

Assessment of Heavy Metals in Deep Groundwater Resources of the Kathmandu Valley, Nepal

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Abstract

A study was carried out to address distribution of some heavy metals in deep groundwater resources of the Kathmandu Valley. Groundwater samples were analyzed for pH, ORP, EC, iron, manganese, zinc, and arsenic in 41 deep groundwater wells during pre monsoon and post monsoon seasons for two consecutive years. The study showed elevated concentrations of iron and manganese in the groundwater of the valley. The occurrence of elevated concentrations of arsenic was also exhibited and observed up to 0.160 mg/L. The spatial distribution patterns demonstrated elevated levels of EC, iron, manganese, zinc, and arsenic in central groundwater district (CGWD) of the valley. The monitored parameters except ORP are not significantly correlated with studied time series, inferring similar distribution of the metals. Correlation analysis and principal component analysis (PCA) were performed to find out relationships among examined parameters and metals. The ORP has strong negative correlations with iron, manganese, and arsenic, suggesting reductive mobilization mechanism of the metals in the groundwater. PCA results showed that iron and manganese with high positive loading factors were due to common natural source of origin of these metals in the groundwater, while negative loading factors of pH and ORP indicated that iron and manganese mobilization was favorable in low pH and reducing environment. Cluster analysis (CA) evidenced high mineralization in most of the wells in the CGWD.

Keywords

Heavy Metals, Deep Groundwater, Principal Component Analysis, Cluster Analysis, Mineralization

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1. Introduction

Heavy metals are commonly defined as those having a specific density of five times higher than water *i.e.*, 5 g/cm³ and denote metals and metalloids that are associated with pollution and toxicity. These also include elements that are required by organisms at rather low concentrations [1]-[3]. However, a heavy metal has little to do with density but concerns with chemical properties. The term heavy metal includes both essential and nonessential trace metals which may be toxic to the organisms depending on their own properties, availability (chemical speciation), and concentration levels [4]. Some heavy metals can become toxic or aesthetically undesirable when their concentrations are only too great. Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives, and their potential to accumulate in different body parts. The environmental exposure to heavy metals is a well-known risk factor for cancer [5]. The heavy metals and metalloids, including arsenic (As), manganese (Mn), lead (Pb), cadmium (Cd), and mercury (Hg), are potentially biohazardous, have their strong toxicity at even low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health [1] [3] [4] [6].

Heavy metal contamination in groundwater either from natural or anthropogenic sources is one of the environmental issues due to its impact in public health [7]. The water supplies around the world possess serious problems due to enhanced heavy metal concentrations [8] [9]. The problems of groundwater pollution, especially from heavy metals have now raised concerns all over the world. The rapid growth of the Kathmandu Valley increases the demand of the water supply. The urbanization rate in the valley is very high. The decadal population growth rate in Kathmandu district is 61.23% [10]. Therefore, there is growing pressure on groundwater resources in the valley. Groundwater is one of the important water resources in the valley. It constitutes 60% - 70% and about 50% of the total water supply during dry and wet seasons, respectively [11] [12].

Many investigators have carried out studies regarding heavy metals in the groundwater of the Kathmandu Valley. An earlier study carried out by Khadka [13] revealed that the deep groundwater contained high concentrations of iron and manganese. The occurrence of elevated concentrations of heavy metals has been detected in the deep groundwater [14]-[20]. However, there have been no long term studies concerning heavy metal contamination in the groundwater resources in the valley.

This study aimed to assess some heavy metals in deep groundwater wells of the Kathmandu Valley during pre monsoon and post monsoon seasons for two consecutive years. The spatial distribution patterns of the metals in northern groundwater district (NGWD), central groundwater district (CGWD), and southern groundwater district (SGWD) of the valley were investigated. Additionally, the study attempted to identify influential physico-chemical parameters and metals using principal component analysis (PCA). Furthermore, the study was also focused on to classify groups of deep groundwater wells by performing multivariate hierarchical cluster analysis (CA) based on major groundwater quality parameters.

