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Macrozoobenthic community responses to sedimentary contaminations by anthropogenic toxic substances in the Geum River Estuary, South Korea

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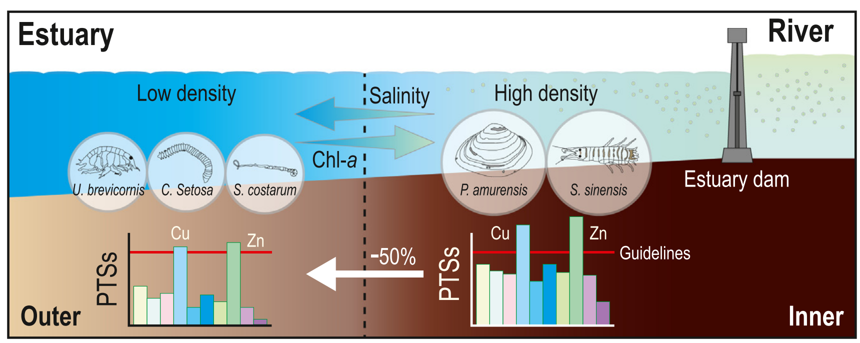
HIGHLIGHTS

- Benthic environment of estuary is clearly divided as the inner and outer parts of estuary.
- PTSs concentrations are obviously high in the inner part of estuary within one year-round.
- Concentrations of Cu and Zn within one year-round pose a potential ecological risk.
- Spatial variation of macrofaunal community prevailed with no seasonal fluctuations.
- Salinity and chlorophyll-*a* were key factors that determine macrofaunal assemblages.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the sedimentary pollution by persistent toxic substances (PTSs) and their potential impacts on the macrobenthic faunal community in the Geum River Estuary, South Korea. Sediment and benthic macrofauna samples were collected from eight sites every two months during the period of February to December in 2015. Target PTSs encompassed metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn), one metalloid (As), polycyclic aromatic hydrocarbons (PAHs), and alkylphenols (APs). The significant difference to the environment of the inner and outer parts of the estuary ($p < 0.05$) was found with relatively high concentrations of PTSs in sediment from the inner estuary. The concentrations of Cu and Zn exceeded the sediment quality guidelines of Korea representing a potential risk to aquatic organisms. The primary source of PAHs was by-products of diesel and gasoline combustion (37%), followed by a coke oven (32%) and oil-burning (31%). The macrofaunal community was spatially distinguished between the inner and outer parts of the estuary ($p < 0.05$), regardless of the season. In the inner part of the estuary, the density of the macrofaunal community was high, due to the increased opportunistic species and/or some indicator species (organic polluted or enrichment), implying that the given environment was disturbed. Among the environmental parameters analyzed by the distance-based linear model (DistLM), salinity, chlorophyll-*a*, and nutrient concentrations were found to be key factors controlling the changes in macrofaunal community structure. Such changes in the closed estuary system would indicate that each taxonomic group had

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to adjust to lower salinities and alternative food sources. Overall, the distribution of PTSs and macrozoobenthic communities in the Geum River Estuary collectively reflected the environmental gradients caused by surrounding activities in the inner part of the estuary together with direct effects by the irregular inflow of freshwater.

1. Introduction

Estuary is a dynamic and productive environment, but one of the most threatened coastal ecosystems primarily due to its geographical feature (McLuski and Elliot, 2006). Various substances are introduced to estuaries, via rivers from the land as a direct or indirect result of human activities, that accumulate in the sediment as major sinks for particle matter (Witt, 1995). Along with freshwater, organic matters, nutrients, and persistent toxic substances (PTSs) are introduced to estuaries, altering the environment. Metals, metalloid (As), polycyclic aromatic hydrocarbons (PAHs), and alkylphenols (APs) are frequently reported as sediment PTSs in contaminated coastal regions, and could adversely affect aquatic wildlife and human health (Tian et al., 2020; Yoon et al., 2020). These PTSs originate from both anthropogenic activities and natural sources, entering estuaries through various routes, such as sewage, industrial wastewater, surface runoff, and atmospheric deposition (Lin and Zhu, 2004; Li et al., 2013; Ghosh et al., 2015; Xu et al., 2016). PTSs that accumulate in sediment have high toxicity, persistency, bioaccumulation, and less biodegradability (White et al., 1994; Bastami et al., 2015; Singh and Kumar, 2017; Yoon et al., 2019), posing potential ecological threats to aquatic organisms.

Benthic macrofauna has an important role in the dynamics of benthic ecosystems, resulting in their being representative taxa (Herman et al., 1999). Benthic macrofauna is sedentary for most of their lives. Because of this low mobility, they must adjust to the surrounding environmental conditions over long timeframes (Gray et al., 1992). Thus, the benthic community serves as a suitable indicator for evaluating the benthic ecological health, facilitating observations of various feeding patterns, life-history, and dominant species (Dauvin et al., 2010; Patrício et al., 2012). Opportunistic species and indicator species often appear in organically enriched and contaminated environments; thus the emergence of specific species is important for interpreting the ecological situation appropriately (Ugland et al., 2008; Pelletier et al., 2010).

The benthic macrofaunal community is influenced by a wide variety of factors by anthropogenic and natural disturbances (including pollution by toxic contaminants and organic enrichment, changes to grain size, hypoxia, and seasonal variation) (Hyland et al., 2005; Sandrini-Neto et al., 2016; Bae et al., 2018; Kim et al., 2020a, 2020b). Many studies have used the benthic macrofauna community to evaluate responses to disturbance, with particular emphasis on the distribution of contaminants of anthropogenic origin (Hyland et al., 2005; Sandrini-Neto et al., 2016; Bae et al., 2017). The responses of the macrozoobenthic communities to contaminated areas have been studied in relation to the distribution of various pollutants, including metals and PAHs, as well as organochlorine pesticides, organotins, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) (Zheng et al., 2011; Wetzel et al., 2012; Ryu et al., 2016; Egres et al., 2019). Although many studies have evaluated how the benthic community responds to contaminants, most only investigate individual pollutants and/or simple relationships (or correlations) between contaminants and diversity indices (Ryu et al., 2011; Rumisha et al., 2012; Bae et al., 2017; Egres et al., 2019).

The Geum River Estuary in South Korea has been subject to continuous development since the construction of the estuary dam in 1990, and the completion of the Gunsan National Industrial Complex in 1992. Gunsan is a city located near the estuary that is a representative city of southwestern Korea. The manufacturing industry of this city continues to grow, in parallel to it being an international trade port. Consequently, the ecosystem of the Geum River Estuary has been impacted by a combination of changes to the physical, geological, and chemical environment, including decreased tidal cycles, changes to seabed topography, the irregular inflow of freshwater, deterioration of water quality, and contamination by PTSs (Lee et al., 1999; Kwon et al., 2001; Kim et al., 2006; Seo and Park, 2007; Shin, 2013; Yoon et al., 2017). Some studies on PTSs in this area demonstrated that, although contamination levels were not high, the degree of contamination in the inner part of the estuary was relatively high (Jeon et al., 2017; Yoon et al., 2017). Meantime, several studies documented the impacts of environmental changes on marine ecosystems, terrestrial origin organic matter on macrobenthos (Yoon et al., 2017) and eutrophication on phytoplankton in the given estuary (Shin, 2013). Of note, however, those earlier studies were limited to survey in a single season and of only a few parameters. Hence, it is necessary to evaluate how the seasonal and spatial distribution of PTSs and benthic communities change with freshwater discharge and the temporary influx of matter of terrestrial origin across all seasons.

The present study aimed to investigate: (1) spatiotemporal distribution of PTSs, (2) sources and fresh input of PTSs, (3) spatiotemporal patterns of macrofaunal assemblages, and (4) key factors influencing the spatiotemporal changes in macrofaunal communities. This study will serve as one few exercises reporting seasonal variations of PTSs and benthic macrofaunal communities, with addressing the ecosystem response to anthropogenic activities in a typical closed estuary of the Yellow Sea.

2. Materials and methods

2.1. Study area and sampling

The Geum River Estuary was specifically targeted for this study. The estuary is located in the southwestern part of Korea, representing a typical estuary area forming where the Geum River meets the Yellow Sea (Fig. 1a). Of note, this estuary has been severely impacted by the construction of an artificial dam. The inner part of the estuary (stations 1 to 3) is surrounded by industrial and urban areas and ports, and the estuary dam. The Geum River Estuary is subjected to higher wave energy in the winter (February and December) compared to the summer (June and August). The water temperature differs by about 20 °C or more between summer and winter, which is one critical environmental feature representing a dynamic oceanographic setting. A salinity gradient also exists due to the irregular discharge of freshwater from the estuary dam (Fig. 1b). Altogether, the very estuary show a dynamic environment in which water quality parameters are directly/indirectly affected by these distinct seasonal differences and/or episodic event of freshwater input to the offshore.

