

POLY AND PERFLUORINATED ALKYL SUBSTANCES AND WASTEWATER TREATMENT PLANTS

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INTRODUCTION

Poly and Perfluorinated alkyl substances (PFAS) are a class of emerging contaminant which has been widely used for a wide range of products and purposes since the 1950s due to their unique surface activity properties.

Perfluorooctane (PFOA) and perfluorooctane sulfonate (PFOS) are the two of the best studied and well known PFAS compounds, but PFAS comprises a large group of compounds which include more than 3000 compounds (Wang *et al.*, 2017) (See Table 1). There are many different of classes or groups of PFAS but a majority of PFAS produced today fall into seven main classes which include perfluorinated carboxylic acids (PFCA), perfluorinated sulfonic acids (PFSA), perfluorinated phosphonic acids (PFPA), fluorotelomer alcohols (FTOH), fluorotelomer sulfonic acids (FTS), polyfluorinated alkyl phosphates (PAP) and perfluorooctane sulfonamide compounds (PFOSA). These different chemical functional groups confer PFAS compounds with different physical properties and allow them to be used for a variety of purposes ranging from stain repellent properties, waterproofing agent, ability to act as a wetting agent, floatation agents in mineral processing, household chemical additives and to be used as firefighting foams (3M, 1999).

Family	Class	Examples	Uses
Perfluoroalkyl acids (PFAA)	Perfluoroalkyl carboxylic acids (PFCA)	PFOA	Surfactant
	Perfluoroalkyl sulfonic acids (PFSA)	PFOS	Surfactant
Polyfluorinated alkyl substances	Fluorotelomers sulfonic acids (FTSA)	8:2 Fluorotelomer sulfonic acid (8:2 FTS)	Surfactant/AFFF
	Fluorotelomer carboxylic acid (FTCA)	6:2 Fluorotelomer carboxylic acid (6:2 FTC)	Immediate product
	Fluorotelomer alcohols	8:2 Fluorotelomer alcohol (8:2 FTOH)	Use for manufacturing PFCA and PFSA
	polyfluorinated alkyl phosphates (PAP)	Zonyl	Paper and Food packaging materials

Notes:

1. Modified from ITRC (2017) *Naming Conventions and Physical and Chemical Properties of Per- and polyfluoroalkyl Substances (PFAS)*. Accessed from https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_naming_conventions__3_16_18.pdf.

Due to their carbon backbone which is surrounded by fluorine atoms, PFAS compounds are relatively chemically inert, resistance to chemical and biological degradation and high temperature. However, the stability of these compounds means that certain PFAS compounds (i.e., PFCA and PFSA compounds) are highly persistence in the environment which leads to poorly reversible ecological exposure in some environments (particularly groundwater)(Wang *et al.*, 2017). PFAS compounds are highly water soluble which allows them to be transported on a vast distance (<5 km from source) and bind to proteins which means they can bioaccumulate in organisms and biomagnify within food chains.

PFOS was listed as a persistent organic pollutant (POP) of the Stockholm Convention in 2009 and PFOA has been proposed for listing.

SOURCES OF PFAS

The NEMP (HEPA, 2018) identifies many different industrial sources of PFAS, but unlike for organochlorine and organobromine substances (MfE, 1999, 2010), no national inventory of PFAS use has been undertaken for NZ. A national inventory of PFAS use has been conducted for Australia (PFAS, 2016) which indicates that the chromium electroplating industry, which uses of PFAS compounds as mist suppression, is the primary user of PFOS compounds in Australia and that the aviation and firefighting industries are relatively minor uses of PFOS compounds. Use of products containing PFAS compounds for water/oil repellent products, fabric and paper treatments, paints, varnishes, surface treatments, floor waxes, and cleaning products for commercial and industrials proposes are also likely to result in significant discharges to either Wastewater Treatment Plants (WWTP) and/or landfills. Landfill leachate can also be a source of PFAS compounds. Landfill leachate from municipal landfills can contain high concentrations of PFCA as well as PFOS compounds (PDP, unpublished data, 2018; EPA, 2018; Gallen *et al.*, 2017). Although landfill leachate can very high concentrations of PFAS compounds (between 73 and 25,000 ng/L (from Gallen *et al.*, 2017)) the relative volume of landfill leachate compared to other waste streams makes landfill leachate a relatively minor contributor to the overall WWTP PFAS load. Fielder *et al.* (2010) found that WWTP receiving trade waste inputs from industrialized catchments can have significantly higher PFAS mass loads than non-industrialise catchments. This data is to be treated with some cautions as the WWTP plants surveyed by Fielder *et al.* (2010) where within Minnesota, where unlike in NZ, significant product of PFAS compounds have occurred.

