

# Evaluating Membrane Filters for Accurate PFAS Air Emission Analysis with OTM-45: Laboratory and Field Investigations



Scan for more OTM-45 data!

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## Introduction

Perfluoroalkyl substances (PFAS) are a class of chemicals utilized in a variety of industries. Their broad use has unfortunately led to persistent accumulation in environmental matrices. Further, mounting evidence of negative health impacts of PFAS combined with regulations evolving at an unprecedented pace have posed a significant analytical challenge.

### Rapidly evolving regulations and new matrices

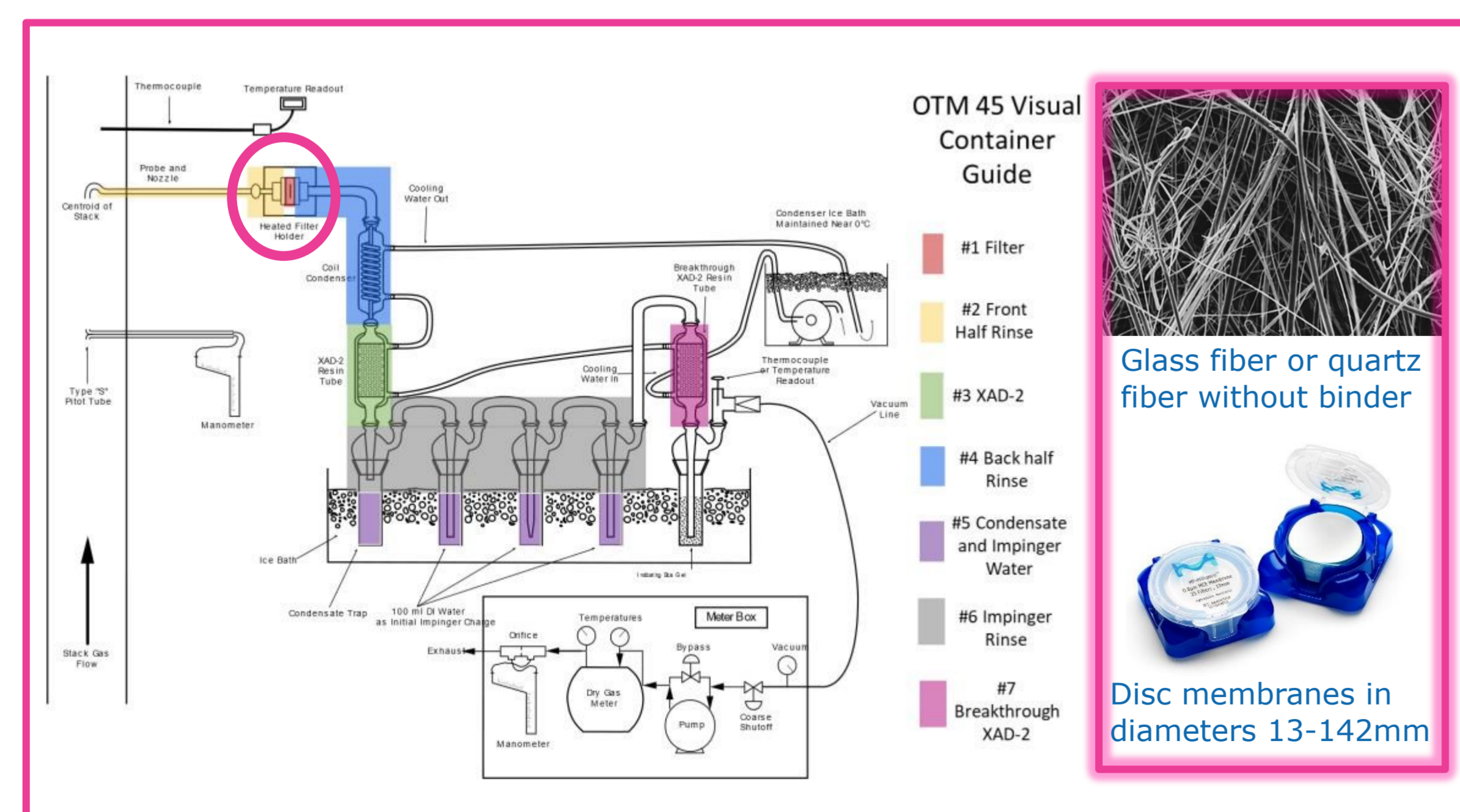
Agencies across the globe have taken action, leading to a recent uptick in analytical methods for PFAS. As drinking water methods were established in testing labs, there was a shift in focus to particulate-laden environmental waters and air. Many of these newer methods require filtration sample preparation to clear samples of particulates or collect particulate phase PFAS. Selected methods involving filters are listed in **Table 1**.

