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Heavy Metal Pollution in Kabini River Sediments

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ABSTRACT: The river Kabini which is tributary of Cauvery drains through industrial area at Nanjangud, Karnataka. Out of the sediment load carried by the river, 2micron the clay fraction was analyzed for total heavy metal contents and advanced statistical techniques such as cluster analysis and correlation matrix were applied in order to investigate the source of heavy metal concentration in the sediments. The river carries natural and anthropogenic pollutants, mainly heavy metal concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn which are released from industrial effluents, agricultural return flows and domestic sewage. The heavy metals find their residence in the colloidal form in water and in 2micron clay fraction in the river bed sediments. Systematic sampling of the river bed sediments at predefined locations has revealed that the metal accumulation is very close to normal and also beyond threshold limits. Compared with the maximum background values in Kabini river sediment, Pb was the highest in terms of contamination level, especially at point of influx of paper mill effluents, followed by Zn and Cu.

Key words: Kabini River, Sediments, Heavy Metals, Physico-Chemical, Accumulation

INTRODUCTION

Heavy metals in aquatic system and sediments have natural and anthropogenic origin; distribution and accumulation of metals are influenced by mineralogical composition, sediment texture, adsorption, desorption processes and oxidation - reduction state and physical transport. Moreover, metals can be adsorbed from the water column into/on fine particle surfaces and later reside and move thereafter towards sediment matrices. Metals also participate in various biogeochemical processes, have significant mobility, can affect the ecosystems through bio-accumulation and bio-magnification processes and are potentially toxic for environment and for human life (Manahan, 2000; Abdul Aziz et al., 2010; Hasan et al., 2010; Resmi et al., 2010; Ahmad et al., 2010; Ahmed and Al-Hajri, 2009; Gaur and Dhankhar, 2009). As a combined result of these factors, metal concentrations in sediments change, with space and time. In fact, during the last few decades, industrial and urban activities have contributed to the increase of metal contamination into aquatic environment and have directly influenced the coastal ecosystems. Various studies have demonstrated that aquatic sediments are contaminated by heavy metals from industrialized coastal areas; therefore, the evaluation of metal distribution in surface sediments is useful to assess pollution in the aquatic environment (Solomons and Forstner, 1984; Zonta et al., 1994, Bellucci et al., 2002). Different studies have widely confirmed the serious contamination of river sediment by heavy metals (Priju and Narayana, 2007; Nabi Bidhendi et al., 2007; Dixit and Tiwari, 2008; Mumba et al., 2008; Kashulin et al., 2008; Mensi et al., 2008; Akoto et al., 2008; Venugopal et al., 2009; Biati et al., 2010; Nouri et al., 2010; Øygard and Gjengedal, 2009). Further studies have been conducted to evaluate the distribution and speciation of heavy metals in sediments. (Buccolieri et al. ,2006; Carman et al. ,2006; Acevedo-Figueroa et al. ,2006; Karbassi et al. ,2007; Yang et al.,2009; Cuculic et al. ,2009). Furthermore, lots of bioassays have indicated the influence of heavy metals on various organisms from different points of view (Murugesan et al., 2008; Opuene and Agbozu, 2008; Vinodhini and Narayanan, 2009; Shetty and Rajkumar, 2009; Abdullahi et al., 2009; Uba et al., 2009; Rahmani et al., 2009). In India, previous studies in Mule Hole, Cauvery and Brahmaputra and Cauvery river basins have focused on mineralogical, geochemical and geophysical studies and chemical composition of sediments (Subramanian et al., 1988; Dekov et al., 1998; Braun et al., 2009). In Mysore, Karnataka the Kabini River is a good example of a site where contributions of pollutants from natural (lithogenic) sources and anthropogenic activity and contribute pollutants two to three fold over values.

