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Trophic transfer of persistent toxic substances through a coastal food web in Ulsan Bay, South Korea: Application of compound-specific isotope analysis of nitrogen in amino acids☆

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ABSTRACT

Trophic magnification factor (TMF) of persistent toxic substances (PTSs: Hg, PCBs, PAHs, and styrene oligomers (SOs)) in a coastal food web (12 fish and four invertebrates) was determined in Ulsan Bay, South Korea. The nitrogen stable isotope ratios ($\delta^{15}N$) of amino acids [$\delta^{15}N_{Glu-Phe}$ based on glutamic acid ($\delta^{15}N_{Glu}$) and phenylalanine ($\delta^{15}N_{Phe}$)] were used to estimate the trophic position ($TP_{Glu-Phe}$) of organisms. The $TP_{Glu-Phe}$ of organisms ranged from 1.64 to 3.69, which was lower than TP estimated by $\delta^{15}N$ of bulk particulate organic matter (TP_{Bulk}: 2.46–4.21). Mercury and CB 138, 153, 187, and 180 were biomagnified through the whole food web (TMF > 1), while other PTSs, such as PAHs and SOs were not (biodilution of SOs firstly reported). In particular, the trophic transfer of PTSs was pronounced in the resident fish (e.g., rock bream, sea perch, Korean rockfish). Of note, CB 99, 101, 118, and 183 were additionally found to be biomagnifying PTSs in these species. Thus, fish residency appears to represent an important factor in determining the TMF of PTSs in the coastal environment. Overall, $\delta^{15}N_{Glu-Phe}$ provided accurate TPs of organisms and could be applied to determine the trophic transfer of PTSs in coastal food webs.

1. Introduction

Trophic magnification factor (TMF) is an important criterion that is used to assess the bioaccumulation and biomagnification potential of pollutants (Gobas et al., 2009), representing the trophic transfer of persistent toxic substances (PTSs) in aquatic ecosystems (Fisk et al., 2001). TMF of PTSs provides valuable information showing implications of bioaccumulation, and several studies have emphasized that it can be incorporated into regulatory decision making (UNEP, 2001). Previous studies also have used TMF as a basis for chemical hazard and risk assessment (Gobas et al., 2009; UNEP, 2001). TMF is estimated by the regression between trophic positions (TP) and concentrations of PTSs in organisms (Fortibuoni et al., 2013; Shao et al., 2016; Wang et al., 2017; Yu et al., 2012). However, so far, studies on TMF have focused on analysis and accuracy for PTSs (the y-axis), and sometimes sample selections, while, the methods for obtaining accurate TP, which is an important factor for correlation, have not been fully discussed (Borgå et al., 2012; Gobas et al., 2009; Won et al., 2018).

TP is typically estimated using the nitrogen stable isotope ratios of bulk tissues ($\delta^{15}N_{Bulk}$) from organisms (Post, 2002). However, estimates of TP based on $\delta^{15}N_{Bulk}$ have some limitations that cause uncertainty in TP. First, the traditional method for calculating TP requires the $\delta^{15}N_{Bulk}$ of baseline organisms such as primary producers (TP = 1), because they are estimated as enriched ^{15}N of consumers relative to baseline organisms. However, the $\delta^{15}N$ values of phytoplankton might be distorted due to the difficulty of pure sampling (Post, 2002). Alternatively, the $\delta^{15}N_{Bulk}$ of zooplankton was used assuming that they are primary consumers (TP = 2), but trophic diversity of zooplankton is still a concern for this issue. Second, the $\delta^{15}N_{Bulk}$ of a given organism is significantly influenced by spatiotemporal variability in baseline $\delta^{15}N$ values (Ishikawa et al., 2018; Won et al., 2018). This phenomenon might alter the TP of organisms, especially in dynamic coastal ecosystems where

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various nitrogen sources exist. Finally, for the trophic discrimination factor (TDF) used to calculate TP, many previous studies have used a TDF of 3.4‰ for $\delta^{15}N$ in marine ecosystems; however, this value can vary depending on species and food quality (Dubois et al., 2007; Post, 2002; Vander Zanden and Rasmussen, 2001).

To address the limitations of traditional methods for estimating the TP of organisms, recent studies have used compound-specific isotope analysis (CSIA). For instance, the $\delta^{15}N$ of amino acids ($\delta^{15}N_{AAs}$) has been proposed as a powerful tool for increasing the accuracy of TP estimates (Ishikawa et al., 2018). This method does not require the $\delta^{15}N$ values of basal organisms, because the difference between the $\delta^{15}N$ of trophic amino acids (i.e., glutamic acid; Glu) and source amino acids (i.e., phenylalanine; Phe) in a given organism is used to calculate TP. In addition, amino acid-based TP uses a relatively constant TDF value (7.6‰), reducing TP variability due to variation in the TDF values of the environment (Blanke et al., 2017). Thus, calculating TP using $\delta^{15}N_{AAs}$ could reduce potential uncertainty and variability compared to the bulk-based method, with it being considered a suitable method for determining the TP of organisms more accurately (Won et al., 2018).

Meanwhile, certain biological factors, such as the uptake routes of food and fish mobility, also impact assessments of the trophic transfer of PTSs (Borgå et al., 2012; McLeod et al., 2015). The carbon stable isotope ratios ($\delta^{13}C$) of organisms retain information about the food sources they consume (Kelly, 2000). Heavier and lighter $\delta^{13}C$ generally indicate benthic and pelagic carbon sources in marine environments, respectively (Hobson et al., 1994). The carbon sources of the organisms might lead to differences in the exposure and bioaccumulation of PTSs between benthic and pelagic organisms (Fan et al., 2017). The spatial variability of pollutants can lead to differences in exposure to pollutants on organisms (Dean et al., 2009). The resident fish reflect local pollution well (Oziolor et al., 2018). However, migratory fish are exposed to a variety of environments with a wide range of pollutants due to inhabiting coastal waters and open seas. Thus, the residency of fish is expected to affect the TMF values of PTSs.

In the present study, we aimed to evaluate the trophic transfer of PTSs through the coastal food web of Ulsan Bay, South Korea. Ulsan Bay is a highly industrialized area that is one of the most polluted areas in Korea. Previous study has reported relatively high concentrations of PTSs in the sediments of Ulsan Bay (Khim et al., 2001). The present study focused on several PTSs, such as mercury (Hg), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and styrene oligomers (SOs). Mercury and PCBs can be biomagnified, having adverse effects on ecosystems and humans due to their great persistence, bioaccumulation, and toxicity (Barron et al., 1995; Driscoll et al., 2013; Muir et al., 2003). Some studies have reported that PAHs are biodiluted in the food web, due to metabolism in organisms (Broman et al., 1990; Kayal and Connell, 1995; Khairy et al., 2014; Nfon et al., 2008; Qadeer et al., 2019), while others have shown that PAHs accumulates through the food web (Wang et al., 2012; Zhang et al., 2015). SOs are emerging compounds that tend to originate from the degradation of polystyrene plastics, and are widely distributed in the environments (Hong et al., 2016; Kwon et al., 2015; Lee et al., 2018). Aquatic wildlife is at potential risk from these pollutants, as they cause genotoxicity and reproduction toxicity (Ohyama et al., 2001). However, the bioaccumulation and biomagnification potential of SOs remain poorly established. In this study, $\delta^{15}N_{AAs}$ were used to estimate the TPs of organisms, and the TMF of PTSs was calculated using TP_{AAs}. We also compared the obtained TMF values with those based on the traditional method (using $\delta^{15}N_{Bulk}$). The results of this study are expected to demonstrate the usefulness of the CSIA of nitrogen in amino acids in evaluating the trophic transfer of PTSs in the coastal food webs.

2. Materials and methods

2.1. Sample collections

Marine fish and potential food sources were sampled in Ulsan Bay during October 2017 (Fig. S1 of the Supplementary Materials (S)). Fishes (n = 14) were collected by fishing, and benthic invertebrates (n = 6) and surface sediment were collected using a Van Veen grab (Table S1). Marine organisms were then classified according to their taxonomy. Twelve fish species were identified, including Japanese horse mackerel (*Trachurus japonicus*), cutlassfish (*Trichiurus lepturus*), stripe rainbowfish (*Halichoeres tenuispinis*), chub mackerel (*Scomber japonicus*), red seabream (*Pagrus major*), greenling (*Hexagrammos otakii*), pearl spot chromis (*Chromis notata*), Korean rockfish (*Sebastes schlegeli*), goby (*Gobiidae*), rock bream (*Oplegnathus fasciatus*), pike eel (*Muraenesox cinereus*), and sea perch (*Ditrema temminckii*). Four invertebrates were identified, including bristle worm (*Neanthes* sp.), razor clam (*Siliqua pulchella*), sea cucumber (*Holothuroidea* sp.), and scutate stermaspid worm (*Sternaspis scutata*).

Seawater samples were collected by a Van Dorn sampler. Bulk particulate organic matter (POM) was sampled by filtering (47 mm GF/F, Whatman, Dassel, Germany) of the seawater after pre-filtration with 100-μm mesh. Size-fractioned POM samples, such as 100–200 μm-POM and >200 μm-POM were collected using plankton nets with different mesh sizes. All samples were stored in dry ice on-site and were then transported to the laboratory. The entire body of benthic invertebrates was used for analysis. Fish samples were dissected, and only muscle tissue was analyzed. All samples for PTSs analysis were freeze-dried and homogenized.

2.2. Analyses of persistent toxic substances

Concentrations of Hg in organisms were measured with a direct mercury analyzer (DMA-80, Milestone, Sorisole, Italy) after weighing approximately 0.015–0.050 g of freeze-dried samples. The detection limit of the instrument was 0.005 ng Hg. For quality control of Hg, the certified reference material (CRM, BCR-277R, estuarine sediment, European Community Bureau of Reference, IRMM, Belgium) was analyzed at the beginning and end of the instrumental analysis. The measured CRM concentrations were within acceptable ranges (96–105%).

For the analysis of PCBs, PAHs, and SOs, freeze-dried samples (approximately 0.4–2.0 g) were weighed and placed in glass thimbles with sodium sulfate and were extracted using Soxhlet extractor for 16 h. For quality control, surrogate standards for PCBs (MBP-MXE, Wellington Laboratories, Guelph, ON, Canada) and PAHs (FRT-525RPM, Chem Service, West Chester, PA) were added before extraction. The extract was separated into subsamples to measure the lipid content of organisms and analyze PTSs. The lipid content of organisms was measured gravimetrically after drying the extract in a weighing dish. The lipids of organic extracts for PTSs analyses were removed using a gel permeation chromatography column (packed with 60 g of Bio-Beads S-X3, Bio-Rad Labs., Richmond, CA) (Reiner et al., 2007). The lipid depleted sample was placed on a column filled with 8 g of activated silica gel, and was cleaned up by passing it through 60 mL mixed solvent (n-hexane:dichloromethane, 80:20, v/v). The eluents were rotary-evaporated and nitrogen-concentrated, and added to an internal standard (2-fluorobiphenyl, Sigma-Aldrich, Saint Louis, MO) for instrumental analysis. Instrumental analysis was performed using a gas chromatography-mass selective detector (7890B GC & 5977B MSD, Agilent Technologies, Santa Clara, CA). Detailed information on instrumental conditions, target compounds, detection limits, and recoveries are provided in Tables S2 and S3.

2.3. Analysis of carbon and nitrogen stable isotopes

Carbon and nitrogen stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) were analyzed for organisms (bulk tissue), size-fractioned POMs, and surface sediments. For $\delta^{13}C_{Bulk}$ analysis, a sample was reacted with 1 M hydrochloric acid to remove inorganic carbon. $\delta^{15}N_{Bulk}$ was analyzed without acid treatment based on a previous study (Choi et al., 2017). Carbon and nitrogen stable isotopes were analyzed using an elemental analyzer (EA-3000, Eurovector, Italy) combined with an isotope ratio mass spectrometer (Isoprime100, Isoprime Ltd., UK). Carbon and nitrogen stable isotope ratios were expressed in δ (‰) notation, based on the following equation (Eq. (1)):

$$\delta X\ (‰) = \left[\left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000\right] \quad (1)$$

where X is ^{13}C or ^{15}N, and R is $^{13}C/^{12}C$ or $^{15}N/^{14}N$. Vienna Pee Dee Belemnite and atmospheric N_2 were used as standards for $\delta^{13}C$ and $\delta^{15}N$, respectively. The analytical errors were 0.06‰ for $\delta^{13}C$ and 0.1‰ for $\delta^{15}N$, which were estimated from working standards (CH6 for $\delta^{13}C$ and N1 for $\delta^{15}N$, International Atomic Energy Agency, Vienna, Austria).

2.4. Compound-specific isotope analysis of amino acids

Nitrogen stable isotope ratios of amino acids ($\delta^{15}N_{AAs}$) were measured for 20 biota samples based on a previously reported method (Chikaraishi et al., 2009). In brief, freeze-dried samples (3–5 mg) were hydrolyzed at 110 °C for 12 h with 12 M hydrochloric acid. Lipids were removed using n-hexane/dichloromethane (3:2, v/v). Hydrolysate was derivatized at 110 °C for 2 h using thionyl chloride/isopropanol (1:4, v/v), followed by pivaloyl chloride/dichloromethane (1:4, v/v). The derivatized amino acids were then extracted with n-hexane/dichloromethane (3:2, v/v). The $\delta^{15}N$ of individual amino acids was measured using gas chromatography (Agilent 6890N, Agilent Technologies) coupled with an isotope ratio mass spectrometer (Isoprime, GV Instruments). The Ultra-2 capillary column (50 m long, 0.32 mm i.d., 0.52 μm film thickness, Agilent) was used, and He was used as the carrier gas at a flow rate of 1.1 mL min^{-1}. The temperatures of combustion and reduction furnaces were set at 980 °C and 650 °C, respectively. The $\delta^{15}N$ of amino acids, including alanine, glycine, valine, leucine, isoleucine, proline, aspartic acid + asparagine, threonine, serine, methionine, Glu, and Phe were measured, and the analytical precision was within 0.5‰. The $\delta^{15}N$ of Glu and Phe were used as trophic and source amino acids for measuring TP of organisms, respectively.

