

## **Australian and New Zealand**

## **Biosolids Partnership**

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## **Assessment of Emergent**

**Contaminants in Biosolids** 

December 2017

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## **EXECUTIVE SUMMARY**

#### Background

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.

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 are short for perfluorooctane sulphonate and perfluorooctanoic acid.

PFOS and PFOA have been commonly used in 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 based on the evidence from animal studies and 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. None-the-less many utilities in the water industry monitor a wide range of unregulated compounds as a precautionary principal. During 2017, these utilities were asked to share with the ANZBP their data on PFOS and PFOA to be used as the basis for this review. A number of major utilities provided data from over 100 samples from 13 different sewage treatment plants around Australia.

	PFOS	PFOA
Units	mg/kg	mg/kg
Number of plants	13	13
Number of samples	109	98
Not detected	17	17
Median	0.003	0.002
Mean	0.021	0.003
Standard deviation	0.062	0.007
Maximum value	0.386	0.050
Minimum value	0.001	0.001

The overall results of the sampling and analysis program are shown in the table below.

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

Of the samples, 17 each did not detect PFOS or PFOA in the biosolids. PFOA was generally found in lower concentrations on most sites. PFOS was found at higher concentrations at two sites with known local PFOS contamination issues.

The results indicate that PFOS and PFOA are generally present in biosolids at detectable levels in Australia.

#### Safe levels

The Australian Government Department of Health (2017) notes that there is no consistent evidence that exposure to PFOS and PFOA causes adverse health effects in humans. As a result of concerns over potential risks from these compounds the Department has set guidelines for safe levels as set out in the table below. 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: 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 eating them.

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 likely the highest risk pathways., It should be noted however that insufficient information on factors such as crop and animal uptake rates, currently exists to accurately assess other exposure pathways.

On the basis of

- a. these exposure pathways,
- b. Australian Government Department of Health recommended daily safe intake of biosolids 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 used to determine safe limits in biosolids are:

- Use the tolerable daily intake levels of PFOS and PFOA set by Australian Government Department of Health;
- Use the NEPM method calculate the health investigation level for PFOS/PFOA in biosolids alone (direct ingestion);
- 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 the table below.

		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 values for PFOS and PFOA for unrestricted use biosolids

The table shows that the limiting Health Investigation Level value for PFOS is 0.3 mg/kg for child exposure. At this level a child eating 100 mg of biosolids per day would ingest 10% of the maximum daily amount of PFOS recommended by the Australian Government Department of Health. It is therefore suggested that this level is an appropriate level for a Grade A or C1 biosolids classification: biosolids suitable for unrestricted use.

In terms of the 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 bar two sites with 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 eating 100 mg of biosolids per day would ingest 10% of the maximum daily amount of PFOS recommended by the Australian Government Department of Health.

In terms of the treatment plants sampled as part of this review the average level of PFOA 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 recorded value approximately one fiftieth of the recommended health investigation level. This data suggests there is a low risk from PFOA in biosolids.

The results of the additional calculations to determine safe levels of PFOS and PFOA in biosolids applied to land are based on soil density of 1.4 tonnes per cubic metre, 100 mm 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 on part biosolids for 70 parts soil.

The assumptions above and the NEPM analysis were 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 the table below.

Parameter	Units	PFOS	PFOA
Health Investigation Level	mg/kg	0.3	2.4
Biosolids limit (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 two sites with a known history of PFOS contamination.

In terms of the treatment plants sampled as part of this review 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 a factor of 3-4 times higher than presented in this review.

#### **Conclusions**

The conclusions of this review and analysis are:

- 1. PFOS and PFOA occur in biosolids at detectable levels. PFOS and PFOA were detected in 92 out of 109 samples from 13 different Australian sewage treatment plants;
- PFOS was detected above the NEPM Health Investigation Level at two sites (3 out of 109 samples) with known PFOS contamination issues. Average values of PFOS measured in Australian biosolids were around 7% of the calculated HIL;
- 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 Australian Government Department of Health. This data suggests that there is little need to monitor PFOA in biosolids with the

maximum recorded value of PFOA being around 2% of calculated Health Investigation Level;

#### **Recommendations**

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

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

Table 5: Recommended PFOS limits in biosolids

mg per kg of dry weight of biosolids
 NSW, QLD, ACT, SA guideline terminology (also TAS for Grade A)
 National, VIC, WA guideline terminology
 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 of PFOS and/or PFOA contamination should monitor these compounds on a case by case basis.



Assessment of Emergent Contaminants in Biosolids <u>RESEARCH REPORT</u>

December 2017

#### **1. INTRODUCTION**

Biosolids are a by-product of the sewage treatment process. Every day, each person contributes around 50 grams of solids to the sewerage system. These solids are treated and managed at sewage treatment works.

The majority of biosolids produced in Australia are beneficially used in agriculture (Darvodelsky, 2011, 2015). The current body of scientific research and practical experience is that this approach is a safe, sustainable and responsible management of the organic matter and nutrients which are present in biosolids.

Other options for disposal of solids include discharge to the sea, land or air (burning). Broadly in Australia discharge to the sea or burning are not favoured approaches and so use or disposal to land are the most common ways of managing biosolids (Darvodelsky 2015). Disposal of biosolids to landfill is also not favoured as it wastes valuable nitrogen, phosphorus and organic matter and creates greenhouse gases (AECOM & ANZBP, 2012).

To ensure the protection of environment and public health, there are strict guidelines for managing biosolids land application, based on the state-of-knowledge at the time of their development. The ANZBP monitors developments in scientific research and concerns which may emerge about biosolids use as our understanding develops.

One area of concern is around new compounds which are used for a broad range of every day applications but are not regulated in the current biosolids guidelines. Some of these compounds have been identified to have potential environmental and/or human health impacts. As a proactive initiative the ANZBP has undertaken this survey to determine whether a range of these new compounds are actually present in Australian biosolids and, if so, whether they are present at levels of concern.

As concern about a number of emergent chemicals has increased over the years, it is timely to apply current techniques (e.g. chemical exposure risk assessment) to assess risks of biosolids land application in Australia. This will provide information on appropriate guideline limits for emerging contaminants and may help allay potential concerns over contaminant risks of land application and open up further end-uses of the product.

The aims of this review are to:

- Review existing literature and data on compounds of concern in biosolids
- Identify those compounds which may pose a risk to human health or the environment
- Gather data on the presence or otherwise in biosolids of the identified compounds
- Provide a better understanding of the potential risks of the beneficial use of biosolids on agricultural land
- Analyse the risks using risk assessment tools and develop safe values for biosolids land application
- Compare guideline values developed in this study to contaminant concentrations measured by Australian water utilities, to determine whether these compounds are found at levels of concern in Australia

#### **2. ACKNOWLEDGEMENTS**

The Australian & New Zealand Biosolids Partnership wishes to thank all those organisations who have contributed data, insight and expertise to this research project.

#### **3. LITERATURE REVIEW**

The stage of this review examined the available literature on compounds of concern, their potential presence in biosolids and possible levels in Australia and other places around the world.

