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Study on Heavy Metal Distribution in the Coastal Environments along the Foremost Places of South-East Coast of India

James Balgan Anand D. [1*], Dr. Mary Jelastin Kala S [2]

Research Scholar, Department of chemistry, St. Xavier's College, Palayamkottai, TamilNadu, India[1]

Assistant Professor, Department of chemistry, St. Xavier's College, Palayamkottai, TamilNadu, India[2]

ABSTRACT: The study of heavy metal distribution in coastal water and surface sediments is an important component in understanding the distribution levels as well as assessing the cause of anthropogenic influences on the marine ecosystem. During the last Twenty Five years, the coastal environment of southeast India had experienced intense developments in industry, urbanization and aquaculture. Several metals are known to be discharged frequently through industrial and domestic effluents along the southeast coast of India. The present study was carried out to determine the Heavy Metal Distribution in the coastal Waters and sediments of Mandapam, Thoothukudi, Arumuganeri and Kanyakumari Coasts. The sampling of coastal water and sediments was carried out from October 2013 to September 2014. The enrichment in the concentration of heavy metals in the samples that are close to the coastal areas indicated that higher concentration was due to the anthropogenic activities in the coastal area. Hence, this present study used to investigate the Heavy metal levels of contamination in this area, and also useful for further impact evaluation.

KEYWORDS: Heavy metals, Seasonal variation, Coastal Waters, Sediments, East-Coast of India.

I. INTRODUCTION

Heavy Metals are naturally occurring elements in the environment and vary in concentrations across the earth. Unlike organic toxins it can be degraded to less harmful components by biological or chemical processes, So Heavy metals are considered to be non-degradable pollutants [1]. Heavy metals are not harmful to the environment, because they play an essential role in tissue metabolism and growth of plants and animals. Metals like Cu, Zn, Fe, Co, MO, and Ni etc. are essential and at the same time it becomes toxic when their level exceeds the limit, and V, Cd, Pb, and Hg are prominently classified as toxic because of their harmful effect even at low concentrations [2]. The distribution of metals within the aquatic coastal environment is managed by complex processes of substantial exchange affected by various natural and anthropogenic activities [3]. Although metals are natural components of our earth and are present in all environments, but their concentrations have been drastically altered by human activities [4]. Since heavy metals are toxic, non-degradable in the environment, and the contamination with sediments create great ecological hazard to coastal marine ecosystem [5]. Such pollution causes severe adverse biological effects, also produce diseases in plant and animal species, leads to loss or modification of habitat [6, 7]. When this toxic metals taken up by marine organisms, entering the food chain and possibly transferred to the different trophic levels, which can be ultimately lead to adverse effects on humans by in taking the contaminated seafood [8].

Industrialization and modern developments along the coast area contributed more heavy metals into the coastal environment. Also, the anthropogenic changes in the coastal environment like land reclamation, dredging and aquaculture cause the metal pollution [9]. Generally the heavy metals in the environment have many sources: Geological weathering of rocks, Industrial effluents, and Solid waste dumping and garbage and Animal and human excreta [10]. Majority of the industries along coastal area discharge the chemical effluents into the aquatic environment which in turn cause changes in habitat, species distribution, and bio-geo chemical cycles. The distribution of heavy metals in the water bodies has been recognized as a major factor for biological risks [11, 12]. Since last Twenty five years, high levels of heavy metals and their compounds, both inorganic and organic, have been released to the Coastal environment by anthropogenic activities [13]. In the environmental point of vision, coastal zones can be considered as

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the topographical space of interaction between earthly and marine ecosystems which is very important for the existence of plants, animals and marine species [14]. Higher heavy metals concentrations in the coastal marine environment are the indicators of anthropogenic impact and potential risk to the natural environment. Therefore, it is important to evaluate the track of these heavy metals in coastal ecosystem [15]. The mode of transfer and distribution of toxic metals between the sediment and water columns is of great importance. Once heavy metals introduced into the aquatic environment, it redistributed throughout the water column, and finally accumulated in sediments [16]. Heavy metal levels in sediments used to identify the history and sources of pollution. Several researches demonstrated that water & sediments from coastal areas, which are greatly contaminated by heavy metals, therefore the evaluation of Heavy metal distribution is necessary to assess pollution levels in the oceanic environment.

