Perfluorinated Compounds' Analysis, Environmental Fate and Occurrence: The Llobregat River as Case Study

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Abstract Perfluorinated compounds are industrial chemicals widely used for more than 60 years. However, during the last decade, due to their high resistance to degradation, bioaccumulation attached to proteins, biomagnification to the food chain and their relation to toxicological effects of these compounds have gained scientific and regulatory attention.

In addition, the difficulty associated with their analysis in complex matrices such as biota, food and human fluids and tissues samples should be mentioned.

This chapter provides a comprehensive examination of the current knowledge on PFCs' analysis, environmental fate and occurrence in aquatic systems, using as a central example the Llobregat River.

Keywords Drinking water, Liquid chromatography, Llobregat River, Mass spectrometry, Perfluorinated compounds, Sediments, Surface water, Wastewater

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S. Sabater et al. (eds.), *The Llobregat: The Story of a Polluted Mediterranean River*, Hdb Env Chem (2012) 21: 193–238, DOI 10.1007/698_2012_147,

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Abbreviations

AcH	Acetic acid
ACN	Acetonitrile
APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photoionization
ASE	Accelerated solvent extractor
DMF	Dimethylformamide
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EPI	Enhanced product ion
EQS	Environmental quality standards
ESI	Electrospray ionization source
Et-FOSA	Ethyl perfluorosulphonamide
EtOAc	Ethyl acetate
FID	Flame ionization detection
FoH	Formic acid
FOSA	Perfluorosulphonamide
FOSE	Perfluorooctane sulphonamide-ethanol
FTOH	Fluorotelomer alcohol
FTUCA	Fluorotelomer unsaturated carboxylate
GC	Gas chromatography
HCl	Hydrochloric acid
HLB	Hydrophilic lipophilic balance
ip-PFNA	Isopropyl perfluorononanoic acid
IT	Ion trap
LC/ARC	Liquid chromatography/accurate radioisotope counting
LC	Liquid chromatography
LC-MS/MS	Liquid chromatography coupled to tandem mass spectrometry
LC-MS	Liquid chromatography–mass spectrometry

LRET	Long-range environmental transport
MeOH	Methanol
MLOD	Method limit of detection
MLOQ	Limits of quantification
MS	Mass spectrometry
MS^2	Mass spectrometry/mass spectrometry
MS^3	Mass spectrometry/mass spectrometry/mass spectrometry
MTBE	Methyl *tert*-butyl ether
N_2	Nitrogen
NaAc	Sodium acetate
NaOH	Sodium hydroxide
N-EtFOSAA	2-(*N*-Ethyl perfluorooctane sulphonamido) acetic acid
NH_4Ac	Ammonium acetate
NH_4OH	Ammonium hydroxide
N-MeFOSAA	2-(*N*-Methyl perfluorooctane sulphonamido) acetic acid
OW	Office of Water
PAPs	Polyfluoroalkyl phosphates
PE	High density polyethylene
PEEK	Polyether ether ketone
PFASAs	Perfluorinated sulphonamides
PFASEs	Perfluorinated sulphonamide ethanols
PFASs	Perfluoro alkyl sulphonates
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulphonate
PFC	Perfluorinated compounds
PFCAs	Perfluoro carboxylic acids
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulphonate
PFEtS	Perfluoroethyl sulphonate
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptane sulphonate
PFHxDA	Perfluorohexadecanoic acid
PFHxS	Perfluorohexane sulphonate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFODA	Perfluorooctadecanoic acid
PFOS	Perfluorooctane sulphonate
PFOSI	Perfluorooctane sulphinate
PFPeA	Perfluoropentanoic acid
PFPrA	Perfluoropropyl acid
PFPrS	Perfluoropropyl sulphonate
PFTeA	Perfluorotetradecanoic acid
PFTOHs	Perfluorotelomers alcohols

PFUnA	Perfluoroundecanoic acid
PHA	Provisional Health Advisories
PLE	Pressurized liquid extraction
POP	Persistent organic pollutant
POSF	Perfluorooctane sulphonyl fluoride
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
QqLit	Hybrid quadrupole linear ion trap
QqQ	Triple quadrupole mass spectrometer
QTOF	Hybrid quadrupole time of flight
RP	Reversed phase
RSD	Relative standard deviation
SCARCE project	Assessing and predicting effects on water quantity and quality in Iberian rivers caused by global change (2009–2014)
SPE	Solid phase extraction
SRM	Selected reaction monitoring
TBA	*tert*-Butyl alcohol
t-Bu-PFOS	*tert*-Butyl perfluorooctane sulphonate
TDI	Tolerable daily intake
TFA	Trifluoroacetic acid
THPFOS	Tetrahydro-perfluorooctane sulphonate
TOF	Time of flight
WAX	Weak anionic exchange
WWTPs	Wastewater treatment plants

1 Introduction: Uses, Production and Global Distribution

Perfluorinated compounds (PFCs) have been manufactured since 1950s. Because of their properties, these compounds are employed for many industrial applications including stain repellents, textile, paints, waxes, polishes, electronics, adhesives and food packaging. Two of the most important PFCs are perfluorooctane sulphonate (PFOS) salts, components of fire-fighting foam concentrates, and perfluorooctane acid (PFOA), primarily used as emulsifier in industrial applications, for example in the production of fluoropolymers such as polytetrafluoroethylene (PTFE). Furthermore, PFOS and PFOA as well as other perfluoro carboxylic acids (PFCAs) are stable degradation products and/or metabolites of neutral PFCs like fluorotelomers alcohols (PFTOHs), perfluorinated sulphonamides (PFASAs) and perfluorinated sulphonamide ethanols (PFASEs). Figure 1 shows the most commonly used PFCs structures.

Because of their use in different industrial applications, these compounds enter to the environment through removal facilities, which are not able to degrade PFCs, or, for example, by their application in agricultural soils or by irrigation with

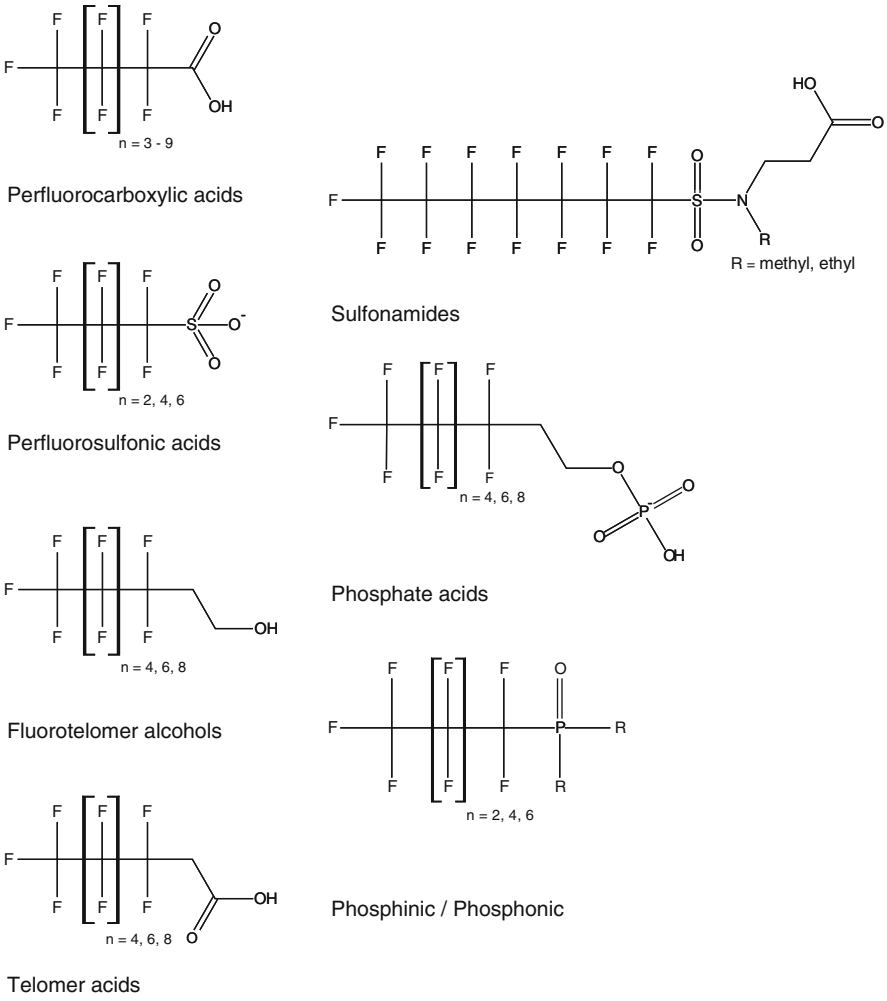

Fig. 1 The most common structures of PFCs

contaminated water. These analytes are widespread around the world in water and soils as well in organism due the high affinity to low weight proteins [1]. The bioaccumulation derives to biomagnification through the food chain and, finally, arrives to human through diet and drinking water [2, 3]. PFCs have been detected in environmental and biological samples. They are present in remote areas as the Arctic (atmosphere [4], Arctic Ocean [5], biological samples [6, 7] and few reviews have been published [8, 9]) or Antarctic (biological samples as penguins or seals [10, 11]). Regarding the presence in human matrices, these analytes have been reported in blood from donors from different countries [12, 13], liver [14], urine, human breast milk [14–17] and cord blood [18, 19] being the breastfeeding and

pregnancy a possible transferability route. Fish is another biological matrix, which has been analysed due to its involvement into marine trophic chain. This is one of the main entrance routes of PFCs into human organisms with other daily products as milk, meat or vegetables [2, 3, 20–23]. In 2006, EPA established the tolerable daily intake (TDI) for PFOA and PFOS [24, 25], and in 2008 the EFSA established as well, TDI levels at 150 ng/kg bw per day in the case of PFOS and 1,500 ng/kg bw for PFOA.

PFCs are considered as emerging organic pollutants since they have not been regulated. However, in the last decade, there are some of them which are proposed to be under regulation [26].

In 2006, EPA and the eight major PFCs producer companies [Arkema, Asahi, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont and Solvay Solexis] launched the "PFOA Stewardship Program". The companies committed to phase out global emissions by 2015 [27]. Recently, PFOS has been included as a persistent organic pollutant (POP) under the Stockholm Convention for global regulation of production and use [28]. PFCs are also prime candidates for chemicals that will need authorization within the REACH regulation [26]. PFOS was added to the Annex III Substances subject to review for possible identification as priority substances or priority hazardous substances of the Directive 2008/105/EC of the European Parliament and Council of 16 December 2008 concerning the environmental quality standards (EQS) in the field water policy [29].

Wastewater has been also identified as a major source of PFCs in the environment since currently their elimination during wastewater treatments in wastewater treatment plants (WWTPs) is not completely achieved, and therefore, important amounts of these compounds can reach the natural environments through the treated effluents. Moreover, also sewage sludge produced in WWTPs is important source of PFCs' contamination, since there is a redistribution of PFOS and long carbon chain PFCs into the sludge [30–32]. Several works during last years have informed about concentrations in sludge in the range between low ng/g and μg/g. These high concentrations are of concern because sewage sludge can be partially used in agricultural lands generating an indirect source of PFCs via consumption of crops, air-borne transport, surface waters and ground waters draining from these sites [33–35]. Clarke et al. scored different groups of organic contaminants commonly found in sewage sludge with respect to their potential significance for agricultural utilization [36], and in this classification PFCs obtained 10 scores over 11, based on their persistence in soil (more than 6 months), their potential accumulation in human food chain, their potential bioaccumulation and their possible soil ecotoxicity [36]. On the other hand, it should be considered that PFCs in sludge amended soil can be mobilized by rainfall [37], reaching phreatic waters.

Drinking water has been identified as one of the major sources of human exposure [38, 39] to PFCs. For this reason, in 2009, the EPA's Office of Water (OW) have set a Provisional Health Advisories (PHA) maximum concentration values for PFOA and PFOS in drinking water. PHA values are 0.4 μg/L for PFOA and 0.2 μg/L for PFOS [40].

To protect human health and the environment against PFCs' contamination, there is a need to assess their presence in the environment and main sources of human exposure and assess possible damages involving their occurrence, bioaccumulation, as well as, their environmental fate and behaviour. In this context, this chapter provides a summary of the state-of-the-art in the analysis of PFCs in environmental samples, and the occurrence of PFCs will be presented and discussed in a typical Mediterranean river: the Llobregat River.

2 Analysis of PFCs

2.1 Sampling Process and Preservation

Storage and conservation of samples for PFCs' analysis present some critical steps because losses or contamination of the samples can easily occur.

Martin et al. [41] summarized the key challenges in trace analysis of PFCs. They include blank contamination issues, purity of reference standards and matrix effects in the ionization process of the mass spectrometer. Blank contamination is one of the most relevant problems associated with PFCs' analysis, and it is associated with fluoropolymer during sampling, storage and materials used in the laboratory. In order to avoid sources of contamination different measures have been suggested, as for example, pre-cleaning of the containers and materials prior sampling by rinsing with semi-polar solvents [38]. It is also important the materials involved during sampling, storage and the analytical process, being polypropylene (PP) containers [34, 42, 43], high density polyethylene (PE) bottles [44–46], or foil containers for solid samples [35] the recommended ones, because these materials cannot contaminate the samples. However, for solid samples losses by sorption to PP and PE containers can be considered negligible [46], whereas for aqueous samples in case of long-chain PFCs is higher [47, 48]. On the other hand, stored aqueous samples in glass have been widely discussed by different authors, whereas some works have reported sorption in glass when prepared samples were tested [49], this phenomena is not expected in real samples with complex matrices [50]. It is also important to consider possible losses due to volatilization of the PFTOHs and short C chain PFCs as PFBA. Therefore, it is recommended to avoid headspace in sampling bottles [51], and kept samples at low temperature after collection [44, 45, 52]. Szostek et al. studied the stability of PFTOHs in water under different storage conditions [53]. In this work it was concluded that aqueous samples can safely be stored in the freezer using glass vials and sealed with a septum lined with alumina foil. In addition, no biodegradation or biotransformation was observed under these conditions [53]. On the other hand, also it was studied the possible benefices associated with the use of biological inhibitors (such as formalin) to preserve the samples, but it was found that some suppress the MS responses during the analysis [54], and therefore should be avoided.

