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Environmental fate and trophic transfer of synthetic musk compounds and siloxanes in Geum River, Korea: Compound-specific nitrogen isotope analysis of amino acids for accurate trophic position estimation

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ABSTRACT

Despite the extensive usage of synthetic musk compounds (SMCs) and siloxanes in various personal care products (PCPs), trophic magnification of such chemicals in aquatic environments remains unexplored. In June and September 2020, eleven SMCs and nineteen siloxanes were measured in water, sediments, and biota. Samples were collected from two sites where levels were expected to be influenced by the distance from the wastewater treatment plant (WWTP) in the Geum River, Republic of Korea, were expected. High concentrations of SMCs and siloxanes entered through WWTP were measured in water, sediment, and biota at the both sites and both seasons. The $\delta^{15}\text{N}$ of amino acids provided a high-resolution food web and accurate trophic position (TP), which is an important factor for determining the trophic magnification factor (TMF). Among 24 TMFs, 19 of them were <1, ranging 0.7–0.8 for 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta- γ -2-benzopyran (HHCB), 0.6–0.8 for 6-Acetyl-1,1,2,4,4,7-hexamethyltetralin (AHTN), 0.7–0.8 for 4-tert-Butyl-3,5-dinitro-2,6-dimethylacetophenone (MK), 0.7–0.9 for octamethylcyclotetrasiloxane (D4), 0.1–0.4 for decamethylcyclotetrasiloxane (D5), and 0.04–0.8 for dodecamethylcyclohexasiloxane (D6), and the remaining ones including HHCB, AHTN, MK, and D4 showed values close to 1 or slightly higher (TMF range: 1.0–2.3) indicating no or a little trophic magnification. The TMFs of these compounds were constant across sites and seasons. The TMF values of PCPs might be affected by species specificity and food web structure rather than by chemical properties such as $\log K_{ow}$, which describes a wide range of TMF values in various environments. This study presents valuable implications for assessing risk and managing environmental fate and trophic transfer of SMCs and siloxanes in freshwater environments.

1. Introduction

Synthetic musk compounds (SMCs) and siloxanes are compounds that have been widely and diversely used in personal care products (PCPs) such as shampoos, sanitizers, cleaners, lotions, perfumes, and cosmetics (Horii and Kannan, 2008; Liu et al., 2014; Lu et al., 2011; Sommer, 2004). SMCs have been identified in various environments owing to their low degradability and high bioaccumulation in the aquatic environment (Duedahl-Olesen et al., 2005; Peck and Hornbuckle, 2004; Stevens et al., 2003). SMCs such as Galaxolide®

(1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta- γ -2-benzopyran, or HHCB) and Tonalide® (6-Acetyl-1,1,2,4,4,7-hexamethyltetralin, or AHTN) are compounds of emerging concern that have been found to impair multixenobiotic resistance in *Mytilus californianus* (Luckenbach et al., 2004; Luckenbach and Epel, 2005). Musk ketone (4-tert-Butyl-3,5-dinitro-2,6-dimethylacetophenone, or MK) consumption causes allergic reactions and hormone disruptions and may be linked to autism spectrum disorders as evidenced by an experiments using human liver cells (Mersch-Sundermann et al., 2001; Sealey et al., 2016). Additionally, siloxanes have

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received substantial attention as they are continually released into surface water through discharge pathways such as wastewater treatment plants (WWTPs) (Lee et al., 2014). D4 and D5 are cyclic siloxanes specifically known as persistent, toxic, accumulative, and high production volume (HPV) compounds (Hamelink, 1992; Wang et al., 2013b).

SMCs have already been approved for use by the Ministry of Environment in Korea. However, its release and potential for bioaccumulation in aquatic environments could vary with discharge characteristics based on usage (Hong et al., 2021). SMCs have been detected in various environmental media such as water, sediment, and biota. SMCs are detected in freshwater environments at concentrated levels and are influenced by pollutant load (He et al., 2021; Hu et al., 2011; Vimalkumar et al., 2021; Zhang et al., 2011) and in coastal (Xie et al., 2007) and marine environments (Zhang and Kelly, 2018) at relatively low concentrations (Tables S1 and S2). Additionally, studies on SMCs toxicity have established the importance of their distribution in the environment and their biological effects (Luckenbach et al., 2004; Wang et al., 2013b). The concentration of chemicals in environmental media significantly regulates body burden in organisms (Borga et al., 2012b) and the feeding habits of organisms can influence bioaccumulation characteristics. Therefore, investigating the chemical concentrations in biota and subsequent ecological assessments are crucial.

Several factors such as bioconcentration factor (BCF), bioaccumulation factor (BAF), and trophic magnification factor (TMF) can be measured to evaluate the relationship among SMCs in environment and biota. TMF is specifically important for assessing the behavior of harmful substances and bioaccumulation potential of pollutants in the food web (Kelly et al., 2009) and regulatory decision-making (Yang et al., 2020). Several studies have been conducted in both freshwater and marine environments to show the transfer of SMCs (Goodbred et al., 2021; Zhang and Kelly, 2018; Zhang et al., 2013) and siloxanes (Borga et al., 2012a, 2013; Cui et al., 2019; He et al., 2021; Jia et al., 2015; McGoldrick et al., 2014; Powell et al., 2018; Powell et al., 2017; Xue et al., 2019) in food webs (Tables S1 and S2). However, TMFs fluctuate with various factors such as seasonal and spatial changes and food web structure (Borga et al., 2012b), affecting chemical fate. The structure of the food web is a particularly important factor that can affect the possible biomagnification through ecosystem because it includes ecological energy flow information, such as feeding relationships among organisms, food chain lengths, and specific trophic position (TP). Accurate TP is important for measuring TMF because it is a value determined by the regression between TP and bioaccumulated pollutants (Borga et al., 2012b; Kelly et al., 2009; Won et al., 2018). $\delta^{15}\text{N}$ values of amino acids (AAs) have specifically been used to compensate for temporal and spatial variability and uncertainty of background nitrogen isotopes determined by the bulk $\delta^{15}\text{N}$ method (Chikaraishi et al., 2009; Elliott et al., 2021; Won et al., 2018).

In this study, we examine the behavior and fate of PCPs including 11 of SMCs and 19 of siloxanes in a river ecosystem to i) investigate the concentrations of SMCs and siloxanes in multi-media samples, ii) determine the fate and distributions in two seasons and different sites affected by WWTP, iii) clarify the trophic transfer characteristics with accurate TP using amino acids, and finally iv) understand the importance of TP for TMF in riverine food web.

2. Materials and methods

2.1. Sampling site

The Geum River is one of the four major rivers in South Korea, with a length of 412 km, a watershed area of approximately 9800 km², and discharges of approximately 6.4×10^9 tons of freshwater into the Yellow Sea annually. There are many cities adjacent to this river, and four WWTPs treat their effluents. The selected sampling site was near the Daejeon WWTP (capacity of approximately 900,000 m³ d⁻¹,

36°22'48.89"N, 127°24'27.71"E), which accounts for approximately 93% of the total capacity of the four WWTPs and is the fifth largest WWTP in Korea. Environmental samples including water, particulate matter in water, and sediment were collected at site (G2) in front of the WWTP and 1 km upstream (G1) and downstream (G3) from G2. The same set of samples was collected above an estuarine dam (G4) as a control site. Sections GB1 and GB2 encompass sampling sites G2–G3 and G4, respectively (Fig. 1).

