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PROMISCES

Preventing **R**ecalcitrant **O**rganic **M**obile **I**ndustrial chemical**S** for **C**ircular **E**conomy in the soil-sediment-water **S**ystem

Start date of the project: **1st November 2021**

Duration: **42 months**

D3.5 - Report on the transfer factor of PFAS compounds from sewage sludge to recovered fertilizers in European WWTP

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Executive Summary

Wastewater treatment plants (WWTPs) can act as a substantial point source of per- and polyfluoroalkyl substances (PFAS) in the environment. However, limited detailed information is available on the distribution and transfer of PFAS in different WWTPs liquid and solid output streams.

This study investigates the presence and transformation of PFAS in sewage sludge and sludge-derived products using advanced analytical techniques, including combustion ion chromatography (CIC), targeted PFAS analysis, and the Total Oxidizable Precursor (TOP) Assay. Results showed that traditional methods, such as CIC-based extractable organic fluorine (EOF) and targeted PFAS analyses, account for only a small fraction of the total organic fluorine (TOF), indicating the presence of numerous unidentified fluorinated compounds. The TOP Assay revealed a significant increase in perfluoroalkyl carboxylic acids (PFCAs), confirming the presence of oxidizable precursors—especially in sludge and compost samples—while struvite fertilizer showed lower PFCA concentrations post-TOP, suggesting reduced precursor content.

Across various WWTP, certain PFAS, including 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) and perfluorooctane sulfonate (PFOS), were consistently detected in digested sludge, which emerged as a primary reservoir of PFAS. However, nutrient recovery processes, such as struvite precipitation, demonstrated high PFAS reduction efficiency—up to 99%—with minimal transfer of PFAS to the final fertilizer product. These results emphasize the importance of integrating non-targeted approaches, like the TOP Assay, for a more comprehensive assessment of PFAS presence and behavior and highlights nutrient recovery as a promising strategy for minimizing environmental and agricultural exposure to PFAS.

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List of abbreviations

AOF : adsorbable organic fluorine

CIC : Combustion Ion Chromatography

EOF : Extractable Organic Fluorine

IF : inorganic fluorine

LC-MS/MS : Liquid Chromatography–Tandem Mass Spectrometry

PFAS : Per- and Polyfluoroalkyl Substances

PFCAs : perfluorocarboxylic acids

PFOS : perfluorooctanesulfonic acid

PFSAs : Perfluorinated Sulfonic Acids.

TF : total fluorine

TOP Assay : Total Oxidizable Precursor Assay

WWTPs : Wastewater Treatment Plants

1 Introduction

Wastewater treatment plants (WWTPs) are recognized as significant sources of per- and polyfluoroalkyl substances (PFAS) in the environment. PFAS have been consistently detected in both liquid effluents and solid byproducts such as sewage sludge. These byproducts are often repurposed as soil amendments, potentially reintroducing PFAS into terrestrial ecosystems (Johnson, 2022). Among the detected compounds, perfluorooctanesulfonic acid (PFOS) is typically the most prevalent in solid matrices, with concentrations reaching up to ~13 ng/g, whereas perfluorobutanoic acid (PFBA) often dominates liquid samples, with levels up to ~53 ng/L (Ozelcaglayan et al., 2024).

Despite increasing awareness of PFAS contamination, comprehensive understanding of their physicochemical properties, environmental fate, and transformation mechanisms remains limited (Gobelius et al., 2023). This knowledge gap continues to hinder the development and optimization of effective remediation technologies.

WWTPs generally employ a multi-stage treatment process, comprising:

- Primary treatment: Physical processes (e.g., settling, filtration) to remove suspended solids.
- Secondary treatment: Biological degradation of dissolved organic matter by microbial communities.
- Tertiary treatment: Advanced filtration or biofiltration for the removal of residual nutrients such as nitrogen and phosphorus.
- Quaternary treatment: High-end technologies including membrane filtration, ozonation, or adsorption to target trace organic micropollutants.

The sludge generated from these treatment stages undergoes further processing, which may include anaerobic digestion, dewatering, composting, or nutrient recovery (e.g., extraction of ammonium and phosphate for fertilizer production). Emerging technologies such as hydrothermal liquefaction, and pyrolysis are currently being explored for their potential to degrade PFAS more effectively (Vogel et al., 2023; Sørmo et al., 2023; Yu et al., 2020; Oza et al., 2025).

Recent studies underscore the influence of specific treatment processes and PFAS properties on their behavior in WWTPs (Kim et al., 2022; Gobelius et al., 2023; Ozelcaglayan et al., 2024). Biological treatments, for instance, can transform PFAS precursors into short-chain perfluorocarboxylic acids (PFCAs), while longer-chain PFAS compounds tend to accumulate in sludge. Understanding these dynamics is essential for enhancing PFAS removal strategies.

This deliverable investigates the distribution and fate of per- and polyfluoroalkyl substances (PFAS) across various output streams from wastewater treatment plants (WWTPs), with a specific focus on sewage sludge, sewage sludge digestate, compost derived from sewage sludge, and recovered fertilizer products like struvite. While the treated effluent is not covered in this report, related findings can be found in the PhD thesis by Babatoundé Idjaton (2024). A key objective of this study is

to assess the transfer of PFAS during nutrient recovery processes, particularly when converting digested sludge into ammonium- and phosphate-based fertilizer as struvite.

Advanced analytical methods developed by Idjaton et al. (2024) have been applied, including:

- **Targeted LC-MS/MS analysis** for quantifying individual PFAS.
- **Total Oxidizable Precursor (TOP) assay** to detect and transform PFAS precursors into measurable perfluoroalkyl acids.
- **Combined LC-MS/MS and TOP assay** to assess precursor presence before and after oxidation.
- **Combustion Ion Chromatography (CIC)** for measuring Extractable Organic Fluorine (EOF), which represents total fluorine content, including unidentified PFAS.

These complementary techniques have been used to analyze real-world WWTP samples, enabling a deeper investigation into PFAS concentrations and transformation pathways in sludge-derived materials and fertilizer products.

2 Methodology

2.1 Sample description

2.1.1 Solid samples collected for TF, EOF and Target PFAS analyses comparison

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). The obtained results may be put into perspective with other methods such as targeted analyses (LC-MS/MS). In order to test this approach, Idjaton et al. (2024) have collected a range of different solid samples from WWTP with a particular focus on the by-products of sewage sludge as source of fertiliser (Table 1). These recovered by-products are produced at different steps of the valorisation process of a mix of sewage sludge and ash into fertilisers.

Table 1: List of different solid samples from WWTP and sewage sludge treatment/valorization units (Idjaton et al., 2024).

Types	Names	Abbreviations	Sources	Parameters determined on them
Solid samples	Sewage sludge 1		From WWTP 1	TF, EOF, Target PFAS
	Sewage sludge 2		From WWTP 2	TF, EOF, Target PFAS
	Sewage sludge 3		From WWTP 3 which treats urban wastewater	TF, EOF, Target PFAS
	Compost		From WWTP 4 which treats urban wastewater and compost the sludge	TF, EOF, Target PFAS
	Ammonium phosphate product	AP product	Produced at different steps of the sewage sludge valorisation/treatment process	TF, EOF, Target PFAS
	Phosphorus Recovery product	PR product		TF, EOF, Target PFAS
	Sewage Sludge Ash	SS Ash		TF, EOF, Target PFAS

The results on these samples are displayed and discussed in section 3.1

2.1.2 Solid samples collected for TOP assay optimization

The TOP (Total Oxidizable Precursor) Assay is increasingly employed as a sample pre-treatment step to provides a quantitative estimate of oxidizable precursors in a sample when paired with targeted analysis before and after the assay. In order to improve the TOP Assay method complex environmental matrices such as sewage sludge, sewage sludge compost and struvite were collected from different sources (Table 2).

Table 2: List of different solid samples from WWTP and sewage sludge treatment/valorization units (Idjaton et al., 2025).

Sample no.	Matrix	Type of samples	Origins /Remarks
1	Solid	Sludge	Municipal WWTP Sludge
2	Solid	Compost	Sludge valorisation product
3	Solid	Fertilizer	Struvite recovered from WWTP out streams

The results on these samples are displayed and discussed in section 3.2 and are fully detailed in Idjaton et al. (2025).

2.1.3 Solid samples collected from WWTP for global and targeted PFAS analyses of digested sludge and struvite.

Samples of WWTP digested sludge and struvite were collected from different WWTPs. The samples were supplied by various partners engaged in the PROMISCES project. Three WWTPs from different countries were studied. However, the samples from 2 WWTPs are presented in this deliverable. The list of samples that were collected is presented in Table 3. Samples were collected over a period of five (5) weeks. Two types of samples were collected from WWTP A (digested sludge and struvite) and only one type of sample has been collected from WWTP C (digested sludge) over a period of 5 weeks.

Table 3: List of samples collected from WWTP A and WWTP C.

