BIOMAGNIFICATION PROFILES OF DIOXIN-LIKE PCBS IN THE COASTAL FOOD WEB OF EASTERN ASIA

Matsuo H[1], Kawano M[1], Omori K[2], Nakajima K[3], Matsuda M[1], Morita M[1] and Takeuchi I[1]

[1]Department of Life Environment Conservation, Faculty of Agriculture, Ehime University, University, 3-5-7 Tarumi, Matsuyama, Ehime 790-8566, Japan; [2]Center for Marine Environment Studies (CMES), Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan; [3]Port of Nagoya Public Aquarium, 1-3 Minato-machi, Minato-ku, Nagoya, Aichi 455-0033, Japan

Abstract

Using stable carbon ($\delta^{13}C$) and nitrogen isotope ratios ($\delta^{15}N$) for trophic characterization, we elucidated biomagnification profiles of dioxin-like polychlorinated biphenyls (DL-PCBs) and normal polychlorinated biphenyls in penta-(P_5) and hepta-(H_6) chlorinated congeners through a coastal food web. The slope of the regression of log-transformed concentration of each of the congeners on the $\delta^{15}N$ value was used to reveal biomagnification profiles through the food web. The slopes ranged from 0.11 ± 0.02 (mean$\pm$SD) to 0.13 ± 0.01 on a wet weight basis, from 0.09 ± 0.02 to 0.11 ± 0.01 on a dry weight basis, and from 0.02 ± 0.00 to 0.03 ± 0.01 on a lipid weight basis. On wet, dry and lipid bases the slopes of DL-PCBs were not significantly different in P_5CBs and H_6CBs from those of normal PCBs. The slopes of the regressions of DL-PCBs against Log Kow were similar to those of earlier work in Bohai Bay, China, but lower than those reported for Tokyo Bay, Japan.

Introduction

In the last two decades, modeling of biomagnifications profiles of anthropogenic chemicals using stable isotope ratios of bio-elements (such as carbon and nitrogen) has advanced rapidly. Recent studies of biomagnification profiles in coastal food webs showed that dioxin-like polychlorinated biphenyls (DL-PCBs) are biomagnified to a significantly greater extent than polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/DFs).[1, 2] Moreover, seafood is reported to be the main intake route for dioxins in the diet of Japanese people; the TEQ of DL-PCBs corresponds to >2/3 of the total TEQ in sea foods consumed in Tokyo.[1, 3] However, there are few quantitative analyses of food web structure that compare biomagnification profiles of DL-PCBs and normal-PCBs. Biomagnification profiles of DL-PCBs are of considerable current concern. Nine congeners of DL-PCBs, DL-P_5 and DL-H_6CBs make up 75% of all DL congeners. Accordingly, we studied the biomagnification profiles of P_5 and H_6CBs congeners of DL-PCBs and normal PCBs in the biota of the ecosystem in the most innermost part of Ise Bay, central Japan. The basic structure of this food web was analysed using $\delta^{13}C$ and $\delta^{15}N$. Our results are compared with biomagnification profiles of DL-PCBs in

Tokyo Bay, Japan[1] and Bohai Bay, China.[2]

Materials and Methods

POM (particulate organic matter), seaweeds, mollusks, crustaceans and fishes were collected in 2006 from the innermost part of Ise Bay, Japan (Fig. 1). The samples were kept frozen at -20°C until analysis. Muscle (POM and seaweed samples were whole) subsamples from animals were dried at 60°C (≥24 h), and lipid in the samples was removed by immersion in a chloroform: methanol (2:1) solution for 24 h. In addition, carbonate in POM and seaweed was removed by immersion in a 1N HCl solution for 24 h. Stable isotopes were measured using an ANCA-SL and a mass spectrometer (PDZ Europa.Ltd). Stable isotope ratios were expressed by δ as ‰ by $\delta X=\{(R_{sample}/R_{standard})-1\}\times 1000(‰)$, where X is ^{15}N or ^{13}C, R_{sample} is the corresponding ratio $^{15}N/^{14}N$ or $^{13}C/^{12}C$ of the sample, $R_{standard}$ for carbon is PeeDee Belemnite (PDB), and $R_{standard}$ for nitrogen is atmospheric nitrogen. About 10g of each of the whole homogenized samples were added to the internal standard and dissolved in 1N KOH/ethanol. The solution was extracted with hexane, and interfering components were removed by treatment with sulfuric acid, and by column chromatography with activated silicagel and alumina. Identifications and quantifications of each of the congeners of P_5 and H_6CBs were performed with a HRGC (HP6890 series, Agilent Ltd) equipped with an HRMS (JMS-800D, JEOL Ltd). An HT8-PCB capillary column (Kanto Chemical Ltd) was used for gas chromatographic separation of target compounds. The slope of the regression of the log-transformed concentration of each congener (on wet, dry and lipid weight bases) on $\delta^{15}N$ represents the biomagnification profile.

