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Transport, Bioaccumulation and Impact of Per- and Polyfluoroalkyl Substances (PFASs) in Birds from South-east Australia

Drew Szabo, PhD Candidate

Clarke Group

Acknowledgement of Country

Research Aims

1. To provide baseline data on the environmental fate of PFASs at a Wastewater Treatment Plants, including temporal trends on inputs.
2. To determine food web model, specifically PFOS, PFOA and PFHxS, their precursors, and novel replacements.
3. To validate novel biological sampling and analysis techniques.
4. To detail the exposure pathways of PFASs in environmental ecosystems, with a particular focus on avian species.

Chapter 1: A review of the global concentrations, exposure and risk of PFAS to marine and terrestrial birds (Literature Review)

Chapter 2: Temporal variation of PFAS in WWTP influent (Research Article)

Chapter 3: Extraction and trace-quantitation of PFASs from µ-volumes of blood (Method Paper)

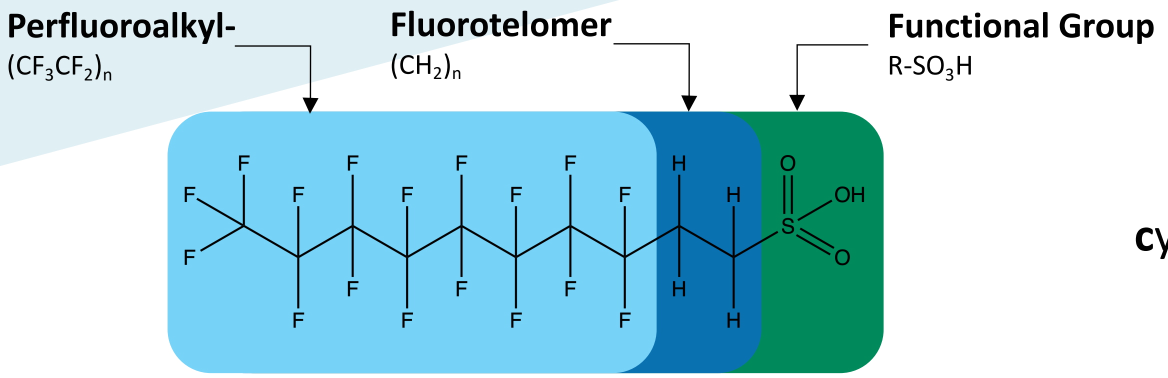
Chapter 4: Contamination of Albert Park Lake and impact to Black Swan population (Research Article)

Chapter 5: Occurrence of PFAS in pacific seabird fledglings (Research Article)

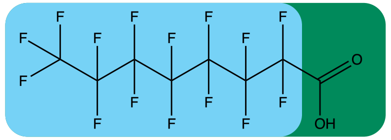
Chapter 6: Occurrence of PFAS in waterfowl from pristine habitat, Tasmania, Australia (Research Article)

Per- and Polyfluoroalkyl Substances

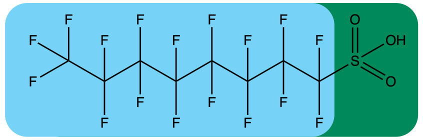
Per- and polyfluoroalkyl substances



PFOA
Perfluorooctanoic acid



PFOS
Perfluorooctanesulfonic acid

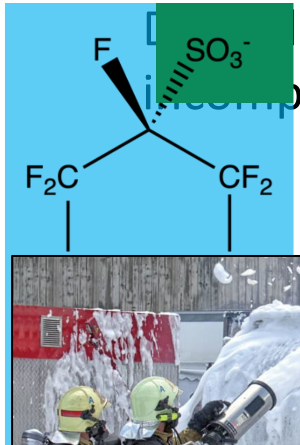


- Persistent (UNEP, 2009)
- Bioaccumulative (Condor *et al* 2008)
- Toxic "multi-system toxicant" (DeWitt *et al* 2015)
- Mobile (Munoz *et al* 2015)

4730 compounds in CAS registry (OECD 2018)

PFECHS
Perfluoro-4-ethyl-cyclohexanesulfonate

Regulation
to replacer
(Barzen-Hanson e



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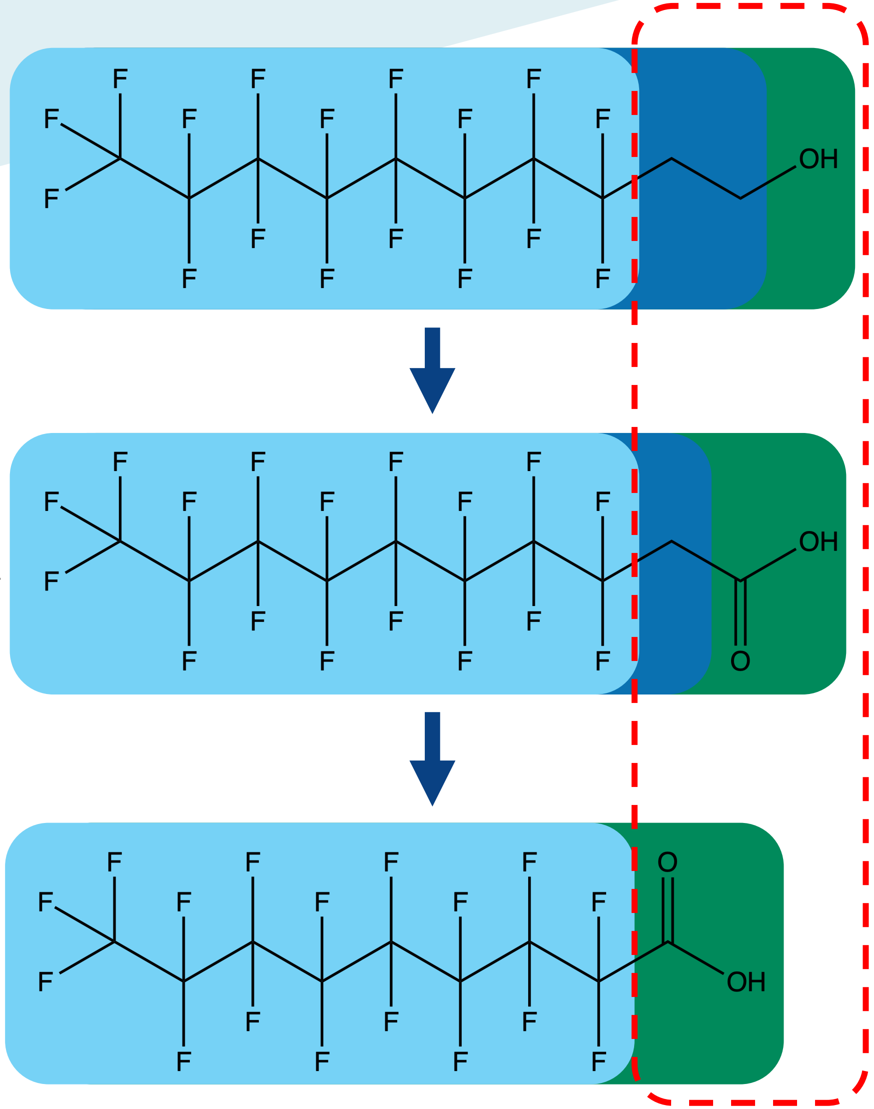
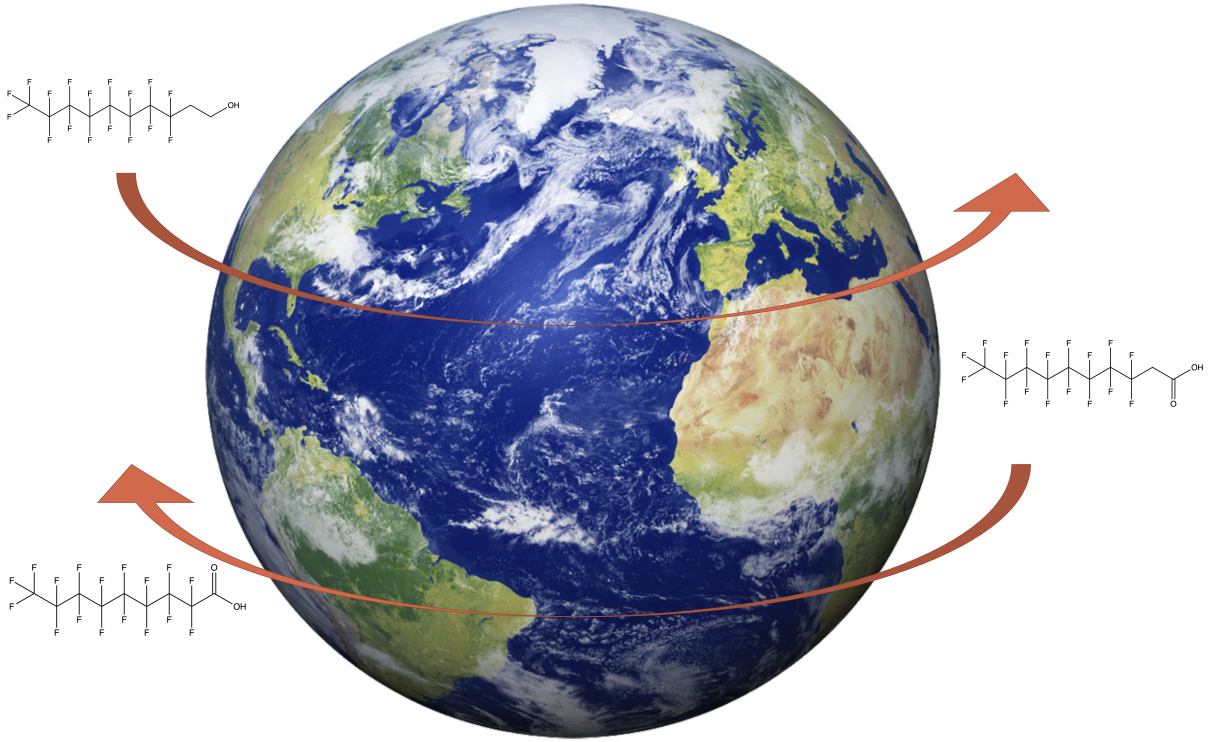
Transformation & Transport

