Some Heavy Metals of the River Water-A Geological Study

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Abstract - **The present study is to prepare heavy metal pollution index (HPI) of the Subarnarekha River (India) flowing through the Indian state of Jharkhand and use the applications of environmetrics, also called multivariate statistical techniques, like principal component analysis (PCA)/factor analysis (FA) and cluster analysis (CA) to identify the sources of heavy metals along the river basin. Seventeen locations were selected along the route of the river covering its full length in the Jharkhand state. Six heavy metals viz. Iron (Fe), Zinc (Zn), Copper (Cu), Lead (Pb), Cadmium (Cd) and Manganese (Mn) were analysed using Atomic Absorption Spectrophotometer. The mean HPI (49.12) was found to be below the critical pollution index value of 100. Lowest HPI (20.89) was recorded near the origin of the river and the highest HPI value (82.40) was obtained at the Mango which is a suburb of the Jamshedpur city, one of the most industrialised and populated cities of India. Fe, Cu, Cd and Pb exceeded the desirable maximum value, prescribed by the Bureau of Indian standards (BIS), at the sites closer to the industrial and urban regions. PCA/FA and CA in combination with metal concentrations and correlation analysis proved to be effective tools for source identification and characterisation. Both natural and anthropogenic sources were found to be contributing to the pollution load of the river with the anthropogenic activities dominating the influence.**

keywords - **Cluster analysis, Drinking water standard, Heavy metals, Pollution index, Principal component analysis, Water contamination.**

Introduction:

Monitoring and assessment of the water pollution has become a very critical area of study because of direct implications of water pollution on the aquatic life and the human beings. The contamination of surface water by heavy metals is a serious ecological problem as some of them like Hg and Pb are toxic even at low concentrations, are non-degradable and can bio-accumulate through food chain. Though some metals like Fe, Cu and Zn are essential micronutrients, they can be detrimental to the physiology of the living organisms at higher concentrations [1, 2]. The spatial study of heavy metals by producing heavy metal pollution index can be helpful in identifying and quantifying trends in water quality [3, 4] and can provide the accumulated information and assessments in a form that resource management and regulatory agencies can use to evaluate alternatives and make necessary decisions. Environmetrics, also called multivariate statistical techniques, like principal component analysis and cluster analysis coupled with metal concentration analysis and correlation analysis can be effective tools for identification of pollution sources, to apportion natural versus anthropogenic or mixed contributions [2, 5, 6].

Subarnarekha River is the smallest of the major inter-state river basins in India with a total catchment area of 19,296 km2. In Jharkhand it passes through some of the most important industrialised belts of India. Ranchi, Jamshedpur and Ghatsila are some of the populated areas located along the course of the river. The Villages situated nearby the river use its water for various daily needs as other alternative sources are lacking. Many mining and processing units are located along the basin as it is rich in mineral deposits. Quarrying of the river bed for construction material and encroachment of the river bed are some of the recent problems that can be seen here. Preparation of current heavy metal profile of the Subarnarekha River water becomes very important for ecological purposes under the above mentioned situations. The objectives of the present study are a step in this direction to prepare the most recent heavy metal pollution index of the Subarnarekha River and to evolve the sources of heavy metals through various multivariate statistical techniques to assess the impacts of various agencies on it. Heavy metal concentrations recorded in some of the rivers around the world are presented in Table 1.

Table – 1 Heavy metal concentrations as recorded in some other rivers

	Parameters					
Rivers	Fe	Cu	Zn	Pb	Cd	Mn
Odra1*	250	8.24	55.4	1.77	0.140	73.3
Gomti2**	0.176	3.13 10^{-3}	0.02272	0.02118	2.6 10^{-4}	0.01534
Keritis3*	-	3.75	21.5	1.44	0.012	-
Hindon4*	350.36	921.2	239.71	276.25	14.73	315.59
Brahmani5*	21.83	1.75	13.61	11.05	1.12	24.34
Euphrates6*	105.60	2.48	10.50	0.10	2.14	6.12
Tsurumi7*	0.241	0.510	-	0.038	-	0.061

Meenachil8**	1.32	0.12	0.16	0.55	0.09	0.31

1= [7]; 2= [8]; 3= [9]; 4= [10]; 5= [4] 6= [11]; 7= [12]; 8= [2]; * = µg/l; ** = mg/l.

