Int. J. Environ. Res., 3(4):581-598, Autumn 2009
ISSN: 1735-6865

Characterization and Risk Assessment Studies of Bed Sediments of River Adyar-An Application of Speciation Study

Venugopal, T.*, Giridharan, L. and Jayaprakash, M.

Department of Applied Geology, University of Madras, Guindy, Chennai - 600 025, India

Received 14 April 2008; Revised 22 Dec. 2008; Accepted 7 July 2009

ABSTRACT: Fractionation studies on the sediment samples provide valuable information on the nature of the metals bound to the sediments. Thirty three sediment samples of River Adyar were collected during two seasons and speciation study was carried out. The industrial and domestic effluents are directed into the river course at many points in the middle and lower of the Adyar River. To ascertain the extent of heavy metal pollution in the bed sediments of the river, total metal content and speciation were evaluated. The summation of the metal recoveries in the sequential extractions was found to be within ±10 % of the total metal content. The mobility factor was evaluated which represents the exchangeable and Carbonate fractions in the sediments. Risk Assessment Code was estimated and the results reveal the extent of risk associated with the heavy metals in the sediments in various stations. The results of speciation shows that Cu and Ni falls in the high risk category at certain stations of the middle and lower part of the river. Except Cr, Fe and Zn, all other heavy metals studied show medium risk with regard to RAC. The effect of monsoon on the concentration of the metals in various fractions had been studied and the significance of seasonal effect is determined using t-test.

Key words: Speciation, River Adyar, Risk assessment , Bioavailability, Metals

INTRODUCTION

River sediments are basic components of our environment as they provide nutrients for living organisms and serve as sinks for deleterious chemical species. Sediments constitute the most important sink of metals originated from weathering and other pollutions. . The concentration of the metals in sediments is augmented to higher levels by anthropogenic activities (Homady *et al.,* 2002). At higher concentration, heavy metals are known to be harmful for both the environment and human health. Severe environmental problems are identified and characterized by several authors due to heavy metal contamination (Shankar and Karbassi, 1991; Karbassi, 1996; Ma and Rao, 1997; Karbassi *et al.*, 2001; Banerjee, 2003; Jiries, 2003; Frignani and Belluci, 2004; Demirbas *et al.*, 2005; Priju and Narayana, 2007; Dixit and Tiwari, 2008). The sediment chemistry is affected by the changes in the physico-chemical parameters of the water column such as pH and redox potential which results in the desorption of some of the trapped metals. Sediments can act as a nonpoint source as it can release the loosely-bound metals and other pollutants to the water column thereby affecting the aquatic organisms. The increase in the concentration of the heavy metals in the sediments occurs from both natural and anthropogenic sources including domestic and industrial effluents, fertilizer remains, river inputs, vehicular emissions, erosion and waste disposal (Mwamburi, 2003; Tokalioglu *et al.*, 2003). Furthermore, in urban agglomerations there is a permanent concern regarding trace metal loads and speciation (Goonetilleke *et al.*, 2005).

Speciation information of heavy metal ions is very important for their toxicity and biological role of a particular elements vary greatly depending on its chemical form. The determination of

*Corresponding author E-mail:t.venu@yahoo.co.in

extractable trace metals in soil or sediment is often used to gain an insight into chemical speciation. The toxicity of metals depends especially on its concentration in various fractions of sediments rather than on their total elemental contents, and therefore, speciation studies increasingly gain importance. It had been demonstrated that physical speciation, i.e. the distribution of an analyte according to physical properties such as size or solubility, controls the overall physical transport of trace metals, while the speciation of dissolved metals, i.e., the distribution of an element amongst defined chemical species in a system, governs its effects on aquatic biota. Therefore, the most important process controlling trace metal effects and fate in aquatic systems is the partitioning between the solid and the aqueous phase. When this competition favors the aqueous phase, metal bioavailability and toxic potential tend to increase. When adsorption predominates, particulate matter acts as the major carrier of trace metals, thus reducing metal toxicity on a short-term basis and changing the ultimate fate of these species.

In this study, the concentration of heavy metals in various fractions of the sediments is determined and the bioavailability of these metals is evaluated from the mobility fractions and categorized the sediments according to the risk assessment code.

MATERIALS & METHODS

The sediment samples of river Adyar is taken up for Geochemical analysis (Fig. 1). River Adyar starts from Malaipattu Dam (80.00^0 latitude and 12.93^0 longitudes) near Manimangalam village, Sriperumbathur taluk, at about 15km west of Tambaram near Chennai. Though it originates from the above point, it assumes the appearance of a stream only after it receives surplus water from the Chembarambakkam tank. It flows through Kancheepuram, Tiruvallur and Chennai districts for a distance of about 50km and enters into the Bay of Bengal near Adyar. The river receives a sizeable quantity of sewage from its neighborhood after it reaches Nandambakkam near Chennai. This river is almost stagnant and do not carry enough water except during rainy season (NW-monsoon). Rapid industrialization and urbanization (Fig.2) along the river course during 80's and 90's of last century has increased the pollution of the river watershed which leads to the present day

