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HEAVY METALS AND THEIR FRACTIONATION PROFILE IN SURFACE SEDIMENTS OF UPPER REACHES IN THE CAUVERY RIVER DELTA, INDIA

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ABSTRACT

A majority of heavy metals resulting from anthropogenic sources in Southern India reaches the River Cauvery, which acts as one of the sinks in the region. This study attempts to document the heavy metal concentrations in the surface sediments in upper reaches of Cauvery river delta region, India, during the pre-monsoon (July 2007) and Post-monsoon (December 2007) season with emphasis on chemical fractionation. The total metal concentrations of chromium, manganese, iron, copper, zinc and lead were recorded up to the maximum levels of 102.64 mg/kg, 341.67 mg/kg, 4860 mg/kg, 12.80 mg/kg, 37.67 and 4.04 mg/kg respectively. Higher concentrations of chromium (102.64 mg/kg) at Kambarasampettai and lead (24.04 mg/kg) at Grand Anaicut were recorded, during post-monsoon. Fractionation experiments revealed notable levels of heavy metals in exchangeable and carbonate fraction. The risk assessment code analysis shows 51% of zinc in the labile fractions signifies that the sediments fall under high and very high risk category. In the case of Iron, manganese, copper, and lead, about 30% was noticed in labile fractions putting the sediments under moderate risk category.

Key Words: *River Sediments, heavy metals, metal fractionation, risk assessment code, Cauvery River*

INTRODUCTION

Freshwater ecosystems in India are largely exploited for domestic and industrial needs and also for disposal of wastes. In particular, contamination caused by heavy metals is a matter of concern today due to their long residence potential and toxicity. Although predominant sources of these metals in sediments are weathering, volcanic eruptions, anthropogenic activities such as agricultural, metallurgical, industrial, mining operations, fuel emissions, domestic sewage and solid waste disposal also contribute to elevated levels of heavy metals. Heavy metals are usually present in different chemical forms which determine their mobilization capacity and bioavailability; 1) easily exchangeable ions 2) metal carbonates 3) oxides, 4) sulphides, 5) organometallics compounds, and 6) ions in crystal lattices of mineral (Lopez-Sanchez et al. 1993; Weisz et al. 2000; Kuang-Chung et al. 2001). This fractionation is influenced by the physico-chemical conditions in the local microenvironment such as pH, redox conditions, and competition for absorption sites among metal ions and absorptive area. Changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present is insoluble. Under oxygen-rich conditions, metals associated with sulfide minerals, oxidation of sulfide minerals leads to release of metals. Metals associated in crystalline phase are available only after weathering or decomposition. In general, the mobility and bioavailability of metals decrease in the order of extraction sequence of exchangeable > carbonate bound > Fe-Mn oxide bound > organic matter bound > lithogenic fraction (Prusty et al. 1994). Sediment characteristics play a significant role in defining the chemical forms of the metals present in the sediments. Significant association with the residual fraction (F5 and F6) and a scavenging action by the Fe-Mn oxide fraction of the sediments were observed in Jhanji River (Baruah et al., 1996). Sediment particle size also influenced the distribution of heavy metal in various fractions (Tsai et al. 2003). Gundersen and Steinne (2001) while experimenting on the influence of pH, Alkalinity and Ca on the

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Speciation and concentration of heavy metals observed that low pH generally induces dissolution, ion exchange and desorption reactions. Cu speciation is more strongly linked to pH variations. Rajendran et al. (1992) in their study on physico-chemical factors controlling the iron and manganese speciation in Skagerrak sediments (northeastern North Sea) observed that Mn in carbonate phase is negatively correlated to CaCO₃. Increased reduction in Mn-oxyhydrates resulted in significant enrichment rate on Mn in pore water.

