PFAS in Air – Method OTM-50

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Agenda

- Background
- PFAS Volatility
- PFAS in Ambient Air Drivers
- SVOA vs VOA compounds
- Methods (OTM-Other Test Methods)
- OTM-50 Analyte List
- OTM-50 Stability of Standards – 23-Week Study
- OTM-50 Detection and Quantitative Reporting Limits
- Sampling Methods
- OTM-50 Sample Train
- OTM-50 Chromatogram
- SVOA Air PFAS - Examples
- Challenges and questions
- Stack Testing Drivers
- Methods
- Summary

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Background
PFAS in Air

Background

- OTM-50
- Based on method TO-15A
- 30 compounds listed
- No specificity on IS or SS
- Use of one IS and SS from TO-15A is acceptable
- Standards are available from two nontraditional vendors
- One traditional vendor resells from one of the vendors
- PIC's and PID's

Background PFAS Volatility

- Remediation
  - Emergency Response Sites
  - Firefighter Training Facilities
  - Former Manufacturing Sites
- Emissions
  - Product Manufacturers
  - Incinerator Facilities
  - Landfill Sites
- Occupational Health/Personal Monitoring
  - Wastewater Treatment Facility
  - Firefighter Training area

Background PFAS in ambient air drivers

- Are air emissions a significant part of the emission profile?
- Both point and non-point source considerations
  - Factories using PFAS
  - Factories producing PFAS
  - Wastewater treatment plants, especially aerators
  - Landfill gas?
  - Other?
- Understanding deposition: PFAS can go very far: Arctic levels linked to mid latitude PFAS
- Early on, no standard methods or EPA development

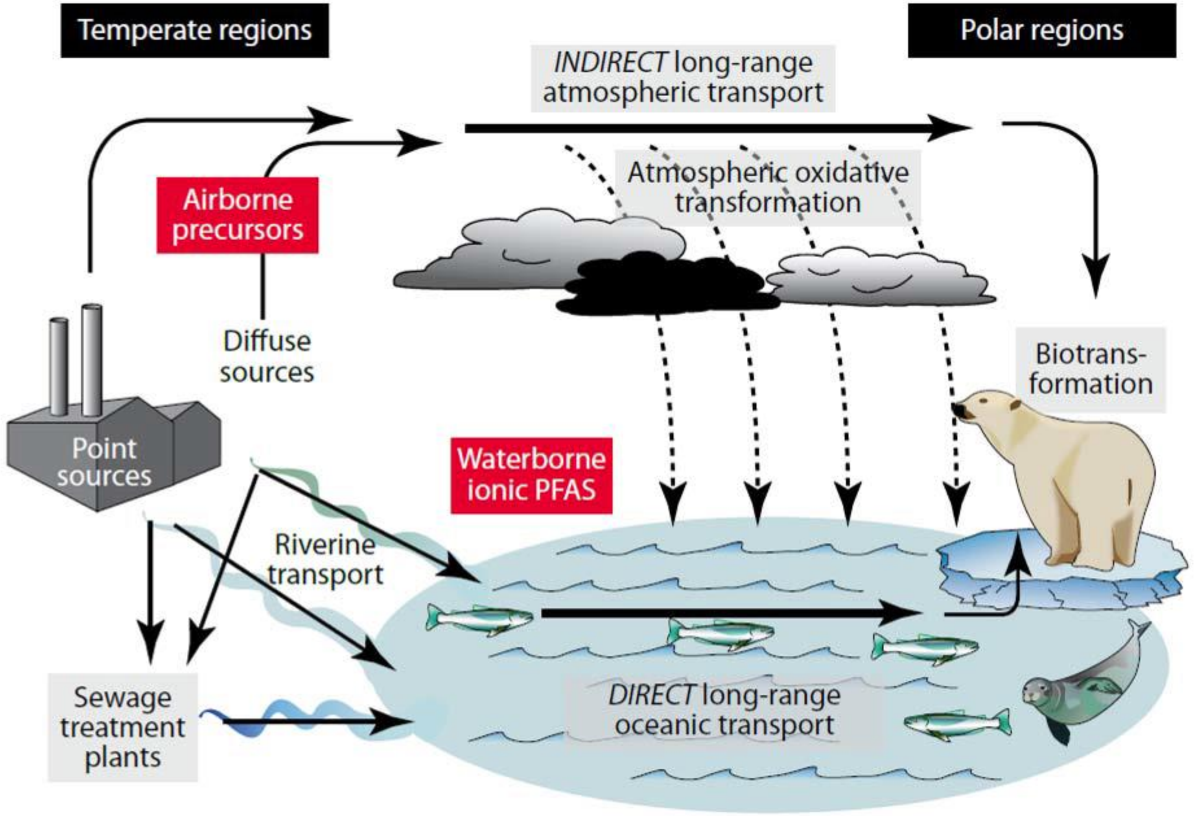
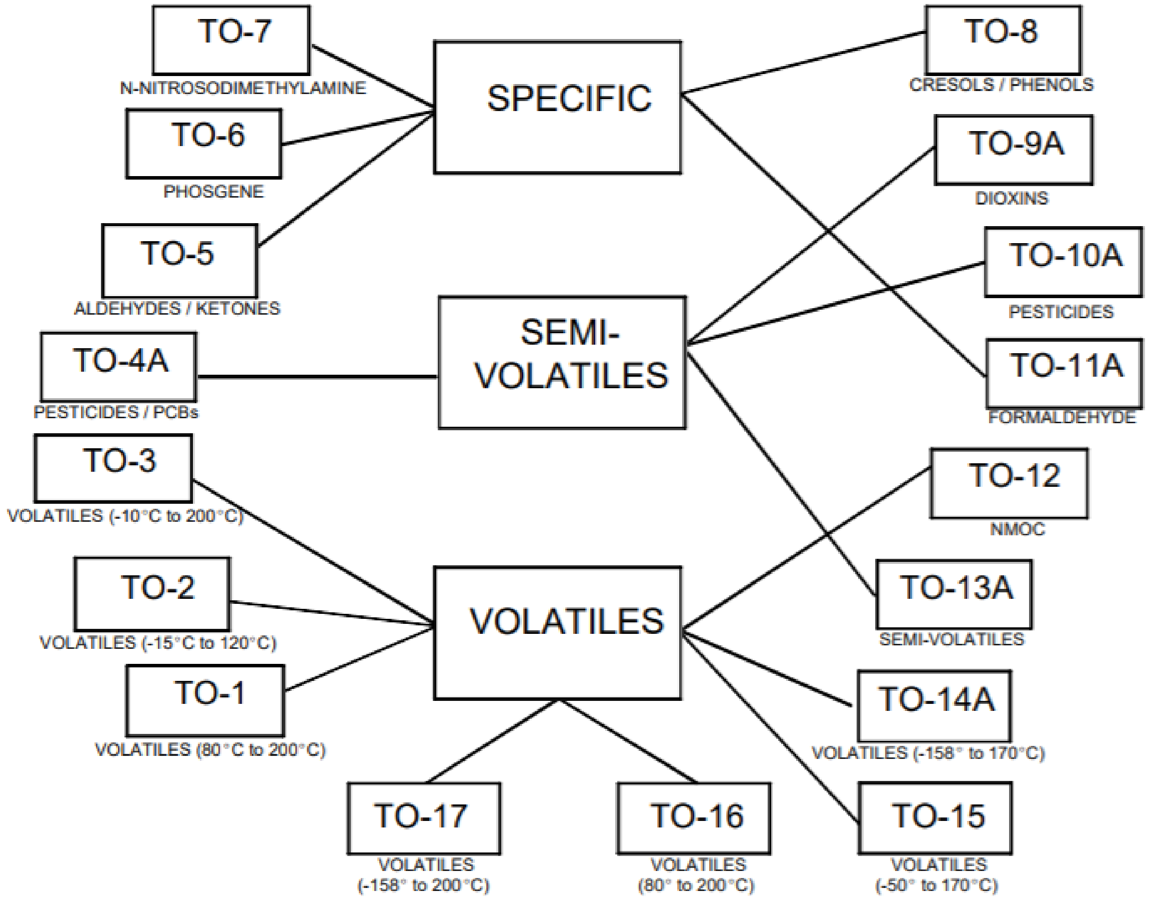


