Centre for Integrated Biowaste Research

Organic Materials Guidelines – Organic Contaminants Review

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Centre for Integrated Biowaste Research

‘Organic Materials Guidelines – Organic Contaminants Review

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EXECUTIVE SUMMARY

The Ministry for the Environment New Zealand Water and Wastewater Association (2003) Guidelines for the Safe Application of Biosolids to Land in New Zealand are designed to safeguard the life-supporting capacity of soils, promote the responsible use of biosolids, protect public health and the environment and minimise risk to the New Zealand economy.
There is a strong perception of risk within the wider community when considering land application or reuse of biosolids. There are concerns about the range of contaminants that those wastes could contain and the uncertainty about the potential health effects and economic consequences. This report critically reviews the pertinence of the organic contaminants that are incorporated in the Guidelines document to recommend amendments that reflect the current level of knowledge to minimise any potential risk associated with the land application of biosolids and other biowastes.

Below are the recommendations for emerging organic contaminants (EOCs) that could form part of the new Organic Materials Guidelines:

- The organic contaminants listed in Table 4.2 of the NZ guidelines can be considered as obsolete in view of the on-going research findings on the sources and fate of POPs in New Zealand;
- Alternatively, new contaminants should be considered for inclusion in view of recent findings on the levels and risk potential of EOCs in biosolids. Based on local and international literature, EOC classes should include endocrine disruptors (e.g. steroids, nonylphenols), flame retardants (e.g. HBCD and selected PDBEs), antimicrobial agent (e.g. triclosan and ciprofloxacin) and pharmaceuticals (e.g. carbamazepine, diclofenac); persistent herbicide (clopyralid); cleaning agent (LAS);
- At this stage, there is not enough information to derive New Zealand specific limits but interim values could be used as per Table 4;
- Other biowastes should be included in the revised guidelines and soil limits should be derived for the specific residue contaminants. The selection of contaminants should be risk-based, i.e. involve estimations of both exposure and effect;
- The revised Guidelines should be based on a flexible and responsive framework to incorporate new and relevant scientific knowledge to facilitate the ongoing acceptance and adoption of the beneficial use of biowastes in NZ. The framework should also facilitate incorporation of social, cultural and community input as the acceptance of the practise will depend on the relevance and risk perception of the various contaminants.

Introduction and context

The *Guidelines for the Safe application of Biosolids to Land in New Zealand* was published in 2003 and a review is conducted to amend the document according to the latest information available in the literature. This report reviews the component of the Guidelines relating to organic contaminants to assess the validity of suggested threshold values and the relevance of chemical targets. In the last 10 years, there has been significant progress in research on organic contaminants in biosolids and their potential risks. This report critically reviews the pertinence of the organic contaminants that are incorporated in the current Guidelines document and recommend amendments that reflect the current level of knowledge to minimise any potential risk associated with the land application of biosolids and other biowastes. There is an emphasis on a group of contaminants referred to as emerging organic contaminants (EOCs). The US Geological Survey has defined an EOC as “any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognised until new detection methods were developed. In other cases, new sources of emerging contaminants can be created through the synthesis of new chemicals or changes in use and disposal of existing chemicals (http://toxics.usgs.gov/regional/emc/).

Aims and Approach

The aims of this report were to:

1. Summarise existing knowledge on organic contaminants in organic wastes relative to the current *Guidelines for the Safe and Application of Biosolids to Land in New Zealand* (2003) (Table 4.2).
2. Review the justification for the inclusion of the following organics: DDT/DDD/DDE; Aldrin; Dieldrin; Chlordane; Heptachlor & Heptachlor epoxide; Hexachlorobenzene (HCB); Hexachlorocyclohexane (Lindane); Benzene hexachloride (BHC); Total polychlorinated biphenyls (PCBs); Total dioxin TEQ (cf Table 4.2 in the Biosolids Guidelines). Provide recommendations for which organic contaminants should and should not be in a new guideline with supporting logic.
3. Determine if other organic wastes contain additional organic contaminants of concern that should be included in a new guideline.
4. Review the allowable concentrations of organic contaminants in biosolids (Table 4.2. in current Biosolids Guidelines); and provide recommendations for any new limits for waste that will not cause waste-amended soil to approach the soil contaminant limits (using the current soil limits in Table 4.2 noting that these might change under the new Soil Health Indicators Envirolink Project).
5. Provide recommendations for the above items 1-4 with supporting logic.

Summary of Existing Knowledge

The *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (New Zealand Water Wastes Association 2003) was written with the purpose to:

- Safeguard the life-supporting capacity of soils;
- Promote the responsible use of biosolids;
- Protect public health and the environment;
- Identify the risks associated with biosolids use and promote best practice for minimising such risks;
- Encourage local authorities to adopt a consistent approach to regulating the application of biosolids to land;
- Create awareness within the community of the benefits and risks of biosolids use;
- Minimise the risk to the economy.

Within these guidelines risks are divided largely into microbiological and chemical categories. This is reflected in the grading system for the biosolids which includes a separate grading for microbiological quality and chemical quality. According to these guidelines biosolids can be awarded 2 levels of microbiological grades (A and B) and 2 levels of organic contaminants grades (a and b). The microbiological risks are dealt with in another Working Group report. As biosolids are likely media to accumulate parts of those products, a recent review of Guidelines commissioned by the ANZ Biosolids Partnership concluded that contaminant levels for each of the grades should be updated in line with up-to-date international, Australian and New Zealand research knowledge (Darvodelsky et al. 2009).