Understanding metal speciation in the environment is important in developing countries like India since traffic, industrial development and mining operations continue to accelerate. Dry and wet deposition airborne metals that reach local and regional water resources are also in the rise. A majority of heavy metals resulting from anthropogenic sources reaches the river basin which acts as one of the sinks. It is extremely essential to determine how the anthropogenic derived metals fractionate in sediments in the river basin. In addition, speciation studies in sediments act as a useful indicator of long and medium term metal flux in industrialized estuaries and rivers, and they help to improve management strategies as well as to assess the success of recent pollution control programs (Ravichandran et al. 1995). Although heavy metal contamination in the environment is widely being reported in India, the studies on fractional distribution of heavy metals are very scarce. It will be further interesting to know the chemical fractionation of heavy metals in the Cauvery Delta Zone. In that context, present work attempted to determine the distribution, geochemical fractionation of six heavy metals (Cr, Mn, Fe, Cu, Zn and Pb) and its associated risk in the upper reaches of Cauvery River delta region.

MATERIALS AND METHODS

Surface sediment samples (up to 5 cm depth) were collected from ten locations (Fig. 1 and Table 1) in the upper reaches of Cauvery River during the pre-monsoon (July 2007) and Post-monsoon (December 2007) season to identify the influence of runoff from watershed. Sediment samples were air dried at room temperature and homogenized using an agate mortar and pestle and sieved using a 63 micron mesh sieve. The sediment samples were examined for pH, total dissolved solids, total organic carbon (TOC) as per standard methods (Jackson 1958). The particles with size less than 63 micron were taken for heavy metal analysis. Samples were digested using microwave digestive system (Auton-Paar, model multiwave 3000, Austria) in a HNO₃-HCl acid mixture and the extracts were analyzed by atomic absorption spectrophotometer (Perkin Elmer Model AAnalyst 300). Metal fractionation analysis was carried out as per sequential extraction procedure developed by Tessier et al. (1979). As per this procedure sediment bound metals are extracted into five fractions viz., exchangeable, carbonate bound, Fe-Mn oxide, organic and residual fractions. After each extraction, separation of the residue from the supernatant was carried out by centrifuging at 6000 rpm for 30 minutes and residue was washed with distilled water and centrifuged for another 30 minutes.

RESULTS AND DISCUSSION

The pH of the sediment samples ranged between 6.7 to 9.19 (Table 2). Total dissolved solids sediment varied between 3.95 to 120 mg/kg with an average value of 25.40 mg/kg. Organic matter of sediments were in range 0.55 - 1.45 % and 0.15 - 0.40%, during pre-monsoon and post monsoon respectively. Comparatively, high organic carbon content recorded during pre-monsoon might be attributed to the decomposition of organic matter deposited in sediment (Rajasegar et al. 2002). Heavy metal concentrations of sediments are shown in Table 3. Iron (Fe) content of samples varied from 2956 to 4196 mg/kg with an average of 3512.5 mg/kg during pre-monsoon and 2782 to 4860 mg/kg with an average of 3537.5 mg/kg at post-monsoon in sediment samples. The results suggest that Fe concentrations are of natural origin. Other regions outside of this study area had higher values in the range 5051 - 239,000 mg/kg (Biksham et al. 1991, Singh et al. 2005), further suggesting that the current samples are considered Fe pristine.

