Environment International 35 (2009) 1142–1149

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Biomagnification of anthropogenic and naturally-produced organobrominated compounds in a marine food web from Sydney Harbour, Australia

Sara Losada [a,b], Anthony Roach [c], Laurence Roosens [a], Francisco Javier Santos [b], Maria Teresa Galceran [b], Walter Vetter [d], Hugo Neels [a], Adrian Covaci [a,e,*]

[a] Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[b] Analytical Chemistry Department, University of Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
[c] Ecotoxicology and Environmental Contaminants Section, Department of Environment and Climate Change, NSW, PO Box 29 Lidcombe NSW 1825, Australia
[d] Institut für Lebensmittelchemie (170b), Universität Hohenheim, Garbenstrasse 28, D-70593 Stuttgart, Germany
[e] Laboratory of Ecophysiology, Biochemistry and Toxicology, Department of Biology, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

ARTICLE INFO

Article history:
Received 18 March 2009
Accepted 10 July 2009
Available online 8 August 2009

Keywords:
Biomagnification
PBDEs
Brominated natural compounds
MeO-PBDEs
PBHDs
Fish
Invertebrates
Australia
Food chain

ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and naturally-produced organobrominated compounds, such as methoxylated PBDEs (MeO-PBDEs), have been scarcely studied in the Southern Hemisphere. Yet, sources of the latter group of compounds were found in Southern regions, specifically in Australia. The environmental distribution and biomagnification potential of organobrominated compounds were therefore investigated in a representative aquatic food chain (invertebrates and fish) from the Sydney Harbour, Australia. Mean PBDE concentrations ranged from 6.4 ng/g lipid weight (lw) in squid to 115 ng/g lw in flounder. BDE 47 was the dominant congener, followed by BDE 100. Mean levels of MeO-PBDEs (sum of congeners 2'-MeO-BDE 68 and 6-MeO-BDE 47) were as high as 110 ng/g lw in tailor, with a slight dominance of 2'-MeO-BDE 68. Polybrominated hexahydroxanthene derivates (PBHDs), another class of naturally-produced compounds, were found at variable concentrations and ranged from 4.7 ng/g lw in fanbelly and 146 ng/g lw in tailor. The tribrominated PBHD isomer dominated in the samples, except for luderick and squid. The lower levels of PBDEs found in luderick from the harbour compared to those obtained from the upper Parramatta River indicated a terrestrial (anthropogenic) origin of PBDEs, while the higher levels of MeO-PBDEs and PBHDs in the samples from the harbour confirmed the marine (natural) origin of these compounds. The highest trophic magnification factor (TMF) was found for sum PBDEs (3.9), while TMFs for sum MeO-PBDEs and sum PBHDs were 2.9 and 3.4, respectively. This suggests that biomagnification occurs in the studied aquatic food chain for anthropogenic brominated compounds, but also for the naturally-produced organobromines.

1. Introduction

In the first half of the 20th century, much of the industry in New South Wales (Australia), including chemical manufacturing, was located around Sydney Harbour and its tributaries, especially in the Parramatta River (Proudfoot, 1982). As a result, previous studies have found significant levels of polychlorinated dibenzo-*p*-dioxins/furans, polychlorinated biphenyls (PCBs) and other chlorinated hydrocarbons in fish, crustaceans and molluscs (Roach and Runcie, 1998; Manning et al., 2007; Roach et al., 2007). The presence of this contamination led to the closure of commercial fishing and restrictions to recreational fishers throughout Sydney Harbour (Manning et al., 2007).

The presence of brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), in the Australian environment has been poorly documented, and more specifically in Sydney Harbour, the largest urban centre in Australia, it has not yet been studied in detail in aquatic biota. In Australian marine wildlife, levels of PBDEs in mammals and other biota, including fish, were lower compared with other corresponding studies (Law et al., 2006; Hermanussen et al., 2008). Concentrations of PBDEs found in sediments were higher in estuarine>freshwater>marine environments, and high in soils dominated by industrial and urban use (Toms et al. 2008a). PBDE concentrations in Australian sewage sludge were similar to European findings (Clarke et al., 2008). Although dust was suggested as an important pathway for PBDE human exposure especially in childhood (Toms et al. 2007; Harrad et al., 2008, Sjödin et al., 2008), the primary cause of PBDE exposure of Australian infants seemed to be maternal transfer and postnatal exposure through breast milk (Toms et al., 2008b).

Additionally, naturally-produced organobrominated compounds (e.g. methoxylated PBDEs, MeO-PBDEs), have been reported in Australian marine environment, but not investigated in detail. MeO-PBDEs were suggested to have a natural origin (Teuten et al., 2005), being detected in sponges (Vetter et al., 2001a, 2002) and algae (Kuniyoshi and Ymaada, 1985; Malmvärn et al., 2005) and could be

* Corresponding author. Fax: +32 3 820 2722.
E-mail address: adrian.covaci@ua.ac.be (A. Covaci).

0160-4120/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envint.2009.07.008

measured in fish and marine mammals worldwide. Other compounds observed in sponges from Australia and the Mediterranean Sea were the polybrominated hexahydroxanthenes (PBHDs) (Melcher et al., 2005, 2007). They were detected in fish from the Mediterranean Sea and Norway (Hiebl et al., 2006; Vetter et al., 2007), but also in fish oil dietary supplements (Covaci et al., 2007). The 2,4,6-tribromoanisole (TBA) was found in red marine algae collected in Australia and is considered also a naturally-produced compound. Similarly, MHC-1, another halogenated compound with suggested natural origin, has been found in marine mammals and fish worldwide (Vetter et al., 2001b, 2008).

For some of these compounds, bioacumulation and biomagnification in aquatic food webs have been documented. Such studies have been carried out previously for PBDEs (Boon et al., 2002; Wolkers et al., 2004), HBCD (Morris et al., 2004) (21), and very recently for MeO-PBDEs (Kelly et al., 2008a; Weijs et al. 2009) and for brominated bipyrroles (Pangallo and Reddy, 2009). For other compounds included in the present work (e.g. PBHDs, TBA and MHC-1), there are only a few studies that have investigated their behaviour in aquatic food webs.

Given the presence of anthropogenic sources of PBDEs in Sydney Harbour and the presence of the naturally-produced compounds (e.g. MeO-PBDEs), their uptake by organisms in the marine food web is possible. Yet, the significance of uptake by lower trophic level organisms (e.g. detritivores and herbivores) and biomagnification by higher trophic level organisms (e.g. piscivores) is unknown. The present study focused on invertebrate and fish species from different trophic levels of the Sydney Harbour food web. We investigated the concentrations, congener profiles and biomagnification of both anthropogenic (i.e. PBDEs and HBCD) and naturally-produced organobromine compounds (i.e. MeO-PBDEs, PBHDs, TBA, and MHC-1) in these species. In addition, we examined the spatial distribution of contaminants in the Sydney Harbour in one fish species to assess the importance of proximity to the marine environment on the levels of these compounds.

2. Materials and methods

2.1. Location and samples

Eight marine species, including six fish species, one crustacean and one mollusc, were sampled from several locations in the eastern part of Sydney Harbour, a marine dominant estuary (Roy et al., 2001) located in New South Wales, Australia (Fig. 1). Samples of one of the species, luderick, were also obtained from the brackish (approx. 15–20‰ salinity) upper Parramatta River. The organisms were sampled between January and March 2006 using commercial fishing methods, immediately transferred to the laboratory and frozen at −20 °C until sub-sampling. A number of 4–5 composite samples of muscle tissue, each being composed from 10 adult individuals, were prepared for each species per sampling location and were freeze-dried prior to analysis.

