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ASSESSMENT OF EMERGENT CONTAMINANTS IN BIOSOLIDS

Recommended PFOS and PFOA levels in biosolids for land application

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INTRODUCTION

Sewage sludge is a by-product of treating wastewater. Once the sewage sludge is sufficiently treated and complies with the relevant State or National guidelines, it is termed 'biosolids' and has a wide range of beneficial uses, including use in agricultural applications.

Over the last 25 years, Australia has successfully and safely developed a sustainable beneficial use program. Nearly 90% of the biosolids produced in Australia are now used as a fertiliser in agriculture or for land rehabilitation (Darvodelsky, 2015). Appropriate biosolids guidelines help to protect the receiving environment (Prichard, 2010).

The water industry is continuously monitoring potential emerging risks from new compounds to ensure biosolids use is safe. This review focusses on two compounds which have received significant attention around the world. Commonly called PFOS and PFOA these acronyms refer to perfluorooctane sulphonate and perfluorooctanoic acid respectively.

PFOS and PFOA have been used in a range of common household products and specialty applications, including in the manufacture of non-stick cookware; fabric, furniture and carpet stain protection applications; food packaging; some industrial processes; and in some types of fire-fighting foam. For example, PFOS was the key ingredient in Scotchgard, a fabric protector until it was phased out in 2000 (3M, 2017).

There is no consistent evidence that exposure to PFOS and PFOA causes adverse human health effects (NSW EPA, 2017). However, there is growing concern based on the evidence from animal studies, and an emerging body of research. Given the persistence of these chemicals in the environment, potential health effects cannot be ruled out. It is therefore important to understand the level of PFOS/PFOA in biosolids.

NATIONAL BIOSOLIDS DATA

PFOS and PFOA are not presently regulated compounds in biosolids in Australia. As a result, there are no recommended safe limits for these compounds in biosolids. Nonetheless many utilities in the water industry monitor a wide range of unregulated compounds as a precautionary principal. During 2017, utilities were asked to share their data on PFOS and PFOA with the Australian and New Zealand Biosolids Partnership (ANZBP), and this was used as the basis for this review. A number of major utilities provided analytical results from over 100 samples from 13 different sewage treatment plants around Australia.

The overall results of the sampling and analysis program are shown in Table 1.

	PFOS	PFOA
Number of plants (#)	13	13
Number of samples (#)	109	98
Number of samples less than limit of reporting (#)	17	17
Median concentration (mg/kg)	0.003	0.002
Mean concentration (mg/kg)	0.021	0.003
Standard deviation (mg/kg)	0.062	0.007
Maximum value (mg/kg)	0.386	0.050
Minimum value (mg/kg)	0.001	0.001

Table 1: Summary of PFOS/PFOA levels measured in Australian biosolids

Of the samples, PFOS or PFOA was not detected in 17 of the biosolid samples. PFOA was generally found at concentrations lower than PFOS on most sites. Two sites (three biosolids samples) had PFOS concentrations at least ten times higher than the mean. These plants were known to have local contamination issues and the customers responsible have since been disconnected from sewer.

The results indicate that PFOS and PFOA are generally present in biosolids at detectable levels in Australia. There was variability in the limit of reporting that was achieved between the different laboratories used by the utilities contributing data.

SAFE LEVELS

The Australian Government Department of Health (2017) note there is no consistent evidence that exposure to PFOS and PFOA causes adverse health effects in humans. Nonetheless, as a result of concerns over potential risks from these compounds, the Department has set guidelines for safe levels which are reported in Table 2. These recommended safe levels form the basis of the analysis in this review.

Toxicity Reference Value	PFOS/PFHxS	PFOA
Tolerable Daily Intake (µg/kg/d)	0.02	0.16
Drinking Water Quality Guideline (µg/L)	0.07	0.56
Recreational Water Quality Guideline (µg/L)	0.7	5.6

Table 2: PFOS and PFOA Guideline values from Australian Government Department of Health (2017)

METHODOLOGY

Analysis of the risk posed by PFOS and PFOA in biosolids depends on how a person might be exposed to these compounds, commonly called 'exposure pathways'. For example, direct ingestion of biosolids is an obvious pathway for people who work closely with biosolids, however this is typically mitigated as workers take precautions to avoid ingesting biosolids particles.