Sediment and benthic macrofauna samples were collected from the bottom water and sediment at eight stations every two months (February, April, June, August, October, and December) during 2015. Bottom water samples were collected using a Niskin bottle for water parameters (temperature, salinity, pH, dissolved oxygen [DO], chemical oxygen demand [COD], suspended sediment [SS], chlorophyll-*a* [Chl-*a*], nitrate [NO_3^-], nitrite [NO_2^-], ammonium [NH_4^+], dissolved inorganic nitrogen (DIN, a sum of NO_3^-, NO_2^-, and NH_4^+), total nitrogen [TN], phosphates [PO_4^{3-}], total phosphorus [TP], and Silica [SiO_2]). Undisturbed sediment samples were collected using a Van Veen grab sampler. These samples were used to analyze PTSs, sediment properties, and macrofaunal assemblages. All samples collected for laboratory analyses were stored using polyethylene bottles and glass bottles in an icebox with ice or

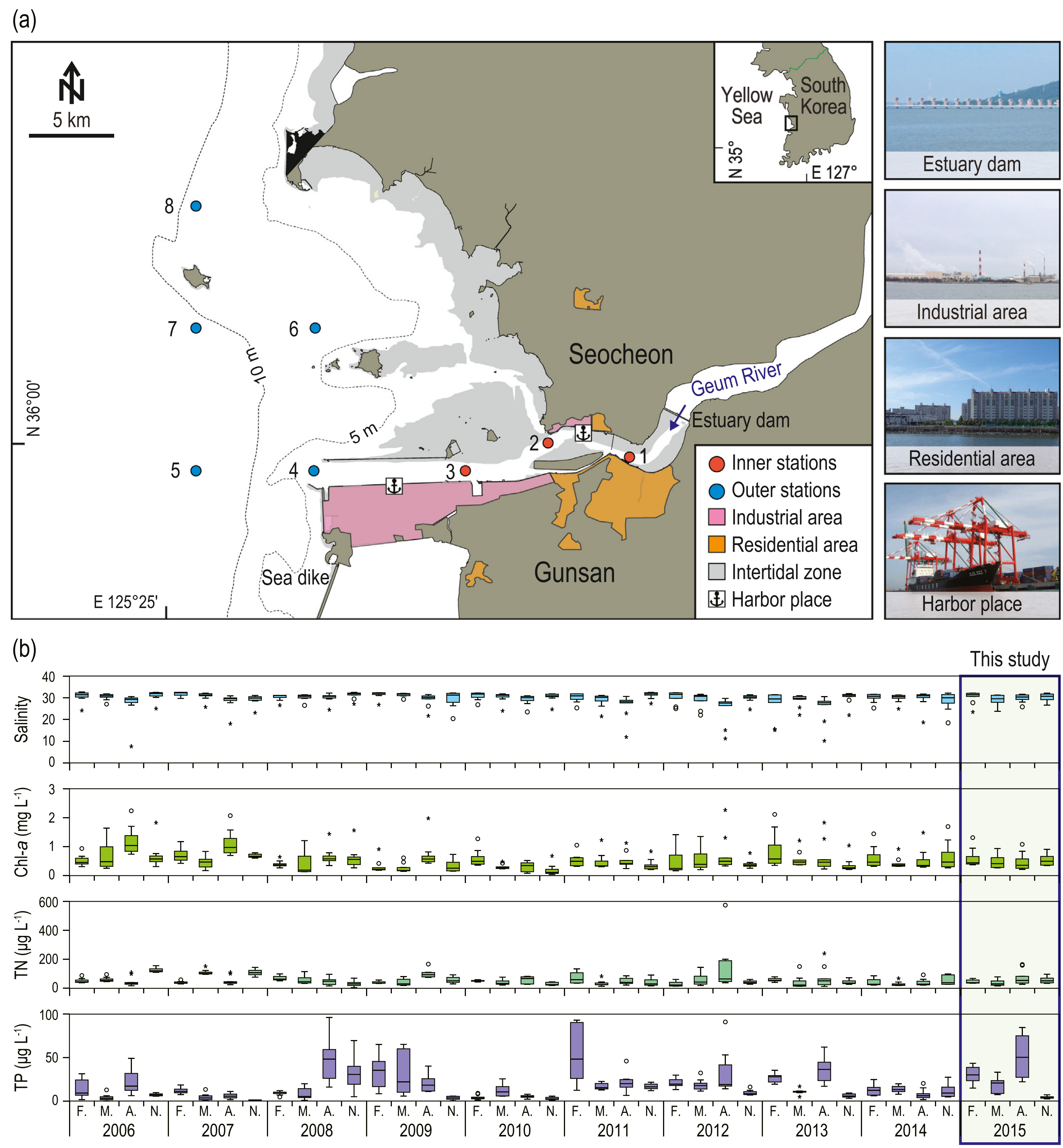

Fig. 1. (a) Map showing the study area and sampling stations in the Geum River Estuary, Korea. Images on the right present the surrounding environment. (b) National monitoring data for salinity, Chl-*a*, TN, and TP in the bottom water of the Geum River Estuary over the last decade.

dry ice. Macrofauna samples were collected after sieving sediment and fixed using buffered formalin. Water temperature, salinity, pH, and DO were measured in situ using YSI 556 Multiprobe System (YSI, Yellow Springs, OH).

2.2. PTS analyses

Sediment samples were prepared to analyze PAHs and APs following an existing method, with minor modifications (Khim et al., 1999). In brief, 10 g freeze-dried sediment was extracted using Soxhlet with 300 mL dichloromethane (DCM) (Burdick & Jackson, Muskegon, MI) and five surrogate standards (acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}, and bisphenol A-d_{16}). Activated copper powder (Sigma Aldrich, Saint Louis, MO) was added, and extracts were fractionated with an activated silica gel column (70–230 mesh, Sigma-Aldrich). After fractionation, 2-fluorobiphenyl was added as an internal standard. We quantified PAHs and APs using an Agilent 7890A gas chromatograph equipped with a mass selective detector

(GC-MSD) (Agilent Technologies, Santa Clara, CA). Details of the instrumental conditions are provided in Table S1 of the Supplementary Materials (S). Method detection limits (MDLs) were determined as standard deviations 3.707 times that of standard samples. The ranges of MDLs were 0.27–0.90 ng g^{-1} for PAHs, and 0.10–0.91 ng g^{-1} for APs. Recoveries for the five surrogate standards and standard reference material 1944 were generally acceptable: 72%–121% (mean = 90%) and 80%–126% (mean = 106%) (Table S2).

Metals in sediments were analyzed in accordance with the Korean Standard Method for Marine Environment (MOF, 2013). In brief, for Cd, Cr, Cu, Li, Ni, Pb, and Zn, 0.2 g freeze-dried and homogenized sediment was conducted on a hot plate with nitric acid (HNO_3, Sigma Aldrich) and perchloric acid ($HClO_4$, Sigma Aldrich) as 3:1 v/v. After evaporation, 2 mL $HClO_4$ and 5 mL hydrofluoric acid (HF, Sigma Aldrich) were added and re-evaporated. The residue was dissolved with 1 mL concentrated nitric acid and diluted with 10 mL HNO_3. Finally, samples were analyzed using an Elan 6100 inductively coupled plasma mass spectrometer (ICP-MS) (Perkin-Elmer SCIEX, Norwalk, CT) and Optima 7300DV ICP-optical emission spectrometer (ICP-OES) (Perkin-Elmer SCIEX). For As and Hg, 0.2 g freeze-dried sediment was dissolved by shaking it with 10 mL of 10% HNO_3 and 50 mL of 1 M hydrochloric acid (HCl, Sigma Aldrich), respectively. Residues were centrifuged, and the supernatant was determined using ICP-MS and a FIMS 100 mercury analysis system (Perkin-Elmer SCIEX), respectively. Recovery of the standard reference material, MESS-3 for sediment, was generally acceptable: 81%–97% (mean = 86%) (Table S2).

2.3. Environment parameters and macrofauna analyses

COD was analyzed using non-filtered seawater with the alkaline permanganate method (MOF, 2013). Other parameters were measured after filtering using GF/F and 0.45 μm membrane filters. Particulate samples for the analyses of SS and Chl-*a* were measured using weight comparisons and a 10-AU fluorescence spectrometer (Turner Design, San Jose, CA), respectively. Concentrations of nutrients were determined by the colorimetric assay method with a spectrophotometer. The grain size of sediment was analyzed following the dry sieve (Ingram, 1971) and pipetted (McBride, 1971) methods. Organic content (OC) was analyzed by burning the sediment for 4 h at 550 °C (Heiri et al., 2001). Macrofauna samples were rinsed and placed in diluted formalin. Identification to the species level (total of 48 species) followed by counting (total of 7986 individuals) was performed using a dissection microscope.

2.4. Data analyses

Based on the distance from the estuary dam and salinity (<30), stations 1–3 were set as being the inner part of the estuary, and stations 4–8 were set as being the outer part of the estuary, for spatial comparison. The concentrations of Cu and Pb in sediment were normalized using Li concentrations following Song and Choi (2017), for comparison with the sediment quality guidelinel of Korea (MOF, 2018). The positive matrix factorization receptor (PMF) model was used to allocate sources to the PAHs (Norris et al., 2014). A detailed method on the PMF model is provided in Yoon et al. (2020). As a result of performing the PMF model, the slope in the linear regression formula ranged from 0.45 to 1.00, with R^2 value ranging from 0.62 to 0.99. These results indicated that the performance of the PMF model applied in this study was satisfactory. Statistical analyses were conducted using the software SPSS 25.0 (SPSS INC., Chicago, IL), PRIMER 6 (PRIMER-E Ltd., Plymouth, UK), and R studio version 3.6.3 (R Development Core Team, 2014).

Pearson correlation was carried out to investigate significant relationships between PTSs and environmental parameters for interval scale variables. The Kruskal-Wallis test and the Mann-Whitney test with Bonferroni correction were used to evaluate differences among the sampling month because the variables did not satisfy normality. In the original data matrix, there were fewer species with <1% total macrofaunal abundance. The abundance data of macrofauna were $\log(x + 1)$ transformed. Two ecological indices were monitored to analyze the benthic communities using the Shannon-Wiener diversity index (H') and Ecological Quality Ratio (EQR) (Ryu et al., 2016). A Bray-Curtis similarity matrix was constructed, and cluster analysis (CA) and non-metric multi-dimensional scaling (nMDS) were used to group sampling stations at spatial and temporal scales. Permutational multivariate analysis of variance (PERMANOVA) was applied with the Monte Carlo test to ascertain whether the composition of the macrofaunal assemblage significantly differed across spatial and temporal scales. The zone (inner part and outer part) and sampling month were fixed factors. The homogeneity of multivariate dispersions was tested using tests of homogeneity of dispersion (PERMDISP).

A distance-based linear model (DistLM) was performed to explore the relationships between the macrofaunal community and environmental variables. The key factors determining the pattern of macrofaunal community assemblages were determined. Variables that had a high correlation (>0.8) were excluded to avoid co-linearity. Step-wise selection and An Information Criterion were applied to determine the influence of different variables. The results of the DistLM was visualized using distance-based redundancy ordination analysis (dbRDA). To identify indicator taxa within each group based on the dbRDA results, indicator value (IndVal) analysis was used (Dufrene and Legendre, 1997). Significant representative relationships delineated by DistLM were tested using canonical analysis of principal coordinates (CAP), to place macrofaunal assemblages along the environmental gradient.

