right solutions.
right partner.

SoBRA Early Careers Webinar – Choosing lab analysis methods for risk assessments

Geraint Williams, Associate

Introduction

- Good practice
- Stability of water samples
- Preservation and field filtering
- Quality control
- Holding times and storage of samples
- TPH
- PFAS
- Vapours

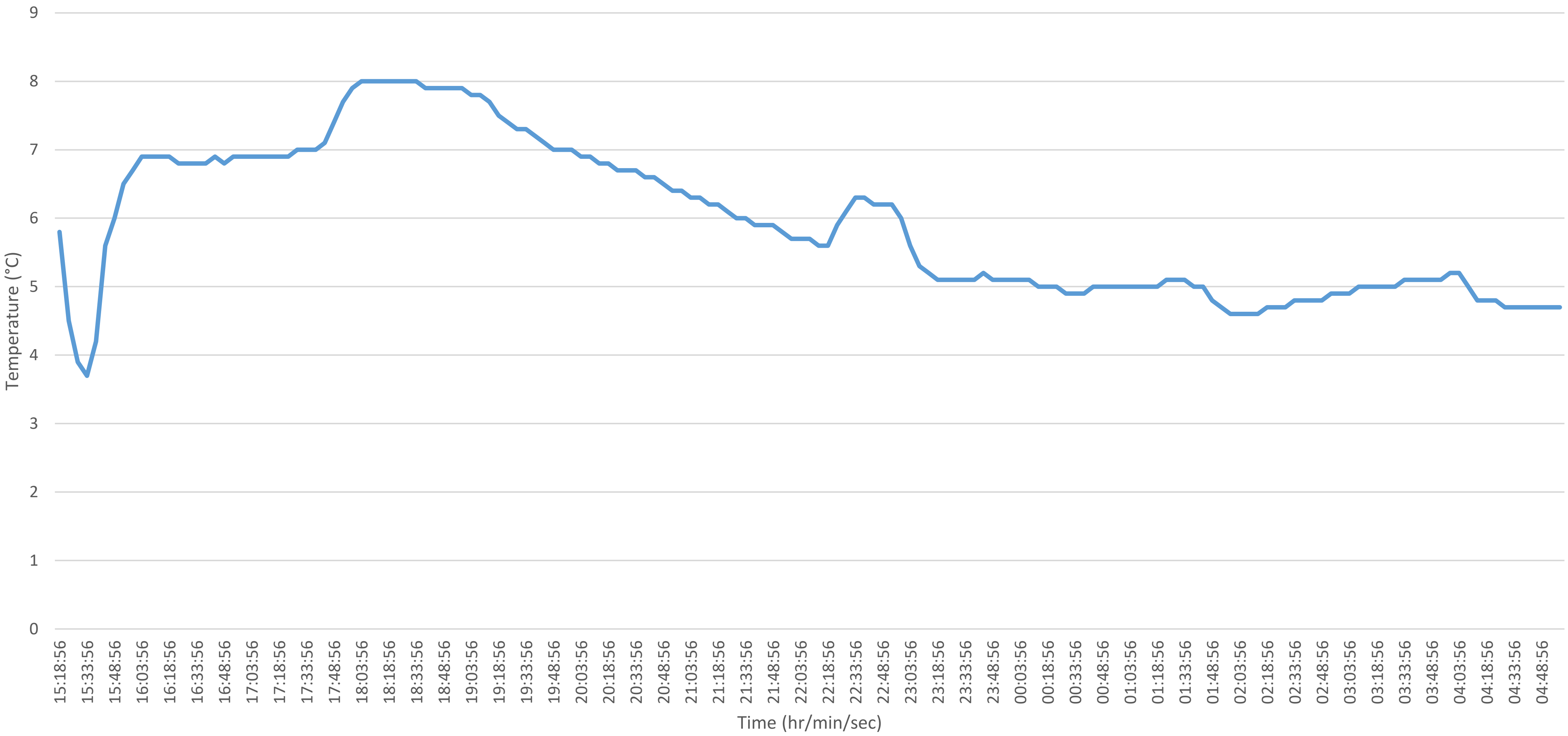
Good Practice

- Collect a representative sample
- Send to laboratory on day of sampling
- Maintain a temperature of 4.5 ± 3.5°C in accordance with MCERTS
    - Use a minimum of four ice packs per cool box
    - Lab records sample temperature upon receipt

