NON-TARGET ANALYSES (NTA) OF PFAS IN AMBIENT AIR AND ATMOSPHERIC DEPOSITION

Report

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Aline Reis de Carvalho
PFAS expert

Samara Fernandes de Souza
PFAS expert

Jelle Hofman
PFAS expert

Griet Jacobs
Senior PFAS expert

Jan Peters
Senior PFAS expert

Patrick Berghmans
Senior PFAS expert

Stefan Voorspoels
Project Manager/Senior PFAS expert
014 335 021 / stefan.voorspoels@vito.be

VITO
Boeretang 200
2400 MOL
Belgium
BTW No: BE0244.195.916
vito@vito.be – www.vito.be
IBAN BE34 3751 1173 5490 BBRUBEBB

AUTHORS

Aline Reis de Carvalho

Samara Fernandes de Souza

Jelle Hofman

Griet Jacobs

Jan Peters

Patrick Berghmans

Stefan Voorspoels

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SUMMARY

At the request of the Flanders Environment Agency (VMM), filters, PUFs and deposition samples of different locations from 2023 and 2024 air monitoring campaigns were subjected to non-target analysis (NTA) for PFAS.

These non-target analyses show that a substantial portion of PFAS-related signals in air and deposition samples cannot be attributed to target compounds currently covered by validated regulatory methods. Across all samples, on average, only 13% of detected PFAS signals corresponded to target PFAS (Confidence Level 1), while 14% were assigned to identified but previously untargeted PFAS classes (CL2 - 4). The remaining 73% of the PFAS signal originated from unknown PFAS (CL5), highlighting the critical importance of NTA to expand the chemical insight beyond conventional monitoring.

Through this NTA approach, several new PFAS classes – such as perfluoroalkyl sulfonamide ethanols (FASEs) and fluorinated pesticides – were identified in ambient air samples. The detection of ultra-short-chain PFAS (e.g., TFA, PFPrA, TFMS) further illustrates the relevance of applying complementary methods to capture highly polar and mobile PFAS, which are difficult to retain using conventional reversed-phase LC-MS.

NTA also revealed a considerable burden of unknown PFAS in locations where PFAS levels were either considered as low or undetected when using only target analysis, indicating that conventional approaches may underestimate the true extent of PFAS contamination. By incorporating PFAS-equivalent calculations, the results enabled a semi-quantitative comparison across samples, further supporting the differentiation of PFAS fingerprints across locations and matrices.

The findings from this study reinforce the added value of NTA as a complementary tool to existing target methods. Integration of NTA into future monitoring programs is essential to improve source identification, support environmental forensics, and guide the development of targeted methods for emerging PFAS classes.

This study represents a first step toward addressing the overarching question: “Is the current target scope a ‘*sufficiently safe*’ proxy for the total PFAS burden in air?”. While the present work cannot directly evaluate the toxicological implications of the unknown PFAS fraction, the findings demonstrate that most of PFAS-related signals in ambient air and deposition samples remain outside the target scope. This indicates that existing regulatory monitoring likely underestimates potential exposure and associated risk related to PFAS compounds. Expanding the analytical coverage through NTA, combined with future effect-based or (in-silico) toxicity evaluations, is therefore essential to assess whether current PFAS monitoring frameworks are protective enough from a health and safety perspective.

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1 CONTENT

At the request of the Flanders Environment Agency, the potential of non-target analysis (NTA) for PFAS estimation in ambient air and deposition samples was explored as a complement to existing measurement methods. NTA enables a qualitative or semi-quantitative assessment of a much broader range of PFAS, including previously unidentified compounds, thereby providing a more comprehensive overview of PFAS contamination at or around specific sites.

Currently, PFAS air monitoring in Flanders relies primarily on target analysis of filters, PUFs, and deposition samples. These methods allow for the quantitative measurement of approximately 50 known PFAS, while thousands of PFAS compounds are documented globally. Since approved laboratories are restricted to the use of validated, target-based methods, NTA cannot yet be performed routinely under the current regulatory framework.

To gain a PFAS "fingerprint" of the contamination at different locations, it is essential to detect and include a broader range of PFAS, beyond those covered by conventional target methods. NTA offers the advantage of broad-spectrum screening without prior knowledge of the analytes present in a sample. Although not all compounds can be captured – limitations exist – it significantly improves the ability to detect emerging, unexpected, or transformation products that result from industrial use and environmental degradation, for example.

Importantly, this study also explores whether the current target scope can be considered a sufficiently safe proxy for the evaluation of the total PFAS burden in air. While direct evaluation of potential health risks associated with unidentified PFAS lies beyond the analytical capability of NTA, the method provides essential insight into the magnitude and diversity of PFAS present beyond the regulated list. In this way, NTA supports a first, science-based step toward understanding whether existing PFAS monitoring approaches adequately reflect potential exposure and safety concerns, even if quantitative risk evaluation remains presently out of reach.

A key challenge in expanding traditional target methods lies in the lack of commercial reference standards for most PFAS compounds, making it difficult to develop validated multi-residue methods. NTA overcomes this limitation by using high-resolution mass spectrometry (HRMS), such as time-of-flight (TOF) or Orbitrap instruments, coupled to ultra-high-performance liquid chromatography (UHPLC). This setup allows detection, tentative identification, and further characterization of unknown PFAS based on their exact mass, isotopic profile and fragmentation patterns.

Additionally, a suspect screening is conducted using the EPA's master list of over 10,000 PFAS compounds[1]. Semi-quantification is performed using structurally related analogues (Cao et al., 2023). For this purpose, the concept of "PFAS equivalents" is introduced and further explained in subsequent sections.

[1] Total 10737 compounds from PFAS Structure lists, https://comptox.epa.gov/dashboard/chemical-lists/PFASSTRUCT.

2 SAMPLES

The sampling campaigns from which the selected samples originate are summarized in Table 1 wherein each 'round' refers to a different point in time when samples were submitted for NTA.

In short, air samples collected either via active pumping (filters for total suspended particles (TSP) or dust fraction, and sorbents PUF + XAD, hereafter referred to as PUF, for the volatile fraction) or passive sampling (deposition (DEP), separated into dust or dry (D) fraction and water or wet (W) fraction) were selected from different locations and had previously been evaluated for target PFAS analysis. These samples were then processed using an NTA-PFAS workflow, which is described in more detail in the following sections.

Table 1. Overview of samples and sampling periods.

	SAMPLE TYPE	LOCATION	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
			Round 1	
1	PUF	ZD08	230608-0020 (R10135)	17/05 – 01/06/2023
2	DEP	ZD08	230613-0005 (R10171)	04/05 – 01/06/2023
3	DEP	ZD08	230712-0005 (D + W) (R10268)	01/06 – 29/06/2023
4	TSP	ZD11	240409-0002 (R11341)	21/03 – 04/04/2024
5	PUF	ZD11	240415-0238 (R11380)	21/03 – 04/04/2024
6	PUF	ZD11	240514-0037 (R11509)	18/04 – 02/05/2024
7	TSP	ZD11	240521-0158 (R11541)	02/05 – 16/05/2024
8	PUF	ZD11	240521-0169 (R11544)	02/05 – 16/05/2024
9	TSP	N016	240522-0059 (R11558)	02/05 – 16/05/2024
			Round 2	
1	DEP	KK01	240419-0058 (D + W) (R11411)	20/03 - 17/04/2024
2	TSP	KK01	240419-0044 (R11409)	31/03 - 14/04/2024
3	TSP	ZD17	240426-0022 (R11451)	14/04 - 21/04/2024
4	DEP	N016	240612-0041 (D + W) (R11664)	02/05 - 30/05/2024
5	TSP	RL18	240718-0001 (R11810)	25/06 - 07/07/2024
6	DEP	RL18	240819-0153 (D) (R11891)	27/06 - 25/07/2024
7	DEP	RS03	240805-0016 (D + W) (R11837)	01/07 - 25/07/2024
8	TSP	R801	240909-0006 (R11958)	20/08 - 03/09/2024
9	DEP	R801	240909-0011 (D + W) (R11959)	08/06 - 04/09/2024
			Round 3	
1	DEP	AL09	240216-0005 (D + W) (R11112)	12/01 - 09/02/2024
2	DEP	AL09	240522-0065 (D + W) (R11559)	04-04 - 02/05/2024
3	DEP	AL09	240819-0146 (D + W) (R11891)	27/06 - 25/07/2024
4	DEP	AL09	240909-0013 (D + W) (R11960)	25/07 - 22/08/2024
5	DEP	AL10	240216-0006 (D + W) (R11112)	12/01 - 09/02/2024
6	DEP	AL10	240612-0040 (D + W) (R11664)	05/02 - 30/05/2024
7	DEP	AL10	240819-0147 (D + W) (R11891)	27/06 - 25/07/2024
8	DEP	ZD01	240216-0008 (D + W) (R11112)	12/01 - 09/02/2024
9	DEP	ZD01	240612-0043 (D + W) (R11664)	05/02 - 30/05/2024
10	DEP	ZD01	240522-0069 (D + W) (R11559)	04-04 - 02/05/2024
11	DEP	ZD01	240819-0150 (D + W) (R11891)	27/06 - 25/07/2024
12	DEP	ZD01	240909-0017 (D + W) (R11960)	25/07 - 22/08/2024
13	DEP	RL19	241106-0006 (D + W) (R12248)	19/09 - 17/10/2024
14	DEP	RL19	241203-0047 (D + W) (R12356)	17/10 - 14/11/2024

Table 2. Overview of the location details.

LOCATION	LOCATION NAME	AREA TYPE	X	Y
N016	Dessel, rural background	non-industry	205542	214045
R801	Borgerhout, urban background	non-industry	154407	211080
KK01	Koksijde, Doornpannestraat	non-industry	30270	202583
AL09	Antwerpen, Van Averbekelaan	non-industry	150544	213321
AL10	Antwerpen, Blancefloerlaan	non-industry	149979	212216
RL18	Roeselare, Regenbeekstraat 7A	industry	65514	181139
RL19	Roeselare, Linkervaartoever	industry	65345	181816
RS03	Ronse, Maghermanlaan	non-industry	95097	159960
ZD01	Zwijndrecht, Binnenplein	non-industry	147056	211744
ZD08	Zwijndrecht, Neerstraat	non-industry	147399	213040
ZD11	Zwijndrecht, Blokkersdijk	industry	148200	213787
ZD17	Zwijndrecht, FLM3M3 (ZO)	industry	148066	213250

* XY-coordinates in Lambert 72 format

3 TARGET ANALYSIS

Analyses for target PFAS compounds were performed based on an adaptation of the WAC/IV/A/025. As of writing, the methods for PFAS measurements in air are not officially recognized measurement methods, although they have been tested and successfully applied for several years.

The compounds PFPrA and PFPrS, known as ultra-short-chain PFAS, were initially included in the target scope as indicative results. Further method development (WAC/IV/A/026) provided a better approach to quantify these substances. For this reason, they are not consistently reported under the target scope and are therefore included in classes 2-4 of the non-target approach (known unknowns).

4 NON-TARGET ANALYSIS (NTA)

The non-target analysis (NTA) is performed on the extracts from the target analysis adapted from WAC/IV/A/025. The extract is analyzed by liquid chromatography with high-resolution mass spectrometric detection (UPLC-HRMS).

The NTA workflow for PFAS consists of several interrelated steps, optimized for the analysis of PFAS compounds using high-resolution mass spectrometry (HRMS) (Figure 1). The method is applicable to a variety of aqueous matrices, including drinking water, surface water, groundwater, and wastewater, as well as extracts from air and deposition samples.

For each sample, full-scan HRMS data and data-dependent MS/MS (dd-MS²) spectra are acquired in negative ion mode, typically including at least one blank and three replicates, where possible. Under optimal conditions, this workflow allows for the elucidation of a molecular formula based on accurate mass and best spectral fit. To ensure focused detection and data quality, a maximum of 50 fluorine atoms per molecule (corresponding roughly to a C25 chain length) is applied as a constraint during formula generation, enabling a broad but relevant coverage of PFAS compounds.

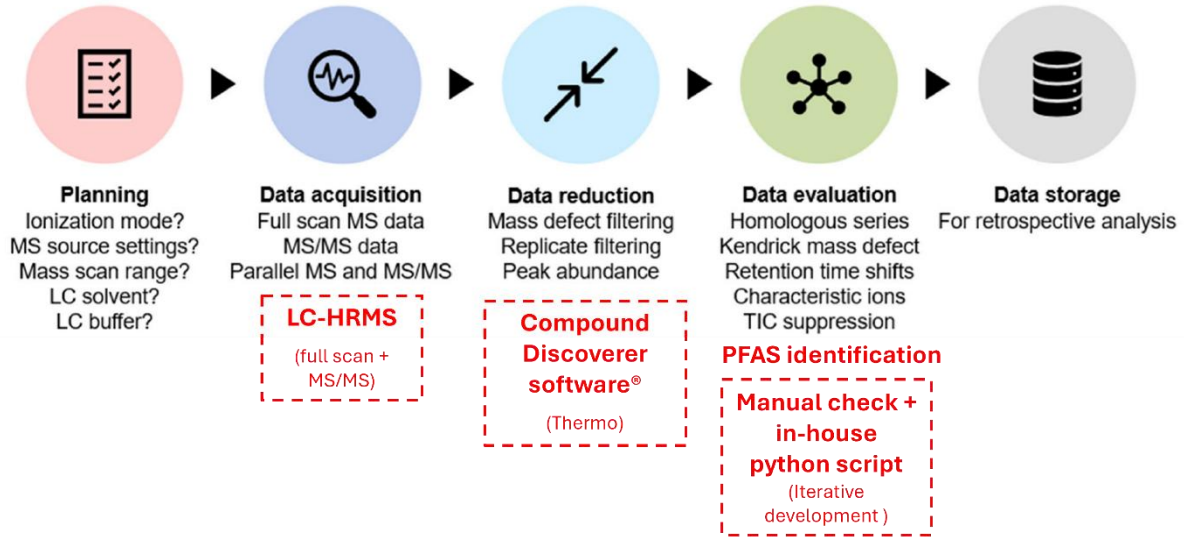


Figure 1. Workflow for NTA-PFAS data processing, adapted from Strynar et al., 2023.

4.1 Sample extraction

The extraction of the filters, PUFs and deposition samples is performed using a method adapted from the WAC/IV/A/025. Extraction with basic (NH_4OH) methanol is applied for filters and PUFs. Typically, 10 µL of the extract is injected into the UPLC-HRMS system.

4.2 Sample analysis

4.2.1 Liquid chromatography

The UPLC-ESI parameters (reversed-phase) are described below:

Type of column:	C18
Column specifications/brand:	ACQUITY Premier BEH Shield RP18 2.1 x100 mm; 1.7 µm
Ionization mode:	ESI Negative
Flow rate (mL/min):	0.30
Mobile phases:	(A) Milli-Q water/MeOH 95/5 (v/v) with 2 mM ammonium acetate (B) Methanol with 2 mM ammonium acetate

4.2.2 Mass calibration of MS instrument

Tuning can be done manually or automatically. The tuning was performed as recommended by the manufacturer.

4.2.3 Data acquisition

Please refer to the manufacturer's manual for details on the instrument-specific procedure. A multicomponent reference standard (containing compounds listed in WAC/IV/A/025) was included in each measurement run to confirm the presence of target PFAS compounds. This serves as a positive quality control check to verify the integrity of the analytical workflow.

Analyses were performed using a negative-mode (H)ESI ion source (QExactive Orbitrap, ThermoFisher). Data acquisition was conducted in full scan mode, and fragmentation data was also collected to improve confidence in the identification of unknown PFAS compounds (Figure 1). The approach to obtaining fragmentation data depends on the instrument manufacturer – for example, using data-dependent MS/MS ($ddMS^2$) or data independent acquisition (DIA), such all-ion fragmentation (AIF) mode.

For each sample, at least one corresponding field blank, when available, or a procedural blank was measured. Additionally, instrumental blanks were measured after every ten samples and were manually inspected for potential carryover. For each sample, at least one injection was performed in full-scan mode and one in $ddMS^2$ mode. The resulting ESI full-scan and $ddMS^2$ data were processed using the corresponding field or procedural blank to account for background features and improve

confidence in compound identification. A peak was only retained for further evaluation if the sample-to-blank signal ratio exceeded 5. Spectra were deconvoluted, retention times aligned, adducts identified, and isotopic patterns and in-source fragments grouped to generate a peak list of detected molecular ions as a function of retention time. This data processing was carried out using the instrument's proprietary software (Compound Discoverer), or in-house script and manual verification by an expert (Figure 1).

4.2.4 Data reduction and data evaluation

The following data filtering strategies can be applied to support the identification of PFAS compounds:

- **Mass defect filtering:** PFAS often exhibit low or even negative mass defects, due to the substitution of hydrogen atoms with fluorine. This deviation from the nominal mass can be used to identify PFAS features in full-scan HRMS spectra.
- **Kendrick Mass Defect (KMD) analysis**: Homologous series of PFAS can be detected using CF_2-normalized KMD plots. This approach, combined with negative mass defect patterns, has been widely applied in PFAS identification using HRMS (Newton et al., 2017).
- **md/C vs. m/C plot** (Kaufmann et al., 2022; Zweigle et al., 2023): This method involves plotting the mass defect per carbon atom (md/C) against the mass per carbon atom (m/C). First, the estimated number of carbon atoms is calculated, based on the molecular formula assigned by the criteria for feature annotation. Then, the monoisotopic mass is divided by the number of carbons to obtain m/C, and the mass defect is similarly normalized to obtain md/C. As explained by Zweigle et al., 2023 compounds with an increased number of heavier elements compared to H are shifted to higher m/C values, while compounds with a higher number of elements with negative md are shifted to a more negative md/C. As an example, a PFAS for which the chemical formula approaches $(CF_2)_n$ would plot at m/C ≈ 50 and md/C ≈ − 0.003 whilea compound mainly composed of $(CH_2O)_n$ would plot at m/C = 30 and md/C = + 0.0106, showing that such a separation generally works.

  Therefore, this plot helps to distinguish true PFAS compounds from non-PFAS, even when some compounds have positive mass defects greater than 0.5 Da, which could otherwise lead to misclassification based on mass defect alone.

  In the case of the presence of compounds with low md/C and high m/C (e.g., halogenated substances, organometallic compounds, and others), a distinct separation from PFAS might not always be possible and false positives might occur when data is filtered using the md/C-m/C approach.

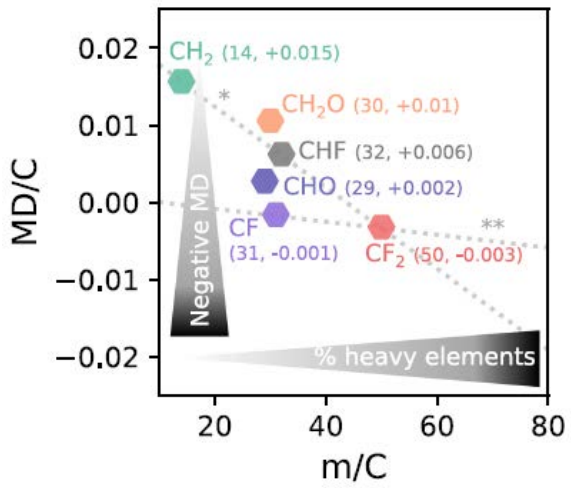


Figure 2. Schematic illustration of the MD/C–m/C plot. Key positions of compounds composed mainly of CH_2, CH_2O, CHO, CHF, CF, and CF_2 are shown. The plot highlights two main trends: (1) increasing m/C with higher percentages of heavy elements (e.g., halogens, O, N, P, S, and heavy metals), and (2) decreasing MD/C with increasing numbers of elements that have a negative mass defect. Obtained from Zweigle et al., 2023.

- **Retention time filtering**: Compounds eluting between 0 - 1 minute are typically salts or other early-eluting interferences and are therefore excluded. Only a limited number of features suspected to be PFAS are retained for further evaluation.

4.3 Compound identification

4.3.1 PFAS Identification

Following feature grouping, the identification of PFAS candidates is carried out in detail, with priority given to the most reliable sources of evidence. The identification of a possible PFAS component (molecular formula) proceeds as follows:

Spectral Database

The experimental fragmentation data and the spectral library are compared. Using the algorithm present in the software, the obtained mass spectrum is compared with the mass spectra present in the libraries of the data station (forward search) or conversely, the extent to which spectra present in the libraries are part of the recorded spectrum is checked (reversed search). If both search options are present in the device software then reversed search is preferred. In order of the degree of similarity between registered spectrum and spectrum found in the library, the data station lists possible candidate compounds along with a value representing the degree of similarity (match factor). Databases with MS/MS data are available (mzCloud, MassBank | MassBank Europe Mass Spectral DataBase, 2020; MzCloud - Advanced Mass Spectral Database, 2020). These contain information for a number of PFAS that may be useful in further identification. Additionally, an in-house spectral database of PFAS was also used for similarity match.

Experimental MS/MS (fragmentation) data are compared with spectral libraries. Using built-in algorithms, the software performs a forward search (comparing the acquired spectrum to those in the library) and, where available, a reverse search (assessing how well library spectra are represented in the acquired data). If both options are available, reverse search is preferred.

Based on spectral similarity (match factor), the software lists candidate compounds. Spectral libraries such as mzCloud and MassBank (MassBank Europe Mass Spectral DataBase, 2020; MzCloud - Advanced Mass Spectral Database, 2020) contain MS/MS data for several PFAS and support more confident identification. Additionally, an in-house PFAS spectral database, built with available standards, was used to improve match reliability.

Mass Lists

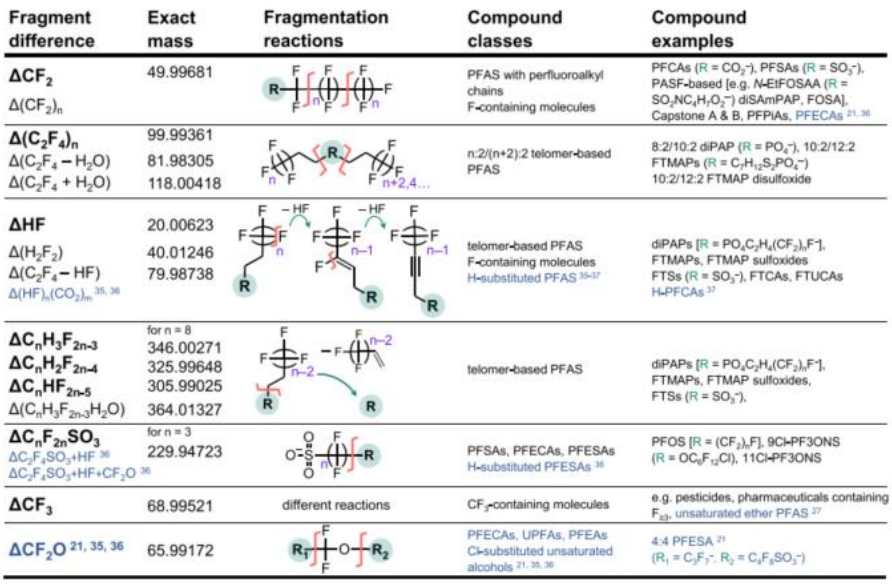
Mass list searches are performed using resources like ChemSpider (EPA DSS TOX), NIST PFAS mass list, or the EPA PFAS master list. Ideally, these lists include structural information to enable comparison between theoretical and experimental fragmentation, though the resulting match scores are often low. Nonetheless, identifying specific PFAS-related fragments can provide useful guidance.

To further confirm candidate structures, in silico tools, such as MetFrag, CFM-ID, and SIRIUS, can predict fragmentation patterns and assist with structure elucidation, especially in the absence of reference standards. Predicted retention time data (Aalizadeh et al., 2021; Mohammed Taha et al., 2022) (Bade et al., 2015) may also be used as supporting evidence.

Isotopic pattern matching is also conducted. A minimum fit of 80% between the proposed isotopic pattern and the experimental data is required to accept the PFAS candidate

Diagnostic fragments and neutral losses

The presence of diagnostic fragments in the product ion spectrum (e.g., $C_2F_5^-$) is a strong indicator of PFAS. In addition, neutral losses characteristic of PFAS can support identification. Typical neutral losses include: CF_2, C_2F_4, HF, $C_nH_3F_{2n-3}$, $C_nF_{2n}SO_3$, CF_3, CF_2O, $HFCH_2CO_2$, and $HFOCH_2CO_2$. An overview of major fragment mass differences and the PFAS classes in which they occur is shown in Figure 3.