Image from AMAP Arctic Pollution 2009

Background Semi-Volatile vs. Volatile



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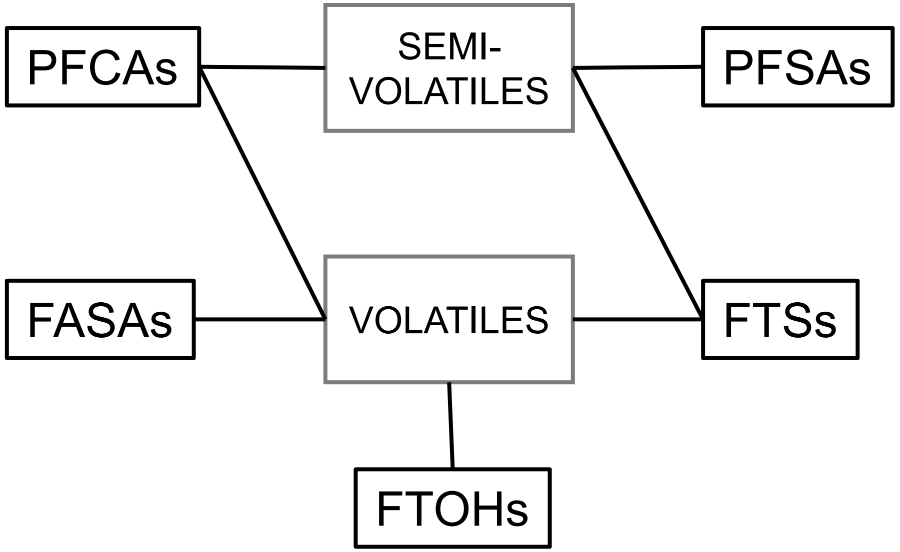

(Roth, 2021)

Key Takeaway

With thousands of PFAS compounds, there will likely need to be more than one analytical method to determine volatile and semi-volatile PFAS concentrations in air.

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Methods

- Analytical Methods:
  - GC/MS Method for OTM-50 (No MRM transitions)(Full scan method) (SGS uses GC/MS/MS)
  - LC/MS/MS
  - LC qTOF HRMS (NTA)
  - GC qTOF HRMS (NTA)

  - OTM-50 (Regular GC/MS method)
  - OTM-45 (EPA 1633)
  - ASTM D8591 (Fluorotelomer Alcohols) (TD)

OTM-50 Analyte List

Compound Name	CAS #	Chemical Formula
Carbon tetrafluoride	75-73-0	CF_4
Hexafluoroethane (FC-116)	76-16-4	C_2F_6
Tetrafluoroethene	116-14-3	C_2F_4
Trifluoromethane (HFC-23)	75-46-7	CHF_3
Octafluoropropane	76-19-7	C_3F_8
Difluoromethane (HFC-32)	75-10-5	CH_2F_2
Fluoromethane (HFC-41)	593-53-3	CH_3F
Pentafluoroethane (HFC-125)	354-33-6	C_2HF_5
Hexafluoropropene	116-15-4	C_3F_6
Hexafluoropropene oxide (HFPO)	428-59-1	C_3F_6O
Decafluorobutane	355-25-9	C_4F_{10}
Dodecafluoropentane	678-26-2	C_5F_{12}
Tetradecafluorohexane	355-42-0	C_6F_{14}
1H-Perfluoropentane	375-61-1	C_5HF_{11}
Hexadecafluoroheptane	335-57-9	C_7F_{16}
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1)	3330-15-2	$C_5HF_{11}O$
1H-Perfluorohexane	355-37-3	C_6HF_{13}
1H-Perfluoroheptane	375-83-7	C_7HF_{15}
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	3330-14-1	$C_8HF_{17}O_2$
1H-Perfluorooctane	335-65-9	C_8HF_{17}
Octadecafluorooctane	307-34-6	C_8F_{18}
1H-Nonafluorobutane	375-17-7	C_4HF_9
1H-Heptafluoropropane	2252-84-8	C_3HF_7
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	$C_2H_2F_4$
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	$C_2H_3F_3$
Chlorodifluoromethane (HCFC-22)	75-45-6	$CHClF_2$
Chlorotrifluoromethane (CFC-13)	75-72-9	CF_3Cl
Octafluorocyclobutane (FC-C318)	115-25-3	C_4F_8
Octafluorocyclopentene (FC-C1418)	559-40-0	C_5F_8
Trichloromonofluoromethane (CFC-11)	75-69-4	CCl_3F

