Analytical Method for Quantifying Legacy & Emerging PFAS in Aqueous and Solid Matrices

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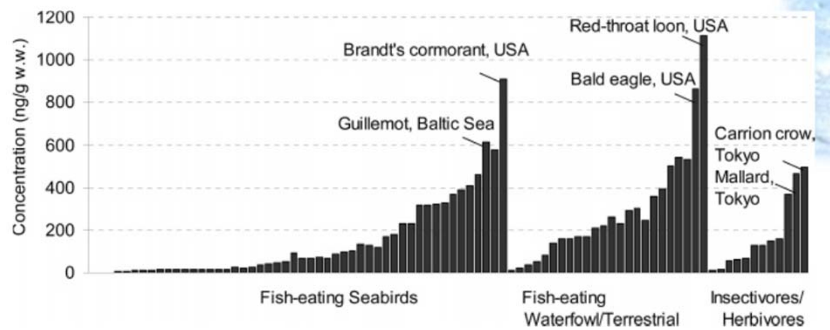
1950s Incorporation of PFAS into wide variety of consumer and industrial products

2001 Accumulation of PFOS in most humans, animals and environmental media
(Giesy, 2001; Kannan, 2001; Houde,2006)

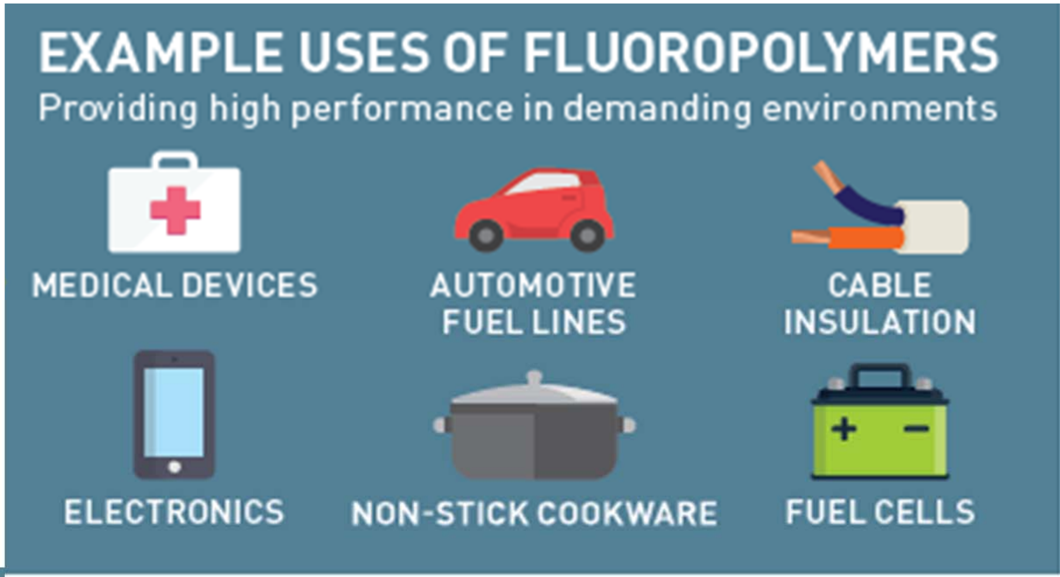


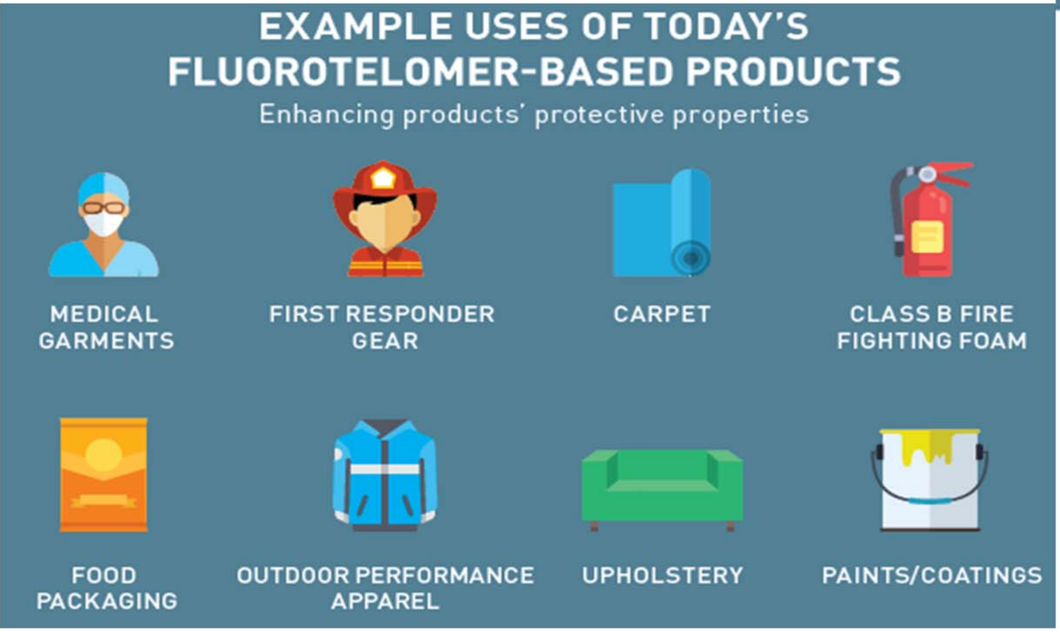
2002 Voluntary phase out of PFOS in the USA

2006 USEPA engaged 8 leading PFAS manufacturers 2010/2015 PFOA Stewardship Program

"…..fluorotechnology is essential technology for many aspects of modern life….."

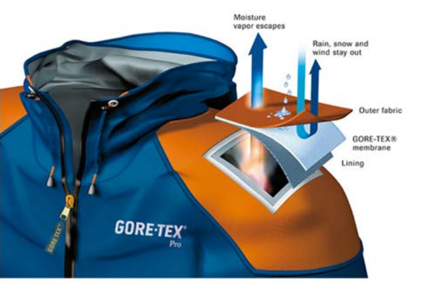
Bowman, 2015





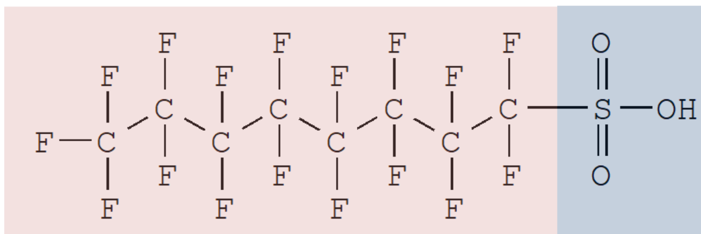
"…..we call on the international community to cooperate in limiting the production and use of PFASs and in developing safer nonfluorinated alternatives."

Blum et al., 2015

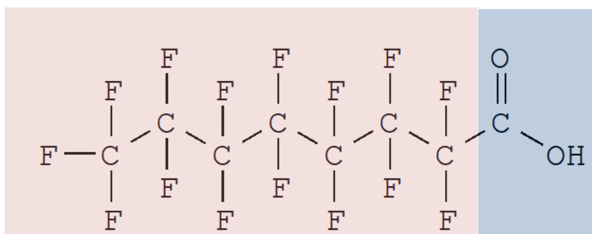


C8 Chemistries

PFOS



PFOA



Properties

- Persistent (UNEP, 2009)
- Mobile (Munoz et al., 2015)
- Bioaccumulative (Conder et al., 2008)
- Toxic (IARC Class 2B Probable Carcinogen)

UNEP Stockholm Convention

- PFOS in 2009
- PFOA under consideration

<u>Replaced with family with varying fluorinated chain length:</u>

- Perfluoroalkylsulfonates (C2-12; PFSA)
- Perfluoroalkylcarboxylic Acids (C4-C22; PFCA)

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Sources of PFAS to the Environment

Point Source

Industry

Defense

Airports

Other Sources

Domestic Environment

WWTPs

Landfill

Potential Contaminated Sites in Australia

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Australian Government
Department of Defence

PFAS Investigation & Management Program
Investigation Process

Queensland
- Army Aviation Centre Oakey
- RAAF Base Townsville
- RAAF Base Amberley
- Lavarack Barracks

Western Australia
- RAAF Base Pearce
- HMAS Stirling
- Naval Communication Station Harold E Holt A & B
- RAAF Base Learmonth
- Gingin Satellite Airfield

New South Wales
- RAAF Base Williamtown
- HMAS Albatross
- RAAF Base Richmond
- RAAF Base Wagga
- Holsworthy Barracks

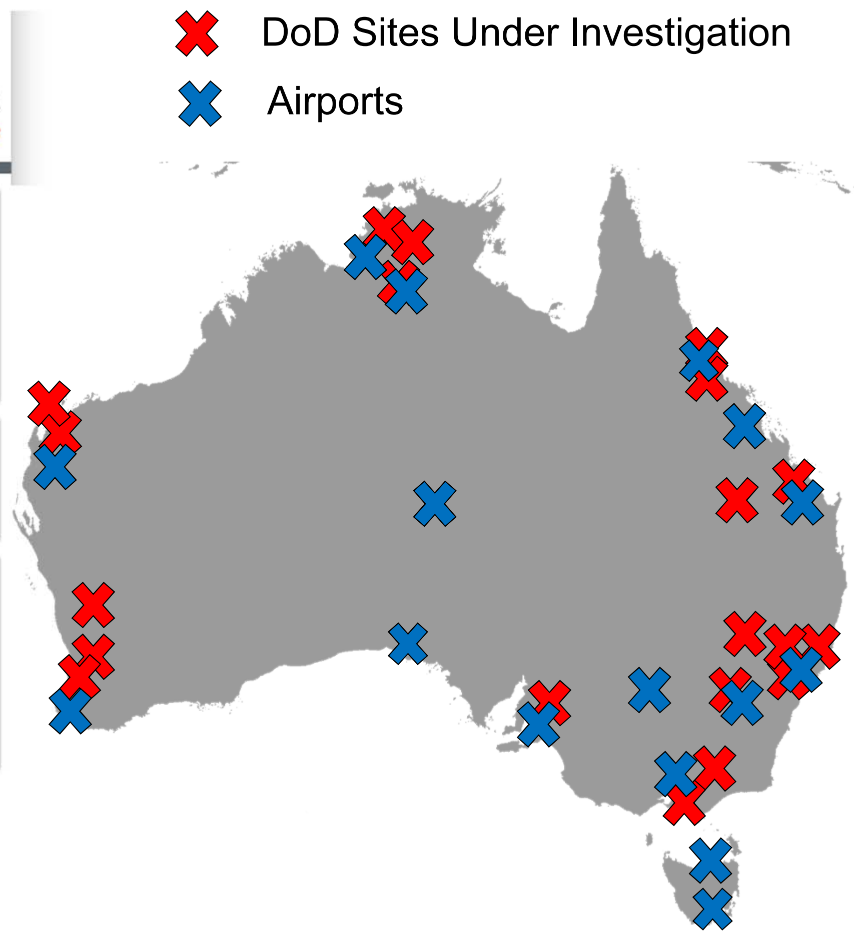
Tasmania
No current PFAS Investigations

South Australia
- RAAF Base Edinburgh

Victoria
- RAAF Base East Sale
- HMAS Cerberus
- Bandiana Military Area

Jervis Bay Territory
- Jervis Bay Range Facility

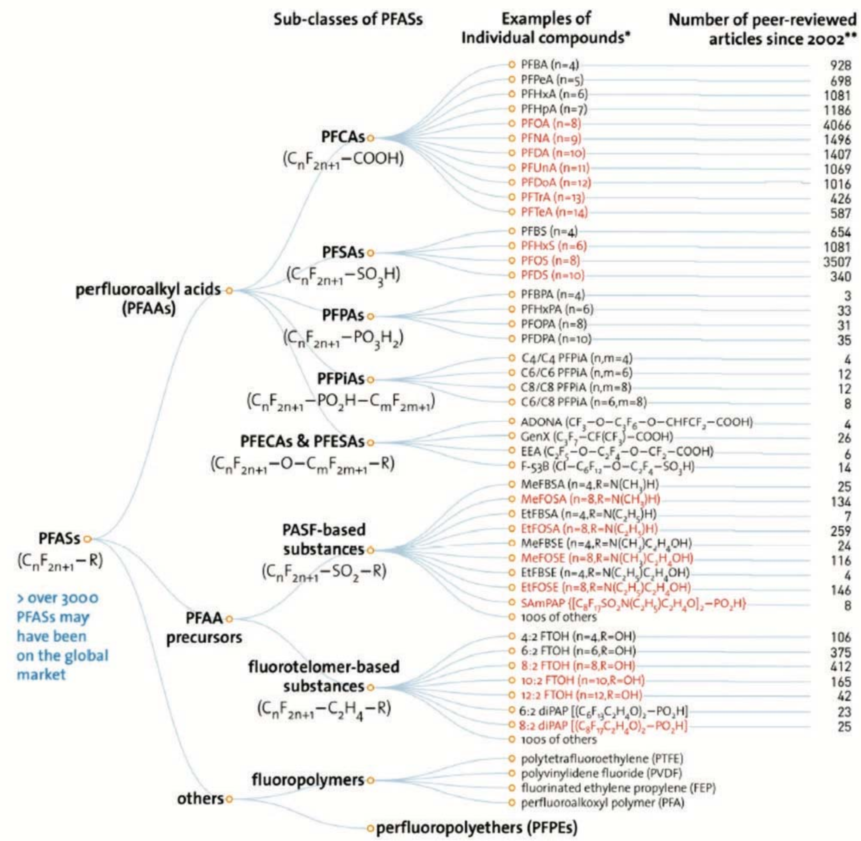
Northern Territory
- RAAF Base Darwin
- RAAF Base Tindal
- Robertson Barracks



