Published in Japan
April 25, 2022 Revised
TG0001ENR2

Technical Guide

FM4: Air Sampler for PFAS

Analysis of Per- and Polyfluoroalkyl Substances in Air

Air Sampler “FM4” Technical Guide

— Analysis of Per- and Polyfluoroalkyl Substances —

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1. Introduction

This document describes a method by which per- and polyfluoroalkyl substances (PFAS) present in atmospheric particulate and gaseous phase are simultaneously captured by an air sampler called FM4 and measured by gas chromatography–tandem mass spectrometry (GC–MS/MS) and liquid chromatography–tandem mass spectrometry (LC–MS/MS).

The proposed method targets the PFAS presented in Section 3. The target PFAS comprise various ionic and neutral PFAS, most of which are linear but some of which are cyclic.

2. References and Citations

Refer to ISO 25101 [1)] and ISO 21675 [2)] for the LC–MS/MS details, such as the instruments, reagents, standards, and detailed parameters; and to Reference [3)] for the GC–MS/MS apparatus conditions.

3. Target Compounds

The measurable ionic and neutral PFAS are as follows.

Ionic PFAS:

- Perfluoroalkyl sulfonic acids (PFSAs); PFEtS, PFPrS, PFBS, PFHxS, PFOS, PFDS
- Perfluoroalkyl carboxylic acids (PFCAs); PFPrA (C3) to PFTeDA (C14), PFHxDA, PFOcDA
- Fluorotelomer sulfonic acids (FTSAs); 6:2 FTSA, 8:2 FTSA
- Fluorotelomer unsaturated carboxylic acids (FTUCAs); 8:2 FTUCA, 10:2 FTUCA
- Perfluorooctanoic sulfonamide acetic acids (FOSAAs); *N*-MeFOSAA, *N*-EtFOSAA

Neutral PFAS:

- Perfluorooctanesulfonamide (FOSA); FOSA, *N*-MeFOSA, *N*-EtFOSA
- Perfluorooctanoic sulfonamide ethanol (FOSE); *N*-MeFOSE, *N*-EtFOSE
- Fluorotelomer alcohol (FTOH); 4:2 FTOH, 4:3 FTOH, 6:2 FTOH, 6:3 FTOH, 8:2 FTOH, 8:3 FTOH, 10:2 FTOH
- Fluorotelomer iodine (FTI); 6:2 FTI, 8:2 FTI, 10:2 FTI
- Fluorinated iodine alkanes (FIAs); PFDoI
- Fluorinated diiodoalkanes (FDIAs); PFBuDiI, PFHxDiI, PFODiI
- Fluorobromine-containing compounds; BTFBB: 1,3-Bis(trifluoromethyl)-5-bromo-benzene ($C_8H_3BrF_6$), BPFB Bromopentafluorobenzene (C_6BrF_5)

4. FM4 Overview

Using FM4, both particulate and gaseous matter in ambient air can be simultaneously collected. Fig. 1 presents a schematic of FM4 (note that FM4 corresponds to the NS20 air sampler described in References [3), 4), 5)]). Particles can be classified by FM4 at a flow rate of 20 L/min into the following three classes: ≥10 µm (Stage I), 2.5–10 µm (Stage II), and 1.0–2.5 µm (Stage III). Stage IV (<1.0 µm) can be added; however, because this stage employs filtration for collection, close attention should be paid to the interaction between particles and gas (precursor) during sampling. This stage should be used only when necessary.

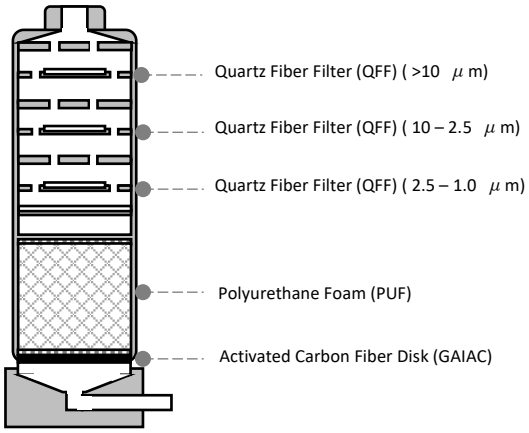


Fig. 1. Schematic Diagram of FM4

The collection media include a quartz fiber filter (QFF) for collecting particulate matter, as well as polyurethane foam (PUF) and an activated carbon fiber disk (GAIAC) for collecting gaseous substances.

When measuring particle weight, the QFF should be weighed before and after sampling. The impactor nozzle is configured to have four holes, and the QFF can be divided into up to four parts depending on the application. If the user changes the target compounds, it is necessary to review the conditions for each additional parameter because different target compounds have different optimum conditions.

5. Pretreatment Process Before Sampling

FM4 and the three materials (QFF, PUF, and GAIAC) used for the sampling process should be pretreated before sampling. Details of the pretreatment process are as follows.

5.1. Sampler (FM4)

1. Disassemble each part and immerse only the metal parts, including the base [except for O-rings and polypropylene (PP) rings], in 50% water/methanol solution.
2. Ultrasonicate the immersed metal parts for 30 min.
3. After ultrasonication, remove each metal part and rinse with methanol.
4. Wipe the O-rings and PP rings with paper moistened with ultrapure water.
5. Air dry each part in an indoor environment without the risk of contamination.

5.2. Quartz Fiber Filter (QFF) – Diameter: 31 mm and 47 mm

1. Bake at 350°C for 3 h.
2. Store in a dry chamber until sampling.

5.3. Polyurethane Foam

1. Immerse in ultrapure water for approximately 30 min, and then discard the solvent.
2. Repeat Step 1 twice.
3. Perform Steps 1 and 2 but with methanol, ethyl acetate, and dichloromethane, in that order.
4. Dry in a vacuum oven (up to 80°C). Replace the gas in the chamber with air or nitrogen (N_2) gas purified by a cartridge filled with silica gel modified with octadecyl groups, by a gas filter filled with activated carbon, or something similar.

5.4. Activated Carbon Fiber Disk (GAIAC)

1. Immerse in ultrapure water, shake slowly for approximately 30 min (approximately 90 rpm), and discard the solvent.
2. Repeat Step 1 twice.
3. Perform Steps 1 and 2 but with methanol, ethyl acetate, and dichloromethane, in that order; care must be taken not to squeeze the GAIAC as it is fragile. No sonication is required.
4. Dry in a vacuum oven (up to 80°C). Replace the gas in the chamber with air or N_2 gas purified by a cartridge filled with silica gel modified with octadecyl groups, by a gas filter filled with activated carbon, or something similar.

6. Extraction

After sampling, the extraction process of each material is as follows.

6.1. Quartz Fiber Filter– Diameter: 31 mm and 47 mm

Fig. 2. Flowchart of QFF Extraction

※ A 15-mL PP tube should be used in the following steps.

1. Place the QFF in PP tube A and add 4 mL methanol (MeOH).
2. Shake the tube (250 rpm) for 30 min at room temperature (20°C–25°C).
3. Stir with vortex for 30 s and centrifuge (3,000 rpm, 15 min).
4. Transfer the supernatant to PP tube B.
5. Add 4 mL of MeOH and repeat Steps 2–4 twice (the final extract volume in PP tube B should be approximately 12 mL).
6. Concentrate the extract in PP tube B to 1 mL at 40°C using N_2 gas. Analyze the obtained extract (Fr1) by LC–MS/MS.

- When injecting each extract into the LC-MS/MS, inject the supernatant obtained by centrifugation if the filters are mixed.
- Previous studies [6] have reported that neutral PFAS are not collected by a QFF; thus, the QFF collects only ionic PFAS.

6.2. Polyurethane Foam (PUF)

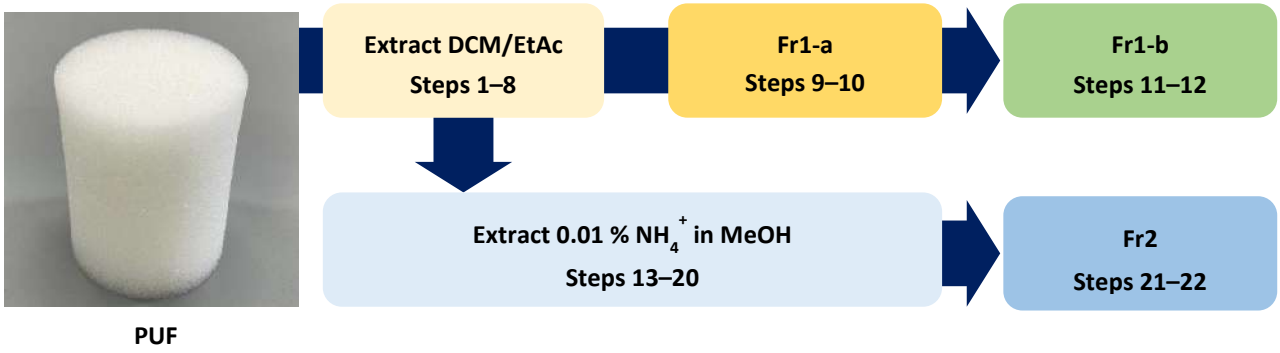


Fig. 3. Flowchart of PUF Extraction

※ A 15-mL PP tube should be used in the following steps.

Fig. 4. 20-mL PP syringe

1. Fill a 20-mL PP syringe (Fig. 4) connected to a stopcock valve (closed) with PUF, and then add 15 mL 50% dichloromethane (DCM)/ethyl acetate (EtAc) and immerse for 1 h.
2. Open the stopcock valve, and drop the extract at a rate of one drop per second, and collect it in PP tube A.
3. When the free fall stops, push the plunger to push out the extract.
4. Add 10 mL 50% DCM/EtAc to the PP syringe.
5. Drop the extract at a rate of one drop per second and collect it in PP tube B.
6. Push the plunger to push out the extract.
7. Add 5 mL 50% DCM/EtAc to the PP syringe.
8. Perform extraction as described in Steps 5 and 6 and obtain two extract aliquots of approximately 15 mL (PP tubes A and B).
9. Concentrate each of the two tubes to approximately 7 mL using N_2 gas (see below), and transfer the entire amount from PP tube B to PP tube A. Then, rinse the inside of PP tube B three times with a small amount of 50% DCM/EtAc (300–350 µL) using a glass pipette; the rinse solution should also be transferred to PP tube A.

Fig. 5. Heating of the test tube

➢ For the concentration of neutral PFAS, set the PP tube in a test tube filled with paper wipers, as shown in Fig. 5, to prevent the PP tube from being exposed to excessive temperature (the temperature of an aluminum block is 35°C).

10. Concentrate PP tube A up to 1 mL using 50% DCM/EtAc, and analyze the extraction (Fr1-a) using GC–MS/MS.
11. Transfer 500 µL of the extract Fr1-a (PP tube A) into PP tube C and evaporate to almost dry using N_2 gas at 40°C.
12. After drying, add 500 µL MeOH, stir with vortex, and homogenize the extract (Fr1-b). Analyze using LC–MS/MS.
13. Add 15 mL 0.01% ammonium methanol (0.01% NH_4^+ in MeOH) to a 20-mL PP syringe containing PUF subject to 50% DCM/EtAc extraction (with the stopcock valve closed), and immerse for 1 h.
14. Open the stopcock valve, drop the extract at a rate of one drop per second, and collect it in PP tube D.
15. When the free fall stops, push the plunger to push out the extract.

