

Assessment and Distribution of Metals Contamination in Groundwater: a Case Study of Busan City, Korea

S. Venkatramanan · S. Y. Chung · T. H. Kim ·
M. V. Prasanna · S. Y. Hamm

Received: 19 April 2014 / Revised: 8 August 2014 / Accepted: 8 August 2014 / Published online: 29 August 2014
© Springer Science+Business Media Dordrecht 2014

Abstract The present research was carried out to assess the pH, electrical conductivity (EC), dissolved oxygen (DO), and metal concentrations of groundwater in Busan City, Korea. Forty groundwater samples were collected at the environs of major residential and recreational area. The physicochemical parameters (pH, EC, and DO) and metals (Fe, Mn, Cu, Cd and Zn) were analyzed. The metals in groundwater were listed in the descending order of concentration like $Zn > Mn > Cu > Fe > Cd$. Groundwater pollution indices (heavy metal evaluation index, heavy metal pollution index and degree of contamination) revealed that most of groundwater samples belonged to the low to medium zones. GIS-based spatial maps suggested that the activities of seawater intrusion and salinized river water are pervasive process in this area. Correlation and cluster analyses were used to assess the intensity and source of pollution in groundwater. It was suggested that groundwater quality was polluted mainly

by seawater intrusion, infiltration of salinized river water, sewage leaked from sewer, and groundwater discharge from the subway. The pollution status of groundwater systems in this case study are of great environmental and health concerns.

Keywords Heavy metals · Groundwater pollution indices · Correlation and cluster analyses · Environmental and health concerns

Introduction

The groundwater quality deterioration gives an adverse effect to growing human populations and economic development, particularly elevating nutrients leading to eutrophication and metal pollution in the aquatic environment (Nriagu and Pacyna 1988; Peierls et al. 1998; Holloway et al. 1998; Li et al. 2008; Pekey et al. 2004). The natural sources of the metals include volcanism, bedrock erosion (Krishna et al. 2009; Pekey et al. 2004) and anthropogenic activities; particularly, mining and mineral processing have dominant influences on the biogeochemical cycles of trace metals (Krishna et al. 2009; Nriagu and Pacyna 1988; Nriagu 1989, 1996). Metal pollution leads to serious human health hazards through the food chain and the loss of biodiversity, and harms the environmental quality. Recent researches of trace elements and metals show highly interesting records (Zhang et al. 2009). Of which, their spatial variability reflects geological parent materials and anthropogenic sources in geographic heterogeneity (Imperato et al. 2003; Prasanna et al. 2012).

The methods of integrating numerous variables associated with water quality in a specific index are increasingly desired in national and international scenarios. Therefore, several researchers have developed various indices, technically referred to as water quality indices (WQIs) (Lermontov

S. Venkatramanan · S. Y. Chung (✉)
Department of Earth & Environmental Sciences,
Institute of Environmental Geosciences,
Pukyong National University, Busan 608-737, Korea
e-mail: chungsy@pknu.ac.kr

S. Venkatramanan
e-mail: venkatramanansenapathi@gmail.com; venkat@pknu.ac.kr

T. H. Kim
K-Water Institute, Korea Water Resources Corporation,
Daejeon 305-730, Korea

M. V. Prasanna
Department of Applied Geology, School of Engineering
and Science, Curtin University, CDT 250, 98009 Miri,
Sarawak, Malaysia

