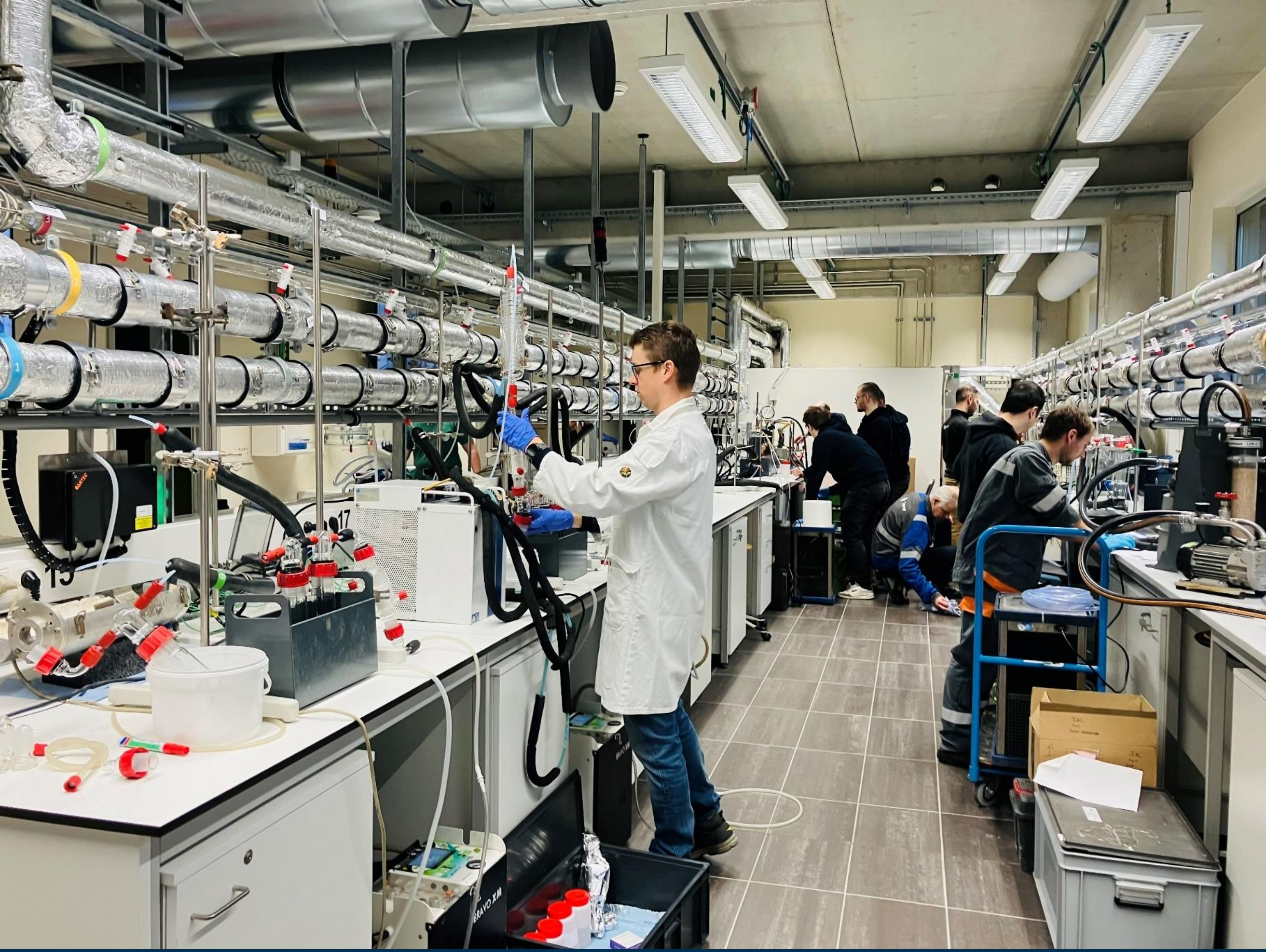

DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN A GUIDED GAS STREAM (LUC/VI/003)

INTERLAB COMPARISON (ILC) 2024

Study accomplished under the authority of Dep OMG
Reference: 2024/EI/R/3336
December 2024

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INTERLAB COMPARISON (ILC) 2024

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SUMMARY

This interlaboratory comparison (ILC) aimed at evaluating the different sampling train variants defined in the Flemish LUC/VI/003 compendium procedure (OTM-45, OTM-45 variant and cooled probe) and applied by the commercial labs in Flanders (SGS, Eurofins, Tauw). Two international labs (INERIS and ANECO) participated with respectively a US EPA OTM-45 and cooled probe variant procedure. The five labs participated with duplo sampling trains, using a sampling train variant of choice. The applied collection media in the sampling trains (filter, XAD2 and water) were spiked by VITO with 50 native (C4-18) PFAS compounds following the WAC/IV/A/0/25 scope and sampled preconditioned air (100°C and 10% RH) following the LUC/VI/003 procedure for sampling, sample collection and prep. While the Flemish labs followed the LUC/VI/003 procedure, INERIS and ANECO had specific deviations from the LUC/VI/003 procedure.

Reported results were evaluated for QA/QC's, internal standard and native spike recoveries (%) and observed measurement uncertainty (U) between the duplo measurements. The number of quantitative compounds (apparent train recovery 70-120% and measurement uncertainty (U) <50%) was considered as quantitative evaluation criterium.

In general, the applied collection media (filter, XAD2 and water) retained the spiked PFAS compounds rather well. Nevertheless, some spike transfer from the water fraction towards the secondary XAD2 was observed for MePFOSA, EtPFOSA and to a lesser extent for PFNA, PFDA, PFDoDA, PFOS and 6:2 FTS for multiple participating labs (VITO, LAB F1, LAB F2, LAB F3).

A varying number of internal standards (15-28) was considered by the participating labs, which generally recovered quite well within the different analytical fractions, except for 13C-MePFOSA,13C-EtPFOSA, 13C-MePFOSAA, 13C-EtPFOSAA, 13C2-6:2FTS and 13C2-8:2diPAP. The hardest analytical fraction (fraction with lowest IS recovery) varied from lab to lab (XAD2, cyclohexane and filter).

All participating labs showed decreasing recoveries with increasing alkyl chain length (both PFCA's and PFSA's) indicating the affinity of long-chain PFAS towards the sampling train glassware (§4.1.3) Recovery gains can be obtained by (i) thorough rinsing of the glassware during sampling collection (3 times MeOH, 3 times cyclohexane, including the sides of the glassware very thoroughly) and (ii) inclusion of more compound-specific internal standards.

The number of quantitative compounds with an apparent train recovery of 70-120% and a measurement uncertainty <50%, varied from 9 to 39 showing the **need for harmonized sampling and analytical procedures to accurately quantify PFAS in emissions and guarantee comparability and repeatability of the results.** The number of quantitative compounds resulting from the sampling train variants defined in the LUC/VI/003, varied between 8-24 (OTM-45 variant sampling train; LAB F1 - LAB F2), 35 (cooled probe variant sampling train; LAB F3) and 38 (OTM-45 sampling train; VITO).

This work is published in the peer-reviewed journal Chemosphere as Hofman et al. (2025):
Hofman, J., Baeyens, B., Aerts, W., Jacobs, G., de Carvalho, A. R., Van den Bergh, G., Voorspoels, S., & Otten, G. (2025). Quantification of per- and polyfluoroalkyl substances (PFAS) in air emissions: An interlaboratory comparison. Chemosphere, 380, 144449.
https://doi.org/10.1016/j.chemosphere.2025.144449

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1 AIM

The aim of this Interlaboratory comparison (ILC) on LUC/VI/003 method *DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN A GUIDED GAS STREAM* was to evaluate:

(i) The equivalence of the different sampling train variants defined in LUC/VI/003 (3) for the entire WAC/VI/A/025 scope (50 PFAS compounds)

(ii) Obtain experimental evidence on the native recovery (%) and associated uncertainty (%) in (i) each of the collection media (filter, XAD2 and water) and (ii) for the sampling train sum.

The LUC/VI/003 compendium method (LUC, 2024) was validated by VITO between 2021 and 2023, turned into force in Flanders since January 15th, 2024, and can be found on the emis online portal in both ENG and NL (https://emis.vito.be/nl/erkende-laboratoria/lucht-gop/compendium-luc). The methodological validation work and field experiences behind LUC/VI/003 are described in Hofman et al. (2025).

2 ILC SETUP

Three Flemish laboratories (F1-F3) and 2 international laboratories (EU1-EU2) participated in this ILC on the 20th and 21st of February. Flemish labs had to foresee 2 sampling trains (cleaned glassware, collection media, rinsing solvents and probe), prepared as described in the Flemish compendium method (LUC/VI/003). International laboratories participated with a method of choice but followed a similar sampling and reporting protocol in order to guarantee comparability of the ILC results.

Table 1 Participating Flemish and international laboratories

Flemish laboratories
Eurofins Air Monitoring Belgium nv
SGS Belgium nv
Tauw België nv
International laboratories
Aneco Institut für Umweltschutz GmbH & Co, Germany
Ineris, France

In the VITO ringlab, preconditioned air (nitrogen), representative for stack conditions (100°C, 10% RH) is provided to the sampling trains of which sampling train media were spiked by VITO (GOAL). Every lab conducts a duplo measurement (2 unique sampling trains) with spiked media (filter, XAD2, impinger water), following the sampling procedure described in LUC/VI/003. Sampling train connections with the ring lab are foreseen by heated lines from the commercial labs. The liners of the heated lines were replaced by PTFE liners from VITO tested in advance by means of MeOH and cyclohexane rinse samples of the cold and heated PTFE (n=4) to evaluate potential contamination of the heated lines.

Native spiking was conducted by VITO on 3 collection fractions (Figure 1): filter (Eppendorf pipet; on top), XAD2 (Hamilton pipet; inside medium) and impinger water (Eppendorf pipet; on top):

- Filter: **10 ng/cpd** → 10 ng x 50 cpds → PFAS total = 500 ng/fraction filter
- XAD2: **10 ng/cpd**→ 10 ng x 50 cpds → PFAS total = 500 ng/fraction filter

- Impinger 1 water (not condensate flask): **50 ng/cpd** → 50mL subsample from a total of 500mL: 5 ng x 50 cpds → PFAS total = 250 ng/fraction impinger

Addition standard solution (WAC-CAL-040; 100 ng/mL/cpd) on media:
- Filter: 100 µL → 10 ng/cpd
- XAD2: 100 µL → 10 ng/cpd
- Impinger 1: 500 µL → 50 ng/cpd → 5ng/cpd after dilution/subsample

TOTAL: 3500 ng/train (70 ng/cpd) → 1250 ng/train (25 ng/cpd) after dilution/subsample

A checklist was foreseen to guarantee proper spiking of all fractions for each of the participating labs. Moreover, spiking controls (additional vials that were spiked during the spiking procedure (Figure 2)) were considered in every sequence to evaluate spiking uncertainty.

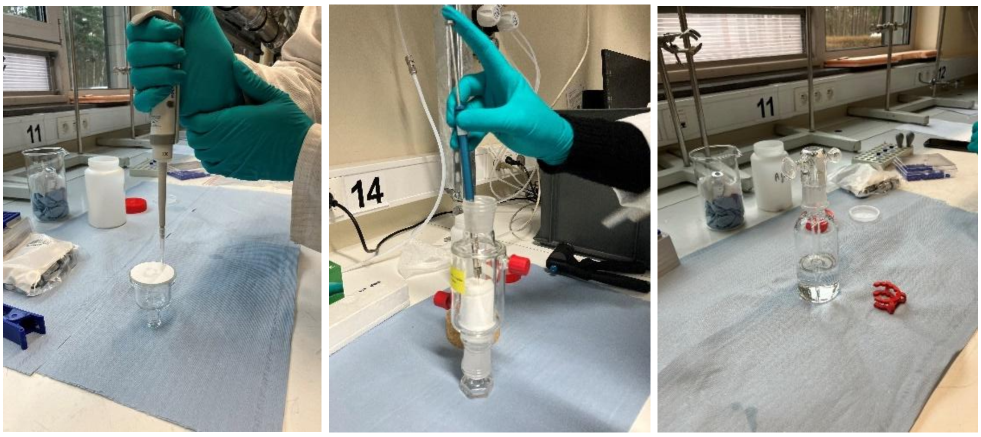


Figure 1 Native spiking of the considered collection media; filter (left), XAD2 (middle) and impinger (right)

Figure 2 Spiking controls (additional vials that were spiked) considered in every sequence

Flemish commercial laboratories (LAB F1, LAB F2 and LAB F3) participated on Feb 20th with 1 measurement in the morning and 1 measurement in the afternoon (Table 2), each consisting of 2h sampling at 12lpm. The commercial laboratories were already present at VITO on the 19th of February to set up their sampling train glassware and replace their heated lines. Non-simultaneous duplo sampling (1 measurement in the morning, 1 in the afternoon) was conducted because not all laboratories had duplo sampling equipment at their disposal at the time of the ILC. International laboratories LAB EU1 and EU2 participated on Feb 21st with 2 simultaneous sampling train setups in the morning consisting of 3h sampling at 12lpm, as prescribed by the LUC/VI/003 compendium method.

VITO participated on both sampling days; each sampling day consisting of 2 spiked sampling trains and 1 unspiked (blanco) sampling train to evaluate potential ringlab or heated line contamination of PFAS during the measurements. An overview of the participating labs, their applied LUC/VI/003 sampling train variant and the timing of the ILC measurements is provided in Table 2. Schematic overviews of the applied sampling train variants, as described in LUC/VI/003, are provided in Figure 3.

Table 2 Participating labs, their sampling train variant (between brackets) and the timing of the ILC measurements.

PARTICIPANTS 20/2/2024		PARTICIPANTS 21/2/2024	
MORNING	***n***	***MORNING***	***n***
VITO (blanco train)	*1*	VITO (blanco train)	*1*
VITO (OTM-45)	*1*	VITO (OTM-45)	*2*
LAB F1 (OTM-45 variant)	*1*	*LAB EU1 (cooled probe variant)*	*2*
LAB F2 (OTM-45 variant)	*1*	*LAB EU2 (OTM-45)*	*2*
LAB F3 (Cooled Probe)	*1*		
AFTERNOON		***AFTERNOON***	
VITO (blanco train)	*1*		
VITO (OTM-45)	*1*		
LAB F1 (OTM-45 variant)	*1*		
LAB F2 (OTM-45 variant)	*1*		
LAB F3 (Cooled Probe)	*1*		

TIMING 20/2/2024		TIMING 21/2/2024	
08:00	Leak test + Field blank collection	09:00	Setup sampling trains
09:00	Spiking media (filter, XAD2, water)	10:00	Leak test + Field blank collection
09:30	Leak test + Measurement (2h, 12lpm): **9u43 – 11u43**	11:00	Spiking media (filter, XAD2, water)
11:43	Field sample collection	11:30	Leak test + Measurement (3h, 12lpm): **12u-15u**
12:30	Lunch	15:00	Field sample collection
13:00	Leak test + Field blank collection	15:30	End ILC
14:00	Spiking media (filter, XAD2, water)		
14:30	Leak test + Measurement (2h, 12lpm): **14u28-16u28**		
16:30	Field sample collection		
17:30	End ILC		

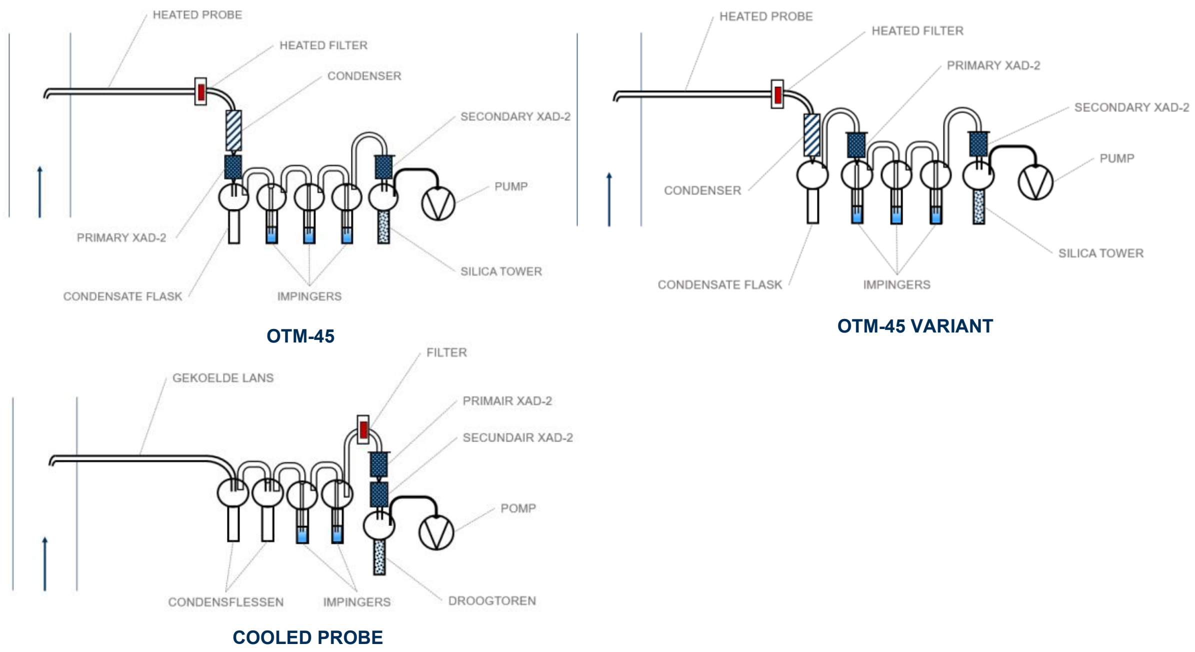


Figure 3 Different sampling train variants (OTM-45, OTM-45 variant & cooled probe) as described in the Flemish compendium method (LUC/VI/003).

