



7th August 2017

Nick Walmsley,
WaterNZ
Ranchhod House,
Level 12,
39 The Terrace
PO Box 1316

Dear Nick,

Review and recommendations on the selection of organic contaminants in the draft Guideline for the Beneficial Use of Organic Waste Products on Land, 2016.

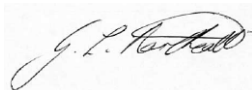
As requested by Water New Zealand find enclosed a report from Northcott Research Consultant's Limited (NRC Ltd) entitled "A reassessment of organic contaminants and their product contaminant concentration limits within the draft Guideline for the Beneficial use of Organic Waste Products on Land".

As directed by the Project Steering Group overseeing the preparation of the draft Guideline this report provides:

- a justification for changing the organic contaminants in the original draft guideline
- a short list of EOCs for monitoring in the new guideline
- Recommended product limits for the short list of EOCs
- Recommended methodology for analysis of the afore mentioned EOCs

Kind regards.

Dr Grant Northcott PhD

A handwritten signature in black ink, appearing to read "G. L. Northcott", is enclosed in a light grey rectangular box.

Director: Northcott Research Consultants Limited
Environmental Chemist: Centre for Integrated Biowaste Research



**A REASSESSMENT OF ORGANIC CONTAMINANTS AND THEIR PRODUCT
CONTAMINANT CONCENTRATION LIMITS WITHIN THE DRAFT GUIDELINE FOR
THE BENEFICIAL USE OF ORGANIC WASTE PRODUCTS ON LAND**

Prepared for Water New Zealand by Dr Grant Northcott

Northcott Research Consultants Limited (NRC Ltd)

August 2017.

EXECUTIVE SUMMARY

Northcott Research Consultants Limited (NRC Ltd) was contracted by Water New Zealand to review and justify the selection of organic contaminants and their respective product contaminant concentration limits specified in the draft Guideline for the Beneficial Use of Organic Waste Products on Land, 2016. (Water New Zealand, 2016).

Specifically, NRC Ltd was directed by the Project Steering Group overseeing the preparation of the draft Guideline to provide:

- a justification for changing the organic contaminants in the original draft guideline
- a short list of EOCs for monitoring in the new guideline
- Recommended product limits for the short list of EOCs
- Recommended methodology for analysis of the afore mentioned EOCs

An assessment of the latest information of their concentration in biowaste, the risk they present to the environment upon biowaste application to land, and regulations for their elimination or restricted use, was completed for those organic contaminants proposed for product concentration limits in the draft Guideline for the Beneficial Use of Organic Waste Products on Land.

Recommendations from this assessment include:

- removing PFOS\PFOA, AOC and polycyclic aromatic hydrocarbons from the list of contaminants requiring product concentration limits in the draft Guideline for the Beneficial Use of Organic By-Products on Land.
- Increasing the product concentration limits for NP\NPE, DEHP, LAS and galaxolide in the draft Guideline for the Beneficial Use of Organic By-Products on Land.

The recommended organic contaminants and respective product contaminant concentration limits proposed for inclusion in the Guideline for the Beneficial Use of Organic By-Products on Land are displayed in the table below.

Contaminant	Parameter	Concentration limit (mg/kg dry weight)
Arsenic		30
Cadmium		10
Chromium		1500
Copper		1250
Lead		300
Mercury		7.5
Nickel		135
Zinc		1500
Nonylphenol and ethoxylates ^A	NP/NPE	50
Phthalate	DEHP	100
Linear alkylbenzene sulphonates ^B	LAS	2600
Musks	Tonalide	15
	Galaxolide	50

^A comprising the sum of technical nonylphenol, NPE10 and NPE20 equivalents

^B comprising the sum of technical C11-C13 homologues and corresponding mixture of isomers

Due to the low risk that NP\NPE, DEHP, LAS and galaxolide present to the environment or human health from the application of biowaste to land, the product contaminant concentration limits for NP\NPE, DEHP, and LAS have been raised to equal those proposed by the European Union in sludge applied to agricultural soil, and to 50 mg/kg for galaxolide.

Guidance on recommended methodological approaches for analysing the recommended organic contaminants in biowaste that reduce the complexity and labour of analysis, and therefore reduce the cost of analysis are provided. This includes general advice on:

- approaches to minimise the number of separate sample extractions required to extract the modified list of organic contaminants from biowaste
- instrumental analysis approaches that reduce the number of separate runs required to analyse the diverse list of organic contaminants in biowaste, and,
- specific recommendations regarding the analysis of residues of industrial mixtures of NP/NPEs and LAS inorganic biowaste, and how to report residues of these industrial mixtures.

INTRODUCTION

The focus on Cl-POPs in the Guidelines for the Safe Application of Biosolids to Land in New Zealand (2003), referred to hereafter as the 2003 Biosolids Guidelines, reflected the goals of NZ Government policy for the regulation and management of organic pollutants at the time the Guidelines were produced.