The key this review sought to address is whether these compounds are present in biosolids at levels of concern.

#### 3.1 Emerging contaminants of concern

Clarke and Smith (2011) reviewed 'emerging' organic compounds in biosolids with the aim of identifying those that may be a risk for biosolids land application. The study identified compounds which may pose a risk on the basis of compounds that were known to be persistent in the environment, may bioaccumulate in food chains and may exhibit toxicity of endocrine disruption and then systematically ranked them according to selected risk based criteria.

The long list of organic compounds identified for review by Clarke and Smith were:

- antibiotics and pharmaceuticals
- benzothiazoles
- bisphenol A
- organotins (OTs)
- polybrominated diphenyl ethers (PBDEs)
- polychlorinated alkanes (PCAs)
- polychlorinated naphthalenes
   (PCNs)

- polydimethylsiloxanes (PDMSs)
- perfluorochemicals (PFAS)
- phthalate acid esters (PAEs)
- quaternary ammonium compounds (QACs)
- steroids
- synthetics musks
- triclosan (TCS) and triclocarban (TCC).

Of these, the emerging chemical class that was of most concern was perfluorochemicals (PFAS). The review highlighted that the degree of water solubility of this group means that they may get into water sources or be taken up by plants or animals.

The main two compounds of concern in the PFAS group are perfluororooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These compounds have been commonly used in 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 (3M, 2017).

Other compounds on Clarke and Smith's list were rated as lower risk and therefore less likely to cause concern than PFAS/PCAs or there were no data available to establish what risk, if any, is posed. The second-ranked chemical of concern was polychlorinated alkanes (PCAs), due to their potential to accumulate in biosolids. Whilst this report focuses solely on PFOS and PFOA, ANZBP continues to monitor and share new research into other compounds in this suite of chemicals of concern.

#### 3.2 What levels of PFAS have been found in biosolids?

The Clarke and Smith (2011) review gives a thorough analysis of literature available at the time, however, as shown in Table 6, the majority of references were from the USA, and there were no indications of published work on Australian biosolids at that time. Gallen et al. (2016) has since published Australian concentrations. This table has been condensed to only show the PFAS compounds. It should be noted that PFAS compounds are not manufactured in Australia (Committee, 2016).

Contaminant Perfluorochemicals	Country	Year	n	Mean	Min	Max	Reference
PFOS	USA	2001	12	0.58	0.06	3.12	3M Environmental Laboratory (2001)
	USA	2006	*	0.100	0.081	0.160	Schultz et al. (2006)
	USA	2006	10	0.031	b0.010	0.065	Sinclair and Kannan (2006)
	USA	2007	8	0.073	0.008	0.110	Loganathan et al. (2007)
	Denmark	2008	7	*	0.005	0.074	Bossi et al. (2008)
	Overall		37	0.196	0.005	3.12	
PFOA	USA	2001	5	0.049	0.002	0.244	3M Environmental Laboratory (2001)
	USA	2006	*	b0.003	*	*	Schultz et al. (2006)
	USA	2006	10	0.107	0.018	0.241	Sinclair and Kannan (2006)
	USA	2007	8	0.068	0.0083	0.219	Loganathan et al. (2007)
	Denmark	2008	7	*	0.001	0.020	Bossi et al. (2008)
	Overall		30	0.075	0.001	0.244	

Table 6 - Concentrations (mg/kg dw) of PFASs in the Clarke and Smith (2011) review in sewage sludge/biosolids

Latimer (2016) highlighted three potential emerging 'persistent organic pollutants' (POPs) that may be a risk in biosolids:

- Polybrominated diphenyl ethers (PBDEs)
- Hexabromocyclododecane (HBCD), and
- Perfluorooctanesulfonic acid and its salts (PFOS)

Latimer (2016) suggested that an appropriate limit for soil would be as low as 0.5mg/kg for PFOS.

Gallen et al. (2016) studied concentrations of selected organic contaminants in biosolids at wastewater treatment plants of a variety of sizes and locations in Australia. The study found

that the concentration of PFOS (0.011-0.37mg/kg) typically exceeded the concentration of PFOA (0.00026 – 0.030mg/kg). The highest concentrations of PFOS were detected at sites where sludge is stored in sludge lagoons or stockpiles for long periods, and the authors suggest that the additional degradation of organic matter in these processes, concentrates the persistent chemicals (Gallen et al., 2016).

#### 3.3 Where do PFAS come from?

PFAS compound are in everyday use and common in home and personal products. They include shampoo, soap, perfumes, toothpaste and fire retardants used in our electronic devices, clothes and a broad range of other products. These compounds are very effective for their intended use, but are thought to have an impact on human health or the environment if their levels are too high (NSW EPA, 2017).

In the USA, land-applied biosolids was found to be the most likely causes of PFAS contamination of agricultural land used for grazing cattle and crops in Decatur, Alabama (Harris et al., 2012). Investigations by the US EPA found that a number of industries in the catchment of the Decatur Utilities Dry Creek Wastewater Treatment Plant either manufacture PFAS or use PFAS as part of their manufacturing processes (USEPA, 2011).

PFAS are not manufactured in Australia, however, they have been imported for a number of uses including in the metal plating, aviation and photography industries and in the local manufacture of non-stick cookware (Committee, 2016). Perhaps the biggest potential source of environmental (typically ground water) contamination is that previously, PFAS were added to certain fire-fighting foams used in Australia. (NSW EPA, 2017)

Organic compounds including PFAS can be found in landfill leachate (Clarke et al., 2015). Leachate can be discharged to wastewater treatment and therefore the compounds potentially present in biosolids. Clarke et al. (2015) measured selected organic pollutants in leachate from five landfills in the USA and found that the mass of PFOA released in the leachate ranged from a low of 0.016 kg/year up to 0.606 kg/year (with an average of 0.16kg/year). Clarke et al. (2015) calculated this gives around 1.5mg PFOA/person/year across the USA. PFOS was much lower in concentration than PFOA, and was not detected at a number of sites, and therefore an estimate of annual load was not calculated.

A similar study of organic pollutants in landfill leachates was conducted in Australia (Gallen et al., 2016). This calculated much lower per capita contributions of 0.164 mg PFOA/person/year and 0.952mg PFOS/person/year. The study concluded that leachate is a 'relatively minor source of PFAS contamination' of land-applied biosolids.

ALS Environmental (2015) conducted a study where they tested for PFAS in landfill leachate samples. In this study, conversely to the previous leachate studies (Clarke et al., 2015; Gallen et al., 2016), PFOS was typically found at slightly higher concentrations than PFOA.

#### 3.4 Leaching of PFAS from different types of biosolids

The type of biosolids can have an impact on leaching of compounds from the biosolids. Gottschall et al. (2010) studied the difference between liquid and dewatered biosolids. The paper focused on fate of polybrominated diphenyl ethers (PBDEs), PFAS, and metals after land application. In Australia, biosolids is rarely applied to land in liquid form, however, some of the outcomes of the paper are still of interest.

