Dioxin-like chemicals in bivalves and sediment collected from around Australia

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Introduction

The aquatic environment is a significant sink for persistent organic pollutants including dioxin-like chemicals. Besides continuous investigations into sources of higher chlorinated PCDD that have initially been found in soils[1], and later in dugong and sediments[2] little is known about the levels of dioxin-like chemicals in Australia's aquatic environment.

In 2002 the National Dioxin Program (NDP) was commissioned by the Department of Environment and Heritage, Australia. One focus of the NDP was to evaluate background levels of dioxin-like chemicals in Australia's environment. One component of the 'Environmental Levels' project aimed to identify dioxin-like chemicals in the aquatic environment including bivalves collected in both marine, estuarine and freshwater systems. Here we report results from the NDP aquatic study with a particular emphasis on the levels of dioxin-like chemicals in bivalves and sediments respectively in areas from where the bivalves were collected.

Sampling Sites and Sampling

The study was part of the NDP and focused on background concentrations of dioxin-like chemicals in regions and aquatic environments that represent different land-uses or contamination levels. While sediment samples were collected from more than 60 locations nationally, bivalves were only found and collected from 18 of these locations. Samples were collected in metropolitan (urban and industrial),

agricultural and remote areas including from freshwater, estuarine and marine environments. Noteably, in some cases (for example in the bivalves collected from the Sydney harbour area), the collection of the sediments was undertaken independantly from collection of the bivalves. Bivalve molluscs were collected whole and unopened by sampling personnel. They were placed immediately on ice and returned frozen to EnTox. On arrival at the EnTox laboratory they were removed from shells using a solvent-washed shucking knife and placed in solvent washed jars before being refrozen for transport to the Australian Govenment Analytical Laboratories (AGAL).

Sediment samples were collected using a stainless steel coring device designed to ensure relatively simple sample collection and maintain a consistent methodology between sampling personnel. The coring device also ensured sediment samples were not handled by sampling personnel, thereby minimising contamination problems. Composite samples were collected at each sampling location, consisting of 10 pooled sediment cores collected over a transect of about at least one km (i.e. distance between cores was greater 100 m). Composite samples were then freeze-dried and sieved through a 2 mm sieve prior to transport to AGAL for analysis.

Analysis of PCDD/PCDF and dioxin-like PCB

The analytical methodology for the determination of PCDD/Fs and PCBs that was used for sample analysis is based on quantification of the analytes through isotopic dilution techniques and is modified from those described by the USEPA methods 1613B and 1668A, respectively. Briefly, samples were freeze dried and mixed to produce a homogenous sample. A sub-sample was removed and spiked with a range of isotopically labeled surrogate standards, and then extracted with toluene using an accelerated solvent extractor. Clean up was effected by partitioning with sulfuric acid then distilled water. For sediment samples sulphur was removed using copper or silver nitrate dispersed on silica gel. Further purification steps included column chromatography on acid and base modified silica gels, neutral alumina and carbon dispersed on celite. After cleanup, the extracts were concentrated to near dryness. Prior to injection, internal standards were added to each extract. Samples were analysed on GCMS (Agilent 6890 GC coupled with a MAT95XL HRMS). A DB-5 (J & W Scientific, Folsom, CA, USA) capillary column (60m x 0.25mm i.d., film thickness 0.25um) was used as the primary analytical column with a DB-Dioxin (J & W Scientific, Folsom, CA, USA) capillary column (60m x 0.25mm i.d., film thickness 0.15um) used as the secondary analytical column for quantification of those 2,3,7,8- CDD & CDF

congeners not completely resolved on the DB-5 column. Resolution was maintained at 10,000 (10 % valley definition) throughout the sample sequence. Multiple ion detection (MID) experiments were performed in the electron impact mode with monitoring of the exact masses of either M+ [M+2]+ or [M+4]+ ions for native and labeled compounds. Individual congeners are identified using the GC retention time and ion abundance ratios with reference to internal standards.

Total organic carbon (TOC) was determined by the Queensland Health Scientific Services (QHSS) laboratory according to a standardized procedure (QHSS, 1996). Inorganic carbonates were removed using acid-catalysed digestion (10% HCl, 1% $FeCl_2$ at 70^{o}C). The remaining material was dried and combusted in the LECO induction furnace with subsequent detection of CO_2 (LECO WR12 CO_2 detector.)

