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Variation Pattern of Heavy Metal Concentrations During Pre- and Post-Monsoon Seasons in the Surface Water of River Indus (Sindh Province)

[1]M. Afzal Farooq, [2]S. Shahid Shaukat, [1]M. Usama Zafar and [1]Qamar Abbas

[1]Department of Environmental Science, Federal Urdu University of Arts, Science and Technology, Gulshan-e-Iqbal Campus Karachi, Pakistan
[2]Institute of Environmental Studies, University of Karachi, Karachi, Pakistan

Abstract: The present study was conducted to analyze heavy metals concentrations from surface water of the Indus River. Forty-one samples were collected from 26 stations. The section of the river surveyed ranged from Kashmor to Keti-Bander. Samples were collected during pre- and post-monsoon seasons in 2011. The six heavy metals cadmium, iron, zinc, lead, mercury and copper were analyzed to study the surface water quality using standard methods of American Public Health Association. The samples were subjected to two multivariate methods, namely Cluster analysis (Ward's method) and Principal Component Analysis (PCA). It was found that cadmium concentration was markedly greater than other heavy metals in pre-monsoon season while lead concentration was found substantially higher compared to other heavy metals during post-monsoon season. Comparison among parameters using cluster analysis and principal component analysis between pre- and post-monsoon seasons showed a substantial correlation with the exception of lead. In pre-monsoon, generally the concentration of cadmium, lead, mercury and copper exceeded the WHO recorded permissible limits while in the post-monsoon samples cadmium, lead and mercury were above the prescribed limits.

Key words: Heavy Metals · Indus River · Pre- and Post-Monsoon · Multivariate Analysis

INTRODUCTION

The availability of good quality water is important for the prevention of diseases and for improving the quality of life [1]. Most of the developed countries have adopted alternative domestic supplies so that the water quality is not so critical while in other parts of the world, particularly in developing countries, alternative supplies are not available for the handling of good quality water for catering the entire urban population [2]. A number of quality parameters that are considered to be the gauge and heavy metals like lead, mercury, arsenic, aluminum, copper, nickel, tin and antimony deteriorate water quality to a large extent [3].

Pakistan is one of the developing countries facing the problem of water quality in its rural and urban areas. The sources of contamination may be due to leakage of supply lines or pollution from damaged sewerage pipes, shallow water tables and due to human activities. The other sources of contamination are agricultural runoff and industrial effluents such as industrial chemicals, dyes, pesticides, arsenic and sewage sludge [4, 5] that contains heavy metals [6, 7]. Health risk due to heavy metals at higher concentrations in soil or water has been widely noticed by many researchers [8, 9, 10].

The quality of surface water is influenced by both anthropogenic activities and natural processes. Indus River is the biggest source of water in Pakistan covering an area of 1,140,000 km^2 and has social and economical value.

Sindh province constitutes lower Indus Basin which lies between 23° to 35° and 28-30° north latitude and 66°42′ and 71°1′-degree east longitude (Fig. 1). It covers 579 kilometers in length from north to south and 442 km in width (a total area of 225,918 km^2). The water from Indus River is used for drinking, domestic, agricultural and industrial purposes. Therefore, from the standpoint of public health it is necessary that the Indus water must be safe for human and animal consumption. Specifically, the water must comply with National Drinking Water Quality Standards in accordance with the standards given in WHO and UNICEF joint report.

Corresponding Author: S. Shahid Shaukat, Institute of Environmental Studies, University of Karachi, Karachi, Pakistan.

