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Seasonal variation of some trace metals in the sediments of the Mandovi River of Goa, India

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Abstract

The bottom sediment samples were collected from the ten sampling stations located along the Mandovi 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.

Keywords: *Mandovi, sediment, Trace metals, Pre-monsoon, Monsoon, Post-monsoon.*

1. Introduction

Trace metals are persistent contaminants: once added to the environment they are not readily converted into something harmless. They are often accumulated in the tissue of the organisms, which, having taken them up, cannot excrete them, and this leads to an amplification of the concentration of them in animals higher up the food chain. Man, as a carnivore at the top of many food chains, therefore is exposed to the risk of taking a diet enriched by these substances, and several metals are accumulative poisons, causing among other things brain damage at low dose rates and death at high.

Sediment is ultimately the depository of many chemical compounds including trace metals from natural and anthropogenic sources. Sediment acts as an indicator of the burden of heavy metals in the aquatic environment as they are the principal reservoir for heavy metals (Fitchiko and Hutchinson, 1975) In the present investigation an humble attempt has been made to study the seasonal variation of some trace metals in the sediments collected from the estuarine regions of Mandovi river of Goa.

STUDY AREA: The Mandovi river originates from the Parwa ghat of the Karnataka part of the Sahyadri Hills and after transversing a stretch of about 70 kms joins the Arabian Sea through the Aguada bay near Panaji. Its width at the mouth of the estuary is 3.2 kms while in upstream it narrows down to 0.25 km. It is fed by monsoon precipitation, and discharges from a catchment area of about 1150 km^2 of which 435 km^2 are forest land. Its basins cover an area of about 1530 km^2 and constitute 42 % of the total land area of Goa. Its post-monsoon and pre-monsoon flow is mainly dominated by the semi diurnal tides having a maximum range of 2.3 m. It has a large tributary system and has a number of islands, sharp turns and shallow depths along its course.

There are total of 108 industries along its banks which discharge 8×10^5 m^3 of effluents per year into the river and its tributaries. About 2/3 of the total mining activities in Goa are located along the Mandovi basin. There are 27 large mines which generate about 1500-6000 tonnes of rejects per day per mine a substantial portion of which can be expected to be dumped into the river (NIO, 1979).

2. Materials and Methods

The area of investigation covers the Mandovi river in Goa (west coast of India). It comprises of ten sampling stations. The stations were named (from mouth to head) ME1, ME2, ME3, ME4, ME5, ME6, ME7, ME8, ME9 and ME10 (extra stations, ME3a, ME9a, ME9b).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. The trace metals from the sediments samples were analysed using Atomic Absorption Spectrophotometer (AAS- Australian Model-GBC 902).

3. Results and Discussion

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

The concentration of zinc ($mg\,g^{-1}$) in sediments varied from 31.67 to 108.0 during pre-monsoon, from 45.33 to 149.67 during monsoon and from 25.0 to 137.33 during post-monsoon. The range and average values of zinc in sediments in the present study is slightly higher when compared with those reported earlier from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988). Seasonal variation of zinc registered highest concentrations during the monsoon followed by pre-monsoon and post-monsoon seasons. High concentrations of zinc during monsoon is 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 (Burton1976). Similar observations were made by Srinivas (1998) in Godavari estuarine sediments and Pondicherry harbour by Senthilnathan and Balasubramanian (1999).

Concentration of iron (%) in different seasons varied from 2.03 to 10.67 during pre-monsoon, from 2.91 to 12.8 during monsoon and from 2.36 to 12.08 during post-monsoon. The range and average values of iron in the present study is slightly higher when compared with those reported earlier from Mandovi estuary (Bukhari, 1994), Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma *et al.,* 1993 & 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 *et al.,*1985). However comparable values were recorded from Zuari estuary (Singh, Khelchandra *et al*, 2009a). Seasonal variation of iron in sediments registered higher values during post-monsoon and monsoon seasons followed by pre-monsoon. Relatively higher concentration during post-monsoon can be attributed to higher organic matter reported from the same estuary (Singh, Khelchandra *et al.*, 2009b). 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, 1997). 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.Spatial distribution of iron increases from mouth to head regions. The decrease in concentration of iron in a seaward direction indicating its terrigenous origin.Further, the loss of metal from the sediment due to solubilization. Such solubilization may come about by the breakdown of organic matter in the estuarine sediments, leading to the formation of soluble organo-metallic complexes in which are released to the estuarine waters (De Groot, 1973). Highest concentration of 10.67%, 12.83% and 12.07% were observed at the sampling stations of ME8, ME7 and ME7 during pre-monsooon, monsson and post-monsoon respectively. All these stations are located in the upstream region of the river.

