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Analysis of zwitterionic, cationic, and anionic poly- and perfluoroalkyl surfactants in sediments by liquid chromatography polarity-switching electrospray ionization coupled to high resolution mass spectrometry

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ABSTRACT

A new analytical method is proposed for the determination of a wide span of fluoroalkylated surfactants (PFASs) of various chain lengths and polarities in sediments, including newly-identified compounds such as zwitterionic and cationic PFASs. Extraction conditions were optimized so as to maintain a common preparation procedure for all analytes (recovery range: 60–110 %). Instrumental analysis was performed with ultra-high performance liquid chromatography coupled to Orbitrap mass spectrometry through polarity-switching electrospray ionization. Calibration curves with excellent coefficients of determination (R^2 > 0.994) were generally obtained over 0.002–10 ng g^{-1} dry weight (dw) and limits of detection were in the range 0.0006–0.46 ng g^{-1} dw. Intra-day precision remained < 9 % and inter-day precision < 23 %. While perfluorooctane sulfonate (PFOS) generally prevailed over other perfluoroalkyl acids (PFAAs) in sediments from mainland France, fluorotelomer sulfonamide amines and fluorotelomer sulfonamide betaines were also ubiquitous in these samples, especially in the vicinity of airports wherein firefighting training activities may occur on a regular basis.

Novelty statement:

Anionic, zwitterionic and cationic PFASs were investigated in sediments from France showing the prevalence of fluorotelomer sulfonamide amines and betaines.

KEYWORDS

Aqueous Film Forming Foams (AFFFs) – Sediments – Zwitterionic and Cationic Fluorosurfactants – Fluorotelomer sulfonamide amines – Fluorotelomer sulfonamide betaines – Optimization

1. INTRODUCTION

Poly- and perfluoroalkyl compounds (PFASs) are strategic chemicals that have been manufactured and used for decades due to their unique surfactant properties (Buck et al., 2011; Krafft and Riess, 2015). Since the first landmark papers suggested their environmental persistence, potential adverse effects and global dissemination (Moody and Field, 1999; Giesy and Kannan, 2001; Renner, 2001), PFASs have garnered considerable attention from the science community, especially medium- to long-chain perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs) due to their bioaccumulation and biomagnification potential (Martin et al., 2004; Tomy et al., 2004; de Vos et al., 2008; Houde et al., 2011).

Heedful of these issues, the United Nations Environmental Program appended the Stockholm Convention in 2009 to include perfluorooctane sulfonate (PFOS) under the list of persistent organic pollutants. The emissions of PFOS are now believed to be on the decline amid increasingly stringent regulations and use restrictions. However, PFOS production is still in effect, for instance in China, and a number of specific sectors (e.g. hydraulic fluids for aircrafts) benefit from derogations due to exemptions from the article restriction under REACH Annex XVII and listed accepted purposes in the Stockholm Convention. Major manufacturers in the world have also committed to the voluntary phase-out of perfluorooctanoate (PFOA) by 2015 (2010/2015 PFOA Stewardship Program). It has been recently suggested that long-chain PFCAs and PFSAs may be increasingly shunted towards the production of shorter-chain homologues (e.g., C_6-based) (Ahrens and Bundschuh, 2014; Sheringer et al., 2014), hence the relatively high occurrence and levels that have sometimes been observed for the latter in surface waters (Ahrens et al., 2009; Möller et al., 2010; Munoz et al., 2015a; Valsecchi et al., 2015). Although these compounds may readily reach groundwater ecosystems due to their higher mobility (Eschauzier et al., 2013; Vierke et al., 2014; Lopez et al., 2015), they are not expected to show as much bioaccumulation potential as their longer-chain homologues.

However, recent observations suggest that the commonly monitored PFSAs and PFCAs only partially reflect the total organic fluorine compounds that can be found in environmental samples (Yeung et al., 2009; Loi et al., 2011; Houtz and Sedlak, 2012; Yeung et al., 2013). For years, the less bioaccumulative fluorotelomer sulfonates (FTSAs) have been used in aqueous film forming foam (AFFF) formulations, leading to elevated levels in groundwater or surface water at specific monitoring sites (e.g., Schultz et al., 2004; Ahrens et al., 2015). In addition, newly-identified PFASs include, but are not limited to, polyfluoroalkyl sulfates (Liu et al., 2015), cyclic perfluoroalkyl sulfonates (De Silva et al., 2011), perfluoroalkyl phosphonic acids (D'eon et al., 2009), perfluoroalkylsulfonamide phosphate diesters (Benskin et al., 2012), short-chain perfluoroalkyl sulfonamides (Houtz et al., 2013; McGuire et al., 2014), hydro- or chlorine-substituted perfluoroalkyl carboxylates (Liu et al., 2015), chlorine-substituted perfluoroalkyl sulfonates (Rotander et al., 2015), and chlorine-substituted fluorotelomer ether sulfonates (Ruan et al., 2015). The advent of unknown compound elucidation through high resolution mass spectrometry recently paved the way for the identification of a variety of zwitterionic and cationic PFASs (Place and Field, 2012; D'Agostino and Mabury, 2014). Although there is still limited data on the environmental occurrence, fate and effects of PFAS alternatives (Ahrens and Bundschuh, 2014; Hoke et al., 2015; Wang et al., 2015), it has been hypothesized that substitutes containing perfluoroalkyl or polyfluoroalkyl moieties may eventually degrade to recalcitrant forms such as PFCAs and PFSAs (Liu et al., 2010; Wang et al., 2011; Liu and Mejia Avendaño, 2013; Mejia Avendaño and Liu, 2015).

To date, only a few papers have reported on the analysis of cationic or amphoteric PFASs in firefighting foam formulations (Place and Field, 2012; D'Agostino and Mabury, 2014), groundwater (Backe et al., 2013), or soils (Moe et al., 2012). One can readily infer that developing a single analytical procedure that can encompass a wide span of PFASs of various chain lengths and different polarities is an essential and delicate task, especially for complex matrices such as sediments. Another obvious pitfall lies in the current lack of available native and isotope-labelled standards for cationic and zwitterionic PFASs, making it challenging to estimate their concentration in environmental samples.

The transfer of PFASs from sediments to aquatic biota is of particular concern, especially for benthic fish or invertebrates that dwell on it (Martin et al., 2004; Bertin et al., 2014). It is therefore essential to document the occurrence and levels of PFASs in sediments, which may subsequently be used to predict the concentration of PFASs in aquatic biota. In this context, a new analytical procedure was developed to investigate the environmental occurrence of a wide spectrum of PFASs in sediment samples. A total of 30 model PFASs were selected for optimization and validation purposes, including 23 legacy PFASs and 7 novel cationic or zwitterionic PFASs. Instrumental analysis was conducted by ultra-high performance liquid chromatography coupled to a Q-Exactive Orbitrap mass spectrometer through a polarity-switching electrospray ionization source, allowing acquisition of all analytes in a single run. The extraction step was also optimized to maintain a common preparation procedure for all PFAS analytes. Method validation included assessment of blank contamination, linearity, detection limits, matrix effects, recovery, accuracy and precision. The newly developed method was subsequently applied to a selection of 12 riverine and lake sediment samples collected at large spatial scale through mainland France (Munoz et al., 2015a). In addition to the 30 PFASs initially used for method optimization and validation, samples were screened for more than 60 infrequently reported PFASs of various chemistries (i.e. chain lengths and functional groups) and contrasted polarities. In particular, the suspect list included zwitterionic and cationic PFASs that have been recently identified in AFFF formulations (Place and Field, 2012; D'Agostino and Mabury, 2014). To the knowledge of the authors, this is the first study to report on the environmental occurrence of cationic and zwitterionic fluorosurfactants in riverine sediments.