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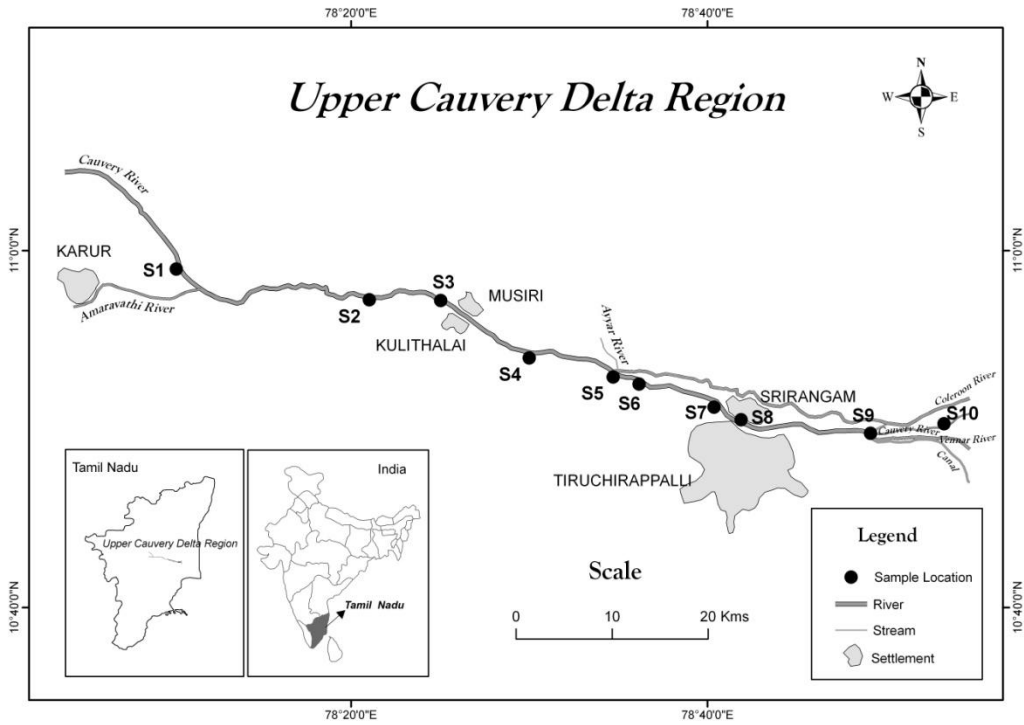


