Trophic Dilution of Polycyclic Aromatic Hydrocarbons (PAHs) in a Marine Food Web from Bohai Bay, North China

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Trophic transfer of polycyclic aromatic hydrocarbons (PAHs) in aquatic ecosystems is an important criterion for assessing their ecological risk. This study analyzed 18 PAHs in phytoplankton/seston, zooplankton, five invertebrate species, five fish species, and one seabird species collected from Bohai Bay, and trophic transfer of the PAHs was determined in the food web, of which the length was approximately 4 on the basis of stable nitrogen isotope values. The concentrations of PAHs $(2-64.5 \text{ nq/q})$ wet weight) in the marine ecosystem were moderate compared with other marine organisms worldwide, and the PAH compositions exhibited species-specific profiles that were related to trophic levels in some organisms. Significant negative relationships were also found between trophic levels and lipid-normalized concentrations for 10 PAH compounds (acenaphthylene, anthracene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene + benzo[k]fluoranthene, benzo[e]pyrene, benzo[a] pyrene, and perylene), and their trophic magnification factors (TMFs) ranged from 0.11 for fluoranthene to 0.45 for acenaphthylene. These results confirm that PAHs undergo trophic dilution in the marine food web, which is likely to be the combined results of low assimilation efficiencies and efficient metabolic transformation at higher trophic levels.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and are released into the environment primarily by incomplete combustion of organic matter $(1-3)$. These contaminants are of special concern since some PAHs elicit potent mutagenic and carcinogenic properties (*4*-*5*) and endocrine-disrupting activity (*6*). In aquatic ecosystems, PAHs partition preferentially to sediments because of their hydrophobicity (log *^K*ow: 3.37-7 (*7*)) and are deposited for a long time with half-lives of 0.2-⁵ years in sediment and soil (*8*-*9*). Being persistent in the sediment, PAHs can continually affect bottom-dwelling organisms and high trophic level animals via food webs. It has been clarified that while relatively high concentrations are often detected in macroinvertebrates, and macroinvertebrates have been widely used as bioindictors to monitor spatial and temporal trends of PAH concentrations (*10*-*11*), the concentration in animals at high trophic levels is relatively

low and the primary concern is the potential of some PAHs' metabolites to cause damage to DNA, RNA, and cellular proteins (*12*).

In addition to their toxicity, environmental persistence, and bioaccumulation, trophic transfer of PAHs in aquatic ecosystem is another vital criterion for assessing the ecological risk of the chemicals. To our knowledge, only a few comprehensive studies on PAH residues in marine food webs have been published (*13*-*15*), which all indicated a relatively low concentration in organisms at high trophic levels compared with those in low trophic organisms. However, the organisms analyzed in the studies mentioned above did not constitute a whole aquatic ecosystem: only three species (seston, mussel, and eider duck) were studied in Broman et al.'s study (*13*), the food web lengths studied by Kayal and Connell (crab, fish, and bird) and by Nakata et al. (fish and invertebrate) were short (*14*, *15*), and the trophic position was just ranked according to the dietary habits, or the trophic level were assigned as an index value. In addition, since PAHs are hydrophobic pollutants, these previous studies all neglected the influence of lipid content, which accounts in part for higher concentrations in upper trophic level organisms (*16*). Total PAHs were studied in previous studies, and no attention was paid to the individual PAH compounds, which would be important for assessing toxic equivalency factors of different compounds. Thus, it is necessary to investigate the exact trophodynamic of each PAH compound on the basis of a relative whole food web including members such as primary producers, macroinvertebrates, fish, and birds.

To provide information on the trophodynamics of PAHs in aquatic ecosystems, this study analyzed 18 PAHs including the 16-priority pollutant PAHs recommended by the U.S. Environmental Protection Agency in a marine food web (including phytoplankton/seston, zooplankton, five invertebrate species, five fish species, and one marine bird) from Bohai Bay, North China. The trophic levels of all organisms were determined by using the stable carbon and nitrogen isotope method (*17*-*19*). Concentrations for biomagnification calculation are expressed in terms of lipid-normalized concentrations, so that the contribution of contaminant concentrations because of different lipid contents can be disregarded. This study presents the first characterization of trophic transfer of PAHs in the marine food web of Bohai Bay.

