



SEASONAL VARIATIONS OF HEAVY METAL POLLUTION IN THE SEDIMENT OF VISAKHAPATNAM COAST, INDIA

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Abstract

Visakhapatnam harbor is one of the Indian leading port for which substantial industrial expansion is proposed over the next decade. However, there has been little attempt to date to assess the extent of contamination in sediment and to characterize the potential impacts of contaminants on marine sediment. In this research work author was observed different sediment qualities in different seasons. The results shows metal levels followed by Post monsoon > Monsoon > Premonsoon during the study period respectively concentration ($\mu\text{g/g}$) of Fe 590.86 ± 91.948 , 398.926 ± 78.101 , 242.375 ± 46.632 , Zn 333.44 ± 68.064 , 253.168 ± 45.819 , 174.331 ± 26.768 , Pb 60.344 ± 8.510 , 39.961 ± 8.650 , 19.177 ± 4.981 , 39.961 ± 8.650 and Cd 0.966 ± 0.156 , 0.739 ± 0.113 , 0.254 ± 0.071 , in spite concentration of metal potential significant at $P < 0.05$ level. These metals variation may be due to the several anthropogenic (urban, agricultural and industrial) activities. In addition, Geo-accumulation Index (I_{geo}) has shown the sediment quality of $I_{geo} > 5$ which are very strongly polluted quality for Cd, Pb and Zn. The metal (Fe) has shown the sediment quality $I_{geo} < 1$ (unpolluted to moderately polluted). These variations were observed due to chemical effluents, solid wastes and debris which entered into the sea from the shore through the runoff of urban, industrial drain and sea tidal waves.

Key words: geo-accumulation index (I_{geo}), marine pollution, sediment, harbor, heavy metals

I. INTRODUCTION

Visakhapatnam Coast is surrounded by 24 large and small scale industries like chemicals, pesticides, fertilizers and petroleum refineries. In addition, Visakhapatnam coast has been built with a big cargo and passenger port. It is one of the big natural ports in India and it is situated in radius of 15 kilometers at Gannavaram to Kailasha Giri Hill. Visakhapatnam city has been connected by the Bay of Bengal, southeast coast of India. The Megadrigedda and Gosthani rivers in the Visakhapatnam urban are lead to severe pollution due to natural hazards, like heavy rains and floods have caused considerable changes in the marine ecosystem by polluting the marine environment with high turbidity and also breaking the coastal vegetations [1].

The quality of water and sediment in the rivers and seas has been seriously affected by pollutants which entered into the coast through the industrial and domestic drain systems [2]. Moreover, solid waste pollution was generating from domestic and commercial activities. Similar observations were found in the United Arab Emirates at Asab Field [3]. These industrial and domestic waste waters, besides other pollutants also contain high concentration of metals. Because of absorption, hydrolysis and co-precipitation only a small portion of free metal ions stay dissolved in water and a large quantity of them get deposited in the sediment. Sediments are ecologically important components of the aquatic habitat and are also a reservoir of contaminants, which play a significant role in maintaining the tropic status of any water body [4], [5].

A study on distribution of heavy metals in seawater is very important to understand the role in various geochemical process of the sea. Significant contributions have been made with reference to oceanic and coastal distribution of various heavy metals [6]. Further studies reveal that heavy metals are biologically non-degradable and through food chain they may finally pass on to man [7]. Considering all the above mentioned facts, the present study shows Seasonal Variations of Heavy Metal Pollution in the Sediment of Visakhapatnam Coast.

II. MATERIALS AND METHODS

2. 1Areas of Sample Collection Points

Monitoring was carried out in 2003 – 2004 during premonsoon (March – June), monsoon (July – October) and post monsoon (November – February) to assess the seasonal variations of metals in marine sediment at Visakhapatnam coast. The samples were collected from 11 sites along the coast (**fig. 1**). The selected location for sample collection is located in between Bheemunipatnam and Gangavaram (Lat $17^{\circ} 30'$ to $18^{\circ} 10'$ N and Long $83^{\circ} 10'$ to $83^{\circ} 30'$ E) adjoining the industrial area and harbor township of Visakhapatnam on East coast of India. The main sampling location was selected at Visakhapatnam port, named as “Main Pollution Source” (MPS) which receives industrial and urban pollutants through the Megadriggedda River. MPS and PLW1, MPS and PRW1, PRW4 and PRW5 are the sites having 2 km distance in between. The rest of the sites are approximately 2 km distance between each site. These sites were selected beside the MPS such as “Pollution Left Wing1 (PLW1) - Pollution Left Wing5 (PLW5). PLW4 and PLW5 sites are receive pollution from agriculture and urban runoff through Gosthani River. These two rivers are effecting indirectly on PLW1, PLW2 and PLW3. Pollution Right Wing5 (PRW5) especially receives industrial waste water through the local channel. PRW1, PRW2, PRW3 and PRW4 affected by shipping activity and tidal waves from MPS and PRW5.

