Inaugural Australasian Land & Groundwater (ALGA) Research & Development Grant

Improving Measurement Reliability of the PFAS TOP Assay

- Implications: Informing Regulation/Guidance

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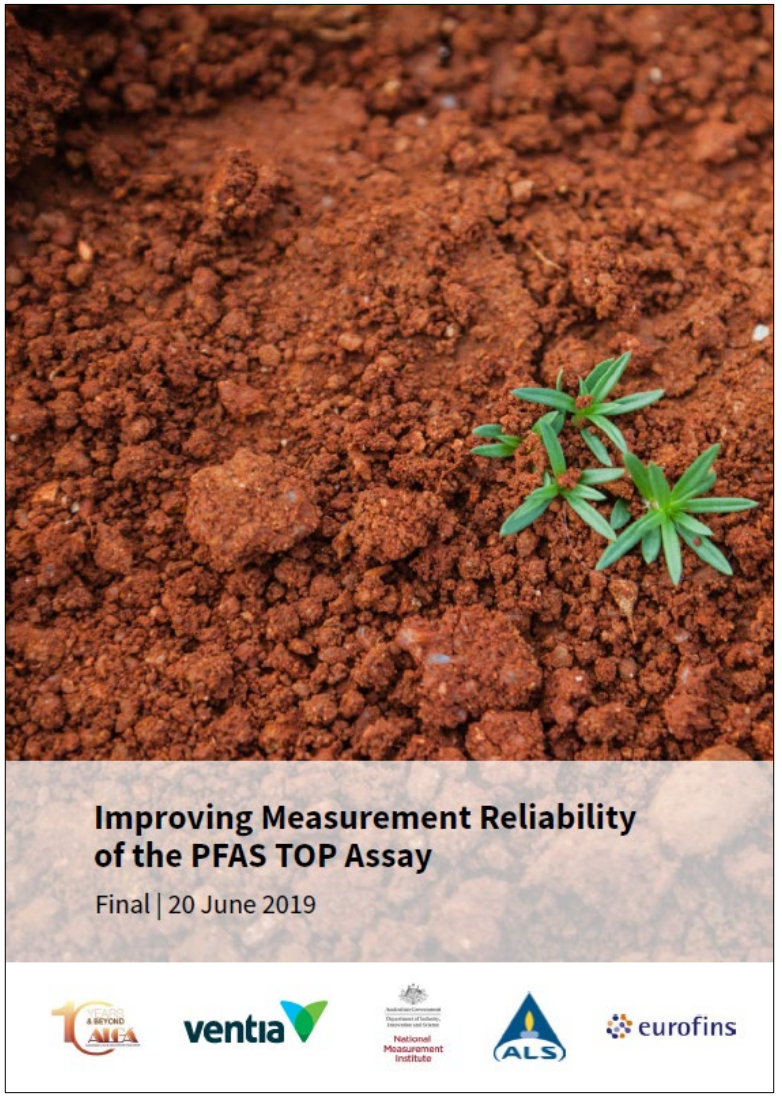
(PREVIOUSLY VENTIA UTILITY SERVICES)

