Occurrence and removal of pharmaceutical compounds in wastewaters in Greece

Christina I. Kosma[1], Dimitra A. Lambropoulou[2] and Triantafyllos A. Albanis[1]

[1]Department of Chemistry, University of Ioannina, Ioannina ,45110

[2]Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, 54124

Emerging contaminants

- A number of new compounds were discovered in water that previously had not been detected, or detected at levels that may be significantly different than expected.
- Not included in the current legislation about water quality.
- Enter the environment and cause known or suspected adverse ecological and (or) human health effects.
- Pharmaceuticals, personal care products, endocrine disrupting compounds, nanoparticles, plasticizers etc.

Pharmaceuticals and Personal care products (PPCPs)

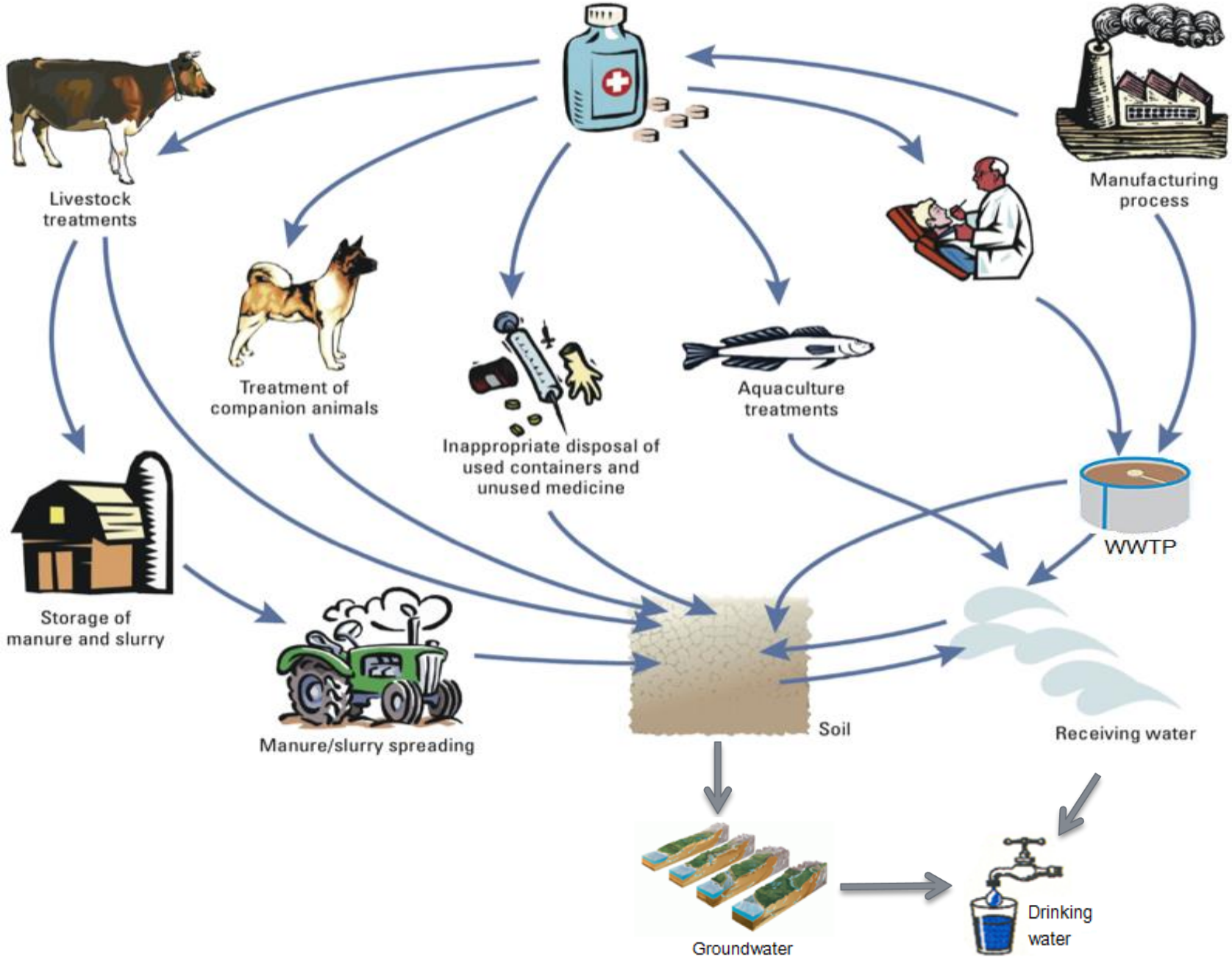
Consumption levels

- ✓ There are 6 million PPCPs commercially available worldwide.
- ✓ Their usage increases 3-4% globally per year.
- ✓ Real consumption rate is higher, since the data are based on uncertain estimation, taking into consideration that many pharmaceuticals are over the counter.

Concentration levels

- ✓ PPCPs are mainly introduced into the environment through WWTPs.
- ✓ Their occurrence in wastewaters were firstly reported in USA., where clofibric acid was detected in concentrations between 0,8-2 μg/L.

Sources, pathways and sinks of PPCPs



Aim of the present study

- ✓ Development, optimization and application of an analytical method for the determination of PPCPs in wastewaters.
- ✓ Monitoring study over 1-year for the determination of eighteen PPCPs in the influents and the effluents of 8 WWTPs of various cities in Greece.
- ✓ Determination of removal efficiencies of PPCPs in WWTPs.
- ✓ Preliminary Environmental Risk Assessment (in terms of acute and chronic toxicity) using risk quotients (RQs).

PPCPs investigated

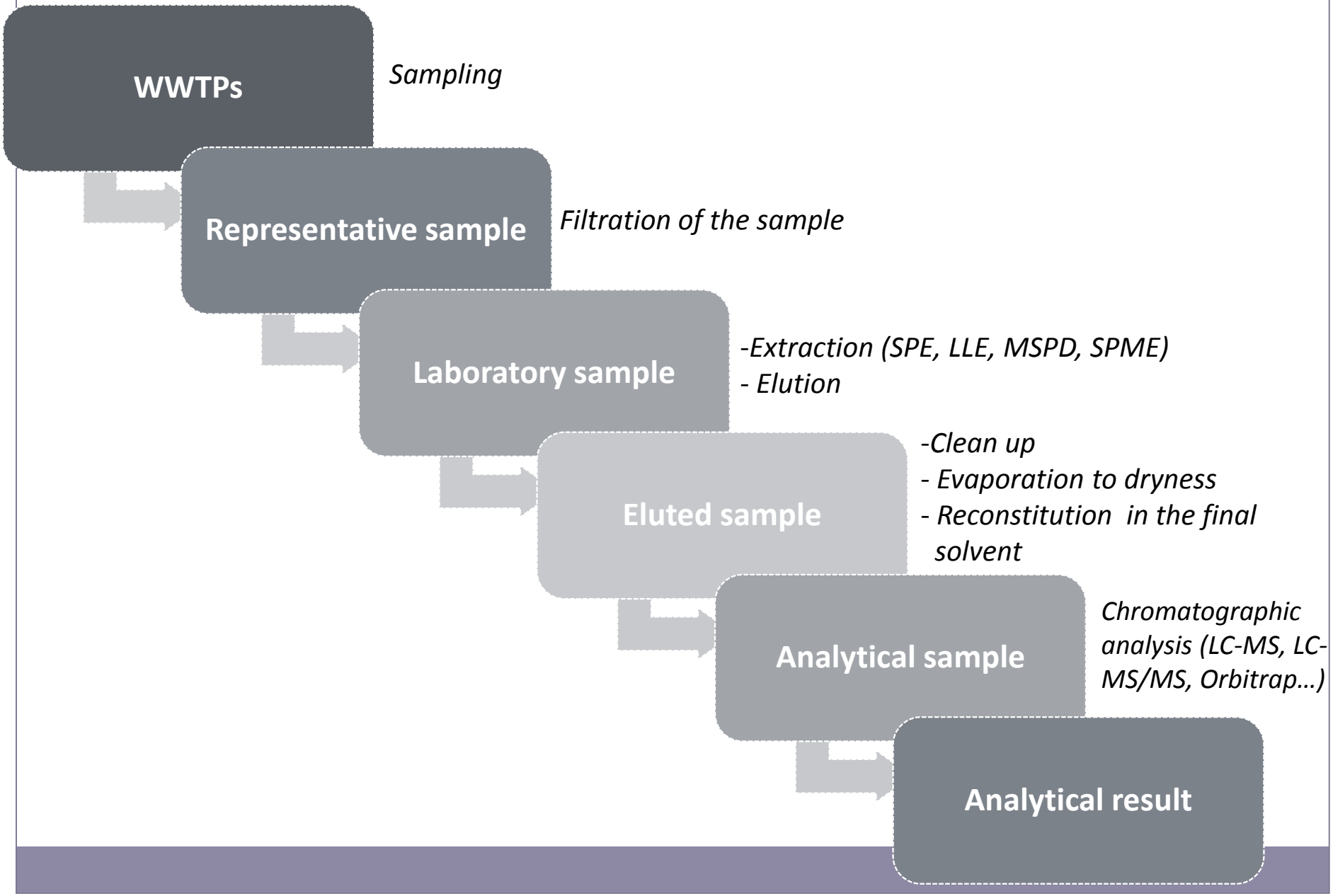
Therapeutic group	Compound
Pharmaceuticals	
Analgesics/ Anti-inflammatory (NSDAIs)	Ibuprofen, diclofenac, paracetamol, naproxen, salicylic acid, phenazone, tolfenamic acid
Antibiotics	Trimethoprim, sulfamethoxazole
Phsychiatrics - antiepileptics	Carbamazepine
Lipid regulators	Clofibric acid, bezafibrate, gemfibrozil, fenofibrate
Psychomotor stimulants	Caffeine
Glucocorticoid steroids	Budesonide
Hypolipidemic statin	Simvastatin
Personal Care Products	
Disinfectants	Triclosan

PPCPs investigated

Selection criteria

- High annual consumption.
- Proved occurrence in wastewaters and environmental concentration levels, according to the existing literature.
- Possible toxicity risk posed in both aquatic organisms and humans.

