Environ Earth Sci (2016) 75:50
DOI 10.1007/s12665-015-4836-2

ORIGINAL ARTICLE

Evaluation of physico-chemical parameters in water and total heavy metals in sediments at Nakdong River Basin, Korea

S. Y. Chung[1] · **S. Venkatramanan**[1] · **N. Park**[2] · **T. Ramkumar**[3] · **S. B. Sujitha**[4] · **M. P. Jonathan**[4]

Received: 2 November 2014 / Accepted: 15 July 2015 / Published online: 21 December 2015

Abstract Fourteen water and sediment samples were collected from the Nakdong River Basin in Korea to evaluate the physico-chemical parameters (pH, dissolved oxygen, chemical oxygen demand, biological oxygen demand, total organic carbon) in water and total heavy metals (Cu, Zn, Pb, Cd, As) in surface sediments. The assessment of physico-chemical parameters indicates that river water and sediments in the study area were strongly impacted by industrial wastewater, irrigational effluents and domestic sewage. The overall average concentrations of metals in sediments were Cu (6.41 mg/kg), Cd (0.11 mg/kg), Pb (4.72 mg/kg), Zn (16.8 mg/kg), As (0.19 mg/kg), and the order of the concentrations was Zn > Cu > Pb > As > Cd. Geo-accumulation index (I_{geo}) indicates that most of samples fall at unpolluted to medium category, while contamination factor values fall at the medium to very high pollution zone. Pollution load index also suggests that all samples fall at progressive pollution sector. Multivariate statistical analysis and pollution index methods were helpful for the classification on the basis of the contamination sources and origin of heavy metals. In conclusion, this study clearly infers the fact that the cause of metal pollution in this region is mainly due to the effluents discharged from factories, agricultural fields and sewers.

Keywords Physico-chemical parameters · Pollution indices · Multivariate analysis · Heavy metals

Introduction

The worldwide water and sediment quality deterioration resulted primarily from growing human populations and economic development, particularly elevating nutrients leading to eutrophication and heavy metal pollution in the aquatic environment (Krishna et al. 2009; Nriagu and Pacyna 1988; Peierls et al. 1998; Holloway et al. 1998; Soylak and Yilmaz 2006; Li et al. 2008; Mendil et al. 2010; Venkatramanan et al. 2012, 2015). The natural sources of heavy metals consist of volcanism, bedrock erosion, atmospheric pollution, and the release from plants and anthropogenic activities. Particularly, mining and mineral processing have dominant influences on the biogeochemical cycles of heavy metals (Nriagu 1989, 1996; Hongyi et al. 2009). Heavy metal pollution leads to serious human diseases through the food chain and the loss of biodiversity, and it also degrades the environmental quality. In recent researches of heavy metals, the spatial variability reflects geological parent materials and anthropogenic sources in a geographically heterogeneous area (Imperato et al. 2003).

Industrialization and unplanned urbanization have also greatly changed the natural environment. In recent times,

---

✉ S. Venkatramanan
venkatramanansenapathi@gmail.com; venkat@pknu.ac.kr

S. Y. Chung
chungsy@pknu.ac.kr

[1] Department of Earth and Environmental Sciences, Institute of Environmental Geosciences, Pukyong National University, 599-1 Daeyeon-dong Nam-gu, Busan 608-737, Korea

[2] Department of Civil Engineering, Dong-A University, 840 Hadan-song Saha-gu, Busan 604-717, Korea

[3] Department of Earth Sciences, Annamalai University, Annamalai Nagar, Tamil Nadu 608 002, India

[4] Centro Interdisciplinario de Investigaciones y Estudios sobre Medio Ambiente y Desarrollo (CIIEMAD), Instituto Politécnico Nacional (IPN), Calle 30 de Junio de 1520, Barrio la Laguna Ticomán, Del. Gustavo A. Madero, C.P. 07340 Mexico, DF, Mexico

the environment has become aggressive, posing a threat to the health and welfare of the people due to the release of pollutants from industries, agricultural fields and urban waste. Their waste waters find their way into surface water bodies via rivers, canals and surface runoff. Thus, these water bodies receive pollutants, and surface sediments become contaminated. The impacts of the heavy metals in sediments were assessed in terms of contamination factor (CFs), geo-accumulation index (I_{geo}) and pollution load index (PLI), which is reported based on the chemical analysis of the bulk sediments. These pollution indices methods have been widely utilized in river and marine sediments (Muller 1969; Bryan and Langston 1992; Buccolieri et al. 2006).

Principal components analysis (PCA) and cluster analysis (CA) have been considered as the most trustworthy approaches for data mining of matrices from environmental quality assessment (Astel et al. 2007, 2008; Simeonova and Simeonov 2007). Thus, PCA and CA are widely used in sediment quality assessment of natural fresh water system. Recently, human population and economic activities have greatly increased in the study area, and sediment and water quality has been continuously threatened from various contamination sources.

Rapid industrialization, urbanization and population increases in the last few decades caused a dramatic increase in the demand for river water, and significant deterioration in water and sediment quality, especially near large industrial complexes and in the lower basin. These trends are expected to be continued, unless appropriate management strategies are carried out to ensure adequate water supplies and to restore water and sediment qualities to appropriate standards for the intended uses (Chun et al. 2001; Venkatramanan et al. 2014). This research evaluates the physico-chemical parameters of river water and the selected heavy metals in surface sediments of Nakdong River in Korea to identify the sources of contaminants, using comparative evaluations of pollution load index (PLI), geo-accumulation index (I_{geo}) and contamination factor (CFs). PCA and CA were also used for this purpose.

