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Determination of organic fluorinated compounds content in complex samples through combustion ion chromatography methods: a way to define a “Total Per- and Polyfluoroalkyl Substances (PFAS)” parameter?

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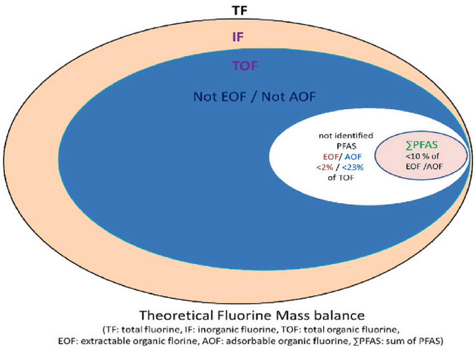
HIGHLIGHTS

- Development of Total (TF), adsorbable (AOF) and extractable (EOF) organic fluorine methods
- A robust AOF method developed and validated for very complex liquid matrices.
- AOF and EOF measured concentrations very low compared to estimated OF.
- AOF and EOF mostly comprised of unknown fluorinated compounds
- Neither AOF or EOF or TF are relevant as a proxy of “total PFAS”.

GRAPHICAL ABSTRACT



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ABSTRACT

Emerging contaminants are a growing concern for scientists and public authorities. The group of per-polyfluoroalkyl substances (PFAS), known as ‘forever chemicals', in complex environmental liquid and solid matrices was analysed in this study. The development of global analytical methods based on combustion ion chromatography (CIC) is expected to provide accurate picture of the overall PFAS contamination level via the determination of extractable organic fluorine (EOF) and adsorbable organic fluorine (AOF). The obtained results may be put into perspective with other methods such as targeted analyses (LC-MS/MS). The impact of pH, the presence of dissolved organic carbon and suspended particles on AOF measurements were explored. The effectiveness of the washing step to remove adsorbed inorganic fluorine (IF) has been proven for samples containing up to 8 mgF.L^{-1}. CIC-based methods showed good repeatability and reproducibility for the complex matrices studied. Environmental applications of these methods have been tested. AOF and EOF analyses could explain between 1 % and 23 % and 0.1 % to 2 % of total organic fluorine (TOF), respectively. The sum of PFAS

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compounds expressed as fluorine could explain from 0.2 % to 11 % and from 0.003 % to 5 % for AOF and EOF, respectively. These results also suggest that some fluorinated compounds are not adsorbed or extractable and/or lost by volatilisation during the application of AOF and EOF analytical procedure. These findings highlight that AOF and EOF are not entirely efficient as proxy to assess "total PFAS" for assessing environmental contamination by PFAS. However, these methods could still be applied to gain a better understanding of the sources and fate of PFAS in the environment.

1. Introduction

Called "forever chemicals" because of their high chemical stability, *per*- and polyfluoroalkyl substances (PFAS) are almost ubiquitous environmental contaminants (Evich et al., 2022). The definition of PFAS has been evolving for several years as new knowledge was acquired. The most recent OECD Recommendations and Practical Guidance published in 2021 indicates: "PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS." (Barnabas et al., 2022; OECD, 2021; Sadia et al., 2023; Wang et al., 2021), which covers a wide range of chemical products.

Since 1940, PFAS have been produced by the chemical industry in high quantities because of the high stability of the carbon-fluorine (C—F) bond and their intrinsic properties, such as thermal resistance (fire-fighting foam, etc.), water repellence (water- and stain-repellent textiles, medical devices, etc.) and oil repellence (laboratory supplies and personal hygiene products, etc.) (Codling et al., 2014; Raheem et al., 2018). Because of the high diversity of PFAS, there is a significant knowledge gap regarding the quantities discharged into the environment. The work of Dalmijn et al. (2024) gives the first complete inventory of emissions of fluorinated organic substances and PFAS from the production of fluoropolymers. They estimate the quantity of fluoropolymers and PFAS emitted in 2021 by the production of fluoropolymers in Europe to be 360 t/yr.

As a result of their intensive use, PFAS can be found in incoming waste streams such as domestic or industrial wastewaters as well as landfill leachates, and thus in wastewater effluent treatment plants, which can become significant gateways of PFAS to the environment (Lenka et al., 2021; Wang et al., 2020). Organising PFAS by chemical group, chain length or other parameters is complex, given the sheer number of descriptors (over 2000) for >7 million PFAS corresponding to the OECD, 2021 definition (Buck et al., 2011; Kibbey et al., 2020; Schymanski et al., 2023; Su and Rajan, 2021; Wang et al., 2017). They are not, consequently, a "single chemical family" which can easily be analysed by one analytical method (Fiedler et al., 2021; Huerta et al., 2022; James et al., 2023).

Most PFAS are not completely degraded by conventional physico-chemical and biological water treatment processes and, consequently, wastewater effluents contain PFAS from both domestic and industrial sources (Arvaniti and Stasinakis, 2015; Coggan et al., 2019; Hu et al., 2016). Conventional water treatment methods can also generate PFAS transformation products (Chen et al., 2018; Kim et al., 2020; Winchell et al., 2022). Consequently, wastewater treatment plants (WWTP) discharge PFAS and transformation products via several routes: treated wastewater, sewage sludge and air by volatilisation (Bastow et al., 2022; Dauchy et al., 2017; Nguyen et al., 2019; Rewerts et al., 2018; Szabo et al., 2023). Through industrial or consumer products, the materials containing PFAS are disposed of at landfill sites (Liu et al., 2022; Rehnstam et al., 2023), and PFAS are partly transferred into the landfill leachate (Lang et al., 2017). There are several thousand of more or less known PFAS, associated to unknown transformation products, disseminating into the environment. There is therefore a need to better characterise the fate of PFAS, their level of contamination in the various source streams, receptor environments and degradation processes. For that, adapted analytical tools are needed as well as good characterisation of the partition of PFAS in the sample.

