Seasonal Behavior of Trace Metals (Cd, Cu,) in the Godavari River, East Coast of India, Bay of Bengal

*Medidi Raja Sekhar, Former Assistant Professor, Department of Chemistry, College of Natural Sciences, Abaya Campus, Gamo Gofa Region, Arba Minch, Ethiopia.

Abstract: The present study was carried out to determine the water quality in terms of seasonal variability and behavior of physico-chemical, nutrients and metal parameters for a period of one year during 2009 in the estuarine waters of Gauthami Godavari along its longitudinal stretch at seven station from the head of the estuary to mouth of the estuary. Trace metals (Cd, Cu,) in general, exhibited a decreasing trend from riverine to estuarine region indicating that dominant occurrence of river water. Relatively high concentrations in monsoon are attributed to the combined effects of precipitation, river runoff and land drainage. Lower concentration of metals during premonsoon season due to its utilization by biological activity, or by chemical and physical activity like desorption or flocculation as pH and salinity are increased during this season. Information of distinct spatial and seasonal variations of particulate trace metals were observed in the monsoon driven estuary like Gauthami-Godavari is essential to assess their involvement in the biogeochemical cycles, their possible accumulations in organisms, and their transfer to human beings through food chain. Suspended particulate matter (SPM) showed an increasing trend from pre-monsoon to monsoon followed by post-monsoon season can be attributed to the high river discharge and land runoff containing significant quantities of terrestrial material into to the estuary. So far there are no detailed seasonal studies of trace metal distribution in the estuarine waters of Godavari; the author has therefore been taken up the present investigation of Gauthami-Godavari.

Keywords: Godavari Estuarine waters, suspended particulate matter, particulate trace metals, Flocculation.

1. INTRODUCTION

The river Godavari receiving the lot of chemicals from the industries located on its banks and also from the agricultural back runoff and from the domestic sewage. All these materials are traveled from the head of the river and settling at the river mouth and dispersed into the sea during flood time of the river. The Godavari is the largest river in south India, largest estuary in the Central East coast of India. The Gauthami-Godavari estuary is a drowned river mouth type of estuary (16041´ - 16056´N, 81045´ - 82021´E), and is characterized by numerous islands and creeks that are separated from the main channel by sand bars (Narasimha Rao, T.V., 2001). It is having a drainage basin of about 3 x 105 Km^2 (Rao *et al*.1975) and has a mean annual discharge at the delta apex (Dowlaiswaram) of 1.05 x 10^{14} liters. In recent years there has been a rapidly growing interest on the heavy metallic content in estuaries and on the nature and the pathways by which they are introduced into the system. Due to anthropogenic input, abnormal concentration of heavy metals in particulate phases result. These high inputs can also affect the adjoining coastal waters due to exchange. Addition of these undesirable heavy metals in excess quantities can disrupt the delicate balance which exist between biomass and trace metals. The author has therefore undertaken a systematic study of the distribution of both dissolved and particulate trace metals like Cadmium and copper with hydrographical and nutrient parameters in the estuarine waters of the Gauthami Godavari over a period of one year during 2009.

2. LITERATURE SURVEY

Considerable work on hydrography, nutrients, major elements of the Godavari-Krishna estuaries and their adjoining coastal regions has been carried out by several workers.

2.1. Godavari and Krishna estuaries:

Godavari and Krishna are the two major rivers, the former constituting the second largest estuarine system next to that of the Ganges in the Peninsular India. They drain over an area of 3.1 x 10^5 and 2.6 x 105 km^2, and have a mean annual discharge at the delta apex (Dowlaiswaram and Vijayawada) of 1.05 x 10^{14} l respectively.

The river Godavari branches out into two major distributaries namely, Gauthami and Vashista at Dowlaiswaram 65 km-from the coast. The Gauthami proper again divides into Vrudha Gauthami, Nilarevu Gauthami and Gauthami proper connected by a seticulate system of tidal creeks. The Vashista again divides into Vainateyam and vashista proper. The tidal portion extends up to 44 km in Gauthami, 42 km in Vashista and 39 km in Vainateyam. Godavari is a typical positive estuary with a mean width of 1.5 km., and an average depth of 12-15m. The estuarine system of Krishna River covers an area of about 320 km^2. The tidal portion extends up to 39 km upstream in the river. It is essentially a shallow one with a mean width of 1.2 km and an average depth of 5-7 m.

