# Non-Target Screening of Fluorinated Ionic Liquids and PFAS in European Wastewaters Using Supercritical Fluid Chromatography

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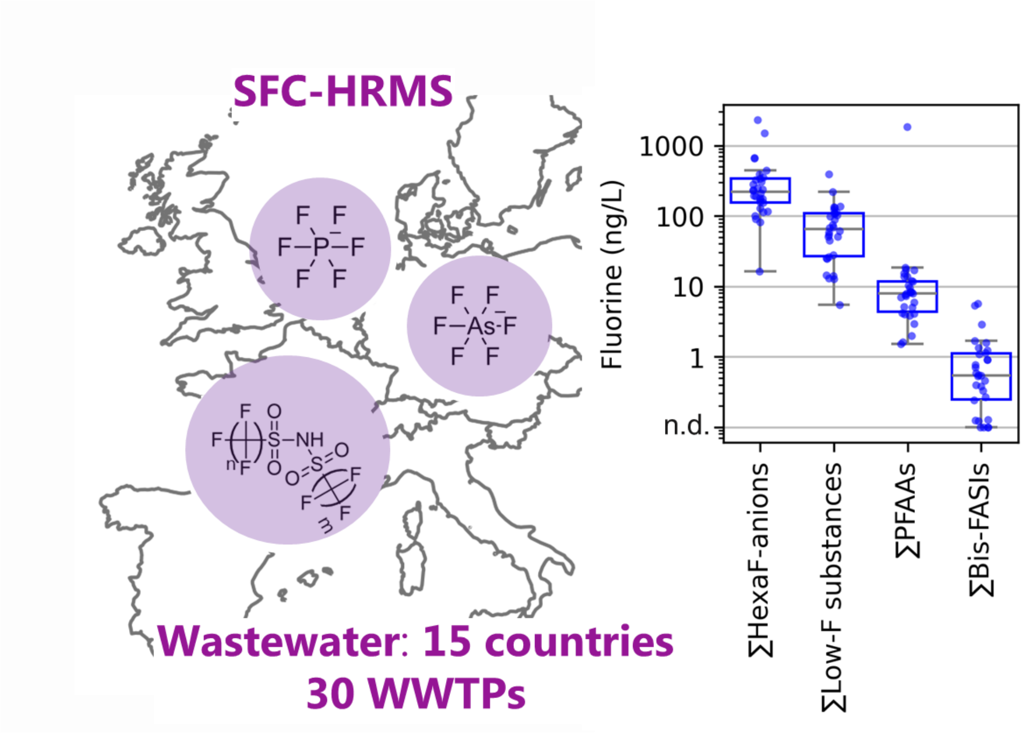
## Graphical Abstract



## Abstract

Per- and polyfluoroalkyl substances (PFAS) and fluorinated ionic liquids are increasingly recognized as persistent environmental contaminants. In this study, municipal effluent samples from 30 wastewater treatment plants (WWTPs) across 15 European countries were analyzed using supercritical fluid chromatography–high-resolution mass spectrometry (SFC-HRMS) for non-target screening of fluorinated compounds. The bis-perfluoroalkyl sulfonimide (bis-FASI) class of ionic liquids was widely detected, including bis(trifluoromethanesulfonyl)imide (NTf$_2^-$), two rarely reported homologues (±2 CF$_2$, namely FSI$^-$ and BETI$^-$), and two previously unreported homologues (±1 CF$_2$, namely FTFSI$^-$ and FTNTf$_2^-$). Bis-FASIs were present in 85% of samples and were more abundant in effluents from larger WWTPs. The fluorinated anion PF$_6^-$, commonly used in ionic liquids, was found in all samples at concentrations up to 3 µg/L. Hexafluoroarsenate (AsF$_6^-$), reported here for the first time in municipal wastewater, was detected in 32% of samples in eight countries. PF$_6^-$ and AsF$_6^-$ concentrations (when present) exceeded those of traditional PFSAs and PFCAs in 97% of samples. Polyfluorinated compounds showed partial removal during treatment, while perfluorinated compounds, inorganic fluorinated anions, and low-fluorinated pharmaceuticals and pesticides showed no removal. Low-fluorinated substances exceeded 100 ng/L in 90% of samples, yet PF$_6^-$ alone surpassed the combined concentration of all low-fluorinated substances in 27 out of 30 samples. These results reveal a significant contribution of unconventional fluorinated substances to the overall fluorine load in wastewater. The dominant contributor, PF$_6^-$, falls outside current PFAS regulatory definitions, underscoring the urgent need to expand monitoring strategies beyond legacy PFAS to include both inorganic and low-fluorinated contaminants.

## Keywords

bis-FASIs, hexafluorophosphate, fluorine mass balance, inorganic fluorinated compounds, ultrashort-chain PFAS

## Synopsis

Our findings show that the major fluorine contribution of identified compounds in wastewater originates from inorganic and low-fluorinated substances, underscoring the need to expand environmental assessments beyond conventional PFAS targets.

## 1. Introduction

Per-and polyfluoroalkyl substances (PFAS) are a class of synthetic, highly persistent compounds widely used in industrial applications and consumer products[1,2]. These substances enter aquatic environments primarily through wastewater treatment plants (WWTPs), receiving PFAS from industrial processes, households, biosolid applications, landfill leachates, aqueous film-forming foams (AFFFs), and mining or drilling operations[3]. Conventional WWTPs often fail to effectively remove PFAS, leading to their presence in effluents and sewage sludge[4–6]. Their widespread use, persistence, and mobility have resulted in a global environmental concern of PFAS[7]. Long-chain perfluoroalkyl acids, such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorohexane sulfonate (PFHxS) have been gradually phased out due to their environmental persistence, bioaccumulation potential, and toxicity[8]. Consequently, alternative PFAS, including fluorotelomers, fluoroalkyl ethers, and short-chain analogues, have emerged[9,10]. While shorter-chain PFAS exhibit lower bioaccumulation potential[11], their high persistence, poor adsorption capacity and increased mobility and water solubility, make them resistant to conventional water treatment processes[9]. The frequent detection of these short-chain PFAS in drinking water emphasises their potential risk to human health[12,13].

In addition to well-characterized PFAS, other fluorinated compounds are gaining increased attention. Many pharmaceuticals and pesticides fall under the OECD PFAS definition - organic substances containing at least one fully fluorinated carbon atom (e.g., $CF_3$ groups)[14]. In this study, compounds are defined as low-fluorinated if their molecular fluorine mass percentage is below 40%, a threshold commonly associated with fluorinated pharmaceuticals and pesticides (Figure S1)[15]. Many of these low-fluorinated compounds can act as precursors to trifluoroacetic acid (TFA)[16,17], and significantly contribute to the total fluorine load in wastewater and sludge[15], as they can occur at concentrations ten to hundred times higher than conventional PFAS[18].