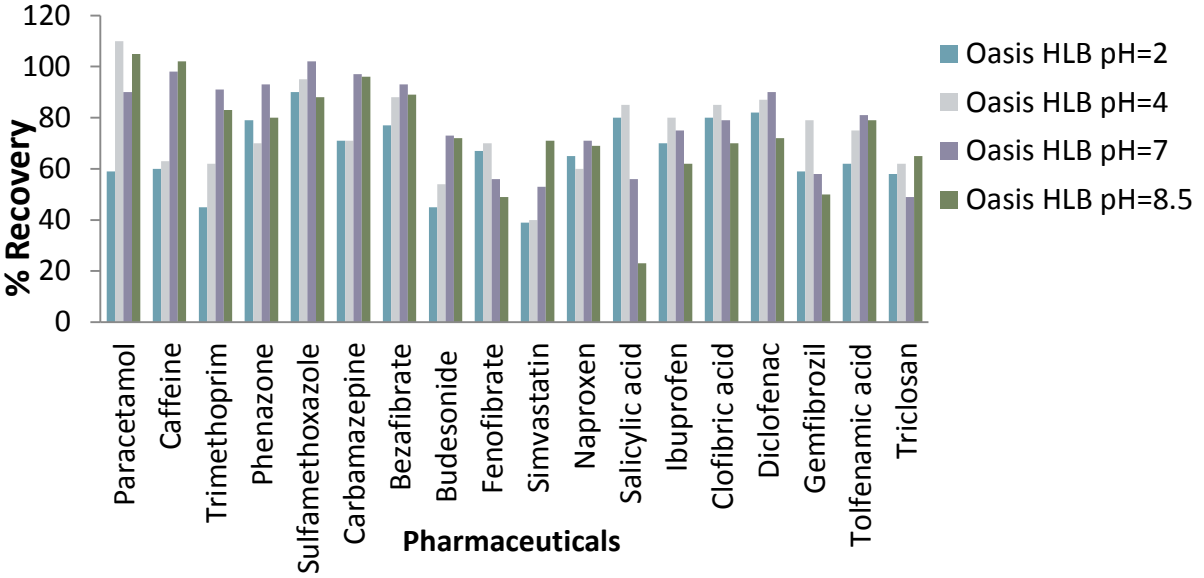
Experimental procedure



Solid Phase Extraction Procedure (SPE)

Cartridges and pH

- ✓ Oasis HLB pH=2
- ✓ Oasis HLB pH=4
- ✓ Oasis HLB pH=7
- ✓ Oasis HLB pH=8,5



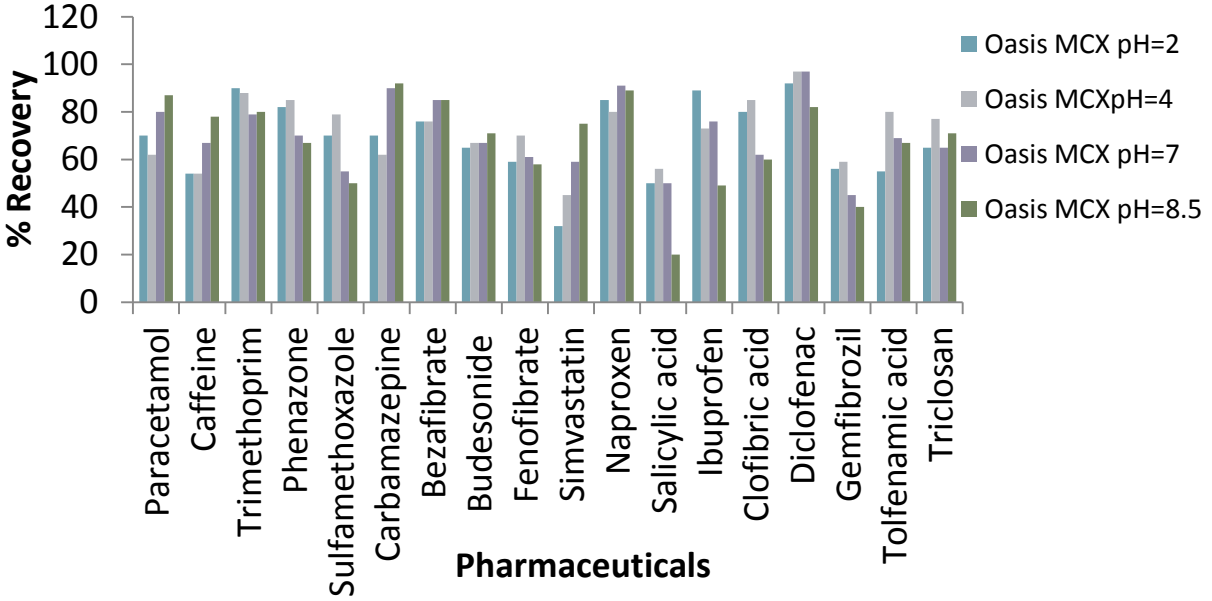
Real samples:

pH: 6.87- 8.39 (mean: 7.57)

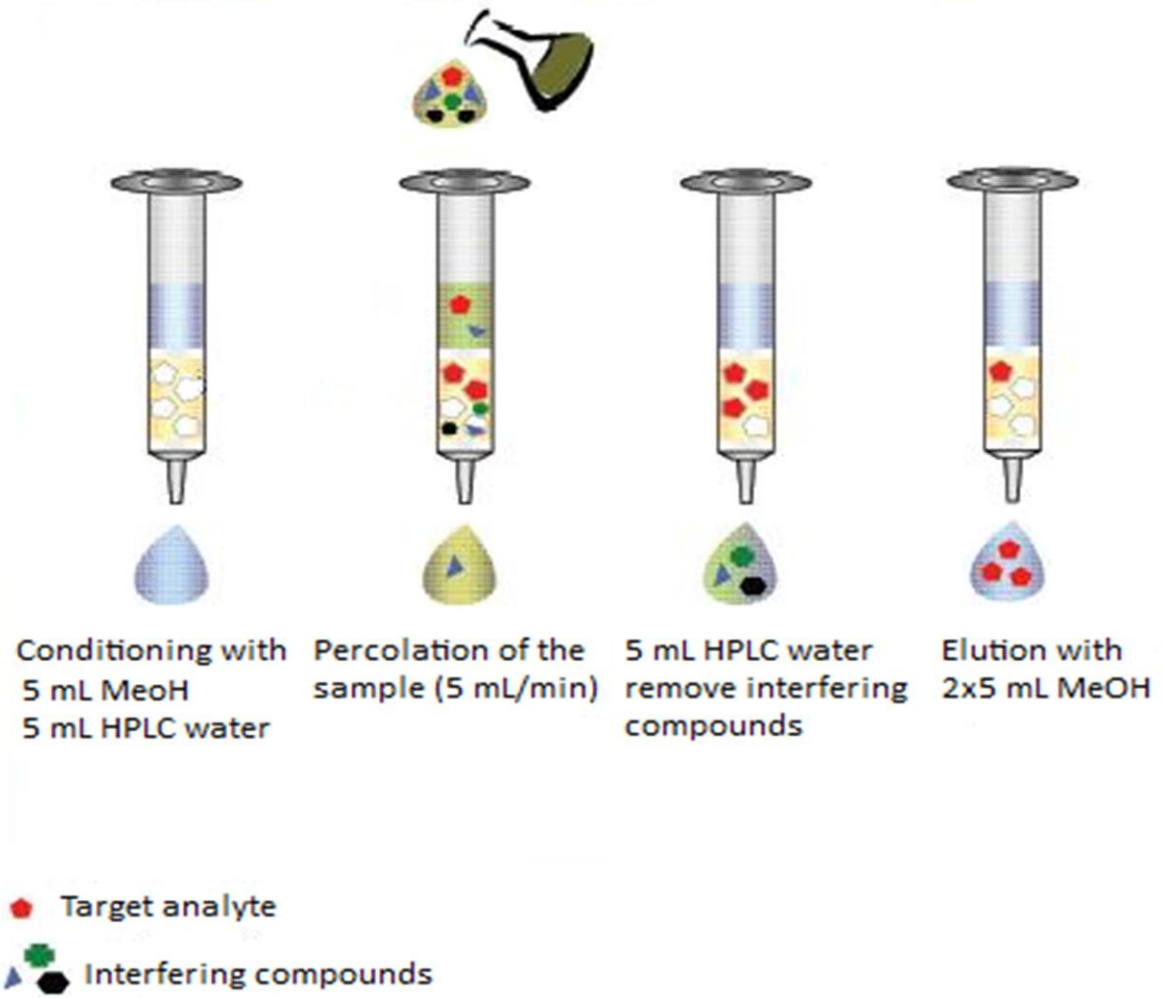
So no pH adjustment was done

- ✓ Extraction volume: 400 mL
- ✓ Elution solvent: Methanol
- ✓ Injection solvent: Methanol: Water = 50: 50

- ✓ Oasis MCX pH=4
- ✓ Oasis MCX pH=7
- ✓ Oasis MCX pH=8,5



Application of SPE



Chromatographic analysis

A. LC-ESI-MS

- ✓ SPD 20A UV-Vis detector coupled in series with the LC-MS 2010EV mass selective detector (*Shimadzu, Kyoto, Japan)*.
- ✓ Atmospheric pressure ionization source electrosprey (ESI) interface.
- ✓ C_{18} (Restek) analytical column 150 x 4.6 mm with 5µm particle size
- ✓ Samples analyzed in **positive(PI)** and **negative(NI)** ionization mode.

