Suspect screening and total oxidizable precursor (TOP) assay as tools for characterization of per- and polyfluoroalkyl substance (PFAS)-contaminated groundwater and treated landfill leachate

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HIGHLIGHTS

- Total Oxidizable Precursor assay for characterizing precursors and persistent PFAS
- Suspect screening revealed 29 persistent PFAS with High-Resolution Mass Spectrometry
- Levels of PFAS in landfill leachate and groundwater determined with MS/MS
- Semi-quantification of PFAS not commonly covered in targeted methods

GRAPHICAL ABSTRACT
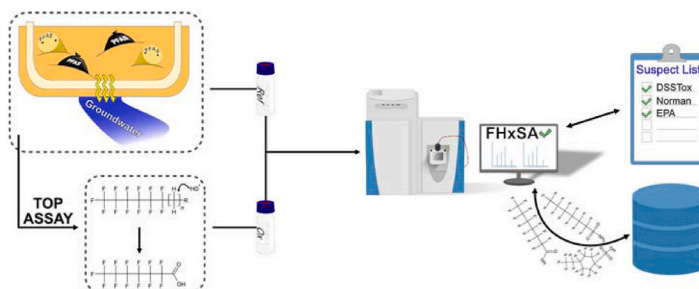
ARTICLE INFO

ABSTRACT

Landfill facilities are a major source of release of per- and polyfluoroalkyl substances (PFAS) to the surrounding environment. In this study, landfill leachate treated in a conventional wastewater treatment plant and PFAS-contaminated groundwater were subjected to suspect screening analysis and semi-quantification using total oxidizable precursor (TOP) assay and liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). TOP assays yielded expected results for legacy PFAS and their precursors, but showed no discernible evidence of degradation of perfluoroethylcyclohexane sulfonic acid. TOP assays also produced significant evidence of presence of precursors in both treated landfill leachate and groundwater, but the majority of precursors had probably degraded into legacy PFAS after many years in the landfill. Suspect screening identified a total of 28 PF AS, of which six were not included in the targeted method and were identified with confidence level (CL) ≥3. Semi-quantification of these six compounds showed very low concentrations, indicating that they are not as great a concern as the target PFAS.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic chemicals characterized by a –CF$_2$- or –CF$_3$ moiety according to the OECD definition (OECD. Reconciling Terminology of the, 2021). PFAS are potential toxic, bioaccumulative, and typically extremely persistent (Podder et al., 2021), and display hydrophilic and hydrophobic properties (Gallen et al., 2017). They are used in many consumer

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products and industrial applications, such as non-stick coating on cookware, food packaging, waterproof coating on outdoor clothes, aqueous film-forming foams (AFFF), functional fluids for machinery, and anti-corrosion agents (Sajid and Ilyas, 2017; Zabaleta et al., 2017; Kotthoff et al., 2015; Houtz et al., 2016; Glüge et al., 2020). The stability and persistence of PFAS has led to their widespread distribution in biota, sediment, soil, fresh and marine water, and groundwater (Nakayama et al., 2019). Typical sources of PFAS in the aquatic environment are municipal and industrial wastewater treatment plants (WWTPs) and landfill facilities (Letcher et al., 2015). Due to the widespread pollution and their toxic properties, PFAS are being partly phased out or increasingly regulated (Gobelius et al., 2018). Monitoring of PFAS by environmental agencies, drinking water plants, WWTPs, and other facilities typically takes the form of targeted analysis using liquid chromatography coupled with mass spectrometry (Mulabagal et al., 2018a). In such monitoring studies on water matrices, a few dozen PFAS are usually included (Mulabagal et al., 2018b), but this represents only a small fraction of the >5000 different PFAS listed by the OECD and in other recent studies (OECD. Reconciling Terminology of the, 2021; Barnabas et al., 2022). Analytical challenges include a lack of authentic standards for non-legacy PFAS and of characterization tools for identification of PFAS in water samples (Ruyle et al., 2021).

Many non-legacy PFAS, so-called PFAS precursors, are not fully fluorinated and can degrade to more persistent PFAS, such as perfluoroalkane sulfonic acids (PFSA) and perfluoroalkyl carboxylic acids (PFCA), which can be detected with target analysis methods (Taylor and Sapozhnikova, 2022). The presence of PFAS precursors can be confirmed using a total oxidizable precursor (TOP) assay, which transforms PFAS precursors into legacy PFAS that can be detected with target analysis methods (Houtz and Sedlak, 2012). However, some studies have investigated the type of PFAS precursors oxidized during TOP assays, mostly by using advanced statistical analyses on observed yields after oxidation, which vary depending on whether the PFAS precursors were produced by fluorotelomerization or electrochemical fluorination (Ruyle et al., 2021; Cortés-Francisco and Caixach, 2015). In addition, most TOP assays to date have been performed on biota, surface water, and AFFF, while studies on wastewater matrices originating from treated landfill leachate are lacking (Ruyle et al., 2021; Koch et al., 2019; Shojaei et al., 2022; Houtz et al., 2018).

A drawback of the TOP assay is that only PFAS which degrade during the oxidization process and can be detected using target analysis methods are considered, whereas for identification of PFAS molecules high-resolution mass spectrometry (HRMS) methods are needed (Krauss et al., 2010). The high resolving power (>10,000) and high mass accuracy (≤5 parts-per-million (ppm)) of HRMS allows a molecular formula to be assigned to observed m/z (Gross, 2017; Liu et al., 2015; Menger et al., 2020). With HRMS, it is possible to employ suspect screening, which relies on accurate masses that are matched to suspect lists containing monoisotopic masses. On the other hand, targeted analysis use reference standards to analyze the target chemicals specifically with retention times and mass spectra. Non-target screening is also a common HRMS technique, which uses prioritization and data-filtering strategies for identification of PFAS (Myers et al., 2014). A commonly used method for prioritization and characterization of PFAS is to calculate Kendrick mass defects, which are derived from the difference between the exact and nominal mass of fluorine. This allows for easy identification of homologous series of PFAS with varying chain length and commonly detected PFAS fragments (e.g., C_2F_5) (Kendrick, 1963; Strynar et al., 2015). Combined suspect and non-target screening has become a widely used method in environmental analytical chemistry, due to the sensitivity, reproducibility, and selectivity it can provide (Nakayama et al., 2019; Liu et al., 2019). However, few studies have applied suspect and non-target screening to matrices such as treated landfill leachate and the groundwater impacted by landfills (Gago-Ferrero et al., 2015).

The overall aim of this study was to identify new PFAS in two complex matrices, groundwater and WWTP-treated landfill leachate, at a landfill site in Sweden. Specific objectives were to (1) investigate degradation of PFAS precursors and legacy PFAS in TOP assays; (2) develop a simple suspect screening workflow for identification of PFAS in complex aqueous matrices; (3) perform prioritization of PFAS based on Kendrick mass defects and homologous series; and (4) identify PFAS with the highest level of confidence possible and semi-quantify their concentrations.

