Supplementary materials

Journal name

Analytical Methods

Article title

A robust multi-residue method for the monitoring of 25 endocrine disruptors at ultra-trace levels in surface waters by SPE-LC-MS/MS

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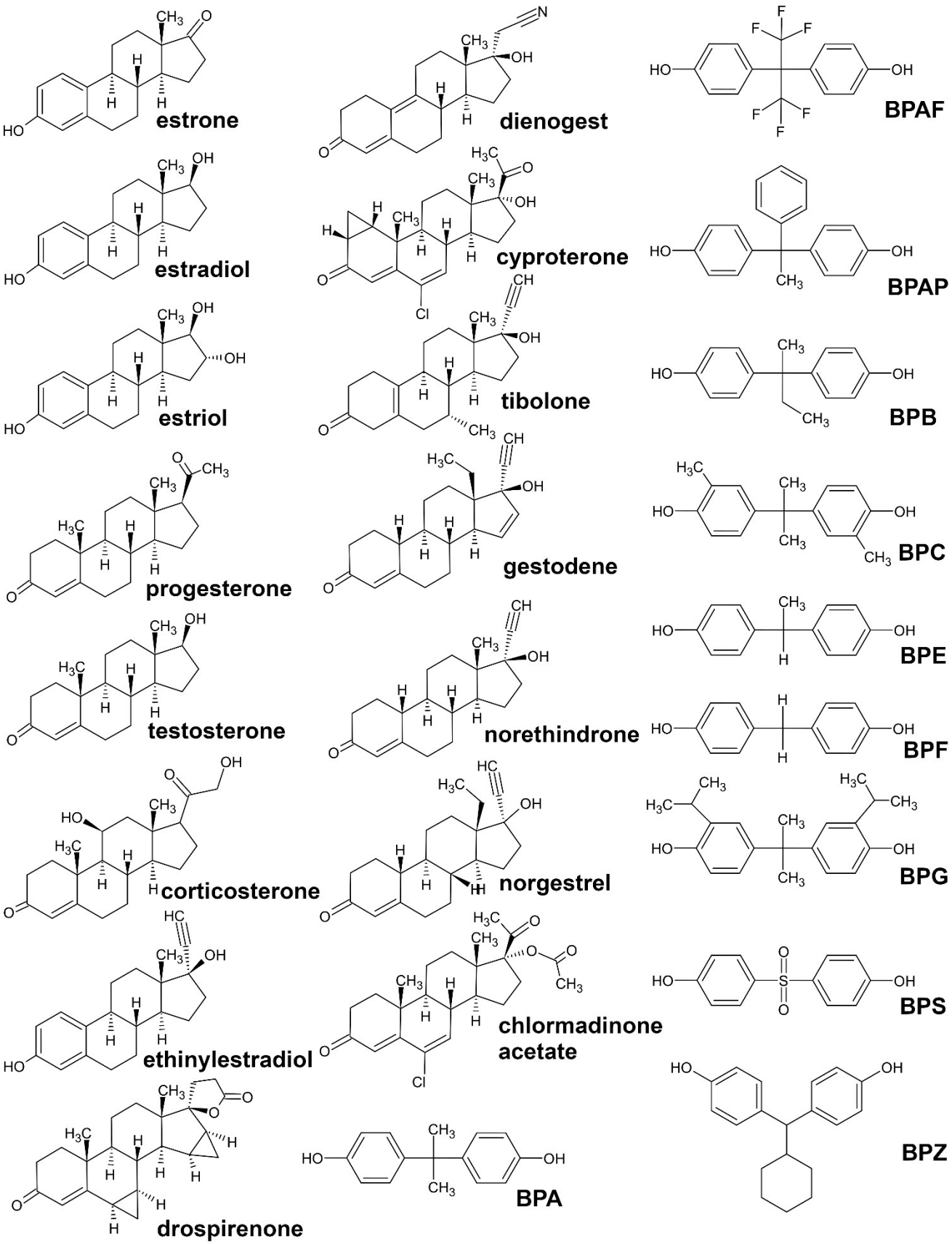
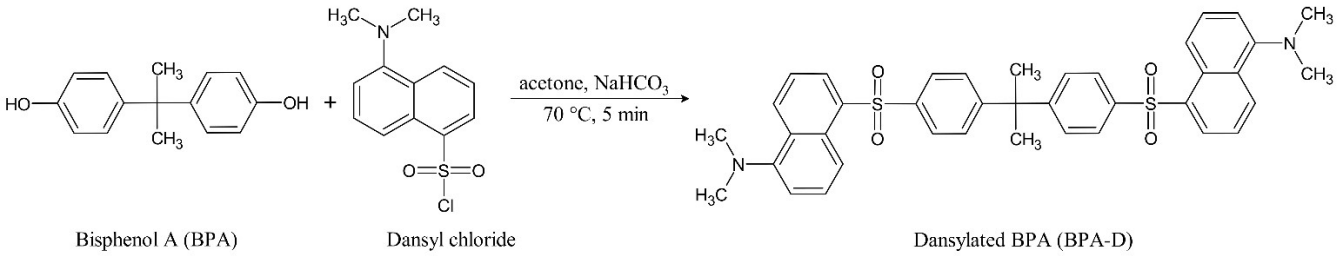


Fig. S1 Chemical structures of selected substances



Bisphenol A (BPA) Dansyl chloride Dansylated BPA (BPA-D)