8:2 FTOH

8:2 FTCA

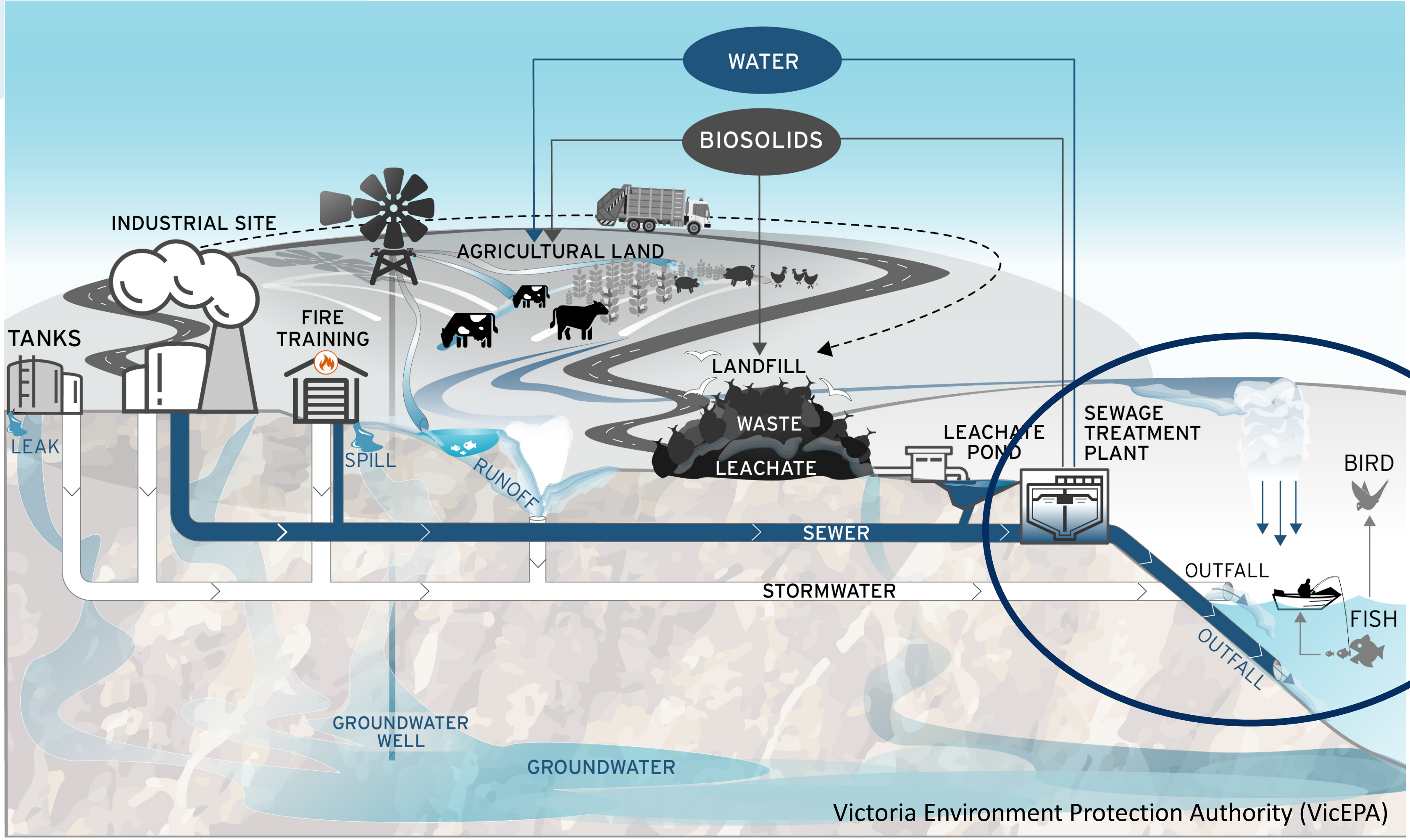
PFNA





Butt *et al.* (2014)

Conceptual Site Model



Birds as Biomonitors

Birds as biomonitors

Large foraging area and feed over multiple trophic levels (Mallory et al. 2010)

Monitor **pollution** (Braune et al, 2005), **fish stocks** (Frederiksen et al., 2007) and **climate change** (Thompson & Ollason, 2001)

Success of reproduction, including fledgling viability, can be related to abundance of prey and time/energy budgets of adults (Einoder 2009)

Overfishing, by-catch and habitat loss are the biggest known drivers for bird population decline.

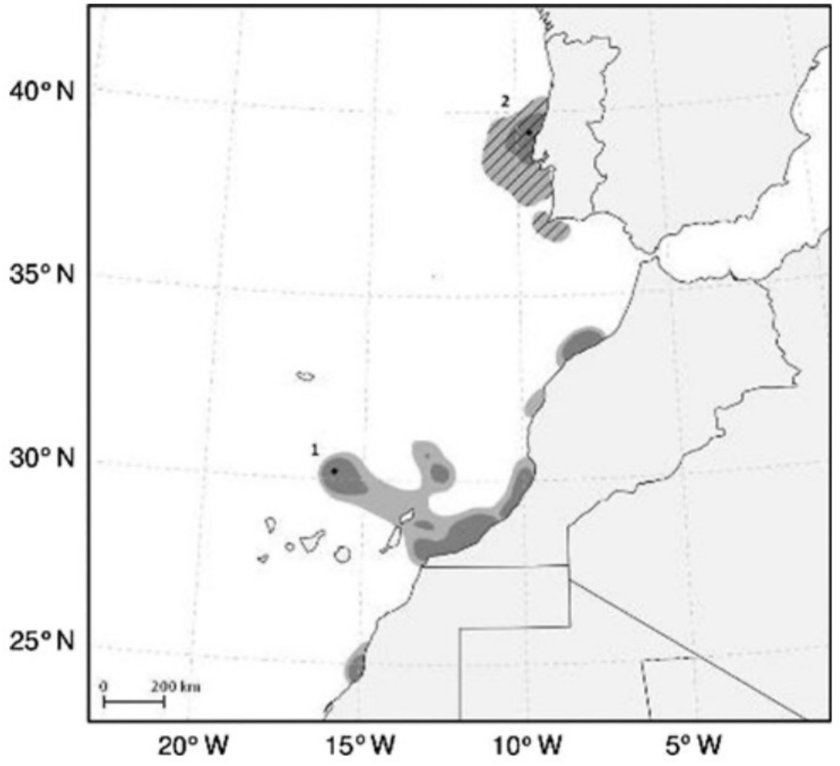
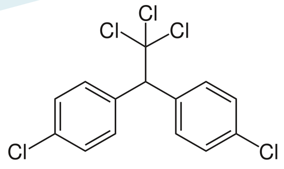
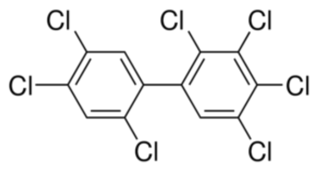
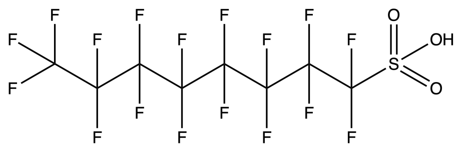
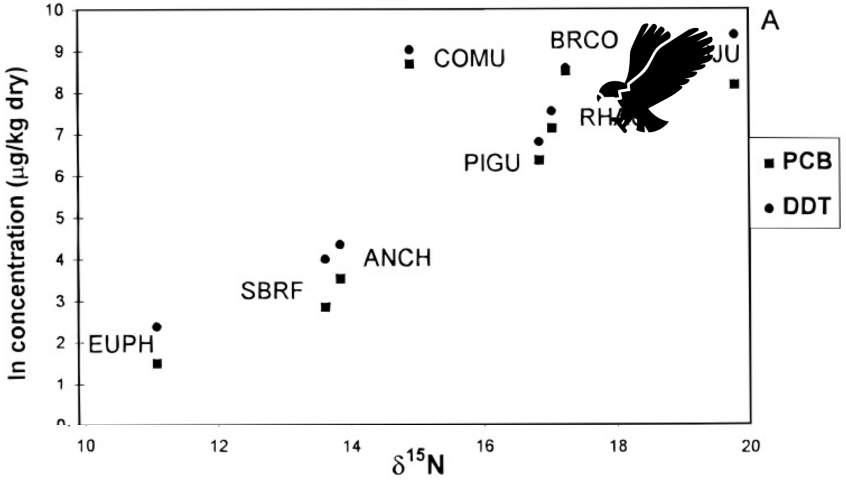


Fig. 4 Foraging areas of Cory's shearwaters, during the chick rearing, in Selvagem Grande (*1*) and Berlenga (*2*) calculated from Kernel density estimation. Density counter plots encompass 50% (*dark gray*) and 75% (*light gray*) of GPS locations. Breeding locations are indicated by the *black dots*

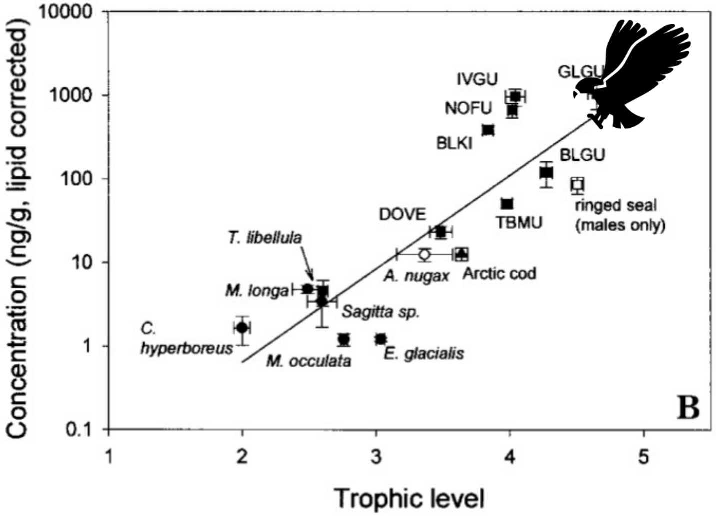
Alonso et al. (2012)

