



Investigating the levels and trends of organochlorine pesticides and polychlorinated biphenyl in sewage sludge

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ABSTRACT

A study was completed to investigate temporal trends of organochlorine pesticides (OCPs; aldrin, chlordane, dieldrin, heptachlor, hexachlorobenzene, and DDT) and polychlorinated biphenyls (PCBs) in sewage sludge. Between 2004 and 2006 the concentration of OCPs and PCBs in Australian sewage sludge ($n=829$) was consistently $<1000 \mu\text{g kg}^{-1}$ dry solids DS. Dieldrin, chlordane and DDE were detected in 68%, 27% and 13% at maximum concentrations of 770, 290 and $270 \mu\text{g kg}^{-1}$ DS, respectively.

Time series analysis (1995–2006) of OCPs and PCBs sewage sludge concentrations ($n=2266$) taken from six wastewater treatment plants (WWTPs) of the same geographic region found that lindane, aldrin HCB, heptachlor, DDT, DDD and PCBs were infrequently detected ($<8\%$). A correlation between dieldrin and chlordane levels was found ($P<0.05$) which provides evidence of similar environmental mechanisms facilitating movement of dieldrin and chlordane through environment compartments. It has taken more than 10 years for dieldrin and chlordane to reduce to less than detectable concentrations in freshly generated sewage sludge in Australia following government restrictions.

Internationally, reported sewage sludge OCP concentrations were consistently low and often less than detection limits. Therefore, OCPs are not considered to be a contaminant of regulatory concern for countries that phased out OCP use several decades ago. Concentrations of PCBs in sewage sludge were also consistently low and rarely exceeded European contaminant limits and therefore, regulatory limits may warrant review. The authors recommend that Australian authorities revise regulatory requirements for OCP and PCBs contaminant levels in sewage sludge destined for beneficial reuse as biosolids.

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1. Introduction

Many countries have contaminant limits for organic pollutants in biosolids (treated sewage sludge) to assess its suitability for beneficial recycling (i.e. applied to land as a fertilizer). Internationally, Australia is the only country to have contaminant limits for organochlorine pesticides (OCPs), which may be a consequence of a relative recent phasing out of these compounds in the 1990s. Many third-world countries continue to use OCPs for malaria control and this study will provide information regarding the expected length of time that environmental contamination will occur. Similar to Australia, a

number of European countries have contaminant limits for polychlorinated biphenyls (PCBs), therefore studies of PCBs in sewage sludge are internationally relevant (European Commission, 2001). Regardless of whether sewage sludge is beneficially recycled, it is an important environmental matrix to monitor for organic chemical pollution.

OCPs are considered to be the second generation of pesticides that took over from the early first generation of insecticides produced from inorganic compounds (arsenic, lead, copper, and sulfur) in the 1940s (Chenier, 2002). The use of these chemicals improved our quality of life by ensuring a regular supply food, as well as protection against insect borne disease. The most infamous OCP, DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane), was found to be remarkably active against a number of insect pests. Ironically, one of the valued properties of DDT was its persistence, reducing the need for frequent applications. DDT became the prototype OCP from which other more toxic pesticides were developed viz. aldrin, dieldrin, lindane, chlordane and heptachlor. Due to the persistence of many OCPs and their potential impact upon human and wildlife health (as carcinogens and endocrine disruptors), international treaties have been

Abbreviation: DDD, 1,1-dichloro-2,2-bis(*p*-chloro-phenyl)ethane; DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; DL, Detection limit; DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; DS, Dry solids; HCB, Hexachlorobenzene; HCH, Hexachlorohexane; LOD, Limit of detection; OCPs, Organochlorine pesticides; PCBs, Polychlorinated biphenyls; WWTP, Wastewater treatment plant.

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developed to prevent further environmental contamination. Despite restrictions for use in most Western nations, OCPs and their breakdown products are still detected in many environmental compartments, including humans, throughout the world (Erickson, 1997; Zitko, 2003; Harden et al., 2005).

PCBs are one of the great environmental pollutants of the twentieth century. The commercial production of PCBs began in the USA in 1929 and their commercially valued properties were electrical resistance, low volatility and resistance to degradation at high temperatures. The commercial product(s) were a complex mixture of PCB isomers and used for a variety of purposes, such as dielectric fluids in capacitors and transformers. It was not until the 1960s that PCBs were found to accumulate in biota globally, entering the food chain through “the backdoor” (Jensen, 1972). Due to their persistence and potential impact on humans and wildlife (carcinogens, endocrine disruptors) in 2001 they were included in the Stockholm Convention on Persistent Organic Pollutants to prevent further environmental contamination (UNEP, 2001). Even though PCB production has been banned in most countries since the 1970s and 1980s, they are still found in infrastructure throughout the world. It is estimated that over 1 million tonnes of PCBs have been generated and about one third of this quantity is thought to be continuing to circulate in the environment (Birkett and Lester, 2003). PCBs are now ubiquitous environmental pollutants, occurring in human and animal tissue, and most environmental compartments (Erickson, 1997).

This paper presents a literature review of OCPs and PCBs in sewage sludge, detailing the typical concentrations and trends observed internationally. This review is pertinent to countries that have regulatory limits for PCBs in sewage sludge (viz., Australia, Germany) and other countries considering such restrictions (European Commission, 2001). This is followed by data obtained from two Australian monitoring studies that have quantified levels and trends of OCPs and

PCBs in Australian sewage sludge and compares them to domestic guidelines and international studies.

2. Methodology

2.1. Historical levels and sources

A comprehensive examination of the scientific peer-reviewed literature is presented that examines OCPs and PCBs sewage sludge concentrations and sources.

2.2. Australian sewage sludge survey 2004–2006

Australian WWTPs must monitor sewage sludge intended for beneficial reuse for OCPs and PCBs. Concentration data ($n = 829$) was obtained from participating WWTPs ($n = 58$) that was released to the authors on condition of anonymity. Results are discussed at an aggregate level, organised according to State and year (Table 1). To ensure comparable data, only freshly generated sewage sludge samples (2004–2006) analysed at National Association of Testing Association (NATA) accredited laboratories have been included.

