Scratching the Surface of PFASs: Closing the mass balance using four techniques on Papers & Textiles

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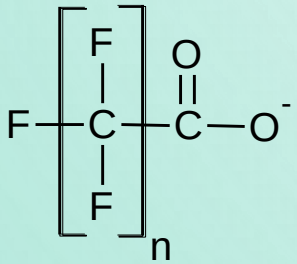
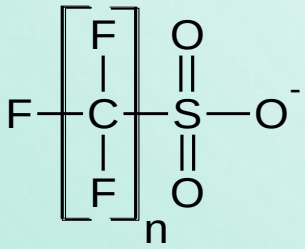
Background

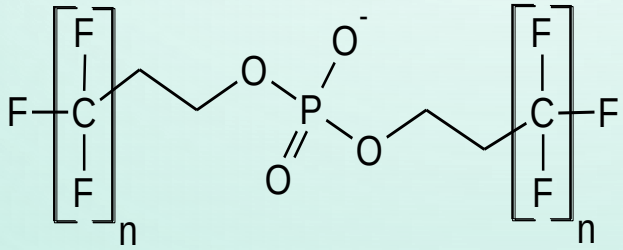
- Per- and Polyfluoroalkyl Substances (PFASs) chemistry
  - Carbon-fluorine chain attached to a polar head group
- Widely present in numerous sources from landfills, wastewater, AFFFs, **consumer products**, etc.
- Non-natural products→ anthropogenic sources



