

**A short cost-effective methodology for tracing the temporal and spatial anthropogenic inputs
of micropollutants to ecosystems: verified mass balance approach applied to rivers confluence
and WWTP release**

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Table S1.The first watch list of the 10 compounds created in the Decision 2015/495/EU.

Name of substance/group of substances		Concentration (ng/L)/ Matrix/ Location
17-Alphaethinylestradiol (EE2)	17-Alphaethinylestradiol (EE2)	<1-8/ WW/ Korea (n = 120), Germany (n.a.), South Africa (n = 12) 0.2-1.9/ SW/ China (n = 3), Korea (n = 120), Germany (n.a.), France (n = 73) 0.5-230/ GW/ France (n = 73), USA (n.a.)
Natural hormones	17-Beta-estradiol (E2)	<1-88/ WW/ China (n = 3), Korea (n = 120), Sweden (n = 3),UK (n.a.), Germany (n.a.) 0.2-10.1/ SW/ China (n = 3), Korea (n = 120), Germany (n.a.), Japan (n = 517), France (n = 71) 0.3-147/ GW/ France (n = 73), USA (n.a.)
	Estrone (E1)	WW/ China (n = 3), Korea (n = 120), Sweden (n = 3), UK (n.a.), Germany (n.a.) 0.5-69.1/ SW/ China (n = 3), Korea (n = 120), Germany (n.a.),France (n = 71) 0.7-79/ GW/ France (n = 73), USA (n.a.)
Diclofenac	Diclofenac	14.9-4425/ WW/ Spain (n.a.), Italy (n = 3), USA (n.a.), Portugal (n = 4) 0.8-1043/ SW/ Spain (n.a.), Vietnam (n.a), Costa Rica (n = 86),Greece (n = 30) 1.17-380/ GW/ Spain (n = 30), France (n = 70)
2,6-di-tert-butyl-4-methylphenol	2,6-di-tert-butyl-4-Methylphenol	49-620/ SW/ USA (n = 19), Sweden (n.a.)
2-ethylhexyl-4-methoxycinnamate	2-ethylhexyl-4-methoxycinnamate	4.7-505/ WW/ China (n = 17), Norway (n = 5) 12-1040/ SW/ Japan (n = 23) 770/ GW/ Spain (n = 7)
Macrolide antibiotics	Azithromycin	0.4-1220/ WW/ Italy (n = 3), Slovakia (n = 3), USA (n.a.), Portugal (n = 4) 0.6-90.8/ SW/ Vietnam (n = 2), China (n = 24) 0.6-1620/ GW/ Spain (n.a), China (n = 69)
	Clarithromycin	54-1890/ WW/ Spain (n.a.), Italy (n = 3), Slovakia (n = 3), USA (n.a) 0.01-778/ SW/ Vietnam (n = 2), Spain (n = 18), China (n = 24) 0.2-20.5/ GW/ Spain (n.a.), China (n = 15)
	Erythromycin	16-147.9/ WW/ Spain (n.a.), Slovakia (n = 3), USA (n.a.), China(n = 3) 0.28-2246/ SW/ Vietnam (n = 2), Spain (n = 18) 4.8-154.3/ GW/ Spain (n = 121), China (n = 54)
Methiocarb		4.73-14.92/ WW/ Spain (n = 55)
Neonicotinoids	Imidacloprid	2-34.44/ WW/ Spain (n = 55) 1.1-105/ SW/ Spain (n = 24), USA (n = 35), Greece (n = 89), Portugal (n.a.), Australia (n = 13)

	Thiacloprid	20-400/ SW/ Australia (n = 13)
	Thiamethoxam	0-1580/ SW/ Brasil (n.a.), Vietnam (n ¼=11), Australia (n = 13)
	Clothianidin	20-420/ SW/ Australia (n = 13)
	Acetamiprid	20-380/ SW/ Australia (n = 13)
Oxadiazon		4-1440/ SW/ Canada (n = 8)
Triallate		n.a.

n.a.: not available

WW: wastewater, SW: surface water, GW: ground water

Table S2. Weather conditions during the four sampling periods.