2.3. Australian sewage sludge time series—1995 to 2006

A time series analysis of OCP and PCBs concentrations in sewage sludge from five Australian WWTPs between 1995 and 2006, and one WWTP between 2001 and 2004, all from the same geographic region and analysed approximately weekly is presented ($n = 2266$). All data were generated from the same NATA accredited laboratory and the detection limit was reduced simultaneously in 2001 from 0.1 mg kg^{-1} dry solids (DS) to 0.01 mg kg^{-1} DS.

Table 1
Concentration of OCPs in international sewage sludge as reported in the scientific literature $\mu\text{g kg}^{-1}$ DS.

Country year	Method	Analyte	Range $\mu\text{g kg}^{-1}$ DS	Mean $\mu\text{g kg}^{-1}$ DS	Median $\mu\text{g kg}^{-1}$ DS	Reference
USA 1976	GC-ECD	Dieldrin	<30 – 2200	0.19	0.27	Furr et al. (1976)
UK 1982	GC-ECD	DDE	<10 – 49	20	40	McIntyre and Lester (1982)
UK 1984	GC-ECD	Dieldrin	<10 – 1260	280	260	McIntyre and Lester (1984)
		Lindane	<10 – 930	210	180	
		Aldrin	<10 – 90,210	30	20	
		Dieldrin	<10 – 52,940	500	130	
Netherlands 1984	GC-ECD	Lindane	<10 – 70,000	410	90	van Luin and van Starkenburg (1984)
		HCB	<50 – 650	360	360	
Switzerland 1993	GC-MS, GC-ECD	Lindane	<50 – 80	*	<50	Frost et al. (1993)
		HCB	nd – 144	21	nd	
		Lindane	nd – 118	21	nd	
Italy 1993	HRGC-MS	Total DDT	nd – 376	70	70	Ottaviani et al. (1993)
		DDE	20 – 90	49	30	
		DDE	5 – 20	12.5	12.5	
Canada 1996	HRGC-MS	HCB	10 – 305	89	10 – 305	Webber et al. (1996)
		DDE	<10 – 13	*	<10	
		HCB	<10 – 33	*	1	
Aldrin, chlordan, heptachlor, DDT were below the detection limit (<10)						
Ireland 2000	GC-ECD	DDE	<10 – 106	51	5	McGrath et al. (2000)
UK 2003	HRGC-LRMS	DDE	6.0 – 28	13	13	Stevens et al. (2003)
		HCB	6.4 – 28	42	22	
Lindane, DDT, DDD, chlordan were “low or at non-detectable levels”						
Greece 2004	HRGC-LRMS	DDE	<dl – 96	27	19	Katsoyiannis and Samara (2004)
		DDD	<dl – 400	78	130	
		Dieldrin	<dl – 86	15	<dl	
		Heptachlor	<dl – 170	41	<dl	
China 2007	HRGC-HRMS	DDE	10.5 – 730.3	142.8	91.2	Wang et al. (2007)
		DDT	<0.10 – 100.7	10.0	2.4	
		HCB	7.5 – 318.7	145.3	133.8	
		Lindane	<0.04 – 7.4	0.6	<0.04	

<dl is used if the detection limit has not been supplied in the text.

3. Results and discussion

3.1. Historical levels and sources

3.1.1. Organochlorine pesticides

A large volume of research investigating OCPs in environmental compartments has been published; however, few studies of levels and trends in sewage sludge have been published. There has been no review undertaken on this subject internationally and in Australia, no published research could be found. The concentration of OCPs in sewage sludge has been reported from the United States of America (USA), the United Kingdom (UK), Sweden, Italy, Greece and recently, China. A summary of English language peer-reviewed articles discussing OCPs in sewage sludge is presented in Table 1.

McIntyre and Lester (1982) were one of the first researchers to report the concentrations of DDE, dieldrin and lindane in UK sewage sludges ($n=40$). DDE was detected in all samples ($10\text{--}40\ \mu\text{g kg}^{-1}$ DS; mean 40), but dieldrin and lindane were not. The maximum concentrations of dieldrin and lindane were slightly higher than the maximum DDE concentration; dieldrin $<10\text{--}1260\ \mu\text{g kg}^{-1}$ DS, lindane $<10\text{--}930\ \mu\text{g kg}^{-1}$ DS (McIntyre and Lester, 1982). McIntyre and Lester (1984) continued this work, reporting the concentration of lindane, aldrin, dieldrin and endrin from a survey of 444 UK sewage sludges. The omission of DDE appears to be an unusual omission, given that DDE was detected in all samples in the earlier survey. The major pesticides detected were lindane and dieldrin and the maximum concentrations were far higher than the previous study: $70,000$ and $52,940\ \mu\text{g kg}^{-1}$ DS respectively. These maximum concentrations were unusual as the mean and median concentrations are more representative of the typical concentrations of UK sludges at the time; median concentration 90 and $130\ \mu\text{g kg}^{-1}$ DS respectively (McIntyre and Lester, 1984).

The nineties saw the improvement in analytical techniques and improved detection limits, which was required due to the decreasing concentrations of most OCPs in sewage sludge. The detection of OCPs was still common in Swedish, Italian and Canadian sludges. In a study of OCPs in Swedish sludge samples, Total DDT, HCB and lindane were detected, albeit at low concentrations $<10\ \mu\text{g kg}^{-1}$ DS (Nylund et al., 1992). HCB and DDE, were detected in Italian sludges ($n=5$) at concentrations ranging from 10 to $310\ \mu\text{g kg}^{-1}$ DS and $20\text{--}90\ \mu\text{g kg}^{-1}$ DS respectively (Ottaviani et al., 1993). DDT and DDD were also detected but interfering analytes prevented the quantification of these compounds. A survey of Canadian sludges in 1996 found that aldrin, chlordane, heptachlor and DDT were below the survey detection limit ($<10\ \mu\text{g kg}^{-1}$ DS). DDE and HCB were detected, but they weren't detected in all samples (median concentration less than detection limit) with concentrations ranging from <10 to $130\ \mu\text{g kg}^{-1}$ DS and $<10\text{--}330\ \mu\text{g kg}^{-1}$ DS respectively (Webber et al., 1996). This sampling event was approximately fifteen years after Canada phased out these compounds, which may provide an indication of the time required for a nation's sewage sludges and environment to undergo natural processes of depuration.