In the years preceding and following the publication of the 2003 Biosolids Guidelines the NZ Government implemented regulations either banning the importation, significantly restricting the use of, or eliminating activities that produce Cl-POPs and polychlorinated dibenzodioxins and Furans (PCDD/Fs) and released them into the environment. These combined controls have resulted in a significant reduction in the release of these chemicals into the NZ environment, and a visible decline in their concentrations within receiving environments in NZ. The concentrations of most Cl-POPs in the NZ environment have continued to decrease and have either reached or are approaching what can be generally considered as “background” environmental concentrations.

This continuing decrease in the quantity of Cl-POPs released into the NZ environment is similarly reflected in their reduction in sewage sludge’s and biosolids.

Phase Two of the 2004 Cross-Departmental Research Programme “Removing the Roadblocks to the Beneficial Use of Sewage Effluent and Biosolids” analysed a wide range of organic contaminants in sewage sludge obtained from ten wastewater treatment plants in New Zealand on three separate occasions. Not one of the thirty analysed sewage sludge’s contained any detectable residues of a suite of Cl-POPs, including those specifically listed for control in the 2003 Biosolids Guidelines. Due to the expense of analysis PCDD/Fs were not analysed within the 2004 CDRP project. However, the US-EPA decided not to regulate dioxins (PCDD/Fs) in biosolids after research demonstrated this source does not pose a significant risk to human health or the environment (USEPA).

The requirement to monitor residues of Cl-POPs and PCDD/Fs in sewage sludges and biosolids in New Zealand was appropriate at the time the 2003 Biosolids Guideline was under development. However, it has since been demonstrated it is no longer necessary to monitor these persistent chlorinated organic pollutants in sewage sludge and biosolids in New Zealand.

In comparison, many new organic chemicals, commonly referred to as emerging organic contaminants (EOCs) that are present in sewage sludge and biosolids, have been identified internationally as high risk or chemicals of concern. In response the Centre for Integrated Biosolids Research (CIBR) completed a review assessing the relevance of the organic contaminants listed in the 2003 Biosolids Guidelines together with high risk EOCs either proposed for regulation or monitoring in overseas countries.

As stated in the 2014 CIBR review, the selection of organic contaminants to include within a revised Organic Materials Guideline new guideline “should be based on a flexible and responsive framework that incorporates new and relevant scientific knowledge”. As such it is expected that new high risk organic contaminants will be assessed and considered for incorporation into the modified Guidelines, and others removed, as our knowledge of the effects and risks of traditional and emerging chemicals increases.

As stated in the 2014 CIBR review of organic contaminants there is not enough information currently available to derive New Zealand specific limits for emerging organic contaminants in biowastes. Instead, the 2014 CIBR review of organic contaminants suggested applying interim values that could be adopted for limiting the concentration of selected EOCs in biowaste as listed in Table 1 (Tremblay et al, 2014). The European guideline limits for organic contaminants were sourced from the review of European

policy on sewage sludge utilisation by Mininni which summarised the limits of selected organic micropollutants in sewage sludge, compost, and digestate adopted by the European Union, and its member countries (Mininni et al, 2015).

The EU definition for compost is the residue remaining after the aerobic decomposition of biomass and digestate is defined as the residue remaining after anaerobic digestion of biomass, typically by fermentation processes. In the EU digestate is most often produced in the operation of biogas plants and consists of the liquid fermentation residue remaining after the separation recovery of fermentation biogases. These digestates are highly valued as fertilisers. In the EU energy crops and liquid manures are predominantly used as feedstock for the production of biogas but in principal all organic materials are suitable feedstock. Under these descriptions the residue produced from municipal sewage sludge subjected to anaerobic digestion could be considered a digestate.

Table 1. Range of guideline limits of organic pollutants for sludge used in agriculture, compost and digestates (mg/kg DM) based on Mininni (Mininni et al. 2014) and compared with NZ biosolids guidelines (New Zealand Water and Wastes Association 2003).

Class	Organic Micropollutant	Limits for EU Countries		Limits for NZ	
		Sewage Sludge	Compost and digestate	Grade A	Grade B
Perfluorinated compounds	PFOS/PFOA	NA	0.01	NA	NA
Absorbable organic halides	AOX	400-500	250-500	NA	NA
Polychlorinated biphenyls	Sum of various congeners	0.10-1.0	0.15- 1.0	0.20	0.20
Chlorinated dioxins and furans	PCDD/Fs	30-100 ^B	20-100 ^A	30 ^A	50 ^A
Polycyclic aromatic hydrocarbons	Sum of various compounds	3.0-6.0	3.0- 10.0	NA	NA
Total nonylphenols	Sum of NP and NPE ^C	10-450	10-25	NA	NA
Phthalate	DEHP	50-100	50	NA	NA
Linear alkylbenzene sulphonates	LAS ^D	1300-5000	1300-1500	NA	NA
Musks	Tonalide	15	NA	NA	NA
	Galaolide	10	NA	NA	NA
Bubber vulcaniser and stabilisers	Mercaptobenzothiazole				
	Hydroxybenzothiazole	0.60	NA	NA	NA

^A Not available, no limit; ^B ng of toxic equivalents (TEQ)/kg dry matter; ^C sum of nonylphenol and nonylphenol ethoxylates, varies between member countries; ^D does not specify which chain length classes are included

The list of proposed organic contaminants and suggested interim limits was subsequently incorporated into the draft Guideline for the Beneficial Use of Organic Waste Products on Land (NZ Water, 2016), hereafter referred to as the draft Guideline. The product contaminant concentration limits contained within Table 5.5 of the draft Guideline are reproduced below in Table 2.

