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A multiresidue method to evaluate emerging micropollutants levels in waters

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Context and objectives

One of the main issue of the Water Framework Directive (WFD, 2000/60/CE) is to reach good ecological and chemical status of waters bodies. The list of WFD priority substances has been amended in 2013 (2013/39/UE) and 2015 (2015/495/UE) by identifying new substances posing a significant risk to, or *via*, the aquatic environment. In fact, these new substances, so called “emerging contaminants”, including numerous pharmaceuticals and pesticides, are frequently detected in rivers and wastewaters in concentrations from ng/L up to several µg/L. Hence, it is now of crucial importance to monitor wastewater treatment plant (WWTP) effluents since they are known one of the main vector of micropollutants to surface water.

➤ Our challenge was to develop a reliable analytical method to quantify emerging contaminants at trace level in various types of waters.

Target compounds: typical indicators of urban domestic pollution

Indicator pesticides and pharmaceuticals were selected according to:

- their frequency of quantification in untreated wastewaters, secondary and tertiary wastewater effluents and in receiving rivers;
- their toxic effect in aquatic and terrestrial ecosystems;
- their large range of physico-chemical properties: octanol-water partition coefficient (log K_{ow}), acid dissociation constant (pK_a) and chemical classes.

➔ 49 selected substances

including 4 priority substances of the WFD and 5 watch-list substances of the WFD daughter directive (2015).

