

Assessment of Pollution and Ecological Risk Index of Heavy Metals in the Surface Sediment of Estuary and the Coastal Environment of Bay of Bengal

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ABSTRACT. The Mahanadi River, surrounding estuaries along the coastal water are important to understand the relationship between heavy metals, ecosystem and human health, as the region being used largely by fisher communities for the potential fishing ground and agriculture. The study evaluates the ecological risk index of heavy metals in the surface sediments along the coastal environment of the Bay of Bengal between 2011 and 2012. The metals concentrations were varied from a maximum in Manganese (4,137 mg/kg) to a minimum in Cadmium (17 mg/kg). The factor analysis result shows that higher concentration of cadmium (Cd), chromium (Cr), Nickel (Ni), lead (Pb), and Zinc (Zn) were significant environmental risk in the study region. The cluster analysis indicated that the creek sediment is heavily polluted than the estuary ecosystem of the coastal environment. Enrichment factor and Geo-accumulation Index of the surface sediment resulted that, the Cd was high enrichment and was moderate to severe in the study region. Pollution load index denoted that the sampling sites in the creek sediment were more polluted than coastal due to the influence of agricultural runoff, industrial and anthropogenic. The Cr, Cu, Ni, Pb, and Cd concentrations result in the potential toxicity to the aquatic organisms based on the comparison with the SQGs. Indicates the average magnitude of the metals in the study period in the decreasing order of Mn, Cr, Cu, Ni, Pb, and Cd which were alarming except iron (Fe) in the estuary and coastal ecosystem of the Bay of Bengal. The present investigation would be a first-hand informant to understand the impact of heavy metals in the ecosystem in the region. The result inputs need to be monitored further in the long term basis for isotopic sediment dating to reconstruct the contamination history for the ecosystem modeling, sustainable ecosystem, and coastal zone management.

Keywords: estuary, heavy metal, pollution index, ecological risk, sediment quality

1. Introduction

Over the past few decades, anthropogenic heavy metal pollution is an alarm condition worldwide for the health of the river, estuary and coastal environment (Ra et al., 2014). Heavy metals pollution into the coastal environment, mostly due to the natural and anthropogenic sources through agricultural runoff, discharge of industrial waste, municipal and domestic wastewater (Satpathy et al., 2012; Yang et al., 2012; Ra et al., 2014). In general, heavy metals are toxic, non-biodegradable in the sediments, and it impacts the biota, the food chain links to the long-term ecosystem vulnerability to the river, estuary and coastal environment (Prange and Dennison, 2000; Sundaramanickam et al., 2016). The sediments of river and estuary play an important role in the re-mobilization of contaminants under positive impact through the interaction of the water column (Ikem et al., 2003). The sediments of rivers, estuaries act as primary reservoir and sink of metals and other pollutants by var-

ious physical-chemical processes (Förstner and Muller, 1974). While a large portion of heavy metal input accumulates in the coastal environment through a river/estuary discharges as the dissolved metal into the fine particles carried out to the sediment (Ra et al., 2014). The marine ecosystem has been found more than 90% load of heavy metals in the sediments (Ra et al., 2014; Zahra et al., 2014). Among the various sizes of the sediments, the average sediment known as grain size plays a major role in the distribution of trace metals in the river, and coastal environment (De Gregori et al., 1996). The heavy metal at highest concentrations found in fine-grained size particle elsewhere, such as clay-silty because of an increase in specific surface properties of this fraction (Cauwet, 1987; De Gregori et al., 1996). Therefore, the monitoring of the metal concentrations and periodic investigations of trace metal distributions to assess the temporal changes of riverine pollutant loads and their associate environmental impacts on large estuaries and coastal ecosystems.

The Mahanadi River is the major river in east-central India and the largest in Odisha. It drains an area of around 141,600 square kilometres (54,672 square miles) and has a total course of 858 kilometres, deposits more silt than any other river in the Indian subcontinent and the third-largest in the peninsula of

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India. The river serves as a major source of the domestic water supply to the cities of the Cuttack, Sambalpur and Paradip and about 0.85 million people depend on this river (Sundaray et al., 2011). Apart from this, a large number of rural and minor urban settlements have been established on the river bank. The river also acts as the primary source of fisheries and agricultural irrigation in the state of Odisha. Major industrial establishments such as Mahanadi Coal Field Ltd., Jagatpur Industrial Estate, Paradeep Phosphates Limited (PPL), and Indian Farmers Fertilizer Cooperative Limited (IFFCO) discharge their effluents into this water body. Fishing harbour activities, municipal sewage, and materials handling in Paradip Port further contribute to the pollution of the water as well as the sediment (Raj et al., 2013).

The investigation attempts to measure the pollution and ecological impact of heavy metals from the surface sediment of the river, estuarine and coastal ecosystem, east coast of India. Several studies have been carried out to understand the role of different urban and industrial effluents upon the water quality of Mahanadi River and the coastal ecosystems (Panda et al., 2006; Sundaray et al., 2006, 2011). A few studies were observed on the basin geology of Mahanadi River (Chakrapani and Subramanian, 1990), geochemical speciation and metal pollution in Mahanadi River, pollution load from industrial and agricultural areas (Sundaray et al., 2006, 2009, 2011). However, the complete study on the metal pollutions in the surface sediment and its impacts on the ecosystem of rivers, estuaries and coastal environment is scanty in the region. Hence, the present study attempts to determine (1) the spatiotemporal variation of heavy metal contaminations in the surface sediment of Mahanadi River, estuary and the coastal environment by using different types of pollution indices and (2) the assessment of the ecological risk measurement in the sediment, compared with

the sediment quality guidelines (SQGs) to sustain the ecological ecosystem in the region. The result would help to develop the baseline data information from two years data and elucidate the estuarine and coastal management. Further inputs can be used for the decision making and policyholders to understand the pollution monitoring for health and protecting the ecological biodiversity of the study region.

2. Materials and Methods

2.1. Study Area

Mahanadi River is the biggest river on Odisha coast in the Bay of Bengal, and it is extended over a zone about 141,600 km². It has a total length of 851 km and an annual runoff of 50×10^9 m³/s with a peak discharge of 44,740 m³/s (Chakrapani and Subramanian, 1990), and it is estimated almost 4.3% of the total geographical area of the country. The annual average rainfall was 150 cm with 85% occurred during the southwest monsoon (Swain, 2014). All tributaries of the river Mahanadi congregate as the mouth of the Bay of Bengal, as shown (Figure 1). The surface sediment samples were collected from fourteen stations in and around the Mahanadi estuary and coastal regions from three different seasons (Summer, Post-monsoon and Winter) used a mechanized boat during 2011 and 2012. The investigation was carried out for studying the pollution level of estuary and coastal region, as the fisherfolk of localities had reduced relatively their fish catch before the study period. The sampling locations were divided into five separate regions such as Mahanadi River (MR1 and MR2), Atharabanki creek (AB1 to AB4), Mahanadi Fishing Jetty (MNFJ), Mahanadi estuary (ME) and Coastal region away from the shore 1, 5, and 10 km (MC-1 to MC-3 and PDC-1 to PDC-3), as shown in the map (Figure 1).