The water generation inside the ringlab was monitored by means of FTIR and resulted in a stable relative humidity of 10% during the morning and afternoon measurements on 20/2/2024 and afternoon measurement on 21/2/2024 (Figure 4).

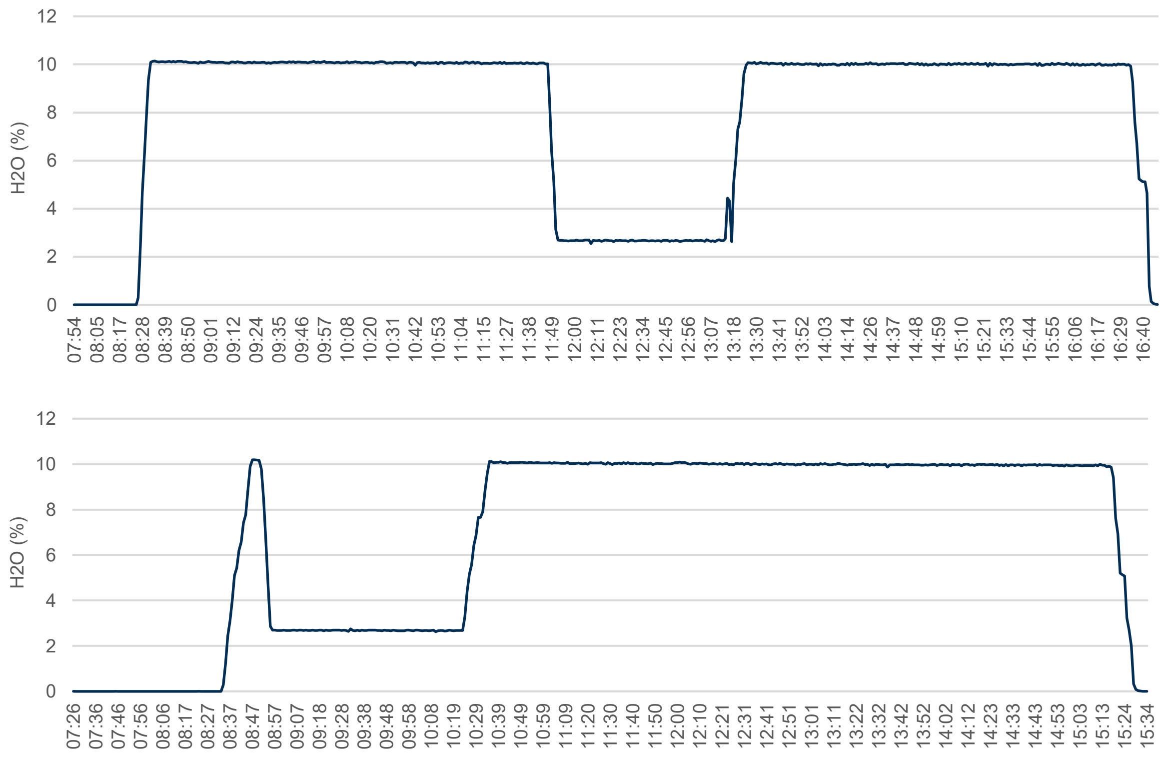


Figure 4 Air humidification (% H_2O) during the morning and afternoon campaign on February, 20th (upper) and morning campaign on February, 21st (lower).

3 SAMPLING TRAIN SETUP

3.1 VITO

The sampling train setup from VITO consists of the "OTM-45" sampling train described in the LUC/VI/003 compendium procedure (LUC, 2024) and consists of a heated probe, followed by a heated filter (120°C), condenser, primary XAD2 resin, condensate flask, 3 impinger flasks filled with 100 mL of ultrapure water, a secondary XAD2 resin, a silica module and pump. The glassware is composed of borosilicate glass. VITO LKM performed the sampling, while VITO GOAL conducted the spiking and lab analysis.

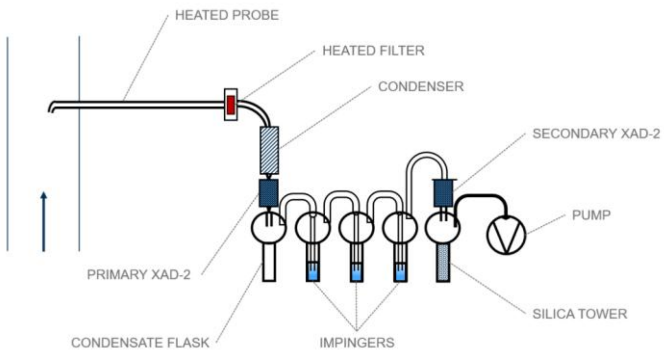


Figure 5 Schematic representation of the "OTM-45" sampling train as described in the LUC/VI/003 compendium procedure (left) and picture of the applied VITO ILC setup (right)

The following fractions were spiked with 50 native PFAS compounds according to the procedure described in §2:

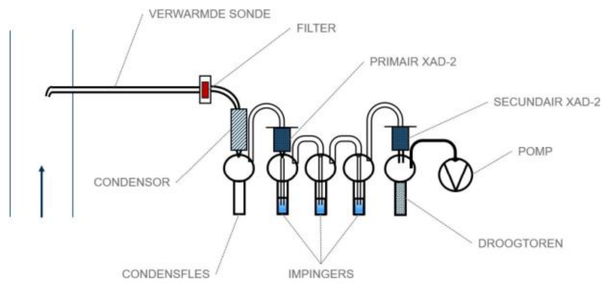
- Filter: 10ng/cpd
- XAD2-1: 10ng/cpd
- Impinger 1: 50 ng/cpd

Resulting in a total train sum spike of 70 ng/cpd.

Three C13-labeled pre-sampling standards (SS), 13C8-PFOA, 13C8-PFOS and 13C3-PFBA are spiked on the primary XAD2 resin and 28 internal standards (IS) are used for the analytical quantification by means of LC-MS/MS. ILC sampling and sample collection was conducted successfully, without notable issues.

3.2 LAB F1

The sampling train setup from LAB F1 consists of the "OTM-45 variant" sampling train described in the LUC/VI/003 compendium procedure and consists of a heated probe, followed by a heated filter (120°C), condenser, condensate flask, primary XAD2 resin, 3 impinger flasks filled with 100 mL of ultrapure water, a secondary XAD2 resin, a silica module and pump. The glassware is composed of borosilicate glass.



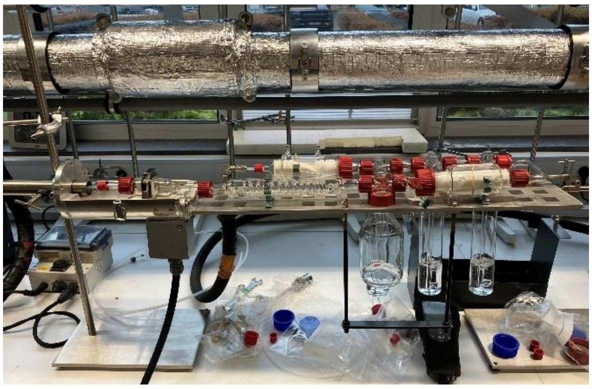


Figure 6 Schematic representation of the "OTM-45 variant" sampling train as described in the LUC/VI/003 compendium procedure (left) and picture of the applied LAB F1 ILC setup (right)

The following fractions were spiked with 50 native PFAS compounds according to the procedure described in §2:

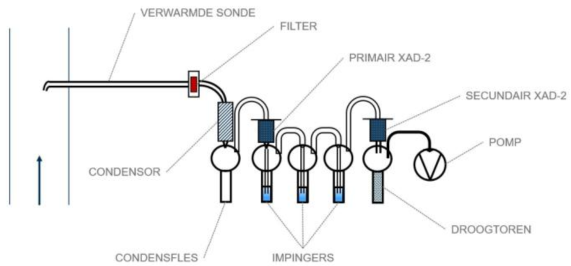
- Filter: 10ng/cpd
- XAD2-1: 10ng/cpd
- Impinger 1: 50 ng/cpd

Resulting in a total train sum spike of 70 ng/cpd.

Three C13-labeled pre-sampling standards (SS), 13C8-PFOA, 13C8-PFOS and 13C3-PFBA are spiked on the primary XAD2 resin and 25 internal standards (IS) are used for the analytical quantification by means of LC-MS/MS. ILC sampling and sample collection was conducted successfully, without notable issues.

3.3 LAB F2

The sampling train setup from LAB F2 consists of the "OTM-45 variant" sampling train described in the LUC/VI/003 compendium procedure and consists of a heated probe, followed by a heated filter (120°C), condenser, condensate flask, primary XAD2 resin, 3 impinger flasks filled with 100 mL of ultrapure water, a secondary XAD2 resin, a silica module and pump. The glassware is composed of borosilicate glass.



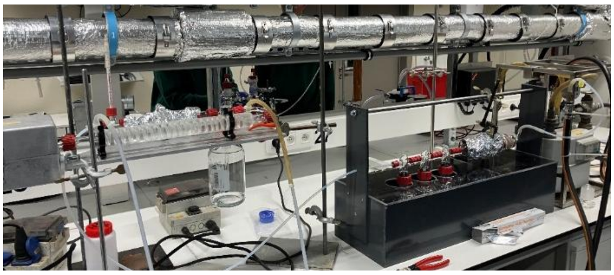


Figure 7 Schematic representation of the "OTM-45 variant" sampling train as described in the LUC/VI/003 compendium procedure (left) and picture of the applied LAB F2 ILC setup (right)

The following fractions were spiked with 50 native PFAS compounds according to the procedure described in §2:

- Filter: 10ng/cpd
- XAD2-1: 10ng/cpd

- Impinger 1: 50 ng/cpd

Resulting in a total train sum spike of 70 ng/cpd.

Three C13-labeled pre-sampling standards (SS), 13C8-PFOA, 13C8-PFOS and 13C3-PFBA are spiked on the primary XAD2 resin and 23 internal standards (IS) are used for the analytical quantification by means of LC-MS/MS. ILC sampling and sample collection was conducted successfully, without notable issues.

3.4 LAB F3

The sampling train setup from LAB F3 consists of the "cooled probe" sampling train described in the LUC/VI/003 compendium procedure comprising of a cooled probe, followed by 2 condensate flasks, 2 impinger flasks filled with 100 mL of ultrapure water, glass wool filter and 2 consecutive XAD2 modules, a silica module and pump. The glassware is composed of borosilicate glass and glass fittings were used instead of Teflon connectors.

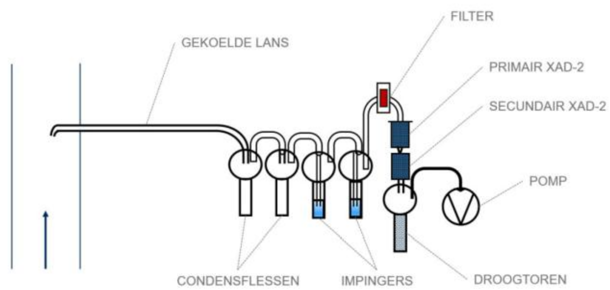


Figure 8 Schematic representation of the "cooled probe variant" sampling train as described in the LUC/VI/003 compendium procedure (left) and picture of the applied LAB F3 ILC setup (right)

The following fractions were spiked with 50 native PFAS compounds according to the procedure described in §2:

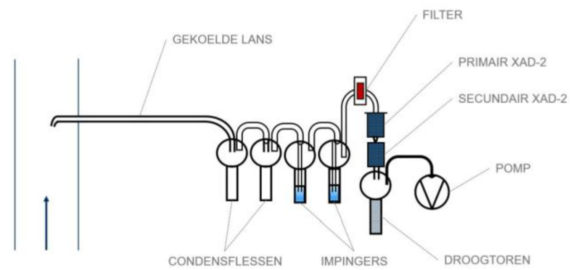
- XAD2-1: 10ng/cpd
- Impinger 1: 50 ng/cpd

Resulting in a total train sum spike of 60 ng/cpd. The glasswool filter was not spiked to avoid cross-medium transfer, as the filter is positioned inside the primary XAD2 module, on top of the XAD2.

Three C13-labeled pre-sampling standards (SS), 13C8-PFOA, 13C8-PFOS and 13C3-PFBA are spiked on the primary XAD2 resin and 18 internal standards (IS) are used for the analytical quantification by means of LC-MS/MS. ILC sampling and sample collection was conducted successfully, without notable issues.

3.5 LAB EU1

LAB EU1 conducted 2 simultaneous measurements on February, 21st, with a variant from the "cooled probe" sampling train described in the LUC/VI/003 compendium procedure comprising of a cooled probe, followed by 1 condensate flask, 3 impinger flasks filled with 100 mL of ultrapure water and 2 consecutive XAD2 modules, a silica module and pump. The glassware is composed of borosilicate glass, blinded for the impingers and XAD2 and glass fittings were applied instead of Teflon connectors. LAB EU1 does not consider a filter but filters the condensate to separately extract dust and adds NaOH to the water compartments (impingers/condensate flask). Normally, the sampling Standard (SS) spike is added to the condensate flask (in NaOH). No SS spike was, however, added during this ILC in order to avoid interference with the VITO spiking.



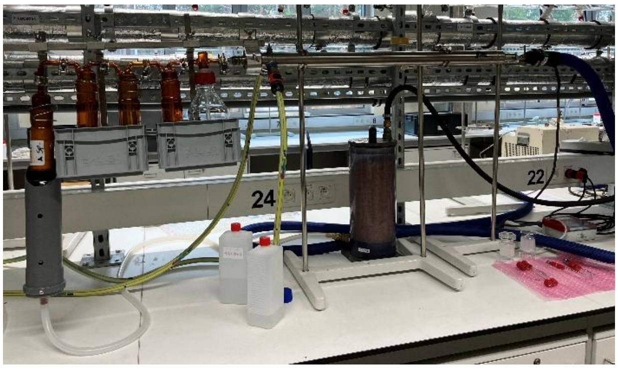


Figure 9 Schematic representation of the "cooled probe variant" sampling train as described in the LUC/VI/003 compendium procedure (left) and picture of the applied LAB EU1 ILC setup (right).

The following fractions were spiked with 50 native PFAS compounds according to the procedure described in §2:

- XAD2-1: 10ng/cpd
- Impinger 1: 50 ng/cpd

Resulting in a total train sum spike of 60 ng/cpd.

No sampling standards (SS) were added and 23 internal standards (IS) are used for the analytical quantification by means of LC-MS/MS. ILC sampling and sample collection was conducted successfully, without notable issues.

