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A new on-line SPE LC-HRMS method for the analysis of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in $PM_{2.5}$ and its application for screening atmospheric particulates from Dublin and Enniscorthy, Ireland

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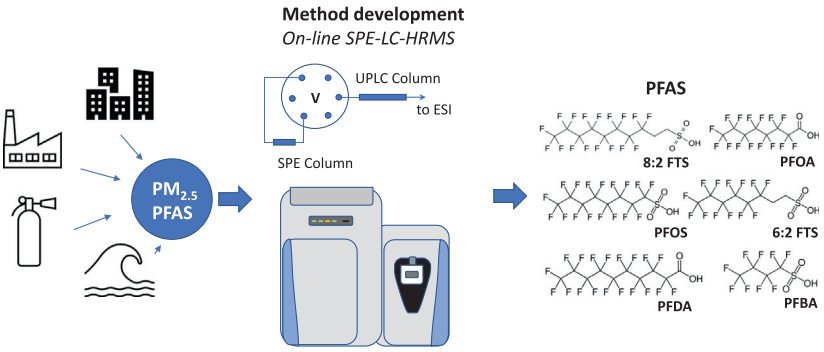
HIGHLIGHTS

- A new method for determination of 16 PFAS in $PM_{2.5}$ has been developed and validated
- The method provides LODs allowing detection of PFAS in $PM_{2.5}$ at low fg/m^3 level
- This is the first study to identify PFAS in $PM_{2.5}$ at urban locations in Ireland
- This is the first study to detect 4:2 and 8:2 fluorotelomer sulfonates in PM2.5
- Our results raise a concern about fluorotelomer persistence and their impact on human health

GRAPHICAL ABSTRACT



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ABSTRACT

A sensitive analytical method has been developed and validated for the determination of 16 polyfluorinated alkyl substances (PFAS) in fine airborne particulate matter ($PM_{2.5}$) using on-line solid phase extraction (SPE) coupled with liquid chromatography (LC) – negative electrospray ionisation high resolution mass spectrometry (−) ESI-HRMS. On-line SPE allows simultaneous sample clean-up from interfering matrices and lower limits of detection (LODs) by injecting a large volume of sample into the LC system without compromising chromatographic efficiency and resolution. The method provides LODs in the range 0.08–0.5 pg/mL of sample extract allowing detection of selected PFAS in aerosol particles at low fg/m^3 level and showed good tolerance to the considered PM matrix. The validated method was applied for analysis of PFAS in ambient $PM_{2.5}$ samples collected at two urban locations in Ireland, i.e., Enniscorthy and Dublin. Several PFAS were observed above the detection limit, including perfluorobutyrate (PFBA), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorobutanesulfonic acid (L-PFBS) and perfluorononanoic acid (PFNA), as well as fluorotelomer sulfonates: 4:2 FTS, 6:2 FTS and 8:2 FTS. The results indicate that some toxic PFAS, such as PFOS and PFOA, are still detected in the environment despite being phased out from production and subject to restricted use in the EU and USA for more than two decades. Observation of fluorotelomer sulfonates (4:2 FTS, 6:2 FTS and 8:2 FTS, which are used as alternatives for legacy PFOA and PFOS) in ambient $PM_{2.5}$ samples raises a concern about their persistence in the atmosphere and impact on human health considering emerging evidence that they could have similar health endpoints as PFOA and PFOS. To our knowledge, this is the first study to identify PFAS in ambient $PM_{2.5}$ at urban locations in Ireland and also the first study to detect 4:2 and 8:2 fluorotelomer sulfonates in atmospheric aerosol particles.

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1. Introduction

Particulate matter (PM) consists of a mixture of solid and liquid particles of different sizes suspended in the atmosphere. Current air quality regulations focus on PM_{10} (particles ≤ 10 μm in diameter) and $PM_{2.5}$ (particles ≤ 2.5 μm in diameter). There is greater concern over $PM_{2.5}$ since these smaller particles can penetrate further into the respiratory system and lead to cardiovascular and respiratory diseases, as well as lung cancer. The World Health Organization (WHO) sets out guideline values of 5 μg/m^3 for an annual mean concentration and 15 μg/m^3 for a 24-hour mean concentration (WHO, 2021). However, the true health risks of exposure to $PM_{2.5}$ are not fully encompassed by $PM_{2.5}$ mass concentration alone because not all fine particles may be equally toxic (Lanphear, 2017; Park et al., 2018). The chemical composition of ambient $PM_{2.5}$ is extremely complex and typically contains thousands of individual organic compounds (Goldstein and Galbally, 2007). Some of these compounds can be extremely toxic, even when present at low concentrations (Smith et al., 2019).

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are a class of emerging contaminants also known as 'forever chemicals'. They have been widely used in a broad range of consumer products and industrial applications (Glüge et al., 2020). PFAS have been detected in a wide variety of environments including soil, biota, water and air samples (Barber et al., 2007; Buck et al., 2011; Gebbink and van Leeuwen, 2020; Kurwadkar et al., 2021). Numerous studies have also shown that exposure to PFAS is associated with a range of human health effects, including reduced immune response, thyroid disease, endocrine-disruption (linked to human fertility) and even kidney and testicular cancer (Bartell and Vieira, 2021). Although, the production and use of some PFAS, e.g., perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been phased out in certain countries and substituted by less toxic alternatives, PFOS and PFOA are still widely observed in the environment (e.g., Sha et al., 2021; Zhou et al., 2021). Despite perfluoroalkyl carboxylic acids and sulfonic acids have low volatility due to their ionic nature (Kissa, 2001; Prevedouros et al., 2006) these compounds have been detected in atmospheric aerosol samples (e.g., Zhou et al., 2021). Their presence in PM can possibly be explained by the photochemical oxidation of volatile precursors (Ahrens et al., 2010) or by solubilising in a liquid particle droplet. There are numerous reports suggesting that newly introduced substitutes for PFOA and PFOS (and their degradation products) can be as toxic as their predecessors (Gomis et al., 2018).

Fluorotelomer sulfonates (FTS), which include 4:2 FTS, 6:2 FTS and 8:2 FTS, are one class of compounds used as substitutes for PFOA and PFOS. The extensive review on FTS by Field and Seow (2017) emphasised that these compounds have been widely marketed since 1970s and are sold for use in paints, coatings, adhesives, waxes, polishes, and industrial cleaning products. FTS have also been found in different environments including drinking and surface waters (Boiteux et al., 2017), landfill leachate (Hamid et al., 2020), influent and effluent of municipal wastewater treatment (WWT) plants (Houtz et al., 2016), soil (Jarjour et al., 2022) and indoor dust (Young et al., 2021). The presence of FTS in soils has previously been attributed to the transport of aerosols emitted from an adjacent WWT plant (Dauchy et al., 2017); however, to our knowledge, there are no previous reports on the presence of 4:2 and 8:2 FTS in atmospheric aerosol particles.

Although some of the FTS, e.g., 6:2 FTS, are not considered to be bioaccumulative, these compounds are found in biota, as well as in regions not impacted by known point sources (Field and Seow, 2017) including remote Artic freshwater samples (Muir et al., 2019). FTS have been found in human blood, serum, plasma and biological tissues (Yeung and Mabury, 2015; Eriksson et al., 2016; Sunderland et al., 2019). It has been suggested that the increasing number of reports of FTS in environmental media and biota is a result of availability of chemical standards and improving analytical methodologies leading to decreased detection limits.

The analysis of PFAS in environmental samples is considered to be challenging due to trace-level concentrations requiring highly sensitive analytical methods. This is especially true when analysing PFAS in the atmosphere, which generally contains significantly lower concentrations than other environmental media. However, dilute atmospheric PFAS can still have a significant impact on human health due to the potential for continuous exposure through inhalation and accumulation of these pollutants in the human body, especially when close to pollution sources. Suitable analytical techniques should also be able to cope with an extremely complex environmental matrix, which often contains thousands of compounds, including naturally occurring chemicals such as humic substances (Weber et al., 2018) that can interfere with the analysis (Escher et al., 2020; Masqué et al., 1998).

Numerous analytical approaches have been proposed for identification of PFAS in waters, sediments, and soils (Winchell et al., 2021) but only a few publications report analytical methods for identification of PFAS in atmospheric samples. One of the earliest methods applied for targeted analysis of PFAS in atmospheric aerosol particles involved ultrasonic extraction of the target analytes from glass fibre filters with methanol, followed by "cleaning" of the extracts by the Powley method, concentration of extracts with rotary evaporation and subsequent analysis by liquid chromatography time of flight mass spectrometry (LC-TOF-MS) and gas chromatography (GC)-MS (Barber et al., 2007). In other studies, off-line solid phase extraction (SPE) was applied to extracts from particles collected by a cryogenic air sampler (Yu et al., 2020) or sorbent-impregnated PolyUrethane Foam (PUF) disc (Goosey and Harrad, 2012), followed by analysis using LC-high resolution (HR)-MS or LC- triple-quadrupole MS, respectively. Recently, the direct analysis of PFAS in atmospheric aerosol particles without prior sample clean-up has been reported, where sample extracts are preconcentrated using evaporation under nitrogen flow and subsequent analysis performed using LC- electrospray ionisation (ESI) TOF-MS (Sha et al., 2022; Zhou et al., 2021).