16. Add 10 mL 0.01% NH_4^+ in MeOH.
17. Drop the extract at a rate of one drop per second and collect it in PP tube E.
18. Push the plunger to push out the extract.
19. Add 5 mL 0.01% NH_4^+ in MeOH.
20. Perform extraction as described in Steps 17 and 18 and obtain two extract aliquots of approximately 15 mL (PP tubes D and E).
21. Concentrate each of the two tubes to approximately 7 mL using N_2 gas at 40°C, and transfer the entire amount from PP tube E to PP tube D. Then, rinse the inside of PP tube E three times with a small amount of MeOH (300–350 µL) using a glass pipette; the rinse solution should also be transferred to PP tube D.
22. Concentrate PP tube D up to 1 mL using MeOH, and analyze the extract (Fr2) using LC–MS/MS.

- When injecting each extract into the LC–MS/MS, inject the supernatant obtained by centrifugation if foreign substances are mixed.

6.3. Activated Carbon Fiber Disk (GAIAC)

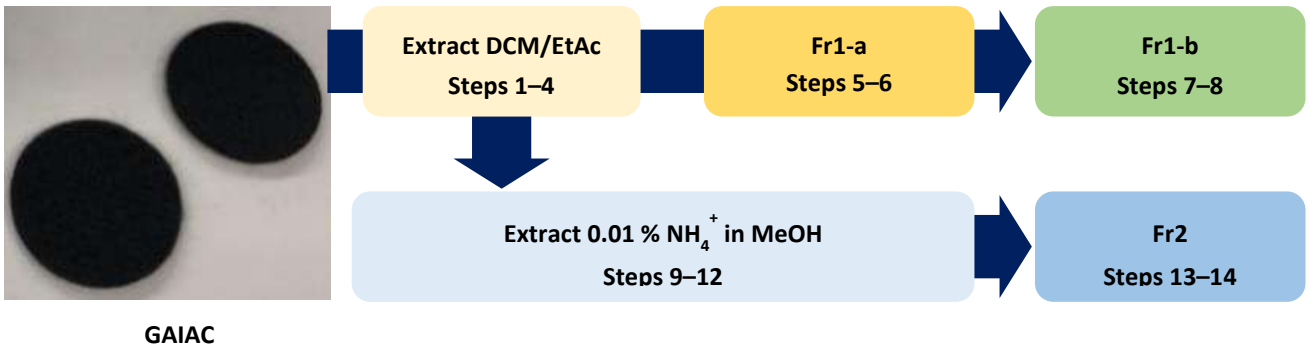


Fig. 6. GAIAC Extract Flowchart

※ A 15-mL PP tube should be used in the following steps.

Fig. 7. 15-mL test tube and GAIAC

1. Place GAIAC into a 15-mL PP tube A, add 10 mL 50% DCM/EtAc, and immerse for 1 h.
2. Shake (250 rpm) for 30 min at room temperature (20°C–25°C) to transfer the extract to PP tube B.
3. Add 10 mL 50% DCM/EtAc to PP tube A and repeat Step 2. Extract that cannot be completely transferred to PP tube B should be transferred to PP tube C.
4. Repeat Step 3. After squeezing the GAIAC of PP tube A with tweezers, remove it and transfer the remaining extract to PP tube C. After the transfer, return the GAIAC to PP tube A, thereby obtaining two extract aliquots of approximately 15 mL (PP tubes B and C).
5. Concentrate each of the two tubes to approximately 7 mL using N_2 gas (see below), and transfer the entire amount from PP tube C to PP tube B. Then, rinse the inside of PP tube C three times with a small amount of 50% DCM/EtAc (300–350 µL) using a glass pipette; the rinse solution should also be transferred to PP tube B.

➢ For concentration neutral PFAS, set the PP tube in a test tube filled with paper wipers, as illustrated in Fig. 5 to prevent the test tube from being exposed to excessive temperature (the temperature of an aluminum block is 35°C).

6. Concentrate PP tube B up to 1 mL using 50% DCM/EtAc, and analyze the extract (Fr1-a) using GC–MS/MS.
7. Transfer 500 µL of the extract Fr1-a (PP tube B) into PP tube D and evaporate to almost dry using N_2 gas at 40°C.
8. After drying, add 500 µL MeOH, stir with vortex, and homogenize the extract (Fr1-b). Analyze using LC–MS/MS.
9. Add 10 mL 0.01% NH_4^+ in MeOH to PP tube A containing GAIAC subjected to 50% DCM/EtAc extraction, and immerse for 1 h.
10. Shake (250 rpm) for 30 min at room temperature (20°C–25°C). Transfer the solvent to a PP tube E.
11. Add 10 mL 0.01% NH_4^+ in MeOH to PP tube A and repeat Step 10. Extract that cannot be completely transferred to PP tube E should be transferred to PP tube F.
12. Repeat Step 11 once more, thereby obtaining two extract aliquots of approximately 15 mL (PP tubes E and F).
13. Concentrate each of the two tubes to approximately 7 mL using N_2 gas at 40°C, and transfer the entire amount from PP tube F to PP tube E. Then, rinse the inside of PP tube F three times with a small amount of MeOH (300–350 µL) using a glass pipette; the rinse solution should also be transferred to PP tube E.
14. Concentrate PP tube E up to 1 mL using MeOH, and analyze the extract (Fr2) using LC–MS/MS.

➢ When injecting each extract into the LC–MS/MS , inject the supernatant obtained by centrifugation if fibers are mixed.

7. Analysis

7.1. Ionic PFAS Analysis

Ionic PFAS and part of the neutral PFAS (FOSAs) can be analyzed using LC–MS/MS. The instrumentation and parameters for LC and MS are summarized in Table 1 and Table 2, respectively. The parameters provided in References [1), 2)] were used for MS/MS monitor ions.

Table 1. Example of Instrumentation and Parameters for Liquid chromatography

System	Exion (SCIEX)
Column	InertSustain AQ-C18 (GL Sciences Inc.) 1.9 µm, 2.1 mm I.D. × 100 mm
Delay Column	Delay Column for PFAS 3.0 × 30 mm (GL Science Inc.)
Mobile Phase (A)	10 mmol/L aqueous ammonium acetate solution
Mobile Phase (B)	Acetonitrile
Column Temperature	40°C
Gradient	**Time (min)** / **0** / **1.5** / **10** / **11** / **11.1** / **15** **A %** / 90 / 70 / 0 / 0 / 90 / 90 **B %** / 10 / 30 / 100 / 100 / 10 / 10
Flow Rate	0.3 mL/min
Injection Volume	2 µL
Sample Cooler	10 °C

Table 2. Example of Instrumentation and Parameters for Mass spectrometry

System	QTRAP 6500+ (SCIEX)	**Collision Gas (CAD)**	12
Ion Source	ESI	**Ion Spray Voltage (IS)**	-4500
Mode	MRM	**Temperature (TEM)**	300 ℃
Polarity	Negative	**Ion Source Gas1**	50
Curtain Gas (CUR)	40	**Ion Source Gas2**	30

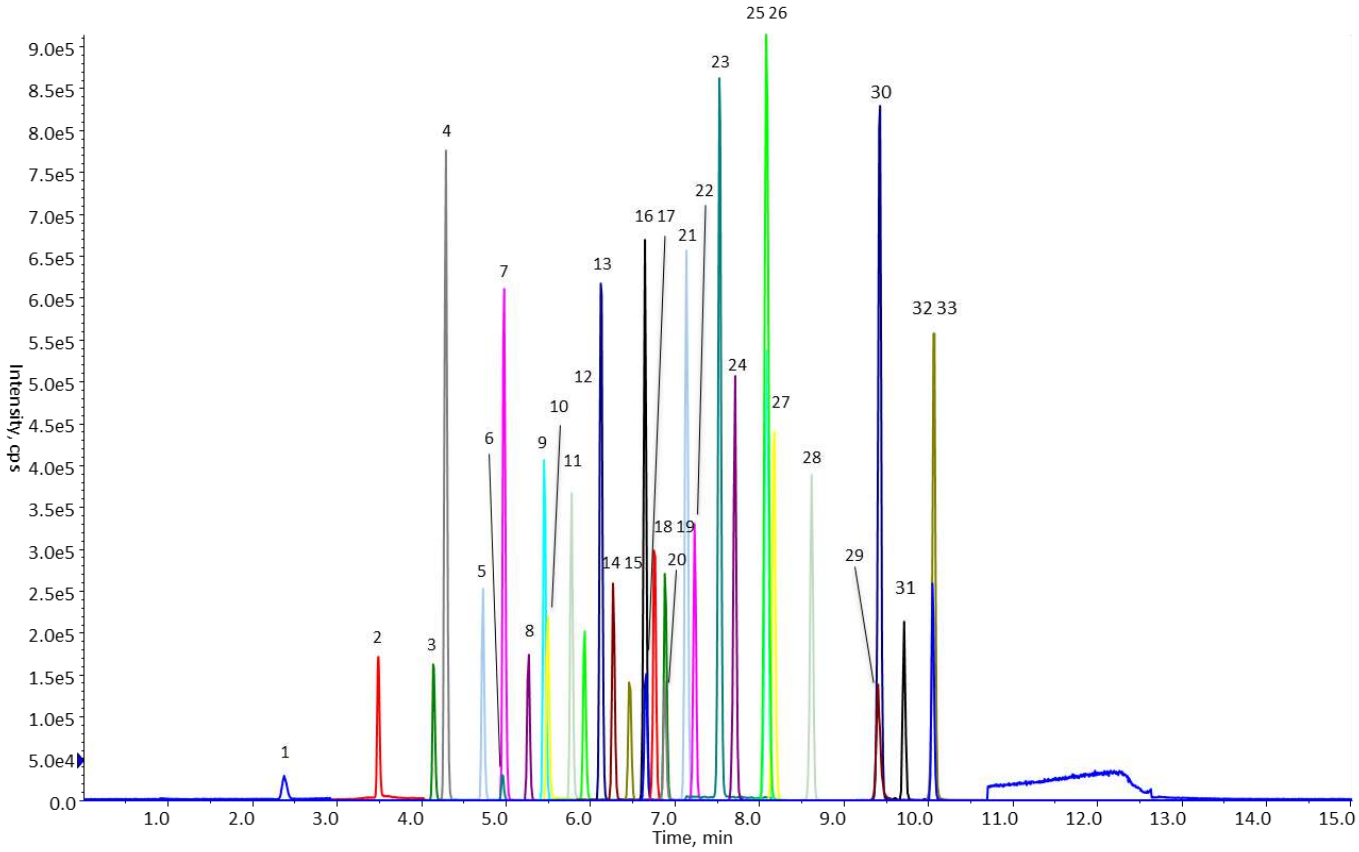


Fig.8 MRM Chromatogram

Table 3. Examples of MRM Transitions and Collision Energy (CE) of Ionic PFAS for LC–MS/MS