2. Materials and Methods

2.1. Study Area

The Kathmandu Valley is roughly circular in shape with diameter of about 25 km and an average altitude of 1300 m (above sea level), located in central Nepal Himalaya within 27°32'N to 27°49'N and 85°12'E to 85°32'E (Figure 1). Its surrounding hills are approximately 2800 m (above sea level). The area of the valley is about 650 km². The valley comprises of Kathmandu, Lalitpur, and Bhaktapur districts. Kathmandu is the largest and the capital city of Nepal.

The Kathmandu Valley is an intermontane basin filled with Pliocene-quaternary fluvio-lacustrine unconsolidated sediments which is up to 500 m thick [21]. Limestones are abundant to the south, whereas to the east and west, the valley is bordered by phyllites and siltstones. Granite gneisses are located on the northern border of the valley [22].

On the basis of hydrochemical and hydrogeological studies, JICA [23] divided the deep groundwater of the Kathmandu Valley into three groundwater districts: NGWD, CGWD, and SGWD. The NGWD has greater potentialities for recharge of the groundwater and is the main aquifer in the valley. About 60 m thick of highly permeable micaceous quartz, sand, and gravel are main upper deposits of the groundwater district. The upper deposits in the CGWD are covered by impermeable thick stiff black clay, named as Kalimati Formation which is rich in organic matter. The groundwater recharge is limited by the presence of the black clay layer in the



Figure 1. Sampling locations in the study area.

CGWD. The major deposits in the SGWD are thick impermeable clays and basal gravels with low permeability. Conversely, there are sand and gravel deposits in some parts of the eastern area of the SGWD which has a potential for groundwater recharge [23]-[25].

2.2. Sampling and Analysis of Groundwater

The samples were collected from 41 deep groundwater wells during pre monsoon and post monsoon seasons in 2012 and 2013 (Figure 1). The depth of the groundwater wells was varied from 84 to 304 m. The high density polyethylene (HDPE) sampling bottles treated with 5% HNO₃ and rinsed with double distilled water were used for sample collection. The samples were collected after pumping the wells for five minutes to get the representative samples. The samples for total iron, total manganese, and total zinc were preserved by adding 1.5 mL/L of conc. HNO₃. The samples for total arsenic were preserved with 2 mL/L conc. HNO₃. The groundwater samples for metals were brought to the laboratory and stored at temperature below 4°C before chemical analysis. Oxidation reduction potential (ORP), electrical conductivity (EC), pH, and temperature (T) were measured in the fields. The ORP and pH were measured by Hanna HI 8314 pH/ORP meter and the EC was measured by Jenway 4200 conductivity meter. The total iron, total manganese, and total zinc were analyzed by Varian AA 240 atomic absorption spectrometer (AAS). The analysis of arsenic was carried out using the AAS with vapor generation accessory Varian VGA-77. The samples for total iron, total manganese, total zinc, and total arsenic were digested with high purity HNO₃ (Merck) within a week of sample collection as per APHA-AWWA-WEF (2005) [26]. The digestion of samples with the HNO_3 ensures total extraction of the metals. The metal standard solutions for AAS (Merck) traceable to standard reference material (SRM) of NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) were used for preparation of calibration solutions. Three replications of each analysis were performed and mean values were used for calculations. Analytical precision was in good agreement, generally better than 5% RSD. The analyses of the metals were carried out at CEMAT Water Laboratory, Kathmandu, Nepal. Statistical packages PASW STATISTICS 18.0 for WINDOWS (SPSS Inc., an IBM Company, Chicago, IL, USA, 2009) and Microsoft Office-Excel 2007 (Redmond, WA, USA) were used for the statistical analyses. ArcGIS 9.3 was used for mapping and spatial analysis.

2.3. Statistical Treatment of Data and Multivariate Analysis

Shapiro-Wilk test was performed to test the goodness of fit of data to normal distribution. Most of the water quality parameters examined were not normally distributed except temperature. Therefore, Spearman's rank correlation coefficient was applied as a non-parametric measure of correlation between the monitored variables [19] [27]. Kaiser-Meyer-Olkin (KMO) and Bartlett's test were employed to examine the suitability of data for PCA. The KMO is a measure of sampling adequacy that indicates the proportion of variance (common variance) which might be caused by underlying factors. High value (close to 1) generally indicates that PCA analysis may be useful [28].

