



PFAS, Total Oxidizable Precursors (TOPs) and Total Organic Fluorine (TOF)

“When to use one over the other?”

Terry Obal, Ph.D., C.Chem.
Bureau Veritas, Mississauga, Ontario, CANADA

Introduction

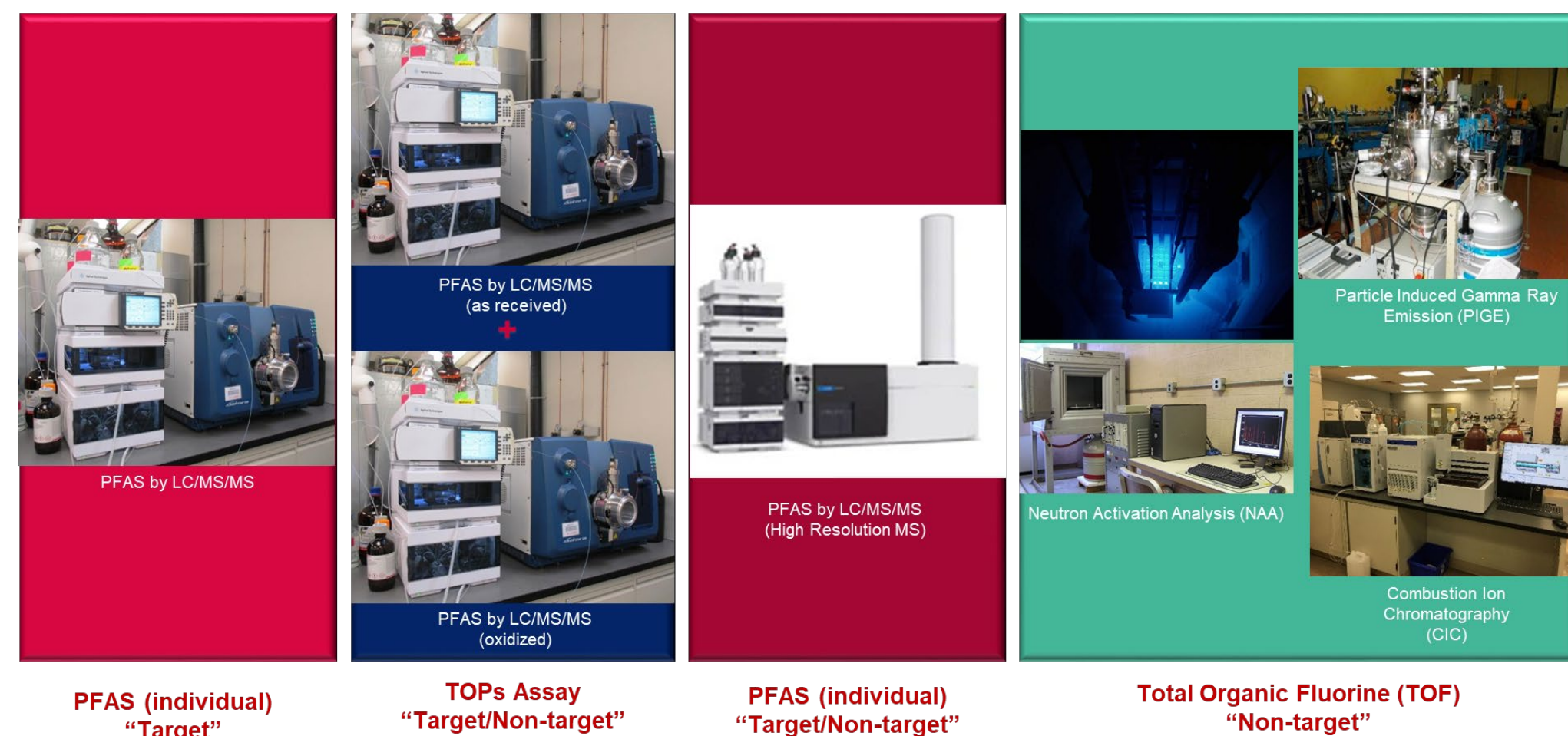
Over the past ten years, there has been an extraordinary amount of attention focused on perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and related per- and polyfluorinated alkyl substances (PFAS), particularly with respect to their characterization, delineation, management and regulation in the environment. Environmental stakeholders are continually developing a better understanding of: occurrence, exposure and toxicity; proper sampling and analysis protocols; and remedial options.