Fragment difference	Exact mass	Fragmentation reactions	Compound classes	Compound examples
ΔCF_2 $\Delta(CF_2)_n$	49.99681		PFAS with perfluoroalkyl chains F-containing molecules	PFCAs (R = CO_2^-), PFSAs (R = SO_3^-), PASF-based [e.g. *N*-EtFOSAA (R = $SO_2NC_4H_7O_2^-$) diSAmPAP, FOSA], Capstone A & B, PFPIAs, PFECAs [21, 36]
$\Delta(C_2F_4)_n$ $\Delta(C_2F_4 - H_2O)$ $\Delta(C_2F_4 + H_2O)$	99.99361 81.98305 118.00418		n:2/(n+2):2 telomer-based PFAS	8:2/10:2 diPAP (R = PO_4^-), 10:2/12:2 FTMAPs (R = $C_7H_{12}S_2PO_4^-$) 10:2/12:2 FTMAP disulfoxide
ΔHF $\Delta(H_2F_2)$ $\Delta(C_2F_4 - HF)$ $\Delta(HF)_n(CO_2)_m$ [35, 36]	20.00623 40.01246 79.98738		telomer-based PFAS F-containing molecules H-substituted PFAS [35-37]	diPAPs [R = $PO_4C_2H_4(CF_2)_nF^-$], FTMAPs, FTMAP sulfoxides FTSs (R = SO_3^-), FTCAs, FTUCAs H-PFCAs [37]
$\Delta C_nH_3F_{2n-3}$ $\Delta C_nH_2F_{2n-4}$ ΔC_nHF_{2n-5} $\Delta(C_nH_3F_{2n-3}H_2O)$	for n = 8 346.00271 325.99648 305.99025 364.01327		telomer-based PFAS	diPAPs [R = $PO_4C_2H_4(CF_2)_nF^-$], FTMAPs, FTMAP sulfoxides, FTSs (R = SO_3^-),
$\Delta C_nF_{2n}SO_3$ $\Delta C_2F_4SO_3+HF$ [36] $\Delta C_2F_4SO_3+HF+CF_2O$ [36]	for n = 3 229.94723		PFSAs, PFECAs, PFESAs H-substituted PFESAs [36]	PFOS [R = $(CF_2)_nF$], 9Cl-PF3ONS (R = $OC_8F_{12}Cl$), 11Cl-PF3ONS
ΔCF_3	68.99521	different reactions	CF_3-containing molecules	e.g. pesticides, pharmaceuticals containing F_{53}, unsaturated ether PFAS [27]
ΔCF_2O [21, 35, 36]	65.99172		PFECAs, UPFAs, PFEAs Cl-substituted unsaturated alcohols [21, 35, 36]	4:4 PFESA [21] (R_1 = C_3F_7-; R_2 = $C_4F_8SO_3^-$)

"R refers to any organic or inorganic rest and is exemplified for several compounds (see right column). Fragment mass differences highlighted in blue were not observed in this study but found in MS/MS spectra from literature. Note: besides the identified fragmentation reactions there might be more that generate these mass differences.

Figure 3. An overview of the main mass differences in fragments and the PFAS classes in which they occur. Obtained from Liu et al., 2019.

Elemental composition

The elemental composition (molecular formula) of detected ions is assigned using the "Seven Golden Rules" for formula prediction (Kind and Fiehn, 2007). An identification is considered acceptable if the isotopic fit (spectral fit) or quality factor exceeds 80%.

When multiple candidate formulas with similarly high match factors are proposed, the most relevant compound is selected based on:

- The sample origin and expected contamination profile.
- The presence of related compounds in the candidate list.
- The overall chromatographic context (e.g., adjacent peaks or known contamination patterns).

Each recorded spectrum is compared to the best library matches. However, in some cases, the top-ranked candidate may not match specific m/z features present in the sample, while lower-ranked candidates may provide better overall agreement. This is considered during the final assignment.

If multiple structural isomers are possible for a given formula, the specific isomer is generally not reported unless:

- Match factors differ significantly (i.e., >10%),
- Retention time data allows for reliable differentiation.

Candidate molecular formulas must meet the following criteria:

- Mass accuracy: The deviation between the measured monoisotopic mass and the theoretical mass must be less than 5 ppm.
- Isotope pattern agreement: The isotope fit score should be greater than 70%.
- Chemical plausibility: Formulas are evaluated for realistic molecular structure, including double bond equivalents (DBE), in line with the Seven Golden Rules.

For match factors between 70% and 80%, additional scrutiny is applied. The proposed structure may still be accepted if:

- It is relevant to the sample context, and
- The most diagnostic fragment ions are present in the recorded spectrum.

4.3.2 Identification confidence levels

Each identified compound is reported with an associated confidence level and assigned to a PFAS class. A clear distinction is made between target PFAS (as defined in WAC/IV/A/025) and previously unreported or unknown PFAS.

The applied confidence scale is adapted from the Schymanski framework (Schymanski et al., 2014), and consists of five levels tailored for PFAS identification (see Figure 4):

- Confidence Level (CL) 1 – Confirmed Structure (by Reference Standard)

  This is the highest confidence level. The identification is confirmed by matching: accurate mass (Kendrick mass defect, md/C-m/C plot), fragmentation data (MS^2), retention time, and reference standard.

- CL 2 – Probable Structure

  A structure is proposed based on a match with a spectral library or mass list, supported by: accurate mass (Kendrick mass defect, md/C-m/C plot), fragmentation data (MS^2), and library or database match.

- CL 3 – Tentative Candidate

  The structure is tentatively assigned based on: accurate mass (Kendrick mass defect, md/C-m/C plot), fragmentation data (MS^2), and retention time. The compound is associated with a likely PFAS class, but structural confirmation is not definitive.

- CL 4 – Molecular Formula

  A molecular formula is proposed based on: accurate mass (Kendrick mass defect and md/C-md/C plot), isotopic fit, and presence of homologous series. A PFAS class is assigned based on the inferred formula, although structural information is lacking.

- CL 5 – Exact Mass only

  Identification is limited to the exact mass, along with Kendrick mass defect (KMD), md/C-m/C plot. No homologous series or isotope match is established. As such, the compound cannot be confidently classified as PFAS and is reported as an unknown possible/probable PFAS-related feature.

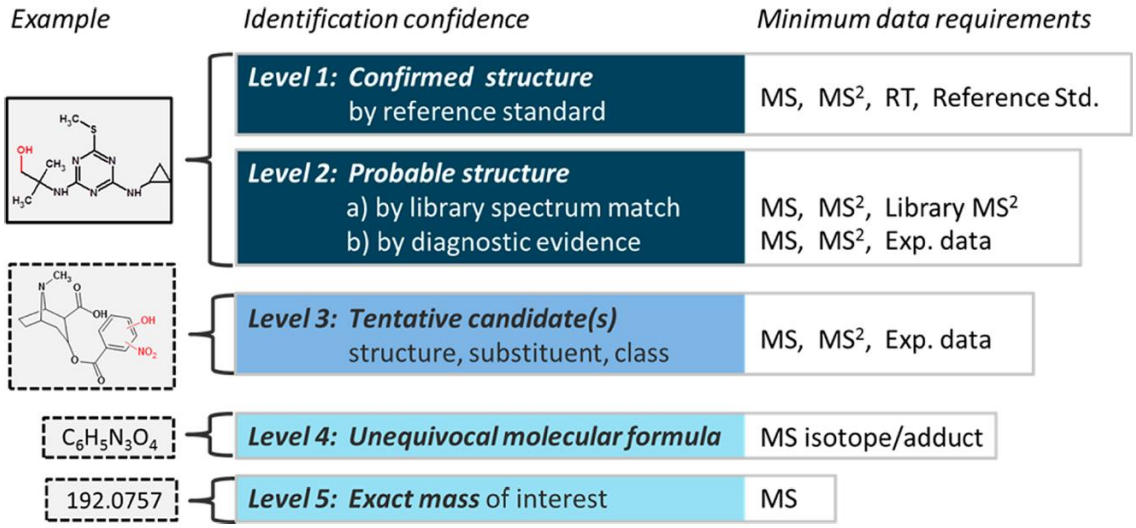


Figure 4. Proposal identification confidence levels in HRMS analysis. Note: MS^2 is intended to also represent any form of MS fragmentation (e.g. MS^e, MS^n). Obtained from Schymanski et al., 2014.

The CLs assigned to PFAS identifications in this study range from CL1 to CL5, each associated with a degree of uncertainty. CL1 represents the highest level of certainty and can only be achieved through confirmation with a reference standard.

The order of increasing uncertainty is: CL1 < CL2 < CL3 < CL4 < CL5, with CL5 reflecting the lowest certainty.

It is important to note that these identifications are based solely on MS (mass spectrometry) data. While MS-based methods offer strong indications, definitive structural confirmation would require additional techniques such as nuclear magnetic resonance (NMR). Nonetheless, the co-occurrence of related PFAS features (e.g., members of the same homologous series) often strengthens confidence in the proposed identifications.

4.3.3 PFAS classes

Potential PFAS compounds are classified by PFAS class, each accompanied by an assigned confidence level (CL1 to CL5). Classification into PFAS classes is based on the presence of a fully (per-) or partially (poly-) fluorinated carbon chain, typically ranging from 2 to 16 carbon atoms in length. These classes are generally defined by their distinct functional groups. The target PFAS compounds for which a certified reference standard was available, their corresponding PFAS classes, and their inclusion or not in WAC/IV/A/025 are listed in Table 3.

While the analytical workflow aims to identify individual compounds, the main results presented in this report are grouped and reported by PFAS class. This approach provides a more robust and interpretable overview of PFAS occurrence across samples. However, when certain PFAS classes stand out - either due to their relevance as emerging substances or their significant contribution to the unknown fraction of a sample - a deeper compound-level investigation can be conducted. Such detailing helps to better understand the composition and potential impact of specific compounds within those classes, without shifting the overall focus from the class-based reporting framework.

Therefore, in this report, PFAS are categorized as follows:

- **CL1**: PFAS included in the validated target list (i.e., in this study, compounds listed in the Table 3, except those from WAC/IV/A/026). These compounds were identified and quantified using certified reference materials.
- **CL2–CL4**: PFAS classes containing PFAS compounds with a high to moderate level of identification certainty, based on varying levels of structural and spectral evidence. This category encompasses:
    - Classes that may correspond to known categories already represented in CL1, but which include compounds not covered by WAC/IV/A/025, such as those listed in the WAC/IV/A/026;
    - New classes for which no certified material was available, but which could be grouped confidently based on matches with our internal spectral and suspect databases;
    - Novel PFAS classes were defined based on groups of compounds exhibiting consistent mass defect patterns and likely shared functional group characteristics - such as common end groups - indicating the presence of homologous series. These series were typically established by detecting at least two related compounds differing by m/z 49.99861, corresponding to the exact mass of a CF_2 unit. Illustrative examples of these newly proposed classes are provided later in the report and are reported as:
        - Unknown PFAS class (AB–CD), where AB and CD represent the last two digits of the detected compounds' m/z values, and the difference (CD – AB) equals approximately 50 (i.e., one CF_2 unit). For example: "Unknown PFAS class (07–57)", which might include compounds with m/z values approximating 157 and 207 when considering only the integer part (ignoring decimal places).

- **CL5**: Unknown compounds reported based solely on exact mass (m/z) and PFAS-like characteristics (e.g., mass defect, md/C and m/C filtering), but lacking sufficient structural or spectral information for more specific classification. Compounds assigned a CL5 (based on accurate mass only) are not classified into PFAS classes due to the absence of supporting features such as homologous series. These compounds may include false positives, and their classification is based solely on PFAS-specific filters: accurate mass, mass defect, and md/C vs. m/C plots. Consequently, they receive the classification “Unknown PFAS cpd (KMD filter CF2)”.Although these compounds are not classified into known PFAS classes and may include false positives, their detection in environmental samples should not be disregarded. Even if they are ultimately not PFAS, they may still represent pollutants or substances of emerging concern that share similar physicochemical characteristics. Their presence may indicate previously unrecognized fluorinated contaminants or other halogenated compounds that warrant further investigation. As such, CL5 compounds contribute valuable insight into the broader chemical burden of environmental samples, and may help guide the prioritization of targets for future analytical development or toxicological assessment.

Table 3. List of compounds considered as target PFAS, including those defined in WAC/IV/A/025 and WAC/IV/A/026, as well as additional compounds for which analytical standards are available but which may not yet be formally included in the WAC scope. All listed compounds were identified with Confidence Level 1 (CL1), except the ultra-short-chain (USC) compounds included in WAC/IV/A/026.

Compound	PFAS class	Molecular formula	WAC [1]	CAS number
bisphenol AF	bisphenol AF	C15H10F6O2	NA	1478-61-1
potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	Cl-substituded perfluoroalkyl sulfonic acids (Cl-PFESA)	C8HClF16O4S	NA	756426-58-1
potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	Cl-substituded perfluoroalkyl sulfonic acids (Cl-PFESA)	C10HClF20O4S	NA	763051-92-9
sodium bis (1H, 1H, 2H, 2H-perfluorooctyl)phosphate	DiPolyfluoroalkyl phosphate ester (diPAP)	C16H9F26O4P	WAC/IV/A/025	57677-95-9
sodium (1H, 1H, 2H, 2H-perfluorooctyl-1H, 1H, 2H, 2H-perfluorodecyl-)phosphate	DiPolyfluoroalkyl phosphate ester (diPAP)	C18H9F30O4P	WAC/IV/A/025	943913-15-3
sodium bis (1H, 1H, 2H, 2H-perfluorodecyl)phosphate	DiPolyfluoroalkyl phosphate ester (diPAP)	C20H9F34O4P	WAC/IV/A/025	678-41-1
Perfluoro-4-oxapentanoic acid (PFMPA)	Ether substituded perfluoroalkyl carboxylic acids (PFECA)	C4HF7O3	NA	377-73-1
Perfluoro-4-oxahexanoic acid (PFMPA)	Ether substituded perfluoroalkyl carboxylic acids (PFECA)	C5HF9O3	NA	863090-89-5
Perfluoro-3,6-dioxaheptanoic acid (NFDHA)	Perfluoroalkyl diether carboxylic acids	C5HF9O4	NA	151772-58-6
2,3,3,3-tetrafluor-2-(heptafluoropropoxy) propaanzuur	Ether substituded perfluoroalkyl carboxylic acids (PFECA)	C6HF11O3	NA	13252-13-6
sodium dodecafluoro-3H-4,8-dioxanonanoate	Diether H-substituted perfluoroalkyl carboxylic acids	C7H2F12O4	NA	919005-14-4
Potassium perfluoro(2-ethoxyethane)sulfonate	Ether substituded perfluoroalkyl sulfonic acids (PFESA)	C4HF9O4S	WAC/IV/A/025	113507-82-7
N-ethylperfluoro-1-octanesulfonamide	N-ethyl perfluoroalkyl sulfonamide (FASAs)	C10H6F17NO2S	WAC/IV/A/025	4151-50-2
N-ethyl perfluorooctanesulfonamidoaceticacid	N-ethyl perfluoroalkyl sulfonamido acetic acids (FASAAs)	C12H8F17NO4S	WAC/IV/A/025	2991-50-6
N-methylperfluoro-1-butanesulfonamide acetaat (N-MeFBSAA-M)	N-methyl perfluoroalkyl sulfonamide acetic acids (FASAAs)	C7H6F9NO4S	WAC/IV/A/025	159381-10-9
N-methyl perfluorooctanesulfonamidoaceticacid	N-methyl perfluoroalkyl sulfonamide acetic acids (FASAAs)	C11H6F17NO4S	WAC/IV/A/025	2355-31-9
N-methylperfluoro-1-butanesulfonamide (N-MeFBSA-M)	N-methyl perfluoroalkyl sulfonamides (FASAs)	C5H4F9NO2S	WAC/IV/A/025	68298-12-4

N-methylperfluoro-1-octanesulfonamide	N-methyl perfluoroalkyl sulfonamides (FASAs)	C9H4F17NO2S	WAC/IV/A/025	31506-32-8
Trifluoroacetic acid	Perfluoroalkyl carboxylic acids (PFCA)	C2HF3O2	WAC/IV/A/026	76-05-1
2,3,3,3-Tetrafluoro-n-propanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C3H2F4O2	WAC/IV/A/026	359-49-9
2,2,3,3-Tetrafluoro-n-propanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C3H2F4O2	WAC/IV/A/026	756-09-2
Pentafluoropropionic acid	Perfluoroalkyl carboxylic acids (PFCA)	C3HF5O2	WAC/IV/A/026	422-64-0
perfluoro-n-butanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C4HF7O2	WAC/IV/A/025	375-22-4
perfluoro-n-pentanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C5HF9O2	WAC/IV/A/025	2706-90-3
perfluoro-n-hexanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C6HF11O2	WAC/IV/A/025	307-24-4
perfluoro-n-heptanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C7HF13O2	WAC/IV/A/025	375-85-9
perfluoro-n-octanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C8HF15O2	WAC/IV/A/025	335-67-1
perfluoro-n-nonanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C9HF17O2	WAC/IV/A/025	375-95-1
perfluoro-3,7-dimethyloctanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C10HF19O2	WAC/IV/A/025	172155-07-6
perfluoro-n-decanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C10HF19O2	WAC/IV/A/025	335-76-2
perfluoro-n-undecanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C11HF21O2	WAC/IV/A/025	2058-94-8
perfluoro-n-dodecanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C12HF23O2	WAC/IV/A/025	307-55-1
perfluoro-n-tridecanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C13HF25O2	WAC/IV/A/025	72629-94-8
perfluoro-n-tetradecanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C14HF27O2	WAC/IV/A/025	376-06-7
perfluoro-n-hexadecanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C16HF31O2	WAC/IV/A/025	67905-19-5
perfluoro-n-octadecanoic acid	Perfluoroalkyl carboxylic acids (PFCA)	C18HF35O2	WAC/IV/A/025	16517-11-6
Sodium bis(perfluorohexyl)phosphinate	Perfluoroalkyl phosphinic acids (x:xPFPi)	C12HF26O2P	NA	40143-77-9
Sodium perfluorohexylperfluorooctylphosphinate	Perfluoroalkyl phosphinic acids (x:xPFPi)	C14HF30O2P	NA	610800-34-5
Sodium bis(perfluorooctyl)phosphinate	Perfluoroalkyl phosphinic acids (x:xPFPi)	C16HF34O2P	NA	40143-79-1
Perfluorohexylphosphonic acid	Perfluoroalkyl phosphonic acids (PFAPAs)	C6H2F13O3P	NA	40143-76-8
Perfluorooctylphosphonic acid	Perfluoroalkyl phosphonic acids (PFAPAs)	C8H2F17O3P	NA	40143-78-0
Perfluorodecylphosphonic acid	Perfluoroalkyl phosphonic acids (PFAPAs)	C10H2F21O3P	NA	52299-26-0
perfluoro-1-octanesulfonamidoacetic acid	Perfluoroalkyl sulfonamide acetic acids (FASAAs)	C10H4F17NO4S	NA	2806-24-8
perfluoro-1-butanesulfonamide	Perfluoroalkyl sulfonamides (FASAs)	C4H2F9NO2S	WAC/IV/A/025	30334-69-1
perfluoro-1-hexanesulfonamide	Perfluoroalkyl sulfonamides (FASAs)	C6H2F13NO2S	WAC/IV/A/025	41997-13-1
perfluoro-1-octanesulfonamide	Perfluoroalkyl sulfonamides (FASAs)	C8H2F17NO2S	WAC/IV/A/025	754-91-6
perfluoro-1-decanesulfonamide	Perfluoroalkyl sulfonamides (FASAs)	C10H2F21NO2S	NA	4262-70-8

Trifluoromethanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	CHF3SO2	WAC/IV/A/026	1493-13-6
Pentafluoroethanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C2HF5SO3	WAC/IV/A/026	354-88-1
Perfluoropropanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C3HF7SO3	WAC/IV/A/026	423-41-6
Perfluorobutanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C4HF9SO3	WAC/IV/A/025	375-73-5
Perfluoropentanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C5HF11O3S	WAC/IV/A/025	2706-91-4
Perfluorohexanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C6HF13O3S	WAC/IV/A/025	355-46-4
Perfluoroheptanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C7HF15O3S	WAC/IV/A/025	375-92-8
perfluoro-4-ethylcyclohexanesulfonate	Perfluoroalkyl sulfonic acids (PFSAs)	C8HF15O3S	WAC/IV/A/025	335-24-0
Perfluorooctanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C8HF17O3S	WAC/IV/A/025	4021-47-0
Perfluorononanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C9HF19O3S	WAC/IV/A/025	68259-12-1
Perfluorodecanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C10HF21O3S	WAC/IV/A/025	335-77-3
perfluoroundecanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C11HF23O3S	WAC/IV/A/025	749786-16-1
perfluorododecanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C12HF25O3S	WAC/IV/A/025	79780-39-5
perfluorotridecanesulfonic acid	Perfluoroalkyl sulfonic acids (PFSAs)	C13HF27O3S	WAC/IV/A/025	791563-89-8
sodium 1H, 1H, 2H, 2H-perfluorooctylphosphate	Polyfluoroalkyl phosphate ester (PAP)	C8H6F13O4P	NA	57678-01-0
sodium 1H, 1H, 2H, 2H-perfluorodecylphosphate	Polyfluoroalkyl phosphate ester (PAP)	C10H6F17O4P	NA	57678-03-2
2-Perfluorohexyl ethanoic acid (6:2) C8H3F13O2	x:2 Fluorotelomer carboxylic acids (x:2FTCA)	C8H3F13O2	NA	53826-12-3
2-Perfluorooctyl ethanoic acid (8:2) C10H3F17O2	x:2 Fluorotelomer carboxylic acids (x:2FTCA)	C10H3F17O2	NA	27854-31-5
2-Perfluorodecyl ethanoic acid (10:2) C12H3F21O2	x:2 Fluorotelomer carboxylic acids (x:2FTCA)	C12H3F21O2	NA	53826-13-4
N-(carboxymethyl)-N,N-dimethyl-N-[3-(1H, 1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-yl]ammonium	x:2 Fluorotelomer sulfonamido betaine (x:2FTAB)	C15H21F13N2O4S	NA	94088-80-9
1H,1H,2H,2H-perfluorohexanesulfonic acid	x:2 Fluorotelomer sulfonic acids (x:2FTS)	C6H5F9O3S	WAC/IV/A/025	757124-72-4
1H,1H,2H,2H-perfluorooctanesulfonic acid	x:2 Fluorotelomer sulfonic acids (x:2FTS)	C8H5F13O3S	WAC/IV/A/025	27619-97-2
1H,1H,2H,2H-perfluorodecanesulfonate	x:2 Fluorotelomer sulfonic acids (x:2FTS)	C10H5F17O3S	WAC/IV/A/025	39108-34-4
sodium 1H,1H,2H,2H-perfluorododecane sulfonate	x:2 Fluorotelomer sulfonic acids (x:2FTS)	C12H5F21O3S	WAC/IV/A/025	120226-60-0
2H-Perfluoro-2-octenoic acid (6:2)	x:2 Fluorotelomer unsaturated carboxylic acids (FTUCA)	C8H2F12O2	NA	70887-88-6

2H-Perfluoro-2-decenoic acid (8:2)	x:2 Fluorotelomer unsaturated carboxylic acids (FTUCA)	C10H2F16O2	NA	70887-84-2
2H-Perfluoro-2-dodecenoic acid (10:2)	x:2 Fluorotelomer unsaturated carboxylic acids (FTUCA)	C12H2F20O2	NA	70887-94-4
3-Perfluoropentyl propanoic acid (3:3)	x:3 Fluorotelomer carboxylic acids	C8H5F11O2	NA	914637-49-3
3-Perfluoroheptyl propanoic acid (3:3)	x:3 Fluorotelomer carboxylic acids	C10H5F15O2	NA	812-70-4
3-Perfluoropropyl propanoic acid (3:3)	x:3 Fluorotelomer carboxylic acids	C6H5F7O2	NA	356-02-5

1 – For compounds not yet covered by WAC/IV/A/025, "NA" is indicated (i.e., no applicable WAC method available).

4.4 Compound semi-quantification (PFAS-equivalents)

Non-catalogued PFAS compounds identified through NTA and subsequently classified, cannot be quantified using conventional methods such as those described in WAC/IV/A/025 and 026. Therefore, an alternative approach was applied to allow for comparative assessment across samples. Specifically, the instrumental response of NTA-identified PFAS was converted into so-called PFAS equivalents (PFAS eq.), as also mentioned in Megson et al., 2025

4.4.1 Technical basis of PFAS-equivalents

The PFAS equivalents approach uses a single internal standard to estimate the relative contribution of unidentified or non-catalogued PFAS. For technical consistency, $^{13}C_4$-PFOA was selected as the internal standard, as it is also used in WAC and CMA methods.

The amount of $^{13}C_4$-PFOA added to each sample is known, and its instrumental response (peak area) is measured. A relative response factor is calculated by dividing the known concentration by the measured peak area of the internal standard. This factor is then multiplied by the peak area of the unknown PFAS compound to estimate its PFAS equivalent concentration.

It is important to note that this approach does not yield absolute quantification but enables semi-quantitative comparison between samples by standardizing the response.

As example of this calculation, when the internal standard $^{13}C_4$-PFOA produces a peak area of 1.447×10^7, corresponding to a concentration of 3.75 µg/L, it results in a factor of 2.59×10^{-6}. The peak area of an unknown PFAS is then multiplied by this factor to estimate its PFAS equivalent concentration.

Some important remarks should be considered when interpreting the PFAS equivalent data:

- Uncertainty in class assignment: Although there are uncertainties in assigning PFAS to specific classes, these are not quantitatively included in the overall uncertainty estimate. This does not affect the total PFAS equivalents, as the cumulative signal is calculated regardless of class assignment.
- Matrix effects: The calculated PFAS equivalents may be influenced by the sample matrix. However, this effect cannot be verified, as the specific PFAS compounds involved are not available as standard references.
- The response of individual compounds in a mass spectrometer varies significantly. Therefore, accurate quantification in targeted PFAS analysis relies on the use of a corresponding isotopically labeled internal standard (typically ^{13}C-labeled) for each PFAS compound. These labeled analogues have matching physicochemical properties and response factors, making it possible to calculate absolute concentrations with high confidence.
- In the context of NTA-PFAS, however, it was decided to use a single labeled internal standard (^{13}C-PFOA) to estimate the concentrations of all detected features (Megson et al., 2025). The resulting values were corrected using the response factor of this internal standard. While this

approach provides a useful approximation, it is well known that response factors vary across different PFAS compounds, depending on their structure, ionization efficiency, and chromatographic behavior. As such, the reported values are expressed in PFAS equivalents—a semi-quantitative metric. These PFAS-equivalent values provide a relative indication of abundance and allow comparative assessment across samples or classes, but should not be interpreted as absolute concentrations. For accurate quantitative data, particularly for compounds identified with confidence level 1, the results from targeted analysis should be used.

4.4.2 Quantification limit of PFAS-equivalents

The quantification limit for PFAS eq. was arbitrarily set at 1 in the sample extract which was measured. The reported LOQ is based on sample level, already applying the sample preparation dilution or concentration factor.

This threshold was chosen based on typical PFAS concentrations observed in target analyses, where known PFAS often yield more than 1,000 PFAS equivalents. In such cases, 1 PFAS equivalent represents 0.1%, which is considered fit-for-purpose for comparative assessment.