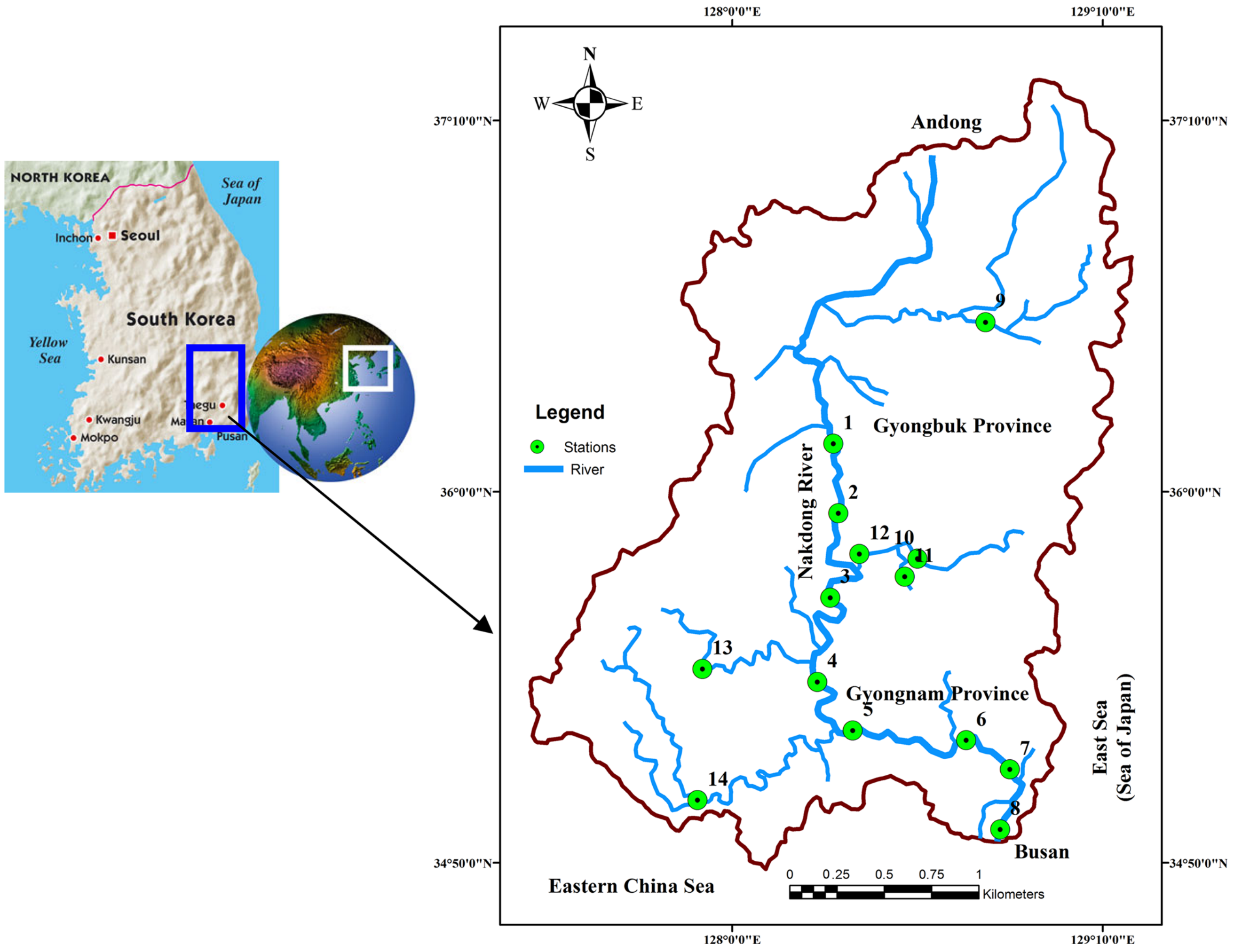

Fig. 1 Map showing Nakdong River Basin and sample stations

Materials and methods

Study area

Nakdong River is the longest river in Korea, which is 525 km in length with the total watershed area of 24,000 km^2 (Fig. 1). Nakdong River originates in the vicinity of Taebaek city in Kangwon Province, and two dams of Andong and Imha Dam were constructed at the upstream of Nakdong River. Those dams are the multipurpose types of water supply, electricity production and flood control for the surrounding area, and also serve the improvement of water quality in the downstream area. The river finally flows into Busan City, and discharges to East China Sea. A barrage was constructed at Nakdong River mouth in 1987 to prevent seawater intrusion and supply fresh water for domestic usage. Nakdong River forms a natural border in the study area, and it supplies a large amount of water to water supply facilities of the surrounding areas.

Heavy flooding was a frequent phenomenon in this river before the construction of 9 small dams. In monsoon season, organic matter/sediments were heavily deposited at the delta area in the downstream of the river. The delta has sedimentary deposits of 60–90 m thickness around the river banks and is composed of backfill, sandy clay, stiff clay, sand and gravel. Most of sediments were deposited from the late Pleistocene Epoch, i.e., the end of 4th glacial period (Oh 1994; Ryu et al. 2011). Basal gravel bed indicates an unconformity between delta sediments and granites of the Cretaceous Period. The thickness of sandy clay ranges from 5 to 10 m, stiff clay from 10 to 30 m, lower sand from 10 to 40 m, and gravel from 5 to 40 m, respectively. Sandy clay is relatively soft and loose, but lower clay is stiff and dense.

Environmental setting

The characteristics of the sampling stations are given in Table 1. The Nakdong River Basin occupies about 24 % of Korean land, and 18.4 % of the land in the basin is used for farming (Ministry of Construction and Transportation 1998). Rice cultivation covers nearly 62 % of the farm land, and dry fields are 38 % of farm land. Building areas and industrial complexes occupy about 1.8 % (430 Km^2) of the total basin area. A total of 149 industrial complexes including 7 multinationals, 51 regional and 91 rural industries inhabit the region. National and regional industrial complexes are located within or near the major urban centers, while rural industrial complexes are characterized by a wide spectrum of small scale industries scattered throughout the basin. The upper Nakdong Basin was developed for electronic industries, the middle basin for textile/dyeing industries and the lower basin for heavy industries and shoemaking. The use of fertilizer was rapidly increased by agricultural growth during the 1970s. However, it has decreased since 1991, because many regions were urbanized and industrialized. Airport and many residential houses are also located in the delta area of the lower Nakdong Basin (Chun et al. 2001).

Table 1 Characteristics of sampling stations at Nakdong river basin

Station no.	Characteristics of the study area
1	Located in the middle of the basin, inhabited by textile/dyeing industries and other small scale industries
2	Located in the middle portion of the study area, and agricultural activities are carried out in spite of the textile/dyeing industries
3	Moderately polluted region in the middle of the basin, busy with textile/dyeing industrial complexes
4	Situated in the lower basin, and it receives huge amounts of effluents derived from leather and heavy industries
5	Located in the lower basin of the river where the contaminant sources are from heavy and shoemaking industrial complexes
6	This station is situated in the lower basin of the study area, and it is surrounded with airports, residential areas and shoemaking industrial complex
7	This station located in the lower part of the basin includes industrial and residential land
8	This station is positioned near the mouth of the river, and it receives the effluents from the city region and the industrial complexes, which is highly polluted
9	Located in the upper basin of Nakdong river is occupied by electronic industries and agricultural activities
10	This station is located in the textile/dyeing and small-scale industrial zone
11	This station is located at the middle of the basin inhabited by human activities and presence of paint industries
12	Station experiences effluents from paint industries and residential areas
13	Located in the lower basin of the river is occupied by many industrial complexes
14	This station is located in the lower basin, which is surrounded by heavy and leather industries with large inputs of urban wastes

Sample collection

A total of 14 water samples were collected during July 2011 (summer season) using a 2-L Van Dorn plastic water sampler. Sample bottles were rinsed with the same sample water before sampling. Samples were preserved by acidifying to pH 2 with the addition of HNO_3 and kept at 4 °C until further analysis. pH and dissolved oxygen (DO) were checked in situ with a portable meter Horiba U-51, Japan. Biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) were measured by complying standard procedures (APHA 1995). Fourteen sediment samples were collected using a Van Veen grab sampler on board with a hired fishing trawler, and the top 5 cm of the sediments were collected from the grab with a plastic spatula. The sediment samples were mixed with $HNO_3 + HCl$ and were digested for 40 min. The final solution was analyzed by atomic absorption spectrometer (AAS, Unicam 989, USA). The accuracy of the analytical method was analyzed by the standard reference material MAG-1 (marine mud from the United States Geological Survey, USA) and National Research Council of Canada Marine sediment reference material BCSS-1. The average recoveries ± standard deviations for each metal were 73 ± 15, 71 ± 14, 79 ± 24, 64 ± 22 and 68 ± 16 (MAG-1) and 62 ± 18, 60 ± 24, 83 ± 16, 65 ± 23 and 58 ± 26 (BCSS-1) for Cu, Cd, Pb, Zn and As, respectively

Evaluation of pollution indices

The pollution indices formulas were developed for evaluating the sediment quality, and many calculation methods have been put forward to quantify the degree of metal enrichments. Various authors (Salomons and Forstner 1984; Muller 1969; Hokanson 1980) have proposed the pollution impact scales or ranges to convert the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity. Sediment quality guidelines provide values that allow quantification of sediment contamination, and that make an overall assessment of the metal contamination degree in river and marine sediments. Contamination factor (CFs), pollution load index (PLI) and geo-accumulation index (I_{geo}) are very useful for the assessment of metal contamination in sediments. PLI and I_{geo} were developed to evaluate the background values of upper continental crust (Wedepohl 1995), and the methods were used for all sampling stations for this study. CF was calculated for an uncontaminated site in the study area.

