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TRACE METALS IN SEDIMENTS OF THE ZUARI RIVER OF GOA, WEST COAST OF INDIA

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ABSTRACT

The bottom sediment samples were collected from the ten sampling stations located along the Zuari river of Goa, west coast of India. The sediment samples were analyzed for some trace metals content viz. Zinc, Iron, Manganese, Cadmium, Cobalt, Copper and Chromium. The collection of the sediment samples were carried out during three seasons viz. Pre-monsoon (February-May), Monsoon (June-September), Post-monsoon (October-January). In general concentrations of the trace metals in the sediments broadly registered highest values during monsoon season except for cadmium and Iron, which showed slightly higher concentrations during the Post-monsoon season. Relatively higher concentration of Iron during the Post-monsoon and monsoon compared to Pre-monsoon can be attributed to mining and shipping activities along with increased river runoff.

KEY WORDS
Biodegradation
Tannery effluent
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INTRODUCTION

Trace metals in aqueous environment may occur in various chemical forms like dissolved, particulate, sediment and interstitial water. The suspended matter can act as a scavenger for heavy metals in water (De Groot *et al.*, 1976). A large part of heavy metals present in the aqueous environment is associated with suspended particles. When the flow velocity slackens, the coarser grained particles and aggregates will settle. This sedimentation takes place especially in estuaries and harbours. This will lead to the accumulation of trace metals in sediments. A large part of the anthropogenic discharge of trace metals into the environment becomes part of the suspended matter and gets deposited in river sediments. Therefore, sediment reflects the extent of the pollution in the given area. Anthropogenic inputs of some heavy metals, however, exceed those of natural inputs due to weathering (De Groot, *et al.*, 1976). Estuarine sediments act as a sink for metals regardless of whether the metal rich waste is discharged into the river as solids or solutions (Elderfield and Hepworth, 1975). The estuarine environment is the last area for the removal of trace metals before their passage from the terrestrial to the marine environment. The role of rivers in transporting material from the continents to ocean is paramount, being 10 times that of glaciers and 100 times that of winds (Goldberg, 1976).

MATERIALS AND METHODS

The Zuari river originates from the Dighi ghat of the Karnataka part of the Sahyadri Hills after flowing through a stretch of 67 kms joins the Arabian Sea near the Mormugao-Donapaula point. Its width at the mouth of the estuary is 5.5 km while, in the upstream, it narrows to less than 0.5 km. Similar to the Mandovi it is fed by monsoon precipitation and also receives the discharge from a catchment area of 550 km^2. Its basin constitutes about 27 % of the total land area of Goa. It carries drainage from 309 km2. of the forest land.There are a total of 127 industries in its basin which discharge about 4.4 x 106 m^3 of effluents per year into the river and its tributaries. There are 10 large mines in its basin which generate 1000-4000 tonnes of rejects per day per mine, of which a good portion can be expected to reach the river. (NIO, 1979).

The station locations in the study area are given in Fig. 1. The area of investigation covers the Zuari river in Goa (west coast of India). It comprises

Table 1: Data on seasonal variation of trace metal in sediments of the Zuari river of Goa, West coast of India