2. EXPERIMENTAL

2.1. Chemicals and Materials

19 native anionic and neutral PFASs were purchased from Wellington Laboratories (Ontario, Canada) and had chemical purities > 98 %; PFAC-MXB contained a mixture of 17 PFASs at 2 µg mL^{-1} in MeOH (for PFSAs, 2 µg mL^{-1} as the salt), including C_4–C_{18} PFCAs and C_4–C_{10} PFSAs; perfluorooctane sulfonamide (FOSA) and sodium 1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FTSA) were purchased separately and were at 50 and 47.4 µg mL^{-1} in MeOH, respectively. Standards of fluorotelomer unsaturated acids (6:2 FTUA, 8:2 FTUA) as well as fluorotelomer carboxylic acids (5:3 FTCA, 7:3 FTCA) were donated by DuPont USA (Wilmington, DE, USA). Isotope-labelled internal standards (IS) were purchased from Wellington Labs (Ontario, Canada) and had chemical purities > 98 % and isotopic purities > 99 % per ^{13}C or > 94 % per ^{18}O. MPFAC-MXB contained 9 IS at 2 µg mL^{-1} in MeOH (for PFSAs, 2 µg mL^{-1} as the salt). Details on analyte name, chemical formula, theoretical and measured exact mass, and corresponding IS are given in the Supporting Information (SI) (**Table S1**).

HPLC-water, HPLC-water containing 0.1 % formic acid (HCOOH), methanol (MeOH), and acetonitrile (ACN) were obtained from Fisher Scientific (Whitby, ON, Canada), as was ammonium hydroxide (NH_4OH, purity 28–30 % in water). Sodium hydroxide (NaOH, purity > 97 %) and HCOOH (purity > 95 %) were from Sigma-Aldrich (St. Louis, MO, USA). Nitrogen (N_2) (purity 99.998 %) was from MEGS Inc. (St-Laurent, QC, Canada). Supelclean ENVI-Carb cartridges (250 mg/6 mL) were obtained from Supelco (Bellefonte, PA, USA).

2.2. Synthesis and Characterization of Model Zwitterionic and Cationic Compounds

Seven model cationic or zwitterionic perfluoroalkyl compounds were custom-synthesized at the Surfactant Institute at Peking University (China) for method optimization and validation purposes, and were all provided at 2 μg mL^{-1} in MeOH (**Fig.1**). Chemical purities (based on NMR data) were > 98 % for perfluorooctaneamido ammonium salt (PFOAAmS, CAS# 335-90-0) and perfluorooctanesulfonamido ammonium salt (PFOSAmS, CAS# 1652-63-7), > 97 % for perfluorooctanesulfonamido amine oxide (PFOSNO, CAS# 30295-51-3), > 96 % for perfluorooctaneamido amine oxide (PFOANO, CAS# 30295-53-5) and perfluorooctanesulfonamide amine (PFOSAm, CAS# 13417-01-1), and > 95 % for perfluorooctaneamido betaine (PFOAB, CAS# 90179-39-8) and perfluorooctanesulfonamido betaine (PFOSB, CAS# 75046-16-1).

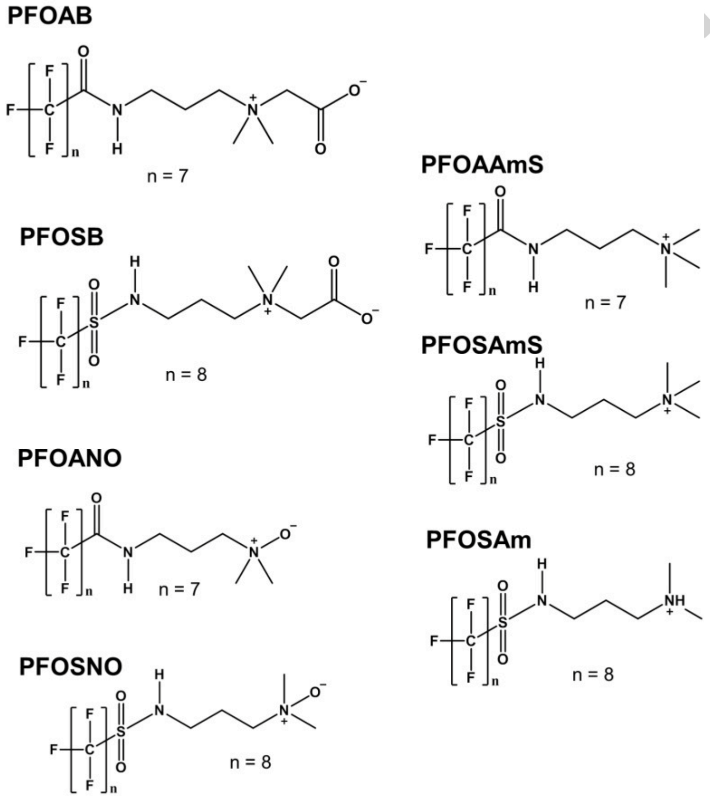

Fig.1. Illustration of the 7 cationic and amphoteric model analytes used for optimization, validation, and quantitation purposes in the present study.

$C_8F_{17}SO_2NHC_3H_6N(CH_3)_2$ is the key intermediate in the preparation of surfactants with a sulfonamide functional group. It was obtained by reacting perfluorooctane sulfonyl fluoride ($C_8F_{17}SO_2F$) with N,N-dimethyl-1,3-propanediamine. The other cationic/amphoteric/non-ionic surfactants were produced by reacting $C_8F_{17}SO_2NHC_3H_6N(CH_3)_2$ with methyl iodide (CH_3I), sodium chloroacetate ($ClCH_2COONa$) and hydrogen peroxide (H_2O_2), respectively. The first two reactions are quaternizations while the last one is an oxidation. In a similar fashion, surfactants with the amide functional group were synthesized using $C_7F_{15}CONHC_3H_6N(CH_3)$ as the key intermediate.

