

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 (pKa) and chemical classes.

➔ 49 selected substances

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

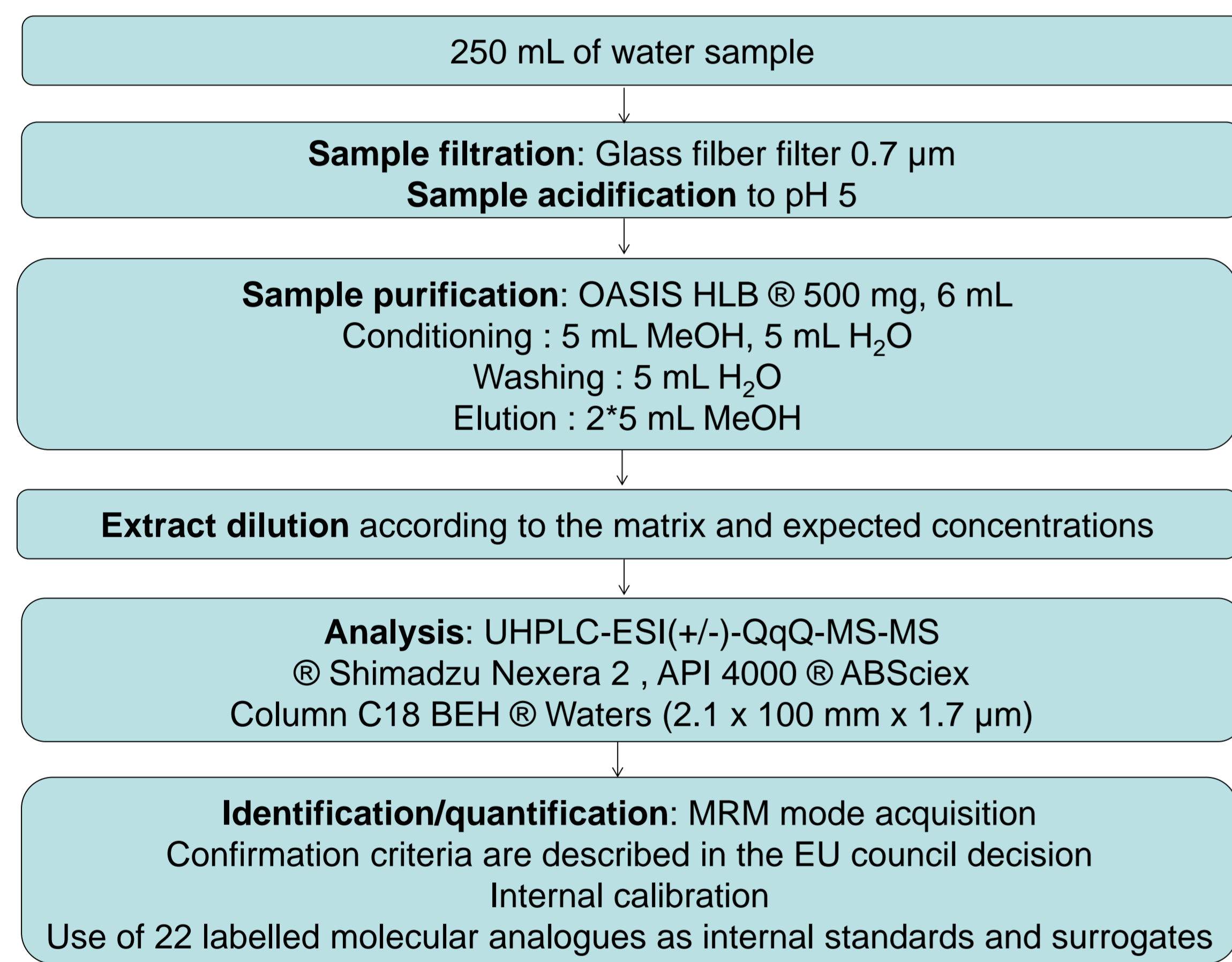
Use	Substances	Abbreviation	Log K _{ow}	pKa	LOQ (ng/L)
Pesticides	Atrazine	ATZ	2.61	1.6	0.1
	Dimethoate	DIM	0.77	-	0.1
	Diuron	DIU	2.68	13.6	0.2
	Imidaclopride	IMI	0.57	-	0.2
	Isoproturon	IPU	2.87	-	0.2
	Mecoprop*	MCPP	3.13	3.3	N.D.
	Pirimicarb	PIRI	1.70	-	0.4
Antibiotics	Simazine	SMZ	2.18	1.6	0.2
	Azithromycin	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
HP	Theophylline	THEO	-0.02	8.8	0.4
	Bezafibrate*	BEZA	4.25	3.3	0.02
	Fenofibrate	FENO	5.19	-	1
	Fenofibrilic Acide	AC FENO	4.00	-	0.02
AC	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.