No.	Compounds	Abbreviation	R.T.	Transition 1	CE	Transition 2	CE
1	2,2,3,3,3-Pentafluoropropionic acid	PFPrA	1.24	163.0>119.0	-16		
2	Perfluorobutanoic acid	PFBA	2.14	213.0>169.0	-14		
3	Sodium prefluoro-1-propanesulfanate	PFPrS	3.95	249.0>80.0	-52	249.0>99.0	-34
4	Perfluoropentanoic acid	PFPeA	4.02	263.0>219.0	-11		
5	Perfluorohexanoic acid	PFHxA	4.73	313.0>269.0	-15	313.0>119.0	-30
6	Perfluorobutanesulfonic acid	PFBS	4.84	299.0>80.0	-59	299.0>99.0	-44
7	Hexafluoropropylene oxide dimer acid	HFPO-DA (GenX)	4.96	329.0>169.0	-16	329.0>285.0	-8
8	Perfluoroheptanoic acid	PFHpA	5.29	363.0>319.0	-14	363.0>169.0	-26
9	4,8-Dioxa-3H-perfluorononanoic acid	ADONA(DONA)	5.44	377.0>251.0	-14	377.0>85.0	-56
10	6:2 Fluorotelomer sulfonic acid	6:2FTS	5.5	427.0>407.0	-34	427.0>81.0	-74
11	Perfluorooctanoic acid	PFOA	5.69	413.0>369.0	-14	413.0>169.0	-26
12	Perfluorohexanesulfonic acid	PFHxS	5.86	399.0>80.0	-80	399.0>99.0	-80
13	8:2 Fluorotelomer unsaturated carboxylic acid	FOUEA (8:2 FTUCA*)	5.9	457.0>393.0	-16	457.0>343.0	-56
14	Perfluorononanoic acid	PFNA	6.07	463.0>419.0	-16	463.0>219.0	-26
15	8:2 Fluorotelomer sulfonic acid	8:2FTS	6.25	527.0>507.0	-40	527.0>81.0	-82
16	Perfluoroheptanesulfonic Acid	PFHpS	6.29	449.0>80.0	-104	449.0>99.0	-70
17	Perfluorodecanoic acid	PFDA	6.43	513.0>469.0	-19	513.0>219.0	-27
18	*N*-methylperfluoro-1-octanesulfonamidoacetic acid	*N*-MeFOSAA	6.56	570.0>419.0	-30	570.0>483.0	-24
19	Perfluorooctanesulfonic acid	PFOS	6.65	499.0>80.0	-97	499.0>99.0	-77
20	2H-perfluoro-2-dodecenoic acid	10:2FTUCA (FDUEA)	6.66	557.0>493.0	-20	557.0>243.0	-52
21	*N*-ethylperfluoro-1-octanesulfonamidoacetic acid	*N*-EtFOSAA	6.78	584.0>419.0	-30	584.0>526.0	-28
22	Perfluoroundecanoic acid	PFUnA	6.81	563.0>519.0	-19	563.0>269.0	-28
23	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	6.95	531.0>351.0	-40	531.0>83.0	-56
24	Perfluorododecanoic acid	PFDoA	7.16	613.0>569.0	-17	613.0>269.0	-29
25	Perfluorodecanesulfonic acid	PFDS	7.38	599.0>80.0	-94	599.0>99.0	-91
26	Perfluorotridecanoic acid	PFTrDA	7.52	663.0>619.0	-19	663.0>269.0	-32
27	Perfluorotetradecanoic acid	PFTeDA(PFTeA)	7.84	713.0>669.0	-19	713.0>319.0	-36
28	Perfluorooctanesulfonamide	FOSA	8.47	498.0>78.0	-85	498.0>169.0	-40
29	Perfluoro-n-hexadecanoic acid	PFHxDA	8.52	813.0>769.0	-20	813.0>319.0	-34
30	Perfluoro-n-octadecanoic acid	PFOcDA (PFODA)	9.1	913.0>869.0	-20	913.0>369.0	-40
31	8:2 Polyfluoroalkyl phosphate diester	8:2 diPAP	9.5	989.0>97.0	-130	989.0>543.0	-36
32	n-methylperfluoro-1-octanesulfonamide	*N*-MeFOSA	9.96	512.0>169.0	-37	512.0>219.0	-34
33	*N*-ethylperfluoro-1-octanesulfonamide	*N*-EtFOSA	10.28	526.0>169.0	-37	526.0>219.0	-34

7.2. Neutral PFAS Analysis

Neutral PFAS were analyzed using GC–MS/MS, and the instrumentation and parameters are summarized in Table 4. Table 5 lists the monitor ions for MS/MS.

Table 4. Example of Instrumentation and Parameters for GC–MS/MS

System	8890/7010B Triple quadrupole GC/MS (Agilent Technologies, Inc)		
Column	InertCap Pure-WAX (GL Science Inc.) 0.25 mm I.D. × 30 m, df = 0.25 µm		
Injection	Splitless		
Injection Vol.	2 µL, 200℃		
Carrier Gas	He, 1.2 mL / min		
Column Temp.	Rate (℃ / min)	Temp (℃)	hold (min)
	0	40	2
	10	200	0
	20	250	20
Ion Source temp.	320℃		
Ion mode	EI		
Mode	MRM		

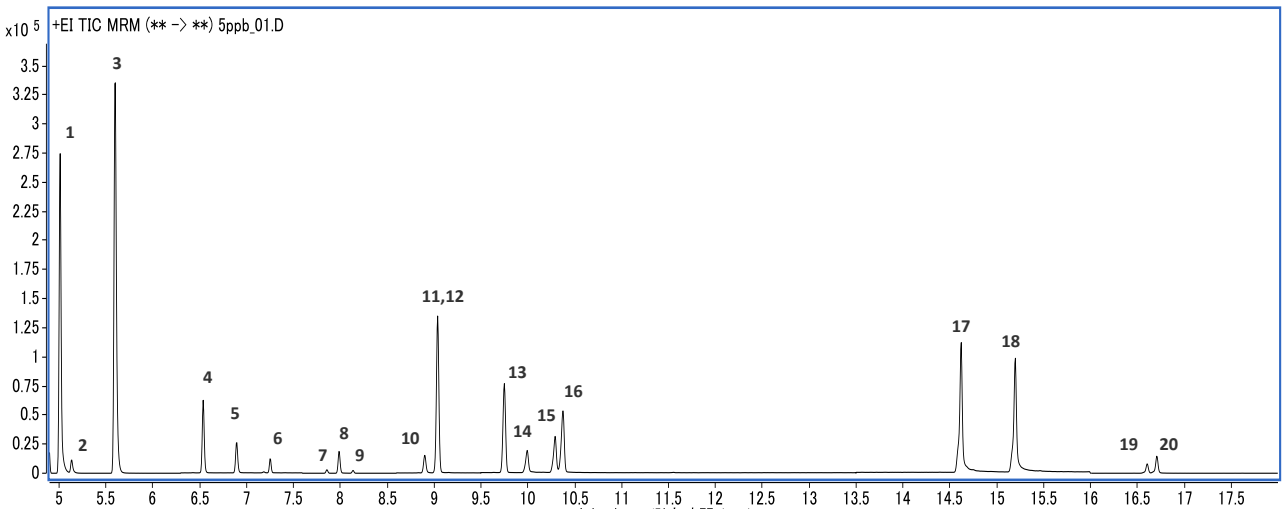


Fig. 8. MRM Chromatogram

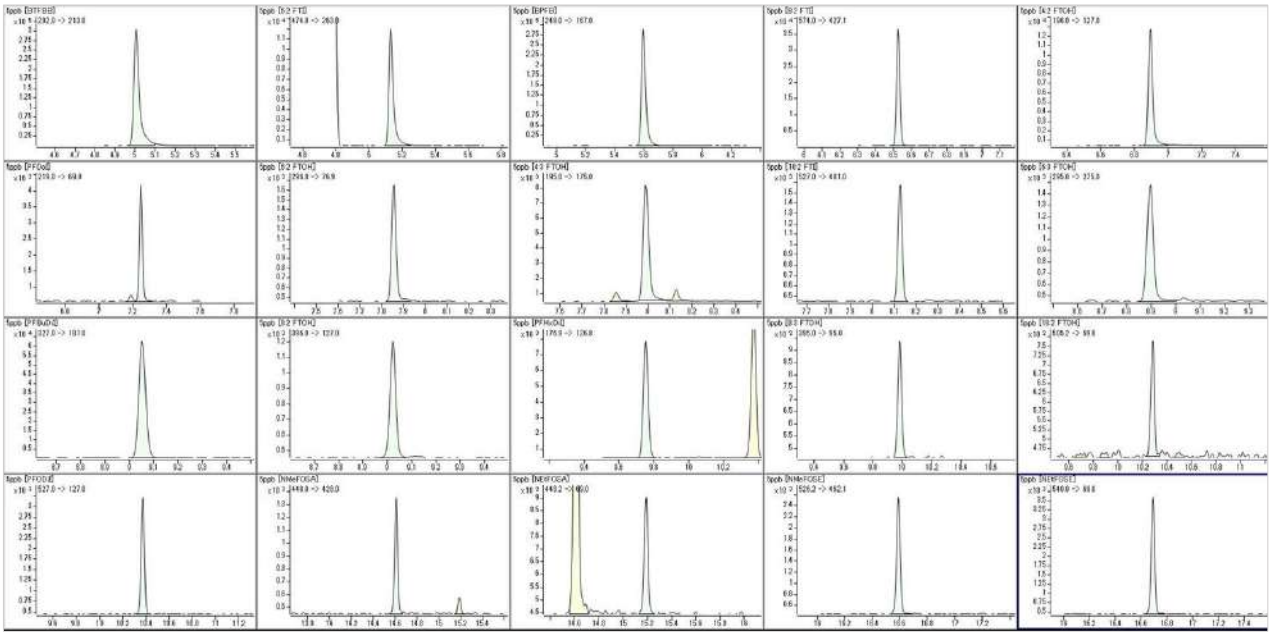


Fig. 9. MRM Chromatogram

Table 5. Examples of MRM Transitions of Neutral PFAS for GC-MS/MS

No.	Compounds	R.T.	Transition 1			Transition 2		
		(min)	Q1	Q3	CE	Q1	Q3	CE
1	BTFBB	5.00	292	213	26	294	213	18
2	6:2FTI	5.13	474	263	28	327	181	16
3	BPFB	5.60	248	167	24	248	117	22
4	8:2FTI	6.53	574	427	8	547	313	20
5	4:2 FTOH	6.90	196	127	10	196	77	26
6	PFDoI	7.25	219	69	28	169	69	16
7	6:2 FTOH	7.86	296	77	26	344	95	24
8	4:3 FTOH	7.99	195	175	8	195	95	24
9	10:2FTI	8.13	527	481	8	527	145	10
10	6:3 FTOH	8.90	295	275	8	295	181	24
11	8:2 FTOH	9.02	396	127	12	131	69	22
12	PFBuDiI	9.05	327	181	8	327	69	60
13	PFHxDiI	9.75	177	127	28	281	181	22
14	8:3 FTOH	9.98	395	95	12	131	69	20
15	10:2 FTOH	10.28	505	669	60	131	69	60
16	PFODiI	10.38	527	127	14	381	69	60
17	*N*-EtFOSA	14.61	448	69	60	131	69	28
18	*N*-MeFOSA	15.19	448	428	12	131	69	28
19	*N*-MeFOSE	16.59	526	462	18	462	93	28
20	*N*-EtFOSE	16.69	540	69	54	540	448	20

7.3. QA/QC

The concentrations of the target PFAS were quantified using an external calibration curve. The calibration curves were based on a PFAS concentration series of 2, 10, 50, 200, 1,000, and 5,000 (pg/mL) for LC–MS/MS and 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2, 5, 20, and 50 (ng/mL) for GC–MS/MS. The deviation of every point from the regression line was less than 20% from theoretical value. The instrumental limit of quantification (I-LOQ) was (i) the smallest concentration of the standard on the calibration curve that could be accurately measured within ±20% of its theoretical value, or (ii) a signal-to-noise ratio of ≥10.

To verify the stability of the instrument, a mixed standard solution adjusted to 1,000 pg/mL for LC–MS/MS and 5 ng/mL for GC–MS/MS was measured for each analysis batch. If the concentration of the mixed standard solution was not within ±20% of the corresponding theoretical value, a new calibration curve was prepared. The material blank (procedural blank) and material recovery (procedural recovery) were analyzed for every batch of samples.

