Supporting information to:

Combination of different chromatographic and sampling modes for high-resolution mass spectrometric screening of organic microcontaminants in water

Verónica Castro[1], José Benito Quintana[1,*], Inmaculada Carpinteiro[1], Julio Cobas[2], Nieves Carro[2], Rafael Cela[1], Rosario Rodil[1,*]

[1] Department of Analytical Chemistry, Institute of Research on Chemical and Biological Analysis (IAQBUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

[2] INTECMAR - Technological Institute for the Monitoring of the Marine Environment of Galicia, Peirao de Vilaxoán S/N, 36611 Vilagarcía de Arousa, Spain

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Figure S8: Number of compounds that would be identified by using different combinations of sampling and chromatographic modes.

Figure S9: Distribution of the compounds identified in surface water samples according to their main application.

Text S1: Chromatographic conditions

RPLC separation was carried out with a ZORBAX Extend-C18 1.8 µm (2.1 x 50 mm) column supplied by Agilent Technologies, connected to a Supelco ColumnSaver 0.5 µm Precolumn Filter (Supelco, Bellefonte, PA, USA). The temperature at the column was fixed at 35 °C and a 2 µL aliquot of the sample was injected. As mobile phases, methanol (A) and water (B) both with 0.1% formic acid (pH 2.7) were used at flow rate of 0.4 mL/min. The gradient elution started with 98% A, increasing to 100% B in 22 min, held for 4 min. Subsequently, it returned to initial conditions (98% A) and was held for 4 min for column back-conditioning.

HILIC separation was adapted from Schulze et al. [1] and carried out with an EC 150/2 NUCLEODUR HILIC 3 µm (2 x 150 mm) column supplied by Macherey Nagel (Düren, Germany), connected to a Supelco ColumnSaver 0.5 µm Precolumn Filter. The temperature at the column was fixed at 35 °C and a 2 µL aliquot of the sample was injected. As mobile phases, a mixture of water-acetonitrile (95:5 v/v) containing 5 mM ammonium formate (apparent pH 2.9) (A) and a mixture of acetonitrile-water (95:5 v/v) also with 5 mM ammonium formate (apparent pH 2.9) (B) were used at flow rate of 0.2 mL/min. The gradient elution started with 100% B, increasing to 50% A in 12 min, held for 8 min. Subsequently, it returned to initial conditions (100% B) and was held for 10 min for column back-conditioning.

MMLC separation was carried out with an Acclaim Trinity P1 3 µm (2.1 x 50 mm) column supplied by Thermo Scientific (San Jose, CA, USA), connected to a Supelco ColumnSaver 0.5 µm Precolumn Filter, based on the work of Montes et al. [2] The temperature at the column was fixed at 35 °C and a 2 µL aliquot of the sample was injected. As mobile phases, a mixture of water- acetonitrile (98:2 v/v) with 5 mM ammonium acetate (apparent pH 5.5) (A) and a mixture of acetonitrile-water (80:20 v/v) with 20 mM ammonium acetate (apparent pH 5.5) (B) were used at flow rate of 0.2 mL/min. The gradient elution started with 98% A, increasing to 100% B in 10 min, held for 10 min. Subsequently, it returned to initial conditions (98% A) and was held for 10 min for column back-conditioning.

SFC separation was carried out with a Torus DIOL 1.7 µm (3.0 x 100 mm) column supplied by Waters Corporation (Milford, MA, USA), connected to a Supelco ColumnSaver 0.5 µm Precolumn, adapting a protocol proposed by Schulze et al. [1]. The temperature at the column was fixed at 45 °C and a 2 µL aliquot of the sample was injected. As mobile phases, supercritical CO_2 (A) and methanol (0.2% ammonia) (B) were used at flow rate of 1.5 mL/min. The gradient elution started with 98% A, increasing to 40% B in 20 min, held for 5 min. Subsequently, it returned to initial conditions (98% A) and was held for 5 min for column back-conditioning. A

mixture of methanol-water (90:10 v/v) (0.1% formic acid) was used as a make-up at a flow rate of 0.2 mL/min. The BPR was maintained at 140 bar and 60 °C.

References:

1. Schulze S, Zahn D, Montes R, Rodil R, Quintana JB, Knepper TP, et al. Occurrence of emerging persistent and mobile organic contaminants in European water samples.Water Res. 2019;153:80–90.
2. Montes R, Rodil R, Cela R, Quintana JB. Determination of persistent andmobile organic contaminants (PMOCs) in water by mixed-mode liquid chromatography–tandem mass spectrometry. Anal Chem. 2019;91(8):5176–83.

Table S2: Compounds identified in the effluent wastewater sample by the different sampling strategies (POCIS sorbent, POCIS membrane and spot water) injected in the four chromatographic modes (RPLC, HILIC, MMLC and SFC). Detections are coded as 1, while non-detections are coded as 0.

Compound name	SPE				POCIS sorbent				POCIS membrane			
	HILIC	SFC	MMLC	RPLC	HILIC	SFC	MMLC	RPLC	HILIC	SFC	MMLC	RPLC
10-Hydroxycarbamazepine	0	0	1	1	1	0	1	1	0	0	0	0
2,4-Dinitrophenol	0	0	1	0	0	0	0	0	0	0	0	0
2,6-Xanthine	0	0	0	0	0	0	0	0	0	0	1	0
3-Hydroxylidocaine	0	0	0	1	0	0	0	1	0	0	1	0
4-Methoxyamphetamine	0	0	1	1	0	0	1	1	0	0	0	0
4-Nitrophenol	0	1	1	1	0	1	0	0	0	0	1	1
5-Hydroxyomeprazole	0	1	0	0	0	1	0	0	0	0	0	0
5-Hydroxypropafenone	0	1	0	0	0	1	1	1	0	0	0	0
8-Hydroxychinolin	0	0	0	0	0	1	0	0	0	0	0	0
8-Hydroxyefavirenz	0	0	0	0	0	1	0	0	0	0	0	0
Acebutolol	1	1	1	1	1	1	1	1	0	0	0	0
Amantadine	1	1	1	1	1	1	1	1	0	0	0	0
Aminocaproic acid	0	0	0	0	0	0	0	0	0	0	1	0
Amitriptyline	1	0	1	1	0	0	1	1	0	0	1	0
Amphetamine	0	1	0	0	0	0	0	0	0	0	0	0
Ampyrone	0	0	0	1	0	0	0	1	0	0	0	0
Articaine	0	0	0	1	0	1	0	0	0	0	0	0
Atenolol	1	1	1	1	1	1	1	1	0	0	0	0
Azithromycin	1	1	1	1	1	1	1	1	0	0	0	0
Benzoylecgonine	0	0	0	0	1	0	0	0	0	0	0	0
Benzydamine	1	0	1	1	0	0	1	1	0	0	0	0
Berberine	0	1	1	1	0	1	0	1	0	0	0	1
Bicalutamide	0	1	0	0	0	1	0	0	0	0	1	0

Bisoprolol	0	1	1	1	0	1	0	1	0	0	0	0
Bupivacaine	0	1	0	0	0	1	0	1	0	0	0	0
Bupropion	0	0	0	1	0	1	0	1	0	0	0	0
Butylscopolaminium	0	0	0	0	0	1	1	0	0	0	0	0
Candesartan	0	1	0	0	0	0	0	0	0	0	0	0
Carbamazepine	0	1	1	1	0	1	1	1	0	0	0	0
Carbamazepine 10,11-epoxide	0	1	0	0	0	1	1	1	0	0	0	0
Carbendazim	0	1	1	1	0	1	1	1	0	1	1	1
Carvedilol	0	0	0	0	0	1	0	0	0	0	1	1
Celiprolol	0	1	1	1	0	1	1	1	0	0	0	0
Cetirizine	0	1	0	0	0	1	0	0	0	0	0	0
Chlorothiazide	0	0	0	0	0	0	1	0	0	0	0	0
Chlorpheniramine	0	1	1	0	1	1	1	1	0	0	0	0
Citalopram	1	1	1	1	0	1	1	1	0	0	0	0
Clarithromycin	1	1	1	1	1	1	1	1	0	0	0	0
Climbazole	0	0	0	0	0	0	1	1	0	0	0	0
Clindamycin	0	1	0	0	0	1	0	0	0	0	0	0
Cloperastine	0	1	0	1	0	0	0	1	0	0	0	1
Clopidogrel	0	0	0	0	0	0	0	1	0	0	0	1
Clorophene	0	0	0	0	0	0	0	0	0	0	1	0
Clozapine	0	1	1	1	1	1	1	1	0	0	0	0
Cyclobenzaprine	0	0	0	0	0	1	0	1	0	0	0	0
Dibenzylpiperazine	0	0	1	0	0	0	0	0	0	0	0	0
Diethyltoluamide (DEET)	0	1	1	1	0	1	1	1	0	0	0	0
Denatonium	1	1	1	1	0	1	1	1	0	0	0	0
(Dex) - ketoprofen	0	1	0	0	0	1	0	1	0	0	0	0
Dextromethorphan	0	0	1	0	0	1	1	0	0	0	0	0
Dextrorphan	1	1	1	1	0	1	1	1	0	0	0	0
Diclofenac	0	1	0	0	0	1	0	0	0	0	0	0

Diltiazem	0	1	0	1	0	1	0	1	0	0	0	0
Diphenhydramine	0	1	0	0	0	1	1	1	0	0	0	0
Diuron	0	1	1	1	0	1	1	1	0	1	1	1
Doxylamine	0	1	1	1	0	1	1	1	0	0	0	0
Eprosartan	1	1	0	1	0	1	0	1	0	0	0	0
Ethambutol	0	0	1	1	0	0	0	0	0	0	0	0
Flecainide	1	1	0	1	0	1	0	1	0	0	0	0
Fluconazole(I)	0	1	0	0	0	1	0	1	0	0	0	0
Fludioxonil	0	0	0	0	0	0	0	0	0	1	1	0
Flufenamic acid	0	1	0	0	0	1	0	0	0	0	0	1
Fluoxetine	0	0	0	0	0	1	0	0	0	0	0	0
Gabapentin	1	1	1	0	0	0	0	0	0	0	0	0
Haloperidol	0	0	0	0	0	1	0	0	0	0	0	0
Harmol	0	0	1	0	0	0	1	0	0	0	0	0
Hydrochlorothiazide	0	1	0	0	0	1	0	0	0	0	0	0
Hydroxybupropion	0	1	1	1	0	1	1	0	0	0	0	0
Hydroxychloroquine	0	0	0	0	1	1	0	1	0	0	0	0
Imidapril	0	0	0	0	0	1	1	0	0	0	0	0
Irbesartan	1	1	1	0	1	1	1	1	0	0	0	0
Isoproturon	0	0	1	0	0	1	1	0	0	0	1	0
Ketamine	0	0	0	0	0	0	0	1	0	0	0	0
Lamotrigine	0	0	1	1	1	1	0	1	0	0	0	0
Levetiracetam	0	1	0	0	0	0	0	0	0	0	0	0
Levofloxacin	0	0	0	1	0	0	0	1	0	0	0	0
Levomethadone	0	0	0	0	1	0	0	0	0	0	0	0
Losartan	0	1	1	0	0	1	1	0	0	0	0	0
Mebendazole	0	1	0	0	0	0	0	0	0	1	0	0
Mecetronium	1	1	0	0	0	0	0	0	0	0	0	0
Memantine	0	0	1	0	0	0	0	0	0	0	0	0

Meperidine	0	0	0	0	0	0	0	1	0	0	0	0
Mepivacaine	1	1	1	1	0	1	1	1	0	0	0	0
Methadone	0	0	1	1	0	0	1	1	0	0	0	0
Methamphetamine	0	1	0	0	1	0	0	0	0	0	0	0
Methyl 4-hydroxybenzoate	0	0	0	0	0	0	0	0	0	0	1	0
Methylendioxymethamphetamine	0	0	1	1	1	0	1	0	0	0	0	0
Methylphenidate	0	1	0	0	0	1	1	0	0	0	0	0
Metoclopramide	0	1	1	0	1	1	1	1	0	0	0	0
Metoprolol	0	1	0	1	0	1	0	1	0	0	0	0
Metronidazole	0	1	0	1	0	0	0	0	0	0	0	0
Minoxidil	1	1	1	1	1	1	1	0	0	0	0	0
Mirtazapine	0	1	1	1	1	1	0	1	0	0	0	0
Mycophenolic acid	0	0	0	0	0	1	0	0	0	0	0	0
N-Desalkylverapamil	0	0	0	0	0	1	0	0	0	0	0	0
Nicotine	0	1	0	1	0	0	0	0	0	0	0	0
Norcitalopram	0	0	1	1	0	1	1	1	0	0	0	0
Nortriptyline	0	0	0	0	0	0	1	0	0	0	0	0
Norverapamil	0	0	0	0	0	1	0	0	0	0	0	0
Octamylamine	0	0	1	0	0	0	0	0	0	0	0	0
O-Desmethyltramadol	0	1	0	1	0	0	0	1	0	0	0	0
Omeprazole	0	1	0	0	0	1	0	0	0	0	0	0
Omeprazole sulfone	0	1	1	1	0	1	1	1	0	0	0	0
Oxazepam	0	1	0	0	0	1	0	0	0	0	0	0
Oxcarbamazepine	0	1	1	1	0	1	0	1	0	0	0	0
Oxybenzone	0	0	0	0	0	0	0	0	0	0	0	1
Paliperidone	0	0	0	1	0	1	0	1	0	0	0	0
Pentoxifylline	0	1	1	1	0	1	1	1	0	0	0	0
Phenethylamine	0	0	0	0	1	1	0	0	0	0	0	0
Propafenone	0	0	0	1	0	1	1	0	0	0	0	0