Geo-accumulation index (I_{geo}) which is a common approach for the estimation of metal enrichment proposed by Müller (1969) is calculated as follows:

$$I_{geo} = \log_2 C_n / 1.5 \times B_n \qquad (1)$$

where C_n is the concentration of a metal in an enriched sample, and B_n is the background value of a metal. The factor 1.5 is introduced to minimize the effect of possible variations in the background values, which may be attributed to lithological variations in the sediments (Müller 1969). Muller's classification suggests that if the value is less than 0, a sediment is unpolluted (Class 0). In case of 0–1, it is unpolluted to moderately polluted (Class 1); 1–2, moderately polluted (Class 2); 2–3 moderately to strongly polluted (Class 3); 3–4 strongly polluted (Class 4); 4–5 strongly to extremely polluted (Class 5) and >5 extremely polluted (Class 6). CF is expressed as

$$\mathrm{CFs} = M_x / M_b \qquad (2)$$

where M_x is the concentration of metal and M_b is the concentration of metal in the selected reference background value. If $\mathrm{CFs} > 1$ for a particular metal, a sediment is contaminated by a metal. If $\mathrm{CFs} < 1$, a sediment is uncontaminated by natural or anthropogenic inputs. The CFs is classified into four groups based on the calculated values (Pekey et al. 2004; Hokanson 1980; Savvides et al. 1995): $\mathrm{CFs} < 1$, low contamination; 1–3, moderate contamination; 3–6, considerable contamination; and >6, very high contamination.

PLI is the summation of several heavy metals and is defined as the nth root of the multiplication of

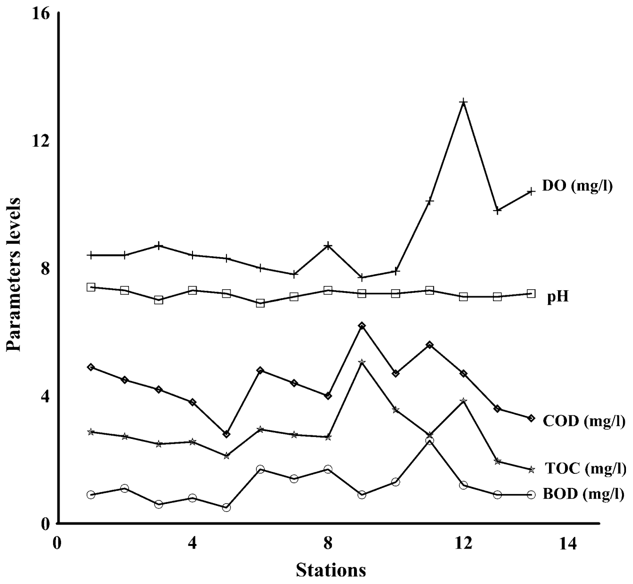

Fig. 2 Variations of primary water quality values according to sample stations in Nakdong River Basin

Table 2 Basic statistics of the primary parameters of water quality and metals of sediments

Parameters	Maximum	Minimum	Mean	Median	SD
pH	7.40	6.90	7.19	7.20	0.14
DO (mg/l)	13.20	7.70	8.99	8.40	1.48
BOD (mg/l)	2.60	0.50	1.18	1.00	0.55
COD (mg/l)	6.20	2.80	4.39	4.45	0.89
TOC (mg/l)	5.04	1.69	2.86	2.75	0.84
Cu (mg/kg)	54.22	0.39	6.41	2.21	13.97
Cd (mg/kg)	0.28	0.03	0.11	0.07	0.08
Pb (mg/kg)	18.91	0.65	4.72	3.73	4.52
Zn (mg/kg)	76.59	1.97	16.77	11.28	19.44
As (mg/kg)	0.45	0.02	0.19	0.20	0.13

concentration factors (CF_{HMk}) (Tomlinson et al. 1980) and is calculated like

$$PLI = n\sqrt{\sum_{k=1}^{n} CF_{HMk}} \tag{3}$$

where CF_{HMk} is the ratio between the concentration of each heavy metal (CHM) and a background value (Taylor and McLennan 1995). When $PLI > 1$, it means that pollution exists. If $PLI < 1$, there is no metal pollution. PLI gives an assessment of overall toxicity status for a sediment (Lu