The proposed product contaminants and their concentration limits were widely discussed during and after a series of National Workshops run by Water New Zealand to publicise and seek input into the draft Guideline for the Beneficial Use of Organic Waste Products on Land.

In the three years following the preparation of the 2014 CIBR report significant advancements have been made in both research and the state of knowledge of EOCs, particularly with respect to their presence in biosolids and other waste materials. Regulatory organisations worldwide have begun responding to the challenges of managing the potential risks EOCs may present to the environment and human health.

Table 2. Product contaminant concentration limits as specified in the draft Guideline for the Beneficial Use of Organic Waste Products on Land, 2016. (Water New Zealand, 2016).

Contaminant	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	PFOA/PFOS	0.01
Adsorbable organic halide	AOX	450
Polycyclic Aromatic Hydrocarbons	Sum of PAHs	5.0
Nonylphenol and ethoxylates	NP/NPE	25
Phthalate	DEHP	75
Linear alkylbenzene sulphonates	LAS	1500
Musks	Tonalide	15
	Galaxolide	10

Source: Water New Zealand, 2016.

In light of these developments it is pertinent to reconsider which organic contaminants to retain, remove, or modify concentration limits for, within the draft Guideline.

The following sections of the report discuss the rationale for reducing the number of organic compounds and testing parameters, and where appropriate modifying the Product contaminant concentration limits, specified within the draft Guideline (Table 2).

General recommendations on methodological approaches that analytical laboratories can adopt to reduce the cost to analyse a modified list of organic contaminants are also provided.

PRODUCT ORGANIC CONTAMINANT LIMITS

The organic contaminants specified for limitation in products within the draft Guideline for the Beneficial Use of Organic Waste Products on Land are discussed in the order they appear in Table 5.5 of the draft Guideline (Table 2 in this report).

Polyfluorinated chemicals- PFOS and PFOA

The environmental persistence and bioaccumulation potential of long chain perfluorotelomers, their degradation products, and perfluoroalkyl acids has seen worldwide enforcement of restrictions and regulations for these chemicals. The extreme level of persistence and high bioaccumulation potential of these perfluorinated chemicals is exemplified by polyfluorooctanoic acid (PFOA) and polyfluorooctane sulphonate (PFOS) which are considered ubiquitous, stable, and toxic environmental contaminants. The profile of perfluorinated chemicals in biosolids and the environment is dominated by PFOA and PFOS.

A summary of concentration of PFOS/PFOA measured in sewage sludge and biosolids in the USA, Australia and Germany is provided below in Table 3.

Table 3. Concentration of PFOS and PFOA in sewage sludge and biosolids

Country	Year	Concentration in mg/kg dry weight		Reference
		PFOS	PFOA	
USA	2001	0.308 - 0.618	0.012 - 0.070	Venkatesan, 2013
Australia	2014	0.011 - 0.370	0.003 - 0.030	Gallen, 2016
Germany	2008- 2013	0.012 - 0.050 (7.6) ^A	0.0003 - 0.016 (1.04) ^A	Ulrich, 2016
Various	Various	0.005- 3.12	0.001-0.244	Clarke, 2001

^A Range of mean concentrations with maximum concentration in brackets

The European Union has not set a concentration limit for perfluorinated chemicals in sewage sludge, compost, or digestate. However, member countries Austria and Germany apply a limit of 0.01 mg/kg for the sum of PFOA/PFOS in compost or digestates (Mininni et al, 2015).

In 2008 the Bavarian State Ministry for the Environment in Germany implemented a policy enforcing the analysis of PFAAs in WWTP sewage sludge and set a precautionary limit of 0.125 mg/kg dry matter for the sum of 11 PFAAs in sewage sludge applied to land or used for the production of compost (Ulrich et al, 2016).

As previously stated PFOS/PFOS contribute the greater proportion of total PFAAs residues in biosolids and the environment. The concentration limit for polyfluorinated organic chemicals in the draft Guideline was set at 0.01 mg/kg for the sum of PFOA/PFOS. Comparison of this limit with the concentration of PFOS and PFOA commonly present in sewage sludge's and biosolids (listed in Table 3) clearly demonstrates this limit would be difficult for most countries to comply with. In comparison a large proportion of the sludge's and biosolids would meet the Bavarian State Ministry for the

Environment precautionary limit of 0.125 mg/kg dry matter for the sum of 11 PFAAs in sewage sludge applied to land or used for the production of compost.

It is important to note the source of the Product Contaminant Concentration Limit of 0.01 mg/kg DM for the sum of PFOS + PFOA was adopted from that set in Austria and Germany for PFOS + PFOA in compost and digestate, and not biosolids. The processing of biosolids to produce compost products, and/or anaerobic digestion of biosolids containing PFOS/PFOA, will reduce the concentration of PFOS/PFOA they contained before they were subject to these processes.

