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ASSESSMENT OF THE CONCENTRATION OF TRACE METALS IN WATER, SEDIMENT AND ZOOPLANKTON OF RUSHIKULYA ESTUARY, ODISHA.

***Sasmita Rath*[1*], *R.C.Panigrahy*[2]**

In the present research the concentration of Cu,Zn,Pb,Cd and Hg were determined in water, sediment and Zooplankton of Rushikulya Estuary,Odisha. Water, sediment and zooplankton samples were collected seasonally premonsoon, monsoon and post monsoon from four fixed stations of this Estuary as it receives contaminated effluents from Chloro-alkali plant (M/S. Jayashree Chemicals Pvt. Ltd.) and residual agrochemicals from its catchment area. In water samples low Cu contents were encountered during the pre-monsoon season and high content found in the monsoon period. Zn, Pb and Cd content were found to be higher in monsoon season than the premonsoon and postmonsoon seasons which could be ascribed to their entry through the surface ranoff. High concentration of Hg was obtained during pre-monsoon season than other seasons due to inputs through the effluents discharged from the nearby Chloro-alkali plant. The positive correlation (p= 0.01) between different metals except Hg denoted their common sources of origin and co-existence. In the sediment sample the season wise pooled data showed that higher concentrations of Cu , Zn, Pb and Cd were found in the monsoon season than premonsoon and postmonsoon season. Higher Hg content was found in premonsoon as compared to monsoon and post monsoon . A strong positive correlation (p = 0.01) was observed between different metals denoting their co existence. But the relationship of Hg with other metals remained inverse. In the Zooplankton sample ,the higher concentrations of Cu , Zn, Pb, Cd and Hg were found in premonsoon season than monsoon and post monsoon season. This was also referred to their accumulation by surface adsorption and ingestion of phytoplankton.

Keywords: *Rushikulya Estuary, Zooplankton, Correlation, Concentration*

INTRODUCTION

The Rushikulya estuary is a shallow tidal estuary situated between Lat 19°22' -19°24' N and Long 85°02'-85°05' E along the South Orissa Coast which opens into the Bay of Bengal near Ganjam, Orissa. It is situated about 20km away towards the north of Gopalpur. This estuary

1. Department of Marine Sciences, Berhampur University, Odisha

2. Department of Marine Science, Berhampur University, Odisha

* Corresponding author: Department of Marine Sciences, Berhampur University, Berhampur, 760007, Odisha . Email: sasmitarath33@gmail.com

remains well mixed during most parts of the year. Since the estuary is fed mainly by a seasonal river, freshwater influx occurs mainly during monsoon and postmonsoon seasons, from July – Nov/Dec. During the peak monsoon period between August – September, the entire bulk of sea water is scrolled out into the sea due to the massive ingress of surface runoff. The inflow of fresh water recedes gradually from November and hardly any riverine input is seen during March - May. Hence marine dominance prevails during the premonsoon period, while total limnetic condition occurred during monsoon period. November to February stands as the salinity recovery period for this estuary. The estuarine sediments are sand dominated both near the mouth as well as in its upper reaches. But the deeper gradient zone the floor has muddy sediments containing silt & clay in different proportions. The geomorphology of the estuary has undergone many visible changes over the years due to change of the mouth position from time to time (Gouda and Panigrahy, 1993). The estuary constitutes one of the important fishing grounds along this coast. About 16, 00 fisher folk families obtain their livelihood through fishing in and around it. This estuary constitutes one of the potential grounds for collection of penaeid prawn seeds used in brackish water farming.The estuary was in receipt Hg contaminated effluents from a Chloro-alkali plant (M/S. Jayashree Chemicals Pvt. Ltd.) and residual agrochemicals from its catchment area. Hg pollution of the estuary has been studied, rather quite elaborately in the past (Gouda and Panigrahy, 1989., 1991; 1995a 1995b, Choudhury, 1980; Shaw *et al.*,1986, 1988; Sahu & Panda, 1987). However very meager information is available on the metal pollution (Pradhan,1999). Hence it was considered proper to include the Rushikulya estuary as one of the study areas of the present investigation..

2. MATERIALS METHODOLOGY

2.1 Study Area

The period of investigation covered three years from January 2009 to December 2011. Samplings were done in January, April, July and October of each year representing the winter, pre-monsoon, monsoon and post-monsoon seasons. During the study period water, sediment and zooplankton samples were collected from fixed stations. They are named as R-1,R-2,R-3,R-4 representing Rushikulya estuary as shown in (Figure-1) and geographic Positions of the Sampling Stations in Table- 1.

Water is an essential requirement of human and industrial development and it is one of the most delicate parts of the environment. In the past few decades there has been a tremendous increase in the demand for fresh water, because most of the rivers all over the world have become dark due to discharge of sewage, oil, chemicals, industrial effluent and agricultural runoff with the passage of time. Organic and inorganic matter began to accumulate in the river, and the biological productivity of the rivers turned to increase. River Karanja is of particular importance in the study of surface water pollution because effluents from sugar, Distillery and pulp & Paper industries and runoff from agriculture are discharged into the reservoir bringing about considerable change in the water quality. These anthropogenic activities on the river karanja pose a serious threat not only to organisms in the reservoir but also the downstream water users.

(A) (B)

Figure-1 (The Map of the study area showing station locations: (A) Odisha coast. (B) Rushikulya estuary).

Table-1 Geographic Positions of the Sampling Stations.

