Supplementary data

Manuscript title:

Simultaneous detection of endocrine disrupting chemicals including conjugates in municipal wastewater and sludge with enhanced sample pretreatment and UPLC-MS/MS

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List of supplementary material:

Table S1

Operational parameters of tandem MS and calibration curves of target EDCs.

Analyte	Formula	Mother ion	Fragmentor (V)	Quantifier (cone energy/eV)	Qualifier (cone energy/eV)	Linear slope [a]	R^2	LOD [b] (pg)
E1	$C_{18}H_{22}O_2$	269.2	160	145.2 (35)	183.2 (45)	478.9	0.9991	2.1
E2	$C_{18}H_{24}O_2$	271.3	170	145.2 (40)	183.2 (40)	514.3	0.9990	8.4
E3	$C_{18}H_{24}O_3$	287.2	170	145.2 (50)	170.9 (34)	466.9	0.9987	9.1
EE2	$C_{20}H_{24}O_2$	295.3	170	145.2 (38)	199.1 (35)	611.0	0.9992	10.5
BPA	$C_{15}H_{16}O_2$	227.3	130	133.0 (30)	211.0 (10)	284.0	0.9982	12.7
NP	$C_{15}H_{24}O$	219.3	125	133.1 (25)	117.1 (55)	568.4	0.9966	20.0
E1-3G	$C_{24}H_{29}O_8Na$	445.2	150	269.1 (35)	113.0 (20)	113.6	0.9997	10.6
E2-3G	$C_{24}H_{31}O_8Na$	447.2	155	113.0 (20)	271.1 (40)	121.5	0.9999	10.0
E2-17G	$C_{24}H_{31}O_8Na$	447.2	165	85.0 (35)	271.1 (40)	231.5	0.9991	5.2
E1-3S	$C_{18}H_{21}O_5NaS$	349.1	110	269.1 (35)	79.9 (55)	751.4	0.9998	1.6
E2-3S	$C_{18}H_{23}O_5NaS$	351.0	170	271.1 (35)	79.9 (35)	451.5	0.9996	2.7
E3-3S	$C_{18}H_{23}O_6NaS$	367.0	165	287.1 (40)	79.9 (35)	709.7	0.9966	1.7

[a] For each estrogen and BPA, a 10-point calibration curve was established (0.5 to 500 ng L^{-1}); while the concentrations of NP were raised by 10 folds.

[b] The instrumental limit of detection was determined by directly injecting serially diluted standards (with MQ water) into the mass spectrometer and then multiplying the concentration at 3:1 of signal to noise ratio by the injection volume (10 μL).

Table S2

Intra- and inter-day precisions evaluated at three concentration levels of target EDCs.

Analyte	Intra-day precision Recovery (RSD[a]) (%/%)			Inter-day precision Recovery (RSD[b]) (%/%)		
	5 ng L^{-1}	50 ng L^{-1}	500 ng L^{-1}	5 ng L^{-1}	50 ng L^{-1}	500 ng L^{-1}
E1	89.2 (4.8) [a]	86.3 (5.9)	98.8 (2.1)	96.6 (13.0)	86.5 (6.1)	93.0 (10.5)
E2	109.9 (0.8)	110.7 (0.3)	100.7 (0.5)	105.1 (5.9)	91.2 (18.1)	99.8 (2.0)
E3	93.7 (1.5)	95.7 (6.6)	101.7 (1.8)	96.0 (7.6)	97.9 (4.6)	99.2 (7.3)
EE2	90.3 (8.7)	88.1 (8.0)	98.3 (3.7)	87.1 (13.7)	91.3 (10.6)	89.7 (4.6)
BPA	94.1 (2.0)	98.7 (2.9)	106.4 (5.5)	92.6 (3.7)	105.0 (5.6)	107.7 (6.3)
NP (/10)	99.0 (2.5)	99.7 (6.7)	101.4 (3.3)	95.7 (11.3)	88.1 (10.3)	102.2 (9.2)
E1-3G	99.0 (2.9)	89.9 (1.9)	98.6 (4.5)	95.0 (5.6)	94.8 (9.6)	96.4 (2.3)
E2-3G	99.8 (0.9)	94.4 (13.2)	96.7 (2.1)	104.1 (7.1)	84.3 (5.9)	101.7 (4.9)
E2-17G	93.6 (9.5)	101.6 (14.3)	92.0 (8.2)	100.6 (7.4)	105.1 (9.0)	92.7 (2.1)
E1-3S	95.0 (2.9)	98.1 (6.5)	98.5 (1.2)	98.1 (5.7)	95.0 (12.3)	94.3 (8.3)
E2-3S	96.9 (1.3)	94.1 (4.4)	93.6 (0.8)	89.4 (8.7)	100.3 (8.6)	95.1 (1.7)
E3-3S	102.8 (2.5)	87.0 (6.6)	102.3 (2.4)	97.3 (4.5)	89.7 (13.9)	101.7 (4.3)

[a] Intra-day repeatability (n = 3).