2.2. Sample collection

Fresh water, sediments, and biota were sampled in June and September 2020 (Fig. 1, Fig. S1, and Table S3). Surface water samples were collected using a Van Dorn water sampler, and surface sediment was collected using a Van Veen grab. Fifteen species of fish including Barbel Steed (*Hemibarbus labeo*), pale chub (*Zacco platypus*), Gobioninae (*Gnathopogon strigatus*), skygager (*Erythroculter hypselonotus*), crucian carp (*Carassius Carassius*), Barbel chub (*Squaliobarbus curriculus*), common carp (*Cyprinus carpio*), largemouth bass (*Micropterus salmoides*), korean piscivorous chub (*Opsariichthys uncirostris*), Light bullhead (*Leiocassis nitidus*), mullet (*Chelon haematocheilus*), flathead grey mullet (*Mugil cephalus*), tone moroko (*pseudorasbora parva*), korean sharpbelly (*hemicultus eigenmanni*), and korean bullhead (*pelteobagrus fulvidraco*) were sampled by netting and are listed in Table S3. Particulate organic matter (POM) was filtered using a 47 mm glass fiber filter (GF/F, Whatman, Dassel, Germany). Only the dissected dorsal muscle of fish samples (whole bodies of small fish <5 cm were used) and sediment samples were freeze-dried and homogenized (Planetary Mono Mill PULVERISETTE 6, Fritsch, Idar Oberstein, Germany). The samples were stored at -80 °C until analysis.

2.3. Chemical analysis

Eleven synthetic musks, namely, five polycyclic musks (HHCB, AHTN, ATHI, ADBI, and AHMI) and six nitro musks (MK, MNN, MA, MX, MM, and MT), and nineteen siloxanes, namely, four cyclic siloxanes (D4, D5, D6, and D7) and fifteen linear siloxanes (L3, L4, L5, L6, L7, L8, L9, L10, L11, L12, L13, L14, L15, L16, and L17) were analyzed (Tables S4 and S5). All the samples were extracted and analyzed using the methods described previously with minor modifications (Lee et al., 2015; Lee et al., 2018). Water samples (600 mL) were extracted twice with 30 mL of dichloromethane (DCM) for 30 min by mechanical shaking. Sediment (~5 g) and biota samples were extracted in a Soxhlet apparatus with a

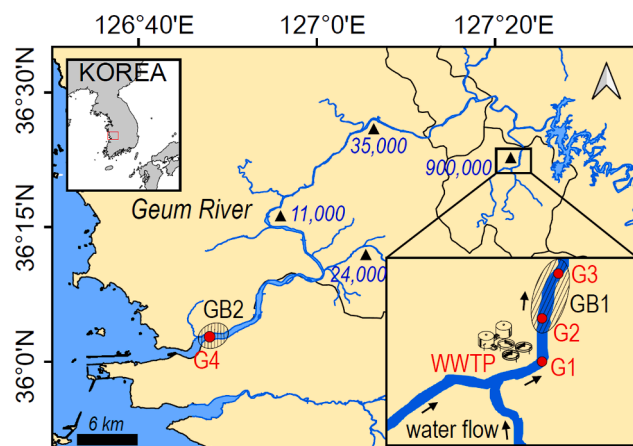


Fig. 1. Sampling sites in Geum River. The red dots are water and sediment sampling sites, and the hatched circles are biota sampling sites. The WWTPs are indicated by a triangle symbols and the WWTPs capacity (m³ day⁻¹) is written in blue letter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mixture of DCM and hexane. Before extraction, tracer standards (100 ng of d_3 -AHTN and d_{15} -musk xylene for SMCs and 200 ng of $^{13}\text{C}_4$ -D4, $^{13}\text{C}_5$ -D5, and $^{13}\text{C}_6$ -D6 for siloxanes) were spiked into the samples. The extract was divided into two aliquots and one aliquot was concentrated to 1 mL and directly analyzed for siloxanes. The other aliquot was used as a clean-up step for synthetic musk analysis. The extract was cleaned up on a silica gel SPE cartridge (Sep-Pak Vac Si cartridge; 1 g 6 cc⁻¹, Waters, Milford, MA, USA) using 12 mL of 50% DCM in hexane. The purified eluants were concentrated and dissolved in 0.5 mL of hexane for instrumental analysis of synthetic musks. The samples were analyzed using an Agilent 7890 gas chromatograph system coupled with an Agilent 5973 mass spectrometer (GC/MS; Agilent Technologies, Wilmington, DE, USA). Analytical conditions GC/MS are presented in the Supplementary Information (Tables S4 and S5).

The compounds of SMCs and siloxanes have relatively high log K_{ow} , mainly accumulated in lipids of biota (Conder et al., 2008). The SMCs and siloxanes concentrations of all biota were normalized with lipid content because there could be differences in weight and size for each individual. For sediment and water sample, lipid-organic carbon equivalent fractions were calculated from the total organic carbon value using following equations proposed by Fremlin et al. (2020) (Eq. (1)):

$$C_{lipid-OC\ eq.} = C_{dry}/OC_{dry}(0.35) \quad (1)$$

where OC is the fraction of total organic carbon. The constant 0.35 represents that organic carbon has approximately 35% the affinity of octanol (Seth et al., 1999).

2.4. Quality control for SMCs and siloxanes

To avoid background contamination of SMCs and siloxanes in the samples, all personnel involved refrained from use of personal care products such as hand lotions, perfumes, and shampoo during the study. Field blanks ($n = 8$) were prepared in same container with real samples using pre-washed Milli-Q water for surface water and sodium sulfate for sediment and biota samples. Procedural blanks ($n = 15$) were processed for every 5 samples with real samples to check for background contamination of SMCs and siloxanes. The levels for chemicals detected in the procedural blanks (HHCB: 26.0 ± 3.24 ng mL⁻¹, AHTN: 5.42 ± 0.79 ng mL⁻¹, D4: 10.9 ± 1.81 ng mL⁻¹, D5: 65.2 ± 8.57 ng mL⁻¹, and D6: 62.9 ± 12.8 ng mL⁻¹) were subtracted from all of the samples. The levels of target chemicals in field blanks were similar with those of procedural blanks, indicating no contamination during sample collection and storage. The recoveries of spiked surrogate standards were $71 \pm 14\%$ for d_3 -AHTN, $66 \pm 14\%$ for d_{15} -musk xylene, for $74 \pm 11\%$ $^{13}\text{C}_4$ -D4, for $73 \pm 9.8\%$ $^{13}\text{C}_5$ -D5, and for $77 \pm 12\%$ $^{13}\text{C}_6$ -D6. The sensitivity was determined by the limit of quantification (LOQ) of instrument at the signal-to-noise (S/N) ratio of 10:1 in water, sediment, and biota for SMCs and siloxanes, respectively (Table S5). Concentrations of SMCs and siloxanes were determined using an external calibration curve, with the concentrations ranging from 1.0 to 2000 ng mL⁻¹ for SMCs and ranging from 1.0 to 5000 ng mL⁻¹ for siloxanes.