Figure 1: Sampling points and location map of the study area

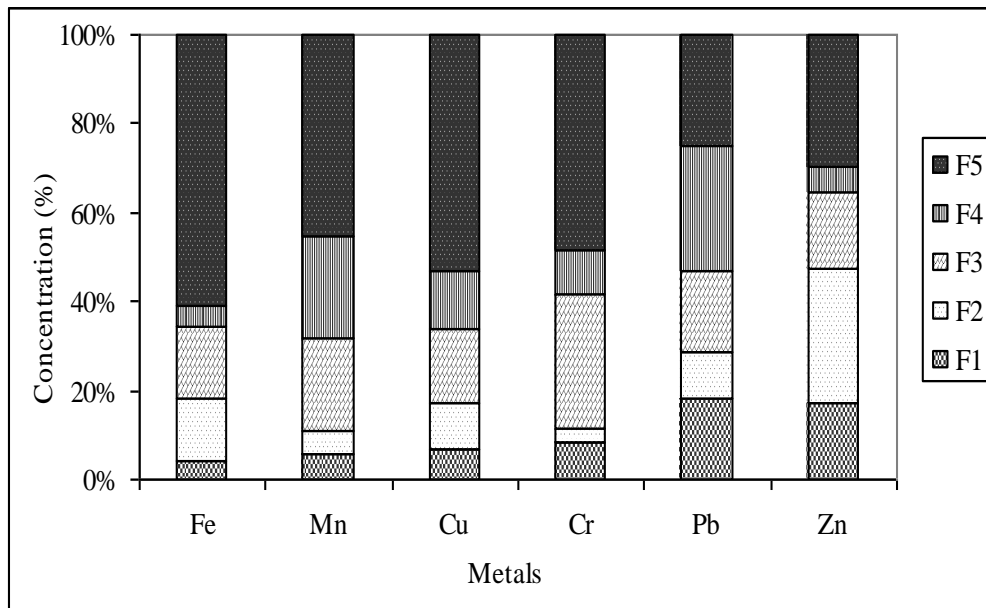


Figure 2: Geochemical fractionation of metals during pre-monsoon season

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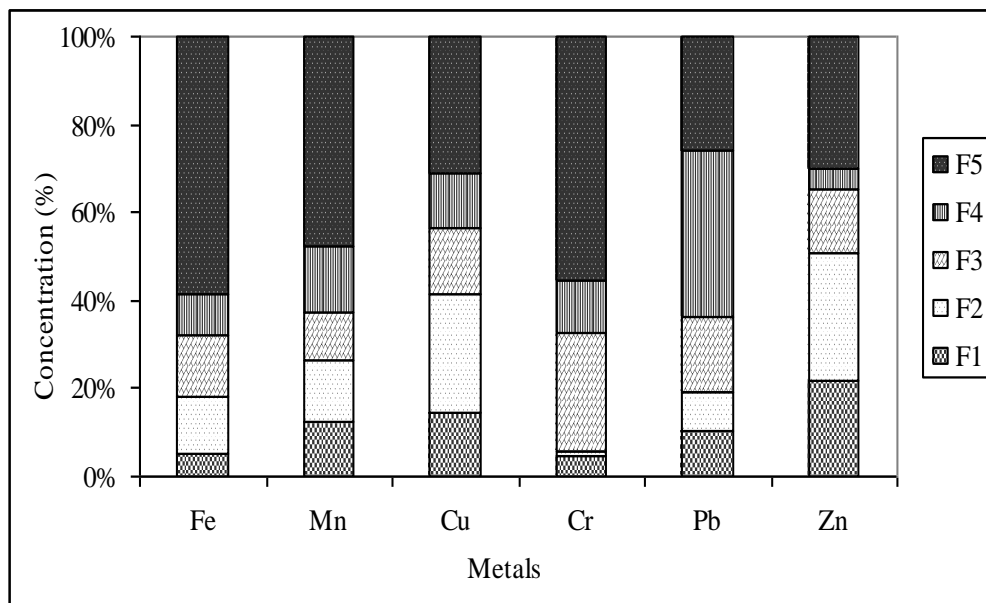


Figure 3: Geochemical fractionation of metals during post monsoon season

Table: 1 Sampling site characteristics

Sample No	Name of station	Land use pattern in the vicinity of sampling station	Possible sources of contamination
S 1	Maravapalayam	Agricultural and residential mixed	Agricultural runoff and sand mining
S 2	Lalapet	Agricultural and commercial mixed	Solid waste dumping and sewage
S 3	Kulithalai	Agricultural and commercial mixed	Sewage and agricultural runoff
S 4	Pettavaithalai	Industrial, commercial, and residential mixed	Industrial effluent and agricultural runoff
S 5	Upper Anicut	Predominantly agricultural area	Agricultural runoff
S 6	Jeyapuram	Agricultural and residential mixed	Agricultural runoff and sewage
S 7	Kambarasampattai	Predominantly residential area	Sewage and runoff from auto garages
S 8	Srirangam	Residential and commercial mixed, pilgrimage site	Sewage and ritual discards by pilgrims
S 9	Grand Anicut	Predominantly agricultural area	Agricultural runoff
S 10	Koviladi	Agricultural and residential mixed	Agricultural runoff

Manganese (Mn) content of samples varied from 49.32 to 203.71 mg/kg during pre-monsoon and 56.88 to 341.67 mg/kg during post-monsoon. Maximum concentration 341.67 mg/kg was recorded at S7 (Kambarasampattai) probably contributed by agricultural runoff. Apart from the natural mineralogical sources, the only predominate source of Mn is macronutrient fertilizers application (Wolters et al. 1989). Goorzadi et al. (2009) reported manganese level in the ranged between 686 and 1650 mg/kg in Tilehbon River, Iran. Mn concentration in the sediments of south platte River basin, USA range lies between 410 to 6700 mg/kg with mean of 1260 mg/kg (Heiny and Tate 1997). When compare to these levels, the Mn observed in the study area falls under unpolluted category. Chromium (Cr) is considered one of the 14 most noxious heavy metals and seventh most abundant element on the earth. Cr levels in the study area ranged from 6.11 to 31.12 mg/kg during pre-monsoon and 10.12 to 102.64 mg/kg during post-monsoon. Comparatively, higher level of Cr in S7 (Kambarasampattai) might be contributed by agricultural and sewage runoff. Earlier reports in Indian River sediments also reported in the range of 115 - 817 mg/kg of

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Cr in R. Ganga (Singh et al. 2002) and 228 - 273 mg/kg in Narmada River (Jain et al. 2008). Hexavalent form of Cr is known to cause wide range of human health effects including mutagenic and carcinogenic risks (Das and Mishra 2008).