Material And Methods:

Spread across the Chottanagpur plateau the Subarnarekha River rises from the eastern slopes at an elevation of 610 metres in Ranchi district of the Jharkhand state, India and passes through two other districts Saraikela Kharswan and Purba Singhbhum before entering West Bengal. Kharkai, which passes through the industrialised belt Adityapur, is the major tributary of the river Subarnarekha and joins it near the Jamshedpur city. Garra, Gurma and Sankh pass through important mining belts and join the river further downwards. The basin is rich in mineral resources and many small and big industrial, mining and processing units are located along the river.

Seventeen sampling locations were selected along the river basin spread across the three districts of Jharkhand where it flows through covering a total distance of about 300 km (Figure 1). Water samples were collected just before the onset of Monsoon in June, 2017 period. The samples were collected at 10-15 cm depth in separate pre-conditioned and acid rinsed clean polypropylene bottles and acidified with concentrated nitric acid to a pH below 2.0 to minimise precipitation and adsorption on container walls. For the determination of total heavy metals in the samples extraction procedures as described in APHA, 2005 were followed [13]. Heavy metal concentrations (Fe, Zn, Cu, Mn, Pb, and Cd) were determined using Atomic Absorption Spectrophotometer (AAS: Varian AA50) with a specific lamp for each metal. Throughout the sampling and analysis procedures all the reagents of only analytical grade were used. Heavy metal pollution index (HPI) was determined as described below [3].

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}$$

Where, *Wi* is the rating or unit weightage for each parameter selected for heavy metal evaluation and is inversely proportional to the recommended standard i.e. highest permissible value for the drinking water (*Si*) of the heavy metals. The rating is a value between zero and one. *Qi*, is the Sub-index of the *ith* parameter and was calculated as shown below.

$$Qi = \sum_{i=1}^{n} \frac{|M_i - I_i|}{S_i - I_i} \times 100$$

Where, *Mi* is the observed value of the *ith* parameter, *Ii* is the maximum desirable value (ideal) of the *ith* parameter and *Si* is the recommended standard of the *ith* parameter. The critical pollution index value is taken to be 100. For the present study the *Si and Ii* values were taken from the Indian drinking water specifications, Bureau of Indian standard, 2004, 10500 [14].

The raw data obtained from the experiments were subjected to statistical analysis to determine various descriptive statistics. Pearson correlation coefficient was used to determine the interrelationships between the metals.

Environmetrics, also called multivariate statistical techniques, like Principal component analysis (PCA)/factor analysis (FA) and agglomerative hierarchal cluster analysis (AHCA), were performed to determine the sources of heavy metals. KMO and Barlett's test of sphericity were initially performed to confirm the appropriateness of water quality data for PCA. The major aim of the PCA is data reduction to better describe the relationship among the variables. PCA was performed with correlation matrix among the variables and VARIMAX normalised rotation to make the results more interpretable [5, 6]. Cluster analysis was done for identifying relatively homogeneous groups of variables based on their similarities. In agglomerative hierarchal cluster method each variables first forms a separate cluster which combine repeatedly until all the variables come under a single cluster. A dendrogram is constructed where cohesiveness and correlations among the variables can be clearly observed [5].

Result And Discussion:

Concentrations of the six studied heavy metals and some basic statistics have been shown in Table 2 and Table 3 respectively. Significant variations in the concentration of metals were obtained spatially along the course of the river. The concentration of Fe was much higher at most of the locations than the highest permissible value for surface water as prescribed by the Bureau of Indian Standards (BIS). The concentrations of Cu, Cd and Pb were found to be below the highest permissible value but above the desirable maximum value. Mn crossed the desirable maximum value only at one location S12. Based on the concentration ranges and abundance heavy metals are ranked as Fe > Cu > Mn > Zn > Pb > Cd (Table 3).