While technically a lower quantification limit could be applied, doing so would substantially increase the number of detected features while reducing confidence in classification and interpretation.

It is important to note that screening approaches, i.e. NTA, are generally less sensitive than targeted methods. As a result, certain PFAS detected by highly sensitive targeted techniques may not be captured in NTA workflows, highlighting the need for complementary use of both approaches.

4.5 Quality assurance/Quality control (QA/QC)

A reference standard mixture is analyzed with each instrumental sequence and should be processed using the same identification workflow as the samples. A minimum of triplicate analyses, including full-scan acquisition and fragmentation (MS/MS) data, is advisable for reliable identification.

4.5.1 False positives and false negatives

4.5.1.1 False positives

It is known that halogenated organic compounds can exhibit mass defects similar to those of PFAS compounds. Additionally, conjugated organic compounds, particularly those containing elements such as oxygen or sulfur, may also display comparable mass defect patterns. This similarity can lead to false positive identifications, which cannot be fully excluded at this time. Further research is needed to improve the discrimination between PFAS and non-PFAS features and to reduce the risk of misidentification in non-target analysis workflows.

4.5.1.2 False negatives

Not all PFAS present in a sample may be detected during non-target analysis (NTA), and it is inherently unknown which compounds may be missed. As such, false negatives cannot be excluded, and acknowledging their sources is key to improving the reliability and completeness of PFAS detection.

As highlighted by Manz et al., 2023, no single NTA method is fully comprehensive. Each step of the analytical workflow, ranging from sampling and sample preparation to chromatographic separation, ionization, and data analysis, introduces selectivity toward specific chemical properties. Consequently, many compounds may go undetected. For example, chromatographic separation (e.g. LC or GC) inherently favors compounds with particular physicochemical properties (e.g., polarity or volatility). Ionization mode determines detectability, with PFAS being typically detected in negative ionization mode via LC-HRMS, whereas pharmaceuticals, pesticides, and flame retardants are more frequently observed in positive ionization mode. This underscores the need for complementary analytical techniques to expand chemical space coverage. Studies using multiple methods (e.g., LC-HRMS in both ionization modes or combined with GC-HRMS) showed broader detection of PFAS, including subclasses less amenable to LC-HRMS negative mode alone (Figure 5).

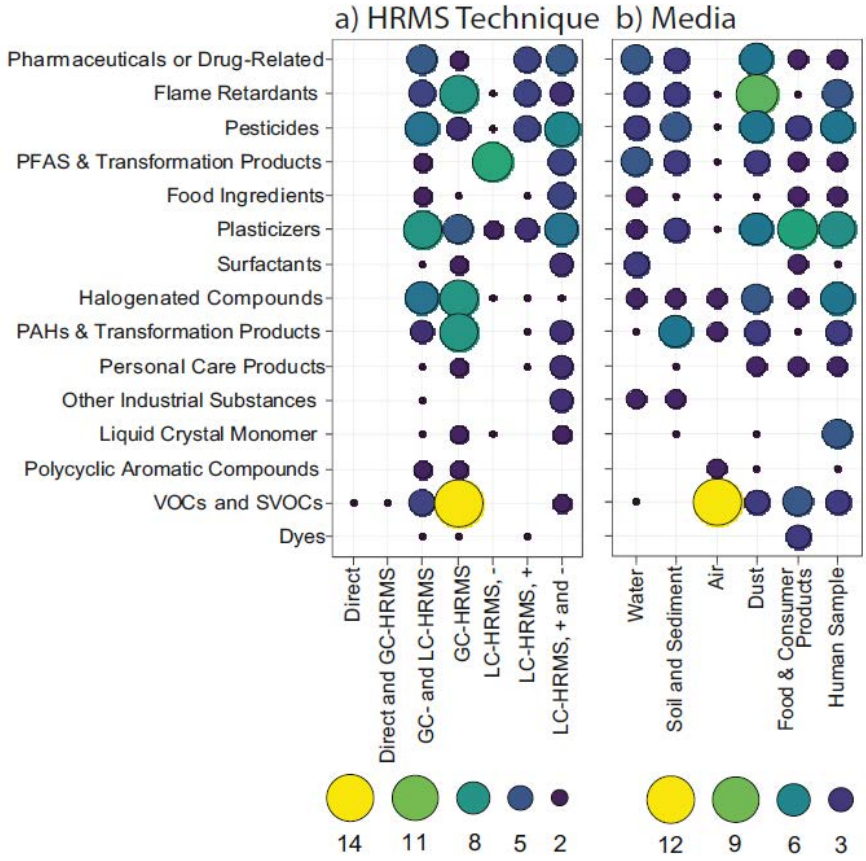


Figure 5. Chemical space detected in NTA by HRMS technique and environmental media. The chemicals detected using NTA by (a) HRMS technique used in the study and the (b) sample media studied. Manz et al. (2025) examined the chemical classes that were detected in each of the 76 NTA studies reviewed herein, and the dot size and color represent the frequency the chemical class was reported in each study. In some studies, multiple chemical classes were reported and all chemical classes reported were considered in the frequency. Obtained from Manz et al., 2023.

The study by Newton et al., 2025 highlighted the need to integrate GC-based non-target analysis (GC-NTA) into PFAS monitoring frameworks to achieve more comprehensive environmental and exposure assessments. Using an LC-ESI-MS amenability model applied to a database of approximately 12,000 PFAS, the study found that less than 10% of known PFAS chemistries are predicted to be amenable to typical LC-MS analysis - such as the one used in the current study. This underscores the limitations of LC-based approaches, particularly in detecting volatile and semi-volatile PFAS, which fall outside the chemical space effectively covered by LC-ESI-MS. These volatile and semi-volatile PFAS are better suited for GC-based techniques, which provide a complementary and orthogonal approach. Notably, such compounds may also act as precursors to less volatile PFAS, which are more likely to be captured by LC-ESI-MS methods.

Moreover, short-chain PFAS are particularly susceptible to matrix effects in reversed-phase LC, often resulting in co-elution with highly polar matrix constituents and significant signal suppression. These compounds typically elute at the very beginning of the chromatographic run, where peak shape and resolution are suboptimal. Consequently, short-chain PFAS may not be detected at all or may be severely underestimated in both qualitative and semi-quantitative assessments.

4.5.2 Sensitivity and selectivity

The applied workflow was developed based on the analysis of a reference standard mixture, with the aim of maximizing both sensitivity and selectivity of the method (Jacob et al., 2021).

4.5.2.1 Sensitivity calculation

Sensitivity, also known as the true positive rate, is a measure of how effectively a screening workflow can detect and correctly annotate PFAS compounds present in a sample. It is calculated using the Equation 1, where true positives (TPs) are the PFAS correctly identified as present and false negatives (FN) are the PFAS present in the sample but not detected by the method (Jacob et al., 2021). A higher sensitivity indicates better performance in capturing the actual PFAS content in a sample.

$$Sensitivity\ (accuracy) = \frac{TP}{TP + FN} \times 100$$

Equation 1. Example of calculating sensitivity.

4.5.2.2 Selectivity calculation

Selectivity is a measure of how effectively a suspect screening workflow can avoid annotating PFAS compounds that are not actually present in a sample. It is calculated by Equation 2, where true positives (TP) are PFAS correctly identified as present and false positives (FP) are PFAS incorrectly annotated as present (Jacob et al., 2021). Higher selectivity reflects greater confidence in the specificity of the screening method, minimizing false detections.

$$Selectivity\ (precision) = \frac{TP}{TP + FP} \times 100$$

Equation 2. Example of calculating selectivity.

4.5.2.3 Method sensitivity and selectivity

The applied PFAS workflow (Figure 1) showed a sensitivity of 87% and selectivity of 76%, which are considered acceptable for its intended use. The sensitivity showed to be higher than methods previously reported in the literature (71%, 89%, 51%), while the selectivity is aligned to what was previously reported (85%, 80% and 82%) (Jacob et al., 2021).

4.6 Interpretation of NTA-PFAS results

The following remarks should be considered when interpreting NTA-PFAS data:

- The results are expressed in PFAS equivalents; **no normalization was applied as function of the air volume that was sampled (ambient air samples) or the duration and area for deposition samples.**
- Dilutions and/or concentration factors applied during sample processing were taken into account when calculating the final PFAS equivalents, as detailed below. As a result, all results are expressed as PFAS equivalents per sample.
    - Filter samples were multiplied by 4 when only a quarter of the filter was processed.
    - PUF samples were multiplied by 10 when a 1/10 sub-fraction of the PUF was analyzed.
    - Water samples (wet deposition) were divided by the enrichment factor, when applied, and subsequently multiplied by the total volume of collected wet deposition.

The purpose of an NTA-PFAS analysis is to obtain an indicative overview of the unknown PFAS compounds present in a sample. To allow comparison between samples, PFAS equivalents have been calculated, and the relative distribution of PFAS classes can be used for cross-sample comparison. However, interpretation of PFAS equivalents should be approached with appropriate caution and expertise.

The results were processed against the field blank, whenever available (i.e., not possible for the wet fraction of atmospheric deposition, where the procedure blank was used instead) to exclude possible background contamination and to filter out the influence of matrix effects.

In general, results are presented as distributions by PFAS class rather than at the individual compound level. However, in certain cases, a more detailed investigation was carried out to identify the main compounds contributing to specific classes. This selection was based on the class's relevance, i.e., its contribution to the total PFAS equivalent amount. It is important to note that branched isomers of compounds listed in WAC/IV/A/025 are not distinguished from their linear counterparts in the current analytical workflow. As a result, they are not considered or highlighted as new compounds in this report.

5 RESULTS PFAS IN AIR

5.1 Site ZD08

5.1.1 Samples

Table 4. Overview of sample types, sample codes and sampling period for samples from site ZD08, processed during different rounds.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
PUF	1	230608-0020 (R10135)	17/05 – 01/06/2023
DEP	1	230613-0005 (R10171)	04/05 – 01/06/2023
DEP	1	230712-0005 (W + D) (R10268)	01/06 – 29/06/2023

5.1.2 Results Target PFAS ZD08

Table 5. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site ZD08. Values marked as "-" could not be reported due to low recovery of the internal standard. Values containing the symbol "+" presented a high response for the specific compound but quantitation could not be performed due to low internal standard recovery. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	230608-0020 (R10135)	230613-0005 (R10171)	230712-0005 (W) (R10268)	230712-0005 (D) (R10268)
PFPrA	1600	+	64	<0.30
PFBA	550	+	27	0.51
PFPeA	22	2.3	3	<0.090
PFHxA	21	4.9	14	0.65
PFHpA	15	6.5	15	0.24
L-PFOA	220	57	79	2.2
T-PFOA	240	63	91	2.5
PFNA	3.3	1.5	1.9	0.17
PFDA	1.2	1.2	0.48	0.21
PFTeDA	<2	<0.30	-	<0.090
PFHxDA	-	<0.40	-	<0.10
PFODA	-	<0.40	-	<0.10
PFPrS	1.6	<0.30	<0.40	<0.080
PFBS	16	3.1	9.8	<0.40
PFPeS	<0.6	0.43	<0.40	<0.070
L-PFHxS	4.3	19	43	0.76
T-PFHxS	5	21	46	0.88
PFHpS	<0.6	6.2	21	0.9
L-PFOS	17	560	1400	250
T-PFOS	30	900	2700	370
PFNS	<0.60	0.36	<0.60	0.57
PFDS	<0.60	0.42	<0.60	0.31
PFUnDS	<0.60	<0.30	<0.60	0.13
PFDoDS	<0.60	0.76	<0.60	0.46
6:2FTS	3.1	NA	NA	NA
PFBSA	92	0.7	7.2	<0.090
MePFBSA	+	0.35	+	-
MePFBSAA	170	17	9.8	0.097
L-PFHxSA	1300	12	24	0.93
T-PFHxSA	1500	13	27	1

L-PFOSA	260	12	9.9	6
T-PFOSA	430	17	14	7.4
L-MePFOSA	+	1.2	-	-
T-MePFOSA	+	2.3	-	-
L-EtPFOSA	+	3.8	-	-
T-EtPFOSA	+	6.9	-	-
L-MePFOSAA	3.1	19	<0.40	4.6
T-MePFOSAA	7.2	24	8.1	5.5
L-EtPFOSAA	2.3	14	5.7	7.9
T-EtPFOSAA	4.9	18	7.3	9.5
8:2diPAP	-	<0.060	<1.0	<0.040
HFPO-DA	150	5.8	3.1	<0.20
BPAF	<0.50	2	0.44	0.31
sum of linear PFAS	**4452**	**752**	**1738**	**277**
sum of total PFAS	**4862**	**1119**	**3070**	**401**

5.1.3 Results NTA PFAS ZD08

5.1.3.1 Confidence level 1 - target PFAS results in ZD08

Table 6 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis. Perfluoroalkylsulfonic acids (PFSAs) were the most frequent PFAS class observed in deposition samples, with a total of 3001 PFAS eq. in wet deposition (R10268) and 994 and 426 in dry deposition (R10171 and R10268, respectively) (Table 6, in light grey).

High PFAS eq. levels of N-methyl-perfluoroalkylsulfonamides (N-Me-FASAs), perfluoroalkylcarboxilic acids (PFCAs), and perfluoroalkylsulfonamides (FASAs) were detected in PUF samples (R10135), with values of 204, 599, and 1092 PFAS eq., respectively (Table 6, in dark grey).

Other PFAS classes, such as ether-substituted perfluoroalkylcarboxylic acids (PFECA), N-ethyl perfluoroalkylsulfonamide acetic acids (N-Et-FASAAs), N-methyl perfluoroalkylsulfonamide acetic acids (N-Me-FASAAs), and x:2 fluorotelomer perfluoroalkylsulfonic acids (x:2FTS) were also detected, though at levels below 100 PFAS eq. or below the limit of quantification (LOQ), which were matrix-dependent.

Table 6. Compounds detected via NTA PFAS analysis in ZD08 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green and the values above 100 PFAS eq. are indicated in grey.

PFAS Classes (PFAS equivalent)	PUF_R10135_230608-0020	DEP_D_R10171_230613-0005	DEP_W_R10268_230712-0005	DEP_D_R10268_230712-0005
Ether substituded perfluoroalkyl carboxylic acids (PFECA)	53	7.0	<6	<1
N-ethyl perfluoroalkyl sulfonamido acetic acids (FASAAs)	<10	<1	<6	2.9
N-methyl perfluoroalkyl sulfonamide acetic acids (FASAAs)	50	17	<6	1.7
N-methyl perfluoroalkyl sulfonamides (FASAs)	204	<1	<6	<1
Perfluoroalkyl carboxylic acids (PFCAs)	599	69	100	<1
Perfluoroalkyl sulfonamides (FASAs)	1092	27	33	7.3
Perfluoroalkyl sulfonic acids (PFSAs)	34	994	3001	426
x:2 Fluorotelomer sulfonic acids (x:2FTS)	<10	<1	17	<1

5.1.3.2 Confidence level 2 – 4 – PFAS results in ZD08

Table 7 below presents the PFAS classes with values above the PFAS eq. LOQ across all ZD08 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with or without supporting fragmentation data.

Considering all these parameters, it can be stated with a high degree of certainty that the identified compounds are PFAS-related substances. These compounds are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but potentially structurally related.

Only known PFAS classes with more than 100 PFAS eq. (highlighted in grey) are discussed in further detail, all of which were found in the PUF sample (R10135).

Table 7. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in ZD08. The values below LOQ are indicated in green and the values above 100 PFAS eq. are indicated in grey.

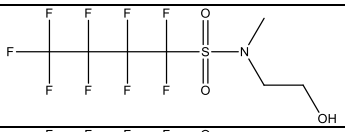
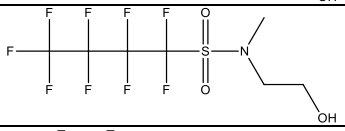
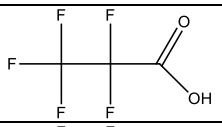
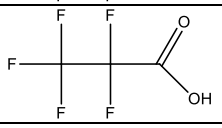
PFAS Classes (PFAS equivalent)	PUF_R10135_230608-0020	DEP_D_R10171_230613-0005	DEP_W_R10268_230712-0005	DEP_D_R10268_230712-0005
H-substituted perfluoroalkyl carboxylic acids (H-subs PFCAs)	410	53	<6	<1
N-ethyl perfluoroalkyl sulfonamide (FASAs)	19	<1	<6	<1
N-ethyl perfluoroalkyl sulfonamide acetic acids (FASAAs)	11	<1	<6	<1
N-methyl perfluoroalkyl sulfonamide ethanol (FASEs)	605	6	<6	<1
Perfluoroalkyl carboxylic acids (PFCAs)	5145	<1	65	<1
Perfluoroalkyl sulfinic acids (PFSIs)	16	<1	<6	<1
Perfluoroalkyl sulfonamides (FASAs)	11	<1	<6	<1
Perfluoroalkyl sulfonic acids (PFSAs)	<10	<1	<6	31
Unknown PFAS class (07-57)	177	<1	<6	<1
Unknown PFAS class (09-59)	184	<1	<6	<1
Unknown PFAS class (32-82)	110	<1	<6	<1
Unknown PFAS class (40-90)	36	<1	<6	<1
Unknown PFAS class (45-95)	68	21	<6	<1
Unknown amine I	71	13	<6	<1
x:2 Fluorotelomer carboxylic acids (x:2FTCAs)	48	<1	<6	<1

One of the PFAS classes observed in the PUF sample (R10135) was the H-substituted perfluoroalkylcarboxylic acids (H-subs PFCAs), with a total of 410 PFAS equivalents. This class of compounds is characterized by the replacement of one or more fluorine atoms with hydrogen atoms within the perfluoroalkylcarboxylic acid (PFCA) structure. Once hydrogen substitution occurs on a carbon atom in the alkyl chain, the resulting compound can no longer be detected by the WAC/IV/A/025 target method, which is limited to perfluoroalkyl substances.

The second class detected was N-methyl-perfluoroalkyl sulfonamide ethanol (N-Me-FASEs), reaching up to 605 PFAS equivalents in the PUF sample (R10135). This is a noteworthy finding, as these compounds have not previously been reported in this context and belong to a class of more volatile PFAS, primarily MePFBSE.

The third class identified the perfluoroalkylcarboxylic acids (PFCAs), mainly composed by ultra-short chain compounds, particularly PFPrA, which showed 5145 PFAS equivalents in the PUF sample (R10135) and 65 PFAS equivalents in the wet deposition sample (R10268).

Table 8. Examples of potential candidates of H-subs.PFCAs, FASEs and PFCAs found in the site ZD08.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	PFAS eq.	RT [min]
H-subs-PFCAs	R10135 (PUF)	H-perfluoropentanoic acid	$C_5H_2F_8O_2$		244.9865	410	1.32
FASEs	R10135	MePFBSE	$C_7H_8F_9NO_3S$		416.02304	605	13.16
FASEs	R10171 (dry deposition)	MePFBSE	$C_7H_8F_9NO_3S$		416.02304	6	12.86
PFCAs	R10135	PFPrA	$C_3HF_5O_2$		162.98387	5145	1.343
PFCAs	R10268 (wet deposition)	PFPrA	$C_3HF_5O_2$		162.98387	65	1.07

Regarding the unknown PFAS classes, the features observed in Table 9 appear to belong to different homologous series, as indicated by their consistent mass differences of m/z 50 (indicating - CF_2 - groups) and similar mass defects, both characteristics of PFAS.

However, caution is required when interpreting these findings. To confidently classify compounds as part of a homologous series, retention time must also align with expected chromatographic behavior. For example, features at m/z 507.96704 (RT 16.309 min) and m/z 557.96472 (RT 16.084 min), classified as *Unknown PFAS class (07-57)*, deviate from the expected trend in reversed-phase liquid chromatography, where heavier molecules within the same chemical class typically show increased retention times. In contrast, the remaining features listed in

Table 9 follow a more consistent retention time progression and show uniform mass differences and defects, supporting the hypothesis that they belong to the same chemical class. These patterns strengthen the likelihood that the compounds are indeed PFAS. Nonetheless, further structural elucidation is necessary to confidently assign them to a specific PFAS subclass.

Table 9. Examples of potential from unknown PFAS classes characterized by homologous series found in the site ZD08 in the PUF sample (R10135).

Class	*m/z*	PFAS eq.	RT [min]
Unknown PFAS class (07-57)	507.96704	10	16.309
Unknown PFAS class (07-57)	557.96472	58	16.084
Unknown PFAS class (07-57)	607.95789	10	18.722
Unknown PFAS class (07-57)	657.95538	98	19.891
Unknown PFAS class (09-59)	209.058	145	4.939
Unknown PFAS class (09-59)	359.0481	23	14.966
Unknown PFAS class (09-59)	409.9879	7	13.137
Unknown PFAS class (09-59)	509.9826	9	17.236
Unknown PFAS class (32-82)	182.9899	61	2.801
Unknown PFAS class (32-82)	282.9829	33	9.592
Unknown PFAS class (32-82)	332.9791	16	13.212

5.1.3.3 Confidence level 5 - unknown PFAS results in ZD08

Table 10 presents the unknown potential PFAS compounds. These compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive compounds. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 10. Unknown compounds (CL5) detected via NTA PFAS analysis in ZD08. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	PUF_R10135 _230608-0020	DEP_D_R10171 _230613-0005	DEP_W_R10268 _230712-0005	DEP_D_R10268 _230712-0005
Unknown PFAS cpd (KMD filter CF2)	1779	1193	<6	50

5.1.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – ZD08

Table 11 presents the total results for ZD08 site. The data show that the target PFAS represented 19%, 84%, 98% and 46% in the PUF, dry and wet deposition (R10268) and dry deposition (R10171), respectively. The unknown identified PFAS classes represented, for the same samples, 64%, 6%, 2% and 4%, respectively. The remaining unknown PFAS fraction represented 17%, 10%, 0% and 50%, for the same samples.

An overview of the distribution of PFAS found into target classes, identified classes and unknown classes is available in Figure 6 (in PFAS eq.) and Figure 7 (in relative distribution of PFAS eq. (%)).

For site ZD08, the deposition samples from R10268 revealed only 2% of PFAS compounds in dry and 6% in wet deposition based on the NTA-PFAS analysis.

In contrast, the dry deposition (R10171) revealed that 54% were potentially PFAS-related molecules, for which 4% could be identified in PFAS classes and 50% remaining unknown.

In the PUF (R10135), only 19% of the total PFAS corresponded to compounds covered by target analysis (within the scope of WAC/IV/A/025), while 64% could be assigned to known PFAS classes.

Table 11. Total PFAS detected, subdivided into target PFAS (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in ZD08. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R10135 _230608-0020	R10171 _230613-0005	R10268 _230712-0005	
	PUF	DEP_D	DEP_W	DEP_D
Results Target PFAS classes (CL1)	2032	1114	3153	438
Results Unknown identified PFAS classes (CL2-4)	6911	93	65	31
Results Unknown PFAS classes (CL5)	1779	1193	<6	50

PFAS Classes (PFAS equivalent)	R10135 _230608-0020	R10171 _230613-0005	R10268 _230712-0005	
	PUF	DEP_D	DEP_W	DEP_D
% Target PFAS classes (CL1)	19%	46%	98%	84%
% Unknown identified PFAS classes (CL2-4)	64%	4%	2%	6%
% Unknown PFAS classes (CL5)	17%	50%	0%	10%

Figure 6. Results in PFAS equivalents (PFAS eq.) per sample in ZD08, subdivided into target PFAS classes (CL1), identified PFAS classes (CL2–CL4), and unknown PFAS classes (CL5).

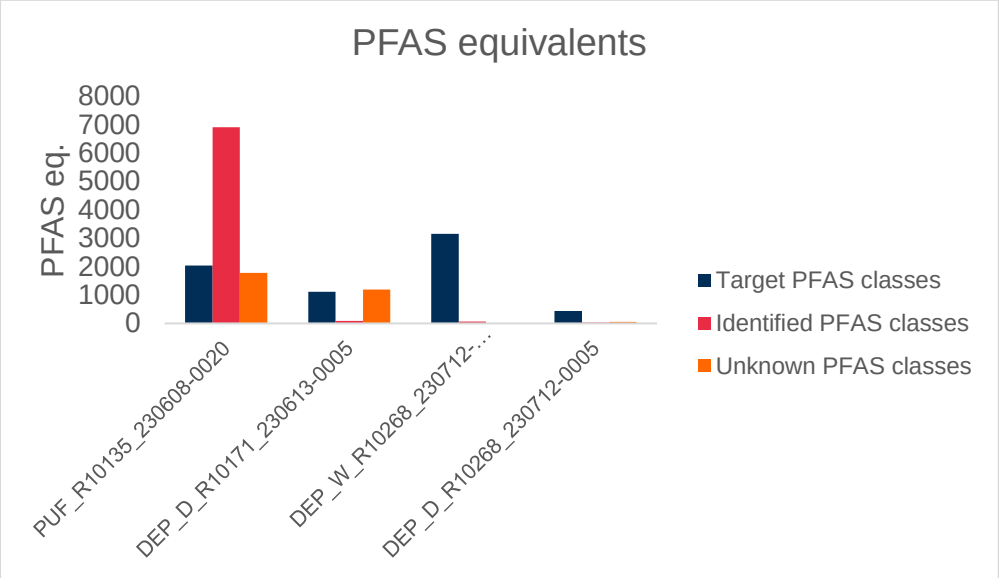
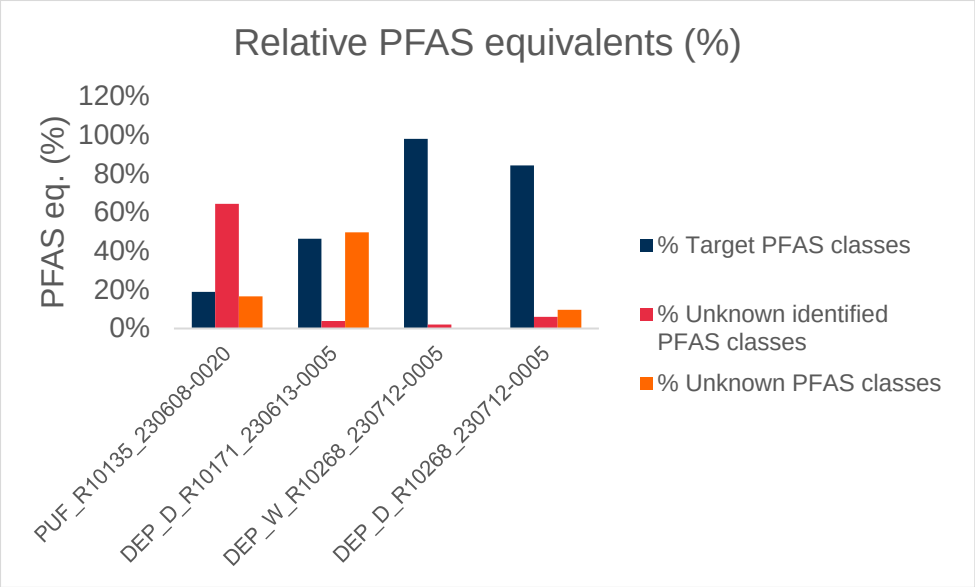


Figure 7. Relative distribution (in %) of PFAS equivalents per sample in ZD08, subdivided into target PFAS classes (CL1), identified PFAS classes (CL2–CL4), and unknown PFAS classes (CL5).