PFAS analysis faces many challenges, due to the thousands of unknown compounds, but also due to the lack of standards and robust analytical methods for quantifying them using conventional methods for targeted compounds. For this purpose, the most commonly used quantitative methods are liquid chromatography combined with mass spectrometry for the analysis of ionic PFAS (i.e. carboxylic and sulfonic acids, PFCA and PFSA), and gas chromatography combined with mass spectrometry methods for the analysis of volatile and semi-volatile PFAS (e.g. fluorotelomer alcohols, FTOH) (Al Amin et al., 2020; Martin et al., 2019; Rewerts et al., 2018). But the combination of all methods concerning targeted PFAS analysis covers <200 compounds, highlighting the need of more global parameters such as organic fluorine content or the "TOTAL PFAS" parameter, introduced in the Drinking Water Directive 2020 (Cioni et al., 2023; DWD, 2020; Shojaei et al., 2022; Trojanowicz et al., 2011; Verwold et al., 2023).

For these global parameters, several approaches have been proposed. Different fractions of the sample can be identified: TF (total fluorine), EOF (extractable organic fluorine) or AOF (adsorbable organic fluorine). Removal of inorganic fluorine (IF) is needed for discriminating organic fluorine from TF content. Fig. 1 provides a comprehensive illustration of the different forms of fluorine compounds according to their inorganic or organic character as well as their adsorptibility or extractability features. Several methods are available for measuring organic fluorinated compounds like high resolution-continuum source-graphite furnace molecular absorption spectrometry (HR–CS–GFMAS) (Simon et al., 2022), high-resolution mass spectrometry (HRMS) (Liu et al., 2019; Wu et al., 2022) and combustion ion chromatography (Aro et al., 2021b; Garg et al., 2023; von Abercron et al., 2019). Based on experience with the determination of global adsorbable organic halogens (AOX) parameter, the combustion ion chromatography (CIC) seemed to be the more reliable method for PFAS compounds. Upon adsorption, activated carbon is combusted and fluorine is converted into hydrogen fluoride (HF), which is then adsorbed in a trapping solution. Subsequently, the analysis of fluoride is carried out using an ion chromatography (IC) method (Gehrenkemper et al., 2021; Wagner et al., 2013).

Even though the analytical principle of CIC is relatively simple, different methodological issues may arise. With CIC, it is impossible to distinguish between IF and OF after combustion. Hence there is a need, when measuring the AOF and EOF parameters, to ensure that IF has been removed. A number of bottlenecks have been identified, on which research work remains to be done. For AOF measurement, the liquid sample is loaded on activated carbon and then washed with a solution to eliminate the IF (Han et al., 2021; von Abercron et al., 2019). However, the washing step efficiency and poor retention of short-chain PFAS compounds has been identified as a major challenge. For AOF measurement, there are no specific studies based on effect of dissolved organic carbon (DOC) and suspended solids (SS). Reliability of the methods is a function of PFAS molecular physico-chemical properties including polarity, carbon chain length, type of functional group, and environmental matrices of concern (Winchell et al., 2021).

From a regulatory point of view, draft standards are currently being drawn up to reduce the disparities observed in the protocols reported in the literature. For example, the draft ISO WD 18127 standard focuses on AOF measurement. It is based on DIN 38409–59, an update of ISO 9562. For EOF measurement on solid matrix, sample preparation is generally carried out by ultrasonication of the sample in different combination of polar solvents, variable depending on samples (Kärrman et al., 2021; Miaz et al., 2020; Ruyle et al., 2023).

The objectives of this study are to validate robust and reliable methods for measuring global organic fluorine based on CIC analysis. Parameters are TF and EOF for solid samples, AOF and TF for liquid samples. For this purpose, representative PFAS are selected to develop method for AOF. Complex matrices such as compost, sewage sludge for solid samples or WWTP influent/effluent for liquid samples have been analysed for matrix effects to evaluate the impact of key factors such as IF, suspended matter and dissolved organic carbon contents. Methods are then applied to real samples and compared with PFAS target analysis method to assess their relevance to better understand the sources and fate of PFAS in the environment.

2. Materials and methods

2.1. Samples

A range of different samples was collected from WWTP (effluent, influent and sludge) and ground water from different European countries, with a particular focus on the by-products of sewage sludge as source of fertiliser (SI1). These recovered by-products are produced at different steps of the valorisation process of a mix of sludge and ash into fertilisers. One litre and 500 g were collected, respectively for liquid and solid samples in high-density polyethylene (HDPE)/polypropylene (PP) containers. Samples were stored at −20 °C until analysis.

2.2. Standards and reagents

81 PFAS standards (59 Natives and 22 Deuterated) were purchased from Wellington (Ontario, Canada), Chiron AS (Trondheim, Norway), Neochema (Darmstadt, Germany), LGC (Manchester, US) and HPC Standards (Cunnersdorf, Germany). More details regarding names and CAS numbers of the considered PFAS are presented in Supplementary Information 2 (SI 2). The Milli-Q water used in the CIC system was produced by a Milli-Q system A10 from Sartorius (Merck, Darmstadt, Germany). Ultrapure water (HPLC grade) and methanol (optima LC-MS grade) were purchased from Fisher Chemical (France). Ammonium acetate (purity 99 %) and glacial acetic acid (purity 99 %) were purchased from Merck (Darmstadt, Germany), ammonia solution (25 %, analytical reagent grade) was purchased from Fisher Scientific (France). The sodium fluoride solution (NaF, ACS reagent, ≥ 99 %) was purchased from Merck (Darmstadt, Germany). The 4-fluorobenzoic acid (AFB) solution (200 μgF.L^{-1}) was purchased from Neochema (Darmstadt, Germany). Pre-packaged activated carbon columns (AOX Pack / Premium Pack) and combustion vessels are from Enviroscience (Dusseldorf, Germany). The humic acid (ref: 041747.14) was purchased from Thermofisher Scientific (Darmstadt, Germany). Glass fiber filter (Acrodisc, Syringe Filter, 25 mm, 1 μm) used for filtration of leachate were purchased from Waters (Guyancourt, France).

