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Worldwide trends in tracing poly- and perfluoroalkyl substances (PFAS) in the environment

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ABSTRACT

Numerous poly- and perfluoroalkyl substances (PFAS) have been manufactured and distributed on the world market. Research on PFAS has highlighted their global distribution and impacts on ecosystems and human health. Following regulations and public concern, PFAS production has shifted toward novel molecules in recent years. New classes of PFAS have been identified in the environment and are gaining worldwide attention. The development of an efficient strategy for identification and quantification of emerging PFAS is essential for risk assessment. This review presents and discusses the most recent analytical method development for PFAS in air, water, abiotic solid matrices and biological matrices, and addresses non-target approaches. Various methods are covered including sampling, pre-treatment (enrichment, extraction and clean-up) and instrumental analysis, and their applications, advantages, shortcomings and future needs are explored.

1. Introduction

Over the last decade, research on poly- and perfluoroalkyl substances (PFAS) has shifted from original PFAS classes such as perfluoroalkyl sulphonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) toward new fluorinated compounds possessing one or more perfluoroalkyl (-C_nF_{2n}-) moieties [1]. According to an Organisation for Economic Co-operation and Development (OECD) survey, the Chemical Abstracts Service (CAS) registers more than 4,000 compounds classified as PFAS that are currently distributed on the global market [2]. Kotthoff et al. explored the chemical properties of diverse alternative PFAS and encouraged further research to identify and characterise them [3]. Wang et al. suggested that PFAS research would never converge since (1) it is difficult to assess the risk of PFAS classes due to a lack of information on mixture effects, total burden, individual hazards, mechanisms of action and the presence of numerous known/unknown PFAS, (2) there are not yet effective techniques to detect decreasing levels of PFAS already present in the environment, or those being continuously discharged, and (3) alternatives with similar structures to existing PFAS will be continuously developed and released into the environment [4]. Both reviews emphasise the importance of prioritising PFAS research due to limited time, funds, man-power and other resources.

To discuss future directions regarding the regulation and management of PFAS, more than 50 international scientists and regulators held a two-day workshop in November 2017 [5]. The workshop report recommends global cooperation on more streamlined research including prioritising certain substances, adopting a group-based approach rather than studying individual substances and updating regulations for highly persistent PFAS sub-classes. Previous review articles have discussed analytical method development including sample preparation and instrumental analysis, environmental occurrence and temporal trends [6–13].

In the early stages of PFAS research, methods were developed for the analysis of original PFAS classes including perfluorooctane sulphonic acid (PFOS) and perfluorooctanoic acid (PFOA) in various matrices such as air, water, solid matrices, human samples, wildlife, foods and consumer products [6,7] (Table 1). In accordance with the shift toward manufacturing alternatives, recent research has focused on the identification of new PFAS and the development of

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Abbreviations

AFFF	aqueous film-forming foam
AMAP	Arctic Monitoring and Assessment Program
APCI	atmospheric pressure chemical ionisation
APPI	atmospheric pressure photoionisation
CAS	Chemical Abstracts Service
CI	chemical ionisation
DI	direct injection
DLLME	dispersive liquid-liquid microextraction
dw	dry weight
EI	electron ionisation
ESI	electrospray ionisation
FUSLE	focused ultrasound solid-liquid extraction
GAPS	Global Atmospheric Passive Sampling
GC-MS	gas chromatography-mass spectrometry
GFF	glass-fibre filter
HDPE	high-density polyethylene
HPLC-MS/MS	high-performance liquid chromatography-tandem mass spectrometry
HRMS	high-resolution mass spectrometry
ILOD	instrumental limit of detection
IPE	ion-pair extraction
LLE	liquid-liquid extraction
LOD	limit of detection
LOQ	limit of quantitation
MDL	method detection limit
MLOD	mass limit of detection
MMF-SPME	multiple monolithic fibre solid-phase microextraction
MSPD	matrix solid-phase dispersion
MTBE	methyl tert-butyl ether
ND	not detected
OECD	Organisation for Economic Co-operation and Development
PCI	positive chemical ionisation
PE	polyethylene
PFAA	perfluoroalkyl acid
PFAS	poly- and perfluoroalkyl substances
PFCA	perfluoroalkyl carboxylic acid
PFSA	perfluoroalkyl sulphonic acid
PLE	pressurised liquid extraction
PP	polypropylene
PUF	polyurethane foam
QA	quality assurance
QC	quality control
QFF	quartz-fibre filter
SBSE	stir bar sorptive extraction
SIM	selected ion monitoring
SIP	solvent-impregnated polyurethane foam
SLE	supported liquid extraction
SPE	solid-phase extraction
SPME	solid-phase microextraction
SVOC	semi-volatile organic compound
TBAS	tetrabutylammonium hydrogen sulphate
TFA	trifluoroacetic acid
TOF	time-of-flight
UHPLC	ultra-high-performance liquid chromatography
UPC^2	ultra-performance convergence chromatography
VALLME	vortex-assisted liquid-liquid microextraction
WAX	weak anion exchange
ww	wet weight
WWTP	wastewater treatment plant

methods that can detect, capture and characterise these alternative molecules. However, analytical methods that are cost-effective and environmentally sound, and can cover a wide range of PFAS species, have proven difficult to develop. Lorenzo et al. evaluated publications from 2011 to 2017 on the challenges of analysing emerging persistent organic pollutants in aquatic environments and concluded that analytical methods covering novel PFAS were scarce [9]. Emphasis was also placed on the importance of inter-laboratory comparison and quality assurance using certified reference materials, since these methods must deal with a wide range of compounds in complex matrices. Numerous publications report improvements in high-resolution mass spectrometry (HRMS) techniques and their successful application to PFAS identification and measurements [14,15]. Novel PFAS have been identified by suspected and non-targeted screening of airborne particles [16], water [17], sediments [17] and biological samples [18,19] (Table 1).

This review summarises recent advances in analytical method development for determination of PFAS in various matrices. It also discusses the advantages and disadvantages of the currently available analytical techniques and their performance characteristics to assist future PFAS research.

2. Air samples

Analytical methods for PFAS outdoor and indoor air samples and airborne particulate matter are summarised in Table 2. There are two review articles on air sampling techniques, published in 2007 [6] and 2009 [7]. These publications cover volatile and neutral PFAS such as fluorotelomer alcohols (FTOHs), perfluoroalkane sulphonamido ethanols (FASEs) and perfluoroalkane sulphonamides (FASAs) in air samples. Typical sampling methods include glass-fibre filters (GFF), quartz-fibre filters (QFF), XAD resin sandwiched by polyurethane foam (PUF) and solid-phase extraction (SPE) cartridges, alone or in combination. Collected PFAS are measured by gas chromatography-mass spectrometry (GC-MS) or high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS).

2.1. Sample collection and preservation

Outdoor and indoor air samples are generally collected by PUF/XAD/PUF using a high-volume air sampler, or by an SPE cartridge using a low-volume air sampler [20,21]. ISOLUTE ENV+ (Biotage AB, Uppsala, Sweden) and Oasis HLB (Waters Inc., Milford, MA, USA) have been widely used to sample neutral PFAS in air. A two-layer SPE consisting of higher carbon (HC)-C18 and weak anion exchange (WAX) material was developed and applied to capture diverse PFAS classes [22]. A typical air sampling volume is 300–2,000 m^3 for outdoor air and 20–200 m^3 for indoor air [6,7]. Sampling volumes for indoor air have decreased to 0.2–8 m^3 in recent studies [20,22,23]. Particulate matter is generally collected on a glass- or quartz-fibre filter [21,24]. Solvent-impregnated polyurethane foam (SIP) developed by Shoeib et al. [25] has been widely used as a passive air sampler for air PFAS monitoring [26] due to its simplicity and low cost. To detect low levels of PFAS in air, eliminating background contamination during washing/preconditioning, storage and transport of samplers is crucial, and indispensable for quality control (QC). For XAD and PUF methods,

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preliminary Soxhlet extraction (24–30 h) is carried out with organic solvent such as methanol, dichloromethane, acetone and petroleum ether, in order to remove contaminants [20]. An SPE cartridge is generally washed with methanol or ethyl acetate and dried with high-purity nitrogen gas before use, and samplers are typically wrapped with aluminium foil or placed in a polypropylene (PP) container and stored at −20°C until analysis [6,7,9,20,22,23].

2.2. Extraction, clean-up and concentration

Soxhlet extraction with organic solvent such as acetone and petroleum ether [20,25,27] and pressurised liquid extraction (PLE) [21] are conventional techniques for XAD and PUF extraction. PFAS collected on an SPE cartridge are usually extracted by organic solvents selected in accordance with target PFAS properties. Neutral PFAS collected by HLB or ISOLUTE ENV + cartridges are generally eluted with methanol [23], whereas ionic PFAS such as PFCAs, PFSAs and polyfluoroalkyl phosphate diesters (diPAPs) collected by a WAX cartridge are usually eluted with methanol containing ammonium solution [22]. For SIP, collected PFAS are subjected to Soxhlet extraction with appropriate organic solvents such as acetone/petroleum ether (1:1), methanol or ethyl acetate, or cold column extraction with ethyl acetate [28,29]. Additional clean-up by ENVI-Carb (Supelco, Bellefonte, PA, USA) is employed in some cases [28,29]. Airborne particulate matter collected on filters is generally subjected to Soxhlet extraction with dichloromethane or ultrasonic extraction with methanol [24,30].

2.3. Instrumental analysis and measurement results

Neutral PFAS are usually detected by GC-MS with either electron ionisation (EI) or chemical ionisation (CI) in selected ion monitoring (SIM) mode [22,25,27–29]. The major detection method for ionic PFAS uses HPLC-MS/MS with electrospray ionisation (ESI) [22,28,29]. For GC separation, most studies employed a WAX column such as DB-WAX (Agilent) with a column size of 0.25 mm in diameter and 30 or 60 m in length and a film thickness of 0.25 μm [20,23,28,29]. Ionic PFAS are generally separated by a C18 column with an aqueous and methanol/acetonitrile mobile phase containing 5–50 mM ammonium acetate. To increase the recovery of short-chain PFCAs (C2–C4), Tian et al. suggested the use of an ion-exchange column (Shodex RSpak JJ-50 2D; Showa Denko America, Inc., New York, NY, USA) for HPLC separation [28].

The Global Atmospheric Passive Sampling (GAPS) survey investigated the global occurrence and long-range atmospheric transport of PFAS [31]. In the survey, SIP samplers were used to monitor various PFAS including PFCAs, PFSAs, FASAs, FASEs and FTOHs at 21 locations around the world. In the 2009–2015 GAPS survey, FTOHs were detected at high concentrations ranging from <0.4 to 21 pg/m^3 in the polar region, and 40–238 pg/m^3 in urban sites [26]. PFSA concentrations in outdoor air displayed increasing trends ($p < 0.001$), but there were no such trends for FTOHs, FASAs, FASEs and PFCAs from 2009 to 2015 [26]. PFAS in Arctic air were collected with an active sampler (GFF + PUF/XAD/PUF) and monitored in the Arctic Monitoring and Assessment Program (AMAP) [32]. In the survey conducted at Alert, Canada (2006–2014), FTOHs, FASAs and FASEs were detected at concentrations < 0.17–30 pg/m^3, <0.014–0.82 pg/m^3 and <0.10–4.8 pg/m^3, respectively, similar to concentrations measured in the GAPS survey [21,26]. Regarding PFAS in indoor air, Yao et al. reported that FTOHs were predominantly detected in both hotels and houses in the range of 246–62,100 pg/m^3. Levels of ionic PFAS differed between study sites; PFCAs and PFSAs ranged from 90.9 to 1,970 pg/m^3 and 86.8–587 pg/m^3, respectively, and were higher in houses, while total FASA/FASE levels were higher in hotels and ranged from non-detectable (ND) to 2,460 pg/m^3 [22].