II. DESCRIPTION OF THE STUDY AREA

The study area Mandapam (latitude 9°16’14”N; longitude 79°7’10”E), Thoothukudi (latitude 8°46’26”N; longitude 78°10’9”E), Arumuganeri (8°59’40”; 78°13’71”) Kanyakumari (latitude 8°4’45”N; longitude 77°32’38”E) are located in the Gulf of Mannar area along the South East Coast of India. Mandapam (nearby by Rameswaram) is situated close to Gulf of Mannar Biosphere. The Biosphere contains 21 islands and also rich in marine biodiversity with estuaries, mudflats, beaches, forests of the near shore environment, including marine components like algal communities, sea grasses, coral reefs, salt marshes and mangroves. Thoothukudi and Arumuganeri are the major industrial areas contains major chemical industries like SPIC, Copper smelting plant, Dharangadhara chemicals ,salt pans, Thermal power station, several small scale industrial units are in Thoothukudi SIPCOT complex. Thoothukudi is one of the important major Ports having a number ship movement. The movement of ships and fishing operation by mechanized boats also release oil effluents and petrochemical products into the sea. The Thermal power station directly dumps its ash into the sea. Likewise the other industries also discharge their wastes into the sea. The effluents from industries in Thoothukudi and Arumuganeri coastal region are discharged directly or indirectly into the sea and hence there is more possibility for accumulation of large concentration of trace metals into the Gulf of Mannar marine ecosystem. Kanyakumari (formerly known as Cape Comorin), lies at the southernmost tip of South East coast of India. It is one of the important Tourist Spot as well as Pilgrim place (Figure 1).

FIGURE-1Sampling Locations and Sampling Points

III. MATERIALS AND METHODS

Monthly variations of Trace metals in Water and sediments are recorded from October 2013 to September 2014. Based on the meteorological events, four seasons are broadly indicated as month wise and they are (1) Post -Monsoon

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(January to March) (2) Summer (April to June) (3) Pre- Monsoon (July to September) (4) Monsoon (October to December). The seawater samples were collected separately in clean Polyethylene containers for heavy metal analyses. They were filtered through a 0.45 µ Millipore membrane filter, acidified and stored until extraction. The samples were pre-concentrated using APDC (Ammonium Pyrrolidine Dithio-Carbamate) and MIBK (Methyl Iso-Butyl Ketone) solutions [17] and estimated by Graphite Furnace Atomic Absorption Spectrophotometer (Perkin-Elmer AAnalyst 700).The heavy metal concentration in sea water were reported as µg/l (PPB).

Sediment samples from the sites were collected in a Polyethyene bag, dried in oven then crushed powdered and mixed thoroughly followed by screening with a 0.5 mm sieve to remove large particles. For metal analysis in sediments a known quantity (1gm) of the above powdered sediment was digested with an acid mixture of $HClO_4$ and HF and the final residue was leached with HCl and made up to the required quantity [18]. Trace metal concentrations (Cd, Cu, Pb, Cr, Ni, and Zn) was measured using flame atomic absorption spectrophotometer (Perkin-Elmer AAnalyst 700) armed with a deuterium background corrector. Suitable internal chemical standards (Merck Chemicals, Germany) were used to calibrate the instrument. All the reagents used were of analytical grade and high purity. The results of the heavy metal concentrations in sediments were determined on a dry weight basis µg /g (PPM).

IV. RESULTS AND DISCUSSION

Heavy metals are considered a major anthropogenic contaminant in coastal and marine environments worldwide [19]. Anthropogenically, heavy metals can be introduced to coastal and marine environments through a variety of sources, including industries, wastewaters, municipal wastes and domestic effluents [20, 21].

1. CADMIUM

Cadmium is a non-essential metal for organisms except some marine diatoms have its biological role in. Cadmium is highly toxic to freshwater and marine organisms. It is bio-accumulative through the food chain. It has been demonstrated as a highly toxic metal to wildlife and carcinogenic to humans [22, 23]. The concentration of Cadmium in the coastal seawater can range from 0.09 to 3.42 (ppb).It was found minimum (0.09 ppb) at Kanyakumari during July/Pre-Monsoon and maximum (3.42 ppb) at Arumuganeri during Feb/Post Monsoon season. Similarly the concentration of Cadmium in sediments range from 0.48 to 6.68 (ppm), and maximum (6.68 ppm) at Arumuganeri during Dec/monsoon season, and minimum (0.48 ppm) at Kanyakumari during July/Pre-Monsoon as shown in the Figure -2.