PCA is an effective pattern recognition technique in multivariate analysis that attempts to explain the variance of a data set of inter-correlated variables with a smaller set of independent variables, principal components (PCs). PCA was performed on the normalized data to compare the monitored groundwater quality variables and to identify the factors that influence each other. The PCs were identified with eigen value >1.0 and factor loading matrix was calculated on the basis of the variables. The application of multivariate statistical technique assists to simplify and organize large data sets by data reduction and interpretation of the variables [29]-[31]. The multivariate statistical techniques were performed on experimental data standardized through z-scale transformation in order to avoid misclassification emerged from wide differences in the dimension of data both numerical values and variance of the variables [32] [33]. The standardization process makes different units of data dimensionless [34], thereby increase or decrease influence of variables whose variance is small or large, respectively [28].

Varimax rotation is used to maximize the variance of the extracted principal axes [35]. The factor-loading matrix is rotated to an orthogonal simple structure through the axis defined by PCA is a varimax rotation which results in varifactors (VFs). The varimax rotation reduces the contribution of less significant variables obtained from PCA increasing the participation of the variables with higher contribution [32] [36].

Multivariate statistical analysis, CA is applied to detect the similarity among different sampling sites. In this study, hierarchical CA was applied and the data were treated after data scaling by z-scale transformation, and Ward's method of linkage with squared Euclidean distance as measure of similarity was used. The clustering procedure generates either cluster or groups based on similar characteristics. The results indicate that CA technique is useful in offering reliable classification of groundwater resources in the study area and are used to find the true groups of data. Dendrogram is constructed on the basis of the levels of the similarity [37].

3. Results and Discussion

3.1. Monitored Groundwater Quality Parameters

The mean of values monitored groundwater quality parameters and the summary of statistical data during pre monsoon and post monsoon of 2012 and 2013 in the groundwater wells are presented in Table 1 and Table 2, respectively. The pH were nearly neutral that ranged from 6.3 to 7.9 (mean = 6.8). The EC ranged from 92 to 1729 μ S/cm (mean = 572 μ S/cm).

Many groundwater wells in the study area contained elevated iron and manganese concentrations. The mean iron and manganese concentration were 3.75 mg/L and 0.44 mg/L, respectively. The groundwater wells were under reduced conditions as indicated by low ORP values which ranged from -190 to 135 mV (mean = -61.3 mV). In an anaerobic environment, reduction of arsenic and Fe/Mn oxyhydroxides would lead to desorption of arsenic, and release of Fe(II) and Mn(II) [38]-[40]. In addition, the chemical composition of the major elements of the sediments: Fe₂O₃ ranged from 1.48 to 9.55 wt% and MnO ranged from 0.01 to 0.18 wt% in the Kathmandu Valley [41] could be related to occurrence of elevated concentration of iron and manganese in the groundwater. Zinc concentration in the study area is relatively lower that ranged from <0.003 to 0.951 mg/L (mean = 0.065 mg/L).

This study revealed a wide variation of arsenic concentrations in the deep groundwater which ranged from

