Occurrence of Poly- and Perfluoroalkyl Substances (PFAS) in Transitional and Marine Waters along the Dublin Coast

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Introduction

Poly- and perfluoroalkyl substances (PFAS) are a large group of anthropogenic compounds consisting of a fully or partially fluorinated carbon backbone attached to varying functional groups. The OECD defines PFAS as any compound with a -CF3 or -CF2- moiety with the exception of H/Cl/Br/I atoms attached to a carbon within the compound. It is the carbon-fluorine bond that renders these compounds resistant to environmental degradation and contributes to their hydrophobic and lipophobic properties [1]. PFAS were first discovered in the late 1930s and are now employed as surfactants across a range of industrial applications, used in firefighting foams and in the production of personal care products and food packaging materials [2]. Due to their widespread use, PFAS are now ubiqitous in the environment and have been detected in drinking waters around the globe as well as in surface waters, from which they are capable of long-range transport [3]. The presence of PFAS in the environment is of concern due to exposure related health impacts including endocrine disruption, altered immune function, developmental issues and cancer [4, 5].

Little information on PFAS pollution in the Irish environment exists, the objective of the INVEST pFASST project is to inform PFAS strategy in Ireland. The first investigation of this project aims to pinpoint PFAS sources by carrying out targeted analysis in transitional waters and assess occurrence in Dublin Bay from which a "fingerprint" of the city's PFAS use can be defined.

Sample Collection and Analysis Methods

Transitional water samples were collected along the River Liffey in Dublin using amber polypropylene bottles and adjusted to a pH of 3 with acetic acid upon return to the laboratory. Samples were stored at -20°C prior to extraction. Samples were extracted and concentrated by Solid Phase Extraction (SPE) using Oasis WAX 6cc 500 mg SPE cartridges as described in Figure 1. Eluates were reconstituted in 1 ml methanol/water (80:20). Extracts were then spiked with 5µl of 1 mg/L internal standard mixture. Analysis of 15 PFAS listed in Table 1 was carried out by LC-MS/MS using HPLC (Agilent 1260 series Infinity binary pump) and triple quadrupole (QQQ) mass spectrometer (Agilent 6470). 10µl of sample was injected onto an Agilent Zorbax Eclipse Plus C18 (3.0 x 50 mm; 1.8 µm) column, a guard column of identical materials was utilized to delay interference by potential instrument contaminants.

LODs using this method range from 0.55 - 15.15 ng/L.

