

# Assessment of the Occurrence and Distribution of Per- and Polyfluoroalkyl Substances in the River Liffey, Ireland

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## INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a large family of widely used legacy and emerging contaminants that are pervasive in aquatic habitats globally. These molecules are chemically very stable and are highly resistant to biological degradation; therefore, they belong to a class of compounds that tend to persist in the environment and potentially may present a risk to the health of humans and wildlife. In Ireland, data on the occurrence of these chemicals in freshwater ecosystems is scarce.

PFAS enter the environment through wastewater disposal and air emissions at manufacturing plants, leaching at landfills or dumpsites, and the spraying of firefighting foams. In order to assess the threat PFAS pose for the environment and public health, this study had the objective of evaluating the occurrence, levels and distribution of fifteen PFAS, both legacy and emerging, in the Liffey river in the city of Dublin. The Liffey flows through agricultural land and into a large urban area, and the sampling points selected contained multiple sources (WWTPs, fire stations, airports, waste facilities, and industry hotspots). A total of 22 samples along a 24 km stretch, from a more rural area to a highly pressure urban area, ending up by Dublin Bay, next to the effluent discharge of the Ringsend WWTP.

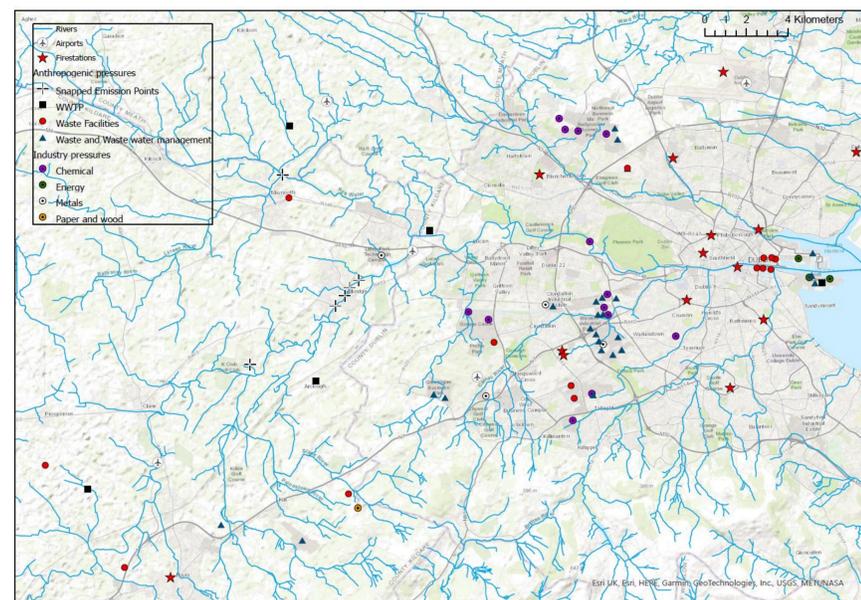


Figure 1. Map of potential pressures - sources of PFAS- on the River Liffey, Dublin (Ireland)

## MATERIALS & METHODS

Occurrence of 15 PFAS was evaluated. Water samples (250 mL) were collected in amber polypropylene bottles. Samples were pH-adjusted (pH=3) and extracted in SPE cartridges Oasis WAX (500 mg). Analytes were eluted with 5 mL of 0.5% ammonia/methanol, and finally reconstituted in 1 mL methanol/ammonium acetate 2mM (10:90), and 5 µL of a 1 mg/L standard mixture containing labelled compounds were added to the extracts as internal standards.

PFAS	Recoveries (% (RSD%))	MLD (ng/L)
PFPeA	101 (10)	1.68
PFBS	99 (12)	0.58
PFHxA	59 (3)	2.13
PFPeS	102 (4)	0.90
GenX	105 (2)	1.74
PFHxS	67 (3)	0.55
PFOA	55 (7)	1.53
PFOS	55 (12)	1.10
PFNA	63 (14)	0.98
PFNS	61 (12)	0.80
PFDA	59 (10)	0.58
PFDS	41 (3)	2.91
FOSA	41 (6)	15.15
PFUdA	51 (6)	1.09
PFDaA	39 (7)	4.93

Table 1. Mean percent recoveries (n=3) of 15 PFAS and method limit of detection (MLD, ng/L)

Extracts were analysed by HPLC (Agilent 1260 series Infinity binary pump) coupled to a triple quadrupole mass spectrometer (Agilent 6470), equipped with an electrospray ionization source in negative mode. Ten microliters were injected in an Agilent Zorbax Eclipse Plus C18 column (3.0 x 50 mm; 1.8 µm), set with a guard column of the same materials. Mobile phases were (A): 2 mM formic acid/ammonium formate (pH 3.2) and (B): methanol at a flow rate of 0.4 mL/min. Details on MDLs, recoveries, etc. can be found elsewhere<sup>1</sup>.

