Geochemical Assessment of Heavy Metal Pollution and Toxicity of Kunda River Sediment at Khargone District, Madhya Pradesh, India

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***Abstract* - The distribution of heavy metals namely Cd, Fe, Mn , Zn, Cu, Cr, and Pb in sediments of Kunda River was studied in 2010. The levels of of selected trace metals were determined using atomic absorption spectrophotometrically. River performing principal component analysis on data set obtained through continuous monitoring of the river water. Sediment samples from upstream and downstream area were collected and analyzed for trace metals. Concentration of heavy metals in water, plants and sediments of Kunda River are reported here and covering the upstream and downstream sites. The degree of contamination in the sediments of the Kunda River, for the metals Cd, Fe, Mn , Zn, Cu, Cr, and Pb, has been evaluated using Enrichment ratio (ER), Pollution load index (PLI) and Geo-accumulation index (Igeo). Results suggested that the river bed sediments are contaminated with heavy metals, which may contribute to sediment toxicity to the freshwater ecosystem of the Kunda River.**

Keywords: ER, PLI, Igeo, Contamination Factor.

1. INTRODUCTION

Pollution of the natural environment by heavy metals is a worldwide problem because these metals are permanent and most of them have toxic effects on living organisms when they exceed a certain concentration (Chakraborty et al.2009). Discharge of greater quantity pollutants into the aquatic environment may result into deterioration of ecological imbalance, changes the physical and chemical nature of the water and aquatic biota (Mitraet al.1996).River sediments are a major carrier of heavy metals in the aquatic environment. Sediments are mixture of several components of mineral species as well as organic debris, represent as ultimate sink for heavy metals dis-charged into environment (F. Abbas 2009 , R. Bettinentti 2003). Chemical leaching of bedrocks, water drainage basins and runoff from banks are the primary sources of heavy metals (K. V. Raju 2012). Mining op-erations, disposal of industrial wastes and applications of biocides for pest are other anthropogenic sources (M. Chakravarty 2009). Heavy metals are serious pollutants because of their toxicity, persistence and nondegradability in the environ-ment (S. Olivares 2005, I. Brunner 2007, A. Idris 2007, S. Morin 2008). Polluted sediments, in turn, can act as sources of heavy metals, imparting them into the water and debasing water quality (A.-P. Zhong, 2006, C. Atkinson 2007). To date, many researchers have conducted extensive surveys of heavy metal con-tamination in sediments (K. V. Raju (2012), P. Harikumar 2010, K. Mmolawa 2011, Y. Wang 2011).

The heavy metal pollution in the rivers from different parts of the world was (also well documented in literature by references (Akcay H 2003, Loska, K. 2003, Woitke, P. 2003, Gonzalez, A.E 2000, Sakai, Hiromitsu 1986, Stamatis, N 2002)

The analysis of river sediments is a useful method of studying environmental pollution with heavy metals. Metal levels are dominated by complex dynamic equilibrium governed by various physical, chemical and biological factors [Murray *et al* (1999)].

Study on the geochemistry of river sediments in the present area has not been undertaken by previous workers so far. However, the sediment chemistry of many Indian rivers has received wide attention in the recent past. River sediments, derived as a result of weathering, are a major carrier of heavy metals in the aquatic environment, the physico-chemical processes involved in their association being precipitation, adsorption, chelation, etc. Besides the natural processes, metals may enter into the aquatic system due to anthropogenic factors such as mining operations, disposal of industrial wastes and applications of biocides for pest. The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon the textural characteristics, organic matter contents, mineralogical composition and depositional environment of the sediments [Trefry and Parsley (1976).].

River borne sediments, especially the suspended matter, act as a major carrier and source of heavy metals in the aquatic system. Geochemical study of sediments, to evaluate the concentration of heavy metals, is necessary as it helps to assess the ecotoxic potential of the river sediments.