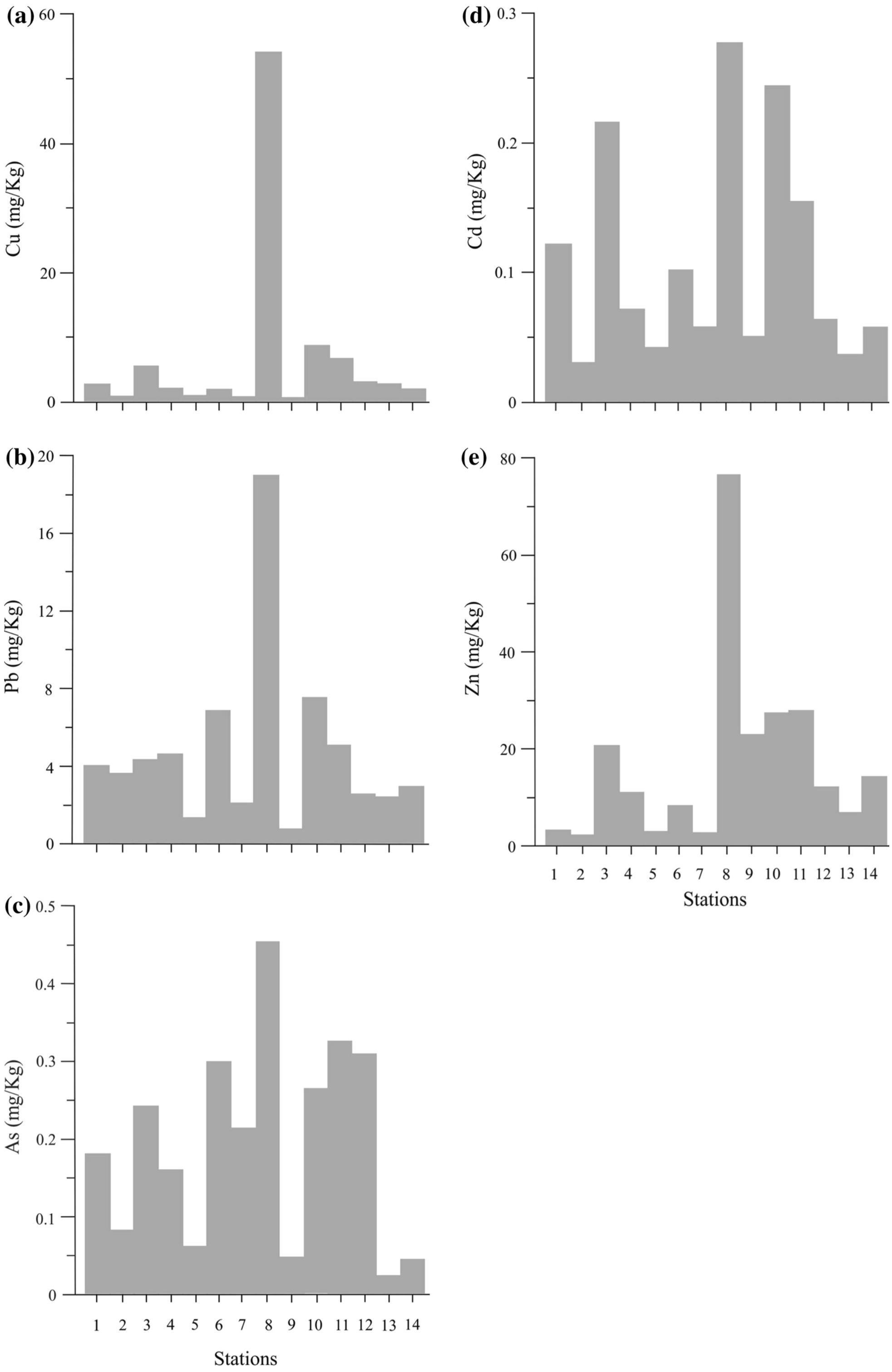

Fig. 3 Variations of heavy metal concentrations in surface sediments according to sample stations in Nakdong River Basin

et al. 2009). In the present study, PLI is a result of the contribution from five heavy metals of Cu, Cd, Pb, Zn and As.

Statistical techniques

The experimental data were subjected to statistical analyses using STATISTICA (Ver. 7) software. PCA was performed with a view to assess compositional differences among physical parameters in water and the variations of heavy metal concentrations in sediment sources. Factor analysis was performed by a varimax orthogonal rotation, which minimized the number of variables with a high loading on each component, and it facilitates the interpretation of PCA results (Howitt and Cramer 2005). Likewise, Pearson's correlation matrix was also used to identify the relationship between different elements.

Cluster analysis was applied to identify groups of samples with similar heavy metal behavior (Panda et al. 2006). It was formulated according to the Ward-algorithmic method, and the rescaled linkage distance was employed for measuring the distance between clusters of similar heavy metal contents. Cluster analysis was used to determine the association of different sediment and water samples.

Results and discussion

Physico-chemical parameters in river water

The distribution of water parameters is shown in Fig. 2, and basic statistical analysis are given in Table 2. Levels of pH, DO, BOD, COD and TOC varies from 6.9 to 7.4, 7.7 to 13.2 mg/l, 0.5 to 2.6 mg/l, 2.8 to 6.2 mg/l and 1.69 to 5.04 mg/l, respectively. pH values exhibit slight alkalinity in the water samples, which is due to the variable inputs from industrial effluents (Santhiya et al. 2011). BOD, COD and TOC were slightly higher than irrigation water quality. DO plays a vital role in supporting aquatic life in surface waters, which is susceptible even to slight environmental changes (Iticescu et al. 2013). DO in water shows lower values as they are consumed for the oxidation of organic matters. Contributions of BOD (0.5–2.6 mg/l), COD (2.8–6.2 mg/l) and TOC (1.69–5.04 mg/l) were derived from agricultural activities, domestic and industrial effluents (Chun et al. 2001).

Heavy metals in sediments

The general grain size characteristics of the sediments from Nakdong Basin exhibit 70–80 % of sand and gravel, and 20–30 % of silt and clay in the upper basin, while the middle and lower part of the basin consists of 30–40 % of sand and gravel, and 60–70 % of silt and clay. Concentrations of Cu, Cd, Pb, Zn and As (all values in mg/kg) in sediments ranged from 0.39 to 54.2, 0.03 to 0.28, 0.65 to 18.9, 1.97 to 76.6 and 0.02 to 0.45, respectively. The order of heavy metal levels with reference to the average values in surface sediment is as follows: Zn > Cu > Pb > As > Cd (Fig. 3). The higher values of Zn (76.6 mg/kg) and Pb (18.9 mg/kg) in river sediments are due to the impacts from textile and heavy industries (e.g., Adamo et al. 2006). Cu, Cd and As present a slightly higher concentration only in sediments of station 8. This is evident due to the presence of a number of heavy and chemical industries in the region as the runoff is lixiviated, precipitated and brought through various unregulated minor channels that drain into the aquatic region (Tuzen et al. 2004; Anithamary et al. 2012, 2013; Jonathan et al. 2013).

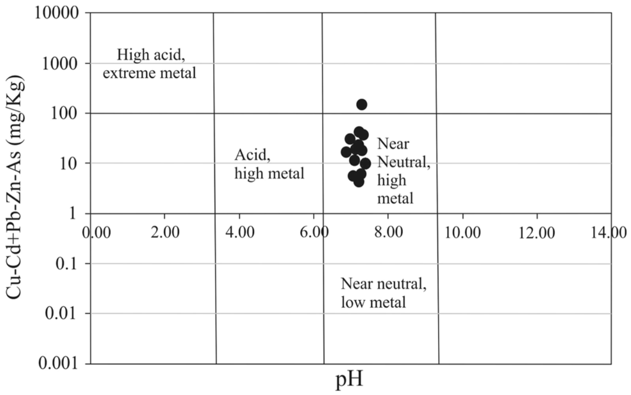

Fig. 4 Classification of samples based on total heavy metals vs. pH

The classification of total heavy metal contents (mg/kg) of Cu + Cd + Zn + Pb + As and pH indicates the near-neutral field of high heavy metal sector (Fig. 4). The above inference reveals that metals are anthropogenic in nature mainly due to the presence of industrial and agricultural fields (Ficklin et al. 1992; Caboi et al. 1999; Jonathan et al. 2013).

Evaluation of pollution indices

Geo-accumulation index of heavy metals was used for the better understanding of the pollution indices (Fig. 5). I_{geo} values ranged from −33.8 to 0.19, and it suggests that the heavy metals are from natural weathering processes (e.g., Zhang and Liu 2002). This method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index.

CF values ranged from 1.41 to 44.32 and it is classified into four categories (e.g., Pekey et al. 2004; Hokanson 1980; Savvides et al. 1995): low (CFs < 1), medium (1–3), considerable (3–6) and high (CFs > 6). Most of samples in

