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Distribution of Particulate Trace Metals like Iron and Nickel in the Estuarine Waters of River Godavari, East Coast of India.

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Abstract: *Godavari is the third largest river on the east coast of India drains in to the Bay of Bengal between the Latitudes 16°.15' to 16°.45' N and longitudes 81°.45' to 82'.25' E, discharging large quantities of fresh water in to the coastal waters of Bay of Bengal particularly during monsoon season. 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 observed during monsoon can be attributed to the high river discharge and land runoff containing significant quantities of terrestrial material into to the estuary. Distinct spatial and seasonal variations of particulate trace metals were observed. Information on the distribution of metals 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. So far there are no detailed seasonal and spatial studies of trace metal distribution in the estuarine waters of Godavari; the author has therefore been taken up the present investigation to assess the spatial and seasonal distribution of particulate trace metals like Iron -and Nickel in the estuarine waters of Gauthami-Godavari.*

Keywords*: Godavari Estuarine waters, Particulate matter, trace metals, Flocculation.*

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I. 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 ($16^0 41'$ - $16^0 56'$N, $81^0 45'$ - $82^0 21'$E), and is characterized by numerous islands and creeks that are separated from the main channel by sand bars (Narasimha Rao., 2001). It is having a drainage basin of about 3×10^5 Km^2 (Rao 1975) and has a mean annual discharge at the delta apex(Dowlaiswaram) of 1.05×10^{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 both dissolved and 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 particulate trace metals like Iron and Nickel along with hydrographical and nutrient parameters in the estuarine waters of the Gauthami Godavari over a period of one year during 2013.

II. Materials And Methods

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.

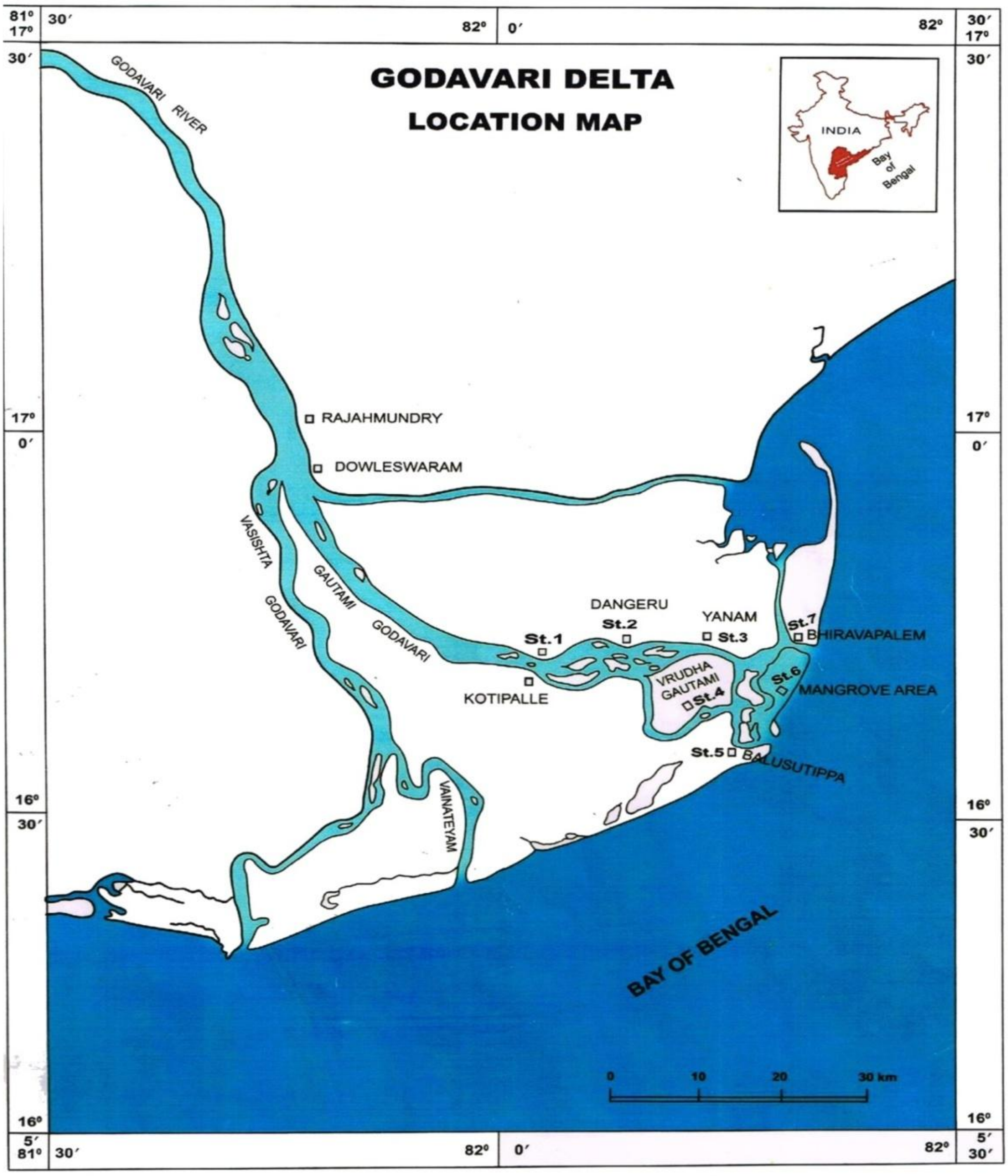
Station 3, is located in the center of the estuary of Gauthami Godavari at **Yanam**, 22 km away from the mouth of the estuary. Yanam is the moderately populated town situatednorthern side of the Gautami Godavari. Most of the domestic effluents are discharging into the estuary. Many fishing boats are 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.



