Factsheet **Project 1121**

Global Water Research Coalition

Water Research AUSTRALIA

PFActS 3 | PFAS in Recycled Water

This is the third and final in a series of factsheets on per- and polyfluoroalkyl substances (PFAS) and their occurrence in catchments, waste streams, drinking water treatment and wastewater treatment and reuse. These factsheets have been designed to assist Australian and global water utilities navigate the risks, regulations, treatment options and monitoring recommendations specifically relating to PFAS. *PFActS 3* is specifically aimed at recycled water providers (RWPs) operating wastewater treatment plants (WWTPs), either municipal or industrial, which produce and supply recycled water for various end uses.

What are PFAS?

PFAS refers to Per- and polyfluoroalkyl Substances that represent a large range of chemicals that historically have been used in applications such as non-stick coatings, textiles, paper products and firefighting foams. Sharing a common structural element of a partial (poly-) or fully (per-) fluorinated carbon chain, these compounds are highly resistant to biological, thermal and chemical degradation, allowing them to persist in the environment and resist removal by the majority of water and wastewater treatment processes.

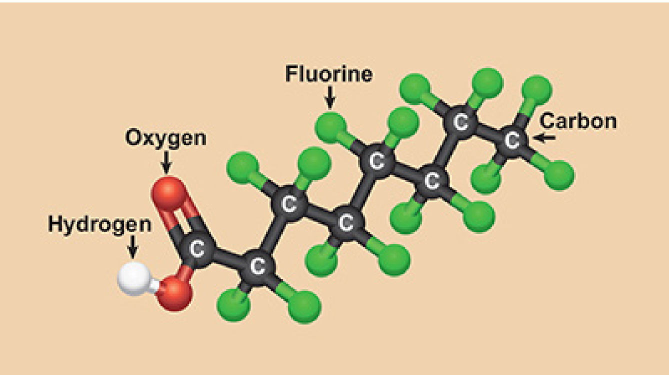

Figure 1 - Perfluorooctanoic acid (PFOA). Image credit: https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm

In general, the vast majority of studies into PFAS substances which have informed global advisory and regulatory limits of PFAS in drinking water, environmental waters and recycled waters are generally focussed on either specific subsets of PFAS chemicals or individual compounds. The most common are listed in Table 1:

Table 1 – Commonly studied PFAS compounds, groups and acronyms

Compound/Subset	Acronym	Notes
Perfluoroalkyl Acids	PFAAs	Covers all of PFHxS, PFOA, PFOS and others
Perfluorinated Carboxylic Acids	PFCAs	PFOA is included in this subset
Perfluorohexanesulfonic Acid	PFHxS	
Perfluorooctanoic Acid	PFOA	
Perfluorooctanesulfonic Acid	PFOS	
Perfluoroalkylsulfonic Acids	PFSAs	PFHxS and PFOS included in this subset
PFHxS/PFOA/PFOS	PFAS3	Refers to three most commonly studied compounds

Information on PFAS in the environment and PFAS in drinking water production can be found in *PFActS 1* and *PFActS 2*, respectively. The ability of PFAS to bioaccumulate combined with uncertainties surrounding long term health and environmental effects make analysis of PFAS risks in recycled water applications particularly challenging. Many applications will require extensive sampling and analysis programmes to quantify PFAS transport throughout receiving environments, and modelling to forecast accumulation rates and inform safe application lifespans which will not result in PFAS levels exceeding guideline values. *PFActS 3* aims to introduce these concepts and provide guidance and resources for RWPs facing PFAS challenges.

PFAS in recycled water and receiving environments

As discussed in more depth in *PFActS 1*, there are four major sources of PFAS: fire training/fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids. Other point and diffuse sources of PFAS exist, and may be significant locally, but generally are expected to be small by comparison to these main four sources[1].

Of high concern to RWPs is the observation that PFAS levels often ***increase*** across WWTPs, with the processes commonly employed for nutrient/contaminant removal also responsible for the oxidation of PFAS precursor compounds into persistent PFAS3 compounds or similar perfluoroalkyl compounds [2] [3]. PFAS can also adsorb and desorb from solids and concentrate in biosolids[2], adding another layer of complexity to risk management and considerations for biosolids applications.

A 2019 study of 19 Australian WWTPs[3] highlights these challenges, finding that several PFAS compounds, including PFOA, increased

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significantly between influent and effluent waters, and linking such increases to the presence of a range of precursor compounds and the amount of trade waste being accepted by the WWTPs. Similar studies conducted on six WWTPs in South Africa with differing treatment processes and influent properties found that PFAS removals varied from 52 – 97% overall, and also noted an increase in PFOA and PFOS across some of the plants[4]. It is worth noting that the highest removals of PFAS were seen in plants with tertiary/advanced treatment processes such as ozonation/activated carbon filtration/nanofiltration/reverse osmosis.

