Caspian Journal of Environmental Sciences
Online ISSN: 1735-3866
Print ISSN: 1753-3033

Multivariate and geostatistical analysis of spatial distribution and potential sources of heavy metals in surface waters

Mohammad Rafiee[1,2], Akbar Eslami[1,2], Reza Saeedi[3], Mehrnoosh Abtahi[2], Mahsa Jahangiri-rad[4]*

1. Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
2. Department of Environmental Health Engineering, School of Public Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran
3. Department of Health Sciences, Faculty of Health, Safety and Environment, Shahid Beheshti University of Medical Sciences, Tehran, Iran
4. Water purification research center, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

** Corresponding author's E-mail: m.jahangiri@iautmu.ac.ir*

ABSTRACT
Although economic growth from industrialization has improved health and quality of life indicators, however, it has intensified the release of chemicals into the environment, with severe effects on health. The present work confers toxic metals contamination levels of surface waters in Zanjan Province, Iran, encompassing several rich mines of lead and zinc. The soluble concentrations of Fe, Cu, Cd, Ni, Pb, Zn and AS in water samples were determined using ICP-MS and the level of contamination was appraised by heavy metal pollution index (HPI). Multivariate statistical methods comprising Pearson's correlation analysis, hierarchical cluster analysis, and principal component analysis were applied to evaluate the relationships between heavy metals. Geostatistical analyses were carried out to conduct the distribution characteristics and the sources of pollution. The results showed that concentrations of studied heavy metals were higher in the spring compared to the winter, however, the calculated HPI values did not exceed the limit of 15. Anthropogenic activities, for the most part, control the quality of water in this study area with minor natural/geogenic input. All the measured heavy metals were strongly homologous in spring based on correlation coefficients. However, this correlation gets weaker in the winter due to a degree of heterogeneity between Zn, Cd, As and other elements. Distribution pattern of the heavy metals pollution index of surface waters with different land uses decreased in the order of: agricultural>dry farming/water bodies>built up areas>forest areas. Multi hotspots for the above mentioned heavy metals were located in the southeast study areas.

Key words: Water quality, Heavy metal pollution index, Geostatistics, Spatial distribution.

INTRODUCTION
Environmental risk factors, notably water pollution, are a momentous source of morbidity and mortality in both developing and industrialized nations. An increasing number of contaminants are entering water resources from human activity and therefore a large number of communities lack access to safe drinking water and sanitation (Shannon *et al.* 2008).

The data pooled from studies, surveys and reports looked at water bodies from different countries shows stunning changes in less than 100 years, with increasing average water quality indices (WQIs) in multiple countries in twenty-first century (Shannon *et al.* 2008; Schwarzenbach *et al.* 2010). The risk of waterborne diseases in many regions, by contrast, is high due to the exposure to traditional compounds such as heavy metals, metalloids and emerging micropollutants (Shannon *et al.* 2008, Schwarzenbach *et al.* 2010, Zhang *et al.* 2010). The increasing

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341
Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

growth of contaminating industries in the human environment, expose these resources to various pollutants (Zhang *et al.* 2010). The entrance of heavy metals (e.g., Pb, Zn, Cd, Cr, Ni, Cu, and Hg) and metalloids (e.g., As and Se) into water resources is one of the issues of public health and environmental concern. The problem is accentuated in many industrial areas, owing to effluent discharge into the aquatic environments and overexploitation of aquifers (Ozmen *et al.* 2004). These metals naturally exist in very small amounts in foods and are useful for human health.

Heavy metal pollution, however, results in serious human health consequences through the food web and the loss of biodiversity and harms the environmental quality (Rodriguez Martin *et al.* 2013; Panigrahy *et al.* 2015). Cadmium, for example, may damage the metabolism of calcium, resulting in cartilage disease and bone fractures as a consequence of calcium deficiency. Pb affects many of the body organs such as kidney and liver, as well as reproductive, nervous, urinary, and immune systems and also the basic physiological processes of cells and gene expression (US EPA 2000). Similarly, Zn and Ni are essential trace elements in the human body. However, they can induce tumor promoting factors in excessive uptake, whose carcinogenesis effects have attracted global concerns (Chen 2011). Acute and chronic arsenic exposure may result in dermal, respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunological, genotoxic, mutagenetic, and carcinogenic effects (Lin *et al.* 2013).

The sources and distribution of heavy metals in water course and soil alter considerably with the weathering of soil parent materials and land use (industrial, urban and agricultural) (Ozmen *et al.* 2004). Development of a monitoring scheme to assist in the planning, development and guiding human activities including industrial as well as agricultural development is thence a cost-effective way to protect the quality of water in order to minimize adverse impacts on water quality. In recent years, a particular attention has been given towards the evaluation of heavy metals and metalloids pollution in ground and surface waters with the development of a heavy metal pollution index (HPI) (Mohan *et al.* 1996).

Statistical approaches, notably multivariate techniques such as principal components analysis (PCA) and cluster analysis (CA), are a more reliable scientific approach for data processing of matrices from environmental quality assessment and can prove useful for interpretation of multiple elements (Astel *et al.* 2007; Simeonova & Simeonov 2007). Geostatistic, on the other hand, is a powerful interpolation tool that can quantifies and reduces sampling uncertainties, simplify source identification, while minimizing investigation cost (Wu *et al.* 2008). At the same time, Iran is industrializing at a rather rapid rate with associated increases in industrial waste. The water situation in Iran is more critical than the global average, since its most part is located among arid and semiarid regions. (Madani 2014). Moreover, water resources in Iran are very unevenly distributed. Iran is at a halfway stage of development at which environmental risks are changing by the quantity and quality, shifting from traditional to modern sources.

In many large cities, new sources of environmental pollution are increasing. Many communities are still exposed to risks from traditional and modern pollutants, neither of which shows signs of abatement. For example, residents of Zanjan Province, our study area, are surrounded by the effluents of modern heavy industries, which have led to heavy metal exposures (Zamani *et al*. 2015). The Zanjan large metalliferous site is considered as a traditional mining region. Horticultural soils of the area have been analyzed for heavy metals, inferring that the soil is naturally enriched with Zinc and lead (Zamani *et al.* 2015). The average background concentration of Cd, Pb and Zn were analyzed as 1.92, 354.98 and 501.10 mg kg^{-1}, respectively (Naderi *et al.* 2017). The distribution of heavy metals in the province agricultural soils was also investigated during the last decade because of the emerging drawbacks of soil contamination which roots from rapid economic growth and industrialization (Delavar & Safari 2016). Mining, transportation of concentrated ore by trucks and smelting units within the province were known as the major contributors to contamination of soils, plants, surface and ground water resources through the distribution of metals by wind action and/or by run-off from tailings (Chehregani *et al.* 2009 ; Zamani *et al.* 2015). However, few studies have sought to the trace metal levels in surface waters of Zanjan which serve as the main sources of water for drinking and agricultural purposes.

Therefore, this study aims to examine (1) the concentrations and spatial distributions of heavy metals in surface water bodies in Zanjan Province in 2015 with different surrounding land uses over a period of two seasons (spring and winter) (2) the efficiency of geostatistic in revealing HMs and HPI variability in the study area (3) probable pollution sources of heavy metals in surface water and to cluster polluted area by local Moran index.

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

METHODOLOGY

Study area

The study area, Zanjan Province with an area of 36,400 km², lies 330 km northwest of Tehran (the capital city of Iran), and approximately 125 km from the Caspian Sea. The province is characterized by numerous surface water bodies which are prone to impacts from human activities which may result in the degradation of the resource. Its capital (Zanjan city) is located about 20 kilometers south of the Qaflankuh Mountain Range. This city has a cold semi-arid climate with hot, dry summers and cold, moist winters. Precipitation is low, and mostly falls between October and May. The average annual rainfall in the winter stands at 72 millimeters, while in the second month of summer, it slips to 3.6 mm. The average humidity stands 74% in the morning, while 43% at noon.

