Trends in Analytical Chemistry 103 (2018) 137–155

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Analytical challenges to determine emerging persistent organic pollutants in aquatic ecosystems

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ARTICLE INFO

Article history:
Available online 10 April 2018

Keywords:
Emerging persistent organic pollutants
Perfluoroalkyl substances
Novel brominated flame retardants
Organophosphorus flame retardants
Aquatic ecosystem
Sample treatment
Extraction
Analytical determination

ABSTRACT

Emerging persistent organic pollutants (ePOPs) include polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonyl fluoride/perfluorooctane sulfonate (POSF/PFOS), which are newly listed in the Stockholm Convention. Other ePOPs, which have not been regulated, include organophosphate flame retardants (PFRs), novel brominated flame retardants (NBFRs) and other perfluoroalkyl substances (PFASs). Often ePOPs data related to occurrence, toxicity, impact or environmental behavior are insufficient or inadequate because of the lack of proper analytical methods to obtain them. Thus, a critical review of the analytical procedures proposed in the last six years (2011–2017) for determining ePOPs by chromatographic methods in the different compartments of the aquatic ecosystems is presented. The overall analytical procedure, from sampling to final determination, is emphasized presenting recent developments in the extraction, pre-concentration, and instrumental detection needed for the accurate quantification of ePOPs in environmental samples. Finally, this review examines the basic challenges we face in order to anticipate future directions and urgent needs of this field.

Abbreviations: μSIS, micro-selected ion storage mode; 1-MP, 1-methyl-piperidine; AA, ammonium acetate; ACE, acetone; ACN, acetonitrile; AcOH, acetic acid; AF, ammonium formate; APCI, atmospheric pressure chemical ionization; APPI, atmospheric pressure photoionization; BTBPE, 1,2-bis-(2,4,6-tribromophenoxy) ethane; CAR, carboxen; CI, chemical ionization; cLC, capillary liquid chromatography; DAD, diode array detection; DBDPE, Decabromodiphenyl ethane; DCM, dichloromethane; DDA, data dependent analysis; DI, direct injection; DIA, data independent analysis; DLLME, dispersive liquid-liquid microextraction; dSPE, dispersive solid-phase extraction; DVB, divinylbenzene; EI, electron ionization; ECNI, electron capture negative chemical ionization; ePOP, emerging persistent organic pollutant; ESI, electrospray ionization; EtAc, Ethyl acetate; FA, formic acid; FOSA, perfluoroalkyl sulfonamides; FOSE, perfluoroalkyl sulfonamide ethanol; FTOH, fluorotelomer alcohols; FUSLE, focused ultrasound solid-liquid extraction; GC, gas chromatography; GCB, graphitized carbon black; GCxGC, comprehensive two-dimensional gas chromatography; GPC, gel permeation chromatography; HBCD, hexabromocyclododecane; HEX, hexane; HPLC, high performance liquid chromatography; HRMS, high-resolution mass spectrometry; HRPS, high resolution product scan; HS, headspace; ICP, inductively coupled plasma; IDA, information dependent acquisition; ILL, immobilized ionic liquid; IMS, ion-mobility mass spectrometry; LC, liquid chromatography; LDTD, laser diode thermal desorption; LLE, liquid-liquid extraction; LLP, Liquid-liquid partition; LOD, limit of detection; LOQ, limit of quantification; MAE, microwave assisted extraction; MeOH, methanol; MS/MS, tandem mass spectrometry; MS, mass spectrometry; MSPD, matrix solid-phase dispersion; MTBE, methyl tert-butyl ether; N-EtFOSA, 2-ethylperfluoro-1-octanesulfonamide; N-EtFOSE, 2-(*N*-ethylperfluoro-1-octanesulfonamido)-ethanol; N-MeFOSA, *N*-methylperfluoro-1-octanesulfonamide; N-MeFOSE, 2-(*N*-methylperfluoro-1-octanesulfonamido)-ethanol; NBFR, novel brominated flame retardant; NCI, negative chemical ionization; nLC, nano liquid chromatography; PBDE, polybrominated diphenyl ether; PBT, pentabromotoluene; PDMS, polydimethylsiloxane; PFAS, perfluoroalkyl substance; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonate; PFCA, perfluoroalkyl carboxylic acids; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFP, pentafluorophenyl; PFR, organophosphate flame retardant; PFSA, perfluoroalkyl sulfonic acids; PLE, pressurized liquid extraction; POP, persistent organic pollutant; POSF, perfluorooctane sulfonyl fluoride; PRM, parallel reaction monitoring; PSA, primary secondary amina; QqLIT, quadrupole linear ion trap; QqQ, triple quadrupole; QqTOF, quadrupole time-of-flight; QuEChERS, quick, easy, cheap, effective, rugged and safe extraction method; RP, reversed phase; SEC, size exclusion chromatography; SFC, supercritical fluid chromatography; SLE, solid-liquid extraction; SPE, solid-phase extraction; SPLE, selective pressurized liquid extraction; SPM, solid particulate matter; SPME, solid-phase microextraction; SRM, selected reaction monitoring; TBAS, tetrabutyl ammonium hydrogen sulphate; TBBPA, tetrabromobisphenol-A; TCEP, tris(2-chloroethyl) phosphate; TCIPP, tris(2-chloroisopropyl) phosphate; TDCPP, tris(1,3-dichloro-2-propyl) phosphate; TEHP, tris(2-ethylhexyl) phosphate; TFC, turbulent flow chromatography; TMPP, tricresyl phosphate; TPhP, triphenyl phosphate; TPP, tripropyl phosphate; t-SIM, targeted selected ion monitoring; UHPLC, ultra-high performance liquid chromatography; UPC^2, ultra-performance convergence chromatography; USE, ultrasound assisted extraction; WAX, weak anion exchange; WW, wastewater.

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https://doi.org/10.1016/j.trac.2018.04.003
0165-9936/

1. Introduction

According to the Stockholm Convention on persistent organic pollutants (POPs) [1], these compounds are resistant to chemical, biological, and photolytic environmental degradation. POPs are stable and persistent, long-distance transportable, bioaccumulative, biomagnifiable in the food chain, and could pose significant impact on human health and the environment [2–7]. Exposure to POPs can cause serious health problems including certain cancers, birth defects and dysfunctional immune and reproductive systems, among others. Tracing the occurrence, distribution and fate of POPs in the environment is challenging because they can occur in different phases [*e.g.*, as a gas, dissolved and attached either to airborne particles or to solid particulate matter (SPM)] and can be exchanged among environmental compartments. Sediments can be considered as a sink of many POPs. Once POPs are released into waterbodies, they may also come into contact with SPM or they can be bioaccumulated in aquatic organisms, producing side effects [8]. Initially, twelve POPs coined as the "dirty dozen" were recognized as causing adverse effects on humans and the ecosystem. These are legacy POPs, the behavior and toxicity of which are well-known and have been banned or strictly regulated under the United Nations Environment Program [1], the European Union [9], the United States Environmental Protection Agency and Environment Canada [10]. However, they are still found in the environment and used in some developing countries.

Currently, there is a rising concern about the presence of new organic synthetic compounds in the environment, the so-called new or emerging contaminants. In many cases, these compounds are present in the environment since long time ago but they have not been identified until the development of new and more sensitive analytical methods. Therefore, most of them are not regulated and their effects on the environment and human health are unknown. These emerging contaminants also included emerging POPs (ePOPs) that are either, very recently or not yet regulated. In 2009, polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonyl fluoride/perfluorooctane sulfonate (POSF/PFOS) were added to the list of Stockholm Convention and hexabromocyclododecanes (HBCDs) listed as candidate. ePOPs include these substances as well as several others widely used in industrial processes and consumer products, such as perfluoroalkyl substances (PFASs), non-PBDEs or novel brominated flame retardants (NBFRs), organophosphate flame retardants (PFRs), Dechlorane plus and related compounds and sort-chain chlorinated paraffin that have been proposed as a replacement alternative for banned formulations [11,12]. The inclusion of some of these group as ePOPs is still controversial. PFRs are prone to be metabolized by liver in organisms [13]. The metabolites of PFRs, mainly diesters, have been found in numerous studies [14]. However, most of the studies considered them as ePOPs. Table 1 classifies ePOPs according to their chemical structure and physico-chemical properties. These compounds have a wide range of physical-chemical properties as water solubility, polarity, volatility, etc. As a whole ePOPs exhibit properties different from legacy POPs. These new POPs belong to several chemical classes with different origins and are often more polar, less volatile, even though some NBFRs, such as DP and DBDPE are lipophilic. This renders to an analytical determination much more demanding and difficult, particularly for the assessment of the aquatic ecosystems introducing a number of analytical matters that need to be solved. Moreover, ultra-trace analysis of these contaminants in aquatic environments is problematic due to the complexity and diversity of natural matrices, including biotic ones that are lipid-rich (the Achilles' heel within efficient extraction).

Due to the high number of ePOPs, this review focuses on NBFRs, PFRs and PFASs because of their widespread use. Previous reviews on analytical aspects of these ePOPs in several matrices can be found for NBFRs [11,15], PFRs [16] and PFASs [17–19]. These reviews are partial, need an update or are not focused on aquatic ecosystems. One book chapter by Guo and Kannan [20] presented an overview of the methodology to analyze traditional and new POPs in environmental matrices, but the wide coverage and the higher number of studies on the former had as a counterpart that methods related to the latter were scarce and less representative. Then, our critical review that provides a broader coverage on analytical challenges for ePOPs would be useful. In it, we outline the most recent extraction techniques, clean-up procedures and instrumental analyses of ePOPs in aquatic environment matrices published since 2011 offering a global overview of the analysis of ePOPs. The review also discusses the advantages and disadvantages of these techniques as well as future prospects related to the extraction and determination of ePOPs.

2. Sample extraction and clean-up

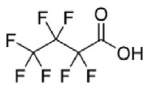
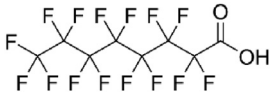
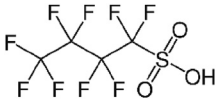
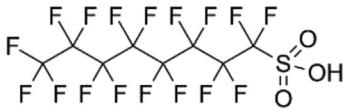
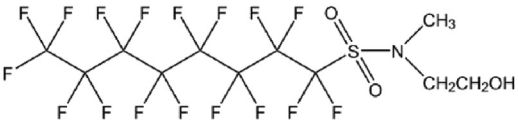
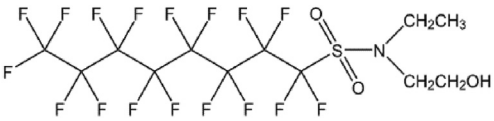
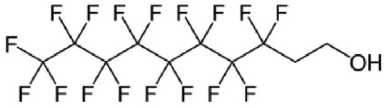
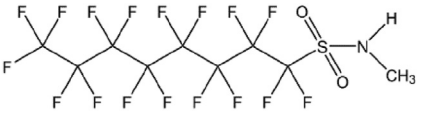
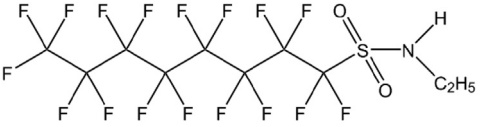
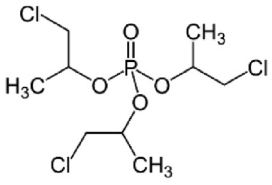
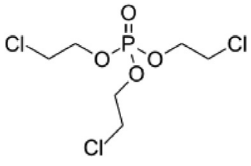
Current extraction and clean-up procedures for the analysis of ePOPs are summarized in Tables 2 and 3 for water and any other aquatic environmental matrices, respectively, and discussed in the following sections.