It has been demonstrated that ESI is prone to matrix effects resulting in, ion suppression or enhancement due to the presence of certain compounds and inorganic salts in the sample (Chekmeneva et al., 2017; Silva et al., 2016). For example, sulfates, nitrates, and ammonium salts are important constituents of atmospheric particles (Pöschl, 2005) and can cause ion suppression and adduct formation if injected into the ESI source (Kourtchev et al., 2020). Such artifacts can potentially be reduced by sample pretreatment (Kubica et al., 2017; Zhao et al., 2013). One of the most frequently applied techniques for removal of interfering substances is SPE (Kraševec and Prosen, 2018). In SPE, a liquid sample is passed through solid phase sorbents and the retained analytes are eluted with an appropriate solvent or a mixture of solvents.

The major drawback of SPE in organic (including PFAS) analysis is possible sample contamination and losses of surface-active PFAS to container walls and other materials (Jahnke and Berger, 2009; Mazzoni et al., 2015). Most of the SPE sorbent containers (e.g., cartridges, tubing, syringes) are made of polymer/plastic material, which can potentially introduce unwanted impurities (including PFAS) into a sample. However, the influence of impurities can be mitigated by fine tuning of the analytical steps (e.g., rinsing cartridges, selecting compatible solvents), thus allowing SPE to be widely applied for PFAS analysis (Sanan and Magnuson, 2020). Another drawback of SPE is that it is a time consuming and laborious process. On-line SPE has been introduced relatively recently and successfully applied to PFAS analysis of water matrices (Takino et al., 2003; Wilson et al., 2007; Gosetti et al., 2010; Enevoldsen and Juhler, 2010; Mazzoni et al., 2015; Sanan and Magnuson, 2020). One of the most commonly used methods for on-line coupling of SPE with LC is achieved through column switching. For this purpose, a small, typically 2–15 mm long and 1–4.6 mm i.d. precolumn used as an SPE column is connected to a conventional LC analytical column via a switching valve (Chen et al., 2009). The use of on-line SPE allows the development of faster methods for screening multiple media more consistently (Grant and Rappold, 2018) which have a higher capacity for multi-analyte determination compared to conventional SPE (Rodriguez-Mozaz et al., 2007). Moreover, it reduces potential contamination from sample handling during off-line SPE sample pretreatment. In on-line SPE mode, efficient cleaning of the extraction system is necessary in order to avoid memory effects (Chen et al., 2009). On-line SPE applications to a wide range of analytical conditions are still not well developed (Sanan and Magnuson, 2020).

The main aims of this work were (1) to develop an on-line SPE-LC-HRMS technique for analysis of PFAS in atmospheric aerosol particles, (2) to expand the analyte detection range of currently applied methods in aerosol analysis with 4:2 and 8:2 FTS (substitutes of PFOA and PFOS) and (3) to apply the developed method for analysis of ambient $PM_{2.5}$ samples collected in urban environments.

2. Method

2.1. Chemical reagents

The following reagents and chemicals were used in this study: EPA-533PAR native analyte primary dilution standard mixture containing 25 PFAS (i.e. Perfluoroalkylcarboxylic acids (C4-C12), Perfluoroalkanesulfonates (C4, C5, C7 linear, C6 & C8 linear and branched isomers), 4:2 FTS, 6:2 FTS, 8:2 FTS, HFPO-DA, NaDONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, PF4OPeA (PFMPA), PF5OHxA (PFMBA), 3,6-OPFHpA (NFDHA), & PFEESA) at concentrations of 0.5 μg/mL and EPA-533ES isotope dilution standard mixture containing 16 mass labelled (^{13}C) PFAS (i.e., M3PFBS, M3PFHxS, M8PFOS, MPFBA, M5PFPeA, M5PFHxA, M4PFHpA, M8PFOA, M9PFNA, M6PFDA, M7PFUdA, MPFDoA, M2-4:2FTS, M2-6:2FTS, M2-8:2FTS and M3HFPO) at concentrations 0.5–2.0 μg/mL (Wellington laboratories Inc.); Optima™ LC/MS grade methanol, water, ammonium acetate and formic acid (99.0 + %), (Fisher Chemical). The full names of listed above abbreviated PFAS and corresponding isotopically labelled compounds are shown in Table S1 of the Supplementary Data.

2.2. Sample collection

Quartz fibre filters (PALL Life Sciences, Pallflex®, Tissuquartz) with a diameter of 150 mm were used for collection of ambient $PM_{2.5}$ in a high volume air sampler (DHA-80, DIGITEL Elektronik GmbH) equipped with a $PM_{2.5}$ size selective inlet and operated at a flow rate of 500 L/min. Aerosol sampling onto filter substrates can be accompanied by positive (e.g., adsorption of organic vapours) and negative (e.g., volatilisation of organic aerosols) artifacts (Chow et al., 2010). However, it has been shown that influence of organic carbon (OC) sampling artifacts on quartz filters is much lower when sampling with a high volume, in comparison to a low volume sampler, due to the higher sampling velocity (Karanasiou et al., 2015). In Enniscorthy the height of the inlet was approximately 2 m above the ground. In Dublin the inlet was at street level, approximately 1 m above the footpath, because it was located in a stairwell below street level. This is the same level that the official air quality monitoring station inlet is located at. Prior to aerosol sampling, the filters were baked in an oven (Carbolite Furnace, Barloworld Scientific) at 650 °C for 24 h to remove any possible organic contaminants. After baking and allowing to cool, the filters were individually wrapped in aluminium foil and stored in a sealed desiccator before transportation to the field. Field blanks were prepared by placing a prebaked filter into a high-volume sampler cartridge with no air sampled through and exposing for as long as the last filter in the stack for every batch. The foil hasn't been precleaned or baked. Field blanks were handled in a similar way to the real samples (e.g., also wrapped into the foil from the same roll). The concentration for most of the tested PFAS (except for PFBA, PFHxA, PFHpA and PFUdA) in the blanks was found to be negligible (below limit of quantification (LOQ)), however, when exceeded limit of detection (LOD), they were subtracted from the values measured in the actual aerosol samples. After sampling, the filters were removed from the high volume sampler, individually wrapped in aluminium foil, placed in a sealed plastic bag to avoid contamination and stored in a freezer at −20 °C until analysis.

2.3. Sampling sites

2.3.1. Pearse Street, Dublin (DUB)

Sampling of ambient $PM_{2.5}$ took place at a roadside location on Pearse Street (53° 20′ 42.3″ N, 6° 15′ 15.3″ W) in the centre of Dublin city from 6 to 21 February 2019. Sampling times were 12 h (06:00–17:59 and 18:00–05:59). The monitoring site was situated on the R802, a main road through Dublin city centre from the Grand Canal Dock to O'Connell Bridge which has a constant flow of traffic and is on almost twenty cross-city and radial bus routes. The majority of the buses run throughout the day, seven days a week. The DART (Dublin Area Rapid Transport) train line runs close to the site, less than 200 m away. Directly to the south of the site is the campus of Trinity College Dublin which is predominantly pedestrianised. To the north of the site is the River Liffey (~300 m), which runs through the heart of Dublin, while Dublin Port is approximately 3 km east of the site.

2.3.2. Enniscorthy, Co. Wexford (ENY)

Sampling of ambient $PM_{2.5}$ took place on the grounds of the public library in the town of Enniscorthy, Co. Wexford (52° 30′ 1.44″ N, 6° 34′ 13.12″ W) in the south-east of Ireland. Samples were collected over 8-hour periods (07:00–15:00, 15:00–23:00, and 23:00–07:00) from 3 to 23 February 2020. The town, which is situated in the valley of the River Slaney, has a population of just over 11,300 according to the census carried out by the Central Statistics Office in 2016 (Census 2016). The sampling site was located near the centre of the town, approximately 520 m southwest of the train station. The M11, which connects Dublin and Wexford, is 3 km east of the monitoring site, while the N30, a national primary road, is approximately 3.5 km to the west.

2.4. Organic carbon and elemental carbon analysis

The $PM_{2.5}$ samples were analysed using an Organic Carbon/Elemental Carbon (OC/EC) laboratory Instrument (Model 5L, Sunset Laboratory Inc.) using the EUSAAR_2 protocol (Cavalli et al., 2010). The accuracy of the measurements was tested using a sucrose solution and found to be within ±10%.