Sl.no.	Stations	Latitude	Longitude
1	R1	19°22'8.45"N	85° 4'0.38"E
2	R2	19°22'22.66"N	85° 3'19.82"E
3	R3	19°22'45.31"N	85° 2'36.00"E
4	R4	19°23'26.22"N	85° 2'4.66"E

2.2 Sample Collection and Analysis

Surface water samples were collected using a precleaned plastic bucket from each station. Samples meant for heavy metal analysis were transported in precleaned polythene bottles and stored for further analysis. Sediment samples were collected with a Peterson's grab sampler. Sediment samples were transferred to precleaned polythene bags and were brought to the laboratory for further analysis. For collection of zooplankton, a conical plankton net with mouth area 0.196 m^2 and mess size 0.33mm was hauled near the surface for about 10-15 minutes. The zooplankton residues retained in the plankton cylinder were transferred into a polythene bottle and were brought to the laboratory for subsequent analysis. For the purpose of heavy metal analysis the water samples were processed in two separate sets, one set for estimation of Hg and another set for other heavy metals. A procedure recommended by Brooks *et al* (1967) was adopted. It is completed in two phases i.e. pre concentration of the samples with APDC-MIBK extraction and then quantitative measurement by Atomic Absorption Spectrophotometry. Calibration curves were prepared by plotting the adsorption against concentration of the working solution of each element. Metal concentrations in the samples were calculated with the help of these calibration curves. The values are expressed as µg/l. About 100g of sediment sample was washed thoroughly with double distilled water for removal of salts and digested with a mixture of 1ml concentrated H_2SO_4, 5 ml concentrated HNO_3 and 2ml of concentrated $HClO_4$. A few drops of HF (Hydrofluoric acid) were added in order to achieve complete dissolution of the metals. The mixture was boiled, evaporated to near dryness and then re suspended in 10ml of 2N HC1. This was passed through a paper filter and made up to 25ml with metal free double distilled water. The resulting solution was then aspirated to a

flame Atomic Absorption spectrophotometer (AA7000) for the determination of Cu, Zn, Pb , Cd & Hg. The values are presented as µg/g. The bulk Zooplankton samples were cleaned with double distilled water (MBD milipore, USA) and oven dried until a constant weight was obtained. Each sample was grounded and dried out. Exactly 0.5gm of sample was taken and digested For mercury determination, the digestion of samples were made as per the procedure given in the Electronic Corporation of India Limited (ECIL) manual and Romes & Nicholas (1986). The values are presented as ng/g.

3. RESULT AND DISCUSSION

3.1 Heavy metal in surface water

The season wise pooled data (Figure -2,Table-2) of the Rushikulya estuary showed concentration of Cu ranged from 9.45 to 13.73µg/l (average12.13 ± 1.31µg/l) during premonsoon season 27.6 to 33.5µg/l (average30.15 ±1.91µg/l) in monsoon and 13.5 to 15.84µg/l (average 15.1 ± 0.78µg/l) in post monsoon season (Table-2).The Low Cu contents were encountered during the pre-monsoon season and high content found in monsoon period. The low Cu in premonsoon season is ascribable to its removal by phytoplankton, the high Cu content in monsoon season substitutes its addition through freshwater influx. During pre-monsoon seasons the hydrographic conditions were relatively stable, and phytoplankton production was reported to be high (Panigrahy and Gouda, 1990; Choudhury and Panigrahy, 1989; Choudhury, 1991; Gouda, 1992). Hence phytoplankton uptake of Cu coupled with adsorped onto the particulates could be the major source of Cu depletion from the medium.water in this environment. Seasonal variations of Zn concentration also showed marked variations in the whole of the study area. The range and mean with standard deviation of metals in the surface waters of Rushi-kulya estuary. The concentrations of Zn varied from 7.15 to 8.6 µg/l (average8.02 ± 0.44µg/l), 15.7 to 17.61µg/ l (average16.82 ± 0.61µg/l) and 9.25 to 11.5 µg/l (average10.51 ± 0.7 µg/l) in premonsoon, monsoon and post monsoon seasons respectively. Its content was found to be higher in the monsoon season than the premonsoon and postmonsoon seasons. This could be due to addition of Zn through surface runoff in the monsoon period. Similar conditions of high concentration of Zn during monsoon season reported in Visakhapatnam harbour (Subramanium and Ananta Laxmi Kumari, 1990) , Vellar estuary (Kanan *et al.* 1992), waters of Ennore and Adyar estuaries of Madras (Joseph and Srivastava .1993) , Aryankuppam estuary in pondichery (G.Ananthan *et al.,*2005) . Zn concentrations during the pre- and post-monsoon periods remained identical in the coastal waters, whereas relatively higher values were obtained during the post-monsoon season than the pre-monsoon season in estuaries. The fall of Zn during the post-monsoon period compared to monsoon period, could be attributed to its removal due to flocculation and precapitation mechanisms.The concentration of Pb in the premonsoon season fluctuated between 1.12-2.28µg/l (average 1.86 ± 0.38 µg/l), while in monsoon season it ranged from 4.12-6.62µg/l (average5.30 ± 0.85µg/l) and in postmonsoon season from 0.45-4.86µg/l (average3.59 ± 1.17 µg/l). High values are observed in monsoon season which could be ascribed to their entry through the surface runoff. The concentrations of Cd in the Rushikulya estuary water ranged from 0.7 to 1.24 µg/l with average value 1.00 ± 0.16 µg/l in premonsoon period while those in monsoon and postmonsoon season ranged from, 0.82 to 1.42 µg/l with an average value of 1.10 ± 0.18 µg/l and 0.76 to 1.28 µg/l with an average value of 1.01 ± 0.16 µg/l.