Materials and Methods

Sampling. The samples were the same as those used in our previous studies, and a detailed description of the samples has been reported previously (*17*-*19*). Briefly, aquatic food web samples were collected in May, June, and September of 2002 in Bohai Bay (39°12′N, 117°59′E). Seabirds were collected in November of 2002 on the coast of Bohai Bay (39°07′N, 117°44′E). The part of the marine food web investigated in this study included primary producers (including phytoplankton/seston and zooplankton), five invertebrate species (crab (*Portunus trituberculatus*), short-necked clam (*Ruditapes philippinarum*), burrowing shrimp (*Upogebia sp.*), veined rapa whelk (*Rapana venosa*), and bay scallop (*Argopecten irradians*)), five fish species (weever (*Lateolabras japonicus*), catfish (*Chaeturichthys sitgmatias*), bartail flathead (*Platycephalus indlcus*), wolffish (*Obontamblyopus rubicundus*), and mullet (*Liza so-iuy*)), and one seabird species (Herring gull (*Larus argentatus*)). Phytoplankton/ seston and zooplankton were obtained from vertical tows (bottom to surface) using 31.6 cm ID \times 140 m length nets

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(77 μ m mesh) and 37 cm ID \times 140 m length nets (160 μ m mesh), respectively, from six locations (39°00′N, 117°53′E; 39°00′N, 118°00′E; 38°45′N, 117°53′E; 38°45′N, 118°00′E; 38°30′N, 117°53′E; and 38°30′N, 118°00′E). The phytoplankton/seston samples mainly consisted of algae of the taxonomic groups Bacillariophyta and Pyrrophyta, and the samples of zooplankton mainly consisted of small copepods (*Acartia bifilosa*, *Paracalanus parvus*, *Labidocera euchaeta*, and *Oithona similis*). Macroinvertebrates and fish were caught with a bottom trawl, and seabirds were captured before their winter migration commenced. All samples were stored at -20 °C prior to analysis.

Chemicals and Reagents.The studied parent PAHs ranged from diaromatics to hexaaromatics: naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (FE), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), chrysene (Ch), benz[a]anthracene (BaA), benzo- [b]fluoranthene (BbF), benzo[k]fluoranthene (BkF) (BbF and BkF could not be separated in our analytical procedure), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Pery), indeno-[1,2,3*-cd*]pyrene (IP), benzo[*ghi*]perylene (BP), and dibenz[*a,h*]anthracene (DA). PAH standards and surrogate standards (acenaphthene-*d*10, phenanthrene-*d*10, chrysene*d*12, and perylene-*d*14) were obtained from AccuStandard (New Haven, CT). All solvents (dichloromethane, methanol, acetonitrile, and hexane) were HPLC grade purchased from Fisher Scientific (NJ). Sodium chloride, sodium sulfate, and aluminum oxide were analytical grade and were heated at 400 °C for 4 h before use.

Sample Preparation for Chemical Analyses. The muscle was chosen for both isotope and chemical analysis except for plankton, because different turnoff rates of isotope ratios exist among tissues, and the turnoff rates in muscle were relatively low (*20*). The whole bodies of phytoplankton/seston and zooplankton; the soft tissues of crabs, burrowing shrimps, short-necked clams, veined rapa whelks, and bay scallops; and the muscles of fish and seabirds (about 10 g wet weight) were homogenized and then were freeze-dried. Then, the samples were spiked with surrogate standards (20 ng acenaphthene-*d*10, phenanthrene-*d*10, chrysene-*d*12, and perylene-*d*14) and were Soxhlet-extracted with a mixture of dichloromethane and methanol (7:3) for 24 h.