Propranolol	0	0	1	1	0	1	1	1	0	0	0	0
Pseudoephedrine	0	1	1	1	0	1	1	0	0	0	0	0
Pyrantel	0	0	0	0	1	0	1	1	0	0	0	0
Quetiapine	0	1	0	1	0	1	1	1	0	0	0	0
Ranitidine	0	1	0	1	0	1	0	0	0	0	0	0
Ritalinic acid	1	1	0	1	0	0	0	0	0	0	0	0
Salazosulfapyridine	0	0	0	0	0	1	0	0	0	0	0	0
Sertraline	0	1	1	1	1	1	0	1	0	1	1	1
Sitagliptin	0	0	1	1	1	1	1	1	0	0	0	0
Sorbitol	0	1	0	0	0	1	0	0	0	0	1	0
Sulfamethoxazole	0	1	0	1	0	1	0	1	0	0	0	0
Sulpiride	0	1	1	1	0	1	1	0	0	0	0	0
Tapentadol	0	1	1	1	0	1	1	1	0	0	0	0
Telmisartan	1	1	1	1	1	1	1	1	0	1	0	1
Terbuthylazine-2-hydroxy	0	0	0	1	1	1	0	1	0	0	0	0
Terbutryn	0	1	1	1	0	1	0	1	0	0	0	0
Tetramisole	0	0	1	1	0	0	1	1	0	0	0	0
Thiabendazole	0	0	0	0	0	0	0	1	0	0	0	0
Tramadol	0	1	0	1	0	1	0	1	0	0	0	0
trans-10,11-Dihydroxy-10,11-dihydrocarbamazepine	0	1	1	0	0	1	1	0	0	0	0	0
Trazodone	0	0	0	1	0	1	1	1	0	0	0	0
Trimethoprim	1	1	1	1	0	1	1	1	0	0	0	0
Trospium	0	0	0	0	0	1	0	1	0	0	0	0
Valsartan	1	1	0	0	1	1	0	1	0	0	0	0
Venlafaxine	0	1	0	1	0	1	0	1	0	0	0	0
Total	21	76	57	67	25	91	56	73	0	6	15	11

Table S3: Physicochemical properties of the 135 compounds identified in wastewater calculated with the JChem add-on for Office (https://chemaxon.com/products/jchem-for-office). N.B., only the most acidic pK_a and most basic pK_a were calculated.

Compound name	CAS	logP	logD (pH 7)	pK_a (acid)	pK_a (basic)
10-Hydroxycarbamazepine	29331-92-8	1.73	1.73	-	-
2,4-Dinitrophenol	51-28-5	1.55	-0.3	4.5	-
2,6-Xanthine	69-89-6	-0.21	-0.25	7.95	-
3-Hydroxylidocaine	34604-55-2	2.54	1.73	10.04	7.73
4-Methoxyamphetamine	64-13-1	1.65	-1.09	-	10.04
4-Nitrophenol	100-02-7	1.61	1.35	7.07	-
5-Hydroxyomeprazole	92340-57-3	1.15	1.15	9.29	3.93
5-Hydroxypropafenone	86384-10-3	2.41	0.67	9.22	9.88
8-Hydroxychinolin	148-24-3	1.83	1.82	9.36	4.83
8-Hydroxyefavirenz	205754-32-1	4.15	4.07	7.66	-
Acebutolol	37517-30-9	1.53	-1.02	13.91	9.65
Amantadine	768-94-5	1.47	-1.48	-	10.71
Aminocaproic acid	60-32-2	-2	-2	4.73	10.21
Amitriptyline	50-48-6	4.81	2.12	-	9.76
Amphetamine	300-62-9	1.8	-0.92	-	10.01
Ampyrone	83-07-8	0.33	0.33	-	0.07
Articaine	23964-58-1	3.25	1.56	11.61	8.68
Atenolol	29122-68-7	0.43	-2.14	-	9.67
Azithromycin	83905-01-5	2.44	-1.99	12.43	9.57
Benzoylecgonine	519-09-5	-0.59	-0.6	3.15	9.54
Benzydamine	642-72-8	3.66	1.42	-	9.26
Berberine	2086-83-1	-1.28	-1.28	-	-
Bicalutamide	90357-06-5	2.71	2.71	11.78	-
Bisoprolol	66722-44-9	2.2	-0.37	-	9.67
Bupivacaine	2180-92-9	4.52	3.47	13.62	8
Bupropion	34911-55-2	3.27	2.03	-	8.22
Butylscopolaminium	149-64-4	-1.94	-1.94	-	-
Candesartan	139481-59-7	5.31	1.04	3.51	1.5
Carbamazepine	298-46-4	2.77	2.77	-	-
Carbamazepine 10,11-epoxide	36507-30-9	1.97	1.97	-6	-
Carbendazim	10605-21-7	1.8	1.8	9.7	4.28
Carvedilol	72956-09-3	3.42	1.69	-	8.74
Celiprolol	56980-93-9	1.5	-1.13	13.55	9.75
Cetirizine	83881-51-0	0.87	0.77	3.59	7.42
Chlorothiazide	58-94-6	-0.44	-0.44	9.19	-
Chlorpheniramine	132-22-9	3.58	1.15	-	9.47
Citalopram	59729-33-8	3.76	1.05	-	9.78
Clarithromycin	81103-11-9	3.24	1.25	12.46	9
Climbazole	38083-17-9	4.34	4.25	-	6.49
Clindamycin	18323-44-9	1.04	0.38	12.41	7.55
Cloperastine	3703-76-2	5.11	3.29	-	8.82

Compound name	CAS	logP	logD (pH 7)	pK_a (acid)	pK_a (basic)
Clopidogrel	113665-84-2	4.03	4.03	-	4.77
Clorophene	120-32-1	4.37	4.36	9.06	-
Clozapine	5786-21-0	3.52	1.06	-	10.08
Cyclobenzaprine	303-53-7	4.61	1.92	-	9.76
Denatonium	47324-98-1	0.41	0.41	12.14	-
(Dex)-ketoprofen	22161-81-5	3.61	0.64	3.88	-
Dextromethorphan	125-71-3	3.49	0.73	-	9.85
Dextrorphan	125-73-5	2.9	0.59	10.46	9.66
Dibenzylpiperazine	1034-11-3	3.49	2.46	-	7.99
Diclofenac	15307-86-5	4.26	1.37	4.00	-
Diethyltoluamide (DEET)	134-62-3	2.5	2.5	-	-
Diltiazem	42399-41-7	2.73	1.53	12.86	8.18
Diphenhydramine	58-73-1	3.65	1.79	-	8.87
Diuron	330-54-1	2.53	2.53	13.18	-
Doxylamine	469-21-6	2.96	1.1	-	8.87
Eprosartan	133040-01-4	3.75	0.67	3.47	6.67
Ethambutol	74-55-5	-0.06	-2.7	-	9.55
Flecainide	54143-55-4	3.19	0.66	13.68	9.62
Fluconazole(I)	86386-73-4	0.56	0.56	12.68	2.3
Fludioxonil	131341-86-1	3.57	3.57	-	-
Flufenamic acid	530-78-9	5.25	2.27	3.88	-
Fluoxetine	54910-89-3	4.17	1.5	-	9.8
Gabapentin	60142-96-3	-1.27	-1.27	4.63	9.91
Haloperidol	52-86-8	3.66	2.58	13.96	8.05
Harmol	487-03-6	1.7	1.64	9.4	6.16
Hydrochlorothiazide	58-93-5	-0.58	-0.58	9.09	-
Hydroxybupropion	357399-43-0	2.9	2.19	10.75	7.61
Hydroxychloroquine	118-42-3	2.89	-0.23	-	9.76
Imidapril	89371-37-9	-0.23	-1.64	3.49	5.22
Irbesartan	138402-11-6	5.39	4.46	5.85	4.12
Isoproturon	34123-59-6	2.57	2.57	13.79	-
Ketamine	6740-88-1	3.35	2.96	-	7.16
Lamotrigine	84057-84-1	1.93	1.89	-	5.89
Levetiracetam	102767-28-2	-0.59	-0.59	-	-
Levofloxacin	100986-85-4	0.09	-0.22	5.35	6.72
Levomethadone	125-58-6	5.01	2.9	-	9.12
Losartan	114798-26-4	5	4.05	5.85	3.85
Mebendazole	31431-39-7	3.26	3.25	8.44	3.93
Mecetronium	10328-33-3	3.04	3.04	-	0
Memantine	19982-08-2	2.07	-0.88	-	10.7
Meperidine	57-42-1	2.46	1.27	-	8.16
Mepivacaine	22801-44-1	3.19	2.75	13.62	7.25
Methadone	76-99-3	5.01	2.9	-	9.12
Methamphetamine	537-46-2	2.24	-0.69	-	10.21
Methyl 4-hydroxybenzoate	99-76-3	1.67	1.66	8.5	-

Compound name	CAS	logP	logD (pH 7)	pK_a (acid)	pK_a (basic)
Methylendioxymethamphetamine	42542-10-9	1.86	-1.03	-	10.14
Methylphenidate	113-45-1	2.25	0.19	-	9.09
Metoclopramide	364-62-5	1.4	-0.64	-	9.04
Metoprolol	37350-58-6	1.76	-0.81	-	9.67
Metronidazole	443-48-1	-0.46	-0.46	-	3.03
Minoxidil	38304-91-5	-0.74	-2.69	13.9	13.09
Mirtazapine	61337-67-5	3.21	3.04	-	6.67
Mycophenolic acid	24280-93-1	3.53	0.35	3.57	-
N-Desalkylverapamil	34245-14-2	2.96	-0.10	-	10.54
Nicotine	54-11-5	1.16	-0.42	-	8.58
Norcitalopram	62498-67-3	3.38	0.32	-	10.54
Nortriptyline	72-69-5	4.43	1.39	-	10.47
Norverapamil	67018-85-3	4.66	1.70	-	10.29
Octamylamine	502-59-0	4.33	1.19	-	10.85
O-Desmethyltramadol	73986-53-5	1.72	0.10	9.62	8.97
Omeprazole	73590-58-6	2.43	2.43	9.29	4.77
Omeprazole sulfone	88546-55-8	2.41	1.96	6.29	4.47
Oxazepam	604-75-1	2.92	2.92	10.61	-
Oxcarbamazepine	28721-07-5	1.82	1.82	13.18	-
Oxybenzone	131-57-7	3.62	3.36	7.07	-
Paliperidone	144598-75-4	1.76	-0.01	13.74	8.76
Pentoxifylline	6493-05-6	0.23	0.23	-	-
Phenethylamine	64-04-0	1.39	-1.21	-	9.79
Propafenone	54063-53-5	3.54	0.93	-	9.72
Propranolol	525-66-6	2.58	0.02	-	9.67
Pseudoephedrine	90-82-4	1.32	-1.13	13.89	9.52
Pyrantel	15686-83-6	1.96	-0.43	-	10.71
Quetiapine	111974-69-7	2.81	2.47	-	7.06
Ranitidine	66357-35-5	0.99	0.13	-	7.8
Ritalinic acid	19395-41-6	-0.36	-0.36	3.73	10.08
Salazosulfapyridine	599-79-1	1.47	-1.37	2.92	4.17
Sertraline	79617-96-2	5.15	2.67	-	9.56
Sitagliptin	486460-32-6	1.26	-0.51	-	8.78
Sorbitol	50-70-4	-3.73	-3.73	12.59	-
Sulfamethoxazole	723-46-6	0.79	0.14	6.16	1.97
Sulpiride	15676-16-1	0.22	-1.07	10.24	8.39
Tapentadol	175591-23-8	2.96	0.72	10.28	9.6
Telmisartan	144701-48-4	6.13	5.17	3.62	5.86
Terbuthylazine-2-hydroxy	66753-07-9	0.28	0.25	12.45	5.83
Terbutryn	886-50-0	2.88	2.70	-	6.72
Tetramisole	5036-02-2	2.36	2.07	-	6.98
Thiabendazole	148-79-8	2.33	2.33	10.28	4.08
Tramadol	27203-92-5	2.45	0.24	13.80	9.23
trans-10,11-Dihydroxy-10,11-dihydrocarbamazepine	58955-93-4	0.81	0.81	12.84	-
Trazodone	19794-93-5	3.13	2.78	-	7.09