During monsoon season comparatively higher values were observed than other season and it could be because of same reason as described above and the Hg content ranged from 5.12 to 6.92µg/l an average of 5.80 ± 0.59 in premonsoon, while those in the monsoon season values ranged from 0.2 to 0.9µg/l with an average value of 0.63 ± 0.21µg/l and in post monsoon season it's values varied from 0.2 to 1.4µg/l with average 0.60 ± 0.39µg/l. Seasonal comparision however, exhibited their. while Pb and Cd contents were found to be more than Hg during the monsoon and post-monsoon periods as noticed during other seasons. The high levels of Pb & Cd during monsoon seasons followed by the post-monsoon and pre-monsoon periods in order suggest that the addition of Pb and Cd occur mainly through surface runoff. The high concentration of Hg during pre-monsoon season in Rushikulya estuary could be due to its input through the effluents discharged from the nearby Chloro-alkali plant. Similar patterns of Hg distribution in this system were also observed by Shaw *et al.,*(1986) and Gouda and Panigrahy (1995) A simple correlation analysis test was performed to understand the interrelationship between different trace metals in the study area. The results of the correlation analysis are presented in (Table -3) .The inter relationship indicated the co-existance of Cu, Zn and Hg in Rushikulya estuary. In this environment the Hg exhibited negative correlation with Zn. The positive correlation (*p*d" 0.01) between different metals except Hg denoted their common sources of origin and co-existence (Table-3)

Table -2 The seasonal variations of heavy metals in surface water (range, mean & SD) of Rushikulya estuary

WATER	Rushikulya Estuary					
	Premonsoon		**monsoon**		**postmon**	
Parameter	min -max, avg ± sd		min -max, avg ± sd		min -max, avg ± sd	
Cu	9.45-13.73	12.13 ± 1.31	27.6-33.5	30.15 ± 1.91	13.5-15.84	15.1 ± 0.78
Zn	7.15-8.6	8.02 ± 0.44	15.7-17.61	16.82 ± 0.61	9.25-11.5	10.51 ± 0.7
Pb	1.12-2.28	1.86 ± 0.38	4.12-6.62	5.30 ± 0.85	0.45-4.86	3.59 ± 1.17
Cd	0.7-1.24	1.00 ± 0.16	0.82-1.42	1.10 ± 0.18	0.76-1.28	1.01 ± 0.16
Hg	5.12-6.92	5.80 ± 0.59	0.2-0.9	0.63 ± 0.21	0.2-1.4	0.60 ± 0.39

Table-3 Correlation matrix of heavy metals in Water.

	Cu	Zn	Pb	Cd	Hg
		Rushikulya Estuary			
Cu	1				
Zn	0.981***	1			
Pb	0.822***	0.830***	1		
Cd	0.277*	0.256*	0.303*	1	
Hg	0.594***	-0.699***	-0.741***	-0.181*	1

*=significant at 0.1 level
**=significant at 0.5 level
***= significant at 0.01 level

3.2 Metals in Sediments

In the season wise data (Figure-3,Table-4) of Rushikulya estuary,the concentration of Cu in sediments fluctuated between 62.25-73.87 µg/g (average 68.76 ± 3.93 µg/g) during premonsoon season, But in the monsoon season it ranged from 95.64-130.98 µg/g (average110.99 ± 10.53 µg/g) and in post monsoon season from 55.24-60.34 µg/g (average58.12 ± 2.02 µg/g). Season wise pooled data showed that higher concentration was found in the monsoon season than premonsoon and postmonsoon season in this environment. justifying in terrestrial sources of origin input through surface runoff.The contents of Zn inside the Rushikulya estuary sediments ranged from 20.24 to 22.37 µg/g with an average value of 21.60 ± 0.67 µg/g during the premonsoon season and from 84.45 to 96.75 µg/g with an average value of 92.40 ± 3.82 µg/g in monsoon season and 29.48 to 39.14 µg/g with an average value of 34.85 ± 2.91 µg/g in postmonsoon respectively. Higher concentration during monsoon than premonsoon and post monsoon season. Similar cases were found in the sediment of Adyar estuary and Ennore estuary.The order of concentration of metals were found to be Zn > Ni > Pb > Cu > Cr > Cd > Hg in Adyar estuary and Zn> Ni >Pb > Cr > Cu > Cd > Hg in Ennore estuary of Madras (Joseph and Srivastava,1993). The contents of Pb in the Rushikulya estuary sediment ranged from 24.22 to 28.36 µg/g with average value 26.37 ± 1.45 µg/g, 50.54 to 56.49 µg/g with an average value of 53.38 ± 1.93 µg/g and 26.38 to 33.65 µg/g with an average value of 31.37 ± 2.14 µg/g in premonsoon, monsoon and postmonsoon season respectively. From the season wise pooled data,high content of Pb values were found in the Monsoon season as compared to other seasons, justifying its terristerial origin and entry through surface runoff. The Cd contents of the Rushikulya estuary sediment ranged from 0.20 to 0.30 µg/g with an average value of 0.25 ± 0.03 µg/g, 0.52 to 0.67 µg/g with an average value of 0.60 ± 0.04 µg/g and 0.29 to 0.45 µg/g with an average value of 0.38 ± 0.05 µg/g relating to the premonsoon,monsoon and postmonsoon seasons respectively. Marked variations were observed with respect to the concentration gradient of Cd & Hg as well. season wise pooled data of Hg varied from 1.25 to 1.48 µg/g with an average value of 1.34 ± 0.07 µg/g in premonsoon season. However the values ranged from 0.10 to 0.22 µg/g with an average value of 0.16 ± 0.04 µg/g) in monsoon season and those in postmonsoon season varied from 0.65 to 1.09 µg/g with an average value of 0.83 ± 0.14 µg/g. The high values in Rushikulya could be due to its addition from the effluents of chloro-alkali plant. strong positive correlation (*p* d" 0.01) was observed between different metals denoting their co existence (Table-5). But the relationship of Hg with other metals was remained inverse .Several works has been done regarding the sediment pollution such as (Satyanarayan *et al.*, 1994; Balachadran ,2003 ; Alagarswamy, 2006 ;Singrare *et al.*,2010 ; venkatesh Raju *et al.* 2012;