The target compounds can be quantified by the internal standard method, and loss in the sampling and extraction processes can be corrected to a limited extent. The timing of adding the internal standard can be determined according to the application (see Table 6). Table 7 presents examples of the internal standard; if the main components are the same, any surrogate can be used regardless of the number and position of ^{13}C.

Table 6. Timing and Purpose of Adding Internal Standard

Timing of Addition		Purpose
Prior to sampling)		
・Ionic PFAS; QFF at Stage I	=>	To correct for loss in the sampling process
・Neutral PFAS; PUF		
Immediately before extraction	=>	To correct for loss in the extraction process

Table 7. Examples of Internal Standard

Internal Standard	Target Compounds
$^{13}C_3$-PFBS	PFBS
$^{13}C_3$-PFHxS	PFHxS
$^{13}C_8$-PFOS	PFOS
$^{13}C_4$-PFBA	PFBA
$^{13}C_5$-PFHxA	PFHxA
$^{13}C_4$-PFHpA	PFHpA
$^{13}C_8$-PFOA	PFOA
$^{13}C_9$-PFNA	PFNA
$^{13}C_6$-PFDA	PFDA
$^{13}C_7$-PFUnDA	PFUnDA
$^{13}C_2$-PFDoDA	PFDoDA
$^{13}C_2$-PFTeDA	PFTeDA
$^{13}C_2$-6:2 FTSA	6:2 FTSA

Internal Standard	Target Compounds
$^{13}C_2$-8:2 FTSA	8:2 FTSA
$^{13}C_4$-8:2 diPAP	8:2 diPAP
$^{13}C_3$-HFPO-DA	HFPO-DA
d_3-*N*-MeFOSAA	*N*-MeFOSAA
d_5-*N*-MeFOSAA	*N*-MeFOSAA
d_3-*N*-MeFOSA	*N*-MeFOSA
d_5-*N*-EtFOSA	*N*-EtFOSA
d_7-*N*-MeFOSE	*N*-MeFOSE
d_9-*N*-EtFOSE	*N*-EtFOSE
d_4-4:2 FTOH	4:2 FTOH
d_2-$^{13}C_2$-6:2 FTOH	6:2 FTOH
d_2-$^{13}C_2$-8:2 FTOH	8:2 FTOH
d_2-$^{13}C_2$-10:2 FTOH	10:2 FTOH

8. Product Data

Consequently, the recovery tests of the target compounds for each material and the blank tests of each material were performed, and real sample measurement was performed as an example. The results are summarized below. This results shown in this chapter are analyzed using the GCMS-TQ8050 GC-MS / MS system (Shimadzu) and LC-MS / MS system configured by the Agilent 1260 Infinity (Agilent) and the Triple Quad 4500 (SCIEX).

8.1. Method Quantification Limit (MQL)

The MQLs in the blank test of each material and the measurement of real samples are summarized in Table 8 and Table 9, respectively. The blank value of each material is an absolute amount (pg) per material, and the real sample concentration is expressed as a relative concentration per air volume (pg/m^3).

Table 8. Method Quantification Limits (MQLs) in Blank Test (pg)

Compounds	MQL (pg)	Compounds	MQL (pg)	Compounds	MQL (pg)
PFEtS	2	PFTeDA	2	4:2 FTOH	250
PFPrS	10	PFHxDA	2	4:3 FTOH	5,000
PFBS	2	PFOcDA	2	6:2 FTOH	250
PFHxS	2	6:2 FTSA	2	6:3 FTOH	2,000
PFOS	2	8:2 FTSA	2	8:2 FTOH	250
PFDS	10	8:2 FTUCA	10	8:3 FTOH	500
PFPrA	200	10:2 FTUCA	2	10:2 FTOH	1,000
PFBA	50	8:2diPAP	2	6:2 FTI	25
PFPeA	10	HFPDA	10	8:2 FTI	50
PFHxA	2	*N*-MeFOSAA	2	10:2 FTI	2,000
PFHpA	2	*N*-EtFOSAA	2	PFDoI	1,000
PFOA	2	FOSA	2	PFBuDiI	100
PFNA	2	*N*-MeFOSA	2,000	PFHxDiI	250
PFDA	10	*N*-EtFOSA	500	PFODiI	1,000
PFUnDA	10	*N*-MeFOSE	250	BTFBB	25
PFDoDA	2	*N*-EtFOSE	100	BPFB	50
PFTrDA	2	-	-	-	-

Table 9. Method Quantification Limits (MQLs) in Real Sample Measurement (pg/m^3)

Compounds	24-hour Sampling (n = 2)			48-hour Sampling (n = 2)			72-hour Sampling (n = 2)		
	Max. (pg)	Min. (pg)	Mean (pg)	Max. (pg)	Min. (pg)	Mean (pg)	Max. (pg)	Min. (pg)	Mean (pg)
PFEtS	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFPrS	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
PFBS	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFHxS	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFOS	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFDS	0.33	0.07	0.20	0.17	0.03	0.10	0.12	0.02	0.07
PFPrA	1.74	6.94	4.34	3.47	0.87	2.17	2.31	0.58	1.45
PFBA	1.74	0.35	1.05	0.87	0.17	0.52	0.58	0.12	0.35
PFPeA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
PFHxA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFHpA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFOA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFNA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFDA	0.07	0.35	0.21	0.17	0.03	0.10	0.12	0.02	0.07
PFUnDA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
PFDoDA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFTrDA	0.07	0.35	0.21	0.17	0.03	0.10	0.12	0.02	0.07
PFTeDA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFHxDA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
PFOcDA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
6:2 FTSA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
8:2 FTSA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
8:2 FTUCA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
10:2 FTUCA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
8:2diPAP	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
HFPDA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
N-MeFOSAA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02
N-EtFOSAA	0.35	0.07	0.21	0.17	0.03	0.10	0.12	0.02	0.07
FOSA	0.07	0.07	0.07	0.03	0.03	0.03	0.02	0.02	0.02

Table 9 (continued)

Compounds	24-hour Sampling (n = 2)			48-hour Sampling (n = 2)			72-hour Sampling (n = 2)		
	Max. (pg)	Min. (pg)	Mean (pg)	Max. (pg)	Min. (pg)	Mean (pg)	Max. (pg)	Min. (pg)	Mean (pg)
***N*-MeFOSA**	69.44	69.44	69.44	34.72	34.72	34.72	23.15	23.15	23.15
***N*-EtFOSA**	17.36	8.68	13.02	4.34	4.34	4.34	2.89	2.89	2.89
***N*-MeFOSE**	8.68	8.68	8.68	4.34	4.34	4.34	2.89	2.89	2.89
***N*-EtFOSE**	3.47	1.74	2.61	0.87	0.87	0.87	0.58	0.58	0.58
4:2 FTOH	8.68	8.68	8.68	4.34	4.34	4.34	2.89	2.89	2.89
4:3 FTOH	347.22	173.61	260.42	86.81	86.81	86.81	57.87	57.87	57.87
6:2 FTOH	17.36	8.68	13.02	8.68	8.68	8.68	5.79	5.79	5.79
6:3 FTOH	69.44	34.72	52.08	17.36	17.36	17.36	11.57	11.57	11.57
8:2 FTOH	34.72	17.36	26.04	17.36	17.36	17.36	11.57	11.57	11.57
8:3 FTOH	34.72	34.72	34.72	17.36	17.36	17.36	11.57	11.57	11.57
10:2 FTOH	34.72	17.36	26.04	8.68	8.68	8.68	5.79	5.79	5.79
6:2 FTI	0.87	0.87	0.87	0.43	0.43	0.43	0.29	0.29	0.29
8:2 FTI	1.74	0.87	1.31	0.43	0.43	0.43	0.29	0.29	0.29
10:2 FTI	69.44	17.36	43.4	34.72	34.72	34.72	23.15	23.15	23.15
PFDoI	34.72	34.72	34.72	17.36	17.36	17.36	11.57	11.57	11.57
PFBuDiI	3.47	1.74	2.61	0.87	0.87	0.87	0.58	0.58	0.58
PFHxDiI	8.68	8.68	8.68	4.34	4.34	4.34	2.89	2.89	2.89
PFODiI	34.72	34.72	34.72	17.36	17.36	17.36	11.57	11.57	11.57
BTFBB	0.87	0.87	0.87	0.43	0.43	0.43	0.29	0.29	0.29
BPFB	1.74	0.87	1.31	0.43	0.43	0.43	0.29	0.29	0.29

8.2. Blank Test

Fig. 10 shows the blanks for each material in the material blank tests, while Fig. 11 shows the blanks for each material in the travel blank tests. In the material blank tests, pretreatment and extraction were performed for each material as stipulated in Sections 5 and 6, followed by instrument measurement. In the travel blank tests, the materials that were pretreated as described in Section 5 were placed in FM4 and extracted as described in Section 6 without air collection, followed by instrument measurement.

Both material blanks and travel blanks were within the MQL or lower, except for some PFCAs, PFBS, and BPFB. Except for 6:2 FTOH, the travel blank was observed at the same level as the material blank, suggesting that the travel blank was derived from the material. The blank values ranged from 0.1 to 18.8 pg/m^3 in the real sample measurement and were 10–100 times lower than the actual concentration level, except for BPFB. For BPFB, the blank values were approximately 2–3 times lower than the actual concentration level; thus, it was considered to be largely due to the blank values.