- List of 30 PFAS. Note that OTM-50 is Rev 0, 1/14/2025

OTM-50 Analyte List

	Compound	Formula
1	Tetrafluoromethane	CF4
2	Hexafluoroethane	C2F6
3	Chlorotrifluoromethane	CClF3
4	Tetrafluoroethylene	C2F4
5	Fluoroform	CHF3
6	Difluoromethane	Ch2F2
7	Octafluoropropane	C3F8
8	Fluoromethane	Ch3F
9	Pentafluoroethane	C2HF5
10	1,1,1-trifluoroethane	C2H3F3
11	Hexafluoropropene	C3F6
12	Hexafluoropropene Oxide	C3F6O
13	Chlorodifluoromethane	CHClF2
14	Octafluorocyclobutane	C4F8
15	Perfluorobutane	C4F10
16	1,1,1,2-tetrafluoroethane	C2H2F4
17	1H-Heptafluoropropane	C3HF7
18	Dodecafluoro-n-pentane	C5F12
19	Trichlorofluoromethane	CCl3F
20	Octafluorocyclopentene	C5F8
21	1H-Nonafluorobutane	C4HF9
22	Tetradecafluorohexane	C6F14
23	1H-Perfluoropentane	C5HF11
24	Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	C5HF11O
25	hexadecafluoroheptane	C7F16
26	1H-Perfluorohexane	C6HF13
27	Perfluorooctane	C8F18
29	1H-Perfluoroheptane	C7HF15
30	2H-Perfluoro-5-methyl-3,6-dioxanonane	C8HF17O2
31	1H-Perfluorooctane	C8HF17

OTM-50 Stability of standards – 23-week study

Table OTM-50-8. Volatile VFC Stability Data for the Targeted Analytes – 30 VFC Standard Mix[1] Target Compound

	Duration (weeks)							
	0	**3**	**5**	**7**	**11**	**13**	**17**	**23**
Carbon tetrafluoride	100%	89%	87%	105%	85%	97%	57%	54%
Hexafluoroethane (FC-116)	100%	102%	95%	88%	93%	81%	76%	78%

The stability of the 30 components in a canister containing the VFC calibration standard was assessed over a period of 23 weeks. All compounds were present in the standard at 20 ppbv except for CF4 (200 ppbv). All compounds were stable through 23 weeks other than the 2 compounds listed above where they tail off at week 17 and 23.

Ref: Method OTM-50

OTM-50 Detection and Quantitative Reporting Limits

Target Compound	CAS #	Canister Concentration (ppbv)1	MDL (ppbv)	MDL (µg/m3)	QRL (ppbv)	QRL (µg/m3)
Carbon tetrafluoride	75-73-0	0.125	0.030	0.109	0.09	0.327
Hexafluoroethane (FC-116)2	76-16-4	0.0125	0.0125	0.072	0.037	0.215
Tetrafluoroethene	116-14-3	0.0125	0.011	0.044	0.033	0.132
Trifluoromethane (HFC-23)4	75-46-7	0.0125	0.050	0.145	0.15	0.435
Octafluoropropane2	76-19-7	0.0125	0.0125	0.098	0.037	0.293
Difluoromethane (HFC-32)	75-10-5	0.0125	0.016	0.034	0.048	0.102
Fluoromethane (HFC-41)	593-53-3	0.050	0.019	0.027	0.057	0.081
Pentafluoroethane (HFC-125)2	354-33-6	0.0125	0.0125	0.062	0.037	0.187
Hexafluoropropene2	116-15-4	0.0125	0.0125	0.078	0.037	0.233
Hexafluoropropene oxide (HFPO)	428-59-1	0.050	0.021	0.146	0.063	0.438
Decafluorobutane2	355-25-9	0.0125	0.0125	0.124	0.037	0.371
Dodecafluoropentane3	678-26-2	0.025	0.023	0.271	0.069	0.813
Tetradecafluorohexane	355-42-0	0.0125	0.016	0.225	0.048	0.675
1H-Perfluoropentane	375-61-1	0.0125	0.016	0.180	0.048	0.54
Hexadecafluoroheptane2	335-57-9	0.0125	0.0125	0.202	0.037	0.605
Heptafluoropropyl-1,2,2,2-tetra Fluoroethyl ether (E1)	3330-15-2	0.0125	0.014	0.165	0.042	0.495
1H-Perfluorohexane	355-37-3	0.0125	0.016	0.206	0.048	0.618
1H-Perfluoroheptane	375-83-7	0.0125	0.011	0.163	0.033	0.489
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)2	3330-14-1	0.0125	0.0125	0.235	0.037	0.705
1H-Perfluorooctane2	335-65-9	0.0125	0.0125	0.218	0.037	0.655
Octadecafluorooctane2	307-34-6	0.0125	0.0125	0.228	0.037	0.683
1H-Nonafluorobutane3	375-17-7	0.0125	0.011	0.097	0.033	0.291
1H-Heptafluoropropane	2252-84-8	0.0125	0.014	0.098	0.042	0.294
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	0.0125	0.016	0.066	0.048	0.198
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	0.050	0.032	0.111	0.096	0.333
Chlorodifluoromethane (HCFC-22)	75-45-6	0.0125	0.011	0.038	0.033	0.114
Chlorotrifluoromethane (CFC-13)2	75-72-9	0.0125	0.0125	0.054	0.037	0.163
Octafluorocyclobutane (FC-C 318)2	115-25-3	0.0125	0.0125	0.104	0.037	0.311
Octafluorocyclopentene (FC-C1418)2	559-40-0	0.0125	0.0125	0.110	0.037	0.331
Trichloromonofluoromethane (CFC-11)	75-69-4	0.0125	0.014	0.079	0.042	0.237

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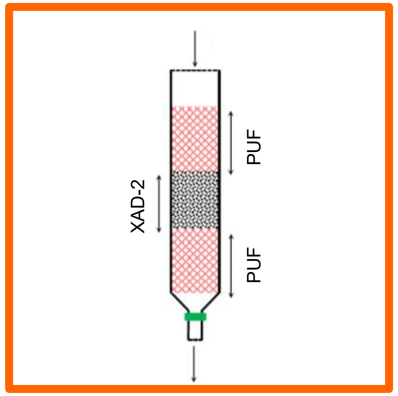
Sampling Methods