The species selected represented differing trophic levels, confirmed using stable isotope analysis (Fig. 2). The fish included flounder (*Pseudorhombus jenynsii*), tailor (*Pomatomus saltator*), yellowfin bream (*Acanthopagrus australis*), fanbelly leatherjacket (*Monocanthus chinensis*), sea mullet (*Mugil cephalus*) and luderick (*Girella tricuspidata*). The crustacean species was the blue swimmer crab (*Portunus pelagicus*) and the squid, Loligo squid (*Loligo* sp).

2.2. Methods

The organobrominated compounds targeted for analysis included PBDE congeners (IUPAC no. 28, 47, 49, 66, 85, 99, 100, 153, 154 and 183), α-HBCD, MeO-PBDE congeners (2'-MeO-BDE 28, 3'-MeO-BDE 28, 4'-MeO-BDE 17, 4-MeO-BDE 42, 3-MeO-BDE 47, 5-MeO-BDE 47, 6-MeO-BDE 47, 4'-MeO-BDE 49, 2'-MeO-BDE 68, 4-MeO-BDE 90, 5'-MeO-BDE 99, 6'-MeO-BDE 99, 5'-MeO-BDE 100, 4'-MeO-BDE 101, 4'-MeO-BDE 103, 6-MeO-BDE 140, 3-MeO-BDE 154, and 6-MeO-BDE 157), 2,4,6-tribromoanisole (TBA), PBHD isomers (2,7-dibromo-4a-bromomethyl-1,1-dimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene (triBHD) and 2,5,7-tribromo-4a-bromomethyl-1,1-dimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene (tetraBHD) and MHC-1.

The procedures used for extraction and clean-up were based on the methods described by Voorspoels et al. (2003), Covaci et al. (2007) and Covaci et al. (2008), with minor modifications to allow the analysis of various organobrominated compounds. Briefly, between 3 and 6 g of freeze-dried tissue was extracted by hot Soxhlet with a mixture of acetone/*n*-hexane, and the extract was further cleaned on 8 g of acidified silica and 1 g of Florisil. After concentration, the cleaned extract was analyzed by gas chromatography-mass spectrometry (GC-MS) by electron-capture negative ion (ECNI) mode (*m/z* 79 and 81) using a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column. For confirmatory purposes, the full scan ECNI spectra (*m/z* 70–650) were acquired using the same chromatographic conditions. For further confirmation of MeO-PBDEs and PBHDs, the extracts were injected into a GC/MS system operated in electron ionization (EI) mode and equipped with a 25 m × 0.22 mm × 0.25 μm HT-8 capillary column (SGE, Zulte, Belgium). The mass spectrometer was used in selected ion monitoring mode with two most intense ions (typically from the molecular ion cluster) acquired for each homologue group or isomer.

Quality Assurance and Quality Control was performed through the analysis of procedural blanks, replicates samples and a standard reference material (SRM 1945, PBDEs in whale blubber). For the replicates and SRM 1945, the relative standard deviations (RSD) were <10%. Recoveries of analytes were between 70 and 100% (RSD <10%) as measured by spiking experiments ($n = 5$) at a concentration of 20 ng/g lipid weight (l w) for each individual compound. Additionally, the method performance was assessed through successful participation in two interlaboratory exercises organized in 2005 and 2007 by NIST (PBDEs in marine mammals). Procedural blanks of PBDEs were consistent (RSD <20%) and therefore the mean value of each analyte in the procedural blanks was used for subtraction. MeO-PBDEs and PBHDs were not present in the procedural blanks. After blank subtraction, the limit of quantification (LOQ) was set at 3*SD of the value obtained in the procedural blanks. Method LOQs ranged from 0.2 to 0.3 ng/g lw for individual PBDE and MeO-PBDE congeners and were 2 ng/g lw for each PBHD isomer.

2.3. Stable isotopes

Ground and dried muscle samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ using a continuous flow-isotope ratio mass spectrometer (Micromass Isoprime EuroVector EA300, Manchester, UK). Stable isotope ratios of samples ($\delta^{13}C$ or $\delta^{15}N$ values [‰]) were assessed against the reference standards ANU sucrose for $\delta^{13}C$ values [‰] and atmospheric N_2 for $\delta^{15}N$ values [‰]. Isotope ratios are expressed as either $\delta^{13}C$ or $\delta^{15}N$, with $\delta X = [(R_{sample}/R_{standard}) - 1] \times 1000]$, where X is ^{13}C or ^{15}N and R is the corresponding ratio $^{13}C/^{12}C$ or $^{15}N/^{14}N$.

Trophic magnification factors (TMFs) were calculated to assess biomagnification potential (Klecka and Muir, 2008). HBCD and MHC-1 were excluded from this analysis because a large percentage of samples had concentrations of these compounds at the LOQ and therefore a reliable analysis could not be done. TMFs were calculated using the following equation: $TMF = e^b$, where b is the slope derived from the ln-linear relationship between the geometric means of the lipid-normalized tissue concentrations (GM) for each species and the corresponding trophic level (TL) in equation $\ln(GM) = a + b^*TL$. Geometric means instead of individual data were used to reduce the influence of non-normally distributed data and obtain normalized mean values on the same scale as the original data. Ln-transformation of contaminant data prior to this analysis has similarly been used by Hop et al. (2002). TL was determined by comparing the enrichment of the stable isotope $\delta^{15}N$ in

