

**“ANALYSIS OF TRACE METAL CONCENTRATION
IN HARBOR WATER AND SEDIMENT OF VERAVAL
COAST, GUJARAT”**

By

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B. F. Sc.



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**A THESIS SUBMITTED TO
JUNAGADH AGRICULTURAL UNIVERSITY IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF
MASTER OF FISHERIES SCIENCE**

**IN
FISHERIES RESOURCE MANAGEMENT**

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ACKNOWLEDGEMENT

I am very grateful for getting an opportunity to carry out my M.F.Sc. studies in the Department of Fisheries Resource Management, College of Fisheries Science, Junagadh Agricultural University, Veraval. All my experiences in the past years have made it an ever-good memory of my life. I wish to thank the many people who in one way or the other made this thesis possible. I express my sincere thanks to our Hon'ble Vice Chancellor **Dr. A. R. Pathak**, Director of Research & P.G. Studies **Dr. V. P. Chovatia**, Junagadh Agricultural University and **Dr. A. Y. Desai**, Dean and Principal College of Fisheries, J.A.U., Veraval for giving me an opportunity and cordial atmosphere to complete the course and research work programme.

It is a genuine pleasure to express my deep sense of thanks and gratitude to my mentor and guide **Dr. D. T. Vaghela**, Associate Professor and Head of Department of Aquatic Environment, College of Fisheries, J.A.U., Veraval. His dedication to work and support had been solely responsible for completing my work. His timely advice and meticulous scrutiny helped me to a very great extent to accomplish this task.

I sincerely express acknowledge the ever willing and sincere help offered my advisory committee members, **Dr. K. H. Vadher**, Associate Professor, Dept. of Aquaculture, **Shri. T. H. Dave**, Assistant Professor, Dept. of Fisheries Resource Management, **Dr. N. J. Rankja**, Associate Professor, Dept. of Agricultural Statistics, College of Agriculture, JAU., Junagadh.

I would like to express my deepest regards and respect to **Dr. B. A. Golakiya**, H.O.D., Food Testing Laboratory, J.A.U., Junagadh for providing me laboratory facilities to carry out sample analysis in its premises, **Shri. Vijay. G. Vyas** elemental cell, Food Testing Laboratory, J.A.U., Junagadh, and their staff for guiding me to perform my analysis. I extend my sincere thanks to **Dr. A. N. Sayani**, **Dr. D. V. Bholia**, **Shri. V. M. Chavda**, **Shri. J. B. Solanki**. I am thankful to all my professors for providing me guidance and suggestion during the entire study period.

I would like to express my honest gratitude and respect to **Shri. Vinay Kumar Vase**, Scientist, Dept. of Fisheries Resource Management, CMFRI, Veraval without his inspiration, expertized training and support I could have never complete statistical work during my studies.

I am thankful to **Shri. A. R. Dodiya and Ms. Deepika Lakdhir** for providing easy access to library and I am also thankful to **Mr. R. B. Vala, Rathod Narendrasinh** and all the staff members of the College of Fisheries Science, JAU., Veraval for their immense help.

I am very much thankful to my seniors, **Ramchandra Khileri, Veerendra Singh, Upasana Vyas, Ganesh Temkar, Milan Masani, Tehsin Panja, Sharman Vagh, Sanisth Sikotariya, Dhaval Jungi, Kalpesh Fofandi, Sunil Vaisya, and Thapetta Sudhakar** for their appreciation and guidance to perform research in better way and teach me in every step when I found difficulties during research and course work. I am also thankful to my dear batch mate **Rutvik, Pargi, Neelmani, Hariprasad, Pravin, Kanak, Mehul, Kiran, Toral, Kinjal, Mira, Ravina and Krishna** for their friendship, encouragement, cooperation and fruitful discussion during different stages of my studies and research. My big thanks goes to my juniors **Yagnesh, Raj, Sarman, Rehan, Naresh, Deepak, Vishal, Sonal, Durga, Pooja, Kinjal, Urmila, Dharmagna, Niharika and Shivani** who have helped me during my research, thank you for your support.

I would like to express my sincere thanks to **Harish Jungi and Nayan Vaisya** for assisting me during my sample collection.

I have no words to express my gratitude to my **Parents, Brother and Sisters** and my **Relatives** for their love, prayer, support, care and encouraging words were helped to me excellent in academics.

Place : Veraval

Date : /09/2019

(MALAMDI MAYUR T.)

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LIST OF ABBREVIATIONS

ABBREVIATIONS	FULL NAME
Al	: Aluminium
Ag	: Silver
°C	: Degree Celsius
ANOVA	: Analysis of Variance
As	: Arsenic
BOD	: Biological Oxygen Demand
Ca	: Calcium
Cd	: Cadmium
cm	: Centi Meter
Co	: Cobalt
COD	: Chemical Oxygen Demand
Cr	: Chromium
Cu	: Copper
DO ₂	: Dissolved Oxygen
<i>et al.</i>	: et all (and others)
Etc,	: et cetera (and other things)
Fe	: Iron
Fig.	: Figure
G	: Gram
GIDC	: Gujarat Industrial Development Corporation
Hg	: Mercury

HM	: Heavy Metal
HNO ₃	: Nitric Acid
H ₂ O ₂	: Hydrogen Peroxide
JAU	: Junagadh Agricultural University
K	: Kilogram
L	: liter
Mg	: Milligrams
Mn	: Manganese
Mo	: Molybdenum
MP-AES	: Microwave Plasma- Atomic Emission Spectrometer
MPN	: Maximum Portable Number
N	: Nitrate
Ni	: Nickle
P	: Phosphate
Pb	: Lead
ppb	: Parts Per Billion
ppm	: Parts Per Million
ppt	: Parts Per Thousand
Ti	: Titanium
Zn	: Zinc

LIST OF SYMBOLS

ABBREVIATIONS	FULL NAME
&	: And
:	: Colon
,	: Coma
°	: Degree
=	: Equal to
~	: Equivalence (approximately)
>	: Greater than
*	: Into
‘	: Left apostrophe
(: Left parenthesis
“	: Left double apostrophe
<	: Less than
×	: Multiplied by
µg	: Micro gram
/	: Per
%	: Percentage
±	: Plus or minus
’	: Right apostrophe
)	: Right parenthesis
”	: Right double apostrophe
;	: Semicolon

CHAPTER-I

INTRODUCTION

Metals are natural constituents of marine and freshwater environment, and are generally found in very low concentrations. The metals normally occur at low levels in the environment are termed as trace metal, because of their presence in trace concentrations. Heavy metals are one of the severe pollutants in natural environment due to their toxicity and persistence. The term heavy metal refers to any metallic chemical element that has a relatively high density (specific density of $>5\text{g/cm}^3$) and is toxic at high concentration (Zeitoun and Mehana, 2014). Examples of metals include cadmium (Cd), mercury (Hg), lead (pb), chromium (Cr), zinc (Zn), iron (Fe), copper (Cu) etc. The impact of anthropogenic disturbance is most strongly felt by estuarine and coastal environments adjacent to urban areas. In coastal environments and estuaries, which are often characterized by large industrial settlements and urban areas, the impact of effluent discharges leads to the accumulation of heavy metals. Discharge of greater quantity pollutants into the aquatic environment may result into deterioration of ecological imbalance, changes the physical and chemical nature of the water and aquatic biota.

1.1 Relation of metal with marine organism and marine environment:

Some metals are essential for life and some are merely beneficial. Adequate amount of trace metals in environment is essential for organism. The metal is regarded as essential if the organism can neither grow nor complete its life cycle without adequate availability of particular metals (Nammalwar, 1983).

The metal element has a direct influence on organism's metabolism. But the same metal element at higher concentrations is become toxic to the organism. Heavy metals are stable and persistent environmental contaminants of coastal waters and sediments. Interest in metals like Zn, Cu, Fe and Mn, which are required for metabolic activity in organisms lies in the narrow window between their essentiality and toxicity. Others heavy metals like Cd, Hg, Cr and Pb, may exhibit extreme toxicity even at low levels under certain conditions, thus necessitating regular monitoring of sensitive aquatic environments (Peerzada et al., 1990).

1.2 Accumulation and magnification of metal in marine environment:

Metals are soluble in water and cannot be eliminated from the water body, and settle at the bottom in high concentrations. The increase in the concentration of a metal in organism overtime in the environment is known as Bio-accumulation. These suspended metals come in contact with the primary food of the organism and passes so on into higher tropic level into the food chain. This phenomenon is called as Bio-magnification. Aquatic organisms, such as fish accumulate pollutants directly from contaminated water and indirectly via the food chain. Occurrence of chemical fertilizers containing trace of heavy metals causes contamination of fish with that metal (Khayatzadeh and Abbasi, 2010). Through the natural process of bio-magnification, minute quantities of metals become part of the various food chains and concentrations become elevated to levels which can prove to be toxic to both human and other living organisms (Ackefors, 1971).

1.3 Source of metal occurrence in water body:

Metals are present constitutently in the natural environment. However, human activity has inevitably increased the levels of metal ions in natural water bodies. Heavy-metal contamination is not a modern problem arising out of industrialization; it began when humans started processing ores (Paul, 2017). Mine drainage, industrial and sewage discards (pesticides, paints, textile, fertilizer, pharmaceuticals) and domestic effluents, agricultural runoff etc. have contributed to the increased metal load in natural water bodies and has ultimately incorporated into the aquatic sediments (Zeitoun and Mehana, 2014). This increase in urbanization and industrialization leads to an increase of marine discharges and therefore, the total load of pollutants being delivered to the sea (McGlashan, 1989). These discharges may contain heavy metals among other pollutants. The organic matter content in the sediments lead to relatively higher concentrations of heavy metals accumulation (Goutam and Ramanathan, 2013). Semi-enclosed coastal areas (harbors and lagoons with a narrow opening to open water) are more sensitive to anthropogenic impacts because of their lower ability to flush the contaminants than coastal areas with open boundaries with the sea (Owen and Sandhu 2000). Port terminals and harbor areas play important roles in the economy worldwide through the transport and storage of traded goods. However, their operating activities extremely harmful to marine and coastal environments. The installation of berths and docks in mangroves areas causes

several negative environmental impacts on the coastal zone such as sediment transport, introduction of exotic species and pollution. Wastewater, petroleum and antifouling paints are also sources of heavy metals (Buruaem *et al.*, 2012).

1.4 Impact of metal on organism and water quality:

High concentrations of metals in water are particularly dangerous to juveniles and may considerably reduce size of fish population, reduce survival rate, and stunted growth of larvae. The effect of metal on marine organism is seen on behavior, migration pattern, physiology, metabolism, reproduction, development and growth. There is also indirect effect on food chain and ecological stress (Khayatzadeh and Abbasi, 2010). In water, the metals are diluted and affected by various surface water components that form insoluble salts or complexes which sink into the bottom sediments (Khayatzadeh and Abbasi, 2010).

1.5 Practical utility of the research problem:

Metal pollution of marine water is less visible but its effect on marine ecosystem is very extensive. Metals get accumulate in bottom sediment from sediments it passes on to plankton and further passed on to fish and from fish to humans. Metals at higher level are harmful for human health in long term exposures which results in carcinogenic diseases; thus, concentrations of metals are needed to be identified within standard limits. Water and sediment of the polluted sites contain various levels of heavy metals. Measurement of heavy metals in both water and sediment samples can show the condition of the ecosystem regard to heavy metal pollution.

Veraval harbor is located on the Southwest coast of Saurashtra, Gujarat coast. Veraval fishing harbor was established for the purpose of harboring 400 fishing vessels (trawlers) only but at present it harbors more than 4000 vessels, which loads and unloads several tons of fish and by catches regularly in the fishing season. The fish caught from local and multi-day trawlers are unload in the harbor itself, where they are washed with water and the waste water is directly discarded into harbor water. Also at the time of loading and unloading of fish ice blocks used for chilling or storing fishes are kept directly on the ground which is washed with water from the ground water source from the harbor thus there may be occurrence of trace metal in

water which is need to be analyzed for healthy running of fishing business in Veraval harbor.

Apart from this, boat making yards are also in function which uses anti-fouling paints which keep boats hulk protected from biodegradable organisms. This anti-fouling paints uses certain metal compounds which gets flushed off slowly with time from the applied paints into the waters. Thus, the present study may help to know the increasing metal concentrations in the area.

Veraval fishing harbor also possess more than 60 fish processing plants in the GIDC area, the waste water from these fish processing plants is discarded after treating into a single effluent treatment plant near the Veraval harbor which act as a drainage point. However, the harbor has the stagnant water condition as there is a one side flow of the waste water into the sea-water with minimal circulation of water, which gets accumulated at small area in the harbor receiving very low amount of tides. This study may help to assess the trace metal concentrations in the harbor water and sediment occurring through possible source sewage discards and effluent plants.

Long term exposure to high concentration of metals leads to gradual and progressive physical, muscular and neurological degenerative process. This study may beneficial to know increasing concentrations of trace metals and it's controlling in Veraval coast, Gujarat.