2.5. Estimations of trophic position and trophic magnification factor

The TP of organisms was estimated according to the following equations (Eqs. (2)–(4)):

$$TP_{Bulk} = \left[\frac{\delta^{15}N_{sample} - \delta^{15}N_{Bulk}}{TDF}\right] + 1 \quad (2)$$

$$TP_{100-200\ \mu m} = \left[\frac{\delta^{15}N_{sample} - \delta^{15}N_{100-200\ \mu m\ POM}}{TDF}\right] + 2 \quad (3)$$

$$TP_{Glu-Phe} = \left(\frac{\delta^{15}N_{Glu-Phe} - \beta}{7.6}\right) + 1 \quad (4)$$

For Eq. (2), $\delta^{15}N$ of bulk POM ($\delta^{15}N_{Bulk}$) was used as the primary producer (TP = 1). For Eq. (3), $\delta^{15}N$ of 100–200 μm POM ($\delta^{15}N_{100-200\ \mu m\ POM}$) was used as the primary consumer (TP = 2). TDF values (3.4‰ for Eqs. (2) and (3); 7.6‰ for Eq. (4)) and β values (3.4‰ in Eq. (4)) were used according to previous studies (Chikaraishi et al., 2009; Minagawa and Wada, 1984).

TMF was calculated using the regression slope (b) between the log-transformed concentrations of the PTSs and the TP of organisms, according to Eqs. (5) and (6). Concentrations of PTSs were dry weight (dw) for Hg and lipid-normalized concentrations for organic pollutants.

$$\text{Log (Concentration of pollutants)} = a + b \times TP \quad (5)$$

$$TMF = 10^{b} \quad (6)$$

2.6. Data analysis

The relative contribution of benthic carbon source to fish was expressed as %B using the two-endmember-mixing model (Eq. (7)) reported in the previous studies (Post, 2002; Wen et al., 2009). Because variability of trophic fractionation factor in carbon stable isotope has reported (McCutchan et al., 2003; Post, 2002); thus, the present study assumed no trophic fractionation of the carbon isotope to reduce potential errors. Endmember for pelagic and benthic carbon sources used the $\delta^{13}C$ values of 100–200 μm POM (−20.8‰) and sea cucumber (−16.0‰), respectively.

$$\%B = \left[\frac{\delta^{13}C_{fish} - \delta^{13}C_{pelagic\ endmember}}{\delta^{13}C_{benthic\ endmember} - \delta^{13}C_{pelagic\ endmember}}\right] \times 100 \quad (7)$$

The fish were grouped according to their mobility based on previous studies (An et al., 2008; Ji et al., 2015; Kang et al., 2015; Lee et al., 2016; Masuda et al., 2010; Park et al., 2002; Suda et al., 1987), and classified into migrant fish with seasonal migration and resident fish that remained in coastal waters (Table S1). Student's t-test was performed to test whether there was a significant difference in the stable isotope ratio between the mobility of fish.

To evaluate whether the PTS concentrations in organisms were classified according to specific compounds or species, principal component analysis (PCA) was performed. The Kaiser-Meyer-Olkin (KMO) and Bartlett's tests were conducted to evaluate the validity of PCA. In order to remove the collinearity of the lipid-normalized concentrations of PTSs in the organisms, the data were pretreated as follows. First, concentrations of below detection limits were set to half of the method detection limit (ng g^{-1} dw) and lipid-normalized. Then, PCBs, PAHs, and styrene oligomers were classified according to the number of Cl (di- to hepta-), the number of aromatic rings (2–6), and molecular mass (dimers and trimers), respectively. Finally, the concentrations were log-transformed and normalized according to the method reported previously (Lattin et al., 2003).

The correlation between the TP and the log-transformed concentration of PTSs was compared to verify the significance of measured TMF using SPSS Statistics (Ver. 24.0, SPSS INC., Chicago, IL). All the tests were conducted after the normality test using Shapiro-Wilk test. Then, Pearson and Spearman correlation analyses were performed for the normal distributed data and the non-normal distributed data, respectively. Statistical significance was set to 0.05.

3. Results and discussion

3.1. Structure of the food web in Ulsan Bay

Bulk $\delta^{13}C$ and $\delta^{15}N$ of organisms and potential food sources showed that the benthic and pelagic food webs were mixed in Ulsan Bay, Korea (Fig. 1a). The $\delta^{13}C_{Bulk}$ of invertebrates and fish ranged from −21.6‰ to −16.0‰ and −20.2‰ to −16.0‰, respectively. Sea cucumber and 100–200 μm POM were considered as benthic and pelagic basal organisms to consumers, respectively. Bulk POM can be composed of pelagic (such as marine phytoplankton), terrestrial, and anthropogenic organic matter in coastal environments. In this study, the $\delta^{13}C$ of bulk POM was −25.2‰; it is indicated that bulk POM contains both allochthonous (i.e., land-derived) and autochthonous (i.e., marine origin) organic matter (Liénart et al., 2016). Thus, we determined the $\delta^{13}C$ value of 100–200 μm POM to be the endmember of pelagic food sources in the study area, rather than bulk POM. In addition, $\delta^{13}C$ of sediment was somewhat similar to that of bulk POM and lower than size-fractioned POM (100–200 μm). The low $\delta^{13}C$ of sediment probably due to allochthonous input. The allochthonous organic matter in sediment is generally less assimilated to benthic organisms due to its low diet quality (Park et al., 2015). Consequently, the $\delta^{13}C$ of benthic organisms were heavier compared to that of sediment in this study. Among the benthos, sea cucumber was the most suitable species as the endmember for benthic organic carbon, as TP is close to "2" (herbivore). Bristle worm was shown higher TP than 2. Razor clam is known as filter feeders that consume pelagic diets, and the $\delta^{13}C$ of scutate stermaspid worm is also similar to pelagic consumer. Previous studies also showed that sea cucumbers consume mainly benthic organic matters (Navarro et al., 2013), and particularly reflect the $\delta^{13}C$ of benthic organic matter (Van Dover et al., 1992). The $\delta^{13}C$ values of benthic and pelagic endmembers were −16.0‰ and −20.8‰, respectively. These values were comparable to the previous studies, with the benthic source having heavier $\delta^{13}C$ compared to the pelagic source (Corbisier et al., 2004; Van Dover et al., 1992).

The contributions of the benthic carbon sources (%B) were relatively high in the fish of the Ulsan Bay (%B: 12–100%, average: 74%, Table 1). In particular, sea perch, greenling, and rock bream had higher %B (88–100%, average: 95%), supporting the results obtained on the feeding behavior of these species in a previous study (Kwak et al., 2005). Japanese horse mackerel had different %B between samples #1 and #2, although both samples were collected in the same region. The higher %B (87%) in the larger specimen (Japanese horse mackerel #1: 23 cm length) than smaller one (Japanese horse mackerel #2: 11.6 cm length; %B = 12%) was found. This result can be explained by the shifts of diet resources and habitats in this

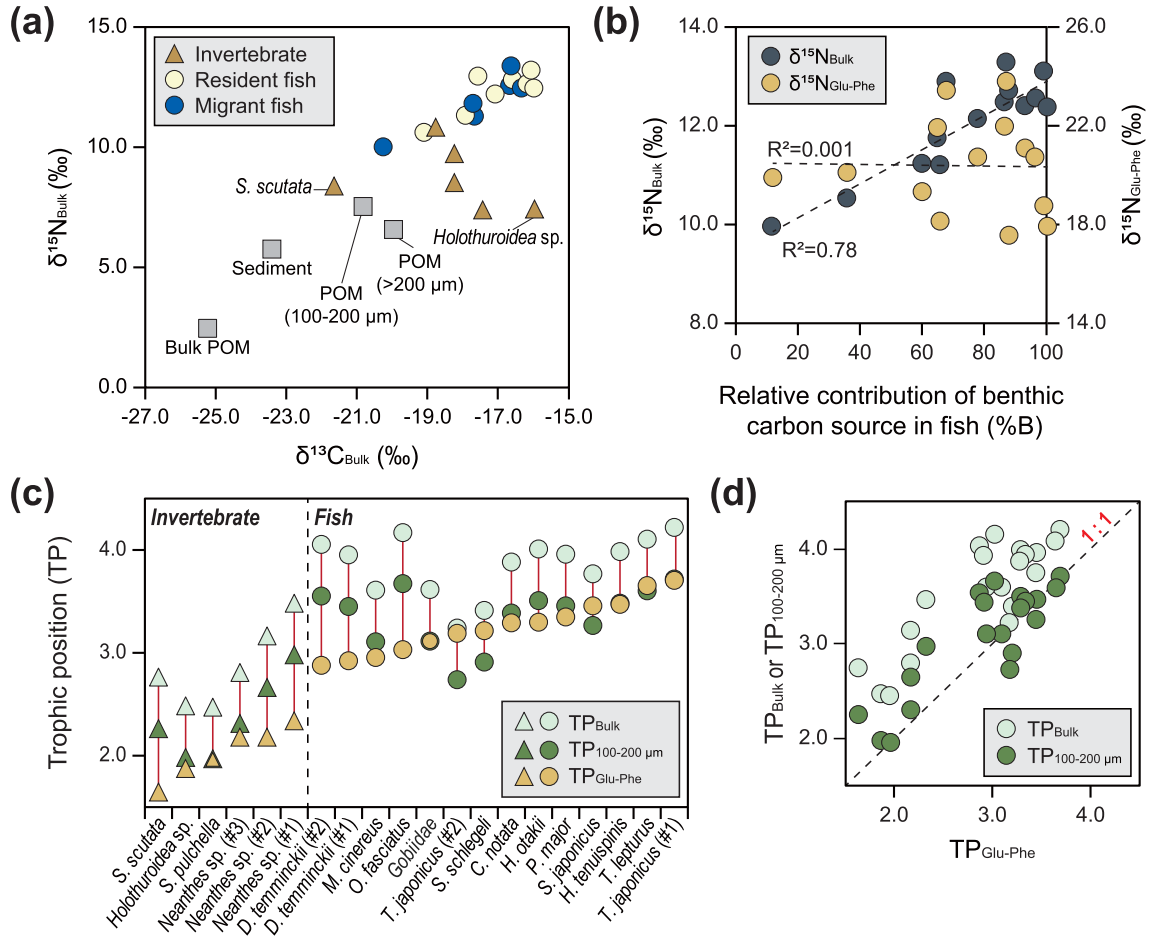

Fig. 1. (a) Structure of the food web in Ulsan Bay, Korea. (b) Correlation between the relative contribution of benthic carbon sources to fish and the nitrogen stable isotope ratios. (c) TPs of organisms calculated from $\delta^{15}N_{Bulk}$, $\delta^{15}N_{100-200\ \mu m}$, and $\delta^{15}N_{Glu-Phe}$. (d) Comparison of bulk-based TP (TP_{Bulk} and $TP_{100-200\ \mu m}$) and amino acids-based TP ($TP_{Glu-Phe}$).

Table 1
Stable isotope ratios of bulk tissue and amino acids, lipid content, trophic position, and biological factors of organisms from Ulsan Bay, Korea.

Common name	Scientific name	Stable isotope ratios (‰)			Trophic positions (TP)			Biological factors of fish	
		$\delta^{13}C_{Bulk}$	$\delta^{15}N_{Bulk}$	$\delta^{15}N_{Glu-Phe}$	TP_{Bulk}[a]	$TP_{100-200\ \mu m}$[b]	$TP_{Glu-Phe}$[c]	%B[d]	mobility
Fish species									
Japanese horse mackerel (#1)	*Trachurus japonicus*	−16.6	13.3	23.8	4.21	3.71	3.69	87	Migrant
Cutlassfish	*Trichiurus lepturus*	−17.6	12.9	23.5	4.09	3.59	3.64	68	Migrant
Stripe rainbowfish	*Halichoeres tenuispinis*	−16.7	12.5	22.0	3.97	3.47	3.45	86	Migrant
Chub mackerel	*Scomber japonicus*	−17.7	11.8	22.0	3.75	3.25	3.44	65	Migrant
Red seabream	*Pagrus major*	−16.3	12.4	21.1	3.95	3.45	3.33	93	Migrant
Greenling	*Hexagrammos otakii*	−16.2	12.6	20.8	3.99	3.49	3.28	96	Resident
Pearl spot chromis	*Chromis notata*	−17.1	12.2	20.7	3.87	3.37	3.28	78	Resident
Korean rockfish	*Sebastes schlegelii*	−19.1	10.6	20.2	3.40	2.90	3.21	36	Resident
Japanese horse mackerel (#2)	*Trachurus japonicus*	−20.2	10.0	19.9	3.23	2.73	3.18	12	Migrant
Goby	*Gobiidae*	−17.9	11.3	19.4	3.60	3.10	3.10	60	Resident
Rock bream	*Oplegnathus fasciatus*	−16.0	13.1	18.8	4.16	3.66	3.02	99	Resident
Pike eel	*Muraenesox cinereus*	−17.7	11.2	18.2	3.60	3.10	2.94	66	Migrant
Sea perch (#1)	*Ditrema temminckii*	−16.0	12.4	17.9	3.94	3.44	2.91	100	Resident
Sea perch (#2)	*Ditrema temminckii*	−16.6	12.7	17.6	4.04	3.54	2.87	88	Resident
Invertebrate species									
Bristle worm (#1)	*Neanthes* sp.	−18.8	10.8	13.5	3.47	2.97	2.33	–	–
Bristle worm (#2)	*Neanthes* sp.	−18.3	9.71	12.3	3.15	2.65	2.17	–	–
Bristle worm (#3)	*Neanthes* sp.	−18.2	8.51	12.3	2.80	2.30	2.17	–	–
Razor clam	*Siliqua pulchella*	−17.4	7.35	10.7	2.46	1.96	1.96	–	–
Sea cucumber	*Holothuroidea* sp.	−16.0	7.41	10.0	2.47	1.97	1.86	100	–
Scutate stermaspid worm	*Sternaspis scutata*	−21.6	8.35	8.24	2.75	2.25	1.64	–	–
POM and sediment									
bulk POM		−25.2	2.4	–	1.00	–	–	–	–
100–200 μm POM		−20.8	7.5	–	2.50	2.00	–	0	–
>200 μm POM		−20.0	6.5	–	–	–	–	–	–
Surface sediment		−23.4	5.7	–	–	–	–	–	–

[a] TP_{Bulk}: trophic positions calculated using $\delta^{15}N_{Bulk}$ of bulk POM as baseline organism (TP = 1).
[b] $TP_{100-200\ \mu m}$: trophic positions calculated using $\delta^{15}N$ of 100–200 μm POM as baseline organism (TP = 2).
[c] $TP_{Glu-Phe}$: trophic positions calculated using the difference between the $\delta^{15}N$ values of trophic amino acid (Glu) and source amino acid (Phe) in organisms.
[d] %B: relative contribution of benthic carbon source in fish species.

