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METAL FRACTIONATION STUDIES IN SURFACIAL AND CORE SEDIMENTS IN THE ACHANKOVIL RIVER BASIN IN INDIA

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Abstract. The Fractionation of Fe, Zn, Cu, Pb, Mn and Cd in the sediments of the Achankovil River, Western Ghats, India using a sequential extraction method was carried out to understand the metal availability in the basin for biotic and abiotic activities. Spatial distribution of heavy metals has been studied. Sediment grain size has significant control over the heavy metal distribution. The fluctuations in their concentration partly depend upon the lithology of the river basin and partly the anthropogenic activities. The sediments are dominated by sand and are moderately to strongly positively skewed and are very leptokurtotic in nature. The quartzite and feldspars are abundant minerals along with significant amount of mica with low clay content. The core sediments show increasing trend of heavy metal concentration with depth due to the recent addition of anthropogenic sources and post-diagenic activities. Significant amount of Cd (18%) was found in carbonate fraction, which may pose environmental problems due to its toxic nature. Small concentrations of metals, except Cd and Cu, are in exchangeable fraction, which indicate low bio-availability. Enrichment Factor (EF) for individual metals shows the contribution from terrregious and in part from anthropogenic sources. Selective Sequential Extraction (SSE) study shows the variation in specific metal distribution pattern, their distribution in different phases and their bio-availability. Maximum amount of the metals were bound to the non-residual fractions (mainly Fe-oxides). Overall, bio-availability of these micronutrients from sediments seems to be very less. Non-residual phase is the most important phase for majority of heavy metals studied. Among the non-residual fraction, maximum amount of the heavy metals bound to Fe-oxides. The study high lights the need for in-depth study of heavy metals distribution and fractionation in the smaller river basins to get precise information on the behavior and transport of heavy metals in the fluvial environment and their contribution to the world ocean.

Keywords: heavy metals, Achankovil River, selective sequential extraction, enrichment factor, anthropogenic factor

1. Introduction

The continental contribution of the heavy metals to the world oceans is large as >70% of the mass transport of metals (Gibbs, 1977) is associated with river sediments. A variety of factors like geology, changes in land use pattern, agricultural activity, industrialization and biological productivity regulate the metal load in the river sediments (Dahlberg, 1968; Garrel *et al.*, 1975; Warren, 1981; Aurada, 1983). Heavy metal inputs may be in particulate form or dissolved form. Because most of the heavy metals tend to accumulate in sediments, their presence in water column is usually the result of recent inputs. Both sorption and desorption are controlled by the nature of the total heavy metal loading to sediment type and the surface water characteristics (Todorovic *et al.*, 2001).

Sediments conserve important environmental information (Gutiérrez *et al.*, 2004) and are increasingly recognized as both carriers and possible sources of contaminants in aquatic system (Tessier *et al.*, 1994). An evaluation of total metal concentration levels after a strong acid digestion of the sediments may be useful for global budget calculation, but it provides little information on the potential availability of metals to biota under various environmental conditions. Since the mobility of trace metals, as well as their bioavailability and related ecotoxicity to plants, critically depends upon the chemical forms in which metals are present in the sediments, considerable interest exists in trace element speciation (Davidson *et al.*, 1994).

Chemical speciation can be defined as the identification and quantification of the different chemical species, forms or phases present in sediment. However, the determination of specific chemical species is difficult and often hardly possible (Loska and Wiechula, 2002). Heavy metals are associated with sediments in different ways, and there association determines their mobility and availability (Ahumuda *et al.*, 1999). Water soluble and exchangeable forms are considered readily mobile and available to fauna, while metals incorporated in the crystalline lattice of sediments appear relatively inactive. The other forms like carbonate bound, occlusion in Fe, Mn and Al oxides, or complexes with OM and Fe-Mn oxides have been found to be the most important components, which influence the media to long term affect and availability (Iyengar *et al.*, 1981). Bioaccumulation of metals can be evaluated by studying the sediments and also by assessing the possible toxicity or risk of environmental pollution by heavy metals present in sediments. This type of association between metals and the sediments can be understood in detail by sequential extraction techniques.

Conceptually, the solid materials can be partitioned into specific fraction, which can be extracted selectively by using appropriate reagents. Several experimental procedures, varying in complexity have been proposed for determining the speciation of metals. The use of sequential extraction, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physico-chemical availability, mobilization and transport of metals. Teisser procedure (Teisser *et al.*, 1979) is widely practiced for sequential extraction procedure. Leleyter and Probst (1999) developed a new procedure which is an improvement of Teisser *et al.* (1979) and Schuman (1985), procedure to determine the speciation of various trace elements.

The aim of the present study is to investigate different types of heavy metals found along with the chemical forms of heavy metals in sediments and to assess their association and bioavailability in the river. In order to assess the impact of sediment components on metal association, relationship between metal accumulation pattern and sediment characteristics have also been investigated. The data presented in this study is the only database available for the speciation of metals in the Achankovil River which will certainly help in better resource management of this river basin in future.

Few studies dealing with hydrology, biogeochemistry and nutrient dynamics are available for this study area (Bala Krishna Prasad and Ramanathan, 2005). Very few studies are available on the sediment chemistry. The studies on heavy metals and their fractionation are not available for this river basin. Hence, an attempt has been made keeping the above aspects in view.

2. Materials and Methods

2.1. STUDY AREA

The state of Kerala lies between 8.5°–11°N and 76°–77°E and is drained by 44 small rivers. Achankovil River (8°.75′–9°.5′N and 76°.25′–76°.75′E) is one of the major rivers of the state with a drainage area of 1484 km^2 and annual average discharge of about 1.5 km^3 y^{-1} bounded by hills on three sides on the south (Figure 1). The elevation varies from 20–120 m above sea level. The climate of the area is humid tropical with mean annual temperature of 23 °C. With an annual rainfall of 2000–5000 mm. The area is influenced by two monsoons: the southwestern (June–Sept.) and the northwestern (Oct.–Dec). The rainfall increases from south to north. The geology of this river basin is dominated by crystalline rocks such as pyroxene, granulites, charnockitic gneiss and khondalites associated with calc-granulite bands. The basin displays dendritic to sub-dendritic and rarely rectangular and trellises drainage patterns. The river discharges into the Vembanad Lake which extends from Cochin (Kochi) to Alleppey (Alapuzha) for a distance of 83 km and is the largest estuary in Kerala. Its width varies from a few hundred meters to 2 km and is elongated and oriented in northwest-southwest direction. The Achankovil River receives discharge from its two important tributaries i.e. Pamba and Manimala. Plantation and agriculture activities are intense in these regions.

2.2. SAMPLING

Surface sediment samples (top 2 cm) were collected from different sampling locations along the Achankovil River. Samples were air-dried in the laboratory. Stones and plant fragments were removed by passing the dried samples through a 2 mm sieve. The sieved samples were powdered and finally passed through standard sieve using ASTM standard sieves. Size fractions of the bed sediments down to 37 μm were separated, and fractions <37 μm were separated by the Astenburg cylinder method based on the Stoke's law (Griffiths, 1967).