Sample collection and aggregation differed from the LUC/VI/003, with four samples (instead of 6) collected after sampling and extracted for analysis:

- NaOH+water from condensate/impingers (F4)
- Rinse condensate/impingers (1% AlkMethanol) (F2)
- Primary XAD2 module (F3)
- Secondary XAD2 module (F5)

In this regard, the method applied by LAB EU1 consiscompared to the LUC/VI/003.

3.6 LAB EU2

LAB EU2 conducted 2 simultaneous measurements on February, 21st, with the OTM-45 method from US EPA (EPA, 2021). The sampling train of this method is identical to the OTM-45 setup described in the LUC/VI/003 compendium procedure and consists of a heated probe, followed by a heated filter (120°C), condenser, primary XAD2 resin, condensate flask, 3 impinger flasks filled with 100 mL of ultrapure water, a secondary XAD2 resin, a silica module and pump. The glassware is composed of borosilicate glass.

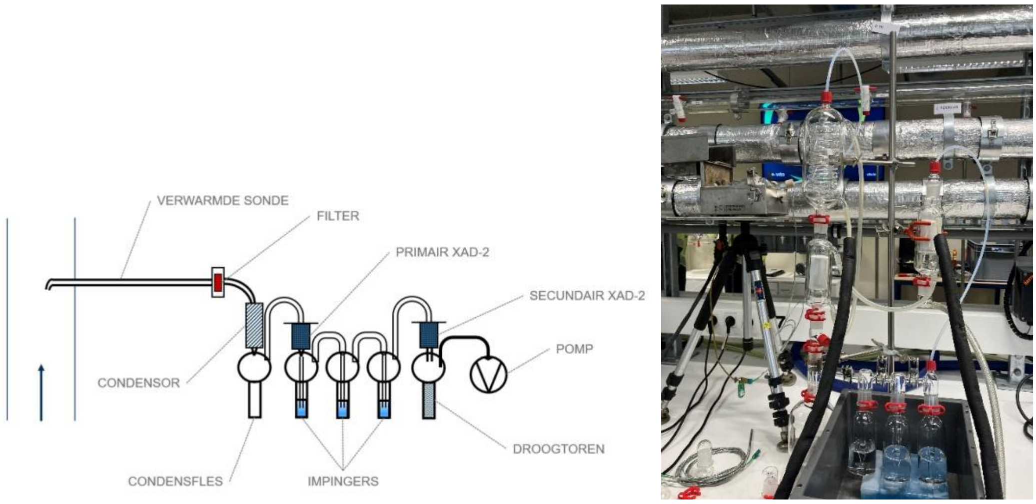


Figure 10 Schematic representation of the "OTM-45" sampling train as described in the LUC/VI/003 compendium procedure (left) and picture of the applied LAB EU2 ILC setup (right).

The following fractions were spiked with 50 native PFAS compounds according to the procedure described in §2:

- Filter: 10ng/cpd
- XAD2-1: 10ng/cpd
- Impinger 1: 50 ng/cpd

Resulting in a total train sum spike of 70 ng/cpd.

As prescribed in the OTM-45, two C13-labeled pre-sampling standards (SS), 13C8-PFOA, 13C8-PFOS are spiked on the primary XAD2 resin and 28 internal standards (IS) are used for the analytical quantification by means of LC-MS/MS. ILC sampling and sample collection was conducted successfully, without notable issues.

4 RESULTS

During the ILC measurements and after leak testing and spiking of their sampling trains, the participating labs conducted proper 2-3h sampling of the preconditioned air (100°C, 10% RH) and sample collection of medium blanks, field blanks, field samples and post-rinse samples as prescribed in the LUC/VI/003 compendium procedure. All labs transported and stored the collected samples in a cool (~4°C) and dark environment awaiting lab analysis.

Following lab analysis of all collected samples, participating labs reported the results in an ILC reporting template, provided by VITO (Annex 1). The ILC reporting template included the following information:

- **"IS-SS"** tab with applied C13-labeled internal (IS) and sampling standards (SS)
- **"LUC_train variant"** tab with quantified mass (ng) and QA/QC's per sample (medium blank, field sample, field blank and post-rinse blank), analytical fraction (see sample aggregation and associated tab) and considered PFAS compound. The lower bound (<LOQ=0) sum of each sample is given automatically below with associated compound-specific breakthrough check (%) and field blank check (%). Sampling standard recoveries should be provided as absolute recovery (%) and corrected for the corresponding internal standard recovery (%).

- **"LUC_train variant_IS LOQ"** tab with internal standard recoveries (%) and LOQ's for the individual samples, analytical fractions and considered PFAS compounds.

The following criteria are evaluated below for each of the participating labs:
- Sampling Standard (SS) Recoveries (%): 50-130%
- Internal Standard (IS) Recoveries (%): >20%, except for 13C-8:2diPAP and 13C-PFHxDA which can be >= 10% following WAC VI/A/003
- Total train recovery (%): between 70-120%
- Observed uncertainty (U) between duplo measurements (k=2): <50%

$$U = |b| + 2\sqrt{(CV_{Rw})^2}$$

With U (%) the combined measurement uncertainty (CI 95%, k=2), b the bias (%) and CV_{Rw}(%) the coefficient of variation for reproducability (standard deviation divided by average of duplo measurements) (WAC/VI/A/002).

If the above criteria are reached for an individual PFAS compound, this compound is considered quantitative. If not, the compound is considered indicative. In a prior validation exercise of the OTM-45 sampling train variant by VITO with a spiked sampling train at a background location, as described in LUC/VI/003 (version 10/2023), 19 quantitative and 22 indicative PFAS compounds were obtained.

Completed ILC reporting templates were returned to VITO on the following dates:
- VITO: 17/4/2024
- LAB F1: 2/4/2024
- LAB F2: 13/5/2024
- LAB F3: 10/5/2024
- LAB EU1: 14/5/2024
- LAB EU2: 30/4/2024

4.1 VITO

VITO participated on both ILC days, with in 4 sampling trains (2 blank trains T1 & T3, 2 spiked trains T2 & T4) on the first day and 3 sampling trains (1 blank train T5, 2 spiked trains T6 & T7) on the second day. Each train consists of field blank, field sample and post-rinse analytical results and associated QA/QC's. ILC reports of the individual measurements can be found in Annex 2.

4.1.1 QA/QC and LOQ's

In terms of QA/QC's, sampling standard spike recovery was within 50-130% for 13C3-PFBA, 13C8-PFOA and 13C8-PFOS in both field blank and field sample XAD2's in all sampling trains (T1-7), except the SS recovery of sample XAD2 of T5 which (184-185%). Internal standard recoveries were all above 20%, except for compounds 13C-PFHxDA, 13C-PFOSA, 13C-MePFOSA,13C-EtPFOSA, 13C-PAP's, 13C-diPAP's. The breakthrough criterium of 30% was never breached.

The field blank criterium (<10%) was not breached for the 4 spiked trains, except for PFHxDA (19%) and PFODA (25%) in T4. Nevertheless, both blank and spiked train field blanks showed the presence of mainly long-chain (>C8) PFCA's in the front half rinse/filter fraction and backhalf/condenser rinse up to 8 ng (T1), 5.8 ng (T2), 10 ng (T3), 11 ng (T4), 1.9 ng (T5), 2 ng (T6) and 1.5 (T7), and PFOS in all analytical fractions. Post-rinse samples were clean (<1ng), except for PFOS in all analytical fractions. As PFOS also appeared in the procedure and medium blanks, PFOS appears to be a compound present in the VITO lab. The LOQ was raised for PFOS (up to 4.6 ng) due to the elevated procedure blank.

LOQ's were derived based on a low calibration standard that is measured before and after every measurement sequence and considering a S/N ratio of 6. If the procedure blank (PB) is higher than this LOQ, the LOQ is elevated to 2x procedure blank concentration. The resulting compound specific LOQ's in the different analysis fractions (filter, MeOH, XAD2 and water) varied between 0.04 ng and 4.6 ng (elevated for PFOS), and highest LOQ's were obtained for the XAD2 fraction. The compound specific LOQ's are provided in the "LUC_OTM-45_IS LOQ" tab of meting 1 (Annex 2).

QA/QC's Spiked trains (T2 and T4):
- SS REC 50-130%: OK
- REC IS (>20%): NOK for PFHxDA, PFOSA, MePFOSA, EtPFOSA, PAP, diPAP
- Field blank (<10% measured): OK (note PFCA's from filter? <9%)
- Breakthrough (<30%): OK (highest for PFOSA 18%)
- Post-rinse: clean (<1 ng), except for PFOS (6-8ng)
- LOQ's

QA/QC's Blank trains (T1 and T3):
- SS REC 50-130%: OK
- REC IS (>20%): NOK for PFOSA, MePFOSA, EtPFOSA, PAP, diPAP
- Field blank (<10% measured): OK
- Breakthrough (<30%): OK (highest for PFOSA 18%)
- Post-rinse: clean (<1 ng), except for PFOS (6-8ng)
- LOQ's: 0.04-0.3 ng → elevated for PFOS (max=4.6 ng)

- **QA/QC's Spiked trains (6 and 7):**
  - SS REC 50-130%: OK
  - REC IS (>20%): NOK for PFHxDA, PFOSA, MePFOSA, EtPFOSA, PAP, diPAP
  - Field blank (<10% measured): OK (<3%)
  - Breakthrough (<30%): OK → highest PFOSA (16%)
  - Post-rinse: clean (<1 ng), except for PFOS (5-7ng)
- **QA/QC's Blank train (5)**:
  - SS REC 50-130%: OK for field blank, NOK for field sample (~180% for all 3 cpds!)
  - REC IS (>20%): NOK for PFOSA, MePFOSA, EtPFOSA, PAP, diPAP
  - Field blank (<10% measured): OK
  - Breakthrough (<30%): OK
  - Post-rinse: clean (<1 ng), except for PFOS (5-7ng)

4.1.2 Internal standard (IS) recovery

The observed internal standard recoveries (%) within each analytical fraction are provided in Figure 11. And show overall good recoveries, except for 13C-PFHxDA, 13C-PFOSA, 13C-MePFOSA,13C-EtPFOSA, 13C-PAP's, 13C-8:2diPAP.

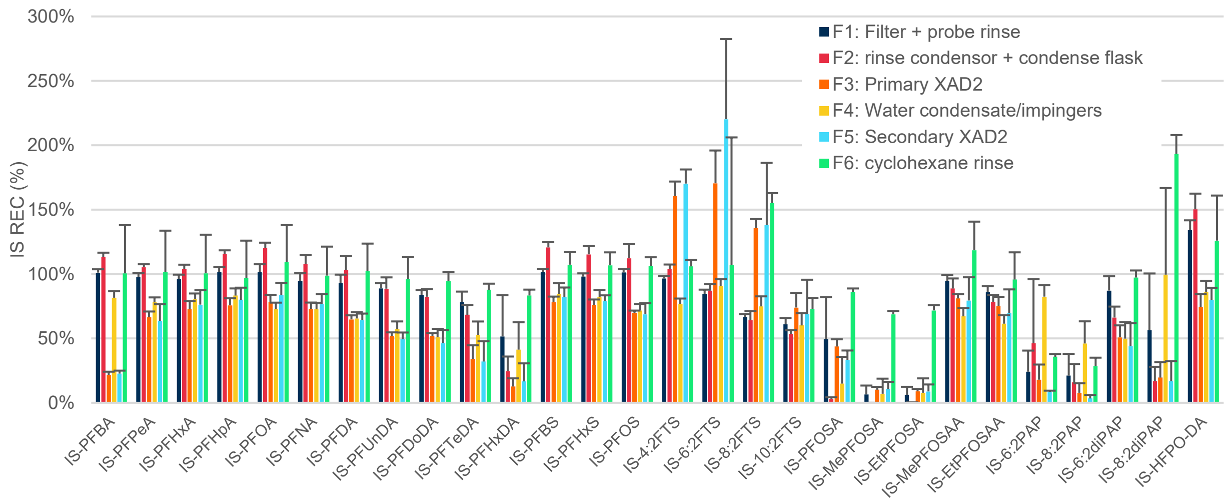


Figure 11 Average internal standard recovery (%) of the 4 spiked sampling trains (T2,T4, T6 and T7), within the different analytical fractions (F1-F6). Error flags denote the standard deviation between the 4 spiked sampling trains (T2,T4, T6 and T7).

4.1.3 Native spike recovery

When evaluating the total train (sum of all analytical fractions) apparent (native) spike recovery (%) between the spiked trains (T2, T4, T6 and T7) in Figure 12, it becomes clear that the spike is generally well recovered (~100%) by the VITO measurements, except for compounds that exhibit bad internal standard recoveries in Figure 11 (e.g. MePFOSA, EtPFOSA, PFHxDA/PFODA). Moreover, apparent recoveries are overestimated for PFBA and long-chain PFCA's, up to 20% for T4 and 80% for T7.

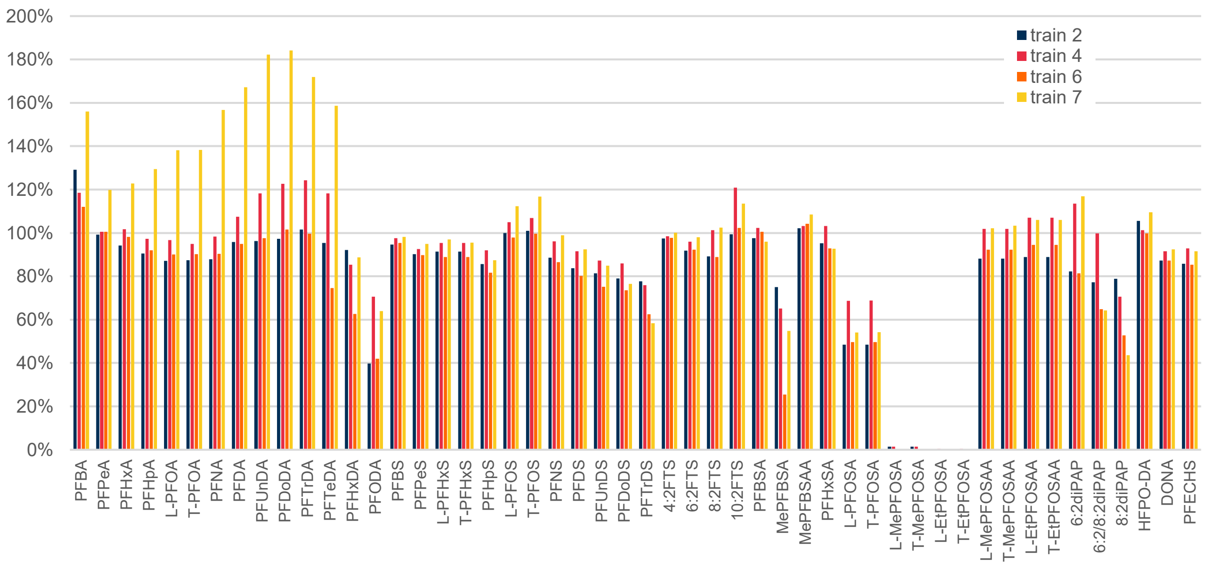


Figure 12 Total train native spike recovery (%) for each of the spiked PFAS compounds and spiked trains (T2, T4, T6 and T7).

Further elucidation within the different analytical fractions (Figure 13) indicates that this overestimation is predominantly observed in the rinse probe + filter fraction (F1) spiked at 10 ng/cpd but recovered up to 23 and 60 ng/cpd for the long-chain PFCA's in train 4 and 7

respectively. Wide error bars represent the variation in observed recoveries for those specific compounds (only train 7 and to a lesser extent train 4 show additional long-chain PFCA's). Remarkably, the filter fraction (F1) contribution of these compounds is much smaller in the associated field blanks (up to 11ng) and post-rinse blanks (up to 0.58ng).
Besides the long-chain PFCA contamination, Figure 13 illustrates that the spiked PFAS compounds are well-retained by the different collection media (filter, XAD2, water) and only limited transfer is observed from the spiked fractions towards other train fractions after 2-3 hours of sampling at 12 lpm (e.g. highest for PFOSA in secondary XAD2).