Sample collection and chemical analyses

Totally 96 samples from surface waters (48 samples in the winter and 48 in the spring) were taken from 48 distinct points (Fig. 1) and inserted the narrow mouth polyethylene bottles (with 100 ml volume). The samples were then passed through 0.45 μm filters and preserved by adjusting pH with nitric acid below 2. It is generally accepted that heavy metals both of geogenic (i.e., natural) origin, like the so-called reference elements, and those introduced anthropogenically are preferentially found (by 85%–95%) in the fine-grain fraction (≤ 20 mm fraction) of aquatic sediments and suspended solids (Adams *et al.* 1992). So that, sampling contaminants in the suspended particulates can sometimes be much more effective than in the water phase. These particles are susceptible to be removed in a common water treatment plant exploiting various physico-chemical and chemical operation and process units (sedimentation, coagulation, flocculation, clarification, filtration, and disinfection), as a multiple barrier approach in environmental health engineering. The remaining soluble fraction, however, would mostly find their way into the produced water, resulting in a health risk for the community exposed. Thus, this last fraction was considered in the present study. The concentration of heavy metals was measured by inductively coupled plasma-mass spectrometry (ICP-MS) (Micromass Platform ICP, Laboratory of Pharmaceutical Sciences, Islamic Azad University, Tehran). The operating conditions of ICP were; Nebulizer gas flow rates 0.9 L min^{-1}, Auxiliary gas flow 1.2 L min^{-1} and plasma gas flow 14 L min^{-1}. Laboratory quality assurance and quality control methods were performed, incorporated the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recuperation of known additions, and analysis of duplicates. All analyses were carried out twice, and the outcomes were expressed as the average of the duplicate. The detection limit was explained as the lowest analytical signal to be discerned qualitatively at a specified confidence level from the background signal (Table 1). The accuracy of analytical procedure was examined by analyzing the standard reference materials. Recovery rates ranged from 82 to 98% for all elements examined.

Data analyses

The pollution level by heavy metals (including Pb, Fe, Cu, Ni, Zn, As, and Cd) was evaluated with the heavy metal pollution index (HPI). HPI is a ranking technique that provides the mixed influence of individual heavy metal on the overall water quality (Horton 1965).

The ranking system is an arbitrary value between zero to one and its assortment depends upon the significance of individual quality considerations in a relative way or it can be estimated by making values inversely proportional to the recommended standard for the comparable parameter (Horton 1965). In HPI calculation, the highest tolerant value for drinking water (S_i) indicates the maximum allowable concentration in drinking water in the absence of any alternate water source. The desirable maximum value (I_i) refers to the standard limits for the same parameters in drinking water. So, HPI is calculatedas Eq. (1) (Mohan. 1996)

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \quad \textbf{(1)}$$

where Q_i is the sub-index of the i^{th} parameter, W_i is the unit weight age of the i^{th} parameter and n is the number of parameters considered. The sub-index (Q_i) of the parameter is calculated by Eq. (2);

$$Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \quad \textbf{(2)}$$

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341
Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

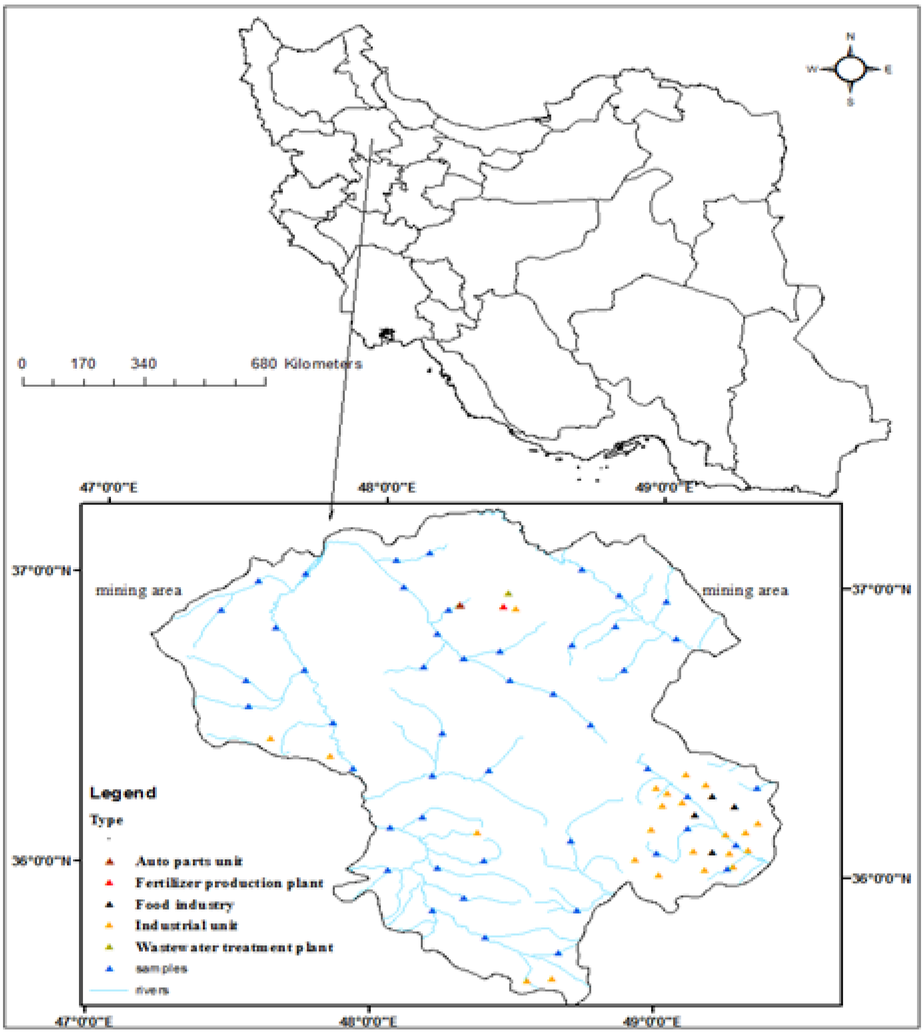

Fig. 1 The study area and sampling site locations in Zanjan Province, I.

Where M_i is the monitored value of heavy metal of ith parameter, I_i is the ideal value (maximum desirable value for drinking water) of the ith parameter and S_i is the standard value (the highest permissive value for drinking water) of the ith parameter. Heavy metal pollution index (HPI) values are typically grouped into ranges, and each range is assigned a descriptor. The critical pollution index of HPI value for drinking water is 100. Nevertheless, the modified HPI scale (Tiwari *et al*. 2015) has been employed in the present study using three classes respectively demarcated as low, medium and high for HPI values <15, 15–30 and >30.

Statistical evaluation

All data were summarized as mean, range and standard deviation for each heavy metal. Non- parametric methods were applied due to the distribution of data. Statistical analysis was performed with IBM PASW Statistics 22 (SPSS Inc. 1993–2007) to analyze the statistical characteristics of the data and to examine the normality of their distributions. Nonparametric Spearman correlation was used to assess correlations among the concentrations of several heavy metals in ground water. Differences were considered significant at a p-value of 0.05 and 0.01 or less. Hierarchical cluster analysis (HCA) was performed for identification of homogeneous subgroups of heavy metals using MVSP version 3.22. The Geostatistical Analyst module of the ArcGIS 10.2 software was applied to analyze the central spatial tendency as well as variogram analysis. Proper interpolation models were selected to perform optimal and impartial spatial interpolation on the concentrations of the seven heavy metals using the geostatistical analyst modules of ArcGIS 10.2.

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341

Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

Table 1. Summary statistics of the measured heavy metals (μg L^{-1}) compared to WHO and Iranian standards for domestic purposes.

		Spring							Winter						
		Pb	**Fe**	**Cu**	**Ni**	**Zn**	**As**	**Cd**	**Pb**	**Fe**	**Cu**	**Ni**	**Zn**	**As**	**Cd**
Mean		3.74	152.39	0.62	8.52	4.26	0.13	0.02	2.31	182.58	0.46	4.32	4.13	0.01	0.005
Std. Deviation		10.84	144.39	0.53	8.47	4.23	0.13	0.02	1.42	118.07	0.29	3.03	2.82	0.02	0.012
Range		0.09-69	23-516	0.04-2.2	0-32.64	0-16.32	0-0.33	0-0.08	0.05-5.83	20-500	0.1-1.5	0-9.8	0-9.36	0-0.08	0-0.05
Percentiles	25	0.09	57	0.19	3.05	1.52	0	0.82	0.82	50.12	0.3	1	0.69	0	0
	50	0.09	90.25	0.47	5.6	2.8	0.1	2.5	2.5	198.5	0.39	4.58	4.5	0	0
	75	0.14	160	0.97	11.6	5.8	0.25	3.28	3.2	249.7	0.56	6.42	6.27	0.01	0.007
WHO (2006)		10	300	2000	20	4000	10	3							
Max desirable		-	300	50	-	5000	10	3							
High Permissible		50	1000	1500	20	15000	50	5							