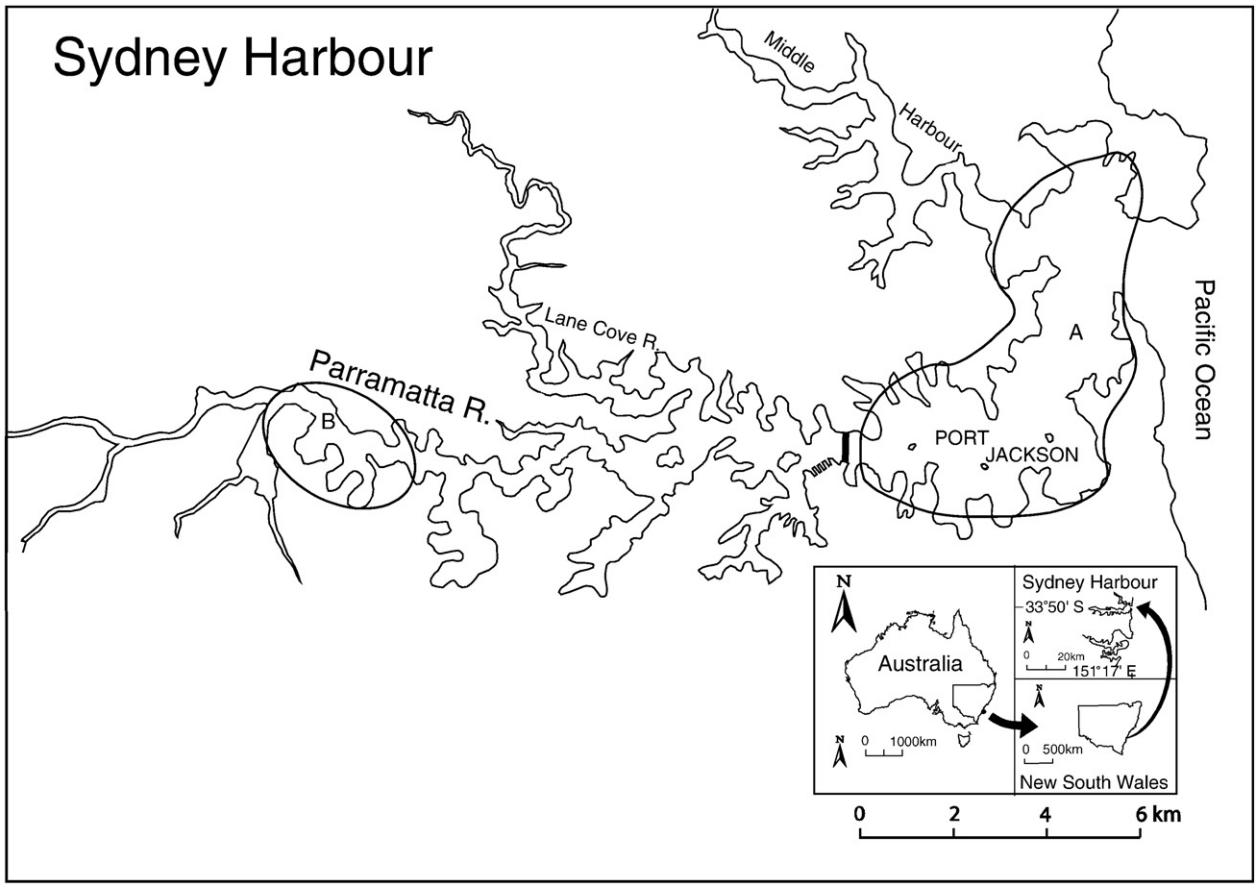

Fig. 1. Map of Sydney Harbour (i.e. Port Jackson and Parramatta River) showing the areas where fish were sampled. Area A is the harbour entrance and area B is the upper Parramatta River.

each species relative to a primary herbivore (Fisk et al., 2001; Hop et al., 2002), in this study a grazing gastropod (*Bembicium auratum*) ($\delta^{15}N = 7.4 \pm 0.32$; mean ± SD), which was assumed to have TL = 2 (Roach, unpublished data). A constant isotopic enrichment factor of 3.4 was used, as suggested by Haukas et al. (2007), for marine food webs. The final relationship obtained for calculating the TL was: $TL = 2 + (\delta^{15}N - 7.4/3.4)$. Overall, lipid-normalized concentrations were used to correct the influence of lipid content, which ranged from 0.3% (flounder) to 14.7% (tailor).

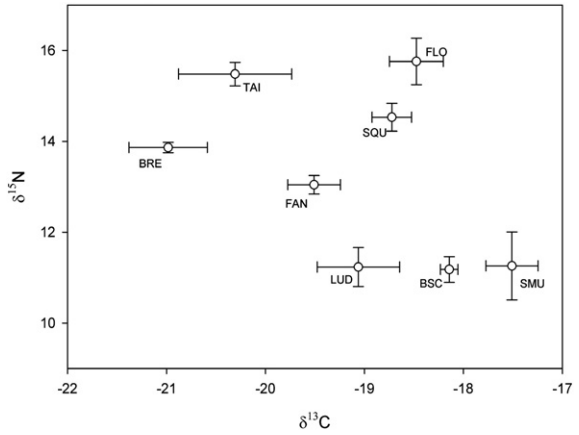

Fig. 2. Plot of the mean $\delta^{15}N$ and $\delta^{13}C$ concentrations (± SD) from stable isotope analysis of aquatic biota analysed in this study. FLO = flounder (*Pseudorhombus jenynsii*), TAI = tailor (*Pomatomus saltator*), BRE = yellowfin bream (*Acanthopagrus australis*), FAN = fanbelly leatherjacket (*Monocanthus chinensis*), SMU = sea mullet (*Mugil cephalus*), LUD = luderick (*Girella tricuspidata*), BSC = blue swimmer crab (*Portunus pelagicus*) SQU = Loligo squid (*Loligo* sp).

2.4. Statistical analyses

Differences in mean concentrations of contaminants in luderick between populations from the harbour and upper Parramatta River were tested using one-way ANOVA. Pearson's correlation coefficients were calculated to obtain the correlations. Concentrations of individual compounds below LOQ were substituted with a value equal to ½ LOQ. All analyses were done using STATGRAPHICS Plus for Windows 4.1 (Statistical Graphics corp., Rockville, MD, USA).

3. Results and discussion

Stable isotope analysis confirmed that the species used in this study represented a range of trophic positions in the Sydney Harbour food web (Fig. 2). Blue swimmer crab, sea mullet and luderick had the lowest $\delta^{15}N$, but varying $\delta^{13}C$ values, indicating that these species are lower in the food chain and have different carbon sources. Blue swimmer crab and sea mullet are largely detritivores, whereas luderick is largely herbivorous. Fanbelly leatherjacket and bream are lower order predators, whereas squid, tailor and flounder are feeding at a higher trophic level. These species also had varying $\delta^{13}C$ values indicating that their carbon sources and therefore their contaminant exposure pathway also varied.

3.1. PBDEs

The highest concentrations were found in flounder and tailor (piscivorous; mean 115 and 107 ng/g lw respectively), followed by bream (piscivorous; 88 ng/g lw), all of them from the highest TLs (Table 1). These concentrations are higher than levels found in Queensland, Australia for tailor (37 ng/g lw) and bream (43 ng/g lw) (Hermanussen

Table 1
Average concentrations of major organobromine compounds (ng/g lw) in various marine species from the Sydney Harbour (Australia).

ng/g lw	LOQ	FLO (n=5)	FBL (n=4)	SQU (n=4)	SMU (n=5)	TAI (n=4)	LUD (n=5)	BSC (n=5)	BRE (n=5)
BDE 28	0.20	2.7	3.8	0.5	1.1	1.2	0.5	0.2	2.0
BDE 49	0.20	4.4	0.3	0.2	0.92	5.5	0.3	0.1	1.7
BDE 47	0.20	78.2	13.2	3.7	17.9	71.6	15.2	11.1	60.0
BDE 66	0.20	1.4	0.6	0.3	0.4	1.3	1.0	1.1	1.7
BDE 100	0.20	18.1	2.4	0.8	4.1	15.0	3.5	1.5	15.3
BDE 99	0.20	4.5	2.4	0.1	0.8	7.3	1.5	1.9	1.4
BDE 85	0.30	1.1	0.3	0.2	0.5	0.5	0.4	0.1	0.9
BDE 154	0.30	3.7	0.5	0.4	1.5	3.4	0.9	0.3	3.7
BDE 153	0.30	1.4	0.3	0.2	0.6	1.6	0.6	0.2	1.6
sum PBDEs		115.4 (63.6)	24.0 (5.0)	6.4 (1.6)	27.8 (13.7)	107.3 (41.2)	24.0 (14.1)	16.4 (3.8)	88.4 (44.5)
2'-MeO-BDE 68	0.20	15.5	0.2	4.9	7.5	66.5	21.9	0.5	0.2
6-MeO-BDE 47	0.20	10.3	0.5	4.0	5.3	43.6	22.6	1.8	10.6
sum MeO-PBDEs		25.8 (14.9)	0.7 (0.6)	8.9 (5.0)	12.8 (10.3)	110.1 (13.9)	44.5 (14.2)	2.3 (1.1)	10.8 (4.3)
TriBHD	2.00	54.2	3.7	16.4	38.02	90.5	5.8	11.5	12.3
TetraBHD	2.00	14.5	1.0	42.7	13.2	55.6	28.5	1.5	5.8
sum PBHDs		68.6 (43.6)	4.7 (3.5)	59.1 (34.6)	51.3 (57.4)	146.0 (34.6)	34.3 (17.2)	13.0 (12.8)	18.1 (7.6)
2,4,6-Tribromo-anisole (TBA)	0.20	19.2 (7.5)	26.3 (27.8)	13.2 (3.3)	30.1 (24.6)	11.7 (5.9)	13.9 (1.9)	29.3 (34.6)	28.4 (3.1)
HBCD	2.00	1.0 (0)	3.0 (2.6)	1.0 (0)	2.7 (0.9)	1.6 (0.9)	1.0 (0)	1.0 (0)	1.4 (0.8)
MHC-1	0.20	1.3 (0.2)	1.0 (1.1)	0.2 (0.1)	0.7 (0.8)	1.6 (1.0)	0.2 (0.3)	0.1 (0)	0.7 (0.5)