Ex. PFOA



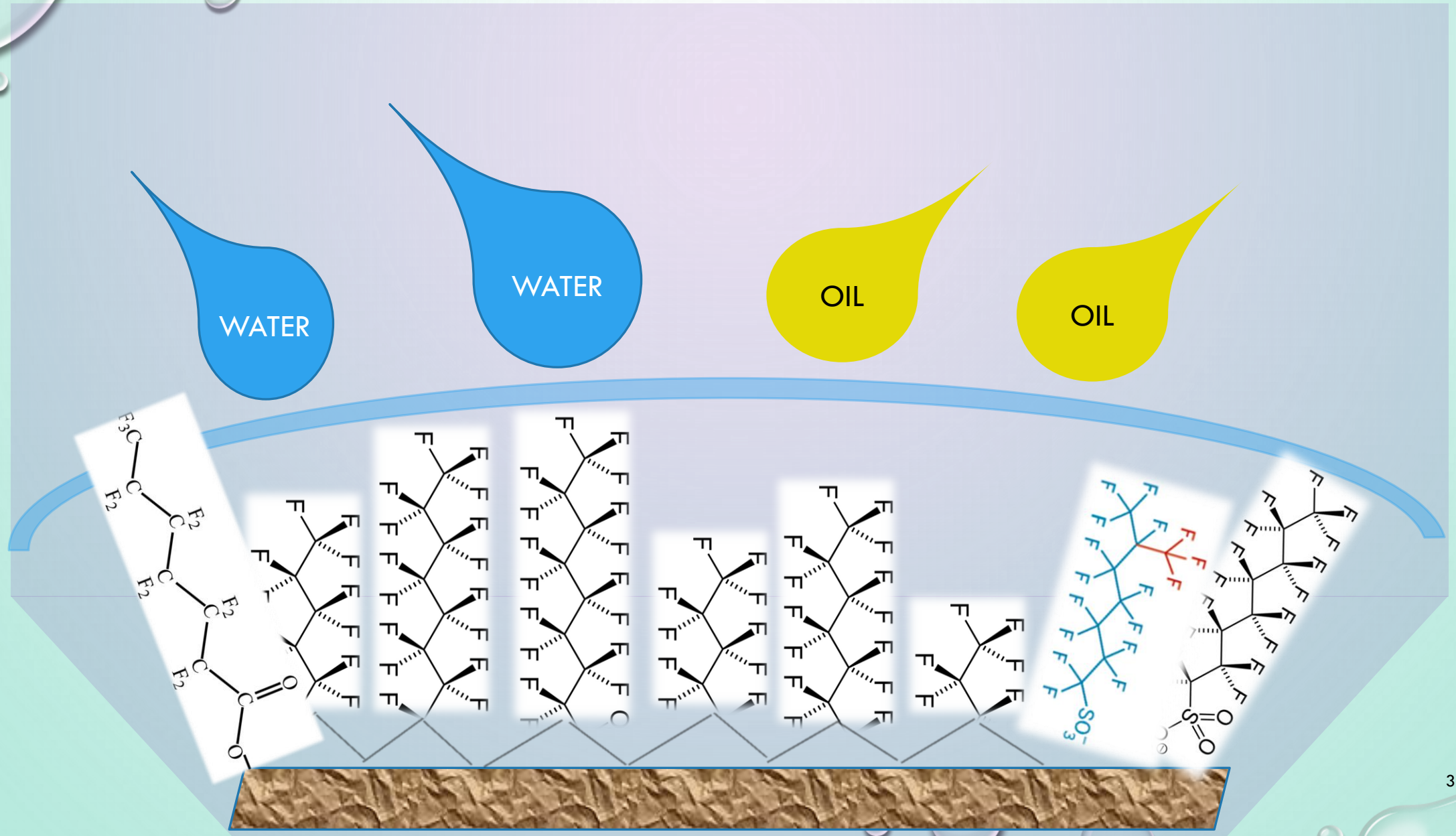
Ex. PFOS



Ex. 6:2 diPAP

Photo credit: google

Allred et. al, 2014, Houtz et. al, 2016, Herzke et. al, 2012, Vestergren et. al, 2015, Trier et. al, 2011, Backe et. al,2013, Van Der Veen, 2016, Begley, 2013


WATER
WATER
OIL
OIL

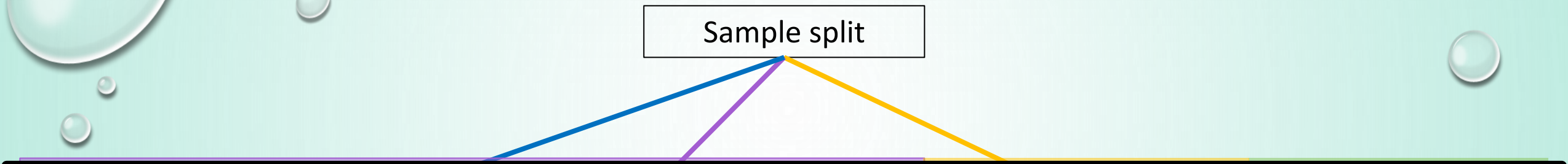
Analytical Tools Available in the Literature

- Extraction methods for quantification of select PFAS
  - Textiles, Food packaging, other consumer goods
- Total fluorine methods are limited, mass balance is challenging
  - TOP Assay, Particle-Induced Gamma-Ray Emission Spectroscopy (PIGE), among others

Allred et. al, 2014, Houtz et. al, 2016, Herzke et. al, 2012, Vestergren et. al, 2015, Trier et. al, 2011, Backe et. al,2013, Van Der Veen, 2016, Begley, 2013

Why is closing the mass balance important?

- Are there more PFASs than those typically measured (PFOS, PFOA, etc.)?
  - LC-MS/MS → Ionic PFASs
  - GC-MS → Volatile PFASs
- Total Fluorine being measured?
  - Total Oxidizable Precursor Assay (TOP Assay), PIGE
- What is present in the current market in comparison to older materials?



For this study 8 papers and 9 textiles were analyzed using these four techniques (e.g. Popcorn Bag):