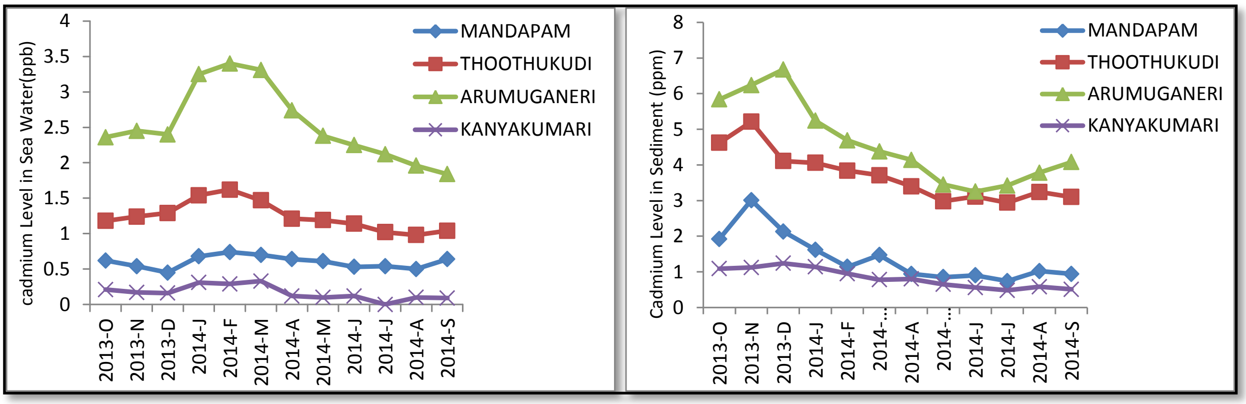

FIGURE-2 Cadmium Levels in Sea water and Sediment from Oct 2013 – Sep 2014

Cadmium may enter the marine environment due to the geology of the catchment soil and runoffs from phosphate fertilized agricultural soils, disposed of nickel cadmium based batteries and cadmium-plated items. The main source of Cd in the coastal environment designates possible anthropogenic sources along with natural crustal origin. The main natural sources are from rock weathering, mineral transport, regional dust transport and events such as forest fires and volcanic eruptions. Anthropogenic inputs in coastal sediment include local waste disposal, Industrial effluent discharge, and human developmental activities near coastal areas [24, 25]. Unlike the other metals in cadmium, the chance of

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adsorption into particulate material is limited, they usually settled to bottom sediment and hence an increased concentration in the sediments [26].

2. LEAD

Lead is also known as a snowballing metabolic poison. Its concentration in the coastal regions has been altered by human activities [27].The concentration of Pb in the coastal seawater can range from 5.32 to 21.60 (ppb). It was found minimum (5.32 ppb) at Kanyakumari during July/Pre-Monsoon and maximum (21.60 ppb) at Thoothukudi during Feb/Post Monsoon season. Similarly the concentration of Pb in sediments range from 14.20 to 52.30 (ppm), maximum (52.30 ppm) at Thoothukudi during Dec/monsoon season, and minimum (14.20 ppm) at Kanyakumari during June/summer season as shown in the Figure - 3.