Table- 4 The seasonal variations of different heavy metals in sediments (range, mean & SD) in Rushikulya estuary.

SEDIMENT	Rushikulya Estuary		
	premonsoon	**Monsoon**	**Postmonsoon**
Parameter	min -max, avg ± SD	min -max, avg ± SD	min -max, avg ± SD
Cu	62.25-73.87 68.76 ± 3.93	95.64-130.98 110.99 ± 10.53	55.24-60.34 58.12 ± 2.02
Zn	20.24-22.37 21.60 ± 0.67	84.45-96.75 92.40 ± 3.82	29.48-39.14 34.85 ± 2.91
Pb	24.22-28.36 26.37 ± 1.45	50.54-56.49 53.38 ± 1.93	26.38-33.65 31.37 ± 2.14
Cd	0.20-0.30 0.25 ± 0.03	0.52-0.67 0.60 ± 0.04	0.29-0.45 0.38 ± 0.05
Hg	1.25-1.48 1.34 ± 0.07	0.10-0.22 0.16 ± 0.04	0.65-1.09 0.83 ± 0.14

Table -5 . Correlation matrix of heavy metals in sediment

	Cu	*Zn*	*Pb*	*Cd*	*Hg*
	Rushikulya estuary				
Cu	1				
Zn	0.913***	1			
Pb	0.902***	0.987***	1		
Cd	0.823***	0.958***	0.949***	1	
Hg	-0.740***	-0.937***	-0.929***	-0.904***	1

*=significant at 0.1 level
**=significant at 0.5 level
***= significant at 0.01 level

3.3 Metals in zooplankton

The contents of Cu in the zooplankton samples of the Rushikulya estuary ranged from 82.68 to 89.77 µg/g yielding average value 87.81 ± 2.19 µg/g in premonsoon season, 33.31 to 63.43 µg/g with an average value of 48.90 ± 10.41 µg/g in monsoon season and 75.68 to 78.84 µg/g with an average value of 77.31 ± 1.23 µg/g in postmonsoon season respectively. The higher concentration of Cu was found in premonsoon period .Seasonally pooled data (Figure-4 Table—6) showed that the contents of Zn in zooplankton of the Rushikulya estuary ranged from177.82 to 188.37 µg/g with average value 183.59 ± 4.14 µg/g in premonsoon season, 84.06 to 93.95 µg/g with an average value of 87.68 ± 4.60 µg/g in monsoon season, From 102.28 to114.42 µg/g with an average value of 106.93 ± 5.57 µg/g in postmonsoon season. The higher concentrationof Zn was found in premonsoon period like Cu.The contents of Pb in the zooplankton of Rushikulya estuary ranged from 12.65 to 14.72 µg/g with an average value 13.82 ± 0.82 µg/g in premonsoon season, while it varied 8.74 to 8.97 µg/g yielding average value of 8.85 ± 0.08 µg/g in monsoon season and 9.66 to 13.42 µg/g with an average

value of 11.53 ± 1.59 µg/g in postmonsoon season. the values are high in Premonsoon period, than other seasons. The contents of Cd inside the zooplankton sample of Rushikulya estuary ranged from 11.45 to 14.87 µg/g with average value 13.44 ± 1.43 µg/g in premonsoon season , 6.24 to7.35 µg/g with an average value of 6.73 ± 0.31 µg/g in moosoonseason and 5.86 to 8.91 µg/g yielding average value of 7.85 ± 1.44 µg/g in postmonsoon season. it showed the same result as the described parameters. Seasonwise pooled data (Table-6) of Hg in the zooplankton of Rushikulya estuary exhibited marked variations .It ranged from 4173.18-5989.00 ng/g an average of 5112.93 ± 769.55 ng/g in premonsoon. However the values ranged from 1755.30 to 2251.12 ng/g with average value 1987.40 ± 212.07 ng/g in Monsoon season and, Its concentration varied from 3440.00 to 4682.00 ng/g with average 4046.70 ±529.07 ng/g in Postmonsoon season . Higher concentration in premonsoon were also seen here. This was also referred to their accumulation by surface adsorption and ingestion of phytoplankton. Again the Zooplankton standing crops were both qualitatively as well as quantitatively richer during the pre-monsoon season than remaining parts of the year (Gouda and Panigrahy, 1995; Mishra, 1995; Choudhury, 1991)