2. Materials and methods

2.1. Target PFAS

In total, 29 PFAS were selected for target analysis, comprising 11 (C_3–C_{13}) perfluoroalkyl carboxylic acids (PFCA) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA), eight (C_4–C_{10}) perfluoroalkane sulfonic acids (PFSA) (PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFECHS), three n:2 fluorotelomer sulfonates (FTSA) (4:2 FTSA, 6:2 FTSA, 8:2 FTSA), two compounds of F–53 B (9Cl-PF3ONS, 11Cl-PF3OUdS), GenX (HFPO-DA), FOSA, MeFOSAA, EtFOSAA, and NaDONA. In addition, two n:2 fluorotelomer phosphate diesters (6:2 diPAP, 8:2 diPAP) were used for TOP assay experiments. For details, full names, and abbreviations, see Table S1 in Supporting Information (SI). For quantification, 20 internal standards (IS) from an IS mixture were added to the calibration standards and samples before extraction (Wellington Laboratories). These were: $^{13}C_4$-PFBA, $^{13}C_5$-PFPeA, $^{13}C_5$-PFHxA, $^{13}C_4$-PFHpA, $^{13}C_8$-PFOA, $^{13}C_9$-PFNA, $^{13}C_6$-PFDA, $^{13}C_7$-PFUnDA, $^{13}C_3$-PFDoDA, $^{13}C_2$-PFTeDA, $^{13}C_3$-PFBS, $^{13}C_3$-PFHxS, $^{13}C_8$-PFOS, $^{13}C_2$-4:2 FTSA, $^{13}C_2$-6:2 FTSA, $^{13}C_2$-8:2 FTSA, $^{13}C_8$FOSA, D_3-MeFOSAA, D_5-EtFOSAA, and $^{13}C_3$–HFPO-DA (for details on abbreviation names and IS purity, see Tables S1 and S2 in SI).

2.2. Sample collection

Treated landfill leachate and groundwater samples were collected at the Hovgården landfill site outside Uppsala, Sweden, in November 2021, using polypropylene bottles. The landfill has opened in 1971 and is still actively used to store mainly ashes from domestic waste incineration. All samples were filtered through Whatman® glass microfiber filters (47 mm diameter, 0.7 μm pore size) and stored at −20 °C until analysis.

2.3. Total oxidizable precursor assay

Before the TOP assay, each sample was split in two. One half was used for the TOP assay and the other was analyzed directly using a targeted PFAS method (used as reference). Both the TOP assay samples and the reference samples were analyzed in triplicate (see Section 2.4). In addition, procedural blank samples were prepared by adding equivalent volumes of Milli-Q water to sample containers. For the precursor analysis, three PFAS precursors (6:2 diPAP, 8:2 diPAP, EtFOSA) and three legacy PFAS (PFECHS, PFUnDA, PFTriDA) were spiked individually into Milli-Q water, to a final concentration of 5 ng/mL, and all samples (TOP assay and reference) were prepared and analyzed in duplicate.

The TOP assay was performed as previously described (Houtz and Sedlak, 2012). In brief, each sample and a blank for each sample were spiked with 1.6 g potassium persulfate (ACS reagent grade, Sigma-Aldrich) and 1.52 mL of 10 mol/L sodium hydroxide monohydrate solution (Suprapur, Merck). The samples were sonicated for 5 min and then placed in a water bath held at 85 °C for 5 h. To stop the reaction, the samples were placed in an ice-bath and the pH was adjusted by adding 300 μL of 30% hydrochloric acid (Suprapur, Merck).

2.4. Sample extraction

Before extraction, 100 μL of IS mixture (c = 50 ng/mL for each IS)

were added to the sample, which was then sonicated for 5 min. Extraction was performed using solid-phase extraction (SPE) with Oasis WAX cartridges (6 mL, 150 mg, 30 μm). After pre-conditioning with 4 mL 0.1% (w/w) ammonium hydroxide in methanol, 4 mL methanol, and 4 mL Milli-Q water, 100 mL of sample were loaded on the cartridge, which was eluted under vacuum at approximately one drop per second. The cartridge was then washed with 4 mL of 25 mM ammonium acetate buffer dissolved in Milli-Q water and dried under vacuum. The sample was eluted into a 15 mL polypropylene (PP) tube with 4 mL methanol, and then 4 mL 0.1% ammonium hydroxide in methanol. To concentrate the final sample, a gentle stream of nitrogen was directed above the PP tube and the sample was concentrated to just below the 1 mL mark. The extract was transferred to a 1.5 mL PP vial.

2.5. Targeted PFAS analysis

Targeted PFAS analysis was carried out using a SCIEX ExionLC Triple Quad 3500 liquid chromatograph coupled to a tandem mass spectrometer (LC-MS/MS), which was operated in negative ionization mode. Injection was performed in triplicate with 20 μL of extracted sample onto a Phenomenex Kinetex (2.0 × 4 mm, 1.7 μm) C18 pre-column, and separation on a Phenomenex Gemini 3 μm C18 (2.0 × 50 mm) analytical column at a constant temperature of 40 °C. The mobile phase consisted of 10 mM ammonium acetate in Milli-Q water and methanol, the flow rate was set 600 μL/min, and the final run time was 9 min. The initial gradient conditions were held at 5% organic modifier for 0.1 min, which was increased to 55% after another 0.1 min. The gradient was then increased to 99% over 4.4 min, held for 3.5 min, decreased to 5% over 0.5 min, and held for an additional 0.5 min (for details of the targeted analysis, see Smith et al. (2022)).

Analysis of variance (ANOVA) was used to compare PFAS concentrations before and after TOP assays for the treated landfill leachate and groundwater samples, with significance level α = 0.05. In some cases, a compound was not detected in all 18 analyses due to being below LOQ. To not exclude too many compounds, compounds that were detected in at least 17 of the 18 samples and replicates were included in ANOVA. All compound data used were tested for normal distribution using quantile-quantile plots.

2.6. Suspect screening using high-resolution mass spectrometry

Suspect screening of PFAS on the reference samples was performed using a Vanquish Horizon UHPLC system coupled to a QExactive Focus Orbitrap mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with an Ion Max heated electrospray ionization source (HESI-II) operated in negative ionization mode. Injection was performed with 10 μL of extracted sample, onto a Waters ACQUITY UPLC C18 1.7 μm (2.1 × 50 mm) analytical column equipped with a ACQUITY UPLC C18 1.7 μm guard column, at a constant temperature of 40 °C. The mobile phase consisted of 5 mM ammonium acetate in Milli-Q water and methanol, using a flow rate of 300 μL/min, with a final run time of 17 min. The initial mobile phase composition was set to 10% organic modifier, which was held for 1 min. Next, a gradient was applied, with a final composition of 95% organic modifier over 12 min, which was held for 2 min. Initial conditions were then applied over 0.1 min and held for 1.9 min. The ion source settings were as follows: sheath and auxiliary gas flow rate was set at 30 and 10 arbitrary units, respectively; spray voltage was set to 3.70 kV; capillary and auxiliary gas heater temperature were both set to 350 °C; and S-lens RF level was set at 55 arbitrary units. The instrument was run using data-dependent acquisition (top N DDA, *n* = 3) in *discovery* mode with resolution of 35,000 at 200 *m/z*, with a full scan ranging from 120 to 1000 *m/z* using resolution of 70,000 at 200 *m/z*. The analysis was performed in two injections on the LC-HRMS, one with stepped absolute collision energies of 20 and 60 eV, and one with stepped absolute collision energies of 10 and 20 eV.

2.7. Quality assurance and quality control

Blank samples (one for TOP assay, one for reference samples, one for the laboratory equipment) were spiked with IS prepared under the same conditions as for the TOP assay or natural samples. Procedural and instrumental blanks were analyzed with the same HRMS methods as the samples, to measure contamination and background signals. Treated leachate and groundwater samples were extracted in triplicate and PFAS precursor-spiked samples were extracted in duplicate, for reproducibility. For quantification of PFAS, the limit of detection (LOD) and limit of quantification (LOQ) were calculated by integrating the signal in the solvent blank:

$$LOD = c(Blank) + 3 \times SD$$

$$LOQ = c(Blank) + 10 \times SD$$

The quality of the TOP assay was checked in an experiment where the calibration curve was spiked into Milli-Q water. The results are shown in Table S3 in SI.