Table: 2 Sediment characteristics of River Cauvery in the upper reaches

Sampling site	pH		TDS (mg/kg)		Organic Matter (%)	
	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
S1	6.7	7.95	25.3	24	1.45	0.15
S2	9.19	8.64	16.7	12.8	0.55	0.25
S3	8.61	7.92	17.7	6.41	0.97	0.17
S4	8.59	8.72	19.3	29.7	0.69	0.40
S5	8.78	8.31	120	17.4	1.10	0.20
S6	8.12	8.54	3.95	13.5	0.90	0.25
S7	6.95	7.91	71.5	9.29	1.24	0.20
S8	8.53	7.74	33.7	8.01	1.38	0.35
S9	6.78	7.67	22.4	13.6	1.38	0.25
S10	9.17	8.49	19.9	22.9	1.03	0.40

Table: 3 Heavy metal concentration (mg/kg) of surface sediments in the upper reaches of Cauvery River

Sample No	Season	Fe	Mn	Cu	Cr	Zn	Pb
S1	A	3797	113.9	12.53	17.17	15.45	9.30
	B	2879	64.06	1.91	12.05	1.41	1.10
S2	A	2956	49.32	1.82	10.21	5.68	7.14
	B	2835	57.68	1.01	11.11	4.34	4.4
S3	A	3122	92.82	3.49	9.71	11.46	6.70
	B	3958	101.3	1.61	23.18	6.96	BDL
S4	A	3592	82.66	3.45	12.17	1.62	6.90
	B	2782	56.88	0.405	10.12	BDL	BDL
S5	A	3090	79.33	1.83	6.11	0.92	2.85
	B	3203	81	0.2	11	2.6	1.3
S6	A	4196	203.7	6.63	31.12	9.84	3.61
	B	2961	82.89	0.102	10.18	BDL	BDL
S7	A	3860	145.8	2.21	24.10	7.63	0.60
	B	4860	341.7	12.81	102.6	28.15	12.81
S8	A	3683	102.9	3.23	11.09	4.03	1.92
	B	3907	143.2	1.90	24.05	9.82	1.60
S9	A	3674	110.6	3.21	15.03	8.66	2.01
	B	3906	152.2	0.91	27.27	37.68	24.04
S10	A	3155	106.4	1.01	11.16	1.52	0.51
	B	3517	101	5.5	11.03	9.9	BDL

*A - Pre-monsoon, *B - Post-monsoon

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Table: 4 Correlation analysis for sediment characteristics and heavy metals

	pH	TDS	OM	Cr	Mn	Pb	Zn	Cu	Fe
Pre-monsoon									
pH	1								
TDS	-.026	1							
OM	-.691	.257	1						
Cr	-.518	-.278	.113	1					
Mn	-.440	-.180	.282	.917	1				
Pb	-.005	-.340	-.319	-.148	-.333	1			
Zn	-.658	-.377	.357	.470	.385	.471	1		
Cu	-.564	-.284	.371	.404	.356	.599	.767	1	
Fe	-.662	-.222	.405	.856	.839	-.127	.420	.539	1
Post-monsoon									
pH	1								
TDS	.366	1							
OM	.103	.402	1						
Cr	-.451	-.435	-.263	1					
Mn	-.466	-.476	-.171	.975	1				
Pb	.202	-.275	-.188	.490	.552	1			
Zn	-.010	-.378	-.095	.636	.725	.936	1		
Cu	-.431	-.213	-.068	.890	.876	.276	.494	1	
Fe	-.484	-.634	-.159	.842	.903	.514	.752	.744	1

The distribution of Cu in the study area varied between 1.01 to 12.53 mg/kg during pre-monsoon and 0.102 to 12.81 mg/kg during post-monsoon. The samples from S7 (Kambarasampettai) recorded higher level (12.80 mg/kg) of Cu compared to rest of the samples during post-monsoon. Cu occurs naturally upto 50 ppm in the earth's crust, which includes soil and parent rock. In the unpolluted region, sediment generally contains <50 ppm in the absence of no known contribution of Cu gained from anthropogenic sources. However, in the polluted areas Cu level may reach upto several thousand ppm (Harrison and Bishop 1984). Rauf et al. (2009) reported in the range between 3.38 to 159.79 mg/kg of Cu concentration in River Ravi, Pakistan. Dauvalter and Rognerud (2001) observed maximum level 6495 mg/kg of Cu in the sediments of Pasvik River, Northern Fennoscandia. While compare with these reports Cu observed in the study area not falls under polluted category.