- 6 volatile analytes
- 73 ionic analytes
- TOP Assay
- PIGE

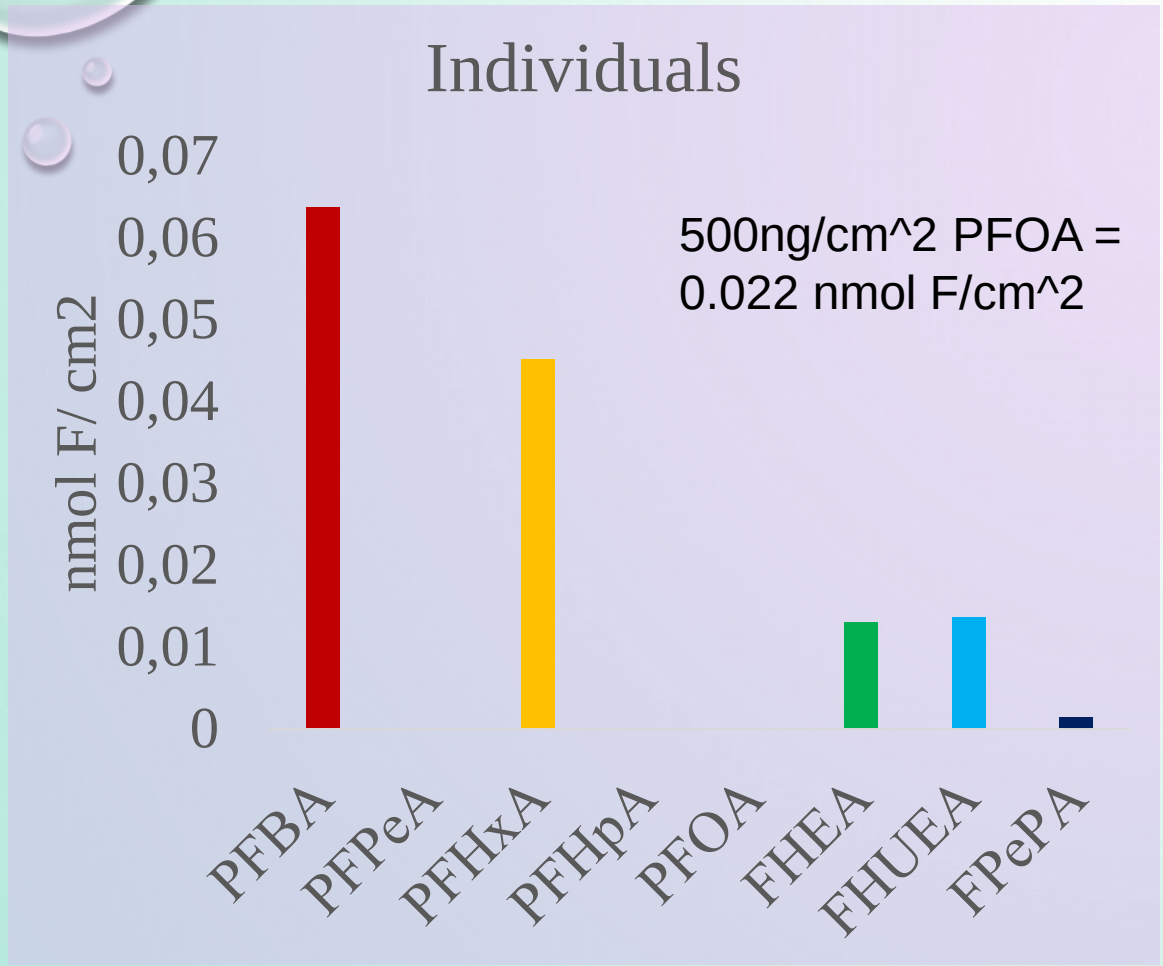
Detector

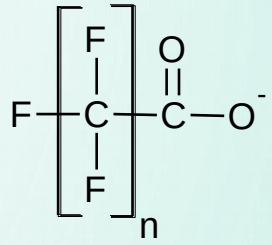
GC-MS analysis for **6 individual** volatile PFASs