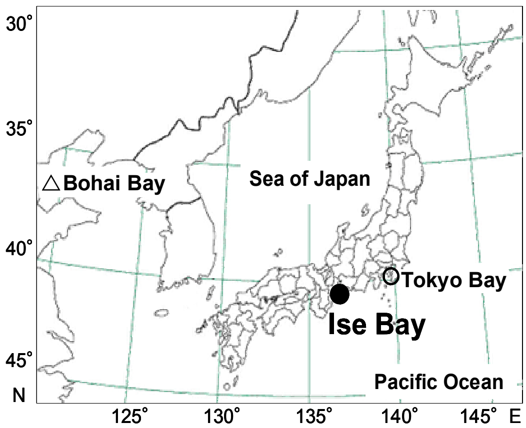


Fig. 1. Sampling location in Japan.

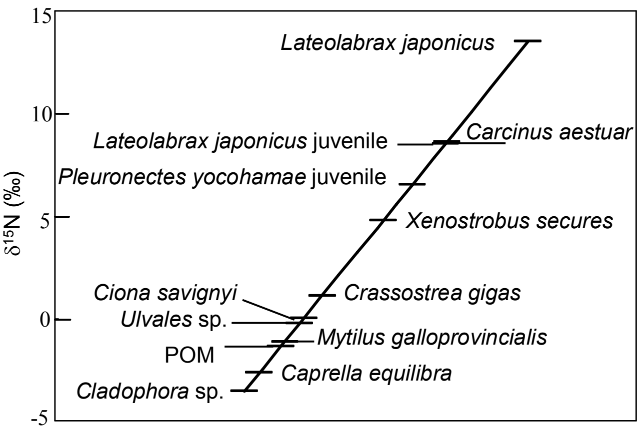


Fig. 2. Food wed structure (based on stable carbon and nitrogen isotope ratios) of the innermost part of Ise Bay, Japan.

Results and Discussion

Among the 88 congeners of P_5 and H_6CBs, 59 were detected in >50% of the biological samples. Calculations of regression slopes of log concentration of congener on stable isotope ratio (Fig. 2) for these 59 congeners indicate were as follows (mean±SD) (Fig. 3): for P_5CBs, the slopes of DL-P_5CB were 0.11±0.02 (wet weight basis), 0.09±0.02 (dry weight basis) and 0.02±0.00 (lipid weight basis) while those of normal-P_5CB were 0.11±0.04, 0.08±0.03 and 0.01±0.03, respectively; for H_6CB, the slopes of DL-H_6CBs were 0.13±0.01, 0.11±0.01 and 0.03±0.01, respectively, while those of normal-H_6CBs were 0.13±0.02, 0.12±0.02 and 0.04±0.02, respectively. There was no significant difference between normal-P_5CBs and DL-P_5CBs in any comparison, or between P_5CBs and H_6CB (t-test; $p > 0.05$).

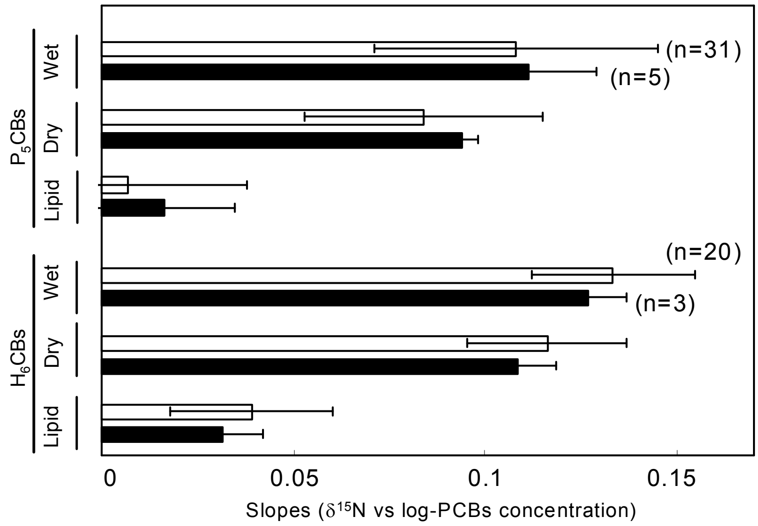


Fig. 3. Average regression (δ^{15}N vs log-PCBs concentration) slopes±SD of P_5 and H_6CBs in normal-PCBs (white bars) and DL-PCBs (black bars).

