



**ENVIRONMENTAL GUIDELINES: USE AND  
DISPOSAL OF BIOSOLIDS PRODUCTS –  
CONTAMINANT REVIEW**

**REPORT TO SHANE RYAN, NSW EPA FROM WCA**

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## EXECUTIVE SUMMARY

The New South Wales Environment Protection Authority (NSW EPA) Environmental Guidelines 'Use and Disposal of Biosolids Products (the Biosolids Guidelines)' were drafted in 1997 with the aim of facilitating the sustainable re-use of biosolids. The guidelines gave a list of contaminants that were deemed to be priorities for routine monitoring and included criteria values for concentrations of the contaminants that enabled grading of the biosolids in relation to use.

This report provides a review of potential contaminants of concern in biosolids from data sources in the open literature, regulatory sources and some Waste Water Industry data. The aim has been to provide an evidence-based, precautionary risk screening assessment to prioritise potential contaminants of concern for routine measurement in NSW biosolids.

There are few Australian-specific data on many potential chemicals of concern in biosolids and there is a need for confirmatory assessment to support the findings in this report. These include the identification of contaminants highlighted by this prioritisation exercise for consideration in future routine monitoring in NSW biosolids, i.e. copper, zinc, dieldrin, triclosan and HHCB (Galaxolide).

There were many chemicals for which uncertainties remained in relation to the assessment and subsequent prioritisation. We categorised these chemicals as requiring occasional 'status' monitoring in NSW biosolids in order to provide a clear evidence-base for either removal or inclusion in routine monitoring. These included cadmium, chromium and PFOS. Further, monitoring for chemicals that showed moderate potential environmental risks or human health hazards should also include benzo(a)pyrene (as representative of PAHs), Cashmeran, decamethylcyclopentasiloxane, DEHP, HBCD, PFOA and Tonalide. For cadmium and chromium these data probably exist already and can be readily processed. Despite an absence of environmental risk, assessment of possible dietary exposure should be undertaken for arsenic, alpha-chlordane, diclofenac and BDE-47 (as a marker for brominated diphenyl ethers) on the basis of human health hazard (as indicated by toxicological potency).

Some chemicals were identified as potentially being of relevance to long-term monitoring in biosolids due to likely persistence in amended soils, but could not be assessed as no reliable ecotoxicity data could be found or exposure concentrations from Australian biosolids estimated. These chemicals were described as being 'parked' and included the trace elements titanium and manganese and the organics BTBPE, TBPH, DEHP, HBB, PCDD/DFs (dioxins and furans), perfluorodecanoate, PFNA, triclocarban and finally microplastics. These chemicals should be periodically reviewed in the future as new information becomes available.

The Australian Waste Water Industry evidence reviewed here, and the data from the open and grey literature support the reduction in the number of contaminants routinely determined in biosolids in NSW. Specifically, the monitoring of lead, nickel, probably arsenic, lindane, BHC, aldrin, heptachlor, DDD, DDE and DDT is considered to be of limited use, based on an informative risk-based exercise undertaken here.

This report should be used as a starting point, rather than a definitive conclusion, regarding the selection of chemicals for inclusion in a routine monitoring determinand suite for biosolids.

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# 1 INTRODUCTION

The chemical characteristics of biosolids generated by a municipal sewage treatment plant are influenced by many factors, including:

- types of treatment process,
- climatic conditions prevailing in the catchment being served by the treatment plant,
- characteristics of discharges from local industry,
- management of runoff from roads and hardstanding; and
- size and cultural and social habits of the population served by the treatment plant.

Over time, the importance and characteristics of these factors will inevitably change and such changes are likely to influence the chemical characteristics of the outputs from the sewage treatment plant, namely the treated effluent and the biosolids.

Changing social and cultural norms across the developed world over the last 20 years have raised researchers interest in the determination of the presence of new groups of chemicals in biosolids. These groups of chemicals include personal care products (e.g. Langdon et al. 2011), industrial organic chemicals (e.g. Kester et al. 2005), mixtures of biocides, human and veterinary medicines, road-wash chemicals from automotive vehicles, plasticisers, flame retardants, etc. (e.g. Clarke and Smith 2011).

The New South Wales Environment Protection Agency (NSW EPA) Environmental Guidelines 'Use and Disposal of Biosolids Products (the Biosolids Guidelines)' were drafted in 1997 with the aim of facilitating the sustainable re-use of biosolids. As part of the guidelines eighteen contaminants are detailed, including nine trace elements (i.e. metals and metalloids) and nine organic micropollutants (mainly organochlorine pesticides), by which the contamination grade of the biosolids is determined (Grades A to D).

This report is aimed at providing a comprehensive review of the contaminants of concern with specific focus on contaminants of concern likely to be present in biosolids applied to land, and the associated risks to agriculture, human health and the environment. A contaminant is defined in the Biosolids Guidelines as "Metals and organochlorine pesticides occurring in biosolids and soils". We have broadened this definition in this review to be inclusive of all chemicals of concern. The term biosolids in this review will be used interchangeably with sewage sludge, yet we will follow the definition as given in the current biosolids guidelines (NSW EPA 1997)<sup>1</sup>.

The first section of this report provides an outline of the review aims and objectives in addition to a broad global background to the project. The strategy followed to select (or deselect)

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<sup>1</sup> Primarily an organic solid product produced by the municipal sewage treatment process, previously referred to as sewage sludge. Solids become biosolids when they come out of a digester or other treatment process and can be beneficially used. The solid content in biosolids should be equal to or greater than 0.5% weight by volume (w/v)



contaminants for routine monitoring in biosolids in NSW is also given. Section 2 details the literature review and searching strategy along with some qualitative criteria to be assigned to literature sources in regard to project relevance. The third section provides a review of the contaminants in biosolids, in line with the classic risk assessment paradigm, focussing on exposure/behaviour and fate and effects. The evidence-based prioritisation of chemicals is detailed in Section 4. Recommendations and conclusions are given in Sections 5 and 6, respectively.

## **1.1 Aims**

The aims of this review are to:

- Use published evidence to identify which chemical contaminants NSW EPA should be concerned about in biosolids and why,
- Determine whether any chemicals on the current list of contaminants in the Biosolids Guidelines should be removed as no longer presenting a potential environmental or human health risk;
- Compile, from the evidence-base, a current list of 'contaminants of concern' for consideration with respect to biosolids in NSW;
- Provide recommendations to align NSW EPA biosolids guidance with current research and best practice on the proper management approaches for the identified contaminants of concern in biosolids.

We recognise that this review would form one component of many in regard to the evidence-base supporting a recommendation for a revised list of contaminants for routine monitoring of biosolids in NSW. Technical aspects not discussed here but potentially of relevance, include the availability of laboratory expertise and costs of chemical analytical methods for specific determinands.

## **1.2 Background**

The re-use of biosolids on land is a balance between sustainable use of a potentially valuable resource and concern over possible degradation of the environment. The evolving technologies at Waste Water Treatment Plants (WWTPs) have reduced the key historic challenges of treatment regarding the effluent, i.e. nutrient enrichment and biological quality. Furthermore, depending on the type of technology, removal of historic trace contaminants, such as metals and organics, can also now be highly effective.

With improvements in analytical techniques and the monitoring of receiving waters downstream from WWTP effluent discharges it has become apparent that a greater variety of different chemicals are now being identified compared to 20 years previously or when the first contaminant guidelines were developed (e.g. Matthiessen and Sumpter 1998).

Recent regulatory studies in Sweden, The Netherlands, and France, have focussed upon the mass balance between pharmaceuticals in WWTP influents, effluents and receiving waters (Fick et al. 2010; ter Laak et al. 2010; Besse et al. 2010). Although there are limited measures of the pharmaceuticals in the biosolids in these studies, the United States Environmental

Protection Agency (USEPA), Canadian Council of Ministers of the Environment (CCME) and the EU through the Joint Research Centre (JRC), have recently performed surveys of biosolids quality in regard to trace chemical composition.

The Targeted National Sewage Sludge Survey performed by the USEPA (2009) measured 164 determinands in sludges randomly sampled from 74 treatment works in 35 states. The determinands included four inorganic anions, 28 trace elements, four polycyclic aromatic hydrocarbons (PAHs), two semi-volatile organics, 11 flame retardants, 72 pharmaceuticals, and 25 steroids and hormones.

The CCME survey was specifically aimed at what are often erroneously defined as 'emerging contaminants', specified as pharmaceuticals, personal care products (PCPs) and industrial contaminants. The term is erroneous as the contaminants are not emerging, they have already emerged and are present and likely been present for some time, it is the fact that no one has actually looked for them previously that is key. Biosolids samples from 11 different WWTPs were analysed for 57 pharmaceuticals, 3 alkylphenolic compounds (including Bisphenol A), 11 synthetic musk fragrances (derived from PCPs) and 11 trace elements.

The recent monitoring programme of biosolids in Europe was undertaken by the JRC; this study investigated chemicals in 63 samples from 15 countries (JRC 2012). The aim of the programme was to perform a random screening of typical European sewage sludges with regard to the occurrence and levels of compounds of concern. These compounds included 22 trace elements and 92 organic compounds including PCPs and pharmaceuticals.

In the UK, the UK water companies (via UK Water Industry Research<sup>2</sup> (UKWIR)) are undertaking a sewage sludge monitoring programme across UK WWTPs for a range of substances including a suite of commonly analysed metals and 21 pharmaceuticals. The results from this monitoring exercise are, however, not yet available.

In addition to these surveys there are numerous open literature sources detailing specific measures of chemicals in biosolids, described in Section 2. Much of this work falls in the category of analytical method development (e.g. Zuloaga et al. 2012) and is perhaps of less relevance in identifying a broad suite of contaminants of concern and determining typical contaminant concentrations in biosolids samples.

The Australian National Biosolids Research Program has been supplemented with recent studies on the presence and concentrations of some of the chemicals now commonly found in biosolids from around the world, including triclosan, nonylphenol (NP) and bisphenol A (Langdon et al. 2011). It was noted that in four of the 14 samples tested the concentration of NP exceeded the European Union limit value for NP in biosolids (50 mg kg<sup>-1</sup>). Other chemicals detected in Australian biosolids include polybrominated diphenyl ethers (PBDEs) (Clarke et al. 2010a), organochlorine pesticides (OCPs: aldrin, chlordane, dieldrin, heptachlor, hexachlorbenzene, and DDT), polychlorinated biphenyls (PCBs) (Clarke et al. 2010b), triclosan (Ying et al. 2007), perfluorinated compounds (PFCs) (Arvaniti et al. 2015) and dioxin-like compounds (Clarke et al. 2008). It was also reported by Clarke et al. (2008) that there was

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<sup>2</sup> <https://www.ukwir.org/69904>

no apparent difference between concentrations of dioxin-like compounds in Australian sludges between 2002 and 2006. Gallen et al. (2016) found decabromodiphenyl ether (BDE-209) and perfluorooctanesulfonate (PFOS) to be the most prevalent chemical in terms of occurrence in 16 Australian wastewater treatment plant biosolids, whilst Liu (2012) reported 3-(4-methylbenzylidene)camphor and octocrylene as the most prevalent of those chemicals determined. This difference between treatment plants was also reported by Ying et al. (2009) who found substantial variations among the concentration of chemicals in biosolids from fifteen Australian STPs.

A working definition for emerging contaminants might be considered to be those chemicals 'which do not have established health standards and whose ecological and/or human health effects are unclear'. This definition is a reasonable one but is intrinsically linked to the regulatory speed at which standards may be derived. Importantly too, many human and veterinary medicines, identified in biosolids more than 15 years previously (e.g. Alcock et al. 1999) still do not have terrestrial limit values. One reason for this in Europe is that the authorisation process of the environmental risk assessment for human medicines rarely ever requires the assessment of terrestrial risks or therefore the generation of terrestrial ecotoxicity data. Therefore, many so called emerging contaminants have largely 'emerged' already. The NORMAN Network<sup>3</sup> in Europe defines emerging substances as "substances that have been detected in the environment, but which are currently not included in routine monitoring programmes at EU level and whose fate, behaviour and (eco)toxicological effects are not well understood". A term used now more widely in regulatory fora that perhaps builds on this definition and encompasses these historical detection is "substances of emerging concern"<sup>4</sup>. This term captures recent research findings, such as change in hazard profile, of a long detected and authorised substance. It is highly likely that we will identify many chemicals that fit with the NORMAN definition due lack behaviour, fate or (eco)toxicological information (Figure 3.1, see chemicals that are "parked").

Braga et al. (2005) observed that 24% of estrone (E1), 43% of 17beta-estradiol (E2), and 100% of 17alpha-ethinylestradiol (EE2) remained associated with the solids fraction in treated effluent after treatment by a coastal Australian WWTP. This was supported by work from Holmes et al. (2010) showing that endocrine disrupting compounds (EDC) removal in a plant in Adelaide, Australia was best achieved using activated sludge and a yeast screen assay for monitoring. Additionally, Leusch et al. (2005) reported that a medium-sized (3800 PE) advanced biological nutrient removal plant in Queensland, Australia decreased estrogenicity to below the limit of detection.

Tan et al. (2007) produced a model on the fate of endocrine disrupting organic compounds in an activated sludge WWTP in South East Queensland, Australia, with the WWTP having a high removal efficiency for all eight compounds that were modelled in this study. The majority removed were via biotransformation, followed by a lesser proportion removed with the primary sludge.

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<sup>3</sup> <http://www.norman-network.net/?q=node/19>

<sup>4</sup> E.g. <https://www.epa.gov/wqc/contaminants-emerging-concern-including-pharmaceuticals-and-personal-care-products>

Cooper et al. (2005) found that when biosolids were applied to soils in New South Wales, there was a significant increase in zinc and copper levels. However, plant material and grain from cereal plants grown in these fields, contained heavy metal levels lower than the maximum stated in the NSW EPA guidance. This was despite Heemsbergen (2009) demonstrating that there was no difference between zinc from biosolids and soluble zinc salt treatments in terms of the concentrations in plant tissue and soil/water partitioning. Oliver et al. (2005) surveyed the availability of elements from Australian biosolids between 1983 and 2001 and found that extractable element concentrations of copper, cadmium, and nickel all fell by 50-72% between 1983 and 2001, while K extractability fell by 35%. Additionally, Donner et al. (2013) investigated the speciation of Ag in new and aged biosolids from the UK, USA and Australia, indicating that when applied to soil, the majority of the Ag will be as Ag-sulfides with low environmental liability.

McLaughlin et al. (2000) reported a bioavailability-based approach to the control of metal contamination of Australian soils and suggested improvements were needed to avoid both over- and under-protective measures. Several states and territories in Australia are looking to adopt bioavailability-based approaches to assess trace element risks in biosolids amended soils (such as South Australia and Western Australia), although NSW is currently not one of these (Mike McLaughlin, pers. comm.).

In NSW and Australian Capital Territory 55% of the biosolids go to agricultural land (Darvodelsky 2012). In Europe some countries, such as The Netherlands, do not recycle their biosolids to agricultural land, due to concerns over the potential for contaminant build up in soils that may have adverse human or environmental effects<sup>5</sup>. Yet, in other parts of Europe agricultural application of sewage sludge has increased. In the UK in 2006 some 62% of sludge was applied to agricultural land and by 2012 this had risen to 80% (Jürgens et al. 2014).

### **1.2.1 Regulated chemicals in biosolids**

Historically, in common with most aquatic monitoring, the monitoring of biosolids destined for agricultural land has focussed upon trace elements. These tend to be straight-forward to analyse for and multiple elements can be determined in a single analysis. As with many historical limit values, the protection goal specifics are not always apparent. However, the earliest limit values for trace elements were most likely determined for the protection of human and livestock health and to reduce risks from food chain transfer (e.g. CEC 1986). Over time, scientific research has led to greater attention upon the protection of the environment and long-term soil fertility. Many countries have recognised this objective and sought to revise or reduce limit values for the trace elements such as copper and zinc (e.g. Chander and Brookes 1993).

In the UK, Department of Environment (DoE 1989) regulations identified 11 trace elements for monitoring in biosolids and amended soils based on a 10-year rolling average that were, in-part, in accordance with the Commission of the European Communities Directive from 1986 (CEC 1986). These 11 elements included copper, cadmium, chromium, arsenic, selenium, fluoride, molybdenum, lead, nickel and mercury. The limit values for nickel, copper and zinc

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<sup>5</sup> <http://www.iwawaterwiki.org/xwiki/bin/view/Articles/Netherlands>

in amended soils were banded with pH. These limit values are still in force in the UK although the evidence that supports them is both opaque and now very outdated. There are no organic chemical limits or monitoring requirements for sludges or amended soils in the UK.