Concerns regarding the persistence and bioaccumulative properties of long chain PFAAs have resulted in worldwide regulations and restrictions on these chemicals. In 2008 the EU prohibited the general use of PFOS and its derivatives, restricted its content in semi-finished and finished products to 50 mg/kg, and provided exemptions for the semiconductor industry, metal plating, and hydraulic fluids. In 2010 the acceptable content was reduced further to 10 mg/kg (EU, 2010) and since 2011 the EU has banned the use of firefighting foams based on PFOS.

In 2009 PFOS and its salts were added to the assessment list of POPs of the United Nations Stockholm Convention and in 2017 were officially classified as new POPs under the Stockholm Convention (UNEP, 2017). In anticipation of this move eight of the major fluoropolymer and telomere manufacturing companies initiated a voluntary phase-out program for PFOA, its pre-cursors, and higher homologues in 2006 with the goal to totally eliminate their use of these chemicals by 2015.

Over the next two years the combined impact of these initiatives and regulations will see a significant reduction in the use of these perfluorinated chemicals, and corresponding reduction in the concentration of PFOS/PFOA in sewage sludge's, biosolids, and products produced from them..

The reduction in the use of PFOA and other higher perfluorinated homologues has been matched by their substitution with alternative shorter chain PFAAs that have the advantage of being less bioaccumulative. However, these shorter chain substitutes remain persistent, display a high level of mobility in the environment, and are more difficult to remove from wastewater because as a result of their reduced adsorption affinity to sewage sludge (Ulrich et al, 2016). Effort should therefore be focused on assessing the environmental and human health risks of shorter chain PFAAs and other perfluorinated chemicals that have been adopted as substitutes for PFOS/PFOA.

In conclusion there is little reason to include a product contaminant concentration limit for PFOS/PFOA in organic wastes within the draft Guideline when these chemicals are being phased out of use and have been officially added to the list of POPs for elimination under the Stockholm Convention.

In 2017 CIBR is initiating a research project to identify and assess the potential risks presented by perfluorinated chemicals in biosolids and biowaste applied to land in New Zealand. The outcomes and recommendations arising from this research will be published and the research papers provided to Water NZ and other end-users for considering whether product contaminant concentration limits need to be considered for perfluorinated chemicals other than PFOS/PFOA within the Guideline for the Beneficial Use of Organic Waste Products on Land.

Adsorbable Organic Halide (AOX)

AOX remains on the list of European list of contaminants in sewage in response to the presence of chemical manufacturing industries within member states and the production of industrial sludge's

containing very high concentrations of halogenated organic chemicals. The AOX test method provides an economic alternative to analysing the multitude of halogenated organic chemicals produced by the chemical industry, and as such has been widely adopted by these industries as a proxy measure.

The reliability of the AOX test method for the analysis of biosolids is a matter of ongoing debate and there is a lot of concern about the reliability of AOX measurements in sewage sludge and biosolids. The suitability of the AOX method depends on halogenated organic chemicals being efficiently extracted from sewage sludge/biosolids by a nitric acid solution, and then being efficiently adsorbed by the activated organic carbon. A large proportion of the halogenated organic chemicals identified in sewage sludge/biosolids are hydrophobic and will not readily partition into the nitric acid extracting solution. Furthermore, the high residual content of humic substances in sewage sludges/biosolids can compete for adsorption sites on the activated carbon, thereby reducing the adsorption of halogenated organic chemicals that are extracted from sewage sludge/biosolids.

The AOX method is intended to extract a wide range of chlorinated organic chemicals from sewage sludge as diverse as chlorinated alkanes, chlorinated benzenes, chlorinated phenols, PCBs and PCDD/Fs. This makes it an almost meaningless parameter to utilise to assess the toxicological risk of chlorinated organic compounds in biosolids and biowaste applied to land because:

1. The heterogeneous nature of biosolids and biowaste means measures of AOX will vary significantly between different WWTPs and processing methods.
2. The compounds included within the AOX analysis display a wide range of very different physico-chemical properties. As such their persistence and fate in soil amended with biowaste will vary widely.
3. Similarly, the compounds encompassed by AOX display widely different modes of toxicity, and toxic potency. For example, chlorinated benzenes are found in biosolids at relatively high concentrations and therefore can make a large contribution to total AOX. However, chlorobenzenes display a relatively low degree of persistence and toxicity in soil amended with biosolids and a correspondingly small contribution to the overall risk of applying biowaste to land.

A requirement to monitor AOX in biowaste within the modified Guideline would not provide any useful information to assist waste practitioners or regulators to reach any meaningful conclusions about the risk of applying biowaste to land. In summary there is little scientific rationale to retain AOX as a product contaminant parameter to monitor in organic waste products within the modified Guideline.

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are often listed as priority contaminants in biosolids in countries where urban storm water is reticulated and directed into WWTPs for treatment, in which case biosolids accumulate high concentrations of combustion and fuel sourced PAHs (for example in the UK). In New Zealand urban storm water drainage networks are typically kept separate from municipal waste water streams, and the concentration of PAHs entering WWTPs in NZ is relatively low. This has been confirmed by recent and unpublished New Zealand data.

