

TOP ASSAY AND RISK ASSESSMENT

Assessing Exposure to Precursors

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10 September 2019

Overview

- Assessing PFAS other than PFOS and PFOA
- Precursors in the environment – pre- and post-TOP Assay data
 - International data
 - Australian data
- Potential contribution to risk

How significant are ‘precursors’ as a contributor to total PFAS exposure?

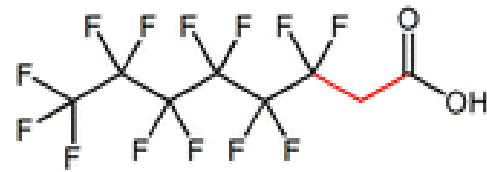
Introduction

- OECD (2018) identified >4,700 individual PFAS compounds
 - Recent study reported >6,300 PFAS now identified
- Standard laboratory methods currently quantify ~30
 - ~400 analytical standards now available (as of mid-2019), but commercial scale volumes still not available
- Many site assessments only measure ‘standard PFAS’
 - Potential proportion of ‘other PFAS’ in the environment not known
 - This may not be a significant data gap for some sites (e.g. some AFFF sources)
- Screening criteria and toxicity values available for only 3 PFAS in Australia

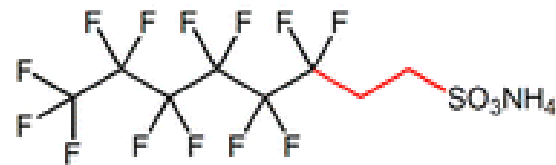
Definitions

Polyfluoroalkyl substances

Non-fully fluorinated alkane compounds (e.g. 6:2 FTS)



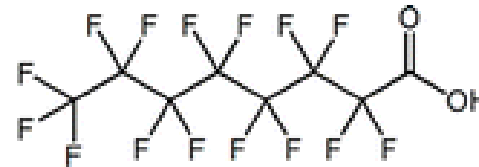
6:2 FTCA



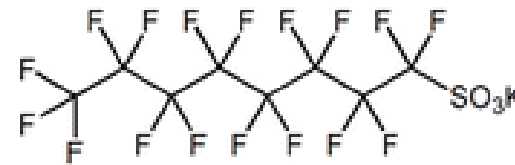
6:2 FTSA

Perfluoroalkyl substances

Fully fluorinated alkane molecules (e.g. PFOS, PFOA)



PFOA



PFOS

Precursors: Polyfluoroalkyl substances that degrade to terminal perfluoroalkyl acids (PFAAs)

Total Oxidisable Precursor (TOP) assay: method to oxidise polyfluoroalkyl substances so they degrade to PFAAs

Measuring ‘other PFAS’

TOP Assay

- TOP Assay treats PFAS samples to degrade ‘precursors’ to form the terminal degradation product
- Oxidised sample can then be analysed with current analytical standards, to provide PFAS specific results

TOF (Total organic fluorine)

- Provides a total concentration of all C-F based compounds in a sample, including PFAS compounds not detected by TOP Assay
- Prone to interference from non-PFAS sources (e.g. pharmaceuticals)

PIGE – Particle-Induced Gamma Ray Emission (PIGE) Spectroscopy

- Limited equipment accessibility, and not able to speciate individual PFAS.

Other methods...? |

Precursors in the Environment

- PFAS manufacturing methods have changed and will continue to do so
- **AFFF concentrates ~ 40-100% precursors** (Houtz et al, 2013; Dauchy et al, 2017).
- **Wastewater Treatment Plant (WWTP) sludges ~ 30-60% precursors** (Houtz et al, 2016; Eriksson et al, 2017).
- **PFAS in precipitation** off Chinese coast in 2018 ~ **50% precursors** (Chen et al, 2019).
- PFAS impacted soil + groundwater **in fire training areas ~ 50% precursors**, incl. >300-500 m down-gradient (Houtz et al, 2013; Weber et al, 2017).
- Precursors have been detected in remote areas, in upper trophic level biota, and in food supplies (Gebink et al, 2015; Boisvert, 2016)
 - Precursors may be present in food due to contamination of land and water and subsequent bioaccumulation
 - Precursors may also be present in food supplies from packaging, processing, etc

Precursors in the Australian Environment

There has been **very little consideration of precursors** in published Australian site assessments

A review of available Australian assessments found **widespread QC issues with TOP Assay results**:

- e.g. decreased concentrations of terminal perfluoroalkyl substances (e.g. PFOS) in post-TOP Assay analyses
- e.g. the presence of precursors such as FtS's or sulfonamides in the post-TOP Assay analyses

Available data indicates that **standard analyses consistently underestimate total PFAS** in soil, sediment, surface and groundwater.

- E.g. a study of surface water near Brisbane reported post-TOP Assay PFOS concentrations at more than double the pre-TOP Assay PFOS concentrations.
- Australian results generally consistent with international literature

TOP Assay of Aquatic Fauna

Qld DES Brisbane Airport study – DES analysed >100 aquatic fauna samples with TOP Assay in 2017

Table 1. Frequency of Detection of Key PFAS in Aquatic Biota, based on Pre- and Post-TOP Assay Results (n = 102)

	Pre-TOP Assay	Post TOP-Assay
PFOS	94%	98%
PFOA	20%	25%
PFBS	1%	1%
PFBA	0%	28%
6:2 FtS	12%	5%



Brisbane Airport AFFF Investigation
Monitoring Sampling Points

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PFOS Concentrations in Biota Pre- and Post-TOP Assay