2.2. Samples Collection Procedure

The sampling points are shown in Fig 1. The sediment samples were collected from premonsoon to post monsoon (Feb. 2003 – Jan. 2004).

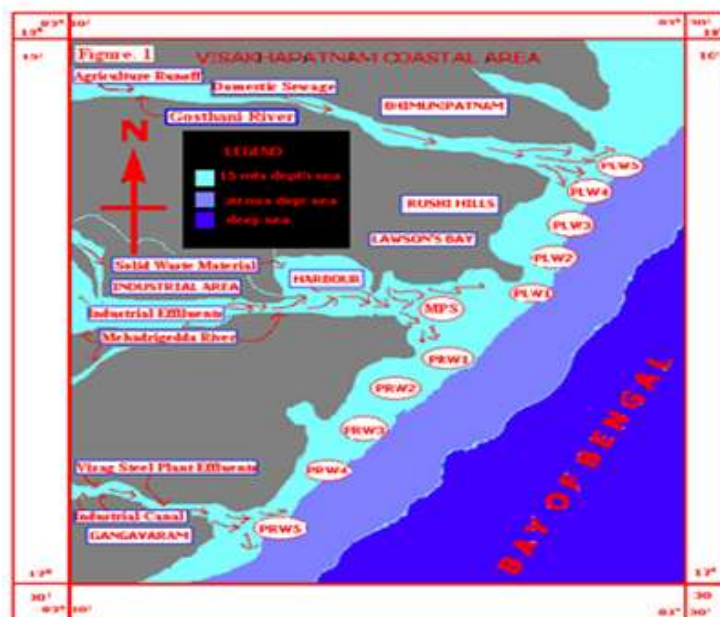


Fig. 1: Visakhapatnam coast and the sampling sites

The samples of the sediment were collected with the help of Grab sampler at each sampling site. The samples were placed in polyethylene bags and transported immediately to the laboratory.

2.3 Extraction of Metals from Marine Sediment

Metals from sediment were extracted by the method of acid digest [8]. 5g dry weight of sediment was taken in crucible and dried at 135°C for 2 hrs. The dry weights were noted first and then were transferred to cool muffle furnace and slowly the temperature was raised to 450°C – 500°C and kept overnight. Then the samples were removed and cooled to room temperature. Next cautiously 2ml of HNO₃ (Anal., Grade supplied by Merck Chem., Lab., India) was added and swirled. They were kept on a hot plate and allowed to evaporate till dry. The dry sample was then transferred to cool furnace, and temperature was slowly raised to 450°C – 500°C. This temperature is maintained for one hour. Crucible was removed from the furnace and cooled. Nitric Acid treatment was repeated three times to obtain clean, carbon free ash. To this 10 ml of 1 N HCl was added and heated cautiously on a hot plate to dissolve the ash. These contents were transferred to 25ml volumetric flask and made up with 1N HCl. The samples were cooled and injected into AAS (Perkin – Elmer 2380) for estimation different heavy metals.

2.4 Statistical Analysis (Duncan’s Multiple Range Test (DMRT))

Duncan’s Multiple Range Test (DMRT) was widely used procedure for comparing all pairs of means is the multiple range test. The results are presented mean ± SD values from three replicates for each sample. The *P* < 0.05 level was selected as the point of minimal statistical significance in all analyses; each site was compared with the rest of remaining all sites in the particular season [9].

2.4.2 Geo-accumulation Index (I_{geo})

The index of geo-accumulation can be calculated by using following equation [10]:

$$I_{geo} = \frac{\log_2 C_n}{1.5 B_n}$$

Where *C_n* is the concentration of the examined metals in the sediment, *B_n* is the geochemical background value of a given metal in shale [11], and 1.5 is the background matrix correction factor.