2.5. Analysis of carbon and nitrogen stable isotope ratios

Carbon and nitrogen stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) analysis was performed for POM, sedimentary organic matter (SOM), and biota according to a previously reported procedure with modifications (Logan and Lutcavage, 2008; Lorrain et al., 2003). For $\delta^{13}\text{C}_{Bulk}$ analysis, the filter samples were acidified with 12 M hydrochloric acid fume for 12 h and neutralized with sodium hydroxide and silica gel for 12 h in a vacuum desiccator, and the sediment and biota samples were reacted with 1 M hydrochloric acid (HCl) to remove inorganic carbon for 12 h followed by neutralization with distilled water. In addition, biota samples were defatted with chloroform/methanol (2:1, v/v). $\delta^{15}\text{N}_{Bulk}$ was analyzed without acidification and removing fats.

The samples were analyzed using an elemental analyzer (EA, Vario PYROcube, Elementar, Germany) combined with an isotope ratio mass spectrometer (IRMS, Isoprime 100, Isoprime, UK) after pretreating each element. The analytical accuracy for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were within $\pm 0.3\%$ for all analysis. International Atomic Energy Agency (IAEA) reference materials, such as CH-3 (cellulose, certified $\delta^{13}\text{C}$: $24.72 \pm 0.04\%$) and N-1 (ammonium sulfate, certified $\delta^{15}\text{N}$: $24.72 \pm 0.04\%$) were analyzed every 10 injections of samples as a running standard to check the accuracy of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively. Standard deviations of CH-3 and N-1 were within $\pm 0.2\%$ and $\pm 0.1\%$, respectively, for all analysis. Finally, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios were expressed as δ (‰), according to Eq. (2):

$$\delta X(\%) = (R_{sample}/R_{standard} - 1) \times 1000 \quad (2)$$

where X is ^{13}C or ^{15}N , and R is the $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ for carbon and nitrogen, respectively. Vienna Pee Dee Belemnite (VPDB) and atmospheric nitrogen (N_2) were used as R standards for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively.

2.6. Analysis of nitrogen stable isotope ratio of amino acids

The $\delta^{15}\text{N}_{AAs}$ analysis was performed according to a previously reported procedure (Chikaraishi et al., 2009; Kim et al., 2019). In brief, 3–5 mg of freeze-dried samples were hydrolyzed for 12 h with 12 M HCl at 110°C and the hydrophobic contents were removed with 3:2n-hexane/DCM (v/v). After drying the residual HCl at 70°C under a N_2 stream, samples were derivatized with 1:4 thionyl chloride/2-propanol (v/v) and 1:4 pivaloyl chloride/DCM (v/v) for 2 h at 110°C. The derivatized amino acids were then extracted with 3:2n-hexane/DCM (v/v). The $\delta^{15}\text{N}$ of each AA was determined by GC (HP 6890 N, Agilent, California, USA) coupled with a combustion furnace (GC5 interface, Elementar, Langensfeld, Germany) and isotope ratio mass spectrometry (Isoprime, Elementar) (Table S6). The running standards were analyzed every 10 injections of samples to check the accuracy. Standard deviations of $\delta^{15}\text{N}$ of glutamic acid ($\delta^{15}\text{N}_{glu}$) and phenylalanine ($\delta^{15}\text{N}_{phe}$) were within $\pm 0.1\%$ and $\pm 0.03\%$, respectively, for all analysis. All analyses were performed at Hanyang University.

2.7. Calculation of TP and TMF

The TP based on the $\delta^{15}\text{N}$ of bulk tissue (TP_{Bulk}) and AAs (TP_{AAs}) was calculated using Equations 3 and 4:

$$TP_{Bulk} = [(\delta^{15}\text{N}_{sample} - \delta^{15}\text{N}_{POM})/TDF] + 1 \quad (3)$$

$$TP_{AAs} = [\delta^{15}\text{N}_{glu} - \delta^{15}\text{N}_{phe} - \beta]/TDF + 1 \quad (4)$$

where 3.4‰ (Minagawa and Wada, 1984) and 6.9‰ (Blanke et al., 2017) are the trophic discrimination factor (TDF) values in bulk tissue and AAs, respectively, and 3.4‰ (Chikaraishi et al., 2009) is the β value, which represents the difference in $\delta^{15}\text{N}$ between glutamic acid and phenylalanine of aquatic primary producers. To determine TP variability, the individual TP (TP_{ind}) was subtracted from the average TP (TP_{avg}) of the organisms, as shown in Equation 5:

$$TP_{variability} = TP_{ind} - TP_{avg} \quad (5)$$

TMF was calculated from the slope of the relationship between TP and the pollutant concentrations following the method of Borga et al. (2012b). (Eqs. (6) and (7)):

$$\text{Log concentration of SMCs and siloxanes} = a + b \times TP \quad (6)$$

$$TMF = 10^b \quad (7)$$

2.8. Statistical analysis

For calculation of total concentrations of SMCs (Σ SMCs; the sum of 11 SMCs) and siloxanes (Σ siloxanes; the sum of 19 siloxanes), the concentration of individual chemical below than LOQ was treated as zero to avoid overestimation of the results. Statistical analyses were performed using IBM SPSS Statistics 23 (2015 SPSS Inc., IBM Corp., Armonk, NY, USA). Significant differences in the parametric variables were determined using one-way analysis of variance (one-way ANOVA) for comparison among spatio-temporal difference of contaminants in biota samples. Pairwise differences were compared by Tukey's honestly significant difference test and Dunnett's test for homogeneity and heteroscedasticity of variances for confirming the significant relationship with TPs and determining the TMF values.

3. Results and discussion

3.1. Spatio-temporal distribution of SMCs and siloxanes in water, sediment, and biota samples

The concentrations of SMCs and siloxane are presented in Fig. 2a and Tables S1, S2, and S7–S10. The highest concentration of SMCs in water samples was detected (384 ng L^{-1}) at G2, which was approximately 26 times higher than that measured at G4 (14.8 ng L^{-1}) in June. The concentrations decreased overall after the rainy season in September, but the trends of concentration distribution remained similar (Fig. 2a). The highest concentration of SMCs in sediment samples was detected ($71.5 \text{ ng g}^{-1} \text{ dw}$) at G3, located 1 km downstream from the WWTP outlet, and was approximately 75 times higher than that at G4 ($0.95 \text{ ng g}^{-1} \text{ dw}$) in