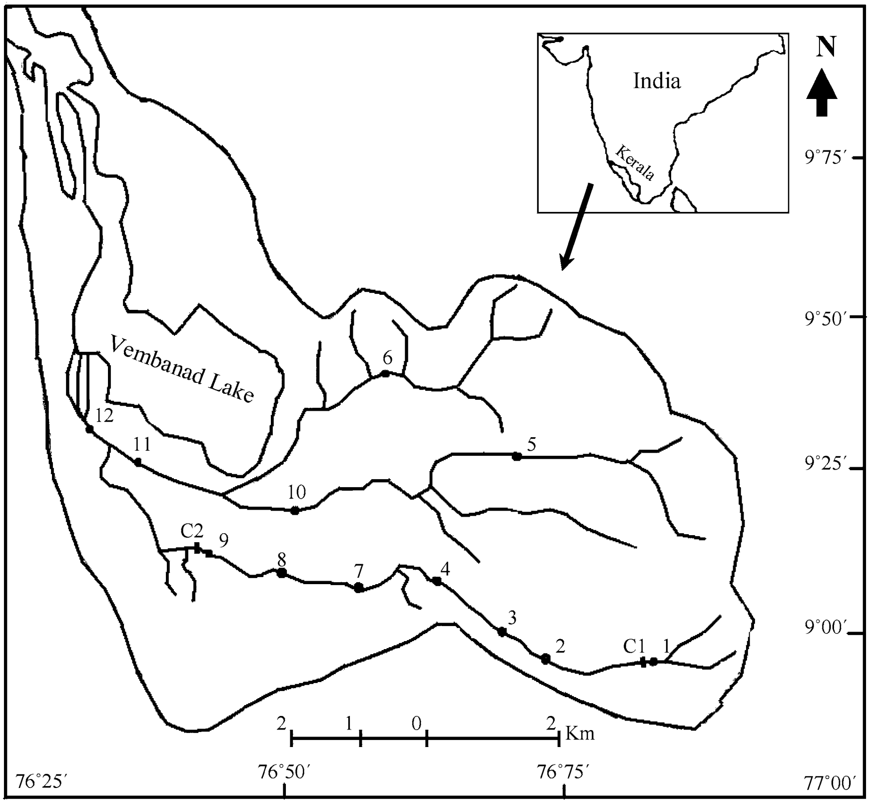

Figure 1. Location of the sediment and core sediment samples sampled in the Achankovil River Basin, Western Ghats, India.

Core sediment from two sampling points were collected in a pre washed (1M HNO_3) polycarbonate tube of 5 cm width and 100 cm length pivoted to ensure a vertical position. All samples were carefully preserved until laboratory processing.

2.3. EXPERIMENTAL

2.3.1. *Total Metal Contents*

Analytical reagent grade solutions were used without further purification. All extractions were carried out in triplicate in acid washed (5% HNO_3) polycarbonate lab ware. The extraction and estimation of metals ware carried out separately for the bed and core sediments. The metal concentration was estimated by total metals and metals from sequential extraction fractions. Digestion was done by aquaregia digestion method (Sterckman and Gomez, 1996) and metal concentrations were determined by Atomic Absorption Spectrophotometer (AAS). Prior to sample analysis, the AAS was calibrated and standardized by using relevant primary standards.

TABLE I
Selective sequential extraction (SSE) procedure

Sediment Fraction	Extractant Conditions	Volume
Water soluble (WAT)	Ultra pure water 20 °C, 30 min, end-over-end shaking	10 ml
Exchangeable (EXCH)	0.1 M KCl 20 °C, 2 h, end-over-end shaking	10 ml
Bound to Mn Oxides (MNOX)	0.1 M NH_4OH HCl at pH 2 20 °C, 30 min, end-over-end shaking	10 ml
Bound to amorphous Fe Oxides (FEOX1)	0.2 M $(NH_4)_2C_2O_4 \cdot H_2O$ + 20 °C, 4 h, end-over-end shaking in dark + $H_2C_2O_4$ at pH 3	10 ml
Bound to crystalline Fe Oxides (FEOX2)	CB: $Na_3C_6H_5O_7 \cdot 2H_2O$ (78.4 g/l) 80 °C, 15 min in dark and after add + $NaHCO_3$ (9.82 g/l), $Na_2S_2O_4$ dithionite, magnetic agitation	50 ml CB
Bound to Organic Matter (OM)	1. 0.2 M HNO_3 – 35% H_2O_2 85 °C for 5 h	1.3–8 ml
	2. 3.2 M NH_4COOCH_3 (20% v/v HNO_3) 85 °C for 30 min.	5 ml
Residual	1. Alkaline fusion for major elements 2. Diacid attack for trace elements	

Calibration was again verified by analyzing a midpoint calibration standard and a calibration blank at every run of 10 samples. Reagent blank was used to assess whether analytes or interference were present. No analyte was found to be present in the reagent blank. One replicate and one blank spike sample were also run after every 10 samples to verify the precision of the method. The precision of metal analysis was checked by triplicate samples in analytical batches, blanks and standard additions. The relative standard deviation of means of the triplicate measurements was around 5%, which was regarded as a satisfactory precision.

2.3.2. *Selective Sequential Extraction*

The partitioning of metals among the compartments of the sediment solid phase was investigated indirectly by selective sequential extractions (SSE) Table I. The SSE procedure was a seven step procedure adapted from Leleyter and Probst (1999), which is a modification of Teisser *et al.* (1979) and Schuman (1985). The SSE was performed with 1 g of ground sediment in 50 ml polypropylene centrifugation tubes to minimize losses of material. All extractions were performed in duplicate on three replications of each treatment. In each extraction series, a standard sample was introduced to follow the reproducibility of the procedure.

After each extraction step, the tubes were centrifuged at 5200 rpm for 20 min. The supernatants were then filtered through 0.45 μm membranes (Sartorius), whereas the residues were washed with 10 ml of ultra pure water, centrifuged again, and then the supernatants were pooled. The leachates (extract and rinsing) were stored in polypropylene bottles or glass vials at 4 °C until chemical analysis. The residues were dried at 40 °C prior to the next extraction step.

Blanks without a sediment sample were used on each extraction step to determine the purity and quality of the procedure.

No satisfactory physicochemical and chemical methods exist to determine unambiguously the distribution of elements within the solid phase. Nevertheless, the present extraction procedure provides an operationally defined soil-phase fractionation which is convenient for comparison of treatments. The chemical forms were labeled according to the targeted geochemical compartments during each extraction step: water soluble (WAT), exchangeable (EXCH), bound to carbonates (CAR) bound to Mn oxides (MNOX), bound to amorphous Fe oxides (FEOX1), bound to crystalline Fe oxides (FEOX2), associated with organics (OM) and residual (RES).

Each element in the different fractions was expressed as micrograms extracted per gram of soil and as percentage of the total amount metal extracted after the seven steps. The elements were analyzed by AAS. Calibration was done with standard solutions analyzed at the beginning of series and after each series of 15-samples.

For a detailed evaluation of the data, the enrichment factor (EF) and the anthropogenic factor (AF) for elements in the sediment and cores were calculated according to the formula

$$\mathrm{EF} = (C_x/C_{\mathrm{Al}})_s/(C_x/C_{\mathrm{Al}})_c$$

where C_x and C_{Al} refer to the concentrations of element x and Al in the surface sediments (s) and earth's crust (c), respectively. Aluminum is used here as the reference element and the anthropogenic factor for the cores were calculated by using the formula

$$\mathrm{AF} = C_s/C_d$$

where C_s and C_d are the concentrations of the element in the surface sediments and sediments at depth in the sediment column.