Table: 1
Sediment Classification

Class	I _{geo} Values	Status
0	0	Practically unpolluted
1	0 – 1	Unpolluted to moderately polluted
2	1 – 2	Moderately polluted
3	2 – 3	Moderately to strongly polluted
4	3 – 4	Strongly polluted
5	4 – 5	Strong to very strongly polluted
6	>5	Very strongly polluted

The factor 1.5 is used for possible variation in the background data due to lithogenic effects. The following description classification is given for the index of geo-accumulation in **table-1** by **Forstner et al. (1990)** [10] as follows:

III. RESULTS

3.1. Sediment Metals Concentration

The seasonal marine sediment metal levels were perceived by the following order; Postmonsoon > Monsoon > Premonsoon. The metals concentration was recorded by the following order; Fe (802.82 µg/g) > Zn (494.76 µg/g) > Pb (80.02 µg/g) > Cd (1.33 µg/g) in all sites during study period (**tables 2-5 & fig. 2-4**). In all metals during the study period, low concentration was found in premonsoon and high in postmonsoon. In all metals during the study period, high concentration was noticed at MPS (main

pollution source) site and low concentration was found at PRW3 (pollution right wing3) site. The cadmium concentration range was 0.15 – 1.33 µg/g during study period (**table 2**).

Table: 2
Cd Concentration (µg/g) in Marine Sediment at Visakhapatnam Coast, India

Seasons	Samples Collection Sites											
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5	
Premonsoon												
DMR Test	a	ba	ca	da	ea	fabcds	gf	habf	iabdfafg	jaf	kcdfhijf	
Mean	0.32	0.28	0.22	0.23	0.23	0.41	0.25	0.19	0.15	0.21	0.30	
SD (±)	0.06	0.04	0.06	0.04	0.04	0.06	0.05	0.03	0.03	0.05	0.06	
Monsoon												
DMR Test	a	b	cab	dab	ea	fbcds	gf	habcdaf	iabcfaf	jabcdaf	kcdfhij	
Mean	0.87	0.80	0.69	0.70	0.75	0.93	0.76	0.61	0.58	0.61	0.83	
SD (±)	0.06	0.05	0.06	0.06	0.06	0.06	0.06	0.05	0.07	0.05	0.06	
Postmonsoon												
DMR Test	a	ba	cab	dab	sab	fabcds	gfa	habfg	iabdfafg	jaf	kbcdafghi	
Mean	1.10	1.01	0.87	0.90	0.91	1.33	0.93	0.83	0.80	0.86	1.09	
SD (±)	0.09	0.06	0.05	0.04	0.06	0.09	0.06	0.05	0.04	0.06	0.06	

The mean value was taken by six individual samples.

DMR Test = a, b, c, d, e, f, g, h, i, j, k (each site testing with the remaining all sites (two-way) individual season (row)).

Significant at $P < 0.05$

SD (±): Standard Deviation.

Table: 3

Fe Concentration (µg/g) in Marine Sediment at Visakhapatnam Coast, India

Seasons	Samples Collection Sites											
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5	
Premonsoon												
DMR Test	a	b	ca	da	e	fabcds	gf	habfg	iabfg	jaf	kcdfhi	
Mean	266.93	247.97	216.55	222.32	230.96	365.94	241.42	201.72	200.68	211.68	259.95	
SD (±)	32.37	24.92	22.33	25.52	26.81	40.58	21.69	23.27	28.05	25.47	26.38	
Monsoon												
DMR Test	a	b	cab	dab	ea	fabcds	gcf	habfg	iabefg	jabfg	kcdfhij	
Mean	451.34	427.81	341.70	364.25	386.26	586.34	408.32	327.68	321.22	331.18	442.09	
SD (±)	48.95	47.00	45.30	39.52	38.32	56.88	51.56	38.64	36.05	33.65	48.61	
Postmonsoon												
DMR Test	a	b	ca	da	ea	fabcds	gaf	habf	iabfg	jaf	kcdefhi	
Mean	674.30	608.77	531.65	558.04	561.42	802.82	579.07	502.34	489.14	526.25	657.15	
SD (±)	67.19	79.41	54.27	57.50	59.40	71.36	53.50	47.62	50.57	53.79	58.68	

The mean value was taken by six individual samples.

DMR Test = a, b, c, d, e, f, g, h, i, j, k (each site testing with the remaining all sites (two-way) individual season (row)).

Significant at $P < 0.05$

SD (±): Standard Deviation.