III. Results and Discussion

Harbor, coastal waters and estuaries act as transition zone in which continental material is trapped and through which some of the material is transported to the open Sea. The chemical composition and variability of suspended particulate matter (SPM) in harbor and coastal water is controlled by complex interplay of physical and biogeochemical processes. Some of the most important geochemical processes influencing variability are mixing of land and riverine suspended matter with marine material, flocculation of colloidal materials (Benoit *et al*., 1994), adsorption and desorption in low salinity zone (Windom *et al*., 1988; Zwolsman *et al*., 1997), production of organic matter by phytoplankton (Balls, 1990; Burton *et al*., 1994), mobilization of Fe-Mn oxides in reducing sediments (Feely *et al*., 1986) and re-suspension of bottom sediments (Balls, 1994; Hatje*et al*., 2001). It is not surprising, that studies of metal behavior in polluted harbor and coastal waters have well documented, but there is a substantial difference from one area to another area. Studies of particulate trace metals are usually based on a single, or a small number of surveys. Moreover, the concentration of particulate metals can be variable, both as a result of changing inputs and or seasonal effects involving biological, geochemical and physical interactions.

Numerous studies on the distribution and behavior of trace metals in various coastal and harbor waters in different parts of the world have revealed that individual metals exhibit contrasting behavior between areas. Factors which have been demonstrated to be important in controlling trace metal behavior include flushing time (Morris, 1990; Owens and Balls, 1997).Very few studies have been made on the distribution of trace metals in the Visakhapatnam harbor and coastal waters. Satyanarayana b *et al*., (1985) studied on the distribution of particulate and dissolved metals in Visakhapatnam harbor waters. Sen Gupta *et al*., (1978) studied the trace metal analysis in the Arabian Sea water. Sanzgiri and Mores (1979) studied the trace metal distribution in the Laccadive Sea. Braganca and Sanzgiri (1980) studied the concentrations of few trace metals in coastal and offshore regions of the Bay of Bengal. Rajandran *et al*., (1982) studied the dissolved and particulate trace metals in western Bay of Bengal. Jegatheesan and Venugopalan (1973) studied the trace elements in the particulate matter of Porto Novo waters.

