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Dioxin-like Compounds in Australian Sewage Sludge –

Literature Review and National Survey

Bradley Clarke^{1,2*}, Robert Symons³, Philip Marriott¹, Judy Blackbeard², Peter
Ades⁴, Nichola Porter^{1,2}

¹School of Applied Sciences, RMIT University, Melbourne, Victoria, Australia

²Co-operative Research Centre for Water Quality and Treatment – Wastewater
Program, Melbourne, Victoria, Australia

³National Measurement Institute, Sydney, NSW, Australia

⁴School of Forest and Ecosystem Science, University of Melbourne, Parkville,
Victoria, Australia

*Corresponding Author

RMIT University

School of Applied Science (Bld 3 Level 1)

Fax +61 9 9925 3747

Phone +61 9 9925 2117

bradley.clarke@student.rmit.edu.au

Keywords

Sewage sludge; dioxins, furans; persistent organic pollutants; biosolids

23   ***Abstract***

24   An Australian survey of dioxin-like compounds in sewage sludge was conducted in
25   two parts (a) a national survey, and (b) a time-study. All sewage sludge samples
26   analysed as part of these studies had low overall concentrations of dioxin-like
27   compounds. Out of thirty-seven samples, all except one, were within the reported
28   concentration range of soil within the Australian environment; 0.05 – 23 WHO₉₈ TEQ
29   ng kg⁻¹ (Muller et al., 2004). The mean concentration of dioxin-like compounds in
30   the Australian sewage sludge survey of 2006 was found to be 5.6 (s.d. 4.5) WHO₀₅
31   TEQ ng kg⁻¹ (n=14) and were within the range of 1.2 to 15.3 WHO₀₅ TEQ ng kg⁻¹.
32   All the Australian sewage sludge samples cited in these studies were below the
33   Victorian EPA “investigation limit” of 50 WHO₉₈ TEQ ng kg⁻¹, well below the
34   European proposed guidelines of 100 WHO₉₈ TEQ ng kg⁻¹, and also below the most
35   stringent guidelines internationally i.e. Canada’s 27 I-TEQ ng kg⁻¹. The burden of
36   dioxin-like compounds in Australian sewage sludge is low and its land application as
37   biosolids is not likely to pose a problem.

38   A general positive relationship was found between population of the town producing
39   the waste and both dioxin-like PCDD/Fs and dioxin-like PCBs. The one exception to
40   this trend was sludge from a town that had a history of smelting that had a relatively
41   high burden of dioxin-like compounds. Sludge from a rural WWTP also had a higher
42   burden of dioxin-like compounds. The treatment plant services a geographically
43   isolated town with a low population and no known emitters of dioxin-like compounds.
44   However, this sample also had a relatively high burden of dioxin-like PCBs, which
45   could be the source of the dioxin-like PCDD/Fs found in this sludge. The time study
46   showed analyzing sludges from three WWTP from the same city between the years
47   2002 and 2006 found no apparent difference between WWTPs but a statistically

48 significant decline of 1.49 WHO₀₅ TEQ ng kg⁻¹ per year. Also, a comprehensive
49 review of the scientific literature, presents typical levels and sources of dioxin-like
50 compounds in international sewage sludges.

51

1. Introduction

Sewage sludge is a useful fertilizer and has many components that can contribute positively to soil health but it can be contaminated with organic pollutants making it unsuitable for land application. One such class of organic pollutants, often referred to as ‘dioxin-like compounds’, includes the twenty-nine most toxic dioxin-like congeners as defined by the World Health Organization (WHO); seven polychlorinated dibenzo-p-dioxins (PCDDs), ten polychlorinated dibenzofurans (PCDFs) and the twelve co-planar “dioxin-like” polychlorinated biphenyls (PCBs) (Van den Berg et al., 2006). Here we present a review of the scientific literature related to dioxin-like compounds in sewage sludge followed by the results of an investigation into dioxin-like compounds within Australian sewage sludge. This investigation was completed in two parts: (1) an Australian survey of dioxin-like compounds in sewage sludge completed in 2006 and (2) an analysis of the concentration of dioxin-like compounds in sewage sludge from three wastewater treatment plants (WWTPs) between the years 2002 and 2006.

The concentration of dioxin-like compounds is reported using Toxicity Equivalency (TEQ) which assigns Toxicity Equivalency Factors (TEFs) to each congener relative to the most toxic congener 2,3,7,8-TCDD (assigned a value of 1), and summing the products to gain a single comparable value. There have been a number of systems, including the International TEQ (I-TEQ) which was largely developed by the United States Environmental Protection Agency (U.S. EPA) (Kutz et al., 1990). The World Health Organization modified that system in 1998 (WHO₉₈ TEQ) by incorporating “dioxin-like” PCBs and this system was updated in 2005 and published in 2006 (WHO₀₅ TEQ) (Van den Berg et al., 1998; Van den Berg et al., 2006). Changes to the TEQ scheme by WHO are relatively few but can make a significant difference to the

77 overall TEQ, particularly with soils and sludges. This is most evident for sewage
78 sludge samples which are high in OCDD, a compound whose TEF was reduced by a
79 factor of ten in formulating WHO₉₈ TEQ factors.

80 While much work has been done on dioxin-like compounds in the Australian
81 environment (DEH, 2005), little work has been completed on dioxin-like
82 concentrations in sludge. Consequently there is little in the form of guidelines for
83 regulating acceptable concentration of dioxin-like compounds in sludge for land
84 application from either the State or Commonwealth regulatory authorities (NRMMC,
85 2004). In 2004, the Victorian Environment Protection Authority (EPA Victoria)
86 proposed an “investigation limit” of 50 WHO₉₈ TEQ ng kg⁻¹ d.w. in their “Biosolids
87 Land Application” guidelines but does not require that testing be conducted
88 automatically (EPA Victoria, 2004). To date there are no other regulatory agencies
89 within Australia that require monitoring of dioxin-like compounds in sludge.

90 Internationally there are varying guidelines for the safe use of sludge. The U.S. EPA
91 had proposed amending management standards by adding a numeric concentration
92 limit of 300 I-TEQ ng kg⁻¹ for dioxin-like compounds in land-applied sewage sludge
93 (Alvarado et al., 2001). However, in 2003, the U.S. EPA stated that “numerical
94 limitations nor requirements for management practices are currently needed to protect
95 human health and the environment from reasonably anticipated adverse effects from
96 dioxin-like compounds and dioxin-like compounds in land applied sewage sludge”
97 (U.S. EPA, 2003). In Canada, levels have been set for dioxin-like compounds in
98 sludge applied to agricultural land on both a restricted and unrestricted basis of 100 I-
99 TEQ ng kg⁻¹ and 27 I-TEQ ng kg⁻¹, respectively. The European Union initially
100 recommended a limit of 100 I-TEQ ng kg⁻¹ for member countries in the third draft of
101 the Working document on sludge which was later recanted (European Union, 2001).

However Germany and Austria did set a maximum limit of 100 I-TEQ ng kg⁻¹ in conjunction with maximum sludge application rates (European Commission, 2001). Regardless of whether or not sewage sludge is used as a fertilizer, it is important to monitor sewage sludge for chemical pollutants as the purpose of wastewater treatment is to contain and prevent pollutants from being re-released into the environment. In addition, sewage sludge is an important sink that can lead to the concentration of these Persistent Organic Pollutants (POPs). As Jensen noted “If sludge had been analysed earlier, PCB might have been discovered [accumulating in the environment] as the result of a systematic search instead of by accident” (Jensen, 1972).

2.1 Historical Levels of Dioxin-like Compounds in Sewage Sludge

Research investigating dioxin-like compounds in sewage sludge has been completed in the U.S.A, Germany, Sweden, England, Spain, Switzerland and more recently, China. In Australia, almost no research has been carried out on the levels of dioxin-like compounds in sewage sludge. Research into dioxin-like compounds is continually evolving with respect to trends, methods and knowledge that can cause difficulties when comparing results. An unfortunate trend has been the omission of raw data (such as isomer and homologue concentrations) due to the summarizing of data to the standards of the day, but these have changed over the last thirty years. The evolution of the three main TEQ systems can make the updating of old literature and its comparison with modern data difficult, particularly if authors only presented TEQ values.