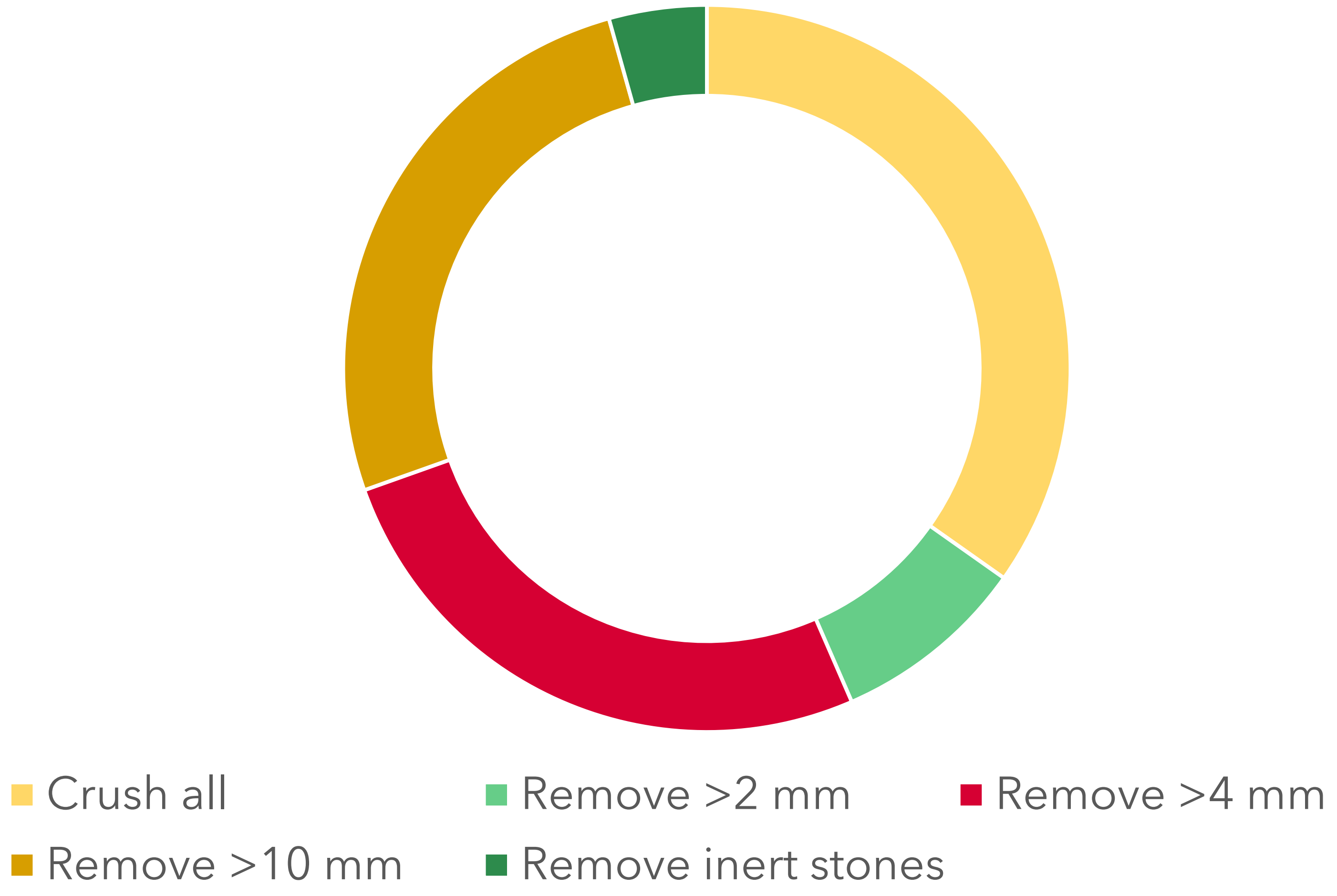
Holding Times and Deviations

- Based on published guidance: BS ISO 18512, BS EN ISO 5667 and USEPA guidance
- UKAS TPS 63 - UKAS Policy on Deviating Samples
- In-house stability trials
- Some testing (such as BOD and microbiological analysis) has a very short holding time

Temperature



AGS survey on soil preparation methods for metals "On Stoney Ground"



https://www.ags.org.uk/2020/02/on-stoney-ground-re-visited/

Stability of Water Samples

Factors affecting stability of water samples:

- Carbon dioxide affecting pH and alkalinity
- pH of the sample
- Temperature
- Exposure to light
- Oxidation
- Precipitation
- Interaction with suspended solids
- Interaction with bottle surface
- Microbial content