By the new millennium, the detection of OCPs in sewage sludge was becoming less common, with some researchers choosing not to monitor for OCPs in national surveys of organic pollutants in sewage sludge (Bright and Healey, 2003). In an analysis of digested sludge from fourteen UK WWTPs HCHs, HCB, endosulfan, DDT, DDD, DDE and chlordane were often below the detectable limit (Stevens et al., 2003). The concentrations of two of the compounds above the detection limit were: HCB (median $22\ \mu\text{g kg}^{-1}$ DS) and DDE (median $13\ \mu\text{g kg}^{-1}$ DS) (Stevens et al., 2003). This observation is consistent with declining use of OCPs in Europe. HCB, like other chlorobenzenes, has some industrial applications, which may account for its continuing presence in all the samples. It is also relatively volatile and ubiquitous in the atmosphere (Stevens et al., 2003).

The latest report of sludge samples analysed for OCPs (HCH, DDT, DDD, DDE and BHC) came from data collected in 2005 from 31 WWTPs in 26 cities of China. Concentrations of HCHs (all four isomers) were not regularly detected and the median concentration was $<\text{LOD}$ for all isomers. The presence of DDTs was detected frequently. The detection of DDT suggests that DDT is still currently being used within China; however, DDT is a contaminant in other pesticides such as diclofop, which may have been a source and is still used in China. HCB was detected in all sludge samples (range: 7.5 to $319\ \mu\text{g kg}^{-1}$ DS). The source of these compounds has been associated with the production of pentachloronitrobenzene and linked to combustion and metallurgical processes involving the use of chlorine (Wang et al., 2007).

The concentration of OCPs has been decreasing in countries where government restrictions have been applied. DDE, dieldrin and lindane are the most commonly detected OCPs. While most OCPs appear to be below current detection limits in sludges, DDE and dieldrin appear to have a much longer half-life since they are still regularly detected in sewage sludges fifteen years after being banned.

A major difference in sewerage systems between nations can be the incorporation of stormwater drains. In countries such as Australia, the sewer system is closed. Therefore, the movement of OCPs directly into the sewerage system is less likely than European systems that also catch and treat rain water. OCPs may enter the WWTP process from industrial discharge or as a component of urban runoff or drainage into the system. However, little research has been carried out to investigate the environmental pathways and source of these compounds in sludge. The most illuminating work was a study by Nylund et al. (1992) that measured the concentration of organic contaminants in sewage sludge during a dry and rainy period. They found that the concentrations of DDT increased from $39\ \mu\text{g kg}^{-1}$ DS in a dry period to $68\ \mu\text{g kg}^{-1}$ DS in a wet period and suggested that atmospheric deposition facilitates the movement of this pesticide to the WWTP. This suggests that a significant portion of DDTs are either

washed out of the atmosphere with rain or the rainfall washes out pesticide residues from the urban environment, or perhaps a combination of both. Determining if DDT was washed out of the atmosphere would be relatively easy by measuring DDT concentrations in rainfall. The concentration of lindane was not significantly different between the two periods (8.7 and $7.8\ \mu\text{g kg}^{-1}$ DS respectively), which suggests that precipitation does not play major role in the movement of lindane. Oddly, the concentration of HCB decreased from 43 to $11\ \mu\text{g kg}^{-1}$ DS from the dry to the wet period. No explanation of this phenomenon was provided but the most likely explanation is dilution.

Various studies have investigated the fate of OCPs within a WWTP. While most OCPs are persistent (Buisson et al., 1986) it was reported that lindane can be effectively removed by wastewater treatment, with reductions of $67\pm 10\%$ (Kipopoulou et al., 2004). Lindane is more water-soluble compared to other OCPs and therefore more biodegradable. Lindane also has a higher vapour pressure so could be volatilised particularly in an aeration basin of an activated sludge WWTP.

3.1.2. Polychlorinated biphenyls

Much work has been conducted into the concentrations of PCBs in sewage sludge, with research published from the USA, the UK, the Netherlands, Italy, Switzerland, Canada, Ireland, Greece and Spain. The majority of this research was directed towards understanding the risk posed by the land application of sewage sludge, as well as quantifying the environmental release of PCBs in sludge and wastewaters. However, a direct comparison of all data is confounded by the different reporting styles. There are a total of 209 individual PCBs and quantification of all 209 is generally not possible or necessary. Concentrations were originally reported in terms of the commercial formulation, Arochlors™. Later, individual isomers were selected as representative of Σ PCB concentration. In this review, the number of isomers included in the total sum of PCBs will be included in brackets, i.e. Σ PCBs (X).

One of the first reports of PCBs in sludge was of six USA sewage sludges (Bergh and Peoples, 1977). The concentrations are high when compared to other reported sludge PCB levels, with a mean concentration of $765,000\ \mu\text{g kg}^{-1}$ DS, ranging between $238,000$ and $1,700,000\ \mu\text{g kg}^{-1}$ DS. At this time in the USA, PCBs were still commonly used and it is possible that reported concentrations were typical of sewage sludge of that period or more likely, that PCB production or industries utilising PCBs were located in the catchment. Another early study of PCBs sludge concentration from the USA reported significantly lower concentrations that were still slightly higher than modern samples (mean $5200\ \mu\text{g kg}^{-1}$ DS, range <10 to $23,000\ \mu\text{g kg}^{-1}$ DS). These concentrations may be more indicative of PCB contaminant levels while it was still unrestricted (Furr et al., 1976). Further studies of PCBs levels in USA sludges were far lower than the earlier Bergh and Peoples (1977) study, with concentrations ranging between $1200\text{--}6200\ \mu\text{g kg}^{-1}$ DS (West and Hatcher, 1980) and $150\text{--}3600\ \mu\text{g kg}^{-1}$ DS (Mumma et al., 1984).

UK research reported concentrations of up $22,000\ \mu\text{g kg}^{-1}$ DS (McIntyre and Lester, 1984) which wasn't typical, as the mean concentrations were less than $1000\ \mu\text{g kg}^{-1}$ in two other separate UK sludge surveys (McIntyre and Lester, 1982; McIntyre and Lester, 1984), which again may be associated with PCB productions or industrial uses in the catchment. Concentrations of PCBs in sludges from the Netherlands were in a similar range to the UK: Σ PCBs (17) ranging from 390 to $1480\ \mu\text{g kg}^{-1}$ DS, mean $880\ \mu\text{g kg}^{-1}$ DS. The concentrations of PCBs in sludges in the 1980s were typically in the low parts-per-million range, which was already far lower than the concentrations reported in the 1970s by Bergh and Peoples (1977).