From an analytical standpoint, testing for PFAS has been primarily through liquid chromatography coupled with tandem mass spectrometry (LC/MS/MS). As a “targeted” analytical technique, the results are limited to a fixed set of parameters. In other words, the results do not necessarily provide a comprehensive measure of the potential magnitude of the total pool of PFAS that may exist in contaminated soils and water, nor does it measure the potential for PFAS formation due to natural transformation of precursor compounds over time to the regulated end products.

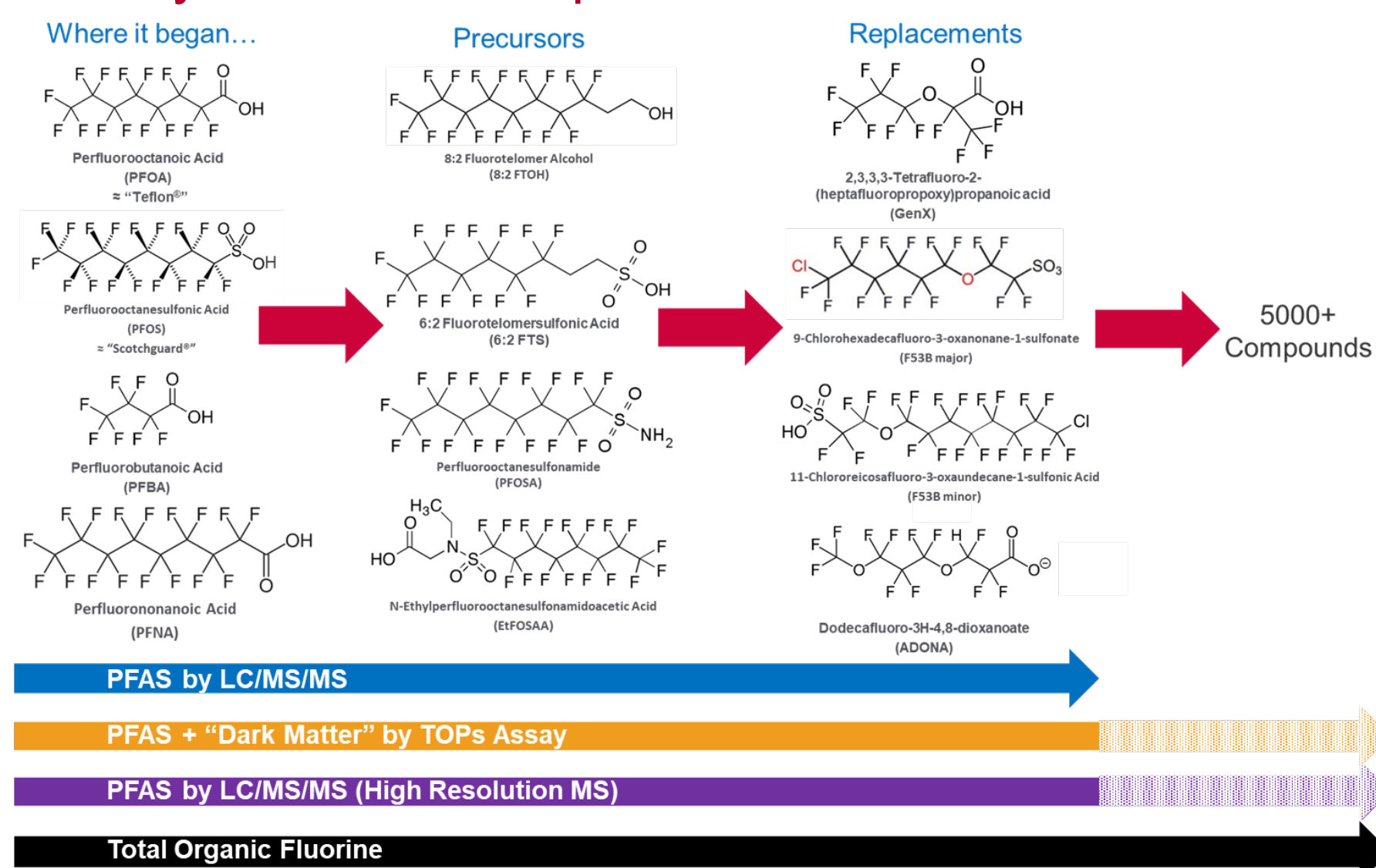
In an attempt to identify the presence of other, non-target PFAS present in a contaminated sample, the total oxidizable precursors (TOPs) assay was developed. More recently, there has been a focus by laboratories to develop and validate lower cost alternatives that also provide a more comprehensive measure of total PFAS impact. This has resulted in several methods for measuring total organic fluorine (TOF) as a proxy for total PFAS contamination.

