LEVELS PBDES IN SEDIMENT FISH AND SEA EAGLES FROM SYDNEY HARBOUR, AUSTRALIA: SPATIAL PATTERNS AND PROFILES.

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Introduction

The catchments and shoreline of Sydney Harbour / Parramatta River experienced extensive industrial development (Proudfoot 1982) as it was the major area of colonisation and population growth in Australia since the early 19th century. This has lead to significant pollution of the environment and its biota by metal and organic contaminants (Roach and Runcie, 1998; Scanes and Roach, 1999; Birch and Taylor, 1999; Birch and Taylor 2000). Notably, recent studies have found high concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs) in its biota (Symons 2005; Roach et. al, 2007). The presence of this contamination has lead to the closure of commercial fishing and the placing of restrictions on the catching and consumption of fish by recreational fishers (FSANZ, 2006; Manning et al. 2007) throughout Sydney Harbour.

For polybrominated diphenyl ethers (PBDEs), for which there is growing concern about their toxicological effects, we have limited data for Sydney Harbour. Our data for these compounds in the environment are restricted to a few samples taken as part of and Australia wide assessment (Toms et al. 2006). A key goal for environmental managers is the reduction and control of the levels of persistent organic pollutants to improve ecosystem health as these compounds may cause significant ecological and human health effects. It is necessary therefore to describe the nature and extent of the existing problem (Hardman-Mountford, et. al., 2005) and establish which congeners are prevalent in the environment in order to develop management strategies which apportion resources and effort in a manner to achieve optimal environmental benefit.

The aim of this study was to help identify patterns of PBDE contamination in sediment to describe environmental contamination gradients, identify the most prevalent congeners. We also compared the profiles of the environmental data with those for two species of fish and one species of bird to identify which of the PBDE congeners have the potential to pose risk to biota.

Materials and methods

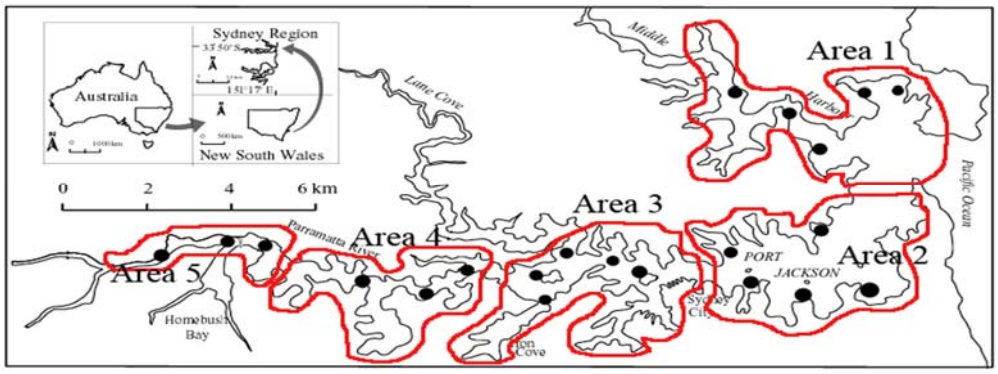
Approximately 200ml of sample from the top 3 cm of the sediment profile was taken from twenty one sites in Sydney Harbour using a stainless steel van veen grab. Sample sites were ascribed at random within one of five zones in Sydney Harbour. Each zone was in the same water body and representative of areas with similar levels of urban/industrial development (Figure 1). Biota samples were analysed to compare congener profiles. Fish samples were collected as part of a wider study for dioxins (Roach et. al, 2007) and the samples described here are for two species, bream (*Acanthopagrus australis*) and flounder (*Pseudorhombus jenynsi),* which were taken from area 4. The White-bellied sea eagle (*Haliaeetus leucogaster*) specimens were opportunistically collected as dead specimens from Homebush Bay on the Parramatta River this study has been described in detail elsewhere (Manning et al., *in press*).