The most basic assumptions about dioxin-like compounds in the environment are that they are anthropogenically produced and released into the environment (IPCS, 1989). Also during the WWTP process, dioxin-like compounds partition almost exclusively

into sewage sludge organic fraction as they are highly lipophilic i.e. K_{OWS} of 4.26 to 12.26 (IPCS, 1989). All results presented in the following discussion are on a dry weight (d.w.) basis unless otherwise stated.

PCDD/Fs levels in sewage sludge were first reported in 1984 by Lamparski et al. who analysed two contemporary (1981, 1982) and one archived sample (1933). Somewhat surprisingly, Lamparski et al. reported similar levels of PCDD/PCDFs in the modern and archived samples, all containing $\sim 60\,000\text{ ng kg}^{-1}$ OCDD (Lamparski et al., 1984). There was an increase in the concentration of 2,3,7,8-TCDD from 2.2 in 1933 to 16 ng kg^{-1} in 1982. In 1985 Weerasinghe et al. reported PCDD/F levels in two New York State sewage sludge samples: one urban and one rural. They found that the urban sludge contained approximately seven times more HxCDD, HpCDD and OCDD than the rural sludge. The OCDD concentrations were $60\,000$ urban and $7\,600$ OCDD ng kg^{-1} d.w. in the rural sludge.

Hagenmaier et al. (1986) were the first to publish the results of contaminated sludges, which be unsuitable for land application, reporting concentrations of 60 to 370 ng kg^{-1} 2,3,7,8-TCDD and up to $200,000\text{ ng kg}^{-1}$ OCDD. In 1989, Rappe et al. monitored the concentration of PCDD/Fs through a WWTP in a highly industrialized area and a WWTP in a rural area, finding similar levels and congener profiles in both (Rappe et al., 1989). In 1988 and 1989, the U.S. EPA conducted the “National Sewage Sludge Survey” of 181 publicly owned treatment works (POTWs) in the United States of America (USA). While the raw data are available, no report with a discussion of results was completed by the U.S. EPA. However, in 1990 Telliard et al. reported selected data from this survey. The data were presented on a wet weight basis without TEQ values, resulting in their data being unsuitable for comparison with other work (Telliard et al., 1990). Nevertheless, they found a positive association between

PCDD/F levels and organic matter (or suspended solids), which supports the theory that dioxin-like compounds will partition almost exclusively onto the organic matter in sludge in preference to water.

In 1994 Rappe et al. continued work into PCDD/F levels in sewage sludge. They reported the results of 30 sewage sludge samples from Switzerland finding that the concentration ranged from 6 to 4100 I-TEQ ng kg⁻¹ (Rappe et al., 1994). Rappe et al. reported the most serious incidences of sewage sludge contamination to that point in time of 1100, 1900, 4100 and 1700 I-TEQ ng kg⁻¹. Rappe et al. followed up this work in 1997 and analyzed samples from the same WWTPs finding that in “eight out of ten samples the PCDD/Fs concentration shows a more or less pronounced decrease” (Rappe et al., 1997).

Sewart et al. (1995) reported the concentration of 12 digested U.K. sludges finding ‘minimal’ contamination; 1 - 3.8 2,3,7,8-TCDD ng kg⁻¹, 650 - 63000 OCDD ng kg⁻¹ and 19 - 206 I-TEQ ng kg⁻¹. The work went further analyzing archived samples from the years 1940 to 1960. The results show an increase in PCDD/Fs in sludge from 1942 (OCDD 1000 ng kg⁻¹) peaking in the mid-1950s (OCDD 170000 ng kg⁻¹) before beginning to decrease to the average 1992 concentration of 12000 OCDD ng kg⁻¹. This is a good example of the effect that the change in TEF weighting can have on reported and perceived PCDD/F burden i.e. 170000 OCDD ng kg⁻¹ is equivalent to 170 I-TEQ ng kg⁻¹ and 17 WHO₉₈ TEQ ng kg⁻¹.

Following on from their earlier work and the U.S. EPA’s earlier national survey, Rappe et al. (1998) reported that the levels of dioxin-like compounds in U.S.A. and Swedish sludge samples had, in general, decreased by 35-50% except at sites that had “historical contamination” (Rappe et al., 1998). This finding was supported by the work of Alvarado et al. (2001) who reported that dioxin-like compounds in U.S.A.

sludges had decreased from an average of 60.5 to 41.1 WHO₉₈ TEQ ng kg⁻¹ between the years 1994 2001, or approximately 32% (Alvarado et al., 2001).

In 1998, Rappe et al. found serious contamination in two sludges from the U.S.A.; I-TEQ of 1270 and 1240 ng kg⁻¹. The concentration of 480,000 OCDD ng kg⁻¹ as reported by Rappe et al. translates to 480 I-TEQ ng kg⁻¹ and 48 WHO₉₈ TEQ ng kg⁻¹. The latest work to be published on the levels of dioxin-like compounds in sludge is by Dai et al. from China. The concentration of dioxin-like compounds reported were low; 2,3,7,8-TCDD <d.l. (n=5) – 7.61 ng kg⁻¹, 34.90 – 828.78 OCDD ng kg⁻¹, 3.47 – 88.24 I-TEQ ng kg⁻¹ (Dai et al., 2007). A summary of literature data is presented in Table 1, including 2,3,7,8-TCDD, OCDD and TEQ concentrations.

In summary, the concentration of dioxin-like compounds has generally declined since measurements and monitoring programs began (1984). There have been incidents of seriously contaminated sludges reported in Germany and U.S.A. with OCDD concentrations exceeding 200,000 ng kg⁻¹ and correspondingly high TEQ values. However, these high levels of contamination are not common and have been associated with a known source. There appears to be a difference in the burden of dioxin-like compounds between rural (~1,000-10,000 OCDD ng kg⁻¹) and urban (60,000 OCDD ng kg⁻¹) sources.

2.2 Sources of Dioxin-Like compounds in Sewage Sludge

The main sources of dioxin-like compounds can be grouped under the headings industrial effluents; surface run-off (including atmospheric deposition); household wastewater; and formation within treatment works. The most common assumption is that dioxin-like compounds are produced as by-products of chlorinated chemical production and combustion processes. However, the sources of dioxin-like

compounds in the various sludges examined are not completely understood, although a wide range of sources have been identified which can explain the bulk of dioxin-like compounds found in sewage sludge. An effective strategy for identifying potential sources of dioxin-like compounds in both sewage sludge and the environment is through congener profiling which compares the ratio of individual PCDD/F congeners in environmental samples with known sources.

Lamparski et al. (1984) found that two contemporary sludges (1981, 1982) and an archived sludge (1933) contained similar concentration of OCDD (60,000 ng kg⁻¹). This result is surprising given that the industrial production of chlorinated chemicals such as PCP and PCBs was still in its infancy in the 1930s; therefore the dioxin-like compounds in the 1933 samples must have had another source. Not only is this the first paper in this area, but it contradicts the established theory of contamination which argues that dioxin-like compounds largely arise as by-products of chlorinated chemical production. Lamparski et al. hypothesized that PCDD/Fs may be formed *in-situ* as by-products of chlorination of wastewater (Lamparski et al., 1984). This suggestion of *in-situ* formation of PCDD/Fs has not received much follow up in terms of further experimental work by other researchers. Rivera et al. (1997) investigated PCDD/F formation resulting from the chlorination of potable water in a real and pilot water treatment plant, with and without pre-chlorination respectively. They found that “the results obtained did not reveal a marked influence of chlorination in the formation of PCDFs/PCDDs”. Interestingly, the concentration of higher chlorinated PCDDs (HpCDD and OCDD) was higher in the pilot WWTP where the treatment process did not include pre-chlorination (Rivera et al., 1997).