2.4. Discussion

Due to simplicity and cost-efficiency, passive samplers employing an SIP disk are widely used for global monitoring of outdoor air. By contrast, SPE cartridges tend to be applied for indoor air monitoring. Sampling and extraction methods for air samples are optimised for anionic and neutral compounds, even though novel PFAS are emerging in other matrices. Most methods reported to date have used extraction of filters to derive particulate fractions for calculating atmospheric PFCA concentrations. Johansson et al. emphasised the potential for overestimation of PFCA concentrations using this method since PFCAs may be adsorbed by the surface of filters [33]. The authors deactivated the GFF by siliconisation in order to eliminate the adsorption of PFCAs to the filter, but this did not completely separate particulate fractionation and adsorption. The main challenge when monitoring PFAS in air is sampling issues. There is no standardised methodology, which hampers comparison of global studies. Development of a globally applicable sampling method and its standardisation are therefore urgently needed.

Furthermore, simultaneous analytical methods for anionic and neutral PFAS in air samples are scarce. To characterise the fate and transport of PFAS in the environment, new analytical methods are needed. Bio-indicators such as vegetation samples (e.g., tree leaves and bark) may become important alternative tools for analysing the atmospheric transport of PFAS [34,35].

3. Aqueous matrices

Analytical methods for PFAS in aqueous matrices such as drinking water, ground water, surface water, seawater and wastewater are summarised in Table 3. According to previous reviews, original PFAS were typically analysed by liquid-liquid extraction (LLE), ion-pair extraction (IPE) or SPE cartridge clean-up followed by HPLC-MS/MS or GC-MS [6,7]. Additionally, fluorotelomer-based substances such as fluorotelomer sulphonic acids (FTSAs), fluorotelomer carboxylic acids (FTCAs) and fluorotelomer unsaturated carboxylic acids (FTUCAs) were typically analysed using these methods. Lorenzo et al. summarised the analytical challenges for emerging persistent organic pollutants such as PFAS in aqueous matrices [9]. They introduced simultaneous analytical techniques for diverse PFAS [36], pre-treatment methods employing green chemistry approaches such as solid-phase microextraction (SPME) [37] and dispersive liquid-liquid microextraction (DLLME) [38] and a separation technique using ultra-performance convergence chromatography (UPC^2) [39]. Methods for novel PFAS including cyclic PFSAs, perfluoroalkyl phosphonic acids (PFPAs), perfluoroalkyl ether sulphonic acids (PFESAs) and perfluoroalkyl ether carboxylic acids (PFECAs) in aqueous samples are summarised in a previous review [10].

3.1. Sample collection and preservation

Aqueous samples are generally collected using pre-cleaned equipment such as a bucket [40], a glass pitcher [14] or an autosampler (Liquiport 2010 CSP44; Endress + Hauser AG, Reinach, Switzerland) [41]. Collected samples are then transferred to a container made of high-density polyethylene (HDPE) [42], PP [43,44] or glass [14,45,46], pre-washed with methanol followed by purified water [41] and stored in a refrigerator at 4–6°C or freezer at about −20°C until analysis [42–46].

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Table 1
List of poly- and perfluoroalkyl substances (PFAS).

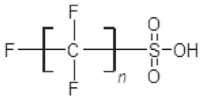
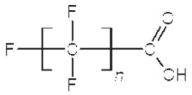
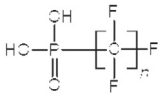
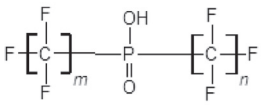
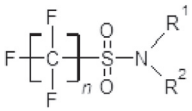
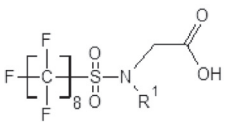
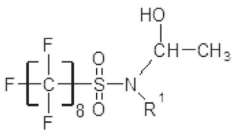
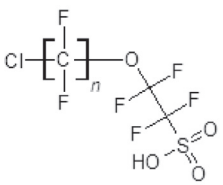
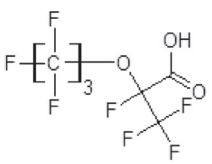
Group	Compound name	Acronym	Structure
Perfluoroalkyl sulphonic acids (PFSAs)	Perfluorobutane sulphonic acid (n = 4)	PFBS	
	Perfluoropentane sulphonic acid (n = 5)	PFPeS	
	Perfluorohexane sulphonic acid (n = 6)	PFHxS	
	Perfluoroheptane sulphonic acid (n = 7)	PFHpS	
	Perfluorooctane sulphonic acid (n = 8)	PFOS	
	Perfluorononane sulphonic acid (n = 9)	PFNS	
	Perfluorodecane sulphonic acid (n = 10)	PFDS	
	Perfluorododecane sulphonic acid (n = 12)	PFDoDS	
Perfluoroalkyl carboxylic acids (PFCAs)	Trifluoroacetic acid (n = 2)	TFA	
	Perfluoropropanoic acid (n = 3)	PFPrA	
	Perfluorobutanoic acid (n = 4)	PFBA	
	Perfluoropentanoic acid (n = 5)	PFPeA	
	Perfluorohexanoic acid (n = 6)	PFHxA	
	Perfluoroheptanoic acid (n = 7)	PFHpA	
	Perfluorooctanoic acid (n = 8)	PFOA	
	Perfluorononanoic acid (n = 9)	PFNA	
	Perfluorodecanoic acid (n = 10)	PFDA	
	Perfluoroundecanoic acid (n = 11)	PFUnDA	
	Perfluorododecanoic acid (n = 12)	PFDoDA	
	Perfluorotridecanoic acid (n = 13)	PFTrDA	
	Perfluorotetradecanoic acid (n = 14)	PFTeDA	
	Perfluorohexadecanoic acid (n = 16)	PFHxDA	
	Perfluorooctadecanoic acid (n = 18)	PFODA	
Perfluoroalkyl phosphonic acids (PFPAs)	Perfluorohexane phosphonic acid (n = 6)	PFHxPA	
	Perfluorooctane phosphonic acid (n = 8)	PFOPA	
	Perfluorodecane phosphonic acid (n = 10)	PFDPA	
Perfluoroalkyl phosphinic acids (PFPiAs)	6:6 Perfluoroalkyl phosphinic acid (m = 6, n = 6)	6:6 PFPiA	
	6:8 Perfluoroalkyl phosphinic acid (m = 6, n = 8)	6:8 PFPiA	
	8:8 Perfluoroalkyl phosphinic acid (m = 8, n = 8)	8:8 PFPiA	
Perfluoroalkane sulphonamides (FASAs)	Perfluorooctane sulphonamide (n = 8, R^1 = H, R^2 = H)	FOSA	
	N-Methyl fluorobutane sulphonamide (n = 4, R^1 = H, R^2 = H)	MeFBSA	
	N-Methyl fluorooctane sulphonamide (n = 8, R^1 = CH_3, R^2 = H)	MeFOSA	
	N-Ethyl fluorooctane sulphonamide (n = 8, R^1 = C_2H_5, R^2 = H)	EtFOSA	
N-Alkyl perfluoroalkane sulphonamido acetic acids (FASAAs)	Perfluorooctane sulphonamidoacetic acid (R^1 = H)	FOSAA	
	N-Methyl fluorooctane sulphonamido acetic acid (R^1 = CH_3)	MeFOSAA	
	N-Ethyl fluorooctane sulphonamido acetic acid (R^1 = C_2H_5)	EtFOSAA	
N-Alkyl perfluoroalkane sulphonamido ethanols (FASEs)	2-(N-Methyl fluorooctane sulphonamido)-ethanol (R^1 = CH_3)	MeFOSE	
	2-(N-Ethyl fluorooctane sulphonamido)-ethanol (R^1 = C_2H_5)	EtFOSE	
Perfluoroalkyl iodides (PFAIs)	Perfluorohexyl iodide (n = 6)	PFHxI	
	Perfluorooctyl iodide (n = 8)	PFOI	
	Perfluorodecyl iodide (n = 10)	PFDI	
Perfluoroether sulphonic acids (PFESAs)	6:2 Chlorinated polyfluorinated ether sulphonic acid (n = 6)	6:2 Cl-PFESA (trade name: F-53B)	
	8:2 Chlorinated polyfluorinated ether sulphonic acid (n = 8)	8:2 Cl-PFESA	
	10:2 Chlorinated polyfluorinated ether sulphonic acid (n = 10)	10:2 Cl-PFESA	
Perfluoroether carboxylic acids (PFECAs)	Hexafluoropropylene oxide dimer acid	HFPO-DA (trade name: GenX)	

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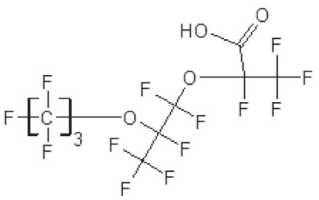
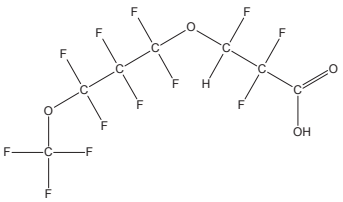
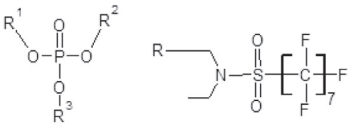
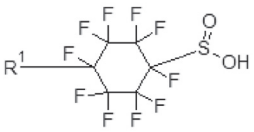
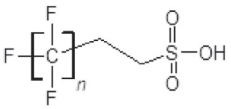
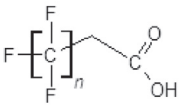
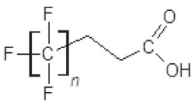
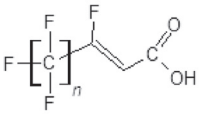
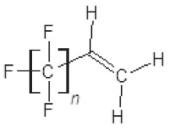
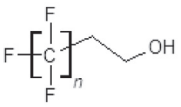
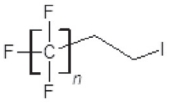
Table 1 (*continued*)