Station	Premonsoon (μg g⁻¹)						Monsoon (μg g⁻¹)						Postmonsoon (μg g⁻¹)					
	Zn	Fe(%)	Mn(%)	Cd	Co	Cu	Cr	Zn	Fe(%)	Mn(%)	Cd	Co	Cu	Cr	Zn	Fe(%)	Mn(%)	Cd	Co	Cu	Cr
ZE1	N.A	N.A	N.A	N.A	N.A	N.A	N.A	84.00	7.598	0.273	N.D	20.667	25.333	149.000	23.667	2.227	0.047	1.667	18.000	9.667	39.333
ZE2	N.A	N.A	N.A	N.A	N.A	N.A	N.A	125.667	9.639	0.551	N.D	12.000	71.667	176.667	73.3333	6.164	0.173	1.333	22.667	32.000	135.000
ZE3	114.333	6.500	0.247	1.260	22.330	43.333	161.000	93.333	8.404	0.240	1.300	35.667	45.000	187.667	165.333	11.735	0.449	1.000	26.333	70.000	144.333
ZE4	N.A	N.A	N.A	N.A	N.A	N.A	N.A	84.667	5.895	0.383	N.D	26.667	37.670	107.667	58.667	5.139	0.323	0.333	22.667	31.667	53.333
ZE5	N.A	N.A	N.A	N.A	N.A	N.A	N.A	121.333	10.529	0.627	1.260	24.667	26.667	135.667	89.000	6.335	0.628	1.260	27.333	7.000	89.000
ZE6	84.667	2.259	0.413	0.330	12.330	36.000	93.333	105.333	6.694	0.159	1.000	29.667	50.667	141.667	29.333	3.788	0.388	0.333	12.333	14.333	70.000
ZE6a	63.333	2.665	0.139	ND	14.667	30.667	165.000	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
ZE7	N.A	N.A	N.A	N.A	N.A	N.A	N.A	71.667	6.023	0.273	1.667	26.000	28.667	137.333	53.000	4.735	0.275	3.333	11.000	12.667	100.333
ZE8	N.A	N.A	N.A	N.A	N.A	N.A	N.A	68.667	5.522	0.290	0.333	34.333	22.667	220.667	150.333	10.459	0.623	1.260	36.330	53.000	132.000
ZE9	86.667	5.667	0.405	2.160	20.670	35.667	175.333	52.667	4.016	0.58	4.600	22.333	18.000	133.333	79.000	9.280	0.323	1.600	22.333	29.667	120.000
ZE9a	N.A	N.A	N.A	N.A	N.A	N.A	N.A	126.000	12.078	0.245	1.260	25.667	74.000	653.000	N.A	N.A	N.A	N.A	N.A	N.A	N.A
ZE10	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	114.333	16.770	0.158	1.300	32.333	35.000	388.000
AVG	87.250	4.273	0.301	0.938	17.499	36.417	148.667	93.330	7.640	0.329	1.142	25.760	40.030	204.260	83.600	7.660	0.338	1.342	23.132	29.500	127.133
Range	(63.33-114.33)	(2.25-6.5)	(0.139-0.413)	(ND-2.16)	(12.33-22.33)	(30.67-43.33)	(93.33-175.33)	(52.667-126)	(4.016-12.07)	(0.159-62)	(N.D-4.6)	(120-35.67)	(18.0-74.0)	(107.67-653.0)	(23.67-165.33)	(2.33-16.7)	(0.04-0.628)	(0.33-3.3)	(11.0-36.33)	(7.0-70.0)	(39.33-388)

Keys: Description; Ze – Zuari Estuary; N. D. – Non-Detectable; N. A. Not Analysed