3. Results and Discussion

3.1. RESULTS

3.1.1. *Total Metal Contents*

The results obtained by acid digestion for total metal content of the Achankovil River are given in Table II. The heavy metals concentration in surface sediments

TABLE II

Heavy metal distribution (mean +SD) (μg/g) in the surface sediments of the Achankovil River

S. no.	Si	Al	Zn	Cu	Fe	Pb	Cd	Mn
1	21(1.8)	4.74 (0.4)	375 (3.7)	247 (5.8)	12273 (4.2)	94 (2.9)	4.2 (0.7)	741 (5.4)
2	32 (0.38)	1.17 (2.9)	489 (2.08)	206 (2.65)	10443 (2.08)	109 (1.53)	5.53 (0.31)	885 (3.06)
3	30 (0.06)	7.21 (0.26)	554 (2.08)	172 (2.52)	11728 (3.06)	86 (3.06)	5.62 (0.3)	767 (1.53)
4	31 (0.22)	5.58 (0.15)	508 (3.51)	216 (4.51)	13747 (7.21)	95 (2.52)	9.73 (0.21)	684 (5.03)
5	26 (0.12)	10.47 (0.07)	340 (5.62)	184 (2.86)	10789 (6.66)	75 (1.53)	6.43 (0.35)	783 (3.21)
6	12.55 (0.04)	2.7 (0.05)	273 (4.36)	163 (3.79)	14516 (5.03)	105 (3.21)	5.82 (0.26)	522 (3.06)
7	31 (0.03)	7.73 (0.05)	448 (3.39)	212 (3.23)	14165 (6.03)	59 (4.04)	6.17 (0.25)	597 (4.57)
8	34 (0.05)	7.03 (0.06)	440 (4.16)	458 (6.58)	11246 (4.36)	35 (2.65)	6.37 (0.31)	722 (3.06)
9	27.66 (3.74)	1.33 (1.26)	389 (6.59)	223 (5.13)	9760 (7.02)	43 (4.02)	11.43 (0.21)	552 (3.06)
10	35 (2.52)	8.47 (0.35)	431 (3.51)	274 (3.06)	11616 (4.04)	75 (2.56)	5.35 (0.46)	742 (3.06)
11	34.33 (0.05)	9.24 (0.18)	419 (5.51)	191 (6.03)	10462 (3.61)	47 (2.39)	3.67 (0.21)	703 (1.53)
12	33 (0.05)	9.23 (0.04)	313 (2.23)	140 (5.03)	11550 (11.53)	46 (2.52)	4.43 (0.35)	692 (8.33)

TABLE III
Heavy metal concentrations (μg/g) in surface sediments of major Indian rivers

River	Fe	Mn	Cu	Pb	Zn	Cd	Reference
Achankovil	11858	699	224	72	415	6	Present study
Godavari	60300	1060	73	13	53	–	Biksham and Subramanian (1988)
Krishna	25100	906	35	9	26	–	Ramesh *et al.* (1989)
Cauveri	17600	319	12	10	26	–	Subramanian *et al.* (1985)
Ganges	33934	669	24	20	67	–	Datta and Subramanian (1998)
Indian average	29000	605	15	15	16	–	Subramanian *et al.* (1985)

of the Achankovil River is compared with other major Indian rivers in Table III. The differences in heavy metal distribution could be assigned to differences in grain size, where the highest concentration of heavy metals occurs in the finer grained sediments (Förster and Wittmann, 1981). Heavy metal distribution in the Achankovil River sediments is lower than other major Indian rivers and Indian average. This clearly indicates the pristine nature of the Western Ghats river system. The average metal concentrations in Achankovil river decreases in the order Fe > Mn > Zn > Cu > Pb > Cd.

The grain size influence was also studied. Sediment samples were divided into various grain size fractions (<2, >2, >32, >67, >125 and >250 μm). The heavy metals were found mostly in the very fine grain fractions (<67). Heavy metals concentration in various grain fractions are given in Figure 2.

3.1.2. *Selective Sequential Extraction of Heavy Metals*

The cumulative amount of elements recovered during the seven steps SSE procedure was up to 85–90% of that obtained by a single step total analysis. The chemical fractionation trends were found to be different for each metal. The average distribution of heavy metals in different chemical fractions is shown in Figure 3. Data obtained by SSE procedure shows following distribution pattern.

Cd: EXCH >FEOXl >CAR >MNOX >OM >RES >WAT >FEOX2
Zn: FEOXl >FEOX2 >OM >MNOX >RES >WAT >CAR >EXCH
Cu: EXCH >RES >WAT> MNOX >FEOX2 >FEOXl >OM >CAR
Mn: OM >FEOXl >RES >MNOX >FEOX2 >WAT >EXCH >CAR
Pb: OM > FEOX1 >RES > MNOX > FEOX2 > WAT >EXCH >CAR
Fe: FEOX1 >FEOX2 >OM >RES >CAR >WAT >EXCH >MNOX

The highest concentration of all heavy metals was found in non-residual fractions. However, significant amounts of Cu (22.28%) and Pb (14%) were found in residual form, bound to silicates and are not in the available fraction.

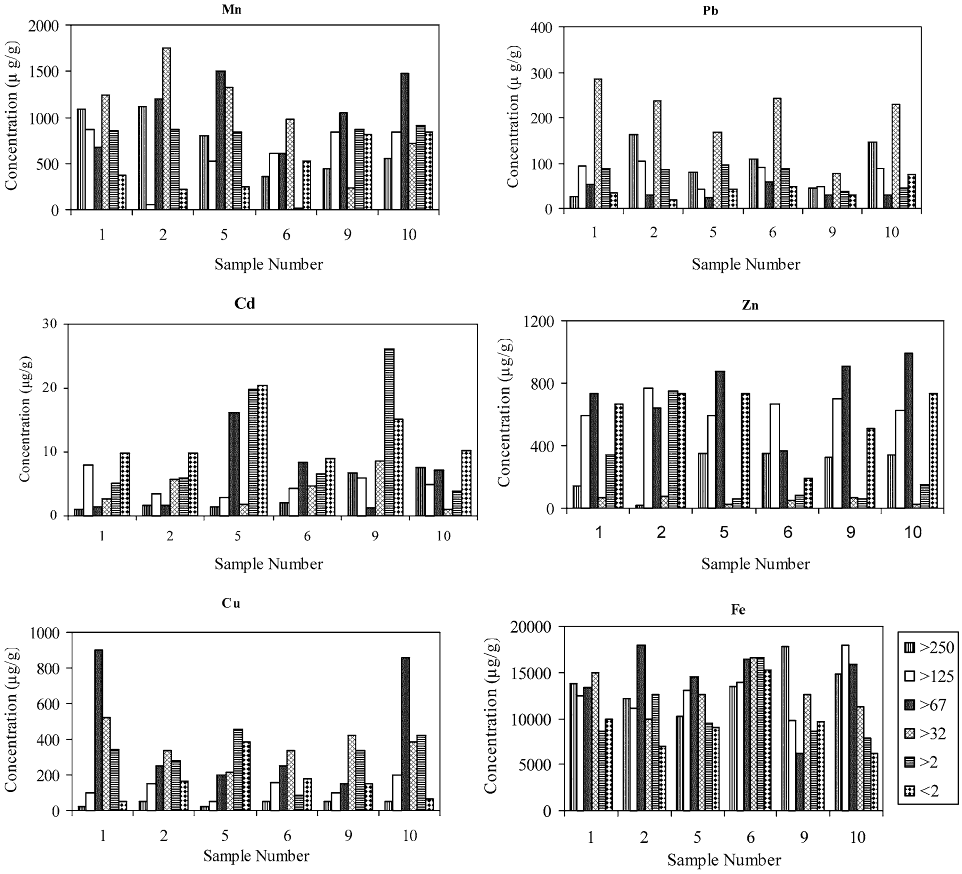

Figure 2. Heavy metals in various grain size fractions of the Achankovil River sediments.