**Table 1:** Selected PFAS methods that involve filters

Method(s)	Matrix/Matrices	Sample Preparation	Analytical Method
ASTM D7968-17a	Environmental solids	Solvent extraction, <b>filtration</b>	LC-MS/MS
ASTM D7979-19	Water matrix (no drinking water)	Solvent extraction, <b>filtration</b>	LC-MS/MS
FDA C-010.03	Foods	QuEChERS, <b>filtration</b>	LC-MS/MS
OTM-45	Stationary sources (Air emissions)	Sampling train: <b>filtration</b> (particulates); Impingers (gaseous)	LC-MS/MS
OTM-50	Stationary sources	Sampling train similar to OTM-45	GC-MS/MS
ASTM D8535-23	Soil, Biosolids	Solvent extraction, <b>filtration</b>	LC-MS/MS
EPA 1633	Aqueous, soil, biosolids, sediment, tissue	SPE, <b>filtration</b>	LC-MS/MS

### OTM-45 is the first method to analyze air matrices

OTM-45<sup>1</sup>, for PFAS in emissions from stationary sources, is based on existing EPA test methods and involves a complex sampling train to collect seven stack gas fractions. The first fraction is a heated filter, critical to collecting particulate phase PFAS (**Fig. 1**). As with any consumable, key considerations of membrane filters are that they (1) **do not introduce PFAS contaminants** into the analysis, and (2) **do not bind PFAS compounds** leading to unanticipated losses<sup>2</sup>.