2.3. Chemical analyses

2.3.1. LC-MS/MS analyses

This method was developed in the laboratory (*publication in prep)* and include 56 PFAS from different chemical families (C_3 to C_{20}) in a single analytical method. The method is inspired from previously published methods by Munoz et al. in 2018 and 2022. Additional and different PFAS are considered in the present study compared to Munoz et al. (2018, 2022). The instrument consisted of an Acquity I-Class Waters® UPLC chain coupled to a Xevo TQXs Waters® tandem mass spectrometer in multiple reaction monitoring (MRM) mode. The chromatographic separation was performed with a BEH C18 column (2.1 mm × 100 mm, 1.7 μm) Waters (France) heated at 35 °C. The delay C18 column (isolator column 50 × 2.1 mm) Waters (France) was used to avoid PFAS contamination from the chromatographic system. The instrumental limit of quantification is ranging from 2 to 10 ng/L for 54 PFAS compounds and 100 ng/L for 2 other compounds (i.e. 6:2FTCA and 8:2 FTCA). Injection volume was 10 μL and the mobile phase was a mixture of 2 mM Ammonium Acetate in H_2O (A) and 2 mM Ammonium Acetate in MeOH (B) at a 0.3 mL/min flow. The gradient elution started with 100 % A, and gradually changed up to 100 % B within 23 min. This ratio was kept for 4 min and then reversed into the initial conditions for 3 min. The ionisation mode used was electrospray. The source conditions were set as the following: desolvation temperature 500 °C, desolvation gas flow 1100 L/Hr, cone gas flow 150 L/Hr, capillary voltage −1000 V. Quantitative analysis is carried out using internal standards. Samples (extract from solid or water) were prepared to obtain a final ratio of 20/80 *v*/v; water/methanol; 0.3 % acetic acid before analysis.

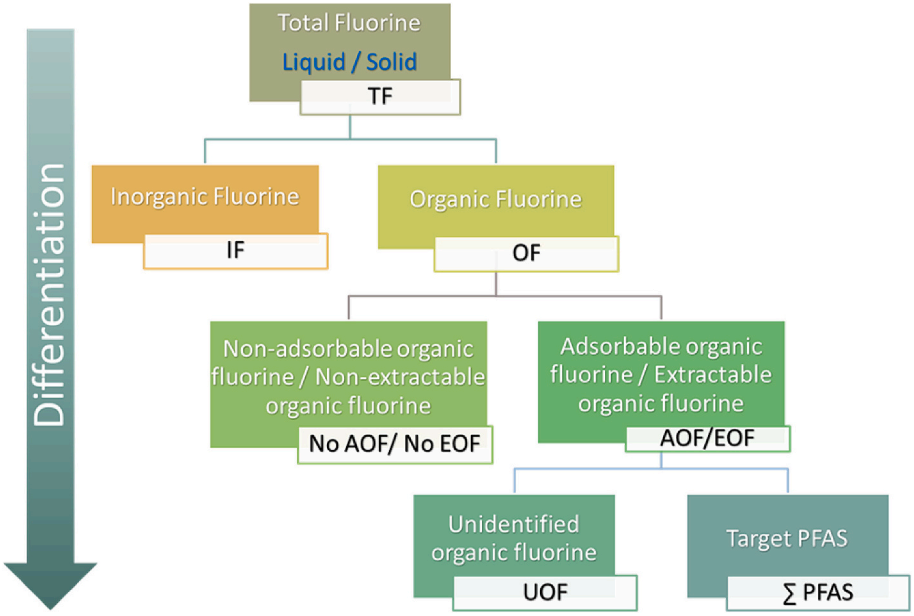

Fig. 1. Overview of the different fluorine chemical species according to their inorganic or organic character as well as their adsorptibility or extractability features of different matrices (liquid or solid) (Modified from Aro et al., 2021a, 2021b).

2.3.2. Total organic fluorine determination by IC methods

The analytical system is constituted of an ASC-2700LS liquid auto sampler, an ABC-210 automatic boat controller, an HF-210 horizontal oven and a GA-211 sample absorption unit, coupled to an ICS 6000 ion chromatography unit (Thermo Scientific). In the case of AOF, samples are pre-concentrated on activated carbon columns using the 5-channel AD enrichment module, all from Envirosciences (Dusseldorf, Germany). Different types of analysis are summarized in Fig. 2.

Ion chromatography (IC) allows fluoride analysis from the fluorine content of the sample. Direct combustion of samples (100 μg or 100 μL) before analysis provides total fluorine (TF) content, while direct injection in the IC provides IF measurement. The determination of organic fluorine is possible after previous sample preparation such as solvent extraction (for EOF) or solid phase extraction (for AOF). Details on the operating conditions are described in the supplementary materials file (SI 3 & SI 4). Briefly, combustion takes place according to the parameters shown in SI 3 & 4. After fluoride absorption in 10 mL of water, 5 mL are injected in the AS 20 column at a flow rate of 0.250 $mL.min^{-1}$.

For EOF, the selected protocol for solid samples is an extraction of 1 g of dry solid with 3 consecutive extraction steps: 10 mL of solvent, ultrasonication for 20 min, centrifugation for 5 min (4612 g) and transfer into a polypropylene 50 mL centrifuge tube. The 3 solvents were MeOH with 10 mM NH_4OH, MeOH with 100 mM CH_3COONH_4 and 10 mL MeOH. The three extracts were combined. An aliquot volume of 10 mL is reduced under nitrogen to 1 mL. One hundred microliter is collected and analysed by CIC to determine EOF.

DOC was measured for liquid sample characterisation using the "CELLULOSE" method outlined in NF EN 1484 standard. In a reactor operating at 97 °C, a strongly oxidising mixture (K_2SO_4) is added to the acidified sample. The CO_2 formed is transferred to the 1010 OI-ANALYTICAL carbon analyser by an inert gas.

2.3.3. Validation of the different parameters for the AOF and EOF methods

To assess differences between IF and OF for IC calibration, two calibrations ranging from 0.005 $mgF.L^{-1}$ to 2.5 $mgF.L^{-1}$ for organic fluorine as 4-fluorobenzoic Acid (FBA) and 0.005 $mgF.L^{-1}$ to 10 $mgF.L^{-1}$ for IF as NaF were compared.

To assess the impact of pH on solid phase extraction (SPE) for AOF preparation step, an ultrapure water solution was spiked with 0.020 $mgF.L^{-1}$ of organic fluorine (PFOA, PFOS, PFBS or AFFF Technical mix). The volume of the test sample was 100 mL. The pH of each solution was adjusted to pH 2 and pH 7 (details in SI4). This experiment aims to compare the effect of pH on the adsorption of perfluorinated compounds onto activated carbon.