Table-6 Seasonal variations of heavy metals in zooplankton (range, mean & SD) in Rushikulya estuary

Zooplankton	**Rushikulya Estuary**		
	Premonsoon	Monsoon	Postmonsoon
	Min-MaxAvg ± SD	Min-MaxAvg ± SD	Min-MaxAvg ± SD
Cu	82.68-89.7787.81 ± 2.19	33.31-63.4348.90 ± 10.41	75.68-78.8477.31 ± 1.23
Zn	177.82-188.37183.59 ± 4.14	84.06-93.9587.68 ± 4.60	102.28-114.42106.93 ± 5.57
Pb	12.65-14.7213.82 ± 0.82	8.74-8.978.85 ± 0.08	9.66-13.4211.53 ± 1.59
Cd	11.45-14.8713.44 ± 1.43	6.24-7.356.73 ± 0.31	5.86-8.917.85 ± 1.44
Hg	4173.18-5989.005112.93 ± 769.55	1755.30-2251.121987.40 ± 212.07	3440.00-4682.004046.70 ± 529.07

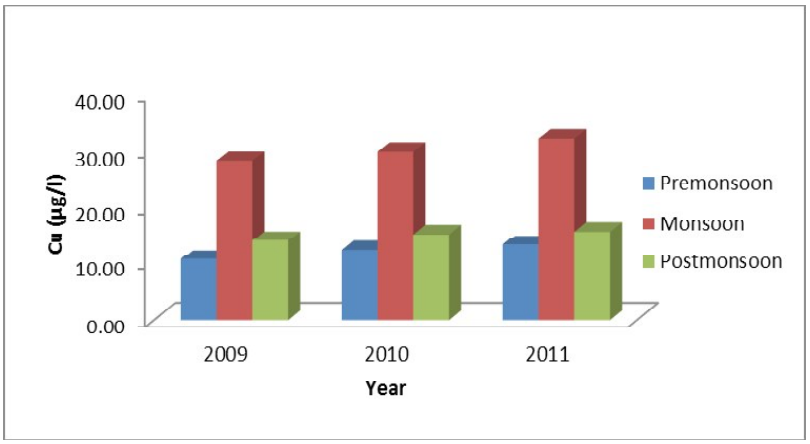
Table -7 Correlation matrix of heavy metal in Zooplankton

	Cu	Zn	Pb	Cd	Hg
	Rushikulya Estuary				
Cu	1				
Zn	0.979***	1			
Pb	0.744***	0.816***	1		
Cd	0.863***	0.922***	0.905***	1	
Hg	0.702***	0.775***	0.848***	0.710***	1

*=significant at 0.1 level
**=significant at 0.5 level
***= significant at 0.01 level

4. CONCLUSION

This study reported the contents of trace metals Cu, Zn, Pb, Cd &Hg in water, sediment and zooplankton of Rushikulya estuary and their variations in premonsoon, monsoon and post monsoon with relation to the environment. The concentrations of metals obtained were compared with the values of other researchers. The results of the present study shows that although the trace metal concentration in water, sediment and zooplankton is not alarming from pollution point of view, their health risk due to trophic transfer to fish and shellfish cannot be ruled out.


40.00
30.00
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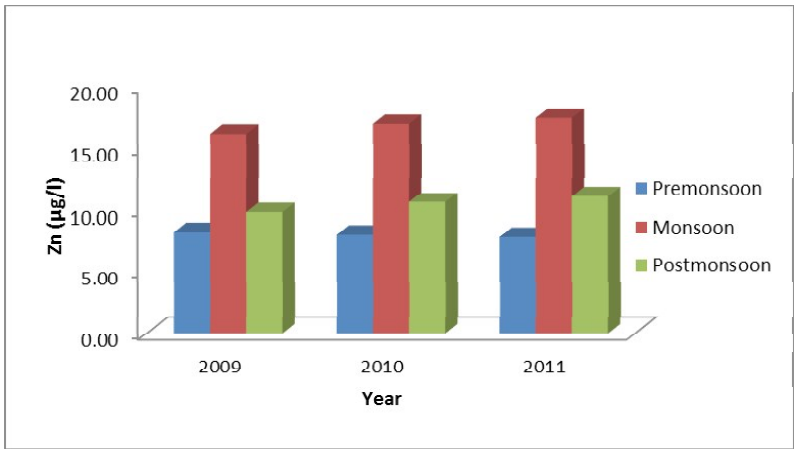
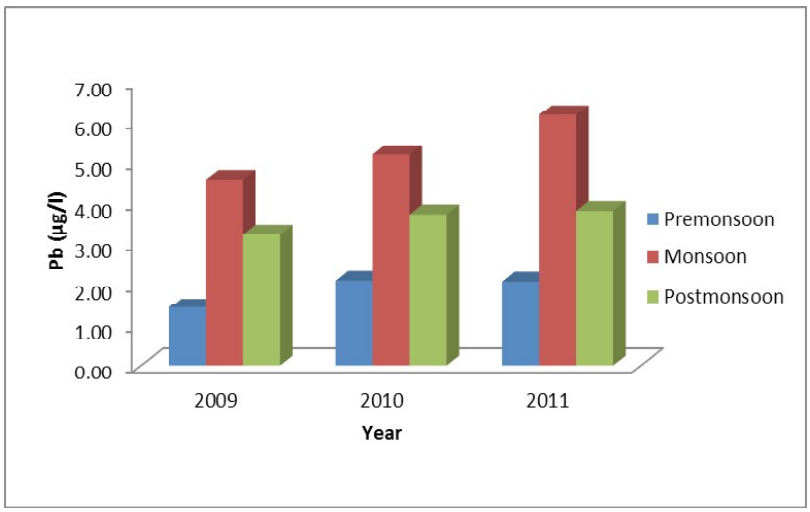
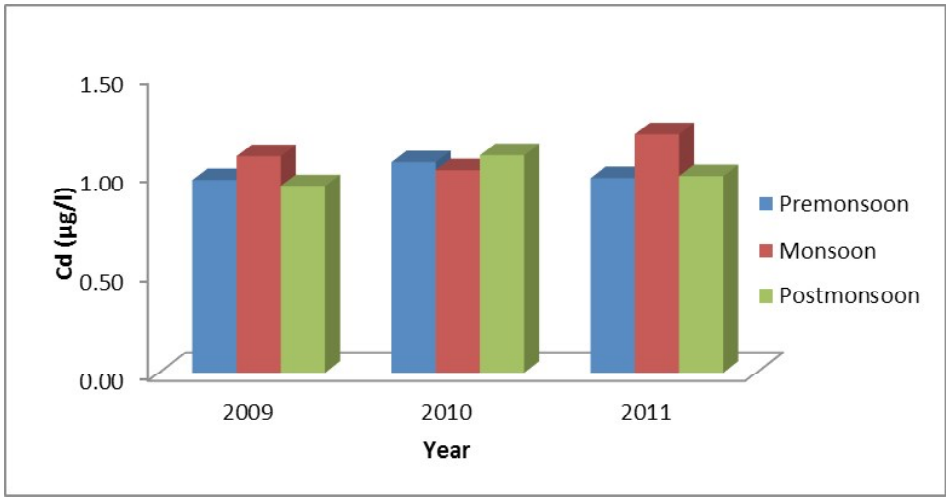
Cu (µg/l)
2009
2010
2011
Year
Premonsoon
Monsoon
Postmonsoon