^{1}H and ^{19}F NMR spectroscopic experiments were performed on a Bruker ARX-400 spectrometer to confirm chemical structures and for purity analysis of final products. For instance, NMR data of PFOSAmS are: ^{19}F NMR (376.47 MHz, $CDCl_3$) δ: -81.3 (ω-CF_3), -112.0(α-CF_2), -121.0 (β-CF_2), -122.1 (3×CF_2), -123.2 (ζ-CF_2), -125.6 (θ-CF_2); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.95 (m, 2H, -CH_2-), 2.87 (m, 2H, -NH-CH_2-), 3.22 (m, 11H, 3×CH_3 & -CH_2-N$(CH_3)_3$). Upon receipt, the identity of each compound was further confirmed by determining its accurate mass using a Q-Exactive Orbitrap mass spectrometer in house.

2.3. Sample Collection

Sediment samples (n = 12) were collected across mainland France, under the framework of the 2012 National Screening Study on Emerging Contaminants (Vulliet et al., 2014; Munoz et al., 2015a). Although only a subset (12/133) of the initially targeted sites was considered in the present study for suspect screening of PFASs, a good geographical coverage was achieved, which encompassed the six French Water Basins: Artois-Picardie (S-1), Rhin-Meuse (S-2), Seine-Normandie (S-3–4), Loire-Bretagne (S-5–7), Adour-Garonne (S-8 and S-12), and Rhône-Méditerranée (S-9–11) (**Fig.2**). At each site, composite sediment samples were collected in aluminum trays from 3 evenly spaced points, the upper layer (1–5 cm) of the sediment being sampled. Samples were stored in a cooling box (5 ± 3 °C), pending shipment to the laboratory. Sediment grain-size (fine fraction content: mass percent fraction of the < 63 µm fraction over the < 2 mm fraction) and total organic carbon (TOC) content were determined as described elsewhere (Munoz et al., 2015a). Sediment samples were freeze-dried, conditioned in 15 mL high density polyethylene (HDPE) tubes, and stored at 4°C until analysis. Details on sample code, location, TOC and grain-size are supplied in the SI (**Table S2**).

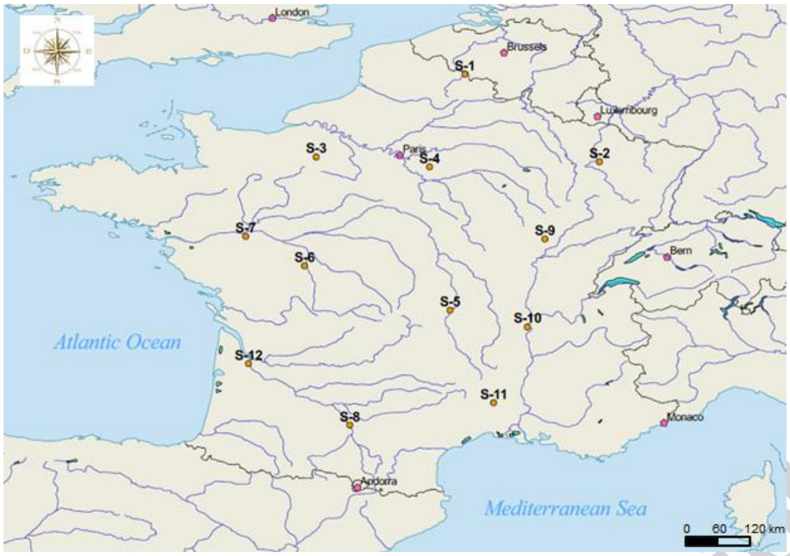

Fig.2. Map showing the spatial distribution of the sampling sites investigated at 12 locations across France.

2.4. Extraction and Clean-up of Sediment Samples

Additions of matrix and standard solutions were systematically controlled by gravimetry. Extraction of sediment samples was based on the ultrasonic extraction method described by Bertin et al. (2014), with some modifications. Sediment samples (1 g dry weight (dw)) were weighed in 15 mL glass tubes. Following the addition of IS (2 ng each) to the samples, the spiked IS were left to equilibrate with the sample material for > 1 h at room temperature. After addition of 5 mL of basic methanol (NaOH 20 mM in MeOH), samples were briefly vortexed and extracted in an ultrasonic bath for 20 min. Extracts were centrifuged (5000 rpm, 3 min) and the supernatants were transferred to clean 15 mL glass tubes. The ultrasonic extraction step was repeated once with 5 mL of basic methanol and a final rinse step was performed with 2 mL of basic methanol. The combined extracts (~12 mL) were evaporated to approximately 2 mL under a gentle stream of N_2 and moderate heating (~40 °C), after which a clean-up step was performed using ENVI-Carb graphite cartridges previously conditioned with 5 mL of MeOH. Extracts were passed through the ENVI-Carb sorbent and collected in 15 mL glass tubes; cartridges were finally rinsed with 5 mL of MeOH and the resulting extracts were neutralized with HCOOH. Extracts were evaporated to a final volume of 200 µL (N_2, ~40 °C), transferred to 250 µL polypropylene vials, and stored at –20 °C until analysis.

2.5. Instrumental Analysis

Chromatographic operating conditions were adapted from a procedure initially developed by Labadie and Chevreuil (2011). The Dionex Ultimate 3000 LC chain was controlled via the Chromeleon 7.2 Software (Thermo Fisher Scientific, Waltham, MA, USA, and Dionex Softron GMbH part of Thermo Fisher Scientific, Germany). A Thermo Hypersil Gold aQ column (100 x 2.1 mm; dp = 1.9 µm) was used for analyte separation. The aqueous mobile phase consisted of HPLC-water with 0.1 % HCOOH (v/v) and the organic mobile phase of ACN with 0.1 % HCOOH (v/v). Flow rate was set at 0.55 mL min^{-1}, injection volume at 5 µL, and column inlet temperature at 40°C. Details on chromatographic gradient elution conditions are supplied in the SI (**Table S3**). The heated electrospray ionization source was used with the following settings: sheath gas flow rate was 40 arbitrary units (a.u.), auxiliary gas flow rate 15 a.u., sweep gas flow rate 0 a.u., capillary temperature 320°C and vaporizer temperature 350°C. Spray voltage was either -4 kV or +4 kV (fast polarity-switching mode). Analyte detection was performed using a Q-Exactive Orbitrap mass spectrometer controlled by the Xcalibur 2.3 software (Thermo Fisher Scientific, Waltham, MA, USA). Orbitrap parameters were set as follows: AGC (maximum capacity in C-trap) was set at 5 x 10^{6}, maximum injection time at 50 ms, and resolution at 70,000 FWHM at 200 m/z (Munoz et al., 2015b). The mass scan range was set at 150–1000 m/z (full scan MS mode).

2.6. Analyte Identification and Quantification

Analytes were quantified using the isotopic dilution method, the IS being added at the beginning of the preparation procedure to correct for potential recovery losses or matrix effects. 1/x weighted linear regressions were used, based on 10-point solvent-based calibration curves which ranged between 0.01–40 ng mL^{-1}.

