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Seawater quality and trends in heavy metal distribution in marine sediment along Alang Sosiya Ship Breaking Yard (ASSBY) region

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ABSTRACT

Alang-Sosiya Ship Breaking Yard (ASSBY), is situated at 21°5' 21°29' north and 72° 5' 72° 15' east on the western Coast of Gulf of Cambay. The sheltered coast here is conducive for forced ship beaching due to suitable tidal amplitude and beach profile, including the availability of around 40,000 workers makes it the largest ship breaking site in the world.[1] The type of ships dismantled includes General Cargo & Bulk carriers; Oil tankers Passenger; Cruisers; Drill Ships et. Since, its inception in 1982, ASSBY has so far recycled 35.61 million of light displacement tonnage (LDT).[2] Ship breaking activity generates hazardous waste like heavy metals which find their way into the marine water and sediment. The present study is to understand the seawater quality and trends in heavy metal distribution in the marine sediments including the net effect over the Gulf of Khambhat region. Samples were analyzed from seawater and sediment samples taken from high tidal, low tidal and offshore region. The samplings were also conducted during pre-monsoon and post-monsoon to analyze the seasonal trends. The paper focuses on the heavy metal distribution in sediment samples over the high tidal, low tidal and offshore region along ASSBY. The results reveal distinct areas of abundance of heavy metals especially along the Alang area.. They study concludes that the high deposition rates in the Gulf of Khambhat, the tidal amplitude and currents and shoreline morphology and the influence of coastal processes overall influences the distribution of heavy metal including a shielding or de-shielding effect due to the sedimentation pattern. The correlations between the coastal process operating in the Gulf (like tides, currents, sedimentation and suspended sediment transport and deposition etc.) with the physico-chemical properties of the marine waters and sediments, the pollutants, as well as the geomorphology of the coastal shorelines, intertidal and offshore regions needs to clearly modeled to control the spread of the pollutants, estimate the net impacts and find solutions for the sustainable development of the coastal areas of the Gulf of Khambhat including ASSBY. The overall metal concentrations are higher than permissible levels and there is a need to move towards cleaner ship breaking or recycling technologies and process.

INTRODUCTION

Alang–Sosiya Ship Breaking Yard (ASSBY), is situated at 21°5' 21°29' north and 72° 5' 72° 15' east on the western Coast of Gulf of Cambay. The coast here enjoys certain distinct characters that makes it conducive for forced ship beaching as well as dismantling. The tidal amplitude at the sheltered coastal area around ASSBY is usually in the range of 10-12 m.; the firm seabed and gentle seaward slope and mud free conditions make it ideal beaching condition. In addition this region has a semi arid climate (usually 7.4 – 47.3 degree C. with mean lowest at 21.9 and mean highest at 34.2 degree C, 558 mm mean rainfall with lot of dry days available which in turn generates continuous working hours and days throughout the year.[1,3]