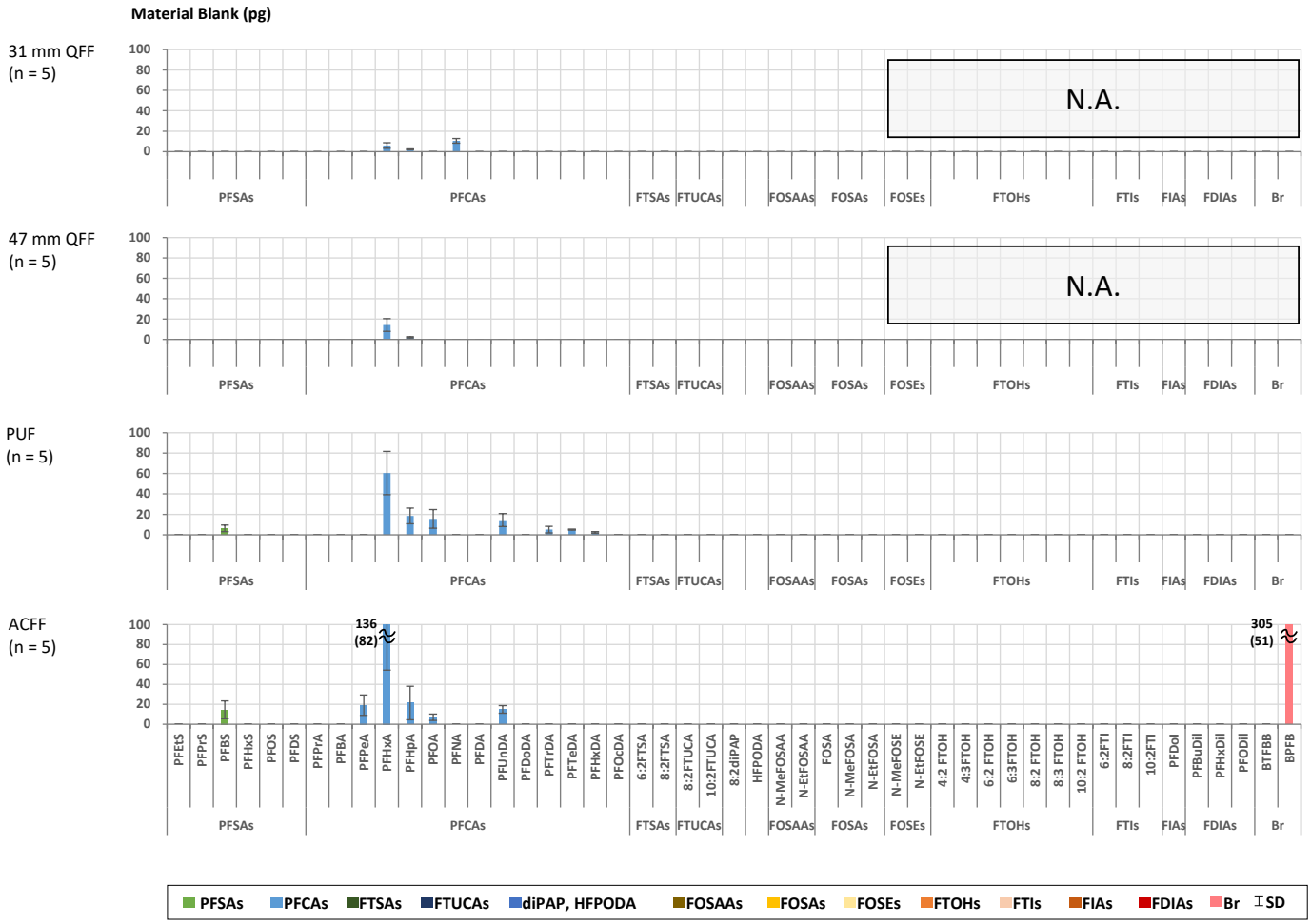


Fig. 10. Material Blank per Material (pg)

- N.A.: Not Analyzed

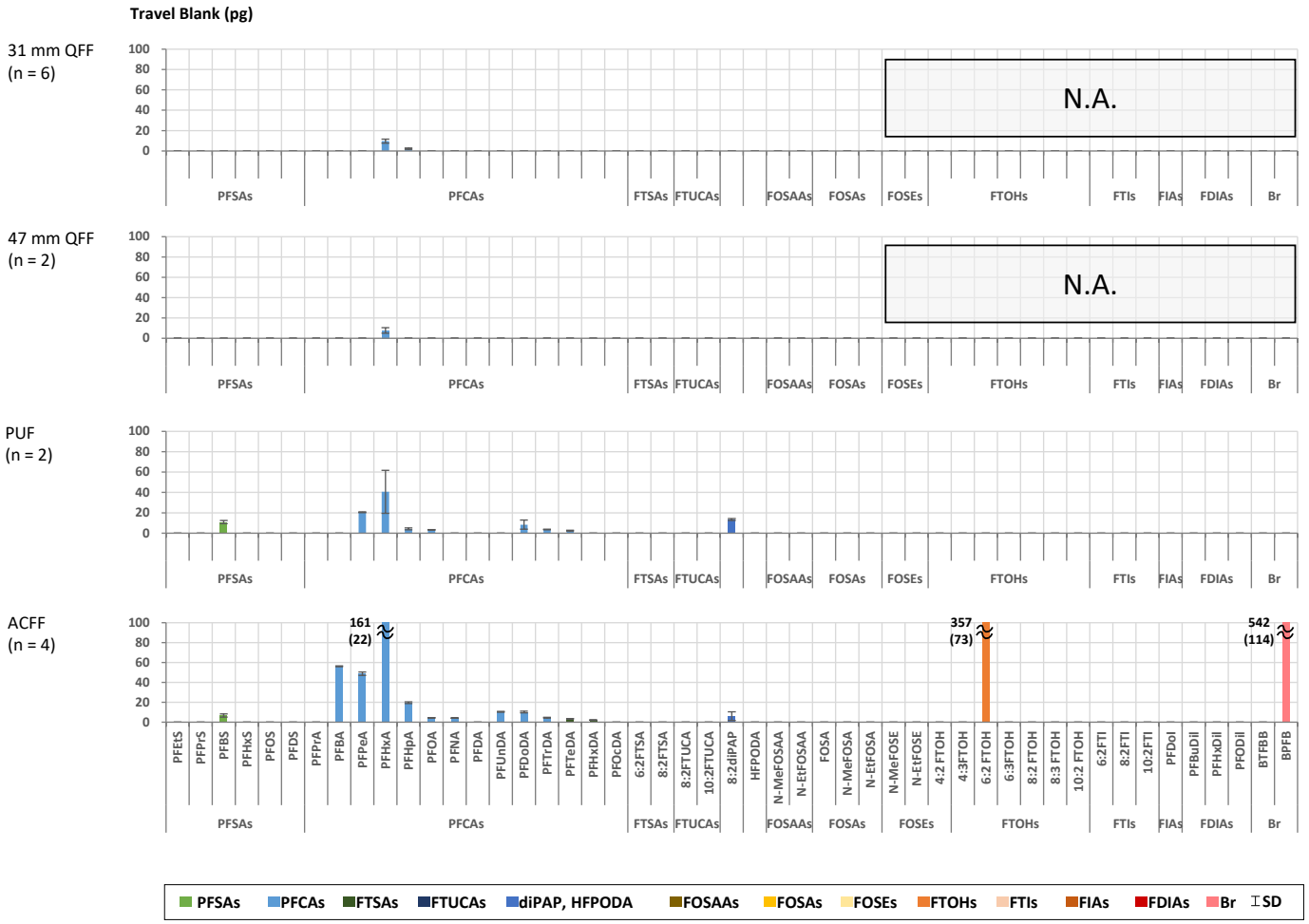


Fig. 11. FM4 Travel Blank per Material (pg)

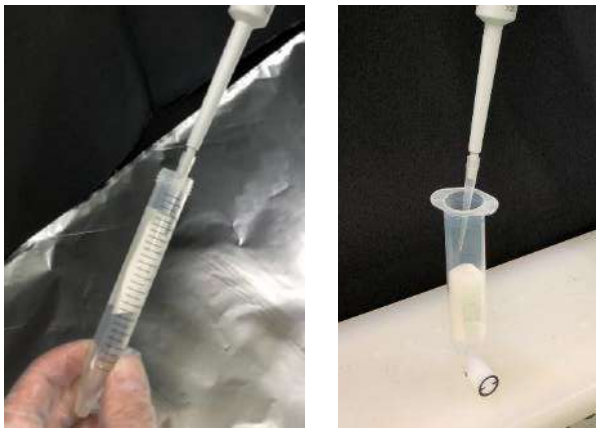
8.3. Recovery Test

8.3.1. Material Recovery test

A known amount of the standard (surrogate or native) was spiked to each material to evaluate the extraction efficiency of each material, thereby obtaining the recovery of the extraction process.

The standard mixture was spiked to each material as follows.

1. Place each material that is pretreated as described in Section 5 in a PP tube or syringe.
2. Spike 1 ng absolute of the standard for ionic PFAS and 5 ng absolute of the standard for neutral PFAS to the material each material (Fig. 13). The mixed standard should be diluted with methanol.
3. Extract as described in Section 6.



a) QFF/GAIAC b) PUF

Fig. 13. Standard mixture spikes on the material

Fig. 12 displays the recovery of the surrogate standard, while Fig. 14 displays the recovery of the native standard. Material recovery ranged from 70% to 120% for most compounds and materials, except for FTUCAs and FDIAs, with an average of 88%. For FTUCAs and FDIAs, the material recovery ranged from 33% to 75%, with an average of 50%. The longer the carbon chain of a substance, the higher the recovery rate.

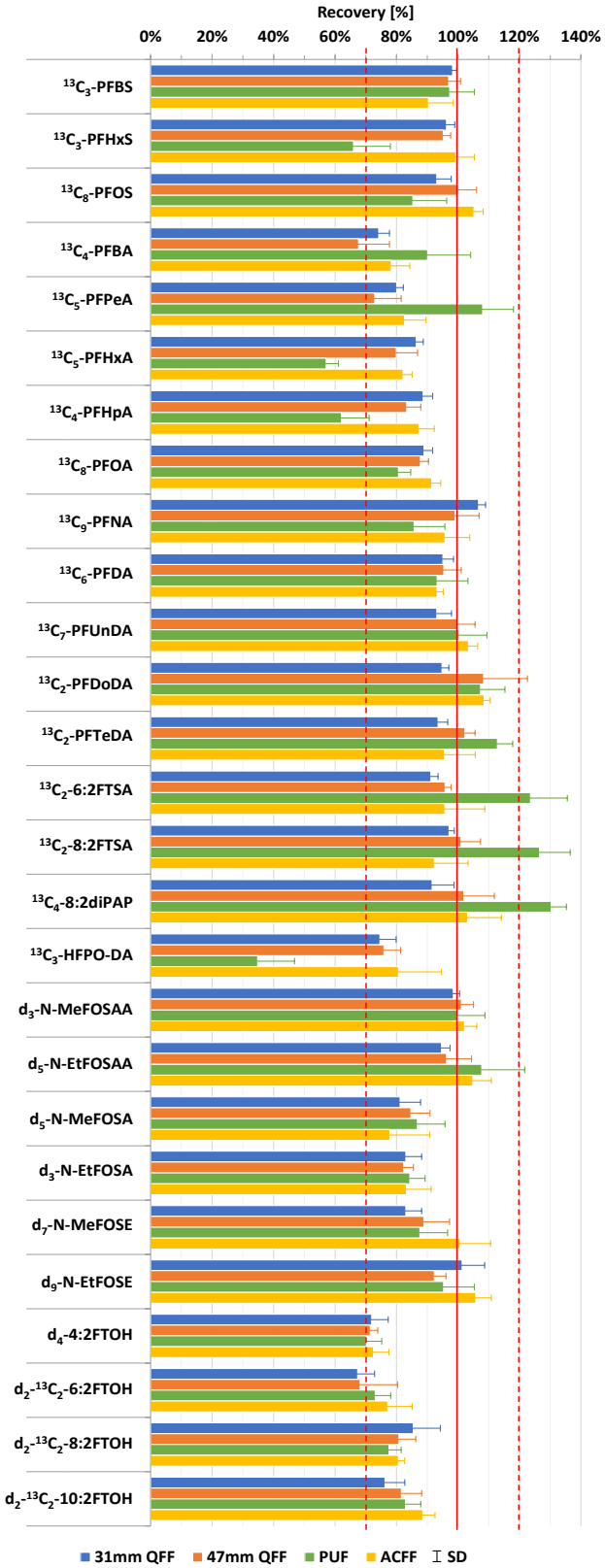


Fig. 12. Material Recovery (%) of Surrogate Standard for Each Material (n = 5)