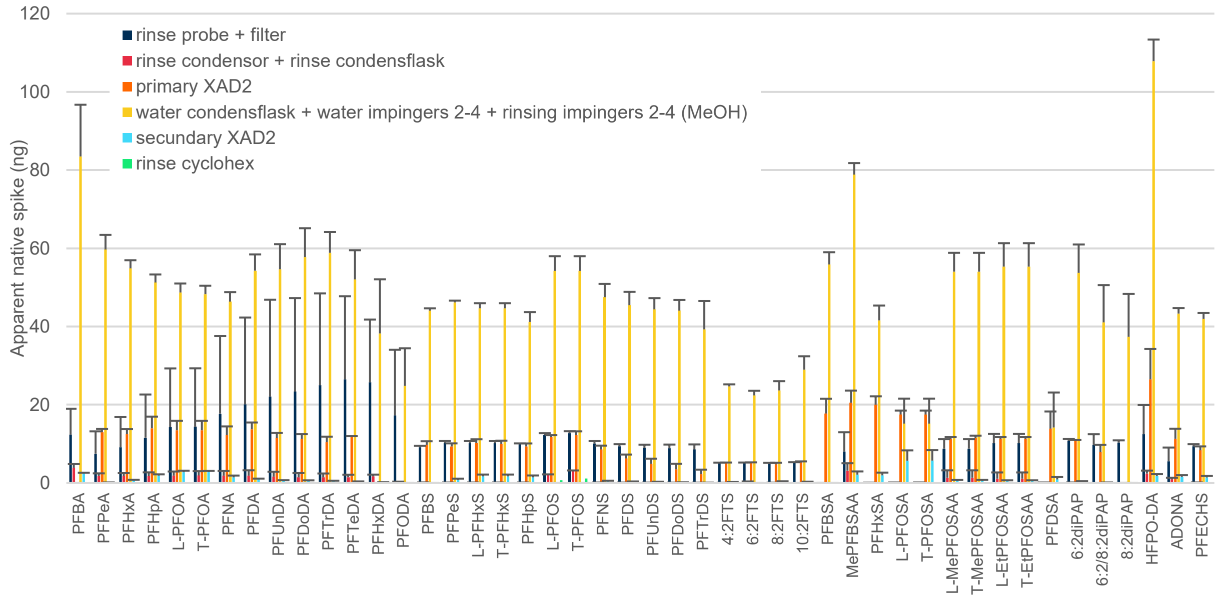


Figure 13 Average apparent spike recovery (ng) within the individual analytical fractions (F1-6) of the spiked sampling trains (T2, T4, T6 and T7). Error flags denote the standard deviation between the 4 spiked sampling trains (T2,T4, T6 and T7).

Potential contamination by long-chain (>C8) PFCA's in the filter fraction (F1) were investigated by evaluating potential external contamination sources:

- Additional filters from same filter batches → <LOQ
- Water used for preconditioning the ILC air → <LOQ
- Rinse samples from the heated inlet PTFE liners (cold/warm, MeOH/cyclohexane) → <LOQ

No detectable PFAS were found when analysing the potential source samples, as can be observed from the analysis reports in Annex 3. When tracing back the glassware, ILC train 7 was used in a previous stack sampling campaign with high emission concentrations of long-chain PFCA's (similar fingerprint). This observation, together with the notion of general prevalence of long-chain PFCA's in the filter fractions from the field blanks and blank ILC trains suggests that, although the LUC/VI/003 washing procedure has strengthened to baking at 450°C and additional cyclohexane rinses to selectively remove long-chain PFAS from the glassware, some long-chain PFCA's remain persistent in the glassware, especially at the filter fraction which forms the first barrier and accumulation location for long-chain PFAS.

Additional glassware extraction experiments confirmed this hypothesis and advocate for replacement of the filter holder glassware (in addition to the probe liner glassware) with every emission measurement. This method optimisation will be added in the next LUC/VI/003 revision (MB2026).

4.1.4 Quantitative evaluation

As train 7 was associated with filter holder glassware contamination, measurement results were rejected from the final evaluation. The apparent train recovery (%) and measurement uncertainty were evaluated on the other 3 spiked filter trains (T2, T4 & T6), resulting in 38 quantitative compounds with apparent train recoveries between 70-120% and measurement uncertainty (U) <50% as can be seen from Figure 14.

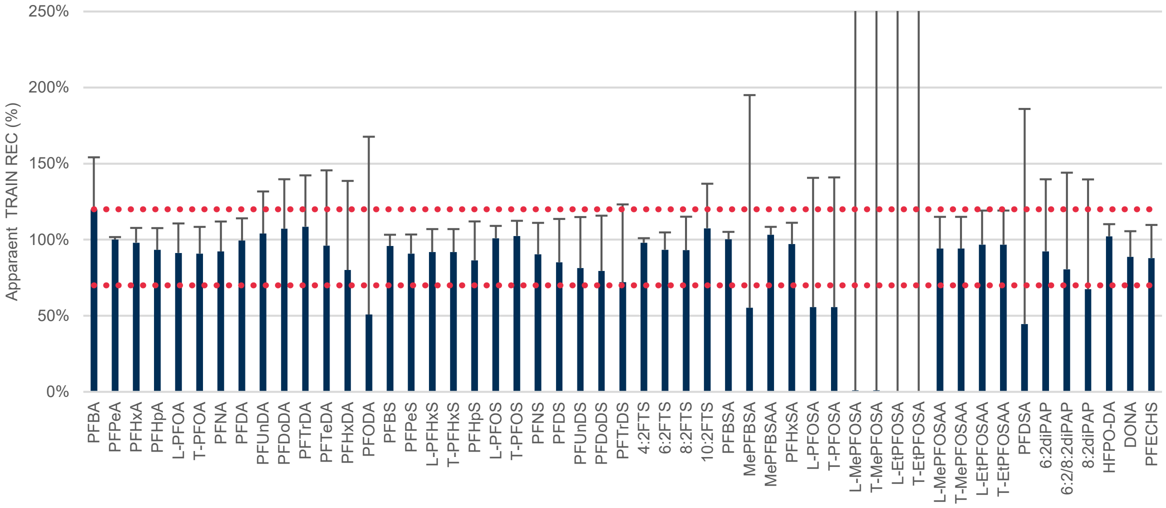


Figure 14 Apparent VITO train recovery (%)with associated error flags representing the measurement uncertainty (U; %) based on the 3 spiked ILC train (T2, T4 & T6) repeats. Red dotted lines denote the quantitative recovery boundaries of 70-120%.

Combined results of all 4 spiked sampling trains were considered in the most recent MB2025 LUC/VI/003 (version 6/2024), resulting in 22 quantitative and 22 indicative compounds (LUC, 2025). After rejecting the train 7 data, this validation exercise results in 28 quantitative compounds which will be added in the next LUC/VI/003 revision (MB2026).

4.2 LAB F1

LAB F1 participated on the first ILC day, with 2 spiked sampling trains (OTM-45 variant). Each train consists of field blank, field sample and post-rinse analytical results and associated QA/QC's. ILC reports of the individual measurements can be found in Annex 4.

4.2.1 QA/QC and LOQ's

In terms of QA/QC's, sampling standard spike recovery was within 50-130% for 13C3-PFBA, 13C8-PFOA and 13C8-PFOS in both field blank and field sample XAD2's in both sampling trains. Internal standard recoveries were generally good (>20%), except for compounds 13C-MePFOSA and 13C-EtPFOSA. 13C2-6:2PAP, 13C2-8:2PAP and 13C2-6:2diPAP were not considered and PFOSAA, PFDSA, 6:2PAP and 8:2PAP were not quantified. Low IS recoveries were observed for the cyclohexane (10-30%) fraction. The breakthrough criterium of 30% was never breached, except for MePFOSA and EtPFOSA of measurement 1.

The field blank criterium (<10%) was not breached for the 2 spiked trains, except for 6:2FTS which was found in the field blank XAD2 of measurement 1 (7.36 ng; 20%) and measurement

2 (2.53 ng; 9%). The post-rinse blank showed no detectable or low concentrations (<1.18ng), for all compounds, except for 6:2diPAP for which 12.08 ng was detected.

LOQ's were derived based on a low calibration standard and varied between 0.1 ng and 1 ng, and highest LOQ's (1 ng) were obtained for the XAD2 fraction. The compound specific LOQ's are provided in the "LUC_OTM-45_IS LOQ" tab of meting 1 (Annex 4).

- QA/QC's:
  - SS REC 50-130%: OK
  - REC IS (>20%): NOK for MePFOSA, EtPFOSA, (PAP, diPAP NA)
    - Lower REC for cyclohexane (~10-30%) and XAD2 (~30-50%)
  - Field blank (<10% measured): OK, except for 6:2FTS
  - Breakthrough (<30%): OK, NOK for MePFOSA and EtPFOSA (measurement 1)
  - Post-rinse: OK, except for 6:2diPAP (12.08 ng)

4.2.2 Internal standard (IS) recovery

The observed internal standard recoveries (%) within each analytical fraction are provided in Figure 15 and show overall good recoveries, except for low recoveries of 13C-MePFOSA,13C-EtPFOSA and rather high recoveries for 13C2-6:2FTS and 13C2-8:2diPAP. Lowest but acceptable IS recoveries are observed in the XAD2 and cyclohexane fraction (Figure 15).

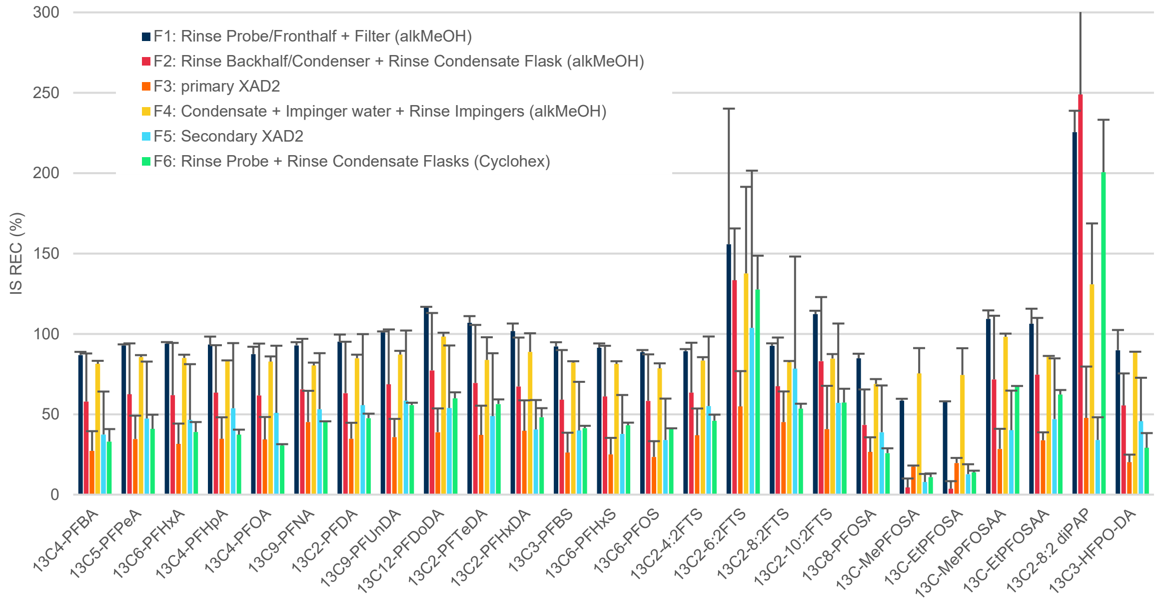


Figure 15 Average internal standard recovery (%) of the 2 spiked sampling trains (T1 and T2), within the different analytical fractions (F1-F6). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.2.3 Native spike recovery

When evaluating the apparent (native) spike recovery (ng) within the different analytical fractions (F1-F6) in Figure 16, it becomes clear that the spike is generally well recovered (<100%) by the LAB F1 measurements. Although the spike recoveries are quite stable in the filter and XAD2 fractions, the water fraction shows a decreasing spike recovery with increasing

chain length of the PFAS compound, observed both for the PFCA's and PFSA's. As this effect is not observed in the long-chain IS recoveries (Figure 15), which are added after sampling, these results suggest that the spike loss is happening during sampling and sample collection. Considering the affinity of long-chain PFAS towards the sampling train glassware (§4.1.3), recovery improvements can be expected by (i) thorough rinsing of the glassware during sampling collection (3 times MeOH, 3 times cyclohexane, taking along the sides of the glassware very thoroughly) and (ii) inclusion of compound-specific internal standards.
Moreover, spike transfer from the water fraction towards the secondary XAD2 is observed for MePFOSA, EtPFOSA and to a lesser extent for PFNA, PFDA, PFDoDA, PFOS and 6:2 FTS.

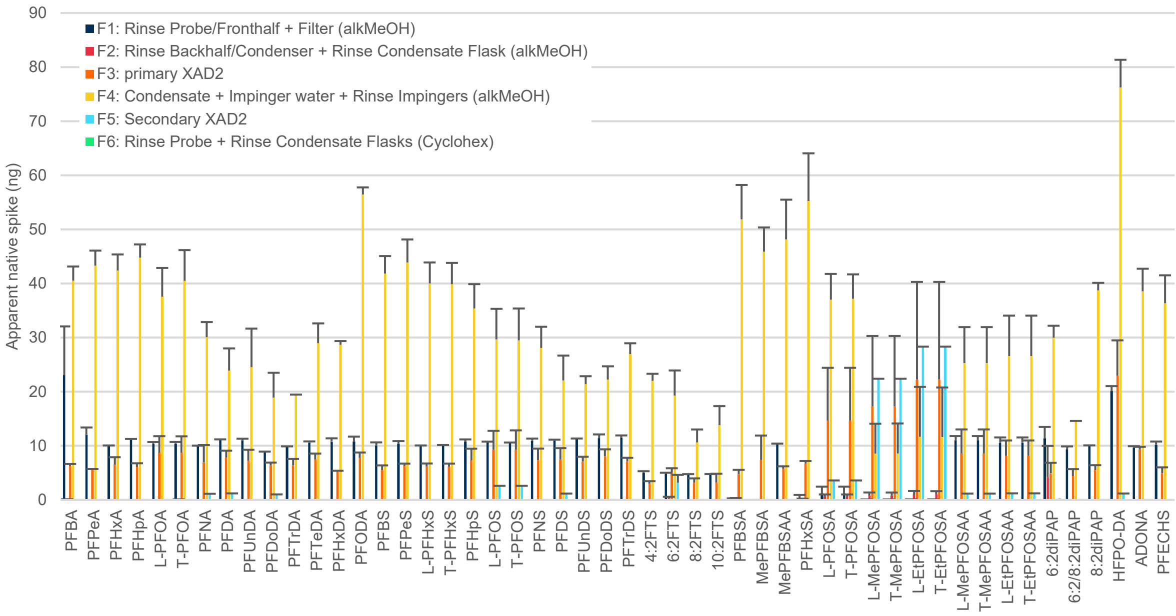


Figure 16 Average apparent spike recovery (ng) within the individual analytical fractions (F1-6) of the spiked sampling trains (T1 and T2). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.2.4 Quantitative evaluation

The apparent train recovery (%) and measurement uncertainty were evaluated on the 2 spiked filter trains (T1 and T2), resulting in 24 quantitative compounds with apparent train recoveries between 70-120% and a measurement uncertainty (U) <50% as can be seen from Figure 17.

Long-chain PFAS recovery (C9-16; both PFCA's and PFSA's) can be optimized in order to obtain more quantitative compounds.