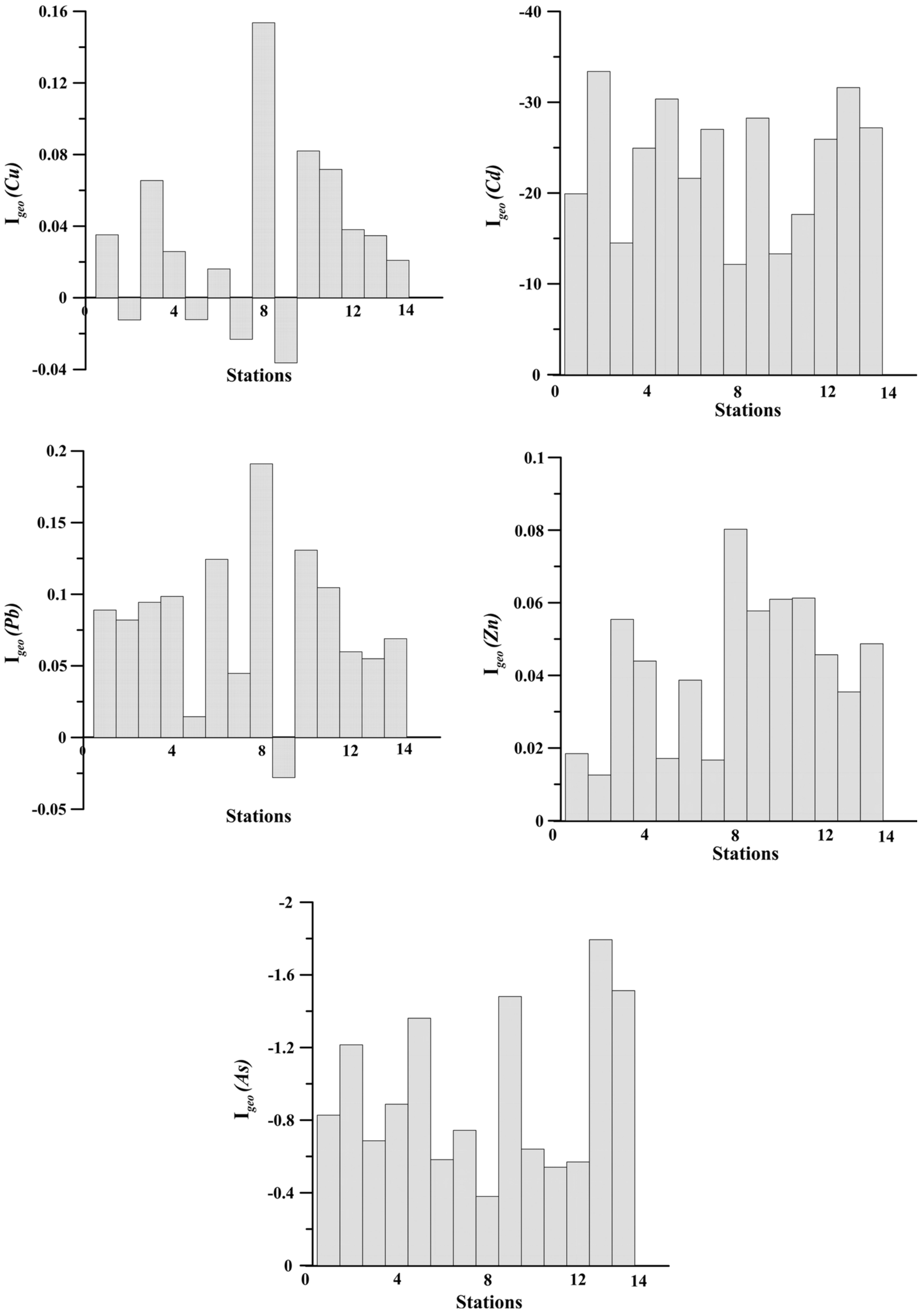

Fig. 5 Geo-accumulation index values of heavy metals in the study area

the study area are moderately polluted, while few samples fall at very high polluted category (Fig. 6a).

PLI was used to determine the synthetic pollution effect at different stations by the metals. In case PLI = 1, heavy metal loads are close to background, and samples are considered as nontoxic. PLI > 1 represents a progressive pollution (Tomlinson et al. 1980). PLI values of all samples in the present study ranged from 1.36 to 2.73 and exhibit a progressive pollution (Fig. 6b).

All samples belong to medium to very high pollution in CFs. CFs and PLI values show almost quite similar trends at various sampling points, but I_{geo} represents a different variation from CFs and PLI. In this study, most of the samples fall in medium to high pollution category, which is

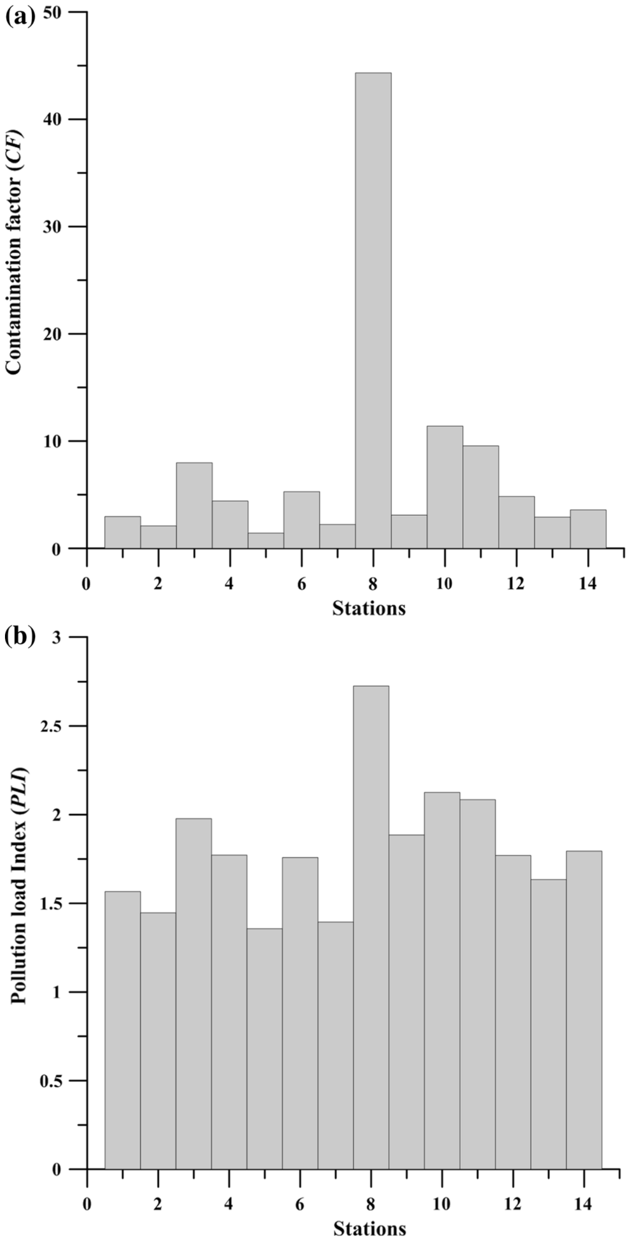

Fig. 6 Variations of heavy metal pollution indices: **a** CF; **b** PLI

attributed to the local point sources associated with industrial and agricultural fields.

Identification of pollution sources

Correlation matrix

The Pearson's correlation coefficient matrices for the analyzed parameters are presented in Table 3. Correlation coefficients less than 0.5 are not included in the table, because they are not at significant levels. The inter-relationship of different parameters is useful in revealing some association of heavy metals with the physico-chemical conditions in the river water. Association of BOD shows significant correlations with As ($r^2 = 0.66$) indicating that it could be directly related to the absorbing capacity of organisms in the study area (Yang et al. 2009). Likewise, COD exhibits good correlation with TOC ($r^2 = 0.81$), suggesting that considerable amount of organic matter is brought by tributaries and industries (Venkatramanan et al. 2014). The association of heavy metals indicates that Cu correlates significantly with Cd ($r^2 = 0.70$), Pb ($r^2 = 0.94$), Zn ($r^2 = 0.93$) and As ($r^2 = 0.65$), suggesting that they have various assimilated contaminants from industrial wastewater, agricultural effluents and municipal sewage (Yalcin et al. 2008; Tariq et al. 2010). The significant correlations among Cu, Zn, and Pb indicate that they may have originated from common sources, preferably from anthropogenic activities. Moreover, it is also due to the textile/dyeing and paint industries, or pesticides (Fukushima et al. 1992).