LC-MS/MS analysis for **73 individual** PFASs

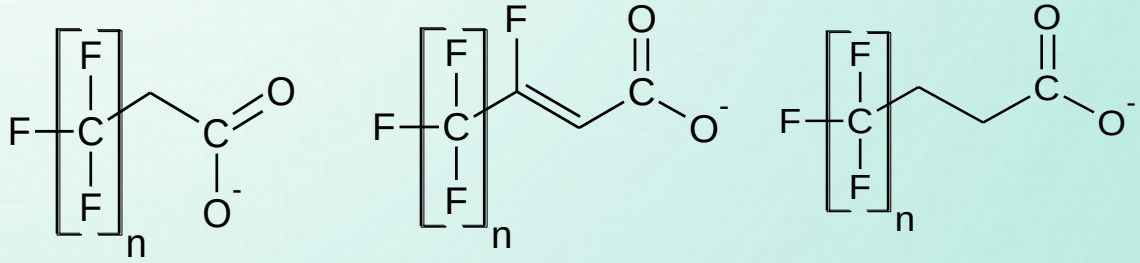
PIGE analysis

Example popcorn bag → LC-MS/MS & GC Data



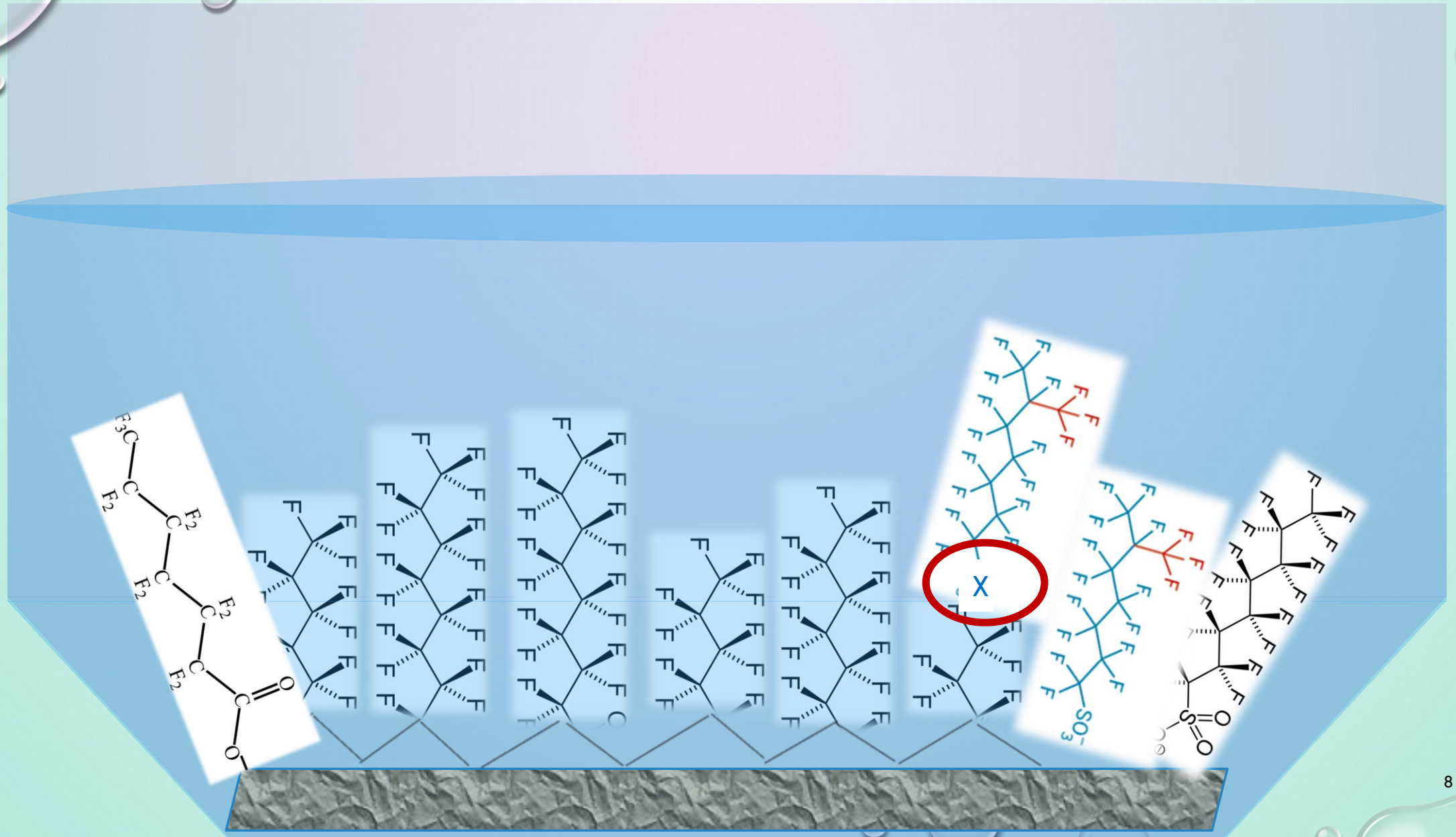


Carbolxylates-PFBA, PFHxA



Fluorotelomer carboxylates-FHEA, FHUEA, FPePA

- 6/73 ionic analytes present
- All analytes <LOQ for GC-MS
- Second instance of saturated and unsaturated acids present as commercial products of commerce (Zabaleta et. al, 2016)


X

What is Total Oxidizable Precursor Assay?