2.1. Understanding types and sources of sample contamination within QC/QA

Sampling procedures have a direct impact on the quality of analytical data. These topics were already detailed in deep in a previous review on legacy and new ePOPs and do not change since many years ago [18]. Relevant samples in the aquatic ecosystems are water and solid samples as sediment and/or biota. Aquatic biota (biofilm, macroinvertebrates, mollusc or fish) is sampled scrapping the rock surface, collected the species from water or using electric fishing and/or contacting to the local associations of fishermen, depending on the type of specimens [21–23]. The most common sediments samples reported to determine ePOPs are superficial samples taken with a grab sampler (dredgers, shovels, scoops, etc.) [23–25]. As these compounds are emerging POPs, deep sediment cores have not been reported yet. ePOPs are at low concentration in water samples, in addition to convention 1 or 2 L grab samples, both higher volume grab samples or passive samplers are commonly used. Even polar PFASs were sampled in Polar Organic Chemical Integrative Samplers (POCISs) filled as receiving phase materials with ionic liquids, HLB, Isolut ENV$^+$, carbonaceous materials, etc. [22,26,27]. To minimize the risks of sample contamination and to ensure sample integrity, basic precautions must be taken. Sample containers should be previously rinsed to eliminate any trace amount of ePOPs and after sampling, they must be sealed [28]. Furthermore, the quality control (QC) can play an important role to avoid contamination during sampling and transport, through the use of field blanks and field duplicate samples.

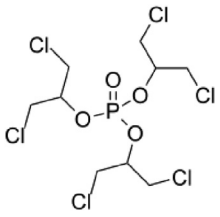
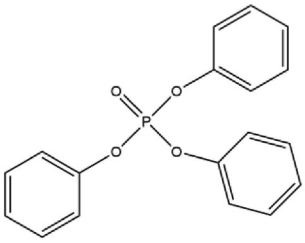
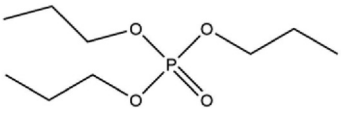
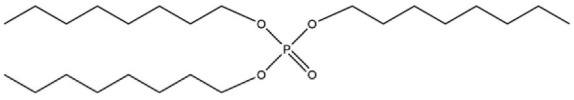
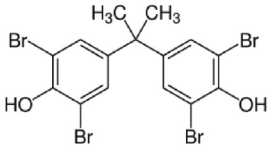
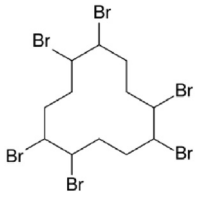
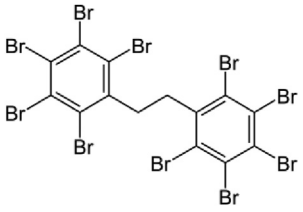
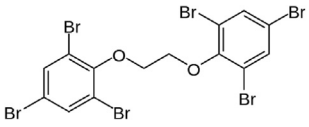
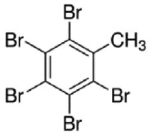
Once in laboratory, blank contamination is an important issue to take into account during the sample preparation process because of the ubiquity of ePOPs in laboratory material and equipment, and their presence in indoor air and dust. Some strategies to avoid or reduce blank contamination are: (i) rinse, heat and keep wrap in aluminum foil the non-volumetric material before use, (ii) minimize surface contact during sample handling, (iii) work in a cleanroom, (iv) reduce the use of plastic materials, or (v) perform a pre-extraction of materials that are used have been reported [16,23,29–35]. In the case of instrumental contamination, the replacement of some pieces by other fabricated with different

Table 1
Chemical structure and physico-chemical properties from selected ePOPs.

Family name	Category	Main examples	Structure	Log K_{OW}	pK_a
Perfluoroalkyl substances (PFASs)	Perfluoroalkyl carboxylic acids (PFCAs)	Perfluorobutanoic acid (PFBA)		−0.62 [a]	<1.6 [b]
		Perfluorooctanoic acid (PFOA)		1.79 [a]	0.5 [b]
	Perfluoroalkyl sulfonic acids (PFSAs)	Perfluorobutane sulfonate (PFBS)		0.14 [a]	<0.3 [b]
		Perfluorooctane sulfonate (PFOS)		2.56 [a]	<0.3 [b]
	Perfluoroalkyl sulfonamide ethanols (FOSEs)	2-(*N*-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)		3.81 [a]	Not available
		2-(*N*-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)		4.17 [a]	Not available
	Fluorotelomer alcohols (FTOHs)	6:2 FTOH		1.62 [a]	Not available
		8:2 FTOH		2.82 [a]	Not available
	Perfluoroalkyl sulfonamides (FOSAs)	*N*-methylperfluoro-1-octanesulfonamide (N-MeFOSA)		3.17 [a]	Not available
		N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)		3.53 [a]	Not available
Organophosphate flame retardants (PFRs)	Halogenated	Tris(2-chloroisopropyl) phosphate (TClPP)		2.59 [c]	Not available
		Tris(2-chloroethyl) phosphate (TCEP)		1.44 [c]	Not available

(*continued on next page*)

Table 1 (*continued*)

Family name	Category	Main examples	Structure	Log K_{OW}	pK_a
		Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)		3.3 [c]	Not available
	Non-halogenated	Triphenyl phosphate (TPhP)		4.59 [c]	Not available
		Tripropyl phosphate (TPP)		1.89 [c]	Not available
		Tris(2-ethylhexyl) phosphate (TEHP)		9.49 [c]	Not available
Novel brominated flame retardants (NBFRs)	Tetrabromobisphenol-A and derivatives	TBBPA		9.69 [c]	7.5–8.5 [c]
	Hexabromocyclodecanes	HBCD		7.92 [c]	Not available
	Others	Decabromodiphenyl ethane (DBDPE)		11.1[c]	Not available
		1,2-Bis (2,4,6-tribromophenoxy) ethane (BTBPE)		8.31[c]	Not available
		Pentabromotoluene (PBT)		6.25[c]	Not available

Data obtained from (a) [87], (b) [88], (d) [89].

Table 2
Sample extraction techniques from water samples.

Matrix	Analytes	Extraction	Clean-up	Separation	Determination	Recoveries	LOD/LOQ (ng L^{-1})	Ref.
WW and surface water (200 mL)	PFASs (n = 2)	SPE Enviro-Clean CUPSA, Oasis WAX, Presep PFC-II and Strata-X-AW Wash: FA and MeOH Elution: MTBE:MeOH 1% NH_4OH 9:1	–	Kinetex-C18 reversed-phase (50 × 3.0 mm, 1.7 μm) ACN (10 mM AF) and MeOH/ACN (1:1) Gradient, 0.3 mL min^{-1}	HPLC-(ESI)Orbitrap-MS in PRM	WW: 99–116% Surface: 98–111%	0.1–0.5[a]	[23]
WW (passive sampling)	PFASs (n = 5)	IIL-sampler: H_2O and vacuum freeze-dried Elution: MeOH (5% NH_4OH) Active sampler (500 mL): Filtered and SPE (WAX cartridge)	–	No data	HPLC–MS/MS	53.7–110%	0.2–0.6[b]	[26]
Surface water (passive sampling)	PFASs (n = 16)	Sorbent was transferred into glass gravity-fiow chromatography columns filled with glass wool. Elution: DCM:MeOH:toluene (8:1:1, v/v)	–	Cogent Bidentate C18 (50 × 2.1 mm, 4 μm) H_2O (0.1% FA) and ACN (0.1% FA) Gradient, 0.3–0.4 μL min^{-1}	LC-(ESI)HRSM(Q Exactive)	Not reported	Not reported	[22]
WW, surface water, ground and drinking	PFASs (n = 9)	Ultracentrifugation 30,000 × g Direct injection	–	Waters Acquity UPLC BEH C18 (100 × 2.1 mm, 1.7 μm) and C18 (100 × 4.6 mm) H_2O:MeOH (2 mM AA) 95:5 and MeOH (2 mM AA) Gradient, 0.5 mL min^{-1}	UHPLC-MS/MS in SRM	Not reported	0.014–0.44[b]	[36]
WW effluent (200 g)	PFASs (n = 52)	SPE Oasis WAX 60 mg Wash: MeOH, MeOH (0.1% NH_3), H_2O Elution: MeOH	–	MZ-Aqua Perfect C18 (50 × 2.1 mm, 5 μm) MeOH:H_2O 5:95 (5 mM AA) and 95:5 MeOH:H_2O (5 mM AA) Gradient, 0.3 mL min^{-1}	HPLC-(ESI)MS/MS(QTrap-QqQ) in scheduled SRM	53-149%	100–1000[b] 200–20000[c]	[34]
Surface water (200 mL)	PFASs	SPE OASIS WAX-SPE cartridge (150 mg) Wash: 0.1% NH_4OH, MeOH and H_2O Elution: MeOH (0.1% NH_4OH)	–	C6–C14 PFASs: Waters Acquity BEH C18 (75 × 2.5 mm, 1.7 μm) H_2O (2 mM AA) and MeOH C2–C14 PFASs: Waters Acquity UPC2Torus DIOL (150 × 3 mm, 1.7 μm) supercritical CO_2 and 0.1% NH_4OH in MeOH Gradient, 1.3 mL min^{-1}	C6–C14 PFASs: UPLC-MS/MS C2–C14 PFASs: UPC^2-MS/MS	84-96%	200–500[c]	[44]
Surface water (200 mL)	PFASs (n = 8)	SPE Oasis WAX Wash: MeOH and 25 mM AcOH:AA Elution: MeOH 0.1% NH_4OH	–	ACQUITY UPLC C18 (100 × 2.1 mm, 1.7 μm) H_2O (1 mM AA) and MeOH (1 mM AA) Multi-step gradient elution, 0.3 mL min^{-1}	LC-(ESI)Orbitrap Tribrid HRMS in full scan MS^1/dd-MS^2 and LC-(ESI)MS/MS(QqQ) in SRM	63-103% (Orbitrap)	Orbitrap: 0.007–0.06[b] QqQ: 0.01–0.05[b]	[45]
WW and surface water (0.25–1 L)	PFASs (n = 15)	SPE Strata X-AW Wash: H_2O Elution: 2x MeOH: H_2O (NH_4OH 0.1%)	Graphite cartridges (WW)	Deposition solvent: EtAc 2 L min^{-1}	LDTD/APCI-HRMS(Orbitrap) in full scan	38-106% (WW)	WW: 0.3–4 Surface water: 0.03–0.2	[46]
WW and surface water (1 L)	PFASs precursors (n = 8)	SPE Oasis HLB (500 mg) Wash: MeOH:H_2O 5:95 Elution: EtAc	–	TraceGold TG-WaxMS (30 m × 0.25 mm, 0.25 μm)	GC-(APCI)MS/MS(QqQ) in SRM mode GC-(APCI)QTOF-MS in SRM mode GC-(EI and CI) EI and CI	80–97%	1-5 fg [d]	[47]