Due to the lack of authentic analytical standards for some of the investigated compounds, analytes were grouped into three categories, following the classification proposed by Backe et al. (2013). Briefly, analytes for which native analytes and suitable corresponding IS were available were classified as quantitative (Qn) analytes (anionic and neutral model analytes, e.g.: PFDS, quantified against $^{13}C_4$-PFOS). Native positive mode analytes such as PFOAAmS, PFOSAmS, PFOAB, PFOSB, PFOANO, PFOSNO and PFOSAm were quantified against $^{13}C_4$-PFOS due to the lack of available isotope-labelled internal standards, and were therefore coined as semi-quantitative (Sq) (**Fig.1**). Qn and Sq analytes were used as model compounds for method optimization and validation purposes, representing a wide spectrum of chemistries (anionic, neutral, amphoteric, cationic) and hydrophobicity (e.g., C_4–C_{18} PFCAs) among PFASs. In addition, the 150-1000 m/z full scan MS acquisition mode enabled the screening of other analytes which were quantified assuming equimolar response to a structurally-related native compound. When an applicable match was used, these analytes were classified as semi-quantitative (Sq), and qualitative (Ql) otherwise (see SI **Fig.S1** and **Tables S5-S6**) (accurate mass tolerance: -4 ppm < δ < +4 ppm). For instance, in the case of fluorotelomer sulfonamide betaines (FTABs), concentrations were estimated using the calibration curve of PFOSB (due to molecular structure similarities, PFOSB being the perfluoroalkyl analogue of 6:2 FTAB) and $^{13}C_4$-PFOS as internal standard. In the case of fluorotelomer sulfonamide amines (FTAs), concentrations were estimated using the calibration curve of PFOSAm (the perfluoroalkyl analogue of 6:2 FTA), and $^{13}C_4$-PFOS as the internal standard. Both FTAs and FTABs were therefore considered as Sq analytes. A full list of investigated Sq or Ql suspect molecules is enclosed in the SI (**Tables S5-S6**).

2.7. Method Validation

A series of 7 procedural blanks were run and consisted of glass tubes (with solvent and IS) that went through the entire analytical procedure except for sediment sample addition. The blank levels observed for PFBA and 6:2 FTSA were quite variable (2.6 ± 1.6 and 0.55 ± 0.42 ng, respectively); therefore, these compounds were only investigated in a qualitative fashion in our final method. Procedural blanks generally showed low to moderate contamination (< 0.03 ng), with the noteworthy exception of PFOA, yet at very reproducible levels (0.50 ± 0.10 ng). None of the cationic or amphoteric Sq or Ql compounds were detected in procedural blanks. For full details on procedural blanks, see **Table S4** of the SI.

When analytes were found in procedural blanks, data were blank-corrected and the limit of detection (LOD) was determined as the standard deviation of the blanks multiplied by the $t_{n-1,95}$ Student coefficient, n being the number of blank replicates (Muir and Sverko, 2006). Otherwise, the LOD was derived from the error on the y-intercept and the slope of the regression of the calibration curve (Fayad et al., 2010).

Linearity was examined through solvent-based and matrix-based approaches: 10-level calibration curves were built, the IS mass added being kept constant and the linearity range tested covering

> 3 decades (0.01–40 ng mL^{-1}). Matrix effects (%) were derived by comparing the slopes obtained by the two approaches.

A sediment sample from the St Lawrence River (Québec, Canada) with relatively low target (Qn) anionic PFAS content (ΣPFAA < 1 ng g^{-1} dw) was used for method validation, following fortification (see below).

Analyte recovery during sample preparation was determined by spiking the sediment matrix at 10 ng g^{-1} dw. For each replicate, recovery (expressed in %) was calculated using Eq.1:

$$Recovery = 100 * \frac{SB-NS}{SA-NS} \text{ (Eq.1)}$$

with SB the analyte to internal standard area ratio observed in a sediment sample spiked before extraction with native analytes, SA the analyte to internal standard area ratio observed in a sediment sample spiked after sample preparation with native analytes, and NS the analyte to internal standard area ratio of the reference (non-spiked sediment sample). In all three cases, the appropriate IS were added after sample preparation.

Method accuracy was evaluated at two concentration levels (1 and 10 ng g^{-1} dw) (n=5) by spiking native analytes jointly with IS to sediment samples at the beginning of the preparation procedure, and was expressed as a percentage of the expected value.

Intra-day precision was assessed likewise and corresponded to the relative standard deviation (RSD) of five replicates analyzed on a same work day. The analysis was repeated on a second and third work day and inter-day precision derived from the overall RSD (n=15).

2.8. Statistics and GIS

Statistical analysis was performed with the R statistical software (R version 2.15.3, R Core Team, 2013). Statistical significance was defined as $p < 0.05$. The ade-4 R-package was used to perform Principal Component Analysis (PCA). Quantum GIS 1.8.0 “Lisbona” (QGIS) was used as a geographic information system, and base maps were downloaded from Natural Earth (URL: <http://www.naturalearthdata.com>).

3. RESULTS AND DISCUSSION

3.1. Method Optimization

Preliminary experiments showed that the polarity switching mode did not adversely affect instrumental detection limits or linearity when compared to the separate acquisition mode, all the while maintaining an acceptable number of points per peak (see SI **Fig.S2** for details). Therefore, positive mode and negative mode PFAS analytes were analyzed within a single run. Acidic mobile phases (containing 0.1 % HCOOH) were preferred to those containing ammonium acetate for the appreciable signal improvement for cationic and amphoteric analytes (SI **Fig.S3**). Another noteworthy progress obtained with the acidic mobile phase was the better retention observed for short-chain compounds (e.g., PFBA, PFPeA), due to the increase of the proportion of these analytes in their neutral form. A minimal injection volume of 5 µL was finally selected, since higher injection volumes (≥ 10 µL) of methanolic extracts induced analyte breakthrough and peak fronting for early eluting analytes (SI **Fig.S4**) which are more prone to viscous fingering effect (Homsy, 1987).

Following the selection of suitable chromatographic conditions, the influence of extraction conditions on analyte recovery was investigated. ACN was discarded for the low recovery rates it yielded for short-chain PFCAs, fluorotelomer carboxylates and 6:2 FTSA, or cationic and amphoteric analytes (< 35 %) (SI **Fig.S5**). MeOH was excellent for a majority of model PFAS analytes (25/30), yet failed to quantitatively recover perfluoroalkyl betaines (PFOAB, PFOSB) and quaternary amines (PFOAAmS, PFOSAmS) (**Fig.3**), presumably a consequence of strong ionic interactions at the sediment surfaces (Smith et al., 1991). Addition of NH_4OH to MeOH had little or no effect on PFOAAmS recovery (< 30 %), and quantitative extraction of the latter (> 65 %) was finally obtained using MeOH/NaOH 20 mM (**Fig.3**). Note that the NaOH concentration was not tested at a level higher than 20 mM because of the recovery loss observed for 6:2 FTUA and 8:2 FTUA at concentrations > 10 mM (**Fig.3**). Using the MeOH/NaOH 20 mM extraction solvent, quantitative recoveries were obtained for all analytes (recovery range: 60–110 %) (**Table 1**).