Origin	Sampling site	Sample type	Sample (Output streams)	Week	Sample name
Country 1	WWTP A (Station A)	Solid	Digested sludge	1	Station A_DigestedSludge_1
Country 1	WWTP A (Station A)	Solid	Digested sludge	2	Station A_DigestedSludge_2
Country 1	WWTP A (Station A)	Solid	Digested sludge	3	Station A_DigestedSludge_3
Country 1	WWTP A (Station A)	Solid	Digested sludge	4	Station A_DigestedSludge_4
Country 1	WWTP A (Station A)	Solid	Digested sludge	5	Station A_DigestedSludge_5
Country 1	WWTP A (Station A)	Solid	Fertiliser (Struvite)	1	Station A_Struvite_1
Country 1	WWTP A (Station A)	Solid	Fertiliser (Struvite)	2	Station A_Struvite_2
Country 1	WWTP A (Station A)	Solid	Fertiliser (Struvite)	3	Station A_Struvite_3
Country 1	WWTP A (Station A)	Solid	Fertiliser (Struvite)	4	Station A_Struvite_4
Country 1	WWTP A (Station A)	Solid	Fertiliser (Struvite)	5	Station A_Struvite_5
Country 2	WWTP C (Station C)	Solid	Digested sludge	1	Station C DigestedSludge_1
Country 2	WWTP C (Station C)	Solid	Digested sludge	2	Station C DigestedSludge_2
Country 2	WWTP C (Station C)	Solid	Digested sludge	3	Station C DigestedSludge_3
Country 2	WWTP C (Station C)	Solid	Digested sludge	5	Station C DigestedSludge_5

Digested sewage sludge samples came from WWTP A and C. The fertiliser (struvite) samples produced from the digested sludge have been delivered only by WWTP A. The results on these samples are displayed and discussed in section 3.3.

2.2 Standards and reagents

A total of 80 PFAS standards (58 native and 22 deuterated) were obtained from various suppliers, including Wellington (Ontario, Canada), Chiron AS (Trondheim, Norway), Neochema (Darmstadt, Germany), LGC (Manchester, USA), and HPC Standards (Cunnersdorf, Germany). Detailed information on the PFAS, including their names and CAS numbers, is provided in Supplementary Information 2 (SI-2). Additional reagents used included sodium fluoride solution (NaF, ACS reagent, ≥99%) and potassium persulfate (99% purity), both sourced from Merck (Darmstadt, Germany). Sodium hydroxide and ammonia solution (25%, analytical reagent grade) were supplied by Fisher Scientific (Loughborough, UK). Ultrapure water (HPLC grade) and methanol (LC-MS Optima grade) were acquired from Fisher Chemical (France). Ammonium acetate (99% purity) and glacial acetic acid (99% purity) were also purchased from Merck. Milli-Q water used in the CIC system was generated using a Milli-Q A10 system from Sartorius (Merck, Darmstadt, Germany).

2.3 Chemical analyses

For the present study, solid samples were subjected to a 72-hour drying process at 35°C and subsequently ground to a particle size of 1 mm prior to extraction. The ground samples were then stored in a refrigerator maintained at a temperature of 5°C before being processed for further sample preparation and analysis.

2.3.1 LC-MS/MS analyses

The LC-MS/MS method used in this study was developed in-house and previously described by Idjaton et al. (2024). It allows for the simultaneous detection of 58 PFAS from various chemical families (ranging from C3 to C20) within a single analytical run. The instrumentation consisted of a Waters® Acquity I-Class UPLC system coupled to a Waters® Xevo TQXs tandem mass spectrometer, operated in multiple reaction monitoring (MRM) mode. Chromatographic separation was performed using a BEH C18 column (2.1 mm × 100 mm, 1.7 µm particle size), maintained at 35 °C and supplied by Waters (France). To prevent PFAS contamination from the chromatographic system, an isolator column (50 × 2.1 mm) from Waters (France) was installed.

The method achieved instrumental limits of quantification ranging from 2 to 10 ng/L for 56 PFAS compounds, and 100 ng/L for two additional compounds (6:2 FTCA and 8:2 FTCA). A 10 µL injection volume was used. The mobile phase consisted of 2 mM ammonium acetate in water (solvent A) and 2 mM ammonium acetate in methanol (solvent B), delivered at a flow rate of 0.3 mL/min. Gradient elution began with 100% A and gradually shifted to 100% B over 23 minutes, held for 4 minutes, and then returned to initial conditions over the following 3 minutes. Electrospray ionization was employed, with the source conditions set as follows: desolvation temperature at 500 °C, desolvation gas flow at 1100 L/h, cone gas flow at 150 L/h, and a capillary voltage of −1000 V.

Quantification was carried out using an internal standard approach. Sample extracts, prepared from either solid or aqueous matrices, were analyzed in a water/methanol solution (0.5% acetic acid) at a final volume ratio of 20:80 (v/v) for liquids, and in 100% methanol (0.5% acetic acid) for solids.

2.3.2 CIC analyses

These methods allow to analyse liquid and solid samples after some sample pre-treatment. The parameters measured by Combustion Ion Chromatography (CIC)—including total fluorine (TF), inorganic fluorine (IF), extractable organic fluorine (EOF), and adsorbable organic fluorine (AOF)—were established in the method developed by Idjaton et al. (2024). CIC analysis involves quantifying these four forms of fluorine. For TF and IF, the sample is first weighed and combusted, converting fluorine compounds into gaseous fluoride, which is then absorbed in Milli-Q water and analyzed via ion chromatography. In the case of IF, liquid samples can be directly injected into the ion chromatograph without combustion. EOF (Extractable Organic Fluorine) is measured by first isolating the organic compounds from the sample following the same detection process as for TF. To analyze AOF in liquid samples, the pH is adjusted to 7 ± 1, and the sample is passed through activated carbon cartridges that have been rinsed with 15 mL of ultrapure water containing 0.01 M $NaNO_3$, in order to remove residual inorganic fluorine. The detailed protocols are illustrated in Figure 1.

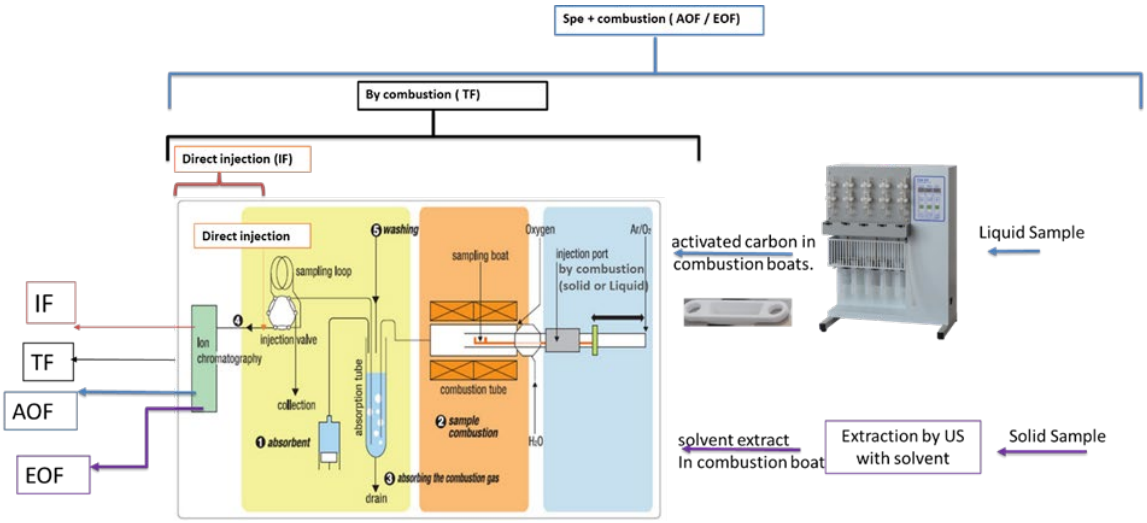

Figure 1: Operating principle of the CIC and analysis processes inspired by Thermo Scientific application n°73481 (US is ultrasonication).

2.3.3 Total Oxidizable Precursor Assay

The TOP (Total Oxidizable Precursor) assay was applied to both liquid and solid samples. For liquid samples, 2.5 mL was collected in 10 mL amber glass vials. The assay involved adding potassium persulfate (240 mM) and sodium hydroxide (600 mM) to the sample, followed by heating at 85 °C for six hours. After cooling in a water bath, the pH was adjusted using hydrochloric acid, and methanol was added. For vial preparation, 200 µL of the treated solution was mixed with 200 µL of methanol, 50 µL of deuterated standards (2 µg/L), and 50 µL of methanol containing 5% acetic acid, yielding a final volume of 500 µL in an 80/20 methanol/water mixture with 0.5% acetic acid. After homogenization and sedimentation, 300 µL of the supernatant was transferred to a clean tube for analysis.

For solid samples, 1 g of dried material was extracted following the method described by Idjaton et al. (2025), using 30 mL of solvent. The methanol extract was then concentrated to 3 mL. From this, 100 µL was used for direct analysis, while 200 µL was evaporated to near dryness and reconstituted with 2.5 mL of HPLC-grade water. The reconstituted solution was then subjected to the same TOP assay conditions as the liquid samples.

2.4 Quantification and characterization of PFAS

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. Figure 2 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.

