ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER OF THE MANDAKINI RIVER CHITRAKOOT USING MULTIVARIATE STATISTICAL TECHNIQUES

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ABSTRACT

The objectives of this study was to apply Principal component analysis and cluster classification techniques to identify the interrelation among a set of the heavy metals concentration Fe, Cd, Pb, As and Hg as potential contaminants of river Mandakani in Chitrakoot and identify the underlying structure of those variables. Water samples were collected from six different sites of river Mandakani. For the determination of total heavy metals in the samples, procedures is described in APHA (2012) was followed. PCA and CA in combination with metal concentration are proved to be effective tools for source identification and characterization. Both natural and anthropogenic sources were found to be contributing to the pollution load of the river with the anthropogenic activities dominating the influence.The pollution in aquatic ecosystem by heavy metals has assumed serious problem due to their toxicity and accumulative behavior.

Keywords: *River Mandakini, Water, Heavy metals, Principal Component Analysis cluster Analysis.*

INTRODUCTION

Wastewater treatment is not given the necessary priority it deserves and, therefore, industrial waste and domestic sewage are discharged into receiving water bodies without treatment, some of these wastes contain heavy metals also which find their way into the aquatic ecosystem. The problem of environmental pollution due to toxic metals has raised widespread concems in different parts of the world and results reported by various agencies have been alarming. "Heavy metals" is a collective term which applies to the group of the metals and metalloids with atomic density greater than 4g/cms **(Nriagu and Pacyna, 1988).** However, being heavy metal has little to do with density but concerns chemical properties. Heavy metals include iron (Fe), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), and mercury (Hg) elements. The main sources of heavy metal pollution are agricultural run off, sewage and discharges of untreated and semi treated effluents ions metal-related industries such as metal electroplating, manufacturing of batteries, circuit boards and car repair. Road is also one of the largest sources of heavy metals **(Farmaki and Thomaidis, 2008).**

Heavy metals have long been recognized as one of the most important pollutants in the river waters because of their toxicity, mutagenic and carcinogenic effects in animals. They constitute the most widely distributed group of highly toxic and retained substances. Almost all heavy metals are toxic but mercury, cadmium and lead are usually considered to be the most dangerous toxicanw **(Baskaran et al., 1990)**. Aquatic organisms have the ability to accumulate heavy metals from various sources including sediments, soil erosion and runoff; air depositions of dust and aerosol and discharges of waste water **(Goodwin et al., 2003)**. Once entered into the aquatic ecosystem, heavy metals persist in sediments, from where these are slowly released into the overlying water. Sediments are recognized as major repository of heavy metals in aquatic systems **(Oyewo and Don-Perdo, 2003).**

Contaminated sediments in river, lakes and coastal regions might directly affect the overlying water where they contaminate the biota, including fish and thus have the potential to ecological and human health risks. These metals after accumulation in the body of aquatic organisms, make their entry into food chain ultimately being consumed by human. Adsorption and accumulation of these elements depend on their concentration, physiochemical properties of water, distribution in body and physiological effects of metals **(Gharib et al., 2003).**

Materials and Methods

Water samples were collected from six sites namely; Sati Anusuiya, Sphatic Shila, Janki Kund, Ram Ghat, Karwi Bridge and Surya Kund of river Mandakini during summer (March, 2015). Water samples were collected the above sites from at 10-15 cm depth in pre-conditioned and acid rinsed clean polypropylene bottles**.** The samples were immediately acidified with concentrated nitric acid to a pH below 2.0 to minimize precipitation and adsorption onto container walls (APHA, 2012). Surface sediment samples were taken at a depth of about 5 cm and immediately transferred into pre-cleaned polythene bags. The collected samples were oven dried at 400C for 48 hours, homogenised, sealed in clean polythene bags and then stored at 40C for further processing. The heavy metal parameters were determined following the standard methods for the examination of water and wastewater (APHA).

