A Field Analysis Technique for the Determination of PFAS Compounds

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Polyfluorinated Compounds

- Polyfluorinated Alkyl Substances (PFAS) are a class of compounds that have been in use since the late 1940's, early 1950's.
- PFAS consists of both perfluorinated and polyfluorinated compounds
- Perfluorinated – all carbons in the chain are fully bonded to fluorine
- Polyfluorinated – not all carbons in the chain are only bonded to fluorine

Polyfluorinated Compounds

PFAS compounds have been used in many applications. They have been used as additives in fluoropolymer production and as surfactants for numerous consumer applications;

- Stain resistant coatings for furniture and carpeting
- Coatings for fast food wrappers and boxes
- Breathable waterproof fabrics
- Insecticides
- Lubricants
- Chromium Plating (mist suppression)

Polyfluorinated Compounds

PFASs were also used in Aqueous Film Forming Foams (AFFF). Developed by 3M and US Navy in the 1960's. The low surface tension and positive spreading coefficient enabled film formation on top of lighter, less dense fuels.

AFFF is a complex, proprietary mix that has been used in large volumes for decades;

- Military
- Airports
- Fire Training Installations
- Oil and Gas Industry
- Chemical Manufacturing

Polyfluorinated Compounds

- PFASs are generally not volatile and not readily detected by gas chromatography/mass spectrometry (GC/MS)
- PFASs are typically ionized at normal environmental pHs, so also not readily extracted by most semi-volatile techniques
- PFASs are measured by liquid chromatography, tandem mass spectrometry (LC/MS/MS) which is well suited for analysis of ionic compounds

Polyfluorinated Compounds

ENVIRONMENTAL Science & Technology LETTERS

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Letter

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Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

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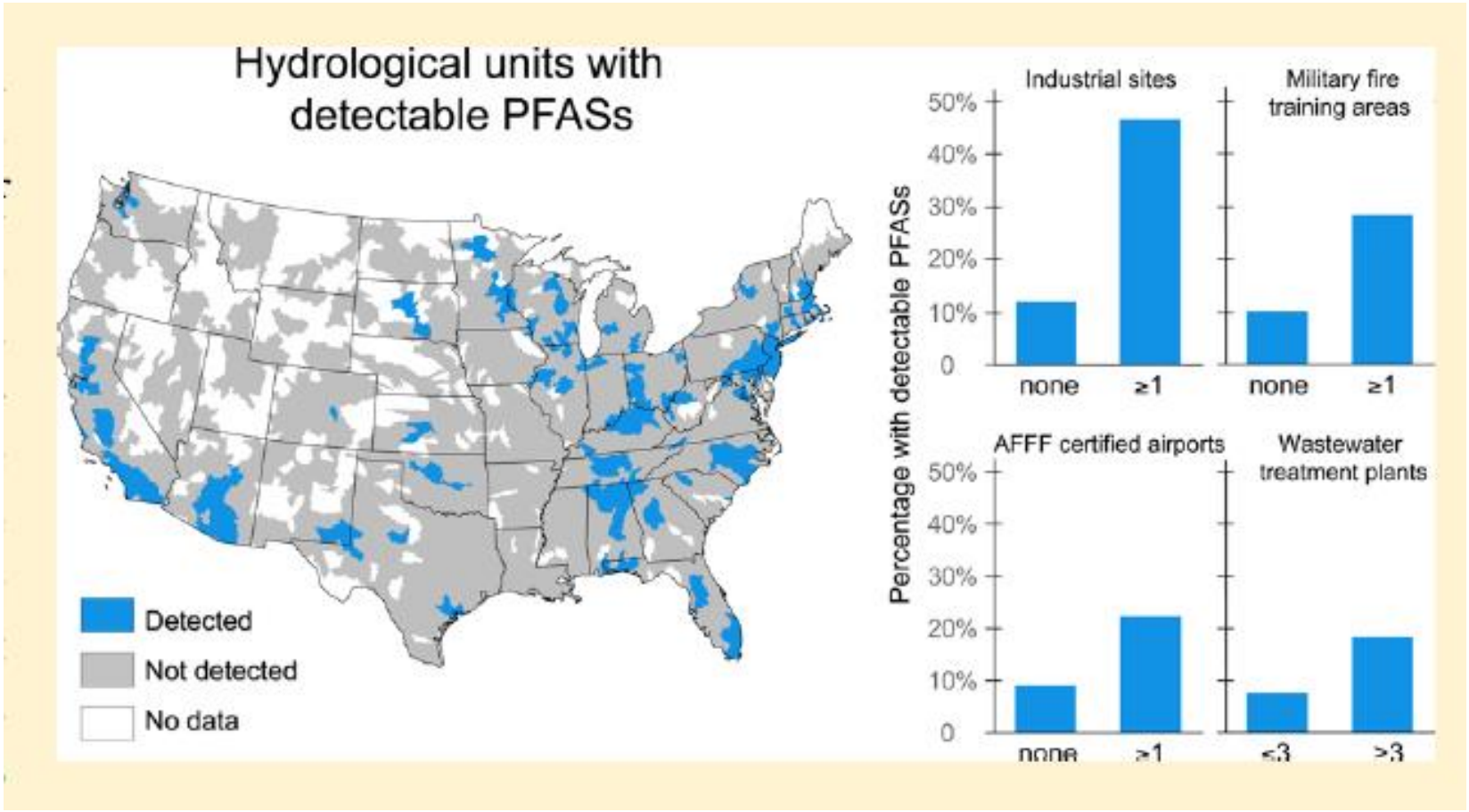
Polyfluorinated Compounds