2.5. Sample extraction

A filter portion (area of 18 cm^2) was placed into a prewashed 20 mL glass vial (Fisherbrand TM, P/N 12971231) and extracted three times with 5 mL of Optima LC/MS Grade methanol in an ultrasonic bath for 1 h (20 min × 3 times). Ultrasonic agitation has been previously applied for PFAS extraction from aerosol samples (Barber et al., 2007). The extracts were filtered using PTFE membrane filters, pore size 0.45 μm (Iso-Disc PTFE-13 − 4, 13 mm × 0.45 μm) into a prewashed 10 mL glass vials (Chromacol 10-HSV, P/N 03–341–956) with metal screw caps (Chromacol 18-MSC, P/N 03–341–957) and polytetrafluoroethylene (PTFE) septa (Chromacol 18-ST101, P/N 03–341–959) from Thermo Scientific (Waltham, MA). This type of septa was previously used in other studies for PFAS analyses and did not adversely affect the method performance relative to the data quality objectives of the treatment studies, including background contamination levels (Sanan and Magnuson, 2020). In our study, we prewashed the septa and glass vials with Optima grade methanol and minimised septa contact with the extracts by avoiding filling the vials with more than 60% of the vial capacity volume. The same type of vial and screw caps was used for all method validation steps described below.

Prior to sample filtration, PTFE filters were purged 3 times with 5 mL of Optima LC/MS Grade methanol (total volume 15 mL). The filtered methanolic extract was topped up with Optima LC-MS grade water to provide a water:methanol ratio of 80:20 (v/v) and spiked with an internal standard (IS), which comprised a mixture of 16 mass labelled (^{13}C) PFAS at concentrations of 5 pg/mL and three telomer sulfonates (M2-4:2 FTS, M2-6:2 FTS and M2-8:2FTS) at 20 pg/mL. The spiked extracts were vortexed and analysed for PFAS. Three field blanks from each sampling site were processed (e.g. extracted, spiked with IS) in a similar way as aerosol samples and analysed for PFAS.

The method extraction efficiencies were assessed by spiking a blank quartz filter (in three replicates) with EPA-533PAR mixture containing 25 native PFAS at 6 pg/mL and extracting for 20 min using an ultrasonic bath. The sonicated extracts were filtered using PTFE filters into a separate

prewashed vial, toped up with Optima grade water, additionally spiked with IS as described above and analysed with on-line SPE LC-MS. The filter that has undergone the first extraction step procedure was extracted for the second time without spiking with a native PFAS mixture for additional 20 min and processed in a similar way as described above. The extraction procedure was repeated for the third time. The recoveries were obtained by calculating ratios of PFAS area response from the extract at each extraction step to that of the solution spiked at the same concentration level injected into on-line SPE directly. The PFAS recoveries from the single-step extraction procedure ranged between 93 and 109% (Fig. S1). The second extraction step resulted in additional 0.75 to 16.3% recoveries for the majority of PFAS analytes. The recoveries from the third extraction step provided insignificant additional recoveries (within the standard deviation range of recoveries from the first extraction step), except for PFBA; therefore, all aerosol samples in this study were extracted three times. The presence of PFBA after the third extraction step (up to 12.6%) suggests that this compound is likely arising from the analytical procedure (sample handling) and on-line SPE LC-MS system as also confirmed by the presence of this compound in the system blanks (see discussion in Section 2.7).

The overall method recoveries at two PFAS spiking concentrations i.e., 6 pg/mL and 15 pg/mL are shown in Table 2.

2.6. Matrix effect

Samples with the lowest PFAS concentration were selected to evaluate matrix effects. Several portions of filter samples were pooled together in a prewashed glass bottle to provide a uniform sample matrix and extracted under ultrasonic agitation with Optima LC/MS Grade methanol for 1 h. The extracts were filtered using PTFE membrane filters treated in a similar manner as outlined above. The PM methanolic extract was topped up with Optima LC/MS grade water to provide a water:methanol ratio of 80:20 (v/v) giving an OC concentration of 3.9 μg/mL. The pooled sample extract was split into several equal portions and spiked with the internal standard described above. The extracts were additionally spiked with a mixture of 25 native PFAS compounds at two concentration levels (6 and 15 pg/mL) in four replicates. All data presented in this work was acquired using on-line SPE.

2.7. On-line-SPE, ultra high pressure liquid chromatography (UHPLC) and MS

On-line SPE and chromatographic separation were carried out on EQuan MAX Plus Thermo Scientific™ Vanquish™ UHPLC system using a Thermo Scientific™ TriPlus™ RSH autosampler equipped with three 6 port VICI valves. A similar analytical procedure was described by Mazzoni et al., 2015. Samples were injected into a 1 mL high volume loop and then transferred onto the preconcentration column by the loading pump (Thermo Scientific VF-P10-A) using 0.1% formic acid in water at 1 mL/min flowrate. After completion of the enrichment step, a 6-way valve on the autosampler switched over and the elution pump (Thermo Scientific VF-P20-A) flowed the elution gradient, composed of two eluents [(A) 2 mM ammonium acetate in 10% methanol and (B) methanol] at 300 μL/min, through the preconcentration column and the analytical column. The loading and the elution gradients are listed in Table 1. The On-line SPE and UPLC columns were Thermo Scientific™ Hypersil GOLD aQ Column, 20 × 2.1 mm, 12 μm and Waters® CORTECS C18 Column, 90 Å, 100 × 2.1 mm, 2.7 μm, respectively. Two replicate sample injections were made for each extract and filter blanks. Prior to aerosol sample and analytical standard analysis, the system was kept continuously running/"flushed though" with a mobile phase (40:60), mobile phases A:B (A-2 mM Ammonium acetate in water with 10% methanol, and B-methanol) at low flow rate (0.01 mL/min and 0.03 mL/min, over the weekend and over the night, respectively) to avoid accumulation of potential PFAS leachables from the system. A series of system ("zero volume") blanks were injected prior to sample analysis, between samples and at the end of the sequence, followed by filter blanks, which resulted in insignificant amounts (below LOQ) for the majority of PFAS from the system after the system flush. The filter blanks showed presence of PFBA, PFHxA, PFHpA and PFUdA above LOQ level, which were subtracted from the values measured in the studied samples. PFDoA, being a late eluting compound (also has lower ionisation efficiency compared to the rest of the considered analytes), showed poor reproducibility at the low concentration range considered in our work and thus was excluded from the final method evaluation and screening of ambient PM samples.

Analysis and method validation were performed using Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ mass spectrometer (Thermo Fisher,

Table 1
On-line SPE, UHPLC and MS conditions for PFAS analysis.

	On-line SPE conditions			UPLC conditions		
Mobile phase	A: 0.1% Formic acid in water B: Methanol			A: 2 mM ammonium acetate in water/methanol, 90/10 (v/v) B: Methanol		
Gradient method	Time, min	%B	Flow, mL/min	Time, min	%B	Flow, mL/min
	0	0	1	0	0	0.3
	5	0	1	1	0	0.3
	5.1	100	3	1.1	33.3	0.3
	6.5	100	3	9	88.9	0.3
	6.6	0	3	12	98.9	0.3
	9	0	3	18	98.9	0.3
	9.1	0	0.5	18.1	0	0.3
				22	0	0.3
Column temp. (°C)	25			35		
Injection vol., mL	1			–		
On-line SPE Pump status						
Time, min		**Loading pump status**		**Eluting pump status**		
0		To SPE column		Direct to analytical column		
1		To waste		To SPE & onto analytical columns		
19.1		To SPE column		Direct to analytical column		
MS conditions						
ESI parameters				**SIM parameters**		
Spray voltage (kV)		3.5		**dd-MS2**	Confirmation	
Sheath gas flow rate		40		**Resolution**	70,000	
Capillary temp. (°C)		325		**Isolation window**	1 *m/z*	
Aux gas flow rate		10		**AGC target**	5e4	
Aux gas heater temp. (°C)		300		**Maximum IT**	Auto	
Sweep gas flow rate		0		**Loop count**	1	
				MSX count	10	

Bremen, Germany) equipped with an ESI source (Thermo Scientific). Acquisition was performed in the negative ionisation mode using selected ion monitoring (SIM) where data were collected at a resolving power of 70,000, quadrupole isolation 1 amu and Orbitrap selectivity of 5 ppm.

Details of the optimised mobile phase conditions, on-line SPE, UPLC and MS parameters are summarised in Table 1. A list of PFAS, internal standards and corresponding target ions and retention times are shown in Table S1.

The autosampler was kept at room temperature to avoid loss of PFAS on the glass vial walls. Even though the majority of fortified PFAS compounds eluted during the first 8 min of the chromatographic run, the gradient was held at 98.9% of organic mobile phase for an additional 6 min before equilibrating back to initial conditions to remove any potential compounds from the analysed sample matrix and to avoid potential carry over. Depending on the aerosol particle loading and matrix composition the total analysis time can be adjusted.