Compound name	CAS	logP	logD (pH 7)	pK_a (acid)	pK_a (basic)
Trimethoprim	738-70-5	1.28	0.92	-	7.16
Trospium	10405-02-4	-0.5	-0.50	11.05	-
Valsartan	137862-53-4	5.27	1.65	4.35	-
Venlafaxine	93413-69-5	2.74	0.84	-	8.91

Table S4: Detection frequency (as obtained after applying the screening workflow) and apparent recoveries in river water spiked samples after SPE and RPLC-QTOF analysis

	100 ng L^{-1}			500 ng L^{-1}		
	Detection %	**Recov %**	**RSD %**	**Detection %**	**Recov %**	**RSD %**
Amisulpride	100	101	5	100	98	2
Amphetamine	100	97	9	100	98	3
Atenolol	0	74	21	0	102	1
Azithromycin	100	35	43	100	67	21
Benzoylecgonine	0	NC	NC	0	95	2
Benzydamine	100	95	8	100	100	3
Berberine	100	85	6	100	95	5
Bezafibrate	20	68	13	80	69	8
Caffeine	0	46	17	100	89	2
Carbamazepine	100	89	6	100	99	2
Carbendazim	100	69	15	100	74	10
Citalopram	0	94	11	0	100	2
Cloperastine	0	68	33	0	78	18
Cocaine	0	98	14	40	102	7
Cotinine	100	95	7	100	100	2
Diclofenac	20	78	15	80	84	7
Flecainide	100	93	8	100	99	1
Irbesartan	100	64	10	100	76	5
Ketoprofen	40	93	8	40	81	1
Levamisole	100	77	16	100	84	6
Lorazepam	20	84	18	80	66	10
Losartan	20	69	9	80	78	4
Metformin	1	12	16	20	3	24
Methadone	0	96	7	0	98	2
Methylphenidate	80	101	13	80	102	1
Mirtazapine	100	94	11	100	98	2
Nicotine	100	105	4	100	99	3
Norcocaine	0	88	16	80	95	2
Omeprazole	20	32	24	20	52	18
Propranolol	80	88	7	80	102	1
Ritalinic acid	100	70	7	100	70	6
Sertraline	100	69	4	100	96	3
Sulfadiazine	0	90	5	100	73	7
Sulfamethoxazole	60	87	1	60	89	1
Sulpiride	100	91	7	100	98	5
Telmisartan	100	87	6	100	97	1
Terbinafine	80	82	5	80	94	4
Terbutryn	80	80	3	100	98	4
Tiapride	20	85	2	20	94	2
Tramadol	100	45	38	100	101	2
Trazodone	0	90	5	60	95	8
Trimethoprim	80	65	8	80	99	2

	100 ng L^{-1}			500 ng L^{-1}		
	Detection %	**Recov %**	**RSD %**	**Detection %**	**Recov %**	**RSD %**
Tri-n-butyl phosphate	100	69	9	100	93	1
Tris(2-butoxyethyl) phosphate	100	52	24	100	77	5
Tris(2-chloroisopropyl) phosphate	100	93	9	100	96	2
Mean	60	78	12	75	88	5

NC: could not be calculated

Table S5: Detection frequency (as obtained after applying the screening workflow) and apparent recoveries in river water spiked samples after SPE and SFC-QTOF analysis

	100 ng L^{-1}			500 ng L^{-1}		
	Detection %	**Recov %**	**RSD %**	**Detection %**	**Recov %**	**RSD %**
Amisulpride	100	60	5	100	65	7
Amphetamine	20	87	9	40	71	4
Atenolol	80	57	6	100	62	3
Azithromycin	100	26	26	100	48	2
Benzoylecgonine	100	81	6	100	80	1
Benzydamine	100	61	4	100	68	5
Berberine	100	44	14	100	56	2
Bezafibrate	0	53	42	0	59	5
Caffeine	20	79	2	80	75	3
Carbamazepine	100	66	12	100	65	5
Carbendazim	100	75	5	100	72	2
Citalopram	100	66	3	100	68	2
Cloperastine	100	58	5	100	72	2
Cocaine	100	87	9	100	89	4
Cotinine	100	83	3	100	82	4
Diclofenac	0	NC	NC	0	66	24
Flecainide	100	55	5	0	71	4
Irbesartan	80	54	7	100	58	6
Ketoprofen	40	68	10	100	63	2
Levamisole	40	83	4	80	84	5
Lorazepam	20	71	5	100	65	2
Losartan	0	77	40	80	62	3
Metformin	20	2	6	80	1	24
Methadone	100	64	3	80	68	3
Methylphenidate	100	61	4	100	76	4
Mirtazapine	100	69	5	100	78	2
Nicotine	100	64	8	100	65	6
Norcocaine	80	36	14	100	75	6
Omeprazole	100	74	5	100	72	1
Propranolol	80	51	8	100	56	6
Ritalinic acid	0	68	2	0	61	2
Sertraline	0	40	13	0	57	7
Sulfadiazine	100	104	3	100	80	2
Sulfamethoxazole	20	60	57	60	67	6
Sulpiride	20	73	22	60	69	6
Telmisartan	100	46	9	100	58	5
Terbinafine	100	75	4	100	53	4
Terbutryn	100	50	7	100	58	2
Tiapride	100	65	5	100	67	3
Tramadol	100	76	2	100	80	3
Trazodone	100	64	5	100	64	7
Trimethoprim	100	43	10	100	80	3

	100 ng L^{-1}			500 ng L^{-1}		
	Detection %	**Recov %**	**RSD %**	**Detection %**	**Recov %**	**RSD %**
Tri-n-butyl phosphate	100	44	17	100	36	26
Tris(2-butoxyethyl) phosphate	100	45	11	100	74	4
Tris(2-chloroisopropyl) phosphate	100	69	4	80	69	4
Mean	74	62	10	83	66	5

NC: could not be calculated

Table S6: List of chemicals identified in the surface water samples. Detections are coded as 1, while non-detections are coded as 0.

Compound name	CAS	Type	Further description	R1	R2	R3	R4	S1	S2	S3	S4
10-Hydroxycarbamazepine	29331-92-8	Metabolite	Metabolite of carbamazepine	1	1	1	1	0	0	0	0
2,4-Dinitrophenol	51-28-5	Multiple sources	Antiseptic, pesticide, industrial intermediate, …	0	0	0	0	0	1	0	0
3-Hydroxycotinine	34834-67-8	Metabolite	Metabolite of nicotine	1	1	1	0	0	0	0	0
4-Hydroxybenzoic acid	99-96-7	Multiple sources	Natural, parabens human metabolite, PCPs, food additive, industrial intermediate	0	0	1	0	1	0	0	1
4-Nitrophenol	100-02-7	Multiple sources	Human metabolite, industrial intermediate, pesticide	1	1	1	1	1	1	1	1
5-Hydroxyomeprazole	92340-57-3	Metabolite	Metabolite of omeprazole	1	1	0	0	0	1	0	0
8-Hydroxyquinoline	148-24-3	Natural product	Bacteriostatic and fungistatic, chelating agent	0	0	0	0	0	1	0	0
Abacavir	136470-78-5	Pharmaceutical	Antiviral	1	1	1	1	0	0	0	0
Acebutolol	37517-30-9	Pharmaceutical	Beta blocker	0	0	1	1	0	1	0	0
Acetaminophen	103-90-2	Pharmaceutical	Analgesic	1	1	1	1	0	1	0	0
Adenosine	58-61-7	Natural product	Pharm. antiarrhythmic and human metabolite	0	0	0	0	0	1	0	0
Amantadine	768-94-5	Pharmaceutical	Antiviral	1	1	0	0	0	1	0	0
Amisulpride	71675-85-9	Pharmaceutical	Antipsychotic	0	0	1	1	0	1	0	0
Amphetamine	300-62-9	Drug of Abuse		1	1	0	0	0	0	0	0
Ampyrone	83-07-8	Metabolite	Metabolite of aminophenazone	1	1	0	0	0	0	0	0
Atenolol	29122-68-7	Pharmaceutical	Beta blocker	1	1	1	1	0	1	0	0
Atorvastatin	134523-00-5	Pharmaceutical	Anticholesteremic	1	1	0	0	0	1	0	0
Atrazine	1912-24-9	Pesticide	Herbicide	0	0	0	0	0	1	0	0
Azelaic acid	123-99-9	Natural product	PCPs, industrial intermediate, Food additive	0	0	0	0	1	0	1	1
Azithromycin	83905-01-5	Pharmaceutical	Antibiotic	1	1	1	1	0	1	0	0
Benzododecinium	10328-35-5	Pharmaceutical	Antiseptic	1	1	0	0	1	1	1	1
Benzoylecgonine	519-09-5	Metabolite	Metabolite of cocaine	1	1	1	1	0	1	0	0
Benzydamine	642-72-8	Pharmaceutical	Anti-inflammatory	1	1	0	0	0	0	0	0
Berberine	2086-83-1	Natural product	Pharm. Supplement and human metabolite	1	1	1	0	0	1	0	0

Compound name	CAS	Type	Further description	R1	R2	R3	R4	S1	S2	S3	S4
Bezafibrate	41859-67-0	Pharmaceutical	Antilipidemic	0	0	0	0	0	1	0	0
Bicalutamide	90357-06-5	Pharmaceutical	Antiandrogen and antineoplastic	1	1	0	0	0	0	0	0
Bisoprolol	66722-44-9	Pharmaceutical	Antihypertensive	0	1	1	1	0	0	0	0
Butylbenzylphthalate	85-68-7	Industrial chemical	Plasticizer	0	0	0	0	0	1	0	0
Butylscopolaminium	149-64-4	Pharmaceutical	Anticholinergic and antispasmodic	0	0	0	0	0	1	0	0
Caffeine	58-08-2	Natural product	Stimulant	0	0	1	1	0	1	0	0
Candesartan	139481-59-7	Pharmaceutical	Antihypertensive	0	0	0	0	0	1	0	0
Carbamazepine	298-46-4	Pharmaceutical	Antiepileptic	1	1	1	1	0	1	0	0
Carbamazepine 10,11-epoxide	36507-30-9	Metabolite	Metabolite of carbamazepine	1	1	1	0	0	1	0	0
Carbendazim	10605-21-7	Pesticide	Funguicide	1	1	0	0	0	1	0	0
Cetirizine	83881-51-0	Pharmaceutical	Antihistamine	1	1	0	0	0	1	0	0
Cetylpyridinium	7773-52-6	Pharmaceutical	Antiseptic	0	0	1	0	0	0	0	0
Chlorpheniramine	132-22-9	Pharmaceutical	Antihistamine	0	0	0	0	0	1	0	0
Citalopram	59729-33-8	Pharmaceutical	Antidepressant	0	0	0	0	0	1	0	0
Clarithromycin	81103-11-9	Pharmaceutical	Antibiotic	1	1	1	1	0	1	0	0
Clindamycin	18323-44-9	Pharmaceutical	Antibiotic	0	0	0	0	0	1	0	0
Cloperastine	3703-76-2	Pharmaceutical	Antitussive	0	0	0	0	0	1	0	0
Clozapine	5786-21-0	Pharmaceutical	Antipsychotic	1	1	0	0	0	0	0	0
Cocaethylene	529-38-4	Metabolite	Metabolite of cocaine	0	1	0	0	0	0	0	0
Cocaine	50-36-2	Drug of abuse		1	1	1	1	0	0	0	0
Cotinine	486-56-6	Metabolite	Metabolite of nicotine	1	1	0	1	0	0	0	0
Denatonium	47324-98-1	Other	Aversive agent in PCPs and repellent in agriculture	0	0	0	0	0	1	0	0
Dexpanthenol	81-13-0	Other	PCPs use in skin disorders	0	0	1	0	1	1	1	0
Dextrorphan	125-73-5	Pharmaceutical	Antitussive	1	1	0	0	0	0	0	0
Diclofenac	15307-86-5	Pharmaceutical	Anti-inflammatory	1	1	1	0	0	1	0	0
Diethyl phthalate	84-66-2	Industrial chemical	Plasticizer	1	1	1	1	1	1	1	0