PFAS Terminology

Common Acronyms

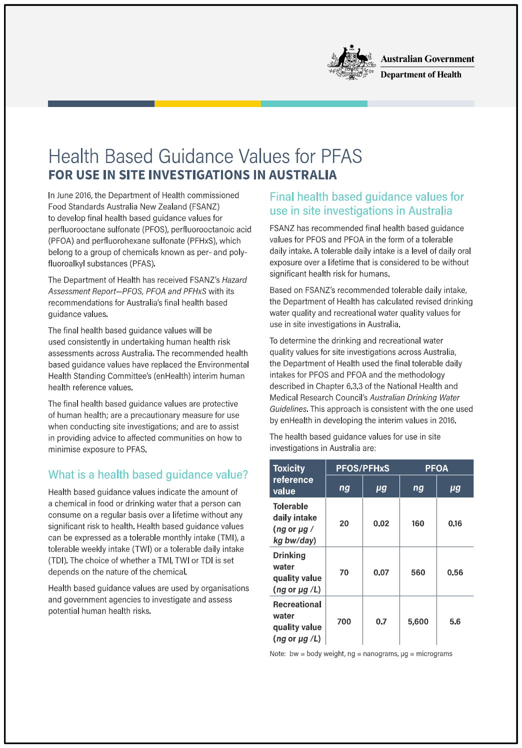
PFCA	Perfluoroalkylcarboxylic acid
PFOA	Perfluorooctanecarboxylic acid
PFAS	Perfluoroalkylsulfonate
PFOS	Perfluorooctanesulfonate
PFASi	Perfluoroalkylsulfinate
FOSA	Perfluorooctanesulfonamide
FOSAA	Perfluorooctanesulfonamidoacetic acid
FOSE	Perfluorooctanesulfonamidoethanol
FTOH	Fluorinated telomer alcohol (-OH functional group)
FTA	Fluorinated telomer acid
FTUA	Fluorinated telomer unsaturated acid
FTS	Fluorinated telomer sulfonate
PFAPA	Perfluoroalkylphosphonic acid
PFPi	Perfluoroalkylphosphinate
PAP	Mono-substituted polyfluoroalkylphosphate ester
diPAP	Di-substituted polyfluoroalkylphosphate ester
PFAI	Perfluoroalkyl iodide
SFA	Semifluorinated alkane
FTI	Fluorinated telomer iodide
FTO	Fluorinated telomer olefin
FTAC	Fluorinated telomer acrylate



Wang, Z *et al.* (2017). *Environ. Sci. Technol.* 51, 2508-2518.

Drinking Water Investigation Levels

Australia



Australian Government
Department of Health

Health Based Guidance Values for PFAS
FOR USE IN SITE INVESTIGATIONS IN AUSTRALIA

In June 2016, the Department of Health commissioned Food Standards Australia New Zealand (FSANZ) to develop final health based guidance values for perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonate (PFHxS), which belong to a group of chemicals known as per- and poly-fluoroalkyl substances (PFAS).

The Department of Health has received FSANZ's *Hazard Assessment Report—PFOS, PFOA and PFHxS* with its recommendations for Australia's final health based guidance values.

The final health based guidance values will be used consistently in undertaking human health risk assessments across Australia. The recommended health based guidance values have replaced the Environmental Health Standing Committee's (enHealth) interim human health reference values.

The final health based guidance values are protective of human health; are a precautionary measure for use when conducting site investigations; and are to assist in providing advice to affected communities on how to minimise exposure to PFAS.

What is a health based guidance value?

Health based guidance values indicate the amount of a chemical in food or drinking water that a person can consume on a regular basis over a lifetime without any significant risk to health. Health based guidance values can be expressed as a tolerable monthly intake (TMI), a tolerable weekly intake (TWI) or a tolerable daily intake (TDI). The choice of whether a TMI, TWI or TDI is set depends on the nature of the chemical.

Health based guidance values are used by organisations and government agencies to investigate and assess potential human health risks.

Final health based guidance values for use in site investigations in Australia

FSANZ has recommended final health based guidance values for PFOS and PFOA in the form of a tolerable daily intake. A tolerable daily intake is a level of daily oral exposure over a lifetime that is considered to be without significant health risk for humans.

Based on FSANZ's recommended tolerable daily intake, the Department of Health has calculated revised drinking water quality and recreational water quality values for use in site investigations in Australia.

To determine the drinking and recreational water quality values for site investigations across Australia, the Department of Health used the final tolerable daily intakes for PFOS and PFOA and the methodology described in Chapter 6.3.3 of the National Health and Medical Research Council's *Australian Drinking Water Guidelines*. This approach is consistent with the one used by enHealth in developing the interim values in 2016.

The health based guidance values for use in site investigations in Australia are:

Toxicity reference value	PFOS/PFHxS		PFOA	
	ng	*μg*	*ng*	*μg*
Tolerable daily intake (*ng* or *μg* / *kg bw/day*)	20	0.02	160	0.16
Drinking water quality value (*ng* or *μg* /L)	70	0.07	560	0.56
Recreational water quality value (*ng* or *μg* /L)	700	0.7	5,600	5.6

Note: bw = body weight, ng = nanograms, μg = micrograms

Toxicity reference value	PFOS/PFHxS		PFOA	
	ng	*μg*	*ng*	*μg*
Tolerable daily intake (*ng* or *μg* / *kg bw/day*)	20	0.02	160	0.16
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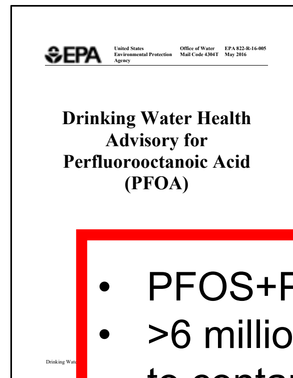
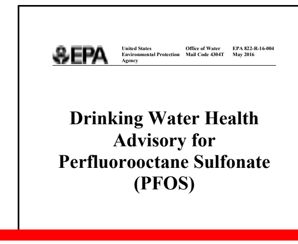
Note: bw = body weight, ng = nanograms, μg = micrograms

- 49% of Australian drinking water samples (n=34) contained PFAS
- None over investigation level (Thompson, 2011)

USA



Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)



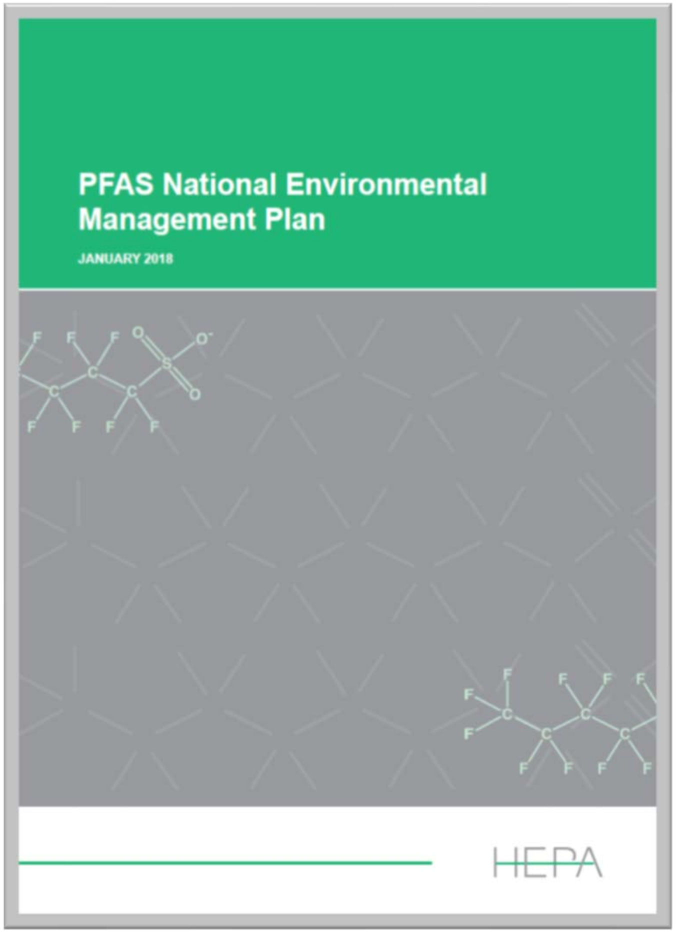
Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)

- PFOS+PFOA = 70 ng/L
- >6 million US citizens exposed to contaminated PFAS drinking water (Hu, 2016)

Methodology

$$[PFAS] = TDI \times BW \times RSC\ (10\%) \times Rate\ (2L)$$

Municipal Wastewater



Exposure scenario	PFOS	PFOA	Exposure scenario	Comments and source
Freshwater	0.00023 µg/L	19 µg/L	99% species protection – high conservation value systems	Australian and New Zealand Guidelines for Fresh and Marine Water Quality – technical draft default guideline values.
	0.13 µg/L	220 µg/L	95% species protection – slightly to moderately disturbed systems	Note 1: The 99% species protection level for PFOS is close to the level of detection. Agencies may wish to apply a 'detect' threshold in such circumstances rather than a quantified measurement.
	2 µg/L	632 µg/L	90% species protection – highly disturbed systems	Note 2: The draft guidelines do not account for effects which result from the biomagnification of toxicants in air-breathing animals or in animals which prey on aquatic organisms.
	31 µg/L	1824 µg/L	80% species protection – highly disturbed systems	Note 3: The WQG advise that the 99% level of protection be used for ...slightly to moderately disturbed systems'. This approach is generally adopted for chemicals that bioaccumulate and biomagnify in wildlife.