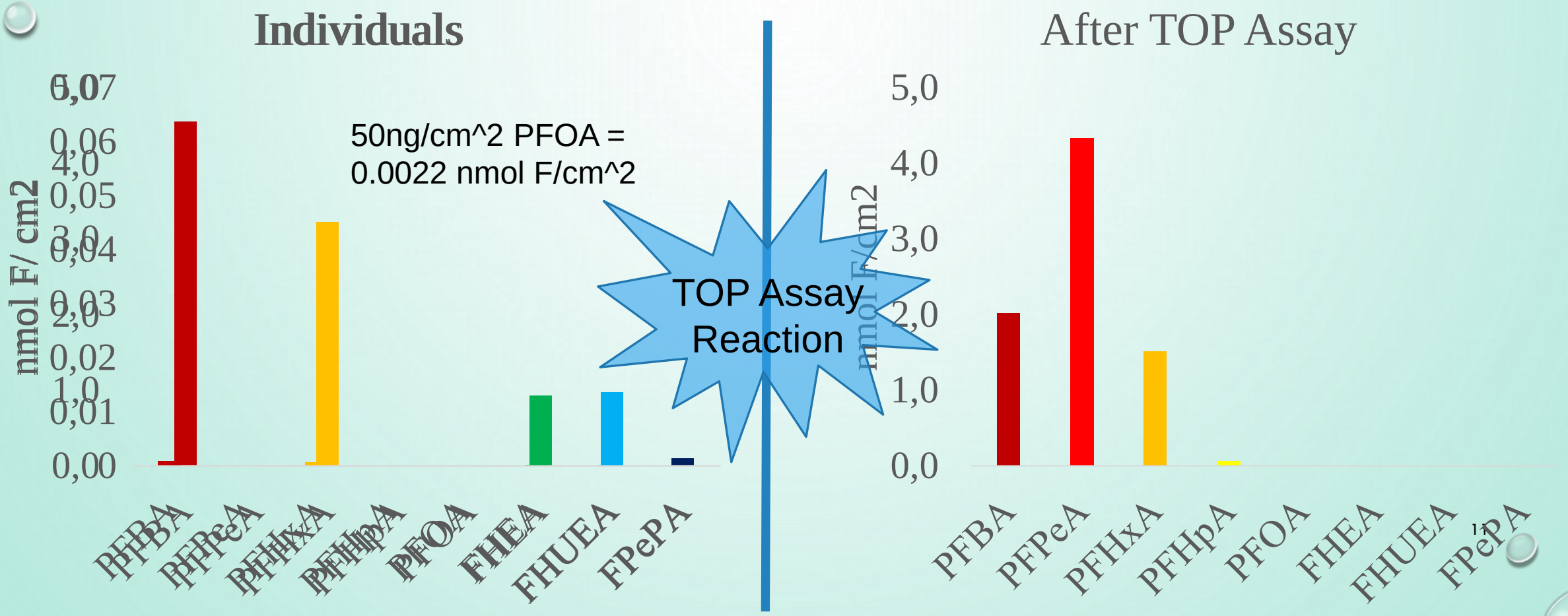
- Novel way of looking at PFASs
- Means of measuring *expected* total fluorine produced through oxidation of precursors to PFCAs and PFSAs
- Quantification of unknown precursors

Closing Mass Balance
How effective is TOP Assay?

Precursor	% Mass Recovered (C/Co)
1	17
2	42
3	36
4	3
5	4
6	45
7 (mix)	24

- Poor mass recovery
- **Need alternative for better accuracy!**

TOP Assay Results for Popcorn Bag



- Of seven food contact papers, LC-MS/MS data is accounting for **0 to 27%** of the TOP Assay
- Representation of total fluorine?

Particle Induced Gamma Ray Emission Spectroscopy (PIGE)

- Total fluorine measure of:
  - volatiles, ionic fraction, total surface bound fraction
- Can we close the mass balance?
- Before and after extraction
  - How efficiently is the material bound to the surface?