Birds as Sentinel Biomonitors

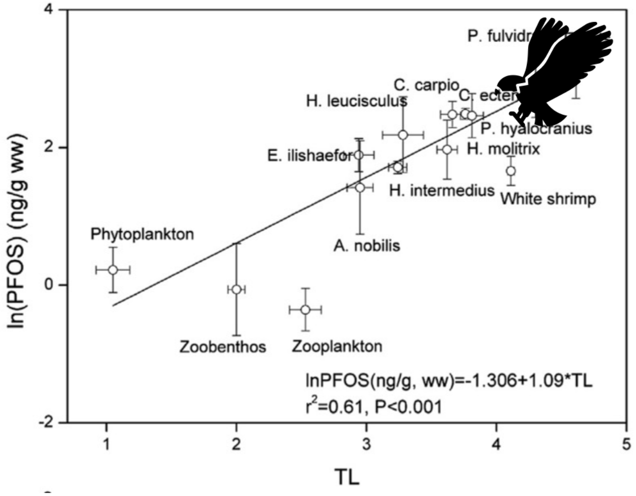
DDT	PCB-180	PFOS
		



Jarman *et al* (**1996**) *Environ. Sci. Technol.*

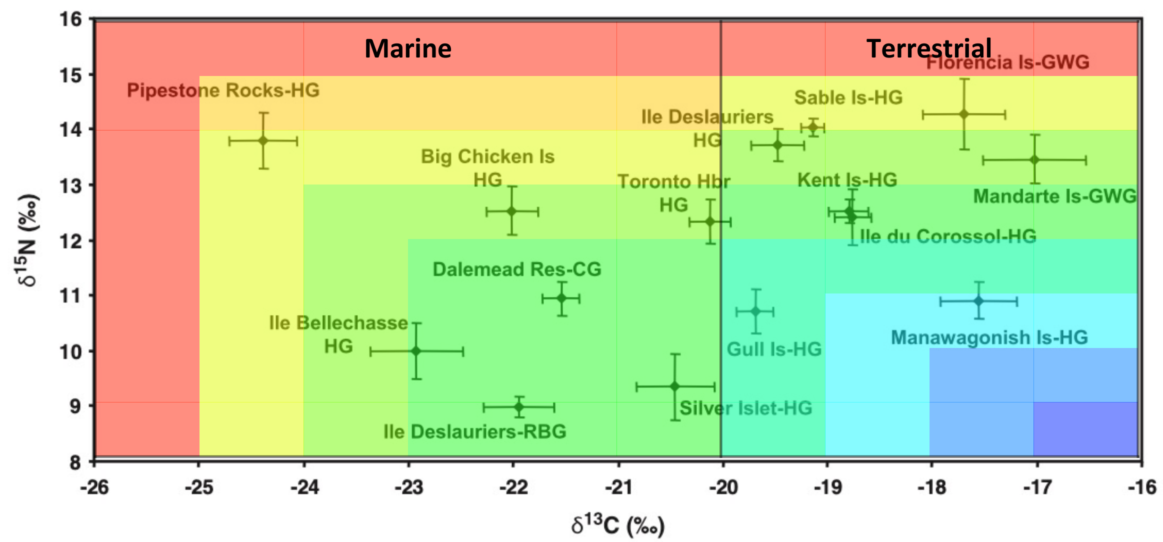


Fisk *et al* (**2001**) *Environ. Sci. Technol.*



Xu *et al* (**2014**) *Environ. Pollut.*

Biomagnification

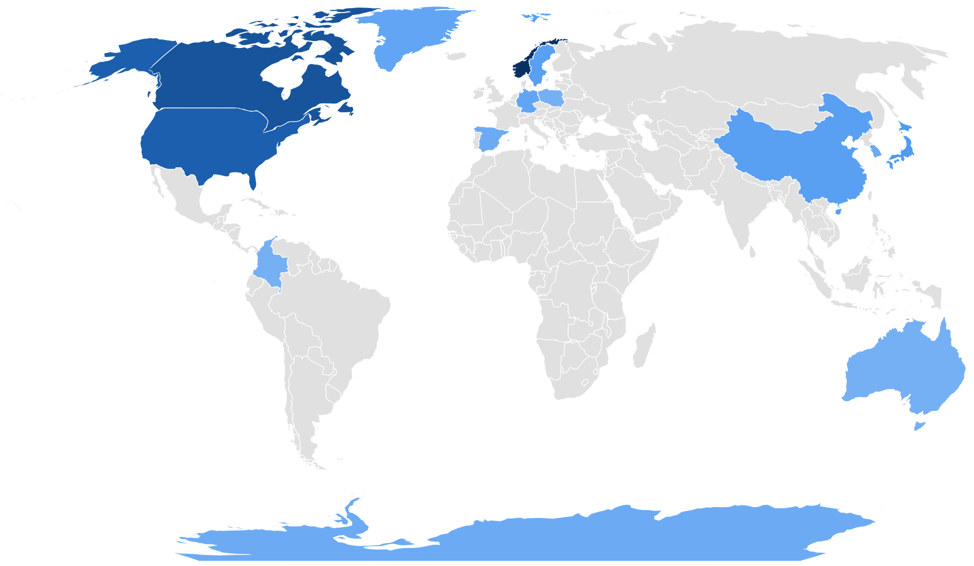


Adapted from Gebbink *et al*. (2011)

Species	BMF	Conc. (ng/g)	Reference
Cod→Kittiwake	(5.1)	1 - 20	Tomy et al. (2004)
Cod→Gull	(9.0)	10 - 33	Tomy et al. (2004)
Overall→Duck	17.4	2 - 25	Kelly et al. (2009)
Cod→Guillimot	10.1	nd - 44	Haukås et al. (2007)
Cod→Gull	38.7	8 - 225	Haukås et al. (2007)
Salmon→Eagle	(5-10)	<7.5 - 1740	Kannan et al. (2005)

Global Distribution

Area	Concentration ng[PFOS]/g	Reference
3M facilities	Great Tit: 5,111 – 187,032 ng/g (egg)	Groffen *et al* (2019)
Great Lakes	Herring Gull: 82 – 390 ng/g (egg)	Remucal (2019)
Arctic	Peregrine Falcon: 40 – 220 ng/g (egg)	Holmström *et al* (2010)
Australia	White Ibis: 12 – 114 ng/g (egg)	Thompson *et al.* (2011)
Antarctic	South-polar Skua: 0.88 ng/mL (serum)	Tao *et al.* (2006)



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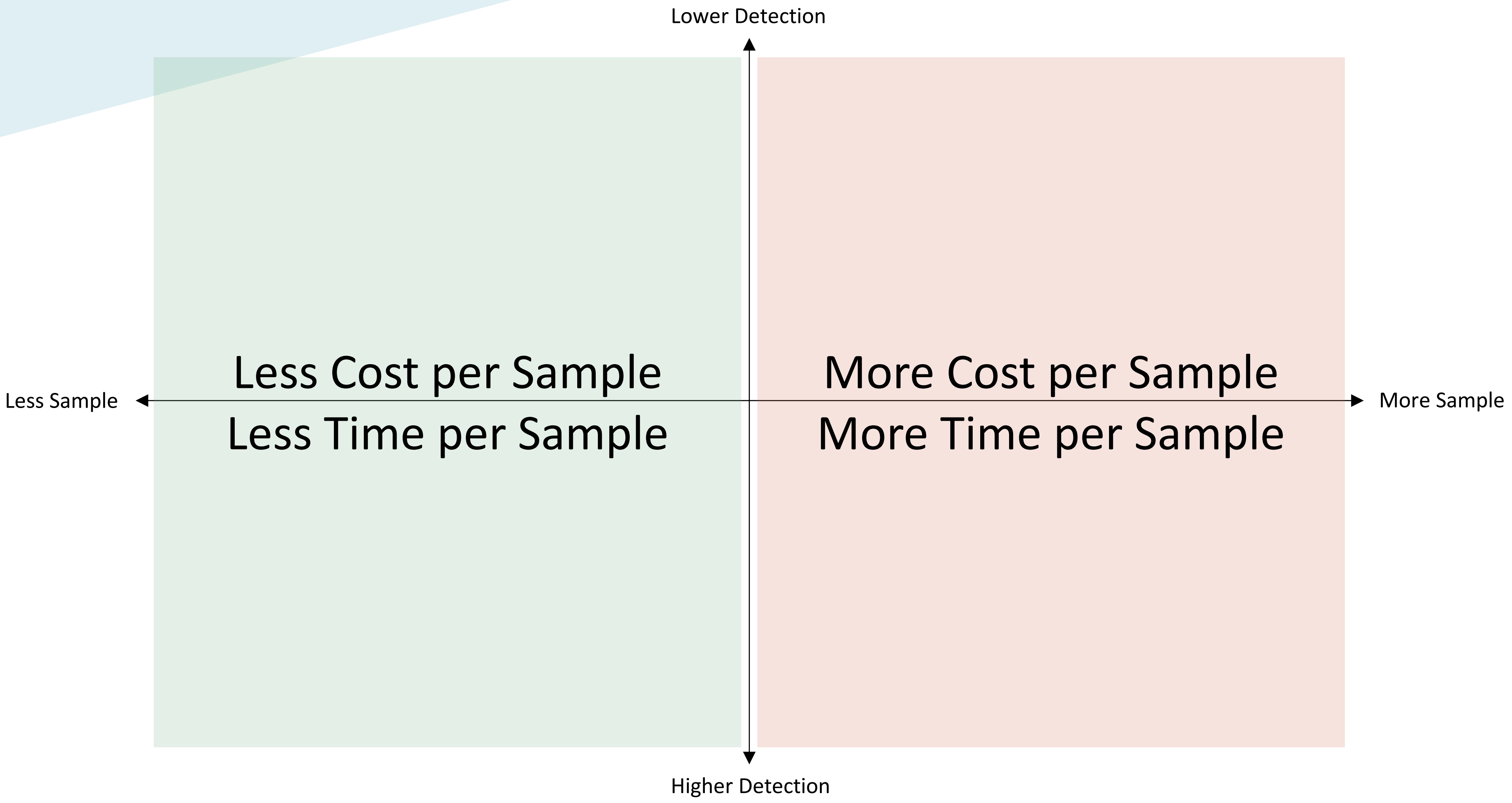
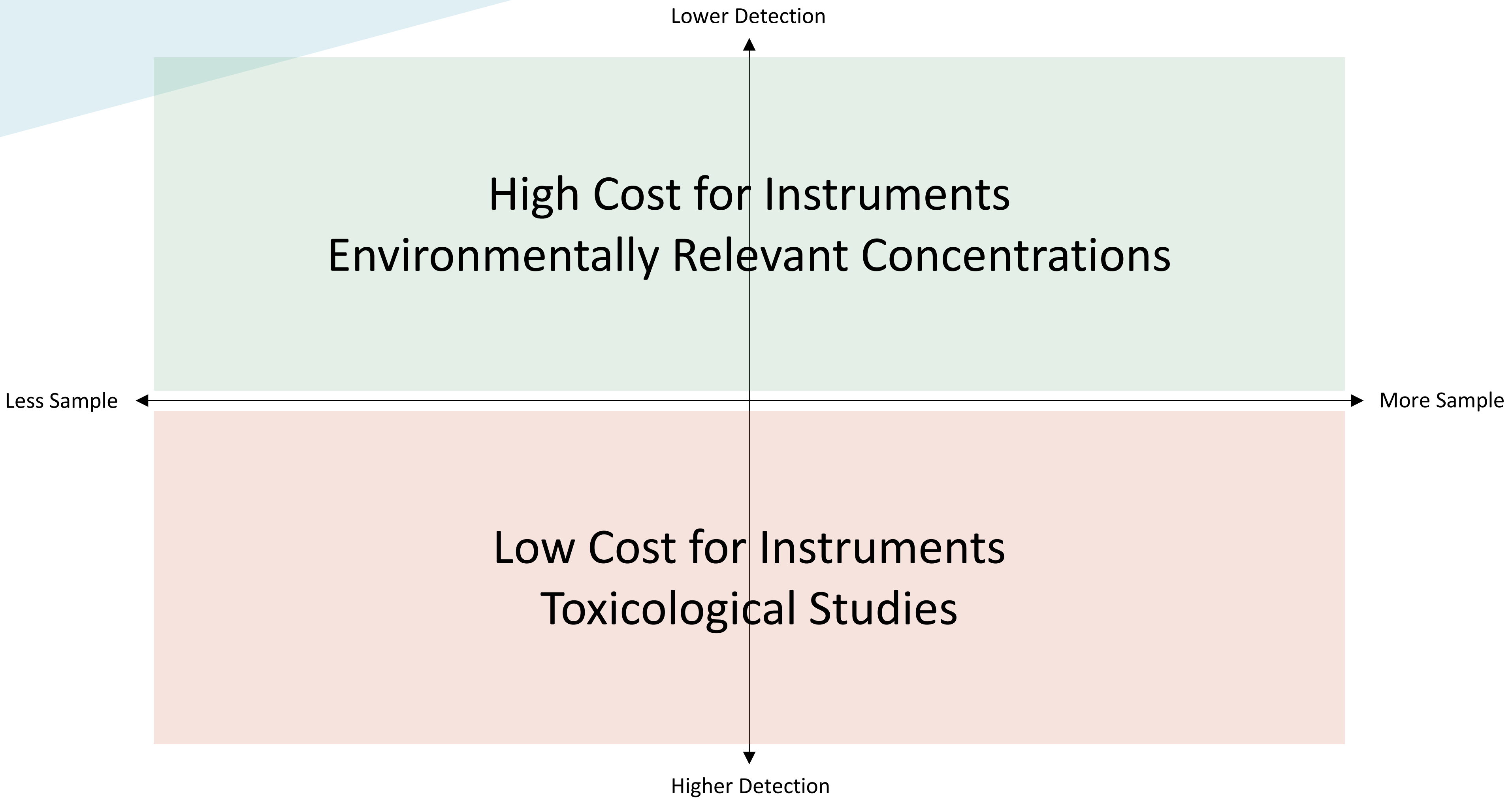
Great Tit ©Francis C. Franklin