Drying procedures are usually applied for solid matrices using room temperature until a constant weight [42, 55], with soft temperature (40°C) along 3–4 days in porcelain bowls [46] or PP containers [34], and in an oven at 103°C overnight [52]. Other specific procedures consisted of direct freeze (−20°C) prior to any treatment in order to perform lyophilization [35, 43] or previous centrifugation to remove supernatant [56] and lyophilization [44]. Dried sludge or sediment is finely ground (<0.5 mm) [46] and homogenized with a mortar and pestle [35, 42–44, 55]. This homogenized sample is subsequently passed through a mesh sieve to remove pebbles or debris [43, 55]. Homogenized samples are kept frozen until analysis in PP containers [35, 42] or high-density PE bottles [44, 46]. Other authors interested in the analysis of PFCs in raw sewage sludge from Wets prepare the sample by centrifugation followed by filtration by GF/B glass filter and stored these filters at 4°C until extraction usually by solid–liquid extraction [45].

2.2 *Sample Pre-treatments*

Table 1 summarizes main sample pre-treatment that can be applied to the analysis of PFCs in different types of environmental matrices.

2.2.1 Water Samples

Extraction procedures for water analysis have been carried out using protocols based on solid phase extraction (SPE). Due to the different polarities of PFCs, different extraction SPE cartridges have been explored. Broadly, good recoveries were reported using Oasis WAX-SPE cartridges including short-chain (C_4–C_6) compound. These cartridges have been applied in many monitoring studies [39, 57, 58]. For longer-chain PFCs, less polar phases (C_{18} and Oasis HLB) may be applied [59–61]. Non-ionic PFCs may be extracted from the matrix by non-polar media (C_{18} SPE). Moderate polar media (Oasis HLB and Oasis WAX-SPE) have also been applied for extraction of non-ionic PFCs. However, one of the critical points in PFCs' analysis is background contamination in the analytical blanks [62–64]. One known source of procedural contamination is contact with laboratory materials made of, or containing, fluoropolymers [54, 62]. Water samples may be filtered [54, 65] to separate solids from the liquid phase. However, filtration can result in losses by adsorption of PFCs on the filters, or on the contrary levels can increase by contamination from the filters, as was found by Schultz et al. for fibre, nylon, cellulose acetate and polyethersulphone filters [54]. They applied centrifugation as an alternative for separating theliquid from the solids.

Controversial studies reported the cross-contamination of samples during PFCs' analysis using different SPE cartridges. Yamashita et al. [66] examined the source of blank contamination at various different steps, including sample collection, extraction and treatment of samples. PFOS and PFOA contamination in the SPE

Table 1 Sample pre-treatments and instrumental analysis of different published works

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
PFBS, PFPA, PFHxA, PFHpA, PFOA, PFNA, ip-PFNA, PFOS, PFDA, PFDS	Water	(1) Filtration (glass microfiber membrane 0.7 μm) (2) SPE by Oasis WAX (conditioning: 4 mL 0.1% NH_4OH MeOH, 4 mL MeOH, 4 mL water; loading: 200 mL; elution: 4 mL 0.1% NH_4OH MeOH (3) Evaporated under N_2 (4) Reconstituted in 0.5 mL MeOH	*LC–MS/MS(QqQ)* • Injection volume: 20 μL • Column: LiChroCARTLiChrospher 100 RP-18 (250 mm × 4 mm; 5 μm) • Mobile phase: water (20 mM NH_4Ac): methanol (20 mM NH_4Ac) • SRM mode	• MLOQ: 0.05 and 5 ng/L • Recoveries: 69–110%	[108]
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFOS	Surface and deep water (lake) and precipitation water	(1) 300 mL sample + Surrogate IS (2) SPE by Oasis HLB (conditioning: 10 mL MeOH, 10 mL water; loading; elution: 10 mL MeOH) (3) Extract reduced to dryness under N_2 (4) Reconstitution in 1 mL MeOH and filtered (0.2 μm) Or (1) 50 L sample (2) XAD resins	*LC–MS/MS(QqLIT)* • Injection volume: 10 μL • Column: C8 Phenomenex guard column C8 Luna (3 μm, C8, 50 mm × 2 mm) • Mobile phase: water (10 mM NH_4Ac): methanol (10 mM NH_4Ac) • SRM mode *GC–MS (for PFCA anilides)* • Column: ZB-5 Zebron fused silica capillary column (30 m × 0.25 mm i.d.) • SIM mode	• MLOD: 0.5 ng/L • Recoveries (XAD-7): 25–160% (1–34 L tap water)	[117]
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFOS	Surface river water	(1) 100 mL sample (pH 7–8 adjusted) + Surrogate IS (2) SPE by Strata-x (200 mg) (conditioning: 2 mL acetone: acetonitrile:FoH (50:50:1),	*LC–MS/MS(QqQ)* • Injection volume: 50 μL • Column: NUCLEODUR SPHINX-RP 2.0 mm × 150 mm, 3 μm	• MLOD: 2 ng/L • Recoveries: 11–117%	[38]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
		3 × 2 mL water (pH 8); loading; elution: 4 × 2 mL acetone:acetonitrile:FoH (50:50:1) (3) Extract reduced to dryness under N_2 (4) Reconstitution in 0.5 mL 10 mM NH_4Ac (water/MeOH, 75/25)	• Mobile phase: water/methanol, 75/25 (10 mM NH_4Ac): acetonitrile/methanol, 75/25 (10 mM NH_4Ac) • SRM mode		
PFOA, PFNA, PFOS, PFDA, PFUdA, FOSA	Surface water	(1) 1 L sample filtered (1 μm glass fibre) + Surrogate IS addition (2) SPE by Oasis HLB 6 cc (conditioning:5 mL MeOH; elution: 15 mL MeOH) (3) Dried under N_2 at 0.5 mL (4) IS addition	*LC–MS/MS(QqQ)* • Injection volume: 3 μL • Column: C_{18} column (5 μm particle size, 50 mm × 2.1 mm) • Mobile phase: water:methanol • SRM mode	• MLOD: 0.1–2.8 ng/L • Recoveries: 49–92%	[118]
PFOS, PFOA, PFNA, PFHxS, PFBS	Surface water	(1) Surrogate IS addition and incubate 12–18 h at 4°C (2) SPE by Oasis HLB 6 cc (conditioning:10 mL MeOH, 15 mL water; elution: 15 mL MeOH) (3) Dried under N_2 (4) Reconstituted in 0.2 mL 70:30 water:acetonitrile	*UPLC–MS/MS(QqQ)* • Injection volume: no data • Column: Acquity UPLC BEH C_{18} column (1.7 μm particle size, 50 mm × 2.1 mm) before injection LiChroCART HPLC RP-18e column (125 μm × 2 μm × 5 μm) • Mobile phase: water (2 mM NH_4Ac): acetonitrile • SRM mode	• MLOD: 0.6–3 pg/L (PFCs) • Recoveries: 60–122% (PFCs)	[59, 60]

Ionic pair extraction					
PFOA, PFNA, PFDA, PFUnA, PFOS, 4:2, 6:2, 8:2, 10:2 diPAP	Sudge from WWTPs	(1) 2 g sludge (2) 4 mL 0.25 M $NaCO_3$ + 1 mL 0.5 M TBA, pH 10 (3) Extraction with 5 mL aliquots of MTBE (4) MTBE aliquots combined (5) Dryness under N_2 (6) Reconstituted in 0.5 mL of MeOH and filtered by 0.2 μm nylon filter	*LC–(−ESI)-MS/MS(QqQ)* • Injection volume: no data • Column: Gemini C_{18} (50 mm × 4.6 mm, 3 μm) and Ascentis Express C_{18} (50 mm × 4.6 mm, 2.7 μm) • Mobile phase: water (10 mM NH_4Ac): MeOH (10 mM NH_4Ac) • SRM mode	• MLOQ: 0.0625 ng/g dw (PFCs) 0.375 ng/g dw (diPAPs) • Recoveries: 17–105% (PFCs) 38–53% (diPAPs)	[73]
PFPeA, PHxA, PFHpA, PFOA, PFNA, PFDoA, PFTeA, 6:2 FTUCA, 8:2 FTUCA, PFBS, PFHxS, PFOS, FOSA, N-MeFOSA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA	Digested sewage sludge from WWTPs	(1) 0.5 g sludge (2) 0.5 mL TBA 0.5 M + 4 mL 0.25 M $NaCO_3$, pH 10) + 2× 5 mL MTBE (3) Evaporated under N_2 (4) Reconstitution in 5 mL MeOH (5) Clean-up by Envicarb cartridges	*LC–(−ESI)-MS/MS(QqQ)* • Injection volume: 20 μL • Column: 70 mm × 2 mm × 3 μm Nucleodur C_{18} gravity • Mobile phases: 2.5 mM NH_4Ac MeOH:water (95:5) and 2.5 mM NH_4Ac water:MeOH (95:5) • SRM mode with collision-induced fragmentation	• MLOQ: 0.6–30 ng/g • Recoveries: 70–169% • RSD: 2–20%	[74]
Solid–acid liquid extraction					
PFHxS, PFOS, PFDS, FOSAA, N-MeFOSAA, N-EtFOSAA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTeA	Digested sludge from WWTP and surface sediments	(1) 0.1 g sludge (2) 7.5 mL 1% AcH (3) Vortexed, sonicated at 60°C (15 min) and centrifugated at 3,000 rpm, 10 min (4) Supernatant separation and repeat steps 2–4 twice; solid part + 1.7 mL MeOH:water (1% AcH) (9:1, v:v) and vortexed, sonicated, and centrifugated (5) Supernatants combination centrifuged 1 h	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 20 μL • Column: 40 mm × 2.1 mm TargaSprite C_{18} (5 μm pore size) and C_{18} guard column • Mobile phase: water (2 mM NH_4Ac):MeOH • SRM mode	• MLOD: 0.7–2.2 ng/g dw (sludge), 0.041–0.246 ng/g dw (sediment) • Recoveries: 73–98% (sediment), 56–89% (aged sediment), 41–91% (digested sludge), 37–98% (primary sludge)	[75]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
		(6) SPE by 500 mg C_{18} (conditioning: 10 mL MeOH, 10 mL 1% AcH; rinsed: 10 mL water and 2 h vacuum; elution: 4 mL MeOH) (7) Concentrated under N_2 to 2 mL (8) 800 μL MeOH + 1,200 μL 0.01% NH_4OHaq + 6 mL MeOH:0.01% NH_4OHaq (70:30) addition (9) Stored at 4°C and before analysis: 500 μL extract + 50 μL IS			
PFBS, PFHxS, PFOS, FOSA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTeA, PFHxDA, PFODA	Sludge from WWTPs	(1) 0.1 g sludge + surrogate (2) 7.5 mL (1% AcH) (3) Sonication 20 min at 60°C (4) Centrifugation at 3,500 rpm, 10 min (5) Supernatant separation and pellet with 1.7 mL MeOH (1% AcH, 90:10), sonication 20 min at 60°C and centrifugation (6) Repeat steps 2–5 twice and combine extracts (7) 7.5 mL 1% AcH addition (8) SPE by Oasis HLB (conditioning: MeOH, 1% AcH; washing: 20% MeOH; elution: 5 mL MeOH) (9) Concentration to 1 mL and filtration by 0.2 μm nylon filter	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 10 μL • Column: Keystone Betasil C_{18} (50 mm × 2 mm; 5 μm) • Mobile phase: mater (2 mM NH_4Ac):MeOH • SRM mode	• Recoveries: 70–130% 37–65% (PFCAs > 11C) • LOQ < 25 ng/g dw	[42]