The Q Exactive™ MS was calibrated using PierceTM ESI Negative Ion Calibration Solution (Thermo Scientific). The mass accuracy of the instrument was routinely checked before analysis using the acceptance criteria of ±1 ppm. LC-MS data was processed using TraceFinder (version 4.2) software package (Thermo Fisher Scientific).

The method was developed and assessed by testing the following elements: linearity, dynamic range (lower limit of quantification (LLOQ) to upper limit of quantification (ULOQ)), accuracy, precision and matrix effects.

Linearity was assessed by evaluating deviation of standards from the nominal concentration and evaluating the slope, intercept, and coefficient of determination (r^2) of the weighted 1/concentration linear regression lines. A series of diluted standard stock solutions of EPA-533PAR mixture containing 25 native PFAS at 7 concentration levels in the range 0.1–10 pg/mL were used. Calibration plots were prepared by calculating area ratios of tested analytes to corresponding ^{13}C labelled compounds serving as internal standards, spiked at 5 or 20 pg/mL and plotted against the corresponding concentration of native compounds and fitted with linear regression.

LOD and LOQ are defined as the lowest concentration of the analyte that can be reliably detected and quantified, respectively. There are several widely accepted approaches for calculating LODs and LOQs, which include but are not limited to assessment of (1) standard deviation of the blanks, (2) standard deviation of response and the slope, (3) the signal-to-noise (*s/n*) ratio and (4) 'visual' evaluation (CPMP/ICH/381/95 ICH, 1995). The most commonly applied method for estimating LOD reported in the literature is establishing *s/n* ratios (Sanchez, 2018). However, this method has significant limitations, e.g., noise may change even over limited periods, it mainly considers peak height measurements, ignores "chemical" noise originated by variations of the signal arising from sample homogeneity and can dramatically change by eventual smoothing or thresholding treatments of the raw data (Desimoni and Brunetti, 2015). In this work, we employed QE Orbitrap MS in SIM mode, which generally provides a very low or no background MS noise and thus if *s/n* is used for estimation of LOD it will provide infinite values. Therefore, the method LOD and LOQ were established using the standard deviation of the response and the slope, calculated using Eqs. (1) and (2).

$$\mathrm{LOD} = 3.3\,\sigma/\mathrm{Slope} \quad (1)$$

$$\mathrm{LOQ} = 10\,\sigma/\mathrm{Slope} \quad (2)$$

where: σ = the standard deviation of the response at low concentrations

Slope = the slope of the calibration curve.

Accuracy was evaluated by calculating the percent deviation from the nominal concentration, and is reported as relative error (RE, %). Precision was determined by calculating the coefficient of variation (CV, %) of replicates within one sample run (intra-day) and between sample runs (inter-day). As per analytical method validation guidelines (e.g., US FDA, 2019; ICH M10, 2019), the mean RE and CV values should be within 15% of the nominal value, except at the Lower Limit of Quantification (LLOQ), where it should be within 20% of the nominal value.

2.8. Air mass trajectories

48-h air mass back-trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) dispersion model (Stein et al., 2015; Rolph et al., 2017) at 500 and 1000 m a.g.l. (above ground level) over the previous 48 h. The results are shown in Figs. S3 and S4 of the SI.

3. Results

3.1. Method development

The summary results from the method validation are presented in Table 2. A typical LC-MS extracted ion chromatogram showing separation of the PFAS standard mixture at 1 pg/mL is shown in Fig. 1. Although, this standard mixture contains 25 PFAS analytes, in this study we only focus on 16 compounds (listed in Table 2) that are detectable by the applied chromatographic and MS conditions. In this work, we used a Hypersil GOLD aQ Column C18 pre-concentration column as an on-line SPE column for PM analysis. This column showed good performance for preconcentrating and recovery of perfluorinated carboxylates and sulphonates in other than PM matrices i.e., drinking and surface waters (Mazzoni et al., 2015; Franke et al., 2019). It allows injection of large sample volumes (up to 1 mL) into LC separation column compared to conventional injection systems, where injection volumes are generally varied between 5 and 25 μL and thus substantially improving method detection limit (Mazzoni et al., 2015; Choi et al., 2016).

A substantial part of the method development was dedicated to sample preparation and extraction. Considering that PFAS can possibly be present in analytical equipment components and consumables (especially in Teflon® containing materials) used during sample preparation and analysis, these components can potentially lead to analytical artifacts e.g., increased blank values and overestimation of PFAS in analysed samples. On the other hand, it has been suggested that glass material (e.g., glass vials) and syringes can potentially adsorb PFAS on their surfaces leading to underestimation of these compounds in analytical samples (ISO, 2009; Shoemaker et al., 2009). As a solution, it has been suggested that these components are substituted with polypropylene (PP) bottles, vials and screw caps (ISO, 2009; Shoemaker et al., 2009). Although this could be suitable for 100% aqueous samples, the presence of an organic solvent in the extracts can potentially lead to leaching out other impurities e.g., glycerol monopalmitate, glycerol monomargarate, Irganox 1010 (Hill et al., 2018; Blázquez-Blázquez et al., 2020) that can accumulate in the system and significantly interfere with the MS analysis by increasing MS background level and affect the detection limit for PFAS with low ionisation efficiencies. This is especially concerning when analysing samples -with potentially low concentrations, such as atmospheric particles and when using semi-targeted or nontargeted screening. Recent study by Lath et al. (2019) examined sorption losses from aqueous PFOA solutions in contact with different commonly used materials in centrifuge tubes (glass and plastics). Contrary to suggestions in the previous literature, Lath et al. indicated that the greatest sorption losses for PFOA occurred on PP (as well as other plasticware i.e., polystyrene (PS), polycarbonate (PC)) whereas losses on glass tubes were much lower.

One of the suggested solutions for reducing the loss of PFAS to glass surfaces, is to add methanol to the aqueous extracts or rinse glassware with methanol to remove any residual analytes that might be lost to the container walls (Sanan and Magnuson, 2020; Shoemaker and Tettenhorst, 2018). However, Sanan and Magnuson (2020) indicated that using methanol during on-line SPE can lead to potential losses of short-chain and more hydrophilic PFAS due to lowered retention by the SPE. In contrast, the authors showed increasing recovery for PFAS with chain lengths above eleven carbons (i.e., PFUdA) with higher methanol percentages, which peaked at

Table 2
Method validation parameters.

PFAS	LOD pg/mL	pg/mL	%Recoveries ± SD		Linearity		[PFAS] = 0.3 pg/mL		[PFAS] = 0.75 pg/mL		[PFAS] = 1.5 pg/mL		[PFAS] = 6 pg/mL	
	pg/mL		[PFAS] = 6 pg/mL	[PFAS] = 15 pg/mL	Range, pg/ml	R^2	Accuracy, RE%	Precision, CV%	Accuracy, %	Precision, CV%	Accuracy, RE%	Precision, CV%	Accuracy, RE%	Precision, CV %
PFBA	0.24	0.80	97.7 ± 3.9	98.7 ± 0.5	0.1–10	0.996	2.1	10.6	−1.6	7.1	1.2	6.7	7.2	5.5
PFPeA	0.37	1.23	106.5 ± 11.4	107.5 ± 6.4	0.2–20	0.997	>20	>20	>20	>20	14.4	8.2	12.7	4.1
L-PFBS	0.08	0.26	104.0 ± 0.9	100.0 ± 2.8	0.1–10	0.996	11.0	4.7	5.3	3.9	14.5	8.2	10.3	4.9
4:2 FTS	0.27	0.89	104.5 ± 1.9	98.6 ± 0.8	0.1–10	0.997	15.6	7.8	2.0	4.6	5.8	3.0	−4.5	1.1
PFHxA	0.33	1.12	108.1 ± 5.0	97.9 ± 3.1	0.1–10	0.996	2.3	16.5	0.6	14.7	7.9	5.2	6.1	3.4
L-PFPeS	0.17	0.58	104.1 ± 3.8	99.3 ± 5.3	0.1–10	0.997	>20	>20	3.8	2.6	9.1	3.5	−6.7	1.5
PFHxS	0.15	0.51	103.1 ± 0.6	100.6 ± 3.6	0.1–10	0.996	3.6	9.9	1.3	5.4	11.3	3.2	7.0	1.1
PFHpA	0.17	0.58	106.3 ± 2.4	97.0 ± 2.7	0.1–10	0.995	4.1	14.9	3.1	9.9	4.4	5.0	−0.2	1.8
6:2 FTS	0.17	0.58	105.6 ± 0.5	97.9 ± 2.3	0.1–10	0.998	5.5	14.6	1.0	12.0	0.6	5.8	9.4	1.6
PFOA	0.18	0.60	104.4 ± 1.4	97.7 ± 0.9	0.1–10	0.995	12.3	13.0	7.5	12.1	3.7	14.6	7.8	1.7
L-PFHpS	0.16	0.54	95.5 ± 8.6	100.3 ± 3.1	0.1–10	0.995	0.3	7.9	2.5	6.5	6.3	3.6	9.6	2.1
PFNA	0.19	0.63	105.3 ± 1.2	96.6 ± 6.16	0.1–10	0.996	9.0	12.8	9.0	8.8	3.1	13.7	2.8	2.2
PFOS	0.11	0.38	113.3 ± 9.3	96.3 ± 2.4	0.1–10	0.995	6.4	14.6	4.1	2.3	13.1	4.8	2.1	2.4
8:2 FTS	0.27	0.90	109.5 ± 10.6	103.1 ± 1.9	0.1–10	0.995	−14.3	14.7	−4.2	12.3	13.0	10.9	2.0	7.7
PFDA	0.39	1.30	99.8 ± 8.5	101.5 ± 1.6	0.5–20	0.995	>20	>20	>20	>20	>20	>20	13.6	1.9
PFUdA	0.51	1.69	95.9 ± 12.6	96.8 ± 15.9	0.5–20	0.997	>20	>20	>20	>20	>20	>20	11.0	4.9