June. The concentrations remained at similar levels overall after the rainy season ($1.65\text{--}62.3 \text{ ng g}^{-1} \text{ dw}$), but unlike during the rainy season, G2 ($62.3 \text{ ng g}^{-1} \text{ dw}$) ranked first as the station with highest SMC concentration instead of G3 ($47.0 \text{ ng g}^{-1} \text{ dw}$) (Fig. 2b). The concentration of SMCs in biota ranged from 771 to $39,000 \text{ ng g}^{-1} \text{ lw}$ (mean $14,000 \pm 15,500 \text{ ng g}^{-1} \text{ lw}$) and 18.3 to $4,750 \text{ ng g}^{-1} \text{ lw}$ ($589 \pm 1,100 \text{ ng g}^{-1} \text{ lw}$) at GB1 and GB2 in June, and $1,000$ to $33,900 \text{ ng g}^{-1} \text{ lw}$ (mean $11,100 \pm 11,300 \text{ ng g}^{-1} \text{ lw}$) and 26.4 to $1,690 \text{ ng g}^{-1} \text{ lw}$ ($684 \pm 537 \text{ ng g}^{-1} \text{ lw}$) at GB1 and GB2 in September, respectively. There were no seasonal differences, but the considerable spatially different results were measured between GB1 and GB2 in each season (June: $p < 0.05$, September: $p < 0.01$, t -test) (Fig. 2c). The high concentration of SMCs at GB1 that decreases with increasing distance from the WWTP indicates that the SMCs in organisms are largely controlled by the source. The concentrations of SMCs in water and sediment samples were similar to those reported from the Haihe River, China (Hu et al., 2011) and three different rivers (Kaveri, Vellar, and Thamiraparani Rivers) in India (Vimalkumar et al., 2021) (Table S1). Meanwhile, the concentrations in biota in this study were much higher than those in biota in the rivers in the above studies, indicating that the bioaccumulation of SMCs was more prevalent in the Geum River. HHCB, AHTN, and MK were mainly detected among a total of 11 SMCs, with dominant concentrations of $66\% \pm 15\%$, $7.7\% \pm 10\%$, and $26\% \pm 14\%$ in water samples; $85\% \pm 11\%$, $12\% \pm 10\%$, and $1.8\% \pm 1.5\%$ in sediment samples; and $83\% \pm 6.7\%$, $10\% \pm 4.9\%$, and $6.0\% \pm 2.5\%$ in biota samples (Fig. S2), respectively, year-round. This is consistent with a recent study reporting that HHCB and AHTN are the most abundant compounds in the aquatic environment with a high usage rate of approximately 95% (Hong et al., 2021; Xie et al., 2007; Zhang et al., 2008). Considering the relative compositions of each

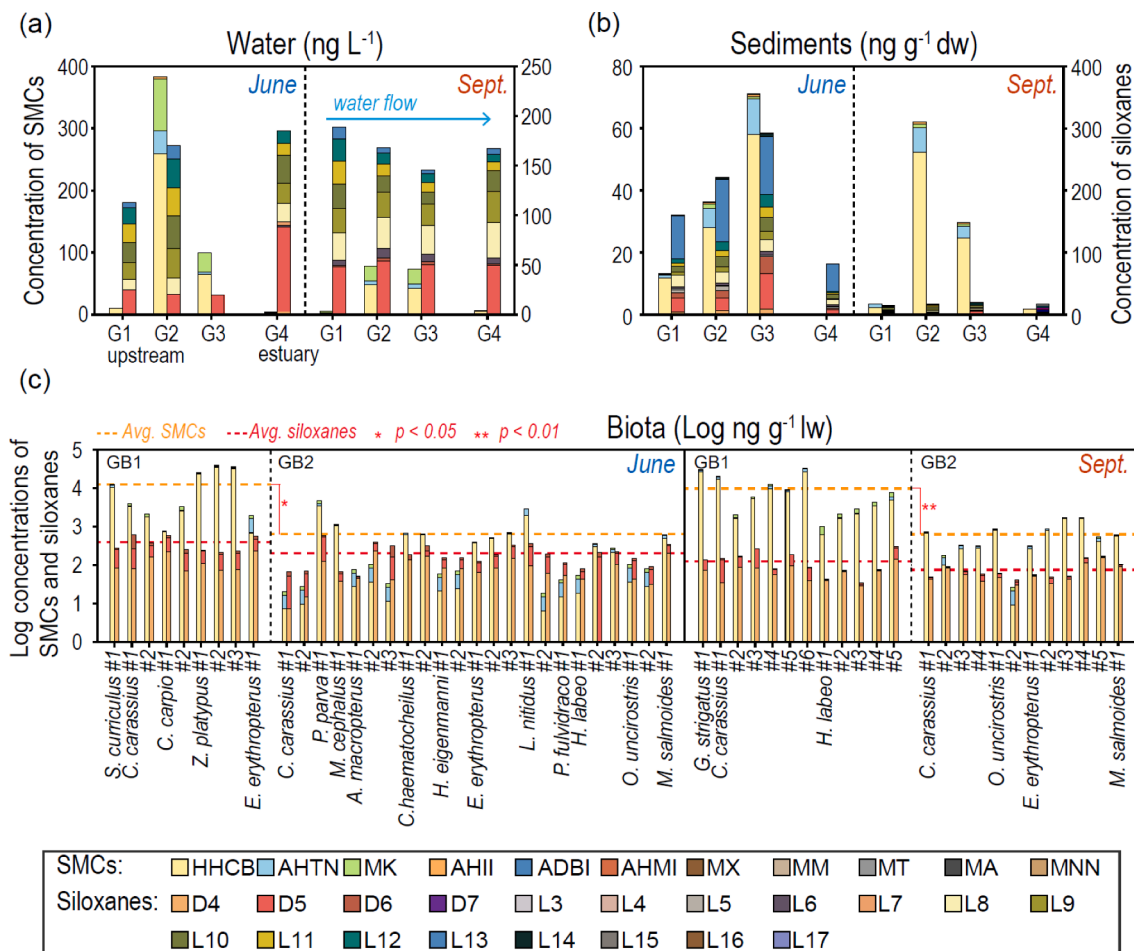


Fig. 2. Concentrations of SMCs and siloxanes of (a) water, (b) sediment, and (c) biota samples in June and September.

compounds, there were no significant differences in SMCs in each medium ($p > 0.05$, one-way ANOVA), but MK concentration was low in sediment and biota samples, which can be attributed to low lipophilicity ($\log K_{ow} = 4.3$) (Tas et al., 1997).

However, the siloxane concentrations in the water samples were largely identical. Concentrations ranged from 114 to 190 ng L^{-1} , showing no difference at all stations except G3 (20.0 ng L^{-1}), with low concentrations in June (Fig. 2a). This seems to be related to the continuous exposure from the WWTP and high persistence under wide aquatic conditions (Wang et al., 2013b). The highest concentration of siloxanes (294 ng g^{-1} dw) in sediment samples were found at G3, which was approximately 3.6 times higher than that at G4 in June. The concentrations decreased overall after the rainy season in September, but the trend remained similar (Fig. 2b). The trend could be attributed to the several factors including the physicochemical properties of each chemical and environmental conditions such as turbidity, inflow of non-point sources, dilution effect, and re-movement of sediment after heavy rain (Fig. S1). Siloxane concentrations in the organisms ranged from 212 to 623 ng g^{-1} lw (mean, $373 \pm 169 \text{ ng g}^{-1}$ lw) and 50.4 to 576 ng g^{-1} lw ($200 \pm 135 \text{ ng g}^{-1}$ lw) at GB1 and GB2 in June, and 43.1 to 298 ng g^{-1} lw ($134 \pm 84.8 \text{ ng g}^{-1}$ lw) and 40.5 to 171 ng g^{-1} lw ($80.1 \pm 42.8 \text{ ng g}^{-1}$ lw) at GB1 and GB2 in September, respectively, with no significant spatial and temporal differences. Therefore, the siloxane concentrations might be affected by water rather than by sediments (Fig. 2c). In addition, the water from the Geum River Estuary is discharged to the coast several times a day and may affect the coastal habitats; hence, it is important to study the biological effects of harmful substances in the estuary (Kim et al., 2019; Kim et al., 2021). Among a total of 19 siloxanes, dominant compounds included D5, L8, L9, L10, L11, L12, and L13 (concentrations of $37\% \pm 25\%$, $13\% \pm 7.2\%$, $13\% \pm 5.8\%$, $12\% \pm 6.0\%$, $8.9\% \pm 5.9\%$, $8.3\% \pm 5.5\%$, and $3.6\% \pm 2.8\%$), suggesting that both cyclic (D-) and linear (L-) siloxanes are discharged from the WWTP and can remain in the aquatic environment to some extent. The highest concentrations of L13 ($44\% \pm 9.1\%$) was observed in sediment samples, especially in June. Only three siloxanes were detected in biota samples, with dominant concentrations of $52\% \pm 19\%$ for D4, $37\% \pm 14\%$ for D5, and $11\% \pm 7.1\%$ for D6 with a detection frequency of $100\% \pm 0\%$, $85\% \pm 12\%$, and $86\% \pm 15\%$, respectively (Fig. S2). Cyclic siloxanes such as D4, D5, and D6 penetrate more easily than linear siloxanes and are highly bioaccumulative (Brooke et al., 2009a, b).