Fig. S2 Reaction of dansylation shown on BPA

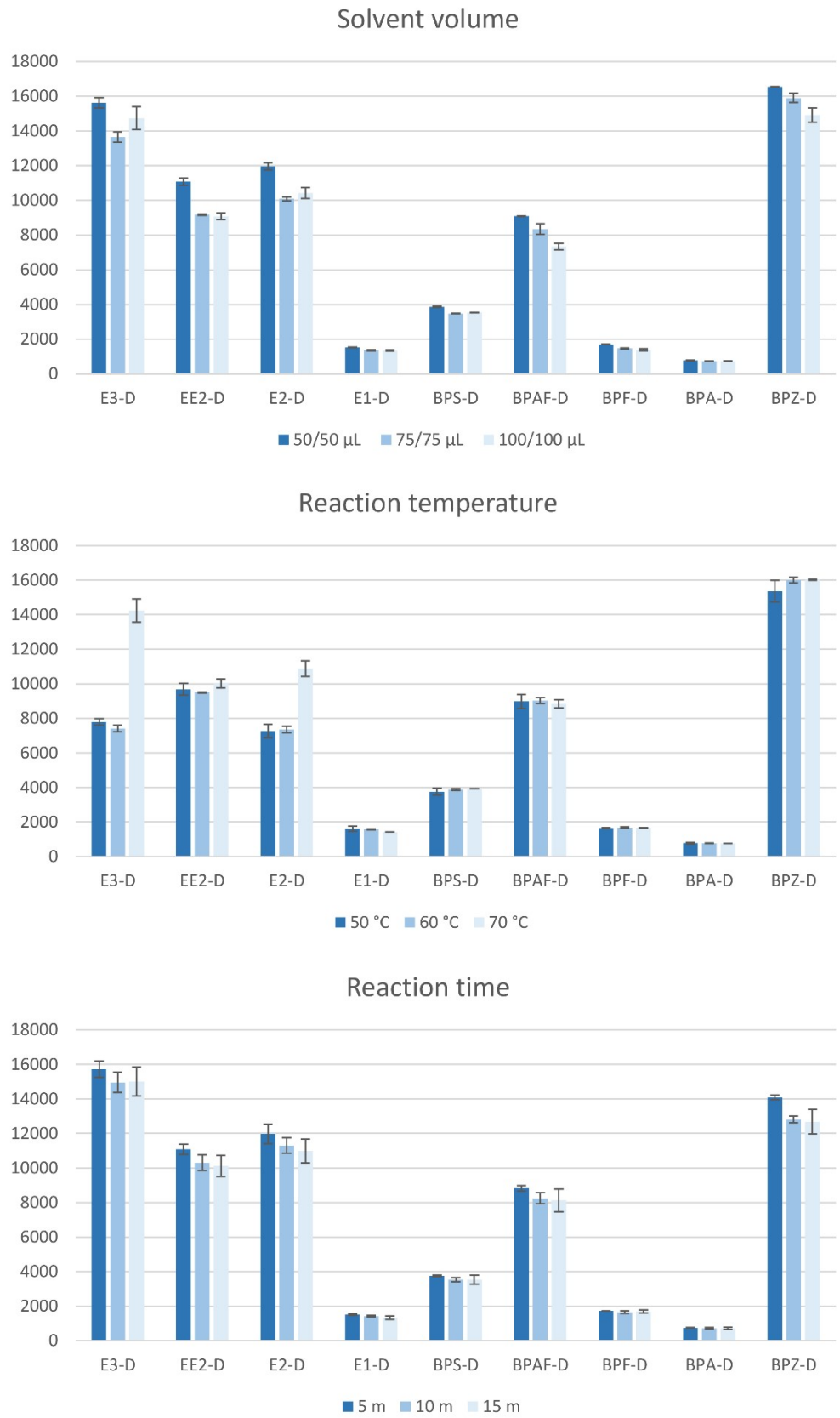


Fig. S3 Signal intensity comparison expressed as slopes of calibration curves of derivatized analytes (with standard deviation error bars) in relation to variations in derivatization parameters

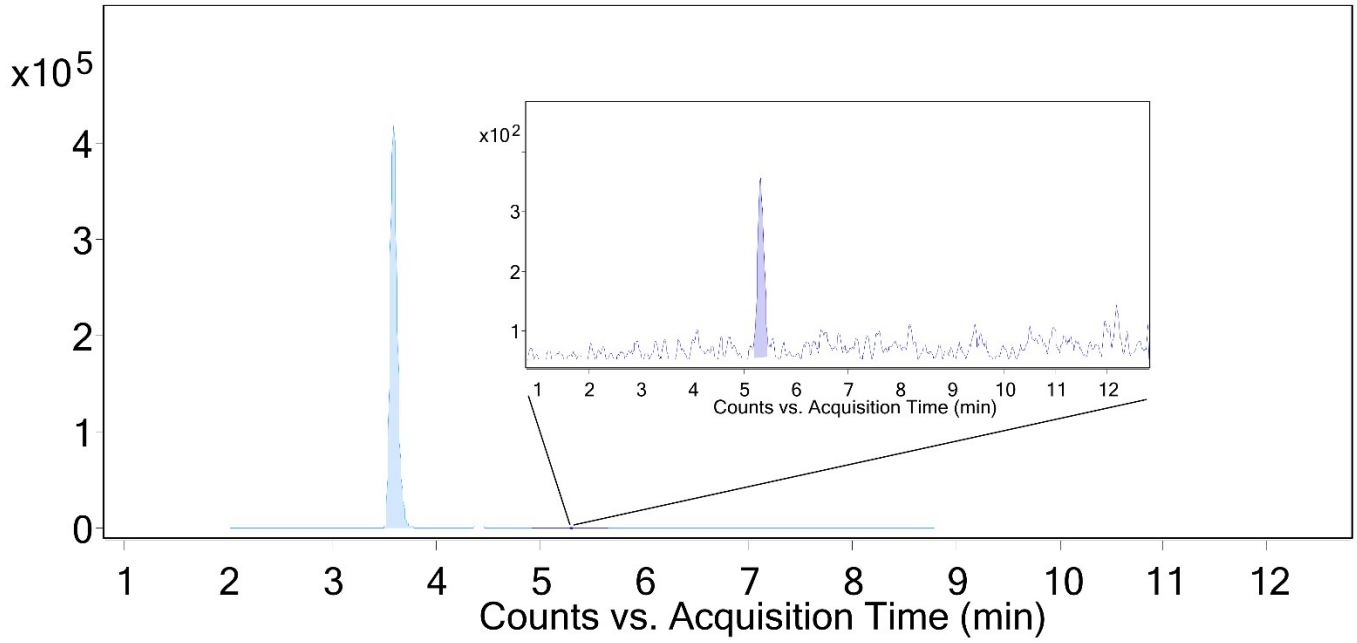


Fig. S4 Derivatization signal gain shown on an example of E2 derivatization. Both peaks represent a sample of a comparable concentration with the one with r_t=3.6 min being the derivatized E2 (E2-D) and the peak with r_t=5.3 min the non-derivatized E2