Environmental Discharge

Water Recycling Programs

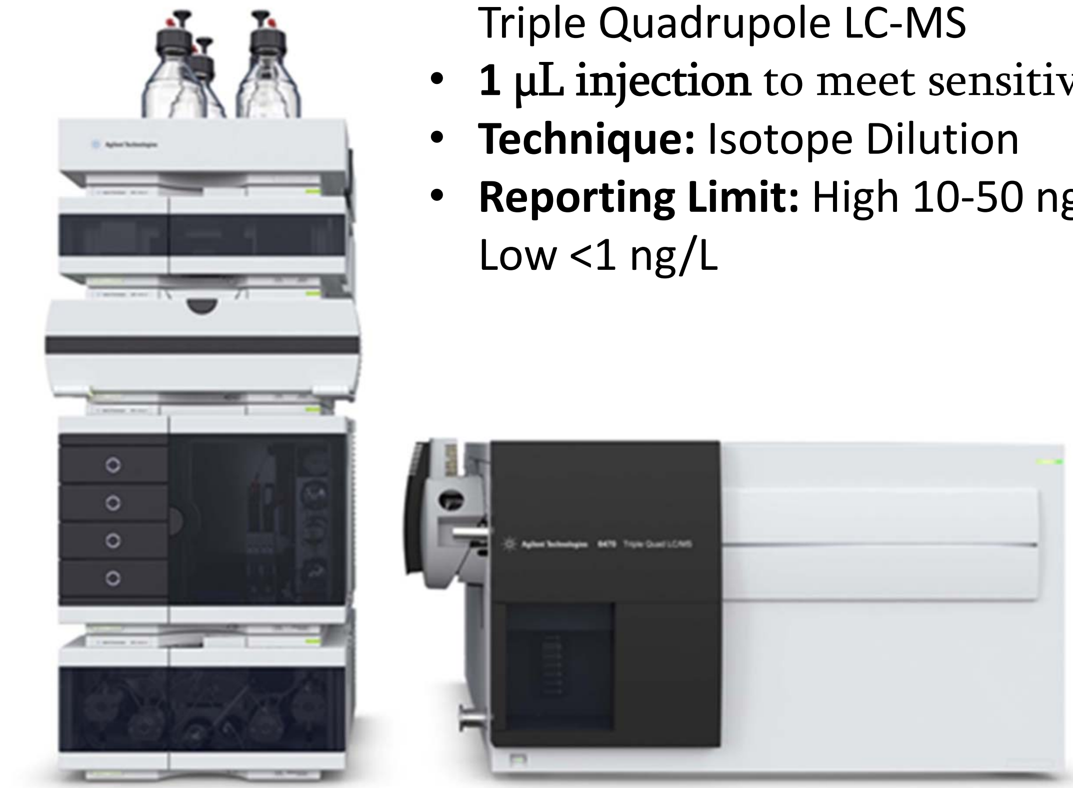
LCMS Analytical Methodology

Standard Methods
- US EPA Method 537.1
- ISO 25101
- ASTM D7968
- ASTM D7979

Total PFAS
- Total Oxidisable Precursor Assay (TOPA)
- Total Organic Fluorine (TOF)

QA/QC: Batch of 9 samples includes matrix spike, laboratory control sample (LCS) & blank

- **Quantification:** Agilent 6495 LC Triple Quadrupole LC-MS
- **1 μL injection** to meet sensitivity
- **Technique:** Isotope Dilution
- **Reporting Limit:** High 10-50 ng/L; Low <1 ng/L



Extraction Techniques

Solid Phase Extraction (SPE)

- **Sample collection:** 250 mL polypropylene bottle
- **Filtration:** 1 µm glass fibre filter
- **Surrogate spike:** 5 ng isotopically labelled PFAS
- **SPE:** 6 cc, 30 µm particle size, 150 mg weak anion exchange resin (WAX)
- **Elution:** 2 mL methanol, 4 mL methanol (0.1% NH_4OH)
- **Evaporation:** Evaporated to dry under gentle stream of N_2, reconstituted to 500-1000uL of MeOH

Solids Extraction

- **Sample collection:** 250 mL polypropylene bottle or 50 mL polypropylene centrifuge tube
- **Preparation:** Sterilise with 2% w/w sodium azide solution, freeze-dry, powderise
- **Surrogate spike:** 25 ng isotopically labelled PFAS
- **Extraction:** 0.5-1 basic MeOH (10 mM NaOH) neutralised after exrtraction with glacial acetic acid.
- **Clean-Up:** dSPE with 100 mg C18 and 50 mg PSA
- **Filter:** 0.45 µm PES syringe filter

QA/QC: Batch of 9 samples includes matrix spike, laboratory control sample (LCS) & blank

IDLs for a consolidated PFAS method on 6495

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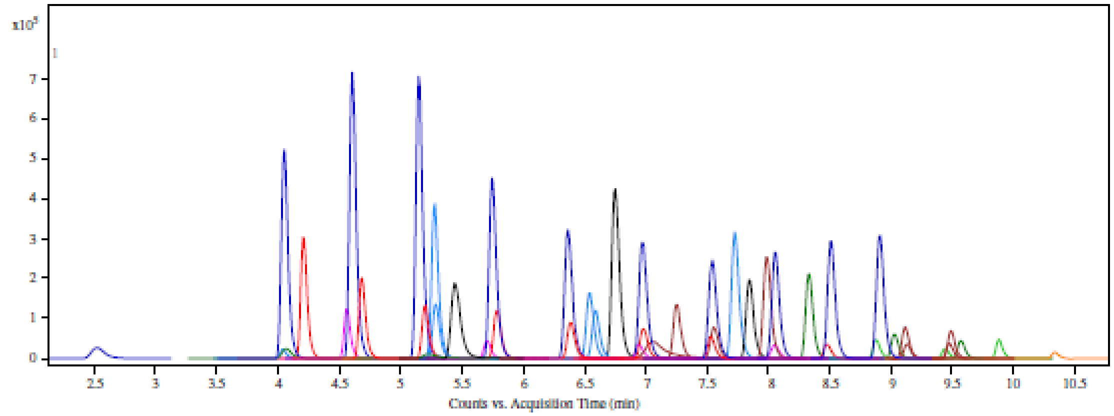
A single analytical method for the determination of 53 legacy and emerging per- and polyfluoroalkyl..

Table 3 Instrument detection limits (IDLs)

Compound	IDL (fg on-column)	Compound	IDL (fg on-column)
PFBA	3.1	PFBS	2.5
PFPeA	4.6	PFPeS	3.9
PFHxA	2.9	PFHxS	2.7
PFHpA	3.8	PFHpS	3.6
PFOA	6.4	PFOS	3.1
PFNA	5.5	PFNS	17
PFDA	12	PFDS	8.8
PFUnA	5.4	PFDoS	14
PFDoA	25	6:2 Cl-PFESA	7.9
PFTrA	23	8:2 Cl-PFESA	9.2
PFTeA	26	4:2 FTS	4.1
ADONA	3.1	6:2 FTS	4.2
6:2 FTCA	436	8:2 FTS	16
8:2 FTCA	469	10:2 FTS	21
10:2 FTCA	320	FOSA	7.2
6:2 FTUCA	46	MeFOSA	11
8:2 FTUCA	59	EtFOSA	20
10:2 FTUCA	40	FOSAA	15
3:3 FTCA	33	MeFOSAA	8.2
5:3 FTCA	18	EtFOSAA	9
7:3 FTCA	72	MeFOSE	73
PFHxPA	19	EtFOSE	28
PFOPA	115	6:6 PFPiA	14
PFDPA	311	6:8 PFPiA	41
6:2 diPAP	18	8:8 PFPiA	23
6:2/8:2 diPAP	12	diSAmPAP	7.7
8:2 diPAP	17		

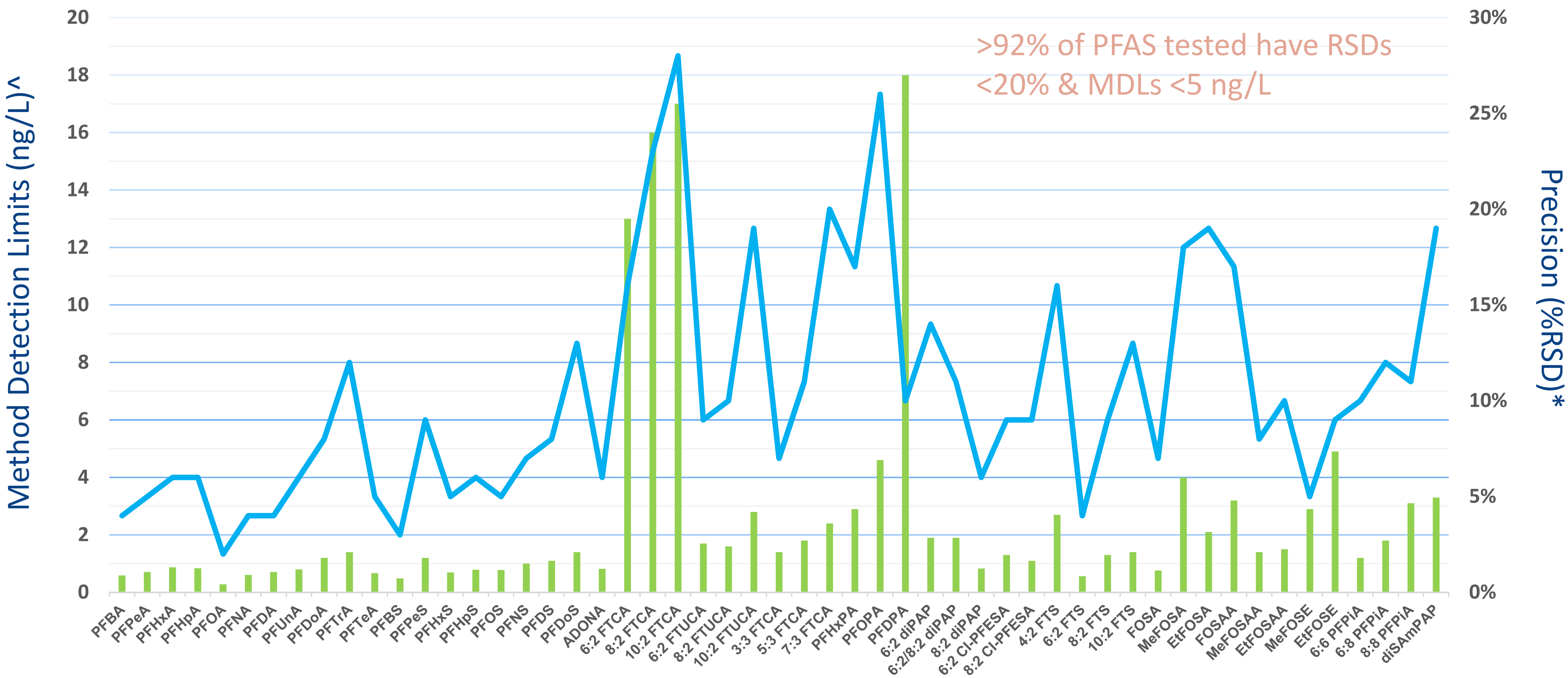
IDL was calculated using replicate injections ($n = 10$) of 10 fg/μL, 25 fg/μL, 50 fg/μL, 250 fg/μL, 500 fg/μL, or 900 fg/μL. Intra- and inter-day variability was assessed using repeat injections of a 5 ng/mL standard in methanol over 1 day and on repeat over three consecutive days, and results are contained in Electronic Supplementary Material, ESM



14 different classes of PFAS including PFCAs (drak blue); PFSAs (red); n:2 FTSs (pink); n:2 FTCA , n:3 FTCA, n:2 FTUCA (light blue); PFECA & Cl-PFESA (black); FASA, FASAA, FOSE (maroon); PFPA, diPAP & PFPiA (green); diSAmPAP (orange)