3.1 PARTICULATE IRON

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

Table 1 Station-wise summary statistics on particulate iron (µg.gr^{-1}) in the estuarine water of Gauthami Godavari during 2013

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	540.50	4788.50	1944.08	1926.87	423.12	2892.25	1207.52	1135.55
Dangeru	282.25	3816.23	1594.79	1515.91	310.27	2058.26	907.69	788.76
Yanam	482.85	3816.23	1594.79	1515.91	310.27	2058.26	907.69	788.76
V.Godavari	477.26	2265.23	1166.37	784.50	302.65	1987.68	835.01	779.71
Balusutippa	389.25	2823.12	1236.67	1088.73	202.15	1635.29	709.57	639.42
Mangrove area	361.75	2777.27	1199.46	1084.42	200.65	598.85	368.83	186.97
Bhiravapalem	343.25	2013.32	915.525	757.60	186.68	1135.26	504.68	430.22

The particulate iron concentrations in the surface waters were in the range of 343.25 to 4788.80 µg.gr^{-1}with an average of 1442.26 µg.gr^{-1}where as in the bottom waters, its concentrations ranged from 186.68 to 2892.30 µg.gr^{-1} with an average of 843.91 µg.gr^{-1}. In general, higher concentrations of particulate iron were observed during monsoon season and were followed by post-monsoon season and pre-monsoon season. Higher concentrations of iron were observed during monsoon season is due to the combined effect of land and river runoff along with anthropogenic inputs of iron. Generally the pH of rain water is lower in comparison to river water average and at lower pH, the rain water dissolves more iron from the rocks of earth surface (Charlson and Rodhe, 1982); Sundaray, 2007), which contributed more particulate/dissolved iron to the river water. This phenomenon is also observed for the Brahamani River by Rath, (2003). Lower values of particulate iron were observed during premonsoon season due to its utilization by plankton, which are more during this season, and precipitation of iron under alkaline pH condition of the estuary (Stumm and Morgan, (1970) and flocculation of iron with dissolved organic matter may also support the lower concentrations of iron during this season.

Similar seasonal variations of iron were also reported by Fang and Lin (2002) in the Tanshui estuary in Northern Taiwan, Zhou *et al*., (2003) in the waters of Conwy estuary, North Wales, Caetano *et al*., (2006) in Guadiana estuary, Beck *et al*., (2010) in a shallow subterranean estuary, South Bay, New York, Sundaray*et al*., (2011) in Mahanadi river estuarine system, India. Raju *et al*., (2013) in the waters of Cauvery river basin.