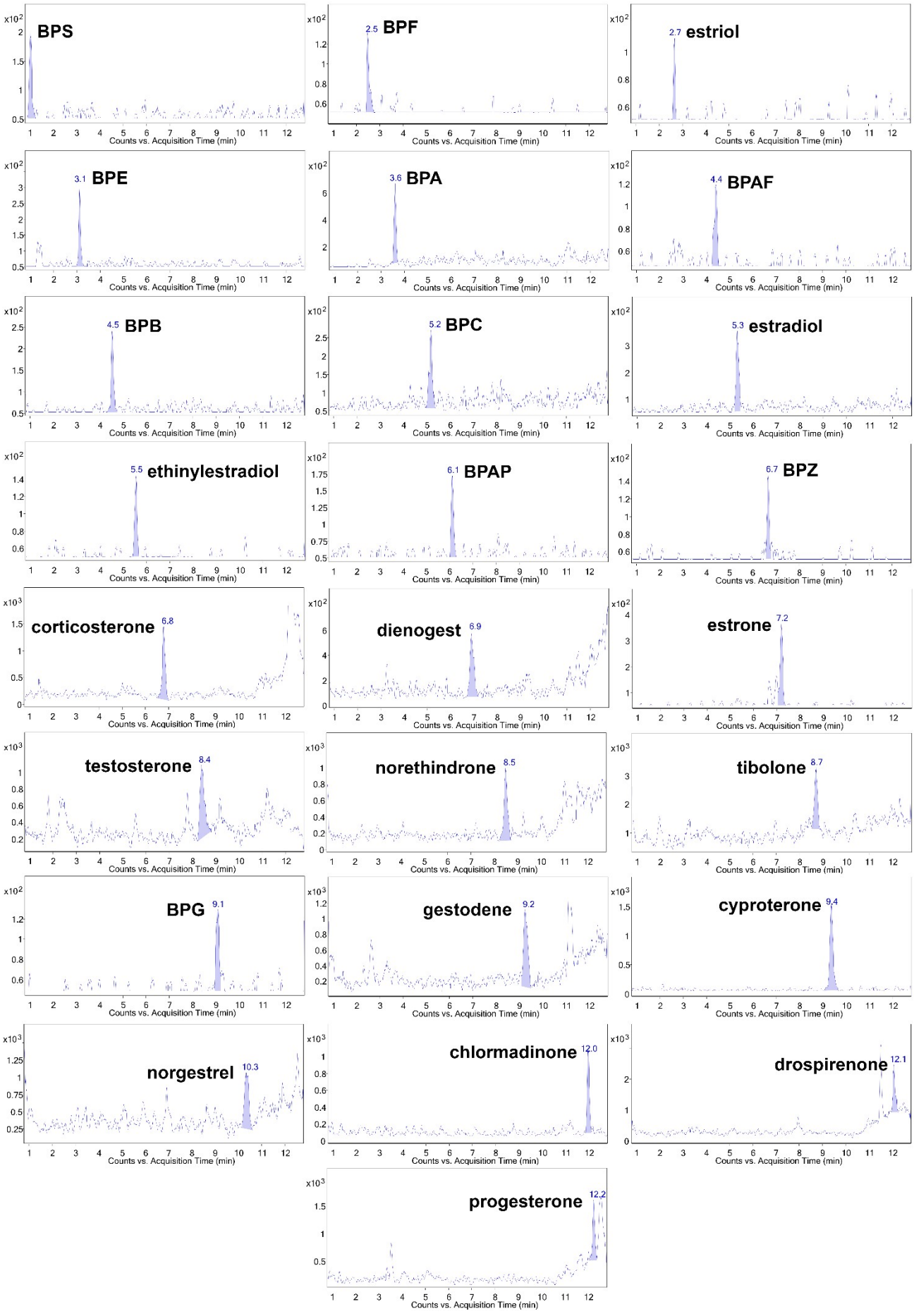

BPS
BPF 2.5
estriol 2.7
BPE 3.1
BPA 3.6
BPAF 4.4
BPB 4.5
BPC 5.2
estradiol 5.3
ethinylestradiol 5.5
BPAP 6.1
BPZ 6.7
corticosterone 6.8
dienogest 6.9
estrone 7.2
testosterone 8.4
norethindrone 8.5
tibolone 8.7
BPG 9.1
gestodene 9.2
cyproterone 9.4
norgestrel 10.3
chlormadinone 12.0
drospirenone 12.1
progesterone 12.2
Counts vs. Acquisition Time (min)

Fig. S5 Representative chromatograms with signal intensities used in calculations of signal to noise (S/N) values for each non-derivatized analyte at their LOQ value. The S/N values for each analyte are as follows: BPS 37, BPF 23, estriol 21, BPE 49, BPA 44, BPAF 27, BPB 41, BPC 27, estradiol 46, ethinylestradiol 56, BPAP 55, BPZ 39, corticosterone 32, dienogest 30, estrone 22, testosterone 14, norethindrone 37, tibolone 10, BPG 19, gestodene 59, cyproterone 205, norgestrel 21, chlormadinone 34, drospirenone 22, progesterone 17