In 1985, Weerasinghe et al. (1985) found that an urban sludge contained about seven times more HxCDD, HpCDD and OCDD than rural sludge (60 000 OCDD ng kg⁻¹;

225 urban, 7 600 OCDD ng kg⁻¹ rural). Weerasinghe et al. (1985) associated these
226 increased PCDD/F levels with pentachlorophenol (PCP) use in wood
227 treatment/preservation in the urban area. This conclusion was supported by research
228 that compared the PCDD/F congener and homologue patterns of 43 German sludges
229 with those of stack emissions from waste incinerators and pentachlorophenol (PCP)
230 use, finding that the main sources of PCDD/F contamination in the sludges they
231 examined were from industrial use of PCP and sodium-pentachlorophenate
232 (Hagenmaier et al., 1986).

233 Tiernan et al. (1997) also found that the urban sludges contained significantly higher
234 concentrations of dioxin-like compounds than rural samples (70-98 % less, n =31).
235 Supporting this, Rappe et al. (1994) published the results of thirty sludge samples
236 finding that “in general the concentrations were found to be higher in the urban areas”
237 and that “the highest inputs could be correlated to local industrial sources”. Attention
238 was focused on the PCDD/F levels of relatively “uncontaminated” sludges. Based on
239 limited evidence, it was asserted that the PCDD/Fs “found in background samples of
240 sewage sludge are best explained by direct contamination by pentachlorophenol and
241 by secondary biological reactions in the sewer system” i.e. the formation of dioxin-
242 like compounds from chlorinated benzenes such as PCP (Rappe et al., 1994). Rappe
243 et al. do not discuss the hypothesis originally proposed by Lamparski et al. (1984),
244 that dioxin-like compounds are formed *in-situ* as a result of chlorination or some other
245 mechanism. The “de novo” formation of dioxin-like compounds *in-vitro* was reported
246 by Oberg et al. (1992) finding the biochemical transformation of eight different
247 chlorophenyls into OCDD (Oberg and Rappe, 1992). While it was recognized early
248 in this field that PCP use in both wood preservation and textiles was a significant

source of contamination, this work identified PCP not only as a primary source of contamination, but also as a secondary source (Oberg and Rappe, 1992).

Since humans are constantly exposed to dioxin-like compounds through their diet, it is possible that they excrete small amounts of dioxin-like compounds through faeces. However, two studies (Wendling et al., 1990; Rappe and Andersson, 1992) found that the levels of dioxin-like compounds in human faeces are extremely low (i.e. approximately 3.9 I-TEQ ng kg⁻¹) and therefore not likely to constitute a major input source of dioxin-like compounds in sludge. However, the congener profile of human faeces was similar to that of “uncontaminated” sludge, with the main congener present being OCDD and almost all the 2,3,7,8- substituted congeners being present (Rappe and Andersson, 1992). Rappe et al. reported a good correlation between the individual congeners found in these samples and in other samples, such as human fat. Rappe et al. argued that the known sources of dioxin-like compounds excreted by the human body cannot alone account for the levels of dioxin-like compounds found in sludge (Rappe and Andersson, 1992).

In 1992, Horstmann et al. published the first of a series of studies that attempted to identify the source of dioxin-like compounds in sewage sludge. The first experiment involved measuring urban particulates including street runoff and atmospheric deposition. They found that while urban runoff may contribute to dioxin-like compounds in sludge, it could not explain the bulk of dioxin-like compounds. In 1993, Horstmann et al. reported that household wastewater had been underestimated as a dioxin-like compound source relative to urban surface water run-off. They reported that the congener pattern in laundry wastewater was virtually identical to the pattern observed in sewage sludge (Horstmann et al., 1993). They also attempted to estimate the contribution of surface runoff to the PCDD/F flux. They measured

PCDD/F concentrations in primary sludge during periods of dry weather and directly after rain events, but found no significant difference. They went further and provided evidence that household waste-water contributed the majority (two to seven times) of the dioxin-like compounds found in sewage sludge compared to other sources. They concluded that grey water from the washing of contaminated clothing (i.e. PCP use in textiles) and subsequently human skin accounted for the majority of dioxin-like compounds found in German sludges (Horstmann and McLachlan, 1995). It is worth noting that countries such as Australia have separate systems to deal with storm-water and sewage, therefore contaminated storm water in Australia, and other country with separate stormwater systems, is a less likely contributor of dioxin-like compounds in sludge.

Research published in 1997 by Rivera et al. showed PCDD/F levels in sludge produced from a potable water treatment plant to be similar to those of sewage sludge (2,3,7,8-TCDD 3.7 ng kg^{-1} , OCDD $2447.0 \text{ ng kg}^{-1}$) (Rivera et al., 1997). The congener profiles of the membrane sludges corresponds well with sewage sludges and suggest a “common source of origin” (Rivera et al., 1997).

Studies have found that certain dioxin-like compounds can be formed through the WWTP process. Klimm et al. found a two-fold increase of OCDD and HpCDD from semi-anaerobic digestion over 192 days (Klimm et al., 1998). They also reported that no other PCDD/Fs were formed and that the formation of HpCDD and OCDD did not occur under strictly aerobic or anaerobic conditions.

In 2001, Stevens reported (UK sewage sludges) that “the homologue group pattern of the PCDD/Fs is dominated by the HpCDD and OCDD and is consistent with that found in most sewage sludges” and that “there appears to be no correlation between the degree of industrial input and the PCDD/F concentration (Stevens et al., 2001).

299 To summarize the conclusions of the above studies it appears that PCDD/F levels in
300 'highly contaminated' sewage sludge (i.e. unsuitable for land application) are
301 associated with industrial wastewater and chlorinated chemical production, in
302 particular, with the industrial use of PCP and sodium-pentachlorophenate. There is a
303 difference in the concentration of dioxin-like compounds between urban and rural
304 samples with no adequate explanation, apart from speculation about industrial inputs.
305 Various studies have shown that this link to industrial inputs is tenuous and the
306 dioxin-like contamination may arise from another source. Horstmann et al. (1993)
307 identified that household wastewater was a significant contributor to dioxin-like
308 compounds in sludge and attributed it to the use of PCP within the textile industry,
309 which is based on the finding that clothing contaminated with dioxin-like compounds
310 can account for the majority of dioxin-like compounds observed in sludge compared
311 to other sources. To date there has been no adequate explanation of the low burden of
312 dioxin-like compounds and its ubiquitous presence in sewage sludge (OCDD < 1000
313 ng kg⁻¹). There is limited evidence that dioxin-like compounds may be formed *in situ*
314 or some other unidentified pathway. The fact that PCDD/F were present in sludge at
315 similar levels in New York in 1933 and 1981 suggests the source of these compounds
316 had been introduced by this period in history, which could be related to
317 industrialisation or urbanisation (Lamparski et al., 1984). Other studies have also
318 reported dioxin-like compounds from archived samples and their origin, as yet, cannot
319 be explained (Muller et al., 2004).

320 In the light of this literature review we've undertaken a study to understand the typical
321 levels of dioxin-like compounds in Australian sewage sludge. The literature review
322 will allow us to place the results of this Australian sludge survey into an appropriate
323 context.

3. Methods

Two different studies of dioxin-like compounds in Australian sewage sludge were undertaken. They were investigations of (a) dioxin-like compounds in an Australian sewage sludge survey that was conducted in 2006 and (b) the levels of dioxin-like compounds measured at three WWTPs between the years 2002 and 2006.

All samples from both studies were analyzed at the National Measurement Institute in Sydney, Australia. The analysis was commissioned by various water utilities and the authors of this report. Sludge samples were extracted using accelerated solvent extraction (ASE) and the extracts were subsequently treated with concentrated sulfuric acid, treated for inorganic and organic sulfur by copper and silver nitrate clean-up techniques respectively and then chromatographically purified using a commercial automated clean-up procedure (PowerPrep™). Analyses were undertaken for PCDDs/PCDFs and dioxin-like PCBs using isotope dilution capillary gas chromatography-electron impact high-resolution mass spectrometry with monitoring of either M⁺, [M+2]⁺ or [M+4]⁺ ions. The analytical procedure was based upon standard U.S. EPA methodologies (U.S. EPA, 1994).