In the 1990s, the concentrations of PCB in sludges were declining and often below $1000\ \mu\text{g kg}^{-1}$ DS. For example, Italian sludges analysed in the early nineties had PCB concentrations between 210 and $1010\ \mu\text{g kg}^{-1}$ DS (Ottaviani et al., 1993). In a follow up survey in the UK the total PCBs concentrations ranged between 110 and $440\ \mu\text{g kg}^{-1}$ DS, which is similar to the concentrations reported by McIntyre and Lester (1984) and later in the nineties by Alcock and Jones (1993). This work was continued in 2003 when Stevens et al. reported the concentration of Σ PCBs in fourteen UK sludges. The concentrations were similar to the studies conducted in the nineties, as well as the eighties and ranged between 110 and $440\ \mu\text{g kg}^{-1}$ DS (Stevens et al., 2003).

Since 1998, the concentration of PCBs in sewage sludge and other environmental matrices has commonly been measured following the inclusion of "dioxin-like" PCBs into World Health Organisation dioxin toxicity equivalence scheme (Van den Berg et al., 1998). For example, the concentrations of the three most toxic co-planar PCB congeners (77, 126, 169) as well as 7 mono- and di-ortho-PCBs (PCB 8, 28, 52, 101, 118, 153, 138, 180) were measured in nineteen sewage sludges from Switzerland. The sum of the seven mono- and di-ortho-PCBs, which are routinely measured as representatives of the PCB fraction, reached levels between 43 and $550\ \mu\text{g kg}^{-1}$ DS (Berset and Holzer, 1996). Sludges that received industrial effluents clearly showed higher PCB levels than rural ones (Berset and Holzer, 1996). The concentrations of 'dioxin-like' PCBs will not be further summarised within this literature review as this information is available in a review of dioxin-like compounds in sewage sludge (Clarke et al., 2008).

By the new millennium, the concentration of PCBs in sludge globally had decreased to be typically lower than $500\ \mu\text{g kg}^{-1}$ DS. For example, in a 2003 survey of Canadian sludges ($n=20$), PCBs were not detected ($\text{dl}=50\ \mu\text{g kg}^{-1}$ DS) in any of the samples (Bright and Healey, 2003).

A survey of Spanish sludges ($n=139$) from twenty WWTPs reported low PCB concentration ranging between 3 and $60\ \mu\text{g kg}^{-1}$ DS (Abad et al., 2005). This is well below the European recommended limit of $800\ \mu\text{g kg}^{-1}$ DS for sewage sludge

beneficial reuse. In fact all European studies from this time had concentrations lower than the European recommended contaminant limit ($800 \mu\text{g kg}^{-1}$ DS). A 2004 French study reported PCB concentrations ranging from 70 to $650 \mu\text{g kg}^{-1}$ DS in sludge samples taken in a WWTP which drains the Paris area (Blanchard et al., 2004) and a 2004 Greek study reported PCB sludge concentrations ranging between 185 and $765 \mu\text{g kg}^{-1}$ DS (Katsoyiannis and Samara, 2004).

A summary of the concentration of PCBs in sewage sludges internationally is presented in Table 2, showing that PCBs levels have declined since measurements were begun. The highest reported concentrations of PCBs in sludges occurred in the USA ($1,700,000 \mu\text{g kg}^{-1}$ DS) in 1977 and are significantly higher than PCBs in other later reported sludge samples and may demonstrate the positive effect of banning these chemicals. There is little variation of PCB sludge concentrations when comparing countries, suggesting that PCB contamination was similar throughout developed countries. Presently, PCB concentrations rarely exceed $1000 \mu\text{g kg}^{-1}$ DS.

Few studies have investigated the origins of PCBs in wastewater treatment facilities. Many European countries do not have separate sewerage and stormwater drainage systems. It is hypothesized that the atmospheric deposition of PCBs is likely to contribute to PCB levels in sewage sludge. The concentration of PCBs ($\Sigma 6$) in two Swedish sludge samples was measured, once during a rainy ($85 \mu\text{g kg}^{-1}$ DS) and once during a dry period ($54 \mu\text{g kg}^{-1}$ DS), and Nylund et al. (1992) reported “the results indicate somewhat increased concentrations of these substances during the rainy period”. This data suggests that the source of PCBs is facilitated by atmospheric deposition by either direct contamination or through increased mobilisation from runoff. Atmospheric deposition as a source of PCBs was supported by research that investigated PCBs in the sewerage system in Paris, France, during 1999–2000. Of the 21.1 kg of PCBs ($\Sigma 7$) detected in sewage sludge 17.6 kg was attributed to atmospheric fallout, suggesting that atmospheric fallout is the dominant source of PCBs in these sludges (Blanchard et al., 2004). The concentration of PCBs in the atmosphere was found to be 40–500% greater in precipitation over urban areas than regional background precipitation (Offenberg and Baker, 1997). If atmospheric deposition of PCBs is the dominant source of PCBs in the sewerage system then it is likely that the concentration of PCBs in sewage will decrease as the atmospheric concentrations decrease. Sweetman and Jones showed this to be the case for the atmosphere over London in which the apparent half lives of the PCBs ranged from 2 to 6 years (Sweetman and Jones, 2000). Loganathan et al. (1997) also investigated the PCB source attributed to wet and dry deposition, finding that contaminated street dust was a major PCB source, particularly in areas that had historical contamination (Loganathan et al., 1997).