In Australia, the National Environment Protection (Assessment of Contaminated Sites) Measure (NEPC, 1999), or NEPM sets out a clear method for assessing emerging contaminants (CRC CARE, 2014). This method was recently updated by the Federal Environmental Health Standing Committee (enHealth) and is used in this review as the basis for determining safe levels of PFOS and PFOA in biosolids.

This review examines two key exposure pathways:

› Direct ingestion of biosolids;

› Direct ingestion of soil in which biosolids have been incorporated.

It is considered in the context of Australian biosolids guidelines and use that these two exposure pathways are the highest risk pathways. It should be noted however that there is insufficient information on factors such as crop and animal uptake rates to accurately assess other exposure pathways. These pathways will be reviewed as data becomes available.

On the basis of:

a. these exposure pathways,

b. Department of Health recommended daily safe intake of biosolids (DoH, 2017), and

c. the NEPM/enHealth methodology;

this review calculates safe levels of PFOS and PFOA in biosolids suitable for unrestricted use, and for application to agricultural land.

The key steps to determine safe limits in biosolids are to:

1. Use the tolerable daily intake levels of PFOS and PFOA set by Department of Health;
2. Use the NEPM method to calculate the health investigation level for PFOS/PFOA in biosolids alone (direct ingestion);
3. Assume typical biosolids application rate, repeat application frequency and incorporation depth for biosolids applied to land;
4. Calculate allowable safe levels of PFOS/PFOA in biosolids applied to agricultural land.

It is notable that the NEPM methodology assumes that any single source of PFOS/PFOA (in this case biosolids) contributes a maximum of 10% of the total intake by any person. This assumption may be considered conservative, but recognises that an exposed individual may also consume PFOS/PFOA from other sources such as water, food and cookware (NSW EPA, 2017).

RESULTS

The results of the NEPM analysis to calculate recommended values for PFOS and PFOA in biosolids which are suitable and safe for unrestricted uses, such as soil replacement, are shown in Table 3.

		CHILD		ADULT	
Parameter	**Units**	**PFOS**	**PFOA**	**PFOS**	**PFOA**
Toxicity Reference Value	mg/kg/d	0.00002	0.00016	0.00002	0.00016
Ingestion Rate	mg/d	100	100	50	50
Health Investigation Level	mg/kg	0.3	2.4	2.8	22.4
Mean value measured in biosolids	mg/kg	0.021	0.003	0.021	0.003
Maximum value measured in biosolids	mg/kg	0.386	0.05	0.386	0.05

Table 3: Recommended maximum concentrations for PFOS and PFOA for the unrestricted use of biosolids

Table 3 shows that the limiting Health Investigation Level value for PFOS is 0.3 mg/kg of biosolids (dry weight) for child exposure. At this level a child ingesting 100 mg of biosolids per day would ingest 10% of the maximum daily amount of PFOS as recommended by the Department of Health. It is suggested that this level is an appropriate level for biosolids suitable for unrestricted use. In the New South Wales, Queensland, Australian Capital Territory, South Australian and Tasmanian biosolids guidelines, this would be the Class 'A' contaminant grade classification and for the National, Victorian and Western Australian terminology it is classified as contaminant grade 'C1'.

For the 13 treatment plants sampled as part of this review, the average level of PFOS measured in biosolids was around 7% of Health Investigation Level for children. The maximum level of PFOS measured at all plants was lower than the suggested Grade A or C1 level at all but two sites, which had a known history of PFOS contamination.

Table 3 shows that the limiting Health Investigation Level value for PFOA is 2.4 mg/kg for child exposure. At this level, a child ingesting 100 mg of biosolids per day would ingest 10% of the maximum daily amount of PFOS as recommended by the Department of Health.

For PFOA, the average concentration measured in biosolids was around 0.1% of the Health Investigation Level. The maximum level of PFOA measured was lower than the suggested Grade A or C1 level at all sites, with the maximum value approximately one fiftieth of the recommended health investigation level. This data indicates there is a low risk from PFOA in biosolids.

Additional calculations to determine safe levels of PFOS and PFOA in biosolids applied to land are based on soil bulk density of 1.4 tonnes per cubic metre, a 100 mm soil depth of incorporation when ploughing biosolids into the soil, and an assumed application rate of 20 tonnes of dry biosolids per hectare every five years. These assumptions give a dilution ratio of one part biosolids to 70 parts of soil.