3. Results and discussion

3.1. Spatiotemporal distributions of metals and the metalloid

All the metals and the metalloid were detected in the sediments of all stations across all months in the Geum River Estuary (Table 1). The concentrations of metals and the metalloid showed no consistent trend across months. Out of the sampling months, statistically significant differences ($p < 0.05$) were only found for As, Hg, and Pb, indicating a slight effect by seasonal factors (Table S3). The concentration of As was statistically high in April, August, and October, while concentrations of Hg and Pb were statistically high in June and October, respectively. These irregular results suggest that the effects of metals and the metalloid are independent of the season, and the result of differences in anthropogenic and/or natural inputs of individual metals and the metalloid (Cheggour et al., 2005). While seasonal variations were unclear, the distribution of metals and the metalloid was clearly distinguished spatially (Fig. S1). Relatively high concentrations of all metals and the metalloid were detected in the inner part of the estuary, with statistically significant values ($p < 0.05$) being recorded for all metals and metalloid, except Cd (Fig. 2a and Table S4). The mean concentrations of metals and the metalloid in the inner part of the estuary (stations 1 to 3) were about 1.3 to 5.9 times higher compared to those in the outer estuary (stations 4 to 8). Thus, industrial complexes, residential areas, and harbors located in the inner part of the estuary likely represent major sources of metals in the sediment (Zhao et al., 2018; Liu et al., 2019). Overall, the distribution of metals and the metalloid in the sediment of the Geum River Estuary was mainly determined by spatial factors, rather than seasonal factors.

The concentrations of most metals and the metalloid were significantly negatively correlated ($p < 0.05$) with salinity and significantly positively correlated ($p < 0.05$) with mud and organic content (Table S5). Some metals showed significant positive correlations with SS (Cr, Ni, and Pb) and negative correlations ($p < 0.05$) with pH (Cr, Hg, Ni, and Pb). Only Hg was significantly correlated with temperature. Thus, the distribution of metals and the metalloid was mainly influenced by spatial factors and sediment properties (Lao et al., 2019; Liu et al., 2019). The results also showed that the fine-grained sediments

Table 1
Data statistics of the selected environmental variables and macrofauna community structure monitored in the Geum River Estuary, Korea, over one-year (2015). Minimum, maximum, mean, and standard deviation of the environmental variables are provided.

Target analytes	All			Month					
	(year total)			2	4	6	8	10	12
	Min	Max	Mean (±SD)	Mean (±SD)					
Sediment									
As (mg kg^{-1})	0.8	4.9	2.2 (±0.9)	2.1 (±0.7)	2.6 (±0.5)	1.2 (±0.3)	2.8 (±1.0)	2.4 (±0.6)	2.4 (±0.9)
Cd (mg kg^{-1})	0.01	0.16	0.06 (±0.04)	0.08 (±0.05)	0.08 (±0.04)	0.09 (±0.05)	0.04 (±0.03)	0.06 (±0.03)	0.04 (±0.03)
Cr (mg kg^{-1})	4.4	73.5	33.7 (±15.2)	23.3 (±11.4)	27.6 (±8.2)	38.1 (±10.2)	32.6 (±11.2)	41.6 (±16.3)	38.9 (±21.0)
Cu (mg kg^{-1})[a]	1.0	480	21.4 (±70.3)	5.6 (±4.0)	80.6 (±157)	7.3 (±5.7)	7.1 (±5.6)	12.4 (±10.5)	15.6 (±26.5)
Hg (μg kg^{-1})	0.8	23.1	6.5 (±4.7)	3.5 (±1.9)	3.6 (±0.9)	13.7 (±6.1)	7.7 (±0.9)	3.8 (±1.5)	6.5 (±3.4)
Ni (mg kg^{-1})	2.3	30.4	12.1 (±6.3)	8.9 (±4.1)	11.3 (±3.8)	12.4 (±4.5)	11.0 (±4.9)	14.8 (±7.5)	14.0 (±9.1)
Pb (mg kg^{-1})	4.5	36.0	17.6 (±5.1)	14.3 (±4.2)	15.5 (±2.6)	18.4 (±2.8)	15.0 (±3.5)	22.5 (±6.2)	19.9 (±4.45)
Zn (mg kg^{-1})[a]	5.5	1078	70.2 (±159)	26.7 (±14.6)	201 (±349)	45.6 (±18.5)	31.4 (±14.7)	52.8 (±34.9)	64.2 (±84.6)
PAHs (ng g^{-1})	ND[b]	205	39.6 (±49.3)	42.4 (±46.8)	38.4 (±37.2)	87.9 (±73.0)	18.8 (±29.3)	29.6 (±26.1)	20.3 (±29.7)
APs (ng g^{-1})	0.6	32.6	7.1 (±6.8)	11.4 (±9.6)	6.4 (±4.8)	10.7 (±8.0)	5.6 (±3.6)	4.4 (±4.8)	4.4 (±3.1)
Mud content (%)	0.0	98.9	26.4 (±26)	16.8 (±18.8)	21.9 (±23.5)	35.4 (±24.6)	20.2 (±19.0)	35.0 (±25.7)	29.1 (±34.8)
Loss on ignition (%)	0.9	6.2	2.2 (±1.2)	1.9 (±0.9)	2.5 (±1.1)	2.6 (±1.0)	1.7 (±0.8)	2.4 (±1.0)	2.2 (±1.7)
Bottom water									
Temperature (°C)	2.7	27.6	14.7 (±7.9)	3.6 (±0.6)	9.9 (±0.9)	21.1 (±1.1)	26.5 (±0.8)	18.3 (±0.9)	8.9 (±0.9)
Salinity (psu)	19.8	32.8	30.3 (±3.2)	29.7 (±4.1)	29.5 (±3.8)	30.1 (±3.1)	30.4 (±2.4)	31.2 (±2.8)	30.8 (±2.1)
pH	7.7	8.5	8.1 (±0.2)	8.2 (±0.1)	8.4 (±0.1)	8.0 (±0.1)	8.0 (±0.1)	7.9 (±0.1)	8.1 (±0.1)
DO (mg L^{-1})	2.9	11.9	7.9 (±2.7)	10.9 (±0.6)	10.2 (±1.2)	5.9 (±1.0)	3.7 (±0.4)	7.3 (±0.3)	9.7 (±0.3)
COD (mg L^{-1})	1.2	8.8	3.7 (±1.7)	1.8 (±0.8)	2.9 (±0.8)	5.0 (±2.2)	3.8 (±1.2)	4.1 (±1.3)	4.9 (±1.0)
SS (mg L^{-1})	4.4	151	27.5 (±28.3)	15.5 (±9.5)	17.7 (±13.5)	23.7 (±17.2)	16.3 (±10.0)	48.8 (±45.3)	43.3 (±31.4)
Chl-*a* (μg L^{-1})	0.7	13.5	4.3 (±3.4)	7.5 (±4.3)	6.0 (±2.1)	3.0 (±1.3)	5.1 (±3.8)	3.0 (±2.0)	1.3 (±0.8)
DIN (μg L^{-1})	15	1460	330 (±323)	542 (±407)	120 (±184)	252 (±285)	264 (±288)	338 (±243)	464 (±290)
TN (μg L^{-1})	326	2040	762 (±370)	863 (±538)	686 (±300)	593 (±221)	801 (±282)	696 (±183)	930 (±448)
PO_4 (μg L^{-1})	0.5	76.6	22.2 (±19.2)	21.2 (±7.0)	2.4 (±2.0)	11.8 (±10.3)	11.0 (±13.1)	41.3 (±13.8)	45.4 (±12.7)
TP (μg L^{-1})	15.2	386	73.4 (±69.1)	41.4 (±6.0)	44.0 (±25.2)	41.9 (±29.7)	57.2 (±32.2)	159 (±116)	96.7 (±39.4)
SiO_2-Si (μg L^{-1})	8.3	1754	500 (±381)	441 (±228)	40.9 (±44.5)	400 (±277)	675 (±468)	684 (±336)	762 (±221)
Macrofauna community structure									
Number of taxa	1	26	14	13	14	15	16	14	12
Mean density (ind.m^{-2})	5	4125	832	830	739	1423	953	688	359
Dominant taxa[c]									
1st	Ann (61.0%)			Ann (50.6%)	Ann (67.9%)	Ann (54.4%)	Ann (58.9%)	Ann (68.5%)	Ann (65.5%)
2nd	Art (23.1%)			Art (31.6%)	Art (22.2%)	Art (68.8%)	Mol (16.7%)	Art (14.6%)	Art (14.9%)
3rd	Mol (9.8%)			Mol (14.9%)	Mol (7.1%)	Mol (5.4%)	Art (16.5%)	Mol (11.1%)	Mol (11.1%)
Ecological indices									
Diversity (*H'*)	0.0	2.0	1.8	1.7	1.9	1.6	1.9	1.8	1.8
Evenness (*J*)	0.3	0.9	0.7	0.6	0.8	0.7	0.7	0.7	0.8
Richness (*R*)	0.0	5.2	2.8	2.6	2.7	3.0	2.9	2.9	2.6
Dominance (*D*)	0.3	1.0	0.6	0.6	0.6	0.6	0.6	0.6	0.6

[a] Concentrations of Cu and Pb in sediments were normalized using concentrations of Li.
[b] ND: Not detected.
[c] Top 3 dominant taxa. Ann: Annelida; Art: Arthropoda; Mol: Mollusca.

in the Geum River Estuary are stable for contaminant retention year-round, regardless of season (Buggy and Tobin, 2008).

