A year-long study of pharmaceutical and personal care products in Irish urban and rural water samples using SPE-LC-MS/MS

Helena Rapp-Wright[a,b], Fiona Regan[a], Blánaid White[a*], Leon Barron[b*]

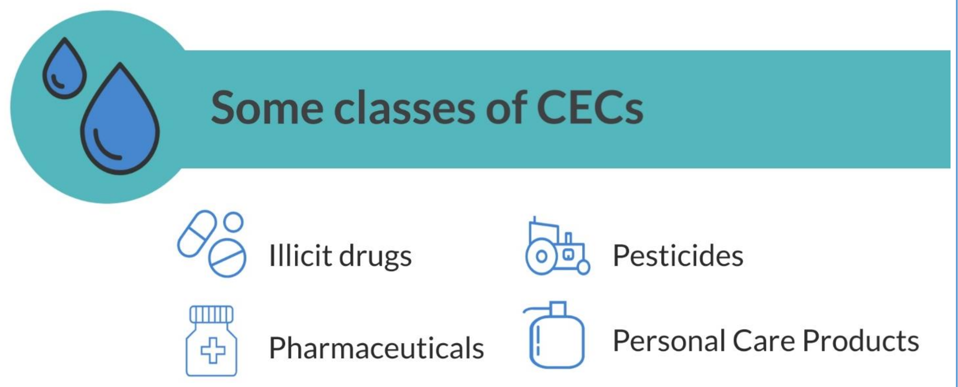
[a] DCU Water Institute and School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland

[b] Analytical & Environmental Sciences Division, King's College London, Franklin-Wilkins Building, 150 Stamford Street, London SE1 9NH, UK

* Email: blanaid.white@dcu.ie; leon.barron@kcl.ac.uk

1. Introduction

- Contaminants of emerging concern (CECs) refer to any chemical not currently being monitored, but which has the potential to enter the environment and cause harm to human, animal and plant life [1].
- Due to their widespread use in many products of everyday use, the increase in consumption continuously releases them into the environment.
- They have been shown to occur in surface waters at ng/L to µg/L concentrations and their risks in the environment require further knowledge.



AIM

The aim of this project is to prioritise CECs in Ireland, using liquid chromatography - mass spectrometry (LC-MS/MS).