Physical parameters (temperature, salinity, currents, tides, flushing time) of Godavari estuary have been investigated by several workers. (Sarma *et al.* 1986) studied the current and temperature structure of Godavari at one station (250m. depth) during September (S.W Monsoon). They observed short term variability of currents and temperature at different depths (15, 115, 240m) in the study area. Studies on salinity and current distribution in Gauthami Godavari estuary (Ranga Rao *et al.* 1988) revealed fairly high river discharge in July (monsoon) resulting in a partially mixed type of estuary. However, in January (post-monsoon), the discharge becomes negligible leading to dominant tidal effect, and making it well mixed type of estuary. The currents were fairly strong at the mouth (55cm.sec^{-1}) and decrease upstream away from the mouth. The flushing and dispersion characteristics of Gauthami Godavari estuary under high (September) and low (December) river discharge conditions have been investigated by (Reddy *et al.* 1994). Total flushing time of the estuary was found to be 4.0 tidal cycles (48 h) in September, and 46 tidal cycles (552 h) in December respectively indicating that the average length of time for the river water to move in the estuary decrease with increase in river discharge. The longitudinal diffusion coefficient was also found to vary with the fresh water discharge.

Physico-chemical characteristics of Vashista Godavari estuary revealed salinity stratification, higher turbidity in the lower reaches, super-saturation of oxygen, and relatively lower concentration of phosphate than nitrate and silicate in the water column (Sai Sastry *et al.* 1990 a). Studies on the suspended matter characteristics of the Gauthami Godavari estuary (Reddy *et al.* 1994) revealed distinct seasonal variation. During pre-monsoon and northeast monsoon seasons, its concentration was mainly controlled by the tidal currents because of minimum river discharge. However, relatively higher concentration of suspended matter in southwest monsoon was attributed to intense fresh water discharge and turbulence caused by wave action and tides. (Rama Sarma D.V., 1970) Studied the diurnal variations of several physico-chemical parameters in the Gauthami Godavari estuary during different seasons. Thought it is evident from the above literature survey that considerable work has been carried out on the distribution and behavior of nutrients and some major elements in the Indian estuaries, the information is very limited and scanty in the Godavari River estuary and its adjoining coastal waters. The author has therefore undertaken a systematic study of these aspects with the following objectives. i) to investigate the distribution of dissolved and particulate trace metals (Cd, Cu) and their inter-relationships among themselves, with salinity and nutrients. ii) to identify the factors controlling the concentration of nutrients and trace metals in the estuarine regions of the Gauthami Godavari.

3. MATERIALS AND METHODS

3.1. Materials:

Gauthami-Godawari estuary is divided into 7 stations they are,

Station 1, is located in the centre of the stretch of Gauthami Godavari at Kotipalle, head of the estuary. It is 41 km away from the mouth of the estuary and minimum tidal action is there. The water is mostly fresh water (less saline). Both sides of the river have villages and have a extensive cultivated agricultural lands. During monsoon season anthropogenic inputs from these villages and agricultural lands are more in to the river.

Station 2, is located in the center of the river Gauthami Godavari at Dangeru, 8 km down to the Kotipalle. Both sides have villages and agricultural lands. Fishing activity is also there. The average depth of the station is 8 m.

Station 3, is located in the center of the estuary of Gauthami Godavari at Yanam, 22 km away from the mouth of the estuary. Yanam is the moderately populated town situated northern side of the Gautami Godavari. Most of the domestic effluents are discharging into the estuary. Many fishing boats are anchored as called boat jetty in the estuary. The tidal influence is more and average depth this station is 12 m.

Station 4, is located in the centre of the river at Vrudha Gautami of the stretch of Gautami Godavari, 5 km down to Yanam. There are many creeks are enter into this area. The average depth of the station is 6 m.

Station 5, is located at the centre of the river channel at Balusutippa. It is 12 km away from the mouth of the estuary. The surrounding areas are fish and shrimp farms, they release appreciable amounts of their effluents into the near creeks and finally come to the main estuary. From this station onwards, mangrove forest are there in both side of the estuary and the average depth of the station is 5 m.

Station 6, is located at the centre of the creek of the mangrove forest area. Dense mangrove forest is there at both side of the creek. The average depth of the creek is 4 m.