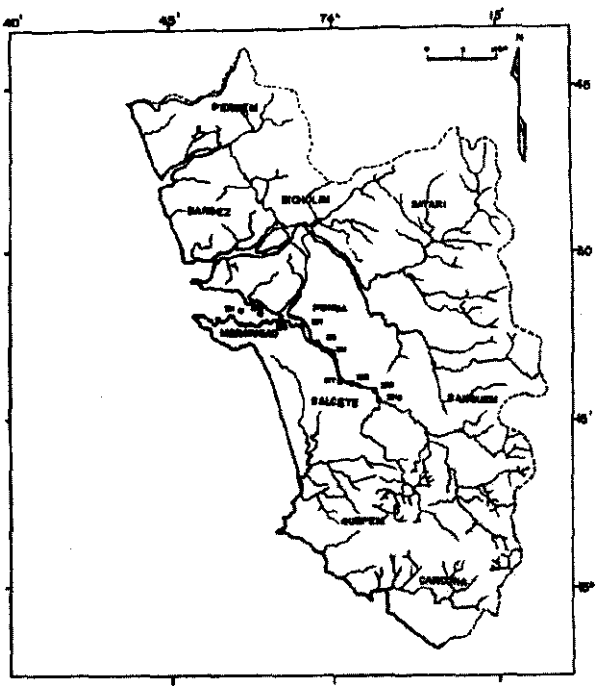


Figure 1: Map showing study area in the Zuari River of Goa, West Coast of India

of ten sampling stations. The stations were named (from mouth to head) ZE1, ZE2, ZE3, ZE4, ZE5, ZE6, ZE7, ZE8, ZE9 and ZE10 (extra stations, ZE4a, ZE6a, ZE9a, ZE9b).These stations cover the entire course of the river i.e. from the head to the mouth region. Sediment samples for the study were collected in three seasons viz. Pre-monsoon (May), Monsoon (July) and Post-monsoon (November). Bottom sediment samples were collected from different stations using a hand operated Van Veen Grab sampler. The analysis of trace metals from the sediments were done according to total decomposition method of Loring and Rantala (1992). In this method hydrofluoric acid (HF) and aquaregia are used to release the total metal content from marine sediments into solutions in a sealed teflon bomb.

RESULTS AND DISCUSSION

The trace metal concentrations of the sediment samples from the estuarine regions of Zuari river in the different seasons are furnished in the Table 1.

Zinc

The concentration of zinc (μg g⁻¹) in sediments varied from 63.33 to 114.33 during pre-monsoon, from 52.67 to 126.0 during monsoon and from 23.67 to 165.33 during post-monsoon. The range and average values of zinc in sediments in the present study (Table 2) is slightly lower when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma

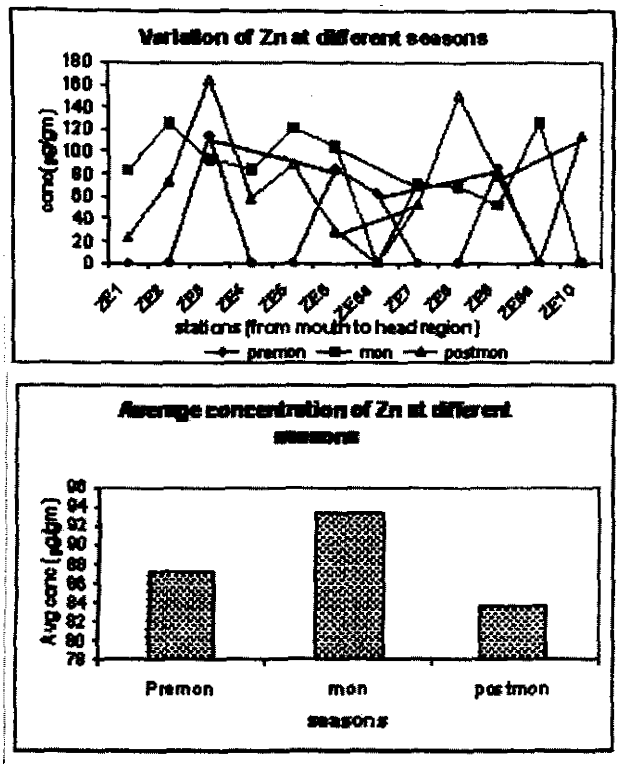


Figure 2a: Seasonal variation of Zinc in sediment of Zuari River of Goa, West coast of India

