

Statistical Assessment of the Heavy Metals Pollution of Water and Sediment in the river Mandakini

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Abstract

The objective 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, Cr, As and Hg as potential contaminants of river Mandakini 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. The principal components analysis in most examined groups showed that the first component describes the change of the heavy metal contents. Other main components emphasized variously the meaning of a given parameter. The results of PCA analysis are in accordance with the results of correlative analysis. Metals analysis of Mandakini river water and sediment was carried out by using multivariate statistical techniques such as principal component analysis (PCA), hierarchical cluster analysis.

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

1. Introduction

Aquatic ecosystems are very vulnerable to water pollution. Most of the fresh water bodies all over the world are getting polluted thus decreasing the suitability of the fresh water. Surface flowing river water, underground water and vast sea water are included in broad subject of water pollution. The degree of contamination of surface water is more comprehensible than ground water. As consequence of human activities, this water gets enriched with several nutrients which set in motion a chain of happenings leading to eutrophication and deterioration of water quality, accumulation of toxic chemicals, shrinkage of surface area and above all a loss of the aesthetic value (Nagapurna and Shashikanth, 2002).

The problem of environmental pollution due to toxic metals has raised widespread concerns 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). 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 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 toxicants (Baskaran et al., 1990). 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. 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).

A Principal Component Analysis used to examine the interrelations among a set of variables (heavy metals) in order to identify the underlying structure of those variables also called factor analysis. Use of this technique on a heavy metals data set with a large number of variables; we can compress the amount of explained variation to just a few components. The higher the component loadings, the more important that variable is to the component. Without the use of Principal Component Analyses these associations would be difficult to determine.

1. Materials and Methods

Water and sediment 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 (Ahdy and Khaled, 2009). 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 (Yongming et al., 2006; Suthar et al., 2009). 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 Scientific, 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 deionised 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 .

3. Results And Discussion

3.1 Heavy metals in the river Mandakini system

The concentration value of heavy metal in water and sediments of river mandakini were presented in Tables 3.1 and 3.2. The values of Fe in water and sediments ranged from 1.10-2.80 ppm, and 123.4-182.5 µg/g, respectively, which was higher than its permissible limit of BIS guideline. The observed values of Cd in water and sediments ranged from N.D.-0.061 ppm and 2.70-5.80 µg/gm respectively. The value of Pb in water and sediment ranged from 0.0029-0.0051 ppm and 17.8-19.9 µg/gm respectively. The values of Cr in water and sediment ranged from N.D. to 0.029 ppm and 3.2-5.1S µg/gm respectively. The value of As in water and sediment ranged from N.D.-0.0041 ppm and 3.2-5.1 µg/gm respectively. The value of Hg in water and sediment ranged from N.D.-0.0007 ppm and 2.0-3.9 µg/gm respectively. The values of Cd, Pb, Cr, As, Hg are within the prescribed permissible limit of BIS guidelines.

Table 3.1: Concentration of heavy metals (ppm) in river Mandakini water in summer 2015

Sites	Heavy metals parameters in water					
	Iron	Cadmium	Lead	Chromium	Arsenic	Mercury
Sati Anusuiya	2.10	0.021	0.0031	0.014	0.0031	0.0001
Sphatik Shila	1.80	0.042	0.0029	0.020	N.D.	0.0001
Janki Kund	1.50	0.051	0.0040	N.D.	0.0034	0.0002
Ram Ghat	2.80	N.D.	0.0051	0.020	0.0039	N.D.
Karwi Bridge	1.70	0.031	0.0031	0.029	0.0051	0.0004
Surya Kund	1.10	0.061	0.0042	0.018	0.0041	0.0007

Table 3. 2: Concentration of heavy metals ($\mu\text{g/gm}$) in river Mandakini sediement in summer 2015

Sites	Heavy metals parameters in sediment					
	Iron	Cadmium	Lead	Chromium	Arsenic	Mercury
Sati Anusuiya	168.0	4.50	19.1	13.5	4.5	2.0
Sphatik Shila	182.5	5.10	17.8	12.8	4.9	2.5
Janki Kund	143.3	2.80	18.5	13.1	3.2	2.9
Ram Ghat	158.0	3.10	18.9	12.9	4.8	3.5
Karwi Bridge	123.4	5.80	19.5	12.5	3.9	2.1
Surya Kund	153.2	2.70	19.9	13.4	5.1	3.9

3.2 Principal Component Analysis of heavy metals in Mandakini water

The results of Principal component analysis of water samples of river Mandakini for summer season 2015 were mentioned in Table 3.4. In this study, 3 PCs contain 92.86 % of the variation of the 6 heavy metals of water. Principal Component 1 explains 46.09% of the variation and highest component loading with Iron (0.60), Cadmium (-0.58) and Mercury (-0.51). This association strongly suggests that these variables have a strong interrelationship. Component 2 explains 26.35%, and Component 3 explains 20.43 %. The remaining 3 components explain only 7.14 %. The results showed in Figure 3.1.