1.6 Objectives:

- 1) To analyze concentration of trace metals (Cd, Cu, Zn) in harbor water and sediment of Veraval coast.
- 2) To examine physico-chemical parameters in harbor water and sediment of Veraval coast.
- 3) To compare seasonal variation of heavy metal concentration in harbor water and sediment in Veraval coast.

CHAPTER-II

REVIEW OF LITERATURE

2.1 Trace metal concentration in harbor water and sediment in World

Poulton (1987) analyzed water and sediment samples collected from Hamilton harbor near west end of Lake Ontario, Canada for the study of heavy metals and trace organic contaminants. The study revealed that in the harbor water copper (Cu) exceeded two-third times while other metals exceeded less frequently. Higher concentrations were found in the southeast part of the harbor near the major industrial and municipal discharges. As a result of mildly reducing conditions at the sediment-water interface, higher concentrations of manganese were found in bottom waters during late summer.

Glasby *et al.* (1988) analyzed 294 sediment samples from selected locations in Manukau and Waitemata Harbors, New Zealand. The data indicated that strong to moderate anthropogenic input of Pb, Zn, and Cu in certain parts of the harbors, particularly into Manukau Harbor and off Point Chevalier, Avondale, and the City Waitemata Harbor.

Angelidis and Aloupi (1995) studied on the metal concentration in sediments of Rhodes Harbor, Greece. The metal concentrations (Cd, Cr, Cu, Fe, Mn, Pb and Zn) were determined in the 0.5 N HCl extractable fractions of surface sediments. The results showed that the metals which were related to human activities (Cu, Pb and Zn) were found in relatively higher concentrations in the harbor sediments and in some cases showed important enrichment compared to the non-polluted coastal sediments indicating anthropogenic sources of metal contamination in polluted coastal areas.

Birch and Taylor (1999) investigated on the heavy metal contamination at port Jackson estuary in Australia. They come to know that the most extensive estuarine contamination occurred adjacent to intense commercial and industrial activity in the catchment, especially in the central city region. They find out that the storm water discharged via large canals with extensive catchments was a major point source of contaminants to the estuary. They observed that the estuarine sediments adjacent to these canals contain the highest concentrations of heavy metals and gradients decline rapidly away from discharge points.

Celo *et al.* (1999) studied heavy metal pollution, based on statistical analysis of concentrations in the sediments from an area along the Albanian coast. They used

Iron (Fe) as reference metal and identified the most significant pollution sources with known potential sources of contamination. They clearly demonstrated that some industrial activities such as mining, harbor and chlor-alkali plant affect the heavy metal concentration in the sediments.

Tanner *et al.* (2000) studied on the physical characteristics, and concentrations of major and trace metal, in 6 m long sediment cores from five marine locations in Victoria Harbor, Hong Kong. The results revealed that the most critical pollutant in the cores, Cu, had normalized enrichment factors between 2.8 and 312 at the five sites. The pollution of Cu, Ni and Cr were largely dated from the post-industrial period. Zn and Pb pollution source had a longer history from the construction, maintenance and anchoring of ships all of them were related to the sources of pollution through anthropogenic activities.

Fatoki and Mathabatha (2001) investigated the distribution of heavy metals (zinc, cadmium, copper, iron, manganese and lead) in seawater and sediments samples from East London and Port Elizabeth Harbors. They revealed that contribution of water drains and streams which carry runoff from industrial, urban, and residential sources in heavy metal pollution. They also suspected that ship repair activities were also responsible for elevated concentrations in the upper reaches of the harbor.

Guerra-Garcia and Garcia-Gomez (2005) investigated on the distribution of heavy metals, nutrients and total hydrocarbons in sediment samples from the harbor of Ceuta, North Africa. Results showed that the sediments inside the harbor of Ceuta were characterized by moderate levels of pollution, mainly hydrocarbons (496–6972 mg/g), nutrients P (282–1350 mg/g), N (100–2600 mg/g) and heavy metals Cu (5–865 mg/g), Pb (10–516 mg/g), Zn (296–695 mg/g), Cr (13–381 mg/g) and Ni (8–671 mg/g). The study revealed that the major sources of contamination was the sewage effluents of urban influence, antifouling paints and accidental oil spills during loading and dumping involved in shipping operations in the harbor.

Santos *et al.* (2005) investigated on the heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. They analyzed three groups of samples: (1) Ferraz surface sediments, with higher content of total trace metals and organic matter; (2) control sediments, with intermediate characteristics; (3) Ferraz soils, with higher bioavailability of most metals due to its

oxidizing condition and low organic matter content. The results showed that the major elements such as Fe, Al, Ca and Ti were present in similar levels in all three groups. Enrichment factor calculations revealed that the paints, sewage and petroleum contamination enhanced metal concentrations in Ferraz surface sediments as followed: Mo, and Pb (>90%); Zn (70–80%); Ni, Cu, Mg, and Mn (30–40%).

Chen *et al.* (2007) investigated distribution and accumulation of heavy metals in the sediments of the estuary in Kaohsiung harbor, Taiwan. They observed that the metal concentration in sediments varied from 0.58 mg kg⁻¹ for Cadmium (Cd) to 596 mg kg⁻¹ for Zinc (Zn) from standard limits. Metal concentrations at the vicinity of river mouths were higher than those of other location. Moreover, they came to know that the metal concentrations correlated closely to the physico-chemical properties of the sediments, which strongly suggested the accumulation of metal due to the industrial and municipal wastewaters discharges, into the harbor.

Zhang *et al.* (2007) studied about the concentrations of selected heavy metals (Cu, Pb, Zn, Cd, Cr, Ni and Fe) in surface sediments from nine sites in western Xiamen Bay and its adjacent Maluan Bay and Yuandang Lagoon, China. They found that the heavy metal concentrations in surface sediments sampled in the western Xiamen Bay and adjacent Maluan Bay and Yuandang Lagoon varied from 19 to 97 mg/kg for Copper (Cu), 45 to 60 mg/kg for Lead (Pb), 65 to 223 mg/kg for Zinc (Zn), 0.11 to 1.01 mg/kg for Cadmium (Cd), 37 to 134 mg/kg for Chromium (Cr), 25 to 65 mg/kg¹ for Nickel (Ni).

Abraham and Parker (2008) analyzed eight sediment cores for study of heavy metal (Cu, Pb, Zn, and Cd) enrichment factor from Tamaki Estuary, New Zealand using downward cored sub-samples. The results indicated a significant upward enrichment in heavy metals with the highest concentrations found in the uppermost 0–10 cm layer. Comparative data for normalized enrichment factors and the modified degree of contamination showed that Tamaki Estuary sediments have suffered significant systematic heavy metal contamination following catchment urbanization. Compared to baseline values the uppermost sediment layers showed four-fold enrichment averaged across eight cores and four analyzed metals.

Guo *et al.* (2010) studied on distribution, enrichment characteristics of heavy metals (such as lead, cadmium, copper, zinc, mercury and arsenic) in the sediments around Dongjiang Harbor, Tianjin in China. The results showed that the sediment enrichment factors of heavy metals were in the order of As > Zn > Cu > Hg > Pb >

Cd. They revealed that the concentration of Cu was low from nature, which was affected by human activities slightly. Hg was affected by human activities and exceeded standard much in many monitoring stations. As and Zn were affected seriously by human activities.

Sekabira *et al.* (2010) investigated pollution of stream sediments and possible sources of pollutants in Nakivubo Channel Kampala, Uganda. Stream sediments sample were collected and analyzed for heavy metal concentration. The results indicated that the sediments had been polluted with lead, cadmium and zinc and it was might be due to high anthropogenic influences.

Buruaem *et al.* (2012) studied on the contamination of port zone sediments by metals from Large Marine Ecosystems of Brazil. They assessed the extent of Al, Fe, Hg, Cd, Cr, Cu, Ni, Pb and Zn contamination in sediments from port zones in northeast (Mucuripe and Pecém) and southeast (Santos) Brazil through geochemical analyses and sediment quality. The results showed that the metal concentrations found in these port zones were higher than those observed in the continental shelf or the background values in both regions. In the northeast, metals were associated with carbonate, while in Santos, they were associated with mud. Geochemical analyses showed enrichments in metals such as Hg, Cd, Cu, Ni and Zn.

Pan and Wang (2012) studied on the trace metal contamination in estuarine and coastal environments in China. The study showed that metal contaminations in the coastal environments were closely associated with accelerated economic growth in the past decades due to elevated metal discharges from various sources such as industrial and domestic sewage discharge, mining, smelting, e-wastes recycling were important sources contributing to coastal pollution in China. High metal contents were detected in the sediments collected across the coasts in China. Alarmingly high metal concentrations were observed in the sediments, water and organisms collected from the heavily industrialized area.

Aly Williams *et al.* (2013) studied on the metal contamination in water, sediment and biota- the common cockle and the Mermaid's glove sponge from a semi-enclosed coastal area in Poole Harbor, UK. The results showed that metal contamination was detected in all environmental compartments. Water was polluted with As and Hg sediment metals were mostly within the possible effect range in which adverse effects occasionally occurred. Cockles had considerable concentrations

of Ni, Ag and Hg in areas close to pollution sources, and sponges were found to be accumulated with Cu and Zn with very high levels.

Esam *et al.* (2015) carried comparative assessment of certain heavy metals such as cadmium (Cd), copper (Cu), zinc (Zn), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni) and cobalt (Co) content in water and sediment from two stations (Al-Kumrah and Al-Shoaibah) in Jeddah, Saudi Arabia Red Sea Coast. The study revealed that there was a significant difference ($p < 0.05$) on the concentration of organic matters in the sediments (%), the highest concentration was detected in Al-Kumrah (17.38%) while the lowest concentration was in Al-Shoaibah (2.04%). These results suggested that the sample collected from Al-Kumrah site might be considered relatively polluted with heavy metals.

2.2 Trace metal concentration in harbor water and sediments in India

Govindasamy *et al.* (1999) studied the seasonal variation of heavy metals in coastal waters of Corromandel coast, Bay of Bengal. The results showed high values of Cu (63.20 $\mu\text{g/gm}$) and Cd (66.80 $\mu\text{g/gm}$) at Mahabalipuram and high values of Zn (130.20 $\mu\text{g/gm}$), Ni (14.60 $\mu\text{g/gm}$), Co (9.60 $\mu\text{g/gm}$) and Hg (0.12 $\mu\text{g/gm}$) at Pondicherry. The metal concentration in seawater were in order of $\text{Zn} > \text{Cu} > \text{Cd} > \text{Ni} > \text{Co} > \text{Hg}$ at Mahabalipuram and $\text{Zn} > \text{Cd} > \text{Cu} > \text{Co} > \text{Cu} < \text{Ni} > \text{Hg}$ at Pondicherry.

Palanichamy and Rajendran (2000) investigated on the heavy metal concentrations in seawater and sediments of Gulf of Munnar and Palk Bay, Southeast coast of India. The results revealed that bottom waters showed higher concentration of Cd and Pb as compared to surface waters in all coastal areas. The results of the sediments showed maximum level of Cd at Arumuganeri (4.33 ppm) and minimum level at Kanyakumari (0.4 ppm). Thus Arumuganeri area was found more polluted as compared to other areas.

Reddy *et al.* (2005) investigated on the seasonal distribution and contamination levels of heavy metals in seawater and dispersed total petroleum hydrocarbons. The results showed that the concentrations of heavy metals and petroleum hydrocarbons were higher in the winter season than in the monsoon and summer season.

Alagarsamy (2006) studied on concentrations and distribution of trace metal in surface sediments of Mandovi Estuary, Goa. Analysis of bulk sediments showed

that the concentrations of iron, manganese, copper, and zinc vary from 2.5 to 45.3 $\mu\text{g/g}$; 11.5 to 77.5 $\mu\text{g/g}$; 19.9 to 83.5 $\mu\text{g/g}$; and 4.5 to 46.5 $\mu\text{g/g}$, respectively. The enrichment of Iron (Fe) and Manganese (Mn) indicated the intensity of anthropogenic activity inputs related to iron ore processing in the upstream region of the estuary. Copper (Cu) and Zinc (Zn) enrichment in river mouth region indicated high organic carbon content indicative of organic waste from municipal sewage discharges into the estuary. He observed that the lowest metal concentrations were found during the monsoon, compared to the pre- and post-monsoon.

Shanmugam *et al.* (2007) studied on the levels of hydrological pollution of Chennai coastal zone in the southeastern part of India. Analysis of physical, chemical and biological parameter indicated that the concentrations of dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), nutrients (nitrate, nitrite and phosphate), turbidity, maximum probable number (MPN) and chlorophyll-a had reached notably high levels at all sample locations. The results for metal analysis showed that the concentrations of trace metals such as manganese, copper, nickel, lead, cadmium and cobalt also reached very high levels as a result of their sub-aqueous disposal in to the coastal areas. Higher concentrations of some elements such as lead, nickel, cobalt and cadmium were influenced due to the industrial wastes discards and had contaminated the coastal waters.