Discussions on revision of the list of contaminants to be monitored in biosolids is on-going in Europe, yet only drafts or working drafts have been produced. Some member states, informed through national monitoring programmes, have include additional contaminants to be monitored and set additional limit values for these respective determinands. For example, in Germany some chemicals, such as polychlorinated biphenyls (PCBs), dioxins and furans (PCDD/Fs) are measured in biosolids, but not used for classification; and some substances are considered to have either high ecotoxicity and are being phased out or have been banned (e.g. DEHP and TBT), or are present in relatively high concentrations (e.g. musk xylenes)<sup>6</sup>. In Denmark, in addition to the usual metal suite, limit values have also been set for alkyl benzene sulfonate (LAS), total PAHs, nonylphenol ethoxylates and DEHP. It is important to stress that the limit values set by each European member state are aimed at protecting human and environmental health, and not just human health (Darvodelsky 2012).

In Canada, the management of biosolids is in a state of flux (CCME 2010), but up to 11 chemicals are routinely monitored in biosolids to determine the grade in relation to human and environmental health. However, most of the management of biosolids re-use is undertaken by individual provincial/territorial acts. The eleven chemicals are effectively the usual trace elements suite<sup>7</sup>, but some jurisdictions also include a requirement for measurement of dioxin, PAH and PCBs for certain biosolids uses. For some of the jurisdictions it is stated that no monitoring in the biosolids is undertaken because, for example for PAHs they are "rarely detected - not deemed of concern". The "not deemed of concern" here may be arguable, but it seems the "rarely detected" is highly unlikely in light of the data recorded in the JRC survey, which detected 3 PAHs in 100% of all of the 31 samples tested and > 84% occurrence for all seven selected PAHs determined in all the samples.

The USEPA require that all biosolids applied to land have concentrations of ten trace elements that are below stated ceiling concentrations<sup>8</sup>. There are no organic chemicals listed and following the examination of long-term biosolids survey data and a full risk assessment the decision was taken by the USEPA not to regulate dioxins in biosolids going to land<sup>9</sup>.

A review undertaken on behalf of the Federal Department of Sustainability, Environment, Water, Population and Communities (Now the Dept. of the Environment and Energy) discussed recent changes in biosolids guidance across Australian states and territories (Darvodelsky 2012). This review identified 22 chemicals that were being routinely monitored in biosolids. South Australia (SA) and Western Australia (WA) have made the most recent revisions to their state biosolids guidance in 2009 and 2010, respectively. The 2012 WA Guidelines for Biosolids Management (DEC 2012) list just six contaminants (four trace elements, two organochlorine

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<sup>6</sup> <http://ec.europa.eu/environment/waste/sludge/>

<sup>7</sup> As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn

<sup>8</sup> [https://www.epa.gov/sites/production/files/2015-05/documents/a\\_plain\\_english\\_guide\\_to\\_the\\_epa\\_part\\_503\\_biosolids\\_rule.pdf](https://www.epa.gov/sites/production/files/2015-05/documents/a_plain_english_guide_to_the_epa_part_503_biosolids_rule.pdf)

<sup>9</sup> <https://www.epa.gov/biosolids/dioxins-sewage-sludge>

pesticides) that require measurement in biosolids in order to undertake the contaminant grading. In this document it is also stated that other groups of chemicals, such as dioxins, pharmaceuticals and personal care products, might be present in biosolids though research “to date has not demonstrated that these contaminants need to be regulated with respect to biosolids application in accordance with best management practices”.

Nevertheless, the exclusion of further chemicals from routine monitoring is based upon evidence outlined in the SA Guidance, which identifies the same six chemicals as WA. The key reason for non-inclusion of arsenic, chromium (III), lead, molybdenum, mercury, cadmium, nickel and selenium is that the average biosolids concentrations of these trace elements, from the National Biosolids Research Program, when applied as a single application would result in a value considerably less than the ambient background concentration of the soil. This logic only applies to a *single application*, and would perhaps suggest no repeat applications of biosolids to the same soils (e.g. Jürgens et al. 2014), few additional inputs of trace elements to soils from other sources, and limited variance about the mean of the trace elements in the biosolids (the mean is not a usual ‘reasonable worst case’ metric for risk assessment) or in the soils, which seems unlikely (NEPM 2011).

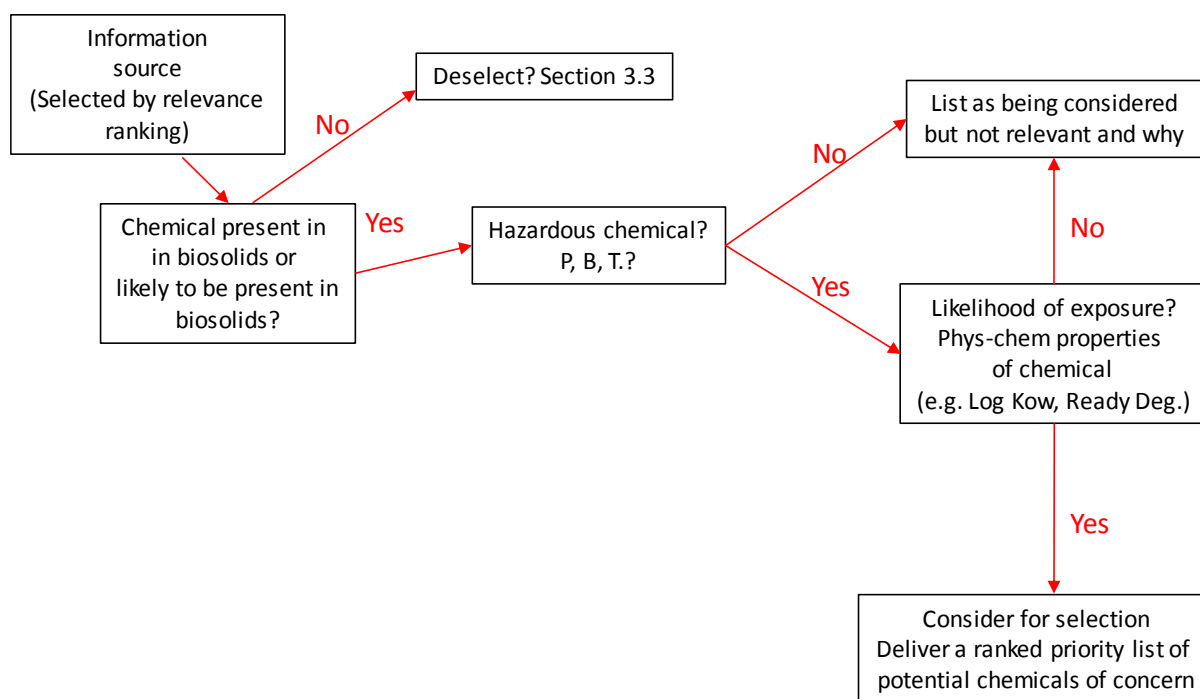
So from a brief review of the regulatory literature it is clear that the historical group of trace elements are still monitored by many jurisdictions and are used to support decisions in relation to the quality or classification of biosolids. Some regulatory jurisdictions also undertake monitoring of a small number of organics, but these are relatively few in number. Importantly, de-selection of chemicals or the decisions not to include contaminants is, aside from the obvious exception of dioxins and the USEPA, not an entirely transparent or evidence-based process (e.g. DEC 2012).

### **1.2.2 Strategy for contaminant selection**

The strategy used here for contaminant selection is based upon an adapted version of criteria set out by Clarke and Smith in their review of ‘emerging’ organic contaminants in biosolids (2011). Figure 1.1 shows a schematic of the process that we will follow in order to deliver a prioritised and ranked list of chemicals of concern. The criteria used and the reasoning for inclusion are set out below:

1. Occurrence – a chemical regularly identified in regulatory surveys or peer-reviewed studies of biosolids, or identified by open literature sources and highly likely (through a brief fate assessment, through use of physico-chemistry) to be present in biosolids;
2. Persistence of the chemical in soil (e.g. the degradation half-life in soil is higher than 120 days, ECHA 2014);
3. Potential risks to the environment or human foodchain from biosolids land application. This will be assessed through a brief review of hazard (health criteria values and terrestrial predicted no effect concentrations (PNECs), including secondary poisoning considerations) and likely exposures in amended soils (simply based on a worst case tonnage per ha basis, e.g. 10t ha<sup>-1</sup> (dry tonnes) and the use of a generic soil scenario with repeat applications over 100 years);

Importantly, we must assume that in considering point 3 that 'good agricultural practice' is followed in the use of the biosolids and that existing guidance is followed. The criteria outlined above will be used to construct a spreadsheet from which the prioritisation of contaminants will be made (Section 3).



**Figure 1.1 Schematic of the process followed in this project (PBT is Persistence, Bioaccumulation and Toxicity).**

## 2 LITERATURE REVIEW AND SUMMARY

This section outlines the method used to undertake the search and review of the open and grey literature sources. In addition, we've provided an outline of the information source ranking that we've used to assign a "relative quality" ranking to the information and data reviewed.

We have date limited the search from the time of completion of the previous contaminant review undertaken on behalf of NSW EPA, which was 1998. Therefore, all searches have been performed from 1997 onwards.

### 2.1 Search strategy

Searches of the published/open literature were conducted in order to identify potentially relevant information. Search strings were devised, and discussed with the Project Board and amended taking into account the search results. This step is important, as if the project is repeated in the future this will offer a starting place for those undertaking the exercise. The initial search string investigated was:

*((biosolid OR sludge) AND (chemical))*

This resulted in 5,590 hits from Toxline for the time period 1997-2016. When using the search tool, Thomson, for the period 1997-2016, there were 11,348 hits.

The volume of hits from Thomson was too large to be downloaded and importantly, appropriately reviewed. Therefore, the search string was separated out, refined and repeated, as follows:

*((biosolid) AND (chemical))* 132 hits

*((sludge) AND (chemical))* 11,318 hits

The results for the *((biosolid) AND (chemical))* string were included. However, the 11,318 hits from the string *((sludge) AND (chemical))* were still too many to be downloaded. The string was then further refined to be:

*((sewage sludge) AND (contaminant))*

There were 194 hits returned from Toxline for the period 1997-2016.

A second string was identified from the criteria used by Clarke and Smith (2011):

*((biosolid OR sludge) AND (persist\* OR bioaccum\* OR ecotox\*))*

This resulted in 737 hits from Toxline for the time period 1997-2016. When using the search tool, Thomson, for the period 1997-2016, there were 1,937 hits were found.

The third string examined was:



*((biosolid OR sludge) AND (PEC OR PNEC OR HCV OR partition coefficient))*

This resulted in 77 hits from Toxline for the time period 1997-2016. When using the search tool, Thomson, for the period 1997-2016, 173 hits were found. A summary of these searches are shown in Table 2.1.

**Table 2.1 Summary of search strings and 'hits' obtained in this project**

String number	Number of hits	
	Toxline	Thomson
<i>((biosolid OR sludge) AND (chemical))</i>	5,590	-
<i>((biosolid) AND (chemical))</i>	-	132
<i>((sewage sludge) AND (contaminant))</i>	-	194
<i>((biosolid OR sludge) AND (persist* OR bioaccum* OR ecotox*))</i>	737	1,937
<i>((biosolid OR sludge) AND (PEC OR PNEC OR HCV OR partition coefficient))</i>	77	173
Total	6404	2436
Number of duplicates	493	0
Total with duplicates removed	5911	2436
Total combined	8347	
Number of duplicates	695	
Total	7652	
No abstract	36	
<b>Final total</b>	<b>7,616</b>	

A second set of additional search strings were investigated following the initiation meeting with the Project Board. Once again, the Thomson and Toxline databases were searched for the period 1997-present. The search strings were:

1. *((sewage sludge OR biosolid) AND (Australia))*
2. *((sewage sludge OR biosolid) AND (microplastic\*))*
3. *((microplastic\*) AND (fate))*
4. *(microplastic\*)*
5. *(nanoplastic\*)*
6. *((nanomaterials) AND (sewage sludge OR biosolids))*

The results from this additional search are shown in Table 2.2.

**Table 2.2 Results of addition search undertaken following the initiation meeting**

String	Number of hits	
	Toxline	Thomson
((sewage sludge OR biosolid) AND (Australia))	100	138
((sewage sludge OR biosolid) AND (microplastic*))	0	1
microplastic* AND fate	10	29
microplastic*	127	405
nanoplastic*	9	15
((nanomaterials) AND (sewage sludge OR biosolids))	24	16
Subtotal	270	604
Duplicates	33	24
Subtotal with duplicates removed	237	580
Combined total	817	
Duplicates	108	
<b>Final total</b>	<b>709</b>	

Therefore, the total number of hits for potentially relevant information for this project from the published/open literature was 8,325.

### 2.1.1 Grey literature sources and Industry information

There are numerous grey and regulatory sources of data that have become available since 1998. Many of these were identified in the recent sludge surveys performed by JRC (2012) and the USEPA (2009). In addition, we performed searches using common search engines to identify further sources. Finally, we contacted regulatory contacts in North America, Europe and Asia to determine awareness of additional work or future activities.

Industry information, in the form of long-term biosolids chemical monitoring data, was provided for the purpose of the project through the NSW EPA Project Team. We have reviewed these data and where possible (i.e. the data was in an understandable and useable format) provided anonymised summaries in Section 3. We are grateful to those organisations that allowed for the use of these data in this review.

## 2.2 Reviewing the information sources

With such an extensive and diverse range of information sources it is imperative that the quality and veracity of the sources is determined to allow ranking in relation to the project aims. The following weighting criteria were used to assess all the literature identified by the above search strings and grey literature searches. Each reference, based on reading the abstract or executive summary, has been assigned a score of 1-4 which are based on the following:

1. A report with this score will be a regulatory report or survey with extensive monitoring data from multiple sites/countries. Any sources that contain relevant Australian data will be given this score;

2. A score of two will have been peer reviewed and published in a high quality journal. This can be applied to both reports and survey data;
3. A reference that is considered less reliable will be assigned a score of 3. An example of when this score will be applied, is a survey where a limited number of sites have been investigated and perhaps only a paper focussed upon a method or an academic study undertaking chemical "stamp collecting". In addition, those references that were considered to be peripheral in regard to relevancy to the project aims would also have been scored 3;
4. This score will be assigned to literature that is not considered relevant to this project.

Only sources scored at 1 or 2 have been used in this project. An Excel sheet of all the abstracts reviewed and the scores given is provided at the end of this report as an embedded file. A tab on this sheet shows all of the references selected for review. The colour coded references on this tab are those, scoring a 1, where the full paper was obtained for use in this report and have been provided to NSW EPA in electronic form. wca was able to obtain numerous references free of charge.

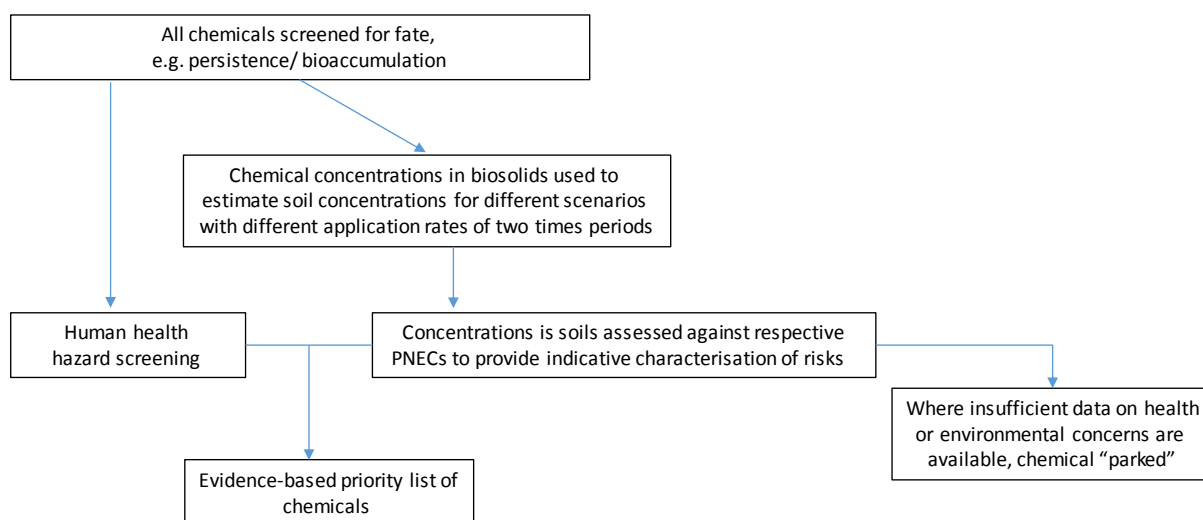
## **2.3 Summary sheets**

As can be seen from Figure 1.1, both hazard and potential exposure information have also been extracted from the literature sources and are summarised in a spreadsheet that is embedded in the appendices at the end of this document.

There are several tabs on this spreadsheet, listing the chemicals measured in biosolids, the maximum or 90<sup>th</sup> percentile concentrations, where they are reported. Physico-chemical properties that are likely to influence behaviour and fate, are provided in addition to both environmental and human health limit values. Finally, the last tabs on this sheet provide a screening level assessment of potential risk following reasonable worst case processes detailed in Section 3.2.

