Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 3, No. 2, p. 53-60, 2013
http://www.innspub.net

RESEARCH PAPER OPEN ACCESS

Assessment of heavy metal study on groundwater in the mining area in Stan Terg, Kosovo

Ahmet Tmava, Sabri Avdullahi*, Islam Fejza

Faculty of Geosciences and Technology, Str. Parku industrial No NN, 40000 Mitrovica, Republic of Kosovo

Article published on February 18, 2013

Key words: groundwater, heavy metal, cluster analysis, principal component analysis, Stan Terg, Kosovo.

Abstract

Groundwater pollution has been an issue of concern for environmentalists, since the pollution could be hardly reformed. The heavy metal analyses of Cu, Pb, Mn, Zn, Ni, Cr and Fe were performed for the water samples. This study presents the application of some selected multivariate statistical techniques and confirmatory analysis to identify the sources of heavy metals in the groundwater in the Stan Terg, Kosovo. Correlation analysis showed that the mean concentration of heavy metals (Cu, Pb, Mn, Zn, Ni, Cr and Fe) in the water springs samples were positive correlated values. Principal cluster analysis and factor analysis investigated the origin of the water quality parameters as due to various mining activities: three principal components were obtained with 92.697% total variance. The results of heavy metals analysis indicated that groundwater is pollution in the Stan Terg. Overall, the results showed that the groundwaters of the Stan Terg in North Kosovo are contaminated with heavy metals, which might affect human health as well as the health of the ecosystem.

***Corresponding Author:** Sabri Avdullahi ✉ sabri.avdullahi@uni-pr.edu

Introduction

Groundwater is globally important for human consumption, and changes in quality with subsequent contamination can, undoubtedly, affect human health. Groundwater pollution has become a major subject of public concern the world over. Despite the large volume of water that covers the surface of the earth, only 1% is inland or fresh and easily available for human use (Bockris, 1978). Heavy metals are involved in various industrial processes, agricultural activities, domestic wastes, and vehicles emission, and they are considered as one of the most serious pollutants due to their persistence in the environment, bioaccumulation and high toxicity (González-Macias *et al.,* 2006; Li *et al.,* 2008). According to the Vadela *et al.,* (1997) one of the most important environmental issues today is ground water contamination and between the wide diversity of contaminants affecting water resources, heavy metals receive particular concern considering their strong toxicity even at low concentrations (Marcovecchio *et al.,* 2007). According to the Marcovecchio *et al.,* (2007) the heavy metals are among the major pollutants of water sources.

Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates (Amman, *et al.,* 2002) from different industries, e.g. tannery, steel plants, battery industries, thermal power plants, etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing the threat on human beings (Lantzy and Mackenzie, 1979; Nriagu, 1979; Ross, 1994) and sustaining aquatic biodiversity (Ghosh and Vass, 1997; Das, *et al.,* 1997).

On the global scale, industrial, agricultural and municipal activities have all resulted in surface and groundwater pollution by a variety of contaminants (Oguzie *et al.,* 2002; Ipinmoroti 1993; Lee *et al.,* 2001; Vidal *et al.,* 2000; Moon *et al.,* 1994; Speir *et al.,* 2003; Razo *et al.,* 2004). Specifically, trace metal contamination of water has emerged as a serious health issue highlighted in published work (Watt et al., 2000; Fernandez *et al.,* 1994; Nriagu and Pacyna 1988). Metals such as iron, copper, zinc and manganese are essential metals, but they may produce toxic effects when their levels exceed certain limits in organisms.

Furthermore, multivariate methods have been used to compare the results coming from the principal component analysis carried out on the concentration data with the experimental indicator variogram applied to some categorical information, in order to relate the concentration of heavy metals to the geology and land use of the area (Armah, *et al.,* 2010a; Armah *et al.,* 2010b).