(*continued on next page*)

Table 2 (*continued*)

Matrix	Analytes	Extraction	Clean-up	Separation	Determination	Recoveries	LOD/LOQ (ng L^{-1})	Ref.
					compared and EI selected			
Surface water (passive sampling) and grab samples (20 mL)	PFRs (n = 7)	Passive samples: SPE Elution: ACE Grab samples: SPE Oasis HLB (200 mg) Elution: ACE	–	Waters BEH C18 column (2.1 × 100 mm, 1.7 μm) H_2O (0.1% FA) and MeOH Gradient, 0.4 mL min^{-1}	UPLC-(ESI)MS/MS(QqQ)	Passive samples: 50.7–76% Grab samples: 48.8–72.5%	50–100[d]	[27]
Environmental water (200 mL)	PFRs (n = 12)	Filtered and SPE Oasis HLB Wash: ACN Elution: ACN	–	Waters BEH C8 (50 × 2.1 mm, 1.7 μm) H_2O (0.1% FA) and ACN (0.1% FA) Gradient, 0.2 mL min^{-1}	LC-(ESI)MS/MS(QqQ) in SRM	40–110%	2–6[b]	[48]
Surface water (250 mL)	PFASs (n = 21)	SPE Strata-X 200 mg Elution: MeOH (0.1% NH_4OH)	–	Kinetex XB-C18 (50 × 4.6 mm, 1.7 μm) H_2O (10 mM AF):MeOH (10 mM AF) Gradient, 0.2 mL min^{-1}	UHPLC-(ESI)MS/MS(QqQ) in SRM	55–94%	0.01–2.00[c]	[25]
Surface water (250 mL)	PFASs (n = 29)	SPE Strata-X AW 200 mg Wash: H_2O Elution: MeOH, MeOH (0.1% NH_4OH) and DCM: C_3H_8O (0.1% NH_4OH) 7:3	–	Waters Acquity BEH C18 (50 × 2.1 mm, 1.7 μm) H_2O (2 mM AA):MeOH 9:1 and MeOH, Gradient, 0.65 mL min^{-1}	UHPLC-(ESI)MS/MS(QqQ) in SRM	15–187%	4–10[c]	[24]
Surface water (10 mL)	PFASs (n = 7)	Derivatization with phosphate buffer, pyridine, propanol and propyl chloroformate to form the esters. HS-SPME CAR/PDMS fiber, Desorption: 290 °C, 10 min Extraction: room temperature, 10 min	–	SPME variables optimization: Varian VF-5MS (30 m × 0.25 mm, 0.25 μm) Calibration and quantification analyses: Thermo TR-5MS (30 m × 0.25 mm, 0.25 μm)	SPME variables optimization: GC-(EI)MS(ion-trap)/MS in full scan Calibration and quantification analyses: GC-(NCI)MS/MS(QqQ) in SRM	81.5–123.7%	0.08–6.6[b] 0.17–14.3[c]	[49]
Surface and tap water (10 mL)	PFAS (n = 14)	HS-SPME DBV/CAR/PDMS Desorption: 240 °C, 10 min Extraction: 50 °C, 30 min		Rxi-624SilMS (30 m × 0.25 mm; 1.4 μm)	GC-(EI)MS(/MS)(QqLIT) in full scan and μSIS	Surface: 64–213% Tap: 76–126%	Surface: 20–100[c] Tap: 20–100[c]	[21]
Surface and tap water (10 mL)	PFAS (n = 26)	DLLME NaCl + HCl Disperser: ACN Extraction: perfluoro-*tert*-butanol	–	Acclaim 120C18 (150 × 4.6 mm, 5 μm) MeOH (50 mM AA) and H_2O Gradient, 1 mL min^{-1}	HPLC-(ESI)MS/MS(QqQ)	Surface: 81.2–120.9% Tap: 85–119.4%	Surface: 0.18–3.3[b] Tap: 0.19–4.2[b]	[57]
Surface water (250 mL)	PFAS (n = 21)	SPE Strata-X 200 mg Elution: MeOH (0.1% NH_4OH)	–	Poroshell EC-C18 (50 × 30 mm, 2.7 μm) H_2O (10 mM AF) and MeOH (10 mM AF) Gradient, 0.3 mL min^{-1}	UHPLC-(ESI)MS/MS(QqQ) in SRM and UHPLC-(ESI)QqTOF-MS in IDA	QqTOF-MS: 67-99%	QqTOF-MS: 0.1–50[c]	[83]
Tap water (10 mL)	PFAS (n = 6) and NBFR (n = 1)	DLLME Disperser: MeOH Extraction: 1-undecanol	–	Zorbax Eclipse XDB–C18 (50 × 4.6 mm,1.8 μm) MeOH and 5 mM AA Gradient, 0.6 mL min^{-1}	HPLC-(ESI)MS/MS(QqQ)	Surface: 15–103% Tap: 15–105%	Surface: 1–324[b] Tap: 1-295[b]	[58]
Surface water (500 mL)	PFRs (n = 13)	Dissolved phase: SPE SERDOLITH PAC 3 (500 mg) Wash: H_2O Elution: 5x DCM or LLE 2x DCM Particulate phase: USE 2x DCM 15 min	–	HP-5MS (30 mm × 0.25 mm, 0.25 μm)	GC-(EI)MS/MS(QqQ) in SRM	45–77%	2.7–26.6[b]	[50]

Surface water (1 L)	PFRs (n = 14)	SPE Envi-18 (500 mg) Wash: H2O Elution: DCM:ACN 1:3	–	Acclaim mixed-mode HILIC-1 (150 × 2.1 mm, 5.0 μm) H_2O and ACN Gradient, 0.25 mL min^{-1}	HPLC-(ESI)MS/MS(QqQ) in SRM	58.6–116.2%	0.3–16[b] 1–35[c]	[51]
River water (160 L)	PFRs (n = 15) and NBFRs (n = 8)	Particle phase: Filtration fiber filter (0.7 μm) Dissolved phase: XAD-2 resin glass column XAD-2 and filters extracted by Soxhlet 30 h/800 mL HEX:ACE 1:1	Silica gel column Elution: HEX, HEX:DCM 1:1 and ACE:DCM 7:3	DB-5MS Ultra Inert (30 m × 0.25 mm, 0.25 μm) for PFRs and RTX-1614 (15 m × 250 μm, 0.1 μm)	GC-(EI)MS(q) for PFRs and GC-(ECNI)MS for NBFRs	PFRs: 57–117% NBFRs: 71–86%	PFRs: 0.02–0.12 NBFRs: 0.00007–0.002	[53]
Seawater (6 L)	NBFRs (n = 4)	Automated SPE SDB-XC disks, 55 °C, 10 min Disks eluted by PLE DCM:HEX 1:1	–	Reverse-phase column C18 (150 × 4.6 mm, 1.8 μm) MeOH and 10 mM AA Gradient, 0.3 mL min^{-1}	LC-(ESI)MS/MS(QqQ)	58-91% (internal standard)	0.03–0.09[b]	[52]
Seawater, tap water and surface water (200 mL)	NBFRs (n = 7)	Filtration (0.45 μm membranes) and LLE 3x DCM	–	ZORBAX Eclipse Plus C18 (150 × 4.6 mm, 5 μm) MeOH (0.1% AcOH) and H_2O (0.1% AcOH) Gradient, 1 mL min^{-1}	HPLC-ICP-MS/MS	67.7–112%	0.71–1.16[b]	[54]

[a] Method reporting level.
[b] Method LOD.
[c] Method LOQ.
[d] Instrumental LOQ.

materials as well as the insertion of a trap column before the injector are the preferred solutions. Reduction of time and method steps during extraction, clean-up and evaporation processes are mandatory. In the case of water samples, direct injection (DI) is another choice to overcome any contamination through sample laboratory handling. However, in DI, matrix effects could be higher affecting significantly sensitivity and precision [36]. There is no consensus or uniformity on the best way to eliminate this background contamination; however, two points are important within all the protocols described (i) eliminate or distinguish the compounds released by laboratory material and instrumental and (ii) avoid sample contamination through pre-treatment and extraction. Despite of these precautions, some analytes are present in laboratory blanks, and minimizing its presence as much as possible is one of the pending issues in the analysis of ePOPs.

The quality assurance and quality control (QA/QC) were of great importance in the method development to support the validity of data during the analysis of ePOPs. Limits of detection (LOD), limits of quantification (LOQ) and recovery values are listed in Table 2 (aqueous samples) and Table 3 (solid matrices). Usually, quantification of ePOPs is performed using the internal standard method that employs commercially labelled standards. Matrix-matched calibration is appropriate when analysing complex matrices. As it mentioned above, laboratory blanks must be analysed at regular intervals to check for potential contamination. Furthermore, it is highly desirable to improve the accuracy and precision for ePOPs determination in aquatic ecosystems and, subsequently, make the obtained results comparable among different laboratories. One of the most important ways to establish a common basis for accuracy measurement and quantification is the existence of a reliable certified reference material (CRM) [23,37–42]. These CRM are still scarce for ePOPs [31]. However, just for further information on the existing matrix CRMs (water, biota and sediment), Ricci *et al.* [37] describe the state of the art availability of matrix CRMs for environmental monitoring laboratories.

World-wide inter-laboratory studies on PFRs [31] and PFASs [43] were already organized to improve the qualitative and quantitative environmental occurrence data. Moreover, these exercises also outline recommendations on how to improve analytical performance, especially to reduce contamination of blanks. These inter-laboratory studies demonstrated to be very helpful to validate the analysis method of ePOPs.

2.2. Extraction and clean-up of aqueous samples

As outlined in Table 2, manual or automated SPE is the most commonly used strategy to concentrate and extract aqueous samples. This strategy is versatile and can be adapted to the analyte characteristics. Main sorbents chosen for PFASs, SPE are the weak anion-exchangers like Oasis WAX [23,34,44,45] and Strata-X AW [23,46] because these compounds are negatively charged at environmental pH. Polymeric reversed phases or hydrophilic-lipophilic sorbents as Oasis HLB [47,48] and Strata-X [25] are also employed. PFASs are the most polar, water soluble and less volatile ePOPs. Their concentrations in water may reach the ng L^{-1} level and then, SPE could be performed passing sample volumes between 100 mL and 1 L. For eluting PFASs, the principal options are either methanol (MeOH) alone [34] or with the addition of 0.1% NH_4OH to ensure ionization and reduce retention of compounds in the sorbent [25,44,45] or both [24].

One important trend in sample extraction framed in the principles of "green analytical chemistry" is the miniaturization of the extraction procedures. Solid-phase microextraction (SPME) with direct immersion in simple matrices as water is common. However, Monteleone *et al.* [49] obtained more intense PFAS peaks when

Table 3
Sample extraction techniques from solid biotic and abiotic matrices.