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The purpose of this paper is to determine the geochemistry, physico-chemical properties and heavy metal thresholds in the Kabini river sediments with an aim to provide additional data and investigate the present level of metal in the area. The Kabini river, a confluence of the tributaries from Panamaram and Mananthavady area originate from western Ghats in the Wynad district of Kerala and passes through the Nanjangud industrial area and flows into the main river Cauvery with its confluence at T.Narasipura down stream. The area lies between north latitude 11° 45´- 12° 30´ and east longitude 75° 45´- 77° 00´.

MATERIALS & METHODS

River bed sediments were collected from the surface along its main stream in the month of April 2009 at seventeen predetermined locations based on GPS (Fig 1). Sampling stations were chosen to provide good area coverage of the background and anthropogenic input values. After sampling, sediments were stored in a plastic vials and frozen at -20° C pending analytical procedures. In the laboratory, sediment samples were defrosted at room temperature, dried at 40 °C up to a constant weight, ground and homogenized in a mortar to a fine powder. Total metals (Cd^{++}, Cr^{+3}, Cu^{++}, Mn^{++}, Ni^{++} ,Pb^{++}, $Fe^{+3}$and Zn^{++}) were determined by Atomic Absorption Spectrophotometer technique after acid digestion. For digestion, 2 g of dried sample was put into a PTFE vessel with 4 ml of nitric acid, 2 ml of hydrochloric acid and 2 ml of hydrofluoric acid. For each digestion program, a blank was prepared with the same amount of acids. After digestion and cooling below extractor hood, samples were filtered and diluted to 100 ml with distilled water and analyzed (Minoia et al., 1993; Daskalova and Boevski, 1999; Mermet, 2001; Bettinelli et al., 2000). Physico-Chemical characteristics including pH, electrical conductivity, Ca^{++}, Mg^{++}, Na^{+}, K^{+} were analyzed by standard methods given by Trivedy and Goel (1986), APHA (1992).

To identify the association between metals, basic statistical tools such as cluster analysis (CA) was exploited on raw data through using MVSP software.