### 3 REVIEW AND ASSESSMENT OF POTENTIAL CONTAMINANTS OF CONCERN

In this section of the report we provide a summary of data on the measured occurrence of chemicals in biosolids. These measured data are used as an input to an indicative risk exercise, following an initial screening that is based upon physico-chemical properties that are related to persistence and bioaccumulation. For the chemicals that pass this screen the measured concentrations are used to calculate predicted environmental concentrations (PECs) in soils following land application of biosolids to Australian soils at different rates and over different time periods. These concentrations are then assessed against predicted no effect concentrations (PNECs) from which we have characterised potential risks and developed a ranked list of potential priority chemicals. Consideration is also made of human health hazard on the basis of toxicological potency. Figure 3.1 shows a schematic of this process. Where no Predicted No Effect Concentrations (PNECs) or Health Criteria Values (HCVs)<sup>10</sup> readily available on which to base the assessment the chemical will be “parked” for future assessment if the information becomes available.



**Figure 3.1 A schematic of the process followed in performing the indicative risk assessment for this project**

A spreadsheet accompanies this report detailing groups of chemicals and individual contaminants identified from the literature search and physico-chemical and fate data for chemicals quantified in high relevance studies. For those chemicals likely to persist in sludge/soil and accumulate in the food chain the spreadsheet details PNECs and HCVs, which are used in semi-quantitative assessment of risks to the environment and human health screening, respectively. The sources of these PNECs and HCVs are given. The sheet is constructed to allow the user to change these values if so required to perform a different specific type of assessment. It is important to stress this assessment is indicative and NOT

<sup>10</sup> Health criteria values (HCVs) are guidance levels set by expert groups. Combined with estimates of exposure, they can be used by assessors to determine the risk to human health, and to consider whether further investigation, assessment, and/or remediation is required.

definitive, numerous assumptions and caveats apply and these are all detailed; it should also be noted be that most assumptions are conservative in nature. For example, in the selection of concentrations in biosolids to be used in the assessment a hierarchy of preferences has been followed:

- Australian specific data;
- 90<sup>th</sup> percentiles (typically used as a reasonable worst case in exposure assessments, see ECHA 2016);
- Maximum concentrations;
- Means, where only these were available.

This conservatism is reasonable and conforms to the classic risk assessment paradigm in that early screening is generally reasonable worst case in regard to assessment inputs ensuring limited false negatives (Type II errors), but enabling refinement when better data becomes available.

### **3.1 Contaminant occurrence in biosolids**

There are 14,457 industrial chemicals currently registered for use under the European REACH legislation<sup>11</sup>. It is perhaps reasonable to consider that many of these may be present in biosolids (Clarke and Smith 2011) and that, without evidence to the contrary the use of chemicals in Australia is similar to Europe. The priority chemicals spreadsheet details the chemicals identified in biosolids from the literature survey and regulatory review. These are discussed in groups below, including those commonly measured and those considered to be less routinely determined. The data from the industry sources are also summarised where appropriate.

It is inevitable, with the likely number of potential chemicals that could be found in biosolids, that some may not be discussed here or have not been identified in our literature searching (or yet identified due to chemical analytical challenges). Further, some of the chemicals could reasonably be allocated to more than one category, but have only be detailed in one, not multiple relevant categories for the sake of clarity.

#### **3.1.1 Dioxins, furans and dioxin-like PCBs**

Dioxins are chlorinated compounds generated as by-products of combustion of organic materials containing chlorine and as trace contaminants during the synthesis of many organochlorine compounds. They are ubiquitous in the environment and would not be anticipated to occur at particularly elevated levels in biosolids. The compounds referred to here as dioxins are restricted to those having a structure and toxicity related to that of the parent compound, 2,3,7,8-tetrachloro-para-dibenzodioxin (TCDD), which is commonly known as dioxin. Polychloro-p-dibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs,

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<sup>11</sup> <https://echa.europa.eu/information-on-chemicals/registered-substances>

commonly known as furans) are related compounds and the presence of four chlorine atoms at positions, 2,3,7 and 8 appears to be responsible for the observed dioxin-like toxicity.

Studies in animals have indicated that the effects of dioxin and dioxin-like compounds have a common mode of action. The 2,3,7,8-TCDD or dioxin molecule displays the most potent toxicity and the potencies of other PCDDs and PCDFs possessing the same mode of action can be characterised relative to TCDD by Toxic Equivalency Factors (TEFs). The potential dioxin-like activity contributed by each congener is determined by multiplying the concentration of the congener by its WHO-designated TEF to yield the dioxin toxic equivalent (TEQ) for that congener. The net TEQ is the sum of the individual TEQs for each dioxin or dioxin-like compound. It should be noted that this is only relevant to the assessment of human health.

No soil screening criteria such as PNECs are available for environmental effects of dioxins due to the complexity of assessing risk to multiple species from a category containing a large number of compounds. Assessment of risk to human health via dietary exposure (due to their known tendency to bioaccumulate) is based on the toxic equivalence approach, by comparison of TEF-adjusted values to a health criteria value (HCV) in terms of TEQ, although dietary risk assessment is very complicated as it entails modelling of all relevant congeners in a number of different foodstuffs. Table 3.1 shows measured concentrations of dioxins in biosolids.

**Table 3.1 PCDD/Fs determined in biosolids**

Chemical	Concentrations in biosolids, Max, ng kg <sup>-1</sup> TEQ (DW)	Source
PCDD/Fs	33.3	Kester et al 2005
	0.189 - 1092	Ju et al 2009

PCBs are a category of chemicals containing a number of dioxin-like compounds (DL PCBs). PCBs have been measured in biosolids in NSW, but from the data reviewed for this report, almost all show non-detections.

### 3.1.2 Halogenated substances

There are many halogenated compounds that have been determined in biosolids, including the perfluoroalkyl substances. Table 3.2 shows a list of those that have been determined in academic research and regulatory monitoring studies. The concentrations shown are either maxima or 90<sup>th</sup> percentiles.

Some of these compounds have also been determined in biosolids by some of the NSW water companies, mean PFOS concentrations and standard deviations from five WWTPs in 2016 were 3.59 ± 2.50 µg kg<sup>-1</sup>, 2.40 ± 2.40 µg kg<sup>-1</sup>, 3.7 ± 0.8 µg kg<sup>-1</sup>, 4.76 ± 2.6 µg kg<sup>-1</sup>, 27 ± 11 µg kg<sup>-1</sup>. For PFOA mean concentrations were less; 1.67 ± 1.21 µg kg<sup>-1</sup>, 1.24 ± 0.72 µg kg<sup>-1</sup>, 1.8 ± 0.8 µg kg<sup>-1</sup>, 1.73 ± 0.8 µg kg<sup>-1</sup>, 2.70 ± 0.89 µg kg<sup>-1</sup>. Perfluoroheptanoic acid and Perfluorohexane sulfonic acid determined in the same samples showed very few detects above the limit of detection (LoD) of 0.0002 mg kg<sup>-1</sup>.

Table 3.2 shows many flame retardants and compounds now classed as Persistent Organic Pollutants (POPs) or banned under certain national and international agreements.

**Table 3.2 Halogenated compounds determined in biosolids and maximum concentrations, or 90<sup>th</sup> percentiles where shown**

Chemical	Concentrations in biosolids, Max, mg kg <sup>-1</sup> (DW)	Source
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	0.021	Lee et al. 2014
1,4 Dichlorobenzene	0.61	Bright and Healey 2003
BDE-153 (2,2',4,4',5,5'-hexabromodiphenyl)	0.41	USEPA 2009
BDE-209 (decabromodiphenyl)	17	USEPA 2009
BDE-47 (2,2',4,4'-tetrabromodiphenyl)	5 x 10 <sup>-6</sup>	USEPA 2009
BDE-99 (2,2',4,4',5-pentabromodiphenyl)	4 x 10 <sup>-6</sup>	USEPA 2009
Decabromodiphenyl ethane (DBDPE)	0.22	Ricklund et al. 2008
Di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH)	1.63	Davis et al. 2012
Hexabromobenzene (HBB)	0.0057	Gorga et al. 2013
Hexabromocyclododecane (HBCD)	36	Zuloaga et al., 2012
m,p-Xylene	5.1	Webber et al. 1996
Octachlorostyrene	0.0115	Kohli et al. 2006
Penta-BDE	2.12	Hale et al. 2012
Pentabromoethylbenzene (PBEB)	0.00233	Gorga et al. 2013
Perfluorodecanoate	0.026	Venkatesan and Halden 2013a
PFNA	0.0068 <sup>#</sup>	JRC 2012
PFOA	0.014 <sup>#</sup>	JRC 2012
PFOS	0.13 <sup>#</sup>	JRC 2012
TBBPA	9.8	Zuloaga et al. 2012
Tris(chloro-isopropyl)phosphate (TCPP)	20	Bester 2005

<sup>#</sup>90<sup>th</sup> percentile

### 3.1.3 Human and veterinary medicines

Human and veterinary medicines have long been targeted for measurement in biosolids and the review by Alcock et al. (1999) summarises the early data. In addition to studies in the open literature, regulatory monitoring studies have also targeted many of these types of chemicals in investigative assessments to determine occurrence and benchmark concentrations. Not surprisingly, with improving analytical methodologies many human and veterinary medicines have been detected in biosolids. Table 3.3 shows mean, maximum or 90<sup>th</sup> percentile concentrations of selected human and veterinary medicines in biosolids. The list here includes beta blockers, antibiotics, antifungal agents, antidepressants, anti-inflammatories, treatments for stomach ulcers and cholesterol lowering drugs.

In the study by Langdon et al. (2011), estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3) and 17 $\alpha$ -ethinylestradiol (EE2) (although none of these are actually pharmaceuticals, they are often considered as such in being biologically active) were determined in 14 selected biosolids sample, but only estrone was detected above the limit of detection (45  $\mu$ g kg<sup>-1</sup>) and that in only four of the samples at an average concentration of 0.13 mg kg<sup>-1</sup>. We have found relatively

few studies that have determined concentrations of these chemicals in Australian biosolids, although it would seem likely that many would be found if analysis were undertaken for them.

Nevertheless, it is important to stress that the presence of a chemical does not indicate potential risk. The chemicals and concentrations listed in Table 3.3 have been taken forward in Section 3.2 for screening as shown by the selection process in Figure 3.1.

**Table 3.3 The concentrations of selected human and veterinary medicines in biosolids**

Chemical	Concentrations in biosolids, Max, mg kg <sup>-1</sup> (DW)	Source
17 a-ethinyloestradiol	0.005*	Clarke and Smith 2011
17 b-oestradiol	0.02*	Clarke and Smith 2011
4-Epitetracycline	4.38	USEPA 2009
Acetylsalicylic acid	0.134 <sup>#</sup> µg kg <sup>-1</sup>	JRC 2012
Azithromycin	5.21	USEPA 2009
Beta Stigmastanol	1330	USEPA
Bezafibrate	0.001 <sup>#</sup> µg kg <sup>-1</sup>	JRC 2012
Caffeine	0.048 <sup>#</sup>	JRC 2012
Campesterol	524	USEPA 2009
Carbamazepine	6.03	USEPA 2009
Chloramphenicol	0.0076	JRC 2012
Cimetidine	8.33	USEPA 2009
Ciprofloxacin	408	USEPA 2009
Cocaine	0.23	Arbeláez et al. 2014
Diclofenac	0.00007 <sup>#</sup>	JRC 2012
Doxycycline	5.09	USEPA 2009
Epicoprostanol	6030	USEPA 2009
Erythromycin	0.18	USEPA 2009
Fluoxetine	0.31	USEPA 2009
Gemfibrozil	0.0094	JRC 2012
Ibuprofen	0.045	JRC 2012
Ketoprofen	0.0086	JRC 2012
Miconazole	9.21	USEPA 2009
Naproxen	7 <sup>#</sup> x 10 <sup>-6</sup>	JRC 2012
Nicotine	0.17	Arbeláez et al. 2014
Norfloxacin	5.28	Chen et al. 2013
Ofloxacin	58	USEPA 2009
Progesterone	0.47	Bevacqua et al. 2011
Propranolol	12* x 10 <sup>-6</sup>	Gottschall et al. 2012
Roxithromycin	1.45	Nieto et al. 2010
Stigmasterol	569	USEPA 2009
Sulfadimethoxine	2.00	Zuloaga et al., 2012
Sulfamethoxazole	1.00	Zuloaga et al., 2012
Tetracycline	2.9 <sup>#</sup>	USEPA 2009
Trimethoprim	0.000710 x 10 <sup>-6</sup> <sup>#</sup>	JRC 2012
Tylosin	1.96	Nieto et al. 2010

\*Mean concentrations



#90<sup>th</sup> percentile

### 3.1.4 Personal care products

As with human and veterinary medicines, there are many compounds from personal care products that are likely to be flushed down the drain and pass through WWTPs. Table 3.4 shows the concentrations of fragrances, biocides, surfactants, sun screens and cosmetics in biosolids from academic and regulatory studies, including some Australian data (e.g. Langdon et al. 2011; Liu et al. 2012). It is not clear as to how many of these chemicals reported in studies from outside Australia are used in Australian personal care products, but they are included here as a 'catch all' at this screening stage.

**Table 3.4 The maximum or 90<sup>th</sup> percentile concentrations of personal care products determined in biosolids**

Chemical	Concentrations in biosolids, Max, mg kg <sup>-1</sup> (DW)	Source
3-(4-methylbenzylidene)camphor	0.962	Liu et al. 2012
4-methylbenzylidenecamphor	5.00	Zuloaga et al., 2012
ATII	0.70*	Kupper et al. 2004
Cashmeran	0.19 <sup>#</sup>	JRC 2012
Celestolide (ADBI)	0.082 <sup>#</sup>	JRC 2012
Decamethylcyclopentasiloxane	22.7 <sup>#</sup>	JRC 2012
DEET	0.0011	Chen et al. 2012
Dodecamethylcyclohexasiloxane	4.74	JRC 2012
Ethylhexyl methoxycinnamate	3.4	Zuloaga et al., 2012
HHCB (Galaxolide)	17.5 <sup>#</sup>	JRC 2012
Methylparaben	0.0605*	Liao et al. 2013
Musk Ketone	1.3*	Di Francesco et al. 2004
Octamethylcyclotetrasiloxane	1.46 <sup>#</sup>	JRC 2012
Octamethyltrisiloxane	0.024	JRC 2012
Octocrylene	0.465	Liu et al. 2012
Octyl-triazone	28	Zuloaga et al., 2012
OTNE	30.7	DiFrancesco et al. 2004
Phantolide (AHDl)	0.065	JRC 2012
Propylparaben	0.044	Albero et al. 2012
Tonalide	1.80 <sup>#</sup>	JRC 2012
Triclocarban	51*	Heidler et al. 2006
Triclosan	3.77	Langdon et al. 2011

\*Mean concentration

<sup>#</sup>90<sup>th</sup> percentile

### 3.1.5 Pesticides

Within the existing list of chemicals to be monitored in biosolids in NSW are several organochlorine pesticides. In addition to these, many other pesticide or plant protection products have been detected in biosolids (Table 3.5).

There are Australia-specific data for pesticides in the open literature (Clarke et al. 2010b) and also routine monitoring data, from the Water Treatment Industry (termed Industry from now). Data have been provided from many NSW WWTPs, for chemicals such as Lindane, BHC, Aldrin, Heptachlor, DDD, DDE and DDT. We have reviewed concentrations since 1997 and almost all were below the levels of detection (LoD). For one WWTP alone for one chemical (Lindane), this equates to 206 (all of them) determinations that have returned a < LoD. Only dieldrin and chlordane gave some returns that are above the LoD. For one WWTP, the mean concentration for dieldrin is 0.068 (0.067 SD) mg kg<sup>-1</sup> from 69 determinations above LoD from 224 samples. For chlordane for the same plant the mean concentration is 0.067 (0.075 SD) mg kg<sup>-1</sup>, with just 18 determinations above LoD from 224 samples. This picture is reflected across all of the biosolids datasets from NSW WWTPs that were investigated.

Therefore, as Lindane, BHC, Aldrin, Heptachlor and DDT are not routinely found in Australian biosolids they have not been included further in the assessment.