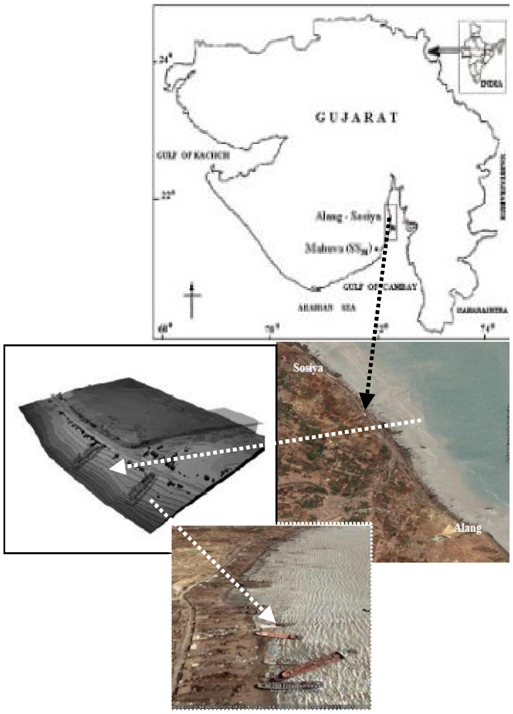


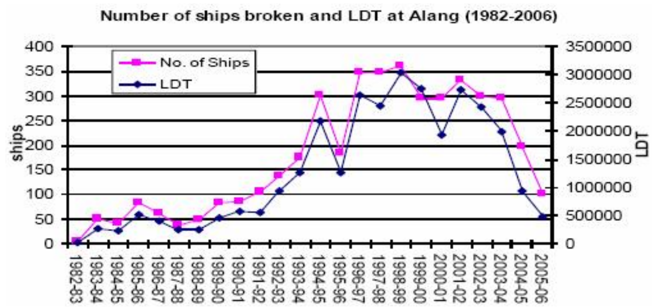
Figure 1 : ASSBY location and ship breaking

Figure 1 indicates the location of ASSBY and helps to visualize the coastal stretch profile including the ship beaching and breaking at individual plots.

ASSBY represented by several plots is built on the shoreline occupying about 14 km stretch. A small creek divides the stretch into two parts. The ship breaking activities initially began in the southern part (Alang) and later new plots were established towards the north (Sosiya). In all there are about 112 plots in and around 80 plots in Sosiya, each having a size of 50-240 m long and 30-120 m width. The first vessel to beach at Alang was M.V. Kota Tenjong on 13th February, 1983. Over, 40,000 workers are involved in the ship breaking yard. The type of ships broken include General Cargo & Bulk carriers (60-65%); Oil tankers (10%); Passenger ship (5%); Cruisers (2-3%); Drill Ships etc. (2%). The LDT of ships usually ranges between 7,000–35,000 tons. The scrap recovered from the ships are indicated in TABLE 1. Since, its inception in 1982, Alang ship breaking yard has so far recycled 35.61 million of light displacement tonnage (LDT). During 2009-10, the yard had dismantled 255 ships up to November 2009 against a total of 264 ships dismantled during 2008-09. With this, Alang ship breaking yard had crossed the milestone of dismantling 5,000 ships before the end of 2009. International price of each LDT ranges between USD 150 and USD 175[2]. The international prices of steel largely moderate the profits earned through ship breaking. Considering the global tonnage of ships broken, Alang emerges as the world's largest ship breaking site. It is projected that ships to be scrapped will increase gradually to 4000 per annum by the year 2010 with an aggregate gross tonnage of 24 million. Around 10% of India's overall steel production is attributed to ASSBY.[2-4]

TABLE 1 : Scrap recovered from ships

Sr. No.	Type of Vessel	RR Scrap %	Melting Scrap %	Cl Scrap %	N.F. Metals %	Machinery	Wooden furniture and other %	WT Loss
1.	General Cargo	56-70	10	1.5-5	0.5-1	4-8	5	9-15
2.	Bulk Carriers	61-75	8-10	1.5-2.5	0.5	1-6	1-5	10-16
3.	Oil tankers	72-81	5-7	1.5-3	0.5-2	0.5-2	1.5-2	10-12



Graph 1 : Ships broken and LDT

While dismantling the ships, various solid, liquid and gaseous hazardous wastes are generated which accumulate over the soil, especially the beach front, high tidal region and then migrate subsequently to the intertidal zone, sub-tidal zone, finally to the deep seawaters and sediments. The main pollutants associated with the ship breaking activity constitute heavy metals and hydrocarbons. Poisonous gases are also generated, especially during open burning of junk material.

The aim of the present study is to understand the seawater quality and distribution and contamination levels of the heavy metals generated in the marine environment due to the ship breaking activities at ASSBY. They study would also consider the seasonal changes, coastal processes operating in the Gulf of Khambhat and try to monitor the variations within the different parameters with respect to the different sampling spots and influences of tides (high and low tide). The observation regarding the correlations for sedimentation pattern along the shoreline and intertidal regions and heavy metals with the sediment nature and distribution would also be attempted. The present paper focuses on the heavy metal distribution in marine sediment samples along the ASSBY region.