PIGE

	Volatile PFASs nmol F /cm^2	Ionic PFASs nmol F /cm^2	TOP Assay nmol F /cm^2	Original PIGE nmol F/cm^2
Popcorn Bag	**0.0**	**0.14**	**7.8**	**450**

50ng/cm^2 PFOA = 0.0022 nmol F/cm^2

- The solvent extractable fraction of PFAS (summation of GC-MS, LC-MS/MS, and TOP Assay) are accounting for **0.0 to 1.8%** of the total fluorine measure by PIGE
- Where are the remaining PFASs?

PIGE Residuals

	Volatile PFASs nmol F /cm^2	Ionic PFASs nmol F /cm^2	TOP Assay nmol F /cm^2	Non-solvent extractable Fraction F/cm^2	Original PIGE nmol F/cm^2
Popcorn Bag	**0.0**	**0.14**	**7.8**	**440**	**450**

50ng/cm^2 PFOA = 0.0022 nmol F/cm^2

- TOP Assay is under representation of total F
- Majority of PFASs remain bound to surface of paper textiles
- Unknown fate of PFASs over time and use

Conclusions

- Out of 8 papers and 9 textiles, accounting for **64-120%** if PIGE is >LOQ
- Closing mass balance-Need combination of Volatile, Ionic, (*limited* by what we know), Unknown Precursors and total fluorine by PIGE
- PIGE is a new and effective way of characterizing total fluorine

Acknowledgements

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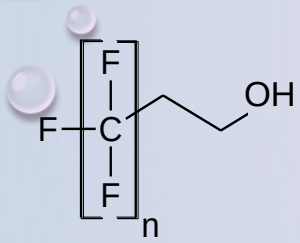
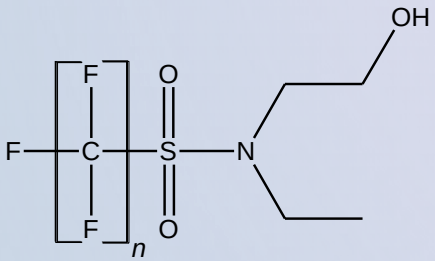
Special Thanks to:
The Field Laboratory
Chris Higgins and Simon Roberts
Tom Webster

GC-MS:



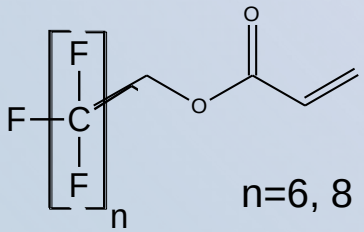
n=6,8,10

Fluorotelomer Alcohols



n=8

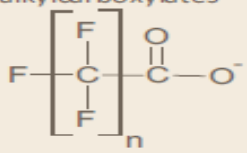
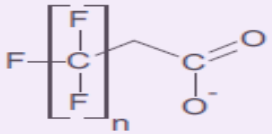
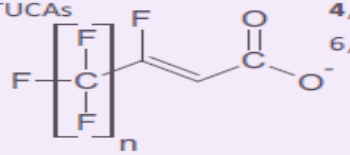
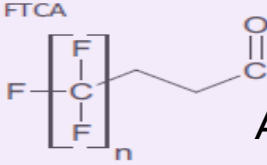
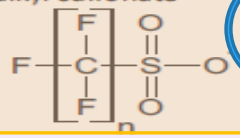
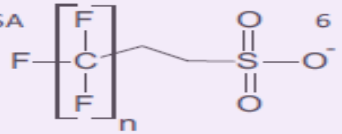
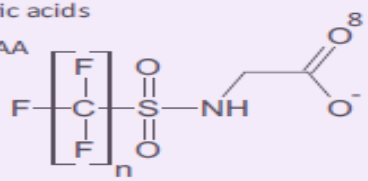
N-Ethyl Sulfonamido Ethanol