The use of chemicals is a key component in the maintenance of our standard of living in modern society. With nearly two thirds of the world's population living in urban areas, cities concentrate multiple human activities and are major contributors of waste by being concentrators, repositories, and emitters of a myriad of chemicals of anthropogenic origin (Diamond & Hodge 2007). Many chemicals are produced from daily domestic activities such as cooking, cleaning, personal grooming, medical care, and gardening. A study investigating contaminants contained in household solid wastes in the UK identified a number of sources including paint, pet products, pharmaceuticals, household cleaners, motor vehicle waste and printer cartridges (Slack et al. 2007). The focus has been on high production volume (HPVs) chemicals in use in household products for their higher potential to accumulate into the environment. The US National Institutes of Health (NIH) list roughly 2800 compounds in daily (household) use, based on a survey of Material Safety Data Sheets (MSDS) of 7000 household products. HPV chemicals are manufactured in or imported into the United States in amounts equal to or greater than 0.5 million kg per year. An extensive study commissioned by the Water Environment Research Foundation (WERF) looked at household chemicals from a list of 720 HPV compounds identified within eight main activities: 1) auto products, 2) inside the home, 3) pesticides, 4) home maintenance, 5) personal care/use, 6) pet care, 7) arts and crafts, and 8) landscape/yard. From the extensive list of HPV chemicals, a two-tiered ranking approach based on production volumes, environmental relevance, and feasibility for analytical quantification was developed. Tier 1 compounds are classified as consumer product chemicals that can be released in high quantities. Tier 2 are organic compounds that are either frequently used in households or are present in household products. Short lists of 11 Tier 1 and 13 Tier 2 chemicals were identified by WERF for future monitoring and are summarised in Tables 1 and 2.

Table 1.Major emerging organic contaminants associated with household wastes- Tier 1 compounds. From WERF report 2009.

Compound	Application
2,6-Di-t-butyl-p-cresol (BHT)	Skin care, hobby supplies
Dibutyl phthalate	Plasticizer, finish, nail care
Atrazine	Herbicide
Bisphenol A (BPA)	plasticizer, epoxy, glue
Benzophenone	Car wash, facial products
Oxybenzone	Skin care, insect repellent
Triclosan	Antibacterial, soap, lotion
Vanillin	Fragrance, cosmetics, various
o-Phenylphenol	germicide, fungicide
2-Phenoxyethanol	Preservatives, cosmetics, fragrance
Hexabromocyclododecane (HBCD)	Flame retardant

Table 2. Major emerging organic contaminants associated with household wastes- Tier 2 compounds. From WERF report 2009.

Compound	Application
Simazine	Herbicide, anti-algae products
DEET	Insect repellent
Hydrocortisone	Anti-itch cream
Butylated hydroxyanisole (BHA)	Antioxidant, various
3-Indolebutyric acid	Fertilizer
Camphor and menthol	Fragrance, various
2-Methylresorcinol	Hair colour, cosmetics
Isobutylparaben	Preservative, cosmetics, various
Acriflavine	Pesticide
Trifluralin	Herbicide
Propylparaben	Preservative, various

Linear alkylbenzene sulfonate (LAS) and triclocarban were also incorporated in the design as model compounds for their specific characteristics (Table 3). LAS can function as a model for complex mixtures and triclocarban is an emerging contaminant model for which only a limited amount of data is available. Several previously studied pharmaceuticals were also studied as indicator compounds of interest (Table 3).

Table 3. Model emerging organic contaminants associated with household wastes used as model and indicator compounds. From WERF report 2009.

Compound	Application
Model Compounds	
Triclocarban	Antibacterial, soap, deodorant
Linear alkylbenzene sulfonate (LAS)	Surfactant, various
Indicator Compounds	
Primidone	Antiepileptic drug
Phenacetine	Anti-inflammatory drug
Carbamazepine	Antiepileptic drug
2-Naphthol	Industrial chemical
Fenofibrate	Blood lipid regulator
Gemfibrozil	Blood lipid regulator
Propyphenazone	Anti-inflammatory drug
Sulfamethoxazole	Antibiotic drug
Ibuprofen	Anti-inflammatory drug
Naproxen	Anti-inflammatory drug
Diclofenac	Anti-inflammatory drug

The removal or transformation of HPV chemicals by biological treatment (activated sludge and membrane bioreactor [MBR]), disinfection (ultraviolet [UV] light, chloramines, chlorine), and advanced oxidation (ozone and ozone/hydrogen peroxide) processes was evaluated. The authors of the WERF report concluded the removal rate of Tier 1 and 2 compounds by MBR and activated-sludge treatments was largely similar at > 80%, indicating high efficacy by biological treatment. Of the conventional disinfection processes, chlorination represents a process for partial transformation of Tier 1 and 2 compounds and is an additional barrier for the removal of contaminants. Ozonation and ozone/hydrogen peroxide treatments can perform well to achieve higher effluent quality but do not eliminate 100% for all compounds (e.g., vanillin). Of the indicator compounds, some exhibited high rates of removal (e.g., ibuprofen, naproxen) and some compounds were not effectively removed (e.g., carbamazepine, primidone, diclofenac). The hydrophobic compounds are likely to be bound to solids and removed during the separation of sewage solids.

List of regulated organic contaminants

The *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) refer to (Paxeus 1996) who identified over 137 organic compounds in the influent of municipal wastewater plants but the authors stated that “a large number of substances present in the wastewater could not be positively identified due to a lack of their reference spectra”.

The only organic contaminants for which recommended limits have been set in the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) include persistent organic pollutants (POPs), namely organochlorine pesticides, polychlorinated biphenyls and polychlorinated dibenzodioxins/furans (Table 2). The limits are based on the contaminant limits set by the New South Wales

Environmental Protection Agency (NSW EPA 1997) and the National Resource Management Ministerial Council of Australia (NRMMC 2003).