5.2 Site ZD11

5.2.1 Samples

Table 12. Overview of sample types, sample codes and sampling period for samples from site ZD11, processed during different rounds.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
TSP	1	240409-0002 (R11341)	21/03 – 04/04/2024
PUF	1	240415-0238 (R11380)	21/03 – 04/04/2024
PUF	1	240514-0037 (R11509)	18/04 – 02/05/2024
TSP	1	240521-0158 (R11541)	02/05 – 16/05/2024
PUF	1	240521-0169 (R11544)	02/05 – 16/05/2024

5.2.2 Results Target PFAS ZD11

Table 13. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site ZD11. Values marked as "-" could not be reported due to low recovery of the internal standard. Values containing the symbol "+" presented a high response for the specific compound but quantitation could not be performed due to low internal standard recovery. Compounds not analyzed for specific samples are represented with a "NA". The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240409-0002 (R11341)	240415-0238 (R11380)	240514-0037 (R11509)	240521-0158 (R11541)	240521-0169 (R11544)
PFBA	<0.50	39	50	<0.40	57
PFPeA	1.1	1.7	2.2	<0.3	2.6
PFHxA	4.6	2.8	4.1	0.92	7.6
PFHpA	6.4	2.1	1.7	2.0	6.0
L-PFOA	61	5.9	6.8	26	59
T-PFOA	66	6.5	6.9	28	63
PFNA	1.3	<0.50	0.55	0.64	1.5
PFDA	0.74	<0.50	<0.50	0.49	<0.90
PFDoDA	<0.20	<0.60	<0.60	0.35	<0.80

COMPOUND	240409-0002 (R11341)	240415-0238 (R11380)	240514-0037 (R11509)	240521-0158 (R11541)	240521-0169 (R11544)
PFHxDA	<0.20	-	<2.0	<0.30	<0.80
PFODA	<0.20	-	<2.0	<0.30	<0.80
PFBS	3.9	4.0	2.3	7.9	4.3
PFPeS	0.28	<0.60	<0.60	0.49	<0.90
L-PFHxS	24	1.8	2.6	28	2.8
T-PFHxS	28	2.1	3.0	32	3.0
PFHpS	4.4	<0.60	<0.60	5.1	<0.90
L-PFOS	410	18	20	360	19
T-PFOS	600	32	36	570	32
PFNS	0.43	<0.60	<0.60	0.85	<0.90
PFDS	0.53	<0.60	<0.60	1.4	<0.90
PFUnDS	<0.30	<0.60	<0.60	0.55	<0.90
PFDoDS	0.58	<0.60	<0.60	1.1	<0.90
6:2FTS	NA	<0.50	17	NA	3.0
PFBSA	<0.50	27	25	<0.40	28
MePFBSA	-	2700	1300	<0.50	1200
MePFBSAA	21	18	15	9.7	54
L-PFHxSA	4.0	65	85	2.5	81
T-PFHxSA	4.2	68	91	2.7	90
L-PFOSA	140	180	190	63	350
T-PFOSA	160	220	250	76	440
L-MePFOSA	-	410	450	9.3	650
T-MePFOSA	-	870	980	18	1400
L-EtPFOSA	-	+	1100	29	1800
T-EtPFOSA	-	+	2300	55	3800
L-MePFOSAA	32	1.2	1.5	89	13
T-MePFOSAA	52	1.6	2.1	120	18
L-EtPFOSAA	65	1.8	2.0	170	18
T-EtPFOSAA	80	2.2	2.5	210	23
8:2diPAP	<0.10	-	<2.0	<0.10	<0.80
BPAF	5.3	<0.90	<1.0	6.1	<2.0
sum of linear PFAS	**787**	**3478**	**3279**	**814**	**4357**
sum of total PFAS	**1041**	**3997**	**5092**	**1149**	**7233**

5.2.3 Results NTA PFAS ZD11

5.2.3.1 Confidence level 1 - target PFAS results in ZD11

Table 14 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.

Perfluoroalkyl sulfonic acids (PFSAs) were the most frequently PFAS class observed in TSP samples (Table 14, light grey), with a total of 221 and 195 PFAS eq. (R11341 and R11541, respectively). High levels of N-ethyl-perfluoroalkyl sulfonamides (N-Et-FASAs), N-methyl-perfluoroalkyl sulfonamides (N-Me-FASAs) and perfluoroalkyl sulfonamide (FASAs) were detected in PUF samples (R11380, R11509 and R11544) (Table 14, dark grey).

Other PFAS classes, such N-ethyl-perfluoroalkyl sulfonamide acetic acids (N-Et-FASAAs), N-methyl-perfluoroalkyl sulfonamide acetic acids (N-Me-FASAAs), perfluoroalkyl carboxylic acids (PFCAs) and x:2 fluorotelomer sulfonic acids (x:2FTS) were also detected at levels below 100 PFAS eq. or below the limit of quantification (LOQ), which were matrix-dependent.

Table 14. Compounds detected via NTA PFAS analysis in ZD11 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green and the values above 100 PFAS eq. are indicated in grey.

PFAS Classes (PFAS equivalent)	TSP_R11341_240409-0002	PUF_R11380_240415-0238	PUF_R11509_240514-0037	TSP_R11541_240521-0158	PUF_R11544_240521-0169
N-ethyl perfluoroalkyl sulfonamide (FASAs)	3.5	229	488	4.7	1966
N-ethyl perfluoroalkyl sulfonamido acetic acids (FASAAs)	7.5	<10	<10	20	<10
N-methyl perfluoroalkyl sulfonamide acetic acids (FASAAs)	8.4	5.0	<10	13	<10
N-methyl perfluoroalkyl sulfonamides (FASAs)	<1	1156	1096	1.7	731
Perfluoroalkyl carboxylic acids (PFCAs)	20	38	38	5.9	98
Perfluoroalkyl sulfonamides (FASAs)	28	315	380	17	649
Perfluoroalkyl sulfonic acids (PFSAs)	227	30	30	195	27
x:2 Fluorotelomer sulfonic acids (x:2FTS)	<1	<10	5.9	<1	<10

5.2.3.2 Confidence level 2 – 4 – PFAS results in ZD11

Table 15 below presents the PFAS classes with values above the PFAS eq. LOQ across all ZD11 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with or without supporting fragmentation data.

Considering all these parameters, it can be stated with a high degree of certainty that the identified compounds are PFAS-related substances. These compounds are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

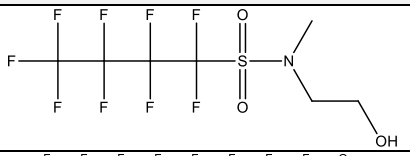
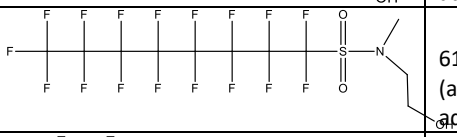
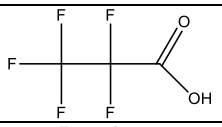
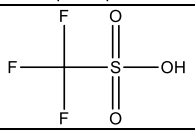
Only known PFAS classes with more than 100 PFAS eq. (highlighted in grey) are discussed in further detail, which were mainly found in PUF samples.

Table 15. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in ZD11. The values below LOQ are indicated in green and the values above 100 PFAS eq. are indicated in grey.

PFAS Classes (PFAS equivalent)	TSP_R11341_240409-0002	PUF_R11380_240415-0238	PUF_R11509_240514-0037	TSP_R11541_240521-0158	PUF_R11544_240521-0169
N-ethyl perfluoroalkyl sulfonamide (FASAs)	<1	13	39	<1	66
N-ethyl perfloroalkyl sulfonamide ethanol (FASEs)	2.0	3.7	12	1.8	34
N-methyl perfluoroalkyl sulfonamides (FASAs)	<1	30	55	<1	99
N-methyl sulfonamide ethanol (FASEs)	2.0	235	186	1.3	244
Perfluoroalkyl carboxylic acids (PFCAs)	<1	437	238	<1	206
Perfluoroalkyl sulfinic acids (PFSIs)	<1	17	<10	<1	8.7
Perfluoroalkyl sulfonamide acetic acids (FASAAs)	<1	4.2	<10	<1	<10
Perfluoroalkyl sulfonamides (FASAs)	<1	3.5	<10	<1	<10
Perfluoroalkyl sulfonic acids (PFSAs)	<1	<10	<10	121	<10
Polyfluoroalkyl phosphate ester (PAPs)	<1	5.3	<10	<1	20
Unsaturated perfluoro carboxylic acids	<1	<10	<10	10	<10
Unknown PFAS class (09-59)	<1	15	24	<1	<10
Unknown PFAS class (19-69)	<1	<10	<10	<1	22
Unknown PFAS class (45-95)	<1	<10	<10	2.0	<10
Unknown PFAS class (47-97)	13	<10	<10	<1	<10
x:2 Fluorotelomer carboxylic acids (x:2FTCAs)	3.8	<10	<10	5.5	<10
x:2 Fluorotelomer sulfonic acids (x:2FTS)	3.7	<10	<10	<1	<10
x:2 Unsaturated fluorotelomer sulfonic acids	14	<10	<10	<1	<10

Two main PFAS classes were identified in PUF samples (R11380, 11509 and 11544), the first one was the N-methyl perfluoroalkyl sulfonamide ethanol (N-Me-FASEs), with a total of 235, 186 and 244 PFAS eq., respectively. The second class was the perfluoroalkyl carboxylic acids (PFCAs), which reached 437, 238 and 206 PFAS eq. in the PUF sample (R11380, R11509 and R11544, respectively). For the TSP samples, the main identified PFAS class was the perfluoroalkyl sulfonic acids (PFSAs), with 121 PFAS eq. in sample R11541. The representative compounds of these classes are displayed in Table 16.

Table 16. Examples of potential candidates of FASEs and PFCAs found in the site ZD11.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
FASEs	R11380 R11509 R11544	MePFBSE	$C_7H_8F_9NO_3S$		416.02304 (acetate adduct)	13.16
	R11380 R11509 R11544	MeFOSE	$C_{11}H_8F_{17}NO_3S$		616.0095 (acetate adduct)	22.26
PFCAs	R11380 R11509 R11544	PFPrA	$C_3HF_5O_2$		162.98387	1.343
PFSAs	R11541	TFMS	CHF_3O_3S		148.95257	0.83

5.2.3.3 Confidence level 5 - unknown PFAS results in ZD11

Table 17 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 17. Unknown compounds (CL5) detected via NTA PFAS analysis in ZD11.

PFAS Classes (PFAS equivalent)	TSP_R11341_240409-0002	PUF_R11380_240415-0238	PUF_R11509_240514-0037	TSP_R11541_240521-0158	PUF_R11544_240521-0169
Unknown PFAS cpd (KMD filter CF2)	130	1283	2121	157	1392

As also noticed for compounds under CL 2-4, the PUF samples presented the highest levels of PFAS eq.

5.2.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – ZD11

Table 18 presents the total results for ZD11 site. The data show that the target PFAS classes (CL1) represented from 43% to 64% from all samples analyzed. The unknown identified PFAS classes (CL 2 – 4) ranged from 8% to 25%, while the remaining unknown PFAS classes, which could not be assigned to any specific class due to the absence of homologous series, ranged from 25% to 45%.

Table 18. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in ZD11.

PFAS Classes (PFAS equivalent)	TSP_R11341_240409-0002	PUF_R11380_240415-0238	PUF_R11509_240514-0037	TSP_R11541_240521-0158	PUF_R11544_240521-0169
Results Target PFAS classes (CL1)	294	1773	2036	257	3471
Results Unknown identified PFAS classes (CL2-4)	39	763	553	141	700
Results Unknown PFAS classes (CL5)	130	1283	2121	157	1392

PFAS Classes (PFAS equivalent)	TSP_R11341_240409-0002	PUF_R11380_240415-0238	PUF_R11509_240514-0037	TSP_R11541_240521-0158	PUF_R11544_240521-0169
% Target PFAS classes (CL1)	64%	46%	43%	46%	62%
% Unknown identified PFAS classes (CL2-4)	8%	20%	12%	25%	13%
% Unknown PFAS classes (CL5)	28%	34%	45%	28%	25%

An overview of the distribution of target PFAS, identified PFAS classes, and unknown PFAS classes is provided in Figure 8 (PFAS eq.) and Figure 9 (relative distribution (%)).

Figure 8. Results in PFAS equivalents (PFAS eq.) per sample of ZD11, subdivided into target PFAS class (CL1), identified PFAS classes (CL2–CL4), and unknown PFAS class (CL5).

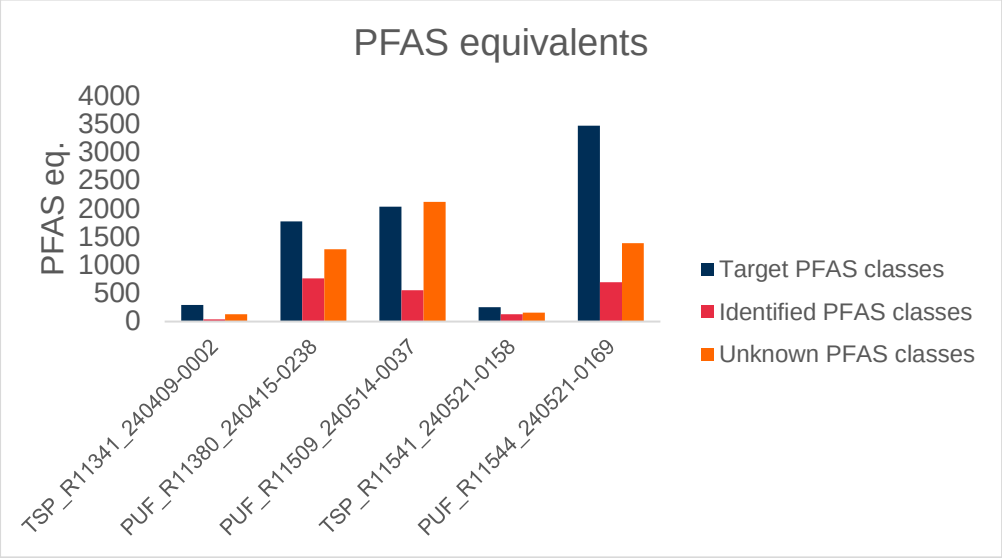
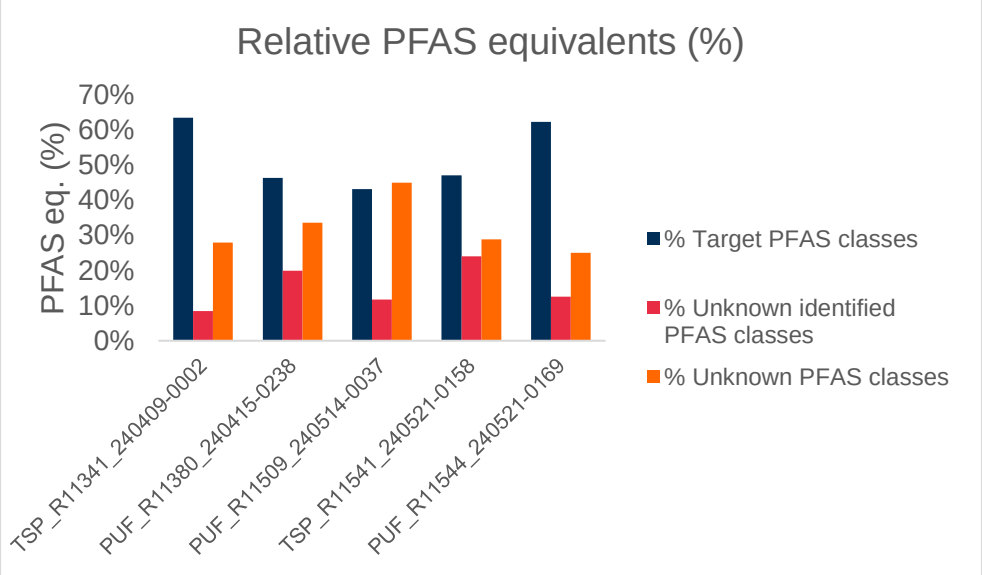


Figure 9. Relative distribution (in %) of PFAS equivalents per sample of ZD11, subdivided into target PFAS class (CL1), identified PFAS classes (CL2–CL4), and unknown PFAS class (CL5).



For site ZD11, the fraction of unknown compounds not previously detected via target PFAS analysis (within the scope of WAC/IV/A/025) ranged from 36% to 57% in TSP and PUF samples. The compounds assigned to identified PFAS classes were mainly represented by short-chain compounds, specifically perfluoroalkyl carboxylic acids (i.e., PFPrA), perfluoroalkyl sulfonic acids (i.e., TFMS) and perfluoroalkyl sulfonamide ethanols (i.e., MePFBSE and MePFOSE).

5.3 Site N016

5.3.1 Samples

Table 19. Overview of sample types, sample codes and sampling period for samples from site N016, processed during different rounds.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
TSP	1	240522-0059 (R11558)	02/05 – 16/05/2024
DEP	2	240612-0041 (D + W) (R11664)	02/05 - 30/05/2024

5.3.2 Results Target PFAS N016

Table 20. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site N016. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240522-0059 (R11558)	240612-0041 (D) (R11664)	240612-0041 (W) (R11664)
PFHxA	<0.20	0.44	<5.0
L-PFOA	0.14	0.22	<2.0
T-PFOA	0.14	0.22	<2.0
PFTrDA	<0.20	0.17	<3.0
PFHxDA	<0.10	<0.20	-
PFODA	<0.10	<0.20	-
PFBS	0.16	<0.10	<3.0
L-PFOS	0.20	0.36	<3.0
T-PFOS	0.67	0.61	3.4
MePFBSA	<0.30	-	<4.0
L-MePFOSA	<0.30	-	-
T-MePFOSA	<0.30	-	-
L-EtPFOSA	<0.30	-	-
T-EtPFOSA	<0.30	-	-
T-MePFOSAA	0.11	<0.10	<3.0
T-EtPFOSAA	0.11	<0.10	<3.0
6:2diPAP	<0.10	-	<10
6:2/8:2diPAP	<0.10	-	<10
8:2diPAP	<0.050	-	-
sum of linear PFAS	**0.34**	**1.2**	**<LOQ**
sum of total PFAS	**0.81**	**1.4**	**3.4**

5.3.3 Results NTA PFAS N016

5.3.3.1 Confidence level 1 - target PFAS results in N016

For this location, there were no PFAS compounds with CL1 found above the LOQ. The determined LOQ was 2, 1 and 40 PFAS eq. for the TSP (R11558), dry and wet deposition (R11664), respectively

5.3.3.2 Confidence level 2 – 4 – PFAS results in N016

Table 21 presents the PFAS classes with values above the PFAS eq. LOQ across N016 sample. These PFAS classes were assigned with a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with supporting fragmentation data and spectra library match.

Considering all these parameters, it can be stated with a high degree of certainty that the identified compounds are PFAS-related substances. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 21. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in N016. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11558 _240522-0059	DEP_D_R11664 _240612-0041	DEP_W_R11664 _240612-0041
Fluazinam (fungicide)	2.3	<1	<40
Flutolanil (fungicide)	10	<1	<40

Two compounds, fluazinam and flutolanil, were identified in TSP sample at site N016. These compounds are classified as broad-spectrum fungicide and are routinely applied during the flowering stage of plants. They were retained as potential PFAS due to the presence of a $-CF_3$ group (trifluoromethyl groups), which, according to the recent OECD definition (Wang et al., 2021), is sufficient for a compound to be considered as PFAS (Table 22).

The main concern with this $-CF_3-$ containing compounds is their potential to release this group in its oxidized state, specifically with a carboxylic acid as an end group. In other words, this could lead to the formation of trifluoroacetic acid (TFA), the shortest perfluoroalkyl carboxylic acid (PFCAs). A recent study conducted by the Pesticide Action Network reported high concentration of TFA in bottles of European wine, strongly suggesting that the use of fluorinated pesticides may be the source[2].

The use of fluazinam is approved in Europe, however, to illustrate recent international concerns, the Environmental Protection Authority of New Zealand (EPA-NZ) recently considered reassessing fluazinam due to new information indicating that risks to operators could not be fully mitigated even with full personal protective equipment (PPE). Potential risks to sediment-dwelling organisms were also identified. Following a preliminary risk assessment of human health impacts related to fluazinam and fluazinam-containing substances, EPA-NZ concluded that most human health risks can be mitigated through the use of full PPE and by applying existing regulatory controls[3].

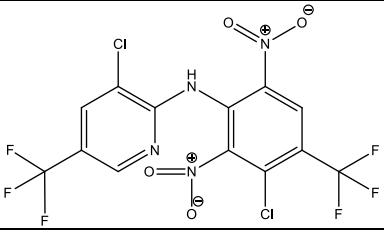
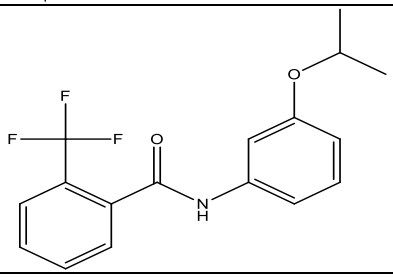
[2] Study reveals alarming surge of forever chemical TFA in European wine (https://www.pan-europe.info/press-releases/2025/04/study-reveals-alarming-surge-forever-chemical-tfa-european-wine)

[3] EPA-NZ: Call for information on fluazinam (https://www.epa.govt.nz/public-consultations/decided/call-for-information-on-fluazinam/)

The current PFAS restriction proposal under REACH[4], submitted by five European countries (Germany, the Netherlands, Denmark, Norway, and Sweden) in early 2023, discuss the inclusion of fluorinated pesticides, specifically those containing perfluoroalkyl moieties such as -CF_3. While the main focus of the REACH restriction proposal is on industrial and consumer uses of PFAS, agricultural applications, including fluorinated active substances in pesticides, are recognized as part of the broader concern, especially due to their persistence and potential degradation into ultrashort-chain PFAS (e.g., TFA). Recently fifty members of the European Parliament have written to the Commission, urging it to ban all PFAS pesticides [5].

Interpretation of PFAS equivalent levels should be approached with caution due to structural differences between the detected compounds and the reference standard ($^{13}C_4$-PFOA) used for semi-quantification. These structural variations can lead to significant differences in instrumental response. Given the specific nature of this class - compounds containing –CF_3 groups - it is recommended to obtain certified reference materials. This would not only enable identification with Confidence Level 1 (CL1) but also support accurate quantification through the use of external calibration curves.

Table 22. Examples of potential pesticides belonging to the PFAS class found in the site N016.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
PFAS – pesticide	R11558	Fluazinam	$C_{13}H_4Cl_2F_6N_4O_4$		462.94410	20.1
PFAS - pesticide	R11558	Flutolanil	$C_{17}H_{16}F_3NO_2$		322.10604	13.6

5.3.3.3 Confidence level 5 - unknown PFAS results in N016

Table 23 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

[4] EFSA – The PFAS restriction proposal in a nutshell (https://www.efsa.europa.eu/sites/default/files/2023-03/7.1f-pfas-restriction-proposal-rivm.pdf)

[5] Urgency of regulating trifluoroacetic acid (TFA) and phasing out PFAS pesticides to safeguard water resilience and public health in the EU. https://www.europarl.europa.eu/doceo/document/E-10-2025-001786_EN.html

Table 23. Unknown compounds (CL5) detected via NTA PFAS analysis in N016.

PFAS Classes (PFAS equivalent)	TSP_R11558_240522-0059	DEP_D_R11664_240612-0041	DEP_W_R11664_240612-0041
Unknown PFAS cpd (KMD filter CF2)	228	38	815

5.3.3.4 Recommendation

The site N016 is a rural background location with generally low PFAS concentrations in ambient air and deposition. For example, the PFAS concentration (T-PFAS all) in sample TSP_R11558_240522-0059 was 0.81 ng/sample (0,002 ng/m³) from previous target analysis and therefore considered as almost PFAS-free. This result was confirmed by the NTA analysis that did not detect any PFAS compounds with CL1. However, the NTA approach revealed the presence of other potential PFAS compounds that had previously gone unnoticed. Given the significance of the unknown fraction at this site, and to maximize the interpretation of these new findings, all detected accurate masses from both active and passive sampling were plotted against their signal intensities and color-coded by sample type (Figure 10).