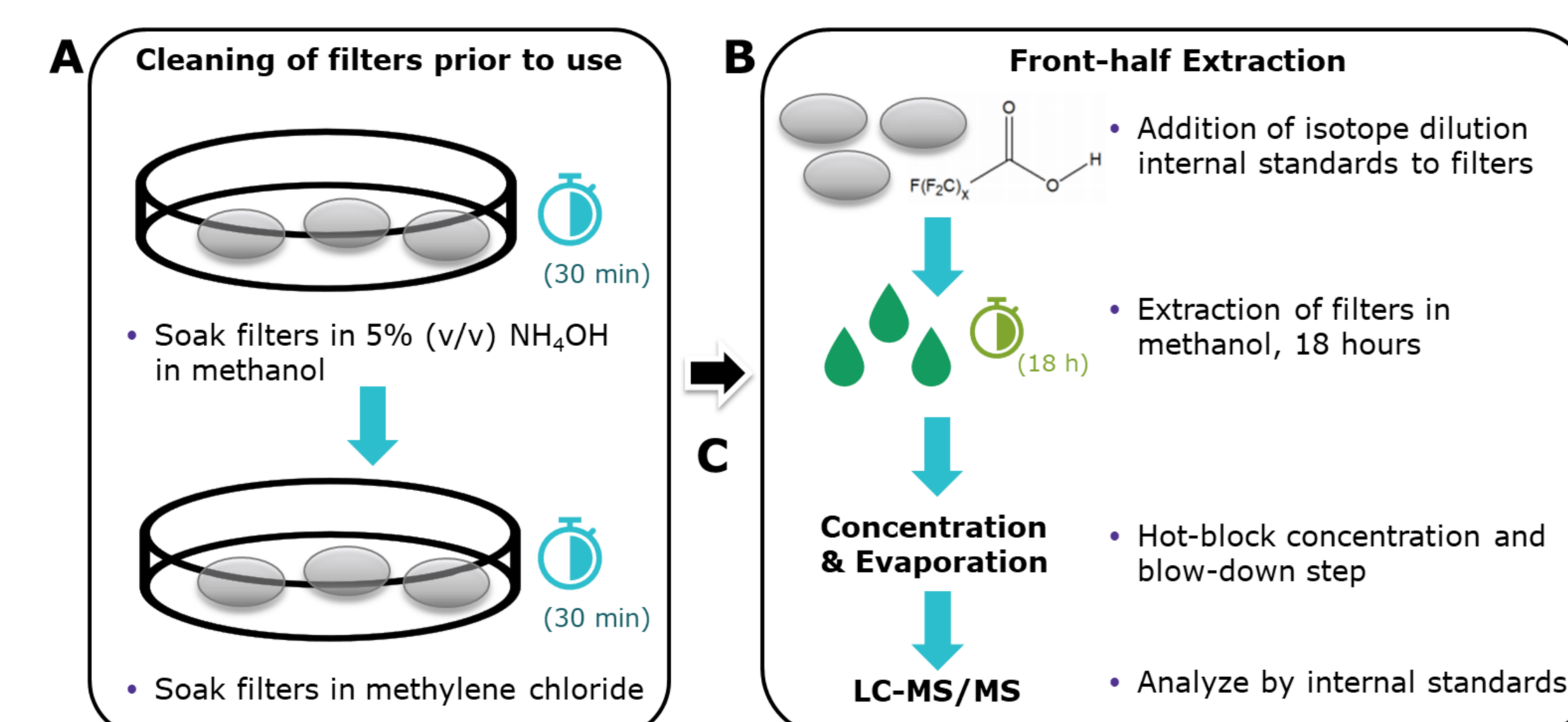
**Fig. 1:** OTM-45 sampling train<sup>1</sup>, the filter fraction in red. To the right is a SEM image of the recommended filter to use for sampling, a glass fiber disc membrane (GFF).

Thus, the goal of this study was to evaluate stability of glass fiber filters (GFFs) for OTM-45 through (1) **laboratory cleaning assessments** and (2) **field pilot investigations**.

## Experimental

A schematic of the methods used to first, analyze cleanliness of Millipore® AP-40 glass fiber filters (GFFs) compared with GFFs from another manufacturer (MFR2), and second, perform field pilot studies at a pyrolyzer site (both in collaboration with Eurofins, Knoxville, TN), is shown in **Fig. 2A-B**.

Membranes, 90 mm diameter, were cleaned with basic methanol and methylene chloride according to internal cleanliness protocols (**Fig. 2A**). For cleanliness tests, these “blank” GFFs were spiked with C-13 labeled standards and analyzed with LC-MS/MS by internal standards after front-half (FH) extraction (**Fig. 2B**) without sampling using the OTM-45 sampling train. For field pilot tests, cleaned GFFs were sent directly to the pyrolyzer site for sampling with the sampling train (**Fig. 2C**) before FH extraction and LC-MS/MS analysis by internal standards. A second pilot site at a scrubber was also tested.



**Fig. 2:** Schematic of testing method. For cleanliness, the cleaning process of GFFs (**A**) was followed by FH extraction of OTM-45 (**B**). For field pilot tests, cleaned GFFs were sent to the sampling train (**C**) before FH extraction.

## Results

### No PFAS contamination detected above reporting limit (RL) in any GFF tested on a per-disc basis<sup>3</sup>

In pooled samples (n=3 discs), however, PFHxA and PFOS were detected in GFFs from both manufacturers between RL and method detection limit (MDL). PFHxA was detected above RL (1.82-2.04 ng/sample). *Data not shown*, see QR code.

