ISSN 2231-5063 Impact Factor : 4.6052 (UIF) Volume - 6 | Issue - 3 | September - 2016

Golden Research Thoughts

# ASSESSMENT OF HEAVY METAL DISTRIBUTION OF COASTAL WATER OF THOOTHUKUDI – GULF OF MANNAR

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**Abstract**

*Water samples collected from five different locations falls along Thoothukudi coast were subjected to study trace metal distribution and associated physic chemical parameters such as pH, acidity, alkalinity, salinity, dissolved oxygen. Nutrient parameters such as nitrogen, phosphorous, calcium, magnesium also measured using standard procedure. The heavy metal distribution level was analyzed based on APHA method using Atomic Absorption Spectrophotometer. The elevated level of nutrients such as nitrate at station IV (23.84mg/l), phosphorous at station IV (0.33 mg/l) calcium (34.26 mg/l) and magnesium content (84.21 mg/l) at station II have been reported. The metal distribution and their environmental concerns were analyzed using various indexes such as Enrichment Factors (EF), Geo accumulation Index (Igeo). The results of these indices indicated that the study area is moderately contaminated with Cu, Pb, Cd.*

**Keywords:***Heavy metals, Thoothu kudi coast, Enrichment Factor, Geo accumulation index.*

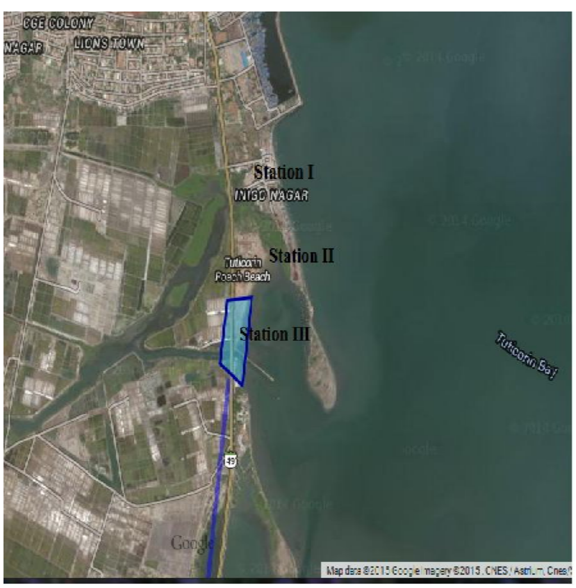
## INTRODUCTION

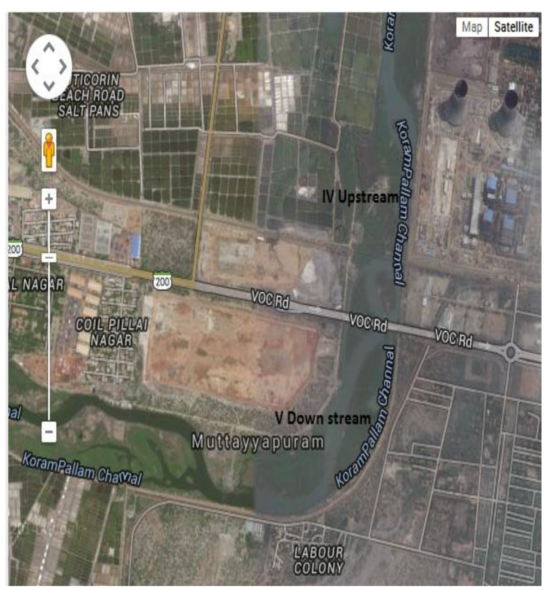
The increasing interest in quantification of heavy metals and the assessment of their potential hazard to environment has come as a result of growing public awareness on impact of industrial development and urbanization. The coastal zones enriched with biodiversity became the site of urbanization and industrialization let out various contaminants particularly heavy metal rich effluents. These contaminants reached to coastal compartments via rivers, and get settled to produce biological effects. Heavy metals pose a serious threat to natural ecosystem because of their toxicity, persistence and bioaccumulation characteristics (Deforest *et al.,* 2007). The way of transfer, and dispersal of these toxic heavy metals between water and sediment are also of great important. Once these heavy metals enter into the aquatic environment and dispersed throughout the water and finally deposited into the sediments. The dynamic accumulation of metal through marine trophic levels and their subsequent hazard to human drastically reduced carbohydrate, protein; amino acid and lipid content even at low concentrations (0.5 to 1 ppm) (Anantharaj *et al.,* 2011). Heavy metal accumulation through food chain can contribute to degradation of marine ecosystems by reducing species diversity and abundance (Hosono *et al.,* 2011). So an understanding of the distribution and their possible coastal ecosystem is paramount important before making any damage to this unique ecosystem. Extensive survey of coastal ecosystem of Thoothukudi has been found the study area was not subjected to understand the distribution and possible sources of physic chemical characteristic including heavy metal and their digenetic reaction of these components between sediment and water above it. So the present study is intended to fill the above mentioned lacuna. The investigation encompasses determining the physico - chemical characteristics including heavy metal distribution and their possible source. The extent of its accumulation and their relation among parameters will be analysed and will be interpreted through relevant statistics. The pollution load indices such as Enrichment factor (EF) (Tang *et al.,* 2010) and Geo accumulation Index (Igeo) with reference to coastal baseline data will be done to confirm the environmental status.