The assumptions above and the NEPM analysis were then used to calculate recommended values for PFOS and PFOA in biosolids which are suitable and safe for restricted use, such as application to agricultural land. The values are shown in Table 4.

Parameter	Units	PFOS	PFOA
Health Investigation Level	mg/kg	0.3	2.4
Biosolids limit (restricted agricultural application)	mg/kg	4.2	33.6
Mean value measured in biosolids	mg/kg	0.021	0.003
Maximum value measured in biosolids	mg/kg	0.386	0.05

Table 4: Recommended Values for PFOS and PFOA in biosolids for use on agricultural land

In terms of the treatment plants sampled as part of this review, the average level of PFOS measured in biosolids was around 0.5% of the calculated safe biosolids level for agricultural use. The maximum level of PFOS measured was lower than the suggested safe level at all sites by a factor of about 11, including the two sites with a known history of PFOS contamination.

The average level of PFOA measured in biosolids was around four orders of magnitude lower than the calculated safe biosolids level for agricultural use. The maximum level of PFOA measured was lower than the suggested safe level at all sites, with the maximum recorded value approximately 0.1% of the recommended health investigation level.

It should be noted that the biosolids application assumptions are conservative. In discussion with major biosolids land application operators, typical incorporation depths are 150-400 mm and maximum repeat application rates are 10-15 tonnes per hectare every 3-5 years. This gives best practice dilution rates 3-4 times higher than presented in this review.

CONCLUSIONS

The conclusions of this review and analysis are:

1. PFOS and PFOA were detected in 92 out of 109 biosolid samples from 13 different Australian sewage treatment plants;
2. PFOS was detected above the NEPM Health Investigation Level (HIL) at two sites (3 out of 109 samples) which had known PFOS contamination issues. Average values of PFOS measured in Australian biosolids were around 7% of the calculated HIL;
3. The data shows that PFOS can occur at sites with contamination issues, and this highlights the need for further investigation and monitoring of PFOS in Australian biosolids;
4. The levels of PFOA detected in this review are significantly lower than Health Investigation Levels suggested by the Department of Health. This data suggests that there is little need to monitor PFOA in biosolids given the maximum measured value of PFOA was approximately 2% of the calculated Health Investigation Level.

RECOMMENDATIONS

It is recommended that limits for PFOS in biosolids be adopted as set out in Table 5 and reviewed regularly on the basis of further data on the levels of PFOS in biosolids.

Allowable use	Grading terminology	PFOS limit (mg/kg)[1]
Unrestricted use	A[2], C1[3]	0.3
Agriculture	C[2], C2[3], B[4]	4.2

Table 5: Recommended PFOS limits in biosolids for different end uses

Notes: (**1**) mg per kg of dry weight of biosolids, (**2**) NSW, QLD, ACT, SA guideline terminology (also TAS for Grade A), (**3**) National, VIC, WA guideline terminology, (**4**) TAS guideline terminology

It is recommended that PFOS is routinely measured in biosolids.

It is recommended that PFOA is not routinely measured in biosolids.

It is recommended that other exposure pathways for PFOS, PFOA and other PFAS be investigated as and when the necessary information becomes available.

It is recommended that sites with a known history or risk of PFAS contamination, monitor these compounds and their precursors on a case by case basis.

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THE AUTHORS

Paul Darvodelsky

Paul Darvodelsky sadly passed away on 24 June 2018. Paul was a chemical engineer with over 35 years' experience in the water industry. He specialised in process design and strategy with a specific focus on biosolids management. Paul was the most experienced biosolids management technologist in the region having completed over 30 major biosolids management strategies involving a total of over 25 million people. He was also involved in the design, construction, procurement, commissioning and operation of over 100 solids handling facilities throughout Europe and Australasia. For many years Paul was Chair of the Australian and New Zealand Biosolids Partnership, the industry's peak organisation for biosolids. He will be sorely missed.

Kelly Hopewell

Kelly is currently a process engineer at the City of Gold Coast, with over 15 years' experience in environmental science/engineering. She is passionate about finding innovative ways to cost-effectively treat sewage and produce fit-for-use recycled water and biosolids, and holds a position on the board of the Australian and New Zealand Partnership.