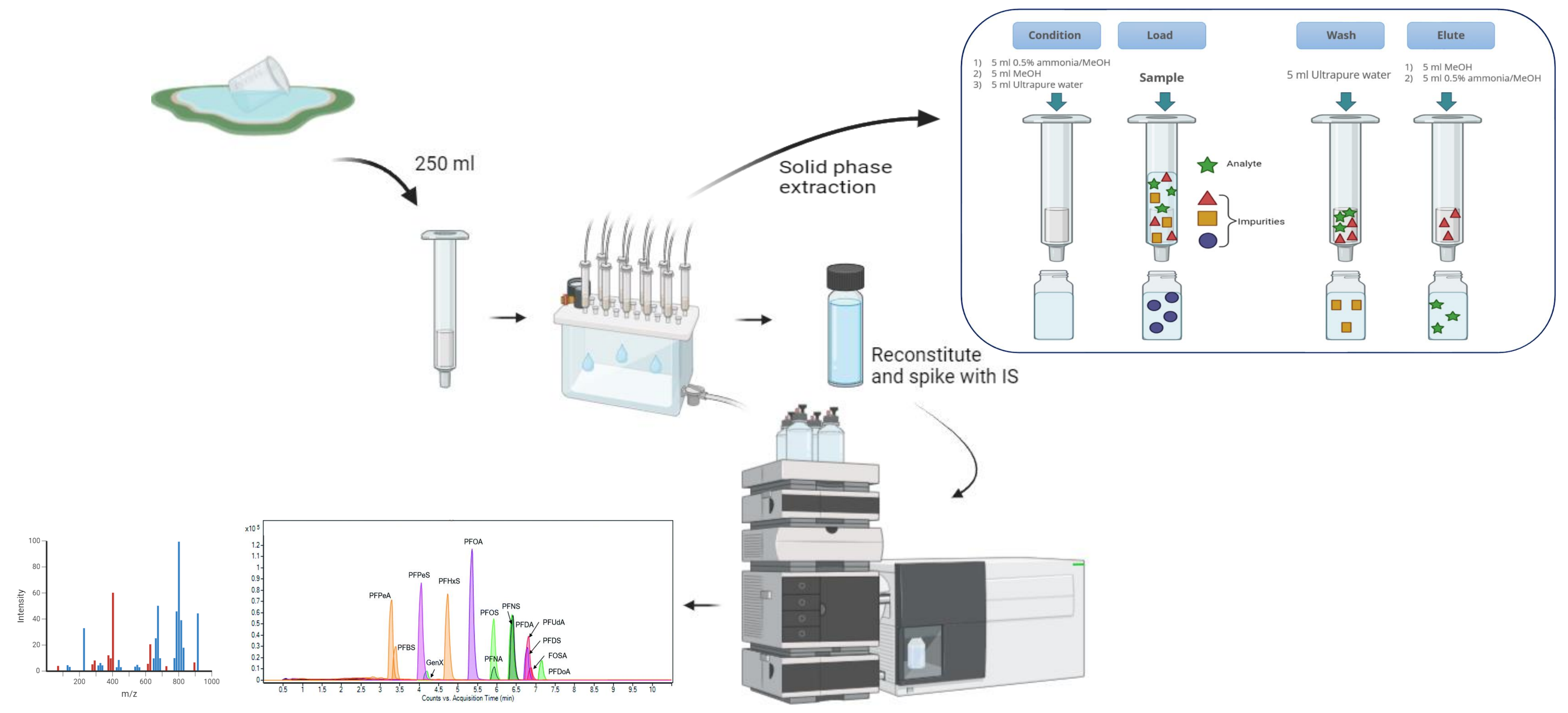


Figure 1 : Targeted analysis method using LC-MS/MS

Target PFAS

Table 1: Target analytes included in the transitional waters study

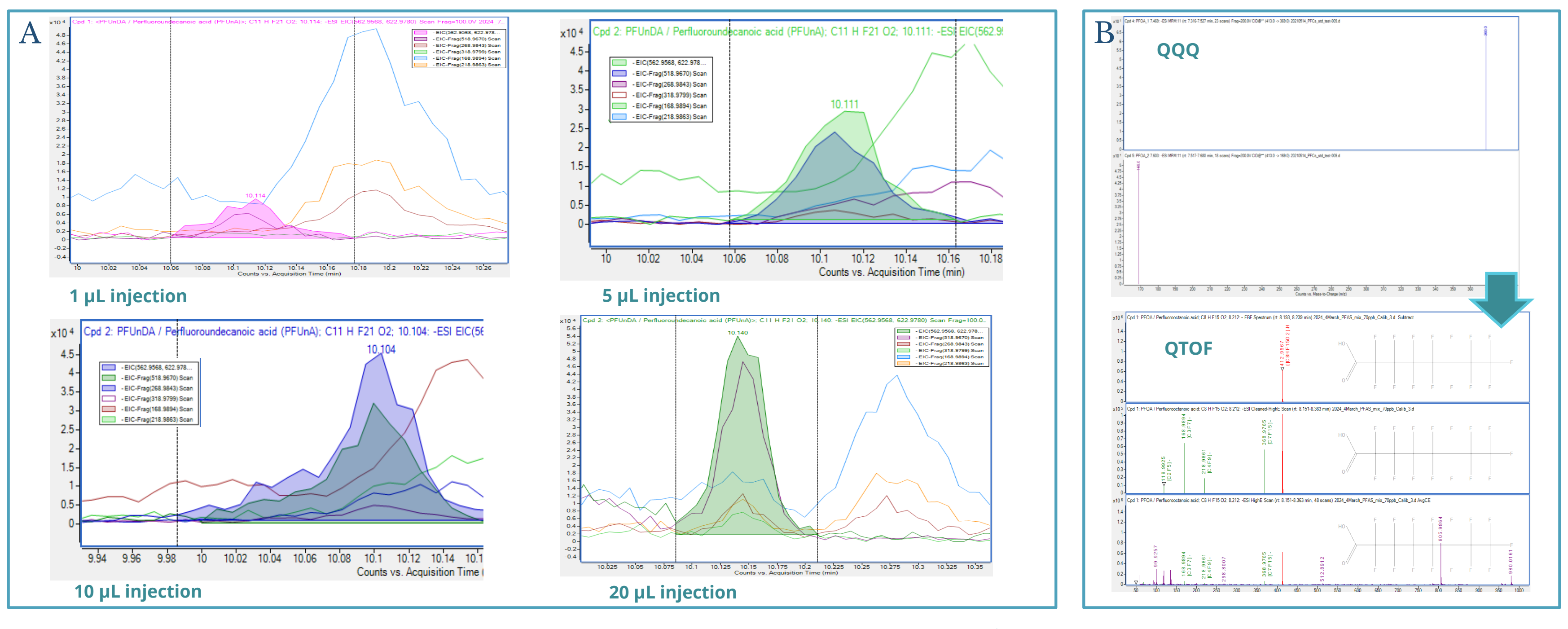
Compound	Acronym	CAS number	Class
Perfluorododecanoate	PFDoA	307-55-1	Acid
Perfluoroundecanoate	PFUdA	2058-94-8	Acid
Perfluorodecanoate	PFDA	335-76-2	Acid
Perfluorononanoate	PFNA	375-95-1	Acid
Perfluorooctanoate	PFOA	335-67-1	Acid
Perfluorohexanoate	PFHxA	307-24-4	Acid
Perfluoropropoxypropanoic acid	Gen X	13252-13-6	Acid
Perfluoropentanoate	PFPeA	2706-90-3	Acid
Perfluorooctanesulfonamide	FOSA	754-91-6	FOSA
Perfluorodecylsulfonate	PFDS	2806-15-7	Sulfonate
Perfluorononylsulfonate	PFNS	98789-57-2	Sulfonate
Perfluorooctylsulfonate	PFOS	4021-47-0	Sulfonate
Perfluorohexylsulfonate	PFHxS	82382-12-5	Sulfonate
Perfluoropentylsulfonate	PFPeS	630402-22-1	Sulfonate
Perfluorobutylsulfonate	PFBS	29420-49-3	Sulfonate