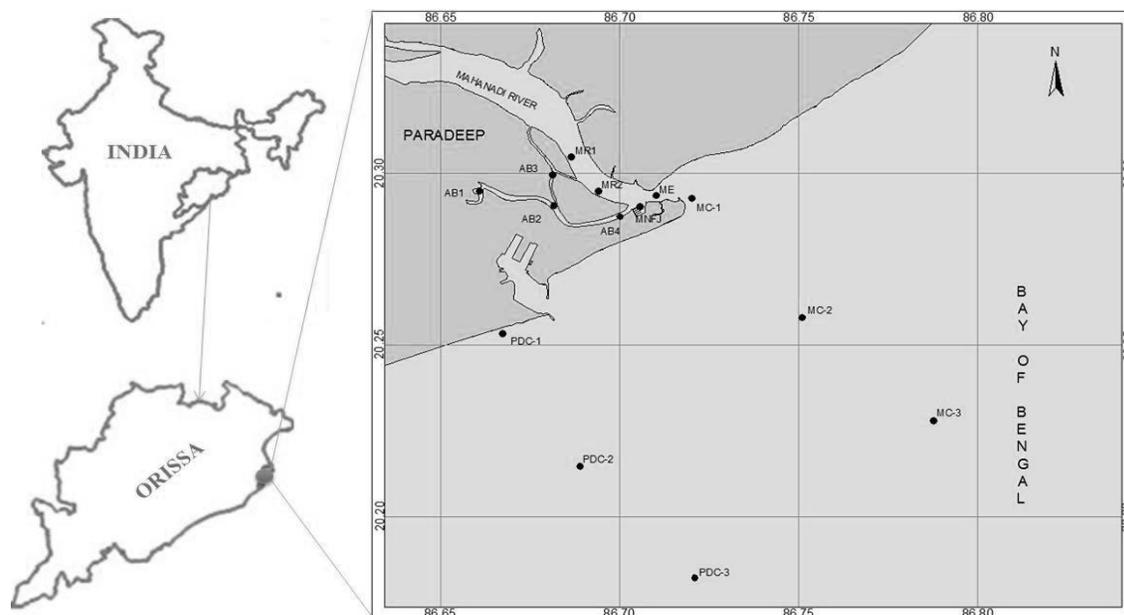


Figure 1. Location of the study area in the Mahanadi River, estuary and coastal environment of the Bay of Bengal during 2011 and 2012.

2.2. Analysis Technique

Sediment samples were collected from all sampling locations using a Van Veen grab and stored in clean polyethylene bags with labelled identifications and brought to the laboratory for further analysis. Before analysis, the samples were well air-dried at room temperature. The samples (~ 50 g) were taken for the grain sizes (sand, silt, and clay) and analyzed for the purpose. Samples were then treated with 35% H₂O₂ and 1N HCl to remove organic matter and carbonate respectively, for further analysis (Andel and Postma, 1954; Jensen et al., 2017). After the treatment, the sediment samples were wet sieved through 230 mesh (0.0625 mm) followed by American Standard Test Sieve Series (ASTM) for the separation. The size analysis of very fine particles (silt and clay) was carried out by the pipette analysis method (Krumbein and Pettijohn, 1961; Switzer, 2013). For the organic carbon (OC) estimation some parts of the sediment samples were oven-dried at 60 °C and powdered with the grinder (Retsch, RM100) followed by Walkley and Black method (Krishan et al., 2009). For the heavy metal analysis the finely powdered sediment samples of 1 g were digested in a mixture of HF-HClO₄-HNO₃ (Loring and Rantala, 1992; Selvam et al., 2012). The Complete digestion was confirmed by repeating the acidification method until a clear solution was obtained to 0.5 M HCl (25 ml). Then samples were analyzed on a flame of atomic absorption spectrophotometer AAS (Analyt 100 Perkin Elmer) after proper calibration with standards. For the cadmium analysis, a Graphite-AAS (ZL 4110 Perkin Elmer) was used. The mercury was determined using the Cold Vapour Atomic Absorption Spectrophotometer (CVAAS) following the standard procedure (USEPA, 1983). The accuracy of the analytical method was estimated considering a triplicate sample using certified reference method (NIST) and standard deviations (SDs).

2.3. Statistical Analysis

The Statistical analysis data were presented in this study area, based on the average of three seasons data sets including error values, explained along with the mean values. The data sets were represented with a 95% confidence label interval. The software SPSS 17.0 was used for the statistical analyses.

Factor analysis (FA), includes principal component analysis (PCA), is one of the most powerful and common techniques used for reducing the large number of variables into a fewer number of factors without losing the original data information (Wunderlin et al., 2001). They follow the general linear model (GLM) forms a linear relationship, where the different variables correlate to the factors. Out of several methods in FA, the PCA is one of the methods, which commonly used for principal component analysis. In the FA, the data results from correlation matrix consider and reorganize them into an order to explain in a structure for principal system produced into a data. The factors, which best explain the variance of the analyzed data (eigen value > 1) and reasonably interpreted, are accepted for further analysis. On the other method of FA also called varifactors (VF), extracted by the PCA, the Varimax rotation was then performed to secure increased principal components of environmental significance.

Cluster analysis (CA) is an unsubstantiated sample detection method that find outs fundamental structure or elemental behavior of a data set without making prior hypothesis about the data, in order to organize the objects of the system into clusters or groups based on their closeness or resemblance (Vega et al., 1998). Hierarchical agglomerative CA was executed on the standardized data set by means of the Ward's method, using squared Euclidean distances as a measure of similarity. The dendrograms generated in CA provides a useful graphical tool determining the number of clusters which describe fundamental process that lead to spatial variation (Sahu et al., 2013). This resulted in the relationship between the heavy metals and different sampling locations to understand its sources (Sahu et al., 2013; Sundararajan et al., 2017).

2.4. Metal Pollution Index

The degree of metal contamination assessment was estimated by various methods based on the average shale values (Müller, 1969; Forstner and Wittmann, 1983). To understand, evaluate and compute the level of the contaminations of heavy metals in the sediment samples were used by many pollution indices such as enrichment factor (*EF*), contamination factor (*CF*), pollution load index (*PLI*), and geo-accumulation index (*I_{geo}*). These indices were intended to use average shale values of metals to measure the degree of pollution level (Turekian and Wedepohl, 1961). The standard contamination factor (*CF*) in river and coastal water is estimated as follows: *CF* < 1 is low; 1 ≤ *CF* < 3 is moderate; 3 ≤ *CF* < 6 is considerable; *CF* ≥ 6 is very high (Hakanson, 1980; Chandrasekaran et al., 2015). The *CF* and degree of contamination were calculated as given below:

$$CF = C_m / B_m \quad (1)$$

$$C_{deg} = \sum \{C_m / B_m\} \times I \quad (2)$$

where *C_m*: measured concentration in water, *B_m*: local background concentration within the actual study area.

Similarly, the enrichment factor (*EF*) is estimated as follows: *EF* < 1 is no enrichment, 1 ~ 3 is minor; 3 ~ 5 is moderate; 5 ~ 10 is moderately severe; 10 ~ 25 is severe; 25 ~ 50 is very severe and > 50 is extremely severe. He reported that the natural mineralogical and granular variability was best compensated by the geochemical normalization of major and trace metal data. The following equation is being used to estimate the *EF* of metals from each sediment stations using Fe as a normalized to correct for differences in sediments grain size and others:

$$EF = (M_e / F_e) \times sample / (M_e / F_e) \times crustal average \quad (3)$$

where (*M_e / F_e*) sample known as: metal concentration in the sediment with respect to *F_e* and (*M_e / F_e*) crustal average known as: metal concentration of crust average values on *F_e*. The crustal average value is considered from the standard calculation followed by (Turekian and Wedepohl, 1961).

