

A study of the SOURCE-TO-SEA occurrence of poly- and perfluoroalkyl substances (PFASs) of emerging concern in Ireland

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Introduction

Poly- and perfluoroalkyl substances (PFASs) are a group of synthetic organic surfactants that have become a global concern because of their toxicity and widespread presence in the aquatic environment and organisms globally. Over the past decades, global manufacturers have started to substitute long-chain PFAS with shorter-chain PFAS or with non-fluorinated substances. This trend has been driven due to the effects of long-chain PFAS on human health and the environment.

However, short-chain PFAS are now thought to have similar or other properties of concern such as fluorinated compounds like Gen X and ADONA (dodecafluoro-3H-4,8-dioxanonanoate). The combined effects of PFAS are not widely studied and relatively unknown. There is also little biological assessment currently done for drinking water and especially marine water.

This project investigates the presence of certain target PFAS in waters in Dublin (Fresh and seawater) with the aim of identifying or grouping sources of these chemical contaminants.

Table 1. PFAS substances and acronyms investigated in this study.

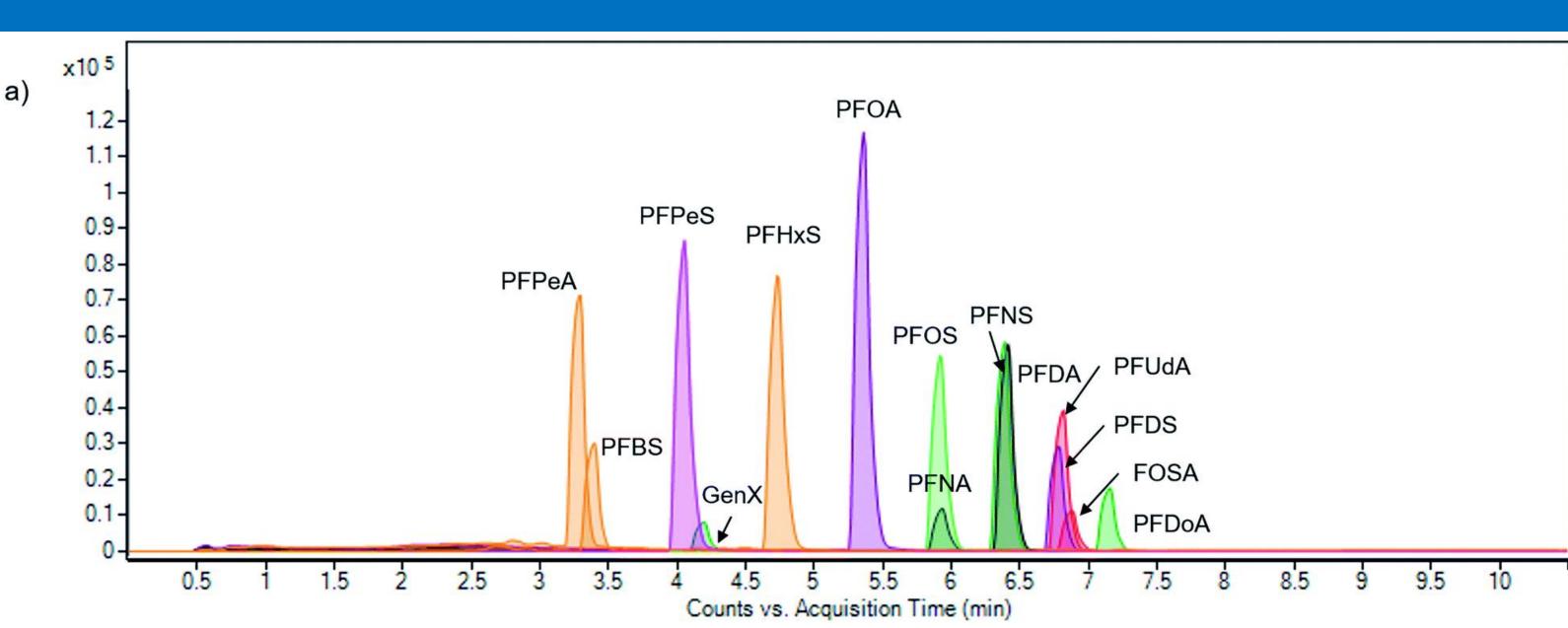
PFAS acronym	PFAS name
PFPeA	perfluoropentanoic
PFHxA	perfluorohexanoic
PFOA	perfluorooctanoic
PFNA	perfluorononanoic
PFDA	perfluorodecanoic
PFUdA	perfluoroundecanoic
PFDoA	perfluorododecanoic
GenX	perfluoropropoxypropanoic
PFBS	perfluorobutanesulfonate
PFOS	perfluorooctanesulfonate
PFDS	perfluorodecanesulfonate
PFPeS	perfluoropentylsulfonate
PFHxS	perfluorohexasulfonate
FOSA	perfluorooctanesulfonamide
PFNS	perfluorononylsulfonate

<u>Sample processing:</u> Sample processing, including collection and solid phase extraction was carried out as previously described [1].