The Transition Towards Suspect and Untargeted Analysis and Simplifying Sample Delivery

In order to widen the lens at which PFAS pollution in the Irish environment can be investigated, a shift towards suspect and untargeted analysis is necessary. Quadrupole time-of-flight (QTOF) mass spectrometry allows for this transition by providing high resolution mass spectral data and operating in full scan mode to return data on a wide range of untargeted ions.

Direct injection of water samples can also enhance research efforts by decreasing sample preparation time and increasing sample turnover while limiting potential contamination during the sample preparation stage [6].

Of the investigated injection volumes (1 – 20 µL), the optimum injection volume was found to be 20 µL as this volume produced multiple confirming peaks for all targeted compounds at 1 µg/L, as represented by PFUdA in Figure 3. 5 µL was the lowest volume to return analyte peaks outside of the instruments noise region. Further tests are required to assess matrix effects as this volume optimisation was carried out using standards in methanol.



1 µL injection
5 µL injection
10 µL injection
20 µL injection

Figure 3: (A) Varying injection volumes for the detection of PFUdA in a 1 µg/L standard solution by direct injection using LC-QTOF-MS. (B) A comparison of mass spectral data of PFOA provided by LC-QQQ-MS and LC-QTOF-MS.

Targeted Results

Of the 15 targeted compounds, 10 PFAS were detected in these transitional water samples with concentrations ranging from low ng/L to µg/L. PFAS occurrence results have been mapped in Figure 2. Data retrieved from sample L8 was disregarded due to suspected extraction issues.

PFBS, PFOA, PFPeA and PFUdA were detected at all transitional sites (excluding L8) with concentrations ranging from 26.0 - 848.9 ng/L, 5.2 - 1393.7 ng/L, 0.9 - 142.0 ng/L and 10.2 - 1217.9 ng/L respectively. PFUdA reached low µg/L levels at multiple sample sites; L2 (1.02 µg/L) L3 (1.22 µg/L) and L10 (1.07 µg/L). The novel PFAS GenX was detected in 6 of the 11 samples at concentrations of 2.4 – 37.8 ng/L.

FOSA, PFDoA, PFDS, PFHxS and PFPeS were not detected in this study.