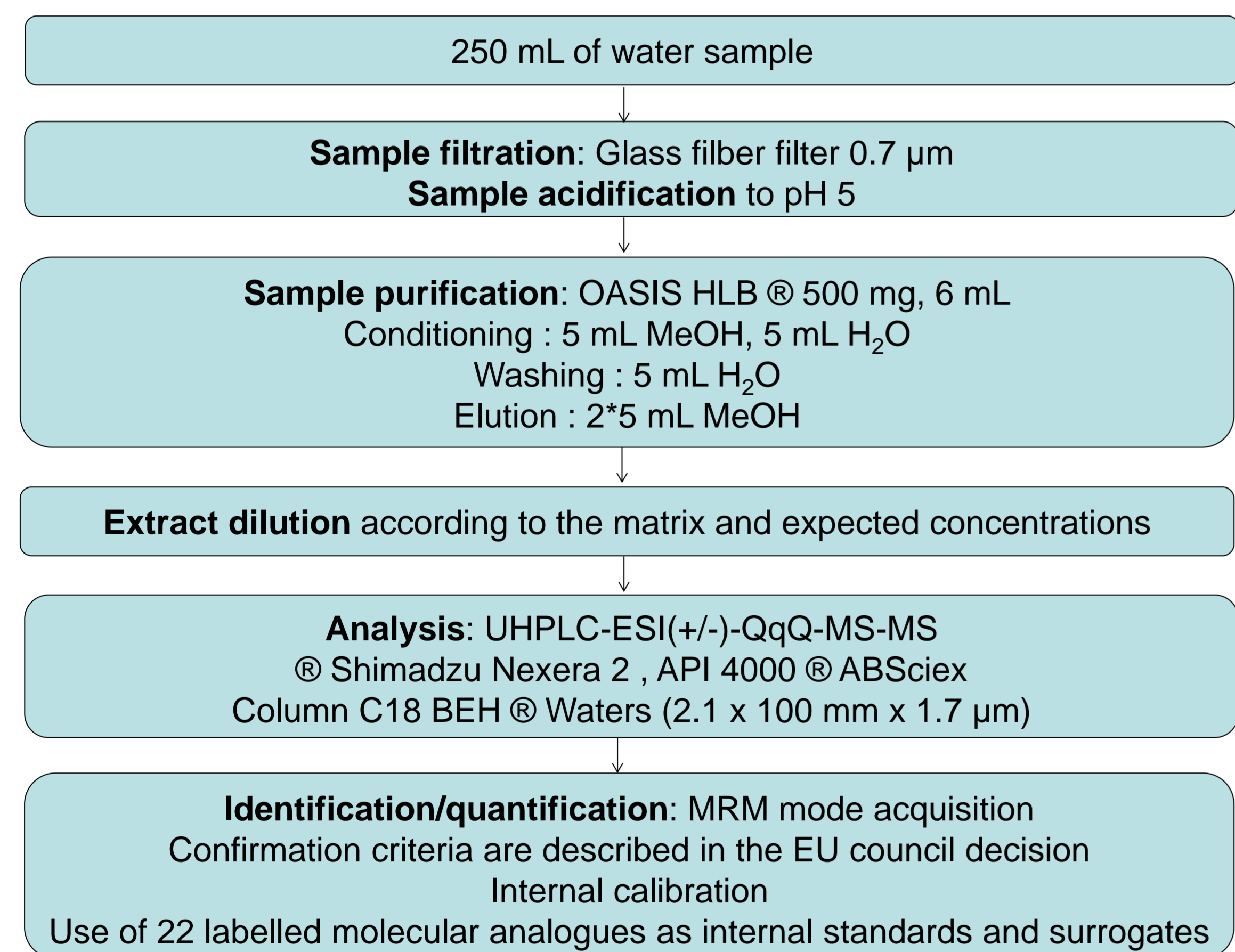
Use	Substances	Abbreviation	Log K _{ow}	pKa	LOQ (ng/L)
Pesticides	Atrazine	ATZ	2.61	1.6	0.1
	Dimethoate	DIM	0.77	-	0.1
	Diuron	DIU	2.68	13.6	0.2
	Imidaclopride	IMI	0.57	-	0.2
	Isoproturon	IPU	2.87	-	0.2
	Mecoprop*	MCPP	3.13	3.3	N.D.
	Pirimicarb	PIRI	1.70	-	0.4
Antibiotics	Simazine	SMZ	2.18	1.6	0.2
	Azithromycin	AZI	4.02	8.7	N.D.
	Ciprofloxacin	CIPRO	0.28	6.1	N.D.
	Clarithromycin	CLARI	3.16	9.0	0.2
	Clindamycin	CLINDA	2.16	-	0.2
	Erythromycin	ERY	3.06	8.9	0.2
	Metronidazole	METRO	-0.02	2.4	0.1
	Norfloxacin	NORFLO	0.46	6.3 / 8.7	10
	Ofloxacin	OFLO	-0.39	6.0 / 9.3	1
	Sulfamethoxazole	SMX	0.89	1.6 / 5.7	0.1
	Trimethoprim	TRIM	0.91	6.6	0.04
	Anti-depressants	Amiripryline	AMI	4.92	9.4
Fluoxetine		FLUOX	4.5	-	1
Betablockers	Acetubutolol	ACE	1.71	9.4	0.1
	Atenolol	ATE	0.16	9.6	0.4
	Metoprolol	MET	1.88	-	0.1
	Propranolol	PROP	3.48	9.4	0.1
	Sotalol	SOT	0.24	-	0.4

