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RESEARCH PAPER

Assessment of Groundwater and Surface Water Pollution by Hazardous Metals using Multivariate Analysis and Metal pollution Index around the old Sidi Kamber Mine, NE Algeria

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Abstract

In order to evaluate the impact on water quality of the abandoned Sidi Kamber mine in Skikda, NE Algeria, Pb, Zn, Cd, Fe, Cu, Mn and Ni metals were collected at surface water and groundwater, from twenty eight sites located near the mine. Conventional hydrochemical methods, heavy metal pollution index (HPI) and multivariate statistical analysis techniques: correlation matrix (CM), principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used. Surface water results show that El-Souk River has a high level of pollution, but Guenitra dam water is less contaminated. Regarding the groundwater results, the wells and springs are not suitable for drinking. The overall quality estimated by HPI values of surface and groundwater are poor; they may pose a potential health risk to the local population. The PCA and HCA suggest that surface water and groundwater are contaminated by two sources: anthropogenic and natural. According to the obtained results, surface water and groundwater pollution state of this area raises serious concerns about health and environment.

Keywords: Groundwater, Mine, Multivariate Statistical, Pollution, Surface Water

INTRODUCTION

The exploitation of various mineral resources has been one of the essential and fundamental activities of humanity life development. However, human intrusion into the environment produces deleterious modifications that always end up being attributed to nature and pose a potential threat to the aquatic and terrestrial environment (Alvarez-Valero et al., 2008). Water resources, either surface or underground, are affected by mining operations at different stages of the mine life cycle or even after closure, including extraction process, flooding operations, dewatering of mine and discharge of untreated water. All those processes are associated with water pollution (Younger et al., 2002; Singh et al., 2016).

The closure of any mine requires special measures to reduce the regeneration processes of acid mine drainage (AMD), which is the main source of metal pollution, with a greater amount than during mining activity. In abandoned mines, the production of AMD can be done by oxidation of existing sulphides in underground and open pit excavations, as well as in tailings and waste

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rock piles (Favas et al., 2017). Tailings are solid wastes produced during mining activity, after the mine closure; these wastes are left on the surrounding soil without any management, which exposes them to environmental factors. (El Khalil et al., 2008). They contain toxic and harmful components that tend to seep through water runoff into the surrounding environment (Zanuzzi et al., 2009; Rowe & Hosney, 2013). This phenomenon may persist for hundreds of years after the mine closure and causes serious environmental problems in the vicinity, such as contamination of soil substrates, destruction of ecological landscape, groundwater and surface water pollution, shortage of nutrient and decrease in biological diversity (Tordoff et al., 2000; Rashed, 2010). Several studies show that heavy metal pollution from mined areas caused damage to inhabitant's health and serious systemic health problems can occur, because of the excessive accumulation of heavy metals in food (Zhuang et al., 2009).

Water pollution by heavy metals in abandoned mines is a major environmental problem, especially in arid and semi-arid areas, where it is more significant since the water resources are limited (Bhuiyan et al., 2010). Like most developing countries, Algeria is not immune to these environment problems. There are many mine sites that are abandoned, particularly in the Skikda area, where the Sidi Kamber mine is located. In this area mining wastes are often abandoned without any treatment, due to the absence of post-mining site rehabilitation (Medjram & khelfaoui, 2014). No studies were carried out on groundwater and surface water quality linked to activities in this area. The unique study having been carried out on surface water pollution is that of El-Souk River (Boukhalfa, 2007).

The objective of this study is to evaluate surface water and groundwater contamination by Fe, Zn, Mn, Cu, Ni, Cd and Pb heavy metals, related to the Sidi Kambar abandoned mine, using conventional hydro chemical methods, Heavy metal Pollution Index (HPI) and multivariate statistical analysis techniques such as Correlation Matrix (CM), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA).

MATERIALS AND METHODS

The old Zn/Pb mine of Sidi Kamber region is situated northeast of Algeria, 60 km from the