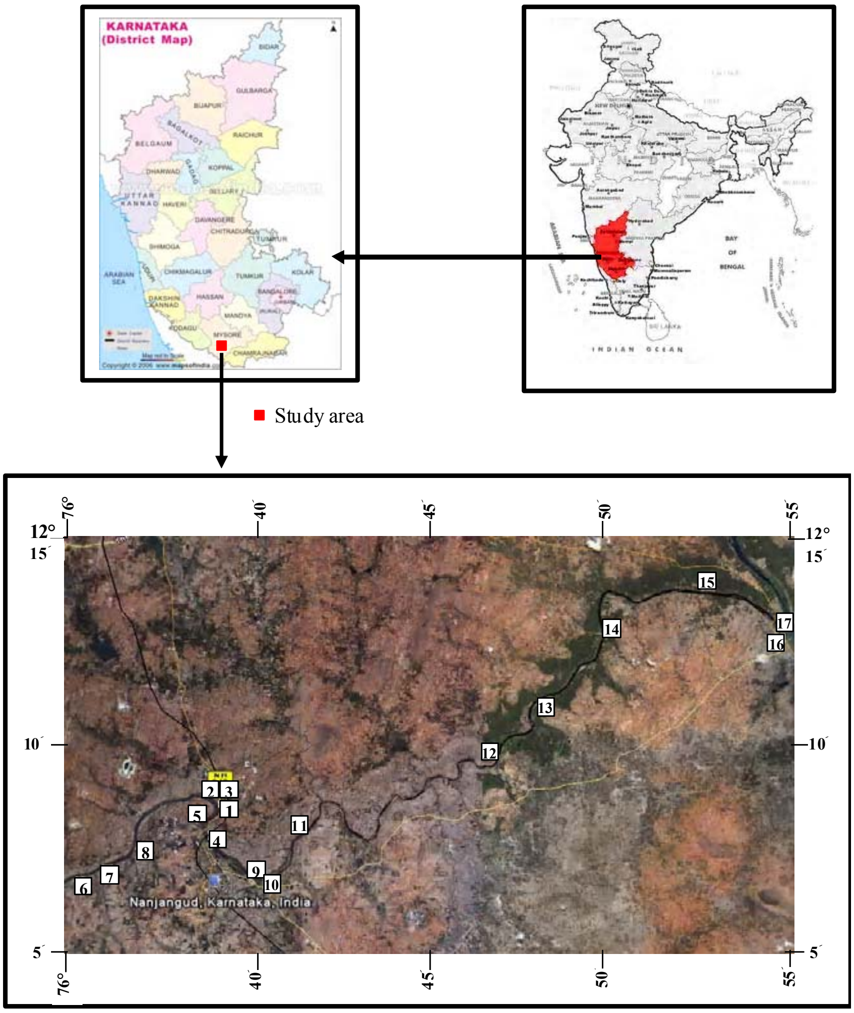


Fig.1. Sample location map of the study area

Table 1. Physico-Chemical Characteristics of water at sampling point in Kabini river-April 2009

No.	Location	pH	Ec	Hardness (mg/lit)	Ca (mg/lit)	Mg (mg/lit)	Na (mg/lit)	K (mg/lit)
1	N.Kattavadipura	8.48	250	544	400	144	31.3	34
2	Chikkayyana Chatra	7.70	327	448	288	160	10.7	12.7
3	Paper mills	7.95	396	740	524	216	16.7	10.8
4	Bridge	8.67	67	188	184	4	8.8	4.9
5	E.Kattavadipura	9.04	82	256	120	136	16.8	5.7
6	Byalaru	8.49	78	220	132	88	9.1	19.5
7	Deburu	8.24	124	432	208	224	21.9	24.7
8	Kallahalli	8.41	68	172	124	48	7.8	6.4
9	Nanjangud Temple	8.76	62	180	148	32	16.7	7.8
10	Hejijige	8.5	135	400	184	216	33.8	30.4
11	Mullur	7.91	64	204	168	36	20.6	4.8
12	Suttur	7.31	64	280	172	108	7.4	10.6
13	Thayur	8.29	112	400	188	212	19.6	35.8
14	Bilagale	8.27	74	208	92	116	1.5	3.8
15	T.Narasipura	8.41	240	220	132	88	5.6	3.4
16	Kabini	8.40	238	400	60	340	6.7	1.2
17	Confluence Cavery & Kabini river	8.46	233	168	100	68	1	1.4