[b] Inter-day repeatability (n = 3).

Table S3

Major characteristics of the influent and effluent of a local WWTP.

Wastewater	COD (mg L^{-1})	NH_4^+–N (mg L^{-1})	TN (mg L^{-1})	TP (mg L^{-1})
Influent	330.4 (2.8)[a]	18.8 (2.1)	33.5 (5.1)	6.2 (0.7)
Effluent	35.8 (4.4)	<LOD[b]	17.5 (0.3)	0.8 (0.1)

[a] Mean concentration (SD), $n = 3$.

[b] LOD = 0.4 mg L^{-1}.

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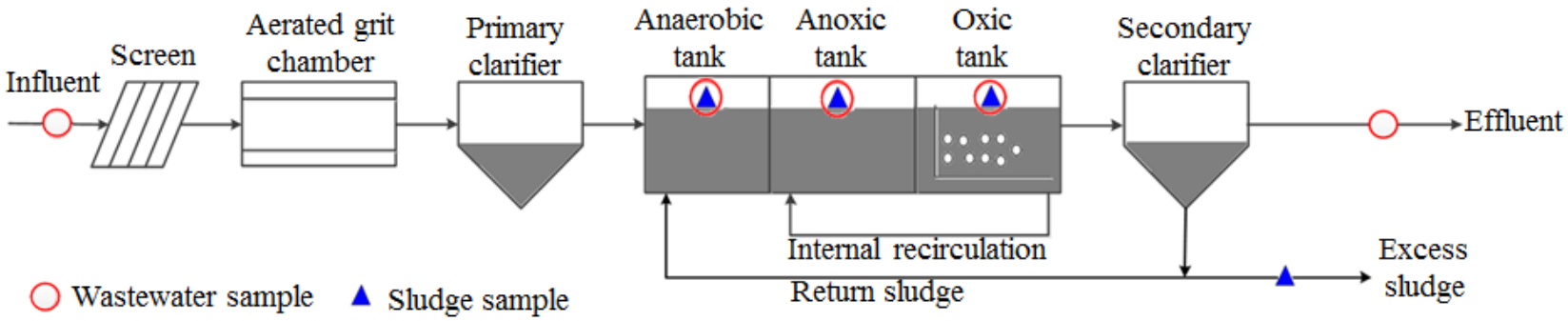

Fig. S1. Sampling points along the A/A/O treatment process in a local WWTP.