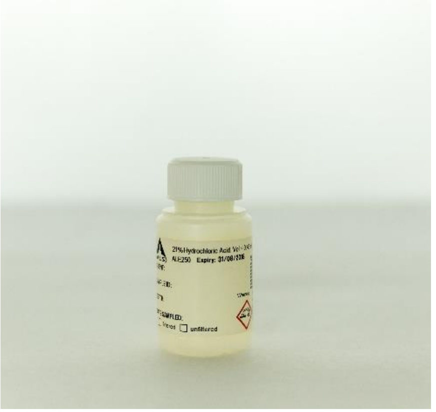
Examples of Preservatives Used

Nitric Acid
preservative

Sulphuric Acid
preservative

Sodium Hydroxide
preservative

Zinc Acetate
preservative



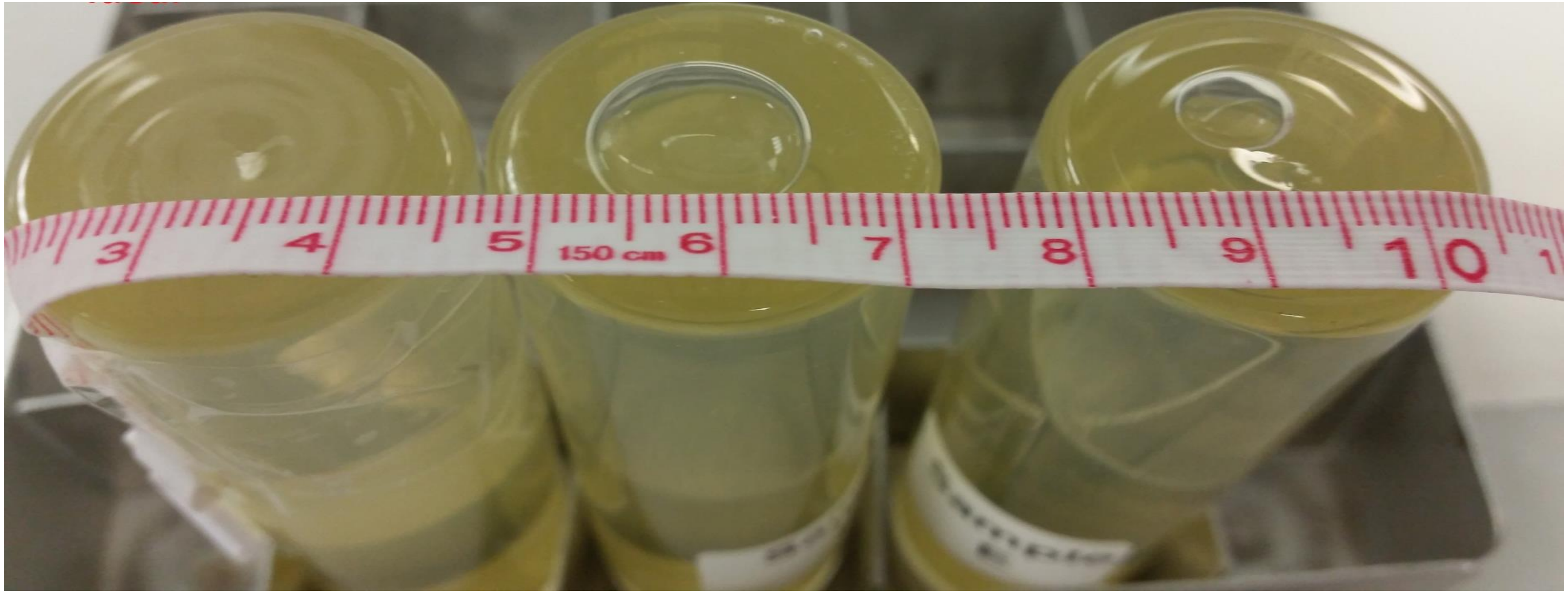
Hydrochloric Acid
preservative

Headspace in Vials

No headspace

> 6 mm is a deviating sample

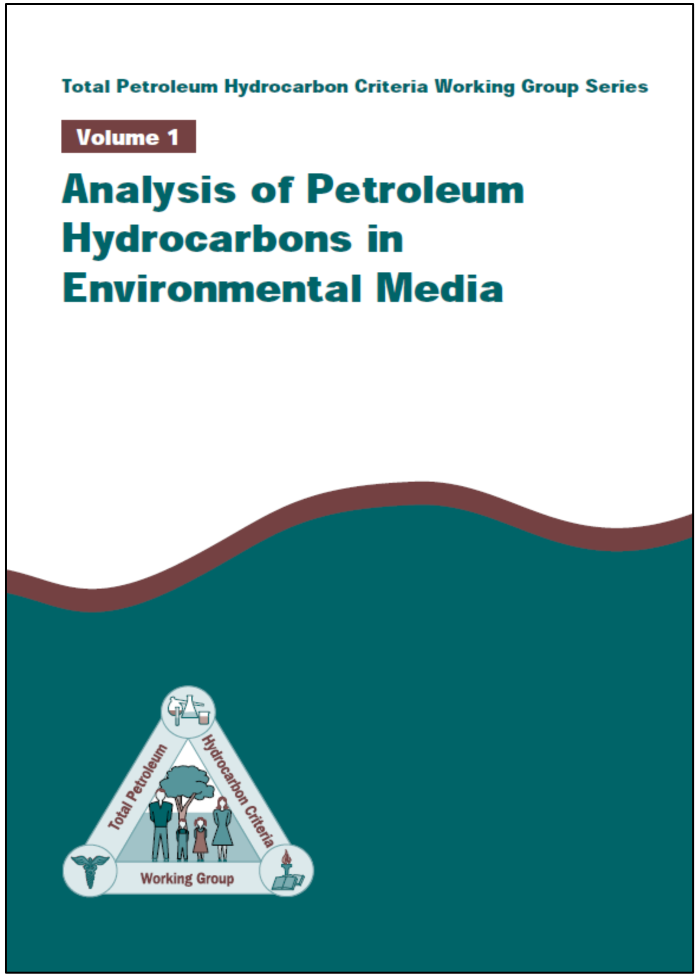
0-6 mm is acceptable range



TPH Analysis

Total Petroleum Hydrocarbon Criteria Working Group (TPH CWG)

- Volume 1 Analysis of Petroleum Hydrocarbons
- Volume 2 Composition of Petroleum mixtures
- Volume 3 Selection of TPH fractions
- Volume 4 Fraction specific classes and reference concentrations
- Volume 5 Risk Evaluation