Instrument: GC HP 6890 coupled to Finnigan MAT 95XL HRMS. Regular analysis is performed with a Phenomenex ZB-5MS column (60m × 0.25mm × 0.25μm) and confirmation is performed using a J&W Dbdioxin column (60m × 0.25mm × 0.15μm). **Injector Temperature** 300°C (ZB-5MS) 270°C (DB-Dioxin) **Injection Volume** 1 μL splitless. **Carrier Gas** Helium, run under constant flow mode. **Temperature Program DB-5:** 100°C for 1min, ramp 40°C/min to 200°C, ramp 3.0°C/min to 235°C, hold for 10min, ramp 5.0°C/min to 310°C, hold for 9 min. **DB-Dioxin:** 120°C for 1min, ramp 50°C/min to 220°C, ramp 2.5°C/min to 270°C, hold for 35min. **Transfer Line** 280°C (DB-5) 250°C (DB-Dioxin) **MS Parameters** Ion

Source: 240°C, Filament Current: 0.7 mA, Electron Multiplier Voltage: Set to produce a gain of 10^6 . Resolution is checked at the beginning and end of each sequence to ensure that the final resolution is not less than 10,000.

3.1 Australian Sewage Sludge Survey 2006

An Australian survey of sewage sludge from operational WWTPs (n=14) was conducted. The fourteen samples were collected from each state (and the Northern Territory) of Australia during 2006 from both urban (population >1,000,000) and rural WWTPs (population < 300,000). The samples were collected in pre-cleaned amber glass jars with Teflon lined lids. The samples were collected by the various WWTP personal and sent via courier to the National Measurement Institute for analysis. Table 2 provides data on the population for each WWTP sampled and a description of the type of treatment process.

3.2 Dioxin-like compounds Variation with Time

Two sewage sludge samples were collected and analyzed for dioxin-like compounds from three WWTPs in Western Australia in the years 2002, 2003, 2005 and 2006. These samples were collected in pre-cleaned amber glass jars with Teflon lined lids. The samples were collected by the various WWTP personal and sent via courier to the laboratory. Table 3 lists the WWTPs from which sewage sludge were analyzed for dioxin-like compounds in the target years.

3.3 Statistical Analysis

Principle component analysis was performed to analyse the relationship among the dioxin-like compounds using the software package NTSYSpc version 2.20 (Exeter Software). The raw concentration data for each compound were standardised to mean zero and standard deviation and the PCA conducted on the correlation matrix. Values

below the detection limit were assumed to be zero for this analysis. Separate principal component analyses were conducted for all the dioxin-like compounds, the dioxin-like PCDD/Fs, and for the dioxin-like PCBs separately. The treatment plant scores for the first principal axis were then regressed on population to test for a relationship between that component and urban community size or urban versus rural sources. In the study of variation in dioxin-like compounds over time, covariance analysis was used to test whether there was a linear trend in TEQ over time and whether the relationship was different for the three WWTPs.

4. Results and Discussion

All sludge samples analysed have a low burden of dioxin-like compounds. TEQ results can be reported with (middle-bound) and without ‘half the detection limit’ (lower-bound). The detection limit is provided within the table of results but has not been used in calculation of the lower bound TEQs. The reproducibility of analysis and sampling methodology was tested by analysis of WWTP B sample in triplicate. The relative standard deviations ranged from 3 to 35% for the dioxin-like compounds and there was a 17% variation of the WHO₀₅ TEQ value calculated (15.3, 16.8 and 12.1 WHO₀₅ TEQ ng kg⁻¹).

4.1 Australian Sewage Sludge Survey 2006

The raw data of the Australian sewage sludge 2006 survey are presented within Table 4. Reported are the results of individual dioxin-like congeners. The toxicity equivalence (TEQ) has been calculated in all three major schemes (I-TEQ, WHO₉₈ TEQ and WHO₀₅ TEQ) as well as the TEQ contribution from the dioxin-like PCDD/Fs and the dioxin-like PCBs. The concentration of homologues has also been provided.

The lower bound sludge concentrations ranged between 1.2 and 16.8 WHO₀₅ TEQ ng kg⁻¹. Twelve of the fourteen samples had 2,3,7,8-TCDD less than the detection limit and the samples with measurable concentrations were 0.772 and 1.6 ng kg⁻¹. These results compare favourably with similar studies conducted in other countries, the proposed international and domestic guidelines, and the background levels of dioxin-like compounds in the Australian environment as discussed in the DEH's "National Dioxin Program" (Muller et al., 2004). In fact, the majority of samples had dioxin-like compounds within the range of soil levels in Australia; 0.05-23 WHO₉₈ TEQ ng kg⁻¹ d.w. middle-bound concentration (Muller et al., 2004). The soil samples also had a similar congener profile to that of sludges, which are dominated by OCDD (Muller et al., 2004).

There was a difference observed between mean congener concentration when comparing urban and rural samples. The mean concentration of all the 2,3,7,8-substituted congeners was lower for the rural samples compared to the urban samples and 5 of the highest 6 concentration were observed in urban sludges. While the urban mean may be skewed due to higher concentrations of dioxin-like compounds from WWTP A, these higher concentrations of dioxin-like compounds appear to be more typical of urban sludge concentrations (based upon the scientific literature). The WHO₀₅ TEQ was higher for the urban samples with 6.9 (s.d. 4.5) compared to 4.6 (s.d. 4.6) WHO₀₅ TEQ ng kg⁻¹.

A positive correlation between OCDD concentration and TEQ systems was found; I-TEQ R = 0.97, WHO₉₈ TEQ R = 0.70, WHO₀₅ TEQ R = 0.82. An extremely strong correlation (R=0.95) was found between the compounds OCDD and OCDF.

Principal component analysis was performed on (1) the dioxin-like PCDD/Fs, (2) the dioxin-like PCBs (Fig. 1a and 1b) and (3) all the dioxin-like compounds (Figure not

shown). For the dioxin-like PCDD/Fs the first three eigenvalues were 64.5%, 11.4% and 7.9% so the biplot (Fig. 1a) in the first two dimensions retains 76% of the total sum of squares of the original data and should provide a very good representation of the relationships between the compounds and the sampled WWTPs. All the dioxin-like compounds were found to be positively correlated to the first principal axis (PCA-I) and all contributed to a similar degree to variation in the two-dimensional space represented in the biplots (i.e. vectors of similar length). Inspection of the eigenvectors indicates that the first principal axis represents overall concentration of the dioxin-like PCDD/Fs while the second axis (PCA-II) is a contrast between OCDD/OCDF and 2378-TCDF/12378-PeCDD/123678-HxCDD/123789-HxCDD. WWTP A has the highest overall concentration of PCDD/Fs and WWTP A has relatively high OCDD/OCDF. Data for 2,3,7,8-TCDD were not included in this analysis as concentrations were below the detection threshold in most samples.

FIGURE 1 NEAR HERE

The PCA analysis of the dioxin-like PCBs (without PCB 169 as it was generally below the detection threshold) was even more strongly dominated by one dimension than that for the dioxin-like PCDD/Fs, with the first two eigenvalues being 83.8% and 7.7%. The biplot on the first two principal axes (Fig. 1b) retains 92% of the original variation. The first principal axis represents average concentration of the dioxin-like PCBs while the second principal axis represents differing composition, essentially a contrast between PCB81 (and to an extent PCB77) and the group of PCBs with PCB156, but variation along this axis is not very important relative to that on the first axis. The curved pattern of the WWTPs in the biplot indicates that their positions in the original space could be summarised even more effectively in only one dimension by a non-linear ordination technique such as non-metric multidimensional

scaling but this would not have shown the relationships among the dioxin-like PCBs as effectively.

The positions of the treatment plants are generally similar in both ordinations.