2. Experimental

2.1 CECs selected

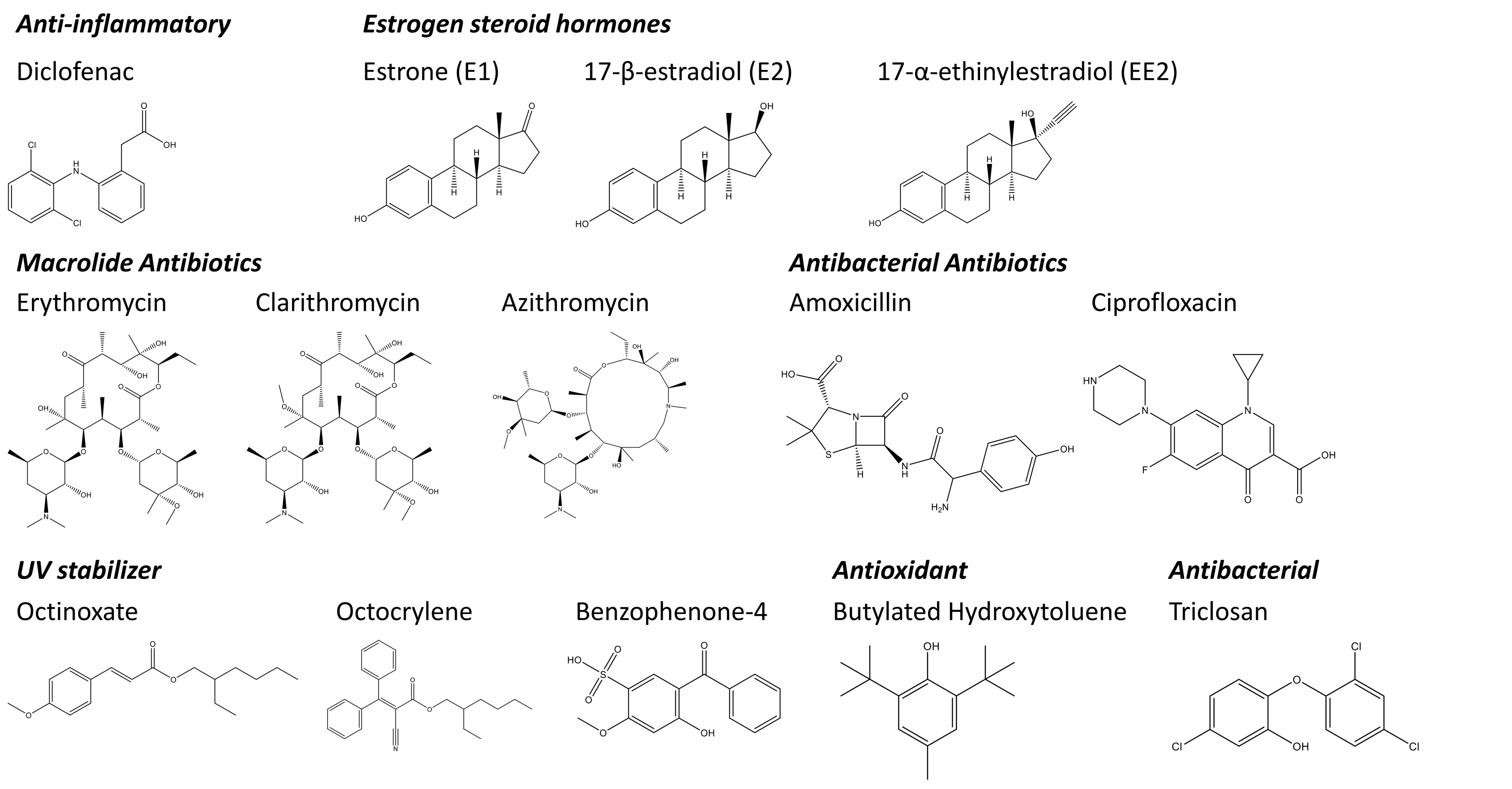


Figure 1. *Chemical structure of Pharmaceutical and Personal Care Products (PPCPs) selected for the study.*

2.2 Sample collection

Monthly surface water and influent and effluent wastewater grab samples were collected for a year from a rural and an urban area in Ireland.

2.3 Sample pre-treatment and solid phase extraction

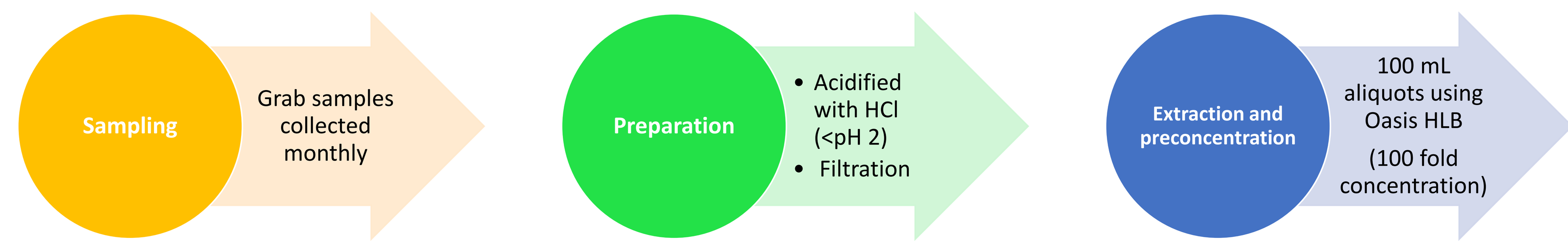


Figure 2. *Schematic of the analytic method developed using an Oasis HLB SPE sorbent weight of 200 mg.*