3.2. Australian sewage sludge survey 2004–2006

3.2.1. Organochlorine pesticides

The summary statistics of OCP and PCBs concentrations measured in Australian sewage sludge between the years 2004, 2005 and 2006 are presented in Table 3. All compounds were less than $1000 \mu\text{g kg}^{-1}$ DS, the highest contaminant limit for beneficial reuse (NRMCC, 2004). The most prevalent OCPs detected in this survey of Australian sewage sludge were dieldrin, chlordane and Total DDT, detected in 68%, 27% and 14% of samples respectively. The maximum concentrations of dieldrin, chlordane and Total DDT were 770, 290 and $270 \mu\text{g kg}^{-1}$ DS respectively. The great majority of samples had concentrations less than the lower contaminant limit, which means that according to Australian biosolids guidelines this material is suitable for a wide range a

beneficial reuses (with respect to these parameters). However, the high frequency of detection of these compounds indicates that they are extremely persistent in the Australian environment. All the other OCPs were detected in less than 3% of samples. In descending order these were: HCB (3%), heptachlor (2%), DDD, DDT, aldrin and lindane (<0.1%). Again, when detected, the concentrations of these compounds were lower than guideline values that would prevent the beneficial reuse of sewage sludge, most being below $200 \mu\text{g kg}^{-1}$ DS (Australia's lowest contaminant limit for unrestricted sewage sludge beneficial reuse). When detected, they were close to the analytical detection limit of $10 \mu\text{g kg}^{-1}$ DS.

Dieldrin was the most prevalent OCP detected in samples from all regions of Australia, at frequencies of 70, 79, 40 and 33% respectively. The higher detection rates in the tropical regions and may reflect the higher use of dieldrin in these areas to combat termites. Aldrin was rarely detected in sewage sludge ($n = 3$); however, this is due to the rapid conversion of aldrin to dieldrin once released in the environment. Therefore, the burden of dieldrin in the sewage sludge is derived from both aldrin and dieldrin (IPCS, 1989b).

Chlordane was only detected in sludges from tropical regions and again, this might be a reflection of higher use in warmer climates for protection of houses against termites.

DDE comprises the majority of the reported ‘Total DDT’, while DDT and DDD are rarely detected (Table 3). This is consistent with the reported breakdown of DDT to DDE in the environment and WWTPs (IPCS, 1989a). Results were obtained that didn't distinguish the contribution of the breakdown products to the Total DDT; however, it is reasonable to assume that the contribution of Total DDT is comprised primarily of DDE. All results are presented as ‘Total DDT’. Total DDT varied according to region, but no consistent trend can be observed. DDT and DDD were only detected in sludges from one region. The presence of DDT in this sludge is surprising given that DDT is expected to be converted to its metabolites in the WWTP (IPCS, 1989a). This suggests that there was recent inappropriate use or disposal of this compound in that area. DDT is also a contaminant in other pesticides such as diclofop and this may be its source in this area, similar to that observed in the recent Chinese study (Wang et al., 2007).

Heptachlor was detected in sludges from three WWTPs. Heptachlor is readily converted in the environment to its metabolite heptachlor epoxide and may be more useful to monitor for this compound.

Overall HCB was detected in 4% of sludge samples from five WWTPs, all of which were in the heavily populated state of New South Wales (NSW). It has been previously reported that one of these WWTP receives contaminated trade waste which may provide an indication of the source of contamination (Connell et al., 2002). It is likely that HCB occurs in sewage sludge as a result of industrial applications and formation as a by-product (i.e. pentachloronitrobenzene) rather than its historical use as a pesticide.

To identify significant trends in the data from 2004, 2005 to 2006, an analysis of variance (ANOVA) was performed on the concentrations of dieldrin, chlordane and Total DDT. Significant differences were observed in the concentration of dieldrin ($P < 0.001$) and chlordane ($P = 0.003$) with years, while no significant difference was observed for Total DDT ($P = 0.157$) and year. The concentration of Total DDT was stable, with a mean concentration of $10 \mu\text{g kg}^{-1}$ DS for the three years. No consistent trends can be observed for the frequency of detection, the mean nor the maximum concentrations over the three years of the study.

The OCPs can be categorized into three groups;

- (1) Frequently detected >5%—dieldrin, chlordane, and DDE
- (2) Low frequency of detection <5%—heptachlor, and HCB; and
- (3) Rarely detected <1%—DDT, DDD, aldrin, and lindane.

Table 2

Concentration of PCBs in sewage sludges globally as reported in the scientific literature reported in $\mu\text{g kg}^{-1}$ DS.

Country year	Method	Analyte	Range $\mu\text{g kg}^{-1}$ DS	Mean $\mu\text{g kg}^{-1}$ DS	Median $\mu\text{g kg}^{-1}$ DS	Reference
USA 1976	GC-ECD	Arochlor 1254	<10 – 23,000	5200	4200	(Furr et al., 1976)
USA 1977	GC-ECD	Arochlor 1016	238,000 – 1,700,000	765,000	*	(Bergh and Peoples, 1977)
USA 1980	GC-ECD	Σ PCBs	1200–6200	3400	3200	(West and Hatcher, 1980)
UK 1982	GC-ECD	Arochlor 1260	20 – 460	160	150	(McIntyre and Lester, 1982)
UK 1984	GC-ECD	Arochlor 1260	10 – 21,500	340	140	(McIntyre and Lester, 1984)
USA 1984	GC-ECD	Σ PCBs	150 – 3600	1200	900	(Mumma et al., 1984)
Netherlands 1984	GC-ECD	(1) PCBs (6) (2) PCBs (17)	210 – 660 390 – 1480	500 880	580 960	(van Luin and van Starkenburg, 1984)
UK 1993	HRGC-ECD	Σ PCBs	106 – 712	292	*	(Alcock and Jones, 1993)
Italy 1993	HRGC-MS	*	210 – 1010	628	565	(Ottaviani et al., 1993)
USA 1994	HRGC-ECD	Σ PCBs	<250 – 4600	<250	<250	(Gutenmann et al., 1994)
Switzerland 1996	HRGC-MS	(1) Co-planar (2) Σ PCBs (7); 28, 52, 101, 118, 153, 138, 180	0.231 – 5.05 43 – 550	* *	* *	(Berset and Holzer, 1996)
Canada 1996	HRGC-MS	Σ PCBs	<10 – 28	*	<10	(Webber et al., 1996)
Ireland 2000	GC-ECD	Σ PCBs	<10 – 105	58	7	(McGrath et al., 2000)
Canada 2003	HRGC-MS	Σ PCBs	<50	*	*	(Bright and Healey, 2003)
UK 2003	HRGC-MS	Σ PCBs	110 – 440	*	*	(Stevens et al., 2003)
France 2004	HRGC-MS	Σ PCBs	70 – 650	*	*	(Blanchard et al., 2004)
Greece 2004	HRGC-MS	Σ PCBs	180 – 765	550	500	(Katsoyiannis and Samara, 2004)
Spain 2005	HRGC-MS	Σ PCBs (7)	3 – 60	*	30	(Abad et al., 2005)

<dl is used if the detection limit has not been supplied in the text, * no data provided.