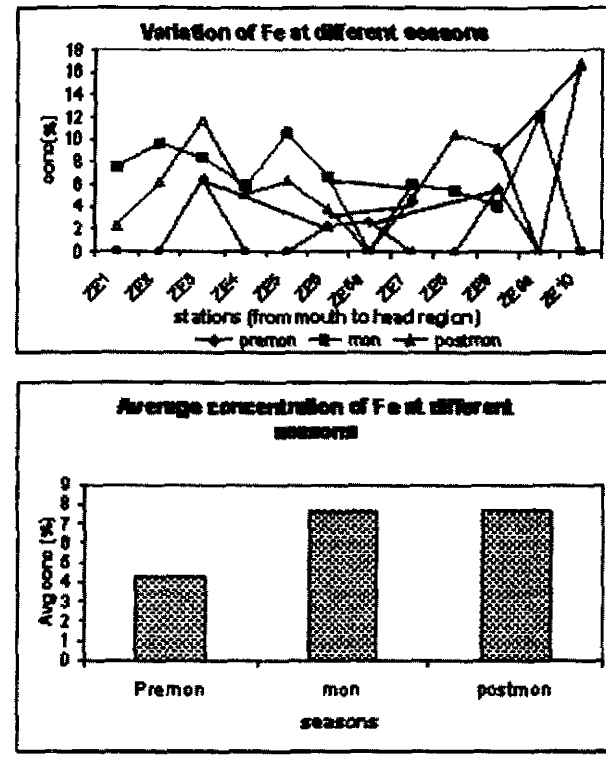


Figure 2b: Seasonal variation of Iron in sediment of Zuari River of Goa, West coast of India

et al., 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Vellar estuary (Mohan, 1995), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979) and Tapti (Subramanian, 1985). The study revealed slightly higher values when compared with those reported earlier from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988), Narmada (Subramanian et al., 1985) and Indian river average (Subramanian *et al.*, 1985).

Seasonal variation of zinc registered highest concentrations during the monsoon followed by pre-monsoon and post-monsoon seasons (Fig.2a). High concentrations of zinc during monsoon are due to the effect of increased inputs of land derived metals due to runoffs. A large part of the anthropogenic discharge of heavy metals into the environment becomes part of the suspended matter in rivers. This suspended matter can act as scavenger for heavy metal in water (Burton and Liss, 1976). Similar observations were made by Srinivas (1998) in Godavari estuarine sediments and Pondicherry harbour by Senthilnathan and Balasubramanian (1999).

Iron

Concentration of iron (%) in different seasons varied from 2.25 to 6.5 during pre-monsoon, from 4.016 to 12.078 during monsoon and from 2.23 to 16.77 during post-monsoon. The range and average values of iron in the present study (Table 2) is slightly higher when compared with those reported earlier from Mandovi estuary (Bukhari, 1994), Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma *et al.*, 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan *et al.*, 1988), Vellar estuary (Mohan, 1995), Tuticorin coast (Ganesan and Kannan, 1995), Narmada (Subramanian *et al.*, 1985), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979) and Tapti (Subramanian, 1985).

Seasonal variation of iron in sediments registered higher values during post-monsoon and monsoon seasons followed by pre-monsoon (Fig 2 b). Concentration of metals in sediments depends on several factors such as local conditions, particle size and organic matter content (Aston and Chester, 1976). Fine grained sediments (clays, clayey silts) are characterized by higher metal concentration in sediment (Deva Varma *et al*, 1993). Relatively high concentration during post-monsoon can be attributed to high organic matter content in sediments. Whereas, higher concentrations during monsoon may be due to the higher inputs from land runoff and influx of metal rich fresh water. The increased particulate matter along with suspended sediment load brought in by the river would also be a possible reason for the abnormally high values during monsoon (Senthilnathan and Balasubramanian, 1994).

Table 2: Comparision of range and average concentrations of trace metals in sediments of mandovi and Zuari rivers of Goa with other regions