S. Y. Hamm
Division of Earth & Environmental System, Pusan National University,
Busan 609-735, Korea

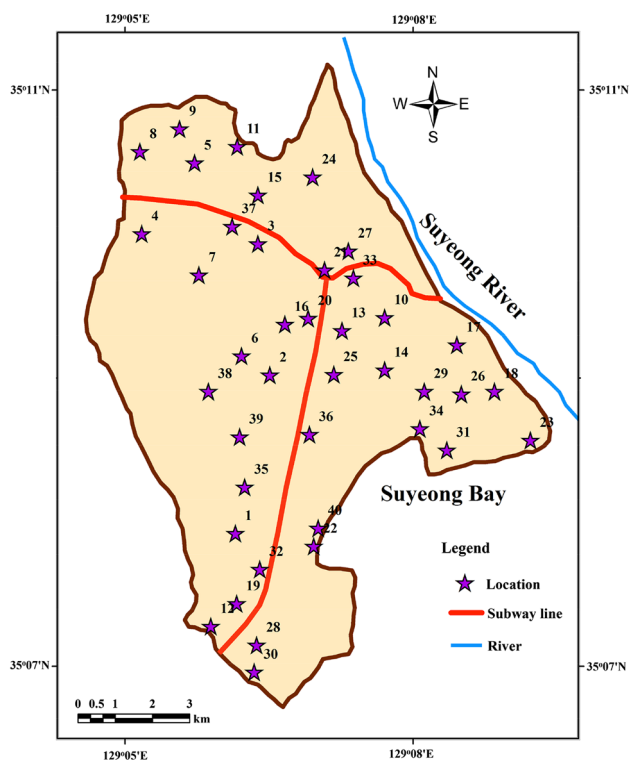


Fig. 1 Location map of the study area

et al. 2009). Usually, water pollution indices are practical and comparatively simple approaches for evaluating the influence and source of overall pollution. The pollution indices were proposed to provide useful and comprehensible guiding tools for water quality executives, environmental managers, decision makers, and potential users of a given water system. The WQI was initially developed in the USA by Horton (1965) and has been widely used in Africa and Asia (Shoji et al. 1966; Handa 1981; Erondy and Nduka 1993; Palupi et al. 1995; Mohan et al. 1996; Li et al. 2009; Prasanna et al. 2012). Correlation and cluster analyses (CA) have been considered as more trustworthy approaches for data mining of matrices from environmental quality assessment (Astel et al. 2007, 2008; Simeonova and Simeonov 2007), and are widely used in water quality assessment.

This study evaluates the metal concentration in groundwater at a coastal area of Busan Metropolitan city, Korea. The main objective of this case study is to assess the groundwater quality using integrated approaches of water quality pollution indices and statistical analyses (Correlation and Cluster analyses). This study also identifies the pollution status and probable sources of metals in the groundwater.

Study Area

The proposed study area, Busan Metropolitan City (Fig. 1) is the second largest city in Korea with a population of 3.7