Sample preparation and analysis of PBDEs

The sample preparation and analytical methodology for the determination of PBDEs in sediment and biota have previously been described in detail (Symons et al. 2004; Toms et al 2006; Manning et al., *in press*) and was based on USEPA Method 1614. Briefly, the samples were freeze dried to remove moisture and mixed thoroughly. After spiking with isotopically labelled surrogates, the samples were extracted with toluene using Accelerated Solvent Extraction (ASE). Clean up was effected by partitioning with sulphuric acid then distilled water. Further purification was performed using column chromatography on acid, base and neutral modified silica gels and basic alumina. After cleanup, the extract was concentrated to near dryness. Immediately prior to injection, internal standards were added to each extract, and an aliquot of the extract was injected into the gas chromatograph (GC). The analytes were separated by the GC and then detected by a high-resolution (≥10,000) mass spectrometer (HRGC/HRMS). The quality of the analysis was assured through reproducible calibration and testing

of the extraction, cleanup, and GC/MS systems. The method is 'performance based'. The detection limits and quantification levels in this method were usually dependent on the level of interferences rather than instrumental limitations. The laboratory is accredited to ISO 17025:2005 for these PBDEs and participates in international interlaboratory studies to benchmark its performance.

Figure 1 Map of Sydney Harbour showing the sampling areas and individual sampling sites.



Results and discussion

Industrial and urban development is most concentrated in the upstream areas of Sydney Harbour (e.g. Areas 3-5). The ∑PBDE concentrations reflect the transition from more to less urban develop with concentrations in Area 1 being less than 5000 pg g^{-1} dw whereas concentrations in Areas 4 and 5 were greater than 40000 pg g^{-1} dw (Table 1). The highest ∑PBDE concentration measured was 87200 pg g^{-1} dw. This is the highest concentration measured in Australia and the mean ∑PBDE found in Areas 4 and 5 exceeds the highest concentrations previously reported for Sydney and Australia (Toms *et al*. 2006). The sampling by Toms et al. (2006) was limited in detail with respect to Sydney Harbour because of its emphasis on Australia wide patterns and as such the values reported here merely reflect the more comprehensive sampling done for this study rather than any change since that study was undertaken.

When compared to the worldwide median values the median ∑PBDE value (excluding BDE 209) for Sydney Harbour was 1200 pg g^{-1} dw which is typical of other areas with a high degree of urban / industrial development (Toms *et al*. 2006). A total of 22 congeners were detected in the sediments but the dominant congener in all areas of Sydney Harbour was BDE 209 which represented between 89 and 96 % of the ∑PBDE. This is typical of the composition of PBDEs reported from other areas of Australia and consistent with previous reports for Sydney (Toms *et al*. 2006). The median BDE 209 value for Sydney Harbour was 25300 pg g^{-1} dw which is among the higher values reported worldwide (Toms *et al*. 2006). Of the other congeners BDE 206 (1.7%), BDE 207 (1.0%), BDE 99(0.6%) and BDE 47(0.4%) generally had the next highest concentrations but the levels were low compared to those reported worldwide (Toms *et al*. 2006).

When the sediment profiles were compared to those in two species fish and one species of bird from Areas 4 and 5 there was a large difference in composition (Figure 2). ∑PBDE concentrations for bream (*Acanthopagrus australis*) and flounder (*Pseudorhombus jenynsi)* were generally low 26 and 36.3 ng g^{-1} lipid. The profiles were dominated by BDE 47 (69%) and BDE 100 (15%) in bream and BDE 47 (57%), BDE 99 (15%) and BDE 100 (8%) in flounder. BDE 209 did bioaccumulate in the fish but it only represents a smaller percentage of the ∑PBDE being 2% in bream and 5% in flounder. The mean concentration of ∑PBDE was high in the White-bellied sea eagle (*Haliaeetus leucogaster*) being 26700 ng g^{-1} lipid (Manning et al., *in press*). The profile differed from both species of fish having a far greater number of congeners being detected and a lower dominance of BDE 47 (31%). They also had notable levels of BDE 183 (21%), BDE 153 (17%) which were low or absent in the fish but they did have comparable levels of BDE 100 (11%). The greater number of congeners found were probably due the overall higher levels of PBDEs in the sea eagles thereby allowing relatively lower level congeners to be detected.