2.8. Orbitrap MS data analysis

The data obtained were processed with Compound Discoverer 3.3 (CD) using a suspect screening workflow tailored for PFAS (Table S4 in SI). Peak picking and deconvolution of the data were performed in this software, where to be considered a feature had to have a signal to noise (S/N) ratio >3 and signal intensity >10,000 counts. Blanks were included with the requirement that a feature had to be five-fold higher in the sample than in the blank. A suspect list with 4676 features was obtained from the Norman Network Substance Database and used as a mass list in Compound Discoverer 3.3. (NORMAN Substance Database) The software matched the accurate masses obtained from the HRMS data and compared these to the monoisotopic masses in the suspect list. The software also allowed use of ChemSpider for connection to various databases (EPA DSSTOx, EPA Toxcast, FDA, Massbank, Molbank, Pubmed, Royal Society of Chemistry, and Sigma-Aldrich) to compare the accurate masses obtained against the monoisotopic mass of known compounds. After the observed accurate masses were matched with monoisotopic masses from the suspect list, the annotated structures of the compounds which had MS (Podder et al., 2021) spectra were automatically evaluated with a CD algorithm running in the background, which gave a score based on how probable the annotation was estimated to be. Additionally, mzCloud, a Thermo Fisher mass spectral database, was used to compare the MS (Podder et al., 2021) spectra obtained to their own curated MS (Podder et al., 2021) spectral library, where a score was given based on the similarity of the spectra. The software was also used to calculate chemical formula when any of the previous methods of identification failed. Once compounds were annotated, the annotation was compared to the predicted isotopic pattern and given a score based on that, which was also visualized when viewing the mass spectra in the software. For all annotation methods, mass accuracy of 3 ppm in full scan was required. Kendrick mass defects (KMD) were calculated for all annotated features, in the case of CF_2 with normal rounding of the values. Fragmentation flagging was also performed with the *Compound Classes* node. CnF_{2n+1}, CnF_{2n-1}, CnF_{2n-3}, CnF_{2n-7}, CnF_{2n-11}, and $CnF_{2n+1}O$ fragments were screened, with n ranging from 1 to 7, 2 to 10, 3 to 11, 5 to 11, 7 to 12, and 1 to 3, respectively. Neutral losses were screened for in the MS (Podder et al., 2021) spectra. Losses from head groups such as carboxylic acids (CO_2), sulfinic acids (SO_2), sulfonic acids (SO_3), and HF were screened.

After data peak picking and feature detection (9668 for treated landfill leachate and 7944 for groundwater), a set of filters was applied to reduce the number of features in the samples to a more manageable level. First, a background subtraction filter was included in the workflow (see Table S4 in SI). Second, a peak rating algorithm was used to rate the shape of the peaks (from 1 to 10) annotated in each sample (version 3.3

of Compound Discovery). The filter required a peak rating of ≥ 6 in the peaks for triplicate samples. Finally, a mass defect filter was used to remove all compounds which did not fall between 0.1 and -0.25 of a CF_2-adjusted KMD (Ng et al., 2022). Each identification of a compound was given a confidence level (CL) value, following Schymanski et al. (2014) as modified for PFAS by Charbonnet et al. (2022) with a more detailed level of identification.

The annotated features were screened manually after filtering to find and remove false negatives and false positives. A Kendrick mass plot was employed to identify homologous series by searching for series differing by m/z of ± 50 ($-CF_2-$) or ± 100 ($-C_2F_4-$). Features that were annotated as possible PFAS with a hit in the suspect list or online databases, but which were lacking MS (Podder et al., 2021) spectra, were added to an inclusion list. An additional analysis was performed for all samples using this newly created inclusion list, with the data-dependent MS (Podder et al., 2021) setting changed from *discovery* to *confirmation*.

3. Results and discussion

3.1. Behavior of precursor and legacy PFAS in TOP assays

Six PFAS were tested individually in spiked Milli-Q water using the TOP assay (Fig. 1). Compound concentrations not covered by the in-house targeted PFAS method were calculated from the known amount spiked into the samples. The three PFAS precursors degraded during the TOP assay, as expected and in agreement with previous studies (Houtz and Sedlak, 2012). Precursor 6:2 diPAP degraded mainly to PFPeA (40% of $\sum$PFAS), PFHxA (28%), PFBA (20%), and PFHpA (12%). Degradation of precursor 8:2 diPAP was slightly different, with PFHpA (38% of $\sum$PFAS), PFOA (26%), PFHxA (18%), PFPeA (13%), and PFBA (5%) as a minor product. Precursor EtFOSA also showed a different degradation pattern, with PFOA (90%) as the major PFAS and a low fraction of PFHxA (5%). This data aligns well with the experiments performed by Houtz and Sedlak (2012) as the major products for 6:2 diPAP and 8:2

diPAP were C_5 and a C_7 precursors, respectively (Houtz and Sedlak, 2012). Additionally, EtFOSA did, unlike the other precursors, result in a yield that was slightly lower to the concentration that was spiked into solution. The cause for this may be due to incomplete oxidation, oxidation into products not covered in the targeted method, or poor recoveries during extraction. It should be noted that PFAS degradation products which were not included in the PFAS targeted method could not be identified using LC-MS/MS.

Two of the three legacy PFAS tested, PFUnDA and PFTriDA, did not show any degradation in the TOP assay, which is in agreement with previous findings (Houtz and Sedlak, 2012). Interestingly, however, the concentration of both PFUnDA and PFTriDA decreased slightly (by 9% and 13%, respectively). The current working theory on this decrease in concentration of legacy PFAS is that the powders introduced into the samples during the TOP assay were partly sorbed. Alternatively, there may have been an analytical error and different recoveries during the extraction.

Relatively little research has been performed on the behavior of PFECHS (perfluoroethylcyclohexane sulfonic acid) in TOP assays. In a study where oilfield samples were analyzed for PFAS, PFECHS was detected in some samples, but none of the samples chosen for TOP assay contained any PFECHS (Meng et al., 2021). In other studies utilizing the TOP assay, PFECHS was not detected and thus more data are needed on this emerging contaminant (Göckener et al., 2022). The analysis performed in the present study is novel in that the TOP assay was performed on PFECHS alone, without any matrix, and the results showed that PFECHS was not affected by the TOP assay. More research on TOP assays of cyclic perfluorinated compounds is needed to explore the behavior of these compounds and determine the mass balance between PFAS precursors and final degradation products.

3.2. TOP assay on treated landfill leachate and groundwater

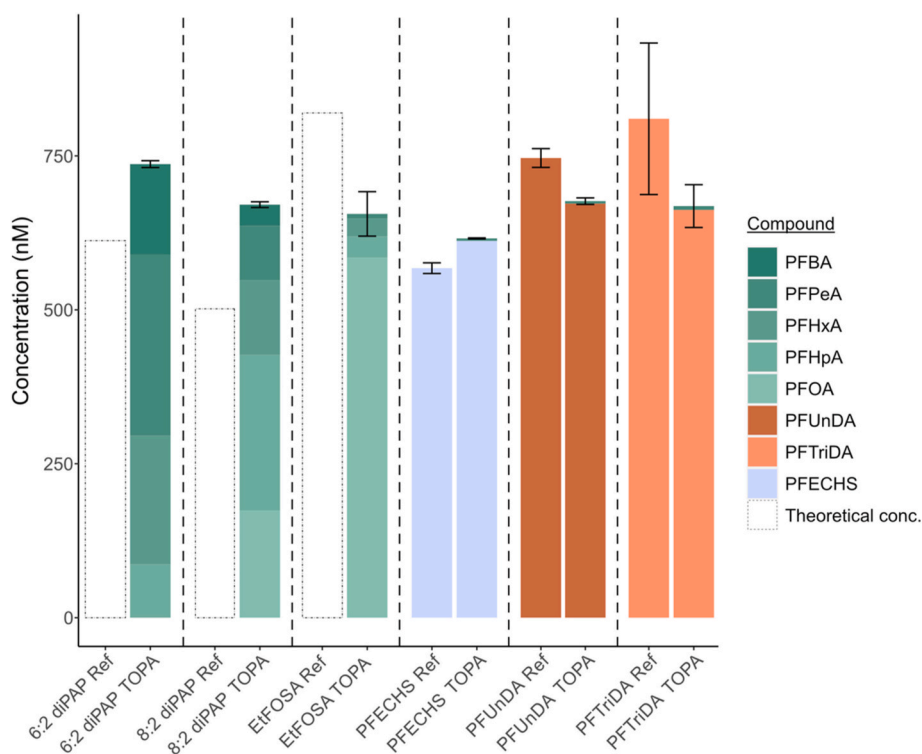Triplicate samples of treated leachate and groundwater were tested