The presence of PFAS compounds in household products used for cleaning and washing (3M, 1999; Fielder *et al.*, 2010) means that domestic wastewater is likely to be a most significant source of PFAS compounds entering WWTPs in terms of mass loadings. However, it is possible the one-off discharges from the activation of fire deluge systems (such as the QANTAS Brisbane incident in 2017) could also mean that there could be transient peaks in PFAS concentrations are some WWTPs.

CONCENTRATION OF PFAS IN WWTPs

The concentration of PFAS discharged from WWTP can vary significantly from each WWTP depending on the number and types of industries within the catchment of the treatment plant. Table 2 shows the composition of PFAS compounds from two small wastewater treatment plants (less than 10,000 residents) with concentrations of PFAS compounds in wastewater discharges in Australia and the United States.

Table 2: PFAS compounds detected in WWTP effluent.			
Compound	NZ (2 WWTP)	Australia²	United States³
Perfluoroalkyl sulfonic acids			
PFPrS	<1	-	-
PFBS	2.2-63	-	
PFPeS	<1-1.4	-	-
PFHxS	3.1-10	20	>310
PFHpS	<1	-	-
PFOS	3.9 -22	25	>790
PFNS	<1 -6.3	-	-
PFDS	<1	-	>15
Sum of PFSA	<9.2-82.2		
Perfluoroalkylcarboxylic acids			
PFBA	<5-19	-	
PFPeA	4.8 -95	-	>0.35
PFHxA	7.3-50	18	>29
PFHpA	2.6-15	3.6	>1,050
PFOA	8.2-17	22	>4,300
PFNA	<1 -3.9	1.3	>8170
PFDA	<1.0	3.0	>10
Sum of PFCA	<22.9-200		
Telomer Sulfonic Acids			
4:2 FTS	<1.0	-	-
6:2 FTS	59	-	-
8:2 FTS	<1.0	-	-
<i>Notes:</i>			
1. Units are ng/L or parts per trillion			
2. Mean concentrations of effluent from Table 1 Gallen <i>et al.</i> , 2018			
3. Information from Rayne & Forest, 2009			

The concentration of the two New Zealand WWTP are similar to the mean of the 14 WWTP sampled by Gallen *et al.* (2018). Gallen *et al.* (2018) found PFHpA and PFOS at all 14 wastewater plants sampled which are also similar to our findings. Although in the two WWTP sampled within New Zealand the concentrations of PFCA were significantly higher than those observed in the 14 Australian WWTP. United States WWTP effluent generally also has higher PFCA concentrations than PFSA (Rayne & Forest, 2009). The higher levels of PFCAs in NZ WWTPs may be in part due to the transformation of unidentified precursor compounds into PFCAs (See Table 3 and Figure 1). The transformation of unidentified PFAS compounds within WTP has been observed in WWTP overseas (Gallen *et al.*, 2018). In some cases, the effluent PFAS concentration can exceed the influent concentration by a factor of

ten (Gallen *et al.*, 2018). Although the average increased in effluent PFAS in NZ was not as high as observed by Gallen *et al.* (2018) it is likely as manufacturers switch PFAS formulation to different types of PFAS compounds (see Table 3) this trend of higher concentrations of PFAS compounds in the effluent is expected to continue.