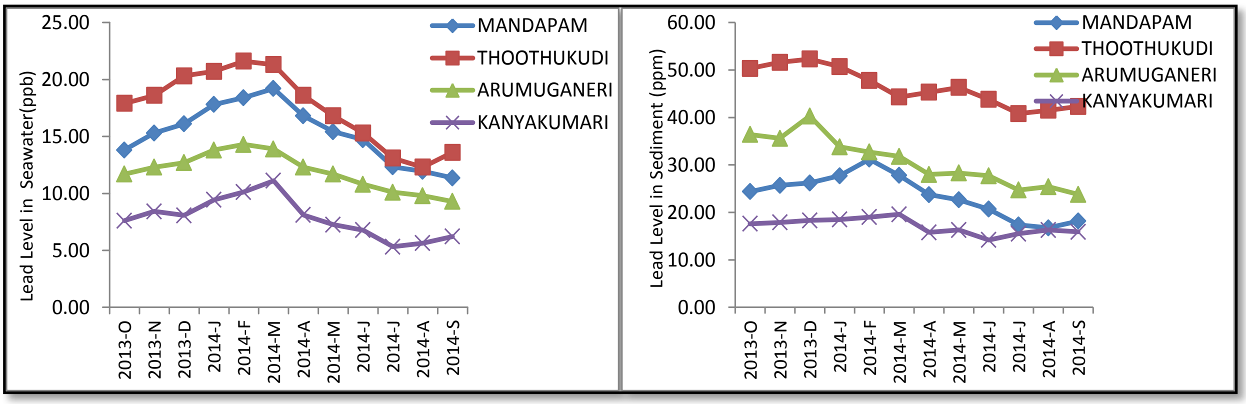

FIGURE-3 Lead Levels in Sea water and Sediment from Oct 2013 – Sep 2014

Lead concentration in coastal environment can be attributed by the sources like automotive exhausts, domestic sewage, agricultural runoff ,power-plant operation , loading and unloading of cargo as well as dredging activities in harbour zones, and leaching from antifouling paints used in fisherman boats and leakage or un-burnt Leaded diesel and petrol from boats [28,29]. This Lead transported through the atmosphere and later settled in the seawater, subsequently wet and dry fallout in sediments. In seawater, it forms colloids which are easily absorbed by planktons.

The high concentration of Lead in the coastal regions are related to the input of industrial effluents from the industries like industrial petrochemical, painting, thermal plant and other chemical industries which also exposed to wave and storm actions [30]. In the absence any industry close to the study sites, the reason for the higher Lead content is due to the substantial increase of automobiles and motor fishing boats usage [31, 32].

3. COPPER

Copper is a micronutrient for aquatic life, but it becomes toxic at higher level. The concentration of Copper in the coastal seawater varied from 0.78 to 4.36 (ppb). It was found minimum (0.78 ppb) at Kanyakumari during May/Summer season and maximum (4.36 ppb) at Thoothukudi during Dec/Monsoon season. The concentration of Copper in sediments can range from 6.49 to 42.73 (ppm), maximum (42.73ppm) at Thoothukudi during Post monsoon season, and minimum (6.49 ppm) at Mandapam during Pre-Monsoon season as shown in the Figure – 4

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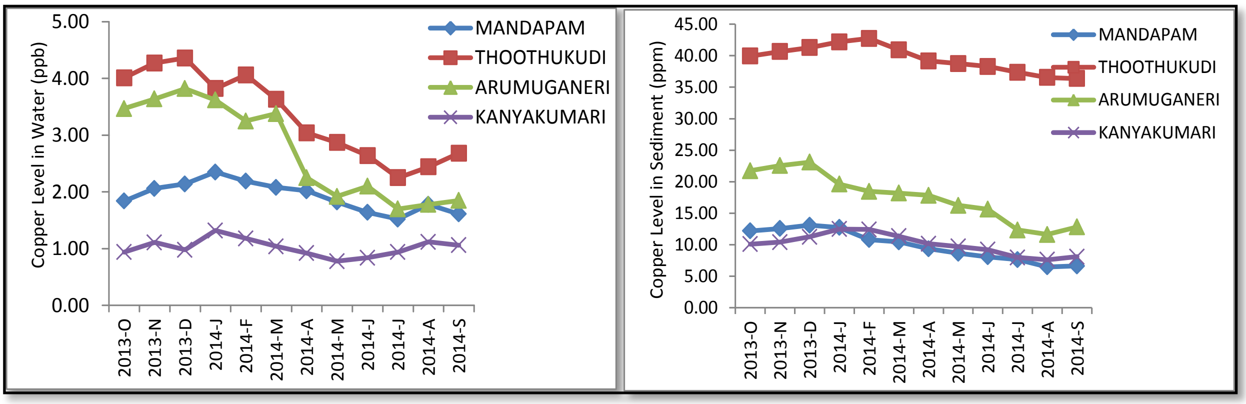

FIGURE-4 Copper Levels in Sea water and Sediment from Oct 2013 – Sep 2014

The observed high concentrations in the coastal transacts is attributed by industrial effluents, Industrial water coolant discharge, Combustion of coal in Power Plants, Municipal domestic sewage and harbour activities-ore handling. Copper is a common ingredient in antibiofouling paints which are applied on the surfaces ships and in offshore engineering [33]. Presence of high organic matter with which copper forms soluble and insoluble metal chelates favours higher concentration in the coastal species samples [35].Another possibility for higher concentration of Copper is due to the usage of copper-based algaecides and herbicides used in the nearby agricultural land and surface runoff in these coastal areas during inter-monsoon fall [30].