Matrix	Analytes	Extraction	Clean-up	Separation	Determination	Recoveries	LOD/LOQ (ng g^{-1})	Ref.
Biota, sediment and sewage sludge (0.5 g)	PFASs (n = 2)	USE 2x (MeOH and 0.2 M NaOH) 15 min	SPE Enviro-Clean CUPSA, Oasis WAX, Presep PFC-II and Strata-X-AW Wash: FA and MeOH Elution: MTBE:MeOH 1% NH_4OH 9:1	Kinetex-C18 (50 × 3.0 mm, 1.7 μm) ACN (10 mM AF) and MeOH/ACN (1:1) Gradient, 0.3 mL min^{-1}	HPLC-(ESI) MS(Orbitrap) in PRM	Sediment: 98–116% Sludge: 88–98% Fish: 97–109%	0.04–0.12[a]	[23]
Fish (0.5 g muscle and liver)	PFASs (n = 16)	Extraction: ACN (1% FA)	–	Cogent Bidentate C18 (50 × 2.1 mm, 4 μm) H_2O (0.1% FA) and ACN (0.1% FA) Gradient, 0.3–0.4 μL min^{-1}	LC-(ESI)HRSM(Q Exactive)	86–130%	Muscle: 0.22–2.8[c] Liver: 0.33–9.8[c]	[22]
Sediment (5 g) and fish (2 g)	PFASs (n = 21)	Sediment: Mechanical agitation and USE AcOH and MeOH Fish: Alkaline digestion (MeOH + NaOH)/4 h + DI	Sediment: SPE (250 mL) Strata-X 200 mg Elution: MeOH (0.1% NH_4OH) Fish: TFC online enrichment with C18 (20 × 2.1 mm, 12 μm)	Sediment: Kinetex XB-C18 (50 × 4.6 mm, 1.7 μm) H_2O (10 mM AF):MeOH (10 mM AF) Gradient, 0.2 mL min^{-1} Fish: Hypersil Gold PFP (50 × 3 mm, 5 μm) H_2O (20 mM AA) and MeOH (20 mM AA) No linear gradient, 0.4 mL min^{-1}	Sediment: UHPLC-(ESI)MS/MS(QqQ) in SRM Fish: TFC-LC-(ESI) MS/MS(QqQ) in SRM	Sediment: 44–100% Fish: 16–135%	Sediment: 0.04–8.00[c] Fish: 0.02–2.26[c]	[25]
Sediment, soil and sludge (0.1–1 g)	PFASs (n = 29)	USE 2x (MeOH:1% AcOH 9:1, vortex, sonicated 15 min/60 °C)	SPE Strata-X AW 200 mg Wash: H_2O Elution: MeOH, MeOH (0.1% NH_4OH and DCM:2-propanol (0.1% NH_4OH) 7:3	Waters Acquity BEH C18 (50 × 2.1 mm, 1.7 μm) and Acquity BEH C18 (5 × 2.1 mm, 1.7 μm) H_2O (2 mM AA):MeOH 9:1 and MeOH Gradient, 0.65 mL min^{-1}	UHPLC-(ESI)MS/MS(QqQ) in SRM	Sediment/soil: 60–108% Sludge: 57–114%	Sediment/soil: 2[c] Sludge: 20[c]	[24]
Sediment (0.5 g)	PFAS (n = 14)	SPME DBV/CAR/PDMS Desorption: 240 °C, 10 min Extraction: 50 °C, 30 min	–	Rxi-624SilMS (30 m × 0.25 mm; 1.4 μm)	GC-(EI)MS(/MS) (Ion trap) in full scan and μSIS	74–125%	1–3[c]	[21]
Sediment (1 g)	PFASs (n = 21)	Mechanical agitation 2x (ACN/0.2M NaOH 3:1)	LLP ion-pair extraction TBAS + 2x MTBE	Restek Ultra C18 (50 × 2.1 mm, 3 μm) H_2O (10 mM AA) and MeOH (10 mM AA) Gradient, 0.25 mL min^{-1}	LC-(ESI)MS/MS(QTrap-QqQ) in SRM	73–120%	0.004–0.2[b]	[59]
European eel (1 g muscle)	PFASs (n = 17)	Mechanical agitation 15 min MeOH (0.01 M KOH)	SPE WAX stationary phase (150 mg) Wash: AA and MeOH Elution: MEOH:NH_4OH 99.5:0.5 and 2nd SPE GCB Envicarb (500 mg) Elution: MeOH:glacial AcOH	Gemini C18 reverse phase (50 × 2.0 mm, 3 μm) MeOH and H_2O (20 mM AA) Gradient, 0.6 mL min^{-1}	LC-(ESI)MS/MS(QqQ) in SRM	65–125%	0.006–1.259[c]	[60]
Sediment	PFASs and isomers/enantiomers (n = 9)	Mechanical agitation ACN:H_2O 3:2	Derivatization of non-volatile PFASs with diazomethane	Columns in tandem: DB-5MS (30 m × 0.25 mm, 0.25 μm) and BGB-172 Analytik chiral (30 m × 0.25 mm, 0.25 μm)	GC-(NCI)MS	Not reported	Not reported	[61]
Soil and sediment (5 g)	PFASs (n = 20)	USE MeOH 3 × 15 min	SPE Strata-X 33 μm 200 mg Wash: MeOH (0.1% NH_4OH), MeOH, H_2O Elution: MeOH (0.1% NH_4OH)	Kinetex-C18 (50 × 2.1 mm, 1.7 μm) H_2O (10 mM AF) and MeOH (10 mM AF) Gradient, 0.2 mL min^{-1}	UHPLC-(ESI) MS/MS(QqQ) in SRM	Sediment: 69–103% Soil: 70–109%	Sediment: 0.02–0.45[c] Soil: 0.01–6[c]	[64]
	PFASs (n = 11)	USE H_2O:ACN 1:9 + FA 15 min				40–133%		[68]

Mollusk (1–10 g)			Online TFC Columns: Thermo Fluoro XL, (50 × 0.5 mm) and Thermo Cyclone (50 × 0.5 mm)	Thermo Hypersil GOLD PFP (50 × 2.1 mm, 1.9 μm) Mobile phases not reported Isocratic, 2 mL min^{-1}	UHPLC-(ESI)MS/ MS(QqQ) in SRM		0.03–0.3[b] 0.1–0.9[c]	
Benthic invertebrates (12–20 mg)	PFASs (n = 2)	Modified QuEChERS 0.5 mL ACN + 0.5 mL H_2O + 0.2 mL HEX + citrate buffer	–	C18 PepMap 100 (15 cm × 75 μm, 3 μm) H_2O (0.1 mM AA) and ACN:MeOH:H_2O (0.1 mM AA) 45:45:10 Gradient, 0.3 mL min^{-1}	NanoLC-(nanoESI) MS/MS(QqLIT) in SRM	92–109%	1.4–3.5[c]	[69]
Biota (0.5 g)	PFASs and precursors (n = 24)	FUSLE ACN:H_2O 9:1/2.5 min/ 10% power/0 °C ice water bath	SPE Evolute-WAX (200 mg) Wash: FA (2%) and H_2O:MeOH 95:5 Elution: ACE 0.1% NH_4OH	ACE UltraCore 2.5 Super C18 (50 × 2.1 mm, 2.5 μm) H_2O:MeOH (95:5) and MeOH:H2O 2 mM AA and 5 mM 1-MP Gradient, 0.3 mL min^{-1}	HPLC-(ESI)MS/ MS(QqQ) in SRM	Liver: 66–111% Mussel: 77–119% Muscle: 83–146%	Liver: 0.1–4.1[b] Mussel: 0.1–3.8[b] Muscle: 0.2–3.2[b]	[70]
Sewage sludge (0.5 g)	PFASs (n = 7)	FUSLE ACN/2 × 20 s/pulsation 0.5/65% power/0 °C ice water bath	PLE MeOH; 2 cycles; 1 min; 70 °C	Waters Acquity BEH C18 (50 × 2.1 mm, 1.7 μm) ACN (0.1% FA) and H_2O (0.1% FA) Gradient, 0.45 mL min^{-1}	UPLC-(ESI)MS/ MS(QTOF)	69–104%	Not reported	[71]
Mollusk (0.5 g)	PFASs (n = 8)	MSPD Diatomaceous earth Elution: ACN	Na_2SO_4 + silica	Ascentis Express C18 (50 × 2.1 mm, 2.7 μm) H_2O (5 mM AA) and MeOH (5 mM AA) Gradient, 0.4 mL min^{-1}	LC-(ESI)MS/ MS(QqQ) in SRM	64–126%	0.05–0.3[b] 0.2–1.0[c]	[72]
Sediment and fish (2 g)	PFASs (n = 21)	Sediment: USE 1st H_2O (1% AcOH), 2nd MeOH ((1% AcOH) and 3rd H_2O (1% AcOH) Fish: Alkaline digestion (MeOH + NaOH)	SPE Strata-X 200 mg Elution: MeOH (0.1% NH_4OH)	Poroshell EC-C18 (50 × 30 mm, 2.7 μm) H_2O (10 mM AF) and MeOH (10 mM AF) Gradient, 0.3 mL min^{-1}	UHPLC-(ESI)MS/ MS(QqQ) in SRM and UHPLC-(ESI) QqTOF-MS in IDA	Sediment: 62–100% Fish: 60–95% (QqTOF)	Sediment: 0.1–2 Fish: 0.01–5 (QqTOF)	[83]
Sediment (2 g)	PFASs (n = 11) and PFRs (n = 2)	USE ACE:MeOH 1:1 30 min and agitation/3 h	SPE GCB cartridge Elution: DCM:MeOH 4:1 (10 mM AF)	Hypersil Gold (50 × 2.1 mm, 1.9 μm) H_2O and MeOH Gradient, 0.3 mL min^{-1}	UHPLC-(ESI)MS/ MS(QqQ) in SRM	75–110%	0.04–2.4[b] 0.14–7.9[c]	[29]
Fish (0.25 g)	PFRs (n = 16)	USE ACE:HEX 1:1 2 × 15 min	Scavenging tandem basic alumina (5 g) and C18 (2 g) cartridges Wash: ACN Elution: ACN	Purosphere Star RP-18 (125 × 2.0 mm, 5 μm) H_2O (0.1% FA) and MeOH (10 mM AA) Gradient, 0.25 mL min^{-1}	LC-MS/MS(QqLIT) in SRM	48–113%	0.3–51.6[b] 1.12–172[c]	[30]
Soil and fish (1 g)	PFRs (n = 9)	USE MeOH 3 × 15 min	SPE Strata-X 33 μm 200 mg Wash: DCM:MeOH 1:1, MeOH, H_2O Elution: MeOH	Kinetex-C18 (50 × 2.1 mm, 1.7 μm) H_2O (0.1% FA) and MeOH (0.1% FA) Gradient, 0.2 mL min^{-1}	UHPLC-(ESI)MS/ MS(QqQ) in SRM	Soil: 50–121% Fish: 47–123%	Soil: 0.01–0.1[b] Fish: 0.01–0.15[b]	[66]
Sediment (1 g) and fish (0.5 g)	PFRs (n = 14)	Sediment: PLE (1 g) ACE:HEX 1:1 Fish: USE (0.5 g) ACE:HEX 1:1 2 × 15 min	Online TFC Columns: CycloneTM-P (0.5 × 50 mm) and C18-XL (0.5 × 50 mm) Solvents: H_2O (0.1% FA) and MeOH (AA)	Purosphere Star RP-18 (125 × 2.0 mm, 5 μm) H_2O (0.1% FA) and MeOH (0.1% FA) Gradient, 0.25 mL min^{-1}	LC-(ESI)MS/ MS(QqQ) in SRM	Sediment: 47–108% Fish: 47–98%	Sediment: 0.02–1.25[b] 0.05–3.44[c] Fish: 0.44–19.3[b] 0.97–24.8[c]	[33]
Lipid-rich biota (applied in fish) (1 g)	PFRs (n = 13)	USE 2x (DCM:HEX 1:1) + NaCl + $MgSO_4$ 10 min	dSPE: PSA 100 mg, PSA 200 mg, PSA 300 mg, Z-Sep+ 300 mg, DSC-18 300 mg and ENVI-Carb 300 mg	Waters Cortecs UPLC C18 (50 × 2.1 mm, 1.6 μm) coupled with ACQUITY UPLC in-line filter kit. H_2O and MeOH Gradient, 0.5 mL min^{-1}	UHPLC-(APCI+)MS/ MS(QqQ) in SRM	Egg: 54–108% Liver: 66–113%	Egg: 0.02–0.13[b] 0.06–0.29[c] Liver: 0.03–0.14[b] 0.05–0.5[c]	[32]