Sample Analysis

For the determination of total heavy metals in the samples, procedures is described in APHA (2012) was followed. Hot plate digestion of water and sediment samples was carried out with tri-acidnitric-sulphuric and perchloric acid mixture. The digested samples were filtered through Whatman No 42 filters and made up to 25 ml by adding distilled water in a volumetric flask. Heavy metal concentrations were determined using atomic absorption spectrophotometer (AAS-303, Thermo Fisher Secentific, pvt Led. Mumbai, India) Chemicals and reagents used were of analytical grades. All glassware were washed with 14% HNO3 and rinsed thoroughly with double distilled and deionised water prior to use. Only double distilled and deionsed water was used for the study.

Statistical Analysis

Statistical techniques was used for principal component analysis (PCA) to association of heavy metals and remove correlation among independent variables, and Hierarchical Cluster classification techniques used to grouping the inter related sites.

Results and Discussion

The result of heavy metals analysis of water samples of river Mandakini during post mansoon were mentioned in Table 1 and depicted in Figures 1 & 2. Concentration of iron in water samples was found to be 1.18 to 3.13 ppm which was higher than its permissible limit, (0.3, WHO, 2006). Iron is the fourth most common element in the earth‘s crust and is highly reactive, so naturally occurring and engineered iron oxides serve as a control on the spread of phosphate, arsenic, and other trace metals and anions (**Cornell and Schwertmann, 1996)**. The average cadmium content in water samples was found to vary between N.D. to 0.040 ppm. The values obtained were found to be under the permissible limit (0.03, WHO, 2006). Absorbed cadmium enters the blood and becomes concentrated in certain parts of the human body (**Moore et. al., 2011)**. The average chromium content in water samples was found to vary between N.D. to 0.040 ppm, which was also above the permissible limit (0.05, WHO, 2006). In the present study, the average concentration of lead in water samples was found to be 0.01 to 0.032 ppm, which was also above the permissible limit ,(0.01, WHO, 2006). This is demonstrated in human beings, consuming water containing more than 50 μg/l of lead (**Anju et. al., 2011**). The average mercury content in water samples was found to vary between N.D. to 0.0004 ppm of the river. The observed values were above the permissible limit (0.001, WHO, 2006). The levels of mercury in fresh water bodies are less than 0.0002 mg/L whereas levels up to 0.03 mg/l have been reported in polluted rivers and lakes (**Krishna et. al., 2010**).The average arsenic content in water samples was found to vary between N.D. to 0.008 ppm. The values obtained were found to be under the permissible limit, (0.01, WHO, 2006). Arsenic is a heavy metal that can cause significant health problems by primarily attacking the immune system (**Hughes, 2002).**

Table 1: Concentration of heavy metals (ppm) in river Mandakini water in post mansoon period, 2014

Parameters / Sites	Iron	Cadmium	Lead	Chromium	Arsenic	Mercury
Sati Anusuiya	3.13	0.0020	0.001	0.003	0.004	0.0002
Sphatik Shila	1.32	0.0028	0.006	0.04	000.	0.0001
Janki Kund	1.513	0.000	0.001	000	0.008	000
Ram Ghat	1.586	0.0026	0.008	0.04	0.005	0.0005
Karwi Bridge	1.692	0.0040	0.002	0.02	0.007	000
Surya Kund	1.186	0.0038	0.003	0.03	0.006	0.0004