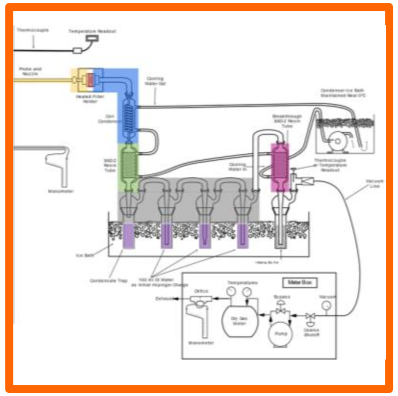
(Roth et. al, 2020)

Filter/XAD/PUF Sampler

- Similar to TO-9/TO-13
- 1-4 Days Sample Duration
- Most widely documented

Thermal Desorption

- Similar to TO-17
- 5-30 Minutes Sample Duration



OTM-45 Sampler

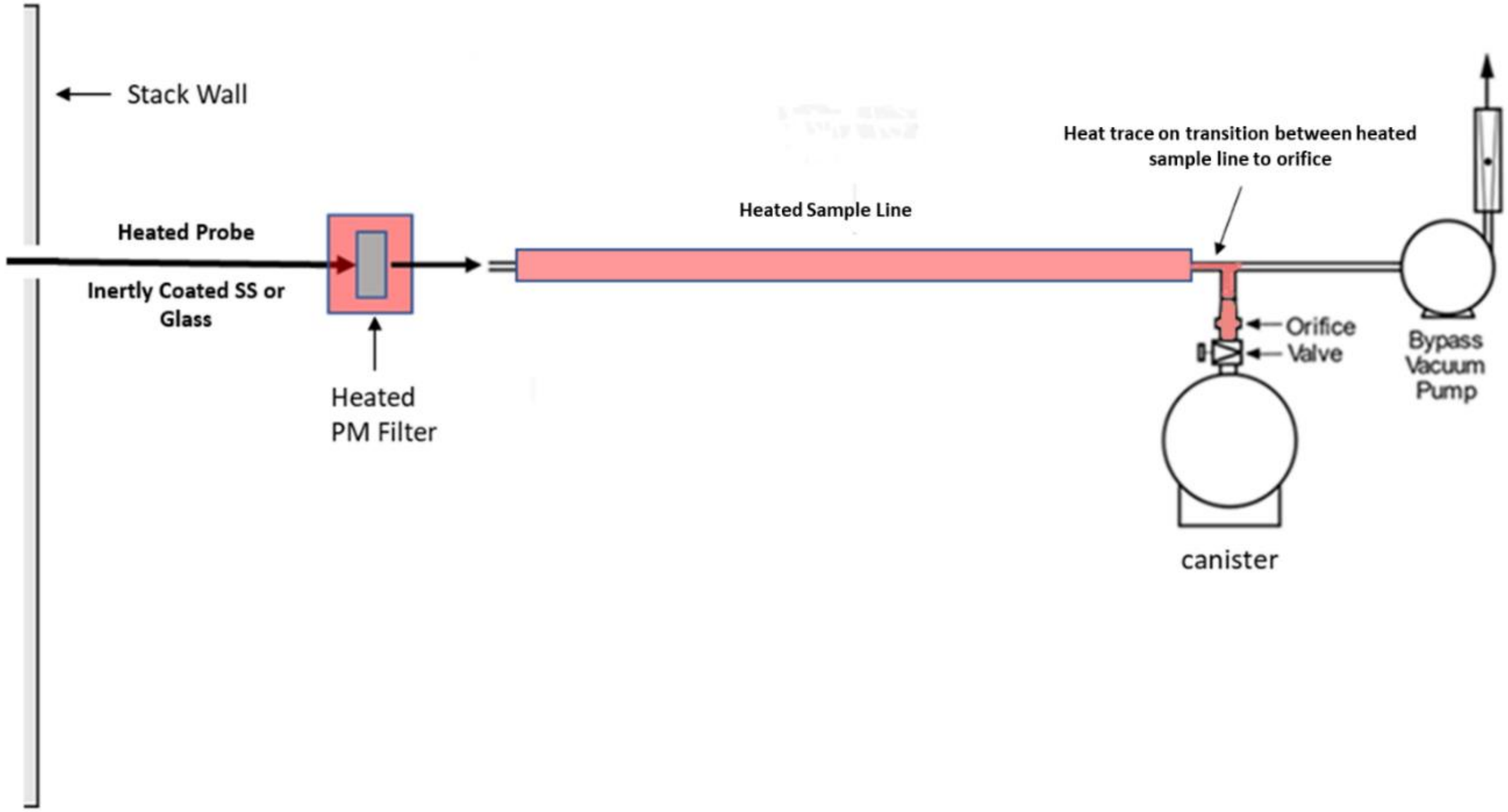
- Modified Method 5
    - Filter
    - XADs
    - Impingers