Since 1996, many more organic contaminants have been identified in biosolids around the world. In recent years, not only sewage effluent but also sewage-derived biosolids have been extensively characterised for organic contaminants. (Eriksson et al. 2008) and (Harrison et al. 2006) reviewed organic contaminants in sewage sludge in peer reviewed publications and government reports, and reported that 516 different EOCs had been determined in sewage sludge. Preliminary results from a New Zealand study looking at the efficacy of a range of sewage treatment technologies indicate that many EOCs including parabens, chloroxylenol and triclosan are poorly removed and still present in treated effluents (J Strong unpublished). EOCs determined in sewage sludge and their concentration ranges have been reported by (Harrison et al. 2006) under the following categories :

- Aliphatic hydrocarbons;
- Chlorobenzenes;
- Dioxins, furans and polychlorinated biphenyls;
- Endocrine disruptors, sterols and stanols;
- Flame retardants;
- Monocyclic hydrocarbons;
- Nitrosamines;
- Organic phosphate esters;
- Organotins;
- Pentachlorophenols (PCPs) and phenols;
- Pesticides;
- Pharmaceuticals and personal care products;
- Phthalates and plasticizers;
- Polycyclic aromatic hydrocarbons (PAHs);
- Polychlorinated biphenyls (PCBs),;
- Surfactants (nonylphenols and nonylphenolethoxylates).

An additional category of EOC were measured in sewage sludge by (Venkatesan & Halden 2013a). This was:

- Perfluoroalkyls (PFASs)

A US study measured 87 different organic chemicals representing a diverse cross section of EOCs that enter wastewater treatment plants in biosolids samples from across the country and demonstrated that biosolids contain higher levels of EOCs (as mass-normalized concentrations) than effluents (Kinney et al. 2006). The major EOC classes identified in biosolids were steroids and detergent metabolites followed by fragrances (Kinney et al. 2006). An survey of Australian biosolids measured similar concentrations of surfactants and triclosan (Langdon et al. 2011). Preliminary results from a New Zealand study measured a range of pharmaceuticals in biosolids (G Northcott unpublished). Some commonly used drugs, like acetaminophen, diclofenac and the beta-blocker metoprolol, were detected at relatively high levels.

In a Canadian biosolids land application study, the fate of 80 pharmaceuticals and personal care products (PPCPs) were monitored in groundwater, tile drainage, soil, and in the grain of wheat grown on the field for 1 year following application of biosolids (Gottschall et al. 2012). Concentrations of several PPCPs declined following exponential decay and none were detected in the grain of wheat (Gottschall et al. 2012). Another land application study on farmland in an arid area in the eastern plains of Colorado indicated that EOCs migrated downward through the soil by 468 days post-application but there was little uptake by mature wheat plants (Yager et al. 2014). The authors stated that more research is required to fully assess the risk of more persistent EOCs, particularly to predict potential effects of those that are persistent or can be mobilized. A recent NIWA study measured the concentrations of a range of EOCs in estuarine sediments from around Auckland found levels similar to those reported world-wide (Stewart et al. 2014). The main source is possibly sewage outfalls but the fact remains that EOCs are transported in the receiving environment and that vigilance is warranted to minimise other potential sources such as land application of biowastes.

Risk assessments

Despite gaps in knowledge, several risk assessments of a wide range of EOCs have been undertaken in order to evaluate the risk they may pose to human health and the environment. These risk assessment processes often require the estimation of exposure levels through likely exposure scenarios. In addition, these risk assessments often need to extrapolate toxic effects to humans and the environment from laboratory based experiments because of the paucity of knowledge about the effects of EOCs.

In addition, this lack of information on the fate and effects of EOCs means that subtle effects that may impact humans and ecosystems are not being considered and incorporated within existing risk assessment frameworks. The subtle effects may include blocking of multixenobiotic transporters leading to chemo-sensitation and allergies (Schirmer et al. 2006), increased aggressive behaviour after selective serotonin reuptake inhibitors such as fluoxetine and sertraline accumulation (Daughton & Ternes 1999; Brooks et al. 2005) or abnormal behaviours due to exposure to endocrine disrupting compounds (Zala & Penn 2004).

Despite their shortcomings, comprehensive risk assessments are a useful tool to identify the potential risks that EOCs may pose on humans and the environment. For example Eriksson *et al*. identified 23 priority pollutants representing different chemical classes by a risk quantification process (Eriksson et al. 2008). These were:

- flame retardants and PCBs (DecaBDE, decabromobiphenyl and PCB 28);
- pesticides (endrin and triclosan);
- endocrine disrupters (17β-estradiol, nonylphenol, nonylphenol mono-ethoxylate, pentachlorophenol);
- phthalates (DEHP and di-(i-nonyl) phthalate);
- PAHs (anthracene, benzo[*a*]anthracene, benzo[*b*] fluoranthene, benzo[*b*]fluorene, benzo[*ghi*] perylene, chrysene, fluoranthene and indeno [1,2,3-*cd*]pyrene);

- alkanes (phytane and pristane);
- cleaning agent linear alkylbenzene sulfonates (LAS).

Clarke and Smith extended this approach and ranked EOCs based on environmental persistence, human toxicity, evidence of bioaccumulation in humans and the environment, evidence of ecotoxicity and the number and quality of international studies focussed on the contaminant (Clarke & Smith 2011). They identified and ranked the following chemicals of concern in decreasing order of priority:

- perfluorinated chemicals (PFOS, PFOA);
- polychlorinated alkanes (PCAs);
- polychlorinated naphthalenes (PCNs);
- organotins (OTs);
- polybrominated diphenyl ethers (PBDEs);
- triclosan (TCS), triclocarban (TCC);
- benzothiazoles;
- antibiotics and pharmaceuticals;
- synthetic musks;
- bisphenol A (BPA);
- quaternary ammonium compounds (QACs);
- steroids;
- phthalate acid esters (PAEs);
- polydimethylsiloxanes (PDMSs).

International legislation

Despite awareness about EOCs in the environment (Daughton & Ternes 1999), international legislations controlling EOCs in sewage sludge are very diverse or non-existent. This may be partly due to the large number of potential contaminants, the relatively low levels of contaminants, and the gap in knowledge about the chronic effects of contaminants on human health and the environment. Overall, UK, USA and Canada claim that typical concentrations of organic micro pollutants in sewage sludge are not hazardous to soil quality, human health or the environment.