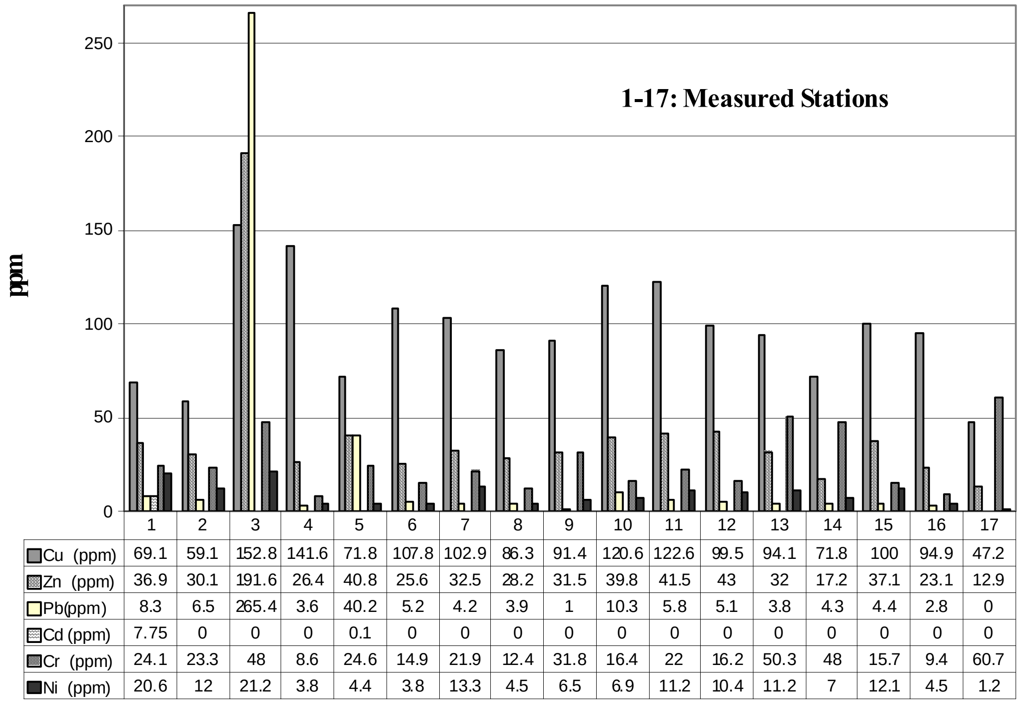
RESULTS & DISCUSSION

There were obvious differences in several measured parameters when the results were compared from site to site. The results of measured physico-chemical parameters are presented in Table 2. The pH of the river sediments vary from 7.31 to 9.04, indicating alkaline nature of the Kabini River. There was also significant difference in electrical conductivity values between the sampling sites (62-396 µmho). High concentrations of exchangeable cations were found in all the samples without any significant difference in the obtained values, except for station 10. There was significant difference in calcium and magnesium values between the sampling sites. However, the calcium values were found higher than magnesium in most of the sampling sites .The highest value of the calcium was observed at station 1 (400 mg/lit). Generally, the higher calcium contents are attributable to microorganisms which play an important role in the calcium exchange at the interface between sediment and overlying water (Elewa, 1988). The value of sodium contents were (1 to 33.8 mg/lit) and significant difference was observed in sodium values. High concentrations of potassium is noticed in the station 1 (34 mg/lit) with significant difference in the obtained values in different station.

Table 2. PEL classification of Sediment quality guideline- quotient (SQG-Q)

Parameter	Level (mg/Kg)
Arsenic	41.6
Cadmium	4.21
Chromium	160
Copper	108
Lead	112
Mercury	0.7
Zinc	271

Table 3 shows the SQGs guideline that it is very useful to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guideline.(Caeiro et al.,2005). Bottom sediments have a high absorption capacity with regard to trace elements, and in fact, it is the bottom sediment that is one of the main factors of water body self-purification from heavy metal compounds. Fig. 2 represents bottom sediment heavy metal parameters. Transitional metals, in particular, Fe and Mn, play a very important role as micronutrients in the biochemistry of plants and animals. At the same time, they are classified as basic technogenic elements. Accumulation levels of these elements are taken into account in estimating the technogenic pollution (Khazheeva et al., 2004). The maximum concentration of Fe (1381 mg/kg) was observed at station 3, in station 1 this value did not exceeded 1360 mg/kg and 1327 mg/kg at station 7, for the rest of the station, the value ranging of Fe is (928-1315 mg/kg). Much of the Fe content are fixed within the crystalline structure of primary and secondary minerals and are totally non reactive. A large portion may be soluble under reduced condition of typical anaerobic sediments and flood soils, but essentially all of the potentially reactive Fe would be oxidized to sparingly soluble ferric oxyhydroxide under upland conditions (Gambrell et al., 1983). The maximum concentration of Mn in the



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Cu (ppm)	69.1	59.1	152.8	141.6	71.8	107.8	102.9	86.3	91.4	120.6	122.6	99.5	94.1	71.8	100	94.9	47.2
Zn (ppm)	36.9	30.1	191.6	26.4	40.8	25.6	32.5	28.2	31.5	39.8	41.5	43	32	17.2	37.1	23.1	12.9
Pb(ppm)	8.3	6.5	265.4	3.6	40.2	5.2	4.2	3.9	1	10.3	5.8	5.1	3.8	4.3	4.4	2.8	0
Cd (ppm)	7.75	0	0	0	0.1	0	0	0	0	0	0	0	0	0	0	0	0
Cr (ppm)	24.1	23.3	48	8.6	24.6	14.9	21.9	12.4	31.8	16.4	22	16.2	50.3	48	15.7	9.4	60.7
Ni (ppm)	20.6	12	21.2	3.8	4.4	3.8	13.3	4.5	6.5	6.9	11.2	10.4	11.2	7	12.1	4.5	1.2