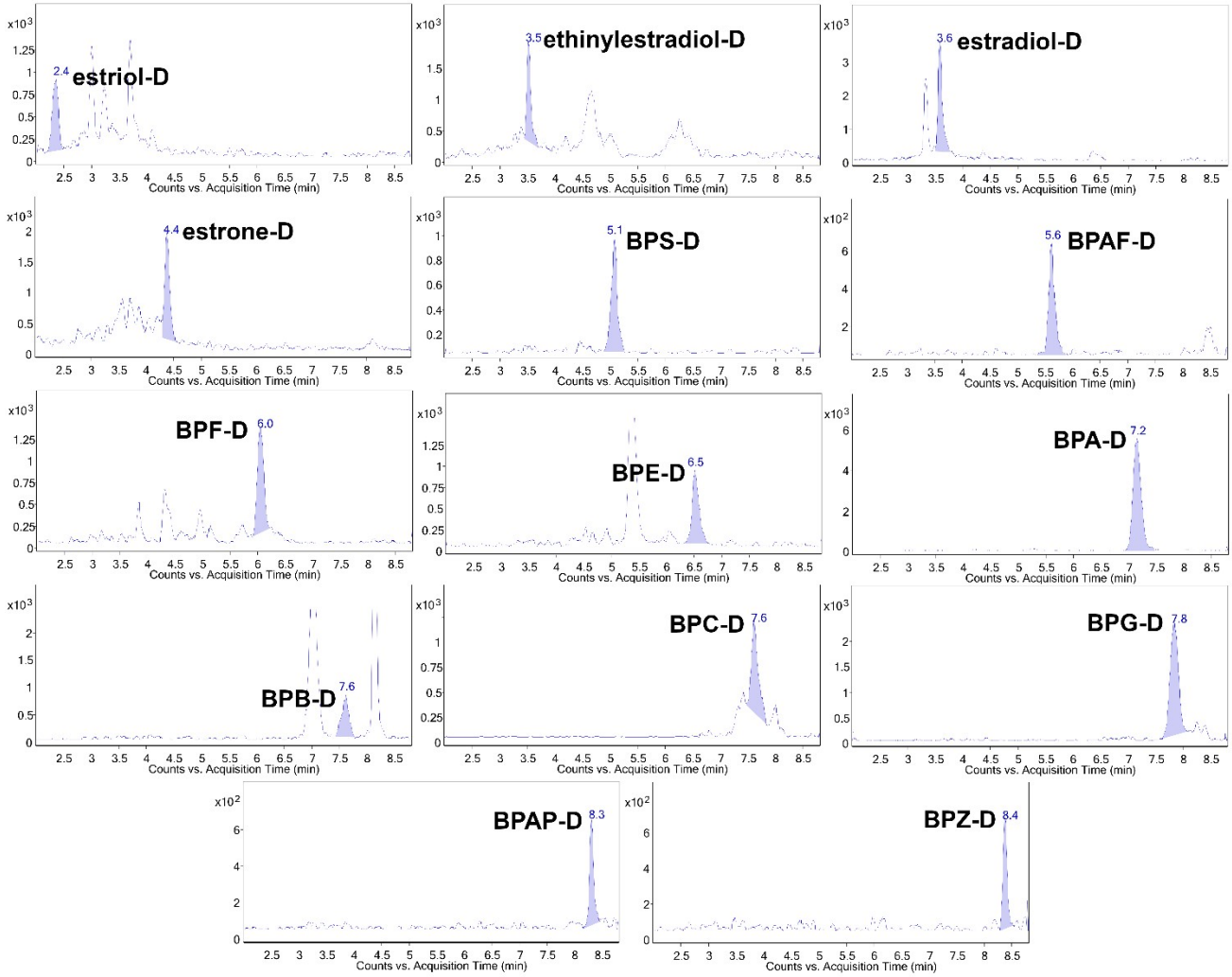


Fig. S6 Representative chromatograms with signal intensities used in calculations of signal to noise (S/N) values for each derivatized analyte (denoted by -D) at their LOQ value. The S/N values for each analyte are as follows: estriol-D 30, ethinylestradiol-D 17, estradiol-D 58, estrone-D 42, BPS-D 77, BPAF-D 144, BPF-D 24, BPE-D 44, BPA-D 1857, BPB-D 51, BPC-D 18, BPG-D 32, BPAP-D 67, BPZ-D 52

Tables

Table S1 Analytical articles with similar analytes found in recent literature and their validation parameters

Source	Number of common / all analytes in the method (with groups)[#]	Linear range [ng/L]	LOQ values [ng/L]	Method of LOQ value determination	Analysis time [min]
(Goeury et al., 2022)	10 / 15 (NH, SH, BPA)	0.3 - 200	0.3 - 1.5	extrapolated[$]	10
(Chafi and Ballesteros, 2022)	8 / 13 (NH, SH)	0.04 - 800	0.03 - 1.0	extrapolated	15
(H. Wang et al., 2022)	9 / 10 (BP)	5000 - 200000	5.6 - 19.3	extrapolated	30
(Q. Wang et al., 2022)	7 / 7 (BP)	1000 - 500000	0.2 - 6	extrapolated	8
(Mirmont et al., 2021)	10 / 23 (NH, SH)	0.25 - 62.5	0.035 - 0.5	extrapolated from 5 ng/L spiked sample	9 + 8(1)
(Corrêa et al., 2021)	5 / 12 (NH, SH, BPA)	2500 - 150000	3.6 - 14.4	extrapolated	N.D. (>25)
(Li et al., 2021)	5 / 6 (NH, SH, BPA)	N.D. - 800	8.3 - 64.1	extrapolated	10
(Glineur et al., 2020)	4 / 4 (NH)	0.1 - 5.0	0.020 - 0.097	extrapolated from low-level samples	N.D. (>20)
(Merlo et al., 2020)	4 / 7 (NH)	10000 - 150000	0.5 - 30	extrapolated from calibrators	27
(Čelić et al., 2020)	4 / 13 (NH, BPA)	0.1 - 500	0.10 - 0.21	extrapolated from 5 ng/L spiked sample	10.5
(Farounbi and Ngqwala, 2020)	3 / 10 (NH, BPA)	N.D.	1.0 - 3.0	N.D.*	N.D.
(Huang et al., 2020)	7 / 15 (BP)	0.1 - 1000000	0.15 - 2.24	extrapolated from 100 ng/L spike	6.5
(Schmidt et al., 2020)	6 / 6 (BP)	N.D.	0.1 - 5.0	extrapolated from lowest calibrator	20
(Tang et al., 2020)	3 / 11 (NH)	10000 - 200000	7.8 - 19.8	extrapolated from 10 ng/L spike	37
(Barreca et al., 2019)	3 / 3 (NH)	3.5 - 224	0.035 - 0.1	extrapolated from low-level samples	8
(Toušová et al., 2019)	4 / 5 (NH)	N.D.	0.2 - 3	N.D.	25
(Ashfaq et al., 2019)	4 / 9 (NH)	N.D.	2.5	N.D.	N.D. (>30)
(Hu et al., 2019)	5 / 8 (NH, BPA)	N.D.	0.1 - 5.7	extrapolated	N.D.
(Luo et al., 2019)	9 / 21 (NH, SH, BPA)	100 - 100000	0.17 - 0.93	N.D.	20 + 26
(Zhang et al., 2019)	5 / 7 (NH)	N.D.	0.03 - 0.24	N.D.	12
(Wee et al., 2019)	6 / 16 (NH, BPA)	5000 - 200000	0.02 - 0.35	extrapolated	10 + 13(2)
(Rico et al., 2019)	4 / 32 (NH, BPA)	N.D.	30 - 300	extrapolated	36 + 18(2)
(Zheng et al., 2019)	6 / 6 (BP)	1000 - 200000	0.53 - 11.1	extrapolated	5
(Česen et al., 2019)	9 / 30 (NH, BP)	1 - 500	0.07 - 3.5	extrapolated from standard line slopes	39.3
(Xu et al., 2019)	5 / 91 (NH, SH, BPA)	200 - 200000	0.05 - 0.49	extrapolated	19 + 8(2)
(Šauer et al., 2018)	7 / 17 (NH, SH)	0.1 - 200	0.06 - 0.51	signal as 1/4 of lowest calibrator (RSD <30%)	22.5
(Weizel et al., 2018)	6 / 60 (SH)	50 - 50000	0.05 - 0.5	extrapolated	35 +35(2)
(Wang et al., 2018)	6 / 7 (BP)	N.D.	5.0 - 20	extrapolated	N.D. (>40)