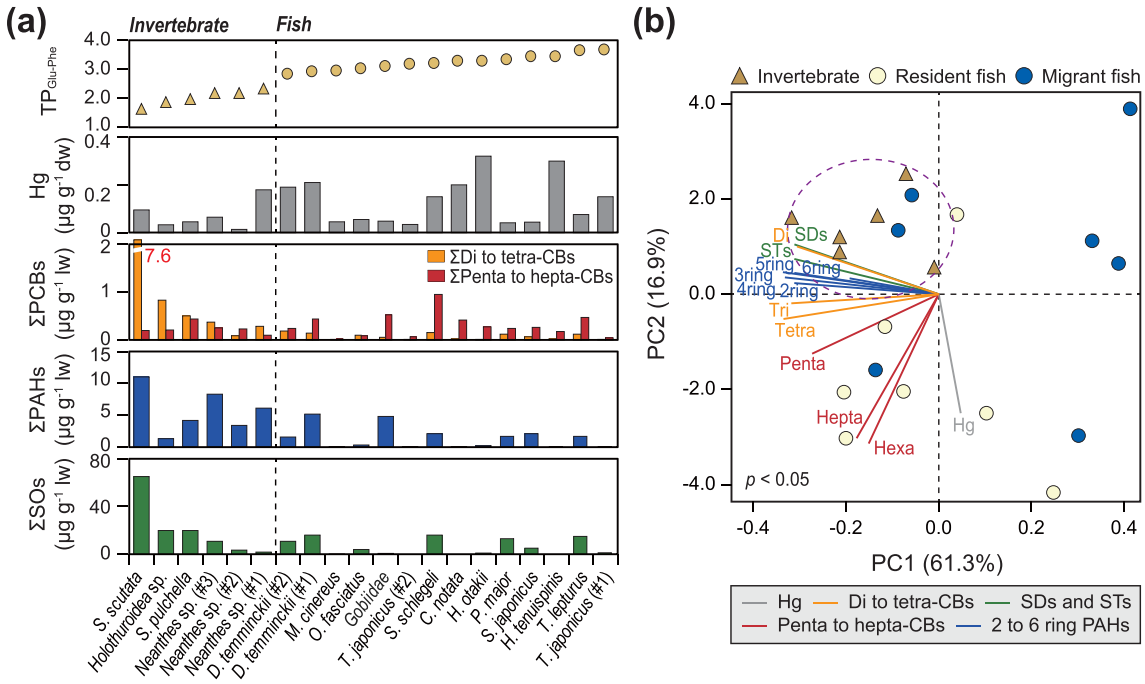

Fig. 2. (a) Concentrations of PTSs and $TP_{Glu-Phe}$ in organisms collected from Ulsan Bay, Korea. (b) Results of the principal component analysis.

species with their growth reported previously (Jiang et al., 2013; Sassa et al., 2008). In addition, $\delta^{15}N_{Bulk}$ differed between the Japanese horse mackerel samples, supporting that the trophic position of this species changes with growth.

The $\delta^{15}N_{Bulk}$ of benthic invertebrates ranged from 7.35‰ to 10.8‰, while the $\delta^{15}N_{Bulk}$ of fish ranged from 10.0‰ to 13.3‰. In

comparison, the $\delta^{15}N_{Glu-Phe}$ of invertebrates ranged from 8.24‰ to 13.5‰, while they ranged from 17.6‰ to 23.8‰ in fish. A positive correlation was obtained between $\delta^{15}N_{Bulk}$ and %B ($r^2 = 0.78$), suggesting that the carbon sources of the organisms affect $\delta^{15}N$ (Fig. 1b). This positive correlation indicated that the ^{15}N content of sediment-associated prey and fecal pellets was high due to microbial activity, with $\delta^{15}N_{Bulk}$ being enriched in organisms with high benthic portions (Vizzini et al., 2002). However, the $\delta^{15}N_{Glu-Phe}$ and %B of organisms were not positively correlated. Thus, the results of the two nitrogen stable isotope ratios (i.e., $\delta^{15}N_{Bulk}$ and $\delta^{15}N_{Glu-Phe}$) show that the $\delta^{15}N_{Glu-Phe}$ of organisms is less affected by variability in nitrogen sources in Ulsan Bay, and could be used to estimate TP with greater accuracy (Chikaraishi et al., 2009). There was no significant difference in $\delta^{13}C$ and $\delta^{15}N$ between migrant and resident fish (Fig. S2). Thus, the mobility of fish might not influence significant changes to carbon sources for fish or estimated trophic positions.

3.2. Trophic position of organisms

The TPs of the organisms calculated from the three equations are shown in Fig. 1c–d. TP_{Bulk} ranged from 2.46 to 3.47 and 3.23 to 4.21 in invertebrates and fish, respectively. Next, $TP_{100-200\ \mu m}$ ranged from 1.96 to 2.97 and 2.73 to 3.71 in invertebrates and fish, respectively. Using this method, the benthic-pelagic integrated TP can be estimated, taking into account the relative portion of benthic and pelagic basal organisms that have the same trophic position (TP = 2) (Munoz et al., 2017). However, this component was not considered separately in this study, because the $\delta^{15}N_{Bulk}$ of the two basal resources was not significantly different. Japanese horse mackerel held the highest TP in the food web (TP_{Bulk} = 4.21; $TP_{100-200\ \mu m}$ = 3.71), followed by rock bream (TP_{Bulk} = 4.16; $TP_{100-200\ \mu m}$ = 3.66), cutlassfish (TP_{Bulk} = 4.09; $TP_{100-200\ \mu m}$ = 3.59), and sea perch (TP_{Bulk} = 4.04; $TP_{100-200\ \mu m}$ = 3.54) (see Table 1 for details).

The TP_{Bulk} of fish was generally higher than $TP_{100-200\ \mu m}$, due to the relatively low $\delta^{15}N$ value of bulk POM (2.4‰). The low $\delta^{15}N$ value of bulk POM might be attributed to the mixing of marine and terrestrial organic matters (Peterson and Howarth, 1987), resulting in the TPs of fish being overestimated. This overestimation of TP reflects the difficulty of pure sampling for primary producers (Post, 2002). In comparison, $TP_{100-200\ \mu m}$ seemed to reduce the effects of terrestrial organic matter due to the selective feeding on the marine phytoplankton by primary consumers (e.g., zooplankton). The distinction between $\delta^{13}C_{Bulk}$ (−25.2‰) and $\delta^{13}C_{100-200\ \mu m}$ (−20.8‰) supports this interpretation, assuming that $\delta^{13}C_{Bulk}$ was affected by terrestrial C3 plants (Fry et al., 1978) and anthropogenic organic matter (Hong et al., 2019).

Finally, the $TP_{Glu-Phe}$ of organisms ranged from 1.64 to 3.69 and was estimated using differences in $\delta^{15}N$ between trophic amino acids ($\delta^{15}N_{Glu}$) and source amino acids ($\delta^{15}N_{Phe}$). $TP_{Glu-Phe}$ values were generally lower than those of TP_{Bulk}; thus, $TP_{Glu-Phe}$ might be more accurate, due to the uncertainty of $\delta^{15}N_{Bulk}$ for baseline organisms being reduced. In particular, differences in TPs for species at the same level (such as Japanese horse mackerel and sea perch) decreased in $TP_{Glu-Phe}$ compared to TP_{Bulk}. Overall, determining the TP of organisms based on $\delta^{15}N_{Glu-Phe}$ seemed to be appropriate, considering the difficulty of sampling for baseline organisms and variations in $\delta^{15}N$ in coastal ecosystems.

3.3. Concentrations and compositions of PTSs in organisms

The concentrations of PTSs in organisms collected from Ulsan Bay were analyzed (Fig. 2a, Tables S4 and S5). Mercury was detected in all biota samples, ranging from 33 to 180 ng g^{-1} dw for invertebrates and 35–320 ng g^{-1} dw for fish. This was similar to the results of previous study conducted in Masan Bay, Korea (9.57–195 ng g^{-1} dw for invertebrates and 10.8–618 ng g^{-1} dw for fish) (Kim et al., 2012). Among benthic invertebrates, polychaetes had the highest concentration of Hg (180 ng g^{-1} dw for bristle worm #1). Higher concentrations of Hg were generally found in demersal fish, such as greenling (320 ng g^{-1} dw) and stripe rainbowfish (300 ng g^{-1} dw), compared to epipelagic fish (e.g., 44 ng g^{-1} dw for chub mackerel) (Table S1). The previous study detected relatively greater concentrations of Hg in benthic organisms, including polychaetes and greenling. In addition, the results of the current study were consistent with a previous study, with higher Hg concentrations being detected in carnivorous and omnivorous organisms compared to herbivorous organisms (Liu et al., 2014).

A total of 25 PCB congeners were detected in the organisms of Ulsan Bay. The highest concentration of ΣPCBs was detected in scutate stermaspid worm (7.8 μg g^{-1} lipid weight (lw)). Specifically, higher concentrations of CB 8 were detected in the invertebrate species, including the scutate stermaspid worm (7.4 μg g^{-1} lw), compared to fish. The concentrations of ΣPCBs detected in fish ranged from 21 to 1200 ng g^{-1} lw, which were higher than those detected in Masan Bay, Korea (1.8–38.5 ng g^{-1} lw) (Won et al., 2020). The most predominant PCB in invertebrates was di-CBs (15–94%), followed by penta-CBs (1.5–54%) and tetra-CBs (2.2–20%). In contrast, for fish species, high-chlorinated CBs were the predominant PCBs, including hexa-CBs (8.5–62%) and penta-CBs (19–71%) (Fig. S3). The distribution patterns of PCB congeners in invertebrate and fish samples were similar to the results of previous studies (Covaci et al., 2006; Miao et al., 2000). Benthic invertebrates that inhabit sediments can be absorbed through the skin by direct contact, as well as through waterborne and dietary exposures. Consequently, relatively low-chlorinated CBs can be introduced more than high-chlorinated CBs. The lipid content of organisms also appeared to influence the bioaccumulation patterns of PCB congeners, with this phenomenon being particularly significant in invertebrate species (Fig. S4). For example, bristle worm (#2) had the highest lipid content (11.5%) of all invertebrates and the lowest CB 8 composition (15%). In comparison, scutate stermaspid worm had the lowest lipid content (1.5%) and highest contribution of CB 8. In addition, different metabolic capacities between marine invertebrates and fish can lead to different PCB congener patterns in organisms (Koenig et al., 2012). Overall, PCBs accumulated in organisms in a species-specific manner, which was dependent on chemical and biological characteristics, including hydrophobicity, bioavailability, exposure routes, and lipid content (Fig. S3) (Miao et al., 2000).

ΣPAH concentrations were greater in invertebrates than those of fish, ranging from 1.3 to 11 μg g^{-1} lw. Similar to PCBs, the highest concentrations of ΣPAHs were detected in the scutate stermaspid worm. High molecular weight PAHs, such as 4-ring PAHs, were predominant in benthic invertebrates, while fish showed different relative compositions between species. Relatively high concentrations of ΣSOs were detected in invertebrates (3.5–65 μg g^{-1} lw). The relative composition of SDs and STs showed no significant differences in organisms. The scutate stermaspid worm had the highest detected PTSs, feeding on detritus in sediments on the seabed. Consequently, this species is considered to be an indicator species of sedimentary pollution (Albayrak et al., 2006).

The PCA approach was performed to determine the characteristics of the PTSs in the organisms of Ulsan Bay, and $a > 0.5$ of KMO (0.688) and significant Bartlett's test ($p < 0.05$) demonstrated its validity. PCA on each grouped compound in organisms showed that PC1 and PC2 accounted for 61.3% and 16.9% of the total variance, respectively (Fig. 2b). The bioaccumulation patterns of PTSs in