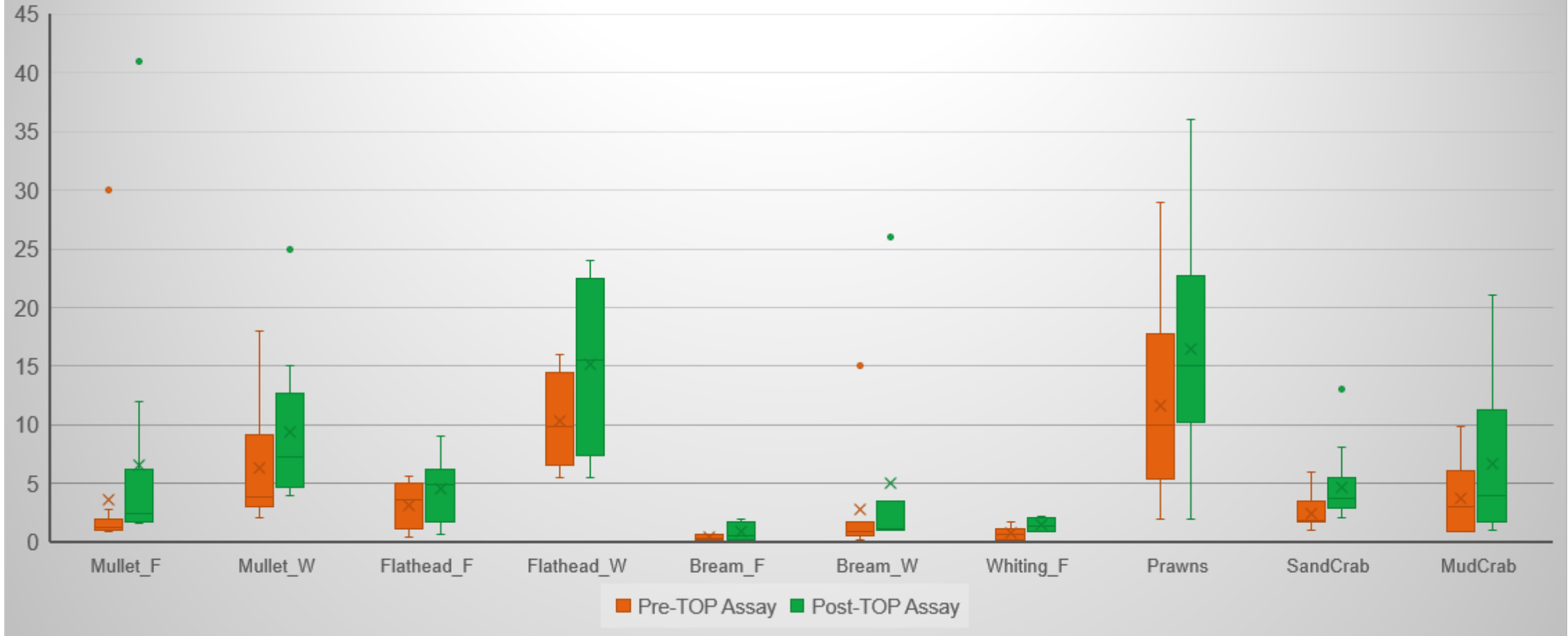


Table 2. Aquatic Fauna TOP Assay Data: PFOS Concentrations Pre- and Post-TOP Assay (µg/kg)

Sample Type	n	Pre-TOP PFOS Conc. (Geometric Mean)	Post-TOP PFOS Conc. (Geometric Mean)	Screening Criteria (µg/kg) ^b	% Increase ^a
Aggregated Data					
All Samples	94	2.7	4.2		192%
All Fish Fillets	33	2.7	4.3	5.2	221%
All Whole Fish	28	3.2	5.0		166%
All Invertebrates	33	3.8	6.4	65	186%
Data Assessed by Species					
Mullet Fillet	13	1.7	3.6	5.2	268%
Mullet Whole	12	5.1	7.9		161%
Flathead Fillet	7	2.5	3.5	5.2	142%
Bream Whole	7	1.1	2.1		209%
Whiting Fillet	7	0.6	1.4	5.2	258%
Whiting Whole	5	1.9	2.6		138%
Prawns	12	9.1	14	65	191%
Sand Crab	15	2.2	4.2	65	189%
Mud Crab	6	2.7	4.3	65	166%
a Calculated from individual paired pre- and post-TOP Assay results; b FSANZ (2017) Proposed Trigger Points for Investigation					

How significant *are* precursors to exposure?

- ‘Standard’ PFAS analyses consistently underestimate total PFAS mass
 - The relative proportion of precursors will change with source type
 - Precursors can be less significant an issue for historic AFFF sources
- Precursors can transport significant distances and can bioaccumulate
- We can’t know the contribution of precursors to exposure if we don’t measure for it...
 - With increasing empirical data, we can target precursor analyses to where it is needed
 - Preferable to assess total intake at point of exposure

The concentrations reported in biota were not significant in the terms of risk to human health ...

if we assume equivalent toxicity

Conclusions

Some **uncertainty** in assessment of PFAS exposure is **acceptable within reasonable bounds**.

An underestimate of total PFAS mass of approximately 30-50% (consistent with accepted analytical uncertainty) is **unlikely to be significant issue** for risk assessment outcomes, **assuming equivalent toxicity**.

Data quality issues need to be managed to ensure oxidation is complete results are reliable.

There is a **lack of assessment for precursors in Australia**, particularly at the point of exposure.

Any risk assessment needs to **ensure that the assessment of exposure is accurate**, notwithstanding limitations in the understanding of toxicity.

Accurate measurement of total PFAS mass via tools such as TOP Assay **will assist in future proofing site investigations** and risk assessment.

Acknowledgements



Tony Bradshaw

Technical Specialist

Regulatory Support

Department of Environment and Science

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QUESTIONS?

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