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341

Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

RESULTS AND DISCUSSION

Trend data analysis

The results of the analysis of heavy metal concentrations in the spring and winter are presented in Table 1. Concentrations of Cu, Zn, As, and Cd in the spring as well as that of Pb, Zn, As, and Cd in the winter have not exceeded the desirable limit. However, in some sampling points, the lead and nickel levels in the spring and that of iron in both seasons were exceeded the limits of national surface water classes and EPA guidelines (EPA 2001). In seven sampling points (14.5%), iron level was exceeded the maximum limit in the spring and winter, while in nine sampling points (18.75%), lead level was more than the threshold value. Meanwhile, in six points (12.5%) the same was observed for nickel level in the spring. Significant amounts of Fe in the spring were related to the sites 13, 14, 21, 30, 35, 43, 45 and 47. In the sites 3, 13, 12, 14, 20, 30, 34, 44 and 45, high lead level were also observed in this season. Elevated concentration of nickel, like iron and lead, was observed in the sampling points 13, 14, 20, 30, 34, 35, 43, 45, respectively. However, significant amounts of iron in the winter were measured with a little change in sites 14, 15, 21, 31, 35, 43, 45. Iron occurs naturally at abundant levels and is thus rarely affected by human activities. The observation made through Fig. 1 suggests that most industrial units in Zanjan Province are located at its southern part. According to the available data, 613 industrial units are active in this province, the most important of which (80%) are food, chemical and metal industries. Thus, it can be concluded that the high nickel and lead levels are related to the industrial discharges which contaminate water resources. Mean concentrations of the analyzed metals were used to calculate the HPI values and its corresponding map in the winter and spring are shown in Fig. 2. As shown in Fig. 2, the ranges of HPI in the winter and spring were 1.57 to 2.25 and 1.61 to 4.65, respectively. The outmost value of HPI was observed in the spring and at sites 17, 18, 19, 21, 24, 28, 43 and 45. The HPI pattern showed irregular seasonal characteristic change between spring and winter especially in the south part of the study area. This indicates that such characteristic variation of HPI was predominantly dictated by anthropogenic activities (Li and Zhang. 2010). Significant values of HPI could result from natural or human activities (Tiwari et al. 2015). Moreover, agricultural activities at site could be a factor to enter high concentrations of heavy metals into the environment. As depicted in Fig. 3, the locations of sample points are plotted on the X, Y plane. This trend analysis provides a three-dimensional perspective of HPI data.
The HPI value of each point is given by the height of a stick in a Z-dimension. The data points are projected onto the perpendicular planes, an east–west and a north–south plane (ESRI 2011). A best-fit line (a polynomial) is drawn through the projected points, showing trends in specific directions. As presented, no significant trend was observed in HPI values in winter. Howbeit, the blue line starts out with lower values at north, increases as it moves toward the center, and then levels off. Similarly, the green line is slightly increasing as it moves east and decreases starting from the center of the state. The trend analysis in spring was clearly more pronounced. The polynomial blue and green lines demonstrate that the HPI values seem to exhibit a strong trend in all directions dedicating higher values in south and north-eastern parts. The results of trend analysis comply with the spatial distribution of HPI shown in Fig. 2. So that, in order to examine the relationship between land use and the spatial distribution of HPI, zonal statistic tool (Arc GIS 10.2) was employed and the results are shown in Fig. 4. The HPI levels for surface waters from lands of different use types reveal that not only industry positioning, but also lands with agricultural uses, farming, and water bodies such as ponds, marshes and lagoons have accounted for the highest value of HPI. Distribution pattern of the heavy metal pollution index of surface waters with different land uses decreased in the order of: agricultural > dry farming / water bodies > built up areas > forest areas. The lowest value of HPI was observed in the forest areas in winter. However, at some sampling points located in the urban (built up) areas (sites 13, 14, and 16) high values of HPI were also observed due to the presence of factories of auto parts and chemical fertilizers as well as a newly wastewater treatment plant that its effluent has somewhat contaminated surface water resources. Elevated heavy metal levels are attributed to residual deposit producing from heavy metal purification processes or excessive use of fertilizers (Hani & Pazira 2011). Application of phosphate fertilizers can increase Cd content (Cai *et al.* 2012), whereas the use of chemical fertilizers escalate Pb and Zn concentration in agricultural soil (Atafar *et al.* 2010). Higher value of HPI in the spring compared to the winter could be due to the higher evaporation or anthropogenic activities (related to the industries or the use of agricultural pesticides) in this season. Besides, due to the presence of zinc and copper mining activities in the east and west parts of Zanjan Province, sites 5, 31 and 33 showed high HPI as depicted in Fig. 2. Additionally, diluting

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

effects of winter rainfall resulted in the decreased concentrations of heavy metals in surface water which in turn may leak into groundwater and pollute them.

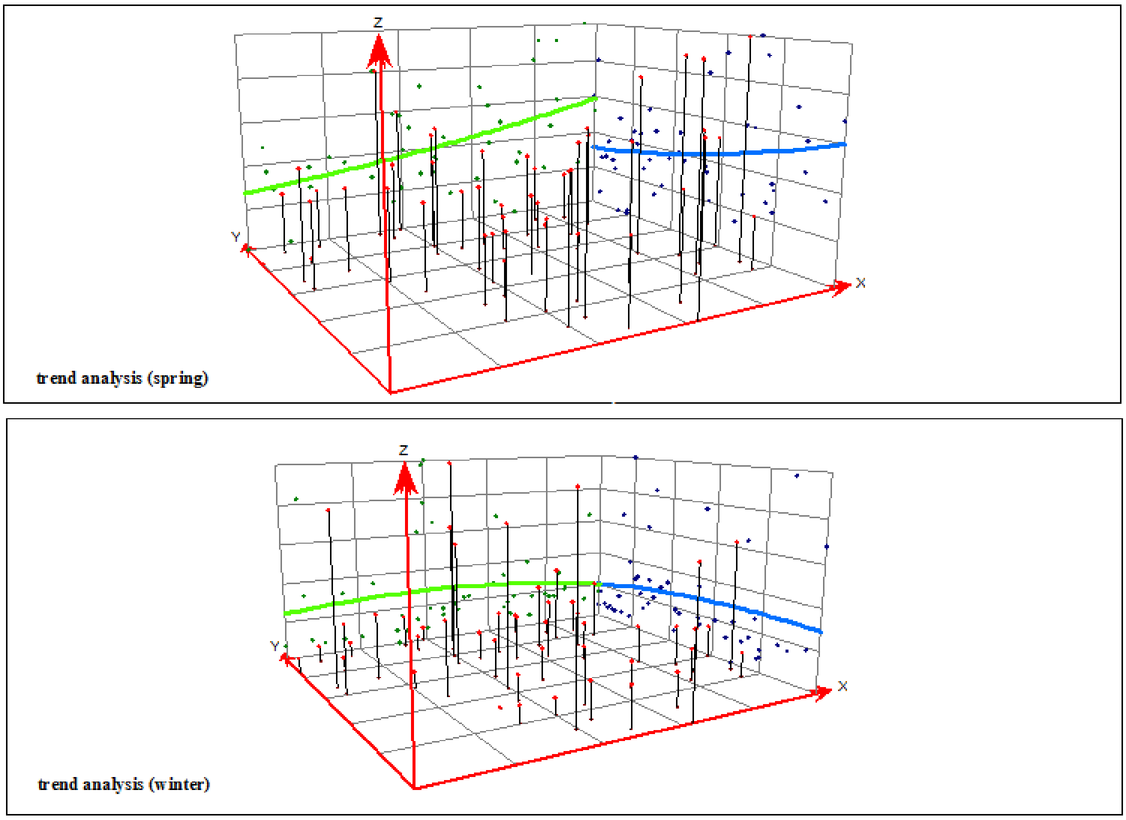

Fig. 3. Trend analysis of HPI data.