3.1.3. *Core Sediment Analysis*

The collected core sediments were divided into 2 cm long sections from top to bottom and analyzed for various heavy metals. Metal distribution in both the samples showed significant variation. The average concentration of all metals was high in core 2 than core 1 except Pb. However, the pattern of distribution in the two core sediments was same and showed the following order:

Cu>Pb>Fe>Mn.

3.2. DISCUSSION

The detrital mineral quartizes and feldspars are found to be most abundant in the Achankovil river sediments. Among the feldspars, orthoclase is more dominant followed by plagioclase feldspars and microclines. Equal distribution of

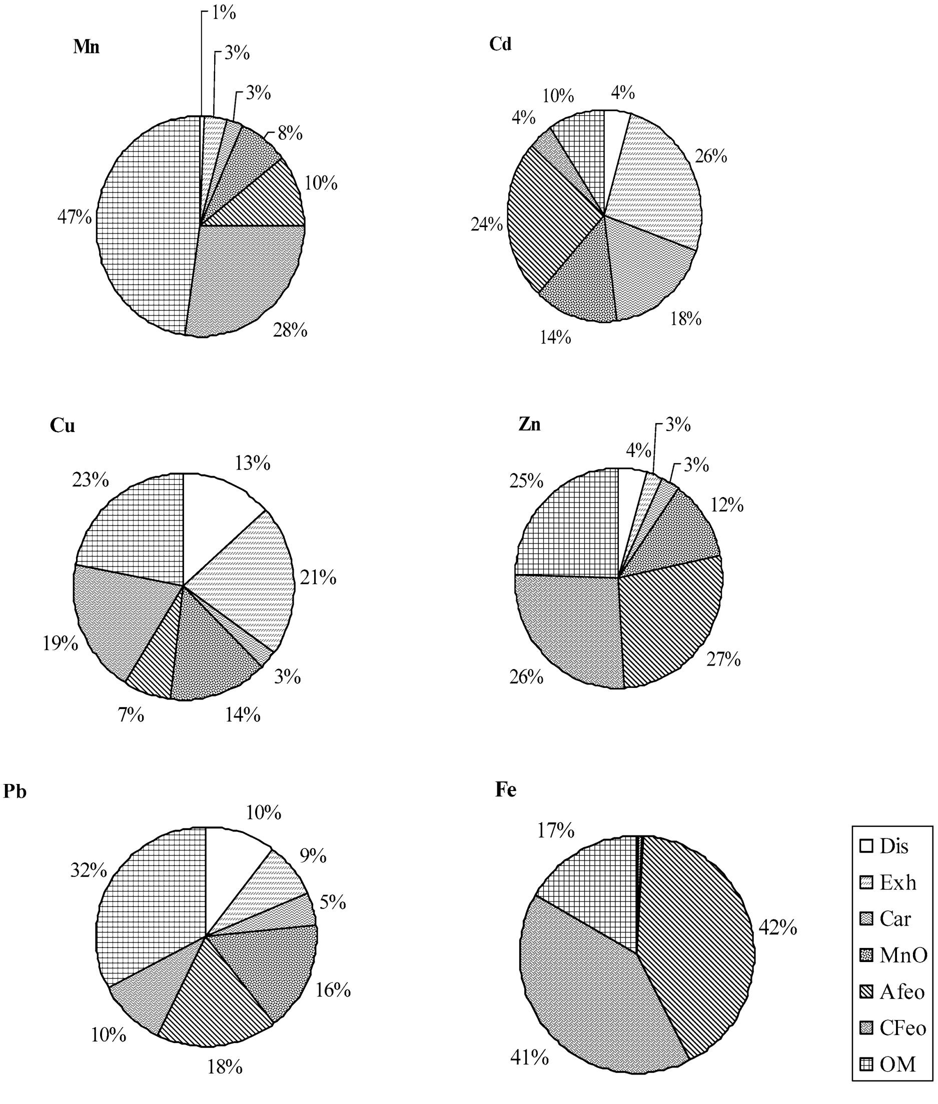

Figure 3. The chemical fractionation of heavy metals in the sediments of Achankovil River.

feldspars and quartizes indicates a high relief tropical weathering conditions in the basin (Table IV). The more resistant K-feldspars dominate the plagioclase feldspars. Muscovite and biotite mica have high concentration indicating the abundance of the metamorphic gneiss (Figures 4 and 5). Chlorite is having equal concentration in comparison to mica indicating the high stability of the minerals in this river draining high latitude tropical area. The fluorspar is reported in most of the areas due to the abundance of the metamorphic rocks. The low concentration of clay indicates the absence of igneous rocks and immature weathering status of

TABLE IV
Mineral composition of Achankovil River sediment (all are in %)

S. no.	Quartz	Orthoclase	Plagioclase	Muscovite	Biotite	Chlorite	Microcline	Fluroapatite	Clay
1	60.51	14.65	9.39	4.05	4.05	1.51	3.92	1.91	<0.1
2	63.55	4.65	14.91	3.47	4.73	–	7.77	0.9	0.2
3	36.57	37.94	3.97	2.86	2.1	2.9	10.7	1.56	0.1
4	21.58	10.97	46.47	6.09	6.09	3.03	3.24	2.51	–
5	35.25	27.78	21.49	1.91	2.42	2.22	5.3	3.62	0.1
6	82.41	5.18	2.31	1.65	2.84	1.41	4.23	–	0.15
7	81.68	3.23	–	–	3.86	–	11.22	–	0.12
8	63.96	18.34	1.38	5.18	4.89	1.53	6.98	0.76	0.2
9	72.03	4.2	–	8.97	3.44	3.14	4.3	3.93	–
10	64.99	5.31	6.87	3.91	2.53	5.28	7.38	3.25	–
11	78.02	3.5	7.36	3.5	4.84	1.03	3.5	–	–
12	72.81	6.24	3.56	4.56	3.1	2.99	–	3.1	0.1

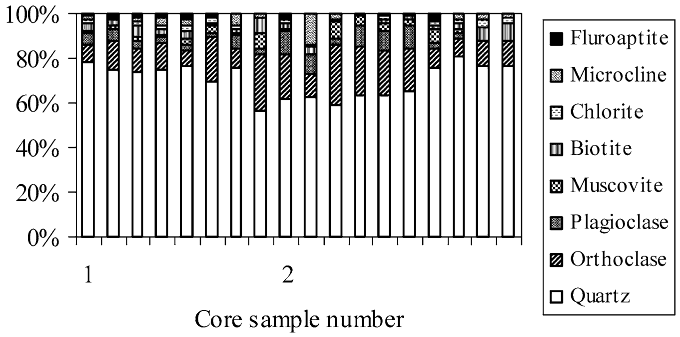

Figure 4. Mineralogy of the core sediments of the Achankovil River.

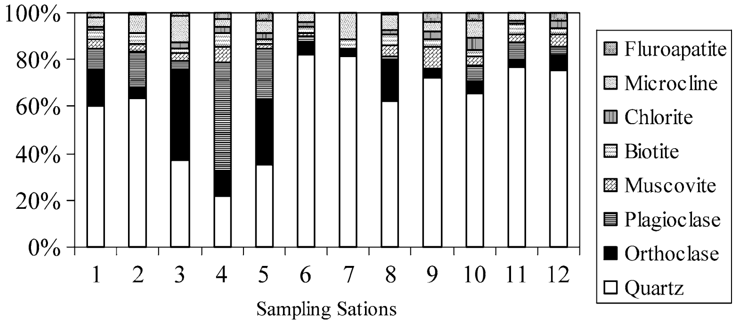

Figure 5. Mineralogy of the surfacial sediments of the Achankovil River.

this drainage basin showing that still an active weathering is progress, which in turn may releases more metals into the system.