20.00
15.00
10.00
5.00
0.00
Zn (µg/l)
2009
2010
2011
Year
Premonsoon
Monsoon
Postmonsoon


7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Pb (µg/l)
2009
2010
2011
Year
Premonsoon
Monsoon
Postmonsoon



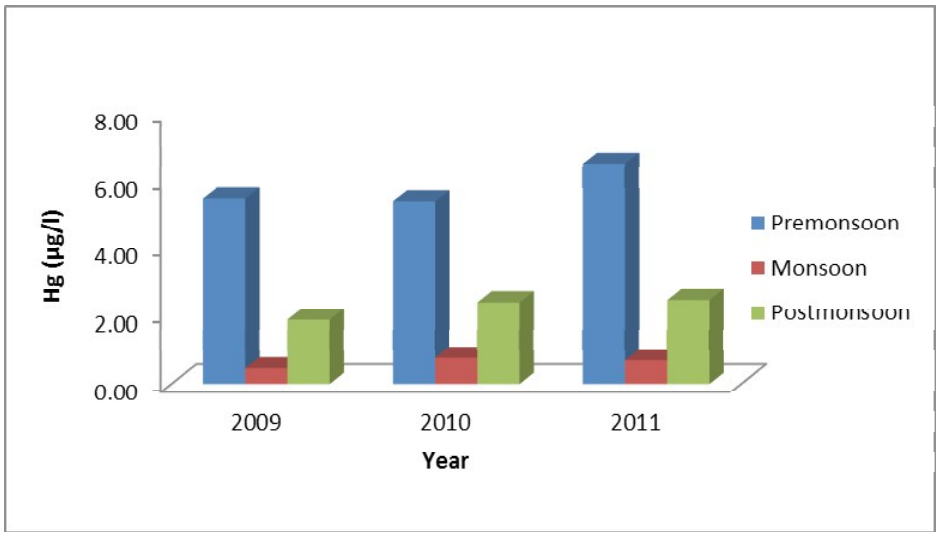
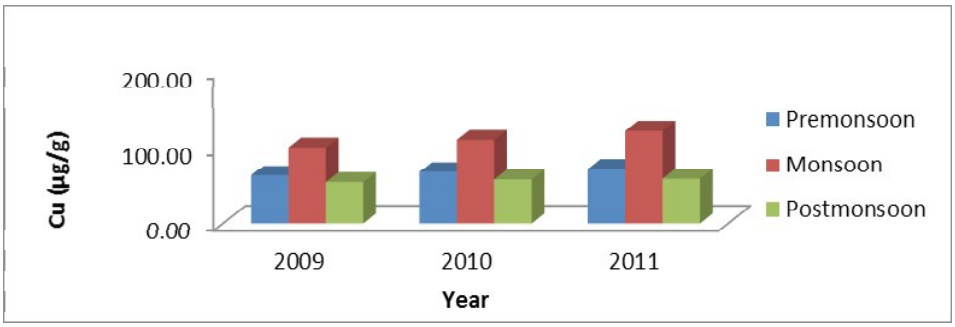


Figure-1 Seasonal variation of Metals (µg/l) in water of Rushikulya Estuary, during 2009-2011