Results and Discussion

Dioxin like chemicals in Australian bivalve samples

Dioxin-like chemicals could be detected in all 18 bivalve samples covering the different regions and various environments of Australia. A summary of the results is provided in Table 1. The levels, expressed as TEQ, ranged from 0.0068 – 3.4 pg TEQ_{Humans} g^{-1} wwt. Highest levels of dioxin-like chemicals were found in a bivalve sample collected from Port Jackson. Although the data are too few to evaluate clear trends with respect to regions or land-use, the geographical distribution of the dioxin-like chemicals in bivalve samples is shown in Figure 2.

Table 1 Summary of result of dioxin-like chemicals in bivalves collected from freshwater, estuarine and marine locations. Results are expressed as median, maximum and minimum values (including 0.5 LOD). Results are given as both wet weight and expressed on a lipid basis (*resampling suggested much lower levels).

	Total (18)		Fresh.(1)		Estuarine (11)		Marine (6)	
	Fresh mass basis	Lipid basis	Fresh mass basis	Lipid basis	Fresh mass basis	Lipid basis	Fresh mass basis	Lipid basis
TEQ_{DF+PCB} FISH Inc. ½ LOD values (pg TEQ g^{-1})	**0.16** (0.0043–1.2)	**12** (0.32–50)	**0.023**	**1.3**	**0.20** (0.0043–1.2)	**12** (0.86–50)	**0.080** (0.012–0.90)	**10** (0.32–38)
TEQ_{DF+PCB} HUMAN Inc. ½ LOD values (pg TEQ g^{-1})	**0.36** (0.0068–3.4*)	**22** (0.59–140)	**0.035**	**2.0**	**0.45** (0.0068–2.7)	**24** (1.4–140)	**0.087** (0.022–3.4)	**24** (0.59–140)
∑PCDD/PCDF Inc. ½ LOD values (pg ∑PCDD/-F g^{-1})	**26** (0.43–230)	**2100** (27–9900)	**9.8**	**540**	**29** (0.43–230)	**2400** (86–9600)	**26** (1.0–90)	**2000** (27–6800)
∑PCB Inc. ½ LOD values (pg ∑PCB g^{-1})	**180** (2.7–7300)	**13000** (150–300000)	**19**	**1100**	**320** (4.7–5600)	**21000** (150–290000)	**89** (2.7–7300)	**8200** (300–300000)

Overall, levels of dioxin-like chemicals in bivalves were well below the benchmark value of 25 pg g^{-1} fresh wt for dioxins in fish set by the U.S. FDA, which was identified as a level with no serious health effects; and therefore also much below the 50 pg g^{-1} fresh wt action level set by the US FDA (US EPA, 1985 quoted in Wenning et al. 2003). However it should be noted that 3 of the 18 bivalve samples exceeded 1 pg TEQ g^{-1} wwt (based on $TEQ_{Mammals}$), a level that, according to information obtained from the US FDA by Wenning et al. (2003), warrants further investigation. Notably, one of the samples originated from a relatively pristine area near the southern part of the Spencer Gulf where levels of dioxin-like chemicals in sediments were extremely low. Re-sampling and analysis of bivalves from this location showed much lower levels in the second oyster sample from this area. The elevated results in the first sample remain unexplained.

Comparison between sediment and bivalve data

Hydrophobic persistent chemicals tend to accumulate in the hydrophobic phases of the environment, such as the organic carbon of the sediment and the lipid in biota. A plot of the concentration in the biota (lipid basis) versus the concentration in the sediment (on a TOC basis) again indicates a general trend of increasing concentration in biota with increasing levels in sediments. However, the levels in biota are, tentatively, less than what would be expected from the sediment concentration for 16 of the 18 sampling sites (Figure 1). This may indicate that the

sediments have become a secondary source for the dioxin-like chemicals in most of these environments. Looking at the accumulation of individual congeners, the data clearly demonstrate a higher accumulation of the lower chlorinated PCBs and PCDD/Fs in biota compared to sediments. For example, using bivalve and sediment samples from the Lower Yarra River, the biota/sediment concentration ratio (pg g^{-1} lipid / pg g^{-1} TOC) range from greater than 1 (lower chlorinated PCBs and TCDF) to below 0.05 for hepta- and octachlorinated PCDD/Fs.