Values in brackets represent standard deviations. Values below LOQ were replaced by ½*LOQ. The following species were investigated: *P. jenynsii* (FLO), *P. saltator* (TAI), *A. australis* (BRE), *M. chinensis* (FBL), *Loligo* sp (SQU), *P. pelagicus* (BSC), *M. cephalus* (SMU), *G. tricuspidata* (LUD).

et al., 2008), but similar to those found in bream from Victorian estuaries (56–250 ng/g lw) (EPA Victoria, 2007). In contrast, fanbelly and luderick (omnivorous/herbivorous) or sea mullet (detritivorous) had lower mean concentrations of PBDEs (24, 24 and 28 ng/g lw, respectively), which were similar to levels found in previous studies for Australian mullet (16 ng/g lw, Hermanussen et al., 2008; 62 ng/g lw, EPA Victoria, 2007).

Blue swimmer crab and squid had total PBDEs concentrations considerably lower than those obtained for fish species (16 and 6.4 ng/g lw, respectively). The low contamination in squid was also seen in other samples from this region, in which lower levels of PBDEs in squid were found compared to other species (Roach et al., 2008). Concentrations observed in the blue swimmer crab were in the range of those observed for mudcrab (10–64 ng/g lw) (Hermanussen et al., 2008). Stable isotope analysis indicated that the blue swimmer crab is largely detritivorous and squid probably consumes similar prey as to mid- to high trophic level fish. Our results indicate also that squid has a low potential to accumulate PBDEs or a high capacity to eliminate them.

The eight PBDE congeners detected in biota were those dominating in the technical Penta-BDE mixture (DE-71) (La Guardia et al., 2006). The high relevance of DE-71 was reflected by the general dominance of BDE 47 in all species and the failure to detect BDE 183 (the key-congener in technical Octa-BDE) (Table 1). BDE 47 contributed between 65 and 68% of the total PBDEs in flounder, tailor and bream, which are at a higher TL (Fig. 2). BDE 100 was found in the fish (9.1–17.3% of the studied PBDEs) at a similar range as in DE-71 (11.5%). Aside from these two congeners, the PBDE pattern was shifted towards the early-eluting PBDEs. For instance, the ratios of BDE 153 to BDE 154 in DE-71 were altered. BDE 153 is more abundant in DE-71 than BDE 154, while the latter generally dominated in fish. The most significant shift was observed for BDE 99 which amounted to 43% of the eight PBDEs to DE-71, while its contribution in the samples ranged only from 1.6 to 11.5%. PBDEs were biotransformed by the reductive debromination as suggested in previous publications (Voorspoels et al., 2003; Stapleton et al., 2004). By contrast, BDE 28 and BDE 47 significantly increased in relevance, with the sum of BDE 28 and BDE 47 contributing with ~70% (66–72%) to the PBDE load. Samples with comparably low BDE 47 contribution were those with the highest BDE 28 contribution (FBL SQU) (Fig. 3).

3.2. HBCD

Levels of HBCD in all samples were very low with concentrations under or close to LOQ. The highest concentrations were seen in fanbelly leatherjacket and sea mullet, with 3.0 and 2.7 ng/g lw, respectively. The samples with the highest HBCD concentrations were not those bearing the highest PBDE load. HBCD has been detected previously in a high trophic level pelagic fish, the skipjack tuna from the Asian-Pacific region, at concentrations from <0.1 to 45 ng/g lw (Ueno et al., 2006), but clearly these higher levels are not reflective of sources in Sydney Harbour.

3.3. MeO-PBDEs

Although congeners from tri- to hexabrominated MeO-PBDEs were analyzed, only two tetrabrominated congeners (2'-MeO-BDE 68 and 6-MeO-BDE 47) could be consistently measured above LOQ in all species (Table 1). The highest concentrations of 2'-MeO-BDE 68 and 6-MeO-BDE 47 (110 ng/g lw for the sum of the 2 MeO-PBDE congeners) were observed in tailor, which is largely piscivorous. Fanbelly leatherjacket and luderick are known to feed on various macroalgae which is a potential source of MeO-PBDEs, but they also feed on varying amounts of macroalgal-associated invertebrate fauna. They showed a large variation in concentrations: luderick showed levels comparable with flounder (45 and 26 ng/g lw, respectively), whereas those found in fanbelly leatherjacket were the lowest observed (0.7 ng/g lw). These differences could be due to their different diets visible in the $\delta^{13}C$–$\delta^{15}N$ plot (Fig. 2) and therefore to the different exposure pathways. Fanbelly leatherjacket is an omnivore feeding more in the pelagic food chain than in the benthic food chain. Corresponding to the $\delta^{15}N$ content, highest concentrations were found for tailor and flounder, followed by bream and squid (Fig. 3). The exceptions were sea mullet and luderick, both with high concentrations of MeO-PBDEs relative to their TL. These species may have increased concentrations of these compounds because they have direct feeding link to a source of MeO-PBDEs. Mullet feed largely on detrital material and luderick are often associated with sea grass communities which are similarly linked to the benthic environment.

All eight species studied had different ratios of 2'-MeO-BDE 68 to 6-MeO-BDE 47 (Table 1), although in general, 2'-MeO-BDE 68 was found at similar or slightly higher concentrations than 6-MeO-BDE 47, with the exception of yellowfin bream. This agrees with reports of marine mammals and reptiles from Australia (Vetter et al., 2001a, 2002; Melcher, et al., 2005), where 2'-MeO-BDE 68 was the dominant congener. Levels of 2'-MeO-BDE 68 and 6-MeO-BDE 47 in samples from Australia and New Zealand were reported in whales (120–3760 ng/g lw and 540–790 ng/g lw), dolphins (220–4160 ng/g lw and 140–1910 ng/g lw), dugong (1–100 ng/g lw and 33 ng/g lw) and shark liver oil (1.6–4 ng/g lw) (Vetter et al., 2001a, 2002; Melcher et al., 2005). Differences among species were probably due to variability in the production of these two congeners from natural sources, in their availability in the food chain and in their uptake or their biotransformation rates.

3.4. PBHDs

Two PBHD isomers (triBHD and tetraBHD), recently reported as belonging to another class of brominated natural products (Hiebl et al., 2006; Covaci et al., 2007; Melcher et al., 2007), were identified in most of the analyzed samples. Concentrations of these two isomers and their ratio exhibited large variation among the investigated species. Tailor had the highest concentrations of total PBHDs (146 ng/g lw) followed by flounder, squid and sea mullet with similar concentrations (69, 59 and 51 ng/g lw, respectively). It is notable that squid and luderick had higher concentrations of tetraBHD than triBHD in comparison with the other species. These concentrations were higher than those found in fish oil dietary supplements (Covaci et al., 2007) (maximum 8.0 and 12 ng/g oil for triBHD and tetraBHD, respectively). However, they were in the range of levels found in fish (between <5 and 1000 ng/g lw for triBHD and between <5 and 560 ng/g lw for tetraBHD) from different locations world-wide (Melcher et al., 2007). In our study, the highest concentrations were found in the species of the highest trophic levels: tailor, flounder and squid (Fig. 3). Surprisingly, the next highest concentrations were found in the species of the lowest trophic levels, sea mullet and luderick (Fig. 2). This could be again related to their feeding habits, since they are reported to be detritivore and herbivore, respectively.