(*continued on next page*)

Table 3 (*continued*)

Matrix	Analytes	Extraction	Clean-up	Separation	Determination	Recoveries	LOD/LOQ (ng g^{-1})	Ref.
Fish (1 g)	PFRs (n = 14)	MAE HEX:ACE 1:1; 1200 W; 130 °C; 20 min	GPC Bio-Beads S-X3 Elution: DCM:HEX and Silica gel column (4 g) Elution: 1st fraction: HEX, 2nd fraction: DCM/HEX 3:7, 3rd fraction: ACE:EtAc 1st, 2nd and 3rd fractions combined	DB-5 MS column (30 m × 0.25 mm, 0.25 μm)	GC-(EI)MS(q) in SIM	39–105%	0.006–0.021[b]	[35]
Sediment and fish (200 mg lipid)	PFRs (n = 9)	PLE DCM:ACE 1:1; 3 cycles; 70 °C	SPE NH_2 cartridge (500 mg) Washed: DCM and HEX Eluted: DCM:HEX 8:2 and DCM	Luna C18 (150 × 3 mm, 3 μm) Mobile phases not reported	HPLC-(ESI)MS/ MS(QqQ) in SRM	Sediment: 71–130% Fish: 43–134%	0.2–29[b]	[38]
Soil and sediment (15 g)	PFRs (n = 11)	PLE ACE:HEX 1:1; 40 min; 35 °C	Florisil column (1 g) Eluted: ACN	ZORBAX Eclipse Plus C18 RRHD (100 × 2.1 mm, 1.8 μm) H_2O (10 mM AA) and MeOH (10 mM AA) Gradient, 0.3 mL min^{-1}	UHPLC-(ESI)MS/MS in SRM	Soil: 56–104% Sediment: 59–103%	0.01–5[c]	[77]
Biota and sediment (0.5 g)	PFASs (n = 6) and NBFR (n = 1)	Mechanical agitation 2x ACN	dSPE C18, hand-shaked and centrifuged 5 min/ 4050 × g	HALO C18 Rapid Resolution (50 × 4.6 mm, 2.7 μm) H_2O (AcOH:AA) and MeOH (AcOH:AA) Gradient, 0.6 mL min^{-1}	HPLC-(ESI)MS/ MS(QqQ) in SRM	80–114%	0.008–4[b] 0.03–13[c]	[62]
Sediment (1.5 g) and sludge (0.1 g)	NBFR (n = 9) and PFRs (n = 10)	USE 2x EtAc:cyclohexane 5:2	Florisil cartridges (5–10 g) Wash and elution: EtAc:cyclohexane 5:2	DB-5MS (15 m × 0.250 mm, 0.10 μm)	GC-(ECNI)MS/ MS(QqQ) in SRM	Sediment: 48–140% Sludge: 64–140%	Sediment: 0.2–80[b] Sludge: 3.7–575[b]	[39]
Bivalve and sediment (5 g)	NBFR (n = 4)	USE 2x DCM:HEX 1:1	Multilayer silica column 1.5% deactivated silica and 44% H_2SO_4 silica Florisil column (used for bivalve when necessary)	RP C18 (150 × 4.6 mm, 1.8 μm) MeOH and 10 mM AA Gradient, 0.3 mL min^{-1}	LC-(ESI)MS/ MS(QqQ)	65–96%	Bivalve: 0.013–0.084[b] Sediment: 0.023 –0.074[b]	[52]
Marine sediment and biota (5–10 g)	NBFR (n = 12)	USE HEX:DCM 1:1	GPC (only biota) Bio-Beads Eluent: HEX:DCM 1:1 Extra clean-up for GC: Deactivated Florisil (8 g) Eluent: HEX:DCM 1:1 and PTFE Cartridge Filter (0.2 μm) for LC	HT-5MS (15 m x 0.25 mm, 0.10 μm) for GC and ZORBAX Eclipse Plus C18 (2.1 × 100 mm^2, 1.8 μm) for LC H_2O and ACN:MeOH 30:70 Gradient, 0.4 mL min^{-1}	GC-EI-MS/MS(QqQ) in SRM and LC-ESI-MS/MS(QqQ) in SRM	Biota: 41–106% Sediment: 31–105%	0.0001–0.33[b]	[65]
Mollusks (0.5 g)	NBFR (n = 6)	MSPD PSA Elution: DCM	Silica, acidified silica (10% H_2SO_4) and Florisil (5% H_2O)	DB-5HT (15 m × 0.25 mm, 0.10 μm	GC-(NCI)MS(Q)	46–120%	0.003–0.6[b] 0.01–2.1[c]	[41]
Marine biota (6–200 g)	NBFR (n = 2)	MSPD Silica gel: Na_2SO_4 4:1 Elution: ACE:HEX 1:1	Multilayer silica column neutral silica, 44% H_2SO_4 silica and 56% KOH silica Elution: HEX	DB-1HT (15 m × 0.25 mm, 0.1 μm)	GC-(APCI)MS/ MS(QqQ) in SRM and GC-(EI)MS/ MS(QqQ) Lower LOD for APCI	Not reported	1–25 fg[b]	[73]

Sediment, sludge, fish and dolphin blubber (1–1.5 g)	NBFR (n = 3)	Sediment: SPLE Sludge, biota: PLE HEX:DCM 1:1; 2 cycles; 10 min; 100 °C	Sludge: Silica (2 g) and alumina (5 g) cartridges Biota: fat removal with H_2SO_4 and SPE with alumina cartridges (5 g)	DB-5MS (15 m × 0.1 mm, 0.1 μm)	GC-(NCI and EI)MS/MS(QqQ) in SRM EI selected as the best ionization mode	Sediment: 103–105% Sludge: 52–66% Fish: 58–80% Dolphin blubber: 71–76%	Sediment: 0.03–0.1[b] Sludge: 0.4–0.9[b] Fish: 0.2–9.6[b] Dolphin blubber: 0.1–1.1[b]	[74]
Sediment (10 g)	NBFR (n = 2)	Soxhlet ACE:HEX (1:1)	Multilayer silica column Elution: HEX:DCM 1:1	DB-XLB (30 m × 0.25 mm, 0.25 μm)	GC-(ECNI)MS in SIM	70–130%	0.056–0.006[b]	[75]
Fish (10 g)	NBFR (n = 14)	Soxtec (automated soxhlet extraction) DCM:HEX 1:1	GPC Bio-Beads S-X3 cycloHEX:EtAc 1:1 and multilayer silica column 44% H_2SO_4 silica and deactivated silica Elution: HEX:DCM 1:1 and ACE	Kinetex reverse-phase C18 (100 × 2.1 mm, 2.6 μm) MeOH:H_2O 60:40 and MeOH:toluene 95:5 Gradient, 0.4 mL min^{-1}	HPLC-(APPI) MS(Orbitrap) in full scan	83–117%	0.001–0.25[c]	[42]
Sediment, fish and seal blubber (10 g)	NBFR (n = 13)	HBCD diastereomers: PLE DCM; 2 cycles; 5 min; 100 °C Other NBFRs: PLE DCM:HEX 1:1; 3 cycles; 5 min; 100 °C	HBCD diastereomers: SEC Envirosep-ABC (350 × 21.1 mm) Elution: DCM and Silica column (2 g) Elution 1st fraction: HEX Elution 2nd fraction: HEX:DCM Elution 3rd fraction: DCM Other NBFRs: SEC Envirogel polymer column (30 × 1.9 cm, 15 μm) Elution: DCM	HBCD diastereomers: Acquity BEH C18 (150 × 2.1 mm, 1.7 μm) H_2O:MeOH 3:1 and MeOH:ACN 1:1 Gradient, 0.2 mL min^{-1} Other NBFRs: DB-5MS (15 m × 0.25 mm, 0.1 μm)	HBCD diastereomers: UPLC-(ESI)MS/MS(QTrap) in SRM Other NBFRs: GC-(ECNI)MS	Sediment: 81–123% Fish: 43–120% Seal blubber: 54–76%	Not reported	[28]
Fish (3 g)	NBFR (n = 3)	PLE HEX:DCM 1:1; 2 cycles; 10 min; 100 °C	Neutral alumina cartridge (5 g) Wash: HEX Elution: HEX:DCM	DB-5MS (15 m × 0.25 mm, 0.1 μm)	GC-(ECNI)MS/MS(QqQ) in SRM	51–98%	0.2–2.1[b] 0.4–6.8[c]	[78]
Fish (10 g) and fish feed (1 g)	NBFR (n = 6)	Modified QuEChERS 5 mL H_2O + 10 mL EtAc + 4 g $MgSO_4$ + 2 g NaCl	Silica gel column (1 g or 5 g) Elution: HEX:DCM (3:1)	Rxi-17Sil MS (30 m × 0.25, 0.25 μm)	UGC-(EI)MS/MS(QqQ) in full scan	82-–01%	0.5–1[c]	[80]
Seal and egg (3 g)	NBFR (n = 21)	Lipid extraction in open glass column HEX:DCM 1:1 in an open glass column	Multilayer silica column Elution: HEX and HEX:DCM 1:1	Rtx-1614 (15 m × 0.25 mm, 0.1 μm)	GC-(APCI)MS/MS(QqQ) in SRM	44–131%	0.001–0.01[b]	[40]

[a] Method reporting level.
[b] Method LOD.
[c] Method LOQ.

they performed the method in headspace (HS) acquisition after the formation of PFAS ester derivatives to form volatile derivatives able to both, HS extraction and further gas chromatography (GC) determination. The ester derivatives are non-polar and volatile, then properly extracted by HS-SPME. In that study, the extraction efficiency of five SPME fibers was also evaluated. Bach *et al.* [21] used HS to extend SPME fiber life and because it can be easily adapted to more complex matrices such as abiotic solid ones. They also assessed different types of SPME fibers and they found that DVB/CAR/PDMS produced the best results. These methods allow a simple, automated and solvent-free extraction, which is advantageous when the analysis of aqueous matrices is carried out by GC. Both experiments showed that more abundant signals for all analytes were clearly obtained using divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and CAR/PDMS fibers. Up to the moment, only scarce miniaturization procedures, such as those previously described, have been reported due to the efficiency and versatility of SPE and the low analyte concentrations present in water that condition robustness and repeatability as the most important parameters.