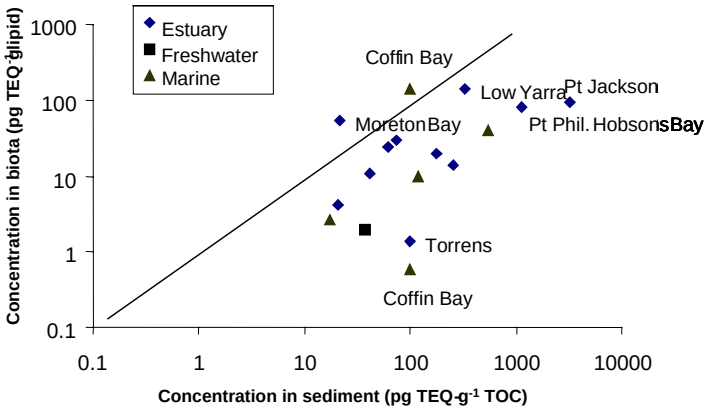

Fig. 1 Plot of the concentration of dioxin-like chemicals in biota (lipid basis) versus the concentration in sediments (TOC basis). (Line represents unity)

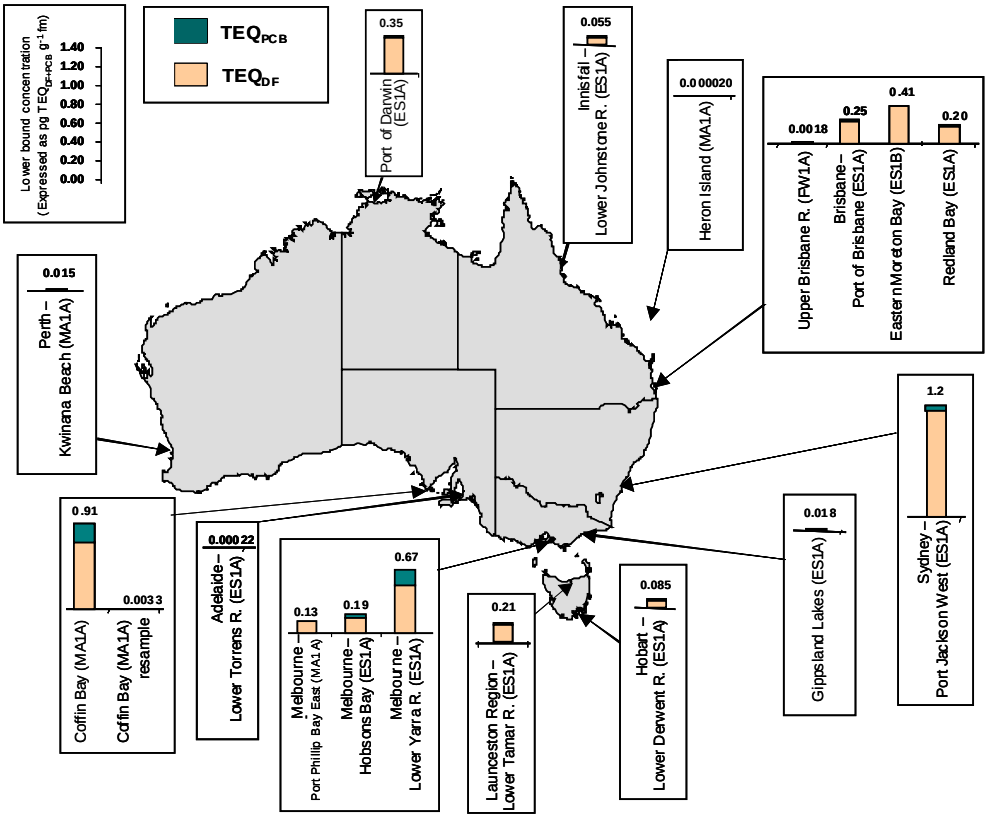

Figure 2 Geographical distribution of the dioxin-like chemicals in bivalve samples (expressed as lower bound $TEQ_{DF\&P}$ using the TEF for fish.)