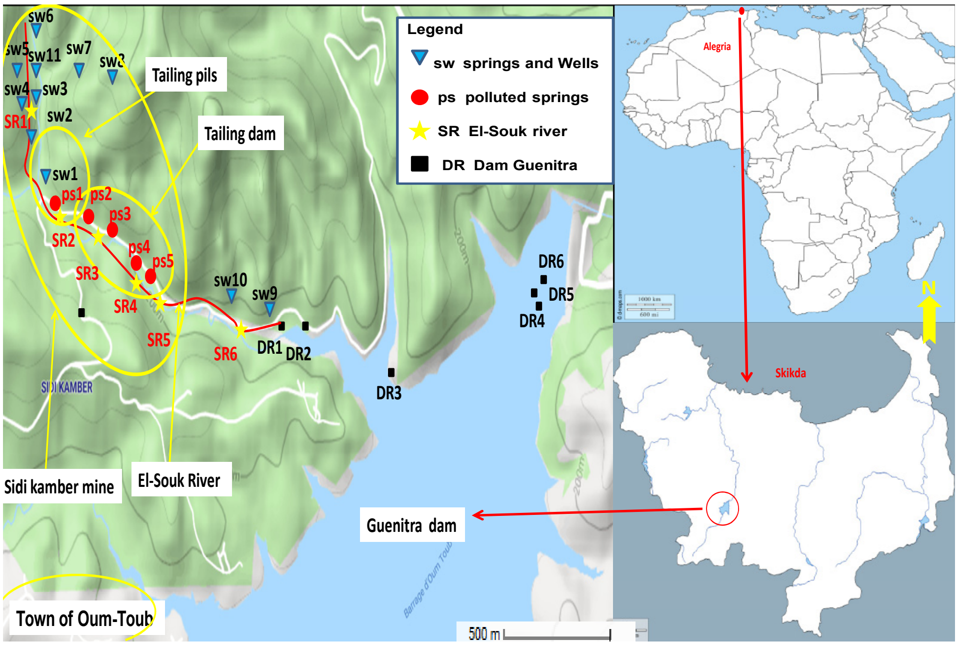

Fig. 1. Location map of the study area

Skikda province (Figure 1). The climate of the Sidi Kamber area is semi-arid with wet winters and dry and hot summers. In 1976, the exploitation of Pb/Zn deposits was stopped, but the open-cast mining production of barite was continued until 1984, when the Sidi Kamber mine was closed (Boukhalfa, 2007). The Guenitra dam is located downstream of the abandoned Sidi Kamber mine in the Oum-Toub locality, about sixty kilometers south of the Skikda chief town, with a surface area of 900 hectares, a gross capacity of 125 million m^3 and a useful capacity of 115.5 million m^3 (Medjram and khelfaoui, 2014). This dam has a dual purpose: it supplies drinking water to the Skikda city (37000m^3), the surrounding urban areas and to the industrial area (16000m^3) and is intended to ensure the irrigation of the Emdjez-Edechich perimeters and the Saf-Saf valley amounting to 5650 hectares. The El-Souk River, one of the tributaries of the Guenitra dam, is still today affected by runoff of mining waste (tailing and waste rock) (Khelfaoui et al., 2020; Oumedjbeur, 1986).

Sampling was conducted in the spring of 2016 and 2017 on twenty eight sampling sites, including sixteen groundwater samples, of which eleven samples are springs and wells water used by inhabitants of the area as drinking water, and five polluted springs (mining leaks) that show a pollution level clearly visible, according to their colors ranging between red, brown and green. The other twelve samples are surface water, including six samples from the El-Souk River and six from the Guenitra dam, which also serves to supply the Skikda area with drinking water. In this study, the average value of four samples for each site is taken, two samples for 2016 and two for 2017. The samples of groundwater and surface water were collected in polyethylene bottles, transported to the laboratory, and stored at 4 °C until analysis. Particular attention was paid to the operations performed during sampling, preservation and analysis processes, in order to avoid the contamination of samples. For this reason, all the material used was soaked in 10% nitric acid, and then rinsed thoroughly with tap water and three times with distilled water.

To assess the impacts of the old abandoned Sidi Kamber mine on the surface water and groundwater quality, all samples were analyzed for concentration of Pb, Zn, Cd, Fe, Cu, Mn and Ni heavy metals, using Atomic Absorption Spectrometry (AAS) of flame equipped with deuterium background correction and graphite furnace (Thermo-scientific 3000), in a laboratory owned by GL1K (Liquefied Natural Gas facility, Algeria). Due to the limited sensitivity of the instrument, preconcentration of the samples was performed by evaporation of 100 mL of water and 8 mL of sample at a hot plate and then the samples were digested by adding 5 mL of concentrated HNO_3 and heated on a hot plate for 30 min. After that, 10 mL of concentrated HCl was added and digestion was continued until the solution became light brown or colorless. Finally, the volume was adjusted to 25 mL by distilled water. In order to assure the precision of the measurement, reference standard solutions with a known concentration of each measured element were used as control samples. In addition, to evaluate the reproducibility of the measurement, each sample was measured at least twice. When the relative standard deviation of measurement exceeds 10%, the water samples should be reanalyzed. In addition, pH and electrical conductivity (EC) of water samples were determined in situ using a conductimeter-pH meter.

Multivariate Statistical Analysis (MSA) was performed on twenty-eight water samples for the following heavy metals: Fe, Zn, Mn, Cu, Ni, Cd and Pb, using statistical software (SPSS) statistic 19, Correlations Matrix (CM) employing Pearson correlation coefficient, Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). The principal component analysis is a multidimensional statistical technique, widely used in hydro chemical and hydrogeological studies to reduce data patterns and decipher patterns within large datasets (Chen et al., 2007; Rakotondrabe et al., 2018). To do this, the data is changed into a bunch of variables or principal components got from linear combinations of the first variables and arranged so that the first major components represent the majority of the variation across the board of original data (Everitt & Hothorn, 2011; Ogwueleka, 2015). Correlation matrix was helpful since it can note the relationship between variables that makes it possible to present very well the overall coherence of dataset (Helena et al., 2000). Hierarchical Cluster Analysis (HCA) is a data classification technique broadly utilized for identifying groups of samples, with similar levels of the components studied (Panda et al., 2006). The results of the similarity levels, at which the observations are merged, are used for the construction of dendrogram (Güler et al., 2012; Moya et al., 2015).

The heavy metals pollution index (HPI) is often used to assess water quality near different mining townships (Prasad et al., 2020) and is assessed by allocating a weightage (Wi) for each heavy metal analyzed. Wi is inversely proportional to the permissible WHO (2011) standard (Si) of each heavy metal (Asare Donkor & Adimado, 2020).

The critical value of HPI or the allowable limit for clean and drinking water is 100 according to studies (Mohan et al., 1996; Leon-Gomez et al., 2020). In this study, we only took samples from the eleven wells analyzed and used for drinking water by the local population. The proposed HPI model is presented by Mohan et al. (1996) and calculated according to the following equation:

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} \mathrm{Wi\ Qi}}{\sum_{i=1}^{n} \mathrm{Wi}}$$

Where:

Wi is the unit weightage defined as the reciprocal value of Si and Si is the standard permissible value for drinking water of ith parameter (adopted standard is the WHO limit 2011) (Kumar et al., 2019), n is the number of parameters analyzed and Qi is the sub index of ith parameter calculated by the following equation: $\mathrm{Qi} = \sum_{i=1}^{n} \left(\frac{\{Mi(-)\mathrm{Ii}\}}{(Si - \mathrm{Ii})} \right)$

Where:

Mi represents the monitored value of heavy metal in μg/L, Ii represents the maximum desirable value, Si represents the standard value of ith parameter in ppb. In this study, the ideal value (Ii) was not considered in the equation, because it is not specified by Algerian drinking water standards.