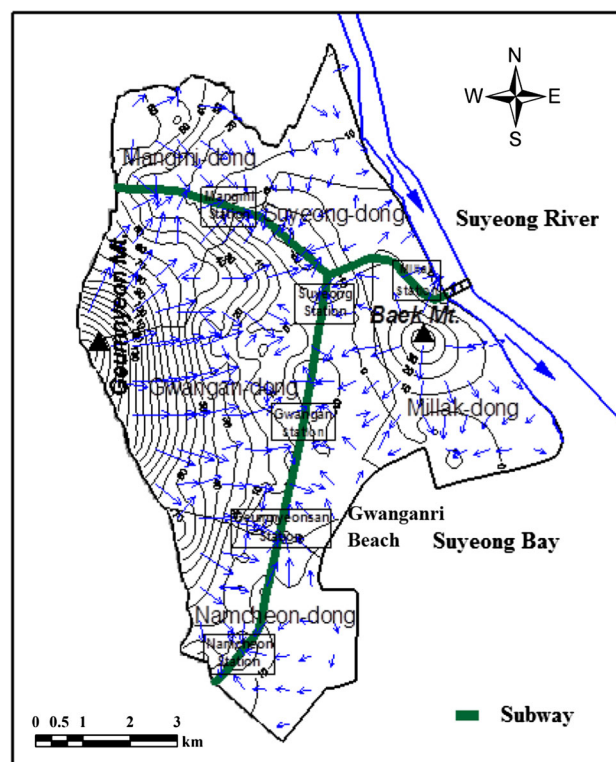


Fig. 2 Groundwater flow direction map of the study area

million and is located at the coast in the southeastern part of the Korean Peninsula. Groundwater utilization has been restricted by seawater intrusion at the coastal area of Busan City (Chung et al. 2014). The city has very long tunnels for three underground subway lines. The total groundwater discharged from the subway lines is approximately 15,000 m³/day (5.5 million m³/year) through subway tunnels of 96 km in length. There is serious groundwater drawdown, and groundwater quality is degraded around the subway tunnels. Many groundwater wells around subway tunnels have been abandoned due to the decrease of groundwater quantity or the deterioration of groundwater quality. Groundwater flow directions are indicated in Fig. 2. Geumnyeon Mountain is a large groundwater recharge area, and Baek Mountain is a small recharge area. Groundwater flows mainly from Geumnyeon Mountain to Gwananri Beach and Suyeong River, but the downstream of groundwater returns to the subway lines. The large drawdown of groundwater level around the subway causes this problem. The seawater intrusion around the beach also disturbs the downstream flow of groundwater. Groundwater flow to the beach is not smooth because of seawater intrusion and return flow to the subway. The geology of the study area is composed of andesitic volcanic breccias, tuffaceous sedimentary rocks, rhyolitic rocks, and intrusive granodiorites and granite porphyries. The geologic time period of the study area is the Cretaceous in Mesozoic Era (Chang et al. 1983; Son et al. 1978).

Materials and Methods

Groundwater Sampling

Groundwater in Busan city is available throughout the year, and utilized mainly for homes, offices, restaurants, hotels, trees, and grasses. Forty groundwater samples were collected during the year of 2010. The drilled bore wells were relatively uniformly distributed throughout the study area. Groundwater was sampled directly from water faucets after pumping for 10 minutes to remove stagnant water (APHA 1995). Groundwater samples were collected from high-quality polyethylene bottle through 0.45 μm cellulose nitric membrane filter to eliminate suspended materials. Most of the borehole wells were developed in bedrock, and the depth of the boreholes ranged from 30 to 350 m. The diameters of the borehole wells were 6–8 inches. Groundwater samples for the analysis of metal components were acidified to pH < 2.0 in the field. All samples were stored in ice chests at 4 °C, and transported directly to the laboratory, where they were analyzed within 2 weeks. pH, EC, and DO were measured in the field using portable instruments: Therm Orion 250A⁺, U.S.A. for pH; TOA CM-14P, Japan for electrical conductivity (EC); and Istek 25D, Korea for dissolved oxygen (DO). Metals were analyzed in the laboratory using Inductively Coupled Plasma–Atomic Emission Spectrometer (ICP–AES, Shimadzu ICPS-1000 III). Accuracy of Quality Assurance (QA) was measured using spiked samples with known concentrations of solutes, and precision was checked by blind duplicate samples from the same site. This is to verify that decontamination procedures and laboratory protocols were adequate (Koterba et al. 1995).

Heavy Metal Evaluation Index

Metal evaluation index provides an overall quality of the water with respect to metals (Edet and Offiong 2002) and is expressed as

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{mac}}$$

where H_c and H_{mac} are the monitored value and maximum admissible concentration (MAC) of the i th parameters, respectively.

Heavy Metal Pollution Index

The index of heavy metal pollution was developed by assigning a rating or weighting (W_i) for each chosen parameter. The rating is an arbitrary value between 0 and 1, and its selection reflects the relative importance of individual quality considerations. It can be defined as inversely proportional to the

standard permissible value (S_i) for each parameter (Horton 1965; Mohan et al. 1996; Reddy 1995). In this present study, the concentration limits (i.e., the standard permissible value (S_i) and highest desirable value (I_i) for each parameter) were taken from the WHO standard. The uppermost permissible value for drinking water (S_i) refers to the maximum allowable concentration in drinking water in the absence of any alternate water source. The desirable maximum value (I_i) indicates the standard limits for the same parameters in drinking water (Bhuiyan et al. 2010). The HPI, assigning a rating or weighting (W_i) for each selected parameter, is determined using the expression below (Mohan et al. 1996):

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i}$$

where Q_i and W_i are the sub-index and unit weight of the i th parameter, respectively, and n is the number of parameters considered. The sub-index (Q_i) is calculated by

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)l_i\}}{S_i - l_i} \times 100,$$

Table 1 Descriptive statistical data of physicochemical parameters (all the values in mg/L except pH and EC (μS/cm)