After liquid biosolids application, the authors did not consider PFAS as a 'considerable loading risk' (Gottschall et al., 2010). Further, the two methods of applying the dewatered biosolids studied did not appear to significantly increase the metal loading to the drainage system according to the data presented (Gottschall et al., 2010).

#### 3.5 PFAS guidance in Australia and New Zealand

The Environmental Health Standing Committee (enHealth) of the Australian Health Protection Principal Committee released a statement in June, 2016, that outlines the reasons for their recommended interim values for PFOS/PFHxS and PFOA. The interim values can be seen in Table 7 below:

Toxicity Reference Value	PFOS/PFHxS	PFOA
Tolerable Daily Intake (μg/kg/d)	0.15	1.5
Drinking Water Quality Guideline (µg/L)	0.5	5
Recreational Water Quality Guideline (µg/L)	5	50

#### Table 7 - Guideline values from EnHealth (2016)

EnHealth (2016) consulted a number of international and national references and decided that as the European Food Safety Authority (EFSA) use a similar risk management approach to that used in Australia, the tolerable daily intake values used in Europe, can be applied to Australian risk assessments.

An independent review of the EnHealth interim health values was conducted by Bartholomaeus (2016), the focus of which was to assess the validity of the values, especially as USEPA values seemed stricter. The review investigated the background to the European and American approaches and concluded that *'the differences between the EFSA and US EPA assessments are not due to new data or information available to the US EPA that was not available to EFSA'* (Bartholomaeus, 2016). The adoption of the European tolerable daily intake values for PFOS and PFOA and the use of these to derive drinking water guidelines was considered 'appropriate' and 'consistent with current risk assessment practices', as an interim limit pending review by Food Standards Australia New Zealand (FSANZ) (Bartholomaeus, 2016).

In April, 2017, these interim guidelines were replaced with new guidelines from the Australian Government Department of Health shown in Table 8. The new values are roughly one tenth of the old values.

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 8 - Guideline values from DoH, 2017

#### 3.6 PFAS guidance in the USA

In response to an investigation of the contamination at Decatur, Alabama, the USEPA released in October 2009 residential soil screening guidance values of 16 mg/kg for PFOA and 6mg/kg for PFOS that are protective of children who might incidentally ingest soils during play, which is generally recognised as the highest risk exposure. (USEPA, 2011).

The soil guidance levels released by the USEPA are significant as they set a safe concentration limit for PFOA and PFOS in soils, based on the assumption that soil may be eaten directly.

#### 3.7 Methods for estimating health risk from chemical compounds

There are a range of methods for estimating the potential health risk from chemical compounds and all are based on how an individual might be exposed to the compound in question.

In Australia, the National Environment Protection (Assessment of Contaminated Sites) Measure (NEPC,1999) referred to as 'NEPM' contains important direction for assessing emerging contaminants (CRC CARE, 2014). The Human Health and Environmental Risk Assessment Framework originally developed by enHealth has a similar approach to the four WHO (2010) Toolkit steps, but includes a final Risk Management step.

enHealth has since refined the Framework and suggests that the more comprehensive model shown in Figure 1 should be used to provide a more structured approach to environmental

health risk assessments. The revised model expands on the previous model's five steps by adding stakeholder involvement and greater connection between the steps.



#### Figure 1: enHealth Revised Framework for Risk Assessments (NEPM, 1999)

As enHealth's most recent NEPM Framework model is the most comprehensive it is proposed that this model is used to assess potential risks, along with a number of exposure methods appropriate for biosolids land-application. The World Health Organisation (WHO) developed the Human health risk assessment toolkit: Chemical hazards (WHO, 2010). The framework requires four usual risk management steps: Hazard identification, Hazard characterisation, Exposure assessment and Risk characterisation.

In the context of biosolids risk assessments, Roccaro and Vagliasindi (2014) use five of the fourteen exposure pathways for 'highly exposed individuals' adopted by previous work by the USEPA (1995). The exposure pathways were chosen to establish the risk to humans from ten compounds found in personal care products, and establish 'reference soil/biosolid concentrations' to compare to measured concentrations in biosolids. The analysis showed that the risk to human health from these individual chemicals was low from these exposure pathways,

#### 3.8 Emerging compounds in the regulations

By their nature, emerging compounds which are of potential concern are not included in biosolids guidelines in Australia. In many cases it is not known what or if these compounds have an impact on human health or the environment. A further difficulty is even if there is a potential risk from a compound, safe levels of that compound are not necessarily known. Regulators are therefore playing 'catch-up' and the need for a precautionary approach is clear.

In Australia the ANZBP and numerous utilities monitor research and proactively investigate potential risks associated with biosolids and indeed, such is the purpose of this report.

Current, typical limits on compounds in biosolids are shown in Table 9 below. These are for all regulated compounds and is taken from the Queensland Department of Environment and Heritage Protection biosolids guidelines, which align closely with many of the existing State guidelines in Australia.

Quality share staristic	MCL (dry mass) in mg/kg				
Quanty characteristic	Grade A	Grade B	Grade C		
Arsenic	20	20	20		
Cadmium	3	5	20		
Chromium (total)	100	250	500		
Copper	100	375	2000		
Lead	150	150	420		
Mercury	1	4	15		
Nickel	60	125	270		
Selenium	5	8	50		
Zinc	200	700	2500		
Total Organic Fluorine	0.39	0.39	0.39		
DDT/DDD/DDE	0.5	0.5	1.00		
Aldrin	0.02	0.2	0.5		
Dieldrin	0.02	0.2	0.5		
Chlordane	0.02	0.2	0.5		
Heptachlor	0.02	0.2	0.5		
НСВ	0.02	0.2	0.5		
Lindane	0.02	0.2	0.5		
BHC	0.02	0.2	0.5		
PCBs	ND	0.3	1.00		

ND = PCB's not detected at a limit of detection of 0.2 mg/kg

 Table 9: Contaminant grading requirements in general beneficial use approval (DEHP, 2016) showing the

 Maximum Contaminant Limit (MCL)

In 2012, Western Australia updated its biosolids guidelines. On the basis of occurrence and risk the guideline regulates six compounds; cadmium, chromium (VI), copper, zinc, dieldrin and chlordane.

In December 2016, New Zealand Water released a draft 'Good Practice Guide for the Beneficial Use of Organic Waste Products on Land' for public comment. This is one of the most recent biosolids guidelines in the world. The guide lists the limit for compounds as shown in Table 10, below. These limits are intended to apply to the 95th percentiles for the data set, with no individual value from the data allowed to exceed the limits by > 20%, with any particular biosolids sample either being 'compliant' or 'non-compliant'.