Concentration of manganese (%) in sediments varied from 0.125 to 0.695 during pre-monsoon, 0.07 to 6.079 during monsoon and from 0.062 to 0.797 during post-monsoon. In general, the ranges and averages of manganese concentrations in the present study broadly agree with those reported from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988), Zuari estuary (Singh, Khelchandra *et al.*, 2009a). But, it revealed slightly higher concentrations when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma *et al.*, 1993 & 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), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979). 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 monsoon period followed by pre-monsoon and post-monsoon. Higher concentration during monsoon season could be due land runoff and influx of metal rich fresh water. About two-thirds of the mining activities in Goa are located located the Mandovi basin. These activities, generates mining rejects and substantial portion of which aredumped into the river. Similarly high concentration of manganese was reported during monsoon and post-monsoon season from Tuticorin coast (Ganesan and Kannan, 1995). Spatial variation of manganese in sediments showed an increasing trend from mouth to head. Highest concentration of 0.695, 6.079 and 0.798 were observed at stations ME8, ME9a and ME10 during pre-monsoon, monsoon and post-monsoon seasons respectively. All these stations are located in the mining areas (i.e in the head region of the estuary). Abnormally high values observed during the monsoon season may be due to spillage of ores during loading along with runoff from mines near the station.

Concentration of cadmium (mg g^{-1}) in different seasons in sediments varied from 0.67 to 2.67 during pre-monsoon, from 0.33 to 3.33 during monsoon and from 0.33 to 4.3 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). However the values are comparable with those reported ealier from Zuari estuary (Singh, Khelchandra *et al*, 2009a). Seasonal variation of cadmium is found to be highest during post-monsoon period followed by pre-monsoon and monsoon. 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, Khelchandra *et al*, 2009b). Spatial distribution of cadmium in sediments showed slightly increasing trend from head to mouth region.

Table 1. **Data on seasonal variation of trace metals in sediments of the Mandovi River of Goa, West Coast of India.**

Station	Pre-Monsoon ($\mu g\ g^{-1}$)						
	Zn	Fe (%)	Mn (%)	Cd	Co	Cu	Cr
ME1	NA	NA	NA	NA	NA	NA	NA
ME2	107.667	3.308	0.303	2.667	3.333	80.667	194.333
ME3	84.333	3.898	0.331	1.670	9.333	27.000	279.333
ME3a	NA	NA	NA	NA	NA	NA	NA
ME4	NA	NA	NA	NA	NA	NA	NA
ME5	NA	NA	NA	NA	NA	NA	NA
ME6	31.667	2.030	0.125	2.300	18.670	3.667	96.667
ME7	NA	NA	NA	NA	NA	NA	NA
ME8	101.000	10.674	0.695	0.670	24.000	38.000	173.667
ME9	NA	NA	NA	NA	NA	NA	NA
ME9a	NA	NA	NA	NA	NA	NA	NA
ME9b	NA	NA	NA	NA	NA	NA	NA
ME10	108.000	9.969	0.433	1.000	17.330	46.000	234.667
AVG	86.533	6.376	0.381	1.661	14.533	39.067	195.733
RANGE	31.67 - 108	2.03 - 10.67	0.125 - 0.695	0.67- 2.67	3.33 - 24	3.67 - 80.67	96.67 - 279.53

Station	Monsoon ($\mu g\ g^{-1}$)						
	Zn	Fe (%)	Mn (%)	Cd	Co	Cu	Cr
ME1	74.667	4.920	0.070	2.300	9.330	35.667	174.333
ME2	45.333	2.905	0.121	1.000	18.330	29.000	151.000
ME3	88.667	4.078	0.258	3.300	19.000	32.333	309.667
ME3a	149.667	6.340	0.233	ND	16.670	32.667	403.000
ME4	64.333	6.293	0.858	2.300	19.330	31.333	324.667
ME5	84.333	8.074	0.197	ND	17.000	31.667	398.333
ME6	117.667	12.298	0.159	ND	12.667	73.000	169.667
ME7	78.000	12.839	0.299	ND	8.000	32.000	366.667
ME8	92.333	10.746	0.984	0.670	15.000	43.333	238.667
ME9	47.000	7.888	0.132	1.670	15.670	28.657	326.000
ME9a	104.333	7.886		0.330	32.000	41.000	301.333
ME9b	140.333	10.693	1.134	0.670	21.667	58.333	198.667
ME10	NA	NA	NA	NA	NA	NA	NA
AVG	90.556	7.914	0.407	1.020	17.139	39.083	280.167
RANGE	45.33 - 149.67	2.905 - 42.8	0.07 - 6.08	ND - 3.33	8 - 32	28.67 - 73	151 - 403