Analytical Techniques

Goals of Analytical Chemistry



Goals of Analytical Chemistry



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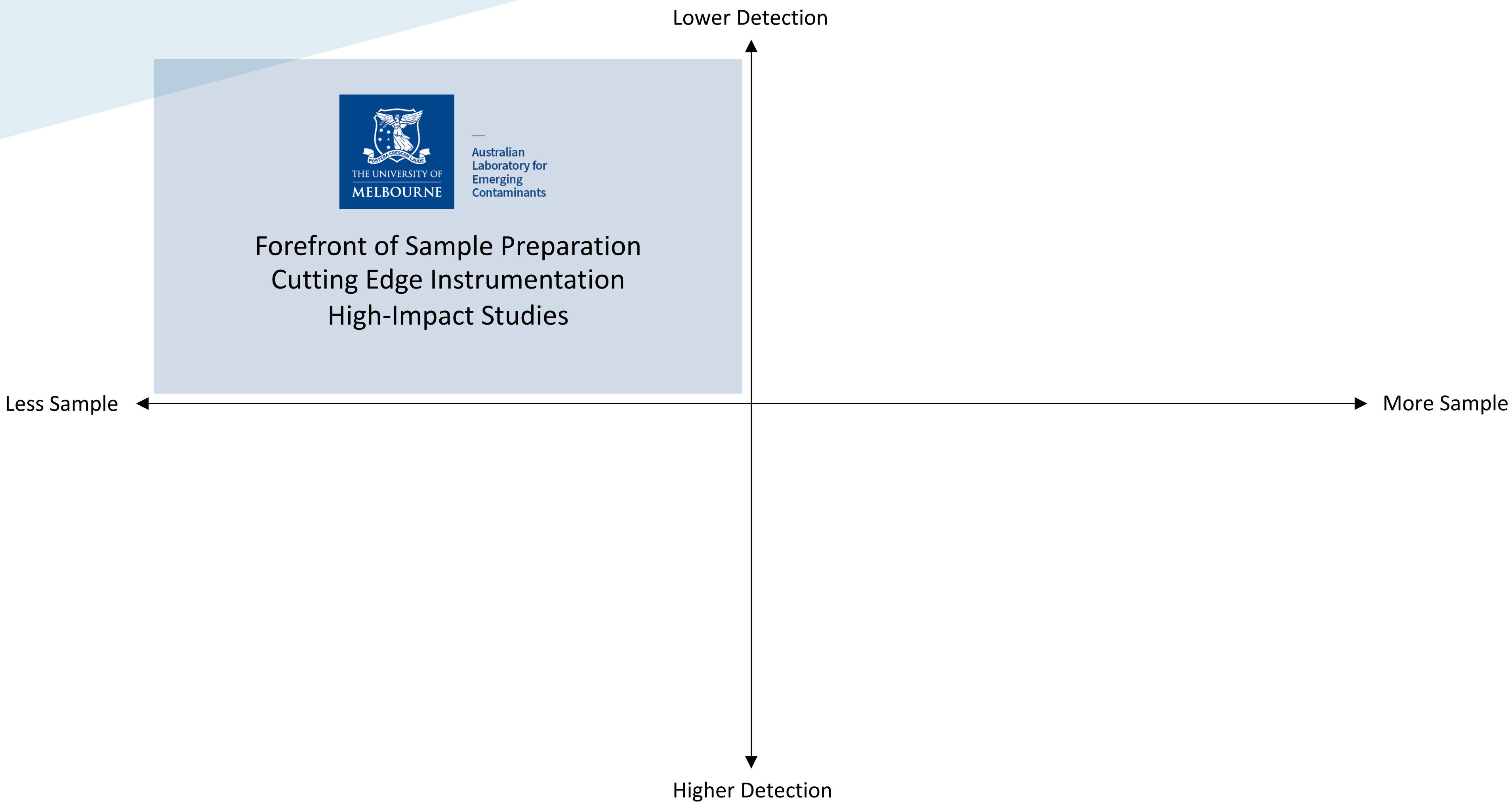


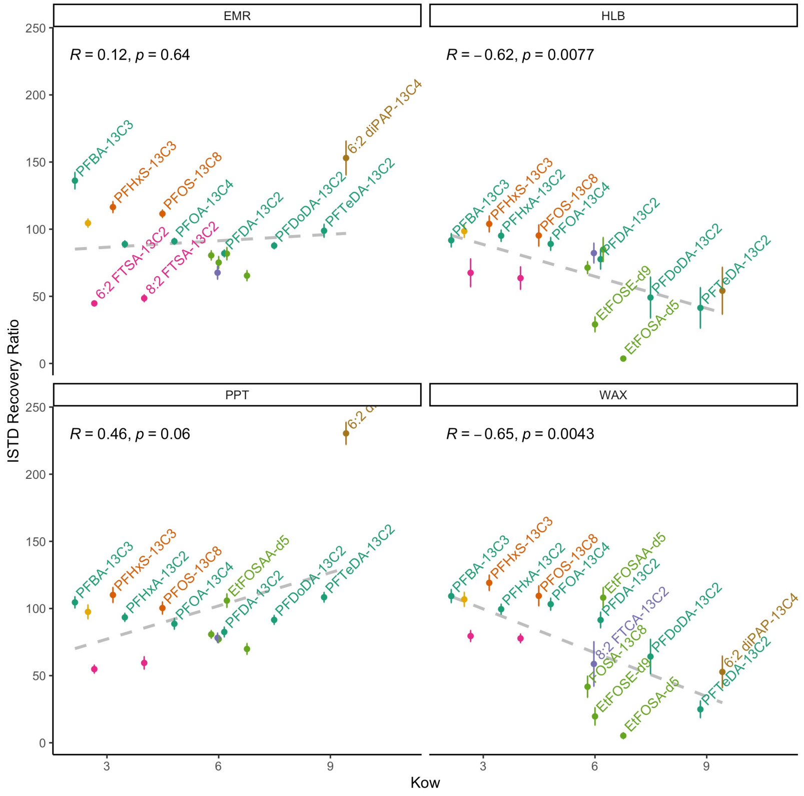
Extraction Methodologies

Aqueous Solid Phase Extraction		Solid QuEChERS	
Surface Water Wastewater	Blood & Serum	Liver & Organs	Soils & Biosolids
50 mL Sample Internal Standard Weak Anion Exchange (WAX) 0.2 – 0.5 mL Methanol	0.2 mL Sample Internal Standard Enhanced Matrix Removal (EMR) 0.2 – 0.5 mL Acetonitrile	1 g ww Sample Internal Standard Salt and Sorbent 5 mL Acetonitrile	1 g dw Sample Internal Standard Salt and Sorbent 5 mL Acetonitrile
Detection Limit = 0.2 ng L^{-1}	Detection Limit = 0.1 ng mL^{-1}	Detection Limit = 0.25 ng g^{-1}	Detection Limit = 0.25 ng g^{-1}

Enhanced Matrix Removal (EMR)

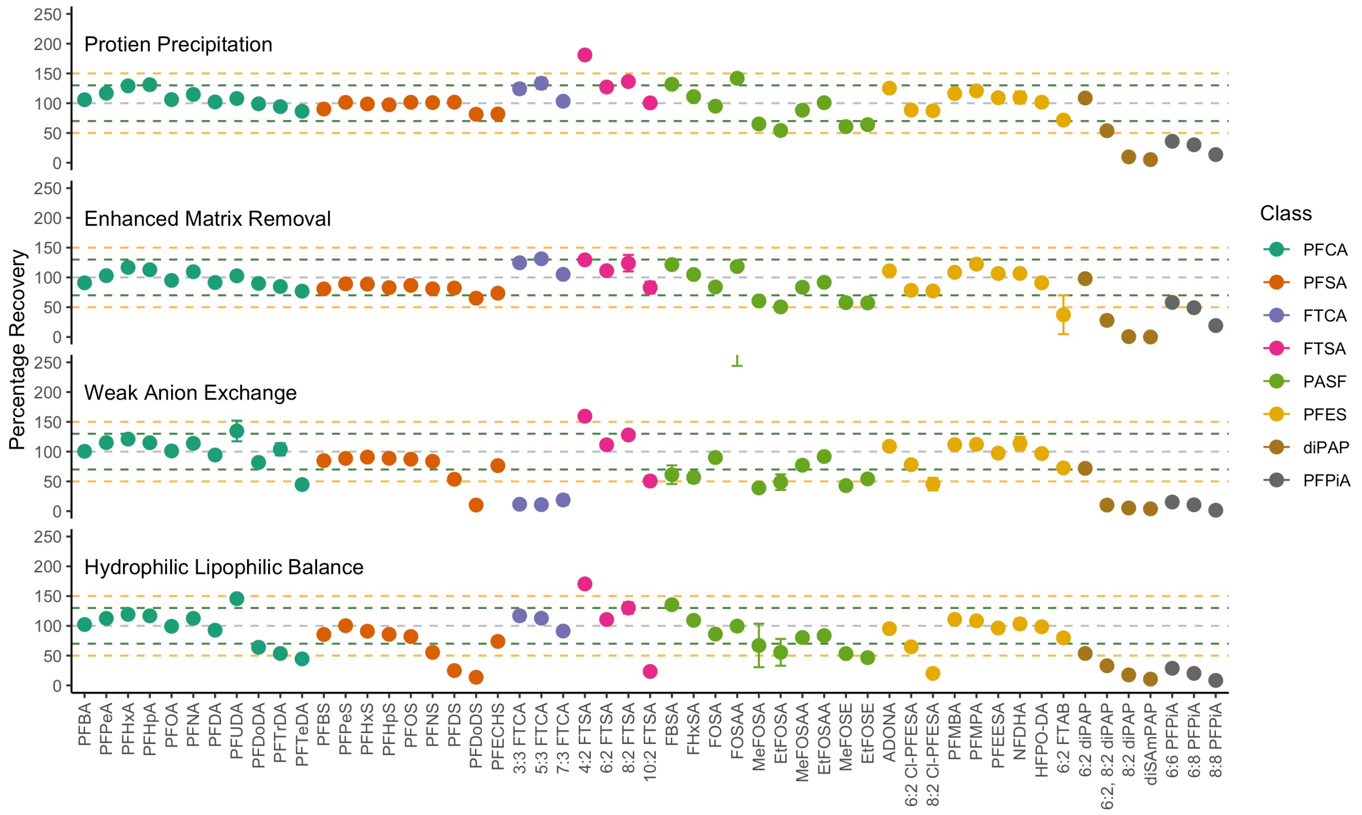
Recovery vs K_{ow}

EMR and PPT performed well overall despite chain-length and HLB and WAX did not for long-chain lengths.