3.2. Effect of seasonally varying baseline organic matter on TP calculation

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of POM and SOM at both sites and in both seasons are described in Table S11. At GB1, located upstream near the WWTP, the $\delta^{13}\text{C}$ of POM ($-26.7\% \pm 0.1\%$) was relatively higher in June and decreased by an average of 1.6% in September (-28.3%). This may be due to the input of a large amount of terrestrial organic matter in Geum River ($\delta^{13}\text{C}$: $-27.2\% \pm 3.5\%$ in Kang et al., 2019) after rainfall. The $\delta^{15}\text{N}$ of POM varied slightly between June ($3.9\% \pm 0.1\%$) and September (4.3%). At GB2, inside the estuary dam downstream, the POM value indicated relatively heavier isotope ratios ($\delta^{13}\text{C}$: $-24.5\% \pm 0.5\%$ and $\delta^{15}\text{N}$: 10.2%) in June, which decreased by an average of 2.6% and 6.0% , respectively, in September (-27.1% for $\delta^{13}\text{C}$ and 4.2% for $\delta^{15}\text{N}$). Generally, the concentration of dissolved inorganic substances (Guo et al., 2015; Mackensen and Schmiedl, 2019), phytoplankton blooms (Wang et al., 2013a), content of POM, and inputs of external pollution sources are factors that affect the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of POM. Since GB2 seems to be a closed system with low water flow owing to the estuary dam, phytoplankton often proliferate from early summer (Han et al., 2016) along with inputs of high $\delta^{15}\text{N}$ from surrounding agricultural areas. These appear to have been the main factors causing heavier carbon and nitrogen stable isotope ratios of POM at GB2 in June. The SOM at GB1, there was a seasonal difference in $\delta^{15}\text{N}$ ($4.7\% \pm 1.1\%$ in June and 2.7% in September) despite $\delta^{13}\text{C}$ ($-23.8\% \pm 1.2\%$ in June

and -23.9% in September) was not changed. Conversely, those showed an insignificant difference in $\delta^{15}\text{N}$ ($6.1\% \pm 0.8\%$ in June and 5.7% in September) but had relatively higher $\delta^{13}\text{C}$ in June ($-22.0\% \pm 2.1\%$) and decreased by an average of 2.5% in September (-24.5%) at GB2. At GB1 and GB2, the dual isotope ratios of SOM presented differing trends between the seasons; this might be due to complex mixing because of the disturbance and resuspension of surface sediments by increased water flow after heavy rain (Table S11). POM and SOM have fluctuations in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values according to regional characteristics and seasons. Since the $\delta^{15}\text{N}$ of baseline organic matter might affect the TP calculation (Equations 3 and 4), additional and complementary methods are particularly required in ecological food web studies based on stable isotope analysis.

Although $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of POM and SOM were relatively enriched in heavy isotopes at GB2 than at GB1 in June ($\Delta\delta^{13}\text{C} = 2.2\%$ and $\Delta\delta^{15}\text{N} = 6.3\%$ for POM, and $\Delta\delta^{13}\text{C} = 1.8\%$ and $\Delta\delta^{15}\text{N} = 1.4\%$ for SOM), there were no significant differences with TP_{Bulk} (2.6 ± 0.4 at GB1 and 2.8 ± 0.5 at GB2 for the crucian carp *Carassius carassius*, and 3.0 at GB1 and 2.5 ± 0.6 at GB2 for the skygager *Erythroculter erythropterus*) at both sites. This means that the values of POM and SOM in June were sufficiently assimilated into the organisms inhabiting this area. The TP_{Bulk} of *E. erythropterus* was 4.5 ± 0.7 in September, which showed a great difference with that in June (2.5 ± 0.6), but such a drastic change over one season is unreasonable (Table S12). This can be attributed to isotope discordance between POM and organisms with a high turnover rate (Gu, 2009). Specifically, the carnivorous *E. erythropterus* has a constant $\delta^{15}\text{N}$ value despite large differences in $\delta^{15}\text{N}$ in POM after the rainy season (Table S11), whereas herbivores such as plankton, could be directly affected by the baseline values of POM. Additionally, the $\delta^{15}\text{N}$ of the stone moroko *Pseudorasbora parva* was less than that of POM, which resulted in a TP_{Bulk} of 0.7 for this species. This is unreasonable for the omnivorous *P. parva*, whose diet generally includes algae, plant detritus, zooplankton, micro-crustaceans, mollusks, fish eggs, and larvae (Xie, 2000; Ye et al., 2007). Meanwhile, the calculated TP_{AAs} was 2.4 for *P. parva* (Table S12).

Overall, the TP_{Bulk} of biota samples from GB1 was 2.2 – 4.0 in June and 2.2 – 4.5 in September and 0.7 – 4.1 and 2.8 – 5.3 at GB2, respectively. The TP_{AAs} of biota samples, however, showed relatively narrow ranges of TP of samples at GB1 which were 2.2 – 3.3 in June and 2.5 – 3.3 in September, and 2.3 – 4.2 and 2.6 – 4.0 at GB2, respectively. Moreover, unlike the TP shown in the steady state in June, as described above, the TP_{Bulk} variability in September explained the temporal uncertainty of the TP_{Bulk} . The range of TP_{Bulk} in three representative species (*C. carassius*, barbel steed *Hemibarbus labeo*, and *E. erythropterus*) collected at both stations was broader than that of TP_{AAs} . The trophic variability of TP_{Bulk} was particularly over $+1$ in September (Fig. S3). The seasonal fluctuation of the isotope baseline could greatly affect TP variability (Lorrain et al., 2015).