LOQ: limit of quantification; N.D.: not determined

Use	Substances	Abbreviation	Log K _{ow}	pKa	LOQ (ng/L)
Anti-inflammatory	Acetaminophen	PARA	0.46	9.4	1
	Diclofenac	DICLO	4.51	4.2	0.1
	Ketoprofen	KETO	3.12	4.5	0.2
	Naproxen*	NAPROX	3.18	4.2	0.1
	Theophylline	THEO	-0.02	8.8	0.4
HP	Bezafibrate*	BEZA	4.25	3.3	0.02
	Fenofibrate	FENO	5.19	-	1
	Fenofibril Acid	AC FENO	4.00	-	0.02
	Gemfibrozil*	GEMFI	4.77	4.8	0.02
	Cyclophosphamide	CYCLOP	0.63	-	0.4
AD	Metformine	METFOR	-0.50	12.4	N.D.
AE	Carbamazepine	CARBA	2.45	13.9	0.2
BD	Salbutamol	SALBU	0.64	10.3	0.2
Anxiolytics	Alprazolam	APZ	2.12	-	0.1
	Diazepam	DIAZ	2.82	3.4	0.2
	Nordiazepam	NDZ	2.93	-	0.1
	Oxazepam	OXA	2.24	1.5 / 10.9	0.2
Diuretic	Furosemide*	FURO	2.03	3.0	0.2
	3,4-Dichloroaniline	DCA	2.69	-	1
Metabolites	Acetylsulfamethoxazole	ACSMX	1.21	-	0.1
	Carbamazepine-EP	CARBA-EP	1.26	-	0.04
	Deisopropylatrazine	DIA	1.50	-	0.1
	Desethylatrazine	DEA	1.51	-	0.2
	Norfloxazine	NFLUOX	3.80	-	1