Table: 4

Pb Concentration (µg/g) in Marine Sediment at Visakhapatnam Coast, India

Seasons	Samples Collection Sites											
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5	
Premonsoon												
DMR Test	a	b	c	d	e	fabcds	gf	haf	iabfg	jf	kfi	
Mean	20.18	19.22	17.02	17.78	18.21	33.23	18.78	15.94	14.24	16.59	19.76	
SD (±)	3.03	2.29	2.10	2.30	3.47	3.47	3.88	2.19	2.40	2.94	2.98	
Monsoon												
DMR Test	a	b	cb	d	e	fabcds	gf	hbdefg	ibdefg	jbfg	kcdfhij	
Mean	46.21	42.09	34.39	38.35	40.03	59.81	40.22	30.42	29.01	33.79	45.25	
SD (±)	5.11	5.57	4.37	3.78	5.46	6.08	5.14	3.80	3.71	5.47	5.47	
Postmonsoon												
DMR Test	a	b	ca	da	e	fabcds	gf	habf	iabfg	jaf	kcdfhij	
Mean	67.24	62.16	55.67	57.22	59.04	80.02	60.15	51.07	50.16	54.91	66.14	
SD (±)	6.64	6.99	5.74	5.79	5.99	8.74	6.95	5.78	7.58	6.31	6.62	

The mean value was taken by six individual samples.

DMR Test = a, b, c, d, e, f, g, h, i, j, k (each site testing with the remaining all sites (two-way) individual season (row)).

Significant at $P < 0.05$
 SD (\pm): Standard Deviation.

Table: 5
Zn Concentration ($\mu\text{g/g}$) in Marine Sediment at Visakhapatnam Coast, India

Seasons	Samples Collection Sites											
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5	
Premonsoon												
DMR Test	a	b	c	d	e	fabcds	gf	haf	iaf	jf	ks	
Mean	187.30	174.45	160.16	162.35	167.10	247.33	170.89	155.57	150.36	158.58	183.55	
SD (\pm)	24.37	21.97	18.28	24.83	18.78	22.18	21.75	18.08	16.66	19.77	20.70	
Monsoon												
DMR Test	a	b	ca	d	e	fabcds	gf	habfg	iahdafg	jahf	kahij	
Mean	273.14	260.50	227.92	245.11	250.21	372.25	252.83	212.48	200.74	221.52	268.35	
SD (\pm)	29.28	32.14	24.85	26.28	25.38	31.11	28.42	30.62	24.72	22.13	26.15	
Postmonsoon												
DMR Test	a	b	ca	d	e	fabcds	gf	habdafg	iahdafg	jahfg	kahij	
Mean	369.933	350.56	302.51	320.45	339.10	494.76	347.08	257.16	247.42	276.28	362.59	
SD (\pm)	6.67	36.95	36.47	33.56	38.85	43.48	38.70	35.27	30.25	29.38	37.05	

The mean value was taken by six individual samples.

DMR Test = a, b, c, d, e, f, g, h, i, j, k (each site testing with the remaining all sites (two-way) individual season (row)).

Significant at $P < 0.05$

SD (\pm): Standard Deviation.

Fe was noticed from 200.68 to 802.82 $\mu\text{g/g}$ (table 3). Pb concentration was found to be 14.24 – 80.02 $\mu\text{g/g}$ (table 4) and Zn range was noticed as 150.36 – 494.76 $\mu\text{g/g}$ (table 5).

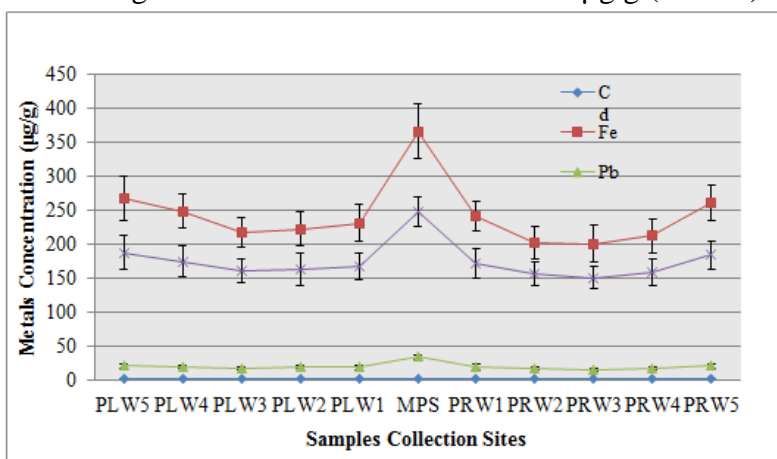


Fig. 2: Premonsoon metals concentration (0 to 450 $\mu\text{g/g}$) in marine sediment of Visakhapatnam Coast, India