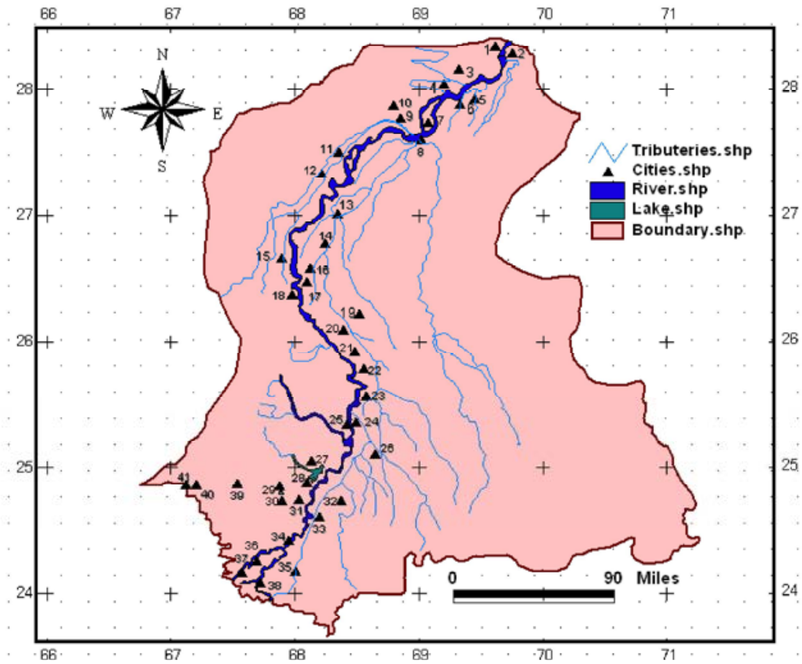

Fig. 1: Map of Sindh showing sampling locatios in lower Indus Basin from Kashmore to Keti-Bandar

In the present study, data sets obtained during one year of monitoring program were subjected to multivariate statistical techniques (cluster analysis and principal component analysis) to evaluate similarities and dissimilarities among the sites, to expose the group structure of samples, to seek gradients of variation and to identify water quality variables responsible for variations in river water quality of lower Indus Basin.

MATERIALS AND METHODS

Sampling: Forty one samples from twenty six sites were collected from Kashmor to Keti-Bander, Sindh (Fig. 1). Water samples were collected the plastic bottles previously rinsed with nitric acid. The plastic bottles were labeled and immediately few drops of nitric acid were added in order to prevent the loss of heavy metals.

Sample Analysis: Heavy metals were detected in water samples using an Atomic Absorption Spectrophotometer (Model PG 990, London, UK). Samples were prepared in nitric acid by heating on a hot plate for thirty minutes.

Statistical Analysis: The data were statistically analyzed using MINITAB (Ver. 11.12) and SPSS (Ver. 11.0) software. Descriptive statistics including mean, standard deviation, standard error, quartile 1 and quartile 3 were computed for each of the variable. Cluster analysis and principal component analysis were performed using the appropriate software mentioned above.

RESULTS AND DISCUSSION

Pre-Monsoon: Table 1 shows the descriptive statistics of pre-monsoon seasons. It is apparent that Pb concentration was much higher than those of other heavy metals. The concentrations of the heavy metals in the pre-monsoon samples were found to be in the order Pb > Hg > Cu > Fe > Cd > Zn (Fig. 2). Correlation matrix (Table 2) shows that out of 15 correlations among parameters 10 were negatively correlated and 5 were positively correlated though the correlations were low and none of them were found significant.

Principal component analysis was applied on the normalized data sets of different sites, (Table 3, Fig. 3). Together the first three components explained 95.5 percent of the total variance. The first component that accounted for 78.1 percent of variance was primarily controlled by Pb, Zn and Cu. The second component explaining 9.1 percent variance was regulated by Cd, Fe and Hg, whereas the third component contributing 8.2 percent variance was basically a function of Cu, Zn and Pb. These results to a great extent are reflected in the two-dimensional PCA ordination (Fig. 3) where Pb by

Table 1: Descriptive statistics of the heavy metal concentrations in Indus River water in pre-monsoon season

Variable	Mean	Median	Standard Deviation	[1]SE	Min.	Max.	[2]Q1	[3]Q3
Cadmium	0.0905	0.0146	0.4864	0.076	0.0123	3.129	0.0142	0.015
Iron	0.1545	0.056	0.2127	0.0332	0.001	0.723	0.019	0.1835
Zinc	0.07787	0.073	0.04104	0.00641	0.006	0.239	0.0565	0.093
Lead	1.163	1.079	0.694	0.108	0.055	2.434	0.52	1.78
Mercury	0.2579	0.273	0.1761	0.0275	0.001	0.525	0.087	0.416
Copper	0.2015	0.12	0.4532	0.0708	0.02	3	0.09	0.16

1-standard error, 2-quartile one, 3-quartile three

Table 2: Correlation matrix between heavy metal concentrations in Indus River water in pre-monsoon

	Cadmium	Iron	Zinc	Lead	Mercury
Iron	0.103				
Zinc	-0.019	-0.265			
Lead	0.026	0.055	0.242		
Mercury	-0.221	-0.076	-0.128	-0.124	
Copper	-0.036	-0.116	-0.054	0.287	-0.035

Table 3: Results of PCA of the heavy metal levels in Indus River samples for pre-monsoon.

