SUPPLEMENTARY MATERIAL

Analytical upgrade of a methodology based on UHPLC-MS/MS for the analysis of endocrine disrupting compounds in greywater

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Supplementary Table 1. Instrumental limits of detection (ILOD) of the previous and the upgraded method.

Class	Compound	ILOD (µg/L)	
		Jakimska et al. 2013	This work
Hormones	Diethylstilbesterol	1.212	0.110
	Estradiol	0.082	0.040
	Estriol	0.363	0.070
	Estrone	0.400	0.060
	Estrone-3-sulfate	0.027	0.030
	Ethinylestradiol	2.232	0.260
	Progesterone	0.360	0.050
Antimicrobial Preservatives	Triclosan	0.350	0.070
	Benzylparaben	0.248	0.040
	Ethylparaben	0.232	0.020
	Methylparaben	0.406	0.190
	Propylparaben	0.086	0.030
Plasticizers	Bisphenol A	0.834	0.330
	Bisphenol AF	0.069	0.020
	Bisphenol B	0.079	0.090
	Bisphenol F	8.706	0.990
	Bisphenol S	0.059	0.140
Chemical biomarker	Caffeine	0.410	0.100
Alkylphenolic compounds	Nonylphenol	2.825	0.811
	Octylphenol	2.671	0.090
Anticorrosives	1H-benzotriazole	0.260	0.020
	Tolytriazole	0.060	0.004
Organophosphorous flame retardants	TBEP	0.630	0.270
	TCEP	0.200	0.100
	TCPP	0.730	0.100

Supplementary Table 2. Therapeutic group, physical and chemical properties of the target compounds.

Therapeutic group	Compounds	Molecular weight (g/mol)[a]	log K_{ow}[a,b]
Hormones	Diethylstilbesterol	268.4	5.07
	Estradiol	272.4	4.01
	Estriol	288.4	2.45
	Estrone	270.4	3.13
	Estrone-3-sulfate	394.4	0.95
	Ethinylestradiol	296.4	3.67
	Progesterone	314.5	3.87
Antimicrobial	Triclosan	298.5	4.76
Preservatives	Benzylparaben	228.2	3.70
	Ethylparaben	166.2	2.47
	Methylparaben	152.2	1.96
	Propylparaben	180.2	3.04
Plasticizers	BPA	228.3	3.32
	BPAF	336.2	4.47
	BPB	242.3	4.13
	BPF	200.2	2.91
	BPS	250.3	1.65
Chemical biomarker	Caffeine	194.1	-0.07
Alkylphenolic compounds	Nonylphenol	220.4	5.76
	Octylphenol	206.3	5.25
Anticorrosives	1H-benzotriazole	119.1	1.44
	Tolytriazole	133.2	1.71
Organophosphorous flame retardants	TBEP	398.5	3.75
	TCEP	285.5	1.63
	TCPP	327.6	2.59

[a]Data extracted from Pubchem (https://pubchem.ncbi.nlm.nih.gov/)
[b]Data extracted from Chemspider (http://www.chemspider.com/)