Table 3Summary statistics of OCP concentrations ($\mu\text{g kg}^{-1}$ DS) in Australian sewage sludges analysed between 2004 and 2006.

Compound	PD	<DL	f	Mean $\mu\text{g kg}^{-1}$ DS	StDev $\mu\text{g kg}^{-1}$ DS	Median $\mu\text{g kg}^{-1}$ DS	Max $\mu\text{g kg}^{-1}$ DS
Aldrin	3	826	0.4	<10	<10	<10	70
Chlordane	227	602	27.4	10	20	<10	290
Dieldrin	567	262	68.4	30	40	20	700
Heptachlor	16	813	2.0	<10	<10	<10	170
HCB	22	807	2.7	<10	10	<10	300
Lindane	0	829	0.0	<10	0	<10	<10
DDT	2	782	0.2	<10	<10	<10	30
DDD	4	780	0.5	<10	<10	<10	60
DDE	103	681	13.1	<10	20	<10	270
Total DDT	112	717	13.5	<10	20	<10	270
Σ PCBs	10	819	1.2	<10	30	<10	410

PD = positive detection, <DL = less than detection limit ($<0.01 \mu\text{g kg}^{-1}$ DS), f = percentage frequency detection; $n = 784$ DDT,DDD,DDE; $n = 829$ Total DDT, Aldrin, chlordane, dieldrin, heptachlor, HCH, lindane.

The overall concentration of all these compounds was consistently low and never exceeded the guideline values for beneficial reuse of sewage sludge. The low frequency of detection for Groups 2 and 3 compounds combined with the low concentrations measured when detected, demonstrates that these compounds are not ubiquitous in Australian sewage sludge. The results of this research should inform future legislative requirements, where compliance monitoring frequency is reduced over a period of time and compliance monitoring for certain compounds may be eliminated entirely.

3.2.2. Polychlorinated biphenyls

The frequency of detection of PCBs in Australian sewage sludge between the years 2004 and 2006 is low and declining, and the concentrations in samples in which PCBs were detected were also low with over 98% of samples having PCB concentrations below $200 \mu\text{g kg}^{-1}$ DS. When PCBs were detected, the concentration of PCBs ranged between 20 and $410 \mu\text{g kg}^{-1}$ DS and had a mean concentration of $260 \mu\text{g kg}^{-1}$ DS. This is lower than all Australian regulations ($500 \mu\text{g kg}^{-1}$ DS) and therefore, according to this parameter these sludges are classified as suitable for beneficial reuse (NRMCC, 2004). Statistically significant differences were observed between PCB concentration and year ($P = 0.001$). Despite the fact that PCBs were only detected in samples from New South Wales and Queensland and from only four WWTPs, the difference between the States was not significant ($P = 0.509$). While PCBs are not frequently detected in sewage sludge they are still contained within Australian infrastructure, and the environmental monitoring of these compounds may still be necessary until they are fully removed and safely disposed. PCBs were detected in 1.2% of the samples analysed and when detected were present at low concentrations.

3.3. Australian sewage sludge time series—1995 to 2006

3.3.1. Organochlorine pesticides

Presented are the OCP concentrations in sewage sludge, analysed approximately weekly at six NSW wastewater treatment plants between the years 1995 and 2006; TS1, TS2, TS3, TS4, TS5. Data from the years 2001 to 2004 have been collected from TS6 ($n = 2266$). The overall summary statistics are presented in Table 4.

Dieldrin, chlordane and Total DDT (primarily DDE) were the main OCPs detected (frequency of detection 69%, 45% and 8% respectively) and they were detected in each of the WWTPs, in all years. OCPs such as aldrin, DDT, DDD, HCB, and lindane were detected infrequently. Lindane was not detected in any of the 2266 sludge samples from six WWTPs between the years 1995 and 2006. Therefore, lindane is not prevalent in Australian sewage sludge from this geographical area and has not been included in the following statistical analysis. Aldrin and heptachlor were rarely detected in over ten years of analysis. Aldrin was detected in 6 of the 2266 sludges analysed (0.26%) and heptachlor was detected in only nine (0.40%), both with maximum concentrations below those restricting land use; aldrin max $410 \mu\text{g kg}^{-1}$ DS, heptachlor $250 \mu\text{g kg}^{-1}$ DS. As a result no further discussion of these compounds will be undertaken.

Dieldrin was the most prevalent compound detected in the data spanning 10 years of analysis, with an overall frequency of detection of 68.6%, ranging between 47.6 and 85.0% for the individual treatment plants. The overall dieldrin concentration from each of the WWTPs wasn't significantly different from one another ($P = 0.327$) with the means ranging between 30 and $100 \mu\text{g kg}^{-1}$ DS. A significant difference was found between years ($P < 0.001$) reducing from a mean concentration of 0.17 mg kg^{-1} DS in 1995 to $<10 \mu\text{g kg}^{-1}$ DS in 2006. A statistically significant linear regression ($P < 0.001$) was obtained that estimates the reduction of dieldrin concentration to be $15.1 \mu\text{g year}^{-1}$ and it is estimated that dieldrin concentration in freshly generated Australian sludges has a half-life of 5.6 years. Factors that will influence the concentration of dieldrin in sewage sludge are the quantities released into the surrounding environment, the mechanisms involved in its environmental transport and its environmental degradation rate. It has taken greater than 14 years following Australian government restrictions, implemented in 1992, for the concentrations of dieldrin in freshly generated sewage sludge to reduce to below detection limits ($<10 \mu\text{g kg}^{-1}$ DS).

