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ASSESSMENT OF HEAVY METAL IN THE WATER SPRINGS, STAN TERG, KOSOVO

Sabri Avdullahi[1], Islam Fejza[1], Ahmet Tmava[1], Mursel Rama[1], Muhamedin Hetemi[1]

[1] Faculty of Geosciences and Technology, Str. Parku Industrial No NN, 40000 Mitrovica, Republic of Kosova

sabriavdullahi@uni-pr.edu

ABSTRACT

This study presents the application of some selected multivariate statistical techniques and confirmatory analysis to identify the sources of heavy metals (Cu, Pb, Mn, Zn, Ni, Cr and Fe) in the water springs 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 86.85% total variance. The results of heavy metals analysis indicated that water springs are pollution in the Stan Terg. Overall, the results showed that the water springs 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. Statistical analysis agrees with discussion based on background value and field survey of point-source, making this statistical discussion more convincing.

Keywords: springs, heavy metal, cluster analysis, principal component analysis, Stan Terg,

1. INTRODUCTION

Water is one of the essentials that supports all forms of plant and animal life (Vanloon & Duffy 2005), and it is generally obtained from two principal natural sources; surface water (lakes, rivers, streams, etc.) and ground water (borehole water and well water) (McMurry & Fay 2004, Mendine 2005). More than one billion people in the world do not have suitable drinking water, and two to three billions lack access to basic sanitation services. About three to five millions die annually from water-related diseases (Kumar & Singh, 2006). In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water and more than 99.9% are stored in sediments and soils (Karbassi *et al*., 2007, Pradit *et al.*, 2010). Heavy metals are among the major pollutants of water sources (Marcovecchio *et al*., 2007).

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 & Mackenzie 1979, Nriagu 1979, Roos 1994) and sustaining aquatic biodiversity (Ghosh & Vas 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 & 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,

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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). The spatial variability of water heavy metal is therefore, an important part of environmental supervision and ecosystem evaluation.

The purpose of this research was: (1) to establish the dissolved heavy metal (Cu, Pb, Mn, Zn, Ni, Cr and Fe) concentrations in natural waters, (2) to estimate significant relationships between trace metals; and (3) to provide a database for pollution control of the area.

2. MATERIAL AND METHODS

2.1. Study area

The Stan Terg is located in the north part of Mitrovica city (Kosovo), the geographic position is between the north latitude 42° 52' 30" 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 Trepca stream.

The amount of rainfall varies from 608mm/y in the plains and 1200mm/y in the mountains (Avdullahi *et al.*, 2008). The annual maximum and minimum temperatures are 32.8°C and -18.5°C, respectively.

Figure 1. Map showing water sampling locations

2.1.1. Geology and hydrogeology

Trepca 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.

2.2. Sample collection and storage

From the studied area, samples are collected and analyzed in 9 springs, one sample is from the water which is extracted from the mine and flows into the river Trepca (Figure 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 μg•L-1 using to flame atomic absorption spectrophotometer (AAS).

2.3. 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

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(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 & Carman 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 & Kazama 2007).

For analysis of surface water quality data set collected from Trepca region, Kosovo using the statistical Package for the Social Sciences –SPSS 19.

2.3.1. 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 (Eniax *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).

2.3.2. 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. The key idea of principal component analysis is to quantify the significance of variables that explain in the observed groupings and patterns of the

Metals	water (μgL^{-1})			
	Mean	Mini	Max	Std. Deviation
Cu	17	10	300	90
Pb	66	19	239	75
Mn	168	10	1460	517
Zn	110	26	790	323
Ni	98	15	320	106
Cr	50	50	90	13
Fe	115	6	1360	49

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. 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.

3. RESULT AND DISCUSSION

3.1. Descriptive Statistic

The statistical summary of the selected metal concentration in the water sample is presented in Table 1. From the descriptive statistics, it is clear that heavy metals dominate the water samples with average concentrations of Mn 168 µg•L-1, Fe 115 µg•L-1, Zn 110 µg•L-1, Ni 98 µg•L-1, Pb 98 µg•L-1, Cr µg•L-1, and Cu 17 µg•L-1. In the water samples; the metal concentration distribution pattern follows the decreasing order: Mn > Fe > Zn> Ni > Pb > Cr > Cu. Manganese, iron, zinc and nickel are the most dominant element of these metals in the water. Lead, chromium and copper have a lower concentration.

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The high concentration of metals in the sampled water may be attributed to the release of effluent directly from the contact of water springs with mineralization of the deposits.