Parameters	Mean	Median	Max.	Min.	Std. dev	MAC
pH	6.95	6.84	7.94	6.19	0.49	6.5–8.5 ^a
EC	1638	521	21400	227	4139	1400 ^a
DO	8.05	7.8	9.9	3.9	2.47	–
Fe	0.009	0.001	0.14	0.001	0.025	200
Mn	0.025	0.001	0.50	0.001	0.091	50
Zn	0.057	0.026	0.26	0.040	0.057	5000
Cu	0.023	0.012	0.24	0.001	0.038	1000
Cd	0.002	0.002	0.003	0.001	0.001	3

MAC Maximum Acceptable Concentration, adopted from Siegel (2002) and ^a WHO (2004)

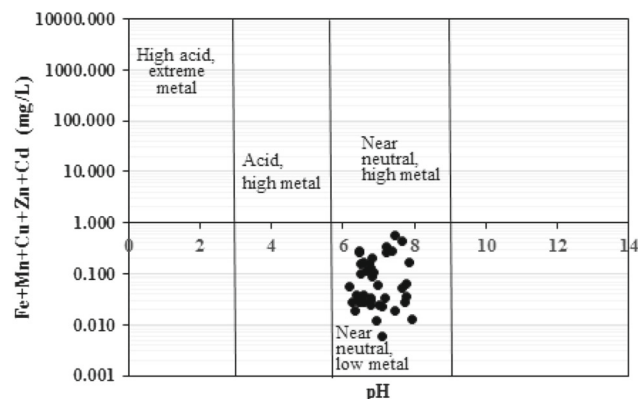


Fig. 3 Classification of groundwater samples based on the plot of metal load and pH