Many studies have investigated the environmental contamination, potential control and remediation measures to manage the environmental impacts of Trepça's former operations. The two main impacts are discharges to surface water of runoff and mining water from tailing ponds with water discharge of high acidity and often heavy metals. But few have paid attention to environmental impacts caused by the discharge of mine waters without prior treatment in the Trepça River. This is the first study that concern with the water pollution of the Trepça River caused by heavy metals from discharge of the mine water. The aim of this study is to determine the levels of Pb, Cu, Zn, Cr, Cd and Ni in the groundwater from the mining area Stan Terg, and water that discharge from mining activities in the Trepça River. Considering that the Trepça River pollution by heavy metals is done continuously for a long time, further studies should focus on the analysis of water and sediment of the river.

Material and methods

Study area

The Stan Terg is located in the north part of Mitrovica city (Kosovo) the geographic position is between the north latitude 42° 56' 20" and east longitude 20° 55' 0". Mining activities and smelting of the silver bearing lead-zinc ore in Kosovo has a long history and can be dated back to even pre-Roman times as the relics of tools and diggings show. The Stan Treg mine is located in the north part of Kosovo; about 800m above sea level and 11km from the near town of Mitrovica. Modern mining began in 1930 at the Stan Terg lead-zinc mine, which is located on the Trepça stream. The amount of rainfall varies from 608mm/y in the plains and 1200mm/y in the mountains. The annual maximum and minimum temperatures are 32.8°C and -18.5°C, respectively.

Table 1. Statistical summary of selected metals concentration in groundwater samples.

Metals	water (mgL^{-1} n=30)			
	Mean	Minimum	Maximum	Std. Deviation
Cu	0.09	0.02	0.41	0.121
Pb	0.22	0.08	0.32	0.078
Mn	0.28	0.19	0.42	0.076
Zn	0.44	0.12	1.74	0.379
Ni	0.06	0.03	0.28	0.088
Cr	0.06	0.03	0.09	0.016
Fe	0.21	0.11	1.55	0.521

Geology and hydrogeology

Trepça deposit is of hydrothermal metasomatic, medium to the high thermal origin created by inflow of solution during the Alpine orgenesis. Tectonic played a major role in deposit formation, spatial distribution, shape and ore body size. Over the body position depends on shale position and that of the limestone so that the over bodies were formed on its contact or in the limestone itself. The principal structural shape in the shale's is of folded type, while in the limestone's faults, fissures and cleavages prevail and this accelerated its karstification.

Hydro geological expiations indicated that water aggravating the mine flows out of the limestones. The water flows out of the fissures, cleavages, fault zones and particularly from karst channels and caverns. Hence, total limestone masses in the deposit are classified as water permeable rocks hydrological collectors because groundwater accumulations in them representing a potential hazard for miner`s safety and aggravates exploitation.

Sample collection and Storage

We have collected 27 groundwater samples in 9 horizons from the total 12 exploitation horizons and 3 samples from the water that is discharged from the mining activities. Groundwater samplings were performed three times for each horizon and from water that discharge from mining in the river in period June, September and December (Fig. 1). Every collected sample was kept in a plastic bottle clearly marked and labeled with references to the sampling points. Similarly, to eliminate differences in the water quality that could arise due to variation in the timing, all the samples were collected during the same period of the day. All the samples were immediately transported to the laboratory under low temperature conditions in ice-box and stored in the laboratory at 4°C until processed analyses. All analyses were completed within a week`s time in the laboratory. The total metal concentration of cupper (Cu), lead (Pb), manganese (Mn), zinc (Zn), nickel (Ni), chrome (Cr), and iron (Fe) in the filtered and digested samples were determined in mg•L-1 using to flame atomic absorption spectrophotometer (AAS).