Significant concentrations of metals were observed in the surface sediments and core sediments of the Achankovil River. A successive downstream variation profile was also found (Figure 6). In general, all metals exhibit enrichment increasing downstream. The down stream regions, representing the combined effect of the lithology, land use patterns and soil conditions, showed higher values compared to the upstream regions. The grain size of the heavy metal distribution is shown in Figure 2. It is clear that the finer fractions of the sediments have a strong control over the metal distribution. The rate of increase and decrease of metals are very less and the peak concentrations were found in <32 μm grain size fractions for Pb and <67 μm for Zn. Mn and Fe were controlled by almost all grain size fractions, where as <2 μm fraction had a high affinity for Cd than any other fractions. In contrast to other elements, Cu was actively influenced by >2 and >32 μm fraction. However for samples 1 and 10, the 32–67 μm fraction was dominant. The variation in the metal concentrations in the bulk sediments and in different grain sizes at different locations simply reflects the changing portioning behavior of the toxic metals in different fractions in response to different mineral composition, lithology

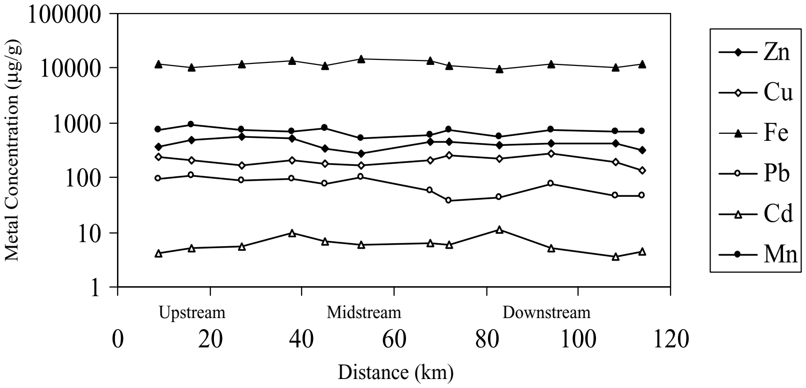

Figure 6. Down stream variation of heavy metals in the Achankovil River basin.

and land use patterns. The grain size distribution indicates equitable fractionation of the metals exceeding Fe and Mn in the sediments. Here, the clay content is very low and the metal enrichment in <37 μm and <67 μm explains lack of preferential sediment size for metal dispersal. However enrichment of Cd and Cu in <2 μm along with Pb in <32 μm size indicates the mixed source of natural weathering and anthropogenic sources like local intensive farming practices. In general the pattern of increasing or decreasing concentrations is found to be associated with a specific range of grain size in the sediments.

Grain size distribution in the sediments indicates that the average grain size is dominated by the medium sand fraction and 50–60% of the sediment population has a grain size >67 μm (Figure 2). The grain size decreases in the downstream direction. The sediments are moderately well sorted, positively skewed and very leptokurtotic (Table V). This sediments indicate the abundance of medium grain sizes, which are better sorted.

The core sediments also showed a decrease in the concentration of anthropogenic elements with depth in the sediment column (Figure 7a and b). The increase of heavy metals in the upper layers of core 1 compared to the lower layers reflects the onset of land use changes due to the agricultural practices which have resulted in heavy metal pollution in the Achankovil river basin. However, in core 2, the vertical distribution of heavy metals was different from core 1. From bottom to top layer, the concentration was found to increase except in 0–2 cm layer. This may be due to the post diagenetic disturbances taking place in this region like bio-accumulation, resuspension etc. This observation suggests that supply of metals in the river system via the sediment dissolution and soil erosion has been a significant factor which has been increasing in the recent times.

The extent of pollution in an aquatic system can be determined by observing the heavy metal load in the sediments, the pre-utilization level, and by enrichment factor (EF) for metal concentration in order to derive the total enrichment caused

TABLE V
Grain size distribution of Achankovil River

S. no.	Mean	Std. Dev.	Skewness	Kurtosis
		Sediment		
1	0.37	0.35	2.205	7.469
2	0.48	0.36	1.783	5.73
3	0.51	0.41	1.441	4.282
4	0.52	0.4	1.321	3.189
5	0.32	0.36	2.532	8.423
6	0.64	0.46	0.969	2.661
7	0.36	0.2	2.842	16.667
8	0.32	0.32	2.478	9.135
9	0.32	0.52	2.542	12.451
10	0.62	0.31	3.414	13.285
11	0.44	0.32	1.915	7.78
12	0.53	0.48	0.975	2.708
		Core sediment		
1	0.37	0.37	2.28	6.91
	0.47	0.36	2.07	5.65
	0.56	0.43	1.42	3.57
	0.53	0.36	1.07	4.37
	0.49	0.38	1.6	4.74
	0.51	0.39	1.51	4.72
	0.57	0.47	1.16	2.77
	0.56	0.46	1.13	2.75
2	0.53	0.37	0.58	3.41
	0.4	0.37	1.81	6.02
	0.42	0.37	1.81	5.7
	0.46	0.44	1.3	5.91
	0.38	0.37	1.51	4.61
	0.45	0.44	1.33	3.74
	0.49	0.42	1.31	3.68
	0.43	0.39	1.57	8.4
	0.33	0.3	1.81	6.83
	0.37	0.31	1.4	5.03

by anthropogenic influences. It is seen that Zn, Cu and Pb, have EF values (Table VI), which are significantly greater than unity and may therefore be considered as mostly anthropogenic in origin. Where as other two metals (Fe and Cd) have EF values less than unity and may therefore be of terrigenous in origin (Szefer *et al.*, 1998). In case of Mn, the EF concentrations ranged from 0.97–1.66 and the average value 1.3, which was almost unity showing both anthropogenic and terrigenous factors. It reflects the fact that heavy metals in the Achankovil River are influenced mainly by natural weathering and to some extent by anthropogenic sources that are