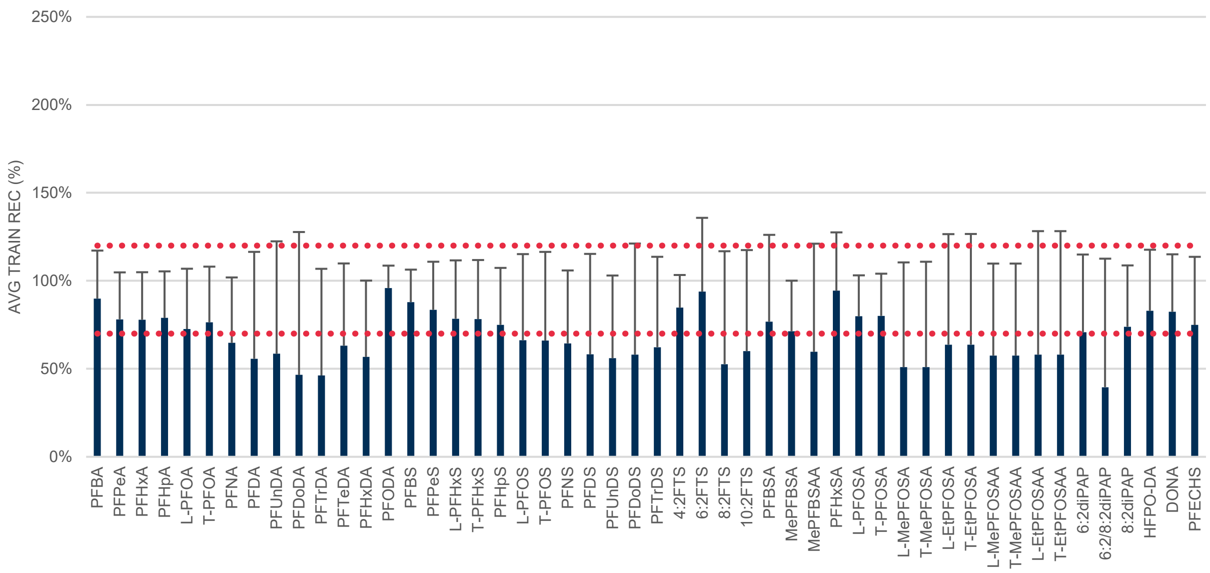


Figure 17 Apparent LAB F1 train recovery (%) with associated error flags representing the measurement uncertainty (U; %) based on the 2 spiked ILC train (T1 and T2) repeats. Red dotted lines denote the quantitative recovery boundaries of 70-120%.

4.3 LAB F2

LAB F2 participated on the first ILC day, with 2 spiked sampling trains (OTM-45 variant). Each train consists of field blank, field sample and post-rinse analytical results and associated QA/QC's. ILC reports of the individual measurements can be found in Annex 5.

4.3.1 QA/QC and LOQ's

In terms of QA/QC's, sampling standard spike recovery was within 50-130% for 13C3-PFBA, 13C8-PFOA in both field blank and field sample XAD2's in both sampling trains and slightly higher for 13C8-PFOS (132-158%). Internal standard (23) recoveries were generally good (>20%), except for compounds 13C-MePFOSAA and 13C-EtPFOSAA. 13C2-6:2PAP, 13C2-8:2PAP and 13C2-6:2diPAP were not considered and PFOSAA, PFDSA, 6:2PAP and 8:2PAP were not quantified. Comparable IS recoveries were observed between the different analytical fractions, except for the sulfonate recovery in the XAD2 fraction which was lower (but still OK). The breakthrough criterium of 30% was never breached, nor was the field blank criterium (<10%) breached. The post-rinse blank showed no detectable (<LOQ) or low concentrations up to 2.51ng (PFUnDA; 2%).

LOQ's were derived from a low calibration standard and varied between 0.05 ng and 0.333 ng. Similar LOQ's were reported for the different analytical fractions. The compound specific LOQ's are provided in the "LUC_OTM-45 variant IS LOQ" tab of meting 1 (Annex 5).

4.3.2 Internal standard (IS) recovery

The observed internal standard recoveries (%) within each analytical fraction are provided in Figure 18 and show overall good recoveries, except for low recoveries of 13C-MePFOSAA,13C-EtPFOSAA. Although the recoveries are quite comparable between the analytical fractions (F1-F6), the sulfonates (13C3-PFBS, 18O2-PFHxS, 13C4-PFOS) exhibit lower but acceptable recoveries in the XAD2 fraction (Figure 18).

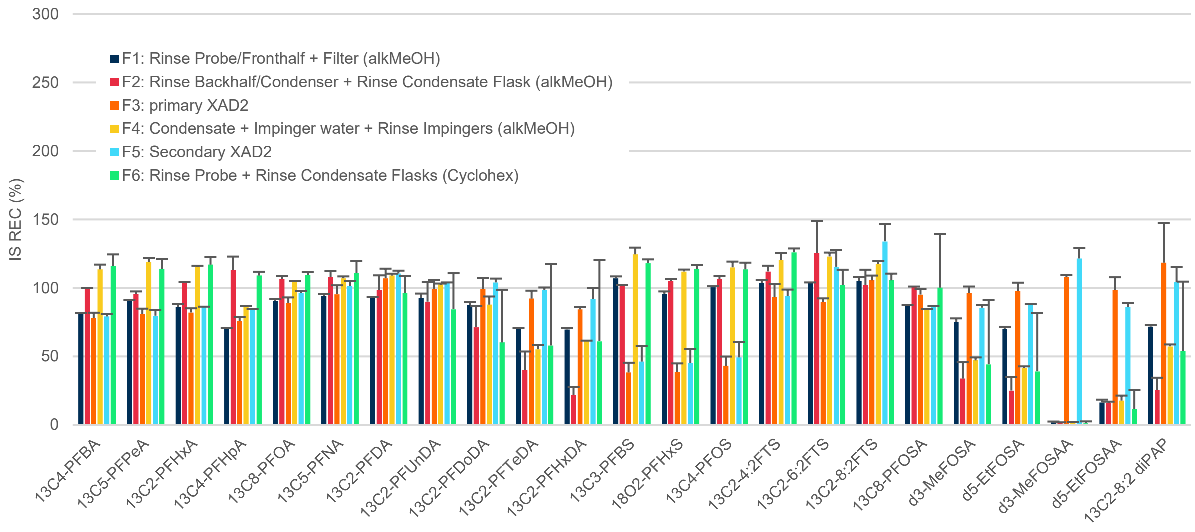


Figure 18 Average internal standard recovery (%) of the 2 spiked sampling trains (T1 and T2), within the different analytical fractions (F1-F6). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.3.3 Native spike recovery

When evaluating the apparent (native) spike recovery (ng) within the different analytical fractions (F1-F6) in Figure 19, it becomes clear that the spike is generally well recovered for the XAD2 and water fractions (<100%), but the filter fraction is significantly overestimated up to 105 ng (PFODA). This overestimation of the filter fraction is much higher for the first measurement, when compared to the second measurement (Figure 20 Apparent spike recovery (ng) within the filter fraction (F1) of the spiked sampling trains (Meting 1 and 2).), and after bilateral discussions with LAB F2, no potential reason could be identified to date. As a lab audit showed that the extraction procedure was not consistent with the LUC/VI/003 procedure, further validation was requested.

The water fraction shows a decreasing spike recovery with increasing chain length of the PFAS compound, observed both for the PFCA's and PFSA's (similar to the LAB F1 measurements). As this effect is not observed in the long-chain IS recoveries (Figure 15), which are added after sampling, these results suggest that the spike loss is happening during sampling and sample collection. Considering the affinity of long-chain PFAS towards the sampling train glassware (§4.1.3), recovery gains can be expected by (i) thorough rinsing of the glassware during sampling collection (3 times MeOH, 3 times cyclohexane, taking along the sides of the glassware very thoroughly) and (ii) inclusion of compound-specific internal standards. Moreover, spike transfer from the water fraction towards the secondary XAD2 is observed for MePFOSA, EtPFOSA and to a lesser extent for PFNA, PFDA, PFDoDA, PFOS and 6:2 FTS.

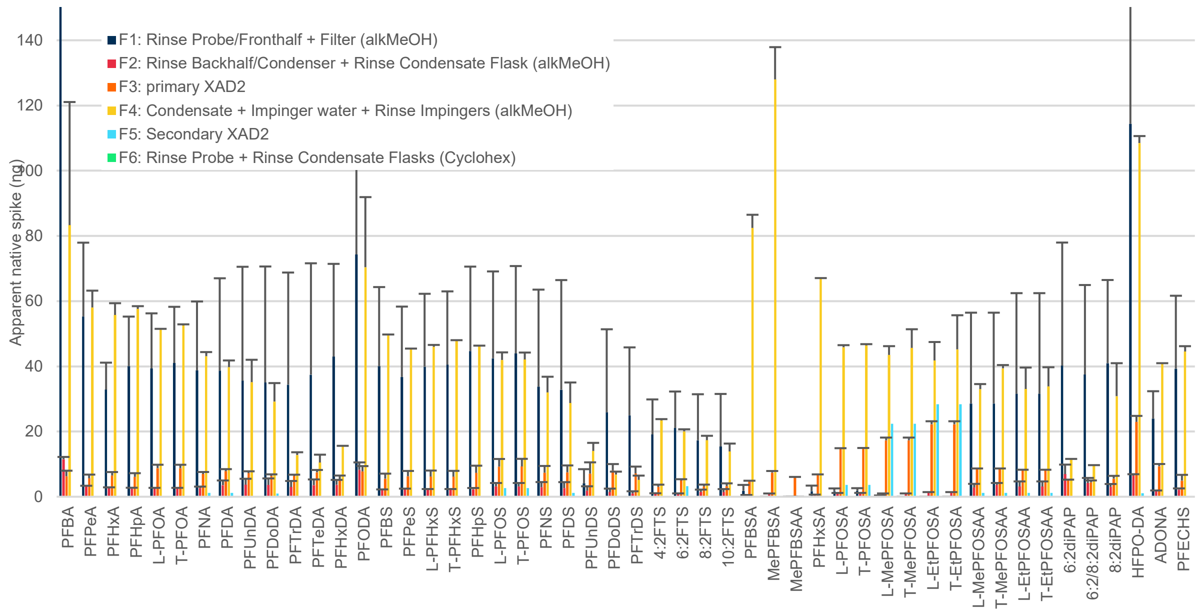


Figure 19 Average apparent spike recovery (ng) within the individual analytical fractions (F1-6) of the spiked sampling trains (T1 and T2). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

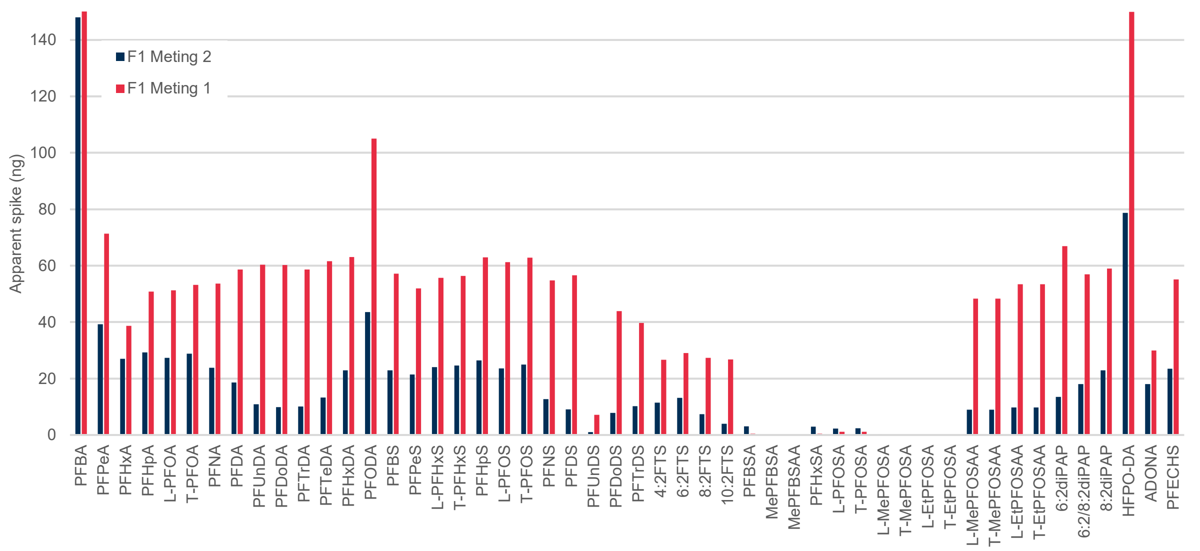


Figure 20 Apparent spike recovery (ng) within the filter fraction (F1) of the spiked sampling trains (Meting 1 and 2).

4.3.4 Quantitative evaluation

The observed spike recovery overestimation in the filter fraction of measurement 1, results in train recovery (%) exceedances and high measurement uncertainties between the duplo measurements, resulting in only 8 quantitative compounds (apparent train recovery 70-120% and measurement uncertainty (U) <50%) as can be seen from Figure 21.

Long-chain PFAS recovery (C9-16; both PFCA's and PFSA's) can be optimized in order to obtain more quantitative compounds.

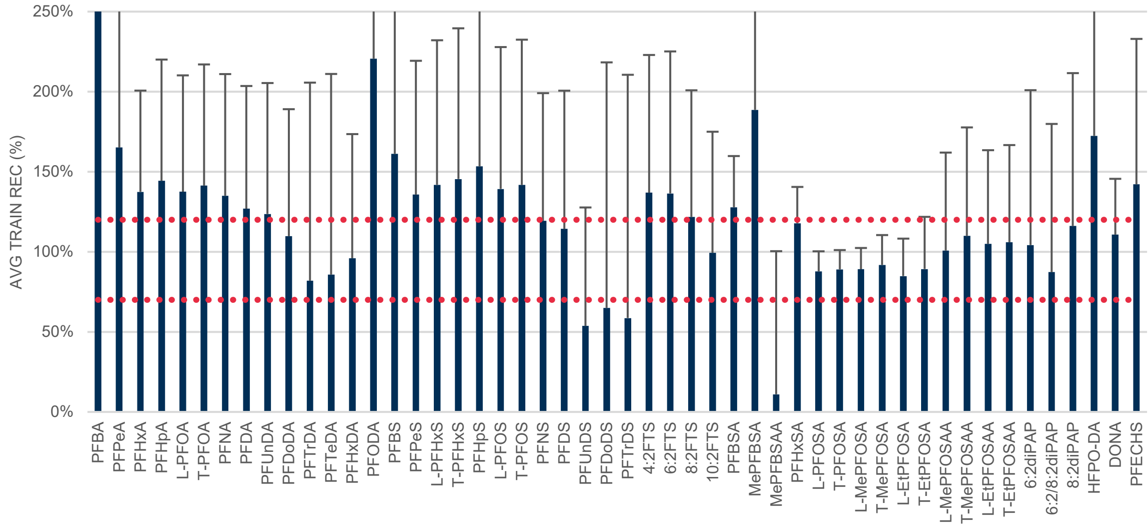


Figure 21 Apparent LAB F2 train recovery (%) with associated error flags representing the measurement uncertainty (U; %) based on the 2 spiked ILC train (T1 and T2) repeats. Red dotted lines denote the quantitative recovery boundaries of 70-120%.

4.4 LAB F3

LAB F3 participated on the first ILC day, with 2 spiked sampling trains (cooled probe). Each train consists of field blank, field sample and post-rinse analytical results and associated QA/QC's. ILC reports of the individual measurements can be found in Annex 6.

4.4.1 QA/QC and LOQ's

In terms of QA/QC's, sampling standard spike recovery was within 50-130% for 13C3-PFBA, 13C8-PFOA and 13C8-PFOS in both field blank and field sample XAD2's from both sampling trains. Internal standard (18) recoveries were good (>20%) for all compounds. 13C-EtPFOSA, 13C-EtPFOSAA, 13C2-6:2PAP, 13C2-8:2PAP and 13C2-6:2diPAP were not considered and PFOSAA, PFDSA, 6:2PAP and 8:2PAP were not quantified. Comparable IS recoveries were observed between the different analytical fractions, with lowest recoveries for the cyclohexane fraction. The breakthrough criterium of 30% was never breached, nor was the field blank criterium (<10%) breached. The post-rinse blank showed no detectable concentrations (<LOQ).

LOQ's were derived from a low calibration standard (signal to noise) and are set at 1 ng for all compounds and all analytical fractions. The compound specific LOQ's are provided in the "LUC_Cooled probe IS LOQ" tab of meting 1 (Annex 6).

- QA/QC's:
  - SS REC 50-130%: OK
  - REC IS (>20%): OK, except for PFBA in medium/field blank
  - Field blank (<10% measured): OK → Medium and field blank <LOQ (1 ng)
  - Breakthrough (<30%): OK
  - Post-rinse: <LOQ (5 ng)

4.4.2 Internal standard (IS) recovery

The observed internal standard recoveries (%) within each analytical fraction are provided in Figure 22 and show good recoveries for all compounds and analytical fractions.

