The occurrence of poly- and perfluoroalkyl substances (PFASs) and potential sources in the River Liffey, Ireland

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Introduction

PFASs (commonly referred to as "forever chemicals") are a group of 4700+ human-made chemicals. There have been decades of unregulated and widespread use of PFASs globally due to their waterproof, oil proof and fire-proof properties [1]. As shown in the commonly regulated compound perfluorooctane sulfonic acid (PFOS) in **Figure 1**, PFAS compounds typically consist of a fully fluorinated hydrophobic tail and a hydrophilic functional head. The carbon-fluorine bond is incredibly strong, making them resistant to break-down under natural environmental conditions. The persistence, bioaccumulation and long-range transportation of PFASs has meant that they are ubiquitous in the environment and have been detected globally in water, soil, air and biota [2], including in the River Liffey, Dublin [3].

There are also concerning links to human health and ecological impacts (including neurotoxicity, endocrine disruption and carcinogenicity) [4].

PFASs have been used in multiple industries and in every-day products. They can enter the environment during manufacturing of the substances, the use of the substances themselves and through disposal. They are found in low concentrations in most environments but to prevent further contamination, it is pertinent to identify potential sources and industries contributing to the most significant contamination [5].

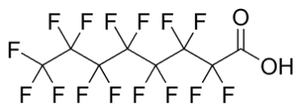

Figure 1: PFOS Structure

Objective 1

To develop a methodology to differentiate between PFAS point sources and background concentrations.

Objective 2

To identify PFAS source trends and contamination hotspots in Ireland to conduct a nation-wide risk asssessment.

Source identification method

STEP 1
Geographical proximity

The River Liffey flows through the centre of Dublin and is known to have legacy contamination associated with a variety of industry. These include known sources of PFAS such as civil sources (fire stations, military training bases and airports), industrial sources (chemical manufacturing plants, paper and wood processing facilities, and other industries with emissions licences), and municipal sources (wastewater treatment plants and other waste facilities) [6]. Using Irish Environmental Protection Agency (EPA) Maps and data, locations that are potential PFAS sources in the Liffey catchment were identified [7].

STEP 2
Chemical footprint

Presently, there are more than 4700 identifiable PFAS compounds. Individual compounds have unique properties and different combinations are used by industries for specific purposes. By identifying unique compounds and distinguishable compound ratios, a specific diffuse PFAS source can be inferred. For example. longer chained perfluoroundecanoic acid (PFuDA) could be linked to fluorinated high density polyethylene (HDPE) containers [8] and PFOS could be linked to aqueous film-forming foams (AFFFs) used in airports or fire-fighting stations [9].

STEP 3
Dimensional calculation

To infer the concentration of an upgradient source (c), such as a stormwater outfall, a mass-balance equation (as shown in **Equation 1**) can be used. The inputs that are required include the total downgradient concentration (T), the background river concentration (C) and seasonal flow rates for the River Liffey (F) and the target outfall (f) [10].

$$T = \frac{FC + fc}{F + f}$$

Equation 1: Mass Balance Equation

STEP 4
Dimensional modelling

Dimensional modelling using programs such as Mike 2D or SWAT+ can allow for further refining of the potential source. Further data inputs would be required to conduct this modelling including:

Environmental factors
- River flow
- Stormwater flows
- Rainfall data
- Temporal data

+

Chemical factors
- Dispersion rates
- Sorption
- Bioavailability
- Solubility
- Bioaccumulation

Literature Review

Potential sources of PFAS in Ireland

Anthropogenic
These sources include anything that humans use, touch and interact with in their daily lives. These include:
- Personal care products
- Non-stick pans
- Detergents
- Waterproof clothing
- 'Widely biodegradable' food and drink packaging

Industrial
These sources reflect a significant input of PFASs into the environment. Known industries that use or process PFASs are:
- Chemical and pharmaceutifcals manufacturers
- Paper and wood processing plants
- IT facilities and data centres

Civil
These sources generally involve the storage and use of AFFFs, often used for training purposes. These locations include:
- Airports
- Fire fighting stations
- Military bases

How does PFAS enter the environment and affect sensitive receptors?

PFAS compounds will pass through multiple municipal waste streams or be applied directly to soil (AFFFs). The waste industry has been identified as being a large contributor to the bioaccumulation and transformation of PFAS in the environment [11]. **Figure 2** shows how PFAS compounds can travel through the environment.