The EU policy on sewage sludge utilization (Mininni et al. 2014) proposed regulation of the following organic micropollutants:

- AOX;
- Sum of 7 PCBs (congeners 28, 52, 101, 118, 138, 153, 180);
- PCDD/F i.e. chlorinated dioxins and furans;
- Sum of 11 Polycyclic aromatic hydrocarbons (PAHs) acenaphthalene, benzo(a)pyrene, benzo(b)anthracene, benzo(ghi)perylene, benzo(j)anthracene, benzo(k)anthracene, fluoranthene, fluorene, indeno (1,2,3-cd)pyrene, phenanthrene and pyrene;
- Nonylphenols (NP) and nonylphenolethoxylates NPE;
- Phthalate (Di(2-ethylhexyl) phthalate – DEHP);
- Linear alkylbenzene sulfonates (LAS).

These organic micro pollutants in sewage sludge have been regulated in Austria, Czech Republic, Denmark, France, Germany and Sweden (Mininni et al. 2014). Regulation limits of organic micro pollutants vary between country and waste source, *i.e.* sewage sludge used in agriculture versus compost (Table 4).

The *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) currently limit selected organics including persistent chlorinated pesticides, PCBs and dioxins. When comparing the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) with EU regulation, it becomes obvious that the NZ Guidelines are heavily slanted towards regulation of chlorinated persistent organic pollutants (Cl-POPs). The focus on Cl-POPs in the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) reflected the goals of the NZ Government policy for the regulation and management of organic pollutants during the time they were produced. The Cl-POPs were the subject of intense international research, prompted by their recognised persistence, bioaccumulation, and toxicity and were identified for elimination by the Stockholm Convention, of which NZ remains a signatory. Major reviews of organochlorine chemicals in the NZ environment undertaken by MfE identified relatively high concentrations of Cl-POPs could be present in NZ sewage sludges. Hence the inclusion of these specific organic chemicals in the Biosolids Guidelines.
In the years following the publication of the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) New Zealand has implemented regulations either banning the importation, significantly restricting the use of, or eliminating activities that produce Cl-POPs and release them into the environment. This has 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 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 reduced concentrations in sewage sludges and biosolids. The US-EPA decided not to regulate dioxins in biosolids after studies demonstrated that this source does not pose a significant risk to human health or the environment (http://www.epa.gov/ost/biosolids/dioxinfs.html).

The requirement to monitor residues of Cl-POPs in sewage sludges and biosolids in New Zealand places a considerable financial burden on biosolids producers to produce data that has limited questionable relevance.

In comparison there are many new organic chemicals of concern within sewage sludge and biosolids that have been identified as high risk or chemicals of concern internationally, and for which we have no or very limited data in New Zealand,

Table 4. Range of guideline limits of organic pollutants for sludge used in agriculture, compost and digestates (mg/kg DM) based on (Mininni et al. 2014) and compared with NZ biosolids guidelines (New Zealand Water Wastes Association 2003).

Class	Organic micro pollutant	Range of EU countries		NZ Sewage sludge and compost	
		Sewage sludge	Compost & Digestate	Grade a	Grade b
Perfluoro compounds	PFOS and PFOA		0.01		
Absorbable organic halogens	AOX	400 – 500	250 – 500		
Polychlorinated biphenyls	PCB sum	0.1 – 1	0.15 – 1	0.2	0.2
Dioxins	PCDD/F (ng/kg DM)	30 – 100	20 – 100	30	50
Polycyclic aromatic hydrocarbons	PAH sum	3 - 6	3 – 10		
Nonyl phenol and - ethoxylates	NP/NPE	10 – 450	10 – 25		
Phthalate	DEHP	50 – 100	50		
Linear alkydbenzene sulphonates	LAS	1300 – 5000	1300 – 1500		
Musks	Tonalide	15			
	Galaxolide	10			
Rubber tires	Mercaptobenzothiazole and hydroxybenzothiazole	0.6			
Pesticides	DDT/DDD/DDE			0.5	0.5
	Aldrin			0.02	0.2
	Dieldrin			0.02	0.2
	Chlordane			0.02	0.2
	Heptachlor and heptachlor epoxide			0.02	0.2
	Hexachlorocyclohexane			0.02	0.2
	Benzene hexachloride			0.02	0.2

The priority organic pollutants identified in the international literature for which regulatory limits need to be established are described in detail in Appendix A.

A list of potential priority organic micropollutants considered to be representative of the main classes of contaminants in sewage sludge (Table 5) has been proposed based on a hazard assessment approach (Eriksson et al. 2008).

Table 5. List of selected target compounds based on expert judgment some of which are included in EU regulations at levels shown in Table 4 (Eriksson et al. 2008).

Group	Selected compound
Aliphatic hydrocarbons	Hexadecane
Dioxins and furans	TCDD
Endocrine disruptors	4-Nonylphenol/nonylphenol Bisphenol A
Flame retardants	Tetrabromobisphenol A DecaDBE
PAH	Benzo[*ghi*]perylene Naphthalene Fluoranthene
Pesticide/antimicrobial	Triclosan
Pharmaceuticals	Ibuprofen
Phthalates and plasticisers	Di-(2-ethylhexyl) phthalate Di-(2-ethylhexyl) adipate
Surfactant	Linear alkylbenzene sulfonate (LAS)

Rationale for Selection and Incorporation of Organic Contaminants into Guidelines

It is challenging to select organic contaminants of concern for inclusion in the guidelines due to the large numbers of chemicals entering sewage systems and the knowledge gaps about their potential fate and effects. The first step is to assess the rationale behind the incorporation of the organic contaminants in Table 4.2 of the Guidelines. The MfE review of organochlorine residues in river and soil samples from across the country showed that environmental levels of PCDDs, PCDFs, PCBs, and organochlorine pesticides are low in New Zealand and markedly lower than concentrations reported in other developed countries (Buckland et al. 1998a; Buckland et al. 1998b).