ALGA BOARD OF DIRECTORS



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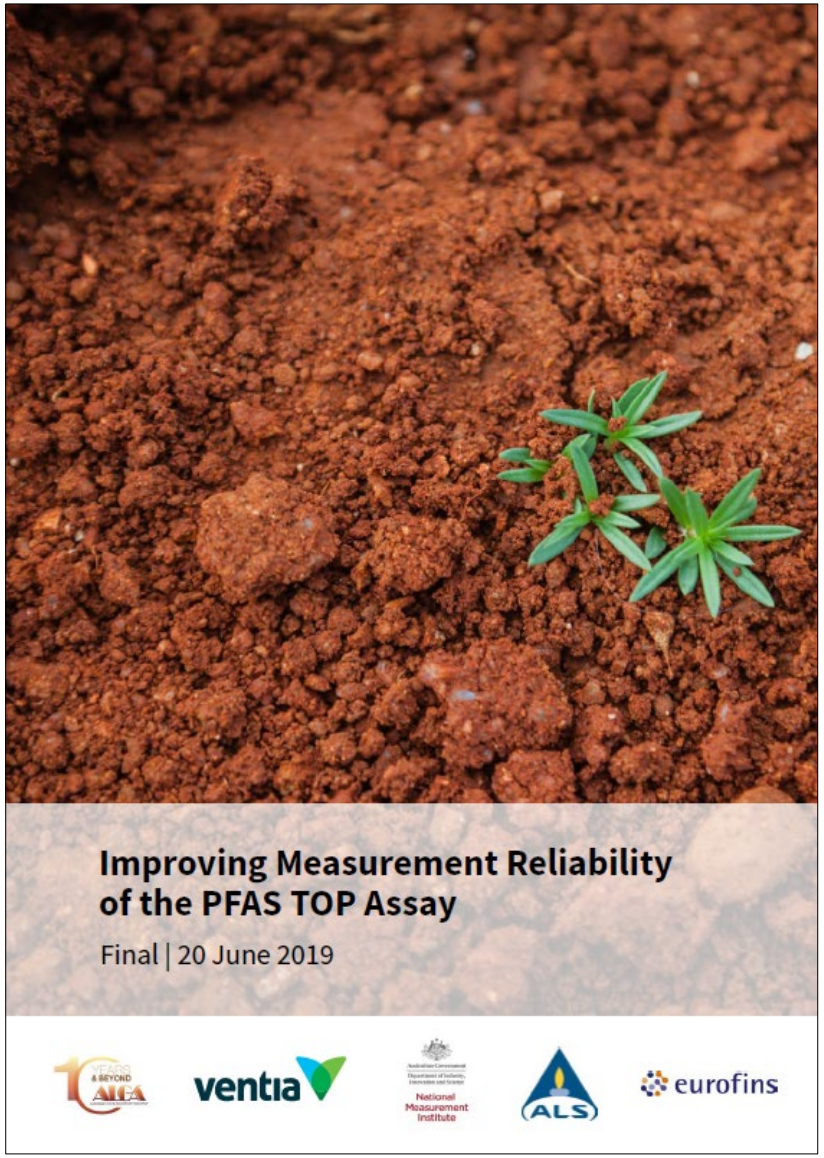