*Note: #. Analyte groups of natural hormones (NH), synthetic hormones (SH), bisphenols (BP) or bisphenol A (BPA). $. Concentration of sample from which the LOQ value was calculated not reported. *. N.D. denotes that the data or calculation method was non-described. (1). Two different mobile phases were used. (2). Two different analytical columns and mobile phases were used.*

Table S2 Mass spectrometry parameters for non-derivatized analytes

Compound Name	Retention time [min]	Corresponding internal standard	Polarity	Precursor Ion [m/z]	Product Ion [m/z]	Fragmentor [V]	Collision Energy [eV]
BPS	1.0	[$^{13}C_6$]-carbamazepine	-	249.0	**108.0**[a] (92.1)[b]	164	**29**[a] (41)[b]
BPF	2.5	[$^{13}C_6$]-carbamazepine	-	199.1	**77.1** (105.1)	138	**25** (21)
estriol	2.7	[$^{13}C_6$]-carbamazepine	-	287.2	**171.1** (145.0)	180	**40** (48)
BPE	3.1	[$^{13}C_6$]-carbamazepine	-	213.1	**198.1** (119.1)	90	**17** (25)
BPA	3.6	[$^{13}C_6$]-carbamazepine	-	227.1	**212.1** (133.1)	148	**17** (21)
[$^{13}C_6$]-carbamazepine*	3.7	/	+	243.1	**199.9**	103	**12**
[$^{13}C_6$]-diclofenac*	4.1	/	+	302.1	**220.0**	100	**15**
BPAF	4.4	[$^{13}C_6$]-diclofenac	-	335.0	**265.1** (69.0)	174	**21** (53)
BPB	4.6	[$^{13}C_6$]-diclofenac	-	241.1	**212.1** (93.0)	130	**17** (57)
BPC	5.2	[$^{13}C_6$]-diclofenac	-	255.1	**240.1** (147.1)	154	**17** (29)
estradiol	5.3	[$^{13}C_6$]-diclofenac	-	271.2	**183.2** (269.2)	180	**44** (36)
ethinylestradiol	5.5	[$^{13}C_6$]-diclofenac	-	295.2	**145** (159.1)	192	**36** (36)
BPAP	6.2	[$^{2}H_5$]-diazepam	-	289.1	**274.1** (195.1)	130	**18** (26)
BPZ	6.7	[$^{2}H_5$]-diazepam	-	267.1	**173.1** (145.1)	174	**25** (41)
corticosterone[$]	6.8	[$^{2}H_5$]-diazepam	+	347.2	**121.2** (77.2)	110	**21** (77)
dienogest[$]	7.0	[$^{2}H_5$]-diazepam	+	312.2	**91.1** (161.2)	170	**65** (21)
estrone	7.2	[$^{2}H_5$]-diazepam	-	269.1	**145** (143.2)	136	**44** (64)
[$^{2}H_5$]-diazepam*	7.9	/	+	290.1	**198.1**	140	**32**
testosterone[$]	8.4	[$^{2}H_4$]-testosterone	+	289.4	**97.0** (109.0)	116	**20** (24)
[$^{2}H_4$]-testosterone*	8.4	/	+	293.2	**98.1**	100	**20**
norethindrone[$]	8.5	[$^{2}H_4$]-testosterone	+	299.2	**77.1** (91.1)	180	**76** (52)
tibolone[$]	8.8	[$^{2}H_4$]-testosterone	+	313.2	**295.2** (65.2)	140	**4** (100)
BPG	9.1	[$^{2}H_4$]-testosterone	-	311.2	**295.1** (175.1)	180	**28** (37)
gestodene[$]	9.3	[$^{2}H_4$]-testosterone	+	311.2	**109.1** (77.3)	80	**25** (73)
cyproterone[$]	9.4	[$^{2}H_4$]-testosterone	+	374.2	**321.3** (43.2)	170	**13** (53)
norgestrel[$]	10.4	[$^{2}H_4$]-testosterone	+	313.2	**77.2** (91.2)	140	**80** (53)
chlormadinone[$]	12.0	[$^{2}H_9$]-progesterone	+	405.2	**309.2** (345.2)	80	**9** (5)
drospirenone[$]	12.1	[$^{2}H_9$]-progesterone	+	367.2	**77.1** (91.1)	100	**92** (72)
progesterone[$]	12.3	[$^{2}H_9$]-progesterone	+	315.2	**109.2** (97.2)	140	**25** (21)
[$^{2}H_9$]-progesterone*	12.3	/	+	324.3	**100.1**	100	**24**

*Note. Both MS1 and MS2 resolutions are 2.5 units for all analytes. *. Denoted analyte is an internal standard. $. Denoted analyte has a positive ionization polarity and is only quantified with the method for non-derivatized analytes. All other analytes are quantified with both methods. a. Value for the Quantifier ion. b. Value for the Qualifier ion.*