After extraction, a proportion of the extract was used for lipid content analysis by evaporating the extract to dryness and by heating it at 65 °C for about 30 min before weighing, and the lipid content was calculated on wet weight basis. Another portion of the extracts was subjected to acetonitrile partitioning to remove lipid as described previously (*15*). The extract for PAH analysis was dried using a rotary evaporator and was redissolved in hexane and then was added to a separatory funnel containing 50 mL of hexane-saturated acetonitrile and 20 mL of hexane. After the solution was shaken and partitioned, the acetonitrile layer was collected. This procedure was repeated, and a total of 100 mL of hexanesaturated acetonitrile was collected. The acetonitrile layer was transferred toa1L separatory funnel containing 500 mL of 10% NaCl solution and 50 mL of hexane. After the solution was shaken, the water layer was removed and hexane was collected. These procedures were repeated, and a total of 100 mL of hexane was obtained. $Na₂SO₄$ was added to the hexane to remove moisture.

The hexane layer described above was concentrated to about 1 mL and was passed through a glass column containing 10 g of 5% $H₂O$ -deactivated active $Al₂O₃$ (aluminum oxide was activated overnight at 450 °C for 4 h and then at 120 °C for 12 h). This column was eluted with 30 mL hexane and 30 mL mixture of hexane and dichloromethane (3:1). This eluant was concentrated to 0.1 mL in hexane for gas chromatography coupled with mass spectrometry (GC-MS) analysis.

GC-MS Analysis. PAHs were analyzed by gas chromatography (GC) coupled with mass spectrometry (MS). The final concentrated extract obtained as described above was injected into a GC-MS (Hewlett-Packard 5890/5971) using a fused silica capillary column (HP-5MS, 60 m \times 0.25 mm \times 0.25 *µ*m film thickness, J&W Scientific, U.S.). A splitless injector was used, and the injector was maintained at 250 °C. The temperature program was from 80 °C to 150 °C at the rate of 10 °C/min, then increased to 280 °C at the rate of 5 °C/min, and then increased to 300 °C at a rate of 1 °C/min. The interface temperature was 300 °C. The carrier gas was helium at a constant flow rate of 1 mL/min. Data acquisition was in electron impact (70 eV) and selected ion monitoring mode (40 ms dwell time).

Quantitation and Quality Assurance Quality Control (QA/QC). All equipment rinses were done with methanol to avoid sample contamination. A procedural blank was analyzed with every set of seven samples to check for interfering peaks and to correct sample values. The procedure described above was validated for recovery experiment by analyzing spiked samples. Since we found that lipid content was the main factor affecting the recovery for analysis because of the emulsion during the extraction, shrimp samples with relatively high lipid content were used for spike experiment. Analyte addition of unlabeled PAHs was made with the criterion of at least three times the original concentration, and the deuterated PAHs were also added to the samples for comparing the recoveries with those of unlabeled surrogates. The three replicate spiked samples and one matrix blank sample were analyzed to determine the general recovery. The recoveries for spiked samples were 69-114% for unlabeled PAHs, 65-66% for acenaphthene- d_{10} , 86-91% for phenanthrene- d_{10} , 114-120% for chrysene- d_{12} , and 74-119% for perylene- d_{14} .

For sample analysis, the concentrations of PAHs were quantified by the internal standard isotope-dilution method using mean relative response factors determined from calibration standard runs. Concentrations of PAHs in blank samples were low compared with those in samples and all results were blank corrected. In this study, for all the biota samples for analysis, the recoveries of deuterated PAHs were $69 \pm 10\%$, $86 \pm 10\%$, $100 \pm 15\%$, and $99 \pm 15\%$ for acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene*d*14, respectively. Method detection limits (MDL) were 10 pg/g wet weight (ww) for Ace, Acy, and F; 20 pg/g ww for An and Fl; 30 pg/g ww for Py; 40 pg/g ww for Ph, BaA, and IP; 50 pg/g ww for Na, Ch, BaP, and Da; 60 pg/g ww for BeP and Pery; and 100 pg/g ww for $BbF + BkF$ and BP in the biota matrices analyzed.