Table 3: Comparison of Influent and Effluent at two WWTPs.

Compound	Influent		Effluent		Change
	Plant A	Plant B	Plant A	Plant B	
Perfluoroalkyl sulfonic acids					
PFPrS	<1	<1	<1	<1	NC
PFBS	15	2	63	2.2	1.1-4.2
PFPeS	1.4	<1	<1	<1	Decrease
PFHxS	16	3.1	10	2.5	0.625-0.8
PFHpS	<1	<1	<1	<1	NC
PFOS	38	2.9	22	3.9	0.69-1.3
PFNS	6.3	<1	<1	<1	Decrease
PFDS	<1	<1	<1	<1	NC
Perfluoroalkyl carboxylic acids					
PFBA	19	<5	19	<5	1
PFPeA	61	2.6	95	4.8	1.5 – 1.8
PFHxA	37	3.2	50	7.3	1.35-2.28
PFHpA	15	<1	15	2.6	Increase
PFOA	9	1.4	17	8.2	1.9-5.9
PFNA	3.2	<1	3.9	<1	1.2
PFDA	<1	<1	<1	1.9	Increase

1. NC = Not calculated

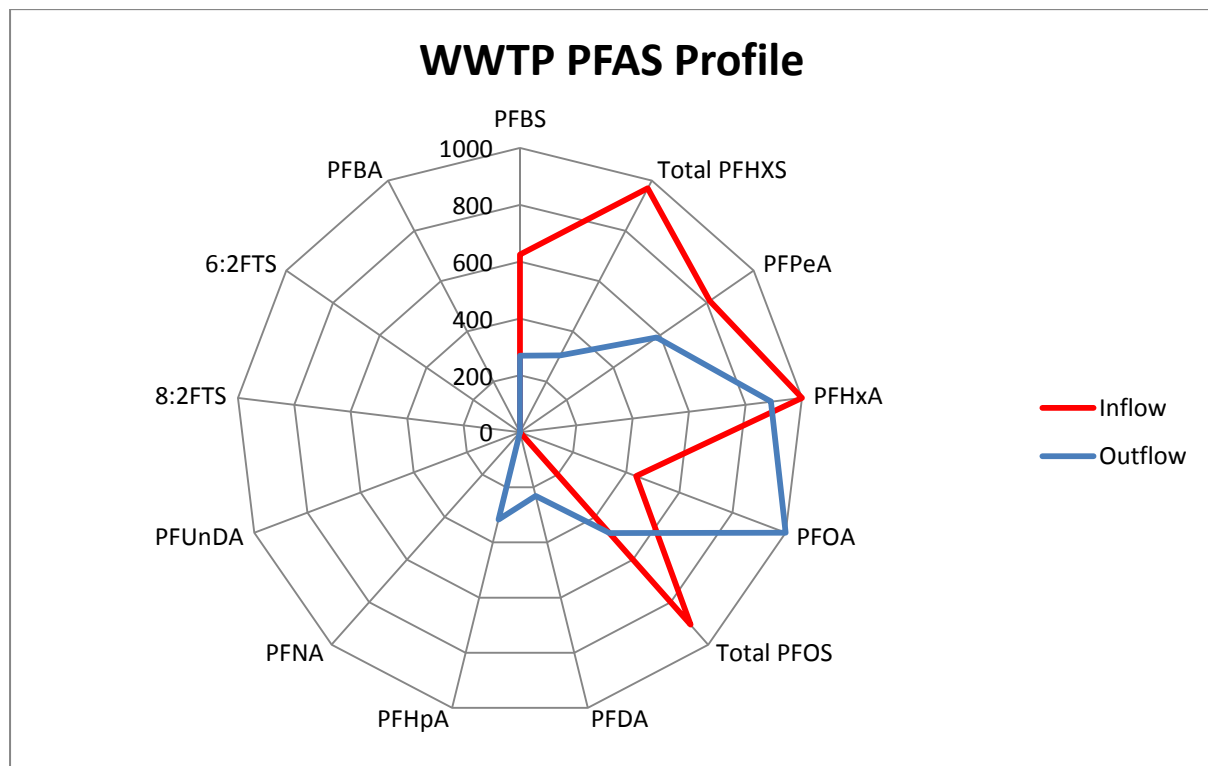


Figure 1. Comparison between PFAS concentration in influent and effluent from a WWTP.