To assess the impact of a washing step during SPE to eliminate IF, 0.020 $mgF.L^{-1}$ of organic fluorine (PFOA, PFOS, PFBS or AFFF Technical mix) as PFAS was together with 2 $mgF.L^{-1}$ of IF in ultrapure water solution adjusted to pH 7. The washing step was performed with 25 and 15 mL of 0.01 $mmol.L^{-1}$ $NaNO_3$ rinsing solution. Tests on real samples with high IF concentrations (up to 8 $mgF.L^{-1}$) have also been conducted.

To assess the impact of high DOC on AOF measurement, ultrapure water adjusted at pH 7 was spiked with different concentrations of humic acid up to 150 $mg.L^{-1}$. Tests on natural samples with very high DOC concentrations (up to 3000 $mg.L^{-1}$) have also been conducted.

Tests were conducted with different PFAS covering different molecular features: carbon chain length: a short one with PFBS (C_4) and a long one with PFOS (C_8); chemical groups: carboxylic (PFOA) and sulfonic (PFOS) and a technical mix with an aqueous film forming foam (AFFF) containing mostly 6:2 FTSA and 6:2 FTAB. The ultra-short-chain PFAS have been identified as a major challenge, but the authors did not analyse PFAS below C_4.

For some wastewater samples, the effects of the presence of high-suspended particles can be significant as PFAS can be sorbed on suspended particle matter (SPM), which is why the impact of SPM has been studied. To reduce the concentration of SPM, two approaches are possible: dilution or centrifugation. Dilution could release adsorbed PFAS, while centrifugation would eliminate them with SPM. For that, a real sample WWTP Influent 1 (SPM 309 $mg.L^{-1}$) was selected for performing this test. The sample was directly analysed in the first condition; in the second one diluted 3 times with ultrapure water before centrifugation (the supernatant was then analysed); and centrifuged followed by 3 times dilution of the supernatant with HPLC water in the third. The set of three results has been compared.

For more solid samples like sewage sludge and products derived from it, as TF includes both OF and IF, leaching tests were performed to measure IF contribution. One gram of solid sample is mixed with 1 mL of 0.5 M $NaNO_3$ vortex for 30 s and filtered through a glass filter. The final volume (≈ 1 mL) was diluted to a volume of 5 mL, and then injected into the IC.

To assess the relevance of the different developed methods, application to real samples and comparison with PFAS target analysis were conducted. For liquid matrices, TOF, AOF and LC-MS/MS (56 targeted PFAS compounds) analysis were compared for the same sample. The TOF value was estimated by deducting the measured IF from the

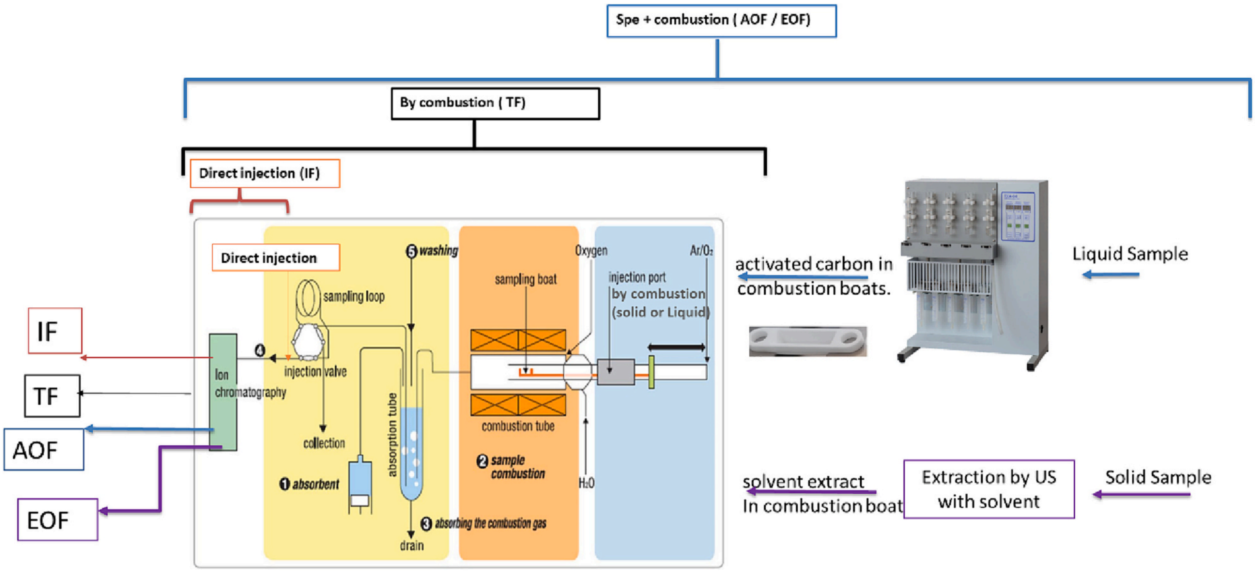

Fig. 2. Operating principle of the CIC and analysis processes inspired by Thermo Scientific application n°73481 (US is ultrasonication).

measured TF. These tests were carried out on different samples (effluent, influent, landfill leachate, treated landfill leachate, ground water) with varying SPM, DOC and IF contents (see SI 5). For solid matrices, the comparison was done between TF (100 mg), EOF and LC-MS/MS targeted analysis. EOF and LC-MS/MS analyses are obtained on the same extract. These tests are carried out on different samples of various types (sludge, fertilisers and intermediates in the recovery process, see SI 6).

2.3.4. *Quality assurance*

Calibration controls were performed for each analytical run. The 20 μgF.L^{-1} (as IF) calibration level is used in each sequence as a quality control (QC) of the reference calibration range used for several analytical runs. Envirosciences, activated carbon and combustion vessel blanks were routinely performed between each analytical run. The limit of quantification (LOQ) of each method was calculated as the average concentration measured in blank extracts plus 10 times its standard deviation. For LC-MS/MS analyses, the controls for the procedural and analytical blanks are integrated into each series of analyses and are PFAS free.