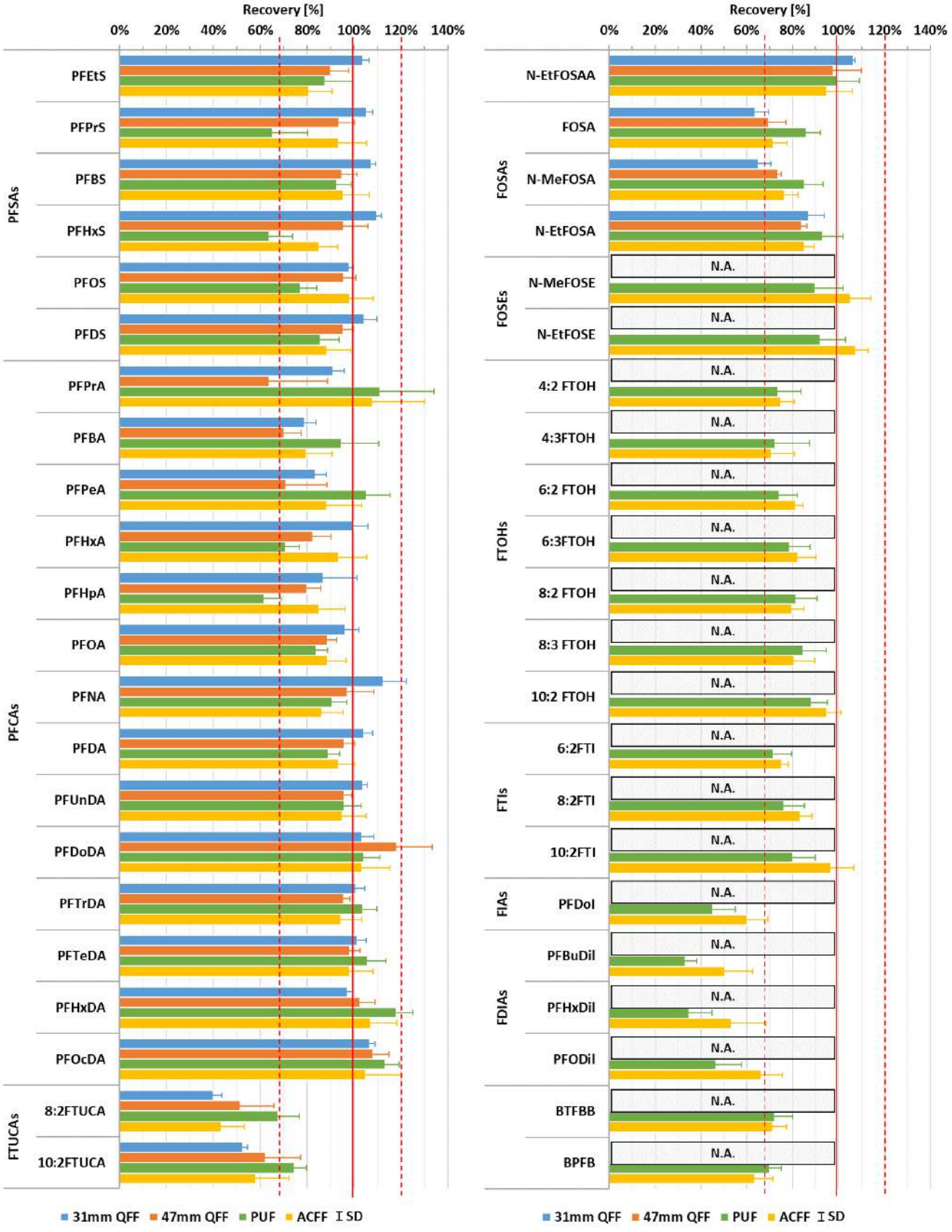


Fig. 14. Material Recovery (%) of Native Standard for Each Material (n = 5)

8.3.2. Sample Recovery Test

Recovery tests were conducted to evaluate the potential losses of the target compounds during sampling.

A known amount of the surrogate standard mixture was spiked into the material, and the ambient air was sampled for 24, 48, and 72 h (n = 6 each) to evaluate the recovery. The surrogate standard mixture was spiked as follows.

1. Spike 1 ng absolute of the ionic PFAS standard to Stage I of QFF (Fig. 16). The standard mixture should be adjusted with methanol.
2. Spike 5 ng absolute of the neutral PFAS standard to PUF (Fig. 16). The standard mixture should be adjusted with methanol.
3. By aspiration with a pump or pressurization of gas, at approximately 20 L/min for approximately 1 minute to volatilize methanol. Then start sampling at 20 L/min.

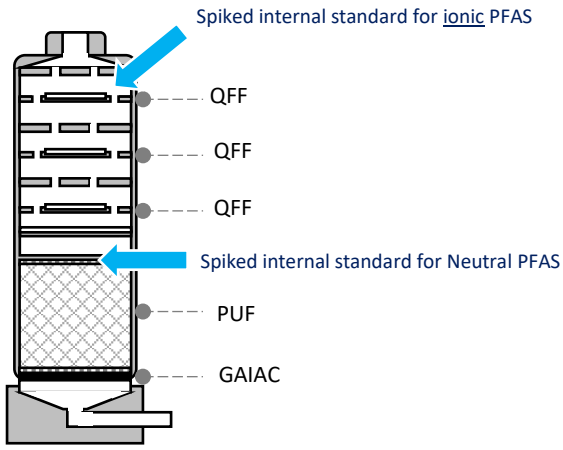


Fig. 16. Addition position of standard solution

Fig. 15 presents the recovery rate of the surrogate standard for sampling. The sample recovery rates ranged from 70% to 120% for most compounds except for short-chain PFCAs and FOSAs, with an average of 88%, which was equivalent to the material recovery rates shown in Fig. 12. This confirms that each material retains PFAS strongly and does not slow recovery after 72 hours of sampling.

For short-chain PFCAs, the recovery ranged from 31% to 68%, with an average of 52%, which was 30% to 50% lower than the material recovery presented in Fig. 12. The results suggest that short-chain PFCAs may have been lost during the sampling process. The recovery tended to increase as the

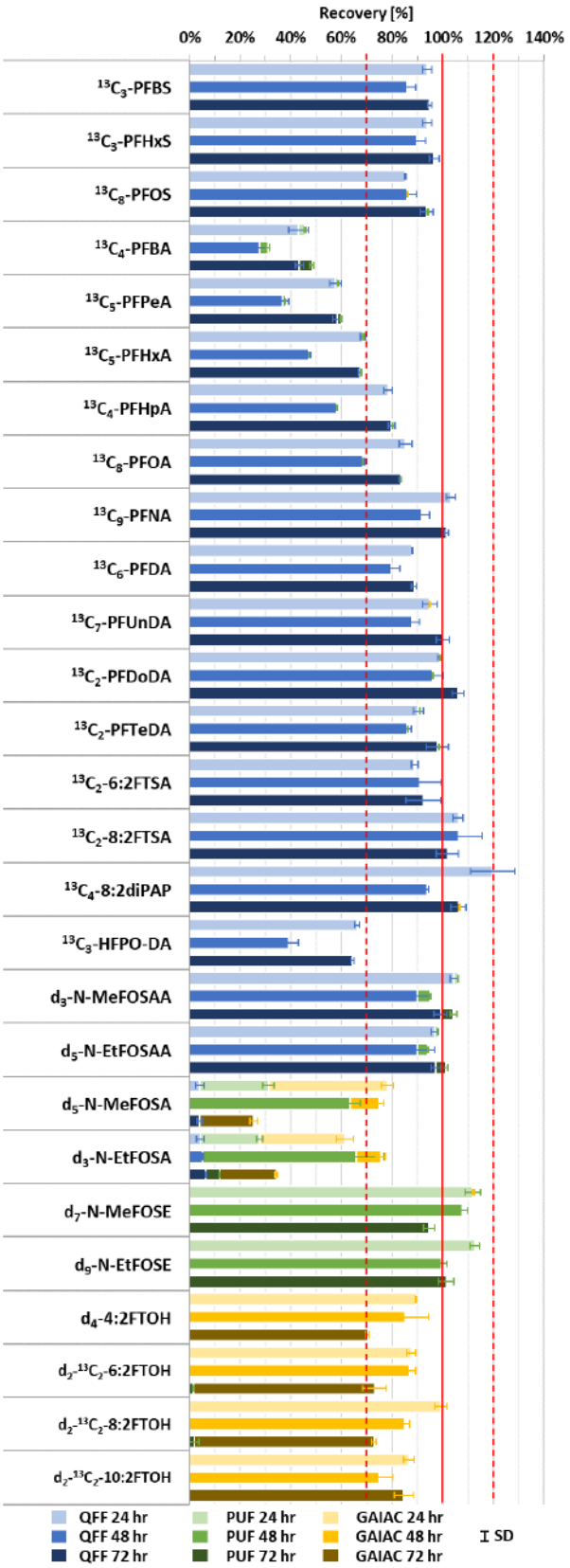


Fig. 15. Recovery (%) of Surrogate Standard for Sampling for 24 Hours, 48 Hours, and 72 Hours (n = 6)

number of carbon atoms increased.

For *N*-MeFOSA and *N*-EtFOSA, the recovery ranged from 45% to 74%, with the standard deviation ranging from 5% to 23% for each material, whose variability was higher than that of the other compounds. It has been confirmed that breakthrough does not occur in GAIAC. Decomposition in the adsorbent may account for the unstable recovery. It has been reported that the structure of substance changes depending on the sampling temperature and time [7]; thus, the obtained results likely reflected the difference in temperature conditions.

8.4. Example of Real Sample Measurement

A real sample was sampled for 24 h, 48 h, and 72 h (n = 3 each) in ambient air at a flow rate of 20 L/min in the same season to verify that the FM4 sampler can be applied to environmental measurement. To sampling were performed for each condition to verify the reproducibility.

Fig. 17 - Fig. 22 present examples of analysis for a real sample in ambient air. Except for BPFB, the concentration of the real sample was 10–100 times higher than the blank value, demonstrating that the FM4 sampler can be employed for the measurement of air samples. Comparable compositions were obtained when n = 1 and n = 2 at each sampling time, indicating good reproducibility.

Regarding the types of compounds detected at each sampling time, 25 compounds were detected in 24-h sampling, whereas 31 compounds were detected in 72-h sampling. The number of compounds detected was increased by extending the sampling time. Fig. 15 demonstrates that there was no change in recovery with respect to the sampling time except for FOSAs, and that it is possible to select a sampling time from 24–72 h depending on the concentration ratio. However, the recovery rate of FOSA may change depending on the sampling time [7].

Ionic PFAS were collected by QFF, while neutral PFAS and ionic PFAS were collected by GAIAC, in which the ratio was 40% to 70%, and PFPrA accounted for a large proportion. Only ionic PFAS were detected in PUF; however, it was considered that neutral PFAS, such as FOSAs and FOSEs, did not exist at this measurement time. Most FOSAs and FOSEs were detected by PUF at the sampling recovery rates displayed in Fig. 15, and it was presumed that they were detected by PUF if they were present in the real sample.

The results thus demonstrate that the proposed method enables simultaneous analysis of particulate and gaseous PFAS and can contribute to the development of new scientific knowledge, such as the elucidation of behavior of PFAS in the environment.