PAHs degrade relatively rapidly in microbially active material and as such many of the stabilisation processes to which organic waste materials (composting, vermicomposting etc.) are subjected should be sufficient to degrade PAHs. Any residues of PAHs remaining in stabilised biowastes added to land will be

degraded further by soil microbes and their bioavailability for uptake into crops and pasture reduced by sorption to the soil matrix and the formation of bound residues.

Research in the United Kingdom has demonstrated the annual mass loading of PAHs into soil resulting from the application of sewage sludge to land at recommended agronomic rates, is significantly less than that attributed to atmospheric deposition of combustion derived PAHs to soil (Duarte-Davidson et al, 1995).

Combustion derived waste material is not a raw organic material and wastes such as these are not listed as suitable organic materials in the modified Guideline. Biochar produced by the reductive combustion of organic wastes (plant material, animal waste etc.) can contain considerable quantities of PAHs. The stability of biochar is such that it is non-compostable and as such the draft Guideline excludes its use as an organic waste material.

In conclusion organic waste materials meeting the definition in the new Guideline should contain relatively low concentrations of PAHs that present little or no risk to the environment or human health, and PAHs can therefore be removed as a product contaminant within the draft Guideline.

Nonylphenols

Alkylphenol ethoxylates are a class of non-ionic surfactants, produced by the reaction of a branched-chain alkylphenols with ethylene oxide. The most commonly used are nonylphenol ethoxylates (NPEs), which make up approximately 80% of the world market. Commercial formulations, commonly referred to as technical nonylphenol ethoxylates, are composed of a complex mixture of homologues, oligomers and isomers containing anywhere between 1 to 50 ethoxy chain lengths.

The use of NPEs in domestic detergents has largely ceased and they are mainly used as industrial surfactants. The starting material for the manufacture of technical NPEs is technical nonylphenol, which is comprised of the same complex mixture of homologues, oligomers and isomers as the technical NPE product.

Technical NPE products are degraded by microorganisms which progressively break down the ethoxy chains to produce as metabolites the original technical NP mixture together with corresponding mixtures of nonylphenol monoethoxylates (NP1EOs) and nonylphenol diethoxylates (NP2EOs). During wastewater treatment processes technical NPEs are rapidly degraded to produce the corresponding mixture of technical NPs, NP1EOs, and NP2EOs. The mixtures of NP1EOs, and NP2EOs are degraded further during anaerobic digestion to produce the corresponding mixture of technical NPs. The composition of technical nonylphenolic compounds in anaerobic digested sludge is typically 95% technical NP and 5% technical NP1EOs and NP2EOs (Ahel et al, 1994).

The principle concern regarding the toxicological risk of nonylphenols is their estrogenicity. The nonylphenol compound exhibiting the highest estrogenic potency is 4-n-nonylphenol. However, 4-n-nonylphenol is only one of many individual nonylphenol compounds present in industrial mixtures of technical-NP, or those produced by the degradation of parent technical mixtures of NPEs. The concentration of 4-n-NP measured in New Zealand biosolids in the 2004 CDRP project ranged from 0.005 to 0.240 mg/kg dry weight biosolids. In comparison the concentration of technical-NPs was orders of magnitude higher and varied from 10.3 to 1843 mg/kg dry weight biosolids.

NPs and NPEs are rapidly biodegraded in biosolid amended soil. A risk assessment of contaminants in sewage sludge applied on Norwegian soils concluded the sum of NP/NP1EOs/NP2EOs at a concentration of 100mg/kg DM in sewage sludge constituted a low risk to the soil ecosystem and didn't constitute a significant risk to aquatic or food producing environments (Norwegian Scientific Committee for Food Safety,2009).

The Product contaminant concentration limit of 25mg/kg NP/NPE specified in the draft Guideline for the Beneficial Use of Organic Waste Products on Land was adopted from the recommendations in the 2014 CIBR review (Tremblay et al, 2014). This concentration limit represents the concentration limit set in Belgium for NP/NPE in digestate (Mininni et al, 2015). In comparison the EU has proposed a concentration limit of 50 mg/kg for NP/NPE in sewage sludge applied to land for agricultural use (EU, 2000).

In conclusion there is no reason to retain a lower product contaminant concentration limit of 25 mg/kg for NP/NPEs in the draft Guideline, and increasing the product contaminant concentration to 50 mg/kg does not present an increased risk to soil ecosystems, the wider environment, or human health.

Linear Alkylbenzene Sulphonates (LAS)

Linear alkylbenzene sulphonates (LAS) are the most widely used anionic surfactant. Similar to NPs/NPEOs, LAS is not a single compound and is composed of a mixture of branched isomers with alkyl chain lengths of 10 to 15 carbon atoms, C11 to C13 being the most common. LAS is one of the major ingredients in domestic and industrial detergents and surfactants and therefore is present at relatively high concentrations in sewage sludge.

LAS are easily degraded under aerobic conditions so the concentration of residual LAS in biosolids is highly dependent on the type of sludge produced and the processes within the treatment works. The concentration of LAS in aerobic digested sludge is typically in the range 100-500 mg/kg but it is significantly greater in anaerobic digested sludge's where it can vary between 5000-15000 mg/kg (Jones and Northcott, 2000). Currently there is no data for the concentration of LAS in sewage sludge and biosolids in New Zealand.