The results show media-specific distribution of unknown features. For instance, in the wet deposition samples (DEP_W), only low-mass compounds (up to *m/z* 350) were observed. In contrast, dust deposition (DEP_D) and TSP samples revealed higher-mass compounds, reaching up to *m/z* 604. These differences likely reflect both the sampling method and the physicochemical properties of the compounds.

To guide further identification efforts, a prioritization strategy may be employed, such as focusing on high-intensity features like *m/z* 324.0396, detected in the TSP sample, which also exhibited the greatest diversity of unknowns. These prioritization steps could be enhanced by incorporating retention time as an additional filtering dimension, improving the robustness of candidate selection and reducing the likelihood of false positives.

Temporal monitoring with higher resolution could also be useful to confirm the consistent presence of prioritized features over time. Nonetheless, all interpretations should be made with caution, as no structural information is currently available. Some compounds may contain only non-perfluorinated carbon atoms and thus may not meet the strict definition of PFAS.

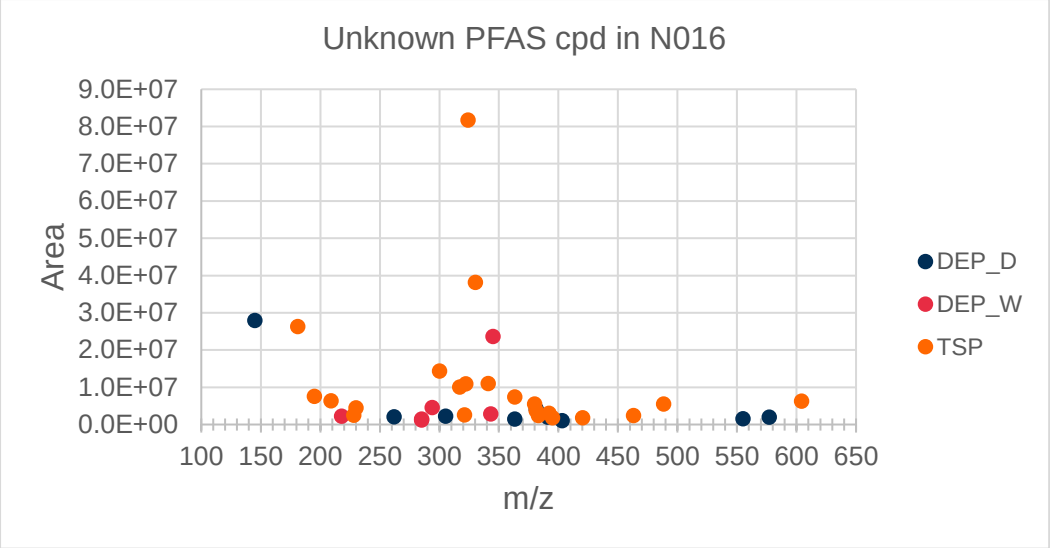


Figure 10. Detected accurate masses in sample N016 across different sample types, with corresponding signal intensities (areas).

5.3.3.5 Overview PFAS results (CL 1 to CL 5) in NTA – N016

Table 24 presents the total results for N016 site. No PFAS were found belonging to target PFAS classes (CL1). The unknown identified PFAS classes (CL 2 - 4) represented 5% in TSP (R11558), while the remaining unknown fraction (CL5) represented 95%, 100%, 100% in TSP, dry and wet deposition (R11664), respectively.

Table 24. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in N016. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11558 _240522-0059	R11664 _240612-0041	
	TSP	DEP_D	DEP_W
Results Target PFAS classes (CL1)	<2	<1	<40
Results Unknown identified PFAS classes (CL2-4)	12	<1	<40
Results Unknown PFAS classes (CL5)	228	38	815

PFAS Classes (PFAS equivalent)	R11558 _240522-0059	R11664 _240612-0041	
	TSP	DEP_D	DEP_W
% Target PFAS classes (CL1)	0%	0%	0%
% Unknown identified PFAS classes (CL2-4)	5%	0%	0%
% Unknown PFAS classes (CL5)	95%	100%	100%

5.4 Site KK01

5.4.1 Samples

Table 25. Overview of sample types, sample codes and sampling period for samples from site KK01.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
DEP	2	240419-0058 (D + W) (R11411)	20/03 - 17/04/2024
TSP	2	240419-0044 (R11409)	31/03 - 14/04/2024

5.4.2 Results Target PFAS KK01

Table 26. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site KK01. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240419-0044 (R11409)	240419-0058 (D) (R11411)	240419-0058 (W) (R11411)
PFBA	<0.10	0.43	3.2
PFPeA	<0.10	0.16	0.51
PFHxA	0.22	0.53	0.80
PFHpA	<0.10	0.29	0.43
L-PFOA	0.20	0.46	0.37
T-PFOA	0.20	0.48	0.36
PFNA	<0.10	6.1	<0.20
PFDA	<0.10	0.35	<0.10
PFUnDA	<0.10	4.6	<0.20
PFDoDA	<0.10	0.14	<0.20
PFTrDA	<0.10	1.9	<0.20
L-PFOS	<0.20	0.33	0.15
T-PFOS	0.41	0.53	0.31
4:2FTS	<0.090	0.15	<0.10
MePFBSA	<0.20	-	<0.20
L-MePFOSA	<0.20	-	<0.20
T-MePFOSA	<0.20	-	<0.20
L-EtPFOSA	<0.20	-	<0.20
T-EtPFOSA	<0.20	-	<0.20
T-MePFOSAA	<0.090	0.068	<0.1
L-EtPFOSAA	<0.080	0.062	<0.10
T-EtPFOSAA	<0.080	0.070	<0.10
ADONA	<0.10	2.0	<0.10
sum of linear PFAS	**0.20**	**18**	**5.5**
sum of total PFAS	**0.61**	**18**	**5.6**

5.4.3 Results NTA PFAS KK01

5.4.3.1 Confidence level 1 - target PFAS results in KK01

Table 27 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.
Specifically, perfluoroalkyl carboxylic acids (PFCAs) and x:2 perfluoroalkyl sulfonic acids (x:2FTS) were the only PFAS classes found, and only in dry deposition (R11411).

Table 27. Compounds detected via NTA PFAS analysis in KK01 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11409_240419-0044	DEP_D_R11411_240419-0058	DEP_W_R11411_240419-0058
Perfluoroalkyl carboxylic acids (PFCA)	<2	10	<2
x:2 Fluorotelomer sulfonic acids (x:2FTS)	<2	11	<2

5.4.3.2 Confidence level 2 – 4 – PFAS results in KK01

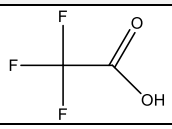
Table 28 presents the PFAS classes with values above the PFAS eq. LOQ across KK01 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with supporting fragmentation data and spectra library match. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 28. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in KK01. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11409_240419-0044	DEP_D_R11411_240419-0058	DEP_W_R11411_240419-0058
x:2 Fluorotelomer carboxylic acids (x:2FTCA)	9.3	<1	<2
Perfluoroalkyl carboxylic acids (PFCA)	<2	745	<2
Perfluoroalkyl sulfonic acids (PFSAs)	<2	18	<2

The main PFAS class found was the perfluoroalkyl carboxylic acids (PFCAs), mainly represented by TFA, in the dry deposition (R11411) (Table 29). That represents an ultra-short chain PFAS, of which its widely spread is already recognized by Environmental agencies (Arp et al., 2024)[6]. The detection of TFA in air samples is particularly relevant, as it may reflect both the atmospheric degradation of volatile PFAS precursors and the direct transport of TFA itself through the atmosphere. Due to its volatility and high water solubility, TFA can undergo long-range transport and be removed from the atmosphere via wet and dry deposition, also impacting remote environments.

Table 29. Examples of potential candidates PFCAs found in the site KK01.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
PFCAs	R11411	TFA	$C_2HF_3O_2$		112.98606	0.902

5.4.3.3 Confidence level 5 - unknown PFAS results in KK01

Table 30 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 30. Unknown compounds (CL5) detected via NTA PFAS analysis in KK01.

PFAS Classes (PFAS equivalent)	TSP_R11409_240419-0044	DEP_D_R11411_240419-0058	DEP_W_R11411_240419-0058
Unknown PFAS cpd (KMD filter CF2)	58	62	82

[6] The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA). https://ovam-english.vlaanderen.be/web/emconsoil/w/the-global-threat-from-the-irreversible-accumulation-of-trifluoroacetic-acid-tfa-
Urgency of regulating trifluoroacetic acid (TFA) and phasing out PFAS pesticides to safeguard water resilience and public health in the EU. https://www.europarl.europa.eu/doceo/document/E-10-2025-001786_EN.html

5.4.3.4 Recommendation

A similar approach to that suggested for the unknown fraction at site N016 could be implemented for KK01 (see in 5.3.3.4), highlighting the potential of using non-target data for monitoring unknown compounds, followed by a prioritization strategy. In the case of KK01, the unknown features appear to be relatively equally distributed across the analyzed sample types (TSP, dry, and wet deposition) at this point in time.

However, it is important to note that, as described in the methodology, the results are expressed in PFAS equivalents and are not normalized to the sampling volume or surface area. This limits direct quantitative comparison between sample types and should be considered when interpreting the distribution patterns.

5.4.3.5 Overview PFAS results (CL 1 to CL 5) in NTA – KK01

Table 31 presents the total results for KK01 site. The target PFAS classes (CL1) represented only 2.5% in dry deposition (R11411) and were only detected in this fraction. The unknown identified PFAS classes (CL 2 - 4) represented 13% in TSP (R11409) and 90% in dry deposition (R11411), while the remaining unknown fraction (CL5) represented 87%, 7% and 100% in TSP, dry and wet deposition, respectively.

Table 31. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in KK01. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11409 _240419-0044	R11411 _240419-0058	
	TSP	DEP_D	DEP_W
Results Target PFAS classes (CL1)	<2	21	<2
Results Unknown identified PFAS classes (CL2-4)	9	762	<2
Results Unknown PFAS classes (CL5)	58	62	82

PFAS Classes (PFAS equivalent)	R11409 _240419-0044	R11411 _240419-0058	
	TSP	DEP_D	DEP_W
% Target PFAS classes (CL1)	0%	2.5%	0%
% Unknown identified PFAS classes (CL2-4)	13%	90%	0%
% Unknown PFAS classes (CL5)	87%	7%	100%

5.5 Site ZD17

5.5.1 Samples

Table 32. Overview of sample types, sample codes and sampling period for samples from site ZD17.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
TSP	2	240426-0022 (R11451)	14/04 - 21/04/2024

5.5.2 Results Target PFAS ZD17

Table 33. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site ZD17. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240426-0022 (R11451)
PFBA	1.9
PFPeA	0.71
PFHxA	2.2
PFHpA	4.6
L-PFOA	40
T-PFOA	43
PFNA	0.95
PFDA	0.32
PFUnDA	0.12
PFDoDA	0.16
PFBS	2.0
PFPeS	0.11
L-PFHxS	9.3
T-PFHxS	10
PFHpS	2.9
L-PFOS	190
T-PFOS	300
PFNS	0.42
PFDS	0.92
PFUnDS	0.31
PFDoDS	0.57
8:2FTS	0.093
MePFBSA	0.85
MePFBSAA	12
L-PFHxSA	4.6
T-PFHxSA	5.0
L-PFOSA	190
T-PFOSA	230
L-MePFOSA	23
T-MePFOSA	44
L-EtPFOSA	150
T-EtPFOSA	290
L-MePFOSAA	62
T-MePFOSAA	78
L-EtPFOSAA	130
T-EtPFOSAA	150
HFPO-DA	0.33
ADONA	0.14
BPAF	2.7
sum of linear PFAS	**833**
sum of total PFAS	**1184**

5.5.3 Results NTA PFAS ZD17

5.5.3.1 Confidence level 1 - target PFAS results in ZD17

Table 34 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.
Perfluoroalkyl sulfonic acids (PFSAs) were the main PFAS class observed (Table 34, in grey), with a total of 371 PFAS eq., follow by perfluoroalkyl sulfonamide (FASAs) and N-ethyl-perfluoroalkyl sulfonamides (N-Et-FASAs), 228 and 160 PFAS equiv., respectively (Table 34, light grey).
Other PFAS classes, such N-ethyl-perfluoroalkyl sulfonamide acetic acids (N-Et-FASAAs), N-methyl-perfluoroalkyl sulfonamide acetic acids (N-Me-FASAAs), perfluoroalkyl carboxylic acids (PFCAs) and x:2 fluorotelomer sulfonic acids (x:2FTS) were also detected at levels below 100 PFAS eq.

Table 34. Compounds detected via NTA PFAS analysis in ZD17 for which a reference standard was available (target PFAS). The values above 100 PFAS eq. are indicated in grey.

PFAS Classes (PFAS equivalent)	TSP_R11451 _240426-0022
N-ethyl perfluoroalkyl sulfonamide (FASAs)	160
N-ethyl perfluoroalkyl sulfonamido acetic acids (FASAAs)	65
N-methyl perfluoroalkyl sulfonamide acetic acids (FASAAs)	45
N-methyl perfluoroalkyl sulfonamides (FASAs)	21
Perfluoroalkyl carboxylic acids (PFCA)	50
Perfluoroalkyl sulfonamide acetic acids (FASAAs)	2.5
Perfluoroalkyl sulfonamides (FASAs)	228
Perfluoroalkyl sulfonic acids (PFSAs)	371
x:2 Fluorotelomer sulfonic acids (x:2FTS)	18

5.5.3.2 Confidence level 2 – 4 – PFAS results in ZD17

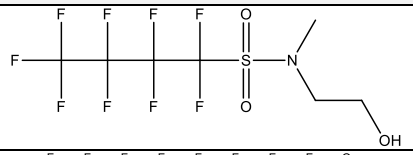
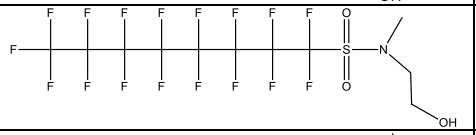
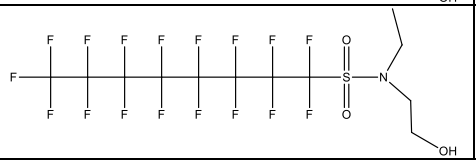
Table 35 below presents the PFAS classes with values above the PFAS eq. LOQ across all ZD11 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with or without supporting fragmentation data. These compounds are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 35. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in ZD17.

PFAS Classes (PFAS equivalent)	TSP_R11451 _240426-0022
Alkylfluorosulfide Perfluoroalkyl (linear) sulfonic acids	4.2
N-ethyl perfluoroalkyl sulfonamide ethanol (FASEs)	51
N-methyl perfluoroalkyl sulfonamide ethanol (FASEs)	38
Perfluoroalkyl sulfinic acids (e.g.PFBSi)	6.0
Perfluoroalkyl sulfonic acids (PFSAs)	4.6
Unknown amine I	3.1
Unknown PFAS class (45-95)	5.1

The two main PFAS classes identified were the N-ethyl perfluoroalkyl sulfonamide ethanol (N-Et-FASEs) and N-methyl perfluoroalkyl sulfonamide ethanol (N-Me-FASEs), with a total of 51 and 38 PFAS eq., respectively (Table 35, in grey). The potential candidates of these classes, MePFBSE, MeFOSE and EtFOSE are displayed in Table 36.

Table 36. Examples of potential candidates of FASEs and PFCAs found in the site ZD17.

Class	Possible compound	Formula	Possible structure	*m/z*	RT [min]
N-Me-FASEs	*MeFBSE*	$C_7H_8F_9NO_3S$		*416.0235 (acetate adduct)*	*13.025*
	MeFOSE	$C_{11}H_8F_{17}NO_3S$		*616.0095 (acetate adduct)*	*20.63 (and isomers)*
N-Et-FASEs	*EtFOSE*	$C_{12}H_{10}F_{17}NO_3S$		*630.0248 (acetate adduct)*	*21.23 (and isomers)*

5.5.3.3 Confidence level 5 - unknown PFAS results in ZD17

Table 37 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 37. Unknown compounds (CL5) detected via NTA PFAS analysis in ZD17.

PFAS Classes (PFAS equivalent)	TSP_R11451_240426-0022
Unknown PFAS cpd (KMD filter CF2)	64

5.5.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – ZD17

Table 38 presents the total results for ZD17 site. The data show that the target PFAS classes represented 85% of the total PFAS Fraction. The unknown identified PFAS classes represented 10%, while the remaining unknown PFAS classes represented 5%.

Table 38. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in ZD17. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11451_240426-0022
Results Target PFAS classes (CL1)	961
Results Unknown identified PFAS classes (CL2-4)	112
Results Unknown PFAS classes (CL5)	64

PFAS Classes (PFAS equivalent)	TSP_R11451_240426-0022
% Target PFAS classes (CL1)	85%
% Unknown identified PFAS classes (CL2-4)	10%
% Unknown PFAS classes (CL5)	5%

5.6 Site RL18

5.6.1 Samples

Table 39. Overview of sample types, sample codes and sampling period for samples from site RL18.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
TSP	2	240718-0001 (R11810)	25/06 - 07/07/2024
DEP	2	240819-0153 (D) (R11891)	27/06 - 25/07/2024

5.6.2 Results Target PFAS RL18

Table 40. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site RL18. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240718-0001 (R11810)	240819-0153 (D) (R11891)
PFBA	<0.20	4.9
PFPeA	<0.10	1.0
PFHxA	0.43	5.4
PFHpA	0.29	1.0
L-PFOA	0.67	2.3
T-PFOA	0.77	2.3
PFNA	0.14	0.38
PFDA	0.13	0.28
PFUnDA	<0.20	0.097
PFDoDA	<0.20	-
PFTrDA	<0.20	-
PFTeDA	<0.10	-
PFHxDA	<0.10	-
PFODA	<0.10	-
PFBS	0.15	0.23
PFPeS	<0.090	-
L-PFHxS	0.13	-
T-PFHxS	0.20	-
PFHpS	<0.090	-
L-PFOS	0.63	1.5
T-PFOS	1.1	2.1
PFNS	<0.10	-
PFDS	<0.10	-
PFUnDS	<0.10	-
PFDoDS	<0.10	-
PFTrDS	<0.10	-
4:2FTS	<0.050	-
8:2FTS	<0.060	-
10:2FTS	<0.090	-
PFBSA	<0.10	-
MePFBSA	<0.20	-
MePFBSAA	<0.090	0.71
L-PFHxSA	<0.30	-
T-PFHxSA	<0.40	-
L-PFOSA	<2.0	-
T-PFOSA	<2.0	-
L-MePFOSA	<2.0	-
T-MePFOSA	<4.0	-
L-EtPFOSA	<9.0	-
T-EtPFOSA	<20	-
L-MePFOSAA	<0.090	0.32
T-MePFOSAA	<0.090	0.37
L-EtPFOSAA	<0.090	0.19
T-EtPFOSAA	<0.090	0.22
PFDSA	<0.10	-

COMPOUND	240718-0001 (R11810)	240819-0153 (D) (R11891)
6:2diPAP	<0.090	-
6:2/8:2diPAP	<0.090	-
8:2diPAP	<0.040	-
HFPO-DA	<1.0	-
ADONA	<0.10	-
PFECHS	<0.10	-
9Cl-PF3ONS	<0.10	-
11Cl-PF3OUnDS	<0.10	-
BPAF	<0.10	-
sum of linear PFAS	**2.6**	**18**
sum of total PFAS	**3.2**	**19**

5.6.3 Results NTA PFAS RL18

5.6.3.1 Confidence level 1 - target PFAS results in RL18

Table 41 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.
Specifically, perfluoroalkyl carboxylic acids (PFCAs) was the only PFAS classes found, and only in dry deposition (R11891).

Table 41. Compounds detected via NTA PFAS analysis in RL18 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11810 _240718-0001	DEP_D_R11891 _240819-0149
Perfluoroalkyl carboxylic acids (PFCA)	<2	3

5.6.3.2 Confidence level 2 – 4 – PFAS results in RL18

Table 42 presents the PFAS classes with values above the PFAS eq. LOQ across RL18 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C-m/C plots, and a mass list match, with supporting fragmentation data and spectra library match. These compounds are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 42. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in RL18. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11810_240718-0001	DEP_D_R11891_240819-0149
Fluazinam (fungicide)	114	<1
N-methyl perfluoroalkyl sulfonamide ethanol (FASEs)	9	<1
Unsaturated perfluoro carboxylic acids	9	<1
x:2 Fluorotelomer carboxylic acids (x:2FTCA)	27	<1
Perfluoroalkyl sulfonamide ethanol (FASEs)	<2	61

The main PFAS class found in dry deposition (R11891) was the perfluoroalkyl sulfonamide ethanol (FASEs), with 61 PFAS eq., represented by the tentatively identified PFBSE. Although following a similar mass defect and a MS2 spectra of the FASEs class, the absence of homologous series and the low retention time (1.426 min) lead to a high uncertainty associated with this identification attribution.
For the TSP sample (R11810), the fungicide fluazinam was found in 114 PFAS eq., and its relevance was already discussed in section 5.3.3.2.

5.6.3.3 Confidence level 5 - unknown PFAS results in RL18

Table 43 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 43. Unknown compounds (CL5) detected via NTA PFAS analysis in RL18.

PFAS Classes (PFAS equivalent)	TSP_R11810_240718-0001	DEP_D_R11891_240819-0149
Unknown PFAS cpd (KMD filter CF2)	114	45

Similarly to what was proposed to KK01, a temporal monitoring of unknown compounds could be used in a prioritization strategy approach for further identification efforts.

5.6.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – RL18

Table 44 presents the total results for RL18 site. The data show that only 3% of the PFAS content in the dry deposition (R11891), at this sampling time, could be previously identified via target analysis. The unknown identified PFAS classes (CL 2 – 4) represented around 57% for both samples analyzed, while the remaining unknown fraction (CL5) represented around 40%.

Table 44. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in RL18. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11810_240718-0001	DEP_D_R11891_240819-0149
Results Target PFAS classes (CL1)	<2	3.3
Results Unknown identified PFAS classes (CL2-4)	160	61
Results Unknown PFAS classes (CL5)	114	45

PFAS Classes (PFAS equivalent)	TSP_R11810_240718-0001	DEP_D_R11891_240819-0149
% Target PFAS classes (CL1)	0%	3.0%
% Unknown identified PFAS classes (CL2-4)	58%	56%
% Unknown PFAS classes (CL5)	42%	41%

5.7 Site RS03

5.7.1 Samples

Table 45. Overview of sample types, sample codes and sampling period for samples from site RS03.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
DEP	2	240805-0016 (D + W) (R11837)	01/07 - 25/07/2024

5.7.2 Results Target PFAS RS03

Table 46. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site RS03. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240805-0016 (D) (R11837)	240805-0016 (W) (R11837)
PFBA	<0.60	5.5
PFPeA	0.20	1.6
PFHxA	0.79	5.2
PFHpA	0.32	4.4
MePFBSA	-	<0.30
L-MePFOSA	-	<0.20
T-MePFOSA	-	<0.20
L-EtPFOSA	-	<0.40
T-EtPFOSA	-	<0.40
6:2diPAP	-	-
6:2/8:2diPAP	-	-
8:2diPAP	<0.20	-
sum of linear PFAS	**1.3**	**17**
sum of total PFAS	**1.3**	**17**

5.7.3 Results NTA PFAS RS03

5.7.3.1 Confidence level 1 - target PFAS results in RS03

For this location, there were no PFAS compounds with CL1 found above the LOQ. The determined LOQ was 1 or 3 PFAS eq. for the dry and wet deposition (R11837), respectively.

5.7.3.2 Confidence level 2 – 4 – PFAS results in RS03

For this location, there were no PFAS compounds with CL 2 – 4 found above the LOQ. The determined LOQ was 1 or 3 PFAS eq. for the dry and wet deposition (R11837), respectively.

5.7.3.3 Confidence level 5 - unknown PFAS results in RS03

Table 47 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 47. Unknown compounds (CL5) detected via NTA PFAS analysis in RS03.

PFAS Classes (PFAS equivalent)	DEP_D_R11837_240805-0016	DEP_W_R11837_240805-0016
Unknown PFAS cpd (KMD filter CF2)	41	162

For the location RS03, only unknown PFAS compounds, not previously identified in target analysis, were detected. Similarly to what was proposed to KK01, a temporal monitoring of unknown compounds could be used in a prioritization strategy approach for further identification efforts.

5.7.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – RS03

Table 48 presents the total results for RS03 site. No compounds were found belonging to the target PFAS classes (CL1) nor to the unknown identified PFAS classes (CL 2 - 4). The remaining unknown fraction (CL5) represented the totality of PFAS compounds found in dry and wet deposition (R11837).

Table 48. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in RS03. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11837_240805-0016	
	DEP_D	DEP_W
Results Target PFAS classes (CL1)	<1	<3
Results Unknown identified PFAS classes (CL2-4)	<1	<3
Results Unknown PFAS classes (CL5)	41	162

PFAS Classes (PFAS equivalent)	R11837_240805-0016	
	DEP_D	DEP_W
% Target PFAS classes (CL1)	0%	0%
% Unknown identified PFAS classes (CL2-4)	0%	0%
% Unknown PFAS classes (CL5)	100%	100%

5.8 Site R801

5.8.1 Samples

Table 49. Overview of sample types, sample codes and sampling period for samples from site R801.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
TSP	2	240909-0006 (R11958)	20/08 - 03/09/2024
DEP	2	240909-0011 (D + W) (R11959)	08/06 - 04/09/2024

5.8.2 Results Target PFAS R801

Table 50. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site R801. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240909-0006 (R11958)	240909-0011 (D) (R11959)	240909-0011 (W) (R11959)
PFBA	<0.30	0.52	3.5
PFPeA	<0.10	<0.070	0.68
PFHxA	<0.20	<0.10	2.6
PFHpA	<0.10	<0.070	1.9
L-PFOA	0.21	0.073	2.4
T-PFOA	0.21	0.089	2.5
PFNA	<0.10	0.092	0.30
PFDA	<0.090	0.21	1.1
PFUnDA	<0.10	0.11	<0.40
PFDoDA	<0.10	0.13	<0.40
L-PFOS	0.32	<0.30	<2.0
T-PFOS	0.56	<0.50	<3.0
MePFBSA	<0.20	-	<0.30
MePFBSAA	<0.30	<0.070	0.80
L-PFOSA	<0.80	0.091	4.0
T-PFOSA	<1.0	0.10	4.0
L-MePFOSA	<0.40	-	<0.90
T-MePFOSA	<0.80	-	<0.90
L-EtPFOSA	<1.0	-	<0.90
T-EtPFOSA	<2.0	-	<0.90
6:2diPAP	<0.070	0.38	-
6:2/8:2diPAP	<0.070	<0.060	-
8:2diPAP	<0.040	<0.050	-
sum of linear PFAS	**0.53**	**1.6**	**17**
sum of total PFAS	**0.77**	**1.6**	**17**

5.8.3 Results NTA PFAS R801

5.8.3.1 Confidence level 1 - target PFAS results in R801

For this location, there were no PFAS compounds with CL1 found above the LOQ. The determined LOQ was 2, 1 or 5 PFAS eq. for the TSP (R11958), dry and wet deposition (R11959), respectively.

