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Seasonal Distribution of Heavy Metals in the Coastal Waters and Sediments along the Major Zones of South East Coast of India

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Abstract

The study of heavy-metal distribution in shore sea water and surface sediments is significant and understanding the distribution levels and also finding the cause of anthropogenic impacts along the marine ecosystem. During the last Twenty-Five years, the coastal environment of southeast India has enormous and rapid developments in urbanization, industry and aquaculture. Numerous heavy metals are to be discharged often through industrial and domestic effluents along the coastal area of 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 along the coastal areas indicated that higher concentration due to the anthropogenic activities. Hence, this present study used to explore the Heavy metal contamination level in this area, and also useful for further impact evaluation.

Keywords: Heavy metals, seasonal, variation, coastal, sea waters, sediments, east coast of India.

Introduction

Heavy Metals are natural compounded elements occurring in the environment and different in concentrations along the earth crust. Dissimilar to organic polymerized toxins it can be degraded slowly by biological or chemical processes, Therefore Heavy metals are considered to be non-degradable pollutants. Due to the availability in nature and it is not harmful to the environment; hence it plays needed role in the tissue metabolism and development 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 its level exceeds the permissible value, also Hg, Cd, Pb and V are significantly assigned as a toxic elements due to its harmfulness even at low levels[1].The dispersal of metals within the coastal environment is governed by multifaceted routes of substantial exchange by several anthropogenic and natural activities[2]. Although metals are natural constituents of our earth and are present in all environs, but their concentrations are drastically altered by man-made actions. Meanwhile heavy metals are toxic, non-degradable in the environs, and the contamination with deposits creates a great ecological hazard to coastal marine ecosystem[3]. Such pollution causes severe adverse biological effects, also create diseases in fauna and flora species, leads to loss or modification of habitat. When these toxic metals taken up by oceanic organisms, and enter into the food chain and probably transferred to the different levels, and ultimately create harmful effects on humans via in taking the metal contaminated seafood chains[4].

Industrialization and modern expansions along the coast area enhance more heavy metals beside the shore environs. Also, the anthropogenic changes in the coastal environment like land renovation, dredging activities and aquaculture causes the metal contamination[5]. Generally Industrial effluents, Geographical weathering of rocks, Solid waste dumping and Human and animal excreta are the major sources for the heavy metals in the coastal area[6].Most of the industries along the coastal area release the chemical effluents into the marine environment cause changes in habitation, species diversity, and biological cycles. The distribution of heavy metals in the aquatic has been considered to be major aspect for the biological threats[7].Since last Twenty five years, due to the anthropogenic activities can release significant levels of heavy metals of organic and inorganic and their compounds released into the Coastal environment. In the environmental point of vision, coastal shore regions are reflected as the topographical place of communication between earthly and aquatic networks and important for the existence of plants, animals and marine species[8].

Higher heavy metals concentrations in the coastal environment are the pointers of anthropogenic influence and prospective danger to the natural environs. Hence it is vital to assess the pathway of these heavy metals in the coastal environment. The way of transfer and dispersal of these toxic heavy metals between water and sediment also great important. Once these heavy metals enter into the aquatic environment and dispersed throughout the water and finally deposited into the sedimets[9]. The presence of Heavy metal levels in sediments used to detect the source and history of pollution. Several researches demonstrated that water & sediments from coastal areas, are contaminated by heavy metals, and hence the assessment of Heavy metal distribution is necessary to evaluate pollution levels in the coastal environment.

Description of the Study area: The study zone 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; rich in marine biodiversity with marine species includes algal populations, corals, sea grass, mangroves and salt marshes. It also covers forests, estuaries, beaches, and forests along the shore environment of the Islands. 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 East coast of India. Also it is the important Tourist Spot as well as Pilgrim place (figure-1).

Material and Methods

Monthly variations of Trace metals in Water and sediments are recorded from October 2013 to September 2014. Based on the climatological factors, four seasons are broadly classified as month wise and they are i. Post -Monsoon (January to March) ii. Summer (April to June) iii. Pre- Monsoon (July to September) iv. 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 filter membrane, little acidified and stored until extraction. The samples were pre-concentrated using APDC (Ammonium Pyrrolidine Dithio-Carbamate) and MIBK (Methyl Iso-Butyl Ketone) solutions [10] 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 mix of $HClO_4$ and HF placed in a Hot Plate, the final residue was percolated with HCl and make up to the requiredquantity[11]. Trace metal concentrations (Cd, Cu, Pb, Cr, Ni, and Zn) were analyzed by Flame Atomic Absorption Spectrophotometer (Perkin-Elmer AAnalyst 700) armed supports with deuterium corrector background. High purity and analytical grade internal standards (Merck Chemicals, Germany) were used for the instrument calibration. The heavy metal concentrations in sediments were expressed as µg /g(PPM).

Results and Discussion

Throughout worldwide anthropogenic input is major source for the heavy metal pollution along the coastal environment[12]. The heavy metals enter into the coastal environment through domestic, municipal wastes and industrial effluents[13].