LAS rapidly degrades in soil with half-lives of 1-3 weeks. Reviews of the fate and effects of LAS in soil conclude they present a low long term risk to soil ecosystems when amended to soil at recommended agronomic rates (de Wolf and Feijtel, 1998; Jensen, 1999; Norwegian Scientific Committee for Food Safety,2009).

The Product contaminant concentration limit of 1500 mg/kg LAS specified in the draft Guideline for the Beneficial Use of Organic Waste Products on Land was adopted from the limit set by Belgium for LAS in compost or digestate. This is lower than the concentration limit of 2600mg/kg set by the EU for LAS in sewage sludge applied to land for agricultural use (EU, 2000).

Similar to the argument presented to increase the product contaminant concentration limit for NP/NPE in the draft Guideline, increasing the product contaminant concentration for LAS to the proposed EU limit of 2600mg/kg does not present an increased risk to soil ecosystems, the wider environment, or human health.

Diethylhexylphthalate (DEHP)

Phthalates esters are incorporated into plastics as plasticisers and Bis-(2-ethyl-hexyl)-phthalate (DEHP) is the most commonly used worldwide

The Product contaminant concentration limit for DEHP of 75mg/kg specified in the draft Guideline for the Beneficial Use of Organic Waste Products on Land appears to be derived from EU concentration limits summarised in the 2014 CIBR review (Tremblay et al, 2014) which varied from 50 to 100 mg/kg in sewage sludge, compost and digestate.

The EU Working Document on Sludge (EU, 2000) proposes a concentration limit of 100 mg/kg dry matter for DEHP in sewage sludge applied to agricultural land. A 'representative mean' concentration for DEHP obtained from studies of sewage sludge in the USA, Canada, Germany and Sweden is about 90 mg/kg (Duarte-Davidson et al., 1995).

DEHP is rapidly degraded in soil and extremely inefficiently transferred into plants and through foodchains (Duarte-Davidson et al., 1995). Risk assessments completed to date on DEHP applied to land in sewage sludge demonstrate there is no increased risk to soil and aquatic ecosystems, or health risks to either animals or humans when sewage sludge is applied to land at agronomically realistic rates (Duarte-Davidson and Jones, 1996; Wilson et al., 1996, Norwegian Scientific Committee for Food Safety, 2009).

Therefore, increasing the product contaminant concentration limit for DEHP in the draft Guideline to the proposed EU limit of 100mg/kg in biosolids and organic biowaste does not present an increased risk to soil ecosystems, the wider environment, or human health.

Musk fragrances (Tonalide and Galaxolide)

Galaxolide (1,3,4,6,7,8-hexahydro- 4,6,6,7,8,8,- hexamethylcyclopenta (γ) – 2 – benzopyrane (HHCB)) and Tonalide (7-acetyl-1,3,4,4,6-hexamethyltetrahydronaphthalene (AHTN)) are the two most widely used polycyclic musk fragrances and are estimated to represent over 95% of the worldwide market for polycyclic musks. Galaxolide and Tonalide are reasonably hydrophobic chemicals that adsorb to and concentrate in sewage sludge.

The concentration of Galaxolide and Tonalide in sewage sludge is typically in the ppm range (mg/kg) and Galaxolide is almost always present at a higher concentration than Tonalide (Table 4) reflecting its more extensive use in personal care products. The concentration of Galaxolide and Tonalide measured in biosolids from WWTPs in New Zealand is comparable to that in sewage sludge and biosolids from other Western countries (Table 4).

Product contaminant concentration limits of 10 and 15 mg/kg are listed respectively for Galaxolide and Tonalide in organic biowaste within the draft Guideline. These concentration limits have been adopted from those applied by Germany for Galaxolide and Tonalide in sewage sludge applied to agricultural land, but no other member country of the EU has implemented such limits for Galaxolide and Tonalide.

The data in Table 4 demonstrates the concentration of tonalide in biosolids worldwide generally falls below the proposed Product contaminant concentration limits of 15 mg/kg in the draft Guideline. In comparison the concentration of galaxolide in New Zealand biosolids and those from most other countries exceeds the Product contaminant concentration limits of 10 mg/kg in the draft Guideline.

Galaxolide is inherently biodegradable in soil (EU, 2008) and rapidly dissipates from sewage sludge amended soils. For example, the half-life of galaxolide in sludge amended US soils, incorporating a three-month period of freezing to simulate winter conditions, was estimated at 141-144 days (DiFrancesco et al, 2004). A half-life of 105 days was obtained for galaxolide in sludge amended soil in New Jersey USA (Envirogen, 1998), and over 90% of galaxolide had dissipated from soil four weeks after amending biosolids to an agricultural field in Ontario (Yang and Metcalfe, 2006).