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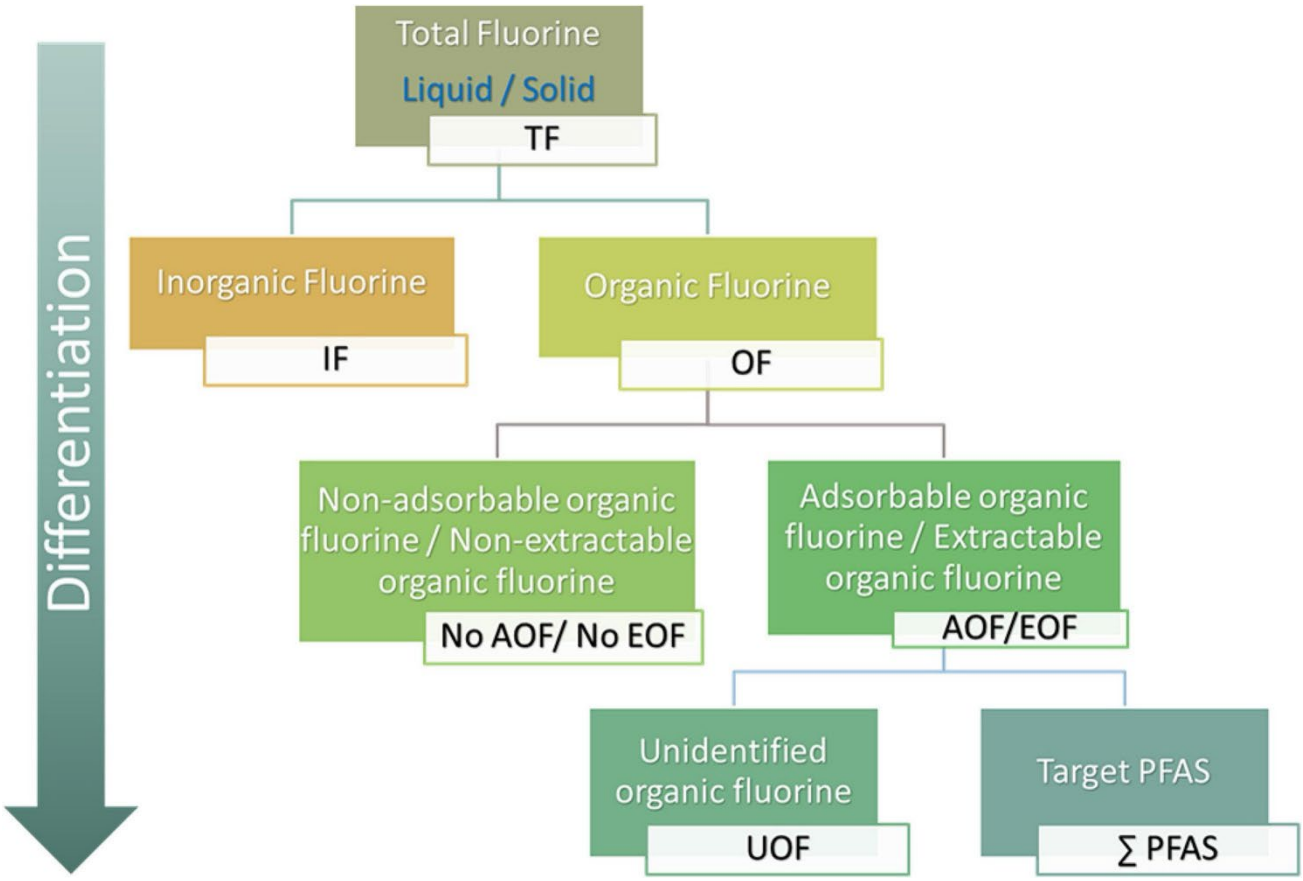

Figure 2: Overview of the different fluorine chemical species according to their inorganic or organic character as well as their adsorptibility or extractability features of different matrices (liquid or solid) (Idjaton et al. 2024)

Global fluorine parameters—including AOF, EOF, TF, and IF—are measured using CIC. For TOP assay, targeted PFAS analyses are conducted both before (To) and after (TOP) the oxidation process using HPLC-MS/MS.

Following quantification, the distribution of PFAS identified through targeted analysis was evaluated for each sample type and WWTP. The compounds detected at least once were then grouped based on the number of carbon atoms in their main chain, allowing comparison of PFAS profiles typically associated with either liquid or solid matrices. Finally, the targeted analysis results were compared with those from the global fluorine measurements to highlight the relevance and potential complementarity of the two analytical approaches.

2.5 Quality assurance and data processing

For both CIC and LC-MS/MS analyses, system blanks, calibration standards, and control standards were included throughout the measurement sequence. A full calibration range was analyzed at both the beginning and end of each analytical run. Additionally, control standards at 20% and 80% of the instrument's linear range were analyzed every 20 samples to ensure accuracy and consistency. The limit of quantification (LOQ) was defined as the lowest concentration at which a compound could be reliably quantified with acceptable uncertainty, under the method conditions described in Babatoundé Idjaton PhD thesis.

Quality control of the TOP Assay involved the use of a deuterated internal standard—commonly EI 8:2 FTSA—to verify the completeness of the oxidation reaction. Data integration for concentration and dilution calculations was carried out using either the Chromeleon or MassLynx software, depending on the instrument used.

3 Results and discussion

3.1 PFAS in sewage sludge and sludge products

The objective of this section is to demonstrate how measurements of Total Fluorine (TF) and Extractable Organic Fluorine (EOF) compare with targeted PFAS analyses. The measurements were applied to real-world samples and evaluated against targeted PFAS analysis to assess their relevance for better understanding the sources and fate of PFAS in wastewater treatment plants (WWTPs). PFAS were analyzed in various complex environmental solid matrices—including sewage sludge, compost derived from sewage sludge, phosphorus based fertilizer products made from sewage sludge, and ashes from sewage sludge incinerators—using CIC to measure EOF as an indicator of total PFAS content. Full methodological details can be found in the work published by Idjaton et al. (2024).

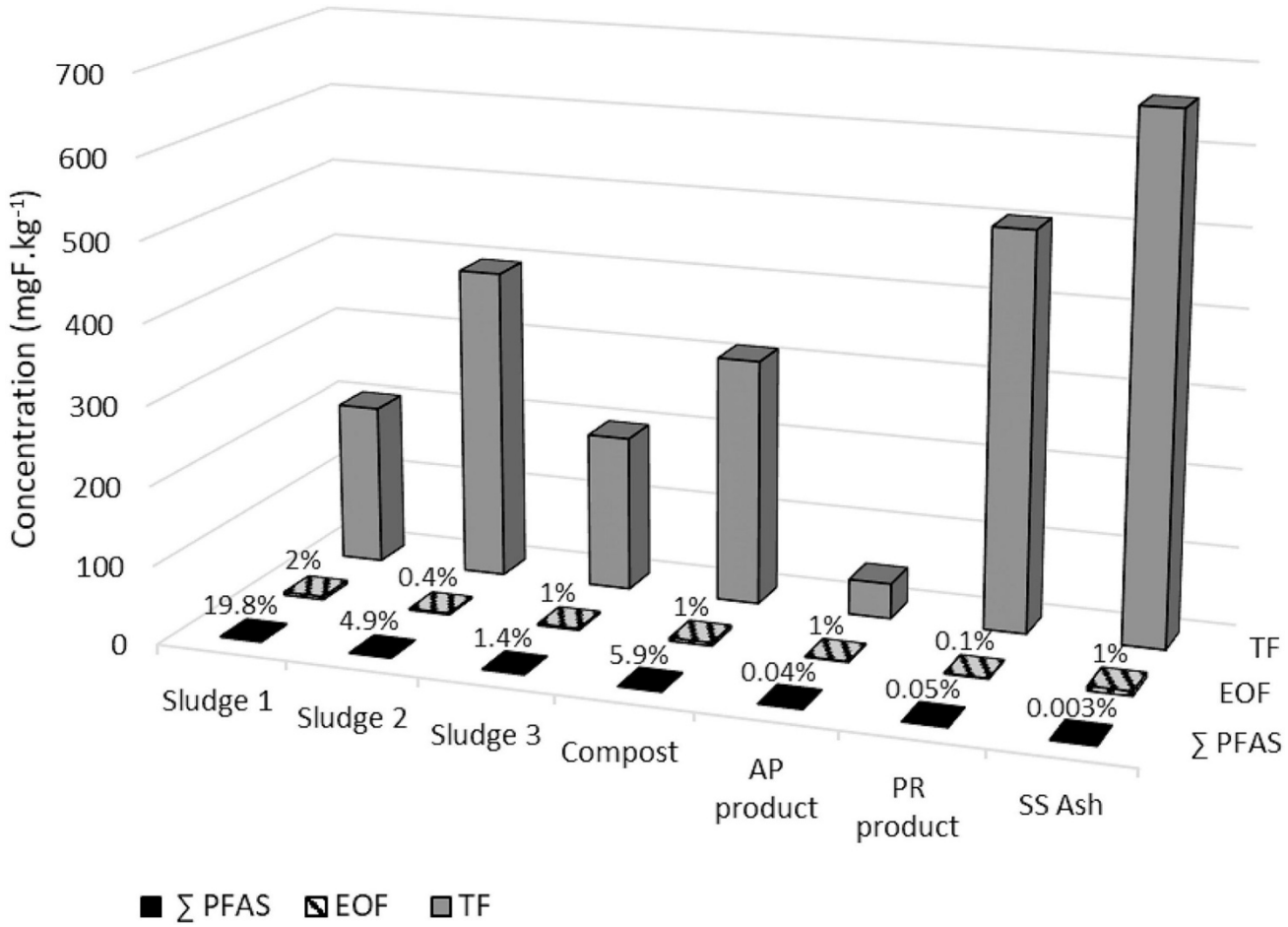

Figure 3 Comparison between TOF, EOF and ∑PFAS analysed by LC-MS/MS expressed as µgF.kg^{-1} on solid samples. (AP: Ammonium phosphate; PR: Phosphorus Recovery; SS: Sewage Sludge). Percentages associated correspond for EOF, to the percentage of TF explained by EOF and for ∑PFAS, to the percentage of EOF explained by ∑PFAS (Idjaton et al., 2024).

