Accreditation against multiple quality standards for legacy and emerging concern contaminants, including PFASs

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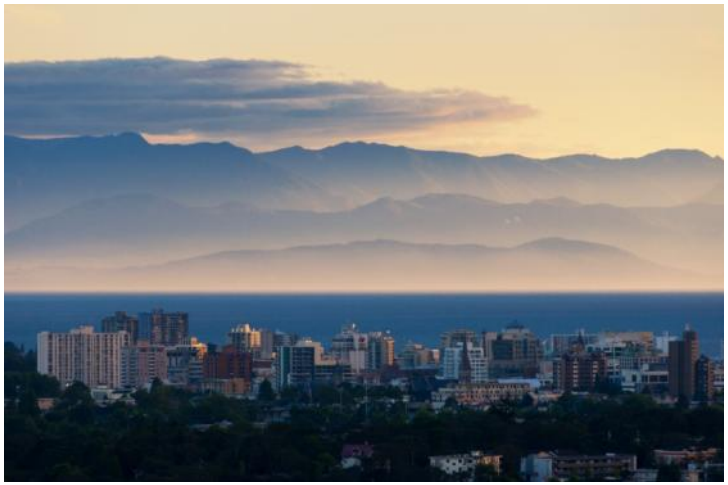
Presentation Outline



- Accreditation requirements/Challenges for Contaminants of Emerging Concern (CECs)
- Use of cooperative/concurrent assessment
- Contaminants of Emerging Concern – Case study: Polyfluorinated Alkylated Substances (PFAS)

CECS: ACCREDITATION REQUIREMENTS/CHALLENGES

Contaminants of Emerging Concern

- Accreditation Requirements/Challenges for CECs
  - A wide scope – Thousands of analytes of interest, increasing every year
  - Concerned stakeholders affected before standards/EPA methods in place
  - What standards to be applied? Proficiency testing?
  - Methods/standards in simple matrices (drinking water) inadequate for multi-compartment investigations in complex matrices, AFFF, tissue, biosolids, etc: Flexibility important
  - Flexibility -> Performance-based rather than prescriptive
  - Learning from US states/other governments and labs on methods/techniques

CECs: Large scope

- Quality Standards, similar but with differences
  - ISO/IEC 17025:2005 standard
  - NELAC – (2003 NELAC and 2009 TNI)- based on ISO 17025 standard
  - DOD-ELAP QSM V5.0- based on ISO/IEC 17025 + NELAC standards
- 3 separate accrediting bodies (ABs)
  - ANSI-ASQ National Accreditation Board (ANAB): ISO/IEC 17025:2005 and DOD-ELAP standards
  - Florida Department of Health, NELAC standard
  - Canadian Association for Laboratory Accreditation (CALA) - ISO/IEC 17025:2005 standard

Combined Assessment Scope (POPs + CECs)

- Accreditation listed against both the AXYS performance based methods and the applicable reference methods:
- Polyfluorinated alkyl substances (PFAS)
  - Perfluorinated carboxylates and sulfonates in water, solids and tissue –AXYS methods MLA-060, MLA-041, MLA-043
  - Fluorotelomer sulfonates in water and solids -AXYS methods MLA-081 and MLA- 089
  - The reference method designation for these is EPA 537 MODIFIED
- Chlorinated dioxins/furans in water, solids and tissue- AXYS method MLA-017; the reference methods are EPA1613 and EPA8290
- PCBs in water, solids and tissue- AXYS method MLA-010; the reference method is EPA 1668
- The CALA 17025 scope
  - Additional emerging and legacy contaminants including: PPCP (MLA-075/EPA 1699), GC-HRMS OC pesticides (MLA-028/EPA 1699), PEM/BPA (MLA-059) and Metabolomics (MLM-001). The matrices include water/solids/tissue/serum-plasma/urine

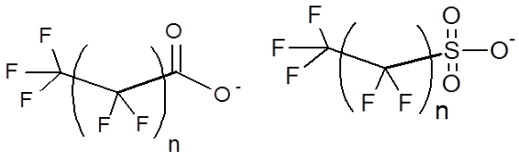
Observations

- Estimated 30% cost savings for the lab on travel/setup costs alone, many other intangible savings
- Significant document review prior to assessment
- Increased efficiency during assessment
  - Reduced disruption
  - Easy scheduling of analysts and management
  - Joint kickoff/findings meetings w/senior management much appreciated
  - Communication/information sharing between assessment agencies

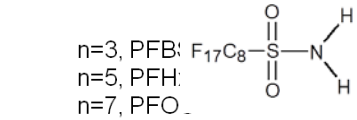
CEC CASE STUDY - PFAS

Per and Highly Fluorinated Compounds - AXYS Methods

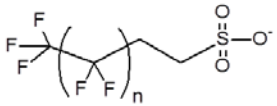
- PFOS and PFOA (approx. 2002)
  - Standard Carboxylates (C4 to C12) and Sulfonates (C4,C6,C8) + PFOSA
- Manufacturing and PFAAs Precursors
  - Telomer Alcohols 4:2 to 16:2 (archived)
  - Precursors - saturated and unsataurated acids, Sulfonamido + acetate + acrylate compounds (Intermediate compounds in metabolism process)
- PFOS speciation (branched / linear, isomers)
- Other AXYS Analysis (sulfonate and carboxylate precursors)
  - Aqueous and Solid Matrices
  - Fluorotelomer Sulfonates (4:2, 6:2, 8:2, 10:2)
  - PFPA, mono and di-PAPS, SAM PAPs
- Other Compound Groups
  - Proprietary Monomers in polymer manufacture (old and new)
  - More complex molecules (ie. FTS +, Fl unsaturated C chains)