Fig. 1. Concentrations (nM) of per- and polyfluoroalkyl substance (PFAS) precursors and legacy PFAS in spiked Milli-Q water processed with a total oxidizable precursor (TOP) assay. Error bars indicate the difference between experimental replicates (n = 2). Transparent boxes with dotted lines indicate theoretical molar concentration of spiked compounds not included in the LC-MS/MS method.

in TOP assays. The overarching trend in the results was that the changes in concentration are largely negligible for PFAS (see Table S5 in SI). In treated leachate, the only compound that increased after the TOP assay was PFPeA with, on average, 11%. In groundwater, two compounds increased after the TOP assay, including PFPeA with 12% and PFHxA with 9%. There was, however, a significant difference ($p < 0.05$) in $\sum$PFAS before and after the TOP assay (see Table S6 in SI). The only compounds that did not show a significant difference ($p > 0.05$) were PFHxA, PFPeS, and PFOA in treated leachate and PFOA in groundwater (see Table S7 in SI). The low occurrence of PFAS precursors in samples from the selected landfill facility (see Section 2.4) may be because it is an old landfill (established 1971). Over time, any PFAS precursors originally present may have already been degraded by biotic and abiotic processes (Allred et al., 2015), during leaching through the landfill or during WWTP treatment of the leachate (Uppsala Vatten, 2021).

Overall, in this study the TOP assay was used as a prioritization strategy of samples for suspect and non-target screening, and hereby prioritize samples which contain a large proportion of unknown PFAS precursors. Although, the difference in concentration from performing the TOP assay was small in this study, the samples were further analyzed for suspect and non-target screening to verify if the TOP assay is a good prioritization strategy for suspect and non-target screening and identify PFAS precursors which are not affected by the TOP assay.

3.3. Suspect screening and non-target screening

Each sample matrix was processed separately and then subjected to the prioritization and quality control process (details of the workflow can be found in Table S4 in SI). Feature detection and peak picking by Compound Discoverer 3.3 using a modified workflow resulted in 9668 features in the treated leachate and 7944 features in the groundwater, with a threshold of S/N ratio = 3 and minimum intensity of 10000 (Fig. 2). Blank subtraction and application of the peak rating filter resulted in a total of 1152 features in the treated leachate and 747 in the groundwater. Prioritization using homologous series by applying a filter which retained features with annotated KMD between -0.25 and 0.10 resulted in 393 features in the treated leachate and 240 in the groundwater, but those figures also included false positives, which were manually screened out and not considered in the final results.

A final total of 28 PFAS were detected in the two matrices with confidence higher than CL = 3 d (Table 1), based on the new PFAS confidence levels (Charbonnet et al., 2022). Ten PFCA ($C_nF_{2n+1}CO_2H$) (C_3–C_{13}) were identified with CL = 1a based on accurate mass, mass defect, isotopic pattern match, a consistent retention time, matching MS (Podder et al., 2021) spectra with an online library, and with a reference standard. Six PFSA (C_nF_{2n+1}-SO_3H) (C_3–C_8) were identified in the matrices, all but one with CL = 1a. The only PFSA that was not

Fig. 3. CF_2-adjusted Kendrick mass defect diagram, where each dot represents a compound found in a homologous series of per- and polyfluoroalkyl substances (PFAS) in groundwater and treated landfill leachate samples. Individual compounds that did not belong to a series are excluded from the diagram.

confirmed with a reference standard was perfluoropropane sulfonic acid. This compound was identified with a CL = 2 b by comparing to a spectral database and having consistent retention time with related homologues. This is in agreement with previous findings that PFCA and PFSA are commonly present in landfill facilities and in the surrounding environment (Gomis et al., 2018; Arias E et al., 2015; Janousek et al., 2019).

Three isomers of PFECHS ($C_8F_{15}SO_3H$) were identified, all with the same m/z. One of these was identified with CL = 1a and two with CL = 3a. The mass spectra of all three isomers are displayed in Fig. S1 in SI. PFECHS has been linked to aviation-grade hydraulic fluids and has been detected at sites related to airports (Szabo et al., 2022). The isomers displayed the same diagnostic ions as the 1a confirmed compound, and thus only a tentative structure could be deduced. Additionally, the three isomers were not baseline-separated in the extracted ion chromatogram (Fig. S1 in SI), indicating that they were isomeric species. The exact position of the perfluorinated ethyl groups could not be confirmed (CL = 3a). The possibility of a perfluorodimethyl group could also not be
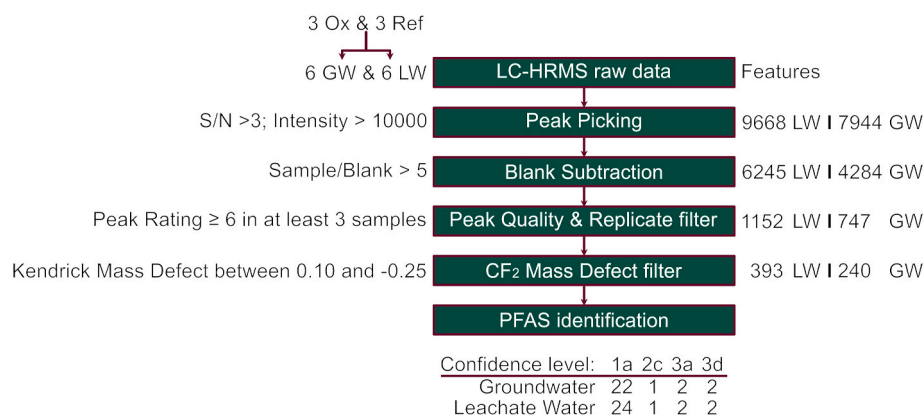