PFHxS, PFOS, FOSA, PFOA, PFNA, PFDA, PFUnA, PFDoA	Sludge from rural and urban areas WWTPs	(1) 0.1 g sludge + surrogate (2) 7.5 mL (1% AcH) (3) Sonication 20 min at 60°C (4) Centrifugation at 3,500 rpm, 10 min (5) Supernatant separation and pellet with 1.7 mL MeOH (1% AcH, 90:10), sonication 20 min at 60°C and centrifugation (6) Repeat steps 2–5 twice and combine extracts (7) 7.5 mL 1% AcH addition (8) SPE by Oasis HLB (conditioning: MeOH, 1% AcH; washing: 20% MeOH; elution: 5 mL MeOH) (9) Concentration to 1 mL and filtration by 0.2 μm nylon filter.	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 10 μL • Column: Keystone Betasil C_{18} (50 mm × 2 mm; 5 μm) • Mobile phase: mater (2 mM NH_4Ac):MeOH • SRM mode	• Recoveries: 59–107% (sludge)	[76]
PFOA, PFOS	Sewage sludge samples from municipal WWTPs	(1) 0.1 g sludge (2) 7.5 mL 1% AcH (3) Vortexed, sonicated at 60°C, 15 min and centrifugation at 3,000 rpm, 10 min (4) Supernatant separation and repeat steps 2–4 twice (5) Solid separated part + 1.7 mL MeOH:water 1% AcH (9:1), vortexed, sonicated and centrifugated (6) Combined supernatants centrifuged 1 h; SPE by 500 mg C_{18} cartridges (conditioning: 10 mL MeOH, 10 mL 1% AcH; rinsed: 10 mL water and 2 h vacuum; elution: 4 mL MeOH)	*HPLC–(−ESI)-MS/MS(QTOF)* • Injection volume: 10 μL • Column: C_{18} reversed phase • Mobile phase: water (NH_4Ac 5 mM):MeOH • SRM mode	• MLOD: 0.5 ng/g (PFOS) 0.8 ng/g (PFOA) • Recoveries: 85–114% (PFOS) 71–98% (PFOA)	[52]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
		(7) Concentrated under N_2 to 2 mL (8) Addition of: 800 μL of MeOH + 1,200 μL of 0.01% NH_4OHaq + 6 mL of MeOH:0.01% NH_4OHaq (70:30) (9) Stored at 4°C (10) Prior analysis, 500 μL extract + 50 μL IS (20–50 ng/mL)			
PFOA, PFOS	Grab samples of primary, activated, secondary and anaerobically digested sludge from sewage treatment plants (STPs)	(1) 0.1 g freeze dried sludge in PP tube (2) 7.5 mL 1% AcH (3) Vortexed, sonicated (60°C) 15 min and centrifugation at 3,000 rpm 10 min (4) Supernatant collection (repeat steps 2–4 twice) (5) Solid part + 1.7 mL [MeOH: water 1% AcH (9:1)], vortexed, sonicated and centrifugated (6) Supernatants centrifuged 1 h (7) Combined extracts (35.1 mL) loaded onto SPE cartridges (Oasis HLB 500 mg) and rinsed with 10 mL water [conditioning: 5 mL MeOH, 10 mL water (1% AcH)] (8) Elution: 2× 2 mL MeOH	*HPLC–(ESI−)-MS/MS(QqQ)* • Injection volume: 10 μL • Column: Zobax Extend C_{18} (150 mm × 2.1 mm; 5 μm) and guard column XDB-C8 (2.1 mm i.d. × 2.5 mm; 5 μm) at 30°C • Mobile phase: water (2 mM NH_4Ac):MeOH • SRM mode	• MLOQ: 1 ng/g dw (PFOS) 5 ng/g dw (PFOA) • Recoveries: 84% (PFOS) 70% (PFOA)	[44]

		(9) Extracts diluted with 6 mL Cl_2CH_2 and loaded onto the silica cartridge [conditioning: 5 mL Cl_2CH_2/MeOH (60:40, v/v)] (10) Eluent concentrated to dryness under N_2 (11) Reconstitution in 1 mL MeOH:water (0.01% NH_4OH) (70:30, v/v) and filtration by 0.2 μm nylon syringe filter			
PFBS, PFPA, PFHxA, PFHpA, PFOA, PFNA, ip-PFNA, PFOS, PFDA, PFDS	Sediment	(1) 1 g homogenized sediment into PP tube (2) 10 mL 1% AcH, vortexed, 40°C sonication (15 min) (3) Centrifuged (4) supernatant mixed with 2× [2.5 mL MeOH:1% AcH (9:1), sonicated 15 min, centrifuged] (5) Supernatant + 10 mL 1% AcH (6) Combined extracts and volume adjusted to 200 mL with water (7) SPE by Oasis WAX (conditioning: 4 mL 0.1% NH_4OH MeOH, 4 mL MeOH, 4 mL water; loading: 200 mL; elution: 4 mL 0.1% NH_4OH MeOH) (8) Evaporated under N_2 (9) Reconstituted in 0.5 mL MeOH	*LC–MS/MS(QqQ)* • Injection volume: 20 μL • Column: LiChroCARTLiChrospher 100 RP-18 (250 × 4 mm; 5 μm) • Mobile phase: water (20 mM NH_4Ac): methanol (20 mM NH_4Ac) • SRM mode	• MLOQ 0.002 and 0.2 ng/g • Recoveries: 62–103%	[108]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
PFOS, PFOA, PFNA, PFHxS, PFBS	Sediments	(1) 1 g (<120 μm particle), in PP tube (2) Surrogate IS addition and incubate 18 h at 4°C (3) 9 mL methanol + 10 mL AcH 1%, mixed and ultrasonicated (4) Centrifuged and supernatant evaporated under N_2 (5) Reconstitution in 1 mL of acetonitrile and incubated in an ultrasonic bath (6) Purification by activated charcoal + 50 μL of AcH, mixed 1 min (7) Centrifuged and 0.15 mL filtered by 2 μm GHP Accrodisc (8) Addition of in 0.35 mL water	*UPLC–MS/MS(QqQ)* • Injection volume: no data • Column: acquity UPLC BEH C_{18} column (1.7 μm particle size, 50 mm × 2.1 mm) before injection LiChroCART HPLC RP-18e column (125 μm × 2 μm × 5 μm) • Mobile phase: water (2 mM NH_4Ac): acetonitrile • SRM mode	• Recoveries: 100% (PFOS) 108% (PFOA)	[59]
PFBS, PFHxS, PFHpS, PFOS, PFDS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA	Sludge from municipal WWTPs, livestock WWTPs and industrial WWTPs	(1) 0.1 g sludge + IS + 7.5 mL 1% AcH (2) Sonication at 60°C, 20 min and centrifugation at 3,500 rpm, 5 min (3) Supernatant separation and solid with 1.7 mL MeOH: 1% AcH (9:1), sonication and centrifugation (4) Repeat step 3 for solid part twice and combine all the extracts (5) SPE by Oasis HLB (6) Extract evaporated under N_2 and reconstitution in 1 mL MeOH	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection: 10 μL • Column: Betasil C_{18} (100 mm × 2.1 mm, 5 μm) and guard column 12.5 mm × 2.1 mm Narrow Bore C_{18} • Mobile phase: water (NH_4Ac 2 mM):MeOH • SRM mode	• MLOQ: 1–5 ng/g • Recoveries: 21%(PFDS) 69–119% the rest of PFCs	[43]

Solid–alkaline liquid extraction

PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFHxS, PFOS	Sludge from WWTP	(1) 0.5 g dw + 0.5 mL NaOH 1 M (2) 30 min sonication/heat and overnight incubation (3) Neutralization (w/HCl) (4) 10 mL ACN:MeOH (1/1, v/v), shaked 1 h (5) Supernatant separation (repeat steps 4–5 one more time) (6) 2 mL of combined extracts (20 mL) + 98 mL water at pH4 (7) Sonicated 30 min (8) SPE by HLB cartridges (conditioning: 5 mL MeOH, 5 mL water; wash step: 5 mL 25% MeOH; elution: 5 mL MeOH) (9) Extract dried under N_2 (10) Reconstitution in 1 mL ACN: water (60:40) + IS addition	*UPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 20 µL • Column: Waters BEH C_{18} (100 mm × 2.1 mm; 2.1 µm) at 35°C and a Waters BEH C_{18} trapping cartridge • Mobile phase: water: ACN (pH4 with HAc) • SRM mode	• MLOQ: 1.8–6.8 ng/g dw • Recoveries: 82–104%	[77]
PFBS, PFHxS, PFHpS, PFOS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, FOSA, N-MeFOSA, N-EtFOSA	Sludge from different WWTPS	(1) 1 g sludge (5 g sediment) + 10 mL MeOH (1% NH_4OH) (2) Vortexed 30 s and sonicated 10 min at 60°C (3) Supernatant + water (1% AcH) (4) Preconcentration under N_2 to 5 mL (5) Purification by dispersed solvent (EnviCarb) and rinse with 2.5 mL MeOH (1% NH_4OH, 1% AcH) (6) Concentrate to 1 mL under N_2	*UPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 10 µL • Column: Waters BEH C_{18} (50 mm × 2.1 mm; 1.7 µm particle size) • Mobile phase: water/MeOH (2 mM NH_4Ac, 95/5):MeOH (2 mM NH_4Ac). UPLC system were replaced by PEEK • SRM mode	• MLOD: 0.14–1.43 ng/g (sludge) 0.03–0.29 ng/g (sediment) • Recoveries: 62–94% (sludge) • RSD: 2–7% (sludge)	[78]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
Solid–liquid extraction					
PFHxS, PFOS, PFDS, PFOA, 9,9,10,10,11,11,12,12,13,13,13-Undecylfluorotredecane-1-sulphonate, *N*-ethyl-*N*-(heptadecafluorooctane)-sulphonyl-glycinic acid, 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorodecane sulphonylamido polyethocylate and polyethocylate methyl ether, partly fluorinated alkyl-ethoxylated (2-perfluoroalkylethanol polyglycol ether), metabolites of partly fluorinated alkylethoxylates	Sludge from WWTP	(1) 2 g sludge (dw) (2) Soxhlet or hot vapour extraction, 6 h [solvent optimization: MeOH, EtOAc, MeOH–HCl] (3) (In parallel to Soxhlet) PLE by ASE [optimization extraction steps: (a) EtOAc–DMF (8:2), (b) MeOH–H_3PO_4 (95:5), (c) MeOH–H_3PO_4 (99:1) and (d) MeOH–H_3PO_4 (99:1)]	*LC–(±ESI or APCI)-MS/MS* • Injection volume: 10 µL • Column: Multospher 100 RP 5-5 (C8, 5 µm, spherical; 250 mm × 4.6 mm i.d.) or using a PF-C8 column (150 mm × 4.6 mm i.d.) filled with spherical perfluorinated RP-C8 material (5 µm) • Mobile phase: MeOH:water • SRM mode	*Soxhlet and hot vapour* • Recoveries: 48–52% *PLE* • MLOQ 10 µg/g (anionic) 20 µg/g (non ionic) • Recoveries: 105% (ionic) 119% (non ionic)	[83]
PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTeA	Liquid sludge	(1) 5 g liquid sludge + surrogates (into PP tube) (2) 20 mL MeOH, wrist-action shaker, mixed 30 min (3) Settled 30 min or centrifugated at 3,000 rpm, 20 min (4) 1 mL supernatant + 25 mg Envi-Carb graphitized carbon adsorbent + 50 µL AcH, vortexed and centrifugated 10,000 rpm, 30 min (5) 500 µL supernatant + 500 µL water, mixed (6) Internal standard addition	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 100–200 µL • Column: Zorbax Rx-C8 (15 cm × 2.1 mm i.d., 5 µm) analytical column and Luna $C_{18}(2)$ (3 cm × 4.6 mm i.d., 3 µm) inserted in the HPLC between the pump and injector to delay any fluorochemicals originating from PTFE instrument components • Mobile phase: ACN (0.15% AcH) • SRM mode	• MLOQ: 1 ng/g • Recoveries: 70–120% • RSD: <20%	[79]

PFOA, PFNA, PFDA, PFUnA, PFOS, FOSA	Sludge	(1) 7 g sludge (dw) + surrogates (into PP tube) (2) 2× (10 mL MeOH, ultrasonic bath) (3) Extracts pooled + 1 L water (4) SPE by C_{18} (conditioning: MeOH, water; eluting: 10 mL MeOH) (5) Evaporated to dryness (6) Reconstitution in 1 mL MeOH:water (2 mM NH_4Ac) (1:1)	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 20 μL • Column: C_{18} Betasil column (2.1 mm × 50 mm) • Mobile phase: H_2O (2 mM NH_4Ac):MeOH (2 mM NH_4Ac) • SRM mode	• MLOD: 0.4–1.7 ng/g (dw) • Recoveries: 83–105% (FOSA) 26% • RSD: 4–8%	[56]
N-EtFOSE, N-EtFOSAA, FOSAA, FOSA, N-EtFOSA, PFOSI, PFOA, PFOS	Aerobic batch assays with WWTPs materials	(1) Lyophilized solids + MeOH (2) Sonication 20 min, 60°C, and centrifugation at 3,600 rpm, 15 min (3) Extract poured into a new tube + 20 mL MeOH (4) Purification by dispersed solvent (ENVI-Carb) (5) Extracts diluted 1/10 with MeOH and again diluted with 3/5 water (0.01% NH_4OH) (6) 0.5 mL in glass autosampler vial (7) (In parallel) SPE from headspace sampling eluted with 10 mL of MeOH and diluted 3/5 with water (0.01% NH_4OH)	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 30 μL • Column: Targa Sprite C_{18} (5-μm pore size equipped with a C_{18} guard column • Mobile phase: H_2O (2 mM NH_4Ac):MeOH • SRM mode	• MLOQ: 0.1 μg/L (vial) 46–49 pmol (microcosm) • Recoveries: 83–119%	[80]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
[1,2-^{14}C] 6:2 FTOH	Sassafras soil	(1) 5 g sample + 15 mL ACN (2–7 days) at 50°C (2) Centrifugation at 657 g, 20 min (3) Supernatant separation and soil with 15 mL ACN: 250 mM NaOH (9:1) at 50°C, shaked overnight (4) 80 μL 5 M HCl and centrifugation at 657 g, 20 min (5) Supernatants stored at −10°C (dark)/Bottle septum experiments with 50 mL ACN at 50°C, 2–7 days/C_{18} Cartridges experiments with 5 mL ACN elution for the first 7 days	• *Radioactivity* by Beckman LS5000 TD liquid scintillation counter • *Liquid* chromatography/ accurate radioisotope counting (LC/ARC) system for the soil CH_3CN extracts and C_{18} cartridge eluent		[82]
TFA, PFPrA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTeA, PFBS, PFHxS, PFOS	Waste sludge and sediments	(1) sonication solvent extraction was used for removing PFCAs from solid matrices (2) SPE was performed to concentrate PFCAs using WAX cartridges (3) The SPE eluent was cleaned up using dispersive carbon sorbent to remove the co-eluted interfering compounds	*HPLC–(−ESI)-MS/MS* • Injection volume: 10 μL • Column: Hypersil Gold C_{18} (150 mm × 2.1 mm; 3 μm pore size) at 30°C • Mobile phase: water (2 mM NH_4Ac):MeOH. HPLC tubing made up of PTFE replaced with PEEK tubing • SRM mode	• MLOQ: 0.10–0.50 ng/g • Recoveries: 66–111% (sediment) 73–112% (soils) 57–115% (sludge) • RSD 1–15% (sediment) 1–19% (soil) 2–18% (sludge)	[55]