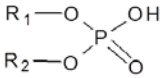
n=2, PFBA; n=3, PFPe
n=4, PFHxA; n=5, PFHp
n=6, PFOA; n=7, PFN
n=8, PFDA; n=9, PFUnD
n=10, PFDoDA;



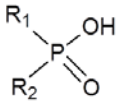
n=3, PFB
n=5, PFH
n=7, PFO



n=3, 4:2 FTS
n=5, 6:2 FTS
n=7, 8:2 FTS



$R_1=C_2H_4C_8F_{17}$, $R_2=C_2H_4C_8F_{17}$ } 6:2 diPAP
$R_1=C_2H_4C_6F_{13}$, $R_2=C_2H_4C_6F_{13}$ } 8:2 diPAP
$R_1=C_2H_4C_6F_{13}$, $R_2=H$ } 6:2 PAP
$R_1=C_2H_4C_8F_{17}$, $R_2=H$ } 8:2 PAP



$R_1=OH$, $R_2=C_6F_{13}$ } PFHxPA
$R_1=OH$, $R_2=C_8F_{17}$ } PFOPA
$R_1=OH$, $R_2=C_{10}F_{21}$ } PFDPA
$R_1=C_6F_{13}$, $R_2=C_6F_{13}$ } 6:6 PFPiA
$R_1=C_6F_{13}$, $R_2=C_8F_{17}$ } 6:8 PFPiA
$R_1=C_8F_{17}$, $R_2=C_8F_{17}$ } 8:8 PFPiA

Method Management Structure – 13 Default PFCA/PFSA example

Common to All Matrices (Isotope Dilution)

Common to All Matrices	1) Instrument programs and QA	2) Materials QA and Calibration / Spiking Standards	3) Personnel and Training	4) Analytes and Surrogates, SPE choice

Specific to Matrix

1) Extraction Fluid and Concentration	2) SPE Size	3) Additional Clean-ups	4) PE programs

May be Custom to a Project

1) Sample Preparation / Creation of Samples	2)Reporting and Flagging Conventions	3) Custom spiking / dilution / handling for high levels, matrix, unique samples

Isotope dilution, cleanup and more

Method	Matrices	Isotopically labeled standards	Recovery Correction	Cleanup
AXYS PFCA/PFSA methods	Aqueous, soil/sediment, WWTP biosolids, tissue	9 (+2 for recovery standard). Standards added with availability	Isotope dilution/surrogate standard quantitation	Weak anion exchange
EPA 537	Drinking water	3	None	SDVB (for extraction)
ASTM	Soil/Sediment	9	Isotope dilution/surrogate standard quantitation	None/Direct injection

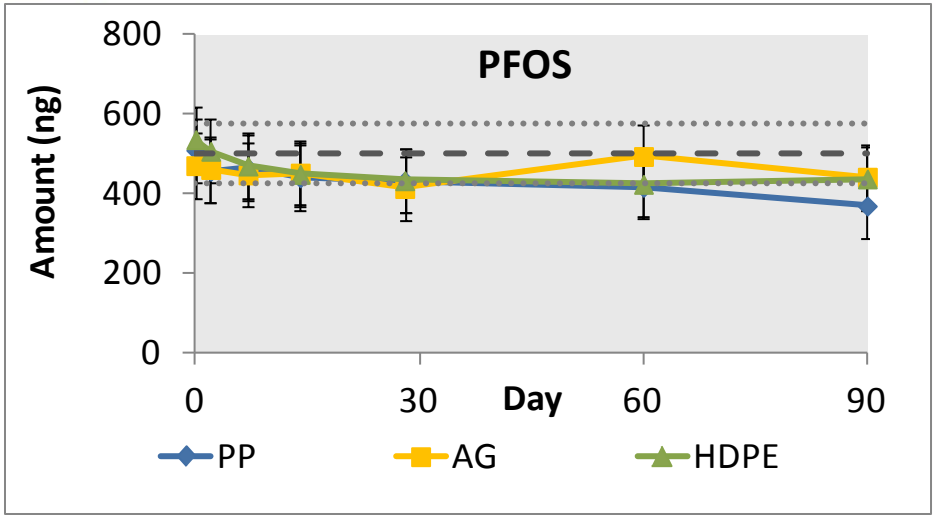
- Each of these methods are validated and fit for stated purpose
- Matrix extensions require careful thought and extension
- Labeled standards account for many matrix issues, better interference detection
- AXYS estimated cost of labeled standards – 5-10% of total method cost (not accounting for reduced rework – Affordable!