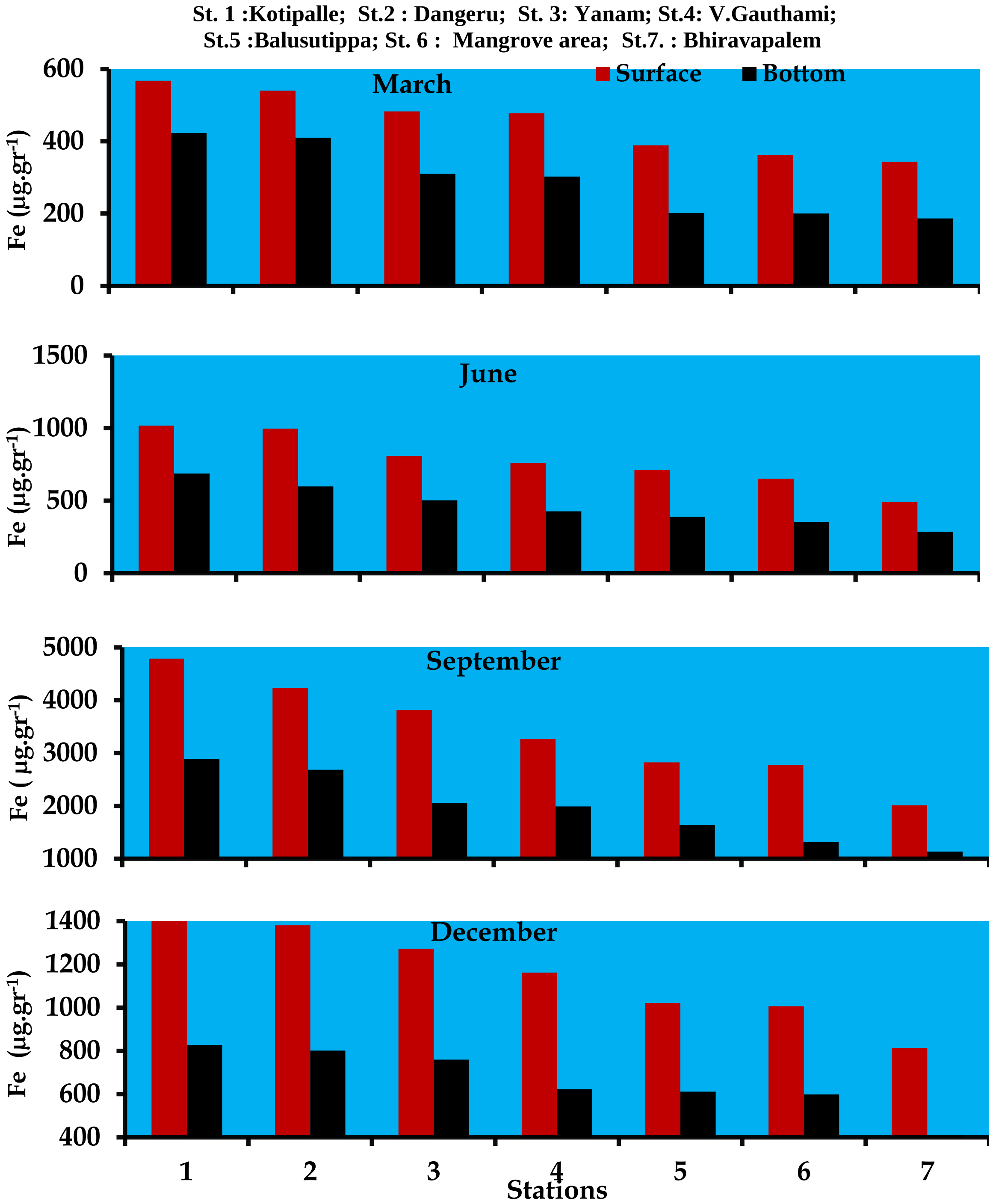


Fig. 1 Seasonal and spatial distribution of particulate Iron in the estuarine waters of the Gauthami Godavari during 2013.

3.2 Relation of particulate Iron with pH:

Significant inverse correlations were observed between the particulate iron with pH in the waters of the Gauthami Godavari ($r = -0.89$, $p < 0.001$) is shown in Fig. 2.Windom *et al.*, 1988 stated that iron removed in the Bang Pakong estuary at Thailand is explained by the decrease the iron solubility at higher pH encountered at higher salinities. The concentration of particulate iron in the present study decreases linearly with increase in pH. It may be attributed due to the large scale rapid removal of iron from river water during estuarine mixing. The river-borne iron consists almost entirely of mixed oxide-organic matter which is stabilized by the organic matter. It is colloidal in nature and the particle size is reported to be less than 0.45 µM. Precipitation occurs on estuarine mixing because the cations present in sea water neutralize the negatively charged iron bearing colloids allowing flocculation.

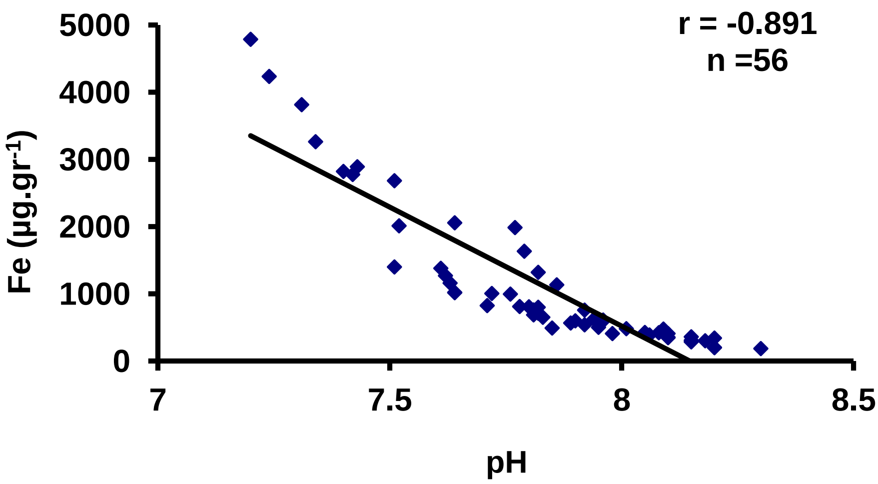


Fig. 2 Relation between pH and particulate iron in the estuarine waters of Gauthami Godavari during 2013

Relation of particulate Iron with salinity:

Significant inverse correlations were observed between the particulate iron with salinity in the waters of the Gauthami Godavari ($r=-0.75$, $p<0.001$) is shown in Fig.3. The particulate iron was observed to be rapidly decreasing in the Gauthami Godavari at higher salinities.

