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Investigating Seasonal Variations of Trace Metals in Particulate Matter: A Study of the Gauthami Godavari Estuary, East Coast of India (Bay of Bengal)

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Abstract The Godavari River, the third largest on the eastcoast of India, drains into the Bay of Bengal, discharging large quantities of freshwater into the coastal water, particularly during the monsoon season. Suspended particulate matter (SPM) has shown an increasing trend from the pre-monsoon to the monsoon season, followed by a decrease in the post-monsoon period in the study areas. The high concentration of SPM observed during the monsoon can be attributed to increased river discharge and land runoff, which carry significant quantities of terrestrial material into the estuary. Distinct spatial and seasonal variations in particulate trace metals have been noted. Understanding the distribution of metals in a monsoon-driven estuary like the Gauthami Godavari is essential for assessing their roles in biogeochemical cycles, their potential accumulation in organisms, and their transfer to humans through the food chain. Until now, there have been no comprehensive seasonal and spatial studies on the distribution of trace metals in the estuarine water of the Godavari. Therefore, this investigation aims to assess the spatial and seasonal distribution of particulate trace metals, specifically Iron, Nickel, Cadmium and Copper in the estuarine water of the Gauthami Godavari.

Keywords: Godavari Estuarine water, Particulate matter, Trace metals

Introduction

The Godavari River receives significant chemical inputs from industries situated along its banks, as well as from agricultural runoff and domestic sewage. These materials travel downstream from the river's source, settling at the river mouth and dispersing into the sea during periods of flooding. As the largest river in South India and the largest estuary on the central east coast of India, the Godavari plays a critical role in the regional ecosystem. Estuaries serve as critical transition zones where continental materials are retained and partially transported to the open sea. The chemical composition and variability of suspended particulate matter (SPM) in these environments are influenced by a complex interplay of physical and biogeochemical processes. Key geochemical factors affecting this variability include the mixing of riverine and marine suspended materials, the flocculation of colloidal substances, and the adsorption and desorption processes occurring in low salinity areas [1, 2]. Additionally, the production of organic matter by phytoplankton, the mobilization of Fe-Mn oxides in reducing sediments, and the resuspension of bottom sediments, further contribute to this complexity [3, 4, 5, 6, 7]. Consequently, research on metal behavior in estuarine waters reveals significant variations across different estuaries. While a few overarching trends have been identified—most notably the removal of iron from low salinity estuarine waters due to flocculation —many studies on particulate trace metals typically rely on limited sampling efforts [8, 9, 10]. Furthermore, the concentrations of particulate metals can fluctuate significantly, driven by varying inputs and seasonal influences that involve biological, geochemical, and physical interactions. Groundwater is susceptible to various pollutants due to its role in the water cycle, which encompasses the atmosphere, ground surface, rocks, and surface water. Over 50% of the global population relies on groundwater for their survival [11]. Toxic elements such as silver (Ag) and lead (Pb) can be harmful even in trace amounts and are often released as effluents from industrial processes [12]. Additionally, reported carcinogenic risks associated with consuming groundwater contaminated by heavy metals in Ogun State, Nigeria [11].

The study area for this research includes various sites along the Gauthami Godavari estuary, each with distinct characteristics:

Site 1 (Kotipalle): Located at the head of the estuary, 41 kilometers from the mouth, this site has minimal tidal activity and primarily fresh water due to low salinity. Surrounding villages and farmland contribute significant human inputs, especially during the monsoon season.

Site 2 (Dangeru): Situated 8 kilometers downstream from Kotipalle, this site is characterized by villages, agricultural land, and substantial fishing activities, with an average depth of 8 meters.

Site 3 (Yanam): Located 22 kilometers from the estuary's mouth, this site experiences considerable household wastewater discharge. Known for its "boat jetty" of anchored fishing boats, it has an average depth of 12 meters and greater tidal influence.

Site 4 (Vrudha Gautami): This site is 5 kilometers downstream from Yanam and features multiple waterways, with an average depth of 6 meters.

