Flushed Through the System: A Sub-Kilometre Investigation of PFAS Pathways from Urban Rivers to Coastal Waters

Helen Burke [1]*, Leila Bowe [1], Yulong Ma [2], M. Isabel Cadena-Aizaga [1], Stuart Harrad [2], Fiona Regan [1]*
[1] DCU Water Institute and School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland
[2] School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK
*Email: helen.burke24@mail.dcu.ie; fiona.regan.dcu.ie

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of man-made chemicals characterised by highly stable carbon-fluorine bonds, which render these compounds resistant to degradation and imparts both hydrophobic and oleophobic properties. These characteristics have led to their widespread use across industrial and commercial applications. Extensive use paired with the environmental persistency of these chemicals has resulted in PFAS becoming ubiquitous in the natural environment.

PFAS enter aquatic environments through multiple pathways, including wastewater effluent, landfill leachate and urban runoff [1, 2 ,3]. Stormwater drainage systems can act as transport pathways for contaminants residing on impervious surfaces, as well as non-stormwater inputs (e.g. industrial discharges, misconnections), into receiving waters [4, 5].

This study investigated the influence of stormwater outfalls on the occurrence of 33 PFAS in the Liffey Estuary (Dublin, Ireland). Sub-kilometre scale sampling was conducted at individual outfalls along the estuary to assess spatial variability in PFAS loadings.

Figure 1 : Map of sample sites and stormwater outfalls along the Liffey Estuary in Dublin, Ireland.

Sample Collection and Analysis Methods

Sixteen water samples were collected along the Liffey Estuary using 1 L polypropylene bottles. Upon return to the laboratory, samples were acidified using glacial acetic acid to a pH of 6.5 +/- 0.5 and stored frozen until extraction and analysis. Samples were extracted in triplicate by Solid Phase Extraction (SPE) and analysed for 33 PFAS using high-performance liquid chromatography coupled with time-of-flight mass spectrometry (HPLC-TOF-MS), as described in Figure 2.

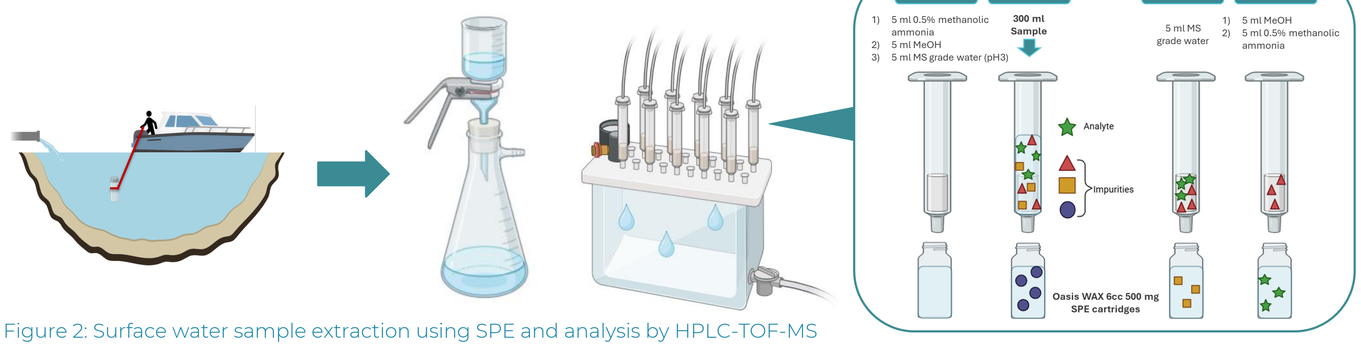
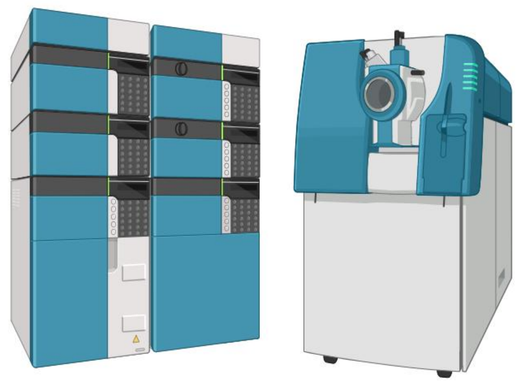