OTM-50

- SUMMA Canisters
- Passive Sampler

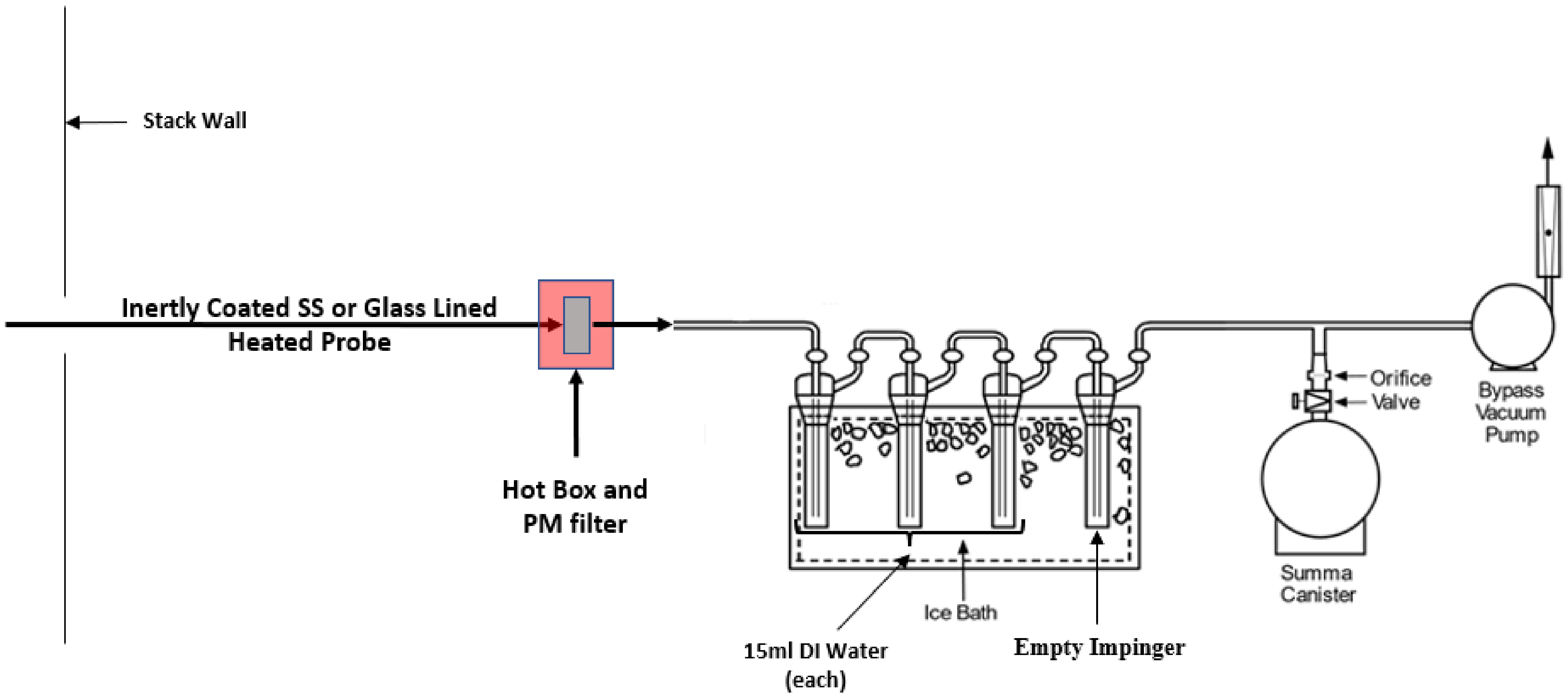
OTM-50 Sample Train

- Direct Sampling System



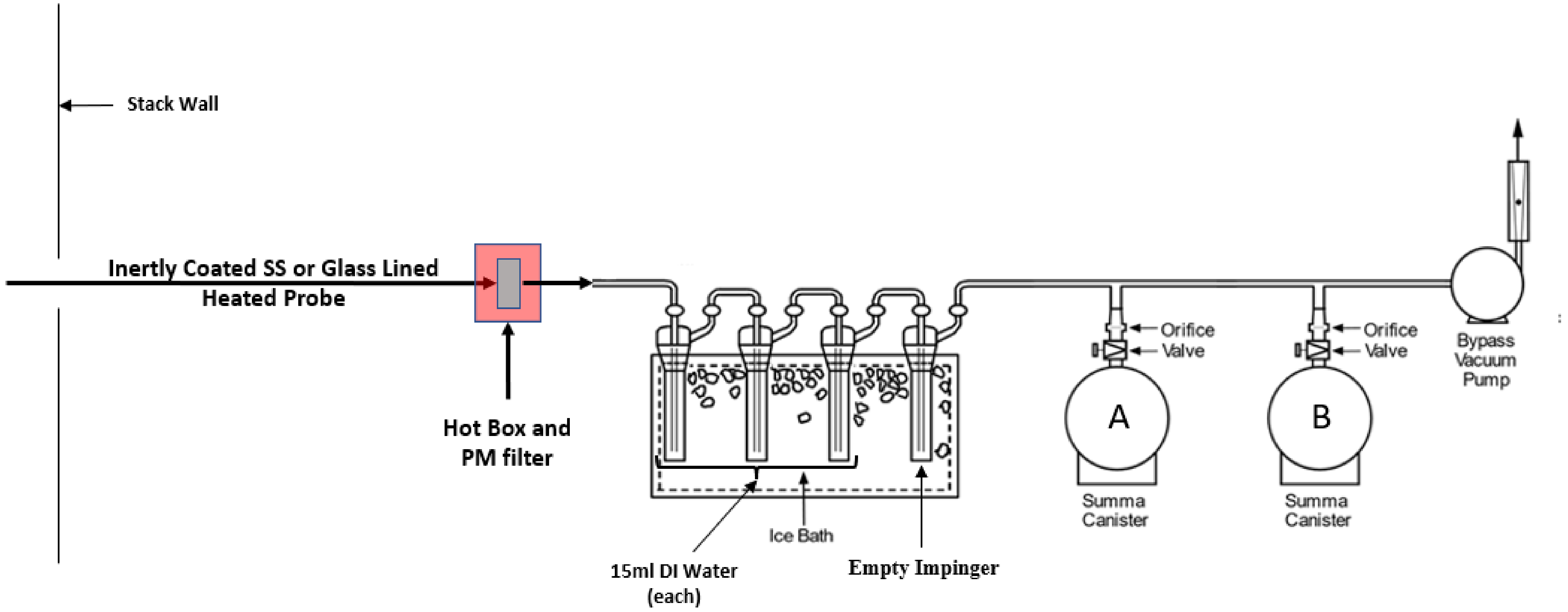
OTM-50 Sample Train

- Canister Sampling System with Water/Acid Gas Management Direct Sampling System