50% methanol. In this work we investigated the effect of methanol content on PFAS recovery by analysing water samples containing 10–50% of methanol, fortified with PFAS mixture at 2 pg/mL and mass labelled ^{13}C-PFAS internal standard mix at 5 pg/mL. Similar to the work of Sanan and Magnuson (2020), we observed increased recoveries at higher methanol content for larger chain PFAS; however, in our study this effect was observed even for compounds with 9 carbon length chain. On the other hand, increasing methanol content significantly decreased recoveries (chromatographic intensities) of short chain PFAS with PFBA, PFPeA, L-PFBS and 4:2 FTS being the most affected (Fig. 2). Interestingly this effect was even more pronounced for corresponding isotopically labelled ^{13}C-PFAS (Fig. S2), with a complete loss of M2-4:2 FTS above 30% of the methanol content. Such unexpected behaviour was confirmed by repeating this experiment and checking for potential shift in retention time caused by a change in solvent composition.

Considering that shorter chain PFAS have lower ionisation efficiencies (as shown by chromatographic intensities, see Fig. 1) than those of larger chain compounds and are appreciably more impacted by increased methanolic content, a 20:80 v/v (methanol:water) ratio was chosen for the online SPE organic mobile phase composition in this study. The difference with Sanan and Magnuson (2020) work can be explained by the difference in the sorbent type used in SPE trap cartridges in this study, i.e., polar endcapped C_{18} stationary phase, which is designed to improve retention of polar compounds in highly aqueous solvents. While C18 polar endcapped stationary phase has a greater selectivity for acidic compounds (Layne, 2002), WAX stationary phase with positively charged diamino ligand has a selective affinity for anionic compounds. PFAS exist in multiple ionic states (e.g. acids, cations, anions) (Blake and Fenton, 2020), so both columns have certain advantages and disadvantages for analysing these pollutants depending on the state they are present in the screened samples. It has been reported that resolution of the peaks for the shortest chain PFAS analytes (including PFBA, HFPO-DA, and PFBS) using WAX SPE requires high pH (~10), which might compromise both SPE and analytical column lifetime (Sanan and Magnuson, 2020). C18 polar endcapped column was selected in our study as it provides very good retention of polar analytes, enhanced hydrogen bonding and silanol activity, increased selectivity for acidic compounds, and increased retention for basic compounds at low pH without a compromise in peak shape (Layne, 2002). Moreover, in our study lower concentration levels of PFAS i.e., 2 pg/mL (equivalent of 2 ng/L) were used for assessment compared to 4–100 ng/L in Sanan and Magnuson (2020).

Solvent extraction of $PM_{2.5}$ from substrates generally involves a filtration step which could be a potential source of contamination by PFAS. Extraction of aerosol from Quartz Fibre filters commonly results in significant amounts of debris as well as non-soluble materials, which need to be removed to avoid an LC column and ESI needle blockage. PTFE membrane filter discs are often used to remove these non-soluble particulates (e.g., Cui et al., 2019; Kourtchev et al., 2016; Wolf et al., 2020). Although centrifugation can also be used to remove these particulates, this step would require transfer of extract into a suitable glass or plastic container, which could lead to additional contamination or losses of analytes. Therefore, in this work we evaluated 0.45 μm Iso-Disc PTFE filters for the potential to leach out PFAS compounds and act as a surface for adsorption of PFAS. The leaching potential was evaluated by purging the PTFE filter with three volumes of 5 mL water:methanol (80:20, v/v) solution and comparing obtained chromatographic areas with those from unfiltered water: methanol solutions. Among 17 tested analytes, four PFAS, i.e., PFOA, PFNA, PFHpA and PFDA were observed in the 1st filter wash solution with analyte areas 2–7 times higher than those in the unfiltered solution. The chromatographic response for these substances dropped to the unfiltered solution levels after the second wash, indicating that the applied filters can be a source of PFOA, PFNA, PFHpA and PFDA, but purging these filters with a methanolic solution reduces the artifacts to a background level. Five individual filters from the same batch were tested and provided variation between replicates from 14 to 21% (based on relative standard deviation).

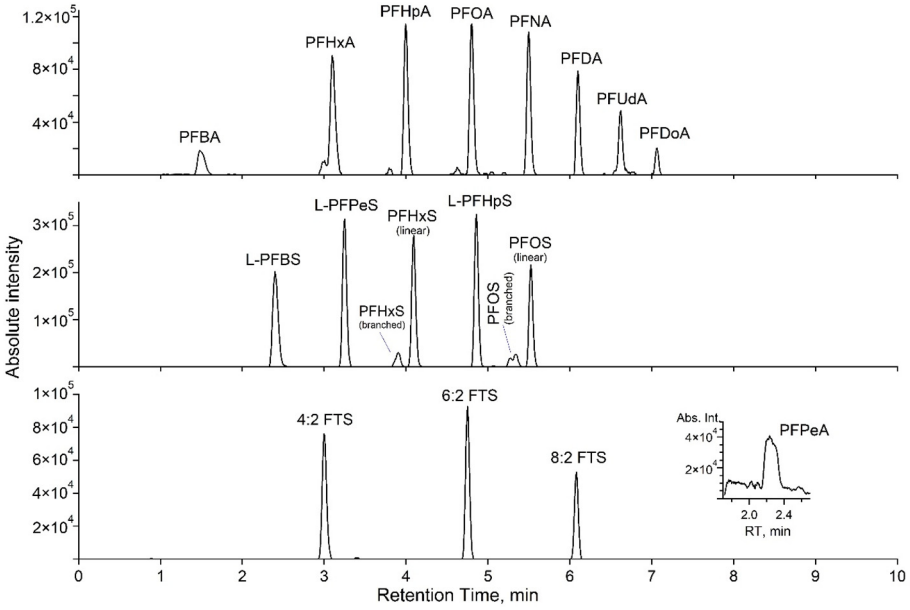

Fig. 1. Typical LC-SIM-(−)ESI-HRMS of a PFAS mixture (water:methanol ratio of 80:20 (v/v)) injected at 1 pg/mL. The injection volume is 1 mL.

The potential of PTFE filters to serve as a sorption surface for PFAS compounds was tested by filtering water:methanol (80:20, v/v) solution fortified with PFAS mixture at 2 pg/mL and ^{13}C-PFAS IS mixture at 5 pg/mL using a prewashed PTFE filter with two volumes of water:methanol (80:20, v/v) solution. Unfiltered PFAS solutions at the same concentration level were used as control samples. For the majority of PFAS analytes the recoveries varied between 96 and 112% (Fig. 3), within the accuracy of the method. The highest values >100% were observed for PFUdA and PFDA during the filtration step, suggesting that PTFE filters can potentially contribute to leaching these species during sample filtration.

3.1.1. Linearity

The linearity of the dynamic range was demonstrated for most of considered analytes ($R^2 \geq 0.995$), except for PFDA, PFUdA and PFPeA. Therefore, concentration ranges for the latter compounds were increased to 0.2–20 pg/mL and 0.5–20 pg/mL (see Table 2) until a linear response with $R^2 \geq 0.995$ was achieved.

3.1.2. LOD and LOQ

Depending on the analyte, the estimated method LOD and LOQ varied between 0.08 and 0.5 pg/mL and 0.25 and 1.7 pg/mL, respectively. The LOD and LOQ for each individual analyte are shown in Table 2.