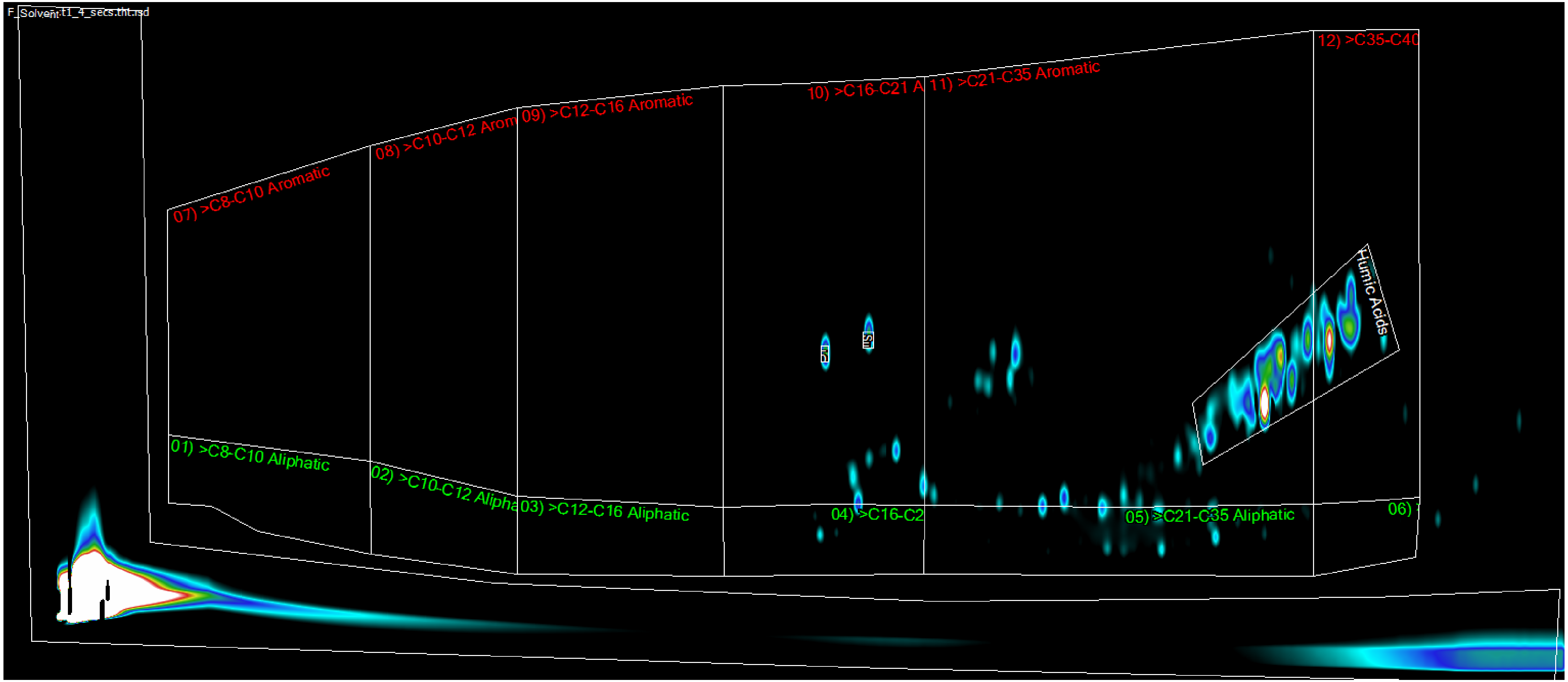
TPH CWG

Aliphatic Fraction	Aromatic Fraction
EC 5-6	EC 5-7
EC >6-8	EC >7-8
EC >8-10	EC >8-10
EC >10-12	EC >10-12
EC >12-16	EC >12-16
EC >16-35	EC >16-21
EC >35-44	EC >21-35
	EC >35-44

Naturally occurring compounds

- Most soils contain biogenic hydrocarbons derived from organic matter (vegetation)
- Humic acids
- Fatty acids both volatile and non-volatile
- Tannic acids – from peat
- Alkanes – from waxy coating on leaves
- Sterols – from plants

GCxGC-FID



F_Solvent t1_4_secs.tht.rsd
07) >C8-C10 Aromatic
08) >C10-C12 Arom
09) >C12-C16 Aromatic
10) >C16-C21 A
11) >C21-C35 Aromatic
12) >C35-C40
Humic Acids
01) >C8-C10 Aliphatic
02) >C10-C12 Alipha
03) >C12-C16 Aliphatic
04) >C16-C2
05) >C21-C35 Aliphatic
06)

Quality Control

PFAS Characteristics

Persistence

Mobility

PFAS

Bioaccumulation

Toxicity

PFAS = Per- and polyfluoroalkyl substances
PFOS = Perfluorooctane sulfonic acid
PFOA = Perfluorooctanoic acid

Industry Profiles

- Aviation and aerospace (military and civil airfields)
- Carpet manufacturing
- Chemical works (cosmetic/personal care products)
- Chrome plating sites
- Electronics manufacturing
- Firefighting – class B firefighting foams (fire training area/fire stations)
- Landfills
- Military bases
- Paper and cardboard manufacturing
- Petrochemical industry
- PFAS production
- Textiles and leather manufacturing
- Wastewater treatment works – biosolids disposal

Sampling Considerations

Below is a summary of items that are likely to contain PFAS and therefore **should not be used** by staff conducting sampling and some acceptable substitutions.

