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PFAS: An update on the Science and Toxicity

Tonkin + Taylor



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A simple name for a complicated family

- Extensive family of chemicals with a broad range of applications.
- Multiple PFAS definitions exist to try and capture the scale of the family (> 10,000 chemicals)
- Environmental behaviour varies with fluorinated chain length and functional groups
- Degradation rate of precursors. Low mobility
 PFAS can transform overtime to higher mobility
- PFAS are pervasive across most waste streams and environmental media.



PCA of PFAS partitioning behaviour, Poyang Lake, China. Reproduced from Tang et al., 2022.







Short-chain (C4-C6) PFAS: PFBS, PFBA, PFPeA, PFHxA, 5:3FTCA and precursors

Ultrashort-chain (>C4) PFAS: TFA, TFMS, PFPrA



PFOS, PFOA and PFHxS – Above the waterline

- Major source is presence C8 fire-fighting foams (AFFF), range of other sources.
- High persistence and long clearance times in humans.
- Method improvements allowed detection of soil, water and food contamination.
- PFOS and PFOA in 100% of tested NZ adults (means: 2.4 ng/ml PFOA, 3.4 ng/ml PFOS; Coakley et al., 2018,).
- First NZ contamination related to AFFF use publicly notified in Dec 2017.
- PFOS, PFOA, PFHxS listed under Stockholm Convention as POPs.
- C8 AFFF to be fully phased out in NZ by 2025.



Please contact the Taranaki DHB Public Health Unit on 0508 834 274 (freephone) or email Health.Protection@tdhb.org.nz if you regularly eat fish or eels from these streams and are worried about your health

TARANAKI District Health Board





Evolving toxicological limits





How low is the USEPA PFOA reference value?





Evolving/diverging toxicology - PFOA

<u>Upto 2016</u>

Tox based on rodent studies: EU: Liver damage; US and Au/NZ: foetal toxicity;

Clearance: rats = 1 hour-6 days; humans 1.2-14 years. Extrapolated rodent doses to humans

Au/NZ/EU: No evidence causes human cancers;

US: Equivocal as to risk of cancer

Difference in health levels mostly from different safety factors



After 2016

EU: Human studies: reduction in vaccination response in infants to diphtheria (Germany),

US: Human studies: reduction in vaccination response in children to tetanus (Faroe Islands)

US: PFOA "Likely to Be Carcinogenic to Humans"





Are PFOA and PFOS immunotoxic?

FSANZ, 2021

- Studies challenged by weak and inconsistent findings,
- Potential for confounding with other immunotoxins, notably PCBs
- Uncertainty over clinical relevance.



• "immunomodulation is not currently considered suitable as a critical endpoint for quantitative risk assessment of PFAS".

Garvey et al., 2023. Expert panel of fourteen epidemiologists and risk assessors:

- All agreed the Faroe Islands studies should not be the primary basis for deriving PFOA/PFOS toxicity values
- PFAS immune epidemiology studies suffer from weaknesses in study design.
- Recommended that animal studies are strong for other health effects;
 "the immune endpoints should not be used for setting toxicity limits"



PFOA and PFOS carcinogenicity?

- Most data for PFOA only on highly exposed populations,
- One new study in 2021 on general population PFOA exposure and kidney tumours.
- PFOS reassigned to "Likely Carcinogen" in 2023. Based on one study of liver tumours in rodents.
- Human data for PFOS is mixed, often confounded by other PFAS being present

Study	Exposure Category					
Mastrantonio et al., 2018	No PFAS in water					
	PFAS in water					Hert
Shearer et al., 2020	0-4 ng/mL					(# 2)
	4-5.5 ng/mL					
	5.5-7.3 ng/mL				(⊢	
	7.3-27.2 ng/mL					
Vieira et al., 2013	0-3.9 ng/mL-yr					
	3.9-89 ng/mL-yr					
	89-198 ng/mL-yr				F	
	198-600 ng/mL-yr					⊢− ∎−−−{
	600-4679 ng/mL-yr					l
Barry et al., 2013	0-219 ng/mL-yr					•
	219-812 ng/mL-yr				H	
	812-5358 ng/mL-yr					
	>5358 ng/mL-yr					
Raleigh et al., 2014	0-29 pg/m^3				H	
	29-150 pg/m^3				-	
	150-790 pg/m^3					
	>790 pg/m^3					
Steenland and Woskie, 2012	0-515 ng/L-years		H			I
	515-1,057 ng/mL-yr					
	1,057-1,819 ng/mL-yr	m				
	>1,819 ng/mL-yr					
Consonni et al., 2013	<80.5 unit-yr				+	
	80.5-559 unit-yr				-	
	>560 unit-yr	-		 		-
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Log Bate Batic and 05% Confidence Interval by Study and Exposure Cat

Log rate ratios for human studies of PFOA and kidney cancer (reproduced from Bartell and Vieira, 2021).



Short-chain PFAS –the emerging problem

- C8 PFAS phase out led to replacement with short-chain PFAS.
- C4-C6 PFAS precursors widely used in society (6:2 FTOH, diPAPs).
- PFAS profile has changed to short-chains in wastewater(Gellen et al., 2022). 23% increase/year in PFBS and 16% in PFHxA (2004-20; Cookson & Detwiler, 2022).
- US EPA report PFBS, PFBA, PFHxA, PFPeA above reporting limits in 6-7% of tested public water supply samples.



Short chain PFAS results in a survey of 131 groundwater wells Adapted from Close & Banasiak, 2023.



Short chain PFAS toxicity

- Anticipated to be cleared much faster in humans than PFOA/PFOS.
- Only US EPA to date has assigned draft/final toxicity reference values
- Potential for common toxicity across different PFAS
- US EPA: PFBS proposed to be added into a mixture assessment approach with PFNA, PFHxS and GenX.
- Other short-chain PFAS (e.g. 5:3 FTCA) have little toxicity data











- Very few studies on formation/occurrence. Potentially wide range of precursors and uses. Highly mobile.
- 5.5 ng/L of PFPrA in New Zealand drinking water and 5-13 ng/L in WW (Lenka et al., 2022)
- High groundwater concentrations associated with AFFF use and landfills (PFPrA: 53 μg/L; PFPrS 15 μg/L; Björnsdotter et al., 2019)
- Toxicity data lacking: ECHA assigned no effect level for TFA of 42 µg/kg bw/day



TFA in North European drinking water sources(adapted from Van Hees et al., 2023).





Profiles of the major PFAS classes (A), and the individual PFAS composition (B) in raw and treated water from 8 DWTPs around the Taihu Lake Basin, China . Reproduced from Jiao et al. 2022.

Concluding points

- PFOS, PFOA and PFHxS have emerged and now being globally phased out.
- Toxicological understanding still developing. Could continue to see divergent positions internationally
- Short-chain PFAS levels increasing, likely to be dominant profile in years to come.
- Short-chain PFAS could be increasingly detected in drinking water, risk assessment needs robust toxicity data.
- Emerging ultra-short chain PFAS. Little toxicity data currently available to judge the risk



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