RESULTS AND DISCUSSION

The results of statistical analysis; min, max, mean, median and standard deviation (SD) of metal concentrations of Fe, Zn, Mn, Cu, Ni, Cd and Pb in surface and groundwater around the abandoned Sidi Kamber mining area are shown in Table 1. These results are represented in box plots form, those of Figure 2 for surface water and those of Figure 3 for groundwater. Knowing that there are two types of surface water: El-Souk River water (SR) and Guenitra Dam raw water (DR), and two types of groundwater: wells and springs waters (SW) which are used for drinking by the area inhabitants and the highly polluted wild springs/ mining leaks (PS).

The results obtained in Table 1 show that the highly polluted water is El-Souk River (SR) surface water and groundwater of mining leaks (PS). Pollution by Fe, Zn and Cd in El -Souk water is heavier than in groundwater of polluted springs (mining leaks), whose maximum concentrations can reach 84.00 mg/l for Fe, 78 mg/l for Zn and 2.67 for Cd. Moreover, Mn, Pb, Ni and Cu metals are higher in groundwater of mining leaks, as compared to El-Souk River surface water, of which the maximum concentration value of polluted spring's waters for each element are: 34.26 mg/l, 5.36 mg/l, 1.11 mg/l and 0.27 mg/l, respectively. This study also shows that the mean concentrations of metals for the four types of water SW, PS, SR and DR follow the order:

Table 1. Descriptive statistics of hazardous metals concentration (mg/l) in the surface water (SW) and groundwater (GW)

	Samples		pH	EC (µS/cm)	Fe	Zn	Mn	Cu	Ni	Cd	Pb
GW	***Springs and wells (SW)*** N= 11	Min	4,57	664	0,00	0,00	0,00	0,00	0,00	0,01	0,00
		Max	7,52	2505	11,03	17,51	12,91	0,02	0,16	0,12	0,16
		Mean	6,80	1169,91	2,39	3,65	1,95	0,005	0,04	0,03	0,02
		Median	6,93	986,00	0,66	0,52	0,08	0,00	0,03	0,01	0,00
		SD	0,82	542,52	3,68	5,53	3,78	0,009	0,05	0,03	0,04
	Polluted Springs (PS) N= 5	Min	2,09	2340,00	23,77	19,81	22,30	0,10	0,21	0,10	0,78
		Max	2,95	3950,00	67,47	26,25	34,26	0,27	1,11	2,05	5,36
		Mean	2,54	2962,20	50,28	21,88	30,67	0,17	0,67	0,66	2,19
		Median	2,53	2945,00	54,48	20,96	32,87	0,17	0,70	0,20	1,73
		SD	0,31	633,69	16,36	2,513	4,816	0,07	0,33	0,82	1,88
SW	***El-souk River (SR)*** N= 6	Min	5,40	750,00	16,20	15,70	0,48	0,00	0,04	0,26	0,09
		Max	7,02	1865,00	84,00	78,00	3,20	0,04	0,11	2,67	0,91
		Mean	6,24	1081,16	37,20	43,53	2,29	0,01	0,06	0,69	0,32
		Median	6,27	978,50	30,55	42,20	2,45	0,01	0,06	0,30	0,22
		SD	0,52	394,64	25,24	20,05	1,03	0,01	0,02	0,96	0,30
	Guenitra Dam Raw (DR) N= 6	Min	7,50	550,00	1,13	0,67	0,10	0,05	0,05	0,00	0,05
		Max	8,06	609,00	15,90	12,30	2,29	0,19	0,14	0,08	0,37
		Mean	7,76	579,83	5,36	3,75	1,00	0,09	0,09	0,03	0,16
		Median	7,75	580,00	1,81	1,43	0,85	0,09	0,09	0,03	0,15
		SD	0,18	19,70	6,22	4,51	0,78	0,04	0,03	0,03	0,11
		WHO standards	6,5-8,5	1500	0,3	3	0,4	2	0,07	0,003	0,01

SD : Standard deviation.

SW : Zn > Fe > Mn >Ni > Cd > Pb > Cu ;
PS : Fe >Mn > Zn > Pb > Ni > Cd > Cu ;
SR : Zn > Fe >Mn > Cd > Pb > Ni > Cu ;
DR : Fe > Zn > Mn > Pb > Cu > Ni > Cd.

According to the results obtained and compared by the WHO standards (2011), waters (PS) and (SR) show very high level of pollution by Fe, Zn, Mn, Cu, Ni, Cd and Pb metals, with max values of 5.36 mg/l of Pb in PS4 and 2.05 of Cd in PS1. This result is due to the location of wild polluted springs in mine wastes areas (tailing pile and tailing dam) of Sidi Kamber abandoned mine. Nowadays, these springs (mining leaks) discharge water polluted by metals, in particular SP1 station, because it is very close to tailing piles. In addition, this spring flows all year round. As for El-Souk River water, it exhibits a considerable level of pollution, especially in SR2 point, which gives very high values for all metals, of which the concentrations of Cd, Fe, and Zn reach the values: 2.67 mg/l, 84 mg/l, and 78 mg/l, respectively. This station SR2 is the common point of polluted springs waters (PS) and tailing piles waters. The point SR1 is also found to exhibit low levels of metals, because this sampling station is a bit far away from mining waste. Guenitra dam water is less contaminated by heavy metals, with deducible concentration at DR1 point, located at the Guenitra dam entrance and the El-Souk River outlet, whose concentration is high and exceeds the WHO standard, 15 mg/l for Fe, 12.30 mg /l for Zn, 2.29 mg/l for Mn, 0.8 mg/l for Cd and 0.37 mg/l for Pb. Besides, wells and springs groundwater is unsuitable for drinking and does