Gradient elution

Time (min)	Elution solvents (PI)	
	Water LC-MS +0,1 % formic acid	Acetonitrile LC-MS +0,1 % formic acid
0	90	10
30	20	80
35	10	90
37	90	10
40	90	10

Time (min)	Elution solvents (AI)	
	Water LC-MS	Acetonitrile LC-MS
0	90	10
5	65	35
12	60	40
15	50	50
20	20	80
25	10	90
27	90	10
30	90	10

Chromatographic analysis

A. LC-ESI-MS

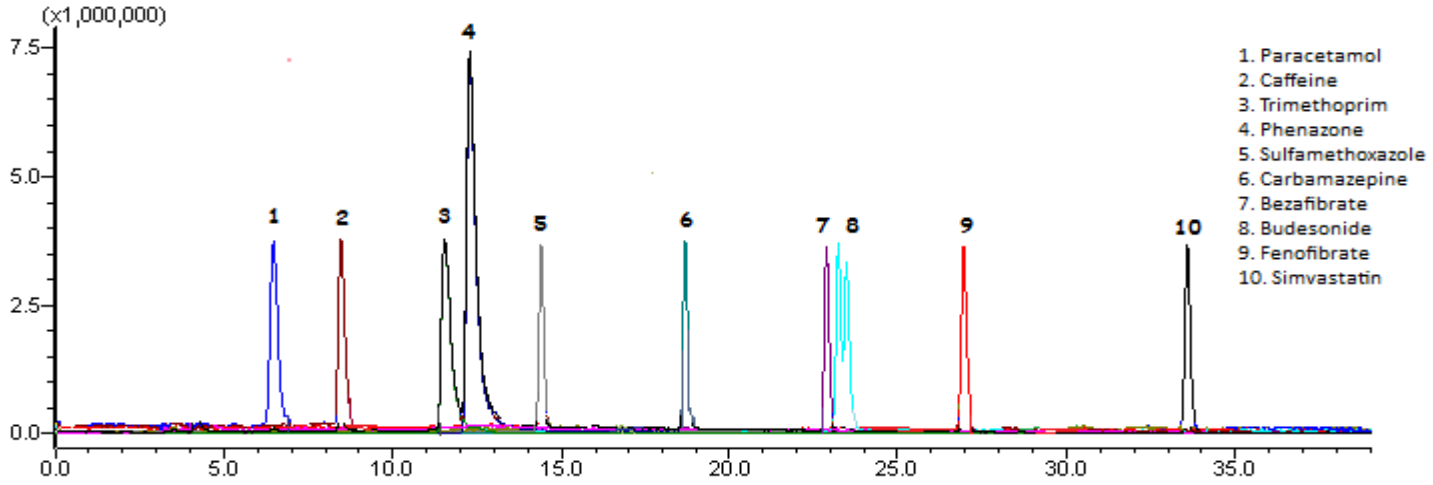
Instrumental parameters for target compounds using LC–MS in SIM mode (Quantitation ions in bold)

PPCPs	Polarity (ESI)	Time (min)	m/z ions	Relative Ion Intensity %
Paracetamol	+	6,267	**152**, 110	100/ 40,09
Caffeine	+	8,425	**195**, 138	100/ 60,16
Trimethoprim	+	11,517	**291,** 261, 230	100/ 51,38/ 36,18
Phenazone	+	12,192	**189**, 147, 56	100/ 86,52/ 12,29
Sulfamethoxazole	+	14,235	**254**, 156, 92	100/ 40,23/ 12,31
Carbamazepine	+	18,692	**237**, 194, 192	100/ 80,39/ 48,59
Bezafibrate	+	22,975	**362,** 276, 316	100/ 25,93/ 14,86
Budesonide	+	23,333	**431**, 413, 323	100/ 98,28/ 29,81
Fenofibrate	+	27,025	**319**	100
Simvastatin	+	33,650	**441**, 419, 267	100/ 98,27/ 97,64
Naproxen	-	12,158	**229**, 185	100/ 80,20
Salicylic acid	-	12,397	**137**, 93	100/ 97,8
Ibuprofen	-	12,437	**205,** 160,161	100/ 90,21/ 71,12
Clofibric acid	-	19,788	**213**, 127	100/ 12,63
Diclofenac	-	22,331	**294**, 295, 250	100/ 40,91/ 12,72
Gemfibrozil	-	24,040	**249**, 121	100/ 82,63
Tolfenamic acid	-	24,318	**260**, 396	100/ 10,12
Triclosan	-	24,715	**287**, 289	100/ 90,86

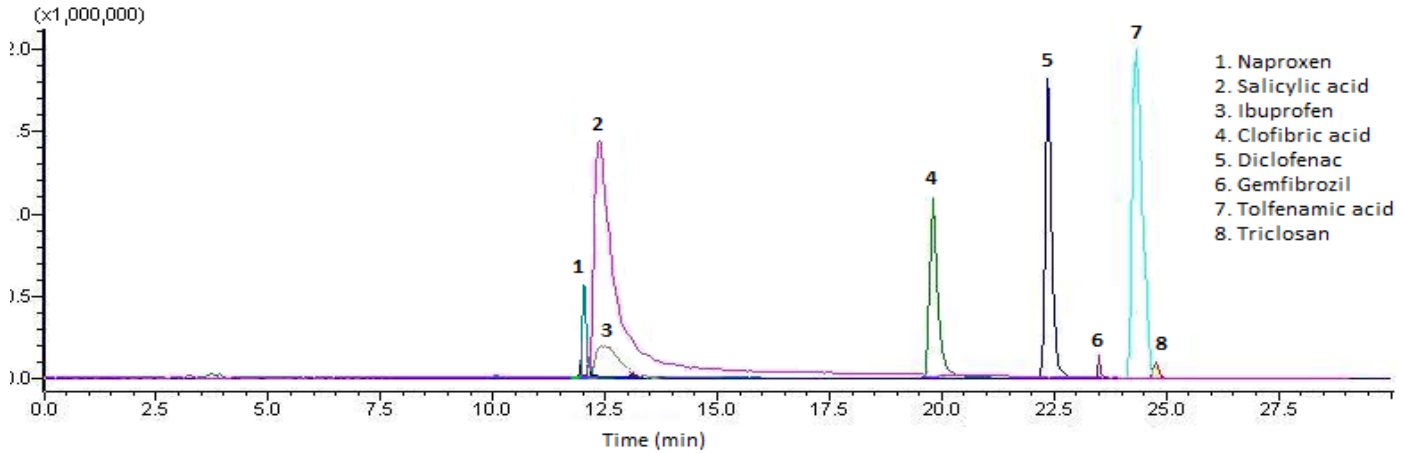
Chromatographic analysis

A. LC-ESI-MS

(a)



(b)



Representative chromatogram of a 500 µg/L spiking extract for the target compounds analyzed under (a) positive and (b) negative ionization mode, in LC-ESI-MS.

Chromatographic analysis

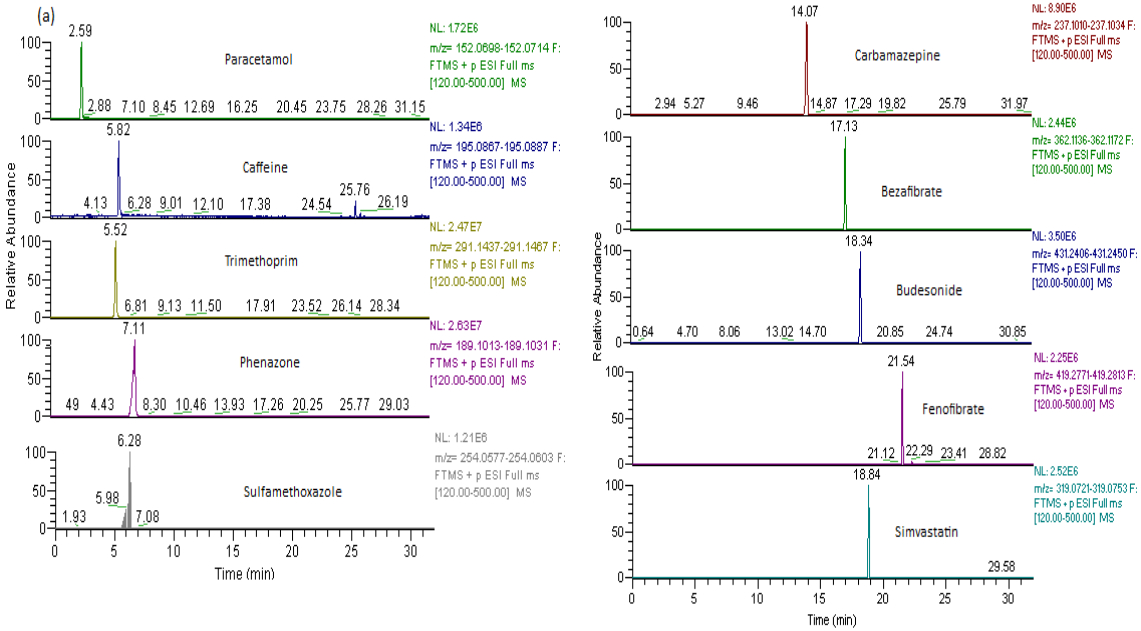
B. UHPLC/LTQ ORBITRAP XL

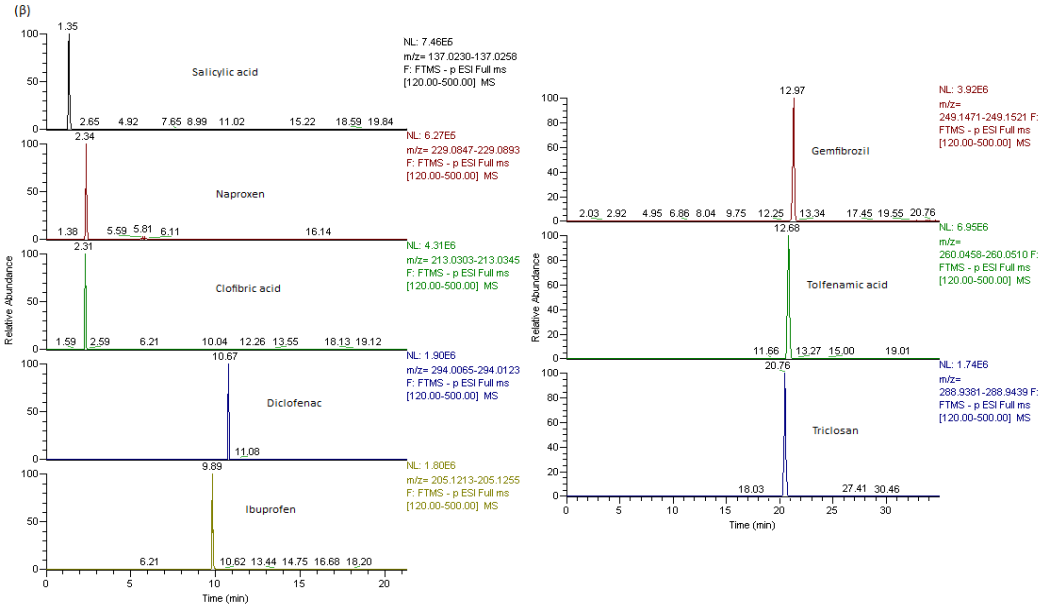
PPCPs and corresponding retention times, exact and accurate mass information, mass error deviation and double bond and ring equivalent number (DBE), for the precursor molecular ions.