Table 4. Concentration of Galaxolide and Tonalide in sewage sludge and biosolids (mg/kg) from New Zealand and other countries

Country	No of WWTP	Sludge description	Galaxolide	Tonalide
New Zealand 2004 ^A	10	Various	1.7- 32.3	0.51- 6.9
Netherlands 1997 ^B	11	Primary	5.4-27	3.3-14
Netherlands 1997 ^B	6	Activated sludge	4.4-63	2.3-34
Netherlands 1999 ^B	8	Primary	6-17	3.7-11.7
Netherlands 1999 ^B	7	Activated sludge	0-21	0-13.5
Netherlands 1999 ^B	2	Digested	19-21	11-13
Germany 1997 ^B	17	Activated	0.1-5.2	0.1-8.9
United Kingdom 2000 ^C	14	Digested	1.9-81	
Denmark ^D	5	Various	11.4-26.5	
Italy 2004 ^E	6	Various	7.7-56	
Spain 2004 ^E	6	Various	12-69	
Greece 2004 ^E		Various	12-39	

Source: ^ACDRP 2005; ^BBalk and Ford, 1999; ^CStevens et al, 2003; ^DMorgensen, 2004; ^EBlok et al, 2005.

A risk assessment of organic contaminants in sewage sludge applied to land in Scotland concluded galaxolide presented a relatively low level of risk to the environment and to human health (WCA, 2014). Similarly, a risk assessment for galaxolide completed for the EU concluded that under normal sludge application conditions the transfer of galaxolide from soil to plants is not relevant and there was no need for risk reduction measures regarding exposure of galaxolide to humans and wildlife from this source to the environment (EU, 2008). The EU risk assessment for galaxolide was completed assuming a concentration of 46.9 mg/kg galaxolide in sewage sludge which is almost five times greater than the Product contaminant concentration limit of 10 mg/kg for galaxolide in organic biowaste in the draft Guideline. Based on the best scientific evidence currently available it is apparent the Product contaminant concentration limit of 10 mg/kg for galaxolide in organic biowaste in the draft Guideline is overly conservative. Based on the outcomes of the EU risk assessment for galaxolide in sewage sludge amended soil it is recommended the product contaminant concentration limit for galaxolide in organic biowaste is increased to 50 mg/kg within the draft Guideline.

Other EOCs.

The CIBR report on EOCs in organic wastes included many other EOCs that have not been included in the Guide, some of which are under the regulatory spotlight in Europe and the USA.

For example, Hexabromocyclododecane (HBCD), a common brominated flame retardant, is now listed in Annex A of the Stockholm convention to which NZ is a signatory. Triclosan (TCS) is the subject of intense

debate and review worldwide and has been banned in many jurisdictions. Regarding phthalate esters there is increasing concern about the environmental and human health impacts of di-isononyl- and diisodecylphthalates which have been produced to replace DEHP.

There is a lack of data on the concentration of these particular EOCs in New Zealand biosolids and biowastes. However, research being undertaken by CIBR will provide data on the concentration of HBCD and TCS in biosolids and biowaste in New Zealand. It is therefore appropriate to exclude these EOCs from the product contaminant list in the draft Guideline until this data is available and the risk these contaminants present to the environment and human health has been assessed.

SUMMARY OF PROPOSED CHANGES TO THE PRODUCT CONTAMINANTS AND CONCENTRATION LIMITS

The recommendations made above for the removal of specific organic contaminants as product contaminants, and modification of product contaminant concentrations for others, are reflected in the modified list of product contaminants and concentration limits in Table 5.

Table 5. Modified Product contaminant concentration limits proposed for inclusion in the Guideline for the Beneficial Use of Organic Waste Products on Land

Contaminant	Parameter	Concentration limit (mg/kg dry weight)
Arsenic		30
Cadmium		10
Chromium		1500
Copper		1250
Lead		300
Mercury		7.5
Nickel		135
Zinc		1500
Nonylphenol and ethoxylates ^A	NP/NPE	50
Phthalate	DEHP	100
Linear alkylbenzene sulphonates ^A	LAS	2600
Musks	Tonalide	15
	Galaxolide	50

^A comprising the sum of technical nonylphenol, NPE10 and NPE20 equivalents

^B comprising the sum of technical C11-C13 homologues and corresponding mixture of isomers

These recommended modifications are based on best available scientific knowledge and reflect the relatively low risk the listed organic contaminants present to the environment or human health from the application of biowaste to land.

Adopting EU limits for the concentration of NP\NPE, DEHP and LAS in sewage sludge applied to agricultural land within the draft Guideline provides the advantages of harmonising contaminant limits with countries that are continuing to reassess the risk organic contaminants in biosolids present to the environment and human health. Any future changes to contaminant limits in sewage sludge implemented by the EU can be justifiably incorporated into future revisions of the New Zealand Guideline for the Beneficial Use of Organic Waste Products on Land.

Similarly, if the outcomes of future research undertaken in New Zealand or overseas demonstrate other organic chemicals in biosolids and organic biowaste represent a high risk to the environment or human health, or our understanding of the risk presented by the organic chemicals in the current list changes, of they can be integrated into

Similarly, as research provides new information on the risk organic chemicals in biosolids and organic biowaste present to the environment or human health it should be evaluated for incorporation into the New Zealand Guideline for the Beneficial Use of Organic Waste Products on Land.

RECOMMENDATIONS FOR THE ANALYSIS OF EOCs IN ORGANIC BIOWASTE

The commercial analytical testing laboratories in New Zealand have the necessary laboratory equipment and analytical instrumentation to analyse the modified list of organic product contaminants proposed in this report. These laboratories have the expertise and capability to develop and validate a targeted organic contaminant protocol to analyse the specified organic contaminants within organic waste products.