2.3.5. *Data processing*

The program Chromeleon or MassLynx, as applicable, immediately incorporates concentration and dilution parameters. In order to compare target analysis with organic fluorine content, PFAS concentrations are converted to fluorine equivalents based on the percentage (%) of fluorine for every compound (Molar mass based). The following formula has been applied:

$$\text{Total } [\text{F}] = \text{Sum of } ([\text{PFAS}] \times \%\text{F}) \quad (1)$$

3. Results & discussion

3.1. *IF and OF calibration*

When the calibration curves for IF and OF are compared, there is no significant difference (see SI 7). These results differ from those obtained by Aro et al. (2021b) who showed that in the same concentration range, there is a significant difference regarding the analytical response for OF and IF by a factor of 0.3. When increasing to 10 mg F.L^{-1}, the IF calibration curve still correlates well with the OF calibration curve. Quality control solutions of PFOA, PFOS, PFBS and AFFF analysed in this IF range confirmed the correct quantification. Therefore, an IF or OF calibration can invariably be used to calibrate the CIC using a polynomial calibration curve.

3.2. *Optimising the extraction methods*

3.2.1. *AOF for liquid samples*

3.2.1.1. SPE conditions (pH and washing step). When comparing the effect of pH (2 vs 7) on the adsorption of perfluorinated compounds onto activated carbon in the absence of inorganic fluorine, pH 7 shows better performance. The sorption efficiency of organic fluorine onto activated carbon is impacted by pH variation, as shown in Fig. 3.

In order to avoid an overestimation of the organic fluorine concentration, the IF should be washed out from the activated carbon, as CIC analysis do not allow to discriminate the different types of fluorine after combustion. The efficiency of the washing solution volume was tested for different PFAS carbon chain lengths and different chemical functions. When comparing the results with 25 mL and 15 mL washing solution, the two volumes showed equivalent results with no particular loss of PFAS, including short chain compounds (i.e. perfluorobutane sulfonic acid (PFBS)). These results are comparable to those reported by Forster et al. (2023). The washing method assessment on a real sample containing a high concentration of IF (7.8 mgF.L^{-1}) showed that a washing solution volume of 15 mL is effective (Fig. 4), showing same results on three (3) different levels of sample dilution (i.e. no overestimation due to presence of IF). Additionally, Fig. 4 demonstrates that the AOF performs well for individual solutions spiked with organic fluorine (i.e. PFBS, PFOS, PFOA and AFFF). These results are similar to the ones reported in the draft of ISO 18127 standard, that does not propose acidification as for other AOX (Cl, Br, etc.).

3.2.1.2. Impact of concentration of dissolved organic carbon (DOC). The first test performed with humic acid did not show any impact on the AOF measurements up to 150 mgC.L^{-1} DOC. The same process was applied to two real samples (with DOC concentrations of 2135 and 3167 mgC.L^{-1}), and the high DOC concentration resulted in a 2 to 4-fold signal extinction, respectively (Fig. 5). This is not very high compared with the increase in DOC concentration, which is 14 to 21 times greater than the maximum concentration tested with humic acid. However, it confirms the necessity of diluting liquid samples containing high concentrations of DOC.

Considering the influence of sample pre-treatment in case of the presence of high SPM content, the results showed that the variability in AOF quantification was below 10 %, whatever the protocol, which is not significant. For this liquid sample (WWTP Influent 1, see SI 1), dilution before or after centrifugation had no statistically significant difference on AOF measurement. However, the fact that the results for these two conditions are also similar to those for the direct sample shows that there

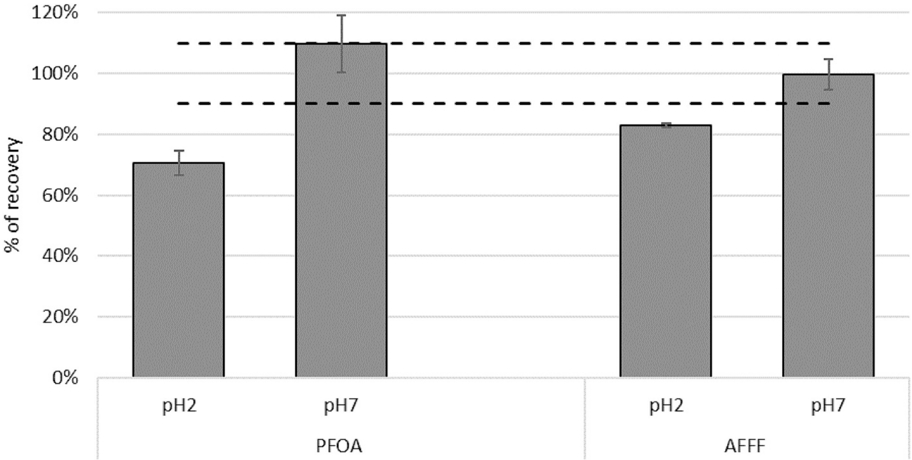

Fig. 3. Impact of pH variation on the adsorption mechanism of Organic Fluorine onto activated carbon ($n = 3$). 90 % and 110 % is the acceptability limits of extraction efficiencies.