Figure 2: Surface water sample extraction using SPE and analysis by HPLC-TOF-MS

Time (min)	%(A/B)
0 - 6	80/20
6.0 - 6.5	5/95
6.5 - 6.51	5/95
6.51 - 8.0	80/20

Restek Raptor C18 column (2.1 mm x 50 mm, 1.2 µm)

(A) 5 mM ammonium formate in water
(B) 5 mM ammonium formate in methanol
Flow rate of 0.4 mL/min



HPLC (Sciex Exion) coupled with TOF-MS (Sciex 5600+ triple TOF-MS)

Results and Discussion

PFAS Occurrence

Twenty-four PFAS were detected across the estuary. Total PFAS concentrations ranged from 6.20 to 91.48 ng/L, with highest total concentrations observed downstream of waste treatment facilities.

6:2 FTS was the most frequently detected analyte, found at all sample sites at concentrations ranging from 4.25 to 90.38 ng/L. As a precursor to perfluoroalkyl acids (PFAAs), 6:2 FTS can undergo environmental transformation into persistent and toxic degradation products [6]. The dominance of this compound suggests widespread urban use. Elevated concentrations downstream of waste facilities indicate that these sites may act as point sources of 6:2 FTS.

Other detected PFAS occurred at lower concentration ranges (figure 4). The restricted compound PFOS was detected at 3 of 16 sites and exceeded the EU environmental quality standard (EQS) surface water limits (0.13 ng/L) [7]. Its short-chain replacement compound, PFBS, was detected at comparable concentrations.

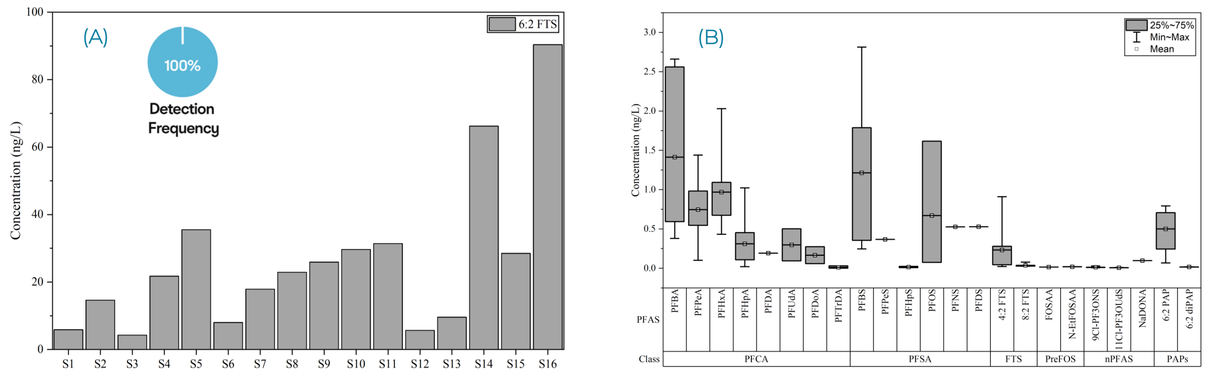


Figure 3: (A) Concentration (ng/L) of 6:2 FTS along the Liffey Estuary. (B) Boxplot displaying the concentration range and mean value of detected PFAS (excluding 6:2 FTS)

Spatial Variability

Clear spatial variation in PFAS class profiles was evident across the estuary, with between 2 and 14 compounds detected per site. PFAS composition and concentrations varied between outfalls located within a few hundred metres of each other, indicating strong localised influences. This variability demonstrates the complexity of the urban drainage system, which can receive inputs from surface runoff and diverse non-stormwater sources.

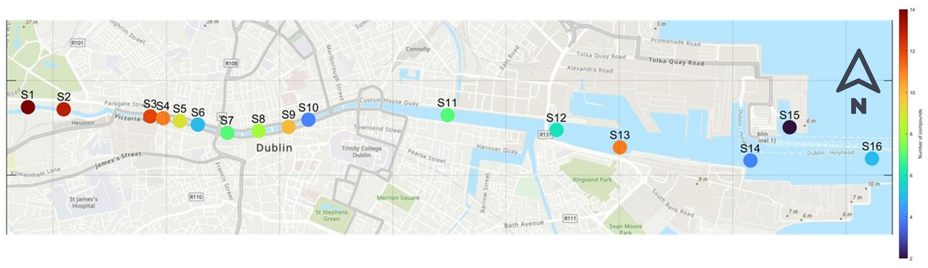
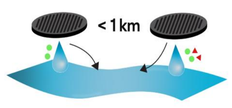


Figure 4: Heatmap displaying the variation in the number of PFAS detected at each sample site targeting individual stormwater outfalls.