Statistical analysis

Multivariate data analysis techniques can be used to assess the complex eco-toxicological processes by showing the relationship and interdependency among the variables and their relative weights (Bartolomeo *et al.,* 2004). PCA is a multivariate method mainly used for data reduction. It aims at finding a few components that explain the major variation within the data (Danielsson *et al.,* 1999). PCA also identified the likely factors that cause variation and also reveal relative significance of the combination of the parameters under study. In our study, PCA/FA was applied to extract the most significant PCs and to reduce the contribution of variables with minimum significance. The PCs obtained were further subjected to varimax rotation to maximize differences between the variables and facilitate easy interpretation of the data (Shrestha and Kazama 2007). For analysis of surface water quality data set collected from Trepça region, Kosovo using the statistical Package for the Social Sciences – SPSS 19.

Cluster Analysis (CA)

Cluster analysis is an exploratory data analysis tool for solving classification problems. Its objective is to sort cases (in this case sampling site) into groups or clusters, so that the degree of association is strong between members of the same cluster and weak between different clusters (Kowalkowski *et al.,* 2005). Cluster analysis may bring our associations and structure in data which, though not previously evident, nevertheless are sensible and useful once found.

Each cluster thus describes, in terms of the data collected, the class to which its members belong; and this description may be abstracted through use from the particular to the general class or type (Einax *et al.,* 1998). Normalized Euclidean distances and the Ward's method were used to obtain dendrograms (Einax *et al.,* 1997). Cluster analysis is not a statistical technique; the results obtained are justified according to their value in interpreting data and indicating patterns (Razmkhah *et al.,* 2009).

Table 2. Linear correlation matrix for selected metals in water samples (n=30).

Minerals	Cu	Pb	Mn	Zn	Ni	Cr	Fe
Cu	1						
Pb	-.164	1					
Mn	-.175	.120	1				
Zn	.919**	.089	-.142	1			
Ni	.066	.232	.611	.207	1		
Cr	-.204	-.319	.807**	-.291	.526	1	
Fe	.715*	-.0.10	.468	.650*	.635*	.380	1

**Correlation in significant at the P< 0.01 level (2-tailed)
*Correlation in significant at the P< 0.05 level (2-tailed)

Table 3. Factor loading of selected metals in water samples.

Metals	Water		
	PC1	PC2	PC3
Cu	-.106	.977	-.144
Pb	.029	-.040	.982
Mn	.928	-.095	.061
Zn	-.088	.961	.138
Ni	.806	.248	.295
Cr	.884	-.178	-.383
Fe	.588	.779	-.012
Eigen value	2.851	2.402	1.236
Loading%	40.274	34.311	17.663
Cumulative%	40.724	75.034	92.697

Extraction Method: PCA

Rotation Method: Varimax with Kaiser Normalization.

Principal Component Analysis (PCA) and Factor Analysis

These two methods are aimed at finding and interpreting hidden complex and casually determined relationships between features in a data set (Einax *et al.,* 1998). The key idea of principal component analysis is to quantify the significance of variables that explain in the observed groupings and patterns of the inherent properties of the individual objects (in this study, sampling sites). On the basis of the dataset, new factors as the linear combination of original parameters are calculated. Owing to this, all information about the objects gathered in the original multidimensional dataset can be performed in the reduced space and explained by a reduced set of calculated factors called principal components (PCs). Identified PCs (e.g. by eigenvalue-one criterion) account for the maximum explainable variance of all original property parameters in a descending order (Marengo *et al.,* 1995). Factor analysis is a useful tool for extracting latent information, such as not directly observable relationships between variables (Einax *et al.,* 1998). The original data matrix is decomposed into the product of a matrix of factor scores plus a residual matrix. In general, by applying the eigenvalue-one criterion, the number of extracted factors is less than the number of measured features. So the dimensionality of the original data space can be decreased by means of factor analysis.