Parameter	Concentration limit (mg/kg dry weight)
Arsenic	30
Cadmium	10
Chromium	1500
Copper	1250
Lead	300
Mercury	7.5
Nickel	135
Zinc	1500
Perfluoro compounds (PFOS and PFOA)	0.01
Absorbable organic halogens (AOX)	450
Polycyclic aromatic hydrocarbons (PAH sum)	5
Nonyl phenol and ethoxylates (NP/NPE)	25
Phthalate (DEHP)	75
Linear alkydbenzene sulphonates (LAS)	1500
Musks – Tonalide	15
Musks – Galaxolid	10
Linear arkydderizene suprionates (LAS) Musks – Tonalide Musks – Galaxolid	15 10

Table 10: Limits for contaminants in the draft New Zealand guidelines (Water New Zealand, 2016)

### 4. APPROACH

#### 4.1 General

The approach to this review included the following steps:

- Data gathering
- Use of NEPM safe exposure limits for compounds where these existed
- Use of the NEPM methodology for PFOA/PFOS in the absence of specific exposure limits for these compounds

The NEPM methodology includes the following broad phases:

- Phase 1 Problem formulation and definition
- Phase 2 Risk assessment
  - Hazard identification
  - Dose response assessment
  - Exposure assessment
  - o Risk characterisation
- Phase 3 Risk management

The problem has been defined as the potential risk of certain unregulated compounds in biosolids. Each of the other phases is described below.

#### 4.2 Data Gathering

This investigation relied on the cooperation of water businesses around Australia to provide data from their own monitoring programs.

An email request was sent to members of the Australian New Zealand Biosolids Partnership (ANZBP) to request access to their data on emergent contaminants and pathogens (see Figure 2: Request for input to research project.). A number of utilities contributed and their data was dereferenced (each plant given a letter instead if a name), and converted to the same units of measurement. As no data regarding pathogens was forthcoming, that part of the analysis was not continued.

Emerging chemicals of concern –
contribute to our biosolids research
the opportunity for these vital industries to come together and explore pressing issues and new innovations.
One of the key issues identified at this event was the recent emergence of a range of chemicals of concern which can now be detected in biosolids products. To date, monitoring activities examining the prevalence of these chemicals tend to indicate their concentrations are below levels which would impact on current biosolids management practices. However there is no consolidated national picture about what this data is telling us or a clear industry position on this suite of chemicals.
It was clear from discussions at the conference that this consolidation of data and clarity about the industry's stance on such chemicals would be hugely beneficial to the industry as a whole. Consequently, the Association's Australian and New Zealand Biosolids Partnership (ANZBP) has embarked upon a project seeking to address this issue.
The ANZBP is aware that a number of organisations have independently collected data on a range of chemicals of concem in biosolids. If you have undertaken such research, we ask that you make this data available to the ANZBP, enabling it to be consolidated into national pictures for Australia and New Zealand. From this, ANZBP will create an industry statement based on the most current and complete data set available.
ANZBP would keep all data confidential and no specific organisation, region or treatment plant would be identified in the subsequent position statement.
In particular we are seeking contributions of data on levels of the following compounds in biosolids found in either Australia or New Zealand:
PFOS and its salts (PFOA, etc)     Tricolosan
Poly brominated diphenyl ethers (PBDEs)     Hexabromocyclododecane (HBCD)
<ul> <li>Dowins/furans</li> <li>Any other compounds your organisation has monitored (which may include those listed on p3 of <u>this document</u> produced by the Water Environment Research Foundation)</li> </ul>
In order to support this work, please submit data and research insights (in any format) to the ANZBP Project Manager, Nicola Helme via <u>admin@hosolids.com.au</u> by <b>Sunday, 15 January 2017</b> . This project will be undertaken by ANZBP advisory board member, Kelly Hopewell of Gold Coast Water, therefore please address technical queries to <u>KHOPEWELL@goldcoast.gld.gov.au</u> .
We hope you will be able to support this initiative to further the collective knowledge of the biosolids industry, ensuring we are able to address any potential risks posed by emergent chemicals of concern in a timely, well informed and proactive manner.
Regards,
Jonathan McKeown CEO – Australian Water Association
Paul Darvodelsky Chair – Australian and New Zealand Biosolids Partnership Advisory Board

Figure 2: Request for input to research project.

#### 4.3 Risk Assessment approach

For compounds which already have safe exposure limits under the Hazard Investigation Level A (Low Density Residential) exposure scenario (NEPM, 1999) these were used in the assessment with a 'dilution factor' for biosolids incorporated into soil.

As there are no specific limits for PFAS, a contaminant risk assessment of PFOS/PFOA was conducted using the methods and assumptions contained in the NEPM (1999). The approach used follows the Hazard Investigation Level A (Low Density Residential) exposure scenario (NEPM, 1999). The assessment used the interim tolerable daily ingestion rates established by EnHealth (2016) and the new guidelines by Australian Government Department of Health (2017).

#### 4.4 PFAS risk assessment approach

The risk analysis approach set out in NEPM has the following main steps:

- Hazard identification
- Dose response assessment
- Exposure assessment
- Risk characterisation
- Risk management

Each of these steps is discussed briefly below.

#### 4.4.1 Hazard Identification

The emergent chemicals of concern known as per- and poly- fluorinated substances (PFAS) have been identified as a potential hazard due to their persistence in the environment, in particular PFOS and PFOA.

Chemical name: Perfluorooctane sulfonate (PFOS)	Chemical name: Perfluorooctanoic acid (PFOA)
Molecular formula: C8F17SO3	Molecular formula: C8 H F15 O2
CAS number: 2795-39-3	CAS number 335-67-1

#### 4.4.2 Dose-response assessment

There is a poor understanding of the mechanism/s of adverse human health impacts from these chemicals, however, there is a body of evidence indicating impacts in animals, and therefore, negative outcomes cannot be ruled out.

The Environmental Health Standing Committee (enHealth) of the Australian Health Principle Committee have assessed available information from a number of sources and provided 'interim' guidance on appropriate safety limits. Food Standards Australia New Zealand (FSANZ) was then commissioned by the New South Wales Department of Health to develop final health based guidance values for per- and poly-fluoroalkyl substances (PFAS), which were released in April, 2017 and are set out in Table 11. These two guidance documents have been used as the basis for safe levels of PFAS.

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 11: Recommended safe levels for PFOS/PFOA Source: New South Wales Department of Health, 2017

#### 4.4.3 Exposure assessment

The exposure assessment looks at the pathway in which a person might be exposed to the compounds in question. PFAS have been found in a number of places and therefore, there are a number of potential exposure pathways for humans. Three main exposure pathways are identified in Table 12, below.

Exposed populations are more likely to be people living in areas with biosolids amended soils, or working with biosolids on a daily basis.

1	Food sources → Human	Food sources
2	Surface Water or Ground Water $ ightarrow$ Human	Human lifetime drinking surface water
3	Biosolids →Soil →Airborne Dust → Human	Adult human lifetime consumption of particles (soil/dust)
4	Biosolids →Human	Child human consumption of particles

#### Table 12: Exposure pathways identified

Pathways 3 and 4 are considered to be the highest risk pathways and therefore are the exposure pathways investigated further in this review.

#### 4.4.4 Risk characterisation

The risk characterisation step is summarised below. This shows for the three significant exposure pathways that PFOS/PFOA is not a risk, with the exception of food which may be sourced from known PFOS contaminated sites.

