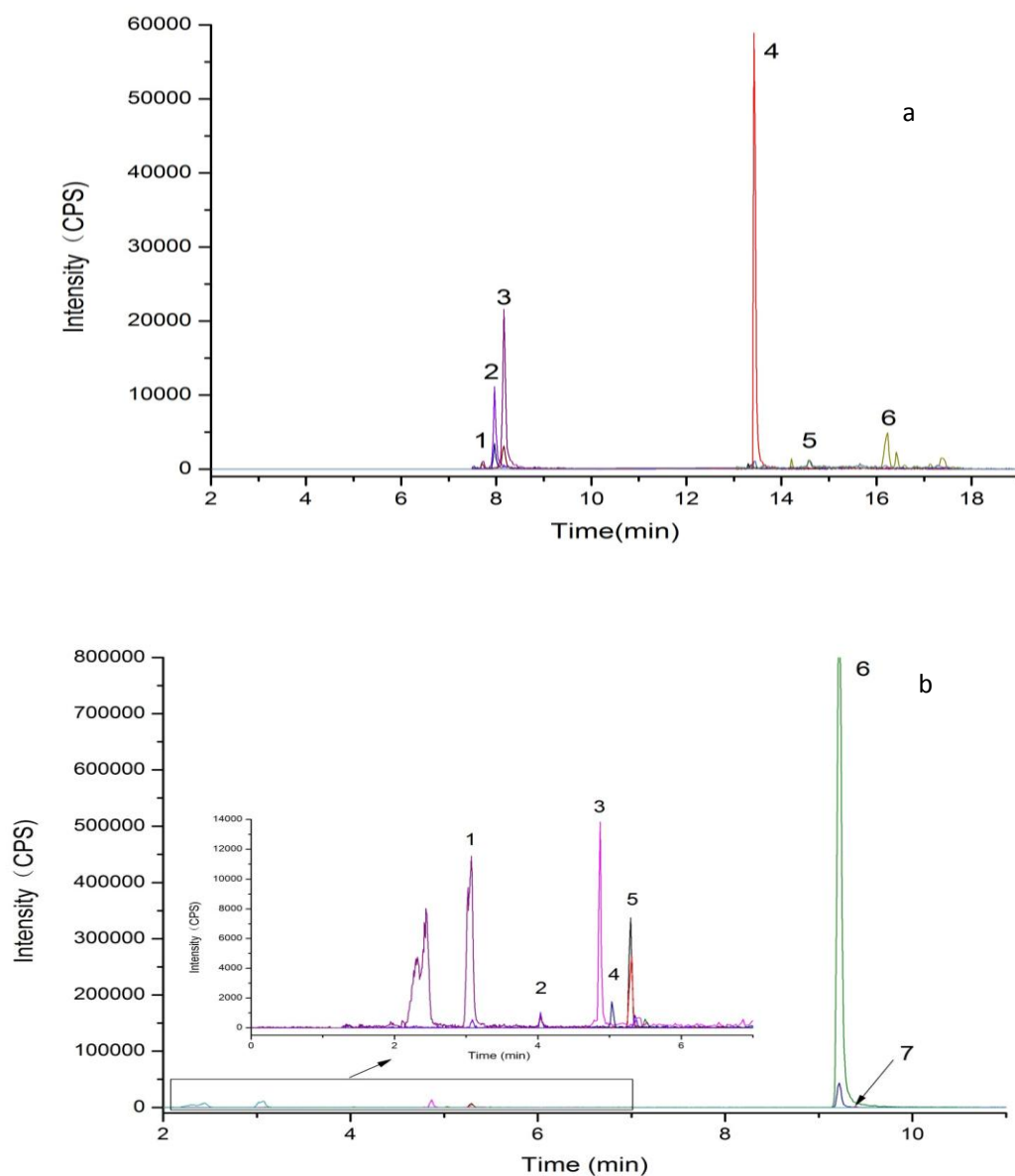


**Fig. S1** Chromatograms of a 100 µg/L standard solutions in methanol (a, positive mode; b, negative mode)

In positive mode: 1 sotalol, 2 atenolol, 3 acetaminophen, 4 codeine, 5 sulfamerazine, 6 metoprolol, 7 pirenzepine, 8 sulfameter, 9 tetracycline, 10 thiabendazole, 11 oxytetracycline, 12 ofloxacin, 13 sulfamethoxazole, 14 clenbuterol, 15 antipyrine, 16 sarafloxacin, 17 sulfadimethoxine, 18 ethenzamide, 19 acetophenone,

20 propranolol, 21 sildenafil, 22 fluoxetine, 23 carbamazepine, 24 propyphenazone, 25 crotamiton, 26 camphor, 27 miconazole, 28 diazepam, 29 loratadine, 30 indomethacine, 31 benzophenone-3, 32 octocrylene.

In negative mode: 1 methyl paraben, 2 clofibric acid, 3 naproxen, 4 ketoprofen, 5 fenoprofen, 6 diclofenac, 7 propyl paraben, 8 bisphenol A, 9 ibuprofen, 10 benzyl paraben, 11 gemfibrozil, 12 triclocarban, 13 triclosan



**Fig. S2** Chromatograms of PPCPs in the sludge collected in September 2012 (a, positive mode; b, negative mode)

In positive mode: 1 tetracycline, 2 oxytetracycline, 3 ofloxacin, 4 camphor, 5 miconazole, 6 octocrylene. In negative mode: 1 methyl paraben, 2 fenoprofen, 3 diclofenac, 4 propylparaben, 5 bisphenol A, 6 triclocarban, 7 triclosan