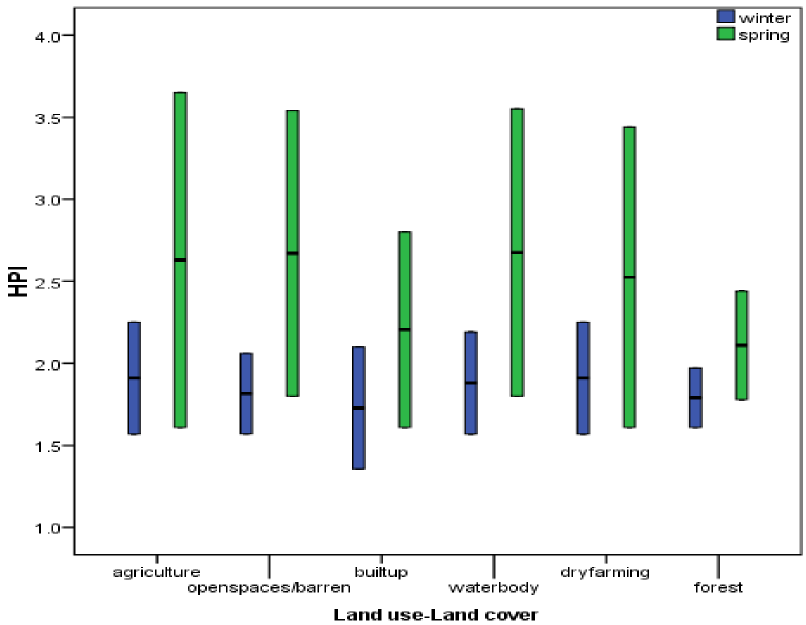

Fig. 4. HPI levels of heavy metals in the surface waters from lands of various use types.

In line with our results, Mohammadian *et al.* (2008) reported lead and cadmium concentrations in 53% and 59% of ground water samples which were higher than the limit of Iranian standards for the same area. HPI values of studied samples in the study area were all lower than 15, indicating low contamination. The findings observed in

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341
Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

this study mirror those of the previous studies that have examined heavy metal pollution in soil and ground water around the Zanjan lead and zinc plants (Parizanganeh *et al.* 2010; Zamani *et al.* 2012).

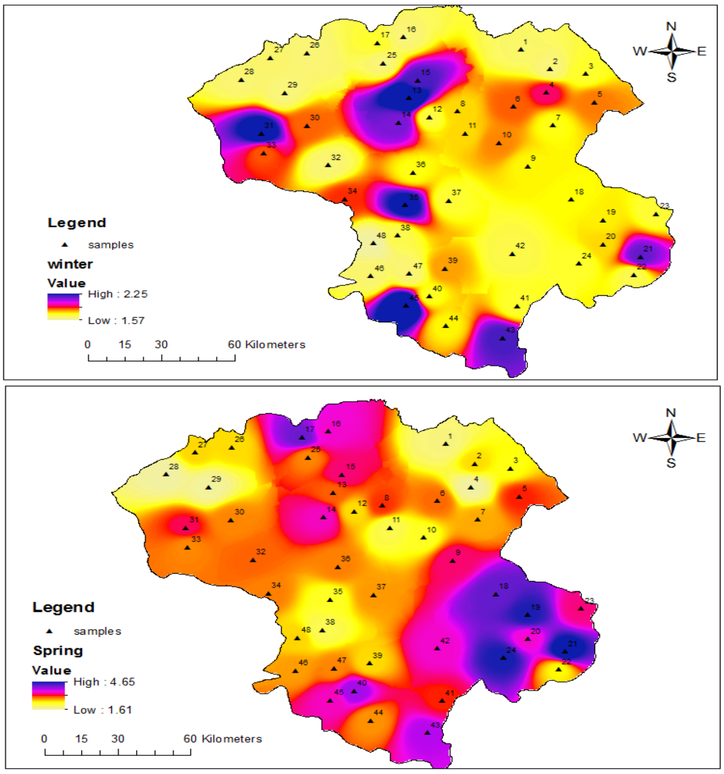

Fig. 2. Heavy metal pollution index spatial map of Zanjan catchment area in the winter and spring

Paired sample t-test

Paired sample T-test was performed to investigate the changes between the concentrations measured in the spring and winter. Table 2 illustrates the mean differences of winter- versus spring seasons heavy metals data for all the seven variables along with the corresponding t values, degrees of freedom (df) and *p* values for two-tailed paired sample t tests. Except for iron, the concentrations of other measured heavy metals in the spring were higher than those in the winter ($p < 0.05$). This implies that the changes in these concentrations were mostly influenced by anthropogenic activities, rather than natural processes (Kohušová *et al.* 2011). However, this difference was not statistically significant for Zn and Pb. It seems that greater agricultural and industrial activities in spring have led to this increase. In some sites, Fe levels in the winter were higher than spring, and these differences were significant. The relationship between anthropogenic activities and high concentrations of some heavy metals in the environment has been frequently reported in the literature (Zhou *et al.* 2007; Sun *et al.* 2010). The comparison of HPI values in the spring and winter shows higher levels of HPI in most sites in the spring, and these differences were quite significant ($p < 0.01$).

The correlation between heavy metals

Spearman correlation coefficient of the studied heavy metals is depicted in Table 3. According to the results, there is a strong correlation between lead and other heavy metals measured in the spring (r = 0.52 to r = 0.72). This correlation indeed exists between other heavy metals. As observed, there was a strong connection between all measured heavy metals in the spring. This correlation got weaker in the winter when there was almost no relationship between Zn, Cd, As and other elements. Furthermore, in the spring, a very strong relationship was observed between Ni and Zn (r = 0.933) as well as between As and Fe (r = 0.832). Cadmium and arsenic formed another highly correlated pair with a correlation coefficient of r = 0.88. Although the significant correlation is not always anticipated being a common source, inter-element relationships could still provide enhancing information on the probable sources and pathways of the metals. Heavy metals having a very strong correlation together may

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

result from the same source. In previous studies, Cluster Analysis (CA) has been exploited to classify heavy metals and to determine the source of their origin and their entrance (Sun *et al.* 2010). The cluster analysis results are respectively presented in Fig. 5(a) and (b) in spring and winter respectively. Surprisingly, Ni and Zn exhibited strong similarity, forming a pair with higher correlation, suggesting that they were probably originated from the same sources. Almost all areas accommodating mining and industrial operations (e.g. electric goods, dying, and insecticides), the studies have explored high levels of metals particularly Zinc and Nickel (Kramer 1976; Schmitt & Finger 1982). The spring cluster can be categorized into four classes. The first class is related to Pb- Fe and Zn, Cu, and Ni. The second class is bound up with As and Cd. The third class is connected to the loaded on As and Cd which is a weaker relationship and the most important component demonstrates lithogenic origin rather than the result of human activities. However, extra concentrations of iron attributed to arsenic and cadmium implies on their anthropogenic sources.

Table 2. Paired t test of the spring versus winter seasons surface water samples.

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	HPI winter –HPI spring	-0.49	0.64	0.09	-0.68	-0.30	-5.33	47	0.000
Pair 2	Pb winter – Pb spring	-1.43	10.62	1.53	-4.51	1.65	-0.93	47	0.356
Pair 3	Fe winter – Fe spring	30.18	92.45	13.34	3.34	57.03	2.26	47	0.028
Pair 4	Cu winter – Cu spring	-0.16	0.40	0.05	-0.27	-0.04	-2.76	47	0.008
Pair 5	Ni winter – Ni spring	-4.19	7.31	1.05	-6.32	-2.07	-3.97	47	0.000
Pair 6	Zn winter – Zn spring	-0.12	3.87	0.55	-1.25	0.99	-0.22	47	0.823
Pair 7	As wintetr – As spring	-0.12	0.13	0.019	-0.15	-0.08	-6.33	47	0.000
Pair 8	Cd winter – Cd spring	-.015	0.015	0.002	-0.01	-.010	-6.81	47	0.000

Finally, all metals present lower relationship with Pb (fourth class). In winter, on the other hand, almost no percent of similarity was observed between arsenic and other clusters due to the fact that most of the arsenic comes from human activities rather than the result of lithogenic origin. The cluster of heavy metals measured in the winter is shown in Fig. 5(b). As shown in Table 3, a strong correlation exists between Pb-Fe-Cu and Zn-Ni. Indeed, a weak and/or no significant correlation existed between As and other elements. There are several possible explanations for the observed dissimilarity between arsenic and other heavy metals. A possible explanation might be that beside the natural sources in the parent materials, non-point sources, like the application of manure, fertilizers, and pesticides also contributed to the elevated amounts of As in the agricultural soils (Hu *et al.* 2013). In accordance with the present results, Zamani *et al.* (2015) examined soil of Zanjan Province for heavy metals and demonstrated that there is no basic natural enrichment for As elements, moderate to severe enrichment by Zn, Fe and Pb.
Principal component analysis (PCA) has been applied to determine the degree of pollution by heavy metals from lithogenic action and anthropogenic sources (Rodríguez *et al.* 2008).
PCA of heavy metals in the spring proved two main categories whose Eigen values are greater than 1 (Table 4). The first category (PC) which includes 83.17% of total sample variance is related to Ni, Cu, Fe, and Zn. This result coincides with the conclusion of the correlation analysis and demonstrates that the source of this category (PC1) may be lithogenic origin rather than the consequence of human activities. Although some parts of zinc and nickel come from natural sources, human activities contribute to their higher concentrations as well, especially in surface waters. The prime anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgic operations involving zinc as well as the use of commercial products containing it (ATSDR 2005). Nickel is a naturally occurring element widely used in many industrial applications for shipbuilding, automobile, electrical, oil, food and chemical industries (ATSDR 2005).