Recovery of PFASs at 5 ng mL^{-1}

PPT and EMR performed best for majority of compounds. HLB and WAX did not perform well for long-chain and novel compounds.



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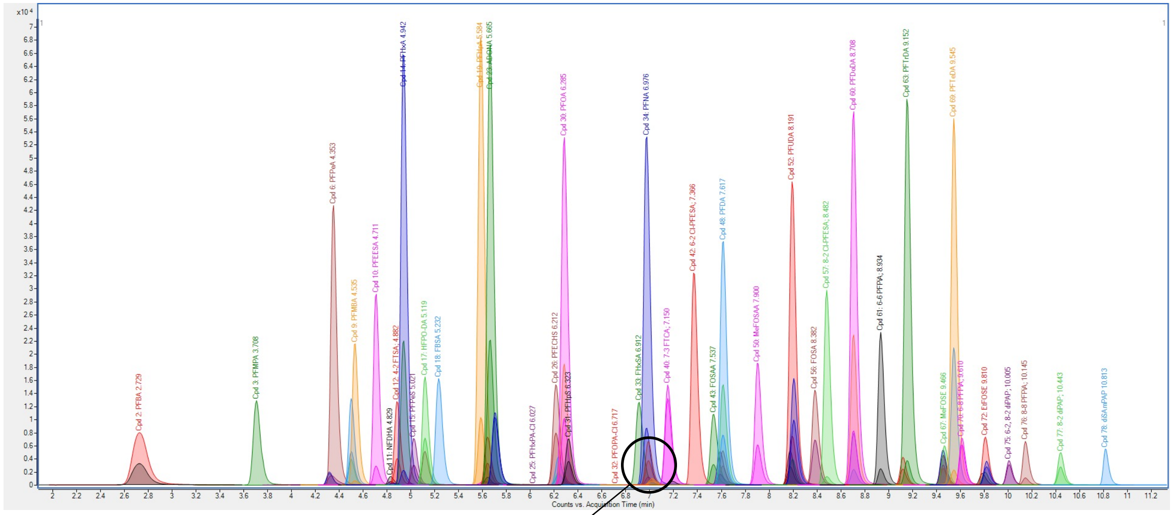
Live Demonstration