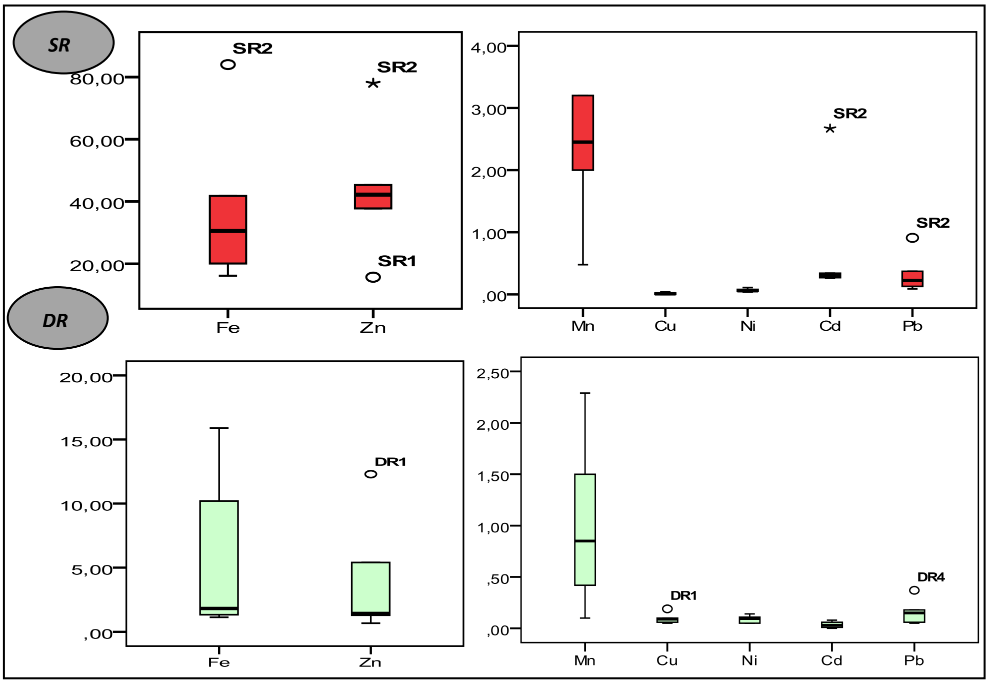

Fig. 2. Box plots of hazardous metals concentration (mg/l) for both types of surface water (SR) and (DR) in study area.

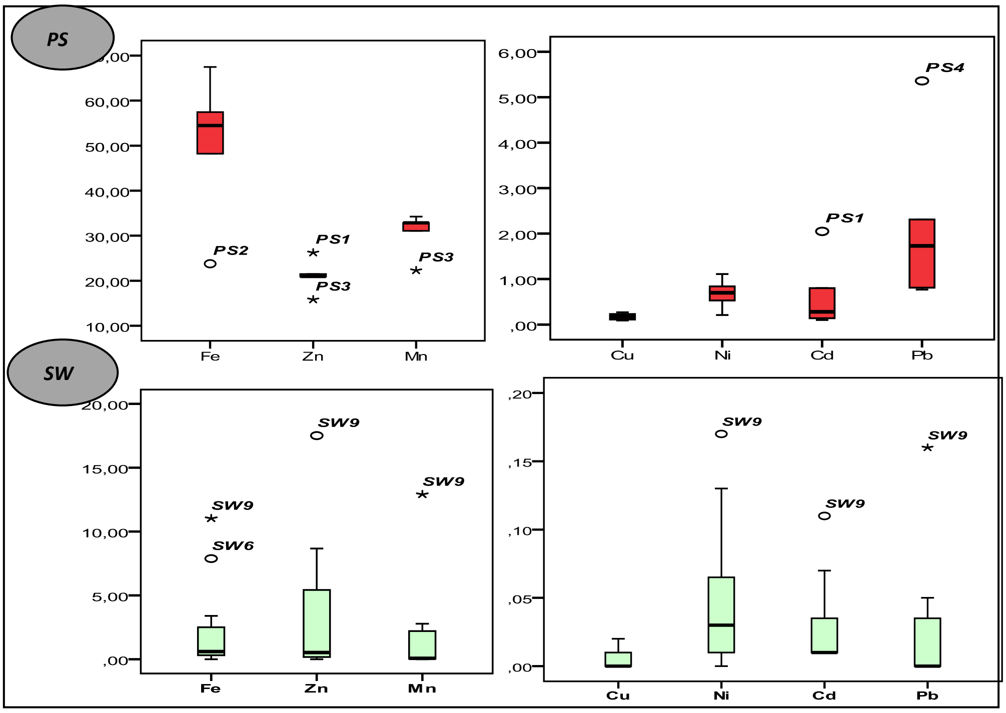

Fig. 3. Box plots of hazardous metals concentration (mg/l) for both types of groundwater (ps) and (sw) in study area.

not comply with WHO standards, especially some stations affected by pollution, such as the old spring SW9 that is sometimes exposed to Guenitra dam flood. At this point, the concentrations exceed the WHO standards for all metals except Cu.

By way of comparison, several similar studies on abandoned mines around the world show high levels of heavy metals in groundwater and surface water, for example, the study of Modoi et al. (2014) on mines in northwestern Romania shows high concentrations of heavy metals in groundwater from wells in villages located downstream from mining dumps. According to the study of Uugwanga et al. (2021), water around abandoned copper mining sites in Klein Aub in Namibia reflects the presence of metals in both types of water. In addition, the study of Rakotondrabe et al. (2018) of water quality in the gold zone of Bétaré-Oya in Eastern Cameroon and the study of Rösner (1998) on historical mining activities in northwestern Arizona show high metal content. The same case for the two studies: Cidu et al. (2009) on the impact of past mining activity on the quality of groundwater in southwestern Sardinia (Italy) and the study of Zhao et al. (2012) on water affected by AMD in the Dabaoshan mine in southern China, which had a high content of heavy metals.