Group	Compound name	Acronym	Structure
	Hexafluoropropylene oxide trimer acid	HFPO-TA	
	4,8-Dioxa-3H-perfluorononanoic acid	ADONA	
Perfluorooctane sulphonamido ethanol-based phosphate esters (SAmPAPs)	Phosphate diester of N-ethylperfluorooctane sulphonamido ethanol (R^1 = R, R^2 = R, R^3 = H) Phosphate triester of N-ethylperfluorooctane sulphonamido ethanol (R^1 = R, R^2 = R, R^3 = R)	SAmPAP diester SAmPAP triester	
Cyclic perfluoroalkyl sulphonic acids (cyclic PFSAs)	Perfluoromethylcyclohexane sulphonic acids ($R^1 = CH_3$) Perfluoroethylcyclohexane sulphonic acids ($R^1 = C_2H_5$)	PFMeCHS PFECHS	
Fluorotelomer sulphonic acids (FTSAs)	n:2 Fluorotelomer sulphonic acids (n = 4, 6, 8, 10)	n:2 FTSA	
Fluorotelomer carboxylic acids (FTCAs)	n:2 Fluorotelomer carboxylic acids (n = 6, 8, 10)	n:2 FTCA	
	n:3 Fluorotelomer carboxylic acids (n = 5, 7)	n:3 FTCA	
Fluorotelomer unsaturated carboxylic acids (FTUCAs)	n:2 Fluorotelomer unsaturated carboxylic acids (n = 6, 8, 10)	n:2 FTUCA	
Fluorotelomer olefins (FTOs)	n:2 Fluorotelomer olefins (n = 6, 8, 10)	n:2 FTO	
Fluorotelomer alcohols (FTOHs)	n:2 Fluorotelomer alcohols (n = 4, 6, 8, 10, 12)	n:2 FTOH	
Fluorotelomer iodides (FTIs)	n:2 Fluorotelomer iodides (n = 4, 6, 8)	n:2 FTI	

(*continued on next page*)

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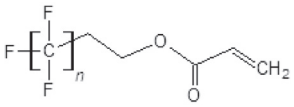
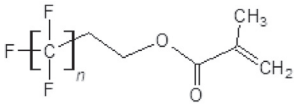
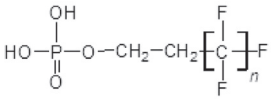
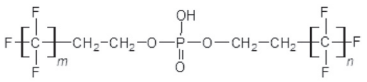
Table 1 (*continued*)

Group	Compound name	Acronym	Structure
Fluorotelomer acrylates (FTACs)	n:2 Fluorotelomer acrylates (n = 4, 6, 8, 10, 12)	n:2 FTAC	
Fluorotelomer methacrylates (FTMACs)	n:2 Fluorotelomer methacrylates (n = 6, 8)	n:2 FTMAC	
Polyfluoroalkyl phosphate monoesters (monoPAPs)	n:2 Polyfluoroalkyl phosphate monoesters (n = 4, 6, 8, 10)	n:2 monoPAP	
Polyfluoroalkyl phosphate diesters (diPAPs)	n:2 Polyfluoroalkyl phosphate diesters (m = n = 4, 6, 8, 10)	n:2 diPAP	
	4:2/n:2 Polyfluoroalkyl phosphate diesters (m = 4, n = 4, 6)	4:2/n:2 diPAP	
	6:2/n:2 Polyfluoroalkyl phosphate diesters (m = 6, n = 6, 8, 10, 12, 14)	6:2/n:2 diPAP	
	8:2/n:2 Polyfluoroalkyl phosphate diesters (m = 8, n = 8, 10, 12)	8:2/n:2 diPAP	
	10:2/10:2 Polyfluoroalkyl phosphate diesters (m = 10, n = 10)	10:2/10:2 diPAP	

3.2. Extraction, clean-up and concentration

To achieve high-throughput and sub-ng/L sensitivity, an SPE cartridge is widely used for sample enrichment and clean-up [6,7,9,15,40,42–45]. A polymer-based SPE cartridge is commonly employed for PFAS analysis [6,7,9]. Oasis HLB series or Strata-X cartridges (Phenomenex, Torrance, CA, USA) tend to be employed for analysis of diverse target compounds [7,9,15,42,45]. Simultaneous analyses of PFAS, pharmaceuticals, personal care products and pesticides were developed using these types of SPE cartridges [15]. Methanol is frequently used as the elution solvent, and for matrix-rich samples, an additional clean-up step with ENVI-Carb can be applied after SPE clean-up [42]. Oasis WAX (Waters, Inc.) and Strata X-AW (Phenomenex) are also used for aqueous sample analysis [40,43,44]. Janda et al. developed an analytical method for short-chain PFCAs such as trifluoroacetic acid (TFA) and perfluoropropanoic acid (PFPrA) in surface water, ground water and drinking water samples using Oasis WAX, resulting in sufficient PFAS recoveries at pH 3–4 [44]. An SPE cartridge filled with bamboo charcoal, a new biomaterial with microporous characteristics, was developed for determination of trace PFAS in environmental water samples [46]. Multiple monolithic fibre solid-phase microextraction (MMF-SPME) using a monolith-based adsorbent that can produce fluorophilic and anion-exchange interactions with PFCAs was evaluated for sensitive detection of ultra-low levels of PFCAs in environmental water and milk samples [47]. LLE is yet another technique frequently applied as a clean-up method for PFAS analysis. Green chemistry methods using DLLME were recently developed [9,38] that utilise less extraction solvent and thereby decrease the environmental burden, achieving sufficient recoveries (80.6%–121% for tap water, river water and urine samples) and relatively low detection limits (0.6–8.7 ng/L for water and urine samples). However, the hydrophobicity of extraction solvents used for DLLME methods tends to decrease the recovery of short-chain PFAS (17%–57% for C4–C6 PFAS). Vortex-assisted liquid-liquid microextraction (VALLME) employs a vortex mixer instead of dispersive solvent, which is much simpler than the two different solvent systems employed in DLLME methods. This technique was applied for PFAS analysis (PFOS, PFOA and FASAs) in seawater, resulting in a method quantitation limit <7 ng/L with a sample volume of 35 mL and 0.85 mL of solvent using an LTQ-Orbitrap HRMS instrument (Thermo Fisher Scientific, Waltham, MA, USA) [14]. In another report, a VALLME method achieved a limit of detection (LOD) of 1.6 ng/L for PFOS in tap, river and well water samples [48]. Stir bar sorptive extraction (SBSE) has been developed as an environmentally friendly technique and applied to PFAS research [49]. Target compounds are extracted from small volume samples by a stir bar coated with adsorbent followed by organic solvent extraction. Yao et al. prepared stir bars coated with adsorbent material and achieved sufficient recoveries for diverse PFAS including PFCAs (C4–C12) and PFSAs (C6 and C8) [50]. A few publications report a direct injection (DI) approach for PFAS analysis, and various water samples including drinking water, ground water, river water, lake water and wastewater have been analysed by DI-LC-MS/MS [41].

3.3. Instrumental analysis and measurement results

Instrumental analysis of PFAS in aquatic matrices has not changed substantially in the past decade. Most studies used HPLC-MS/MS [40–44,46,47,50], although some studies used HRMS such as Orbitrap- or time-of-flight (TOF)-MS for quantitative and qualitative analyses [14,15]. Since most target PFAS are anionic, MS is generally operated in ESI-negative mode. For neutral PFAS such as FASAs, FASEs and FTOHs, atmospheric pressure chemical ionisation (APCI) and atmospheric pressure photoionisation (APPI) have also been tested [45]. As PFAS manufacturing has moved from Western to Asian countries, an increasing number of studies have been conducted in Asia. Cai et al. summarised recent reports regarding PFAS levels in Asian water samples collected during 2010–2016 [51]. Elevated levels of PFOS (0.13–881 ng/L) and PFOA (1.28–24,700 ng/L) were detected in water samples collected in 2016 from 65 rivers and 34 coastal drain outlets around the Bohai Sea, China [52]. Mean concentrations of seven PFCAs (C6–C12) and two PFSAs (C4 and C6) in Australian wastewater treatment plant (WWTP) influents and effluents were found to be 0.3–20 ng/L and

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0.11–25 ng/L, respectively [42]. Tap water samples (n = 14) were analysed for 14 PFAS, including four PFSAs (C4–C10) and 10 PFCAs (C5–C14), in South Korea in 2017, and concentrations from ND to 189.6 ng/L were reported [53]. The total concentrations of 14 PFAS, including original PFAS and two novel PFAS comprising 6:2 chlorinated polyfluorinated ether sulphonic acid (6:2 Cl-PFESA) with the trade name of F-53B and 6:2 FTSA, in ground water samples (n = 102) collected from 13 non-industrialised cities in Jiangsu Province, China, were 2.69–556 ng/L [43]. Concentrations of novel PFAS in aqueous samples, including cyclic PFSAs, PFPAs, PFESAs and PFECAs, from publications up to 2017 are summarised in a previous review article [10]. The worldwide distribution of PFESAs and PFECAs in surface water was investigated using 160 samples collected between September and December 2016. Hexafluoropropylene oxide dimer acid (HFPO-DA), hexafluoropropylene oxide trimer acid (HFPO-TA) and 6:2 Cl-PFESA were widely detected in all countries including China (n = 106), the United States (n = 12), the United Kingdom (n = 6), Sweden (n = 10), Germany (n = 14), the Netherlands (n = 6) and South Korea (n = 6), with median values of 0.95, 0.21 and 0.31 ng/L, respectively. The hydrogen-substituted analogue of 6:2 Cl-PFESA (6:2 H-PFESA) was only detected in China with a high detection rate (>95%) [54]. Short-chain PFCAs (C2–C8) were detected in the range of 0.056 μg/L (PFPrA) to 2.2 μg/L (TFA) from ground water (n = 5) collected at polluted sites in the state of Baden-Wurttemberg, Germany, with TFA and PFOA the predominant analytes [44].

3.4. Discussion

The most notable development for PFAS analysis in aqueous matrices during the last decade is the miniaturisation of extraction procedures such as DLLME, VALLE and micro-SPE, which has decreased the required sample volume and the amount of extraction solvent needed [14,15]. Simultaneous instrumental detection techniques have also attracted attention for the analysis of a wide range of 'new' PFAS, such as 6:2 Cl-PFESA, HFPO-DA and HFPO-TA, and 'legacy' PFAS. However, it is still difficult to optimise the methods for entire target analytes. For example, recovery of short-chain PFCAs is low with DLLME (C2–4), PFBS and 4:2 FTCA [38]. Short-chain PFAS are also more susceptible to matrix effects that cause ionisation suppression, resulting in lower analytical sensitivities [44]. Short-chain PFAS (C6 or shorter) have been increasingly manufactured and used worldwide as alternatives for long-chain PFAS. Since these compounds are more volatile and therefore diffuse and distribute widely, more research is needed to determine their environmental fate and their effects on organisms. Short-chain PFAS are more likely to persist in wastewater treatment [44]. Therefore, developing robust analytical methods that can capture both original and novel PFAS possessing broad chemical properties in aqueous matrices is a priority.

4. Abiotic solid matrices

Analytical methods for PFAS in abiotic solid matrices such as sediments, soil, sludge and dust are summarised in Table 4. The use of aqueous film-forming foam (AFFF) in firefighting training sites has attracted attention as an important source of PFAS contamination in the environment [55]. Recent PFAS research in this field has focused on identifying and quantifying PFAS in soil matrices [55,56], evaluating the adsorption of PFAS to solid matrices [57–59] and optimising extraction methods for novel PFAS [60]. Several studies have investigated original PFAS [61] and alternative substances [62,63] in soil and sediment samples collected from non-firefighting training sites. Meanwhile, earth core samples have been investigated to estimate the temporal trends of both original and novel PFAS [64]. Newly developed analytical methods for identifying and measuring novel PFAS in solid matrices are summarised in recent review articles [9,10]. Regarding dust analysis, one comprehensive review has covered survey sites, concentrations and daily intake of semi-volatile organic compounds (SVOC) including PFAS [13], but dust analysis methods have not been thoroughly explored.