Unsupervised PCA also revealed clusters that appeared to coincide roughly to urban vs rural, with a few exceptions such as WWTP B that had a relatively high burden of dioxin-like compounds. WWTP B has a low population (142,000) and is in a region where previously there was a large smelting industry, which is a known source of dioxin-like compounds (IPCS, 1989). Another exception is WWTP N, which had a higher dioxin-like PCDD/F burden than expected and therefore also had a high PCAI score. WWTP N is in a geographically isolated area, has a very low population (14,000) and no known industrial emitters dioxin-like compound and its relatively high burdens are unexplained. However the dioxin-like PCBs PCAI score was also high for WWTP N, which may explain the higher burden of dioxin-like PCDD/Fs.

One possible explanation is that PCBs may have been inappropriately disposed of in the area causing elevated concentrations of dioxin-like PCDD/Fs as well as dioxin-like PCBs. A plot of PCAI vs population for the dioxin-like PCDD/Fs indicated a generally positive association with one unusual point, WWTP B (Fig. 2). If WWTP B is left out then the regression of PCAI on population size is highly statistically significant ($P < 0.01$). The trend line shown in Fig. 2a is the linear regression omitting point B. PCAI effectively summarises overall PCDD/F concentration so there is a general positive relationship between dioxin-like PCDD/F burden in sewage sludge and population. An equivalent graph of the PCBs PCAI against population indicated a weaker relationship (Fig. 2b). WWTP B was again an unusual point, having a much higher PCAI score than other plants in population centres of similar size, but WWTP N also had a very high score. If WWTP B is deleted from the

analysis there is a significant ($P=0.042$), positive regression and this trend line is shown in the Fig. 2b.

FIGURE 2 NEAR HERE

The burden of dioxin-like compounds increases with population, and this is likely to be related to urbanisation and not specifically population. This source of dioxin-like compounds in the urban environment must also have been present in 1933, given that similar levels have been detected in an archived sludge sample (Lamparski et al., 1984), as well as one archived Australian soil sample of the same period (Muller et al., 2004). The correlation of dioxin-like PCDD/Fs with dioxin-like PCBs suggests that these compounds are also being produced and emitted by the same, as yet, unidentified source. All the Australian sewage sludge samples cited in this study are below the Victorian EPA “investigation limit” of 50 WHO₉₈ TEQ ng kg⁻¹, well below the European proposed guidelines of 100 WHO₉₈ TEQ ng kg⁻¹, and also below the most stringent international guidelines e.g. the Canadian guideline of 27 WHO₉₈ TEQ ng kg⁻¹. The mean concentration of dioxin-like compounds in sewage sludge in this survey is 5.6 WHO₀₅ TEQ ng kg⁻¹.

4.2 Dioxin-like Compounds Variation with Time

In the study of Western Australian sludge samples there was little change in the concentration of dioxin-like compounds during the years 2002-2006. As found in other studies OCDD, OCDF and 1,2,3,4,6,7,8-HpCDD were the dominant congeners present. The concentration of dioxin-like compounds within this study ranged from 2.5 to 20.6 WHO₀₅ TEQ ng kg⁻¹. Generally speaking this is slightly higher than the national mean of 5.6 WHO₀₅ TEQ ng kg⁻¹. Table 5 presents the concentration of individual congeners and presents the concentration of each homologue.

Independent linear regressions of WHO₀₅ TEQ on year for each treatment plant, a single slope but independent intercepts, and a single overall regression were tested in an analysis of covariance. There was no evidence for differences in either slope or intercept among treatment plants but the single overall regression was highly significant ($P < 0.01$). On average WHO₀₅ TEQ declined by 1.49 ng kg⁻¹ each year. The data and the fitted regression line are shown in Figure 3. There was markedly more variation between samples in 2002 and 2005. There is a large variation in the WHO₀₅ TEQ in the years 2002 and 2005, particularly when compared to 2003 and 2006, which have very similar results (Fig. 3). This suggests that the flux of dioxin-like compounds in sewage sludge is associated with a random event (i.e. such as bushfires) rather than industrial. It is expected that industrial emitters of dioxin-like compounds would be consistent in their industrial processes and emissions.

FIGURE 3 NEAR HERE

4.3 General Discussion

There has been a variety of different systems for reporting the results of chlorinated dioxins and furans as well as the dioxin-like PCBs and this can make comparison of historical data difficult. One compound that has been routinely monitored and reported is OCDD, and it is suggested that this compound could be a marker for contamination to facilitate discussion and comparison of historical and contemporary data, even as TEQ systems continue to evolve. From our data set we have found a positive correlation between OCDD concentration and TEQ systems; I-TEQ $R = 0.97$, WHO₉₈ TEQ $R = 0.70$, WHO₀₅ TEQ $R = 0.82$. This correlation has also been identified by Fuentes et al who included the contribution of OCDF to predict the I-TEQ burden (Fuentes et al., 2007). In our data set all the dioxin-like PCDD/Fs and PCBs were positively correlated. In fact principle component analysis revealed that

that the total variation was mainly due to overall differences in overall load of dioxin-like compounds, with differences in relative concentrations of individual compounds contributing only a minor component to the overall variation between sludges. Effectively the variation in dioxin-like compounds in sewage sludge can be summarised in just a single dimension, i.e. the total concentration of dioxin-like compounds. Furthermore OCDD is a good choice of dioxin-like compound marker as its magnitude relative to other dioxin-like compounds means the variance in reported concentrations is far lower than other dioxin-like compounds with smaller magnitudes. Therefore, a crude classification of sewage sludge contamination based upon OCDD concentration is proposed (See Table 6). Equivalent I-TEQ have been calculated using $I\text{-TEQ ng kg}^{-1} = 0.053(OCDF \text{ ng kg}^{-1} \text{ d.w.})^{0.36}(OCDD \text{ ng kg}^{-1} \text{ d.w.})^{0.49}$ (Fuentes et al., 2007); OCDF concentrations were estimated based upon the average ratio of OCDD to OCDF from our survey data.

5. Conclusions

A general positive relationship was found between population of the town producing the waste and both dioxin-like PCDD/Fs and dioxin-like PCBs. The one exception to this trend was sludge from a town that had a history of smelting that had a relatively high burden of dioxin-like compounds. Sludge from WWTP N also had a higher burden of dioxin-like compounds. The treatment plant services a geographically isolated town with a low population and no known emitters of dioxin-like compounds. However, this sample also had a relatively high burden of dioxin-like PCBs, which could be the source of the dioxin-like PCDD/Fs found in this sludge. All sewage sludge samples analysed as part of these studies had low overall concentrations of dioxin-like compounds. Out of thirty-seven samples, all except one, were within the reported concentration range of soil within the Australian

environment ($0.05 - 23 \text{ WHO}_{98} \text{ TEQ ng kg}^{-1}$ middle bound concentration) (Muller et al., 2004). The mean concentration of dioxin-like compounds in Australian sewage sludge survey of 2006 was found to be $5.6 \text{ (s.d. 4.5) WHO}_{05} \text{ TEQ ng kg}^{-1}$ ($n=14$) and were within the range of 1.2 to $15.3 \text{ WHO}_{05} \text{ TEQ ng kg}^{-1}$. All the Australian sewage sludge samples cited in these studies were below the Victorian EPA “investigation limit” of $50 \text{ WHO}_{98} \text{ TEQ ng kg}^{-1}$, well below the European proposed guidelines of $100 \text{ WHO}_{98} \text{ TEQ ng kg}^{-1}$, and also below the most stringent guidelines internationally i.e. Canada’s $27 \text{ I-TEQ ng kg}^{-1}$. The burden of dioxin-like compounds in Australian sewage sludge is low and its land application as biosolids is not likely to pose a problem.