3.3 Principal Component Analysis of heavy metals in Mandakini Sediment

The results of Principal component analysis of water samples of river Mandakini for summer season 2015 were mentioned in Table 3.5. In this study, 3 PCs contain 86.58 % of the variation of the 6 heavy metals of water. Principal Component 1 explains 40.46 % of the variation, and highest component loading with Mercury (0.54), Cadmium (-0.57) and Chromium (0.47). This association strongly suggests that these variables have a strong interrelationship. Component 2 explains 29.79 %, and Component 3 explains 16.33 %. The remaining 3 components explain 13.42 %. The results showed in Figure 3.2

Table 3.3: Principal component analysis of heavy metals in Mandakini water in summer 2015

Heavy metals	PC ₁	PC ₂	PC ₃
Iron	0.60	0.04	0.025
Cadmium	-0.58	-0.15	-0.14
Lead	0.19	0.49	-0.55
Chromium	0.089	0.25	0.81
Arsenic	-0.05	0.73	-0.01
Mercury	-0.51	0.38	0.14
Percent of total	46.09	26.35	20.43
Cumulative variance explain %	46.09	72.44	92.86

Table 3.4: Principal component analysis of heavy metals in Mandakini sediment in summer 2015

Heavy metals	PC ₁	PC ₂	PC ₃
Iron	0.22	0.70	0.05
Cadmium	-0.54	0.20	-0.47
Lead	0.20	-0.54	-0.59
Chromium	0.47	0.06	0.08
Arsenic	0.34	0.38	-0.65
Mercury	0.54	-0.18	0.07
Percent of total	40.46	29.79	16.33
Cumulative variance explain %	40.46	70.25	86.58

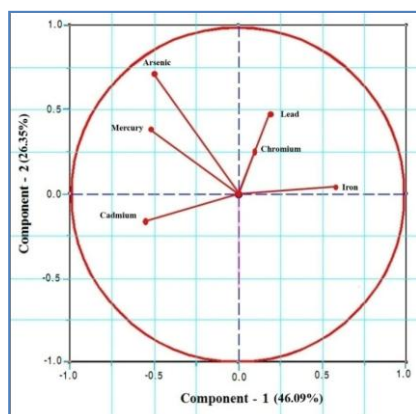


Figure 3.1: Principal component analysis of heavy metals in river Mandakini water in summer 2015

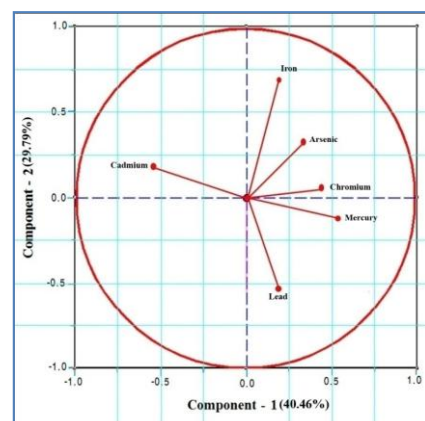


Figure 3.2: Principal component analysis of heavy metals in river Mandakini sediment in summer 2015

3.4 Classification techniques Cluster analysis of Water

Clustering 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 3.6). 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, Sphatik Shil and Janki Kund 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 Karwi Bridge and Surya 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 one member Sati Anusuiya found heavy metal concentration in consistent (Fig. 3.3).

3.5 Classification techniques Cluster analysis of sediment

Cluster analysis of Sediment 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 3.7). 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 . Therefore, within group-III shows dissimilarity from other group's members with contain one member Karwi Bridgefound heavy metal concentration in consistent (Figure.3.4). It observed that the cluster analysis of sites Janki Kund, Ram Ghat and Surya Kund found in a same group and considered as group-II. The metal concentrations were significantly different between sampling locations. Moore and Rastmanesh (2011) a similar result found in total of nine samples were collected from sediments deposited from Khoshk River Iran. The main objectives of this study are evaluating heavy metal contents (Cd, Cr, Cu, Ni, Mo, Pb and Zn) and locations can be categorized two clusters.