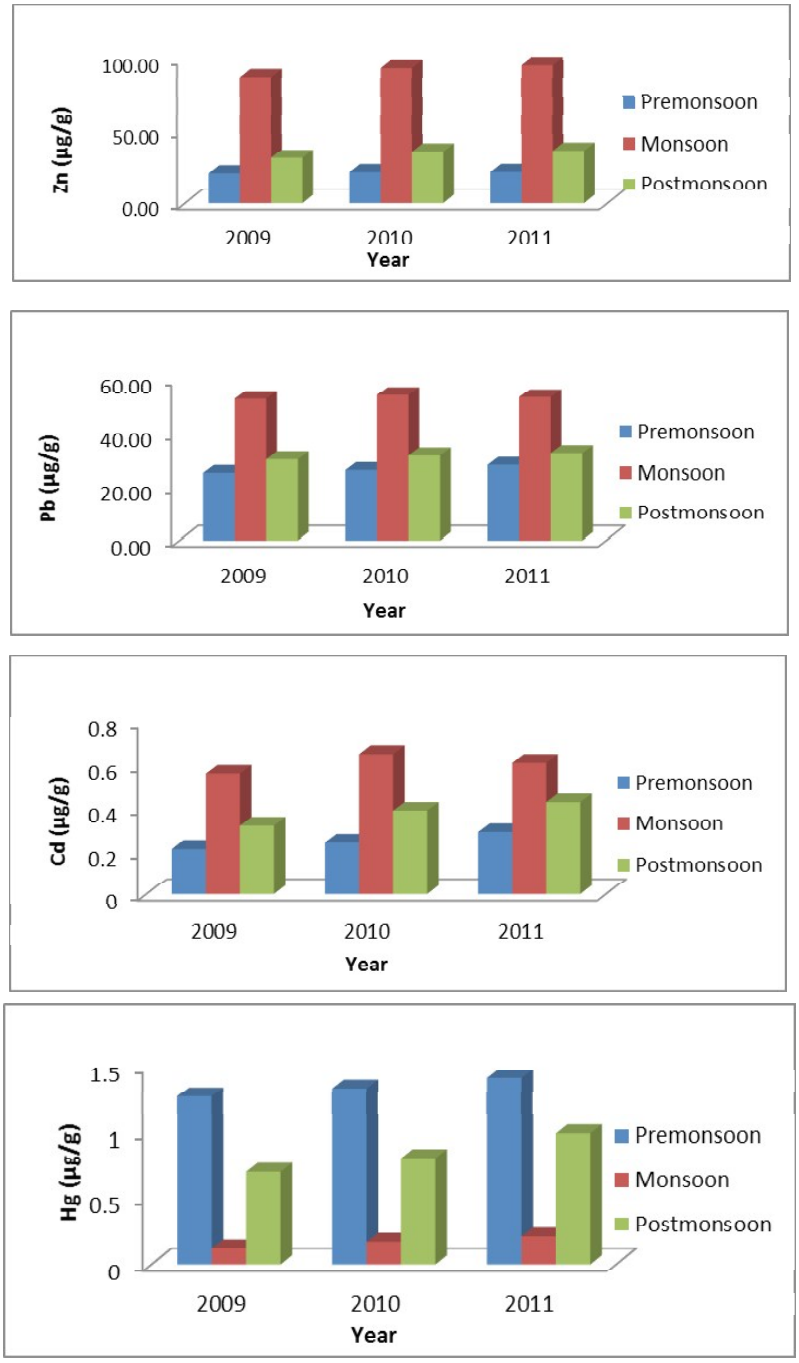
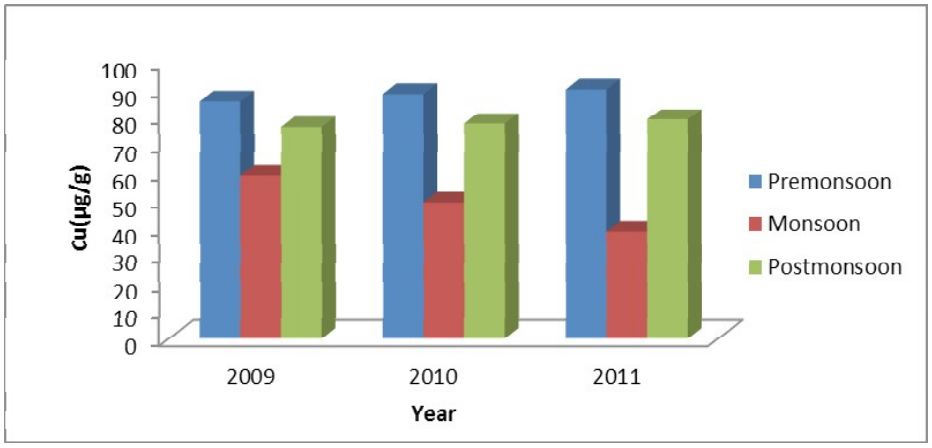
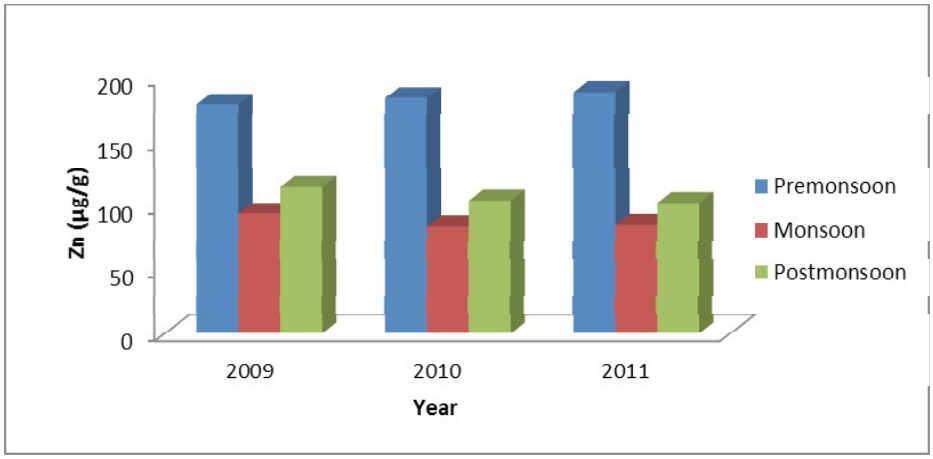
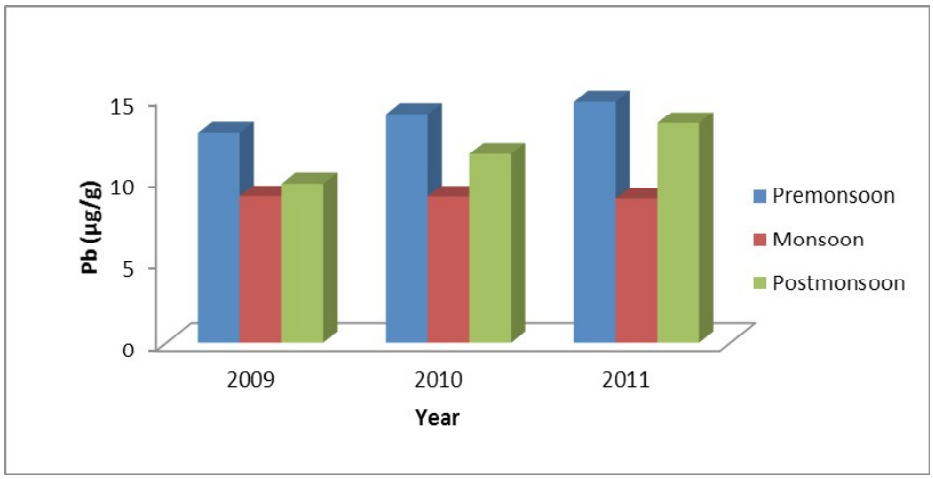