Table S3 Mass spectrometry parameters for derivatized analytes

Compound Name	Retention time [min]	Corresponding internal standard	Polarity	Precursor Ion [m/z]	Product Ion [m/z]	Fragmentor [V]	Collision Energy [eV]	MS1 resolution	MS2 resolution
estriol-D[c]	2.3	[$^2H_4$]-estriol-D	+	522.2	**171.2**[a] (156.1)[b]	196	**37**[a] (65)[b]	1.2	2.5
[$^2H_4$]-estriol-D*	2.3	/	+	526.2	**171.2**	196	**37**	0.7	2.5
ethinylestradiol-D	3.5	[$^2H_4$]-ethinylestradiol-D	+	530.2	**171.2** (156.1)	200	**37** (65)	1.2	2.5
[$^2H_4$]-ethinylestradiol-D*	3.5	/	+	534.2	**171.2**	200	**37**	0.7	2.5
estradiol-D	3.6	[$^2H_5$]-estradiol-D	+	506.2	**171.2** (156.1)	196	**33** (61)	0.7	2.5
[$^2H_5$]-estradiol-D*	3.6	/	+	511.2	**171.2**	196	**33**	0.7	2.5
estrone-D	4.4	[$^2H_4$]-estrone-D	+	504.2	**171.2** (156.1)	92	**37** (57)	1.2	2.5
[$^2H_4$]-estrone-D*	4.4	/	+	508.2	**171.2**	92	**37**	0.7	2.5
BPS-D	5.0	[$^2H_{16}$]-BPA-D	+	717.1	**171.2** (156.1)	246	**41** (80)	0.7	2.5
BPAF-D	5.6	[$^2H_{16}$]-BPA-D	+	803.2	**171.2** (156.1)	246	**53** (80)	0.7	2.5
BPF-D	6.0	[$^2H_{16}$]-BPA-D	+	667.2	**171.2** (156.1)	192	**41** (77)	0.7	2.5
BPE-D	6.6	[$^2H_{16}$]-BPA-D	+	681.1	**171.2** (156.1)	220	**44** (82)	0.7	2.5
BPA-D	7.2	[$^2H_{16}$]-BPA-D	+	695.2	**171.2** (156.1)	246	**53** (77)	0.7	0.7
[$^2H_{16}$]-BPA-D*	7.2	/	+	709.2	**171.2**	246	**53**	0.7	2.5
BPB-D	7.7	[$^2H_{16}$]-BPA-D	+	709.3	**171.2** (156.1)	220	**52** (86)	0.7	2.5
BPC-D	7.7	[$^2H_{16}$]-BPA-D	+	723.3	**171.2** (156.1)	246	**53** (80)	0.7	0.7
BPG-D	7.9	[$^2H_{16}$]-BPA-D	+	779.4	**171.2** (156.1)	240	**56** (92)	0.7	2.5
BPAP-D	8.3	[$^2H_{16}$]-BPA-D	+	757.4	**171.2** (156.1)	250	**54** (88)	0.7	2.5
BPZ-D	8.4	[$^2H_{16}$]-BPA-D	+	735.3	**171.2** (156.1)	246	**49** (77)	0.7	2.5

*Note. *. Denoted analyte is an internal standard. a. Value for the Quantifier ion. b. Value for the Qualifier ion. c. Analytes denoted with -D are derivatized with dansyl chloride.*

Table S4 Concentrations (ng/L) of calibrators and QC samples. QC_L is the low and QC_H the high concentration QC sample. A.U. denotes arbitrary units, showing the concentration relations of each individual calibrator and QC level

Calibrators								QC samples	
								QC_L	QC_H
A.U.	**0.5**	**1.5**	**5**	**15**	**50**	**175**	**500**	**10**	**200**
BPS	0.3	0.9	3	9	30	105	300	6	120
BPF	0.4	1.2	4	12	40	140	400	8	160
E3	0.075	0.23	0.75	2.25	7.5	26.3	75	1.5	30
BPE	0.3	0.9	3	9	30	105	300	6	120
BPA	0.3	0.9	3	9	30	105	300	6	120
BPAF	0.3	0.9	3	9	30	105	300	6	120
BPB	0.3	0.9	3	9	30	105	300	6	120
BPC	0.3	0.9	3	9	30	105	300	6	120
E2	0.4	1.2	4	12	40	140	400	8	160
EE2	0.075	0.23	0.75	2.25	7.5	26.3	75	1.5	30
BPAP	0.3	0.9	3	9	30	105	300	6	120
BPZ	0.2	0.6	2	6	20	70	200	4	80
corticosterone	0.85	2.55	8.5	25.5	85	298	850	17	340
dienogest	0.4	1.2	4	12	40	140	400	8	160
estrone	0.03	0.09	0.3	0.9	3	10.5	30	0.6	12
testosterone	0.1	0.3	1	3	10	35	100	2	40
norethindrone	0.75	2.25	7.5	22.5	75	263	750	15	300
tibolone	0.7	2.1	7	21	70	245	700	14	280
BPG	0.6	1.8	6	18	60	210	600	12	240
gestodene	0.55	1.65	5.5	16.5	55	193	550	11	220
cyproterone	1.25	3.75	12.5	37.5	125	438	1250	25	500
norgestrel	0.5	1.5	5	15	50	175	500	10	200
chlormadinone	3.5	10.5	35	105	350	1225	3500	70	1400
drospirenone	0.4	1.2	4	12	40	140	400	8	160
progesterone	0.1	0.3	1	3	10	35	100	2	40
E3-D	0.075	0.23	0.75	2.25	7.5	26.3	75	1.5	30
EE2-D	0.075	0.23	0.75	2.25	7.5	26.3	75	1.5	30
E2-D	0.4	1.2	4	12	40	140	400	8	160
E1-D	0.03	0.09	0.3	0.9	3	10.5	30	0.6	12
BPS-D	0.3	0.9	3	9	30	105	300	6	120
BPAF-D	0.3	0.9	3	9	30	105	300	6	120
BPF-D	0.4	1.2	4	12	40	140	400	8	160
BPE-D	0.3	0.9	3	9	30	105	300	6	120
BPA-D	0.3	0.9	3	9	30	105	300	6	120
BPB-D	0.3	0.9	3	9	30	105	300	6	120
BPC-D	0.3	0.9	3	9	30	105	300	6	120
BPG-D	0.6	1.8	6	18	60	210	600	12	240
BPAP-D	0.3	0.9	3	9	30	105	300	6	120
BPZ-D	0.2	0.6	2	6	20	70	200	4	80

*Notes: *. Analytes denoted with -D are derivatized with dansyl chloride.*

Table S5 Concentration ranges of analytes in the derivatized and non-derivatized method

Compound Name	Derivatized calibration range [ng/L]	Non-derivatized calibration range [ng/L]
BPS	0.3 - 105	0.3 - 300
BPF	0.4 - 140	4.0 - 400
E3	0.075 - 26	2.3 - 75
BPE	0.3 - 105	1.5 - 300
BPA	0.3 - 105	0.8 - 300
BPAF	0.3 - 105	1.5 - 300
BPB	0.3 - 105	1.5 - 300
BPC	1.5 - 105	9.0 - 300
E2	0.4 - 140	40 - 400
EE2	0.075 - 26	25 - 75
BPAP	0.3 - 105	0.4 - 300
BPZ	0.2 - 70	2.0 - 200
corticosterone	N.D.	0.9 - 850
dienogest	N.D.	0.4 - 400
E1	0.03 - 11	3.0 - 30
testosterone	N.D.	0.1 - 100
norethindrone	N.D.	0.8 - 750
tibolone	N.D.	2.0 - 700
BPG	0.6 - 210	6.0 - 600
gestodene	N.D.	0.55 - 550
cyproterone	N.D.	1.25 - 1250
norgestrel	N.D.	0.5 - 500
chlormadinone	N.D.	3.5 - 3500
drospirenone	N.D.	0.4 - 400
progesterone	N.D.	0.1 - 100

Notes: N.D. analyte not suitable for derivatization.