The concentrations of metals and metalloid in sediments obtained from the present study were similar or less compared to those previously reported in the other regions of South Korea, including Jinhae Bay, the west coast of Korea, and the coastal area of the Yellow Sea (Bae et al., 2017; Kim et al., 2020a, 2020b; Tian et al., 2020). In addition, the concentrations of metals and the metalloid in the Geum River Estuary were generally lower compared to their background concentrations in Korean sediments (Fig. S2) (Woo et al., 2019). The range of <MDL–22.9% (mean: 10.7%) for all metals and the metalloid exceeded the corresponding background concentrations, indicating low contamination. Thus, anthropogenic sources appeared to weakly affect the distribution of metals and the metalloid in the Geum River Estuary, suggesting that they were of mostly natural origin. The contamination status of metals and the metalloid in the sediment of the Geum River Estuary was lower compared to that previously reported (Seo and Park, 2007). Cr, Cu, Ni, Pb, and Zn concentrations decreased by 62–82% compared to the mid-2000s, implying that the benthic environment of the Geum River Estuary had improved. However, comparison with the sediment quality guidelines of Korean marine environmental standards (MOF, 2018) showed that contamination of metals in the sediments of the Geum River Estuary was of potential ecological risk. Out of all of the metals and metalloid, only Cu and Zn concentrations exceeded the threshold effects level (TEL) and probable effects level (PEL) in both the inner and outer parts of the estuary (Fig. 2b). Cu concentrations exceeded the guideline threshold in April, October, and December, while Zn concentrations exceeded the guideline threshold in April, June, October, and December. Thus, although the overall contamination level was low, the potential risk to aquatic organisms in the Geum River Estuary has sporadically occurred from past to present.

3.2. Spatiotemporal distributions of PAHs and APs

PAHs had a 91% detection frequency, while APs were detected in the sediments of all stations across all months (Fig. 3a). The concentrations of PAHs and APs ranged from <MDL to 205 ng g^{-1} dw (mean: 39.6 ng g^{-1} dw) and from 0.6 to 32.6 ng g^{-1} dw (mean: 7.1 ng g^{-1} dw), respectively. The concentrations of PAHs and APs were not correlated with the season and had a similar distribution to metals. (Table 1). No statistically significant difference ($p < 0.05$) was found (Table S3) among sampling months, suggesting that the influx of similar

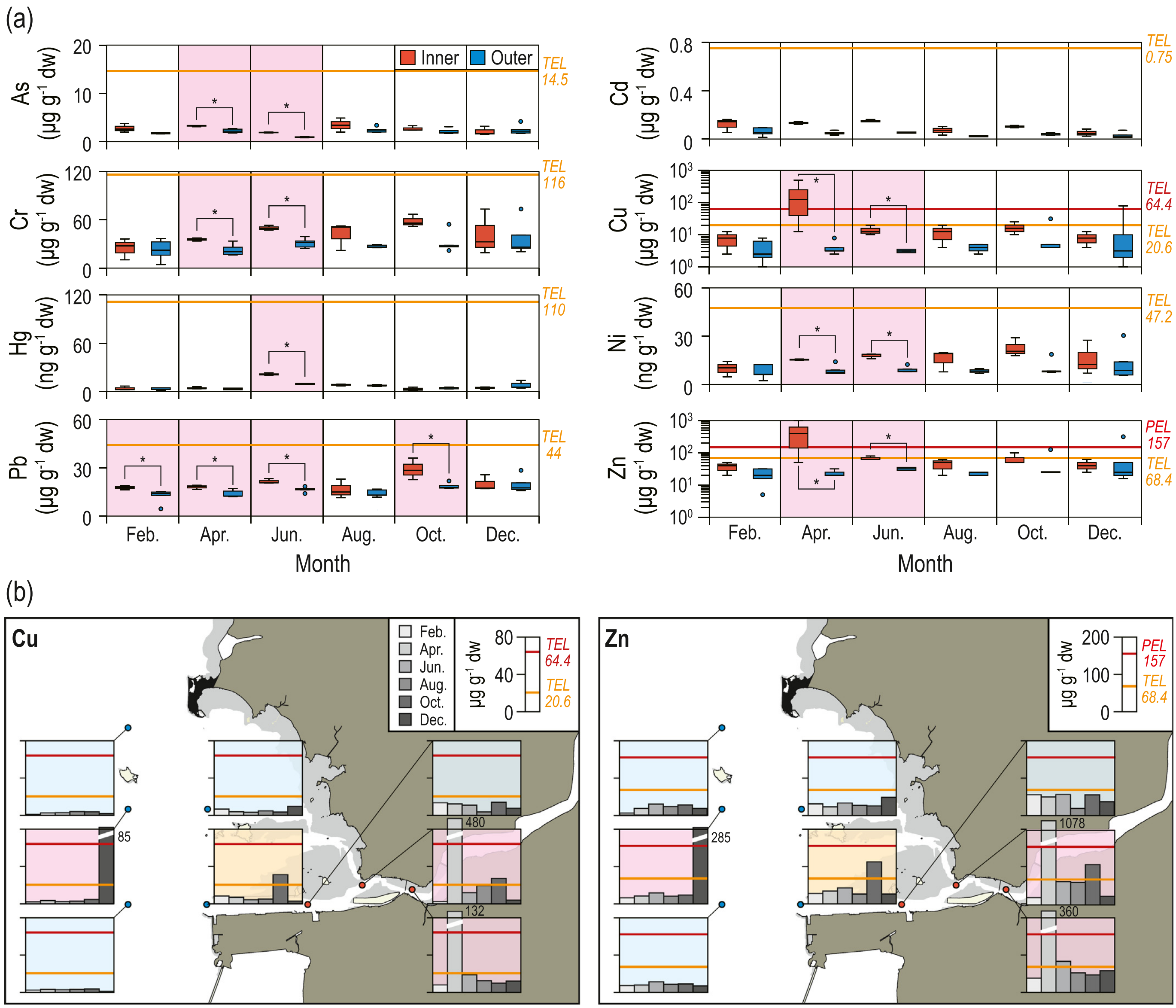

Fig. 2. Spatiotemporal distribution of metals and the metalloid in the sediments of the Geum River Estuary, Korea. Blue and yellow backgrounds indicate that concentrations did and did not exceed TEL, respectively; red background indicates that concentrations exceeded PEL. The graph at the top shows the concentrations in the inner and outer parts of the estuary each month. The red background on the graph indicates a case where the concentration between the inner and outer parts of the estuary was significantly different.

sources continued, regardless of time. The spatial distributions of PAHs and APs were clearly divided, irrespective of time (Fig. S3). Relatively high concentrations of PAHs and APs were detected in the inner part of the estuary with significant differences ($p < 0.05$) (Fig. 3a and Table S4). The means concentrations of PAHs and APs in the inner part of the estuary were about 4.3 and 2.9 times compared to those in the outer part of the estuary, respectively. Thus, the main sources of PAHs and APs were likely industrial complexes, residential areas, and harbors around the inner part of the estuary (Ashley and Baker, 1999; Yoon et al., 2020). The concentrations of PAHs and APs were significantly correlated ($p < 0.05$) with salinity (negative), mud content (positive), and organic content (positive) (Table S5). Thus, the distribution of PAHs and APs in the Geum River Estuary was likely regulated by spatial factors and sediment properties (Xu et al., 2006; Liu et al., 2013). Overall, the distribution of PAHs and APs in the sediment of the Geum River Estuary were space-dependent, not seasonal.

The concentrations of PAHs and APs in sediments of Geum River Estuary were similar or less compared to other regions of South Korea, including Lake Sihwa, Masan Bay, west coast of Korea, and the coastal area of the Yellow Sea (Lee et al., 2017, 2018; Kim et al., 2020a, 2020b; Yoon et al., 2020). In addition, the concentrations of PAHs and APs detected in all sampling periods did not exceed the interim sediment quality guidelines (ISQG) of the Canadian Council of Ministers of the Environment (CCME, 2001, 2002). In addition, the concentrations of PAHs and APs detected in the present study were similar to those previously reported for the intertidal zone and subtidal zone of the Geum River Estuary since 2010 (Jeon et al., 2017; Yoon et al., 2017). PAHs and APs levels were in the sediment of the Geum River Estuary in the 2010s were predicted not to impact the benthic ecosystem.

The composition of PAHs was similar in time, with some spatial differences between the inner and outer parts of the estuary (Fig. S3). Throughout the entire period, four- to six-ring PAHs were predominated (61.9–91.7%) and were dominant in the inner part of the estuary. This result was attributed to the hydrophobic nature of high molecular mass PAHs, which tend to accumulate around the source (Bixian et al., 2001; Yoon et al., 2017). The contribution of PAH sources varied with time, showing some spatial differences. The PMF model results showed that the Q_{True}/Q_{Exp} values of 2–5 factors were 2.06 1.99, 2.27, and 2.40,