Pharmaceuticals	Elemental Composition	RT (min)	Exact mass (theoritical)	Accurate/nominal mass (detected)	Error (ppm)	DBE	Ionization mode
Paracetamol	$C_8H_9NO_2$	2.59	152.0706	152.0712	3.452	4.5	+
Trimethoprim	$C_{14}H_{18}N_4O_3$	5.52	291.1452	291.1462	3.548	7.5	+
Caffeine	$C_8H_{10}N_4O_2$	5.82	195.0877	195.0883	3.321	5.5	+
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	6.28	254.0594	254.0600	2.407	6.5	+
Phenazone	$C_{11}H_{12}N_2O$	7.80	189.1022	189.1027	2.435	6.5	+
Carbamazepine	$C_{15}H_{12}N_2O$	14.08	237.1022	237.1030	3.207	10.5	+
Bezafibrate	$C_{19}H_{20}ClNO_4$	17.13	362.1154	362.1170	4.522	9.5	+
Budesonide	$C_{25}H_{34}O_6$	18.34	431.2428	431.2440	2.747	8.5	+
Fenofibrate	$C_{17}H_{16}ClO_4$	18.84	319.0737	319.0742	3.249	9.5	+
Simvastatin	$C_{25}H_{38}O_5$	21.54	419.2792	419.2809	4.065	6.5	+
Salicylic acid	$C_7H_6O_3$	1.35	137.0244	137.0249	3.620	5.0	-
Clofibric acid	$C_{10}H_{11}ClO_3$	2.31	213.0324	213.0332	3.778	5.5	-
Naproxen	$C_{14}H_{14}O_3$	2.34	229.0870	229.0879	3.852	8.5	-
Ibuprofen	$C_{13}H_{18}O_2$	9.89	205.1234	205.1234	-0.015	5.5	-
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	10.67	294.0094	294.0101	2.356	9.5	-
Tolfenamic acid	$C_{14}H_{12}ClNO_2$	12.68	260.0484	260.0492	3.155	9.5	-
Gemfibrozil	$C_{15}H_{22}O_3$	12.97	249.1496	249.1502	2.337	5.5	-
Triclosan	$C_{12}H_7Cl_3O_2$	20.76	286.9439	286.9442	1.095	8.5	-

Chromatographic analysis

B. UHPLC/LTQ ORBITRAP XL

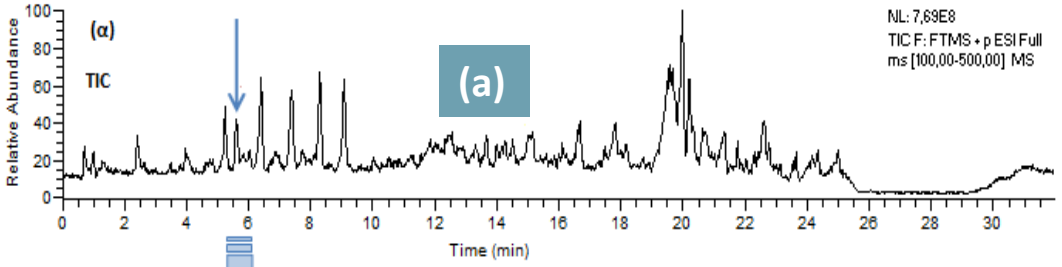




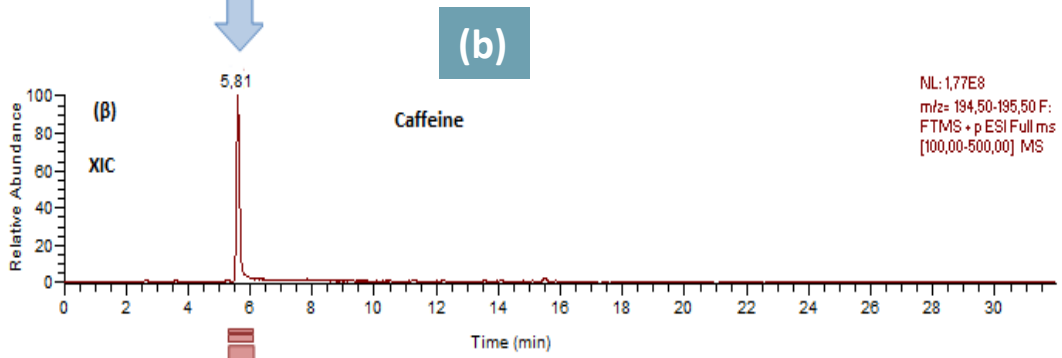
UHPLC/ LTQ-Orbitrap XL chromatograms of PPCPs standard (500 ppb) in (a) positive and (b) negative ionization mode, based on accurate mass with a mass window of 5 ppm. The chromatograms were extracted from total ion current (TIC).

Arta WWTP - Influent in May

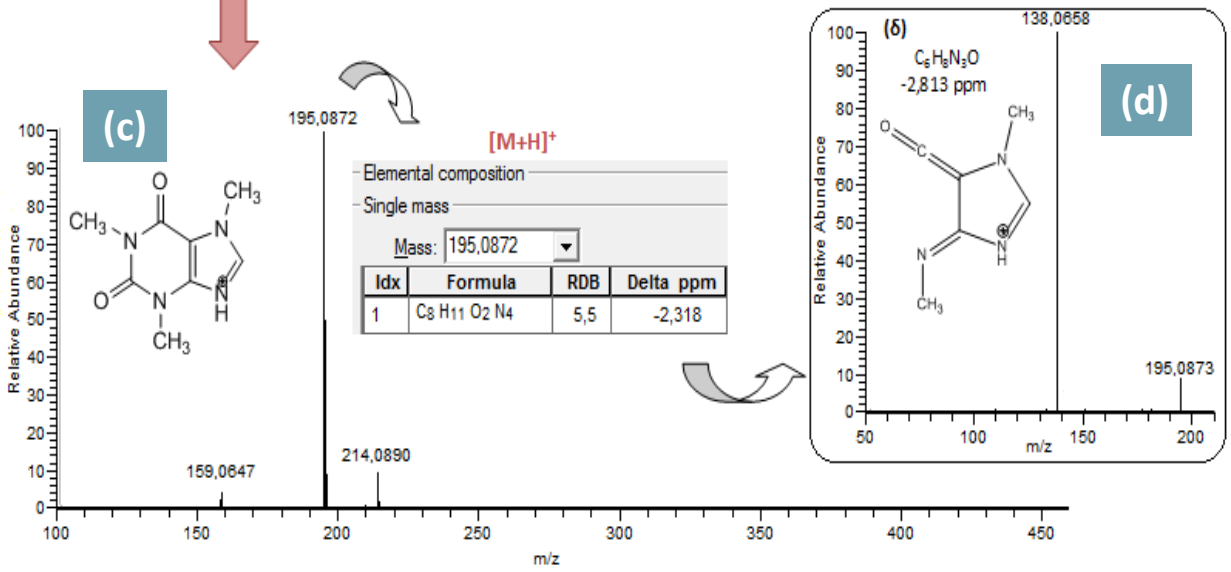
UHPLC/LTQ ORBITRAP XL



(a) Total Ion Chromatogram (TIC)



(b) Extracted Ion Chromatogram(XIC)



(d) MS^2 Spectrum

(c) Exact mass of the precursor ion and its elemental composition

Method validation

LC-ESI-MS

Limits of detection (**LOD**) and limits of quantification (**LOQ**) in distilled water, influent and effluent wastewater and precision (RSD in the same day ($\mathbf{RSD_r}$) and RSD in different days ($\mathbf{RSD_R}$)) in effluent wastewater.

	LOD (ng/L)			LOQ (ng/L)			RSDr (%)	RSD_R (%)
PPCPs	DW	WWI	WWE	DW	WWI	WWE	(n=5)	(n=5)
Paracetamol	11,3	39,7	28,8	35,0	119,1	89,3	9,3	13,0
Caffeine	9,4	12,0	8,7	28,8	37,2	27,8	5,1	8,6
Trimethoprim	1,9	3,4	2,1	5,9	10,9	6,2	2,3	4,7
Phenazone	1,8	2,9	2,0	5,5	9,0	6,6	1,8	4,0
Sulfamethoxazole	3,3	4,0	3,5	10,2	12,4	10,5	2,5	3,0
Carbamazepine	4,5	4,9	4,8	13,5	15,8	15,4	2,1	3,1
Bezafibrate	5,6	7,5	6,1	17,9	24,8	18,9	3,1	8,8
Budesonide	6,4	7,9	8,2	19,8	25,4	26,1	4,0	10,1
Fenofibrate	8,3	9,1	9,0	25,6	28,4	27,7	5,3	11,7
Simvastatin	4,10	5,33	4,92	12,8	16,6	15,4	6,3	7,0
Naproxen	16,1	26,4	19,1	159,4	79,4	57,3	12,1	14,3
Salicylic acid	46,7	85,0	69,2	144,8	272,0	210,6	3,6	6,1
Ibuprofen	70,7	112,9	78,3	233,3	350,0	250,6	4,8	4,9
Clofibric acid	20,1	30,6	22,8	61,1	91,8	69,8	2,0	2,7
Diclofenac	15,9	25,1	18,5	50,9	77,8	55,5	5,0	11,9
Gemfibrozil	37,8	60,5	40,7	114,5	187,6	126,2	9,0	11,4
Tolfenamic acid	9,0	13,2	12,1	27,9	42,2	37,5	4,4	9,9
Triclosan	32,5	49,2	41,8	100,8	147,6	129,6	4,1	5,0