Component	Eigenvalue	Percentage variance	Cumulative percentage variance	First 3 eigenvector coefficients	Associated variables
1	32.027	78.1	78.1	-0.606	Pb
				-0.501	Zn
				-0.408	Cu
2	3.729	9.1	87.2	-0.593	Cd
				-0.566	Fe
				0.513	Hg
3	3.380	8.2	95.5	0.651	Cu
				-0.524	Zn
				0.315	Pb

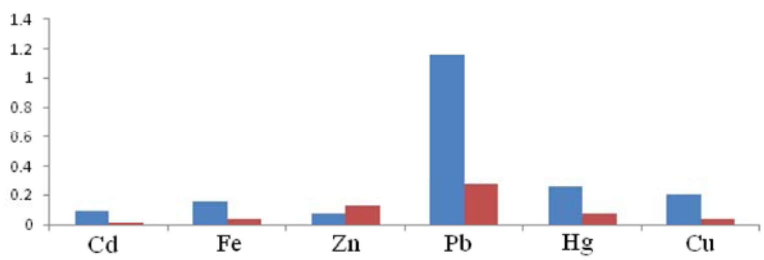

Fig. 2: Graph shows the association between pre- and post- monsoon seasons. Blue line shows mean values of all parameters during pre-monsoon season while red line represents mean values during post-monsoon season

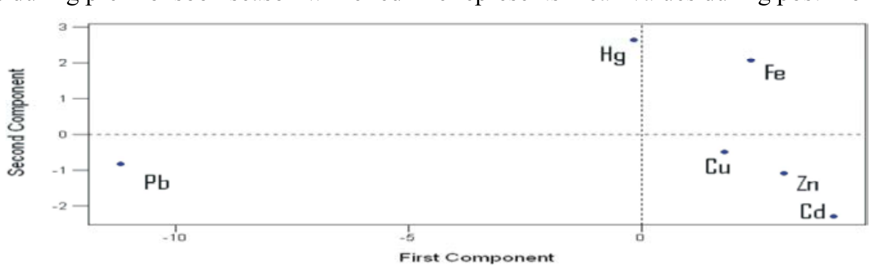

Fig. 3: Principal component analysis of heavy metals in Indus River water in pre-monsoon season

itself is situated in the extreme left, whereas the other five heavy metals tend to form a loose group on the right of the ordination diagram. The dendrogram (Fig. 4) derived from the cluster analysis confirms the result of PCA ordination where Pb forms an isolated individual while the rest of the heavy metals form a cluster. The latter represent heavy metals with relatively lower concentrations.

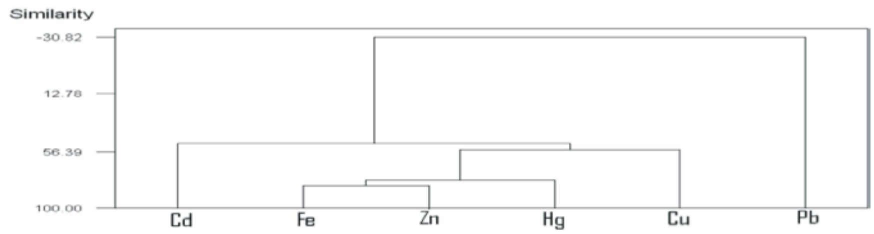

Fig. 4: Dendrogram of heavy metals in Indus River water in pre-monsoon season

Table 4: Descriptive statistics of the heavy metal concentrations in Indus River water in the post-monsoon season

Variable	Mean	Median	Standard Deviation	SE	Min.	Max.	Q1	Q3
Cadmium	0.0069	0.0055	0.0043	0.0006	0.0006	0.0166	0.0030	0.0109
Iron	0.0378	0.03	0.0450	0.0070	0	0.2	0.01	0.05
Zinc	0.1229	0.11	0.099	0.0156	0.02	0.7	0.09	0.125
Lead	0.2736	0.2876	0.086	0.0135	0.0127	0.4002	0.2198	0.3349
Mercury	0.0725	0.0736	0.0395	0.0061	0.0020	0.2371	0.0495	0.0914
Copper	0.0347	0.0396	0.0267	0.0041	0	0.0923	0	0.0533

Table 5: Correlation matrix of between heavy metal concentrations in Indus River water in post-monsoon

	Cadmium	Iron	Zinc	Lead	Mercury
Iron	-0.033				
Zinc	-0.019	-0.174			
Lead	-0.339	-0.048	-0.026		
Mercury	-0.082	-0.068	-0.09	0.082	
Copper	0.227	-0.273	0.186	-0.262	-0.003

Table 6: Results of PCA of the heavy metal levels in Indus River samples for post-monsoon

Component	Eigenvalue	Percentage variance	Cumulative percentage variance	First 3 eigenvector coefficients	Associated variables
1	35.061	85.5	85.5	-0.630	Cu
				0.450	Fe
				-0.410	Zn
2	3.038	7.4	92.2	-0.570	Pb
				0.496	Fe
				0.456	Cd
3	1.436	3.5	96.4	0.762	Hg
				0.491	Zn
				0.356	Cd

Post-Monsoon: Table 4 shows the descriptive statistics of post-monsoon seasons. Correlation matrix (Table 5) shows that there were 15 correlations among parameters out of which 12 were negatively correlated and 3 were positively correlated but significant correlations were not found. The order of heavy metal concentration during post-monsoon season was in the order Pb > Zn > Hg > Cu > Fe > Cd (Fig. 2).