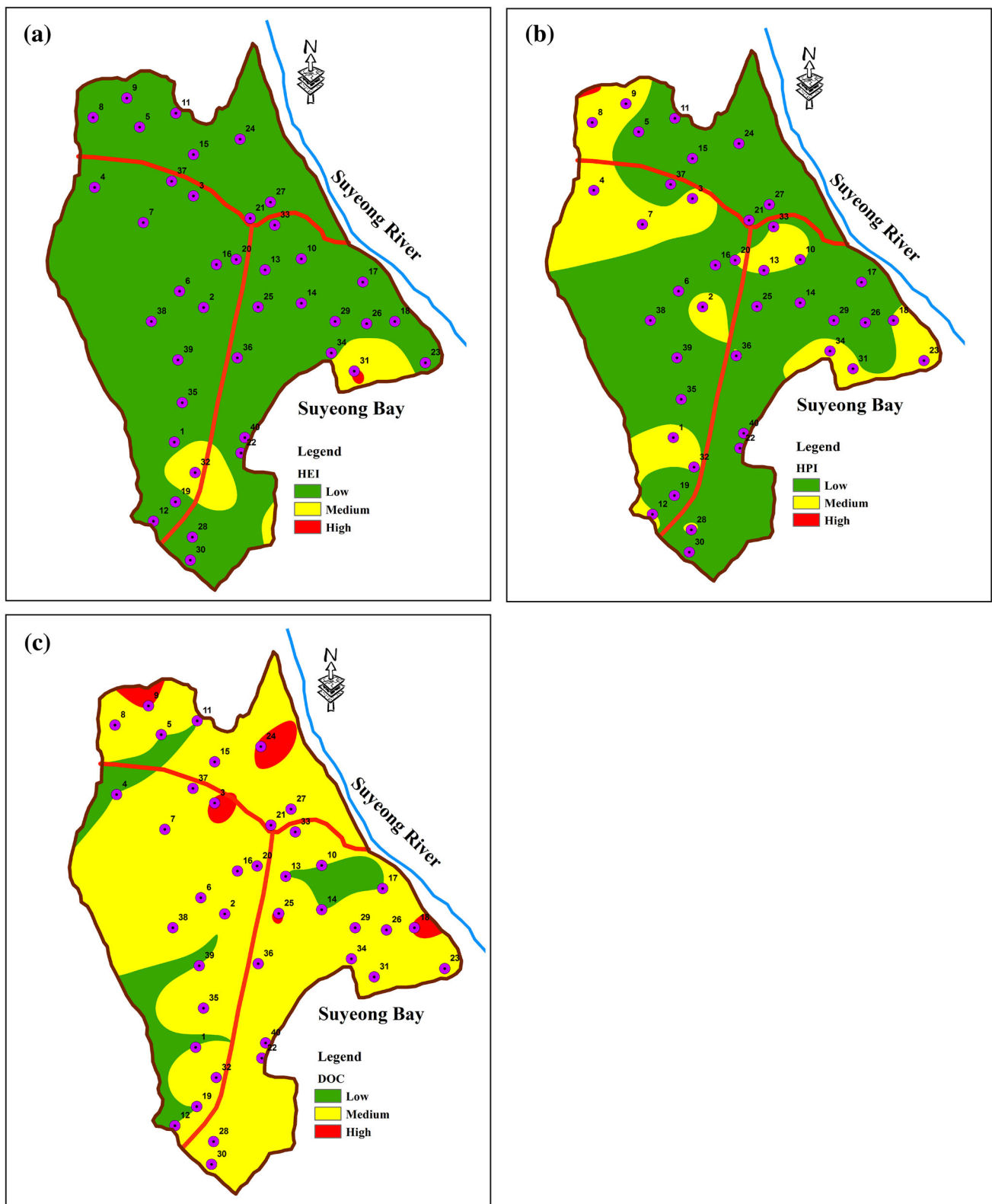


Fig. 4 Distribution of pollution indices of groundwater samples (a) HEI (b) HPI (c) DOC

where M_i , I_i and S_i are the monitored heavy metal, ideal, and standard values of the i th parameter, respectively. The sign (−) indicates numerical difference of the two values, ignoring the algebraic sign. Generally, pollution indices are estimated for any specific use of the water. The proposed index is intended for the purpose of water quality. The critical pollution index value of water quality is 100.

Degree of Contamination (DOC)

The contamination index (DOC) summarizes the combined effects of several quality parameters considered harmful to domestic water (Backman et al. 1997) and is calculated as follows:

$$Cd = \sum_{i=1}^n C_{fi}$$

with

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

where C_{fi} , C_{Ai} and C_{Ni} represent contamination factor, analytical value and upper permissible concentration of the i th component, respectively. N denotes the ‘normative value’ and C_{Ni} is taken as MAC. Finally, GIS based maps were developed for the pollution indices extracted from DOC, HEI and HPI of the data set using Arc GIS (ver.10.2).

Statistical Analyses

The analytical data were subjected to statistical analyses using Statistica software ver.8 (StatSoft 1999). Cluster analysis was applied to identify groups of samples with similar heavy metal contents. CA was formulated according to the Ward-algorithmic method, and the rescaled linkage distance was employed for measuring the distance between clusters of similar metal contents. Q-mode CA was used to determine the association of different groundwater quality parameters and pollutant sources. Pearson’s correlation matrix was also used to identify the elements’ relationship.

Results and Discussion

Metal Distributions

The descriptive statistical values of physical parameters and metal concentrations are presented in Table 1. The analytical results indicate that pH of groundwater samples varied between 6.19 and 7.94, which is a little acidic to alkaline. EC varied from 227 to 21,400 μ S/cm due to the influences of seawater and sewage leaked from sewers. The level of DO (3.9–9.9 mg/L) in groundwater samples is more or less low,

and it could infer the presence of pollutants that consume the oxygen in water (Akinbile and Yusoff 2011). The mean concentrations of metals in groundwater are in the descending order as Zn > Mn > Cu > Fe > Cd. The relationship between metal loads (Fe + Mn + Cu + Zn + Cd) and pH for the groundwater samples is shown in Fig. 3, and all samples were plotted in the field of near-neutral and low metal sector (Ficklin et al. 1992; Caboi et al. 1999).