Compound name	CAS	Type	Further description	R1	R2	R3	R4	S1	S2	S3	S4
Diethyltoluamide (DEET)	134-62-3	Pesticide	Insecticide	0	1	1	1	0	1	0	0
Diltiazem	42399-41-7	Pharmaceutical	Antihypertensive	1	1	1	1	0	1	0	0
Dimethoate	60-51-5	Pesticide	Insecticide	0	0	1	0	0	0	0	0
Dinoterb	1420-07-1	Pesticide	Herbicide	0	0	0	0	1	0	1	1
Diuron	330-54-1	Pesticide	Herbicide	0	1	0	0	0	1	0	0
Doxylamine	469-21-6	Pharmaceutical	Antihistamine	0	0	1	0	0	1	0	0
Empenthrin	54406-48-3	Pesticide	Insecticide	0	0	0	0	0	1	0	0
Enalapril	75847-73-3	Pharmaceutical	Antihypertensive	1	1	1	0	0	0	0	0
Ephedrine	299-42-3	Pharmaceutical	Stimulant, bronchodilator, appetite suppressant	1	1	1	1	0	1	0	0
Eprosartan	133040-01-4	Pharmaceutical	Antihypertensive	1	1	0	0	0	0	0	0
Erythromycin	114-07-8	Pharmaceutical	Antibiotic	1	1	0	0	0	0	0	0
Estrone sulfate	481-97-0	Natural product	Hormone	0	0	1	0	0	0	0	0
Flecainide	54143-55-4	Pharmaceutical	Antiarrhythmic	1	1	1	1	0	1	0	0
Fluconazole (II)	86386-73-4	Pharmaceutical	Antifungal	1	1	1	0	0	1	0	0
Flucytosine	2022-85-7	Pharmaceutical	Antifungal	1	1	0	0	0	1	0	0
Flufenamic acid	530-78-9	Pharmaceutical	Analgesic	0	1	1	0	0	1	0	0
Furosemide	54-31-9	Pharmaceutical	Diuretic	0	0	0	0	0	1	0	0
Gabapentin	60142-96-3	Pharmaceutical	Antiepileptic	0	0	0	0	0	1	0	0
Haloperidol	52-86-8	Pharmaceutical	Antipsychotic	0	0	0	0	0	1	0	0
Harmol	487-03-6	Metabolite	Metabolite of harmine	0	0	0	0	0	1	0	0
Hydrochlorothiazide	58-93-5	Pharmaceutical	Antihypertensive	1	1	1	1	0	1	0	0
Hydroxybupropion	357399-43-0	Metabolite	Metabolite of bupropion	0	0	0	0	0	1	0	0
Imidapril	89371-37-9	Pharmaceutical	Antihypertensive	0	0	0	0	0	1	0	0
Iminostilbene	256-96-2	Metabolite	Metabolite of carbamazepine	1	1	0	0	0	1	0	0
Iopromide	73334-07-3	Pharmaceutical	Contrast medium	1	1	1	0	0	0	0	0
Irbesartan	138402-11-6	Pharmaceutical	Antihypertensive	1	1	1	0	0	1	0	0
Ketoprofen	22071-15-4	Pharmaceutical	Anti-inflammatory	0	1	0	0	0	0	0	0

Compound name	CAS	Type	Further description	R1	R2	R3	R4	S1	S2	S3	S4
Labetalol	36894-69-6	Pharmaceutical	Antihypertensive	0	0	0	0	0	1	0	0
Lamivudine	134678-17-4	Pharmaceutical	Antiviral	0	0	0	0	0	1	0	0
Levamisole	14769-73-4	Pharmaceutical	Antihelminthic	0	0	0	0	0	1	0	0
Levetiracetam	102767-28-2	Pharmaceutical	Anticonvulsant	1	1	0	0	0	0	0	0
Levomethadone	125-58-6	Pharmaceutical	Analgesic and antitussive	0	1	0	0	0	0	0	0
Levorphanol	77-07-6	Pharmaceutical	Analgesic	0	0	1	0	0	0	0	0
Lidocaine	137-58-6	Pharmaceutical	Anesthesic	1	1	1	1	0	1	0	0
Loratadine	79794-75-5	Pharmaceutical	Antihistamine	1	1	0	0	1	0	1	1
Lorazepam	846-49-1	Pharmaceutical	Ansiolitic	0	0	0	0	0	1	0	0
Losartan	114798-26-4	Pharmaceutical	Antihypertensive	1	1	1	0	0	1	0	0
Mecetronium	3006-10-8	Pharmaceutical	Bactericide and antiseptic	0	0	0	0	0	1	0	0
Melamine	108-78-1	Multiple sources	Industrial chemical, food adulterant, fertilizer	0	0	0	0	0	1	1	0
Memantine	19982-08-2	Pharmaceutical	Antidementia	0	0	0	0	0	1	0	0
Mepivacaine	22801-44-1	Pharmaceutical	Anesthesic	1	1	1	1	0	0	0	0
Metformin	657-24-9	Pharmaceutical	Antidiabetic	1	1	1	1	0	1	0	0
Methadone	76-99-3	Pharmaceutical	Analgesic, desintoxication drug	1	1	1	0	0	1	0	0
Methenamine	100-97-0	Pharmaceutical	Urinary tract infections	0	0	0	0	0	1	0	0
Methylendioxymethamphetamine	42542-10-09	Drug of abuse		1	1	1	1	0	1	0	0
Methylphenidate	113-45-1	Pharmaceutical	Stimulant	1	1	0	0	0	0	0	0
Metoclopramide	364-62-5	Pharmaceutical	Antivomiting	0	0	0	0	0	1	0	0
Metoprolol	37350-58-6	Pharmaceutical	Beta blocker	0	0	0	0	0	1	0	0
Metronidazole	443-48-1	Pharmaceutical	Antibiotic	1	1	1	1	0	1	0	0
Minoxidil	38304-91-5	Pharmaceutical	Antihypertensive	1	1	1	1	0	1	0	0
Mirtazapine	61337-67-5	Pharmaceutical	Antidepressant	1	1	0	0	0	0	0	0
Mycophenolic acid	24280-93-1	Pharmaceutical	Immunosuppresant	0	0	0	0	0	1	0	0
N-Desalkylverapamil	34245-14-2	Metabolite	Metabolite of verapamil	1	1	0	0	0	0	0	0
Nicotine	54-11-5	Natural product	Stimulant	1	1	1	1	0	0	0	0

Compound name	CAS	Type	Further description	R1	R2	R3	R4	S1	S2	S3	S4
Norcitalopram	62498-67-3	Metabolite	Metabolite of citalopram	1	1	0	1	0	0	0	0
Norcocaine	18717-72-1	Metabolite	Metabolite of cocaine	1	1	0	0	0	0	0	0
Norethindrone acetate	51-98-9	Pharmaceutical	Hormone	0	0	0	0	0	0	1	0
O-Desmethyltramadol	73986-53-5	Metabolite	Metabolite of tramadol	1	1	1	1	0	1	0	0
Omeprazole	73590-58-6	Pharmaceutical	Antacid	0	0	0	0	0	1	0	0
Omeprazole sulfone	88546-55-8	Metabolite	Metabolite of omeprazole	1	1	1	0	0	1	0	0
Oxazepam	604-75-1	Pharmaceutical	Ansiolitic	1	1	0	0	0	1	0	0
Oxcarbamazepine	28721-07-5	Pharmaceutical	Antiepileptic	1	1	1	1	0	1	0	0
Palmidrol	544-31-0	Pharmaceutical	Anti-inflammatory	1	0	0	0	0	0	0	0
Paraxanthine	611-59-6	Metabolite	Metabolite of caffeine	0	0	0	1	0	0	0	0
Pentoxifylline	6493-05-6	Pharmaceutical	Anti-inflammatory	1	1	1	1	0	0	1	0
Phenethylamine	64-04-0	Multiple sources	Natural product, human metabolite, food additive	0	0	0	0	0	0	1	0
Piperine	94-62-2	Natural product	Food additive	1	1	1	0	0	0	0	0
Propranolol	525-66-6	Pharmaceutical	Beta blocker	1	1	0	0	0	0	0	0
Psilocine	520-53-6	Natural product	Psychoactive	1	1	0	0	0	0	0	0
Quetiapine	111974-69-7	Pharmaceutical	Antipsychotic	1	1	1	0	0	1	0	0
Ranitidine	66357-35-5	Pharmaceutical	Antacid	1	1	0	0	0	0	0	0
Rhein (cassic acid)	478-43-3	Natural product		0	0	0	0	0	1	0	0
Ritalinic acid	19395-41-6	Metabolite	Metabolite of methylphenidate	1	1	1	1	0	1	0	0
Saccharin	81-07-2	Other	Artificial sweetener	1	1	1	1	0	0	0	0
Salicylic acid	69-72-7	Pharmaceutical	Keratolytic, antiseptic. Intermediate and food preservative	1	1	0	1	1	0	1	1
Sertraline	79617-96-2	Pharmaceutical	Antidepressant	0	1	0	0	0	1	0	0
Sitagliptin	486460-32-6	Pharmaceutical	Antidiabetic	0	0	1	1	0	0	0	0
Sotalol	3930-20-9	Pharmaceutical	Beta blocker	1	1	0	0	0	1	0	0
Sulfadiazine	68-35-9	Pharmaceutical	Antibiotic	1	1	0	0	0	0	0	0
Sulfamethoxazole	723-46-6	Pharmaceutical	Antibiotic	1	1	1	0	0	1	0	0
Sulfapyridine	144-83-2	Pharmaceutical	Antibiotic	0	0	0	0	0	1	0	0

Compound name	CAS	Type	Further description	R1	R2	R3	R4	S1	S2	S3	S4
Sulpiride	15676-16-1	Pharmaceutical	Antipsychotic	1	1	1	1	0	1	0	0
Tapentadol	175591-23-8	Pharmaceutical	Analgesic	1	1	1	1	0	1	0	0
Telmisartan	144701-48-4	Pharmaceutical	Antihypertensive	1	0	1	1	0	1	0	0
Terbinafine	91161-71-6	Pharmaceutical	Antifungal	0	1	0	0	0	0	0	0
Terbuthylazine-2-hydroxy	66753-07-9	Metabolite	Metabolite of terbuthylazine	0	0	0	1	0	1	0	0
Terbutryn	886-50-0	Pesticide	Herbicide	1	1	1	1	0	0	0	0
Theobromine	83-67-0	Natural product	Stimulant	1	1	0	0	0	0	0	0
Theophylline	58-55-9	Natural product	Stimulant and bronchodilator	1	1	0	0	0	0	0	0
Thiabendazole	148-79-8	Pharmaceutical	Antifungal	0	0	0	0	0	1	0	0
Tiapride	51012-32-9	Pharmaceutical	Antipsychotic	1	1	1	1	0	1	0	0
Tramadol	27203-92-5	Pharmaceutical	Analgesic	0	0	1	1	0	1	0	0
trans-10,11-Dihydroxy-10,11-dihydrocarbamazepine	58955-93-4	Metabolite	Metabolite of carbamazepine	1	1	1	0	0	1	0	0
Trazodone	19794-93-5	Pharmaceutical	Antidepressant	1	1	0	0	0	1	0	0
Triamterene	396-01-0	Pharmaceutical	Diuretic	0	0	0	0	0	1	0	0
Tri-iso-butyl phosphate	126-71-6	Industrial chemical	Plasticizer/ flame retardant	1	0	1	1	1	1	1	1
Trimethoprim	738-70-5	Pharmaceutical	Antibiotic	1	1	1	0	0	0	0	0
Tri-n-butyl phosphate	126-73-8	Industrial chemical	Plasticizer/ flame retardant	1	1	1	1	1	0	1	1
Triphenyl phosphate	115-86-6	Industrial chemical	Plasticizer/ flame retardant	0	0	0	0	0	1	0	0
Tris(2-butoxyethyl) phosphate	78-51-3	Industrial chemical	Plasticizer/ flame retardant	1	1	1	1	0	1	0	1
Tris(2-chloroisopropyl) phosphate	13674-84-5	Industrial chemical	Plasticizer/ flame retardant	0	1	1	1	0	0	0	0
Umbelliferone	93-35-6	Natural product	PCPs	1	1	0	1	0	0	0	0
Usnic acid	125-46-2	Natural product	PCPs	0	1	0	0	0	0	0	0
Valsartan	137862-53-4	Pharmaceutical	Antihypertensive	1	1	1	1	0	1	0	0
Venlafaxine	93413-69-5	Pharmaceutical	Antidepressant	1	1	1	1	0	1	0	0