Recently, fluorinated ionic liquids have emerged as concerning environmental pollutants[19]. Their diverse industrial applications, particularly in lithium-ion batteries for electric vehicles, are rapidly increasing alongside the increasing global demand for energy storage solutions[20]. Despite their rising production, knowledge regarding their environmental fate remains limited. Recent studies have reported widespread occurrence of ionic liquids in the environment, such as bis(trifluoromethylsulfonyl)imide ($NTf_2^-$) which has been detected in 46% of tap water samples across multiple countries[21], and hexafluorophosphate ($PF_6^-$) has been found ubiquitously in German river waters[22]. Ionic liquids are suspected to account for a substantial fraction of the environmentally persistent “PFAS dark matter”[20,23]. This term refers to the fraction of the fluorine mass balance (determined for example by extractable organic fluorine (EOF)[24,25]) that cannot be explained by routinely monitored PFAS. Current targeted PFAS monitoring typically accounts for <50% of EOF, highlighting the urgent need for broader analytical strategies[26]. This includes the screening of both emerging PFAS and inorganic fluorinated compounds such as $PF_6^-$, using suspect and non-target screening (NTS) methods[27].

Highly polar PFAS compounds, apart from TFA, are often overlooked by current analytical strategies[28]. Conventional reversed-phase liquid chromatography (RP-LC) offers limited retention for these polar analytes, highlighting the need for dedicated analytical approaches[29]. Supercritical fluid chromatography (SFC) has been proven as a valuable tool for detecting ultra-short-chain ($C_1$–$C_3$) PFAS at low detection limits[30]. This demonstrates the potential of SFC for NTS to detect short-chain PFAS in environmental samples.

This study investigates the occurrence and fate of PFAS and other fluorinated compounds in wastewater effluent from Europe using SFC coupled to quadrupole time-of-flight mass spectrometry (SFC-QTOF-MS). A non-target screening approach was employed to cover a wide polarity range, with particular emphasis on highly polar PFAS. By identifying a broader spectrum of PFAS, including previously undetected PFAS analogues and ionic liquids, this research advances the understanding of their widespread environmental presence. The study provides the first comprehensive overview of environmental occurrence and persistence of these fluorinated ionic liquids in 30 wastewater treatment plants across 15 European countries.

## 2. Materials and Methods

### 2.1. Sampling and sample preparation

A pan-European wastewater sampling campaign was performed within the Partnership for the Assessment of Risks from Chemicals (PARC). The campaign was conducted from March to September 2024. It investigated 72-hour composite samples (time or volume proportional) of raw (influent) and treated (effluent) wastewater from 30 conventional WWTPs with primary and secondary treatment from 15 European countries. In each country, two WWTPs were investigated: one smaller plant (<100,000 population equivalents, PE) and one larger plant (>100,000 PE), except in the Netherlands, where both WWTPs were large. Participating countries included Austria, Belgium, Czechia, Denmark, France, Germany, Great Britain, Italy, Netherlands, Poland, Slovakia, Slovenia, Spain, Sweden and Switzerland. Further details about sampling and sample preparation can be seen in S2.1 in Supporting Information (SI). In short, samples were collected under standardized conditions across all sites, spiked with internal standards (list of concentrations and compounds in Table S2) and processed via solid-phase extraction (Oasis HLB, Waters) and enriched 100-fold before analysis. Field blanks (LC-MS grade water) were individually prepared in each participating country following the same procedure ($n$ =1, per sampling site, S2.1). The sample preparation was carried out within the framework of a joint study covering a wide spectrum of analytes and was therefore not specifically optimized for PFAS analysis. Recovery experiments were performed to evaluate SPE extraction efficiency for PFAS, as described in S2.1. Recoveries in wastewater influent and effluent were calculated specifically for compounds detected in the samples and for which analytical standards were available. High recoveries (>75%) were achieved for perfluoroalkyl sulfonic acids (PFSAs) and fluorotelomer sulfonic acids (FTSAs) with chain lengths between $C_4$ and $C_7$, and for perfluorohexanoic acid (PFHxA, $C_6$) in both influent and effluent samples (Figure S2). Lower recoveries were found for PFOS (50-60 %) and PFBA (26-30 %). Hexafluorophosphate ($PF_6^-$) had the lowest recovery, on average only 5% (standard deviation 0.07) in effluent. Hexafluoroarsenate ($AsF_6^-$) showed consistently higher recovery than $PF_6^-$, with average recoveries of 50% (Figure S1). Due to the low recovery of $PF_6^-$, which makes concentration correction highly sensitive, additional recovery experiments were conducted in Sweden, Slovenia and

Switzerland (Section S2.1) using different matrices (wastewater effluent and tap water). The average recoveries of 6%, 5%, and 2% were consistent with the 5% average recovery observed in the experiments conducted in Denmark. Concentrations in effluent samples were adjusted based on observed recoveries for compounds below 75%. Specifically, measured concentrations for $PF_6^-$, PFBA, and $AsF_6^-$ were corrected by factors of 0.05, 0.26, and 0.50, respectively. Influent samples were used solely to determine effluent-to-influent ratios. Therefore, no recovery correction was applied for removal calculations as absolute concentrations were not required.

### 2.2. SFC-QTOF analysis

Two SFC-QTOF setups, both with a BEH column (3 × 100 mm, 1.7 µm), were used for analysis of wastewater effluent samples. SFC 1 (Acquity UPC$^2$ coupled to G2-Si Synapt QTOF, Waters) operated in data-independent acquisition (DIA), while SFC 2 (1260 infinity II SFC coupled to 6546 LC/QTOF, Agilent Technologies) operated in data-dependent acquisition (DDA) mode. For both SFC setups, data were acquired in negative ionization mode. The use of two SFC systems allowed: (1) cross-validation of compound detection (a compound detection was considered valid only if detected on both platforms), and (2) collection of additional fragmentation data. Details about the two SFC-QTOF methods can be seen in S2.2 in SI.

### 2.3. Screening workflow for effluent wastewater samples

PFAS and other fluorinated compounds were screened in effluent wastewater. Data from both instruments were processed by MS-DIAL[31] (version 4.9, parameters detailed in Table S1). The screening workflow (Fig. 1) integrated targeted, suspect, and NTS approaches.

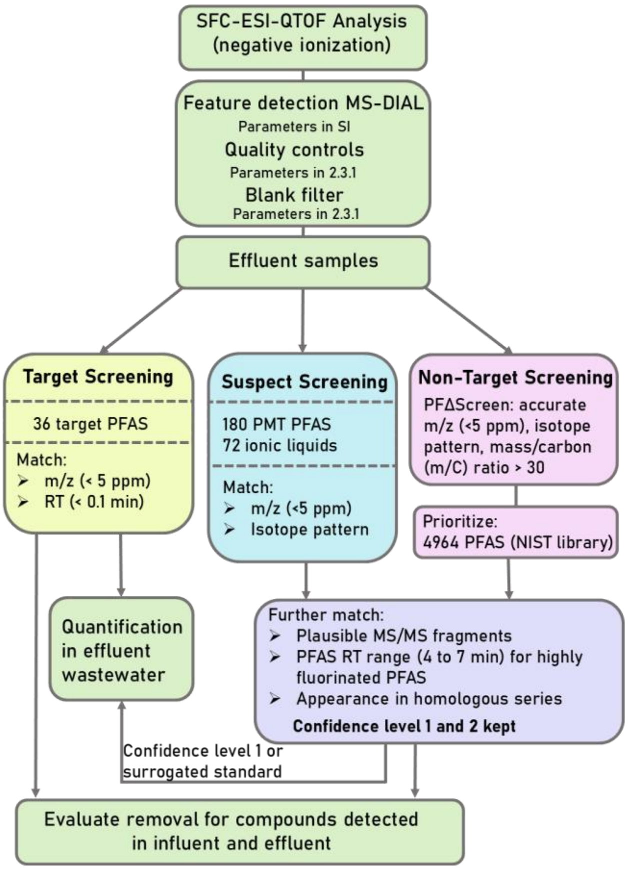


**Figure 1:** Workflow for identification and evaluation of PFAS detected in wastewater effluent. The suspect lists are public available: PMT PFAS [32], ionic liquid[33], NIST library [34].