Location	Zn	Fe(%)	Mn (%)	Cd	Co	Cu	Cr	References
Mandovi estuary	25.0-149.67 (87.827)	2.03-12.8 (7.909)	0.062-6.079 (0.37)	ND-4.3 (1.389)	3.33-32.0 (15.506)	3.67-80.67 (36.987)	68.0-403 (264.47)	Present study
Zuari estuary	23.67-165.33 (88.264)	2.23-16.7 (7.09)	0.04-0.62 (0.329)	Nd - 4.6 (1.191)	12.0 - 36.33 (22.583)	7.0-74.0 (35.0)	60.33-388.0 (162.86)	Present study
Mandovi estuary	21.0-83.5	2.2-49.7	0.01-1.18	-	2.5-45.3	12.9-77.5	-	Alagarsamy, 1988
Mandovi estuary	38.0-102	3.15-11.05	0.085-1.01	-	15-35	31-88	224-580	Bukhari, 1994
Godavari estuary	66.0-323.0 (207.0)	2.67-8.03 (5.77)	0.04-0.17 (0.1)	-	22.0-89.0 (50.0)	61.0-157.0 (107.0)	88.0-243.0 -137	Srinivas, 1998
Vamsadhara estuary	50.0-250.0 (152.0)	3.20-7.10 (5.28)	0.04-0.09 (0.05)	-	20.0-45.0 (32.0)	25.0-55.0 (37.0)	8.0-128.0 (106.0)	Devavarma *et al.*, 1991 and 1993
Krishna	97	6.6	0.2	-	29	124	114	Krishna Rao and estuary Swamy, 1991
Cauvery estuary	-	1.35-7.6	0.02-0.14	-	10.0-200.0	10.0-50.0	20-220.0	Ramanathan *et al.*, 1988
Vellar estuary	196	3.93	0.4854	7	48	45	222	Mohan, 1995
Tuticorin coast	-	0.224-0.432 (0.316)	0.029-0.125 (0.078)	-	-	-	-	Ganesan and Kannan, 1995
Narmada	50	3.14	0.0514	-	36	46	55	Subramanian *et al.*, 1985
Tapti	118	10.9	0.13	-	64	126	108	Subramanian et al., 1985
Indian Average	16	2.9	0.06	-	31	28	87	Subramanian *et al.*, River 1985
World river Average	350	4.8	0.105	-	20	100	100	Martin and Maybeck, 1979
Surficaial	129	3.59	0.07	-	13	32	97	Martin and Maybeck, Rock 1979

N. D - Non-detectable; All values in parentheses are average values' All values in $\mu g\ g^{-1}$ except Fe and Mn.

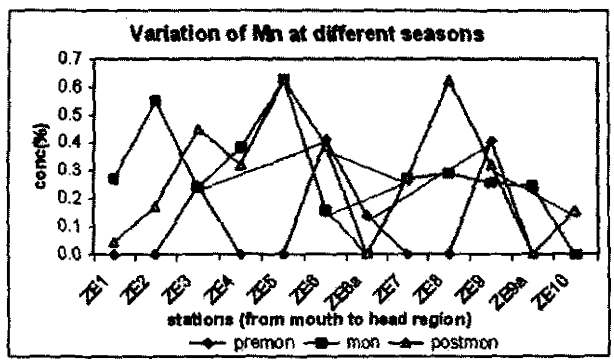
Ganesan and Kannan (1995) had reported high content of iron during monsoon and post-monsoon in Tuticorin coast, which is attributed to increasing land runoffs. Srinivas (1998) while studying Godavari estuarine sediments observed higher concentrations during monsoon seasons.

Manganese

Concentration of manganese (%) in sediments varied from 0.139 to 0.413 during pre-monsoon, from 0.159 to 0.62 during monsoon and from 0.047 to 0.62 during post-monsoon. In general, the ranges and averages of manganese concentrations in the present study (Table 2) broadly agree with those reported from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988). But, it revealed slightly higher concentrations when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma *et al.*, 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan *et al.*, 1988), Tuticorin coast (Ganesan and Kannan, 1995), Narmada (Subramanian *et al.*, 1985), Narmada (Subramanian *et al.*, 1985) World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979) and Tapti

(Subramanian, 1985). However, slightly lower values were observed when compared with that reported earlier from Vellar estuary (Mohan, 1995).