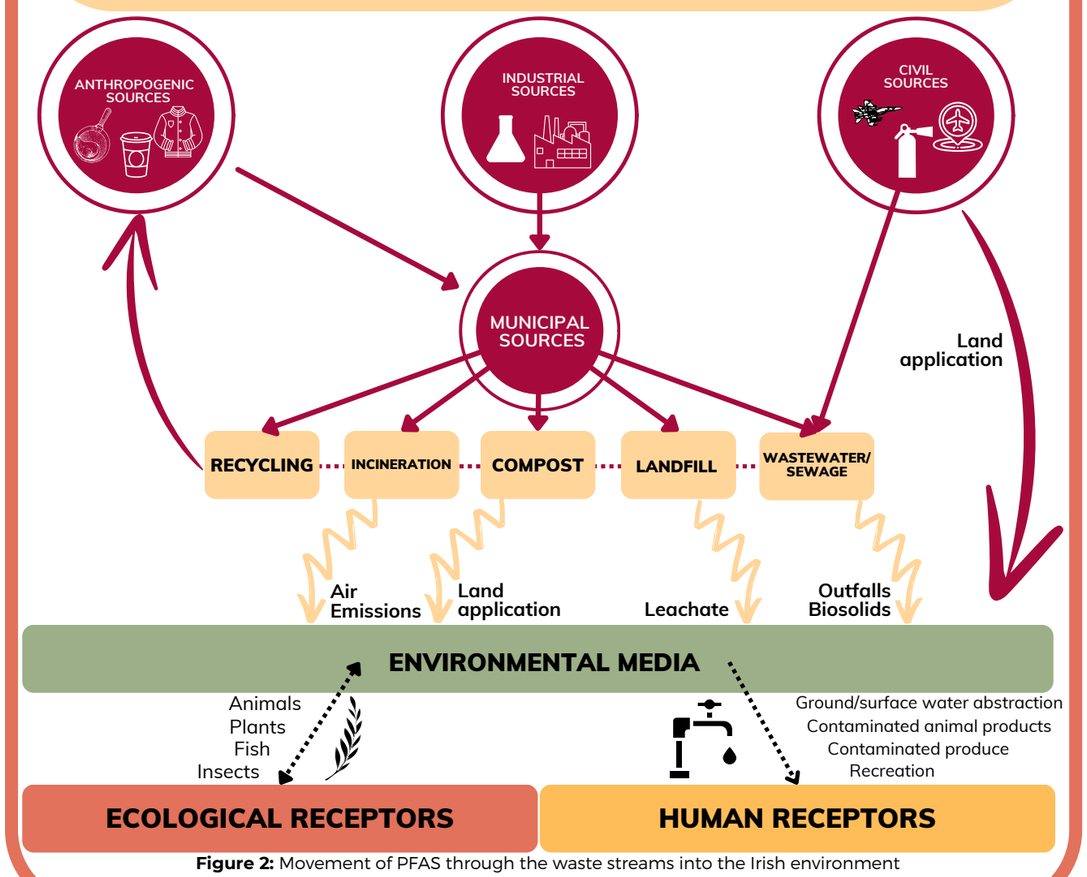

Figure 2: Movement of PFAS through the waste streams into the Irish environment

Results

STEP 1 - Geographical Proximity

A total of 20 samples were selected to be representative of the movement of the River Liffey from the headwaters to Dublin Bay. Step 1 involved assessing whether elevated Total PFAS concentrations are within close proximity to known sources and whether there are feasible pathways for the compounds to enter the environment, such as runoff, outfalls and stormwater drains. EPA Maps were used to identify IPC Emission Points and PRTR facilities. Inverse distance weighted (IDW) technique was utilised to create contamination contour maps on ArcGIS geoprocessing tool, as shown in **Figure 3 and 4**.