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

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 (Figure 2). Cluster I consists of sites S1, S2, S4, S9 and S10, cluster II by sites S5, S7 S8, and S3, and cluster III, sites S6. 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 site S6 have the highest value of heavy metals (Mn and Fe).

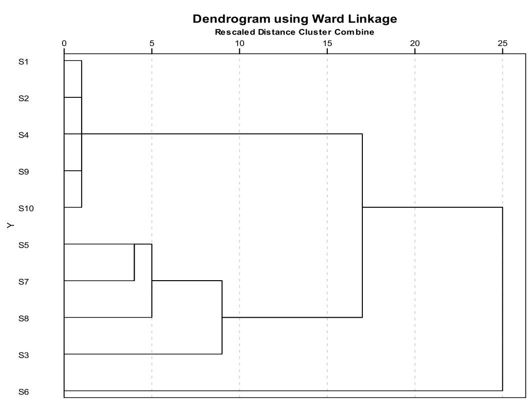

Figure 2. Dendrogram of selected metals in the water samples using ward`s method

The Pearson correlation coefficient matrix for heavy metals in the sources of the Trepça area is presented in Table 3. The relationship between the heavy metals studied offer remarkable information on the sources and pathway of the heavy metals. Fe was significantly correlated with Ni (r = 0.864), Mn (r = 0.737), and Zn (r = 0.595). Zn was significantly correlated with Mn (r = 0.878). The rest three metals: copper, lead and chrome do not show obvious relativity between each other. The significant positive correlation between the heavy metals indicates that the water springs have contact with lead-zinc ore deposits. The correlation matrix provides a justification for the use of principal component analysis to simplify the data.

In all the Principal component analysis generated three significant factors (Table 4). Three PC are separated for the water samples, with a cumulative variance of more than 86.85%. PC 1 exhibits high loading for Ni, and Fe with a maximum contribution of 44.69% of total variance. PC 2 (26.07% of total variance), accounts for high contribution of Cu, Mn, and Zn, reflects the control of parent materials weathering progress. PC 3 exhibits 16.52 % of the total variance with positive loading on Pb and negative loading on Cr. This would be presumably due to the characteristic that heavy metals resulting from contact of the springs with the mineralization in this area.

Table 3. Pearson correlation matrix of heavy metals in μgL^{-1}

Minerals	Cu	Pb	Mn	Zn	Ni	Cr	Fe
Cu	1						
Pb	-.347	1					
Mn	.484	.218	1				
Zn	.404	.240	.878**	1			
Ni	-.277	.063	.502	.401	1		
Cr	.370	-.345	-.105	-.188	-.097	1	

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Fe	-.099	.177	.737*	.595*	.864**	-.189	1

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

Tabela 4. Factor loading of selected metals in water samples

Metals	Water		
	PC1	PC2	PC3
Cu	-.334	**.792**	-.474
Pb	.020	.104	**.836**
Mn	.463	**.864**	.120
Zn	.351	**.849**	.226
Ni	**.977**	.060	.022
Cr	-.091	.030	**-.790**
Fe	**.902**	.334	.146
Eigen value	3.129	1.821	1.131
Loading%	44.693	26.007	16.152
Cumulative%	44.693	70.700	86.852

Extraction Method: PCA
Rotation Method: Varimax with Kaiser Normalization.

4. 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 spring waters samples showed significant higher values of heavy metals contents that the control. All water springs pass through inhabited areas and discharged into the river.

Based on the results of the study, it is strongly suggested that the chemistry of waters spring 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 water springs of Stan Terg to the Ibri River.

REFERENCES

1. Amman A.A., Michalke B., Schramel P. 2002. Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. Anal. Biochem. 372(3), 448-452.
2. Armah F.A., Obiri S., Yawson D.O., Onumah E.E., Yengoh G.T., Afrifa E.K., Odoi J.O 2010a. Anthropogenic sources and environmentally relevant concentrations of heavy metals in surface water of a mining district in Ghana: A multivariate statistical approach. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng, 45, 1804-1813.
3. Armah F.A., Obiri S., Yawson D.O., Pappoe A.N.M., Akoto B. 2010b. Mining and heavy metal pollution: Assessment of aquatic environments of Tarkwa, Ghana using multivariate statistical analysis. J. Environ. Statistics, 1(4), 1-13.
4. Avdullahi S., Fejza I., Syla A. 2008. Water resources in Kosova. Journal of International Environmental Application & Science, 3(6), 51-56,
5. Bartolomeo A.D., Poletti L., Sanchini G. 2004. Relationship among parameters of lake polluted sediments evaluated by multivariate statistical analysis. Chemosphere, 15, 1323-1329.
6. Danielsson A., Cato I., Carman R. 1999. Spatial clustering of metals in the sediments of the Skagerrak/Kattegat. Applied Geochemistry, 14, 689-706.
7. Das R.K.; Bhowmick S.; Ghosh S P.; Dutta S. 1997. Coliform and fecal coliform bacteria 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.
8. Einax J W., Truckenbrodt D., Kampe O. 1998. "River Pollution Data Interpreted by Means of Chemometric Methods," Microchemistry Journal, 58(3), 315-324.
9. Einax J.W., Zwanziger H.W., Geiss S. 1997. "Chemomet-rics in Environmental Analysis," Wiley, Weinheim,
10. Fernandez H., Conti L.F., Patchineelam S.R. 1994. An assessment of the pollution of heavy metals in Jacarepagua Basin, Rio De Janeiro, Brazil: A