The relatively low percentage of BDE 209 in the biota, compared to that in the environment, reflects that it is a large molecule and with a low tendency to bioaccumulate. Whilst it has been suggested that its physiochemical properties would preclude it from bioaccumulating these results add to the growing

list of studies which have found it in biota (D'Silva et al., 2004). The BDEs other 209 and 207 individually represented less than 1% of the ∑PBDE in the environment but there was marked variation among congeners in biota. This variation among species appears to reflect variation in physicochemical properties as a function of the degree of bromination and probably variation in pathways of exposure and transformation in fish and birds. The relatively high percentage of BDE 47 in biota compared to sediment is indicative of its stability and propensity to bioaccumulate. This congener is frequently found at high concentrations in organisms of a high trophic level (D'Silva et al., 2004) as was shown in the White-bellied sea eagle. The other dominant congener in fish and sea eagles was BDE 100 and to a lesser extent BDE 85 they generally had similar percentages in fish and sea eagles. The higher brominated BDEs 183 and 153 were found at a relatively higher percentage in sea eagles compared to the fish and the environment. The biota data emphasize the potential from lower brominated BDEs even at low environmental concentrations and highlight the need for monitoring biota as well as environmental levels.

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Table 1. Summary of the mean (±SD) concentrations (pg g-1 dw) PBDE congeners in sediment from Sydney Harbour. ND = not detected.

	Area 1		Area2		Area3		Area4		Area5	
BDE17	5.5	5.1	21.8	14.0	20.4	5.7	42.0	19.7	165.7	142.6
BDE28-33	ND	ND	ND	ND	ND	ND	56.7	98.1	57.7	32.3
BDE47	ND	ND	64.0	143.1	44.0	98.4	300.0	305.1	576.7	386.6
BDE49	9.8	13.4	69.6	43.9	61.2	17.5	115.7	41.8	316.7	181.8
BDE66	ND	ND	10.0	9.9	10.8	3.0	17.9	7.1	50.0	39.9
BDE71	0.8	1.8	1.9	4.2	5.2	1.2	2.1	3.6	16.3	11.7
BDE85	ND	ND	ND	ND	1.0	2.3	3.3	5.7	34.7	30.7
BDE99	ND	ND	58.0	129.7	133.2	30.4	250.0	88.9	906.7	776.8
BDE100	ND	ND	41.8	27.1	34.6	8.8	57.7	23.1	177.3	149.7
BDE153	3.4	7.6	24.4	17.4	25.4	7.1	71.3	52.7	180.0	121.7
BDE154	ND	ND	30.6	18.7	26.2	5.1	42.0	12.2	125.0	116.9
BDE180	ND	ND	ND	ND	ND	ND	10.3	17.9	2.9	5.1
BDE183	13.0	9.2	40.6	21.2	47.4	36.0	237.0	239.7	250.0	91.7
BDE184	ND	ND	ND	ND	ND	ND	ND	ND	5.3	9.2
BDE 196	ND	ND	36.0	80.5	13.6	30.4	156.7	171.6	173.3	75.1
BDE 197	4.6	10.3	30.8	28.3	42.0	35.3	126.7	135.8	158.3	74.2
BDE201	ND	ND	20.8	20.7	13.0	17.8	40.0	34.8	52.0	45.1
BDE203	ND	ND	38.0	85.0	14.6	32.6	70.0	121.2	113.3	196.3
BDE206	61.6	56.4	592.4	716.3	592.0	209.8	740.0	417.6	823.3	287.3
BDE207	44.0	40.8	162.6	162.5	250.0	66.3	406.7	181.5	690.0	141.8
BDE208	12.6	17.3	46.2	78.0	96.8	27.4	223.3	179.3	333.3	116.8
BDE209	3112	2697	28854	28734	35600	16192	45000	33173	42733	4724
∑PBDE	3267	2826	30143	30246	37031	16550	47969	33966	47941	5137

Figure 2 Comparison of the composition of PBDEs in sediment, fish and birds. Note: Plotted on log scale to emphasize the BDEs which make up a small percentage of the ∑PBDE. Non detects shown as zero for convenience.