**Table 3.5 The maximum or 90<sup>th</sup> percentile concentrations of pesticides determined in biosolids**

Chemical	Concentrations in biosolids, Max, mg kg <sup>-1</sup> (DW)	Source
1H-benzo-triazole	1.01 <sup>#</sup>	JRC 2012
1-methyl-1H-benzotriazole	0.021 <sup>#</sup>	JRC 2012
Alpha- chlordane	400 x 10 <sup>-6</sup>	Kohli et al. 2006
Carbendazim	0.00224 <sup>#</sup>	JRC 2012
Clofibric acid	0.0105	JRC 2012
Diazinon	0.015	Diaz-Cruz and Barcelo 2006
Dichlorodiphenyl dichloroethane	0.0148	Ju et al. 2009
Dichlorodiphenyldichloroethylene	0.270	Clarke et al. 2010b
Dieldrin	0.770	Clarke et al. 2010b
Diuron	0.00230 <sup>#</sup>	JRC 2012
MCPA	0.0022	JRC 2012
Mecoprop	0.0012	JRC 2012

<sup>#</sup>90<sup>th</sup> percentile

### 3.1.6 Other organics

This category is a 'catch all' for many industrial chemicals, intermediates and ubiquitous compounds such as PAHs, which have natural and anthropogenic sources. Regulatory survey data have primarily been used to populate Table 3.6, with only a few data from Australian biosolids (Langdon et al. 2011).

**Table 3.6 The maximum or 90<sup>th</sup> percentile concentrations of general chemicals determined in biosolids**

Chemical	Concentrations in biosolids, Max, mg kg <sup>-1</sup> (DW)	Source
2,4-dinitrophenol	0.0022 <sup>#</sup>	JRC 2012
2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB)	3.75	Davis et al. 2012
4-Chloroaniline	5.90	USEPA 2009

4-nonylphenol	58.7*	Langdon et al. 2011
4-tert-octylphenol	3.08*	Langdon et al. 2011
Acesulfame K	0.034 <sup>#</sup>	JRC 2012
Anthracene	0.19 <sup>#</sup>	JRC 2012
Benzo(a)pyrene	0.87 <sup>#</sup>	JRC 2012
Benzo(a)anthracene	0.98 <sup>#</sup>	JRC 2012
Benzo(b)fluoranthene	0.64 <sup>#</sup>	JRC 2012
Benzo(e)pyrene	0.74 <sup>#</sup>	JRC 2012
Benzo(g,h,i)perylene	0.73 <sup>#</sup>	JRC 2012
Benzo(k)fluoranthene	0.64 <sup>#</sup>	JRC 2012
Benzothiazole	0.174	Stasinakis et al. 2013
Bisphenol A	0.47*	Langdon et al. 2010
Chrysene	1.08 <sup>#</sup>	JRC 2012
Coprostanol	43700	USEPA 2009
Coronene	0.36 <sup>#</sup>	JRC 2012
Di(2-ethylhexyl) phthalate	58*	Clarke and Smith 2011
Dibenz(a,h)anthracene	0.31 <sup>#</sup>	JRC 2012
Dibenzo(a,e)pyrene	0.073	JRC 2012
Dibenzo(a,h)pyrene	0.26 <sup>#</sup>	JRC 2012
Dibenzo(a,l)pyrene	0.060	JRC 2012
Diphenhydramine	5.73	USEPA 2009
Diphenyl ether	100	Di Francesco et al. 2004
Oestriol (E3)	0.01	Zuloaga et al., 2012
Oestrone (E1)	0.37	Langdon et al. 2011
Ethylbenzene	5.5 <sup>Y</sup>	EU RAR 2007 <sup>12</sup>
Fluoranthene	2.08 <sup>#</sup>	JRC 2012
Indeno(1,2,3-cd)pyrene	0.76 <sup>#</sup>	JRC 2012
Nitrophenol	0.022	JRC 2012
N-nitrosodimethylamine	0.50	Venkatesan et al. 2014
N-nitrosodi-n-propylamine	0.51	Venkatesan et al. 2014
N-nitrosodiphenylamine	0.15	Venkatesan et al. 2014
N-nitrosopiperidine	1.19	Venkatesan et al. 2014
Nonylphenol	534	Venkatesan and Halden 2013b
Nonylphenol diethoxylate	297	Bennie et al. 1998
Nonylphenol ethoxylate	437	Bennie et al. 1998
Octylphenol	1.26*	Langdon et al. 2010
Perylene	0.28 <sup>#</sup>	JRC 2012
Phenanthrene	0.98 <sup>#</sup>	JRC 2012
Phenol	220	Kester et al. 2005
Pyrene	14	USEPA 2009
Saccharin	0.020 <sup>#</sup>	JRC 2012
Sucralose	0.0044 <sup>#</sup>	JRC 2012

<sup>12</sup> <https://echa.europa.eu/documents/10162/f9b4577b-c57f-439b-b15a-9e268b1d0a58>

Toluene	737	Kester et al. 2005
Tolyltriazole	0.12	Asimakopoulos et al. 2013

#90<sup>th</sup> percentile

\$Mean concentration

¥Median

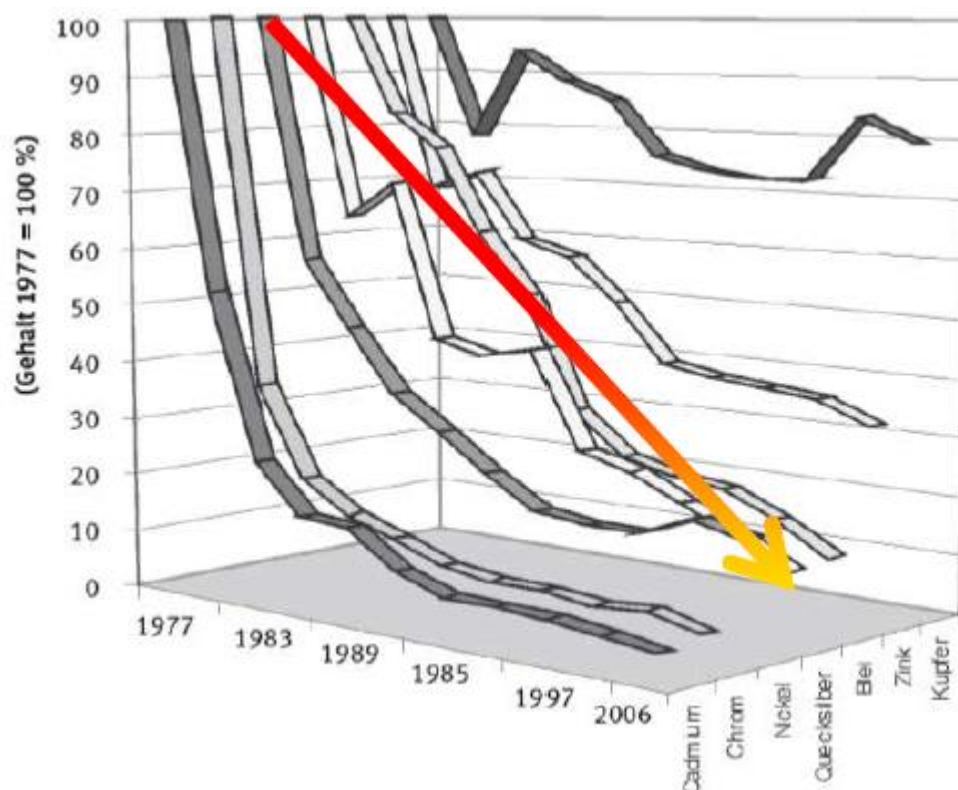
### 3.1.7 Trace elements<sup>13</sup>

The simultaneous measurement of multiple trace elements in biosolids is relatively simple and can be achieved at low cost, and it has been indicated to wca that the requirement for measurement of trace elements in NSW is likely to persist. This section is focussed upon those trace elements commonly measured in regulatory programmes and reported in the open literature and also some of those less common elements and forms of elements (such as the precious metals). The trace elements covered here are not an exhaustive list, but measured concentrations are shown from regulatory surveys in Table 3.7.

In the developed world, trace element concentrations in biosolids have generally been falling over the last twenty years. This perhaps shouldn't be too much of a surprise as industrial discharges are subject to greater regulatory controls or the original industrial sources have declined. Figure 3.2 shows a graph from a presentation by the German Association of Water, Wastewater and Waste that reflects these changes. The figure also shows, aside from perhaps for copper, a relative plateauing of the concentrations over time of these commonly monitored trace elements. This is especially the case for cadmium and chromium with multiple, low level, diffuse sources of these metals being the only remaining inputs to the WWTPs.

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<sup>13</sup> Generally, a trace element is one whose average concentration in environmental media is of less than 100 mg kg<sup>-1</sup>



**Figure 3.2** Concentrations of trace elements in German biosolids with time, where the 100% concentrations are taken as those from 1977 (Gerhalt 1977) and the order of metals on the x-axis is cadmium, chromium, nickel mercury, beryllium, zinc and copper (DWA, German Association of Water, Wastewater and Waste<sup>14</sup>)

The absolute changes in some trace metal concentrations in biosolids across many developed countries obviously reduces the potential environmental exposures but without appropriate effects measurement this does not necessarily mark a reduction in any potential environmental risks.

**Table 3.7** Trace element concentrations measured in biosolids from samples from Europe, the USA and NSW monitoring data

Trace element	Concentrations in biosolids, 90 <sup>th</sup> percentiles, mg kg <sup>-1</sup> (DW)	Source	NSW EPA (90 <sup>th</sup> percentile) <sup>§</sup>
Antimony	9.1	JRC 2012	-
Arsenic	56	JRC 2012	11.0
Barium	350	JRC 2012	-
Beryllium	2.3 <sup>^</sup>	USEPA 2009	-
Cadmium	1.3	JRC 2012	4.52
Chromium	81	JRC 2012	80.2
Cobalt	11	JRC 2012	-
Copper	418	JRC 2012	424
Lead	81	JRC 2012	66.4

<sup>14</sup> <http://ec.europa.eu/environment/waste/sludge/>

Manganese	604	JRC 2012	-
Mercury	0.7	JRC 2012	1.30
Molybdenum	86.4 <sup>^</sup>	USEPA 2009	-
Nickel	35	JRC 2012	27.0
Selenium	2.7 <sup>^</sup>	USEPA 2009	7.00
Silver	8	JRC 2012	-
Titanium	764	JRC 2012	-
Vanadium	135 <sup>^</sup>	JRC 2012	-
Zinc	1200 <sup>^</sup>	JRC 2012	976

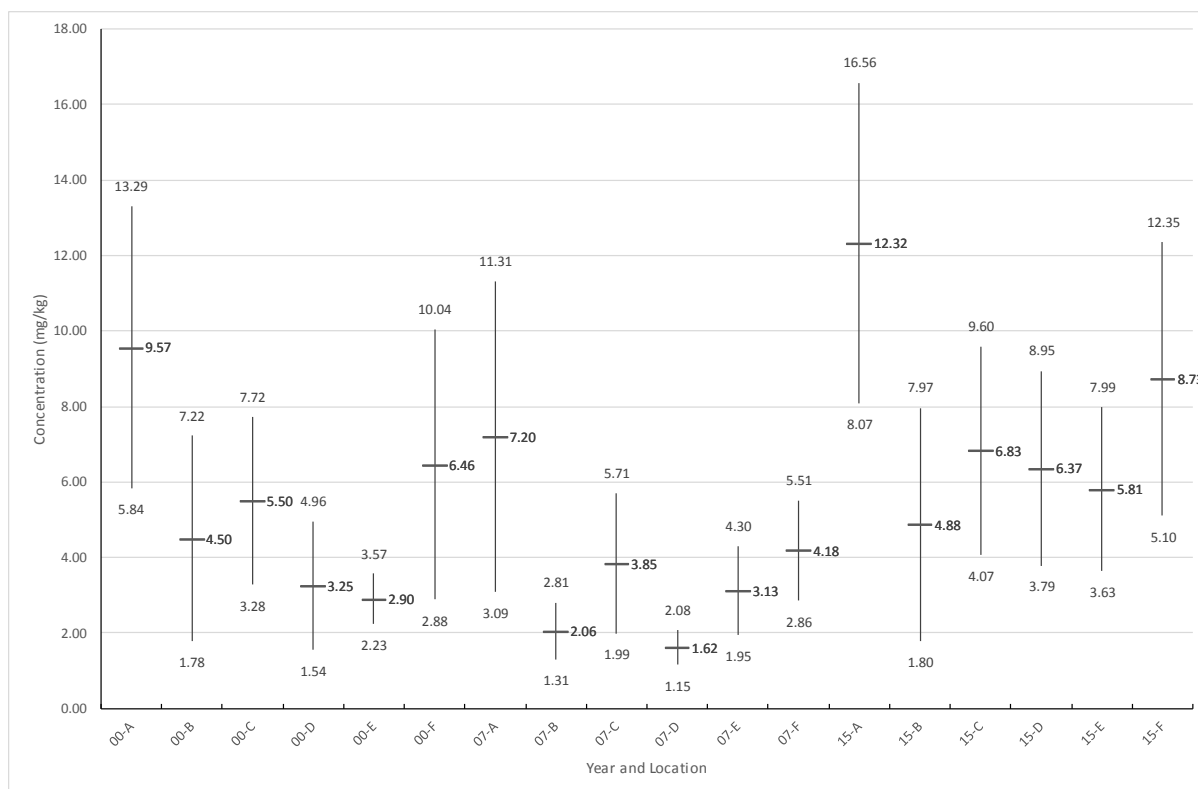
\$These percentiles are calculated from six locations in NSW for which measured data were available for 2000, 2007, 2015.

<sup>^</sup>Maximum concentrations

Similar patterns of reduction in concentrations of trace elements to those noted in Germany have been reported by Oliver et al. (2005) for Australian biosolids from multiple sources for copper, cadmium and nickel. Trace element concentrations for selected trace elements in biosolids from NSW are presented in Table 3.7. Data from a total of six WWTPs have been summarised in this table for the years 2000, 2007 and 2015 and the 90<sup>th</sup> percentiles calculated. These data are from a range of operations with different treatment processes and different sizes and catchment characteristics and therefore are simply indicative of 'likely' trace element concentrations in NSW biosolids. Importantly, wca were informed by the NSW EPA project team, that the biosolids from these operations have been or are likely to be applied to agricultural land.

**Arsenic** has historically been routinely monitored in biosolids in NSW and elsewhere. Historically, arsenic products were used widely as insecticides and in formulations to treat wood products to prolong service life. However, there are relatively few existing authorised uses of arsenic in most developed countries.

Industry data for concentrations of arsenic in biosolids from six locations in NSW are shown in Figure 3.3 as means and standard deviations for each anonymised location for a time series. There appears to be no clear pattern of change in these data in regard to concentrations or the variance as depicted by the standard deviations. Of course, this simply could be a reflection of the variation in baseline levels of arsenic in biosolids from diffuse and low level anthropogenic inputs. Unfortunately, there are not enough data here to be able to definitively make that statement.



**Figure 3.3 Arsenic concentrations in biosolids, as means (horizontal bars) and  $\pm 1$  standard deviations (as vertical lines) for six WWTPs in NSW over three separate years, 2000, 2007 and 2015**

Routine monitoring of chemicals in environmental matrices is performed for many reasons that can include classifications, determination of the state of the environment, regulatory compliance assessment and risk assessments (e.g. ISO 2008). The routine and regular monitoring of a chemical, such as arsenic, in a material destined for application to agricultural land is especially important if the concentration of that chemical is shown to be highly variable and that variability spans the range at which it might be expected to present potential human or environmental risks (e.g. Environment Agency 2009). Conversely, if the concentration of the chemical is relatively constant, showing little if any variability over an extended time period (however that is determined) and below any estimated risk limit then routine monitoring could be justifiably reduced or ceased.

**Cadmium** use in many industrial processes across the developed world has decreased considerably in the last 20 years. Remaining domestic uses in batteries and some electronic componentry are also largely being reduced. Not surprisingly the biosolids concentrations of cadmium reflect this phasing out with data from Germany and Australia (Oliver et al. 2005) showing concentrations decreasing with time to a plateau in concentrations probably reflecting ambient background and very diffuse latent sources of cadmium exposure. The 90<sup>th</sup> percentile concentration from the Australian data within the same order of magnitude as the EU data.