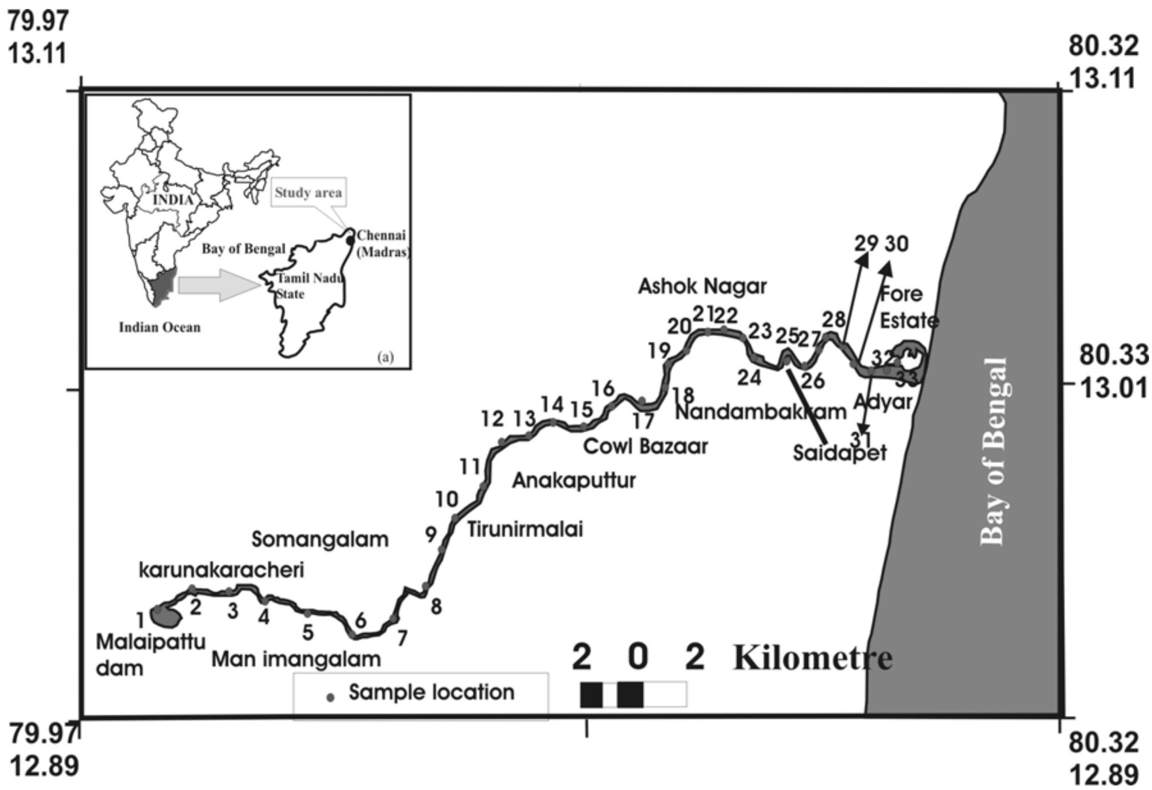


Fig. 1. Base Map of Adyar River depicting the sample locations

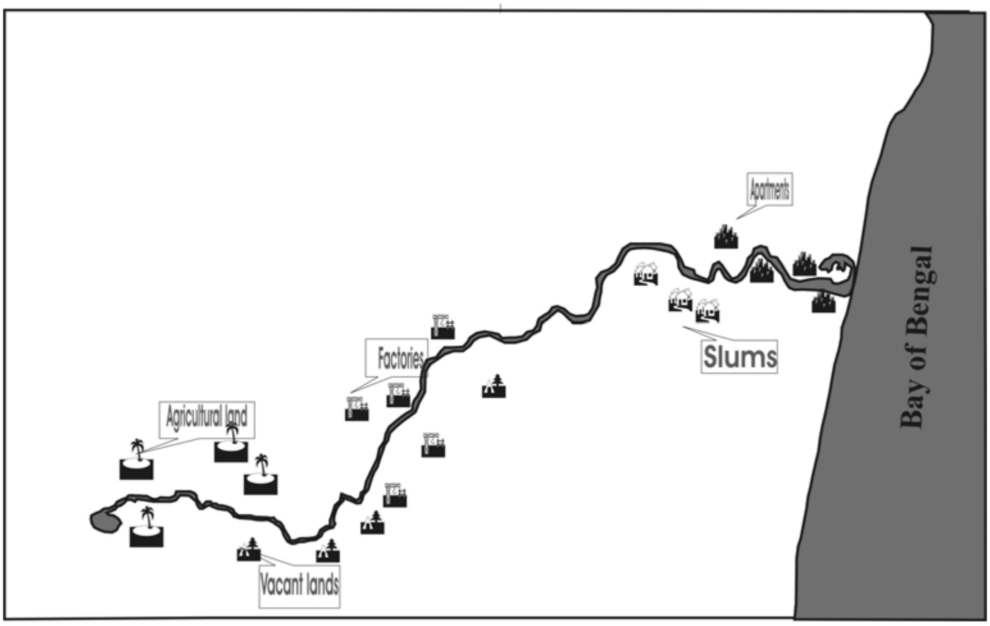


Fig. 2. Map showing the Pollution sources of Adyar River

deteriorated condition of water level. River water near the midstream is found to be contaminated by the industrial and domestic effluents directed into the river course and the lower part of the river water is observed to be polluted by domestic effluents and saline water intrusion (Fig.2).

Thirty three sediment samples were collected in September 2005 (pre-monsoon) and in February 2006 (post monsoon) from the origin of the river to the confluence point (Fig.1). For the collection of bed sediments, the standard methods were adopted (Chapman, "1992"). Samples were collected from the subsurface at a depth of 10-15 cm. About 250 g of the samples were collected in polythene bags and were kept frozen to preserve their chemical integrity until analysis. The sediment samples were air dried at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris. The sediments were then ground until all particles pass through a 200-mesh nylon sieve. Tessier sequential extraction procedure was used in this study (Tessier *et al.*, 1979). The sediments were analyzed for the chemical partitioning of Cr, Cu, Fe, Mn, Ni, Pb and Zn. The five fractions viz., Exchangeable, carbonate bound, Fe-Mn oxide, organic and residual fractions were evaluated. The separation of the residue from the supernatant of each fraction was performed by centrifuging at 4000 rpm for 30 minutes. The residue was washed with double distilled water and again centrifuged for 25 minutes. This wash water was discarded and the separated supernatants were made up to the recommended volume (Tessier *et al.*, 1979) in each fraction. The concentrations of heavy metals in each fraction were determined using Graphite Furnace Atomic Absorption Spectrophotometer (Perkin-Elmer AAnalyst 700). Multi element Perkin-Elmer standard solutions were used for the estimation of Trace metals. Precision of the analysis was monitored by running triplicates for every 20 samples and it was found that the results are <7% relative standard deviation. The total metal content was also determined to assess the quality of the study. The percent ratios of the sum of concentrations of five fractions to the total concentrations measured separately of Cr, Cu, Fe, Ni, Mn, Pb and Zn were 96, 108, 97, 93, 109, 94 and 92%, respectively.

RESULTS & DISCUSSION

The results of statistical parameters on the chemical partitioning data of Cr, Cu, Fe, Ni, Mn, Pb and Zn in bed sediments of River Adyar is summarized in Table 1.

The effect of season on the various sediment fractions of the heavy metals is determined using t-test. The result demonstrates that Cu, Fe and Ni shows significance to seasonal effect in almost all the fractions. The percentage abundance of

Table 1. Summary statistics of the analytical data

Parameters (µg/g)		Pre monsoon				Post monsoon				t	R
		Min	Max	Mean	σ	Min	Max	Mean	σ		
Cr	I F	1.00	6.40	2.80	1.40	0.08	4.96	1.87	1.26	2.9	S
	II F	1.00	7.80	3.50	1.60	0.16	6.24	2.58	1.33	2.5	S
	III F	2.20	65.30	18.70	14.10	1.20	59.60	16.51	13.00	0.7	N
	IV F	1.10	74.70	22.80	21.70	0.80	72.40	20.89	20.92	0.4	N
	V F	65.50	232.10	152.00	44.30	58.50	206.00	139.94	43.57	1.1	N
Cu	I F	1.86	16.98	9.88	4.20	1.52	12.00	6.77	2.72	3.6	S
	II F	1.26	6.98	3.76	1.44	0.96	4.32	2.42	1.01	4.4	S
	III F	6.57	21.26	11.33	3.45	5.20	15.80	7.89	2.24	4.8	S
	IV F	8.16	75.26	22.48	13.74	5.60	64.60	17.49	12.53	1.5	N
	V F	10.21	42.35	23.51	7.99	7.75	36.25	19.51	7.14	2.2	S
Fe	I F	149.00	563.00	333.00	110.00	30.00	483.00	222.00	116.00	4.0	S
	II F	155.00	698.00	431.00	148.00	57.00	477.00	248.00	111.00	5.7	S
	III F	6958	21652	12842	3305	4668	18452	9230	3186	4.5	S
	IV F	3125	8564	5969	1300	2170	5894	3437	858	9.3	S
	V F	12954	48962	37856	8935	10180	45700	34241	8661	1.7	N
Mn	I F	2.48	15.62	8.85	3.49	0.64	8.40	4.53	1.83	6.2	S
	II F	2.24	82.54	28.12	23.55	0.96	77.28	21.90	20.29	1.2	N
	III F	5.21	369.59	103.86	99.77	1.26	333.20	78.00	79.71	1.2	N
	IV F	4.11	152.37	46.72	48.80	1.76	112.46	35.07	37.72	1.1	N
	V F	34.29	242.51	110.96	43.09	24.75	202.00	89.23	38.55	2.2	S
Ni	I F	3.88	18.47	8.86	3.03	2.64	14.25	5.91	2.13	4.6	S
	II F	2.21	15.36	7.55	3.33	1.52	9.56	4.30	1.92	4.9	S
	III F	7.89	24.11	16.67	4.60	5.20	18.42	11.66	3.80	4.8	S
	IV F	3.22	34.33	14.33	5.36	1.56	29.00	10.16	4.66	3.4	S
	V F	17.25	45.69	27.76	6.34	12.65	37.84	20.72	5.93	4.7	S
Pb	I F	0.35	2.31	0.93	0.45	0.19	2.69	0.96	0.60	-0.2	N
	II F	0.21	1.85	0.81	0.37	0.16	1.35	0.63	0.35	2.0	N
	III F	0.82	14.20	5.52	4.22	0.59	12.37	4.42	3.54	1.2	N
	IV F	1.13	15.80	10.08	3.53	0.85	14.68	8.40	2.99	2.1	S
	V F	3.65	19.34	14.50	3.83	1.35	16.34	9.76	2.98	5.6	S
Zn	I F	0.29	0.98	0.56	0.19	0.22	0.69	0.42	0.14	3.5	S
	II F	1.34	13.54	6.37	2.82	0.88	8.26	4.20	1.95	3.7	S
	III F	32.15	215.61	88.26	47.40	17.80	199.68	81.42	45.08	0.6	N
	IV F	1.29	112.34	28.89	26.92	0.26	109.68	24.61	25.69	0.7	N
	V F	26.51	235.89	128.92	58.75	20.23	238.60	119.81	57.98	0.6	N

t stands for t-test Critical two-tail- 2.01 σ- standard deviation S-significant, N-non-significant, R- Result