Figure-1
Sampling Locations and Sampling Points

Cadmium: Cadmium is a non- vital metal for the species 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, also highly toxic to animals and carcinogenic to human beings[14]. The concentration of cadmium in the coastal seawater can range from 0.10 to 3.32 (ppb).It was found minimum (0.10ppb) at Kanyakumari during Pre-Monsoon and maximum (3.32 ppb) at Arumuganeri during Post Monsoon season (figure-2). Similarly the concentration of cadmium in sediments range from 0.52 to 6.25 (ppm), and maximum at Arumuganeri during monsoon season, and minimum at Kanyakumari during pre-monsoon as shown in the figure -3.

Cadmium may enter the marine environment due to the geology of the catchment soil and runoffs from phosphate fertilizer agricultural soils, disposed of nickel cadmium based batteries and cadmium-plated items.

Apart from natural earth crust diffusion, anthropogenic is the major cradle for the cadmium source in the coastal marine environment. Natural calamities like rock dispersal, volcanic explosion, forest fire, and massive flood water input through estuary also increase the cadmium content. The major anthropogenic includes industrial effluent discharge, municipal waste dumping, and man-made activities along the coastal environment[15]. Unlike the other metals, in cadmium the chance of adsorption into particulate material is limited, they usually settled to bottom sediment and hence an increased concentration in the sediments.

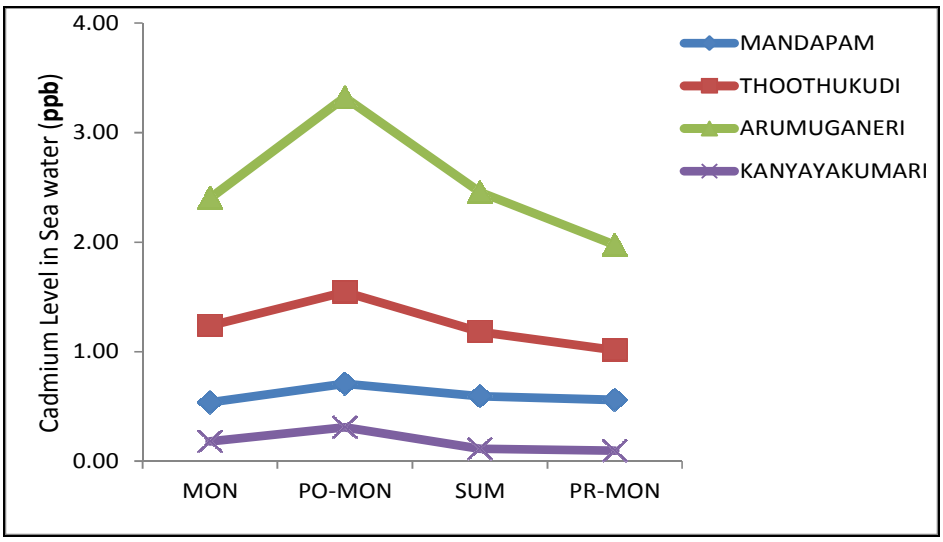

Figure-2
Cadmium Levels in Sea water at different seasons (ppb) (Oct 2013 – Sep 2014)

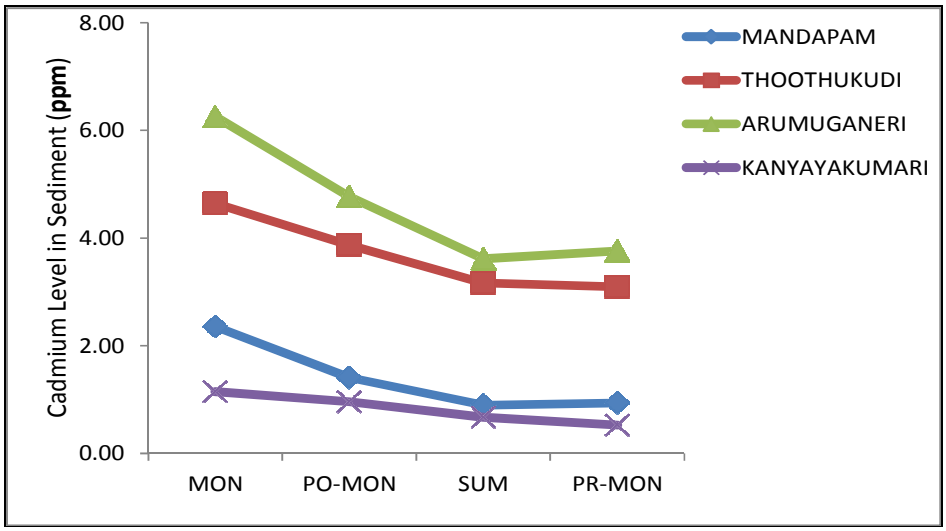

Figure-3
Cadmium Levels in Sediment at different seasons (ppm) (Oct 2013 – Sep 2014)

Lead: Lead is recognized as a snowballing toxin in the metabolic activities of living beings. Lead level in the coastal environment is influenced by man-made activities[16]. The concentration of Lead in the coastal seawater can range from5.72 to 21.20 (ppb). It was found minimum (5.72 ppb) at Kanyakumari during pre-monsoon and maximum (21.20 ppb) at Thoothukudi during Post Monsoon season (figure-4). Similarly the concentration of lead in sediments range from 15.43 to 51.40 (ppm), maximum at Thoothukudi during monsoon season, and minimum at Kanyakumari during summer season as shown in the figure-5.