PFBS, PFHxS, PFHpS, PFOS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA	Anaerobically stabilized sewage sludge from municipal WWTPs	(1) 0.5 g sludge (dw) in a 15 mL PP tube + 0.5 mL water + IS (2) Sequentially extraction by 2.5, 1.5 and 1.0 mL of MeOH (shaking the slurry 10 min and sonication 20 min at 40°C) (3) Centrifugation at 3,500 rpm, 8 min (4) Combined extracts + Envicarb graphitized carbon adsorbent (300 mg) (5) Shaked 20 min, centrifugation at 3,500 rpm along 30 min (6) 4 mL supernatant + IS + 1 mL water (0.01% NH_4OH) (7) Stored at −4°C before analysis	*LC–(−ESI)-MS/MS(QqQ)* • Injection volume: 20 μL • Column: Nucleodur C_{18} gravity column (70 mm × 2 mm; 3 μm) • Mobile phase: 2.5 mM NH_4Ac MeOH:water (95:5) and 2.5 mM NH_4Ac water: MeOH (95:5) • SRM with collision-induced fragmentation	• MLOQ: 0.5–17 ng/g • Recoveries: 94–115% (PFSAs) 21–109% (PFCAs)	[81]
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFHxDA, PFODA, PFBS, PFHxS, PFOS, PFDS, FOSA	Sewage sludge from a domestic WWTP	(1) 0.5 g sludge (dw) + surrogates (2) PLE (MeOH solvent at 70°C, two cycles, 1 min static time, 100 bar) (3) Evaporation to 1 mL + 30 mL water (4) SPE by Oasis WAX (conditioning: 4 mL MeOH (NH_4OH), 4 mL water; loading: under gravity conditions; eluting: 4 mL MeOH(NH_4OH)) (5) Dried under N_2 (6) Reconstitution in initial mobile phase conditions + IS	*HPLC–(−ESI)-MS/MS(QqLIT)* • Injection volume: 10 μL • Column: LiChroCART® 125-2, Pusopher® STAR, RP-18e (5 μm) • Mobile phase: water (20 mM NH_4Ac):MeOH • SRM mode	• MLOQ: 50–2,772 pg/g • Recoveries: 65–111% • RSD: 4–30%	[35]

(continued)

Table 1 (continued)

Analytes	Matrices	Pre-treatment	Instrumental analysis	Quality parameters	Reference
PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS	Sludge from industrial WWTP	(1) Suspended solid and dried sludge (2) Extraction by PLE (MeOH solvent, three cycles, 15 min, 2,000 psi at 100°C) (3) 60–80 mL of extract diluted into 1 L of water (4) SPE extraction	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 10 μL • Column: Agilent Eclipse XDB-C_{18} (2.1 mm × 100 mm; 5 μm) • Mobile phase: water (5 mM NH_4Ac):ACN • SRM mode		[84]
PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, FOSA, N-MeFOSA, N-EtFOSA	Sewage sludge samples from WWTPs	(1) 1 g sludge + surrogates + 10 mL MeOH in a PP tube (2) Shaked 10 min, ultrasonic bath at 40°C for 30 min and centrifugation at 3,000 rpm (15 min) (3) Supernatant separated and solid part with 9 mL MeOH in an ultrasonic bath and centrifugation (4) Repeated step 3 one more time and combine all the extracts (5) Purification by disperse solvent (EnviCarb) (6) Eluted extract + 1 L water (7) SPE by Oasis WAX [conditioning: 12 mL MeOH (0.1% NH_4OH), 12 mL water; cleaning: 12 mL 25 mM NaAc (pH4); elution: 8 mL MeOH (0.1% NH_4OH)] (8) aliquot + IS	*HPLC–(−ESI)-MS/MS(QqQ)* • Injection volume: 20 μL • Column: Varian Polaris C_{18} analytical column (50 mm × 2.0 mm; 3 μm particle diameter) at 40°C • Mobile phase: water (2 mM NH_4Ac):MeOH • SRM mode	• MLOQ: 0.02–0.71 ng/g • Recoveries: 64–129% • RSD: 3–22%	[34]

Other extraction procedures					
PFHxA, PFOA, PFNA, PFOS, PFBS, PFUnA, FOSA, 6:2 FTS, 6:2 FTOH, 8:2 FTOH	Activated sludge from WWTP	(1) PFCAs were extracted from supernatant of the sludge experiments (2) SPE by C_{18} cartridges (conditioning: 10 mL MeOH, 10 mL water; elution: 10 mL MeOH) (3) Reduced under a gentle stream of N_2 and filtered before analysis	*HPLC–(−ESI)-MS* • Mobile phase: water (5 mM NH_4Ac):MeOH • FTOHs detected as acetate adducts	• Recoveries: ($^{13}C_2$-PFOA) $>$ 60%	[119]
PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA	Suspended soil and mixed liquor suspended solid from WWTPs	(1) Suspended soil and mixed liquor suspended soil filtered by GF/B filter (2) PLE (ASE200, Dionex, USA) of GF/B filter (three static cycles, MeOH solvent, 100°C, 2,000 psi, 10 min) (3) Extract dried to reduce $<$10 mL (60°C, water bath) (4) Reduced extract + 1 L water (5) SPE by Oasis HLB plus and PrepSepC-Agri (short) in tandem (6) Elution with 4 mL of MeOH under gravity conditions (7) Dryness under N_2 (8) Reconstitution in 1–2 mL of water:ACN (6:4) and vortexed	*HPLC–(ESI−)-MS/MS(QqQ)* • Injection volume: 10 µL • Column: Agilent Eclipse XDB-C_{18} (2.1 mm × 100 mm; 5 µm) at 40°C • Mobile phase: water (5 mM NH_4Ac):ACN • SRM mode	• MLOQ: 0.02–0.22 ng/g • Recoveries: 64–112% • CV $<$20%	[88]

cartridges, OASIS HLB and Sep-Pak (C_{18}), was evaluated. Both SPE cartridges were a cause of contamination by PFOS and PFOA. However, higher concentrations of PFOS and PFOA were reported for Sep-Pak cartridges. In the case of the Oasis HLB, PFOS, PFOA, PFHxS and PFBS were detected, but at lower concentrations than those found in the Sep-Pak cartridges. On the other hand, Taniyashu et al. [67] evaluated Oasis HLB and Oasis WAX columns for the extraction of PFCs. In this study, few target PFCs were detected in procedural blanks at a few pg/L in the final extract. However, PFOA, PFDA and PFUnA were still found at relatively high concentrations. In general, the performance of these columns was comparable. Recoveries were good (70–100%) for most compounds, but for short-chain PFCAs recoveries using Oasis WAX-SPE cartridges were higher. Losses due to evaporation during analysis and adsorption to the polypropylene sample container surface as discussed earlier were suggested causes for the lower recoveries.

2.2.2 Solid Samples

Sample pre-treatment in complex matrices as sludge or sediments is required to minimize matrix effects. It is important to be sure that transformation processes do not occur during this process. For example, the hydrolysis of fluorotelomer compounds to fluorotelomer alcohol during solvent extraction of soils was reported by Dasu et al. [68]. General approaches can be summarized in four different pre-treatments based on solid–liquid extraction or supernatant liquid extraction:

1. Ionic-pair extraction
2. Solid–acid liquid extraction
3. Solid–alkaline liquid extraction
4. Solid–liquid extraction

Table 1 summarizes the pre-treatments that can be found in some published works. The first four extraction procedures are based on the extraction of lyophilized or dried solid. The last one corresponds to non-dried solid extraction procedures.

Ionic-Pair Extraction

Ylinen et al. developed an ion-pair extraction procedure employing tetrabutyl ammonium (TBA) counter ions for the determination of PFOA in plasma and urine in combination with gas chromatography (GC) flame ionization detection (FID). Later on Hansen et al. [69] improved the sensitivity of the ion-pair extraction approach using methyl tertiary butyl ether (MTBE) and by inclusion of a filtration step to remove solids from the extract making it amenable for liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) determination. Ion-pair extraction procedure has been the basis of several procedures for biota [70, 71] and food samples [72]. However, this method has shown some limitations, such as

(1) co-extraction of lipids and other matrix constituents, (2) the absence of a clean-up step to overcome the effects of matrix compounds and (3) the wide variety of recoveries observed, typically ranging from <50% to >200%. Sludge samples usually contain high amounts of interferences and, once the sample is reconstituted, a filtration step previous to the analysis [73] or an additional clean-up step by Envicarb cartridges [74] is necessary. This pre-treatment improves the limits of quantification (MLOQ). Using this last approach, Eon et al. obtained recovery rates between 17% and 105% [73].

Solid–Acid Liquid Extraction

Current methods are based on the procedure described by Higgins et al. [75]. This method is based on the extraction of dried soils using acetic acid 1% at 60°C in an ultrasonic bath. Then, the mixture is centrifuged and the supernatant collected. The extraction of the solid residue is repeated twice; the extracts are combined and after centrifugation are cleaned up using SPE. Sometimes, a filtration step could be also required in order to eliminate the non-dissolved matter [44, 76]. This methodology has been used in the sludge characterization of different PFCs including PFCAs, PFSAs and fluorinated sulphonamides [43, 44, 52, 75, 76]. The recoveries were in most of the cases between 40% and 119%. In general, this treatment allows better quality parameters than ionic-pair extraction.

Solid–Alkaline Liquid Extraction

This procedure has been used for the analysis of acids, sulphates and sulphonamides fluorinated compounds by different authors. In general, alkaline methanol (with NaOH or NH_4OH) is used. After the alkaline treatment, a neutralization step with HCl (if NaOH is used) [77] or acetic acid at 1% (if the alkaline digestion has been carried out by NH_4OH) is needed [78]. Some more details can be found in Table 1. As a last clean-up step, SPE or dispersive-SPE (EnviCarb) is performed. The alkaline extraction allowed method limit of detection (MLOD) in the range of 0.14–1.43 ng/g dw in sludge [78] and MLOQ between 1.8 and 6.8 ng/g dw [77]. The recoveries ranged from 62% to 104% with RSDs between 2% and 7% (Table 1).

Solid–Liquid Extraction

This is the most commonly used methodology in the extraction of non-volatile PFCs from solid matrices due the facility and simplicity of the extraction and the required solvents. Some published works performed the extraction by methanol or acetonitrile with a shaker [79], in an ultrasonic bath with temperature between 40°C

and 60°C along 20–30 min [34, 55, 56, 80, 81] or at 50°C along 2–7 days [82], depending on the analysed compounds.

In some other works, the extraction is performed using pressurized liquid extraction (PLE) by accelerated solvent extractor (ASE) [35, 83, 84]. The use of PLE instead of Soxhlet or hot vapour extraction allows decrease in the time of extraction due to the use of high pressure. The most frequent solvent extractor is methanol using a different number of cycles, temperatures (between 70°C and 100°C) and pressures (between 1,500 and 2,000 psi). After extraction, a clean-up process is in general required to decrease the matrix effects [35, 74], using SPE (C_{18}, anionic exchange (WAX)) or by using Envicarb graphitized carbon adsorbent. The methodology allows, in general, a MLOQ between 0.05 and 2.77 ng/g of PFCs, recoveries ranging from 57% to 120% in most of the cases and 2–30% of RSD (see Table 1).

2.3 Instrumental Analysis

During this step is important minimize possible sources of contamination due Teflon or PVDF tubing other materials as PEEK. Other precaution that can be considered is the addition of extra chromatographic column prior to the injector in order to delay PFCs peaks due to system contamination [79].

Liquid chromatography-mass spectrometry (LC-MS) or LC-MS/MS has been in general the techniques of choice for the analysis of PFCs. Therein detailed information about the main experimental conditions used for analysis such as LC-MS/MS precursor-product ion transitions.

LC separation of PFCs has been mainly carried out with C_{18} and C_8 columns. In spite of the wide use of RP-C_{18} columns for PFCs' analysis, the interference producing the enhancement of spectral signal has been reported. RP columns with shorter alkyl chain bonded phases (e.g., C_8, C_6, phenyl and phenylhexyl) also separated the branch isomers, but to a lesser extent. To minimize the separation of branched isomers, the authors increased the LC column temperature to 35°C or 40°C [85, 86]. Taniyasu et al. [87] explored the chromatographic properties and separation of short-chain PFAs on RP-C_{18} and ion-exchange columns. The results showed that using RP-C_{18}, the peaks of PFPrA and PFEtS were broad and not adequately resolved, whereas that of TFA was not retained in the analytical column eluting with the solvent front. This suggested that RP columns are not suitable for the analysis of short-chain PFAs, especially TFA. As a proper alternative, ion-exchange columns have superior retention properties for more hydrophilic substances enabling the analysis of short-chain PFCAs, TFA, PFPrA, PFBA, PFEtS, PFPrS and PFBS together with several long-chain PFCAs, in water samples.

Due to the complexity of environmental samples, it is possible that the co-occurrence of certain compounds can interfere the analyte determination. This problem has been partially solved using LC–MS/MS. However, certain interferences can affect the analyte ionization producing ion suppression or

enhancement [35, 74]. The use of labelled PFCs during analytical process (surrogates or internal standards) helps to assess and normalize these instrumental effects.