Agrichemicals that have been identified as persistent organic pollutants (or POPs) wastes are deregistered and banned from use in New Zealand as per the Stockholm Convention on POPs of which New Zealand is a signatory. Safe, effective collection and disposal of these chemicals is required for New Zealand to meet its obligations under the Stockholm Convention (http://chm.pops.int). The 12 organochlorine chemicals initially listed as POPs under the Stockholm Convention in 2004 are aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, hexachlorobenzene, toxaphene, PCBs, dioxins and furans. The elimination of these POPs in New Zealand is underpinned by managing their inputs to WWTPs via trade waste controls implemented by regional councils and territorial authorities. In general, the largest current day sources of POPs into the New Zealand environment are background atmospheric deposition and urban run-off.Therefore, it is unlikely that most of the organics listed in Table 4.2 of the Guidelines would accumulate within biosolids and their relevance is questionable. Most of the POPs listed in Table 4.2 have very few identifiable current day sources into biosolids in New Zealand, and those that exist can be effectively managed at the source. Currently the greater proportion of POPs entering WWTPs in New Zealand occurs via diffuse background atmospheric deposition and depuration from the human population.

In comparison to POPs the use of products containing EOCs continues to grow in New Zealand with the result that increasing volumes enter WWTPs. There is a need to regulate EOCs because of the significant knowledge gaps regarding their fate and effects in the environment and the high perception of risk they pose, e.g. potential for EOCs in the soil to transfer to crops, contamination of drinking water.

The main reasons to regulate the concentration of organic contaminants in biosolids are if they:

- pose a risk to human and environment health, or the economy;
- accumulate in the environment through a lack of degradation or sufficiently high usage in relation to their degradation rate;
- pose a risk to groundwater.

The EOCs identified from the literature as priority organic micropollutants in sewage sludge (Table 5; Appendix A) provide insights into the type of chemicals to consider setting regulatory limits

Other Organic Wastes

In the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003), biosolids are defined as “sewage sludges or sewage sludges mixed with other materials that have been treated and/or stabilised to the extent that they are able to be safely and beneficially applied to land”.

The term ‘biosolids’ and the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) therefore do not apply to other solid biowastes such as untreated raw sewage sludges or sludges derived solely from industrial processes, animal manures, food processing and abattoir wastes.

Each organic waste type may contain specific types and concentrations of contaminants associated with particular practices. Nevertheless, the organic contaminants may have some similarity especially if blended products remain regulated under the Guidelines.

Organic waste comprised of animal manure has excellent fertilizer and soil conditioning qualities that are comparable to sewage sludge derived biosolids. However, overseas studies showed that many antibiotics enter the soil environment with the land application of poultry and pig manure. The concentration of veterinary medicines and antibiotics in animal manures are generally high because they are used as animal food supplements for growth promotion and therapeutic treatment. Pig manures in Austria, Germany and China have been demonstrated to contain a wide range of antibiotics (enrofloxacin, sulfamonomethoxine, oxytetracycline, tetracyclines, sulphonamides, chlortetracycline and sulfadimidine) with maximum concentrations ranging from 4 to 59 mg/kg (Heuer et al. 2011). The concentrations of antibiotics in animal manure are often more than 10 times greater than that in sewage sludge.

In New Zealand, 47% of total antibiotics use (amounting to 75,000 kg) is associated with farmed animal production with approximately half consumed as growth promoters and prophylaxis (Sarmah *et al.* 2006). Nevertheless, only 6% of these antibiotics are used on ruminant animals and therefore it can be expected that sheep, beef, cattle and deer manure contains negligible amounts of antibiotics. In contrast, 19% of veterinary antibiotics are used on pigs and 74% on poultry (Sarmah et al., 2006). Therefore pig manure and particularly poultry manure can be expected to contain antibiotic residues that may require monitoring and the setting of appropriate concentration limits.

Organic wastes comprised of compost containing greenwaste and in particular grass clippings can contain a range of pesticides used to control weeds and insects These pyridine carboxylic acids, in particular aminopyralid, clopyralid and picloram are found consistently in compost from grass clippings that have been sprayed for broad leaf weeds. These compounds have a long active life and degradation, especially in biosolids can take up to 3 or 4 years. They remain active after animal and human excretion and after compost processing. Since the quality of compost will be included in any new Organic Waste Guideline and this group of herbicides is detected in compost pyridine carboxylic acids will need to be controlled in order to avoid damage to plants that the herbicide containing compost is applied to. The composting standards already refer to the contaminants from the Biosolids guidelines and there are already mechanisms in place to assess residual herbicidal activity including a plant bioassay and commercially available herbicide screen analysis.

Organic waste from viticulture, horticulture, crops, and vegetable processing may also contain some pesticides depending on the source but since they are applied to food crops regulation of pesticide application is likely to have been controlled during the food production cycle.

The forestry and the pulp and paper industries produce a range of organic wastes from sawdust and, bark through to residual fibres and organic biomass from treatment ponds. Common contaminants in sawdust, depending on its source are the heavy metals copper chromium and arsenic which are regulated in the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) and the New Zealand Timber Preservation Council Best Practice Guideline for the Safe Use of Timber Preservatives & Antisapstain Chemicals (2005).

Historically pulp and paper mills employed elemental chlorine to bleach pulp. This resulted in pulp mill effluent and sludges containing dioxins. However, since the late 1980s, elemental chlorine bleaching has been replaced by more environmentally friendly bleaching processes. These process changes have resulted in a significant reduction of effluent and sludge toxicity and impacts (van den Heuvel and Ellis 2002; Sandstrom and Neuman 2003). Pulp and paper mill sludges generally contain an abundance of resin acids and other extractives derived from wood lignin. Pulp mill solids exhibit low toxicity to oat, earthworm and enchytraeid worm test models, indicating that application of this material to land presents a low risk to terrestrial ecosystems (Fraser, 2007).