Figure S1: Location of the surface water samples included in this study. Map source: https://www.sergas.es/Saude-publica/GIS-Cartografia-Galicia-formato-vectorial-SHP?idioma=es

Code	Water body	UTM 29T (X)	UTM 29T (Y)
R1	Cervantiños creek	556090	4731814
R2	Sar river	530127	4745069
R3	Sar river	527852	4732827
R4	Sar river	527205	4729974
S1	Ria de Arousa	512963	4715028
S2	Ria de Arousa	507343	4717335
S3	Ria de Arousa	503322	4711089
S4	Ria de Arousa	513064	4707213

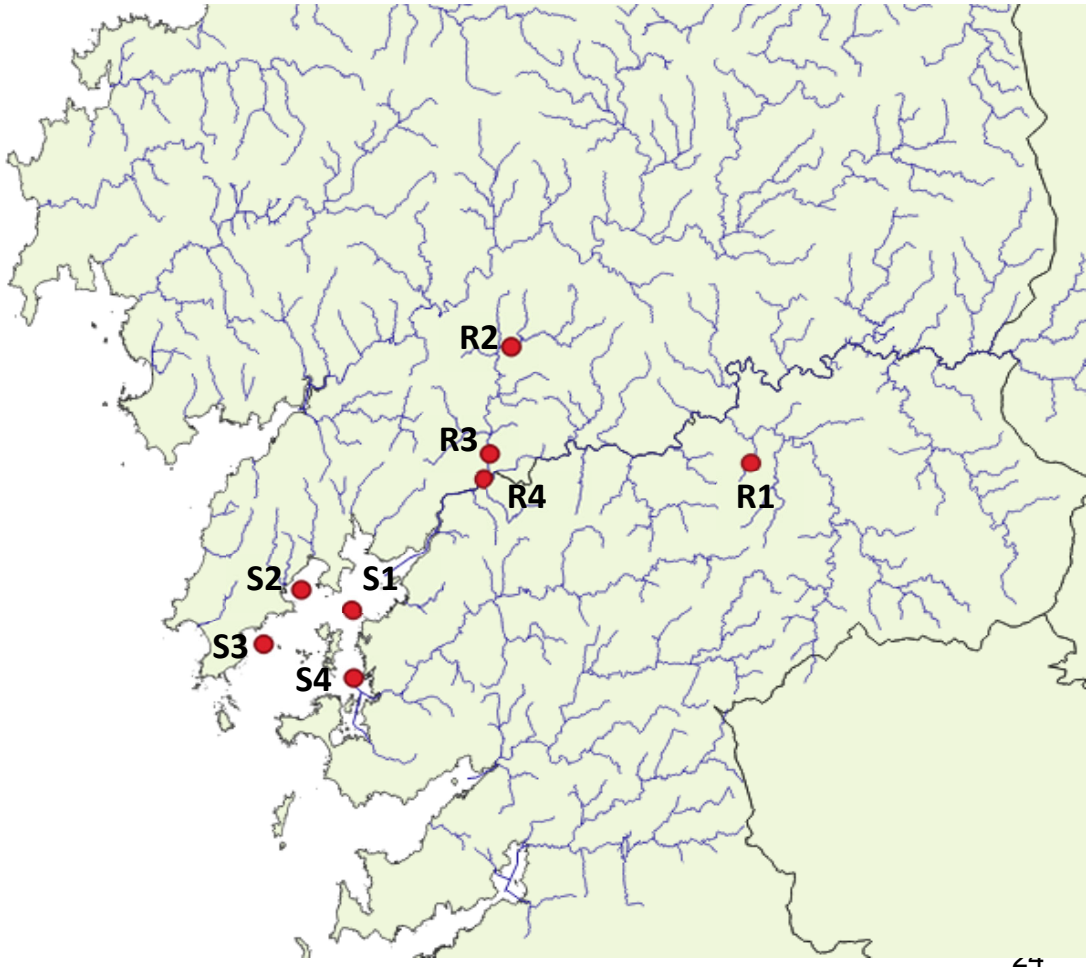
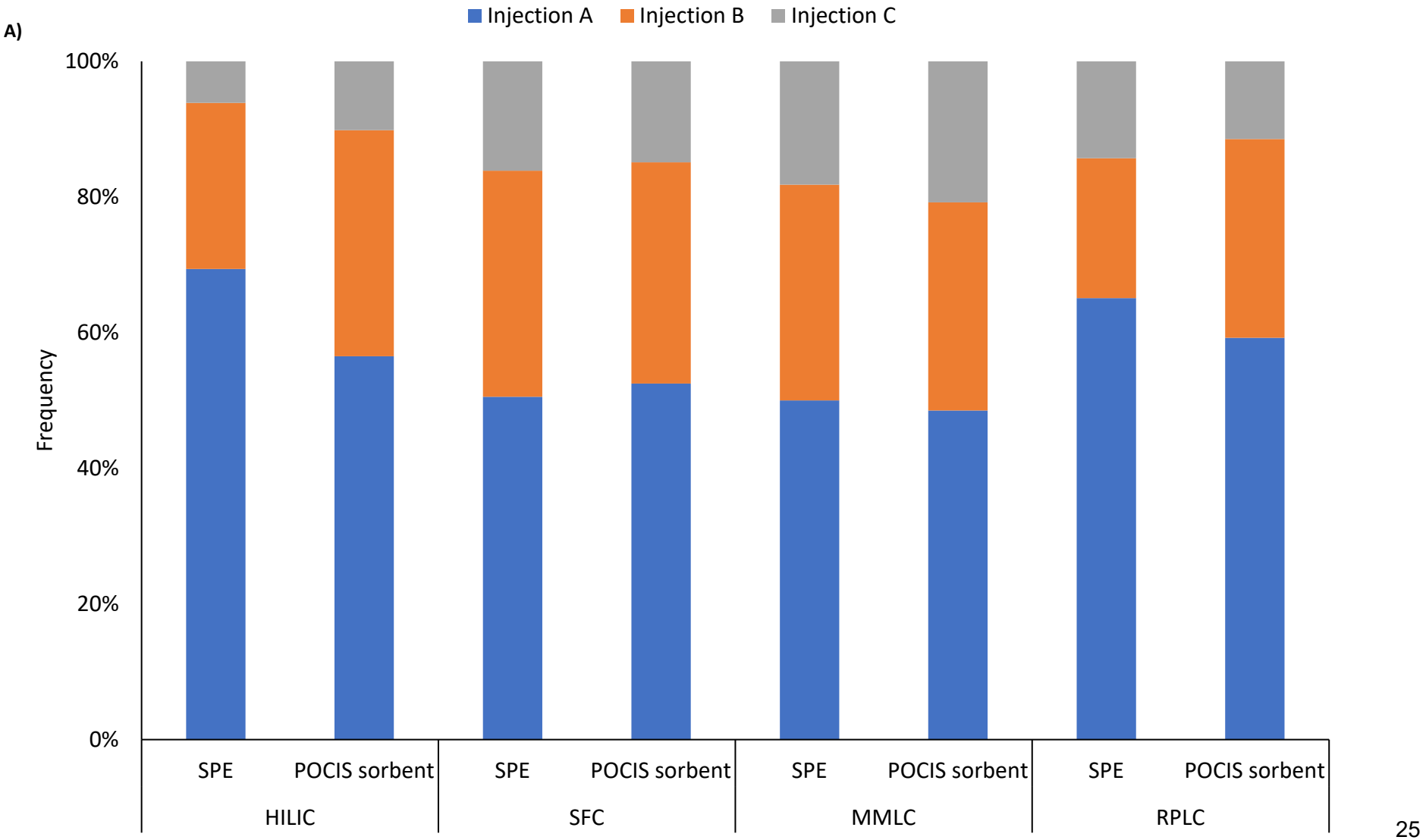


Figure S2: Percentage of compounds found in each iterative injection in the different retention and sampling modes. (A) positive polarity and (B) negative polarity. N.B.: First injection: injection A; second injection: injection B and third injection: injection C.



B)

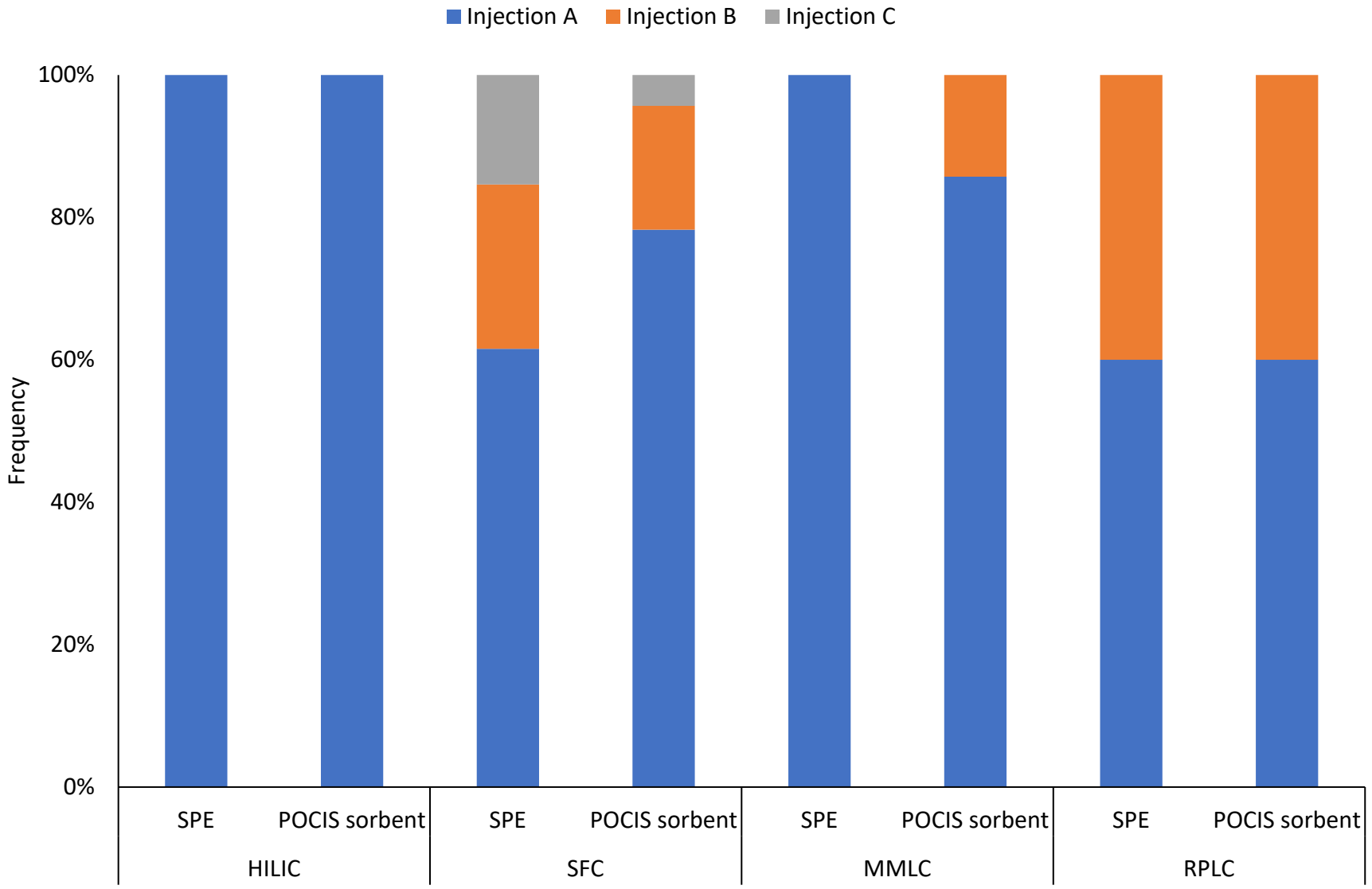

Injection A
Injection B
Injection C
100%
80%
60%
40%
20%
0%
Frequency
SPE
POCIS sorbent
SPE
POCIS sorbent
SPE
POCIS sorbent
SPE
POCIS sorbent
HILIC
SFC
MMLC
RPLC

Figure S3: Box and whiskers of the log D (pH 7) values of the compounds detected onto POCIS membrane, POCIS sorbent and SPE extracts.