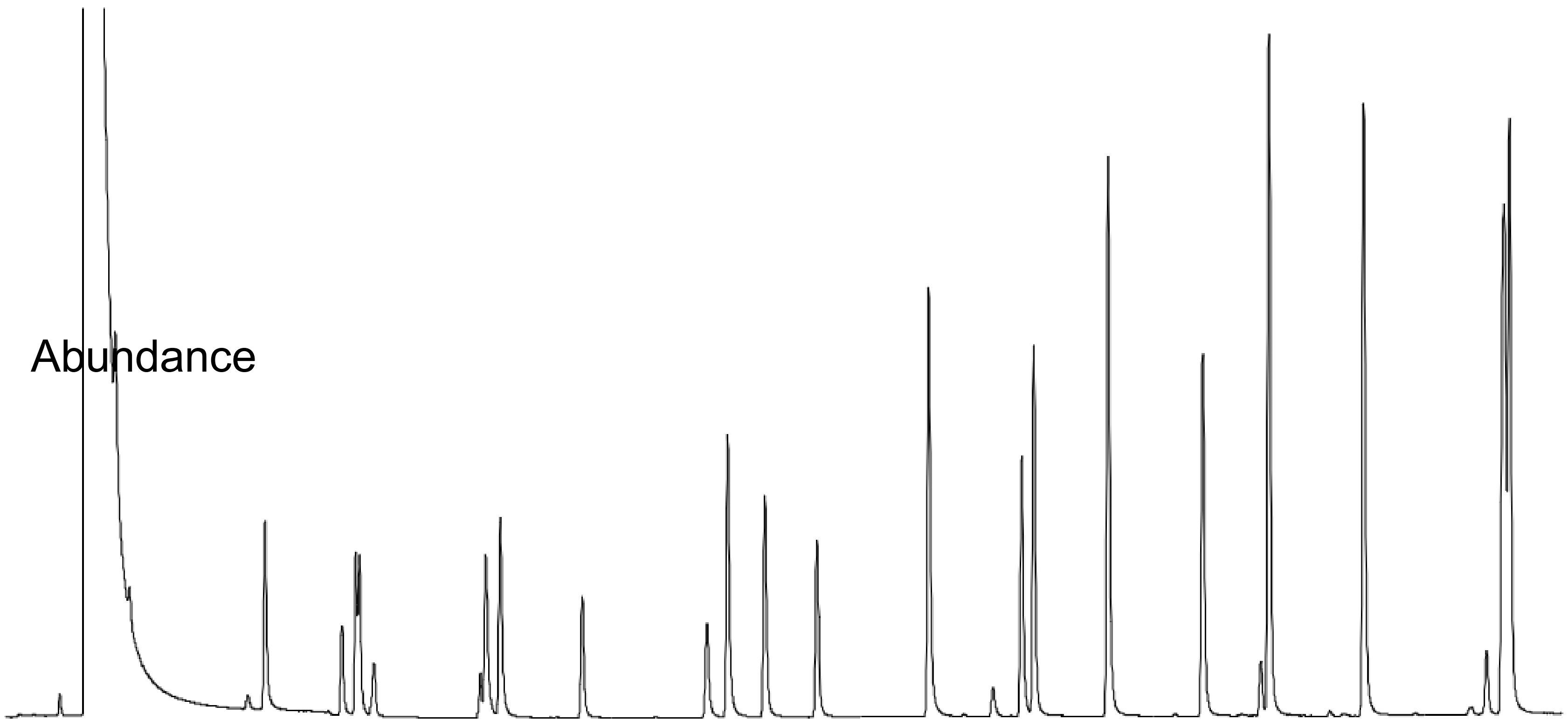


OTM-50 Sample Train

- Canister Sampling System with Multiple Canisters



OTM-50 Chromatogram

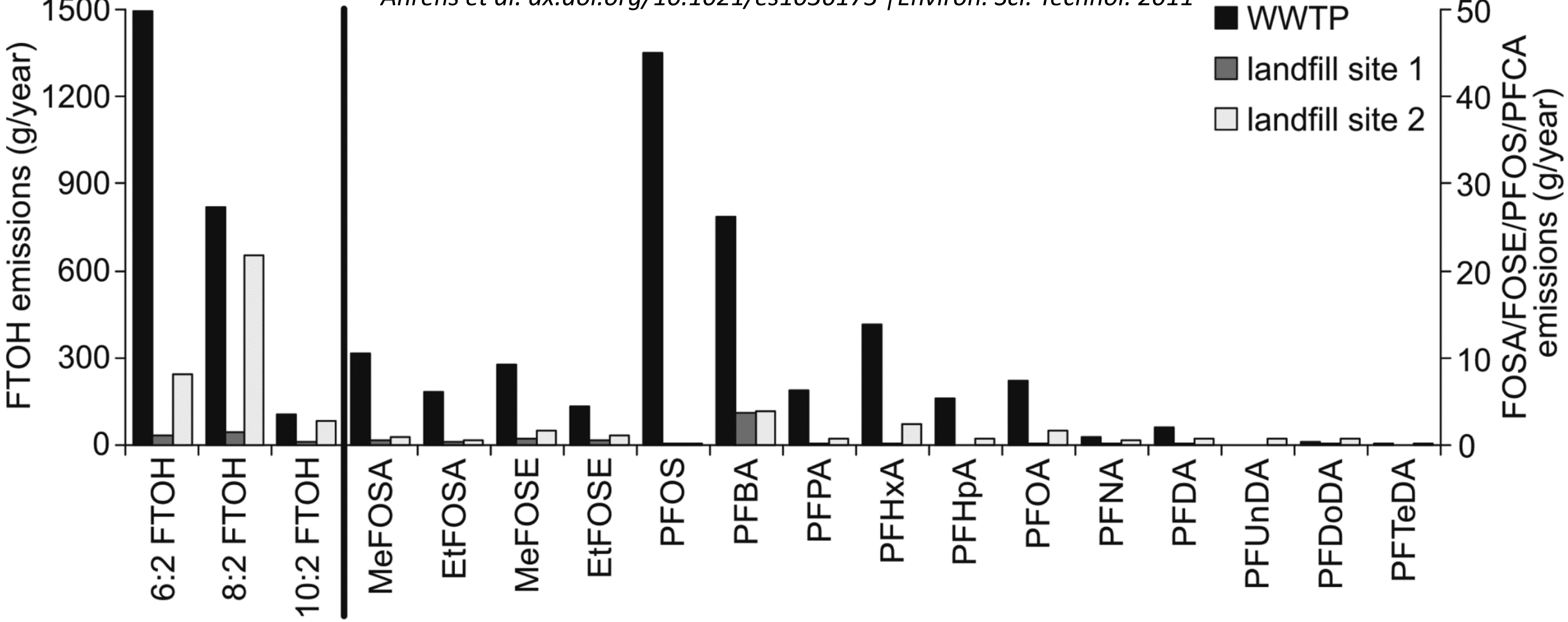


Ref: Markes International Application Note 177

Examples of PFAS in Air (SVOA)