Site 5 (Balusutippa): Positioned 12 kilometers from the estuary's mouth, this area includes shrimp and fish farms that discharge wastewater into nearby streams before reaching the estuary.

Site 6: Located in a mangrove forest area, this creek has dense mangrove vegetation and an average depth of 4 meters.

Site 7: Situated at the mouth of the estuary, this site connects to the clean coastal waters of the Bay of Bengal. It is bordered by an oil industry to the north and a mangrove forest to the south, with an average depth of 8 meters.

These diverse sites highlight the varying influences of human activity, freshwater input, and tidal dynamics throughout the Gauthami Godavari estuary [13].

1. Methods

Preparation of metal standards

Stock standard solutions (1000 mg/ml) of the target elements (Cd, Cu, Fe, Ni, Pb, and Zn) were prepared from high-purity metals or their salts by dissolving specific amounts in a 1:1 HNO_3 solution and diluting to a final volume of 100 ml with double-distilled water, ensuring the overall acidity remained at 1N with respect to HNO_3. A working mixed standard solution (5 ppm) was created by combining 5.0 ml of each stock solution in a 1000 ml volumetric flask and diluting to the mark with double-distilled water, again maintaining an overall acidity of 1N with respect to HNO_3. Six samples (1000 ml) of trace metal-free water, prepared as described, were placed in separate 2-liter funnels. Each sample was spiked with 0.0, 0.4, 0.8, 1.2, 1.6, and 2.0 ml of the mixed standard solution (5 ppm) using a calibrated pipette, resulting in final trace element concentrations of 0.0, 2.5, 5.0, 7.5, 10.0, and 12.5 ppb (mg/dm^3), respectively. The pH of each solution was adjusted to between 3 and 4, and they were then transferred to six pre-cleaned 50 ml screw-capped polyethylene bottles. The standards underwent the same treatment as the samples. Each solution was aspirated into the instrument under optimal operational conditions, utilizing the appropriate fuel-air mixture, wavelength, and cathode lamp, with absorbance measurements recorded in Table 1.1. The calibration curves (absorbance versus concentration) established for each element were found to be linear up to 12.5 ppb. The concentrations of trace metals in the samples were determined using these calibration curves, with all metal concentrations reported in mg/L.

Table 1.1: Optimal instrumental conditions for elemental analysis using Atomic Absorption Spectroscopy (AAS).

Element	Wave length (nm)	Flame	Detection limit
Cadmium	228.8	Air-Acetylene	0.001

Copper	324.7	Air-Acetylene	0.010
Iron	248.3	Air-acetylene	0.010
Nickel	232.0	Air-Acetylene	0.009
Lead	283.3	Air-Acetylene	0.030
Zinc	213.0	Air-Acetylene	0.002

Accuracy and precision of analytical methods

The accuracy and precision of the above methods were established by replicate (six) analysis and expressed as standard deviation and percent coefficient of variation (C.V) and standard error using the following equation and the data are incorporated in Table 1.2.

Standard deviation (σ) = $\sqrt{\frac{\sum\left(X_i - \overline{X}\right)^2}{n-1}}$

Coefficient of variation (C.V.) = $\frac{\sigma}{\overline{X}} \times 100$

Standard error (S.E) = $\frac{\sigma}{\sqrt{n}}$

Where Xi represents the 'i' th determined value, $\overline{X}$ is arithmetic mean an 'n' is the number of determinations.

It is evident from the statistical data (Table 1.2) that the methods adopted and the data obtained in the present study are fairly accurate. Further, the deviations obtained in the replicate determinations are within the permissible experimental limits.

Results & Discussion:

Total Suspended Particulate Matter (TSPM):

The station-wise summary statistics on total suspended particulate matter in the estuarine waters of the Gautami Godavari during the study period was given in Table 1.3. The seasonal and spatial variations of TSPM in surface and bottom waters are shown in Fig. 1.1. The TSPM values in the surface waters were in the range of 9.97 to 12500 mg./L with an average of 35.73 mg/L where as in the bottom waters, the TSPM ranged from 6.24 to 49.00 mg./L with an average of 31.03 mg./L .