The variations in pH and conductivity in surface water and groundwater around the Sidi Kamber mine and its surrounding areas are shown in Table 1. The pH values of surface water indicate a range of acidic to basic characteristics, varying between 5.40 and 7.02 in the El-Souk River and between 7.50 and 8.06 in the Guenitra dam, with an average values of 6.24 and 7.76 for each type of water, while groundwater has a pH ranging from 4.57 to 7.52 for the wells and springs surrounding the study area. Moreover, they range from 2.09 to 2.95 for the polluted springs (PS), whose results show that most of (PS) is acidic, especially at the sampling site PS1. Electrical conductivity of groundwater from natural wells and springs is between 664 and 2505 µS/cm, with an average of 1169 µS/cm; this type of water is very poorly mineralized. However, the highest electrical conductivity values are found in the mining leaks, PS1, PS2, PS3, PS4 and PS5. They are affected by metals pollution from natural deposits in the study area, which could reach up to 3950 µS/cm for the sampling point PS1. Electrical conductivity of Guenitra reservoir surface water is generally relatively low, whereas El-Souk River surface water has some deducible values in some sampling points located in mine waste areas such as RS2 and RS4.

The multivariate statistical methods such as the correlation matrix, principal component analysis and cluster analysis were widely applied to study environmental phenomena and to interpret hydro geochemical data. They are very effective in representing geochemical data for water pollutants and geochemistry (Gular et al., 2002; Kumar and Riyzuddin. 2008).

The correlation matrix is useful because it can point out associations between variables that can show the overall coherence of dataset and identify the influence factors, which help identifying the sources of different elements (Chen et al., 2007; Rakotondrabe et al., 2018). Tables 2 and 3 present the correlation matrix of the seven metal variables in groundwater and surface water, respectively. Only those with correlation values greater than 0.50 are taken into account.

In groundwater, the metal correlation matrices show that different metal pairs have strong positive correlations between Fe and all other metals including Fe-Zn (r = 0.882), Fe-Mn (r = 0.913), Fe- Cu (r = 0.964), Fe - Ni (r = 0.841), Fe - Cd (r = 0.725), Fe - Pb (r = 0.782). Zn is strongly and positively correlated with Mn (r = 0.933), Cu (r = 0.850), Ni (r = 0.848) and moderately with

Table 2. Correlation matrix calculated using Pearson coefficients (groundwater).

	Fe	**Zn**	**Mn**	**Cu**	**Ni**	**Cd**	**Pb**
Fe	1,000						
Zn	0,882**	1,000					
Mn	0,913**	0,933**	1,000				
Cu	0,964**	0,850**	0,914**	1,000			
Ni	0,841**	0,848**	0,917**	0,922**	1,000		
Cd	0,725**	0,625*	0,606*	0,776**	0,769**	1,000	
Pb	0,782**	0,664*	0,730**	0,745**	0,628*	0,628*	1,000

Table 3. Correlation matrix calculated using Pearson coefficients (surface water).

	Fe	Zn	Mn	Cu	Ni	Cd	Pb
Fe	1,000						
Zn	0,948**	1,000					
Mn	0,604*	0,757**	1,000				
Cu	-0,323	-0,488*	-0,209	1,000			
Ni	0,175	-0,035	-0,041	0,784**	1,000		
Cd	0,899**	0,799**	0,431*	-0,206	0,242	1,000	
Pb	0,809**	0,732**	0,497*	-0,165	0,136	0,902**	1,000

* Correlation is significant at the 0.05 level.

** Correlation is significant at the 0.01 level.

Cd (r = 0.625) and Pb (r = 0.664). Mn is positively correlated with Cu (r = 0.914), Ni (r = 0.917), Pb (r = 0.730) and moderately with Cd (r = 0.606). Cu is strongly and positively correlated with Ni (r = 0.92), Cd (r = 0.776) and Pb (r = 0.745). Ni is positively correlated with Cd (r = 0.769) and Pb (r = 0.628). Cd is correlated is with Pb (r = 0.628). The results obtained show that metals in groundwater had similar hydro chemical characteristics in this area and suggest that they have a common source. Similarly, in surface water, correlation matrices show that some metals pairs have positive significant correlations like Fe -Zn (r =0,948), Fe - Mn (r=0,604), Fe - Cd (r=0,899), Fe - Pb (r=0,809), Zn-Mn (r = 0,757), Zn-Cd (r = 0,799), Zn - Pb (r = 0,732), Cu-Ni (r = 0,784) and Cd- Pb (r = 0,902).These results indicate the variation and contribution of metal origins of surface water pollution. It can be attributed to natural or geological processes such as oxidation of sulphide minerals and rocks containing metallic ores, and anthropogenic origins such as acid drainage of tailing and all mining waste.

In this case, the principal component analysis and factor analysis were performed for seven variables on twenty-eight observation points. The size of ours dataset is not that big , but this study depends on the number of stations available in the mining area, especially groundwater, for example the number of existing wells and springs is only 11. In addition, the study period is limited. The values of Bartlett's test of sphericity and KMO allow us to run PCA (KMO values are greater than 0.5, whose; 0.693 for groundwater and 0.595 for surface water). Varimax rotation was used to maximize the sum of the factor coefficients variance, which better explains the possible groups/sources that influence water systems (Chidambaram et al., 2015). Factor load, eigenvalues, percentage of variance and cumulative percentage for extracted factors are shown in Table 4 for groundwater and Table 5 for surface water. However, the Figure 4, A, B, C, D shows the results obtained from the PCA analysis of the variables studied for surface water and groundwater. Factor analysis provides a powerful way to detect similarities between variables or samples for hydro geochemical data aims to explain the observed relationship and expresses it as a new set of variables called factors (Varol & Davraz, 2015). The contribution of a factor is said to be significant when the corresponding eigenvalue is greater than unity (Briz-Kishore & Murali. 1992).