4. CHROMIUM

Domestic and industrial products are rich in Chromium. The bioavailability of Chromium is complicated by its speciation [Cr (III) and Cr (VI)] and its redox behaviour [36].The concentration of Chromium in the coastal seawater can range from 0.54 to 3.24 (ppb). It was found minimum (0.54 ppb) at Kanyakumari during Nov/Monsoon and maximum (3.24 ppb) at Thoothukudi during Feb/Post Monsoon season. Similarly the concentration of Chromium in sediments ranges from 5.84 to 30.67 (ppm), maximum (30.67 ppm) at Thoothukudi during Mar/Post-monsoon season, and minimum (5.84 ppm) at Kanyakumari during Sep / Pre-monsoon season as shown in the Figure -5.

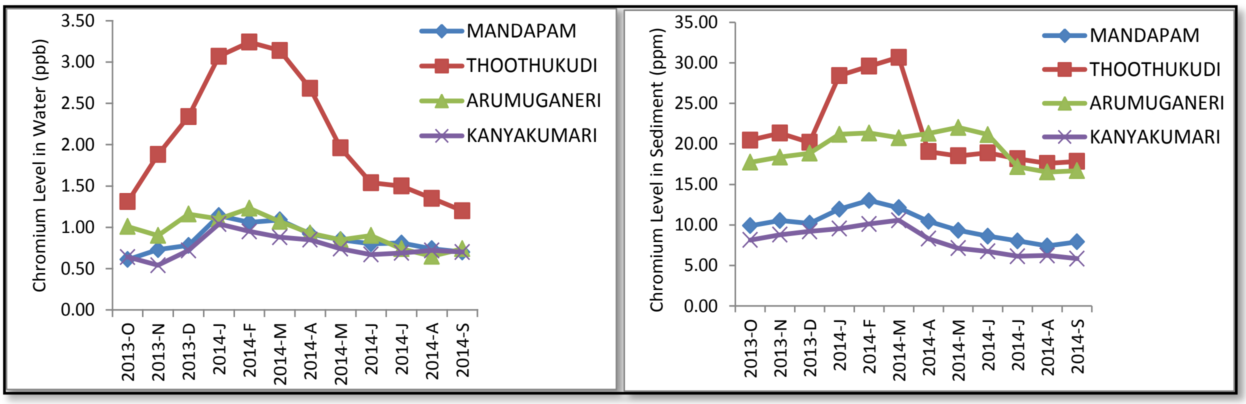

FIGURE-5 Chromium Levels in Sea water and Sediment from Oct 2013 – Sep 2014

The effluent of metal finishing industry, corrosion of building materials, domestic and Municipal sewage play an important role in increasing the chromium concentration in the marine environment [37]. Land run off during monsoon season also increasing Chromium concentration. Elemental Chromium is used as a marker of metal industry. Moreover, in addition to iron and steel industries, sewages also contribute equally to the contamination of Chromium [38].The precipitation processes of high organic and inorganic suspended matter adsorb chromium and other heavy metals from water and increase the sediment concentration of these metals [39].

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5. NICKEL

Nickel is known to be a nutritional requirement for many eukaryotic and prokaryotic organisms, which is necessary for plants to metabolize urea [40].The concentration of Nickel in the coastal seawater varied from 0.40 to 3.77 (ppb). It was found minimum (0.40 ppb) at Kanyakumari during July/Pre-Monsoon and maximum (3.77 ppb) at Thoothukudi during Mar/Post Monsoon season. The concentration of Nickel in sediments can range from 7.16 to 27.13 (ppm), maximum (27.13 ppm) at Thoothukudi during Jan/Post-monsoon season, and minimum (7.16 ppm) at Mandapam during Aug/ Pre-Monsoon season as shown in the Figure - 6.