Polyfluorinated Compounds

- Many sites across the US that have been impacted by PFASs from AFFF
- PFOA and PFOS in particular (due to Health Advisory Levels) are monitored for
- Analytical technique of preference is LC/MS/MS
- Requires sending sample out to lab, extraction, TAT concerns and getting analytical results
- Often, do not really know where a plume is or the extent of the plume
- Therefore, plume delineation may involve multiple field mobilizations and/or analysis of more samples than might be needed
- Sample cost $250-$300 for 2-3 week TAT with prices doubling for expedited TAT

Alternative

- Thought was for a real time monitoring tool
- Something that could be on-site and target specific compounds (PFOA/PFOS)
- Would not need to demonstrate sensitivity to the LC/MS/MS level, but low enough to help delineate plume (ppb)
- Collaboration between Geosyntec, Eurofins Eaton Analytical and Eurofins Lancaster Laboratories Environmental

Alternative



DIONEX

Technical Note 73

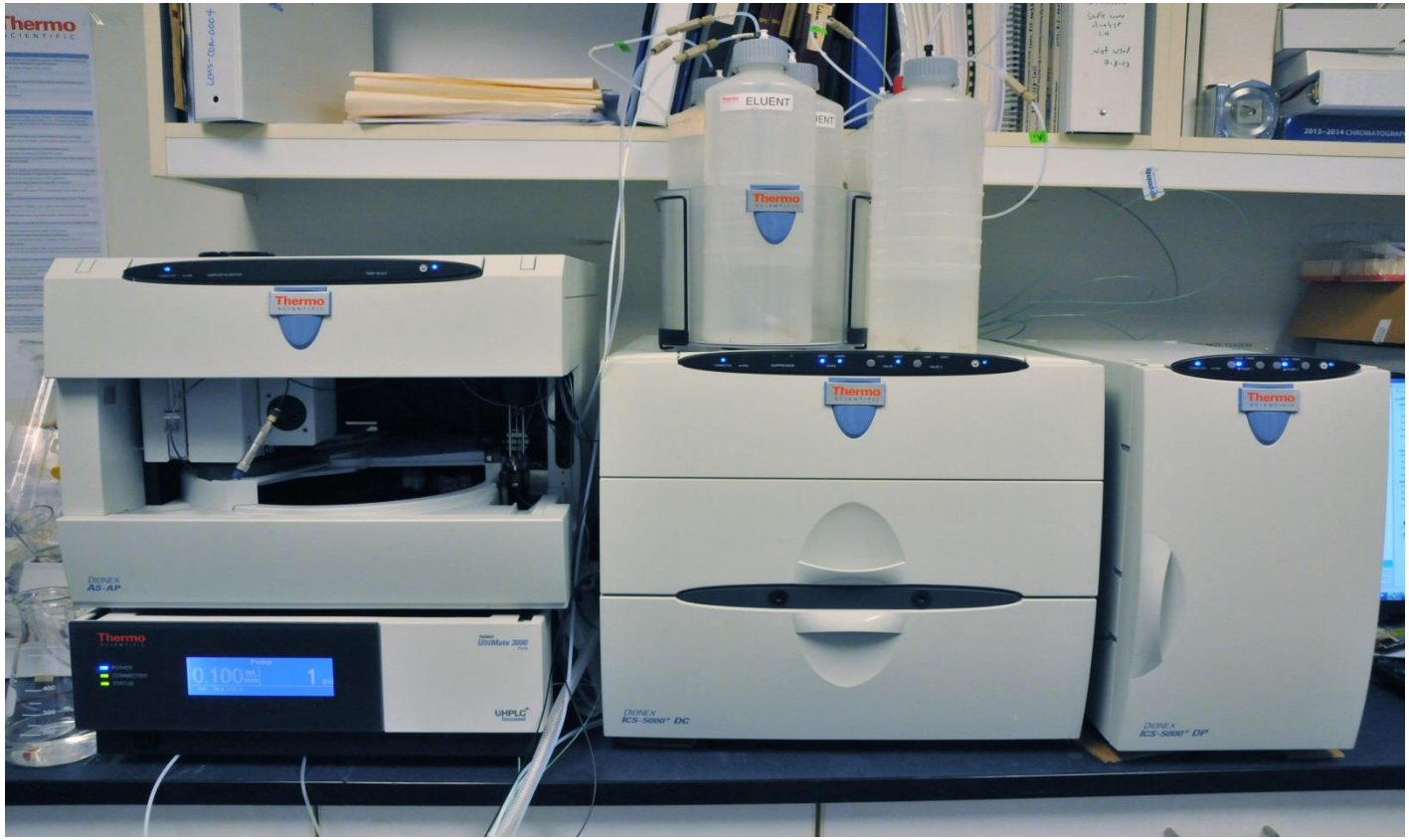
Determination of Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS) in Water Samples Using On-Line Sample Concentration, Reversed-Phase Liquid Chromatography, and Suppressed Conductivity Detection