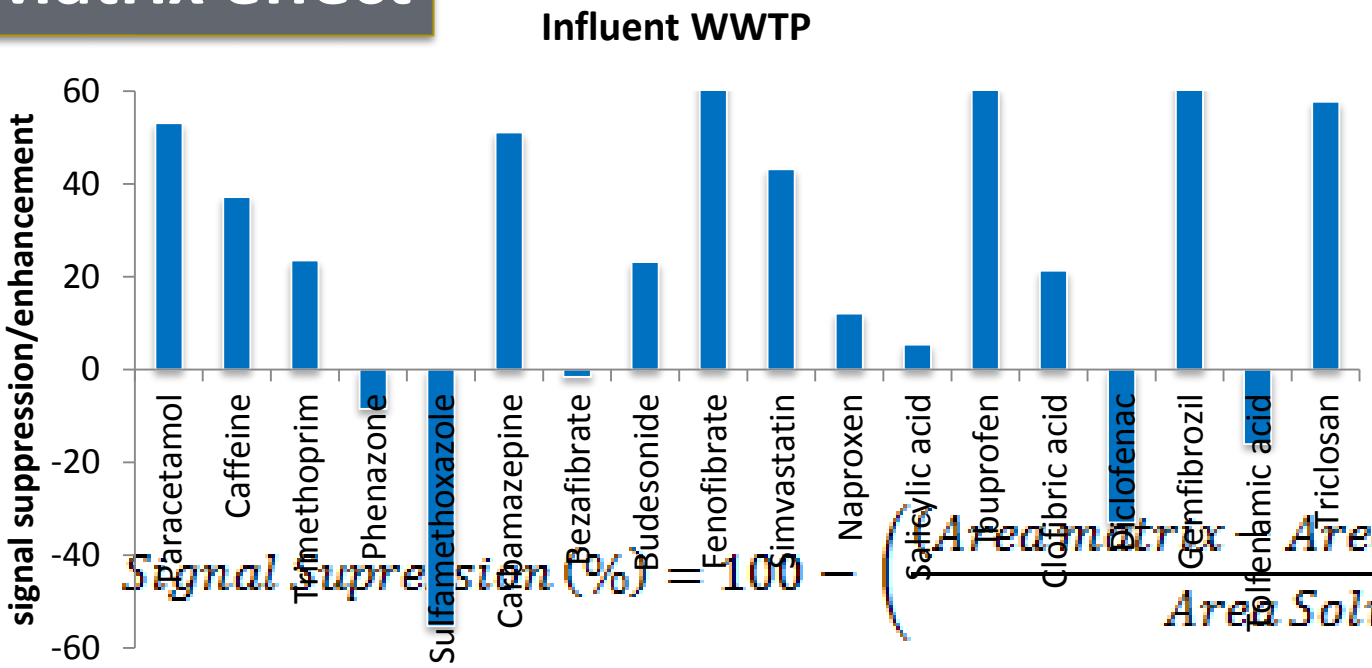
Method validation

LC-ESI-MS

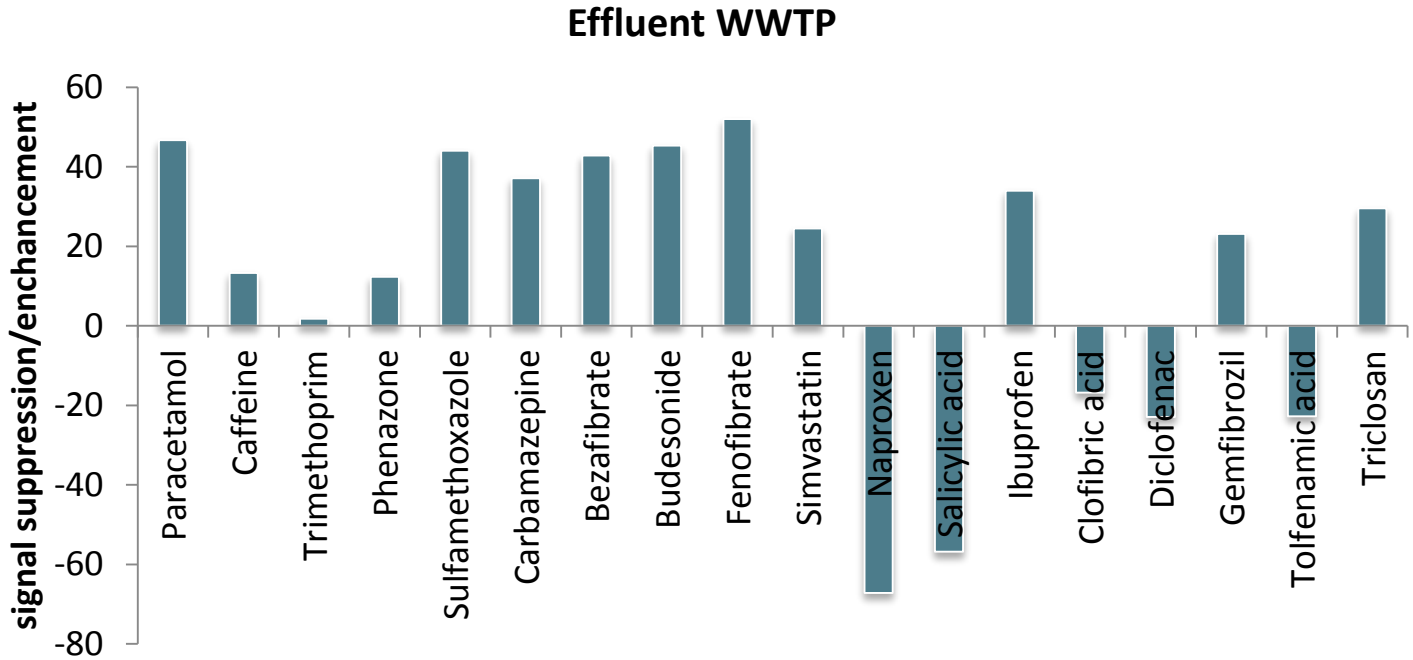
Mean recoveries (%) and RSD (%) in distilled water, influent and effluent wastewater after spiking with 0.2 and 2 µg/L (n=3).

PPCPs	% Recoveries after spiking with 0,2 µg/L (RSD %)			% Recoveries after spiking with 2 µg/L (RSD %)		
	DW	WWI	WWE	DW	WWI	WWE
Paracetamol	76,2 (5,2)	80,1 (8,6)	74,4 (9,3)	82,6 (6,3)	89,5 (9,4)	77,2 (7,1)
Caffeine	87,2 (6,1)	93,6 (7,9)	95,0 (5,3)	99,0 (3,0)	102,3 (2,2)	114,2 (2,3)
Trimethoprim	81,2 (6,8)	88,4 (5,2)	86,0 (3,6)	95,5 (12,2)	95,1 (9,0)	90,9 (7,8)
Phenazone	90,3 (3,8)	72,6 (9,8)	84,9 (3,3)	98,7 (11,2)	96,3 (4,0)	91,7 (6,1)
Sulfamethoxazole	91,6 (4,3)	88,5 (4,2)	80,5 (3,9)	100,8 (3,3)	112,1 (1,2)	112,6 (7,9)
Carbamazepine	95,5 (9,1)	99,3 (7,2)	92,6 (5,0)	99,3 (7,5)	108,0 (7,0)	97,7 (7,1)
Bezafibrate	78,1 (8,2)	65,3 (4,3)	72,1 (1,5)	96,4 (8,5)	91,0 (4,3)	95,5 (1,2)
Budesonide	62,7 (9,0)	60,5 (3,3)	57,1 (6,0)	75,9 (9,9)	70,7 (8,3)	73,1 (10,2)
Fenofibrate	52,1 (3,8)	48,0 (2,5)	49,5 (6,9)	61,3 (8,6)	52,7 (7,4)	56,1 (12,5)
Simvastatin	58,1 (6,7)	55,3 (5,9)	69,2 (6,5)	61,1 (10,0)	66,7 (4,3)	70,5 (7,2)
Naproxen	70,1 (6,7)	61,2 (3,2)	51,0 (10,9)	70,9 (9,4)	68,2 (2,1)	56,6 (5,4)
Salicylic acid	58,7 (3,2)	43,3 (8,0)	51,6 (8,8)	59,3 (4,3)	56,2 (7,6)	49,8 (9,4)
Ibuprofen	64,3 (4,7)	72,6 (4,3)	65,7 (2,1)	84,9 (3,1)	90,0 (6,8)	82,3 (5,2)
Clofibricacid	81,7 (11,1)	88,2 (6,0)	81,4 (9,4)	99,3 (3,1)	93,3 (6,0)	90,2 (9,0)
Diclofenac	101,4 (9,2)	87,0 (6,8)	121,4 (10,2)	97,3 (5,0)	92,1 (6,2)	126,5 (8,1)
Gemfibrozil	58,3 (9,7)	49,8 (12,4)	58,2 (6,8)	77,2 (2,2)	65,6 (4,4)	73,0 (4,1)
Tolfenamicacid	88,2 (3,0)	75,1 (5,6)	77,14 (8,7)	85,8 (11,7)	78,7 (2,9)	81,3 (5,0)
Triclosan	49,4 (12,7)	50,5 (9,0)	45,5 (8,1)	58,6 (6,7)	52,7 (8,5)	53,1 (7,0)

Matrix effect

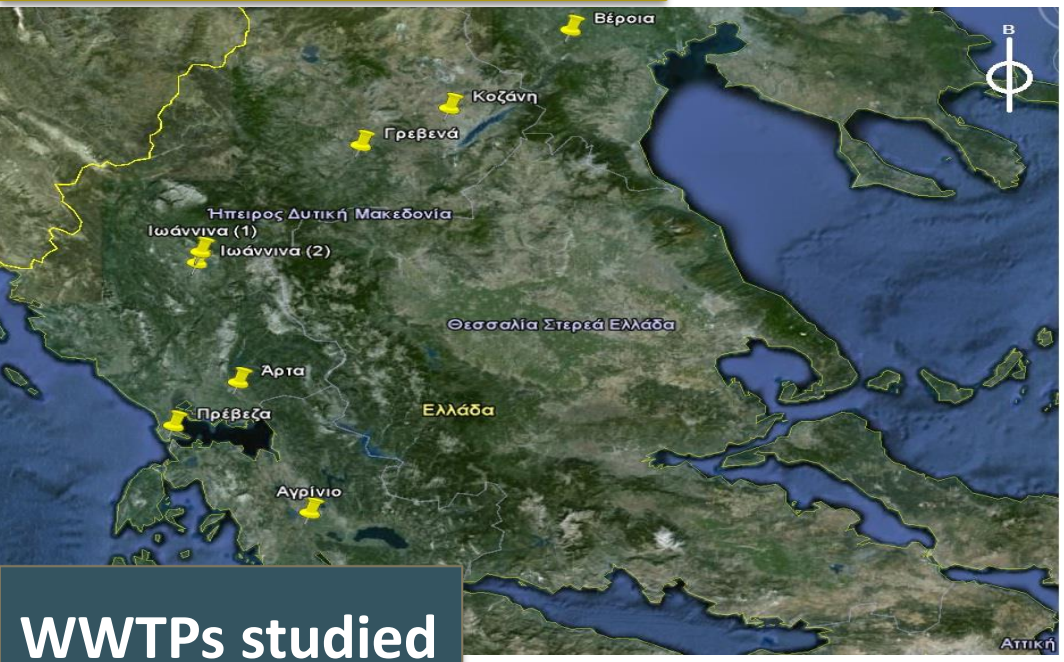


$$Signal\ suppression\ (\%) = 100 - \left(\frac{(Area\ matrix - Area\ Blank) \times 100}{Area\ Solvent}\right)$$