5.8.3.2 Confidence level 2 – 4 – PFAS results in R801

Table 51 presents the PFAS classes with values above the PFAS eq. LOQ across R801 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with supporting

fragmentation data and spectra library match. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 51. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in R801. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11958_240909-0006	DEP_D_R11959_240909-0011	DEP_W_R11959_240909-0011
Fluazinam (fungicide)	80	<1	<5
Unsaturated perfluoro carboxylic acids	4	<1	<5
x:2 Fluorotelomer carboxylic acids (x:2FTCA)	43	<1	<5
Perfluoroalkyl sulfonamides (FASAs)	<2	<1	<5
Unknown PFAS class (15-65)	5	<1	<5

The only PFAS compounds classified into classed with CL 2-4 were detected in TSP sample (R11958). The main PFAS class found (43 PFAS eq.) was the X:2 fluorotelomer perfluoroalkyl carboxylic acids (x:2 PFCAs). The fungicide fluazinam was found in 80 PFAS eq., and its relevance was already discussed in section 5.3.3.2.

5.8.3.3 Confidence level 5 - unknown PFAS results in R801

Table 52 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 52. Unknown compounds (CL5) detected via NTA PFAS analysis in R801.

PFAS Classes (PFAS equivalent)	TSP_R11958_240909-0006	DEP_D_R11959_240909-0011	DEP_W_R11959_240909-0011
Unknown PFAS cpd (KMD filter CF2)	537	2	82

In R801, high amounts of unknown PFAS (537 PFAS eq.) were found in the TSP sample (R11958), followed by lower levels in wet (82 PFAS eq.) and dry (2 PFAS eq.) deposition (R11959). However, it's worth nothing that, as described in our methodology, the results displayed are in PFAS eq. not normalized for the sampling volume or area.
A similar approach as for the N016 unknown fraction could be followed for this location, illustrating the potential temporal monitoring of unknown compounds in TSP samples, which could therefore be used in a prioritization strategy for compound identification.

5.8.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – R801

Table 53 presents the total results for R801 site. No compounds were found belonging to the target PFAS classes (CL1). The unknown identified PFAS classes (CL 2 - 4) represented 20% in TSP sample (R11958). The remaining unknown fraction (CL5) represented 80%, 100%, 100% in TSP (R11958), dry and wet deposition (R11959).

Table 53. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in R801. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	TSP_R11958_ 240909-0006	DEP_D_ R11959_240909-0011	DEP_W_ R11959_240909-0011
Results Target PFAS classes (CL1)	<2	<1	<5
Results Unknown identified PFAS classes (CL2-4)	133	<1	<5
Results Unknown PFAS classes (CL5)	537	2	82
PFAS Classes (PFAS equivalent)	**TSP_R11958_ 240909-0006**	**DEP_D_ R11959_240909-0011**	**DEP_W_ R11959_240909-0011**
% Target PFAS classes (CL1)	0%	0%	0%
% Unknown identified PFAS classes (CL2-4)	20%	0%	0%
% Unknown PFAS classes (CL5)	80%	100%	100%

5.9 Site AL09

5.9.1 Samples

Table 54. Overview of sample types, sample codes and sampling period for samples from site AL09.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
DEP	2	240216-0005 (D + W) (R11112)	12/01 - 09/02/2024
DEP	2	240522-0065 (D + W) (R11559)	04/04 - 02/05/2024
DEP	2	240819-0146 (D + W) (R11891)	27/06 - 25/07/2024
DEP	2	240909-0013 (D + W) (R11960)	25/07 - 22/08/2024

5.9.2 Results Target PFAS AL09

Table 55. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site AL09. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240216-0005 (D) (R11112)	240216-0005 (W) (R11112)	240522-0065 (D) (R11559)	240522-0065 (W) (R11559)	240819-01406 (D) (R11891)	240819-01406 (D) (R11891)	240909-0013 (D) (R11960)	240909-0013 (W) (R11960)
PFBA	0.3	8.7	0.71	9.7	0.25	3.7	<0.10	5.9
PFPeA	<0.20	<1.0	0.13	0.93	<0.090	<0.40	<0.060	<2.0
PFHxA	<0.60	<1.0	0.16	2.0	0.29	2.0	<0.10	4.8
PFHpA	<0.080	<1.0	<0.10	0.95	<0.10	1.2	<0.060	2.8
L-PFOA	1.2	<0.90	<0.090	1.4	0.30	2.1	<0.060	7.2
T-PFOA	1.2	<0.90	0.16	1.8	0.34	2.5	<0.060	8.3
PFNA	<0.10	<1.0	<0.080	<0.80	0.14	<0.40	<0.060	<2.0
PFDA	<0.10	<1.0	<0.10	<0.90	0.21	<0.40	<0.060	4.4
PFTeDA	-	<1.0	-	<1.0	<0.20	<0.60	<0.070	<3.0
PFHxDA	-	<1.0	-	<1.0	-	<0.70	<0.070	<5.0
PFODA	-	<1.0	-	<1.0	-	<0.70	<0.070	<5.0
PFPeS	0.1	<1.0	<0.080	<0.80	<0.10	<0.30	<0.060	<2.0
L-PFOS	<5.0	<6.0	0.40	2.0	1.5	<2.0	<0.30	<10
T-PFOS	<7.0	6.9	0.51	3.2	1.9	<2.0	<0.50	<20
PFBSA	<0.10	<1.0	<0.20	<0.90	-	0.75	<0.060	<2.0
MePFBSA	-	<2.0	-	<0.90	-	<0.50	-	<2.0
MePFBSAA	<0.080	<1.0	<0.080	1.3	<0.20	2.0	<0.050	<2.0
L-PFHxSA	<0.10	<1.0	<0.20	<0.90	-	<0.50	<0.20	<9.0
T-PFHxSA	<0.10	<1.0	<0.20	<0.90	-	<0.50	<0.20	<9.0
L-PFOSA	<0.10	<3.0	<0.20	<2.0	-	<2.0	0.11	16
T-PFOSA	<0.10	<3.0	<0.20	<2.0	-	<2.0	0.12	16
L-MePFOSA	-	<2.0	-	<1.0	-	<0.70	-	<7.0
T-MePFOSA	-	<2.0	-	<1.0	-	<0.70	-	<7.0
L-EtPFOSA	-	<2.0	-	<1.0	-	<0.70	-	<7.0
T-EtPFOSA	-	<2.0	-	<1.0	-	<0.70	-	<7.0
L-MePFOSAA	<0.080	<1.0	<0.080	<1.0	0.25	<0.40	<0.050	<2.0
T-MePFOSAA	<0.080	<1.0	<0.080	<1.0	0.29	<0.40	<0.050	<2.0
L-EtPFOSAA	<0.090	<1.0	<0.10	<1.0	0.38	<0.40	<0.050	<2.0
T-EtPFOSAA	<0.090	<1.0	<0.10	<1.0	0.46	<0.40	<0.050	<2.0
PFDSA	<0.10	<1.0	<0.20	<0.90	-	<0.50	<0.060	<2.0
6:2diPAP	-	<1.0	-	<1.0	-	-	-	<5.0
6:2/8:2diPAP	-	<1.0	-	<1.0	-	-	-	<5.0
8:2diPAP	-	<2	<0.20	<1.0	-	<0.70	<0.020	<4.0
sum of linear	**1.6**	**8.7**	**1.4**	**18**	**3.3**	**12**	**0.11**	**41**
sum of total	**1.6**	**16**	**1.7**	**20**	**3.9**	**12**	**0.12**	**42**

5.9.3 Results NTA PFAS AL09

5.9.3.1 Confidence level 1 - target PFAS results in AL09

Table 56 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.
The only PFAS class found was the x:2 perfluoroalkyl sulfonic acids (x:2FTS) in the wet phase of deposition (R11960).

Table 56. Compounds detected via NTA PFAS analysis in AL09 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_240216-0005		R11559_240522-0065		R11891_240819-0146		R11960_240909-0013	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
x:2 Fluorotelomer sulfonic acids (x:2FTS)	<1	<18	<1	<13	<1	<6	<1	23

5.9.3.2 Confidence level 2 – 4 – PFAS results in AL09

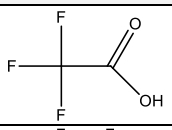
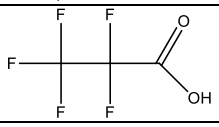
Table 57 presents the PFAS classes with values above the PFAS eq. LOQ across AL09 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with supporting fragmentation data and spectra library match. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 57. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in AL09. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_240216-0005		R11559_240522-0065		R11891_240819-0146		R11960_240909-0013	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
N-methyl perfluoroalkyl sulfonamide ethanol (FASEs)	2.7	<18	<1	<13	<1	<6	<1	<15
Perfluoroalkyl carboxylic acids (PFCA)	<1	<18	19	147	<1	<6	<1	<15
Unknown PFAS class (29-79)	<1	<18	<1	<13	<1	<6	7.1	<15

The main PFAS class found was the perfluoroalkyl carboxylic acids (PFCAs), represented by TFA in the wet deposition (R11559) and PFPrA in dry deposition (R11559) (Table 58).

Table 58. Examples of potential candidates of PFCAs found in the site AL09.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
PFCAs	R11559	TFA	$C_2HF_3O_2$		112.9863	0.824
		PFPrA	$C_3HF_5O_2$		162.983	1.119

5.9.3.3 Confidence level 5 - unknown PFAS results in AL09

Table 59 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 59. Unknown compounds (CL5) detected via NTA PFAS analysis in AL09.

PFAS Classes (PFAS equivalent)	R11112_24021_6-0005		R11559_24052_2-0065		R11891_24081_9-0146		R11960_24090_9-0013	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
Unknown PFAS cpd (KMD filter CF2)	35	1899	93	184	18	253	556	477

For the first three sampling periods, the amount of unknown compounds was higher in the wet deposition than in the dry deposition, while similar PFAS eq. levels between both fractions were found for the last sampling period analyzed.

5.9.3.4 Recommendation

Given the relatively high temporal resolution for this location, compared to other sites, the unknown compounds could be monitored over time. This offers a valuable opportunity for temporal monitoring, which is particularly useful for prioritizing features for further identification efforts. As an illustration of this approach, Table 60 shows features (accurate mass, m/z) classified as *Unknown PFAS cpd (KMD filter CF2)*, signal intensity expressed in PFAS equivalents, and retention time (RT) as detected across different sampling campaigns.

In the wet deposition samples (DEP_W), one notable example is the feature with m/z 294.0655, which was consistently detected over time and exhibited a peak PFAS eq. intensity of 9.9 in sample R11891.

Table 60. Examples of features with corresponding intensity and retention time detected over time at site AL09. The feature with m/z 294.0654 is highlighted in yellow. "n.d." indicates "not detected".

Request	Sampling period	Sample type	m/z	PFAS eq.	RT [min]
R11112	12/01 - 09/02/2024	DEP_D	313.07187	10.6	16.794
R11559	04/04 - 02/05/2024	DEP_D	313.07187	n.d.	n.d.
R11891	27/06 - 25/07/2024	DEP_D	313.07187	n.d.	n.d.
R11960	25/07 - 22/08/2024	DEP_D	313.07172	0.95	16.664
R11112	12/01 - 09/02/2024	DEP_D	335.22034	2.2	21.569
R11559	04/04 - 02/05/2024	DEP_D	335.22034	n.d.	n.d.
R11891	27/06 - 25/07/2024	DEP_D	335.22034	n.d.	n.d.
R11960	25/07 - 22/08/2024	DEP_D	335.22012	2.5	21.458
R11112	12/01 - 09/02/2024	DEP_D	350.10328	8.5	13.251
R11559	04/04 - 02/05/2024	DEP_D	350.10328	n.d.	n.d.
R11891	27/06 - 25/07/2024	DEP_D	350.10328	n.d.	n.d.
R11960	25/07 - 22/08/2024	DEP_D	350.10315	1.6	13.216
R11112	12/01 - 09/02/2024	DEP_D	417.02847	2.6	6.425
R11559	04/04 - 02/05/2024	DEP_D	417.0282	2.0	6.37
R11891	27/06 - 25/07/2024	DEP_D	417.0282	n.d.	n.d.
R11960	25/07 - 22/08/2024	DEP_D	417.0282	n.d.	n.d.
R11112	12/01 - 09/02/2024	DEP_D	537.11829	6.3	16.936
R11559	04/04 - 02/05/2024	DEP_D	537.11835	3.8	17.074
R11891	27/06 - 25/07/2024	DEP_D	537.11835	n.d.	n.d.
R11960	25/07 - 22/08/2024	DEP_D	537.11835	n.d.	n.d.
R11112	12/01 - 09/02/2024	DEP_W	245.10301	n.d.	n.d.
R11559	04/04 - 02/05/2024	DEP_W	245.10301	n.d.	n.d.
R11891	27/06 - 25/07/2024	DEP_W	245.10301	24	1.183
R11960	25/07 - 22/08/2024	DEP_W	245.10307	11	1.122
R11112	12/01 - 09/02/2024	DEP_W	259.11871	n.d.	n.d.
R11559	04/04 - 02/05/2024	DEP_W	259.11871	7.1	1.21
R11891	27/06 - 25/07/2024	DEP_W	259.11871	n.d.	n.d.
R11960	25/07 - 22/08/2024	DEP_W	259.11874	15	1.206
R11112	12/01 - 09/02/2024	DEP_W	294.06552	2.9	6.966
R11559	04/04 - 02/05/2024	DEP_W	294.06552	3.7	6.869
R11891	27/06 - 25/07/2024	DEP_W	294.06552	9.9	6.849
R11960	25/07 - 22/08/2024	DEP_W	294.0654	1.9	6.214

This recurring detection suggests the potential environmental relevance of this feature and supports its prioritization for structural elucidation. Additional discussion of the temporal monitoring strategy is provided in Section 6.5.

5.9.3.5 Overview PFAS results (CL 1 to CL 5) in NTA – AL09

Table 61 presents the total results for AL09 site. The target PFAS classes (CL1) represented only up to 4.7% of the total PFAS amount detected, only in wet deposition (R11960). The unknown identified PFAS classes (CL 2 - 4) varied from 0% to up 44% in wet deposition (R11559). The remaining unknown fraction (CL5) represented more than 90% in two out of the eight samples analyzed.

Table 61. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in AL09. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_240216-0005		R11559_240522-0065		R11891_240819-0146		R11960_240909-0013	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W

Results Target PFAS classes (CL1)	<1	<18	<1	<13	<1	<6	<1	23
Results Unknown identified PFAS classes (CL2-4)	2.7	<18	19	147	<1	<6	7.1	<15
Results Unknown PFAS classes (CL5)	35	1899	93	184	18	253	556	477

PFAS Classes (PFAS equivalent)	**R11112_240216-0005**		**R11559_240522-0065**		**R11891_240819-0146**		**R11960_240909-0013**	
	DEP_D	**DEP_W**	**DEP_D**	**DEP_W**	**DEP_D**	**DEP_W**	**DEP_D**	**DEP_W**
% Target PFAS classes (CL1)	0%	0%	0%	0%	0%	0%	0%	4.7%
% Unknown identified PFAS classes (CL2-4)	7%	0%	17%	44%	0%	0%	1%	0%
% Unknown PFAS classes (CL5)	93%	100%	83%	56%	100%	100%	99%	95%

5.10 Site AL10

5.10.1 Samples

Table 62. Overview of sample types, sample codes and sampling period for samples from site AL10.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
DEP	2	240216-0006 (D + W) (R11112)	12/01 - 09/02/2024
DEP	2	240612-0040 (D + W) (R11664)	05/02 - 30/05/2024
DEP	2	240819-0147 (D + W) (R11891)	27/06 - 25/07/2024

5.10.2 Results Target PFAS AL10

Table 63. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site AL10. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240216-0006 (D) (R11112)	240216-0006 (W) (R11112)	240612-0040 (D) (R11664)	240612-0040 (W) (R11664)	240819-0147 (D) (R11891)	240819-0147 (W) (R11891)
PFBA	0.33	7.9	0.84	6.7	0.28	4.9
PFPeA	<0.20	<0.80	0.14	<1.0	0.071	0.66
PFHxA	<0.50	<0.90	0.23	8.7	0.24	2.4
PFHpA	<0.080	<0.70	<0.10	4.2	0.12	1.2
L-PFOA	1.6	<0.70	0.063	2.2	1.2	1.7
T-PFOA	1.6	<0.70	0.063	3.1	1.2	2.1
PFNA	<0.090	<0.80	<0.060	<1.0	0.29	<0.10
PFDA	<0.10	<0.80	<0.070	<2.0	0.21	<0.10
PFUnDA	<0.10	<0.80	<0.080	<2.0	0.10	<0.20
PFDoDA	<0.10	<0.90	<0.090	<2.0	<0.10	-
PFTrDA	<0.10	<0.90	0.12	<2.0	<0.10	-
PFTeDA	-	<0.90	<0.050	<2.0	<0.090	-
PFHxDA	-	<1.0	<0.070	<2.0	<0.60	<0.20
PFODA	-	<1.0	<0.070	<2.0	<0.70	<0.20
PFBS	<0.20	<0.80	<0.060	<1.0	<0.070	0.58
L-PFHxS	<0.080	<0.80	<0.060	<1.0	<0.070	0.11
T-PFHxS	<0.080	<0.80	<0.060	<1.0	<0.070	0.11
L-PFOS	<5.0	<4.0	0.50	3.9	1.8	0.60
T-PFOS	<7.0	6.1	0.70	6.3	2.3	1.1
4:2FTS	<0.10	<0.90	<0.070	2.1	<0.080	<0.060
8:2FTS	<0.070	<0.80	<0.060	<1.0	<0.060	-
10:2FTS	<0.10	<0.90	<0.070	<2.0	<0.060	-
PFBSA	<0.10	<0.80	<0.20	<3.0	<0.10	0.32
MePFBSA	-	<1.0	-	<2.0	-	0.19
MePFBSAA	<0.080	<0.80	<0.060	2.5	<0.070	1.1
L-PFHxSA	<0.10	<0.80	<0.080	<2.0	<0.10	0.17
T-PFHxSA	<0.10	<0.80	<0.080	<2.0	<0.10	0.18
L-PFOSA	<0.10	<2.0	0.30	<2.0	0.48	<0.60
T-PFOSA	<0.10	<2.0	0.37	<2.0	0.72	<0.60
L-MePFOSA	-	<1.0	-	<2.0	-	<0.20
T-MePFOSA	-	<1.0	-	<2.0	-	<0.20
L-EtPFOSA	-	<1.0	-	<2.0	-	<0.20
T-EtPFOSA	-	<1.0	-	<2.0	-	<0.20
L-MePFOSAA	<0.080	<0.80	<0.060	<2.0	0.21	<0.10
T-MePFOSAA	<0.080	<0.80	<0.060	<2.0	0.26	<0.10
L-EtPFOSAA	<0.080	<0.90	<0.060	<2.0	0.17	<0.10
T-EtPFOSAA	<0.080	<0.90	<0.060	<2.0	0.19	<0.10
6:2diPAP	<0.20	<1.0	<2.0	<2.0	-	<0.20
6:2/8:2diPAP	<0.20	<1.0	<0.20	<2.0	-	<0.20
8:2diPAP	-	<1.0	-	<3.0	-	<0.10
sum of linear	**1.9**	**7.9**	**2.2**	**30**	**5.2**	**14**
sum of total	**1.9**	**14**	**2.5**	**34**	**6.0**	**15**

5.10.3 Results NTA PFAS AL10

5.10.3.1 Confidence level 1 - target PFAS results in AL10

Table 64 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.
The two PFAS classes found were the x:2 perfluoroalkyl sulfonic acids (x:2FTS) in wet deposition (R11664) and perfluoroalkyl carboxylic acids (PFCAs) in dry deposition (R11112).

Table 64. Compounds detected via NTA PFAS analysis in AL10 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_240216-0006		R11664_240612-0040		R11891_240819-0147	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
Perfluoroalkyl carboxylic acids (PFCA)	1.7	<14	<1	<32	<1	<2
x:2 Fluorotelomer sulfonic acids (x:2FTS)	<1	<14	<1	37	<1	<2

5.10.3.2 Confidence level 2 – 4 – PFAS results in AL10

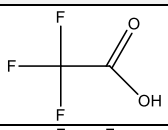
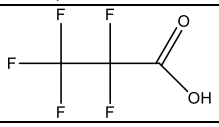
Table 65 presents the PFAS classes with values above the PFAS eq. LOQ across AL10 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with supporting fragmentation data and spectra library match. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 65. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in AL10. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_240216-0006		R11664_240612-0040		R11891_240819-0147	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
Perfluoroalkyl carboxylic acids (PFCA)	<1	41	<1	631	<1	<2
x:2 Unsaturated fluorotelomer sulfonic acids	<1	<14	<1	<32	22	<2
Unknown PFAS class (01-51)	<1	<14	<1	69	<1	<2

The main PFAS class found was the perfluoroalkyl carboxylic acids (PFCAs), represented by TFA in the wet deposition (R11664) and PFPrA in wet deposition (R11112) (Table 66).

Table 66. Examples of potential candidate of PFCAs found on the site AL10.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
PFCAs	R11664 (DEP_W)	TFA	$C_2HF_3O_2$		112.98639	0.835
	R11112 (DEP_W)	PFPrA	$C_3HF_5O_2$		162.98267	1.107

5.10.3.3 Confidence level 5 - unknown PFAS results in AL10

Table 67 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 67. Unknown compounds (CL5) detected via NTA PFAS analysis in AL10.

PFAS Classes (PFAS equivalent)	R11112_240216-0006		R11664_240612-0040		R11891_240819-0147	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
Unknown PFAS cpd (KMD filter CF2)	21	4008	12	493	1077	10

For the first two sampling periods, the amount of unknown compounds was higher in the wet deposition than in the dry deposition, while an opposite profile was observed in the third sampling period analyzed. A similar temporal monitoring approach as described in 5.9.3.3 could be applied to this location, ideally in a higher temporal resolution, in order to identify relevant features for further investigation.

5.10.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – AL10

Table 68 presents the total results for AL10 site. The target PFAS classes (CL1) represented up to 8% of the total PFAS amount detected, in dry deposition (R11112). The unknown identified PFAS classes (CL2 - 4) varied from 0% to 57% in wet deposition (R11664). The remaining unknown fraction (CL5) represented more than 90% in five out of the six samples analyzed.