### 2.3.1. Quality control, matrix effect, and blank corrections

To assess signal drift during the analysis, quality control (QC) samples (prepared as described in S2.1) were injected regularly: for influent and effluent samples, the corresponding QC (influent QC or effluent QC) was injected after every seventh samples. In addition, both influent and effluent QCs were injected after every 20th sample to allow correction of signal intensity between the two sample types. Samples were injected in duplicates and randomized throughout the sequence. On SFC 1 (effluent samples only), signal intensity decreased ~40% over time, requiring correction via a second-degree polynomial function based on QC sample intensities[35]. After drift correction, the median RSD for features in duplicate injections was 8 %. SFC 2 showed no signal drift (median QC variation 15%). Duplicate injections of effluent samples had median of RSD 10%, whereas influent samples had median RSDs of 11% (undiluted) and 14% (five-fold diluted).

For comparing influent and effluent data (SFC 2), intensities were aligned by using the pre-extraction spiked internal standards: n-butylparaben D4 (0.88 min), bisphenol A D16 (3.06 min), acetamiprid D3 (3.9 min), p-toluene-sulfonamide D4 (1.45 min), bentazone D6 (4.45 min), and 4-nitrophenol D4 (1.0 min). Peak intensities were adjusted relative to the internal standard peak intensities of the first QC sample in the effluent batch. Undiluted influent peak intensities required no correction (median internal standard peak intensity was 83% of effluent with values between 71% and 98%), while five-fold diluted influent peak intensities (median 44%, with values between 36% and 50%) were corrected by dividing by 0.44. All batches were filtered for false positives by retaining only features with intensities at least five times the average field blank and three times the highest field blank.

The RSD for internal standard signals between effluent samples and field blanks was ~20% for most compounds, except acetamiprid-D3, which had an RSD of about 30% (most likely due to its low signal intensities (<1000 counts)) (Figure S3). Given that the internal standards were spiked before sample preparation and the SPE enrichment was performed across 15 laboratories using wastewater from 30 WWTPs, these variations were considered acceptable, and matrix effects in effluent samples were concluded to be minor. Therefore, applying additional corrections using non-matching internal standards could introduce bias by artificially altering peak intensities and was thus avoided. In contrast, undiluted influent samples showed higher internal standard variability (RSD up to 40%), making matrix effect corrections necessary. Influent samples were used solely to screen for compounds identified in the effluent, allowing for an evaluation of their removal in WWTPs. For assessing removal efficiency (comparison between influent and effluent), influent peak intensities were adjusted using the average response of the two internal standards closest in retention time. For compounds with peak intensities above a threshold of 1000, the accuracy of this correction was validated by comparing signal ratios between five-fold diluted (corrected by multiplying signal intensity by five) and undiluted samples (Table S3). Validation was considered successful if the ratios fell within 80–150%. However, three compounds (6:2 fluorotelomer amido betaine (FTAB), celecoxib, and PFOS) exceeded this range, with average ratios of 226%, 268%, and 290%, respectively (Table S3), showing two to three times higher normalized peak intensity for diluted samples compared to undiluted samples. Thus, in undiluted influent samples, incomplete matrix effect correction may lead to higher uncertainty in the calculated removal efficiencies for these compounds, wherefore 6:2 FTAB, celecoxib, and PFOS were excluded from removal calculations.

### 2.3.2. Target, Suspect, and Non-Target Screening of PFAS and fluorinated ion liquids

For target screening, analytical standards matched by retention time (±0.1 min) and accurate mass (<5 ppm) were used and further confirmed with the presence of matching fragment ions (Table S4). In suspect screening, features were matched to accurate mass (<5 ppm) using two suspect lists (Table S5 and S6). Depending on the charge of the suspect, either the deprotonated or monoisotopic mass for negatively charged molecules, which is often the case for ionic liquids, was used for screening (both lists are available in NORMAN Suspect List Exchange (NORMAN-SLE)[32,33,36]). Isotope patterns were investigated manually for potential hits to ensure the detection of molecules without isotopic patterns, which might not be prioritized by the NTS workflow. The absence of isotopes could result from low signal intensities, which is expected for suspected fluorine-rich compounds as they have less carbon atoms. In case of ionic liquids, such as hexafluoroanions, even no carbon atoms are present, which means a complete lack of isotopes.

For NTS of organic fluorinated compounds the PFΔ*Screen* software[37], adapted for MS-DIAL outputs[38] was used. MS-DIAL has proven reproducible results for feature detection for SFC data in environmental analysis[39]. The suspect list used in PFΔ*Screen* was the NIST PFAS suspect list, containing 4964 entries[34]. Features prioritized for identification either matched accurate mass/isotope pattern criteria (5 mDa/ >90%) or appeared in PFAS-specific regions of MD/C-m/C plots and Kendrick mass defect series ($CF_2$ repeats)[40–42].

For compounds prioritized by suspect and non-target screening, retention time was used to increase confidence: in SFC analysis (BEH column), PFAS are eluting in a specific retention time area: in our study, 34 target PFAS from $C_1$ to $C_{13}$ eluted within 4 to 6 minutes (Table S4). Thus, a retention time window from 3 to 7 min was determined (±1 min of target PFAS), as specific region where highly fluorinated PFAS are likely to elute. For prioritized compounds, fragments were investigated manually (either DDA or DIA) and compared with characteristic PFAS fragments, fragment mass differences or common losses[43,44].

Finally, PFAS were kept if confirmed by analytical standard (confidence level 1) or high confidence in identification (confidence level 2a/b)[45,46]. Confidence level 2 was assigned to PFAS identified by matching libraries, or characteristic fragments for structural identification. In addition, this level of confidence was also given to compounds that were part of a homologous series in which at least one homologue had been confirmed using an analytical standard.