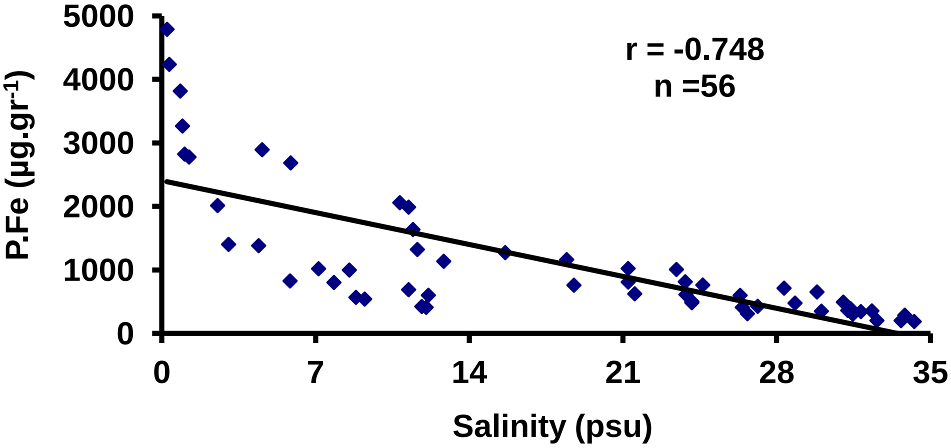


Fig. 3. Relation between particulate iron with salinity in the Estuarine waters of Gauthami Godavari during 2013

In general, the rapid removal of iron from solution is commonly observed in estuarine waters (Byrd *et al*., 1990; Windom *et al.*, 1971, 1988; Yeats and brewers 1976; Boyle *et al.*, 1977) and has been attributed to the flocculation and precipitation of colloidal iron oxy hydroxides with organic matter (Sholkovitz, 1976; Sholkovitz and Cop land, 1981). The dissolved and particulate iron is known to show highly non-conservative behavior in most estuarine environments due to destabilization of humid substances with which it is complexed (Liu, 1996). The removal process of iron is an adsorption on to suspended matter in the estuarine region, enhanced by the pH gradient (Bourg, 1983; Tessier *et al*., 1985). The similar removal process is also observed in Tamar and Beaulieu estuaries in England (Liu *et al*., 1998; Turner *et al*., 1998), Conwy estuary, North Wales (Zhou *et al*., 2003), in the coastal environment of Orissa, India (Nayak *et al*., 2004), in the Mandove and Zuari estuary (Kessarkar*et al*., 2010, 2013) in Mangrove estuary (Shynu *et al*., 2012.

PARTICULATE NICKEL:

The station-wise summery statistics on particulate nickel in the estuarine waters of the Gauthami Godavari during the study period were given in Table 2. The detailed seasonal distributions at seven individual stations are shown in Fig.4. The particulate nickel concentrations in the surface waters were in the range of 3.78 to 34.65 $\mu g.gr^{-1}$ with an average of 16.70 $\mu g.gr^{-1}$ where as in the bottom waters, its concentrations ranged from 2.10 to 23.650 $\mu g.gr^{-1}$ with an average of 10.01 $\mu g.gr^{-1}$.

Table. 2 Station-wise summary statistics on particulate nickel (µg.gr^{-1}) in the estuarine water of Gauthami Godavari during 2013

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	12.96	34.65	21.89	9.34	7.36	23.65	13.86	7.01
Dangeru	11.98	33.12	20.85	9.16	7.01	22.79	13.15	6.86
Yanam	9.67	30.15	18.89	8.79	6.35	21.02	11.32	6.66
V.Godavari	7.25	27.65	16.53	8.55	4.93	19.63	10.12	6.65
Balusutippa	5.38	26.34	14.70	8.86	3.65	17.54	8.38	6.31
Mangrove area	4.15	24.98	13.18	8.89	2.45	15.35	6.86	5.81
Bhiravapalem	3.78	12.42	10.90	6.11	3.10	14.63	6.58	5.43