The different properties of the organic chemicals in the modified list of EOCs in Table 5 means they are unable to be extracted by a common solvent and instead it will be necessary to apply two separate extraction methods. The extraction of NPs/NPEs, DEHP, and tonalide and galaxolide from organic biowaste can be accomplished with standard solvent extraction methods for semi-volatile organic contaminants using dichloromethane or a mixture of acetone and hexane as the extracting solvent.

Due to their high polarity the extraction LAS from organic biowaste will require the use of methanol as the extraction solvent.

Extraction techniques recommended and approved by the USPEA including soxhlet extraction, sonication extraction, and pressurised liquid extraction are all suitable for extracting the EOCs in the modified product contaminant list from organic biowaste.

The extent to which the solvent extracts of organic biowaste will need to be purified before instrumental analysis will be dependent upon the extraction method and solvent that is employed, and the properties of the biowaste being analysed. However, the product contaminant concentrations for the proposed EOCs are relatively high compared to normal environmental concentrations, and as such it may be possible to overcome the negative effects of co-extractive matrix components by simply diluting the raw sample solvent extracts before analysis.

Following extraction from organic biowaste the specified EOCs can be analysed using gas chromatography-mass spectrometry (GCMS) and/or liquid chromatography-mass spectrometry (LCMS).

Analysis of the listed EOCs by LCMS provides the advantage that it would not be necessary to chemically derivatise any of the EOCs prior to analysis and it may be possible to analyse all five compounds/classes of EOCs in a single chromatographic run.

Analysis of LAS by GCMS will require chemical derivatisation of LAS to their respective trifluoro-sulphonates or sulphonated alkyl esters using appropriate procedures.

Analysis of LAS using the colorimetric methylene blue assay to obtain total anionic surfactant content is not recommended as this will have limited application to organic wastes due to the myriad of interferences it is subject to.

With the appropriate choice of injection solvent and instrumental and chromatographic conditions the analysis of NP/NPE, DEHP, galaxolide and tonalide can be accomplished by GCMS in a single chromatographic run without derivatisation. Alternatively, DEHP, NP1EOs, NP2EOs, galaxolide and tonalide can first be analysed and the extract subsequently derivatised for the analysis of technical-NP as the corresponding alkyl, alkylhalide, or alkylsilyl ethers.

The combined cost to analyse the organic contaminants in the modified Product Contaminant list at the specified concentration limits should be somewhat less than the previous combined cost to analyse total PCBs, Dioxin TEQ, and the chlorinated organic contaminants previously specified in the 2003 Biosolids Guidelines.

Specific recommendations regarding quantitating and reporting of technical NP/NPEs and LAS residues

As discussed previously NP/NP1EOs/NP2EOs and LAS are not single chemicals and are instead technical industrial mixtures comprising a series of branched alkyl chain isomers in the case of NP/NP1EOs/NP2EOs, and for LAS a series of alkyl chain homologues containing a series of isomers.

Using standard GCMS analysis up to 22 individual NP compounds can be detected in Technical mixtures of NP but the resulting total ion chromatogram is typically dominated by 8 to 12 peaks.

The linear alkyl chain of LAS consists primarily of C10 to C13 homologues, typically in the ratio of 13:30:33:24, and commercial products commonly contain around 20 individual compounds.

NP/ NP1EOs / NP2EOs are most often analysed and reported as “equivalents” of the corresponding technical mixtures. In the case of technical-NP common mass ions selected from the dominant 8 to 12 peaks in a chromatogram of a technical-NP mixture are acquired and the mass contribution of each peak determined to produce calibration curves for the dominant peaks. The mass ion responses obtained from analysis of a sample are integrated and quantitated against the calibration curves. The masses obtained for each individual peak are summed, and this “total” is reported as the mass of technical-NP equivalents. The same approach is applied for the analysis of the corresponding mixtures of NP1EOs and NP2EOs.

The same approach is used for the analysis of LAS, but LAS is typically reported as equivalents of the individual C10, C11, C12 and C13 homologues. This procedure has persisted from the original HPLC analysis methods for LAS that were able to resolve the C10 to C13 homologue series, but not the individual isomers within each homologue group.

Modern LCMS instruments will be able to resolve the individual LAS isomers within each homologue group on the basis of mass-ion differentiation, and therefore LAS can be reported as both the individual isomers and their respective total within each homologue group.

Following chemical derivatisation of LAS, the increased chromatographic resolution provided by glass capillary gas chromatography columns enables the individual isomers within each homologue groups of commercial mixtures of LAS to be analysed by GC-based methods.

Analytical standards of representative industrial mixtures of NP/NP1EOs/NP2EOs and LAS are available from providers of specialist analytical standards. These same suppliers often provide standards of selected individual compound isomers which should be purchased and used to validate the performance of the analytical method. Similarly, isotopically labelled standards available from specialist suppliers

should be used as internal and recovery standards to improve the performance of the analytical method, and to normalise the effects of signal enhancement and/or suppression arising from the presence of residual co-extracted matrix in solvent extracts of organic biowaste.

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