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 harbor zones, and leaching from antifouling paints used in fisherman boats and leakage or un-burnt Leaded diesel and petrol from boats [17]. Atmosphere is the transportation vehicle for the Lead particle emitted and fall on the aquatic surfaces finally settle in the sediments. In seawater, it forms colloids which are easily absorbed by planktons.

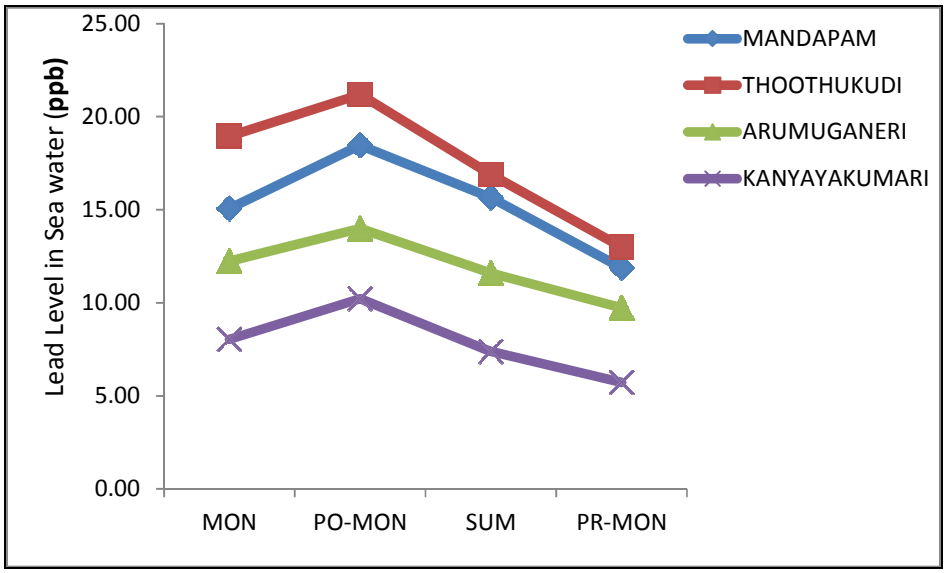

Figure-4
Lead Levels in Sea water at different seasons (ppb) (Oct 2013 – Sep 2014)

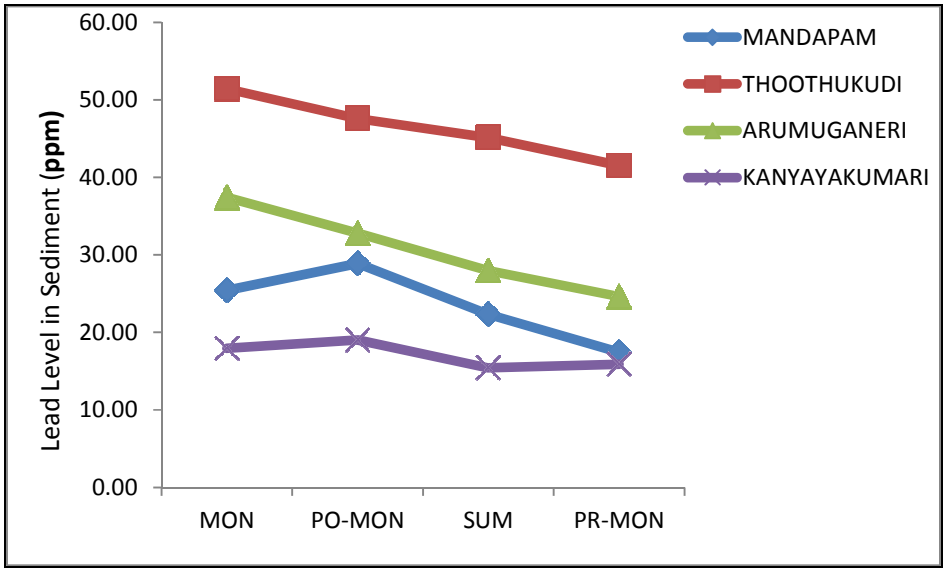

Figure-5
Lead Levels in Sediment at different seasons (ppm) (Oct 2013 – Sep 2014)

Discharge and dumping of Industrial effluents from thermal power plant, paints and pigments, petrochemical and other allied chemical industries along the coastal environments leads to high concentration of Lead levels. By wave and tide actions it slowly enters into water media[18]. 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[19].

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 1.01to 3.84 ppb). It was found minimum (1.01 ppb) at Kanyakumari during Monsoon and maximum (3.84 ppb) at Thoothukudi during Post Monsoon season (Figure-6). The concentration of Copper in sediments can range from 6.92 to 41.94 (ppm), maximum at Thoothukudi during Post monsoon season, and minimum at Mandapam during Pre-Monsoon season as shown in the figure-7.

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 harbor activities-ore handling.