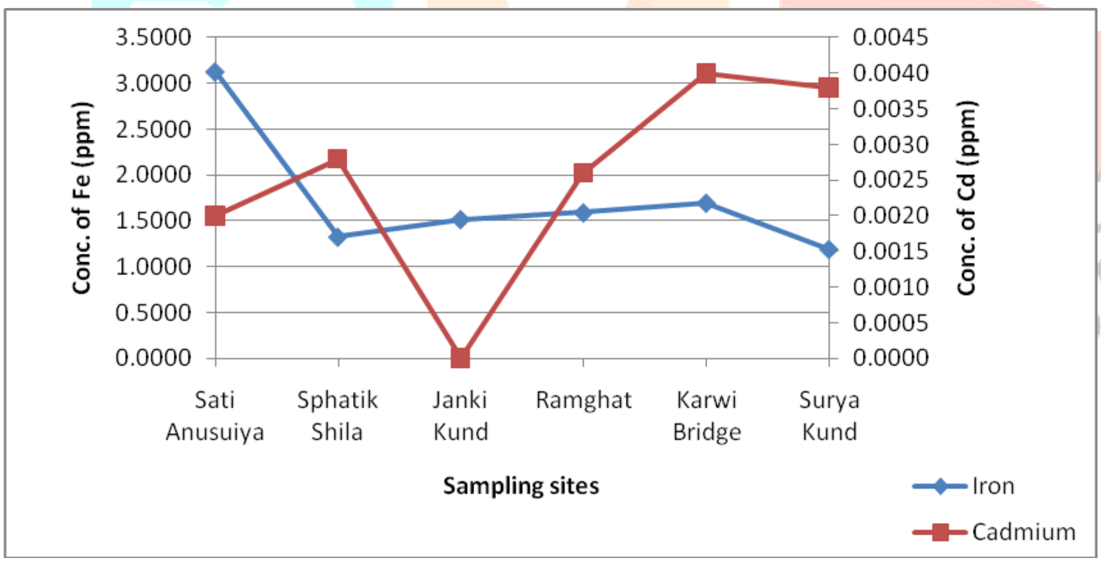

Figure 1: Concentration of heavy metals-Fe/Cd in river Mandakini water in post mansoon period, 2014

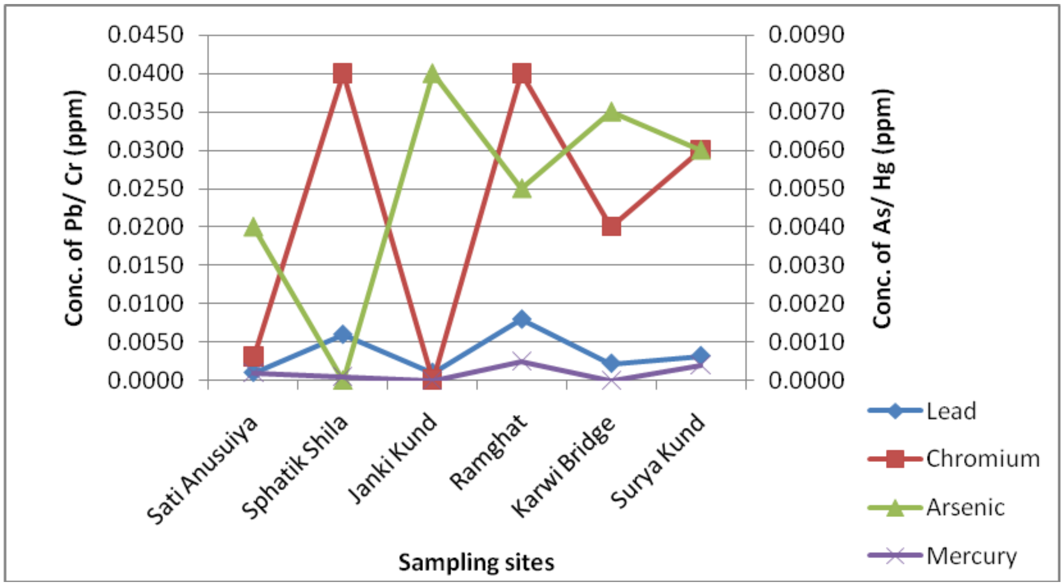

Figure 2: Concentration of heavy metals-Pb/Cr/As/Hg in river Mandakini water in post mansoon period, 2014

Principal Component Analysis (PCA) using PC_1, PC_2, eigenvalue and eigenvector was conducted for commonsource identification. The heavy metals are correlated with two principal components in which 74.18 % of the total variance in the data was found. The Principal component analysis of heavy metals of post mansoon period in the year 2014 is given in Table 2 and Figure 3.