Table – 2 Heavy metal concentrations at different locations of the Subarnarekha River

Sampling Location	Parameters					
	Fe (mg/l)	Zn (mg/l)	Cu (mg/l)	Pb (mg/l)	Cd (mg/l)	Mn (mg/l)
S1	0.613	0.016	0.010	0.012	0.002	0.054

S2	3.332d	0.054	0.014	0.018	0.005	0.058
S3	1.771	0.022	0.012	0.015	0.004	0.056
S4	0.441	0.015	0.010	0.013	0.002	0.050
S5	1.814	0.020	0.016	0.020	0.006	0.059
S6	1.243	0.021	0.013	0.019	0.004	0.051
S7	3.445	0.015	0.015	0.022	0.006	0.100
S8	5.162	0.034	0.018	0.035	0.007	0.136
S9	6.654	0.037	0.020	0.038	0.008	0.054
S10	4.642	0.028	0.015	0.020	0.006	0.051
S11	4.281	0.027	0.013	0.018	0.004	0.050
S12	4.076	0.040	0.024	0.026	0.005	0.221
S13	3.592	0.022	0.035	0.022	0.003	0.057
S14	5.342	0.072	1.445	0.035	0.007	0.116
S15	5.136	0.031	0.061	0.032	0.006	0.075
S16	3.971	0.022	0.035	0.030	0.004	0.058
S17	1.472	0.014	0.027	0.018	0.003	0.052

Table – 3 Basic statistics for the heavy metals determined

Parameters	Mean	Median	SD	Skewness	Kurtosis	Min	Max	Range
Fe	3.352	3.592	1.83	-0.113	-0.971	0.441	6.654	6.213
Zn	0.029	0.022	0.015	1.679	3.005	0.014	0.072	0.058
Cu	0.105	0.016	0.346	4.114	16.943	0.010	1.445	1.435
Pb	0.023	0.020	0.008	0.564	-0.894	0.012	0.038	0.026
Cd	0.0048	0.005	0.002	-0.002	-0.862	0.002	0.008	0.006
Mn	0.076	0.057	0.045	2.440	6.330	0.050	0.221	0.171

Fe and Cd showed moderately negative skewness values indicating bulk of the values on the higher right side of the frequency distribution curve. Pb showed positive moderately skewed behaviour (Table 3). These things point to a common relationship between the three elements as they approach normal distribution with their lower skewness. Higher positive skewness values were observed for Zn, Cu and Mn which indicated bulk of the values on the lower left side of the distribution curve (Table 3). Thus, Fe-Cd-Pb and Zn-Cu-Mn formed two groups based on their frequency distribution curves. Similar trends can be observed in the Kurtosis values (Table 3).

Heavy metal pollution index is an effective tool to characterise the surface water pollution [3, 4] as it combines several parameters to arrive at a particular value which can be compared with the critical value to assess the level of pollution load. In Table 4 the methodology of HPI calculation has been presented in detail. Mean concentrations of the six heavy metals were used for the HPI determination. Overall HPI for the Subarnarekha River was found to be 49.12, which is below the critical value of 100. HPI was also calculated separately for each sampling location to compare the pollution load and assess the water quality of the selected stations (Table 5). Though overall HPI value indicates that the Subarnarekha River is not critically polluted with respect to these heavy metals, comparatively very high HPI values were obtained at S8 (72.01), S9 (82.40), S14 (73.05) and S15 (62.38). Least HPI was recorded at S1, the place near the origin of the river, and highest HPI was observed at S9 (Mango), a suburb of the highly populated, industrialised and urbanised Jamshedpur city.

Table – 4 Mean HPI of the Subarnarekha River

Parameters	Mean	Highest* permissive value ( )	Desirable# maximum value( )	Unit weightage ( )		
Fe	3352.00	1000	100	0.001	361.35	0.361
Zn	29.00	15000	5000	0.000067	49.71	0.003
Cu	105.00	1000	50	0.001	5.78	0.006
Pb	23.00	50	-	0.02	46.36	0.920
Cd	4.80	10	-	0.1	48.20	4.800
Mn	76.00	300	100	0.0033	11.83	0.039
				= 0.12536		= 6.156

HPI = 49.12; * and # taken from Bureau of Indian Standards (BIS), 2004, IS: 10500

Table – 5 HPI recorded at different sampling locations

Sampling locations	HPI	Mean deviation	% Deviation
S1	20.89	-28.23	-57.47
S2	49.10	-0.02	-4.07