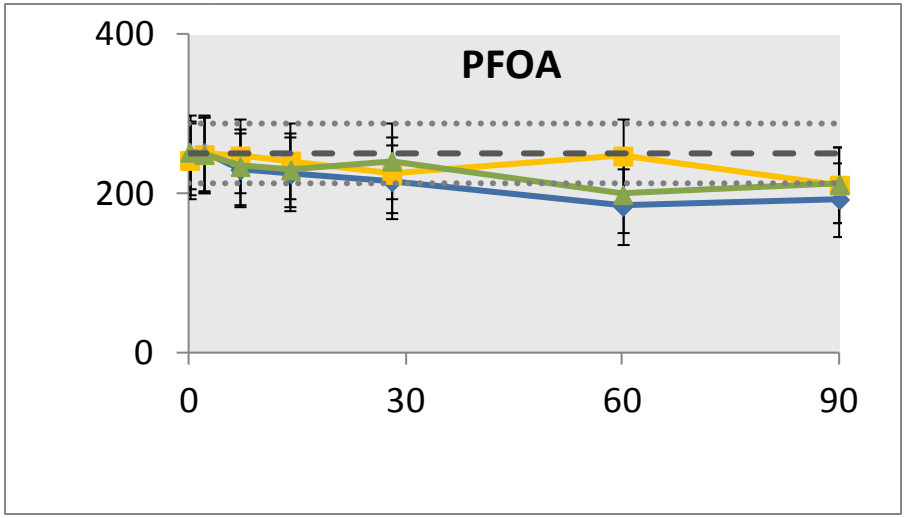
Stability/Holding Time – AXYS Dupont Study

- Method validation: Validated in three aqueous matrices, at three concentrations, in triplicate, and at three different days.
- Hold time study:
  - Analytes – C4-C12 PFCA, C4-C8 PFSA
  - Matrix = reagent water
  - Container types = polypropylene (PP), amber glass (AG), and High Density Polyethylene (HDPE)
  - Hold time intervals = 0, 2, 7, 14, 28, 60 and 90 Days
  - # of samples analyzed = 3 samples per hold time interval
  - Storage temperature = 4°C

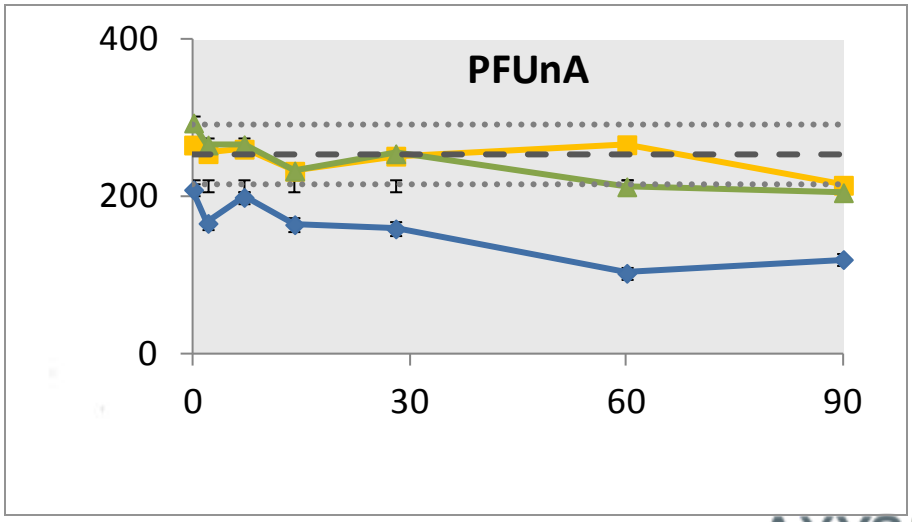
Berger et al. 2011. Analytical and Bioanalytical Chemistry 400 (6): 1625–35