Seasonal variation of manganese in sediments showed highest concentration during post-monsoon and monsoon periods compared to pre-monsoon (Fig 2 c). Higher concentration during post-monsoon season can be



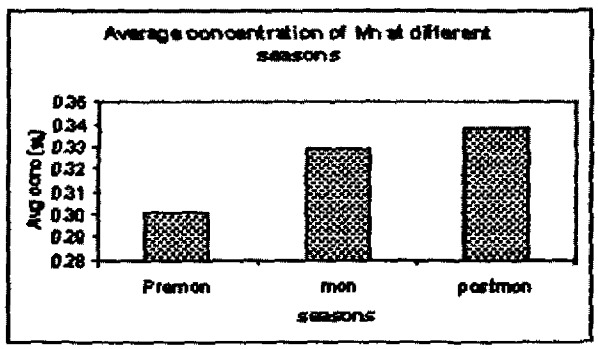


Figure 2c: Seasonal variation of Manganese in sediment of Zuari River of Goa, West coast of India

attributed to high organic matter content during post-monsoon season. Srinivas (1998) reported high concentration of manganese in sediment during monsoon and post-monsoon in Godavari estuary. Similarly high concentration of manganese was reported during monsoon and post-monsoon season from Tuticorin coast (Ganesan and Kannan, 1995).

Cadmium

Concentration of cadmium ($\mu g\ g^{-1}$) in different seasons in sediments varied from ND (Non Detectable) to 2.16 during pre-monsoon, from ND to 4.6 during monsoon and from 0.33 to 3.3 during post-monsoon.The range and average values obtained in the study is slightly lower when compared with that reported earlier from Vellar estuary (Mohan, 1995).

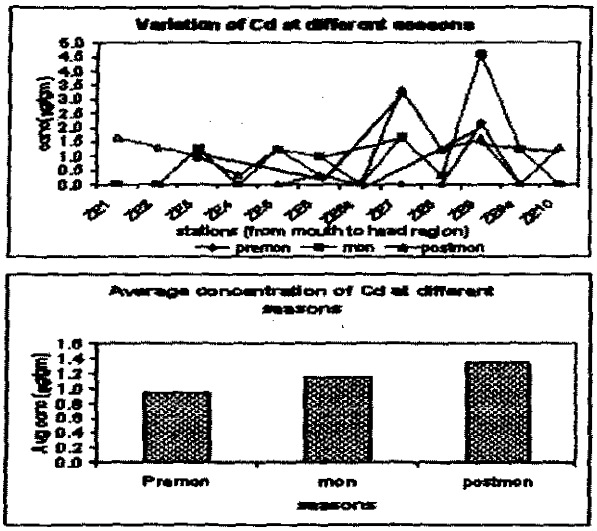


Figure 2c: Seasonal variation of Cadmium in sediment of

Seasonal variation of cadmium is found to be highest during post-monsoon period followed by monsoon and pre-monsoon (Fig 2d). Higher values during post-monsoon could be due to higher organic matter content in both the estuaries. This is also supported by significant positive correlation exhibited between cadmium and organic carbon during post-monsoon season in the Mandovi estuary (Singh, 2000). Senthilnathan and Balasubramanian (1999) while studying heavy metal distribution in Pondicherry harbour reported higher concentration of cadmium in sediments during monsoon and lower in summer. This was attributed to land runoff and influx of metal rich water.

Cobalt

Concentration of cobalt ($\mu g\ g^{-1}$) varied from 12.33 to 22.33 during pre-monsoon, from 12.0 to 35.67 during monsoon and from 11.0 to 36.33 during post-monsoon. The ranges and averages values of cobalt in sediments in the present study (Table 2) is slightly lower when compared with those reported earlier from Godavari estuary (Srinivas, 1998),