S3	38.61	-10.51	-21.40
S4	21.36	-27.76	-56.51
S5	56.35	+7.23	+14.72
S6	39.70	-9.42	-19.18
S7	57.89	+8.77	+17.85
S8	72.01	+22.89	+46.40
S9	82.40	+33.28	+67.75
S10	58.26	+9.14	+18.61
S11	42.07	-7.05	-14.35
S12	53.24	+4.12	+8.39
S13	34.23	-14.89	-30.02
S14	73.05	+23.93	+48.71
S15	62.38	+13.26	+27.00
S16	45.16	-3.96	-8.06
S17	31.26	-17.86	-36.36

ΣHPI = 49.12

Pearson's correlation coefficients of heavy metals studied in the Subarnarekha River water have been summarised in the Table 6. Correlation analysis showed very strong correlation between Fe-Pb (r = 0.857), Fe-Cd (r = 0.798) and Cd-Pb (r = 0.784) at $P < 0.01$ level forming one group of Fe-Pb-Cd.

Another group represented by Zn-Cu also displayed a significant strong correlation (r = 0.727, $P < 0.01$). Heavy metals showing very high correlation may indicate same source. Zn also showed positive correlations with Fe (r = 0.596), Pb (r = 0.544) and Cd (r = 0.565) at $P < 0.05$ level indicating its relationship with the Fe-Pb-Cd group. Fe-Pb-Cd comes mainly from industrial activities/effluents though untreated domestic sewage discharges and traffic sources also contribute to it. Zn-Cu finds its main source from mining and processing units and chemical weathering of the minerals.

Cu and Zn, dominating in the PC2, come under second cluster and are highly correlated which also indicates their common source. The concentration of Cu started increasing after S12 which crossed desirable maximum value at S14 and S15. S14 is located close to a copper factory and S15 further downstream to it. Zn shows a similar trend and is highly correlated to Cu. This shows that industrial effluents are increasing the pollution load of Cu and Zn. The river passes through a large mining belt after S12 and some mineral processing units are located along the basin. Its tributaries also pass through some used and abandoned mining areas and drain directly into it carrying the minerals along with them. This shows mixed sources of these elements in the Subarnarekha River.

Mn forms a somewhat independent group within the Zn-Cu-Mn cluster as observed in correlation analysis and PCA. Mn shows similar values at most of the sampling locations but its concentration becomes higher at sampling locations nearby heavy industrial units. This clearly points to industrial activities being predominantly responsible for its increased concentration in river water.

Table – 6 Correlations between the heavy metals

	Fe	Zn	Cu	Pb	Cd	Mn
Fe	1	0.596*	0.295	0.857**	0.798**	0.333
Zn		1	0.727**	0.544*	0.565*	0.405
Cu			1	0.397	0.321	0.230
Pb				1	0.784**	0.409
Cd					1	0.339
Mn						1

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

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

Table – 7 KMO and Barlett's tests

Kaiser – Meyer – Olkin measure of sampling adequacy		0.690
Barlett's test of sphericity	Approx. Chi square	54.736
	Degree of freedom	15
	Significance	0.000

Table – 8 Total variance explained (Two components selected)

Components	Initial Eigen values			Rotation sum of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	3.621	60.350	60.350	2.802	46.703	46.703
2	1.015	16.919	77.269	1.834	30.567	77.269

3	0.781	13.013	90.283			
4	0.270	4.493	94.776			
5	0.223	3.710	98.485			
6	0.091	1.515	100.00			

Extraction method: Principal component analysis

Table – 9 Factor loadings of the components extracted

Parameters	**Original components**		**Rotated components**		**Communalities**
	1	**2**	**1**	**2**	
Fe	0.874	-0.351	0.921	0.200	0.887
Pb	0.888	-0.282	0.894	0.264	0.869
Cd	0.853	-0.318	0.885	0.215	0.830
Mn	0.540	0.060	0.414	0.352	0.296
Cu	0.612	0.722	0.102	0.941	0.895
Zn	0.820	0.433	0.437	0.818	0.860

Conclusion

Overall HPI calculated based on the mean concentration of the heavy metals was found to be 49.12 which is below the critical pollution index value of 100. However, very high HPI values were obtained at S8, S9, S14 and S15 sampling locations compared to other sampling stations. Though the water was not found to be critically polluted with respect to heavy metals, the situation is still a matter of concern as concentrations of most of the metals were found to be above the desirable maximum value prescribed for the water by BIS. The concentration of Fe exceeded even the highest permissible value for water.