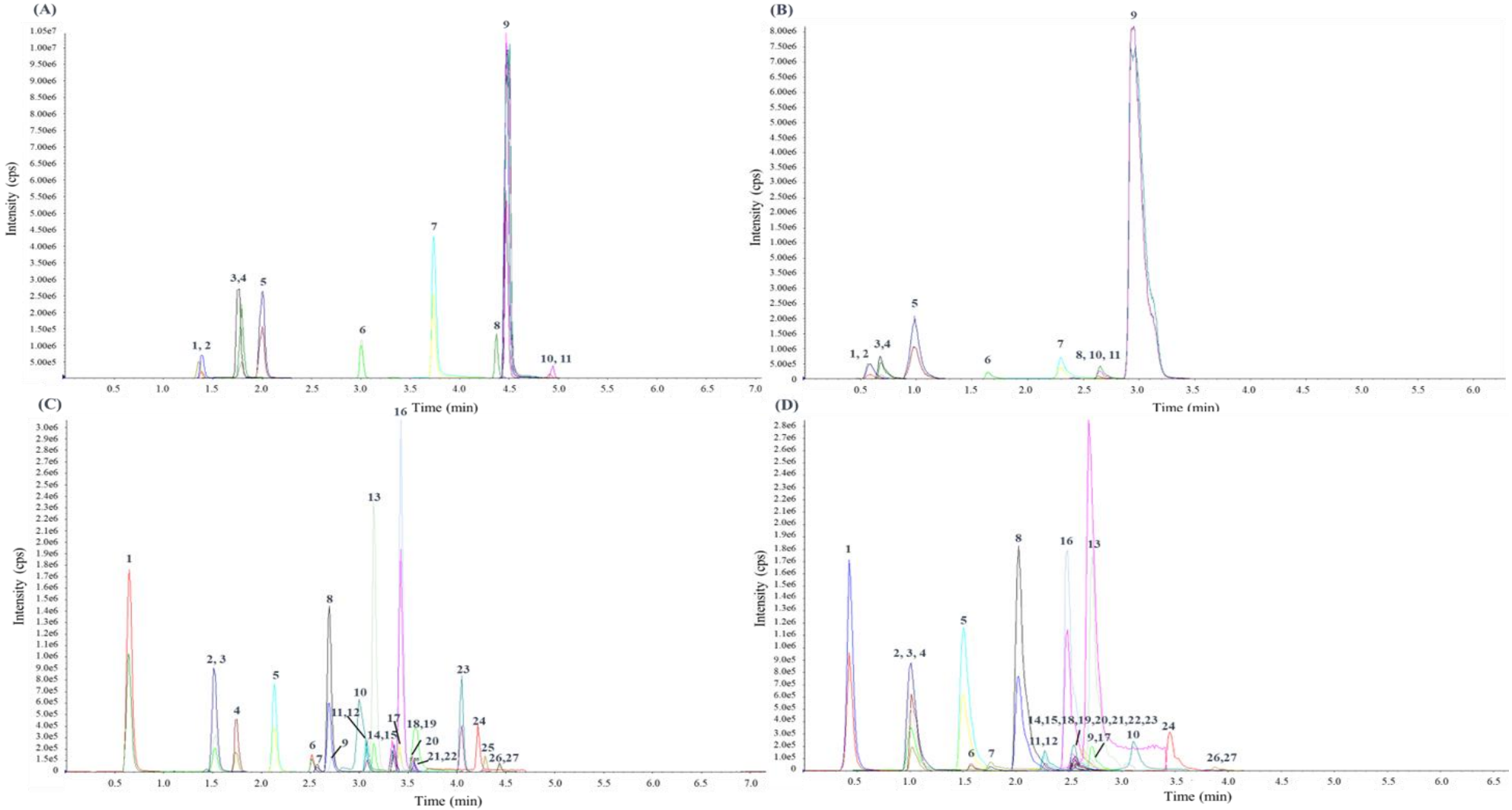
Supplementary Table 3. Physico-chemical characterization of Sh-GW, Ki-GW and La-GW.

	Sh-GW	Ki-GW	La-GW
pH	7.70	7.50	9.65
Conductivity (µS/cm)	724	491	1452
TSS[a] (mg/L)	30.0	115	1366
COD[b] (mgO_2/L)	50.0	NA	161
NO_2^- (mg/L)	3.90	0.02	0.07
NO_3^- (mg/L)	NA	0.95	0.93
PO_4^{3-} (mg/L)	0.65	0.07	0.11
Cl^- (mg/L)	114	45.5	89.5
SO_4^{2-} (mg/L)	16.0	16.7	86.4
NH_4^+ (mg/L)	2.84	0.13	0.57
Na^+ (mg/L)	NA	32.9	NA
K^+ (mg/L)	NA	10.5	NA
Mg^{2+} (mg/L)	9.30	9.71	9.69
Ca^{2+} (mg/L)	51.0	51.5	42.6

[a]Total Suspended Solids
[b]Chemical Oxigen Demand
NA: Not available

Supplementary Table 4. Recovery (%), method limit of detection (MDL) and quantification (MQL) for three types of greywater samples. Sh-GW: shower, Ki-GW: kitchen, La-GW: laundry. n.r.: not recovered.