MATERIALS AND METHODS

Selection of sample sites

Identification and selection of sampling spots were based on the following specific factors that were to be studied as a part of the monitoring work;

- Quantification of the various physical and chemical parameters related to seawater and sediments
- Determination of pollutant load, quantification and distribution
- Distribution of various parameters especially, pollutants with respect to coastal processes like tides, current pattern and sedimentation
- Distribution of the parameters season wise including climatic conditions
- Effect of the industrial activity
- Influence of the shoreline configuration, intertidal extent and offshore processes
- Linkages with the various processes, especially sedimentation patterns existing within the Gulf of Khambhat.

For the present study, initially, the seawater samples (during high tide and low tide) as well as sediments (along the shore) were collected. Seawater samples were collected at intervals of 200mt. from the beginning of ASSBY (i.e. Plot 84C) to Sosiya end (Plot V). The shore sediments were also collected, mainly to observe about the content, moisture levels and determine the nature of the sediments and to get other relevant information. Gopnath and Gogha which lie on extreme and considerable distance from ASSBY were considered for studying control effects. The admiralty map No. 1486 & 2736 of approaches to Gulf of Khambhat was studied for the oceanographic conditions. The shore sediments were collected in the winter months when the net sedimentation is observed towards the shore. The visual study of the sediments along with the ground observations and the shoreline configuration helped in observing the linkages between sediment deposition, transportation and erosion along the shore. This further helped in fixing selected sampling spots at ASSBY and offshore regions, especially for sediment analysis. The results were validated with the study of the moisture content variations noted across the shore line sediments during the winter phase. Further, the intertidal region and the near shore water region were studied by taking a boat during the high tide and observing the bottom profiles and nature of sediments and their deposition. Discussions were made with the fishermen and labourers from the local area about their experiences and observations of the nature of the current pattern, patches were rocky substrata were available, tidal influence, sedimentation phenomenon, climate, local fauna and socio-economic issues. This helped in getting an overall view about the study area and correlating the coastal processes operating in the Gulf of Khambhat with the study area.

Based on the above observations and analytical results, it was observed that the sedimentation pattern along the shore was based on the tidal influence (high tide – low tide), seasonal effect, intertidal and onshore bottom topography, shoreline currents and the shoreline morphology. Further, there was a typical distribution of the fine and coarse sediment particles along the shoreline because of the above factors. This had an implication on the quantification and distribution of important parameters like metals and oil and grease. The analytical analysis of the sediment texture and concentrations of metal and oil and grease revealed distinct correlations existing amongst them. Hence, for sediment analysis; the sampling spots were selected based on the Zones of Accumulation (ZA) and Zones of transportation and erosion (ZT and ZE) of sediments along the shoreline of ASSBY. The sampling spots are referred to as; Alang Beginning, Alang Mid, Alang End,

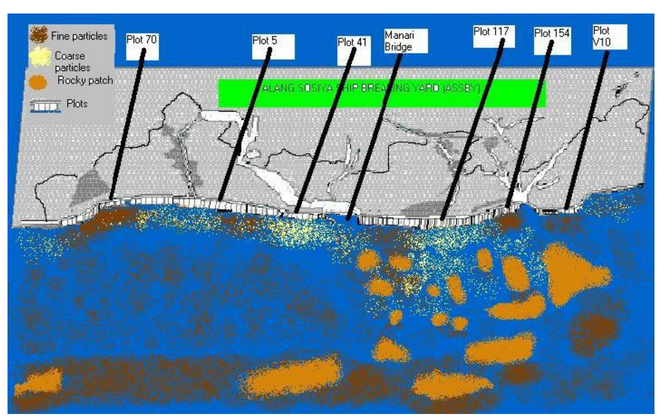


Figure 2 : Sediment distribution pattern based on personal observations.