Similar research into aquifer health below irrigation districts serviced by recycled water found that PFAS levels in the groundwater, particularly around the centre of the irrigation district, had risen to above background levels and were comparable to WWTP effluent levels[5]. These findings show that not only human health concerns, but also environmental health and sustainability must be considered in recycled water applications. In Australia, the PFAS National Environmental Management Plan[6] is an excellent resource for RWPs conducting site risk assessments; other guidelines and resources are also available for many jurisdictions[7].

Unlike potable water applications, where a utility can refer to local advisory PFAS levels in finished water as a target and implement risk management strategies to assure these targets are met, the situation for RWPs is complicated by the need to consider long term PFAS accumulation, proliferation and routes to human ingestion. This means that RWPs will need to have detailed knowledge of PFAS levels in soils, aquifers, and surface waters in the receiving environment. Due to the persistence of PFAS, they are found in soils around the world in varying levels, with results of a global survey given in Table 2[8].

Table 2 – PFCA and PFSA levels in global soils

Continent	Range PFCAs (includes PFOA), µg/kg dry soil	Range PFSAs (includes PFOS and PFHxS), µg/kg dry soil	Average PFCAs (includes PFOA), µg/kg dry soil	Average PFSAs (includes PFOS and PFHxS), µg/kg dry soil
North America	0.15 – 6.08	0.04 – 1.99	1.82	0.41
Europe	0.006 – 3.64	0.00 – 3.27	1.00	0.81
Asia	0.13 – 14.30	0.08 – 0.42	4.71	0.18
Africa	0.12 – 1.49	0.00 – 0.14	0.55	0.07
Australia	0.08 – 1.26	0.04 – 0.30	0.67	0.15
South America	0.03 – 0.32	0.03 – 0.05	0.14	0.04
Antarctica	N/A (n = 1)	N/A (n = 1)	0.19	0.01

Further information on PFAS levels in global surface and groundwaters can be found in *PFActS 1*.

PFAS risks and advisory guidelines for recycled water providers

RWPs are encouraged to conduct their own risk assessments based on the proposed end use for their product. Given that PFAS represents a chemical risk, appropriate resources for management of such risks in recycled water applications are available, with the US EPA[9], European Union [10], and a multidisciplinary Australian council [11] having published extensive guidelines. In addition to routine sampling and testing, other control measures could include identification of major contributors and ensuring trade waste agreements are sufficient to control the volumes of PFAS entering waste waters that are processed by RWPs. It may be that large polluters require pre-treatment onsite prior to discharge to ensure that the onus for PFAS control does not fall on RWPs.

It is important to note that not only PFAS need to be considered in risk assessment sampling protocols; as discussed there are a wide range of precursor compounds which ultimately degrade to PFAS in receiving environments and across WWTPs. Most commercial environmental testing laboratories can now offer analyses that cover both a suite of common PFAS compounds and a total organic precursor assay (TOPA) to identify compounds which may increase PFAS levels upon degradation.

Common uses of recycled water[12] and the potential PFAS risks associated with each use are given in Table 3. Based on the risks associated with each application, relevant local guidelines for advisory PFAS levels in soils, surface and groundwaters can be found using the ITRC database described in *PFActS 2*. For any PFAS risk assessment, the most important outcome is to ensure that the application does not lead to the advisory tolerable human consumption guidelines being exceeded. Presented in Table 4, these vary globally, and are extrapolated from studies conducted on animals and hence guidelines for best practice rather than legislated limits. It is also important to consider the health of the receiving environment, and the potential for the application to introduce or increase PFAS in otherwise healthy environments.

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Table 3 – PFAS risks associated with common recycled water applications

Recycled Water Use	Potential PFAS risks
Agricultural	Human consumption Groundwater leaching Environmental
Forestry	Environmental Groundwater leaching
Non-potable urban uses	Human contact (likely low risk)
Industrial	Environmental (cooling water discharge receiving waters) Human contact (in textiles etc)
Fisheries	Human consumption
Recreational	Human contact
Environmental	Terrestrial biota Freshwater organisms Marine organisms
Residential	Human contact
Landscape irrigation	Human contact Groundwater leaching Sensitive receiving environments
Fire control	Environmental/ Run-off Groundwater leaching

Table 4 – Global recycled water and human consumption guidelines for PFAS3

	Tolerable Daily Intake (µg/kg/day)			
Country	PFOA	PFHxS	PFOS	Notes
Australia [13]	0.16	0.02	0.02	One of few countries with PFHxS guidelines; ΣPFOS + PFHxS < 0.02
US [14], [15]	0.02	None	0.02	Oral non cancer reference dose ΣPFOS + PFOA < 0.02
Europe [16]	0.1	None	0.03	European Food Safety Authority
UK [17]	1.5	None	0.15	Likely to adopt European limits [18]

Practical guide for recycled water providers

Risk analysis exercises for a given recycled water application will follow a similar philosophy for those conducted for drinking water treatment, as discussed in *PFActS 2*. This is outlined below, with additional considerations for recycled water applications included. If RWPs require additional treatment processes to remove PFAS to acceptable levels, technologies are discussed in *PFActS 2*.