### After sampling at a pyrolyzer, PFAS hits for both manufacturers were on the same order of magnitude with the exception of PFDA<sup>3</sup>

Of the two runs studied at the pilot site, R1 with Millipore® AP-40 GFFs and R2 with GFF from MFR2, most of the hits detected on a per-disc basis (9 hits above RL in R1 and 10 in R2) were shorter chained perfluoroalkyl carboxylic acids (PFCAs) (**Table 2**). For PFDA, 1.28 ng and 0.599 ng were detected in R1 and R2, respectively. More variation was observed between GFF runs in quantification of PFAS categories other than PFCAs. Similar trends for the scrubber were observed.

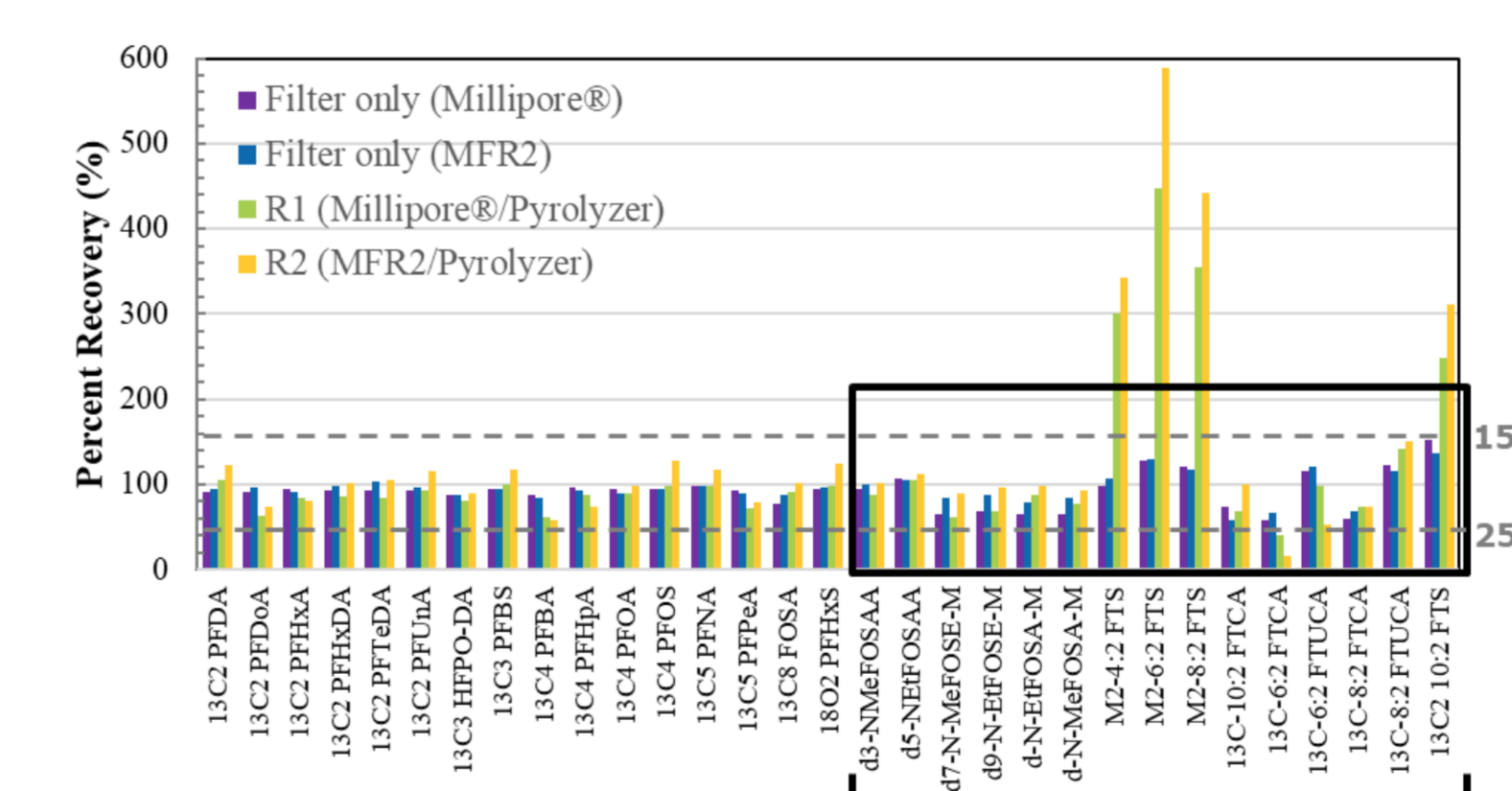
For both GFFs, recovery of C-13 labeled standards was compared between the cleanliness and field pilot tests (**Fig. 3**). For many compounds, recoveries were within acceptable QC range, 25-150%, and differences were observed with compounds that did not have 1:1 direct internal standards or have been known to cause difficulties in quantification, including FTUCA intermediates.