LC-MS/MS performed using triple quadrupole mass spectrometer (QqQ) combined with multiple selected reaction monitoring (SRM) is one of the more widely applied analyzer [34, 43, 44, 73–78, 80, 81, 84, 88], as well as, to be one of the better suited for quantification of PFCs. Nowadays the performance of hybrid quadrupole linear ion trap (QqLit) [35] or hybrid quadrupole time of flight (QTOF) [52] has been also considered for trace quantification of PFCs. PFCs contain carboxylic, sulphonic, hydroxy or sulphonamide group. They have acidic properties and can therefore dissociate. Consequently, electrospray ionization in the negative mode (ESI(−)) has been the interface most widely used for the analysis of anionic perfluorinated surfactants, allowing limits of detection in the pg to ng/g range, although atmospheric pressure chemical ionization (APCI) and positive ESI have been employed for specific PFCs' analysis [83]. In addition, ESI has been optimized for the determination of neutral compounds such as the sulphonamides FOSA, Et-FOSA and *t*-Bu-PFOS. The use of atmospheric pressure photoionization (APPI) has been explored in few works [68–70]. Takino et al. [68] found as the main advantage of this technology the absence of matrix effects, but the limits of detection were considerably higher than those obtained by LC–ESI-MS/MS.

Pseudomolecular ions are formed such as $[M-K]^-$ for PFOS (*m*/*z* 499), $[M-H]^-$ for PFOA (*m*/*z* 413) and FOSA (*m*/*z* 498), which are generally selected as precursor ions for MS^2 experiments using ion trap and a triple quadrupole instruments. Berger et al. [89] have presented a comparison between IT, QqQ and TOF instruments. Tandem mass spectrometry showed excellent specificity, but the background is eliminated by the instrument, and thus it cannot be visualized. Applying TOF-MS gives an estimation of the amount of matrix left in the extract, which could impair the ionization performance and the high mass resolution of the TOF-MS instrument offers excellent specificity for PFCs' identification after a crude sample injection. Recently, the analytical suitability of three different LC–MS/MS systems: QqQ, conventional 3D-IT and QqLIT, to determine trace levels of PFCs in fish and shellfish was compared [90]. In this study, the accuracy was similar in the three systems, with recoveries always over 70%. Precision was better for the QqLIT and QqQ systems (7–15%) than for the IT system (10–17%). The QqLIT (working in SRM mode) and QqQ systems offered a linear dynamic range of at least three orders of magnitude, whereas that of the IT system was two orders of magnitude. The main advantage of QqLIT system is the high sensitivity, at least 20-fold higher than the QqQ system. Another advantage of QqLIT systems is the possibility to use enhanced product ion (EPI) mode and MS^3 modes in combination of SRM mode for confirmatory purposes of target analytes in complex matrices.

Other instrumental tools have been employed by Liu et al. [82] in the study of aerobic biodegradation of [^{14}C] 6:2 PFTOH in a flow-through soil incubation system. The instrumental analysis was carried out by radioactivity and liquid chromatography/accurate radioisotope counting (LC/ARC).

3 Environmental Fate of PFCs

Partitioning and reactivity properties are important to understand and model the environmental behaviour of PFCs. Just during the recent years, it has been initiated the study of the reactivity properties of these compounds, and in addition should be pointed out that some data continue being contradictory. A starting point to study the mechanistic properties of PFCs, as well as, to evaluate and assess properties of new emerging PFCs is the study of selected physicochemical properties.

The perfluoro alkyl sulphonates (PFASs) and PFCAs are strong acids that exist in equilibrium between the neutral form and the anionic form. In general, both the anionic and neutral forms, as it happens with PFOA, are soluble in water. Although the Henry's law constant values suggests partitioning to air for the neutral, protonated form, predicting the amount that partitions into air is complicated because there is uncertainty over the degree to which carboxylic and sulphonic acids partition from the water to atmosphere. The uncertainty arises with regard to the value of the acid dissociation constant (i.e. pK_a), or the fraction of the acid form present at environmentally relevant pH. PFCA and PFAS have been detected in air, water and soil samples collected throughout the world. The oceans have been suggested as the final sink and route of transport for perfluorinated carboxylic and sulphonic acids, where they have been detected on the surface and at depths over 1,000 m [91].

Some PFAS/PFCA have the potential for long-range environmental transport (LRET) by a combination of dissolved-phase ocean and gas-phase atmospheric transport; however, determining which is the predominant transport pathway is complicated by the uncertainty over water to atmosphere partitioning. Furthermore, there is evidence that transport and subsequent oxidation of volatile alcohol PFAS/PFAC precursors may contribute to the levels of PFAS/PFCA in the environment.

The evaluation of PFCs in remote areas such as the Antarctica peninsula is one of the very few forms of evaluation of LRET. The global fate of POPs is associated with different biogeochemical cycles and geophysical drivers. The occurrence of PFCs into remote areas such as the Antarctica could be partially explained by the theory of *cold condensation*, concerning the chemical movements or chemical transformations from sources under the impact of environmental forces, such as temperature, and interaction with other environmental compartments (soil, oceans, etc.) [92]. In addition, the physicochemical characteristics of PFCs should be considered, since these properties dictate their environmental behaviour [5].

Just few previous studies have reported the presence of PFCs in different biota samples from the Antarctica continent [11, 70, 93], whereas this information could be of importance to establish Global PFCs' distribution and also the basis of LRET of these compounds.

Different studies have shown that PFTOH can be degraded by microorganisms and by abiotic processes. 8:2 FTOH and FTOH of other chain lengths, and related chemicals in mixed microbial cultures, activated sludge and soil systems have been shown to be easily degraded to form PFOA and related perfluorinated acids. Some studies have also shown that $–CF_2-$ groups can be mineralized, forming

shorter-chain perfluoro acids. If FTOH are absorbed from ingestion, inhalation, dermal or ocular exposure or formed in vivo by from other compounds they can be metabolized by mammals and other organisms to form perfluorinated acids and other fluorinated compounds. FTOH can be degraded by abiotic processes in water and air to produce PFCA and various intermediates. FTOH are fairly volatile. Based on atmospheric half-lives determined in chamber studies, FTOH can be transported globally. Deposition or degradation in areas far from the source can result in PFCA contamination in high latitudes and other remote locations and contribute to global background levels of PFCA and PFAS.

Therefore, two mechanisms should be considered to explain the LRET capabilities of PFCs. The first suggests atmospheric distribution of neutral, volatile compounds (*flyers*), such as fluorotelomer alcohols and perfluorinated sulphonamido alcohols. *Flyer* compounds are susceptible to suffer atmospheric long-range transport because of their partitioning properties (log K_{aw} values estimated between 0 and 1 and log K_{ow} around 5), which indicate that these classes of chemicals can be classified as *flyers* according to the Globo-POP model [5, 92]. This is also in agreement with the findings of Dreyer et al. (2009). Then, after their transport and cold condensation, these *flyer* compounds can biodegrade as it has already been indicated in previous studies [80] or suffer in situ oxidation to form ionic PFCs [94].

The second mechanism is related to the properties of ionic PFCs (negligible vapour pressure, water solubility and moderate sorption to solids), which predicts their accumulation in surface waters (*swimmers*) [95, 96]. Some studies have evaluated the influence of these mechanisms and have been revealed that the dominant phenomenon is the hydrospheric transport for PFOS, PFOA and PFNA [97]. For example, fluorotelomer alcohols have short atmospheric lifetimes in the order of 10–20 days [98]. The geographical isolation of Antarctica combined with both, short atmospheric lifetimes of fluorotelomer alcohols and the low yield of the oxidation pathway, significantly reduces the potential for effective atmospheric delivery to the Antarctic continent. Therefore, atmospheric input of flyer PFCs to the Antarctica is principally a function of rapid and direct delivery of contaminated wind masses.

Concerning to degradation processes, some recent data show that perfluorooctane sulphonyl fluoride (POSF) and its derivatives can be degraded under environmental conditions to form perfluoroalkyl sulphonates and carboxylic acids. Reaction of POSF ($CF_3(CF_2)_n$-SO_2F) with methyl or ethyl amines is used to produce *N*-ethyl or *N*-methyl perfluorooctane sulphonamidoethanols. Similar reactions are used to make shorter- and longer-chain analogues to POSF and POSF derivatives. FOSE compounds, such as *N*-methyl and *N*-ethyl FOSEs can be degraded though a series of intermediates to form both PFCAs and perfluoroalkyl sulphonates. Other chemical intermediates produce other FOSA derivatives, including phosphate esters, fatty acids esters, silanes, carboxylates and polymers with acrylate, urethane and other linkages.

Longer- and shorter-chain perfluoro sulphonyl derivatives have also been produced intentionally and as unintended reaction products. Based on existing data

from the open literature and CBI data, it is expected that most, if not all, of these POSF and other chain length sulphonyl fluorides and their derivatives will be degraded to carboxylic acids and/or sulphonate over time. Most of these compounds will have environmental and metabolism half-lives of weeks to months. Some will be degraded faster and some will degrade more slowly, but all will eventually be degraded.

Very little data are available on the behaviour of other perfluorochemicals in the environment and in vivo but the existing data suggest that they will also be degraded to form PFAC. For example, recent studies have shown that ingested mono- and di-polyfluoroalkyl phosphates (PAPs) can be degraded in rats to form PFOA and other PFAC in the body. They can also be degraded by microbial processes in soil and wastewater to form perfluorinated acids [99].

A limited number of studies on the degradation of fluorotelomer-based polymers have been submitted, but some studies have shown that fluorotelomer-based polymers are subject to hydrolysis, photolysis and biodegradation to some extent. Studies have shown half-lives of a few days to hundreds of years. In addition, preliminary research on degradation of fluorotelomers has shown that some urethanes and acrylates biodegrade; however, half-lives and kinetics of the fluorotelomers are not yet well defined.

These studies have shown that the perfluorinated portion of some polymers is released as the polymer is degraded by microbial or abiotic processes to form telomer alcohols or other intermediates and that they eventually form PFCA. Polymers based on POSF and other chain length chemistries show similar degradation rates and release intermediates that further degrade to form perfluorinated acids and sulphonates. Studies have shown that some polymers can undergo indirect photolysis in soil and in aquatic systems and be degraded with half-lives of days to several years.

4 Occurrence of PFCs: The Llobregat River as Case Study

During the last decade, an important work has been carried out in order to assess the occurrence of PFCs in the aquatic environment. In this section, the occurrence of PFCs in river basins will be revised taken as central example the Llobregat River, as example of a Mediterranean river suffering a high industrial pressure.

Different examples of works assessing the occurrence of PFCs in river water are summarized in Table 2.

Due to their persistency and wide use in the past PFOS and PFOA are the best-studied compounds. Currently, the use and production of these two compounds are almost stopped; however, due to their high resistance to degradation and because they are the end products of other PFCs in use, PFOS and PFOA continue being present in high concentrations in surface waters and sediments. Due to their physicochemical characteristics PFOA is mainly found in water, whereas PFOS is retained in higher proportion into the sediments.

Table 2 PFCs – published works

Analytes	Origin	Matrices	Results		Reference
Llobregat River					
PFBS, PFHxS, PFOS, PFOA, PFNA	Rivers: Muga, Fluvià, Ter, Besós, Llobregat, Ebro Different WWTPs (2009) Catalonia (Spain)	Surface river water and effluent water from WWTP	*Surface river*: PFBS = 0.07–0.88 ng/L PFHxS = 0.03–0.64 ng/L PFOS = 1.09–9.56 ng/L PFOA = 0.79–9.63 ng/L PFNA = 0.06–1.62 ng/L	*Effluent WWTP*: PFBS = 0.07–2.03 ng/L PFHxS = 0.03–25.3 ng/L PFOS = 0.03–72.1 ng/L PFOA = 3.47–61.9 ng/L PFNA = 0.06–14.1 ng/L	[60]
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFHxDA, PFODA, PFBS, PFHxS, PFOS, PFDS, FOSA	WWTPs from Catalonia, Spain (2010)	Sewage sludge ($n = 5$)	PFBA ≤ MLOD − 22.6 ng/g dw PFPeA ≤ MLOQ − 17.2 ng/g dw PFHxA ≤ MLOD − 4.8 ng/g dw PFHpA ≤ MLOQ − 4.5 ng/g dw PFOA = 7.0–30.3 ng/g dw PFNA = 1.0–2.4 ng/g dw PFDA = 6.1–23.5 ng/g dw PFUnA ≤ MLOQ − 12.2 ng/g dw PFDoA = 2.7–11.3 ng/g dw	PFTrA ≤ MLOQ PFTeA ≤ MLOQ − 5.0 ng/g dw PFHxDA ≤ MLOQ − 4.9 ng/g dw PFODA ≤ MLOD − 0.9 ng/g dw PFBS ≤ MLOD − 7.6 ng/g dw PFHxS ≤ MLOQ PFOS = 53–121.1 ng/g dw PFDS ≤ MLOD − 7.5 ng/g dw FOSA ≤ MLOD − 10.7 ng/g dw	[35]
Other Spanish areas					
PFOS, PFHxS, PFBS, PFOA, PFNA	Northern Spain: Asturias, Cantabria and Basque Country (Spain)	Sea emissaries ($n = 3$) Ports ($n = 5$) Sewage treatment plant effluent ($n = 3$) Industrial WW effluent ($n = 1$)	PFOS = 0.01–5.11 ng/L PFHxS ≤ MLOD − 0.31 ng/L PFBS ≤ MLOD − 5.08 ng/L	PFOA = 0.03–3.53 ng/L PFNA = 0.01–1.40 ng/L	[59]
PFBS, PFHxA, PFHpA, PFHxS, THPFOS, PFOA, PFNA, PFOS, FOSA, PFDA, PFUnA, PFDS, PFDoA, PFTrA	Ebro River (Garcia and Mora) Francolí River Cortiella River (Spain)	Surface river water	PFBS ≤ MLOQ PFHxA ≤ MLOQ PFHpA = MLOQ − 3.38 ng/L PFHxS = MLOQ − 0.78 ng/L THPFOS ≤ MLOQ PFOA = MLOQ − 24.9 ng/L PFNA = MLOQ − 0.64 ng/L	PFOS = MLOQ − 5.88 ng/L FOSA = MLOQ − 0.20 ng/L PFDA = MLOQ − 0.82 ng/L PFUnA ≤ MLOQ PFDS ≤ MLOQ PFDoA ≤ MLOQ PFTrA ≤ MLOQ	[39]