Fig. 2. Summary of the suspect screening workflow showing the prioritization strategies used and the number of features identified in groundwater (GW) and treated landfill leachate (LW) after prioritization and application of quality control filters.
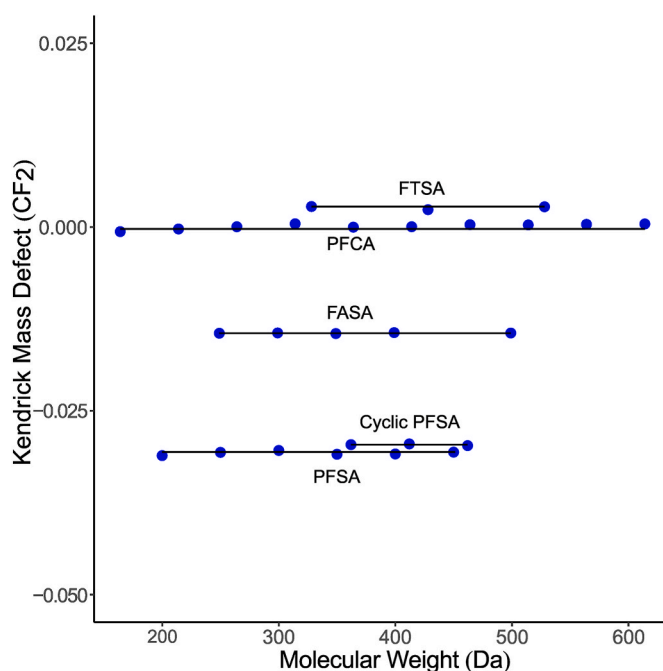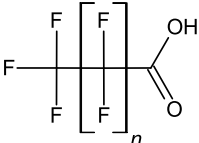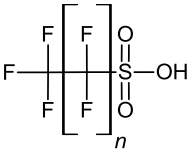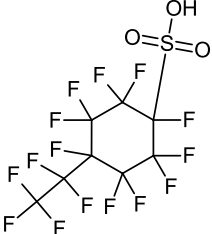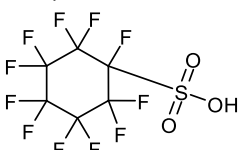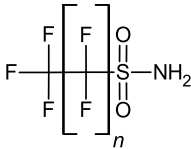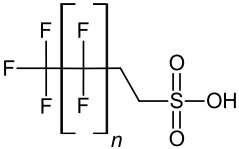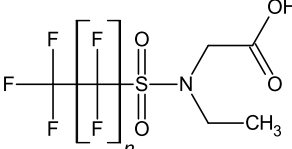
Table 1

Summary of findings from suspect screening of per- and polyfluoroalkyl substances (PFAS) in treated landfill leachate and groundwater samples. Class name, structure, parameters used for identification, confidence level, in silico-determined log K_{OW} according to EPI Suite v. 4.1, United States Environmental Protection Agency, 2021 and examples of uses for the identified PFAS.

Abbreviation	Proposed structure	n	Confidence level (Charbonnet et al., 2022)	Log K_{OW}	Examples of uses
PFCA		2; 3; 4; 5; 6; 7; 8; 9; 10; 11	1a; 1a; 1a; 1a; 1a; 1a; 1a; 1a; 1a	1.47; 2.14; 2.81; 3.48; 4.15; 4.81; 5.48; 6.12; 6.82; 7.49	In textiles: n = 2–11. Guo et al., 2009; Herzke et al., 2009; AFFF: n = 3–11. (Backe et al., 2013; Mumtaz et al., 2019)
PFSA		2 3; 4; 5; 6; 7	2 b; 1a; 1a; 1a; 1a 1a	0.48; 1.15; 1.82; 2.49; 3.16; 3.82; 4.49	AFFF: n = 2–7. (Backe et al., 2013; Barzen-Hanson and Field, 2015)
PFECHS		–	1a	4.42	Mist suppressant (Anich and Sierakowski, 1995); Surfactant (Tubergen and Benjamin, 1985) Aviation-grade hydraulic fluid. (Szabo et al., 2022)
PFECHS isomers	–	–	3a	–	–
PFMeCHS		–	3a	1.54	Surfactant (Tubergen and Benjamin, 1985)
PFCHS		–	2c	1.60	Etching agent for manufacturing semiconductor devices. (Hopkins et al., 1985)
FASA		2; 3; 4; 5; 7	3 d; 1a; 3 d; 1a; 1a	2.46; 3.13; 3.79; 4.46; 5.80	Etching agent for manufacturing semiconductor devices: n = 4. (Parent et al., 2002)
FTSA		4; 6; 8	– 1a; 1a; 1a	1.32; 2.66; 4.00	Indoor carpets: n = 4, 6, 8. (Wu et al., 2020)
EtFOSAA		7	1a	6.22	Stain and water repellant. (Boulanger et al., 2005)

confirmed due to the lack of any such fragments in MS (Podder et al., 2021) (Fig. 4). The only fragments were [M-HSO$_3$]$^-$ with a mass corresponding to a C$_n$F$_{2n-1}$ fragment and a FSO$_3^-$ fragment. Considering the [M-HSO$_3$]$^-$ fragment, following the C$_n$F$_{2n-1}$ pattern, and lack of additional C$_n$F$_{2n-1}$ fragments, which would indicate a double bond, the evidence was deemed indicative of a cyclic PFAS (Charbonnet et al., 2022). Two more cyclic PFAS were identified, which also followed the C$_n$F$_{2n-1}$ fragmentation pattern, indicating the same ring double bond equivalents, and which had [M-HSO3]$^-$ and FSO$_3^-$ fragments. They also followed a homologous series, with similar mass defect and decreasing
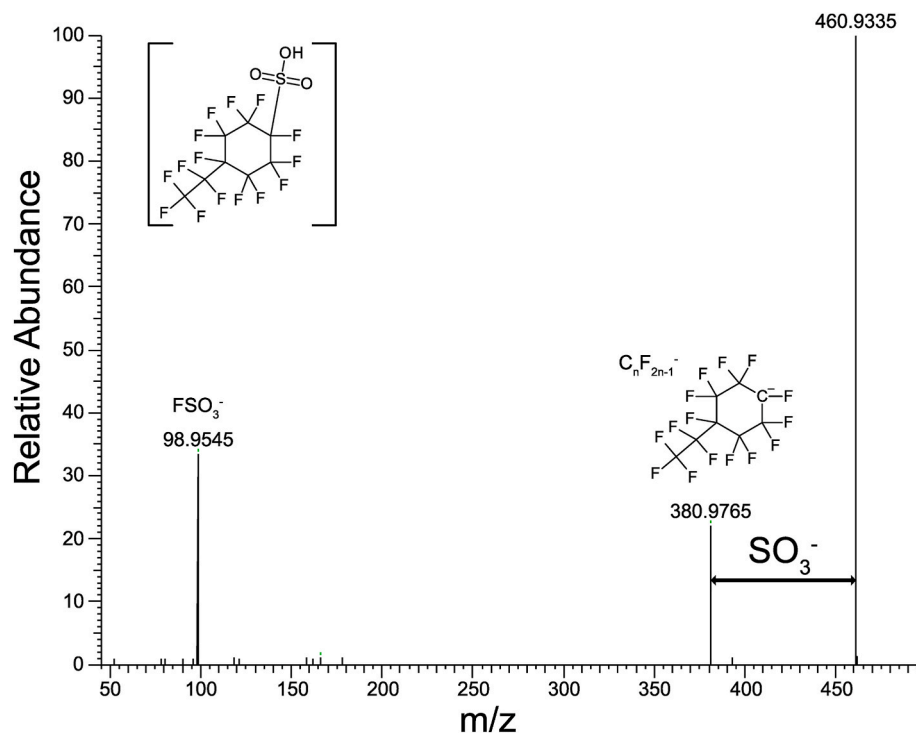
Fig. 4. MS (Podder et al., 2021) spectrum of perfluoroethylcyclohexane sulfonic acid (PFECHS) obtained from treated landfill leachate, with annotated fragments and their possible structure and formula (CL = 1a).

in nominal m/z by 50 in the series. They were identified as decreasing in chain length of the ethyl group to methyl group, and to without any alkyl group attached to the PFCHS. Due to the lack of any other functional groups on PFCHS apart from sulfonic acid, the structure could be identified with CL = 2c. Extracted ion chromatograms and related mass spectra of cyclic PFSAs can be seen in Fig. S2 in SI.