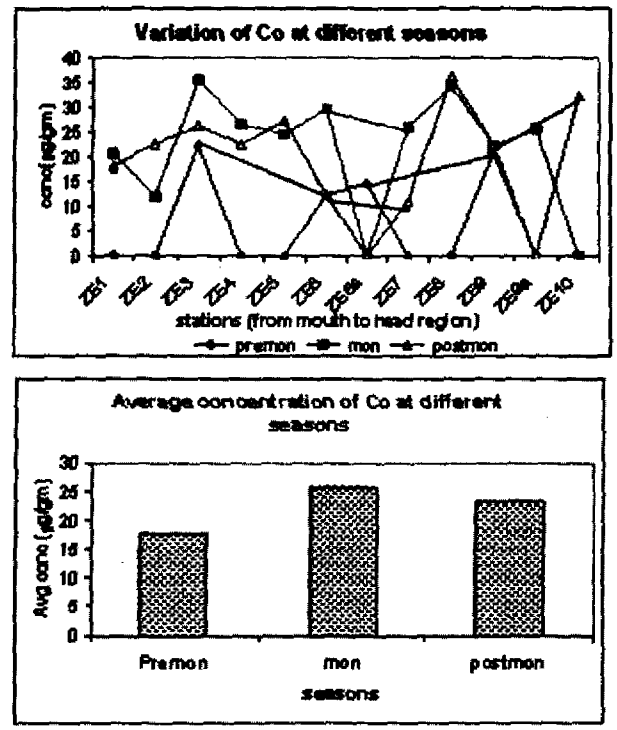


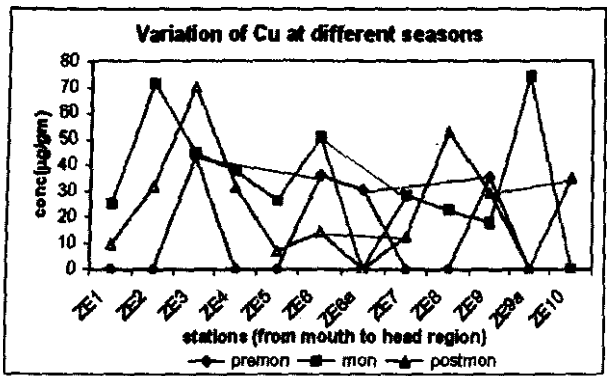
Figure 2c: Seasonal variation of Cobalt in sediment of Zuari River of Goa, West coast of India

Vamsadhara estuary (Devavarma *et al.*, 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan *et al.*, 1988), Vellar estuary (Mohan, 1995), Narmada (Subramanian *et al.*, 1985), Tapti (Subramanian, 1985) and Indian river average (Subramanian *et al.*, 1985). However, the ranges and average values of cobalt observed in the present broadly agree with those reported earlier from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979).

Seasonal variation of cobalt is found highest during monsoon period followed by post-monsoon and pre-monsoon (Fig 2e). The higher concentration of cobalt during monsoon period may be attributed to the land runoff and influx of metal rich fresh water. Similarly highest concentration of cobalt during monsoon season has been reported from Godavari estuary (Srinivas, 1998).

Copper

Concentration of copper ($\mu g\ g^{-1}$) varied from 30.67 to 43.33 during pre-monsoon, from 18.0 to 74.0 during monsoon and from 7.0 to 70.0 during post-monsoon. The ranges and averages values of copper obtained in the present study broadly agree with those reported earlier from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988), Vamsadhara estuary (Devavarma *et al.*, 1993 and 1991), Cauvery estuary (Ramanathan et al., 1988), Vellar estuary (Mohan, 1995), Indian river average (Subramanian *et al.*,



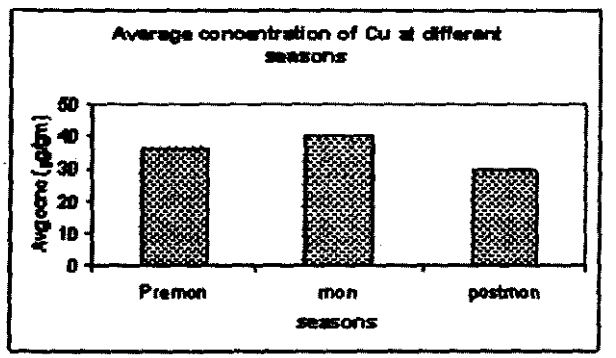
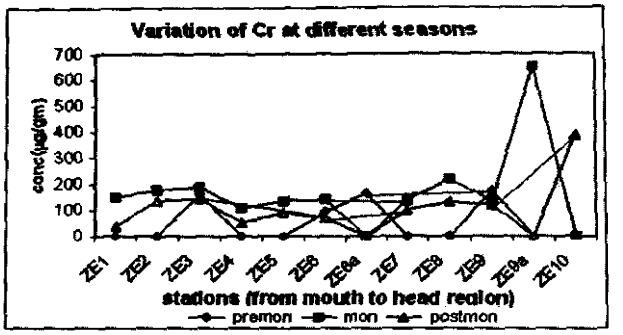