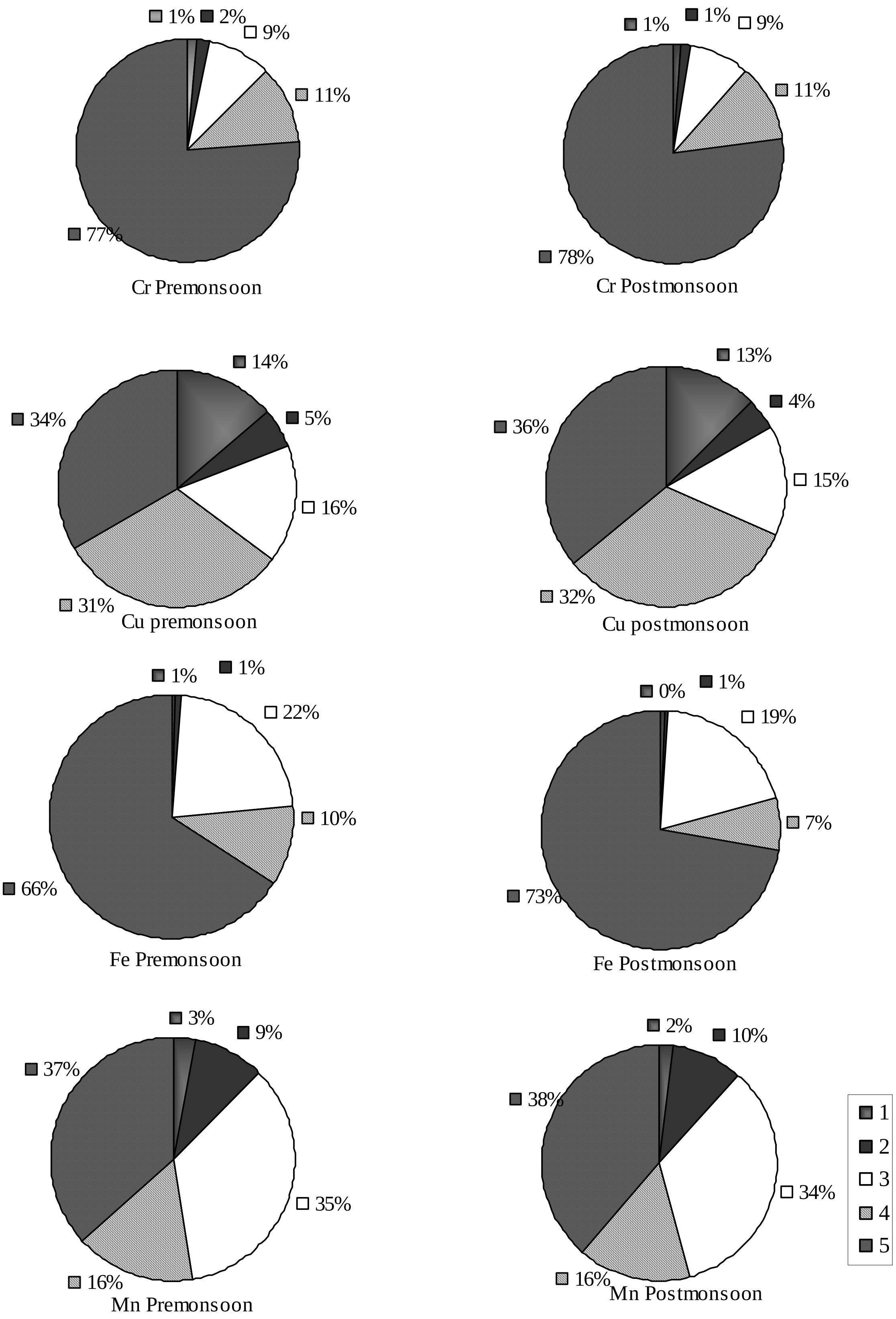
the heavy metals in various fractions is presented in pie diagram (fig.3). The spatial variation of heavy metals in various fractions is represented in figs. 4 & 5 for pre monsoon and post monsoon respectively. In the study area, during pre-monsoon, the exchangeable and carbonate bound fractions of Cr ranges from 1.0 to 6.4 with a mean of 2.8 µg/g and 1.0 to 7.8 with a mean of 3.5 µg/g respectively. The spatial variation of pre-monsoon with respect to this metal in the exchangeable fraction is found to be distributive with some of the stations (stations 2, 3, 10, 19, 25 and 30) shows higher values both in the upper and lower part of the river. The concentration of Cr in the carbonate bound fraction is also in line with the exchangeable fraction demonstrating high concentration of this metal in the upper to lower part of the river sediments at stations 1-4, 11, 12, and 27-29. During post monsoon, the concentration of metals bound to these fractions are found to be slightly decreased and it ranges from 0.08 to 4.96 with a mean of 1.87 µg/g and 0.16 to 6.24 with a mean of 2.58 in the I and II fractions respectively. The distribution pattern of post monsoon is in line with the pre-monsoon in the exchangeable fraction having higher concentration at stations 3, 10, 19, 24, 25 and 31. The carbonate bound fraction has significant values of Cr in certain stations at upper, middle and lower part of the river at stations 1-4, 10-12 and 26-29. The spatial-variation with regard to Cr in these fractions is found to be distributive with some of the station showing higher values in the middle and lower part of the river.

In the case of post monsoon, III and IV fraction have values ranging from 1.2 to 59.6 with a mean of 16.51 and 0.80 to 72.4 with a mean of 20.89µg/g respectively.Fig. 5 reveals that the stations 3, 10, 11 & 24-31 shows higher values in the Fe-Mn fraction and the organic fraction have higher values at stations 19-21 in the middle part and station 24-26 & 28-33 in the lower part of the river. The middle and lower part of the river runs through the urban area. In the suburban area, it is found that there are many small and tiny tanneries and the effluents from these tanneries are found to be rich in chromium. The surface run-off of these effluents due to precipitation and also in certain points, it is observed that the effluents are directly directed into the river water. This increases the concentration of the metal in the bed sediment of the river.

In the residual fraction, the concentration of Cr ranges from 65.5 to 232.1 with an average value of 152µg/g and 58.5 to 206 with an average value of 139.9 µg/g during pre-monsoon and post monsoon respectively. There is only a slight decrease in the values and the seasonal effect is not found to be significant in this fraction. The spatial-temporal variation results show that in both the seasons, the residual fractions is found to be predominant and the contribution of the other four fractions to the total concentration is only minimal. During pre-monsoon, the residual fraction shows an increase in the Cr concentration from the upper to the lower part of the river bed sediments. Station 1-3 of the upper part shows higher concentration of Cr and stations falling in the lower part of the river sediments shows high values. Post monsoon also follows the same pattern but with reduced values. Though the total concentration of the chromium in the sediments is not alarming, the slight increase in the lower part may be attributed to the influence of the industrial effluents into the river water near the urban area.

The speciation pattern of Cr reveals that during pre-monsoon, 3% of the metal was present in the exchangeable and Carbonate bound fractions whereas post monsoon records 2% with these fractions. About 77% of the metal was bound to residual fraction in both the seasons and irrespective of the regions (upper and lower part of the river); there is no much change in the fractionation with regard to this metal. The speciation results clearly shows that the chromium content in the bed sediments can only be attributed to the background metal concentration in many of the stations except in the lower part where there is a slight increase in the concentration due to anthropogenic activities.

During pre-monsoon, the exchangeable and carbonate bound fractions of Cu ranges from 1.86 to 16.98 with a mean of 9.88µg/g; and 1.26 to 6.98µg/g with a mean of 3.76µg/g respectively. The spatial-temporal variations show that the exchangeable fraction is found to be high near the middle and lower part of the river. The stations 10-18 and 21-27 show high values with regard to Cu. The concentration of Cu in the carbonate bound fraction is found to have distributive pattern. During post monsoon, the concentration of metals bound to these fractions are found to be slightly



1-I fraction 2-II fraction 3-III fraction 4-IV fraction 5-V fraction

Fig. 3. Percentage distribution of metals in various fractions (Continues)