Table 68. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in AL10. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_240216-0006		R11664_240612-0040		R11891_240819-0147	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
Results Target PFAS classes (CL1)	**1.7**	**<14**	**<1**	**37**	**<1**	**<2**
Results Unknown identified PFAS classes (CL2-4)	**<1**	**41**	**<1**	**700**	**22**	**<2**
Results Unknown PFAS classes (CL5)	**21**	**4008**	**12**	**493**	**1077**	**10**

PFAS Classes (PFAS equivalent)	R11112_240216-0006		R11664_240612-0040		R11891_240819-0147	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
% Target PFAS classes (CL1)	8%	0%	0%	3%	0%	0%
% Unknown identified PFAS classes (CL2-4)	0%	1%	0%	57%	2%	0%
% Unknown PFAS classes (CL5)	92%	99%	100%	40%	98%	100%

5.11 Site ZD01

5.11.1 Samples

Table 69. Overview of sample types, sample codes and sampling period for samples from site ZD01.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
DEP	2	240216-0008 (D + W) (R11112)	12/01 - 09/02/2024
DEP	2	240612-0043 (D + W) (R11664)	05/02 - 30/05/2024
DEP	2	240522-0069 (D + W) (R11559)	04-04 - 02/05/2024
DEP	2	240819-0150 (D + W) (R11891)	27/06 - 25/07/2024
DEP	2	240909-0017 (D + W) (R11960)	25/07 - 22/08/2024

5.11.2 Results Target PFAS ZD01

Table 70. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site AL09. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	240216-0008 (D, R11112)	240216-0008 (W, R11112)	240522-0069 (D, R11559)	240522-0069 (W, R11559)	240612-0043 (D, R11664)	240612-0043 (W, R11664)	240819-0150 (D, R11891)	240819-0150 (W, R11891)	240909-0017 (D, R11960)	240909-0017 (W, R11960)
PFBA	0.23	7.9	0.31	12	0.54	<1.0	0.29	4.5	<0.10	3.6
PFPeA	<0.20	<0.70	0.68	3.2	0.46	<1.0	0.45	5.4	<0.060	1.1
PFHxA	<0.40	1.1	0.78	11	0.58	6.0	1.5	11	0.32	4.5
PFHpA	<0.060	<0.70	<0.10	2.4	<0.10	<3.0	0.25	2.0	<0.060	1.6
L-PFOA	<0.40	<0.60	0.11	1.8	0.080	<1.0	1.2	1.4	<0.060	1.7
T-PFOA	<0.40	<0.60	0.18	2.0	0.080	<1.0	1.2	1.6	<0.060	1.8
PFNA	<0.090	<0.70	<0.080	<0.60	<0.080	<1.0	0.25	<0.080	<0.060	<1.0
PFDA	<0.080	<0.70	<0.10	<0.70	<0.050	<2.0	0.23	<0.080	<0.060	<1.0
PFTrDA	<0.20	<0.80	<0.20	<0.80	0.058	<2.0	<0.080	<0.090	<0.060	<1.0
PFTeDA	-	<0.80	-	<0.80	<0.050	<2.0	<0.080	<0.10	<0.060	<1.0
PFHxDA	-	<0.90	-	<2.0	<0.060	<3.0	<0.50	<0.20	<0.070	<2.0
PFODA	-	<0.90	-	<2.0	<0.060	<3.0	<0.60	<0.20	<0.070	<2.0
PFBS	<0.10	<0.70	<0.080	<0.60	<0.050	<1.0	<0.070	0.15	<0.060	<1.0
PFPeS	0.068	<0.70	<0.090	<0.60	<0.050	<1.0	<0.070	<0.070	<0.060	<1.0
L-PFHxS	<0.060	<0.70	<0.090	<0.60	<0.050	<1.0	<0.070	0.12	<0.060	<1.0
T-PFHxS	<0.060	<0.70	<0.090	<0.60	<0.050	<1.0	<0.070	0.15	<0.060	<1.0
L-PFOS	<4.0	<4.0	0.55	3.1	0.29	3.0	2.2	0.60	<0.30	<7.0
T-PFOS	<5.0	5.2	0.72	4.6	0.45	5.1	2.7	1.2	<0.50	<10
4:2FTS	0.16	<0.80	<0.060	<0.60	<0.060	<1.0	<0.070	<0.040	<0.060	<1.0
PFBSA	<0.080	<0.70	<0.20	<0.70	<0.10	<3.0	<0.10	0.37	<0.060	<1.0
MePFBSA	-	<0.90	-	<0.70	-	<2.0	-	0.29	-	<1.0
MePFBSAA	<0.040	<0.70	<0.070	1.8	<0.050	<2.0	<0.070	1.4	<0.040	<1.0
L-PFHxSA	<0.080	<0.70	<0.20	<0.70	<0.060	<2.0	<0.10	0.096	<0.20	<5.0
T-PFHxSA	<0.080	<0.70	<0.20	<0.70	<0.060	<2.0	<0.10	0.11	<0.20	<5.0
L-PFOSA	<0.080	<2.0	0.29	<1.0	<0.20	<2.0	0.39	<0.40	<0.060	<6.0
T-PFOSA	<0.080	<2.0	0.39	<1.0	<0.20	<2.0	0.63	<0.40	<0.060	<6.0
L-MePFOSA	-	<0.90	-	<1.0	-	<2.0	-	<0.10	-	<3.0
T-MePFOSA	-	<0.90	-	<1.0	-	<2.0	-	<0.10	-	<3.0
L-EtPFOSA	-	<0.90	-	<2.0	-	<2.0	-	<0.10	-	<3.0
T-EtPFOSA	-	<0.90	-	<2.0	-	<2.0	-	<0.10	-	<3.0
L-MePFOSAA	<0.040	<0.70	0.17	<0.70	<0.050	<2.0	0.13	<0.070	<0.040	<1.0
T-MePFOSAA	<0.040	<0.70	0.19	<0.70	<0.050	<2.0	0.15	<0.070	<0.040	<1.0
L-EtPFOSAA	<0.040	<0.80	0.20	<0.70	<0.050	<2.0	0.12	<0.080	<0.050	<1.0
T-EtPFOSAA	<0.040	<0.80	0.22	<0.70	<0.050	<2.0	0.13	<0.080	<0.050	<1.0
6:2diPAP	-	<0.80	-	<0.90	<2.0	<3.0	-	-	<0.040	<4.0
6:2/8:2diPAP	-	<0.80	-	<0.90	<0.10	<3.0	-	-	<0.040	<4.0
8:2diPAP	-	<1.0	-	-	-	<3.0	-	<0.20	<0.020	<4.0
sum of linear PFAS	**0.46**	**9.0**	**3.1**	**35**	**2.0**	**9.0**	**7.0**	**27**	**0.32**	**13**
sum of total PFAS	**0.46**	**14**	**3.5**	**37**	**2.2**	**11**	**7.8**	**28**	**0.32**	**13**

5.11.3 Results NTA PFAS ZD01

5.11.3.1 Confidence level 1 - target PFAS results in ZD01

Table 71 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.
The only PFAS class found was the perfluoroalkyl carboxylic acids (PFCAs) in wet deposition (R11891).

Table 71. Compounds detected via NTA PFAS analysis in ZD01 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_ 240216-0008		R11559_ 240522-0069		R11664_ 240612-0043		R11891_ 240819-0150		R11960_ 240909-0017	
	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W
Perfluoroalkyl carboxylic acids (PFCA)	<1	<13	<1	<11	<1	<31	<1	15	<1	<20

5.11.3.2 Confidence level 2 – 4 – PFAS results in ZD01

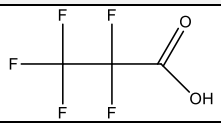
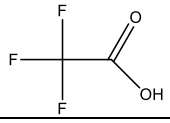
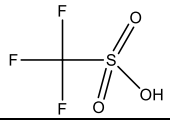
Table 72 presents the PFAS classes with values above the PFAS eq. LOQ across AL09 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C-m/C plots, and a mass list match, with supporting fragmentation data and spectra library match. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 72. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in ZD01. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_ 240216-0008		R11559_ 240522-0069		R11664_ 240612-0043		R11891_ 240819-0150		R11960_ 240909-0017	
	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W
Perfluoroalkyl carboxylic acids (PFCA)	<1	46	<1	<11	<1	<31	<1	37	<1	<20
Perfluoroalkyl sulfonic acids (PFSAs)	<1	<13	<1	<11	<1	<31	481	<2	<1	<20

The main PFAS class found was the perfluoroalkyl sulfonic acids (PFSAs), represented by TFMS, in dry deposition (R11891). The perfluoroalkyl carboxylic acids (PFCAs) were also found, represented by PFPrA in the wet deposition (R11112) and TFA in the wet deposition (R11891) (Table 73).

Table 73. Examples of potential candidate of PFCAs found in the site ZD01.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
PFCAs	R11112	PFPrA	$C_3HF_5O_2$		162.98283	1.109
PFCAs	R11891	TFA	$C_2HF_3O_2$		112.98622	0.895
PFSAs	R11891	TFMS	CHF_3O_3S		148.95216	0.838

5.11.3.3 Confidence level 5 - unknown PFAS results in ZD01

Table 74 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 74. Unknown compounds (CL5) detected via NTA PFAS analysis in ZD01.

PFAS Classes (PFAS equivalent)	R11112_ 240216-0008		R11559_ 240522-0069		R11664_ 240612-0043		R11891_ 240819-0150		R11960_ 240909-0017	
	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W	DEP_ D	DEP_ W
Unknown PFAS cpd (KMD filter CF2)	146	223	100	314	244	359	14	18	38	387

The amount of unknown compounds was slightly lower for the fourth sampling period evaluated (R11891), and always higher in the wet deposition than in the dry deposition. A future analysis could focus on tracking unknown compounds over time (see in 5.9.3.4). Such a temporal monitoring approach would be particularly valuable for prioritizing features for compound identification. As a potential direction, a database could be prepared (example in Table 60), containing key characteristics, such as accurate mass (m/z), intensity (PFAS eq.), and retention time (RT) across multiple sampling events. This would enable the identification of persistent or recurring unknowns and support more targeted follow-up efforts (also see discussion in Section 6.5.).

5.11.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – ZD01

Table 75 presents the total results for ZD01 site. The target PFAS classes (CL1) were found only in the wet deposition (R11891) and represented 21%. The unknown identified PFAS classes (CL 2 - 4) represented 17%, 97% and 53% in wet deposition (R11112), dry and wet deposition (R11891), respectively. The remaining unknown fraction (CL5) represented more than 90% in seven out of the ten samples analyzed.

Table 75. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in ZD01. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R11112_ 240216-0008		R11559_ 240522-0069		R11664_ 240612-0043		R11891_ 240819-0150		R11960_ 240909-0017	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
Results Target PFAS classes (CL1)	<1	<13	<1	<11	<1	<31	<1	15	<1	<20
Results Unknown identified PFAS classes (CL2-4)	<1	46	<1	<11	<1	<31	481	37	<1	<20
Results Unknown PFAS classes (CL5)	146	223	100	314	244	359	14	18	38	387

PFAS Classes (PFAS equivalent)	R11112_ 240216-0008		R11559_ 240522-0069		R11664_ 240612-0043		R11891_ 240819-0150		R11960_ 240909-0017	
	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W	DEP_D	DEP_W
% Target PFAS classes (CL1)	0%	0%	0%	0%	0%	0%	0%	21%	0%	0%
% Unknown identified PFAS classes (CL2-4)	0%	17%	0%	0%	0%	0%	97%	53%	0%	0%
% Unknown PFAS classes (CL5)	100 %	83%	100 %	100%	100 %	100%	3%	26%	100 %	100%

5.12 Site RL19

5.12.1 Samples

Table 76. Overview of sample types, sample codes and sampling period for samples from site RL19.

SAMPLE TYPE	ROUND	SAMPLE CODE (REQUEST)	SAMPLING PERIOD
DEP	2	241106-0006 (D + W) (R12248)	19/09 - 17/10/2024
DEP	2	241203-0047 (D + W) (R12356)	17/10 - 14/11/2024

5.12.2 Results Target PFAS RL19

Table 77. Results target PFAS (according to WAC/IV/A/025) in ng/sample for samples from site RL19. Values marked as "-" could not be reported due to low recovery of the internal standard. The sum of PFAS is calculated using the lower-bound principle.

COMPOUND	241106-0006 (D) (R11248)	241106-0006 (W) (R11248)	241203-0047 (D) (R12356)	241203-0047 (W) (R12356)
PFBA	< 0.30	3.9	< 0.20	9.3
PFPeA	< 0.20	0.98	0.21	< 1.0
PFHxA	< 0.40	2.5	< 0.30	< 2.0
PFHpA	< 0.10	1.0	< 0.20	< 1.0
L-PFOA	0.28	1.5	0.27	1.7
T-PFOA	0.28	1.6	0.40	2.6
PFDA	0.21	< 0.80	< 0.50	< 1.0
PFHxDA	< 0.20	< 1.0	-	< 4.0
PFODA	< 0.20	< 1.0	-	< 4.0
PFBS	< 0.070	0.86	< 0.20	< 0.70
T-PFHxS	< 0.060	< 0.30	0.19	< 1.0
L-PFOS	0.17	< 2.0	1.3	< 1.0
T-PFOS	0.25	< 2.0	2.3	< 1.0
MePFBSA	-	< 0.90	< 0.50	< 2.0
L-MePFOSA	-	< 0.90	< 0.50	< 2.0
T-MePFOSA	-	< 0.90	< 0.50	< 2.0
L-EtPFOSA	-	< 1.0	-	< 2.0
T-EtPFOSA	-	< 1.0	-	< 2.0
ADONA	0.36	0.39	< 0.080	< 0.70
PFECHS	0.084	< 0.40	< 0.20	< 1.0
sum of linear	1.1	11	1.8	11
sum of total PFAS	1.2	11	3.1	12

5.12.3 Results NTA PFAS RL19

5.12.3.1 Confidence level 1 - target PFAS results in RL19

Table 78 presents the compounds listed in WAC/IV/A/025, for which reference standards were available (complete list in Table 3), that were also detected through NTA PFAS analysis.

The only PFAS class found was the x:2 perfluoroalkyl sulfonic acids (x:2FTS) in the wet phase of deposition (R12248).

Table 78. Compounds detected via NTA PFAS analysis in RL19 for which a reference standard was available (target PFAS). The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R12248_241106-0006		R12356_241203-0047	
	DEP_D	DEP_W	DEP_D	DEP_W
x:2 Fluorotelomer sulfonic acids (x:2FTS)	<1	9	<1	<12

5.12.3.2 Confidence level 2 – 4 – PFAS results in RL19

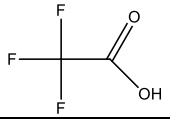
Table 79 presents the PFAS classes with values above the PFAS eq. LOQ across RL19 samples. These PFAS classes were assigned a confidence level between 2 and 4, meaning they were identified based on homologous series patterns, mass defect, md/C–m/C plots, and a mass list match, with supporting fragmentation data and spectra library match. These components are not included in the target method but may belong to the same chemical classes. In other words, they are PFAS compounds not listed in WAC/IV/A/025, but for which we may have the reference standard, and which are potentially structurally related.

Table 79. Unknown compounds with identified PFAS class (CL2 to CL4) detected via NTA PFAS analysis in RL19. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R12248_241106-0006		R12356_241203-0047	
	DEP_D	DEP_W	DEP_D	DEP_W
Perfluoroalkyl carboxylic acids (PFCA)	<1	73	<1	<12

The only identified PFAS class found was the perfluoroalkyl carboxylic acids (PFCAs), represented by TFA, in the wet deposition (R12248) (Table 73).

Table 80. Examples of potential candidates of PFCAs found in the site RL19.

Class	Sample	Possible compound	Formula	Possible structure	*m/z*	RT [min]
PFCAs	R12248	TFA	$C_2HF_3O_2$		112.98614	0.83

5.12.3.3 Confidence level 5 - unknown PFAS results in RL19

Table 81 presents the unknown potential PFAS compounds. It should be noted that these compounds could not be assigned to any known PFAS class – for example, due to the absence of homologous series – and there is a possibility that some represent false-positive unknown PFAS. Classification was based on PFAS filtering criteria, including accurate mass, mass defect, and the md/C vs. m/C plot. The confidence level is 5, based solely on accurate mass.

Table 81. Unknown compounds (CL5) detected via NTA PFAS analysis in RL19.

PFAS Classes (PFAS equivalent)	R12248_241106-0006		R12356_241203-0047	
	DEP_D	DEP_W	DEP_D	DEP_W
Unknown PFAS cpd (KMD filter CF2)	91	151	171	94

The amount of unknown compounds was higher in the wet deposition than in the dry deposition, in the first sampling period analyzed, while the opposite was observed for the second sampling period, with overall low PFAS eq. levels. A similar temporal monitoring approach as described in 5.9.3.4 could be applied to this location, ideally in a higher temporal resolution, in order to identify relevant features for further investigation (see discussion in Section 6.5.).

5.12.3.4 Overview PFAS results (CL 1 to CL 5) in NTA – RL19

Table 82 presents the total results for RL19 site. The target PFAS classes (CL1) represented only 3.7% of the total PFAS amount detected, in wet deposition (R12248). In the same sample, the unknown identified PFAS classes (CL 2 - 4) represented 31%. For the other three samples, the total amount of PFAS found represented unknown PFAS classes.

Table 82. Total PFAS detected, subdivided into target PFAS classes (CL1), unknown identified PFAS classes (CL 2 to 4) and unknown PFAS classes (CL 5), as identified via NTA PFAS analysis in RL19. The values below LOQ are indicated in green.

PFAS Classes (PFAS equivalent)	R12248_241106-0006		R12356_241203-0047	
	DEP_D	DEP_W	DEP_D	DEP_W
Results Target PFAS classes (CL1)	<1	8.6	<1	<12
Results Unknown identified PFAS classes (CL2-4)	<1	73	<1	<12
Results Unknown PFAS classes (CL5)	91	151	171	94

PFAS Classes (PFAS equivalent)	R12248_241106-0006		R12356_241203-0047	
	DEP_D	DEP_W	DEP_D	DEP_W
% Target PFAS classes (CL1)	0%	3.7%	0%	0%
% Unknown identified PFAS classes (CL2-4)	0%	31%	0%	0%
% Unknown PFAS classes (CL5)	100%	65%	100%	100%

6 DISCUSSION

6.1 Overview of NTA-PFAS results by confidence levels

As a result of the PFAS-NTA approach, new compounds could be identified within known PFAS classes (CL 2-4), while others were highlighted as potential PFAS compounds requiring further investigation (CL 5). An overview of the results for all samples is displayed in Table 83 (in PFAS eq.) and Table 84 (in relative PFAS eq. (%)).

It should be noted that, in several cases, PFAS detected at low concentrations in target analyses were not detected in the corresponding NTA results (i.e., CL 1 compounds). This discrepancy is likely related to the higher detection limits and lower sensitivity of the HRMS-based NTA workflow compared to targeted quantification methods. Consequently, NTA results reported as below detection limit should be interpreted with caution, as they do not necessarily indicate the absence of these compounds but rather reflect inherent higher detection limits in the applied NTA-PFAS workflow.

Table 83. Overview of NTA-PFAS results expressed in PFAS equivalents for all samples analyzed in this study, categorized by confidence level of identification, with averages, standard deviations, and minimum and maximum values also reported

Site	Request and sample code	Sample type	Target PFAS (CL1) (PFAS eq.)	Unknown identified PFAS (CL2-4) (PFAS eq.)	Unknown PFAS (CL5) (PFAS eq.)
ZD08	**R10135_230608-0020**	**PUF**	2032	6911	1779
ZD08	**R10268_230712-0005**	**DEP_D**	438	31	50
ZD08	**R10268_230712-0005**	**DEP_W**	3153	65	<6
ZD08	**R10171_230613-0005**	**DEP_D**	1114	93	1193
ZD11	**R11341_240409-0002**	**TSP**	294	39	130
ZD11	**R11380_240415-0238**	**PUF**	1773	763	1283
ZD11	**R11509_240514-0037**	**PUF**	2036	553	2121
ZD11	**R11541_240521-0158**	**TSP**	257	141	157
ZD11	**R11544_240521-0169**	**PUF**	3471	700	1392
N016	**R11558_240522-0059**	**TSP**	<2	12	228
N016	**R11664_240612-0041**	**DEP_D**	<1	<1	38
N016	**R11664_240612-0041**	**DEP_W**	<40	<40	815
KK01	**R11409_240419-0044**	**TSP**	<2	9	58
KK01	**R11411_240419-0058**	**DEP_D**	21	762	62
KK01	**R11411_240419-0058**	**DEP_W**	<2	<2	82
ZD17	**R11451_240426-0022**	**TSP**	961	112	64
RL18	**R11810_240718-0001**	**TSP**	<2	160	114
RL18	**R11891_240819-0149**	**DEP_D**	3.3	61	45
RS03	**R11837_240805-0016**	**DEP_D**	<1	<1	41
RS03	**R11837_240805-0016**	**DEP_W**	<3	<3	162
R801	**R11958_240909-0006**	**TSP**	<2	133	537

R801	**R11959_240909-0011**	**DEP_D**	<1	<1	2
R801	**R11959_240909-0011**	**DEP_W**	<5	<5	82
AL09	**R11112_240216-0005**	**DEP_D**	<1	2.7	35
AL09	**R11112_240216-0005**	**DEP_W**	<18	<18	1899
AL09	**R11559_240522-0065**	**DEP_D**	<1	19	93
AL09	**R11559_240522-0065**	**DEP_W**	<13	147	184
AL09	**R11891_240819-0146**	**DEP_D**	<1	<1	18
AL09	**R11891_240819-0146**	**DEP_W**	<6	<6	253
AL09	**R11960_240909-0013**	**DEP_D**	<1	7.1	556
AL09	**R11960_240909-0013**	**DEP_W**	23	<15	477
AL10	**R11112_240216-0006**	**DEP_D**	1.7	<1	21
AL10	**R11112_240216-0006**	**DEP_W**	<14	41	4008
AL10	**R11664_240612-0040**	**DEP_D**	<1	<1	12
AL10	**R11664_240612-0040**	**DEP_W**	37	700	493
AL10	**R11891_240819-0147**	**DEP_D**	<1	22	1077
AL10	**R11891_240819-0147**	**DEP_W**	<2	<2	10
ZD01	**R11112_240216-0008**	**DEP_D**	<1	<1	146
ZD01	**R11112_240216-0008**	**DEP_W**	<13	46	223
ZD01	**R11559_240522-0069**	**DEP_D**	<1	<1	100
ZD01	**R11559_240522-0069**	**DEP_W**	<11	<11	314
ZD01	**R11664_240612-0043**	**DEP_D**	<1	<1	244
ZD01	**R11664_240612-0043**	**DEP_W**	<31	<31	359
ZD01	**R11891_240819-0150**	**DEP_D**	<1	481	14
ZD01	**R11891_240819-0150**	**DEP_W**	15	37	18
ZD01	**R11960_240909-0017**	**DEP_D**	<1	<1	38
ZD01	**R11960_240909-0017**	**DEP_W**	<20	<20	387
RL19	**R12248_241106-0006**	**DEP_D**	<1	<1	91
RL19	**R12248_241106-0006**	**DEP_W**	8.6	73	151
RL19	**R12356_241203-0047**	**DEP_D**	<1	<1	171
RL19	**R12356_241203-0047**	**DEP_W**	<12	<12	94
		Average all	920	449	438
		STD all	1126	1293	728
		Max all	3471	6911	4008
		Min all	2	3	2
		Average DEP_D	316	164	193
		Average DEP_W	647	158	556
		Average TSP	504	86	184
		Average PUF	2328	2232	1644

Table 84. Overview of NTA-PFAS results expressed in relative PFAS equivalents (%) for all samples analyzed in this study, categorized by confidence level of identification, with averages, standard deviations, and minimum and maximum values also reported

Site	Request and sample code	Sample type	Target PFAS (CL1) (%)	Unknown identified PFAS (CL2-4) (%)	Unknown PFAS (CL5) (%)
ZD08	**R10135_230608-0020**	**PUF**	19%	64%	17%
ZD08	**R10268_230712-0005**	**DEP_D**	84%	6%	10%
ZD08	**R10268_230712-0005**	**DEP_W**	98%	2%	0%
ZD08	**R10171_230613-0005**	**DEP_D**	46%	4%	50%
ZD11	**R11341_240409-0002**	**TSP**	64%	8%	28%
ZD11	**R11380_240415-0238**	**PUF**	46%	20%	34%
ZD11	**R11509_240514-0037**	**PUF**	43%	12%	45%
ZD11	**R11541_240521-0158**	**TSP**	46%	25%	28%
ZD11	**R11544_240521-0169**	**PUF**	62%	13%	25%
N016	**R11558_240522-0059**	**TSP**	0%	5%	95%
N016	**R11664_240612-0041**	**DEP_D**	0%	0%	100%
N016	**R11664_240612-0041**	**DEP_W**	0%	0%	100%
KK01	**R11409_240419-0044**	**TSP**	0%	13%	87%
KK01	**R11411_240419-0058**	**DEP_D**	2.5%	90%	7%
KK01	**R11411_240419-0058**	**DEP_W**	0%	0%	100%
ZD17	**R11451_240426-0022**	**TSP**	85%	10%	5.6%
RL18	**R11810_240718-0001**	**TSP**	0%	58%	42%
RL18	**R11891_240819-0149**	**DEP_D**	3.0%	56%	41%
RS03	**R11837_240805-0016**	**DEP_D**	0%	0%	100%
RS03	**R11837_240805-0016**	**DEP_W**	0%	0%	100%
R801	**R11958_240909-0006**	**TSP**	0%	20%	80%
R801	**R11959_240909-0011**	**DEP_D**	0%	0%	100%
R801	**R11959_240909-0011**	**DEP_W**	0%	0%	100%
AL09	**R11112_240216-0005**	**DEP_D**	0%	7%	93%
AL09	**R11112_240216-0005**	**DEP_W**	0%	0%	100%
AL09	**R11559_240522-0065**	**DEP_D**	0%	17%	83%
AL09	**R11559_240522-0065**	**DEP_W**	0%	44%	56%
AL09	**R11891_240819-0146**	**DEP_D**	0%	0%	100%
AL09	**R11891_240819-0146**	**DEP_W**	0%	0%	100%
AL09	**R11960_240909-0013**	**DEP_D**	0%	1%	99%
AL09	**R11960_240909-0013**	**DEP_W**	4.7%	0%	95%
AL10	**R11112_240216-0006**	**DEP_D**	8%	0%	92%
AL10	**R11112_240216-0006**	**DEP_W**	0%	1%	99%
AL10	**R11664_240612-0040**	**DEP_D**	0%	0%	100%
AL10	**R11664_240612-0040**	**DEP_W**	3%	57%	40%
AL10	**R11891_240819-0147**	**DEP_D**	0%	2%	98%
AL10	**R11891_240819-0147**	**DEP_W**	0%	0%	100%

ZD01	**R11112_240216-0008**	**DEP_D**	0%	0%	100%
ZD01	**R11112_240216-0008**	**DEP_W**	0%	17%	83%
ZD01	**R11559_240522-0069**	**DEP_D**	0%	0%	100%
ZD01	**R11559_240522-0069**	**DEP_W**	0%	0%	100%
ZD01	**R11664_240612-0043**	**DEP_D**	0%	0%	100%
ZD01	**R11664_240612-0043**	**DEP_W**	0%	0%	100%
ZD01	**R11891_240819-0150**	**DEP_D**	0%	97%	3%
ZD01	**R11891_240819-0150**	**DEP_W**	21%	53%	26%
ZD01	**R11960_240909-0017**	**DEP_D**	0%	0%	100%
ZD01	**R11960_240909-0017**	**DEP_W**	0%	0%	100%
RL19	**R12248_241106-0006**	**DEP_D**	0%	0%	100%
RL19	**R12248_241106-0006**	**DEP_W**	3.7%	31%	65%
RL19	**R12356_241203-0047**	**DEP_D**	0%	0%	100%
RL19	**R12356_241203-0047**	**DEP_W**	0%	0%	100%
		Average all	13%	14%	73%
		STD all	25%	24%	35%
		Max all	98%	97%	100%
		Min all	0%	0%	0%
		Average DEP_D	6.8%	13%	80%
		Average DEP_W	6.9%	11%	82%
		Average TSP	28%	20%	52%
		Average PUF	43%	27%	30%

Across all analyzed samples (n = 51), on average 13% (± 25%) of detected features were attributed to target PFAS classes (CL 1), 14% (± 24%) to identified but previously untargeted PFAS classes (CL 2–4), and 73% (± 35%) to unknown PFAS classes (CL 5) (Table 84). In some samples and locations where no PFAS were previously detected using targeted methods, the unknown fraction (CL 5) accounted for the entirety of the PFAS-related signal. This distribution underscores the critical role of NTA in capturing the full spectrum of PFAS present in environmental samples, particularly in identifying compounds beyond the scope of traditional target-based approaches.