(continued)

Table 2 (continued)

Analytes	Origin	Matrices	Results		Reference
PFBS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, ip-PFNA, PFOS, PFDA, PFDS	L'Albufera de Valencia (Spain)	Surface water	PFBS ≤ MLOD − 5.50 ng/L PFPeA ≤ MLOD − 5.40 ng/L PFHxA ≤ MLOQ − 6.90 ng/L PFHpA ≤ MLOQ − 18.4 ng/L PFOA = 0.99–120.2 ng/L	PFNA = 0.02–18.5 ng/L ip-PFNA ≤ MLOD − 5.44 ng/L PFOS = 0.94–58.1 ng/L PFDA ≤ MLOD − 10 ng/L PFDS ≤ MLOD − 1.29 ng/L	[108]
PFBS, PFHxA, PFHpA, PFHxS, THPFOS, PFOA, PFNA, PFOS, FOSA, PFDA, PFUnA, PFDS, PFDoA, PFTrA	Reus, Tarragona, Tortosa and Valls (Spain)	Drinking tap water	PFBS ≤ MLOQ PFHxA ≤ MLOQ PFHpA = MLOQ − 0.40 ng/L PFHxS ≤ MLOQ THPFOS ≤ MLOQ PFOA = MLOQ − 0.67 ng/L PFNA = MLOQ − 0.20 ng/L	PFOS ≤ MLOQ FOSA ≤ MLOQ PFDA = MLOQ − 0.63 ng/L PFUnA ≤ MLOQ PFDS ≤ MLOQ PFDoA ≤ MLOQ PFTrA ≤ MLOQ	[39]
PFOS, PFHxS, PFBS, PFOA, PFNA	Northern Spain (Asturias, Cantabria and Basque Country)	Sediment emissaries ($n = 3$) Port sediment ($n = 4$) River sediment ($n = 3$)	PFOS ≤ MLOD − 0.13 ng/g PFHxS ≤ MLOD PFBS = 0.01 ng/g PFOA ≤ MLOD − 0.06 ng/g PFNA ≤ MLOD − 0.08 ng/g		[59]
PFBS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, ip-PFNA, PFOS, PFDA, PFDS	L'Albufera de Valencia, Spain	Sediment	PFBS ≤ MLOD − 0.02 ng/g PFPeA ≤ MLOD − 0.02 ng/g PFHxA ≤ MLOQ − 0.10 ng/g PFHpA ≤ MLOQ − 0.95 ng/g PFOA = 0.03–10.9 ng/g	PFNA ≤ MLOD − 1.24 ng/g ip-PFNA ≤ MLOD − 1.52 ng/g PFOS = 0.10–4.80 ng/g PFDA ≤ MLOD − 1.25 ng/g PFDS ≤ MLOD − 2.00 ng/g	[108]
PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, FOSA, N-MeFOSA, N-EtFOSA	Twenty WWTPs from Spain (2006)	Sewage sludge	PFPeA ≤ 0.05–4.69 ng/g dw PFHxA ≤ 0.03–2.60 ng/g dw PFHpA ≤ 0.01–2.04 ng/g dw PFOA ≤ 0.03–7.94 ng/g dw	PFNA ≤ 0.01–10.23 ng/g dw PFDA ≤ 0.04–24.29 ng/g dw PFHxS ≤ 0.01–18.20 ng/g dw PFOS ≤ 0.01–286.81 ng/g dw	[34]
Other countries					
PFOA, PFNA, PFOS, PFDA, PFUnA, FOSA	Conasauga River, Altamaha River and streams and ponds of Dalton (Georgia, USA)	Surface river	PFOA = 2.6–1,280 ng/L PFNA = 0.6–456 ng/L PFOS = 0.2–368 ng/L	PFDA = 0.1–160 ng/L PFUdA = 0.1–117 ng/L FOSA = 10.7–420 ng/L	[118]

PFOS	Rivers: Tone, Arakawa, Tama (Tokyo, Japan)	Surface river water	PFOS = 0.5–58 ng/L		[61]
PFOS, PFOA, PFHpA, PFNA, PFDA, PFDoA, PFHxS	Rivers from Northern of China	Surface river water	PFOS ≤ MLOD − 31 ng/L PFOA = 0.43–82 ng/L PFHpA ≤ MLOD − 35 ng/L PFNA ≤ MLOD − 4.9 ng/L	PFDA ≤ MLOD − 5.7 ng/L PFDoA ≤ MLOD − 0.29 ng/L PFHxS ≤ MLOD − 5.8 ng/L	[120]
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFOS	Rhine river, Mohene river and tributaries, Ruhr area	Surface river, lake water and drinking water	*Rhine*: PFBA = 2–3 ng/L PFPeA = 2–42 ng/L PFHxA = 2–77 ng/L PFHpA = 2–11 ng/L PFOA = 2–48 ng/L PFBS = 2–46 ng/L PFOS = 2–26 ng/L *Ruhr area*: PFBA = 2–143 ng/L PFPeA = 2–1,638 ng/L PFHxA = 2–1,248 ng/L PFHpA = 25–148 ng/L PFOA = 9–3,640 ng/L PFBS = 3–71 ng/L PFOS = 5–193 ng/L	*Mohene river and tributaries*: PFBA = 9–200 ng/L PFPeA = 25–2,670 ng/L PFHxA = 73–3,040 ng/L PFHpA = 46–989 ng/L PFOA = 11–33,900 ng/L PFBS = 17–1,450 ng/L PFOS = 2–5,900 ng/L *Drinking water*: PFBA = 2–11 ng/L PFPeA = 3–77 ng/L PFHxA = 3–56 ng/L PFHpA = 2–23 ng/L PFOA = 2–519 ng/L PFBS = 3–20 ng/L PFOS = 3–22 ng/L	[38]
PFBS, PFHxS, PFHpS, PFOS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, FOSA, N-MeFOSA, N-EtFOSA	WWTPs from Hong Kong • Plants (A) and (B): secondary treatment by activated sludge method • Plant (C): chemically enhanced primary treatment (2008)	Sludge	PFBA = 3.1–111.4 ng/g PFPeA = 0.5–10.1 ng/g PFHxA = 0.3–27.8 ng/g PFHpA = 0.4–4 ng/g PFOA = 1.3–15.7 ng/g PFNA = 0.5–23 ng/g PFDA = 0.3–15.2 ng/g PFUnA = 0.4–7.8 ng/g PFDoA = 0.6–8.6 ng/g PFTrA = 0.2–19 ng/g	PFTeA = 0.2–46 ng/g FOSA = nd N-MeFOSA = nd N-EtFOSA = nd PFBS = 0.6–6.4 ng/g PFHxS = nd PFHpS = 106.6 ng/g (one sample) PFOS = 3.1–7304.9 ng/g PFDS = nd	[78]

(continued)

Table 2 (continued)

Analytes	Origin	Matrices	Results		Reference
PFPeA, PHxA, PFHpA, PFOA, PFNA, PFDoA, PFTeA, 6:2 FTUCA, 8:2 FTUCA, PFBS, PFHxS, PFOS, FOSA, N-MeFOSA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA	WWTPs from Zürich, Switzerland (2008)	Digested sewage sludge	∑PFCAs = 16.9–21.6 ng/g dw (PFOA = 5.0–9.1 ng/g dw) (PFOA > PFDoA > PFHxA > PFNA > PFHpA) PFOS = 117–670 ng/g dw 6:2 FTUCA = 2.1–3.4 ng/g dw 8:2 FTUCA = 5.4–14.8 ng/g dw FOSA = 2–5 ng/g dw		[74]
PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS	WWTPs from industrial zones in Thailand	Samples from: • Activated sludge • Sludge	*Activated sludge concentrations* PFPeA = 7.6–29.4 ng/L PFHxA = 0.5–79.4 ng/L PFHpA = 1.7–43.3 ng/L PFOA = 13.7–142.0 ng/L PFNA = 12.1–308.4 ng/L PFDA = 4.8–81.3 ng/L PFUnA = 11.9–338.2 ng/L PFDoA = 7.6–48.4 ng/L PFHxS = 26.8–27.5 ng/L PFOS = 348.7–672.9 ng/L	*Sludge concentrations* PFPeA = 2.9–3.3 ng/g PFHxA = 0.3–99.9 ng/g PFHpA = 1.6–52.6 ng/g PFOA = 11.3–136.0 ng/g PFNA = 5.1–512.8 ng/g PFDA = 3.8–327.7 ng/g PFUnA = 45.2–78.2 ng/g PFDoA = ND-310.6 ng/g PFHxS = 36.6–157.7 ng/g PFOS = 396.9–552.6 ng/g	[84]

4.1 Waste Water Treatment Plants

Wastewater treatment plants (WWTPs) are major sources of PFCs to the natural environment, through treated effluents and also when contaminated sludge is used in agricultural lands. The first work assessing the occurrence of PFCs in sewage sludge was performed by Higgins et al. [75] who studied the occurrence PFCs in sediments and sludge from WWTPs in San Francisco (1998–2004) [75]. Concentrations from 1.2 to 2,610 ng/g dw, were reported, being PFOS the compound at higher concentrations. Following this work, several works have been devoted to assess the content of PFCs in sewage sludge. PFOS is exceptionally stable chemical compound that is highly resistant to degradation and due to its higher partition coefficient in comparison with other PFCs, especially PFCAs, is present in high concentrations in sewage sludge worldwide. Furthermore, PFOS is the end-point of the degradation of fluorochemicals used in a variety of industrial and commercial applications. Compounds that may be transformed to PFOS are 2-(*N*-ethyl perfluorooctane sulphonamido) acetic acid (N-EtFOSAA) and 2-(*N*-methyl perfluorooctane sulphonamido) acetic acid (N-MeFOSAA), among others. These compounds have been also identified in general in WWTP sewage sludge at levels often exceeding PFOS. This could indicate that part of the PFOS is directly generated in the degradation process of related products.

Llorca et al. [35] investigated the presence of PFCs in sewage sludge from five WWTPs along the Llobregat River. The results showed that PFCs longer than 10 C chains were at lower ng/g concentration levels, or below. In general, the concentrations of perfluorocarboxylic acids were ranging from 0.4 to 30.3 ng/g. PFOA, PFNA, PFDA and PFDoA were present in all the samples at concentrations higher than 1.0 μg/kg. These high concentrations were in agreement with other works. For example, Zhang et al. [100], Guo et al. [101], Li et al. [55] or Ma et al. [102]. On the other hand, in most of the samples the long-chain acidic compounds were not detected and just PFOA was found to be in high amounts, but this concentration can be associated with the biodegradation of other long-chain congeners currently in use [103, 104]. This predominance of shorter C chains is supported by Ma et al. [78]. The authors found a dominance of even-chain length PFCAs in all of the WWTP sludge samples investigated. It is suggested that a strong aerobic degradation of fluorotelomer alcohols in WWTPs ends in shorter fluorinated compounds. In addition, developing substitute materials to replace long-chain PFCs, or new processes to eliminate their presence as impurities in other products, has been a significant technical challenge. There has been considerable progress in the development and introduction of substitutes and alternatives. Many substitutes are shorter-chain compounds that still provide the needed functionality, but lack the bioaccumulation potential of the long-chain PFCs. In this sense, considerable amounts of these products can also reach sludge of WWTP, partially contributing to these concentrations. In spite of the lack of data reporting the profile of PFCs present in sewage sludge during the past, available data seem to show a strong decrease in the presence of long-chain PFCs, and at the same time an

increase in short C-chain compounds. In the studies of Llorca et al. in the sewage sludge of WWTP discharging into the Llobregat River, FOSA was another of the more frequently found compounds, with concentrations ranging from 0.3 to 10.7 μg/kg. There was not found perfluorosulphonates at higher levels than MLOQ with an exception of PFOS, which was detected at concentrations ranging from 53 to 121 ng/g, being the compound that was present at higher levels, as it was expected. Picó et al. within the Framework of the SCARCE project also analysed sewage sludge from the WWTP of Igualada in the Anoia tributary of Llobregat and also found PFOS at concentration as high as 1,790 ng/g. Zhou et al. [30] reported the sorption of PFCs on the heterogeneous protein composition of activated sludge and the different sorption kinetics according to their carbon chain length and different functional groups [105], which could explain the high concentrations of PFOS found by Llorca et al. [35] and other authors. There is a general agreement among results in sewage sludge were the concentrations of PFOS is in general three to ten times higher than the concentrations of PFOA. This difference could be associated with the different sorption kinetics in function the different functional groups, in agreement with Zhou et al. [105].

The lack of total elimination of PFCs in wastewater treatments has been proved, and many works have reported high concentrations of PFCs in treated effluents, being therefore one of the main inputs to receiving waters.