It was found that EOF accounted for only a small portion of TOF, ranging from 0.1% to 2%. The sum of PFAS (expressed as fluorine from the targeted analyses) explained only 0.003% to 5% of the TOF (Figure 3). These results suggest that some fluorinated compounds in solid matrices are not captured by the EOF method due to limited extractability or loss through volatilization. Even if the CIC-based EOF method is not fully efficient as a proxy for total PFAS content in solid environmental samples, it can still be useful for understanding PFAS sources and environmental behaviour. Additionally, the targeted PFAS analyses, which include the quantification of regulated PFAS compounds, only account for a very small proportion of the total organic fluorine content in the studied samples.

3.2 Comparison pre-TOP and post-TOP Assay analyses in sewage sludge and sludge products

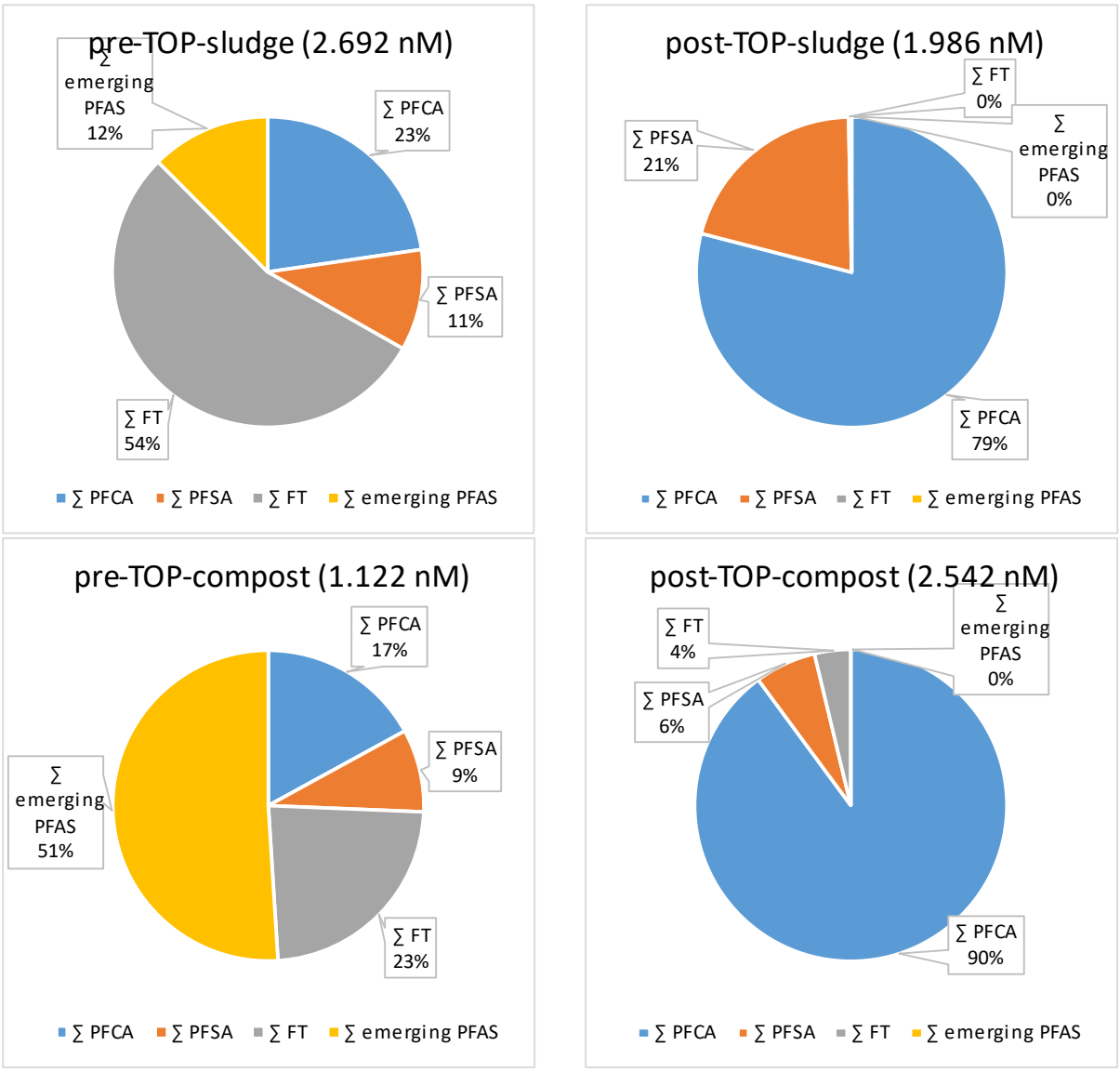

Figure 4 Comparison of the distribution of the sum of PFAS by family before (pre-TOP) and after (post-TOP) expressed in molar concentration (sample volume 5 mL) for the complex solids (sewage sludge, compost) tested. (∑FT = sum of fluorotelomers).

Figure 4 illustrates the molar proportion of PFAS classes in digested sewage sludge and compost samples, comparing results before and after the TOP assay (pre- and post-TOP). A summary of the molar proportions for all solid samples is presented in Table 4. Notably, the proportion of perfluoroalkyl carboxylic acids (PFCAs) increased post-TOP across all solid samples, following the sequence: sewage sludge < compost < fertilizer (struvite). However, despite the higher PFCA proportion in post-TOP struvite, the absolute molar concentration was over 99% lower than that of sludge (Table 4). This suggests that struvite recovery processes significantly reduce PFAS and precursor concentrations. Only 6:2 FTSA was quantified pre-TOP and only PFOA post-TOP in fertilizer samples, further indicating the impact of recovery processes on PFAS profiles. Across all solid

samples, the molar concentrations of PFCAs increased after oxidation, with increases ranging from 157% to 1856%. Specifically, sludge and compost showed increases of 45% and 67%, respectively, while the fertilizer sample exhibited a 100% decrease. Fluorotelomers and other PFAS precursors—such as 7:3 FTCA and 6:2 FTAB—generally showed a 100% reduction post-TOP, except in the compost sample, where the sum of fluorotelomers remained at 64%. The residual 6:2 FTSA detected in the compost post-TOP may represent an intermediate oxidation product derived from other precursors. These findings highlight the effectiveness of the TOP assay in revealing the presence of unknown PFAS precursors in complex solid environmental samples.

Table 4: Sum of molar concentration for pre-TOP and post-TOP analysis, per chemical group for solid samples (Individual compounds are below the LQ).

nmol/g	pre-TOP-fertilizer	post-TOP-fertilizer	pre-TOP-compost	post-TOP-compost	pre-TOP-sludge	post-TOP-sludge
∑ PFCA	<LQ	0.002	0.191	2.285	0.611	1.570
∑ PFSA	<LQ	<LQ	0.097	0.161	0.284	0.410
∑ FT	0.001	<LQ	0.262	0.095	1.462	0.006
∑ Emerging PFAS	<LQ	<LQ	0.572	<LQ	0.335	<LQ

3.3 Distribution and transfer of PFAS from sludge to struvite recovery unit

This section presents the global analyses results as well as the targeted analyses before and after the TOP Assay solid samples. The global and target analyses data for all samples from station A and station C are presented.

3.3.1 Occurrence of individual PFAS

All the digested sludge samples show a high diversity of PFAS based on the target analyses. Figure 5 shows the most detectable PFAS by target analyses before TOP Assay (To) for WWTP A. Figure 5a shows the concentration of PFCA and PFSA measured, while Figure 5b shows the concentration of PFAS precursors measured. High concentrations are reported for 5:3 FTCA and 6:2 FTAB, ranging from 11 ng/g dw to 26 ng/g dw and from 8 ng/g dw to 13 ng/g dw, respectively. The samples from WWTP C (Figure 6), show that PFOS and 6:2 FTAB are the compounds displaying the highest concentrations. The concentrations of PFOS and 6:2 FTAB range from 105 ng/g dw to 136 ng/g dw and 37 ng/g dw to 74 ng/g dw, respectively, before TOP Assay (To) (Figure 6). The PFAS 6:2 FTAB is a recurring compound in all the sludges analysed. For all the sludge samples, the variability over time shows a very low variability ranging between 8 % and 22%.