3.5. MHC-1 and TBA

MHC-1 was detectable in all fish samples, but at very low concentrations, up to 1.6 and 1.3 ng/g lw in tailor and flounder, respectively. In squid and crab, it was below LOQ. It is

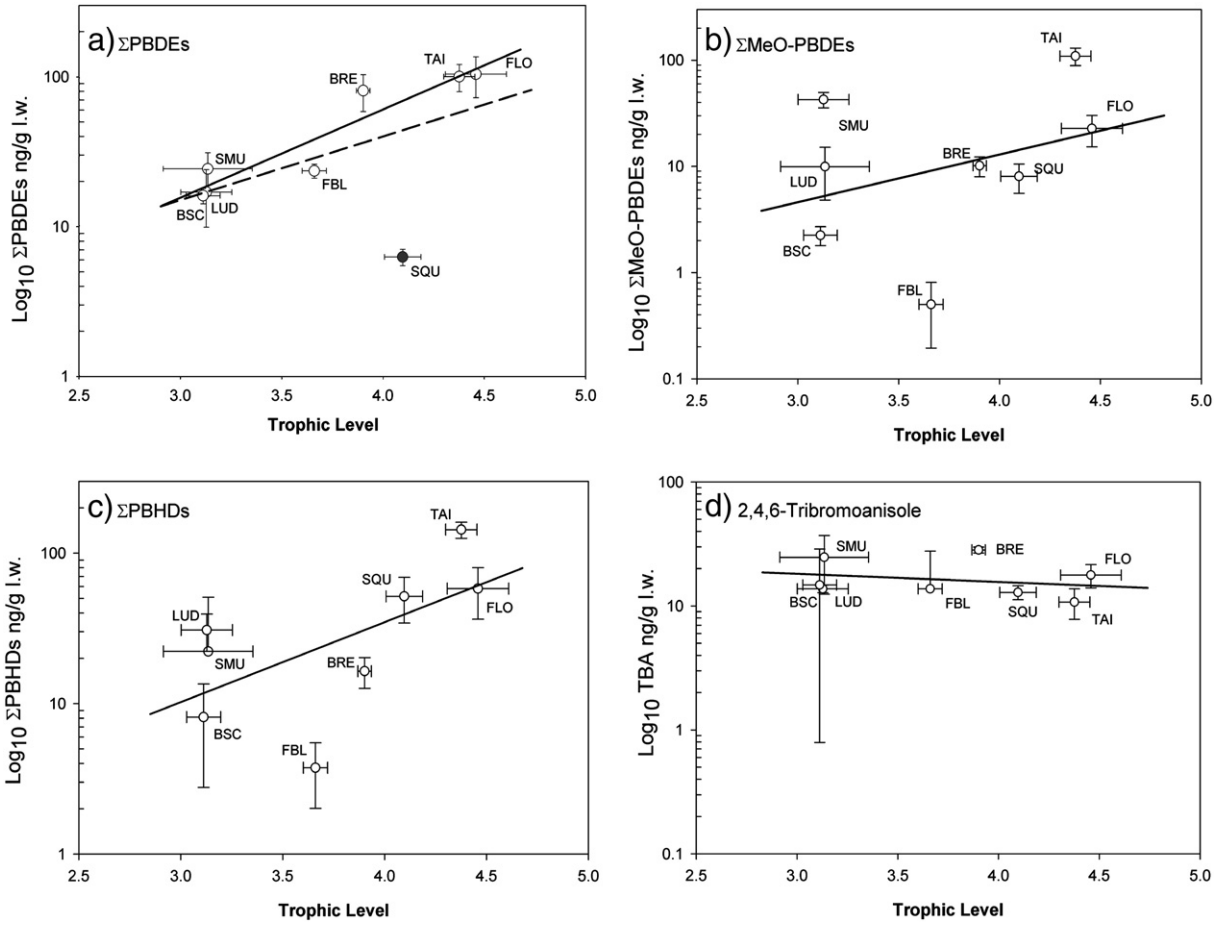

Fig. 3. Plots of the chemical concentrations in organisms from Sydney Harbour (ng/g lipid weight) versus trophic level (TL) for a) PBDEs, b) MeO-PBDEs, c) PBHDs and d) 2,4,6-Tribromoanisole. The solid line represents linear regression of the concentration versus trophic level. Data points are geometric means, and error bars are 1 standard deviation. In the plot a) PBDEs, the dashed line represents the regression with squid included and the solid line is the regression without squid. FLO = flounder (*Pseudorhombus jenynsii*), TAI = tailor (*Pomatomus saltator*), BRE = yellowfin bream (*Acanthopagrus australis*), FAN = fanbelly leatherjacket (Monocanthus chinensis), SMU = sea mullet (*Mugil cephalus*), LUD = luderick (*Girella tricuspidata*), BSC = blue swimmer crab (*Portunus pelagicus*) SQU = Loligo squid (*Loligo* sp).

notable that the levels found in bream were similar to those of sea mullet, although they belong to different TLs and thus having different feeding patterns.

TBA was detected in all samples in concentrations between 12 and 30 ng/g lw. The high concentrations in sea mullet compared to higher trophic level organisms suggest a benthic source and low ability to biomagnify. The concentrations of polybrominated anisoles (2,4-dibromoanisole, TBA and pentabromoanisole) were determined in marine fish, shellfish, and sediments collected in Japan (Watanabe et al., 1983). TBA was found in 14 out of 24 fish and shellfish samples, with a range of 0.1–5.4 μg/g on a wet weight basis.

3.6. Comparison river vs. harbour

In previous studies of contamination of Sydney Harbour, a gradient in the concentrations of dioxins was observed with the decreasing distance from Homebush Bay in the upper Parramata River (Roach et al., 2007; Manning et al., 2007). In that study, luderick showed a strong relationship between distance from source and tissue levels (Roach et al., 2007) indicating that they have a restricted home range and are suitable biomonitors for these substances. For this reason, samples of luderick were collected in the present study from both the harbour entrance and the upper Parramatta River (Fig. 1) to compare levels of brominated compounds in populations with different degrees of marine influence. Results can be seen in Fig. 4, except for HBCD, for which concentrations were below LOQ.

Total mean concentrations of PBDEs were higher in luderick from the upper river zone (59 ng/g lw) than those from the harbour (24 ng/g lw) ($p<0.05$, one-way ANOVA). Congener profiles in fish from both zones were similar: all compounds except BDE 183 were found in all fish samples, with dominance of BDE 47 (39 ng/g lw and 15 ng/g lw mean concentrations for river and harbour, respectively), followed by BDE 100, BDE 99 and 154 (2.9–9.7 and 0.9–3.5 ng/g lw in river and harbour, respectively). Inversely, the mean concentration of MeO-PBDEs in luderick from the harbour zone (45 ng/g lw) was higher than from the upper river zone (13 ng/g lw). The patterns for both groups were also similar, with slightly higher concentrations of 6-MeO-BDE 47. Similarly to MeO-PBDEs, the PBHD concentrations of luderick from the harbour zone (mean of 34 ng/g lw) were also significantly higher than those from the river zone (mean of 4.1 ng/g lw) ($p<0.05$, one-way ANOVA). The concentrations of triBHD in luderick were similar to tetraBHD in the river zone (3.1 and 1.0 ng/g lw, respectively), while the concentrations of triBHD were lower than tetraBHD in the harbour zone (5.8 and 29 ng/g lw). Concentrations of TBA and MHC-1 found in both zones were very similar: 14 ng/g lw in harbour and 17 ng/g lw in river for TBA, and 0.2 ng/g lw and under the LOQ (0.2 ng/g lw) for MHC-1 in harbour and upper river, respectively.