For the estimation of geo-accumulation index (I_{geo}) followed the standard method (Müller, 1979). Which the entire assessment has been classified into seven categories (0 ~ 6), i.e., background concentrations to evaluate very heavily polluted, (Class 0: Less than 0) is a background concentration; (Class 1: 0 ~ 1) is moderate; (Class 2: 1 ~ 2) is moderately polluted; (Class 3: 2 ~ 3) is a moderate to high polluted; (Class 4: 3 ~ 4) is a heavily polluted, (Class 5: 4 ~ 5) is a highly to very highly polluted, (Class 6: 5 ~ 6) is a very heavily polluted. Based upon this elsewhere the similar result has been found in the river, estuary and coastal water (Kumar and Edward, 2009; Chandrasekaran et al., 2015; Shang et al., 2015; Sundararajan et al., 2017). The geo-accumulation index (I_{geo}) was used to assess metal pollutions in the sediments and the equation was given below:

$$I_{geo} = \text{Log}_2(C_n / 1.5 \times B_n) \quad (4)$$

where C_n is measured the concentration of heavy metal in the sediment, B_n is the geochemical background value in average shale (Turekian and Wedepohl, 1961) of element and 1.5: the correction in the factor of background matrix due to lithogenic effects.

The assessment of the contamination extent by metals in sediments was further calculated using the Pollution Load Index (Tomlinson et al., 1980), which results in the cumulative indication of the overall level of heavy metal pollution in the particular sample. Pollution Load Index (PLI) has been calculated for the area under investigation for considering the least toxicity by the most prolific metals (Fe). The PLI is evaluated using below the equation (Tomlinson et al., 1980):

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \dots \times CF_n} \quad (5)$$

(CF = contamination factor and n = number of metals)

2.5. Ecological Risk Index

The several indices were applied to assess the ecological risk of heavy metal contamination known as the chemical speciation of the heavy metal in the sediment. Sediment quality guidelines (SQGs) were introduced to estimate the trace metal contaminations in sediment that cause risk to an aquatic organisms and the ecosystems (Long et al., 1995; Sundararajan et al., 2017). It consists of a threshold effect level (TEL), probable effect level (PEL), effect range low (ERL), and effect range median (ERM). The TEL is below which adverse biological effects were not expected to occur and PEL is an adverse biological effect was projected to occur more often than there is no unpleasant effect occur. As per the SQGs the degree to which the sediment-associated chemical status, adversely affected aquatic organisms and ecosystems, understands in the interpretation of sediment quality (CCME, 1995). Such SQGs were successfully used in designing the monitoring plans, interpreting historical data, conducting remedial investigations, including the developing sediment quality remediation objectives (Jahangir et al., 2015).

In the present study to understand and assess the ecological status of the aquatic environment of the region, the metal concentrations of Cr, Cu, Ni, Cd, Zn, and Pb in the sediments were compared to the numerical sediment quality guidelines such as effect range low (ERL), effect range medium (ERM), threshold effect level (TEL) and probable effect level (PEL) as followed (Long et al., 1998; MacDonald et al., 2000). The concentration of samples below the ERL and TEL values were considered as nontoxic, below ERL and above than TEL were considered as rarely toxic and above than ERL and PEL values were considered as potentially toxic (Sundararajan et al., 2017).

3. Results and Discussion

3.1. Sediment Texture

The physical-chemical process of transportation and deposition in the estuary and coastal body primarily was influenced the sedimented nature and particle size. The spatial and seasonal variations of texture quality (Mean \pm SD) in the Mahanadi estuary, and coastal sediment were presented in Table S1 and Table S2. The average percentage of the sand fraction (99.30%) found highest along the Mahanadi River during winter season followed by Mahanadi coastal, estuary and creek sediment (Figure 2). The highest silt fraction (19.52%) was observed in the Mahanadi coast during the winter and the least fraction (0.15%) was in river sediment during post-monsoon due to low energy and heavy flow of freshwater carrying from the upstream to estuary than coastal (Hossain et al., 2014). The average percentage of higher clay value (57.90%) was recorded in creek sediment during summer 2012. The sand and clay fraction were consistently dominated in the summer (Figure 2). The Atharabanki Creek sediment was the higher clay content followed by the estuary, coastal and river (Figure 2). Among the textural compositions, sand particle was dominated (> 90%) in 2011 and 2012 followed by silt and clay fraction in the ecosystem during the study period (Raj et al., 2013). It was observed that the size fractioned samples of lower dimensions present larger pollutant concentrations to their higher specific area (De Gregori et al., 1996). The gradual reduction of grain size towards downstream of the river sediments were considered to be the progressive decrease of river transporting capacity, and hence the reduction size in downstream current side drawing transportation is almost axiomatic (Seetharamaiah, 1989). It was concluded that the downstream grain size reduction in Mahanadi River sediment, due to the presence of Hirakud reservoir at the upstream of the study area (Sundaray et al., 2006).

3.2. Sediment Organic Carbon (OC) and Organic Matter (OM)

During 2011, the annual average of organic carbon (OC) concentration varied from 0.82 to 6.76% and the organic matter (OM) from 1.23 to 11.65%. Similarly, the organic carbon 0.81 ~ 6.46% and organic matter 1.40 ~ 11.14% in 2012 (Figure 2). The OC (7.09%) and the OM (12.21%) were found higher in the Creek and estuarine sediment during winter followed by summer and post-monsoon (Figure 2) due to the litterfall from mangroves and anthropogenic inputs from the township in the

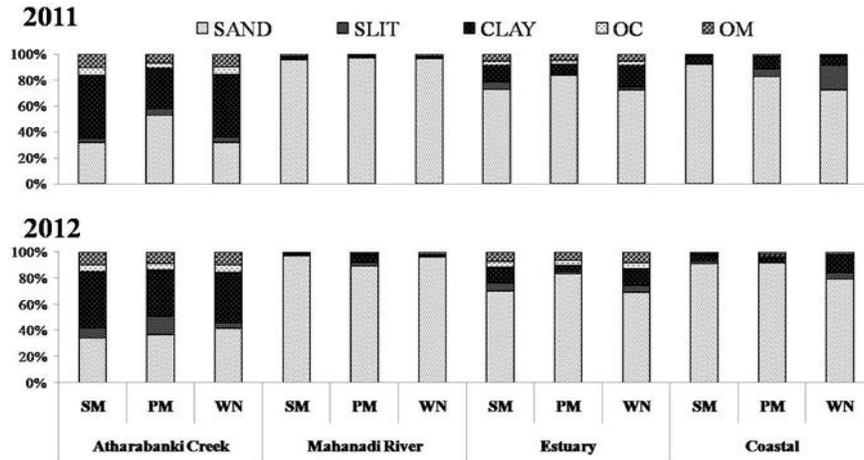


Figure 2. Seasonal and spatial variation of texture quality in Mahanadi estuarine and coastal environments.