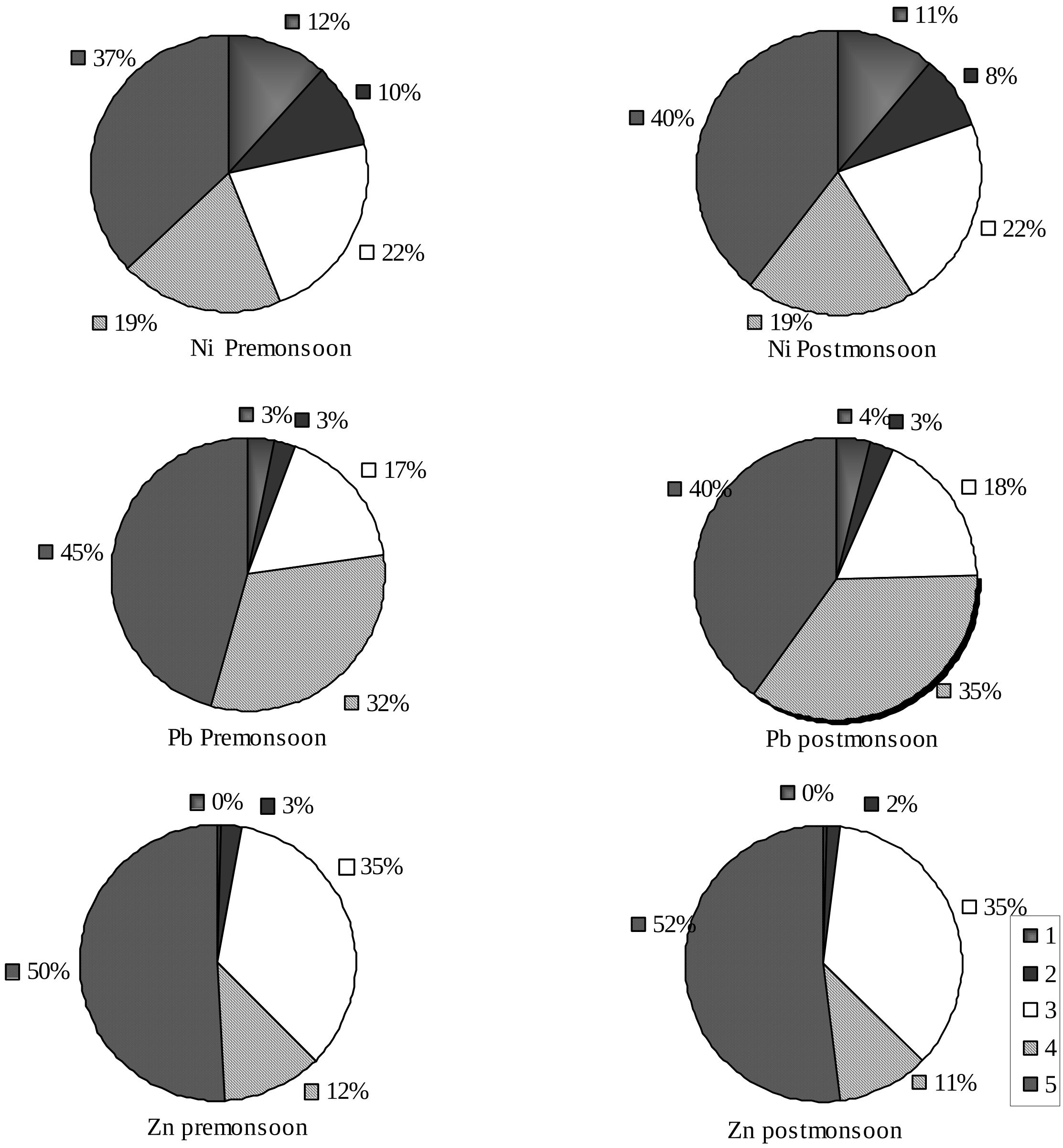


Fig. 3. Percentage distribution of metals in various fractions(Continuation)

decreased and it ranges from 1.52 to 12.0 with a mean of 6.77 µg/g and 0.96 to 4.32 with a mean of 2.42 in the I and II fractions respectively. The spatial diagram shows a distributive pattern of exchangeable fraction with some of the stations showing slightly higher values in the middle and lower part of the river. Stations 10-16, 21, 26 & 27 show high values with regard to the concentration of this metal in this fraction. The concentration of the metal in the carbonate bound fraction is observed to be lesser than the exchangeable fraction and the spatial diagram shows some significant values of Cu in the lower part of the river sediments.

In the moderately bound fractions viz., Fe-Mn oxide and organic fractions, during pre-monsoon, the concentration of the metal ranges from 6.57 to 21.26 with a mean of 11.33 and 8.16 to 75.26 with a mean of 22.48 µg/g respectively. The spatial variation with regard to this metal in Fe-Mn oxide fraction is found to be distributive with some of the stations showing higher values in the middle part of the river. The distribution diagram of the organic fraction shows higher values in the lower part of the river at stations 26-32. In the case of post monsoon, Cu value ranging from 5.2 to 15.8 with a mean of 7.89 and 5.6 to 64.6 with a mean of 17.49 µg/g in III and IV fractions respectively.

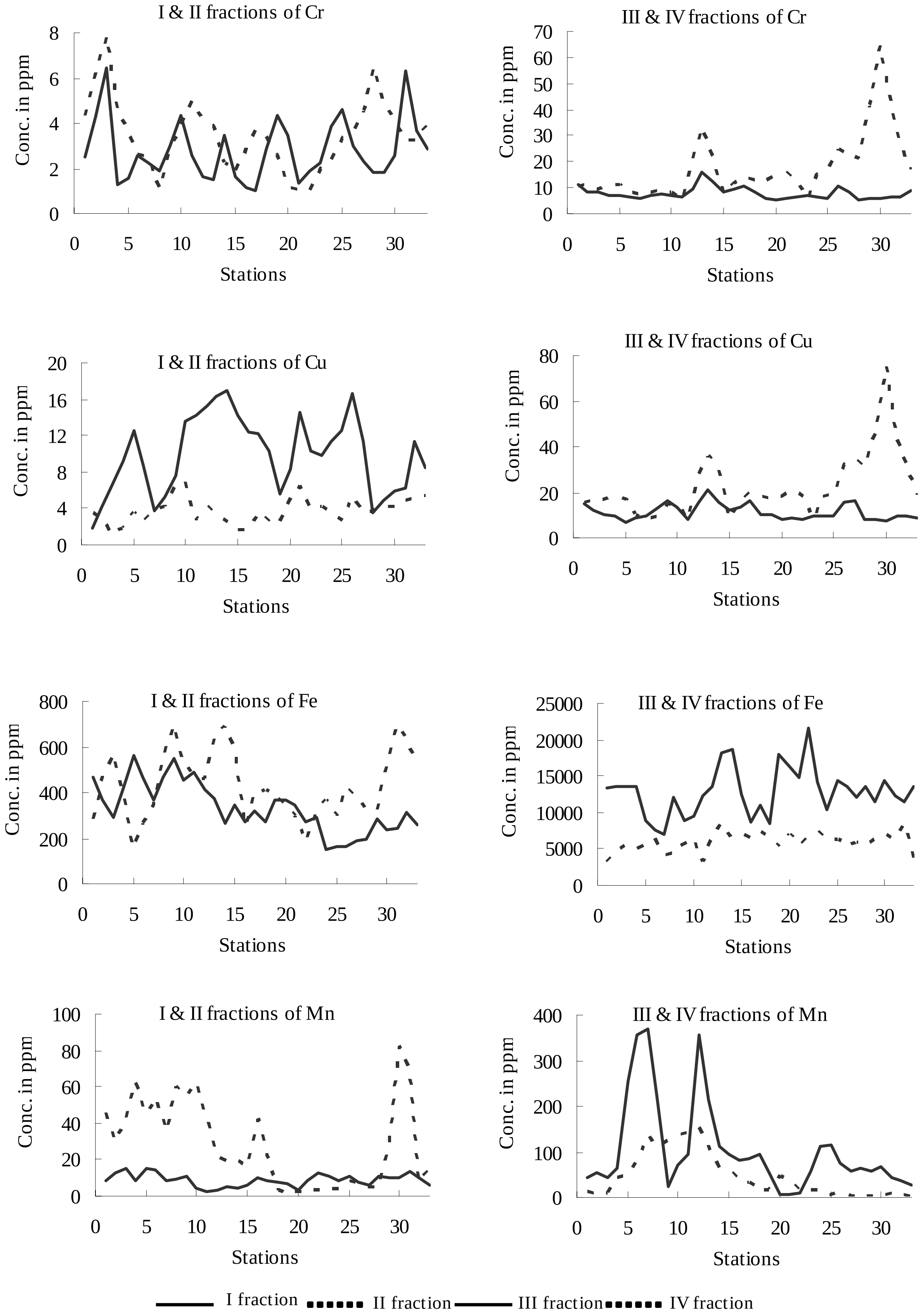


Fig . 4. Spatial variation of fractions in sediments of River Adyar – pre-monsoon(Continues)