**Table 2:** Comparison of PFAS detected at a pyrolyzer site by FH extraction and LC-MS/MS analysis, of samples collected using Millipore® AP-40 GFF (R1) and GFF from MFR2 (R2). *Showing hits only\**.

Compound	RL (ng/)	MDL (ng/)	R1/FH (Millipore®)	R2/FH (MFR2)
<b>Perfluoroalkyl Carboxylic Acids (PFCAs)</b>				
Perfluoro-n-heptanoic acid (PFHpA) <sup>a</sup>	0.99	0.62	<b>2.43</b>	<b>1.41</b>
Perfluoro-n-butyric acid (PFBA)	1.98	1.29	<b>6.57 (I)</b>	<b>3.05 (I)</b>
Perfluoro-n-pentanoic acid (PFPeA)	0.99	0.18	<b>1.95</b>	<b>1.45</b>
Perfluoro-n-hexanoic acid (PFHxA)	0.99	0.21	<b>3.72</b>	<b>3.42</b>
Perfluoro-n-octanoic acid (PFOA)	0.99	0.65	<b>9.12</b>	<b>7.61</b>
Perfluoro-n-nonanoic acid (PFNA)	0.99	0.08	<b>1.98</b>	<b>1.17</b>
Perfluoro-n-decanoic acid (PFDA)	0.99	0.25	<b>1.28</b>	<b>0.599 (J)</b>
Perfluoro-n-undecanoic acid (PFUnDA)	0.99	0.17	<b>0.651 (J)</b>	<b>0.222 (J)</b>
Perfluoro-n-dodecanoic acid (PFDoDA)	0.99	0.10	<b>0.689 (J)</b>	<b>0.252 (J)</b>
Perfluoro-n-tridecanoic acid (PFTeDA)	0.99	0.14	<b>0.531 (J)</b>	<b>0.231 (J)</b>
Perfluoro-n-tetradecanoic acid (PFTeDA)	0.99	0.17	<b>0.278 (J)</b>	ND
Perfluorohexadecanoic acid (PFHxDA)	0.99	0.29	ND	<b>0.656 (J)</b>
<b>Perfluoroalkyl Sulfonic Acids (PFSAs)</b>				
Perfluoro-n-butanesulfonic acid (PFBS)	0.99	0.88	ND	<b>1.4 (I)</b>
Perfluoro-n-pentanesulfonic acid (PFPeS)	0.99	0.12	ND	<b>5.4 (I)</b>
Perfluoro-n-nonanesulfonic acid (PFNS)	0.99	0.12	ND	<b>0.717 (J I)</b>
Perfluoro-n-decanesulfonic acid (PFDoS)	0.99	0.11	ND	<b>2.62 (I)</b>
<b>Perfluoroalkane Sulfonamides / Perfluoroalkane Sulfonamidoacetic Acids / Perfluoroalkane Sulfonamido Ethanols</b>				
N-EtFOSAA	0.99	0.14	<b>0.914 (J)</b>	<b>0.553 (J)</b>
N-MeFOSE	4.96	4.86	<b>13.1</b>	<b>9.6</b>
N-EtFOSE	0.99	0.12	<b>0.262 (J)</b>	<b>0.436 (J)</b>
<b>Fluorotelomer Sulfonic Acids (FTSs)</b>				
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	4.96	3.97	<b>5.05</b>	<b>4.67 (J)</b>
<b>Per- and Polyfluoroether Carboxylic Acids / Per- and Polyfluoroether Sulfonic Acids / Fluorotelomer Carboxylic Acids (FTCA) / Fluorotelomer Unsaturated Carboxylic Acids (FTUCA) / Next-Generation PFAS</b>				
6:2 Fluorotelomer unsaturated carboxylic acid (6:2 FTUCA)	0.99	0.14	ND	<b>0.297 (J I)</b>
n-3-Perfluoroheptyl propanoic acid (7:3 FTCA)	0.99	0.35	<b>0.517 (J*+)</b>	ND (*+)
2H,2H,3H,3H-Perfluorooctanoic acid (5:3 FTCA)	0.99	0.48	ND (*+)	ND (*+)