Dioxin like chemicals in bivalves - comparison with previous studies.
Limited data are available on dioxin-like chemicals in bivalves from Australia. Mosse and Haynes[3] collected samples from inshore waters of Bass Strait adjacent to the Victorian coastline but only analysed for TCDDs and TCDFs which were not detectable. Haynes and Toohey[4] evaluated the temporal variation of PCDD/Fs in cultured mussels from Port Phillip Bay, Victoria and reported levels between 0.23 and 0.71 pg I-TE g^{-1} wwt which is slightly higher than the concentration that we found in this study in bivalves from Hobson Bay and Eastern Port Phillip Bay (i.e. 0.19 and 0.13 pg TEQ g^{-1} wwt using human TEFs).

In the New Zealand Organochlorines Program levels of dioxin-like chemicals in bivalves from 26 sites in estuaries around New Zealand were collected and a

median level of 0.032 pg I-TE g^{-1} wwt with levels ranging from 0.015 to 0.26 pg I-TE g^{-1} wwt (0.5 LOD) were found[5].

From Europe, concentrations ranging between 0.07 and 0.13 pg I-TE g^{-1} wwt were reported for bivalves collected from a north-south transect of the western Adriatic Sea[6]. Karl et al. [7]reported 0.39 pg TEQ g^{-1} wwt in pooled mussel samples from Denmark whereas Knutzen et al. [8] found between 1.6 and 3.0 pg TEQ g^{-1} wwt in mussels collected from Norway's south coast. The German Umweltbundesamt reported that PCDD/Fs in 13 mussel samples from the River Elbe showed levels ranging from 0.55 – 0.96 pg I-TE g^{-1} wwt [9].

From North America, Wenning et al.[10] reported levels of PCDD/Fs in commercial oysters from Arcata Bay, California with highest mean levels up to 2.1 pg TEQ g^{-1} wwt in June 2002 in Pacific Diploids and up to 0.22 pg TEQ g^{-1} wwt in samples of the same species collected 4 months later. Litten et al. [11]showed results for mean values of 81 mussel samples collected in 4 different parts of the New York/New Jersey area with mean levels ranging from 1.5 – 38 pg TEQ g^{-1}. Notably the authors did not provide whether the results are on a dry weight, wet weight or lipid weight basis hence we could not include it here until further information is available.

From China Wu et al. [11] analysed PCDD/Fs in mussels from a lake and found 0.34 and 0.43 pg I-TE g^{-1} wwt. The Japanese survey study also included bivalves in their study however in their reporting combined all biota results including fish with levels from 0.002 – 30 pg TEQ g^{-1} wwt (median 1.1 pg TEQ g^{-1} wwt) [12]. Tsutsumi et al. [13] determined the levels of PCDD/Fs in oysters and short-necked clams and found concentration ranging from 0.22 – 1.1 and 0.07 – 0.14 pg TEQ g^{-1} wwt respectively. Finally, Choi et al. [14] analysed oysters and mussels from marine locations in Korea and reported levels from 0.001 – 1.2 pg TEQ_{DF} g^{-1} wwt.

Figure 3 depicts the levels of dioxin-like chemicals in bivalve samples from different continents.

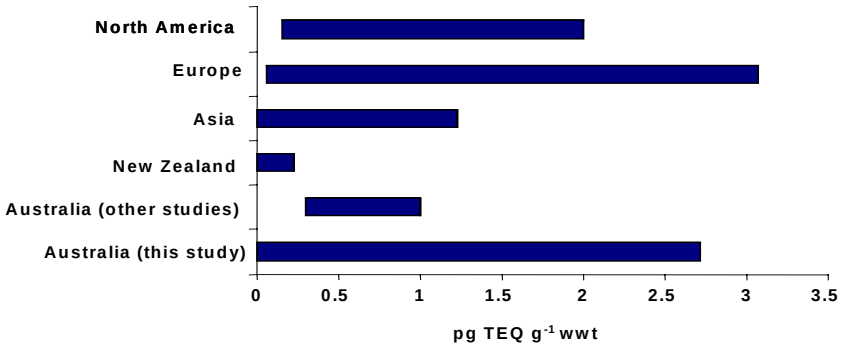

Figure 3 Comparison of levels of dioxin-like chemicals in bivalve samples from different continents. It should be noted that the maximum value in this study includes dioxin-like PCBs whereas most other studies did not included PCBs. The PCBs contributed up to 80% of the TEQ.

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