Results and discussion

Descriptive statistic

The statistical summary of the selected metal concentration in the groundwater sample is presented in Table 1. From the descriptive statistics, it is clear that heavy metals dominate the groundwater samples with average concentrations of Zn 0.44 mg•L-1, Mn 0.28 mg•L-1, Pb 0.22 mg•L-1, Fe 0.21 mg•L-1, Cu 0.09 mg•L-1, Cr mg•L-1, and Ni 0.06 mg•L-1. In the groundwater samples; the metal concentration distribution pattern follows the decreasing order: Zn > Mn > Pb> Fe > Cu > Cr > Ni. Zinc, manganese, lead and iron are the most dominant element of these metals in the groundwater. Copper, chromium and nickel have a lower concentration. The high concentration of metals in the sampled groundwater may be attributed to the release of effluent directly from the contact of the water with mineralization of the deposits.

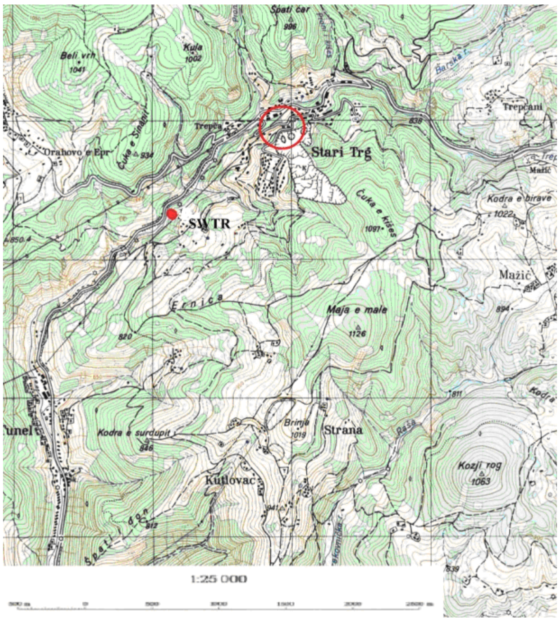

Fig. 1. Map showing water sampling locations.

With the cluster analysis, the relationship between various sites in the water springs can be clearly explained and the source of origin of the ions, that is, whether they are anthropogenic or natural, can be evaluated. Using the CA, the locations of different pollution sites may be clearly distinguished. The dendrogram shows that the sampling sites could be mainly grouped into three main clusters (Fig. 2). Cluster I consists of sites GW8, GW9, GW10, GW4 and GW6, cluster II by sites GW3, GW5 and GW1, and cluster III, sites SWRT. It is seen from the dendrogram that cluster III is characterized by the biggest Euclidean distance to the other clusters (high significance of clustering). This cluster could be categorized as highly polluted because the surface water of Trepca River has the highest value of heavy metals (Zn and Fe). Cluster II (sites GW3, GW5 and GW1) have lower values of the heavy metals and not have directly contact with mineralization.

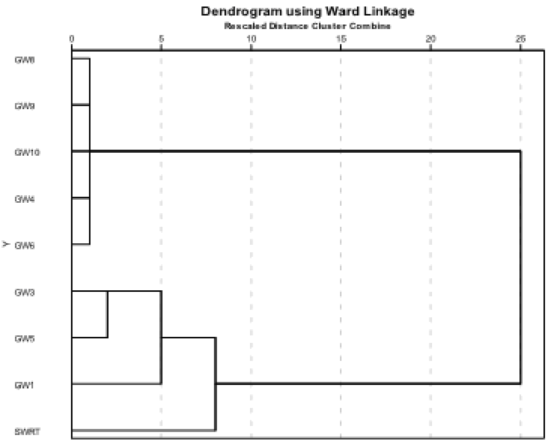

Fig. 2. Dendrogram of selected metals in the water samples using Ward`s Method.

The Pearson correlation coefficient for heavy metals in the sources of the Trepça area is presented in Table 2. The relationship between the heavy metals studied offer remarkable information on the sources and pathway of the heavy metals. Fe ($r = 0.715$, $P<0.05$) was significantly correlated with Zn ($r = 0.650$, $P<0.05$), and Ni ($r = 0.635$, $P<0.05$). Zn was significantly correlated with Cu ($r = 0.919$, $P<0.01$), and Cr have significantly correlated with Mn ($r = 0.807$, $P<0.01$). The rest three metals: copper and chrome do not show obvious relativity between each other. The significant positive correlation between the heavy metals indicates that the groundwater have contact with lead-zinc ore deposits. The correlation matrix provides a justification for the use of principal component analysis to simplify the data.