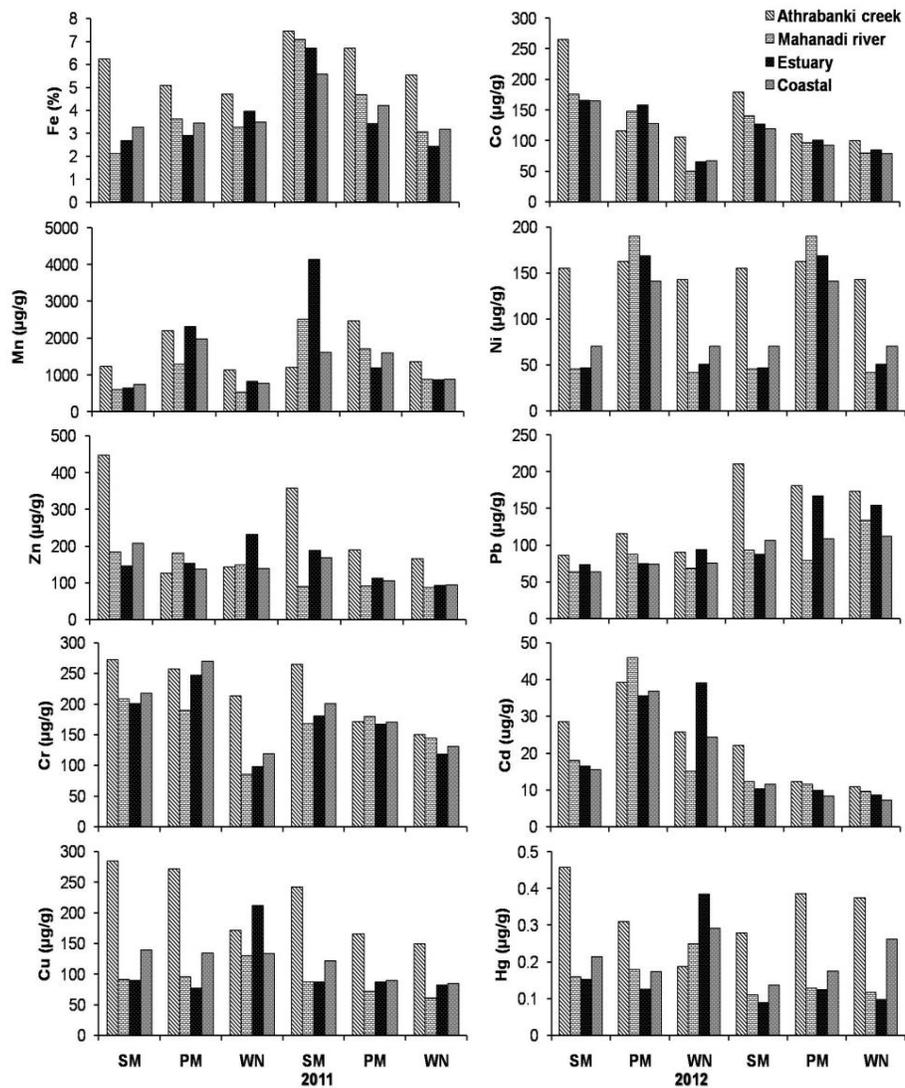


Figure 3. Seasonal and spatial variation of heavy metals in Mahanadi estuarine and coastal environment. (AB: Atharabanki creek, MR: Mahanadi River, ME: Estuary, CS: Coastal; SM: Summer, PM: Post Monsoon and WN: Winter.)

study region (Hossain et al., 2014). A higher percentage of OM observed at Atharabanki Creek in the systems during the sampling periods, probably owing to the influx of high organic load from the sewage of Paradip Port Township and Cuttack town (Jameel, 2001). High concentrations of OM can also result in low levels of decay, associated with anaerobic metabolic processes (Hossain et al., 2014). There is no significant change during the study period. The textural parameter plays a significant role in the distribution of OM, as the clay was an excellent adsorbing capacity of OM (Kemp, 1971).

3.3. Trace Metals

The seasonal and spatial distribution of heavy metals concentrations (Mean \pm SD) in the Mahanadi River, creek, estuary and coastal sediments during the study period are presented in Table S3 and Table S4. The variations of trace metals were found along with the minimum in cadmium (17 mg/kg) and maximum in manganese (4,137 mg/kg) as shown in Figure 3. The magnitude of heavy metals was observed in a decreasing order such as Fe > Mn > Cr > Zn > Cu > Co > Ni > Pb > Cd > Hg in 2011, and similar trends of Fe > Mn > Cr > Zn > Pb > Ni > Cu > Co > Cd > Hg in 2012. In the study area, the percentage of iron was found higher (7.44%) during 2012 compared to 2011 (Figure 3). This distribution could be the impact of the effluent load from fertilizer plants and anthropogenic input from Paradip port township. Its concentration was always greater than that of the river in the sediments in the study period during summer and post-monsoon (Figure 3). The results trend was found similar to that earlier reported elsewhere (Sundaray et al., 2011). This has been predicted due to weathering of ferruginous laterite and transports the products through freshwater river discharges which might have resulted in an increase in the iron concentration during post-monsoon followed by summer and winter (Padma and Periakali, 1999). In the system at the study region, it is observed that a decreasing trend of iron concentrations from coastal to towards the offshore, because of the increasing effect of salinity and impacts of anthropogenic input from Township into the Mahanadi estuary (Sholkovitz, 1987). The highest concentrations of manganese (Mn) were found (4,137 mg/kg) in summer, followed by post-monsoon and winter in the study area during 2012 (Figure 3). The Mn concentration was found higher in 2012 compared to 2011. The increasing trend of manganese concentration was noticed in upstream and estuary stations nearby major urban settlement irrespective of all seasons. In Mahanadi estuary, the Mn concentration was found decrease in coastal sediments because of the decreasing oxidative precipitation. The seasonal variation showed that Zn concentration was the maximum (448.5 mg/kg) during the summer season (Figure 3) in 2011 compared to 2012, maybe on account of the input of more terrigenous materials collected from its river discharges. An increasing concentration of Zn was recorded in the downstream channels, which may be the accumulation of terrigenous materials coming through anthropogenic drainages. In the study area, the input of organic waste into the estuary, which come from municipal sewage and fertilizer plants, significantly contributed of enhanced Zn concentration in the sediments (Alagarsamy, 1991).

The Chromium (Cr) concentration was marginally higher during 2011 compared to 2012 (Figure 3). In 2011 the concentration Cr was observed higher (330 mg/kg) in the coastal sediment during post-monsoon, but during summer it was highest at Atharabanki creek sediment in 2012. Overall, the highest Cr concentration was found in Atharabanki creek followed by the river, estuary and coastal sediments due to the anthropogenic impact. The highest values of copper (Cu) were recorded in Atharabanki river (283 mg/kg) during summer in 2011, while the lowest concentrations were recorded in coastal locations (43.67 mg/kg) during the winter in 2012 (Figure 3). The seasonal average of Cu concentration was found to be decreasing trend from the river towards the sea. However, it was (except Atharabanki) shown an increasing trend from summer to winter period (Figure 3), possibly due to the combined influence of the agriculture, wastewater runoff, and industrial activities (Sundaray et al., 2011).

Table 1. VARIMAX Rotated Factor Analysis for Texture and Heavy Metals in the Mahanadi Estuarine and Coastal Environment, 2011

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Sand	-0.89	-0.06	-0.10	0.00	0.43
Slit	0.08	-0.12	-0.15	0.05	-0.95
Clay	0.95	0.10	0.16	-0.02	-0.13
OC	0.93	0.21	0.23	0.08	0.05
OM	0.93	0.21	0.23	0.08	0.05
Fe	0.73	0.29	0.35	0.22	0.08
Mn	0.11	0.88	0.10	-0.25	0.06
Zn	0.28	0.15	0.87	0.27	0.04
Cr	0.22	0.45	0.38	-0.72	0.06
Cu	0.65	0.30	0.38	0.37	0.16
Co	0.29	0.19	0.84	-0.14	0.16
Ni	0.47	0.71	0.32	-0.01	0.10
Pb	0.59	0.41	0.07	0.50	0.24
Cd	0.18	0.88	0.11	0.23	0.04
Hg	0.31	0.08	0.32	0.81	-0.10
Total	7.68	2.23	1.56	1.16	0.81
Variance %	51.22	14.89	10.37	7.72	5.37
Cumulative %	51.22	66.10	76.47	84.19	89.56