4.1. Sample collection and preservation

Sampling tools for sediment, soil and sewage sludge include a stainless-steel grab sampler [65], bottom sampler [62], hand trowel [65] and knife [66], all pre-cleaned before use. Earth core samples can be collected using a Model MC-400 Multi-corer [67] or by a diver with an acryl tube [62]. After sampling, core samples are sliced with a stainless-steel tool into specimens of appropriate thickness (0.5–5 cm) [63,64,67], then placed in a polyethylene (PE) or PP bag [62] or a PP tube [66] or wrapped in aluminium foil [61,64,65,68] and refrigerated at around 4°C [65] or frozen at −20°C [62,64,66,68,69] until analysis. Prior to extraction, samples are generally freeze-, air- or vacuum-dried, then sieved and homogenised. Dust is often collected from houses, offices and shops to estimate human exposure to PFAS [13]. Dust collection is generally carried out using a vacuum cleaner [22,70].

4.2. Extraction, clean-up and concentration

Few remarkable developments in pre-treatment procedures have occurred in the last decade. Sample pre-treatment methods essentially consist of Soxhlet extraction, PLE or supported liquid extraction (SLE), followed by additional clean-up procedures using graphite carbon materials such as ENVI-Carb, SLE or IPE [6,7]. The predominant combination is SLE followed by ENVI-Carb or an SPE cartridge (e.g., OASIS WAX, OASIS HLB or C18) under neutral or basic conditions. Wang et al. compared SPE (WAX, HLB and C18) with solvent extraction and filtration as a pre-treatment method and concluded that solvent extraction achieves better recoveries [61]. The sample pre-treatment procedure should be capable of capturing PFAS with diverse properties, especially highly hydrophobic compounds, cations and zwitterions [60,62]. Dust samples are analysed for both volatile and non-volatile PFAS; hence methods tend to be more complex and involve fractionating with different extracting solvents and/or repeated extraction steps [22,70,71].

4.3. Instrumental analysis and measurement results

GC-MS is the predominant method for volatile PFAS analysis in solids. For ionic PFAS, instruments are similar to those used for analysis of aqueous matrices by HPLC-negative ESI-MS/MS. A few studies used Orbitrap-MS [68] or TOF-MS [17]. LC conditions are generally similar to those adopted for air and aqueous matrices. Zhang et al. reported that an alkyl perfluorinated C8 column (Epic FO LB, ES Industries, Inc., West Berlin, NJ, USA) achieved better separation characteristics for PFAS isomers than a C18 column [69].

Studies between 2005 and 2018 reported sediment PFOS and PFOA concentrations in the range of ND to 623 ng/g dry weight (dw) and ND to 16 ng/g dw, respectively [58,59]. A systematic review evaluated temporal trends and suggested increasing trends for PFOS and some PFCAs in sediment core samples in the period 1850–2013 [11]. Marine sediment core samples collected in China and Korea displayed similar trends, with higher levels of PFAS detected in surface layers [64]. PFAS levels were measured in core sediment samples collected from the Great Lakes region of North America in 2006 and 2009, and were also higher in the top layers

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Table 2
Analytical methods for PFAS in air.

Compounds			Matrix	Sample volume	Sampling device	Absorbent	Elution/clean-up	Instrument	LOD/LOQ	QA/QC	Misc.	Reported level		Reference
PFCAs[a]	PFSAs[a]	Other										n	Concentration[b]	
4–14, 16, 18	4, 6, 8, 10	n:2 FTOHs, n:2 FTACs (n = 6, 8, 10), FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE, 6:2 FTSA	Outdoor air	1200, 2000 m^3	High-volume sampler	GFF, XAD	PLE, sonication (MeOH): GFF	GC-PCI-MS UHPLC-ESI(−)-MS/MS UHPLC-ESI(−)-TOF-MS	0.008–4.2 pg/m^3	Field blanks, laboratory blanks recoveries	Extraction using PLE	801	FTOH (median): 3.8 pg/m^3 FASE (median): 0.49 pg/m^3 FASA (median): 0.13 pg/m^3 FTAC (median): 0.24 pg/m^3 FOSA (median): 0.12 pg/m^3	[21]
–	–	n:2 FTOHs (n = 6, 8, 10), MeFOSA, EtFOSA, MeFOSE, EtFOSE	Indoor air/ personal air	7.2/1.44 m^3	Low-volume sampler	SPE (ENVI+)	MeOH	GC-PCI-MS	0.03–71 pg/m^3 (indoor air) 1.4–350 pg/m^3 (personal air) (MDL)	Breakthroughs, field blanks	SPE air sampling	76	FTOH: 170 –446,000 pg/m^3 FASA: <MDL –78,300 pg/m^3 FASE: <MDL –38,800 pg/m^3	[23]
4–12	4, 6, 8	MeFOSA, EtFOSA, MeFOSE, EtFOSE, n:2 FTOHs (n = 6, 8, 10), n:2 FTUCAs, n:2 diPAPs (n = 6, 8)	Indoor air	0.172 –8.33 m^3	Low-volume sampler	SPE (WAX/HC-C18)	Ethyl acetate 0.5% NH_4OH MeOH	GC-PCI-MS HPLC-ESI(−)-MS/MS	0.9–26.3 pg/average 3 m^3 (MDL)	Procedure blanks, breakthroughs recoveries	Two-layer SPE air sampling	67	ΣFTOH: 249 –62,100 pg/m^3 ΣPFCA: 121 –8,670 pg/m^3 ΣPFSA: 71.2 –1,780 pg/m^3 ΣdiPAP: ND –125 pg/m^3 ΣFASA/E: ND –2,460 pg/m^3 ΣFTUCA: ND –413 pg/m^3	[22]
–	–	8:2 FTO, n:2 FTOHs (n = 4, 6, 8, 10, 12), n:2 FTACs (n = 6, 8), MeFBSA, MeFOSA, EtFOSA, MeFBSE, MeFOSE, EtFOSE	Outdoor air	–	Passive air sampler	SPE (SIP disk)	EtOAc (cold column extraction) ENVI-Carb	GC-PCI-MS	0.09–1.85 pg/m^3	Field blanks, laboratory blanks recoveries	–	46	ΣFTOH: 51.4 –1,210 pg/m^3 ΣFTAC: 0.20 –15.3 pg/m^3 ΣFASA: 3.22 –831 pg/m^3 ΣFASE: 7.44 –172 pg/m^3	[29]
2–12	4, 6, 8	n:2 FTOHs (n = 6, 8, 10), n:2 diPAPs (n = 6, 8), MeFOSA, EtFOSA, MeFOSE, EtFOSE	Outdoor air	–	Passive air sampler	SPE (SIP disk)	Soxhlet: EtOAc, MeOH ENVI-Carb	GC-PCI-MS HPLC-ESI(−)-MS/MS	0.02–0.22 pg/m^3	Field blanks, procedure blanks recoveries	Sampling short-chain PFAS using SIP	12	ΣFTOH: 58 –2,100 pg/m^3 FASA: ND–13 pg/m^3 ΣPFAS (C ≥ 4): 280 –820 pg/m^3 diPAP: <MDL –12 pg/m^3 TFA: 1.4–3.0 ng/m^3	[28]

											PFPrA: 0.064 −0.36 ng/m^3	
7–12	6, 8	–	Outdoor air (aerosol)	No information	Cascade impactor	QFF	MeOH shaking, sonication filtration	HPLC-ESI(−)-MS/MS	0.08–2.89 pg/m^3	Procedure blanks Field blanks Recoveries	Sampling aerosol	19	0.26–1.98 ng/m^3	[24]

Abbreviations: diPAP, polyfluoroalkyl phosphate diester; ESI, electrospray ionisation; EtFOSA, N-ethyl fluorooctane sulphonamide; EtFOSE, 2-(N-ethyl fluorooctane sulphonamido)-ethanol; EtOAc, ethyl acetate; FASA, perfluoroalkane sulphonamide; FASE, N-alkyl perfluoroalkane sulphonamido ethanol; FOSA, perfluorooctane sulphonamide; FTAC, fluorotelomer acrylate; FTI, fluorotelomer iodide; FTMAC, fluorotelomer methacrylate; FTOH, fluorotelomer alcohol; FTO, fluorotelomer olefin; FTSA, fluorotelomer sulphonic acid; FTUCA, fluorotelomer unsaturated carboxylic acid; GC-MS, gas chromatography-mass spectrometry; GFF, glass-fibre filter; HPLC-MS/MS, high-performance liquid chromatography-tandem mass spectrometry; LOD, limit of detection; LOQ, limit of quantitation; MDL, method detection limit; MeFBSA, N-methyl fluorobutane sulphonamide; MeFBSE, 1-(N-methyl fluorobutane sulphonamido)-ethanol; MeFOSA, N-methyl fluorooctane sulphonamide; MeFOSE, 2-(N-methyl fluorooctane sulphonamido)-ethanol; MeOH, methanol; ND, not detected; NH_4OH, ammonium hydroxide; PCI, positive chemical ionisation; PFAS, poly- and perfluoroalkyl substances; PFCA, perfluorinated carboxylic acid; PFDI, perfluorodecyl iodide; PFHxI, perfluoro-n-hexyl iodide; PFOI, perfluorooctyl iodide; PFPrA, perfluoropropanoic acid; PFSA, perfluoroalkane sulphonic acid; PLE, pressurised liquid extraction; PUF, polyurethane foam; QA, quality assurance; QC, quality control; QFF, quartz-fibre filter; SIP, solvent-impregnated polyurethane foam; SPE, solid-phase extraction; TFA, trifluoroacetic acid; TOF, time-of-flight; UHPLC, ultra-high-performance liquid chromatography; WAX, weak anion exchange; WWTP, wastewater treatment plant.

[a] Carbon chain length.

[b] Median or concentration range (depending on reference).

than the deeper layers [63]. Moreover, diPAPs and perfluoroalkyl phosphinic acids (PFPiAs) were detected in the most recent layer. Perfluorooctane sulphonamido ethanol-based phosphate (SAmPAP) diester and triester were detected in freshwater sediments from Taihu Lake in the range of <0.03–4.3 ng/g dw and <0.024–1.13 ng/g dw, respectively. Novel PFAS such as 6:2 Cl-PFESA and its analogues, and 6:2 fluorotelomer sulphamide alkylbetaines (FTABs), have been detected in abiotic solid matrices [10]. Regarding PFAS in dust samples, concentrations and composition differ at different collection sites; samples collected from hotels show higher levels of FTOHs (24.8–678 ng/g), while those from houses contain more short-chain PFCAs (41.6–226 ng/g) and much fewer FTOHs [22], and diPAPs are also frequently detected in dust samples [70,72].