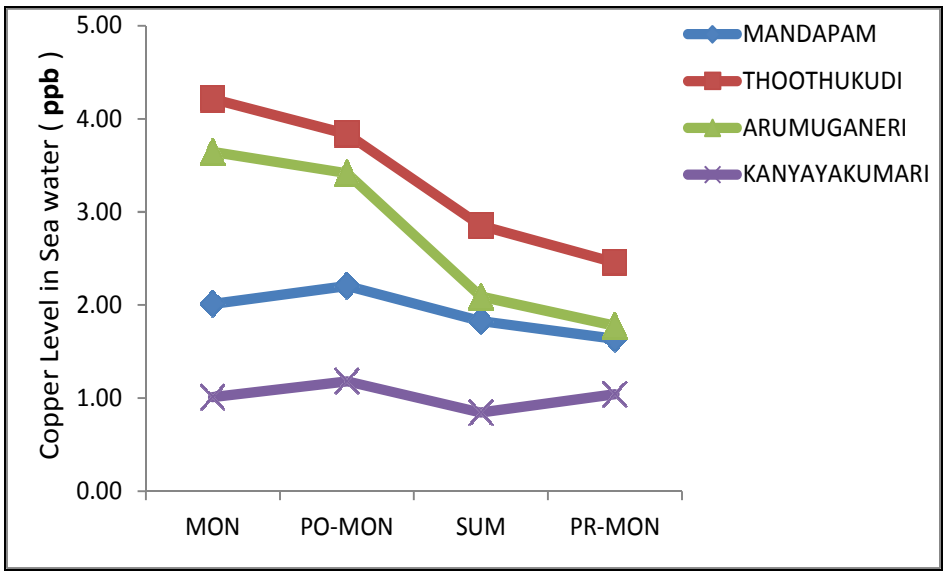

Figure-6
Copper Levels in Sea water at different seasons (ppb) (Oct 2013 – Sep 2014)

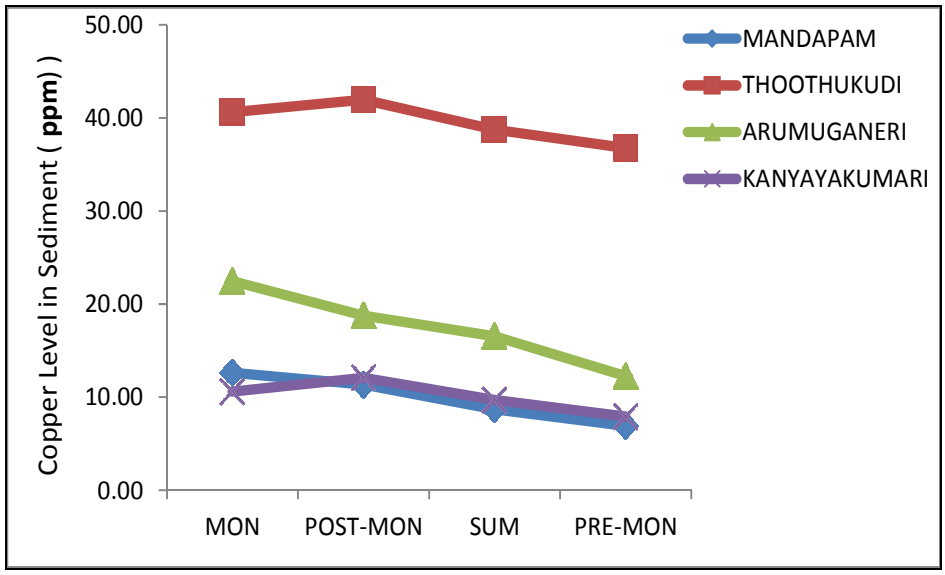

Figure-7
Copper Levels in Sediment at different seasons (ppm) (Oct 2013 – Sep 2014)

There is a possible dispersion of copper from the marine vessel, boats surface and offshore platforms which was coated with antibiofouling paints containing copper pigments[20]. Copper undergoes chelation with organic matter present in the effluent discharge and forms soluble and insoluble metal matrix also increase copper content in the coastal environs[21]. During the monsoon season the runoff from the surface and agricultural land which contains copper based pesticides also upturns the copper concentration in the coastal areas[18].

Chromium: Home usable and engineering products contain chromium. The bio-availability of chromium is complexed by its species [Cr (III) and Cr (VI)] and its redox behavior[22].The concentration of chromium in the coastal seawater can range from 0.63 to 3.15 ppb). It was found minimum (0.63 ppb) at Kanyakumari during Monsoon and maximum (3.15ppb) at Thoothukudi during post monsoon season (figure-8). Similarly the concentration of chromium in sediments ranges from 7.39 to 29.56(ppm), maximum at Thoothukudi during post-monsoon season, and minimum at Kanyakumari during summer season as shown in the figure-9.