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Table 1

Concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), octachlordibenzo-p-dioxin (OCDD) and toxicity equivalence (I-TEQ or WHO₉₈ TEQ) in international sewage sludge as reported in scientific literature relating to dioxin-like compounds in sewage sludge

Nation	Author Year	2,3,7,8-TCDD ng kg ⁻¹	OCDD ng kg ⁻¹	TEQ (I-TEQ or WHO ₉₈ TEQ) ng kg ⁻¹
America	Lamparski et al. 1984	1933 – 2.2 1981 – 11 1982 – 16	1933 – 59000 1981 – 50,000 1982 – 60,000	
America	Weerasinghe et al. 1985		60,000 7,600	
Germany	Hagenmaier et al. 1986		18,200 19,400 3,700 5,600 51,000 7,700 5,000 2,500 4,000 3,700 17,900 28,000 12,200 17,800 6,900	
Sweden	Rappe et al. 1989	0.72 <0.48	9,100 7,400	
Sweden	Broman et al. 1990	1.5 2.2 1.7 1.3	328,644 16,354.4 30,765.7 12,829.2	
Canada	Ho et al. 1990		0.6 to 309 n=99	
Sweden	Naf et al. 1990	1	750	
Germany	Hagenmaier et al. 1992			I-TEQ mean: 0.047 n = 13
Switzerland	Rappe et al. 1994		5,700 4,300 5,000 1,400 17,000 24,000 22,00 26,000 4,900 9,800 14,000 5,400 5,700 19,000 8,600 11,000 67,000 19,000 3,300 15,000 4,300 630 3,800 8,500 24,000 20,000 51,000 360 20,000 27,000	I-TEQ 21 15 25 9 46 71 130 1100 17 43 57 79 53 1900 30 35 4100 230 190 55 11 8 14 53 120 57 150 6 390 1700
United Kingdom	Sewart et al. 1995	1.9 3.8 1.4 2.9 1.0 2.1 1.0 2.9	11,000 23,200 650 63,000 6,500 15,400 7,500 1,820	I-TEQ 29 29 23 0.7 9.9 29 15 0.4

Switzerland	Rappe et al. 1997	<1.5 <0.12 1.7 0.65 1.2 0.31 34 54 77 75 0.34 23 6.2 0.86 25 2.2 5.8 0.91 0.92 1.3 0.27 <4.2 0.75	4,300 1,400 5,700 1,800 22,000 870 26,000 27,000 5,400 19,000 650 67,000 20,000 890 19,000 360 410 3,800 1,500 24,000 1,400 51,000 2,200	I-TEQ 15 9.7 21 8.4 130 10 1200 1700 2200 1900 16 1400 390 22 230 6.2 120 14 6.1 120 14 6.1 120 15 150 23
America	Rappe et al. 1998	2.1 <0.06 2.0 0.84 1.9 0.17 2.0 <0.58 5.3 4.1 1.6 0.30 <0.13 0.17 <0.051 0.076 1.0 <0.35	7,400 7,400 4,300 1,800 7,700 2,700 9,300 6,800 480,000 420,000 3,500 3,300 1,400 1,900 560 2,600 4,400 27,000	I-TEQ 23.7 27.6 26.4 13.7 30.9 4.83 36.7 37.7 1270 1240 31.7 7.40 2.67 6.18 2.26 3.35 33 70.4
Spain	Eljarrat et al. 1999	1.5 0.8 0.4 ND ND 1.0 4.6 1.5 ND 0.5 1.9 1.1 0.6 0.6 ND 1.0 3.8 0.5 8.7	5,700 2,000 4,600 2,500 5,100 7,800 6,000 15,000 9,600 1,100 1,600 2,000 1,000 19,000 4,700 3,800 3,9500 4,900 1,800	I-TEQ 23 23 24 6.9 43 58 70 150 86 7.8 13 14 51 130 18 46 160 14 110
United Kingdom	Stevens et al. 2001	1.1 5.6 1.6 2.6 3.3 0.8 1.6 0.8 0.7 1.0 2.1 1.2 1.0 1.1	4,460 51,500 2,990 3,120 31,400 4,150 9,990 6,280 13,500 2,320 2,900 3,020 4,800 2,610	I-TEQ 53.4 225 49.2 23.0 153 19.9 40.5 30.2 45.1 40.3 29.2 24.7 152 19.9
Canada	Bright et al. 2003	range: 0.3 to 3.9 mean: 1.1 n = 26 f = 100%	range: 730 to 16,000 mean: 4,500 n = 26 f = 100%	range: I-TEQ 5.5 to 250 mean: 40 n = 26 f = 100%
Spain	Eljarrat et al. 2003	nd 0.12 0.23 0.15 0.32 0.35 0.39 0.20	852 527 785 609 943 647 556 1603	WHO ₉₈ TEQ 20.8 5.43 7.18 4.90 6.92 8.06 7.18 14.1
China	Dai et al. 2007	7.61 <0.17 <0.18 <0.10 <0.14 <0.08	503.76 106.41 210.59 316.36 262.55 34.90	I-TEQ 88.24 3.47 4.13 32.80 5.30 7.07
Spain	Fuentes et al. 2007	0.5 0.4 0.3 0.1 1.2 0.7 0.6 0.6 0.5 0.5 0.4 0.2 0.2 0.3 0.4 3.0 0.8 0.62 1.3 0.6 1.4 1.9 1.3 1.5 1.0 1.0 0.4 0.5 1.3 0.2 0.1	2220.8 1796.1 852.2 830.8 1172.3 1677.7 1666.1 773.5 827.9 1875.4 774.8 1396.5 1470.6 816.3 976.2 866.3 820.0 2285.5 705.3 550.7 204.3 167.7 4470.6 3047.5 4074.9 7279.1 27306.8 1991.3 1679.9 2262.0 1469.2	I-TEQ 11.9 9.6 6.8 6.8 12.3 12.3 9.3 4.8 6.3 7.6 5.1 5.6 6.3 5.9 7.1 12.9 8.8 10.1 9.3 8.2 5.1 5.1 17.1 19.5 23.6 23 48.8 28.7 35.6 43.6 346

Table 2**Australian Sewage Sludge Survey 2006 - Type of treatment process and source of wastewater**

WWTP	Population ¹	Treatment Method
A	4,297,000	Anaerobically digested and freshly dewatered.
B	142,000	Stored in a lagoon for 6 months. Dewatered by centrifuge and stockpiled for 4 months. 92% domestic 8% trade waste.
C	106,000	Dewatered by vacuum filtration
D	27,000	Activated sludge. Dewatered. Domestic source.
E	1,811,000	Dewatered. Composition industrial and domestic.
F	35,000	Aerobic digestion. Dewatered. Domestic and light industrial.
G	1,139,000	Activated sludge. Dissolved air-flotation filtration. Mixture of domestic and industrial and some groundwater runoff.
H	1,139,000	Integrated fixed-film activated sludge. Mixture of domestic and industrial and some groundwater runoff.
I	202,000	Chemically stabilized with lime.
J	52,000	Dewatered and chemically stabilized (lime). Mainly domestic.
K	3,850,000	Activated sludge plant. Anaerobically digested primary and secondary sludge. Dewatered in sludge drying pans. Stockpiled for >3 years. Source industrial and domestic
L	5,000	Activated sludge and lagoon process. Land dried.
M	1,508,000	Activated sludge. Mechanically dewatered. Chemically stabilized (lime). Mainly domestic, ~5% industrial.
N	14,000	Oxidation treatment pond. Solar dried.