Station 7, is located at the centre of the mouth of the estuary, it is connected to the coastal waters of the Bay of Bengal, relatively very clean waters are prevailed. North side of this station oil industrial activity is there and southern side is mangrove forest. The average depth of this station is 8 m

3.2. Methods:

Metals in suspended particulate matter (µg/l):

An aliquot of seawater sample (1 litre) containing different metals were filtered through a pre-weighed 0.45 µm membrane kept in polyethylene petri dishes stored in deep freeze until their digestion. The filters containing suspended particulate matter were dried and kept in a vacuum desiccators over silica gel and weighed to an accuracy of 0.001 mg. Filter containing particulate matter and blanks were digested with a mixture of perchloric acid and nitric acid and evaporated to almost dryness. The residues are diluted to 25 ml with HCl (0.1N) and then subjected to trace metal analysis (Loring *et al.* 1977) using ICP-MS. The concentrations of trace metals were computed from calibration curves. The particulate trace metals in seawater were expressed $\mu g.dm^{-3}$.

4. RESULTS AND DISCUSSIONS

4.1. Particulate Cadmium: The station-wise summery statistics on particulate iron in the estuarine waters of the Gauthami Godavari during the study period was given in Table 1. The detailed seasonal distribution at the seven individual stations was shown in Fig. 1

The concentrations of particulate cadmium in these waters during pre-monsoon season (March) varied from 1.86 to 5.91 µg/l with an average of 4.03 µg/l and in its bottom waters, its concentrations varied from 0.88 to 3.21 µg/l with an average of 2.08 µg/l. During the onset of monsoon (June), the particulate cadmium concentrations of the surface waters ranged from 2.18 to 6.58 µg/l with an average of 4.69 µg/l, and in its bottom water, the cadmium concentrations varied from 1.02 to 3.54 µg/l with an average of 2.49 µg/l. During the monsoon season (September), the particulate cadmium concentrations of the surface waters, varied from 3.28 to 9.70 µg/l with an average of 6.45 µg/l and in its bottom water, its concentrations ranged from 2.21 to 5.01 µg/l with an average of 3.56 µg/l. The cadmium concentrations during postmonsoon season (December), in the surface water varied from 3.02 to 7.65 µg/l with an average of 5.55 µg/l and in its bottom waters, its concentration varied from 1.12 to 4.01 µg/l with an Table average of 3.02 µg/l. Particulate cadmium concentrations in the study area decreased from the Kotipalle (Head) to Bhairavapalem (Mouth). This may be due to desorption and solubilization of particulate metals as salinity and dissolved oxygen concentrations increase. This process could be expected in estuaries due to chloride and sulphate complexation and ionic strength effects. Similar behavior of the cadmium was also observed by (Ramana *et al* 1989) during estuarine mixing. Cadmium mobilization is well documented in estuaries in the Amazon plume (Comans *et al* 1988); in the Chang Jiang estuary (Boyle *et al.* 1982) in the lower part of the Scheldt estuary (Edmond *et al.* 1985) (Duinker *et al.* 1982) in the Gironde and Huanghe estuaries. (Salomaons *et al.* 1986) in the Mississippi estuary (Elbazpoulichet *et al.* 1987) etc., The concentrations of particulate cadmium observed in the present study are lower or higher than in the estuarine waters reported elsewhere. (Shiller *et al.* 1991) reported that the particulate cadmium concentrations in Scheldt estuary varied from 1.10 to 13.9 µg/l in fluvial end member; and it is found to be less than 0.5 to 2.0 in the marine end member composition. reported the particulate concentrations, varied from 0.28 to 0.30 µg/l. (Zwolsman *et al.* 1999) reported that the particulate cadmium concentrations varied from 25.3 to 236 (103 mol. year-1) at Gironde estuary, 19.2 to 218 (103 mol year-1) at Girone river system and 5.67 to 18.0 (103 mol year-1) at Dordogne river systems. (Schafer *et al.* 2002) reported the particulate cadmium concentrations varied from 5.02 to 7.03 µg/dm3 at Kakinada Bay, 5.52 to 8.05 µg/dm^3 at Gauthami Godavari estuarine region, 6.01 to 8.50 µg/dm3 at mangrove area, (Abdallah M., 2008) reported particulate cadmium concentrations, it is varied upto 6.71 µg/l, Seasonal higher concentrations of particulate cadmium were observed during monsoon season followed by post-monsoon and premonsoon season due to influx of fresh water into the estuary.