Conditions	Sampling 1	Sampling 2	Sampling 3	Sampling 4
Date	11 September 2015	5 January 2016	14 October 2016	17 March 2017
Weather	Sunny	Rainy	Cloudy	Clear
Weather days before	Sunny	No rain, cold	Some rain	Clear
Temperature	22 °C	7 °C	8 °C	11 °C

Table S3. Parameters of the LC-MS/MS instrument, including mobile phases and eluent programs. The notation “min” corresponds to minutes.

	Positive ionization mode	Negative ionisation mode
Column	Zorbax Eclipse Plus C18 (Agilent)	
Oven temperature	40 °C	
Flow	0.25 mL/min	
Volume of injection	25 µL	
Eluents	A: Water + 0.1 % formic acid B: Methanol + 0.1 % formic acid	A: Water + 2.5 mM ammonium acetate B: Acetonitrile
Eluent program	0 min 10 % B – 2 min 10 % B – 10 min 30 % B – 14 min 95 % B – 16 min 95 % B – 17 min 10 % B – 28 min 10 % B	0 min 30 % B – 1 min 30 % B – 3 min 50 % B – 8 min 80 % B – 9 min 95 % B – 11 min 95 % B – 12 min 30 % B – 15 min 30 % B

Table S4. The Concentrations (C) in ng/L and mass fluxes (F) in g/day for the 21 micropollutants in 5 sampling sites on 3 sampling dates.

Compound	Value	A3	A2	A1	B2	B1
September 2015	Q (m³/s)	13.5	5.4	3.9	8.08	8.08
Bisphenol A	F	155	15	15	165	48
	C	133	31.7	44.3	236	69.1
Estradiol-beta	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Estrone	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Ethinylestradiol	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Carbamazepine	F	58	10	8	38	15
	C	49.2	21	23.1	54.1	21.8
Carbamazepine-10,11-epoxide	F	-	-	-	-	-
	C	n.q	n.q	n.q	2.99	n.q
Clarithromycin	F	97	-	-	103	19
	C	83.5	n.q	n.q	148	27.3
Cyclophosphamide	F	-	-	-	-	-
	C	n.q	n.q	n.q	2.04	n.q
Diclofenac	F	33	-	2	61	5
	C	28.6	n.q	7.06	87.4	6.86
Erythromycin	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Ibuprofen	F	9	2	2	7	6
	C	7.63	5	5.7	9.33	8.18
Ketoprofen	F	-	-	-	12	-
	C	n.q	n.q	n.q	16.9	n.q
Lidocaine	F	44	12	14	40	13
	C	37.4	25.6	41	57.2	18.3
Naproxen	F	19	-	-	21	11
	C	16.4	n.q	n.q	29.6	15.2
Sulfadimethoxine	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Sulfadimidine	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Sulfamethoxazole	F	52	4	2	45	11
	C	44.6	8.96	6.63	64.6	15.8
Sulfathiazole	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Triclosan	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
PFOA	F	-	-	-	-	-
	C	n.q	8.52	n.q	n.q	n.q
PFOS	F	19	7	7	10	9
	C	15.9	16	21.9	14.1	12.3
Compound	Value	A3	A2	A1	B2	B1
January 2016	Q (m³/s)	124	90.5	58.5	30.3	30.3
Bisphenol A	F	435	366	246	241	117