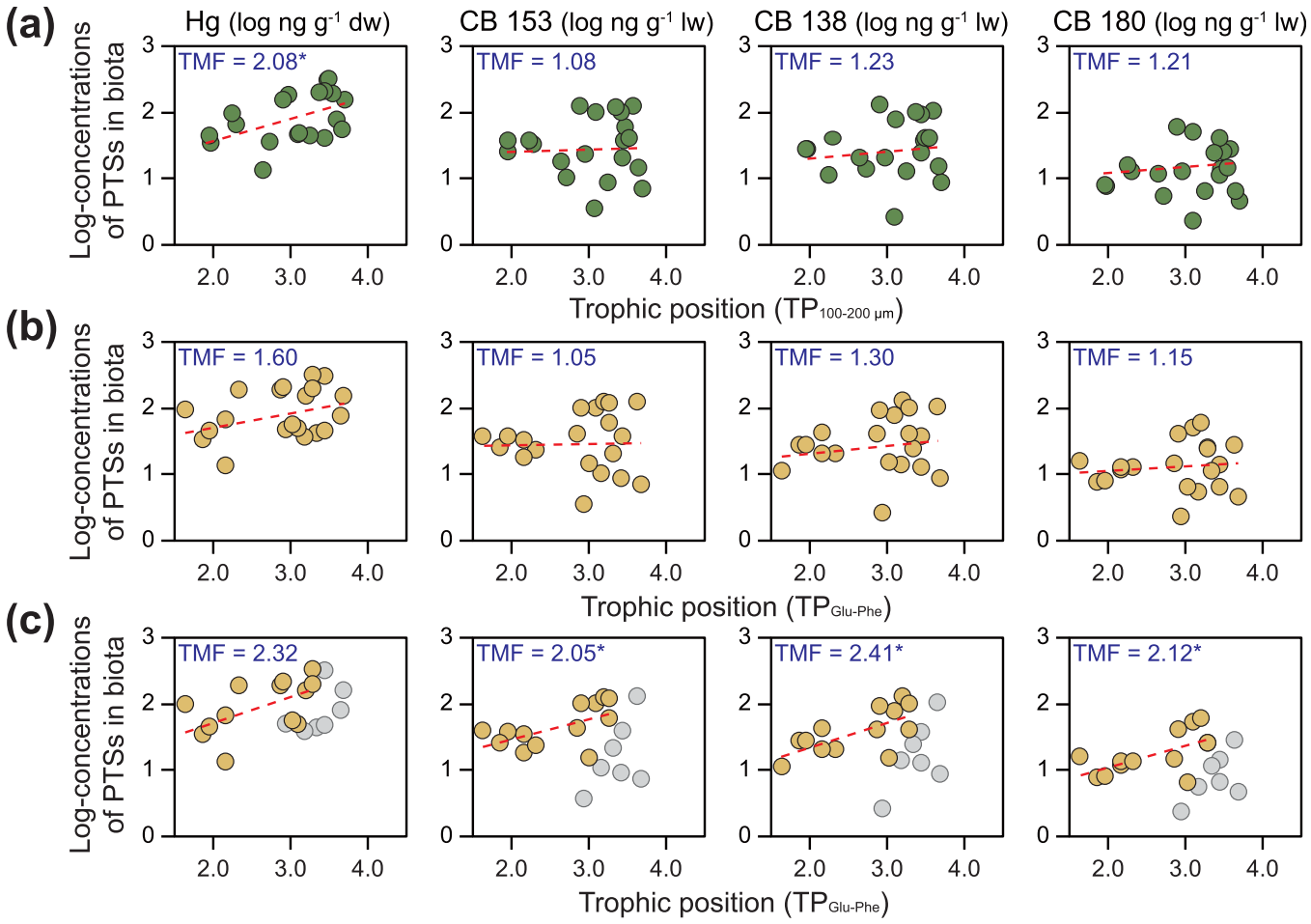

Fig. 3. Scatter plots for the trophic positions of organisms [(a) $TP_{100\text{-}200\ \mu m}$ and (b) $TP_{Glu\text{-}Phe}$] and log-concentrations of selected PTSs (Hg, CB 153, 187, and 180) in organisms collected from Ulsan Bay, Korea. (c) TMF considering resident fish only (grey: migrant fish).

invertebrates were distinct to those of fish. However, there was no significant difference in PTS accumulation between fish species. Factor loading plots showed that the bioaccumulation patterns of PTSs in organisms were compound-specific, and formed two groups [Group 1: Hg and high-chlorinated CBs (penta to hepta-CBs); Group 2: low-chlorinated CBs (di to tetra-CBs), PAHs, and SOs]. Thus, the results indicated that bioaccumulation profiles of PTSs were associated with the biological factors of organisms, including differences in the metabolic capacity and habitats (Windsor et al., 2019). In addition, the chemical properties of PTSs, such as lipophilicity and polarity, seemed to influence the bioaccumulation pattern (Miao et al., 2000).

3.4. Trophic transfer of PTSs through the food web

The assessment of trophic transfer for PTSs through the food web was performed using both $TP_{100–200\ \mu m}$ and $TP_{Glu–Phe}$. TMF values for Hg, 14 PCBs, 7 PAHs, and 10 SOs were estimated (Table S6). These compounds had a detection frequency greater than 50% in organisms. The five PTSs, Hg, CB 153, 138, 187, and 180, exhibited a trophic magnification potential in the food web of Ulsan Bay, with TMF values based on $TP_{100–200\ \mu m}$ ($TMF_{100–200\ \mu m}$) being greater than 1. The TMF values of PTSs based on $TP_{Glu–Phe}$ ($TMF_{Glu–Phe}$) showed similar trends to $TMF_{100–200\ \mu m}$. Previous studies showed that Hg and PCBs are significantly magnified through food webs in various aquatic ecosystems, including marine and freshwater (Coelho et al., 2013; Kobayashi et al., 2015; Nfon et al., 2009; Zhou et al., 2019). The TMF values of PCBs obtained from this study were similar to those in Omuta River, Japan (range: 0.90–3.28; Kobayashi et al., 2015) and fishing grounds in China (range: 0.56–4.41; Zhou et al., 2019). However, these TMFs were slightly lower than those in Lake Hartwell, USA (range: 1.46–6.63; Walters et al., 2011), Lake Como, Italy (range: 1.6–5.9; Villae et al., 2011), and Masan Bay, Korea (range: 0.6–9.9; Won et al., 2020) (see Table S7 for details). Such differences to the TMFs of PCBs across regions might be associated with the uptake routes of PCBs in organisms, range (length) of TPs, or spatial variation in PCBs (Borgå et al., 2012). Thus, it is necessary to reduce the uncertainty caused by these environmental and biological factors to estimate the TMFs of pollutants accurately.

$TMF_{100–200\ \mu m}$ values for seven PAHs and 10 SOs were less than one (TMF: 0.19–0.57 for PAHs and 0.14–0.74 for SOs). Statistically significant decreasing trends of the concentrations of these compounds as a function of TP were obtained from Ant, Chr, BkF, and DbahA ($p < 0.05$). In other words, these PAH and SO concentrations decreased as they reached organisms at higher levels in the food web. Similarly, the $TMF_{Glu–Phe}$ values of PAHs and SOs were below 1, ranging from 0.17 to 0.60 and from 0.08 to 0.62, respectively. Previous studies suggested that PAHs are biodiluted compounds in the aquatic food web (Fan et al., 2017; Takeuchi et al., 2009), which was supported by the results of this study. These compounds might be metabolized more in higher TP organisms (Wan et al., 2007). To

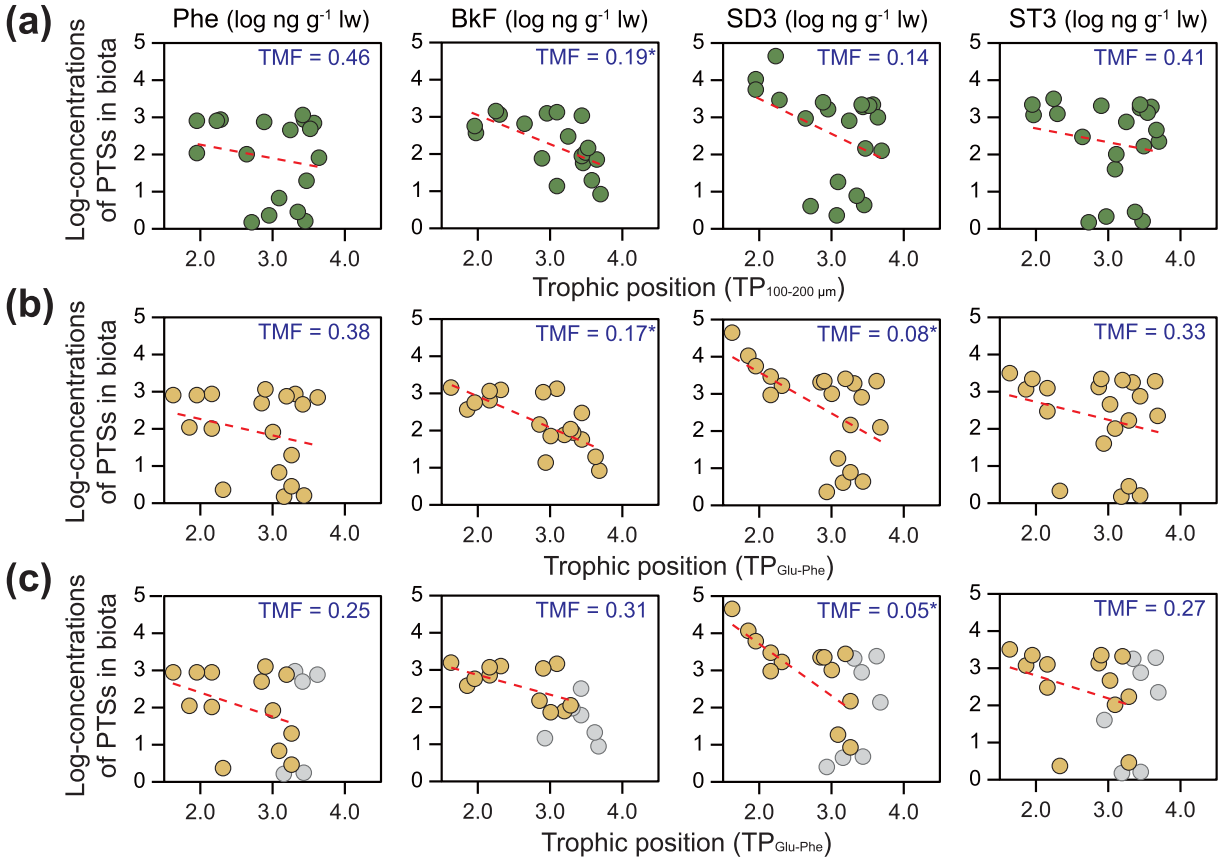

Fig. 4. Scatter plots for the trophic positions of organisms [(a) $TP_{100–200\ \mu m}$ and (b) $TP_{Glu\text{-}Phe}$] and log-concentrations of selected PTSs (Phe, BkF, SD3, and ST3) in organisms collected from Ulsan Bay, Korea. (c) TMF considering resident fish only (grey: migrant fish).

the best of our knowledge, previous studies did not investigate the trophic transfer of SOs through the marine food web. The current study indicated that SOs tend to decrease through the food web, due to biodilution and/or biotransformation processes. Indeed, styrene compounds undergo metabolism by oxidation through the action of some cytochromes in mammalian cells (Andersen et al., 2017). Overall, $TMF_{Glu-Phe}$ does not show a significant difference with the $TMF_{100–200\ \mu m}$, suggesting that various factors that can influence the calculation of TP did not have a great influence for the TMF in the study sites.

3.5. Potential effects of biological factors on TMF

Estimations of TMF could be affected by the mobility of fish, due to the spatial variation of PTSs in the environment, different duration of being exposed to PTSs, and their different uptake routes. Here, for further interpretation on the trophic transfer of PTSs, we tried to explore how fish mobility and the contributions of carbon sources affect the trophic magnification of PTSs in the food web. First, for %B, which reflects the major carbon sources of organisms, the Japanese horse mackerel (# 2) and the Korean rockfish had the lowest contributions (12% and 36%, respectively), and were distinguished from the other fish samples with greater %B (>60%) (Tables 1 and S6). In high %B organisms, where the uptake route is considered to be strongly linked to the benthic pathway, Hg and high chlorinated PCBs had TMF values above 1. However, the TMF values of PTSs in fish were not significantly different between higher %B fish and lower %B fish species (Table S6). Previous studies suggested that the additional bioaccumulation of contaminants through sediment uptake might occur in benthic organisms, resulting in higher TMF values (Fan et al., 2017); however, this phenomenon was not detected in this study. Thus, in the study area, the trophic transfer of PTSs through the food web seemed to be less affected by the direct contact and ingestion of sediments associated with benthic pathways. However, because there were not enough samples with major contributions to the pelagic carbon source, further studies are needed.

To determine how fish residency affects TMF values, fishes were classified into two groups (migrant and resident fish; Table 1). The TMF values of PTSs based on $TP_{Glu\text{-}Phe}$ in the whole food web were compared with those of resident fish only (excluding migrant fish). Because migrant fish inhabit a relatively wider range, we were not able to collect enough potential food sources (i.e., invertebrate) for this group. TMF values of Hg, CB 101, 99, 118, 153, 138, 187, 183, and 180 in resident fish food web exceeded 1, which was about 1.5–2.0 times greater than those in the whole food web (Fig. 3, Table S6). A previous study suggested that TMF calculated in food webs containing mobile species, such as fish, reflects the exposure of species to pollutants from outside the study area, which might distort TMF values (Borgå et al., 2012). In addition to spatial variation in the exposure of pollutants, the non-steady state of $\delta^{15}N$ in mobile organisms might affect TMF (Fisk et al., 2001). Variability of $\delta^{15}N$ in organisms due to such spatial variation could be reduced by using $\delta^{15}N_{Glu-Phe}$ (Chikaraishi et al., 2009).

Biodiluted compounds in the food web, such as PAHs and SOs, showed no significant difference in the calculated TMF values for

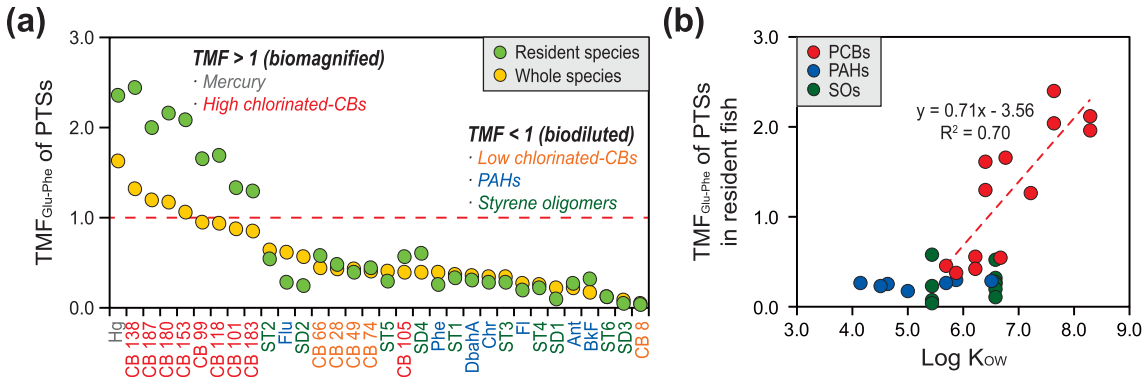

Fig. 5. (a) Comparison of $TMF_{Glu\text{-}Phe}$ values of PTSs in the whole food web and resident fish species (excluded migrant fish). (b) Relationship between $TMF_{Glu\text{-}Phe}$ values of PTSs in resident fish and log K_{OW} values of PTSs (Red dotted line indicates fitted line for log K_{OW} values of PCBs and TMFs). Log K_{OW} values referred from Walters et al. (2011) for PCBs, ChemSpider, 2020(available online at http://www.chemspider.com/) for PAHs, and Hong et al. (2016) for SOs.

fish mobility (resident or migrant), with TMF values of less than 1 being commonly found (Figs. 4 and 5a, Table S6). Despite spatial changes to pollutants and $\delta^{15}N$, these results suggest that other factors might drive the trend in trophic transfer of these compounds. Previous study suggested that certain biological factors, including the efficient metabolism in fish cause to decline the concentrations of pollutants (e.g., PAHs) through the food web (Wan et al., 2007). In addition, the TMF values of PTSs were found to be dependent on the log K_{OW} values of PTSs (Fig. 5b), and this relationship between TMF and log K_{OW} of PTSs has been described in a previous study (Walters et al., 2011); and this trend is pronounced in resident fish.