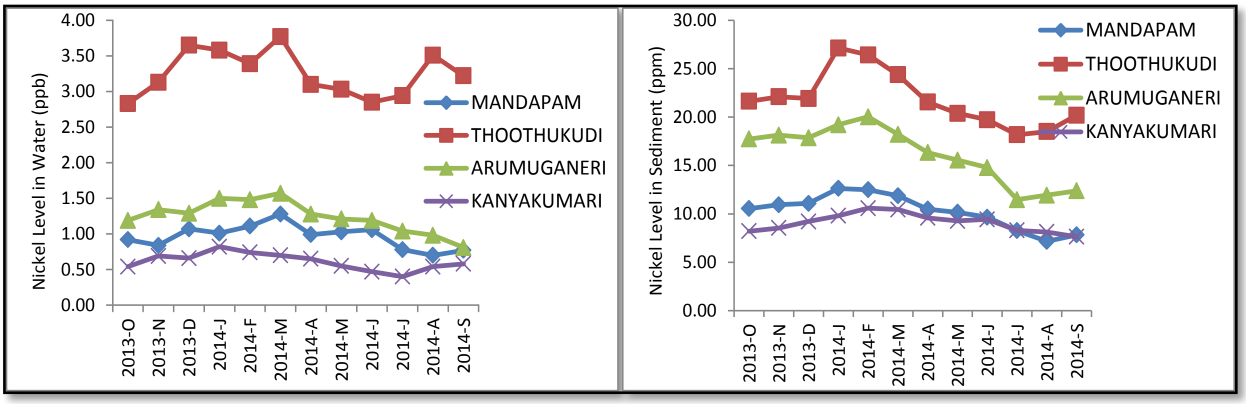

FIGURE-6 Nickel Levels in Sea water and Sediment from Oct 2013 – Sep 2014

Higher concentration Nickel along the coastal region due to the discharge of industrial effluents and domestic sewage, land run off and its gradual diffusion on the nearby coastal region. Moreover, lower values of Nickel shows that low intense activity of chemical weathering of the source rock which is a common phenomenon in the environment [41]. The petroleum related activities also bring Nickel and contaminate the environment.

6. ZINC

Zinc is present in all organisms and also essential trace element for metabolic processes. The concentration of Zinc in the coastal seawater can range from 1.19 to 21.48 (ppb). It was found minimum (1.19 ppb) at Mandapam during Sep/Pre-Monsoon and maximum (21.48 ppb) at Thoothukudi during Jan/Post Monsoon season. Similarly the concentration of Zinc in sediments ranges from 10.31 to 31.45 (ppm), maximum at Thoothukudi during Nov/monsoon season, and minimum at Mandapam during July/Pre-monsoon season as shown in the Figure-7.

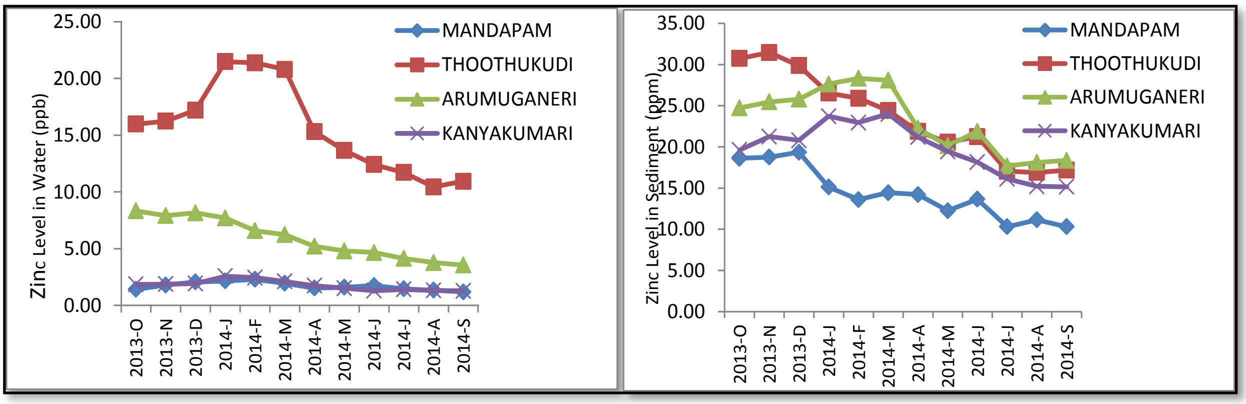

FIGURE-7 Zinc Levels in Sea water and Sediment from Oct 2013 – Sep 2014

The high concentration of Zinc observed in the coastal environment is from the domestic sewage, municipal waste, the coal powered thermal power plant, atmospheric deposition of fly ash, anthropogenic sources and dredging and dumping