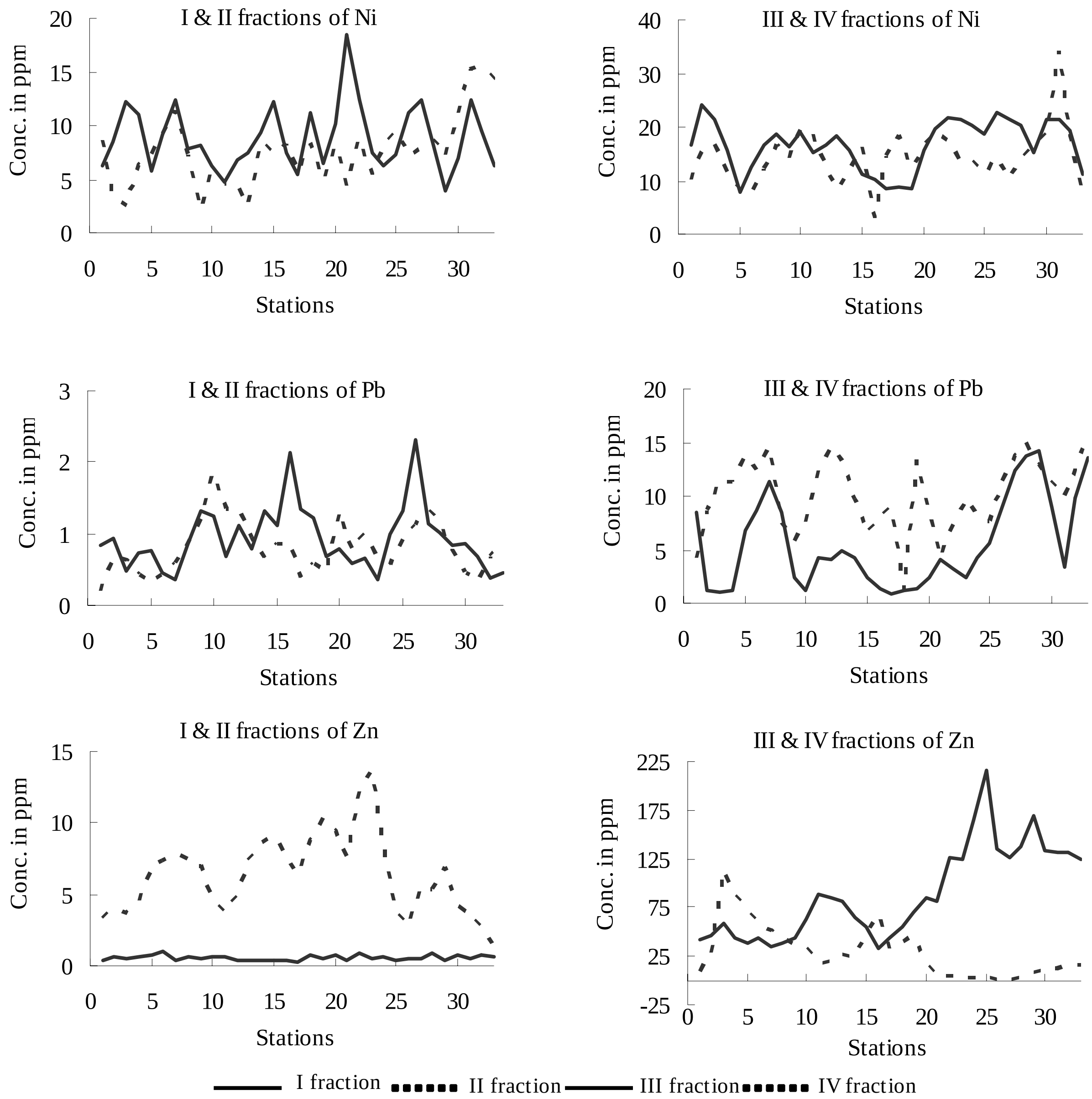


Fig . 4. Spatial variation of fractions in sediments of River Adyar – pre-monsoon(Continuation)

Spatial variation diagram of Fe-Mn oxide fraction shows a distributive pattern at stations 1, 13, 14, 17 and 26. In the case of organic fraction, Cu shows higher values in the middle and lower part of the river at stations 12-14 and 26-32. In the residual fraction, the concentration of Cu ranges from 10.21 to 42.35 with an average value of 23.51 µg/g and 7.75 to 36.25 with an average value of 19.51 µg/g during pre-monsoon and post monsoon respectively. There is only a slight decrease in the values and the seasonal effect is not found to be significant in this fraction.

The partitioning percentage of Cu in the sediments is of the order: residual > organic > Fe-Mn oxide > carbonate > exchangeable. In general, the concentration of Cu is found to be high in certain stations falling in the middle and lower part of the river. This region falls in the urban area and both industrial and domestic effluents are found to be directed into the river water. Exchangeable fraction shows a distributive pattern with respect to the stations. In these sediments, copper is largely bound to the oxidize-able fraction reflecting the availability of high organic matter in the sediments and the formation of stable organometallic

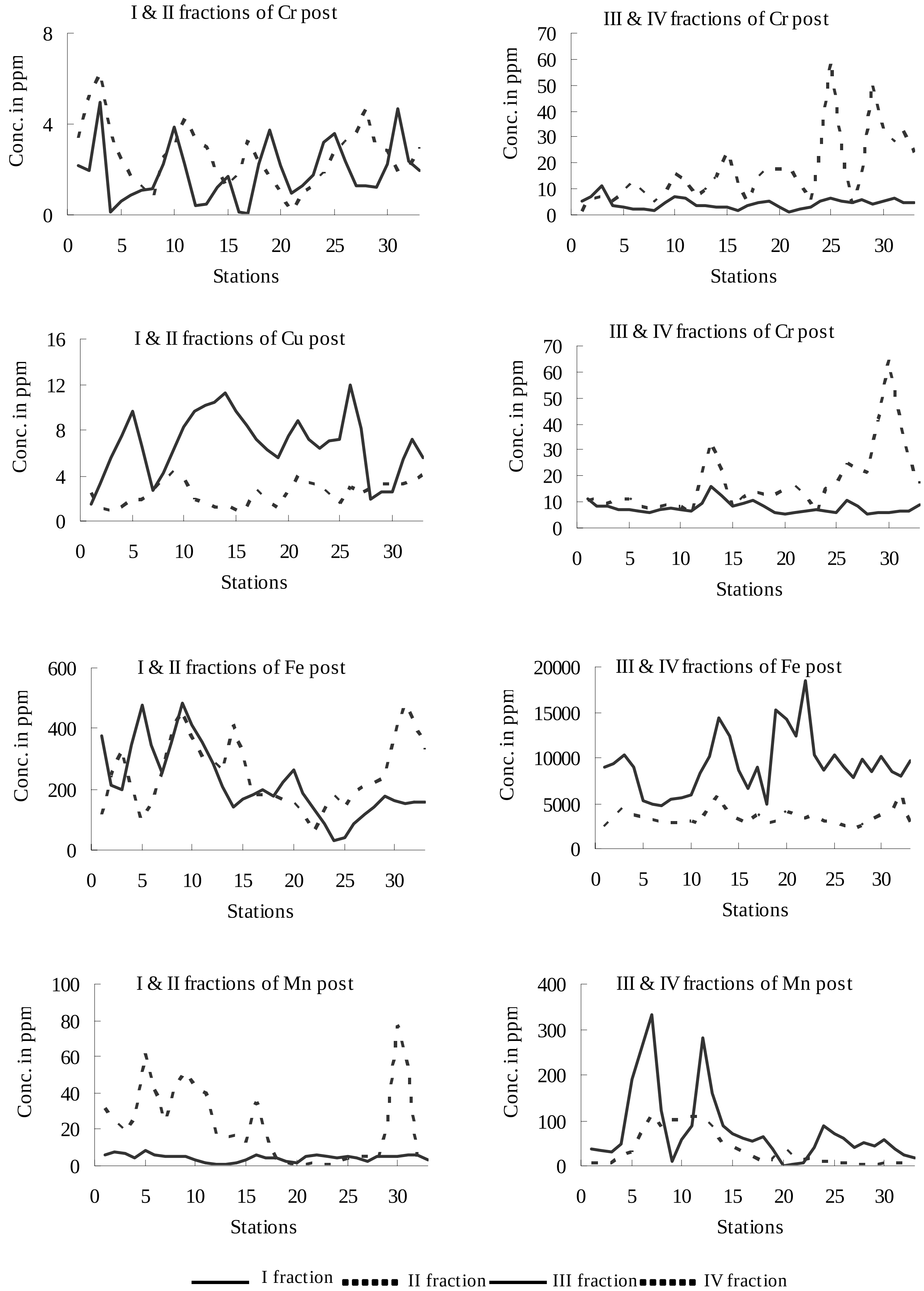


Fig. 5. Spatial variation of fractions in sediments of River Adyar – post monsoon(Continues)