The other ePOPs are more apolar, less water soluble (almost insoluble) and more volatile, and as a consequence their concentrations in water are in the pg L^{-1} level. Their low concentrations could mostly be detected using high sample volumes. For analyzing large water volumes of 10–200 L, in the case of PFRs, some non-traditional sorbents such as SERDOLITH PAC 3, an hydrophobic resin similar to Amberlite, have been used [50]. The cartridges are usually washed with ultra-pure water [34,44,46,47,50,51]. In the case of PFRs, predominant eluents are acetonitrile (ACN) [48], dichloromethane (DCM) [50], or their mixtures [51]. Within this group of large water volume techniques, Gu *et al.* [52] developed a method to determine tetrabromobisphenol-A (TBBPA) and HBCDs extracting 6 L of seawater with an automated SPE system, and using a styrene divinyl benzene disk (SDB-XC, 3M). Once the analytes retained, the disk was dried in an oven, and the analytes eluted by pressurized liquid extraction (PLE) using a mixture of DCM and hexane (HEX) (1:1, v/v). PFRs, NBFRs and other POPs were also extracted from high water volumes (up to 160 L) using a XAD-2 resin packed on a glass column. Then, resins were extracted by Soxhlet with a mixture of HEX and acetone (ACE) (1:1, v/v) over a period of 30 h [53]. The use of so high sample volumes also conditions an increase in the potential matrix interference compounds. Then, the need of an additional clean-up step is quite common. For example, in the previous mentioned method, after extraction, matrix interferences were eliminated by passing the samples through a silica gel column eluted with HEX, HEX:DCM (1:1, v/v) and ACE:DCM (7:3, v/v). Similarly, to extract PFASs from 1 L wastewater influent, Munoz *et al.* 2015 [46] applied an extra clean-up step using graphite cartridges for wastewater samples.

Liquid-liquid extraction (LLE) or liquid partitioning using DCM is also reported in different aqueous matrices for the analysis of PFRs [50], TBBPA and their main derivatives [54] even through this technique requires high volume of expensive, high purity and toxic organic solvent, is long and tedious, prone of emulsion formation and needs more exhaustive concentration step that sometimes could be a source of analyte losses [55]. However, LLE successfully extract these compounds from river water, sea water and tap water samples with satisfactory recoveries. The main drawbacks of LLE are the large amount of solvent required and the evaporation step. Miniaturized extraction methods as dispersive liquid-liquid microextraction (DLLME) have attracted the interest in the last years because of their simplicity, low cost and environment-friendly characteristics [56]. DLLME based on the unique fluorous-affinity property was established for the extraction of PFASs from water samples [57]. Furthermore, a novel DLLME technique based on the solidification of a floating organic drop (DLLME-SFO) has been applied for a multiresidue extraction of PFASs and HBCD, among others [58]. The number of applications using DLLME platform is expected to rise.

2.3. Extraction and clean-up of biotic and abiotic solid matrices

As shown in Table 3, solid-liquid extraction (SLE) is the most common procedure to extract ePOPs from solid matrices such as sediment, sewage sludge, soil and SPM. SLE includes mechanical agitation [25,59–62] and ultrasound assisted extraction (USE) [63]. USE is the most common technique to facilitate the extraction of ePOPs from abiotic matrices [24,64,65], as well as to facilitate it in those methods that could be indistinctly used for both, biotic and abiotic matrices [23,25,33,52,66,67]. Some authors applied USE for combined extraction of PFRs and PFAS [29] or PFRs and NBFRs [39]. MeOH and acetic acid (AcOH) are the main organic solvents to extract PFASs while less polar solvents as DCM and HEX are more employed for the analysis of PFRs and NBFRs. Some authors used several cycles to improve the efficiency of extraction [23,24,30,32,33,52,59,64,66,67]. However, although there are also works that employ USE in biota samples [30,32,68], extraction procedures for these matrices also exploit other alternatives since they are the most complex ones. These techniques can be as simple as a modified quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction method —a user-friendly alternative to traditional SLE— employed for the extraction of PFASs from homogenized benthic invertebrates [69].

Focused ultrasound solid-liquid extraction (FUSLE) is a “green” extraction method based on the application of high power focused ultrasonic waves with a micro-tip immersed directly in the extraction mixture to form cavitation bubbles unlike the ultrasonic bath where there is no direct contact with the extraction solution. Then, FUSLE can easily couple approx. 20,000 W/L into the processed medium providing a focused and uniform ultrasounds power input whilst an ultrasonic bath provides a weak sonication with approx. 20–40 W/L and a very non-uniform distribution. It has been successfully applied for determining PFAS from sewage sludge and biota using a few milliliters of a mixture ACN:H_2O (9:1, v/v) at 0 °C [70,71]. FUSLE demonstrated to be a fast, low-cost and efficient extraction technique.

Different solid supports or dispersing agents as diatomaceous earth [72], primary secondary amina (PSA) [41], and a mix of silica and Na_2SO_4 [73] have been used prior to SLE to break-up the sample matrix and improve the solvent-sample interaction. A technique widely used to extract PFASs and NBFRs from marine biota is matrix solid-phase dispersion (MSPD) based on this principle. The homogenous mixtures are placed in syringes or columns and the analytes are desorbed with different organic solvents as ACN, DCM and ACE:HEX 1:1 (v/v). Furthermore, the placement of a layer of Na_2SO_4 and silica gel [72], or a combination of silica, acidified silica and Florisil [41] in the bottom of the syringe achieves an in-line clean-up.

More exhaustive and continuous techniques as PLE [74], microwave assisted extraction (MAE) [35], Soxhlet [75], or their automatized version Soxtec [42] are applied for the extraction of most non-polar compounds with mixtures ACE:HEX or DCM:HEX. PFRs and NBFRs have more affinity for lipids and they need more energy to be extracted. PLE is widely used in biotic matrices for the extraction of PFRs and NBFRs, being the sample amount lower in the extraction of biotic samples (0.2–10 g) than of abiotic ones (1–15 g) [76]. The extraction solvents comprise DCM and mixtures as ACE:HEX, ACE:DCM and HEX:DCM [28,33,38,74,77,78]. The PLE have some common points with the MSPD because the sample is also frequently dispersed in a sorbent and placed in a stain steel

cell. In the case of sediment, selective pressurized liquid extraction (SPLE) that includes the in-line clean-up step within the stain steel cell is frequently applied. However, this methodology could not be applied for biota because it requires a more complex clean-up and lipid content determination [74].

Analysis of ePOPs in solid matrices requires the removal of SPM and co-extracted matrix compounds that can interfere in their determination, especially if liquid chromatography (LC) and mass spectrometry (MS) or tandem MS (MS/MS) is used. Clean-up strategies are also detailed in Table 3. In solid sample extracts, SPE has been used as the main clean-up strategy [23–25,29,38,39,60,64,66,70,71,74,78]. As for water samples extraction, in the case of PFASs the most used sorbents are the weak anion-exchangers [24,38,60,70] and polymeric reversed phases [25,64,66]. Couderc *et al.* [60] applied SPE with a WAX stationary phase followed by a second SPE composed of graphitized carbon black (GCB). GCB is considered both a reverse phase and an anion-exchanger sorbent due to its structure and somewhat positively charged surface [79]. Cavaliere *et al.* [29] used GCB to retain from nonpolar to very polar endocrine-disrupting compounds, which include PFASs and PFRs. Neutral and very weak acids were eluted with a small volume of a mixture of DCM:MeOH. Weak and strong acids were eluted with DCM:MeOH but with formic acid (FA) or ammonium formate (AF), respectively. Zacs and Bartkevics [23] evaluated four SPE cartridges with weak anion-exchange properties to retain perfluorooctanoic acid (PFOA) and PFOS from environmental samples. Enviro-Clean CUPSA cartridges showed less effectiveness in comparison with Oasis WAX, Presep PFC-II and Strata X-AW SPE columns. They also applied the SPE cartridge in combination with a SPE column filled with GCB to improve the extracts clean-up. Although significant changes in terms of signal suppression or enhancement were not reported, better chromatographic peak shape and stability of retention times of the analytes were observed.

PFR and NBFR compounds are accumulated in lipids. Polar sorbents in the normal phase, such as silica gel [28,35,40,42,52,73,75,80], alumina [78] and Florisil [39,65,77], used alone or in combination [30,74], have been employed to separate the analytes from lipids in biotic matrices. The most common elution solvent is the mixture of HEX:DCM [65,75,78,80]. Several authors use 2–3 elution fractions and combine the extracts [28,35,40,42].

Size exclusion chromatography (SEC) or gel permeation chromatography (GPC) reduce matrix interferences in biota samples previous to PFR and NBFR analyses [28]. Styrene divinylbenzene copolymer are the most common columns (*e.g.* Bio-Beads S-X3). The disadvantages of GPC are its high solvent-consumption and its inability to remove lipid-related substances (additional clean-up with Florisil [65], silica gel [35] or multilayer silica column [42] is required).

Dispersive solid-phase extraction (dSPE) is a green clean-up technique suitable for lipid-rich matrices. This approach is based on the addition of the sorbent material to an aliquot of the sample solution. Several dSPE sorbents (three different PSA based, Z-sep$^+$, DSC_{18} and ENVI-Carb) were tested for the isolation of PFRs from fish samples and showed that the highest efficiency was obtained by ENVI-Carb; however, this sorbent adsorbed some benzene ring-containing PFRs [*e.g.* triphenyl phosphate (TPhP) and tricresyl phosphate (TMPP)]. By contrast, PSA (100, 200 and 300 mg) showed higher recoveries for all PFRs and acceptable lipid adsorption efficiency from fish [32]. In the case of PFASs, dSPE was used to clean-up marine biota and marine sediment testing one reversed-phase sorbent (C_{18}), one mixed mode sorbent (PSA) and three normal-phase sorbents (Florisil, alumina and silica). The best results were obtained with C_{18}, which can be explained by PFASs more acidic nature [62].

New techniques, as turbulent flow chromatography (TFC), are used for on-line sample pretreatment. This technique uses high solvent flow rates (4–6 mL min^{-1}) through columns packed with large particle size sorbents. TFC is a useful technique to discard large sample compounds such as proteins, peptides and lipids. Once analytes are trapped on the turbulent flow column, they are subjected to a back-flushing elution that desorbs them towards the analytical column for chromatographic separation. TFC has been mainly used in studies involving the extraction of biota samples [25,33,68].