Zinc is an essential trace metal for the growth of humans and animals, it plays a vital role for the function of numerous metalloenzymes. However, enhanced level of Zn may leads to pancreatitis, anemia and acute renal failure (Pais and Jones 1997). The concentration of Zn lies between 0.92 to 15.45 mg/kg and below detectable limit to 37.68 mg/kg, during pre monsoon and post monsoon respectively. Maximum level of 37.68 mg/kg was recorded at S9 (Grand Anicut) during post-monsoon season. Since, sampling site (S9) is located in vicinity of agricultural hub contribution from agricultural runoff might be the probable source of Zn. Major sources of Zn are industrial emissions, composted materials and agrochemicals (Romic and Romic 2003). Level of Zn in the sediments of Hindon River recorded in the range between 3.98 to 85.0 mg/kg (Suthar et al. 2009). However, Olivares-Rieumont et al. (2005) reported in the range of 86.1 to 708.8 mg/kg of Zn in the sediments of Almendares River, Cuba.

Lead is second among the top 20 priority list of hazardous substances (ATSDR 1999). In the present study, Pb content figured between 0.51 to 9.3 mg/kg during pre-monsoon and below detectable level to 24.04 mg/kg during post monsoon. S9 (Grand Anicut) recorded highest Pb concentration of 24.04 mg/kg in post-monsoon season. Concentrations of Pb in River sediments have been estimated about 23 mg/kg (EPA 1982). However, level of Pb in the top layers of sediments differs based upon the deposition and

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accumulation of atmospheric particulates from anthropogenic sources. According to Khan (2001), apart from leaded gasoline, sewage sludge and agricultural runoff are the major sources of Pb contamination in the watersheds. Singh et al. (2005) reported 75.30 mg/kg as a maximum concentration of Pb in the sediments of Gomti River, India. The values obtained in this study belong to the category of unpolluted with respect to Pb while comparing with observations in the polluted sediments.

Paired T- test not yielded statistically significant difference among heavy metals between sampling events and sampling stations. It suggests that the disturbance of the river base and transport of sediment towards downstream lead by monsoon dominated high flow rate in the River. The results of correlation matrix for pre-monsoon and post-monsoon are presented in Table 4. The positive correlation between iron and other heavy metals in both sampling events might be contributed by high adsorption capacity of its oxides (Algan et al. 2004). Positive correlation between Cu, Zn and Pb, suggests its similar ionic radii and geochemical behaviour during pedogenesis (Kabata-Pendias and Pendias 2001; Kucuksezgin et al. 2007). The positive correlation between Mn and Cu in the both seasons indicates that Mn is possibly one of the geochemical support phases, while Cu is associated with Mn, it may co-precipitate or adsorbed on manganese oxide/ hydroxide (Lin and Benjamin 1992; Bertin and Bourg 1995). There was no notable correlation between heavy metals and organic matter in the both sampling events.

To assess the extent of metal contamination, contamination factor was calculated for sediments using measured concentration of metals and respective world shale average reported by Turkian and Wedephol (1961). However, the pollution levels in the sampling sites were calculated based on Tomlinson et al. (1980) developed Pollution Load Index (PLI).

$$CF = C_m / C_b$$

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n}$$

Where CF=contamination factor, n =number of metals; C_m = metal concentration in polluted sediments; C_b = background value of that metal. The study result showed that the CF values of Mn, Fe, Cu, Zn and most of Cr and Pb values are less than 1 in both sampling events. However, CF values exceed 1 at S7 (1.14) for Cr and S9 (1.20) for Pb during post-monsoon and pre-monsoon respectively. The PLI values are in the range of 0.05 - 0.19 during pre-monsoon while post-monsoon values are recorded between 0.01- 0.37.