In general, a PFAS risk assessment for a RWP will involve:

1. Collate all relevant local regulatory and advisory guidelines and limits concerning PFAS. ***These will also need to include surface, groundwater and soil screening levels***.
2. Conduct sampling and PFAS analysis on raw water source(s) and finished waters, ***as well as receiving environments – surface and groundwaters, and receiving soils***.
3. Use results as input into risk analysis exercises to estimate the likelihood of producing finished water with PFAS levels close to or exceeding relevant guideline limits, ***or the tolerable daily intake where recycled water is used for irrigation***.
4. If action is required to lower PFAS risks, it would be preferable to investigate primary PFAS sources (industry/military/fire training sites/landfill) within the catchment and assess measures to minimise PFAS contamination of raw waters.
5. If additional treatment barriers are required for ongoing management of PFAS risks, conduct laboratory and pilot scale studies to identify optimum treatment technologies.
6. If possible, apply Hazard Analysis and Critical Control Point (HACCP) philosophy to new treatment processes such that they can be run within set operational parameters and deliver a verified and validated PFAS removal, minimising ongoing sampling and analysis costs.
7. ***Consider predictive modelling for PFAS accumulation in receiving environments to assess lifespan of recycled water application before risk of exceeding relevant advisory limits is approached***.

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Case Study – Risk Assessment of Recycled Water for Irrigation

The most difficult recycled water application which relates directly to human ingestion of PFAS is the use of recycled water for irrigation of stock feed and human food crops, as this application poses the risk of the tolerable daily intake levels of PFAS in humans being exceeded. Furthermore, the pathway of PFAS from recycled water to human consumption varies with soil type, crop type, and dietary habits; meaning the use of recycled water for irrigation poses variable risks.

A recent study was undertaken by WaterRA, led by Atura, to develop trigger points for investigation (TPI) for PFAS in recycled water for the protection of stock feed and human food crops [19]. The PFAS Exposure Model for Irrigation (PEMI) was developed to assess human exposure of PFOA, PFOS and PFHxS (PFAS3) via irrigation of animal feed and human food crops with recycled water. Using PEMI, it was found that irrigation of milk pasture crops and green vegetables posed the highest risks, with root vegetables also a moderate risk.

A TPI (trigger point investigation) was derived for recycled water (TPIRW) and soil (TPISOIL) that included all exposure pathways and an adjusted TPIRW that excluded the milk and green vegetable exposure pathways (i.e. highest exposure pathways). The adjusted TPIRW allows higher PFAS3 loads to be applied through irrigation for lower risk crops and products. However, an adjusted TPIRW also increases the soil concentration of PFOS and PFHxS to a level where the production of milk or green vegetables may be restricted in the future.

The 50-year exposure was considered appropriate for setting the TPIRW. Changes to this approach may be warranted in the future based on new information. Current efforts to restrict PFAS use should also lead to lower concentrations in recycled water within this time frame. The TPI proposed are summarised below in Table 5 [19].

Table 5 – Proposed trigger points for investigation (TPI) for median concentrations of PFOA, PFOS and PFHxS in recycled water

TPI	Years of application	Units	TPI A			TPI adjusted A		
			PFOA	PFOS	PFHxS	PFOA	PFOS	PFHxS
TPIRW	50	ng/L	122	22	10	122	34	14
TPISOIL	50	mg/kg	0.006	0.0025	0.00027	0.006	0.0039	0.00035

TPIRW50 = recommend medium-term trigger point for investigation. A TPIRW values are driven primarily by green vegetables and milk production, if these exposure routes are not relevant then the TPI adjusted value is appropriate to use, however, the soils concentrations may prevent change to these uses in the future. Both the TPIRW and TPISOIL should be used to assess site for irrigation with recycled water to ensure historical contamination is considered.

Based on the effluent quality of the 17 Australian WWTPs included in the study, it was found that 80% of recycled water source data supplied by water utilities would not exceed the TPIRW. However, further analysis is required for 60% of these sources to confirm this, due to limitations to the analytical data provided. For sites where recycled water has already been used for irrigation and PFAS3 concentrations in recycled water could have been historically high, the TPISOIL should also be assessed.

The fact that 80% of WWTP in this study could achieve the TPIRW based on the 50-year time frame indicates its likely to be an achievable, conservative TPI for the water industry, while providing medium-term protection that will allow the refinement of the PEMI and the TPI as the science for PFAS3 matures.