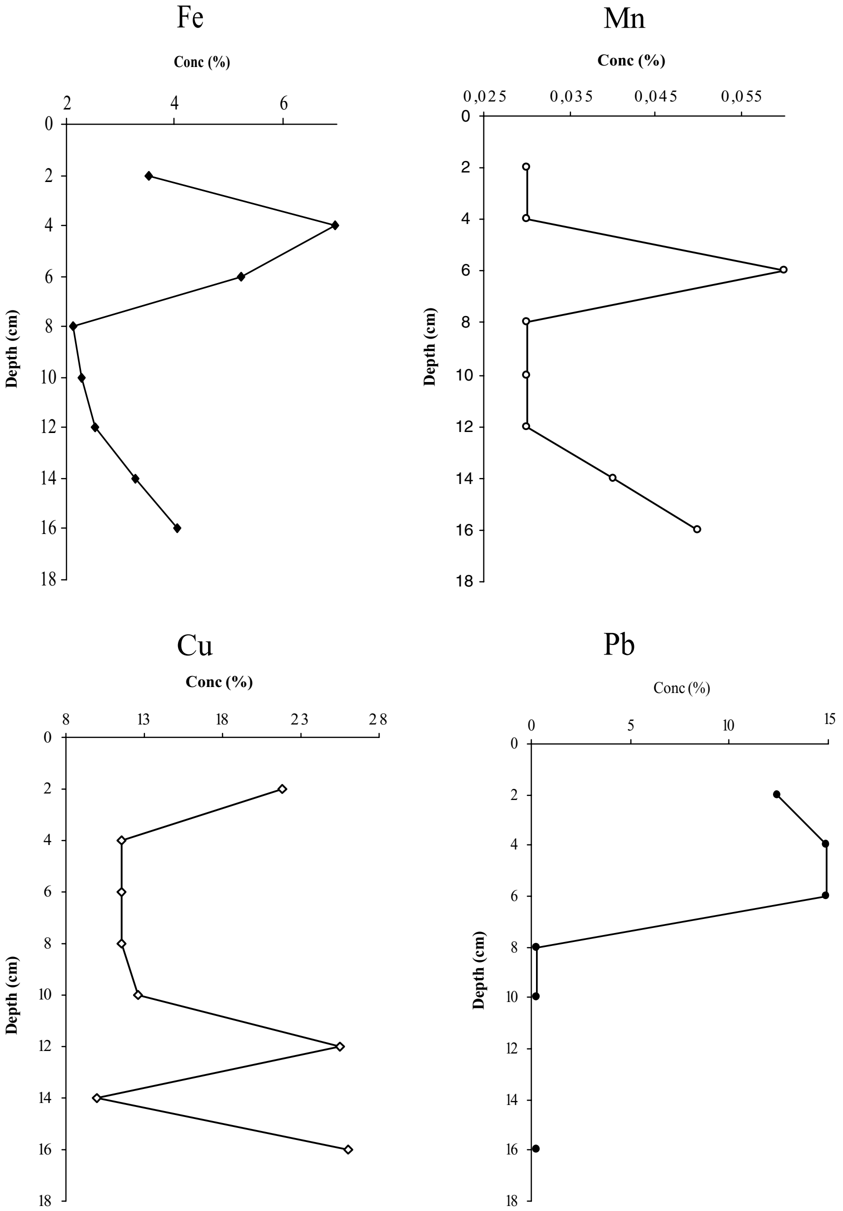

Figure 7. (a) Depth profiles of heavy metals in Core 1. (b) Depth profiles of heavy metals in Core 2.

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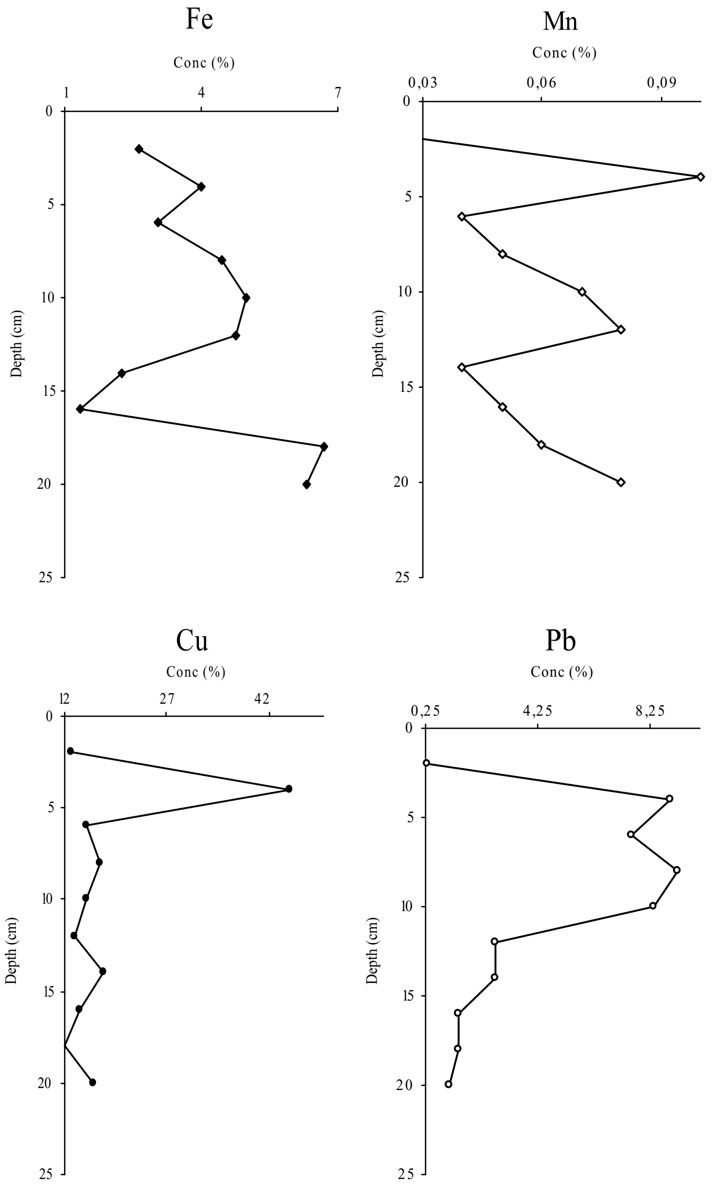

Figure 7. (*Continued*)

contributing considerable amounts of heavy metals to this aquatic system. The EF values for these elements are in the sequence Pb>Zn>Cu>Mn>Fe>Cd.

The enrichment factors were also calculated for core sediments (Table VII). Majority of elements show gradual increase in EF from top to bottom layers. In core 1, there was a uniform gradation in EF values for Pb and Fe than Cu and Mn.

TABLE VI
Enrichment factors (EF) for the surfacial sediments in the Achankovil River, India

Site	Fe	Zn	Cu	Pb	Mn	Cd
1	0.41	7.77	5.4	9.74	1.4	0.072
2	0.35	10.29	4.57	22.89	1.66	0.089
3	0.39	11.67	3.85	18.06	1.43	0.096
4	0.46	10.58	4.75	20.37	1.24	0.168
5	0.36	7.14	4.12	15.96	1.46	0.117
6	0.49	5.84	3.72	21.84	0.97	0.103
7	0.48	9.41	4.75	12.18	1.12	0.106
8	0.38	9.26	5.78	7.77	1.35	0.105
9	0.33	8.17	4.97	9.03	1.03	0.199
10	0.39	8.73	6.2	16.17	1.39	0.089
11	0.35	8.8	4.26	9.87	1.31	0.062
12	0.39	6.57	3.11	9.66	1.3	0.075

TABLE VII
Enrichment factors (EF) for the core sediments in the Achankovil River, India

Core no.	Depth (cm)	Cu	Pb	Fe	Mn
1	2	0.25	1.34	0.61	0.29
	4	0.13	1.6	1.2	0.29
	6	0.13	1.6	0.9	0.57
	8	0.13	0.03	0.36	0.29
	10	0.14	0.03	0.39	0.29
	12	0.29	0.27	0.44	0.29
	14	0.11	0.41	0.56	0.38
	16	0.3	0.03	0.69	0.48
2	2	0.29	0.06	0.87	0.55
	4	1	1.86	1.33	1.85
	6	0.34	1.57	1.01	0.74
	8	0.38	1.92	1.48	0.92
	10	0.34	1.73	1.66	1.29
	12	0.3	0.56	1.58	1.48
	14	0.39	0.56	0.75	0.74
	16	0.31	0.3	0.45	0.92
	18	0.27	0.3	2.23	1.11
	20	0.36	0.23	2.1	1.48

Uniform vertical increasing trend for EF values from top to bottom was observed. This indicates that the EF enrichment of metal in this core sediment is not of recent origin. Core 2 also exhibits a clear gradual vertical gradation. In middle layers the EF values were higher than in the top and bottom layers. From this it may be inferred that the rate of sedimentation has been quite rapid for some time in the past. By contrast, a different pattern emerges when anthropogenic factors (AF) are considered. The difference in these patterns may be attributed to different method of calculation of these two parameters. In case of EF, the enrichment of elements is normalized relative to Al in the sediments, whereas in case of AF, the enrichment is normalized relative to the concentration of metals in the depth of the sediment core. The anthropogenic factors data for the two core sediments are given in Table VIII. The data indicates that the anthropogenic enrichment of Pb in the sediment should have occurred over a longer time period than that of Cu, Fe and Mn.