Occurrence, seasonal variation and removal of PPCPs in eight WWTPs of Greece

Sampling stations



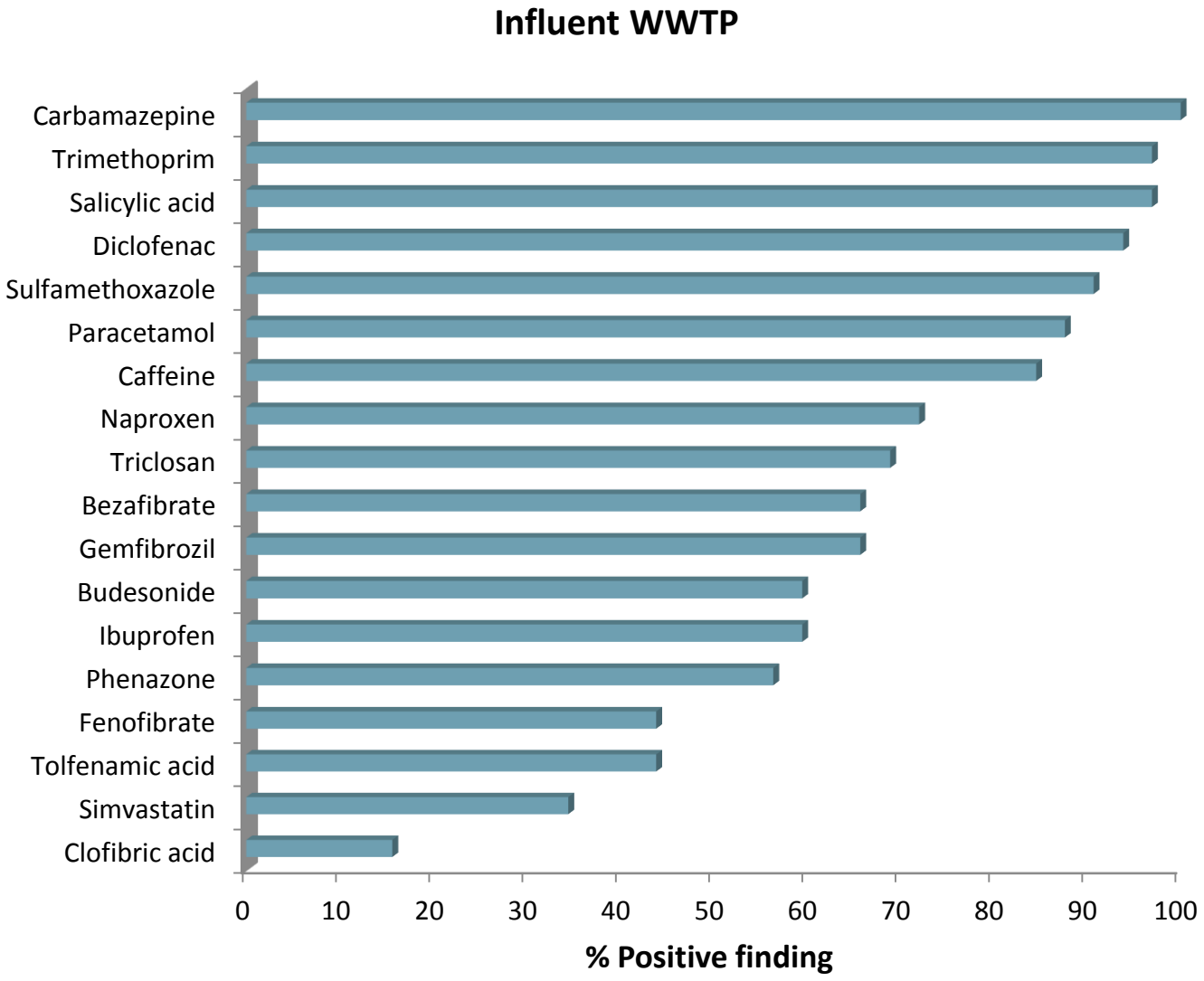
WWTPs studied

Sample collection

- **Influent and effluent wastewaters**
- Autumn 2010 *(Ocotber)*
- Winter 2011 *(February)*
- Spring 2011 *(May)*
- Summer 2011 (*July)*

WWTPs	Population served	Average flow (m^3/d)	Treated wastewater	SRT (d)	HRT (h)	Primary treatment	Secondary treatment	Final receiver
Ioannina city	100,000	25,276	Urban and industrial	11	1,5 - 4	Grit removal-primary settling	Activated sludge	Kalamas River
Ioannina hos.	800	550	Hospital	1,5	6	Grit removal	Activated sludge	Urban network
Arta	38,000	11,500	Urban	18	4	Grit removal	Activated sludge	Arachthos River
Preveza	25,000	7,000	Urban	28	20	Grit removal	Activated sludge	Ioanian Sea
Agrinio	90,000	14,000	Urban	1-3	24	Grit removal	Activated sludge	Acheloos River
Grevena	20,000	4,000	Urban	20	16	Grit removal	Activated sludge	Grevenitis River
Kozani	70,400	10,000	Urban	25	39	Grit removal	Activated sludge	Polifitos Lake
Veroia	45,000	9,800	Urban	20	22	Grit removal-primary settling	Activated sludge	Stank 66 – Aliakmonas River

Positive findings in the influents of the eight WWTPs



Mean concentration values in the influents of the eight WWTPs

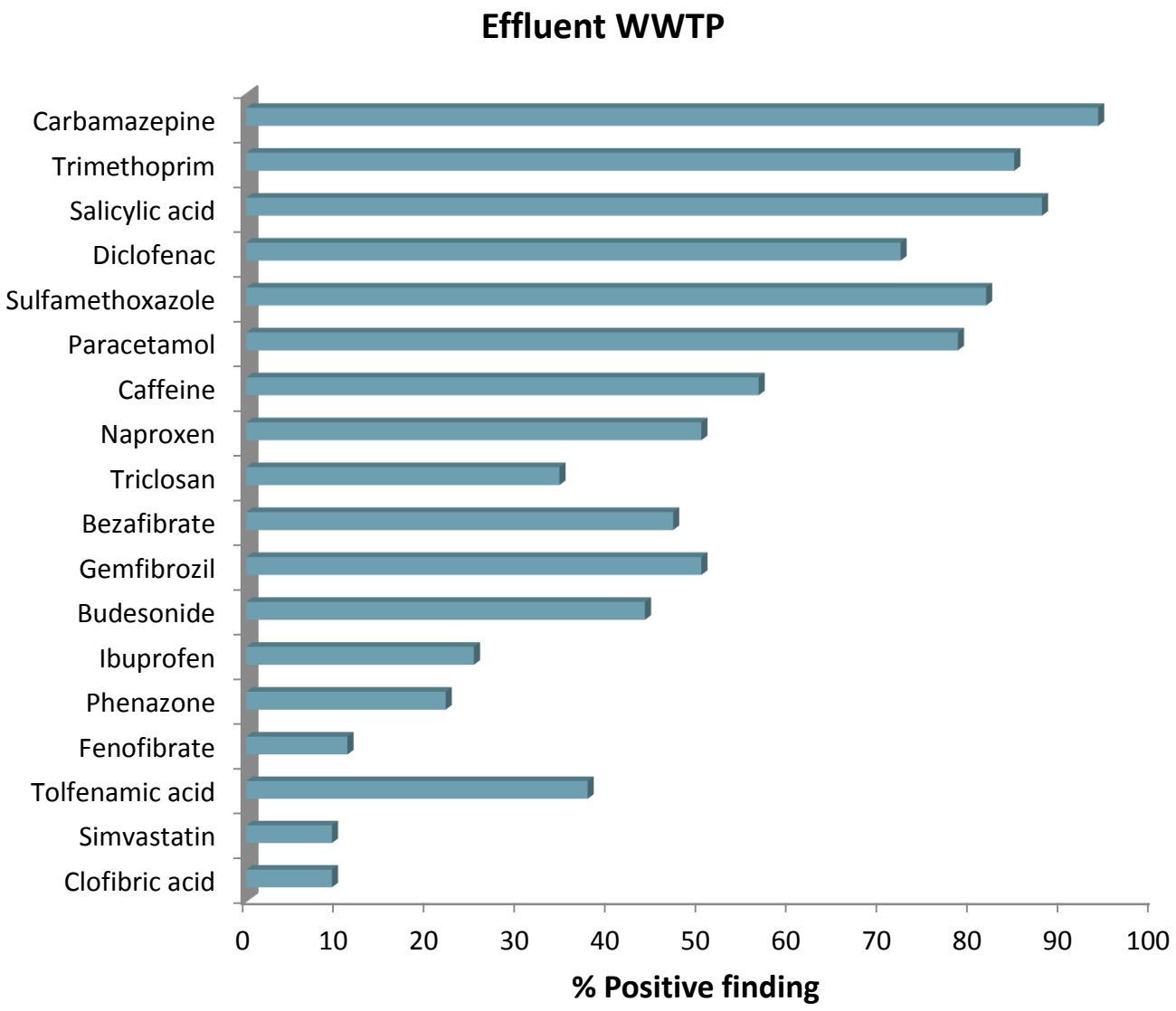
SA	42348,1	32064,6	1464,0	348,1	362,7	619,4	395,9	1261,6
IBU	2633,4	2048,5	177,0	279,9	56,5	494,6	κ.ο.α.	κ.ο.α
PARA	2872,5	2519,6	8313,2	293,0	139,9	3047,2	4184,9	30353,6
NPX	230,3	1469,8	544,4	1814,0	324,6	306,6	574,5	1583,7
DCF	100,8	180,7	106,9	1346,0	98.8	78,3	83,1	κ.ο.π.
TA	κ.ο.π.	κ.ο.π.	κ.ο.π.	κ.ο.π.	κ.ο.π.	κ.ο.α	κ.ο.π.	κ.ο.α.
PNZ	102,1	66,0	7,4	κ.ο.α.	5,1	5,7	6,4	7,7
GMF	347,1	515,2	κ.ο.π.	κ.ο.π.				
FNB	93,0	κ.ο.π.	κ.ο.π.	31,2				
BZF	429,8	315,4	60,8	210,4				
CA	κ.ο.π.	κ.ο.α.	κ.ο.α.	κ.ο.π.				
TMP	132,1	621,8	23,1	16,2				
SMX	904,2	1464,5	112,2	19,5				
CBZ	98,8	77,7	59,7	21,8				
CAF	26107,5	28214,1	58087,5	361,7	615,0	642,6	24556,5	14928,7
BUD	70,5	114,7	26,6	59,1	26,3	27,5	κ.ο.α.	κ.ο.α.
TCS	202,7	452,6	κ.ο.π.	κ.ο.π.	κ.ο.π.	113,2	κ.ο.π.	681,2
SIM	24,9	26,9	25,7	17,9	κ.ο.α.	26,2	39,6	κ.ο.α.