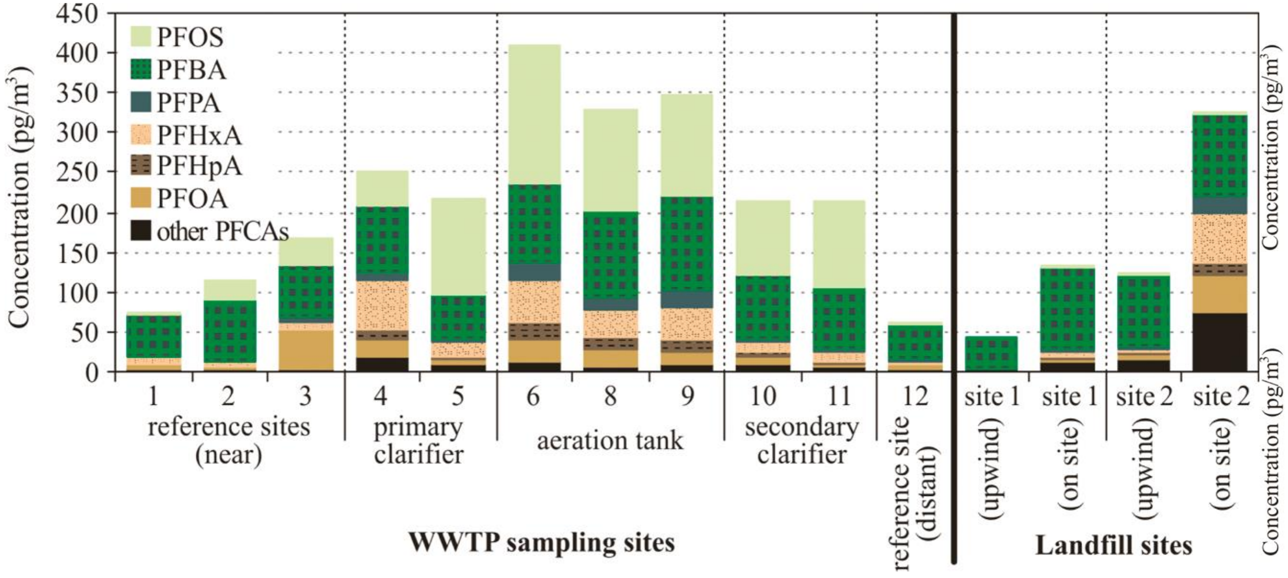
PFAS from WWTP/landfills

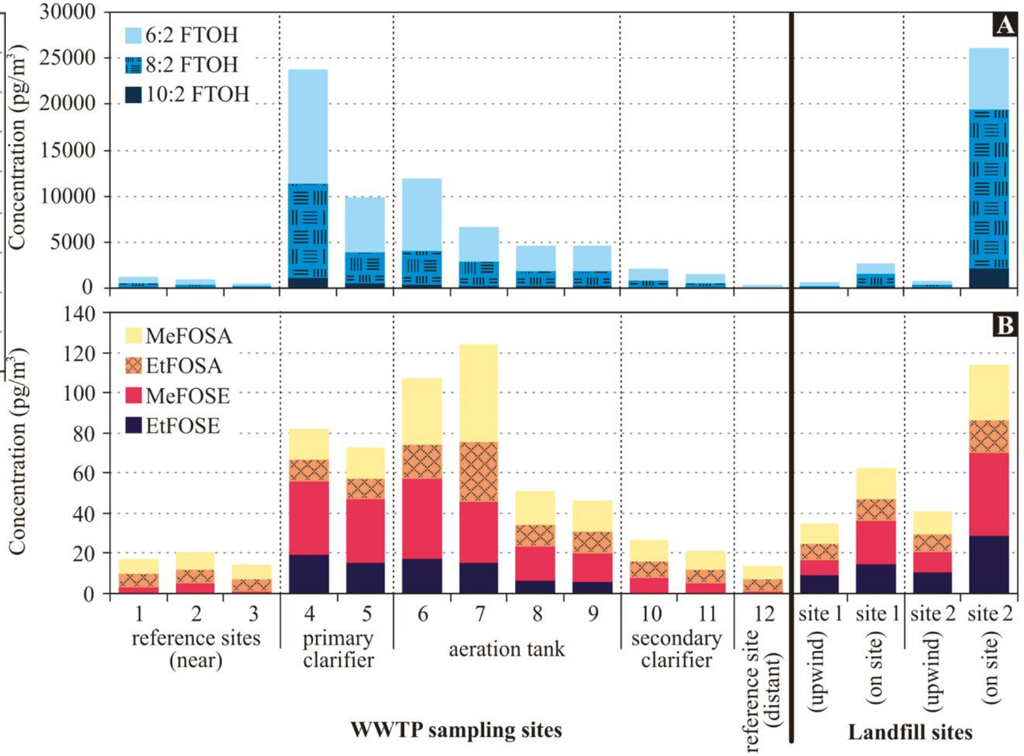
Ahrens et al. dx.doi.org/10.1021/es1036173 |Environ. Sci. Technol. 2011



2560 g PFAS/year for the WWTP tested, mostly FTOHs. Compared with 200-15000 g/year from effluent + biosolid (Guerra et al. 2014),