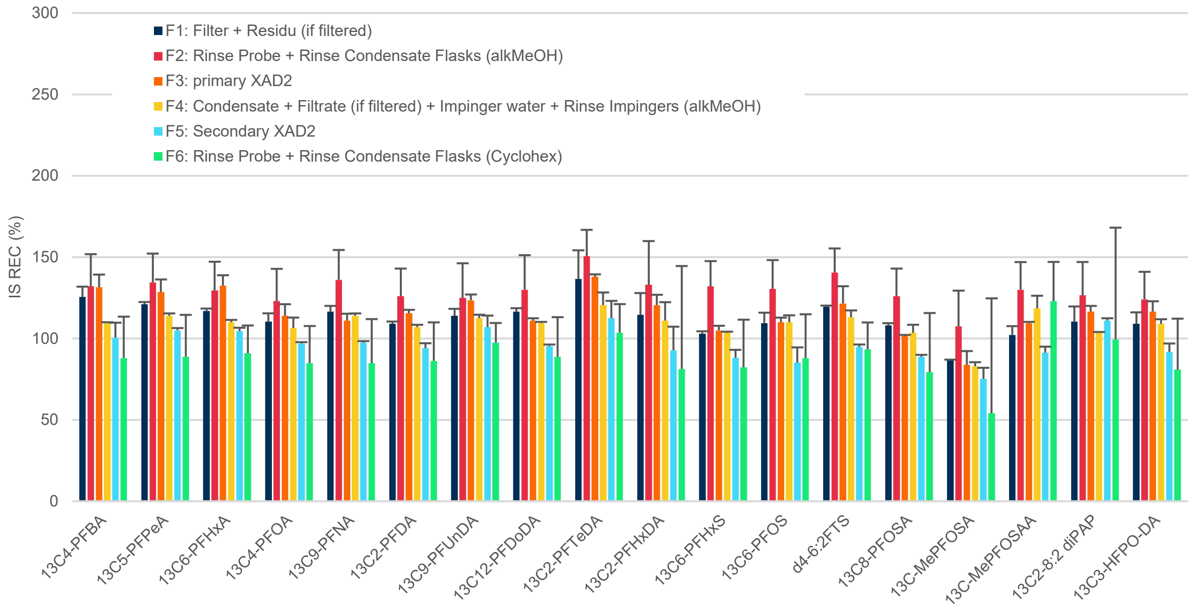


Figure 22 Average internal standard recovery (%) of the 2 spiked sampling trains (T1 and T2), within the different analytical fractions (F1-F6). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.4.3 Native spike recovery

When evaluating the apparent (native) spike recovery (ng) within the different analytical fractions (F1-F6) in Figure 23, it becomes clear that the spike is generally well recovered in the XAD2 and water fractions (glasswool filter was not spiked), except for MePFOSA and EtPFOSA for which we observe spike transfer from the water towards the primary XAD2 (similar to LAB F1 and LAB F2).

Moreover, the water fraction shows a decreasing spike recovery with increasing chain length of the PFAS compound, observed both for PFCA's and PFSA's (similar to the LAB F1 and LAB F2 measurements). As this effect is not observed in the long-chain IS recoveries (Figure 22), which are added after sampling, these results suggest that the spike loss is happening during sampling and sample collection. Considering the affinity of long-chain PFAS towards the sampling train glassware (§4.1.3), recovery gains can be expected by (i) thorough rinsing of the glassware during sampling collection (3 times MeOH, 3 times cyclohexane, taking along the sides of the glassware very thoroughly) and (ii) inclusion of compound-specific internal standards.

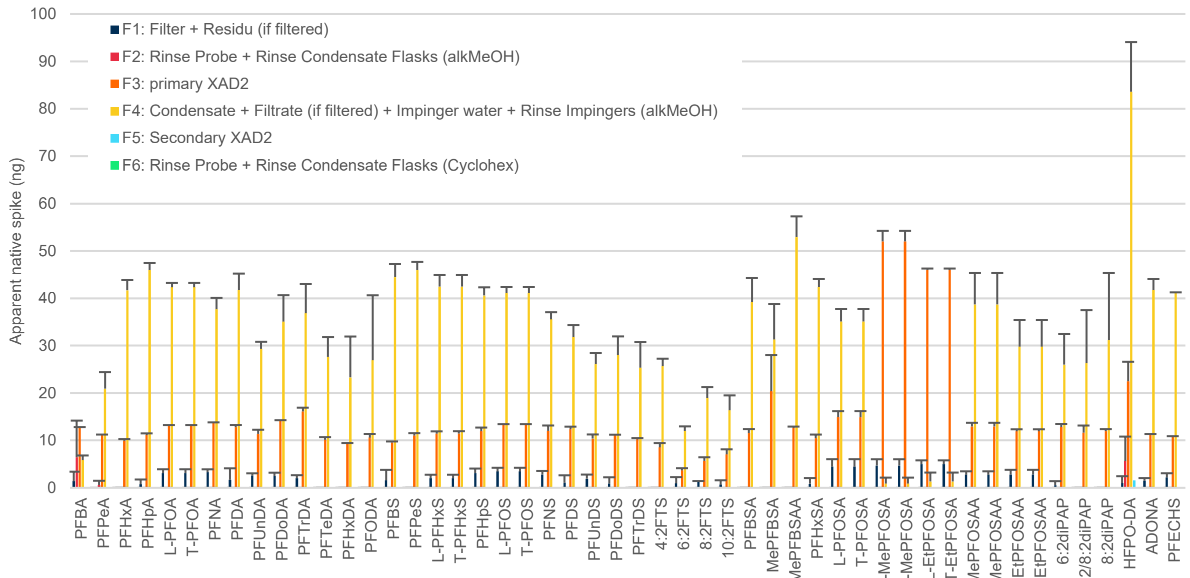


Figure 23 Average apparent spike recovery (ng) within the individual analytical fractions (F1-6) of the spiked sampling trains (T1 and T2). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.4.4 Quantitative evaluation

The apparent train recovery (%) and measurement uncertainty were evaluated on the 2 spiked filter trains (T1 and T2), resulting in 35 quantitative compounds (apparent train recovery 70-120% and measurement uncertainty (U) <50%) as can be seen from Figure 24.

Long-chain PFAS recovery (C9-16; both PFCA's and PFSA's) can be optimized to include more quantitative compounds.

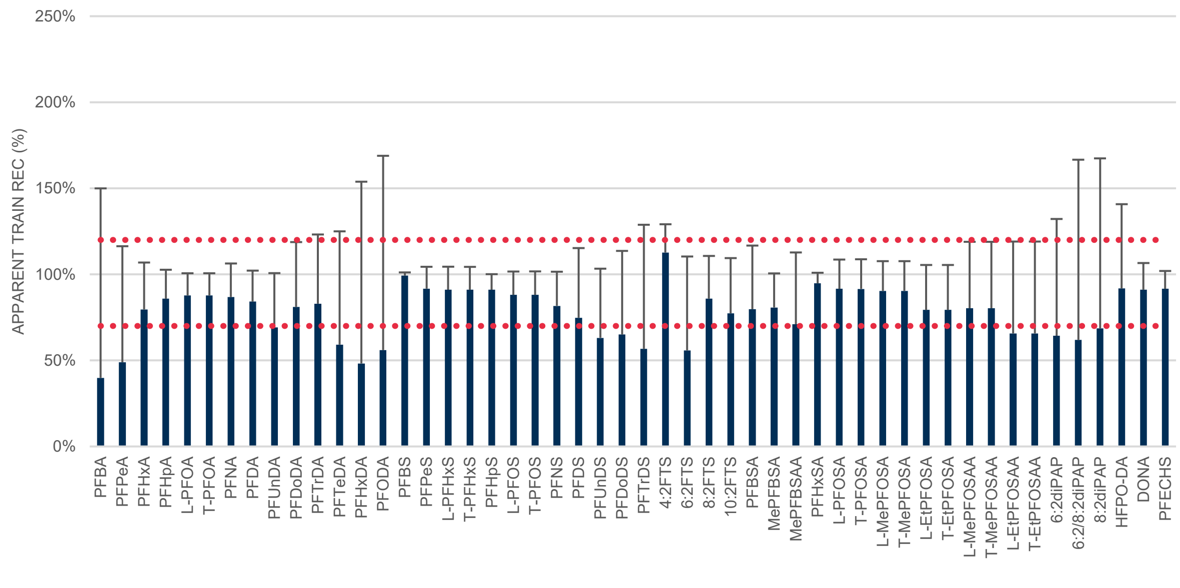


Figure 24 Apparent LAB F3 train recovery (%) with associated error flags representing the measurement uncertainty (U; %) based on the 2 spiked ILC train (T1 and T2) repeats. Red dotted lines denote the quantitative recovery boundaries of 70-120%.

4.5 LAB EU1

LAB EU1 participated on the second ILC day, with 2 spiked sampling trains (cooled probe). Each train consists of field blank, field sample and post-rinse analytical results and associated QA/QC's. LAB EU1 only considers 4 of the 6 LUC/VI/003 analytical fractions (no filter and cyclohexane fraction). ILC reports of the individual measurements can be found in Annex 7.

4.5.1 QA/QC and LOQ's

In terms of QA/QC's, no sampling standard spikes were added by LAB EU1. Internal standard (23) recoveries were good (>20%), except for d3-MePFOSA, d5-EtPFOSA, d3-MePFOSAA and d5-EtPFOSAA in the solvent (MeOH) and/or water fractions. PFOSAA, PFDSA, 6:2PAP and 8:2PAP were not quantified. Comparable IS recoveries were observed between the different analytical fractions, with lowest recoveries for the cyclohexane fraction. The breakthrough criterium of 30% was never breached, nor was the field blank criterium (<10%) breached with a maximum of 0.71 ng for PFOSA. The post-rinse blank (1 aggregated MeOH rinse sample) showed no detectable (<LOQ) or low concentrations up to 0.89 (PFTeDA).

LOQ's were derived based on a low calibration standard and varied between 0.05 ng and 0.333 ng. Similar LOQ's were reported for the different analytical fractions. The compound specific LOQ's are provided in the "LUC_OTM-45 variant IS LOQ" tab of meting 1 (Annex 7).

- QA/QC's:
  - SS REC 50-130%: OK
  - REC IS (>20%): OK, except for PFBA in medium/field blank
  - Field blank (<10% measured): OK → Medium and field blank <LOQ (1 ng)
  - Breakthrough (<30%): OK
  - Post-rinse: <LOQ (5 ng)

4.5.2 Internal standard (IS) recovery

The observed internal standard recoveries (%) within each analytical fraction are provided in Figure 25 and show good recoveries for all compounds and analytical fractions, except for d3-MePFOSA, d5-EtPFOSA, d3-MePFOSAA and d5-EtPFOSAA in the solvent (MeOH) and/or water fractions (Figure 25). Note that the analytical fractions of LAB EU1 (4) deviate from the LUC/VI/003 procedure. Moreover, no filter and cyclohexane fraction are included.

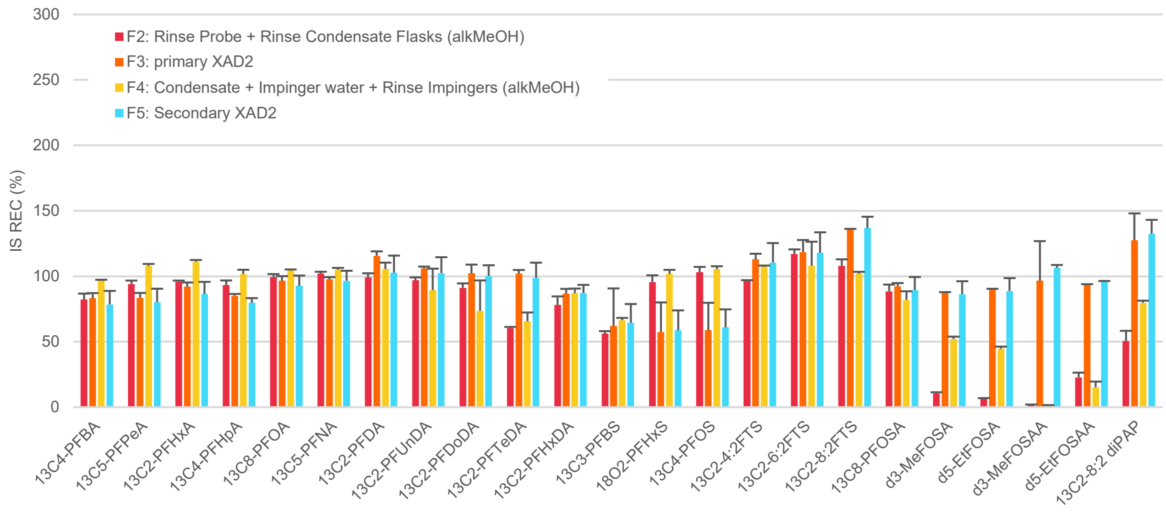


Figure 25 Average internal standard recovery (%) of the 2 spiked sampling trains (T1 and T2), within the different analytical fractions (F1-F6). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.5.3 Native spike recovery

When evaluating the apparent (native) spike recovery (ng) within the different analytical fractions (F2-F5) in Figure 26, it becomes clear that the spike is generally well recovered in the XAD2 and water fraction (no filter present/spiked), except for PFBA, PFODA, PFPeS, PFBSA and MePFBSA which were overestimated in the water fraction. Although spike transfer from the water fraction towards the primary XAD2 seems to have occurred for MePFOSA and EtPFOSA, the impact seems smaller compared to LAB F1, LAB F2 and LAB F3.

The water fraction shows decreasing spike recoveries with increasing chain length of the PFAS compound, observed both for PFCA's and PFSA's (similar to the LAB F1, LAB F2 and LAB F3 measurements). As this effect is not observed in the long-chain IS recoveries (Figure 25), which are added after sampling, these results suggest that the spike loss is happening during sampling and sample collection. Considering the affinity of long-chain PFAS towards the sampling train glassware (§4.1.3), recovery gains can be expected by (i) thorough rinsing of the glassware during sampling collection (3 times MeOH, 3 times cyclohexane, taking along the sides of the glassware very thoroughly) and (ii) inclusion of compound-specific internal standards.

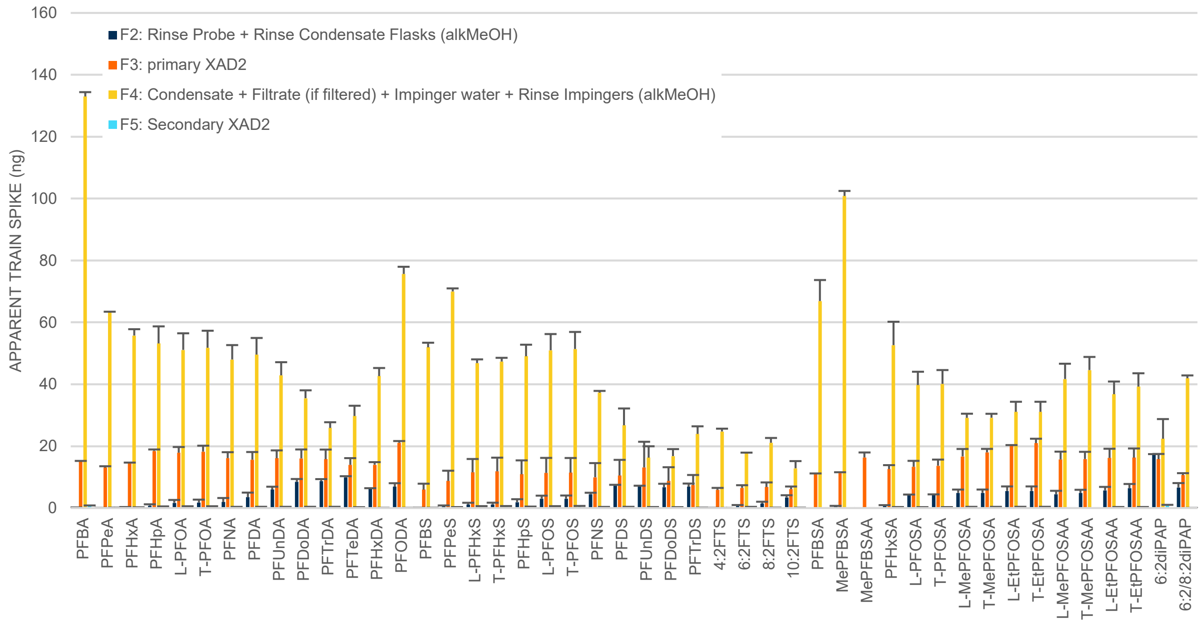


Figure 26 Average apparent spike recovery (ng) within the individual analytical fractions (F1-6) of the spiked sampling trains (T1 and T2). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.5.4 Quantitative evaluation

The apparent train recovery (%) and measurement uncertainty were evaluated on the 2 spiked filter trains (T1 and T2), resulting in 39 quantitative compounds (apparent train recovery 70-120% and measurement uncertainty (U) <50%) as can be seen from Figure 27.