The geochemical associations of metals during pre-monsoon and post-monsoon season samples are given in Fig. 3 and 4. Irrespective of seasons, exchangeable fraction of Fe, Mn, Cu, Cr, Pb and Zn recorded in the range between 0.8-6.5%, 4.2-13%, 6.4-18%, 3-9%, 8-19% and 15-24%, respectively. Metals extracted in this fraction are the most mobile and readily available for biological uptake in the environment (Purushothaman and Chakrapani 2007). Notable level of exchangeable fractions indicates their possible pollution risks to the aquatic environment.

Fractionation profile of Fe, Mn, Cu and Cr indicates significant proportion is constituted by residual fraction. The residual fraction is a main carrier of metals in most aquatic systems and largely controlled by the mineralogy and weathering. Concentration of metal bound in this fraction is not affected by anthropogenic contributions (Gibbs 1977). Zn and Pb are mainly associated with carbonate bound (26 to 30%) and organic matter bound fractions (28 to 39%), respectively. Carbonates bound metal fraction is susceptible to pH changes with the lowering of pH may lead to the release of metal cations. Many studies had also reported that the higher level of carbonate fraction of Zn in the sediments (Modak et al. 1992; Vaithyanathan et al. 1993; Panda et al. 1995).

While comparing the post-monsoon samples high level of Pb is recorded in the exchangeable fraction during pre-monsoon. Higher level of exchangeable fraction of Pb during pre-monsoon might be attributed to large proportion of atmospheric deposition. Previous reports also hinted fractionation of Pb is found to be variance probably due to atmospheric deposition (Davidson et al. 1994; Marin et al. 1997). Ramos et al. (1999) observed high level of exchangeable fraction of Pb in the Ebro River sediments because of its anthropogenic origin. In all the studied metals, moderate level of Fe-Mn bound fraction is observed in the both season indicates that this fraction accumulates metals from the aqueous system by the mechanism of

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adsorption and co-precipitation and it act as a significant sink for heavy metals in the aquatic system (Bordas and Bourg 2001).

Based on the percentage contribution the order of various geochemical fractions of metals is observed in the order following

Pre-monsoon

Fe: residual > Fe-Mn oxide > carbonate > organic > exchangeable

Mn: residual > organic > Fe-Mn oxide > carbonate = exchangeable

Cu: residual > Fe-Mn oxide > organic > carbonate > exchangeable

Cr: residual > Fe-Mn oxide > organic > exchangeable > carbonate

Pb: organic > residual > Fe-Mn oxide = exchangeable > carbonate

Zn: residual > carbonate > Fe-Mn oxide = exchangeable > organic

Post-monsoon

Fe: residual > Fe-Mn oxide > carbonate > organic > exchangeable

Mn: residual > organic > carbonate > exchangeable > Fe-Mn oxide

Cu: residual > carbonate > Fe-Mn oxide = exchangeable > organic

Cr: residual > Fe-Mn oxide > organic > exchangeable > carbonate

Pb: organic > residual > Fe-Mn oxide > exchangeable > carbonate

Zn: residual > carbonate > exchangeable > Fe-Mn oxide > organic

The results of the metals fractionation studies reveal that the metals in sediments are bound to different fractions with different strengths (Jain 2004). Further, it can give a clear indication of sediment reactivity which is known as a vital component to assess the risk associated with the presence of metals in an aquatic system. In order to assess the metals availability and associated risk connected with heavy metal presence in the study area risk assessment code (RAC) was applied. As per RAC classification, sum of exchangeable and carbonate bound fractions if figured <1% of the total metal is considered as no risk for the environment, 1–10% shows low risk, 11–30% indicates medium risk, 31–50% high risk and >50% corresponds to very high risk. The risk assessment code as applied to the present study reveals 37 to 51% of Zn fractions in the labile fractions and therefore it falls under high and very high risk during pre-monsoon and post-monsoon, respectively. The association of Zn with exchangeable and carbonate fraction may cause harmful effects to aquatic life. Fe, Mn, Cu, and Pb fractionation profile indicates labile fractions contribution up to 30%, so these metals come under moderate risk category.

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