2.4 Sample analysis

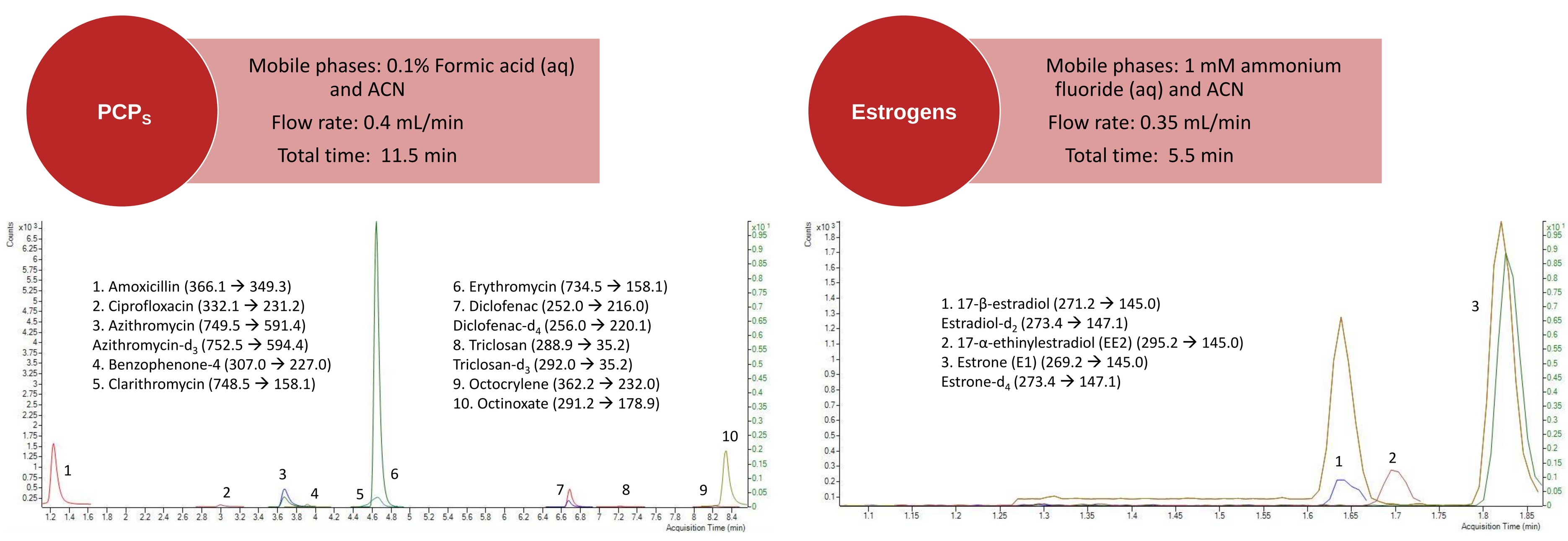


Figure 3. *Schematic of the LC-MS/MS analytic methods developed using an InfinityLab Poroshell 120 EC-C18 (2.1 x 150 mm, 1.9 µm) LC column and an UHPLC InfinityLab Poroshell 120 EC-C18 guard column (2.1 mm, 1.9 um) (Agilent Technologies, Cork, Ireland) at 30°C. Chromatograms include compounds separation and MRM quantification transitions. Standard of PPCPs at 250 ng/L and estrogens at 15 ng/L, both prepared in water: acetonitrile (10:90, v/v).*

3. Method performance

3.1 Effluent wastewater

Compound	Recovery (%)	SD (%)	ME	ME (%)	R^2	Range (ng/L)	LOD_{method} (ng/L)	LOQ_{method} (ng/L)
Diclofenac	114	26	2.69	269	0.9918	0.03 - 5	0.176	0.534
Azithromycin	89	18	0.41	41	0.9954	0.03 - 5	0.471	1.43
Erythromycin	93	43	0.07	6.93	0.9929	0.03 - 5	0.813	2.46
Triclosan	183	54	1.16	116	0.9870	0.035 - 1	0.223	0.675
Octocrylene	364	44	0.1	10	0.9834	0.035 - 1	0.252	0.763
Octinoxate	155	48	0.96	96	0.9872	0.03 - 1	0.225	0.680
Ciprofloxacin	115	12	1.57	157	0.9607	0.03 - 5	1.97	5.99
Amoxicillin	104	49	0.67	67	0.9702	0.035 - 5	1.70	5.16