A PC analysis indicated that the first PC (PC_1) has an eigenvalue of 2.36 and explains 39.34 % of the total variation in data set (Table 2). This is relatively large eigenvalue and suggests that PC_1 represents the equivalent of 2 individual heavy metal viz. Arsenic and Iron (Figure 3 in Table 2). This association strongly suggests that these variables havea strong interrelationship.The second component (PC_2) contributes cadmium and Lead (Figure 3 in Table 2) at 34.84 % variance, and has eigenvalue > 1.0 which alsoinfers the strong correlation between this metal pair. Principal component analysis one of the multivariate statistical analytical tools used to assess metal behaviour in sediments (**Liu *et al*., 2003**), and it is applied to detect the hiddenstructure and associations of elements in the data set, in anattempt to explain the influence of latent factors on the data distribution (**Kapaj *et al*.,** 2006).

Table 2: Principal csomponent analysis of heavy metals in river Mandakini water in post mansoon period, 2014

Heavy metals	**PC_1**	**PC_2**	**PC_3**
Iron	**0.46**	0.38	0.34
Cadmium	-0.25	**0.58**	-0.25
Lead	0.25	**0.54**	-0.45
Chromium	-0.47	0.40	0.19
Arsenic	**0.59**	0.15	0.29
Mercury	-0.31	0.23	**0.729**
Eigenvalue	**2.36**	**2.09**	**1.16**
Percent of total	**39.34**	**34.84**	**19.38**
Cumulative variance explain %	**39.34**	**74.18**	**93.56**

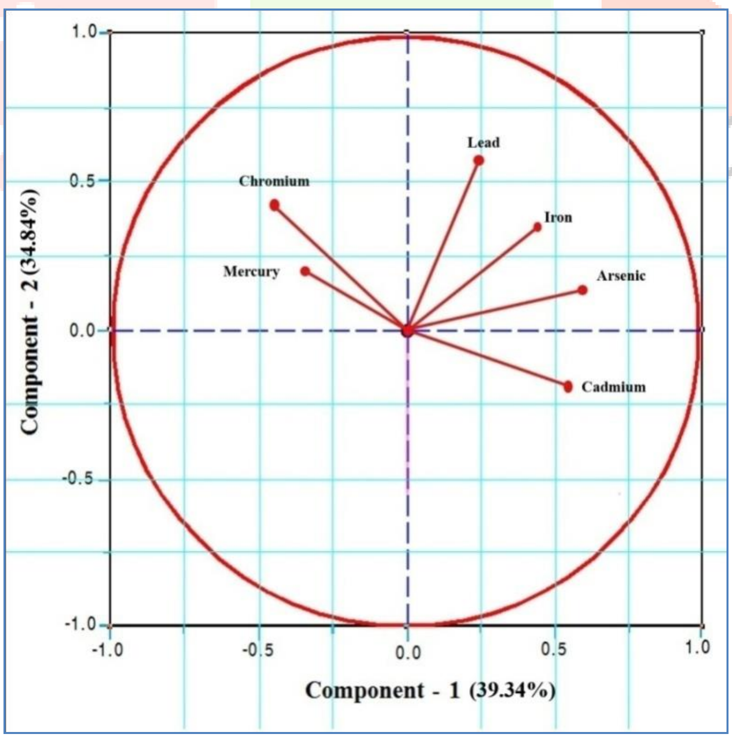

Figure 3: Principal component analysis of heavy metals in river Mandakini water in post mansoon period, 2014

Cluster analysis of heavy metal concentration calculated from six different sites of river Mandakini can be separated into 3 groups respectively for response pattern across the sites and across metals (Table 3).

The taking a cluster, classified as three groups (I, II and III) has significant different response in terms of metal distribution over all different sites. The dendrogram indicated a close relationship between the Sati Anusuiya and Sphatik Shila was grouped individually and different among all sites in their heavy metals response in river Mandakini group–I . It observed that the cluster analysis of sites Janki Kund found in a same group and considered as group-II. The metal concentrations were significantly different between sampling locations.Therefore, within group - III shows dissimilarity from other group's members with contain Ram Ghat, Karwi Bridge and Surya Kundfound heavy metal concentration in consistent (Figure 4).