	C	40.6	46.8	48.7	92.1	44.5
Estradiol-beta	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Estrone	F	-	-	-	-	-
	C	n.q	n.q	n.q	7.55	2.8
Ethinylestradiol	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Carbamazepine	F	264	123	66	84	59
	C	24.6	15.7	13	32.2	22.5
Carbamazepine-10,11-epoxide	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Clarithromycin	F	825	426	237	367	214
	C	77	54.5	46.9	140	81.6
Cyclophosphamide	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Diclofenac	F	340	257	142	131	43
	C	31.7	32.9	28	50	16.6
Erythromycin	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Ibuprofen	F	287	138	174	255	148
	C	26.8	17.6	34.5	97.3	56.7
Ketoprofen	F	83	13	19	49	15
	C	7.71	1.63	3.79	18.7	5.69
Lidocaine	F	268	315	194	-	-
	C	25	40.3	38.3	n.q	n.q
Naproxen	F	216	136	53	118	55
	C	20.2	17.4	10.4	45	21.1
Sulfadimethoxine	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Sulfadimidine	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Sulfamethoxazole	F	168	80	69	61	37
	C	15.7	10.2	13.7	23.2	14.2
Sulfathiazole	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Triclosan	F	903	-	-	157	186
	C	84.3	n.q	n.q	59.8	71.2
PFOA	F	77	112	79	-	-
	C	7.19	14.3	15.7	n.q	n.q
PFOS	F	185	146	124	73	43
	C	17.3	18.7	24.6	27.8	16.5

Compound	Value	A3	A2	A1	B2	B1
October 2016	Q (m³/s)	21	10.8	6.46	9.28	9.28
Bisphenol A	F	71	35	7	64	25
	C	39.1	37.4	12.3	80.3	31.6
Estradiol-beta	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Estrone	F	7	-	-	5	-
	C	3.8	n.q	n.q	6.18	n.q
Ethinylestradiol	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Carbamazepine	F	58	16	10	55	30
	C	31.96	17.1	17.4	68.92	37.2
Carbamazepine-10,11-epoxide	F	-	-	-	-	-
	C	n.q	n.q	n.q	3.1	n.q
Clarithromycin	F	495	34	32	512	95
	C	253	36.23	57.49	639	118.2
Cyclophosphamide	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Diclofenac	F	88	-	7	104	19
	C	48.5	n.q	12.4	129	24.27
Erythromycin	F	847	717	148	734	494
	C	467	768.8	264.37	914.9	615.7
Ibuprofen	F	22	5	2	15	14
	C	12.2	4.9	4.1	18.8	17.2
Ketoprofen	F	-	-	-	6	-
	C	n.q	n.q	n.q	6.99	n.q
Lidocaine	F	46	12	19	38	5
	C	25.4	12.4	33.4	47.8	6.7
Naproxen	F	-	-	-	11	11
	C	n.q	n.q	n.q	13.7	13.6
Sulfadimethoxine	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Sulfadimidine	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Sulfamethoxazole	F	33	6	3	26	6
	C	18.1	5.9	5.58	32.2	7.92
Sulfathiazole	F	-	-	-	-	-
	C	n.q	n.q	n.q	n.q	n.q
Triclosan	F	22	-	5	11	7
	C	12.1	n.q	8	13.1	8.4
PFOA	F	9	4	3	2	2
	C	5.2	4.47	5.8	3	2.1
PFOS	F	47	19	19	16	16
	C	26	20	34	20	20

Table S5. The concentrations (ng/L), mass fluxes F (g/day), flux F_{iWWTPt} (g/day) and flux F_{iWWTPt} per inhabitant (g/day.Inhabitant) of the quantified micropollutants upstream and downstream the WWTP during the three sampling periods. The sum represents the sum of the mass fluxes for all the micropollutants upstream WWTP and from WWTP, and the percentages are calculated with respect to the total sum downstream WWTP. The letter F refers to mass flux and C to concentration. A dash '-' is used when C_{it} at the site is < LOQ.