Table.1.3: Station-wise summary statistics on TSPM (mg/L) in the estuarine water of Gauthami Godavari during 2021

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	12.8	156	85	43.89	23.46	48	39.57	29.32
Dangeru	11.72	141.9	32.65	45.07	12.35	53	52.45	37.41
Yanam	10.58	148.66	85.31	28.11	15.2	32.7	28	23.74
V.Godavari	8.32	78.8	74.76	37.34	30	32.4	28.47	42.67
Balusutippa	16.46	69.4	35.47	43.87	19.3	48.8	59.94	32.41

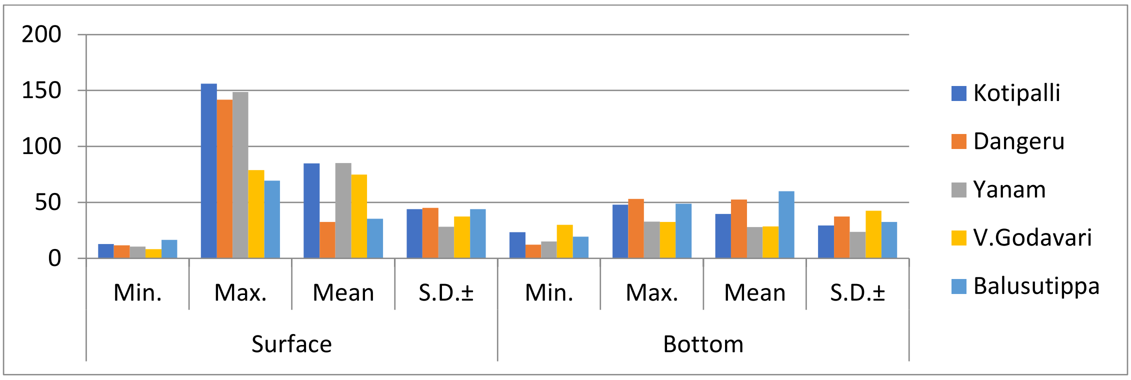

Fig. 1.1

Relation of suspended particulate matter with pH:

Significant negative correlations were observed between suspended particulate matter with pH of the estuarine waters (r = -0.87, p < 0.001). It was observed that the concentration of SPM decreases with increasing in pH of the estuarine waters due to its flocculation at the mouth area of the estuary. An increase in pH was observed during summer and this may be due to associated with photosynthesis of planktonic blooms. The lower pH values were observed during monsoon season due to the higher river discharge (22,456 m^3/sec) holds the domestic sewage having large amounts of suspended matter in the estuary.

Relation of suspended particulate matter with salinity:

Significant negative relation was observed between suspended particulate matter with salinity (r= -0.72, p < 0.001) in the present study. The decrease of suspended particulate matter with increasing salinity is primarily caused by mixing of fluvial matter with marine waters, and also caused by desorption of suspended particulate matter with higher salinities at estuarine mouth area. Similar behavior was also reported in the waters of many tropical estuaries.

Particulate cadmium (µg/L):

Cadmium is the least abundant among the metals studies. The station-wise statistics on particulate cadmium in the estuarine waters of the Gautami Godavari during the study period were given in Table 1.4.

Table 1.4: Station-wise statistics on particulate cadmium (µg/L) in the estuarine water of Gauthami Godavari during 2021.

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	8.23	9.70	7.46	1.66	3.21	5.01	3.94	0.78
Dangeru	6.39	8.85	6.89	1.52	3.01	4.86	3.76	0.82
Yanam	3.25	7.28	5.88	1.14	2.23	4.24	3.31	0.85
V.Godavari	9.56	6.12	5.13	0.82	2.08	3.56	2.88	0.65
Balusutippa	2.96	5.65	4.67	0.92	2.04	2.85	2.38	0.42
Mangrove area	2.62	4.28	3.67	0.75	1.12	2.43	1.96	0.62
Bhiravapalem	1.86	3.28	2.59	0.67	0.88	2.21	1.31	0.61