Expressing method LOD through mass of PFAS per extract volume (pg/mL) is a more reliable approach than that per air volume (pg/m^3) for several reasons. Firstly, the contribution of OC to ambient $PM_{2.5}$ mass concentration can vary significantly (from 20 to 90%), depending on location and sampling period (Jimenez et al., 2009). Secondly, the contribution of specific organic compounds to particle mass and thus the air volume required for analysis can also be impacted by the same parameters. Moreover, emission of unique pollutants can occur over short periods of time (e.g., an

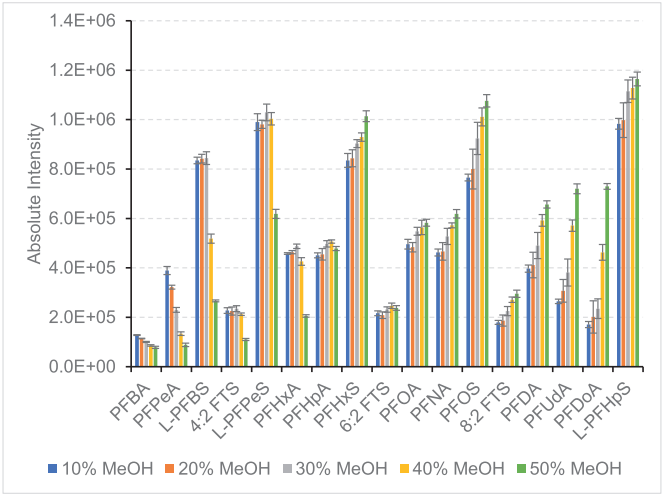

Fig. 2. Effect of methanol (MeOH) content in the solution loaded to SPE-LC-HRMS on chromatographic intensities of 17 PFAS. Standard deviation bars correspond to variations within 5 replicate solution injections at 2 pg/mL. Due to unexpected behaviour of the corresponding isotopically labelled compounds used as internal standards, the data is not corrected using internal standards (see Fig. S3 for details).

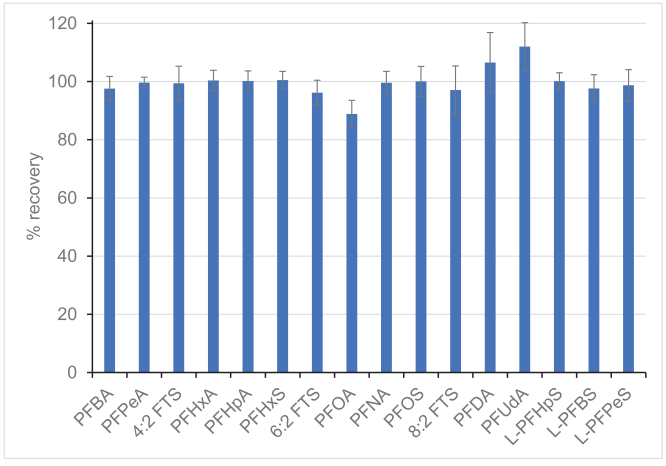

Fig. 3. Percent recovery of 16 PFAS after filtration with a prewashed Iso-disc 0.45 μm PTFE syringe filter. Recoveries were calculated using the formula: $\frac{A}{B} * 100\%$, where *A* and *B* are average ratios of PFAS chromatographic areas to that from the ^{13}C-PFAS internal standard obtained from the filtered solution and B from unfiltered solution, respectively. The results are obtained by using four individual filters from the same batch.

air plume from waste incineration) while ambient filter sampling is generally set to a specific time interval (e.g., 12 h or 24 h) which often exceeds these time periods and can lead to underestimation of a pollutant concentration expressed per volume of air (m^3) when total filter collection time is considered.

3.1.3. Accuracy and precision

The Quality Control (QC) samples used to evaluate method accuracy and precision were prepared at 4 concentration levels within the calibration curve range: at LLOQ level, within three times of the LLOQ (low QC), around 30% of the calibration curve range (medium QC) and at least 60% of the ULOQ (high QC): 0.3 pg/mL, 0.75 pg/mL, 1.5 pg/mL and 6 pg/mL.

Twelve out of seventeen tested PFAS showed acceptable accuracy and precision (CV, % and RE below 20%) at 0.3 pg/mL and for all evaluated analytes at 6 pg/mL (Table 2).

3.1.4. Matrix effect

It has been previously demonstrated that inorganic salts and organic matter can impact on analysis and accurate measurements of PFAS (Sanan and Magnuson, 2020). These types of chemical species are usually present in ambient $PM_{2.5}$. For example, inorganic components (e.g., Na^+, Cl^-, $Ca2^+$, NH_4^+, and SO_4^{2-}) and organic matter are important constituents of atmospheric PM (Pye et al., 2020) and depending on the sampling location can significantly contribute to a total particle mass and thus potentially impact the analysis and quantitation of PFAS.

Therefore, in this study we evaluated the analytical method for matrix effects using ambient $PM_{2.5}$ extracts. Samples that showed lowest concentration of PFAS were selected and spiked with a native PFAS test mixture at two concentration levels (low and high levels, see Table 3). In addition, the samples were spiked with IS (^{13}C-PFAS internal standard mix) at 5 pg/mL. The spiking lowest level of PFAS in the matrix was at 6 pg/mL, which is the concentration when all analytes showed CV and RE below 15% in the "non-matrix" samples. The matrix effect was estimated by comparing the response of the analyte in standard solution prepared in water: methanol (80:20, v/v) to that of $PM_{2.5}$ extract spiked with the analyte at the same concentration using Eq. (3).

$$Matrix\ Effect(\%) = \left(\frac{B}{A} - 1\right) \times 100 \quad (3)$$

where, A is a peak response of the analyte in the solvent standard and B is a peak response of the analyte in the matrix matched standard (i.e., spiked into the $PM_{2.5}$ sample post-extraction).

When ME<0 then the analyte response is suppressed by the matrix whereas if ME > 0 the analyte response is enhanced by the matrix. It is recommended that an action is taken (e.g., additional sample clean up) if |ME| > 20%, to minimize the error in mis-reporting accurate concentrations (US FDA, 2019). At 6 pg/mL, a slight enhancement for all 16 analytes by the sample matrix was observed (Table 3). At higher spiking level i.e., 15 pg/mL, the ME values for most of the analytes were negative and ranged from −5.6 to 2.4% indicating minimal suppression by the sample matrix. Enhancement at the low concentration level can be explained by the cumulative contribution of PFAS already present in the matrix with that from the spiked solutions. This effect becomes less significant at higher spiking concentrations as the contribution to the total analyte area in the spiked solution becomes smaller. A very small suppression (ME ≤ 5.6%) observed for analytes at higher spiking concentration range and is within the method's accuracy and precision thus it is likely to be related to the method accuracy.

It should be noted that sample matrix composition can be influenced by multiple factors e.g., sampling location and duration, meteorological parameters, presence of atmospheric oxidants and contribution of different pollution sources. Therefore, while the reported ME values can be used as a relative measure of the method performance, these values can be significantly impacted by a sudden and unexpected change in the $PM_{2.5}$ composition due to e.g., change in air masses that can bring other chemical substances to the sampling site. Therefore, setting additional criteria, for example, requiring internal standard recoveries to be 50–150% when compared with calibration standards can be used. If obtained values exceed these criteria, method modifications need to be considered e.g., sample dilution, calibration with standards including matrix match, high salt concentrations, and determining method reporting limits accordingly (Cortese et al., 2020; Sanan and Magnuson, 2020).

3.2. Method application for screening $PM_{2.5}$ sample analysis from urban environments

$PM_{2.5}$ samples from Dublin and Enniscorthy were analysed for 16 target PFAS compounds and their concentrations are shown in Table 4. Eight compounds were observed above the method detection limit. These include PFBA, PFOA, PFOS, L-PFBS, PFNA, and three fluorotelomer sulfonates: 4:2 FTS, 6:2 FTS and 8:2 FTS. It should be noted that PFOS and LBPFS were only observed in samples from Dublin. To the best of our knowledge this is the first study reporting PFAS compounds in $PM_{2.5}$ collected in urban areas in Republic of Ireland (ROI). Previous studies have reported PFAS in PM samples collected at Mace Head Atmospheric Research Station, located on the west coast of the country (Barber et al., 2007; Jahnke and Berger, 2009). In all our ambient samples, the recoveries of internal standards (see Table S2) were within acceptance criteria (50–150%) of the

Table 3
Sample matrix effect at 6 and 15 pg/mL PFAS spiked concentrations. Organic carbon (OC) concentration in the spiked samples with PFAS solutions is 3.9 μg/mL.