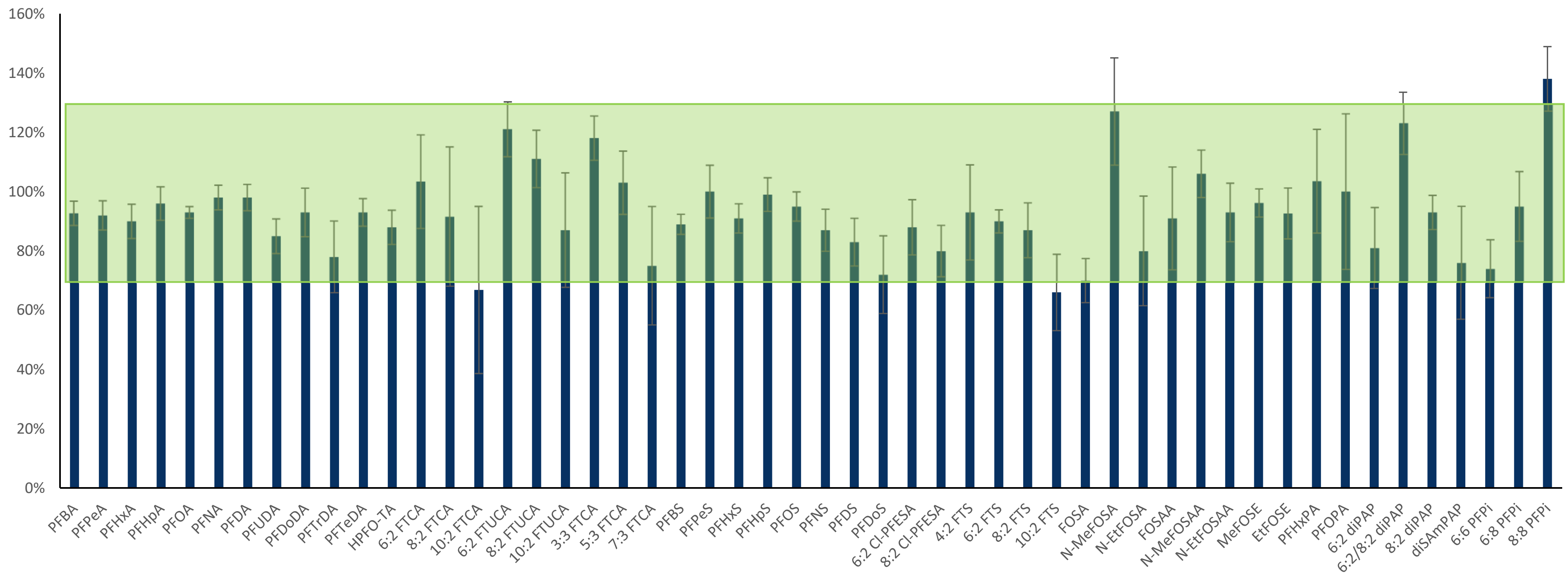
Coggan *et al.* (2019) Anal Bioanal Chem, 3507-3520

Analysis of >50 PFAS in Water
Method Performance (1 uL injection of extract)



** Seven replicates at 5 ng/L spiked into 250 mL water samples; followed by SPE and injection of 1 uL onto 6495 LC-MS/MS; ^ based on USEPA 40 CFR Part 136 Appendix B Revision 2*

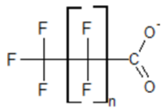
SPE Method accuracy – 5 ng/L spike* (n=7)



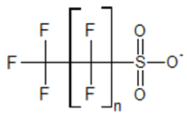
Accuracy:
49 of 52 between 70 – 130 %
*n:2 FTCAs and FOSEs spike 20 ng/L

MDL (US EPA 40 CFR part 136, rev 2):
Between 0.28 – 17 ng/L

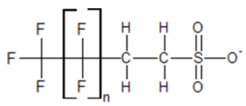
Target compounds



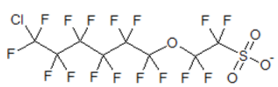
PFCAs



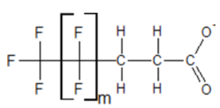
PFSAs



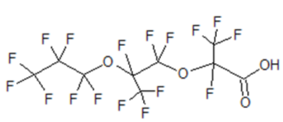
FTSs



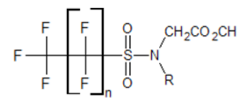
Cl-PFESAs



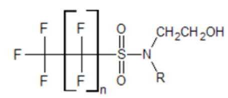
FTCAs/FTUCAs



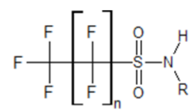
HPFO-TA



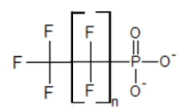
FASAAs



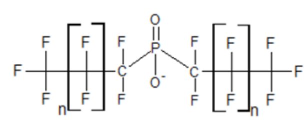
FASEs



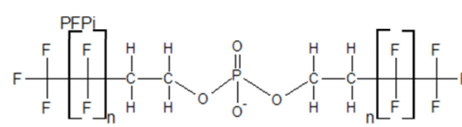
FASAs



PFPAs



PFPis



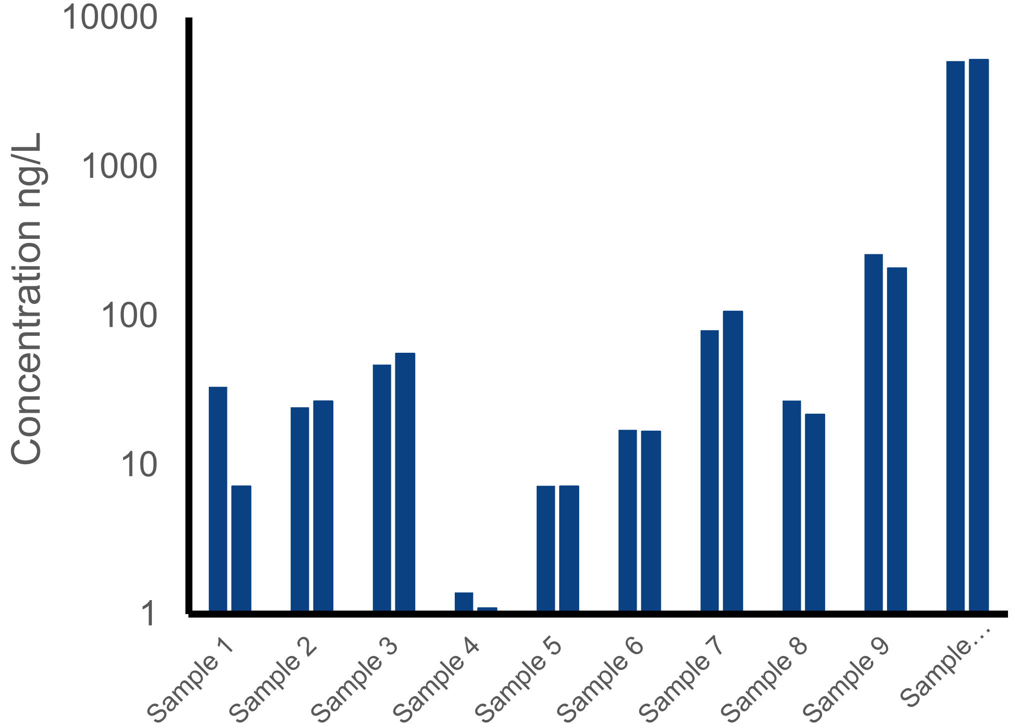
diPAPs & diSAmPAP

Coggan *et al.* (2019) Anal Bioanal Chem, 3507-3520

Method Validation - PFOS

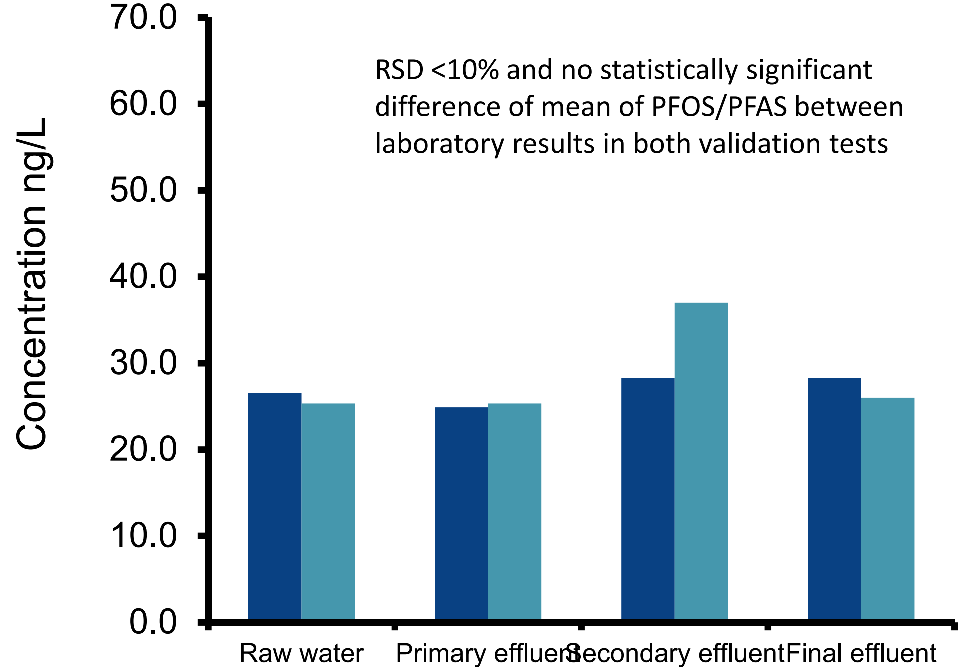
Groundwater

RMIT-Contract Lab 1



Wastewater

RMIT-Contract Lab 2



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Project Overview

(1) Analytical Method Development

- SPE Extraction for liquids
- Alkaline digestion for solids
- Validated with two external comparisons
- Quantifying 55-60 PFAS

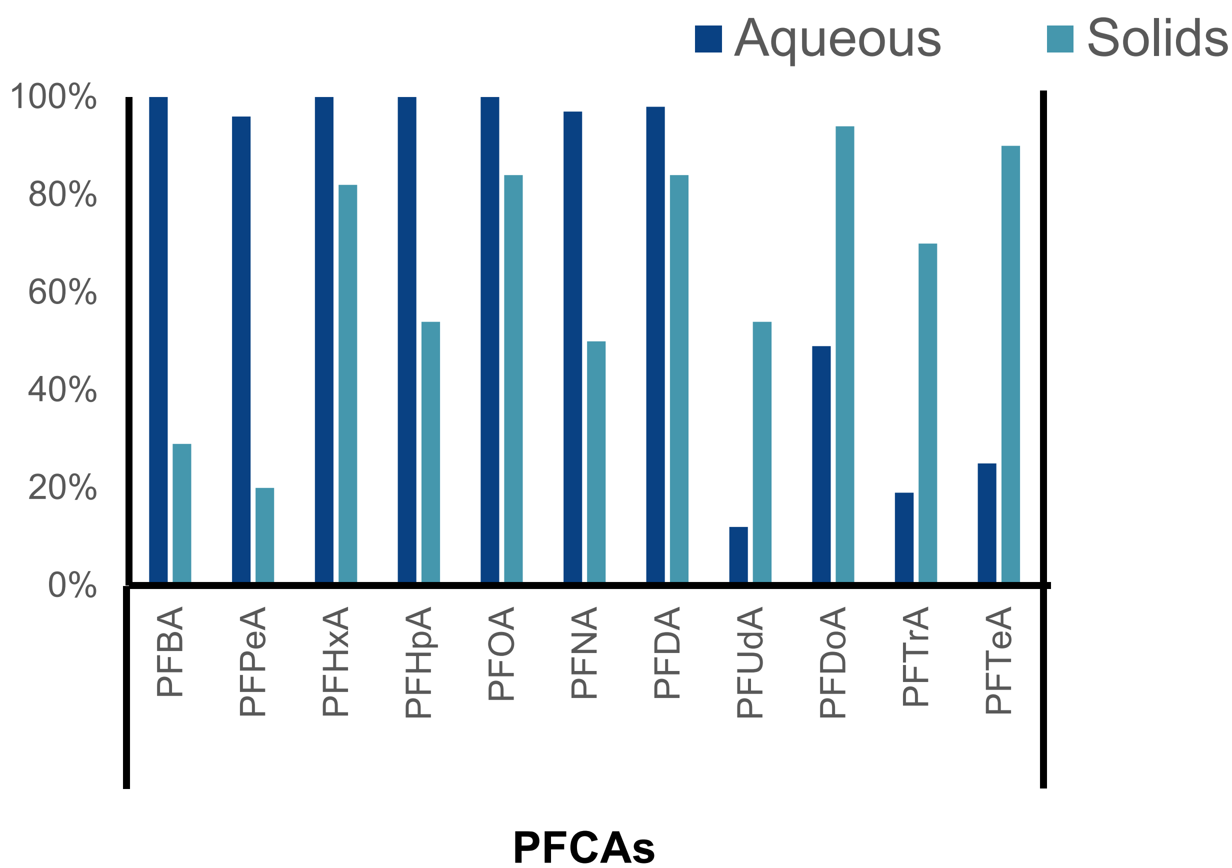
(2) PFAS Mass Flux at Australian WWTPs

- Mass balance studies at 19 WWTPs (22 PFAS)
- Mass balance studies at 5 WWTPs (55 PFAS)
- Untargeted analysis using Q-TOF
- Australian biosolids survey for PFAS