**Chromium** 90<sup>th</sup> percentile concentrations shown in Table 3.7 for both the European and Australian biosolids are remarkably similar, although this is probably something of a coincidence. Figure 3.2 shows the German biosolids chromium concentrations decreasing

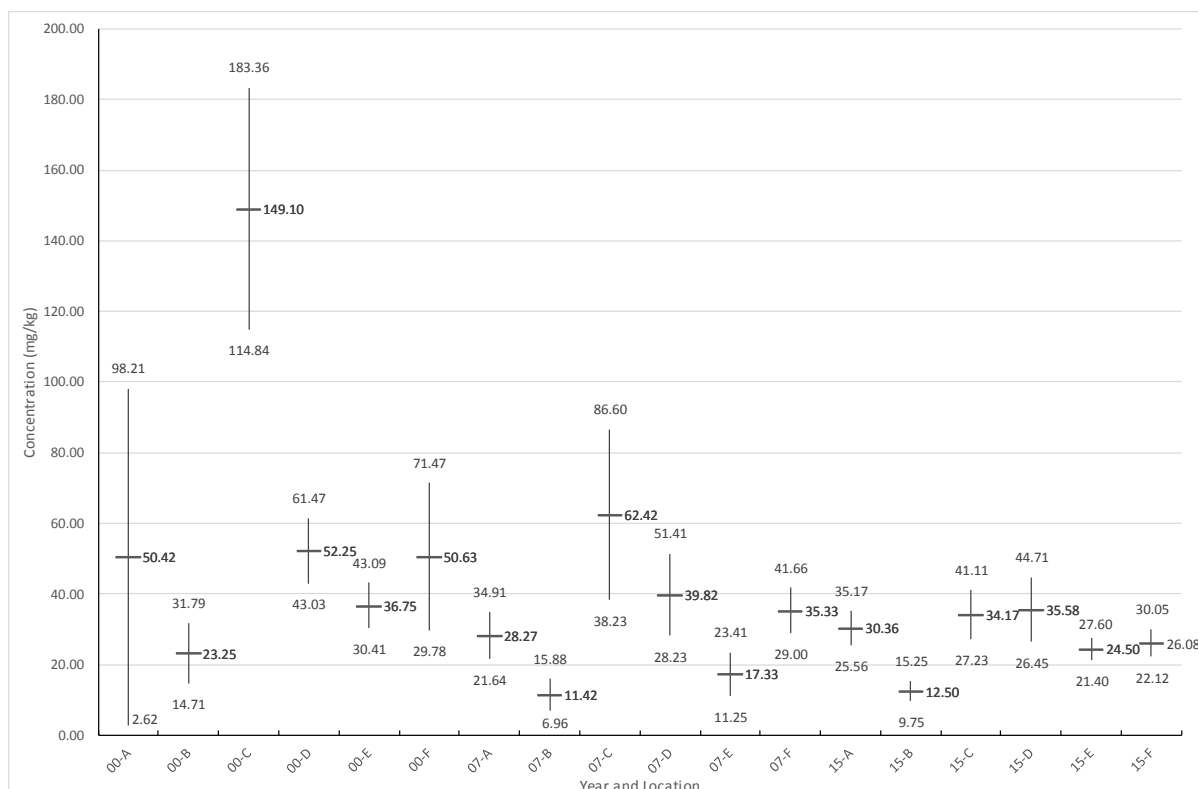
rapidly to a plateau. With an increased data set in both size and coverage for NSW biosolids a similar pattern may emerge.

**Copper** is one of the few elements to show no decrease with time in Figure 3.2. The extensive use of copper in domestic plumbing (now being replaced largely by plastic) has probably meant that there has been little discernible reduction in copper concentrations in many biosolids. Again, the concentrations at the 90<sup>th</sup> percentile for both the EU and NSW biosolids are very similar. Nevertheless, Oliver et al. (2005) did not report reductions in copper concentrations in Australian biosolids from multiple interstate WWTPs.

**Lead** use has greatly reduced over the last decades and this coupled with a gradual move in developed countries away from the burning of coal means less lead is likely to be entering WWTPs. Figure 3.4, summarising the Australian biosolids lead concentrations from the six WWTPs, indicates both a reduction in total lead concentrations in biosolids and importantly a considerable reduction in variability in concentrations, as indicated by reductions in the standard deviations for data from 2000 to 2015. These data would suggest that, dependent also on the final characterisation of potential risks, the on-going monitoring of lead in biosolids is perhaps not warranted.

**Molybdenum** is not determined routinely in Australian biosolids, but tends to be measured in Europe and the UK (Table 3.7). It is a relatively data rich metal, in regards to terrestrial hazard assessment, but one of the key concerns in regard to its measurement in UK biosolids is in relation to the prevention of molybdenosis in grazing livestock. If this has not been identified as a potential challenge in Australia, then there would be little reason to begin routinely monitoring molybdenum in biosolids. The concentration at which this occurs is determined in part by the concentrations of copper also present in the soil.





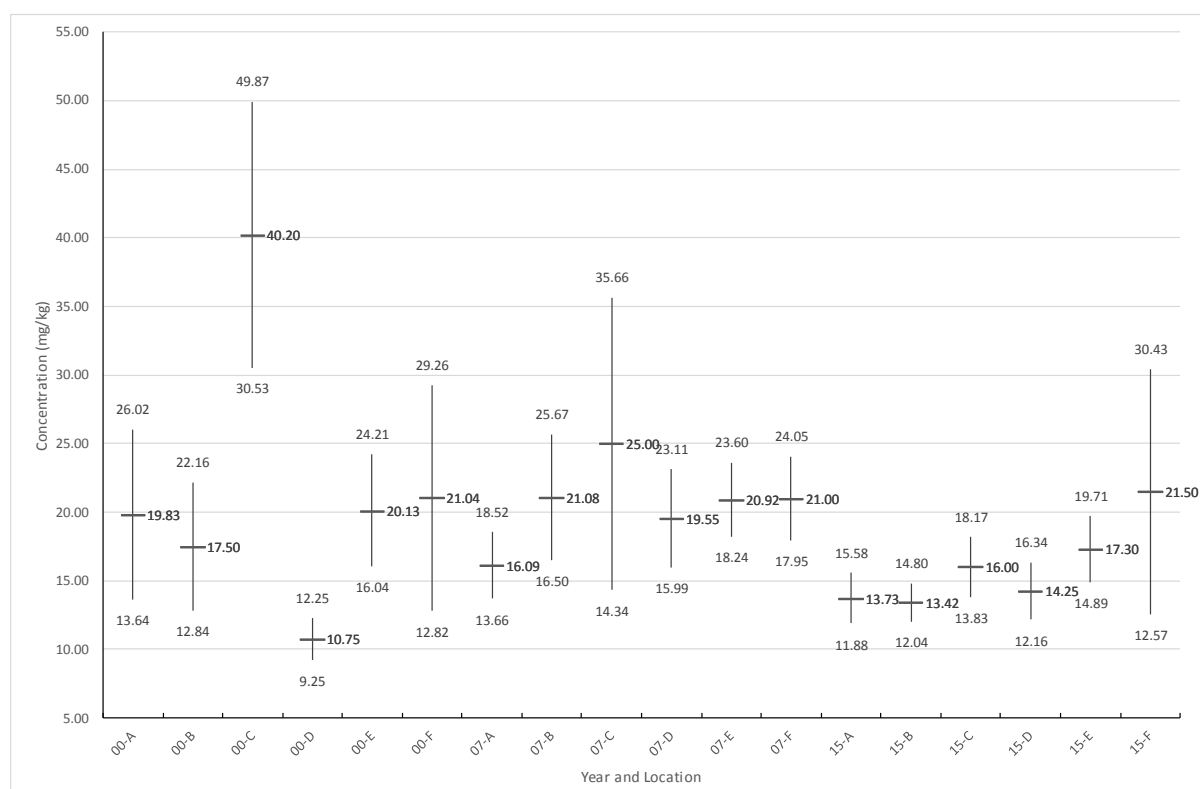
**Figure 3.4** Lead concentrations in biosolids, as means (horizontal bars) and  $\pm 1$  standard deviations (as vertical lines) for six WWTPs in NSW over three separate years, 2000, 2007 and 2015

**Nickel** concentrations in biosolids, like cadmium, have been shown to be decreasing in both German and Australian biosolids (Oliver et al. 2005) over recent decades. The 90<sup>th</sup> percentile concentrations in both the European and Australian biosolids subset are very similar. When the concentrations over the three time periods, 2000, 2007 and 2015 are plotted (Figure 3.5) a similar pattern to lead is seen in the decreasing concentration and variance, as given by the standard deviations, for all but the last sample in the sequence.

**Silver** has been measured in biosolids from several regulatory surveys and academic studies (nano forms of silver are discussed below, Section 3.1.8.1)(Table 3.7). Considerable recent academic and political interest in silver, as an environmental hazard, has led to suggestions of including silver as a routine regulatory monitoring determinand (e.g. the Environment Agency in the UK and the European Union, both only for aquatic monitoring at the moment).

Removal efficiencies, specifically from waters and into sludges and biosolids, of silver in WWTP have been modelled and measured to be in the region of 35% to 98% (Peters et al. 2011; Barton et al. 2015). It was suggested that these differences could be related to treatment technology (Peters et al. 2011), although Johnson et al. (2014) suggested no clear plant related effect in a survey of nine UK WWTP. However, retentions of greater than 90% of the silver entering the plant as influent, irrespective of silver form, seem to be very typical (e.g. Hedberg et al. 2014; Barton et al. 2015) and so much of the silver entering the treatment plant will be present in the biosolids.

In terms of the behaviour and fate of the silver in biosolids, Doolette et al. (2013) noted, through the use of solid-speciation techniques, the sulphidation of the nanosilver particles during bench top batch reactor experiments and total sulphidation during anaerobic digestion. This latter finding was also confirmed in a more recent study by Ma et al. (2014) who observed that regardless of the form of silver entering a pilot waste water treatment set up the silver in the anaerobically digested sludge was present as silver sulphide. However, it is also clear that before entering the WWTP transformation reactions, especially sulphidation, has already begun during the transportation process of the influent to the treatment plant (e.g. Kaegi et al. 2013).



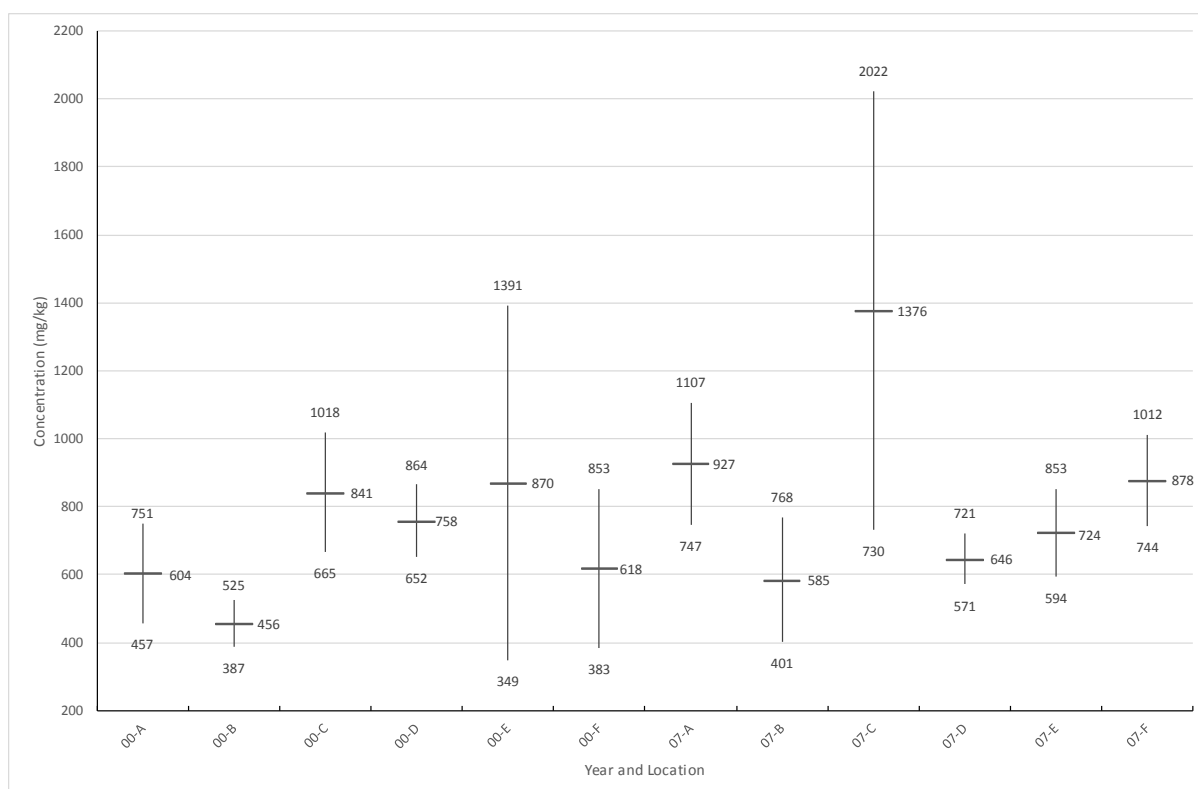
**Figure 3.5 Nickel concentrations in biosolids, as means (horizontal bars) and  $\pm 1$  standard deviations (as vertical lines) for six WWTPs in NSW over three separate years, 2000, 2007 and 2015**

As with all other trace elements, soil factors may influence silver bioavailability in soils. These factors have been investigated in a range of European and Australian soils (e.g. Langdon et al. 2014). The most important soil properties influencing the bioavailability of ionic silver were deemed to be soil pH, organic carbon content and effective cation exchange capacity. Importantly, many of the reactions that took place in soil with silver occurred rapidly and resulted in relatively non-bioavailable forms of silver for many soils. These silver forms in the biosolids and soils, in the medium term at least, have been shown to be relatively stable (e.g. Sekine et al. (2015), although it has been suggested that longer term studies focussing upon organic matter turnover may indicate potential silver release (Claus Svendsen pers. comm.).

There are many point and diffuse sources of **Zinc** that may enter WWTPs. Concentrations of zinc in German biosolids have been shown to have decreased over the last 30 years, perhaps

to a plateau concentration. Figure 3.6 shows the mean concentrations of zinc in biosolids from the six NSW WWTPs and indicates limited change over time. It is perhaps noteworthy that the variance, as indicated by the standard deviations, in zinc concentrations is also relatively large compared with some of the other trace elements.

The maximum concentrations of zinc in European biosolids and the 90<sup>th</sup> percentile of the Australia subset of data are again relatively similar.



**Figure 3.6 Zinc concentrations in biosolids, as means (horizontal bars) and  $\pm 1$  standard deviations (as vertical lines) for six WWTPs in NSW over three separate years, 2000, 2007 and 2015**

**Other** trace elements have been measured in biosolids, although less routinely than those shown in the surveys used to populate Table 3.7. Precious metals, such as platinum and palladium, have been determined in biosolids with concentrations shown to vary with catchment characteristics (e.g. Lottermoser 1994). These elements can present a considerable challenge to risk assessors in that currently relatively little is known about them in regard to environmental hazard. Lottermoser (1994) noted concentrations in German biosolids in the range of  $< 10 - 1070 \mu\text{g Pt kg}^{-1}$  and  $38-4700 \mu\text{g Pd kg}^{-1}$ . Additional studies on the behaviour and fate of these precious metals in WWTPs are being performed for the fulfilment of the European REACH regulation and should report with the next 18 months (Stutt et al. 2016). We accounted for this group of chemicals in Section 4.

### 3.1.7.1 Nano trace element forms

A great deal of academic and research resource has been invested recently in understanding the behaviour and fate of nano trace element forms, including silver, zinc oxide and titanium dioxide in the environment (e.g. Batley et al. 2013; Barton et al. 2014). Of all the nano materials studied in waste water treatment systems, silver has received perhaps the greatest attention.

However, there is perhaps a need for some context in relation to nano trace element forms and especially silver. Manufactured nanosilver materials represent a very minor percentage of the total tonnages of silver likely to be entering the WWTP. Indeed, in Europe nanosilver

accounts for less than 0.002% of the total tonnage of silver in use. From the occurrence data (Table 3.7) it can be seen that the total silver concentrations are relative low, when compared to the nanosilver concentrations used in many academic studies (e.g. 1-100 mg Ag L<sup>-1</sup>, Gu et al. 2014). A recent study by Navarro et al. (2014) assessing the release of ionic and nanosilver from biosolids and two biosolid amended soils in Australia noted limited release of nano particulate silver into solution post amendment.

The limited solubility of silver in biosolids is supported by the relatively low levels of microbial effects noted to the microbial populations at sewage treatment plants at relevant concentrations. We have therefore focussed on the assessment of the whole trace element potential risks, which will include some nano forms, rather than specific size fractions. Although the evidence at the moment the PNECs for the specific trace element which is generally derived for the most bioavailable form (the most soluble ion), such as silver or zinc, has been deemed to be protective of any nano specific effects.

### **3.1.8 Microplastics<sup>15</sup>**

The environmental fate of microplastics, especially in the marine environment, has become of increasing scientific interest over the last decade (e.g. Browne et al. 2008; Graham and Thompson 2009; Clark et al. 2016). Relatively little of this interest has focussed upon the behaviour of microplastics in biosolids.

Nevertheless, a recent study investigated the fate of synthetic microfibers and particles at a municipal WWTP through comparison with influent and effluent loads (Talvitie and Heinonen 2014). This pilot study showed a considerable reduction from the influent load (467 fibres, 160 synthetic particles and 3,160 black particles per litre of waste water) compared with the effluent discharged (16 fibres, 7 synthetic particles and 125 black particles were found per litre of wastewater). The authors suggested that much of the retained material would be destined for the biosolids. This finding is further supported by a study performed in California by Carr et al. (2016) looking at the fate of microplastics in eight WWTPs. Table 3.8 shows a summary table of the fate of the microplastics in the WWTPs from which it can be seen that relatively limited amounts are discharged in the final effluent, but considerable quantities are being removed to the biosolids and other solid fractions. The authors of this study characterised the microplastics and identified one of the key sources as being from toothpastes.