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of sediments [44]. Zinc can enter the aquatic environment from a number of sources including industrial discharges, sewage effluents and terrestrial runoff [45]. Increase in Zinc content particularly during monsoon period coincided with relatively high organic content observed. This identifies that land runoff, agricultural waste and drainage are the sources of Zinc like Copper.

7.CONTAMINATION FACTOR

Sediments are generally used as indicator for the Heavy metal contamination. The metal accumulation in the sediment has been controlled by the nature, Physico-Chemical environments, level of suspension and precipitation process. The presence of Heavy metals in the sediments gives the impact on water and species in the marine environment. The contamination factor (CF) which gives the level of contamination in the sediment. It was computed for soil samples using the measured concentrations of metals in sediments and their corresponding values in rock samples [42].The range of contamination factor (CF) for the sediments is shown in the Table-1.

$$CF = \frac{Metal\ \ concentration\ in\ \ \ sediment}{Background\ or\ crustal\ value\ of\ the\ metal}$$

When CF >1 for a particular metal, it means that the sediment is contaminated by the element and if CF < 1, then there is no metal enrichment less contamination. For calculating the CF of the sediments, the world crustal average proposed by Martin and Meybeck [43] is considered as background value of the metal.

The CF was classified into four groups

- 1 ⩽ CF low contamination factor
- 1 ⩽ CF<3 moderate contamination factor
- 3 ⩽CF<6 considerable contamination factor
- 6 ⩾ CF very high contamination factor

8.POLLUTION LOAD INDEX (PLI):

Pollution load index (PLI), for a particular site, has been calculated by the following method proposed by Tomilson [34]. Pollution load index (PLI) is expressed as

$$PLI = [CF_1 x\ CF_2\ x\ CF_3\ x\ \ldots\ldots\ldots..\ x\ CF_n]^{1/n}$$

Where, CF_1, CF_2, CF_3 …is the Contamination factor. “n” is the number of metals. The value of PLI > 1 shows the site was anthropogenically polluted and PLI <1 indicates less pollution. The Pollution Load Index (PLI) for the sites is shown in the Table-1.

CONTAMINATION FACTOR (CF) FOR SEDIMENTS (OCT 2013-SEP 2014)							POLLUTION LOAD INDEX (PLI)
SITES	Cd	Pb	Cu	Zn	Cr	Ni	
MANDAPAM	6.95	1.47	0.31	0.11	0.14	0.21	**0.40**
THOOTHUKUDI	18.45	2.90	1.24	0.18	0.31	0.45	**1.12**
ARUMUGANERI	23.00	1.92	0.55	0.18	0.27	0.33	**0.83**
KANYAKUMARI	4.15	1.07	0.32	0.16	0.11	0.19	**0.34**

TABLE-1
CONTAMINATION FACTOR AND POLLUTION LOAD INDEX FOR SEDIMENTS

V. CONCLUSION

Observing the results obtained during the present study, it is evident that the monsoon plays a prominent role in the distribution of heavy metals. There is a noticeable seasonal change in the metal concentration. The accumulation of heavy metals found to be high in the near shore sediment mainly due to the land based activities. Due to the expansion of Industries, Tuticorin Port Trust, Thermal power station, Copper smelter Industry, Petrochemicals, Alkali Industry and other allied small industries around Thoothukudi and Arumuganeri will be the main source for the anthropogenic input in future. Because of the Heavy metals result of Thoothukudi and Arumuganeri transacts gradually increases, especially Cadmium and Copper levels. Even though our "Sea is the universal dustbin" at the same time nearly forty to fifty present of human life completely depends on sea including sea foods. Hence the gradual rise in heavy metal levels in the sea creatures have chance to enter human life through food web. Therefore coastal region should be given great attention to control the anthropogenic input into the coastal environment. Continuous monitoring of near shore coastal area recommended for future studies and proper monitoring required for the effluent treatment in the industry.

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