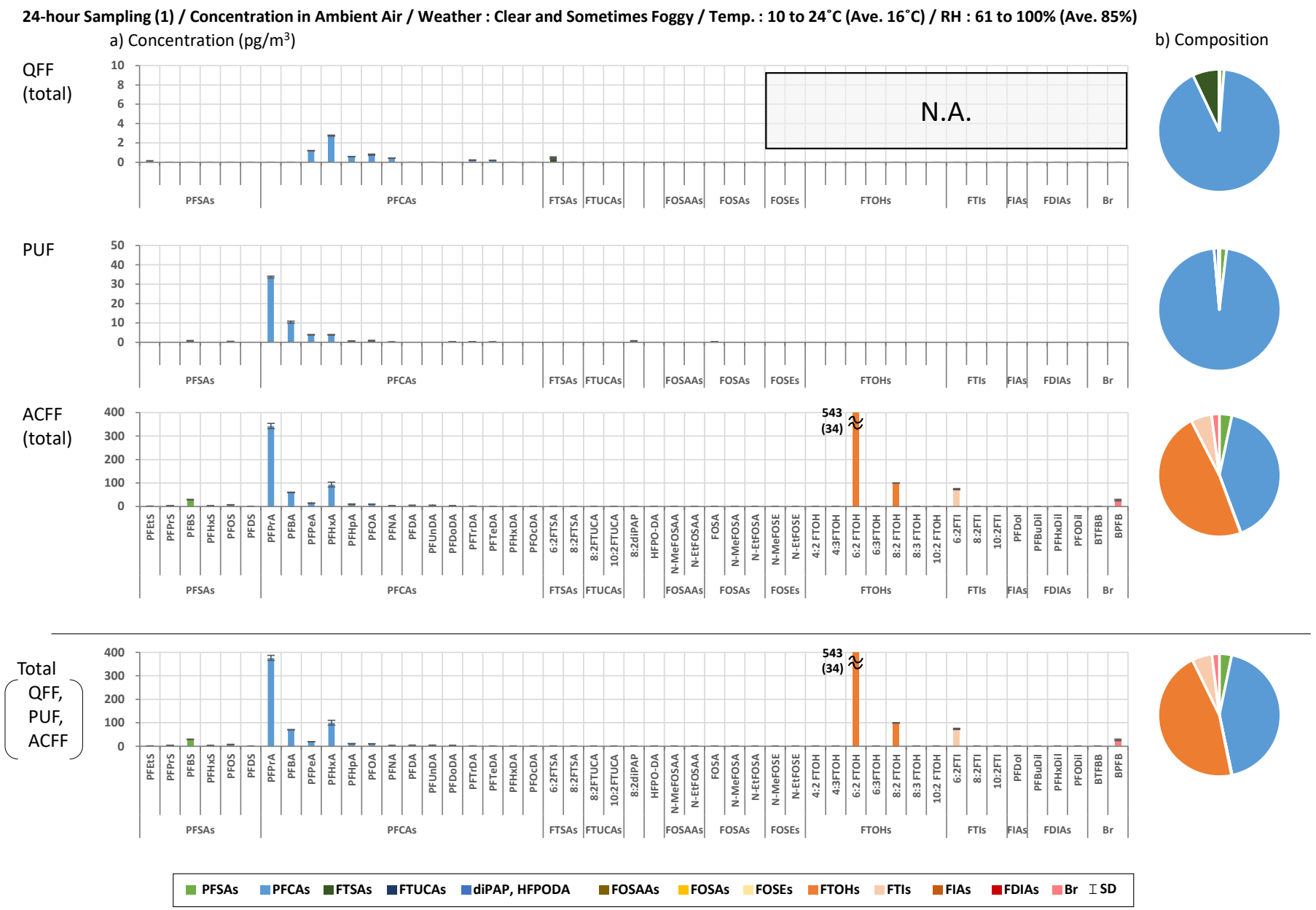


Fig. 17. Example Analysis (1) for 24-hour Sampling (n = 3)

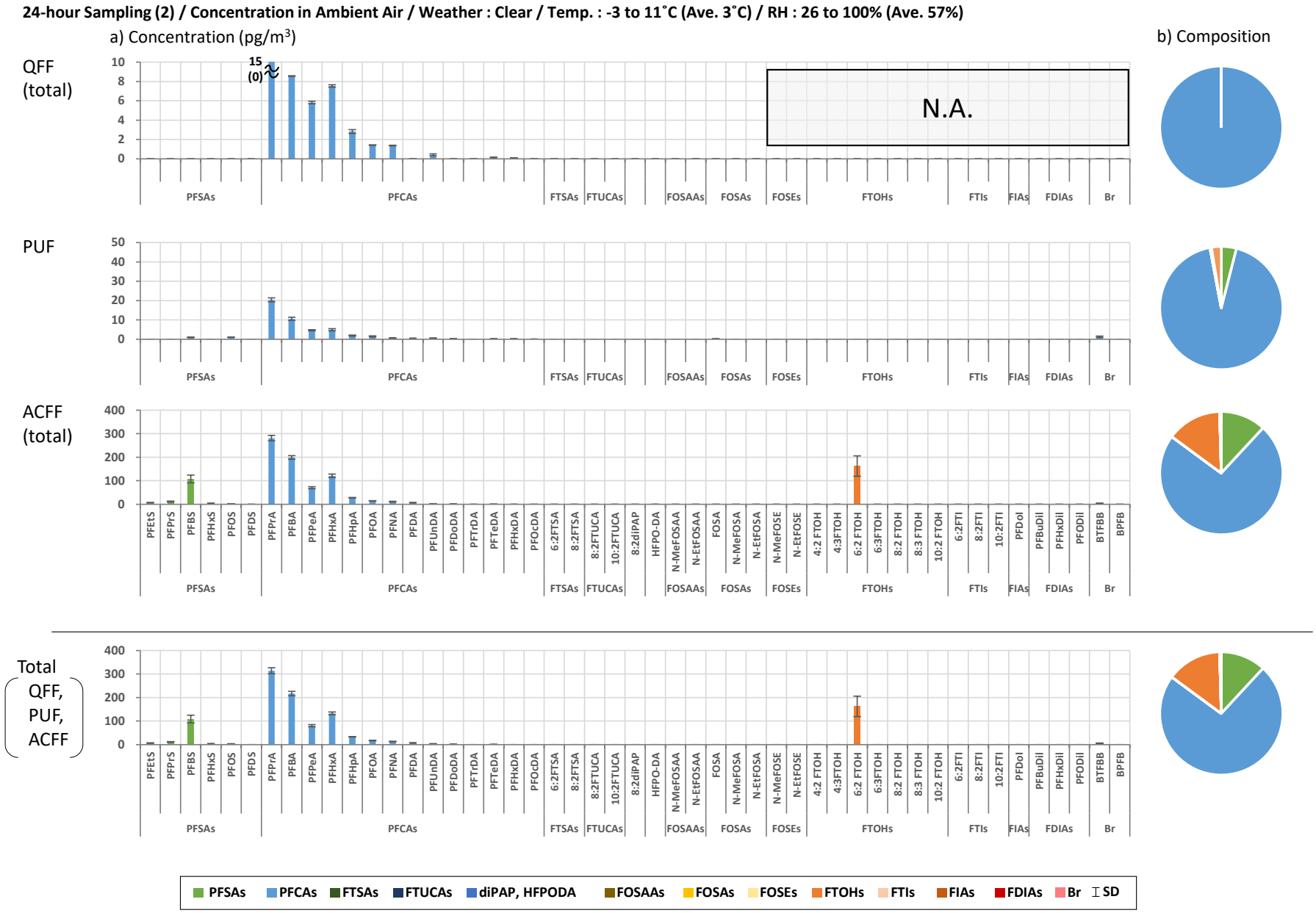


Fig. 18. Example Analysis (2) for 24-hour Sampling (n = 3)

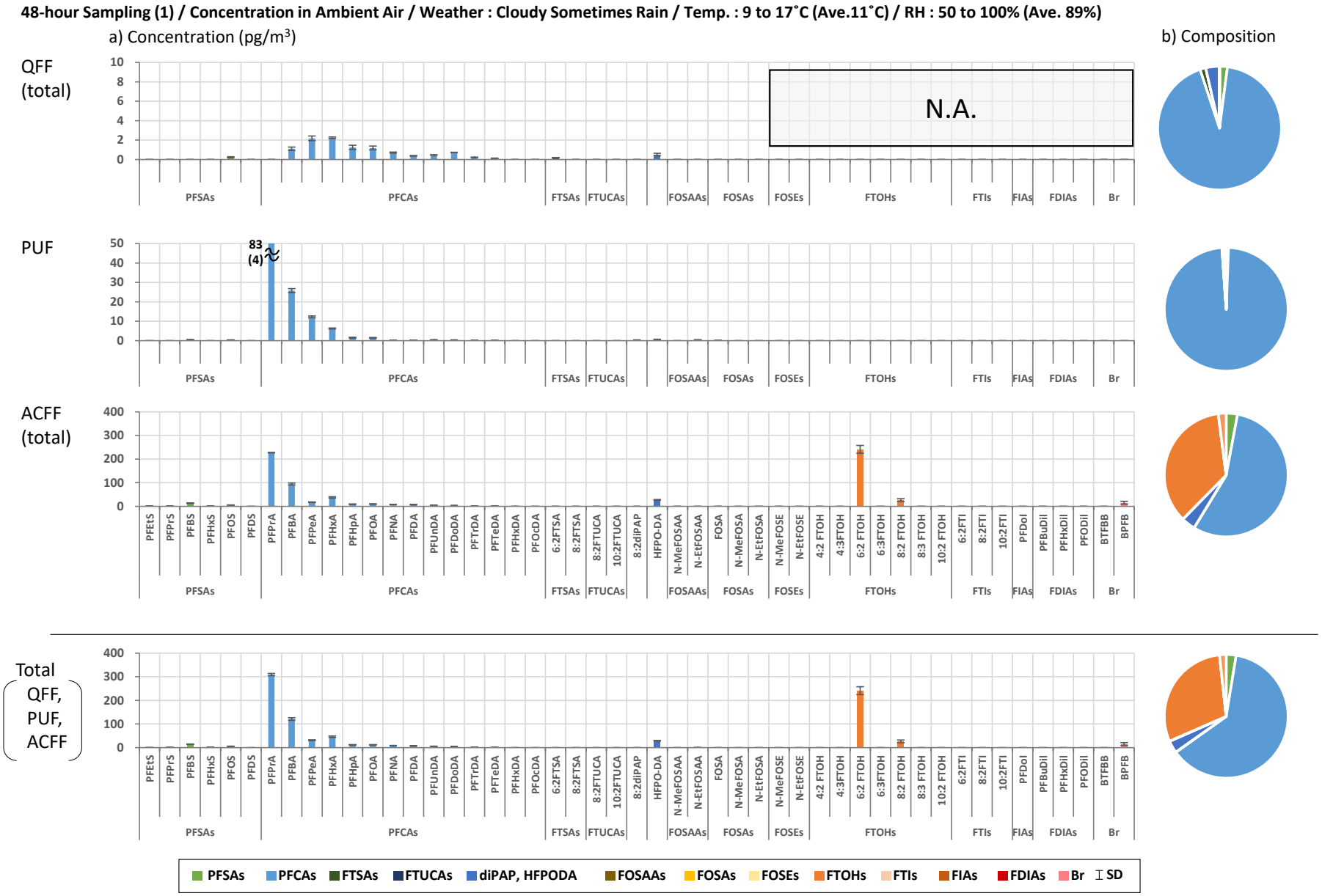


Fig. 19. Example Analysis (1) for 48-hour Sampling (n = 3)