Fig. 2. Heavy metal Characteristics of sediments at sampling points in Kabini river April 2009

Table3. Correlation matrix between metal concentrations in the area of study

Pearson Correlations	CU	ZN	PB	CD	CR	NI	MN	FE
CU	1							
ZN	0.58	1						
PB	0.50	0.99	1					
CD	-0.26	-0.024	-0.056	1				
CR	-0.30	0.26	0.34	-0.038	1			
NI	0.25	0.63	0.54	0.52	0.14	1		
MN	-0.37	-0.057	-0.093	0.28	-0.097	0.27	1	
FE	0.27	0.49	0.36	0.31	-0.004	0.73	0.31	1

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

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

bottom sediment (435.64 mg/kg) was determined at station 2, as well as in station 1 (227.55 mg/kg) and station 10 (204 mg/kg).

Copper is an essential nutrient for plants growth, but may be toxic under certain conditions. Station 3 showed significant higher concentration of copper (152.8 mg/kg) compared to that of other stations. The lowest concentration of copper is at station 7 (47.2 mg/kg). As is known, the concentration of Cu in non-contaminated sea and river bottom sediments does not exceed 20 mg/kg .

The maximum value of Pb concentration in station 3 (265.4) mg/kg was observed that is exceeds the SQG standard level. Highest appreciable values of Zn concentration (191.6 mg/kg) is also observed at station 3,in other stations the concentration of Zn varied from 12.9 to 43 mg/kg, relatively high concentration of Cr was observed at station 16 (60.7 mg/kg) whereas in other stations this value varies from 8.6-50.3 mg/kg. The concentration of Nickel at station 3 was the highest with value of 21.2 mg/kg the lowest Ni concentration was at station 17 with a value of 1.2 mg/kg, value ranging from 3.8-20.6 mg/kg.

In the present study CA was carried out on sediment samples in order to identify similarities in metal contents between the analyzed sediment samples. The aim in performing CA was to identify the samples which represented different areas where metal contents followed a similar pattern (anthropogenic metal influence, background lithogenic metal levels, etc.). Fig.3. shows dendrograms summarizing samples from 17 sampling sites which were grouped into significant clusters of statistically similarity. The clustering of elements indicates common anthropogenic sources.

Metal–metal properties and relationships were analyzed by correlation matrix (Tables 3).In general, correlations between metals agreed with the results obtained by CA. Therefore in present study correlation matrix was useful to confirm some new associations between metals that were not clearly stated in previous analysis. Thus, Cu ,Zn and Pb were highly correlatable,

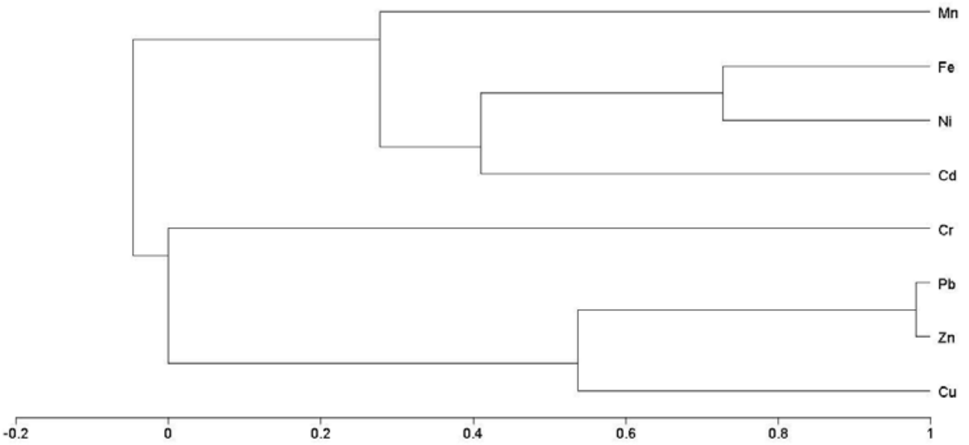


Fig. 3. Hierarchical cluster results or dendrogram obtained by CA of the sediment samples