2. MATERIALS AND METHODS

STUDY AREA

Khargone is located at South-West border of Madhya Pradesh, 283 meters above sea level. It is spread over an area of 8030 km^2. Towards North it borders Dhar, Indore and Dewas districts. Towards South it borders Maharashtra, in East Khandwa and Burhanpur and Barwani in West.

Khargone is in the middle of Narmada river vally with Vindhyachal Mountain Range on North and Satpura on South. River Narmada flows in a path of 50 km inside the district. Veda and Kunda are other main rivers in the district.

The study area is bounded by latitudes 21° 29′ 24″ N and longitudes 75° 21′ 36″ E. Samples were collected from the river bed along the seventh order segment of the Kunda river flowing through the Km in Formation (Upper Siwaliks) and the Quaternaries comprising the Pleistocene and Recent deposits Fig 1.

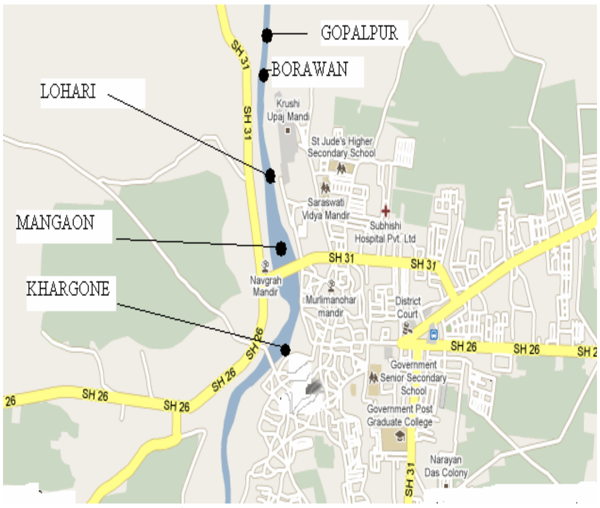

Fig.1 Location of the sampling station on Kunda River, Khargone

Samples were collected from five (5) locations, viz., Khargone, Mangaon, Lohari, Borawan and Gopalpur during both the monsoon (August) and non-monsoon (January) periods.

The sediments samples were collected in winter and spring 2012. The samples were placed in polyethylene bags and transported to the laboratory under frozen condition (at 4°C). The samples were dried in the laboratory at 104°C for forty eight hours, ground to a fine powder and sieved through 106 µm stainless steel mesh wire. The samples were then stored in a polyethylene container ready for digestion and analysis. Closed vessel microwave assisted acid digestion technique under high temperature and pressure has become routine (S. Valeria 2003) which avoids the ex- ternal contamination and requires shorter time and smaller quantities of acids, thus improving detection lim- its and overall accuracy of the analytical method (H. Feng 2004). 0.5 gram of sediment sample was put into the reference ves- sel. Then 25 ml of mixture ($HCl:H_2SO_4:HNO_3$, 3:2:2) were added to reaction vessel which was inserted into the microwave unit. The digested solution was cooled and filtered. The filtered sample was then made up to 50 ml with distilled water and stored in a special containers. We used AAS (Atomic Absorption Spectrometry) in-strument to detect and measure heavy metal content in the sediment samples.

Assessment of contamination has been done on the basis of mean concentration values of these two periods (Table 1).

The metal content has been determined by Atomic Absorption Spectrometer (AAS).

The degree of contamination in the sediments is determined with the help of three parameters - Enrichment Ratio (ER), Pollution Load Index (PLI) and Geo-accumulation Index (Igeo).