4.1.1. Relation of particulate cadmium with salinity

Significant inverse correlations for particulate cadmium with salinity in the waters of the Gauthami Godavari (r = -0.78, p <0.001 (for dissolved cadmium); r = -0.71, p <0.001 for particulate cadmium). These values are incorporated in the Fig. 3. From the data present in the figure it may be seen that the concentrations of dissolved cadmium decrease with increase in salinity. It is known that with increase in salinity there is greater desorption and solubulization of particulate metals. (Zwolsman *et al.* 1993) mentioned that there is overwhelming evidence, both from laboratory experiments and field investigations, that cadmium bound on to suspended matter is (partially) desorbed when river water mixes with sea water due to formation of chloro-complexex (Turner *et al.* 1991) (Ramana *et al.* 1989). Several field studies on the chemistry of dissolved cadmium in the Scheldt have confirmed this hypothesis (Kerdjik *et al.* 1981) (Edmond *et al.* 1985); (Zwolsman *et al.* 1999); (Zwolsman *et al.* 1993).

Similar relationships between salinity particulate cadmium have been observed in the estuarine waters of Scheldt (Salomons *et al.* 1981); (Elbazpoulichet *et al.* 1987). (Reign Pierre *et al.* 1993) and in many estuaries both in Europe and in USA, (Olsen *et al.* 1989), (Schoer J.H., 1990), (Turner *et al.* 1991), (Paalman *et al.* 1992), in the estuarine waters of Gironde estuary by (Krapile *et al.* 1997) it is well known that these behaviors are primarily related to physical mixing of fluvial and marine particulates at the mouth of the estuaries and also caused by flocculation and desorption of particulate metals into the sediments in the Scheldt estuary, South west Netherlands, (Shiller *et al.* 1991), in the estuarine waters of Gironde reported by (Michael *et al.* 2000); in Bay waters of Galveston reported by (Tang *et al.* 2000); in the estuarine waters of Gironde (SW France) reported by (Stephen Audry *et al.* 2007) in the waters of Mediterranean-Climate Coastal Bay, Elmex Bay, Egypt and its coastal environment (Abdallah M., 2008).

4.1.2. Relation of particulate cadmium with pH:

Significant inverse correlations were observed between the dissolved and particulate cadmium with pH in the waters of the Gauthami Godavari, r=-0.80; p<0.001and these values are incorporated in Fig. 4.6. It was observed that the dissolved cadmium concentrations decrease with increase in pH due to dilution of estuarine waters with sea water at mouth of the estuary. Similar relationships between pH and particulate cadmium have been observed in the Scheldt estuary (Salmons *et al.* 1981); (Edmond *et al.* 1985) (Reign Pierre *et al.* 1993), and also in many estuaries both in Europe and in USA, (Olsen *et al.* 1989) (Schoer *et al.* 1990); (Turner *et al.* 1991) (Paalman *et al.* 1992). Relatively higher pH values in the Gauthami Godavari was observed during summer (premonsoon). The higher values are probably associated with photosynthesis during plankton blooms. The decrease of pH was observed in Gauthami Godavari with increasing distance from the mouth (Bhairavapalem). This is due to the high partial pressure of CO_2 related to the respiration of organic matter occurring in the upper part of estuary. The influence of ionic strength on the dissociation constants of carbonic acid also contributes to the pH drop (Turner *et al.* 1991).

4.2. Particulate Copper:

The station-wise summery statistics on particulate iron in the estuarine waters of the Gautami Godavari during the study period was given in Table 2.