The only perfluoroalkane sulfonamide (FASA) initially identified in suspect screening was FOSA, but four more FASA were identified by implementing NTS strategies, in this case an inspection of the KMD plot, which showed a homologous series (Fig. 3). Authentic reference standards were only available for three FASA (FOSA, perfluorobutane sulfonamide (FBSA), and perfluorohexane sulfonamide (FHxSA)), while the other FASA were identified with CL = 3 d. The lack of diagnostic ions, which is inherent with FASA, limited the evidence to homologous series of the 1a identified compounds, accurate mass, mass defect, isotopic match, and consistent retention time (Charbonnet et al., 2022). Three FTSA were identified (4:2 FTSA, 6:2 FTSA, 8:2 FTSA), all with CL = 1a. FTSA have previously been identified as biodegradation products of fluorotelomer thioether amido sulfonic acids (FtTAoS) (Harding-Marjanovic et al., 2015). In other studies, FTSA have been found in AFFF extracts and in AFFF-contaminated waters (Mulabagal et al., 2018b; Barzen-Hanson et al., 2017). EtFOSAA was also identified through the suspect list and then confirmed with an authentic standard. EtFOSAA has previously been documented as a transformation product deriving from aerobic biotransformation of N-ethyl perfluorooctane sulfonamidoethanol. This indicates that there were several processes co-occurring in the landfill (Rhoads et al., 2008).

In a similar study conducted in Guangzhou, China, where leachate and groundwater at three landfills were sampled, many emerging PFAS were identified but, as in this study, most of these were legacy PFAS (Liu et al., 2022). In another study that analyzed PFAS in landfill (Koelmel et al., 2020), the screening results were very similar to the classes identified in this study with the exception of MeFOSAA, which was not identified using suspect screening but was detected in the targeted analysis (Koelmel et al., 2020). In another study involving targeted analysis where 70 PFAS were targeted in a simulated landfill containing

PFAS products, the overall PFAS concentration was shown to increase over time (Lang et al., 2016).

3.4. Quantification and semi-quantification of PFAS in groundwater and treated landfill leachate

In total, 13 and 11 PFAS were quantified in levels above the LOQ in the treated leachate and groundwater (reference) samples, respectively (Table 2). Other PFAS were also detected, but due to their detection in blank samples they are not reported here (for details, see Table S8 in SI). Semi-quantification of compounds that were not included in the targeted LC-MS/MS method (i.e. FASA and cyclic PFSA) was performed using HRMS. For semi-quantification of FASA, the FOSA calibration curve and IS were used, while semi-quantification of the cyclic PFAS was performed using the calibration curve of PFECHS and additionally the IS $^{13}C_3$-PFHxS.

In treated landfill leachate, the dominant PFAS group was PFCA (76% of $\sum$PFAS), with PFOA showing the highest concentration (420 ng/L). The second largest PFAS group in treated leachate was PFSA (21% of $\sum$PFAS), with ~3.5 times lower concentration (400 ng/L for $\sum$PFSA) compared with PFCA (1400 ng/L for $\sum$PFCA). Dominance of PFCA and PFSA has been observed in other studies on leachate from e.g., waste-to-energy stockpiles in the UK and Spain, and from a landfill in Spain (Björklund et al., 2021; Fuertes et al., 2017). However, most previous studies have generally found higher concentrations of PFHxA than PFOA (Gallen et al., 2017; Björklund et al., 2021; Lang et al., 2017), which was not observed in this study. The other PFAS groups were generally present in lower concentrations (PFECHS 28 ng/L, $\sum$FASA 34 ng/L). The semi-quantified PFAS (i.e., PFMeCHS, PFCHS, FPrSA, FBSA, FPeSA, and FHxSA) had a total concentration of only 46 ng/L, which indicates lower presence of other PFAS groups than PFCA and PFSA, or lack of identification of other PFAS groups.

In groundwater, the $\sum$PFAS concentration was higher by a factor of ~1.5 (3420 ng/L for $\sum$PFAS) than in landfill water (1910 ng/L for $\sum$PFAS). The reasons for this difference could be that the treated landfill leachate was more diluted by precipitation and that the PFAS were

Table 2

Concentrations (ng/L ± standard deviation) of per- and polyfluoroalkyl substances (PFAS) in treated landfill leachate (LW) and groundwater (GW), sum according to targeted quantitative (Q) LC-MS/MS analysis and semi-quantitative (semiQ) LC-HRMS analysis, and overall total concentration. Compounds marked with "*" have high uncertainty due to being below method quantitation limit but above method detection limit. These compounds were not added to the concentration sum. For method limits see Table S8 in SI.

Compound	LW			GW		
PFBA	170	±	6.6	230	±	5.4
PFPeA	190	±	7.4	260	±	6.5
PFHxA	390	±	29	570	±	30
PFHpA	220	±	8.0	360	±	32
PFOA	420	±	16	940	±	68
PFBS	97	±	4.6	160	±	9.6
PFPeS	21	±	1.8	70	±	6.3
PFHxS	98	±	8.3	330	±	14
PFHpS	7.4	±	0.53	22	±	2.3
PFOS	150	±	14	250	±	17
PFECHS	28	±	2.7	39	±	3.8
EtFOSAA	19	±	1.1	<LOD		
MeFOSAA	5.1	±	0.52	<LOD		
4:2 FTSA*	<LOD			74	±	7.2
6:2 FTSA*	<LOD			59	±	3.3
Q sum	1820			3230		
PFMeCHS	2.2	±	0.14	4.1	±	0.05
PFCHS	10	±	0.45	20	±	0.97
FPrSA	4.2	±	0.28	23	±	1.7
FBSA	17	±	3.5	43	±	4.4
FPeSA	4.3	±	0.52	11	±	0.96
FHxSA	8.0	±	1.2	9.8	±	1.0
semiQ sum	46			110		
Overall total	**1860**			**3340**		

further diluted during WWTP treatment. The PFAS concentrations in groundwater were higher due to the direct impact from the waste stored in the landfill and other contributing sources. The dominant PFAS group in groundwater was PFCA (73% of ∑PFAS), followed by PFSA (26% of ∑PFAS). The other PFAS groups were generally detected in lower concentrations (PFECHS 39 ng/L, FASA 86 ng/L). The semi-quantified PFAS had a total concentration of 110 ng/L.

The composition profile of PFAS in the treated leachate and groundwater differed in terms of the dominant PFSA. In the groundwater, PFHxS (11% of ∑PFAS), followed by PFOS (7.9% of ∑PFAS) were the dominant PFSA. In the treated leachate, on the other hand, PFOS (8.4% of ∑PFAS), followed by PFHxS (5.8% of ∑PFAS) were the dominant PFSA. Furthermore, FASA and cyclic-PFSA were lower in concentration in treated leachate and higher in the groundwater, following the general trend of the other quantified PFAS. The two precursors MeFOSAA and EtFOSAA were detected above the LOQ only in the treated leachate samples and most likely these two compounds were formed either during the WWTP process or by reactions which occurred in the landfill (Allred et al., 2015; Rhoads et al., 2008; Hamid et al., 2018). This indicates that the source of PFAS was different for treated landfill leachate and groundwater, or that the composition profile changed during treatment at the WWTP or during leaching to groundwater. Semi-quantification proved useful by identifying additional PFAS which were not covered in the targeted method.

4. Conclusions

A workflow to identify and (semi)-quantify new PFAS in treated leachate and groundwater using TOP assay and suspect screening was developed and tested in this study. As expected, the PFAS precursors 6:2 diPAP and 8:2 diPAP showed almost complete degradation during the TOP assay and long-chain PFCA did not degrade significantly. The cyclic PFAS PFECHS also did not degrade during the TOP assay. Thus more studies are needed to determine the behavior of cyclic PFAS in TOP assays and their environmental persistence. In TOP assays, treated

landfill leachate and groundwater showed very few PFAS with increasing concentrations, indicating that biotic and abiotic processes within the landfill over time have already degraded any PFAS precursors initially present.