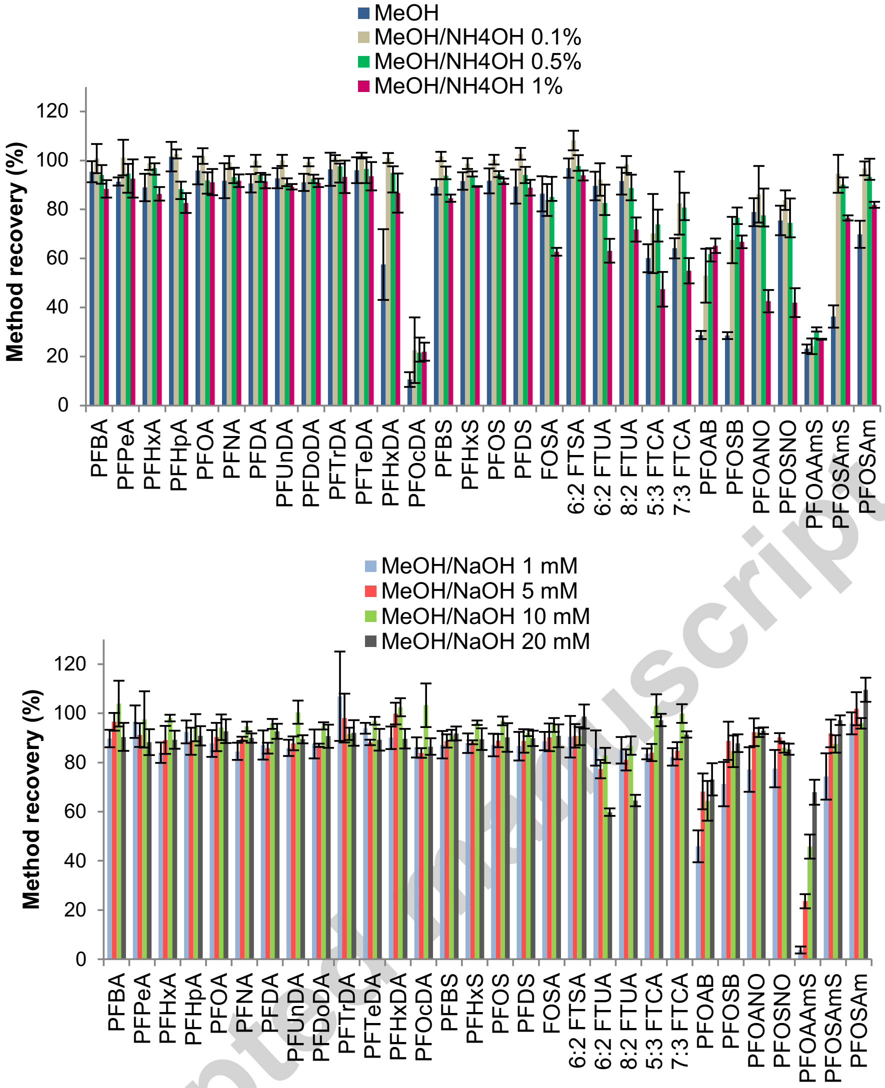

Fig.3. Influence of NH_4OH and NaOH addition to methanol on whole method recovery rates for Quebec sediment samples spiked at 10 ng g^{-1} dw with PFAS analytes. Error bars indicate standard deviation (n=3).

3.2. Assessment of Linearity and Matrix Effects

Five- to ten-point calibration curves (1/x weighted linear regressions) were built for both solvent-based and matrix-based approaches. Excellent coefficients of determinations (R^2) were obtained (0.9947–0.9999) and residuals generally deviated < ± 20 % from the calculated trend line over the whole linearity range which spanned 2–3 orders of magnitude. Note that the deviation at the highest calibration level tested was always < 5 %, suggesting that the linear domain may extend beyond 40 ng mL^{-1} for all analytes. Full details on R^2, linearity range, as well as information on the deviation between observed and calculated-back relative response, are outlined in the SI (**Tables S7-S8**). Matrix effects were acceptable overall, the matrix-based calibration curve slope being comprised between ± 20 % of the solvent-based one for most analytes, with the exception of PFOANO and PFOSNO (-38 and -41 %) (SI **Fig.S6**). Therefore, it was deemed acceptable to quantify analytes in sediment samples from a solvent-based calibration curve instead of the standard addition approach which is in practice cumbersome to implement.

3.3. Method Performance

Key figures of merit for the method performance (accuracy, intra-day and inter-day precision) are supplied in the SI (**Table S9**).

LODs were in the range 0.00056–0.24 ng g^{-1} dw for negative mode Qn analytes and 0.0091–0.46 ng g^{-1} dw for positive mode Sq analytes (**Table 1**). Limits of quantification (LOQs) were then defined as the most severe of the two following approaches: i) 3.3 times the LOD or ii) derived from the lowest level of the linearity range (**Table 1**).

Since no standard reference materials are currently available for the analysis of PFASs in sediment matrices, our extraction procedure was validated on sediment samples fortified at two levels (1 and 10 ng g^{-1} dw) (SI **Table S9**). Accuracy rates were excellent for Qn analytes, remaining between 80–120 % for 19/21 analytes (range 68–124 % for all Qn analytes), and were not influenced by the spike level. The lower accuracy rates observed for several positive mode Sq analytes (e.g., 43–55 % for perfluoroalkyl betaines, 25–50 % for perfluoroalkyl amido amine oxides) somewhat reflect matrix effects or losses during the preparation procedure that were not compensated for by ^{13}C-PFOS. These results further underscore the need for appropriate isotope-labelled standards to improve quantification performances. Regardless of the spike level, repeatability and reproducibility were excellent, intra-day precision being always better than 9 % and inter-day precision always better than 23 % for all model analytes (SI **Table S9**).

Table 1. Limits of detection (LODs), limits of quantification (LOQs), and recovery rates and corresponding relative standard deviations (RSD, %) of the herein described method.