The highest concentration of cobalt (Co) was found in Atharabanki creek in the summer followed by the Mahanadi River, estuary and coastal surface sediment during the study period. The Co concentration recorded the highest (265.8 mg/kg) in summer and showed an increasing trend towards post-monsoon and winter (Figure 3). The concentration of Co was higher in 2012 compared to 2011 and was elevated in post-monsoon at Mahanadi River followed by the estuary, Atharabanki creek and coastal area. The cadmium (Cd) was a higher concentration in the Mahanadi River (45.9 mg/kg) due to the effluent discharge from fertiliser plants. It was recorded maximum in 2011 compared to 2012 in the study area. In sediments, the concentration was observed elevated in winter followed by post-monsoon and summer (Figure 3). The concentration of Cd was shown a decreasing trend toward the open seawater, which

could be due to the influence of urban settlement near the study area. One of the major sources of Cd in the sediment was phosphatic fertilizers due to the presence of urban and Phosphate Limited plant, which might be a source for the study region. The nickel concentration (Ni) observed decreasing trend from post-monsoon to summer (Figure 3). Its levels in the Atharabanki creek, Mahanadi River, and coastal sediments were higher values than Cu, but lower than Zn. The annual average of Ni concentration was higher recorded in 2011 followed by 2012 in the surface sediments. Indicated, the concentration could be due to the anthropogenic and industrial activities in the study area. The seasonal variations of lead (Pb) concentrations were higher during summer, followed by post-monsoon and winter (Figure 3). The highest value of Pb was recorded in Atharabanki creek (210 mg/kg) irrespective of the seasons, in the summer during 2012, mostly attributed to anthropogenic inputs from the Paradip Township, and the atmospheric deposition of aerosols containing Pb from the nearby highway of Paradip town. During seasonal, the mercury (Hg) concentration was found high values in surface creek sediment followed by the river, estuary and coastal (Figure 3). This disputation might be ascribed to waste incineration. The higher concentration of Hg was recorded at the Atharabanki creek (0.39 mg/kg) and the concentration was elevated in post-monsoon during 2012 compared to 2011.

Table 2. VARIMAX Rotated Factor Analysis for Texture and Heavy Metals in the Mahanadi Estuarine and Coastal Environment, 2012

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Sand	-0.29	-0.90	-0.01	-0.14	-0.23
Slit	0.09	0.80	0.23	0.15	0.31
Clay	0.32	0.88	-0.04	0.14	0.21
OC	0.49	0.85	0.05	0.04	0.02
OM	0.49	0.85	0.05	0.04	0.02
Fe	0.60	0.48	0.46	0.24	0.09
Mn	0.28	-0.02	0.94	0.01	0.00
Zn	0.82	0.28	0.17	0.36	0.22
Cr	0.43	0.15	0.03	0.85	-0.10
Cu	0.71	0.46	0.06	0.28	0.28
Co	0.77	0.25	0.34	0.36	0.08
Ni	0.77	0.41	0.35	0.21	0.08
Pb	0.87	0.33	0.09	-0.04	0.10
Cd	0.88	0.28	0.19	0.26	0.03
Hg	0.22	0.48	0.00	-0.12	0.80
Total	9.75	2.08	0.94	0.63	0.46
Variance %	65.03	13.84	6.29	4.17	3.08
Cumulative %	65.03	78.87	85.16	89.33	92.41

3.4. Statistical Perspectives

3.4.1. Factor Analysis (FA)

Factor loading larger than 0.4 was considered statistically significant (Heidam, 1982). The factor was extracted from five basic components (F1 ~ F5) with eigenvalue > 1, accounting for 89.56% of the total variance during 2011 (Table 1). Factor 1 was accounted for 51.22% of the total variance with the significant positive loading towards clay, OC, OM, Cu, Ni, and

Pb. The strong loading of clay and OC along with these metals in the first factor were evaluated that the inflation of fine-grained minerals and organic matter on the distribution of heavy metal in the sediment (Zhuang and Gao, 2014). Factor 2 was elucidated 14.89% of the total variance in the study region along with positive loadings of Mn, Cr, Ni, Pb and Cd is indicated their sinks/source properties. A similar pattern of metal loading was observed during the year of 2012, with 92.40% of the total variance (Table 2). Factor 1 was explained that 65.02% with strong positive loading found all most all the metals (except Mg and Hg) with clay and organic carbon. While, Factor 2 was accounted for 13.84% of the total variance in the region with strong loading of silt, clay, OC, OM, Fe, Cu, Co, and Hg. This analysis clearly shows that the grain size of these metals is with dominant controlling factors like OC and Fe oxyhydroxides (Selvam et al., 2012). Factor 1 revealed that the accumulation pattern of metals was mainly from terrestrial sources. Factor 2 explained that they were from terrestrials' input, agriculture runoff, and anthropogenic sources.

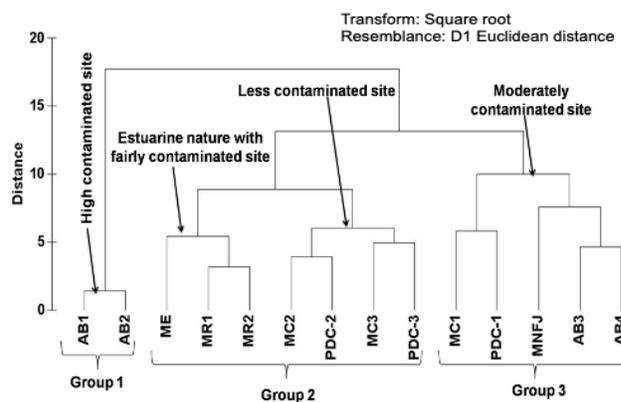


Figure 4. Cluster diagram showing the Euclidean distance between sampling stations during 2011.

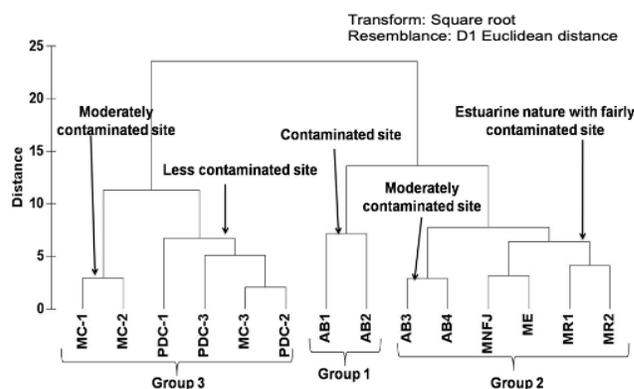


Figure 5. Cluster diagram showing the Euclidean distance between sampling stations during 2012.

3.4.2. Cluster Analysis (CA)

Hierarchical Cluster Analysis is mostly used for environmental analysis to identify the group of samples, as per their similarity. The result of the study site based on the data of metal

concentrations was observed during 2011 and 2012 (Figure 4 and Figure 5). During 2011, cluster showed three groups such as Group-1: AB1 and AB2 (Creek) highly contaminated, in the Group-2, the locations ME, MR1, MR2 were estuarine in nature with fairly contaminated sites, and the stations MC2, MC3, PDC2, PDC3 were less contaminated. In the Group-3, the stations MC-1, PDC-1, MNFJ, AB3, AB4 were represented moderately contaminated sites in the study area. Similarly, in 2012 in Group-1, AB1 and AB2 sites (Creek) were indicated maximum pollution and in Group-2, the sites AB3 to AB4 indicated moderate pollution and the sites MR1, MR2, MNFJ, ME were identified as estuarine in nature with fairly polluted. In Group-3, the locations from MC-1 to MC-2 were moderately polluted, stations MC3, PDC-1 to PDC-2 represented moderately polluted, and was represented less contaminated relatively in the river, estuary and coastal of the study region. Therefore, it was accomplished that the heavy metals contamination was mostly contributed from agriculture, river runoff and anthropogenic sources such as urban sewage, industrial effluent discharge from townships and two fertilizer industries in the study area.