**Table 3.8 Results from assessment of microplastic fate in Californian WWTPs (From: Carr et al. 2016)**

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<sup>15</sup> Microplastics are particles that are generally smaller than 1 mm down to the micrometre range.

Location	Sample	MPP counts	Estimated total daily MPP counts
Grit	2.1 g	1 <sup>a</sup>	$\sim 7.78 \times 10^6$
1 <sup>o</sup> Skimming	5 g	20 <sup>a</sup>	
2 <sup>o</sup> Skimming	5 g	None found <sup>a</sup>	
CTS <sup>b</sup> influent	100 mL	51	
Thickened centrate	100 mL	267	
Biosolids	5 g	5 <sup>a</sup>	$\sim 1.09 \times 10^9$
Final effluent	$4.23 \times 10^5$ L	373	$\sim 0.93 \times 10^6$
$\Sigma$ Grit + biosolids + final effluent			$1.10 \times 10^9$ per day
Grit + biosolids			$1.10 \times 10^9$ per day ( $\sim 99.9\%$ removal by the plant)
Influent			One particle per liter

<sup>a</sup> Average number of 2 or 3 replicates.

<sup>b</sup> Centrate thickening system.

Defining the potential microplastic environmental hazard, and exposure loading in a solid material, is currently not straight-forward.

From a scientific perspective, not identifying a chemical of concern in biosolids, because it has never been looked for, does not mean that it does not present a potential environmental or human health risk (e.g. Darvodelsky 2011). We have included microplastics in the 'parked' section of this assessment, as these require greater information to be able to make an evidence-based assessment (Section 4).

## 3.2 Hazard and exposure

The potential for chemicals detected in biosolids to pose a risk following application to agricultural land is assessed in two stages with an initial screen based on fate and behaviour properties followed by preliminary environmental risk assessment and screening of potential human health hazard.

### 3.2.1 Fate Screening

An initial screening for the organic chemicals is performed by review of physico-chemical properties and environmental fate and behaviour characteristics. The following criteria are used to screen out chemicals from further consideration that are considered unlikely to persist and accumulate in sludge and agricultural soils:

- Log Kow <4.5;
- Readily or inherently biodegradable;
- Half-life <120d in soil, sludge or compost (ECHA 2016).

Chemicals meeting these criteria are considered unlikely to accumulate in agricultural soil following application of sludge and are screened out from further consideration (these chemicals are shown in the spreadsheet, Chemicals\_physchem tab). Those that meet these

criteria have been taken forward to the next stage of the assessment and are detailed in Section 4.1.

### **3.2.2 Indicative environmental risk assessment**

A simple generic environmental risk assessment has been performed for those chemicals selected by the initial screening (see above) and for which PNECs are available (as per Figure 3.1). All of the trace elements listed in Table 3.7 were included in this indicative assessment.

The references for the PNECs are all provided in the reference section at the end of this report. They are from a range of regulatory jurisdictions, with a mix of protection goals and regulatory purposes, but are suitable for use in this precautionary generic level risk assessment (Environment Agency 2016). For some of the trace elements, bioavailability correction approaches are available for use, both for the PNECs used here and also for use specifically with Australian biosolids (e.g. in South Australia), although these are not yet widely available. For some of the chemicals, it has not been possible to obtain a suitable PNEC (see spreadsheet, PNECs tab), and these chemicals will be 'parked' for further investigation as new information becomes available.

Exposure concentrations of all the chemicals passing the first screen following application of sludge to land were calculated from a generic use scenario for a generic soil considering two application rates. Table 3.9 gives the parameters that have been used to calculate the exposure concentrations of chemicals over an area of 1 ha. The exposure concentrations in the soils were calculated for each of four scenarios (1 year of 8 tonnes, 1 year of 50 tonnes, 10 years of 8 tonnes per ha per year and 10 years of 50 tonnes per ha per year) and no losses were assumed (this is a very conservative assumption as it disregards degradation and volatilisation of organic chemicals and leaching of trace elements). These concentrations were then compared to the respective PNECs and risk characterisation ratios (RCRs) calculated<sup>16</sup>. The results of this assessment are given in Section 4 and can be found in the embedded spreadsheet at the end of this report (on the 'Risk' tab).

When undertaking such an assessment it is imperative to assume that at all times 'good practice' has been followed in the biosolids use. In a screening level assessment, it is not practically feasible to consider other types of behaviour. The data detailed in Table 3.9 refer to the existing biosolids guidelines (NSW EPA 1997) and take account of some of the typical soils in the region<sup>17</sup>. These data have been used in the screening level environmental risk assessment set out in the spreadsheet (see the Risk tab).

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<sup>16</sup> RCR = PEC/PNEC

<sup>17</sup> E.g. <http://www.soilquality.org.au/au/nsw>

**Table 3.9 The default parameters and assumptions used in the estimation of exposure concentrations of organic chemicals in soils amended with biosolids for this project**

Parameter	Value	Reference
Application rate of biosolids, as dry tonnes ha <sup>-1</sup>	8 and 50* t ha <sup>-1</sup>	Environment Agency 2009
Bulk density of soil receiving organic material	1.333 g cm <sup>-3</sup>	NSW EPA 1997, Table S4-3
Depth of incorporation	0.075m	NSW EPA 1997, Table S4-3
Area of incorporation	1 ha	NSW EPA 1997, Table S4-3

\* These have not been changed as they represent hypothetically 'typical' and relatively large application rates.

There are several assumptions made in performing the screening approach as presented here and in the accompanying spreadsheet that may be considered to influence the assessment in particular ways. These assumptions and the likely direction they might influence the assessment include;

- No account has been taken for the ambient background concentrations of chemicals already present within the soil, this would include all the trace elements and some of the organics, this would result in a lack of conservatism;
- No account has been taken for degradation or loss of any of the chemicals from the biosolids or in the amended soils, this would have relatively a precautionary influence on the outcome;
- Generally, maximum or 90<sup>th</sup> percentile concentrations of chemicals in the biosolids have been used for the derivation of the predicted environmental concentrations (PECs), this is reasonable worst case;
- Only a limited amount of exposure data have been sourced specifically from Australian biosolids, the influence of this on the assessment is uncertain and makes any definitive conclusions on substance selection also uncertain;
- Three of the PNECs used in the assessment (dieldrin, dichlorodiphenyl dichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE) are specific to Australia (NSW EPA 1997), this is due to an absence of a readily available source of PNECs to use for all the chemicals from Australia and the dated nature of many of the PNECs that are available;
- Bioavailability for some of the trace elements in the final amended soils has been considered as a refinement (Section 4.3, in the spreadsheet TMbioav tab), but using very generic soil properties from NSW<sup>18</sup>. So, we have simply taken the mid-range of the properties as an input to the bioavailability calculation tools<sup>19</sup> (e.g. pH in CaCl<sub>2</sub> 5.5, CEC 5 meq/100g soil, 15% clay, total organic carbon 1.5%). Clearly, this is a fictitious

<sup>18</sup> <http://www.soilquality.org.au/au/nsw>

<sup>19</sup> <http://www.arche-consulting.be/en/our-tools/soil-pnec-calculator/>



'soil type', and represents a very generic and indicative assessment. A potential refinement would be to use a range of common soil types representing typical soils that might receive biosolids amendments.

- No account for bioavailability has been taken for the organic chemicals in this report. However, this can be undertaken through normalisation of the PNEC to a specific soil organic carbon content<sup>20</sup>.

### 3.2.3 Indicative human health ranking

Risk assessment for human health has the objective of assessing dietary exposure resulting from the presence of contaminants in sewage sludge applied to agricultural land. This considers the potential for trace elements or persistent organic pollutants with high bioaccumulative potential present in sludge to transfer and accumulate through the food chain and increase dietary exposure to these contaminants. Full quantitative risk assessment would require a detailed modelling exercise which is beyond the scope of this project. Instead an indicative human health screening has been undertaken for the selected contaminants, based on a ranking system comprising of an assessment of toxicity and exposure potential.

Contaminants are ranked by their toxic potency according to a scoring scheme devised for Health Criteria Values (HCVs) and other similar measures of toxicological potency (ADIs<sup>21</sup>, RfDs<sup>22</sup>). For substances with a readily available HCV or similar accredited level of acceptable human exposure, scores are allocated to each contaminant according to the following scheme for oral HCVs (Table 3.10).

**Table 3.10 Potency scoring scheme for contaminants with HCVs**

Health Criteria Value ( $\mu\text{g kg}^{-1} \text{ bw day}^{-1}$ )	Ranking Score
< 0.01	10 (high)
1 to 0.01	8
1 to 10	6
10 to 100	4
>100	2 (low)

<sup>20</sup> For the PNECs used here, this is generically set as 3.4% soil organic matter content, which is a value used in the EU, but may not be suitable in Australia.

<sup>21</sup> Acceptable Daily Intake (ADI is a measure of the amount of a specific substance (originally applied for a food additive, later also for a residue of a veterinary drug or pesticide) in food or drinking water that can be ingested (orally) on a daily basis over a lifetime without an appreciable health risk.

<sup>22</sup> Reference Dose (this terminology is commonly used by the US Environment Protection Agency for oral exposure; Reference Concentration, RfC, is used for inhalation exposure)

## 4 PRIORITISATION OF CHEMICALS

This section provides an outline of the results from the screening and indicative risk assessment and provides a prioritised, evidence-based, list of chemicals to monitor in biosolids in NSW.

### 4.1 Chemicals 'screened in'

Following the initial screening exercise undertaken on the basis of physico-chemical properties (Section 3.2.1) the following chemicals from the initial list of 158 found in biosolids were deemed likely to persist in soils amended with biosolids. The values for vapour pressure listed in the spreadsheet were treated only with secondary importance and were not used to screen out chemicals on the basis of a potential to volatilise soil; this conservative approach was taken as partitioning occurs between different compartments in soil (e.g. partitioning to organic carbon may retard tendency to volatilise). All of the trace elements were taken forward as all are effectively persistent. Where groups had initially been identified in the occurrence data, only one chemical was taken forward as being representative of that group (for example BaP rather than all PAHs) to ensure the list was a manageable practical size. Highlighted chemicals in Table 4.1 are those screened in for further assessment (24 organic compounds).

**Table 4.1 Organic substances screened into risk assessment**

Substance	Category and representative (if relevant)
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	
Alpha- chlordane	
BDE-153 (2,2',4,4',5,5'-hexabromodiphenyl)	BDEs
BDE-209 (decabromodiphenyl)	BDEs
BDE-47 (2,2',4,4'-tetrabromodiphenyl)	BDEs - representative
BDE-99 (2,2',4,4',5-pentabromodiphenyl)	BDEs
Benzo(a)anthracene	PAHs
Benzo(b)fluoranthene	PAHs
Benzo(a)pyrene	PAHs - representative
Benzo(e)pyrene	PAHs
Benzo(g,h,i)perylene	PAHs
Benzo(k)fluoranthene	PAHs
Cashmeran	
Chrysene	PAHs
Decabromodiphenyl ethane (DBDPE)	
Decamethylcyclopentasiloxane	
Di(2-ethylhexyl) phthalate	
Di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH)	
Dibenz(a,h)anthracene	PAHs
Dibenzo(a,e)pyrene	PAHs
Dibenzo(a,h)pyrene	PAHs
Dibenzo(a,l)pyrene	PAHs
dichlorodiphenyl dichloroethane (DDD)	
Dichlorodiphenyldichloroethylene (DDE)	
Diclofenac	
Diieldrin	
Dodecamethylcyclohexasiloxane	

Fluoranthene	PAHs
Hexabromobenzene (HBB)	
Hexabromocyclododecane (HBCD)	
HHCB (Galaxolide)	
Indeno(1,2,3-cd)pyrene	PAHs
Penta-BDE	BDE
Perfluorodecanoate	
Perylene	PAHs
PFNA	
PFOA	
PFOS	
Pyrene	PAHs
Tonalide	
Triclocarban	
Triclosan (TCS)	

## 4.2 Initial selection of chemicals for environmental risk assessment

For the list of chemicals highlighted in Table 4.1, and all of the trace elements identified in Table 3.7, PNECs were identified (where possible) to provide an initial indicative environmental risk assessment. From this assessment of the four generic scenarios, the chemicals for which a risk characterisation ratio (RCR) of 1 or greater (i.e. indicative of potential environmental risk) are shown in Table 4.2. Only selenium and mercury are identified as potentially being an issue at the lowest application rate, but as the rates and application numbers increased so the number of chemicals with RCR>1 increases. However, even at the highest rate of biosolids application over ten years, several chemicals give RCR values below 1 and so represent low risks, and can be discounted from further consideration for inclusion in the routine monitoring, these were:

- Alpha- chlordanedecabromodiphenyl ethane (DBDPE),
- Diclofenac,
- Dodecamethylcyclohexasiloxane,
- Dichlorodiphenyl dichloroethane (DDD),
- Dichlorodiphenyldichloroethylene (DDE),
- BDE-47,
- Antimony,
- Lead, and
- Nickel.

**Table 4.2 Chemicals for which an RCR of 1 or greater was estimated for each biosolids application scenario**

<b>8t ha<sup>-1</sup>, 1 application</b>	<b>8 t ha<sup>-1</sup>, 10 applications</b>	<b>50 t ha<sup>-1</sup>, 1 application</b>	<b>50 t ha<sup>-1</sup>, 10 applications</b>
Mercury Selenium	Mercury Selenium Dieldrin HHCB (Galaxolide) PFOS Triclosan Barium Molybdenum Silver Vanadium Zinc	Dieldrin HHCB (Galaxolide) Triclosan Barium Mercury Selenium Silver Vanadium Zinc	Mercury Selenium Benzo(a)pyrene Cashmeran Decamethylcyclopentasiloxane Di(2-ethylhexyl) phthalate Dieldrin Hexabromocyclododecane (HBCD) HHCB (Galaxolide) PFOA PFOS Tonalide Triclosan Arsenic Barium Beryllium Cadmium Chromium Cobalt Copper Molybdenum Silver Vanadium Zinc

The following trace elements and organics did not have readily available PNECs meaning that it was not possible to include them in the indicative environmental risk assessment:

- Titanium,
- Manganese,
- 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE),
- di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH),
- Hexabromobenzene (HBB),
- PCDD/DFs (dioxins and furans),
- Perfluorodecanoate,
- PFNA, and
- Triclocarban.

Therefore, despite these having been identified by the chemical properties screening exercise (Section 3.2.1) as being of potential relevance, we have not been able to consider them further (they are therefore considered 'parked' for consideration at a later date if additional information becomes available).

### **4.3 Refinement of potential priority list of chemicals**

In terms of the organic chemicals included in the indicative risk assessment, none were identified as being of potential risk for a single application of 8 t ha<sup>-1</sup> of biosolids (see Table 4.2). However, potential risks were identified at every other scenario, with dieldrin, HHCB (Galaxolide) and triclosan being common to all.

The synthetic musk HHCB has a PEC that has not been calculated from Australian data, meaning that it has a potentially low level of relevance for this study. The triclosan PEC has been derived from the limited survey of Australian biosolids by Langdon et al. (2011) and that for dieldrin from Clarke et al. (2010b) also from Australian data. The triclosan PNEC used has been recently derived by the UK Environment Agency (2016), but is from a relatively limited ecotoxicity dataset. These three organic chemicals are the only ones for which RCRs of greater than 10 have been estimated for the highest rates of application and therefore clearly represent the highest potential concern for environmental risk following application of sludge to soil. Despite the HHCB PEC not being generated from Australian data (it comes from JRC 2012), it has been included as a prioritised chemical as it has the highest RCR, at 28, of any of the organic chemicals considered at the highest application rate.

The only other organic identified as presenting potential environmental risks, for both sets of repeat applications, is the perfluorinated compound, PFOS. This compound has the next highest RCR compared to three chemicals discussed above, but is less than 10 for both long term application scenarios. The data used for the assessment of the effects and also the exposures for PFOS are not Australian, being sourced from Europe. Therefore, a refinement of the assessment performed for PFOS would be to use local data before making a prioritisation decision.

At the highest application rate for repeat applications the chemicals that were identified as being potentially a risk were benzo(a)pyrene, cashmeran, decamethylcyclopentasiloxane, di(2-ethylhexyl) phthalate, hexabromocyclododecane (HBCD), PFOA and Tonalide. None of the PEC data identified for these chemicals were taken from Australian studies, and importantly, the PEC for di(2-ethylhexyl) phthalate is calculated from a mean value, and so cannot be considered to be 'reasonable worst case' (making it probably a less than conservative assessment). We therefore suggest that these chemicals are given further consideration, ideally using Australian PECs (and where available, PNECs).

For mercury and selenium both PNECs used in the indicative assessment are based upon secondary poisoning and are also associated with high level of relative regulatory uncertainty. Specifically, this would make the inclusion of these chemicals in any routine regulatory monitoring very uncertain and it is likely to be more appropriate that site-specific assessments should be undertaken where they may be of particular concern.