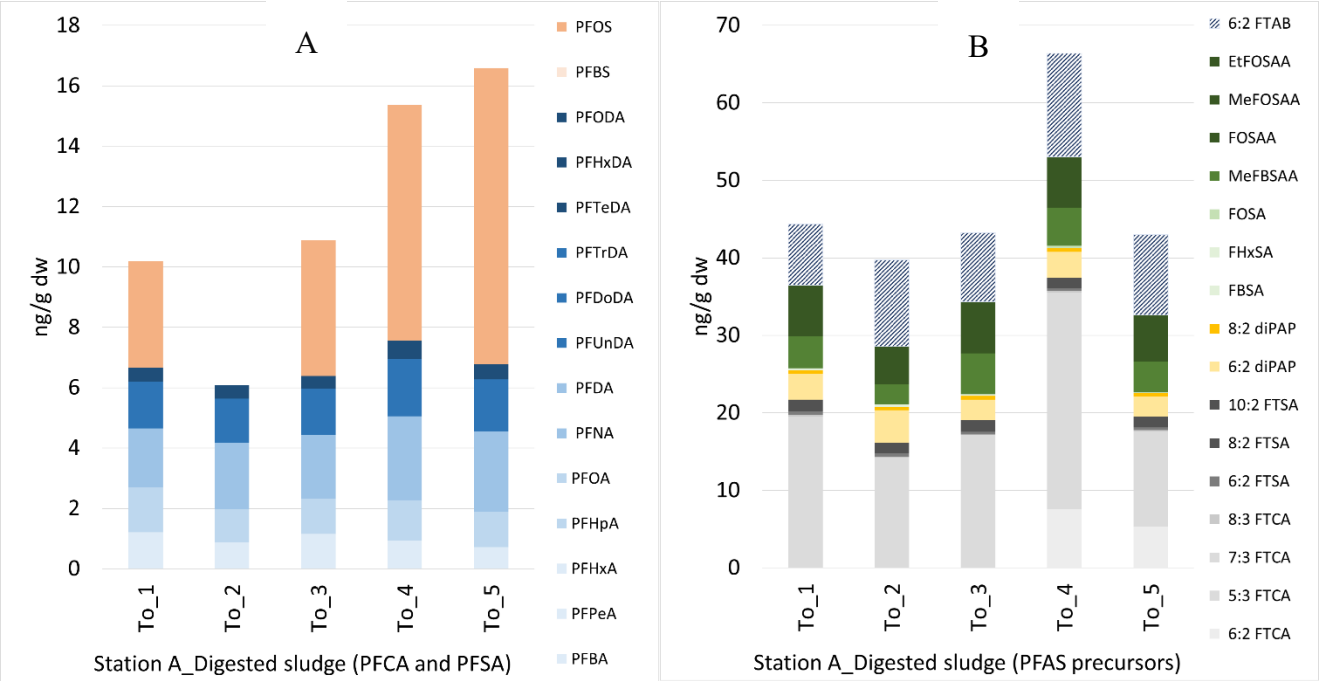

Figure 5: Target analyses results for digested sludge from WWTP A (sample 1 to 5) before TOP assay (To = pre-TOP).

The concentration levels in the investigated samples are comparable to those reported by published studies referring to digested sludge (Arvaniti et al. 2024). Digested sludge appears to be the main outlet for PFAS from wastewater treatment plant discharges. Legislation varies from one country to another; in France, it allows sludge to be land-spread for agricultural purposes at the end of the treatment plant, whereas in the Netherlands, for example, the spreading of sludge is prohibited. The characterization of all WWTP discharges for PFAS is therefore an important issue.

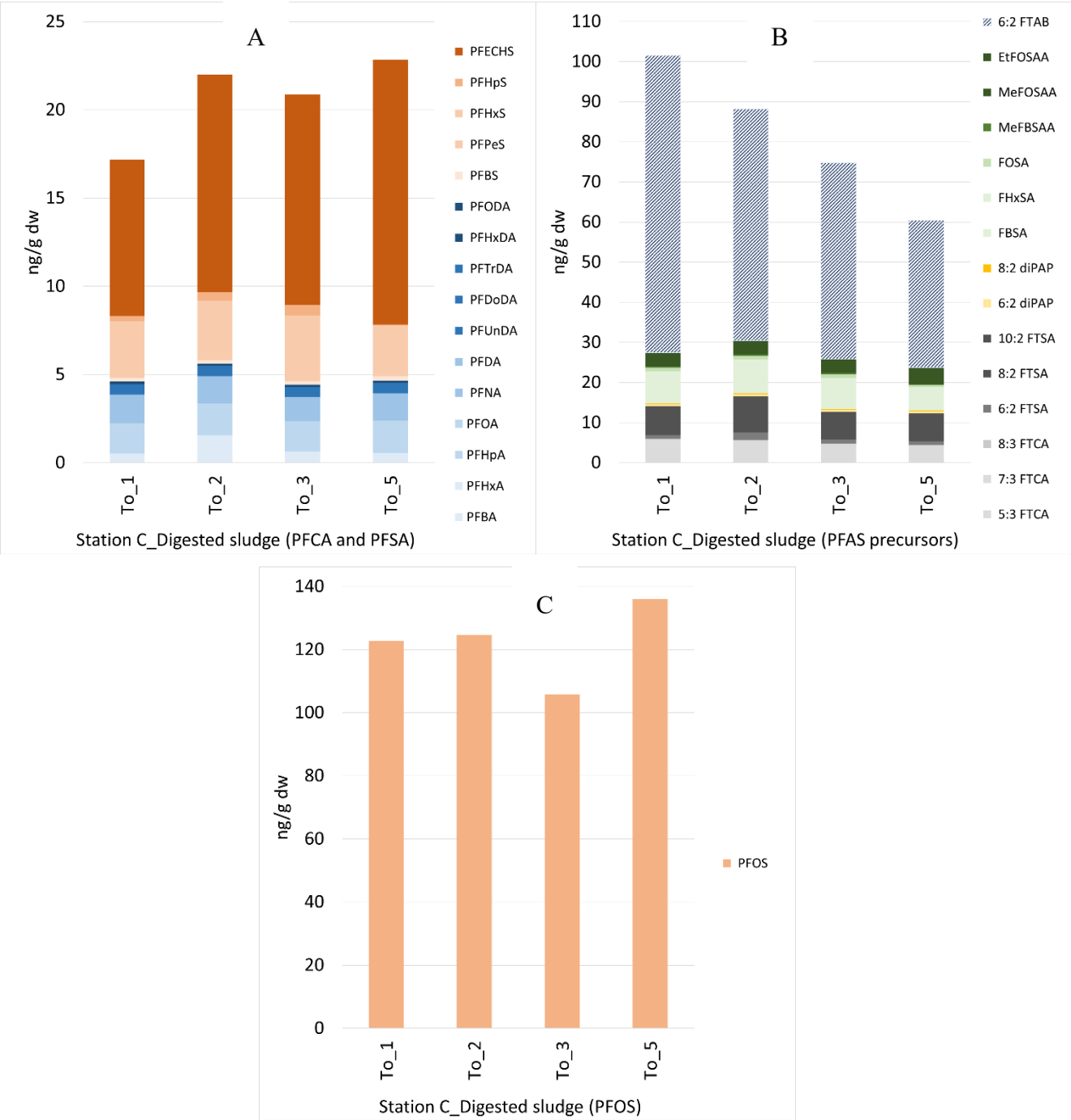

Figure 6: Target analyses results for the digested sludge from station C. Sample 4 was not collected (Figure 6A is displayed without PFOS to make the figure more legible).

3.3.2 PFAS precursors in digested sewage sludge

The weekly variations in the digested sludge samples from stations A after the TOP Assay are presented in Figure 7. With the exception of the sample from week 3 and 5 for which the targeted analysis after TOP Assay showed PFDA, all the PFCAs formed were less than or equal to C8. Although the variability in the PFAS composition of digested sludge from the WWTP is low (RSD 22%), variations in PFCA formed after TOP Assay were observed (Figure 7). These differences may be due to the absence of precursors or variations in the oxidation mechanism of the precursors present. In the

absence of oxidisable precursors, PFCAs would be oxidised due to the high oxidant/oxidisable compound ratio.

The increase in PFCA at all stations after TOP Assay is clear evidence of the presence of oxidisable precursors (only Station A is shown in this report). By comparing the profiles observed after oxidation with the oxidation profiles, we can proceed with further work on deconvolution to characterise the type(s) of precursor(s). This allows to determine likely PFAS precursors that would have oxidised. The current difficulty is that the oxidation protocols are not standardised and, above all, the percentages of PFCA formation after oxidation vary according to the protocols and matrices.