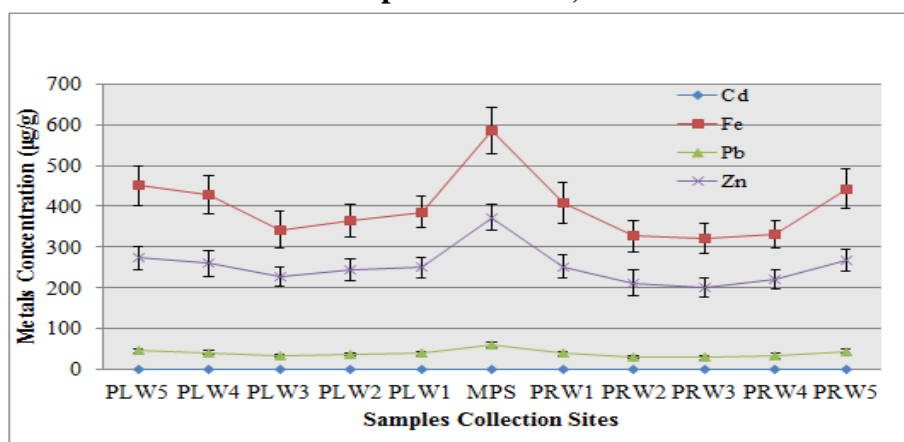


Fig. 3: Premonsoon metals concentration (0 to 700 $\mu\text{g/g}$) in marine sediment of Visakhapatnam Coast, India

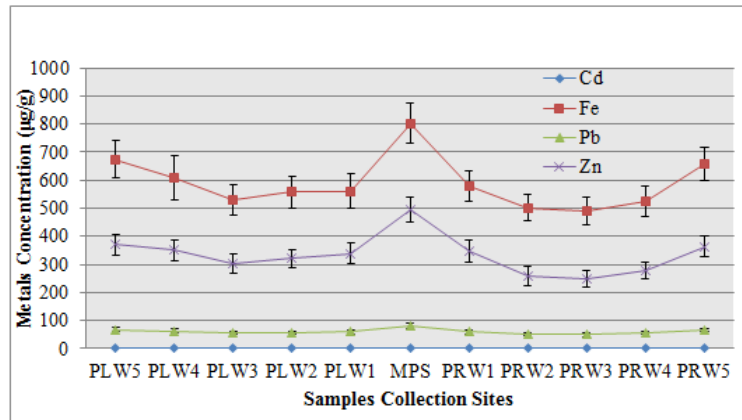


Fig. 4: Premonsoon metals concentration (0 to 1000 µg/g) in marine sediment of Visakhapatnam Coast, India

3.2. Sediment Metals Geo-accumulation Index (I_{geo})

In the present work different classes of sediments were found in table 1. And statistical analysis (t -test) revealed significant ($P > 0.05$) levels between the sites. The metals noticed different classes of sediment pollution index (I_{geo}) from practically unpolluted to very strongly polluted (0 - >5) in the tables 6, 7 & 8. Cd, Pb and Zn concentrations found very strongly polluted sediment class (>5) in the tables 6, 7 & 8. Fe found specific value of sediment pollution index (I_{geo}) <1 (unpolluted to moderately polluted) in the tables 6, 7 & 8.

Table: 6
 Sediment Metals Geo-accumulation Index (I_{geo}) in Premonsoon Season at Visakhapatnam Coast, India

Seasons	Samples Collected Sites										
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5
Cd	-2715	-3032	-3640	-3587	-3499	-2144	-3333	-3993	-4562	-3715	-2868
Fe	0.083	0.082	0.080	0.080	0.081	0.087	0.081	0.078	0.078	0.079	0.082
Pb	36.126	118.588	34.078	34.078	65.276	42.106	35.262	33.286	31.955	33.765	35.871
Zn	30.501	30.087	29.589	29.668	29.668	32.121	29.967	29.420	29.229	29.551	30.383

Table: 7
 Sediment Metals Geo-accumulation Index (I_{geo}) in Monsoon Season at Visakhapatnam Coast, India

Seasons	Samples Collected Sites										
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5
Cd	-326	-527	-898	-863	-681	-174	-649	-1201	-1317	-1195	-448
Fe	0.090	0.090	0.086	0.087	0.088	0.094	0.089	0.086	0.085	0.086	0.090
Pb	46.064	44.957	42.532	43.841	44.348	49.184	44.414	41.054	40.483	42.319	45.815
Zn	32.700	32.559	31.645	32.069	32.189	34.505	32.237	31.237	30.893	31.475	32.598