Wastewater treatment plants as sources

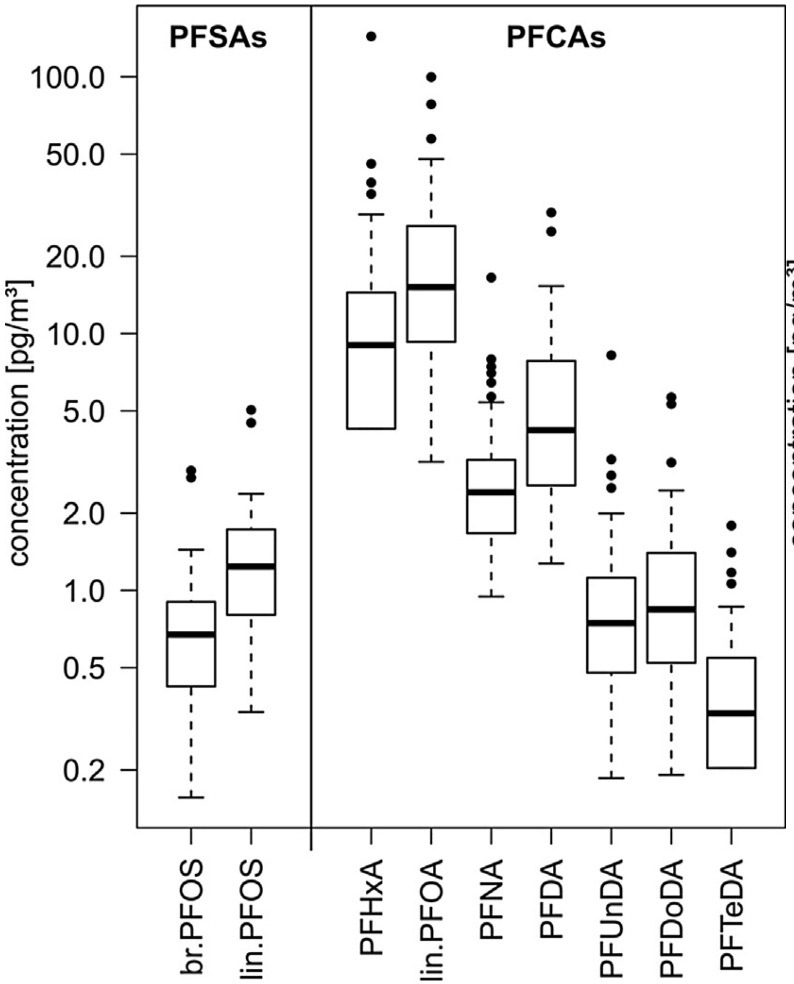


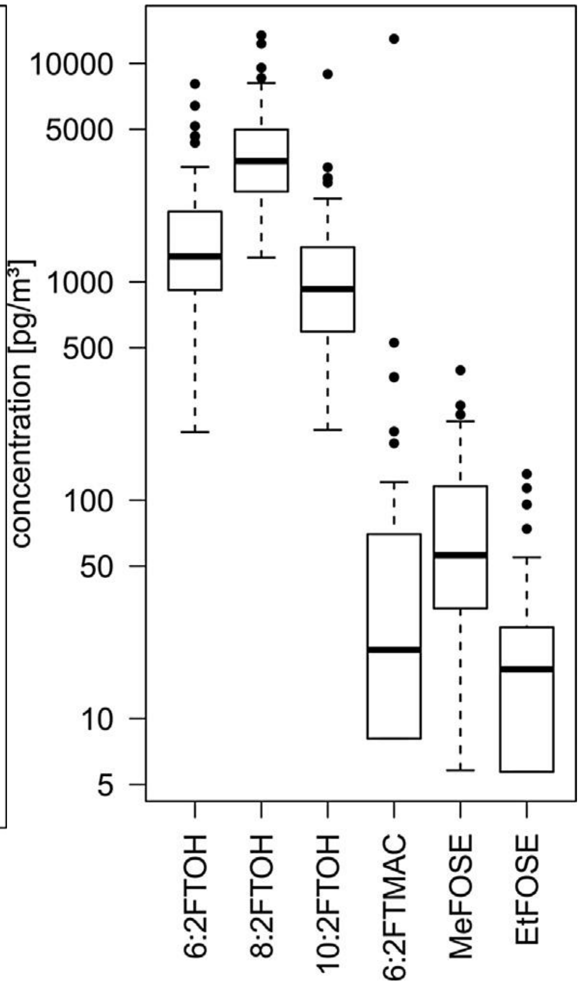


Ahrens et al. dx.doi.org/10.1021/es1036173 |Environ. Sci. Technol. 2011

- Of target PFAS, fluorotelomer alcohols 2 orders of magnitude higher

Indoor environments (Children's bedrooms)





- More carboxylates than sulfonates in indoor air
- FTOH predominate
- High variability due to varied sources

Winkens et al.. Environmental Pollution. 2017 .

Challenges and questions

Sampling

- How? What sampling media?
- For how long? Flow rate?
- Breakthrough, filter sorption, other

Measurement

- What targets to measure?
- Field standards
- PFAS methods
- Specific issues with air

Modeling and Data interpretation

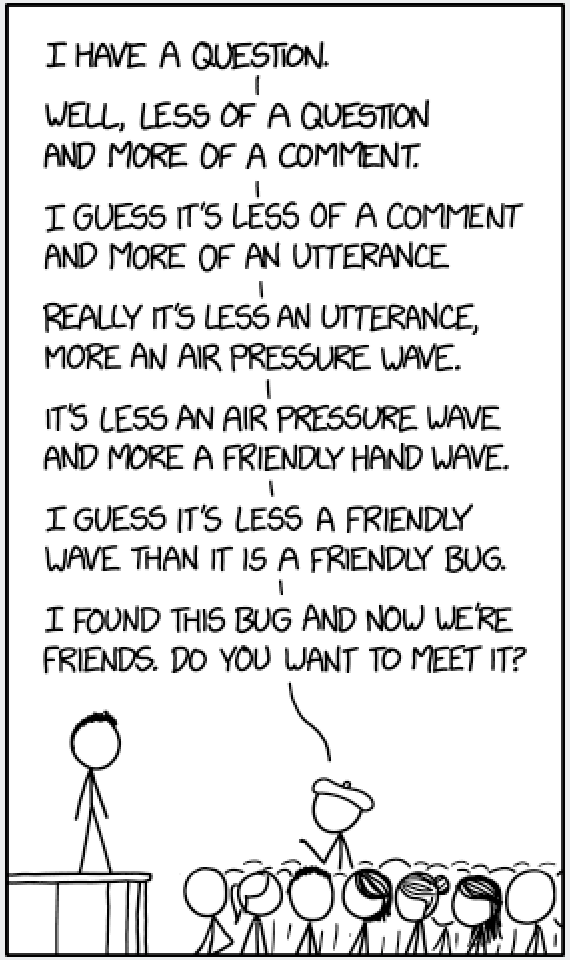
- Big uncertainties in dispersion, calculated partitioning coefficients, other modeling parameters
- Role of precursor transformation

Stack testing drivers

- Incinerators, especially those handling AFFF and hazardous waste
- Factories producing PFAS or polymers
- Factories using PFAS
- Still very early, mostly driven by PFAS measured in soil/water adjacent to sites
-

Summary

Summary



https://xkcd.com/2191/

- Complex Analysis
- Develop method-specific technical (and robust QC) requirements
- Even though the method is based on TO-15 it is comparatively complex
- Standards for the 30 compounds
- Management of CO2
- OTM-50 is not prescriptive as written (revisions must be made)

Thank you!

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