Application of the suspect screening workflow to groundwater and treated landfill leachate samples resulted in identification of a total of 28 PFAS with confidence level ≥3 d. To our knowledge, this is one of the first few suspect screening study to analyze groundwater and treated landfill leachate from an active landfill site. Monitoring of PFAS in the waste sector should be continued, as PFAS are included in many household and commercial products and may be released into the environment from landfills or other waste facilities over time. The TOP assay can be useful as a method to improve and widen the scope of conventional targeted analysis and as a tool for preselecting samples although the information obtained may be limited depending on the matrix and source of PFAS. The samples discussed in this paper yielded little information regarding precursors using the TOP assay but through suspect screening precursor were detected. Semi-quantification is a useful method to estimate the concentrations of newly identified PFAS, so structured semi-quantification methods need to be developed.

Author contributions

Svante Rehnstam: Writing – Original Draft, Visualization, Formal analysis, Data Curation, Mai-Britt Czeschka: Investigation, Formal analysis, Writing – Review & Editing, Lutz Ahrens: Conceptualization, Methodology, Writing – Review & Editing, Supervision, Funding acquisition.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.138925.

References

Allred, B.M.K., Lang, J.R., Barlaz, M.A., Field, J.A., 2015. Physical and biological release of poly- and perfluoroalkyl substances (PFASs) from municipal solid waste in anaerobic model landfill reactors. Environ. Sci. Technol. 49, 7648–7656.

Arias E, V.A., Mallavarapu, M., Naidu, R., 2015. Identification of the source of PFOS and PFOA contamination at a military air base site. Environ. Monit. Assess. 187.

Backe, W.J., Day, T.C., Field, J.A., 2013. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC-MS/MS. Environ. Sci. Technol. 47, 5226–5234.

Barnabas, S.J., et al., 2022. Extraction of chemical structures from literature and patent documents using open access chemistry toolkits: a case study with PFAS. Dig. Dis. 1, 490–501.

Barzen-Hanson, K.A., Field, J.A., 2015. Discovery and implications of C2 and C3 perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. Environ. Sci. Technol. Lett. 2, 95–99.

Barzen-Hanson, K.A., et al., 2017. Discovery of 40 classes of per- and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. Environ. Sci. Technol. 51, 2047–2057.

Björklund, S., Weidemann, E., Yeung, L.W., Jansson, S., 2021. Occurrence of per- and polyfluoroalkyl substances and unidentified organofluorine in leachate from waste-to-energy stockpile - a case study. Chemosphere 278.

Boulanger, B., Vargo, J.D., Schnoor, J.L., Hornbuckle, K.C., 2005. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. Environ. Sci. Technol. 39, 5524–5530.

Charbonnet, J.A., et al., 2022. Communicating confidence of per- and polyfluoroalkyl substance identification via high-resolution mass spectrometry. Environ. Sci. Technol. Lett. 9, 473–481.

Cortés-Francisco, N., Caixach, J., 2015. Fragmentation studies for the structural characterization of marine dissolved organic matter. Anal. Bioanal. Chem. 407, 2455–2462.

Fuertes, I., Gómez-Lavín, S., Elizalde, M.P., Urtiaga, A., 2017. Perfluorinated alkyl substances (PFASs) in northern Spain municipal solid waste landfill leachates. Chemosphere 168, 399–407.

Gago-Ferrero, P., et al., 2015. Extended suspect and non-target strategies to characterize emerging polar organic contaminants in raw wastewater with LC-HRMS/MS. Environ. Sci. Technol. 49, 12333–12341.

Gallen, C., et al., 2017. Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates. J. Hazard Mater. 331, 132–141.

Glüge, J., et al., 2020. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). Environ. Sci. Process. Impacts 22, 2345–2373.

Gobelius, L., et al., 2018. Per- and polyfluoroalkyl substances in Swedish groundwater and surface water: implications for environmental quality standards and drinking water guidelines. Environ. Sci. Technol. 52, 4340–4349.

Göckener, B., Fliedner, A., Rüdel, H., Badry, A., Koschorreck, J., 2022. Long-term trends of per- and polyfluoroalkyl substances (PFAS) in suspended particular matter from German rivers using the direct total oxidizable precursor (dTOP) assay. Environ. Sci. Technol. 56, 208–217.

Gomis, M.I., Vestergren, R., Borg, D., Cousins, I.T., 2018. Comparing the toxic potency in vivo of long-chain perfluoroalkyl acids and fluorinated alternatives. Environ. Int. 113, 1–9.

Gross, Jurgen H., 2017. Mass Spectrometry, A Textbook, third ed. Springer International Publishing.

Guo, Z., Liu, X., Krebs, kenneth a., 2009. US EPA's perfluorocarboxylic acid content in 116 articles of commerce. http://books.google.com/books?hl=e n&lr=&id=KoE5lJx1NjIC&oi=fnd&pg=PR7&dq=textile+finishes+and+ fluorosurfactants&ots=HjGrfP9WTo&sig=Zbs6nN8UYQPkhTM4PJH6tffADn0% 5Cnfile:///Users/Jerry/Documents/Library.papers3/Articles/2009/Epa/2009 Epa. pdf%5Cnpapers3://pub.

Hamid, H., Li, L.Y., Grace, J.R., 2018. Review of the fate and transformation of per- and polyfluoroalkyl substances (PFASs) in landfills. Environ. Pollut. 235, 74–84.

Harding-Marjanovic, K.C., et al., 2015. Aerobic biotransformation of fluorotelomer thioether amido sulfonate (lodyne) in AFFF-amended microcosms. Environ. Sci. Technol. 49, 7666–7674.

Hopkins, R.J., Thomas, E.G., Kieta, H.J., 1985. Soluble Fluorinated Cycloalkane Sulfonate Surfactant Additives for NH4. US Pantent US4620934A.

Herzke, D., Posner, S., Olsson, E., 2009. Survey , screening and analyses of PFCs in consumer products. Swerea IVF Project report 09/41. Available from: https://www. miljodirektoratet.no/globalassets/publikasjoner/klif2/publikasjoner/2578/ta2578. pdf [Accessed: 25 May 2023].

Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ. Sci. Technol. 46, 9342–9349.

Houtz, E.F., Sutton, R., Park, J.S., Sedlak, M., 2016. Poly- and perfluoroalkyl substances in wastewater: significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. Water Res. 95, 142–149.

Houtz, E., Wang, M., Park, J.S., 2018. Identification and fate of aqueous film forming foam derived per- and polyfluoroalkyl substances in a wastewater treatment plant. Environ. Sci. Technol. 52, 13212–13221.

Janousek, R.M., Mayer, J., Knepper, T.P., 2019. Is the phase-out of long-chain PFASs measurable as fingerprint in a defined area? Comparison of global PFAS concentrations and a monitoring study performed in Hesse, Germany from 2014 to 2018. TrAC, Trends Anal. Chem. 120, 115393.

Kendrick, E., 1963. A mass scale based resolution mass spectrometry of organic compounds. Anal. Chem. 35, 2146–2154.

Koch, A., et al., 2019. Point source characterization of per- and polyfluoroalkyl substances (PFASs) and extractable organofluorine (EOF) in freshwater and aquatic invertebrates. Environ. Sci. Process. Impacts 21, 1887–1898.

Koelmel, J.P., et al., 2020. Toward comprehensive per- A nd polyfluoroalkyl substances annotation using FluoroMatch software and intelligent high-resolution tandem mass spectrometry acquisition. Anal. Chem. 92, 11186–11194.