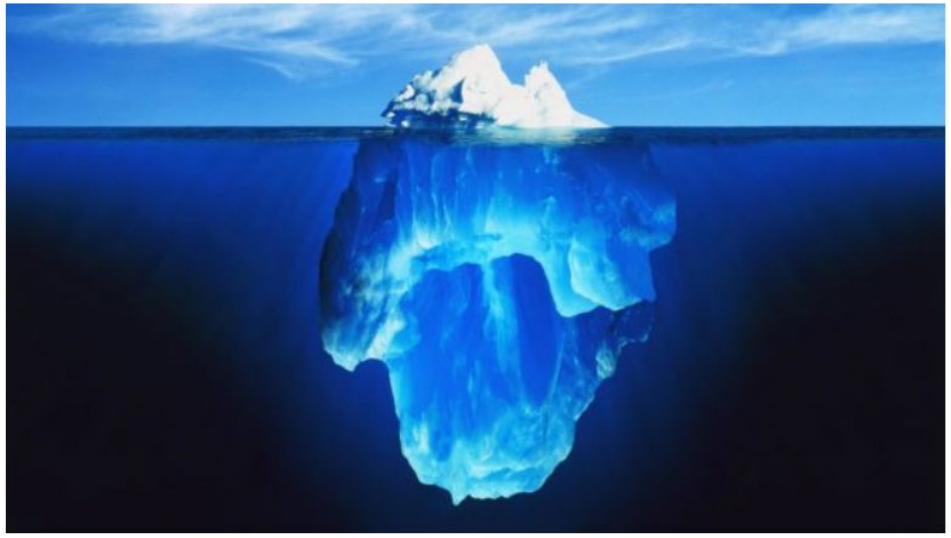
Summary

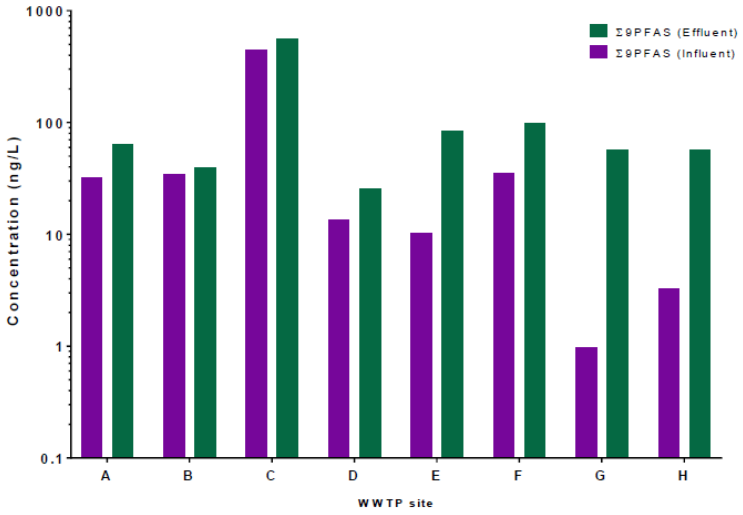
- Why is there an issue with precursors?
- Why was there a need for this project?
- Implications - Informing Regulation/Guidance
- Implications for site investigations

Improving Measurement Reliability of the PFAS TOP Assay

Why is there a problem?

- Over 4700 PFAS identified (OECD 2018)
- ~90% may be precursors
- Standard USEPA method covers 14 PFAS





WWTP PFAS levels higher in effluent compared to influent (Gallen *et al.* 2018)

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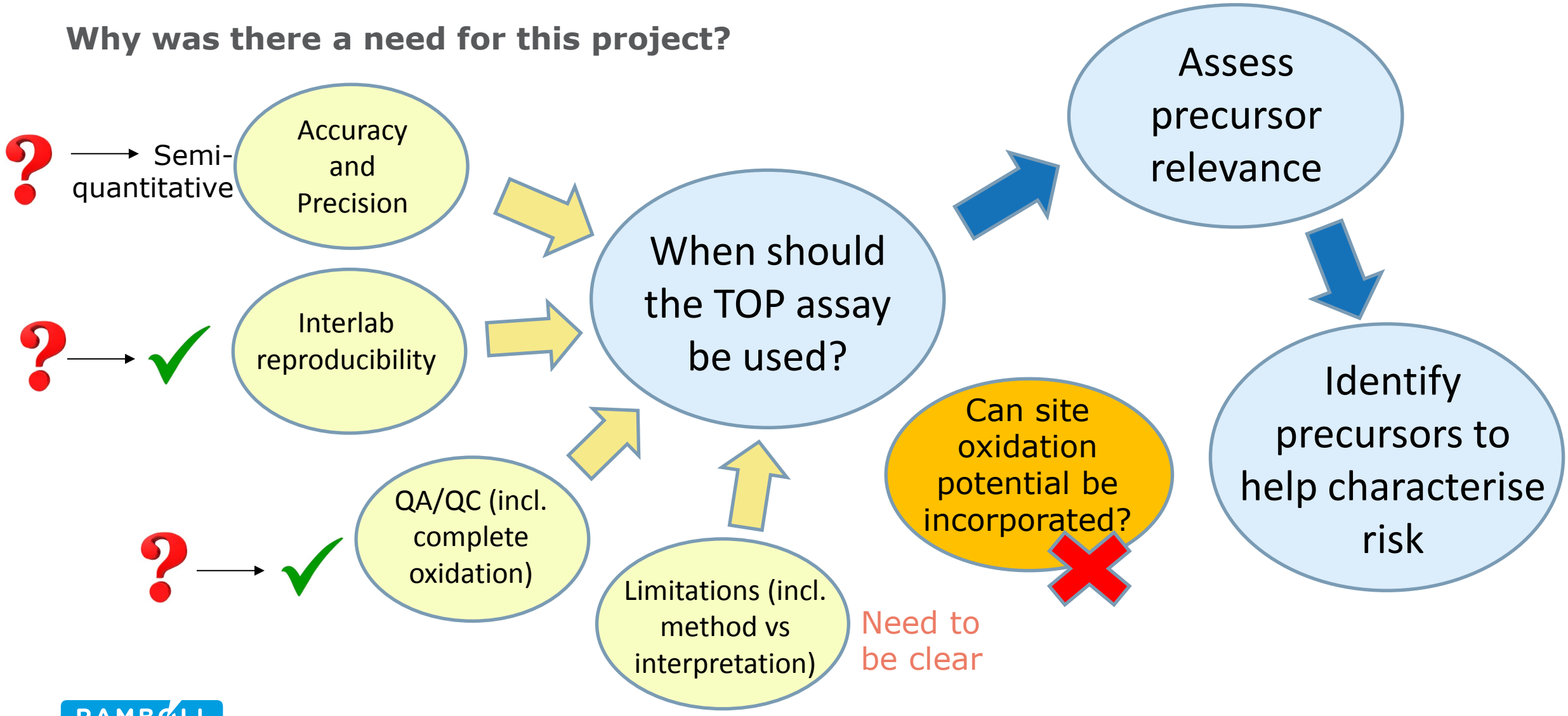
Why was there a need for this project?