The spatial distribution patterns of PBDEs in luderick corresponded with that in sediment (Roach et al. 2008) and hence can be explained by proximity to the source of contamination in the river zone due to industrial activities. In contrast, natural compounds (MeO-PBDEs and PBHDs) had high concentrations in the zone with greater marine influence, demonstrating the marine origin of these compounds (Haglund et al., 1997; Teuten et al., 2005; Hiebl et al., 2006; Covaci et al., 2007; Melcher et al., 2007). TBA (natural origin) and HBCD (flame retardant), however, showed no difference in concentrations between the harbour and upper river zones. The results for TBA suggest that the producers of this compound maybe be widely distributed through the Sydney Harbour/Parramatta River system. HBCD levels were generally low and therefore this may indicate that there are few sources and no specific source within the system. MHC-1 appears to have a marine signature, but concentrations were low. As MHC-1 shows a trophic effect and luderick are of lower trophic position, a species like flounder, which may also be found upstream and downstream, but is of a higher trophic level, would have been a better choice to study MHC-1.

3.7. Biomagnification

There was a significant relationship between mean tissue concentrations and TL for some PBDEs ($p<0.05$) (Fig. 3; Table 2). The individual PBDE congeners, with exception of BDE 28 and BDE 85, also showed a strong relationship between tissue concentration and TL (Table 2). Squid was eliminated from further calculations as it had an atypical pattern with respect to its trophic level and its presence significantly distorted the general relationship for PBDEs (Fig. 3). For example its inclusion made the R^2 change from 0.90 to 0.54 for PBDEs. These data suggest that squid, a cephalopod with a

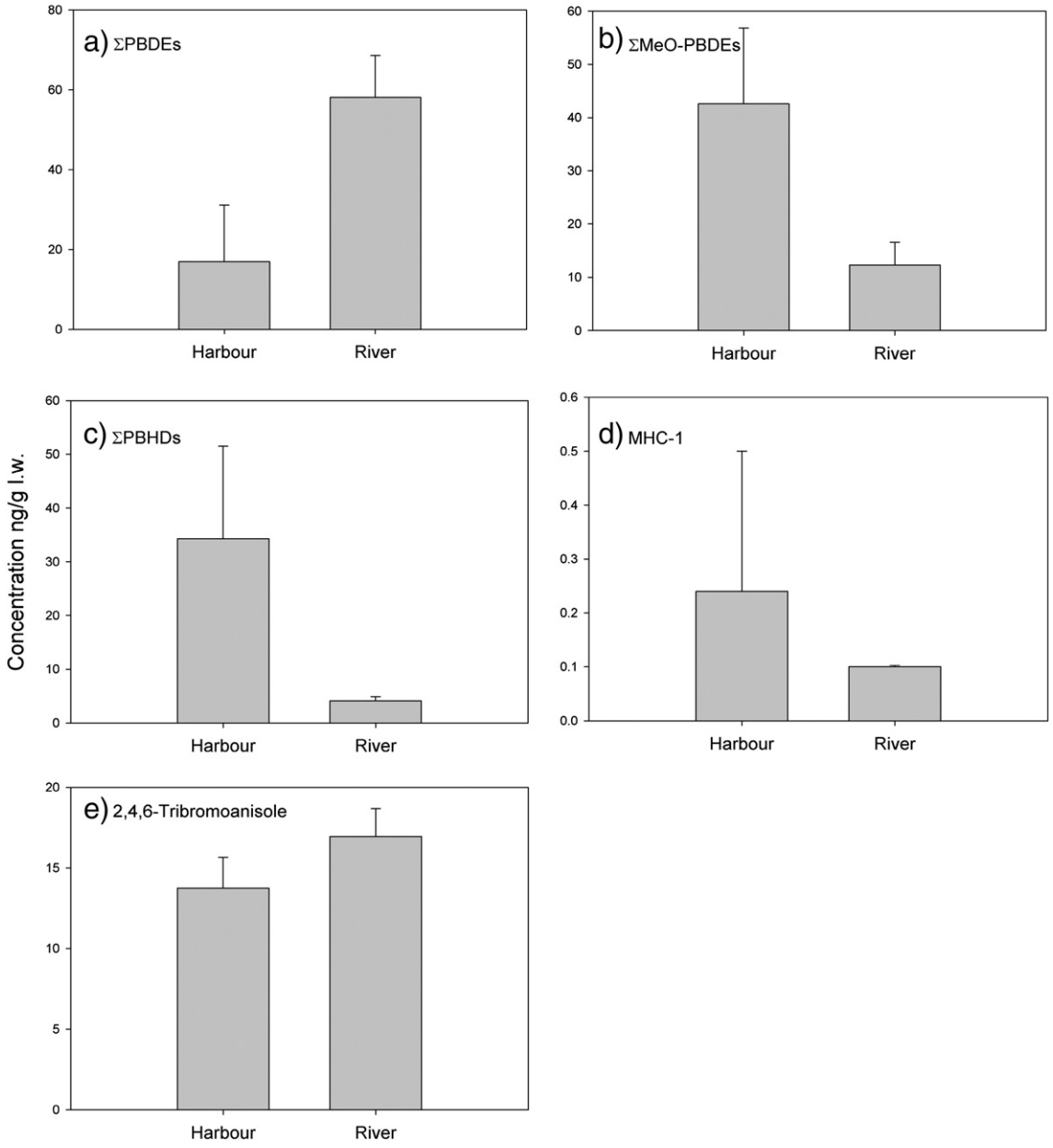

Fig. 4. Plots of the chemical concentrations of in luderick (*Girella tricuspidata*) (ng/g lipid weight) from the harbour entrance and the upper Parramatta River. Data points are geometric means and error bars are 1 standard deviation.

comparatively high TL, may either uptake or excrete PBDEs at different rates compared to the other organisms studied. Debruyn and Gobas (2006) found that squid display a high growth dilution rate. However, this cannot explain the pattern observed here as it appears to be specific to PBDEs, but not the other compounds measured in this study. For the other compounds, no statistically significant relationship with TL was found.

No significant relationships between tissue concentrations and TL were observed for MeO-PBDEs and PBHDs ($R^2 = 0.13$ and 0.35, respectively, $p > 0.1$), mainly due to the low concentrations found in fanbelly leatherjacket relative to its TL (Fig. 3). This species was identified as an herbivore (Fig. 2) and is known to feed among the rocky reef macroalgal communities and therefore linked to the pelagic food web. However, the observed MeO-PBDEs and PBHDs trends in the fanbelly leatherjacket were different to the other pelagic (i.e. bream) or herbivore (i.e. luderick) species. These differences are possibly due to a high capacity to metabolize these two groups of compounds or reflect a lack of an exposure pathway to these naturally occurring compounds.

TMFs calculated for these compounds were greater than 1 (Table 2) largely due to the tailor, having higher concentrations than all other species (Fig. 3). The highest TMFs were found for sum PBDEs (3.9), followed by sum MeO-PBDEs and sum PBHDs (2.9 and 3.4, respectively). In contrast, concentrations of TBA presented no correlations with TL, while the low levels of HBCD did not allow the studying of its behaviour. This contrasts with the negative trend between concentrations and TL was seen for the γ-HBCD diastereoisomer (Tomy et al., 2008) and with the suggested biomagnification potential of HBCD (Morris et al., 2004; Covaci et al., 2006; Tomy et al., 2004.).