3.3. TP and relations examined by stable isotopes of bulk and amino acids

When the TP_{Bulk} and TP_{AAs} were compared with the global TP dataset from FishBase (<http://www.fishbase.in>), the $\text{TP}_{\text{Bulk-Fishbase}}$ significantly increased with increasing TP_{Bulk} ($R^2 = 0.6$, $p < 0.01$) and presented differences at one TP level ($\Delta\text{TP} = 0.92 \pm 0.58$), while the differences between TP_{AAs} and $\text{TP}_{\text{fishbase}}$ ($\text{TP}_{\text{AAs-Fishbase}}$) were lower ($\Delta\text{TP} = 0.47 \pm 0.29$) (Fig. 3). This indicates that reliable TP can be derived by stable isotope ratios of AAs, where baseline values cannot be sufficiently reflected in the ecosystem. Incidentally, the relationship between TP_{Bulk} and TP_{AAs} showed a significant linear correlation with a slope of 0.4 ($R^2 = 0.5$, $p < 0.01$), with respect to the 1:1 line, and compared to TP_{AAs} , TP_{Bulk} was overestimated from $\text{TP} > 2.7$ (Fig. 3a). This reflects our finding that the reduced trophic fractionation of $\delta^{15}\text{N}$ in carnivores with a TP of 3 or higher (Chikaraishi et al., 2009) suggests the need for further studies. Recent studies have explained that trophic AAs are also known to experience TDF compression; it has been suggested that the TDF

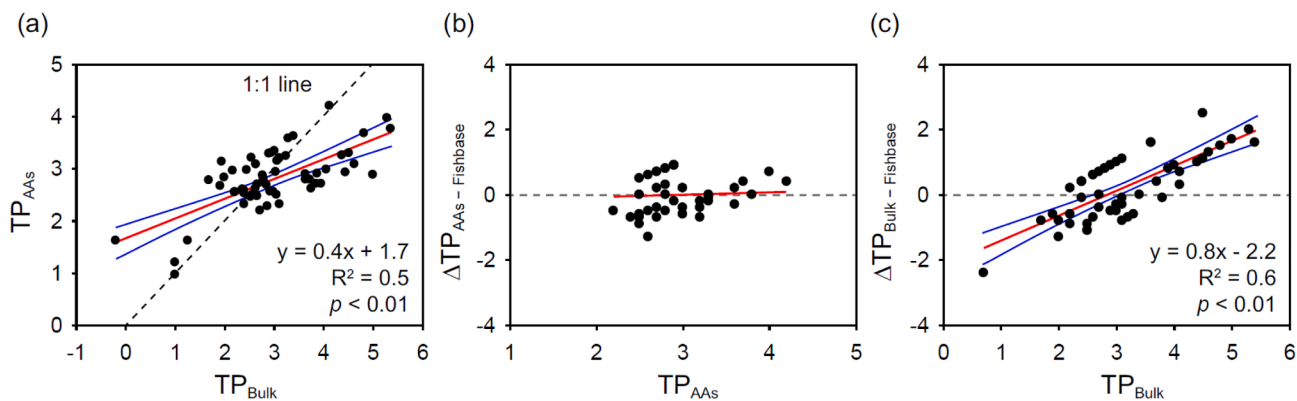
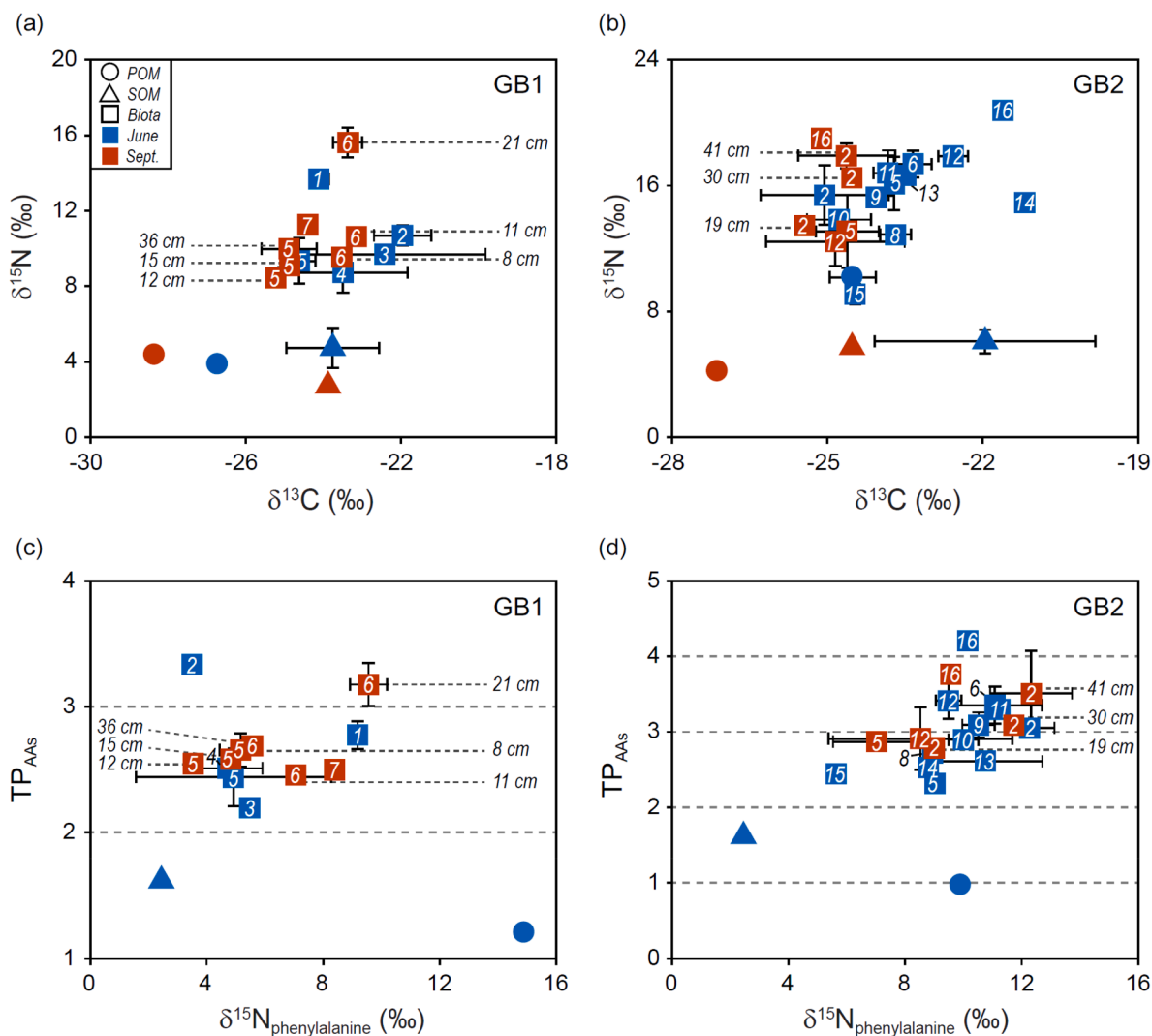


Fig. 3. Relationships between (a) TP_{Bulk} and TP_{AAs} , (b) TP_{AAs} and $\Delta TP_{AAs-Fishbase}$, and (c) TP_{Bulk} and $\Delta TP_{Bulk-Fishbase}$. The red and blue line indicate a linear regression line and 95% confidence interval, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



1. *Z. platypus*; 2. *E. erythropterus*; 3. *S. curriculus*; 4. *C. caprio*; 5. *C. carassius*; 6. *H. labeo*; 7. *G. strigatus*; 8. *C. haematocheilus*; 9. *L. nitidus*; 10. *H. eigenmanni*; 11. *P. fulvidraco*; 12. *O. uncirostris*; 13. *A. macropterus*; 14. *M. cephalus*; 15. *P. parva*; 16. *M. salmoides*

Fig. 4. Dual plots of $\delta^{13}C$ and $\delta^{15}N$ in (a) GB1 and (b) GB2 and of $\delta^{15}N_{phenylalanine}$ and TP_{AAs} in (c) GB1 and (d) GB2.

should be adjusted for carnivorous fish (Bradley et al., 2014; McMahon and McCarthy, 2016). TP_{Bulk} , which has been widely used in ecology, is limited in that there is a time gap to completely reflect the baseline nitrogen isotope of diet sources caused by the sudden environmental change (Chikaraishi et al., 2009; Won et al., 2020). Some studies that were conducted in a constant environment with little influence from the surrounding organic matter sources showed stable feeding relationships in which the TP_{Bulk} was reasonably calculated. However, there are many

inputs, such as allochthonous substances, anthropogenic pollutants, and increased primary production in estuary dam systems in this study area. Accurate examination of TP is essential owing to these effects, and it is especially important to clarify the accumulation of hazardous substances according to TP.