Each of these analytical approaches offers distinct advantages for environmental practitioners. At the same time, the limitations of each need to be considered when assessing their utility in different situations.

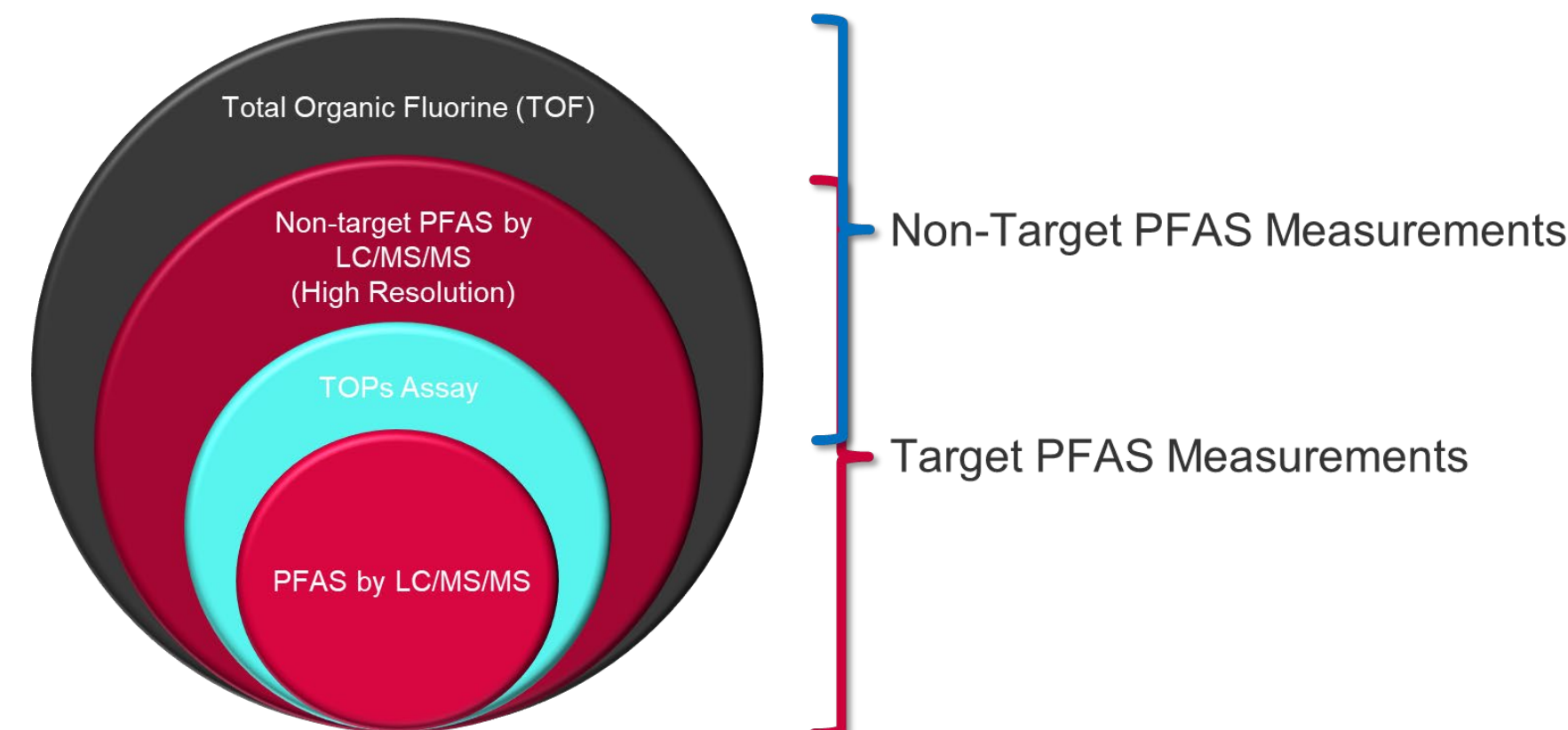
PFAS Analytical Toolkit



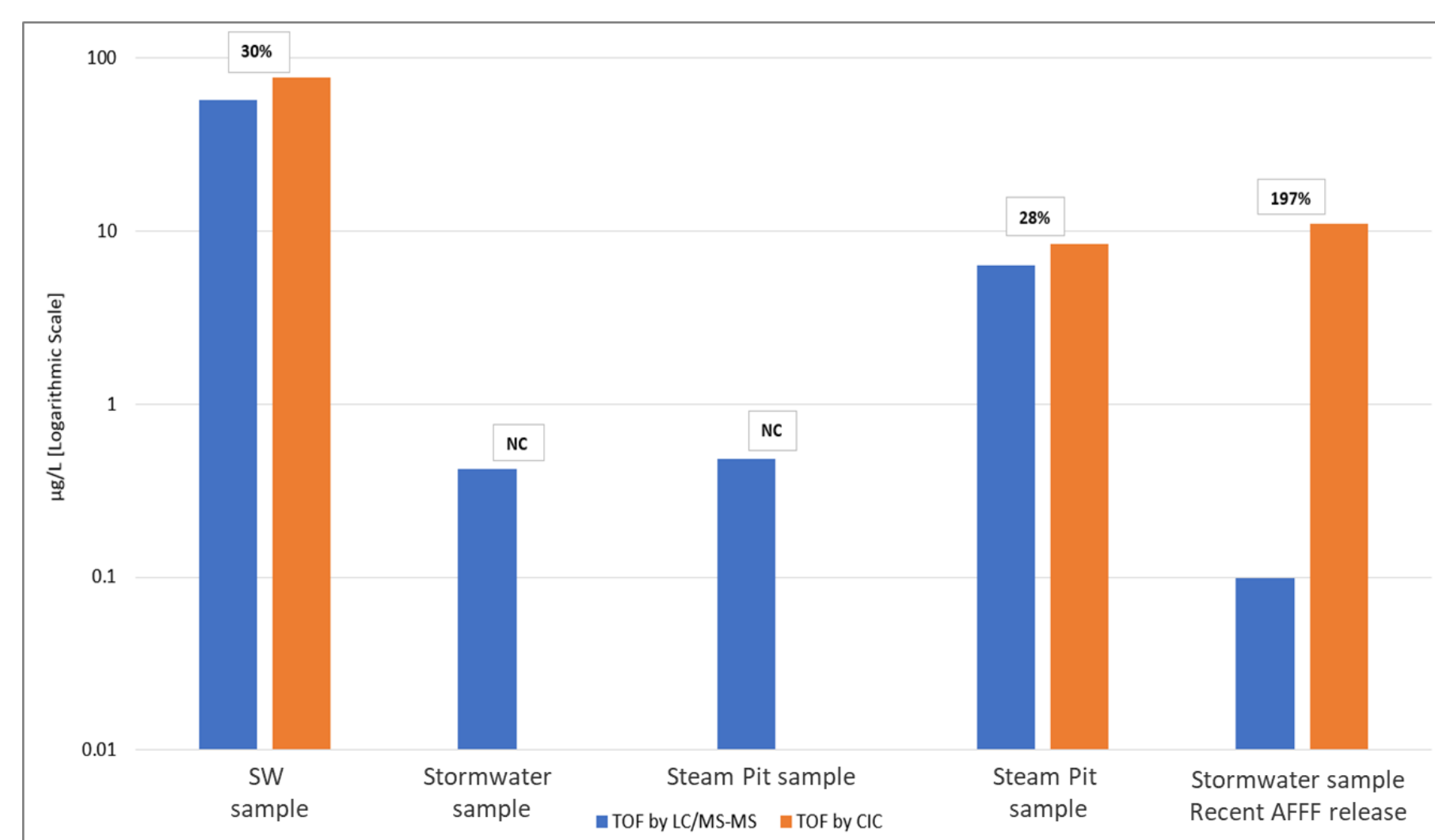