The highest TMFs found in this study were for BDE 49 (9.6), followed by BDE 100 (4.7) and BDE 47 (4.1). TMFs for individual PBDEs congeners found in other works ranged from 0.4 to 1.6 (Kelly et al., 2008a), 1.6 and 7.2 (Wan et al., 2008) and 0.3 and 2.5 (Tomy et al., 2008). The TMF of sum PBDEs found in the present study (3.9) was very similar to values found by Law et al. (2006) and Wan et al. (2008) (3.7 and 3.5, respectively). The biomagnification potential of PBDEs was observed previously by Boon et al. (2002), Wolkers et al. (2004) and Burreau et al. (2004, 2006). TMFs found in the present study for MeO-PBDEs were similar to ones found by Kelly et al. (2008b) (2.3 for 2'-MeO-BDE 68; 2.6 for 6-MeO-BDE 47). However, the pattern was different, with higher TMF found for 2'-MeO-BDE 68 than for 6-MeO-BDE 47, probably reflecting the inverse ratios between these two compounds seen in samples from the Southern Hemisphere (Vetter et al. 2002). For triBHD and tetraBHD, TMF values were 4.2 and 3.4, respectively.

In summary, among the organobromine compounds analyzed for this study, PBDEs and MHC-1 exhibited the strongest relationship with trophic level. Trophic relationships were not evident for MeO-PBDEs and PBHDs, although their TMFs indicate capacity of biomagnification. For TBA and HBCD, no relationship was found between the trophic level and concentrations. PBDEs were found to have a terrestrial source, while MeO-PBDEs, PBHDs and MHC-1 seem to have a marine origin, according with their anthropogenic and natural origin, respectively. For TBA and HBCD, no relationship was found with terrestrial or marine contribution. Levels of some of the compounds investigated were very low, especially for HBCD and MHC-1. Due to the relationship of some of them with the trophic level, it would be interesting to study pathways using fish samples from higher trophic

Table 2
Statistical results of the regression analysis between ln (lipid-normalized concentrations) and trophic level (TL) in the studied species.

	Slope	R^2	p	TMF[a]
BDE 28	1.186	0.397	0.130	3.3
BDE 49	2.261	0.756	0.011	9.6
BDE 47	1.402	0.849	0.003	4.1
BDE 66	0.969	0.714	0.017	2.6
BDE 100	1.544	0.777	0.009	4.7
BDE 99	1.147	0.692	0.020	3.2
BDE 85	0.765	0.387	0.136	2.2
BDE 154	1.364	0.569	0.050	3.9
BDE 153	1.022	0.598	0.041	2.8
sum PBDEs	1.360	0.883	0.002	3.9
2´-MeO-BDE 68	1.190	0.090	0.470	3.3
6-MeO-BDE 47	0.867	0.099	0.449	2.4
sum MeO-PBDEs	1.053	0.125	0.390	2.9
TriBHD	1.433	0.473	0.059	4.2
TetraBHD	1.227	0.219	0.243	3.4
sum PBHDs	1.216	0.353	0.121	3.4
2,4,6-Tribromoanisole (TBA)	−0.122	0.043	0.624	0.9

[a] TMF: Trophic magnification factor.

levels or a longer trophic web to obtain clearer results about their behaviour in the food chain.

Acknowledgements

Anke Gelbin (Accustandard) is kindly acknowledged for the generous gift of MeO-PBDE standards. Adrian Covaci was financially supported through a postdoctoral fellowship from the Research Scientific Foundation - Flanders (FWO). Sara Losada is grateful to the Spanish Ministry of Science and Technology for a FPI PhD grant and project no. CTM2006-00753/TECNO. The NSW Department of Primary Industries is thanked for organizing sample collection and providing funds for the stable isotope analysis. Leroy Gonsalves and Amanda Rose (DECC) are thanked for their assistance with sample preparation. Rene Diocares (Griffith University) is thanked for the stable isotope analyses.

References

Boon JP, Lewis WE, Tjoen-A-Choi MR, Allchin CR, Law RJ, de Boer J, et al. Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. Environ Sci Technol 2002;36:4025–32.

Burreau S, Zebühr Y, Broman D, Ishaq R. Biomagnification of PBDEs and PCBs in food webs from the Baltic Sea and the northern Atlantic Ocean. Sci Tot Environ 2006;366:659–72.

Burreau S, Zebühr Y, Broman D, Ishaq R. Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studied in pike (*Esox lucius*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*) from the Baltic Sea. Chemosphere 2004;55:1043–52.

Clarke B, Porter N, Symons R, Marriott P, Ades P, Stevenson G, et al. Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge. Chemosphere 2008;73:980–9.

Covaci A, Gerecke AC, Law RJ, Voorspoels S, Kohler M, Heeb NV, et al. Hexabromocyclodecane (HBCDs) in the environment and humans: a review. Environ Sci Technol 2006;40:3679–88.

Covaci A, Losada S, Roosens L, Vetter W, Santos FJ, Neels H, et al. Anthropogenic and naturally-occurring organobrominated compounds in two deep-sea fish species from the Mediterranean Sea. Environ Sci Technol 2008;42:8654–60.

Covaci A, Voorspoels S, Vetter W, Gelbin A, Jorens PG, Blust R, et al. Anthropogenic and naturally-occurring organobrominated compounds in fish oil dietary supplements. Environ Sci Technol 2007;41:5237–44.

Debruyn AMH, Gobas FPC. A bioenergetic biomagnification model for the animal kingdom. Environ Sci Technol 2006;40:1581–7.

EPA Victoria, 2007. Technical Report: Maribyrnong and Yarra estuaries: Investigation of contaminants in fish. http://epanote2.epa.vic.gov.au/EPA/Publications.nsf/PubDocsLU/ 1094?OpenDocument.

Fisk AT, Hobson KA, Norstrom RJ. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. Environ Sci Technol 2001;35:732–8.

Haglund PS, Zook DR, Hu J. Identification and quantification of polybrominated diphenyl ethers and methoxy-polybrominated diphenyl ethers in Baltic biota. Environ Sci Technol 1997;31:3281–7.

Harrad S, Ibarra C, Diamond M, Melymuk L, Robson M, Douwes J, et al. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zeeland, United Kingdom and United States. Environ Int 2008;34:232–8.

Haukas M, Berger U, Hop H, Gulliksen B, Gabrielsen GW. Bioaccumulation of per-and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. Environ Pollut 2007;148:360–71.

Hermanussen S, Matthews V, Päpke O, Limpus CJ, Gaus C. Flame retardants (PBDEs) in marine turtles, dugons and seafood from Queensland, Australia. Mar Pollut Bull 2008;57:409–18.

Hiebl J, Melcher J, Gundersen H, Schlabach M, Vetter W. Identification and quantification of polybrominated hexahydroxantene derivatives ad other halogenated natural products in commercial fish and other marine samples. J Agric Food Chem 2006;54:2652–7.

Hop H, Borga K, Gabrielsen GW, Kleivane L, Skaare JU. Food web magnification of persistent organic pollutants in poikilotherms and homeotherms from the Barents Sea. Environ Sci Technol 2002;36:2589–97.

Kelly BC, Ikonomou MG, Blair JD, Gobas FAPC. Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. Sci Total Environ 2008a;401:60–72.

Kelly BC, Ikonomou MG, Blair JD, Gobas FAPC. Hydroxylated and methoxylated polybrominated diphenyl ethers in a Canadian Arctic marine food web. Environ Sci Technol 2008b;42:7069–77.