PFAS compound	[PFAS] = 6 pg/mL				[PFAS] = 15 pg/mL			
	ME, %	SD	Accuracy, RE%	Precision, CV%	ME, %	SD	Accuracy, RE%	Precision, CV%
PFBA	9.8	4.4	9.7	1.2	−1.7	1.4	2.7	1.3
PFPeA	6.9	2.9	8.1	2.3	−1.4	2.0	2.5	0.9
L-PFBS	12.7	5.9	−4.0	2.8	2.4	3.8	1.5	1.6
4:2 FTS	2.5	2.3	−6.8	2.3	−0.5	2.4	2.9	2.0
PFHxA	10.6	6.7	−5.3	5.7	−4.4	4.2	5.7	1.6
L-PFPeS	4.8	4.1	−11.1	4.8	1.5	2.8	0.5	2.7
PFHxS	5.6	2.8	1.0	2.1	−0.5	2.6	1.4	2.3
PFHpA	7.3	4.5	−7.5	3.5	−2.0	1.0	3.5	0.9
6:2 FTS	5.8	1.0	11.0	0.9	−0.2	2.2	2.5	3.0
PFOA	4.4	3.9	8.1	3.5	−1.0	2.2	1.8	1.4
L-PFHpS	4.8	3.5	16.0	3.3	−3.8	7.6	0.6	4.8
PFNA	8.1	2.5	−5.6	1.7	−1.4	2.3	3.8	3.0
PFOS	5.6	1.5	12.0	1.7	−1.0	2.5	2.7	1.2
8:2 FTS	5.4	7.3	−3.9	0.6	0.0	2.6	1.8	1.5
PFDA	7.4	2.6	5.2	1.6	−1.3	4.3	2.7	2.5
PFUdA	12.8	3.9	8.5	2.9	−5.6	2.2	5.5	2.3

ME and SD are Matrix Effect and Standard Deviation, respectively.

Table 4
Sampling period, air volume, OC and PFAS concentrations in analysed $PM_{2.5}$ samples from Enniscorthy and Dublin, Ireland.

Sample name	Sampling period dd-mmm hh-min		Air volume, m^3	OC, $\mu g/m^3$	PFAS concentration, pg/m^3							
	Start	Finish			PFBA	L-PFBS	4:2 FTS	6:2 FTS	PFOA	PFOS	PFNA	8:2 FTS
ENY13_14*	07-Feb 15:00	08-Feb 06:59	479.5	1.10	–	–	0.013	0.121	0.056	–	0.022	0.074
ENY15_16*	08-Feb 07:00	08-Feb 22:59	479.5	0.79	–	–	0.009	0.078	0.052	–	0.020	0.067
ENY17_18*	08-Feb 23:00	09-Feb 14:59	479.5	0.75	0.094	–	0.010	0.067	0.050	–	0.020	0.064
ENY19_20*	09-Feb 15:00	10-Feb 06:59	479.5	2.04	0.199	–	0.027	0.140	0.026	–	0.012	0.151
ENY21_22*	10-Feb 07:00	10-Feb 22:59	479.5	3.06	0.091	–	0.023	0.140	0.010	–	0.009	0.103
ENY23	10-Feb 23:00	11-Feb 06:59	239.5	1.17	–	–	–	–	0.749	–	0.007	0.006
ENY24	11-Feb 07:00	11-Feb 14:59	239.5	2.82	–	–	–	–	0.506	–	0.004	0.063
ENY25	11-Feb 15:00	11-Feb 22:59	239.5	11.97	–	–	–	–	1.140	–	0.004	0.061
DUB11_12*	06-Feb 18:00	07-Feb 17:59	719.5	1.52	0.092	0.006	0.015	0.081	0.042	0.012	0.023	0.076
DUB 13_14*	07-Feb 18:00	08-Feb 17:59	719.5	1.27	0.074	0.006	0.012	0.071	0.041	0.015	0.030	0.141
DUB 15_16*	08-Feb 18:00	09-Feb 17:59	719.5	1.11	0.065	0.005	0.016	0.077	0.029	0.006	0.010	0.077
DUB 17_18*	09-Feb 18:00	10-Feb 17:59	719.5	2.12	0.032	0.006	0.013	0.082	0.037	0.007	0.029	0.118
DUB 19_20*	10-Feb 18:00	11-Feb 17:59	719.5	1.69	0.012	0.007	0.012	0.081	0.069	–	0.066	0.067
DUB 21	11-Feb 18:00	12-Feb 05:59	359.5	4.04	–	–	–	0.015	1.524	–	0.038	0.045
DUB 22	12-Feb 06:00	12-Feb 17:59	359.5	2.90	–	–	–	0.016	3.209	–	0.049	0.059
DUB 23	12-Feb 18:00	13-Feb 05:59	359.5	2.41	–	–	–	0.024	3.322	–	0.055	0.053
DUB 24	20-Feb 18:00	21-Feb 05:59	359.5	1.73	–	–	–	0.025	1.970	–	0.030	0.029

ENY and DUB correspond to samples from Enniscorthy and Dublin, respectively. The samples from Enniscorthy and Dublin were collected in 2020 and 2019, respectively. Samples marked with '*' correspond to pooled filter samples. Air volume values are cumulative numbers corresponding to total air passed through all filter portions used for analysis.

calibration standards, suggesting that potential matrix changes caused by variability of emission sources at both sites was not significant.

PFOA was the most abundant PFAS with concentrations in the range 0.03 and 3.32 pg/m^3 in Dublin and 0.01–1.14 pg/m^3 in Enniscorthy. PFOA was previously identified as the dominant PFAS in PM collected in several European countries (e.g., Barber et al., 2007), US (e.g., Zhou et al., 2021) and Asia (e.g., Lin et al., 2020). The observed concentrations of PFOA in our study are mostly lower than those reported from other European urban and semi-rural sites. For example, reported average concentrations of PFOA in 7-day integrated atmospheric samples from Hazlerigg, Lancaster, England (semi-rural), Manchester, (urban), Mace Head, ROI (rural) are 101 pg/m^3 (552 pg/m^3 in February–March 2005), 15.7 (341 pg/m^3 in February–March 2005) and 8.9 pg/m^3, respectively (Barber et al., 2007). Such high concentrations of PFOA at Hazlerigg and Manchester, were attributed to the proximity of the sampling sites to a fluoropolymer production plant at Thornton–Cleveleys. Interestingly, PFOA concentrations at both Dublin and Enniscorthy were on average lower than those reported for the regional background site at Mace Head where PFAS concentrations were correlated with air masses that spent significant time in-land, and potentially linked to PTFE coating plants in Galway (Barber et al., 2007).

Fluorotelomer sulfonates i.e., 4:2 FTS, 6:2 FTS and 8:2 FTS, were the second most prominent class of compounds after PFOA, with ΣFTS average concentrations of 0.16 and 0.14 pg/m^3 in Enniscorthy and Dublin, respectively. The observed concentration of 6:2 FTS at both Dublin and Enniscorthy (0.05 and 0.08 pg/m^3, respectively) are higher than those reported at Mace Head (<0.02 pg/m^3) and Hazlerigg (Feb–March 2005, 0.01 pg/m^3) but lower than in Manchester (1.2 ng/m^3) and Hazlerigg in (Nov 2005–Feb 2006, 1.9 pg/m^3) (Barber et al., 2007). Higher concentrations of 6:2 FTS in $PM_{2.5}$ were measured in residential and industrial areas of Elche and Alicante (Spain) during April–July 2010 by Beser et al. (2011). The later study emphasised that 6:2 FTS was the most frequently detected compound (>60%) in 41 analysed samples.

There are several studies reporting 4:2 and 8:2 fluorotelomer olefins and fluorotelomer alcohols in atmospheric particles (Barber et al., 2007; Li et al., 2011); however, to the best of our knowledge this is the first study reporting 4:2 and 8:2 fluorotelomer sulfonates in ambient $PM_{2.5}$.

PFOS and L-PFBS were observed only in Dublin samples at average concentrations of 10 fg/m^3 and 6 fg/m^3, respectively. It is worth noting that both compounds were only observed in the pooled samples (above LOD, and at a concentration three times greater than that found in blanks) indicating that their detection most likely requires sufficient particle mass to be determined by the method. On average, the pooled samples have almost 50% larger volume of air passed through the filter compared to unpooled samples (see Table 4). In general, higher concentrations of PFOS and L-PFBS were reported in the literature for both compounds (Barber et al., 2007; Zhou et al., 2021). For example, Barber et al. (2007) detected PFOS at Mace Head, Hazlerigg and Manchester at average concentrations 1.8, 7.1 and 1.6–44.5 pg/m^3, respectively. In a more recent study of $PM_{2.5}$ in the US during 2018–2019, PFOS was detected at average concentration of 4.75 pg/m^3 and 1.37 pg/m^3 in Wilmington and Research Triangle Park, North Carolina, respectively. With regards to PFBS, significantly higher concentrations were observed in Mace Head, Hazlerigg, and Manchester at average concentrations below 1.0, 2.6 and 1.6 pg/m^3, respectively.

PFNA was observed in all of the $PM_{2.5}$ samples collected in Dublin and Enniscorthy, with average concentrations of 12 and 37 fg/m^3, respectively. This compound was previously observed in PM collected at the remote background site in Mace Head; however, at significantly higher concentrations (average 3.3 pg/m^3, Barber et al., 2007). Moreover, higher PFNA concentrations were reported for Hazlerigg (Feb-March 2005, 13.8 pg/m^3) and Manchester (26.6 pg/m^3) during February–March 2005. In addition, higher concentrations of PFNA (range 1.4–11.8 pg/m^3) were reported for $PM_{2.5}$ at the coastal sites in Elche and Alicante, Spain during 2011 (Beser et al., 2011).