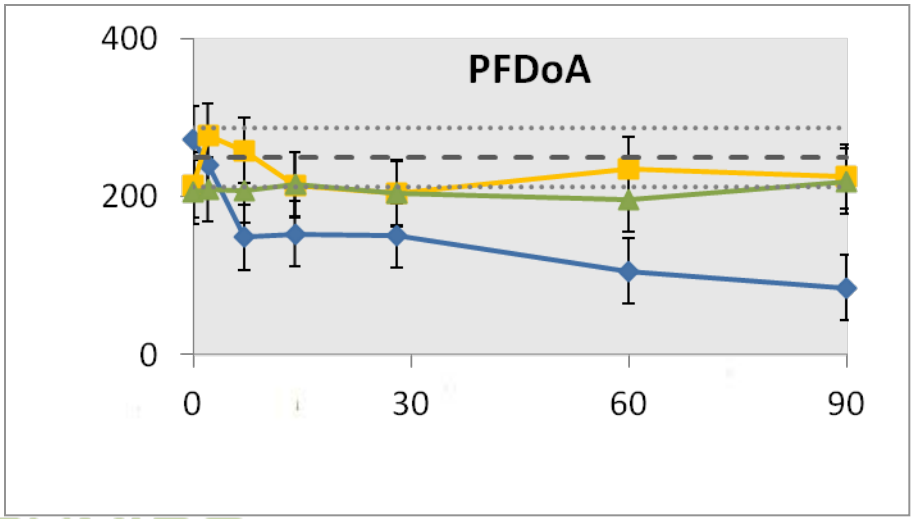
Hold Time Results



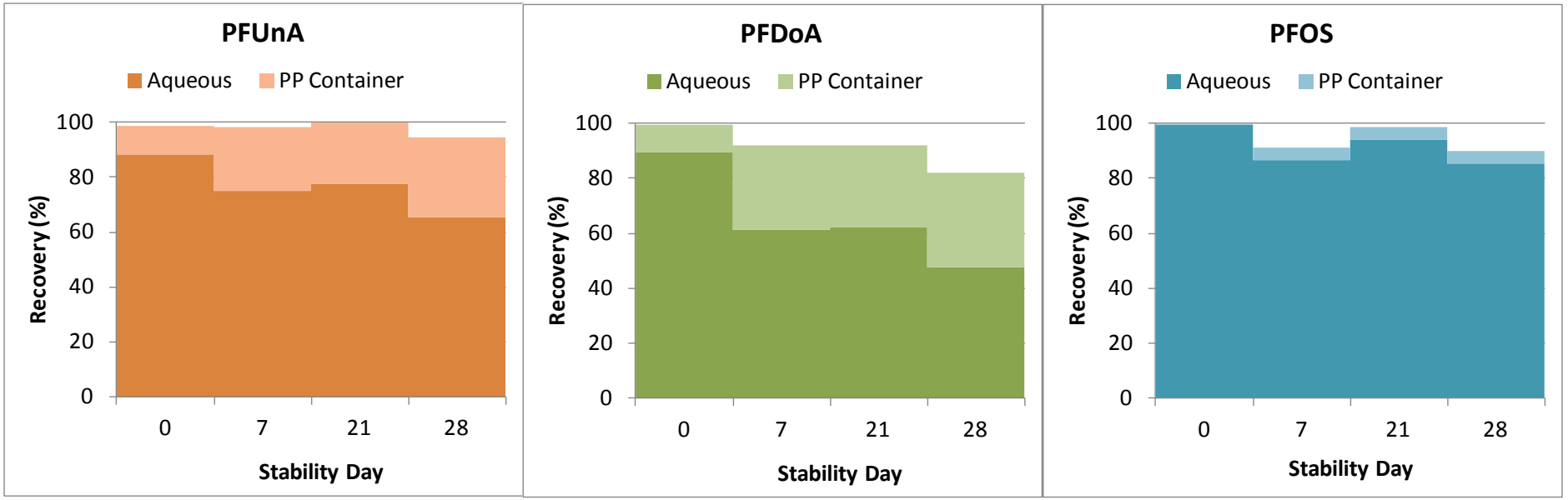


Amber glass, HDPE work well. Significant losses in Polypropylene





Adsorption to Polypropylene Containers Reversible



- Long chain PFCA adsorbs on polypropylene containers
- Methanol rinse shows adsorption is reversible (EPA 537 requires rinse

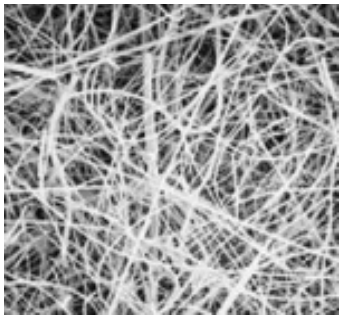
Hold Time/Stability Conclusions

- Aqueous samples stable up to 90 days at 4°C
- Amber glass and HDPE container show best performance
- Polypropylene containers sorb longer chain PFCAs
- Sorption is reversible with methanol container rinse

Filter aqueous samples or not?

- Why filter?
  - Because we must, sometimes – SPE capacity limited
  - Different questions: Whole water vs. dissolved phase vs. phase partitioning studies