In this study, for surface water in Figure 4, C and Table 5; two independent factors are extracted, which explains 84.82% of the total variance. The first, responsible for 58.80% of the total variance, was well represented by Mn, Fe, Pb, Cd and Zn with a high load Fe (r = 0.964), Zn (r = 0.966), Mn (r = 0.712), Cd (r = 0.907) and Pb (r = 0.876). Most metals with strongly positive PC1 charges are generally in the form of oxyanions soluble in oxidizing waters, they can be qualified as an anthropogenic source, associated with the processes of generation of acid and sulphide oxidation mines. Likewise, this factor determines the level of AMD contamination in water as a function of pH and the concentration of toxic metals (Chen et al., 2007; Bhuiyan et al., 2010).The second explains 26.01% of the total variance and was mainly represented by Ni and Cu, heavily loaded with Ni (r = 0.967) and Cu (r = 0.877). It can therefore be considered as a geogenic source component and could be released by the chemical alteration of the base materials. For groundwater samples Figure 4, A and Table 4; only one of the main components was identified, of which 82.71% of the total sample variance (82.71% for PC1), represented by all metals: Mn, Fe, Pb, Cd, Zn, Ni and Cu, with a very high positive charge of Fe (r = 0.963), Zn (r = 0.917), Mn (r = 0.951), Cd (r = 0.800), Pb (r = 0.808), Ni (r = 0.935) and Cu (r = 0.973).

These results clearly indicate that the only metallic origin of groundwater pollution is the anthropogenic source, associated with existing mine waste near this well and springs, of which all polluted springs are positioned in the tailing dam. This could be explained by complex mineralization from water - rock interaction and Fe - Mn redox reactions (Huang et al., 2016). These results confirm those obtained by the correlation matrix.

The projection of individuals on the factorial plan F1–F2 in Figure 4 B, D allows identifying three distinct groups of surface water samples and three of groundwater. Positive scores in PCA indicate that water samples are affected by the presence of the parameters that are significantly loaded on a specific factor/component, whereas negative scores suggest that water quality is essentially unaffected by those parameters. For surface water in Figure 4, D, the positive side contains group

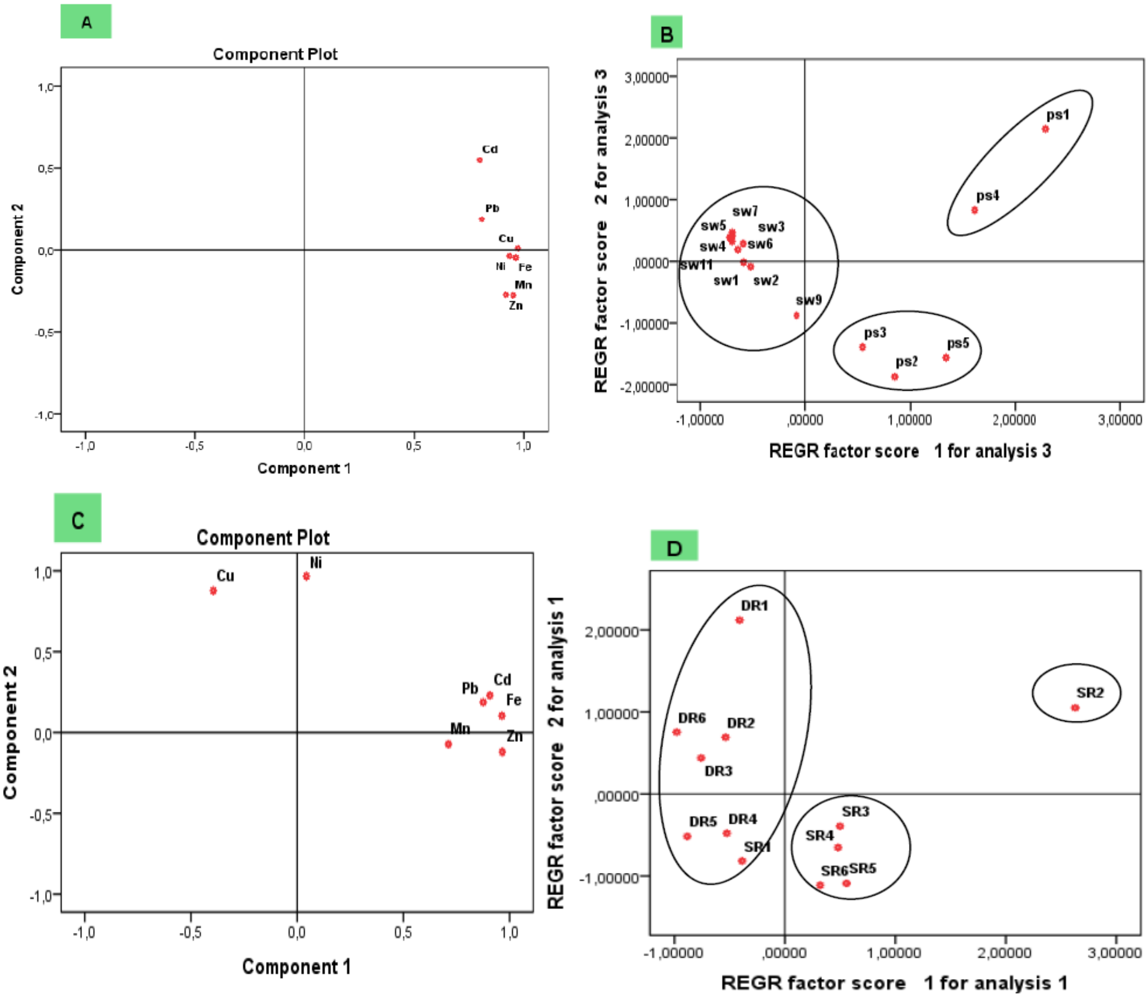

Fig. 4. Principal Component Analysis (PCA) for surface water (SW) and groundwater (GW): in the left projection of variables on the factorial plan F1–F2; and in the right projection of individuals on the factorial plan F1–F2.