Concentrations <bql:

Tolfenamic acid

PARA: Veroia

Positive findings in the effluents of the eight WWTPs



Mean concentration values in the effluents of the eight WWTPs

SA	327,7	332,6	κ.ο.π.	κ.ο.π.	κ.ο.α	κ.ο.π.	κ.ο.π.	κ.ο.π.
IBU	κ.ο.π.	κ.ο.π.	κ.ο.α.	κ.ο.π.	κ.ο.π.	κ.ο.π.	κ.ο.α.	κ.ο.α.
PARA	96,1	κ.ο.π.	195,7	192,3	κ.ο.π.	166,0	209,7	368,7
NPX	κ.ο.α.	216,8	128,0	170,7				534,0
DCF	98,0	63,2	162,5	56,1				145,6
TA	κ.ο.π.	κ.ο.π.	κ.ο.π.	κ.ο.π.				κ.ο.α.
PNZ	κ.ο.π.	κ.ο.α.	κ.ο.π.	κ.ο.α.				κ.ο.α.
GMF	κ.ο.π.	168,4	κ.ο.α.	κ.ο.π.				κ.ο.π.
FNB	κ.ο.π.	κ.ο.α.	κ.ο.α.	κ.ο.α.				κ.ο.α.
BZF	128,0	111,8	κ.ο.π.	71,8				κ.ο.π.
CA	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	25,8
TMP	59,8	186,7	11,6	8,0	8,3	κ.ο.π.	κ.ο.π.	10,0
SMX	23,7	205,7	21,8	15,9	κ.ο.π.	11,0	21,8	30,6
CBZ	119,9	147,4	211,9	57,7	61,7	224,8	76,6	110,5
CAF	335,2	348,9	415,8	κ.ο.π.	κ.ο.π.	50,3	440,2	189,9
BUD	288,6	254,7	κ.ο.α.- κ.ο.π.	90,4	κ.ο.π.	κ.ο.π.	κ.ο.α.	κ.ο.α.
TCS	κ.ο.π.	133.6	κ.ο.π.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	139,2
SIM	κ.ο.π.	κ.ο.π.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.	κ.ο.α.

Concentrations <bql:

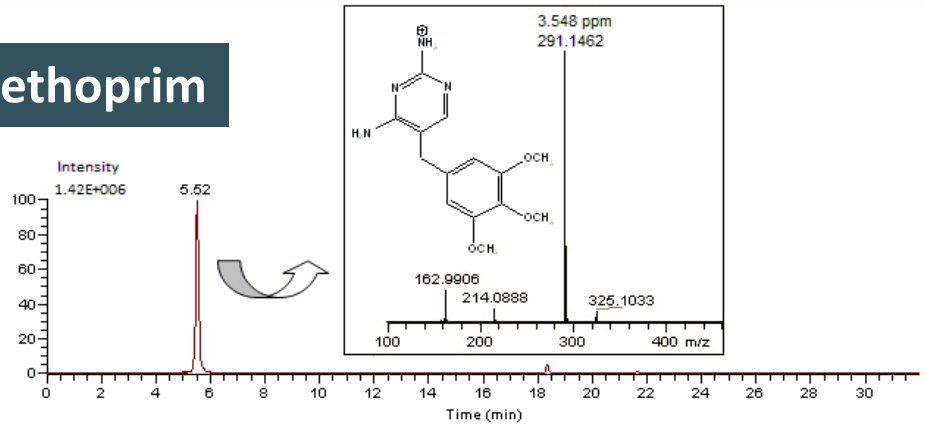
Tolfenamic acid

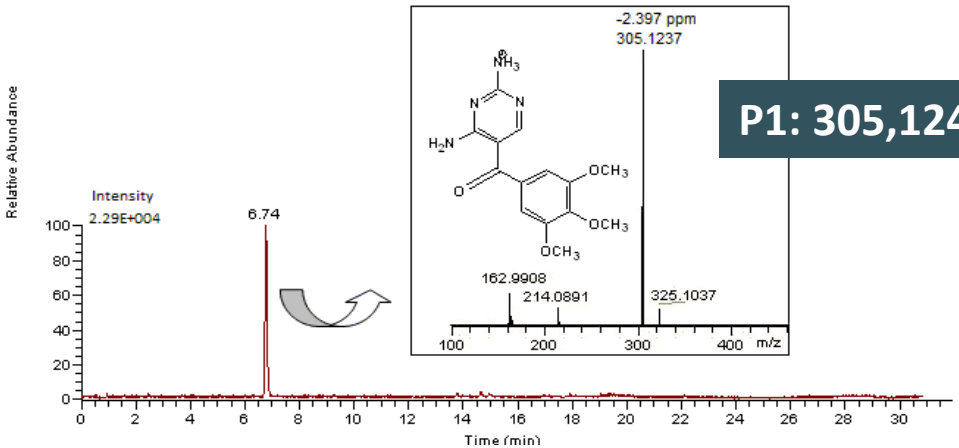
Fenofibrate

Simvastatin

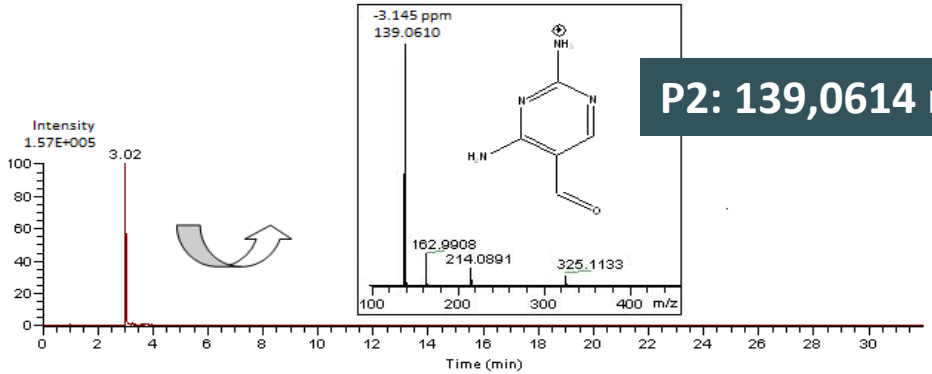
Transformation products (TPs) of trimethoprim in WWTPs

Trimethoprim





P1: 305,1244 m/z



P2: 139,0614 m/z

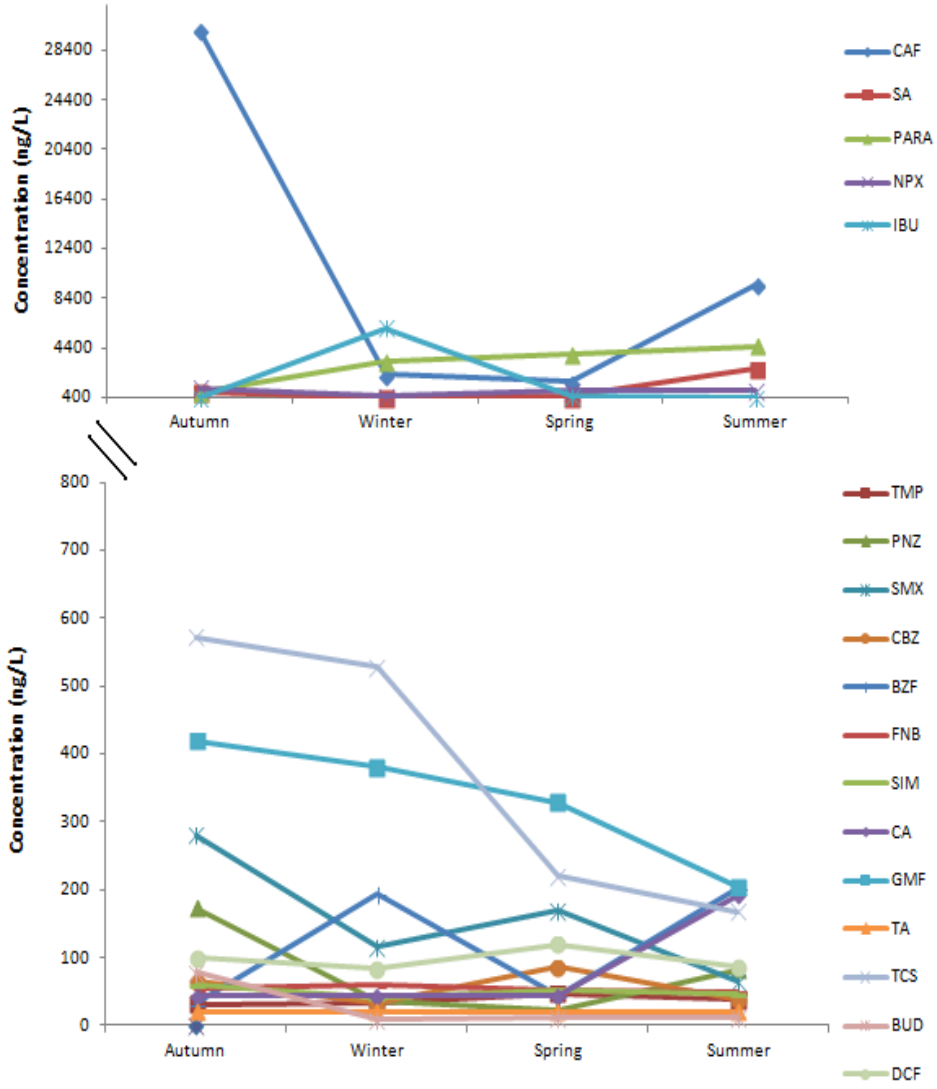
LTQ Orbitrap MS

Non target analysis

WWTP Effluent

(Ioannina – Veroia in Summer)

Seasonal variation of PPCPs in WWTPs



Median concentrations of PPCPs in the influents of the WWTPs

❑ **Caffeine:** Presented by far the highest loads in autumn (29969.6 ng/L) maybe due to the fact that in this season coffees and beverages are consumed even cold or hot. Also in the summer (9478.7 ng/L) the consumptions are much higher because the daylight conditions in Greece are elevated.