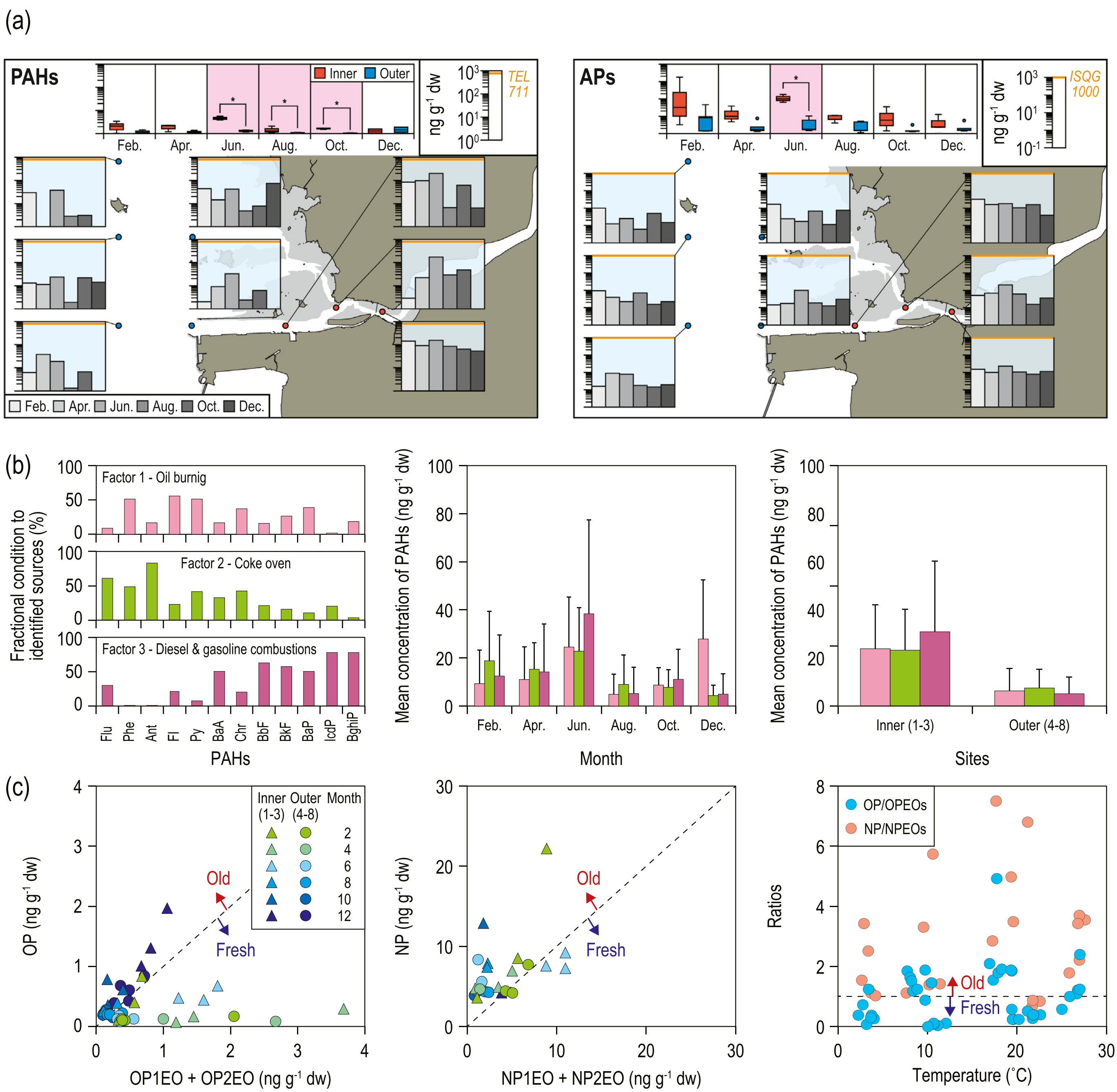

Fig. 3. (a) Spatiotemporal distribution of PAHs and APs in the sediments of the Geum River Estuary, Korea. The blue background indicates that the concentration did not exceed sediment quality guidelines. The graph at the top shows the concentrations in the inner and outer parts of the estuary each month. The red background on the graph indicates a case where the concentration between the inner and outer parts of the estuary was significantly different. (b) The quantitative contribution of the identified sources by positive matrix factorization receptor (PMF), and monthly and spatial distribution of each source. (c) Fresh (recent) input ratios of APs and the relationship between water temperature and fresh input ratios.

respectively. The smallest Q_{True}/Q_{Exp} value was found in the result of 3-factor, indicating the most reliable model (Crilley et al., 2017). Thus, 3-factor was selected for source identification of PAHs in Geum River Estuary. The PMF model analysis classified PAHs sources as oil burning, coke oven, and diesel & gasoline combustion (Fig. 3b) (Khalili et al., 1995; Harrison et al., 1996; Ravindra et al., 2008). Diesel and gasoline combustion had the highest contribution, representing 36.3% of total PAHs concentration detected in present study, followed by coke oven (32.4%) and oil burning (31.3%). Diesel and gasoline combustion was relatively high in June and October, coke oven in February, April, and August, and oil burning in December. This result indicated that various sources affected sediment seasonally. Diesel and gasoline combustion accounted for 39.6% of PAHs in the inner part of the estuary, while the most influential source in the outer part of the estuary was the coke oven (39.7%). Thus, diesel and gasoline combustion were the primary sources of PAHs in the hotspot of the Geum River Estuary, with spatially different intensities.

Fresh inputs of APs were evaluated based on the ratios of degraded chemicals (OP: octylphenol and NPs: nonylphenols) and fresh chemicals (OPEOs: octylphenol ethoxylates and NPEOs: nonylphenol ethoxylates) (Fig. 3c) (Isobe et al., 2001). Fresh inputs of OP were confirmed in February, April, and June. In comparison, fresh inputs of NPs were rarely detected in any of the sampling months. For both NPs and OP, the diagnostic ratio did not show any specific relationship with water temperature. Thus, fresh inputs of

Table 2
Result of the PERMANOVA and PERMDISP test based on the data of taxon diversity and abundance of macrofauna in the Geum River Estuary, Korea. Zo: Zone (inner part and outer part); Sm: Sampling month; df: degree of freedom; P-F: Pseudo-F; ECV: Estimate Components of Variation; Sqrt: square root of ECV; Bold values: $P < 0.05$.

Target	Term	PERMANOVA					PERMDISP	
		df	P-F	ECV	Sqrt	*P*	P-F	*P*
Taxon diversity	Zo	1	50.8	200	14.2	**0.001**	12.5	**0.003**
	Sm	5	0.7	−3.1	−1.8	0.631	1.7	0.568
	Zo × Sm	5	1.3	8.6	2.9	0.245		
	Res	36		90.4	9.5			
Density	Zo	1	14.8	1166	34.1	**0.001**	0.40	0.573
	Sm	5	1.4	106	10.3	**0.042**	0.51	0.837
	Zo × Sm	5	1.1	58.4	7.6	0.292		
	Res	36		1898	43.6			

APs in the Geum River Estuary may be influenced by a particular time event (rather than a season), such as increased decomposition rates through microbial activity (Ying et al., 2002). The Korean government officially banned the use of NP in household products in 2007 and industrial products in 2016 (Kim et al., 2020a, 2020b). Thus, Fresh inputs of APs in the present study showed that government policy had a positive effect. However, this study also confirmed that chemicals that are not yet fully regulated are being continuously introduced to the environment.

3.3. Spatiotemporal patterns of macrofaunal assemblages

The distribution of the macrofaunal community in the Geum River Estuary reflected both spatial and seasonal differences (Table 1). Spatially different taxon diversity occurred in the inner part of the estuary versus in the outer part of the estuary (df = 1, Pseudo-F = 50.8, $p < 0.05$); however, there was no difference between sampling months (df = 5, Pseudo-F = 0.7, $p > 0.05$) (Table 2). No interaction between zone and sampling month was found. A significant dispersion difference was detected by the PERMDISP test in the zone of taxon diversity ($p < 0.05$). This phenomenon might be attributed to heterogeneous variation, rather than a real factor effect. The number of species tended to increase from the inner part of the estuary to the outer part of the estuary, indicating that the benthic communities of the inner and outer parts of the estuary were distinct (Fig. 4a). The largest group of species was Annelida, followed by Arthropoda, Mollusca, others, and Echinodermata. Density significantly differed with respect to zone (df = 1, Pseudo-F = 14.8, $p < 0.05$) and sampling month (df = 5, Pseudo-F = 1.4, $p < 0.05$), with no interaction between zone and sampling month (Table 2). The PERMDISP test showed no significant difference in dispersion between zone and sampling month. Annelida dominated (mean: 442 ind. m^{-2}), but Arthropoda (mean: 222 ind. m^{-2}) and Mollusca (mean: 134 ind. m^{-2}) were predominant in the inner part of the estuary. This result could be explained by the appearance of opportunistic species, due to dynamic environmental changes

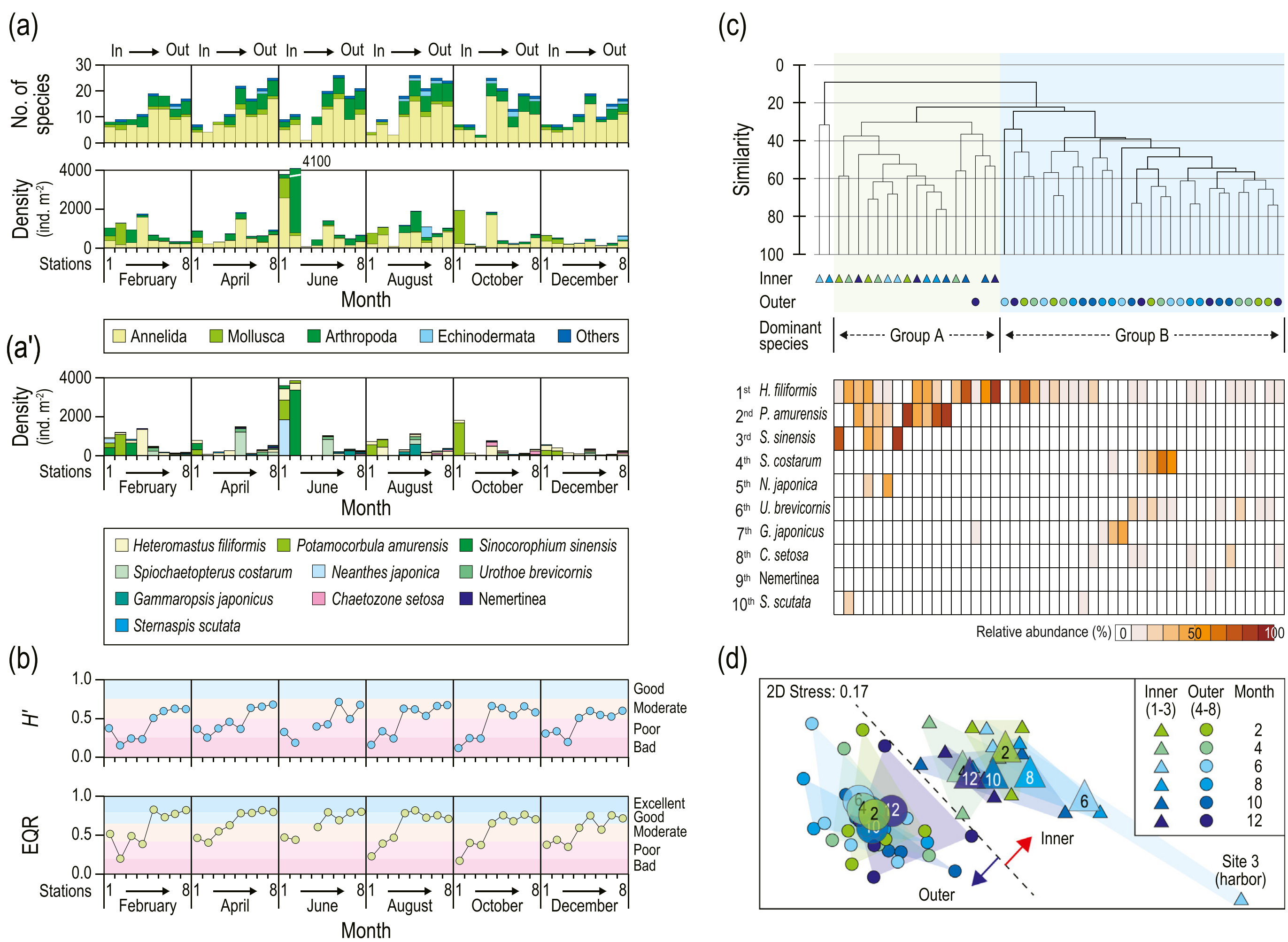

Fig. 4. (a) Number of species, density, and (a') density of top 10 dominant species. (b) Ecological quality status as represented by Shannon-Wiener diversity index (H') and Ecological Quality Ratio (EQR). (c) Cluster analysis showing the two groups of macrofaunal assemblages, with the top 10 dominant species. (d) Non-parametric multi-dimensional scaling (nMDS) ordination plot based on relative abundance.