	LOD* **(ng g^{-1} dw)**	**LOQ**** **(ng g^{-1} dw)**	**Recovery rates***** **(%)**	**RSD****** **(%)**
PFPeA	0.0067^{b}	0.020^{c}	88	6
PFHxA	0.038^{a}	0.11^{c}	89	4
PFHpA	0.0077^{a}	0.023^{c}	91	4
PFOA	0.24^{a}	0.72^{c}	93	5
PFNA	0.011^{b}	0.033^{c}	90	2
PFDA	0.0034^{a}	0.010^{c}	93	3
PFUnDA	0.0043^{a}	0.013^{c}	89	2
PFDoDA	0.0059^{a}	0.017^{c}	91	5
PFTrDA	0.0025^{a}	0.0075^{c}	92	6
PFTeDA	0.0049^{a}	0.015^{c}	89	5
PFHxDA	0.030^{a}	0.090^{c}	90	4
PFOcDA	0.055^{a}	0.17^{c}	86	4
PFBS	0.0020^{b}	0.0060^{c}	92	3
PFHxS	0.0021^{a}	0.0063^{c}	89	5
PFOS	0.00090^{a}	0.0027^{c}	90	6
PFDS	0.0036^{b}	0.011^{c}	90	3
FOSA	0.00056^{a}	0.0020^{d}	91	5
6:2 FTUA	0.059^{b}	0.18^{c}	60	2
8:2 FTUA	0.020^{b}	0.060^{c}	65	4
5:3 FTCA	0.046^{b}	0.14^{c}	97	3
7:3 FTCA	0.042^{b}	0.13^{c}	91	1
PFOAB	0.015^{b}	0.05^{c}	73	9
PFOSB	0.033^{b}	0.10^{d}	88	4
PFOANO	0.0091^{b}	0.027^{c}	93	1
PFOSNO	0.019^{b}	0.10^{d}	85	3
PFOAAmS	0.46^{b}	1.4^{c}	68	7
PFOSAmS	0.048^{b}	0.14^{c}	97	2
PFOSAm	0.034^{b}	0.10^{c}	110	4

*LODs were derived (a) from the standard deviation of 7 procedural blanks multiplied by the $t_{6;95\%}$ Student coefficient, or (b) from the calibration curve, based on the error on the y-intercept and the slope of the regression. **The LOQ was either set at 3 x LOD (c) or at the lowest point of the linearity range (d). ***Based on sediment samples spiked at 10 ng g^{-1} dw with Qn and Sq model analytes (for more details on recovery experiments, see also **Section 2.7**). ****Relative standard deviation (%) on replicate recovery tests (n=3).

3.4. Method Demonstration and Suspect Screening of PFASs in Sediments

Investigation of Qn and Sq analytes

With the exception of fluorotelomer carboxylates (6:2 FTUA and 8:2 FTUA), all Qn model analytes were quantified at least once in the 12 sediment samples targeted. PFOS and long-chain PFCAs (C_{10}-C_{14}) were systematically or near-systematically detected while short-chain PFCAs (C_5-C_7) were only anecdotally reported, akin to the PFAS occurrence generally described for sediments (e.g., Ahrens et al., 2010; Labadie and Chevreuil, 2011). PFOS was dominant in most samples, accounting on average for 44 ± 25 % of $\Sigma PFASs^{-}$ (total of anionic and neutral Qn analytes), PFOS concentrations varying substantially across sites (0.084–23 ng g^{-1} dw) (**Table 2a**). Sediment S-10 from the Rhône River exhibited a starkly divergent profile with the predominance of PFCAs (> 98 % $\Sigma PFASs^{-}$), especially PFTrDA (35 % of ΣPFCAs). We attribute this peculiar signature to a fluorochemical plant operating in this watershed (Dauchy et al., 2012; Munoz et al., 2015a). A number of other anionic compounds were screened in full scan MS mode but were either not detected in sediment samples or comparable to the procedural blanks (see SI **Table S6** for the full list of investigated Sq or Ql suspects). Model positive mode analytes were only sporadically detected in these samples (PFOSB: 3/12; PFOANO: 2/12; PFOSAmS: 1/12; PFOSAm: 1/12), remaining at sub ng g^{-1} dw levels (**Table 2b**).

Suspect screening of newly-identified PFASs

Suspect screening in full scan MS mode led to the identification of a series of homologous fluorotelomer sulfonamide betaines (FTABs) in most sediment samples. The pattern of ~ + 1 min observed between retention times was consistent with an increase of two $-CF_2$ units (**Fig.4**), and the deviation from nominal mass remained comprised between -1.5 and +0.60 ppm (SI **Table S5**). For confirmation purposes, sediment extract S-9 was reanalyzed in t-MS^2 positive ionization mode (normalized collision energy (NCE) = 30 %) and three characteristic fragment ions were identified for each FTAB: loss of fragment 1 (betaine group: $[(CH_3)_2NHCH_2COOH]^+$, m/z=104.07061) to form fragment 2, and subsequent ethylene loss to form fragment 3 (**Fig.4**) (see also D'Agostino and Mabury, 2014). 6:2 FTAB was detected in 12/12 samples, with a maximum estimated concentration of 3.9 ng g^{-1} dw at site S-5, nearly ten-fold higher than that of PFOS. Other FTABs, such as 8:2 FTAB, 10:2 FTAB and 12:2 FTAB were also frequently reported, displaying maximum estimated concentrations at site S-9 (4.5, 7.6 and 6.8 ng g^{-1} dw, respectively) (**Table 2b**).

Table 2a. Concentrations (ng g^{-1} dw) of quantitative (Qn) anionic and neutral PFAS analytes in the sediment samples investigated (not detected: 6:2 FTUA and 8:2 FTUA). When applicable, concentrations were blank-corrected.

	S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	**S-10**	**S-11**	**S-12**
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.062	<LOD	0.15	0.035	<LOD	0.041
PFHx	<LOD	4.3	<LOD	<LOD	0.13	<LOD	<LOD	<LOD	<LOD	0.32	<LOD	<LOD
PFHpA	<LOD	<LOD	<LOD	<LOD	<LOD	0.0032	<LOD	<LOD	0.096	0.13	<LOD	0.064
PFOA	0.56*	<LOD	<LOD	0.43*	0.35*	0.28*	0.36*	<LOD	<LOD	1.3	0.50*	0.37*
PFNA	<LOD	<LOD	0.086	0.22	<LOD	<LOD	0.14	0.068	0.34	0.37	<LOD	0.044
PFDA	0.092	0.17	0.067	0.96	0.086	0.013	2.0	0.39	0.45	2.8	0.034	0.17
PFUnDA	0.054	0.20	0.045	0.22	0.075	0.020	0.66	0.28	0.39	0.99	<LOD	0.24
PFDoDA	0.32	1.38	0.085	0.75	0.28	0.042	0.82	0.65	2.2	1.3	0.028	0.24
PFTrDA	0.069	0.14	0.021	0.13	0.057	0.0073*	0.17	0.084	0.37	4.2	0.018	<LOD
PFTeDA	0.13	0.39	0.032	0.28	0.088	0.011*	0.084	0.12	0.92	0.42	0.0091*	0.24
PFHxDA	0.12	0.099	< LOD	0.10	0.033*	<LOD	<LOD	<LOD	0.19	0.13	<LOD	<LOD
PFOcDA	0.23	0.12*	<LOD	0.064*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	0.0030*	0.011	0.0037*	0.0071	<LOD	0.0057	0.012	<LOD	0.011	<LOD	<LOD	0.053
PFHxS	0.039	0.073	0.023	0.090	0.114	0.013	0.074	0.037	0.30	0.0025*	0.021	0.53
PFOS	1.3	0.96	1.0	3.9	0.40	0.37	2.9	2.7	4.2	0.084	0.81	23
PFDS	0.014	0.018	0.015	0.012	0.0064*	0.014	0.0048*	0.035	0.16	<LOD	<LOD	0.27
FOSA	<LOD	0.23	0.011	0.053	0.053	0.021	0.013	0.038	0.24	0.0024	0.042	0.55
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	0.078*	<LOD	0.42	<LOD	<LOD	0.090*	<LOD	<LOD
7:3 FTCA	0.19	<LOD	<LOD	0.37	0.32	<LOD	0.36	<LOD	0.42	<LOD	<LOD	<LOD
ΣPFASs^{-} (Qn)	**3.2**	**8.1**	**1.4**	**7.6**	**2.1**	**0.79**	**8.0**	**4.4**	**11**	**12**	**1.5**	**25**

*Tentatively determined concentrations (comprised between LOD and LOQ).