Figure -2 Seasonal variation of metals(µg/g) in Sediment of the Rushikulya estuary, during 2009-2011


Cu(µg/g)
100
90
80
70
60
50
40
30
20
10
0
2009
2010
2011
Year
Premonsoon
Monsoon
Postmonsoon


Zn (µg/g)
200
150
100
50
0
2009
2010
2011
Year
Premonsoon
Monsoon
Postmonsoon


Pb (µg/g)
15
10
5
0
2009
2010
2011
Year
Premonsoon
Monsoon
Postmonsoon

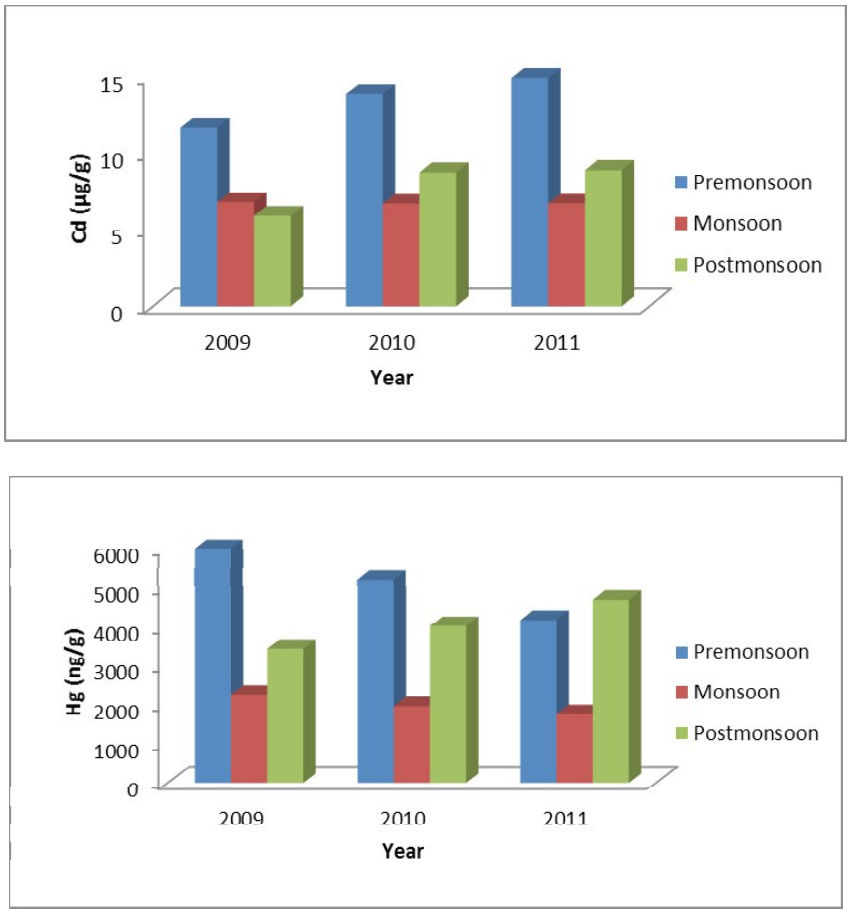


Figure-3 Seasonal variations of metals (ng/g) in Zooplankton of the Rushikulya estuary, during 2009-2011

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