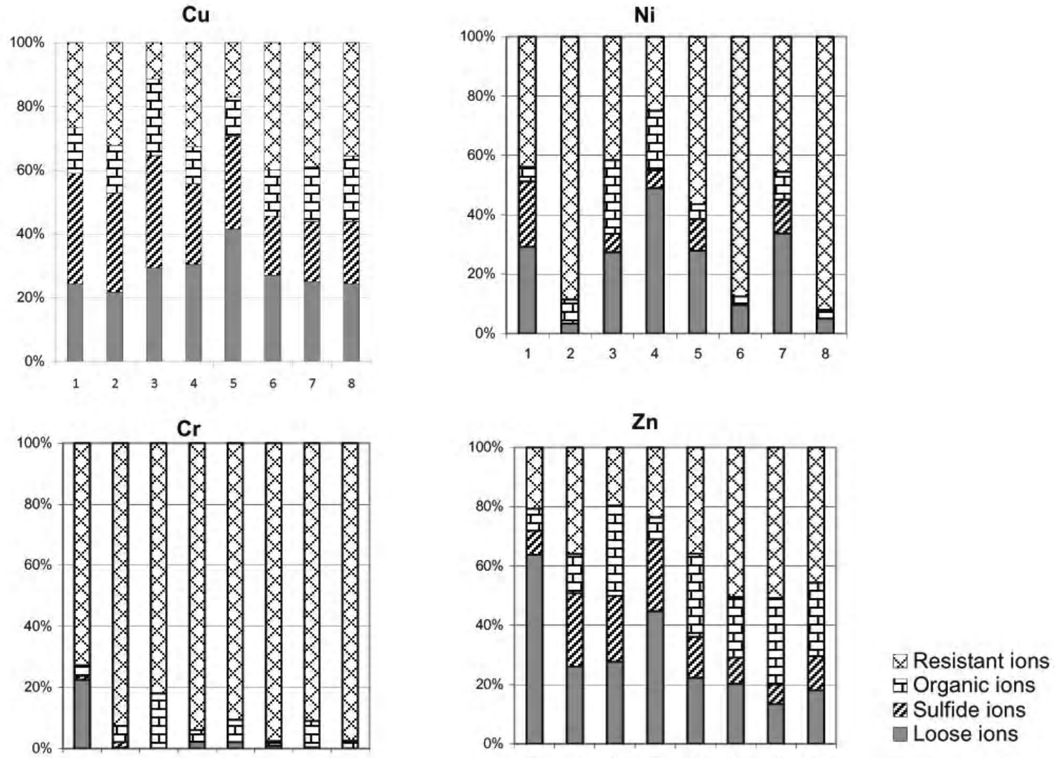


Fig. 4. Partitioning patterns of Cu, Cr, Ni and Zn in 8 samples sites of the Kabini River

which shows that Cu content in sediment was not only due to its presence in the parent rocks but also due to anthropogenic effluents of industrial area, and confirms the combination of metal affiliation of varied origin . Besides, Cd and Pb also correlated with Ni. It has been shown that the concentration of Pb in sediments is contribution of effluents from a particular industry involving manufacture of paints and pigments and on the other hand, Cd and Ni may result from a variety of industrial activities.

Metal fractionation

Chemical partitioning patterns for each metal and sampling point are shown in Fig. 4. In the present study, the resistant ion was predominant for Cu, Cr, Ni and Zn in most sites. For Cu and Zn, the very different partitioning patterns in various samples can be observed. These metals were mostly concentrated at the resistant ion at points 6 (39.9% for Cu) and 7 (50.7% for Zn) both in lower reaches, while at points 3 the relative percentage values in this fraction were 11.3% for Cu and 19.6% for Zn respectively. The next important phase of detective was, Cu as the loose ion. Cr showed a homogeneous distribution in all samples. Cr was mostly bound to resistant ion (72.7 to 97.6%) and to loose ion (13.3– 63.6%). Only small amounts of Cr were bound to the organic fraction (1.3–18.4%). The loose ions and sulfide ion account for less than 10% of total Cr with the exception of points 1.