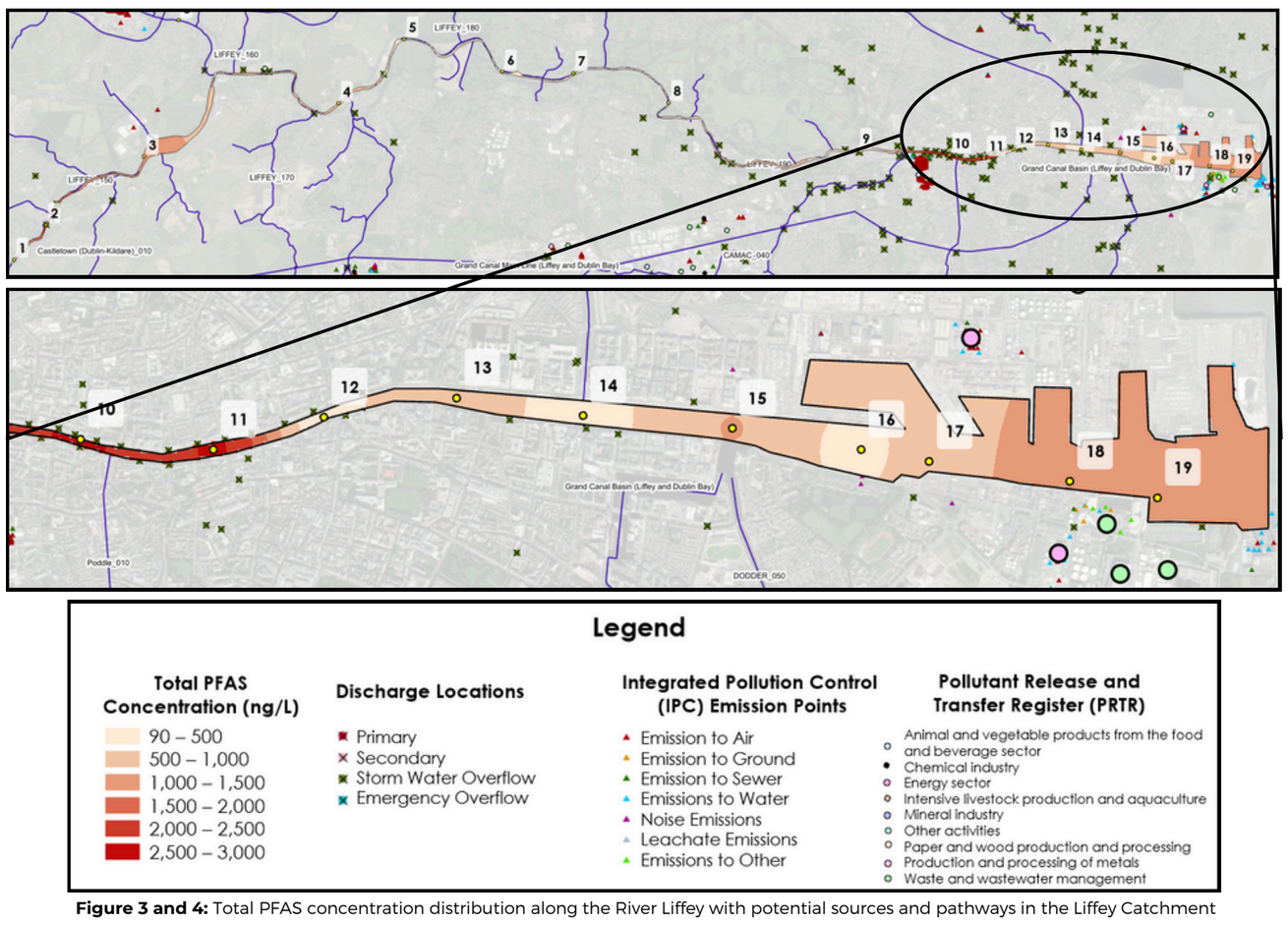

Figure 3 and 4: Total PFAS concentration distribution along the River Liffey with potential sources and pathways in the Liffey Catchment

STEP 2 - Chemical Footprint

Step 2 involved identifying unique compounds and distinguishable compound ratios, the origin of the contamination can be inferred. Longer chained PFuDA was identified in 19 locations and PFOS was detected in 3 samples above the Annual Average concentration in the Irish Environmental Quality Standards [12].

Compound	FOSA	GenX	PFBS	PFDA	PFDoA	PFDS	PFHxA	PFHxS	PFNA	PFNS	PFOA	PFOS	PFPeA	PFPeS	PFUdA	∑PFAS
Number of locations detected	0	11	19	16	0	0	6	0	17	2	19	3	20	0	19	20

STEP 3 and 4 - Dimensional Calculations and Modelling

There is a trend of elevated Total PFAS concentrations being linked to a higher number of stormwater overflows. To refine the source, further data inputs and targeted sampling will be required.

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