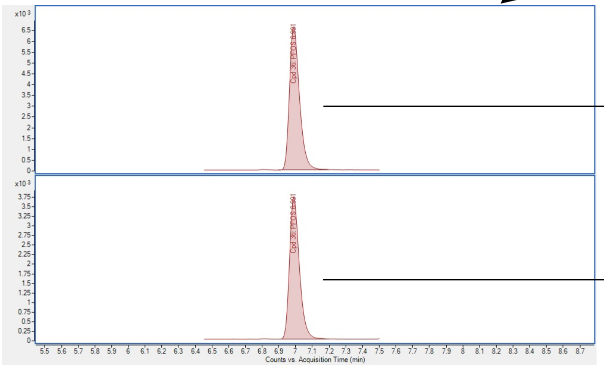
Analytical Quantification

C18 Reverse Phase Chromatography

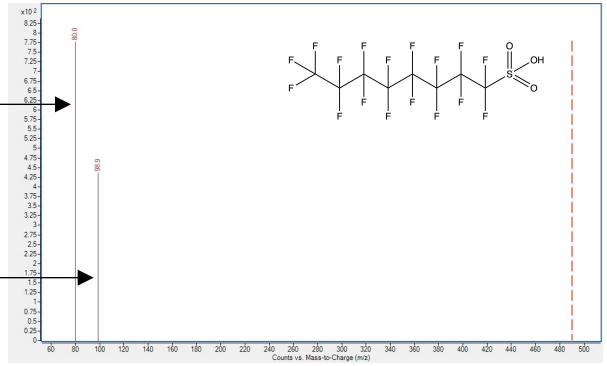
Sample Chromatogram



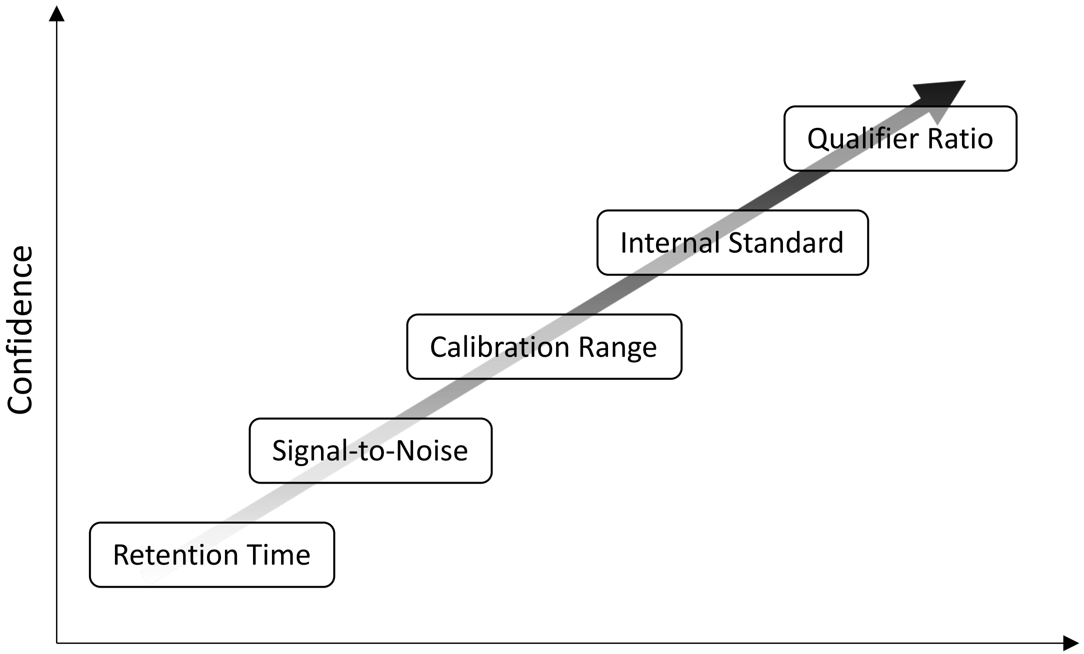
PFOS MRM Chromatogram

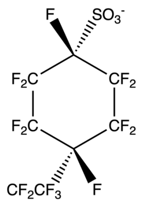


PFOS MRM Mass Spectrum



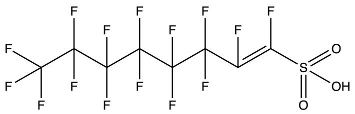
Quantification Confidence





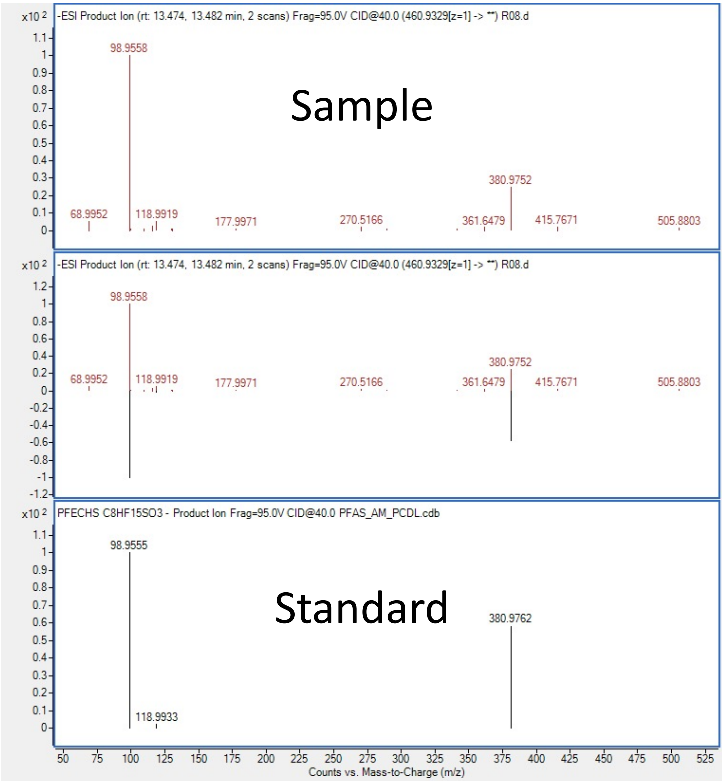
PFECHS

m/z = 460.9



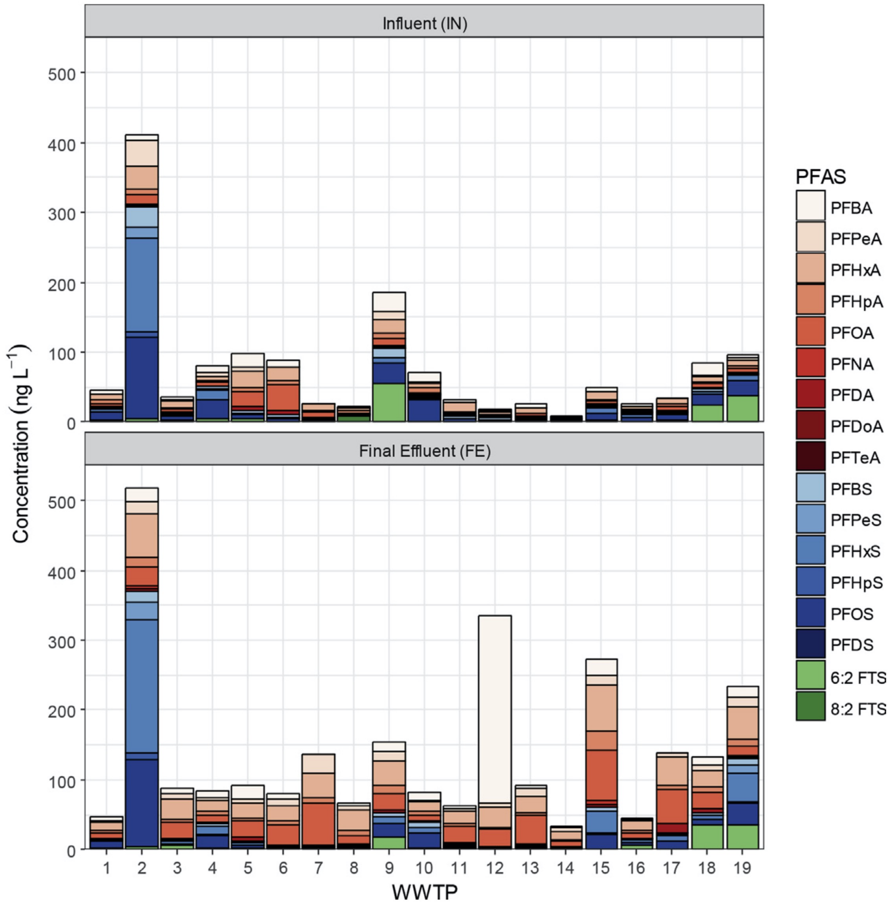
UPFOS

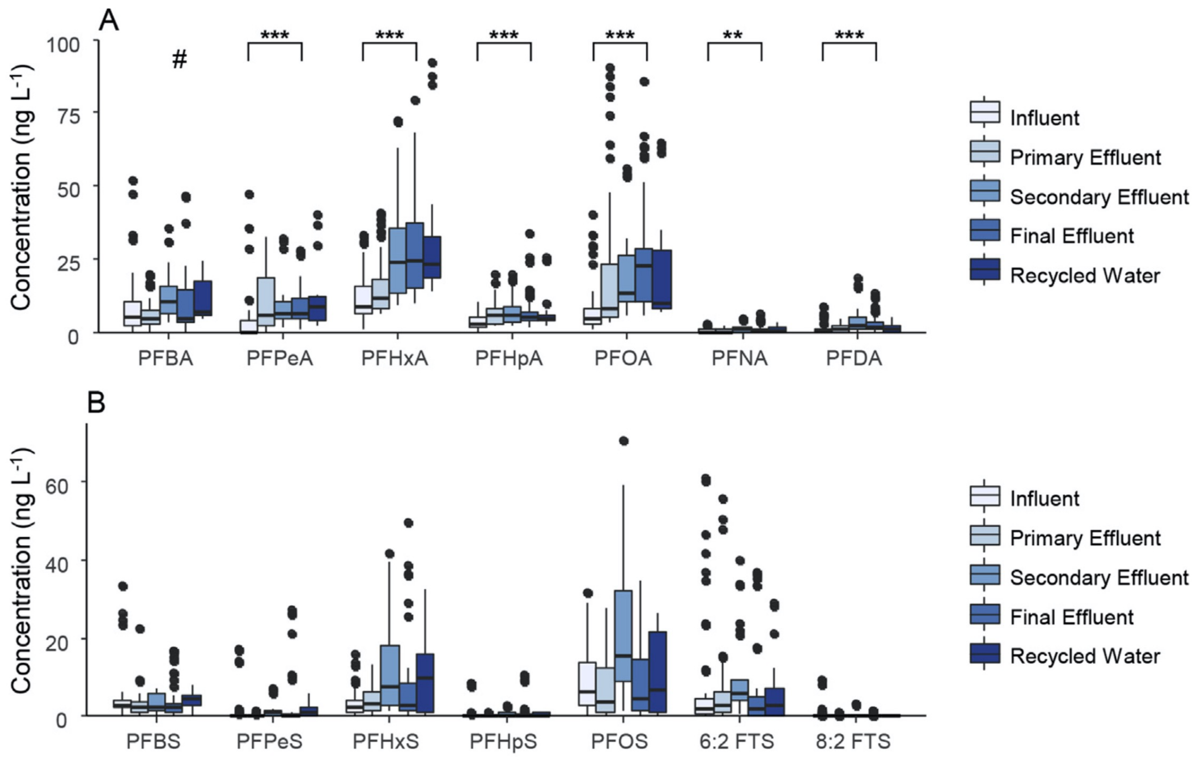
m/z = 460.9



Wastewater Treatment Plant

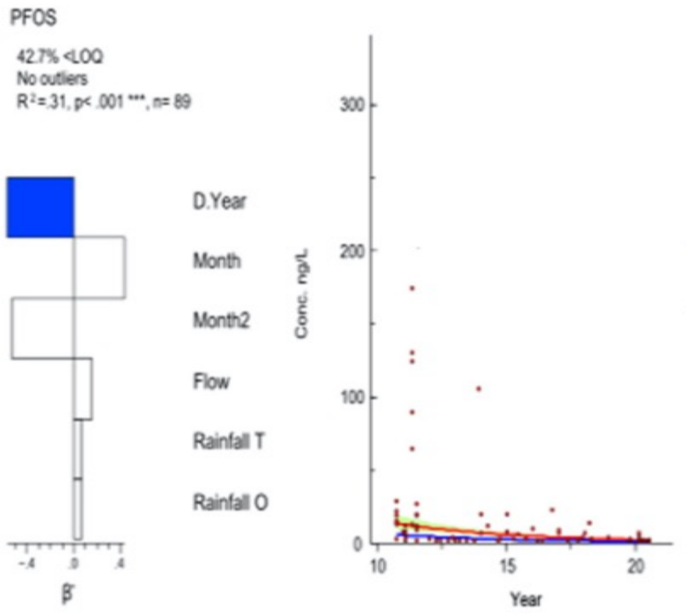
PFASs in Australian WWTPs



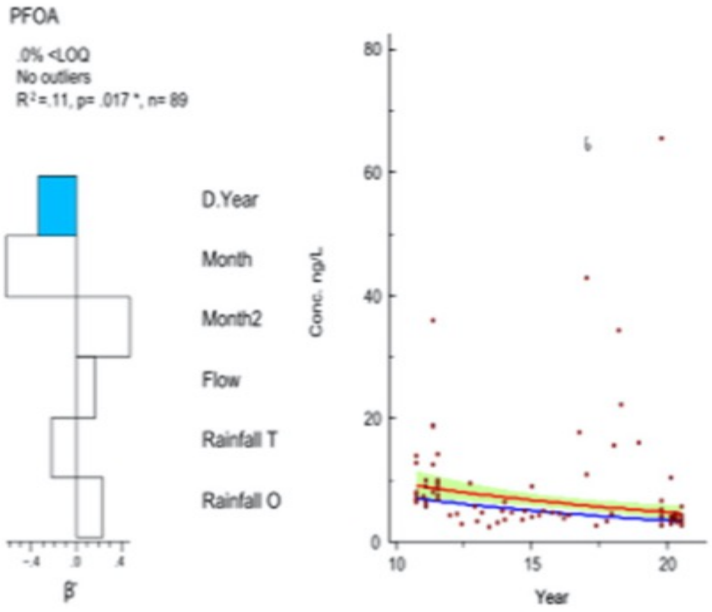


Coggan *et al* 2019. *Heliyon*

Long-term Trends



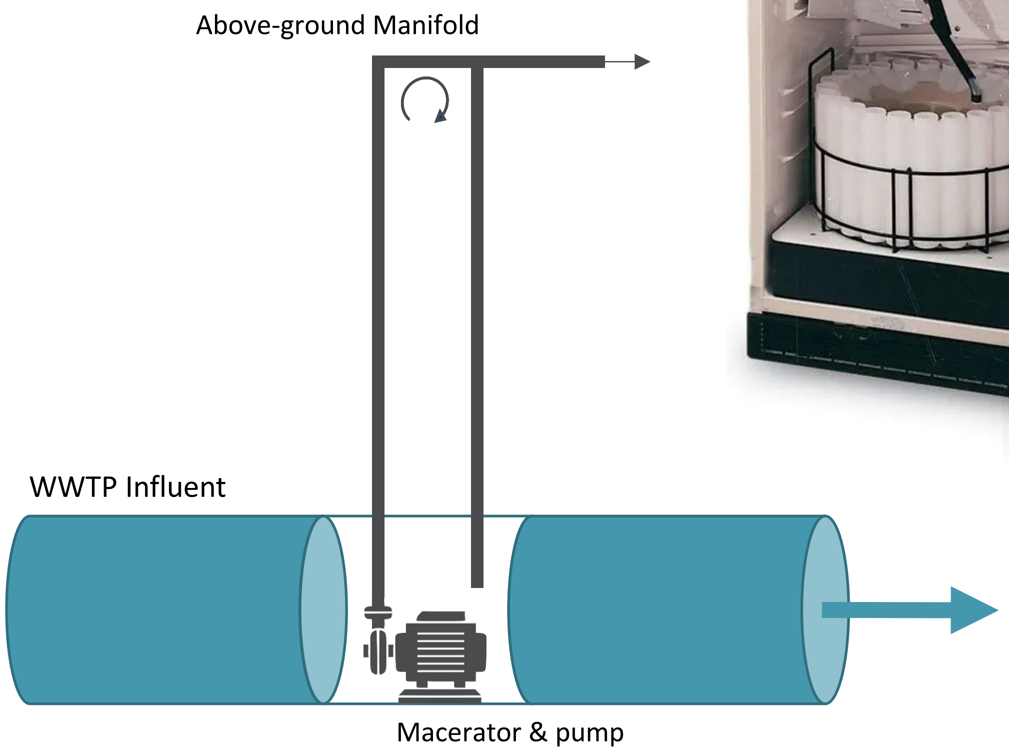
-18% annual change



-6.7% annual change

Gallen *et al* 2021. *Sci. Tot. Environ.*

Hourly Sampling Campaign



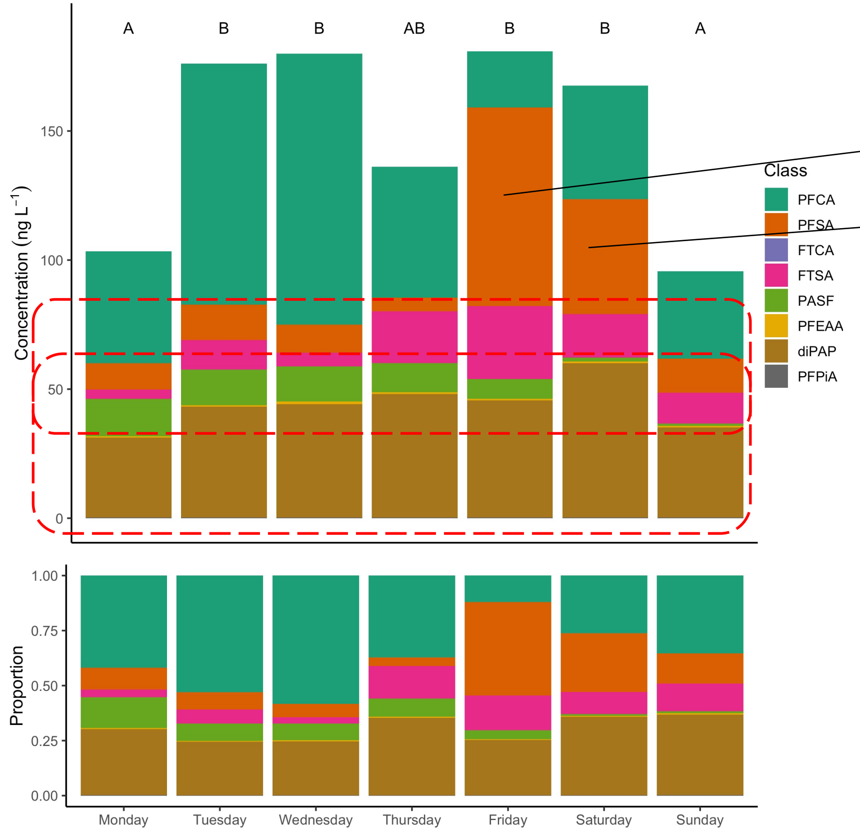
11 Nov – 17 Nov 2019

Hourly influent samples for 7-days (n = 168)
System is purged before sampling
PVC and silicone plumbing from pump
Sample taken every hour in HDPE containers
Low Precipitation
No Public Holidays
Pre-COVID (Business-as-Usual)

Variability in WWTP Sampling

Concentrations of PFASs per Day

The sum total PFAS concentrations change of average throughout the week (n = 168)



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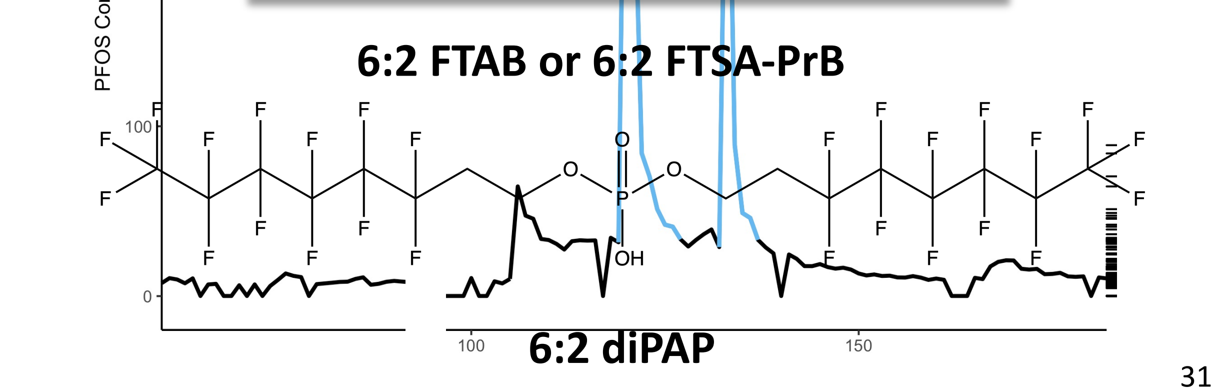