Principal component analysis (PCA)

PCA varimax orthogonal rotation (Gotelli and Ellison 2004) was used to maximize the sum of the variance of the factor coefficients which explained the possible groups/sources in the Nakdong River Basin. Four factors were extracted from the chemical data set based on eigenvalues. The calculated factor loadings, together with percentages of variance, and cumulative percentage of variance by each factors, are listed in Table 4.

PC1, PC2, PC3, and PC4 show 40, 22, 20, and 15 % of total variance, respectively. PC1 is heavily loaded on Cd and Pb, which are mostly distributed in sample stations of 6, 9, 10, 11 and 12. PC1 components are derived from mixed sources of industrial wastewater, agricultural effluents and municipal sewage. PC2 is loaded on Cu and Zn, which may be derived from the pesticides and industries (e.g., Jonathan et al. 2004; Jayaprakash et al. 2007). These parameters are importantly distributed in sample stations from 11 to 14. PC3 contributed by pH and As represents direct anthropogenic source from the industries and agriculture, which are significantly distributed in sample stations of 1, 2, 4, 8 and 11. PC4 is loaded on DO only, which occurs as an important parameter in sample station 1, 9 and 12, which directly reflects the influence of irrigation runoff. When sampling sites were plotted on the plane of the first two principal components (PCA 1 vs. PCA 2) of the Q-mode PCA, PCA 1 separated 3, 4, 5, 13 and 14 from the other stations (Fig. 7a), indicating that heavy metals are derived from external sources such as agricultural and industrial region of the basin.

Table 3 Correlation matrices for primary water quality parameters and heavy metals

	pH	DO	BOD	COD	TOC	Cu	Cd	Pb	Zn	As
pH	1.00									
DO	–	1.00								
BOD	–	–	1.00							
COD	–	–	–	1.00						
TOC	–	–	–	0.81	1.00					
Cu	–	–	–	–	–	1.00				
Cd	–	–	–	–	–	0.70	1.00			
Pb	–	–	–	–	–	0.94	0.78	1.00		
Zn	–	–	–	–	–	0.93	0.77	0.87	1.00	
As	–	–	0.66	–	–	0.65	0.75	0.75	0.65	1.00

$p < 0.05$

Table 4 Q and R modes principal component analysis of primary water quality parameters and heavy metals

Parameters	PC1	PC2	PC3	PC4
R-mode				
pH	0.09	−0.28	**0.91**	0.28
DO	−0.06	**0.87**	0.04	**0.50**
BOD	**0.57**	**0.50**	0.33	**−0.56**
COD	**0.97**	−0.04	−0.04	0.02
TOC	**0.85**	−0.20	−0.27	0.35
Cu	0.04	**0.70**	0.34	−0.20
Cd	**0.58**	0.05	0.15	−0.30
Pb	**0.62**	0.07	0.31	−0.37
Zn	0.24	**0.56**	0.28	−0.16
As	0.38	0.38	**0.58**	−0.34
Eigenvalues	2.01	1.12	1.32	1.06
Cumulative %	40.12	62.47	76.83	87.94
Q-mode				
1	0.31	−1.00	**1.23**	**0.64**
2	0.01	−0.59	**0.74**	0.08
3	−0.92	−0.21	−1.47	−0.06
4	−0.88	−0.78	**0.65**	0.33
5	−2.23	−0.77	−0.02	0.17
6	**0.66**	0.42	−1.68	−1.62
7	0.11	−0.28	−0.45	−0.96
8	0.03	0.12	**1.14**	−0.53
9	**2.79**	−1.53	−0.87	**0.98**
10	**0.87**	−0.69	−0.09	−0.17
11	**1.93**	**1.59**	**1.62**	−0.98
12	**0.78**	**2.30**	−0.76	**1.85**
13	−1.53	**0.61**	−0.40	−0.03
14	−1.92	**0.82**	0.38	0.30

* Significant values are in boldtype face

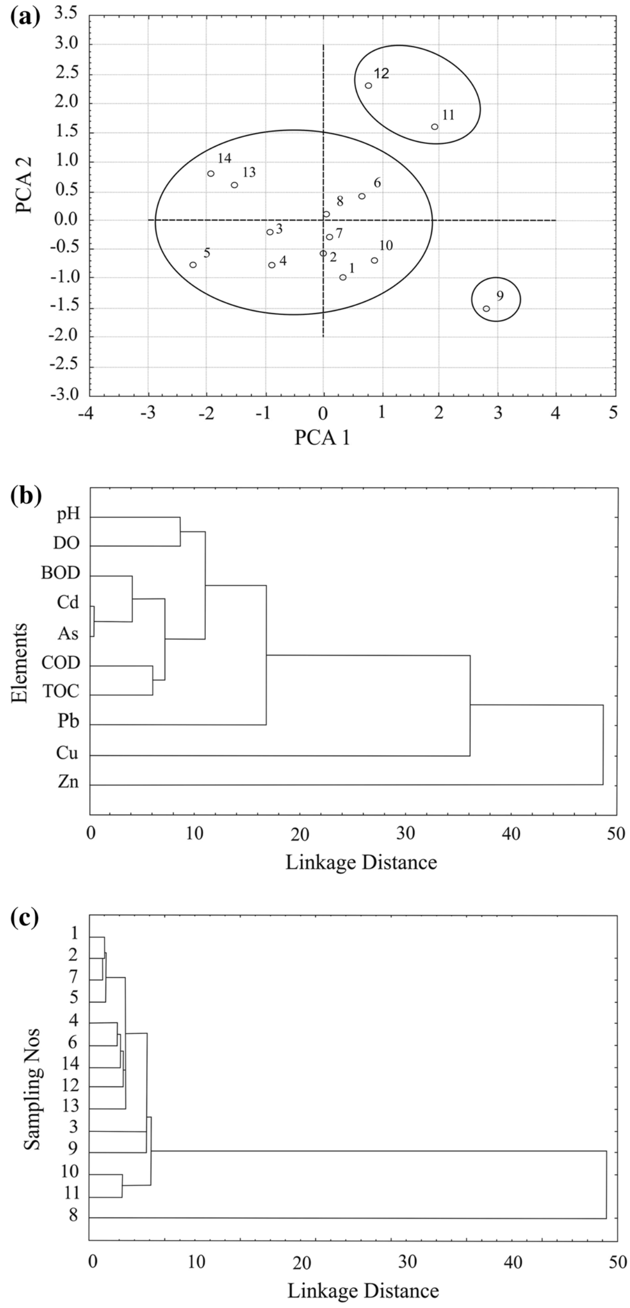

Fig. 7 Multivariate statistical analysis of water and sediment samples: **a** PCA; **b** dendrogram of R-mode; **c** dendrogram of Q-mode

Cluster analysis (CA)

Cluster analysis was also performed to understand the chemical components and heavy metals groupings in the data set (Fig. 7b, c). Parameters in the same cluster are likely to originate from a common source. The R-mode CA performed on the samples produced four clusters. Cluster 1 includes pH and DO; cluster 2 consists of BOD, Cd and As; cluster 3 contains COD and TOC; cluster 4 includes Pb, Cu and Zn. Cluster 1 is related with PC3 and PC4 of R-mode PCA, and Cluster 2 and 3 are related with PC 1 of R-mode PCA. Cluster 4 is related with PC1 and PC2 of R-mode PCA, reflecting the influence of anthropogenic sources and minor natural input.