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

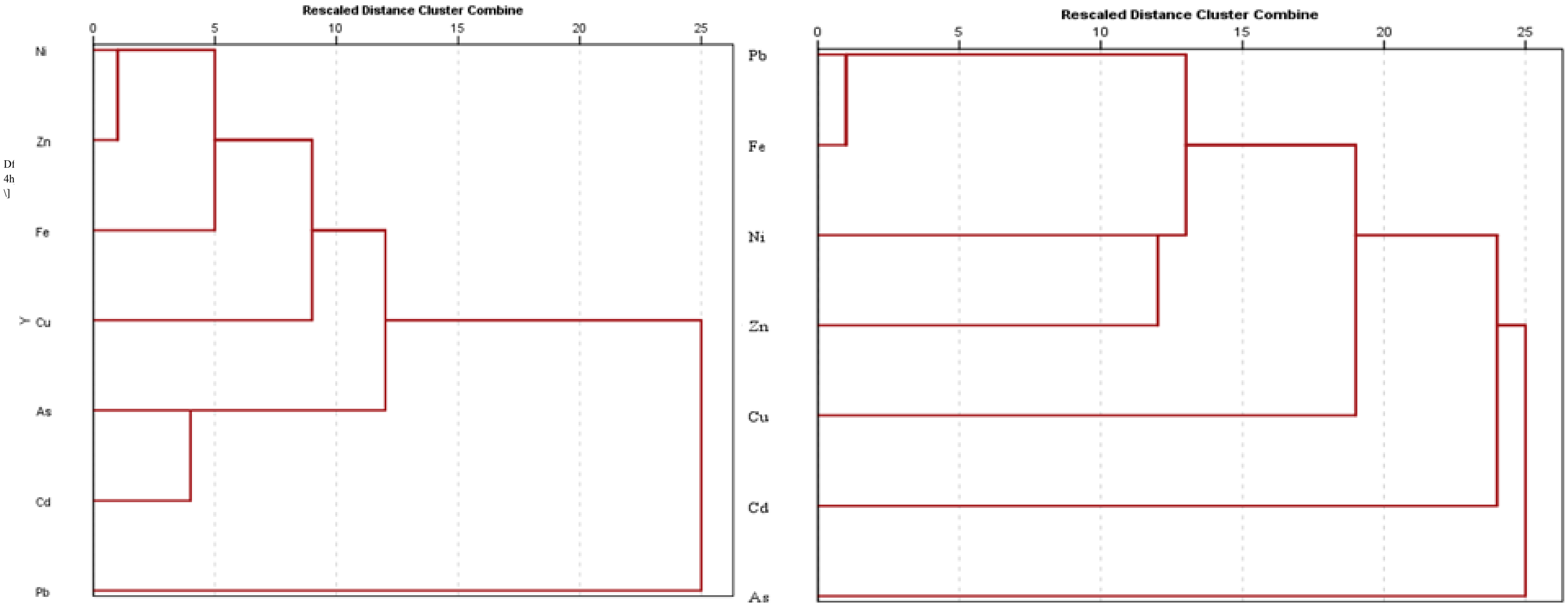

Fig. 5. Hierarchical dendogram of the heavy metals obtained by the single-linkage clustering method in spring (a) and winter (b).

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

Table 3. Spearman correlations matrix among heavy metal levels measured in surface water a (spring, n = 48), b (winter, n = 48).

(a)	Pb	Fe	Cu	Ni	Zn	As	Cd
Pb	1.000						
Fe	0.524	1.000					
Cu	0.522	0.653	1.000				
Ni	0.614	0.662	0.678	1.000			
Zn	0.614	0.662	0.678	0.933	1.000		
As	0.596	0.832	0.635	0.642	0.642	1.000	
Cd	0.728	0.768	0.618	0.657	0.657	0.880	1.000

(b)	Pb	Fe	Cu	Ni	Zn	As	Cd
Pb	1.000						
Fe	0.788	1.000					
Cu	0.608	0.590	1.000				
Ni	0.446	0.469	0.393	1.000			
Zn	0.424	0.458	0.440	0.524	1.000		
As	0.350	0.391	0.304	0.188	0.164	1.000	
Cd	0.449	0.607	0.393	0.202	0.228	0.218	1.000

Domestic wastewater treatment plant effluents and metal smelters are the major sources of Ni in the waters which later are accumulated in the biota, particularly in the phytoplankton or other aquatic plants (Cempel & Nikel 2006). The variability in these metal levels in the surface water might be primarily controlled by the parent materials of the soils.

The second category (PC_2) which includes 7.48% of total sample variance is related to Pb. However, the high Pb level in PC_2 is probably linked to industrial and agricultural activities, especially in the spring. According to Rodríguez *et al*. (2008), lead is a toxic metal mainly used as an anti-knock agent in gasoline (Lead tetraethyl – $Pb(C_2H_5)_4$) and in batteries. Principal component analysis in the winter is observed with two general categories in which Eigen values are greater than 1. PC_1 is closely related to Zn, Cu, Fe, and Pb which includes 81.46% of the total sample variance, while PC_2 is connected to Cd which includes 5.58% of the total sample variance. In the second component, Cd revealed much higher values than other heavy metals. The correlation analysis also indicated that As showed no significant correlation with the other six heavy metals, that implies on the different anthropogenic origins of As. The origin of cadmium in surface waters might be from other pollution sources, such as fertilizer usage and irrigation. Lu *et al.* (1992) reported that the phosphate fertilizers were generally the major source of trace metals among all inorganic fertilizers, and much attention has also been paid to Cd level in phosphate fertilizers. The main anthropogenic sources of Cd in cultivated soils are phosphorus-fertilizers, atmospheric deposition, animal manures, and to a smaller extent liming agents, sewage sludge, and bio waste. Cadmium has also been employed in various industrial activities (Lu *et al.* 1992).

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341

Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

The major industrial applications of cadmium comprise the production of alloys, pigments, and batteries. More assigned appraisal finds that samples highly polluted with Pb, Cd, Cu, Zn, and Ni were mainly located in the urban and industrial areas, as well as agricultural lands, approving that human activities contributed pronouncedly to the accumulation of these heavy metals in the surface waters. This is consistent with other studies exploring the relationship between the concentration of heavy metals in the environment and anthropogenic sources, mainly application of metal-containing pesticides on agricultural lands (Cheng & Hu 2010; Hu *et al*. 2013).

Distribution test, trend analysis and interpolation models of heavy metals

The untransformed and transformed data were examined for compliance with normal distribution using SPSS. The results exhibited that Pb, Cu, Ni and Zn in the spring, and Ni, Zn and HPI in the winter followed normal distribution (Table 5). Based on the geostatistical rules if the raw data or the logarithmic or exponential transformation of the data showed a normal distribution, the ordinary kriging model can be applied; if the data are not normally distributed but exhibited a central tendency, the universal kriging model is appropriate; and if the data are not normally distributed and follow no central tendency, the disjunctive kriging model is suitable (ESRI 2011). Semivariogram which clarifies the variations between two observed values at different distances was used to explain the spatial variability of the water heavy metal pollution (Goovaerts 1999). The main application of geostatistics to water science is the estimation and mapping of water qualirt attributes in unsampled areas. Prediction is made possible by the existence of spatial dependence between observations as assessed by the semivariogram. Table 5 denotes the fitted optimal semivariogram theoretical model and its associated parameters, obtained by fitting the measured concentrations of the seven heavy metals. The C_0/C_0+C values were also calculated. These values for Fe, Cu, Zn, As in the spring and Fe, Cu, Ni, Zn and As in the winter were less than 25% which shows strong spatial correlation. The C_0/C_0+C values for HPI were 0.36 and 0.2, respectively; thus exhibited moderate and high spatial correlation in the spring and winter, respectively.