#### **Exposure Pathway 3: Consumption of soil/dust**

NEPM (1999) provides the assumptions and guidelines to assess the hazards of consumption of soil/dust from contaminated sites. The calculation of the Hazard Investigation Level uses an excel spreadsheet provided on the website, and the following assumptions are used (Table 13).

Summary of Exposure P	arameters	Abbreviation	units	Parameter	References/Notes
Soil and Dust Ingestion	- Young children (0-5 vears)	IRSC	mg/dav	100	Schedule B7. Table 5
hate	- Adults	IRSA	mg/day	50	Schedule B7, Table 5
Body weight	- Young children (0-5 years)	BWC	kg	15	Schedule B7, Table 5
	- Adults	BWA	kg	70	Schedule B7, Table 5
Exposure Frequency		EF	days/year	365	Schedule B7, Table 5
Exposure Duration	- Young children (0-5 years)	EDC	years	6	Schedule B7, Table 5
	- Adults	EDA	years	29	Schedule B7, Table 5
A				ED*265	Calculated based on ED for each relevant age group, multiplied by 24 hours for the assessment of
Averaging Time (non-car	cinogenic)	AII	days	ED*365	Inhalation exposures
					years, multiplied by 24 hours for the assessment of
Averaging Time (carcino	genic)	ATNT	days	25550	inhalation exposures

Table 13: Selection of Parameters of Exposure from NEPM (1999)

The calculation of the Hazard Investigation Level for ingestion is based on Equation 1 below (NEPM, 1999).

$$HIL ingestion \left(\frac{mg}{kg}\right) = \frac{TRV \times (100\% - BI) \times BW \times AT}{IR \times BA \times CF \times EF \times ED}$$
Where:  
TRV = toxicity reference value in mg/kg/d  
BI = background intake (% from other sources)  
BW = body weight (kg)  
AT = Averaging time (d)  
IR = Ingestion Rate (mg/d)  
BA = Bioavailability (oral) %  
CF = conversion factor (from mg to kg)  
EF = exposure frequency (d/y)  
ED = exposure duration (y)

Equation 1 - Hazard Investigation Level for ingestion

Typically when setting drinking water and soil guidelines it is assumed that not more than 10% of the daily intake of the contaminant comes from drinking water or soil (e.g.Danish Ministry of the Environment, 2015), therefore, the calculation uses a 'background ingestion' of 90% (i.e. only 10% contribution from soil). Table 14, below, shows the results of the calculations with this consevative assumption of background ingestion.

	Youth		Ac	Units	
	PFOS	PFOA	PFOS	PFOA	
TRV	0.00002	0.00016	0.00002	0.00016	mg/kg/d
Background Ingestion	90.0%	90.0%	90.0%	90.0%	% of TRV
Ingestion Rate	100	100	50	50	mg/d
BA Bioavailability (Oral)	100%	100%	100%	100%	
Conversion Factor	0.000001	0.000001	0.000001	0.000001	kg/mg
Exposure Frequency	365	365	365	365	d/y
Exposure Duration	6	6	29	29	у
Body Weight (BW)	15	15	70	70	kg
Averaging Time	2190	2190	10585	10585	d
Contribution from soil	0.30	2.40	2.8	22.4	mg/kg

**Table 14: Analysis of Acceptable Soil Concentration** 

The youth exposure scenario using a 90% background injestion with only a 10% contribution expected from soil is more consevative than the adult exposure scenario. It could be argued that the youth scenario is less likely to occur on broad acre farming applications, however, this value has been carried through as the acceptable soil concentration of PFOS and PFOA of 0.30mg/kg and 2.40 mg/kg, respectively.

Due to complexities associated with the rate of uptake and biomagnification from soil to food products it is recommended that further work be conducted on the likelhood of this concentration impacting human health through food exposure pathways.

#### 4.4.5 Risk Management

The exposure pathway that involved biosolids was the incidental consumption of biosolidsamended soil, and the previous sections have outlined the assumptions used to calculate an 'acceptable risk' concentration of PFOS/PFOA concentrations in soil. The acceptable limits of the two chemicals in soil with the exposure scenarios for youth and adult are shown in Table 15 below.

Exposed person	Youth		Units
	PFOS	PFOA	
Soil concentration			
acceptable risk	0.30	2.40	mg/kg

Table 15: Summary of acceptable risk concentration in soil

Biosolids are typically applied to limit the nutrients and contaminants to an appropriate standard taking into account the 'dilution' of the biosolids with the soil. The 'agreed' figures to calculate dilution of biosolids in soil according to the Environmental Risk Assessment Guidance Manual in Lee-Steere (2009) is 10 tonnes/ ha/ year (or 1kg/m<sup>2</sup>/yr) at a soil mixing depth of 0.1m, assuming a soil bulk density 1500kg/m3. This means the 10 tonnes of biosolids is diluted in 1500 tonnes of soil (the biosolids:soil ratio is 1:150 – scenario A). The manual did recognise the need to revise these values as use of biosolids changes (Lee-Steere, 2009).

To calculate the 'dilution' rate with biosolids and soil, QLD DEHP uses an application rate of '20 tons/ha (dw) and biosolids incorporation depth of 30cm (assuming homogeneous mixing)' (Sharma, 2016). While the soil density used by DEHP was not provided, it could be back-calculated as 1600kg/m3. Therefore 20 tons of biosolids is mixed or 'diluted' with 4800 tonnes of soil (the biosolids:soil ratio is 1:240 – scenario B).

The Victorian and NSW biosolids guidelines both use the same assumptions to convert the concentration of the contaminant into a biosolids application rate and the assumption is an incorporation depth of 7.5cm, bulk density of 1333kg/m<sup>3</sup> and therefore the soil mass to dilute is 1000 dry tonnes per hectare. Therefore, if 10 or 20 dry tonnes of biosolids was applied there would be a 1:100 or 1:50 dilution (scenario C and D). There is the provision to increase the incorporation depth on a case-by-case basis, but a note that states the incorporation depth would not typically exceed 25cm.

The lack of agreement between the soil densities is understandable in different parts of the country, however, it makes a difference to the soil dilution calculations that influences the acceptable biosolids calculation. The depth of incorporation is also site-specific and therefore, it is prudent to select typical but conservative values to ensure protection. The website <u>www.soilquality.org.au</u> provides information on the soil bulk density in areas across Australia.

In Queensland, the majority of sites tested had a bulk density <1.2 g/cm3 in the top 10 cm. This was particularly the case in areas where biosolids application is commonplace, although some were higher at between 1.2 and 1.4 g/cm3. 40% of sites in NSW were between 1.2 and 1.4 g/cm3, and 39% were higher at between 1.4 and 1.6 g/cm3.