Source Attribution

Multivariate analysis identified stormwater outfalls as diffuse sources of PFAS to the Liffey Estuary, along with unique PFAS profiles being attributed to localised inputs such as waste facilities, tributary confluences and marina activities.

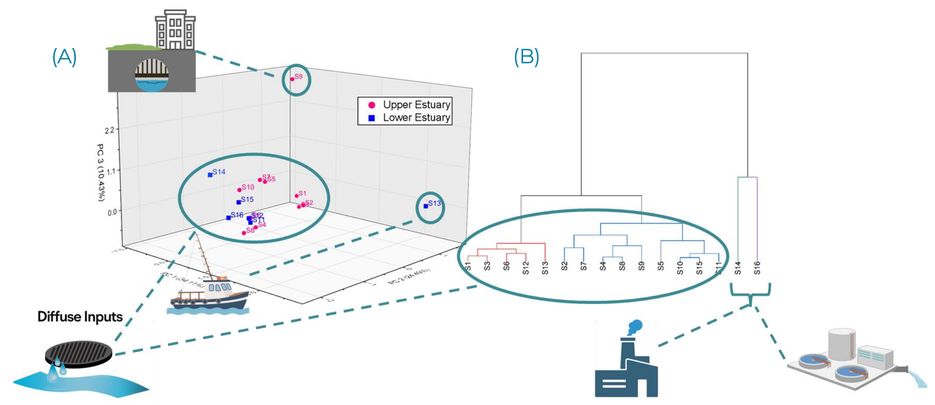


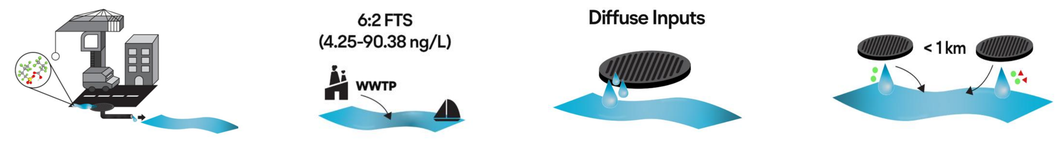
Figure 5: Multivariate analysis of PFAS in the Liffey Estuary. (A) Score plot of sample sites from principal components analysis (PCA). (B) Hierarchical clustering dendrogram revealing relationships between analytes detected at each site

Conclusions

High-resolution spatial monitoring is essential for improved PFAS source attribution and understanding transport pathways of contaminants in urban surface waters.

Stormwater outfalls were identified as diffuse sources of PFAS, with spatial variability observed between sites.

The development and implementation of treatment or filtration systems within stormwater drainage networks may help mitigate PFAS inputs to receiving waters.



References

[1] E. Tavasoli, J. L. Luek, J. P. Malley and P. J. Mouser, Environmental Science: Processes & Impacts, 2021, 23, 903–913.
[2]T. Stoiber, S. Evans and O. V. Naidenko, Chemosphere, 2020, 260, 127659.
[3] Y. Zushi, T. Takeda and S. Masunaga, Chemosphere, 2008, 71, 1566–1573.
[4] S. E. Kali, H. Österlund, M. Viklander and G.-T. Blecken, Water Research, 2025, 271, 122973.
[5] D. Li, L. C. Van De Werfhorst, J. Ervin, A. Poresky, B. Steets, C. Rivers, G. Sharp, J. Smith and P. A. Holden, Environmental Pollution, 2023, 337, 122521.
[6] S. Zhang, X. Lu, N. Wang and R. C. Buck, Chemosphere, 2016, 154, 224–230.
[7] European Union, European Union Environmental Objectives (Surface Waters) (Amendment) Regulations 2019, S.I. No. 77 of 2019, 2019.

Acknowledgements

EPA Research Project Code: 2022-HE-1148