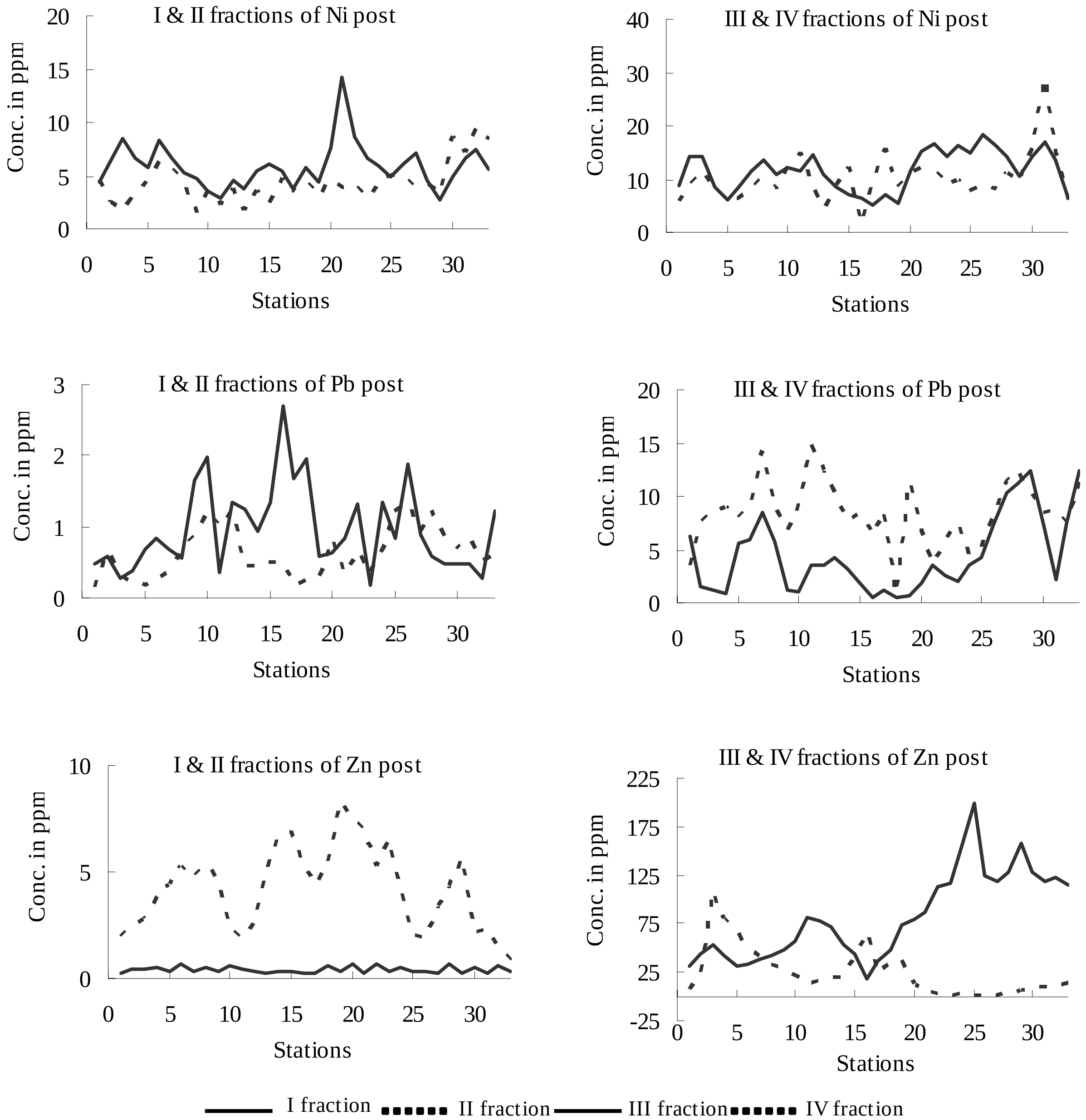


Fig. 5. Spatial variation of fractions in sediments of River Adyar – post monsoon(Continuation)

complexes. The high stability constant of organic copper compounds results in stable complex formation (Morillo *et al.*, 2004). The exchangeable and Carbonate fraction of the Cu in the sediment during pre-monsoon are 14% and 5% whereas during post monsoon, there is a slight decrease in these fractions to 13% and 4%. Residual fraction accounts for 34% and 36% during pre and post monsoon seasons. Since the contribution of the residual fraction to the total metal content is low, it could be suggested that there is an increase from the background value. Hence it is proposed that Cu would have been introduced into the river sediments largely from the anthropogenic sources. Higher percentage values in the exchangeable and carbonate fractions indicate that the metal in the river sediments are potentially more available for exchange and/or release into the riverine environment.

During pre-monsoon, the exchangeable and carbonate bound fractions of Fe range from 149 to 563 with a mean of 333 µg/g and 155 to 698 with a mean of 431 µg/g respectively. The spatial-temporal variations with regard to exchangeable and carbonate bound fractions are found to be of distributive pattern. During post monsoon, the concentration of metals bound to the exchangeable and carbonate bound fractions are found to be slightly decreased and it ranges from 30 to 483 with a mean of 222 µg/g and 57 to 477 with a mean of 248 µg/g respectively. The distribution pattern of post monsoon is in line with the pre-monsoon results. The stations 1, 4-6, 8-11 show high value with regard to the concentration of this metal in the exchangeable fraction. The carbonate bound fraction show high value at station 8-11, 14, 15, 30-33 with regard to Fe.

In the moderately bound fractions, viz., Fe-Mn oxide and organic fractions, during pre-monsoon, the concentration of the metal ranging from 6958 to 21652 with a mean of 12842 and 3125 to 8564 with a mean of 5969 µg/g respectively. The spatial variation with regard to this metal in the Fe-Mn oxide fraction shows high value at stations 13, 14, 19-23 and 30. Fe concentration in the organic fraction shows higher values at the middle and lower part of the river at stations 13, 17, 23, 30 and 32. In the case of post monsoon, III and IV fraction have values ranging from 4668 to 18452 with a mean of 9230 and 2170 to 5894 with a mean of 3437 µg/g respectively. The concentration of the metal in the organic fraction is found to be low as compared to the Fe-Mn fraction. These fractions have higher values at station 3 in the upper part; 12, 13 and 20 in the middle part and station 31 & 32 in the lower part of the river.

In the residual fraction, the concentration of Fe ranges from 12954 to 48962 with an average value of 37856 µg/g and 10180 to 45700 with an average value of 34241 µg/g during pre-monsoon and post monsoon respectively. The results show that in both the seasons, the residual fraction is found to be predominant and the contribution of the other four fractions to the total concentration is only minimal. During pre-monsoon, the residual fraction shows higher values at Station 2, 3, 8-10, in the upper part; 15-17 in the middle part; 21, 28-30 in the lower part of the river. Post monsoon also follows the same pattern but with reduced values. Though the total concentration of the iron in the sediments is not alarming, the slight increase in some of the stations may be attributed to the influence of the industrial effluents into the river water near the urban area.

The speciation diagrams depicts that the fractions does not show much variability with regard to the seasons. The residual fraction shows higher values near the upper part of the river during pre-monsoon. The partitioning of Fe in the sediments is in the order: residual > Fe-Mn oxide > organic> carbonate / exchangeable. During pre-monsoon, the exchangeable and carbonate bound fractions shows 2% whereas in the case of post monsoon, a reduction in the value is observed in these fractions from 2 to 1%. Since the concentration of Fe in the mobile fraction is found to be very low, it may be concluded that the sediment is not polluted with regard to this metal. Post monsoon recorded a high residual fraction than that of the pre-monsoon reflecting the deposition of fresh soil sediments due to the heavy precipitation during this period. The high percent availability of Fe in the residual fraction indicates that the concentration of the metal in the sediments can be attributed to the background value. In both the seasons and in all the fractions, the Fe content in the sediments is found to be distributive and there is not much variation of Fe concentration in the upper and lower part of the river.

During pre-monsoon, the exchangeable and carbonate bound fractions of Mn range from 2.48 to 15.62 with a mean of 8.85 µg/g and 2.24 to 82.54 with a mean of 28.12 µg/g respectively. The spatial-temporal variations show that the exchangeable fraction is found to be high near the upper and lower part of the river. The concentration of Mn in the carbonate bound fraction demonstrates high values near the upper and lower part of the river at stations 1-10 and 29-31. During post monsoon, the concentration of metals bound to these fractions are found to be slightly lower. It ranges from 0.64to 8.40 with a mean of 4.53 µg/g and 0.96 to 77.28 with a mean of 21.90 µg/g in the I and II fractions respectively. The spatial diagram shows a distributive pattern with regard to Mn in the exchangeable fraction with some of the stations showing slightly higher values in the upper and lower part of the river. The carbonate bound fraction has significant values of Mn in the lower part of the river at stations 5, 6, 8-10, 30 & 31.

In the moderately bound fraction viz., Fe-Mn oxide and organic fraction, during pre-monsoon, the concentration of the metal ranging from 5.21to 369.59 with a mean of 103.86 µg/g and 4.11 to 152.37 with a mean of 46.72µg/g respectively. The spatial variation with regard to this metal in Fe-Mn oxide fraction is found to be high at stations 5-8 in the upper part; 12-14 in the middle part; 24 & 25 in the lower part. The distribution diagram of the organic fraction shows higher values in the upper part of the river at stations 7-13. In the case of post monsoon, Mn values ranging from 1.26 to 333.20 with a mean of 78.0 and 1.76 to 112.46 with a mean of 35.07 µg/g in III and IV fractions respectively. Spatial variation diagram of Fe-Mn oxide fraction show similar pattern as that of pre-monsoon with higher values at stations 6-8, 12, 13 and 25. The organic fraction also falls in the same line with the pre-monsoon pattern showing higher values in the upper part of the river at stations 7-13. In the residual fraction, the concentration of Mn ranges from 34.29 to 242.51 with an average value of 110.96 µg/g and 24.75 to 202.0 with an average value of 89.23 µg/g during pre-monsoon and post monsoon respectively. There is only a slight decrease in the values and the seasonal effect is found to be only moderately significant in this fraction.

The partitioning percentage of Mn in the sediments is in the order: residual > Fe-Mn oxide > organic > carbonate > exchangeable. The speciation pattern of pre-monsoon show that the exchangeable fraction of the sediment has 3% of the total metal whereas the carbonate fraction has high concentration of the metal with 9%. A slight variation in these fractions is observed during post monsoon with 2% and 10% in exchangeable and carbonate fractions respectively. About 37% of the total metal falls under the residual category suggesting that there is an increase in the Mn concentration from the background value of the study area. It is apparent from the data that the concentration of Mn in all the fractions shows higher values in the upper and lower part of the river sediments. Indiscriminate usage of fertilizers and pesticides containing trace metal impurities near the catchment areas and the mixing of industrial and domestic effluents into the river water influences the concentration of this metal in the river bed sediments.