The indicative soil density to be applied in this assessment has been chosen as 1.4 g/cm3 or 1400kg/m3, however, other densities are equally valid and potentially site specific testing should be relied on. Therefore, using the conservative depth of incorporation of 10cm, the incorporation solids mass becomes 1400kg/ha and the biosolids application rate of 20 dry tonnes/ha (maximum) is diluted at a ratio of 1:70 (scenario E). Scenario E is a more conservative dilution than the previous scenarios and the dilution greatly impacts the acceptable biosolids concentration (Table 16).

It is assumed that the concentration in the soil prior to biosolids application is less than the detection limit, and therefore the concentration in the biosolids that could be applied and mixed with the soil on one occasion and still be an acceptable level of risk is shown in Table 16, for five application dilution rates.

	Scenario	Assumed soil density (kg/m3)	Incorporation depth (cm)	Application rate (dt/ha)	PFOS (mg/kg)	PFOA (mg/kg)
	Soil concentration					
	acceptable risk (Youth					
	exposure scenario)				0.30	2.40
Α	Acceptable biosolids					
	concentration (dilution					
	rate provided by Sharma,					
	2016) 1:240	1600	30	20	72	576
В	Acceptable biosolids					
	concentration (after Lee-					
	Steere, 2009) 1:150	1500	10	10	45	360
С	Acceptable biosolids					
	concentration using					
	NSW/Vic assumptions					
	(10 dt/ha) 1:100	1333	7.5	10	30	240
D	Acceptable biosolids					
	concentration using					
	NSW/Vic assumptions					
	(20dt/ha) 1:50	1333	7.5	20	15	120
Ε	Acceptable biosolids					
	concentration using this					
	study's assumptions	1 4 4 9 9	10	20	24	4.60
	(20t in 1400t) 1:70	1400	10	20	21	168

Table 16: Summary of acceptable risk concentration in biosolids

Using the most likely biosolids:soil dilution rate of 1:70 (application rate used in 'E'), Table 16 shows that the acceptable biosolids concentration to protect the 'youth' exposure scenario is PFOS of 21mg/kg and PFOA of 168mg/kg, for a once off application. To ensure that multiple applications of biosolids in the same area do not contribute to a higher than acceptable load of contaminant, it is assumed that there is no degradation of contaminant over time and that the biosolids is applied every 5 years for 20 consecutive years (five applications), and therefore the final acceptable concentration in biosolids is divided by 5, as shown in Table 17.

Exposed person		Units	
	PFOS	PFOA	
Soil concentration acceptable risk	0.30	2.40	mg/kg
Acceptable biosolids concentration 'E' (20 dt/ha at 10cm depth and 1400kg/m3 1:70			
'one application'	21	168	mg/kg
Recommended Biosolids guideline concentration	4.2	33.6	mg/kg

Table 17: Recommended biosolids PFOS and PFOA guideline concentrations

#### 5. **RESULTS**

#### 5.1. Results of data collation

A number of water utilities provided access to their own data. This data has been dereferenced and presented in this report to protect the confidentiality of the utilities, as requested.

Table 18 shows the results of the synthesis of results the PFOS and PFOA. A number of plants recorded results that were less than the limit of detection for the method of analysis (i.e. the contaminant was not detected in the sample). Plant D and Plant S had the highest PFOA results with maximum of 0.01 and 0.011 mg/kg respectively. Plant S and Plant J had the highest concentration of PFOS, with maximum results of 0.386 and 0.32 mg/kg respectively.

	Perfluorooctane sulfonate	Perfluorooctanoic Acid
	001763-23-1	335-67-1
	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	C 8HF15O2
	PFOS	PFOA
Plant A	< 0.005	< 0.005
Plant B	0.007	< 0.005
	< 0.005	< 0.005
Plant d median	< 0.0016	0.006
Plant d min	0.05	0.01
Plant d n	17	0.005 6
Plant F	< 0.005	< 0.005
Plant H	0.003	< 0.005
Plant G St 3	0.021	< 0.005
Plant G St 5	0.014	< 0.005
Plant J median	0.0745	< 0.0017
Plant J max	0.32	< 0.05
Plant J min	0.018	< 0.0013
Plant J n	8	8
Plant L	0.011	< 0.005
Plant S median	0.235	0.00845
Plant S max	0.386	0.011
Plant S min	0.0401	0.0051
Plant S n	4	4
Plant U median	0.00265	0.00145
Plant U max	0.01	0.0056
Plant U min	0.0012	0.0005
Plant U n	14	14
Plant V mediah	0.0015	0.001
Plant V min	0.0097	
Plant V n	0.0003	0.0003
Plant W median	0 003	0.0016
Plant W max	0.0104	0.0052
Plant W min	0.0012	< 0.0005
Plant W n	28	28
Plant Y median	0.0041	0.004
Plant Y max	0.0106	0.0016
Plant Y min	0.0015	0.0006
Plant Y n	13	13

Table 18: PFOS and PFOA results from biosolids at Australian STPs

# 5.2. Synthesis of Results - Comparison of PFOS/PFOA results against previous guidelines

The concentrations established from the risk assessment should be strict enough to ensure safety for the 'youth' exposure scenario. The scenario outcomes were presented in Table 16Table 16 in the previous section, and they have been repeated in Table 19, below compared to other guideline values presented in Section 2.

	Recommen ded (this study)		USEPA (2011)		NZ Draft organics guidelines		WA		Danish guidelines		QId DEHP	Units
	PFO S	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA	TOF (total organic fluorine)	
Tolerable Daily Intake	<b>0.02</b>	<b>0.16</b> <sup>1</sup>	0.02	0.02					0.03	0.1		ug/kg/day
Soil concentration acceptable risk	0.3 <sup>2</sup>	2.40	6	16			4 <sup>3</sup> (sum of PFOS and PFHxS)	40	0.39 <sup>4</sup>	1.3	<lor (&lt;0.005)</lor 	mg/kg
Acceptable biosolids concentration unrestricted use	0.3	2.4			0.01	0.01					0.39	
Acceptable biosolids concentration application to agricultural land	<b>4.2</b> <sup>5</sup>	33.6										mg/kg

Table 19: Summary of acceptable risk concentration in biosolids

<sup>1</sup> DOH, 2017

<sup>2</sup> To protect 'youth' scenario

<sup>3</sup> For 'residential' in as found in DER (2017)

<sup>4</sup> Using a 'youth' scenario of 13kg (Danish Ministry of the Environment, 2015)

<sup>5</sup> Using dilution rate of 1:70 and application with no degradation five applications over 20 years

As discussed previously, the tolerable daily intake used to establish the biosolids concentration is that proposed by DoH (2017). Using the slightly different tolerable daily intake values and the soil guidelines developed by the Danish study (and the same assumptions of a dilution factor of 1:70 and 5 applications) acceptable biosolids concentrations are slightly higher for PFOS but lower for PFOA than those proposed in this study (5.5 mg/kg for PFOS and 18.2 mg/kg for PFOA). Cooperative Research Centre (CRC) for Contamination Assessment and Remediation of the Environment had set health screening levels of 22 mg/kg PFOS and 220 mg/kg PFOA based on the previous interim tolerable daily intake. The CRC's website states that these will be revised down, and using the same calculator as they previously used (PFAS HSL spreadsheet tool) the revised values would be 3 mg/kg and 24 mg/kg which is a factor of ten higher than the values in this study, due to their assumption that allows 100% of the tolerable daily intake to come from this source (where this study is allowing only 10%, in line with development of other guidelines).