### 2.3.3. Quantification via Non-Target Screening workflow

Compounds with available analytical standards were quantified using five-point calibration curves (0.1-10 µg/L in 100-fold enriched extracts, equivalent to 1–100 ng/L in the original, non-enriched samples). The limit of quantification was estimated as the lowest calibration level that could be reliably detected and showed a linear response consistent with the higher concentration standards. For compounds lacking analytical standards, structurally similar surrogate standards from the same homologous series were used. Peak intensities within compound classes PFSAs, perfluoroalkylether sulfonic acids (PFESAs), fluorotelomer sulfonic acids (FTSAs), sulfonamides, and fluorinated anions varied less than 9% across homologues or analogous (P vs. As) (Figure S4). This consistency likely results from similar chromatographic behavior and ionization efficiency under the employed SFC conditions. However, if compound classes are forming in-source fragments as perfluorocarboxylic acids (PFCAs), the variability in response factors is higher due to chain-length-dependent in-source fragmentation [47]. For none of the compound classes used for surrogate standards in-source fragmentation was observed. Four bis-FASIs ($BETI^-$, $FSI^-$, $FTFSI^-$, and $FTNTf2^-$) were quantified using

$NTf_2^-$ as the surrogate due to their shared core structure and classification within the same homologous series (with no evidence of in-source fragmentation). The PFESA compound 1:2 H-PFESA was quantified using PFBS as a surrogate, due to its structural similarity as a hydrogen-substituted C3-ether sulfonic acid within the same PFAS class. Celecoxib was quantified with the sulfonamide n-ethyl perfluorooctane sulfonamidoacetic acid (N-Et-FOSAA). Hexafluoroisopropanol could not be quantified, as no structurally similar standard was available. In conclusion, 21 compounds (all with confidence level 1) were quantified based on their analytical standard, six compounds were quantified based on surrogated standards ($BETI^-$, $FSI^-$, $FTFSI^-$, and $FTNTf2^-$, 1:2 H-PFESA and celecoxib) and one compound was not quantified. Concentrations were reported using two significant digits. The uncertainty is expected to be higher than in conventional targeted analyses, even when analytical standards are used, due to the absence of matching internal standards in non-target screening.

# 3. Results and discussion

## 3.1. Identification and occurrence of PFAS and inorganic ion liquids

In this study, we prioritized compounds identified with the selected workflow (HLB-SPE for sample preparation and SFC-HRMS for analysis) with high confidence (levels 1 or 2a/b). In total, 28 PFAS were identified (Figure 2, Table S7 and available as Norman SLE list[48]). These included nine ionic liquids, containing two inorganic fluorinated anions (HexaF-anions), five bis-FASI anions, hexafluoroisopropanol (HFIP), and trifluoromethanesulfonic acid (TFMS). Additionally, four PFSAs and two PFCAs were detected, along with several replacement PFAS: two FTSAs, two PFESAs and one sulfonamide. The analysis also revealed eight low-fluorinated PFAS of pharmaceutical, biocides, or industrial origin.

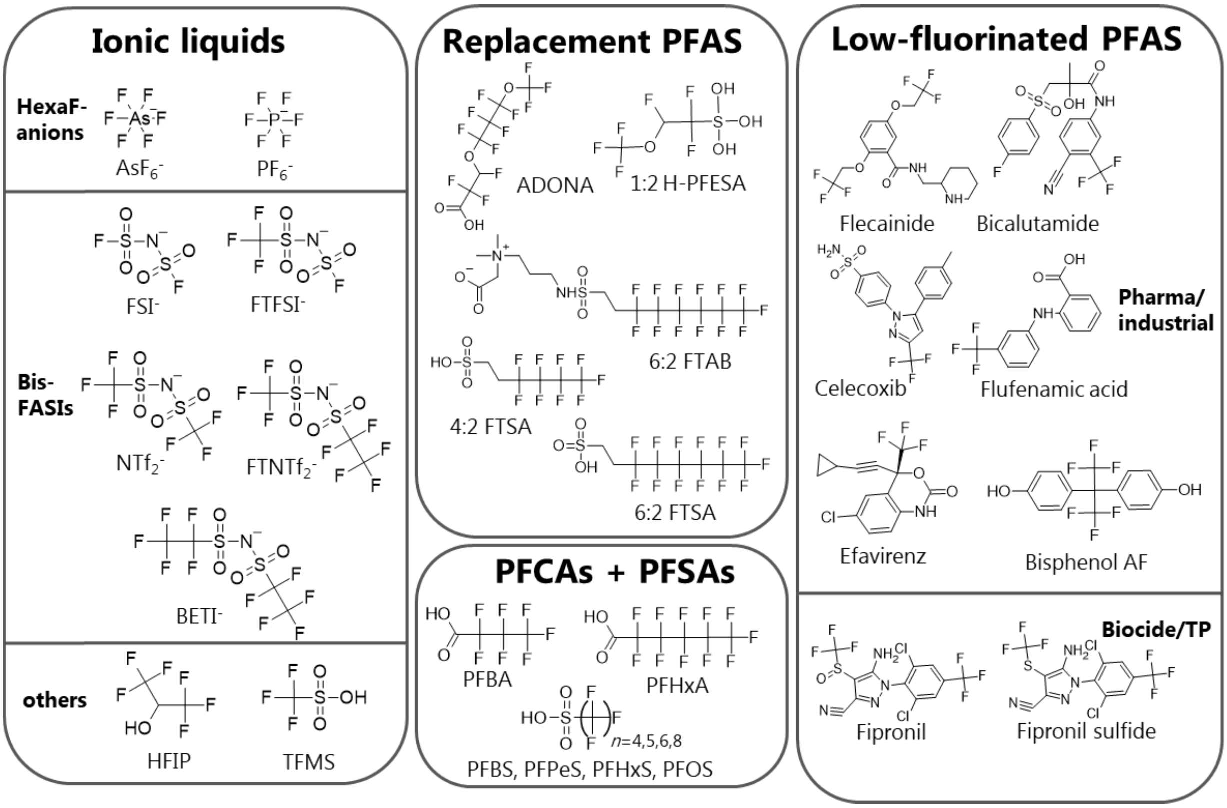


**Figure 2:** Chemical structures of PFAS and inorganic fluorinated compounds identified in European wastewater effluent samples, available as the SFCPFASFIONS list[48].

*Ionic liquids*

In this study, nine compounds were identified as related to ionic liquid use. Ionic liquids are salts dissolved in solvents and used as electrolytes in various applications including electronics and energy storage[19]. $NTf_2^-$ (bistriflimide), was detected in 22 of 30 samples (75% detection frequency), and is commonly used in electronic devices and electric vehicles due to its high ionic conductivity and electrochemical stability[21]. While $NTf_2^-$ has historically been infrequently reported in environmental samples, recent studies indicate ubiquitous contamination in environmental samples, including samples near e-waste recycling facilities[49], landfill leachate[50], and surface waters[51]. Reported concentration in these previous studies (around 10 ng/L) are in accordance with the highest concentrations observed in this study (13 ng/L, Belgium). Additionally, $NTf_2^-$ raises environmental concerns due to its polarity and high degree of fluorination, which have been linked to increased toxicity for photobacterium *vibrio fischeri*: Montalbán et al. (2016)[52] demonstrated this in their study on 29 ionic liquids, showing that anionic counterions with greater fluorination exhibited the highest toxicity levels.

In addition to $NTf_2^-$, several other bis-FASIs were identified (Figure 3A). Similar peak intensities were observed for the structurally related bis-FASI, namely $FSI^-$ (two fewer $CF_2$ units) and $BETI^-$ (two additional $CF_2$ units compared to $NTf_2^-$). As $FSI^-$ is an inorganic ion and has no carbon atoms it is not considered as PFAS according to the OECD definition. These analogues ($FSI^-$ and $BETI^-$) have been synthesized and used since the 2010s, extending their application beyond lithium to include sodium, potassium, and zinc batteries[19,53,54]. Like $NTf_2^-$, $BETI^-$ has been detected previously in surface water near production sites [53]. Two previously unreported homologues were also identified: $NTf_2^-$–$CF_2$ ($FTFSI^-$) and $NTf_2^-$+$CF_2$ ($FTNTf_2^-$). $FTFSI^-$ has known ionic liquid applications[54], while $FTNTf_2^-$ has not been previously described.