(3) Environmental and Ecological Impact

- Literature review of ecotoxicology report
- PFOS/PFOA/GenX fish update/depuration study with Australian fish
- Environmental fate in the marine environment from treatment

19 WWTP Frequency of Detection

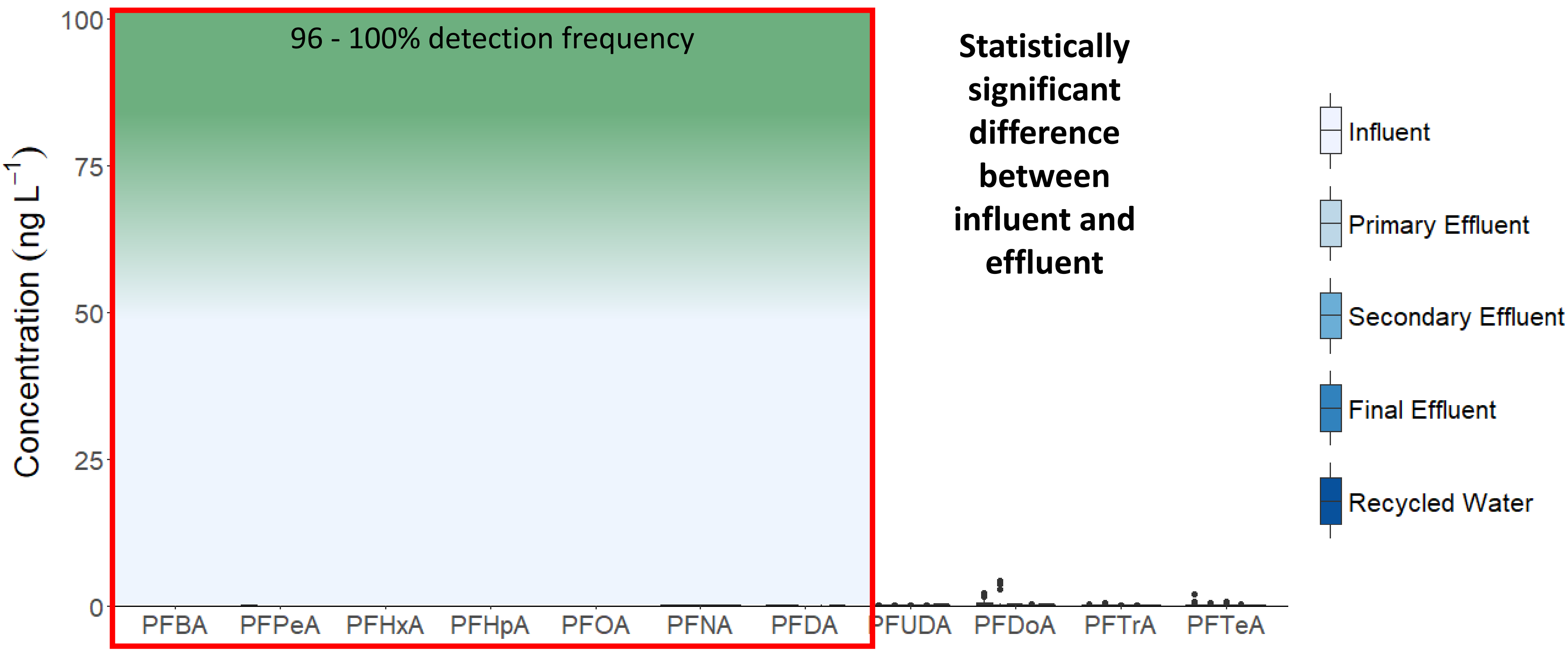


Coggan et al. *2019*

Σ_{18}PFAS Concentration in WWTPs

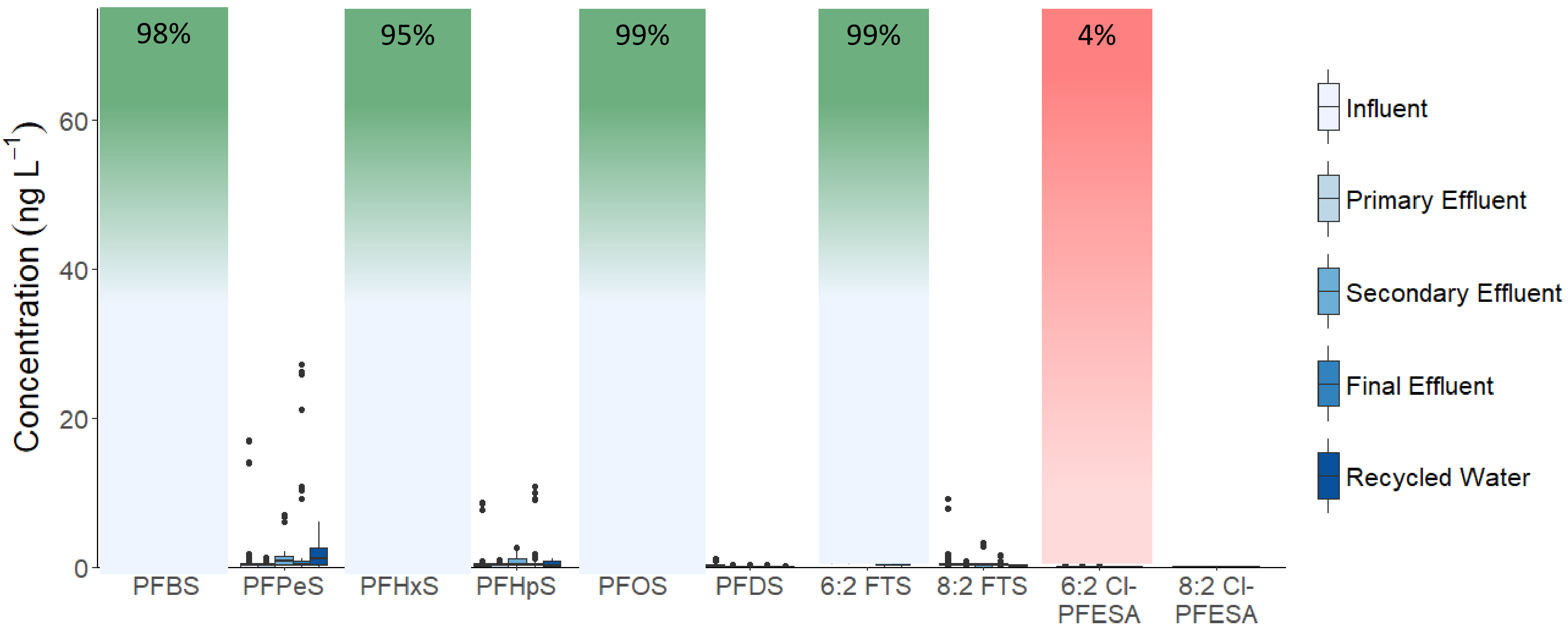
Coggan et al. *Under Review*

PFCAs: 19 WWTPs Aqueous Samples



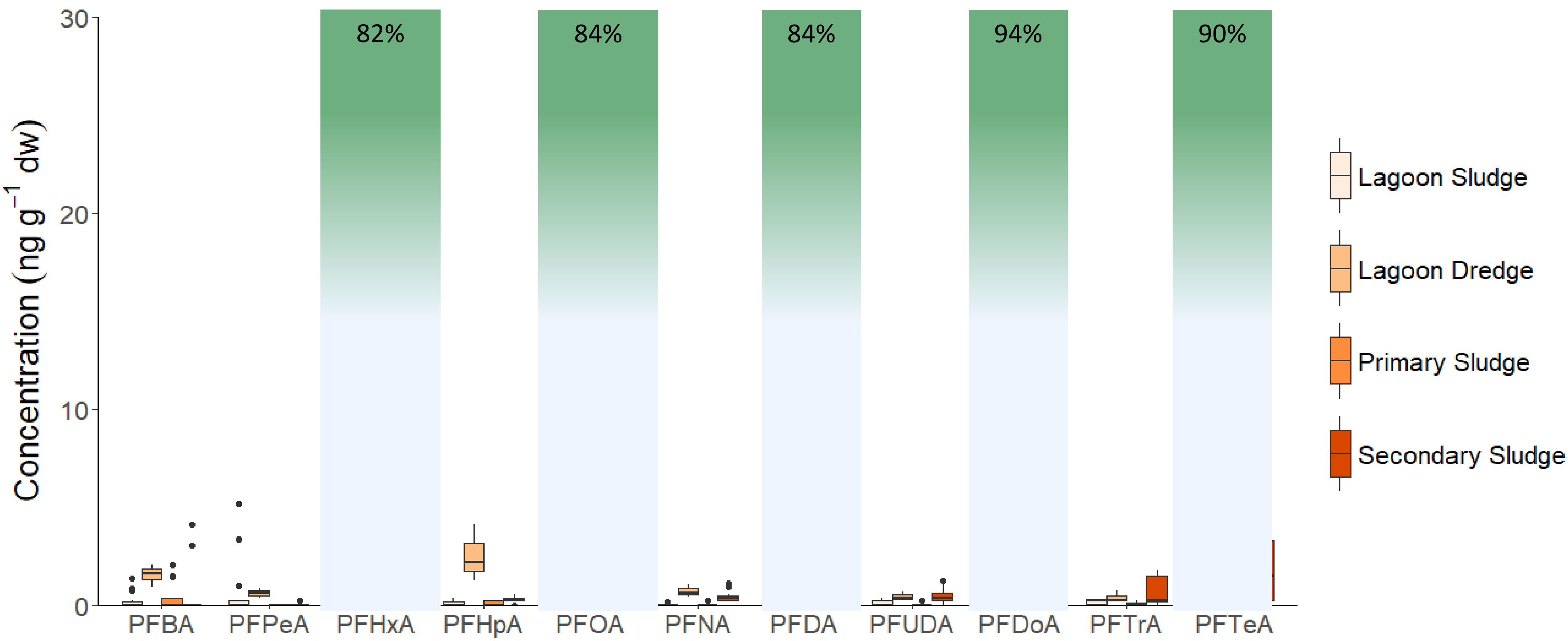
Coggan et al. *Under Review*

PFSAs: 19 WWTPs Aqueous Samples



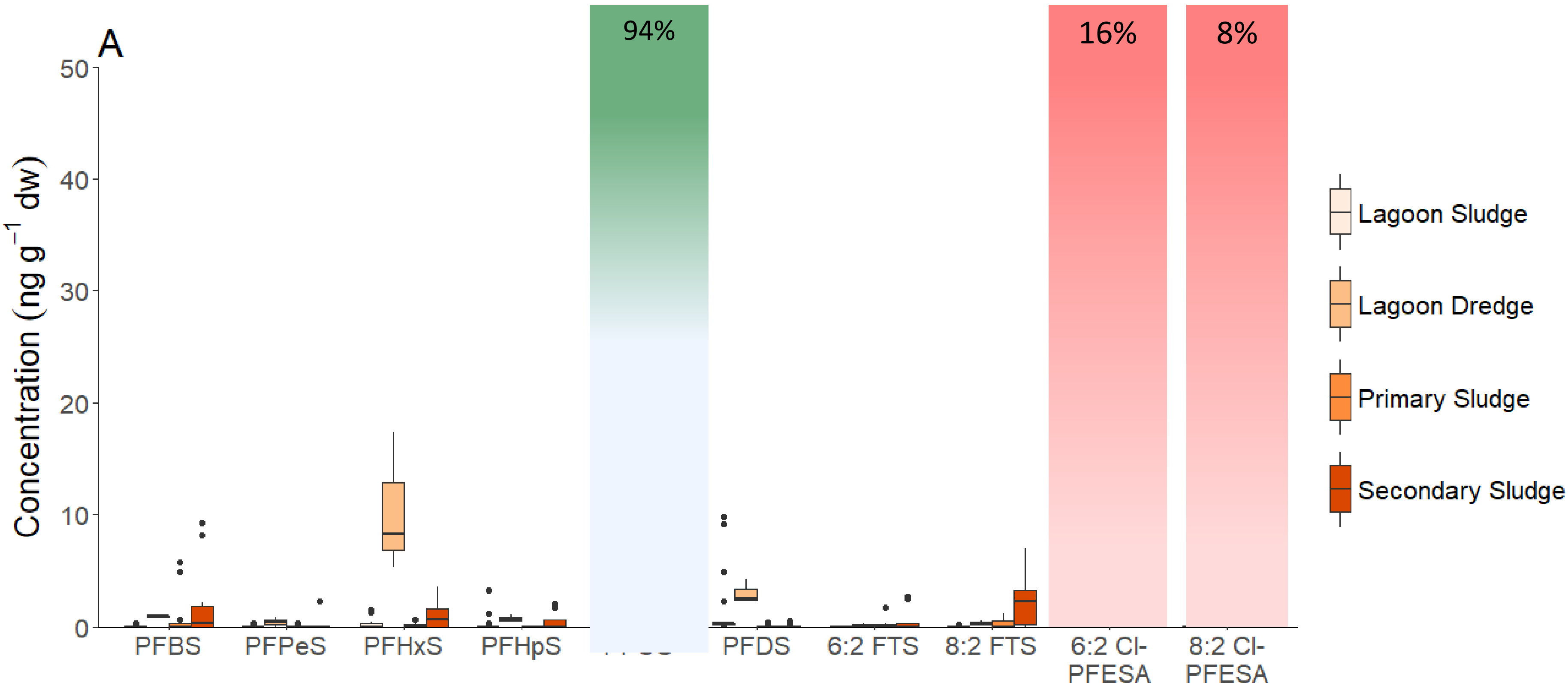