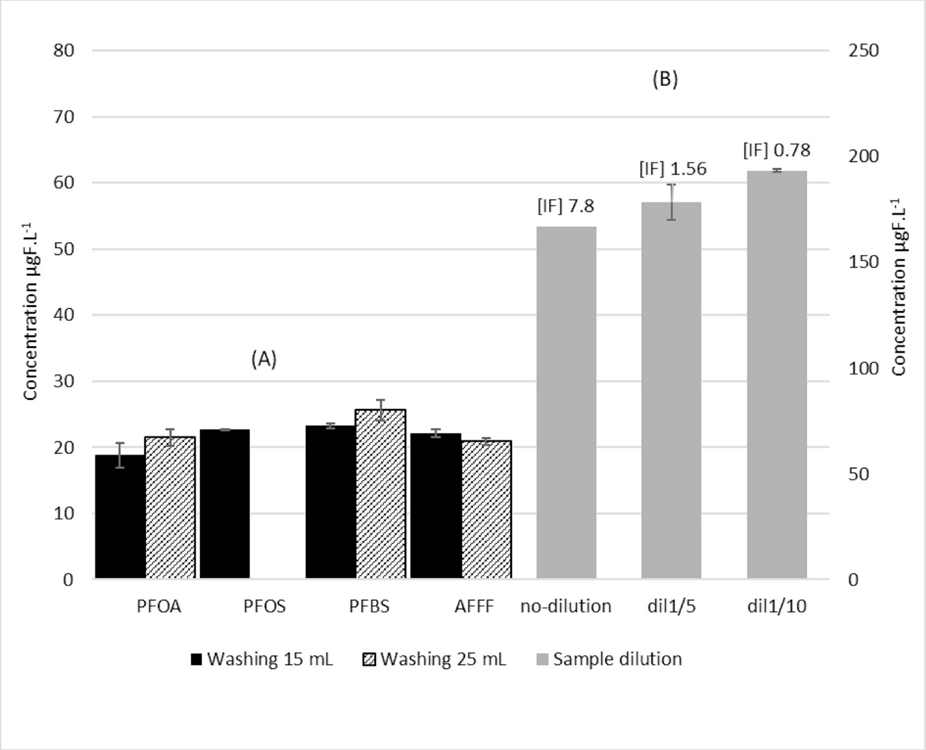

Fig. 4. (A) Measured concentration of AOF in spiked water with different PFAS expressed in µgF.L^{-1} depending on washing volume (n = 3). (B) Efficiency of washing step on real liquid sample analysed by AOF at 3 levels of dilution (results are corrected by the dilution factor). [IF] concentration in each sample is expressed in mg F. L^{-1}. (Only washing 15 mL for PFOS are realise).

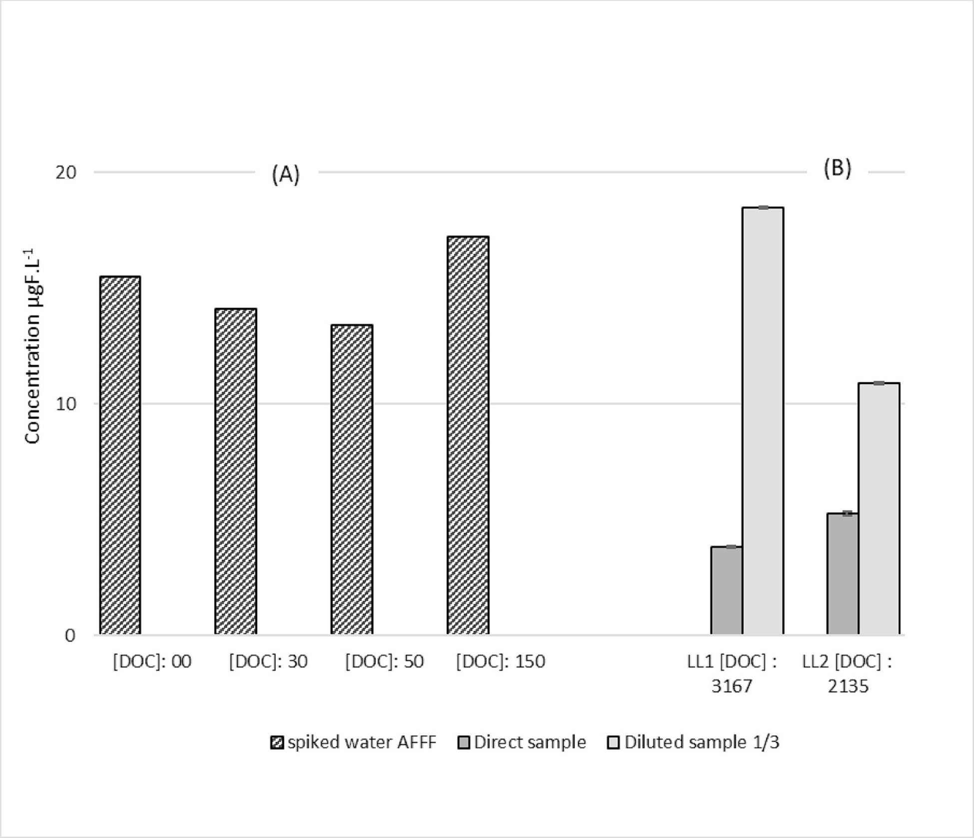

Fig. 5. (A) Measured concentration of AOF in spiked water with AFFF mix, expressed in µgF.L^{-1} depending on [DOC] ($n = 1$). (B) Measured concentrations of AOF in landfill leachates (LL1 and LL2) before (direct) and after dilution. [DOC] indicated below each value (for direct sample) is expressed in mgC.L^{-1}.

is no contribution of organic fluorine by the SPM, which explains the inconclusive nature of the experiment. New tests should therefore be carried out with different samples.

3.2.2. Analysis on solids

Analysis of IF in the leachable fraction highlights very low concentrations. For example, in the sample "SS Ash" low IF concentration was measured (0.2 mgF.kg^{-1}) compared with TF (661.5 mgF.kg^{-1}), that can be considered insignificant. Leachability of all IF fractions is not guaranteed by the selected protocol. In parallel, the requirement to dilute the liquid fraction (1 mL) for analysis (5 mL) results in an enhancement of the LOQ to 0.025 mgF.kg^{-1}, which can make low concentrations undetectable. Considering these results, we have chosen to consider that TF and TOF were equivalent in all experiments.

3.3. Quality assurance

To ensure the quality of the analytical work several blanks were analysed. A protocol for cleaning the combustion-absorption tube of the CIC was carried out before each series of analyses. Particular attention was paid to the memory effect after eluting a highly concentrated sample, which requires a blank analysis after each sample. The addition of a systematic blank afterwards eliminates the residual effect of high fluoride concentrations.

Multiple assays on the analysis of individual consumables (reused boat, new boat, activated carbon) have shown that contamination level for the analytical parts is $<0.21 \pm 0.06$ µgF.L^{-1} for combustion boat and 0.47 ± 0.12 µgF.L^{-1} for entire process (combustion boat + activated carbon).