Not to be used	Acceptable alternative
Teflon™ tubing/equipment	HDPE tubing/equipment
Decon 90	Ensure PFAS-free cleaning products
LDPE or glass sample containers	HDPE or other lab approved containers ** ensure no Teflon™ liner
Waterproof or plastic field book	Electronic data capture/metal clipboard
Markers	E-scheduling/Ball point pen
Water resistant or treated gloves / clothing	Powderless nitrile gloves/cotton clothing
Cosmetics, creams, sunscreen and related products	--
Pre-packaged food, aluminum foil, fast food wrappers or containers	--
Plastic bags	Polyethylene bags (Ziplock®)

**This is not a full comprehensive list of all potential sources of PFAS contamination

AGS Environmental Sampling Guidance https://www.ags.org.uk/item/ags-guide-to-environmental-sampling/

ES&T Field Sampling Materials Unlikely to be a Source of Contamination in Samples: https://pubs.acs.org/doi/pdf/10.1021/acs.estlett.0c00036

The Challenges

Environmental Science & Technology
Article
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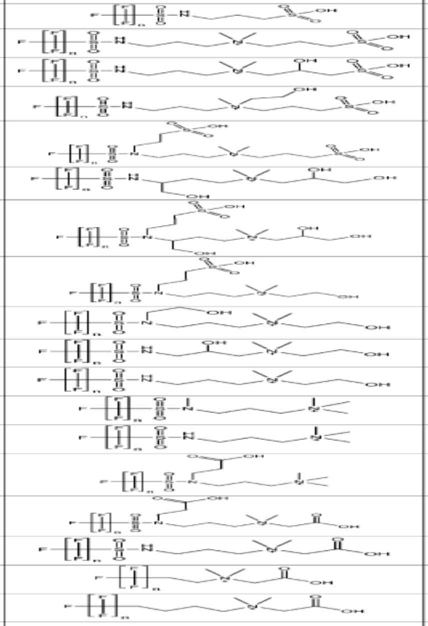
Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson,[†] Simon C. Roberts,[∇,‡] Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,[∥] Nicole Riddell,[∥] Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,[*,‡] and Jennifer A. Field[*,#]



Class Number	Structure	$n^{a,b}$	Acronym[c]	Confidence Level[d,e]	AFFF/CP Found In
1		3–6	N-SP-FASA	2b	B, C
2		3–8	N-SPAmP-FASA	2b	A, B, C, F
3		3–9	N-SHOPAmP-FASA	3[f]	C, D, E, F, G
4		4–6	N-SPHOEAmP-FASA	3	B, C
5		3–8	N-SPAmP-FASAPS	2b	A, B, C
6		3–6	N-diHOPAmHOB-FASA	3	B, C, O
7		2–6	N-diHOPAmHOB-FASAPS	3	A, B, C
8		2–8	N-HOEAmP-FASAPS	2b	A, B, C
9		2–8	N-HOEAmP-FASE	2b	A, B, C, D, E
10		4–6	N-HOEAmHOP-FASA	3	B, C
11		2–8	N-HOEAmP-FASA	2b	A, B, C, D, E
12		4–8	N-TAmP-N-MeFASA	3	B
13		3–8	N-TAmP-FASA	3	A, B, C, D, E, F, G
14		3–6	N-TAmP-FASAP	3	D, E, F, G
15		4–6	N-CMAmP-FASAP	2b	D, E, F, G
16		3–6	N-CMAmP-FASA	2b	D, E, F, G
17		6, 8, 10	CMAmEt-FA	2b	L
18		4, 6, 8	CMAmB-FA	3	L
19	$C_{n+8}H_{16}O_2SN_2F_{2n+1}$	6, 8, 10	Not applicable	4	I, J
20	$C_{n+10}H_{20}O_7SN_2F_{2n+1}$ or $C_{n+10}H_{18}O_4SN_2F_{2n+1}$	Un-known	Not applicable	5	I, J

DOI: 10.1021/acs.est.6b05843

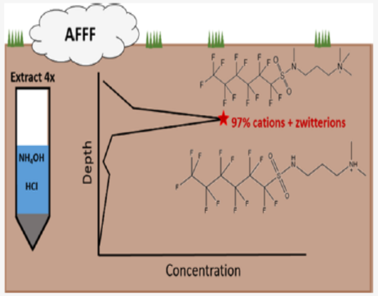
Environmental Science & Technology
pubs.acs.org/est
Article

Enhanced Extraction of AFFF-Associated PFASs from Source Zone Soils

Anastasia Nickerson, Andrew C. Maizel, Poonam R. Kulkarni, David T. Adamson, John J. Kornuc, and Christopher P. Higgins*