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Well ID	рН	EC (µS/cm)	ORP (mV)	T (°C)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	As (mg/L)
1	7.1	649	-152	23.8	0.90	0.17	0.020	BDL
2	7.3	511	-116	25.0	1.61	0.23	0.041	0.143
3	6.6	958	-105	25.2	6.41	0.81	0.043	0.015
4	7.2	403	-81	23.2	2.15	0.23	0.057	0.056
5	7.8	165	106	21.9	0.06	BDL	0.029	BDL
6	6.6	1122	-71	24.1	4.14	1.50	0.020	0.012
7	6.5	800	-81	26.0	6.86	0.77	0.647	0.011
8	6.9	1041	-113	25.7	4.14	0.89	0.060	0.007
9	6.6	1051	-83	26.5	3.80	0.55	0.075	0.007
10	6.4	482	104	21.4	0.29	0.70	0.494	BDL
11	6.8	185	-58	23.7	1.51	0.16	0.018	0.003
12	6.7	393	-74	24.4	4.43	0.25	0.031	0.005
13	6.7	751	-88	24.6	4.83	0.38	0.026	0.007
14	6.5	326	-70	21.5	6.66	0.30	0.025	BDL
15	6.8	186	-58	25.0	0.97	0.13	0.019	0.004
16	6.6	225	-53	24.4	1.38	0.19	0.051	0.006
17	6.7	193	-72	23.9	1.60	0.19	0.011	0.004
18	6.7	462	-67	24.9	2.63	0.19	0.019	0.006
19	6.6	408	-86	27.1	2.20	0.45	0.012	0.011
20	6.6	232	-67	23.6	2.38	0.20	0.012	0.008
21	6.5	923	-97	24.3	6.27	1.08	0.043	0.011
22	6.6	757	-99	25.9	6.70	0.77	0.017	0.037
23	6.5	902	-94	25.6	7.21	1.08	0.013	0.009
24	7.1	441	-114	22.2	4.87	0.66	0.053	0.019
25	6.5	985	-118	24.8	7.95	0.61	0.040	0.006
26	6.6	1707	-114	25.4	8.08	0.26	0.023	0.003
27	6.8	882	-102	23.1	5.02	0.46	0.060	0.056
28	6.5	1097	-107	25.0	7.22	1.10	0.018	0.010
29	6.6	1300	-102	24.9	5.42	0.44	0.049	0.004
30	/.1	/64	-143	23.3	3.69	0.46	0.032	0.025
31	6.9	439	-58	25.1	1.89	0.29	0.025	0.004 DDI
32	0.5	240	-00	22.1	5.11	0.35	0.019	BDL
33 24	0.7	169	-40	21.5	5.24	0.11	0.017	0.005
34 25	0.5	615	-87	25.5	5.54	0.45	0.019	0.005
33 26	0./	90 150	38 42	21.0	0.52	0.02	0.022	BDL
30 27	0.9	150	-42	22.5	1.01	0.05	0.100	DDL
31 20	7.0 7.5	10/	-09	24.0	3.25	0.13	0.015	0.003
30 30	1.5 7.6	18C 207	04 Q1	20.0 18.4	0.11	0.04 BDI	0.027	BDI
37 40	7.0	207	01	10.4	0.07		0.095	עם זמק
40 71	7.0 6.8	297 185	-85	22.0	2.50	0.85	0.237	BDL
41	0.0	10.2	-0.2	L1.1	11.44	V	0.011	לות

 Table 1. Mean values of monitored groundwater quality parameters during pre monsoon and post monsoon of 2012-2013.

BDL = Below detection limit.

Table 2. Summary of statistical data for monitored groundwater quality parameters.							
Variable	Unit	Min.	Max.	Median	Mean	SD	
pH		6.3	7.9	6.7	6.8	0.35	
EC	µS/cm	92	1729	461	572	381	
ORP	mV	-190	135	-82	-61.3	70.1	
Т	°C	16.8	28.6	23.9	23.9	2.27	
Fe	mg/L	BDL	12.99	3.15	3.75	2.81	
Mn	mg/L	BDL	1.75	0.34	0.44	0.37	
Zn	mg/L	BDL	0.951	0.026	0.065	0.186	
As	mg/L	BDL	0.160	0.005	0.013	0.024	

Min. = Minimum, Max. = Maximum, SD = Standard deviation, BDL = Below detection limit.

<0.003 to 0.160 mg/L; the mean concentration being 0.013 mg/L. Arsenic concentration in about 27% of the examined wells exceeded World Health Organization (WHO) guideline value for drinking water of 0.010 mg/L [42]. Arsenic concentration in the sediments of the valley averages 8 mg/kg (ranging from 3 to 25 mg/kg) [43] could be the probable source of arsenic in the groundwater. The widespread lacustrine clay in the valley is rich in organic matter [44]. The presence of organic matter results in the reduction of iron and manganese in groundwater [45]. Arsenic is either adsorbed into the surface or coprecipitated in Fe/Mn oxyhydroxides [39] [46] and its dissolution or desorption in reducing environment was observed by many researchers [47]-[50]. Several investigators have reported the elevated arsenic concentrations in the groundwater of the Kathmandu Valley [15] [16] [18] [20].