Pollution Indices

Evaluations of water quality pollution were carried out using heavy metals of groundwater samples (Edet and Offiong 2002). The study area was classified into three categories according to HEI values, that is, low (<10), medium (10–20), and high (>20) categories. HEI values ranged from 0.34 to 10.63. According to HEI distribution, 97 % of the samples fall in a low pollution zone, and only 3 % of the groundwater samples are included in medium and high pollution zones. The medium and high pollution zones are located at the south and east parts (Fig. 4a). HPI values of all groundwater samples were calculated using MAC (maximum acceptable concentration), (Siegel 2002). The values are useful to assess the groundwater quality in each sample point. The study area was classified into three zones according to HPI values, that is, low (<90), medium (90–180), and high (>180) categories. HPI value ranged between -3 and 135. According to HPI distribution (Fig. 4b), 57 and 42 % of the samples fall in low and medium pollution zones, respectively, and only 1 % of samples are above the critical limit of 100 proposed by Prasad and Bose (2001). The sampling stations (1–4, 7–10, 12, 13, 18, 20, 23, 28, 31–34, 36) in a medium category are considered as polluted groundwater. The above mentioned sampling points are located near the sea and the subway. They were contaminated by seawater intrusion, salinized river water, and sewage leaked from sewers. The study area was classified into three zones according to DOC values, that is, low (<1), medium (1–3), high (>3) categories. According to DOC distribution

Table 2 Correlation coefficients for parameters of groundwater samples

	pH	EC	DO	Fe	Mn	Cu	Zn	Cd
pH	1.00							
EC	0.17	1.00						
DO	−0.01	0.13	1.00					
Fe	0.36	−0.11	0.50	1.00				
Mn	0.34	0.65	0.12	−0.05	1.00			
Cu	0.04	0.18	0.04	0.18	0.34	1.00		
Zn	−0.08	−0.11	0.36	0.32	0.01	0.32	1.00	
Cd	0.24	0.08	−0.04	0.22	0.19	0.11	0.13	1.00

* Significant values are in bold

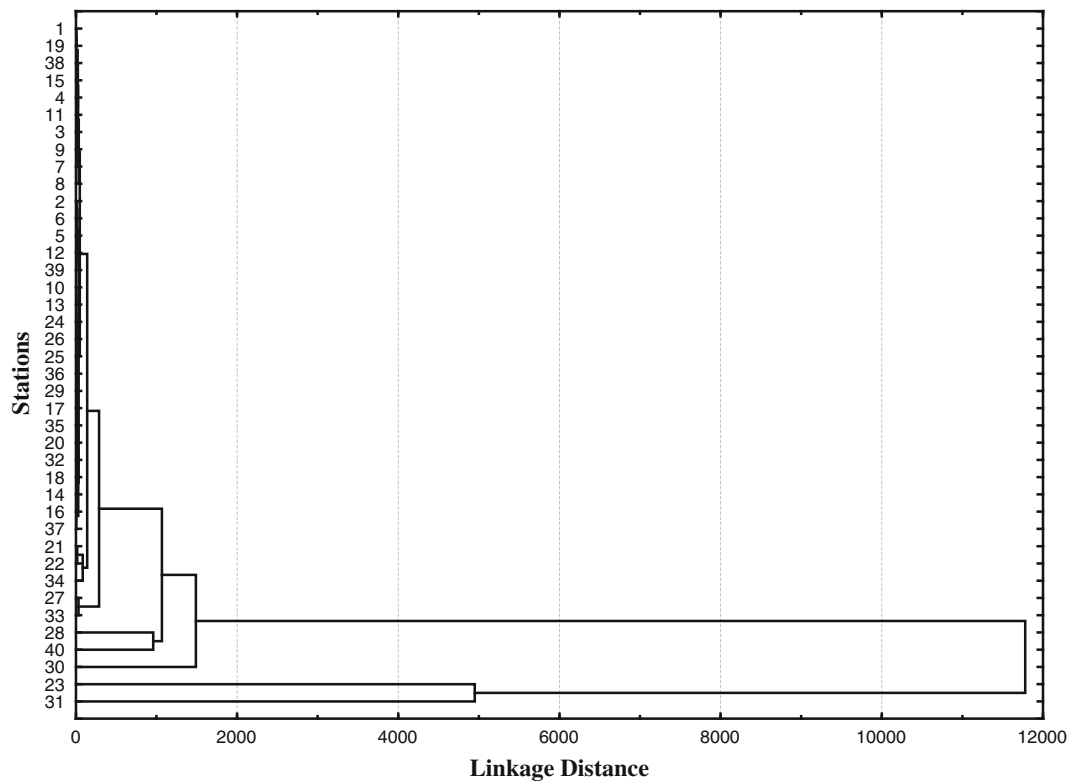


Fig. 5 Dendrogram analyses of the groundwater samples

(Fig. 4c), 85 % of the samples fall in a medium zone, 10 % in a low zone, and 5 % in a high pollution zone. The sampling stations (3, 9, 18, 24, 25) in high pollution zones are located near residential area, the subway or the Suyeong River effluents. Groundwater in the zones were affected by salinized river water and leaked sewage.