Table S6 Comparison of recoveries (top) and precisions (bottom) from different SPE cartridges expressed as percentages (%). The recovery is calculated by comparing the slope obtained in the extraction with each cartridge and the slope of a standard solution of the same concentration

Recovery (%)

	E3	EE2	E2	E1	BPS	BPAF	BPF	BPA	BPC	BPZ	corticosterone	dienogest	testosterone	norethindrone	tibolone	gestodene	cyproterone	norgestrel	chlormadinone	drospirenone	progesterone
Strata X	91	91	92	91	103	96	98	97	103	102	99	90	93	94	83	96	97	91	86	112	80
Oasis HLB	99	93	90	91	100	96	95	92	98	85	97	83	97	87	61	89	97	86	80	123	44
Chromabond HR-X	81	88	86	74	81	76	87	76	78	82	89	74	86	79	74	88	76	69	64	120	49
Chromabond HLB	80	85	84	76	84	75	82	61	69	81	95	73	86	78	72	89	73	68	80	109	70

Precision (%)

	E3	EE2	E2	E1	BPS	BPAF	BPF	BPA	BPC	BPZ	corticosterone	dienogest	testosterone	norethindrone	tibolone	gestodene	cyproterone	norgestrel	chlormadinone	drospirenone	progesterone
Strata X	6	4	4	1	2	2	2	5	11	3	2	3	2	1	2	2	2	2	1	9	2
Oasis HLB	76	64	68	9	41	26	17	34	54	24	3	4	5	3	5	5	5	4	4	7	7
Chromabond HR-X	7	23	11	1	1	1	3	3	32	5	3	3	3	3	9	4	4	4	7	9	9
Chromabond HLB	13	24	8	5	10	8	2	5	44	5	6	8	3	4	17	5	6	6	4	13	2

Table S7 Comparison of recoveries (top) and precisions (bottom) of representative analytes at different loading volumes and flow rates, all expressed as percentages (%). The analytes missing in the table are synthetic hormones (except EE2) as they were added later in method development. Each condition was performed in 2 parallel experiments

Recovery (%)

	BPS	BPF	E3	BPA	BPAF	BPC	E2	EE2	BPZ	E1	testosterone	progesterone
100 mL	94	84	83	118	64	103	88	104	54	100	63	69
200 mL	93	94	84	102	95	94	96	99	96	94	88	81
500 mL	92	97	82	94	96	99	82	81	92	94	78	79
700 mL	81	87	82	78	87	92	82	69	97	93	66	61
1000 mL	84	91	79	81	92	87	73	72	101	88	69	60
2.5 mL/min	99	77	86	108	103	64	97	81	94	113	71	75
5 mL/min	95	97	86	99	94	96	92	92	95	94	87	83
10 mL/min	100	112	33	95	84	73	104	73	66	86	77	77
20 mL/min	102	111	22	91	81	72	105	86	70	88	25	74

Precision (%)

	BPS	BPF	E3	BPA	BPAF	BPC	E2	EE2	BPZ	E1	testosterone	progesterone
2.5 mL/min	0	5	10	6	8	15	3	8	10	3	6	3
5 mL/min	5	12	1	7	2	13	4	4	3	4	3	5
10 mL/min	2	20	17	13	1	25	7	6	23	8	10	15
20 mL/min	27	21	14	12	2	24	7	5	9	8	2	11

Table S8 Values of acceptance parameters of calibrator samples at the limit of quantitation

	Analyte concentration [ng/L]	Signal to noise ratio	Signal to blank ratio	Precision [%]	Accuracy [%]
BPS	0.24	37	16	0	75
BPF	4.0	23	8.7	17	90
E3	2.25	21	55	2	96
BPE	1.5	49	19	2	126
BPA	0.84	44	5.6	9	153
BPAF	1.5	27	7.2	7	95
BPB	1.5	41	20	14	97
BPC	9.0	27	14	14	80
E2	40	46	16	1	77
EE2	26	56	23	17	71
BPAP	0.42	55	15	3	90
BPZ	2.0	39	6.6	2	79
corticosterone	0.68	32	39	38	74
dienogest	0.32	30	19	22	61
E1	3.0	22	40	18	61
testosterone	0.14	14	7.9	9	51
norethindrone	0.60	37	20	25	81
tibolone	1.96	10	7.8	10	87
BPG	6.0	19	5.6	12	146
gestodene	0.44	59	16	27	145
cyproterone	1.0	205	39	14	78
norgestrel	0.40	21	18	14	118
chlormadinone	2.8	34	8.3	18	63
drospirenone	0.32	22	8.8	15	66
progesterone	0.080	17	11	19	56

	Analyte concentration [ng/L]	Signal to noise ratio	Signal to blank ratio	Precision [%]	Accuracy [%]
E3-D*	0.060	30	8.4	38	121
EE2-D	0.060	17	7.7	24	121
E2-D	0.32	58	17	24	55
E1-D	0.084	42	5.5	10	119
BPS-D	0.24	77	5.4	9	90
BPAF-D	0.24	144	23	8	80
BPF-D	0.32	24	32	16	114
BPE-D	0.24	44	89	13	108
BPA-D	0.24	1857	5.1	16	117
BPB-D	0.24	51	27	11	72
BPC-D	1.5	18	39	18	55
BPG-D	0.48	32	12	13	55
BPAP-D	0.24	67	12	6	109
BPZ-D	0.16	52	18	17	100

*Notes: *. Analytes denoted with -D are derivatized with dansyl chloride.*

Table S9 Comparison of matrix effect in drinking water (DW) and river water (RW) calculated with and without taking into account the addition of internal standards