The temporal variation of the monitored physicochemical parameters and metals during pre monsoon and post monsoon seasons of 2012 and 2013 were evaluated through time-parameter Spearman's correlation matrix. The parameters were not significantly (p > 0.05) correlated with studied time series except for ORP (r = 0.262, p < 0.01), implying that there is no temporal variation of pH, EC, iron, manganese, zinc, and arsenic in the groundwater.

Spearman's rank correlation coefficients were determined to establish the relationships of monitored parameters in the groundwater (Table 3). The pH has strong negative correlations with iron and manganese, which can be explained by dissolution of the metals in acidic media. The pH has no significant correlation with zinc. Zinc is one of the most mobile heavy metals in groundwater because it is available as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control

Table 3. Spearman's rank correlation coefficients of monitored groundwater quality parameters ($n = 164$).							
Parameter	рН	EC	ORP	Fe	Mn	Zn	As
pH	1.000						
EC	-0.286**	1.000					
ORP	-0.001	-0.589**	1.000				
Fe	-0.472**	0.576**	-0.566**	1.000			
Mn	-0.395**	0.682**	-0.404**	0.677**	1.000		
Zn	0.121	0.211**	0.011	-0.068	0.135	1.000	
As	-0.032	0.477**	-0.512**	0.375**	0.468**	0.096	1.000

**Significant value at p < 0.01.

zinc solubility [51]. Arsenic has weak negative correlation with the pH. On the contrary, many investigators have observed positive correlation between arsenic and pH in groundwater, which is probably due to desorption processes at higher pH values [52]-[54]. In this study, the weak negative correlation indicates that there is minimal effect of pH in release of arsenic. Arsenic is positively correlated with iron and manganese, suggesting common geogenic origin of these metals. The ORP has strong negative correlations with iron, manganese, and arsenic, which is attributed to the release of these metals in reducing environment in the groundwater. Zinc has no significant correlation with ORP.

3.2. Spatial Distribution of Major Monitored Groundwater Quality Parameters

The spatial distribution patterns of major groundwater quality parameters including iron, manganese, zinc, and arsenic are illustrated in **Figures 2-7**. Most of the groundwater wells of the CGWD exhibited higher concentrations of metals and EC value, and lower ORP value. The elevated concentrations of the metals are attributed to the reducing environment in the CGWD. In addition, the contents of Fe_2O_3 in the sediments are generally high (ranges <0.5 to 15 wt%), and are uniformly higher in the fine sediments of the central basin (average 7 wt%) [55]. Though, the concentrations of zinc are lower in all the examined groundwater wells, the spatial distribution pattern of zinc reveals that few groundwater wells in the CGWD exhibited relatively higher concentrations, indicating that the higher zinc abundances in fine-grained sediments. Zinc abundances are <10 mg/kg in most sand and gravel sediments, whereas in the fine-grained sediments (e.g., silty clay) are relatively higher (up to 94 mg/kg) [43]. Many groundwater wells in the NGWD and SGWD have lower iron, manganese, and arsenic concentrations. The finer particles and trace elements in the sediments of the central part of the valley are high [43]. The decrease in grain size tends to increase the concentration of metals in the sediments [43] [56] [57], because smaller particles in the sediments collectively hold larger surface area available for the formation of metal hydroxide coatings and to adsorb metal ions. Therefore, variation in grain size has an important role in the mobilization of metals in groundwater.



Figure 2. Spatial distribution pattern of EC.

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Figure 7. Spatial distribution pattern of arsenic.