Figure 5 explains the principal component analysis and Fig. 6 cluster analysis of post monsoon season respectively. Again lead concentration was found to be high as obtained in the results of pre-monsoon data. Copper, cadmium, iron and mercury show similarities in their concentrations.

Table 6 explained the results of principal component analysis of post monsoon applied on normalized data sets. The cumulative variance explained 85.5% with the highest variance 96.4%. The first component was controlled by Cu, Fe and Zn. The second component which explained 7.4% variance was regulated by Pb, Fe and Cd while third component having percent variance 3.5% was basically a function of Hg, Zn and Cd. Dendrogram using cluster analysis (Fig. 6) confirms the results of PCA again lead was separated from other heavy metals concentration.

A number of workers have attempted the water analysis of various rivers, lakes and other water bodies throughout the world [11, 12]. The present study focuses

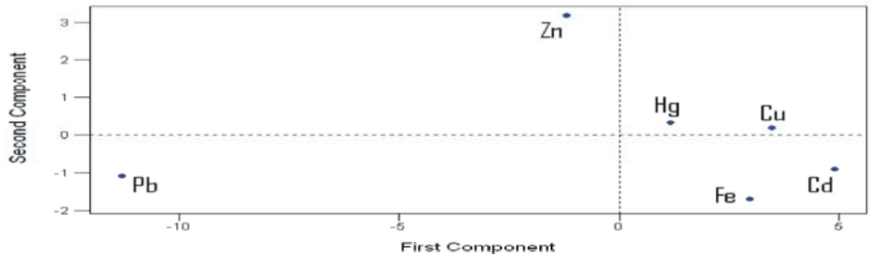

Fig. 5: Principal component analysis of heavy metals of Indus River water in post-monsoon season

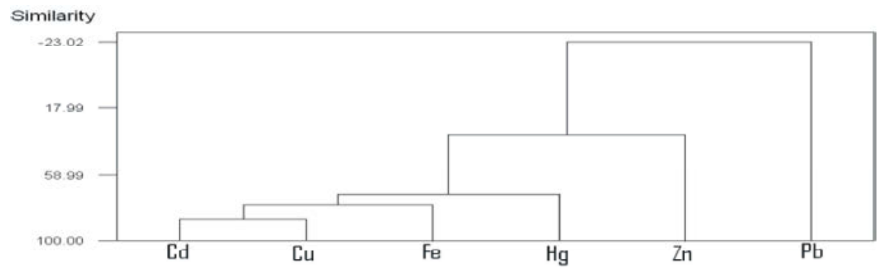

Fig. 6: Dendrogram of heavy metals of Indus River water in post monsoon season

on the water characteristics and quality of the River Indus from Kashmoor to KT-Bunder, near Karachi, in the province of Sindh.

The important consideration is that heavy metal concentrations were found to be high with respect to permissible limits set by WHO [13] with the exception of iron and zinc in both pre- and post-monsoon seasons. Of all the parameters, lead concentration was found to be high as compared to others during both seasons. Fig. 3 also explains that mean values of pre-monsoon season are higher than those of the mean values of post-monsoon season. Presumably, this is the result of excessive floods and inflow of water into the river after the heavy monsoon rains that would cause the heavy metal concentrations to be diluted. These results seem to be supported by the following study. Impact of storm water on ground water quality was assessed by Zubair *et al.* [14] from ground water samples taken from 33 monitoring wells during pre- and post-monsoon seasons. Recharge by storm water infiltration decreased the concentration of heavy metals such as Fe, Pb and Zn in background water. However, it did not result in appreciable risk of ground water contamination. The results of heavy metals in this study do not agree with these results as Pb, Hg and Cd concentrations were found to be greater in our samples, particularly those obtained in pre-monsoon period. However, the results of the present study support those of Zubair *et al.* [15] who found elevated concentrations of Pb and Zn in well water in both pre- and post-monsoon periods. The decrease in heavy metal concentrations in the post-monsoon period found in the current study may be the result of flooded water due to heavy rains that occurred in the year 2011.

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