## STUDY AREA

Thoothukudi is an industrial town located between latitude 8º 45'N & 9º02'3'N and longitude between 78º07'17'' E and 78º19'18''. This coast is sheltered by Sri Lanka. Thoothukudi port is one of the Fastest growing Major Ports in India. Thoothukudi is an "Emerging Energy and Industrial hub of South India". It is also called as "Sea Gateway of Tamil Nadu". A number of major and minor industries are located in and around its coast. The 21 islands between Thoothukudi and Rameswaram shores in the Gulf of Mannar are noted as the first Marine Biosphere Reserve of India, and have around 36,000 species of flora and fauna exist in the region covered with mangroves, sandy shores, sea grass beds that are conducive for turtle nesting. This protected area is called Gulf of Mannar Marine National Park. Fishing is one of the largest contributors to the local economy. In addition to this there are several small scale and large scale industries of the city such as Thermal power plants, Coastal Energen, Sterlite Industries Captive power plant, Southern Petrochemical Industries Corporation, Thoothukudi Alkali Chemicals, Heavy Water Board Plant, Sterlite Industries, Madura Coats and Mills, Dhrangadhra Chemical works, Kilburn Chemicals, Thoothukudi Spinning Mills Ltd and KSPS Salts are located along these limited coastal stretch. The study area ranges between Inigo nagar to Korampallam Creek (Fig. 1) falls along Thoothukudi coast. The study area is colonized well flourished mangrove vegetation. It is extended to all sides by major industries such as Thermal power station, salt pan activities, sea food processing etc. Besides, the mangrove strands forms a major dumping ground for municipal waste and sewage disposal activities. Recently salt pan, roads and walking track expanding activities the mangrove vegetation was slowly destroyed, however the remaining mangroves are with stand healthily under these threatened condition.

**Plate 1 Maps showing the sampling stations**



## MATERIALS AND METHODS

Surface water from fifty different locations of 5 different stations along the mangrove ecosystem was collected during Pre monsoon, 2014. The collected water samples in the pre cleaned acid washed poly ethylene bottles were refrigerated at 4ºC until further analysis. Physico – chemical parameters such as pH, EC & Salinity were determined using digital pH meter (Model No: C/128), Digital pH - conductivity & Temperature meter 181 and titrimetric method respectively. Determination of DO was performed *insitu* by fixing the DO of the water in special DO bottles (Winkler's method). The nutrient parameters such as nitrate, phosphorous (Stickland and Panson 1978) were analyzed using standard procedures. The heavy metals of water sample were extracted by applying APHA (1978) method. The resultant solution was utilized for analyzing metals such as Cu, Zn, Pb, Fe, Mn, Cd, Cr and As using AAS (Model No: SL 168). The detection limit of these metals is 0.001 ppm. For quality assurance, suitable internal chemical standards (Chemical concentration) were used to calibrate the instrument. The analytical grade chemicals were used. The data are subjected to statistical analysis to derive better interpretation terms of origin, mobilization and distribution using computer package (SPSS), version 19 and Microsoft Excell 2007. Various pollution monitoring indices were used to understand the heavy metal status of the study area in terms of pollution load.