¹Population refers to the population of the town/city and not just the feeding population of the WWTP

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Table 3

Wastewater treatment plants from Perth, Australia, where sewage sludge samples were collected and analysed for dioxin-like compounds between the years 2002 to 2006

Beenyup WWTP	110 ML/day, mesophilic anerobic digestion, centrifuge dewatering, ~2% industrial input
Subiaco WWTP	60 ML/day dewatered and chemically stabilized. Mainly domestic. ~5% industrial input
Woodman Point WWTP	120 ML/day mesophilic anerobic digestion, centrifuge dewatering, ~9% industrial input

Table 4

Concentration of dioxin-like congeners (ng kg⁻¹ d.w.) in 14 sewage sludge samples collected from Australian sources 2006

	Wastewater Treatment Plant															
Congeners	A	B	C	D	E	F	G	H	I	J	K	L	M	N	Mean	Sd
2,3,7,8-TCDF	2.6	3.9	2.1	0.83	1.5	1.3	1.1	1.2	<0.4	0.6	11	0.775	<0.6	1.3	2.4	2.9
2,3,7,8-TCDD	1.6	0.72	<0.3	<0.4	<.5	<0.5	<.6	<0.5	<0.4	<0.4	<1	<0.3	<0.3	<0.3	1.2	0.6
1,2,3,7,8-PeCDF	0.75	1.4	<0.3	<0.3	0.43	<0.3	<0.5	0.66	<0.1	<0.2	0.65	0.35	<0.1	0.77	0.7	0.3
2,3,4,7,8-PeCDF	0.8	2.1	<0.4	<0.6	<0.7	<0.4	0.89	<0.4	<0.4	<0.7	2	>0.3	<0.3	1.4	1.4	0.6
1,2,3,7,8-PeCDD	0.91	1.7	<0.4	0.72	<2	<0.6	<0.6	1.2	<0.9	<1	1.2	1	0.56	<1	1.0	0.4
1,2,3,4,7,8-HxCDF	2.9	2.4	<0.3	<0.5	1.1	<0.6	1	0.84	<0.5	<0.6	1.4	0.83	0.61	<2	1.4	0.8
2,3,4,6,7,8-HxCDF	2.1	2.9	<0.4	0.82	1.9	0.82	1.3	1	0.6	0.67	2.9	0.97	0.43	1.6	1.4	0.8
1,2,3,6,7,8-HxCDF	1.7	4.1	<0.3	1.5	1.6	1.5	2	1.5	<1	<1	1.1	0.62	<0.4	2.2	1.8	0.9
1,2,3,7,8,9-HxCDF	<0.2	1.3	<.2	<0.2	<0.3	<0.2	<0.2	0.15	<0.4	<0.3	<0.1	<0.08	<0.3	<0.7	0.7	0.8
1,2,3,4,7,8-HxCDD	1.2	2.5	0.22	0.72	<2	<0.7	0.64	0.51	<0.4	0.5	1.1	0.63	<0.4	<0.7	0.9	0.7
1,2,3,6,7,8-HxCDD	4	7.4	1	3.3	2.3	2.1	2.6	3	<2	3.1	6.4	5	3.7	3.3	3.6	1.8
1,2,3,7,8,9-HxCDD	1.7	5.2	<0.5	1.1	1.3	<2	1.3	2.7	<0.6	<1	3.5	1.8	1.3	<2	2.2	1.4
1,2,3,4,6,7,8-HpCDF	42	53	8.6	15	27	28	32	32	16	18	24	18	14	48	27	13
1,2,3,4,7,8,9-HpCDF	1.6	1.6	<0.3	0.46	1.2	0.76	0.99	0.97	<0.7	0.39	1.8	1.5	<0.2	0.9	1.1	0.5
1,2,3,4,6,7,8-HpCDD	150	230	30	26	61	59	68	75	50	67	130	150	63	95	90	57
OCDF	400	160	34	23	76	77	68	96	19	36	79	84	22	170	96	99
OCDD	20900	7820	540	190	1290	1940	690	1180	420	640	2560	1410	500	1990	3005	5495
WHO ₉₈ TEQ ΣPCDD/Fs	8.6	10.2	0.8	2.0	2.0	1.7	2.5	3.5	0.8	1.4	6.8	3.9	2.0	3.2	3.5	2.9
WHO ₀₅ TEQ ΣPCDD/Fs	12.7	11.3	0.9	2.0	2.3	2.1	2.5	3.8	0.9	1.5	6.9	4.2	2.1	3.4	4.0	3.7

PCB 77	19	37	2.9	4.7	18	7.3	27	13	6.1	9.2	18	5	3.4	24	14	10
PCB 81	<1	<0.6	<0.5	2.3	1.8	<1	3	0.76	<0.9	<0.8	1.5	0.48	<0.2	2.6	2	1
PCB 126	1650	2400	210	110	1270	280	950	790	560	670	1210	260	250	1920	895	712
PCB 169	110	130	12	21	160	29	57	100	45	53	90	28	19	150	72	51
PCB 105	4480	5790	540	410	3250	730	2840	2150	1390	1640	3010	700	660	4850	2317	1772
PCB 114	81	120	8.6	6.3	56	2	42	41	29	32	70	12	8	77	42	35
PCB 118	900	850	88	100	400	130	340	210	98	140	360	84	87	860	332	311
PCB 123	150	240	23	22	90	27	80	52	23	33	85	19	17	200	76	72
PCB 156	280	320	26	30	130	37	120	75	31	51	130	31	28	260	111	103
PCB 157	100	45	5.4	8.2	29	10	20	14	9.6	13	20	6.6	<4	49	25	27
PCB 167	8.6	10.2	0.8	2.0	2.0	1.7	2.5	3.5	0.8	1.4	6.8	3.9	2.0	3.2	3.5	2.9
PCB 189	12.7	11.3	0.9	2.0	2.3	2.1	2.5	3.8	0.9	1.5	6.9	4.2	2.1	3.4	4.0	3.7
WHO ₉₈ TEQ ΣPCBs	3.1	5.2	0.4	0.6	2.6	0.9	3.4	1.8	0.9	1.3	2.5	0.7	0.5	3.7	2.0	1.5
WHO ₀₅ TEQ ΣPCBs	2.2	4.0	0.3	0.6	2.0	0.8	3.0	1.5	0.7	1.0	2.0	0.6	0.4	2.8	1.6	1.1
I-TEQ	27.3	16.5	1.3	1.8	3.2	3.5	3.2	4.1	1.2	2	8.6	4.8	2.2	5.2	6.1	7.3
WHO₉₈ TEQ (ΣPCDD/Fs + ΣPCBs)	11.8	15.3	1.2	2.6	4.7	2.6	5.9	5.3	1.7	2.7	9.3	4.6	2.5	7	5.5	4.1
WHO₀₅ TEQ (ΣPCDD/Fs + ΣPCBs)	14.9	15.3	1.2	2.6	4.3	2.8	5.4	5.2	1.6	2.6	8.9	4.8	2.5	6.1	5.6	4.5
Total TCDD	18	29	9.7	58	39.5	16	41	16	10	10	7.9	7.8	97	10	26	26
Total TCDF	42	70	7.7	37	32	9.7	87	39	3.2	13	110	16	31	5.8	36	33
Total PeCDD	19	31	13	26	13	12	21	15	42	81	14	6.1	16	140	32	36
Total PeCDF	66	45	4.6	34	17	7	43	41	5.4	8	260	14	27	7.3	41	66

Total HxCDD	35	86	9.3	23	22	13	28	28	14	23	60	38	37	21	31	20
Total HxCDF	45	46	4.6	23	15	29	21	20	8.5	11	66	16	24	6.2	24	18
Total HpCDD	280	530	56	50	120	130	30	160	87	120	260	270	200	110	172	132
Total HpCDF	78	98	8.6	16	41	29	53	56	16	19	69	58	49	14	43	27
Total PCDD/Fs	21900	8920	690	480	1640	2260	1180	1650	630	960	3490	1920	2640	840	3514	5709

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Table 1. Concentrations of *dioxin* congeners (pg/g d.w.) in sewage sludge from three wastewater treatment plants from Western Australia during 2002, 2003, 2005 and 2006.