4. Conclusions

This study demonstrated that the $\delta^{15}N$ of amino acids could be objectively used to determine the trophic transfer of PTSs through the food web. In fish samples from Ulsan Bay, the relationship between $\delta^{15}N$ values (bulk and amino acids) and %B showed that $\delta^{15}N$ of amino acids provide stable information on the TP of organisms. However, the TMF values of PTSs based on $TP_{Glu-Phe}$ were not significantly different from those of TP_{Bulk}. The reason for this result seems to be due to the small number of samples used in this study. Although we could not collect a large number of samples, we believe that this study has conducted relatively successful sampling and TMF measurements because it covers about three trophic hierarchies in the food web. Fish residency could affect the trophic transfer of PTSs due to spatial variation in pollutants and TP variability. Overall, we suggest that future studies should implement a sampling strategy and study design considering uptake routes of PTSs and residency of fishes into account when assessing the trophic transfer of PTSs.

CRediT authorship contribution statement

Yoonyoung An: Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing - original draft. **Seongjin Hong:** Conceptualization, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition, Supervision. **Youngnam Kim:** Investigation, Formal analysis, Data curation. **Mungi Kim:** Formal analysis, Data curation. **Bohyung Choi:** Conceptualization, Writing - review & editing. **Eun-Ji Won:** Conceptualization, Writing - review & editing. **Kyung-Hoon Shin:** Conceptualization, Writing - review & editing, Project administration, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2020.115160.

References

Albayrak, S., Balkis, H., Zenetos, A., Kurun, A., Kubanç, C., 2006. Ecological quality status of coastal benthic ecosystems in the Sea of Marmara. Mar. Pollut. Bull. 52, 790–799.

An, H.S., Kim, M., Hong, S.W., 2008. Genetic diversity of rock bream *Oplegnathus fasciatus* in Southern Korea. Genes Genom. 30, 451–459.

Andersen, M.E., Cruzan, G., Black, M.B., Pendse, S.N., Dodd, D., Bus, J.S., Sarang, S.S., Banton, M.I., Waites, R., McMullen, P.D., 2017. Assessing molecular initiating events (MIEs), key events (KEs) and modulating factors (MFs) for styrene responses in mouse lungs using whole genome gene expression profiling following 1-day and multi-week exposures. Toxicol. Appl. Pharm. 335, 28–40.

Barron, M.G., Galbraith, H., Beltman, D., 1995. Comparative reproductive and developmental toxicology of PCBs in birds. Comput. Biochem. Phys. C 112, 1–14.

Blanke, C.M., Chikaraishi, Y., Takizawa, Y., Steffan, S.A., Dharampal, P.S., Vander Zanden, M.J., 2017. Comparing compound-specific and bulk stable nitrogen isotope trophic discrimination factors across multiple freshwater fish species and diets. Can. J. Fish. Aquat. Sci. 74, 1291–1297.

Borgå, K., Kidd, K.A., Muir, D.C., Berglund, O., Conder, J.M., Gobas, F.A., Kucklick, J., Malm, O., Powell, D.E., 2012. Trophic magnification factors: considerations of ecology, ecosystems, and study design. Integr. Environ. Asses. 8, 64–84.

Broman, D., Näuf, C., Lundbergh, I., Zebühr, Y., 1990. An in situ study on the distribution, biotransformation and flux of polycyclic aromatic hydrocarbons (pahs) in an aquatic food chain (seston-*Mytilus edulis* L.-*Somateria mollissima* L.) from the baltic: an ecotoxicological perspective. Environ. Toxicol. Chem. 9, 429–442.

ChemSpider, 2020. Royal Society of Chemistry 2015. Available online at. http://www.chemspider.com/.

Chikaraishi, Y., Ogawa, N.O., Kashiyama, Y., Takano, Y., Suga, H., Tomitani, A., Miyashita, H., Kitazato, H., Ohkouchi, N., 2009. Determination of aquatic food-web structure based on compound-specific nitrogen isotopic composition of amino acids. Limnol. Oceanogr-Meth. 7, 740–750.

Choi, B., Ha, S.Y., Lee, J.S., Chikaraishi, Y., Ohkouchi, N., Shin, K.H., 2017. Trophic interaction among organisms in a seagrass meadow ecosystem as revealed by bulk δ^{13} C and amino acid δ^{15} N analyses. Limnol. Oceanogr. 62, 1426–1435.
Coelho, J., Mieiro, C., Pereira, E., Duarte, A., Pardal, M., 2013. Mercury biomagnification in a contaminated estuary food web: effects of age and trophic position using stable isotope analyses. Mar. Pollut. Bull. 69, 110–115.
Corbisier, N.T., Petti, M.A.V., Skowronski, R.S.P., Brito, T.A.S., 2004. Trophic relationships in the nearshore zone of Martel Inlet (King George Island, Antarctica): δ^{13}C stable isotope analysis. Polar Biol. 27, 75–82.
Covaci, A., Gheorghe, A., Hulea, O., Schepens, P., 2006. Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta, Romania. Environ. Pollut. 140, 136–149.
Dean, K.E., Suarez, M.P., Rifai, H.S., Palachek, R.M., Koenig, L., 2009. Bioaccumulation of polychlorinated dibenzodioxins and dibenzofurans in catfish and crabs along an estuarine salinity and contamination gradient. Environ. Toxicol. Chem. 28, 2307–2317.
Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Toxicol. Chem. 47, 4967–4983.
Dubois, S., Jean-Louis, B., Bertrand, B., Lefebvre, S., 2007. Isotope trophic-step fractionation of suspension-feeding species: implications for food partitioning in coastal ecosystems. J. Exp. Mar. Biol. Ecol. 351, 121–128.
Fan, S., Wang, B., Liu, H., Gao, S., Li, T., Wang, S., Liu, Y., Liu, X., Wan, Y., 2017. Trophodynamics of organic pollutants in pelagic and benthic food webs of Lake Dianchi: importance of ingested sediment as uptake route. Environ. Sci. Technol. 51, 14135–14143.
Fisk, A.T., Hobson, K.A., Norstrom, R.J., 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. Environ. Sci. Technol. 35, 732–738.
Fortibuoni, T., Noventa, S., Rampazzo, F., Gion, C., Formalewicz, M., Berto, D., Raicevich, S., 2013. Evidence of butyltin biomagnification along the Northern Adriatic food-web (Mediterranean Sea) elucidated by stable isotope ratios. Environ. Sci. Technol. 47, 3370–3377.
Fry, B., Joern, A., Parker, P.L., 1978. Grasshopper food web analysis: use of carbon isotope ratios to examine feeding relationships among terrestrial herbivores. Ecology 59, 498–506.
Gobas, F.A., de Wolf, W.e., Burkhard, L.P., Verbruggen, E., Plotzke, K., 2009. Revisiting bioaccumulation criteria for POPs and PBT assessments. Integr. Environ. Asses. 5, 624–637.
Hobson, K., Piatt, J., Pitocchelli, J., 1994. Using stable isotopes to determine seabird trophic relationships. J. Anim. Ecol. 63, 786–798.
Hong, S., Lee, J., Lee, C., Yoon, S.J., Jeon, S., Kwon, B.O., Lee, J.H., Giesy, J.P., Khim, J.S., 2016. Are styrene oligomers in coastal sediments of an industrial area aryl hydrocarbon-receptor agonists? Environ. Pollut. 213, 913–921.
Hong, S., Lee, Y., Yoon, S.J., Lee, J., Kang, S., Won, E.-J., Hur, J., Khim, J.S., Shin, K.-H., 2019. Carbon and nitrogen stable isotope signatures linked to anthropogenic toxic substances pollution in a highly industrialized area of South Korea. Mar. Pollut. Bull. 144, 152–159.
Ishikawa, N.F., Chikaraishi, Y., Takano, Y., Sasaki, Y., Takizawa, Y., Tsuchiya, M., Tayasu, I., Nagata, T., Ohkouchi, N., 2018. A new analytical method for determination of the nitrogen isotopic composition of methionine: its application to aquatic ecosystems with mixed resources. Limnol. Oceanogr-Meth. 16, 607–620.
Ji, H.S., Kim, J.K., Oh, T.Y., Choi, K.H., Choi, J.H., Seo, Y.I., Lee, D.W., 2015. Larval distribution pattern of *Muraenesox cinereus* (Anguilliformes: Muraenesocidae) leptocephali in waters adjacent to Korea. Ocean Sci. J. 50, 537–545.
Jiang, R.J., Jin, H.W., Zhou, Y.D., Xue, L.J., Guo, A., 2013. Feeding habits of *Trachurus japonicus* in the East China sea. J. Appl. Ecol. 24, 2015–2024.
Kang, P.J., Kim, C.K., Hwang, S.W., 2015. Fish assemblages collected by bottom trammel gill net around Gampo in the East Sea of Korea. Korean J. Environ. Biol. 33, 27–33.
Kayal, S., Connell, D.W., 1995. Polycyclic aromatic hydrocarbons in biota from the Brisbane River Estuary, Australia. Estur. Coast. Shelf Sci. 40, 475–493.
Kelly, J.F., 2000. Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. Can. J. Zool. 78, 1–27.
Khairy, M.A., Weinstein, M.P., Lohmann, R., 2014. Trophodynamic behavior of hydrophobic organic contaminants in the aquatic food web of a tidal river. Environ. Sci. Technol. 48, 12533–12542.
Khim, J.S., Lee, K.T., Kannan, K., Villeneuve, D.L., Giesy, J.P., Koh, C.H., 2001. Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity, Korea. Arch. Environ. Con. Toxicol. 40, 141–150.
Kim, E., Kim, H., Shin, K.H., Kim, M.S., Kundu, S.R., Lee, B.G., Han, S., 2012. Biomagnification of mercury through the benthic food webs of a temperate estuary: Masan Bay, Korea. Environ. Toxicol. Chem. 31, 1254–1263.
Kobayashi, J., Imuta, Y., Komorita, T., Yamada, K., Ishibashi, H., Ishihara, F., Nakashima, N., Sakai, J., Arizono, K., Koga, M., 2015. Trophic magnification of polychlorinated biphenyls and polybrominated diphenyl ethers in an estuarine food web of the Ariake Sea, Japan. Chemosphere 118, 201–206.
Koenig, S., Fernández, P., Solé, M., 2012. Differences in cytochrome P450 enzyme activities between fish and crustacea: relationship with the bioaccumulation patterns of polychlorobiphenyls (PCBs). Aquat. Toxicol. 108, 11–17.
Kwak, S.N., Baeck, G.W., Klumpp, D.W., 2005. Comparative feeding ecology of two sympatric greenling species, *Hexagrammos otakii* and *Hexagrammos agrammus* in Eelgrass *Zostera marina* beds. Environ. Biol. Fish. 74, 129–140.
Kwon, B.G., Koizumi, K., Chung, S.Y., Kodera, Y., Kim, J.O., Saido, K., 2015. Global styrene oligomers monitoring as new chemical contamination from polystyrene plastic marine pollution. J. Hazard Mater. 300, 359–367.
Lattin, J., Douglas, C.J., Green, P.E., 2003. Analyzing Multivariate Data. Thomson Learning, Inc.
Lee, S., Kim, J., Han, S., 2016. Distribution of mackerel, *Scomber japonicus* eggs and larvae in the coast of Jeju island, Korea in spring. J. Korean. Soc. Fish. Ocean Technol. 52, 121–129.
Lee, J., Hong, S., Kwon, B.O., Cha, S.A., Jeong, H.D., Chang, W.K., Ryu, J., Giesy, J.P., Khim, J.S., 2018. Integrated assessment of persistent toxic substances in sediments from Masan Bay, South Korea: comparison between 1998 and 2014. Environ. Pollut. 238, 317–325.
Liénart, C., Susperregui, N., Rouaud, V., Cavalheiro, J., David, V., Del Amo, Y., Duran, R., Lauga, B., Monperrus, M., Pigot, T., Bichon, S., Charlier, K., Savoye, N., 2016. Dynamics of particulate organic matter in a coastal system characterized by the occurrence of marine mucilage – a stable isotope study. J. Sea Res. 116, 12–22.
Liu, J., Xu, X., Yu, S., Cheng, H., Hong, Y., Feng, X., 2014. Mercury pollution in fish from South China Sea: levels, species-specific accumulation, and possible sources. Environ. Res. 131, 160–164.
Masuda, R., Shiba, M., Yamashita, Y., Ueno, M., Kai, Y., Nakanishi, A., Torikoshi, M., Tanaka, M., 2010. Fish assemblages associated with three types of artificial reefs: density of assemblages and possible impacts on adjacent fish abundance. Fish. Bull.-NOAA 108, 162–173.
McCutchan Jr., J.H., Lewis Jr., W.M., Kendall, C., McGrath, C.C., 2003. Variation in trophic shift for stable isotope ratios of carbon, nitrogen, and sulfur. Oikos 102, 378–390.
McLeod, A.M., Arnot, J.A., Borgå, K., Selck, H., Kashian, D.R., Krause, A., Paterson, G., Haffner, G.D., Drouillard, K.G., 2015. Quantifying uncertainty in the trophic magnification factor related to spatial movements of organisms in a food web. Integr. Environ. Asses. 11, 306–318.
Miao, X.S., Swenson, C., Woodward, L.A., Li, Q.X., 2000. Distribution of polychlorinated biphenyls in marine species from French Frigate Shoals, North Pacific Ocean. Sci. Total Environ. 257, 17–28.
Minagawa, M., Wada, E., 1984. Stepwise enrichment of ^{15}N along food chains: further evidence and the relation between δ^{15}N and animal age. Geochim. Cosmochim. Acta 48, 1135–1140.
Muir, D., Savinova, T., Savinov, V., Alexeeva, L., Potelov, V., Svetochev, V., 2003. Bioaccumulation of PCBs and chlorinated pesticides in seals, fishes and invertebrates from the White Sea, Russia. Sci. Total Environ. 306, 111–131.
Munoz, G., Budzinski, H., Babut, M., Drouineau, H., Lauzent, M., Menach, K.L., Lobry, J., Selleslagh, J., Simonnet-Laprade, C., Labadie, P., 2017. Evidence for the trophic transfer of perfluoroalkylated substances in a temperate macrotidal estuary. Environ. Sci. Technol. 51, 8450–8459.
Navarro, P.G., García-Sanz, S., Barrio, J.M., Tuya, F., 2013. Feeding and movement patterns of the sea cucumber Holothuria sanctori. Mar. Biol. 160, 2957–2966.
Nfon, E., Cousins, I.T., Broman, D., 2008. Biomagnification of organic pollutants in benthic and pelagic marine food chains from the Baltic Sea. Sci. Total Environ. 397, 190–204.
Nfon, E., Cousins, I.T., Järvinen, O., Mukherjee, A.B., Verta, M., Broman, D., 2009. Trophodynamics of mercury and other trace elements in a pelagic food chain from the Baltic Sea. Sci. Total Environ. 407, 6267–6274.
Ohyama, K.I., Nagai, F., Tsuchiya, Y., 2001. Certain styrene oligomers have proliferative activity on MCF-7 human breast tumor cells and binding affinity for human estrogen receptor. Environ. Health Perspect. 109, 699–703.
Oziolor, E.M., Apell, J.N., Winfield, Z.C., Back, J.A., Usenko, S., Matson, C.W., 2018. Polychlorinated biphenyl (PCB) contamination in Galveston Bay, Texas: comparing concentrations and profiles in sediments, passive samplers, and fish. Environ. Pollut. 236, 609–618.
Park, C.S., Lee, D.W., Hwang, K., 2002. Distribution and migration of hairtail, *Trichiurus lepturus* in Korean waters. J. Korean Soc. Fish. Res. 5, 1–11.
Park, H.J., Kwak, J.H., Kang, C.K., 2015. Trophic consistency of benthic invertebrate among diversified vegetational habitats in a temperate coastal wetland of Korea as determined by stable isotopes. Estuar. Coast 38, 599–611.
Peterson, B.J., Howarth, R.W., 1987. Sulfur, carbon, and nitrogen isotopes used to trace organic matter flow in the salt-marsh estuaries of Sapelo Island, Georgia. Limnol. Oceanogr. 32, 1195–1213.
Post, D.M., 2002. Using stable isotopes to estimate trophic position: models, methods, and assumptions. Ecology 83, 703–718.
Qadeer, A., Liu, M., Yang, J., Liu, X., Khalil, S.K., Huang, Y., Habibullah-Al-Mamun, M., Gao, D., Yang, Y., 2019. Trophodynamics and parabolic behaviors of polycyclic aromatic hydrocarbons in an urbanized lake food web, Shanghai. Ecotoxicol. Environ. Saf. 178, 17–24.
Reiner, J.L., Wong, C.M., Arcaro, K.F., Kannan, K., 2007. Synthetic musk fragrances in human milk from the United States. Environ. Sci. Technol. 41, 3815–3820.
Sassa, C., Tsukamoto, Y., Konishi, Y., 2008. Diet composition and feeding habits of *Trachurus japonicus* and *Scomber* Spp. larvae in the shelf break region of the East China Sea. Bull. Mar. Sci. 82, 137–153.
Shao, M., Tao, P., Wang, M., Jia, H., Li, Y.F., 2016. Trophic magnification of polybrominated diphenyl ethers in the marine food web from coastal area of Bohai Bay, North China. Environ. Pollut. 213, 379–385.
Suda, Y., Shimizu, M., Nose, Y., 1987. Morphological variations of the Japanese Jack Mackerel *Trachurus japonicus*. Nippon Suisan Gakk 53, 1913–1919.
Takeuchi, I., Miyoshi, N., Mizukawa, K., Takada, H., Ikemoto, T., Omori, K., Tsuchiya, K., 2009. Biomagnification profiles of polycyclic aromatic