According to the table 3, PC is separated for the water samples, with a cumulative variance of more than 92.697%. PC 1 exhibits high loading for Mn, Ni and Cr with a maximum contribution of 40.724% of total variance. PC 2 (34.311% of total variance), accounts for high contribution of Cu and Fe, reflects the control of parent materials weathering progress. PC 3 exhibits 17.663 % of the total variance with positive loading on Pb. This would be presumably due to the characteristic that heavy metals resulting from contact of the groundwater with the mineralization in this area.

Conclusions

Descriptive statistics of all the parameter's understudy revealed that the main water quality pollution in the studied area can be attributed mainly to the mineralization of the area and discharged water from the mining operation. Principal component analysis and factor analysis was proven as a feasible technique in source's apportionment: it is a useful method that could assist decision makers in determining the extent of pollution via practical pollution indicators. Correlation matrix, together with other multivariate analyses, seems to point towards a common source for heavy metals. The results of the factor analysis performed on the data also appear to explain fairly well the factors that may have accounted for the chemistry of the water in the study area. The groundwater samples showed significant higher values of heavy metals contents that the control. All groundwater from the mining activity discharged in the Trepca River and pass thru the living area. Based on the results of the study, it is strongly suggested that the chemistry of groundwaters is largely influenced by the specific geologic settings of the area. So to preserve the environment of the Mitrovica from deterioration, the main act is to prevent the discharge of groundwater from the mining area in Stan Terg to the Ibri rivers.

References

Amman AA, Michalke B, Schramel P. 2002. Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. Analytical Biochemistry **372(3)**, 448-452.

Armah FA, Obiri S, Yawson DO, Pappoe ANM, Akoto B. 2010a. Mining and heavy metal pollution: Assessment of aquatic environments of Tarkwa, Ghana using multivariate statistical analysis. Journal of Environmental Statistics **1(4)**, 1-13

Armah FA, Obiri S, Yawson DO, Onumah EE, Yengoh GT, Afrifa EK, Odoi JO. 2010b. Anthropogenic sources and environmentally relevant concentrations of heavy metals in surface water of a mining district in Ghana: A multivariate statistical approach. Journal of Environmental Sciences Health. A Toxic/Hazardous Substance Environmental Engineering **45,** 1804-1813

Bartolomeo AD, Poletti L, Sanchini G. 2004. Relationship among parameters of lake polluted sediments evaluated by multivariate statistical analysis. Chemosphere **15,** 1323–1329.

Bockris JOM. 1978. Environmental chemistry. New York, Premium Press 332.

Danielsson A, Cato I, Carman R. 1999. Spatial clustering of metals in the sediments of the Skagerrak/Kattegat. Applied Geochemistry **14,** 689–706.

Das RK, Bhowmick S, Ghosh SP, Dutta S. 1997. Coliform and fecal coliform bacterial load in a stretch of Hooghly, in K. K Vass and M. Sinha, (Eds.), Proceedings of the National seminar on changing perspectives of inland fisheries, Inland Fisheries Society of India, Barrackpore.

Einax JW, Zwanziger HW, Geiss S. 1997. "Chemomet-rics in Environmental Analysis," Wiley, Weinheim.

Einax JW, Truckenbrodt D, Kampe O. 1998. "River Pollution Data Interpreted by Means of Chemometric Methods," Microchemistry Journal **58(3),** 315-324.

Fernandez H, Conti LF, Patchineelam SR. 1994. An assessment of the pollution of heavy metals in Jacarepagua Basin, Rio De Janeiro, Brazil: A statistical approach. Environment & Technology **269**, 87–94

Ghosh S, Vass KK. 1997. Role of sewage treatment plant in Environmental mitigation. K. K. Vass and M. Sinha (Eds.), Proceedings of the national seminar on changing perspectives of inland fisheries, Inland Fisheries Society of India, Barrackpore 36-40.