Table 4. Factor loadings of PCA analysis of groundwater samples

Variable	F1	F2
Fe	0,963	-0,048
Zn	0,917	-0,274
Mn	0,951	-0,277
Cu	0,973	0,010
Ni	0,935	-0,039
Cd	0,800	0,547
Pb	0,808	0,187
Eigenvalues	5,790	0,490
% variance explained	82,711	6,996
% cumulative variance	82,711	89,707

Table 5. Factor loadings of PCA analysis of surface water samples

Variable	F1	F2
Fe	0,964	0,104
Zn	0,966	-0,120
Mn	0,712	-0,073
Cu	-0,394	0,877
Ni	0,043	0,967
Cd	0,907	0,229
Pb	0,876	0,187
Eigen values	4,117	1,821
% variance explained	58,807	26,013
% cumulative variance	58,807	84,820

1 (SR3, SR4, SR5 and SR6) and the group 2 (SR2). These samples show El-Souk river water, which are affected by acid mine drainage from mine waste. The group 2 of SR2 point is highly polluted, because it is the common point between the polluted water by tailing piles and the polluted spring PS2 of ground water. The negative side contains group 3, which consists of Guenitra dam water samples, DR2, DR3, DR4, DR5 and DR6 and SR1 point taken from El-Souk River, upstream of the mine and very far from all sources of pollution. This group contains the water samples with low concentrations of metals except DR1 point, with considerable concentration of metals. This latter is at the entrance of the dam and the outlet of El-Souk River. for ground water in Figure 4, B, group 1 (PS1 and PS4) and group 2 (PS2, PS3, PS5) in the positive side indicate very high levels of pollution, especially PS1 point which exhibits a real risk for the environment, because this spring flows during the whole year and discharges large amounts of metals and sulphates. In addition, well and spring waters in the negative side (SW1, SW2, SW3, SW4, SW5, SW6, SW7, SW8, SW10, SW11) have low level of metal pollution, with the exception of the point (SW9), which could be attributed to the closeness of the well to the Guenitra dam and sometimes to its exposure to dam flooding which submerges it with sediments containing fairly high concentrations of metals. For this reason, the concentrations of (SW9) are high and exceed the norm.

The cluster analysis has been successfully used to classify the water samples and formulate the geochemical models, by identifying the spatial similarity between the sampling sites, according to the chemical concentration levels of heavy metals (Armah et al., 2010; Nasrabadi & Abbasi

Maedeh. 2014; Singh et al., 2016). It allows to clearly distinguishing the locations of the different pollution sites.

In this study, cluster analysis was also conducted to visualize metals groupings and to detect the spatial similarities and site grouping in surface water and groundwater datasets. The results are illustrated in Figure 5, A, B, C and D.

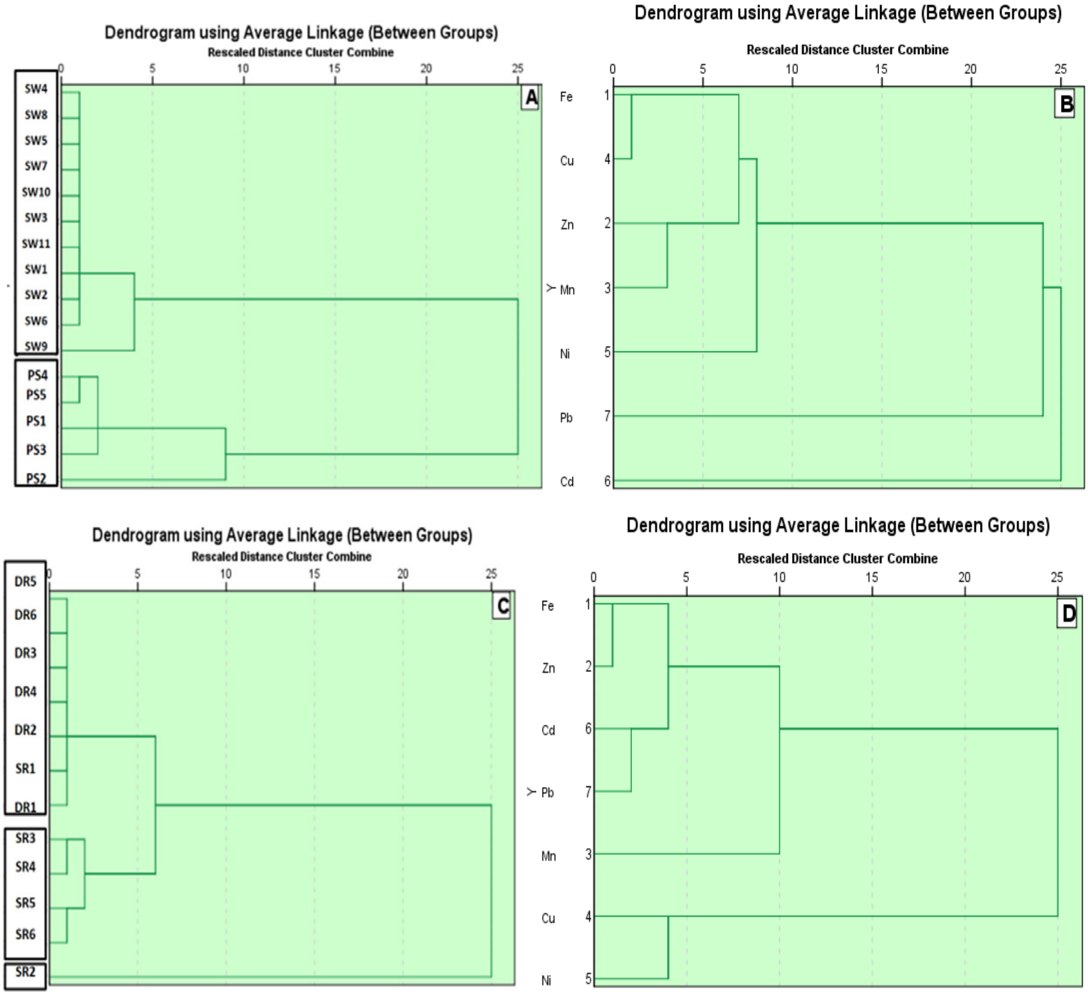

Fig. 5. Dendrogram of Hierarchical Cluster Analysis of surface water (SW) and groundwater (GW) for metals and sampling stations from area