Nickel occurs principally as Ni^{2+} in surface sea waters, but oxidation states ranging from Ni^{1+} to Ni^{4+} have been reported from time to time (Moore, 1991). Under reducing conditions in surface water, nickel forms insoluble sulphides, provided that sulphur is present in excess. Under aerobic conditions and pH < 9, nickel complexes with hydroxides, carbonates, sulphates, and naturally occurring organic ligands. This has been observed both in fresh waters and estuarine waters (Luther *et al*., 1986). Above pH 9 (rarely found in surface waters), the hydroxide and carbonate complexes precipitate.

Seasonally higher concentrations of particulate nickel were observed during monsoon followed by post-monsoon and pre-monsoon seasons. Higher concentrations were observed during monsoon season due to the combined effect of land and river runoff along with domestic and industrial effluents are more during this season. Lower values of particulate nickel were observed during pre-monsoon season due to its precipitation under alkaline pH condition of the estuary (Stumm and Morgan, 1970), and flocculation with dissolved organic matter.

The removal of nickel by co-precipitation with manganese oxides also observed in the oxic and suboxic interphase in salt marshes of the Scheldt estuary (Zwolsman *et al*., 1993). The concentrations of the particulate metals in estuaries generally decrease seaward due to the mixing of river-borne suspended matter containing higher metal concentrations with marine suspended matter which contains relatively low metal concentrations (Regnier and Wollast, 1993).

Similar variation of nickel were also reported by Fang and Lin (2002) in the Tanshui estuary in Northern Taiwan, Zhou *et al*., (2003) in the waters of Conwy estuary, North Wales, Caetano *et al*., (2006) in Guadiana estuary, Sundaray *et al*., (2011) in Mahanadi river estuarine system, India. Raju*et al*., (2013) in the waters of Cauvery river basin.

Relation of particulate nickel with pH:

Significant inverse correlations were observed between the particulate nickel with pH in the waters of the Gauthami Godavari (r = -0.97, p <0.001) is shown in Fig. 4.14. In the high pH range, particulate nickel concentrations decreased due to dilution with sea water (Abdullah, 2008). The concentration of particulate nickel in the present study decreases linearly with increase of pH. It may be attributed to the large scale rapid removal of nickel from river water and it is a general phenomenon during estuarine mixing. Precipitation of particulate nickel occurs on estuarine mixing because the sea water cations neutralize the negatively charged nickel bearing colloids allowing flocculation.

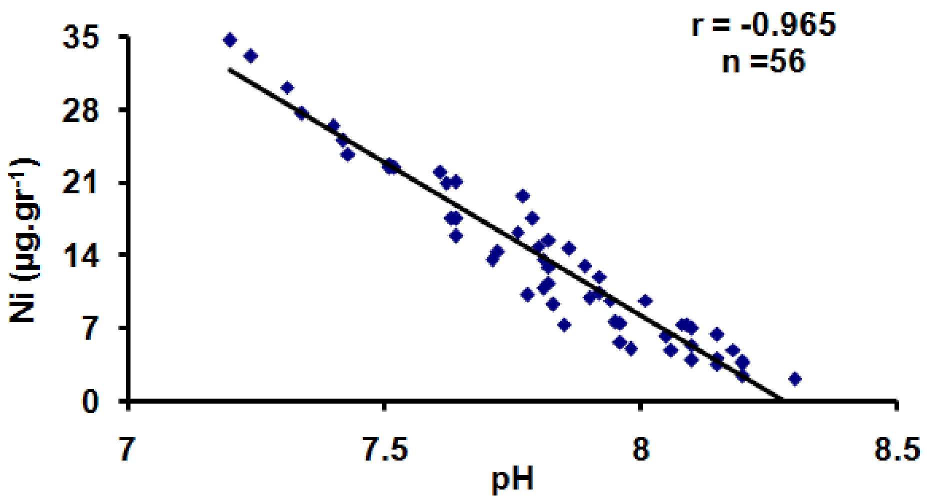


Fig.3. Relation between pH and particulate Nickel in the estuarine waters of Gauthami Godavari during 2013

Relation of particulate nickel with salinity:

Significant inverse correlations were observed between the particulate nickel with salinity in the waters of the Gauthami Godavari (r = -0.86, p <0.001) is shown in Fig. 4.15. It indicates that the particulate nickel behaves non-conservatively in Gauthami Godavari estuary. Nickel may be partially associated with sulphides, (Zwolsman *et al.*, 1997). These nickel sulphides are gradually oxidized during restoration of dissolved oxygen with increasing salinity, resulting in releasing of trace metals to the dissolved phase. At the same time Mn hydroxides which are very effective scavengers of trace metals are also formed. The close relationship between Ni, Co and Mn in the suspended matter of the lower estuary indicates that the Ni, mobilized from the lower estuary but it is scavenged back by Mn oxides. Co-precipitation of Ni with Mn oxides was also formed near the oxic-suboxic interface in salt marshes of the Scheldt estuary as reported by (Zwolsman *et al.*, 1999).

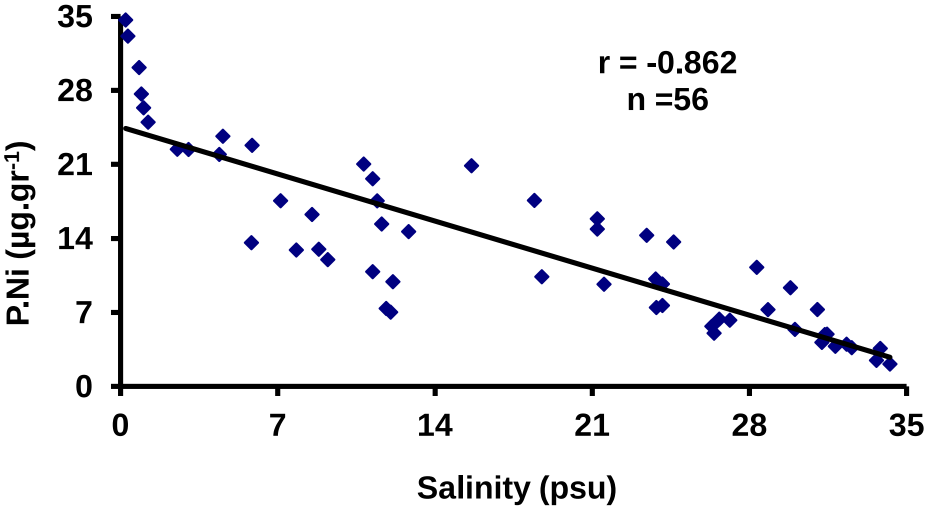


Fig. 4. Relation between particulate nickel with salinity in the Estuarine waters of Gauthami Godavari during 2013

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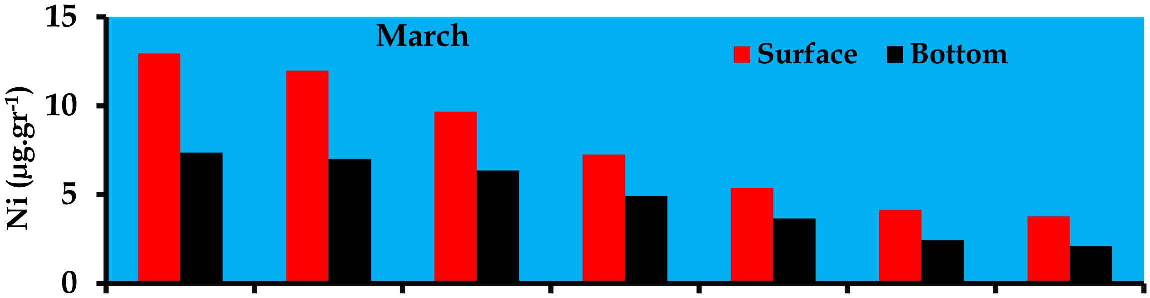
A distinct spatial and seasonal variation of particulate trace metals like iron and nickel were observed in the present study. Relatively higher concentrations of these metals were observed in head of the estuary and low concentrations in mouth of the estuary. Higher concentrations of particulate trace metals like iron and nickel were observed during monsoon season followed by onset of monsoon and post-monsoon seasons, Lower concentrations of these metals were observed during pre-monsoon season. Higher concentrations of all these metals during monsoon season due to the river and land runoff along with domestic and agricultural, industrial effluents are more during this season. Lower concentration during pre-monsoon 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.