Limitations of HPI confirmed that environmetrics like principal component analysis and cluster analysis, in combination with metal concentration analysis and correlation analysis can be effective tools for the characterisation of the sources of the pollutants. Fe, Pb and Cd were found to have anthropogenic origin and mainly came from industrial activities, though municipal sewage, domestic wastes, traffic sources and atmospheric depositions also contributed to them. Zn and Cu showed mixed origin from both natural and anthropogenic sources. Chemical weathering of minerals, mining activities and industrial discharges increased their concentration in water. Industrial activities were predominantly responsible for the high concentrations of Mn in water.

The study revealed the impact of various human activities on the quality of water and indicated a trend to undertake further studies on the affects of polluted river water on the aquatic life.

References

1. Kar, D., Sur, P., Mandal, S.K., Saha, T. & Kole, R.K. (2008). Assessment of heavy metal pollution in surface water. Int. J. Environ. Sci. Tech., 5(1):119-124.
2. Nair, I.V., Singh, K., Arumugam, M., Gangadhar, K. & Clarson, D. (2010). Trace metal quality of Meenachil River at Kottayam, Kerala (India) by principal component analysis. World Appl. Sci. J., 9(10):1100-1107.
3. Prasad, B. & Kumari, S. (2008) .Heavy metal pollution index of ground water of an abandoned open cast mine filled with fly ash: A case study. Mine Water Environ., 27 (4): 265-267.
4. Reza, R. & Singh, G. Heavy metal contamination and its indexing approach for river water. (2010). Int. J. Environ. Sci. Tech., 7(4):785-792.
5. Yongming, H., Peixuan, D., Junji, C. & Posmentier, E.S. (2006). Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci. Total Environ., 355(1-3):176 – 186.
6. Yalcin, M.G., Tumuklu, A., Sonmez, M. & Erdag, D.S. (2010). Application of multivariate statistical approach to identify heavy metal sources in bottom soil of the Seyhan River (Adana), Turkey. Environ. Monit. Assess., 164(1-4):311 – 322.
7. Adamiec, E. & Helios-Rybicka, E. (2002). Distribution of pollutants in the Odra river system part IV. Heavy metal distribution in water of the upper and middle Odra River, 1998-2000. Pol. J. Environ. Stud., 11(6):669-673.
8. Singh, V.K., Singh, K.P. & Mohan, D. (2005). Status of heavy metals in water and bed sediments of River Gomti – A tributary of the Ganga River, India. Environ. Monit. Assess., 105(1-3):43 – 67.
9. Papafilippaki, A.K., Kotti, M.E. & Stavroulakis, G.G. (2008). Seasonal variations in dissolved heavy metals in the Keritis River, Chania, Greece. Global Nest J., 10(3):320-325.
10. Suthar, S., Nema, A.K., Chabukdhara, M. & Gupta, S.K. (2009). Assessment of metals in water and sediments of Hindon River, India: Impact of industrial and urban discharges. J. Hazard. Mater., 171(1-3):1088 – 1095.
11. Hassan, F.M., Saleh, M.M. & Salman, J.M. (2010). A study of physicochemical parameters and nine heavy metals in the Euphrates River, Iraq. E-J. Chem., 7(3):685-692.
12. Mohiuddin, K.M., Zakir, H.M., Otomo, K., Sharmin, S. & Shikazono, N. (2010). Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. Int. J. Environ. Sci. Tech., 7(1):17 – 28.
13. APHA (2005). Standard methods for the examination of water and waste water. 21st ed. American Public Health Association, Washington. DC, USA.
14. Indian standard drinking water specification IS: 10500. 2004. (New Delhi: Bureau of Indian Standards).
15. Arumugam, N., Fatimah, M.A., Chiew, E.F.C. & Zainalabidin, M. (2010). Supply chain analysis of fresh fruits and vegetables (FFV): Prospects of contract farming. Agr. Econ., 56(9):435 – 442.
16. DeCoster, J. (1998). Overview of factor analysis. Retrieved on August 29, 2011, from http://www.stat-help.com/notes.html.