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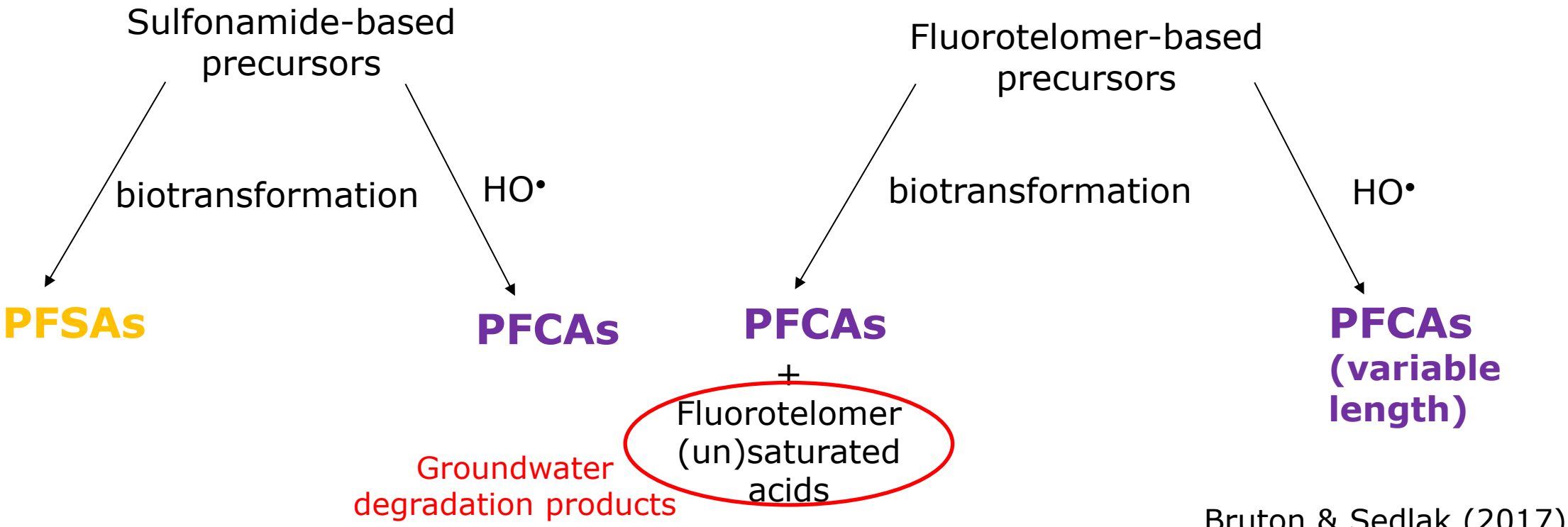
Can site oxidation potential be incorporated? ✗