3.2.1. *Chemical Fractionation of Metals*

The biogeochemical behavior of the heavy metals and their chemical forms can be studied with the help of fractionation. The metals present in water soluble, exchangeable and carbonate fractions are considered to be weekly bound and may

TABLE VIII

Anthropogenic Factor (AF) for the core sediments in the Achankovil River, India

Core No.	Depth (cm)	Cu	Pb	Fe	Mn
1	2	1.35	42.86	0.56	0.38
	4	0.71	51.24	1.1	0.38
	6	0.71	51.24	0.82	0.75
	8	0.71	1	0.33	0.38
	10	0.78	1	0.36	0.38
	12	1.57	8.62	0.4	0.38
	14	0.62	13.1	0.52	0.5
	16	1.61	1	0.64	0.63
2	2	0.81	0.26	0.42	0.38
	4	2.79	8.07	0.63	1.25
	6	0.94	6.82	0.48	0.5
	8	1.06	8.32	0.7	0.63
	10	0.94	7.51	0.79	0.88
	12	0.84	2.44	0.75	1
	14	1.1	2.44	0.36	0.5
	16	0.87	1.31	0.21	0.63
	18	0.74	1.31	1.06	0.75
	20	1	1	1	1

be having equilibrium with the aqueous phase and become readily available to the biological systems. Some amounts of heavy metals are strongly bound to Fe and Mn oxides and organic matter which act as internal reservoirs. On the other hand, the metals in the residual fraction are not available under normal conditions. The hydrous Mn-oxide fraction exhibits more isotropic substitution than amorphous Fe-oxide and shows greater conditional equilibrium constants for heavy metals than crystalline Fe-oxide (Kotoky *et al.*, 2004). The chemical partitioning trend was found to be different for each metal. The concentrations are given in μg/g determined at each extraction step in the sediment samples, Table III.

The Cu content of the sample ranges between 0.18–95.2 μg/gm for all sampling sites and for all fractions. Highest concentration of Cu was observed at the second stage of the extraction procedure. This indicates that the Cu is derived from natural as well as anthropogenic sources. Metals bound to these different phases will behave differently in the sedimentary and diagenetic environment, and thus have different potentials for re-mobilization and for uptake by biota. Thus, it is readily available and relatively mobile for biological uptake, a process facilitated by the lowered pH (Copeland and Ayers, 1972). After the exchangeable fraction, residual fraction is dominant. A significant amount of Cu is associated with the reducible fractions (MNOX, FEOX1 and FEOX2) either by co-precipitation or by sorption onto preexisting coatings under existing physicochemical conditions (Panda *et al.*, 1995). During early diagenesis, microbially mediated redox reactions quickly result in the reduction of some of the insoluble Fe(III) and Mn (II) oxides, and the release of Fe(II) and Mn(II) species to the pore water (Canfield, 1989). Dissolution will also release metals associated with Fe and Mn oxides to the overlying water column (Petersen *et al.*, 1995) and to the benthic biota. A significant amount of Cu is associated with organic matter and carbonates. Copper is preferentially retained on the organic matter by complexation rather than by ion exchange (Balasoiu, 2001; Wu *et al.*, 1999). This strong effect can also be attributed to the fact that copper easily forms complexes with the organic matter due to high stability constant of organic Cu compounds (Kotoky, 2004). Organic matter exhibits a high degree of selectivity for divalent ions and hence the organic bound Cu fraction is an important fraction in the sediments and is not available to the biological activity (Mcbride, 1994). $CaCO_3$ in the carbonate phase is not a significant contributing factor to the heavy metal content of sediments (Paropkari *et al.*, 1980). The same trend has also been observed for Zn, Mn and Pb.

In sediment samples, the concentration of Cd was in the range of 3.67–12.73 μg/g. Cd was found to be most frequently associated with Sulfur (40%) followed by exchangeable fraction as also reported by Fytianos and Lourantou (2004). The thermodynamic approach also suggests similar trend (Sahuquillo *et al.*, 1999). In this study, the exchangeable fraction is the major fraction (25–31%) for Cd.

Fe and Zn, the two most abundant of the metals analyzed, are distributed in a similar manner with the reducible, the oxidisable and to a lesser extent in residual fractions, carbonate bound and exchangeable fractions seem to be of greater significance. The iron oxide bound fractions (FEOX1 + FEOX2) are dominant with concentrations 51% and 77.2% for Zn and Fe respectively. Relatively higher concentrations of Zn and Fe in this phase may be attributed to the flocculation of colloids of Zn and Fe in the Achankovil river system which may have been transported to the river via ephemeral streams. The organic matter also contains significant amount of zinc and iron. The Zn concentration up to 5% is reported to be bound in the humic acid fraction of the soil (Bodek *et al.*, 1988). The high amount of zinc in the organic fraction may be due to the scavenging effect. Singh and Subramaniam (1984) explained that Mn-Fe oxides act as efficient scavengers for many of the heavy metals (Fe, Mn, Cu, Ni, Zn etc). Relatively higher concentration of Zn and other heavy metals associated with this fraction are caused by the adsorption of these elements by the colloids of Mn and Fe (Jenne, 1968). The sorption of zinc with iron in the sediment may strongly hinder their mobility in the aquatic environment. A minor amount of Zn is associated with carbonate and exchangeable fractions. Calcium carbonate forms complexes with zinc as a double salt ($CaCO_3 \cdot ZnCO_3$) in the sediment (Li *et al.*, 2000). The association of the metals with the carbonate phase is less, which may be due to the low carbonate in the sediment. Low concentration in exchangeable fractions indicates low bio-availability of Zn.

Manganese is also one of the abundant metals with concentration ranging from 521.6–925.3 μg/g. The highest concentration values (45–85%) of Mn were observed in organic bound fraction. This indicates that Mn occurred in the form of stable organic complexes and metal sulphides. Under an oxic water column a significant amount of the metal (40%) reaching the sediment interface may be returned to the overlying water column by mineralization of the host organic matter at the surface, and in the oxic upper layers of the sediment (Petersen *et al.*, 1995). A smaller fraction of sediment Zn may be remobilized due to the same reason. Microbial oxidation of the organic substrate may release more Zn, Fe and Cd to the system (Jones and Turkie, 1997). Significant concentrations of MNOX, FEOX1 and FEOX2 fractions are observed: 7.53%, 10% and 26.71% respectively for Mn and 14%, 15.33% and 8.65% respectively for Pb. However, FEOX2 fraction for Pb and MNOX fraction for Mn are less significant compared to the other two.