The detailed seasonal distribution at the seven individual stations was shown in Fig. 2. The particulate copper in the surface waters during pre-monsoon season (March) varied from 13.68 to 26.52 µg/l with an average of 20.33 µg/l and its bottom waters, the copper concentrations varied from 6.02 to 15.62 µg/l with an average of 10.95 µg/l. During the onset of monsoon (June), the copper concentrations of the surface waters ranged from 20.32 to 38.26 µg/l with an average of 29.98 µg/l, and its bottom water, the copper concentrations varied from 8.65 to 20.85 µg/l with an average of 15.08 µg/l, and in the monsoon (September), the copper concentrations of the surface waters, varied from 30.15 to 52.32 µg/l with an average of 43.84 µg/l and its bottom water, the copper concentrations ranged from 21.65 to 35.16 µg/l with an average of 28.53 µg/l, and during post-monsoon season (December), the copper concentrations of the surface water varied from 22.15 to 43.21 µg/l with an average of 34.04 µg/l and its bottom concentrations of copper varied from 16.32 to 28.32 µg/l with an average of 23.30 µg/l.

The oxidation of metals sulphides in the oxic ozone also plays an important role in the release of several particulate toxic elements (Cu, Cd, Pb) during estuarine mixing (Zwolsmen *et al.* 1993). Seasonally, higher concentrations of particulate copper were observed during (monsoon), September, lower concentrations were observed during pre monsoon season, March and intermediate concentrations were observed in the (onset of monsoon season) June and (post monsoon season) December. Higher concentrations of particulate copper were observed in the surface waters due to the desorption of copper on the organic matter in the surface waters is more. A higher concentration of copper is increased seasonally. Speciation calculations suggest that desorption of particulate cadmium during estuarine mixing is due to the formation of chloro-complexes (Turner *et al.* 1991) (Ray *et al.* 2006) reported the particulate copper concentrations varied from 28.5 to 32.5 µg/dm^3 at KKD Bay, 28.0 to 31.0 µg/dm^3 at GGE Region, 26.5 to 39.0 µg/dm^3 at mangrove area. (Gomez- Parra *et al.* 2000) reported the particulate copper concentrations varied from 8.45 to 9.85 µg/l. (Baeyans *et al.* 1998) reported that the surface dissolved cadmium concentrations varied from 112.0 to 278.0 µg/l at 0-2 (psu), 47.0 to 95.0 µgl at 10-20 (psu), 101.0 to 273.0 µgl at 30 (psu). (Martin *et al.* 1993) the surface dissolved concentrations in Lena river are varied from 24.0 to 48.0 ppm.

4.2.1. Relation of particulate copper with salinity:

Significant inverse correlations observed between the dissolved and particulate copper with salinity in the waters of the Gauthami Godavari (r = -0.8 1, p <0.001 (for particulate copper) have been graphically shown in Fig. 4. Both dissolved and particulate copper behaves non-conservatively in these waters. The non-conservative behavior has been observed in the small river dominant estuaries (Window *et al.* 1983). The concentrations of particulate copper gradually decreased towards the lower reaches of estuary may be due to salinity-induced solubilization of the particulates associated organic matter (Duinker *et al.* 1977). Relationship between copper and salinity tough reciprocal, cannot be established convincingly. Yet, the fact that most heavy metals flocculate in high saline waters (Rantala *et al.* 1985) substantiates the decrease in copper concentrations with increase in salinity levels (Vansantha, M. 2008).

The high concentrations of Particulate copper estuarine and Mangrove environments could be due to the re-mineralization from sediments and organic matter in the low salinity region (Chakraborty *et al.* 2009). Distribution of copper in particulate phase clearly shows a non-linear pattern. This may be due to the desorption and solubilization of particulate metals as salinity and dissolved oxygen increases (Zwolsman *et al.* 1993).

4.2.2. Relation of particulate copper with pH.

Significant inverse correlations were observed between the dissolved and particulate copper with pH in the waters of the Gauthami Godavari (r = -0.95, p <0.001) are shown in Fig. 5. Dissolved copper in the estuarine water is largely complexed with organic matter (Kramer *et al.* 1984), (Valenta *et al.* 1986), (Vanden Berg *et al.* 1987), (Zwolsman *et al.* 1993) and one may expect that desorption of particulate copper is enhanced at increasing pH, in accordance with the known characteristics of humic compounds (Bourg A.C.M., 1983).

The strong association between dissolved copper and organic ligands suggests that copper is mainly bound to organic matter of riverine origin which progressively mineralized during its transport to the sea. The particulate copper concentrations were decreased with increasing pH due to dilution of estuarine waters with sea water at mouth of the estuary (Kerdjik *et al.* 1981). The oxidation of metal sulphides in the oxic zone plays an important role in the release of several particulate toxic elements (Cd, Cu, Pb) during estuarine mixing (Zwolsman *et al.* 1999).