González-Macias C, Schifter I, Lluch-Cota DB, Mendez-Rodriguez L, Hernandez-Vazquez S. 2006. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico, Environmental and Monitoring Assessment **118**, 211–230.

Ipinmoroti KO. 1993. Water quality of shallow wells located close to dumpsite in Akure, Nigeria. Pakistan Journal of Scientific and Industrial Research **36**, 137–141.

Kowalkowski T, Zbytniewski R, Szpejna J, Buszewski B. 2005. "Application of Chemometrics in River Water Classification". Water Research **40(4),** 744-752

Lantzy RJ, Mackenzie FT. 1979. Atmospheric trace metals: global cycles and assessment of man's impact, Geochimica et Cosmochimica Acta **43,** 511-525.

Lee C, Chon H, Jung M. 2001. Heavy metal contamination in the vicinity of the Daduk Au–Ag–Pb– Zn mine in Korea. Applied Geochemistry **16,** 1377–1386.

Li S, Xu Z, Cheng X, Zhang Q. 2008. Dissolved trace elements and heavy metals in the Danjiangkou Reservoir, China. Environmental Geology **55,** 977–983.

Marcovecchio JE, Botte SE, Freije RH. 2007. Heavy metals, major metals, trace elements. In handbook of water analysis. 2nd edition. Edited by Nollet LM. London: CRC Press; 275-311.

Marengo E, Gennaro MC, Giacosa D, Abrigo C, Saini G, Avignone MT. 1995. "How Chemometrics Can Helpfully Assist in Evaluating Environment Data Lagoon Water," Analytica Chimica Acta Anal **317(1-3),** 53-63

Moon CH, Lee YS, Yoon TH. 1994. Variation of trace Cu, Pb and Zn in sediment and water of an urban stream resulting from domestic effluents. Water Research **28,** 985–991.

Nriagu JO, Pacyna JM. 1988. Quantitative assessment of world-wide contamination of air, water and soils by trace metals. Nature **333,** 134–139

Nriagu JO. 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature **279,** 409-411

Oguzie EE, Agochukwu IB, Onuchukwu AI, Offem JO. 2002. Ground water contamination: A simulation study of buried waste metallic contaminant penetration through the aquifers. Journal of the Chemical Society of Nigeria **27,** 82–84.

Razmkhah H, Abirishamchi A, Torkian A. 2009. "Evalua-tion of Spatial and Temporal Variation in Water Quality by Pattern Recognition Techniques: A Case Study on Ja-jrood River (Tehran, Iran)". Journal on Environmental Management **91(4),** 852-860.

Razo I, Carrizales L, Castro J, Díaz-Barriga F, Monroy M. 2004. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water, Air and Soil Pollution **152,** 129–152.

Ross SM. 1994. Toxic metals in soil-plant systems, Wiley, Chichester, U. K

Shrestha S, Kazama F. 2007. Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. Environmental Modelling & Software **22**, 464-475.

Speir TW, Van Schaik AP, Percival HJ, Close ME, Pang L. 2003. Heavy metals in soil, plants and ground water following high-rate sewage sludge application to land. Water Air and Soil Pollution **150,** 319–358

Vidal M, Melgar J, Lopez A, Santoalla MC. 2000. Spatial and temporal hydrochemical changes in ground water under the contaminating effects of fertilizers and wastewater. Journal of Environmental Management **60,** 215–225

Vodela JK, Renden JA, Lenz SD, Mcelhenney WH. Kemppainen BW. 1997. Drinking water contaminants. Poultry Science **76,** 1474-1492

Watt GCM, Britton A, Gilmour HG, Moore MR, Murray GD, Robertson SJ. 2000. Public health implications of new guidelines for lead in drinking water: A case study in an area with historically high water lead levels. Food and Chemical Toxicology **38,** S73–S79.