Particulate cadmium concentrations in surface waters ranged from 1.86 to 9.70 µg/L, with an average of 5.18 µg/L. In contrast, bottom water concentrations ranged from 0.88 to 5.01 µg/L, averaging 2.79 µg/L. Throughout all seasons and stations, higher concentrations of cadmium were consistently observed in surface waters compared to bottom waters. The study found that particulate cadmium concentrations decreased from Kotipalle (the head) to Bhairavapalem (the mouth), likely due to the desorption and solubilization of particulate metals as salinity increases. This phenomenon is common in estuaries, influenced by chloride and sulfate complexation and variations in ionic strength.

Particulate Copper (µg/L):

Copper is essential for healthy growth of plankton, but elevated concentrations can be toxic to marine organisms [14]. Similar to Iron in hemoglobin, copper plays a vital role in the oxygen transport system of animals. Invertebrates use copper in their hemocyanin, which acts as an oxygen carrier. In open ocean waters, particulate copper concentrations typically do not exceed 8 µg/L [15]. However, significantly higher levels can be found in coastal and estuarine waters, especially in areas affected by pollution. A substantial fraction of Cu (II) may exist as complexes with dissolved organic compounds. In this study, particulate copper concentrations in surface waters ranged from 53.68 to 92.32 µg/L, with an average of 32.05 µg/L. In contrast, bottom water concentrations ranged from 8.02 to 45.16 µg/L, averaging 39.46 µg/L.

The station-wise statistics on particulate copper in the estuarine waters of the Gautami Godavari during the study period was given in Table 1.5.

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	22.12	65.32	42.08	12.88	26.16	35.86	34.99	12.55
Dangeru	31.15	55.13	38.12	15.30	31.12	43.25	29.65	18.57
Yanam	20.18	47.38	30.45	18.32	36.02	32.10	42.32	27.86
V.Godavari	42.21	55.46	39.22	21.36	22.10	36.82	35.26	17.83
Balusutippa	24.33	34.16	45.29	19.66	18.36	26.19	25.16	22.75
Mangrove area	45.32	39.25	23.36	22.40	34.12	35.24	32.15	167.94
Bhiravapalem	25.36	35.12	28.31	16.82	26.13	36.12	21.33	27.15

Generally, higher concentrations of particulate copper were recorded during the monsoon season, while lower concentrations were observed in the pre-monsoon season. The elevated levels during the monsoon can be attributed to a combination of land and river runoff, along with anthropogenic inputs of copper. In contrast, the lower values in the pre-monsoon season may result from copper utilization by plankton or the complexation of copper ions with organic matter.

While the increased copper concentrations during the monsoon can benefit plankton growth due to nutrient availability, they also pose risks of toxicity to marine organisms if levels become too high. On the other hand, lower concentrations during the pre-monsoon can indicate a healthier ecosystem, as copper is being utilized effectively, but this may also lead to reduced availability for organisms that rely on copper for essential functions. Balancing these factors is crucial for maintaining the health of marine ecosystems.

Particulate Iron (µg/L):

Table 1.6 presents the station-wise statistics for particulate iron in the estuarine waters of the Gautami Godavari during the study period. Particulate iron concentrations ranged from 253.25 to 5758.80 µg/L, with an average of 2342.26 µg/L. In contrast, bottom water concentrations ranged from 186.68 to 2892.30 µg/L, averaging 953.31 µg/L. Overall, particulate iron concentrations in surface waters were higher than those in bottom waters.