Sulochanan *et al.* (2007) studied on effect of anthropogenic activity at two stations each in Palk bay and gulf of Munnar, one referred as a non-polluted site and other as polluted site. The mean level of trace metals in sediments from polluted site were found in the concentration of Cd-1.23 ppm, Cu-5.42 ppm, Pb-15.52, and Zn-7ppm. The mean level of trace metals in clam tissue were Cd-1.12ppm, Cu-14.47, Pb-24.03, and Zn-267.2 ppm. The maximum level in seawater from polluted site were in the concentrations of Cd-1.11 ppb, Cu-26.78, Pb-21.35 ppb, Zn-247.12 ppb. Analysis of variance (ANOVA) showed that there was no significant difference in the trace metal levels in water, clam tissue, and sediments between polluted site and reference site.

Raj and Jayaprakash (2008) studied concentrations of heavy metals (Fe, Mn, Cr, Cu, Ni, Pb, Zn, Co and Cd) in sediments of Ennore shelf, Bay of Bengal to understand the metal contamination due to heavily industrialized area of Ennore, South-east coast of India. The concentration of metals showed significant variability and ranged from 284 to 460 $\mu\text{g/g}$ for Mn, 148.6 to 243.2 $\mu\text{g/g}$ for Cr, 385 to 657 $\mu\text{g/g}$

for Cu, 19.8 to 53.4 µg/g for Ni, 5.8 to 11.8 µg/g for Co, 24.9 to 40 µg/g for Pb, 71.3 to 201 µg/g for Zn and 4.6 to 7.5 µg/g for Cd. They concluded that the major sources of metal contamination were land based anthropogenic ones, such as discharge of industrial wastewater, municipal sewage and runoff.

Asha *et al.* (2010) studied concentration of heavy metals in sea water, sediment, and bivalves off Tuticorin coast. They revealed that the concentration were in order of $FE > MN > Zn > Cu > Pb > Cd > Ni$. High concentrations of Fe, Mn, Mg, Cu, Pb, and Zn were observed during monsoon season. The mean values of heavy metal concentration in the tissue, sediment and seawater samples in the three stations for Cd in the water (1.01 µg/gm) and sediment (1.65 µg/g); Cu in the water (7.45 µg/g) and clam tissue (17.97 µg/g) and Zn in the water (27.83 µg/g) samples were the highest. One-way ANOVA indicated statistically significant differences ($p < 0.01$) among the samples in the concentrations of Cu, Fe, Mn, Pb and Zn. Except for Cd and Cu, no significant difference was noticed in the seasonal variation of other metals.

Nobi *et al.* (2010) studied on the spatial distribution of metal concentrations in the surface sediment samples collected from marine locations covering different coastal ecosystems such as mangroves, sea grasses, dead coral and sandy beaches of the Andaman islands, India. Contamination Factor of heavy metals revealed different levels of accumulation viz. Al: 0.01–0.22, Mg: 0.38–1.85, Fe: 0.06–0.74, Mn: 0.04–1.18, Cu: 0.18–2.93, Cr: 0.52–12.6, Zn: 0.3–1.39, Ni: 0.06–0.89, Pb: 0–0.74, Co: 0.1–0.35 and Cd: 2.3–12.9. They concluded that the metal concentration were less in these ecosystems when compared to similar ecosystems of mainland of India. Concentration of some metals like Cr and Cd were comparatively higher than the background values.

Magesh *et al.* (2011) investigated impact of industrial effluents on the Tamiraparani estuary, Thoothukudi in Tamil Nadu by determining the degree of trace element contamination in the estuarine sediments. Vulnerability maps prepared from the index of geo-accumulation values revealed that the estuary is extremely contaminated with Cd and moderately contaminated with Zn and Pb. They concluded that the sources of these metals were associated with nearby chemical plants and harbor activities.

Balasubramanian (2012) studied on the wastewater toxicants especially heavy metals in water, particulate, zooplankton and in sediment from the southern Kerala coast, India. The heavy metal concentrations followed the hierarchy

Zn>Mn>Pb>Cu>Cd>Hg; Pb>Zn>Mn>Cu>Cd>Hg; Zn>Pb>Mn>Cu>Cd>Hg and Pb>Al>Cd>Hg in seawater, particulate matter, zooplankton and sediment respectively. The results revealed that in all transacts (except Cochin) the heavy metal concentrations were below the threshold levels associated with the toxicological effects and the regulatory limits. The calculation of enrichment factor, geo-accumulation index and pollution load index revealed minor to moderately severe enrichment of Cd, Pb and Hg in the industrial zones of the coastal stretches especially at Cochin.

Satpathy *et al.* (2012) studied on the variations of heavy metals in the marine sediments off Kalpakkam, East Coast of India. Heavy metal values showed maximum variation for Fe and minimum for Cd. The metal values showed the decreasing trend: Fe>Cu>Zn>Pb>Cr>Ni>Cd. This study showed that the major source of metals at Kalpakkam coast were land-based anthropogenic ones, such as, discharge from industrial waste, agricultural waste, urban, municipal and slum sewage into the Buckingham canal, which in turn discharges into the sea through backwater.

Bastami *et al.* (2014) studied spatial distribution, enrichment factor index (EFI), pollution load index (PLI) and potential ecological risk (PER) in two different seasons of the year (winter and summer) in surface sediments along southeast coast of the Caspian Sea. The results indicated that there were significant differences between concentrations of As, Ni and Pb in two different seasons. Considering reports of PER and PLI, during their study, sediments from southeast Caspian coast had low ecological risk and sediment from the southeast coast had no pollution.

Venkatramanan *et al.* (2014) analyzed surface sediments at the Tirumalairajan river estuary, Tamil Nadu, India and their surrounding coastal areas for the bulk metal concentration. The sediments were collected from pre- and post-monsoon seasons. The results revealed that metals such as Fe, Mn, Cu, Pb, and Zn demonstrated an increased pattern from the estuary when compared to the coastal area. The dominances of heavy metals were in order as: Fe > Mn > Zn > Pb > Cu in both seasons from estuary and coastal area. The contamination factor and geo-accumulation index showed that Zn, Pb, and Cu were unpolluted to moderately polluted from the sediments in estuarine part. The results showed that the major sources of metal contamination in catchment area were related to anthropogenic ones, such as agriculture runoff, discharge of industrial wastewater, and municipal sewage through the estuary and adjoining coastal area.

CHAPTER-III

MATERIALS AND METHODS

3.1 Experimental details:

3.1.1. Materials:

The materials used for conducting the experiment were as followed:

- a) Bucket
- b) Sampling bottles
- c) Polyethene bag
- d) Chemicals and Reagents
- e) Refractometer (ERMA 0-100% Salinity)
- f) Thermometer
- g) Digital pH meter (ANALAB Digital pH meter)
- h) Peterson grab
- i) Spectrophotometer (MP-AES)
- j) Sterile glassware

3.1.2. Location : Veraval Harbor
(Lat - 20°53'6 0.00N, Lon - 70°22'0.00E)

3.1.3. Year and season of Experiment : August - 2018 to March - 2019
August to September (Monsoon season)
October to December (Post-monsoon)
January to March (Pre-monsoon)

3.1.4. Number of replication : Three replications at monthly interval

3.2 Methodology:

Study Area-

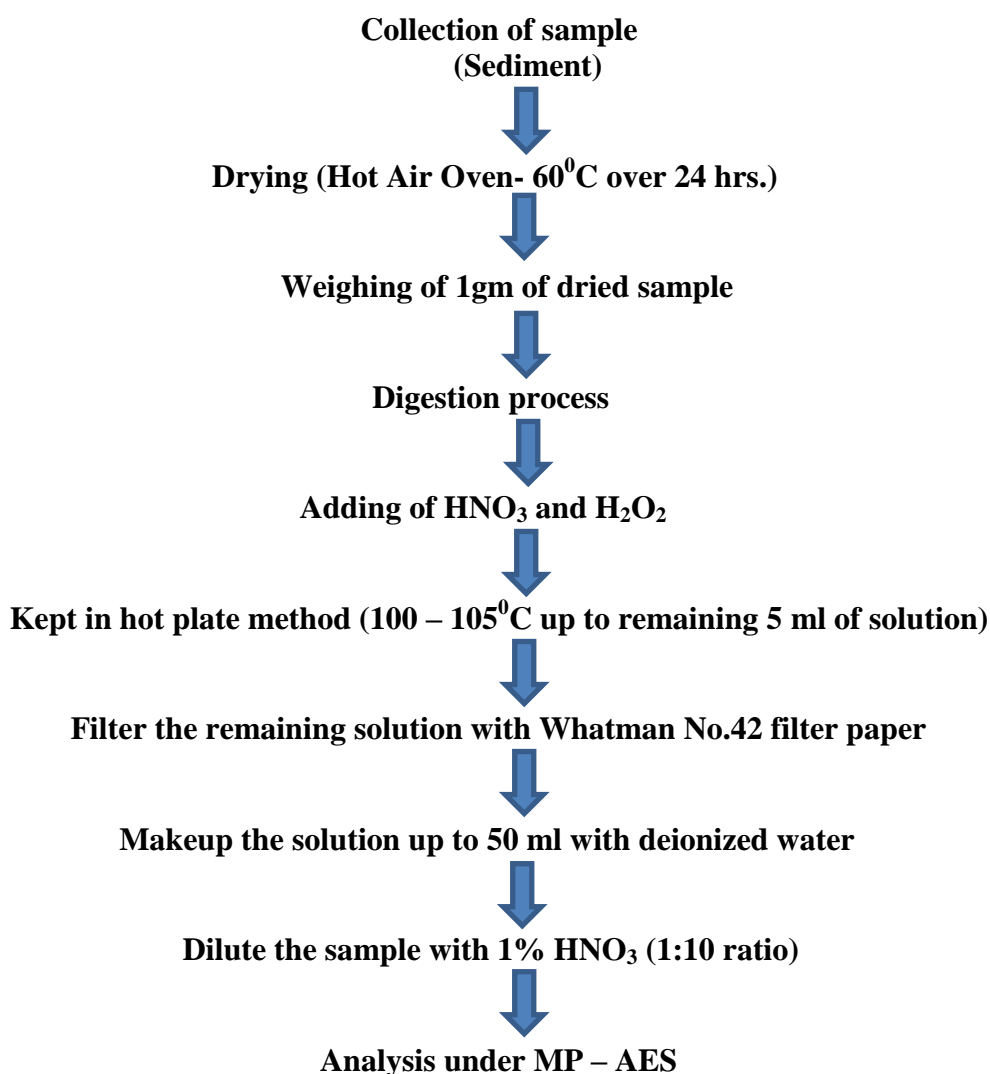
Veraval is located at 20.9°N and 70.37°E on the southwest coast of Gujarat, India. The main activities performed at the Veraval coast are processing and exporting of fish, which constitute a significant source of economy to the fisher population. The harbor has the stagnant water condition, due to siltation at the mouth, lack of turbulence, wind action and tidal effect in and around the jetty because of its inappropriate design, which makes dilution an impossible task for tides coming towards the jetty. During study period of 8 months the seasonal data set from the study sites was taken considering weather condition of the region, representing the periods of monsoon season (August to September), post-monsoon season (October to

December) and pre-monsoon season (January to March) comprising of all seasonal effect on harbor. Water and sediment samples was collected from three different stations as one at the mouth of the harbor, second middle point of the harbor and third end point of harbor in Veraval and was analyzed with the help of standard methods.

3.2.1 Methodology for Trace metal Analysis in sediment from harbor area

The sediment samples from the different stations were collected using Peterson grab operated manually from the deck of the fishing vessel anchored in harbor. The grab was held down in water until sediment surface bed is reached then the grab was pulled up and sediment sample was collected, collected sample was kept in polythene bag and taken to the laboratory for preservation under refrigeration and then further analysis was done.

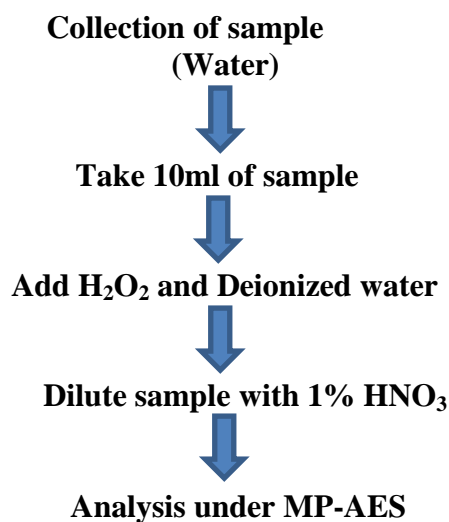
Methodology for trace metal analysis in sediment sample:



3.2.2 Methodology for Trace metal Analysis in harbor water.

The water sample from the different stations as station-1, station-2 and station-3 were collected using water sampling bottles. The collected sample for trace metal analysis was taken to the laboratory and preserved under refrigeration and then further analysis was done.

Methodology of trace metal analysis in water sample:



3.2.3 Methodology for Analysis of physico-chemical parameters.

pH- The pH of harbor water surface was measured on site with the help of Digital pH meter by holding it in the water surface 2 - 4 cm deep in water for 2 minutes and after removing, the recorded value obtained in pH meter was noted.

Temperature- The surface temperature of harbor water was measured using thermometer still in water surface up to 2cm for about 2 minutes and after removing, the indicated temperature in thermometer was noted.