Figure 2c: Seasonal variation of Copper in sediment of Zuari River of Goa, West coast of India



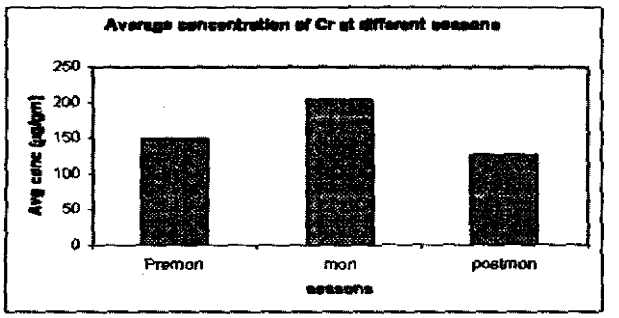


Figure 2c: Seasonal variation of Chromium in sediment of Zuari River of Goa, West coast of India

1985), Surficial Rocks (Martin and Maybeck, 1979). However, they are found to be lower when compared with those of Godavari estuary (Srinivas, 1998), Krishna estuary (Krishna Rao and Swamy, 1991) and World river average (Martin and Maybeck, 1979).

Seasonal variation of copper showed maximum values during monsoon followed by pre-monsoon and post-monsoon seasons (Fig 2f). This slight increase in the concentrations of copper in the sediments during the monsoon period may be due to downstream transport along with the monsoonal discharge. Settling of trace metals at the area of confluence between river and seawater could lead to such effects. Senthilnathan and Balasubramanian (1999) also reported higher concentration of copper in sediments from Pondicherry harbour during monsoon and lower in summer. This was attributed to land runoff and influx of metal rich water. Similarly, higher concentrations of copper in sediments were reported from Godavari estuary during monsoon season (Srinivas, 1998).

Chromium

The concentrations of chromium ($\mu g\ g^{-1}$) in different seasons varied from 93.33 to 175.33 during pre-monsoon, from 107.67 to 653.0 during monsoon and from 39.33 to 388.0 during post-monsoon. The ranges and averages values of chromium in the present study (Table 2) are slightly higher when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma et *al.*, 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan et *al.*, 1988), Vellar estuary (Mohan, 1995), Narmada (Subramanian *et al.*, 1985), Tapti (Subramanian, 1985), Indian river average (Subramanian et al., 1985), World river average (Martin and Maybeck, 1979) and Surficial Rocks (Martin and Maybeck, 1979). But, the range is found to be in broad agreement when compared with the earlier values reported from Mandovi estuary (Bukhari, 1994).

Seasonal variation in the concentrarions of chromium registered highest values during the monsoon period followed by those in pre-monsoon and post-monsoon (Fig 2g). High concentrations observed during monsoon can be attributed to the land runoff and influx of metal rich fresh water. The increased particulate matter along with suspended sediment load brought in by the river would also be a possible reason for the abnormally higher values during monsoon (Senthilnathan and Balasubramanian, 1997). Similarly, Srinivas (1998) reported higher concentrations of chromium in sediments from Godavari estuary during monsoon season.

CONCLUSION

The range and average values obtained from the estuarine region of Zuari river for the trace metals in sediments are in broad agreement with those in other Indian estuarine and coastal sediments. In general, seasonal variation of all metals except for iron and cadmium showed higher

concentrations during monsoon followed by those in pre-monsoon and post-monsoon. High concentrations of metals during monsoon can be attributed to the large land runoff, the suspended matter from the catchment areas along with the runoffs from mining areas. The increased particulate along with suspended sediment load brought in by river would be the possible reason for the abnormally higher values during monsoon. Relatively higher concentration of iron during post-monsoon and monsoon compared to premonsoon can be attributed to the increased river runoff and the associated high organic carbon content along with above factors.

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