These bis-FASI homologues showed characteristic retention time shifts (Figure 3A), with decreasing retention as the number of $CF_2$ units increased (less polar), typical for normal-phase SFC. The complete homologous series of bis-FASIs, including $FTFSI^-$ and $FTNTf_2^-$, was exclusively found in one wastewater effluent sample from Czech Republic (CZ1, Figure 3B). Their infrequent occurrence and lower peak intensities compared to $NTf_2^-$, $FSI^-$, and $BETI^-$, suggest that they may represent impurities or transformation products rather than intentional ionic liquid ingredients. In general, the sample CZ1 showed the highest sum concentration of bis-FASIs (18 ng/L).

Out of the 26 samples in which bis-FASIs were detected, $NTf_2^-$ had the highest peak intensities in 20 samples (Figure 3B). However, in six samples, either $FSI^-$ or $BETI^-$ showed higher intensities. Notably, $NTf_2^-$ comprised <5% of total bis-FASI intensity at the smaller WWTP sites in Denmark, Austria, Switzerland, and both sites in Czech Republic, reflecting regional differences in bis-FASI composition. Specific sources of these ionic liquids were not known at any of the sampling locations.

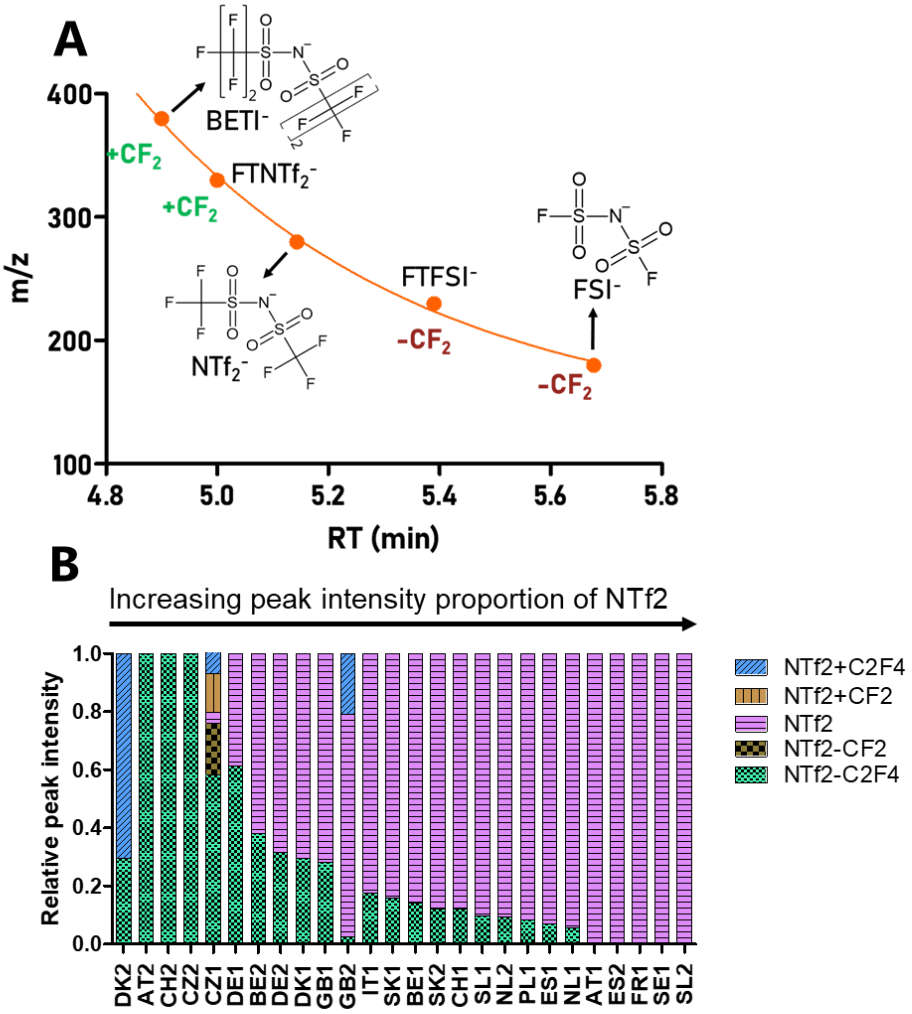


**Figure 3:** A) m/z and retention times of bis-FASIs belonging to a homologous series centered around $NTf_2^-$, detected in wastewater effluent. B) Relative peak intensities of NTf2$^-$-2CF$_2$ (FSI$^-$), NTf2$^-$-CF$_2$ (FTFSI$^-$) NTf2$^-$, NTf2$^-$+CF$_2$ (FTNTf$_2^-$) and NTf2$^-$+2CF$_2$ (BETI-) in wastewater effluent samples across Europe.

A second class of ionic liquids identified in this study consisted of inorganic hexafluorinated anions, $PF_6^-$ and $AsF_6^-$ (Figure 2). Lithium $PF_6^-$ is widely used as the primary electrolyte salt in lithium-ion batteries due to its high ionic conductivity and ability to passivate aluminum current collectors[19]. In this study, the widespread presence of $PF_6^-$ in the environment was confirmed by the occurrence in all samples (Figure 4). Muschket et al. (2024) [22] reported $PF_6^-$ occurrence in >80% of river water and 97% of wastewater samples in Germany, with median concentrations of 0.2 µg/L and 2.6 µg/L, respectively. Consistent with these findings, our study identified the highest $PF_6^-$ concentrations in samples from Germany (2.0 and 3.0 µg/L). Except for one sample from Sweden, all samples exceeded 0.1 µg/L.

$AsF_6^-$ is less commonly used than $PF_6^-$, but also functions as an ionic liquid component, a superacid in organic synthesis, and is used in crystal glass production[19]. To our knowledge, this is the first report of $AsF_6^-$ in municipal wastewater effluents. It has previously been detected in lake water impacted by contaminated wastewater discharged through a former crystal glass factory[55]. In the current study, $AsF_6^-$ was detected at lower concentrations than $PF_6^-$, with a median concentration of 17 ng/L in samples where it was detected. Its presence was confirmed in 32% of effluent samples in eight countries, including Belgium, the Czech Republic, Germany, Spain, Italy, Poland, Sweden, and Slovakia.

Hexafluoroisopropanol (HFIP) was identified with confidence level 2a. Its first environmental detection was reported in German drinking water[56], and has since been found in soils near e-waste recycling sites, suggesting a possible link to electronic manufacturing and recycling[57]. In this study, HFIP was detected in single effluent samples from Spain and Slovakia.

Trifluoromethansulfonic acid (TFMS), detected in samples from Switzerland and at the highest concentration in Spain (15 ng/L), is used in lithium-ion batteries since the 1970s as the salt $LiSO_3CF_3$ (triflate)[19]. However, even though it is already detected at several locations in the water cycle, environmental sources of TFMS remain unclear[56].