Similarly, multiple tests of AOF blanks including entire protocol (extraction and analysis) before and after real samples were carried out with HPLC water. They demonstrated excellent repeatability (<12 %, $n = 11$) and good control of residual contamination (by cleaning enrichment module after each sample elution) leading to a background level of fluoride of 0.88 ± 0.11 µgF.L^{-1}, called "procedural blank" which constrains the limits of quantification (LOQ) for the different measurements.

Considering LOQ from apparatus sensitivity (5 µgF.L^{-1}) and analytical parameters of each method, theoretical LOQ for AOF will be 0.5 µgF.L^{-1} for 100 mL sample, 500 µgF.kg^{-1} for TF (sample mass of 100 mg) and 500 µgF.L^{-1} for EOF extract injected (sample volume of 100 µL).

For AOF, calculation of LOQ based on residual contamination leads to 1.98 µgF.L^{-1}. Then the LOQ set as 2 µgF.L^{-1} for 100 mL sample is therefore driven by the system blank. For TF and EOF, the method blank value was 136 ± 29 µgF.kg^{-1}, leading to a LOQ of 500 µgF.kg^{-1} for TF (sample 100 mg) and 500 µgF.L^{-1} for EOF (sample 100 µL extract injected). The LOQ for IF in the leachate from solid is 0.025 mgF.L^{-1}.

3.4. Comparison of information by method

3.4.1. Liquid matrices

For liquid samples, IF was determined by direct injection into the IC. TF was used to calculate TOF by deducting measured IF from TF. Fig. 6 presents the comparison between TOF and AOF for liquid samples. The proportion of TOF explained by AOF is still low, with a high variability between analysed samples. From 1 % to 23 % of TOF can be explained by the AOF. These results are comparable to those of Gehrenkemper et al. (2021), Han et al. (2021), von Abercron et al. (2019).

The difference between TOF and AOF could be due to the ultrashort chain PFAS, such as trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA) or trifluoromethane sulfonic acid (TFMS) which are poorly adsorbed onto activated carbon, about 9 % according to (Pan and Helbling, 2023). These ultrashort chain PFAS are used in industry or are generated from the degradation of longer chain PFAS in WWTP, or in the environment (Wu et al., 2022). Other compounds such as fluorinated ionic liquids can also explain the gap between AOF and TOF (Neuwald et al., 2020).

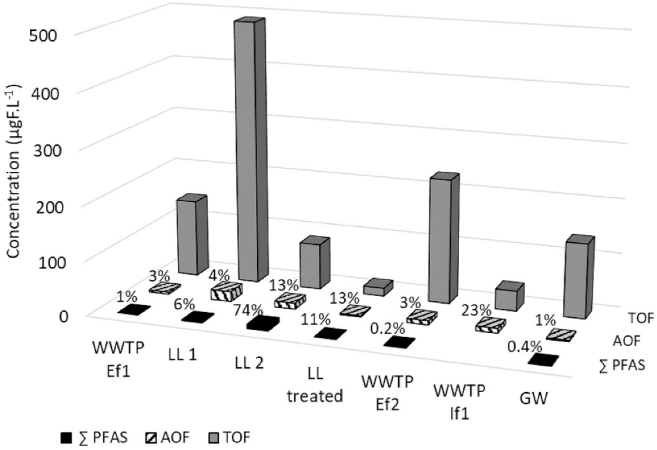

Fig. 6. Comparison between TOF, AOF and ∑PFAS analysed by LC-MS/MS expressed as µgF.L^{-1} on liquid samples. (LL: Landfill Leachate; Ef: Effluent; If: Influent; GW: Ground water). Percentages associated correspond, for AOF, to the percentage of TOF explained by AOF and for ∑PFAS, the percentage of AOF explained by ∑PFAS.

Considering the targeted PFAS quantification by LC-MS/MS, Fig. 6 highlights the comparison between AOF and sum of PFAS expressed in F. Except for one sample where LC-MS/MS explained 74 % of the F contained in AOF, all the others were explained from 0 % to 11 %.

The difference between AOF and the PFAS expressed in fluorine is due to unidentified PFAS, which are not considered by the targeted analysis methods. Even if 56 PFAS considered as the most relevant and abundant were analysed, the results show that other PFAS are likely present in the sample. Other fluorinated compounds can also be sorbed onto activated carbon that are not PFAS, making interpretation more complex.

3.4.2. Solid matrices

Fig. 7 shows high variability between samples where 0.1 % to 2 % of the TF can be explained by the EOF. The gap between TF and EOF could be attributed to the loss of volatile PFAS (e.g. fluorotelomer alcohol, FTOH) during evaporation's step, as demonstrated by Pan and Helbling (2023), Weed et al. (2022). It may also be due to the presence of fluorinated organic compounds that are strongly adsorbed onto the SPM and then not correctly extracted by the analytical method used (Koch et al., 2020).

On real solid samples, the same extract has been used for LC-MS/MS and CIC measurements. The Fig. 7 shows the comparison between EOF and sum PFAS expressed in µgF.L^{-1}. Except for one sample where LC-MS/MS explained 20 % of the fluorine contained in the EOF, all the others were explained from 0.003 % to 5 %. These results are comparable to those of Aro et al. (2021a), Herzke et al. (2022), Kärrman et al. (2021) and Swedish Chemicals Agency (2021).

The difference between the EOF and the sum of PFAS can be explained, as for AOF, by occurrence of unknown PFAS, or other fluorinated organic compounds not considered in target analysis.