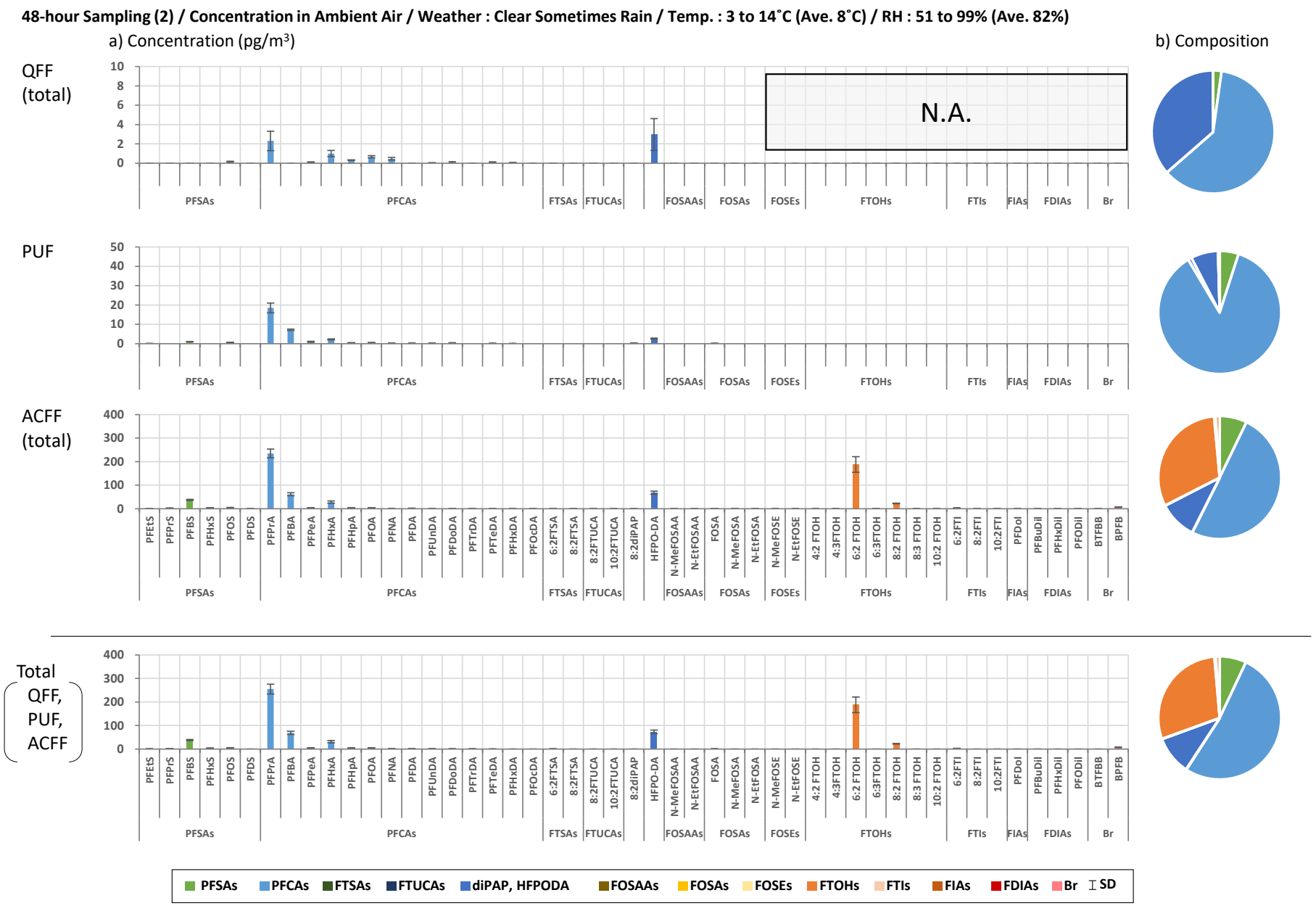


Fig. 20. Example Analysis (2) for 48-hour Sampling (n = 3)

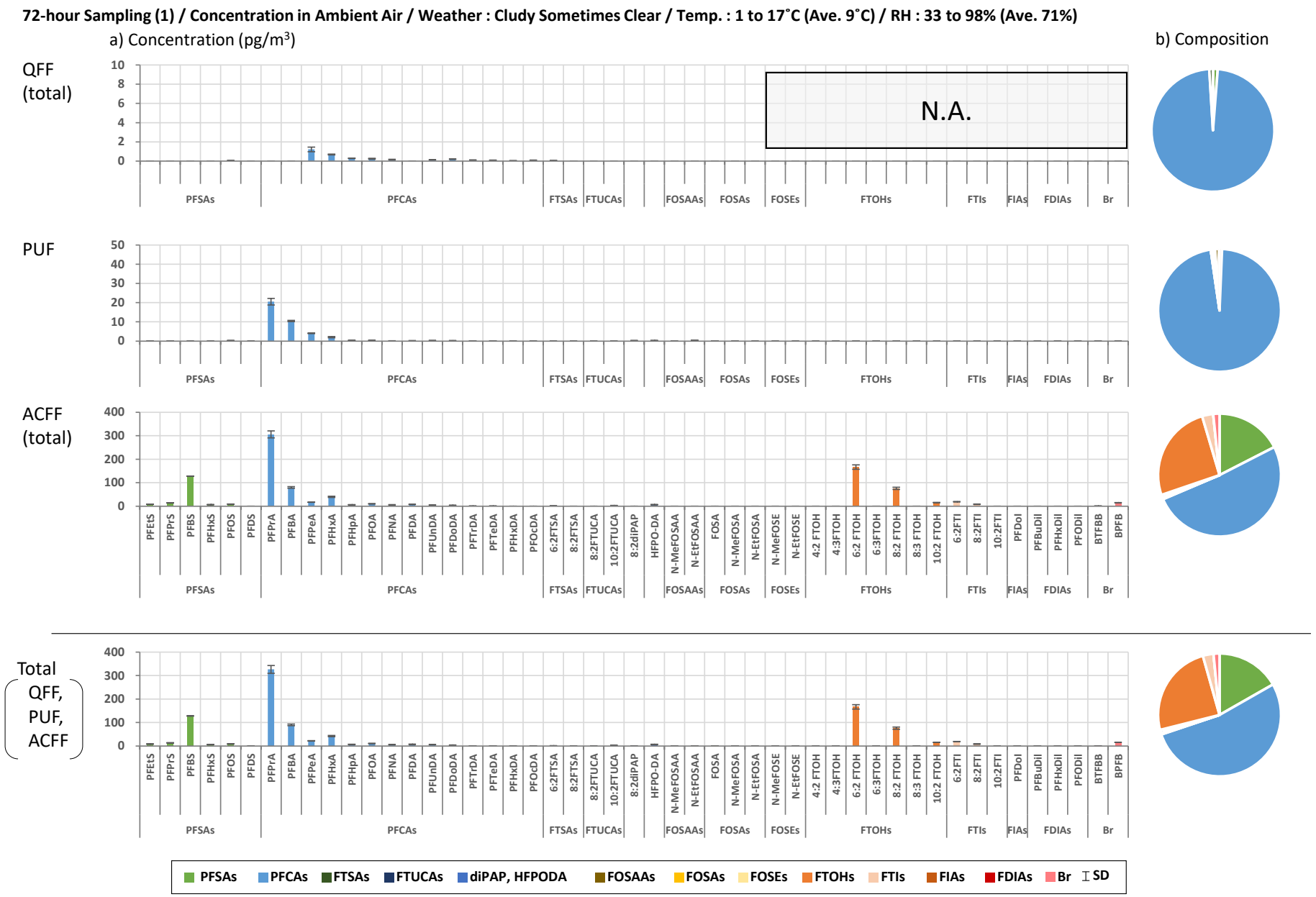


Fig. 21. Example Analysis (1) for 72-hour Sampling (n = 3)

72-hour Sampling (2) / Concentration in Ambient Air / Weather : Clear Sometimes Foggy / Temp. : 1 to 15˚C (Ave. 6˚C) / RH : 37 to 100% (Ave. 82%)

a) Concentration (pg/m^3)

b) Composition

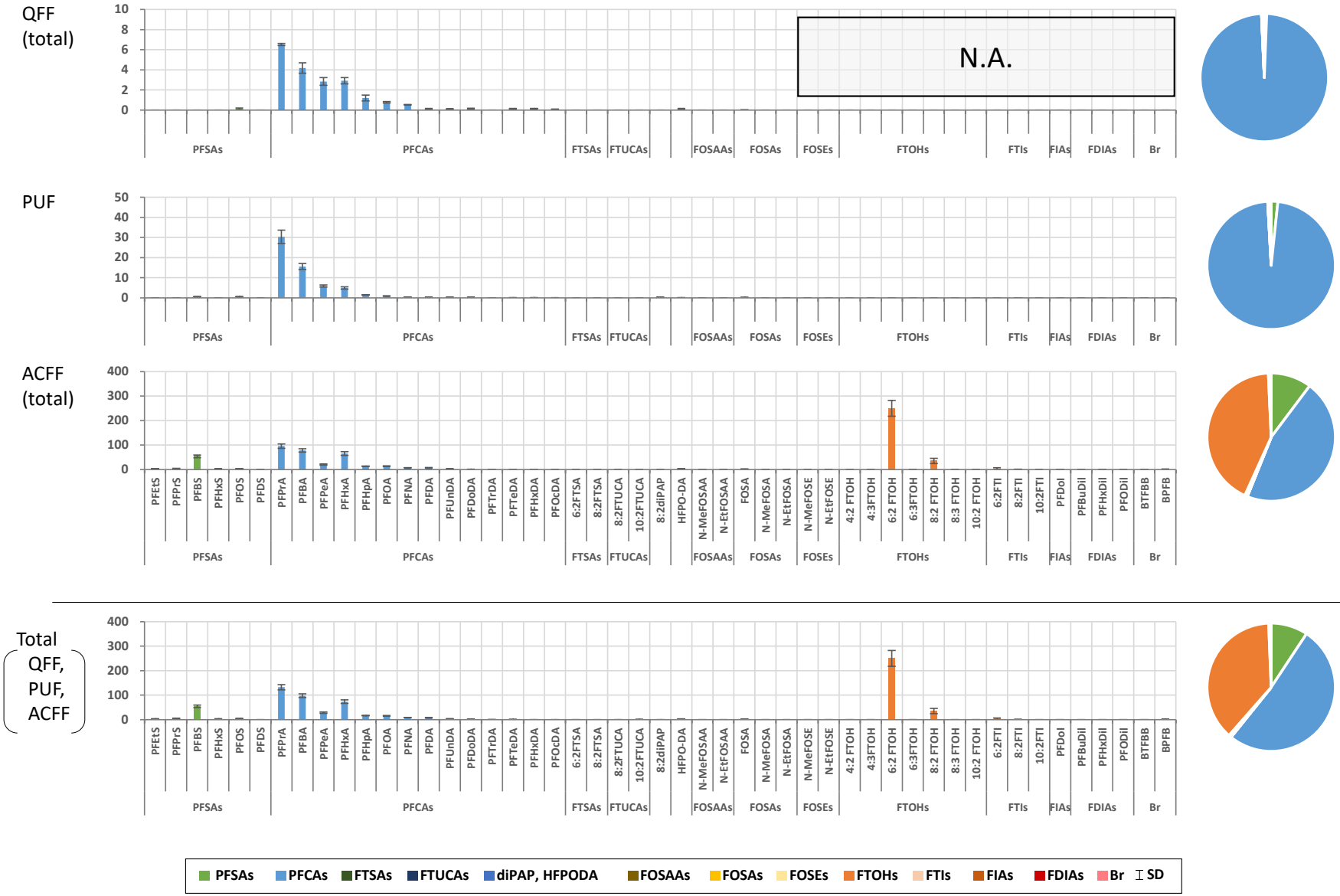


Fig. 22. Example Analysis (2) for 72-hour Sampling (n = 3)

9. Conclusion

- The FM4 sampler can be applied at a flow rate of 20 L/min for 24–72 h.
- Blank values for FM4 and trap material were barely detected except for some compounds. Even the detected compounds were 10-100 times lower than the actual sample concentrations. The FM4 sampler is useful for PFAS measurements in air samples (excluding BPFB).
- It was shown that each compound with different composition could be collected for each material, and it is possible to analyze particulate and gaseous PFAS.

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Published in Japan, April 25, 2022
TG0001ENR2