Biotransformation ≠ TOP assay oxidation



Bruton & Sedlak (2017)

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QA Guidance I -

…validation of the method's oxidation using detectable oxidisable precursors (e.g. labelled internal standards)…

- Not straightforward in practice due to limited available standards.
- Commercially available labelled standards –
  - will oxidise to unlabelled native PFCAs, thereby positively interfering with target analytes.
  - could oxidise to interfere with labelled internal standards or surrogates used for quality assurance.

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QA Guidance II -

[Total PFAS] post-TOPA should be ≥ [total PFAS] pre-TOPA…

- This is dependent on what PFAA precursors are present and in what proportions -
  - During conversion to PFAAs, some mass is typically lost:
    - PFAS compounds can be degraded to <C4
    - <C4 PFAS will be unaccounted for by standard LC-MSMS analysis.

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QA Guidance III -

[Sum PFCAs post-TOPA] should be ≥ [Sum PFCAs pre-TOPA]

- Signifies any precursors being converted to PFCA products

- A more appropriate measure than the preceding criterion.
- 'Equal' is defined as within normal analytical variability.

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QA Guidance IV -

[Sum PFSAs post-TOPA] should approximate [Sum PFSAs pre-TOPA]

– Signifies that precursors do not convert to PFSA products

- This assumes no PFSAs will be produced from precursors, which is not always the case -
  - For example, fabric treatments based on acrylic polymers with perfluoroalkyl sulfonamide side branches attached.
  - Therefore ≥ criterion specified for PFCAs also applicable for PFSAs.

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QA Guidance V -

…where near complete oxidation is acceptable, minimal PFAA precursors are detectable post oxidation…

- ***for aqueous samples, [Sum PFAA precursors] ÷ [Sum Total PFAS] < 5%***
- ***for soil samples, [Sum PFAA precursors] ÷ [Sum Total PFAS] < 10%***

- Valuable measures of assay efficacy.
- Using [Sum Total PFAS] could mask poor performance of the assay and is dependent on the PFAS analytes reported by a particular laboratory.
- Changing [Sum Total PFAS] to **[Sum Total PFAAs]** recommended, representing a more relevant and consistent approach across laboratories.
- Laboratories only report a selection of PFAA precursors in their analytical suit
  - A more appropriate designation is **[Sum <u>measured</u> PFAA precursors]**

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QA Guidance V -

…where near complete oxidation is acceptable, minimal PFAA precursors are detectable post oxidation…

Suggested changes to wording:

- ***for aqueous samples, [Sum measured PFAA precursors] ÷ [Sum Total PFAAs] < 5%***
- ***for soil samples, [Sum measured PFAA precursors] ÷ [Sum Total PFAAs] < 10%***

(greater leniency may be applied for samples where PFAS detected ≤ 10 times LOR)

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Implications for investigations -

- TOP assay has limitations but can be a useful tool for investigations.
- Laboratories need to report on QA/QC based on appropriate guidance.
- Review QA/QC data to ensure results are fit-for-purpose.
- TOP assay is not simple and straightforward -
  - Multiple oxidations and/or dilutions may be required.
  - LORs and turn around times may be impacted.
- TOP assay results have greater uncertainty than conventional PFAS analyses.
- Useful as a semi-quantitative indication - much better than an order of magnitude variability.
- Application of TOP assay to guidelines/regulation?
  - Needs to be risk-based.

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THANK YOU