## RESULT & DISCUSSION

Throughout the world anthropogenic input is major source for the heavy metal pollution along the coastal environment (Ruilian *et al.,* 2008). The heavy metals enter into the coastal environment through domestic, municipal wastes and industrial effluents (Vinithkumar *et al.,* 1999). Once reached into the water body their distribution is governed by physical and chemical factors like temperature, salinity, pH, dissolved oxygen, conductivity, redox potential ionic strength and biological activities operating both in sediment and water (Goksu. L.Z. 2003). Based on this prediction our study has been aimed and estimated the physico chemical characteristics of sea water and the results obtained were presented in Table 1.

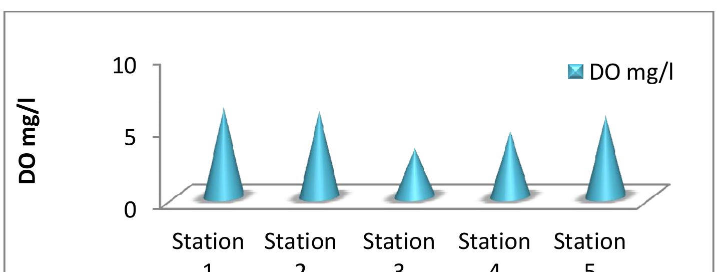
**Table 1 Physico - chemical parameters in water sample**