5. CONCLUSION

Suspended particulate matter (SPM) showed an increasing trend from pre-monsoon to monsoon followed by post-monsoon season in the study area. High concentration of SPM in monsoon can be attributed to the high river discharge and land runoff containing significant quantities of terrestrial material during this season. Its concentration in general, showed a decreasing trend from head to mouth of the estuary. This trend is attributed to the adsorption of particulate matter at head of the estuary and its desorption at the estuarine mouth due the pH and salinity variations. In general, suspended particulate matter showed relatively higher values at surface when compared with those in bottom waters. From the findings of the present study, it is known that the estuarine waters of Gauthami Godavari are not polluted. Further increase of the metal concentrations poses a serious threat to the aquatic organisms and especially water quality of the estuary. The results would form a useful tool for the eradication of pollution

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Table1. Seasonal changes of particulate Cadmium in the waters of the Gouthami estuary of river Godavari

Area	March		June		September		December	
	S	B	S	B	S	B	S	B
Kotipalli	5.91	3.21	6.58	3.54	9.70	5.01	7.65	4.01
Dangeru	5.28	3.01	6.23	3.26	8.85	4.86	7.21	3.89
Yanam	4.68	2.23	5.28	3.12	7.28	4.24	6.28	3.65
V.Godavari	4.35	2.08	4.56	2.65	6.12	3.54	5.48	3.21
Balusutippa	3.54	2.04	4.35	2.02	5.65	2.62	5.12	2.85
Mangrove	2.62	1.12	3.65	1.87	4.28	2.41	4.12	2.43
Bhiravapalem	1.86	0.88	2.18	1.02	3.28	2.21	3.02	1.12

Table 2. Seasonal changes of particulate Copper in the waters of the Gouthami estuary of river Godavari

Area	March		June		September		December	
	S	B	S	B	S	B	S	B
Kotipalli	26.52	15.62	38.26	20.85	52.32	35.16	43.21	28.32
Dangeru	24.89	14.98	36.89	19.35	50.13	34.12	41.65	27.89
Yanam	22.32	12.36	32.65	18.63	48.37	30.12	38.25	25.94
V.Godavari	20.54	12.02	30.85	14.84	45.65	28.63	34.62	24.35
Balusutippa	18.56	9.12	26.32	12.34	41.64	25.65	31.15	21.66
Mangrove	15.84	6.54	24.56	10.87	38.65	24.35	26.28	18.63
Bhiravapalem	13.68	6.02	20.32	8.65	30.15	21.65	23.15	16.32