Table 3: The groups of heavy metals having similar response pattern over all sites for river Mandakini in post mansoon period, 2014

Groups	Cluster No.	Cluster Members
I	2	Sati Anusuiya and Sphatik Shila
II	1	Janki Kund
III	3	Ram Ghat, Karwi Bridge and Surya Kund

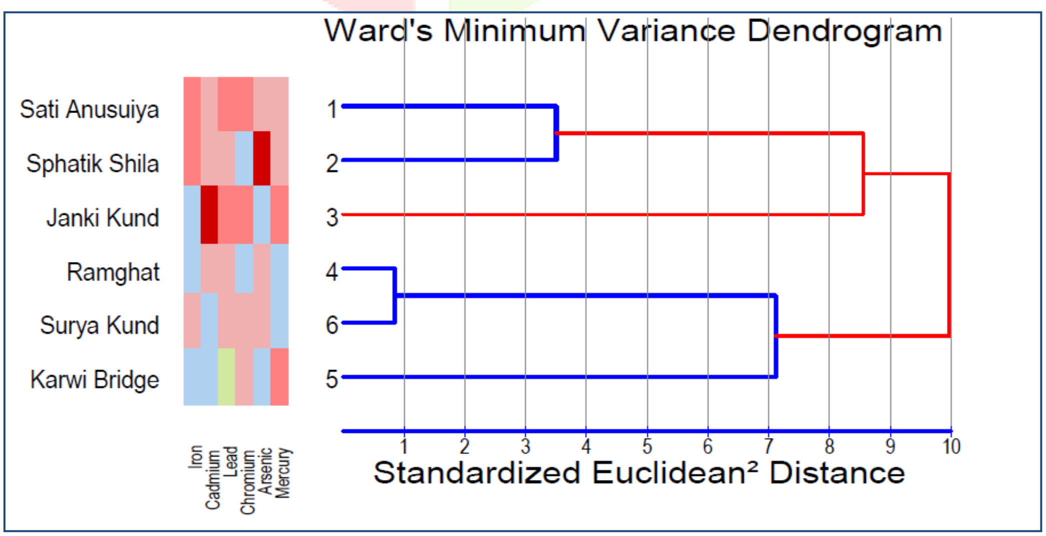

Figure 4: Dendrogram for the classification of sites in across heavy metals in water sample of Mandakini in post mansoon period, 2014

CONCLUSION

The increasing trend of concentrations of all heavy metals in water levels has been recorded Mercury < Arsenic< Chromium<Cadmium< Lead< Iron.

Multivariate statistical techniques (PCA and Cluster) were used to investigate the water quality of the River Mandakini. Principle component analysis identifies the sources responsible for variations in river heavy metals. Three Principal components generated from the principal component analysis point to that the heavy metals responsible for deterioration of water quality are largely attributed to anthropogenic activities associated with urbanization, industrialization, agriculture and mining activities. Therefore, this study observed that the multivariate statistical techniques were valuable for analysis and interpretation of heavy metals to evaluate water quality and identify contamination sources as well as understanding the variations in water quality for efficient river water quality management.

The PCA results suggest that the studied heavy metals in river water and sediments are of anthropogenic origin and cluster analysis also confirms the PCA results. PC_1 is related with Iron.Lead, Chromium whir PC_2 with Iron and Cadmium in river water. The PCA results suggest that the studied heavy metals in river sediments are PC_1 is loaded with Iron, Chromium and Mercury; PC_2 with Iron and Arsenic in river water.

The source of PC_1 loading variables can be considered as mixed source of anthropogenic inputs particularly for industrial effluents, municipal waste and agricultural activities in the study area. On the contrary PC_2 and PC_3 can be considered as assorted source from both lithogenic and anthropogenic inputs.

Cluster analysis categorized the six sites into three clusters based on the similarity of heavy metals characteristics to three clusters to identify the relationship among the various sites and their possible sources. Based on obtained information, optima.