Cite This: Environ. Sci. Technol. 2020, 54, 4952–4962
Read Online

ABSTRACT: Poly- and perfluoroalkyl substances (PFASs) derived from aqueous film-forming foam (AFFF) are increasingly recognized as groundwater contaminants, though the composition and distribution of AFFF-derived PFASs associated with soils and subsurface sediments remain largely unknown. This is particularly true for zwitterionic and cationic PFASs, which may be incompletely extracted from subsurface solids by analytical methods developed for anionic PFASs. Therefore, a method involving sequential basic and acidic methanol extractions was developed and evaluated for recovery of anionic, cationic, and zwitterionic PFASs from field-collected, AFFF-impacted soils. The method was validated by spike-recovery experiments with equilibrated soil-water-AFFF and



https://dx.doi.org/10.1021/acs.est.0c00792

Typical UK PFAS suites

PFOS & PFOA

PFAS suite

TOP Assay suite

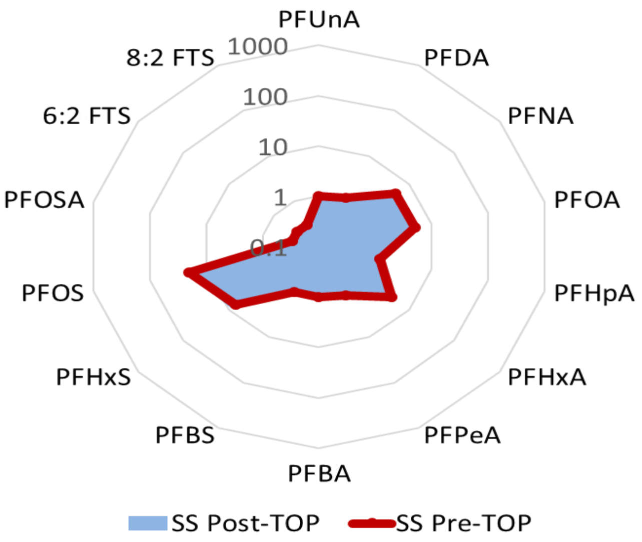
LC-MS/MS = Liquid chromatography coupled with triple quadrupole mass spectrometer
TOP assay = Total Oxidisable Precursors Assay

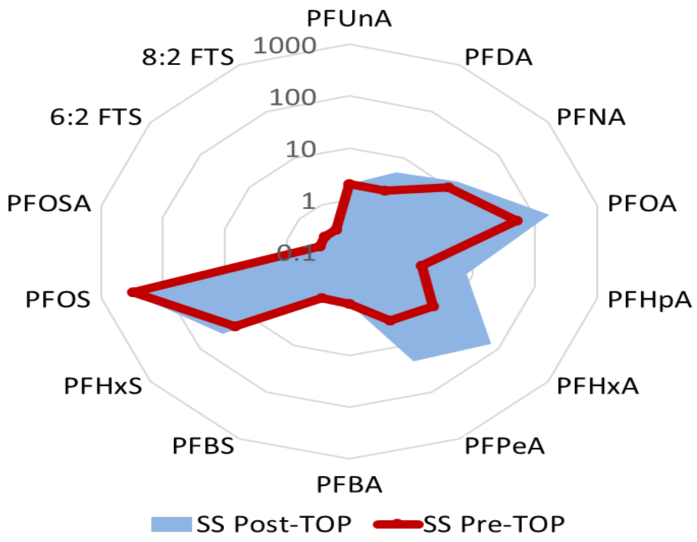
Typical UK PFAS suites

No	PFAS	CAS No.	LODs
1	PFBA	375-22-4	2
2	PFPA	2706-90-3	1
3	PFHxA	307-24-4	1
4	PFHpA	375-85-9	1
5	PFOA	335-67-1	0.65
6	PFNA	375-95-1	1
7	PFDA	335-76-2	2
8	PFUnA	2058-94-8	2
9	PFDoA	307-55-1	2
10	PFTrDA	72629-94-8	3
11	PFTeA	376-06-7	1
12	PFHxDA	67905-19-5	1
13	PFODA	16517-11-6	1
14	PFBS	375-73-5	1
15	PFPeS	2706-91-4	1
16	PFHxS	355-46-4	1
17	PFHpS	375-92-8	1
18	Linear PFOS	N/A	0.65
19	Branched PFOS	N/A	0.65
20	Total PFOS	1763-23-1	0.65
21	PFNS	68259-12-1	1
22	PFDS	335-77-3	2
23	PFUnDS	749786-16-1	2
24	PFDoS	79780-39-5	2
25	PFTrDS	174675-49-1	2

No	PFAS	CAS No.	LODs
26	HFPO-DA	13252-13-6	2
27	HFPO-TA	13252-14-7	5
28	ADONA	919005-14-4	1
29	PFMOPrA	377-73-1	1
30	NFDHA	151772-58-6	3
31	PFMOBA	863090-89-5	1
32	PFecHS	133201-07-7	1
33	3:3 FTCA	356-02-5	2
34	5:3 FTCA	914637-49-3	5
35	7:3 FTCA	812-70-4	5
36	PFEESA	113507-82-7	1
37	9Cl-PF3ONS	756426-58-1	1
38	11Cl-PF3OUdS	763051-92-9	2
39	4:2 FTS	757124-72-4	1
40	6:2 FTS	27619-97-2	1
41	8:2 FTS	39108-34-4	2
42	FBSA	30334-69-1	2
43	FHxSA	41997-13-1	1
44	PFOSA	754-91-6	1
45	N-MeFOSA	31506-32-8	1
46	N-EtFOSA	4151-50-2	1
47	MeFOSE	24448-09-7	10
48	EtFOSE	1691-99-2	10
49	MeFOSAA	2355-31-9	2
50	EtFOSAA	2991-50-6	2