	With IS		Without IS	
	DW	RW	DW	RW
BPS	-9.4	-17.8	-5.3	-28.0
BPF	9.4	17.4	15.7	15.2
E3	5.9	22.2	9.6	21.7
BPE	6.5	24.2	11.9	31.1
BPA	0.3	17.1	5.7	24.9
BPAF	-5.8	20.9	-3.4	26.2
BPB	8.3	16.5	9.6	12.1
BPC	-12.0	19.6	15.5	25.3
E2	8.6	19.5	11.3	21.2
EE2	5.2	10.2	10.0	30.1
BPAP	-3.6	6.1	4.4	9.3
BPZ	-5.5	0.6	5.4	12.3
corticosterone	5.1	-13.4	7.9	-36.7
dienogest	-8.0	-20.6	-9.4	-28.0
E1	-1.3	21.0	7.6	-15.4
testosterone	-3.3	1.7	4.8	-21.4
norethindrone	-4.6	5.8	-11.9	-5.6
tibolone	6.0	10.7	11.3	-20.0
BPG	-17.6	14.0	-13.5	-33.7
gestodene	-3.1	8.3	5.0	-7.7
cyproterone	2.8	8.5	3.3	-21.3
norgestrel	-5.6	13.0	12.3	-32.3
chlormadinone	-2.4	12.3	4.7	-24.1
drospirenone	-7.6	6.5	14.2	-27.9
progesterone	-7.9	-0.6	23.0	-33.9
E3-D*	-5.3	0.5	14.8	-34.6
EE2-D	-2.1	23.4	-5.5	-14.6
E2-D	-10.5	-5.4	-11.5	-14.1
E1-D	6.2	13.7	12.5	-20.7
BPS-D	-1.8	-12.1	-10.2	-26.4
BPAF-D	9.7	-8.4	3.1	-14.7
BPF-D	-8.9	2.5	-16.2	7.9
BPE-D	-4.8	4.4	-13.1	9.1
BPA-D	-4.0	-1.8	-11.6	-4.5
BPB-D	0.0	1.8	-14.5	6.3
BPC-D	-10.1	20.2	-18.6	28.0
BPG-D	-17.1	22.7	-16.8	43.4
BPAP-D	9.9	-9.6	-20.2	-18.2
BPZ-D	1.7	-2.8	-17.7	-15.5

*Notes: *. Analytes denoted with -D are derivatized with dansyl chloride.*

Table S10 Autosampler stability after 24 and 48 h at 8 °C, expressed as a percentage (%) compared to the signal at t=0 h. QC_L is the low and QC_H the high concentration QC sample

	BPS	BPF	E3	BPE	BPA	BPAF	BPB	BPC	E2	EE2	BPAP	BPZ	corticosterone	dienogest	E1	testosterone	norethindrone	tibolone	BPG	gestodene	cyproterone	norgestrel	chlormadinone	drospirenone	progesterone
QC_L																									
24h	94.3	106.7	124.3	117.3	93.0	97.7	97.7	97.3	94.7	103.7	99.3	84.7	101.3	99.7	90.7	98.3	95.7	96.3	102.3	98.3	98.7	97.0	106.3	101.7	101.7
48h	106.3	111.7	98.7	100.7	110.0	98.3	104.3	98.3	102.7	108.3	103.7	85.0	102.7	102.3	79.3	98.7	101.0	100.0	111.3	98.3	97.3	94.3	104.7	101.7	98.3
QC_H																									
24h	100.3	100.0	98.0	102.3	100.0	94.7	98.3	96.3	91.7	105.7	101.3	104.7	103.7	101.7	104.0	96.0	97.0	95.7	98.7	97.0	96.7	96.0	98.0	96.7	97.3
48h	103.3	101.0	104.7	102.0	100.3	108.0	96.3	101.0	94.7	103.0	97.3	103.0	101.7	101.3	101.7	99.0	99.0	102.7	98.7	97.7	99.3	94.0	94.0	92.0	91.0

	E3-D	EE2-D	E2-D	E1-D	BPS-D	BPAF-D	BPF-D	BPE-D	BPA-D	BPB-D	BPC-D	BPG-D	BPAP-D	BPZ-D
QC_L														
24h	93.7	96.0	96.0	104.3	95.0	94.3	98.3	97.7	97.0	102.0	102.7	97.3	115.7	114.3
48h	100.3	98.7	96.3	108.7	108.7	103.3	110.3	103.3	95.0	104.3	95.0	101.3	115.3	110.7
QC_H														
24h	103.3	100.0	100.0	99.7	98.3	96.7	98.7	100.3	100.0	103.0	103.7	104.7	114.3	114.0
48h	100.3	98.0	97.3	101.7	97.3	94.7	97.3	96.0	93.0	97.7	96.7	100.0	103.7	111.0

*Notes: *. Analytes denoted with -D are derivatized with dansyl chloride.*

Table S11 Concentrations of detected analytes (ng/L) from three representative surface water samples calculated from calibration curves and by the standard addition principle. The quotient of values calculated from calibration curves divided by values obtained from standard addition is presented as a percentage (%)

	BPS	BPA	testosterone	norethindrone	norgestrel	drospirenone	progesterone	E3-D	EE2-D	E2-D	E1-D	BPS-D	BPF-D	BPA-D	BPG-D
CR	2.4	9.0	0.22	5.8	<LOQ	3.9	0.63	0.26	<LOQ	0.23	4.0	2.4	0.55	10.2	1.1
BR	3.7	21	0.24	6.1	3.1	4.6	0.65	0.70	0.75	0.24	5.7	3.6	0.54	19.8	<LOQ
LA	2.8	18	0.33	5.8	<LOQ	3.1	0.53	0.45	<LOQ	0.24	5.4	2.9	0.69	16.3	<LOD
CR-A*	2.6	9.3	0.19	4.8	/	3.9	0.64	0.25	/	0.24	4.2	2.3	0.50	9.9	0.94
BR-A	3.7	18	0.23	6.8	3.0	4.2	0.58	0.80	0.63	0.26	5.0	3.5	0.49	16.5	0.32
LA-A	2.5	19	0.29	5.3	/	3.1	0.57	0.47	/	0.26	5.2	2.6	0.87	16.8	0.22
Comparison CR	91%	96%	113%	121%	/	100%	99%	106%	/	96%	95%	105%	109%	103%	117%
Comparison BR	101%	119%	105%	89%	104%	108%	113%	87%	119%	92%	113%	102%	111%	120%	/
Comparison LA	113%	93%	114%	109%	/	100%	92%	95%	/	94%	104%	110%	80%	97%	/
Comparison average	102%	103%	111%	106%	104%	103%	101%	96%	119%	94%	104%	106%	100%	107%	117%

*Notes: CR clean river sample. BR burdened river sample. LA lake sample. *. Concentrations denoted with -A are calculated by the standard addition principle*