The spatial distribution maps of the investigated elements (Fig. 6) were used for identifying metal enriched areas. The spatial patterns of the six heavy metals exhibited comparable trends (except for Fe) with the highest concentrations (lightest grey color) in the south, central and to some extent eastern part. As and Cd were accumulated mainly in the south and central areas, near the industrial plants. A very close geographical patterns were observed for Ni and Zn. This finding verifys the association between metals observed in the spearman correlation.

Table 4. Total variance explained and component matrices for the heavy metals in surface waters from the Zanjan rivers.

Heavy metals components	Spring		Winter	
	PC1	**PC2**	**PC1**	**PC2**
Pb	0.14	0.86	0.46	0.09
Fe	0.72	0.07	0.54	0.2
Cu	0.43	-0.018	0.43	-0.17
Ni	0.41	0.12	0.40	-0.31
Zn	0.41	0.12	0.41	-0.31
As	0.38	-0.35	0.17	0.31
Cd	0.36	-0.35	0.16	0.63
Eigen value	11.23	1.01	15.91	1.09
Total variance, %	83.17	7.48	81.46	5.58

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

A completely irregular distribution pattern was maintained for iron which indicate that soil parent materials and pedogenic processes are the main factors influencing its distribution.

Point pattern analysis using Kernel Density Estimation (KDE)

Density analysis takes known quantities of some phenomenon and spreads them across the landscape based on the quantity that is measured at each location and the spatial relationship of the locations of the measured quantities (ESRI 2011).

Density surfaces show which point(s) or line features are concentrated.

Kernel density estimation (KDE), on the other hand, transforms a dot pattern into a continuous surface, providing useful information of pollution distributions to allow easier detection of possible pollution hot spots. The resulting surfaces surrounding each point in kernel density are based on a quadratic formula with the highest value at the center of the surface (the point location) and tapering to zero at the search radius distance (ESRI 2011). The spatial patterns of Kernel density revealed Ni, Pb and Fe hot spots distributed in the study area (Data not shown). The sites with Ni, Fe and Pb hot spots were particularly located in the south, central and western parts. Furthermore, the results obtained enough evidence on multiple hot spots associated with these three heavy metals in the area. In addition, the spatial patterns revealed that Ni provided the largest set of hot spots near industrial and mining plants. The sites with Pb hot spots were in the central, west and south parts in the vicinity of the industrial plants and wastewater treatment facilities, while chemical fertilizer industry located in the central part. Hot spots of Ni were particularly highly distributed throughout the south part. The sites with Fe hot spots, on the other hand, were close both to the industrial plants and agricultural activities. Areas with high susceptibility of pollution were marked on these maps adjacent to the industrial plants and the agricultural activities (irrigation systems) as well.

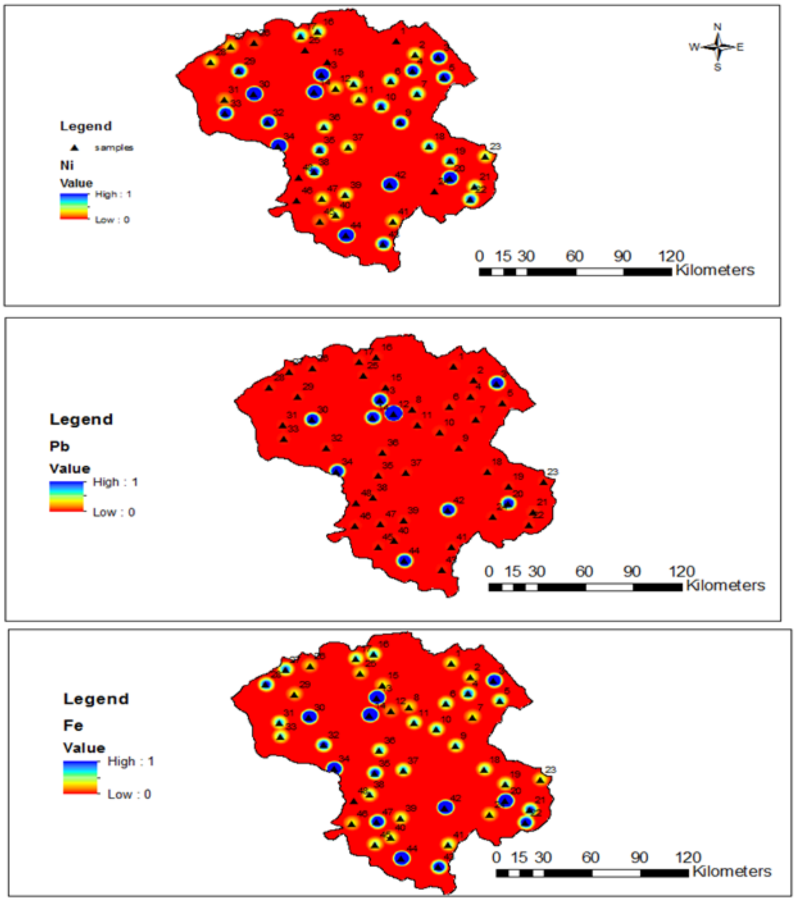

Fig. 6. Kernel density maps of Ni, Pb, and Fe (in spring).

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341

Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

Table 5. Statistical distribution, optimal statistical analysis and Theoretical semivariogram models of heavy metals.

	Element	Untransformed		Logarithmic transformed		Normal distribution status	Central tendency	Interpolation	Theoretical mode	Nugget (C_0)	Sill (C_0+C)	Range	$C_0/(C_0+C)$	Coefficient of determination
		Skewness	kurtosis	Skewness	kurtosis									
Spring	Pb	0.22	-0.5	-1.39	4.8	Basic normality	-	Ordinary kriging	Gaussian	1.65	1.48	4456	1.11	0.853
	Fe	0.46	-0.03	-0.6	2.12	Right- skewed	exist	Universal kriging	Exponential	123	558	191433	0.2	0.921
	Cu	1.92	4.44	0.07	3.15	Logaritmic- normality	-	Ordinary kriging	Gaussian	27	141	20326.3	0.19	0.956
	Ni	-0.02	-1.14	-1.01	0.05	Logaritmic- normality	-	Ordinary kriging	Exponential	3.35	4.14	24805	0.81	0.9
	Zn	-0.09	-1.12	-1.03	1.54	Logaritmic-normality	-	Ordinary kriging	Gaussian	145.5	2200	90236	0.065	0.932
	As	2.01	3.25	0.03	4.18	Right-skewed	Not exist	disjunctive kriging	Exponential	1.33	7.006	227365	0.189	0.9
	Cd	2.27	4.5	1.57	3.06	Right-skewed	exist	Universal kriging	Gaussian	0.06	0.05	53980	1.2	0.846
	HPI	1.58	4.54	0.03	1.06	Left- skewed	Not exist	disjunctive kriging	Exponential	0.34	0.92	3089	0.36	0.936
Winter	Pb	0.23	-0.5	1.63	3.82	Right-skewed	exist	Universal kriging	Exponential	150.3	31.45	90.6	0.34	0.911
	Fe	0.48	-0.35	0.59	2.55	Right-skewed	Not exist	Disjunctive kriging	Gaussian	7.1	85.02	68086	0.083	0.932
	Cu	1.09	5.05	-0.4	2.29	Left-skewed	exist	Universal kriging	Exponential	35.5	150	55362	0.23	0.9
	Ni	-0.02	-1.14	-0.08	0.65	Basic normality	-	Ordinary kriging	Gaussian	5.25	23.5	90656	0.22	0.902
	Zn	-0.09	-1.12	1.23	2.11	Basic normality	-	Ordinary kriging	Gaussian	121.3	670	24581	0.181	0.941
	As	2.06	3.25	-1.87	0.44	Right- skewed	-	Ordinary kriging	Exponential	145	780.4	73650	0.185	0.832
	Cd	2.27	4.53	0.18	2.46	Right- skewed	exist	Universal kriging	Gaussian	0.04	0.06	23410	0.66	0.855
	HPI	0.55	3.08	-0.06	2.36	Basic normality	-	Ordinary kriging	Gaussian	0.013	0.05	13373	0.2	0.966

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341
Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