Prior work done by Dionex in 2008 used Ion Chromatography (IC) with a conductivity detector

Alternative

- IC methodology uses conductivity detector so there should be significant differences in responses of compounds
- Theoretically should be simpler to operate than an LC/MS/MS
- Should be relatively field portable as just needs electricity
- Technical note cited sensitivities to low ppb

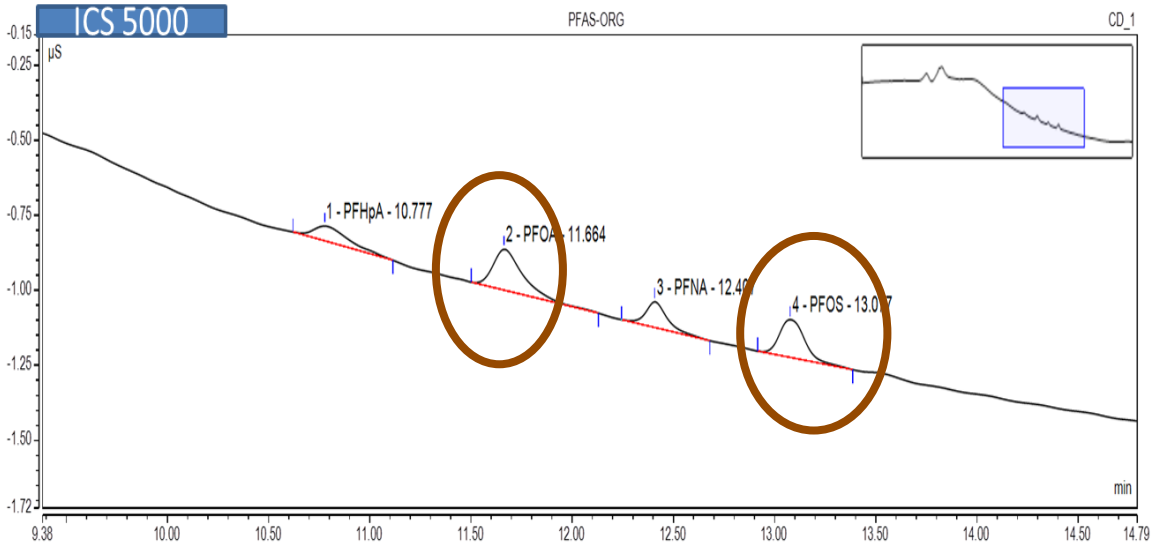
Ion Chromatography



Set-up is similar to an LC/MS/MS but a smaller footprint
Picture from the Eurofins Eaton facility

IC Separation

- Chromatogram showing co-elution (peak = PFOA+PFHxS & PFOS+PFDA)