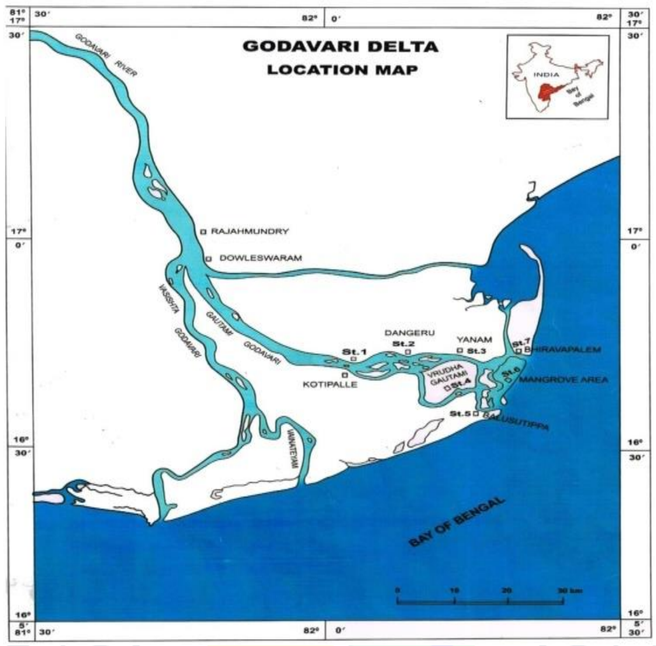


Fig 2

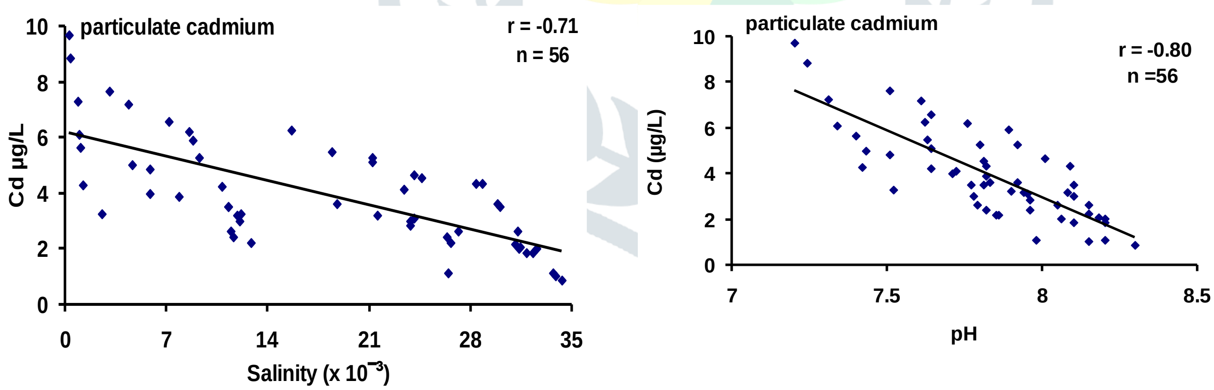


Fig.3. Relation between particulate cadmium with salinity and pH in the estuarine waters of Gautami Godavari during 2009.