4. Discussion

Our observation of PFOA in $PM_{2.5}$ collected at both sampling sites and PFOS in Dublin raises a question about their potential emission sources, since the production of both compounds has been phased out and restricted in Europe (OECD, 2019). Zhou et al. (2021) also observed PFOS and PFOA in $PM_{2.5}$ at several locations in the US almost two decades after their production was phased out there. Zhou et al. (2021) listed several possible sources of PFOA and PFOS in their atmospheric samples, which included long-range transport from countries where these chemicals are still produced, volatilisation from contaminated soils and sediments, landfills, rivers, oceans, and biota due to legacy manufacturing and continued use of PFOS- and PFOA-containing products, as well as microbial degradation of precursors to more stable end products such as PFOS.

Moreover, additional sources of PFOS and PFOA in $PM_{2.5}$ include emissions from activities at local fire departments, airports, and military facilities involving the use of PFOS-based aqueous film forming foam (AFFF) from old stock (Young et al., 2021; Zhou et al., 2021). A further possible source is water-to-air transfer via sea spray aerosol (SSA) emission, which

was recently suggested to play a role in the contribution of PFAS to atmospheric aerosol. Laboratory simulation experiments have demonstrated that PFAS concentrations in submicron SSA can be several orders of magnitude higher than that in water (Johansson et al., 2019; Sha et al., 2021). Using laboratory-derived enrichment factors and reported median concentrations in seawater, the estimated fluxes of PFOA and PFOS from SSA to the atmosphere were found to be comparable to direct emission from manufacturing sources and degradation from volatile precursors. A recent study by Sha et al. (2022) screened more than 100 atmospheric samples collected between 2018 and 2020 from two coastal sites in Norway and found a strong correlation between the SSA tracer ion (Na^+) and PFAS concentrations, supporting the assertion that SSA is an important source of atmospheric PFAS especially at coastal areas. Additional possible sources of PFOA at Dublin sampling site may include a waste incineration facility and power plants located to the East of Pearse street in Dublin.

Although all of the sources listed above could potentially be responsible for the PFAS observed at the sites studied in this work, the higher concentration of PFOA in samples from Dublin compared to Enniscorthy and the presence of PFOS only in Dublin, supports the proposed hypothesis of SSA emissions as a significant source for both species. The sampling site in Dublin is only 2–3 km from the Irish sea, while Enniscorthy is 30–35 km from the coast. During the sampling period air masses arriving at Enniscorthy were mainly from a westerly direction, passing over land and any marine aerosols were thus diluted or influenced by inland emission sources. The air masses experienced in Dublin also predominantly originated from a westerly direction, but they were more dispersed and the impact of the sea is still expected to be noticeable at such short proximity to the coast (see Supplimentary Data).

Observation of the fluorotelomer sulfonates i.e., 4:2 FTS, 6:2 FTS and 8:2 FTS in the samples deserves further attention, as these compounds were introduced as substitutes for the more toxic species, perfluorooctane sulfonate (PFOS) (Wienand et al., 2013; Fath et al., 2016). It is worth noting that FTS were shown to be resistant to ozonolysis treatment processes (Boiteux et al., 2017). On the other hand, 6:2 FTS was found to be completely degraded under ultraviolet (UV) irradiation with hydrogen peroxide (Yang et al., 2014). Although oxidation via reaction with ozone and the hydroxyl radical (which is formed though photolysis of H_2O_2) are major removal processes for hydrocarbons in the atmosphere, the photolysis study by Yang et al. (2014) did not report the intensity of the lamps that were used to oxidise 6:2 FTS. Another study reporting successful photochemical degradation of 6:2 FTS was conducted using a mercury lamp with wavelength peak at 254 nm (Jin et al., 2017), which has little relevance to the lower tropospheric oxidative chemistry. Therefore, it is difficult to extrapolate these results to the potential removal processes for FTS in the atmosphere and link their presence to either fresh emissions or long-range transport. Recent work on analysis of PFAS in dust and wipe samples collected at a fire station in Massachusetts (USA), reported all three FTS, with 6:2 or 8:2 FTS as the most predominant species (Young et al., 2021). It is difficult to determine the exact emission source for these species in both Enniscorthy and Dublin. Even though the sampling site in Enniscorthy is in close proximity to the fire stations, observation of 8:2 FTS in all samples (from day and night and in both Enniscorthy and Dublin) suggests a continuous emission source, at least for this species, which is highly unlikely to be a fire station. 4:2 FTS and 6:2 FTS were mainly observed in the pooled samples suggesting there is likely insufficient particle loading in the unpooled extracts to provide FTS for detection by the analytical method. However, it must be noted that one of the unpooled samples from Enniscorthy (i.e., from 11 February) had almost 50% more OC loading than that of the highest in the pooled samples. Interestingly, occurrence of both 4:2 FTS and 6:2 FTS was anticorrelated with PFOA which was mainly observed in the unpooled samples.

The concentration of PFNA in the Dublin samples was, on average, three times higher concentration than that observed in Enniscorthy (Table 4). PFNA occurrence in the environment was previously attributed to direct manufacturing discharges, transport of sea spray aerosols and degradation of precursors (Johansson et al., 2018). PFNA is used as a surfactant for the production of the fluoropolymer polyvinylidene fluoride (Prevedouros et al., 2006) and it can be formed from the degradation of 8:2 fluorotelomer alcohol (Henderson and Smith, 2007) as well as from other PFAS precursors in the atmosphere (Thackray et al., 2020). The higher concentration of PFNA observed in Dublin can potentially be explained by the higher number of industrial activities in the location (as expected for a larger city) and its proximity to the sea.

5. Conclusions

In this work, we present the development and application of a rapid analytical method for determination of 16 PFAS in atmospheric aerosol particles using an on-line SPE-LC-(−)ESI-HRMS. The on-line SPE allows simultaneous sample clean-up from interfering matrices and decreasing limits of detection (LODs) by injecting a large volume of sample (1 mL) into a LC system without compromising chromatographic efficiency and resolution. Analytical aspects that are important for implementation of this method have been assessed and discussed. These include the use of solvents, glassware, and sample filtration. Method limits are comparable to those reported elsewhere for on-line SPE techniques applied to other matrices e.g., water (Sanan and Magnuson, 2020). The method showed good tolerance to the sample matrix and was used for targeted analysis of $PM_{2.5}$ collected at two Irish urban locations, Enniscorthy and Dublin.

Our results indicate that despite some of the toxic PFAS, i.e., PFOS and PFOA, being restricted and phased out from production in Europe and the USA for more than two decades, they are still detected in the environment (air samples), although at significantly smaller concentrations than those reported over a decade ago. While our sample dataset is not extensive, the results suggest that the restriction and control policies have had an impact on the occurrence of these species in atmosphere. Additional longer-term measurements are needed to support this conclusion. It must be noted that in this study we evaluated $PM_{2.5}$ samples that were collected on filters with a relatively low time resolution (8 and 12 h) and combined several filter samples to obtain enough organic material for LC-MS analysis. As a result, the peak concentrations of PFAS could be much higher than the average reported values, especially given the highly episodic nature of some emission sources, such as plumes released from waste incineration plants. It must be noted that this limitation applies to most of the off-line measurement reports.

To our knowledge, this is the first study reporting PFAS in atmospheric $PM_{2.5}$ at urban locations in Ireland. Moreover, this is the first study reporting 4:2 and 8:2 fluorotelomer sulfonates in atmospheric $PM_{2.5}$ samples. Observation of the fluorotelomer sulfonates, which were introduced as "safer" substitutes for toxic PFOA and PFOS, raises a concern about their persistence in the atmosphere and impact on human health. This is especially concerning as more evidence becomes available regarding the toxicity of fluorotelomer sulfonates, coupled with the fact that some of these compounds were recently detected in human blood and biological tissues. Although observed concentrations for PFAS in our study are generally lower than those reported at other locations in Europe and USA, these compounds can potentially accumulate in human organs and the environment leading to long-term exposure to these pollutants. More studies are needed to understand the concentrations and fate of these pollutants in the atmosphere and their potential impact on human health.

CRediT authorship contribution statement

Ivan Kourtchev: Conceptualisation, Methodology, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualisation, Supervision, Project administration. **Stig Hellebust:** Investigation, Resources, Data curation, Writing – review & editing, Supervision, Project administration. **Eimear Heffernan:** Investigation, Resources, Data curation. **John Wenger:** Resources, Supervision, Data curation, Writing – review & editing, Project administration. **Sam Towers:** Resources. **Evangelia Diapouli** and **Konstantinos Eleftheriadis:** Resources and Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155496.

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