TRANSFORMATION AND TREATABILITY OF PFAS WITHIN WWTPs

Polyfluorinated alkyl substances can be readily transformed into PFAAs under oxidizing conditions, particularly fluorotelomer alcohols found in many new AFFF firefighting foams. The transformation of polyfluorinated substances into terminal PFAAs is the why the concentration of PFAS substances in the effluent is higher than what is measured in the influent. Some estimates (Rayne and Forest, 2009) indicate that between 60 to 90% of the organofluorine mass entered WWTP is unquantified and therefore what happens to these compounds within WWTP is unknown. PFAA resist degradation and sorption onto sludge is they only mechanism likely to remove them from the wastewater (Rayne and Forest, 2009). Due to varying chain length and functional groups, PFAS compounds display a range of sorption preferential onto particulate matter (Gallen *et al.*, 2018). Shorter chain PFAS compounds and PFCA are less likely to bind to the particulate matter than longer chain PFAS compounds and PFSA (Gallen *et al.*, 2018). Short-chain PFAS (PFHxA, PFHxS, and PFHpA) show very poor removal efficiency by biosolids (less than 1%), while moderate chain length PFAS compounds (PFOA, PFOS, and PFNA) show moderate sorption to biosolids (9-36%) (Gallen *et al.*, 2018). PFAS compounds with the chain length of C10 or higher have a higher affinity towards biosolids than they do the liquid phase (Gallen *et al.*, 2018). This variety of properties and potential transformation makes treatment of PFAS compounds difficult. The global shift to short chain PFAS compounds and polyfluorinated compounds like GenX means that in future the treatability of PFAS compounds within WWTP.

ISSUES ASSOCIATED WITH PFAS

The lack of information and policy around managing PFAS compounds does pose a number of different issues for WWTP operators these include:

1. Disposal of Biosolids
2. Discharges limits when applying for consent renewals
3. Trade waste limits

Disposal of Biosolids

Current and proposed Guidelines for the land application of biosolids do not provide any guidance on the management of PFAS within biosolids. In the interim EPA (2018) has recommended interim limits for PFOS in biosolids of 0.3 mg/kg dry weight for unrestricted use and 4.2 mg/kg dry weight for agricultural land.

The development of new US EPA Leaching Environmental Assessment Framework (LEAF) Methods 1313 and 1316 as well as Australian Standard Leaching Procedure (ASLP) do

provide tools for assessing potential leaching from biosolids. However, there is a lack of policy and guidance for using these tools in New Zealand, and there is no clear methodology to incorporate these test methods into NZ EPA interim biosolid guidelines.

Discharge Limits of Wastewater Treatment Plants

There are currently draft recommendations for freshwater water quality guidelines for PFOS and PFOA within the PFAS National Environmental Management Plan (NEMP) (HERA, 2018). However, the lack of intergenerational toxicity testing is retarding the development of suitable marine water quality guidelines. Also, some PFAS compounds have shown the potential to bioaccumulate in fish. The ANZECC (2000) recommends that the 99% ecosystem protection level (0.000 23 ug/L for PFOS) is used for protection of aquatic ecosystems from bioaccumulation. However, there are three problems with this recommendation:

1. It may be below ambient background levels.
2. Some current laboratory analytical detection limits are not sensitive to measure that low.
3. Data for some species shows that the concentration of PFAS compounds below this value can result in fish tissue residues exceeding health-based guideline values for human consumers.