In case of Q-mode analysis, the 14 sampling stations in Nakdong River Basin are classified into four major clusters. Cluster 1 consists of four sampling points (1, 2, 5 and 7). These sites receive inputs from industries (1, 2) and agricultural contaminants via irrigation (5, 7). Cluster 2 consists of five sampling points (4, 6, 12–14), whereas cluster 3 consists of four stations (3, 9, 10, 11). This indicates the accumulation of metal loads from industrial effluents, metal-laden agricultural runoff and domestic sewage. Cluster 4 consists of only one station (8) because this station lies in mouth of the river, where the contaminants accumulate through flocculation and coagulation process (Venkatramanan et al. 2014).

Comparison of heavy metals with world regions

Heavy metal concentrations of present study were compared with other regions around the world, indicating higher values for Cu (54.2 mg/kg) than other regions expect Pearl River, China. In the case of Cd (0.28 mg/kg), it is on the lower side than the other regions. Pb (18.9 mg/kg) and Zn (76.6 mg/kg) values in this study were lower than other regions expect Uppanar River and Thirumalairajan River, India. According to ecotoxicological values, Cu concentration exhibits LEL and ERL and the rest of metals are below the toxic condition (Table 5).

Conclusion

Heavy metal pollution indices and multivariate statistical analysis were used to assess the intensity and sources of pollution in the Nakdong River Basin. The sediment quality of the River Basin at Busan City (St.no 8) had the highest concentration of metals. The order of primary water quality parameters and heavy metal levels in descending order is as follows: DO > COD > TOC > BOD (water) and Zn > Cu > Pb > As > Cd (sediment), respectively. The pH values and metals concentrations of this river basin exhibited near-neutral high metal sector. Heavy metal pollution indices seemed to be promising and beneficial in assessing the enrichment/contamination status of sediments in terms of heavy metals. CFs suggested that all samples fell in medium to very high polluted zone. Otherwise, PLI showed that all samples belonged to progressive pollution. I_{geo} revealed that all samples fell in the unpolluted to moderately polluted sector. Multivariate statistical analysis indicated that anthropogenic impact was responsible for

Table 5 Comparison of heavy metal concentrations in surface sediments of Nakdong River with those of other rivers in the world

Study areas	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	As (mg/kg)	References
Nakdong River, South Korea (avg.)	6.41	0.11	4.72	16.77	0.19	Present study
Nakdong River, South Korea (range)	0.39–54.2	0.03–0.28	0.65–18.9	1.97–76.6	0.02–0.45	Present study
Uppanar River, India	6.52	0.41	6.60	6.93	–	Ayyamperumal et al. (2006)
Tirumalairajan River, India	2.9	–	1.02	9.5	–	Venkatramanan et al. (2012)
Seine River, Paris	33	0.6	41	153	9.4	Le Cloarec et al. (2009)
Elbe River, German	38	–	139	391	–	Pache et al. (2008)
Pearl River, China	348	1.72	102	383	–	NIU Hongyi et al. (2009)
Upper continental crust	25	0.102	14.8	52	2	Wedepohl (1995)
Ecotoxicological values						
Lowest effect level (LEL)	16	–	31	120	–	USEPA (2001)
Severe effect level (SEL)	110	–	250	820	–	USEPA (2001)
Effects range low (ERL)	34	1.2	46.7	150	–	Long et al. (1995)
Effects range medium (ERM)	270	9.6	218	410	–	Long et al. (1995)

controlling the variability of primary water quality parameters and total heavy metal contents in this study region. Sediment quality analysis clearly states that the heavy metals are released from industrial wastewater, irrigation effluents and domestic sewage. The contamination of surface sediments by heavy metal pollutants could generate serious threats to human health and ecological habitat in this river basin. In conclusion, this research represents that the combination of pollution index methods and multivariate statistical analysis is an important tool to identify contamination sources and origins.

Acknowledgments This research was supported by a grant (code 15AWMP-B066761-03) from AWMP Program funded by Ministry of Land, Infrastructure and Transport of Korean government. The chemical data of the Nakdong River water and sediment were supplied by the Busan Metropolitan City. The authors express a sincere gratitude to the Busan Metropolitan City.

References

Adamo P, Zampella M, Gianfreda L, Renella G, Rutigliano FA, Terribile F (2006) Impact of river overflowing on trace element contamination of volcanic soils in south Italy: part I. Trace element speciation in relation to soil properties. Environ Pollut 144:308–316

American Public Health Association (APHA) (1995) Standard methods for the examination of water and waste water, 19th edn. Public Health Association, Washington

Anithamary I, Ramkumar T, Venkatramanan S (2012) Distribution and accumulation of metals in the surface sediments of Coleroon River estuary, east coast of India. Bull Environ Contam Toxicol 88:413–417

Anithamary I, Ramkumar T, Venkatramanan S, Vasudevan S (2013) Assessment of heavy metal concentrations in surface sediments of Coleroon estuary of Tamilnadu, east coast of India. Carpathian J Earth Environ Sci 8:39–46

Astel A, Tsakovski S, Barbieri P, Simeonov V (2007) Comparison of self-organizing maps classification approach with cluster and principal components analysis for large environmental data sets. Water Res 41:4566–4578

Astel A, Tsakovski S, Simeonov V, Reisenhofer E, Piselli S, Barbieri P (2008) Multivariate classification and modeling in surface water pollution estimation. Anal Bioanal Chem 390:1283–1292

Ayyamperumal T, Jonathan MP, Srinivasalu S, Armstrong-Altrin JS, Ram-Mohan V (2006) Assessment of acid leachable trace metals in sediment cores from River Uppanar, Cuddalore, South east coast of India. Environ Pollut 143:34–45

Bryan GW, Langston WJ (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ Pollut 76:89–131

Buccolieri A, Buccolieri G, Cardellicchio N, Atti AD, Leo AD, Maci A (2006) United States Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). Mar Chem 99:227–235

Caboi R, Cidu R, Fanfani L, Lattanzi P, Zuddas P (1999) Environmental mineralogy and geochemistry of the abandoned Pb–Zn Montevecchio-Ingurtosu mining district, Sardinia, Italy. Chron Rech Min 534:21–28

Chun KC, Chang RW, Williams GP, Chang YS, Tomasko D, LaGory K, Ditmars J, Chun HD, Lee BK (2001) Water quality issues in the Nakdong River Basin in the Republic of Korea. Environ Eng Policy 2:131–143

Ficklin DJ, Plumee GJ, Smith KS, McHugh JB (1992) Geo-chemical classification of mine drainages and natural drainages in mineralized areas. In: Kharaka YK, Maest AS (eds) Water–rock interaction, vol 7. Balkema, Rotterdam, pp 381–384

Fukushima K, Saino T, Kodama Y (1992) Trace metal contamination in Tokyo Bay. Jpn Sci Total Environ 125:373–389

Gotelli NJ, Ellison AM (2004) A primer of ecological statistics, 1st edn. Sinauer Associates, Sunderland, p 492

Hokanson L (1980) Ecological risk index for aquatic pollution control, a sedimentological approach. Water Res 14:975–1001