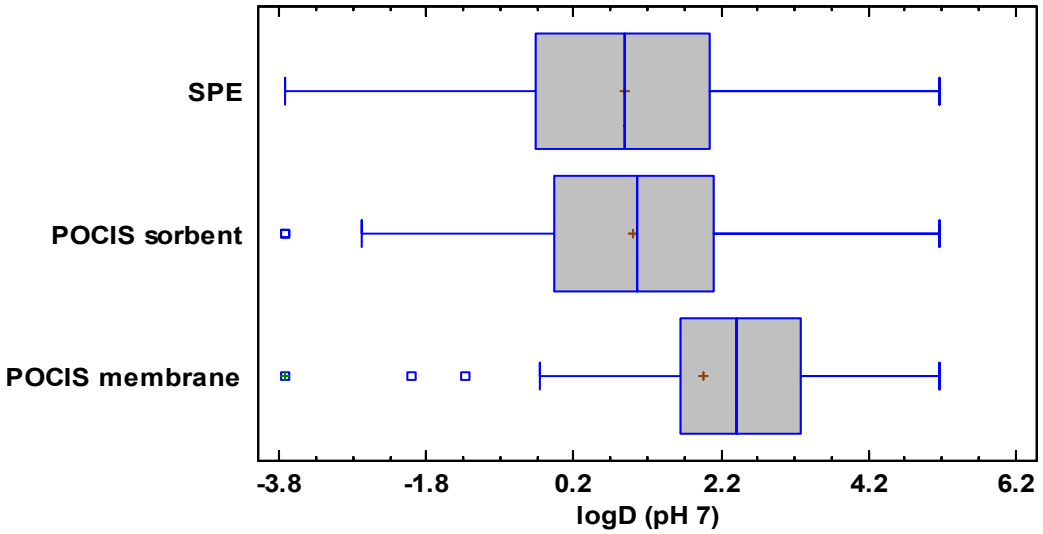
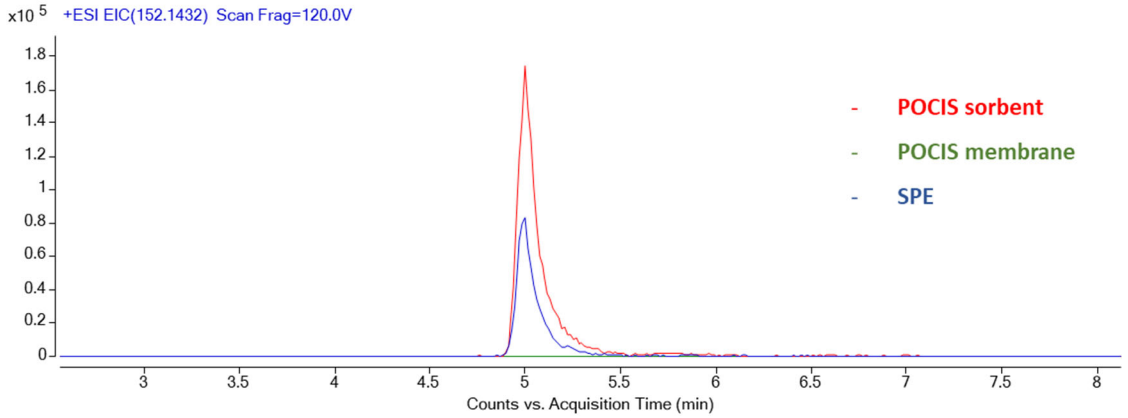
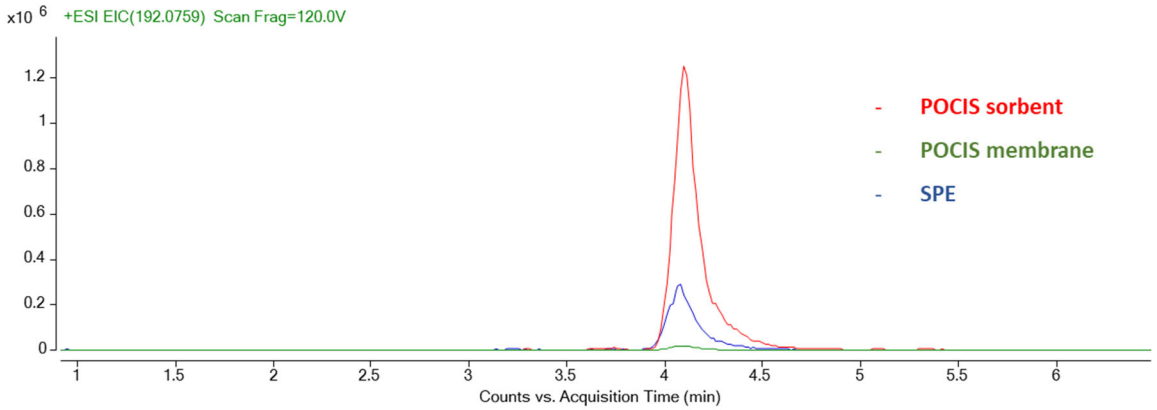


Figure S4: Extracted ion chromatograms (EIC) obtained for POCIS sorbent, POCIS membrane and SPE extract of wastewater by RPLC for (a) Amantadine , (b) Carbendazim, (c) Climbazole, (d) Ritalinic acid and (e) Fludioxonil

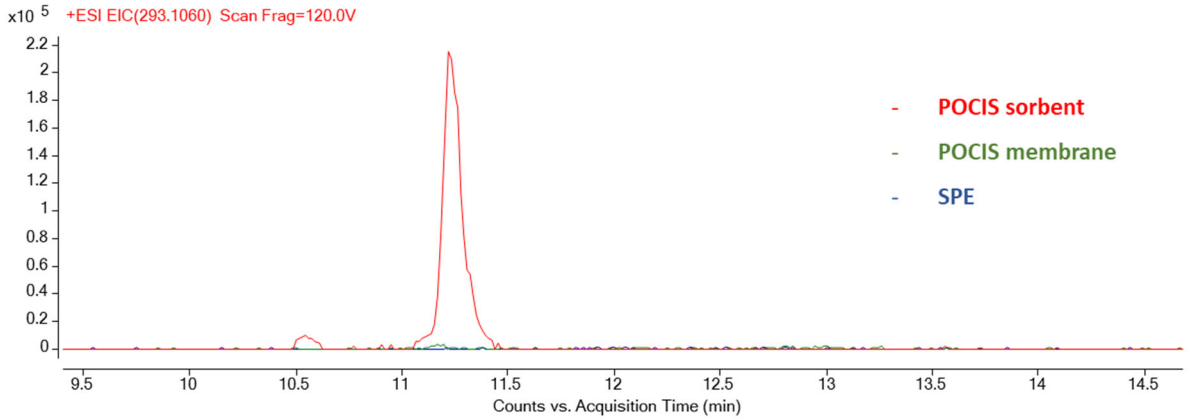
(a) Amantadine



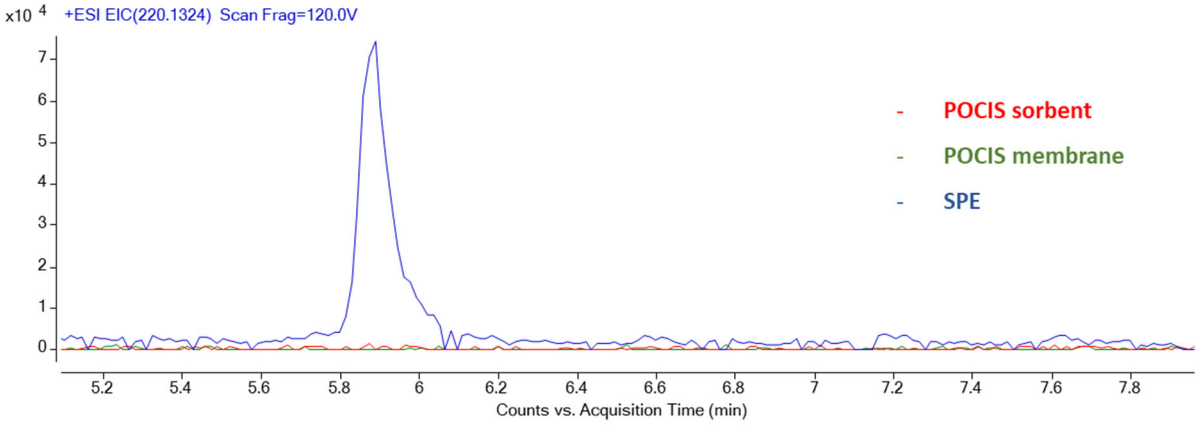
(b) Carbendazim



(c) Climbazole



(d) Ritalinic acid



(e) Fludioxonil

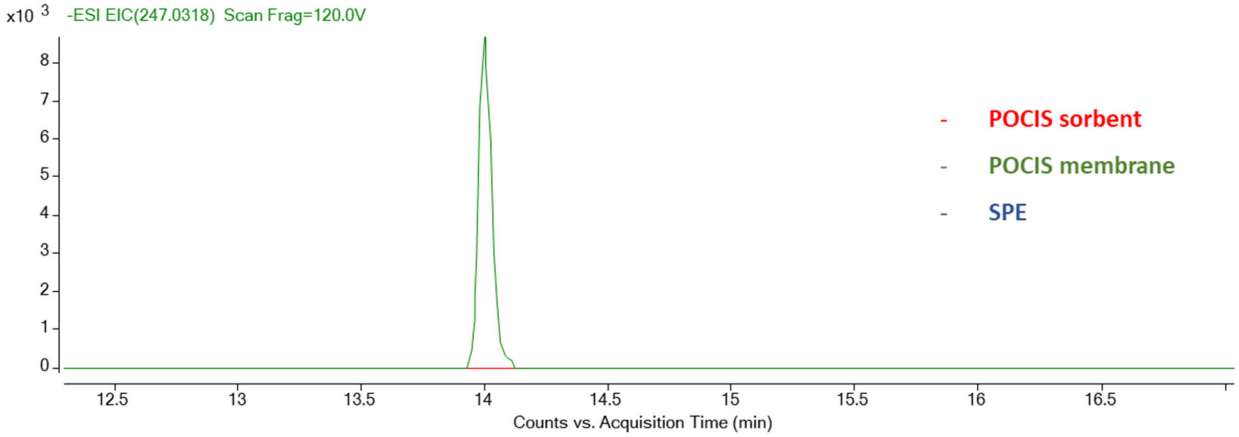
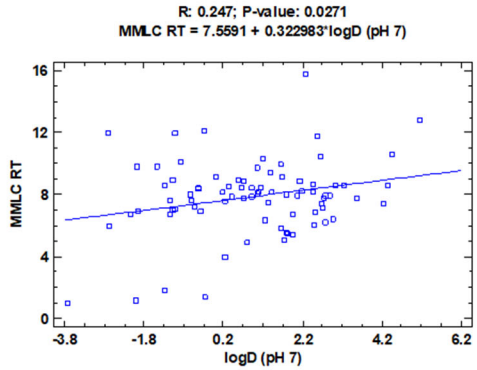
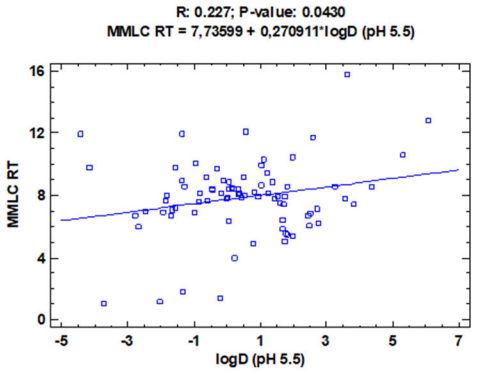
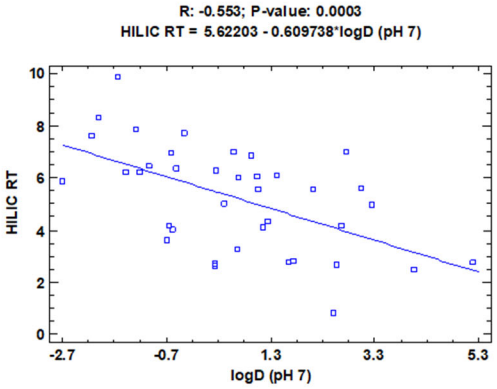
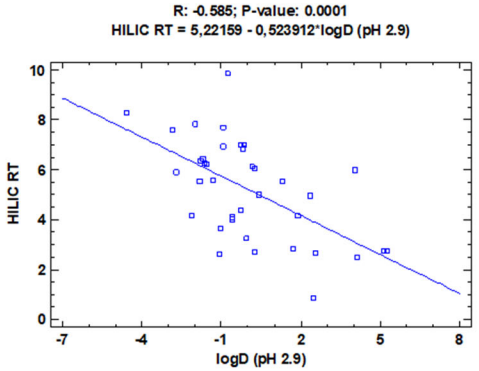