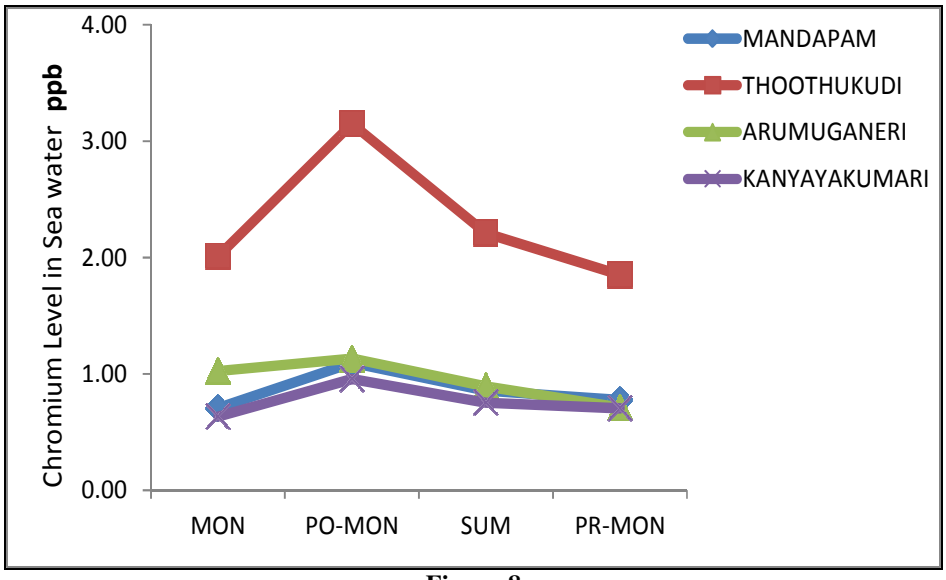

Figure-8
Chromium Levels in Sea water at different seasons (ppb) (Oct 2013–Sep 2014)

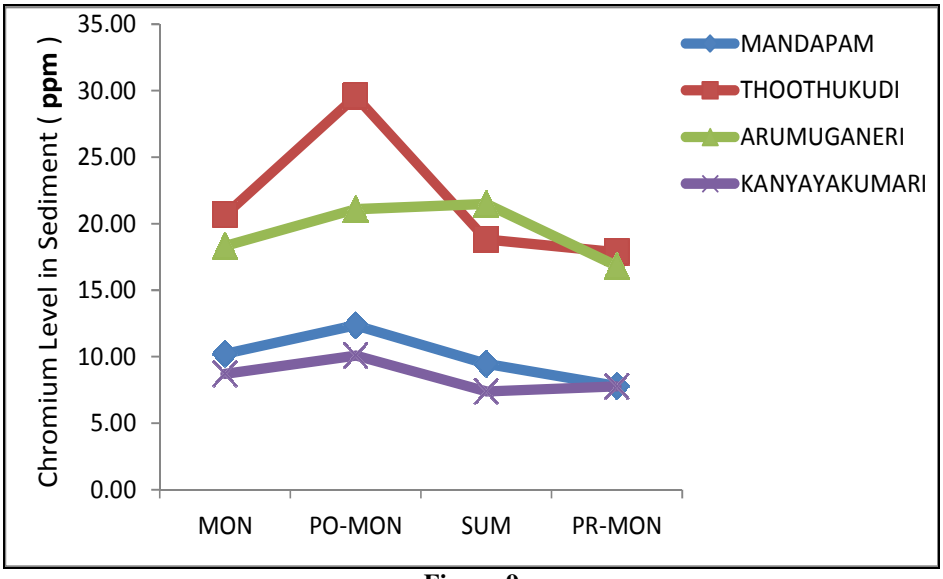

Figure-9
Chromium Levels in Sediment at different seasons (ppm) (Oct 2013–Sep 2014)

The effluent of metal finishing industry, corrosion of building materials, domestic and municipal sewage are the significantpart in increasing the chromium concentration along the marine environment. Land run off during monsoon season also increasing chromium concentration. In metal industry elemental chromium is used as a marking material. Besides the wastages from metal ore, iron and steel industries, municipal sewages also increase the chromium load in shore areas[23]. The precipitated organic and inorganic suspended matter adsorbs chromium metal in the water media and thus increases the metal content in sediment[24].

Nickel: Nickel is known to be a nutritional requirement for many eukaryotic and prokaryotic organisms, which is necessary for plants to metabolize urea [25]. The concentration of nickel in the coastal seawater varied from 0.51 to 2.52 (ppb). it was found minimum (0.51 ppb) at Kanyakumari during pre-monsoon and maximum (2.52 ppb) at Thoothukudi during post monsoon season (figure-10). The concentration of Nickel in sediments can range from 6.07 to 25.98 (ppm), maximum at Thoothukudi during monsoon season, and minimum at Mandapam during pre-monsoon season as shown in the figure-11.