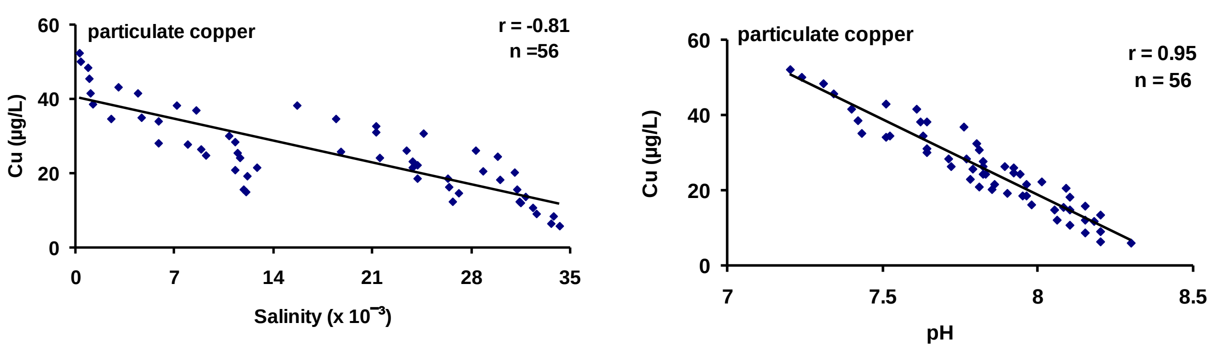
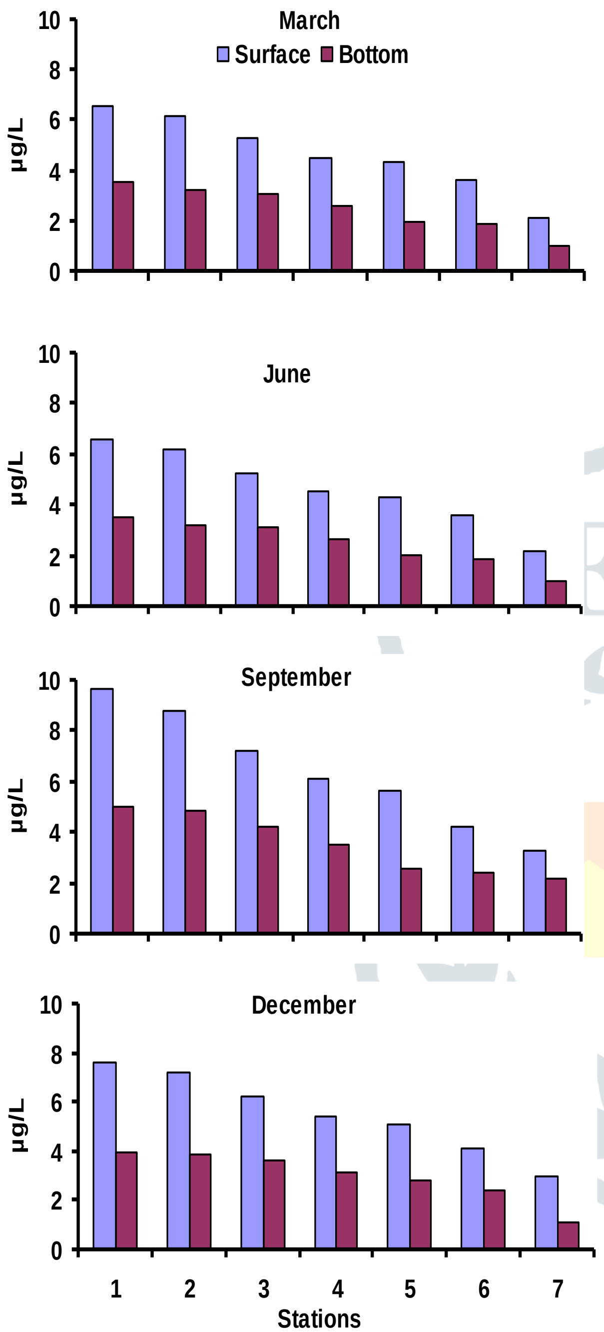
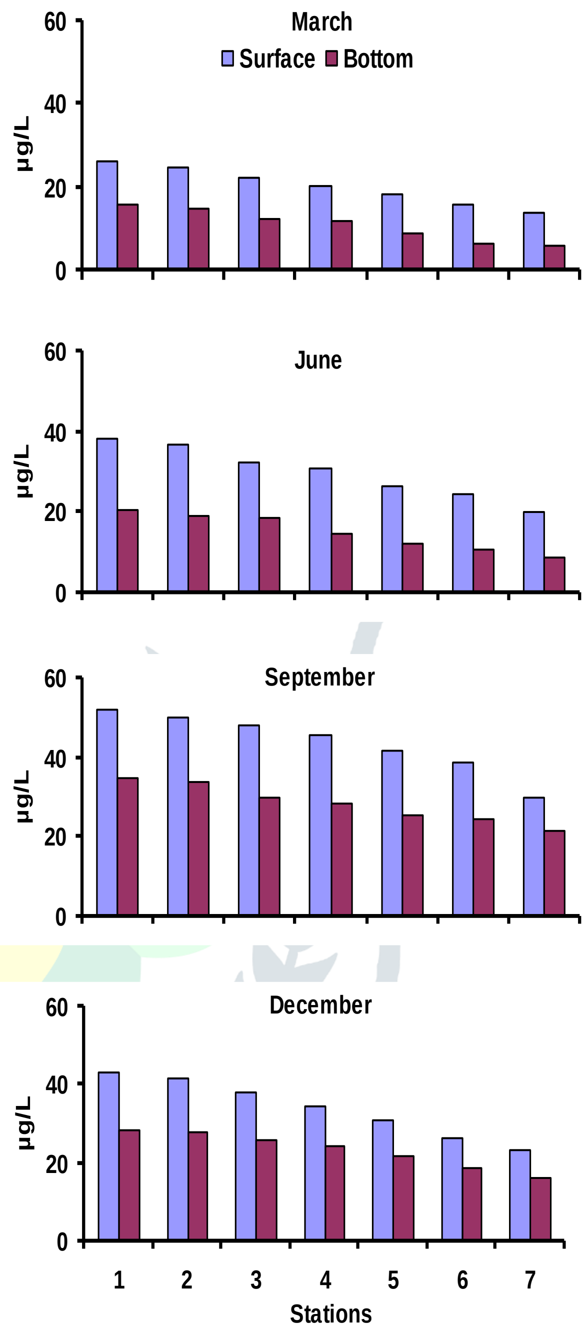


Fig.4. Relation between particulate copper with salinity and pH in the estuarine waters of Gautami Godavari during 2009.

St.1: Kotipalle, St.2: Dangeru, St.3: Yanam, St.4: V.Gauthami, St.5: Balusutippa, St.6: Mangrove Area, St.7: Bhairavapalem.





Seasonal variations of particulate cadmium and copper in the estuarine waters of Gauthami Godavari during 2009.

Figure 1 cadmium **Figure 2 copper**