REFERENCES

APHA, Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington D.C, 22 ND Ed., 2012.

Anju, A. K., Dipu, S. and Sobha ,V.,Seasonal variation of heavy metals in Cochin Estuary and adjoining Periyar and muvattupuzha rivers, Kerala, India, Global J. Enviro. Res., 5 (1), 15-20, 2011.

Baskaran, P., Vasanthi, R., Muniandy, D.M.S. and Palanichamy, S., Impact of environmental pollutants on growth and protein conversion efficiency in the Feshwater fish Oreochromismossambicus. in: environmental concern and tissue injury part I ed, R. Prakash and S.M. Choubey,1990.

Cornell, R.M., and Schwertmann, U., The iron oxides: structure, properties, reactions, occurrence and uses. VCH, New York, pp. 28–29, 1996.

Farmaki, E. G. and Thomaidis, N. S., Current status of the metal pollution of the environment of Greece- a review, Global Nest J., 10(3), 366-375, 2008.

Gharib, A.G., Fatoorechian, S. and Ahmadiniar, A.,Determination of essential major and trace elements in daily diets by comparative methodologies and alterations, Trance elements Med. 4(1)21-32, 2003.

Goodwin, T.H., Young, A.R., Holmes, M.G.R., Old, G.H. and Hewitt, N., The temporal and spatial variability of sediment transport and yields within the Bradford Beck catchment, West Yorkshire, Sci. Total Environ., 314, 475-494,2003.

Hughes, M.F., Arsenic toxicity and potential mechanism of action, Toxicilogy Letters. 133, 1-6, 2002.

Kapaj, S. Peterson, H. Liber, K. and Bhattacharya, P., Human health effects from chronic arsenic poisoning- a review, J. Environ Sci Health 41A, 2399–2428, 2006.

Krishna ,A.K., Mohan, K.R. and Murthy , N.N., A multivariate statistical approach for monitoring of heavy metals in sediments a case study from Wailpalli watershed , Nalgonda, district A. P. , India , Res. J. Environ.and Earth Sci., 3(2),103-113,2010.

Liu, L., Fasheng, L., Xiong, D., Heavy metal contamination and their distribution in different size fractions of the surficial sediment of Haihe river, China, Environ. Geol, 50,431-438, 2006.

Moore, F. and Rastmanesh, F., Anthropogenic sources of heavy metals in deposited sediments from runoff and industrial effluents, Shiraz, SW Iran, Inter. Conference on Environ. Sci. and Techno., 5, 215-219,2011.

North 24-Parganas, one of the nine arsenic affected districts of West Bengal, Ind. J. Environ. Sci. Health, 28 A, 25–59, 2003.

Nriagu, J.O. and pacyna, J., Quantitative assessment of wordwide contamination of air, water and soil by trace metals, Nature, 333, 134-139,1988.

Oyewo, E. O. and Don-Pedro, K. N., Lethal and sub lethal effects of copper to the Afiican catfish (Clarinsgarienpnus), Appl. Ecol., 4, 115-123,2003.

Rajmohan, N. and Elango, L., Distribution of iron, manganese, zinc and atrazince in groundwater in parts of Palar and Cheyyar river basins, Souhindia. Environ. Monit. Assess., 107,115-131,2005.

Ram, P. and Singh, A, K., Studies on distribution of heavy metals in Ganga water and its bed sediments along the Patna stretch, J. Environ. Sci. and Eng.,49(3), 211-214, 2007.

Sameer, V., Yamakanamardi, Hampannavar, U.S, and Purandara. B. K.; Assessment of chloride concentration in groundwater, a case study for Belgaum city; Inter. J. Environ. Sci., 2(1), 283-292,2011.

Singh, D., RanjanaSinha, P.K. and Rawat, N.S., Water and sediment quality of rivers Damodar and Barakar with respect to heavy metals distribution, Ind. J. Environ.l Prot., 13 (8), 594-600,1993.

W.H.O. Guidelines for drinking water quatity,1(2),Geneva, 2006.