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References

[1] ITRC, "Environmental Fate and Transport of Per- and Polyfluoroalkyl Substances," [Online]. Available: https://pfas-1.itrcweb.org/fact_sheets_page/PFASFact_Sheet_Fate_and_Transport_April2020.pdf.

[2] C. Gallen, G. Eaglesham, D. Drage, T. Nguyen and J. Mueller, "A mass estimate of perfluoroalkyl substance (PFAS) release from Australian wastewater treatment plants," Chemosphere, vol. 208, pp. 975-983, 2018.

[3] T. Coggan, D. Moodie, A. Kolobaric, D. Szabo, J. Shimeta, N. Crosbie, E. Lee, M. Fernandes and B. Clarke, "An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs)," Heliyon, vol. 5, p. e02316, 2019.

[4] Water Research Commission, "WRC Report no TT 742/3/17: Emerging Contaminants in Wastewater Treated for Direct Potable Reuse: The human health risk priorities in South Africa," Water Research Commission, Gezina, South Africa, 2018.

[5] D. Szabo, T. Coggan, T. Robson, M. Currell and B. Clarke, "Investigating recycled water use as a diffuse source of per- and polyfluoroalkyl substances (PFASs) to groundwater in Melbourne, Australia," Science of the Total Environment, vol. 644, pp. 1409-1417, 2018.

[6] Heads of EPAs Australia and New Zealand (HEPA), "PFAS National Environmental Management Plan Version 2.0," HEPA, January 2020.

[7] Interstate Technical Regulatory Council , "ITRC PFAS Regulations, Guidance and Advisory Values," May 2020. [Online]. Available: http://pfas-1.itrcweb.org. [Accessed June 2020].

[8] K. Rankin, S. Mabury, T. Jenkins and J. Washington, ""A North American and Global Survey of Perfluoroalkyl Substances in Surface Soils: Distribution Patterns and Mode of Occurrence," Chemosphere, vol. 161, pp. 333-341, 2016.

[9] USEPA, "Guidelines for Water Reuse," USEPA, Washington, D.C., 2012.

[10] European Commission Joint Research Centre Institute for Environment and Sustainability, "Water Reuse in Europe: Relevant Guidelines, needs for and barriers to innovation," European Union, Luxembourg, 2014.

[11] N. R. M. M. C. A. H. M. C. Environment Protection and Heritage Council, "National Guidelines for Water Recycling: Managing Health and Environmental Risks," Environment Protection and Heritage Council, Natural Resource Management Ministerial Council, Australian Health Ministers' Conference, Canberra, 2006.

[12] Z. Chen, H. Ngo and W. Guo, "A Critical Review on the End Uses of Recycled Water," Critical Reviews in Environmental Science and Technology, vol. 43, no. 14, pp. 1446-1516, 2013.

[13] Australian Government Department of Health, "Health Based Guidance Values for PFAS," September 2019. [Online]. Available: https://www1.health.gov.au/internet/main/publishing.nsf/Content/2200FE086D480353CA2580C900817CDC/$File/HBGV-Factsheet-20190911.pdf. [Accessed June 2020].

[14] USEPA, "Fact Sheet: PFOA & PFOS Drinking Water Health Advisories," November 2016. [Online]. Available: https://www.epa.gov/sites/production/files/2016-06/documents/drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf. [Accessed June 2020].

[15] USEPA, "Technical Fact Sheet - Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)," November 2017. [Online]. Available: https://www.epa.gov/sites/production/files/2017-12/documents/ffrrofactsheet_contaminants_pfos_pfoa_11-20-17_508_0.pdf. [Accessed June 2020].

[16] European Food Safety Authority, "Contaminants Update: First of two opinions on PFAS in food," 2018. [Online]. Available: https://www.efsa.europa.eu/en/press/news/181213. [Accessed June 2020].

[17] United Kingdom Drinking Water Inspectorate, "Guidance on the Water Supply (Water Quality) Regulations 2000 specific to PFOS (perfluorooctane sulphonate) and PFOA (perfluorooctanoic acid) concentrations in drinking water," October 2009. [Online]. Available: http://www.dwi.gov.uk/stakeholders/information-letters/2009/10_2009annex.pdf. [Accessed June 2020].

[18] CL:AIRE, "Technical Bulletin 19: Managing Risks and Liabilities associated with Per- and Polyfluoroalkyl Substances (PFASs)," February 2019. [Online]. Available: https://www.claire.co.uk/. [Accessed June 2020].

[19] Water Research Australia, "PFAS Exposure Modelling and Trigger Points for investigation in recycled water irrigation applications. Executive Summary Project # 3043," Water Research Australia, Adelaide , 2020.