Enrichment Ratio (ER): The enrichment ratio (ER), defined as the ratio of grade of a metal element in a deposit to the crustal abundance of the metal, is proposed for assessing mineral resources. According to the definition, the enrichment ratio of a poly metallic deposit is given as a sum of enrichment ratios of all metals. Enrichment factor analysis, a method proposed by [Simex and Helz (1981)] to assess trace element concentration, is mathematically expressed as:

Enrichment ratio (ER) =(Cx/Fe)sample/ (Cx/Fe)background

Where, Cx stands for concentration of metal 'x'. The background value is that of the world surface rock average [Martin and Meybeck (1979)] given in Table 1. in case of Fe, particularly the redox sensitive iron-hydroxide and oxide under oxidation condition constitute significant sink of heavy metals in aquatic system [Forstner and Wittmann (1983]. Even a low percentage of $Fe(OH)_3$, in aquatic system, has a controlling influence on heavy metal distribution. Therefore, Fe is taken as a normalization element while determining enrichment ratio (ER).

Pollution Load Index (PLI):

Pollution load index (PLI), for a particular site, has been evaluated following the method proposed by Tomilson et al. (1980) [6] . This parameter is expressed as:

$$PLI = (CF1x\ CF2\ x\ CF3\ x \ldots\ldots\ldots.. x\ CFn)^{1/n}$$

Where, n is the number of metals (nine in the present study) and CF is the contamination factor.

Contamination Factor (CF):

The level of the pollution of the sediments calculated by the contamination factor. The contamination factor represents the individual impact of each metal on the sediment [Haknson (1980)].

The contamination factor can be calculated from the following relation:

CF (Contamination factor) = Metal concentration in the sediments / Background value of the metal

Geo-accumulation Index (Igeo):

A quantitative measure of metal pollution in river sediments was introduced by Muller (1988), which is called index of geo-accumulation. It is widely used to study pollution level of trace metals in sediments, The geo-accumulation index (Igeo), has been used by various workers in their studies[Rath *et al* (2005)] ,[Tomilson *et al* (1980)], [Glasby *et al* (1988)].

Igeo is mathematically expressed as: Igeo = $\log_2 Cn/1.5Bn$,

Where, Cn is the concentration of element 'n' and Bn is the geochemical background value [world surface rock average given by Martin and Meybeck (1979)]. The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect.

The geo-accumulation index (Igeo) scale consists of seven grades (0-6) ranging from unpolluted to highly polluted.

3. RESULTS AND DISCUSSION

In order to assess the metal content in river sediments, it is important to establish the natural levels of these metals. Apart from natural contribution, heavy metals may be incorporated into the aquatic system from anthropogenic sources such as solid and liquid wastes of industries. Some degree of contamination may be caused from fall out of industrial emissions from the atmosphere.

Trace metal contents:

Metal contamination in the Kunda river sediments has been assessed for Al, Fe, Mn, Zn, Cu, Cr, and Pb. Metal concentration values are the mean values of concentration of individual metals in the monsoon and non-monsoon periods (Table 1). The mean concentration levels of Al, Fe, Mn, Zn, and Cr in sediments of all the locations are lower than the background values. Concentration of Cu and Pb are uniformly higher than the background value. Higher concentrations of Cu and Pb are reflected in higher CF values (>1) (Table 3). Mean concentration of heavy metals in the Kunda river sediments are given in Fig 2.

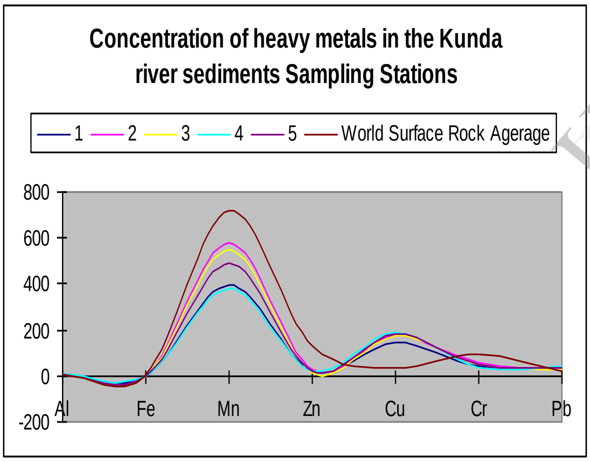

Fig.2 Mean concentration of heavy metals in the Kunda river sediments

Table 1. Mean concentration of heavy metals in the Kunda river sediments and their and their world surface rock average