3.5. Metal Index Analysis

3.5.1. Contamination Factor (CF)

The pollution grade CF values in the surface sediments were presented in Figure S1. The estimated CF values of Mn,

Fe, and Hg were > 1 which indicated refusal contaminations. The CF for Zn, Cr, Pb, and Cu < 6 indicated a moderate degree of contamination. The Cd magnitude was observed higher than 6, indicated very high CF (Hakanson, 1980) in the river sediment, and followed by estuary, river, and coastal sediment during 2011. In Atharabanki creek contamination factor for both Cd and Co were found higher than other regions of the coastal areas. All the metals were observed very high contamination during post-monsoon due to the anthropogenic inputs as a discharge from municipality sewage, organic wastes from the fish jetty, fishing communities and industrial effluents situated on the river bank (Sundaray et al., 2011). Similar results have been observed in the present study area, however, Cd was very high contamination in 2011, compared to 2012 (Figure S1).

3.5.2. Enrichment Factor (EF)

The seasonal variations of EF of Mahanadi River, estuary and coastal in the surface sediments were presented in Figure S2. The seasonal variations of annual average EF values of Co, Cu, Pb, Ni, Zn, Cr, and Mn in the sediments of the study area were shown moderate to severe enrichment during 2011 and 2012. Except for Cr, the coastal sediments were observed least EF value compared to river, estuary and creek sediment. The Cd was found high enrichment, but Pb was the minor enrich-

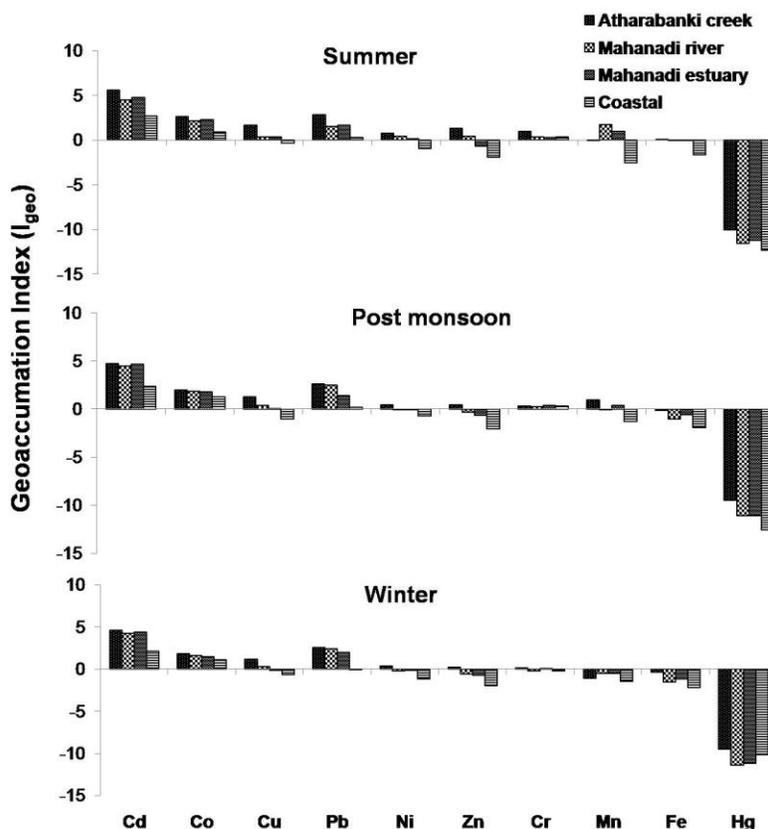


Figure 6. Seasonal and spatial variation of geo-accumulation index (I_{geo}) in the study area, Bay of Bengal. Note: 0 ~ 1 (Class 1) unpolluted, 1 ~ 2 (Class 2) moderately polluted, 2 ~ 3 (Class 3) moderately to highly polluted, 3 ~ 4 (Class 4) highly polluted, 4 ~ 5 (Class 5) highly to very highly polluted, 5 ~ 6 (Class 6) very highly polluted.

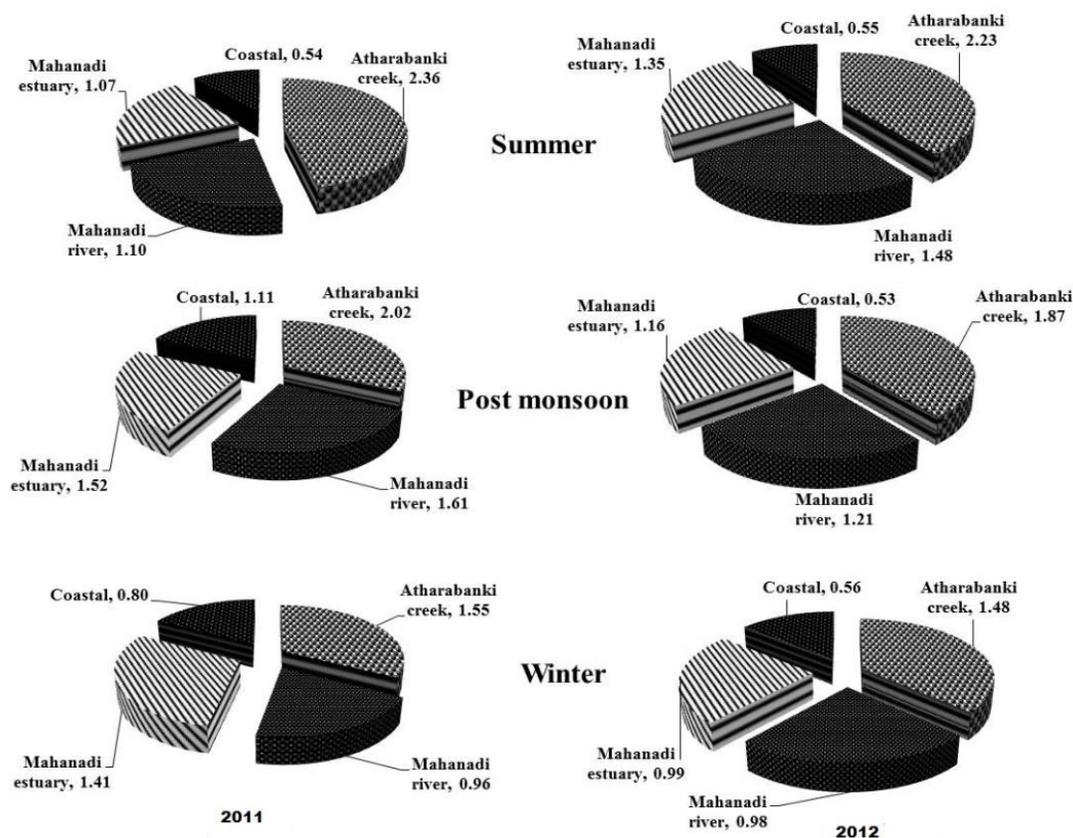


Figure 7. Seasonal and spatial variation of Pollution load index (*PLI*) in the study area, Bay of Bengal.

ment in the region indicated that the source of these metals were anthropogenic and industrial inputs. The results imply that the coastal sediment of Mahanadi was polluted by Cr and acts as a sink. The Co, Cu, Pb, Ni, Zn, Cr and Mn were higher value of EF in the river and estuary sediments due to the effluent discharge from the fertilizer, heavy metal processing plants, pesticides, petrol refining chemical industries and anthropogenic activities.