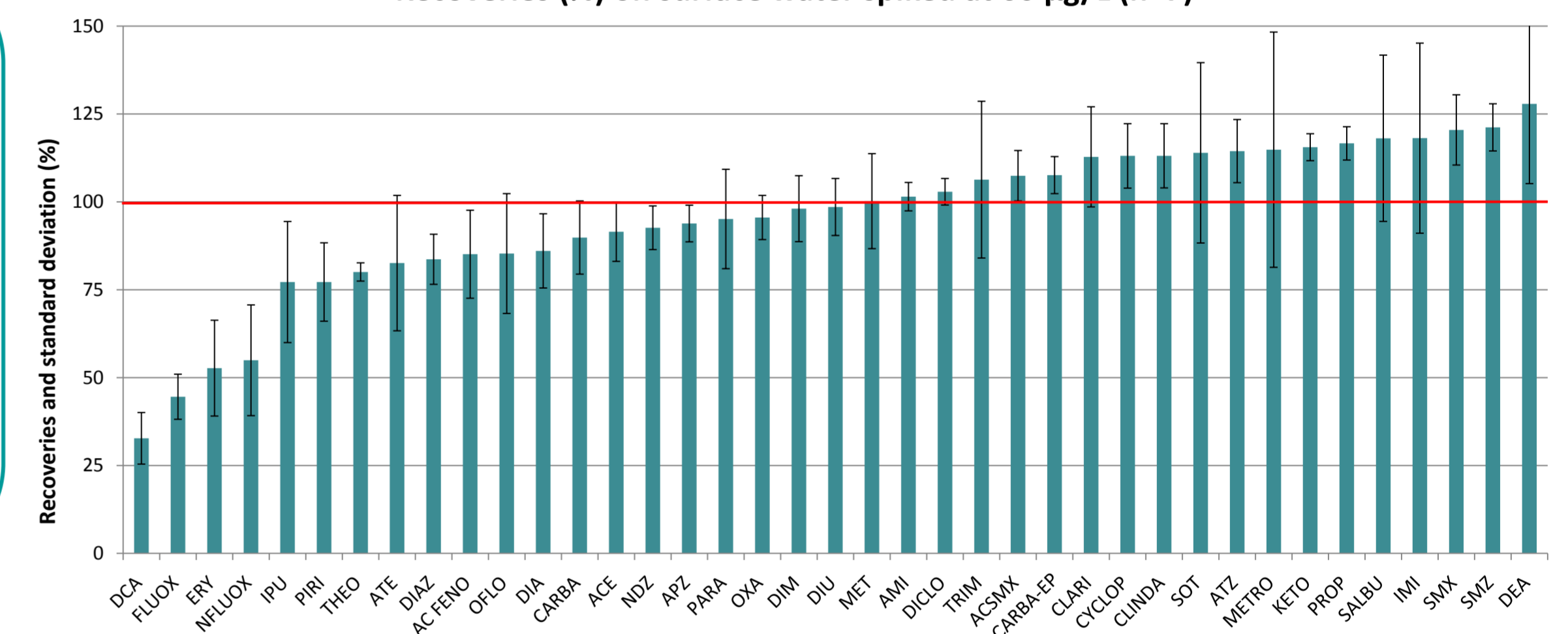


water sample



UHPLC-MS-MS system

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

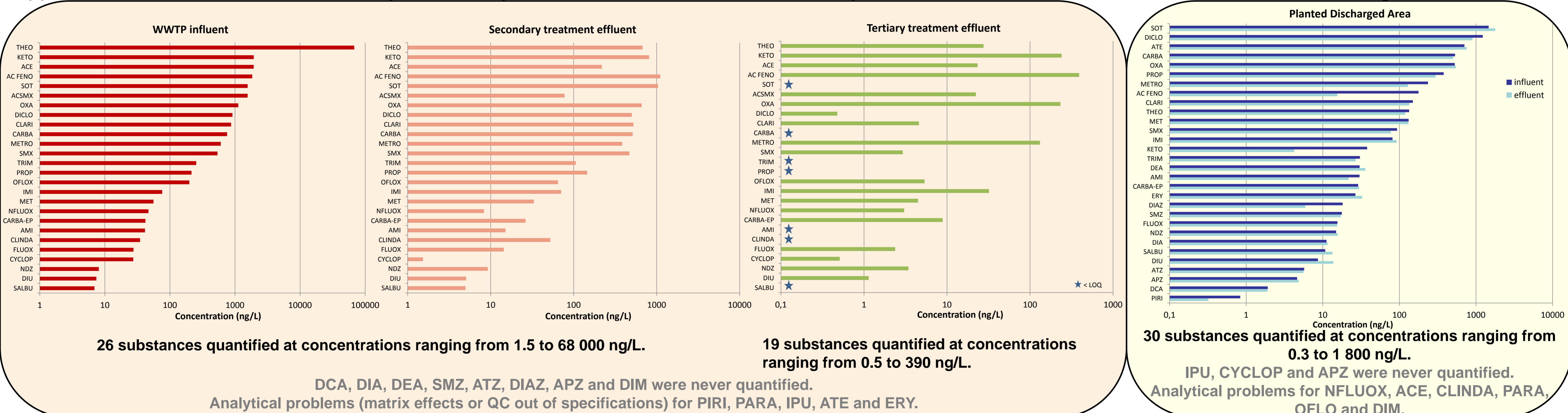


Quality controls (QC):

- 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.



26 substances quantified at concentrations ranging from 1.5 to 68 000 ng/L.

19 substances quantified at concentrations ranging from 0.5 to 390 ng/L.

30 substances quantified at concentrations ranging from 0.3 to 1 800 ng/L.

DCA, DIA, DEA, SMZ, ATZ, DIAZ, APZ and DIM were never quantified.
Analytical problems (matrix effects or QC out of specifications) for PIRI, PARA, IPU, ATE and ERY.

IPU, CYCLOP and APZ were never quantified.
Analytical problems for NFLUOX, ACE, CLINDA, PARA, OFLO and DIM.

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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