3. Determination

To detect and get an accurate quantification of ePOPs in environmental samples, compounds must be isolated. The use of sensors is a rapid way of determination. However, the LODs reported (mostly for PFASs) are far away of the trace concentrations detected in environmental matrices [81]. Because of their higher sensitivity, selectivity, and efficiency, chromatographic based separations, especially those using GC and high-pressure LC are clearly the most widely used for ePOPs separation. Tables 2 and 3 overview the most relevant determination techniques from 2011 onwards.

3.1. Liquid chromatography-mass spectrometry and related techniques

Most of the analytical methods to determine PFASs and PFRs in environmental samples are based on LC coupled to MS. Reversed phase LC is usually employed for the ePOPs separation. Bonded silica (C18) is the preferred non-polar stationary phase column. Few studies use high-density diol [44], C8 [82], hydrophobic alkyl chain with diol called mixed-mode HILIC-1 [51] or pentafluorophenyl (PFP) [68]. Regarding the mobile phase composition, water is usually employed as base and polar solvents such as MeOH, ACN and their mixtures are added in fixed or varying proportions. The most common modifiers added to the mobile phase to improve peak shape are 1-Methyl-piperidine (1-MP), ammonium acetate (AA), AF and FA. FA is the first choice for LC-MS at low-acid pH. AA is the most used buffer because it can cover a wide pH range ($2.0 < pH < 3.8$ and $5.8 < pH < 8.0$) and is normally used for silica-based columns. AF ($2.7 < pH < 3.7$) fills the pH gap of AA. Both, together with 1-MP [70] are also ion-pairing agents used in the mobile phase to increase the chromatographic resolution and detection sensitivity for anionic PFASs [3,23–25,29,34,36,44,45,64,70,83]. Recent advances related to separation –mostly based on reducing the particle size or the inner diameter of the LC columns– have been also implemented within the field of ePOPs determination. Since their introduction in 2004, ultra-high performance liquid chromatography (UHPLC) has become a routine technique [24,25,29,32,36,64,66,68,77,83]. Among the benefits of this technique include its faster separation and higher resolution through the use of columns of low particle diameter (<2 μm) [84]. It also provides better achievable sensitivity and high-resolution separation of ePOPs in complex samples [24,25,29,32,64,66,68,77,83]. The ability to use less solvent and sample means that UHPLC can be considered a “green” LC platform. The application of capillary LC (cLC) and nano LC (nLC) to the determination of PFASs in water is already a reality. Their benefits are a reduction of the extra-column band broadening (due to use of narrower and shorter connection tubing) and an increase of the chromatographic efficiency (because of the narrowed diameter at increased length of the columns). Compared to UHPLC-MS/MS, both attain better resolution and comparable or even improved sensitivity (due to the narrower and higher peaks obtained) providing a viable and economical alternative [69,85].

As already mentioned, one important issue is the background contamination coming from the LC system. Several authors applied a trap column on the high performance LC (HPLC) system in order to distinguish background contamination from that of the samples

[66]. Trap columns employed to distinguish PFRs in the sample of those coming from the instrument also required washing and blank solvent injections before use to remove residual contamination [29]. Capillaries and tubes of the HPLC system that can contain PFASs or PFRs are provisionally replaced when possible [23].

The most used ionization technique for identification of ePOPs is electrospray ionization (ESI). Only few studies apply atmospheric pressure chemical ionization (APCI) to analyze PFRs [32], and atmospheric pressure photoionization (APPI) to analyze NBFRs [42]. Zacs and Bartkevics [23] analyzed PFOA and PFOS in various environmental samples and evaluated ESI, APCI and APPI. Although ESI systems are more susceptible to matrix interferences, in comparison with APCI and APPI techniques, ESI was chosen for the sample ionization because it provided the highest instrumental sensitivity.

Among the different mass analyzers available, LC coupled to triple quadrupole (QqQ) or quadrupole linear ion trap (QqLIT) MS/MS is considered one of the most used for ePOPs detection and quantification [24,25,29,32–34,38,45,51,52,57–60,62,64,66–68,70,72]. The low environmental concentrations of these compounds make the sensitivity one of the most important parameters to be taken into account, and this mass analyzer achieves the lowest LODs.

However, MS/MS sometimes shows inadequate selectivity and some authors have proposed the use of a high resolution MS (HRMS) technique, as time-of-flight (TOF)-MS or Orbitrap-MS, as alternative tools for (ultra-)trace analyses of PFASs and NBFRs in complex environmental matrices [23,42,46,67]. Fig. 1 shows the identification of perfluorobutanoic acid, one of the compounds for which QqQ is not selective enough since it only fragments to one ion [83]. HRMS provides accurate mass and then, information on the most probable empirical formula. Although HRMS instruments are not feasible to provide MS/MS their hybridation with quadrupoles or linear ion-traps has achieved the MS, pseudo MS/MS (two parallel MS at low and high energy) and real MS/MS fragmentation with high mass accuracy as well as acquisition in data dependent or independent analyses (DDA or DIA). Zacs *et al.* [42] also proved the efficiency of three different detection modes: full scan, targeted selected ion monitoring (t-SIM), and DIA using the parallel reaction monitoring (PRM) mode. They found high background noise and significant interference on the chromatograms when analyzing complex matrices by t-SIM and full scan modes, and then selected PRM mode. On the contrary, the same authors reported that PRM mode was less sensitive when screening NBFRs in fish samples [42]. The HRMS instrument provided higher LODs but it has the unquestionable advantage to be able to detect and identify other non-target ePOPs, as well as their metabolites and transformation products as long as the instrument works in full scan acquisition. The Q Orbitrap have also demonstrated to be able to determine PFASs in fish and passive samplers operating in high resolution product scan (HRPS) mode to selectively detect the target compounds [22]. However, the high number of other compounds in the matrix and the low concentrations of ePOPs, makes that most studies use selected reaction monitoring (SRM). Only two studies use full scan acquisition [42,45].

Although MS detection is the most widespread detector, there are some special cases, such as TBBPA and its derivatives, which are not properly determined neither by GC-MS (thermolability) or LC-MS (lack of analyte ionization in the source). Liu *et al.* [54] established a new and sensitive method for these compounds by

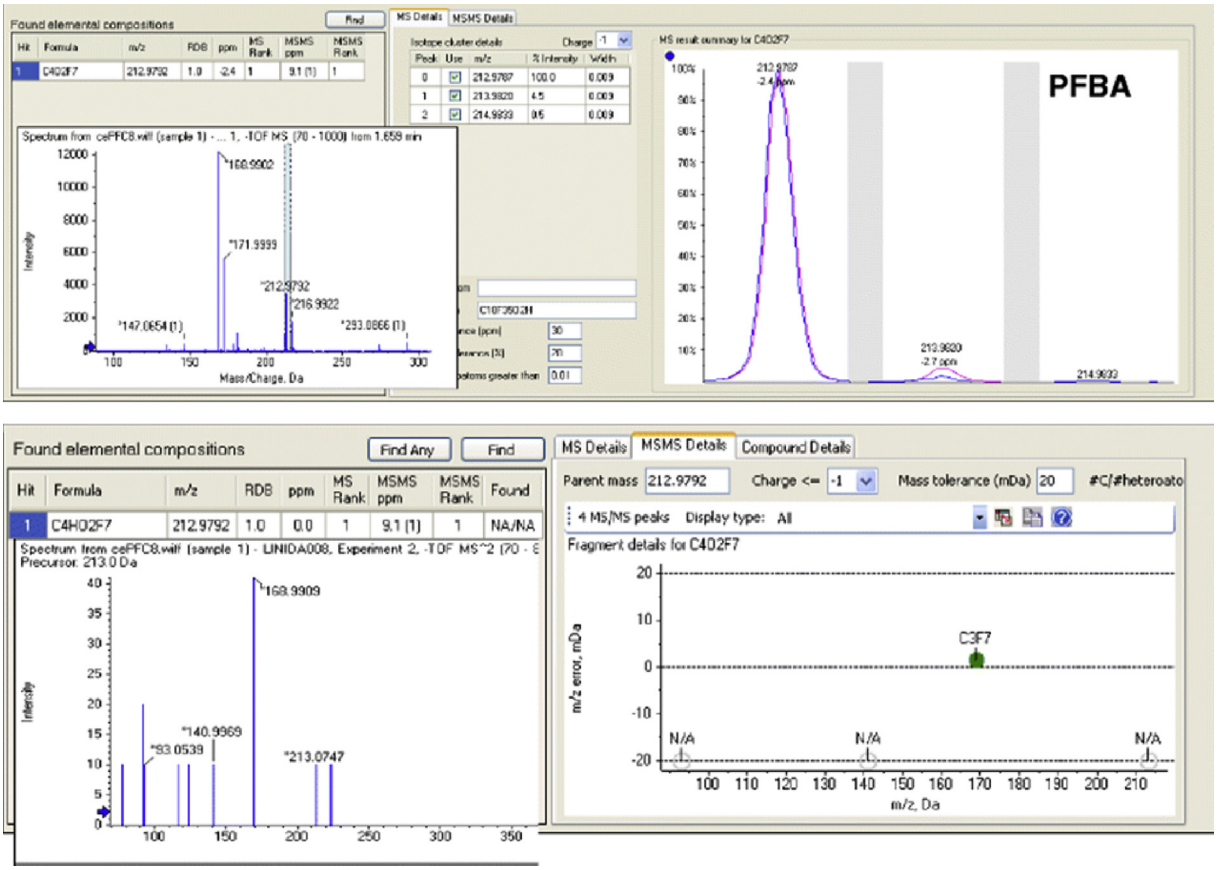


Fig. 1. Water sample: PFBA was identified using Formula Finder and combining TOF-MS and TOF-MS/MS information. Reproduced with permission from Ref. [83]. Copyright (2015) Springer.

coupling HPLC separation with inductively coupled plasma (ICP)-MS detection technique. In comparison with the traditional quantification methods, such as MS/MS or diode array detection (DAD) detector, the ICP-MS has obvious advantages in sensitivity for the quantification of TBBPA and its derivatives, especially TBBPA-BAE and TBBPA-BDBPE. Fig. 2 shows the proper peak shape and sensitivity obtained for these compounds. The determination of bromide was carried out using helium in the plasma because significantly eliminated the interferences and decreased the baseline values of ^{79}Br and ^{81}Br in comparison with the no gas mode.

As last innovation within the field of related techniques, the ultra-performance convergence chromatography (UPC^2) [an updated supercritical fluid chromatography (SFC)] is increasing used for those compounds not retained in LC columns, such as ultrashort-chain PFASs (C2–C3) [44]. In this technique, the separation is achieved by manipulating the density of a supercritical fluid (generally CO_2) and composition of the supercritical fluid and a modifier (co-solvent). Compared to reported LC-MS/MS methods, the new method has a lower detection limit (0.4 pg trifluoroacetate on-column), narrower peak width (3–6 s), and a shorter run time (8 min) and if extended to longer-chain compounds, attain separation of many different classes of PFASs. As the UPC^2 improves, it is expected the development of new methods that will extend the current possibilities to the sensitive and selective detection of ePOPs.