hydrocarbons, alkylphenols and polychlorinated biphenyls in Tokyo Bay elucidated by $\delta^{13}C$ and $\delta^{15}N$ isotope ratios as guides to trophic web structure. Mar. Pollut. Bull. 58, 663–671.
UNEP (United Nations Environment Program), 2001. Final Act of the Conference of Pleniopotentiaries on the Stockholm Convention on Persistent Organic Pollutants. UNEP, Geneva (CG), p. 44.
Van Dover, C.L., Grassle, J.F., Fry, B., Garritt, R.H., Starczak, V.R., 1992. Stable isotope evidence for entry of sewage-derived organic material into a deep-sea food web. Nature 360, 153–156.
Vander Zanden, M.J., Rasmussen, J.B., 2001. Variation in $\delta^{15}N$ and $\delta^{13}C$ trophic fractionation: implications for aquatic food web studies. Limnol. Oceanogr. 46, 2061–2066.
Villa, S., Bizzotto, E.C., Vighi, M., 2011. Persistent organic pollutant in a fish community of a sub-alpine lake. Environ. Pollut. 159 (4), 932–939.
Vizzini, S., Sarà, G., Michener, R.H., Mazzola, A., 2002. The role and contribution of the seagrass *Posidonia oceanica* (L.) Delile organic matter for secondary consumers as revealed by carbon and nitrogen stable isotope analysis. Acta Oecol. 23, 277–285.
Walters, D.M., Mills, M.A., Cade, B.S., Burkard, L.P., 2011. Trophic magnification of PCBs and its relationship to the octanol–water partition coefficient. Environ. Sci. Technol. 45, 3917–3924.
Wan, Y., Jin, X., Hu, J., Jin, F., 2007. Trophic dilution of polycyclic aromatic hydrocarbons (PAHs) in a marine food web from Bohai Bay, North China. Environ. Sci. Technol. 41, 3109–3114.
Wang, D.Q., Yu, Y.X., Zhang, X.Y., Zhang, S.H., Pang, Y.P., Zhang, X.L., Yu, Z.Q., Wu, M.H., Fu, J.M., 2012. Polycyclic aromatic hydrocarbons and organochlorine pesticides in fish from Taihu Lake: their levels, sources, and biomagnification. Ecotoxicol. Environ. Saf. 82, 63–70.
Wang, Q., Chen, M., Shan, G., Chen, P., Cui, S., Yi, S., Zhu, L., 2017. Bioaccumulation and biomagnification of emerging bisphenol analogues in aquatic organisms from Taihu Lake, China. Sci. Total Environ. 598, 814–820.
Wen, Z., Xie, P., Xu, J., 2009. Contributions of pelagic and benthic dietary sources to freshwater mussels: evidence from stable carbon isotope analysis. J. Freshw. Ecol. 24 (3), 425–430.
Windsor, F.M., Pereira, M.G., Tyler, C.R., Ormerod, S.J., 2019. Biological traits and the transfer of persistent organic pollutants through river food webs. Environ. Sci. Technol. 53 (22), 13246–13256.
Won, E.J., Choi, B., Hong, S., Khim, J.S., Shin, K.H., 2018. Importance of accurate trophic level determination by nitrogen isotope of amino acids for trophic magnification studies: a review. Environ. Pollut. 238, 677–690.
Won, E.J., Choi, B., Lee, C.H., Hong, S., Lee, J.H., Shin, K.H., 2020. Variability of trophic magnification factors as an effect of estimated trophic position: application of compound-specific nitrogen isotope analysis of amino acids. Environ. Int. 135, 105361.
Yu, Y.X., Zhang, S.H., Huang, N.B., Li, J.L., Pang, Y.P., Zhang, X.Y., Yu, Z.Q., Xu, Z.G., 2012. Polybrominated diphenyl ethers and polychlorinated biphenyls in freshwater fish from Taihu Lake, China: their levels and the factors that influence biomagnification. Environ. Toxicol. Chem. 31, 542–549.
Zhang, Y., Cui, B., Zhang, Q., Liu, X., 2015. Polycyclic aromatic hydrocarbons in the food web of coastal wetlands: distribution, sources and potential toxicity. CLEAN Soil Air Water 43, 881–891.
Zhou, S., Zhu, H., Huang, S., Zhou, J., Zhang, S., Wang, C., 2019. Biomagnification and risk assessment of polychlorinated biphenyls in food web components from Zhoushan fishing ground, China. Mar. Pollut. Bull. 142, 613–619.

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Supplementary Materials for

Trophic transfer of persistent toxic substances through a coastal food web in Ulsan Bay, South Korea: Application of compound-specific isotope analysis of nitrogen in amino acids

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References

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Supplementary Tables

Table S1. Biological information of biota samples collected from Ulsan Bay, Korea.

Common name	Scientific name	Water contents (%)	Lipid contents (%)	Length (cm)	Mobility	Habitat
Fish						
Japanese horse mackerel (#1)	*Trachurus japonicus*	69.8	15.0	23.0	Migrant	Epipelagic
Cutlassfish	*Trichiurus lepturus*	80.1	2.9	59.5	Migrant	Demersal
Stripe rainbowfish	*Halichoeres tenuispinis*	77.7	10.3	15.5	Migrant	Demersal
Chub mackerel	*Scomber japonicus*	71.9	9.5	21.5	Migrant	Epipelagic
Red seabream	*Pagrus major*	78.7	5.4	11.8	Migrant	Demersal
Greenling	*Hexagrammos otakii*	76.4	8.4	19.5	Resident	Demersal
Pearl spot chromis	*Chromis notata*	78.8	5.8	9.5	Resident	Demersal
Korean rockfish	*Sebastes schlegelii*	77.6	6.1	12.1	Resident	Demersal
Japanese horse mackerel (#2)	*Trachurus japonicus*	74.4	11.3	11.6	Migrant	Epipelagic
Goby	*Gobiidae*	79.3	2.5	15.0	Resident	Demersal
Rock bream	*Oplegnathus fasciatus*	75.6	15.0	14.0	Resident	Demersal
Pike eel	*Muraenesox cinereus*	75.1	19.9	27.0	Migrant	Demersal
Sea perch (#1)	*Ditrema temminckii*	78.7	5.5	17	Resident	Demersal
Sea perch (#2)	*Ditrema temminckii*	77.9	6.8	11.9	Resident	Demersal
Invertebrate						
Bristle worm (#1)	*Neanthes* sp.	-	7.5	-		
Bristle worm (#2)	*Neanthes* sp.	-	11.5	-		
Bristle worm (#3)	*Neanthes* sp.	-	5.4	-		
Razor clam	*Siliqua pulchella*	-	2.9	-		
Sea cucumber	*Holothuroidea* sp.	-	5.6	-		
Scutate stermaspid worm	*Sternaspis scutata*	-	1.5	-		

Table S2. GC/MSD conditions for the analyses of polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and styrene oligomers in biota samples.

Instrument	Agilent 7890B GC / 5977B MSD	
Column	HP-5MS UI (30 m long × 0.25 mm i.d × 0.25 μm film)	
Gas flow	1 mL min^{-1} He	
Injection mode	splitless	
Injection volume	1 μL	
Oven temperature program	PCBs	60 °C (hold 1 min) → 5 °C/min to 140 °C (hold 1 min) → 30 °C/min to 200 °C (hold 1 min) → 4 °C/min to 250 °C (hold 5 min)
	PAHs	60 °C (hold 2 min) → 6 °C/min to 300 °C (hold 13 min)
	SOs	60 °C (hold 2 min) → 6 °C/min to 300 °C (hold 3 min) 20 °C/min to 300 °C (hold 6 min)

Table S3. Target compounds, abbreviations, and target ions in the instrumental analysis, and method detection limits and recovery of surrogate standards.

Target compounds	Abbreviation	Target ions (m/z)		Method detection limit (ng g^{-1} dw)
		Quantification ion	Confirmation ion	
Polychlorinated biphenyls (PCBs)				
2,4'-Dichlorobiphenyl	CB 8	222	224	0.23
2,4,4'-Trichlorobiphenyl	CB 28	256	258	0.34
2,2',5,5'-Tetrachlorobiphenyl	CB 52	292	290	0.16
2,2',4,5'-Tetrachlorobiphenyl	CB 49	292	290	0.22
2,2',3,5'-Tetrachlorobiphenyl	CB 44	292	290	0.25
3,4,4'-Trichlorobiphenyl	CB 37	256	258	0.17
2,4,4',5-Tetrachlorobiphenyl	CB 74	292	290	0.16
2,3',4',5-Tetrachlorobiphenyl	CB 70	292	290	0.12
2,3',4,4'-Tetrachlorobiphenyl	CB 66	292	290	0.30
2,3,4,4'-Tetrachlorobiphenyl	CB 60	292	290	0.29
2,2',4,5,5'-Pentachlorobiphenyl	CB 101	326	328	0.20
2,2',4,4',5-Pentachlorobiphenyl	CB 99	326	328	0.18
2,2',3,4,5'-Pentachlorobiphenyl	CB 87	326	328	0.21
3,3',4,4'-Tetrachlorobiphenyl	CB 77	292	290	0.14
2,2',3,3',4-Pentachlorobiphenyl	CB 82	326	324	0.30
2,3',4,4',5-Pentachlorobiphenyl	CB 118	326	328	0.35
2,3,4,4',5-Pentachlorobiphenyl	CB 114	326	328	0.19
2,2',4,4',5,5'-Hexachlorobiphenyl	CB 153	360	362	0.17
2,3,3',4,4'-Pentachlorobiphenyl	CB 105	326	324	0.16
2,2',3,3',5,6,6'-Heptachlorobiphenyl	CB 179	396	394	0.27
2,2',3,4,4',5'-Hexachlorobiphenyl	CB 138	360	362	0.15
2,3,3',4,4',6-Hexachlorobiphenyl	CB 158	360	362	0.32
3,3',4,4',5-Pentachlorobiphenyl	CB 126	326	328	0.25
2,3,4,4',5,6-Hexachlorobiphenyl	CB 166	360	362	0.17
2,2',3,4',5,5',6-Heptachlorobiphenyl	CB 187	394	396	0.20
2,2',3,4,4',5',6-Heptachlorobiphenyl	CB 183	394	396	0.17
2,2',3,3',4,4'-Hexachlorobiphenyl	CB 128	360	362	0.23
2,3,3',4,4',5-Hexachlorobiphenyl	CB 156	360	362	0.22
2,2',3,4,4',5,5'-Heptachlorobiphenyl	CB 180	394	396	0.30
3,3',4,4',5,5'-Hexachlorobiphenyl	CB 169	360	362	0.27
2,2',3,3',4,4',5-Heptachlorobiphenyl	CB 170	394	396	0.25
2,3,3',4,4',5,5'-Heptachlorobiphenyl	CB 189	394	396	0.27
Polycyclic aromatic hydrocarbons (PAHs)				
Acenaphthylene	Acl	152	151	0.06
Acenaphthene	Ace	153	154	0.12
Fluorene	Flu	166	165	0.15
Phenanthrene	Phe	178	176	0.06
Anthracene	Ant	178	176	0.07
Fluoranthene	Fl	202	200	0.09
Pyrene	Py	202	200	0.12
Benzo[a]anthracene	BaA	228	226	0.06
Chrysene	Chr	228	226	0.03
Benzo[b]fluoranthene	BbF	252	253	0.08
Benzo[k]fluoranthene	BkF	252	253	0.20
Benzo[a]pyrene	BaP	252	253	0.09
Indeno[1,2,3-cd]pyrene	IcdP	276	138	0.09
Dibenz[a,h]anthracene	DbahA	278	276	0.07
Benzo[g,h,i]perylene	BghiP	276	138	0.12