Instrumental analysis:

All 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 μ m), 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. The gradient elution was: 0–1.5 min, 90–45% A; 1.5–7.0 min, 45–10% A; 7.0–8.5 min, 10–0% A; 8.5–10 min, 0% A; 10–11 min return to initial conditions; 11–12 min, equilibration of the column. A separation chromatogram of standard mixtures and example calibration curve is shown in Fig. 1.

Methods & Methods



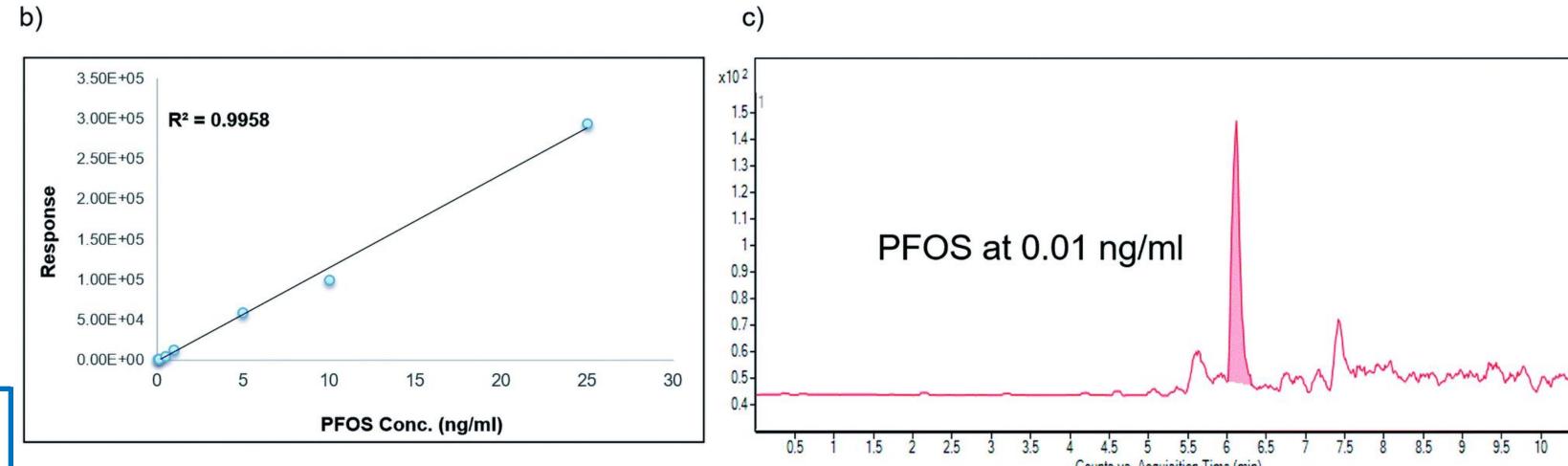


Fig 2. (a) Compound peaks obtained by injecting a standard mixture at 100 ng mL⁻¹; (b) PFOS calibration curve (levels 0.01 to 25 ng mL⁻¹), with an $R^2 > 0.99$; (c) PFOS chromatogram extracted at a concentration of 0.01 ng mL⁻¹.