Salinity- The salinity of harbor water was measured using hand held Refractometer which was calibrated before using. Water sample was taken in pipette dropper and was filled into cover flap of refractometer. After closing the flap the refractometer was held horizontally towards light source and through eyepiece the reading was noted.

Total Suspended Solid- TSS of harbor water was measured in laboratory by mass balance method (APHA, 1995) in TSS measurement unit. A well-mixed sample was filtered through glass fiber filter and residue was retained on filter was dried to a constant weight at 103-105⁰C. The TSS was determined by increase in weight of filter and was calculated using below given equation.

Calculation of TSS:

$$\text{Total Suspended Solids (mg/L)} = \frac{(\text{W1}-\text{W2}) \times (1000)}{\text{Sample volume (ml)}}$$

Where,

W1 =Weight of dried glass fiber filter + residue

W2 = Weight of dried glass fiber filter disk before filtering

Dissolved Oxygen- The collected sample in tightly capped DO bottles were brought to laboratory and DO was measured following Winkler's method. The cap was removed from DO bottle and 1ml each of Winkler A and Winkler B was added to the sample. The bottles were shake gently until precipitation formed was evenly distributed then 2ml concentrated sulfuric acid was added and yellow to brown-orange color was appeared. From this 50ml sample was pipette out in conical flask and was titrated against 0.025N sodium thiosulphate solution until color became pale yellow. Then 1ml of starch solution was added and titration was continued until blue color was disappeared. Reading was noted and calculated using below given equation.

Calculation of DO:

$$\text{Dissolved Oxygen (mg/L)} = \frac{\text{ml of Titrant} \times \text{N2} \times 1000 \times 8}{\text{Volume of sample taken}}$$

Where: N2 = Normality of titrant (0.025)

3.3 Statistical Analysis

Random sampling was done. The collected data was analyzed by using Completely Randomized Design method along with arithmetic mean, standard deviation, coefficient variance and test of significance (Snedecor and Cochran, 1967).

CHAPTER-IV

RESULTS AND DISSCUSION

The concentration of trace metals cadmium (Cd), copper (Cu) and zinc (Zn) in harbor water and sediment from Veraval coast, Gujarat were analyzed for a period of eight months from August,2018 to March,2019 comprising of monsoon season (August-September), post-monsoon season (October-December) and pre-monsoon season (January-March). Water and sediment samples were collected from three different stations as one at the mouth of the harbor, second middle point of the harbor and third end point of harbor in Veraval and were analyzed with the help of standard methods. Significant differences between stations and between months were calculated using Tukey method at 5% level. The harbor has the stagnant water condition, due to siltation at the mouth, and minimal circulation of water in and around the jetty due to its inappropriate design, making dilution a difficult task for tides coming towards the jetty.

4.1 Cadmium

Cadmium is a chemical element with the symbol Cd. It is a trace metal widely distributed in the Earth's crust at an average concentration of about 0.1 mg kg^{-1} and is commonly found in association with zinc. Higher levels are present in sedimentary rocks viz. marine phosphates. Weathering and erosion by rivers result in the transport of large quantities of cadmium to the world's oceans. The vertical distribution of dissolved cadmium in ocean waters is characterized by a surface depletion and deep water enrichment, which corresponds to the pattern of nutrient concentrations in these areas (Boyle *et al.*, 1976).

4.1.1 Cadmium concentration in sediment of harbor area, Veraval Coast Gujarat.

Cadmium concentration in the sediment from three different stations in harbor area was analyzed during the study period. The highest mean concentration of (Cd) was observed in post-monsoon season (0.72 ppm) at station-3 in November and lowest concentration in monsoon season (0.01 ppm) at station-1 in August (Table 4.1; Fig.4.1). Similar work was carried out by Sundarajan *et al.*, (2017) at Veraval harbor and the concentration of cadmium was found as 0.628 ppm in sediment.

Table 4.1 Trace metal Cadmium (Cd) concentration (ppm) in sediment of harbor area, Veraval coast, Gujarat.

Season	Month	Station-1 Mean \pm SE	Station-2 Mean \pm SE	Station-3 Mean \pm SE
Monsoon	Aug.18	0.01 \pm 0	0.02 \pm 0.007	0.02 \pm 0
	Sep.18	0.17 \pm 0.056	0.15 \pm 0.063	0.20 \pm 0.014
Post-Monsoon	Oct.18	0.29 \pm 0.134	0.29 \pm 0.091	0.23 \pm 0.042
	Nov.18	0.45 \pm 0.056	0.32 \pm 0.106	0.72 \pm 0.049
	Dec.18	0.54 \pm 0.042	0.38 \pm 0.021	0.38 \pm 0.056
Pre-Monsoon	Jan.19	0.15 \pm 0.049	0.20 \pm 0.049	0.27 \pm 0.035
	Feb.19	0.15 \pm 0.042	0.22 \pm 0.014	0.28 \pm 0.014
	Mar.19	0.12 \pm 0.056	0.21 \pm 0.063	0.19 \pm 0.056

(The values were average of three samples with standard error)

Fig 4.1 Monthly variation of Cadmium (Cd) concentration (ppm) in sediment between three stations in harbor area, Veraval coast, Gujarat.

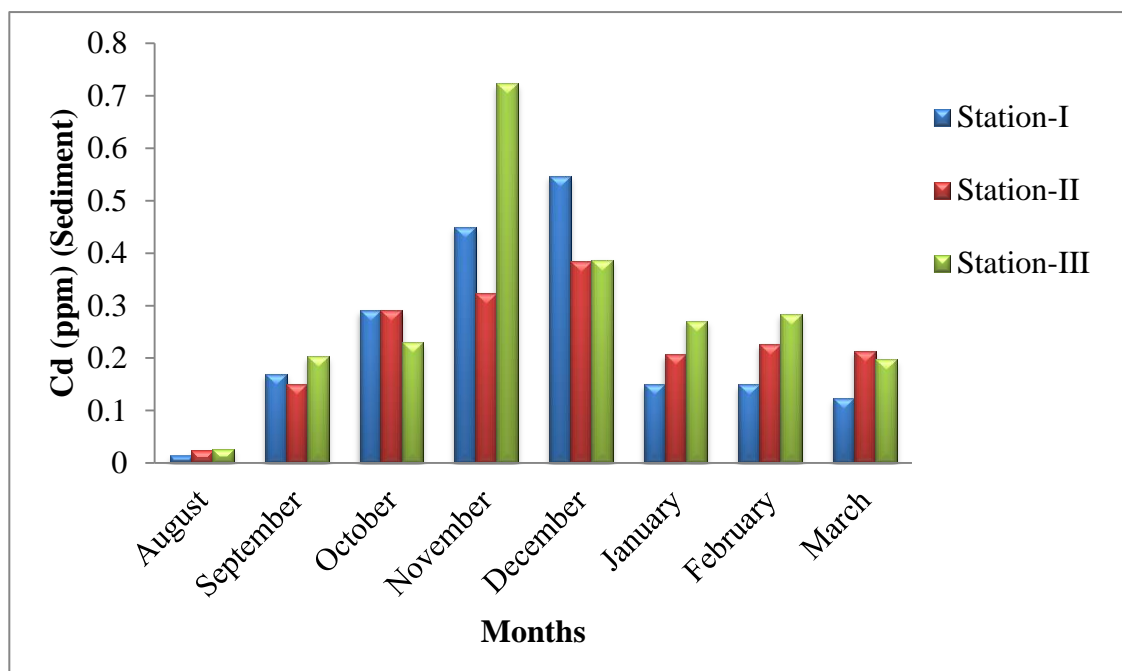


Table 4.2 One-way ANOVA of sediment versus station

One way ANOVA sediment versus station					
Source	DF	SS	MS	F	P
Station	2	0.0603	0.0301	1.07	0.347
Error	69	1.9342	0.280		
Total	71	1.9945			
S= 0.1674	R-Sq= 3.02 %	R-Sq (adj) = 0.21 %			

No **Significant differences** were observed among the **stations** in **sediment** during collection of sample (One-way ANOVA, df=2, F=1.07, P>0.05).

Table 4.3 One-way ANOVA of sediment versus months

One way ANOVA sediment versus months					
Source	DF	SS	MS	F	P
Station	7	1.472	0.21035	25.79	0.000
Error	64	0.522	0.00816		
Total	71	1.994			
S= 0.09031	R-Sq= 73.83 %	R-Sq (adj) = 70.96 %			

Significant differences were observed surrounded by the **months** in **sediment** during collection of sample (One-way ANOVA, df=7, F=25.79, P<0.05).

4.1.2 Cadmium concentration in harbor water of harbor area, Veraval Coast Gujarat.

Cadmium concentration was below detection limit (< 0.1 ppm) thus it was not detected in harbor water sample collected during the study period from all three stations in Veraval harbor, Gujarat. The similar concentration of Cd in seawater (0.15 ppm) at Veraval harbor was found by Majithiya *et al.* (2018) during their study period.

4.2 Copper

Copper is a chemical element with the symbol Cu. It is a trace metal present naturally in earth's crusts. Copper may exist in a natural water system, either in the dissolved form as the cupric ion or as suspended particles when present as a

precipitate or absorbed to organic matter (Mance and Yates, 1984a). Copper enter the aquatic environment through natural sources or by anthropogenic sources which may led to significant concentrations entering the aquatic environment either directly via sewage or industrial discharges or through atmospheric deposition.

4.2.1 Copper concentration in sediment of harbor area, Veraval Coast Gujarat.

The highest and lowest levels of Copper (Cu) concentration in sediment sample collected from Veraval harbor were found in December (307.70 ppm) in post-monsoon season at station-3 and in August (16.60 ppm) in monsoon season at station-1 respectively (Table 4.4; Fig.4.2).

Chen *et al.*, (2007) analyzed sediment samples from six locations in the Kaohsiung harbor, Taiwan and the concentration of Cu was observed between (5 - 946 ppm) from these locations. The concentration of (300 ppm) and (411.3 ppm) was recorded at location-4 and location-5 respectively by them.

Table 4.4 Trace metal Copper (Cu) concentration (ppm) in sediment from harbor area, Veraval coast, Gujarat.

Season	Month	Station-1 Mean ± SE	Station-2 Mean ± SE	Station-3 Mean ± SE
Monsoon	Aug.18	16.60 ± 0.212	46.63 ± 0.565	112.86 ± 2.757
	Sep.18	20.40 ± 1.202	52.56 ± 6.858	130.20 ± 3.040
Post-Monsoon	Oct.18	31.03 ± 0.827	86.87 ± 18.186	247.78 ± 43.57
	Nov.18	29.33 ± 1.343	93.20 ± 19.798	263.76 ± 11.66
	Dec.18	38.35 ± 8.711	94.64 ± 31.247	307.70 ± 41.81
Pre-Monsoon	Jan.19	18.40 ± 1.060	52.26 ± 0.141	117.43 ± 6.363
	Feb.19	18.60 ± 0.141	53.06 ± 0.494	126.26 ± 4.808
	Mar.19	17.10 ± 4.030	52.40 ± 5.091	162.86 ± 46.66

(The values were average of three samples with standard error)

Fig 4.2 Monthly variation of Copper (Cu) concentration (ppm) in sediment between three stations at harbor area, Veraval coast, Gujarat.

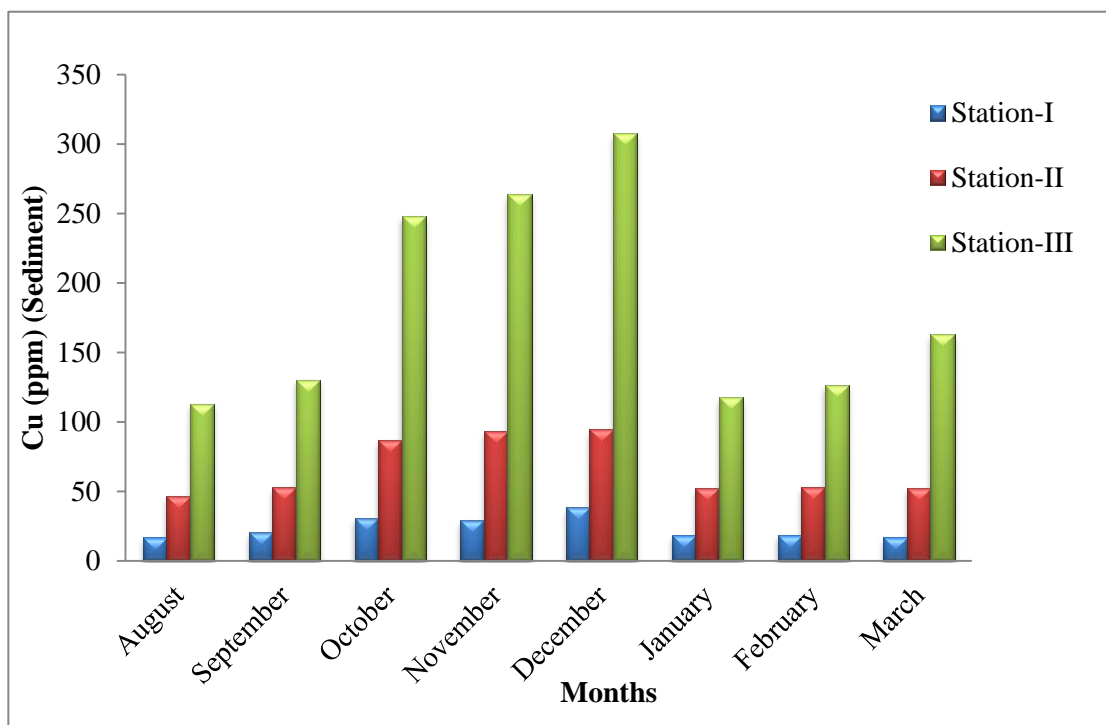


Table 4.5 One-way ANOVA of sediment versus station

One way ANOVA Sediment versus station					
Source	DF	SS	MS	F	P
Station	2	328914	164457	76.39	0.000
Error	69	148544	2153		
Total	71	477458			
S= 46.40	R-Sq= 68.89 %	R-Sq (adj) = 67.99 %			

Significant differences were observed among the **stations** in **sediment** during collection of sample (One-way ANOVA, df=2, F=76.39, P<0.05).