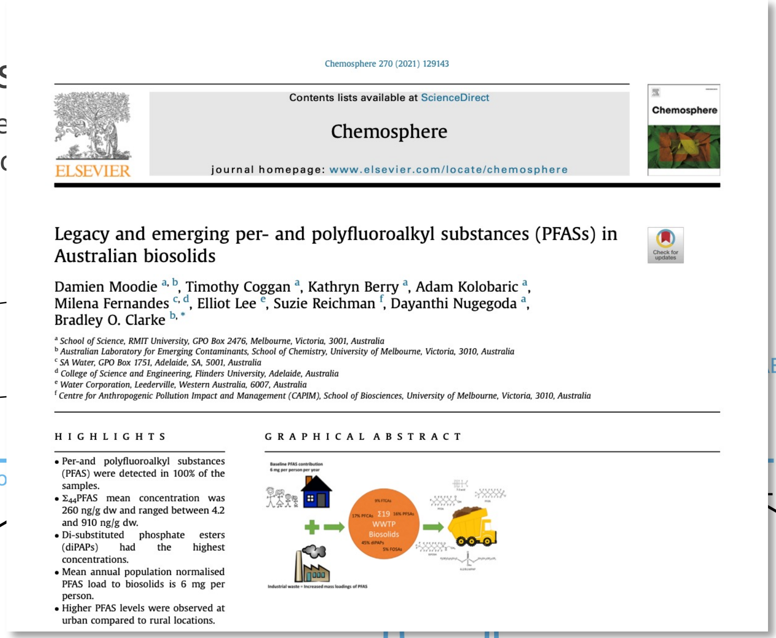

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Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Australian biosolids

Damien Moodie [a, b], Timothy Coggan [a], Kathryn Berry [a], Adam Kolobaric [a], Milena Fernandes [c, d], Elliot Lee [e], Suzie Reichman [f], Dayanthi Nugegoda [a], Bradley O. Clarke [b, *]

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[d] College of Science and Engineering, Flinders University, Adelaide, Australia
[e] Water Corporation, Leederville, Western Australia, 6007, Australia
[f] Centre for Anthropogenic Pollution Impact and Management (CAPIM), School of Biosciences, University of Melbourne, Victoria, 3010, Australia

HIGHLIGHTS

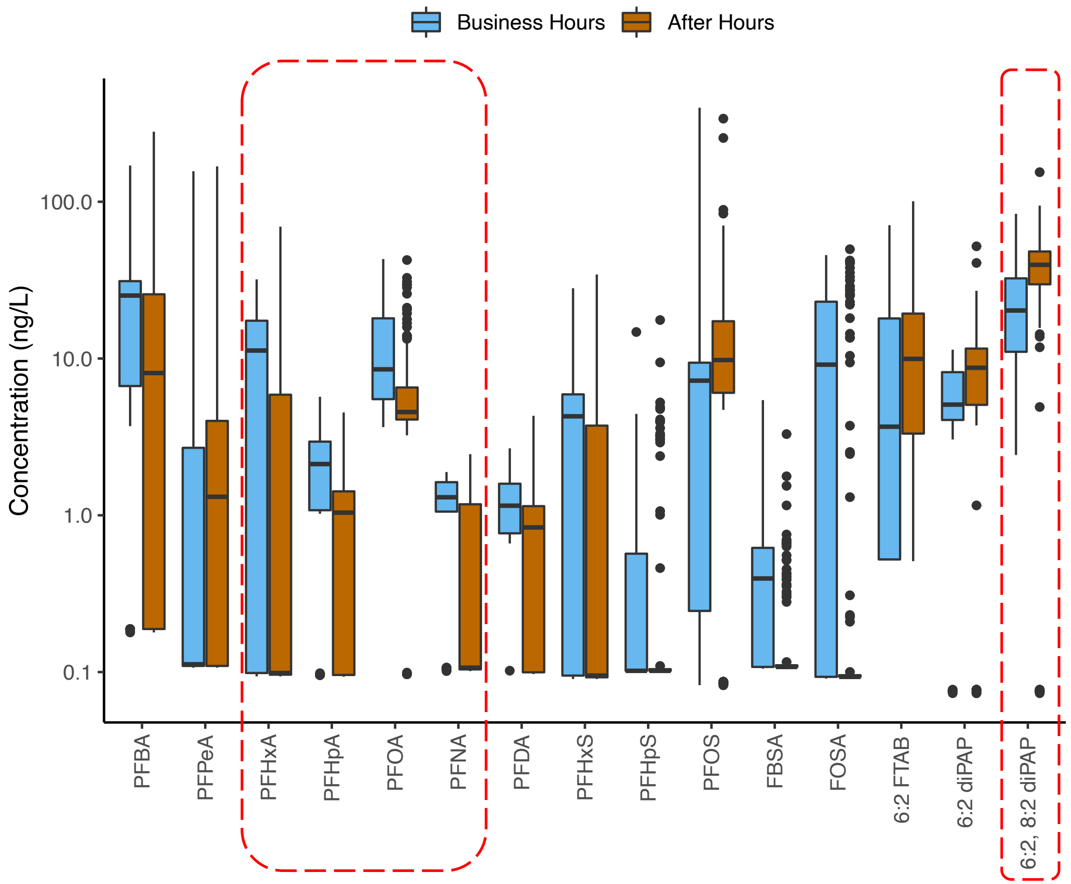
- Per-and polyfluoroalkyl substances (PFAS) were detected in 100% of the samples.
- Σ_{44}PFAS mean concentration was 260 ng/g dw and ranged between 4.2 and 910 ng/g dw.
- Di-substituted phosphate esters (diPAPs) had the highest concentrations.
- Mean annual population normalised PFAS load to biosolids is 6 mg per person.
- Higher PFAS levels were observed at urban compared to rural locations.

GRAPHICAL ABSTRACT

Variability in WWTP Sampling

Potential Sampling Bias

Difference in concentrations for most frequently detected compounds between Business Hours (9AM – 5PM, Mon – Fri) and After Hours.