Holloway JM, Dahlgren RA, Hansen B, Casey WH (1998) Contribution of bedrock nitrogen to high nitrate concentrations in stream water. Nature 395:785–788

Hongyi NIU, Wenjing D, Qunhe WU, Xingeng C (2009) Potential toxic risk of heavy metals from sediment of the Pearl River in South China. J Environ Sci 21:1053–1058

Howitt D, Cramer D (2005) Introduction to SPSS in psychology: with supplement for releases 10, 11, 12 and 13. Pearson, Harlow

Imperato M, Adamo P, Naimo D, Arienzo M, Stanzione D, Violante P (2003) Spatial distribution of heavy metals in urban soils of Naples city (Italy). Environ Pollut 124:247–256

Iticescu C, Georgescu LP, Topa CM (2013) Assessing the Danube water quality index in the city of Galati, Romania. Carpathian J Earth Environ Sci 8:155–164

Jayaprakash M, Jonathan MP, Srinivasalu S, Muthuraj S, Ram-Mohan V, Rajeshwara-Rao N (2007) Acid-leachable trace metals in sediments from an industrialized region (Ennore Creek) of Chennai city, SE coast of India: an approach towards regular monitoring. Estuar Coast Shelf Sci 76:692–703

Jonathan MP, Ram Mohan V, Srinivasalu S (2004) Geochemical variations of major and trace elements in recent sediments, off the Gulf of Mannar, the southeast coast of India. Environ Geol 45:466–480

Jonathan MP, Roy PD, Rodriguez-Espinosa PF, Sarkar SK, Munoz-Sevilla NP, Navarrete-Lopaz M, Srinivasalu S, Thangadurai N (2013) Evaluation of trace elements concentration (acid leachable) in sediments from River Panuco and its adjacent lagoon areas, NE Mexico. Environ Earth Sci 68:2239–2252

Krishna AK, Satyanarayanan M, Govil PK (2009) Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India. J Hazard Mater 167:366–373

Le Cloarec MF, Bonte PH, Lestel L, Lefevre L, Ayrault S (2009) Sedimentary record of metal contamination in the Seine River during the last century. Phys Chem Earth 36:515–529

Li S, Xu Z, Cheng X, Zhang Q (2008) Dissolved trace elements and heavy metals in the Danjiangkou Reservoir, China. Environ Geol 55:977–983

Long ER, MacDonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manage 19:81–97

Lu S, Wang H, Bai S (2009) Heavy metal contents and magnetic susceptibility of soils along an urban-rural gradient in rapidly growing city of eastern China. Environ Monit Assess 58:91–101

Mendil D, Unal TF, Tuzen M, Soylak M (2010) Determination of trace metals in different fish species and sediments from the River Yeşilirmak in Tokat, Turkey. Food Chem Toxicol 48:1383–1392

Ministry of Construction and Transportation (1998) An investigation on the status of Nakdong River water utilization. Ministry of Construction and Transportation, Kwachon, Republic of Korea. p 18

Muller G (1969) Index of geo-accumulation in the sediments of the Rhine River. Geo-journal 2:108–118

Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. Nature 338:47–49

Nriagu JO (1996) A history of global metal pollution. Science 272:223–224

Nriagu JO, Pacyna JM (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace-metals. Nature 333:134–139

Oh GH (1994) The paleoenvironment of the northern part of the Nakdong River delta. Korean J Quat Res 8:33–42

Pache T, Brockamp O, Clauer N (2008) Varied pathways of river-borne clay minerals in a near-shore marine region: a case study of sediments from the Elbe- and Weser rivers, and the SE North Sea. Estuar Coast Shelf Sci 78:563–575

Panda UC, Sundaray SK, Rath P, Nayak BB, Bhatta D (2006) Application of factor and cluster analysis for characterization of river and estuarine water systems—a case study: Mahanadi River (India). J Hydrol 331:434–445

Peierls BL, Caraco NF, Pace ML, Cole JJ (1998) Human influence on river nitrogen. Nature 350:386–387

Pekey H, Karakas D, Ayberk S, Tolun L, Bakoglu M (2004) Ecological risk assessment using trace elements from surface sediments of Izmit Bay (Northeastern Marmara Sea) Turkey. Mar Pollut Bull 48:946–953

Ryu CK, Kang S, Chung SG, Jeon YM (2011) Late Quaternary depositional environmental change in the northern marginal area of the Nakdong River delta, Korea. J Geol Soc Korea 47:213–233

Salomons W, Forstner U (1984) Metals in hydro-cycle. Springer, Berlin, pp 63–98

Santhiya G, Lakshumanan C, Jonathan MP, Roy PD, Navarrete-Lopaz M, Srnivasalu S, Uma-Maheswari B, Krishnakumar P (2011) Metal enrichment in beach sediments from Chennai Metropolis, SE coast of India. Mar Pollut Bull 62:2537–2542

Savvides C, Papadopoulos A, Haralambous KJ, Loizidou M (1995) Sea sediments contaminated with heavy metals: metal speciation and removal. Water Sci Technol 32:65–73

Simeonova P, Simeonov V (2007) Chemometrics to evaluate the quality of water sources for human consumption. Microchim Acta 156:315–320

Soylak M, Yilmaz S (2006) Heavy metal levels in sediment samples from Lake Palas, Kayseri-Turkey. Fresenius Environ Bull 15:340–344

Tariq SR, Shaheen N, Khalique A, Sha MH (2010) Distribution, correlation, and source apportionment of selected metals in tannery effluents, related soils, and groundwater—a case studies from Multan, Pakistan. Environ Monit Assess 166:303–312

Taylor SR, McLennan SM (1995) The geochemical evolution of the continental crust. Rev Geophys 58:241–265

Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index. Helgol Meeresunters 63:566–575

Tuzen M, Sari H, Soylak M (2004) Microwave and wet digestion procedures for atomic absorption spectrometric determination of trace metals contents of sediment samples. Anal Lett 37:1925–1936

United States Environmental Protection Agency (USEPA) (2001) The role of screening-level risk assessments and refining contaminants of concern in Baseline ecological risk assessments, Publication 9345 0–14, EPA 540/F-01/14, June 2001

Venkatramanan S, Ramkumar T, Anithamary I, Vasudevan S (2012) Heavy metal distribution in surface sediments of the Tirumalairajan river estuary and the surrounding coastal area, east coast of India. Arab J Geosci 7:123–130

Venkatramanan S, Chung SY, Lee SY, Park N (2014) Assessment of river water quality via environmentric multivariate statistical tools and water quality index: a case study of Nakdong River Basin, Korea. Carpathian J Earth Environ Sci 9:125–132

Venkatramanan S, Chung SY, Ramkumar T, Gnanachandrasamy G, Kim TH (2015) Evaluation of geochemical behavior and heavy metal distribution of sediments: the case study of the Tirumalairajan river estuary, southeast coast of India. Int J Sedim Res 30:28–38

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232

Yalcin MG, Narin I, Solylak M (2008) Multivariate analysis of heavy metal contents of sediments from Gumusler creek, Nigde, Turkey. Environ Geol 54:1155–1163

Yang Z, Wang Y, Shen Z, Niu J, Tang Z (2009) Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. J Hazard Mater 166:1186–1194

Zhang J, Liu CL (2002) Riverine composition and estuarine chemistry of particulate metals in China – weathering features, anthropogenic impact and chemical fluxes. Estuar Coast Shelf Sci 54:1051–1070