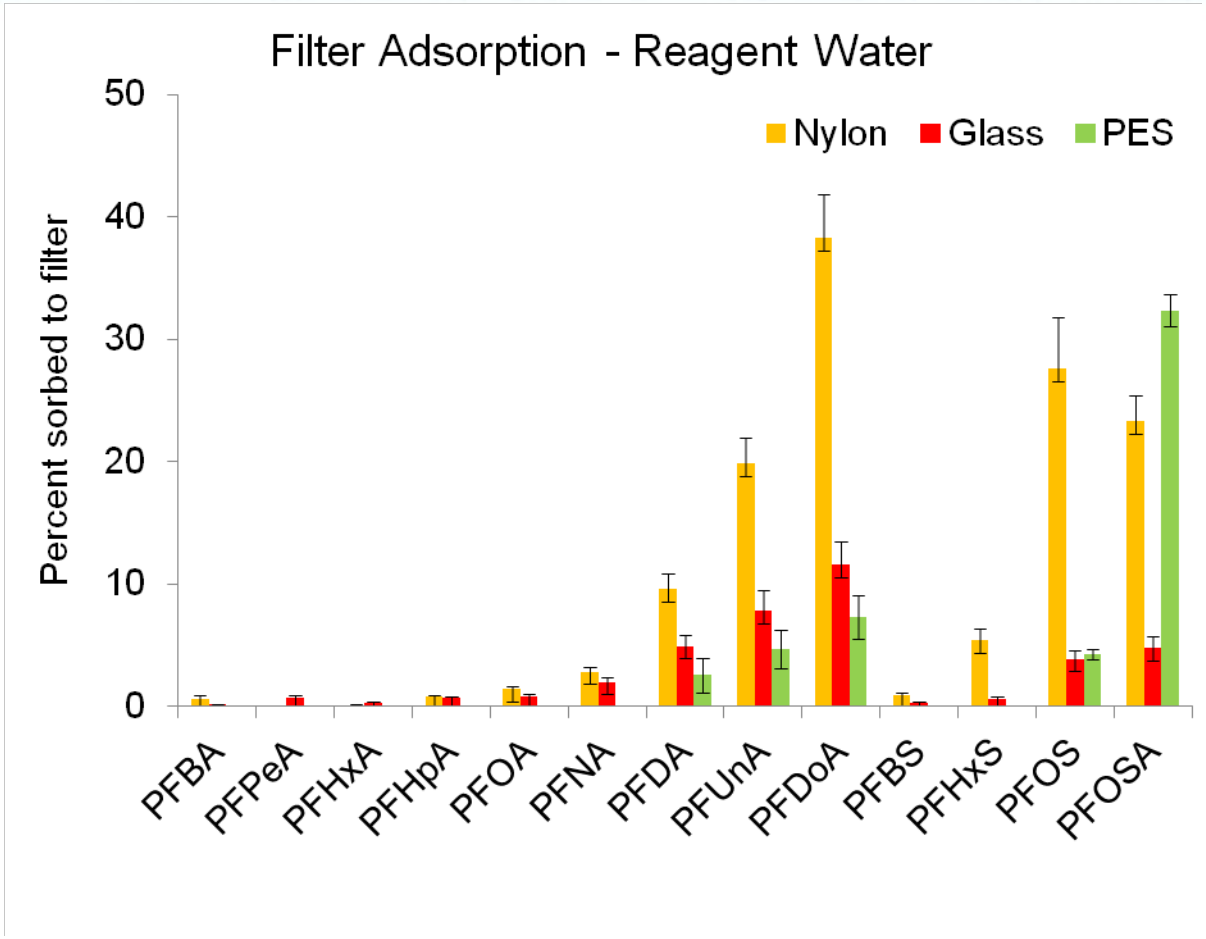
Water filtration study



- Filters (approx 0.45 µm)
  - Nylon (Nalgene kits)
  - PES (Nalgene Kits)
  - Teflon (Sterlitech)
  - Glass (Sterlitech)
- Matrices
  - Reagent/Drinking water
  - Surface water (non AFFF)
  - WWTP Effluent
  - Groundwater from AFFF-impacted site
- Analytes
  - PFCA, PFSA, PFOSA
  - FTS
  - monoPAPs, diPAPs, PFPAs, and PFPiAs

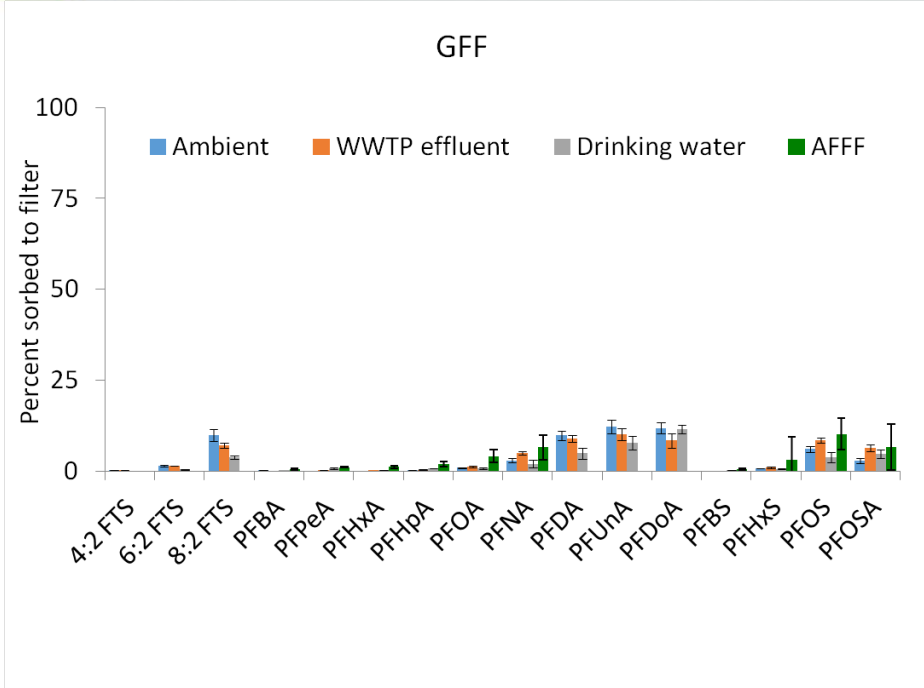
Chandramouli et al. Environmental Toxicology and Chemistry 34 (2015) 30–36.