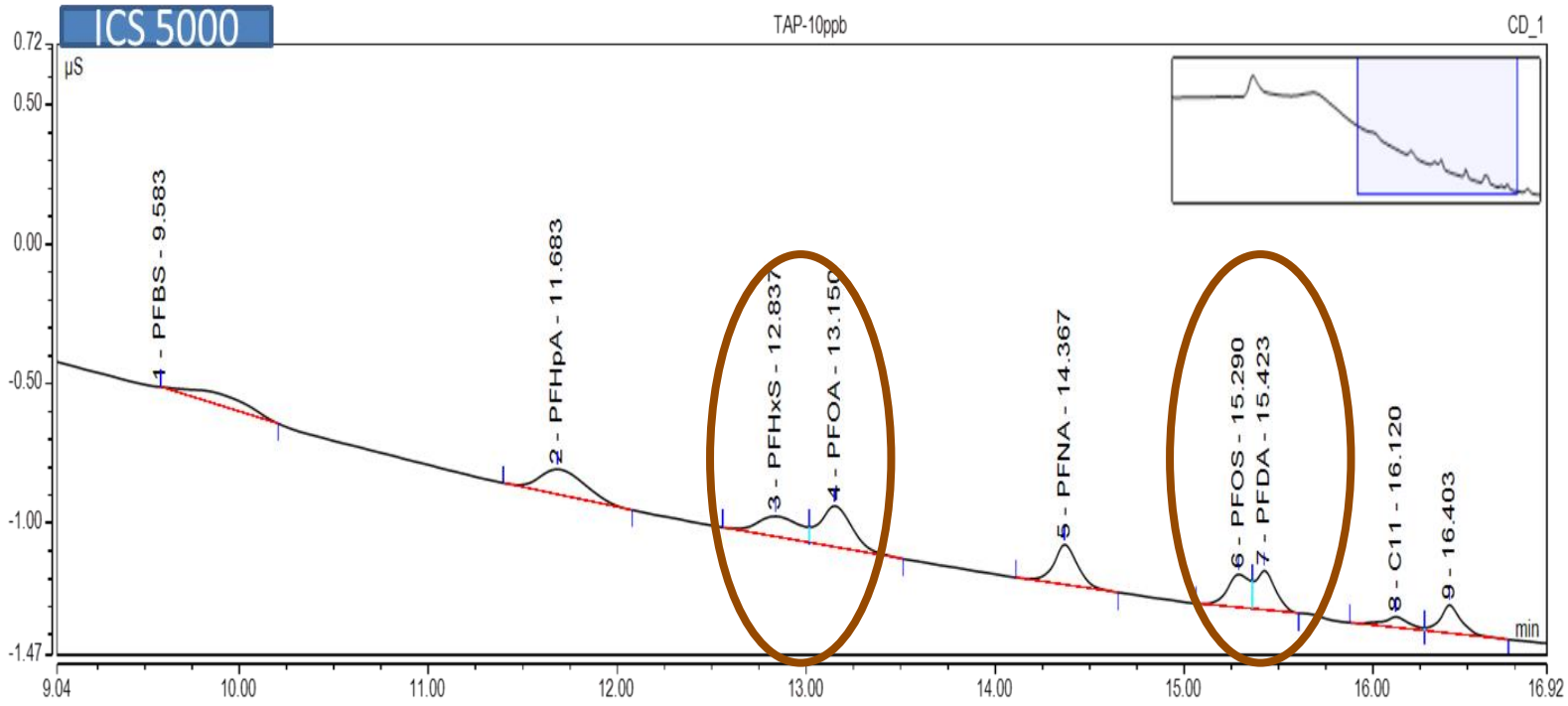
- Need to optimize using four variables that control the elution sequence