4.4. Discussion

Temporal studies and model predictions suggest that sediments, soils and sludges are an important environmental sink for PFAS [73]. A considerable number of novel PFAS, including cationic and zwitterionic species, have been detected in recent studies [60,74]. These substances tend to exhibit strong adsorption to solid matrices [57]. It is therefore necessary to develop a method that can extract diverse classes of PFAS for long-term monitoring. Dust is one of the most important routes of human exposure; hence a method suitable for both volatile and non-volatile PFAS is warranted.

5. Wildlife and humans

Analytical methods for PFAS in biological samples are listed in Table 5. Since biological samples consist of complex matrices, development of efficient extraction and clean-up methods has attracted more attention than for other sample types [6,7,9]. IPE and alkaline digestion followed by LLE has been widely employed as a pre-treatment method in the last decade [75,76], and eluates are usually subjected to an additional clean-up with an SPE cartridge containing HLB, WAX or ENVI-Carb resin. Numerous studies have investigated not only original PFAS but also PFAS isomers [77] and different classes of PFAS such as PFECAs and PFESAs [77–80], perfluoroethylcyclohexane sulphonate (PFECHS) [81,82], PFPAs [82,83], PFPiAs [82], polyfluoroalkyl phosphate monoesters (monoPAPs) and diPAPs [83,84]. Furthermore, identification of novel PFAS in biological samples, including cations and zwitterions, has been initiated in various matrices [18]. To reduce the environmental burden from PFAS research, development of analytical techniques using a green chemistry approach is warranted, as it is for other matrices. For this purpose, several techniques were introduced in a recent review article, including focused ultrasound solid-liquid extraction (FUSLE) and turbulent flow chromatography (TFC) [9]. Plasma, serum and breast milk represent the major target matrices investigated thus far [6], but an increasing number of studies are focusing on non-invasive samples such as urine, hair and nail for human biomonitoring [85,86].

5.1. Sample collection and preservation

For collection of biological samples, greater attention has been paid to contamination from sampling equipment during collection and storage, since the adsorption of target compounds to sample containers and equipment can be minimised by the matrix content [6]. After sampling, wildlife samples from fish, frog, eel, marine organisms and others are immediately transported to the laboratory, dissected with stainless-steel tools [78,80] and homogenised [81,87]. Fish samples are collected with equipment such as a

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Table 3
Analytical methods for PFAS in aqueous matrices.

Compounds			Matrix	Sample volume	Pre-treatment	Extraction	Clean-up	Instrument	LOD/LOQ	QA/QC	Misc.	Reported level		Reference
PFCAs[a]	PFSAs[a]	Other										n	Concentration[b]	
5–12	4, 6, 8	FOSA, PPCPs, Pesticide, Food additives	Drinking water	5000 mL	–	SPE (Oasis HLB, Bond-Elut ENV)	–	UPLC-ESI(−)-QTOF-MS	~2.9 ng/L (MDL PFPeA)	Blanks, recoveries matrix effects	Multiresidue analytical method for simultaneous determination, large volume extraction comparison, Oasis HLB vs. Bond-Elut ENV	16	PFCA: <MDL −4.2 ng/L PFSA: <MDL −9.8 ng/L FOSA: 0.02 −0.30 ng/L	[15]
–	–	MeFOSA, EtFOSA, MeFOSE, EtFOSE, n:2 FTSAs (n = 4, 6, 8, 10), 7-Me-FTOH	River water	500 mL	–	SPE (Oasis HLB)	Column wash	HPLC-APCI(−)/APPI-MS/MS	0.3–6 ng/L (MLOD)	Blanks, recoveries, triplicates	Comparison, APCI vs. APPI, ionisation	5	4:2 FTSA: 30 ± 1 ng/L EtFOSA: 780 ± 12 ng/L	[45]
6–12	6, 8	–	Wastewater	50–100 mL	Adjusted to pH 7	SPE (Oasis HLB, Strata-X)	ENVI-Carb	HPLC-ESI(−)-MS/MS	–	Blanks, replicates	Method for WWTP influents, effluents, biosolids	14	PFCA: 0.17 −60 ng/L PFSA: 0.63 −240 ng/L Σ9PFAS: 0.98 −560 ng/L	[42]
4–12, 14, 16, 18	4, 6, 8	F-53B (6:2 Cl-PFESA), 6:2 FTSA	Ground water	2000 mL	Filtration	SPE (Oasis WAX)	Column wash	HPLC-ESI(−)-MS/MS	0.1–0.5 ng/L (LOD)	Blanks, recoveries	Large volume extraction, simultaneous determination	102	PFCA: <LOD −290 ng/L PFSA: <LOD −143 ng/L F-53B, 6:2 FTSA: 0.17 −8.54 ng/L	[43]
4–14, 16, 18	4, 6, 8, 10	FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE, FOSAA, MeFOSAA, EtFOSAA, 6:2 FTSA	Wastewater, surface water	500 mL	Filtration	SPE (Oasis WAX)	Column wash	HPLC-ESI(−)-MS/MS	0.05–1.79 ng/L (LOD)	Recoveries, replicates	Method for WWTP influents, effluents and surface water, simultaneous determination	10	PFCA: <LOD −4.1 ng/L PFSA: <LOD −3.9 ng/L ΣPFAS: 1.0 −14 ng/L	[40]
2–8	–	–	Surface water, ground water, drinking water	50 mL	Adjusted to pH 3.9 ± 0.1	SPE (Oasis WAX)	–	HPLC-ESI(−)-MS/MS	0.1–3.3 ng/L (LOD)	Blanks, recoveries, matrix effects repeatability, reproducibility	Simultaneous determination of short-chained PFCA	5	0.056–2.2 μg/L (ground water)	[44]
7–10	6, 8	–	Drinking water, tap water, pond water	100 mL	–	SPE (bamboo charcoal)	Column wash	HPLC-ESI(−)-MS/MS	0.01–1.15 ng/L (LOD)	Recoveries, repeatability reproducibility	Development of new adsorbents for SPE	4	ND–4.61 ng/L	[46]
4–5, 7–10	–	–	Tap water, river water, wastewater	20 mL	Adjusted to pH 7	MMF-SPME	–	HPLC-ESI(−)-MS/MS	0.40–4.40 ng/L (LOD)	Blanks, recoveries matrix effects, repeatability, reproducibility	Development of new adsorbents for SPE	3	ND–0.014 μg/L	[47]

8	8	MeFOSA, EtFOSA	Seawater	35 mL	–	VALLME	Filtration	HPLC-ESI(−)-LTQ-Orbitrap HRMS	0.22–3.0 ng/L (M-LOD)	Blanks, recoveries matrix effects, repeatability	12	–	[14]
4–12	6, 8	–	Lake water, river water	5 mL	Diluted by MeOH, adjusted to pH 3	SBSE	Washed with deionised water	HPLC-ESI(−)-MS/MS	0.06–0.40 ng/L (LOD)	Recoveries, replicates	2	PFCA: ND −38 ng/L PFAS: 0.30 −5.84 ng/L	[50]
5–10	4, 6, 8	–	Wastewater, surface water, ground water, drinking water	0.1 mL	Ultracentrifugation	–	–	DI-UHPLC-ESI(−)-MS/MS	0.013–0.44 ng/L (MDL)	Blanks, recoveries, matrix effects	Direct large volume injection (100 mL)	52	Wastewater: <MDL −132.5 ng/L surface water: <MDL–4.7 ng/L ground water: <MDL–20.8 ng/L drinking water: <MDL–12.8 ng/L	[41]

Abbreviations: APCI, atmospheric pressure chemical ionisation; APPI, atmospheric pressure photoionisation; ESI, electrospray ionisation; EtFOSA, N-ethyl fluorooctane sulphonamide; EtFOSAA, N-ethyl fluorooctane sulphonamidoacetic acid; EtFOSE, 2-(N-ethyl fluorooctane sulphonamido)-ethanol; FOSA, perfluorooctane sulphonamide; FOSAA, perfluorooctane sulphonamidoacetic acid; FTOH, fluorotelomer alcohol; FTSA, fluorotelomer sulphonic acid; HPLC-MS/MS, high-performance liquid chromatography-tandem mass spectrometry; HRMS, high-resolution mass spectrometry; LOD, limit of detection; LOQ, limit of quantitation; MDL, method detection limit; MeFOSA, N-methyl fluorooctane sulphonamide; MeFOSAA, N-methyl fluorooctane sulphonamidoacetic acid; MeFOSE, 2-(N-methyl fluorooctane sulphonamido)-ethanol; 7-Me-FTOH, 1H,1H,2H,2H-perfluoro-7-trifluoromethyl-octan-1-ol; MLOD, mass limit of detection; MMF-SPME, multiply monolithic fibre solid-phase microextraction; ND, not detected; PFAS, poly- and perfluoroalkyl substances; PFCA, perfluorinated carboxylic acid; PFESA, perfluoroether sulphonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulphonic acid; PFSA, perfluoroalkane sulphonic acid; PPCP, pharmaceutical and personal care product; QA, quality assurance; QC, quality control; SBSE, stir bar sorptive extraction; SD, standard deviation; SPE, solid-phase extraction; TOF, time-of-flight; UHPLC, ultra-high-performance liquid chromatography; VALLME, vortex-assisted liquid-liquid microextraction; WAX, weak anion exchange; WWTP, wastewater treatment plant.

[a] Carbon chain length.

[b] Mean ± SD or concentration range (depending on reference).

bottom trawl [78] and gill nets [81] or obtained from a local market [87]. Human samples such as blood and urine are collected in a PP tube or bottle and stored at −20°C until analysis. Nail and hair samples are collected using a pre-cleaned stainless-steel nail cutter or scissors and stored in a PP centrifuge tube at room temperature until analysis. To remove external contamination, nail and hair samples are often washed with water or acetone and dried before analysis [79,85,87].

5.2. Extraction, clean-up and concentration

Various extraction methods such as SLE, LLE, IPE, alkaline digestion and acetonitrile protein precipitation have been investigated for clean-up of multiple coexisting matrices [79,80,85,87]. One study suggested that low-temperature clean-up at −30°C for 2 h after clean-up with an SPE cartridge was effective for the removal of lipid components [87]. A recent trend for biological samples, especially for human biomonitoring, is the simplification of pre-treatment steps and employment of high-throughput analysis, including online SPE techniques. The sample volume required for PFAS analysis in blood has decreased during the last decade from millilitres to tens of microlitres.

5.3. Instrumental analysis and measurement results

HPLC-MS/MS is mainly used for biological sample analysis. To obtain data that are representative of human and wildlife populations, high-throughput techniques such as online SPE or dual-column systems coupled with HPLC-MS/MS are often employed [84,88]. A systematic review of temporal trends reported a decrease in blood PFOS and PFOA levels in human samples from the Northern hemisphere, despite the fact that environmental media have shown no such clear decreasing trend [11]. In China, there has been an increasing trend in PFAS levels in both human blood and wildlife samples, close to sites where PFAS are currently manufactured [11,78]. In addition to original PFAS, novel PFAS have been detected in biological samples in accordance with the phasing out of original PFAS and a shift toward manufacturing alternatives [18,78,80,82,83].