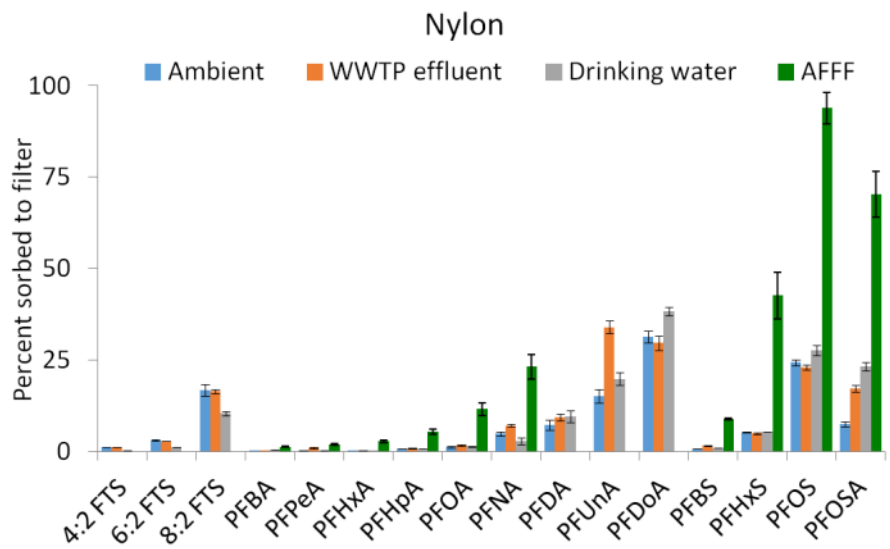
Filtration results – Drinking water



- GFF highly recommended, 10% or lower for analytes observed
- Avoid polymeric media – unpredictable results PES and PFOSA, for example

Filtration Results – Matrix Effects

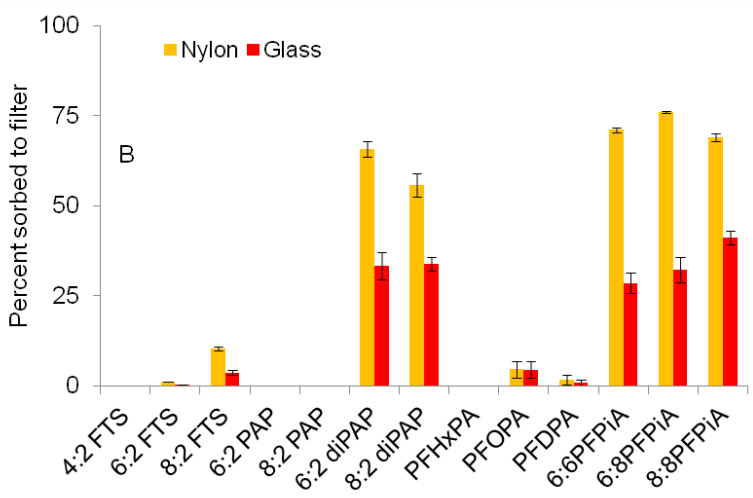




- GFF show 10-12% adsorption in the worst case for PFOS
- Significant matrix effects seen
  - Matrix effects muted in glass, predictable.
  - In general, more adsorption with increasing matrix
  - **High surfactant AFFF samples behave very differently in Nylon and polymeric filtration media**