The Western Australian Department of Environmental Regulation has developed guidelines for residential soil contaminants from the interim EnHealth tolerable daily intake guidelines (DER, 2017). Therefore, the values they established are slightly higher than those developed in this study using the Department of health tolerable intake guidelines.

The guideline value presented in DEHP (2016) for total organic fluorine in biosolids is taken from the Danish guideline for soil (Sharma, 2016). The Danish soil guideline was used as the biosolids guideline and then back-calculated to find an appropriate soil guideline limit (which was less than the typical limit of reporting) (Sharma, 2016). This gives a limit which is overly conservative compared to the risk assessment that was conducted in this study, however, comment was made that the guidelines could be reviewed in future (Sharma, 2016).

#### 5.3 Results of the NEPM analysis

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 20 below.

		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 20: Recommended values for PFOS and PFOA for unrestricted use biosolids

The table shows that the limiting Health Investigation Level value for PFOS is 0.3 mg/kg for child exposure. At this level a child eating 100 mg of biosolids per day would ingest 10% of the maximum daily amount of PFOS recommended by the Australian Government Department of Health. It is therefore suggested that this level is an appropriate level for a Grade A or C1 biosolids classification: biosolids suitable for unrestricted use.

In terms of the treatment plants sampled as part of this review the average level of PFOS measured in biosolids was around one fifteenth of Health Investigation Level. The maximum level of PFOS measured at each was lower than the suggested Grade A or C1 level at all bar two sites with a known history of PFOS contamination.

The table shows that the limiting Health Investigation Level value for PFOA is 2.4 mg/kg for child exposure. At this level a child eating 100 mg of biosolids per day would ingest 10% of the maximum daily amount of PFOS recommended by the Australian Government Department of Health.

In terms of the treatment plants sampled as part of this review the average level of PFOA measured in biosolids was around one eight hundredth of 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 recorded value approximately one fiftieth of the recommended health investigation level. This data suggests there is a low risk from PFOA in biosolids.

The results of the additional calculations to determine safe levels of PFOS and PFOA in biosolids applied to land are based on soil density of 1.4 tonnes per cubic metre, 100 mm 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 on part biosolids for 70 parts soil.

The assumptions above and the NEPM analysis were 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 21 below.

Parameter	Units	PFOS	PFOA
Health Investigation Level	mg/kg	0.3	2.4
Biosolids limit (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 21: 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 one two hundredth 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 11including two sites with a known history of PFOS contamination.

In terms of the treatment plants sampled as part of this review 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 one seven hundredth 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 in the 10-15 tonnes per hectare every 3-5 years. This gives best practice dilution rates a factor of 3-4 times higher than presented in this review.

#### 6. CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

The conclusions of this review and analysis are:

- PFOS and PFOA occur in biosolids at detectable levels. PFOS and PFOA were detected in 92 out of 109 samples from 13 different Australian sewage treatment plants;
- PFOS was detected above the NEPM Health Investigation Level (HIL) at two sites (3 out of 109 samples) with known PFOS contamination issues. Average values of PFOS measured in Australian biosolids were around one fifteenth of the calculated HIL;
- 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;
- The levels of PFOA detected in this review are significantly lower than Health Investigation Levels suggested by the Australian Government Department of Health. This data suggests that there is little need to monitor PFOA in biosolids with the maximum recorded value of PFOA being around one fiftieth of calculated Health Investigation Level.

#### 6.2 Recommendations

 It is recommended that limits for PFOS in biosolids be adopted as set out in Table 22 below and reviewed regularly on the basis of further data on the levels of PFOS in biosolids.

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

Table 22- Recommended PFOS limits in biosolids

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) Tasmania 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 of PFOS and/or PFOA contamination should monitor these compounds on a case by case basis.

### 7. REFERENCES.

3M. (2017). *3M and Fluorochemicals*. [ONLINE] Available at: <u>https://www.3m.com/3M/en\_US/sustainability-us/policies-reports/3m-and-fluorochemicals/</u>. [Accessed 24 September 2017].

ALS Environmental. (2015). Perfluorinated Compounds (PFCs) in Landfill leachate. [ONLINE] Available at: <u>https://www.alsglobal.com/-/media/als/resources/services-and-products/environmental/enviromails-au/enviromail-86---perfluorinated-compounds-pfcs-in-the-landfill-leachate.pdf</u> [Accessed 28 September 2017].

Australian Government Department of Health. (2017). Health Based Guidance Values for Per- and Poly-Fluoroalkyl Substances (PFAS). [ONLINE] Available at: <u>http://www.health.gov.au/internet/main/publishing.nsf/content/ohp-pfas-hbgv.htm</u>. [Accessed 28 September 2017].

Bartholomaeus, A. (2016). Procedural Review of Health Reference Values Established by enHealth for PFAS. [ONLINE] Available

at: <u>http://www.health.gov.au/internet/main/publishing.nsf/content/2200FE086D480353CA2580C900817CDC/\$F</u> <u>ile/eHealth-interim-full.pdf</u> [Accessed 30 November 2017].

Clarke, B. O., Anumol, T., Barlaz, M., & Snyder, S. A. (2015). Investigating landfill leachate as a source of trace organic pollutants. *Chemosphere*, *127*, 269-275. doi:<u>http://dx.doi.org/10.1016/j.chemosphere.2015.02.030</u>

Clarke, B. O., & Smith, S. R. (2011). Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environment International*, *37*(1), 226-247. doi:<u>http://dx.doi.org/10.1016/j.envint.2010.06.004</u>

CRC CARE. (2014). *Development of guidance for contaminants of emerging concern*. [ONLINE] Available at: <u>http://www.crccare.com/files/dmfile/CRCCARETechnicalReport32-</u> DevelopmentofGuidanceforContaminantsofEmergingConcern.pdf. [Accessed 28 September 2017].

Darvodelsky, P. (2011). *Biosolids Snapshot*. [ONLINE] Available at: <u>http://www.environment.gov.au/system/files/resources/2e8c76c3-0688-47ef-a425-5c89dffc9e04/files/biosolids-snapshot.pdf</u> [Accessed 28 September 2017].

Darvodelsky, P. (2015). *ANZBP Biosolids Survey*. [ONLINE] Available at: <u>https://www.biosolids.com.au/biosolids-atlas/statistics/</u> [Accessed 28 September 2017].

Darvodelsky, P. 2017. *Australian Biosolids Statistics*. [ONLINE] Available at: <u>https://www.biosolids.com.au/guidelines/australian-biosolids-statistics/</u>. [Accessed 28 September 2017].