Calculations of Trophic Magnification Factor. Because the trophic magnification factor (TMF) represents the average rate of increase per trophic level (TL) rather than specific predator-prey relationships (*21*), we used it to describe the food-web biomagnification of chemicals. The continuous integrative measures of trophic position were obtained according to stable nitrogen isotope ratios reported previously (*22*), and the detail descriptions for the analysis were provided in the Supporting Information. The factors are based on the relationships between the trophic level and the PAH concentration using single linear regression:

log PAH concentration (lipid-normalized) = $a + b \times TL$ (1)

where *a* and *b* represent intercept and slope of the regression, respectively. The concentrations below the detection limit were treated as half of the detection limit (Table 1). The *b* in eq 3 was used to calculate TMF by the following equation

$$
TMF = 10^b \tag{2}
$$

indlcus); CS = catfish (Chaeturichthys sitgmatias); LJ = weever (Lateolabras japonicus); LA = herring gull (Larus argentatus). TL = trophic level; data were expressed as mean ± standard deviation (SD) of three

replicates. Lipid content was calculated on wet weight basis.

PC₂ \square AI \bullet RV $\overline{2}$ $TL: 1.61 - 2.15$ TL: 3.01-3.88 \blacksquare RP \Diamond \ddagger Δ US PC2 loadings $\mathbf{1}$ \times Δ □ \Box \triangle PT θ \circ LS $\mathbf{0}$ $\overline{PC1}$ \circ \bullet OR $\therefore 2.17$ -3.10 $-PI$ -1 \times CS $+_{Li}$ -2 $*_{LA}$ -2 \overline{c} $\overline{3}$ -1 $\mathbf{0}$ PC1 loadings **FIGURE 1. Varimax rotated loadings of principal components, PC1 and PC2, for aquatic organisms collected from Bohai Bay, North** China. PK = phytoplankton/seston + zooplankton; AI = bay scallop
(*Arnonecten irradians*): RV = veined rana whelk (*Ranana venosa*): **(Argopecten irradians); RV**) **veined rapa whelk (Rapana venosa); RP**)**short-necked clam (Ruditapes philippinarum); US**)**burrowing shrimp (Upogebia sp .); PT**) **crab (Portunus trituberculatus); LS**) **mullet (Liza so-iuy); OR**) **wolffish (Obontamblyopus rubicundus);**

3

 \Diamond PK

Statistical Analysis. Correlations between PAH concentration and trophic level were examined by Pearson's rank correlation test, and when the *p* value was below 0.05, the linear regression between the PAH concentration and trophic level was regarded as significant. **and LA**) **herring gull (Larus argentatus).**

PI) **bartail flathead (Platycephalus indlcus); CS**) **catfish (Chaeturichthys sitgmatias); LJ**) **weever (Lateolabras japonicus);**

PAH profile patterns were evaluated by principal component analysis (PCA) for all samples. The analyses were performed on log-transformed data. In the case of missing values (e.g., below the detection limit), the concentrations were treated as half of the detection limit. The software used was SPSS 11.0 (SPSS Inc., Chicago, IL).

Results and Discussion

PAH Concentrations. Table 1 and Supporting Information Table 1 show the mean biological parameters and the PAH concentrations (ng/g dry weight (dw)) in target organisms from Bohai Bay. The highest and lowest total PAH concentrations were found in zooplankton (644.6 ng/g dw) and weever (8.7 ng/g dw), respectively. When the concentrations were expressed on a lipid weight basis, the highest concentrations were detected in phytoplankton/seston and zooplankton (1321 and 3503 ng/g lipid weight (lw)), followed by macroinvertebrates (66 -770 ng/g lw), birds (370 ng/g lw), and fish (43 -247 ng/g lw). To our knowledge, PAH concentrations in primary producers from aquatic ecosystems have only been reported in a food chain from the Baltic Sea (*13*), and the mean concentrations in phytoplankton/seston and zooplankton were much lower than those in seston from the Baltic Sea (202 340 ng/g lw) (*13*). Of all the organisms, the concentration in phytoplankton/seston and zooplankton was the highest, and the same observation was also reported in the food chain from the Baltic Sea where the concentrations of PAHs in mussel and duck were 2282 ng/g lw and 110 ng/g dw (dry weight) (*13*), indicating that primary producers are very important for the distribution of PAHs in natural aquatic environments. The PAHs in macroinvertebrates in this study (19.3–215.3 ng/g dw) were comparable to those in mussels
from the Mediterranean Sea (25.1–390 ng/g dw) (23–24) from the Mediterranean Sea (25.1 -390 ng/g dw) (*²³* -*²⁴*) and in bivalve species from the Gulf of Oman $(17-173 \text{ ng/g})$
dw) (25) and were slightly bigher than those in clam, ovster dw) (*25*) and were slightly higher than those in clam, oyster, and crab from the Ariake Sea (3.4 -5.1 ng/g ww) (*15*). In the present study, the PAH concentrations in fish (8.7 -58.8 ng/g