Sosiya Mid and accordingly sediments samples were collected at High Tide, Low Tide and Offshore regions during winter (phase-I) and summer (phase-II). Discussions about the correlations are mentioned separately in the results section.

Sediment sampling spots along ASSBY shore.[Alang Beginning (Plot 70); Alang Mid (Plot 5); Alang End (Plot 41, Manari); Sosiya Mid (Plot 117, 154)].

The above zone demarcation of sampling spots helps in understanding the existing seawater quality and sediment status of an individual sampling spot as well as its surrounding areas. Further, any patterns or changes existing in the parameters within each zone as well as between the zones can be easily discernable. The procedure helps in bringing out the overall water and sediment quality status of the entire region and also predicts existing patterns and future patterns for changes or trends in some of the parameters. Another important feature of the zone demarcation is that it facilitates easy identification of sites that show extreme or unique conditions for certain parameters.

Sample frequency

Samples were collected from the predetermined spots identified as per the criteria discussed in the above sections. Seawater and sediment samples were taken during Phase I (i.e. December which is the winter season and also the post monsoon time) and during Phase II (i.e. during April, which is the summer season and also the pre monsoon time). The samples collected and parameters analyzed are given below.

Seawater Analysis

Phase-I (i.e. December-2000) Low tide
Phase II (i.e. April -2001) Low tide
Phase-I (i.e. December-2000) High tide
Phase-II (i.e. April -2001) High tide
Phase-I (i.e. December-2000) Off Shore Status
Phase II (i.e. April -2001) Off Shore Status
Parameters selected are pH, Turbidity, Salinity, S.S., NO2, PO4, DO, COD, BOD, Oil & Grease and Heavy metals like Zn, Mn, Cu, Co, Pb, Ni, Cd, As, Cr, and Hg.

Sediment Analysis

Phase-I (i.e. December-2000) Low tide
Phase II (i.e. April -2001) Low tide
Phase-I (i.e. December-2000) High tide
Phase-II (i.e. April -2001) High tide
Phase-I (i.e. December-2000) Off Shore Status
Phase II (i.e. April -2001) Off Shore Status
General parameters selected are, oil/grease, Heavy Metals, Sediment texture analysis.

Sampling procedures

Looking at variables like high current, high tidal difference and large inter tidal region (also the sediment pattern and personal observations of sediment texture of shore line), a strategy of collection of seawater and sediment samples was prepared. All high tide water samples were collected from approximately one meter depth during the approximately two hours span of high tide. Composite sediment samples were prepared of selected group of plots based on sediment texture. All low tide samples were collected similarly. A boat was hired to collect samples and it was ell equipped with samplers (water samplers, grab-sediment samplers).

Sample preservation

The collected samples were preserved as per standard methods. TABLE 2 outlines the preservation techniques.

TABLE 2 : Sample preservation and storage

Parameters	Sample container	Sample Volume	Sample Type	Sample treatment	Analysis period
BOD	P	1000	G	Refrigerate	6 h/48 h
COD	P	100	g, c	Analyze as soon as possible, or add H_2SO_4 to pH<2; refrigerate	7 d/28 d
Metals, general	P(A)	500	G	For dissolved metals filter immediately with 0.45 µ filter paper, add 1.5 ml con. HNO_3 to pH<2 and refrigerate at 4^0C	6 months
Mercury	P(A)	500	G	2ml /L 20% $K_2Cr_2O_7$ prepared in 1:1 HNO_3 and refrigerate at 4 ^{0}C	28 d
Nitrite	P	500	g, c	Refrigerate; add H_2SO_4 to pH<2	7 d/28 d
Oxygen, dissolved Winkler method	BOD bottle	300	G	Analyze immediately Titration may be delayed after acidification	0.5 h/stat 8 h/8 h
pH	P	50	G	Analyze immediately	2 h/stat
Phosphate	G(A)	100	G	For dissolved phosphate filter immediately; refrigerate	48 h/N.S.
Turbidity	P	100	g, c	Analyze same day; store in dark up to 24 h, refrigerate	24 h/48 h
S.S	P	100	G, c	Analyze same day; store in dark up to 24 hours, refrigerate	24h /48h
Salinity	P	100	G, c	Analyze within 24 hours Refrigerate; analyze at 480^0C for gravimetric method or analyze at room temp (27 ^{0}C) by conductivity meter	24h /48h

