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Trophic magnification of polychlorinated biphenyls and polybrominated diphenyl ethers in an estuarine food web of the Ariake Sea, Japan

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HIGHLIGHTS

- TMFs of 57 PCBs and 9 PBDEs in an estuary were determined.
- TMFs of PCB in the estuarine food web were lower than those in marine food webs.
- Negative relationships between TMF and log K_{OW} values observed for PCB congeners.

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ABSTRACT

To evaluate trophic biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in an estuary of the Ariake Sea, Japan, we measured concentrations of 209 PCB congeners and 28 PBDE congeners, and nitrogen stable isotope ($\delta^{15}N$) levels in living aquatic organisms. The trophic magnification factor (TMF) for ΣPCBs (all 209 congeners) was 1.52, and TMFs for 58 PCB congeners ranged from 0.90 to 3.28. In contrast, TMF for ΣPBDEs was 1.17, and TMFs for 7 PBDE congeners ranged from 0.46 to 1.66. TMFs of PCB and PBDE congeners in this study were lower than those in marine food webs, and were similar to those in a lake food web. However, although negative relationships were observed between TMF and log octanol–water partition coefficient (K_{OW}) values among PCB congeners in this study (log K_{OW} up to 7), positive relationships have been reported in several other studies. In the present estuary, PCB concentrations in sea bass may not reach a steady state because sea bass are migratory species. Therefore, TMFs of highly chlorinated congeners with high log K_{OW} values take longer to reach the steady state and may not increase with increasing log K_{OW}.

1. Introduction

Among aquatic environments, estuaries are the most abundant in nutrients from rivers, and are important for the growth of a wide variety of aquatic organisms that are important food sources for humans. However, estuaries also receive persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), and POPs would transfer to aquatic organisms. Thus, assessments of biomagnification through the food chain and subsequent risk management are critical for the health of humans and wildlife.

Ratios of stable nitrogen isotopes ($^{15}N/^{14}N$ or $\delta^{15}N$) that can derive trophic level of organism are a powerful indicator to assess biomagnification of POPs through aquatic food web (Fisk et al., 2001; Hop et al., 2002; Kelly et al., 2008). Trophic magnification factor (TMF) is derived by using slope of relationship between tropic levels (TL) and pollutant concentrations in organisms, and a TMF > 1 indicates biomagnification of pollutants through the food web. In previous studies, various PCB congeners were observed to have TMFs > 1 in a Barents Sea food web, a Canadian Arctic marine food web, and in a lake trout food web from North America (Fisk et al., 2001; Hop et al., 2002; Houde et al., 2008). However, TMFs of ΣPCB in a riverine food web were lower than those in marine and lake food webs (Walters et al., 2008). PBDE congeners (BDE 47) with TMF > 1 were limited, although 7 PBDE congeners had TMFs ranging from 1.56 to 7.24 in a Bohai Bay food

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web (Wan et al., 2008), and from 0.7 to 1.6 in a Canadian Arctic food web (Kelly et al., 2008). Thus, TMFs vary between food webs and target chemicals. However, few studies show trophic magnification of PCB and PBDE in riverine and estuarine food webs (Walters et al., 2008; Wan et al., 2008; Mizukawa et al., 2009), warranting further comparisons of TMFs among aquatic food webs.

PCBs and PBDEs are appropriate models of biomagnification, with 209 congeners displaying a wide range of physico-chemical properties such as octanol–water partition coefficients (K_{OW}) (Walters et al., 2011). In addition, because PBDEs are more easily metabolized than PCBs, their food web biomagnification properties differ. Therefore, modes of food web biomagnification of PBDEs may not be appropriately expressed according to K_{OW} values alone (Wu et al., 2009). In this study we clarified differences in biomagnification potential between contaminants, and quantitatively determined structure activity relationships using K_{OW} values.

The Ariake Sea is located in the northwestern part of Kyusyu Island, Japan. The Omuta River flows into the Ariake Sea, and mainly flows through urban and industrial areas with large-scale chemical plants. High concentrations of PCBs, nonylphenol, and polycyclic aromatic hydrocarbons have been observed in the river, and high concentrations of vitellogenin have been observed in male mudskipper and goby (Nakata et al., 2002; Takao et al., 2010).

In this study, we compared degrees of trophic biomagnification between PCB and PBDE in an estuarine food web, and assessed associated differences in TMFs between freshwater and marine food webs. Specifically, TMFs for PCB and PBDE congeners were evaluated in an estuary, and the relationship between TMF and log K_{OW} was determined and is discussed in terms of PBDE metabolism

2. Materials and methods

2.1. Sampling

The Omuta River has a length of 7.65 km and a catchment area of 10.8 km^2 (Fig. S1). Fish were collected using a casting net at a range of approximately 3000 m (salinity 19.7–29.5) from the river mouth during October 2012. Javelin goby (*Acanthogobius hasta*, $n = 3$), yellowfin goby (*Acanthogobius flavimanus*, $n = 4$), spotnape ponyfish (*Nuchequula nuchalis*, $n = 5$), grey mullet (*Mugil cephalus*, $n = 3$), and sea bass (*Lateolabrax* sp., $n = 7$) were collected, and snails (*Cerithidea rhizophorarum*, $n = 10$) were handpicked from the same location. Fish were immediately placed in an icebox and were transported to the laboratory. After measurements of lengths and body weights, fish were stored below −20 °C until analysis. Snail samples were stored in filtered seawater overnight to purge gut contents and were then stored below −20 °C until analysis. Fish ages were determined using an otolith-surface reading method with a microscope.