For the trace elements, accounting for bioavailability was undertaken for those metals for which it was possible to do so, and that showed a potential risk for one of the scenarios shown in Table 4.2. Using the generic soil properties given previously (Section 3.2.2) a brief refinement of the PNECs (which are specifically derived for use with bioavailability consideration) for molybdenum, copper, cobalt and zinc was undertaken using the Arche Soil PNEC calculator (see the TMBioav tab on the spreadsheet). In accounting for bioavailability, potential risks are only identified at the highest rate (50 t ha<sup>-1</sup>) for the longest period (10

years) for copper and zinc. For zinc (and vanadium too) this is a relatively conservative assessment as the PNEC is an 'added' PNEC, that requires the addition of the local ambient background concentration. Even for copper and zinc the values of the RCR are also relatively low (2.8 and 4.6, respectively). Through the use of more Australian-specific biosolids monitoring data a more relevant PEC could be determined, thereby refining the assessment. Nevertheless, copper and zinc should be prioritised on the basis of the evidence reviewed here.

For silver, a simple tool does not yet exist to account for the influence of soil factors on bioavailability, although that is expected soon as it is currently being worked up by the Environment Agency in the UK (Ian Martin pers. comm.). Nevertheless, from the work by Langdon et al. (2014) it is clear that soil factors can influence the PNEC by over an order of magnitude. Therefore, we would 'park' silver at present until an appropriate assessment, accounting for the latest scientific evidence, can be considered; although we would expect this to be of low priority as soil bioavailability of silver tends to be relatively low.

Chromium is identified as a potential risk at the highest application rate of 50 t ha<sup>-1</sup>. The PEC used is for Australian data, but no account has been taken for bioavailability with the PNEC. The decrease in chromium concentrations in German biosolids may also be a trend reflected in Australia, making the use of the 90<sup>th</sup> percentile of the subset of data used here a conservative assumption. However, chromium should remain under consideration until this comparison can be made.

Cadmium, like chromium, is only a risk under one of the scenarios above (Table 4.2) and as was indicated by Oliver et al. (2005) has been shown to be decreasing in biosolids in Australia. Nevertheless, due its potential for food chain transfer cadmium should remain under consideration, perhaps along with chromium, for occasional status monitoring in the biosolids.

For many of the trace elements that have been identified as potential priorities at the higher rates of application, such as barium, beryllium and vanadium the PECs have been generated using non-Australian data and/or PNECs have high relative regulatory uncertainty for a region-specific assessment. This is important context but does not remove the need for further 'local' consideration and so these trace elements should reasonably be parked and not removed from further assessment.

## **4.4 Ranking for human health hazard**

As detailed in Section 3.2.3, contaminants are ranked by their toxicological potency according to a scoring scheme devised for Health Criteria Values (HCVs) and other similar intake values (e.g. ADI and RfDs). The output of this ranking exercise is detailed below in Table 4.3 and in the 'HCVs' tab of the spreadsheet. It should be noted that all of the organic compounds considered here have log Kow>4.5 and therefore have some potential to bioaccumulate in the food chain. Quantitative assessment of this exposure pathway and possible risks to human health from dietary intake would require a detailed modelling exercise that it beyond the scope of this project.

Trace elements accumulate to varying extents in different food types and plant uptake is influenced by a variety of factors such as chemical speciation and soil properties. A number of studies are available in the literature that quantify plant uptake of trace elements and a search should be undertaken to identify those that could be considered relevant to soils in NSW that biosolids may be applied to. These parameters could then be used in detailed risk assessment of this exposure pathway.

It is recommended that any detailed assessment of dietary intake starts with the most toxicologically potent compounds highlighted by this ranking exercise.

**Table 4.2 Ranking of prioritised chemicals for toxicological significance**

<b>Score = 10</b> <b>Very high</b> <b>potency</b>	Benzo(a)pyrene, PCDD/DFs (dioxins and furans)
<b>Score = 8</b> <b>High</b> <b>potency</b>	Alpha-chlordane, Diclofenac, Dieldrin, BDE-47, PFOS, arsenic, cadmium
<b>Score = 6</b> <b>Moderate</b> <b>potency</b>	DEHP, DDD, DDE, HBB, PFOA, antimony, beryllium, lead, mercury, molybdenum
<b>Score = 4</b> <b>Low</b> <b>potency</b>	HHCB, Tonalide, nickel, selenium, silver, vanadium
<b>Score = 2</b> <b>Very low</b> <b>potency</b>	Decamethylcyclopentasiloxane, Dodecamethylcyclohexasiloxane, Triclosan, barium, copper, zinc, manganese,
<b>'Parked'</b> <b>No HCV</b>	BTBPE, Cashmeran, DBDPE, TBPH, HBCD, Perfluorodecanoate, PFNA, Triclocarban, chromium (species dependent), cobalt, titanium

## 4.5 Chemicals prioritised for potential monitoring in biosolids

We have divided the chemicals in biosolids reviewed here into four categories that reflect the evidence-base and assessment results. The first category is for those chemicals prioritised, i.e. those for which there is clear evidence that these chemicals should, at the minimum, be considered for assessment locally in Australian biosolids, using Australian specific PECs/PNECs, before inclusion in a routine monitoring list. The second category is for chemicals for which further consideration might be necessary as one aspect of the assessment is not matched directly to Australian or NSW specific data. It is likely that a limited, but specific, action would be to move these chemicals to the first category or down to the fourth. Such action might even include 'status' monitoring where occasional measurements in biosolids are made to support non-inclusion in the routine monitoring category. The third category is for those chemicals for which one part of the indicative risk assessment has not been possible, but for which more information in the future might mean a change in category for the respective chemical. The fourth category is for chemicals that have been assessed, using relatively precautionary assumptions, and have been shown to present a low risk for the scenarios presented.

The results of the indicative environmental risk assessment for organic compounds detected in biosolids indicate that dieldrin, HHCB (Galaxolide) and triclosan should be considered as highest priority for routine monitoring. Human health hazard prioritisation also indicates dieldrin to have relatively high toxicological potency. Additional compounds that should be given further consideration and local assessment include PFOS and then benzo(a)pyrene, Cashmeran, decamethylcyclopentasiloxane, DEHP, HBCD, PFOA and Tonalide (PFOS and BaP are also considered to have high and very high toxicological potency, respectively). Those 'parked' and requiring additional data are dioxins and furans (as detailed in Section 3, assessment of these compounds is a detailed and involved process and there is no specific reason for their presence at elevated concentrations in biosolids), BTBPE, TBPH, Hexabromobenzene (HBB), perfluorodecanoate, PFNA and Triclocarban. Those that present low potential risk to the environment include alpha-chlordane, DBDPE, Diclofenac, dodecamethylcyclohexasiloxane, DDD, DDE and BDE-47. On a purely environmental basis these chemicals would not be considered for routine monitoring but the toxicological potency of alpha-chlordane, diclofenac and BDE-47 means that they should be given further consideration and possibly assessed for dietary exposure and risk to human health.

On the basis of the indicative risk assessment and consideration of bioavailability the trace elements that should continue to be monitored routinely would be copper and zinc. Those that might be considered further are chromium and cadmium and those that are 'parked' requiring more data and local assessment would include selenium, mercury, silver (bioavailability assessment), barium, beryllium, vanadium (and perhaps the precious metals). Those that should not be continually monitored on the basis of presenting low potential environmental risk include cobalt, lead, molybdenum, nickel and probably arsenic (however, arsenic is recommended for further consideration on the basis of high toxicological potency).

For some of the precious metals (e.g. platinum, palladium) there is evidence of presence in biosolids but not yet sufficient terrestrial ecotoxicological data from which to derive a reliable PNEC to make the assessment.



**Table 4.3 Chemicals in biosolids categorised from the evidence reviewed in this report, in regard to inclusion in a routine monitoring determinand suite**

Chemicals prioritised	Chemicals for further consideration?	Chemicals 'parked'	Chemicals presenting low potential environmental risks
Copper Zinc Dieldrin* HHCB (Galaxolide) Triclosan	Cadmium* Chromium PFOS* Benzo(a)pyrene* Cashmeran Decamethylcyclopentasiloxane DEHP HBCD PFOA Tonalide  <u>On the basis of toxicological potency:</u> Alpha- chlordane* Arsenic* Diclofenac* BDE-47*	Silver Barium Beryllium Vanadium. Titanium Manganese Selenium Mercury 1,2-bis(2,4,6-Tribromophenoxy)ethane (BTBPE), di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH), Hexabromobenzene (HBB), Perfluorodecanoate PCDD/DFs & dioxin-like PCBs* PFNA Triclocarban Precious metals (Pt, Pd, etc.) Microplastics	Decabromodiphenyl ethane (DBDPE) Dodecamethylcyclohexasiloxane Dichlorodiphenyl dichloroethane (DDD) Dichlorodiphenyldichloroethylene (DDE) Antimony Cobalt Lead Molybdenum Nickel

\*Indicates high or very high human health hazard score

## 5 RECOMMENDATIONS

From this assessment we would recommend:

- Following a confirmatory assessment using biosolids data specifically from NSW, routine monitoring of copper, zinc, dieldrin, triclosan and HHCb (Galaxolide).;
- We would recommend occasional 'status' monitoring for cadmium, chromium and PFOS. This exercise could also be undertaken with slightly lower priority (based on lower RCRs from the indicative environmental risk assessment) for benzo(a)pyrene (as representative of PAHs), Cashmeran, decamethylcyclopentasiloxane, DEHP, HBCD, PFOA and Tonalide. These data can be used to inform decisions about inclusion or removal on a finalised routine monitoring list. For cadmium and chromium these data probably exist already and can be readily processed;
- Some chemicals were identified as potentially being of relevance to long-term monitoring in biosolids due to likely persistence in amended soils, but could not be assessed as no reliable PNECs could be found or PECs estimated. These chemicals were described as being 'parked' and included the trace elements titanium and manganese and the organics 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH), di(2-ethylhexyl) phthalate, hexabromobenzene (HBB), PCDD/DFs (dioxins and furans), perfluorodecanoate, PFNA, triclocarban and also microplastics. These chemicals (and the microplastics) should be periodically reviewed in the future as new information becomes available;
- Before any additional or changed monitoring burden is implemented it is imperative that an assessment is made to ensure that analytical capabilities at local NSW commercial/in-house laboratories are available and that the costs for additional determinands are not prohibitive;
- The PNECs used in this study to assess potential trace element risks have been derived for a specific screening purpose in a regulatory framework in the UK. It would increase the relevancy and realism of this assessment if those trace element PNECs derived in Australia, using Australian biosolids, on Australian soils were to be used to provide confirmatory support for the findings detailed here;
- Despite an absence of environmental risk, assessment of the dietary exposure pathway should be undertaken for arsenic, alpha-chlordane, diclofenac and BDE-47 (as a marker for brominated diphenyl ethers) on the basis of human health hazard (as indicated by toxicological potency). Furthermore, local assessments of environmental risk are recommended for mercury and selenium, for which key exposure routes are secondary poisoning.
- The Australian Water Industry evidence reviewed here, and the data from the open and grey literature support the reduction in the number of contaminants routinely determined in biosolids in NSW. Specifically, the monitoring of lead, nickel, probably arsenic, lindane, BHC, aldrin, heptachlor, DDD, DDE and DDT is considered, based on

an informative risk-based exercise of biosolids as a source of these chemicals, to be of limited use;

- This report should be used as a starting point, rather than a definitive conclusion, regarding the selection of chemicals for inclusion in a routine monitoring determinand suite for biosolids. We have detailed many assumptions and opportunities for refinement and we understand that much of the information may be available with which to achieve this (specifically on the PECs). By providing the spreadsheets in an unlocked form, changes and refinements to the assessment can be readily made in a transparent way.

## **6 CONCLUSIONS**

This report has provided an evidence-based screening of chemicals in biosolids, from the perspective of environmental risks and human health hazard. For many of the chemicals measured in biosolids there are few, if any, data for biosolids from NSW. Therefore, a conclusion from this report would be the identification of a need to deliver a broad assessment of chemicals in regional biosolids. Such surveys have been undertaken in Europe and the USA and are important in light of the large proportion of biosolids produced in NSW that go to agricultural land. To ensure long-term sustainability and consumer confidence in biosolids use such a survey would seem necessary.

A relatively short list of chemicals has been prioritised for routine monitoring in biosolids. The chemicals on this list have been identified through an evidence-based, precautionary, screening risk assessment for the environment and hazard ranking for human health. This process, as with all risk assessments, is suitable for further iteration and refinement. We strongly suggest this refinement is undertaken and the assumptions we have made robustly challenged using more regional specific information (including application rates, soil properties and exposure concentrations).

We have identified some chemicals which may present potential risks, but for which there exist too few data to draw, even tentative, conclusions.

The existing list of contaminants for which routine monitoring is undertaken in biosolids from NSW is probably not reflective of the potential environmental and human health risks that may be present from land applying biosolids. Indeed, of the existing list only copper, zinc and dieldrin should probably remain.

## REFERENCES

- Albero B, Pérez RA, Sánchez-Brunete C, Tadeo JL. 2012. Occurrence and analysis of parabens in municipal sewage sludge from wastewater treatment plants in Madrid (Spain). *J Hazard Mater.*, 239-240:48-55.
- Alcock RE, Sweetman A, Jones KC. 1999. Assessment of organic contaminant fate in waste water treatment plants. I: Selected compounds and physicochemical properties. *Chemosphere*, 38: 2247-2262.
- Arbeláez P, Borrull F, Maria Marcé R, Pocurull E. 2014. Simultaneous determination of drugs of abuse and their main metabolites using pressurized liquid extraction and liquid chromatography-tandem mass spectrometry. *Talanta*, 125:65-71.
- Arvaniti OS, Stasinakis AS. 2015. Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. *Science of the Total Environment*, 524: 81-92.
- Asimakopoulos AG, Ajibola A, Kannan K, Thomaidis NS. 2013. Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece. *Sci Total Environ.*, 452-453: 163-171.
- Bailey, HC, Krassoi, R, Elphick, JR, Mulhall, AM, Hunt, P, Tedmanson, L, Lovell, A, Whole effluent toxicity of sewage treatment plants in the Hawkesbury-Nepean watershed, New South Wales, Australia, to *Ceriodaphnia dubia* and *Selenastrum capricornutum*, *Environmental Toxicology and Chemistry*, 19: 72-81.
- Barton LE, Auffan M, Durenkamp M, McGrath S, Bottero JY, Wiesner MR. 2015. Monte Carlo simulations of the transformation and removal of Ag, TiO<sub>2</sub>, and ZnO nanoparticles in wastewater treatment and land application of biosolids. *Science of the Total Environment*, 511: 535-543.
- Batley GE, Kirby JK, McLaughlin MJ. 2013. Fate and risks of nanomaterials in aquatic and terrestrial environments. *Accounts of Chemical Research*, 46: 854-862.
- Bennie DT, Sullivan CA, Lee H, Maguire RJ. 1998. Alkylphenol polyethoxylate metabolites in Canadian sewage treatment plant waste streams. *Water Quality Research Journal of Canada*, 33: 231-252.
- Besse JP, Kausch Barreto C, Garric J. 2008. Exposure assessment of pharmaceuticals and their metabolites in the aquatic environment: Application to the French situation and preliminary prioritization. *Journal of Human and Ecological Risk Assessment*. 14:665-695.
- Bester K. 2005. Comparison of TCPP concentrations in sludge and wastewater in a typical German sewage treatment plant—comparison of sewage sludge from 20 plants. *J. Environ. Monit.*, 7: 509-513.
- Braga O, Smythe GA, Schafer AI, Feitz AJ. 2005. Fate of steroid estrogens in Australian inland and coastal wastewater treatment plants. *Environ. Sci. Technol.*, 39:3351-3358.
- Bright DA, Healey N. 2003. Contaminant risks from biosolids land application: Contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia. *Environmental Pollution* 126: 39–49.
- Browne MA, Dissanayake A, Galloway TS, Lowe DM, Thompson RC. 2008. Ingested Microscopic Plastic Translocates to the Circulatory System of the Mussel, *Mytilus edulis* (L.) *Environmental Science & Technology*, 42, 5026–5031.
- Carr SA, Liu J, Tesoro AG. 2016. Transport and fate of microplastic particles in wastewater treatment plants. *Water Research*, 15: 174–182.
- CCME (Canadian Council of Ministers of the Environment). 2010. A Review of the Current Canadian Legislative Framework for Wastewater Biosolids. PN 1446.
- CEC (Commission of the European Communities). 1986. Council directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Official Journal of the European Communities*, Directive 86/278/EEC, No L 181/6-12.
- Chander K, Brookes PC. 1993. Residual effects of zinc, copper and nickel in sewage sludge on microbial biomass in a sandy loam. *Soil Biology and Biochemistry*, 25: 1231-1239.