PFAS Analytical Toolkit Capabilities



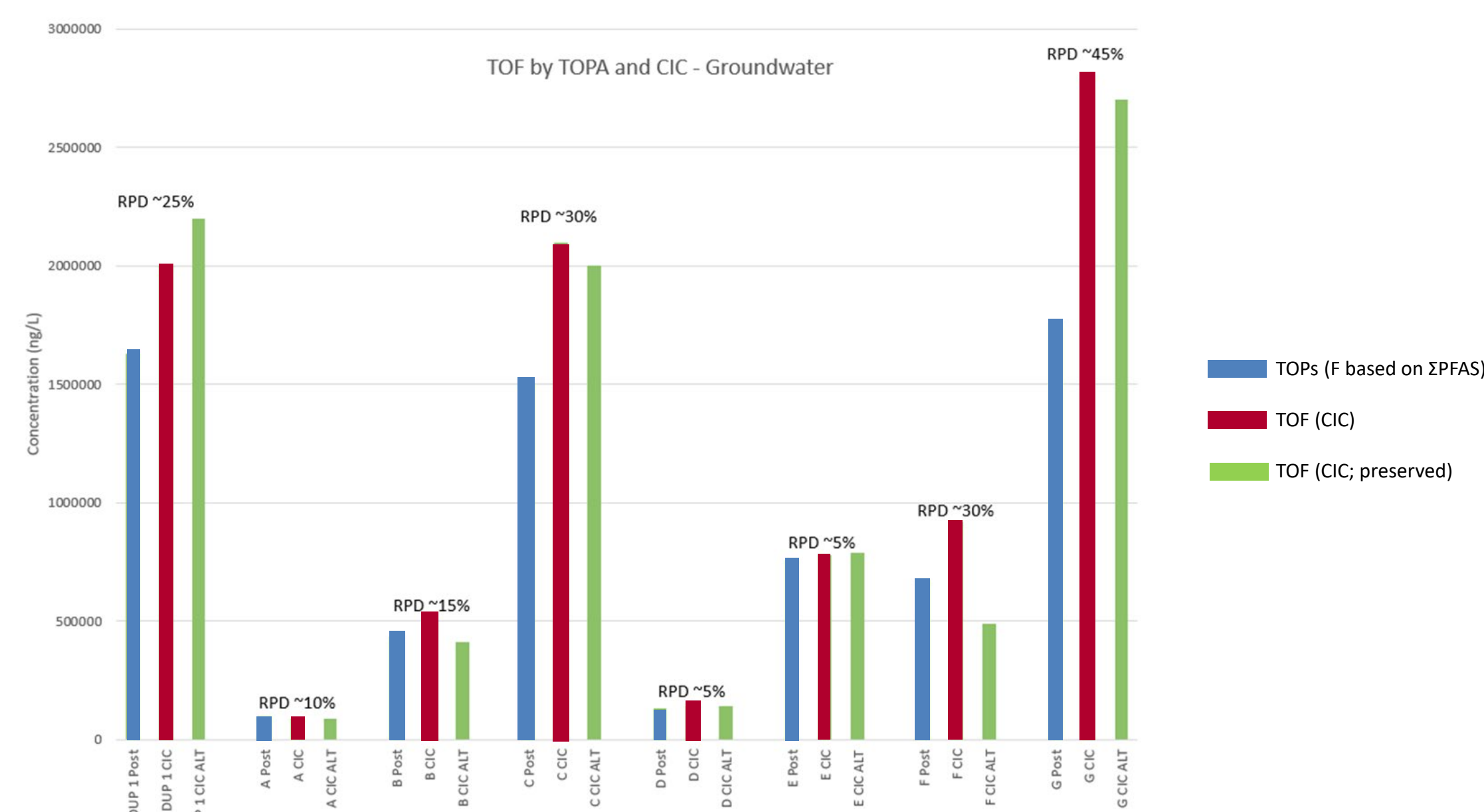
Target vs. Non-Target PFAS Analysis



TOF (Σ PFAS by LC/MS/MS) vs. TOF (CIC)