AXYSENVIRO

Filtration conclusions



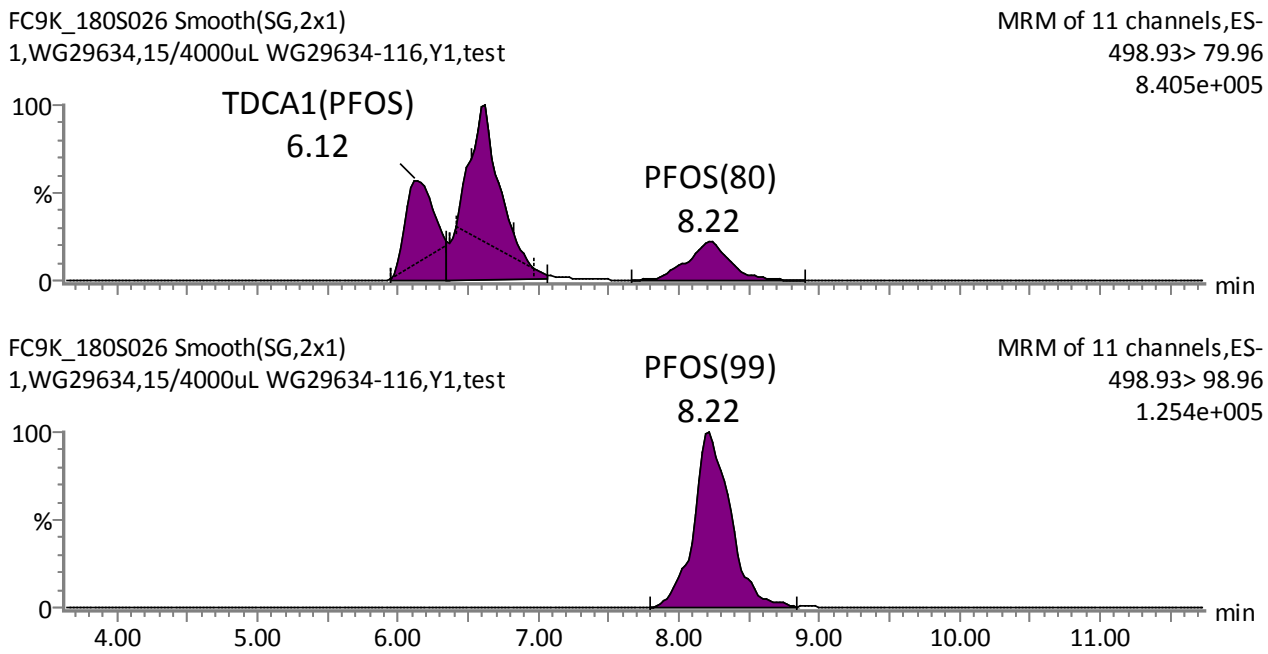
- Use whole water methods when practical
- If excessive particulate expected/dissolved phase data needed
  - Use GFF
  - When possible, validate with site-relevant samples
- CECs vary greatly in chemical/physical properties, so every method that includes filtration MUST test for artifacts

Tissue LC MS/MS Interferences

- False positives of up to 120 ng/g PFOS detected in eggs
- PFOS and Taurine-conjugated Acid (TDCA)
  Same MW, Common Transition

Compound	Parent	Ion 1	Ion 2	Ion 3
Taurochendeoxycholate	498.2	79.8	106.8	123.8
Taurodeoxycholate	498.2	79.8	106.8	123.8
Tauroursodeoxycholate	498.2	79.8	106.8	123.8
PFOS	498.9	79.9	98.9	N/A

TDCA + PFOS – Full workup

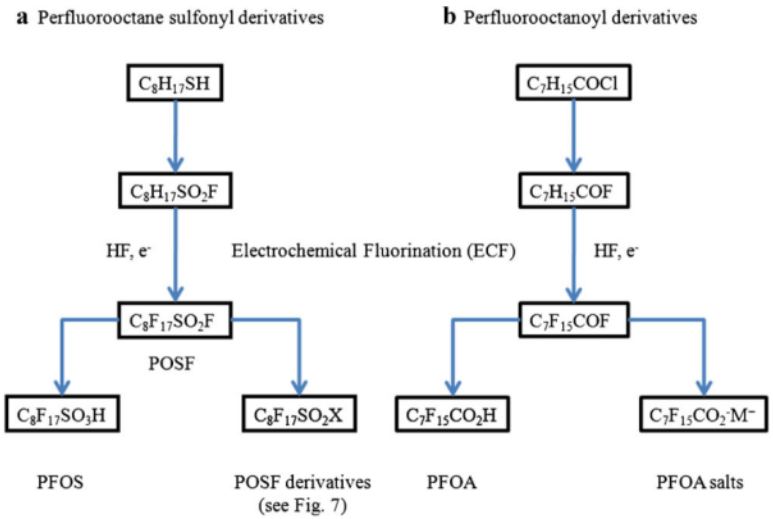


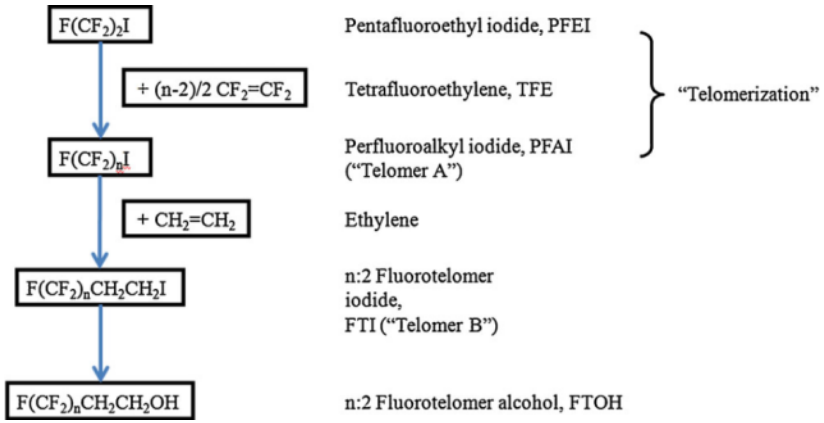
- AXYS method separates out TDCA by >2 minutes – Enables use of more sensitive transition for quantitation and 499 -> 99 transition for confirmation
- Recovery of TDCA through WAX cleanup 70-130%: Chromatographic separation/use of 499 -> 99 transition required
- Use of multiple transitions can mitigate against interferences, but sensitivity hit on older instrumentation