Chlordane was the next most frequently detected compound, detected in 45% of samples. The overall mean concentration was $110 \mu\text{g kg}^{-1}$ DS and ranged from <10 to $730 \mu\text{g kg}^{-1}$ DS. There was no significant difference between the chlordane concentration and WWTP mean ($P = 0.729$) but there was a difference between years ($P < 0.001$), reducing from $170 \mu\text{g kg}^{-1}$ DS in 1995 to $<10 \mu\text{g kg}^{-1}$ DS in 2006. A statistically significant linear regression ($P < 0.001$) was performed that estimates the chlordane concentration to be declining by $18.1 \mu\text{g year}^{-1}$ and has an estimated half-life of 4.7 years. It has taken at least 11 years for the concentration of chlordane in freshly generated Australian sewage sludge to reduce to less than detectable concentrations ($<10 \mu\text{g kg}^{-1}$ DS) following government restriction introduced in 1995.

The frequency of detection of Total DDT was lower than in the collated data survey. While Total DDT was found in 7.7% of samples, DDT, DDD and DDE were detected in only 1.3, 3.9 and 5.7% of samples. Similar to the collated data, DDE was the most prevalent of the DDTs, with the exception of WWTP TS6. At TS6, both DDT and DDD were detected in 4.6 and 15.8% of samples respectively. This finding is unusual and suggests that DDT was being used within the area or that DDT had been recently released as a by-product of other pesticides such as dicofol. DDT and DDD were rarely detected in samples from the other WWTPs, which is similar to the data from the collation of Australian OCP sewage sludge concentrations (2004–2006) survey.

The concentration of Total DDT was significantly different between WWTPs ($P < 0.001$) ranging from 10 to $40 \mu\text{g kg}^{-1}$ DS. Total DDT concentration was also significantly different between years ($P < 0.001$), peaking in 1996 with a mean of $70 \mu\text{g kg}^{-1}$ DS and declining to $<10 \mu\text{g kg}^{-1}$ DS in 2006.

The concentrations of dieldrin and chlordane in sewage sludge generated from each of the WWTP analysed between the years 1995 and 2006 were all highly correlated ($P < 0.05$). The other feature that is apparent is the change in detection limit between 1995 and 2001 ($dl = 10 \mu\text{g kg}^{-1}$ DS) and 2001–2006 ($dl = 10 \mu\text{g kg}^{-1}$ DS). The lower frequency of detection (88% and 97% detection of dieldrin and chlordane in 2006 reducing to 69% and 22% in 2006 respectively) and the statistical methodology employed (i.e. treating $<dl$ as half the detection limit) combine so that the mean concentrations are lower when comparing the two periods. Given that the sampling events did not occur on the same day or with the same frequency the statistical analysis of this data is problematic. Treatment of samples less than the detection limit will also affect the quality of the statistical analysis. Regardless of the statistical approach undertaken the trend observed is consistent. Values below the detection limit treated as missing data (*) amplify the apparent concentration and does not utilize all the available information. Treating values below the detection limit as zero is also

Table 4Summary statistics of OCP and PCB concentrations ($\mu\text{g kg}^{-1}$ DS) in Australian sewage sludge sampled from six wastewater treatment plants from the same geographic region between the years 1995 and 2006.

Variable	f	<DL	Mean $\mu\text{g kg}^{-1}$ DS	StDev $\mu\text{g kg}^{-1}$ DS	Median $\mu\text{g kg}^{-1}$ DS	Max $\mu\text{g kg}^{-1}$ DS
Aldrin	0.26	2260	40	50	<10	70
Dieldrin	68.58	712	<10	<10	20	770
Chlordane	44.84	1250	10	20	<10	29
Heptachlor	0.40	2257	<10	<10	<10	170
HCB	7.72	2091	<10	10	<10	300
Lindane	0.00	2266	<10	0	<10	<10
DDT	1.30	2237	<10	<10	<10	30
DDD	3.93	2177	<10	<10	<10	60
DDE	5.69	2137	<10	20	<10	270
Total DDT	7.68	2092	<10	20	<10	270
Σ PCBs	5.6	2140	5.6	300	<10	1400

f = percentage detection, <DL = less than detection limit ($<10 \mu\text{g kg}^{-1}$ DS).

unrealistic, particularly with respect to changes in the detection limit in 2001. Treating values below the detection limit as half the detection limit was seen as the best approach as it incorporates this data into the overall average.

The analytical approach was to create a categorical variable of month-year using half the detection limit. All samples were analysed at the same laboratory and the change in detection limit occurred simultaneously for all WWTPs. Using this categorical variable, it was determined that not only are the concentrations of dieldrin and chlordane correlated within each of the WWTPs, they are also correlated between the respective WWTPs ($P < 0.05$) (Fig. 1). This work provides clear evidence that dieldrin and chlordane have moved in same way from the environment and into the WWTPs. Within Australia, both these compounds were primarily used on wood in domestic properties for the treatment of termites. The correlation between the rainfall and concentration was tested and no correlation was established.

3.3.2. Polychlorinated biphenyls

The concentration of PCBs in sewage sludge was measured approximately weekly at six WWTPs from the same geographic region (radius 100 km) between the years 1995 and 2006 (TS1–TS5) and another WWTP between the years 2001 and 2004 (TS6). The overall summary statistics are presented in Table 4.

PCBs were detected in four of the six WWTPs and at a much greater frequency in TS5 (16.0%) and TS1 (11.0%) than the other WWTPs or determined as part of the 2004–2006 data collation survey. PCBs were not detected in two WWTPs (TS2, TS6) and detected at low frequency in the remaining two (TS3, TS4). A correlation analysis was performed to determine if a relationship existed between PCB concentrations and WWTPs, but no correlation was observed. Overall, the mean and maximum concentration decreases with time. When PCBs were detected in sewage sludge it was usually below Australian regulatory levels for beneficial reuse. Only ten samples out of 2266 had concentrations that exceeded the guideline value of $500 \mu\text{g kg}^{-1}$ DS, Fig. 2a (NRRMMC, 2004).