Novel PFAS (6:2 Cl-PFESA and HFPO-TA) were detected in various tissues from black spotted frogs collected in a rice paddy field near a large-scale fluorochemical production site in China [80]. Liver samples (n = 56) collected from all sampling sites contained 6:2 Cl-PFESA in the range of 0.13–119 ng/g wet weight (ww), while HFPO-TA was found in samples (n = 4) from only one site (Huantai) in the range of 6.51–27.30 ng/g ww. Another study investigated various biological samples collected from the Bohai Sea near China (n = 152) [78], revealing that 6:2 and 8:2 Cl-PFESA and PFOS have bioaccumulated and been biomagnified in the marine ecosystem. Levels of 6:2 Cl-PFESA were in the range of ND to 3.84 ng/g ww, comparable to those of PFOS. Fish, birds and dolphins collected between 2004 and 2011 in various regions of North America were analysed for PFPAs and PFPiAs [82], and PFPiAs were detected in all animals at levels 1–2 orders of magnitude lower than those of PFCAs and PFSAs, while levels of most PFPAs were below the LOD.

Regarding human biomonitoring, most (~90%) studies published in the past two decades measured PFAS in blood samples, while a few studies employed breast milk, urine, hair and nail samples [12]. One study analysed 39 matched human matrices comprising serum, urine, hair and nail to explore the most appropriate specimens for biomonitoring, and concluded that nail was an ideal matrix for PFOS biomonitoring [89]. In another study, urine, hair and nail were evaluated in two populations with different exposure conditions [79], and 6:2 Cl-PFESA was detected in 88%–95% of samples.

Table 4
Analytical methods for PFAS in abiotic solid matrices.

Compounds			Matrix	Sample volume	Pre-treatment	Extraction	Clean-up	Instrument	LOD/LOQ	QA/QC	Misc.	Reported level		Reference
PFCAs[a]	PFSAs[a]	Other										n	Concentration[b]	
5–14, 16, 18	4, 6, 8, 10	–	Sediment	5 g	–	SLE (MeOH), shaking, sonication	ENVI-Carb	HPLC-ESI(−)-MS/MS	2–10 pg/g (LOQ)	Blanks, recoveries matrix spikes	Historical trends of PFAS in coastal environments	90	ΣPFAS (mean): 77.0–339 pg/g dw	[64]
6–14	6–8	FOSA, EtFOSA, FOSAA, EtFOSAA, EtFOSE, SAmPAPs (diester, triester)	Sediment	1 g	Freeze-drying, sieving	SLE (MeOH), shaking	ENVI-Carb	UHPLC-ESI(−)-MS/MS	0.005–0.027 ng/g (MDL)	Blanks, recoveries matrix effects	Determination and microbial degradation of SAmPAP in sediments	41	ΣPFAS: 0.27–18.2 ng/g dw SAmPAP diester: <0.027–4.3 ng/g dw SAmPAP trimester: <0.024–1.13 ng/g dw	[62]
–	4, 6–8, 10	n:2 FTSAs (n = 6, 8), n:2 Cl-PFESAs (n = 6, 8, 10)	Sludge	0.5 g	Lyophilisation, homogenisation	SLE (ACN: 1 M NaOH), shaking	ENVI-Carb	UHPLC-ESI(−)-MS/MS UHPLC-ESI(−)-Orbitrap HRMS	25.2–135 pg/g (MQL)	Blanks, recoveries matrix effects	Screening to identify potential PFOS alternatives	56	ΣPFSA: ND–220 ng/g dw ΣFTSA: ND–18.9 ng/g dw ΣCl-PFESA: 0.31–241 ng/g dw	[68]
4–14, 16	4, 6, 8, 10	FOSA, FOSAA, MeFOSAA, EtFOSAA, MeFOSE, EtFOSE	Sediment	2.5 g	Lyophilisation, homogenisation removal of large material	SLE (MeOH/acetic acid solution), sonication	Oasis HLB	HPLC-ESI(−)-MS/MS	NA	Blanks, recoveries	Clean-up using SPE for polymeric reversed-phase	102	ΣPFAS (mean): 1.5–10.9 ng/g dw	[67]
8	8	Oestrogens, phenolic compounds	Sediment	1 g	–	SLE (MeOH), sonication	Oasis HLB	HPLC-ESI(−)-MS/MS	PFOA: 0.09 ng/g dw PFOS: 0.27 ng/g dw (LOD)	Blanks, recoveries triplicates	–	30	PFOA: <LOQ–0.88 ng/g dw PFOS: <LOQ	[65]
4–14, 16, 18	4, 6, 8, 10	FOSA, MeFOSA, EtFOSA, FOSAA, MeFOSAA, EtFOSAA, MeFOSE, EtFOSE, n:2FTSAs (n = 6, 8, 10)	Soil	2 g	Freeze-drying, homogenisation	SLE (NaOH in MeOH), shaking	Oasis WAX	HPLC-ESI(−)-MS/MS	0.0049–8.78 ng/g dw (MDL)	Blanks, triplicates	Simultaneous determination of PFAS including FASA, FASAA and FASE in soil	31	PFCA: <MDL–8.3 ng/g dw PFSA: <MDL–1.7 ng/g dw FASA: <MDL–0.65 ng/g dw FASAA: <MDL–0.88 ng/g dw FASE: <MDL FTSA: <MDL–2.96	[66]
4–16	3–10, 12	PFECHS, FOSA, FHxSA, MeFOSA, EtFOSA, FOSAA, MeFOSAA, EtFOSAA, n:2 FTSAs (n = 4, 6, 8, 10), n:2 FTUCAs (n = 6, 8, 10), n:3 FTCAs (n = 3, 4, 5, 7), PFASAms (n = 3, 4, 5, 6), PFOSAmS, PFOSNO, PFOANO, PFOSB, PFOAB, n:2 FTABs (n = 6, 8, 10, 12), n:2 FTSASs (n = 6, 8, 10), n:2 FTAs (n = 6, 8, 10), n:3 FTBs (n = 5, 7, 9,	Soil	1 g	Homogenisation, sieving	SLE (400 mM CH_3COONH_4 in MeOH), vortexing sonication (*3 times)	ENVI-Carb	UHPLC-ESI(+/−)-Orbitrap HRMS	0.03–0.6 ng/g (MDL)	Blanks, recoveries matrix effects, precision, matrix spikes	Method optimisation for 86 PFAS including 24 chemical classes	5	Σ_{86}PFAS (mean): 110–8,200 ng/g dw	[60]

		11, 13), n:1:2 FTBs (n = 5, 7, 9, 11, 13), PFAAAms (n = 5, 6, 7), 6:2 FTSAS-sulphoxide, 8:2 FTSAS-sulphoxide, O-PFOS, O-PFNS, Cl-PFOS, 6:2 FTSHA, 8:2 FTSHA, PFHxSi, PFASACs (n = 3, 4, 5, 6, 8)											
5–13	6, 8, 10	n:2 diPAPs (n = 6, 8, 10), PFPAs (n = 6, 8, 10), 6:6 PFPiA, 6:8 PFPiA, 8:8 PFPiA	Sediment	1 g	Air-drying, homogenisation	SLE (0.2 M NaOH solution/ ACN), shaking	Centrifugation, IPE (TBAS/ MTBE)	HPLC-ESI(−)-MS/MS	0.004–0.2 ng/g (MDL)	Blanks, recoveries duplicates	Final extract was separated into two fractions and diluted. Fraction 1 (MeOH): diPAP Fraction 2 (60% MeOH): Other PFAS	–	PFAS (mean): 0.51 –13.1 ng/g dw	[63]
8	6, 8	Eight branched isomers of PFOA, branched isomers of PFHxS, nine branched isomers of PFOS	Biosolids, soil plants	0.5 g (biosolids and plants), 2 g (soil)	Freeze-drying, sieving	SLE (NaOH solution/ Na_2CO_3/ $NaHCO_3$ buffer, pH 10), sonication	IPE (TBAS/ MTBE), Oasis WAX, centrifugation	UHPLC-ESI(−)-MS/MS	Biosolids: 10 –55 pg/g dw Soil: 3–13 pg/g dw	Blanks, recoveries duplicates, reproducibility	Simultaneous determination of PFAS including branched isomers, comparison of IPE vs. alkaline digestion methods	2	E.g., biosolids L-PFOA: 204.5 ng/g dw PFOA-isomers: <MDL– 3.21 ng/g dw L-PFHxS: 3.39 ng/g dw PFHxS-isomers: 0.538 ng/g dw L-PFOS: 47.3 ng/g dw PFOS isomers: <MDL– 7.41 ng/g dw	[69]
4–15	4, 6, 8, 10	(LC) br-PFHxS, br-PFOS, br-PFOA, FOSA, br-FOSA MeFBSA, br/l-EtFOSA, br/l-MeFOSAA, br/l-EtFOSAA, n:3 FTCAs (n = 3, 5, 7), ADONA, n:2-PFESAs (n = 6, 8), FTSAs (n = 6, 8), n:2 monoPAPs (n = 4, 6, 8, 10), n:2 diPAPs (n = 4, 6, 8, 10), m:2/n:2 diPAPs (m = 4, 6, 8, n = 6, 8, 10, 12, 14), (GC) 6:2 FTAC, 6:2 FTMAC,	Dust	110 mg (mean)	Sieving	SLE (ENVI-Carb/ethyl acetate), vortexing, sonication, centrifugation, SLE (ethyl acetate) vortexing, sonication	Filtration	UHPLC-ESI(−)-MS/MS, GC-MS	MDL (LC): 0.02 –82.9 ng/g MDL (GC): 5.5 –34.8 ng/g	Blanks, recoveries accuracy (SRM2585)	Total estimated daily intake via dust (EDI dust) and air (EDI air) of PFAS was calculated for 10.5-year-old children	65	PFAS (LC): <MDL –1,360 ng/g PFAS (GC): <MDL –514 ng/g	[70]

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Table 4 (*continued*)

Compounds			Matrix	Sample volume	Pre-treatment	Extraction	Clean-up	Instrument	LOD/LOQ	QA/QC	Misc.	Reported level		Reference
PFCAs[a]	PFSAs[a]	Other										n	Concentration[b]	
		n:2 FTOHs (n = 4, 6, 8, 10), MeFOSA, EtFOSA, MeFOSE, EtFOSE												
4–14	4, 6, 8, 10	br-PFOS, FOSA, MeFOSA, EtFOSA brominated, flame retardants (BFRs)	Dust	50 mg	Impurities (hair, crumbs, etc.) and other non-dust components are removed with tweezers	–	MSPD Florisil (Fraction 1: n-Hex:DCM 15, 85 v/v Me-/Et-FOSA; Fraction 2: MeOH): Other PFAS	UHPLC-ESI(−)-MS/MS	LOQ: 0.25 −1 ng/g	Blanks, recoveries repeatability	A novel approach for analysis of 27 BFRs and 18 PFAS in indoor dust	18	Σ_{18}PFAS: 1.58 −236 ng/g (median: 10.6 ng/g)	[71]
4–14, 16, 18	4, 6, 8, 10	FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE, 6:2 FTSA, n:3 FTCAs (n = 5, 7), n:2 FTUCAs (n = 6, 8, 10), n:2 monoPAPs (n = 6, 8, 10), n:2 diPAPs (n = 6, 8, 10), m:2/n:2 diPAPs (m = 2, 4, 6, 8, n = 6, 8, 10, 12, 14), n:2 triPAPs (n = 6, 8), 6:2/6:2/8:2 triPAPs, 6:2/6:2/10:2 triPAPs, 6:2/8:2/8:2 triPAPs	Dust	0.1 g	Sieving, impurities (hair, fibres, etc.) are removed	SLE (0.2 M NaOH solution/ MeOH), neutralising sonication	SPE (Oasis WAX and Oasis HLB)	UHPLC-ESI(−)-MS/MS	LOD: 0.005 −24.2 ng/g	Blanks, recoveries precision, matrix effects, matrix-matched calibration curves	Comparison of world-wide indoor dust	72	PFCA: <0.1 −779 ng/g PFSA: <0.1− 1,177 ng/g monoPAP: <12 −5,946 ng/g diPAP: 1.6 −4,841 ng/g FTCA/FTUCA: <0.1 −26 ng/g FASA/FASE: <0.1 −6,772 ng/g 6:2 FTSA: <2.0 −20 ng/g FOSA: <1.4− 28 ng/g	[72]