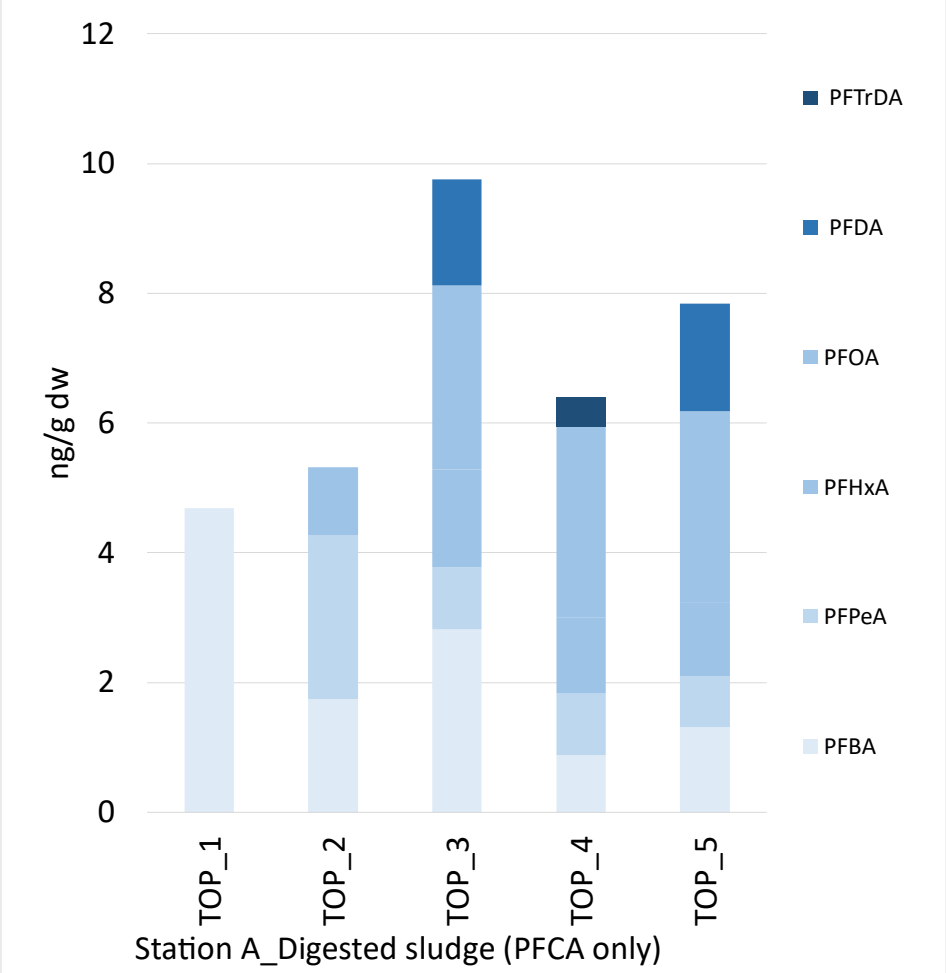

Figure 7: TOP Assay (TOP) results of PFCA for the digested sludge from station A (sample 1 to 5).

3.3.3 Comparison of global and target analysis

The global and target analyses comparison shows that there are many unknown molecules that are not quantified by the target analysis.

The TF concentrations variation is 8% and 5%, respectively for WWTP A and C, when comparing for all weeks sampled. The TF concentrations range from 88 mg-F/kg dw to 189 mg-F/kg dw (Table 6). The EOF parameters showed variations of 7% and 2%, respectively for WWTP A and C. The EOF concentrations range from 0.13 mg-F/kg dw to 0.43 mg-F/kg dw (Table 6).

Table 5 shows the percentage of fluoride explained by the targeted analysis. Liquid chromatography (LC) target analyses explain up to 0.15% of TF across all samples pre-TOP and pre-TOP assay. Except for samples from station C, where target PFAS analysis by LC explains up to 33% of the EOF before TOP Assay while it explains less than 7% of the EOF for WWTP A. Target analyses after TOP Assay (TOP) explain up to 0.13% of the TOF and up to 7% of the AOF, except for samples from station C, where it explains up to 27%.

Table 5 Percentages of fluorine explained by LC-MS/MS analysis in relation to TF and EOF.

	pre-TOP	pre-TOP	pre-TOP	pre-TOP
Solid	**LC/TF**	**LC/EOF**	**LC/TF**	**LC/EOF**
WWTP A_DigestedSludge_1	0%	5%	0%	1%
WWTP A_DigestedSludge_2	0%	5%	0%	2%
WWTP A_DigestedSludge_3	0%	5%	0%	3%
WWTP A_DigestedSludge_4	0%	7%	0%	7%
WWTP A_DigestedSludge_5	0%	6%	0%	6%
WWTP C DigestedSludge_1	0.2%	32%	0.1%	24%
WWTP C DigestedSludge_2	0.1%	33%	0.1%	25%
WWTP C DigestedSludge_3	0.1%	29%	0.1%	27%
WWTP C DigestedSludge_5	0.1%	31%	0.1%	21%

3.3.4 PFAS transfer from sludge to struvite

The concentrations of TF in struvite sampled from WWTP A display a variation of 11% when comparing all samples. The EOF values show a variation of 9%. The TF and EOF concentrations range from 44 mg-F/kg dw to 58 mg-F/kg dw and 0.13 mg-F/kg dw to 0.15 mg-F/kg dw, respectively (Table 6). IF was not determined and consequently, TOF could not be calculated.

Table 6: Global analyses results for samples from Station A. LOQ for solid: TF = 0.500 mg-F/kg, EOF = 0.100 mg-F/kg (n.a. = not analysed).

Sample name	Concentration unit	Total fluorine (TF)	Inorganic fluorine (IF)	Extractible organic fluorine (EOF)	Total organic fluorine (TOF= TF-IF)
WWTP A_DigestedSludge_1	mg-F/kg	187	n.a.	0.6	n.a.
WWTP A_DigestedSludge_2	mg-F/kg	161	n.a.	0.6	n.a.
WWTP A_DigestedSludge_3	mg-F/kg	189	n.a.	0.7	n.a.
WWTP A_DigestedSludge_4	mg-F/kg	163	n.a.	0.7	n.a.
WWTP A_DigestedSludge_5	mg-F/kg	178	n.a.	0.6	n.a.
WWTP A_Struvite_1	mg-F/kg	55	n.a.	0.2	n.a.
WWTP A_Struvite_2	mg-F/kg	58	n.a.	0.1	n.a.
WWTP A_Struvite_3	mg-F/kg	53	n.a.	0.2	n.a.
WWTP A_Struvite_4	mg-F/kg	44	n.a.	0.1	n.a.
WWTP A_Struvite_5	mg-F/kg	49	n.a.	0.1	n.a.

The results before (To) and after (TOP) the TOP Assay for the struvite fertiliser samples show that only PFOA, PFHxA, EtFOSAA, 6:2 FTSA and 5:3 FTCA were quantified, but at concentrations below 1 ng/g dw (See Supplementary Information 1). Among them, PFOA was detected with concentrations ranging from 0.2 ng/g dw to 0.3 ng/g dw. While the digested sludge from which they were derived had a PFOA concentration of between 0.9 ng/g dw and 2 ng/g dw. This represents up to a 74% reduction in PFOA.

The main precursors in digested sludge were 6:2 FTAB, 5:3 FTCA, MeFBSAA, EtFOSAA, and 6:2 diPAP, with concentrations reaching up to 13 ng/g dw (see Supplementary Information 1). In contrast, the quantities of these precursors in the recovered struvite were substantially lower, indicating a high separation efficiency. Overall, the results demonstrate a reduction efficiency of 97% to 100% for all known precursors from the list of 58 compound-dependent PFAS, and a total PFAS concentration reduction exceeding 99%.

Following the TOP assay, an increase in PFCA concentrations was observed in samples 2, 3, and 4 of the fertiliser (struvite). The initial non-quantification of PFCAs in the target analysis before the TOP assay (To) can be attributed to the higher limit of quantification (LOQ), which increased from 0.1 ng/g dw to 0.2 ng/g dw. However, the PFCA profiles detected after the TOP assay (TOP) differ between samples. Specifically, sample 2 contained PFBA (0.5 ng/g dw) and PFOA (1 ng/g dw); sample 3 contained PFBA (0.5 ng/g dw) only; and sample 4 contained PFPeA (1 ng/g dw), PFHxA (0.7 ng/g dw), and PFODA (0.1 ng/g dw). These concentrations are significantly lower than those measured in the digested sludge after the TOP assay, indicating that the nutrient recovery process is effective in substantially reducing the concentrations of PFAS precursors—by more than 96%. It should be noted that this reduction refers to concentration, not to total PFAS load transfer.

In addition to the four PFAS compounds quantified in the struvite samples, the sewage sludge originally contained 33 PFAS. This means that 29 of the 33 PFAS detected in the digested sludge prior to the TOP Assay (To sample) were no longer quantifiable in the struvite. The observed reduction in PFAS concentrations in struvite compared to sewage sludge can be attributed to the removal of PFAS—particularly long-chain PFAS—during sludge digestion. These compounds are less mobile and more likely to adsorb onto solid phases. It is important to note that struvite is harvested by sedimentation in a settler, which may further limit the transfer of PFAS into the final struvite product.

4 Conclusions

This work investigates the occurrence, behavior, and transformation of per- and polyfluoroalkyl substances (PFAS) in sewage sludge and related sludge-derived products, using a combination of analytical techniques, including combustion ion chromatography (CIC), targeted PFAS analysis, and the Total Oxidizable Precursor (TOP) Assay.