Table 4.6 One-way ANOVA of sediment versus months

One way ANOVA sediment versus months					
Source	DF	SS	MS	F	P
Station	7	78308	11186.866	1.794	0.104
Error	64	399150	6236.721		

Total	71	477458		
S= 78.97	R-Sq= 16.40 %	R-Sq (adj) = 7.26 %		

No Significant differences were observed surrounded by the **months** in **sediment** during collection of sample (One-way ANOVA, df=7, F=1.794, P>0.05).

4.2.2 Copper concentration in harbor water of harbor area, Veraval Coast Gujarat.

The highest and lowest levels of Copper (Cu) concentration in harbor water collected from Veraval harbor were found in March (1.65 ppm) in pre-monsoon season at station-2 and in January (0.06 ppm) in pre-monsoon season at station-3 respectively (Table 4.7; Fig.4.3).

Chan (1992) studied on the heavy metal concentration in seawater with distance from Inner Tolo Harbor, during his study period the concentration of Cu (11.8 ppm) was observed.

Table 4.7 Trace metal Copper (Cu) concentration (ppm) in harbor water from harbor area, Veraval coast, Gujarat.

Season	Month	Station-1 Mean ± SE	Station-2 Mean ± SE	Station-3 Mean ± SE
Monsoon	Aug.18	1.52 ± 0.233	1.49 ± 0.332	1.53 ± 0.325
	Sep.18	1.57 ± 0.021	1.15 ± 0.042	1.33 ± 0.098
Post- Monsoon	Oct.18	1.30 ± 0.452	0.59 ± 0.374	0.63 ± 0.459
	Nov.18	0.49 ± 0.056	0.56 ± 0.091	0.70 ± 0.247
	Dec.18	0.60 ± 0.148	0.53 ± 0.049	0.23 ± 0.091
Pre- Monsoon	Jan.19	0.18 ± 0.035	0.08 ± 0.014	0.06 ± 0.035
	Feb.19	1.36 ± 0.127	1.22 ± 0.014	1.10 ± 0.007
	Mar.19	1.45 ± 0.091	1.65 ± 0.282	1.30 ± 0.410

(The values were average of three samples with standard error)

Fig 4.3 Monthly variation of Copper (Cu) concentration (ppm) in harbor water between three stations in harbor area, Veraval coast, Gujarat.

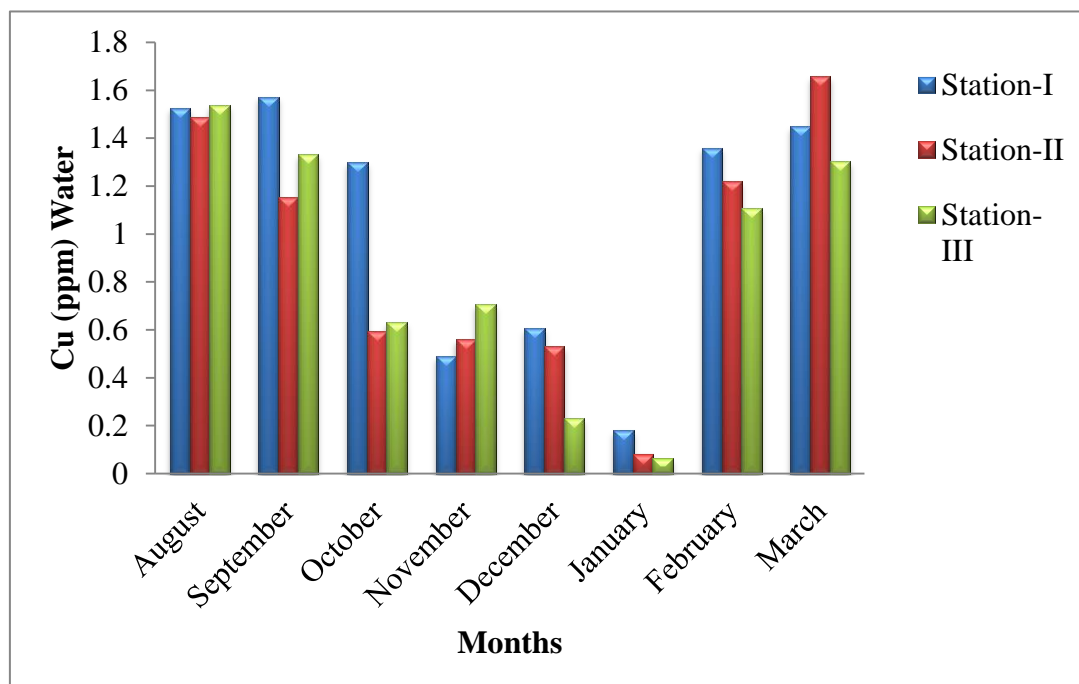


Table 4.8 One-way ANOVA of water versus stations

One way ANOVA water versus stations					
Source	DF	SS	MS	F	P
Station	2	0.507	0.253	0.83	0.442
Error	69	21.140	0.306		
Total	71	21.647			
S= 0.5535	R-Sq= 2.34 %	R-Sq (adj) = 0.00 %			

No significant differences were observed among the stations in water during collection of sample (One-way ANOVA, df=2, F=0.83, P>0.05).

Table 4.9 One-way ANOVA of water versus months

One way ANOVA water versus months					
Source	DF	SS	MS	F	P
Station	7	17.3649	2.4807	37.08	0.000

Error	64	4.2819	0.0669		
Total	71	21.6468			
S= 0.2587	R-Sq= 80.22 %	R-Sq (adj) = 78.06 %			

Significant differences were observed surrounded by the **months** in **water** during collection of sample (One-way ANOVA, df=7, F=37.08, P<0.05).

4.3 Zinc

Zinc is a chemical element with the symbol Zn. It is a ubiquitous element occurring in many rocks in Earth's crust and as a trace constituent in the oceans and the atmosphere. It may enter the aquatic environment in both dissolved forms and associated with suspended particles (Mance and Yates, 1984b) through natural or anthropogenic sources, including sewage and industrial discharges.

4.3.1 Zinc concentration in sediment of harbor area, Veraval Coast Gujarat.

In sediment collected from three different stations at Veraval harbor, the highest concentration of metal (Zn) was found in post-monsoon season (704.92 ppm) at station-3 in December and lowest concentration was found in monsoon season (22 ppm) at station-1 in August (Table 4.10; Fig.4.4).

The concentration of zinc (603 ppm) in sediment was found by Sundarajan *et al.* (2017) during their study period in Veraval harbor, Gujarat.

Table 4.10 Trace metal Zinc (Zn) concentration (ppm) in sediment from harbor area, Veraval coast, Gujarat.

Season	Month	Station-1	Station-2	Station-3
		Mean ± SE	Mean ± SE	Mean ± SE
Monsoon	Aug.18	22 ± 2.12	111.86 ± 3.04	229.46 ± 20.7
	Sep.18	25.43 ± 3.60	127.10 ± 12.5	261.63 ± 10.1
Post-Monsoon	Oct.18	53.38 ± 13.82	190.37 ± 84.2	476.50 ± 24.0
	Nov.18	59.53 ± 3.04	221.83 ± 82.8	514.23 ± 28.8
	Dec.18	72.58 ± 22.9	230.98 ± 62.7	704.92 ± 176.2

Pre-Monsoon	Jan.19	24.56 ± 5.37	121.36 ± 1.76	249.10 ± 21.3
	Feb.19	22.46 ± 1.76	121 ± 5.79	250.66 ± 50.06
	Mar.19	23.36 ± 6.15	121.36 ± 1.34	229.10 ± 33.09

(The values were average of three samples with standard error)

Fig 4.4 Monthly variation of Zinc (Zn) concentration (in ppm) in sediment between three stations at harbor area, Veraval coast, Gujarat.

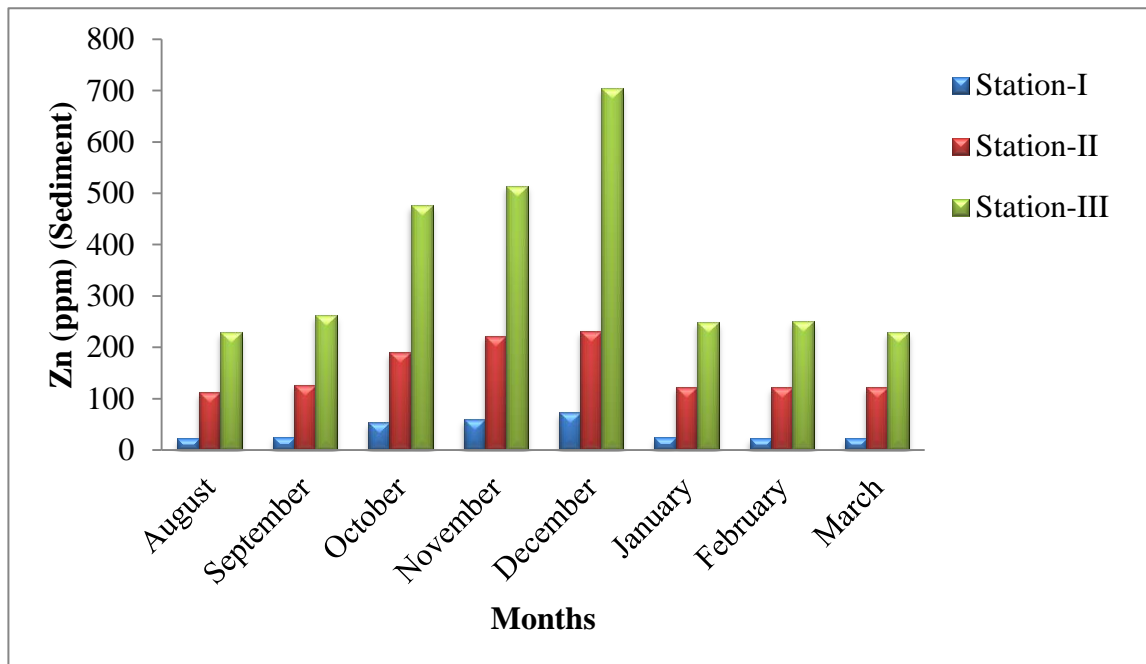


Table 4.11 One-way ANOVA of sediment versus station

One way ANOVA sediment versus station					
Source	DF	SS	MS	F	P
Station	2	1312565	656282	52.71	0.000
Error	69	859182	12452		
Total	71	2171747			
S= 111.6	R-Sq= 60.44 %	R-Sq (adj) = 59.29 %			

Significant differences were observed among the **stations** in **sediment** during collection of sample (One-way ANOVA, df=2, F=52.71, P<0.05).

Table 4.12 One-way ANOVA of sediment versus months

One way ANOVA sediment versus months					
Source	DF	SS	MS	F	P
Station	7	431644.225	61663.461	2.268	0.040
Error	64	1740102.889	27189.108		
Total	71	2171747.114			
S= 164.9	R-Sq= 19.88 %	R-Sq (adj) = 11.11 %			

Significant differences were observed surrounded by the **months** in **sediment** during collection of sample (One-way ANOVA, df=7, F=2.268, P<0.05).

4.3.2 Zinc concentration in harbor water of harbor area, Veraval Coast Gujarat.

In harbor water sample collected from three different stations at Veraval harbor, during the study period the highest concentration of metal (Zn) was recorded in post-monsoon season (3.32 ppm) at station-2 in November and lowest concentration was recorded in monsoon season (0.07 ppm) at station-1 in August (Table 4.13; Fig.4.5).

Table 4.13 Trace metal Zinc (Zn) concentration (ppm) in harbor water from harbor area, Veraval coast, Gujarat.