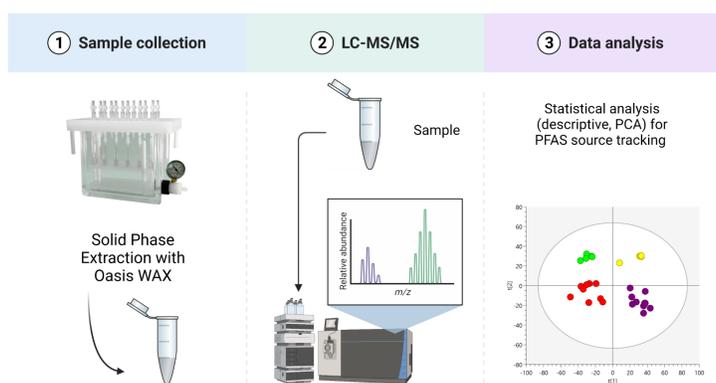


Figure 2. Analytical Methodology

## CONCLUSIONS

- Eight PFAS were consistently detected in the ng/L to µg/L range. PFUdA, PFOA and PFBS were the compounds with the highest concentrations.
- Future steps involve the study of how potential sources close to the sampling sites impact the composition profile of PFAS in the River Liffey.

## RESULTS & DISCUSSION

Out of 15 PFAS, 8 were detected at least once. FOSA, PFDaA, PFDS, PFHxS, PFNS and PFPeS were not detected. Concentrations ranged between low ng/L to µg/L for some compounds. Highest concentrations were detected for the compound PFUdA (up to 1.8 µg/L). PFOA was detected almost in every sample, with a maximum of 1.2 µg/L in L12 (urban area). PFBS was detected consistently in almost all samples, with a maximum concentration of 0.8 µg/L. No concentrations were detected in two sampling sites, most probably due to an extraction problem.

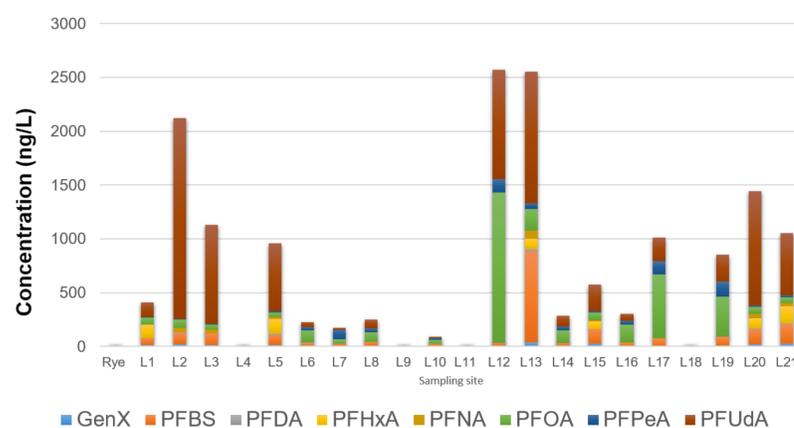
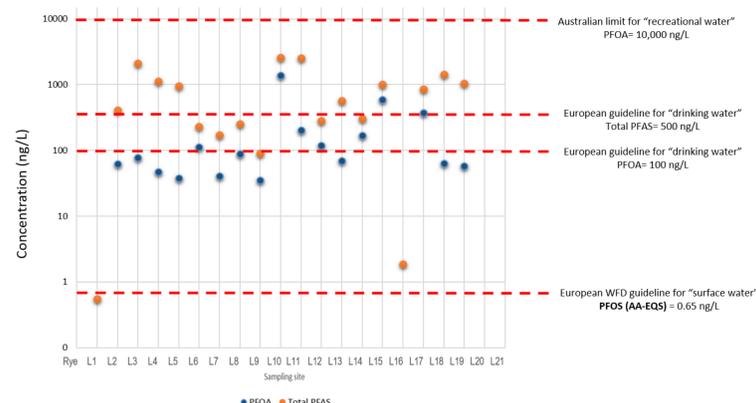


Figure 3. PFAS concentrations (ng/L) in the River Liffey. Sampling sites are labelled as L1 to L21, from upstream (L1) to Dublin Bay (L21). Rye is a small tributary of the Liffey

Figure 4. Comparison of mean concentrations (ng/L) of PFOA and total PFAS concentration against several European and Australian guidelines for PFAS occurrence in drinking and inland waters



## REFERENCES

- <sup>1</sup> Huerta et al., 2022. "Development and application of an LC-MS method to the determination of poly- and perfluoroalkyl substances (PFASs) in drinking, sea and surface water samples". Analytical Methods, 2022. Accepted.

## ACKNOWLEDGEMENTS

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