Klecka GM, Muir DCG. Science-based guidance and framework for the evaluation and identification of PBTs and POPs: summary of a SETAC Pellston workshop. Summary of the SETAC Pellston Workshop on Science-Based Guidance and Framework for the Evaluation and Identification of PBTs and POPs. SETAC Pellston Workshop on Science-Based Guidance and Framework for the Evaluation and Identification of PBTs and POPs. Pensacola Beach, FL: Society of Environmental Toxicology and Chemistry (SETAC); 2008. Jan 28–Feb 1.

Kuniyoshi M, Ymaada KH. Biologically active diphenyl ether form the green alga *Cladophora fascicularis*. Experientia 1985;41:523–4.

Law K, Halldorson T, Danell R, Stern G, Gewurtz S, Alaee M, et al. Bioaccumulation and trophic transfer of some brominated flame retardants in a lake Winnipeg (Canada) food web. Environ Toxicol Chem 2006;25:2177–86.

La Guardia MJ, Hale RC, Harvey E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol 2006;40:6247–54.

Malmvärn A, Marsh G, Kautsky L, Athanasidou M, Bergman A, Asplund L. Hydroxylated and methoxylated brominated diphenyl ethers in the red algae *Ceramium tenuicorne* and blue mussels from the Baltic Sea. Environ Sci Technol 2005;39:2990–7.

Manning T, Roach A, Ferrell D. Dioxins in fish and other seafood from Sydney Harbour, Australia. Organohalogen Compd 2007;69:343–6.

Melcher J, Janussen D, Garson MJ, Hiebl J, Vetter W. Polybrominated hexahydroxanthene derivatives (PBHDs) and other halogenated natural products from the Mediterranean sponge *Scalarispongia scalaris* in marine biota. Arch Environ Contam Toxicol 2007;52:512–8.

Melcher J, Olbrich D, Marsh G, Nikiforov V, Gaus C, Gaul S, et al. Tetra- and tribromophenoxyanisoles in marine samples from Oceania. Environ Sci Technol 2005;39:7784–90.

Morris S, Allchin CR, Zegers BN, Haftka JJH, Boon JP, Belpaire C, et al. Distribution and fate of HBCD and TBBPA brominated flame retardants in North Sea estuaries and aquatic food webs. Environ Sci Technol 2004;38:5497–504.

Pangallo KC, Reddy CM. Distribution patternes suggest biomagnification of halogenated 1'-methyl-1, 2'-bipyrroles (MBPs). Environ Sci Technol 2009;43:122–7.

Proudfoot PR. Development of Botany Bay as a second seaport for Sydney. Aust Geog 1982;15:159–69.

Roach AC, Runcie J. Levels of selected chlorinated hydrocarbons in edible fish tissues from polluted areas in the Georges/Cooks Rivers and Sydney Harbour, New South Wales. Australia. Mar Pollut Bull 1998;36:323–44.

Roach A, Ferrell D, Manning T. The interaction between life history and dioxin levels in fish from Sydney harbour, Australia. Organohalogen Compd 2007;69:1560–5.

Roach A, Symons R, Stevenson G, Manning T. Levels of PBDEs in sediment, fish and sea eagles from Sydney Harbour, Australia: Spatial patterns and profiles. Organohalogen Compd 2008;70:114–7.

Roy P, Williams R, Jones A, Yassini I, Gibbs P, Coates B, et al. Structure and function of south-east Australian estuaries. Est Coast Shelf Sci 2001;53:351–84.

Sjödin A, Päpke A, McGahee E, Focant J, Jones RS, Pless-Mulloli T, et al. Concentrations of polybrominated diphenyl ethers (PBDEs) in household dust from various countries. Chemosphere 2008;73:S131–6.

Stapleton HM, Letcher RJ, Baker JE. Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (*Cyprinus carpio*). Environ Sci Technol 2004;38:1054–61.

Teuten EL, Xu L, Reddy CM. Two abundant bioaccumulated halogenated compounds are natural products. Science 2005;307:917–20.

Toms LL, Harden FA, Symons RK, Burninston D, Fürst P, Müller JF. Polybrominated diphenyl ethers (PBDEs) in human milk from Australia. Chemosphere 2007;68:797–803.

Toms LL, Mortimer M, Symons RK, Paepke O, Mueller JF. Polybrominated diphenyl ethers (PBDEs) in sediment by salinity and land-use type from Australia. Environ Int 2008a;34:58–66.

Toms LL, Harden F, Paepke O, Hobson P, Ryan JJ, Mueller JF. Higher accumulation of polybrominated diphenyl ethers in infants than in adults. Environ Sci Technol 2008b;42:7510–5.

Tomy GT, Budakowski W, Halldorson T, Whittle DM, Keir MJ, Marvin C, et al. Biomagnification of α- and γ-hexabromocyclododecane isomers in a lake Ontario food web. Environ Sci Technol 2004;38:2298–303.

Tomy GT, Pleskach K, Oswald T, Halldorson T, Helm PA, Macinnis G, et al. Enantioselective bioaccumulation of hexabromocyclododecane and congener-specific accumulation of brominated diphenyl ethers in an Eastern Canadian Arctic marine food web. Environ Sci Technol 2008;42:3634–9.

Ueno D, Alaee A, Marvin C, Muir DCG, Macinnis G, Reiner E, et al. Distribution and transportability of hexabromocyclododecane (HBCD) in the Asia-Pacific region using skipjack tuna as a bioindicator. Environ Pollut 2006;144:238–47.

Vetter W, Scholz E, Gaus C, Müller JF, Haynes D. Anthropogenic and natural organohalogen compounds in blubber of dolphins and dugongs (*Dugong dugon*) from Northeastern Australia. Arch Environ Contam Toxicol 2001a;41:221–31.

Vetter W, Hiebl J, Oldham NJ. Determination and mass spectrometric investigation of a new mixed halogenated persistent component (MHC-1) in fish and seal. Environ Sci Technol 2001b;35:4157–62.

Vetter W, Stoll E, Garson MJ, Fahey SJ, Gaus C, Müller JF. Sponge halogenated natural products found at parts-per-million levels in marine mammals. Environ Toxicol Chem 2002;21:2014–9.

Vetter W, von der Recke R, Herzke D, Nygard T. Natural and man-made organobromine compounds in marine biota from Central Norway. Environ Int 2007;33:17–26.

Vetter W, Rosenfelder N, Kraan S, Hiebl J. Structure and origin of the natural halogenated monoterpene MHC-1 and its concentrations in marine mammals and fish. Chemosphere 2008;73:7-13.

Voorspoels S, Covaci A, Schepens P. Polybrominated diphenyl ethers in marine species from the Belgian North Sea and the Western Scheldt estuary: Levels, profiles, and distribution. Environ Sci Technol 2003;37:4348–57.

Wan Y, Hu J, Zhang K, An L. Trophodynamics of polybrominated diphenyl ethers in the marine food web of Bohai Bay, North China. Environ Sci Technol 2008;42:1078–83.

Watanabe I, Kashimoto T, Tatsukawat R. Polybrominated anisoles in marine fish, shellfish, and sediments in Japan. Arch Environ Contam Toxicol 1983;12:615–20.

Weijs L, Losada S, Das K, Roosens L, Neels H, Blust R, et al. Biomagnification of naturally-occurring methoxylated polybrominated diphenyl ethers (MeO-PBDEs) in a fish-marine mammal food chain from the North Sea. Environ Int 2009;35:893–9.

Wolkers H, van Bavel B, Derocher A, Wiig O, Kovacs K, Lydersen C, et al. Congener-specific accumulation and food chain transfer of polybrominated diphenyl ethers in two Arctic food chains. Environ Sci Technol 2004;38:1667–74.