Styrene oligomers (SOs)				
1,3-Diphenylpropane	SD1	105	196	0.19
cis-1,2-Diphenylcyclobutane	SD2	78	208	0.19
2,4-Diphenyl-1-butene	SD3	104	208	0.89
trans-1,2-Diphenylcyclobutane	SD4	78	208	0.11
2,4,6-Triphenyl-1-hexene	ST1	117	194	0.63
1e-Phenyl-4e-(1-phenylethyl)-tetralin	ST2	129	207	0.66
1a-Phenyl-4e-(1-phenylethyl)-tetralin	ST3	129	207	0.31
1a-Phenyl-4a-(1-phenylethyl)-tetralin	ST4	129	207	0.70
1e-Phenyl-4a-(1-phenylethyl)-tetralin	ST5	207	105	0.41
1,3,5-Triphenylcyclohexane	ST6	117	104	0.88
Internal standard				
2-Fluorobiphenyl	IS	172	171	
Standard materials		**Quantification ion**	**Confirmation ion**	**%Recovery (Mean ± SD)**
Surrogate standards				
^{13}C-labeled CB 28		268	270	80 ± 18
^{13}C-labeled CB 52		304	302	80 ± 18
^{13}C-labeled CB 101		338	340	84 ± 18
^{13}C-labeled CB 153		372	374	88 ± 19
^{13}C-labeled CB 138		372	374	90 ± 19
^{13}C-labeled CB 180		406	408	94 ± 20
^{13}C-labeled CB 209		440	442	92 ± 19
Acenaphthene-d10		164	162	73 ± 13
Phenanthrene-d10		188	189	75 ± 8.0
Chrysene-d12		240	236	87 ± 12
Perylene-d12		264	270	88 ± 11

Table S4. Concentrations of Hg and PCB congeners in organisms collected from Ulsan Bay, Korea.

Samples	**Concentration of individual compounds**																								
	Hg	Polychlorinated biphenyls (ng g $^{-1}$ lw)																							
	(ng g^{-1} dw)	CB 8	CB 28	CB 52	CB 49	CB 44	CB 74	CB 70	CB 66	CB 101	CB 99	CB 87	CB 77	CB 82	CB 118	CB 153	CB 105	CB 179	CB 138	CB 158	CB 187	CB 183	CB 128	CB 156	CB 180	CB 170
Bristle worm (#1)	180	210	5.7	nd[a]	13	14	15	11	24	8.2	4.1	4.3	nd	nd	6	23	7.2	1.6	19	2.1	7.5	3	nd	nd	13	nd
Bristle worm (#2)	13	50	3.9	nd	10	nd	12	nd	17	9.3	5.5	2.2	nd	nd	12	18	150	nd	20	nd	6	2.3	nd	nd	12	nd
Bristle worm (#3)	65	270	10	12	13	14	35	4.9	25	16	13	3.2	nd	nd	23	33	100	4.9	40	3.3	10	5.3	nd	nd	13	nd
Razor clam	45	400	nd	nd	7.1	31	52	7.3	33	14	5.1	nd	nd	44	15	37	280	nd	27	nd	13	7.8	nd	nd	7.7	nd
Sea cucumber	33	790	10	nd	10	17	30	4	14	12	6.6	1.2	nd	nd	8.1	25	110	3.5	27	nd	13	4.1	nd	nd	7.4	nd
Scutate stermaspid worm	95	7400	57	nd	59	nd	58	22	37	36	17	nd	nd	nd	31	37	37	nd	nd	nd	11	16	nd	nd	16	nd
Japanese horse mackerel (#1)	150	2.1	nd	nd	nd	nd	nd	nd	nd	3.1	1.8	0.6	nd	0.8	3	7	3.6	0.7	8.4	0.7	3.5	1.5	3.2	1.4	4.5	2.3
Cutlassfish	76	48	nd	nd	13	nd	38	nd	25	39	11	5.6	nd	27	48	120	6.8	nd	100	4.2	42	11	25	nd	28	19
Stripe rainbowfish	300	nd[a]	nd	nd	3.7	nd	5	4	7.2	19	13	4.6	nd	nd	18	38	2.5	2.3	36	1.9	12	3.4	5.8	3.3	14	7.7
Chub mackerel	44	17	5.6	11	4.4	nd	14	2	9	5.7	4.5	nd	nd	nd	4.7	8.1	220	nd	12	nd	5.7	2.4	nd	nd	6.3	nd
Red seabream	41	50	nd	36	9.2	nd	32	nd	nd	7.2	4.3	nd	nd	26	8.4	21	130	nd	23	nd	10	1.2	nd	nd	11	nd
Greenling	320	1.5	nd	nd	2.3	nd	nd	1.1	7.6	11	8.6	1.3	3.5	nd	19	60	65	nd	39	2.6	16	6.4	7.7	2.9	25	14
Pearl spot chromis	200	nd	nd	nd	2.5	nd	2.9	2.5	10	36	25	8	nd	nd	43	120	9.2	5.8	97	4.5	28	13	11	5.6	25	10
Korean rockfish	150	39	11	15	15	nd	49	5.9	28	44	29	6.4	nd	40	50	120	390	nd	120	7	46	16	26	14	60	30
Japanese horse mackerel (#2)	35	nd	nd	nd	nd	nd	nd	2.6	nd	5.9	4.1	0.8	3.4	nd	4	10	4.8	1.3	13	1.1	4.8	2	1.2	2.1	5.4	2.6
Goby	48	nd	nd	nd	nd	nd	27	1.6	21	28	23	5.3	nd	4.3	55	98	93	nd	73	5.8	45	11	18	12	51	25
Rock bream	55	63	3.9	nd	1.2	nd	21	2	4.2	8.4	4	1.9	nd	8.9	7.9	15	3.6	1.1	14	0.7	5.7	2	6.3	2.1	6.2	2.9
Pike eel	46	nd	nd	nd	nd	nd	nd	0.3	nd	0.9	1	nd	nd	nd	2.3	3.5	2.7	nd	2.5	nd	0.8	1.1	nd	nd	2.2	nd
Sea perch (#1)	210	49	8.9	15	14	nd	39	nd	19	34	22	5.3	1.1	nd	33	97	24	6.2	87	5.8	50	13	10	nd	39	26
Sea perch (#2)	190	121	6.8	23	nd	nd	23	4	12	20	12	3.8	nd	26	18	41	42	3.3	40	4.2	12	5.1	nd	nd	14	13

[a] nd: not detected.

Table S5. Concentrations of PAHs and SOs in organisms collected from Ulsan Bay, Korea.

Samples	**Concentration of individual compounds**																							
	Polycyclic aromatic hydrocarbons (ng g $^{-1}$ lw)															Styrene oligomers (ng g $^{-1}$ lw)									
	Acl	Ace	Flu	Phe	Ant	Fl	Py	BaA	Chr	BbF	BkF	BaP	IcdP	DbahA	BghiP	SD1	SD2	SD3	SD4	ST1	ST2	ST3	ST4	ST5	ST6
Bristle worm (#1)	nd[a]	nd	nd	nd	38	6	72	140	420	1400	1200	1400	830	nd	540	nd	nd	1600	nd	54	nd	nd	nd	nd	200
Bristle worm (#2)	3.2	5	53	96	8	98	48	90	340	1100	650	530	46	280	52	460	270	890	380	170	50	280	430	60	480
Bristle worm (#3)	9	44	360	820	46	410	170	230	1000	1300	1100	1100	440	780	450	1600	920	2900	1400	560	220	1200	1500	230	430
Razor clam	21	36	580	800	65	170	nd	nd	420	nd	540	250	270	760	310	2800	1600	5500	2400	950	370	2100	2600	280	1200
Sea cucumber	9	nd	140	100	62	60	31	nd	180	nd	350	nd	nd	370	nd	1500	870	11000	1200	520	200	1100	1400	300	1900
Scutate stermaspid worm	nd	nd	310	800	430	160	150	320	590	nd	1400	2000	1600	1700	1200	3700	2300	41000	3100	1600	640	3000	3600	930	5000
Japanese horse mackerel (#1)	nd	nd	nd	nd	3.4	nd	nd	nd	nd	nd	8	nd	nd	nd	nd	2.7	130	120	450	180	150	210	71	98	nd
Cutlassfish	10	61	310	670	41	69	nd	nd	45	nd	20	nd	nd	470	nd	1900	1300	2200	2300	970	490	1900	1900	260	1600
Stripe rainbowfish	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	55	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chub mackerel	7.2	11	170	430	7.7	105	23	670	180	nd	290	120	nd	79	nd	290	470	800	990	400	240	710	640	190	310
Red seabream	6.7	14	310	830	nd	110	nd	nd	200	nd	86	nd	nd	140	nd	1600	1200	1900	2300	890	630	1800	1700	430	980
Greenling	nd	nd	33	19	11	nd	nd	nd	10	nd	110	nd	nd	47	nd	7.5	91	140	410	140	96	160	50	54	33
Pearl spot chromis	nd	nd	nd	nd	4.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Korean rockfish	nd	11	220	710	22	180	76	nd	152	nd	74	nd	nd	680	nd	2400	1500	2500	2200	980	420	2000	2300	350	1700
Japanese horse mackerel (#2)	nd	nd	nd	nd	4.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Goby	nd	nd	nd	nd	110	nd	nd	450	870	nd	1300	nd	880	200	960	nd	83	nd	320	150	77	98	140	nd	nd
Rock bream	nd	6.4	40	80	2.5	nd	nd	nd	20	nd	68	nd	nd	130	nd	570	340	970	500	220	85	440	540	66	240
Pike eel	nd	nd	nd	nd	6.1	nd	nd	nd	nd	nd	13	nd	nd	7.3	nd	nd	26	nd	80	27	33	40	5.5	nd	nd
Sea perch (#1)	nd	9.1	310	1100	40	370	110	56	490	580	1000	590	90	240	150	1500	1300	2100	3200	1200	830	2100	1700	620	1200
Sea perch (#2)	nd	nd	270	460	50	76	nd	nd	140	nd	140	340	nd	170	nd	1200	860	2000	1800	690	380	1300	1200	330	1400

[a] nd: not detected.

Table S6. Trophic magnification factor values for selected PTSs based on $TP_{100–200\ \mu m}$ and $TP_{Glu–Phe}$ in the food web of Ulsan Bay, Korea.

Compounds	Whole food web		Including resident fish		Including high %B fish	
	$TMF_{100–200\ \mu m}$[a]	**$TMF_{Glu–Phe}$[b]**	**$TMF_{100–200\ \mu m}$**	**$TMF_{Glu–Phe}$**	**$TMF_{100–200\ \mu m}$**	**$TMF_{Glu–Phe}$**
Hg	**2.08***	**1.60**	**2.33***	**2.32**	**2.37***	**2.21**
Polychlorinated biphenyls (PCBs)						
CB 8	0.08*	0.05*	0.07*	0.03*	0.10*	0.08*
CB 28	0.46*	0.43*	0.51	0.47*	0.58*	0.56*
CB 49	0.46*	0.42*	0.44*	0.39*	0.57*	0.57*
CB 74	0.44	0.40	0.44*	0.43	0.45	0.41*
CB 66	0.45*	0.43*	0.51*	0.56	0.46*	0.47*
CB 101	0.89	0.86	**1.06**	**1.31**	0.98	0.94
CB 99	0.93	0.93	**1.23**	**1.63**	**1.01**	0.96
CB 118	0.96	0.92	**1.19**	**1.67**	**1.02**	0.98
CB 153	**1.08**	**1.05**	**1.40**	**2.05***	**1.10**	**1.06**
CB 105	0.24*	0.39	0.26*	0.56	0.18*	0.23
CB 138	**1.23**	**1.30**	**1.53**	**2.41***	**1.08**	**1.06**
CB 187	**1.12**	**1.17**	**1.32**	**1.97**	**1.07**	**1.11**
CB 183	0.80	0.83	**1.95**	**1.28**	0.92	0.95
CB 180	**1.21**	**1.15**	**1.57**	**2.12***	**1.30**	**1.23**
Polycyclic aromatic hydrocarbons (PAHs)						
Flu	0.57	0.60	0.37	0.28	0.62	0.61
Phe	0.46	0.38	0.26	0.25	0.44	0.33
Ant	0.23*	0.22*	0.28*	0.26*	0.29*	0.30*
Fl	0.29	0.27	0.19	0.19	0.26*	0.21*
Chr	0.29*	0.34*	0.29	0.28	0.30*	0.33
BkF	0.19*	0.17*	0.42	0.31	0.21*	0.19*
DbahA	0.31*	0.34	0.30*	0.30*	0.39*	0.38*
Styrene oligomers (SOs)						
SD1	0.16	0.22	0.11	0.09	0.19	0.12
SD2	0.38	0.55	0.22	0.24	0.44	0.37
SD3	0.14	0.08*	0.10*	0.05*	0.17*	0.11*
SD4	0.41	0.38	0.64	0.59	0.49	0.39
ST1	0.50	0.36	0.37	0.33	0.48	0.39
ST2	0.74	0.62	0.50	0.54	0.71	0.62
ST3	0.41	0.33	0.25	0.27	0.36	0.27
ST4	0.29	0.25	0.20	0.21	0.27	0.20
ST5	0.49	0.40	0.32	0.29	0.53	0.41
ST6	0.19	0.12*	0.20	0.12*	0.22	0.14*

* $p < 0.05$

[a] TMF values calculated between $TP_{100–200\ \mu m}$ and log concentration of pollutants.