FIGURE 2. PAH concentrations (ng/g lw) and trophic level relationships for the marine food web in Bohai Bay. The lines represent linear regression used for calculating trophic magnification factors (TMF) in Table 2. Only data sets of compounds with significant slopes were plotted.

dw) were slightly lower than those in fish from the Mediterranean Sea (14.7-139 ng/g dw) and the Gulf of Oman (17-173 ng/g dw) (*23*-*25*). For birds, the concentrations of PAHs in herring gulls (37.8 \pm 12.5 ng/g ww, 107.9 \pm 35.7 ng/g dw) were also comparable with those in duck from the Baltic Sea (*13*) and were slightly lower than those in Australian pelican (75 ng/g ww) and Silver gull (85 ng/g ww) from the Brisbane River estuary (*14*). Conclusively, the organisms in Bohai Bay are moderately contaminated by PAHs compared with other marine organisms worldwide.

TABLE 2. Statistical Results of Regression Analysis between Logarithm of Concentration and Trophic Level (Slope, *p***-Value of Slope) and TMFs for PAHs**

compound	slope (b)	r^2	TMF	р
Na	-0.30	0.10	0.50	0.288
Acy	-0.35	0.46	0.45	0.011
Ace	0.01	0.06	1.02	0.747
FE	0.06	0.01	1.15	0.810
Ph	-0.37	0.16	0.43	0.182
An	-0.47	0.52	0.34	0.005
FI	-0.94	0.51	0.11	0.006
Py	-0.76	0.57	0.17	0.003
BaA	-0.70	0.67	0.20	0.001
Сh	-0.58	0.58	0.26	0.002
$BbF + BkF$	-0.57	0.53	0.27	0.005
BeP	-0.61	0.60	0.25	0.002
BaP	-0.49	0.42	0.32	0.016
Perv	-0.62	0.35	0.24	0.034
IP	-0.09	0.01	0.81	0.727
ΒP	-0.19	0.05	0.65	0.450
DA	-0.07	0.07	0.85	0.786
^a p values in bold print represent statistically significant increases				

or decreases of the lipid-normalized concentration (i.e., <0.05).

PAH Composition. It was found that the proportions (calculated as percentage of total PAHs) of medium-to-high molecular compounds were relatively high, for example, Py: ²-17%, BaA: 2-12%, Ch: 3-47, BbF + BkF: 2-11, BeP: ⁴-13%, and BaP: 2-8%. BeP and Pery (not belonging to the 16 priority PAHs) also showed relatively high proportions: ⁴-13% and 0.1-14%, respectively. Because the PAH distributions in the present study do not have clearly dominant compounds, we conducted principal component analysis (PCA) to further evaluate the PAH profiles and found that each species had a specific profile. Four principal components (PC1, PC2, PC3, and PC4) were identified after varimax rotation and accounted for 30.9, 26.1, 18.0, and 10.4%, respectively, of the total variance. PC1 was associated mainly with Na, An, Fl, Py, BaA, and Ch; PC2 was dominated by BbF + BkF, BeP, BaP, Pery, IP, BP, and DA; PC3 was characterized by high loadings of Ace, FE, and Ph; and PC4 was correlated with Acy. A similar species-specific profile of PAHs was also reported for a Norwegian fjord (*26*), and it was possibly due to trophic levels, and therefore to diet, and biotransformation capacities of the animals, in addition to bioavailability of the compounds (*24*). Figure 1 shows the scatter plots of the component scores on PC1/PC2, showing that intraspecific variability was present in all species, especially for crab and wolffish. For the species with small individual differences, the samples can be classified to three groups: phytoplankton/ seston, zooplankton, and bay scallop (TL: 1.61-2.15); veined rapa whelk, short-necked clam, and crab (TL: 2.17-3.10); and burrowing shrimp, mullet, Bartail flathead, catfish, weever, and herring gulls (TL: 3.01-3.88), which were found to be related to their trophic levels. This suggested that the trophic level would be the main factor determining the species-specific profile of PAHs in these organisms.