4. Practical applicability of the developed methods

The present results raise the question of whether AOF and EOF are effective parameters for assessing the occurrence of global PFAS contamination. Because the AOF and EOF are not exhaustive, they do not accurately represent the fluorine contamination determined by TOF or TF. The comparison demonstrates that there is still a large gap between AOF or EOF and TOF. AOF and EOF do not take into account all PFAS (such as ultra-short chain, volatile, non-adsorbable…). Especially

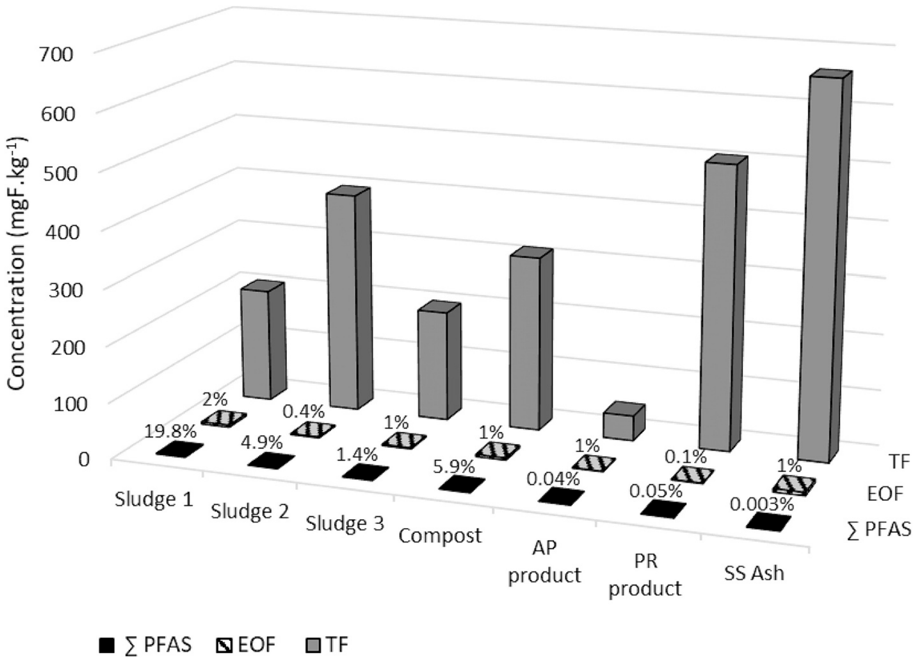

Fig. 7. Comparison between TOF, EOF and ∑PFAS analysed by LC-MS/MS expressed as µgF.kg^{-1} on solid samples. (AP: Ammonium phosphate; PR: Phosphorus Recovery; SS: Sewage Sludge). Percentages associated correspond for EOF, to the percentage of TF explained by EOF and for ∑PFAS, to the percentage of EOF explained by ∑PFAS.

because TF involves the combustion of all fluorinated compounds without discrimination, these parameters include organic fluorinated compounds other than those covered by the definition of PFAS (OECD, 2021). In parallel for solids, a non-leachable IF fraction can occur that lead to the overestimation of TOF.

As the AOF does not integer all PFAS, other solid phase extraction (SPE) methods can be carried out using other polymer cartridges and/or activated carbon. These methods can favour the inclusion of a greater number of compounds and fill the gaps between TOF/AOF and TF/EOF measurements (Koch et al., 2020; Ruyle et al., 2023).

As the comparison of CIC and LC-MS/MS analyses highlights the important part of unknown compounds, other analytical approaches can be considered.

Total Oxidisable Precursors Assay (TOP Assay) developed over several years by (Houtz et al., 2013) has been applied in a large variety of applications. By including this method, the gap between the global CIC parameters and LC-MS/MS can be better explained (Al Amin et al., 2023; Antell et al., 2023; Ateia et al., 2023; Dauchy et al., 2017; Janda et al., 2019; Tsou et al., 2023).

Another source of information can be non-target analysis (HRMS) to identify fluorinated compounds not yet included in target analysis (Al Amin et al., 2023; Bangma et al., 2023; Bugsel and Zwiener, 2020; Charbonnet et al., 2022)Therefore, it is necessary to combine several analytical approaches (CIC, LC-MS/MS, LC-HRMS) to obtain a comprehensive screening of PFAS (Aro et al., 2021a; Gehrenkemper et al., 2021; Koch et al., 2020; Wang et al., 2016). Winchell et al. (2021) proposes approaches to integrate different analytical workflows.

5. Conclusion

To provide more accurate sustainable remediation of emerging contaminants and reduce the spread of PFAS in the environment to achieve zero pollution targets, this paper developed and compared different analytical approaches for monitoring PFAS in complex sample matrices. Robust and reliable methods have been developed for both liquid and solid matrices. In particular, AOF method demonstrates a good activated carbon adsorption efficiency for selected PFAS, as well as robustness with both high DOC and SPM concentrations. It also shows an effective removal of IF in complex liquid matrices containing up to 8 mgF.L^{-1}. All tested methods show good reproducibility. For AOF, the objective of a LOQ of 2 µgF.L^{-1} is reached but cannot be lowered because of the procedural blank.

The present study compares measurements of TOF, AOF and the amount of organic fluorine explained by targeted analysis of complex liquid samples. For complex solid samples, the same comparison was performed on measurements of TF, EOF and the amount of organic fluorine explained by targeted analysis.

When considering the literature review and the results of the present study the following conclusions can be drawn:

The AOF and EOF measured concentrations are low compared to TOF/TF measured concentrations. Therefore, there is currently no method that responds alone to the “total PFAS” parameter.

The target analysis of 56 PFAS by LC-MS/MS allow to quantify a very small fraction of the fluorinated compounds contained in AOF/EOF, depending on the complex matrices studied. The ultra-short-chain PFAS have been identified as a major challenge and it would be important for future studies to take them into account in order to assess their potential contribution.

The difficulty of discriminating the IF content is a limitation for determining the real TOF fraction.

In view of the present results, these validated analytical methods will be implemented to study the fate of PFAS in WWTP output streams and will form part of an overall robust monitoring strategy for determining the PFAS transfer factors from sewage sludge to different recovered products including fertilisers or organic amendments.

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CRediT authorship contribution statement

Babatoundé I.T. Idjaton: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Anne Togola:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization. **Jean Philippe Ghestem:** Writing – review & editing, Validation, Methodology. **Laura Kastler:** Resources, Data curation. **Sébastien Bristeau:** Resources, Conceptualization. **Mariska Ronteltap:** Writing – review & editing, Data curation. **Stéfan Colombano:** Writing – review & editing, Methodology, Data curation. **Nicolas Devau:** Methodology, Conceptualization. **Julie Lions:** Project administration, Funding acquisition. **Eric D. van Hullebusch:** Writing – review & editing, Validation, Methodology, Investigation, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.172589.

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