Abbreviations: ADONA, 4,8-dioxa-3H-perfluorononanoic acid; ACN, acetonitrile; BFR, brominated flame retardant; Cl-PFOS, chloro-perfluorooctane sulphonic acid; DCM, dichloromethane; diPAP, polyfluoroalkyl phosphate diester; dw, dry weight; ESI, electrospray ionisation; EtFOSA, N-ethyl fluorooctane sulphonamide; EtFOSAA, N-ethyl fluorooctane sulphonamidoacetic acid; EtFOSE, 2-(N-ethyl fluorooctane sulphonamido)-ethanol; FASA, perfluoroalkane sulphonamide; FASAA, N-alkyl perfluoroalkane sulphonamido acetic acid; FASE, N-alkyl perfluoroalkane sulphonamido ethanol; FHxSA, perfluorohexane sulphonamide; FOSA, perfluorooctane sulphonamide; FOSAA, perfluorooctane sulphonamidoacetic acid; FTAB, fluorotelomer sulphonamidoalkyl betaine; FTAC, fluorotelomer acrylate; FTA, fluorotelomer sulphonamidoalkyl amine; FTB, fluorotelomer betaine; FTCA, fluorotelomer carboxylic acid; FTMAC, fluorotelomer methacrylate; FTOH, fluorotelomer alcohol; FTSA, fluorotelomer sulphonic acid; FTSAS, fluorotelomer thioether amido sulphonate; FTSHA, fluorotelomer thioether hydroxyammonium; FTUCA, fluorotelomer unsaturated carboxylic acid; GC-MS, gas chromatography-mass spectrometry; HPLC-MS/MS, high-performance liquid chromatography-tandem mass spectrometry; HRMS, high-resolution mass spectrometry; IPE, ion-pair extraction; LOD, limit of detection; LOQ, limit of quantitation; MDL, method detection limit; MeFBSA, N-methyl fluorobutane sulphonamide; MeFOSA, N-methyl fluorooctane sulphonamide; MeFOSAA, N-methyl fluorooctane sulphonamidoacetic acid; MeFOSE, 2-(N-methyl fluorooctane sulphonamido)-ethanol; MeOH, methanol; monoPAP, polyfluoroalkyl phosphate monoester; MQL, method of quantitation limit; MSPD, matrix solid-phase dispersion; MTBE, methyl tert-butyl ether; Na_2CO_3, sodium carbonate; $NaHCO_3$, sodium hydrogen carbonate; NaOH, sodium hydroxide; ND, not detected; n-Hex, normal hexane; O-PFNS, oxa-perfluorononane sulphonic acid; O-PFOS, oxa-perfluorooctane sulphonic acid; PFAAAm, perfluroalkyl amidoalkyl amine; PFAS, poly- and perfluoroalkyl substances; PFASAC, perfluroalkyl sulphonamidoalkyl amino carboxylic acid; PFASAm, perfluoroalkyl sulphonamidoalkyl amine; PFCA, perfluorinated carboxylic acid; PFECHS, perfluoroethylcyclohexane sulphonic acids; PFESA, perfluoroether sulphonic acid; PFHxSi, perfluorohexane sulphonate; PFOA, perfluorooctanoic acid; PFOAB, perfluorooctane amidoalkyl betaine; PFOANO, perfluorooctane amidoalkyl amine oxide; PFOS, perfluorooctane sulphonic acid; PFOSAmS, perfluorooctane sulphonamidoalkyl ammonium; PFOSB, perfluorooctane sulphonamidoalkyl betaine; PFOSNO, perfluorooctane sulphonamidoalkyl amine oxide; PFPA, perfluoroalkyl phosphonic acid; PFPiA, perfluoroalkyl phosphinic acid; PFSA, perfluoroalkane sulphonic acid; QA, quality assurance; QC, quality control; SAmPAP diester, phosphate diester of N-ethylperfluorooctane sulphonamide ethanol; SAmPAP triester, phosphate triester of N-ethylperfluorooctane sulphonamide ethanol; SD, standard deviation; SLE, supported liquid extraction; SRM, standard reference material; TBAS, tetrabutylammonium hydrogen sulphate; triPAP, tri-substituted polyfluorinated phosphate ester; UHPLC, ultra-high-performance liquid chromatography; WAX, weak anion exchange.

[a] Carbon chain length.

[b] Median or concentration range (depending on reference).

5.4. Discussion

Method development is clearly needed to facilitate analysis of the exposure of wildlife and humans to both original and novel PFAS possessing diverse chemical properties. Especially in Asian countries where most fluoropolymer production is now carried out, it is important to measure exposure to PFAS alternatives such as PFESAs, PFECAs and PFPiAs through biomonitoring. Discovery of over 300 novel PFAS belonging to 10 different classes in pooled fish liver samples collected in China [18] highlights the need for a breakthrough in this field, not only to keep up with industrial development, but also to implement precautionary measures against it. Advancement in this area will require the development of efficient pre-treatment methods, more robust ionisation techniques for MS analysis and non-invasive biological sample collection.

In recent decades, numerous publications on the analysis of wildlife and humans for legacy and novel PFAS using LC-MS/MS have been reported. However, due to the wide variety of chemical properties of PFAS, it is not easy to develop a sufficient pre-treatment method that eliminates matrix suppression/enhancement of lipophilic components in samples. To overcome this problem, many studies have improved quantitation results using isotope dilution [83,87,88] and matrix-matched calibration curve approaches [84]. However, problems remain since not all isotope-labelled reference standards are currently available, and matrices representative of all samples are also not available. Loss of sensitivity caused by ionisation suppression results in an increase in non-detection. Removal of lipid components by sample freezing after SPE clean-up [87], graphite carbon (e.g., ENVI-Carb) clean-up [83] and addition of 1-methyl piperazine to the LC-MS/MS mobile phase [83,84] have been suggested to overcome these problems, but none are perfect solutions. The most promising approach for minimising matrix effects is reducing the volume of the initial sample and the amount of extract injected. Thus, a sensitive method that covers a wide range of PFAS using a small sample volume is in great demand.

6. Non-target and non-specific analyses

6.1. Non-target analysis

Recent PFAS studies have revealed that numerous PFAS are continuously used and discharged into the global environment [10,54,90]. Thanks to improvements in HRMS performance, identification of as-yet-unknown PFAS by non-target analysis has become one of the main streams of PFAS research [8,9,91]. A pioneer study on novel PFAS identification in AFFF formulations used fast atom bombardment (FAB)-MS and quadrupole TOF-MS [92]. Following this study, diverse novel PFAS including anions, zwitterions, cations and neutral species were identified in AFFF samples [92,93], Fluorad surfactants [94], water [17], airborne particulate matter [16], fish [18] and circulating blood [19]. A recent report identified four new classes of PFAS consisting of more than 165 PFAS compounds in pooled fish samples collected downstream from a fluorochemical manufacturing site [18].

Several pre-treatment methods have been adopted for non-target analysis including dilution [94], SPE clean-up (e.g., Oasis WAX) [17,18], SLE [19] and SLE followed by activated carbon clean-up [16,17], similar to those employed for target analysis. These pre-treatment procedures initially optimised for anionic PFAS measurement are susceptible to loss of PFAS when applied to novel PFAS possessing different chemical properties [16,17]. Indeed, one study that attempted to develop a method for analysing firefighting foam in soils found that recoveries of cationic and zwitterionic PFAS were low when using a conventional pre-treatment method optimised for anionic PFAS [60]. It is important to select a pre-treatment procedure that can effectively reduce interference matrices and simultaneously capture a broad range of PFAS [16].

Multidimensional analysis techniques such as GC × GC or LC × LC followed by TOF-MS have been developed for non-target analysis of environmental contaminants in dust samples [95]. These methods are expected to work for non-target analysis of PFAS. Ruan and Jiang summarised the current status of non-target methods for PFAS [8]. In-source fragmentation flagging scans for anionic PFAS have proved effective in some recent studies [18]. Another study investigated high-resolution parent (precursor) ion searches using a TOF-MS system with continuously interleaving scans at low and high collision energies (MS^E) [94], which led to the identification of 47 new and 43 infrequently reported PFAS, including 40 non-ionic, 30 cationic, 15 zwitterionic and 5 anionic compounds.

6.2. Non-specific analysis

To overcome the challenge of the ever-increasing number of PFAS, non-specific inclusive approaches have been applied to analyse all known PFAS. Such methods include combustion ion chromatography (CIC), total oxidisable precursor (TOP) assays, particle-induced gamma ray emission (PIGE) spectroscopy and fluorine-19 nuclear magnetic resonance (19F NMR) spectroscopy. McDonough et al. summarised the advantages and disadvantages of non-specific methods previously employed for water analysis [96]. One of the most common non-specific methods is the extractable organic fluorine (EOF) assay using CIC that has been used for the analysis of water, sediment and biological samples since it was first reported by Miyake et al., in 2007 [97]. Different types of organic compounds are extracted prior to EOF assay to improve selectivity. Most recently, the technique was applied to detect PFAS in cosmetics [98]. Another method using CIC, the adsorbable organic fluorine (AOF) assay, utilises activated carbon adsorbent, but the authors did not directly compare EOF and AOF assays using the same samples to evaluate differences between the two methods.

The TOP assay originally developed by Houtz and Sedlak achieved greater detection selectivity but only for substances that can be oxidised to specific perfluoroalkyl acids (PFAAs) by comparing samples before and after oxidation by hydroxyl radicals [99]. This method has advantages over CIC since it does not require any specific instruments other than a simple LC-MS/MS system, and it can target precursors of specific PFAAs. Most recently, the TOP assay was applied to groundwater samples to evaluate seepage of PFAS through the soil of a firefighter training site to assess groundwater contamination [100]. PIGE spectroscopy and 19F NMR spectroscopy are promising non-destructive and non-specific methods, but few publications utilising these approaches have been reported to date.

6.3. Discussion

The most recent development in the analysis of PFAS is the discovery of 'new' PFAS in the environment using non-target approaches, made possible by the advancement of exact mass spectrometry instruments, including improved fragmentation techniques, increased instrumental sensitivity and better software. Promisingly, these non-target approaches have identified many novel PFAS, but the technology remains in its infancy. Sample pre-treatment methods and data analysis procedures are not yet standardised; hence this approach can be used for discovery rather than comprehensive analysis of PFAS at present. Developing a comprehensive technique capable of quantitative non-target

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Table 5
Analytical methods for PFAS in wildlife and human specimens.