Kotthoff, M., Muller, J., Jürling, H., Schlummer, M., Fiedler, D., 2015. Perfluoroalkyl and polyfluoroalkyl substances in consumer products. Environ. Sci. Pollut. Res. 22, 14546–14559.

Krauss, M., Singer, H., Hollender, J., 2010. LC-high resolution MS in environmental analysis: from target screening to the identification of unknowns. Anal. Bioanal. Chem. 397, 943–951.

Lang, J.R., Allred, B.M.K., Peaslee, G.F., Field, J.A., Barlaz, M.A., 2016. Release of per- and polyfluoroalkyl substances (PFASs) from carpet and clothing in model anaerobic landfill reactors. Environ. Sci. Technol. 50, 5024–5032.

Lang, J.R., Allred, B.M.K., Field, J.A., Levis, J.W., Barlaz, M.A., 2017. National estimate of per- and polyfluoroalkyl substance (PFAS) release to U.S. Municipal landfill leachate. Environ. Sci. Technol. 51, 2197–2205.

Letcher, R.J., et al., 2015. Perfluorinated sulfonate and carboxylate compounds and precursors in herring gull eggs from across the Laurentian Great Lakes of North America: temporal and recent spatial comparisons and exposure implications. Sci. Total Environ. 538, 468–477.

Liu, Y., Pereira, A.D.S., Martin, J.W., 2015. Discovery of C5-C17 Poly- and perfluoroalkyl substances in water by in-line Spe-HPLC-Orbitrap with in-source fragmentation flagging. Anal. Chem. 87, 4260–4268.

Liu, Y., D'Agostino, L.A., Qu, G., Jiang, G., Martin, J.W., 2019. High-resolution mass spectrometry (HRMS) methods for nontarget discovery and characterization of poly- and per-fluoroalkyl substances (PFASs) in environmental and human samples. TrAC, Trends Anal. Chem. 121, 115420.

Liu, T., et al., 2022. Non-target and target screening of per- and polyfluoroalkyl substances in landfill leachate and impact on groundwater in Guangzhou, China. SSRN Electron. J. 844, 157021.

Meng, Y., Yao, Y., Chen, H., Li, Q., Sun, H., 2021. Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Dagang Oilfield: multimedia distribution and contributions of unknown precursors. J. Hazard Mater. 412, 106735.

Menger, F., Gago-Ferrero, P., Wiberg, K., Ahrens, L., 2020. Wide-scope screening of polar contaminants of concern in water: a critical review of liquid chromatography-high resolution mass spectrometry-based strategies. Trends Environ. Anal. Chem. 28, e00102.

Mulabagal, V., Liu, L., Qi, J., Wilson, C., Hayworth, J.S., 2018a. A rapid UHPLC-MS/MS method for simultaneous quantitation of 23 perfluoroalkyl substances (PFAS) in estuarine water. Talanta 190, 95–102.

Mulabagal, V., Liu, L., Qi, J., Wilson, C., Hayworth, J.S., 2018b. A rapid UHPLC-MS/MS method for simultaneous quantitation of 23 perfluoroalkyl substances (PFAS) in estuarine water. Talanta 190, 95–102.

Mumtaz, M., et al., 2019. Per- and polyfluoroalkyl substances in representative fluorocarbon surfactants used in Chinese film-forming foams: levels, profile shift, and environmental implications. Environ. Sci. Technol. Lett. 6, 259–264.

Myers, A.L., Jobst, K.J., Mabury, S.A., Reiner, E.J., 2014. Using mass defect plots as a discovery tool to identify novel fluoropolymer thermal decomposition products. J. Mass Spectrom. 49, 291–296.

Nakayama, S.F., et al., 2019. Worldwide trends in tracing poly- and perfluoroalkyl substances (PFAS) in the environment. TrAC, Trends Anal. Chem. 121.

Ng, K., et al., 2022. Target and suspect screening of 4,777 per- and polyfluoroalkyl substances (PFAS) in river water, wastewater, groundwater and biota samples in the Danube River Basin. J. Hazard Mater. 436, 129276.

Anich, A.T., Sierakowski, M.J., 1995. Mist Suppressant for solvent extraction metal electrowinning. US Patent 5,468,353.

NORMAN Substance Database. https://www.norman-network.com/nds/susdat/.

Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, 2021. OECD. www.oecd.org/chemic alsafety/.

Parent, M., Savu, P., Flynn, R., 2002. Fluorinated Surfactants for Buffered Acid Etch Solutions.

Podder, A., Sadmani, A.H.M.A., Reinhart, D., Chang, N. Bin, Goel, R., 2021. Per and poly-fluoroalkyl substances (PFAS) as a contaminant of emerging concern in surface water: a transboundary review of their occurrences and toxicity effects. J. Hazard Mater. 419, 126361.

Rhoads, K.R., Janssen, E.M.L., Luthy, R.G., Criddle, C.S., 2008. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. Environ. Sci. Technol. 42, 2873–2878.

Ruyle, B.J., et al., 2021. Isolating the AFFF signature in coastal watersheds using oxidizable PFAS precursors and unexplained organofluorine. Environ. Sci. Technol. 55, 3686–3695.

Sajid, M., Ilyas, M., 2017. PTFE-coated non-stick cookware and toxicity concerns: a perspective. Environ. Sci. Pollut. Res. 24, 23436–23440.

Schymanski, E.L., et al., 2014. Identifying small molecules via high resolution mass spectrometry: communicating confidence. Environ. Sci. Technol. 48, 2097–2098.

Shojaei, M., Joyce, A.S., Ferguson, P.L., Guelfo, J.L., 2022. Novel per- and polyfluoroalkyl substances in an active-use C6-based aqueous film forming foam. J. Hazard. Mater. Lett. 3, 100061.

Smith, S.J., Wiberg, K., McCleaf, P., Ahrens, L., 2022. Pilot-Scale continuous foam fractionation for the removal of per- A nd polyfluoroalkyl substances (PFAS) from landfill leachate. ACS Environ. Sci. Technol. Water. 2, 841–851.

Strynar, M., et al., 2015. Identification of novel perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass spectrometry (TOFMS). Environ. Sci. Technol. 49, 11622–11630.

Szabo, D., Moodie, D., Green, M.P., Mulder, R.A., Clarke, B.O., 2022. Field-based distribution and bioaccumulation factors for cyclic and aliphatic per- and polyfluoroalkyl substances (PFASs) in an urban sedentary waterbird population. Environ. Sci. Technol. 56, 8231–8244.

Taylor, R.B., Sapozhnikova, Y., 2022. Comparison and validation of the QuEChERSER mega-method for determination of per- and polyfluoroalkyl substances in foods by liquid chromatography with high-resolution and triple quadrupole mass spectrometry. Anal. Chim. Acta. 1230, 340400.

Tubergen, T.S., Benjamin, T.A., 1985. Process for Metallizing Plastics.US Patent: US4610895A.

Estimation Programs Interface SuiteTM for Microsoft® Windows, vol. 4, 2021. United States Environmental Protection Agency. US EPA, 11. (2022).

Uppsala Vatten. Hovgårdens Avfallsanläggning Hovgårdens Avfallsanläggning. https ://www.uppsalavatten.se/globalassets/dokument/hushall/blanketter-och-trycks aker/anlaggningspresentation-hovgarden-2021.pdf.

Wu, Y., Romanak, K., Bruton, T., Blum, A., Venier, M., 2020. Per- and polyfluoroalkyl substances in paired dust and carpets from childcare centers. Chemosphere 251, 126771.

Zabaleta, I., et al., 2017. Screening and identification of per- and polyfluoroalkyl substances in microwave popcorn bags. Food Chem. 230, 497–506.