Table 3.5: The groups of heavy metals having similar response pattern over all sites for river Mandakini in summer 2015

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

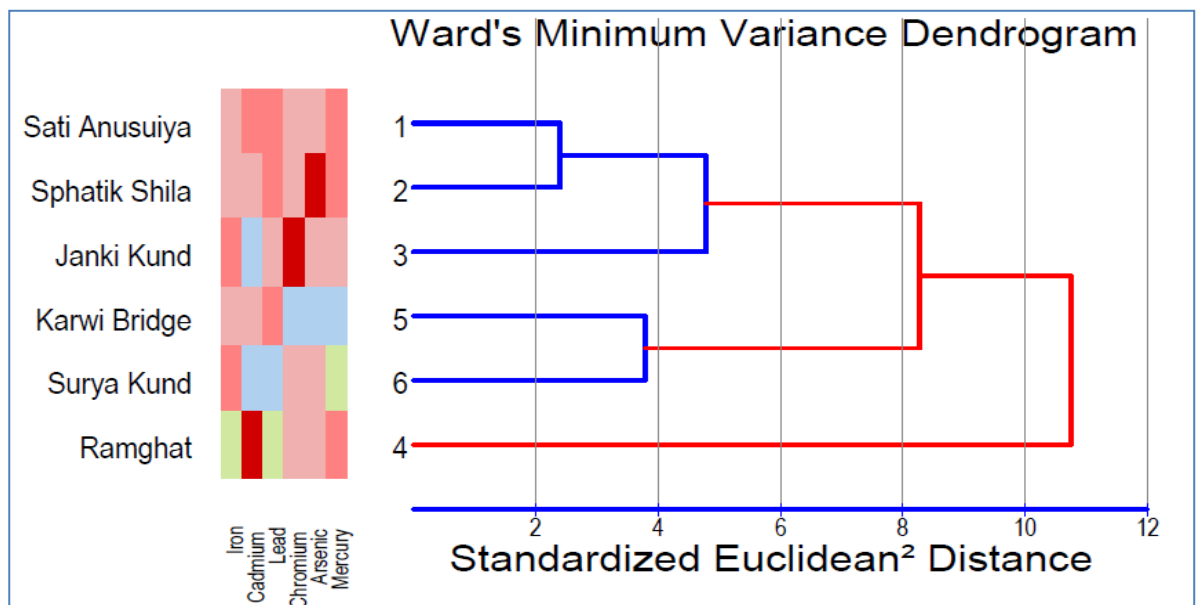


Figure 3.3: Dendrogram for the classification of sites in across heavy metals in water sample of Mandakini in summer 2015

Table 3.6s: The groups of heavy metals having similar response pattern over all sites for river Mandakini summer 2015

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

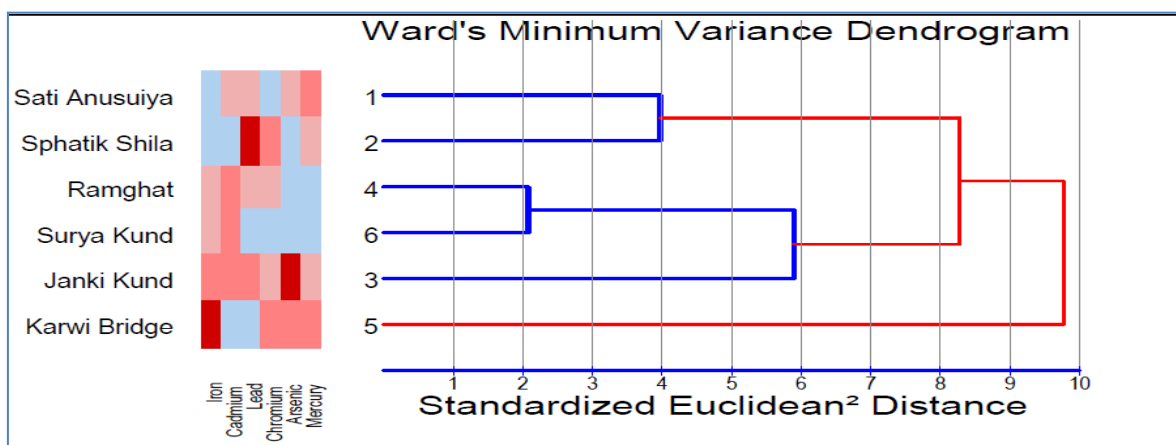


Figure3.4: Dendrogram for the classification of sites in across heavy metals in sediment sample of Mandakini in summer 2015

4. Conclusion

The increasing trend of concentrations of all heavy metals in water sediment levels has been recorded Mercury < Arsenic < Chromium < Cadmium < Lead < Iron. 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. PC₁ is related with Iron, Lead, Chromium whir PC₂ with Iron and Cadmium in river water. The PCA results suggest that the studied heavy metals in river sediments are PC₁ is loaded with Iron, Chromium and Mercury; PC₂ with Iron and Arsenic in river water. The source of PC₁ 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 PC₂ and PC₃ can be considered as assorted source from both lithogenic and anthropogenic inputs.