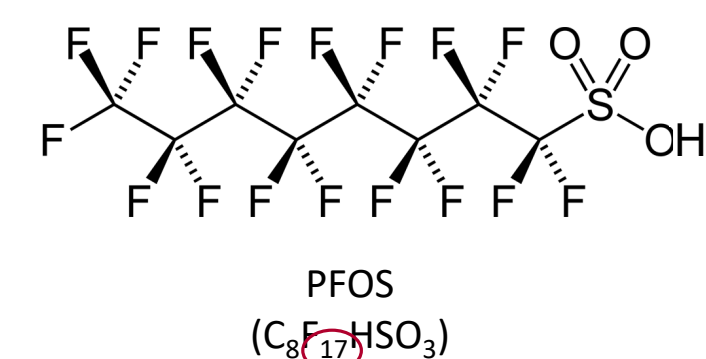


TOPs Assay (Σ PFAS) vs. TOF (CIC)



Remember...

TOF by CIC is measuring the fluorine contribution from all of the fluorine-containing compounds in the sample



PFOS (Mol. Wt.) = 500 g/mol
Fluorine (Mol. Wt.) = 19 g/mol
17 x Fluorine = 323 g/mol
Fluorine Contribution = $\frac{323}{500} = 64.6\%$

PFOS TOF equivalent (TOF-EQ) ~65%

PFOS (by LC/MS/MS) = 250 ng/L PFOS \rightarrow F_{total} (by CIC) = $0.646 \times 250 \text{ ng/L} = 162 \text{ ng/L F}$

Considerations

Test	Questions Answered	Advantages	Limitations
PFAS by LC/MS/MS	<ul style="list-style-type: none"> Identification and quantitation of target PFAS at ultra trace levels Regulatory compliance Risk Assessment 	<ul style="list-style-type: none"> Provides accurate concentrations for individual PFAS 1-2 ng/L reporting limits meets all current regulatory standards 	<ul style="list-style-type: none"> Higher cost test “Targeted” analysis 30-40 individual compounds ...out of a potential 5000+ PFAS
Total Oxidizable Precursors (TOPs) Assay	<ul style="list-style-type: none"> Identification and quantitation of target PFAS at ultra trace levels Regulatory compliance <i>Indication</i> of total PFAS 	<ul style="list-style-type: none"> Provides accurate concentrations for individual PFAS Indicates the presence of PFAS not measured by LC/MS/MS (“Dark Matter”) 	<ul style="list-style-type: none"> High cost Labor intensive assay...longer turnaround times High sample variability Not fully quantitative Does not necessarily provide a “total” PFAS result
PFAS by LC/MS/MS (High Resolution MS)	<ul style="list-style-type: none"> Identification and quantitation of target PFAS at ultra trace levels Regulatory compliance Risk Assessment Characterization of non-target PFAS at ultra trace 	<ul style="list-style-type: none"> Characterization of non-target compounds “Target” and “non-target” analysis 	<ul style="list-style-type: none"> High capital cost = High cost test
Total Organic Fluorine (TOF)	<ul style="list-style-type: none"> <i>Measure</i> of total PFAS “Is my sample “PFAS-free?” 	<ul style="list-style-type: none"> Provides concentration of organic fluorine, which is <u>representative</u> of the presence or absence of PFAS Less labour intensive Lower priced analysis 	<ul style="list-style-type: none"> Current Reporting limits: <ul style="list-style-type: none"> 600 ng/L (total F) in water 200-700 ng/g (total F) in soil Non-selective analysis Some lower recoveries observed for high organic content soils

PFAS by LC/MS/MS, TOPs Assay (Σ PFAS) or TOF (CIC)?

Analytical Need	PFAS by LC/MS/MS	TOPs Assay	TOF by CIC
Regulatory Compliance	✓		
Site Characterization	✓	✓	
Contaminant Delineation	✓	✓	✓
Completeness of Remedial Action	✓	✓	✓
Site Risk (Future Liability)	✓	✓	✓
PFAS-Free AFFF			✓