Long-chain PFAS recovery (C9-16) of the PFSA's can be further optimized to include more quantitative compounds.

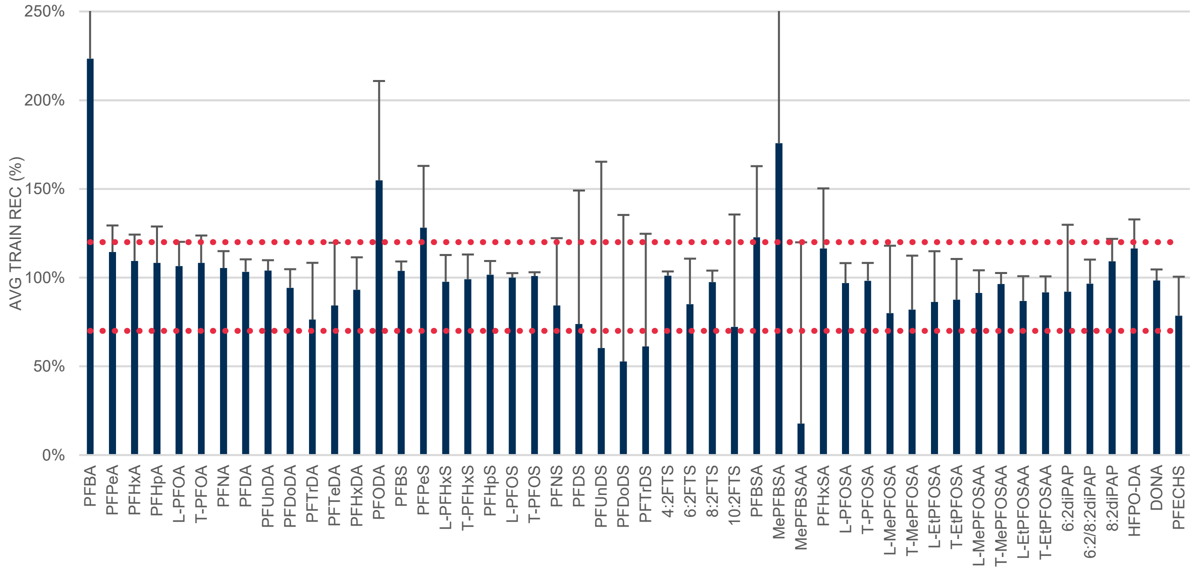


Figure 27 Apparent LAB EU1 train recovery (%) with associated error flags representing the measurement uncertainty (U; %) based on the 2 spiked ILC train (T1 and T2) repeats. Red dotted lines denote the quantitative recovery boundaries of 70-120%.

4.6 LAB EU2

LAB EU2 participated on the second ILC day, with 2 spiked sampling trains (T1, T2) following the US EPA OTM-45 procedure (2021 version). LAB EU2 considers 4 analytical fractions (no cyclohexane fraction), 2 instead of 3 sampling standard (SS) recoveries and 15 internal standards. PFHxDA, L-PFOS, L-PFHxS, PFBSA, MePFBSA, MePFBSAA, PFHxSA, L-(Me/Et-)PFOSA's, (Me-/Et-)PFOSAA's, PFDSA, PAP's, diPAPs and PFECHS were not quantified. Each train consists of field blank, field sample and post-rinse analytical results and associated QA/QC's. ILC reports of the individual measurements can be found in Annex 8.

4.6.1 QA/QC and LOQ's

In terms of QA/QC's, the applied sampling standard (SS) recoveries of 13C8-PFOA, 13C8-PFOS were good (50-130%) for both sampling trains. Internal standard (15) recoveries were good (>20%) but IS compounds that exhibited recovery issues for other labs (MePFOSA, EtPFOSA, MePFOSAA) were not considered by LAB EU2. and EtPFOSAA and PFOSAA, PFDSA, 6:2PAP and 8:2PAP were not quantified. The filter fraction exhibits the lowest IS recovery. PFBA was detected in the medium (104 ng) and field (57 ng) blank XAD2. The breakthrough criterium of 30% was never breached, except for 6:2FTS (15.4 ng; 47%) in T1 and PFOSA (18 ng; 44%) in T2. The field blank criterium (<10%) was breached for PFBA (57 ng; 25%) and 6:2FTS (8.4 ng; 55%). The post-rinse blank showed detectable concentrations in train 2 (line 2) for PFBA (23 ng), PFHpA (7.1 ng), T-PFOA (8 ng), PFNA (12.1 ng), PFDA (15 ng), PFUnDA (11.9 ng), PFDoDA (10.4 ng), PFTrDA (6.2 ng), T-PFOS (14.4 ng), PFNS (12.4 ng), PFDS (15.6 ng) PFUnDS, (9.9 ng), PFDoDS (6.3 ng).

LOQ's were determined by the lowest value on the calibration curve. To validate this value, a quality control (QC) is performed at the end of each sequence, with a maximum deviation of 30% allowed. The limit of quantification for each fraction or media is calculated by multiplying the analytical LOQ by the maximum volume for each fraction. For filter and XAD2, the LQ is based on the highest volume of extraction obtained. For solvent, the LOQ is expressed in ng/L. This procedure resulted in LOQ's ranging between 2.3-120 ng/L depending on the analytical fraction.

- QA/QC's:
    - SS REC 50-130%: OK PFOA/PFOS (no PFBA)
    - REC IS (>20%): OK, NOK for filter line 1 (leak on ASE cell)
    - Field blank (<10% measured): NOK for PFBA and 6:2FTS
    - Breakthrough (<30%): NOK for PFBA, PFHxA, 6:2FTS line 1, NOK for PFOSA line 2
    - Post-rinse: OK for line 1 (high LOQ's!), NOK for line 2 (5-23 ng)

4.6.2 Internal standard (IS) recovery

The observed internal standard recoveries (%) within each analytical fraction are provided in Figure 28 and show good recoveries for all compounds and analytical fractions. Lowest recoveries are observed in the filter fraction (Figure 28). Note that the analytical fractions of LAB EU2 (4) deviate from the LUC/VI/003 procedure (no cyclohexane fraction).

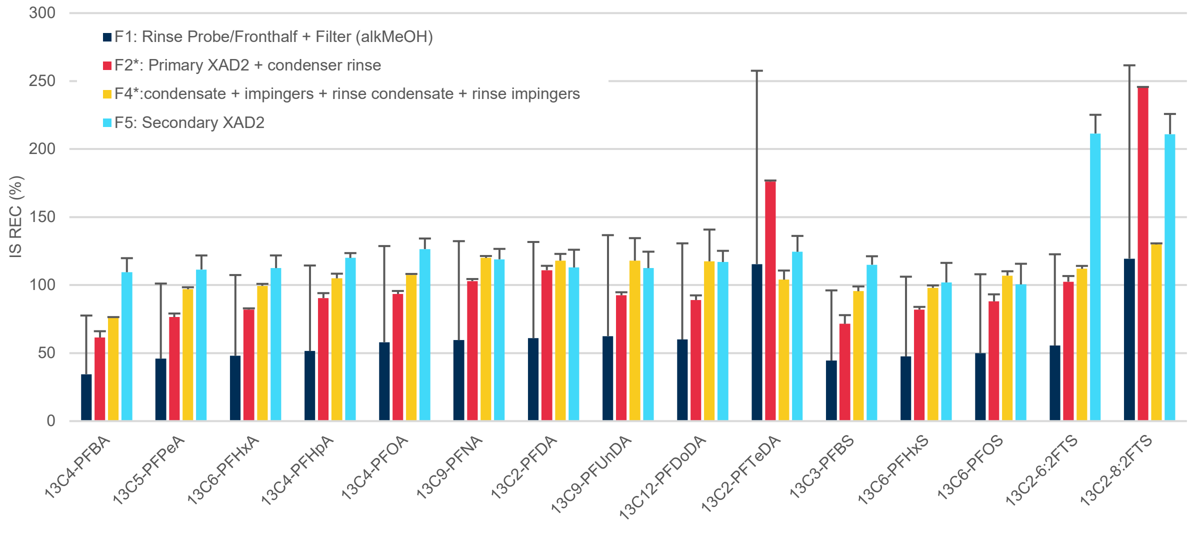


Figure 28 Average internal standard recovery (%) of the 2 spiked sampling trains (T1 and T2), within the different analytical fractions (F1-F5). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.6.3 Native spike recovery

When evaluating the apparent (native) spike recovery (ng) within the different analytical fractions (F1-F5) in Figure 29, highly variable recoveries are observed in the spike fractions. PFBA and HFPO-DA are significantly overestimated in all analytical fractions, while some of the compounds are only detected in one/some of the spiked fractions (e.g. PFPeA, PFOA, PFODA) due to the high LOQ's and spike transfer to the secondary XAD2 module is observed for several compounds (e.g. PFBA, 6:2FTS, PFPeS, ADONA).

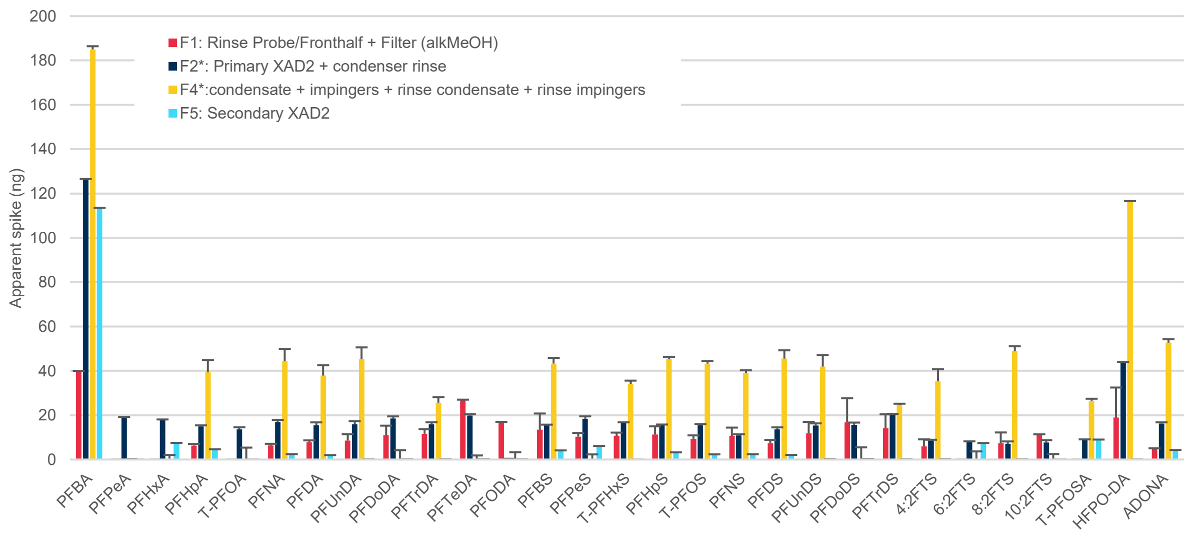


Figure 29 Average apparent spike recovery (ng) within the individual analytical fractions (F1-6) of the spiked sampling trains (T1 and T2). Error flags denote the standard deviation between the 2 spiked sampling trains (T1 and T2).

4.6.4 Quantitative evaluation

The low number of internal standards and high LOQ's result in varying recoveries in the various fractions (Figure 29). As a results, apparent train recovery (%) and measurement uncertainty result in only 9 quantitative compounds (apparent train recovery 70-120% and measurement uncertainty (U) <50%) as can be seen from Figure 30. Both sampling and analytical optimisations will be needed in order to improve the apparent recovery and associated measurement uncertainty of the considered PFAS compounds.

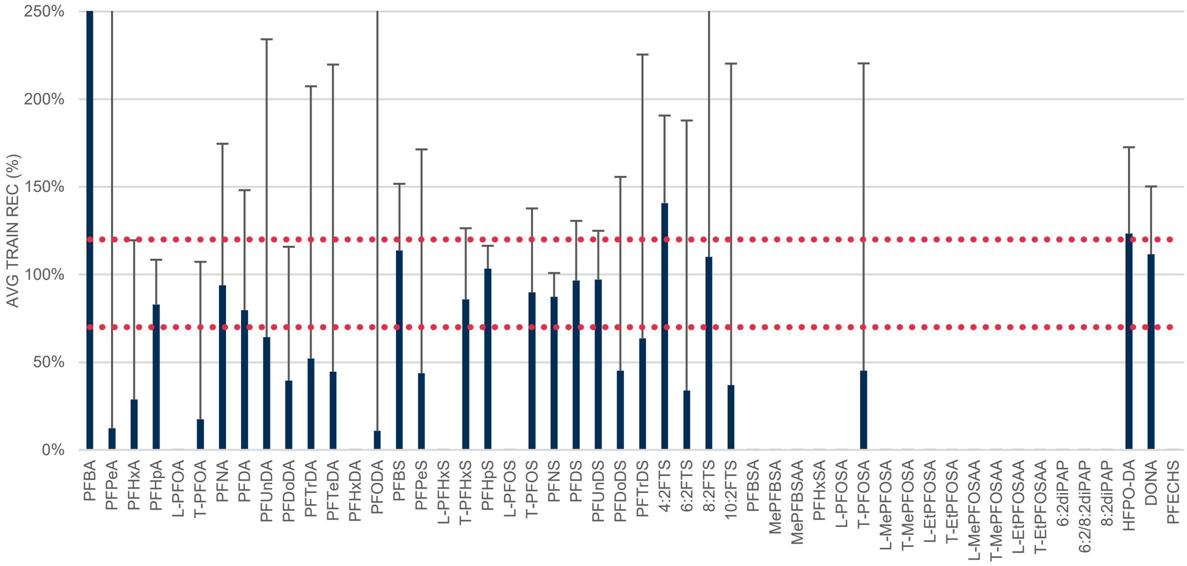


Figure 30 Apparent LAB EU2 train recovery (%) with associated error flags representing the measurement uncertainty (U; %) based on the 2 spiked ILC train (T1 and T2) repeats. Red dotted lines denote the quantitative recovery boundaries of 70-120%.

5 CONCLUSION

This interlaboratory comparison (ILC) aimed at evaluating the different sampling train variants defined in the Flemish LUC/VI/003 compendium procedure (OTM-45, OTM-45 variant and cooled probe) and applied by the commercial labs in Flanders (SGS, Eurofins, Tauw). Two international labs (INERIS and ANECO) participated with respectively a US EPA OTM-45 and cooled probe variant procedure.

The five labs participated with duplo sampling trains, using a sampling train variant of choice. The applied collection media in the sampling trains (filter, XAD2 and water) were spiked by VITO with 50 native (C4-18) PFAS compounds following the WAC/IV/A/0/25 scope and sampled preconditioned air (100°C and 10% RH) following the LUC/VI/003 procedure for sampling, sample collection and prep. INERIS and ANECO had specific deviations from the LUC/VI/003 procedure.

Reported results were evaluated for QA/QC's, internal standard and native spike recoveries (%) and observed measurement uncertainty (U) between the duplo measurements. The number of quantitative compounds (apparent train recovery 70-120% and measurement uncertainty (U) <50%) was considered as quantitative evaluation criterium.

In general, the applied collection media (filter, XAD2 and water) retained the spiked PFAS compounds rather well. Nevertheless, some spike transfer from the water fraction towards the secondary XAD2 was observed for MePFOSA, EtPFOSA and to a lesser extent for PFNA, PFDA, PFDoDA, PFOS and 6:2 FTS for multiple labs (VITO, LABS F1, F2 and F3).