3.3. Principal Component Analysis

The KMO measure of sampling adequacy was 0.682, which shows that PCA analysis is useful in data interpretation and analysis. Bartlett's test of sphericity was significant (p < 0.05), indicating that PCA can achieve significant reduction in the dimensionality of the original data set [32]. In the groundwater wells, VFs were indentified with eigen value >1.0, accounting almost 73.6% of the total variance, and factor loading matrix is calculated on the basis of the groundwater quality parameters measured during pre monsoon and post monsoon in 2012 and 2013 (Table 4). In the first VF, 38.8% of the total variance is contributed by positive loadings of EC, iron, and manganese. The contribution of EC is indicated by its high loading factor and is due to the presence of dissolved ions. The high loading factors of iron and manganese reveals that these metals have common natural source of origin in the groundwater. The concentrations of iron and manganese in the groundwater are more likely due to the dissolution and weathering process of the minerals. Additionally, moderate negative loading factors of pH and ORP indicate that iron and manganese mobilization is favorable in low pH and reducing environment. Reducing environment is responsible for the release of iron and manganese, and Fe/Mn oxyhydroxide precipitation and its ability to adsorb metals are the major controlling factors that lead to metal contents in groundwater [58]. This may exhibit the influence of geochemical processes and hydrodynamic behavior of iron and manganese in groundwater. The second VF accounting for 19.8% of total variance is contributed by high loading factor of zinc and moderate loading factor of ORP. In oxidizing environment, dissolution of zinc is favorable and it readily precipitates under reducing conditions [51]. The third VF contributing for 15.0% of total variance is contributed by strong positive loading factor of arsenic. This VF represents only arsenic, which indicates that mobilization of arsenic in groundwater is distinctive and can be related to reduction of Fe/Mn oxyhydroxides.

3.4. Cluster Analysis

In the present study, CA is based on the major groundwater quality parameters of the deep groundwater samples. Hierarchical CA was performed to construct dendrogram (Figure 8). CA classified two statistically significant

Table 4. Loadings of monitored variables of first three rotated principal components (varifactors) (n = 164).							
Variables	VF 1	VF 2	VF 3				
pH	-0.620	-0.043	0.495				
EC	0.791	0.016	0.141				
ORP	-0.636	0.538	-0.248				
Fe	0.824	-0.148	-0.114				
Mn	0.772	0.306	0.004				
Zn	0.101	0.912	0.003				
As	0.078	-0.033	0.928				
Eigen value	2.71	1.38	1.05				
% Variance	38.8	19.8	15.0				
% Cumulative variance	38.8	58.6	73.6				



Figure 8. Dendrogram of hierarchical cluster analysis using Ward's method.



Figure 9. Box and whisker plot of EC, ORP, and metals of group (A) and (B) resulting from CA representing min, max, median, 25th, and 75th percentile.

groups of groundwater wells: Groups (A) and (B). The variations of EC, ORP, and metals in between the groups are shown in **Figure 9**. The groundwater wells from group (B) exhibit higher concentrations of iron, manganese, zinc, and arsenic. In addition, the group (B) observes higher EC and lower ORP value. Therefore, group (A) and group (B) are classified as groundwater of low mineralization and high mineralization, respectively. The classification of groundwater wells reveals groundwater quality varies according to natural hydrogeological conditions in the study area. Most of the groundwater wells of group (B) with high mineralization are located in CGWD, whereas many groundwater wells of group (A) with low mineralization are located in the NGWD and SGWD (**Figure 10**). Chapagain *et al.* [19] also reported similar result in the groundwater of the valley, indicating that the high mineralization in the CGWD. The high mineralization in the CGWD may be attributed to geochemical heterogeneity of the sediment in groundwater districts of the Kathmandu Valley where there is a presence of finer particles and trace elements in the sediments of central part of the valley [43]. Furthermore, the low ORP values in the CGWD would contribute to the mobilization of metals in the groundwater.



Figure 10. Classification of groundwater wells on the basis cluster analysis.

4. Conclusion

The study observed elevated concentrations of iron and manganese in the groundwater of the Kathmandu Valley. The occurrence of elevated concentrations of arsenic in some groundwater wells was also detected. The spatial distribution patterns demonstrated the higher concentrations of iron, manganese, and arsenic in the CGWD of the valley. Correlation analysis showed arsenic was positively correlated with iron and manganese, suggesting common geogenic origin of these metals. The ORP shows strong negative correlations with iron, manganese, and arsenic, which is attributed to reductive mobilization mechanisms of the metals in the groundwater. The results of the PCA with varimax rotation rendered the reduction of the data matrix to three important VFs. In VF 1, the high loading factors of iron and manganese reveal that these metals have common natural source of origin in groundwater. Additionally, negative loading factors of pH and ORP indicate that iron and manganese mobilization is favorable in low pH and reducing environment. The results of CA classified groundwater wells into two major groups of low and high mineralization. Many groundwater wells of the NGWD and SGWD are classified as wells of high mineralization. The metals are not significantly correlated with studied time series, inferring no temporal variation of metals in the groundwater.

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