PFASs in Australian Birds

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Albert Park and Lake

40,000 ya
Corroboree

1864
Public Park

1890s – 1950s
Municipal Tip

WWII
ADF Site

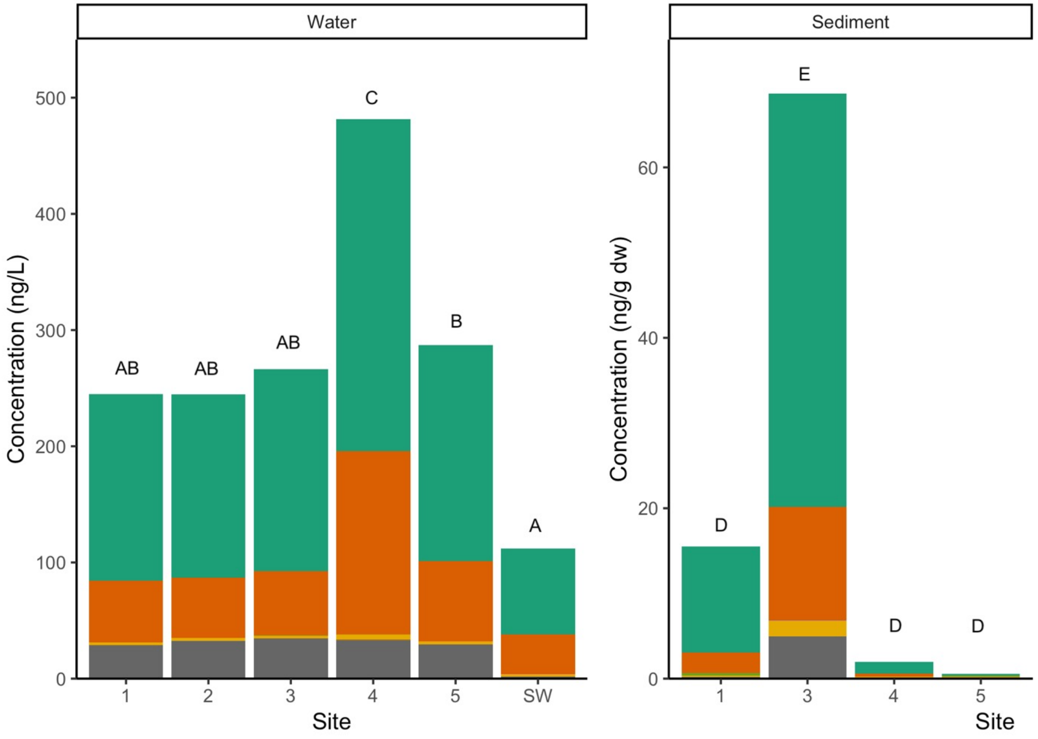
1996
Formula One Circuit

2008
Stormwater Diversion

Results

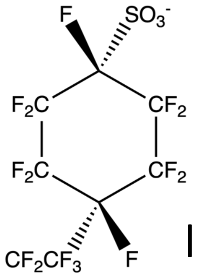
Environmental PFAS

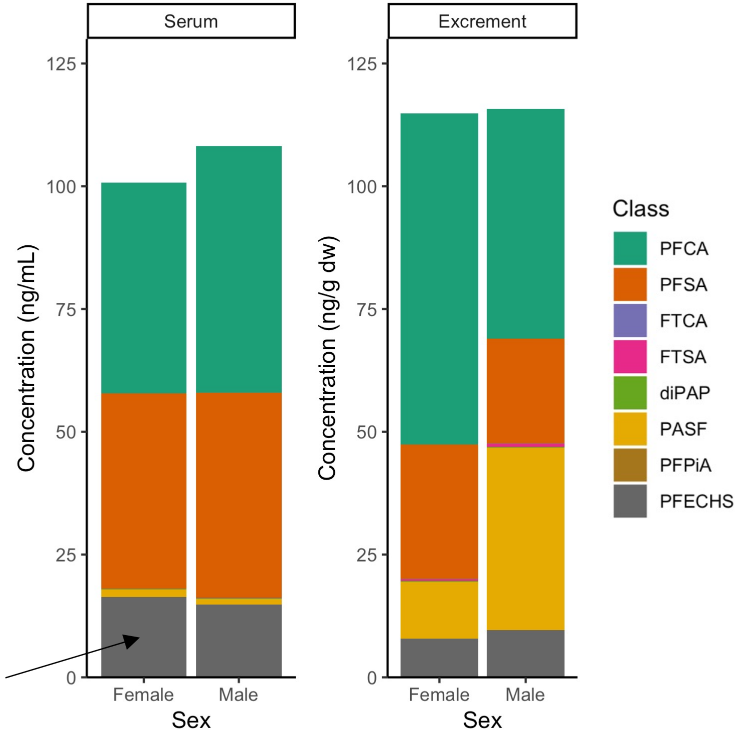
Concentrations of PFCAs, PFSAs and PFECHS are elevated in water and sediment from Albert Park Lake.



Biological PFAS

Exposure has led to equally elevated PFAS concentrations in swan serum and excrement.



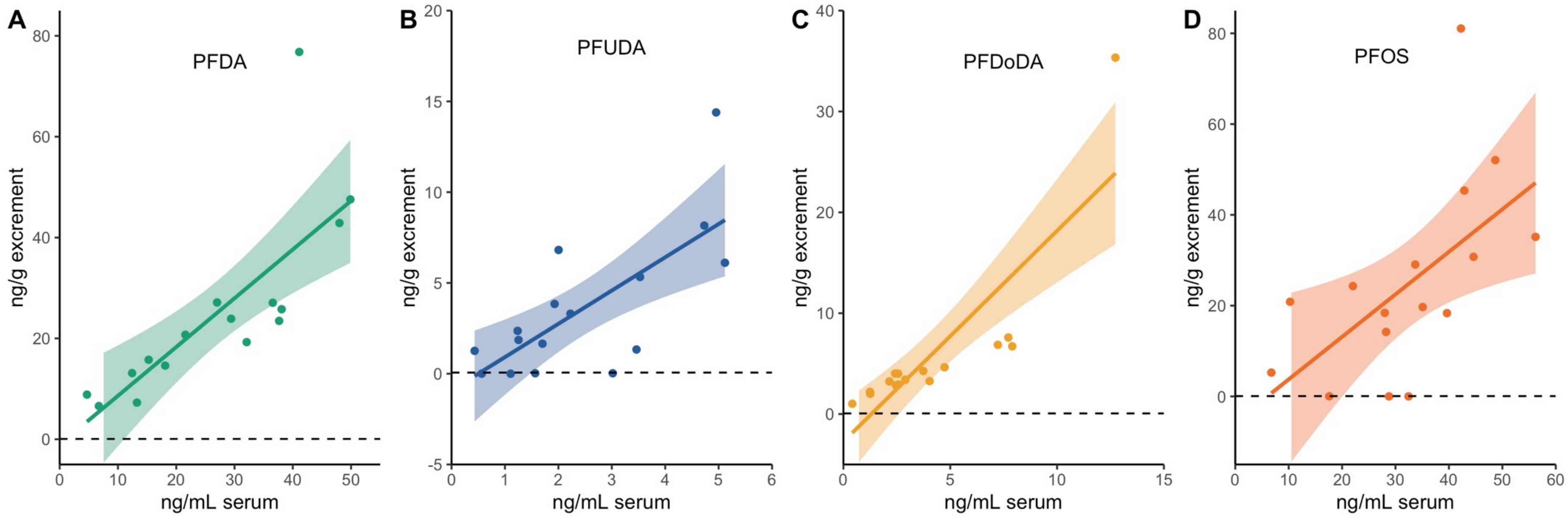


log BAF = 2.8 L kg^{-1}

Excrement as Indicator

Serum vs. Excrement

Concentrations of four PFAS, including long-chain PFCAs and PFOS, in excrement are a good indicator for total body burden with potential for less invasive biomonitoring applications.



PFECHS in surface water

Great Lakes
Water: 0.16 to 5.65 ng L^{-1}
Whole Fish: <0.10 to 2.5 ng g^{-1} ww
log BAF: 2.8 L kg^{-1}
De Silva *et al* (2011)

Hamilton
Water: 1.7 to 20.0 ng L^{-1}
Amphipod: 0.05 to 30.6 ng g^{-1} ww
log BAF: 2.72 L kg^{-1}
de Solla *et al* (2012)

Montreal
Water: 1.11 to 1.23 ng L^{-1}
Houde *et al* (2014)

Beijing
Water: <0.13 to 195.1 ng L^{-1}
Sediment: <0.28 to 1.86 ng g^{-1} dw
log K_d: 1.74 L kg^{-1}
Whole Fish: 36.43 ng g^{-1} ww
log BAF: 2.67 L kg^{-1}
Wang *et al* (2016)

Canada Ice Cap
Water: 0.020 ng L^{-1}
MacInnis *et al* (2017)

Resolute Bay
Water: 0.05 to 4.3 ng L^{-1}
Invertebrates: 0.29 to 0.32 ng g^{-1} ww
Lescord *et al* (2015)

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Sources of PFAS to Albert Park Lake

Final Thoughts

Future of PFASs in birds

Overall, peer-reviewed literature on the occurrence of PFASs in wildlife from the southern hemisphere is lacking, particularly birds.

Populations near sources of PFASs, such as *wastewater treatment plants* and *defence sites*, are more at risk and need to be monitored.

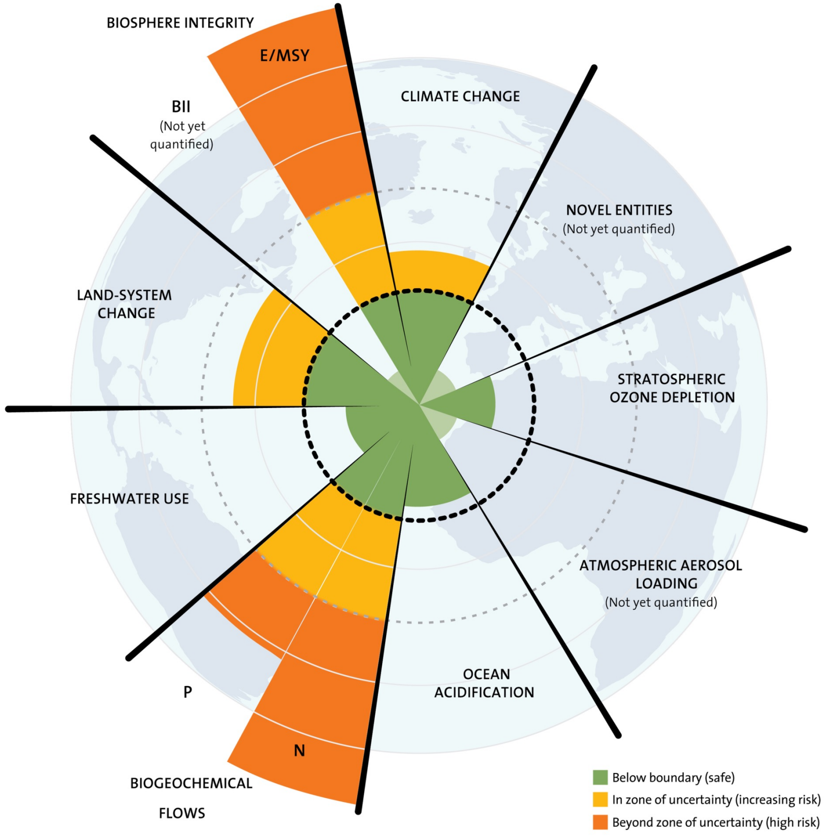
Consumption of waterfowl can pose a risk to human health in areas where hunting is permitted.

The total risk of PFASs to the adult birds are unknown due to lacking toxicological data.

Global Context

Planetary Boundaries

Introduction of Novel Entities into the global environment is currently not well understood. Impacts of PFASs are firmly in this category.



Adapted from Steffen *et al* 2015. *Science*

ALEC Class of 2021

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Jerry Zweigenbaum

Aus Team
Thomas Hennessey
Eric Li
Damian Pomeroy
Dragan Krsta (formerly)

Kris Coventry

ALS Global
Jason Glenn
John Tarascio

Green Lab
Beth Finger

Kathryn Hassel
Andrew Harford
Tom Cresswell

Carolyn Bellamy

Adrift Lab
Jennifer Lavers
Peter Puskic