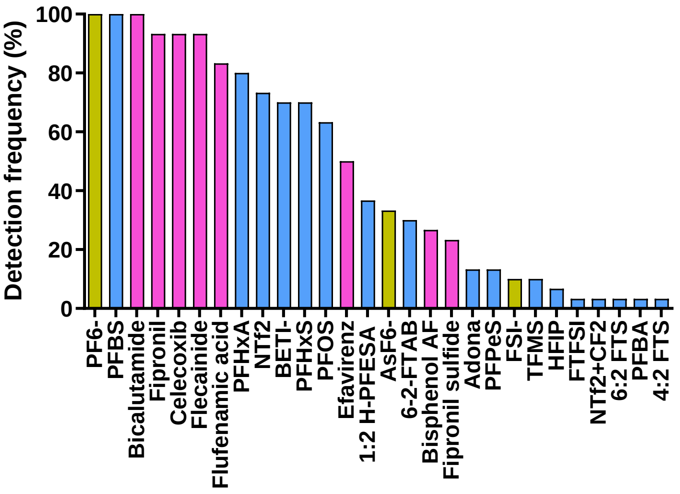


**Figure 4:** Detection frequency of identified compounds in the 30 wastewater effluent samples. Gold=inorganic fluorinated substances, pink= low-fluorinated substances, blue= other PFAS

*Replacement PFAS and transformation products (TPs)*

In response to restrictions on long-chain PFAS, replacement products have been developed, including Gen-X (hexafluoropropylene oxide dimer acid, HFPO-DA), ADONA (dodecafluoro-3H-4,8-dioxanonanoate), and F53-B (6:2 chlorinated polyfluoroalkyl ether sulfonate)[58]. In this study, ADONA was detected in four samples: both from the Czech Republic (60 and 170 ng/L), Slovakia (145 ng/L), and Great Britain (60 ng/L). While ADONA is a well-known replacement PFAS, environmental data remain limited primarily from China [50]. In a study of 10 Belgian WWTPs, ADONA was not detected, and its detection frequency was low in surface water samples worldwide (15 out of 160 samples[59]). However, widespread occurrence was reported in German rivers[60]. Gen-X was part of the target screening method, but not detected in any sample.

The compound 1:2 H-PFESA, previously reported in wastewater from Belgium[61] and China[62], is suspected to be a TP of F53-B. Wang et al (2020)[62] identified 1:2 H-PFESA via homologues series analysis, where the main compound was 6:2 H-PFESA, a known TP of the main component of F53-B (6:2 Cl-PFESA)[10]. In this study, we confirmed the structure of 1:2 H-PFESA based on characteristic fragment ions (Figure S5) and retention time trends following known PFSA standards (standards with the same core structure but missing ether bond (Figure S6)), facilitating identification to confidence level 2b. 1:2 H-PFESA was detected in 35 % of the samples, including both Belgian samples, with the highest peak intensities in samples from France (Figure 4 and Table S8).

Fluorotelomers, another group of PFAS partly used as replacements, are characterized by a hydrocarbon ($C_2H_4$) spacer between the perfluoroalkyl chain and functional group. In this study, 6:2 FTSA (160 ng/L), 4:2 FTSA (3 ng/L) and 6:2 FTAB (31 ng/L) were identified in a composite wastewater sample from the large WWTP in Spain. Both 6:2 FTSA and 6:2 FTAB have been previously reported in wastewater from AFFF-impacted sites in France[63]. 6:2 FTAB, a known constituent of AFFF formulations (e.g., Capstone product B), is frequently found in high levels in AFFF contaminated environments[64]. Additionally, 4:2 FTSA has been reported in effluents from AFFF-impacted WWTPs in the U.S.[65] and in 6% of wastewater effluent samples in Italy[66]. In this study, 6:2 FTAB was detected in both Austrian and Swiss samples, and in approximately 30% of the larger WWTPs in the other countries, with the highest concentrations observed in Great Britain (380 ng/L).

*Perfluoroalkyl sulfonic and carboxylic acids (PFSAs and PFCAs)*

PFBS ($C_4$ PFSA) was detected in all wastewater effluent samples, followed by PFHxS ($C_6$ PFSA) in >70% and PFOS ($C_8$ PFSA) in 60% of the samples. PFPeS ($C_5$ PFSA) was detected in only four samples. Notably, samples from the Czech Republic were the only ones where PFBS as only PFSA was detected. Consistent with previous reports on wastewater, short-chain PFSAs were generally found at higher concentrations than their long-chain analogues[61]. This trend was also observed here, with average concentrations of 4 ng/L (PFBS), 3 ng/L (PFHxS), and 2 ng/L (PFOS).

Besides PFSAs, PFCAs are among the most frequently reported PFAS in wastewater globally[58]. However, they are analytically challenging for NTS due to in-source fragmentation, blank contamination[47], and lower SPE recovery. In this study, PFBA ($C_3$ PFCA), PFHxA ($C_5$ PFCA), and PFOA ($C_7$ PFCA) were detected. PFOA, however, was excluded from further analysis as peak intensities in samples were <3 times the intensity found in in field blanks, indicating background contamination. PFBA was only detected above threshold in the small WWTP in Austria, with a concentration exceeding 2 µg/L, approximately 20 times higher than typical levels reported in wastewater[58], suggesting a point source. PFHxA was more widespread, detected in 80% of samples, with the highest concentration observed in the Czech republic (12 ng/L).

*Low-fluorinated substances*

In this study, low-fluorinated substances were categorized as PFAS with a fluorine mass percentage below 40% (Figure S1 and S7). According to this definition, the identified low-fluorinated substances included five pharmaceuticals, one biocide (fipronil) along with its transformation product (TP), and one industrial compound, bisphenol AF. All compounds had at least on perfluorinated methyl group. While TFMS (38% F), $FTFSI^-$ (33% F) an $FSI^-$ (21% F) fall under this threshold as well, they are discussed separately as they belong to the compound class of ionic liquids. Maximum concentrations ranged from 56 ng/L for fipronil sulfide (Slovakia) to 630 ng/L for the prostate cancer drug bicalutamide (Sweden), and up to 2000 ng/L for the anti-arrhythmic drug flecainide (Germany). Bicalutamide has been recently reported among the top ten priority chemicals in Swedish domestic effluent waters with measured concentrations frequently exceeding the respective PNEC of 93 ng/L[67]. The highest concentrations of fipronil were detected in Slovakia (140 ng/L), along with its TP fipronil sulfide (56 ng/L). Flufenamic acid, celecoxib, flecainide, and bicalutamide were detected in >85% of samples across Europe.

Bisphenol AF, a structural analogues of bisphenol A containing two $CF_3$-groups, was detected in 25% of samples, with 59 ng/L as highest concentration (Slovakia). Bisphenol AF is even more environmentally persistent[68] and may exhibit equal or greater endocrine-disrupting potential than bisphenol A [69].

### 3.2. Fate of PFAS in conventional treatment processes

Among the identified compounds present in both influent and effluent, removal through conventional treatment was observed for the fluoroether 1:2 H-PFESA and the fluorotelomers 6:2 FTSA. This is consistent with earlier studies showing partial degradation of fluortelomers like 6:2 FTSA, which can transform into fully fluorinated perfluoroalkyl acids [3].