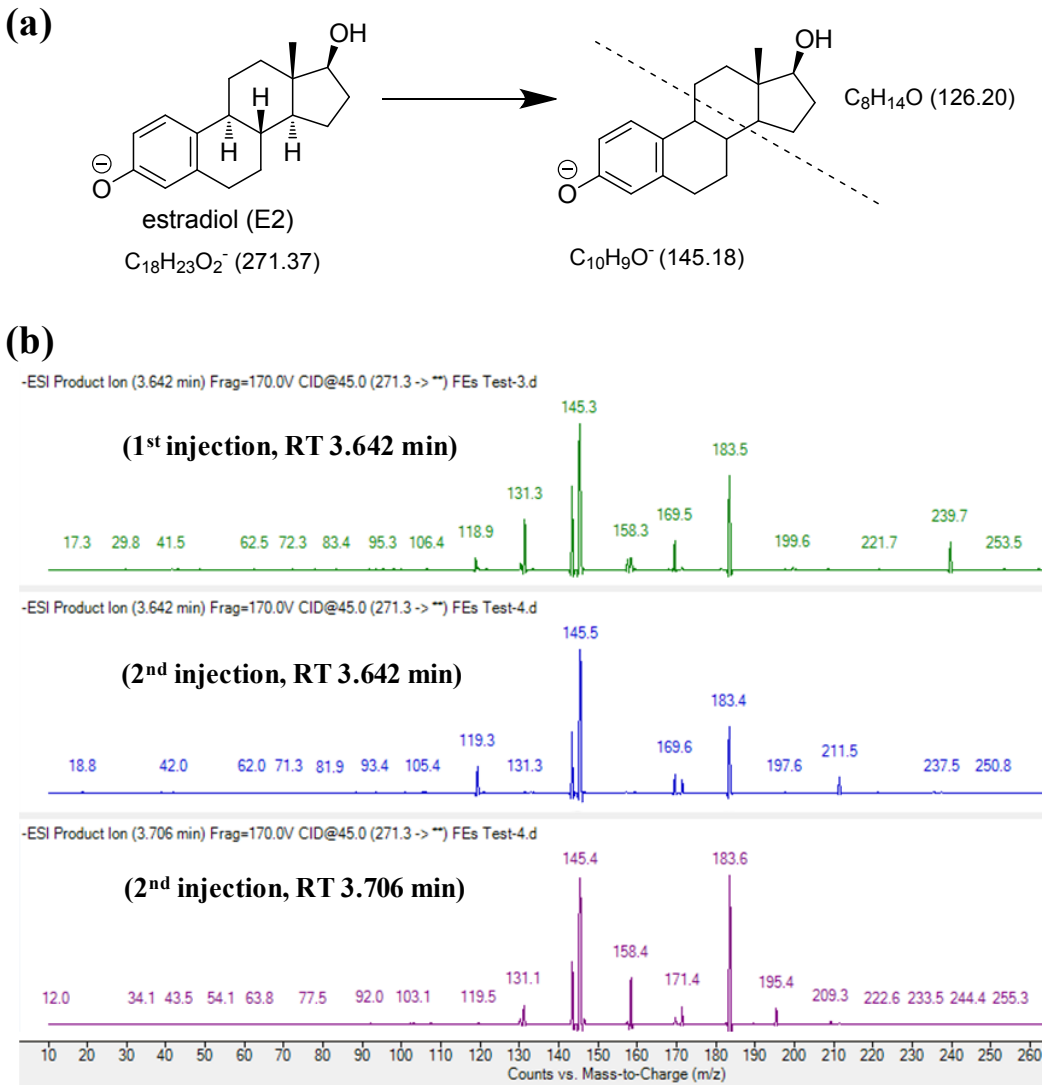

Fig. S2. (a) Illustration of E2 fragmentation to produce the 145.18 m/z ion; and (b) mass chromatograms of the product ions of E2 in the MS2 scan mode.

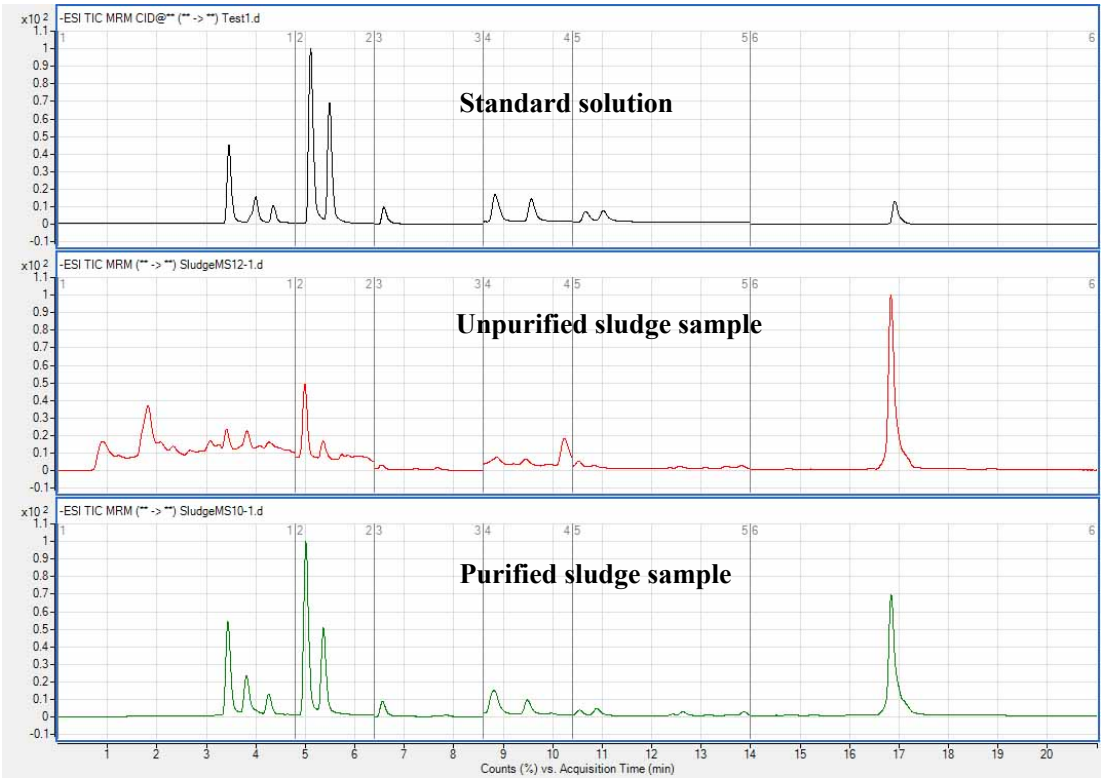

Fig. S3. Total-ion MRM chromatograms of 12 target EDCs (100 μg L^{-1} each) in standard solution (prepared in MQ water), unpurified sludge sample, and purified sludge sample.