		PFOA	PFOS
pH	4.5-8.5	+	>+
mM	10 to 30	+	>+
temp	30-45	=/>	<
MeCN	elution	25%	35%

Data acquired by Ali Haghani, Eurofins Eaton Analytical

IC Separation

Separation achieved at higher pH. RT = 18 minutes

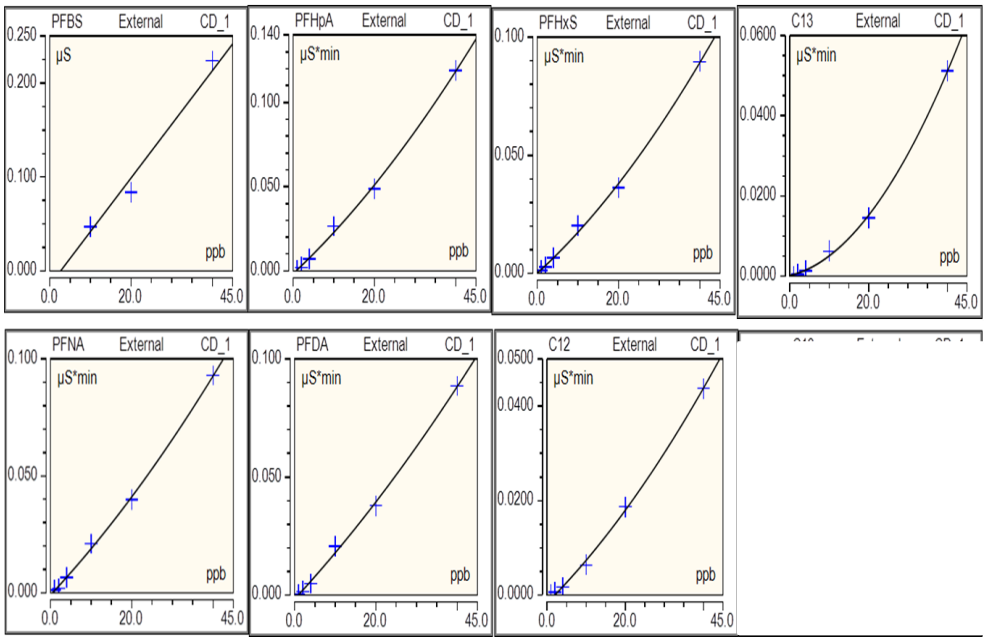


Data acquired by Ali Haghani, Eurofins Eaton Analytical

Calibration



Good linear calibration achieved for detected PFAS

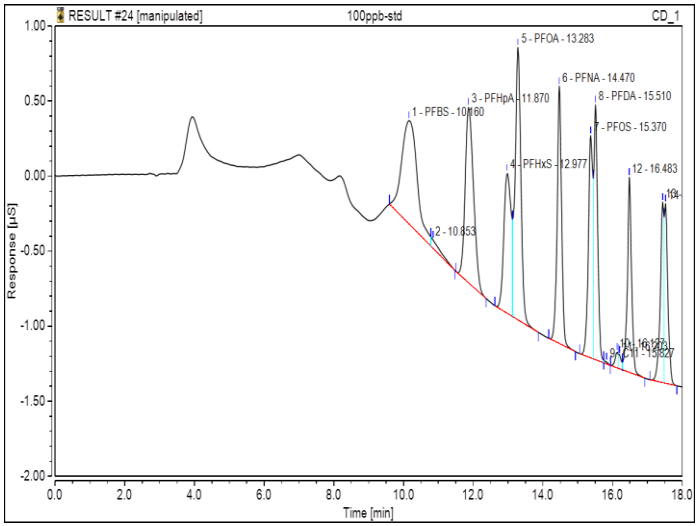


Injection Name	Amount ppb CD_1	
	PFOA	
CAL-1	0.940	
CAL-2	1.950	
CAL-4	4.275	
CAL-10	10.660	
CAL-20	18.797	
CAL-40	40.379	
%Coeff.Det.		99.7591

Injection Name	Amount ppb CD_1	
	PFOS	
CAL-1	1.079	
CAL-2	1.432	
CAL-4	3.694	
CAL-10	11.409	
CAL-20	19.254	
CAL-40	40.085	
%Coeff.Det.		99.8114