 ISSN 2305-8269

International Journal of Engineering and Applied Sciences

www.eaas-journal.org

statistical approach. Environment & Technology, 269, 87-94.

11. Ghosh S.; Vass K.K. 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.
12. Ipinmoroti K.O. 1993. Water quality of shallow wells located close to dumpsite in Akure, Nigeria. Pakistan Journal of Scientific and Industrial Research, 36, 137-141.
13. Karbassi A., Ayaz G., Nouri J. 2007. Flocculation of trace metals during mixing of Talar river water with Caspian Seawater. International Journal of Environmental Research, 1(1), 66-73.
14. Kowalkowski T., Zbytniewski R., Szpejna J., Buszewski B. 2005. "Application of Chemometrics in River Water Classification," Water Research, 40(4), 744-752
15. Kumar R., Singh R.N. 2006. Municipal water and wastewater treatment. New Delhi: Capital Publishing Company,
16. Lantzy R.J. Mackenzie F.T. 1979. Atmospheric trace metals: global cycles and assessment of man's impact, Geochim. Cosmochim. Acta, 43, 511- 525.
17. 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.
18. Marcovecchio J.E., Botte S.E., Freije R.H: 2007. Heavy metals, major metals, trace elements. In handbook of water analysis. 2nd edition. Edited by Nollet LM. London,
19. Marengo E., Gennaro M.C., Giacosa D., Abrigo C., Saini G., Avignone M.T. 1995. "How Chemometrics Can Helpfully Assist in Evaluating Environment Data Lagoon Water," Analytica Chimica Acta Anal, 317(1-3), 53-63.
20. McMurry J., Fay R.C. 2004. Hydrogen, Oxygen and Water. In: McMurry Fay Chemistry. K.P. Hamann, (Ed.). 4th Edn. New Jersey: Pearson Education, 575-599.
21. Mendie U. 2005. The Nature of Water. In: The Theory and Practice of Clean Water Production for Domestic and Industrial Use. Lagos: Lacto-Medals Publishers, 1-21.
22. Moon C.H., Lee Y.S., Yoon T.H. 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.
23. Nriagu J.O. 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, Nature, 279, 409-411
24. Nriagu J.O., Pacyna J.M. 1988. Quantitative assessment of world-wide contamination of air, water and soils by trace metals. Nature, 333, 134–139
25. Oguzie E.E., Agochukwu I.B., Onuchukwu A.I., Offem, J.O. 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.
26. Pradit S., Wattayakorn G., Angsupanich S., Baeyens W., Leermakers M. 2010. Distribution of trace elements in sediments and biota of Songkhla Lake, Southern Thailand. Water, Air, & Soil Pollution, 206(1), 155-174.
27. 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.
28. 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.
29. Ross S.M. 1994. Toxic metals in soil-plant systems, Wiley, Chichester, U. K.
30. Shrestha S., Kazama F. 2007. Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. Environ. Modell. Softw, 22, 464-475.
31. Speir T.W., VanSchaik A.P., Percival H.J., Close M.E., 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
32. Vanloon G.W., Duffy S.J. The Hydrosphere. 2005. In: Environmental Chemistry: A Global Perspective. 2nd Edn. New York: Oxford University Press, 197-211.
33. Vidal M., Melgar J., Lopez A., Santoalla M.C. 2000. Spatial and temporal hydrochemical changes in ground water under the contaminating effects of fertilizers and wastewater. Journal of Environmental Management, 60, 215–225
34. Watt G.C.M., Britton A., Gilmour H.G., Moore M.R., Murray G.D., Robertson S.J. 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

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