TOP Assay





Pre-Oxidation Analysis

TOP Assay (Oxidation)

Post Oxidation Analysis

Emerging PFAS options

TOF-CIC

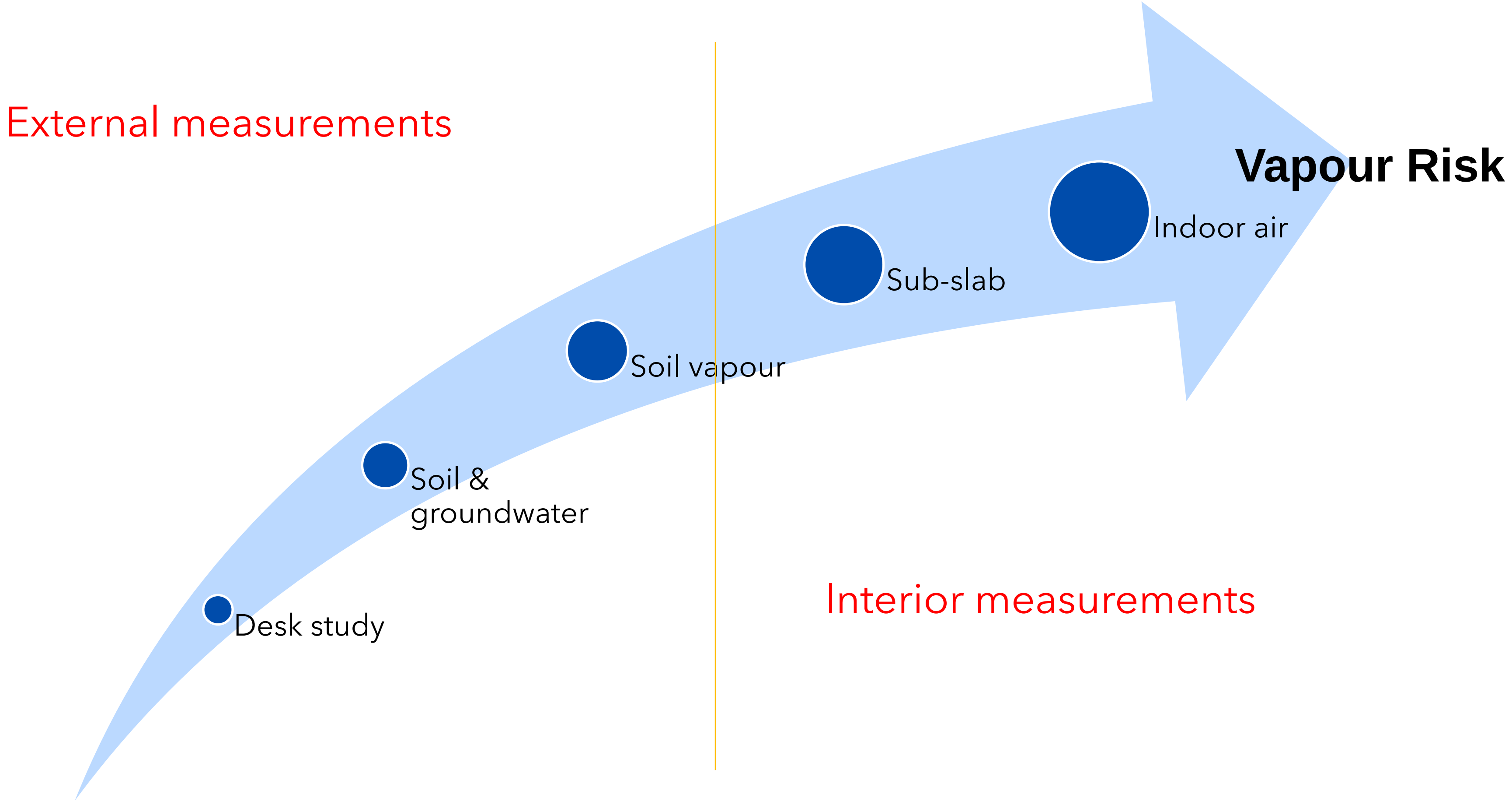
HRMS

TOF-CIC – Total Organofluorine Combustion Ion Chromatography
HRMS - High Resolution Mass Spectrometry