A varying number of internal standards (15-28) was considered by the participating labs, which generally recovered quite well within the different analytical fractions, except for 13C-MePFOSA,13C-EtPFOSA, 13C-MePFOSAA, 13C-EtPFOSAA, 13C2-6:2FTS and 13C2-8:2diPAP. The hardest analytical fraction (fraction with lowest IS recovery) varied from lab to lab (XAD2, cyclohexane and filter).

All participating labs showed decreasing recoveries with increasing alkyl chain length (both PFCA's and PFSA's) indicating high affinity of long-chain PFAS towards the sampling train glassware (§4.1.3) Recovery improvements can be obtained by (i) thorough rinsing of the glassware during sampling collection (3 times MeOH, 3 times cyclohexane, including the sides of the glassware very thoroughly) and (ii) inclusion of more compound-specific internal standards.

The number of quantitative compounds with apparent train recoveries between 70-120% and a measurement uncertainty <50%, varied between 9 and 39 which shows the need for harmonized sampling and analytical procedures to accurately quantify PFAS in emissions and guarantee comparability and repeatability of the results. The number of quantitative compounds resulting from the sampling train variants defined in the LUC/VI/003, varied between 8-24 (OTM-45 variant; LAB F1 and F2), 35 (cooled probe; LAB F3) and 38 (OTM-45; VITO).

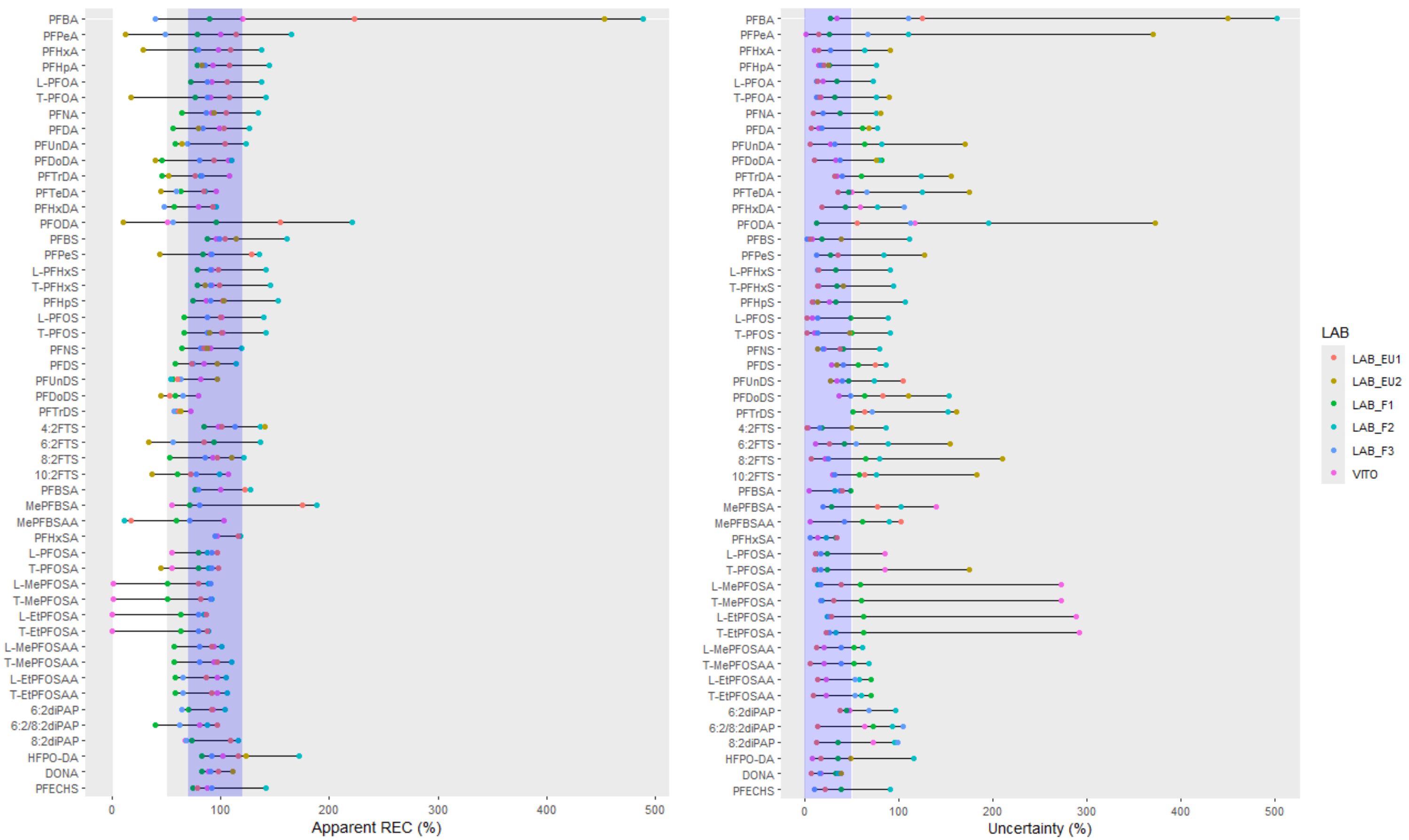


Figure 31 Lab comparison of observed apparent (total train) recoveries (%; left) and measurement uncertainties (%; right) for each PFAS compound. Blue highlighted areas denote the quantitative recovery (70-120%) and uncertainty (<50%) objectives.

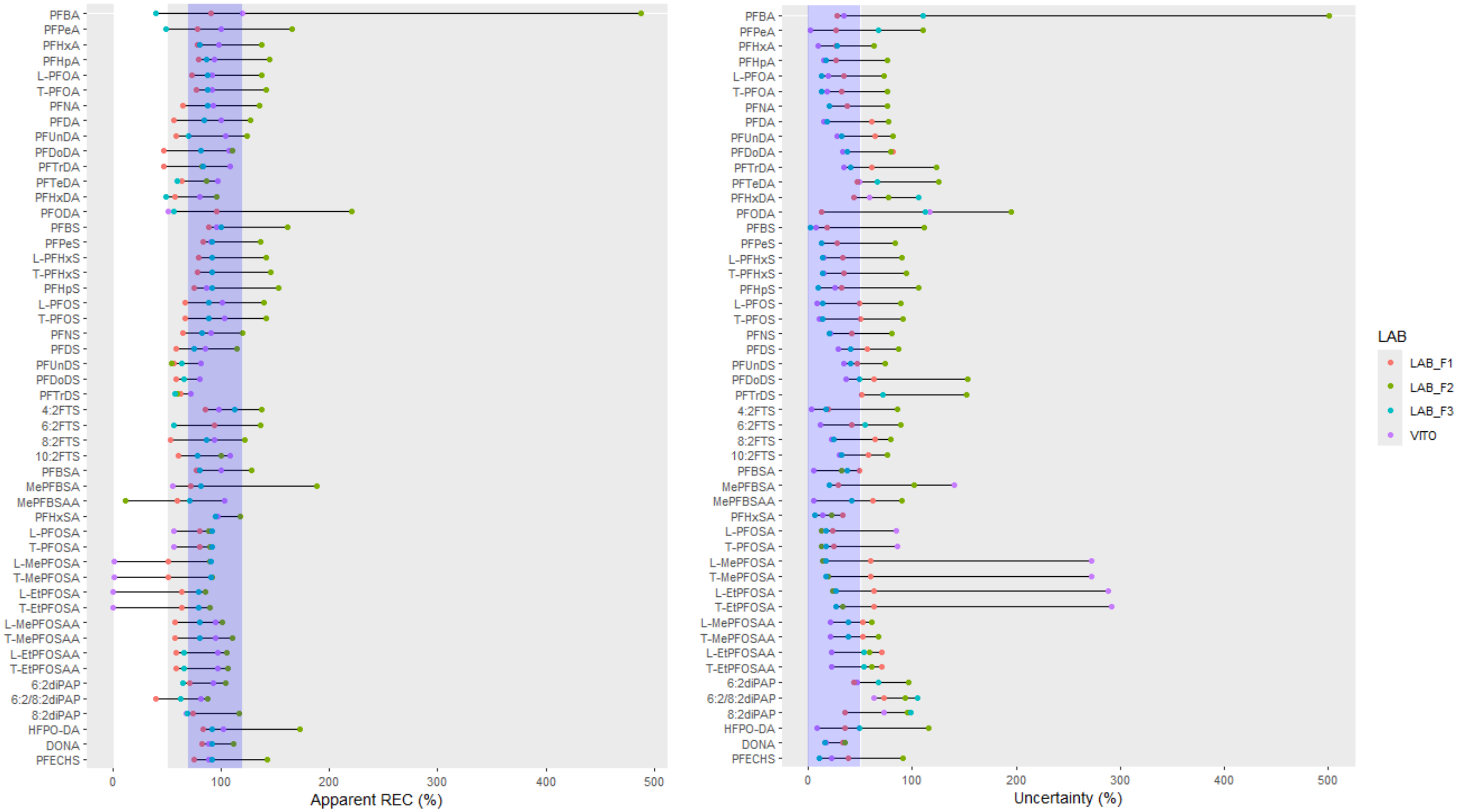


Figure 32 Flemish lab comparison of observed apparent (total train) recoveries (%; left) and measurement uncertainties (%; right) for each PFAS compound. Blue highlighted areas denote the quantitative recovery (70-120%) and uncertainty (<50%) objectives.

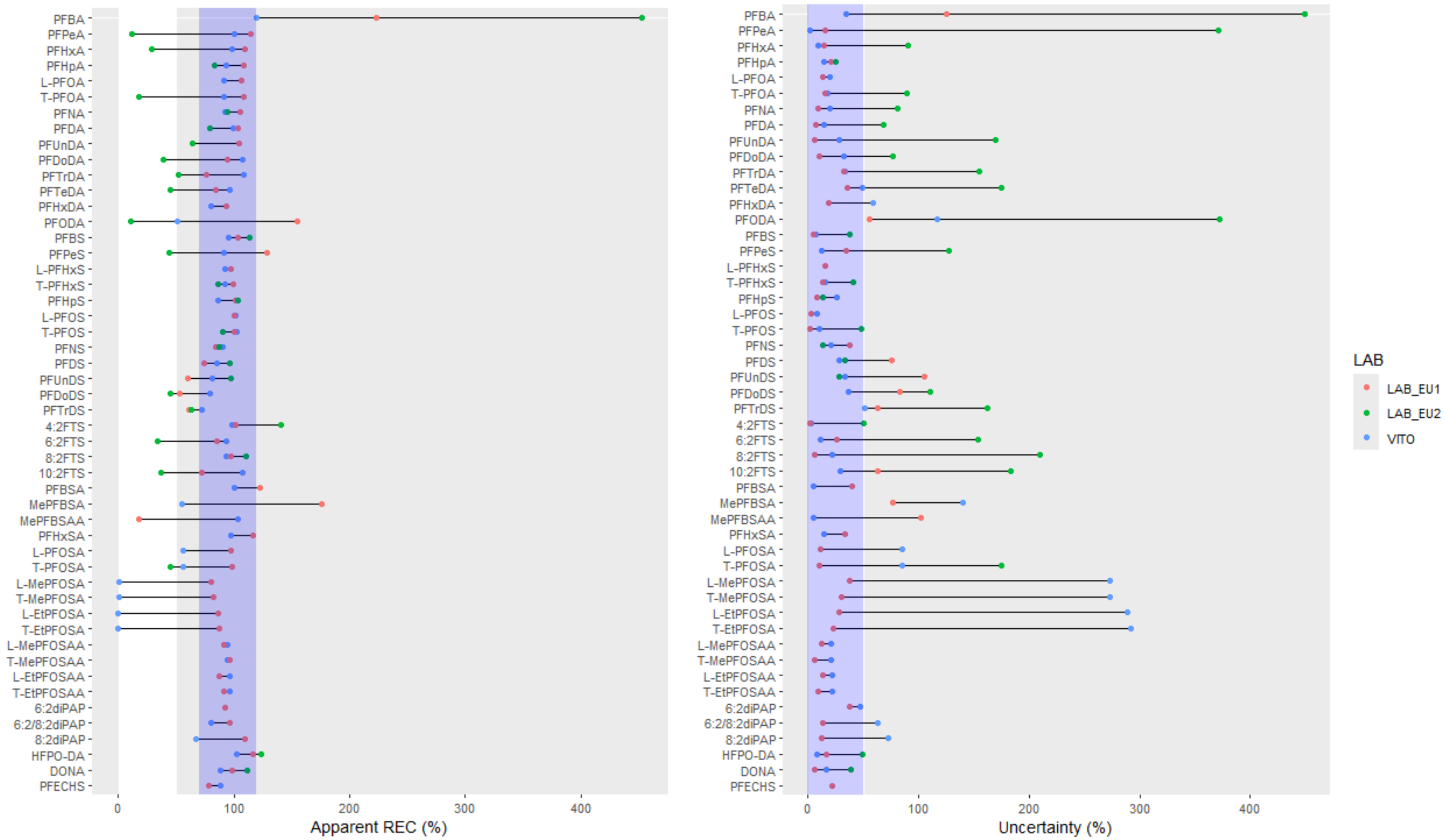


Figure 33 International lab comparison of observed apparent (total train) recoveries (%; left) and measurement uncertainties (%; right) for each PFAS compound. Blue highlighted areas denote the quantitative recovery (70-120%) and uncertainty (<50%) objectives.

LIST OF LITERATURE

EPA. (2021). Other Test Method 45 (OTM-45) Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources. https://www.epa.gov/sites/production/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

Hofman, J., Baeyens, B., Aerts, W., Jacobs, G., de Carvalho, A. R., Van den Bergh, G., Voorspoels, S., & Otten, G. (2025). Quantification of per- and polyfluoroalkyl substances (PFAS) in air emissions: An interlaboratory comparison. Chemosphere, 380, 144449. https://doi.org/10.1016/j.chemosphere.2025.144449

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LUC. (2025). Compendium voor de monsterneming, meting en analyse van lucht (LUC): Bepaling van de concentratie aan per- en polyfluoralkylverbindingen (PFAS) in een geleide gasstroom. Compendium for the sampling, measurement and analysis of air (LUC)(LUC/VI/003). https://reflabos.vito.be/2025/LUC_VI_003.pdf

ANNEX 1

ILC reporting template

ILC2024 PFAS
Reporting Template_F

ANNEX 2

Individual VITO measurements on 20/2/2024 (T1, T2, T3 and T4) and 21/2/2024 (T5, T6 and T7)

ILC2024 PFAS VITO meting 1.xlsx

ILC2024 PFAS VITO meting 2.xlsx

ILC2024 PFAS VITO meting 3.xlsx

ILC2024 PFAS VITO meting 4.xlsx

ILC2024 PFAS VITO meting 5.xlsx

ILC2024 PFAS VITO meting 6.xlsx

ILC2024 PFAS VITO meting 7.xlsx

ANNEX 3

Additional PFAS analyses to evaluate potential contamination sources:

- Filters

R11400_blanco_filters
_reported_20240521_(

- Water for air conditioning of ringlab

R11316_water_report
ed_20240417_ARC.xlsı

- Heated line (cold/warm, MeOH/cyclohexane)

R11127_R11132_R111
35_spoelteflon_2_repc

ANNEX 4

Individual LAB F1 measurements conducted on 20/2/2024 (T1 and T2)

ILC2024 PFAS F1 meting 1.xlsx

ILC2024 PFAS F1 meting 2.xlsx

ANNEX 5

Individual LAB F2 measurements conducted on 20/2/2024 (T1 and T2)

F2-meting1_ILC2024
PFAS Reporting Temp

F2-meting2_ILC2024
PFAS Reporting Temp

ANNEX 6

Individual LAB F3 measurements conducted on 20/2/2024 (T1 and T2)

ILC2024 PFAS
Reporting Template_v

ANNEX 7

Individual LAB EU1 measurements on 21/2/2024 (T1 and T2)

EU1_1_ILC2024 PFAS Reporting Template_v

EU1_2_ILC2024 PFAS Reporting Template_v

ANNEX 8

Individual LAB EU2 measurements on 21/2/2024 (T1 and T2)

EU2_ILC2024 PFAS
Reporting Template_F

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