Sucralose was used as a benchmark compound (Figure 4) due to its well-documented persistence in WWTPs [18] and its elution within the PFAS retention time window of 4 to 6 min (5.2 min for sucralose). Its removal varied around 0 ± 20%, supporting the reliability of the removal efficiency assessment in this study. Variations may arise from discrepancies in hydraulic retention time between influent and effluent samples, or from inadequate correction for matrix effects. Due to these potential variations, and in line with a previous NTS study[35], a compound was considered "removed" if the median removal exceeded 50%.

All other compounds, including NTf2$^{-}$ and the inorganic fluorinated anions (FSI$^{-}$, $PF_6^-$, and $AsF_6^-$), remained persistent in wastewater treatment. This observation aligns with findings from Muschket et al. (2024)[22], who reported that $PF_6^-$ persists through riverbank filtration, even when many other contaminants are effectively removed. In this study, $AsF_6^-$ showed similar persistence to $PF_6^-$. Data on the environmental persistence of bis-FASIs remains limited, but their stability is supported by the fact that they were not degraded in the total oxidizable precursor (TOP) assay[53]. Low-fluorinated substances showed also little to no removal. Fipronil sulfide, the TP of fipronil, had negative % removal, which indicated formation of this chemical due to transformation of fipronil.

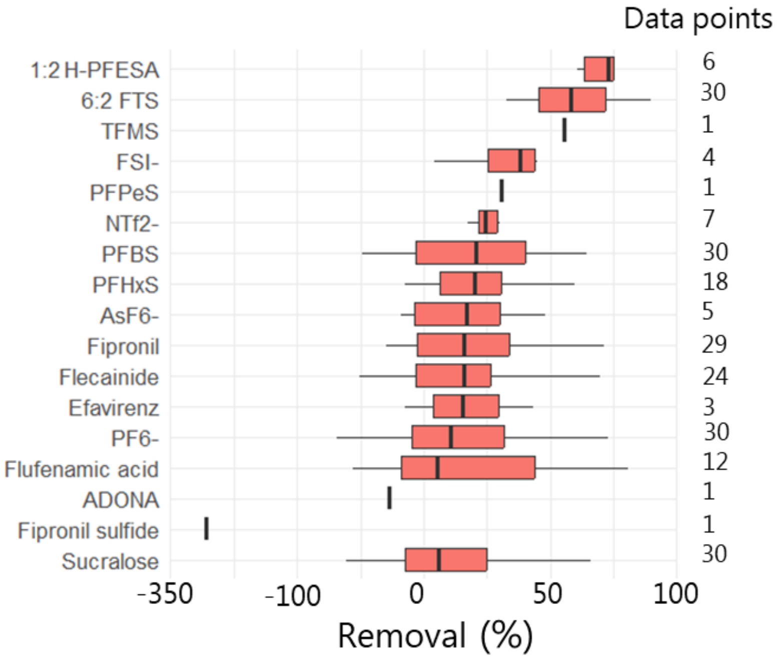


**Figure 5:** Removal of identified compounds detected in both influent and effluent samples from the same WWTP in comparison to the persistent benchmark compound sucralose. Negative removal (<0%) indicates higher concentrations in the effluent, suggesting possible formation or release during treatment. The number of data points refers to the total number of removal values (%) calculated across sampling sites. The full names can be seen in Table S8.

### 3.3. Patterns of PFAS occurrence, sources, and implications

Overall, PFSAs and PFCAs were detected at the lower end of concentrations typically reported in literature[58]. This may be attributed to the dry weather sampling conditions, which likely limited PFAS inputs from diffuse sources such as runoff and landfill leachates [70]. Additionally, unlike hotspot investigations, e.g., sites near airports, this study was not focused on areas with potentially high PFAS contamination.

$PF_6^-$, PFBS, and bicalutamide were detected in all effluent samples (Figure 4). Notably, the inorganic hexafluoroanions $PF_6^-$ and $AsF_6^-$ were present at higher concentrations than any PFSAs or PFCAs in 97% of the samples. When calculating fluorine equivalents based on compound classes, $PF_6^-$ and $AsF_6^-$ contributed to 27 times more fluorine than PFSAs and PFCAs, after recovery correction (Figure 6). On average, these hexafluoroanions exhibited five times higher concentrations than those of PFSAs and PFCAs, contributing to more than 50% of the total fluorine equivalent concentration in 26 out of 30 samples (Figure S8). Although $PF_6^-$ and $AsF_6^-$ are inorganic, they are still enriched by SPE (e.g., using WAX or HLB cartridges) and could be detected during EOF analysis. This raises an important consideration: if these hexafluoroanions are co-extracted and measured alongside organic fluorine, they may have a major contribution to EOF values. Consequently, their presence could partially explain the often-observed discrepancy between total EOF measurements and concentrations from conventional targeted PFAS analyses. While some uncertainty in HLB recovery of $PF_6^-$ is expected in this study, even without applying recovery correction, the inorganic anions still represent a larger share of the fluorine mass balance as PFSAs and PFCAs (Figure 6). For EOF, WAX is used for enrichment, which showed higher recovery of 77% for $PF_6^-$ (S2.1). Additionally, the inorganic ionic liquid anion tetrafluoroborate ($BF_4^-$) was recovered with high efficiency (98%) using WAX, whereas it could not be detected in our study using HLB, likely due to the very low recovery (<1%, S2.1).

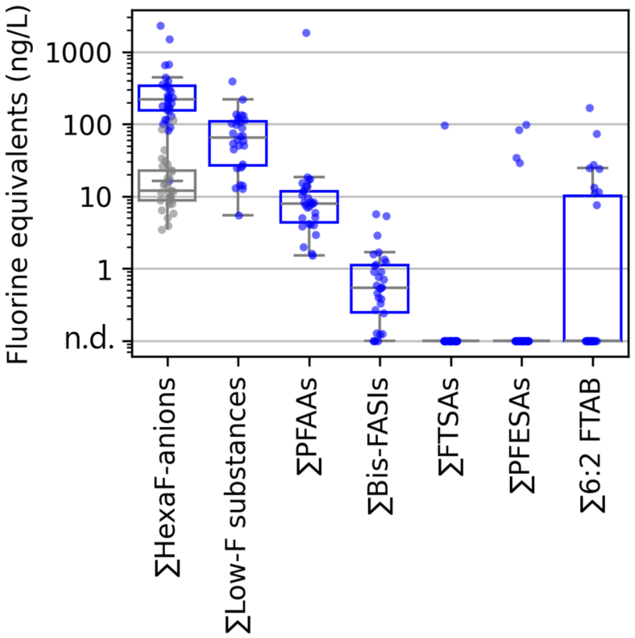


**Figure 6:** Fluorine equivalents calculated from the molecular formulas of identified and quantified compounds from wastewater effluent (*n* = 32). PFAA= PFSAs+PFCAs. $PF_6^-$ concentrations were corrected for recovery losses. The grey bar indicates fluorine equivalents for hexafluoride (hexaF) anions ($PF_6^-$ and $AsF_6^-$) based on uncorrected $PF_6^-$ concentrations.

Additionally, low-fluorinated substances such as pharmaceuticals, pesticides, and the plasticizer bisphenol AF were the second largest contributors to the overall fluorine load, frequently exceeding 100 ng/L in summed concentrations (Figure 6 and Figure S8). Fluorine mass balance studies have shown that inclusion of low-fluorinated PFAS and even less fluorinated pharmaceuticals (not defined as PFAS) can increase the explained fraction of EOF in WWTP sludge from 2% to 27% [15]. However, $PF_6^-$ alone exceeded the combined concentration of all here identified low-fluorinated substances in 27 of 30 samples, showing its ubiquitous occurrence and potential significance in fluorine mass balances in wastewater.