	Beenyup								Subiaco								Woodman Point					
	2002		2003		2005		2006		2002		2003		2005		2006		2002		2003		2005	
PCDF	4.6	11.4	7.5	7.4	6	5.1	2.6	2.4	<3	<2	4.5	3.9	4.5	<1	<0.6		<1.6	<2.0	2.6	2.3	2.6	3
	0.7	1	0.26	0.32	<0.6	0.85	<0.8	<1	9.3	<0.1	0.48	0.63	8.3	<0.4	<0.3		<0.5	<0.2	0.35	0.26	0.68	<1
PCDF	1.1	<6	1.7	1.6	<0.9	<0.6	<1	<0.7	0.7	<0.2	0.5	0.56	1.2	<0.3	<0.1		<0.9	2.1	1.1	1	1.1	<0.8
PCDF	1.7	13	1.8	1.6	1.4	1.4	<0.9	<2	<1	<0.7	0.87	0.93	1.2	0.69	<0.3		<0.8	3.2	1.1	1.2	1.4	1.4
PCDF	1.2	2.8	1.5	1.5	1.2	<1	<2	<2	<0.7	<0.4	1.3	1.2	<0.9	<0.8	0.56		0.9	2.3	1.4	1.1	2.2	1.9
PCDF	2.8	6.8	1.5	<3	2.2	2.6	<0.8	<0.8	<3	<3	0.27	<0.1	1.6	1.3	0.61		2	5.2	<2	<1	2.5	2.2
PCDF	2	6.7	2	1.7	1.1	1.5	<0.9	<1	0.8	<0.4	0.775	0.87	0.75	<0.5	0.43		<0.6	4.4	1.8	1.8	1.5	1.6
PCDF	2.7	8	<3	<3	2.2	2.9	<2	<2	1.2	1	<1	<1	1.5	1.3	<0.4		1.8	6.7	2.7	<2	2	2
PCDF	<0.4	<3	<0.4	<0.3	<0.4	<0.3	<0.5	<0.8	<0.3	<0.2	<0.4	<0.1	<0.3	<0.2	<0.3		<0.3	0.7	<0.3	0.23	<0.3	<0.5
PCDD	<0.5	1.3	0.58	0.61	<0.5	<0.5	<0.8	<0.8	<0.2	<0.1	0.71	0.72	0.45	<0.4	<0.4		<0.3	<2	0.75	0.63	1.4	<0.7
PCDD	3	5.3	3.9	3.7	3.2	3.1	<2	2.5	2.6	1.8	4.5	4.8	5	5.4	3.7		3.2	13	4.2	4.3	4.6	4.3
PCDD	<0.5	1.33	<0.9	<0.7	<1	1.5	<0.8	<0.7	<1	<0.2	<1	<2	<2	<2	1.3		1.8	<2	<2	<3	3	3.8
pCDF	72	92	110	99	71	72	47	44	30	29	43	43	35	32	14		68	99	99	99	58	54
pCDF	1.3	1.9	1.4	1.3	1.4	1.4	<0.6	<2	0.7	<0.5	<0.8	0.9	<0.6	0.82	<0.2		1.5	4.3	1.6	1.4	1.5	1.6
pCDD	87	104	88	85	82	85	62	52	60	65	110	110	150	160	63		83	188	100	100	86	81
	333	379	340	330	240	250	170	150	137	137	170	170	60	78	22		321	389	330	320	170	180
	882	1110	860	790	810	830	580	500	592	769	1270	1200	1000	1210	500		900	1160	999	990	740	780

PCDD/Fs	6.0	16.5	6.4	6.0	5.0	4.9	1.4	1.5	10.8	1.3	5.0	5.0	12.3	3.2	2.0	3.4	10.1	5.7	5.1	7.0	5.8	
PCDD/Fs	5.9	14.2	6.3	5.9	4.9	4.8	1.6	1.6	10.9	1.5	5.1	5.1	12.2	3.3	2.1	3.7	9.7	5.7	5.1	6.8	5.7	
	294	373	190	190	180	180	300	190	255	208	98	95	130	110	53	481	587	230	230	210	200	
	14.9	40.3	8.4	8.4	7.9	8.5	13	8	25.1	8.43	7.4	6.6	11	5.1	2.1	15.9	23.4	9.9	9.5	9.4	8.3	
	24.2	61	17	16	16	17	12	11	34.1	9.65	22	13	11	8.7	3.4	26.5	31.8	18	19	20	19	
	<3	<10	2	2.3	2.2	1.9	<1	<1	<2	<2	2.3	1.4	<1	0.85	<0.2	3.35	<5	2.2	2.4	<2	2.4	
	1970	2100	860	820	1000	1030	680	580	1240	1290	810	770	680	680	250	1760	2250	1230	1300	1700	1780	
	130	135	58	70	72	67	49	43	79	87.4	67	64	48	42	19	148	172	120	100	130	120	
	3780	4710	2280	2110	2330	2400	1810	1490	2680	2600	2200	2280	1590	1410	660	3880	5040	3560	3190	4190	4010	
	91	144	48	45	61	61	29	29	55.6	52.8	51	60	49	44	8	124	84.4	<100	73	99	97	
	629	726	320	300	360	320	220	200	408	387	270	310	220	200	87	623	684	440	390	570	560	
	119	161	100	72	80	89	49	45	80.2	<70	7	63	47	45	17	<100	161	75	110	140	150	
	767	797	240	380	150	150	68	68	497	420	360	340	63	100	28	719	929	490	540	210	220	
	35.5	31	16	15	19	20	16	<10	19.7	<20	<10	14	13	<10	<4	33.9	38.6	<20	24	23	27	
PCBs	3.5	7.4	2.3	2.2	2.2	2.3	1.6	1.5	4.1	1.6	2.7	1.9	1.5	1.2	0.5	0.0	3.7	4.5	2.6	2.7	3.0	3.0
PCBs	2.7	6.4	1.9	1.8	1.8	1.9	1.3	1.2	3.6	1.1	2.4	1.5	1.2	1.0	0.4	0.0	3.0	3.5	2.1	2.2	2.2	2.2
ΣPCBs)	6.5	16.5	6.7	6.3	5.4	5.9	2.1	2.1	11.4	2.1	5.6	5.7	13.3	4.4	2.2	4.1	10.3	6.2	5.7	6.7	5.7	
	9.5	23.9	8.7	8.2	7.3	7.2	3.1	3.0	14.9	2.9	7.7	6.9	13.8	4.4	2.5	7.1	14.6	8.3	7.8	10.0	8.7	
	8.6	20.6	8.2	7.7	6.8	6.7	2.9	2.8	14.5	2.6	7.5	6.6	13.4	4.3	2.5	6.7	13.2	7.8	7.2	9.1	7.9	
	13	66	16	14	9.7	8.4	<4	<6	18	13	48	50	32	22	5.8	14	28	19	18	26	20	
	28	219	41	39	33	32	23	19	19	14	26	23	120	20	10	22	19	27	24	21	19	

	21	59	23	22	28	11	0.7	10	38	9.9	45	110	730	7710	7.3	5.6	45	19	19	15	28
	12	119	31	27	23	18	8	9.7	11	10	17	18	30	16	140	10	29	23	22	21	22
	23	77	40	36	25	25	20	16	13	9.6	31	34	30	32	6.2	13	119	35	44	53	1
	20	59	38	29	21	23	15	17	10	5.1	15	14	11	10	21	14	43	29	28	21	20
	159	198	180	170	150	160	110	89	109	119	220	220	240	260	14	154	348	200	200	160	160
	117	136	170	150	100	110	66	58	49	48	36	38	49	49	110	111	152	160	150	89	84
ts	1610	2420	1740	1610	1440	1470	1000	870	996	1130	1880	1880	2300	2410	840	1560	2330	1840	1820	1320	1350

Table 6

Contamination grading for sewage sludge based on octachloro dibenzo-p-dioxin (OCDD) concentration ng kg⁻¹ d.w. and compared to calculated I-TEQ ng kg⁻¹ concentration

Grading	OCDD	I-TEQ ¹
Very Low	150-1,000	1 – 5
Low	1,000-10,000	5 – 38
Moderate	10,000-60,000	38 – 171
High	60,000 -200,000	171 – 475
Extremely High	200,000+	475 +

¹I-TEQ calculated by formula $I-TEQ \text{ ng kg}^{-1} = 0.053(OCDF \text{ ng kg}^{-1})^{0.36}(OCDD \text{ ng kg}^{-1})^{0.49}$ (Fuentes et al., 2007); OCDF concentration calculated by average ratio of OCDF/OCDD.

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