Coggan et al. *Under Review*

PFCAs: 19 WWTPs Solids Samples

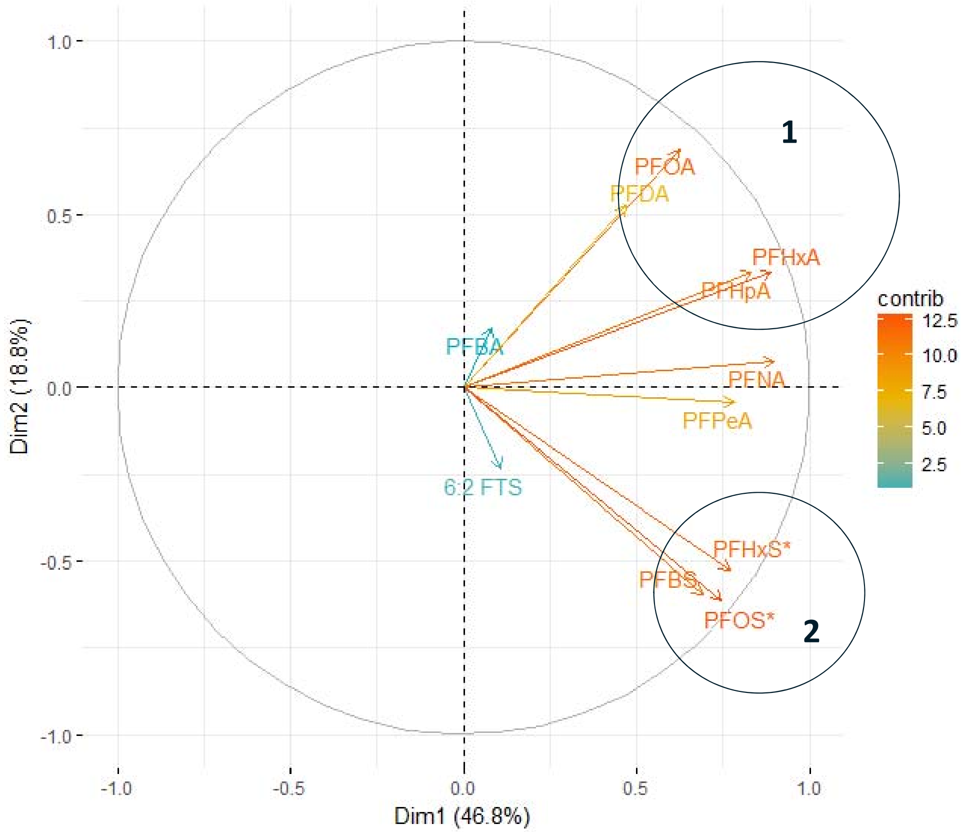


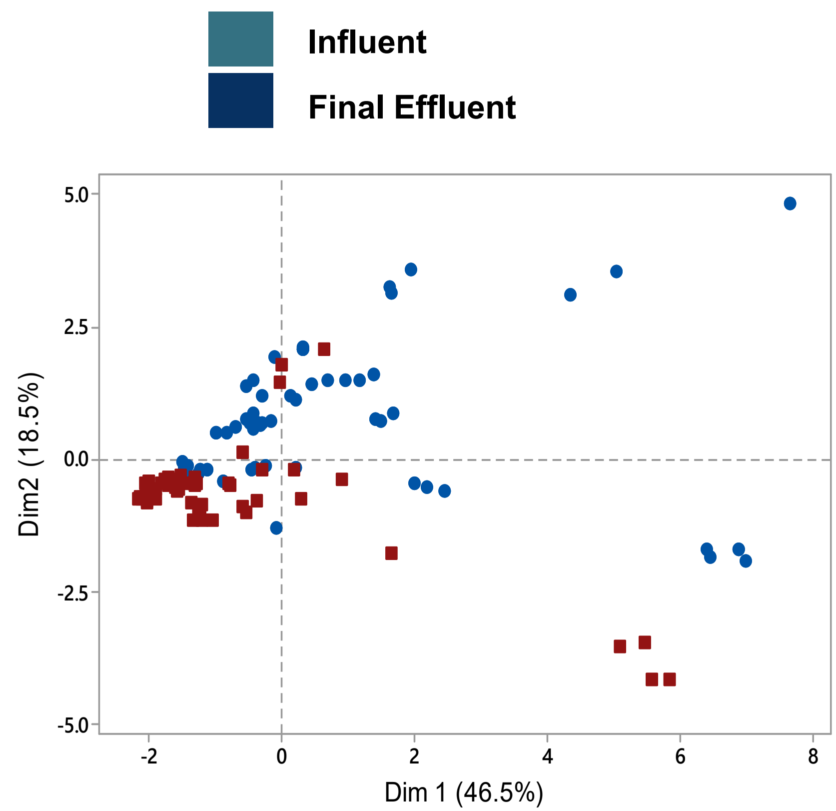
Coggan et al. *Under Review*

PFSAs: 19 WWTPs Solids Samples



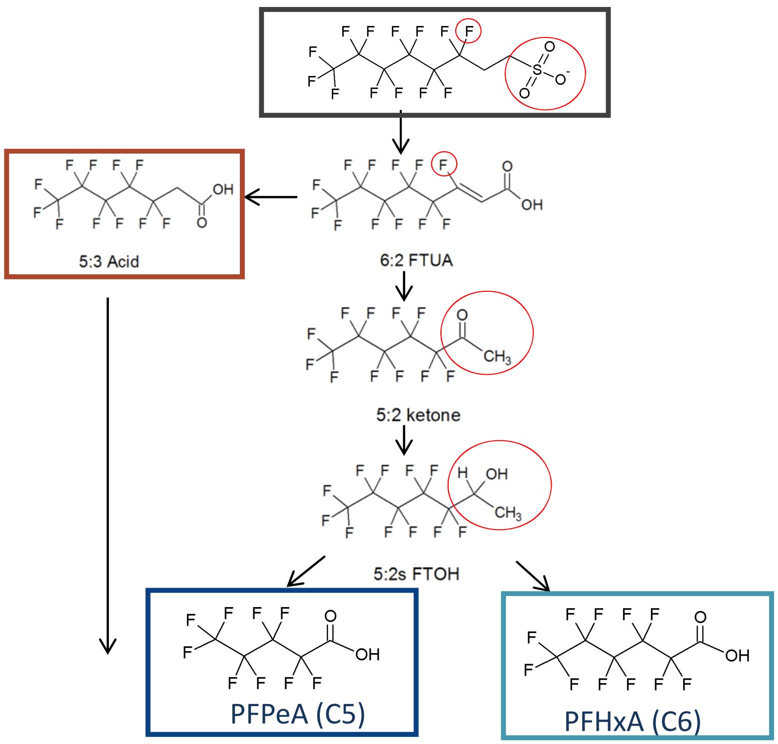
Coggan et al. *Under Review*



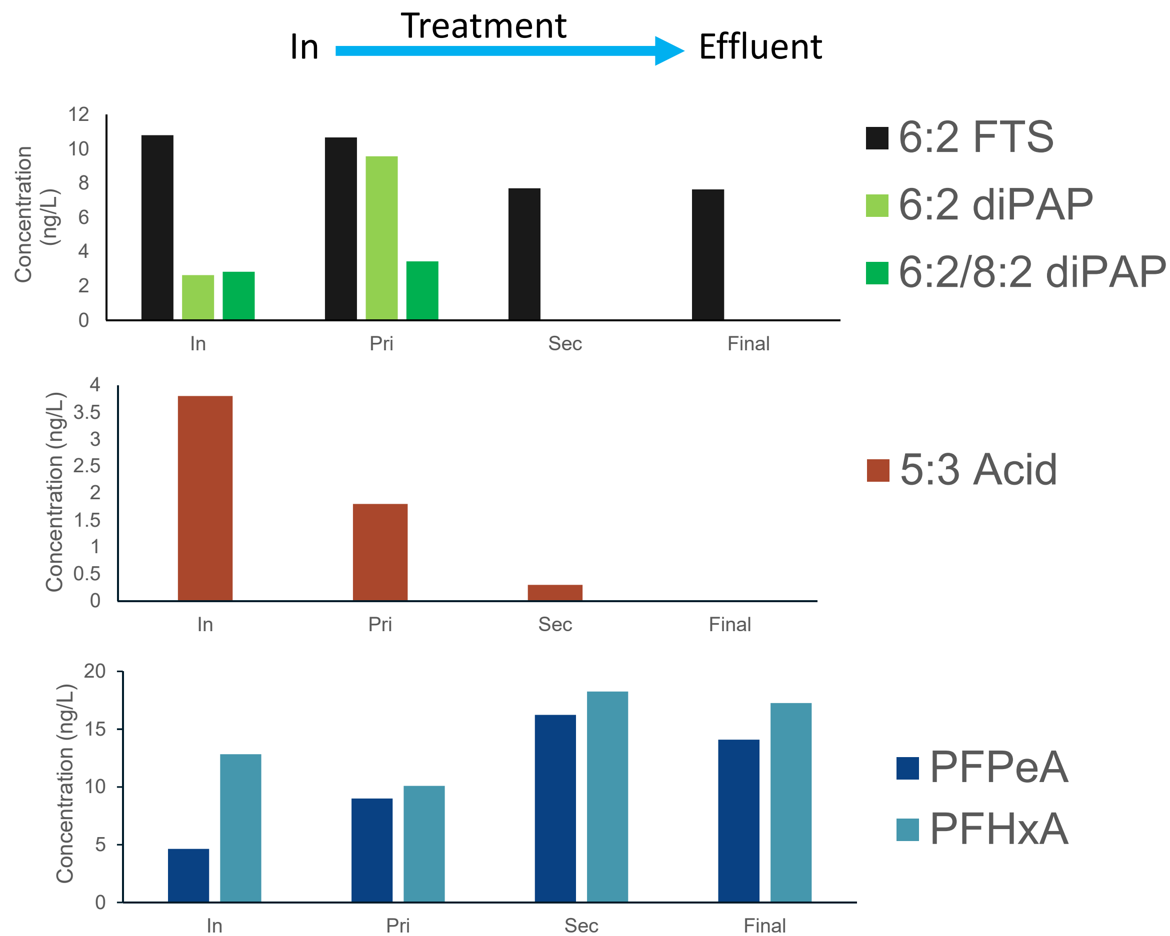


Coggan et al. *Under Review*

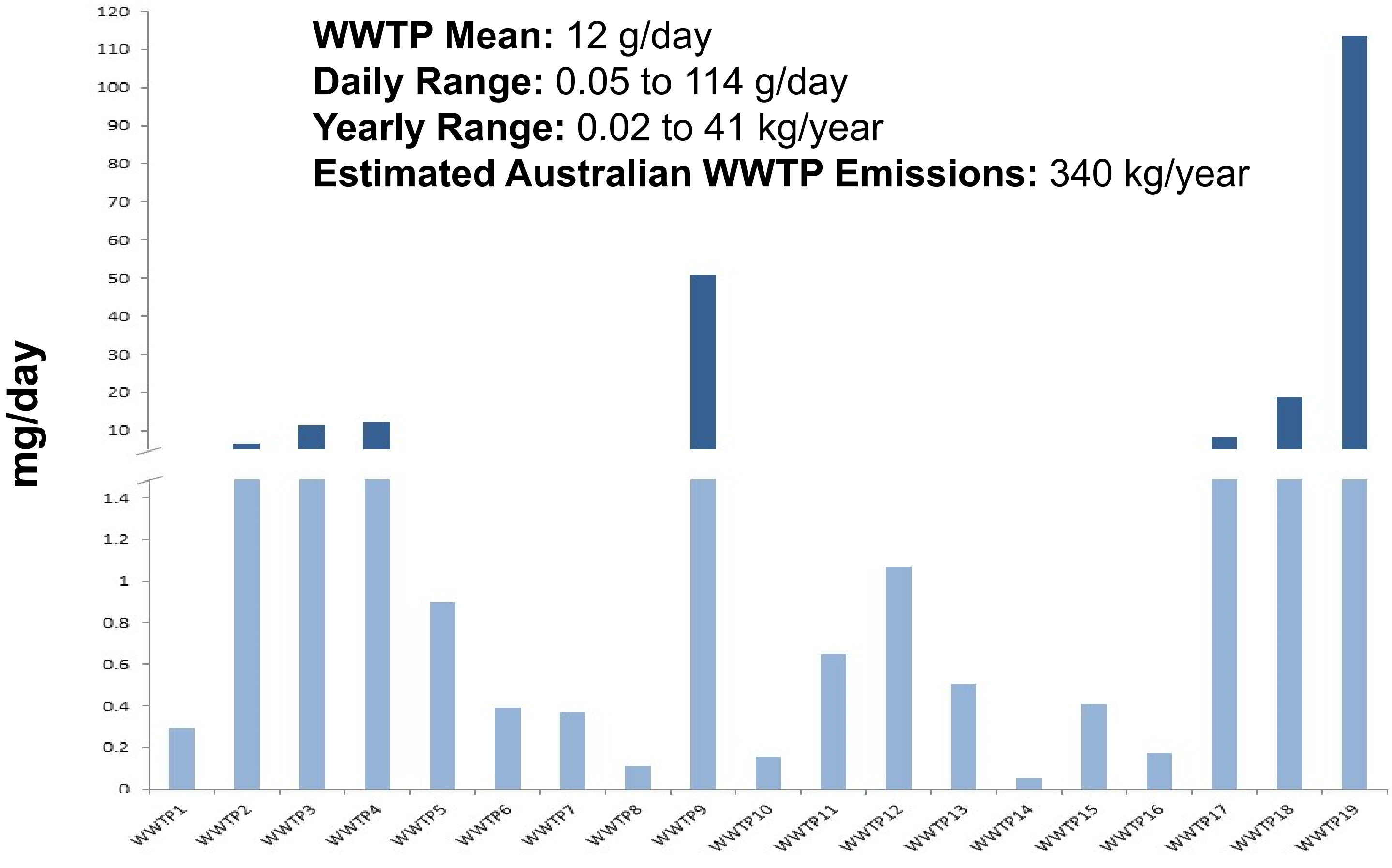
Biotransformation – 6:2 FTS in a WWTP



Transformation pathway from
Wang et al., *Chemosphere,* 2011



WWTP Effluent Environmental Discharges



Suspect Screening and Untargeted Analysis

- Agilent 6545 LC/Q-TOF
- Custom PFAS database