Table 1. Slopes for regressions of log-concentration of DL-PCBs on δ^{15}N.

	Non-ortho-DL-PCBs				*Mono-ortho*-DL-PCBs							
IUPAC. No	#81	#77	#126	#169	#123	#118	#114	#105	#167	#156	#157	#189
Number of Cl	4	4	5	6	5	5	5	5	6	6	6	7
log Kow[4]	6.42	6.34	6.93	7.54	6.74	6.83	6.77	6.64	7.47	7.26	7.24	7.86
Slope (wet wt basis)	—	0.08	0.08	—	0.11	0.12	0.12	0.12	0.13	0.13	0.12	0.10
Slope (dry wt basis)	—	0.06	0.06	—	0.09	0.11	0.10	0.10	0.12	0.11	0.10	0.08
Slope (lipid wt basis)	—	−0.02	−0.01	—	0.02	0.03	0.03	0.03	0.04	0.04	0.02	0.00

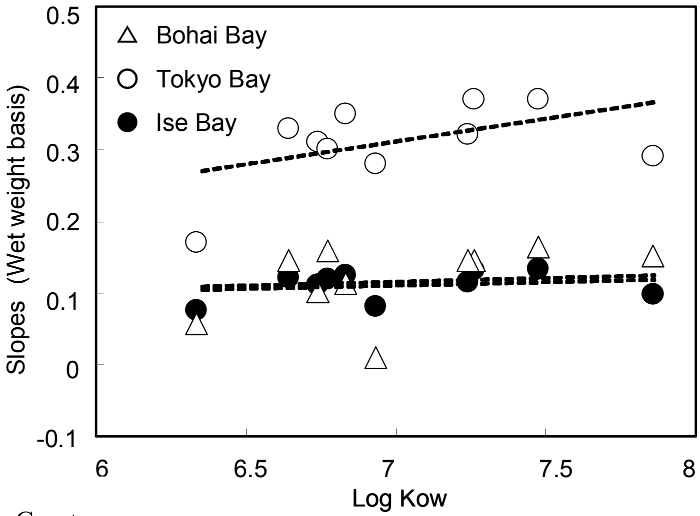
The inequalities among slopes of DL-PCBs congeners detected may be represented as follows (congeners in bold indicate non-ortho-DL-PCBs; other congeners [not bold] are for mono-ortho-DL-PCBs): **#77**<**#126**<#189<#123<#157<#114<#105<#118<#156<#167. In general the slopes increased as congener number increased. This trend was also found in Tokyo Bay and Bohai Bay**:**

Tokyo Bay[1]: **#81<#77<#169<#126**<#189<#123<#114<#157<#105<#118<#156<#167

Bohai Bay[2]: **#81<#77<#126**<#118<#167<#105<#156<#157<#189<#123<**#169**<#114

The log transformed octanol-water partition coefficient (log Kow) is considered one of the most useful indices in estimating biomagnification through a food web. In general, a chemical with log Kow between 5 and 6 is thought to biomagnify through a food web.[5] However, the regression slopes for DL-PCBs (wet weight basis) varied little (0.08 to 0.13) across a wide range of log Kow values (Fig. 4). This was also true for Bohai Bay[2] data, and about half of those from Tokyo Bay.[1] $\delta^{15}N$ values for the biota from Tokyo Bay[1] spanned 6‰, which covers <2 trophic levels (a span of 3.4$\pm$1.1‰ in $\delta^{15}N$ represents 1 trophic level[6]). In contrast, the $\delta^{15}N$ ranges in the biota from Bohai Bay[2] and Ise Bay were 9.8 and 17.1‰, respectively, corresponding closely to 3 and 5 a trophic level food web structure. Accordingly, the shortness of the food chain in Tokyo Bay[1] may lead to an overestimate bias in the regression slopes. Moreover, the slope estimates are thought to vary with several environmental factors, i.e., seawater temperature, concentrations of PCBs in the shallow water ecosystems etc. Because of this, there is an urgent need for further studies of factors driving variation in the regression slopes.

Fig. 4. Slope of regressions plotted against log Kow. Data for Tokyo Bay and Bohai Bay are from Naito et al.[1] and Wan et al.,[2] respectively.



Acknowledgements

The present study was partially supported by Grants-in-Aid for Scientific Research from Japan Society for the Promotion of Science (Nos. 16310042, 19310024).

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