3.2 Influent wastewater

Compound	Recovery (%)	SD (%)	ME	ME (%)	R^2	Range (ng/L)	LOD_{method} (ng/L)	LOQ_{method} (ng/L)
Diclofenac	87	13	2.38	238	0.9740	0.03 - 5	1.56	4.74
Azithromycin	111	12	1.23	123	0.9843	0.03 - 5	0.272	0.823
Erythromycin	92	9	1.43	143	0.9947	0.03 - 5	0.708	2.14
Benzophenone-4	97	15	4.27	427	0.9937	0.03 - 5	0.762	2.31
Octocrylene	43	28	0.001	0.106	0.9883	0.003 - 1	0.211	0.639
Octinoxate	20	65	0.001	0.145	0.9957	0.03 - 5	0.632	1.92
Ciprofloxacin	111	12	0.64	64	0.9442	0.03 - 5	0.523	1.58
Amoxicillin	79	17	0.12	12	0.9867	0.03 - 5	1.11	3.37

3.3 Surface waters

Compound	Recovery (%)	SD (%)	ME	ME (%)	R^2	Range (ng/L)	LOD_{method} (ng/L)	LOQ_{method} (ng/L)
Diclofenac	100	20	0.75	75	0.9979	0.03 - 5	0.378	1.15
Azithromycin	137	100	1.71	171	0.9981	0.03 - 5	0.185	0.561
Erythromycin	50	71	0.09	9	0.9792	0.1 - 5	1.43	4.32
Benzophenone-4	131	20	1.11	111	0.9953	0.1 - 5	0.656	1.99
Octocrylene	118	22	0.998	100	0.9957	0.1 - 5	0.641	1.94
Octinoxate	109	17	1.05	105			No linear	
Ciprofloxacin	134	29	12.0	1175	0.9934	0.03 - 5	0.795	2.41
Amoxicillin	84	9	12.0	1178	0.9837	0.03 - 5	1.07	3.23

Tables 1, 2 and 3. *Method performance tables including recovery ± standard deviation (SD) in %, matrix effect (ME), linearity (R^2), range of the calibration line and limits of detection and quantification of the method in ng/L (calculated from the calibration lines).*

4. Sample analysis

4.1 PPCPs found

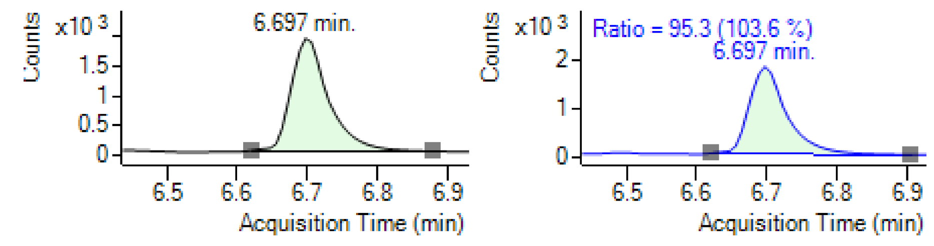


Figure 4. *Example of a chromatogram of diclofenac in an effluent wastewater sample collected in October 2018 in an urban area. On the left the quantification ion and on the right the qualifier ion, confirming its presence in the sample.*

5. Conclusions

- Method developed for 14 PPCPs selected.
- Method performance implemented in three different matrices (surface waters, influent and effluent wastewater).
- Sample analysis performed for a year worth of samples from two different areas.

References

1. Raghav, M. et al, Water Resources Research Center, College of Agriculture and Life Sciences, The University of Arizona; 2013; p 12.

6. Further work

- Finish method performance experiments for missing compounds.
- Perform quantification on sample analysis.

IMPACT – Innovative monitoring to prioritise contaminants of emerging concern for Ireland

This project is funded under the EPA Research Programme 2014-2020. The EPA Research Programme is a Government of Ireland initiative funded by the Department of Communications, Climate Action and Environment.

@IMPACT_DCU Water Institute epaResearch Climate - Water - Sustainability