PFAS in Concrete

Refinement of the CSM

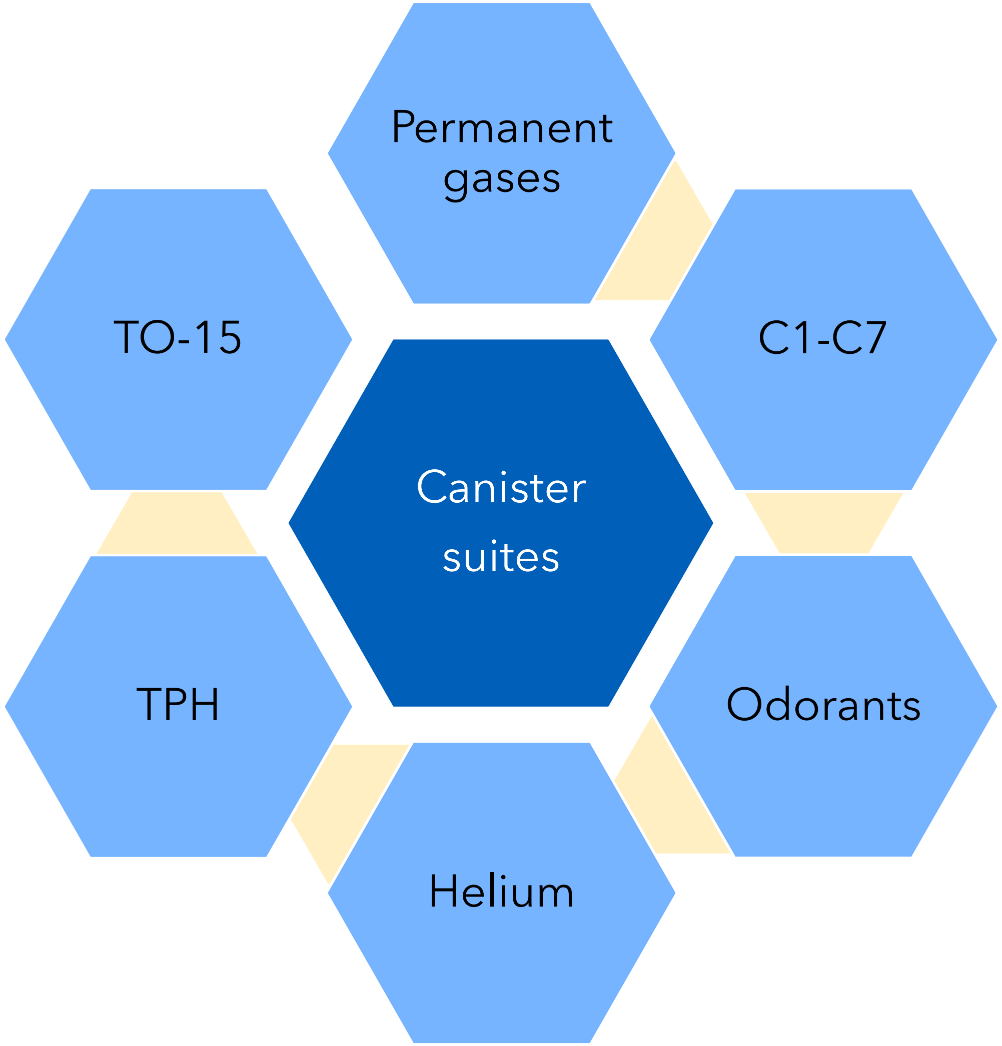
Decreasing VI assessment conservatism



Model if you must, measure if you can

Types and Sizes of Canisters

Typical Canister Suites



TO-15

Difluorochloromethane	Methylene Chloride	Carbon Tetrachloride	Tetrachloroethene
Dichlorodifluoromethane	Trichlorotrifluoroethane	Cyclohexane	Chlorobenzene
Chloromethane	Carbon Disulfide	2-Pentanone	Ethylbenzene
1,2-Dichlorotetrafluoroethane	1-Propanol	Pentanal	Xylenes (m/p & o)
Vinyl Chloride	Methylacrolein	3-Pentanone	Bromoform
Isobutene	trans-1,2-Dichloroethene	1,2-Dichloropropane	Styrene
1,3-Butadiene	MTBE	Trichloroethene	1,1,2,2-Tetrachloroethane
Bromomethane	1,1-Dichloroethane	Bromodichloromethane	1,3,5-Trimethylbenzene
Chloroethane	Vinyl Acetate	cis-1,3-Dichloropropene	1,2,4-Trimethylbenzene
Acetonitrile	Butanal	4-Methyl-2-pentanone	Benzyl Chloride
Acrolein	2-Butanone (MEK)	trans-1,3-Dichloropropene	1,4-Dichlorobenzene
Acetone + Propanal	cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,3-Trimethylbenzene
Trichlorofluoromethane	Hexane	Toluene	1,2-Dichlorobenzene
Pentane	Chloroform	3-Hexanone	1,2,4-Trichlorobenzene
Isoprene	1,2-Dichloroethane	2-Hexanone	Naphthalene*
Iodomethane	1,1,1-Trichloroethane	Hexanal	1,4-Dioxane*
1,1-Dichloroethene	Benzene	1,2-Dibromoethane	Hexachlorobutadiene*

Laboratory Analysis

In Conclusion

- Early communication with the lab is key
- Determine the analytical technique most suited to what the data is being used for (human health, waste classification)
- Better understand the preparation method used and assess importance to results
- Visual and olfactory observations are important – these should be correlated with lab results (along with any site measurements)
- Ensure sufficient allowance is made for QC samples (especially for PFAS)
- Only use de-ionised water supplied by the lab.
- Ensure full chain of custody procedures are followed (standard forms or on-line portals)

Accreditation Window

SoBRA's Accreditation Window is now open until 31 August

https://sobra.org.uk/accreditation/

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Questions?

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Geraint Williams, Associate

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