in the inner part of the estuary (Dauer, 1993). The most dominant species were *Heteromastus filiformis*, accounting for 16.8% of total abundance, followed by *Potamocorbula amurensis* (14.6%), *Sinocorophium sinensis* (12.3%), *Spiochaetopterus costarum* (7.1%), and *Neanthes japonica* (5.2%). (Fig. 4a'). These species were opportunistic, organic pollutant or enrichment indicator species, or brackish water species, which were predominantly found in the inner part of the estuary (Pearson and Rosenberg, 1978). Thus, the benthic environment in the Geum River Estuary is likely influenced by freshwater and is in a state of organic enrichment due to the inflow of terrestrial organic matter (Hermand et al., 2008). The next dominant species were *Urothoe brevicornis* (3.3%), *Gammaropsis japonicas* (2.8%), *Chaetozone setosa* (2.8%), Nemertinea (1.9%), and *Sternaspis scutata* (1.4%), which predominantly occurred in the outer part of the estuary. The H' and EQR showed that the benthic environment in the inner part of the estuary was mostly "Bad" to "Moderate" and mostly "Moderate" to "Excellent" in the outer part of the estuary (Borja et al., 2004; Borja and Dauer, 2008) (Fig. 4 b). Thus, the macrofaunal community in the inner and outer parts of the Geum River Estuary was spatially separated, with the outer part of the estuary being ecologically more valid and stable compared to the inner part of the estuary.

The ordination of macrofauna assemblages using CA and nMDS clearly showed that the inner and outer parts of the estuary differed (Fig. 4c and d). However, no seasonal trend was detected among stations, even though the PERMANOVA test showed significant differences among sampling months. The cluster results were largely divided into the inner (group A) and outer parts (group B) of the estuary, except for station 3, where few individuals of macrofauna were detected. Group A was dominated by *P. amurensis*, *S. sinensis*, and *N. japonica* were predominated, and in group B, *S. costarum*, *U. brevicornis*, *G. japonicas*, and *C. setosa*. *H. filiformis* was the most dominant species and indicator of organic enrichment in both groups A and B. These results confirmed that the macrofaunal community spatially differed, with the community in the inner part of the estuary being disturbed by the dominance of opportunistic species and indicator species (organic polluted or enrichment) (Pearson and Rosenberg, 1978; Dauvin et al., 2009). In the nMDS space, each month had a relatively wide distribution range in the inner part of the estuary compared to the outer part of the estuary, with June and August (summer) differing to other months. This phenomenon could be explained by the increasing influence of freshwater from the Geum River, and the increased stress due to high water temperature and low water depth in summer (Rundle et al., 1998).

3.4. Key factors influencing the spatiotemporal pattern of macrofaunal assemblages

Many factors determined the spatiotemporal distribution of the macrofaunal community in the present study. Out of the 18 input variables, DistLM showed that TN, mud content, Chl-*a*, salinity, Hg, APs, and SiO_2 accounted for significant variations in macrofauna assemblages across all sampling stations and months (Table S6). Collectively, these seven environmental variables explained 44% of the total variability in macrofauna assemblages. Thus, various substances from the Geum River likely have a strong influence on the distribution of benthic communities (Montagna and Kalke, 1992). For instance, previous studies in the same area reported the origin of sediment organics as the main factor controlling benthic communities (Yoon et al., 2017). The dbRDA showed that the distribution of benthic communities differed inner (Group 1) and outer parts (Group 2) of the estuary, depending on the main environmental variables (Fig. 5a). The factors determining the benthic community structure included TN, Chl-*a*, mud content, and salinity (Fig. 5a), but salinity and mud content seemed to be primary factors apparently explaining the spatial distribution of some opportunistic and/or indicator species between inner and outer regions. Out of the dominant species in each group, five species were selected by identifying the indicator taxa corresponding to $P < 0.01$ (Table S7). The indicator taxa representing the Geum River estuary were *P. amurensis* and *S. sinensis* in Group 1 (freshwater inflow, organic enrichment, fine-grained sediment), and *U. brevicornis*, *C. setosa*, and *S. costarum* in Group 2 (No freshwater inflow event, little organic matter, coarse sediment). Opportunistic species and indicator species (organic polluted or enrichment) were identified as indicator taxa, both in the inner and outer parts of the estuary, indicating that the benthic environment in the Geum River Estuary was disturbed (Pearson and Rosenberg, 1978; Dauvin et al., 2009).

The macrofaunal assemblages were clearly distributed in relation to environmental variables (Fig. 5b). Salinity and Chl-*a* gradients clearly changed in relation to macrofaunal assemblages, with a canonical correlation of $\delta = 0.78$ ($m = 7$, $r = 0.88$, $p < 0.001$) and $\delta = 0.70$ ($m = 13$, $r = 0.83$, $p < 0.001$), respectively. In contrast, macrofaunal assemblages were not strongly correlated with sediment properties and PTSs, with a canonical correlation of $\delta = 0.49$ ($m = 6$, $r = 0.70$, $p < 0.001$) and $\delta = 0.43$ ($m = 5$, $r = 0.66$, $p < 0.001$), respectively. At low salinity, Mollusca dominated, while under normal salinity, Annelida and Arthropoda dominated. The change to the macrofaunal community due to salinity indicates that the ability to adapt to low salinity varies across taxonomic groups. Previous studies also documented this trend (Rosenberg and Möller, 1979; Montagna and Kalke, 1992; Kennish et al., 2009). The apparent increase of Mollusca (mostly filter feeders) with increasing Chl-*a* concentration could be explained by the result of adaptation to the environment in which the amount of prey increased (Essink and Bos, 1985). The inconsistent changes to the macrofaunal community in relation to sediment properties and PTSs might be attributed to the greater influence of freshwater inflow and low levels of pollution. Even under similar PTSs contamination, the degree of exposure, due to sediment resuspension or bioturbation, would vary and consequently, the continuous release of industrial and urban wastes in the region might act differently (Cabrini et al., 2017). The type of compound is also a factor that influences the impact of benthic community change (Fusi et al., 2016). The insensitivity of macrofauna could also be explained as one reason. In the previous study, the responses of meiofauna and macrofauna to PTSs contamination showed a greater change in the meiofauna community structure (Egres et al., 2019). Thus, considering these factors, it is necessary to carefully approach the understanding of benthic community response associated with PTSs contamination. Studies conducted in coastal areas with a relatively stable environment and highly polluted areas have reported that the distribution of benthic communities is controlled by the characteristics of sediments or the distribution of pollutants (Zheng et al., 2011; Wetzel et al., 2012; Fusi et al., 2016; Cabrini et al., 2017; Camargo et al., 2017). Overall, changes to the macrofaunal community in the Geum River Estuary mainly depended on phenomena caused by freshwater inflow. In comparison, the sediment properties and the contamination levels of PTSs had relatively minor effects.

4. Conclusions

The present study demonstrated the spatiotemporal distribution of PTSs and macrofaunal assemblages and identified how the community responds to the surrounding environment. We showed that, regardless of season, the inner part of the estuary was a hotspot for PTSs. We also showed that, in some instances, PTSs present a potential risk to the aquatic ecosystem. The main source of PAHs was diesel and gasoline combustion, and less fresh input of APs was identified on the seasonal scale. We confirmed that the benthic community in the Geum River Estuary was mainly influenced by spatial factors, not seasonal factors. In addition, disturbance to the environment of the inner part of the estuary was confirmed by the emergence of opportunistic and indicator species (organic polluted or enrichment). Salinity and Chl-*a* were the natural variables that primarily drove spatial variation of macrofaunal assemblages, regardless of the season. Consequently, the present study