The dominance of the resistant ion for Ni is clear over the other fractions (25–92%), with exception of sampling point 4 where the loose ion fraction is predominant (49%). The next Important phase of this element in the samples was the organic fraction (1.3–18.4%). The other fractions were found associated with loose ion, 3.3 49%; sulfide ion fraction, 0-21.9%.

CONCLUSION

The major sources of pollution of the Kabini river are the industrial effluents, (return flows), agricultural runoff, domestic and municipal sewage besides pedogenic background contributions. A case study where contamination of coconut trees by heavy metals released by industrial effluents soaking soils and draining into river Kabini near Nanjangud is on record. (Fazeli et.al.,1991). The provenance or source of heavy metals in Kabini river bed sediments (RBS) is normally envisaged as additional inputs from anthropogenic sources over and above natural or lithogenic sources. The heavy metal averages of RBS are above and more concentrated than the combined averages contributed by lithogenic sources .Table 4 gives the sources of heavy metals, the matrices involved and the mechanism of pollutants entering various matrices. Kabini River is degraded in quality due to the industrial discharge and anthropogenic effluents. In this study, hierarchical clustered analysis helped to show that groups of elements were significantly interrelated. Also, partitioning study indicate the metals under study were present mostly in the least mobilized fraction to the overlying water and it is assumed that trace metals in these sediments are to a great extent derived from derived from multisource anthropogenic inputs besides geochemical background contributions . In addition,

Table 4. Sources of heavy metals in river bed sediments of Kabini River

Provenance (source)	Source category		Pollutant types									Matrices involved	Mechanism of pollution
	point	Non point	Cu	Cd	Cr	Ni	Co	Pb	Zn	Fe	Mn		
A. NATURAL (LITHOGENIC) Amphibolites Granites, Gneisses, Ultra basic rocks & Carbonates			✓	✓	✓	✓	✓	✓	✓	✓	✓	River water, Suspended load, bed sediment Soil, Ground water, Biomass	Dissolution Suspension Deposition Reprecipitation
B. ANTHROPOGENIC													Flows,
1- Industrial													Land spreading,
a) Textile	✓		✓	✓	✓	✓			✓			Soil,	Soaking,
b) Paper	✓		✓		✓	✓		✓	✓			Suspended load	Sorption, CEC,
c) Distillery	✓		✓	✓	✓	✓	✓		✓	✓	✓	Bed Sediment	Seepage, Plumes,
d) Miscellaneous	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	Biomass	Suspension
2- Municipal													
a) Sewage effluent	✓	✓	✓	✓	✓	✓			✓			Suspended load	Mixing, Dispersion,
b) Sewage sludge	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	Bed sediment	Soaking,
c) Garbage dumps	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	Soil, Ground water	Sorption, Seepage
3- Agricultural													
a) Return flows		✓											
b) Stockpiles	✓		✓	✓	✓	✓	✓		✓	✓			

analysis indicates that Cu was not only due to weathering of parent rocks but also due to anthropogenic effluent of industrial area and other pollutants contributed to the river. Whereas Zn originated from the discharge at point sources pollutants along the river, particularly in the industrial area, Pb showed the anthropogenic sources of heavy metal in the sediments. It could have come from non- point sources such as atmospheric deposition (aerosols carrying insecticides and pesticides) and surface draining toxic chemicals within industrial areas. Although total amounts of the heavy metals investigated were found to be normal, those station showing accumulation beyond threshold limits presented by SQG standard level, assumes greater significance. Some measured stations show anomalies in heavy metal levels accumulations beyond threshold limits posing potential danger and contamination and possibility reentering into aquatic and solid food chain. It may, however be added that higher metal values might also be contributions from the already adsorbed metals in the deposited sediments due to turbulence generated by scavenging organisms at the sediment water interface.

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