HP: Hypolipemiant; AC: Anticarcinogen; AD: Antidiabetic; AE: Antiepileptic; BD: Bronchodilator
*: negative ionization (ESI⁻)

Materials and methods: an efficient multiresidue method



Validation:

- Linearity checked from LOQ values to 200 ng/L.
- Recoveries evaluated on a surface water spiked at 60 µg/L under reproducibility conditions (n=7):
 - Only qualitative analysis for NORFLO, CIPRO, METFOR, AZI, FENO.
 - Work in progress for negative ionization compounds.

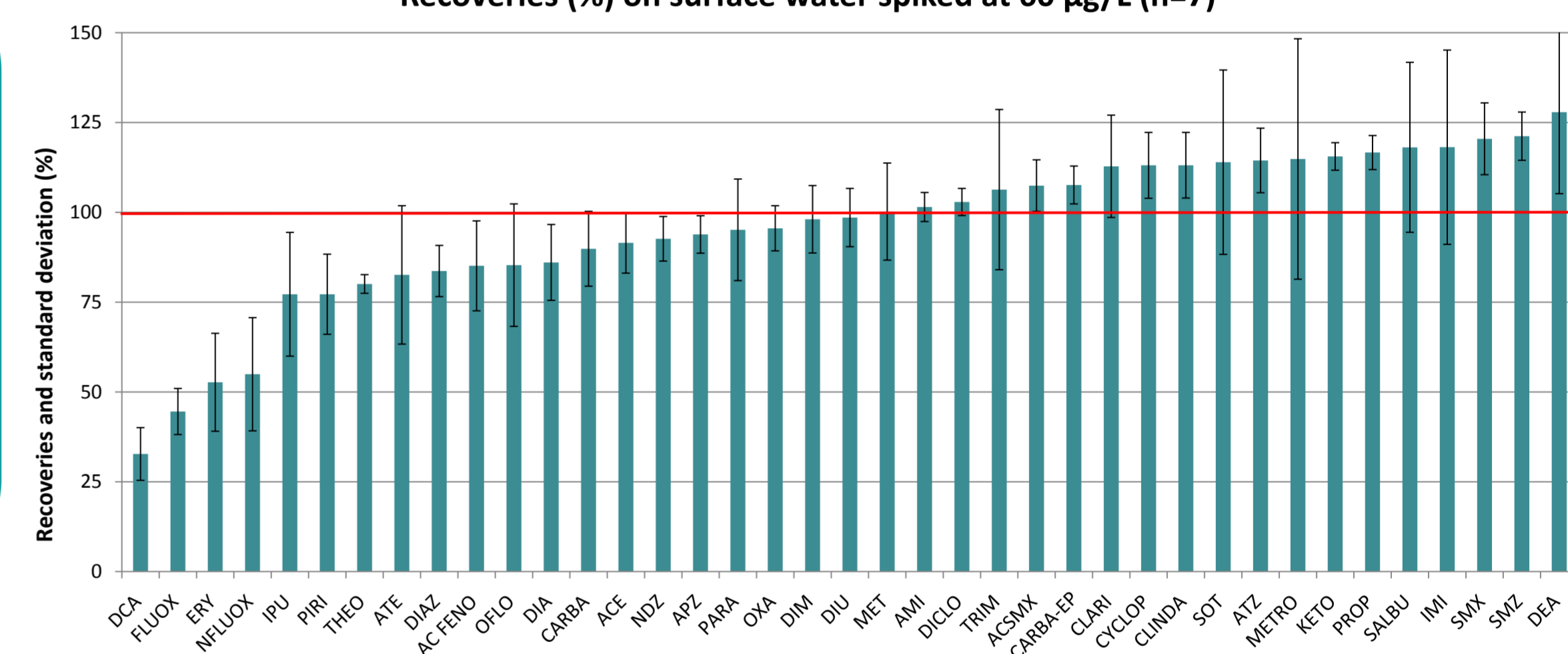


water sample



UHPLC-MS-MS system

Recoveries (%) on surface water spiked at 60 µg/L (n=7)

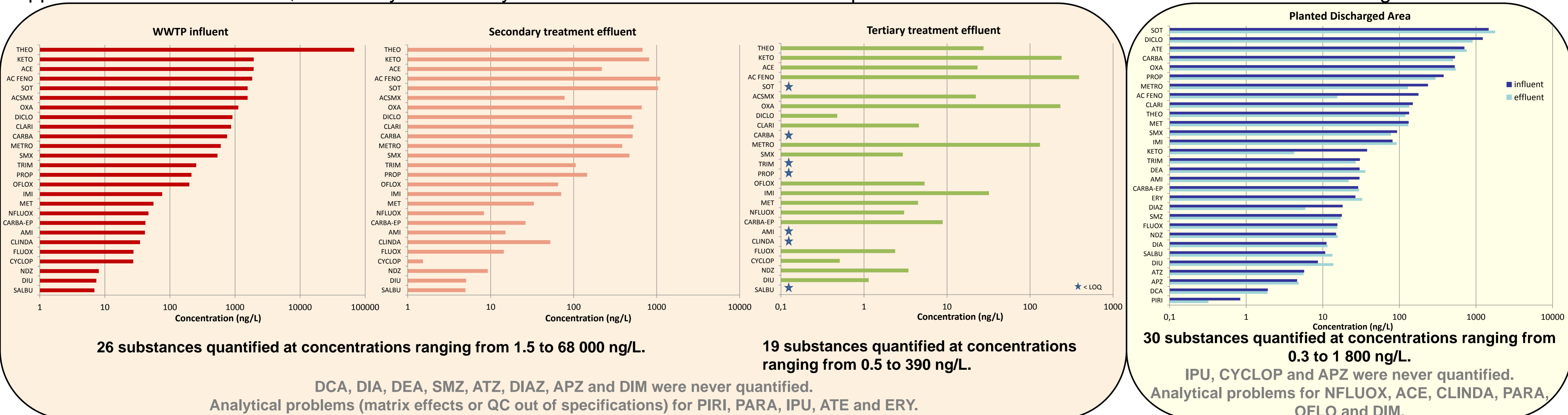


Quality controls (QC):

- Laboratory blanks (source water) to check non contamination.
- Spiked samples to check recoveries.
- QC standard solutions at 2 ng/L and 40 ng/L every 6 samples to check accuracy of the analysis and non deviation of instrumental measure. Acceptation criteria for QC standard solution: between 70 and 130 %.

Application to different types of wastewaters: concentration levels

Application to WWTP influent, secondary and tertiary treatment effluents of an ozonation process and to influent and effluent of a Planted Discharge Area.



Conclusions

- This study showed that our multiresidue analytical method is suitable for the quantification of 41 emerging micropollutants from ng/L to 100 µg/L in various water matrices.
- Further work is needed to better appreciate matrix effects on various aqueous matrices.
- This method will be adapted for biota matrices (*Gammarus fossarum*) and passive samplers extracts (Polar Organic Chemical Integrative Sampler).

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