Station	Post-Monsoon ($\mu g\ g^{-1}$)						
	Zn	Fe (%)	Mn (%)	Cd	Co	Cu	Cr
ME1	127.333	7.983	0.062	3.667	5.667	51.333	
ME2	25.000	2.356	0.092	1.333	10.670	17.333	68.000
ME3	95.667	8.697	0.271	4.300	12.330	23.000	299.333
ME3a	NA	NA	NA	NA	NA	NA	NA
ME4	78.333	9.071	0.569	3.000	8.333	31.000	326.000
ME5	102.000	9.500	0.459	1.670	14.330	24.667	345.667
ME6	66.000	7.655	0.239	0.333	20.670	17.000	364.000
ME7	82.000	12.075	0.350	0.333	17.330	41.667	307.667
ME8	62.000	7.547	0.625	1.333	17.000	25.667	383.333
ME9	76.333	9.762	0.155	0.333	15.330	33.000	338.000
ME9a	NA	NA	NA	NA	NA	NA	NA
ME9b	NA	NA	NA	NA	NA	NA	NA
ME10	137.333	12.073	0.796	0.667	18.670	67.667	171.000
AVG	85.200	8.672	0.362	1.697	14.033	33.433	280.067
RANGE	25 - 137.33	2.36 - 12.58	0.062 - 0.79	0.33 - 4.3	5.6 - 20.67	17 - 67.67	68 - 383.33

KEYS	DESCRIPTION
ME	Mandovi Estuary
N.D.	Non-Detectable
N.A.	Not Analysed

Concentration of cobalt (mg g^{-1}) varied from 3.33 to 24.0 during pre-monsoon , from 8.0 to 32.0 during monsoon and from 5.6 to 20.67 during post-monsoon. The ranges and averages values of cobalt in sediments in the present study is slightly lower when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma *et al.*, 1993 & 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 *et al* ., 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), Zuari estuary (Singh, Khelchandra, 2000), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979). Seasonal variation of cobalt is found highest during monsoon period compared to post-monsoon and pre-monsoon. 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).Spatial distribution of cobalt in sediments showed an irregular trend from mouth to head region. However, highest concentration of 32.0 is recorded from head region during monsoon season in Mandovi estuary.

Concentration of copper (mg g^{-1}) varied from 3.67 to 80.67 during pre-monsoon, from 28.67 to 73.0 during monsoon and from 17.0 to 67.67 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), Zuari estuary (Singh, Khelchandra *et al*, 2009a), Vamsadhara estuary (Devavarma *et al.*, 1993 & 1991), Cauvery estuary (Ramanathan *et al.*, 1988), Vellar estuary (Mohan, 1995), Indian river average (Subramanian *et al.*, 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 and pre-monsoon seasons. 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 was reported from Godavari estuary during monsoon season (Srinivas, 1998).

The concentrations of chromium (mg g^{-1}) in different seasons varied from 96.67 to 279.33 during pre-monsoon, from 151.0 to 403.0 during monsoon and from 68.0 to 383.33 during post-monsoon. The ranges and averages values of chromium in the present study are slightly higher when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma *et al.*, 1993 & 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan *et al.*, 1988), Vellar estuary (Mohan, 1995), Narmada (Subramanian *et al.*, 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). The highest concentration of chromium is observed during monsoon and postmonsoon seasons. 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. Spatial distribution of chromium in sediments showed an irregular trend from mouth to head region. However, highest concentration during pre-monsoon and monsoon seasons were recorded from the mouth region.

4. Conclusions

The range and average values obtained from the estuarine region of Mandovi 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 pre-monsoon can be attributed to the increased river runoff and the associated high organic carbon content along with above factors.This is also supported, though not significant by a positive correlation between cadmium and organic carbon content during post-monsoon season (Singh, Khelchandra *et al*, 2009b). Spatial variation of trace metals in sediments observed no significant trend from mouth to head region in the present study. However, iron and manganese showed slightly increasing trend from mouth to head region. This is believed to be due to the terrigenous origin of metals. Highest concentration in all seasons is recorded from the stations located in the mining areas (i.e. upstream region). Loading of ores is also done in this region. This indicates the inputs of these metals from mining activities.

5. References

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