During pre-monsoon, the exchangeable and carbonate bound fractions of Ni range from 3.38 to 18.47 with a mean of 8.86µg/g and 2.21 to 15.36 with a mean of 7.55µg/g respectively. The spatial-temporal variations shows that the exchangeable fraction is found to have a distributive pattern with higher values at stations 3, 7, 15, 21, 22, 27 and 31. Carbonate bound fractions shows significant values at stations 11, 30-33. During post monsoon, the concentration of metals bound to these fractions are found to be slightly decreased and it ranges from 2.64 to 14.25 with a mean of 5.91µg/g and 1.52 to 9.56 with a mean of 4.30µg/g in the I and II fractions respectively. The spatial diagram with respect to exchangeable fraction shows higher values in the lower part of the river. Stations 3, 6, 21, 22, 27 and 32 show high values with regard to the concentration of this metal in this fraction. The carbonate bound fraction demonstrates distributive pattern of Ni values and the higher concentrations are observed at stations 6, 30-33. In the moderately bound fractions viz., Fe-Mn oxide and organic fractions, during pre-monsoon, the concentration of the metal ranging from 7.89 to 24.11 with a mean of 16.67 and 3.22 to 34.33 with a mean of 14.33 µg/g respectively. The spatial variation with regard to this metal in Fe-Mn oxide fraction is found to have higher values in the lower part of the river sediments at stations 2,3, 22-24, 26-28, 30 & 31. The distribution diagram of the organic fraction demonstrates a distributive pattern with higher values at stations 10, 11, 18, 21, 30-32. In the case of post monsoon, Ni values ranging from 5.20 to 18.42 with a mean of 11.66 and 1.56 to 29.0 with a mean of 10.16 µg/g in III and IV fractions respectively. Spatial variation diagram of Fe-Mn oxide fraction shows similar pattern as that of pre-monsoon with higher values in the upper and lower part of the river at stations 2, 3, 14, 21-28 & 30. The organic fraction also fall in the same line with the pre-monsoon pattern showing higher values in the middle and lower part of the river at stations 10, 15, 18, 30 and 32. In the residual fraction, the concentration of Ni ranges from 17.25 to 45.69 with an average value of 27.76 µg/g and 12.65 to 37.84 with an average value of 20.72 µg/g during pre-monsoon and post monsoon respectively. The residual fraction shows higher concentration of Ni in the middle part of the river in both the seasons.

The partitioning percentage of Ni in the sediments is of the order: residual > Fe-Mn oxide > organic > exchangeable > carbonate. The speciation pattern of Ni shows that the exchangeable fraction is high with 12% and 11% during pre and post monsoon respectively. The carbonate fraction of the metal recorded 8% and these first two fractions accounts for about 20% reflecting the bioavailability of the metal. About 38% of the total metal falls under the residual category suggesting that there is an increase in the Ni concentration from the background value of the study area. It is apparent from the data that the concentration of Ni in all the fractions shows higher values in the m and lower part of the river sediments.

During pre-monsoon, the exchangeable and carbonate bound fractions of Pb range from 0.35 to 2.31 with a mean of 0.93 µg/g and 0.21 to 1.85 with a mean of 0.81 µg/g respectively. The spatial-temporal variations shows that the exchangeable fraction shows high values near the middle and lower part of the river. Carbonate bound fractions also shows higher values at stations 9-12, 20, 26-28. During post monsoon, the concentration of metals bound to these fractions are found to be slightly decreased and it ranges from 0.19 to 2.69 with a mean of 0.96 µg/g and 0.16 to 1.35 with a mean of 0.63 µg/g in the I and II fractions respectively. The spatial diagram of exchangeable fraction shows higher values in the middle and lower part of the river. Stations 9, 10, 12, 13, 15-18, 24 & 26 shows high values with regard to the concentration of the metal in this fraction. The carbonate bound fraction has significant values of Pb in the lower part of the river at stations 25-28.

In the moderately bound fractions viz., Fe-Mn oxide and organic fractions, during pre-monsoon, the concentration of the metal ranging from 0.82 to 14.20 with a mean of 5.52 and 1.13 to 15.80 with a mean of 10.08 µg/g respectively. The spatial variation with regard to this metal in Fe-Mn oxide fraction is found to be high in the lower part of the river at stations 7, 27-29 & 33. The spatial diagram of the organic fraction indicates a distributive at stations 3-7 in the upper part; 11-13, 19 in the middle part; 26-30, 32 & 33 in the lower part of the river sediment. In the case of post monsoon, Pb values ranging from 0.59 to 12.37 with a mean of 4.42 and 0.85 to 14.68 with a mean of 8.40 µg/g in III and IV fractions respectively. Spatial variation diagram of Fe-Mn oxide fraction show similar pattern as that of pre-monsoon with higher values in the lower part of the river at stations 27-29 and 33. The organic fraction also shows higher values at stations 7, 11-13, 19, 27-29 and 33.

In the residual fraction, the concentration of Pb ranges from 3.65 to 19.34 with an average value of 14.50 µg/g and 1.35 to 16.34 with an average value of 9.76 µg/g during pre-monsoon and post monsoon respectively. The residual fraction shows a distributive pattern with regard to the concentration of Pb in both the seasons. It is observed from the data that during both the seasons, the concentration of Pb is found to be high in the middle and lower part of the river. In this region, the river water is highly polluted as the domestic sewage water and industrial effluents are directly directed into the river. Moreover, this region falls in the urban area where the automobile exhaust containing lead particles and the urban run-off due to precipitation increases the metal concentration in the river sediments. The partitioning of Pb in the sediments is in the order: residual > organic > Fe-Mn oxide >carbonate/ exchangeable. The speciation diagram shows higher percentage of oxidize-able fraction 32% and 35% during pre and post monsoon reflecting that the organic load in the water binds the metal and would have settled in the organic fraction of the bed sediments. The exchangeable and carbonate fraction during pre-monsoon shows 6% and in the case of post monsoon, these fractions accounts for 7%. These values suggest that the sediments are moderately contaminated by anthropogenic activities.

During pre-monsoon, the exchangeable and carbonate bound fractions of Zinc range from 0.29 to 0.98 with a mean of 0.56 µg/g and 1.34 to 13.54 with a mean of 6.37 µg/g respectively. The spatial-temporal variations show that the exchangeable fraction is found to have a distributive pattern. Carbonate bound fractions shows significant values in the middle and lower part of the river sediments at stations 19, 22 and 23. During post monsoon, the concentration of metals bound to these fractions are found to be slightly decreased and it ranges 0.22 to 0.69 with a mean of 0.42 µg/

g and 0.88 to 8.26 with a mean of 4.20 µg/g in the I and II fractions respectively. The spatial diagram follows in line with the pre-monsoon and demonstrates a distributive pattern with regard to exchangeable fraction. The carbonate bound fraction has significant values of Zn in the middle part of the river at stations 19-21.

In the moderately bound fractions viz., Fe-Mn oxide and organic fractions, during pre-monsoon, the concentration of the metal ranging from 32.5 to 215.61 with a mean of 88.26 and 1.29 to 112.34 with a mean of 28.89 µg/g respectively. The spatial variation with regard to this metal in Fe-Mn oxide fraction is found to be high in the lower part of the river at stations 22-33. The distribution diagram of the organic fraction shows higher values in the upper and middle part at stations 3-8, 15, 16 & 19. In the case of post monsoon, Zn values ranging from 17.8 to 199.68 with a mean of 81.42 and 0.26 to 109.68 with a mean of 24.61 µg/g in III and IV fractions respectively. Spatial variation diagram of Fe-Mn oxide fraction shows higher values near the lower part of the river at stations 22-33. The organic fraction also fall in the same line with the pre-monsoon pattern with higher values at stations 3-9, 15, 18 and 19. In the residual fraction, the concentration of Zn ranges from 26.51 to 235.89 with an average value of 128.92 µg/g and 20.23 to 238.6 with an average value of 119.81 µg/g during pre-monsoon and post monsoon respectively. The residual fraction shows a distributive pattern with regard to Zn in both the seasons.

The partitioning of the sediments is in the order: residual > Fe-Mn oxide > organic >carbonate >exchangeable. The speciation pattern of Zn shows that the exchangeable and carbonate fractions show 3% and 2% during pre and post monsoon periods suggesting lower bioavailability of the metals in the mobile fraction. About 51% of the total metal falls under the residual category indicating that there is an increase in the Zn concentration from the background value of the study area. It is apparent from the data that the concentration of Zn in all the fractions shows higher values in the middle and lower part of the river sediments.