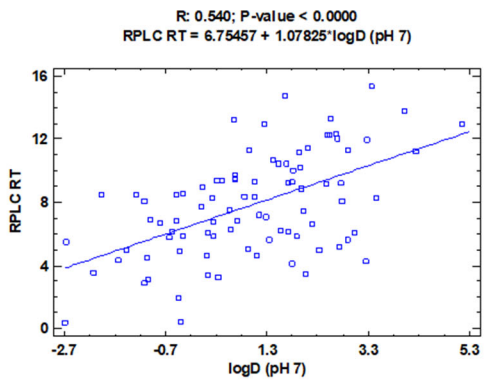
Figure S5: Relationship between the logD and the retention time (RT) of the compounds detected by HILIC, MMLC, SFC and RPLC. Left: logD at pH 7. Right: logD at the pH of the chromatographic aqueous eluent (in the case of SFC a pH of 11 was used as that would be approximately the pH of an 0.2% ammonia aqueous solution)

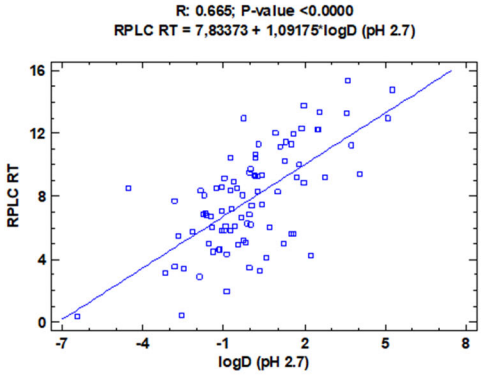


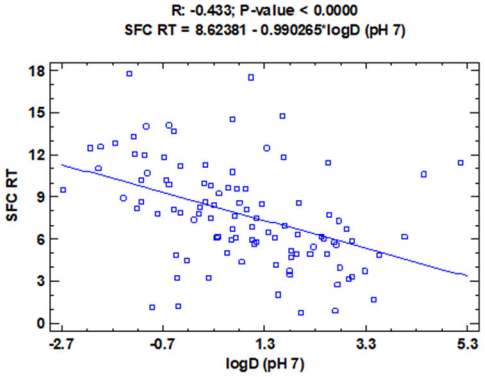







R: 0.540; P-value < 0.0000
RPLC RT = 6.75457 + 1.07825*logD (pH 7)
RPLC RT
logD (pH 7)
16
12
8
4
0
-2.7
-0.7
1.3
3.3
5.3


R: 0.665; P-value <0.0000
RPLC RT = 7,83373 + 1,09175*logD (pH 2.7)
RPLC RT
logD (pH 2.7)
16
12
8
4
0
-7
-4
-1
2
5
8


R: -0.433; P-value < 0.0000
SFC RT = 8.62381 - 0.990265*logD (pH 7)
SFC RT
logD (pH 7)
18
15
12
9
6
3
0
-2.7
-0.7
1.3
3.3
5.3

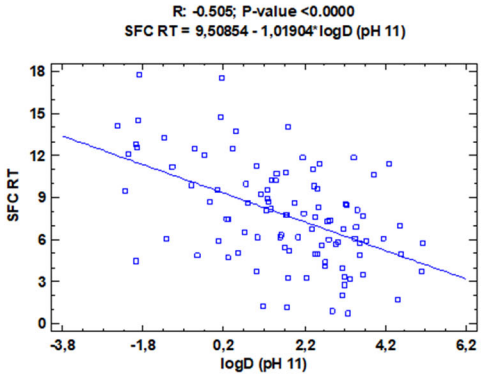

R: -0.505; P-value <0.0000
SFC RT = 9,50854 - 1,01904*logD (pH 11)
SFC RT
logD (pH 11)
18
15
12
9
6
3
0
-3,8
-1,8
0,2
2,2
4,2
6,2

Figure S6: Distribution of the logD (pH 7) calculated values of the identified compounds according to chromatographic mode.

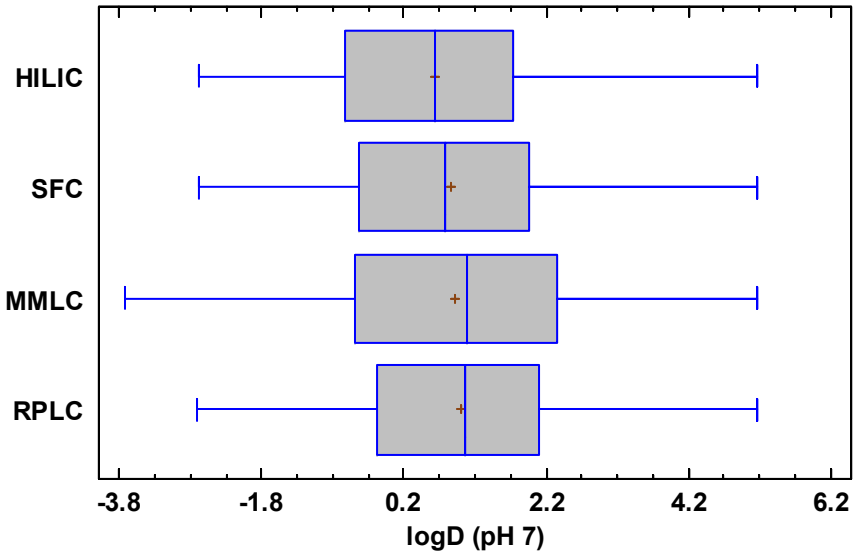
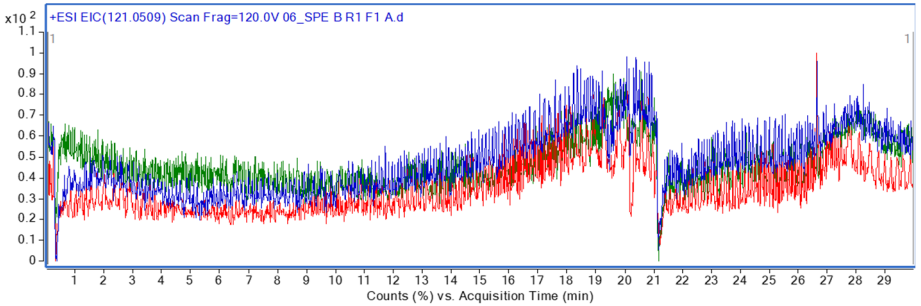
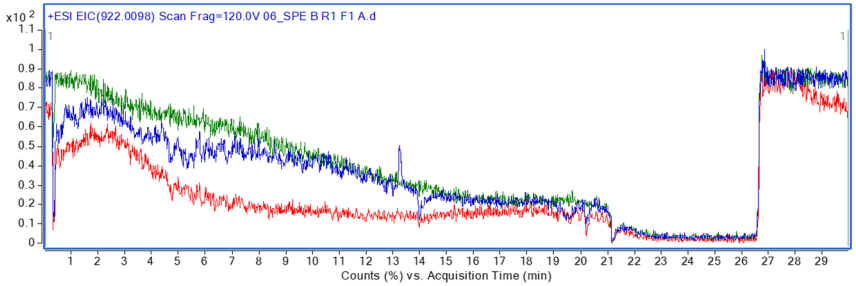


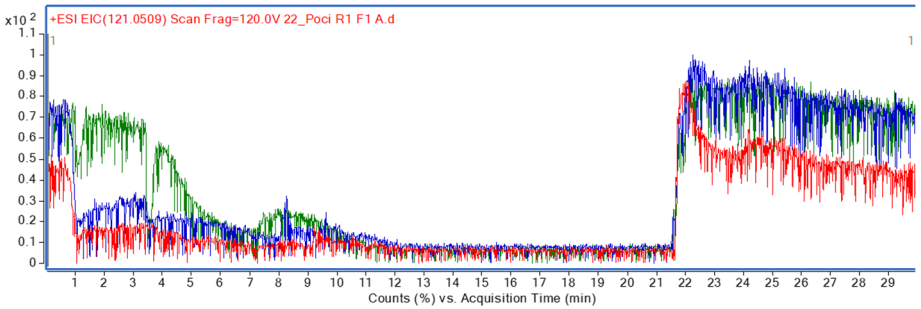
Figure S7: Extracted ion chromatograms (EIC) obtained for the reference calibration solution during the analysis of a methanol solvent (green line), a POCIS extract (red line) and a SPE extract (blue line) in positive mode by (a) RPLC, (b) MMLC, (c) HILIC and (d) SFC and in negative mode by (e) RPLC, (f) MMLC, (g) HILIC and (h) SFC.

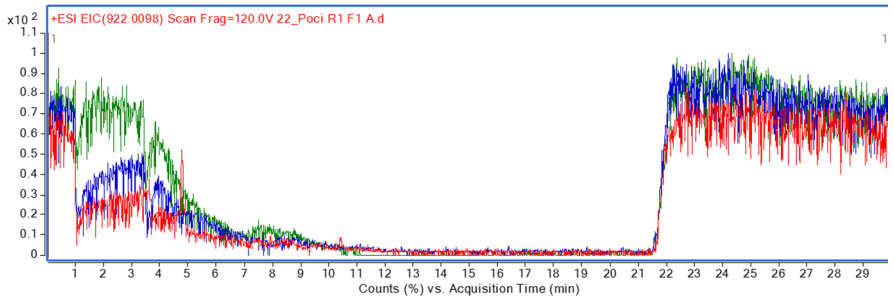
(a)



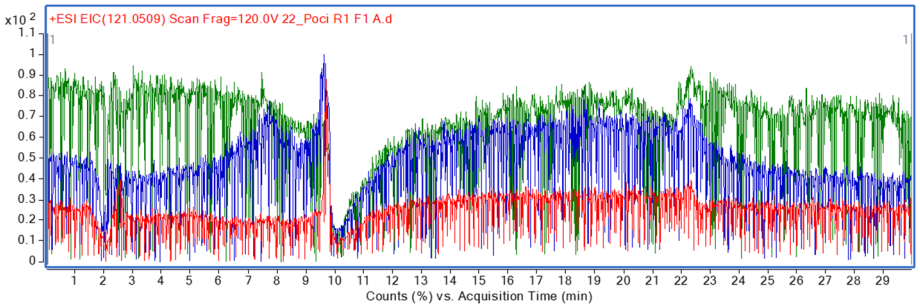


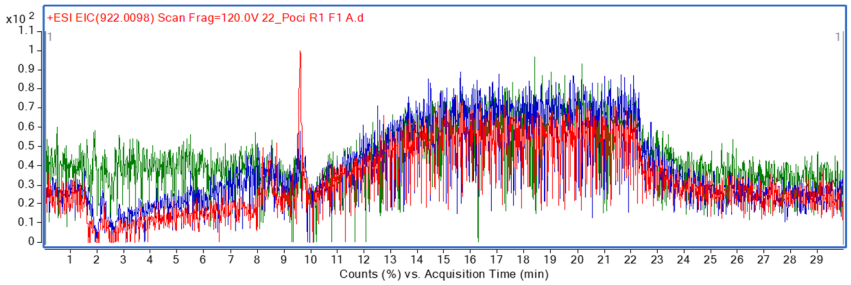
(b)



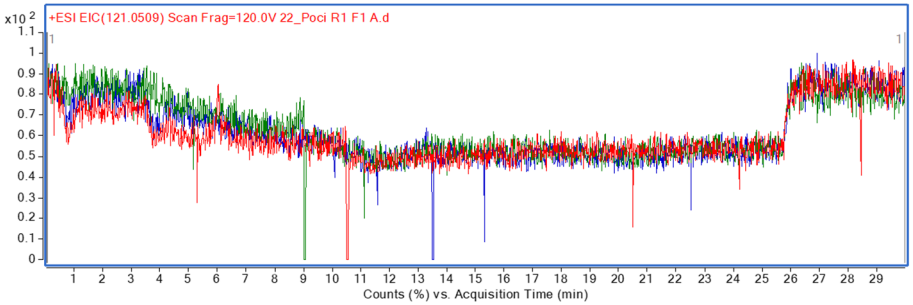


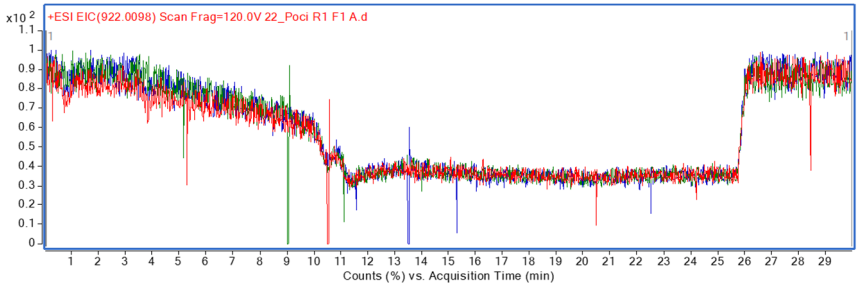
(c)


x10 2
+ESI EIC(121.0509) Scan Frag=120.0V 22_Poci R1 F1 A.d
Counts (%) vs. Acquisition Time (min)