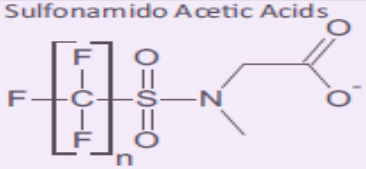
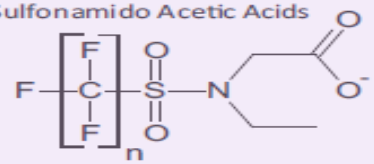
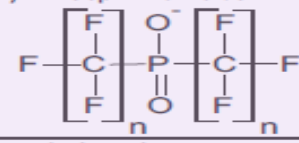
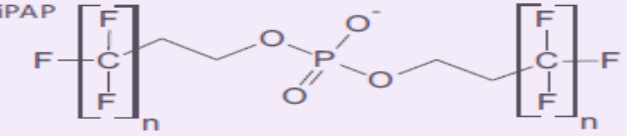
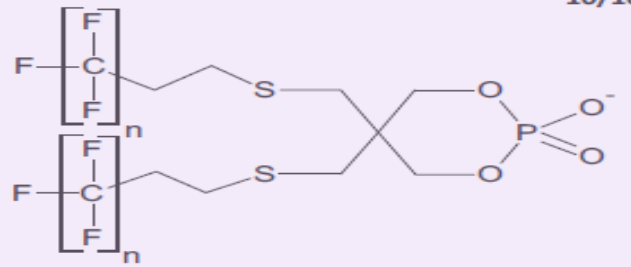
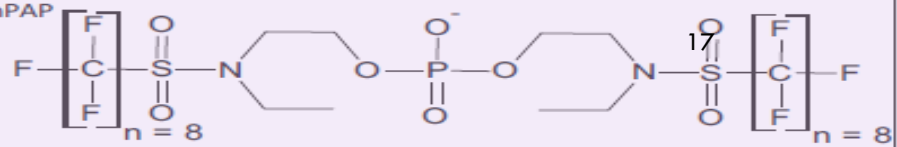
n=6, 8

Fluorotelomer Acrylates

LC-MS/MS

Compound Class	n	Data Quality
Perfluoroalkylcarboxylates	3-12	Qn
PFCAs 	13, 15, 17	Sq
	14, 16	Ql
Fluorotelomer Carboxylates	4	Sc
n:2 FTCA 	6, 8, 10	Qn
n:2 FTUCAs 	4, 10	Sc
	6, 8	Qn
n:3 FTCA 	3	Ql
	5, 7	Qn
	9	Sc
Perfluoroalkyl sulfonate	4, 6, 8, 10	Qn
PFSA 	5, 7, 9	Ql
Fluorotelomer Sulfonate	4, 8, 10	Sq
n:2 FTSA 	6	Qn
Fluoroalkyl sulfonamido acetic acids	4-7	Sc
		Sq
FASAA 		

Added C2, C3

Compound Class	n	Data Quality
N-Methyl Fluoroalkyl Sulfonamido Acetic Acids	4	Sq
MeFASAA 	5-7	Sc
	8	Qn
N-Ethyl Fluoroalkyl Sulfonamido Acetic Acids	4-7	Sc
EtFASAA 	8	Qn
Disubstitued Perfluoroalkyl Phosphinic Acids	4/4	Sc
PFPIA 	4/6	Ql
	6/6, 6/8, 8/8	Qn
Di-Substitued Polyfluorinated Phosphate Esters	4/4, 4/6	Sc
diPAP 	6/6, 8/8	Qn
	6/8, 8/10, 10/10	Ql
Fluorotelomer Mercaptoalkyl Phosphate Esters	6/6-10/10	Ql
FTMAP 		
N-ethyl perfluorooctanesulfonamidoethanol-based polyfluoroalkyl phosphate diester	8/8	Ql
SAmPAP 		

Allred, B. McKay, Lang, Johnsie R., Barlaz, Morton A., Field, Jennifer A. (2014). Orthogonal zirconium diol/C18 liquid chromatography-tandem mass spectrometry analysis of poly and perfluoroalkyl substances in landfill leachate. *Journal of Chromatography A, 1359*, 202-211.

Future Directions

- Mass balance
  - Identifying and adding individual species
  - TOP Assay fraction, identification understanding transformation toward exposure
- Binding process to materials is quite efficient, but may not be bound indefinitely
  - Preliminary findings in older textiles have higher mobile fractions, unknown in food contact materials
- Time Course study of older materials, (use/ “weathering” over time) to identify the longevity or break-down of bound fraction

Conversion Factor

nmol F/cm^2=

$$\frac{(Instrument\#)ng}{L} * dilution\ factor * Extract\ volume(L) * \frac{1g}{1E{-}9ng} * \frac{mol}{molecular\ weight\ (g)} * \frac{1E9nmol}{1mol} * \frac{1}{sample\ quantity\ in\ cm^2} * \#fluorine\ atoms\ present\ per\ molecule$$