- MS/MS spectra and retention time data available for a subset of compounds

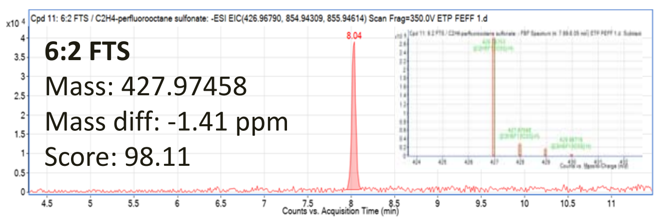
Moving Beyond Monitoring Legacy Per and Polyfluoroalkyl Substances (PFAS): Screening Strategies for the Growing List.

James Pyke, Tuesday 11:00 AM

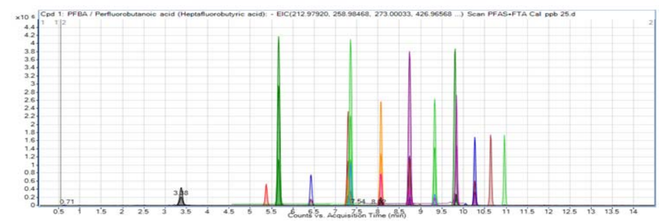
Continuing work

Known knowns
Expanded targeted
list (~50 compounds)

Known unknowns
Expanded PFAS database

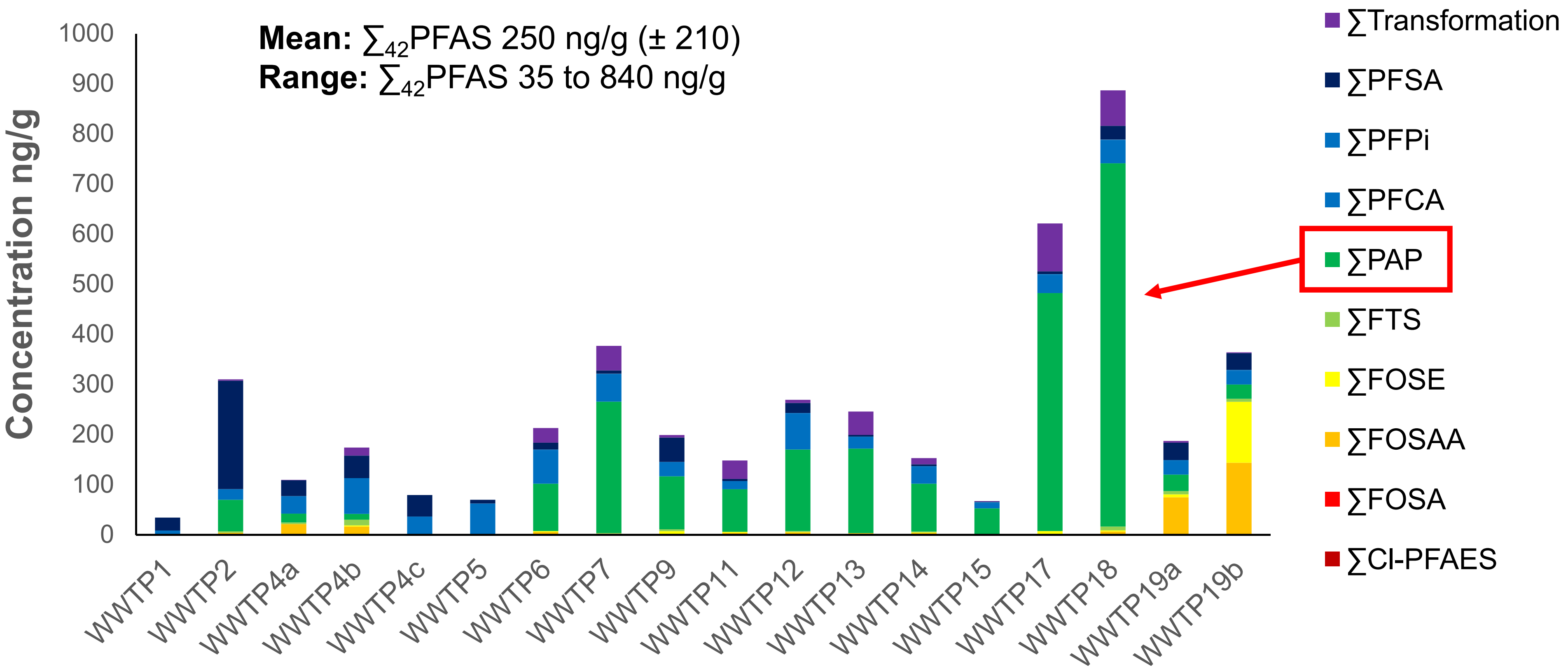


Continually refining
targeted method



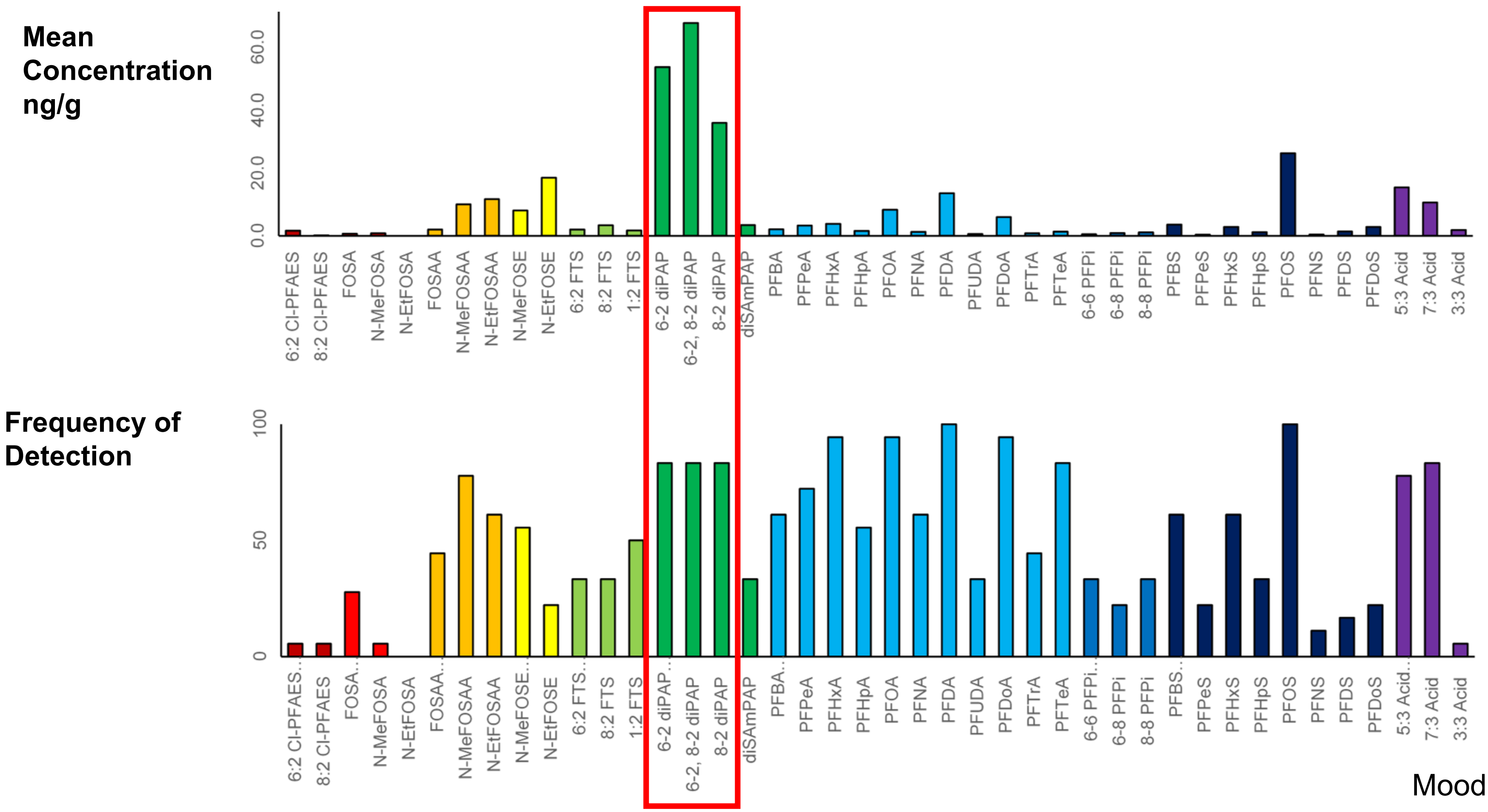
Unknown unknowns
Adding identified
compounds to database list