Matrix effects – Not all tissues are equal

Matrix (2g sample)	Split	Performance
Salmon	None	Acceptable
Ling Cod	None	Acceptable
Pike-Perch	None	Acceptable
Carp	None	Marginal for 13C-PFBA
Carp	50%	Acceptable
Walleye	50%	Not satisfactory for 13C-PFBA
Trout	50%	Not Satisfactory for 13C-PFBA
Invertebrates whole	None	Not Satisfactory for multiple analytes
Invertebrates whole	50%	Not satisfactory for 13C-PFHxA, PFOS, PFHxS, marginal for 13C-PFBA
Pig Liver	None	Not satisfactory for multiple analytes
Pig Liver	50%	Marginal for 13C-PFBA
Beef	50%	Acceptable for PFOA, 13C-PFOA and 13C-PFBA
Cormorant Eggs	10%	Acceptable.
Sturgeon Muscle	50%	Acceptable
Sturgeon Liver	50%	Unacceptable - Low recovery across the board, 13C-PFBA disappears
Sturgeon Liver	10%	Acceptable
Liver (ALL)	50%	Not recommended
All tissues	10%	Acceptable, exceptions not correlated to tissue type

Linear vs. Branched



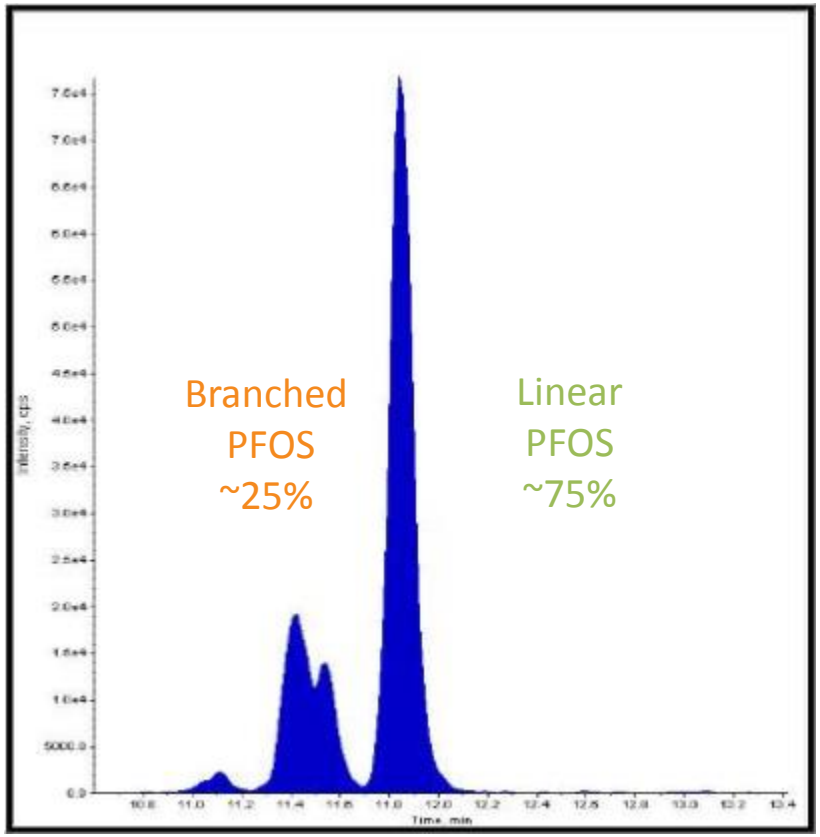


Electrochemical Fluorination – Produces linear and branched

Telomerization – Produces linear

Guide to PFASs in the Environment, Buck et al. —Integr Environ Assess Manag 7, 2011

Linear vs. Branched



- Eleven *known* isomers of PFOS in ECF process
- 499>80 and 499>99 transitions have different relative response factors for the linear and the branched isomers.
- Quantitative biases possible depending on standard type and MRM transitions used for quantitation
- Distribution/half lives in tissue are different

Riddell, N. et. al, Environ Sci. Technol. 2009 (43) 7902-7908.

Linear vs. Branched: Current AXYS Approach

- Default option uses a mixed standard where available, does not separate linear vs. branched
- Method options allow for flexibility on instrument runs to separate linear from all branched PFOS , other PFCA/PFCA depends
- Don’t see current need to separate out individual branched isomers
- Need for community to standardize approach

CEC Analyses – Take home messages

- Comprehensive Isotope dilution/surrogate standard quantification where available (and push standards manufacturers to make more)
- Matrix validation is very important
- Use confirming MRM transitions/more to increase detection certainty – But ratios are instrument dependent at times, so caution is advised
- Important to perform AND fund stability and storage studies
- Variety of analyte chemistries => important to test and validate all steps
- CECs are not always predictable – Experimental data is critical
- Data sharing on best practices most efficient, let's learn from each other

Questions?

LIVING > TRAVEL

Why Victoria, British Columbia, Should Be Your Next Weekend Getaway

APRIL 7, 2016 3:03 PM
by ALYSSA SCHWARTZ

Vogue Magazine, 2016
http://www.vogue.com/13423997/victoria-british-columbia-weekend-getaway-travel-guide/