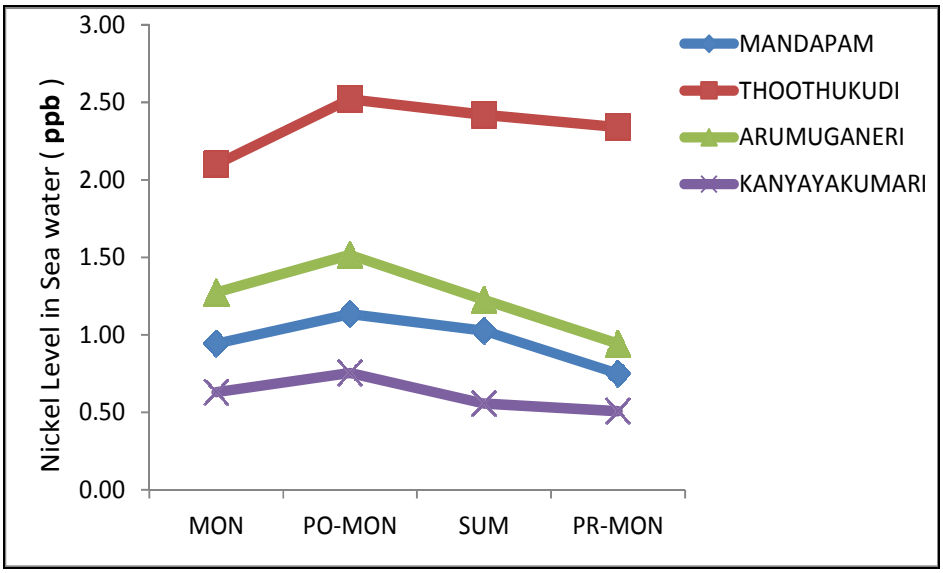

Figure-10
Nickel Levels in Sea water at different seasons (ppb) (Oct 2013 – Sep 2014)

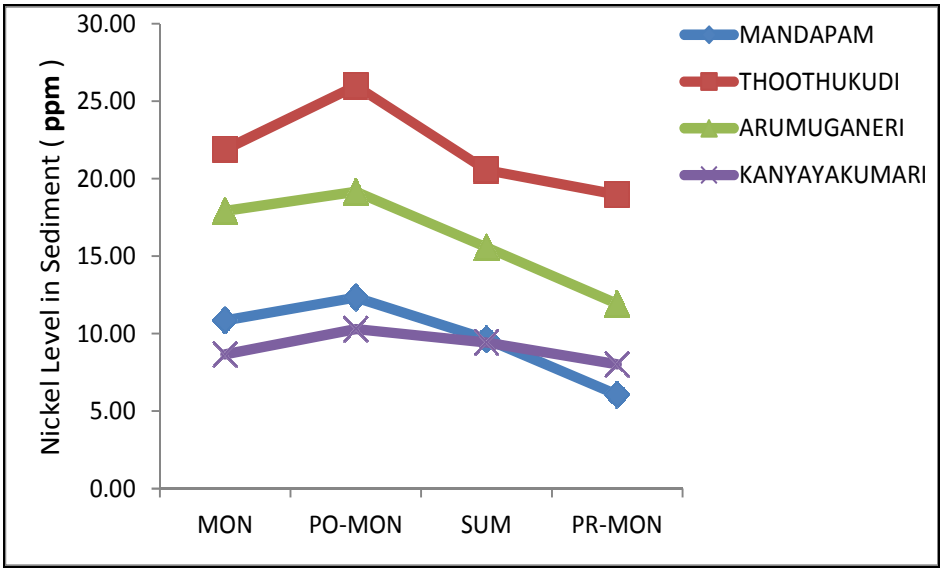

Figure-11
Nickel Levels in Sediment at different seasons (ppm) (Oct 2013 – Sep 2014)

Due to the diffusion of industrial effluent, land run-off, urban and domestic sewage increase the Nickel concentration along the coastal environment. Commonly, the low levels of nickel in the environment are due the chemical weathering of rocks and mountains[26]. The petroleum allied activities also fetch nickel and pollute the marine environment[27].

Zinc: Zinc is the vital element and present in all living beings and involved in the metabolic activities. The concentration of zinc in the coastal seawater can range from 1.33 to 21.22 (ppb). It was found minimum (1.33ppb) at Mandapam during Pre-monsoon and maximum (21.22 ppb) at Thoothukudi during Post monsoon season (figure-12). Similarly the concentration of Zinc in sediments ranges from 10.59 to 30.68 (ppm), maximum at Thoothukudi during monsoon season, and minimum at Mandapam during pre-monsoon season as shown in the figure-13.

The high concentration of zinc observed in the coastal environment is from the domestic sewage, municipal waste, Fly-ash deposition by atmosphere, Coal fuelled Thermal Power stations, and dredgingactivities[28]. From the sources like sewage,