In Figure 7, concentrations of selected PFAS across 15 European countries are compared, grouped by WWTP size. Bis-FASIs were frequently detected, although generally at low concentrations (<20 ng/L). Their environmental relevance remains uncertain due to unknown SPE recovery. However, they were consistently found at higher concentrations in large WWTPs compared to smaller ones (Figure 7), indicating a potential link to urban or industrial inputs. The sample with the highest number of detected features (small WWTP in France; Figure S9) did not exhibit the highest PFAS diversity or concentration. This suggests that PFAS originate from distinct sources and are not necessarily indicators of chemically complex or matrix-rich wastewater samples. No bis-FASIs were detected in that sample, and PFSA and PFCA levels were below 8 ng/L. However, 1:2 H-PFESA was detected at a high concentration of 250 ng/L, showing the influence of specific sources.

While sampling hotspots were not specifically targeted, a PFAS production facility upstream of the large Spanish WWTP likely influenced the local PFAS profile. This sample showed the highest peak intensities for $AsF_6^-$ (used in ionic liquids) and HFIP (linked to electronics recycling), associated with electronic manufacturing. It also had the second-highest concentration of PFBS and uniquely contained both 6:2 FTSA and 4:2 FTSA, which are commonly associated with AFFF use, suggesting an additional PFAS input source. In contrast, low fluorinated pharmaceuticals showed lower peak areas, ranging from 3% to 55% of the highest peak intensity detected in effluent.

The findings of this study demonstrate that the dominant part of the fluorine load in European wastewater effluents might come from fluorinated ionic liquids or low-fluorinated compounds, and not from traditional target PFAS. Their ubiquitous occurrence also raises the question of so far unknown sources of these compound classes as the majority of wastewater originates from households where no typical sources of these compounds are known. In the context of the PFAS definition proposed by the OECD, it is noteworthy that the inorganic fluorinated substances detected by SFC originates from compounds not currently classified as PFAS. Many of these substances are neither regulated nor routinely monitored. Their consistent detection across diverse countries and WWTPs underscores the urgent need to broaden the scope of PFAS screening strategies, investigate their sources and uses, and to incorporate these compound classes into future environmental monitoring.

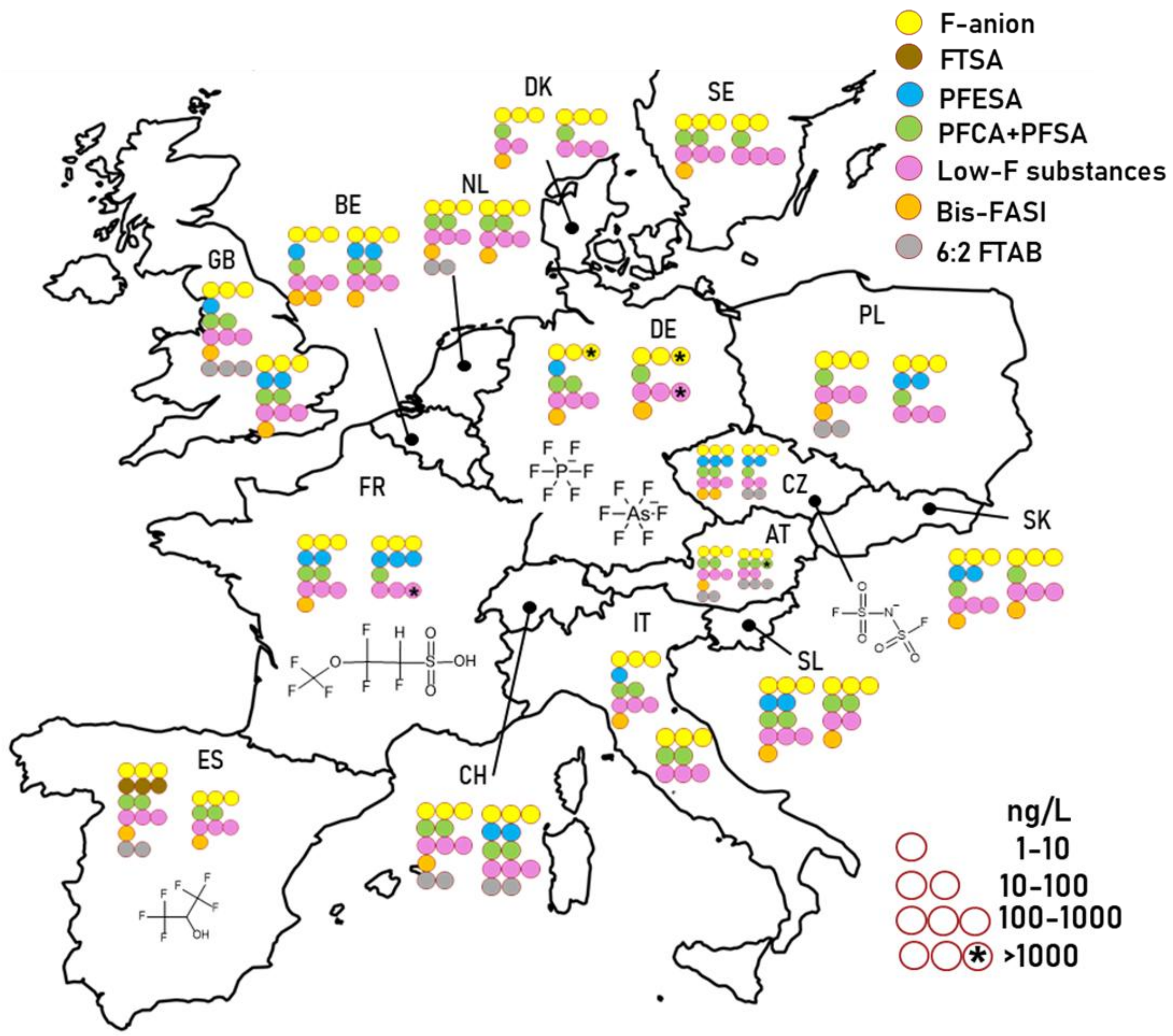


**Figure 7:** Concentration range of the identified PFAS across European wastewater effluent samples. Left and right point scales belong to the big and small WWTP per country, respectively. PFAS are displayed with their structure in the country of highest occurrence.

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## Supporting Information

Additional details on sample preparation, result plots, and supplementary figures are provided in SI_A (Word document). Supporting tables related to materials and methods, as well as results, are available in SI_B (Excel file).

## Author Contributions

**ST:** conceptualization, data acquisition and analysis, investigation, methodology, visualization, writing-original draft**. JZ:** investigation, visualization, writing- review & editing; **MKG**: data acquisition, validation; **SF, WB, BKH**: conceptualization, project administration, writing- review & editing; **EB, CM, JH, TK, PL, AK**: validation, writing- review & editing; **ELS**: data curation, writing- review & editing; **ES, DE, HE, TB, AC, HO, HFQ, FYL, LZ, AA, FB:** writing- review & editing; **JHC**: supervision, writing- review & editing.

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