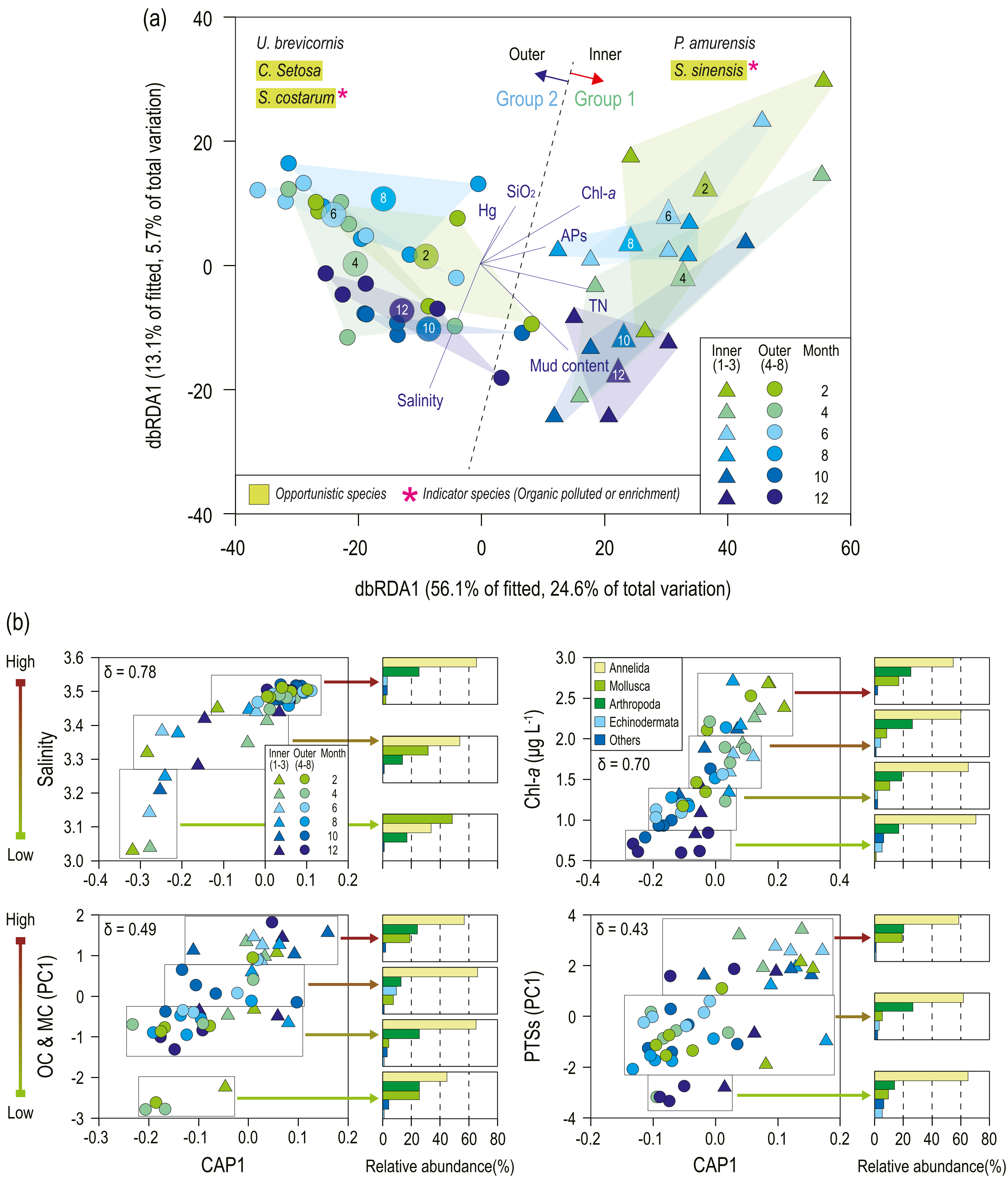

Fig. 5. (a) Distance-based redundancy analysis (dbRDA) ordination based on environmental parameters and the relative abundance of macrofauna. Only significant environmental variables were marked as vectors. Indicator taxa identified through IndVal analysis is displayed in each group. (b) Variation in macrofaunal assemblages along the canonical gradient in relation to salinity, Chl-*a*, organic & mud content, and PTSs. Bar graph on the right side indicates the proportional abundance for five taxa at the Phylum level.

indicated that contamination levels and responses of macrofaunal assemblages in estuarine areas are influenced by the estuary dam. The present study provides baseline information on how benthic macrofaunal communities respond to anthropogenic toxic substances at a 1-year timescale in an estuarine area subjected to various anthropogenic pressure, including the estuary dam where freshwater was irregularly discharged. Although the present study suggests that the freshwater input is the major impact that controls the macrofaunal community, further study would be needed in more polluted areas and/or more sensitive benthic community to confirm the identified key factors.

CRediT authorship contribution statement

Seo Joon Yoon: Conceptualization, Investigation, Formal analysis, Statistical analyses, Visualization, Writing – original draft. **Seongjin Hong**: Conceptualization, Writing – review & editing, Visualization. **Hyeong-Gi Kim**: Visualization, Statistical analyses. **Junghyun Lee**: Investigation, Formal analysis. **Tawoo Kim**: Investigation, Formal analysis. **Bong-Oh Kwon**: Writing – review & editing. **Jaeseong Kim**: Writing – review & editing, Project administration. **Jongseong Ryu**: Writing – review & editing, Project administration. **Jong Seong Khim**: 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 to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142938.

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<Supplementary Materials>

Macrozoobenthic community responses to sedimentary contaminations by anthropogenic toxic substances in the Geum River Estuary, South Korea

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Supplementary Tables

Table S1. Instrumental conditions of the gas chromatograph equipped with a mass selective detector for the analyses of PAHs and APs.

GC/MSD system	**Agilent 7890A GC and 5975C MSD**
Column	DB-5MS UI (30 m long, 0.25 mm i.d., 0.25 μm film thickness)
Gas flow	1 mL/min He
Injection mode	Splitless
Injection volume	2 μL
Injector temperature	300 °C
Ionization	EI mode (70 eV)
MS temperature	180 °C
Detector temperature	230 °C
Oven temperature (PAHs)	60 °C hold 2 min Increase 6 °C/min to 300 °C 300 °C hold 13 min
Oven temperature (APs)	60 °C hold 5 min Increase 10 °C/min to 100 °C Increase 20 °C/min to 300 °C
Targeted PAHs (16)	Acenaphthylene (Acl), Acenaphthene (Ace), Fluorene (Flu),, Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fl), Pyrene (Py), Benzo[*a*]anthracene (BaA), Chrysene (Chr), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Benzo[*a*]pyrene (BaP), Perylene (Pery), Indeno[*1,2,3-c,d*]pyrene (IcdP), Dibenz[*a,h*]anthracene (DbahA), and Benzo[*g,h,i*]perylene (BghiP)
Targeted APs (6)	4-tert-Octylphenol (OP), 4-tert-Octylphenol monoethoxylate (OP1EO), 4-tert-Octylphenol diethoxylate (OP2EO), Nonylphenols (NPs, isomer mix), Nonylphenol monoethoxylates (NP1EOs, isomer mix), and Nonylphenol diethoxylates (NP2EOs, isomer mix)

Table S2. Certified and measured concentrations for selected PAHs and metals in standard reference material (SRM) to check the accuracy of the method.

PAHs	Certified concentration	Measured concentration	Recovery (%)
SRM-1944[a]			
Phenanthrene	5.3 ± 0.2	4.6 ± 0.3	87 ± 5.3
Fluoranthene	8.9 ± 0.3	7.8 ± 0.1	87 ± 1.6
Pyrene	9.7 ± 0.4	7.9 ± 0.3	81 ± 2.9
Benz[*a*]anthracene	4.7 ± 0.1	4.8 ± 0.2	102 ± 5.1
Chrysene	4.9 ± 0.1	4.1 ± 0.2	85 ± 3.3
Benzo[*b*]fluoranthene	3.9 ± 0.4	4.7 ± 0.2	121 ± 6.4
Benzo[*j*]fluoranthene	2.1 ± 0.4	2.1 ± 0.1	103 ± 3.6
Benzo[*k*]fluoranthene	2.3 ± 0.2	2.9 ± 0.2	126 ± 7.7
Benzo[*a*]pyrene	4.3 ± 0.1	5.3 ± 0.2	122 ± 5.1
Benzo[*e*]pyrene	3.3 ± 0.1	4.0 ± 0.1	122 ± 4.1
Perylene	1.2 ± 0.2	0.9 ± 0.1	80 ± 4.9
Indeno[1,2,3-*c,d*]pyrene	2.8 ± 0.1	3.3 ± 0.2	119 ± 4.9
Dibenz[*a,h*]anthracene	4.2 ± 0.1	5.1 ± 0.1	121 ± 1.8
Benzo[*g,h,i*]perylene	4.8 ± 0.1	3.5 ± 0.1	122 ± 2.7
MESS-3[b]			
Cd	0.24 ± 0.01	0.20 ± 0.01	83 ± 4.2
Cr	105 ± 4.0	87.0 ± 2.0	83 ± 1.9
Cu	33.9 ± 1.6	29.3 ± 2.9	86 ± 8.6
Li	73.6 ± 5.2	65.8 ± 0.7	89 ± 1.0
Ni	46.9 ± 2.2	45.3 ± 0.7	97 ± 1.5
Pb	21.1 ± 0.7	17.4 ± 0.3	82 ± 1.4
Zn	159 ± 8.0	128 ± 2.9	81 ± 1.8

[a] ng g^{-1} dry weight
[b] mg kg^{-1} dry weight

Table S3. Statistical relationships of seasonal differences among months. The bold text highlights statistically significant relationships ($p < 0.05$).

PTSs	Kruskal-Wallis test		Month (*Post hoc* Mann-Whitney)						
	F-value	P value	2 – 6	2 – 8	2 – 10	4 – 6	6 – 8	6 – 10	8 – 10
As	21.2	**0.001**				**0.025**	**0.002**	**0.001**	
Cd	13.0	**0.024**							
Cr	6.68	0.245							
Cu	3.49	0.626							
Hg	30.8	**<0.001**	**<0.001**	**0.019**		**0.001**		**0.002**	
Ni	4.27	0.511							
Pb	17.9	**0.003**			**0.036**				**0.015**
Zn	6.97	0.223							
PAHs	10.7	0.057							
APs	6.89	0.229							

Table S4. Mann-Whitney test for comparison of monthly inner- and outer-stations. Values in bold indicate that the correlation was significant at $p < 0.05$.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	PAHs	APs
February	0.710	0.250	1.000	0.250	1.000	0.571	**0.036**	0.143	0.393	0.393
April	**0.036**	0.250	**0.036**	**0.036**	0.143	**0.036**	**0.036**	**0.036**	0.114	0.071
June	**0.036**	0.393	**0.036**	**0.036**	**0.036**	**0.036**	**0.036**	**0.036**	**0.036**	**0.036**
August.	0.393	0.143	0.571	0.250	0.250	0.250	1.000	0.571	**0.036**	0.143
October	0.143	0.071	0.071	0.250	0.393	0.071	**0.036**	0.250	**0.036**	0.071
December	0.393	0.786	1.000	0.571	0.393	0.786	1.000	0.571	1.000	0.143

Table S5. Pearson correlation analysis between the persistent toxic substances and environmental parameters in bottom water and sediment. Values in bold indicate that the correlation was significant at $p < 0.05$.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	PAHs	APs
Temperature	-0.001	-0.094	0.218	-0.087	**0.461****	0.091	0.093	-0.080	0.071	-0.085
Salinity	**-0.290***	**-0.610****	**-0.327***	-0.240	-0.153	**-0.422****	**-0.372****	-0.263	**-0.565****	**-0.408****
pH	-0.010	-0.098	**-0.446****	0.206	**-0.437****	**-0.333***	**-0.420****	0.184	-0.275	-0.171
SS	0.087	0.263	**0.531****	0.061	-0.032	**0.558****	**0.656****	0.084	0.200	0.138
Mud content	**0.533****	**0.727****	**0.731****	0.071	**0.346***	**0.771****	**0.581****	0.100	**0.705****	**0.584****
Organic content	**0.491****	**0.674****	**0.826****	-0.007	**0.355***	**0.832****	**0.673****	0.028	**0.693****	**0.578****

* $p < 0.05$, ** $p < 0.01$.