Other Considerations

The *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) are designed to safeguard the life-supporting capacity of soils, promote the responsible use of biosolids, protect public health and the environment and minimise risk to the New Zealand economy. The tools that are available for this are limiting exposure through:

- Controlling manufacturing and importation of products containing EOCs of concern;
- Improved wastewater and sewage sludge treatment;
- Imposing limits on annual loading rates of biosolids to land;
- Imposing limits on the specific contaminants of concern within biosolids.

This last option is used in the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (2003) and requires a well-defined and rational approach focusing on the more significant contaminants presenting a risk. The implications of requirements for costly analytical tests could hinder the beneficial recycling of organic wastes to land. Consequently, land application reuse option would continue to be too costly and alternative ways of disposal will continue to be favoured (e.g. landfill, incineration). It is therefore important to focus efforts and resources on selected indicator compounds that represent EOC classes associated with significant risk. By strategically choosing components to be included in the new Organics Waste Guideline, the on-going monitoring costs will not outweigh the benefits associated with land application options. There is on-going research investigating the fate and effects of EOCs and it would be beneficial to design a process within the Guidelines' framework allowing flexibility and responsiveness to incorporate and integrate outcomes from new scientific knowledge leading to reduced risk.

There is an increasing number of potentially harmful chemicals listed in the ingredients of domestic household products which has been identified as a point-source of EOCs in biosolids (Glegg & Richards 2007; Tremblay et al. 2013). It is a priority to engage with the wider community to assist them making better and more sustainable choices when purchasing household products. There are more initiatives to provide better information on the ingredients that are more likely to persist in the waste and represent human and environmental health risks (Goldsmith et al. 2014).

Conclusions and Recommendations

There is a strong perception of risk within the wider community when considering land application or reuse of organic wastes, especially biosolids. There are concerns about the range of contaminants that those wastes could contain and uncertainty about their potential health effects and adverse economic consequences related to environmental degradation. A study reported that there was significant risk with the application of biosolids to land as EOCs measured in the biosolids bioaccumulated in earthworms (Kinney *et al.* 2012). However, it is not feasible to characterise and regulate all organic compounds when considering land application of organic wastes. Furthermore, even if all compounds were measured, there is still limited knowledge to suitably assess the risks of EOCs on the receiving ecosystems and human health (Tremblay et al. 2013).

The recommendations for organic contaminants to be monitored in a new Organic Waste Guideline are:

- The organic contaminants listed in Table 4.2 of the NZ guidelines can be considered as obsolete in view of the on-going research findings on the sources and fate of persistent organic pollutants in New Zealand;
- Alternatively, new and representative contaminants should be considered for inclusion in view of recent findings on the concentration and risk potential of EOCs in biosolids. Based on local and international literature, EOCs classes should include endocrine disruptors (e.g. nonylphenols and steroid hormones), flame retardants (e.g. HBCD and selected PDBEs), antimicrobial agents (e.g. triclosan and ciprofloxacin) and pharmaceuticals (e.g. carbamazepine , diclofenac); persistent herbicides (e.g. clopyralid); cleaning agent (LAS);
- At this stage, there is not enough information to derive New Zealand specific limits but interim values could be used as per Table 4;
- The derivation of New Zealand specific EOC limits should be based on actual risk. This process should be implemented by the development of a risk assessment framework;
- Other biowastes should be included in the revised guidelines and soil quality limits derived for the specific residue contaminants;
- The revised Guidelines should be based on a flexible and responsive framework to incorporate new and relevant scientific knowledge to facilitate the continued beneficial use of biowastes.

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Appendix A: Organic Micropollutants

Perfluoro chemicals (PFCs)

Perfluorinated chemicals are a family of synthetic chemicals that do not occur naturally. They have been used since the late 1950’s to make products resistant to heat, oil, stains, grease and water. They are very resistant to degradation even more than other halogen compounds that include bromine, chlorine (Clarke & Smith 2011). The perfluorinated chemicals can degrade to release in particular the environmentally persistent perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA). These monomers were identified as the top priority pollutant by (Clarke & Smith 2011) and PFOS concentrations were detected in all biosolids from 32 US states at levels averaging 403 ng/kg DM (Venkatesan & Halden 2013a). In addition, field investigation have demonstrated that PFCs in sludge amended soil can be mobilised by rainfall (Gottschall et al. 2010).

However, there are analytical difficulties associated with quantification of PFCs in sewage sludge(Clarke & Smith 2011). This may impact on the applicability of including PFOS and PFOA in any regulating guidelines. It may however be more practical and cheaper to measure a sum of halogens and regulate these. The sum of absorbable halogens AOXs have been regulated in various EU countries (Table 4).

Chlorinated dioxins and furans

Dioxins and furans are lipophilic compounds and will adsorb strongly to the soil phase. The compounds are very slowly degradable and thus bioaccumulate. The US EPA 2003 (http://www.epa.gov/fedrgstr/EPA-TOX/2003/October/Day-24/t26923.pdf) has decided not to regulate dioxin and dioxin-like compounds in sewage sludge. Nevertheless, chlorinated dioxin compounds were identified on the OSPAR (2002) list of substances of possible concern (Eriksson et al. 2008) and have been included in the regulations of various EU countries (Mininni et al. 2014). TCDD was chosen as a representative for this group because TCDD has the highest bioaccumulation factor and the highest measured soil sorption of the investigated dioxins (Eriksson et al. 2008). It is thus prone to accumulate in sludge amended soil.

In 2006, dioxin-like compounds were surveyed in Australian sewage sludge (Clarke et al. 2008). The average was found to be 5.6 ng TEQ/kg and were within the range of 1.2–15.3 ng TEQ/kg (n = 14). All the Australian sewage sludge samples were below the Victorian EPA ‘‘investigation limit” of 50 ng TEQ/kg, and well below the EU proposed guidelines (Table 1). Based on this study, (Clarke et al. 2008) concluded that the burden of dioxin-like compounds in Australian sewage sludge is low and its land application as biosolids is not likely to pose a problem (Clarke et al. 2008).