Correlation and Cluster Analyses

Pearson's correlation coefficient matrices for the analyzed parameters are presented in Table 2. The statistically significant level is $p < 0.05$. pH correlated with Fe ($r = 0.36$) and Mn ($r = 0.34$). The solubility of Fe and Mn minerals was strongly redox controlled, particularly at near neutral pH (Prasanna et al. 2012). EC also shows significant correlated with Mn ($r = 0.65$). DO correlated with Fe and Zn. Metal pairs Fe–Zn, Mn–Cu, and Cu–Zn show good correlations with respective correlation coefficient (r) values of 0.32, 0.34, and 0.32, respectively, due to the interaction between rock and groundwater.

Cluster analysis (CA) was also performed to understand the pH, EC, DO and metals groupings in the data set and the results are presented in Fig. 5. The Q-mode CA performed on the samples produced four clusters. Cluster 1 consists of 13 stations (1, 19, 38, 15, 4, 11, 3, 9, 7, 8, 2, 6, 5). It reflects the influence of sewage leaked from sewers. Cluster 2 includes

of stations of 12, 39, 10, 13, 24, 26, 25, 36, 29, 17, 35, 20, 32, 18, 14, 16, 37, 21, 22, 34. This is due to the accumulation of metals from bedrocks in groundwater. Cluster 3 contains stations of 27 and 33, and it shows the influence of groundwater discharged from the subway. Cluster 4 includes stations of 28, 40, 30, 23, 31. It indicates contamination by seawater intrusion.

Conclusion

Groundwater quality in the study area was influenced by various kinds of contamination sources such as seawater intrusion, sewage leaked sewers, salinized river water, and groundwater discharged from the subway. By metal load and pH, groundwater quality was characterized in the near-neutral and low metal sector. The calculated values of HPI showed that 43 % of samples were above the critical index value (100), and 57 % of samples were within the low HPI zone. Based on the HEI, 3 % of samples fell in medium and high pollution zones, and 97 % of samples existed in a low pollution zone. DOC suggested that 95 % of the groundwater samples fell in low and medium zones, and 5 % of the samples located in highly polluted zones. Correlation and cluster analyses clearly elucidated that seawater intrusion, sewage leaked from sewers and salinized river acted as the definite

donors of this metals. This present case study underscored the importance of an integrated approach of pollution indices and statistical analyses for groundwater quality.

Acknowledgments This work was supported by the Pukyong National University Research Fund in 2012 (PK-2012-0571).