Class	Compound	Sh-GW			Ki-GW			La-GW		
		Recovery ± SD (%)	MDL (ng/L)	MQL (ng/L)	Recovery ± SD (%)	MDL (ng/L)	MQL (ng/L)	Recovery ± SD (%)	MDL (ng/L)	MQL (ng/L)
Hormones	Diethylstilbesterol	17 ± 8	4.32	14.4	n.r.	n.r.	n.r.	78 ± 10	10.9	36.5
	Estradiol	101 ± 0	6.54	21.8	103 ± 0	15.6	52.0	105 ± 17	23.6	78.6
	Estriol	84 ± 4	4.61	15.4	24 ± 4	15.8	52.8	110 ± 12	15.2	50.6
	Estrone	100 ± 9	8.61	28.7	115 ± 1	20.1	66.9	102 ± 17	13.2	44.1
	Estrone-3-sulfate	75 ± 18	4.67	15.6	95 ± 12	13.1	43.6	97 ± 10	8.94	29.8
	Ethinylestradiol	107 ± 3	6.72	22.4	102 ± 19	13.6	45.5	104 ± 6	27.3	91.1
	Progesterone	107 ± 4	4.05	13.5	104 ± 4	12.3	40.9	114 ± 13	21.6	72.1
Antimicrobial	Triclosan	n.r.	n.r.	n.r.	76 ± 9	17.9	59.8	93 ± 6	29.1	97.0
Preservatives	Benzylparaben	72 ± 16	4.26	14.2	76 ± 8	15.9	53.1	103 ± 8	6.94	23.1
	Ethylparaben	113 ± 3	4.74	15.8	n.r.	n.r.	n.r.	114 ± 14	3.94	13.1
	Methylparaben	100 ± 5	7.51	25.0	107 ± 2	26.1	86.9	99 ± 3	29.0	96.7
	Propylparaben	103 ± 3	5.36	17.9	n.r	n.r	n.r	63 ± 13	19.5	64.8
Plasticizers	BPA	108 ± 6	6.84	22.8	96 ± 15	37.5	124	103 ± 11	25.7	85.5
	BPAF	21 ± 7	2.88	9.60	n.r.	n.r.	n.r.	68 ± 13	105	349
	BPB	80 ± 12	6.89	23.0	n.r.	n.r.	n.r.	93 ± 13	131	438
	BPF	122 ± 3	12.0	39.9	n.r.	n.r.	n.r.	81 ± 12	141	469
	BPS	88 ± 9	6.03	20.1	n.r.	n.r.	n.r.	94 ± 14	19.2	64.1
Stimulant	Caffeine	86 ± 3	6.05	20.2	n.r.	n.r.	n.r.	93 ± 5	27.0	90.0
Alkylphenolic	Nonylphenol	27 ± 2	16.7	55.6	110 ± 8	6.8	22.6	90 ± 3	8.05	26.8
compounds	Octylphenol	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	146 ± 9	17.1	57.0
Anticorrosives	1H-benzotriazole	73 ± 3	2.01	6.71	54 ± 1	17.9	59.7	72 ± 10	54.5	181
	Tolytriazole	99 ± 3	3.73	12.4	148 ± 0	21.6	72.0	94 ± 7	6.59	22.0
Organophosphorous	TBEP	n.r.	n.r.	n.r.	30 ± 0	3.88	12.9	123 ± 12	0.27	0.92
flame retardants	TCEP	n.r.	n.r.	n.r.	97 ± 2	9.39	31.3	109 ± 3	3.43	11.4
	TCPP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.



Supplementary Figure 1. Representative total ion chromatograms (TIC) of a 25 µg/L standard mixture of the selected EDCs analyzed under PI and NI mode

using the upgraded method of this study (A and C), and the previous method[33] (B and D), respectively. For PI: 1. 1H-benzotriazole-d_4; 2. 1H-benzotriazole; 3. caffeine-d_3; 4. caffeine; 5. tolytriazole; 6. TCEP; 7. TCPP; 8. TCPP-d_{15}; 9. TBEP; 10. progesterone-d_8; 11. progesterone. For NI: 1. BPS; 2. methylparaben; 3. methylparaben-d_4; 4. estrone-3-sulfate; 5. ethylparaben; 6. estriol; 7. BPF; 8. propylparaben; 9. octylphenol-d_{17}; 10. triclosan-d_3; 11. BPA-d_4; 12. BPA; 13. BPAF; 14. BPB-d_8; 15. BPB; 16. benzylparaben; 17. diethylstibesterol; 18. estradiol-d_2; 19. estradiol; 20. estrone-d_4; 21. ethinylestradiol-d_4; 22. ethinylestradiol; 23. estrone; 24. triclosan; 25. octylphenol; 26. nonylphenol-d_4; 27. nonylphenol.