	September 2015					January 2016					October 2016					
	Site		FiWWTPt per inhabitant × 10 ⁻⁵			Site		FiWWTPt per inhabitant × 10 ⁻⁵			Site		FiWWTPt per inhabitant × 10 ⁻⁵			
	Upstream of the WWTP	Downstream of the	Value	C	F	Upstream of the WWTP	Downstream of the	Value	C	F	Upstream of the WWTP	Downstream of the	Value	C	F	
C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F	
Carbamazepine	21.8	15	54.1	38	23	8.9	23	84	9.7	25	37.2	30	68.9	55	25	9.7
Clarithromycin	27.2	19	148.4	103	84	32.6	84	367	59.4	153	118.2	95	639	512	417	161.9
Diclofenac	6.9	5	87.4	61	56	21.7	56	131	34.1	88	24.3	19	129	104	85	33
Ibuprofen	8.2	6	9.3	7	1	0.3	1	255	41.5	107	17.2	14	18.9	15	1	0.3
Ketoprofen	-	-	16.9	12	12	4.6	12	49	13.2	34	-	-	7	6	6	2.3
Lidocaine	18.3	13	57.2	40	27	10.4	27	-	-	-	6.7	5	47.8	38	33	12.8
Naproxen	15.2	11	29.6	21	10	3.8	10	118	24.4	63	13.6	11	13.7	11	0	0
Sulfamethoxazole	15.9	11	64.6	45	34	13.2	34	61	9.3	24	7.9	6	32.3	26	20	7.7
Bisphenol A	69.1	48	236.2	165	117	45.4	117	241	48.1	124	31.6	25	80.3	64	39	15.1
Estrone	-	-	-	-	-	-	-	20	5	13	-	-	6.2	5	5	1.9
PFOS	12.3	9	14.2	10	1	0.38	1	73	11.6	30	20.1	16	20.1	16	0	0
Sum in %	27 %		73 %		53 %		47 %		26 %		74 %					

Table S6. Concentration of micropollutants in A1 on January and October.

Micropollutant Concentration (ng/L)	January	October
Bisphenol A	48.7	12.3
Estradiol-beta	n.q	n.q
Estrone	n.q	n.q
Ethinylestradiol	n.q	n.q
Carbamazepine	13.0	17.4
Carbamazepine-10,11-epoxide	n.q	n.q
Clarithromycin	46.9	57.49
Cyclophosphamide	n.q	n.q
Diclofenac	28.0	12.4
Erythromycin	n.q	264.37
Ibuprofen	34.5	4.1
Ketoprofen	3.79	n.q
Lidocaine	38.3	33.4
Naproxen	10.4	n.q
Sulfadimethoxine	n.q	n.q
Sulfadimidine	n.q	n.q
Sulfamethoxazole	13.7	5.58
Sulfathiazole	n.q	n.q
Triclosan	n.q	8.0
PFOA	15.7	5.8
PFOS	24.6	34

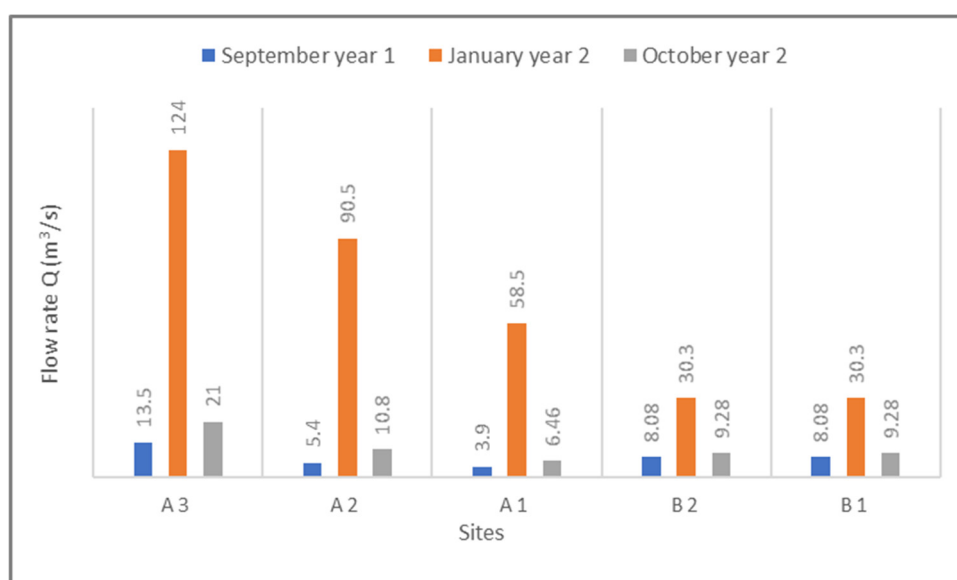


Figure S1. The variation of the flow rate during the three sampling periods at the five sampling sites.