Furthermore, the evolution of MS interface coupled to LC brings a new direct analysis, which is able to determine the compounds directly in the extract eliminating the LC separation. PFASs were already successfully determined by laser diode thermal desorption method (LDTD) [46]. Environmentally relevant LODs were obtained. Furthermore, the elimination of the chromatographic step prior to MS analysis reduced solvent consumption and potential contamination risk from tubing and mobile phases, as well as analysis times, making it a relevant alternative for sample screening of PFASs. Other novelties within the field of MS coupled to LC such as the incorporation of ion-mobility mass spectrometry (IMS) are not reported. These techniques would be less useful for the most non-polar ePOPs. However, this technique could be applied to PFASs determination since they are ionic substances.

3.2. Gas chromatography-mass spectrometry

The selection of GC instead of LC depends on the analyte properties, PFRs [3,35,39,50,53] and NBFRs [3,39–41,53,65,74,75,78,80] are commonly determined using GC-MS because they are thermostable and volatile. However, PFASs may require derivatization because even that they are volatile enough to be chromatographed by GC, their ionic nature provides wide and tailing peaks difficult to quantify. Although some columns (*i.e.* ultra-inert columns or FFAP-type columns) have improved the analysis of carboxylic acids, up to our knowledge they have not been applied yet to the determination of PFASs or any other ePOP [86]. The rapid and sensitive determination of perfluoroalkyl carboxylic acids in aqueous matrices by GC-QqQ-MS is, up to the moment, achieved transforming the carboxylic groups in their esters. This technique is combined with a selective HS-SPME extraction that is also favored by the derivatization of the PFASs [49].

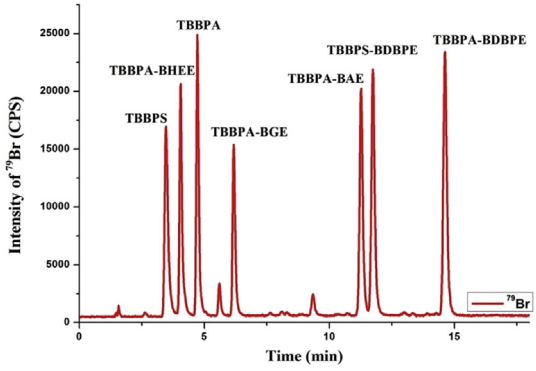


Fig. 2. HPLC-ICP-MS chromatography of mixed standard solutions of TBBPA, TBBPA-BHEE, TBBA-BGE, TBBPA-BAE, TBBPA-BDBPE, TBBPS, and TBBPS-BDBPE (100 μg L^{-1}) under the optimized conditions. Reprinted from Ref. [54]. Copyright (2017) with permission from Elsevier.

In GC, electron ionization (EI) has been described as the most frequently used GC technique for the identification of any type of substance. However, ePOPs are more labile than legacy ones and then, softer ionization techniques are preferred, for example electron capture negative chemical ionization (ECNI) is generally used for the analysis of NBFRs [28,39,53,75,78]. Recently, the new combination of GC with APCI sources has opened a new horizon within the analysis of these compounds [40,47,73]. The most used mass analyzer in GC is the single quadrupole. However, QqQ [39,40,47,49,50,65,73,78] and TOF [47] have been recently reported in some applications.

Portolés *et al.* [73] compared both EI and APCI sources for the analysis of NBFRs. In contrast to EI sources, APCI provides the molecular $[M]^{+\bullet}$ and quasi-molecular $[M+H]^+$ ions as base peak of the spectrum. If combined with a QqQ both ions might be selected as precursor ion for MS/MS. This ionization mode strongly improves sensitivity (LODs lower than 10 fg on column) and selectivity in contrast to GC-EI-MS/MS. The same research group [47] also studied ionization and in source-fragmentation behavior of fluorotelomer alcohols and perfluoroalkyl sulfonamides. In Fig. 3 the EI full-scan spectra showed a high fragmentation pattern, positive CI mode showed MS spectra with an intense $[M+H]^+$ protonate molecule and in positive APCI the fragmentation dismiss and the intensity of the protonated molecule increases. They also performed comparison of GC-QTOF to GC-QqQ operating in APCI mode for the analysis of PFASs precursors. The application of GC-QTOF to water samples attain identification of several related compounds showing the potential of HRMS even in combination with GC.

It is noteworthy within this field, that recent advances in GC separation, as comprehensive two-dimensional gas chromatography (GCxGC) or fast GC have not been tested yet. However, many of the previously described techniques are only in the earlier stages of the application to ePOPs and still we expect that the new techniques will be applied to soon to the ePOPs determination.

4. Conclusion and future prospects

A significant issue in quantitation of ePOPs is that they occur at very low concentration levels (sub-ng L^{-1} range) in water, what means that a highly sensitive method is needed to their accurate quantitation. This issue forces to work with high sample volumes and as a consequence, the method usually requires time consuming and expensive clean-up before analysis in order to achieve the high level of sensitivity required. The abiotic and biotic environmental matrices in which ePOPs are commonly examined are often complex. These matrices such as sediments, soils and biota are problematic because usually contain interfering compounds such as humic and fulvic acids, organic matter, lipids, proteins, pigments, etc. (depending on the sample). Hence, the sample preparation and extraction of ePOPs are time consuming. It also means that these compounds need efficient separation and retention away from interfering compounds, which can cause further problems with

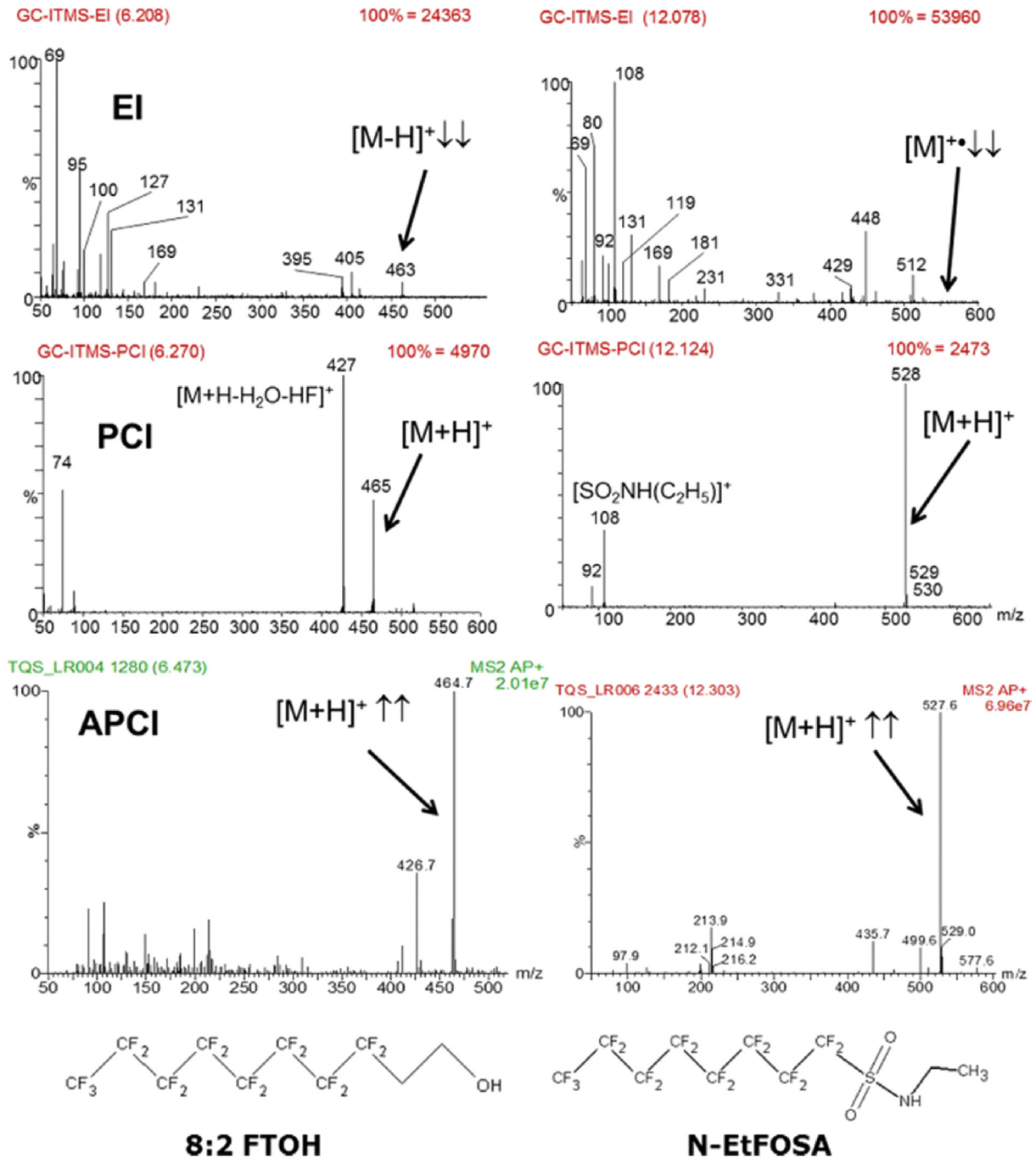


Fig. 3. Spectra of 8:2 FTOH (left) and N-EtFOSA (right) under EI (up), PCI (middle) and APCI (bottom) conditions. Reprinted from Ref. [47] Copyright (2015), with permission from Elsevier.

detection. Since LLE and SPE require high volumes of eluting solvents and are time consuming, extractions based on SPME have gained increased attention. However, the need for complete and exhaustive sample preparation is still a great challenge to provide efficiency, accuracy, and precision for a wide range of analytes, and microextraction approaches are still scarce. Much work needs still to be done to adapt ePOPs extraction to the more eco-friendly ongoing trends of "green methods".

MS techniques have turned into indispensable tools for ePOPs determination in aquatic ecosystems, due to its high accurate mass determination for compositional analysis, the ability of MS/MS fragmentation techniques for structural identification, and the possibility to couple with separation techniques like LC or GC. Recently, a promising methodology to quantify brominated ePOPs has also been published combining LC, ICP and MS. The particularity and somewhat less non-polar character of ePOPs, in comparison to legacy POPs, have marked that many of the determinations apply LC. Additionally, in the case of GC the implementation of interfaces that produce a soft fragmentation of molecules, such as CI and APCI, is favored. In this regard, the recent developed alternative techniques to LC, GC and their combination with MS, such as multidimensional approaches (including LC × LC and GC × GC), IMS or direct analysis techniques could offer complementary selectivity and thus, information that would help to

increase the ePOPs coverage. These innovative techniques are not well implemented yet. However, it is expected that examples start to appear in the near future.

Acknowledgements

This work has been supported by the Spanish MINECO and the ERDF through the project CGL2015-64454-C2-1-R (ECO2risk-dss). M. Lorenzo was supported by the Foundation "Tatiana Pérez de Guzmán el Bueno" (Predoctoral Grant 2014).

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