Season	Month	Station-1 Mean ± SE	Station-2 Mean ± SE	Station-3 Mean ± SE
Monsoon	Aug.18	0.07 ± 0.007	0.12 ± 0.021	0.14 ± 0.014
	Sep.18	0.26 ± 0.070	0.34 ± 0.141	0.39 ± 0.049
Post- Monsoon	Oct.18	1.12 ± 0.777	2.39 ± 0.318	1.92 ± 0.275
	Nov.18	0.49 ± 0.134	3.32 ± 1.060	1.30 ± 0.070
	Dec.18	0.43 ± 0.360	2.72 ± 0.530	1.54 ± 0.707
Pre- Monsoon	Jan.19	0.74 ± 0.275	1.05 ± 0.028	0.74 ± 0.643
	Feb.19	0.88 ± 0.226	2.52 ± 0.664	1.37 ± 0.346
	Mar.19	0.85 ± 0.127	1.46 ± 0.565	1.28 ± 0.134

(The values were average of three samples with standard error)

Fig 4.5 Monthly variation of Zinc (Zn) concentration in harbor water between three stations at harbor area, Veraval coast, Gujarat.

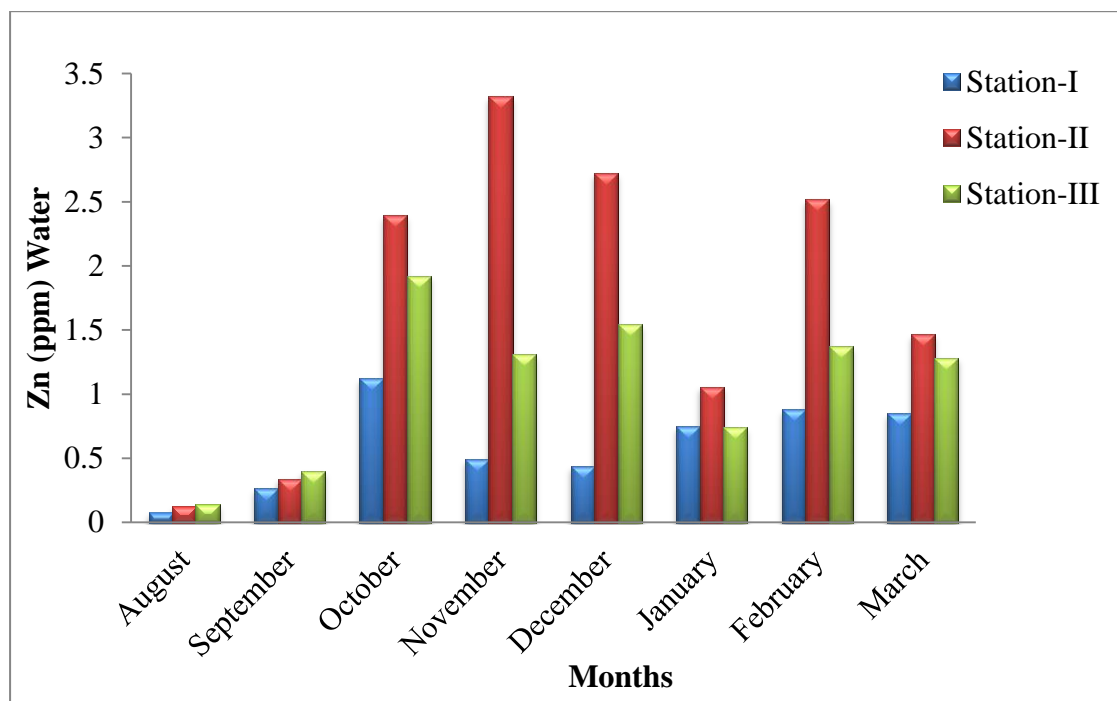


Table 4.14 One-way ANOVA of water versus station

One way ANOVA water versus station					
Source	DF	SS	MS	F	P
Station	2	15.560	7.780	11.60	0.000
Error	69	46.266	0.671		
Total	71	61.826			
S=	R-Sq= 25.17 %	R-Sq (adj) = 23.00 %			
0.8189					

Significant differences were observed among the **stations** in **water** during collection of sample (One-way ANOVA, df=2, F=11.60, P<0.05).

Table 4.15 One-way ANOVA of water versus month

One way ANOVA water versus month					
Source	DF	SS	MS	F	P
Station	7	26.552	3.793	6.882	0.000

Error	64	35.273	0.551		
Total	71	61.826			
S= 0.7424	R-Sq= 42.95%	R-Sq (adj) = 36.71 %			

Significant differences were observed surrounded by the **months** in **water** during collection of sample (One-way ANOVA, df=7, F=6.882, P<0.05).

Physico-chemical parameters at harbor area Veraval coast, Gujarat.

Physico-chemical parameters such as (pH, Salinity, Temperature, Dissolved Oxygen and Total Suspended Solids) in harbor water sample collected from three different stations at Veraval harbor area, Veraval coast, Gujarat were analyzed with standard methods.

4.4 pH

During the study period the lowest value of pH was stated in pre-monsoon season in the month of January (7.36) at sation-3 and highest was observed in post-monsoon season in the month of November (7.96) at station-1 (Table 4.16.; Fig 4.6).

Table. 4.16 Monthly variations in pH between three stations at harbor area, Veraval coast, Gujarat.

Season	Month	Station-1	Station-2	Station-3
Monsoon	Aug.18	7.86	7.66	7.53
	Sep.18	7.90	7.63	7.53
Post-Monsoon	Oct.18	7.93	7.60	7.46
	Nov.18	7.96	7.46	7.40
	Dec.18	7.96	7.50	7.40
Pre-Monsoon	Jan.19	7.86	7.53	7.36
	Feb.19	7.93	7.53	7.46
	Mar.19	7.96	7.60	7.40

Fig. 4.6 Monthly variations in pH between three stations at harbor area, Veraval coast, Gujarat

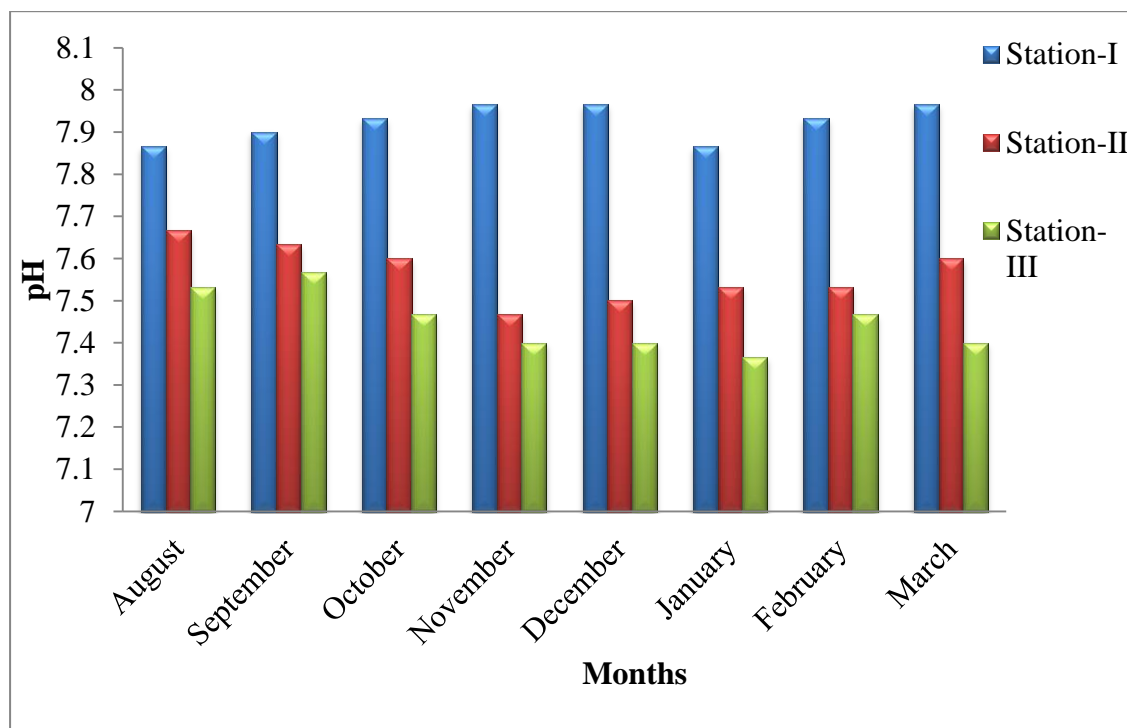


Table 4.17 One-way ANOVA of pH versus station

One way ANOVA pH versus station					
Source	DF	SS	MS	F	P
Station	2	2.94111	1.47056	231.49	0.000
Error	69	0.43833	0.00635		
Total	71	3.37944			
S= 0.07970	R-Sq= 87.03 %	R-Sq (adj) = 86.65 %			

Significant differences were observed among the **stations** in **pH** during collection of sample (One-way ANOVA, df=2, F=231.49, P<0.05).

Table 4.18 One-way ANOVA of pH versus months

One way ANOVA pH versus months					
Source	DF	SS	MS	F	P
Station	7	0.0928	0.0133	2.26	0.968
Error	64	3.2867	0.0514		
Total	71	3.3794			
S= 0.2266	R-Sq= 2.75 %	R-Sq (adj) = 0.00 %			

No Significant differences were observed surrounded by the **months** in **pH** during collection of sample (One-way ANOVA, df=7, F=2.26, P>0.05).

4.5 Temperature

In pre-monsoon season, in the month of March highest temperature (28.1 °C) at station-3 was recorded and lowest temperature was recorded in post-monsoon season in the month of December (24.1 °C) at station-1 (Table 4.19.; Fig 4.7).

Table. 4.19 Monthly variations in harbor water temperature (°C) between three stations at harbor area, Veraval coast, Gujarat.

Season	Month	Station-1	Station-2	Station-3
Monsoon	Aug.18	24.3	24.5	24.4
	Sep.18	25.6	25.8	25.9
Post-Monsoon	Oct.18	26.2	26.7	27
	Nov.18	26.3	26.2	26.2
	Dec.18	24.1	24.4	24.3
Pre-Monsoon	Jan.19	24.2	25.9	25.9
	Feb.19	27.2	27.3	27.
	Mar.19	27.7	27.9	28.1

Fig. 4.7 Monthly variations in harbor water temperature (°C) between three stations at harbor area, Veraval coast, Gujarat.

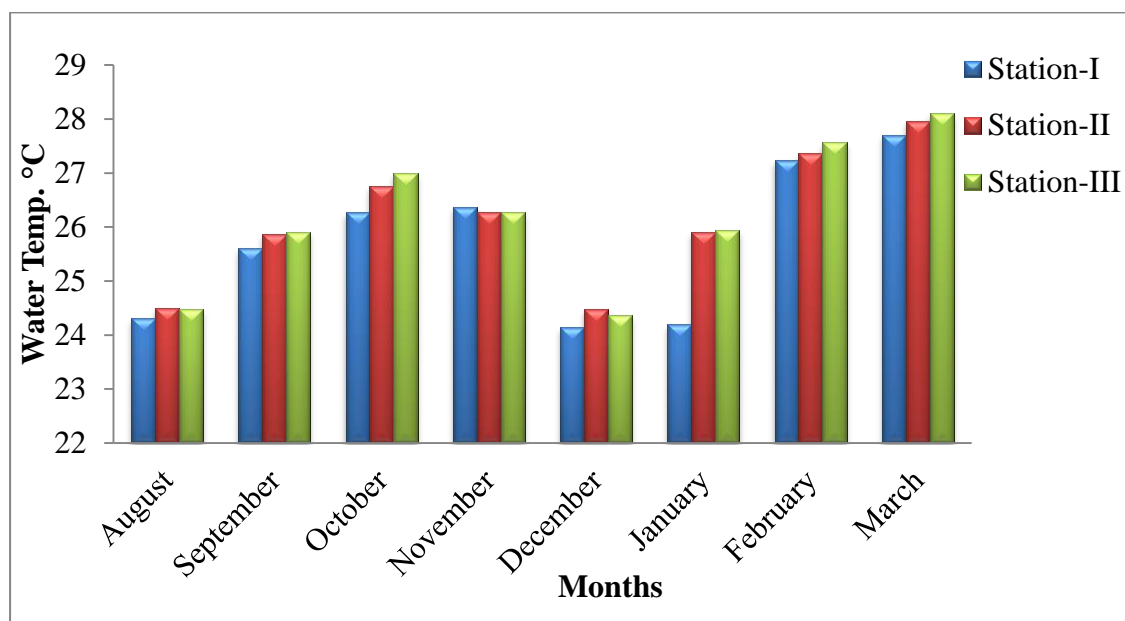


Table 4.20 One-way ANOVA of temperature versus station

One way ANOVA temperature versus station					
Source	DF	SS	MS	F	P
Station	2	3.04	1.52	0.92	0.403
Error	69	112.08	1.65		
Total	71	115.12			
S= 1.284	R-Sq= 2.64 %	R-Sq (adj) = 0.00 %			

No significant differences were observed among the **stations** in **temperature** during collection of sample (One-way ANOVA, df=2, F=0.92, P>0.05).

Table 4.21 One-way ANOVA of temperature versus months

One way ANOVA temperature versus months					
Source	DF	SS	MS	F	P
Station	7	106.938	15.277	117.58	0.000
Error	64	8.185	0.130		
Total	71	115.123			
S= 0.3605	R-Sq= 92.89 %	R-Sq (adj) = 92.10 %			

Significant differences were observed surrounded by the **months** in **temperature** during collection of sample (One-way ANOVA, df=7, F=117.58, P<0.05).