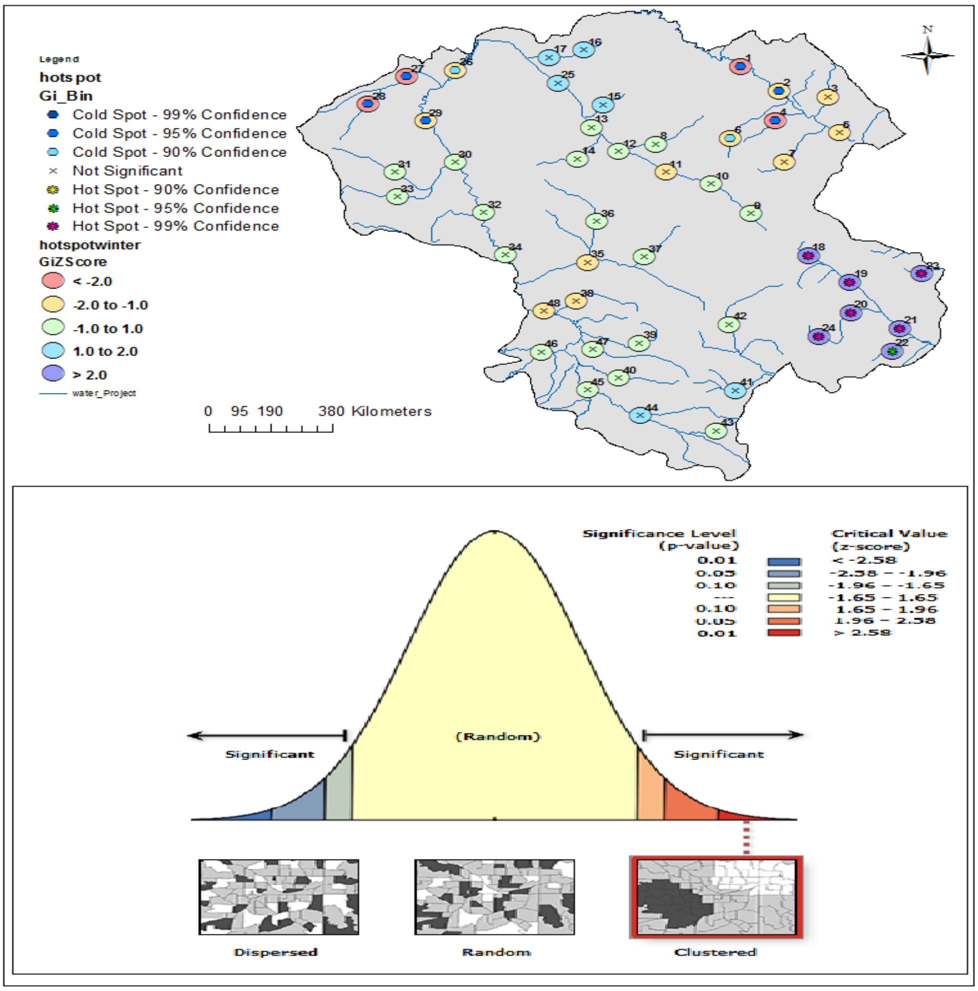

Fig. 7. Spatial distribution map of significant hotspots and cool spots for data.

Hot Spot Analysis

This in-depth analysis identifies statistically significant spatial clusters of high (hot spots) and low (cold spots) values. A high z-score and small *p*-value for a feature indicates a spatial clustering of high values. In effect, they suggest whether the observed spatial clustering of high or low values is more pronounced than one would expect in a random distribution of those same values. A low negative z-score and small *p*-value demonstrate a spatial clustering of low values. The higher (or lower) z-score, the more intense clustering. A z-score near zero participates in a demonstration of no apparent spatial clustering. The map of cluster analysis is shown in Fig. 5. As depicted in this Fig., HPI is clustery distributed in winter due to the high z score ($z > 2.58$) and low *p*-value (< 0.01). The cluster analysis showed seven sampling points located in the south east part of Zanjan Province (Fig. 7). According to their corresponding Z scores (> 2), all of these samples statistically are highly significant. This pattern corresponds to the industrial complexes and agricultural practices in the study area. Generally, most samples in the central and west parts were insignificant. This might be due to the lack of industrial units in these parts as compared to other ones.

There are also cold spots in northeast and northwest parts located in the forest and built-up areas where the HPI values were low.

CONCLUSION

On the basis of the results presented and discussed in this study, the following conclusions can be drawn:

The occurrence and spatial distribution of heavy metals (Fe, Cd, Cu, Ni, Pb and Zn) as well as As in Zanjan surface waters, Iran, were investigated over a period of two seasons (winter and spring). Among measured heavy

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

metals, the lead and nickel levels in the spring were higher than the values of Class I and II thresholds, while iron level in both seasons exceeded the value of Class I. However, the iron, lead and nickel level during spring, generally exceeded the Class I standard values in 14.5%, 18.75% and 12.5% of the sampling sites, respectively. The seasonal variations of heavy metals occurrence were detected. Most heavy metals showed higher concentration in the spring than in winter. The higher dilution rate in the cold season owing to the more precipitation might contribute the lower heavy metal levels. The seasonal variations of the heavy metal occurrences were also observed due to the agricultural an industrial effects on the surrounding areas especially in the spring. Significantly higher heavy metal levels were observed in water samples collected from southern and central regions compared to the other parts, pointing out the contribution of industrial complexes, agricultural activities, and mines besides natural resources suggesting that higher heavy metal levels could be discharged into the surrounding water during warm seasons.
The spatial dependency levels for the measured heavy metals showed strong relation on space as the ratio of the random variance (nugget) to the total variance were < 0.25 for most of variable except for Cd and Pb which indicates a weak spatial dependency.

ACKNOWLEDGEMENT
This work forms a part of the comprehensive project entitled 'Water and Soil Contamination Atlas of Zanjan Province.
The study was partially funded by Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran (2015–2016).
The authors are also thankful to Geographical Organization of Iran for providing topographic maps.

REFERENCES
Adams, WJ, Kimerle, RA & Barnett, JW 1992, Sediment quality and aquatic life assessment. *Environmental Science and Technology*, 26: 1865–1875.
Atafar, Z, Mesdaghinia, A, Nouri, J, Homaee, M, Yunesian, M & Ahmadimoghaddam, M 2010, Effect of fertilizer application on soil heavy metal concentration. *Environmental Monitoring and Assessment,* 160: 83–89.
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 Research,* 41: 4566–4578.
ATSDR 2005, U.S. Department of health and human services, Agency for toxic substances and disease registry.
Cai, L, Xu, Z, Ren, M, Guo, Q, Hu, X Hu, G, Wan, H & Peng, P 2012, Source identification of eight hazardous heavy metals in agricultural soils of Huizhou, Guangdong Province, China. *Ecotoxicology and Environmental Safety,* 78: 2–8.
Cempel, M & Nikel, G 2006, Nickel: a review of its sources and environmental toxicology. *Polish Journal of Environmental Studies,* 15: 375–382.
Chehregani, A, Noori, M & Yazdi, H 2009, Phytoremediation of heavy-metal-polluted soils: Screening for new accumulator plants in Angouran mine (Iran) and evaluation of removal ability. *Ecotoxicology and Environmental Safety,* 72: 1349 - 1353.
Chen, YF 2011, Review of the research on heavy metal contamination of China's city soil and its treatment method. *China Population, Resources and Environment,* 21: 536-539.
Cheng, H & Hu, Y 2010, Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environmental Pollution,* 158: 1134–1146.
Delavar, MA & Safari, Y 2016, Spatial distribution of heavy metals in soils and plants in Zinc Town, northwest Iran. *International Journal Environmental Science Technology,* 13: 297–306.
ESRI. 2011 www.esri.com/legal/li- censing/ software-license.html
Goovaerts, P 1999, Geostatistics in soil science: State of the art and perspectives. *Geoderma*, 89: 1-45.
Hani, A & Pazira, E 2011, Heavy metals assessment and identification of their sources in agricultural soils of Southern Tehran, Iran. *Environmental Monitoring and Assessment*, 176: 677–691.
Horton, PK 1965, An index-number system for rating water quality. *Journal of the Water Pollution Control Federation,* 37: 300–06.

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

Hu, Y, Liu, X, Bai, J, Shih, K, Zeng, EY & Cheng, H 2013, Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. *Environmental Science and Pollution Research,* 20: 6150–6159.

Kohušová, K, Havel, L, Vlasák, P & Tonika, J 2011, A long term survey of heavy metals and specific organic compounds in biofilms, sediments, and surface water in a heavily affected river in the Czech Republic. *Environmental Monitoring and Assessment.* 174: 555–572.

Kramer, RL 1976, Effects of century old Missouri Lead mining operations upon the water quality sediments, and biota of Flat River Creek, M.S. Thesis, University of Missouri, Rolla, Missouri.

Li, S & Zhang, Q 2010, Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. *Journal of Hazardous Materials*, 181(1): 1051–1058.