References

- Akinbile CO, Yusoff MS (2011) Environmental impact of leachate pollution on groundwater supplies in Akure, Nigeria. *Int J Environ Sci Dev* 2:81–86
- APHA (1995) Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, New York
- 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
- Backman B, Bodis D, Lahermo P, Rapant S, Tarvainen T (1997) Application of a groundwater contamination index in Finland and Slovakia. *Environ Geol* 36:55–64
- Bhuiyan MAH, Parvez L, Islam MA, Dampare SB, Suzuki S (2010) Heavy metal pollution of coal mine affected agricultural soils in the northern part of Bangladesh. *J Hazard Mater* 173:384–392
- Caboi R, Cidu R, Fanfani L, Lattanzi P, Zuddas P (1999) Environmental mineralogy and geochemistry of the abandoned Pb–Zn Montevicino-Ingurtosu mining district, Sardinia, Italy. *Chron Rech Miniere* 534:21–28
- Chang TW, Kang PC, Park SH, Hwang SK, Lee DW (1983) The Geological Map of Busan and Gadeog (1:50,000). Korea Inst of Energy Resour, 22 p
- Chung SY, Venkatramanan S, Kim TH, Kim DS, Ramkumar T (2014) Influence of hydrogeochemical processes and assessment of suitability for groundwater uses in Busan city. *Environment, development and sustainability*, Korea. doi:10.1007/s10668-014-9552-7
- Edet AE, Offiong OE (2002) Evaluation of water quality pollution indices for heavy metal contamination monitoring. A study case from Akpabuyo-Odukpani area, Lower Cross River Basin (southeastern Nigeria). *Geo J* 57:295–304
- Erondu ES, Nduka EC (1993) A model for determining water quality index (WQI) for the classification of the New Calabar River at Aluer-Port Harcourt, Nigeria. *J Environ Stud* 44:131–134
- Ficklin DJ, Plumee GS, Smith KS, McHugh JB (1992) Geochemical 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
- Handa BK (1981) An integrated water-quality index for irrigation use. *Indian J Agric Sci* 51:422–426
- Holloway JM, Dahlgren RA, Hansen B, Casey WH (1998) Contribution of bedrock nitrogen to high nitrate concentrations in stream water. *Nature* 395:785–788
- Horton RK (1965) An index system for rating water quality. *J Water Pollut Control Fed* 37:300–306
- 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
- Koterba MT, Wilde FD, Laphan WW (1995) Groundwater data collection protocols and procedures for the national water quality assessment program. collection and documentation of water quality samples and related data. US Geological Survey Open file report, 95–399, p 113.
- 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
- Lermontov A, Yokoyama L, Lermontov M, Machado MAS (2009) River quality analysis using fuzzy water quality index: Ribeira do Iguape river watershed, Brazil. *Ecol Ind* 9:1188–1197
- 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
- Li Z, Fang Y, Zeng G, Li J, Zhang Q, Yuan Q, Wang Y, Ye F (2009) Temporal and spatial characteristics of surface water quality by an improved universal pollution index in red soil hilly region of South China: a case study in Liuyanghe River watershed. *Environ Geol* 58:101–107
- Mohan SV, Nithila P, Reddy SJ (1996) Estimation of heavy metal in drinking water and development of heavy metal pollution index. *J Environ Sci Health* 31:283–289
- 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
- Palupi K, Sumengen S, Insuwiasri S, Agustina L, Nunik SA, Sunarya W, Quraisyn A (1995) River water quality study in the vicinity of Jakarta. *Water Sci Technol* 39:17–25
- Peierls BL, Caraco NF, Pace ML, Cole JJ (1998) Human influence on river nitrogen. *Nature* 350:386–387
- Pekey H, Karaka D, Bakoglu M (2004) Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses. *Mar Pollut Bull* 49:809–818
- Prasad B, Bose JM (2001) Evaluation of the heavy metal pollution index for surface and spring water near a limestone mining area of the lower Himalayas. *Environ Geol* 41:183–188
- Prasanna MV, Praveena SM, Chidambaram S, Nagarajan R, Elayaraja A (2012) Evaluation of water quality pollution indices for heavy metal contamination monitoring: a case study from Curtin Lake, Miri City, East Malaysia. *Environ Earth Sci* 67:1987–2001
- Reddy SJ (1995) *Encyclopedia of environmental pollution and control*, vol 1. Environmental media, Karlia.
- Shoji H, Yamamoto T, Nakakaga N (1966) Factor analysis of stream pollution of the Yodo River system. *Air Water Soil Pollut* 10: 291–299
- Siegel FR (2002) *Environmental geochemistry of potentially toxic metals*. Springer, Berlin
- Simeonova P, Simeonov V (2007) Chemometrics to evaluate the quality of water sources for human consumption. *Microchim Acta* 156: 315–320
- Son CM, Lee SM, Kim YK, Kim SW, Kim HS (1978) The Geological map of Dongrae and Woelnae (1:50,000). Korea Res Inst of Geol and Miner Res
- StatSoft (1999) *Statistica computer program*, version 8. StatSoft, Tulsa, Oklahoma
- World Health Organization (WHO) (2004) *Guidelines for drinking water quality* (3rd edn.) (ISBN: 9241546387). Retrieved from http://www.who.int/water_sanitation_health/dwq/guidelines/en/
- Zhang W, Feng H, Chang J, Qu J, Xie H, Yu L (2009) Heavy metal contamination in surface sediments of Yangtze River intertidal zone: an assessment from different indexes. *Environ Pollut* 157:1533–1543