❑ **Ibuprofen και bezafibrate:** Higher concentrations in winter (6023,9 and 195,0 ng/L, respectively).

❑ **Triclosan:** Showed higher concentrations in autumn (571.9 ng/L) and winter (527.9 ng/L) than in spring (220.6 ng/L) and summer (167.8 ng/L), maybe due to its antimicrobial and antibacterial usage against contagious and infectious viruses.

Environmental Risk Assessment

- ✓ Risk Quotient method was applied:

$$RQ = \frac{exposure}{toxicity} = \frac{MEC}{PNEC}$$

- ✓ Both the ***acute*** and ***chronic*** toxicity were estimated, for three trophic levels (fish, invertebrates and algae)

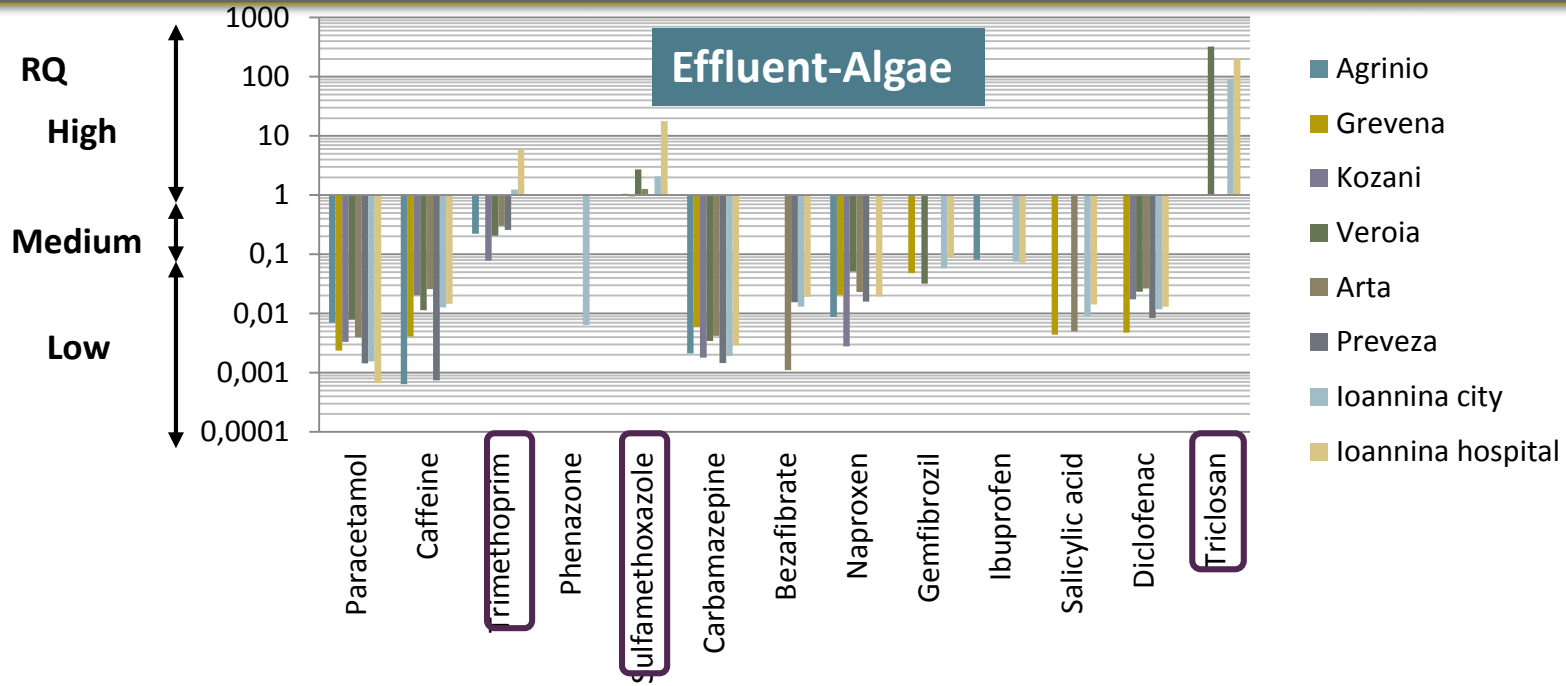
- ✓ Risk levels taking into consideration:

RQ≤0.01 → Low risk

0.01 ≤RQ ≤1 → Medium risk

RQ≥1 → High risk

Acute toxicity risk in the influents and the effluents of the eight WWTPs



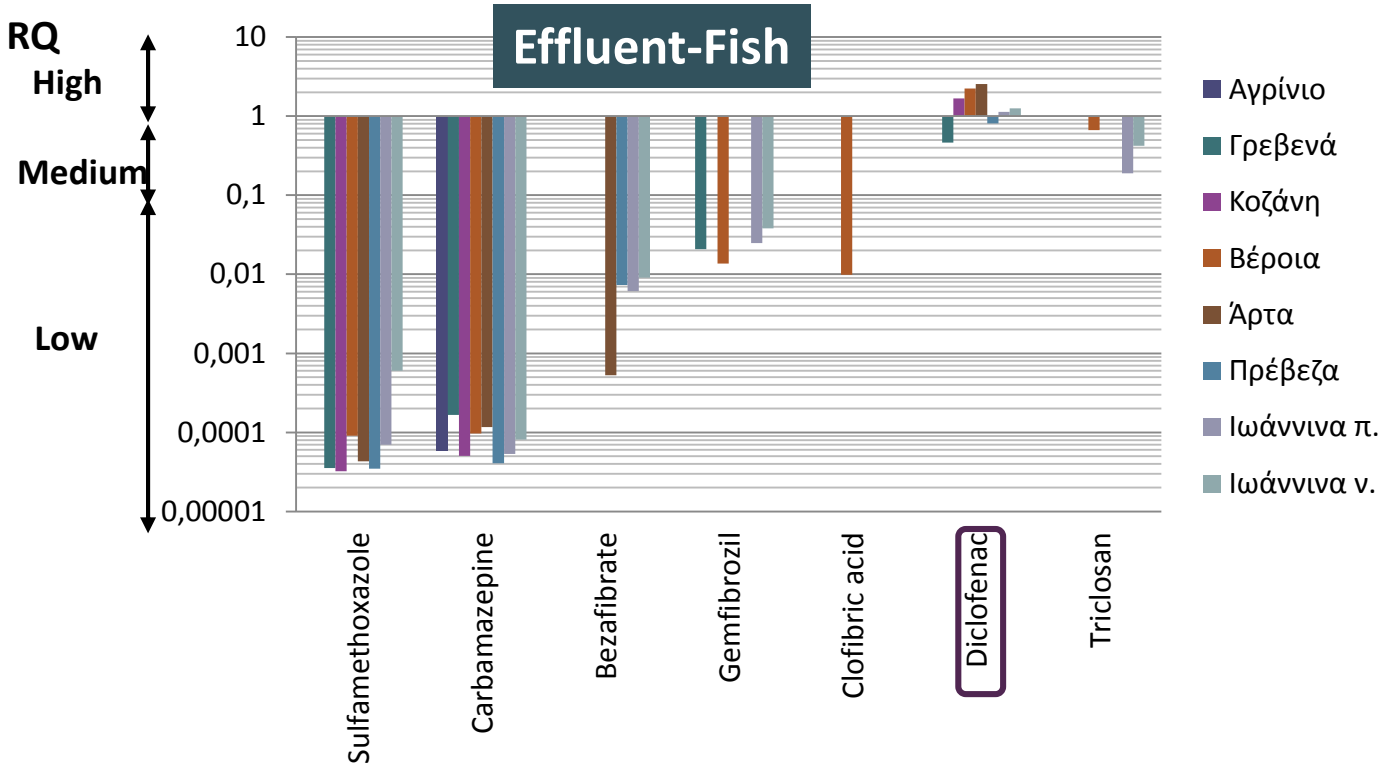
Influent

Fish	Invertabrates	Algae
Paracetamol	Paracetamol	Caffeine
Ibuprofen	Caffeine	Trimethoprim
Salicylic acid	Trimethoprim	Sulfamethoxazole
Triclosan	Salicylic acid	Fenofibrate
	Clofibric acid	Ibuprofen
	Triclosan	Salicylic acid
		Triclosan

Effluent

Fish	Invertabrates	Algae
Triclosan	Trimethoprim	Trimethoprim
	Triclosan	Sulfamethoxazole
		Triclosan

Chronic toxicity risk in the influents and the effluents of the eight WWTPs

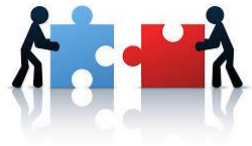


Influent	
Fish	**Algae**
Diclofenac	Sulfamethoxazole
Triclosan	Triclosan

Effluent	
Fish	**Algae**
Diclofenac	Triclosan

Conclusions

- Development and optimization of an SPE/LC-ESI-MS method for the determination of 18 PPCPs in wastewaters.
- The method proved to be sensitive, reliable and robust (low LOD, LOQ, RSDr, RSD_R values and satisfactory recoveries).
- Further confirmation of positive findings was accomplished by using UHPLC-LTQ-Orbitrap MS.
- The extensive screening campaign in the eight WWTPs confirmed the presence of almost all the target compounds in the influents and the effluents.



Conclusions

- Concentration levels ranged from 9.3 to 96648.3 ng/L in the influents and 6.6 to 1076.0 ng/L in the effluents.
- Most detected compounds were: carbamazepine, salicylic acid, paracetamol, trimethoprim και sulfamethoxazole.
- Hospital WWTP of Ioannina was a significant contributor of PPCPs in the wastewaters of the city.
- Low seasonal variation for most of the compounds, due to the fact that belong to those therapeutic categories that are used for therapeutic reasons throughout the year.

Conclusions

- Removal efficiencies varied from relatively high rates, to medium or low ones.
- Acute toxicity for 9 compounds in the influents and 3 in the effluents, respectively.
- Chronic toxicity for 3 compounds in the influents and 2 in the effluents, respectively.
- Triclosan: most critical compound in terms of acute and chronic toxicity.

Acknowledgments

A. *This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program:* ***Heracleitus II****. Investing in knowledge society through the European Social Fund.*

B. *The authors would like to thank the Unit of Environmental, Organic and Biochemical high resolution analysis-****ORBITRAP-LC–MS*** *of the University of Ioannina for providing access to the facilities.*

Thank you for your attention!