

## Supplementary Materials

**Table S1:** Quantification and diagnostic ions used in GC-MS analyses. The relative abundance of ions ( $m/z$ ) is indicated between brackets (detailed information in Rocha et al. 2013).

Compound	MDL (ng/L)	$t_R$ (min)	Molecular mass	Quantification ions ( $m/z$ )	Diagnostic ions ( $m/z$ )	Segment [time (min)]
4-t-OP	1.46	10.8	206.3	207 (100)	-	8.5-17.2
4-NP	3.50	11.5-12.5	220.4	207 (100)	179 (84.9), 193 (31.9), 221 (31.9)	8.5-17.2
4-OP	5.47	12.9	206.3	179 (100)	180 (17.7)	8.5-17.2
4-n-NP	0.60	14.2	220.4	179 (100)	292 (35.9)	8.5-17.2
OP1EO	5.29	14.8	250.4	251 (100)	207 (97.2), 135 (68.9)	8.5-17.2
NP1EO	1.84	15.8-16.6	264.4	251 (100)	265 (64.4), 207 (59.5), 135 (45.5)	8.5-17.2
BPA-d16	-	17.9	244.3	368 (100)	369 (34.7), 386 (9.1)	17.2-22.5
BPA	0.73	18.1	228.3	357 (100)	358 (30.8)	17.2-22.5
OP2EO	0.94	18.6	294.4	295 (100)	207 (76.5), 115 (55.2)	17.2-22.5
NP2EO	2.07	19.6-19.9	308.5	295 (100)	207 (74.9)	17.2-22.5
E1	0.97	24.7	270.4	342 (100)	357 (55.1)	22.5-25.3
E2-d2	-	24.9	272.4	287 (100)	418 (75.2), 328 (72.8)	22.5-25.3
E2	0.86	25.0	274.4	285 (100)	416 (85.2), 326 (48.4)	22.5-25.3
EE2	1.34	27.3	296.4	425 (100)	285 (48.0), 426 (34.7)	25.3-29.0
FORM	2.61	28.6	268.3	340 (100)	339 (76.0), 355 (22.6)	25.3-29.0
BIO-A	1.38	30.5	284.3	356 (100)	341 (34.3)	29.0-35.0
DAID	1.25	30.5	254.2	398 (100)	383 (76.0), 355 (22.6)	29.0-35.0
GEN	1.14	30.8	270.2	471 (100)	473 (19.9)	29.0-35.0
SITO	2.01	43.4	414.7	396 (100)	486 (53.4), 255 (49.4)	35.0-45.0

**Table S2:** Data referring to PCA of EDCs in Douro River estuary.

Estrogens	PC 1	PC 2	PC 3	Phytoestrogens & SITO	PC 1	PC 2	PC 3	PC 4	PC 5
E1	0.68	-0.22	0.70	FORM	0.53	-0.08	-0.21	-0.23	0.78
E2	0.26	0.96	0.04	BIO-A	0.53	-0.06	-0.13	-0.60	-0.58
EE2	0.69	-0.16	-0.71	DAID	0.51	0.09	-0.37	0.74	-0.22
				GEN	0.12	0.96	0.22	-0.08	0.05
				SITO	0.39	-0.23	0.87	0.19	0.00
OPs & OPEOs	PC 1	PC 2	PC 3	PC 4	NPs & NPEOs	PC 1	PC 2	PC 3	PC 4
4-t-OP	-0.27	0.92	0.18	0.20	4-NP	0.54476	-0.39	-0.26	-0.69
4-n-OP	0.59	0.35	-0.06	-0.72	4-n-NP	0.48237	-0.55	0.42	0.53
OP1EO	0.51	-0.07	0.80	0.31	NP1EO	0.43909	0.62	0.61	-0.24
OP2EO	0.56	0.15	-0.57	0.58	NP2EO	0.52702	0.40	-0.62	0.43