The organisms showed species specificity in the dual isotope plot, indicating that the levels of trophic ecology had size-dependent results (Fig. 4a and b). In *C. carassius* and *H. labeo*, $\delta^{15}N$ values increased as the

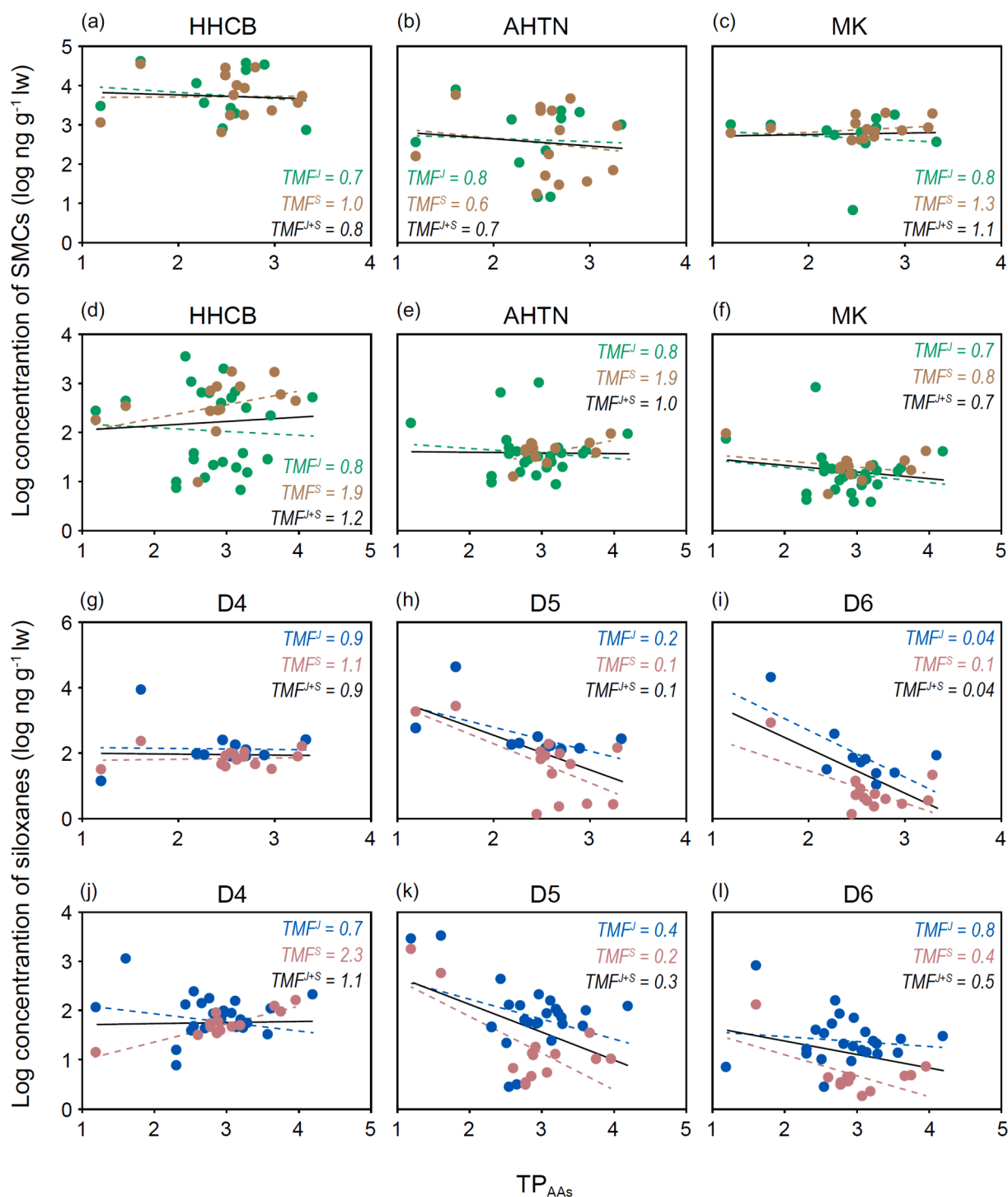


Fig. 5. Trophic magnification factors of SMCs including HHCB, AHTN, and MK in (a, b, and c) GB1 and (d, e, and f) GB2, and siloxanes including D4, D5, and D6 in (g, h, and i) GB1 and (j, k, and l) GB2. The green and blue indicate the plots of June (TMF^J) and the brown and purple indicate those of September (TMF^S), and the sum of June and September were expressed in black (TMF^{J+S}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

length of fish increased. Incidentally, $\delta^{15}\text{N}$ of *H. labeo* (21 cm) was more positive than that of smaller fish (<11 cm), whereas $\delta^{13}\text{C}$ values were identical, which could be misinterpreted as these species have a constant food source. Several studies have established that the bulk carbon values reflect various source information, but integrated values can be similar (Fogel and Tuross, 2003; Guiry, 2019; Larsen et al., 2013). Considering that the isotope values of AAs indicate source information, we found that large *H. labeo* (21 cm) had higher values of $\delta^{15}\text{N}_{\text{phenylalanine}}$ (2.5–4.0; which provides food source information) than the smaller *H. labeo* (<11 cm) (Fig. 4c). Diet size and feeding habits can be influenced by the length of fish, which is closely related to age (Hickley and Dexter, 1979; Mummert and Drenner, 1986). Therefore, as *H. labeo* aged and its body length increased and mouth developed, it is likely that the feeding habits shifted to benthic organisms with high $\delta^{15}\text{N}_{\text{phenylalanine}}$. It is possible that feeding habits influence other carnivores that depend on a high-quality diet. This is highly significant because the inflection points of diet shift and physiological changes could affect the TP of aquatic organisms. The barbel chub *Squaliobarbus curriculus* had a wide range of $\delta^{13}\text{C}$ values, indicating that they have a wide migratory range of up to 50 km (Jang et al., 2012) and feed on various carbon sources. The enriched $\delta^{15}\text{N}$ of adult *E. erythropterus* (41 cm) at GB2 was similar to that of *C. carassius* and *H. labeo* at GB1 (Fig. 4d). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}_{\text{phenylalanine}}$ values of the flathead gray mullet *Mugil cephalus*, a euryhaline species known to move in a wide radius in the brackish zone (Yoon et al., 2015), which contains POM and SOM, indicate that this species might feed on complex food sources (Oliveira et al., 2014). In this study, nitrogen isotopes of AAs were applied to reliably interpret the feeding behavior of various fish species and to clarify the fate and trophic transfer of hazardous materials.