Department of Health, (DoH, 2017), *Health Based Guidance Values for PFAS for use in site investigations in Australia*, [ONLINE] Available at:

https://www.health.gov.au/internet/main/publishing.nsf/Content/2200FE086D480353CA2580C900817CDC/\$Fil e/fs-Health-Based-Guidance-Values.pdf [Accessed 30 November 2017].

DEHP, D. o. E. a. H. P. (2015). *Model Operating Conditions ERA 63—Sewage Treatment*. [ONLINE] Available at: <u>http://www.ehp.qld.gov.au/assets/documents/regulation/pr-co-sewage-treatment.pdf</u>. [Accessed 30 November 2017].

DEHP, D. o. E. a. H. P. (2016). *General beneficial use approval for Biosolids*. (ENBU06949016). Queensland. [ONLINE] Available at: <u>http://www.ehp.qld.gov.au/assets/documents/regulation/wr-ga-biosolids.pdf</u>. [Accessed 30 November 2017].

DER WA (2017). Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS). 168 St Georges Terrace, Perth, Western Australia. [ONLINE] Available at: <a href="https://www.der.wa.gov.au/images/documents/your-environment/contaminated-sites/guidelines/Guideline">https://www.der.wa.gov.au/images/documents/your-environment/contaminated-sites/guidelines/Guideline on Assessment and Management of PFAS v2.1.pdf</a>. [Accessed 30 November 2017].

EnHealth. (2016). Interim national guidance on human health reference values for per- and poly-fluoroalkyl substances for use in site investigations in Australia. In E. H. S. C. o. t. A. H. P. P. Committee (Ed.), [ONLINE] Available at: <u>http://www.health.nsw.gov.au/environment/factsheets/Documents/pfas-interim-health-values-ahppc.pdf</u>. [Accessed 30 November 2017].

FSANZ, F. S. A. N. Z. (2016). Food Standards Australia New Zealand 24th Australian Total Diet Study. [ONLINE] Available at:

http://www.foodstandards.gov.au/publications/Documents/24th%20Total%20Diet%20Study\_Phase%202.pdf [Accessed 30 November 2017].

FSANZ, F. S. A. N. Z. (2017). *Consolidated Report - Perflourinated Chemicals in Food* [ONLINE] Available at: http://www.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-hbgv.htm#final <u>Consolidated</u> <u>Report - Perfluorinated Chemicals in Food</u> . [Accessed 30 November 2017].

Gallen, C., Drage, D., Kaserzon, S., Baduel, C., Gallen, M., Banks, A., . . . Mueller, J. F. (2016). Occurrence and distribution of brominated flame retardants and perfluoroalkyl substances in Australian landfill leachate and biosolids. *Journal of Hazardous Materials, 312*, 55-64. doi:<u>http://dx.doi.org/10.1016/j.jhazmat.2016.03.031</u>

Gottschall, N., Topp, E., Edwards, M., Russell, P., Payne, M., Kleywegt, S., . . . Lapen, D. R. (2010). Polybrominated diphenyl ethers, perfluorinated alkylated substances, and metals in tile drainage and groundwater following applications of municipal biosolids to agricultural fields. *Science of The Total Environment, 408*(4), 873-883. doi:<u>http://dx.doi.org/10.1016/j.scitotenv.2009.10.063</u>

Harris, K., Gunter, K., Golubski, G., Grams, B., Lau, C., Mills, M., . . . Hundal, L. (2012). P65—Measuring for perfluorinated chemicals in land-applied biosolids and plants. *Reproductive Toxicology*, *33*(4), 623. doi:<u>http://dx.doi.org/10.1016/j.reprotox.2011.11.099</u>

Latimer, G. (2016). *Persistant Organic Pollutants (POPs) in Biosolids: Risks for Australian Wastewater Managers*. Paper presented at the Australian Water Association Biosolids Conference, Melbourne November 2016.



Lee-Steere, C. (2009). *Environmental Risk Assessment Guidance Manual for industrial chemicals*. Commonwealth of Australia [ONLINE] Available at:

http://www.nepc.gov.au/system/files/resources/bffdc9e9-7004-4de9-b94f-b758140dbc8c/files/cmgt-nchemeragm-industrial-chemicals-200902.pdf. [Accessed 30 November 2017].

NEPC. 1999. National Environment Protection (Assessment of Site Contamination) Measure. [ONLINE] Available at: <u>http://www.nepc.gov.au/nepms/assessment-site-contamination</u>. [Accessed 28 September 2017].

NSW EPA. (2000). *Environmental Guidelines: Use and Disposal of Biosolids Products*. [ONLINE] Available at: <u>http://epa.nsw.gov.au/resources/water/BiosolidsGuidelinesNSW.pdf</u>. [Accessed 30 November 2017].

New South Wales EPA. 2017. *PFAS investigation program FAQs*. [ONLINE] Available at: <u>http://www.epa.nsw.gov.au/mediainformation/pfasinvestigationfaqs.htm</u>. [Accessed 28 September 2017].

Roccaro, P., & Vagliasindi, F. G. A. (2014). Risk Assessment of the Use of Biosolids Containing Emerging Organic Contaminants in Agriculture. *Chemical Engineering Transactions*, *37*, 817-822. doi:10.3303/CET1437137

Sharma, I. (2016, Thu 15/12/2016 4:52 PM). [Email: 1. Response to query regarding Organic Fluorine (TOF) limits].

USEPA, U. E. P. A. (1994). *Biosolids Recycling: Beneficial Technology For A Better Environment*. [ONLINE] Available at: <u>https://www.epa.gov/sites/production/files/2015-</u> <u>06/documents/biosolids recycling beneficial technology for a better environment.pdf</u> [Accessed 30 November 2017].

USEPA, U. E. P. A. (1995). A Guide to Biosolids Risk Assessments for the EPA Part 503 Rule. [ONLINE] Available at: <u>https://www.epa.gov/biosolids/guide-biosolids-risk-assessment-epa-part-503-rule</u> [Accessed 30 November 2017]

USEPA, U. E. P. A. (2011). Fact Sheet - Perfluorochemical (PFC) Contamination of Biosolids Near Decatur, Alabama. [ONLINE] Available at:

https://archive.epa.gov/pesticides/region4/water/documents/web/pdf/epa\_decatur\_fact\_sheet\_final.pdf [Accessed 30 November 2017]

Water New Zealand. (2016a). *Beneficial Use of Organic Waste Products on Land – Volume 1 Guide (Draft)*. [ONLINE] Available at: <u>http://www.waternz.org.nz/Attachment?Action=Download&Attachment\_id=1745</u>. [Accessed 30 November 2017]

Water New Zealand. (2016b). *Beneficial Use of Organic Waste Products on Land – Volume 2 Technical Manual (Draft)*. [ONLINE] Available at:

http://www.waternz.org.nz/Attachment?Action=Download&Attachment\_id=1746. [Accessed 30 November 2017]

WHO, W. H. O. (2010). *WHO human health risk assessment toolkit: chemical hazards*. [ONLINE] Available at: <u>http://www.who.int/ipcs/methods/harmonization/areas/ra\_toolkit/en/</u>. [Accessed 30 November 2017]



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