Data acquired by Ali Haghani, Eurofins Eaton Analytical

Linearity and Sensitivity



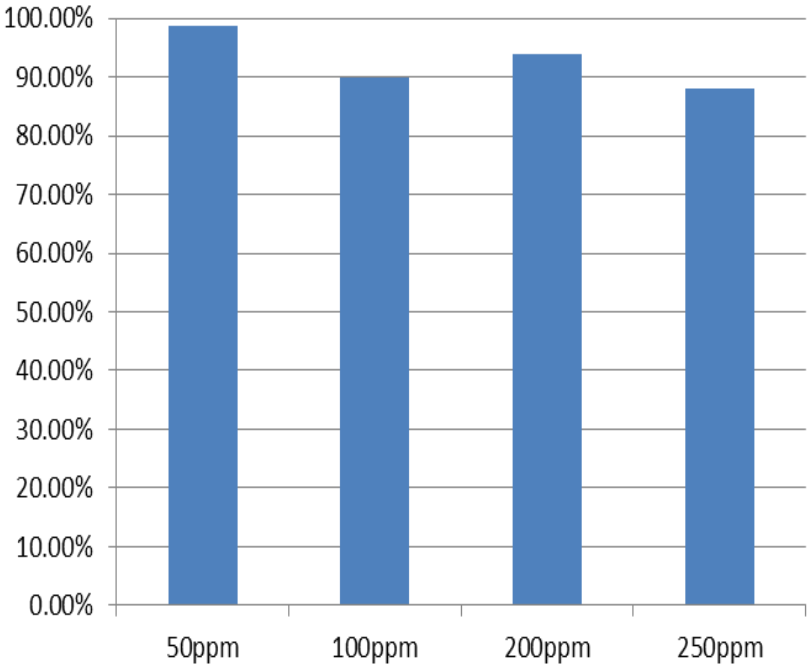
No	Peak Name	Retention Time (min)	Amount (ppb)
1	PFBS	10.2	104.0
3	PFHpA	11.9	99.9
4	PFHxS	13.0	99.9
5	PFOA	13.3	104.8
6	PFNA	14.5	99.9
7	PFOS	15.4	99.9
8	PFDA	15.5	99.9
9	PFUnA	15.8	100.0
13	PFDoA	17.4	99.8
14	PFTrDA	17.5	100.0

- Good linearity up to 100 ppb (no need for dilution)
- Sensitivity for PFOA (1 ppb) and PFOS (2 ppb)

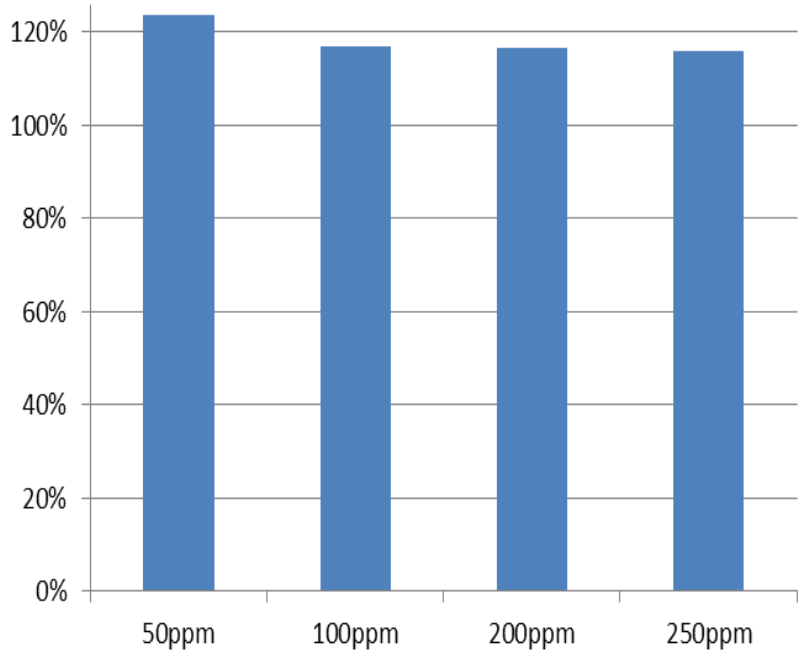
	PFOA	PFOS	
Avg	0.9	1.5	
% Rcvy	89%	74%	
Stdv	0.054	0.063	
% RSD	6.0%	4.3%	
IPR	0.21	0.25	
Upper PIR	111%	87%	< 150%
Lower PIR	68%	62%	> 50%
MDL	0.17	0.20	

Ruggedness

PFOA



PFOS



Synthetic Water Containing Ca, Mg, Cl, SO4 at the concentration indicated
No negative impact observed with increased TDS

Conclusions

- Ion Chromatography has yielded promising results in the lab to date
- Able to achieve sensitivity to 1 ppb for PFOA and 2 ppb for PFOS
- 18 minute run time translates to 3 samples per hour. Little to no sample preparation
- TDS has little impact on sensitivity or separation
- Not shown here but preliminary comparison to LC/MS/MS results looks very promising
- TAT will be less than achieved with external lab
- Costs should be less due to reduction of field costs

Future

- Unit has been tansferred to ELLE
- Ruggedness and method validation work (lab to lab, analyst to analyst) ongoing
- Details of mobilization to field being finalized
- Deployment

Acknowledgements

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Questions