3.4. TMF of SMCs and siloxanes

The TMFs were derived from the relationships between TP and the log concentrations of chemicals, and the TMFs of each compound of SMCs (HHCB, AHTN, and MK) and siloxanes (D4, D5, and D6) were determined at GB1 and GB2 in June and September, respectively (Fig. 5). Among 24 TMFs, 19 showed biodilution tendencies in which TMF was <1 (HHCB = 0.7–0.8, AHTN = 0.6–0.8, MK = 0.7–0.8, D4 = 0.7–0.9, D5 = 0.1–0.4, and D6 = 0.04–0.8), and the remaining including HHCB, AHTN, MK, and D4 showed tendencies close to 1 or slightly higher (TMF range: 1.0–2.3). The TMF values were similar to those values in previous studies that were conducted in Lake Taihu, China (HHCB: 1.1, AHTN: 0.7) and Lake Mead, USA (HHCB: 0.4, AHTN: 0.06) (Goodbred et al., 2021; Zhang et al., 2013). D4, D5, and D6, which account for a large proportion of siloxane bioaccumulation, also showed trophic dilution (0.7–0.8) in the food webs of Lake Erie, Canada and Lake Chaohu, China (He et al., 2021; McGoldrick et al., 2014), indicating rapid metabolism of these compounds and low transfer into higher trophic organisms. However, there were also opposite results showing trophic magnification trends in studies conducted in Lake Mjøsa, Randsfjorden, Norway (TMF = 2.3–3.0 and 2.3 for D5 and D6) (Borga et al., 2012a, 2013) and Shuangtaizi Estuary, China, with extreme magnifications of D5 (TMF = 11) and D6 (TMF = 7.1) (Xue et al., 2019). The high TMF values in the Shuangtaizi Estuary were one or two orders higher than those of D5 and D6 in this study. This may be due in different ecosystems to the species specificity of organisms and food web structure, resulting in biodilution or biomagnification of SMCs and siloxanes in the food web (Borga et al., 2012b). This large difference in TMF values of PCPs could be also caused by physio-chemical properties including log K_{ow} and molecular weight. Log K_{ow} is considered as one of the major factors affecting the accumulation and trophic transfer of chemicals in aquatic food webs. Chemicals with log K_{ow} > 4–5 tend to be magnified owing to high phospholipid permeability (Conder et al., 2008). In the freshwater food web of Lake Taihu, China, the TMFs of the organic contaminants (bisphenols, brominated diphenyl ethers [BDEs], and polychlorinated biphenyls [PCBs]) increased until the log K_{ow} was 7

before decreasing (Wang et al., 2017), showing a bell-shaped curve (Kelly et al., 2009; Yu et al., 2012). In Fremlin et al. (2020), a strong positive relationship ($p < 0.01$) between TMFs and the log K_{ow} of legacy persistent organic pollutants (POPs) including PCBs, organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) was also observed. However, there was no significant correlation between log K_{ow} (SMCs: 4.3–5.9, siloxanes: 4.5–9.1) and TMFs of SMCs (Goodbred et al., 2021; Zhang and Kelly, 2018; Zhang et al., 2013) and siloxanes (Borga et al., 2012, 2013; Cui et al., 2019; He et al., 2021; Jia et al., 2015; McGoldrick et al., 2014; Powell et al., 2018; Powell et al., 2017; Xue et al., 2019) in the previous and the present studies (Fig. S4). In addition to chemical properties such as log K_{ow} , the ecological (trophic) niche of organisms considerably affects the calculation of TMF. Previous studies have shown that TMF could be dependent on whether the samples were selectively (Xue et al., 2019) or non-selectively (Kim et al., 2020) used in aquatic food webs. As discussed in the previous section, the results of the stable isotope analysis indicated that the food web structure and feeding relationship could significantly affect the trophic transfer of harmful substances in various aquatic ecosystems. The traditional and widely used calculation method of TP using bulk $\delta^{15}\text{N}$ could not overcome the errors caused by species specificity, such as the tissue turnover rate and ontogenetic shift. In this study, the relationship between the accurate TP and concentration of bioaccumulated harmful substances was determined with high-resolution by considering the growth stage of the organism and the feeding characteristics using AAs.

Furthermore, despite the spatial and temporal differences in background concentrations of contaminants in the environmental media, there was no trend of TMFs across sites or seasons (Fig. 5). In five rivers located in southeastern France, the TMFs of poly- and perfluoroalkyl substances were determined using constant values regardless of the sites (Simmonet-Laprade et al., 2019). The TMFs of ionizable pharmaceutical products and PCPs were independent of distance from the WWTP (0.24, 2.3, and 21 km) and seasons in Salt Lake City, USA (Haddad et al., 2018). There are some critical factors determining the TMF value of contaminants besides the background concentrations in environment. Therefore, accumulating different spatio-temporal TMF values in food webs with accurate TP estimation is essential to clarify bioaccumulation characteristics and trophic transfer and magnification.

4. Conclusion

In this study, we investigated the fate of SMCs and siloxanes introduced through WWTP discharge, and the ecological impacts on habitats. Several key findings on the characteristics of distribution and trophic transfer of SMCs and siloxanes in Geum River were obtained i) great concentration of SMCs and siloxanes entered through WWTP discharge, ii) they were widespread in the estuary in multiple media, e.g. water, sediments and particulates, and iii) the bioaccumulation and trophic transfer were observed even though trophic magnification was not shown in the Geum River. Both SMCs and siloxanes had different composition ratios in multi-media samples, respectively. While HHCB was a major compound of SMCs in all samples, the secondary dominance of MK in water samples changed to AHTN in sediments and biota. Siloxane compounds were relatively evenly distributed in water and sediments, but D4 predominates, followed by D5 and D6 in biota. Most of the six compounds with significant concentrations detected in biota had TMFs <1 or slightly higher, indicating biodilution was more dominant than biomagnification. Overall, this study investigated the pollution sources, environmental fate, and bio-transfer of PCPs including SMCs and siloxanes in the Geum River. It also provided that accurate estimation of TP is important to determine the TMF in food web structure. In order to understand the characteristics of bioaccumulation, trophic transfer, and trophic magnification, it is essential to accumulate TMF values in food webs and spatio-temporal conditions.

CRediT authorship contribution statement

Dokyun Kim: Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing – original draft, Writing – review & editing. **Ha-Eun Cho:** Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing – original draft, Writing – review & editing. **Eun-Ji Won:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Hye-Jin Kim:** Investigation, Data curation. **Sunggyu Lee:** Formal analysis, Data curation, Writing – original draft. **Kwang-Guk An:** Investigation, Writing – review & editing. **Hyo-Bang Moon:** Conceptualization, Formal analysis, Writing – review & editing. **Kyung-Hoon Shin:** Conceptualization, Writing – original draft, 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 material is available free of charge on the Elsevier website. Additional details of the instrumental conditions, raw data of chemical concentrations and isotopes, and other helpful materials are given in Tables S1–S12 and Figs. S1–S4. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2022.107123>.

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