Table 6. HPI of groundwater of wells in the abandoned mine area

Heavy metal	Mean value (ppb) *Mi*	Standard permissible value (ppb) *Si*	Unit weightage (*Wi*)	Sub index (*Qi*)	*Wi* × *Qi*
Fe	2390	300	0.0033	796.66	2.6528
Zn	3650	3000	0.0003	121.66	0.0364
Mn	1950	400	0.0025	487.5	1.2187
Cu	5	2000	0.0005	0.25	0.00012
Ni	47	70	0.0142	67.143	0.9587
Cd	30	3	0.33	1000	330
Pb	26	10	0.2	260	26
			Σ *Wi* = 0.45		Σ *Wi* × *Qi* =360.86

HPI = 800.14

Table 7. HPI of surface water of raw water of Guenitre dam in the abandoned mine area

Heavy metal	Mean value (ppb) *Mi*	Standard permissible value (ppb) *Si*	Unit weightage (*Wi*)	Sub index (*Qi*)	*Wi* × *Qi*
Fe	5365	300	0.0033	1788.333	5.9014
Zn	3755	3000	0.0003	125.166	0.0375
Mn	1001	400	0.0025	250.25	0.6256
Cu	96	2000	0.0005	4.8	0.0024
Ni	90	70	0.0142	128.5714	1.8257
Cd	35	3	0.33	1166.666	384.999
Pb	160	10	0.2	1600	320
			Σ *Wi* = 0.45		Σ *Wi* × *Qi* =713.354

HPI = 1585.23

The Dendrogram of 16 sampling sites for groundwater is divided into two major clusters in Figure 5, A, one very large and one very small. Cluster 1 consists of 11 sampling points: SW1, SW2, SW3, SW4, SW5, SW6, SW7, SW8, SW9, SW10 and SW11. These sites are wells and springs used by the area residents for drinking, although some of these latter contain a high content of heavy metals, whereas cluster 2 consists of five sampling points: PS1, PS2 PS3, PS4 and PS5. These sites are springs highly polluted by mine wastes in this area, which contain large amounts of heavy metals. The CA retained three main clusters for the surface water samples in Figure 5; C. Cluster 1 consists of sampling points: DR1, DR2, DR3, DR4, DR5, DR6 and SR1. These sites represent dam water and the first point of El-Souk River. These waters are not affected or slightly affected by metals pollution. Cluster 2 consists of SR3, SR4, SR5 and SR6 of El-Souk River samples. These sites are closer to the abandoned mine in Figure 1. However, cluster 3 consists only of SR2. This point of El-Souk River is highly polluted because it is very close to mining wastes and probably fed by groundwater from polluted springs. It is slightly different from the other group members. According to these results, there is no difference between spatial groupings obtained from the multivariate analysis.

The CA performed on groundwater samples (Figure 5, B) comprises two clusters: cluster 1 includes Cu, Ni, Pb, Fe, Zn and Mn, cluster 2 consists only of Cd. For the surface water in Figure 5, D, two main clusters were obtained: cluster 1 contains Cu and Ni and cluster 2 consists of Zn, Pb, Mn, Cd and Fe. Therefore, the results of the CA are largely in agreement with those of the PCA. Table 6 and 7 provide the details of Wi values calculations, maximum allowable values (Si) and HPI values of metals analysis in wells groundwater and Guenitra dam surface water in the abandoned mine area.

In this study, in order to determine the HPI values, the mean concentrations of heavy metals (Fe, Mn, Pb, Cu, Zn, Cd and Ni) are used. According to the results obtained, the value of HPI is much higher than the value of critical pollution index of 100 (Nasrabadi. 2015; Rakotondrabe et al., 2018; Bhardwaj et al., 2017); if the HPI value is greater than 100, the overall pollution level is considered to be unacceptable. This is due to the Sidi Kamber abandoned mine, which affected wells and Guenitra dam waters and caused them to be of poor quality and seriously polluted with heavy metals. The estimated HPI values for Guenitra dam surface water are higher than wells groundwater in the mining area. Therefore, the quality of dam water is poorer than that of wells. These high values of HPI must be taken into account by the authorities, since there is a serious threat to human health and environment.

CONCLUSION

This study assessed the quality of surface water and groundwater near the abandoned Sidi Kamber lead/zinc mine in northeast Algeria, by determining the levels of hazardous metals and revealing the source of metals for all existing water types: El-Souk River, Guenitra dam, springs and wells, using correlation matrix, principal component analysis and Heavy metal pollution index, in order to suggest the necessary management measures. The results obtained show that the concentrations of hazardous metals: Pb, Zn, Cd, Fe, Cu, Mn and Ni in most samples from the El-Souk River and polluted springs are very high. Guenitra dam water is less contaminated by metals. Groundwater from wells and springs is unsuitable for drinking and does not comply with (WHO) standards, especially some pollution-affected points such as the old springs (SW9), (SW1) and (SW6) that largely exceed WHO standards. PCA and HCA analysis identified anthropogenic (tailings piles and tailing dam) and natural/geogenic (base material alteration) sources of metal concentration in surface water. However, the only anthropogenic source (mine wastes) of heavy metals is identified for groundwater. Correlation matrix shows very strong correlation between groundwater metals and average correlation for surface water metals. It is concluded from the estimated HPI values that groundwater and surface water of the study area are greater than the critical pollution index value. This indicates that water is critically polluted with heavy metals. The water quality analysis clearly shows that toxic metals, released from mine effluents, pose a high contamination risk to surface water and groundwater. This serious threat directly impacts ecological habitat and exhibits a potential risk to human health of populations residing in the vicinity of these mining areas. Therefore, this alarming situation requires special attention and effective corrective measures to cope with the serious metals pollution in the abandoned mines in Algeria.

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CONFLICT OF INTEREST

All authors declare that they have no conflict of interest.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research

REFERENCE

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