Table 2b. Estimated concentrations (ng g^{-1} dw) of semi-quantitative (Sq) amphoteric and cationic PFAS analytes in the sediment samples investigated (not detected Sq analytes: PFOAB, PFOSNO, PFOAAmS).

	S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	**S-10**	**S-11**	**S-12**
PFOSB	<LOD	<LOD	<LOD	<LOD	0.31	<LOD	<LOD	<LOD	0.35	<LOD	<LOD	0.95
PFOANO	<LOD	<LOD	<LOD	<LOD	0.15	<LOD	<LOD	<LOD	0.14	<LOD	<LOD	<LOD
PFOSAmS	<LOD	<LOD	<LOD	<LOD	1.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOSAm	<LOD	<LOD	<LOD	<LOD	1.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTA	0.95	1.5	0.078	0.021	6.1	0.032	0.079	1.7	4.8	0.076	0.0092	1.2
8:2 FTA	0.068	0.077	ND*	ND	0.17	ND	ND	0.026	0.38	ND	ND	ND
6:2 FTAB	0.54	0.54	0.23	3.5	3.9	0.023	3.0	1.9	2.2	0.23	0.12	0.26
8:2 FTAB	0.84	0.43	0.042	1.0	2.5	ND	0.35	2.1	4.5	0.077	ND	ND
10:2 FTAB	1.7	0.89	ND	0.77	0.66	ND	ND	1.9	7.6	0.15	ND	ND
12:2 FTB	0.93	0.67	ND	0.48	0.087	ND	ND	1.3	6.8	0.019	ND	0.11
ΣPFASs^{+} (Sq)	**5.0**	**4.1**	**0.35**	**5.8**	**16**	**0.055**	**3.4**	**8.9**	**27**	**0.55**	**0.13**	**2.5**

*ND: Not detected. Since that no standards were available for FTAs and FTABs, no LODs were reported for the latter in the present study.

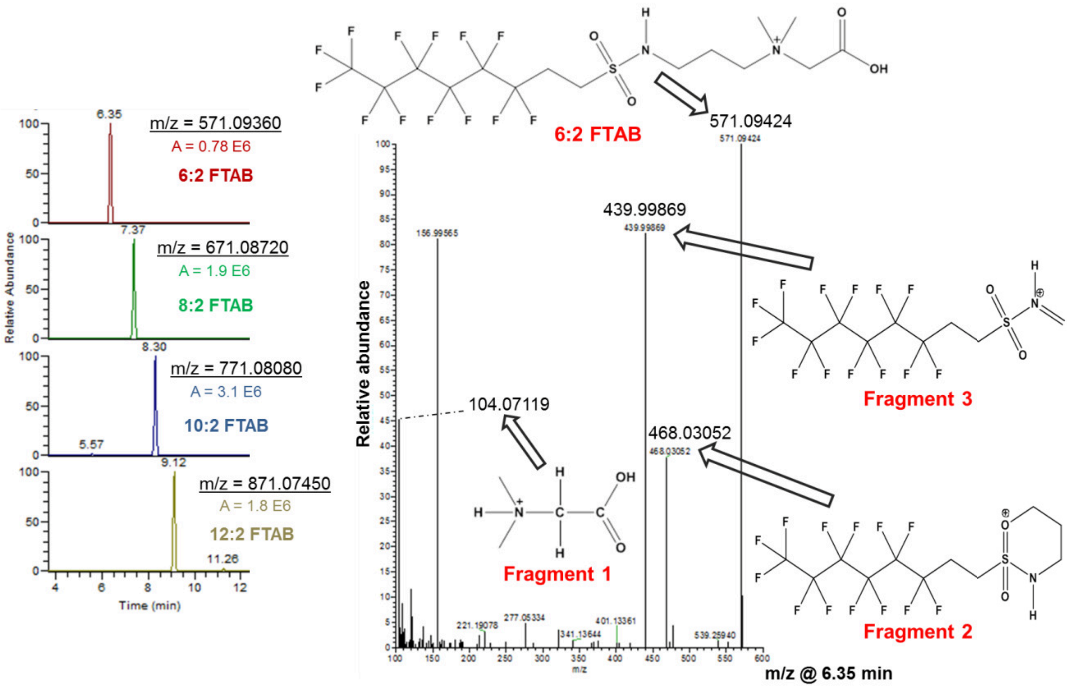

Fig.4. Identification of a series of homologous fluorotelomer sulfonamide betaines in sediment sample S-9 from the Rhône water district with accurate mass and observation of retention time patterns and illustration of the Orbitrap t-MS² spectrum obtained at 6.35 min for structural confirmation of 6:2 FTAB, also in sediment sample S-9.

Similarly, 6:2 and 8:2 fluorotelomer sulfonamide amines (FTAs) were identified based on retention time patterns (+1.08 min between the latter two) and accurate mass (SI **Fig.S7**), the observation of characteristic fragments in t-MS² mode providing further confirmation (SI **Fig.S8**) (see also SI **Table S5**). Sites S-5 and S-9 exhibited elevated levels of 6:2 FTA (6.1 and 4.8 ng g^{-1} dw, respectively), while 8:2 FTA was less prominent (0.17–0.38 ng g^{-1} dw) (**Table 2b**). Overall, these results may suggest the predominance of telomerization-based AFFFs rather than electrochemical fluorination-based AFFFs in metropolitan France (Place and Field, 2012). Note that although fluorotelomer betaines (FTBs) were included in the suspect list, these compounds were not detected (SI **Table S6**). These results provide the first evidence of the widespread occurrence of these novel PFASs in freshwater ecosystems.

Investigation of spatial distribution and sources to aquatic environments

The average ΣPFASs^{+} (total of amphoteric and cationic Sq analytes) was 6.1 ng g^{-1} dw (median: 3.8 ng g^{-1} dw; range: 0.055–27 ng g^{-1} dw), similar to that of ΣPFASs^{-} (total of anionic and neutral Qn analytes) (mean: 7.0 ng g^{-1} dw; median: 6.0 ng g^{-1} dw; range: 0.79–25 ng g^{-1} dw).