4.6 Salinity

During the study period especially in pre-monsoon season in the month of March highest salinity (33.46 ppt) was recorded at station-1 and lowest salinity (28.83 ppt) was recorded in monsoon season in the month of September at station-1 (Table 4.18.; Fig 4.8).

Table. 4.22 Monthly variations in Salinity (ppt) between three stations at harbor area, Veraval coast, Gujarat.

Season	Month	Station-1	Station-2	Station-3
Monsoon	Aug.18	29.83	29.93	30.0
	Sep.18	28.83	29.83	30.06
Post-Monsoon	Oct.18	30.06	30.0	30.13
	Nov.18	31.20	30.06	31.10
	Dec.18	31.06	32.03	30.13
Pre-Monsoon	Jan.19	32.03	32.30	30.10
	Feb.19	33.43	32.06	30.13
	Mar.19	33.46	32.16	30.26

Fig. 4.8 Monthly variations in Salinity (ppt) between three stations at harbor area, Veraval coast, Gujarat.

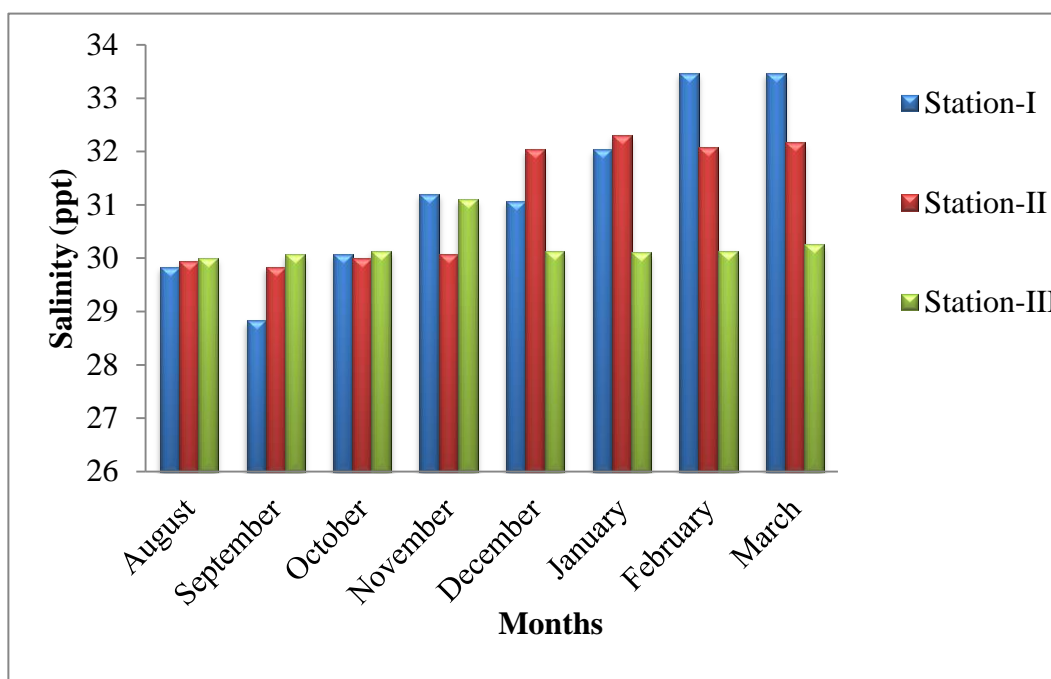


Table 4.23 One-way ANOVA of salinity versus station

One way ANOVA salinity versus station					
Source	DF	SS	MS	F	P
Station	2	13.09	6.54	4.98	0.010
Error	69	89.29	1.31		
Total	71	102.37			
S= 1.146	R-Sq= 12.78 %	R-Sq (adj) = 10.22 %			

No **Significant differences** were observed among the **stations** in **salinity** during collection of sample (One-way ANOVA, df=2, F=4.98, P>0.05).

Table 4.24 One-way ANOVA of salinity versus months

One way ANOVA salinity versus months					
Source	DF	SS	MS	F	P
Station	7	51.435	7.348	9.09	0.000
Error	64	50.939	0.809		
Total	71	115.123			
S= 0.8992	R-Sq= 50.24 %	R-Sq (adj) = 44.71 %			

Significant differences were observed surrounded by the **months** in **salinity** during collection of sample (One-way ANOVA, df=7, F=9.09, P<0.05).

4.7 Total Suspended Solids

In pre-monsoon season in the month of March highest TSS (84.63 mg/L) at station-3 was recorded and lowest was recorded in monsoon season in month of August (70.63mg/L) at station-1 (Table 4.25.; Fig 4.9).

Table. 4.25 Monthly variations in TSS (mg/L) between three stations at harbor area, Veraval coast, Gujarat.

Season	Month	Station-1	Station-2	Station-3
Monsoon	Aug.18	70.63	72.40	79.50
	Sep.18	73.93	72.76	80.06
Post-Monsoon	Oct.18	71.33	72.86	80.06
	Nov.18	72.56	74.33	82.40
	Dec.18	73.13	75.70	83.30
Pre-Monsoon	Jan.19	74.33	75.70	83.40
	Feb.19	74.83	75.80	84.03
	Mar.19	75.3	75.83	84.63

Fig. 4.9 Monthly variations in TSS (mg/L) between three stations at harbor area, Veraval coast, Gujarat.

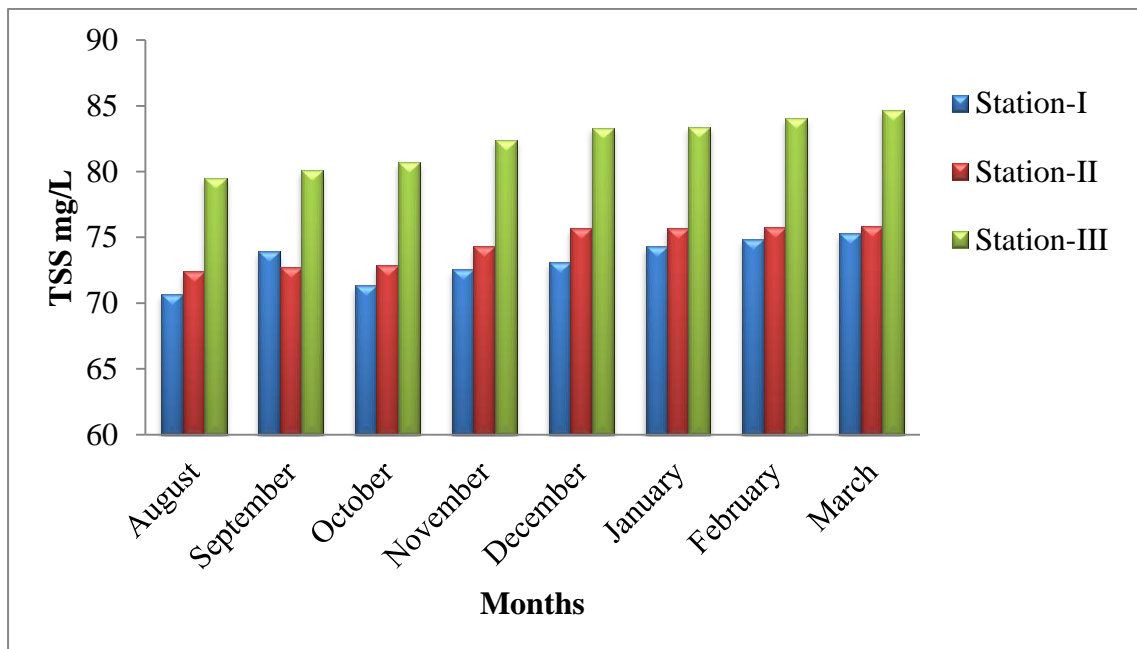


Table 4.26 One-way ANOVA of TSS versus station

One way ANOVA TSS versus station					
Source	DF	SS	MS	F	P
Station	2	1147.53	573.77	161.97	0.000
Error	69	244.42	3.54		
Total	71	1391.96			
S= 1.882	R-Sq= 82.44 %	R-Sq (adj) = 81.93 %			

Significant differences were observed among the **stations** in **TSS** during collection of sample (One-way ANOVA, df=2, F=161.97, P<0.05).

Table 4.27 One-way ANOVA of TSS versus months

One way ANOVA TSS versus months					
Source	DF	SS	MS	F	P
Station	7	164.4	23.5	1.22	0.303
Error	64	1227.6	19.2		
Total	71	1392.0			
S= 4.380	R-Sq= 11.81 %	R-Sq (adj) = 2.16 %			

No Significant differences were observed surrounded by the **months** in **TSS** during collection of sample (One-way ANOVA, df=7, F=9.09, P>0.05).

4.8 Dissolved oxygen

In monsoon season in the month of August highest DO (2.43 mg/L) at station-1 was recorded and lowest was recorded in pre-monsoon season in all three months January, February and March (0.20 mg/L) especially at station-2 and station-3 (Table 4.28.; Fig 4.10).

Table. 4.28 Monthly variations in Dissolved oxygen (mg/L) between three stations at harbor area, Veraval coast, Gujarat.

Season	Month	Station-1	Station-2	Station-3
Monsoon	Aug.18	2.43	0.30	0.30
	Sep.18	2.33	0.26	0.30

Post-Monsoon	Oct.18	2.20	0.26	0.23
	Nov.18	2.26	0.23	0.20
	Dec.18	2.13	0.20	0.20
Pre-Monsoon	Jan.19	2.13	0.20	0.20
	Feb.19	2.16	0.20	0.20
	Mar.19	2.20	0.20	0.20

Fig. 4.10 Monthly variations in Dissolved oxygen (mg/L) between three stations at harbor area, Veraval coast, Gujarat.

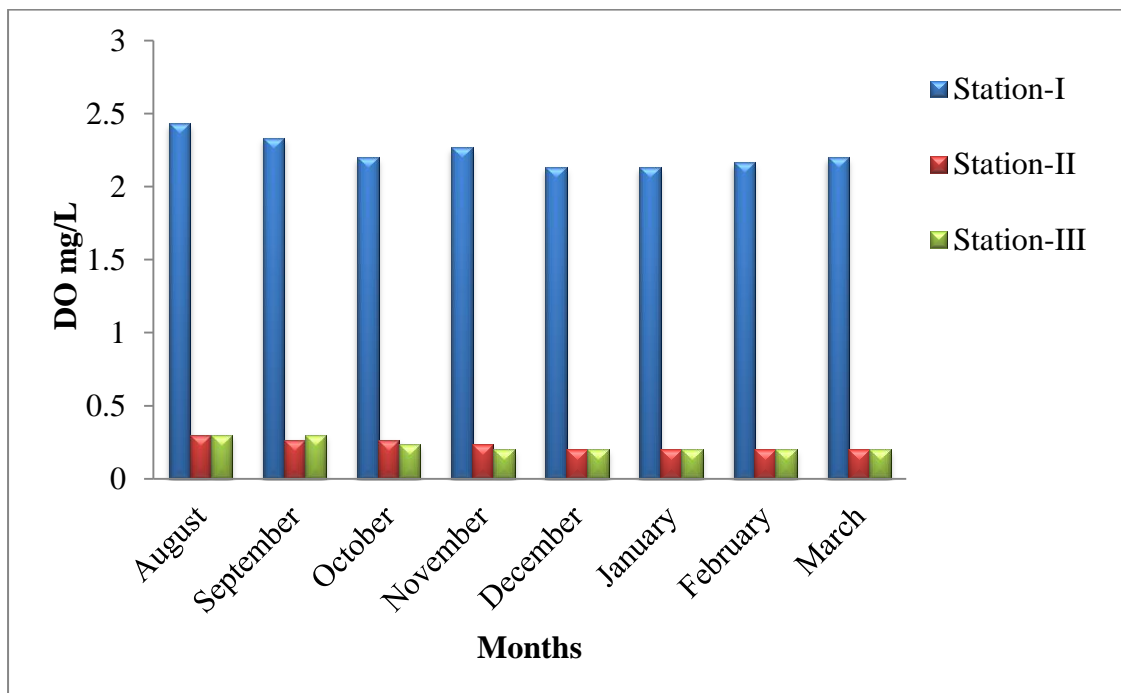


Table 4.29 One-way ANOVA of DO versus station

One way ANOVA DO versus station					
Source	DF	SS	MS	F	P
Station	2	64.13361	32.06681	5315.58	0.000
Error	69	0.41625	0.00603		
Total	71	64.54986			
S= 0.07767	R-Sq= 99.36 %	R-Sq (adj) = 99.34 %			

Significant differences were observed among the **stations** in **DO** during collection of sample (One-way ANOVA, df=2, F=5315.58, P<0.05).

Table 4.30 One-way ANOVA of DO versus month

One way ANOVA DO versus month					
Source	DF	SS	MS	F	P
Station	7	0.23	0.03	0.03	1.000
Error	64	64.32	1.00		
Total	71	64.55			
S= 4.380	R-Sq= 11.81 %	R-Sq (adj) = 2.16 %			

No Significant differences were observed surrounded by the **months** in **DO** during collection of sample (One-way ANOVA, df=7, F=0.03, P>0.05).