- Chen Y, Yu G, Cao Q, Zhang H, Lin Q, Hong Y. 2013. Occurrence and environmental implications of pharmaceuticals in Chinese municipal sewage sludge. *Chemosphere*. 93:1765-1772.
- Clark JR, Cole M, Lindeque PK, Fileman E, Blackford J, Lewis C, Lenton TM, Galloway TS. 2016. Marine microplastic debris: a targeted plan for understanding and quantifying interactions with marine life. *The Ecological Society of America*. 14: 317–324.
- Clarke B, Porter N, Symons R, Blackbeard J, Ades P, Marriott P. 2008. Dioxin-like compounds in Australian sewage sludge-review and national survey *Chemosphere*, 72:1215-1228.
- Clarke BO, Porter NA, Symons RK, Marriott PJ, Stevenson GJ, Blackbeard JR. 2010a. Investigating the distribution of polybrominated diphenyl ethers through an Australian wastewater treatment plant, *Sci. Total Environ.*, 408:1604-1611.
- Clarke BO, Porter, NA, Marriott, PJ, Blackbeard, JR. 2010b. Investigating the levels and trends of organochlorine pesticides and polychlorinated biphenyl in sewage sludge, *Environment International*, 36: 323-329.
- Clarke BO, Smith SR. 2011. Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environment International* 37:226-247.
- Cooper JL. 2005. The effect of biosolids on cereals in central New South Wales, Australia. 2. Soil levels and plant uptake of heavy metals and pesticides, *Australian Journal of Experimental Agriculture*, 45: 445-451.
- Darvodelsky P. 2012. Biosolids Snapshot. Department of Sustainability, Environment, Water, Population and Communities. ACT, Australia.
- Davis EF, Klosterhaus SL, Stapleton HM. 2012. Measurement of flame retardants and triclosan in municipal sewage sludge and biosolids. *Environ Int.*, 40:1-7.
- DEC (Department of Environment and Conservation). 2012. Western Australian guidelines for biosolids management. Department of Environment and Conservation. Perth, Western Australia. 91pp.
- Diaz-Cruz MS, Barcelo D. 2006. Highly selective sample preparation and gas chromatographic-mass spectrometric analysis of chlorpyrifos, diazinon and their major metabolites in sludge and sludge-fertilized agricultural soils. *J. Chromatography*, 1132: 21-27.
- Di Francesco AM, Chiu PC, Standley LJ, Allen HE, Salvito DT. 2004. Dissipation of fragrance materials in sludge-amended soils. *Environ Sci Technol.*, 38:194-201.
- DoE (Department of the Environment). 1989. Code of practice for agricultural use of sewage sludge. HMSO. London.
- Doolette CL, McLaughlin MJ, Kirby JK, Batstone DJ, Harris HH, Ge HQ, Cornelis G. 2013. Transformation of PVP coated silver nanoparticles in a simulated wastewater treatment process and the effect on microbial communities. *Chemistry Central Journal*, 7.
- Durenkamp M, Pawlett M, Ritz K, JHarris JA, Neal AL, McGrath SP. 2016. Nanoparticles within WWTP sludges have minimal impact on leachate quality and soil microbial community structure and function. *Environmental Pollution*, 211: 399-405.
- Donner E, Scheckel K, Sekine R, Popelka-Filcoff RS, Bennett JW, Brunetti G, Naidu R, McGrath SP, Lombi E. 2015. Non-labile silver species in biosolids remain stable throughout 50 years of weathering and ageing. *Environmental Pollution*, 205: 78-86.
- ECHA. 2014. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB assessment Version 2.0 November 2014. Helsinki, Finland.
- ECHA. 2016. Guidance on information requirements and Chemical Safety Assessment. Chapter R.16: Environmental exposure assessment. Version 3.0 February 2016. Helsinki Finland.
- Environment Agency. 2003. Risk Assessment. BIS(PENTABROMOPHENYL) ETHER. Performed under the Existing Substances Regulations. Pp26.
- Environment Agency. 2008. Guidance on the use of soil screening values in ecological risk assessment. Science Report SC070009/SR2b. Environment Agency, Bristol, UK.

- Environment Agency. 2009. Assessment of MBT input and output quality. Report: SC030144/R4. Environment Agency, Bristol, UK.
- Environment Agency. 2016. Derivation and Use of Soil Screening Values for Assessing Ecological Risks. Report – ShARE id26. Environment Agency, Bristol, UK.
- Fick J, Lindberg RH, Kaj L, Brorström-Lundén E. 2011. Results from the Swedish National Screening Programme 2010 Subreport 3: Pharmaceuticals. IVL Swedish Environmental Research Institute.
- Gallen C, Drage D, Kaserzon S, Baduel C, Gallen M, Banks A, Broomhall S, Mueller JF. 2016. Occurrence and distribution of brominated flame retardants and perfluoroalkyl substances in Australian landfill leachate and biosolids. *J. Haz. Mats.*, 312: 55-64.
- Gorga M, Martínez E, Ginebreda A, Eljarrat E, Barceló D. 2013. Determination of PBDEs, HBB, PBEB, DBDPE, HBCD, TBBPA and related compounds in sewage sludge from Catalonia (Spain). *Sci Total Environ.*, 444:51-59.
- Graham ER, Thompson JT. 2009. Deposit- and suspension-feeding sea cucumbers (Echinodermata) ingest plastic fragments. *Journal of Experimental Marine Biology and Ecology*, 368: 22–29.
- Gu L, Li Q, Quan X, Cen Y, Jiang X. 2014. Comparison of nanosilver removal by flocculent and granular sludge and short- and long-term inhibition impacts. *Water Res.*, 58:62-70.
- Hale RC, La Guardia MJ, Harvey E, Chen D, Mainor TM, Luellen DR, Hundal LS. 2012. Polybrominated diphenyl ethers in U.S. sewage sludges and biosolids: temporal and geographical trends and uptake by corn following land application. *Environ Sci Technol.*, 46:2055-2063.
- Hedberg J, Baresel C, Wallinder IO. 2014. Transport and fate of silver as polymer-stabilised nanoparticles and ions in a pilot wastewater treatment plant, followed by sludge digestion and disposal of sludge/soil mixtures: A case study. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering*, 49: 1416-1424.
- Heemsbergen DA, Warne MS, Broos K, Bell M, Nash D, McLaughlin M, Whatmuff M, Barry G, Pritchard D, Penney N. 2009. Application of phytotoxicity data to a new Australian soil quality guideline framework for biosolids, *Sci. Total Environ.*, 1407: 2546-256.
- Heidler J, Sapkota A, Halden RU. 2006. Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment. *Environ Sci Technol.*, 40:3634-3639.
- Holmes M, Kumar A, Shareef, A, Doan H, Stuetz R, Kookana R. 2010. Fate of indicator endocrine disrupting chemicals in sewage during treatment and polishing for non-potable reuse. *Water Science and Technology*, 62: 1416-1423.
- INERIS. 2011. Chlordane. Fiche de données toxicologiques et environnementales des substances chimiques. DRC-11-117259-10253A. Version N°2 - Septembre 2011. INERIS, Paris, France.
- ISO (International Organisation for Standardisation). 2008. Water quality - Sampling: Part 20: Guidance on the use of sampling data for decision making -Compliance with thresholds and classification. International Organization for Standardization. ISO 5667-20:2008(E). Switzerland.
- JRC (Joint Research Centre) 2012. Occurrence and levels of selected compounds in European Sewage Sludge Samples: Results of a Pan-European Screening Exercise (FATE SEES). Report EUR 25598 EN. JRC, Ispra, Italy.
- Ju JH, Lee IS, Sim WJ, Eun H, Oh JE. 2009. Analysis and evaluation of chlorinated persistent organic compounds and PAHs in sludge in Korea. *Chemosphere*, 74:441-447.
- Johnson AC, Jurgens MD, Lawlor AJ, Cisowska I, Williams RJ. 2014. Particulate and colloidal silver in sewage effluent and sludge discharged from British wastewater treatment plants. *Chemosphere*, 112: 49-55.
- Jürgens MD, Johnson AC, Lawlor AJ, Thacker SA, Williams RJ, Pereira MG, Barnett CL, Beresford NA. 2014. Assessment of current exposure of the British natural environment to silver (CB0464). Silver in sewage sludge, soil and river bed-sediments. Defra, London. 32pp.

- Kaegi R, Voegelin A, Ort C, Sinnet B, Thalmann B, Krismer J, Hagendorfer H, Elumelu M, Mueller E. 2013. Fate and transformation of silver nanoparticles in urban wastewater systems. *Water Research*, 47: 3866-3877 Sp. Iss.
- Kester GB, Brobst RB, Carpenter A, Chaney RL, Rubin AB, Schoof RA, Taylor DS. 2005. Risk characterization, assessment, and management of organic pollutants in beneficially used residual products. *Journal of Environmental Quality* 34:80-90.
- Kohli J, Lee HB, Peart TE. 2006. Organic contaminants in Canadian municipal sewage sludge. Part II. Persistent chlorinated compounds and polycyclic aromatic hydrocarbons. *Water Quality Research Journal of Canada*, 41: 47-55.
- Kupper T, Berset JD, Etter-Holzer R, Furrer R, Tarradellas J. 2004. Concentrations and specific loads of polycyclic musks in sewage sludge originating from a monitoring network in Switzerland. *Chemosphere*, 54:1111-1120.
- Langdon KA, Warne MS, Smernik RJ, Shareef A, Kookana RS. 2011. Selected personal care products and endocrine disruptors in biosolids: An Australia-wide survey. *Science of the Total Environment* 409:1075-81.
- Langdon K, McLaughlin MJ, Jason K, Merrington G. 2014. The effect of soil properties on the toxicity of silver to the soil nitrification process. *Environmental Toxicology and Chemistry*, 33: 1170-1178.
- Lee S, Song GJ, Kannan K, Moon HB. 2014. Occurrence of PBDEs and other alternative brominated flame retardants in sludge from wastewater treatment plants in Korea. *Sci Total Environ*, 470-471:1422-9.
- Leusch FD, Chapman HF, Korner W, Gooneratne SR, Tremblay LA. 2005. Efficacy of an advanced sewage treatment plant in southeast Queensland, Australia, to remove estrogenic chemicals. *Environ. Sci. Technol.*, 39:5781-5786.
- Liao C, Lee S, Moon HB, Yamashita N, Kannan K. 2013. Parabens in sediment and sewage sludge from the United States, Japan, and Korea: spatial distribution and temporal trends. *Environ Sci Technol*, 47:10895-10902.
- Liu YS, Ying GG, Shareef A, Kookana RS. 2012. Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant, *Environ. Pollut.*, 165:225-232.
- Lottermoser BG. 1994. Gold and platinum in sewage sludges. *Int. J. Environ. Studies*, 46: 167-171.
- Ma R, Levard C, Judy JD, Unrine JM, Durenkamp M, Martin B, Jefferson B, Lowry GV. 2013. Fate of zinc oxide and silver nanoparticles in a pilot wastewater treatment plant and in processed biosolids. *Environmental Science and Technology*, 48: 104-112.
- Matthiessen P, Sumpter JP. 1998. Effects of estrogenic substances in the aquatic environment. Chapter in *Fish Ecotoxicology*, Volume 86 of the series EXS. Springer, Basel. pp 319-335.
- McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL. 2000. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research*, 38: 1037-1086.
- Navarro DA, Kirby JK, McLaughlin MJ, Waddington L, Kookana RS. 2014. Remobilisation of silver and silver sulphide nanoparticles in soils. *Environ. Pollut.*, 193:102-110.
- NEPM (National Environment Protection (Assessment of Site Contamination) Measure). 2011. Schedule B1. Guideline on Investigation Levels For Soil and Groundwater. Draft for Consultation. National Environment Protection Council, ACT, Australia.
- Nieto A, Borrull F, Pocurull E, Marcé RM. 2010. Occurrence of pharmaceuticals and hormones in sewage sludge. *Environ Toxicol Chem.*, 29: 1484-1489.
- NSW EPA (Environmental Protection Authority New South Wales). 1997. Environmental guidelines: use and disposal of biosolids products. Sydney, Australia.
- Oliver IW, McLaughlin MJ, Merrington G. 2005. Temporal trends of total and potentially available element concentrations in sewage biosolids: a comparison of biosolid surveys conducted 18 years apart. *Sci. Total Environ*, 337: 139-45.



- Peters A, Simpson P, Merrington G, Rothenbacher K, Sturdy L. 2011 Occurrence and concentration of dissolved silver in rivers in England and Wales. *Bulletin of Environmental Contamination and Toxicology* 86: 637-647.
- Ricklund N, Kierkegaard A, McLachlan MS. 2008. An international survey of decabromodiphenyl ethane (deBDethane) and decabromodiphenyl ether (decaBDE) in sewage sludge samples. *Chemosphere*, 73:1799-1804.
- RIVM. 2008a. Risk Assessment. 1,3,4,6,7,8-HEXAHYDRO-4,6,6,7,8,8-HEXAMETHYLCYCLOPENTA-γ-2-BENZOPYRAN, (1,3,4,6,7,8-HEXAHYDRO-4,6,6,7,8,8-HEXAMETHYLIN-DENO[5,6-C]PYRAN - HHCB). Performed under the Existing Substances Regulations. Pp251.
- RIVM. 2008b. Risk Assessment. 1-(5,6,7,8-TETRAHYDRO-3,5,5,6,8,8-HEXAMETHYL-2-NAPHTHYL)ETHAN-1-ONE (AHTN). Performed under the Existing Substances Regulations. Pp259.
- Stasinakis AS, Thomaidis NS, Arvaniti OS, Asimakopoulos AG, Samaras VG, Ajibola A, Mamais D, Lekkas TD. 2013. Fate of selected pharmaceuticals and synthetic endocrine disrupting compounds during wastewater treatment and sludge anaerobic digestion. *J Hazard Mater.*, 244-245:259-267.
- Stutt E, Wilson I, Merrington G, Rothenbacher K. 2016. Determining the removal of platinum group metals in industrial effluent during sewage treatment. Poster Presented at SETAC Nantes, May 2016.
- Sweden Chemicals Agency. 2008. Risk Assessment. Hexabromocyclododecane. Performed under the Existing Substances Regulations. Pp507
- Talvitie J, Heinonen M. 2014. Preliminary study on synthetic microfibers and particles at a municipal waste water treatment plant. HELCOM 2014, BASE project 2012-2014.
- Tan BL, Hawker DW, Müller JF, Leusch FD, Tremblay LA, Chapman HF. 2007. Modelling of the fate of selected endocrine disruptors in a municipal wastewater treatment plant in South East Queensland, Australia. *Chemosphere*, 69: 644-654.
- ter Laak T, van der Aa M, Houtman C, Stoks P, van Wezel A. 2010. Temporal and spatial trends of pharmaceuticals in the Rhine. RIWA. RIWA-Rhine, The Netherlands.
- UKWIR. 2014. Risk Based Prioritisation of Pharmaceuticals. UKWIR. ISBN: 1 84057 735 5, London, UK.
- USEPA. 2009. Targeted National Sewage Sludge Survey Statistical Analysis Report 2009. [http://water.epa.gov/scitech/wastetech/biosolids/upload/2009\\_04\\_23\\_biosolids\\_tnsss-overview.pdf](http://water.epa.gov/scitech/wastetech/biosolids/upload/2009_04_23_biosolids_tnsss-overview.pdf).
- Venkatesan AK, Halden RU. 2013a. National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. *J Hazard Mater.*, 252-253:413-418.
- Venkatesan AK, Halden RU. 2013b. National inventory of alkylphenol ethoxylate compounds in U.S. sewage sludges and chemical fate in outdoor soil mesocosms. *Environ Pollut.*, 174: 189-193.
- Venkatesan AK, Pycke BF, Halden RU. 2014. Detection and occurrence of N-nitrosamines in archived biosolids from the targeted national sewage sludge survey of the U.S. Environmental Protection Agency. *Environ Sci Technol.*, 48: 5085-5092.
- Webber MD, Goodin JD, Fowlie PJA, Hong-You RL, Legault J. 1996. Persistence of volatile organic compounds in sludge treated soils. *Water quality research journal of Canada*, 32: 579-597
- Ying GG, Kookana RS. 2007. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants, *Environ Int.*, 33:199-205.
- Ying GG, Kookana RS, Kolpin DW. 2009. Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies, *J Environ Monit.*, 11:1498-1505.
- Zuloaga O, Navarro P, Bizkarguenaga E, Iparraguirre A, Vallejo A, Olivares M, Prieto A. 2012. Overview of extraction, clean-up and detection techniques for the determination of organic pollutants in sewage sludge: A review. *Analytica Chimica Acta* 736: 7– 29.

## APPENDICES – Excel Sheets



Microsoft Excel  
97-2003 Worksheet

*Risk/Hazard Assessment 1*



Microsoft Excel  
97-2003 Worksheet

*Literature survey 1*