3.5.3. Geo-Accumulation Index (I_{geo})

Seasonal variation of the Geo-accumulation index (I_{geo}) was presented in Figure 6 in the Mahanadi River and coastal environment during 2011 and 2012. All the sediments except coastal areas were found to be moderately to highly polluted by Cd. Sediments of Atharabanki creek were found to be moderately to highly polluted by Cd, Cu, Co, Pb, and Zn, especially during the summer. The entire study area was found to be mostly unpolluted on Hg, irrespective of seasons. During the winter, most of the sediments except for the Atharabanki creek was found to be relatively unpolluted by Cu, Cd, Pb, Zn, and Cr. The results indicated that anthropogenic threats were contaminated to these sediments.

3.5.4. Pollution Load Index (*PLI*)

The seasonal variations of *PLI* were calculated for the sediment of the Mahanadi River, estuary and coastal sediments

were shown in Figure 7. The values of *PLI* were recorded for creek, river, estuary and coastal surface sediments that ranged between 0.54 ~ 2.36 during 2011 and 0.53 ~ 2.23 during 2012 (Figure 7). The lowest *PLI* values were found in the coastal sediment (mostly < 1), irrespective of season and year. This is indicated by the fact that these coastal sediments were far away from the various sources of heavy metals from the river runoff, which gets diluted with relatively fresh seawater. High values were observed in these sediments of the creek, river, and estuary during the study period. Indicated, that the accumulation of metals in the sediments because of the discharges from an agricultural runoff, industrial effluents and anthropogenic inputs from domestic sewages. The *PLI* values for metals were high concentrations in the surface sediments during summer and revealed an alarming status of the sites on the creek, river and estuary sediments than less polluted in coastal regions.

The average concentrations of metals in Mahanadi River, estuary and coastal sediment compared with the other river, estuary and coastal sediment around the world, and average has presented in Table 3. The average contraction of Cr, Cd, Ni, and Pb were observed higher than the Indian and world rivers and also world average value. Zn concentration was found higher compared to all Indian rivers, but lower with the Yangtze River, China, Buriganga River, Bangladesh, and average world value. The average contraction of Cr, Cu, Cd, Ni, and Pb found higher compared with all Indian and world's estuaries whereas lower concentration found with a world average except Cu and

Pb. The concentration Zn found higher compared with all Indian estuaries. The all metal concentrations of Atharabanki Creek sediment were higher than the Thane and Ennore Creek. In coastal sediments, all-metal values recorded greater than the Indian and other parts of world coasts except for Fe. Ni (93 mg/kg) and Cd (16.53 mg/kg) were greater than the average shale standard and earth crust concentrations in the sediments (Table 4).

3.5.5. Ecological Risk Index in the Sediment Quality Guidelines (SQGs)

In the study period, the result showed that Zinc (Zn) concentration was above the threshold effect level (TEL) and effect range was low (ERL), but it was less than from the probable effect level (PEL), and effects range was median (ERM) during the summer. While the concentrations were lesser than TEL, PEL, ERM and ERL in pre-monsoon and winter. The chromium (Cr) concentration was higher than the TEL, PEL, and ERL whereas low from the ERM during summer and post-monsoon. In winter, it was higher than TEL and ERL whereas lower than PEL and ERM. The copper (Cu) concentration was elevated than the TEL, PEL, ERL and lower than the ERM during the summer. However, in post-monsoon and winter it was higher than the TEL, ERL and similar concentration to the TEL but lower than the ERL. The concentration of Nickel (Ni) and cad-

mium (Cd) were above the TEL (15.9 mg/kg), PEL (42.8 mg/kg), ERL (51.6 mg/kg) and ERM (20.9 mg/kg), and the results indicated the potential toxicity for aquatic organisms and ecosystems in the Mahanadi estuarine and coastal sediment (Zahra et al., 2014; Sundararajan et al., 2017) throughout the study period (Table 5). The Lead (Pb) concentration was higher than TEL and ERL, whereas lower than PEL and ERM in the estuarine and coastal sediment in different seasons.

During the analysis of the stations, the result indicated that the Zn concentration was higher than the TEL and ERL but lower than the PEL and ERM in Atharabanki creek. The Cu, Cr and Pb concentrations were higher than TEL, PEL, and ERL whereas lower than ERM. The Ni and Cd were higher from all ecological indexes in Atharabanki creek sediments. In Mahanadi River, Zn concentration was higher than the TEL and less than from ERL, PEL, ERM. The Cr and Pb concentrations were shown higher than the values of TEL, PEL, ERL and lower than the ERM. The Cu concentration was greater than TEL and ERL, but lesser than the PEL and ERM. The Ni and Cd concentrations were higher, and Zn was lesser than the all ecological indexes in the river sediments. The Cr was higher than the TEL and ERL, and similar concentration to the PEL and lesser than the ERM. The Cu and Pb concentrations were higher than the TEL and ERL, But lesser than the PEL and ERM. The Ni and Cd concentrations were maximum and Zn and Pb concentrations

Table 3. Comparative Studied of Heavy Metal Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ except Fe%) of Mahanadi River, Estuary, Creek and Costal Surface Sediment with River, Estuary, Creek and Costal of India and Asian Countries

River, Estuary, Creek, and Coastal	Fe	Mn	Zn	Cr	Cu	Co	Ni	Pb	Cd	Hg	References
Yangtze, China	-	-	230	109	60.3	-	41.9	49.2	1.0	-	Wang et al., 2011
Buriganga, Bangladesh	-	-	502	101	184.4	-	79.8	-	0.8	-	Saha and Hossain, 2011
Euphrates, Iraq	0.23	-	48	126	18.6	-	67.1	22.6	1.9	-	Salah et al., 2012
Ganga, India	216	400	46	52	21	22	20	-	-	-	Subramanian et al., 1988
Godavari, India	6.03	1060	53	140	73	50	52	25	-	-	Biksham and Subramanian, 1991
Cauvery, India	1.76	3190	26	129	12	64	64	9	-	-	Vaithyanathan et al., 1993
Mahanadi, India	3.26	778	7735	34	14	24	24	48	1.0	-	Sundaray et al., 2009
Mahanadi	5.33	2068	131	246	77	104	110	136	29	0.10	Present study
World average	5.74	975	303	126	122.9	-	102	230.8	1.4	-	Martin and Meybeck, 1979
Pearl river estuary, China	3.76	673	140	88	46.8	15	34.8	47.9	-	-	Ip et al., 2007
Godavari estuary, India	4.25	429	54	2	40.2	31	20.7	46.7	-	-	Ray et al., 2006
Ganga estuary, India	2.80	503	53	40	22	18	34	23.4	2.0	-	Banerjee et al., 2012
Rusikulya estuary, India	2.06	-	-	-	-	20	22.9	43.9	-	-	Pradhan et al., 1998
Mahanadi estuary, India	4.60	1095	101	45	17	26	26.8	48	1.7	-	Sundaray et al., 2009
Mahanadi estuary	4.93	1705	89	164	73	106	101	103	11.1	0.32	Present study
Thane Creek, India	5.45	-	198	85	134	-	-	119.9	-	-	Athalye et al., 2001
Ennore Creek, India	-	-	97	50	22	-	17.7	31.8	-	-	Jayaprakash et al., 2008
Atharabanki Creek	5.94	1602	239	221	213	146	150	143	23.1	0.33	Present study
Chennai coast, India	-	-	101	102	37.12	-	28.4	24.9	-	-	Veerasingam et al., 2012
Bay of Bengal, India	3.90	529	-	84	26	-	64	-	-	-	Sarin et al., 1979
Hong Kong coast	2.90	524	148	49	119	-	25	53	0.3	0.19	Zhou et al., 2007
Coastal belt, Pakistan	-	-	68	171	64.2	-	34	45	0.4	-	Ali et al., 2015
Pearl coast, China	2.60	491	72	47	10.4	9	30.4	21.7	-	-	Ip et al., 2007
Coastal sediment	2.18	571	38	152	45.4	63	54.8	21	2.5	0.14	Present study
Indian average	2.90	605	16	87	28	31	37	11	-	-	Subramanian, 1987
World Average	4.80	1050	350	100	100	20	90	150	1.0	-	Martin and Meybeck, 1979