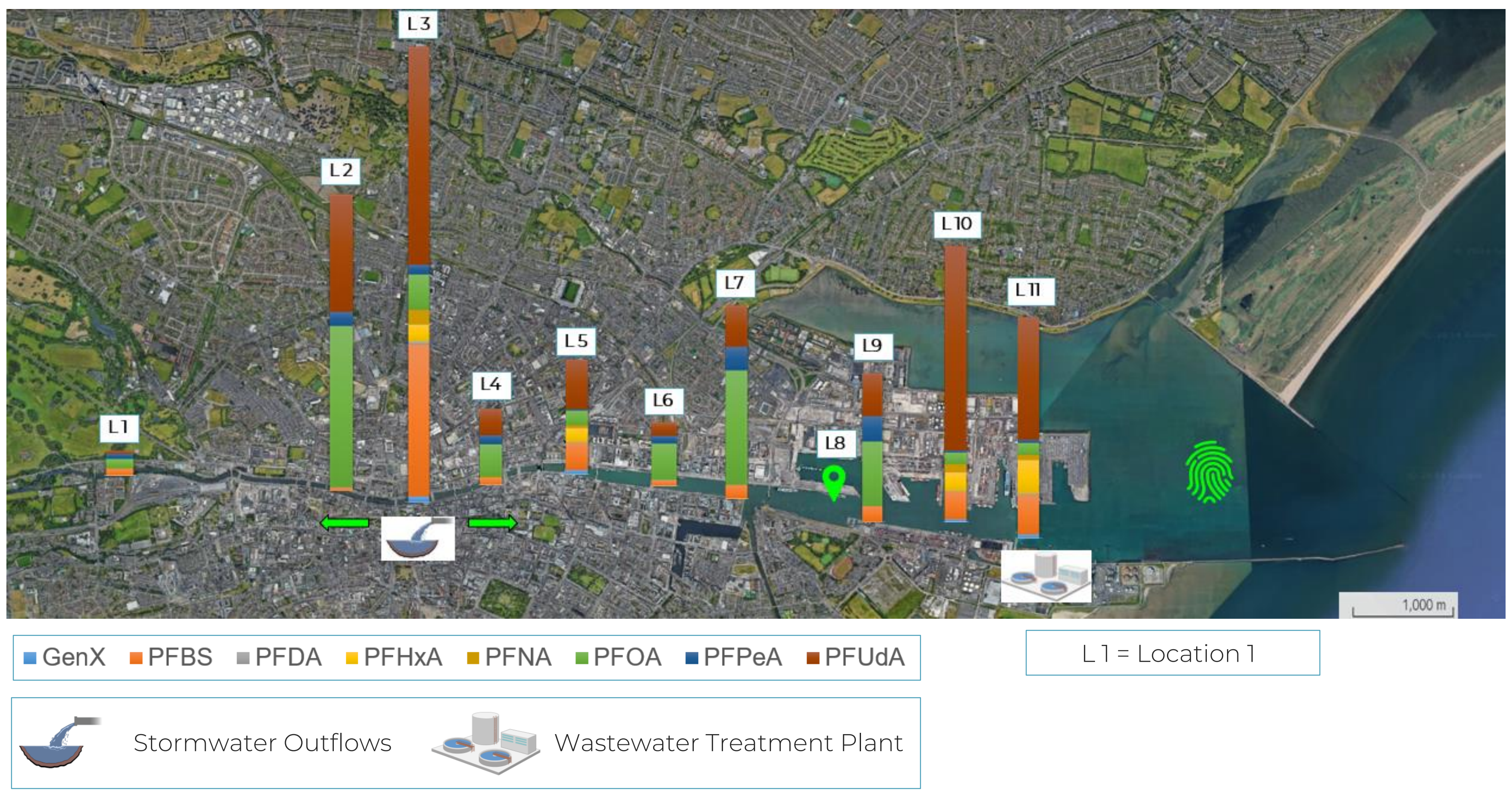


Figure 2: Mapped results of detected PFAS along the River Liffey and possible sources

Conclusions

PFAS are present in Irish Transitional waters, with PFOA and PFUdA reaching to µg/L levels at multiple sites. Possible PFAS sources along this study site include stormwater outflows and the Ringsend Wastewater Treatment Plant.

A shift towards untargeted analysis is necessary to gain full understanding of PFAS pollution in Ireland. Simplifying sample delivery by direct injection can aid in increasing both coverage and frequency of monitoring.

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