\*Compounds not shown that were ND <MDL: PFODA, PFHxS, PFHpS, PFOS, PFDoS, PFOSA, N-EtFOSA, N-MeFOSA, N-MeFOSAA, 4:2 FTS, 8:2 FTS, 10:2 FTS, ADONA, GenX, 9CI-PF3ONS, 11CI-PF3OUs, 10:2 FTCA, 8:2 FTCA, PFESA, 8:2 FTUCA, PFMPA, PFMBA, 6:2 FTCA, 3:3 FTCA, PFECBS, NFDHA. <sup>a</sup>PFHxA identified in blank filters (<0.68 ng).

Abbreviations: GFF = glass fiber filter; FH = front half; RL = reporting limit; MDL = minimum detection limit; ND = not detected above MDL & RL; J = less than RL but greater than MDL/concentration provided is approximate; I = value is the estimated maximum possible concentration; \*+ = laboratory control sample or laboratory control sample duplicate is outside acceptance limits



**Fig. 3:** Percent recovery of internal standards, comparing cleanliness (Millipore®, purple & MFR2, blue) and pyrolyzer sampling study (Millipore® R1, green & MFR2 R2, yellow) results. QC range of 25-150% is indicated by a dotted line.

## Summary & Conclusion

Cleanliness tests demonstrated similar levels of PFAS in GFFs from different manufacturers. Further, field sampling showed consistent results across manufacturers in detection levels and types of PFAS. These data demonstrate that Millipore® AP-40 glass fiber filters are suitable for use in the OTM-45 sampling train for analysis of PFAS compounds in stationary sources.

## References

- [1] US EPA. 2021. Other Test Method 45 (OTM-45).
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- [5] Van Leeuwen S.P.J., De Boer, J. *Chrom. A*, **2007**, 1153, 172-85.
- [6] Johansson, J.H., Berger, U., Cousins, I.T. *Env. Poll.*, **2017**, 224, 779-86.

## Discussion

- ❖ PFHxA, PFOS and PFHpA in GFFs from both manufacturers; possibly from processing
- ❖ Uncertainty in quantifying certain volatile compounds (FTS, FTCA, FTUCA) such as M<sub>2</sub>-4:2 FTS and <sup>13</sup>C<sub>2</sub> 10:2 FTS
- ❖ More long-chain PFCAs detected in R1 vs. R2 (2-3 fold), indicating differences in GFF retention<sup>3</sup>
- ❖ Adsorption of organic vapors due to GFF structure may make it difficult to interpret data through positive artefacts<sup>4-5</sup>
- ❖ Membrane pressure drop during sampling<sup>6</sup> can introduce volatile losses