Cluster analysis categorized based on obtained information, optimal sampling strategy can be designed, which could reduce the number of sampling sites and related costs. In water and sediment, the result of cluster, classified as three groups (I, II and III) has significant different responses in terms of metal distribution over all different sites. The most of results indicated a close relationship between the Sati Anusuiya, Sphatik Shila and Janki Kund grouped individually and clearly found that different among all sites in their heavy metals response in river Mandakini group-I. The sites Karwi Bridge considered as a group-II and remaining sites Surya Kund and Ram Ghat considered as group-III.

In sediment, the result of cluster, classified as three groups (I, II and III) and most of

results indicated a close relationship between the Sati Anusuiya and Sphatik Shila grouped individually and clearly found that different among all sites in their heavy metals response in river Mandakini group -I. The sites Janki Kund and Ram Ghat considered as group-II and remaining sites Karwi Bridge and Surya Kund were considered as group-III.

References

- [1] Abhay, H. and Khaled, A. (2009), Heavy metals contamination in sediments of the western part of the Egyptian mediterranean sea. *Australian Journal of Basic and Applied Sciences*. Vol (3) pp: 3330-3336.
- [2] Baskaran, P., Vasanthi, R., Muniandy, D. M. S. and Palanichamy, S., (1990). Impact of environmental pollutants on growth and protein conversion efficiency in the Freshwater fish *Oreochromis mossambicus*. in: environmental concern and tissue injury part I Ed, R. Prakash and S.M. Choubey.
- [3] Gharib, A.G., Fatoorechian, S. and Ahmadiniar, A., (2003). Determination of essential major and trace elements in daily diets by comparative methodologies and alterations, *Trance elements Med*. 4(1) 21-32.
- [4] Goodwin, T.H., Young, A.R., Holmes, M.G.R., Old, G.H. and Hewitt, N. (2003). The temporal and spatial variability of sediment transport and yields within the Bradford Beck catchment, West Yorkshire. *Sci. Total Environ*, 314, 475-494.

- [5] Indian Standards for Drinking Water-Specification (Second Revision) Bureau of Indian Standards (2012). 10002 ICS13.060.20, New Delhi.
- [6] Kamal, D., Khan, A. N., Rahman, M. A. and Ahamed, F. (2007). Study on physico-chemical properties of water of Mouri River, Khulna, and Bangladesg. *Pak. J. Biol. Sci.*, 10 (5), 710-717.
- [7] Kapaj, S. Peterson, H. Liber, K. and Bhattacharya, P. (2006). Human health effects from chronic arsenic poisoning- a review, *J. Environ Sci Health* 41A, 2399–2428.
- [8] Kataria, H.C. (1995). Heavy metals contamination and pollution in Betwa River, *Indian J. Environ. Prot.*, 15 (1) 34-38.
- [9] Manual on Sampling, Analysis and Characterisation Hazardous Wastes (2000). Central Pollution Control Board, Delhi.
- [10] Moore, F. and Rastmanesh, F.(2011). 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.
- [11]Nagaprapurna and Shashikanth, K. (2002). Pollution level in HussainSagar lake of Hyderabad- A case study, *Pall. Res.*, 21(2), 187-190.
- [12]Nriagu, J.O. and pacyna, J.(1988). Quantitative assessment of worldwide contamination of air, water and soil by trace metals, *Nature*. 333, 134-139.
- [13]Oyewo, E. O. and Don-Pedro, K. N.(2003). Lethal and sub lethal effects of copper to the Afiican catfish (*Clarinsgarienpnus*). *Appl. Ecol.*, 4, 115-123.
- [14]Pradhan, U. K., Shirodkar, P. V. and Sahu, B. K. (2009). Physico-chemical characteristics of the coastal water of Devi estuary, Orissa and evaluation of its seasonal changes using chemometric techniques, *Current Sci.*, 96 (9), 1203-1209.
- [15]Styblo, M., Razzo, L.M., Vega, L., Germolec, D.R., LeCluyse, E.L and Hamilton, G.A. (2000). Comparative toxicity of trivalent and pentavalent inorganic and methylated arsenicals in rat and human cells, *Arch. Toxicol*, 74, 289–299.
- [16]Suthar, S, Nema A. K., Chabukdhara, M. and Gupta, S. K. (2009). Assessmenta of Metals in water and sediments of Hindon River, India: Impact of Industrial and Urban Discharges. *Journal of Hazardous Materials*, 171 1088-1095.
- [17]Yongming, H, Pexuan D, Junji, C. and Posmentier, E. S. (2006). Multivariate Analysis of Heavy Metal Contamination in Urban Dusts of Xi' an, Central China. *Science of the Total Environment*, 355 176-186