Table: 8
 Sediment Metals Geo-accumulation Index (I_{geo}) in Post monsoon Season at Visakhapatnam Coast, India

Seasons	Samples Collected Sites										
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5
Cd	233	19	-326	-244	-222	692	-166	-453	-527	-376	214
Fe	0.096	0.095	0.093	0.094	0.094	0.099	0.094	0.092	0.092	0.093	0.096
Pb	50.593	49.635	48.323	48.639	49.026	52.680	49.248	47.285	47.061	48.157	50.383
Zn	34.469	34.155	33.296	33.631	33.962	36.163	34.097	32.350	32.124	32.767	34.352

Table: 8
 Sediment Metals Geo-accumulation Index (I_{geo}) in Post monsoon Season at Visakhapatnam Coast, India

Seasons	Samples Collected Sites										
	PLW5	PLW4	PLW3	PLW2	PLW1	MPS	PRW1	PRW2	PRW3	PRW4	PRW5
Cd	233	19	-326	-244	-222	692	-166	-453	-527	-376	214
Fe	0.096	0.095	0.093	0.094	0.094	0.099	0.094	0.092	0.092	0.093	0.096
Pb	50.593	49.635	48.323	48.639	49.026	52.680	49.248	47.285	47.061	48.157	50.383
Zn	34.469	34.155	33.296	33.631	33.962	36.163	34.097	32.350	32.124	32.767	34.352

IV. DISCUSSION

The increased concentrations of metals were observed during the study period of post monsoon season shown in tables 2, 3, 4 & 5. The high concentrations of all metals were observed at Main Pollution Source (MPS) site during the study period. The metals might have been increased due to the man made activities like industrial, agriculture, urban activities and natural disasters [12], [13]. All metals-concentrations were observed to be significant ($P < 0.05$) between the sites (for specific seasons and metals).

Cadmium was present in environment through different activities, i.e. agriculture, industrial and export and import [14]. In the present research work Cd concentration values were observed above the tolerance limits and were significant at $P > 0.05$ between the sites in particular season. Cd high concentration was observed in postmonsoon. These variations of heavy metal concentrations may be due to the continuous stirring of sediments by the high speed of sea tidal actions [12]. The marine sediment geo-accumulation index (I_{geo}) value > 5 was found in post monsoon. This value represented that the quality of sediment was polluted very strongly in post monsoon in particular sites (PLW5, PLW4, MPS and PRW5 (table 8)). This could be due to the entry of cadmium contaminants into particular sites. Cadmium constituent was found in fungicides, industrial effluent, solid wastes and phosphoric fertilizers [15]. Those pollutants entered into the sea through different local canals, seasonal streams and rivers [6].

The present work reveals that significant concentrations of Iron were found in the marine sediment (table 2 & figs. 2-4). In sediment the concentration of iron is very high compared to other metals.

This high concentration of iron could be exhibited in to the sea from different industrial pollution sources like steel, pesticides and agrochemicals [16]. Fe geo-accumulation Index (I_{geo}) value < 1 was

recorded in sediment. However, it has decreased the quality of sediment from unpolluted to moderately polluted (tables 6- 8). Similar results were found from Sediment of River Gomati – A tributary of the Ganga River, India [17].

Lead and Zinc high concentrations were found in post monsoon during the study period. And their trends were observed similarly. Various significant ($P > 0.05$) concentrations were observed in all sites in particular season (tables 5 & 6). In the sediment metals concentration was noticed above limits. Besides this, the marine sediment status ($I_{geo} > 5$) of Pb and Zn was found very strongly polluted during the study period (tables 6-8). According to Xivanand[18] these metal variations could be due to the presence of major metal pollution sources of intensive human activities of municipal waste and industrial effluents which entered into the sea.

V. CONCLUSION

This present study shows varying quantities of heavy metals pollution causing damage to marine ecosystem in different seasons. However, marine sediment quality is decreasing according to different seasons. The current research work reveals the fall of marine sediment quality from moderate to very strongly pollute due to the various metal contaminations. These results and discussions have concluded that apart from the contaminated water, debris, solid waste and effluents are also responsible in the marine coastal pollution. This comparable metal pollution research work has been recorded the seasonal metal variations and levels. This coastal data is important in designing the management and conservation policies of the Visakhapatnam coast.

VI. ACKNOWLEDGEMENTS

The authors are thankful to Head and Staff Members, Department of Environmental Science, Sri Venkateswara University, Tirupati, India for constant encouragement.

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