With the integration of NTA-PFAS data, the PFAS fingerprint of samples can be significantly expanded and refined, offering a more robust basis for forensic and source-tracking applications. To illustrate this, two media (i.e., PUF and filter) from ZD11 location were selected for comparison between PFAS fingerprints obtained via the adapted WAC/IV/A/025 target method and those generated through the NTA-PFAS workflow (Figure 11).

At location ZD11, both methods - target analysis (Figure 11A) and non-target screening (Figure 11B) - initially produced similar PFAS fingerprints when restricted to the subset of compounds included in the WAC/IV/A/025 scope. This consistency was observed for both the PUF (+ XAD) (Figure 11, outer circle) and TSP filter matrices (Figure 11, inner circle). The differences in PFAS profiles between TSP (filter) and air (PUF) samples were anticipated and reflect the distinct partitioning behavior of PFAS across particulate and gas phases. Slight deviations in profiles are expected and were observed, as this relative distribution is based on PFAS equivalents, a semi-quantitative approach, rather than direct quantification (described in more detail in Section 4.4.)

However, when additional compounds classified under confidence levels CL 2 to CL 5 were included (Figure 11C) the PFAS fingerprint diverged notably from the one obtained via target analysis (Figure 11A). Specifically, Figure 11C presents the PFAS composition in samples incorporating all identified and unidentified compounds (CL 2–5).

For example, PUF samples were dominated by the N-Et-FASAs class, which accounted for 59% of the total PFAS signal in the target analysis (outer circle, Figure 11A). In contrast, this proportion decreased to 37% when considering the NTA dataset (outer circle, Figure 11C). For TSP samples, the main class was PFSAs, with similar proportions in both the target and NTA analyses, 55% and 59%, respectively (inner circles, Figure 11A and 10C). However, the inclusion of NTA results significantly altered the overall PFAS class distribution, particularly through the emergence of a substantial unknown fraction, which accounted for 29% of the PFAS signal in this matrix. This example underscores the added value of NTA in capturing a broader and potentially more representative chemical fingerprint, thereby improving environmental interpretation and enabling more informed regulatory and forensic assessments.

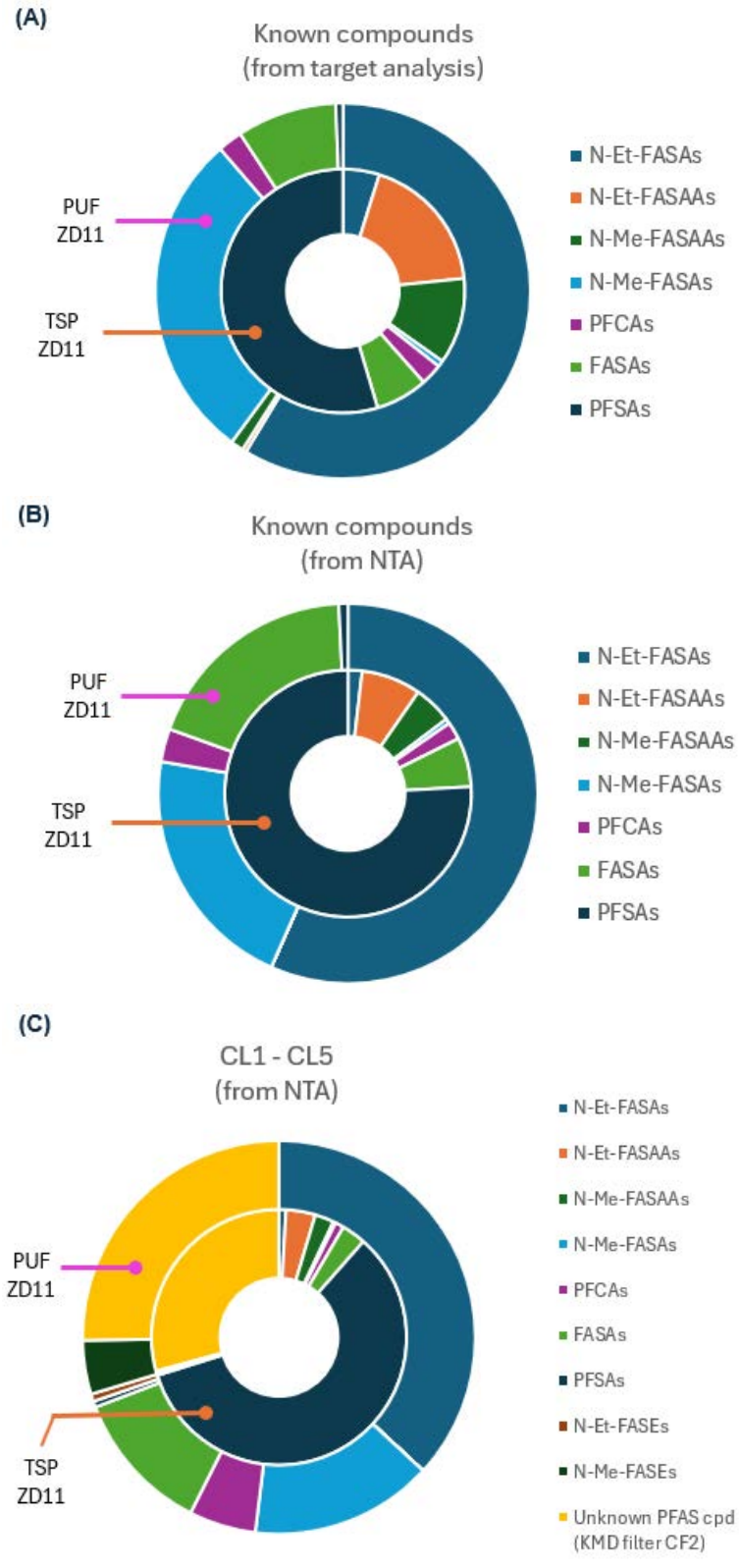


Figure 11. Relative PFAS class distribution at location ZD11 for TSP (inner circle) and PUF (outer circle) samples. Panel (A) compares the target approach (left, based on WAC/IV/A/025) with the non-target approach (right). Panel (B) shows results from the non-target approach, including all compounds with confidence levels CL 1–5 (left) and only known unknowns (CL 1–4) (right). Results from the non-target analysis are based in PFAS equivalents.

6.2 New PFAS class: FASEs and fungicides

As an outcome of the NTA-PFAS study, several new PFAS classes were identified with Confidence Levels (CL) 2 to 4. One notable group is the perfluoroalkyl sulfonamide ethanols (FASEs), which are considered neutral PFAS and exhibit higher volatility. Traditionally, these compounds are not detected using conventional reversed-phase LC-MS methods, and a GC-MS approach is generally recommended for their analysis.

However, results from our interlaboratory comparison trial, conducted within the framework of the NORMAN network, demonstrated that FASEs (i.e., MePFBSE (CAS 34454-97-2), MeFOSE (CAS 24448-09-7) and EtFOSE (CAS 1691-99-2)) can be detected via acetate adduct formation in the LC-MS ionization source. Based on these findings, compounds from this class were added to our PFAS suspect list and incorporated into our spectral library, and subsequently included in this NTA-PFAS study. These compounds were detected mainly in PUFs (ZD11 and ZD08 locations) and in TSP (ZD17).

In addition to FASEs, perfluoroalkyl fluorotelomer alcohols (FTOHs) are also considered relevant in air samples, especially due to their ubiquitous presence in indoor environments (Morales-McDevitt et al., 2021; Wang et al., 2022). Further research is needed to integrate this class into both GC-based non-target screening (NTA) and targeted analytical workflows. For the latter, ongoing efforts under the D.O. reference task have led to the development of a new GC-MS method for quantifying 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH in water samples (WAC/IV/A/032 – Bepaling van neutrale PFAS in water met GC-MS, currently under development). Additionally, two compounds from the FASEs group, MeFOSE and EtFOSE, are included within the scope of method WAC/IV/A/032.

Given that FASEs are among the most frequently detected PFAS in air samples, along with FTOHs and FASAs (Wallace et al., 2024), and considering their successful detection using LC-based non-target screening, we recommend further research to develop a dedicated quantification and targeted method for FASEs in air matrices.

A second group of emerging interest includes fluorinated pesticides, which were detected only in TSP samples from several locations (N016, RL18, and R801). Their identification in air samples reinforces concerns about their relevance as atmospheric PFAS contributors. While these compounds, fluazinam (CAS 79622-59-6) and flutolanil (CAS 66332-96-5) are traditionally regulated under pesticide legislation, the presence of trifluoromethyl groups bring them into the scope of PFAS (Wang et al., 2021) (see discussion in 5.3.3.2). It is also recommended to purchase the reference standard material and proceed with the identification to confidence level 1 (Schymanski et al., 2014) and the quantification with external calibration curve.

Their detection through NTA highlights the need to integrate such substances into PFAS monitoring frameworks and suspect lists, with a focus on understanding their environmental behavior, potential transformation into ultrashort-chain PFAS (e.g. TFA), and implications for future policy development.

6.3 Ultra-short chain PFAS

The detection of ultra-short chain (USC) PFAS – specifically trifluoroacetic acid (TFA), perfluoropropanoic acid (PFPrA), and trifluoromethanesulfonic acid (TFMS) – highlighted the relevance of these highly mobile compounds in air samples. These substances were primarily detected in the PUF matrix and in deposition samples: TFA and PFPrA were more prominent in wet deposition, while TFMS appeared in dry deposition (ZD01). Notably, they were observed at several locations, including ZD08, ZD11, ZD01, AL09, AL10, and KK01.

It is well known that the reversed-phase liquid chromatography (LC) approach used in this study and aligned with the WAC/IV/A/025 method, is not ideally suited for detecting such small, highly polar compounds. For this reason, dedicated methods (e.g., WAC/IV/A/026 and WAC/IV/A/035) have been developed for target quantification of USC PFAS in water, mainly by optimizing chromatographic retention through alternative LC conditions.

Given this limitation, it is important to acknowledge that false negatives for USC PFAS are likely under the current analytical approach. This is primarily due to the data processing filters applied during peak selection, which prioritize chromatographic features that exhibit Gaussian-like shapes. Since USC PFAS typically elute at the very beginning of the LC run, co-eluting with salts and other matrix constituents, their peak shapes are often asymmetric, reducing the likelihood that they are flagged by the automated screening algorithm. As a result, these compounds may be underrepresented or missed entirely in the current dataset.

This issue is even more pronounced in samples with high matrix load, where early-eluting interferences are more intense and likely to mask or distort the signal of USC PFAS. Consequently, the detection of these compounds in the current study should be interpreted as conservative, and the true occurrence may be underestimated.

6.4 Expanding the chemical space coverage

Despite recent advances in NTA for PFAS, incomplete coverage of the PFAS chemical space remains a major challenge that may lead to false negatives and underestimation of total PFAS burden in environmental samples. This limitation arises from both methodological and instrumental constraints that influence which compounds are detected and identified. Each stage of the NTA workflow, ranging from sampling, extraction, chromatographic separation, and ionization, to data acquisition and processing, introduces selectivity toward certain compound classes. As shown by Megson et al., 2025, these limitations mean that even widely used techniques such as LC-HRMS, capture only a fraction of the chemical space. Their review of 76 NTA studies showed that: 51% used only LC-HRMS, 32% used only GC-HRMS, 16% used both LC- and GC-HRMS, and only 1% used direct injection (Figure 12).

Newton et al., 2025 highlight the critical role of gas chromatography-mass spectrometry (GC-MS) in extending chemical space coverage of PFAS. Their study underscores that while PFAS NTA has historically focused on LC-MS, GC-MS offers complementary detection capabilities, particularly for:

- Volatile and semivolatile PFAS,
- Neutral compounds,
- And transformation products not captured by LC-HRMS.

In fact, Newton et al. show that less than 10% of the ~12,000 known PFAS are predicted to be amenable to LC-MS under typical conditions. This statistic illustrates the large data gap in PFAS monitoring that GC-MS is well-suited to address. GC-NTA is especially relevant for emissions from fluorochemical manufacturing, thermal treatment and incineration of PFAS-containing materials, consumer product surveillance, and atmospheric monitoring, where volatile PFAS and products of incomplete combustion (PICs/PIDs) are of concern.

A comprehensive view of PFAS contamination requires multidimensional analytical strategies. The limitations of LC-HRMS, particularly for polar, and volatile compounds, necessitate expanding the current methodological toolbox. While NTA using LC-HRMS remains a powerful tool, it is clear that no single platform can cover the full spectrum of PFAS in environmental and industrial samples.

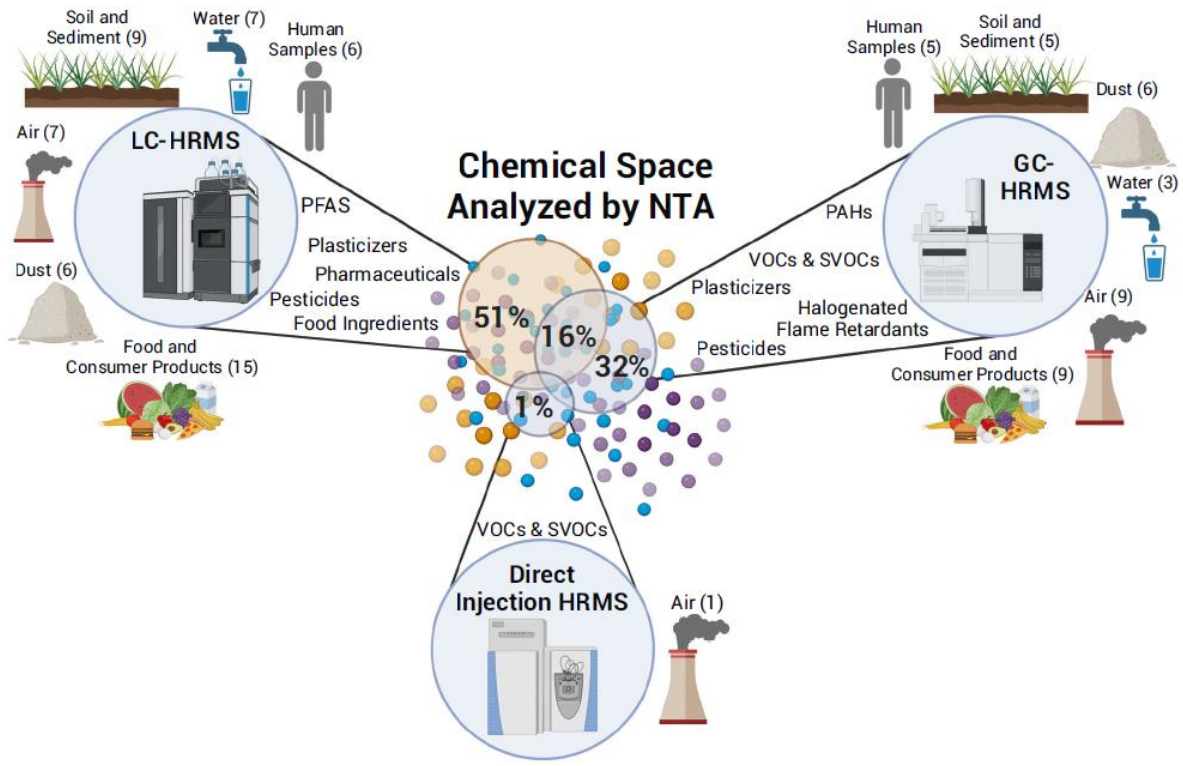


Figure 12. Schematic diagram of the chemical space analyzed by HRMS using NTA. The number and percentage of studies using liquid chromatography (LC), gas chromatography (GC), or direct injection paired with high-resolution mass spectrometry (HRMS) are shown, including the types of chemicals that were detected and the media that have been characterized using each approach. Figure created with BioRender.com, obtained from Manz et al., 2023.

To address this, a coordinated investment strategy focusing on expanding the chemical space accessible through NTA is recommended. Specifically:

- LC-based NTA method optimization for:
    - Highly polar and early-eluting PFAS, such as ultra-short-chain compounds,
    - Development and implementation of alternative chromatographic approaches (e.g., HILIC, mixed-mode LC, or ion-exchange chromatography) to improve retention, separation, and detectability of polar PFAS.
- Advance GC-based NTA methods to:
    - Capture volatile, semivolatile, and neutral PFAS not amenable to LC-MS,
    - Support the characterization of emissions from PFAS manufacturing, waste incineration, and other high-temperature processes where volatile fluorinated byproducts are likely to occur,
    - Develop PFAS-specific spectral libraries with retention index data and reference materials for compounds currently lacking commercial standards.

6.5 Temporal monitoring and feature highlighting

It is important to emphasize that compounds classified under Confidence Level 5 (CL5) require further investigation to confirm their classification as PFAS. Although limited information is currently available for these compounds – typically just accurate mass, isotopic pattern, and retention time – the unknown fraction (CL5) may contain valuable signals that warrant additional exploration and potential inclusion in future monitoring campaigns.

To enhance the long-term utility of these findings, compiling the available features of CL5 compounds into a structured database is strongly recommended. This would enable follow-up assessments and targeted identification efforts as analytical capabilities evolve.

In order to prioritize which unknowns should be investigated further, a strategy based on temporal monitoring with increased sampling frequency was proposed (see Section 5.9.3.4). This approach helps to identify recurring or trend-relevant features, e.g. m/z 294.0655, which may indicate environmentally significant or emerging compounds (*Figure 13*). A similar approach was recently highlighted by Armin et al., 2025, where compounds in the influent originating from a particular wastewater treatment plant were prioritized and their intensity profiles were monitored (Armin et al., 2025). As emphasized in that study, routine downstream monitoring combined with regular trend analysis can support the identification and prioritization of new, emerging compounds originating from high-risk sources.

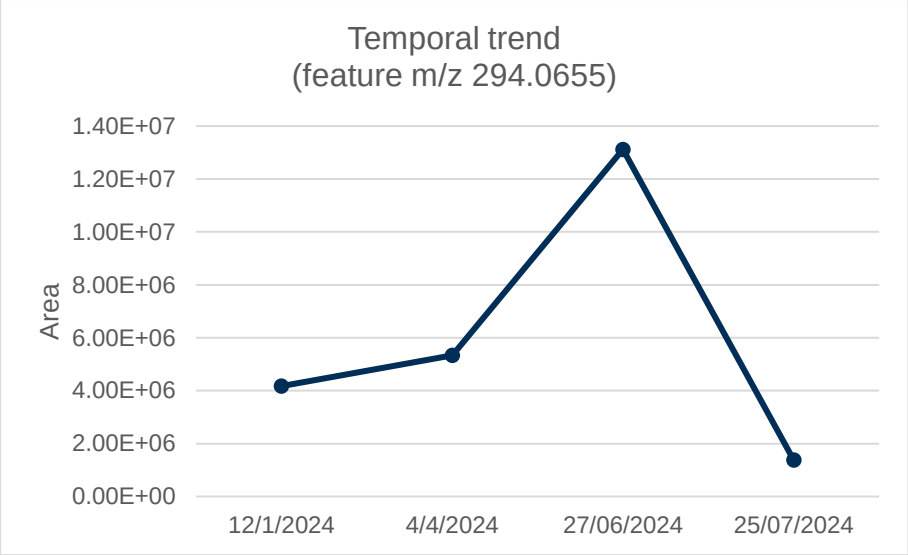


Figure 13. Monitoring of feature 294.0655 over time, in wet deposition in location AL09.

When deeper structural insights are warranted, due to toxicological relevance or elevated concentrations, orthogonal techniques such as ion mobility spectrometry, nuclear magnetic resonance (NMR), or high-resolution tandem MS with authentic standards may be applied. However, such approaches can be resource-intensive and limited by the availability of reference materials. In the context of PFAS, the complexity of fluorinated compound chemistries, combined with limited standard availability, has led the community to propose PFAS-specific adaptations of the five-level identification confidence scheme (Charbonnet et al., 2022). These adaptations provide more detailed classification criteria, supporting future efforts to track, prioritize, and potentially identify unknown PFAS-related features currently captured under CL5.

7 CONCLUSION AND RECOMMENDATIONS

This study demonstrates the **added value of non-target analysis (NTA)** as a complementary approach to conventional target PFAS monitoring methods **in better understanding the total (ionizable) PFAS present in air samples**. While existing regulatory frameworks in Flanders currently rely on validated, target-based methodologies that cover only a limited number of known PFAS compounds, NTA enables the detection of a broader spectrum of substances, including unknowns and emerging compounds that would otherwise remain undetected.

The results of 51 air samples revealed that, on average, over 80%, 52% and 30% of the PFAS-related signal corresponded to unidentified compounds (Confidence Level 5), for deposition, TSP and PUF matrices, respectively. On average, 13%, 20% and 27% are assigned to identified PFAS classes in DEP, TSP, and PUF, respectively, while 7%, 28%, and 43% were attributed to known target PFAS classes. These findings indicate that **conventional approaches significantly underestimate the full PFAS burden in air, and that NTA can help fill this gap by offering a more comprehensive chemical**

fingerprint. This proved to be particularly valuable for sites where no PFAS were previously detected using target methods. In some case all PFAS found were unknown compounds discovered by NTA.

Several notable outcomes emerged from the NTA-PFAS workflow. **New classes of PFAS, such as perfluoroalkyl sulfonamide ethanols (PFASEs) and fluorinated pesticides, were identified in ambient air for the first time within this monitoring context**. Their discovery underscores the dynamic and evolving nature of PFAS occurrence and supports the future inclusion of such compounds in suspect lists, regulation and screening programs. Likewise, the **presence of ultra-short chain PFAS**, despite the current analytical limitations, illustrates the need for further method development to ensure future monitoring of these highly mobile substances.

Temporal monitoring offers a promising strategy for compound prioritization and improving environmental assessments. However, such temporal monitoring approach needs coupling with systematic data collection, database structuring of unknown features, and development of extensive data processing tools. Recurring features, particularly those linked to emission sources, can then serve as early warning indicators and can guide risk mitigation strategies.

Considering these findings, **NTA can become an essential component of future PFAS monitoring and policy development in Flanders**. **Its integration into long-term surveillance programs will support the early identification of emerging contaminants, enhance source tracking and forensic analyses, and strengthen the scientific basis for regulatory decision-making**.

The central question underlying this study is whether the current target scope used in regulatory monitoring provides a sufficiently safe proxy for the actual PFAS burden - and, by extension, whether it adequately reflects potential health risks. Although direct toxicological assessment of the PFAS fraction was beyond the scope of this project, our results clearly show that a large portion of PFAS-related signals remains unknown. This implies that **the present target list may not capture all compounds of toxicological relevance**, and that relying solely on target analysis may underestimate potential exposure.

From a **precautionary standpoint**, it is therefore not possible to conclude that the current target scope is “safe enough.” However, this study provides the first crucial step toward answering that question: expanding the chemical space and revealing the presence of numerous yet-unknown PFAS. Only by first identifying what is there can subsequent work assess their potential risks. This highlights **the need to couple NTA findings with effect-based analysis** and **toxicity prediction assays and computational tools**, enabling a more integrated chemical-biological risk framework.

Ultimately, the successful implementation of NTA in routine workflows depends on overcoming existing challenges related to data interpretation, normalization, and regulatory acceptance. Nevertheless, the insights gained in this study illustrate the technique’s transformative potential. Moving forward, **collaboration between government agencies, scientific institutions, and international networks** will be critical to scaling up NTA capacity, improving methodologies, and ensuring that the evolving landscape of PFAS contamination is comprehensively addressed.

The **following tailored recommendations** are based on the findings of this project:

- Incorporate NTA into PFAS research efforts to identify compounds missing from the target scope and possibly establish their abundance by semi-quantification.
- Promote harmonization and QA/QC alignment across laboratories performing PFAS-NTA to ensure comparability and reproducibility of results, which is essential for policy acceptance. In this regard, interlaboratory studies are particularly valuable.
- Systematically monitor unknown PFAS by compiling features data into a searchable database to enable future identification and regulatory tracking.
- Prioritize recurring unknown features through temporal monitoring to highlight compounds of potential concern and focus efforts on their identification. Use NTA results as early-warning evidence for potential PFAS emissions, supporting precautionary and risk-based regulatory actions.
- Develop targeted methods for relevant emerging PFAS classes (e.g., those that are abundant in the environment and/or associated with potential health risks), including:
    - PFASEs (e.g., MeFOSE, EtFOSE)
    - Fluorinated pesticides (potential precursors to ultrashort-chain PFAS)
- Incorporate ultra-short-chain PFAS, such as TFA, PFPrA, and TFMS, into future monitoring plans of air samples using better methods (e.g., WAC/IV/A/026 and WAC/IV/A/035), given current analytical limitations.
- Expand the chemical scope with the implementation of GC-based target and NTA approaches, which are particularly suited to detect volatile and semi-volatile PFAS that may not be accessible through LC-MS techniques. This includes compounds such as fluorotelomer alcohols, fluorinated ethers, or volatile degradation products that are likely to escape detection under standard LC conditions. The integration of GC-based methods will enable a more complete coverage of the PFAS chemical space and help capture previously overlooked emission profiles, especially in complex air matrices.
- Integrate effect-based and predictive toxicity tools into PFAS research efforts to help prioritize relevant unknowns detected by NTA, particularly those that are abundant and/or potentially associated with health risks. This will support the evaluation of whether the current target scope provides a sufficiently safe proxy for regulatory monitoring.

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