Results & Discussion

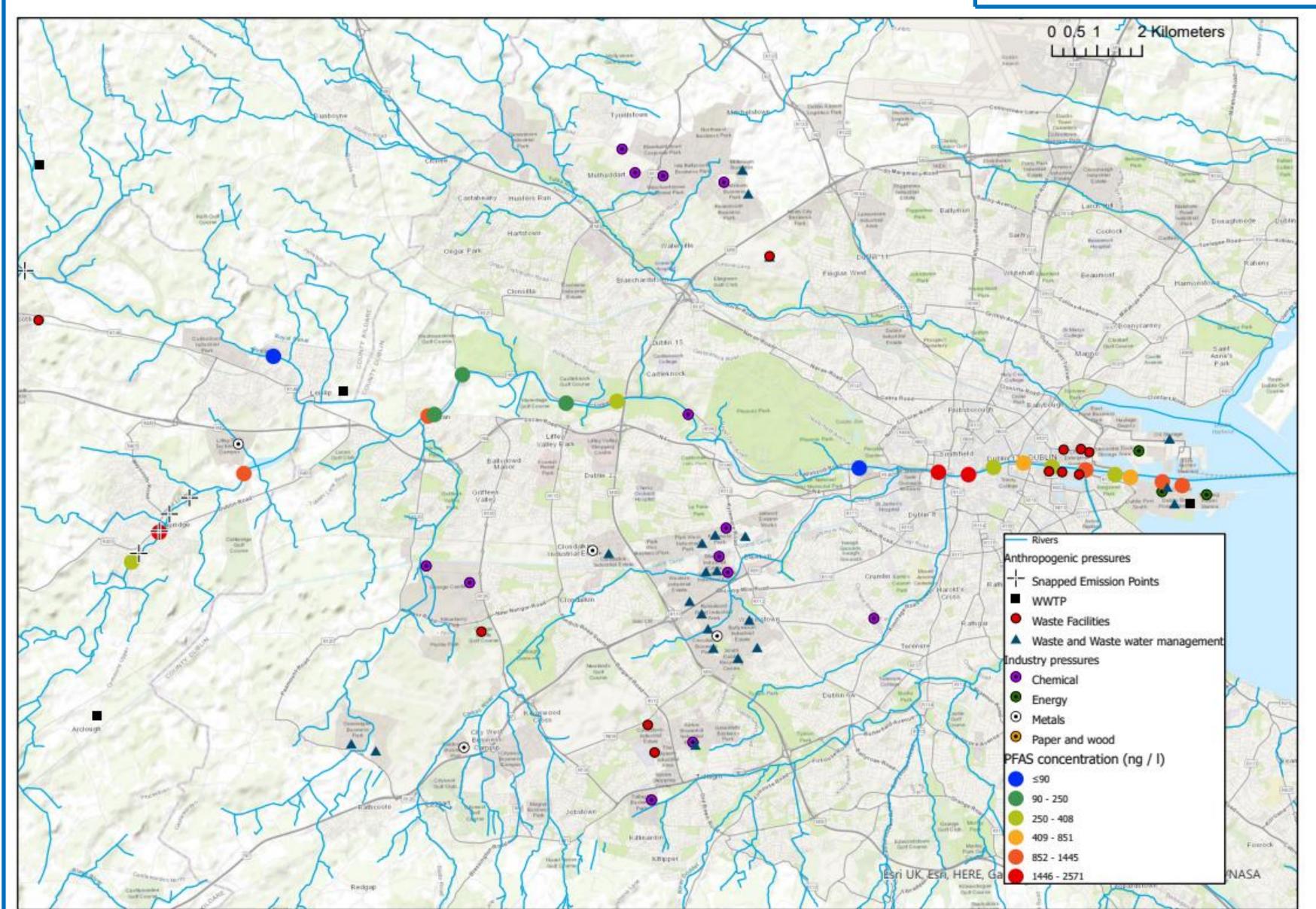


Fig 2. PFAS concentration and occurrence along the River Liffey, Ireland. Map illustrates potential sources of PFAS compounds in the area of the study.

Concentrations were found ranging in the low ng/L to μ g/L. The highest concentrations were detected for the compounds PFUdA of up to 1.8 μ g/L. PFOA was detected in almost every sample, reaching a maximum concentration of 1.2 μ g/L. PFBS was detected consistently in almost all samples (up to 0.8 μ g/L).

The potential sources discharging PFAS have been identified as airports, fire stations, anthropogenic pressures (i.e., WWTPs, waste facilities), and industry pressures (i.e., chemical, energy, metals, paper and wood).

Conclusion

This study demonstrates the determination of the occurrence and fate of legacy and novel per and polyfluoroalkyl substances (PFAS) to asses likely human exposure levels in the aquatic environment.

References:

[1] Huerta, B., McHugh, B., Regan, F., Development and application of an LC-MS method to the determination of poly- and perfluoroalkyl substances (PFASs) in drinking, sea and surface water samples. *Anal. Methods*, 2022,14, 2090 – 2099.