Table S6. Results of the DistLM analysis used to explore the relationship between macrofauna and environmental variables. *P*-values were obtained using 999 permutations of residuals under the best model (forward selection based on the AIC test). Bold numbers indicate significant values; V: Variables; AIC: Akaike information criterion; P-F: Pseudo-F; Cum: Cumulation; BS: Best Solution.

Macrofauna				
V	AIC	P-F	*P*	Cum.
TN	370.1	10.5	**0.001**	0.19
Mud content	368.7	3.38	**0.001**	0.24
Chl-*a*	367.3	3.23	**0.001**	0.29
Salinity	366.8	2.26	**0.004**	0.33
Hg	366.7	1.89	**0.032**	0.36
APs	366.5	1.90	**0.022**	0.39
PO_4	366.5	1.71	0.056	0.41
SiO_2	366.3	1.83	**0.034**	0.44
B.S	AIC	R^2	V	
	366	0.44	7	

Table S7. IndVal analysis listing indicator taxa within specific environmental groups for macrofauna. Bold numbers indicate significant values. Environmental groups were defined by the results of the dbRDA routine (Fig. 5).

Group	Indicator taxa	IndVal	*P*
1	*Potamocorbula amurensis*	0.69	**0.001**
	Sinocorophium sinensis	0.53	**0.009**
2	*Urothoe brevicornis*	0.82	**0.001**
	Chaetozone setosa	0.74	**0.008**
	Spiochaetopterus costarum	0.69	**0.003**

Supplementary Figures

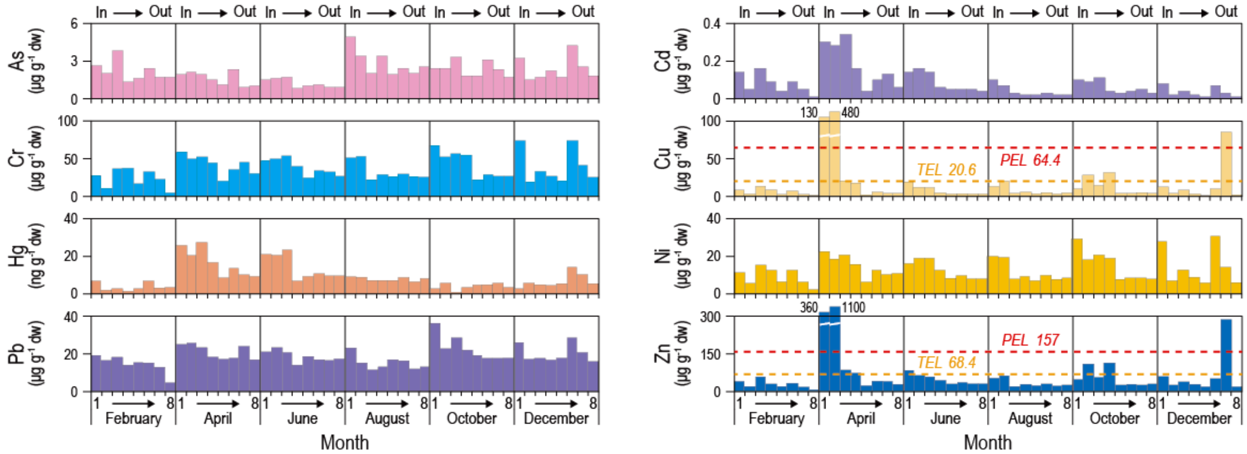

Fig. S1. Distribution of metals and a metalloid in sediment based on the distance from the inner part to the outsider part of the Geum River Estuary, Korea.

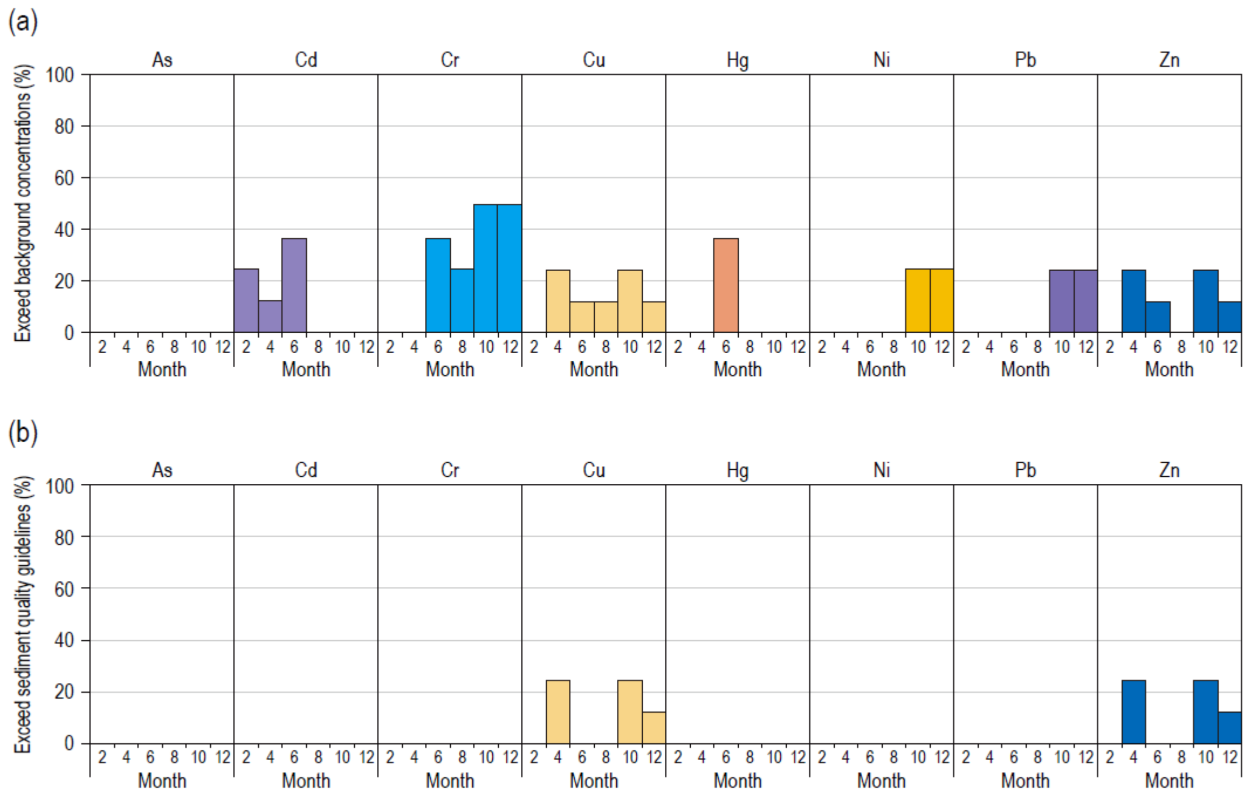

Fig. S2. Percentages of metals and metalloids in the sediments of the Geum River Estuary (a) exceeding background concentrations and (b) exceeding the sediment quality guidelines of Korea.

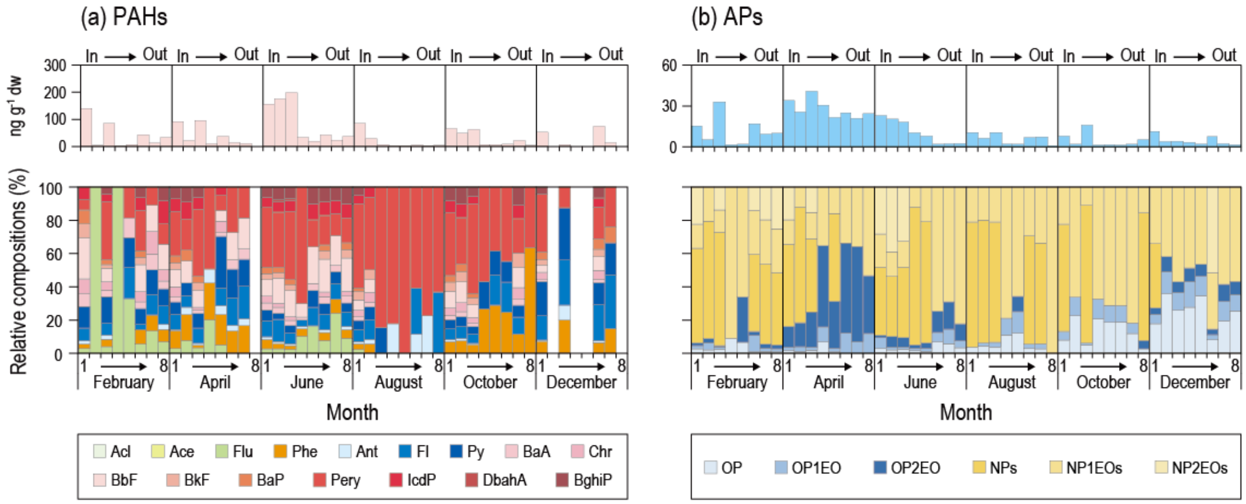

Fig. S3. Distribution and relative composition of (a) PAHs and (b) APs in the sediment based on the distance from the inner part to the outer part of the Geum River Estuary, Korea.