PFCs have been studied in effluent water from Llobregat WWTP located in El Prat de Llobregat by Sanchez-Avila et al. [60]. The sampling point was located near to river surface water sampling point location which was also investigated by the same author. The WWTP effluent values were below 0.77 ng/L for PFBS, below 0.03 ng/L for PFHxS, 14.1 ng/L for PFOS, 61.9 ng/L for PFOA and below 0.06 ng/L for PFNA. Comparing the levels found in surface river water and in effluent water, the concentrations in this last one were higher. These results suggested that PFCs are discharged into the river through WWTPs effluents arriving to potable water treatment plants and, finally, to humans through tap water. However, the WWTPs processes redistribute some of the PFCs from influent water to sludge. The study realized by Zhou et al. [30] showed the favourable sorption of PFCs on the heterogeneous protein composition of activated sludge which could be explain the highest levels found by Llorca et al. [35] in WWTPs from Llobregat River. Zhou et al., in another published work, studied the different sorption kinetics in function of carbon chain length and different functional groups [105]. The calculated distribution coefficients indicate that PFOS had a higher sorption tendency to activated sludge than PFOA. Becker et al. [106] studies supported this last result. The authors showed that, in WWTP, the calculated mass flow of PFOA was fully discharged into the river while about half of PFOS was retained in the sewage sludge. The study carried out by Pico et al. in the WWTP of Anoia also showed that PFOS was accumulated in the sludge whereas PFCAs including PFHpA, PFOA, PFNA and PFDA were mostly in water.

4.2 Surface Waters

In general, concentration gradients can vary up to several orders of magnitude between different areas along the same river or lake, reflecting in general proximity to known industrial sources and WWTPs concentrated near populated regions. For example, different Japanese works found PFOS and PFOA in surface river samples with concentrations in the range from 0.30 to 157 ng/L for PFOS, or between 1.6 and 104 ng/L also for PFOS and 3.8–311 ng/L for PFOA [65]. The study carried out by Skutlared et al. [38] in the Ruhr River in Europe should be mentioned. In this study the occurrence of 12 PFCs was assessed including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS and PFOS. The results showed extremely high concentrations of some compounds. PFOA was present at concentrations till 33,900 ng/L in the Moehne River, and the authors found the main source of contamination in an agricultural area near Brilon-Scharfenberg. In addition, it was proved that this source of contamination leads to the consecutive pollution of Lake Moehn, the Ruhr River and corresponding drinking waters. In another example in China Wang et al. [107] studied the environment around a manufacturing facility. The authors also observed a decreasing trend of the PFOS, PFOA and PFHxS concentrations in soils, water and chicken eggs with the increased distance to the production factory, indicating the production site to be the primary source of PFCs in the region.

Regarding the occurrence of PFCs in the Llobregat River, very few works have assessed the content of PFCs. In 2009 Sanchez-Avila et al. [60] investigated the levels of PFBS, PFHxS, PFOS, PFOA, PFNA, in surface waters from Catalonia, including a sample from an industrialized area of the Llobregat River. In this sampling site, PFOS and PFOA were the compounds found at higher concentrations, but should be mentioned that all the compounds investigated were also found at quantifiable concentrations: 0.88 ng/L for PFBS, 0.64 ng/L for PFHxS, 9.13 ng/L for PFOS, 9.63 ng/L for PFOA and 1.62 ng/L for PFNA. The concentration levels reported in this study were comparable with the data reported for other river waters from industrialized areas. However, the profile of compounds was quite different than the one found in other European countries, such as Germany, where the occurrence of PFOA in surface water is generally found in higher concentrations than PFOS.

Recently, under the frame of the SCARCE project Picó et al. have investigated the presence of 21 PFCs in different sampling sites along the Llobregat River during 2 sampling campaigns. In this case, PFOA was one of the more frequently found compounds. However, PFOS was found at higher concentrations up to 2.7 μg/L. The presence of these compounds showed an important spatial distribution. In agreement with data reported in other European rivers. However, the Llobregat River is affected in a great manner by climate episodes, such as flows, which can re suspends contaminants in general contained in the sediments. The higher concentrations were found near the mouth as it was expected, because it corresponds to a heavily populated and industrialized area. The compound found in

higher concentration was PFHpA with concentrations around 30 ng/L in more polluted samples. In general, more frequent compounds and also those in higher concentration were short-chain compounds, indicating a tendency to replace more persistent long-chain PFCs by new short-chain ones.

4.3 Sediments

There are few available data reporting the levels of PFCs in sediment samples from Llobregat River basin within the SCARCE project. Different PFCAs including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA and PFDoA were detected in sediment samples but at concentrations up to 7.5 ng/g. Although the number of PFSAs is restricted to PFBS and PFOS, they reach concentrations up to 11 ng/g. However, other related works indicated that these compounds are distributed between the two compartments, water and sediment. An example was published by Picó et al. [108]. The authors investigated different points from l'Albufera de Valencia (Spain) assessing the presence of PFCs between MLOD and 10.9 ng/g where the highest values corresponded to PFOA and PFOS. In the same study, the levels of PFCs in surface waters were assessed showing the distribution of these compounds between water and sediments. Another study performed by Gómez et al. [59] focused the investigation on the analysis of different sediments from Cantabrian Sea samples (North of Spain). The results of PFCs were in most of the cases below MLOD in sediment river samples.

4.4 Drinking Water

In order to elucidate the possible source of PFCs in drinking water, some authors have compared the levels found in the catchment sites in surface river or lakes and in tap water, and it was showed that certain relations can be established. This reveals the ineffective removal of PFCs by the purification processes performed at water purification plants [38, 109]. For example, Skutlarek et al. [38] showed extremely high concentrations for PFOA in tap water in the zone of Ruhr area, which is in agreement with the concentrations found in environmental surface waters of the same areas. In another example PFOS and PFOA were measured at concentration levels around 9 and 3 ng/L, respectively, in The Lake Maggiore (Switzerland), and the results of the analysis of drinking water produced from the lake gave almost identical results revealing the poor performance of sand filtration and chlorination which is applied by the local waterworks [109].

Similar conclusion can be extracted from the work carried out by Takagi et al. [110], who studied the presence of PFCs in different waters including raw water and drinking water from Japan. In raw water the results for PFOS and PFOA were between 0.26–22 ng/L and 5.2–92 ng/L, respectively, and in tap water similar

results were also obtained in the ranges between 0.16–22 ng/L and 2.3–84 ng/L for PFOS and PFOA, respectively. In addition, other PFCs that in general are not assessed and that are generated during the water treatment processes should be considered [48, 103, 111, 112].

Regarding the study of the Llobregat River, the occurrence of PFCs in drinking water produced from Llobregat River has been assessed by Llorca et al. under the frame of the SCARCE project. Among the 21 compounds considered in this study, the presence of PFBA, PFPeA, PFOA, PFNA, PFBS, PFHxS and PFOS has been found in final drinking water at concentrations between 0.07 and 35 ng/L. The more polluted drinking waters were those corresponding to catchment locations in more industrialized and polluted areas, such as Barcelona city, as it was expected.

These results were in agreement with a previous work carried out by Ericson et al. [39, 57] who studied the presence of these contaminants in drinking water from different areas of Catalonia. In the study performed by Ericson et al., the concentrations of PFCs were in the range between 0.02 and 69 ng/L in tap waters.

5 Future Trends

In recent years, the research has been focused on the study of degradation mechanisms of fluorochemicals as PFOA and PFOS. Cheng et al. found that sonolysis (sonochemical) is able to decompose PFOS and PFOA present in groundwater beneath a landfill following a pseudo first-order rate constant [113].

Because of the poor degradability of these ones in the treatment facilities, these compounds are discharged directly into the rivers. Once these recalcitrant compounds reach the environment, they can arrive to the drinking water through the drinking water prepared from surface water [114] or enter into food chain through the irrigation of agricultural lands with contaminated waters [115] or by the bioaccumulation, and consequent biomagnification, through the food chain [3]. The study of these compounds in river waters as well in flora and fauna is of high importance since they are not regulated and should be under control in order to elucidate possible focuses of PFCs into, for example, the Llobregat River [116].

Acknowledgement This work was funded by the project "Assessing and predicting effects on water quantity and quality in Iberian Rivers caused by global change" SCARCE (CSD-2009-00065).

References

1. Prevedouros K (2006) Sources, fate and transport of perfluorocarboxylates. Environ Sci Technol 40(1):32–44
2. Kantiani L (2010) Emerging food contaminants: a review. Anal Bioanal Chem 398(6): 2413–2427

3. Pico Y Perfluorinated compounds in food: a global perspective. Crit Rev Food Sci Nutr 51:605–625
4. Shoeib M, Harner T, Vlahos P (2006) Perfluorinated chemicals in the arctic atmosphere. Environ Sci Technol 40(24):7577–7583
5. Wania F (2007) A global mass balance analysis of the source of perfluorocarboxylic acids in the Arctic Ocean. Environ Sci Technol 41(13):4529–4535
6. Sonne C (2010) Health effects from long-range transported contaminants in Arctic top predators: an integrated review based on studies of polar bears and relevant model species. Environ Int 36(5):461–491
7. Martin JW (2004) Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. Environ Sci Technol 38(2):373–380
8. Stemmler I, Lammel G (2010) Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources. Atmos Chem Phys 10(20):9965–9980
9. Butt CM (2010) Levels and trends of poly- and perfluorinated compounds in the arctic environment. Sci Total Environ 408(15):2936–2965
10. Schiavone A (2009) Perfluorinated contaminants in fur seal pups and penguin eggs from South Shetland, Antarctica. Sci Total Environ 407(12):3899–3904
11. Tao L (2006) Perfluorooctanesulfonate and related fluorochemicals in albatrosses, elephant seals, penguins, and polar skuas from the southern ocean. Environ Sci Technol 40(24):7642–7648
12. Kubwabo C, Vais N, Benoit FM (2004) A pilot study on the determination of perfluorooctanesulfonate and other perfluorinated compounds in blood of Canadians. J Environ Monit 6(6): 540–545
13. Ericson I (2007) Perfluorinated chemicals in blood of residents in Catalonia (Spain) in relation to age and gender: a pilot study. Environ Int 33(5):616–623
14. Kärrman A (2009) Biomonitoring perfluorinated compounds in Catalonia, Spain: concentrations and trends in human liver and milk samples. Environ Sci Pollut Res 1–9
15. Tao L (2008) Perfluorinated compounds in human breast milk from several Asian countries, and in infant formula and dairy milk from the United States. Environ Sci Technol 42 (22):8597–8602
16. Llorca M (2010) Infant exposure of perfluorinated compounds: levels in breast milk and commercial baby food. Environ Int 36(6):584–592
17. So MK (2006) Health risks in infants associated with exposure to perfluorinated compounds in human breast milk from Zhoushan, China. Environ Sci Technol 40(9):2924–2929
18. Inoue K (2004) Perfluorooctane sulfonate (PFOS) and related perfluorinated compounds in human maternal and cord blood samples: assessment of PFOS exposure in a susceptible population during pregnancy. Environ Health Perspect 112(11):1204–1207
19. Monroy R (2008) Serum levels of perfluoroalkyl compounds in human maternal and umbilical cord blood samples. Environ Res 108(1):56–62
20. Carabias-Martínez R (2005) Pressurized liquid extraction in the analysis of food and biological samples. J Chromatogr A 1089(1/2):1–17
21. EFSA (2008) Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts Scientific Opinion of the Panel on Contaminants in the Food chain. EFSA Guidelines 653:2–131
22. Ericson I (2008) Human exposure to perfluorinated chemicals through the diet: intake of perfluorinated compounds in foods from the Catalan (Spain) market. J Agric Food Chem 56(5): 1787–1794
23. Lacina O (2011) Simple, high throughput ultra-high performance liquid chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish. J Chromatogr A 1218(28):4312–4321

24. Committee on Toxicity of Chemicals in Food Environment (2006) COT statement on the tolerable daily intake for perfluorooctane sulfonate. Available on line at http://www.food.gov.uk/multimedia/pdfs/cotstatementpfos200609.pdf
25. Committee on Toxicity of Chemicals in Food, C.P.a.t.E. (2006) COT statement on the tolerable daily intake for perfluorooctanoic acid. Available on line at http://www.food.gov.uk/multimedia/pdfs/cotstatementpfoa200610.pdf
26. Commission decision of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Off J Eur Union L221/8
27. USEPA (2006) 2010/15 Stewardship Program. Environmental Protection Agency. Available on line at http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html
28. UNEP (2010) New POPs SC-4/17: listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. In: United Nations Environment Programme: Stockholm Convention on Persistent Organic Pollutants (POPs). Geneva, Switzerland
29. European Union Directive 2008/105/EC on the environmental quality standards in the field of water policy, amending and repealing Council Directives: 82/176/EEC, 83/513/EEC, 84/156/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and Council-348/84, Brussels, 2008
30. Zhou Q (2010) Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated sludge. Chemosphere 81(4):453–458
31. Rayne S, Forest K (2009) Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. J Environ Sci Health A Tox Hazard Subst Environ Eng 44(12):1145–1199
32. Ruan T (2010) Presence and partitioning behavior of polyfluorinated iodine alkanes in environmental matrices around a fluorochemical manufacturing plant: another possible source for perfluorinated carboxylic acids? Environ Sci Technol 44(15):5755–5761
33. Yoo H (2011) Quantitative determination of perfluorochemicals and fluorotelomer alcohols in plants from biosolid-amended fields using LC/MS/MS and GC/MS. Environ Sci Technol 45:7985–7990
34. Navarro I, Sanz P, Martínez MÁ (2011) Analysis of perfluorinated alkyl substances in Spanish sewage sludge by liquid chromatography-tandem mass spectrometry. Anal Bioanal Chem 400(5):1277–1286
35. Llorca M (2011) Analysis of perfluorinated compounds in sewage sludge by pressurized solvent extraction followed by liquid chromatography-mass spectrometry. J Chromatogr A 1218(30):4840–4846
36. Clarke BO, Smith SR (2011) Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. Environ Int 37(1):226–247
37. Gottschall N (2010) Polybrominated diphenyl ethers, perfluorinated alkylated substances, and metals in tile drainage and groundwater following applications of municipal biosolids to agricultural fields. Sci Total Environ 408(4):873–883
38. Skutlarek D, Exner M, Färber H (2006) Perfluorinated surfactants in surface and drinking waters. Environ Sci Pollut Res 13(5):299–307
39. Ericson I (2008) Levels of perfluorochemicals in water samples from Catalonia, Spain: is drinking water a significant contribution to human exposure? Environ Sci Pollut Res 15(7):614–619
40. USEPA (2009) Provisional Health Advisories (PHA) for PFOA and PFOS. Environmental Protection Agency. Available on line at http://www.epa.gov/oppt/pfoa/pubs/pfoainfo.html
41. Martin JW (2004) Analytical challenges hamper perfluoroalkyl research. Environ Sci Technol 38(13):248A–255A
42. Sinclair E, Mayack DT, Roblee K, Yamashita N, Kannan K (2006) Arch Environ Contam Toxicol 50:398–410