St. 1 :Kotipalle; St.2 : Dangeru; St. 3: Yanam; St.4: V.Gauthami;
St.5 :Balusutippa; St. 6 : Mangrove area; St.7. : Bhiravapalem



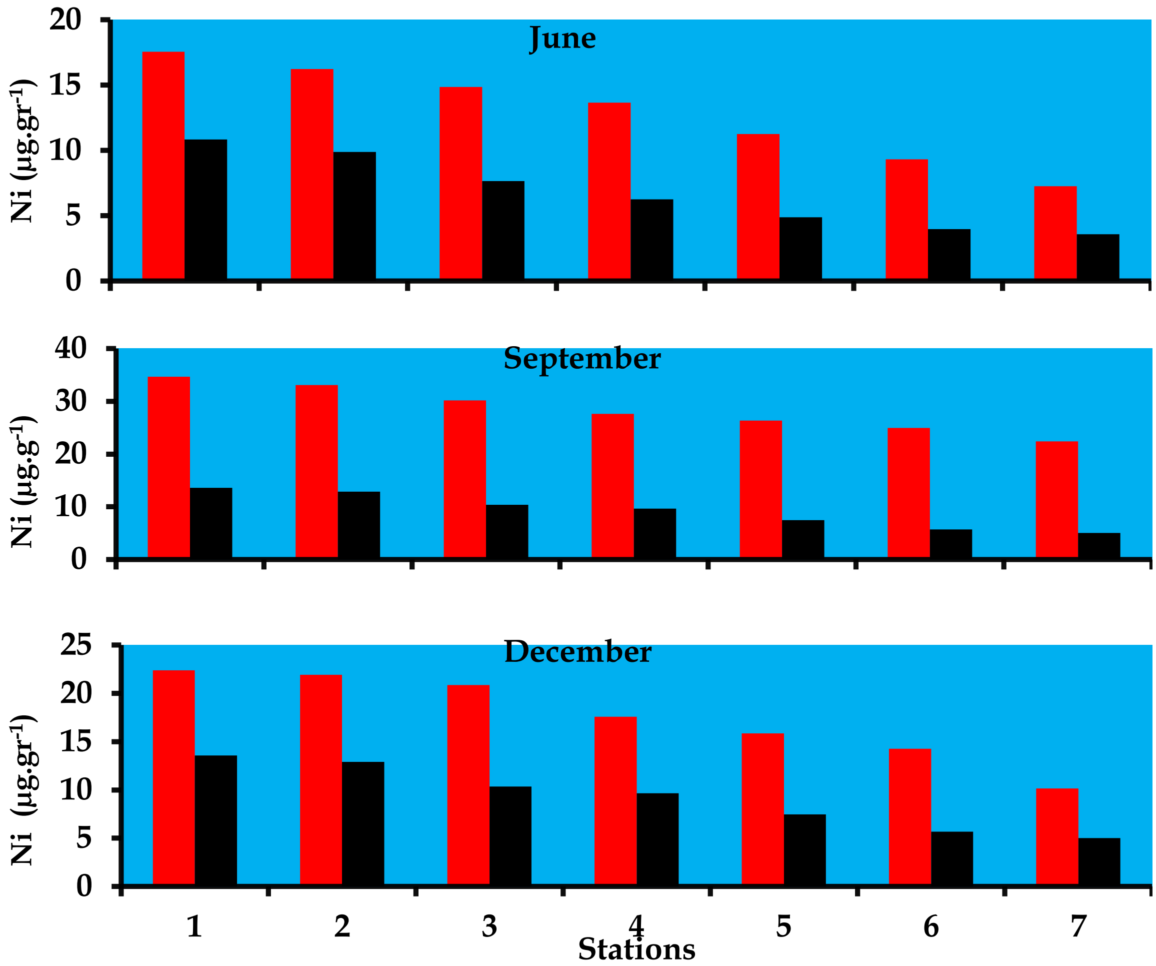


Fig. 4. Seasonal and spatial distribution of particulate nickel in the estuarine waters of Gauthami Godavari during 2013.

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