2.2. Chemical analysis

2.2.1. Chemicals

Native PCB standard (BP-MXP), [^{13}C]PCB standards (MBP-MXP (CBs 3, 8, 28, 52, 101, 118, 138, 153, 180, 194, 206, and 209) and PCB-IS-A (CB 70)), native PBDE standard (BDE-MXC) and [^{13}C]PBDE standard (MBDE-MXC (BDEs 3, 15, 28, 47, 99, 153, 154, 183, 197, 207, and 209)) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). All solvents (pesticide analysis grade) and 22% H_2SO_4-silicagel were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2.2. Sample preparation

Whole fish were analyzed after removal of the stomach and gastrointestinal tract. Whole sea bass of more than 200 mm (3 of 7 samples) were difficult to homogenize, and analyses were performed in the muscle tissue and carcass (after removal of head, stomach, gastrointestinal tract, and bone). Analyses were performed in soft tissue from snails. Small-bodied organisms (spotnape ponyfish and snail) were analyzed as combined samples.

Fish samples were slowly thawed in a refrigerator; were homogenized using a T18 basic ULTRA-TARRAX® IKA®-Werke homogenizer (GmbH & Co. KG, Germany); and PCB, PBDE, and stable isotope (SI) levels were analyzed.

2.2.3. PCB and PBDE analysis

Biota samples of 2–4 g were dehydrated with diatomite (Hydromatrix; Varian Inc., CA, USA), packed into stainless cells, and spiked with 50 μL of a decane solution containing 1000 pg of $^{13}C_{12}$-labeled internal standards (MBP-MXP and MBDE-MXC). Samples were extracted using an accelerated solvent extractor (ASE; ASE200, Thermo Fisher Scientific Inc, MA, USA) with a 1:1 (v:v) dichloromethane and hexane solution. Extracts were dehydrated using powdered Na_2SO_4, and were then evaporated to approximately 2 mL in a rotary evaporator. These concentrated extracts were passed through a column containing 6 g of 22% sulfuric acid-impregnated silica gel and 6 g of anhydrous Na_2SO_4. The column was pre-eluted with 80 mL of hexane, and was further eluted with another 80 mL of hexane. Eluates were evaporated in a rotary evaporator and were transferred to 10-mL glass tubes. Subsequently, 50 μL of decane was added and the solution was concentrated under a gas stream of ultrapure N_2 to a volume of approximately 50 μL. Finally, 50-μL aliquots of decane solution containing 1000 pg of $^{13}C_{12}$-labeled injection internal standard (PCP-IS-A) were added to 10-mL glass tubes for gas chromatography (GC)/mass spectrometry (MS).

All 209 PCB congeners and 28 PBDE congeners were identified and quantified using GC/high-resolution MS (HP6890, Agilent Technologies, Santa Clara, CA, USA, and JMS 700, JEOL Ltd., Tokyo, Japan), and 209 PCB congeners were separated into 192 peaks using an HT8-PCB column (60 m × 0.25 mm i.d., film thickness; unpublished, Kanto Chemical Co., Inc.). Oven temperatures, MS conditions, and peak assignments were as detailed in Kobayashi et al. (2010), and the PCB numbering system was implemented according to Ballschmiter and Zell (1980). PBDE congeners were separated using a DB5-ms column (15 m × 0.25 mm i.d., 0.10 μm filmthickness; Agilent Technologies). Oven temperatures and MS conditions were as shown in Iwamura et al. (2009). Concentrations of both chemicals were determined using a mass spectrometer in electric ionization mode and selected ion monitoring mode at a mass resolution of $R > 10000$ (10% valley). Quantitation was performed using isotope dilution or internal standard methods. Blank values for PCBs were confirmed to contain negligible compound contamination (<0.6 ng g-lipid^{-1}). Blank values for PBDEs were subtracted from the analytical values of all fish samples. The recovery rates (mean ± standard deviation) for [^{13}C]PCB and [^{13}C]PBDE ranged from 37% ± 14% (CB 3) to 105% ± 27% (CB 118) and from 18% ± 14% (BDE 3) to 57% ± 19% (BDE 99), respectively. Detailed recovery rates of internal standards were described in Supplementary material. The low recoveries and large standard deviations of [^{13}C]PBDEs may be caused by volatilization during the concentration processes. However, the internal standard method could reliably quantify PCBs and PBDEs despite a range of relatively low recoveries. The coefficient of variation for triplicate analyses of a fish sample was 2.1% for ΣPCBs and ranged from 1.0% to 48% for 62 CB congeners, and it was 9.0% for ΣPBDEs and ranged from 2.0% to 36% for 8 BDE congeners.