Chemicals and glassware

All chemicals used in the investigation were of AR grade either from E-Merck or from BDH. The stock solutions was prepared in double distilled water and used as and when required. For metal extraction, liquid-liquid extraction with APDC followed by MIEK and stock solutions of metals (1g/ml Metal) and deionized water having 18-25mho conductivity, along with standard electrolyte solutions were used.

Methodology

The samples were analyzed using standard methods including titrimetric, gravimetric, instrumental analysis, spectroscopy and biological methods. The methodology applied is outlined in TABLE 3.

TABLE 3 : Outline of methodology applied

Parameter	Method Applied for the present work
Turbidity	Nephelometry method
Solids	Laboratory Method
Metal ions (Zn, Mn, Cd, Pb, As, Al, Fe, Cu, Hg)	Electro analytical Method AAS applied(S.W.,D.P.P. and Stripping) and ICP,
Anions (Cl,NO_2,NO_3,PO_4,SO_4,F,NH_4)	Ion Chromatography, I.S.E.
Dissolved Oxygen	Iodometry, and Ion selective electrode
Bio-chemical Oxygen Demand	5-Day BOD Test
Chemical Oxygen Demand	Closed Reflux Titrimetric Method
Salinity	From Electrical conductivity, RI, Method

Metal analysis in sediment samples

The sediment samples were first air dried, later on oven dried at 110° C for 24 h. The dried samples were grounded to fine powder in agate mortar & pestle and sieved. The sieved homogenized fine powder was used in heavy metal analysis by Flame Emission Atomic Absorption Spectrophotometer (AAS) with back ground correction (Shimadzu AA-680) and X-ray fluoresce (XRF)spectrometer (Bruker AXS Spectrometer S4 Pioneer XRF). The procedure out lined Jones and Turki20 were followed for heavy metal analysis. To a weighed (~ 1 g) quantity of grounded sediment taken in a 250 ml Teflon beaker, 4m of 40% hydrofluoric acid (HF), 2 ml of 30% perchloric acid ($HClO_4$) 5 ml of 60% nitric acid (HNO_3) and 5 ml of 60% hydrochloric acid (HCl) were added in the sequence and heated to dryness after the addition of each of the above analytical grade (Merck) acids, respectively. The final residue was dissolved in 50 ml of 0.1 N Hydrochloric acid (HCl) and quantified by Flame Emission Atomic Absorption Spectrophotometer with background correction (Shimadzu AA-680). The sample was diluted suitably as and when necessary and carried out the analysis. External standards of each metal were prepared from their (1000 mg/kg) stocks as procured from Merck, and used in the calibration of AAS. All precautions were under taken during the sample collection, treatment and analyses of them in order to reduce potential contamination.

RESULTS AND DISCUSSION

The results are presented in order to understand the seawater quality and also the heavy metal distribution trend in the marine sediments. The seasons are represented as Phase –I which is during December 2000 (winter season) and is also the post monsoon period. Phase – II which is during April 2001 (summer season) and is also the pre monsoon period. The sampling from the study areas during the above phases are represented as the High Tide region (HT), Low Tide region (LT) and offshore.

Sea water analysis

Average Values of 25 samples (collected over selected sampling spots corresponding to specific plots ranging from 84C at Alang to V10 at Sosiya) are given in TABLE 4.