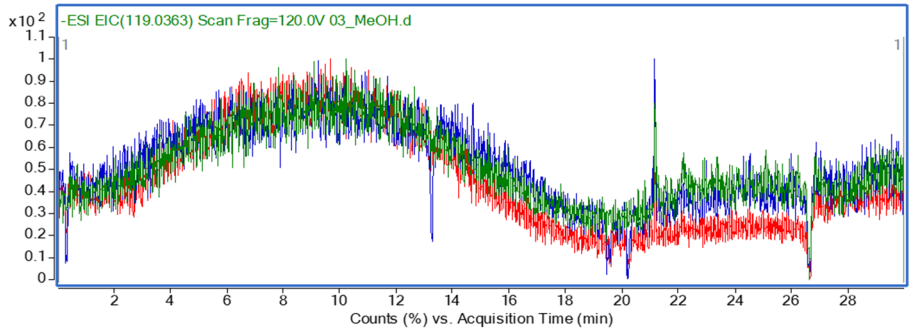

x10 2
+ESI EIC(922.0098) Scan Frag=120.0V 22_Poci R1 F1 A.d
Counts (%) vs. Acquisition Time (min)

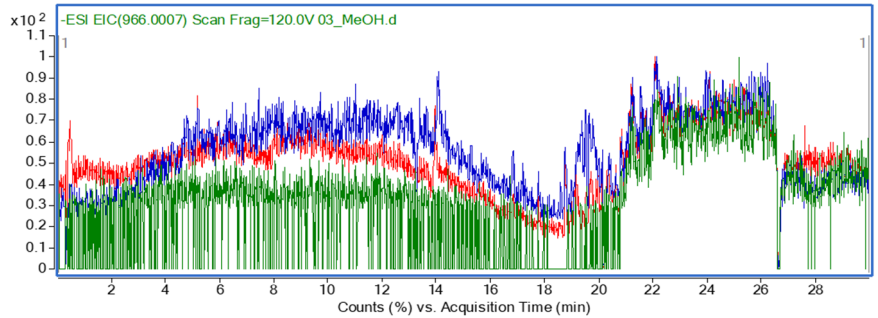
(d)


x10 2
+ESI EIC(121.0509) Scan Frag=120.0V 22_Poci R1 F1 A.d
Counts (%) vs. Acquisition Time (min)

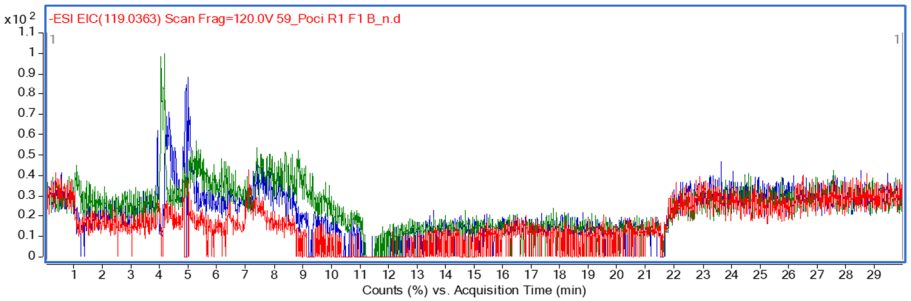

x10 2
+ESI EIC(922.0098) Scan Frag=120.0V 22_Poci R1 F1 A.d
Counts (%) vs. Acquisition Time (min)

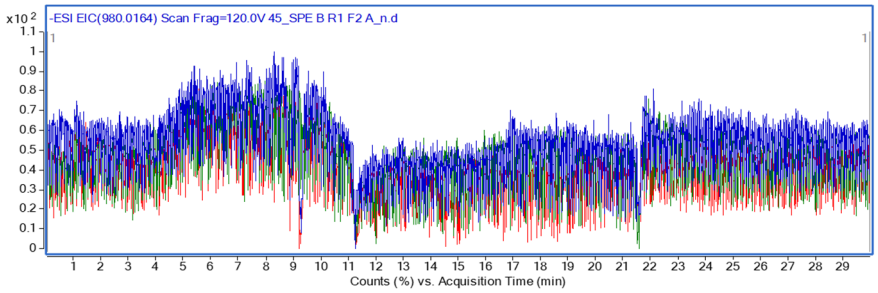
(e)


x10 2
-ESI EIC(119.0363) Scan Frag=120.0V 03_MeOH.d
Counts (%) vs. Acquisition Time (min)

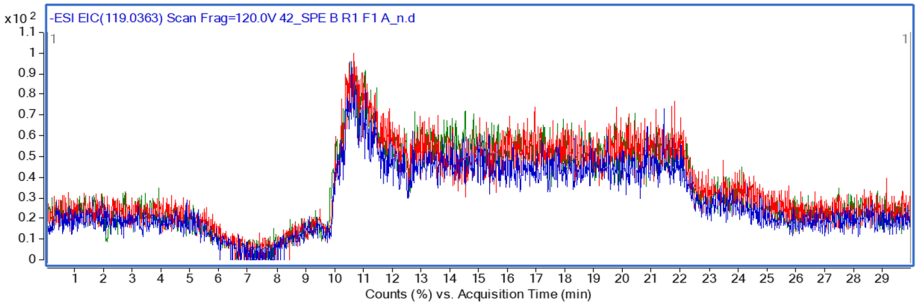

x10 2
-ESI EIC(966.0007) Scan Frag=120.0V 03_MeOH.d
Counts (%) vs. Acquisition Time (min)

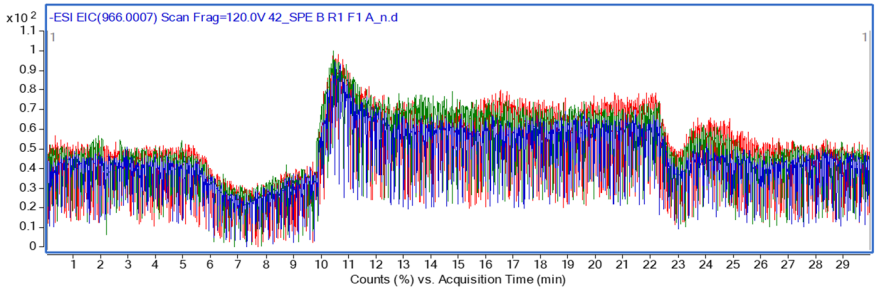
(f)


-ESI EIC(119.0363) Scan Frag=120.0V 59_Poci R1 F1 B_n.d
x10 2
Counts (%) vs. Acquisition Time (min)

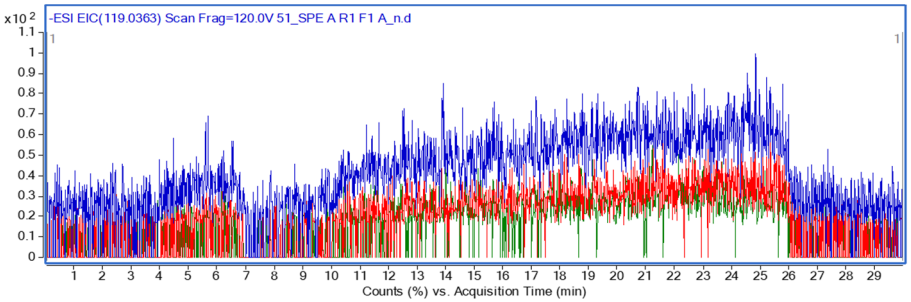

-ESI EIC(980.0164) Scan Frag=120.0V 45_SPE B R1 F2 A_n.d
x10 2
Counts (%) vs. Acquisition Time (min)

(g)


-ESI EIC(119.0363) Scan Frag=120.0V 42_SPE B R1 F1 A_n.d
x10 2
Counts (%) vs. Acquisition Time (min)


-ESI EIC(966.0007) Scan Frag=120.0V 42_SPE B R1 F1 A_n.d
x10 2
Counts (%) vs. Acquisition Time (min)

(h)


-ESI EIC(119.0363) Scan Frag=120.0V 51_SPE A R1 F1 A_n.d
x10 2
Counts (%) vs. Acquisition Time (min)

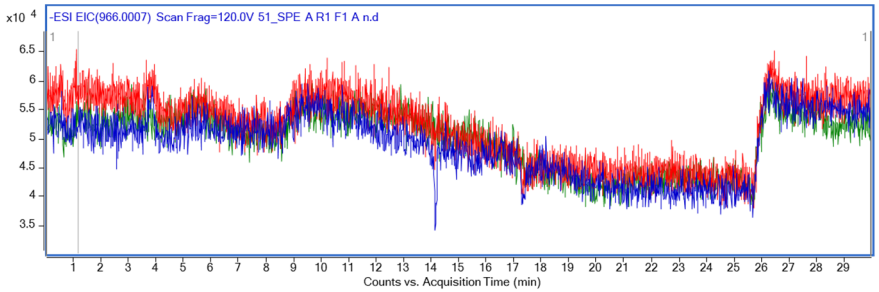

-ESI EIC(966.0007) Scan Frag=120.0V 51_SPE A R1 F1 A n.d
x10 4
Counts vs. Acquisition Time (min)

Figure S8: Number of compounds that would be identified by using different combinations of sampling and chromatographic modes.

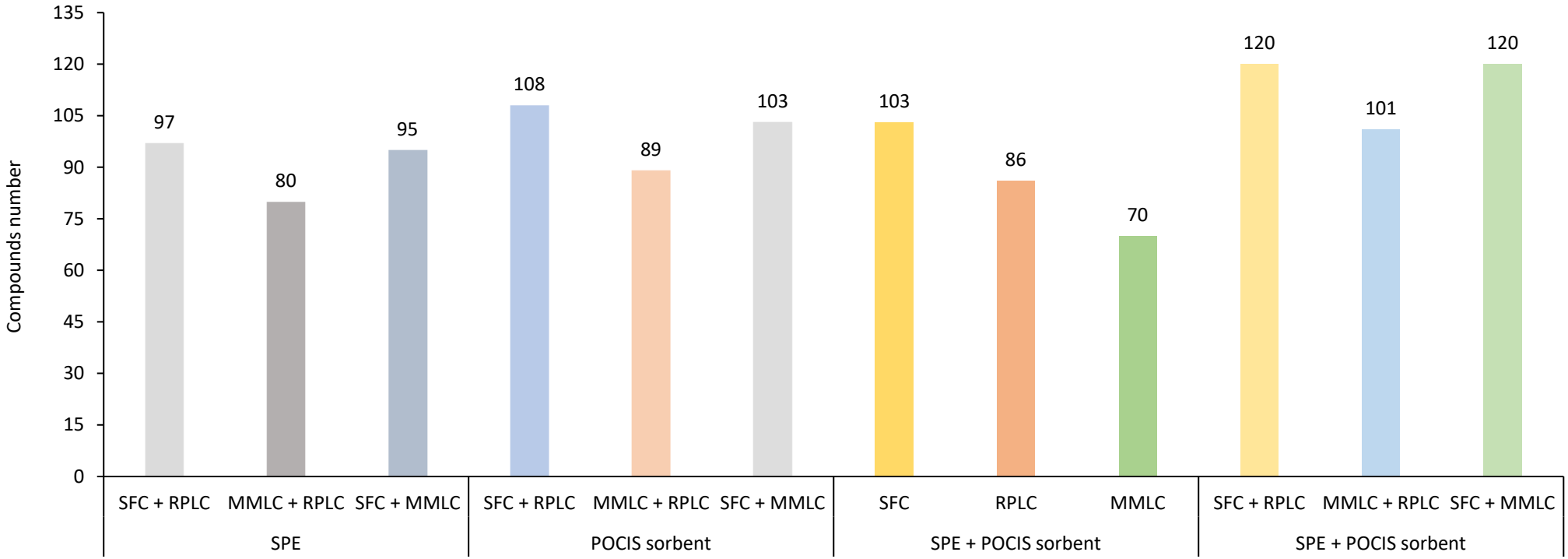


Figure S9: Distribution of the compounds identified in surface water samples according to their main application.