[b] TMF values calculated between $TP_{Glu–Phe}$ and log concentration of pollutants.

Table S7. Values of trophic magnification factors for Hg and PCBs reported in previous studies.

Study area (Country)	year(s)	Organisms in food web	TP[a]	TP estimation		Target compounds	TMF (Mean±SD or min–max)	References
				$TP_{baseline}$	TDF (‰)[b]			
Mercury								
Baltic Sea	1991–1993	Fish, Crustacean, Plankton	2–3.98	2	3.5	THg	1.50	Nfon et al., 2009
Tropical coastal ocean (Brazil)	2008–2010	Fish, Mollusca, Crustacean, Plankton	1.0–3.8±0.1	1	3.4	THg	6.84	Di Beneditto et al., 2012
Coastal lagoon (Portugal)		Fish Crustacean, Invertebrate, Primary producer	0.9–3.2	1	3.4	THg	1.02–1.17	Coelho et al., 2013
Offshore of southwest, Florida (US)	2007–2010	Fish, Invertebrate	1.50–4.15	2	3.4	Hg	5.05	Thera et al., 2014
Ulsan Bay (Korea)	2017	Fish, Invertebrate	1.64–3.69	1	7.6	THg	1.60	This study
Polychlorinated biphenyls (PCBs)								
Reservoir in e-waste recycling site (China)	2006	Reptile, Fish, Crustacean, Gastropoda	2.0–4.60	2	3.4	tri-CB tetra-CB penta-CB hexa-CB hepta-CB	2.03–2.40 2.17–4.83 2.70–4.68 1.69–5.10 3.12–4.73	Wu et al., 2009
Lake Hartwell (US)	2005, 2006	Fish, Invertebrate	1.6–4.1	2	3.4	di-CB tri-CB tetra-CB penta-CB hexa-CB hepta-CB	1.95 1.46–2.68 1.97–3.57 3.10–5.07 3.90–6.24 4.38–6.63	Walters et al., 2011
Lake Como (Italy)	2007	Fish, plankton	2.0–3.9	1 or 2	3.4	tri-CB tetra-CB penta-CB hexa-CB hepta-CB	1.6 2.1 2.6–5.9 1.8–4.7 2.9–4.3	Villa et al., 2011
Omuta River (Japan)	2012	Fish, Gastropoda	2.0–3.5±0.52	2	3.4	di-CB tri-CB	2.81–3.28 1.61–2.88	Kobayashi et al., 2015

						tetra-CB penta-CB hexa-CB hepta-CB	1.25–2.39 1.09–1.59 1.02–1.70 0.90–1.18	
Lake Nam Co (Tibet)	2014	Fish, Invertebrate, Plankton	1.0–3.6	1	3.4	hexa-CB hepta-CB	2.7–2.9 3.5	Ren et al., 2017
Zhoushan fishing ground (China)	2011	Mammal, Fish, Crustacean, Zooplankton	2.00±0.07 –3.81±0.27	1	3.4	tri-CB tetra-CB penta-CB hexa-CB hepta-CB	0.70–0.83 0.56–1.37 0.62–1.94 1.24–4.41 1.03–1.50	Zhou et al., 2019
Masan Bay (Korea)	2016	Fish, Invertebrate	2.0–3.1	AAs[c]	7.6	di-CB tri-CB tetra-CB penta-CB hexa-CB hepta-CB octa-CB nona-CB Deca-CB	0.6 0.6–0.7 0.7-0.9 2.1–6.3 4.6-7.1 6.1-9.9. 0.6-0.7 0.7 0.8	Won et al., 2020
Ulsan Bay (Korea)	2017	Fish, Invertebrate	1.64–3.69	AAs	7.6	di-CB tri-CB penta-CB hepta-CB	0.05 0.43 0.86–0.93 0.83–1.17	This study

[a] TP: trophic position of the organism. [min–max (or mean ± SD)]
[b] TDF: trophic discrimination factor.
[c] AAs: based on compound-specific analysis of amino acids.

Supplementary Figures

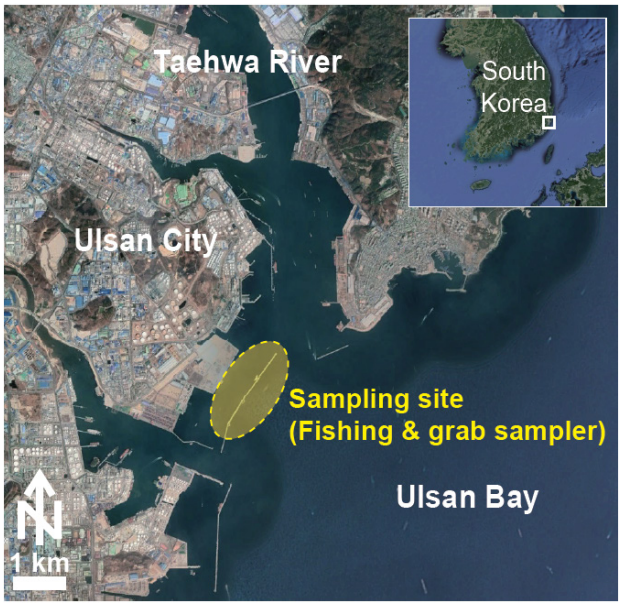

Fig. S1. Map showing the sites where biota were sampled in Ulsan Bay, Korea (October, 2017).

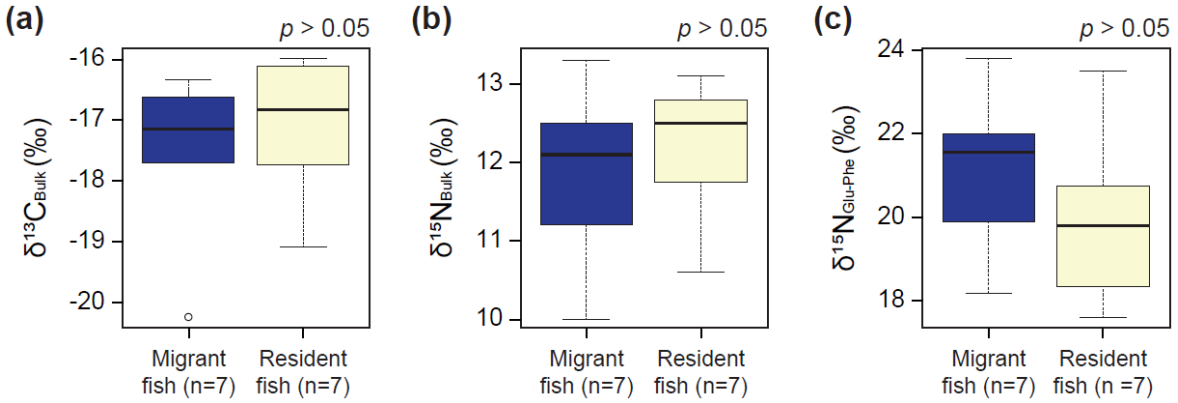

Fig. S2. Comparison of stable isotope ratios between migrant and resident fish collected from Ulsan Bay, Korea. (a) $\delta^{13}C_{Bulk}$, (b) $\delta^{15}N_{Bulk}$, and (c) $\delta^{15}N_{Glu\text{-}Phe}$.

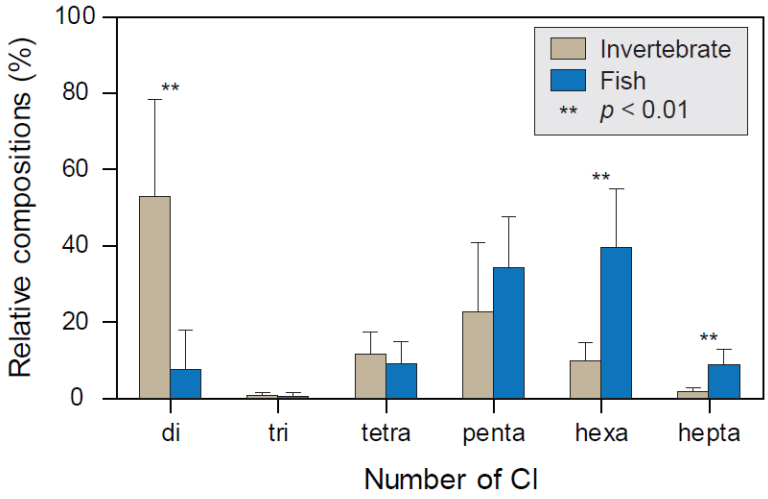

Fig. S3. Relative composition of PCB congeners in invertebrate and fish samples (*p* value verified by unpaired t-test).

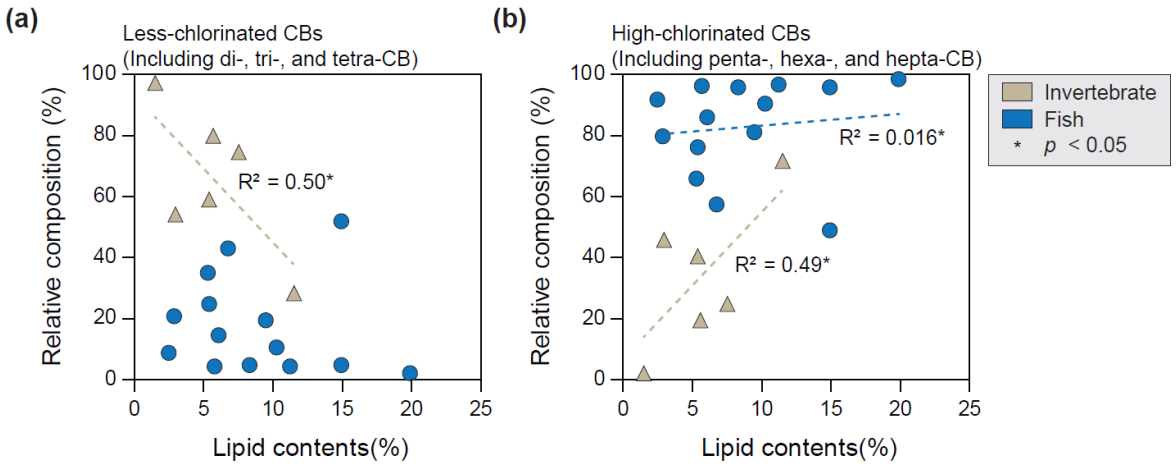

Fig. S4. Correlation between the lipid content and the relative composition of PCBs in organisms collected from Ulsan Bay, Korea: (a) less-chlorinated CBs; (b) high-chlorinated CBs.

References

Coelho, J.; Mieiro, C.; Pereira, E.; Duarte, A.; Pardal, M., 2013. Mercury biomagnification in a contaminated estuary food web: Effects of age and trophic position using stable isotope analyses. Mar. Pollut. Bull. 69, (1-2), 110-115.

Di Beneditto, A. P.; Bittar, V. T.; Camargo, P. B.; Rezende, C. E.; Kehrig, H. A., 2012. Mercury and nitrogen isotope in a marine species from a tropical coastal food web. Arch. Environ. Con. Tox. 62, (2), 264-271.

Kobayashi, J.; Imuta, Y.; Komorita, T.; Yamada, K.; Ishibashi, H.; Ishihara, F.; Nakashima, N.; Sakai, J.; Arizono, K.; Koga, M., 2015. Trophic magnification of polychlorinated biphenyls and polybrominated diphenyl ethers in an estuarine food web of the Ariake Sea, Japan. Chemosphere 118, 201-206.

Nfon, E.; Cousins, I. T.; Järvinen, O.; Mukherjee, A. B.; Verta, M.; Broman, D., 2009. Trophodynamics of mercury and other trace elements in a pelagic food chain from the Baltic Sea. Sci. Total Environ. 407, (24), 6267-6274.

Ren, J.; Wang, X.; Wang, C.; Gong, P.; Wang, X.; Yao, T., 2017. Biomagnification of persistent organic pollutants along a high-altitude aquatic food chain in the Tibetan Plateau: Processes and mechanisms. Environ. Pollut. 220, 636-643.

Thera, J. C.; Rumbold, D. G., 2014. Biomagnification of mercury through a subtropical coastal food web off southwest Florida. Environ. Toxicol. Chem. 33, (1), 65-73.

Villa, S.; Bizzotto, E. C.; Vighi, M., 2011. Persistent organic pollutant in a fish community of a sub-alpine lake. Environ. Pollut. 159, (4), 932-939.

Walters, D. M.; Mills, M. A.; Cade, B. S.; Burkard, L. P., 2011. Trophic magnification of PCBs and its relationship to the octanol−water partition coefficient. Environ. Sci. Technol. 45, 3917-3924.

Won, E. J.; Choi, B.; Lee, C. H.; Hong, S.; Lee, J. H.; Shin, K. H., 2020. Variability of trophic magnification factors as an effect of estimated trophic position: Application of compound-specific nitrogen isotope analysis of amino acids. Environ. Int. 135, 105361.

Wu, J.-P.; Luo, X.-J.; Zhang, Y.; Yu, M.; Chen, S.-J.; Mai, B.-X.; Yang, Z.-Y., 2009. Biomagnification of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls in a highly contaminated freshwater food web from South China. Environ. Pollut. 157, (3), 904-909.

Zhou, S.; Zhu, H.; Huang, S.; Zhou, J.; Zhang, S.; Wang, C., 2019. Biomagnification and risk assessment of polychlorinated biphenyls in food web components from Zhoushan fishing ground, China. Mar. Pollut. Bull. 142, 613-619.