Table 1.6: Station-wise statistics on particulate iron (µg/L) in the estuarine water of Gauthami Godavari during 2021

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	450.50	22788.50	2644.08	2226.87	323.12	3292.25	1222.52	1135.55
Dangeru	382.25	2816.23	3294.79	2515.91	210.27	2958.26	925.69	788.67
Yanam	452.85	4816.23	4194.79	3515.91	410.27	2558.26	912.69	788.67
V.Godavari	277.26	2265.23	3266.37	684.50	502.65	4987.68	853.01	779.17
Balusutippa	289.25	2823.12	1636.67	1588.73	102.15	2635.29	790.57	639.24
Mangrove area	461.75	3777.27	2299.46	2284.42	212.65	588.85	386.83	186.79
Bhiravapalem	343.25	3013.32	855.525	667.60	450.68	3235.26	540.68	430.26

In general, higher concentrations of particulate iron were observed during the monsoon season, followed by the post-monsoon and pre-monsoon seasons. The elevated iron levels during the monsoon can be attributed to the combined effects of land and river runoff, as well as anthropogenic inputs of iron.

Lower concentrations of particulate iron were observed during the pre-monsoon season, primarily due to its utilization by plankton, which are more abundant during this time. Additionally, the precipitation of iron under alkaline pH conditions in the estuary and the flocculation of iron with dissolved organic matter may also explain the reduced iron concentrations in this season.

Particulate Nickel (µg/L):

Nickel occurs principally as Ni^{2+} in surface waters, but oxidation states ranging from Ni^{+1} to Ni^{+4} have been reported from time to time. 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 saline estuaries [16, 17]. Above pH 9 (rarely found in surface waters), the hydroxide and carbonate complexes precipitate.

The station-wise summary statistics on particulate nickel in the estuarine waters of the Gautami Godavari during the study period were given in Table 1.7.

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Kotipalli	24.96	43.65	31.89	12.34	12.36	23.56	16.86	17.01
Dangeru	32.98	33.12	29.85	19.16	17.01	22.97	23.15	26.86
Yanam	19.67	32.15	26.89	18.79	21.35	21.20	13.32	16.66
V.Godavari	27.25	22.65	32.53	21.55	24.93	19.36	21.12	21.65
Balusutippa	15.38	36.34	24.70	28.86	23.65	17.45	28.38	20.31
Mangrove area	34.15	29.98	15.18	16.89	22.45	15.53	21.86	15.81
Bhiravapalem	23.78	19.42	22.90	22.11	31.10	14.36	26.58	25.43

The particulate nickel concentrations in the surface waters were in the range of 4.88 to 54.65 µg/L with an average of 26.70 µg/L where as in the bottom waters, its concentrations ranged from 4.12 to 33.255 µg/L with an average of 25.21 µg/L. The particulate concentrations of nickel in surface waters were higher than that of bottom waters. Seasonally higher concentrations of particulate nickel were observed during monsoon followed by post-monsoon and premonsoon 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 in this season. Lower values of particulate nickel were observed during pre monsoon season due to its precipitation under alkaline pH condition of the estuary, and flocculation with dissolved organic matter.

Conclusions:

Suspended particulate matter (SPM) exhibited an increasing trend from the pre-monsoon to the monsoon season, followed by a decrease in the post-monsoon period in the study area. The elevated concentrations of SPM during the monsoon can be linked to high river discharge and land runoff, which carries substantial amounts of terrestrial material. Generally, SPM concentrations decreased from the head to the mouth of the estuary. This pattern is likely due to the adsorption of particulate matter at the estuary's head and its subsequent desorption at the mouth, influenced by variations in pH and salinity. Notably, SPM levels were consistently higher in surface waters compared to bottom waters. The study also revealed distinct spatial and seasonal variations in dissolved and particulate trace metals (Cd, Cu, Fe, Ni, Pb, Zn). Higher metal concentrations were found at the head of the estuary, with lower levels at the mouth. The monsoon season had increased concentrations of both dissolved and particulate trace metals, followed by the onset and post-monsoon periods, while pre-monsoon concentrations were lower. The higher metal levels during the monsoon can be attributed to river and land runoff, as well as increased domestic, agricultural, and industrial effluents. The reduced metal concentrations observed in the pre-monsoon season may result from biological uptake and various chemical and physical processes such as desorption or flocculation, driven by rising pH and salinity. This was further supported by significant negative correlations between both dissolved and particulate metals and pH and salinity, alongside significant positive correlations between metal concentrations and nutrients, indicating that they likely originate from similar sources.

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