PFAS in Biosolids



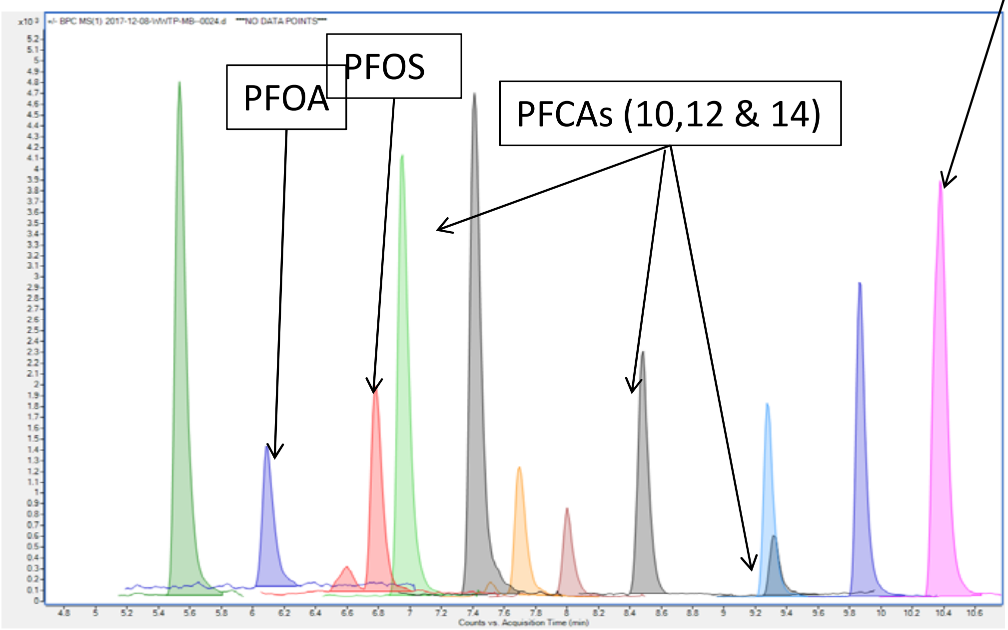
Moodie et al. *in prep*

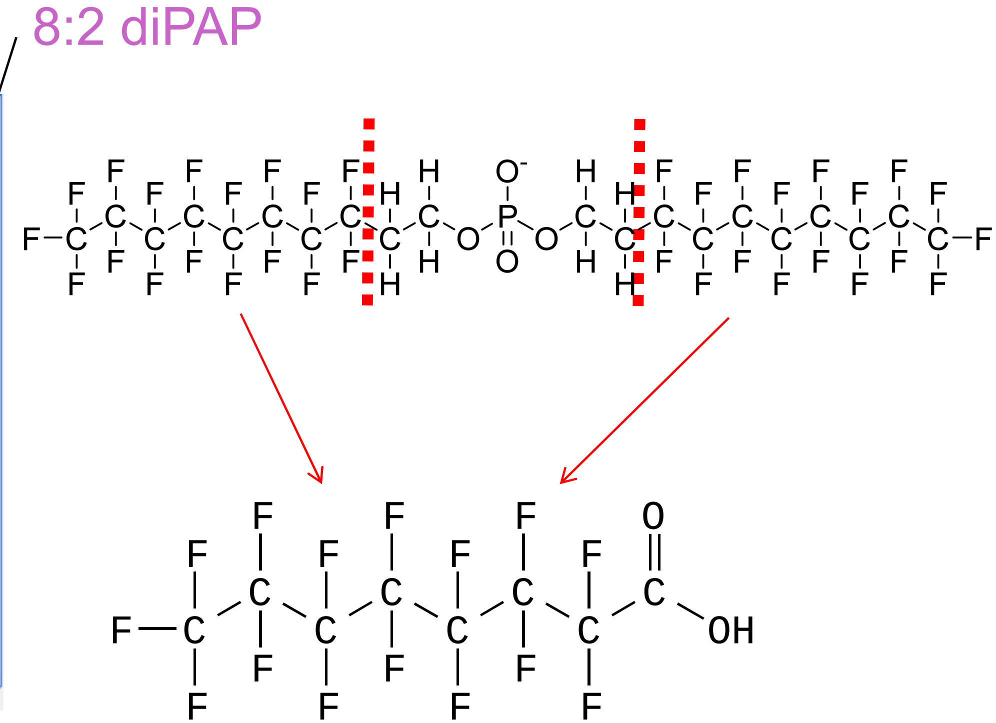
PFAS in Biosolids



Moodie et al. *in prep*

PFAS in a WWTP Solid Sample

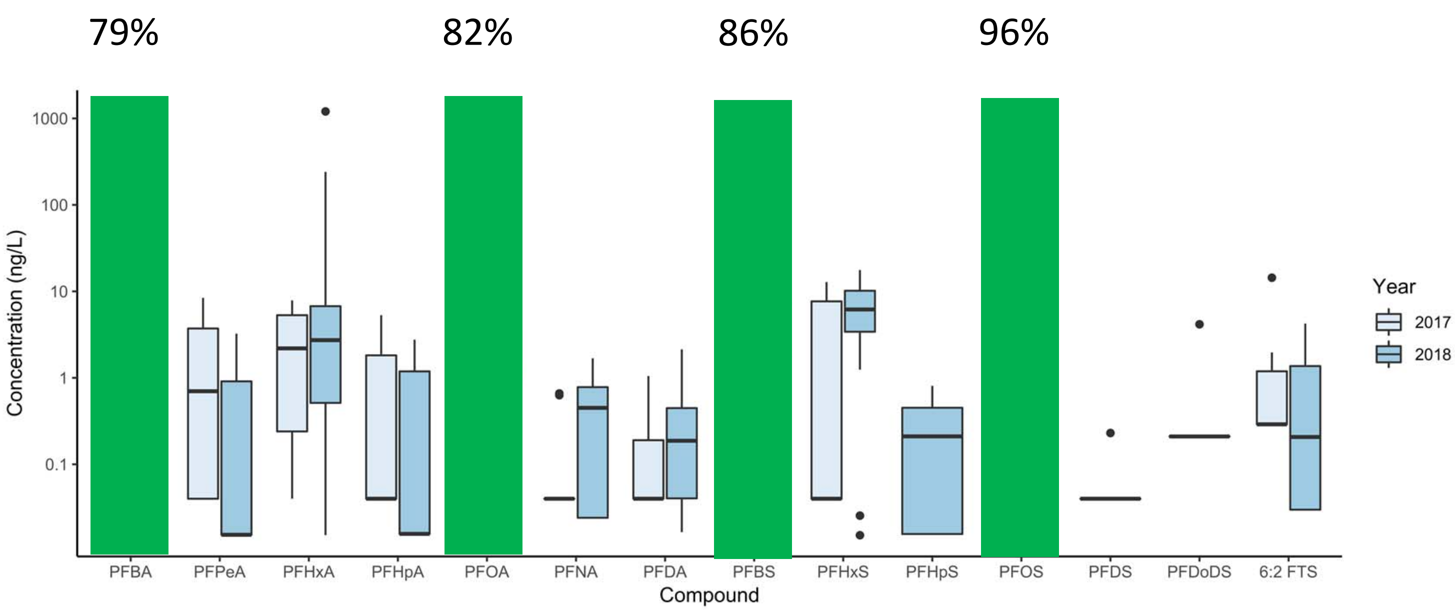




PreFAS: 5:3 Acid 7:3 Acid Et FOSAA Me FOSAA 6:2 diPAP 8:2 diPAP 6:2/8:2 diPAP

Will breakdown to form PFOA and other PFCAs

PFASs in WWTP Impacted Groundwater

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Investigating recycled water use as a diffuse source of per- and polyfluoroalkyl substances (PFASs) to groundwater in Melbourne, Australia

Drew Szabo [a], Timothy L. Coggan [a], Timothy C. Robson [b], Matthew Currell [a], Bradley O. Clarke [a,*]

HIGHLIGHTS

- PFASs were detected in 100% of groundwater samples impacted by recycled water.
- PFOS, PFBS, PFOA and PFBA were the most frequently detected compounds.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

1. Introduction

THE UNIVERSITY OF MELBOURNE

Analytical and Bioanalytical Chemistry
https://doi.org/10.1007/s00216-019-01829-8

RESEARCH PAPER

Check for updates

A single analytical method for the determination of 53 legacy and emerging per- and polyfluoroalkyl substances (PFAS) in aqueous matrices

Timothy L. Coggan[1] · Tarun Anumol[2] · James Pyke[2] · Jeff Shimeta[1] · Bradley O. Clarke[1]

Received: 30 November 2018 / Revised: 27 February 2019 / Accepted: 3 April 2019

Abstract
A quantitative method for the determination of per- and polyfluoroalkyl substances (PFAS) using liquid chromatography (LC) tandem mass spectrometry (MS/MS) was developed and applied to aqueous wastewater, surface water, and drinking water samples. Fifty-three PFAS from 14 compound classes (including many contaminants of emerging concern) were measured using a single analytical method. After solid-phase extraction using weak anion exchange cartridges, method detection limits in water ranged from 0.28 to 18 ng/L and method quantitation limits ranged from 0.35 to 26 ng/L. Method accuracy ranged from 70 to 127% for 49 of the 53 extracted PFAS, with the remaining four between 66 and 138%. Method precision ranged from 2 to 28% RSD, with 49 out of the 53 PFAS being below <20%. In addition to quantifying > 50 PFAS, many of which are currently unregulated in the environment and not included in typical analytical lists, this method has efficiency advantages over other similar methods as it utilizes a single chromatographic separation with a shorter runtime (14 min), while maintaining method accuracy and stability and the separation of branched and linear PFAS isomers. The method was applied to wastewater influent and effluent; surface water from a river, wetland, and lake; and drinking water samples to survey PFAS contamination in Australian aqueous matrices. The compound classes FTCAs, FOSAAs, PFPAs, and diPAPs were detected for the first time in Australian WWTPs and the method was used to quantify PFAS concentrations from 0.60 to 193 ng/L. The range of compound classes detected and different PFAS signatures between sample locations demonstrate the need for expanded quantitation lists when investigating PFAS, especially newer classes in aqueous environmental samples.

Keywords PFAS · Wastewater · Surface water · Drinking water · LC-MS/MS

Coggan et al. (2019) Anal Bioanal Chem, 3507-3520

Application Note
Environmental

Agilent
Trusted Answers

Analysis of >50 Legacy and Emerging PFAS in Water Using the Agilent 6495B Triple Quadrupole LC/MS

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Melbourne, VIC, Australia

Tarun Anumol and
James Pyke
Agilent Technologies, Inc.

Abstract
The contamination of the environment with per- and polyfluoroalkyl substances (PFAS) is a serious concern to regulators, scientists, and the public worldwide; due to their ubiquitous presence, persistence, and toxicity.[1-3] Robust analytical techniques that can accurately and precisely quantify these pollutants at trace levels are necessary for understanding their environmental fate, ecological impacts, and impacts on public health. Appropriate analytical techniques and the fundamental data they generate allow scientists and regulators to make informed assessments of PFAS use in modern society.

This Application Note describes a sensitive and reliable method for the simultaneous quantitation of 53 legacy and emerging PFAS from 14 compounds classes. The method uses isotope dilution on an Agilent 1290 Infinity II LC coupled to an Agilent 6495B triple quadrupole LC/MS.[4]

Application: 5994-0919EN

THE UNIVERSITY OF MELBOURNE

Thank you

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