The fractionation of Pb shows that its major fractions are associated with organic matter followed by amorphous iron oxide, residual fraction and Mn-oxides. A significant quantity of Pb probably originates from Manganese oxides and amorphous iron oxides, which were estimated in the fourth phase, but a smaller amount also comes from crystallized iron oxides, which were extracted in the fifth phase. The significant concentrations of Pb in Mn-Fe-oxides are due to the formation of a stable complex (LopezSanchez *et al.*, 1996; Jones and Turkie, 1997). Further, the positive correlation of Pb with the microelements (Mg and Fe), suggests that lead carbonates are incorporated with manganese oxides and amorphous iron oxides as also reported by Todorovic *et al.* (2001). The lower concentration of Pb in the exchangeable fraction suggests its low bio-availability. Fairly higher concentration in carbonate fraction indicates a change in the physiochemical parameters of the ecosystem that may also dissolve the carbonate bound fraction in water becoming a potentional hazard to the biological production.

Residual fractions of heavy metals accumulate on fine particles sizes and can be attributed to the large aggregation of particles (Panda *et al.*, 1995), provided the sediments contain a significant fraction of flocculent, aggregate particles that can have abnormally high adsorptive capacities. Since the clay content is very less, it could be studied separately to understand the preferential control of the metal distribution by various fractions. Some deviation from conventional grain size/concentration relationship may be expected. Source materials primarily control the heavy metal concentrations in this residual fraction. This feature reflects the predominance of physical weathering and high erosion rates in the drainage basin. The metals present in the residual fraction can be used as a baseline data for the assessment of the degree of the contamination of the system. Greater percentage of metals present in the residual category indicates lower pollution, because this inert phase corresponds to detrital or lattice bound metals that cannot be remobilized. Occurrence of metals in the residual fractions is in the following order: Cu>Pb>Fe>Zn>Cd>Mn. The results show the relatively unpolluted nature of the Achankovil river environment at present. The high concentrations of Cu and Pb may be attributed to the discriminate use of pesticides and insecticides from the agriculture practices. Thus, it can be concluded that the concentration of heavy metals in the Achankovil River sediments are controlled by mineralogy of the land derived fragments and by the man made enrichment, which seems to be minimal.

The comparative study of heavy metal distribution in Achankovil river with other major rivers of India indicate that the heavy metal are enriched more here than other major and medium rivers (Table III). It reflects the contribution form the weathering of metamorphic rocks and partially by land use changes and anthropogenic sources especially in the upstream stretches as discussed earlier. This river is very small compared to others but is receives sediment and metals from two equally mighty tributaries of its size which drains in different land use patterns and lithology. This in turn increases many folds its discharge compared to its size which is almost equal to the discharge of other major rivers of India (Bala Krishna Prasad and Ramanathan, 2005). The metal enrichment in different grain size fractions show the enrichment of metals in the coarser grains which is significantly anomalous when compared with other Indian rivers where the smallest grain size shows enrichment (Table IX). This may be due to the differential mineral assemblage and varied land use patterns. The Chemical fractionation studies also show that the exchangeable and carbonate fraction holds high amount of metals in comparison to other Indian rivers which also confirm the contributing from varied land use patterns beside the weathering sources (Table X). The Achankovil river is significantly different in metal enrichments than other rivers of India which shows the need for the micro level studies on smaller rivers to get insight into the natural weathering process and for the global budget of the metal and micro nutrients to the adjacent estuaries

TABLE IX

Comparison of heavy metal distribution in different grain size fractions (μm) in the surfaces sediments of major Indian rivers (all are in μg/g)

Size fraction	River	Cd	Mn	Zn	Cu	Fe	Pb
>67	1[a]	6.00	1084	753	434	14061	38
	2[b]	–	1360	73	91	58000	–
	3[c]	–	1070	100	70	47200	70
	4[d]	–	404	72	20	39000	17
	5[e]	–	668	68	22	30800	14
>32	1	4.10	1042	51	368	12979	207
	2	–	1140	64	102	57500	–
	3	–	835	110	70	53500	65
	4	–	907	147	57	23000	26
	5	–	–	–	–	–	–
>2	1	11.25	724	240	321	10600	73
	2	–	1600	100	139	84000	–
	3	–	950	100	70	52600	65
	4	–	887	307	507	53750	70
	5	–	–	–	–	–	–
<2	1	12.38	504	594	165	9523	42
	2	–	1,300	117	143	91,000	–
	3	–	720	100	75	52,800	45
	4	–	887	307	507	39,250	45
	5	–	–	–	–	–	–

[a] Present study.

[b] Godavary-Biksham and Subramanian (1988).

[c] Mahanadi–Chakrapani and Subramanian (1993).

[d] Cauvery–Ramanathan *et al.* (1993).

[e] Ganges-Datta and Subramanian (1998).

and the world ocean. Thus, the land use pattern, lithology and anthropogenic factors are together responsible for the heavy metal concentration. This study reveals that the role of smaller rivers are very significant which has been ignored over the years and need to be addressed immediately in terms of metal contribution to the world oceans. So far, only the major rivers have been considered for this purpose. Further, it has been suggested that each river has its own land use stress and anthropogenic pressure which also may modify the present perception of the river biogeochmical cycling of heavy metals and their budget. Hence, this type of studies is highly important to assess the differential environmental changes taking place in and around the smaller river basins on the sustainable development of the regional environment.

TABLE X
Comparison of heavy metal distribution in different chemical fractions in the surfaces sediments of major Indian rivers (all are in μg/g)

River	Metal	Exch	Car	Fe-Mn Oxides	Org	Res
Achankovil	Cd	1.72	1.17	0.89	0.63	0.32
Cauvery		6	6.4	2.67	5.34	80
Mahanadi		–	–	–	–	–
Yamuna		–	–	–	–	–
Achankovil	Mn	23	18	103	322	23
Cauvery		2.67	4	3.5	1.5	90
Mahanadi		–	60	162	105	575
Yamuna		5	8	9	16	62
Achankovil	Zn	9.03	9.74	76	85	18
Cauvery		3	5	5.67	5.67	82
Mahanadi		8.32	4.9	5.2	–	91
Yamuna		2	3	4	26	65
Achankovil	Cu	59	8.05	38	62	54
Cauvery		3.34	5.7	3	4.67	83
Mahanadi		15.4	5.1	6.53	5.83	37
Yamuna		6	3	5	17	69
Achankovil	Fe	17	29	3160	1915	793
Cauvery		0.67	–	4.67	–	95
Mahanadi		4	2	8	4	82
Yamuna		2	1	15	23	58
Achankovil	Pb	7.40	4.12	13	29	14
Cauvery		6.33	4	4.33	8.67	77
Mahanadi		3.36	4.1	–	2.8	47
Yamuna		7	5	6	12	70

4. Summary and Conclusions

Quartz and orthoclase are the dominant mineral fractions in both surfacial and core sediments. The grain size study reveals that sand is the dominant fraction. The concentration and distribution of the heavy metals in the Achankovil River sediments is influenced both by natural and anthropogenic sources as evident from the EF and AF factors. Fe and Cu are the dominant heavy metals in the surfacial and core sediments. Less than 67 μm grain size fraction of the sediment has a strong control over the distribution and availability of the heavy metals in the Achankovil River basin. The average pattern of distribution of heavy metals in various SSE fractions decreases in the order of FEOX1>FEOX2>OM>MNO>EXCH>WAT>CAR. Most of the metals seem not to be available for the biological activities from the sediment-water interactions. The metal distribution in the surfacial sediments is mostly in the residual and carbonate phases. Metals like Cu, Cd and Pb are also present in the exchangeable phase and may they become potential pollutants in the river system in near future. Although, it is a smaller river in comparison to the other Indian rivers, the enrichment of total heavy metal concentration in different fractions emphasized the greater role of the small rivers in modifying the global budget of heavy metals to the world ocean.

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