TABLE 4 : Average values of 25 seawater samples collected from selected sites

Parameters	Phase-I		Phase-II		Permissible limits
	Average Value*		Average Value*		
	L. T.	H. T.	L. T.	H. T.	
pH	8.34	8.239	8.71	8.62	5.5-9.0
Turbidity ***	202.5	229.8	137.24	142.1	-
Salinity *	30.7	30.9	32.06	31.75	-
S. S.	618	518	480	430	200
NO_2^{-1} **	0.0138	0.015	0.036	0.029	10
PO_4^{-3} **	41.9	41.01	54.5	53.3	5
DO **	4.83	4.75	4.9	4.92	6-8
COD **	60.3	63.1	54.1	56.8	250
BOD **	6.54	7.3	7.3	7.05	100
Oil & Grease **	63.96	64.61	95.2	98.5	20

*** (g/Kg at 280C) ** (mg/L) *** (NTU)**

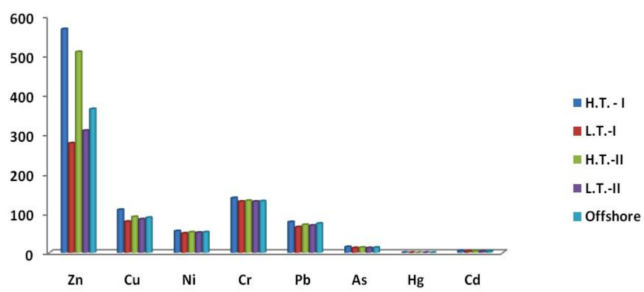
The results indicate that the overall turbidity levels are very high mostly due to the heavy sediments and churning of the sediments due to the tidal currents and amplitude. The salinity levels are slightly lower due to the freshwater inputs into the coast due to Manari river. Organic matter contamination is relatively low due to non-contamination from sewage or other domestic waste. The lower values of phosphates and nitrates also collaborate this result. However, the net oil and grease levels are extremely high (about 3 times more than permissible limits) and the area is heavily contaminated with hydrocarbons. This could be because of the direct discharge of oil and grease and other crude oil into the seawater during high tide. This practice therefore needs to be monitored and measures taken to treat the waste oil separately and disposed of safely inland.

Sediment analysis

Average values of metal concentration in sediment samples are compiled and discussed as below:

TABLE 5 : Average metal concentration (mg/Kg) in sediment samples

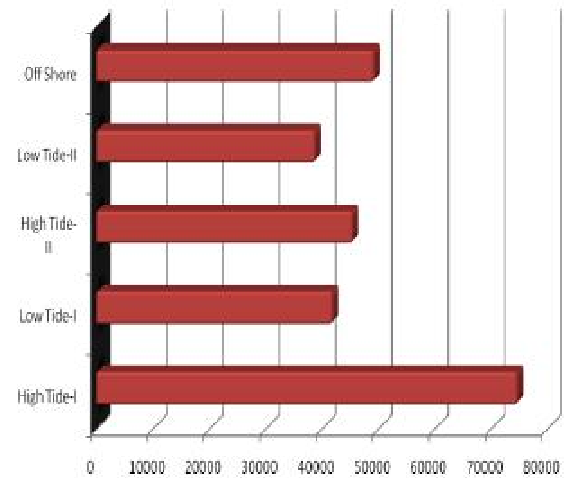
Metal Ions	H.T. - I	L.T.-I	H.T.-II	L.T.-II	Offshore
Zn	568	278	510	310	365
Cu	109	79	91	85	89
Ni	55	49	52	51	52
Cr	139	130	132	130	131
Pb	78.16	65	71	69	74
As	14.8	12	13	12	13
Hg	0.26	0.17	0.16	0.18	0.16
Cd	4.5	3.58	3.83	3.5	3.53