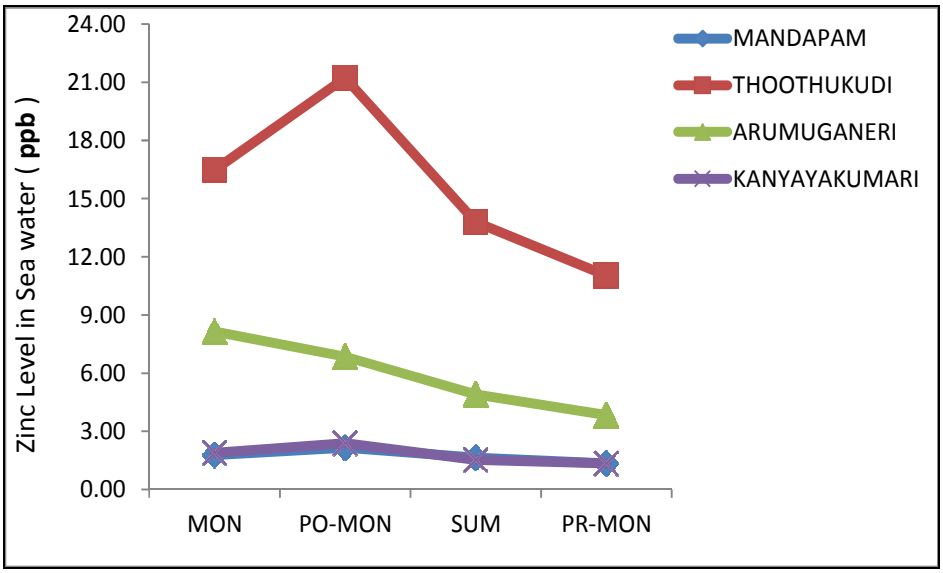

Figure-12
Zinc Levels in Sea water at different seasons (ppb) (Oct 2013 – Sep 2014)

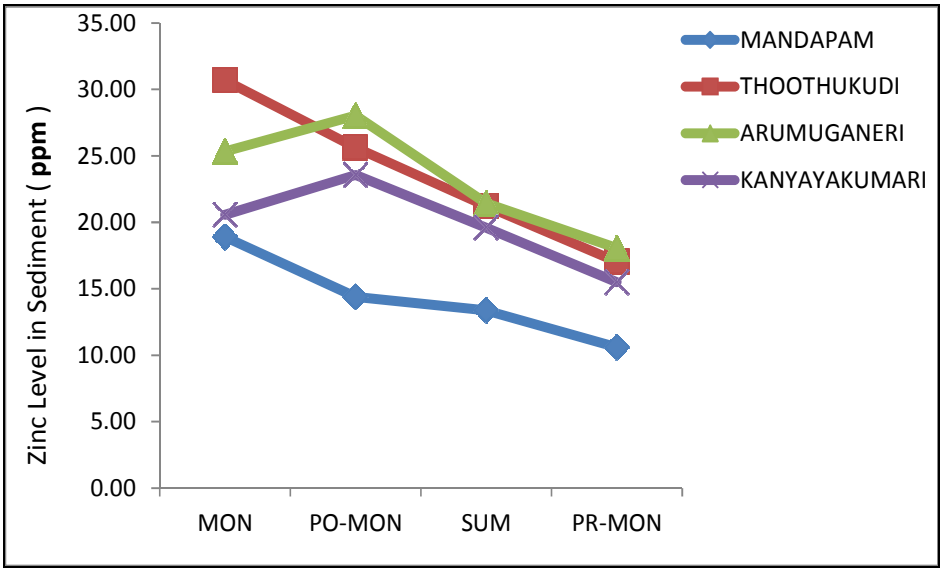

Figure-13
Zinc Levels in Sea water and Sediment at different seasons (ppm) (Oct 2013 – Sep 2014)

continental runoff, industrial effluent discharges zinc enters into the coastal aquatic environment[29]. During monsoon period high organic load was observed along coastal zone as well as estuary area, concurrently increase the zinc level. This shows that the anthropogenic sources also increase the zinc content like Copper.

Conclusion

Examining the trend of results obtained during the present study, it is visible that the monsoon acts a prominent role in the distribution of heavy metals in coastal waters and sediment. Therefore, an obvious seasonal change varies the metal concentration. Due to the man-made land based; activities accumulate more heavy metal concentration in the shore water and sediment. Furthermore, the expansion of chemical 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 key source for the anthropogenic input in the 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. The gradual rises in heavy metal levels in the sea creatures have the chance to enter human life through the food web. Great attention should be given along the coastal region in order to control the anthropogenic sources. Proper monitoring is essential along the coastal zone is recommended for future studies, and Industries must treat their effluent appropriately before the discharge point.

References

1. Michael HC, Heavy metal in encyclopedia of earth. edited by Monosson Cleveland C., Washington DC : National Council for Science and the Environment, **(2010)**

2. Ip C.C.M., Li X.D., Zhang G., Wai O.W.H and Li Y.S., Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal areas, South China, *Environmental Pollution*, **147**, 311–323 **(2007)**

3. Lamb T., Bickham J.W. and Gibbons J.W., Genetic damage in a population of slider turtles (Trachemysscripta) inhabiting a radioactive reservoir, *Archives of Environmental Contamination and Toxicology,* **20**, 138-142 **(1991)**

4. Bryan GW, Bioaccumulation of marine pollutants, *Phil Trans R Soc Lond B* 1979, **286**, 483–505 **(1979)**

5. Antonio Cobelo Garcia and Ricardo Prego, Heavy metal sedimentary records in Galician Ria (NW Spain) : Background values and recent contamination, *Marine Pollution Bulletin***, 46,** 1253–1262 **(2003)**

6. Forstner U and Wittmann G T W, Metal pollution in the aquatic environment (*Berlin: Springer*), 486, **(1981)**

7. Ananthan G, Sampathkumar P, Palpandi C and Kannan L, Distribution of heavy metals in Vellar estuary, Southeast coast of India, *J Ecotoxicol Environ Monit*, **16**, 185–191 **(2006)**