The results of sediment speciation reveal the presence of metals in various fractions. This fractionation of metals facilitates to determine the mobility of the heavy metals by evaluating the percentage of metals in the weakly bound fractions (A and B) with the total metal content. Since these fractions are easily mobilized, they form a potential threat to the environment (Tessier *et al.,* 1979; Kabala and Singh, 2001). Kabala and Singh (2001) proposed a mobility factor (MF) to assess the behavior of the metal in soil and sediments which was used by several authors (Ettler *et al.,* 2005; Chrastny *et al.*, 2006).

$$MF = [(A + B)/(A + B + C + D + E)] \times 100(\%)$$

Where A, B, C, D and E are the concentration of the metals present in exchangeable, carbonate, reducible, oxidize-able and residual fractions respectively.

In this study, the Risk Assessment Code (RAC) which takes into account the mobility fraction of the metal was evaluated in order to identify the extent of risk associated with the percentage of metals present in the sediments. A sediment containing less than 1% of exchangeable and carbonate fractions is considered safe for the environment; 1-10% of these fractions is regarded as low risk; medium risk category falls in 11-30% of these fractions; mobile fractions with values 31-50% and more than 50% are considered as high risk and very high risk categories respectively since the metals found in these fractions are bio-available and it may easily enter into the food chain. In the study area, the results of RAC (Table 2) reveals that Cr during both pre and post monsoon periods falls in the category of low risk in all the stations. Fe shows that many of the stations falls in the low risk and no risk category. Seasonal effect is significant as many of the post monsoon stations falls in the no risk category. In the case of Cu, seasonal effect is found to be apparent and during pre-monsoon, 28 stations falls in the category of medium risk with 3 stations in the high risk region. Post monsoon follows almost the same pattern but with a reduced number of stations in the high risk category. In the case of Mn, 17 stations are in the medium risk category and 16 stations are in the low risk category during both pre-monsoon and post monsoon. Most of the stations falls in the medium risk category for the metal Ni with 3 stations are observed to be in the high risk category during pre-monsoon. In the case of post monsoon, the number of high risk stations reduced from 3 to 2. The speciation results of Pb shows those 28 stations and 5 stations are found to be in the low risk and medium risk category respectively during pre-monsoon. In the case of post monsoon, 25 stations and 8 stations fall in the low and medium risk category. Zn illustrates moderate seasonal effect and most of the stations are found to be in the low risk category. The speciation results of Cu and Ni shows that some of the stations are found to be in the high risk category which is a concern for the environment and human health.

The results of I_{poll} (karbassi *et al.*, 2008) supplements the speciation data where it has been observed that the pollution index is very high in the case of Ni during both pre and post monsoon periods (Table 3). Chromium, Fe and Pb shows low I_{poll} values indicating that the river sediments are not much affected with regard to these metals. The moderate I_{poll} values obtained for Mn and Zn are in line with the speciation results.In general, many of the medium risk and high risk stations with regard to the heavy metals are found to be in the middle and lower part of the river where both industrial and urban domestic effluents are found to be directly directed into the river water. Necessary control and remedial action is required

Table 2. Distribution of the number of stations in each risk category

Risk category	Cr		Cu		Fe		Mn		Ni		Pb		Zn	
	pre	post	pre	post	pre	post	pre	post	pre	post	pre	post	pre	post
No risk					6	18							1	4
Low risk	33	33	2	3	27	15	16	16			28	25	32	29
Medium risk			28	29			17	17	30	31	5	8		
High risk			3	1					3	2				
Very high risk														

Table 3. I_{poll} value for pre-monsoon and post monsoon of sediment of river Adyar

Element	Pre-monsoon	Post Monsoon
Cr	0.27	0.19
Cu	0.73	0.60
Fe	0.40	0.33
Mn	0.94	0.80
Ni	1.52	2.36
Pb	0.43	0.51
Zn	0.71	0.69

in this region since more of stations fall in the risk category.

CONCLUSION

The results of speciation study of the sediments of River Adyar throw more light on the nature and origin of the heavy metals. The study highlights the significance of the fractionation of metals providing the vital bioavailability data. The seasonal variation of the heavy metals in each fraction was not carried out in the sediments of River Adyar previously and hence the result gains more significance. The t-test carried out on the various fractions shows that Fe, Ni and Zn illustrates significant seasonal effect on all the fractions. Interestingly, Mn shows non-significance towards the seasonal effect for all the fractions except exchangeable fraction. Among the five fractions, the study highlights the significance of the mobility fraction which encompasses the exchangeable and Carbonate bound fractions. Since in these two fractions, metals can easily be desorbed and hence the bioavailability of the metals in the sediment can be determined.

Based on this, Risk assessment was evaluated for the heavy metals and the results shows that Cr and Fe does not have much risk impact on the environment. Cu and Ni demonstrate medium risk at about 30 stations. Manganese shows medium risk at about 17 stations. The fractionation results of Copper and Nickel in the river sediments shows high risk at about 3 stations. In general, the medium and high risk stations fall in the middle and lower part of the river which is found to be highly polluted due to the mixing of industrial and domestic effluents. From the results of the study, it is highly recommended to periodically monitor the level of pollution and action is highly warranted to control the mixing of effluents in order to halt the augmentation of the concentration of heavy metals in this region.

REFERENCES

Banerjee, A. D. K. (2003). Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environ. Poll., **123**, 95-105.

Chapman, D. (1992). Water quality assessment. In: Chapman, D. (Ed.), on behalf of UNESCO, WHO and UNEP, Chapman & Hall, London, 585.

Chrastny, V., Komarek, M., Tlustos, P. and Svehla, J. (2006). Effects of flooding on lead and cadmium speciation in sediments from a drinking water reservoir. Environ. Monit. Assess., **118**, 113-123.

Demirbas, A., Pehlivan, E., Gode, F., Altun, T., and Arslan, G. (2005). Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd (II) from aqueous solution on Amberlite IR-120 synthetic resin. Journal of Colloid and Interface Science., **282**, 20-25.

Dixit, S. and Tiwari, S. (2008). Impact Assessment of Heavy Metal Pollution of Shahpura Lake, Bhopal, India. Int. J. Environ. Res., **2(1),** 37-42.

Ettler, V., Van˘ek, A., Mihaljevi˘c, M. and Bezdi˘cka, P. (2005). Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. Chemosphere., **58**, 1449-1459.

Frignani, M. and Belluci, L. G. (2004). Heavy metals in marine coastal sediments: Assessing sources, fluxes, history and trends. Annali di Chimica., **94(7-8)**, 479-486.

Goonetilleke, A., Thomas, E., Ginn, S. and Gilbert, D. (2005). Understanding the Role of Land Use in Urban Stormwater Quality Management. J. Environ. Manage., **74**, 31-42.

Homady, M., Hussein, H., Jiries, A., Mahasneh, A., Al-Nasir, F. and Khleifat, K. (2002). Survey of some heavy metals in sediments from vehicular service stations in Jordan and their effects on social aggression in prepubertal male mice. Environ. Res., **89**, 43-49.

Jiries, A. (2003). Vehicular contamination of dust in Amman, Jordan. The Environmentalist., **23(3)**, 205-210.

Kabala, C. and Singh, B. R. (2001). Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter, J. Environ. Qual., **30**, 485-492.

Karbassi, A. R., (1996). Geochemistry of Ni, Zn, Cu, Pb, Co, Cd, V, Mn, Fe, Al & Ca in sediments of North Western part of the Persian Gulf. Intl. J. Env. Studies., **54,** 205-212.

Karbassi, A. R., Monavari, S. M., Nabi Bidhendi, Gh. R., Nouri, J. and Nematpour, K. (2008). Metal pollution assessment of sediment and water in the Shur River. Environ. Monit. Assess., **147**, 107-116.

Karbassi, A. R., Shankar, R. and Manjunatha, B. R. (2001). Geochemistry of shelf sediments off Mulki on southwestern coast of India and their palaeo-environment significance. Journal of the Geological Society of India, **58,** 37-44.

Ma, L. Q. and Rao, G. N. (1997). Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. J. Environ. Qual., **26**, 259-264.

Morillo, J, Usero, J. and Gracia, I. (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere., **55**, 431-442.

Mwamburi, J. (2003). Variations in trace elements in bottom sediments of major rivers in Lake Victoria's basin, Kenya. Lakes and Reservoirs. Res. Manage., **8**, 5-13.

Priju, C. P. and Narayana, A. C. (2007). Heavy and Trace Metals in Vembanad Lake Sediments. Int. J. Environ. Res., **1(4)**, 280-289.

Shankar, R. and Karbassi, A. R. (1991). Geochemistry and magnetic susceptibility of surficial sediments of the new Mangalore Port. J. Geol. Soc. Ind., **38,** 412-417.

Tessier, A., Campbell, P. G. C. and Bisson, M. (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Anal. Chem. **51**, 844-851.

Tokalioglu, S., Kartal, S. and Birol, G. (2003). Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. Turk. J Chem., **27**, 333-346.