Analytical findings and limitations

1. Limited scope of conventional PFAS analyses

- Combustion Ion Chromatography (CIC) and targeted PFAS analysis captured only a small fraction of total organic fluorine (TOF)—0.1–2% for EOF and as low as 0.003–5% for targeted PFAS.
- This reveals a large proportion of unidentified organofluorine compounds in sludge and derived products, indicating that current methods severely underestimate total PFAS burden.

2. TOP Assay unveils hidden PFAS precursors

- The Total Oxidizable Precursor (TOP) Assay revealed significant increases in perfluorocarboxylic acid (PFCA) concentrations—up to +1856% in sludge—demonstrating the presence of substantial precursor compounds.
- Compost and sludge exhibited considerable precursor conversion post-TOP, while struvite showed reduced PFCA concentrations, indicating low precursor content.

3. PFAS profile in sludge across WWTPs

- Recurrent detection of PFAS such as 6:2 FTAB and PFOS in digested sludge from multiple wastewater treatment plants (WWTPs) confirms that sludge is a consistent PFAS sink.
- These values align with existing literature, strengthening the case for considering digested sludge a major PFAS reservoir.

4. PFAS removal during struvite recovery

- Struvite showed a substantial reduction in PFAS concentrations—up to 99% total PFAS removal compared to digested sludge.
- Post-TOP analyses of struvite revealed minimal residual precursor activity, implying effective separation during struvite precipitation.

Implications for sludge valorization and risk management

1. Analytical limitations demand broader monitoring approaches

- The gap between TOF and known PFAS concentrations underscores the importance of incorporating techniques like TOP Assay and non-targeted fluorine analysis in environmental monitoring.

2. Struvite precipitation reduces PFAS risk in sludge valorization

- Compared to compost or direct land application of digested sludge, struvite offers a significantly cleaner end-product in terms of PFAS contamination.
- The low PFAS content in struvite—both before and after oxidation—suggests it is a safer option for agricultural valorization.

3. Rethinking sludge valorization strategies

- Traditional valorization methods (e.g., composting, landspreading) may retain or even concentrate PFAS and precursors.
- Struvite recovery, due to its selective precipitation and phase separation, limits PFAS carryover and presents a viable pathway to produce low-risk fertilizers from wastewater sludge.

4. Policy and treatment implications

- Results support the prioritization of recovery technologies like struvite precipitation in circular economy strategies.
- Regulation of PFAS in biosolids should consider not just known compounds but also precursor and unknown organofluorine content.

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Supporting information (SI)

SI1 - PFAS concentrations before and after TOP Assay for solid sample from station A, expressed in ng/g dw.

Sample name	Acronym	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	P37DMOA	PFUnDA	PFDoDA
Station A_DigestedSludge_1	To_1	0.2	0.1	1	<LOQ	2	0.3	2	<LOQ	1	1
Station A_DigestedSludge_2	To_2	0.2	<LOQ	1	0.1	1	0.4	2	<LOQ	1	1
Station A_DigestedSludge_3	To_3	0.2	0.1	1	0.1	1	0.3	2	<LOQ	1	1
Station A_DigestedSludge_4	To_4	0.1	<LOQ	1	0.3	1	0.4	2	<LOQ	1	1
Station A_DigestedSludge_5	To_5	0.1	<LOQ	1	0.3	1	0.4	2	<LOQ	1	1
Station A_DigestedSludge_1 after TOP assay	TOP_1	5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_2 after TOP assay	TOP_2	2	3	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_3 after TOP assay	TOP_3	3	1	2	<LOQ	3	<LOQ	2	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_4 after TOP assay	TOP_4	1	1	1	<LOQ	3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_5 after TOP assay	TOP_5	1	1	1	<LOQ	3	<LOQ	2	<LOQ	<LOQ	<LOQ
Station A_Struvite_1	To_1	<LOQ	<LOQ	<LOQ	<LOQ	0.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2	To_2	<LOQ	<LOQ	0.1	<LOQ	0.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_3	To_3	<LOQ	<LOQ	<LOQ	<LOQ	0.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4	To_4	<LOQ	<LOQ	<LOQ	<LOQ	0.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5	To_5	<LOQ	<LOQ	<LOQ	<LOQ	0.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2 after TOP assay	TOP_2	0.5	<LOQ	<LOQ	<LOQ	1	<LOQ	<LOQ	0.2	<LOQ	<LOQ
Station A_Struvite_3 after TOP assay	TOP_3	0.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4 after TOP assay	TOP_4	<LOQ	1	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5 after TOP assay	TOP_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

SI1 PFAS concentrations before and after TOP Assay for all sample from station A, (continued 1), expressed in ng/g dw.

Sample name	Acronym	PFTrDA	PFTeDA	PFHxDA	PFODA	PFPrS	PFBS	PFPeS	PFHxS	PFHpS	PFOS
Station A_DigestedSludge_1	To_1	0.1	0.2	0.1	0.2	3	<LOQ	<LOQ	<LOQ	<LOQ	4
Station A_DigestedSludge_2	To_2	<LOQ	0.2	0.1	0.2	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_3	To_3	<LOQ	0.2	0.1	0.1	2	<LOQ	<LOQ	<LOQ	<LOQ	5
Station A_DigestedSludge_4	To_4	<LOQ	0.3	0.1	0.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8
Station A_DigestedSludge_5	To_5	<LOQ	0.3	0.1	0.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10
Station A_DigestedSludge_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5
Station A_DigestedSludge_2 after TOP assay	TOP_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6
Station A_DigestedSludge_3 after TOP assay	TOP_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5
Station A_DigestedSludge_4 after TOP assay	TOP_4	0.5	<LOQ	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	10
Station A_DigestedSludge_5 after TOP assay	TOP_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	<LOQ	8
Station A_Struvite_1	To_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2	To_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_3	To_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4	To_4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5	To_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2 after TOP assay	TOP_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ
Station A_Struvite_3 after TOP assay	TOP_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4 after TOP assay	TOP_4	<LOQ	<LOQ	<LOQ	0.1	2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5 after TOP assay	TOP_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

SI1 PFAS concentrations before and after TOP Assay for all sample from station A, station B and station C (continued 2), expressed in ng/g dw.

Sample name	Acronym	PFECHS	PFNS	6:2 FTCA	5:3 FTCA	7:3 FTCA	8:3 FTCA	8:2 FTUCA	6:2 FTSA	8:2 FTSA	10:2 FTSA
Station A_DigestedSludge_1	To_1	<LOQ	<LOQ	<LOQ	18	2	0.2	<LOQ	0.5	1	1
Station A_DigestedSludge_2	To_2	<LOQ	<LOQ	<LOQ	13	2	0.2	<LOQ	0.4	1	1
Station A_DigestedSludge_3	To_3	<LOQ	<LOQ	<LOQ	16	2	<LOQ	0.1	0.4	1	1
Station A_DigestedSludge_4	To_4	<LOQ	<LOQ	8	26	1	0.2	0.1	0.3	1	1
Station A_DigestedSludge_5	To_5	<LOQ	<LOQ	5	11	1	0.1	0.2	0.4	1	1
Station A_DigestedSludge_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_2 after TOP assay	TOP_2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_3 after TOP assay	TOP_3	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_4 after TOP assay	TOP_4	<LOQ	2	<LOQ	28	2	1.50	<LOQ	2	2	3
Station A_DigestedSludge_5 after TOP assay	TOP_5	<LOQ	<LOQ	<LOQ	23	1	1.51	<LOQ	1	<LOQ	3
Station A_Struvite_1	To_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2	To_2	<LOQ	<LOQ	<LOQ	0.3	<LOQ	<LOQ	<LOQ	0.2	<LOQ	<LOQ
Station A_Struvite_3	To_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4	To_4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5	To_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2 after TOP assay	TOP_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_3 after TOP assay	TOP_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4 after TOP assay	TOP_4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5 after TOP assay	TOP_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

SI1 PFAS concentrations before and after TOP Assay for all sample from station A (continued 3), expressed in ng/g dw.

Sample name	Acronym	6:2 diPAP	8:2 diPAP	FBSA	FHxSA	FOSA	MeFBSAA	FOSAA	MeFOSAA	EtFOSAA	PFHxSAM	6:2 FTAB
Station A_DigestedSludge_1	To_1	3	0.5	0.2	0.1	<LOQ	4	1	2	4	<LOQ	8
Station A_DigestedSludge_2	To_2	4	0.5	0.2	0.1	<LOQ	3	1	1	3	<LOQ	11
Station A_DigestedSludge_3	To_3	3	0.5	0.2	<LOQ	<LOQ	5	1	2	4	<LOQ	9
Station A_DigestedSludge_4	To_4	3	0.5	<LOQ	<LOQ	0.3	5	1	2	4	<LOQ	1
Station A_DigestedSludge_5	To_5	3	0.4	<LOQ	<LOQ	0.2	4	1	2	4	<LOQ	10
Station A_DigestedSludge_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_2 after TOP assay	TOP_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ
Station A_DigestedSludge_3 after TOP assay	TOP_3	3	<LOQ	<LOQ	<LOQ	<LOQ	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_DigestedSludge_4 after TOP assay	TOP_4	4	0.2	<LOQ	<LOQ	<LOQ	3	<LOQ	2	3	<LOQ	<LOQ
Station A_DigestedSludge_5 after TOP assay	TOP_5	3	0.2	<LOQ	<LOQ	<LOQ	2	<LOQ	3	2	<LOQ	<LOQ
Station A_Struvite_1	To_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.2	<LOQ	<LOQ
Station A_Struvite_2	To_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_3	To_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.4	<LOQ	<LOQ
Station A_Struvite_4	To_4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5	To_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_1 after TOP assay	TOP_1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_2 after TOP assay	TOP_2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_3 after TOP assay	TOP_3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_4 after TOP assay	TOP_4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Station A_Struvite_5 after TOP assay	TOP_5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

SI2 -List of PFAS analysed by LC-MS/MS.