8. Castro H., Aguilera P.A., Martinez J.L. and Carrique E.L., Differentiation of clams from fishing areas an approximation to coastal quality assessment, *Environmental Monitoring and Assessment*, **54**, 229-237 **(1999)**

9. Eugenia JO, Sanchez G and Marcado G, Cleaner production and environmental sound biotechnology for the prevention of upstream nutrient pollution in the Mexican coast of the Gulf of Mexico, *Ocean Coastal Manag.,* **47**, 641–670 **(2004)**

10. Brooks R.R., Presley B.J. and Kaplan I.R., Determination of microgram amounts of some transition metals in sea water by methyl iso-butyl ketone-nitric acid successive extraction and flameless atomic absorption spectrophotometer, *Talanta,* **14**, 809–814 **(1967)**

11. Tessier A, Campbell PGC and Bisson M., Sequential extraction procedure for the speciation of particulate trace metals, *Anal Chem,* **51**, 844–851 **(1979)**

12. Ruilian Y., Xing Y., Yuanhui Z., Gongren H. and Xianglin T., Heavy metal pollution in intertidal sediments from Quanzhou Bay, China, *J. Environ. Sci.,* **20**, 664–669 **(2008)**

13. Vinithkumar N.V., Kumaresan S., Manjusha M. and Balasubramanian T., Organic matter, Nutrients and major ions in the sediments of corals reefs and seagrass bed of Gulf of Mannar Biosphere Reserve, Southeast coast of India, *Indian J. Mar. Sci.,* **28**, 383-393 **(1999)**

14. Palanichamy S. and Rajendran A., Heavy metal concentrations in seawater and sediments of Gulf of Mannar and Palk Bay, Southeast coast of India, *Indian J. Mar. Sci.,* **29,** 116-119 **(2000)**

15. Kennish M.J., Practical handbook of Estuarine and Marine Pollution, 525, Boca Raton, FL: CRC **(1996)**

16. Fernandez C, Monna F, Labanowski J, Loubet M and van Oort F, Anthropogenic lead distribution in soils under arable land and permanent grassland estimated by Pb isotopic compositions, *Environ Pollut,* **156**, 1083–1091 **(2008)**

17. Abu-Hilal A.H., Distribution of trace elements in nearshore surface sediments from the Jordan Gulf of Aqaba (Red Sea), *Mar. Poll. Bull*, **18(4),** 190–193 **(1987)**

18. Selvaraj K, Ram-Mohan V, Srinivasalu S, Jonathan, MP and Siddartha R., Distribution of non-detrital trace metals in sediment cores from Ennore creek, southeast coast of India, *Journal of Geological Society of India,* **62**, 191–204 **(2003)**

19. Jayaprakash M, Jonathan MP, Srinivasalu S, Muthu Raj S, Ram- Mohan V and Rajeshwara Rao N., Acid-leachable trace metals in sediments from an industrialized region (Ennore Creek) of Chennai City, SE coast of India : An approach towards regular monitoring, *Estuar Coast Shelf Sci* ., **76,** 692–703 **(2008)**

20. Raman A.V. and Ganapati P.N., Pollution effects on ecobiology of benthic polychaetes in Visakapatanam harbour (Bay of Bengal), *Mar Poll Bull*, **14,** 46-52 **(1983)**

21. Jurgen Ritterhoff and Gerd-Peter Zauke, Influence of Body length, Life-history status and sex on trace metal concentrations in selected zooplankton collectives from the Greenland Sea., *Marine Pollution Bulletin,* **34(8),** 614-621 **(1997a)**

22. Wang W-X and Fisher NS, Assimilation efficiencies of chemical contaminants in aquatic invertebrates: a synthesis, *Environ Toxicol Chem*, **18**, 2034–45 **(1999a)**

23. El Nemr A, Khaled A and El Sikaily A., Distribution and statistical analysis of leachable and total heavy metals in the sediments of the Suez Gulf, *Environ Mon Ass,* **118**, 89–112 **(2006)**

24. Turkoglu M. and Parlak H., Accumulation and distribution of total chromium in seawater, sediment, and some organisms and its behaviour processes in Izmir Bay (Aegean Sea), *Ege Univ. J. Fish. Aquat. Sci.*, **16(1-2),** 47-58 **(1999)**

25. Thomson A.J., Proteins containing nickel, *Nature,* **298**, 602-603 **(1982)**

26. Achyuthan H, Richardmohan D, Srinivasalu S and Selvaraj K ., Trace metals in the sediment cores of estuary and tidal zones from northern part of southeast coast of India, *Indian J Mar Sci,* **31**, 141–149 **(2002)**

27. Muthu Raj S and Jayaprakash M., Distribution and enrichment of trace metals in marine sediments of Bay of Bengal, off Ennore, south-east coast of India, *Environ Geol,* **56**, 207–217 **(2008)**

28. Boxall A.B.A., Comber S.D., Conrad A.U., Howcroft J. and Zaman N., *Inputs, Bulletin,* **37,** 393–403 **(2000)**

29. John SG, Park JG, Zhang Z, Boyle EA., The isotopic composition of some common forms of anthropogenic zinc, *Chem Geol,* **245**, 61–69 **(2007)**