Lin, HJ, Sunge, T, Cheng, CY, Guo & HR 2013, Arsenic levels in drinking water and mortality of liver cancer in Taiwan. *Journal of Hazardous Materials*, 262:1132-8.

Lu, RK, Xiong, LM & Shi, ZY 1992, A review about studies on cadmium in soil-crop ecosystem. *Soils,* 24: 129–132 (In Chinese).

Madani, K 2014, Water management in Iran: what is causing the looming crisis? *Journal of Environmental Studies and Sciences,* 4: 315–328

Mohammadian, M, Nouri, J, Afshari, N, Nassiri, J & Nourian, M 2008, Investigation of heavy metals concentrations in the water wells Close to Zanjan zinc and lead smelting plant. *Iranian journal of health and environment,* 1: 51-56.

Mohan, SV, Nithila, P, Reddy & SJ 1996, Estimation of heavy metal in drinking water and development of heavy metal pollution index. *Journal of Environmental Science and Health, Part A,* 31: 283–289.

Naderi, A, Delavar, MA, Kaboudin, B & Askari, MS 2017, Assessment of spatial distribution of soil heavy metals using ANN-GA, MSLR and satellite imagery. *Environmental Monitoring and Assessment,* 189(5): 214-220.

Ozmen, H, Kulahci, F, Cukurovali, A & Dogru, M 2004, Concentrations of heavy metal and radioactivity in surface water and sediment of Hazar Lake (Elazig, Turkey). *Chemosphere*, 55(3): 401–408

Panigrahy, BP, Singh, PK, Tiwari, AK, Kumar, B & Kumar, A 2015, Assessment of heavy metal pollution index for groundwater around Jharia coalfield region, India. *Journal of Biodiversity and Environmental Sciences,* 6: 33–39.

Parameters of water quality. Interpretation and Standards. Environmental Protection Agency (EPA) 2001. Published by the Environmental Protection Agency, Ireland.

Parizanganeh, A, Hajisoltani, P & Zamani, A 2010, Assessment of heavy metal pollution in surficial soils surrounding Zinc Industrial Complex in Zanjan-Iran. *Procedia Environmental Sciences,* 2: 162-166.

Rodriguez Martin, JA, Ramos-Miras, JJ, Boluda, R & Gil, C 2013, spatial relations of heavy metals in arable and greenhouse soils of a Mediterranean environment region (Spain). *Geoderma,* 200-201: 180-188.

Rodríguez, JA, Nanos, N, Grau, JM, Gil, L & López-Arias, M 2008, Multiscale analysis of heavy metal contents in Spanish agricultural topsoil. *Chemosphere,* 70: 1085–1096.

Schmitt, CJ & Finger, SE 1982, The dynamics of metals from past and present mining activities in the big and black river watersheds, Southeastern Missouri. U.S., Fish and Wildlife Service. Columbia National Fisheries Research Laboratory. Columbia, USA.

Schwarzenbach, RP, Egli, T, Hofstetter, TB, von Gunten, U & Wehrli, B 2010, Global Water Pollution and Human Health. *Annual Review of Environment and Resources,* 35: 109–136.

Shannon, MA, Bohn, PW, Elimelech, M, Georgiadis, JG, Marin, BJ & Mayes, AM 2008, Science and technology for water purification in the coming decades. *Nature,* 452.

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

Sun, YB, Zhou, QX, Xie, XK & Liu, R 2010, Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *Journal of Hazardous Materials,* 174: 455-462.

Tiwari, AK, Maio, MD, Singh, PK & Mahato, MK 2015, Evaluation of Surface Water Quality by Using GIS and a Heavy Metal Pollution Index (HPI) Model in a Coal Mining Area, India. *Bulletin of Environmental Contamination and Toxicology,* 95: 304–310.

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41 Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
DOI: 10.22124/cjes.2019.3341 Article type: Research

US EPA 2000, Supplementary guidance for conducting health risk assessment of chemical mixtures, Risk Assessment Forum Technical Panel.

Zamani, AA, Yaftian, MR & Parizanganeh, A 2012, Multivariate statistical assessment of heavy metal pollution sources of groundwater around a lead and zinc plant. *Journal of Environmental Health Science and Engineering,* 9: 29-36.

Zamani, AA, Yaftian, MR & Parizanganeh, A 2015, Statistical evaluation of topsoil heavy metal pollution around a lead and zinc production plant in Zanjan province, Iran. *Caspian journal of environmental sciences,* 13(4): 349-361.

Zhang, J, Mauzerall, DL, Zhu, T, Liang, S, Ezzati, M & Remais, JV 2010, Environmental health in China: progress towards clean air and safe water. *Lancet,* 375: 1110–1119.

Zhou, JM, Dang, Z, Cai, MF & Liu, CQ 2007, Soil heavy metal pollution around the Dabaoshan Mine, Guangdong Province, China. *Pedosphere,* 17: 588–594.

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341

Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research

تجزیه و تحلیل چند متغیره و زمین آماری توزیع فضایی فلزات سنگین و منابع بالقوه مولد آنها در آبهای سطحی

محمد رفیعی[۱]، اکبر اسلامی[۱]، رضا سعیدی[۲]، مهرنوش ابطحی[۱]، مهسا جهانگیری راد[۳*]

۱- مرکز تحقیقاتی کنترل عوامل مخاطره آمیزمحیطی و شغلی، دانشگاه علوم پزشکی شهید بهشتی، تهران، ایران
۲- دانشکده بهداشت و ایمنی، دانشگاه علوم پزشکی شهید بهشتی، تهران، ایران
۳- مرکز تحقیقات آب، دانشگاه آزاد اسلامی واحد علوم پزشکی تهران، ایران

(تاریخ دریافت: ۹۷/۰۷/۱۰ تاریخ پذیرش: ۹۷/۱۲/۰۶)

چکیده

اگرچه رشد اقتصادی ناشی از صنعتی‌شدن جوامع سبب ارتقای بهداشت و شاخص‌های کیفیت زندگی شده است، ولی از طرف دیگر باعث پخش آلاینده‌های شیمیایی تهدید کننده زندگی انسان به محیط زیست گشته است. مطالعه حاضر سطوح آلایندگی فلزات سمی را در حوضه شهر زنجان که به عنوان منبع غنی از سرب و روی است، بررسی می‌کند. غلظت فلزات محلول Fe, Cu, Cd, Pb, Zn, As در نمونه‌های آب توسط دستگاه ICP-MS سنجش، و سپس و میزان آلودگی به فلزات سنگین توسط شاخص HPI محاسبه شد. آنالیزهای آماری چند متغیره شامل آزمون همبستگی پیرسون، آنالیز سلسله مراتبی و عنصر معیار برای تعیین ارتباط بین غلظت‌های فلزات سنگین استفاده شد. آنالیزهای زمین آماری برای بررسی نحوه پراکندگی و منابع احتمالی آلودگی به کار رفت. نتایج نشان داد که غلظت فلزات سنگین در فصل بهار نسبت به زمستان بیشتر بود، هرچند که شاخص HPI در این مدت از محدوده ۱۵ فراتر نرفت. فعالیت‌های انسانی در بیشتر مواقع مسبب اصلی تغییر کیفیت آب در محدوده مورد مطالعه بوده و در برخی مواقع، فعالیت‌های طبیعی با منشا زمینی بر اساس ضریب همبستگی به دست آمده، ارتباط قوی بین فلزات سنگین در ماه بهار دیده شد و این ارتباط در زمستان به دلیل اثرات Cd, As Zn, با دیگر فلزات کاهش نشان داد. میزان شاخص آلودگی در محدوده مورد نظر به صورت زیر کاهش نشان داد: مناطق جنگلی < مناطق ساخته شده < پیکره‌های آبی < مناطق کشاورزی. مناطق با بیشترین بار فلزات سنگین اندازه‌گیری شده در جنوب منطقه مورد مطالعه مشخص شد.

*مؤلف مسئول

Bibliographic information of this paper for citing:

Rafiee, M, Eslami, A, Saeedi, R, Abtahi, M, Jahangiri rad, M 2019, Multivariate and geostatistical analysis of spatial distribution and potential sources of heavy metals in surface waters. Caspian Journal of Environmental Sciences, 17: 23-41

Caspian J. Environ. Sci. Vol. 17 No. 1 pp. 23~41
DOI: 10.22124/cjes.2019.3341
Received: Oct. 02. 2018 Accepted: Feb. 25. 2019
Article type: Research