Sample Location	Al	Fe	Mn	Zn	Cu	Cr	Pb
1	3.955	1.518	398	22	145	39	32.6
2	3.234	1.623	578	29	175	55	29.4
3	3.01	1.561	547	12	178	48	25
4	3.56	1.632	378	19	189	35	41
5	3.0	1.562	490	20	185	49	35
Std. Dev.	0.406	0.074	88.465	6.107	17.343	8.074	6.003
World Surface Rock Agerage	6.93	3.59	720	129	32	97	20

Enrichment Ratio:

The ER values, given in Table 2 and graphically shown in Fig 3, show depletion trend for Ni and Zn (<1). The ER of Cr is about normal, while that in case of Al, Mn and Ti shows mild enrichment (>1). Cu shows very high ER values (>10) indicating its high contamination in sediments. The ER of Pb is also fairly high (>3). Almost uniformly high values along the entire reach negate the presence of local enrichment factors.

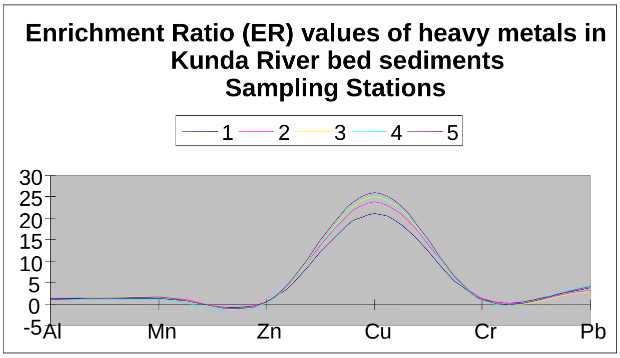

Fig.3 Enrichment Ratio (ER) values of heavy metals in Kunda River bed sediments

Table.2 Enrichment Ratio (ER) values of heavy metals in Kunda River bed sediments

Sample Location	Al	Mn	Zn	Cu	Cr	Pb
1	1.35	1.307	0.403	21.09	0.951	3.855
2	1.032	1.775	0.497	23.80	1.255	3.252
3	0.999	1.747	0.214	25.17	1.138	2.875
4	1.13	1.155	0.324	25.56	0.794	4.509
5	0.995	1.564	0.356	26.15	1.161	4.022

Pollution Load Index:

There is, in general, a decrease in PLI values downstream indicating dilution and dispersion of metal content with increasing distance from source areas. However, relatively higher PLI values at Mangaon (0.63) and Gopalpur (0.59) might be due to increased human activity since these are township area having higher population and establishments. The pollution load index does not show much fluctuation. Lower values of PLI imply no appreciable input from anthropogenic sources.Pollution Load Index of heavy metals in Kunda River bed sediments are given in Fig. 4.

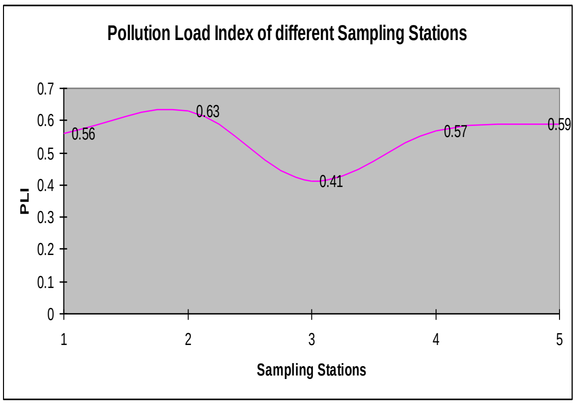

Fig 4. Pollution Load Index of heavy metals in Kunda River bed sediments

Table.3 Average concentration (A), Contamination Factor (B), standard deviation of metal concentration (SD), Back Ground value (BG) and pollution load index (PLI) of the metals in the sediments of kunda River