43. Guo R, Sim W-J, Lee E-S, Lee J-H, Oh J-E (2010) Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants. Water Res 44:3476–3486
44. Yu J, Hu J, Tanaka S, Fujii S (2009) Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Res 43:2399–2408
45. Hu J, Yu J (2010) An LC-MS-MS method for the determination of perfluorinated surfactants in environmental matrices. Chromatographia 72:411–416
46. Sun H (2011) Long-chain perfluorinated chemicals in digested sewage sludges in Switzerland. Environ Pollut 159(2):654–662
47. Loveless SE (2006) Comparative responses of rats and mice exposed to linear/branched, linear, or branched ammonium perfluorooctanoate (APFO). Toxicology 220(2–3):203–217
48. Frömel T, Knepper TP (2010) Fluorotelomer ethoxylates: sources of highly fluorinated environmental contaminants. Part I: biotransformation. Chemosphere 80(11):1387–1392
49. Holm A (2004) Determination of perfluorooctane sulfonate and perfluorooctanoic acid in human plasma by large volume injection capillary column switching liquid chromatography coupled to electrospray ionization mass spectrometry. J Sep Sci 27(13):1071–1079
50. Kärrman A (2006) Perfluorinated chemicals in relation to other persistent organic pollutants in human blood. Chemosphere 64(9):1582–1591
51. Liu J, Lee LS (2005) Solubility and sorption by soils of 8:2 fluorotelomer alcohol in water and cosolvent systems. Environ Sci Technol 39(19):7535–7540
52. Guo R, Zhou Q, Cai Y, Jiang G (2008) Determination of perfluorooctanesulfonate and perfluorooctanoic acid in sewage sludge samples using liquid chromatography/quadrupole time-of-flight mass spectrometry. Talanta 75:1394–1399
53. Szostek B, Prickett KB, Buck RC (2006) Determination of fluorotelomer alcohols by liquid chromatography/tandem mass spectrometry in water. Rapid Commun Mass Spectrom 20(19): 2837–2844
54. Schultz MM, Barofsky DF, Field JA (2006) quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry characterization of municipal wastewaters. Environ Sci Technol 40(1):289–295
55. Li F (2010) Quantitative characterization of short- and long-chain perfluorinated acids in solid matrices in Shanghai, China. Sci Total Environ 408(3):617–623
56. Bossi R (2008) Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. Environ Int 34(4):443–450
57. Ericson I, Domingo J, Nadal M, Bigas E, Llebaria X, van Bavel B, Lindström G (2009) Levels of perfluorinated chemicals in municipal drinking water from Catalonia, Spain: public health implications. Arch Environ Contam Toxicol 57(4):631–638
58. D'Eon JC (2009) Perfluorinated phosphonic acids in Canadian surface waters and wastewater treatment plant effluent: discovery of a new class of perfluorinated acids. Environ Toxicol Chem 28(10):2101–2107
59. Gómez C (2011) Occurrence of perfluorinated compounds in water, sediment and mussels from the Cantabrian Sea (North Spain). Mar Pollut Bull 62(5):948–955
60. Sánchez-Avila J, Meyer J, Lacorte S (2010) Spatial distribution and sources of perfluorochemicals in the NW Mediterranean coastal waters (Catalonia, Spain). Environ Pollut 158(9): 2833–2840
61. Takazawa Y (2009) Occurrence and distribution of perfluorooctane sulfonate and perfluorooctanoic acid in the rivers of Tokyo. Water Air Soil Pollut 202(1–4):57–67
62. Villagrasa M, López De Alda M, Barcelo D (2006) Environmental analysis of fluorinated alkyl substances by liquid chromatography–(tandem) mass spectrometry: a review. Anal Bioanal Chem 386(4):953–972
63. Suja F, Pramanik BK, Zain SM (2009) Contamination, bioaccumulation and toxic effects of perfluorinated chemicals (PFCs) in the water environment: a review paper. Water Sci Technol 60:1533–1554
64. Taniyasu S (2003) A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. Environ Sci Technol 37(12):2634–2639

65. Saito N (2003) Perfluorooctane sulfonate concentrations in surface water in Japan. Arch Environ Contam Toxicol 45(2):149–158
66. Yamashita N (2004) Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. Environ Sci Technol 38(21):5522–5528
67. Taniyasu S (2005) Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. J Chromatogr A 1093(1–2):89–97
68. Dasu K (2010) Hydrolysis of fluorotelomer compounds leading to fluorotelomer alcohol production during solvent extractions of soils. Chemosphere 81(7):911–917
69. Hansen KJ (2001) Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. Environ Sci Technol 35(4):766–770
70. Giesy JP, Kannan K (2001) Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 35(7):1339–1342
71. Yeung LWY (2009) A survey of perfluorinated compounds in surface water and biota including dolphins from the Ganges River and in other waterbodies in India. Chemosphere 76(1):55–62
72. Guruge KS (2008) Species-specific concentrations of perfluoroalkyl contaminants in farm and pet animals in Japan. Chemosphere 73(Suppl 1):S210–S215
73. Crozier P, Furdui V, Reiner E, Libelo EL, Mabury S (2009) Observation of a commercial fluorinated material, the polyfluoroalkyl phosphoric acid diesters, in human sera, wastewater treatment plant sludge, and paper fibers. Environ Sci Technol 43:4589–4594
74. Zhang T, Sun H, Gerecke AC, Kannan K, Müller CE, Alder AC (2010) Comparison of two extraction methods for the analysis of per- and polyfluorinated chemicals in digested sewage sludge. J Chromatogr A 1217:5026–5034
75. Higgins CP (2005) Quantitative determination of perfluorochemicals in sediments and domestic sludge. Environ Sci Technol 39(11):3946–3956
76. Loganathan BG (2007) Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res 41(20):4611–4620
77. Yoo H, Washington JW, Jenkins TM (2009) Analysis of perfluorinated chemicals in sludge: method development and initial results. J Chromatogr A 1216:7831–7839
78. Ma R, Shih K (2010) Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong. Environ Pollut 158:1354–1362
79. Powley CR (2005) Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. Anal Chem 77(19):6353–6358
80. Rhoads KR (2008) Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. Environ Sci Technol 42(8):2873–2878
81. Sun H, Gerecke AC, Giger W, Alder AC (2011) Long-chain perfluorinated chemicals in digested sewage sludges in Switzerland. Environ Pollut 159(2):654–662
82. Liu J, Wang N, Buck RC, Wolstenholme BW, Folsom PW, Sulecki LM, Bellin CA (2010) Aerobic biodegradation of [14C] 6:2 fluorotelomer alcohol in a flow-through soil incubation system. Chemosphere 80:716–723
83. Schröder HF (2003) Determination of fluorinated surfactants and their metabolites in sewage sludge samples by liquid chromatography with mass spectrometry and tandem mass spectrometry after pressurised liquid extraction and separation on fluorine-modified reversed-phase sorbents. J Chromatogr A 1020(1):131–151
84. Kunacheva C (2011) Mass flows of perfluorinated compounds (PFCs) in central wastewater treatment plants of industrial zones in Thailand. Chemosphere 83(6):737–744
85. Kuklenyik Z (2004) Automated solid-phase extraction and measurement of perfluorinated organic acids and amides in human serum and milk. Environ Sci Technol 38(13):3698–3704
86. Calafat AM (2006) Perfluorochemicals in pooled serum samples from United States residents in 2001 and 2002. Environ Sci Technol 40(7):2128–2134
87. Taniyasu S (2008) Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (C5–C18). Anal Chim Acta 619(2):221–230

88. Shivakoti BR (2010) Occurrences and behavior of perfluorinated compounds (PFCs) in several wastewater treatment plants (WWTPs) in Japan and Thailand. J Environ Monit 12(6):1255–1264
89. Berger U, Haukås M (2005) Validation of a screening method based on liquid chromatography coupled to high-resolution mass spectrometry for analysis of perfluoroalkylated substances in biota. J Chromatogr A 1081(2):210–217
90. Llorca M (2010) Study of the performance of three LC-MS/MS platforms for analysis of perfluorinated compounds. Anal Bioanal Chem 398(3):1145–1159
91. Yamashita N (2005) A global survey of perfluorinated acids in oceans. Mar Pollut Bull 51 (8–12):658–668
92. Lohmann R (2007) Global fate of POPs: current and future research directions. Environ Pollut 150(1):150–165
93. Bengtson Nash S (2010) Perfluorinated compounds in the Antarctic region: ocean circulation provides prolonged protection from distant sources. Environ Pollut 158(9):2985–2991
94. Wallington TJ (2006) Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8:2 fluorotelomer alcohol. Environ Sci Technol 40(3):924–930
95. Yamashita N (2008) Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70(7):1247–1255
96. Ahrens L (2010) Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. Mar Pollut Bull 60(2):255–260
97. Armitage J (2006) Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. Environ Sci Technol 40(22):6969–6975
98. Ellis DA (2003) Atmospheric lifetime of fluorotelomer alcohols. Environ Sci Technol 37(17):3816–3820
99. D'Eon JC, Mabury SA (2007) Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): exploring routes of human contamination. Environ Sci Technol 41(13):4799–4805
100. Zhang T (2010) Comparison of two extraction methods for the analysis of per- and polyfluorinated chemicals in digested sewage sludge. J Chromatogr A 1217(31):5026–5034
101. Guo R (2010) Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants. Water Res 44(11):3476–3486
102. Ma R, Shih K (2010) Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong. Environ Pollut 158(5):1354–1362
103. Lee H, Deon J, Mabury SA (2010) Biodegradation of polyfluoroalkyl phosphates as a source of perfluorinated acids to the environment. Environ Sci Technol 44(9):3305–3310
104. Frömel T, Knepper TP (2010) Biodegradation of fluorinated alkyl substances. Rev Environ Contam Toxicol 208:161–177
105. Zhou P (2009) Fluorine bonding – how does it work in protein-ligand interactions? J Chem Inf Model 49(10):2344–2355
106. Becker AM (2010) Perfluorooctanoic acid and perfluorooctane sulfonate released from a waste water treatment plant in Bavaria, Germany. Environ Sci Pollut Res 17(9):1502–1507
107. Wang Y (2010) Distribution of perfluorooctane sulfonate and other perfluorochemicals in the ambient environment around a manufacturing facility in china. Environ Sci Technol 44(21):8062–8067
108. Pico Y (2011) Occurrence of perfluorinated compounds in water and sediment of L'Albufera Natural Park (València, Spain). Environ Sci Pollut Res 1–12.
109. Loos R, Wollgast J, Huber T, Hanke G (2007) Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy. Anal Bioanal Chem 387(4):1469–1478

110. Takagi S, Adachi F, Miyano K, Koizumi Y, Tanaka H, Mimura M, Watanabe I, Tanabe S, Kannan K (2008) Perfluorooctanesulfonate and perfluorooctanoate in raw and treated tap water from Osaka, Japan. Chemosphere 72(10):1409–1412
111. Dinglasan MJA (2004) Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. Environ Sci Technol 38(10):2857–2864
112. Wang N (2005) Fluorotelomer alcohol biodegradation – direct evidence that perfluorinated carbon chains breakdown. Environ Sci Technol 39(19):7516–7528
113. Cheng J (2008) Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in landfill groundwater: environmental matrix effects. Environ Sci Technol 42(21):8057–8063
114. Houtman CJ (2011) Emerging contaminants in surface waters and their relevance for the production of drinking water in Europe. J Integr Environ Sci 7(4):271–295
115. Ferré-Huguet N (2008) Assessment of metals from consuming vegetables, fruits and rice grown on soils irrigated with waters of the Ebro River in Catalonia, Spain. Biol Trace Elem Res 123(1):66–79
116. Petrovic M (2011) Combined scenarios of chemical and ecological quality under water scarcity in Mediterranean rivers. Trends Anal Chem 30(8):1269–1278
117. Scott BF (2006) Analysis for perfluorocarboxylic acids/anions in surface waters and precipitation using GC-MS and analysis of PFOA from large-volume samples. Environ Sci Technol 40(20):6405–6410
118. Konwick BJ (2008) Concentrations and patterns of perfluoroalkyl acids in Georgia, USA surface waters near and distant to a major use source. Environ Toxicol Chem 27(10): 2011–2018
119. Saez M, De Voogt P, Parsons JR (2008) Persistence of perfluoroalkylated substances in closed bottle tests with municipal sewage sludge. Environ Sci Pollut Res 15(6):472–477
120. Wang T (2011) Perfluorinated compounds in surface waters from Northern China: comparison to level of industrialization. Environ Int