Bioaccumulation of PFAS compounds within fish species (Table 4) and watercress has been observed downstream of PFAS contaminated sites. It is possible that WWTP discharge of WWTP could also result in elevated PFAS tissue concentrations. Therefore it would be advisable test representative food species if there are food gathering areas downstream of WWTPs.

Table 4: Biota Sampling Results - Per- and Poly-Fluoroalkyl Substances (PFAS) - Freshwater Fish ^{1,2}								
Sample Results ⁴	Tissue Residues				Bioconcentration Factor ³			
	Species							
	Carp	Shortfin Eels	Longfin Eel ⁵	Bully	Carp	Shortfin Eels	Longfin Eel ⁵	Bully
Medium-chain PFAS Compounds								
PFBS	<LOR	<LOR	<LOR	<LOR	NC	NC	NC	NC
Sum of Total PFHxS+PFOS ^{6,7}	23 - 81	19 - 1600	30	13 - 17	NC	9 - 727	40	23 - 591
PFNS	<LOR	<LOR -20	<LOR	<LOR	NC	NC - 12500	NC	NC

Long-chain PFAS Compounds

PFBA	<LOR	<LOR - 0.56	<LOR	<LOR	NC	NC	NC	NC
PFHxA	<LOR	0.25 - 0.45	<LOR	<LOR	NC	1 - NC	NC	NC
PFOA	<LOR	0.37 - 0.69	0.35	<LOR	NC	9 - 69	4	NC
PFNA	0.31 - 0.96	<LOR - 4.3	0.5	<LOR - 0.4	NC	NC - 123	25	NC - 20

Notes:

1. All values in μ/L .
2. Results are shown as a range of minimum and maximum concentrations.
3. Bioconcentration Factor calculated by dividing tissue residue concentrations by surface water concentrations at the same locations.
4. Only selected compounds.
5. Result is from one sample only.
6. Total PFOS is calculated by summing monoethyl, dimethyl and linear isomers. Where an isomer is below the detection limit it is not added to the summation. This is following the method in the reported lab results.
7. Summations are made by adding compounds Total PFOS (7), Total PFHxS (3) together. Where one compound is below detection, it is not included in the summation.

<LOR
NC

Less than the Limit of Reporting

Not Calculated due to results less than the limit of reporting in fish and / or surface water samples.

Trade waste Limits

Current trade waste guidelines (NZS 9201.23:2004) do not have any limits for PFAS compounds but the Ministry for the Environment. However, EPA has proposed interim trade waste limits for PFAS compounds (See Table 5).

Table 5: Interim Tradewaste Discharge Limits

PFOS	0.1 ug/L
PFOA	0.1 ug/L
PFAS (total)	1 ug/L

Anecdotal evidence indicates that some trade waste discharges already exceed those limits (particularly for landfills) and some landfill is now refusing to accept PFAS contaminated soils. Also, newer generation PFAS compounds (Such as GenX, F35B, Zonyl) cannot be detected by analytical test available in NZ. The undetected mass of PFAS compounds can pose a problem for WWTP as these compounds could be potentially transformed into PFAA within the treatment plant and result in the elevated concentration of PFAS in the discharges from WWTPs. Total oxidisable precursor assay (TOPA) offer a means to assess the oxidisable PFAS load into WWTP but this test is still costly and not provided in NZ.

SUMMARY

Discharge of PFAS compounds from industrial and domestic sources are likely to result in the elevated concentration of PFAS in WWTP effluent. Current data suggests that wastewater treatment plants effluent are likely to similar to those seen in Australia. However, it is possible some WWTP which receive trade waste inputs for specific industries (i.e., chromium electroplaters) may discharge effluent which is higher than those reported so far observed in Table 2. PFAS concentrations at currently observed levels have the potential to accumulate in fish tissue downstream of WWTPs and it is possible that some species may exceed FSANZ guideline values.

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