Trophodynamics of PAHs. Regression analysis was also conducted between the lipid-normalized concentrations of PAHs (log-transformed) and the trophic level, as shown in Figure 2, and the statistical results of the regression analysis are listed in Table 2. Lipid-normalized concentrations of total PAH concentrations decreased significantly with increasing trophic level ($p = 0.018$). Regarding individual PAHs, significant negative relationships for 10 individual PAH compounds (*p*: 0.001-0.034) were also obtained, as shown in Figure 2, and the TMF values ranged from 0.11 for fluoranthene to 0.45 for acenaphthylene, as shown in Table 2. These results indicate that PAHs undergo trophic dilution in the marine food web.

FIGURE 3. Relationships between log ^Kow values and trophic magnification factors (TMFs) of PAHs in the marine food web from Bohai Bay. log ^Kow values were taken from Neff and Burns (7). O**: no statistically significant relationships between lipid-normal**ized concentration and trophic levels; \bullet : statistically significant **decreases of the lipid equivalent concentration with trophic levels.**

Generally, the octanol-water partition coefficient ($log K_{ow}$) can be used to assess the biomagnification potential of pollutants in the environment (*27*-*28*). However, the TMF values of PAHs were much lower than those of recalcitrant organochlorines with similar log K_{ow} (e.g., DDTs, HCB, and coplanar PCBs), which were all higher than 1 (*17*-*18*). Figure 3 shows the relationships between the log K_{ow} and TMFs of PAHs. Although positive relationships have been found between the TMFs and log K_{ow} of most organochlorines in the Northwater Polynya marine food web (*29*), no relationships were obtained for PAHs. These results all indicate that the trophic transfer characterization of PAHs was different from those of organochlorines in the marine food web.

As shown in Figure 3, 10 PAH compounds, with log *K*ow values ranging from 3.5 to 6.5, showed significant food web trophic dilution, which was similar to the trophodynamics of non-2,3,7,8-substituted (Polychlorinated Dibenzo-*p*dioxins, Dibenzofurans) (PCDD/Fs) in the same food web (*17*). For the medium molecular-weight phthalate esters and 2,3,7,8-substituted PCDD/Fs with the same range of log K_{ow} as PAHs, no significant food web trophic dilution was reported (*17*, *30*). The different biomagnification potential for these chemicals with similar $\log K_{ow}$ indicates that the $\log K_{ow}$ was not the only factor to decide the bioaccumulation potential of a chemical, although most models rely on the octanolwater partition coefficient to estimate bioaccumulation (*31*). Cytochromes P450, which can catalyze the oxidation of various chemicals, have been found throughout nature (*32*), and the metabolic transformation of PAHs was an important factor influencing their trophic transfer in ecosystems (*33*). In fact, the half-lives (2.6-15.6 days) of PAHs in macroinvertebrates were relatively low compared with those of low molecular weight coplanar PCBs (28-60 days) (*34*-*35*), which exhibit high biomagnification potentials in the same food web (*17*). Besides metabolic transformation, gut assimilation efficiency is another important factor as exemplified by the previous bioaccumulation models of PAHs (*36*). The assimilation efficiencies of PAHs with log K_{ow} values ranging from 4.5 to 6 were lower than those of PCBs with same range of log *K*ow (*36*), and these PCBs were shown to biomagnify in marine food webs (*17*, *29*). So, trophic dilutions of PAHs in marine food web are likely because of both their low assimilation efficiencies and efficient metabolic transformation in animals at higher trophic levels.

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Supporting Information Available

Stabile isotope analysis, trophic level calculation, and a table showing PAH concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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