Compounds			Matrix	Sample volume	Pre-treatment	Extraction	Clean-up	Instrument	LOD/LOQ	QA/QC	Misc.	Reported level		Reference
PFCAs[a]	PFSAs[a]	Other										n	Concentration[b]	
4–14	4, 6, 8, 10	FOSA, MeFOSAA, EtFOSAA	Fish	1 g	Remove head, skin, viscera, bone homogenisation	SLE (ACN), centrifugation	Oasis WAX, filtration	UHPLC-ESI(−)-MS/MS	2–120 pg/g (MDL)	Blanks, recoveries matrix effects, accuracy, precision	Simultaneous determination of 21 PFAS, including PASF-based substances	20	Σ9PFAS: 0.04 –2.14 ng/g ww	[87]
4–14	4, 6, 8	HFPO-TA, n:2 Cl-PFESAs (n = 6, 8)	Frog	0.2–0.8 g	Muscle separated from other tissues, cleaned with Milli-Q water homogenisation	For muscle, SLE (10 mM KOH/MeOH), sonication centrifugation For other tissues, SLE (0.5 M TBAS + $NaHCO_3$/Na_2C), O_3 buffer (pH 10), MTBE, shaking, centrifugation	Oasis WAX	UPLC-ES(−)-MS/MS	0.005–0.627 ng/g ww (LOQ)	Blanks, recoveries	Novel PFAS determination in biological samples	56	All tissues ΣPFCA: 1.92 –85.42 ng/g ww ΣPFAS: 0.27 –27.26 ng/g ww HFPO-TA (liver): 6.51–27.30 ng/g ww ΣPFESA: 0.21 –21.71 ng/g ww	[80]
4–7, 9–14	4, 6, 8	6:2 Cl-PFESA, FOSA, four branched isomers of PFOA and PFOS, br-FOSA	Fish	0.2 g	Homogenisation, freeze-drying	SLE (10 mmol/L KOH/MeOH), sonication shaking	Oasis WAX	HPLC-ESI(−)-MS/MS	0.002–0.66 ng/g (MQL)	Blanks, spikes, recoveries	–	43	–	[77]
–	8	n:2 Cl-PFESAs (n = 6, 8)	Marine organisms	0.5 g	–	SLE (10 mM KOH/MeOH), shaking	Oasis WAX	HPLC-ESI(−)-MS/MS	0.056 –0.093 ng/g (MDL)	Blanks, recoveries	Monitoring novel PFAS (Cl-PFESA) in various marine organisms	152	PFOS: 0.062 –0.932 ng/g ww 6:2 Cl-PFESA: 0.069 –0.351 ng/g ww 8:2 Cl-PFESA: <MDL–0.033 ng/g ww	[78]
4–14,	4, 6, 8, 10	PFPAs (n = 6, 8, 10), 6:6 PFPiA, 8:8 PFPiA, 6:8 PFPiA, PFECHS	Animal plasma	0.15–1 g	–	PFPA/PFPiA: LLE (ACN, MTBE), centrifugation vortexing, PFCA/PFSA: LLE (MeOH)	PFPA/PFPiA: ENVI-Carb	UHPLC-ESI(−)-MS/MS	PFCA/PFSA: 0.067–0.34 ng/g PFPA: 2.3 –6.7 ng/g PFPiA: 0.025 ng/g PFECHS: 0.17 ng/g (LOD)	Blanks, recoveries matrix effects	Monitoring novel PFAS (PFPA, PFPiA and PFECHS) in plasma from birds, fish and dolphins	141	ΣPFCA: 65 –3,171 ng/g ww ΣPFAS: 96 –2,337 ng/g ww PFPA: <LOD ΣPFPiA: 0.33 –5.0 ng/g ww	[82]
6–14	4, 6, 8, 10	PFECHS	Fish	0.2–0.3 g	Homogenisation	SLE (MeOH)	ENVI-Carb	HPLC-ESI(−)-MS/MS	MDL: 8 PFCA: 0.42 ng/g 9 PFCA: 0.14 ng/g Others: 0.10 ng/g	Blanks, recoveries	Simple method for determination of PFCA, PFAS and PFECHS	40	PFCA: <MDL –6.1 ng/g ww PFAS: <MDL –96 ng/g ww PFECHS: <MDL –3.7 ng/g ww	[81]
4–10	4, 6, 8	PFPAs (n = 6, 8, 10), FOSA, n:2 monoPAPs, n:2 diPAPs, n:2 FTUCAs (n = 6, 8), 6:2 FTCA, 8:2 FTCA, 5:3 FTCA, 7:3 FTCA	Mussel, fish muscle, liver	0.5 g	Freeze-drying	SLE (ACN/water), homogenising using FUSLE filtration	Oasis WAX, ENVI-Carb	UPLC-ESI(−)-MS/MS	0.1–3.8 ng/g (MDL)	Blanks, recoveries	Pre-treatment using FUSLE and tandem SPE clean-up (WAX + ENVI-Carb)	10	PFNA, PFDA: ND–2 ng/g PFOS: ND –1,062 ng/g FOSA: <MDL –15 ng/g 8:2 PAP: ND –86 ng/g	[83]

4–14	4–10, 12	FOSA	Serum	50 μL	Formic acid addition	Automated *m*-SPE (Oasis WAX)	Plate wash	UHPLC-ESI(−)-MS/MS	0.006 −0.339 ng/mL (MDL)	Blanks, matrix effects recoveries, accuracy, precision	Automated high-throughput SPE microelution	40	ΣPFOS: 0.13 −118 ng/mL ΣPFOA: 0.53 −3.44 ng/mL ΣPFHxS: 0.18 −11.6 ng/mL PFNA: 0.03 −2.06 ng/mL	[88]
4–14, 16, 18	4–10, 12	n:2 FTSAs (n = 4, 6, 8, 10), n:2 monoPAPs (n = 6, 8), diPAPs (6:2, 6:2/8:2, 8:2), PFPAs (n = 6, 8), PFPiAs (6:6, 6:6/8:8, 8:8), FOSA, MeFOSA, EtFOSA, FOSAA, MeFOSAA, EtFOSAA, n:2 Cl-PFESAs (n = 6, 8)	Serum	25 μL	Dilute with Milli-Q water, centrifugation	In-line SPE (Cyclone-P)	–	HPLC-ESI(−)-MS/MS	PFCA: 0.013 −0.089 ng/mL (LOD)	Blanks, matrix-matched calibration curves recoveries, accuracy, precision	Column switch online SPE matrix-matched calibration	30	PFCA: <LOD −2,140 ng/mL PFSA: <LOD −10,449 ng/mL FTSA: <LOD −171 ng/mL monoPAP: <LOD −0.19 ng/mL diPAP: <LOD−0.94 ng/mL PFPA: <LOD PFPiA: <LOD −0.09 ng/mL FASA: <LOD −0.97 ng/mL FASAA: <LOD −0.72 ng/mL Cl-PFESA: <LOD −1.39 ng/mL	[84]
8	8	–	Serum	1 mL	–	IPE (TBAS/MTBE)	–	UHPLC-ESI(−)-MS/MS	0.02 ng/mL (LOD)	Blanks, recoveries	Application of hair, nail and urine as biological indicators	64	0.26–35.15 ng/mL	[85]
			Urine	1 mL		Formic acid addition, sonication, centrifugation	Oasis WAX		1.1–2.1 ng/L (LOD)			63	<LOQ–159.9 ng/L	
			Hair	0.1 g	Rinse with water and acetone, air-drying	SLE (ACN), sonication			0.03 ng/g (LOD)			53	<LOQ–6.74 ng/g	
			Nail	0.1 g	grinding	Alkaline digestion (NaOH/MeOH)			0.04–0.05 ng/g (LOD)			63	<LOQ–5.09 ng/g	
4–14	4, 6, 8	n:2 Cl-PFESAs (n = 6, 8, 10)	Urine	50 mL	Dilute with water (50 mL)	SPE (Oasis WAX)	–	HPLC-ESI(−)-MS/MS	0.003 −0.035 ng/L (MQL)	Blanks, recoveries	Application of hair, nail and urine as biological indicators	41	<MQL–64.37 ng/mL	[79]
			Hair	0.1 g	Rinse with water and acetone, air-drying	SLE (ACN)	Oasis WAX		0.005 −0.110 ng/g (MQL)			41	<MQL–51.07 ng/mL	
			Nail		cutting and grinding	Alkaline digestion SLE (MeOH)	Oasis WAX		0.018 −0.339 ng/g (MQL)			41	<MQL–29.18 ng/g	

Abbreviations: ACN, acetonitrile; diPAP, polyfluoroalkyl phosphate diester; ESI, electrospray ionisation; EtFOSA, N-ethyl fluorooctane sulphonamide; EtOAc, ethyl acetate; FASA, perfluoroalkane sulphonamide; FASAA, N-alkyl perfluoroalkane sulphonamido acetic acid; FOSA, perfluorooctane sulphonamide; FOSAA, perfluorooctane sulphonamidoacetic acid; FTCA, fluorotelomer carboxylic acid; FTSA, fluorotelomer sulphonic acid; FTUCA, fluorotelomer unsaturated carboxylic acid; FUSLE, focused ultrasound solid-liquid extraction; HFPO-DA, hexafluoropropylene oxide dimer acid; HFPO-TA, hexafluoropropylene oxide trimer acid; HPLC-MS/MS, high-performance liquid chromatography-tandem mass spectrometry; HRMS, high-resolution mass spectrometry; IPE, ion-pair extraction; KOH, potassium hydroxide; LLE, liquid-liquid extraction; LOD, limit of detection; LOQ, limit of quantitation; MDL, method detection limit; MeFOSA, N-methyl fluorooctane sulphonamide; MeOH, methanol; monoPAP, polyfluoroalkyl phosphate monoester; MQL, method of quantitation limit; MTBE, methyl tert-butyl ether; Na_2CO_3, sodium carbonate; $NaHCO_3$, sodium hydrogen carbonate; NaOH, sodium hydroxide; ND, not detected; PASF, perfluoroalkane sulfonyl fluoride; PFAS, poly- and perfluoroalkyl substances; PFCA, perfluorinated carboxylic acid; PFESA, perfluoroether sulphonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulphonic acid; PFPA, perfluoroalkyl phosphonic acid; PFPiA, perfluoroalkyl phosphinic acid; PFSA, perfluoroalkane sulphonic acid; QA, quality assurance; QC, quality control; SD, standard deviation; SLE, supported liquid extraction; TBAS, tetrabutylammonium hydrogen sulphate; UHPLC, ultra-high-performance liquid chromatography; WAX, weak anion exchange; ww, wet weight.

[a] Carbon chain length.

[b] Mean or concentration range (depending on reference).

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analysis remains a future target, but until then, non-specific approaches are useful for screening fluorinated substances in the environment and various biological matrices. A vital shortcoming of non-specific methods is that their results cannot be used for estimating toxicological effects, preventing them from being used for regulatory purposes at present. A method that bridges non-specific analysis and toxicological evaluation is therefore greatly needed.

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