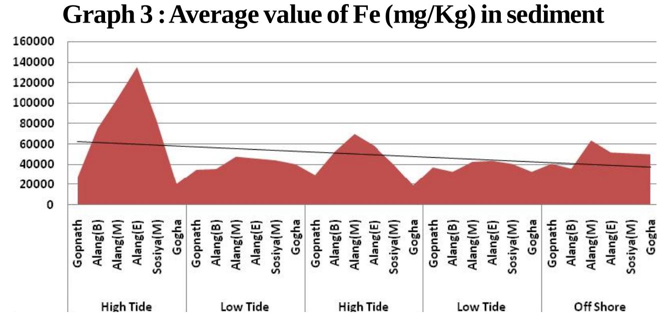
Graph 2 : Concentration (mg/Kg) of heavy metals in sediment

The results reveal all the sediment samples to have heavy metal values higher than the permissible limits, indicating heavy metal pollution in the region due to the ship breaking activities. The status of iron (Fe) is found extremely high that the results can not be compiled while comparing with the other metals mentioned above. The concentration of Fe is discussed separately.

From graph 3 it can be inferred that Fe concentrations reach an average of approximately 50,000 mg/Kg of dry sediment sample. If the values of only Alang area is considered, then the higher value reaches to 1,35,642 which shows approximately 10 % of the sediment weight is due to iron. It may be inferred that the heavy metals, especially Fe is most likely to be found as chunks (i.e. undissociated or undissolved) part in the sediments. This indicates that a substantial amount of Fe and other heavy metals contaminate the marine environment because of the unrestricted disposal of scrap and other metal wastes directly on the beach face or the immediate high tidal region. The current practice of cutting the ships on the high tidal slope is dangerous and therefore steps may be taken to construct dry docking methods or to take measures to dispose the metal waste and other scrap safely in the inland region, rather than disposing it on the beach front itself.



Graph 3 : Average value of Fe (mg/Kg) in sediment



Graph 4 : High concentration of Fe heavy metal at Alang compared to Gopnath and Gogha

Graph 4 reveals the trend of heavy metal (Fe) distribution. It indicates high concentration of iron at the sites Alang (B) and (M) compare to other sites like Gopnath and Gogha. Clearly the overall spread of heavy metal concentration in the marine sediments originate from Alang and spreading over to the offshore region. The sedimentation pattern, including the tidal currents and net sediment-deposition behavior would influence the availability of the heavy metals in the sediments. Steps must be taken to contain the metal contamination of sediments by incorporating appropriate metal scrap disposal methods, particularly to prevent it from being disposed directly into the beach front or high tidal area.

CONCLUSION

From the observations of the study area, analytical results, preliminary analysis of data and their correlation, it could be concluded that the suspended particles, entering to the gulf, from the number of river runoff water in the monsoon season plays an important role in overall natural quality of the seawater. The direct discharge of crude oil into the high tide waters during shipbreaking causes the spread of oil and grease in the marine water columns, including the offshore areas. The fluctuations in the turbidity levels in seawater across the different phases indicates that there is a typical movement of suspended solids in the period between high and low tides and net migration is found also affected with respect to seasons. This suspended particle have specific trend of settlement on the shoreline and high tidal and intertidal area. This creates specific sedimentation pattern and plays role in shielding-deshielding of pollutants. Thus, a specific correlation is observed between suspended particles and oil pollution. This is also observed for a specific correlation between suspended particles and metal pollution. The ASSBY shoreline would also be having zones of erosion, accumulation and transportation of sediments, which might directly have an implication on the availability of heavy metal in such zones.

Overall, the oil and grease content in the seawater and the heavy metal concentration in the marine sediments are extremely higher than the permissible levels and this calls attention for practicing cleaner ship breaking and recycling technologies and processes. The overall tidal amplitude and coastal processes operating in the Gulf of Khambhat makes the net pollutants to be dispersed out of the gulf or trapped in the offshore sediments, which might therefore make the marine waters and environment to be less polluted compared to the net amount of pollutant input during ship breaking activity. In such a situation continuous monitoring of the spread of pollutants is recommended and cleaner technologies and processes for ship recycling to be pursued.

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