Table 4. Mean Concentrations of Heavy Metals ($\mu\text{g}\cdot\text{g}^{-1}$ except Fe%) Compared with Ecological Risk Assessment of Surface Sediment of Mahanadi Estuarine and Coastal Environment

Seasons & Regions	Fe	Mn	Zn	Cr	Cu	Co	Ni	Pb	Cd	Hg
Summer	4.22	1078	174	209	125	135	88	82	12.51	0.17
Post monsoon	3.69	1767	117	224	108	108	115	86	21.86	0.17
Winter	3.22	804	110	123	103	72	76	89	15.22	0.29
Mean Sediment	3.71	1216	134	185	112	105	93	86	16.53	0.21
Mahanadi	5.33	2068	131	246	77	104	110	136	29.00	0.10
Mahanadi estuary	4.93	1705	89	164	73	106	101	103	11.10	0.32
Atharabanki Creek	5.94	1602	239	221	213	146	150	143	23.07	0.33
Mahanadi Coastal	21.8	571	38	152	45	63	55	21	2.52	0.14
Avg. shale standard ¹	4.60	950	95	90	40	na	68	20	0.30	na
Earth Crust ²	5.63	850	70	100	55	25	75	13	0.15	na
TEL ³	na	na	124	52.3	19	na	15.9	30	0.70	na
PEL ³	na	na	271	160	108	na	42.8	112	4.20	na
ERM ⁴	na	na	410	370	270	na	51.6	218	9.60	na
ERL ⁴	na	na	150	81	34	na	20.9	47	1.20	na

TEL: Threshold Effect Level; ERL: Effects Range Low; PEL: Probable Effects Level; ERM: Effect Range Median. Turekian and Wedepohl, 1961; Taylor, 1964; Long et al., 1998; MacDonald et al., 2000.

Table 5. Ecological Risk Assessment of Cu, Cr, Ni, Pb and Zn on the Basis Sediment Quality Guidelines Benchmarks (P: Potentially Toxic, R: Rarely Toxic, N: Nontoxic)

Seasons and Regions	Zn	Cr	Cu	Ni	Pb	Cd
Summer	P	P	P	P	P	P
Post monsoon	N	P	P	P	P	P
Winter	N	P	P	P	P	P
Mean Sediment	R	P	P	P	P	P
Mahanadi	R	P	P	P	P	P
Mahanadi estuary	N	P	P	P	P	P
Atharabanki Creek	P	P	P	P	P	P
Mahanadi Coastal	N	P	P	P	N	P

were lower than all ecological indexes in the Mahanadi estuarine sediments. The Cr concentration was higher than the value of TEL and ERL, equivalent to the PEL and lower than the ERM. The Cu and Cd concentrations were higher than the TEL and ERL whereas lower than the PEL and ERM. The Ni concentration was greater than all ecological indexes in the coastal sediments (Table 4). Creek sediment was the highest level of ecological risk followed by the estuary, river and coastal. However, in the present study Cr, Cu, Ni, Pb, and Cd concentrations were indicated potentially toxic in all sites of Mahanadi estuarine and coastal sediment (Table 5), which was harmful to marine flora and fauna during the study period (Veerasingam et al., 2012; Zahra et al., 2014; Sundararajan et al., 2017).

The average concentrations of metals in Mahanadi River, estuary and coastal sediment compared with the other river, estuary and coastal sediment around the world (Table 5). The average contraction of Cr, Cd, Ni, and Pb observed in the study area was higher than the Indian and world rivers. The average Zn concentration was found higher in study site compared to other Indian rivers, but lower with the Yangtze River, China, Buriganga River, Bangladesh, and other rivers of the world. The average contractions of Cr, Cu, Cd, Ni, and Pb in Mahanadi estuary were higher compared to other Indian and world's

estuaries. However the average lower concentration of Cu and Pb were found lower compared to other world estuaries, but the Zn concentration found higher in the study region compared to other Indian estuaries. However, in the Mahanadi River basin the total erosion rate of metals was $128.645 \text{ kg km}^{-2} \text{ year}^{-1}$ and the geochemical speciation of Cd, Ni, Co, and Pb was indicated a high environmental risk because of higher availability in the exchange fraction (Sundaray et al., 2012). This resulted in a severe impact on the ecosystem. The Cd was mostly bound in exchangeable, carbonate and Fe-Mn oxide fractions were in the non-residual phase due to bioavailability of the metals to the marine organisms in the river. The relative abundance the metals were observed in the decreasing order $\text{Fe} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Cu} > \text{Pb} > \text{Cr} > \text{Co} > \text{Cd}$ for river, whereas in case of estuaries, the order is $\text{Fe} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cu} > \text{Co} > \text{Cr} > \text{Cd}$ (Sundaray et al., 2012). In the present study, all metal concentrations of Atharabanki Creek sediments were higher compared to the Thane and Ennore Creek. In coastal sediments, all-metal values recorded greater than the Indian and other parts of world coasts except for Fe and Ni (93 mg/kg) and Cd (16.53 mg/kg), which were greater than the average shale standard and earth crust concentrations in the sediments (Table 5) due to the influence of industries and anthropogenic sources.

4. Conclusions

The study significantly evaluated the heavy metal pollutions and ecological risk assessment using metal indices based on the SQGs. The sediment texture showed the seasonal and spatial variation in the study region and the geochemical circulations of heavy metals which were mainly controlled by organic carbon and fine sediments. The fluvial discharges were extensively shifted towards the coastal sediment (finer sediment) and transported to the downstream, caused the increase of the salinity and resulted in the flocculation as well as resuspension. The metal concentrations in Mahanadi River and estuaries of the sediment were found a higher amount than the coastal re-

gion of the Bay of Bengal due to the discharge of industrial effluents of fertilizer, refinery, smelters and anthropogenic runoff in the region. The Cd concentration was observed a high ecological concern in the study environment. The Enrichment factor (EF) and Geo accumulation index (I_{geo}) revealed that the creek region of the study area was highly polluted than the river, estuary and coastal surface sediment. The pollution load index in Atharabanki creek was identified as a critical point of contamination representing both urban and industrial point sources and contributes substantially to the environment. This resulted that the environment was a potential eco-toxicological risk for benthic organisms in the sediment. Ecological index based on SQGs suggested that Cr, Cu, Ni, Pb, and Cd concentrations are assumed potential toxicity to aquatic organisms in the environment. A further study on the bio-availability of metals with their potential toxicity in higher trophic levels is needed to assess the sediment and water quality of the environment. Hence, the findings suggested that the need of proper industrial planning, management and the safe disposal of industrial and urban wastes, through regular monitoring and comprehensive policies, would help to reduce the metal concentrations that alarming level in the estuarine and coastal environment of Bay of Bengal. Based the datasets from present investigation in the major river like Mahanadi and its adjacent, creek, estuary and the coastal site would further use as a platform to extend the study in the region to understand the biomarkers of pollution level of the bioavailability of metals, point sources and their preclusion for the safeguard of fisherfolks, sustainable ecosystem and coastal zone management.

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