Analytical costs of chlorinated dioxins in New Zealand are extremely high compared to analytical costs of other compounds. (Clarke et al. 2008) found that there generally was a positive relationship between towns producing the waste and both dioxin-like PCDD/Fs and dioxin-like PCBs. This connection between PCBs and dioxins could utilise to save on analytical costs if it is decided that dioxins and PCB need to be regulated.

Polychlorinated biphenyls (PCB)

PCB is not included for assessment by (Eriksson et al. 2008)., as PCBs have been phased out in most countries, though some diffuse long-term leakage from existing buildings and installations may take place, it will not be in focus for substitution or improved source control

Polycyclic aromatic hydrocarbons (PAHs)
PAHs are included in the sludge related legislation in some EU countries, for example Denmark, and France. (Eriksson et al. 2008) suggest to choose 3 PAHs as measurable representative for high, medium, and low molecular weight PAHs as well as to cover a range of octanol–water partition coefficients and evaporation potential; (naphthalene, fluoranthene and benzo[ghi]perylene). These PAH compounds stem from urban runoff and air pollution due to combustion for heating and transportation purposes as well as other combustion and charring processes such as food preparation which results in a heavy load of PAHs in wastewater. Redirecting the stormwater away from municipal wastewater treatment plants will reduce the total load of PAHs found in sewage sludge (Eriksson et al. 2008).

Flame retardants
Polybrominated diphenyl ethers (PBDEs) are a class of fire retardants used in many products. There are 209PBDE congeners. These compounds have low vapour pressures, and are highly lipophilic. They were listed as Persistent Organic Pollutants in the United Nations Environment Programme in 2008 (Clarke & Smith 2011). These PBDEs are routinely found in sewage sludge in the low mg/kg DM range and values have been reported in Sweden, Germany, Netherlands, China, Australia, Kuwait, Antartica (Clarke and Smith, 2011) and US (Venkatesan & Halden 2014). Health risks associated with exposure to the most bioactive congeners (tri- to octa BDE) include thyroid hormone disruption, neuro-development defects and cancer (Clarke and Smith, 2011). The primary congener of decaBDE formulation (BDE209) is consistently detected in the highest concentrations in sewage sludge. Action in Europe has been taken to ban pentaBDE and octaBDE (Directive 2003/11/EC) and it is expected that their presence in sewage sludge will decrease (Clarke & Smith 2011). However decaBDE is a flame retardant compound that is still allowed to be used in the European Union (Eriksson et al. 2008). Therefore the high production volume compounds decaBDE and tetrabromobisphenol A were chosen by Eriksson et al. (2008) as compounds to represent flame retardants for monitoring or regulation purposes.

Surfactants (nonylphenols and nonylphenolethoxylates)
Alkylphenol ethoxylates (APEOs) are extensively used as surfactants in commercial and industrial products. Nonylphenol ethoxylates (NPEOs) represent about 80-85% of all APEOs, with an annual consumption estimated at 123,000 - 168,000 metric tonnes in the US. Due to their widespread use, significant amounts of APEOs enter sewage treatment plants, where they readily undergo biotransformation to alkylphenols (primarily nonylphenol) and their short chained ethoxylates (mono- and diethoxylates). Nonylphenol was the most abundant analyte (534±192mg/kg) in a biosolids survey across 32 US states (Venkatesan & Halden 2013b), followed by its mono- and di-ethoxylates (62.1±28 and 59.5±52 mg/kg, respectively). Nonylphenol compounds showed observable loss from sewage sludge/soil mixtures (1:2), with mean half-lives ranging from 301 to 495 days (Venkatesan & Halden 2013b). (Eriksson et al. 2008), identified 4-nonylphenol as a potential risk in a recent hazard assessment. Nonyl phenol and –ethoxylates are regulated under European regulations (Mininni et al. 2014).

Surfactant levels in US sewage sludge were 10 times in excess of European regulations and (Venkatesan & Halden 2013b) argued that these levels in excess of EU regulations, substantial releases to U.S. soils, and prolonged half-lives found under field conditions would be a good reason to regulate these chemicals in the US.

Pharmaceuticals and antibiotics

Pharmaceuticals are bioactive compounds by their very nature. They are often not fully metabolised and enter the environment via sewage effluent and sewage sludge. There are many different pharmaceuticals and their fate depends on the individual characteristics of each compound, their partitioning coefficients and biodegradability. (Eriksen et al. 2009) evaluated 1400 pharmaceutical compounds based upon a tired approach where chemicals were screened against consumption, volume wastewater of influent, human metabolism, biodegradation and behaviour in sewage treatment plants. They identified 14 pharmaceuticals for further risk assessment. These were: atorvastatin cholesterol lowering medication); carisoprodol, gabapentin (analgesic/pain killer); mesalazin (anti-inflammatory); chlorprothixene (anti-psychotic); ciprofloxacin, tetracycline (antibiotic); ranitidine (inhibits stomach acid production); levetiracetam (anticonvulsant/epilepsy); and dipyridamole, losartan, fexofenadinesotalol, metoprolol (blood and heart treatments).

The most abundant pharmaceutical and personal care products detected in sewage sludge across 32 US states were the disinfectants triclocarban and triclosan, with mean concentrations ranging from 12 to 36 mg/kg. The second most abundant class were antibiotics. In order of decreasing concentration these were ciprofloxacin, 4-epitetracycline, tetracycline, minocycline, doxycycline, azithromycin, miconazole and norfloxacin (McClellan & Halden 2010) with corresponding mean contents ranging from 0.3 mg/kg to 7 mg/kg . In a Swiss study, norfloxacin and ciprofloxacin were also detected in sewage sludge and in soil 21 months after land application of sewage sludge (Golet et al. 2002; Golet et al. 2003). The most abundant non-antibiotic pharmaceuticals in decreasing order were cimetidine caffeine, carbamazepine, gemfibrozil and naproxen. The mean contents of these compounds ranged from 0.2 to 0.5 mg/kg (McClellan & Halden 2010). Especially carbamazepine, is very persistent during sewage treatment and in soils, and is only retained by soils high in organic matter (Gielen et al. 2009) and it was found to be translocated into the aerial components of plants (Dolliver et al. 2007; Winker et al. 2010).