Interestingly, maximum ΣPFASs⁻ concentrations did not necessarily imply high ΣPFASs$^+$ concentrations, and conversely, as shown in the multivariate analysis approach. The first factorial component of the PCA (Dim 1: 42.8 % of inertia) corresponded to high ΣPFASs$^+$ levels, highlighting sites S-5 and S-9, and, to a lesser extent, site S-8 (SI **Fig.S9**). The second factorial component (Dim 2: 21.9 % of inertia) highlighted sampling sites affected by strong urban pressures (S-12: ΣPFSAs = 24 ng g^{-1} dw) or urban/industrial pressures (S-10, downstream from a polyvinylidene fluoride manufacturing plant). In sediment S-5 (Le Bédat à Saint-Laure), ΣPFASs$^+$ was estimated at 16 ng g^{-1} dw (8 x > ΣPFASs$^-$). The Bédat river is a shallow river characterized by a low water flow rate (mean < 2 m^3 s^{-1} over the 2000-2015 period) (<hydro.eaufrance.fr>) and a small scale watershed (< 400 km²). Before flowing through the Saint-Laure commune, the Bédat River receives waters from a small brook (Ruisseau des Ronzières) which passes just a few hundred yards from the Clermont-Ferrand main wastewater treatment plant (WWTP) (nominal capacity: 425,000 population equivalents). In addition to urban and industrial inputs, this WWTP likely receives waters from the adjacent Clermont-Ferrand airport wherein firefighting activities involving AFFFs may occur on a regular basis. Even if sediment sample S-5 exhibited low organic content (0.91 %) and coarse grain-size characteristics (fine fraction content < 3 %), the small dilution capability of the Bédat River may partly explain the high ΣPFASs$^+$ observed at this location. Maximum ΣPFASs$^+$ was observed at site S-9 (27 ng g^{-1} dw) (L'Ouche à Crimolois). The River Ouche is also characterized by a rather low water flow rate (mean < 9 m^3 s^{-1} over the 1963–2015 period) (<hydro.eaufrance.fr>) and flows through the town of Dijon before reaching Crimolois. While the relatively high PFOS concentration (4.2 ng g^{-1} dw) likely reflects urban inputs from the Dijon conurbation, the specific FTAB signature (ΣFTABs = 21 ng g^{-1} dw) may be attributed to the presence of the Dijon-Bourgogne airport, situated < 2 km upstream from S-9. Similarly, firefighting activities at Toulouse-Blagnac airport may partly explain the substantial ΣPFASs$^+$ (8.9 ng g^{-1} dw) observed in the Garonne River at site S-8, although urban sources may also contribute to the PFAS load.

Correlations between PFAS sedimentary levels and sediment characteristics were tentatively assessed via the calculation of Spearman's rank order coefficients (SI **Table S10**). ΣPFSAs was strongly related to fine fraction content or TOC, concurring with previous observations for metropolitan France (Munoz et al., 2015a). Significant correlation coefficients were reported for ΣFTABs/ΣFTAs (rho = 0.65), pointing to similar sources or environmental fate. The 6:2 FTA to 8:2 FTA ratio was highly variable (29 ± 22 on average; number of matching pairs n_{mp} = 5/12). Based on differences in perfluoroalkyl chain length and the hydrophobic properties thereof, even higher

6:2 FTA to 8:2 FTA ratios might be expected in the dissolved phase, although other confounding factors such as different degradation kinetics under environmental conditions make it difficult to speculate; these preliminary findings should therefore be taken with caution since only a limited number of sampling sites were considered in the present survey (n=12).

4. CONCLUSIONS

The proposed analytical procedure has proven robust and reliable for the trace-level determination of a wide spectrum of amphoteric, cationic, neutral and anionic PFASs in sediments. Regardless of analyte chain-length or polarity, excellent recovery rates could be obtained for all model analytes (60–110 %) while matrix effects remained moderate (comprised between ± 25 % for most compounds), making it eligible for routine analyses using solvent-based calibration curves. Arguably, the herein described method could also be transposed to other mass spectrometry platforms. The method was suitable for suspect screening of a large range of PFASs within a single run, which led to the identification of several polyfluoroalkyl cationic or zwitterionic analytes in sediment samples. In addition, the satisfactory chromatographic retention observed even for PFBA, PFPeA or PFBS through the use of an acidic mobile phase also suggests that the instrumental conditions of the proposed method could be applied as-is for the analysis of even shorter-chain congeners without any additional chromatographic requirements, provided one operates at low injection volumes to circumvent viscous fingering effects.

Given its broad geographical coverage in France, this survey provides a valuable source of information on the widespread occurrence of amphoteric and cationic PFASs in hydrosystems. In particular, fluorotelomer sulfonamide amines and fluorotelomer sulfonamide betaines were ubiquitous in these samples. Hot spots of positive mode compounds (ΣPFASs^{+} range: 8.9–27 ng g^{-1} dw) were associated with low-flow watercourses in the vicinity of airports, suggesting the existence of firefighting activities involving AFFFs at these sites. Natural attenuation of amphoteric and cationic PFASs is expected through biodegradation of the fluorine-free moiety, yet may entail the formation of more environmentally persistent forms. The partitioning behavior of amphoteric and cationic PFASs warrants future research on their fate, including determination of water-sediment partitioning coefficients or degradation kinetics under environmentally relevant conditions. Biomonitoring and ecotoxicological studies are also needed to dispel or validate concerns about the bioaccumulation, biomagnification potential and toxicity of newly-identified fluorosurfactants.

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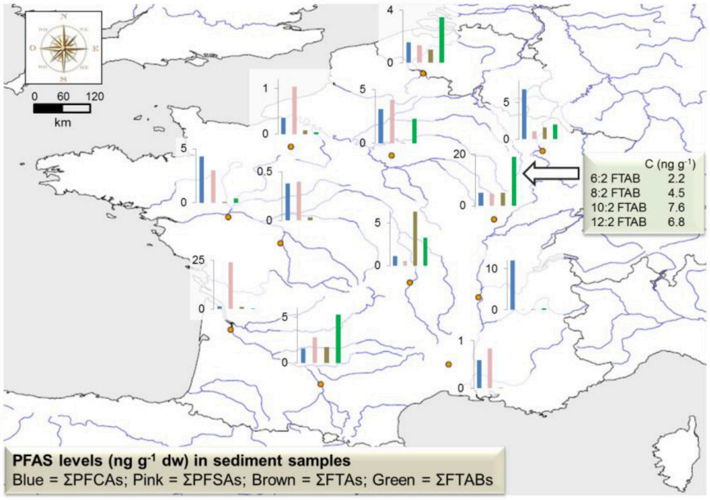
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Anionic, zwitterionic and cationic PFASs were investigated in sediments from France
- Following sonication with basic methanol, extracts were cleaned-up with graphite
- Quantitative recovery of a wide range of PFASs was realized (60–110 %)
- Limits of detection were comprised between 0.0006–0.46 ng g^{-1} dw
- Fluorotelomer sulfonamide amines and betaines were prevalent in these samples