Sampling location	Al		Fe		Mn		Zn		Cu		Cr		Pb		PLI
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
1	3.96	0.571	1.52	0.423	398	0.553	22	0.171	145	4.531	39	0.402	32.6	1.63	0.56
2	3.23	0.467	1.62	0.452	578	0.803	29	0.225	175	5.469	55	0.567	29.4	1.47	0.63
3	3.01	0.056	1.56	0.435	547	0.76	12	0.093	178	5.563	48	0.495	25	1.25	0.41
4	3.56	0.514	1.63	0.455	378	0.525	19	0.147	189	5.906	35	0.361	41	2.05	0.57
5	3	0.433	1.56	0.435	490	0.681	20	0.155	185	5.781	49	0.505	35	1.75	59
SD	0.406		0.047		88.465		6.107		17.343		8.074		6.006		
BG	6.93		3.59		720		129		32		97		20		

Geo-accumulation Index:

This index provides a simple and quick method to determine the extent of pollution by means of the trace elements load in sediments.

The calculated Igeo values, based on the world surface rock abundance, are presented in Table 4 and the variations are shown graphically in Fig 5. It is evident from the figure that the Igeo values for Al, Fe, Mn, Zn, and Cr fall in class '0' in all the five sampling locations indicating that there is no pollution from these metals in the Kunda river sediments. The Igeo values of Pb fall in the range 0-1, while those in case of Cu have an almost uniform Igeo value of near about 2. This suggests negligible pollution from Pb, The above findings show no contamination from Al, Fe, Mn, Zn, and Cr. High Cu content in the sediment samples, as revealed from the three parameters, could be mainly due to dispersion or lithogenic influx from the upper catchments since contribution from anthropogenic factors appears negligible in the absence of major industrial establishments Fig 5.

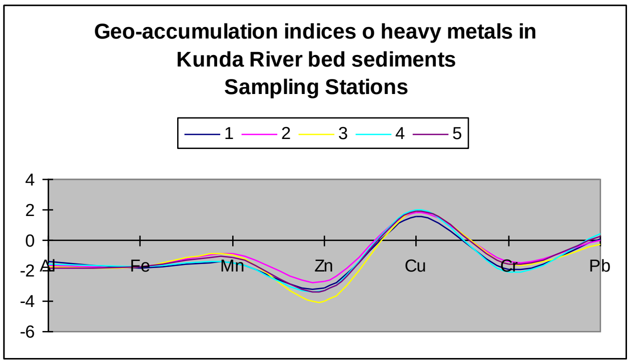

Fig. 5. Geo-accumulation indices of heavy metals in Kunda river sediments

High runoff due to heavy rainfall might have served as an efficient agent for dispersion of Cu from its source area downstream. The concentration level of Pb along the entire reach is also high. In the absence of major industrial activity, high concentration of Pb can also be attributed predominantly from domestic waste a discharge appears to be insignificant. Free metallic complexes influence the solubility of metal 'lead' by forming insoluble complexes.

4. CONCLUSION

Identification and quantification of heavy metal sources, as well as the fate of those heavy metals, are important environmental scientific issues. The present study presents useful tools, methods, and indices for the evaluation of sediment contamination. This study also provides a powerful tool for processing, analyzing and conveying raw environmental information for decision-making processes and management involving natural resources.

The results obtained in this work have allowed us to evaluate the degree of metal contamination of sediments in the Kunda River. Digestion of sediment samples using two protocols of digestion is efficient for determination of heavy metals. The results of assays are reproductible by AAS.

From the above observations, it is clear that the concentrations of all the metals showed sustained levels of pollution. The results of this study proved that the urban might have been responsible for the elevated levels of all the metals in the sediment samples. It is most likely that the food web in this study environment might be at highest risk of induced heavy metal contamination.

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