Several pharmaceuticals found in sewage sludge are antibiotics and the main concern with antibiotics is their ability to cause antibiotic resistance in the receiving environment. Many antibiotics, however, enter the soil environment with the land application of animal manure. Antibiotic levels in animal manure are generally high because antibiotics are used as animal food supplement for growth promotion in addition to therapeutic treatments. In Austria, Germany and China pig manure was analysed for a range of antibiotics (enrofloxacin, sulfamonomethoxine, oxytetracycline, tetracyclines, sulphonamides, chlortetracycline and sulfadimidine) and maximum levels ranged from 4 to 59 mg/kg (Heuer et al. 2011). The abundance of antibiotics in manure is often more than 10 times larger than antibiotics levels found in sewage sludge.

Applying manure increased the numbers of resistant genes but there was already a considerable pool of resistance genes in soils (Heuer et al. 2011). The usage of antibiotics in animal husbandry has promoted the development and abundance of antibiotic resistance in farm environments. Manure has become a reservoir of resistant bacteria and antibiotic compounds, and its application to agricultural soils is assumed to significantly increase antibiotic resistance genes and selection of resistant bacterial populations in soil. The human exposure to soil-borne resistance has yet to be determined, but is likely to be severely underestimated (Heuer et al. 2011).

(Eriksen et al. 2009) suggested that pharmaceutical substances in sewage sludge are sufficiently lower than predicted effects concentrations and therefore constitute a low risk to the soil compartment. In addition, it is impossible to regulate all bioactive compounds. Nevertheless, the selection of a few key components would give a good indication on a general abundance. Therefore it is proposed to choose 3 indicators; triclosan(or tricloban) because they are the most abundant bioactive compound; ciprofloxacin because it was one of the most abundant antibiotic; and carbamazepine because it has a real potential to contaminate groundwater (Gielen et al. 2009).

Phthalates and plasticizers

Phthalate acid esters have been used for over 50 years mainly in the manufacturing of resins and plastics (PVC), paints, rubber, adhesives and some cosmetics. Phthalate acid esters such as di-(2-ethylhexyl) phthalate (DEHP), soften plastics without chemically binding and the PAEs content generally ranges from 20% to 40% and in some cases 55% (Clarke, et al., 2011). These phthalates easily leach from plastics and in a sewage treatment plant partition strongly to sewage sludge. The levels of DEHP, the most common phthalate, in sewage sludge ranges from the low mg/kg to 200 mg/kg (Clarke, et al., 2011). Phthalates are classified as endocrine disruptors. However, phthalates are not environmentally persistent and can be degraded in sewage sludge and soil both aerobically and anaerobically (Clarke, et al., 2011). Nevertheless, phthalates can be taken up in plants but phthalates are readily metabolised in mammals. Mammals ingesting high doses of phthalates were able to quickly remove them from body tissues once the chemical was excluded from the feed (Clarke, et al., 2011). This would indicate that the risks from continuous supply rather than from accumulation would need to be considered.

Endocrine disruptors, sterols and stanols

Bisphenol A is widely found in households and industry among others in the coating of metal cans to prevent the metal contact with food. It is found in raw sewage and surface waters primarily because it is continuously released into the environment and not because it is environmentally persistent. Bisphenol A is found in sewage sludge at levels ranging from low µg/kg to mid mg/kg levels. It has been included as a compound of possible concern because of its endocrine disrupting abilities (Clarke & Smith 2011) and is included in the OSPAR List of substances of possible concern. Bisphenol A is an endocrine disruptor that can be found in the human body (Lee et al. 2008), but exposure primarily occurs in the domestic environment and via direct ingestion. Transfer to humans from biosolids-amended soil is unlikely since there is little evidence that bisphenol A is environmentally persistent or bioaccumulates via the food-chain (Clarke & Smith 2011).

Natural hormones from animals are spread with manure. It was found that these natural hormones contribute much more than sewage sludge to the total land application of hormones in Denmark (Eriksen et al. 2009). Therefore natural hormones are unlikely in need of regulation.

Organotins

Organotin compounds have been used since the 1960s for industrial and agricultural purposes such as polyvinyl chloride (PVC) stabilisers, fungicides, bactericides, insecticides, industrial catalysts and wood preservatives. During sewage treatment, these organotin compounds are effectively concentrated in the sewage sludge fraction. Organotin compounds have been reported in sewage sludge in Switzerland, France, Canada, and the UK (Clarke & Smith 2011). Levels are generally below 1 mg/kg and are predicted to decline with the internationally decrease in the use of compounds like tributyltin (Clarke & Smith 2011).

Pentachlorophenols (PCPs)

PCP is abandoned in many countries and therefore not considered relevant in spite of it high score in environmental risk assessments (Eriksen et al. 2009).

Pesticides

The contribution to land via sewage sludge application is in comparison to the direct application considered of minor importance. These compounds and their risks are often controlled by banning the import and sales. In the EU, this is the case for Endrin, which was identified as a high environmental risk, and was banned in the EU. In time, this will decrease exposure (Eriksen et al. 2009).

Despite that the use of pesticides is mostly controlled, there is a group of herbicides found consistently in compost from grass clippings that have been sprayed for broad leaf weeds. These compounds have a long active life and degradation, especially in biosolids can take up to 3 or 4 years. The group of herbicides are pyridine carboxylic acids, in particular aminopyralid, clopyralid and picloram are persistent. They remain active after animals and humans excretion and after compost processing. Since the quality of compost is included in the NZ Biosolids Guidelines, and this group of herbicides is detected in compost pyridine carboxylic acids will need to be controlled in order to avoid damage to plants that the herbicide containing compost is applied to.