N° CAS	Acro	Name	Formula	Internal standards
375-22-4	PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$	PFBA $^{13}C_4$
2706-90-3	PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$	PFHxA $^{13}C_2$
307-24-4	PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$	PFHxA $^{13}C_2$
375-85-9	PFHpA	Perfluoroheptanoic acid	$C_7H_4F_{13}NO_2$	PFOA $^{13}C_4$
335-67-1	PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$	PFOA $^{13}C_4$
375-95-1	PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$	PFNA $^{13}C_5$
335-76-2	PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	PFDA $^{13}C_2$
2058-94-8	PFUnDA	Perfluoro undecanoic acid	$C_{11}HF_{21}O_2$	PFUnDA $^{13}C_2$
307-55-1	PFDoDA	Perfluoro dodecanoic acid	$C_{12}HF_{23}O_2$	PFDoDA $^{13}C_2$
72629-94-8	PFTrDA	Perfluoro tridecanoic acid	$C_{13}HF_{25}O_2$	PFDoDA $^{13}C_2$
376-06-7	PFTeDA	Perfluoro-tetradecanoic acid	$C_{14}HF_{27}O_2$	PFDoDA $^{13}C_2$
67905-19-5	PFHxDA	Perfluoro-hexadecanoic acid	$C_{16}HF_{31}O_2$	PFHxDA $^{13}C_2$
16517-11-6	PFODA	Perfluoro-octadecanoic acid	$C_{18}HF_{35}O_2$	PFHxDA $^{13}C_2$
423-41-6	PFPrS	Perfluoropropane sulfonate	$C_3HF_7O_3S$	PFBS $^{13}C_3$
375-73-5	PFBS	Perfluorobutane sulfonic acid	$C_4HF_9O_3S$	PFBS $^{13}C_3$
2706-91-4	PFPeS	Perfluoropentane sulfonic acid	$C_5HF_{11}O_3S$	PFBS $^{13}C_3$
355-46-4	PFHxS	Perfluorohexane sulfonic acid	$C_6HF_{13}O_3S$	PFHxS $^{18}O_2$
375-92-8	PFHpS	Perfluoroheptane sulfonic acid	$C_7HF_{15}O_3S$	PFOS $^{13}C_4$
1763-23-1	PFOS	Perfluorooctane sulfonic acid	$C_8HF_{17}O_3S$	PFOS $^{13}C_4$
68259-12-1	PFNS	Perfluorononane sulfonic acid	$C_9HF_{19}O_3S$	PFOS $^{13}C_4$
335-77-3	PFDS	Perfluorodecane sulfonic acid	$C_{10}HF_{21}O_3S$	PFOS $^{13}C_4$
749786-16-1	PFUnDS	Perfluoroundecane sulfonic acid	$C_{11}HF_{23}O_3S$	PFOS $^{13}C_4$
79780-39-5	PFDoDS	Perfluorododecane sulfonic acid	$C_{12}HF_{25}O_3S$	PFOS $^{13}C_4$
791563-89-8	PFTrDS	Perfluorotridecane sulfonic acid	$C_{13}HF_{27}O_3S$	PFOS $^{13}C_4$
356-02-5	3:3 FTCA	3:3 fluorotelomer carboxylic acid	$C_6H_5F_7O_2$	PFHxA $^{13}C_2$
914637-49-3	5:3 FTCA	5:3 fluorotelomer carboxylic acid	$C_8H_5F_{11}O_2$	PFHxA $^{13}C_2$
812-70-4	7:3 FTCA	7:3 fluorotelomer carboxylic acid	$C_{10}H_5F_{15}O_2$	PFOA $^{13}C_4$
34598-33-9	8:3 FTCA	8:3 fluorotelomer carboxylic acid	$C_{11}H_5F_{17}O_2$	PFOA $^{13}C_4$
53826-12-3	6:2 FTCA	6:2 fluorotelomer carboxylic acid	$C_8H_3F_{13}O_2$	8:2 FTCA $^{13}C_2$
27854-31-5	8:2 FTCA	8:2 fluorotelomer carboxylic acid	$C_{10}H_3F_{17}O_2$	8:2 FTCA $^{13}C_2$
70887-84-2	8:2 FTUCA	8:2 fluorotelomer unsaturated carboxylic acid	$C_{10}H_2F_{16}O_2$	8:2 FTUCA $^{13}C_2$
757124-72-4	4:2 FTSA	4:2 fluorotelomer sulfonic acid	$C_6H_5F_9O_3S$	4:2 FTSA $^{13}C_2$
27619-97-2	6:2 FTSA	6:2 fluorotelomer sulfonic acid	$C_8H_5F_{13}O_3S$	6:2 FTSA $^{13}C_2$
39108-34-4	8:2 FTSA	8:2 fluorotelomer sulfonic acid	$C_{10}H_5F_{17}O_3S$	8:2 FTSA $^{13}C_2$
120226-60-0	10:2 FTSA	10:2 fluorotelomer sulfonic acid	$C_{12}H_5F_{21}O_3S$	8:2 FTSA $^{13}C_2$
57677-95-9	6:2 diPAP	6:2 fluorotelomer phosphate diester	$C_{16}H_9F_{26}O_4P$	6:2 diPAP $^{13}C_4$
678-41-1	8:2 diPAP	8:2 fluorotelomer phosphate diester	$C_{20}H_9F_{34}O_4P$	8:2 diPAP $^{13}C_4$
958445-44-8	ADONA	4,8-dioxa-3H-perfluorononanoic acid	$C_7H_5F_{12}NO_4$	PFHxA $^{13}C_2$
13252-13-6	HFPO-DA	Hexafluoropropylene oxide dimer acid	$C_6HF_{11}O_3$	HFPO-DA $^{13}C_3$
73606-19-6	6:2Cl-PFESA	6:2 chlorinated perfluoroalkylether sulfonic acid	$C_8ClHF_{16}O_4S$	PFOS $^{13}C_4$
83329-89-9	8:2 Cl-PFESA	8:2 chlorinated perfluoroalkylether sulfonic acid	$C_{10}ClHF_{20}O_4S$	PFOS $^{13}C_4$

N° CAS	Acro	Name	Formula	Internal standards
646-83-3	PFECHS	Perfluoro-4-ethyl-hexanesulphonic acid	$C_8HF_{15}O_3S$	PFOS $^{13}C_4$
30334-69-1	FBSA	Perfluoro-1-butanesulfonamide	$C_4H_2F_9NO_2S$	FOSA$^{13}C_8$
68298-12-4	MeFBSA	N-Methyl perfluorobutane sulfonamide	$C_5H_4F_9NO_2S$	FOSA$^{13}C_8$
41997-13-1	PFHxSA	perfluorohexanesulfonamide	$C_6H_2F_{13}NO_2S$	FOSA$^{13}C_8$
754-91-6	FOSA	Perfluorooctane sulfonamide	$C_8H_2F_{17}NO_2S$	FOSA$^{13}C_8$
31506-32-8	MeFOSA	N-Methyl perfluorooctane sulfonamide	$C_9H_4F_{17}NO_2S$	MeFOSA D_3
4151-50-2	EtFOSA	N-Ethyl perfluorooctane sulfonamide	$C_{10}H_6F_{17}NO_2S$	MeFOSA D_3
159381-10-9	MeFBSAA	N-Methyl Perfluorobutane sulfonamidoacetic acid	$C_7H_6F_9NO_4S$	MeFOSA D_3
2806-24-8	FOSAA	Perfluorooctane sulfonamidoacetic acid	$C_{10}H_4F_{17}NO_4S$	MeFOSA D_3
2355-31-9	MeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	$C_{11}H_6F_{17}NO_4S$	MeFOSA D_3
2991-50-6	EtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	$C_{12}H_8F_{17}NO_4S$	MeFOSA D_3
50598-28-2	PFHxSAm	Perfluorohexane sulfonamidopropyl amine	$C_{11}H_{13}F_{13}N_2O_2S$	6:2 FTAB D_6
1546-95-8	HPFHpA	7H-perfluoroheptanoic acid	$C_7H_2F_{12}O_2$	PFOA $^{13}C_4$
172155-07-6	P37DMOA	Perfluoro-3,7-dimethyloctanoic acid	$C_{10}HF_{19}O_2$	PFDA $^{13}C_4$
34455-29-3	6:2 FTAB	6:2 fluorotelomer sulfonamide betaine	$C_{15}H_{20}F_{13}N_2O_4S$	6:2 FTAB D_6