Discussion

The concentration of trace metals (Cd, Cu and Zn) were analyzed in water and sediment were comparable with three different stations at harbor area, Veraval Coast, Gujarat. Harbor area in Veraval exposes various forms of pollution, most importantly waste discharge from harbor activities and urban and industrial run-off. Findings of this study, Cd concentrations were not detected in harbor water sample at all three stations in all seasons, while Cu and Zn concentrations were in detectable level. In sediments all three metal concentrations were detected considerably in higher levels than in water. The variation in trace metals was higher in the end point of the harbor (station-3) and lowest in the mouth of the harbor (station-1). Concentration of trace metals in the harbor sediment showed a wide variation; an increasing trend from middle point of the harbor (station-2) to the end point of the harbor (station-3). The seasonal variation in trace metal concentrations were higher in the post-monsoon season, followed by pre-monsoon and monsoon seasons, which might be due to industrial activity and major pollution sources such as effluents from industries and fish-processing plants and sewage input from the urban area situated near the harbor of Veraval.

CHAPTER-V

SUMMARY AND CONCLUSION

The concentration of trace metal (Cd, Cu and Zn) in sediment and water sample and physico-chemical parameters of harbor was carried out in present study. The brief summary and conclusion of the study are given below.

5.1 Summary

The sediment and harbor water sample was collected from three different stations at Veraval harbor. The collected sample was analyzed under MP-AES for trace metal concentrations for selected metals Cd, Cu and Zn.

- 1) In sediment, all three metals Cd, Cu and Zn were concentrated in high levels, whereas in water Cd was not detected and Cu and Zn were concentrated at certain levels.
- 2) The highest concentration of Cd in sediment was found in post-monsoon season (0.72 ppm) at Station-3 in November and lowest concentration occurred in monsoon season (0.01 ppm) station-1 in August.
- 3) In case of Cu the highest concentration in sediment observed in post-monsoon season (307.70 ppm) at Station-3 in December and lowest concentration occurred in monsoon season (16.6 ppm) at station-1 in August.
- 4) The concentration of Cu in water was highest in pre-monsoon season (1.65 ppm) at Station-2 in November and lowest concentration observed in pre-monsoon season (0.06 ppm) at Station-3 in January.
- 5) In case of Zn the highest concentration in sediment reported in post-monsoon season (704.92 ppm) at Station-3 in December and lowest concentration occurred in monsoon season (22 ppm) at Station-1 in August.
- 6) The concentration of Zn in water was highest in post-monsoon season (3.32 ppm) at Station-2 in November and lowest concentration occurred in monsoon season (0.07 ppm) at Station-1 in August.
- 7) The highest concentration of all three metals Cd, Cu and Zn in sediment reported during post-monsoon season at Station-3.
- 8) The lowest concentration of all three metals Cd, Cu and Zn in sediment recorded during monsoon season at Station-1.

- 9) The seasonal variation in trace metal concentration was higher in the post-monsoon, followed by pre-monsoon and monsoon season.
- 10) The lowest value of pH was observed in pre-monsoon season in the month of January (7.36) at station-3 and highest value was noted in post-monsoon season in the month of November (7.96) at station-1.
- 11) The highest temperature (28.1°C) was recorded at station-3 in pre-monsoon season in the month of March and lowest temperature (24.1°C) was recorded in post-monsoon season in the month of December at Station-1.
- 12) The highest salinity (33.46 ppt) at station-1 was recorded in pre-monsoon season in the month of March and lowest (28.83 ppt) was recorded in monsoon season in the month of September at station-1.
- 13) The highest DO in the month of August (2.43 mg/L) at station-1 was recorded and lowest (0.20 mg/L) was recorded in pre-monsoon season in all three months January, February and March at station-2 and station-3.

5.2 Conclusion

Based on the results obtained from the experiment the current study showed that the metals Cd, Cu and Zn in sediment were having high levels of concentrations at station-3 in post-monsoon season and low levels of concentrations at station-1 in monsoon season. The concentration of Cd in water was not detected during study period which indicating negligible or minute levels in the harbor water. The DO level in water was below 0.2 mg/L at station-2 and station-3 that showed about the anoxic condition of harbor water in all seasons. The present study suggested that the high concentrations of metals during post-monsoon season might be due to the excess industrial discharge and domestic wastewater runoff due to the running of processing units after closed (monsoon) season in the harbor area of Veraval.

CHAPTER-VI

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**“ANALYSIS OF TRACE METAL CONCENTRATION IN HARBOR WATER
AND SEDIMENT OF VERAVAL COAST, GUJARAT”**

ABSTRACT

The present study on trace metal concentrations in water and sediment was conducted at Veraval, Coast Gujarat. The purpose of study was to measure the increasing concentration of metals in harbor. The analysis of concentrations of trace metals (Cd, Cu and Zn) at three different stations in Veraval harbour was done under MP-AES. Some physico-chemical parameters such as pH, Salinity, Temperature, TSS and DO₂ were recorded in different seasons for eight months. The highest concentration of Cd in sediment was observed in Post-monsoon season (0.72 ± 0.049) at Station-3 in November and in water the levels of Cd was not detected. In case of Cu the highest concentration in sediment recorded in Post-monsoon season (307.70 ± 41.81) at Station-3 in December Zn had the highest concentration in sediment in Post-monsoon season (704.92 ± 176.2) at Station-3 in December. The concentration of Cu in water was highest in Pre-monsoon season (1.65 ± 0.282) at Station-2 in November. The concentration of Zn in water was highest in Post-monsoon season (3.32 ± 1.060) at Station-2 in November. It was noted that the highest concentration of all three metals Cd, Cu and Zn in sediment occurred at Station-3 during Post-monsoon season and lowest at Station-1 during Monsoon season. Thus, results revealed that seasonal variation in trace metal concentrations was observed in all stations.

Key words: Trace metal concentration, harbor water, sediment, seasonal variation.

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CERTIFICATE-I

This is to certify that the thesis entitled “**ANALYSIS OF TRACE METAL CONCENTRATION IN HARBOR WATER AND SEDIMENT OF VERAVAL COAST, GUJARAT**” submitted by **MALAMDI MAYUR TULSIDAS** in partial fulfillment of the requirements for the award of the degree of **MASTER OF FISHERIES SCIENCE** in the subject of **FISHERIES RESOURCE MANAGEMENT** to the Junagadh Agricultural University is a record of bonafied research work carried out by under my guidance and supervision and the thesis has not previously formed the basis for the award of any degree, diploma or other similar title. The candidate had fulfilled all prescribe requirements. The assistance and help received during the course of investigation have been fully acknowledged. He has successfully completed the comprehensive/ preliminary examination held on **3rd May 2019** as required under the regulation for post-graduate studies. He has submitted *kachcha* bound thesis on **June 18, 2019**.

Place: Veraval

Date: 18/06/2018

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Date: /06/2019

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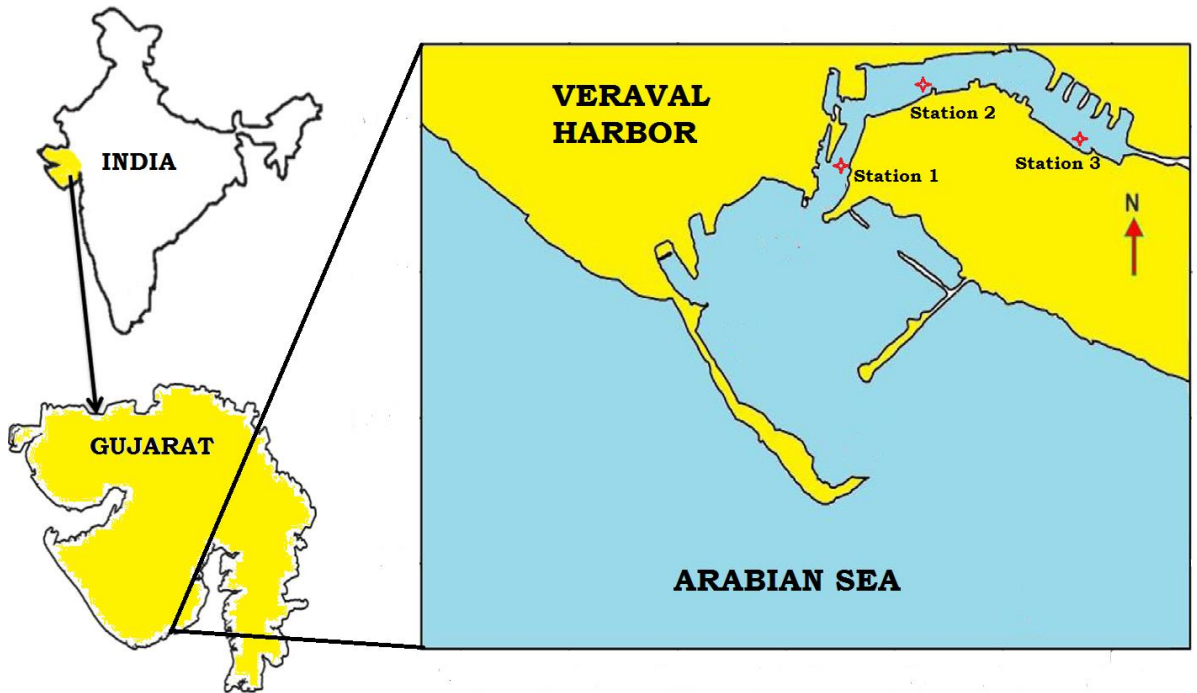
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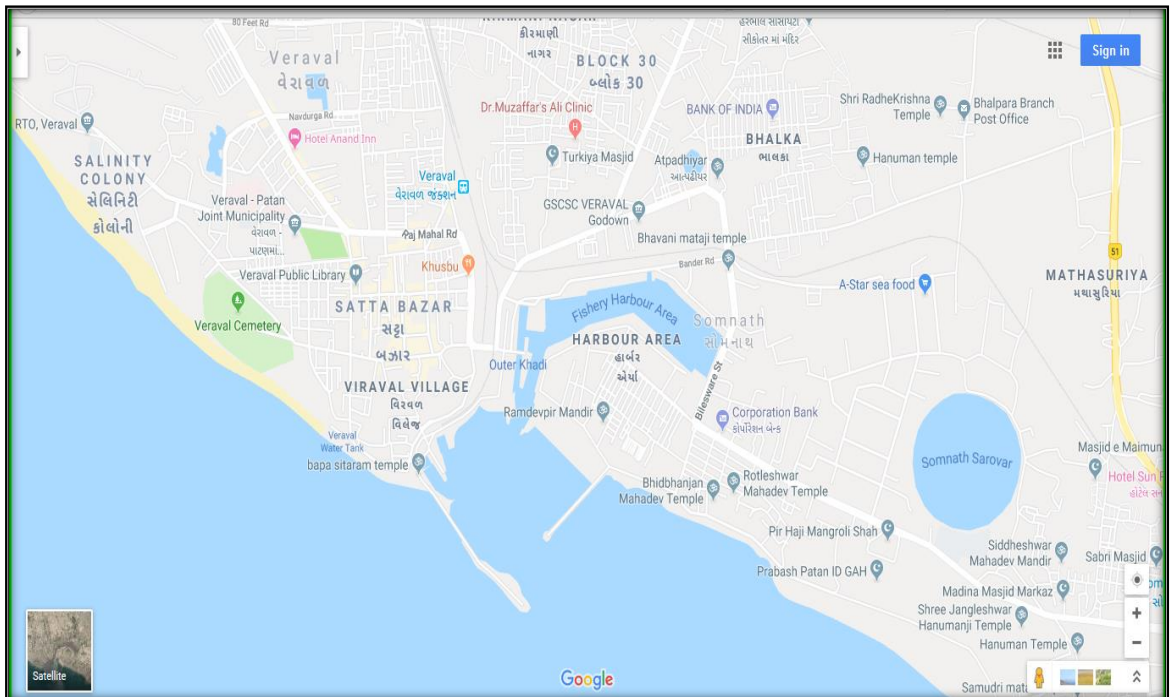
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PLATE 1



A. Location of Study area



B. Google Map View of Veraval Harbor

PLATE 2



A. Station-1 (Mouth of Harbor)



B. Station-2 (Middle Point of Harbor)



C. Station-3 (End Point of Harbor)

PLATE 3



A. Sampling Bottle (Water)



B. Polyethene Bag (Sediment)



C. Water Sample Bottle



D. Sediment Sample Polyethene Bag



E. DO₂ Bottle



F. Chemicals and Reagent

PLATE 4



A. Sediment Collection Grab



B. Weight Balance



C. Refractometer



D. pH meter



E. Thermometer



F. TSS Measurement Unit

PLATE 5



A. Water Sample Collection



B. Adding of H_2O_2

PLATE 6



A. Dilution of Sample with 1% HNO₃



B. Analysis under MP-AES

PLATE 7



A. Sediment Sample Collection



B. Drying Sample in Hot Air Oven



C. Weighing of 1gm Sediment sample



D. Adding of HNO_3 and H_2O_2

PLATE 8



A. Kept in Hot Plate until 5ml sample remain



B. Filter Solution with Whatman filter paper



C. Makeup Solution up to 50ml with deionized water



D. Dilution with 1% HNO_3



E. Analysis under MP-AES