While no statistical correlation was determined between PCB concentrations and WWTP, two PCB spikes occurred. The first spike in PCB concentration occurred simultaneously between September 1999 and August 2000 in WWTPs TS1 and TS5 for approximately 1 year (Fig. 2a Mean PCB concentrations ($\mu\text{g kg}^{-1}$ dw) at six NSW WWTPs (between the years 1995 and 2006) from the same geographic region. Error bars represent maximum and minimum concentrations observed; if the mean was less than detection limit then this value has been used for graphical purposes. Red lines represent Australian ($500 \mu\text{g kg}^{-1}$ dw) and European ($800 \mu\text{g kg}^{-1}$ dw) polychlorinated biphenyl contaminant limit (European Commission, 2001; NRRMMC, 2004) (Fig. 2b). Since these WWTPs are approximately 100 km apart, it is possible that PCBs were released into the local environment during this period or that PCBs were inappropriately disposed of into the sewerage system. The length of time (1 year) taken for PCBs to fall below the detection limit may provide some indication of the time taken for PCBs to be depurated from the environment, once released. A second smaller spike in concentration appears at three WWTPs (TS1, TS5, and TS4) all occurring in 2002. The time of PCB occurrence and duration was more variable than the first PCB spike (Fig. 2b).

4. Conclusion

Dieldrin, chlordane and DDE were frequently detected in Australian sewage sludges ($n = 829$) between 2004 and 2006. They were detected in 68%, 27% and 13% of samples at maximum concentrations of 770, 290 and $270 \mu\text{g kg}^{-1}$ DS, respectively. Many other OCPs were rarely detected and lindane was not detected in any samples in this survey, including in analysis of sludge over ten years from six WWTPs ($n = 2266$). Again, in sludges monitored for OCPs and PCBs generated from 6 WWTPs of the same geographic region between 1995 and 2006,

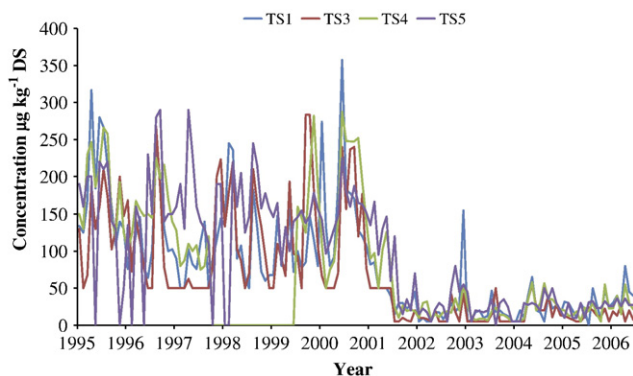


Fig. 1. Comparison of dieldrin concentration mg kg^{-1} DS between the years 1995 and 2006 at WWTP TS1, TS2, TS3, TS4 and TS5.

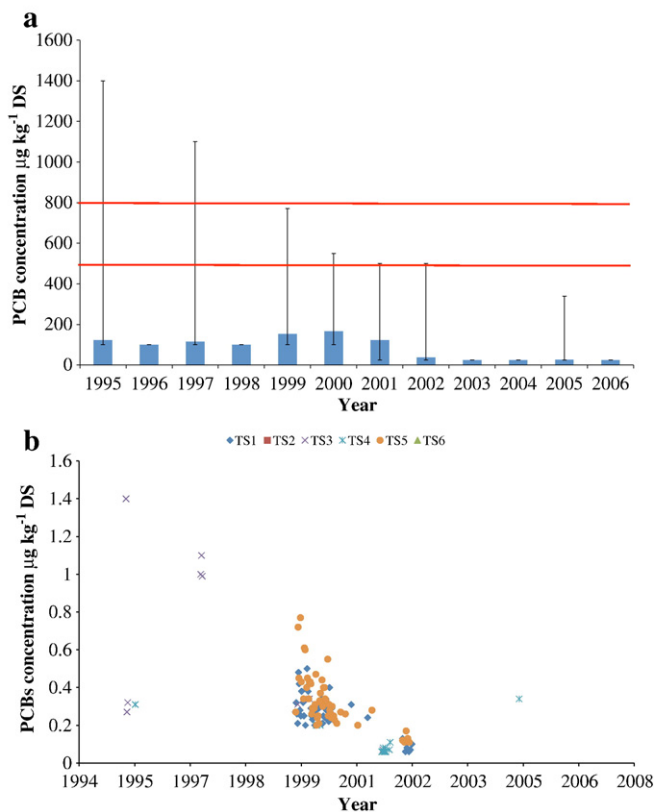


Fig. 2. a Mean PCB concentrations ($\mu\text{g kg}^{-1}$ DS) at six NSW WWTPs (between the years 1995 and 2006) from the same geographic region. Error bars represent maximum and minimum concentrations observed; if the mean was less than detection limit then this value has been used for graphical purposes. Red lines represent Australian ($500 \mu\text{g kg}^{-1}$ DS) and European ($800 \mu\text{g kg}^{-1}$ DS) polychlorinated biphenyl contaminant limit (European Commission, 2001; NRRMMC, 2004). b PCB concentrations ($\mu\text{g kg}^{-1}$ DS) at six Australian WWTPs between 1995 and 2006 from the same geographic region. Sample concentrations below detection limit have not been plotted and comprise 94.4% of samples analysed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dieldrin and chlordane were the most common compounds detected. Other compounds such as lindane, aldrin HCB, heptachlor, DDT and DDD were rarely detected. PCBs were detected in 5.6% of samples and only ten were above the threshold of $500 \mu\text{g kg}^{-1}$ DS limit preventing beneficial reuse. A statistically significant correlation ($P < 0.05$) was found between the concentration of dieldrin and chlordane in sludges from each WWTP, as well as, between WWTPs of the same geographic region. This study has demonstrated that dieldrin and chlordane have moved from the environment into WWTP in the same way and likely as a result of the same environmental influence i.e., temperature, rainfall, air pressure. It has taken more than 16 and 11 years for dieldrin and chlordane to reduce to less than detectable concentrations in freshly generated sewage sludge in Australia following government restrictions respectively.

This research demonstrates OCPs and PCBs are no longer causing significant contamination of Australian sewage sludge. Of the OCPs that were regularly detected, the concentrations and frequency of detection have been declining since 1995. Given this, there is a case for reviewing the necessity of compliance monitoring for these compounds in sewage sludge when destined for beneficial reuse. The authors suggest that the frequency of compliance monitoring for OCPs and PCBs can be reduced and phased out over a five to ten-year period.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envint.2010.01.004.

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