| Station | Sites | pH | EC 20 ms | Acidity ppm | Alkalinity mg/l | Salinity ppm | Nitite mg/l | Nitratemg/l | Orthophosporous mg/l | Ca (mg/l) | Mg (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 1 | 7.34 | 11.50 | 0.3 | 1.7 | 4.8 | 7.5 | 24 | 0.44 | 26.88 | 75.84 |
| | 2 | 7.27 | 11.72 | 0.1 | 1.4 | 4.6 | 8.0 | 3.8 | 0.1 | 21.44 | 84.74 |
| | 3 | 7.30 | 11.33 | 0.4 | 2.0 | 5.3 | 9.0 | 23.9 | 0.21 | 36.76 | 79.93 |
| | 4 | 7.38 | 11.62 | 0.3 | 1.6 | 5.7 | 6.6 | 25.5 | 0.1 | 20.25 | 77.75 |
| | 5 | 7.24 | 10.76 | 0.2 | 1.2 | 5.5 | 7.2 | 22.0 | 0.1 | 29.00 | 77.06 |
| | 6 | 7.28 | 11.38 | 0.2 | 2.2 | 5.3 | 6.26 | 16.4 | 0.26 | 17.65 | 72.18 |
| | 7 | 7.27 | 11.52 | 0.3 | 1.6 | 3.8 | 8.4 | 22.0 | 0.17 | 24.84 | 71.49 |
| | 8 | 7.38 | 11.26 | 0.3 | 1.4 | 5.2 | 7.6 | 20.6 | 0.20 | 28.52 | 69.31 |
| | 9 | 7.30 | 11.42 | 0.1 | 1.4 | 6.2 | 8.5 | 18.2 | 0.1 | 21.64 | 64.50 |
| | 10 | 7.36 | 11.40 | 0.4 | 1.3 | 5.4 | 7.6 | 22.0 | 0.26 | 21.86 | 73.40 |
| | **Average** | **7.31** | **11.39** | **0.26** | **1.58** | **5.18** | **7.66** | **19.84** | **0.19** | **24.88** | **74.62** |
| II | 1 | 7.27 | 11.22 | 0.5 | 3.0 | 7.1 | 9.0 | 24.4 | 0.24 | 26.16 | 85.43 |
| | 2 | 7.17 | 12.04 | 0.3 | 2.4 | 6.2 | 8.3 | 22.0 | 0.10 | 32.28 | 94.33 |
| | 3 | 7.39 | 12.06 | 0.4 | 2.7 | 5.9 | 9.9 | 24.4 | 0.21 | 45.07 | 89.52 |
| | 4 | 7.42 | 16.04 | 0.2 | 3.3 | 7.4 | 8.6 | 23.0 | 0.18 | 26.11 | 87.34 |
| | 5 | 7.28 | 10.16 | 0.4 | 2.7 | 6.6 | 7.7 | 24.0 | 0.10 | 43.24 | 86.65 |
| | 6 | 7.26 | 10.00 | 0.6 | 3.4 | 6.4 | 9.6 | 23.6 | 0.14 | 30.28 | 81.77 |
| | 7 | 7.42 | 13.22 | 0.2 | 2.5 | 8.0 | 8.2 | 26.4 | 0.20 | 31.10 | 81.08 |
| | 8 | 7.26 | 11.26 | 0.5 | 3.1 | 6.8 | 8.3 | 25.2 | 0.14 | 39.28 | 78.90 |
| | 9 | 7.32 | 13.04 | 0.2 | 2.7 | 6.1 | 9.7 | 22.4 | 0.10 | 36.12 | 74.09 |
| | 10 | 7.32 | 14.00 | 0.3 | 2.4 | 5.9 | 7.9 | 20.2 | 0.22 | 33.00 | 82.99 |
| | **Average** | **7.31** | **12.30** | **0.36** | **2.82** | **6.64** | **8.7** | **23.56** | **0.16** | **34.26** | **84.21** |
| III | 1 | 7.91 | 13.34 | 0.3 | 1.2 | 8.1 | 12.9 | 19.2 | 0.1 | 29.08 | 78.34 |
| | 2 | 8.01 | 11.24 | 0.2 | 1.1 | 8.2 | 12.5 | 20.0 | 0.33 | 32.16 | 74.57 |
| | 3 | 7.98 | 14.06 | 0.2 | 0.9 | 7.8 | 13.2 | 18.0 | 0.33 | 27.19 | 81.89 |
| | 4 | 7.89 | 11.34 | 0.3 | 1.1 | 7.4 | 13.8 | 17.4 | 0.21 | 11.06 | 83.00 |
| | 5 | 8.03 | 11.52 | 0.3 | 1.2 | 5.9 | 13.2 | 23.9 | 0.1 | 14.92 | 85.02 |
| | 6 | 7.56 | 13.20 | 0.2 | 0.8 | 7.3 | 13.4 | 20.4 | 0.2 | 16.42 | 68.78 |
| | 7 | 7.93 | 11.02 | 0.2 | 1.3 | 8.6 | 12.6 | 18.3 | 0.3 | 36.19 | 70.80 |
| | 8 | 8.46 | 14.06 | 0.3 | 1.4 | 6.9 | 12.8 | 17.8 | 0.14 | 27.48 | 71.91 |
| | 9 | 8.21 | 11.00 | 0.2 | 1.2 | 7.8 | 13.6 | 22.4 | 0.22 | 24.92 | 79.23 |
| | 10 | 7.62 | 12.26 | 0.3 | 0.9 | 6.8 | 13.2 | 19.6 | 0.18 | 39.01 | 75.46 |
| | **Average** | **7.96** | **12.3** | **0.25** | **1.1** | **7.48** | **13.12** | **19.7** | **0.21** | **27.50** | **76.90** |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IV | 1 | 7.26 | 11.28 | 0.4 | 1.5 | 7.0 | 7.5 | 26.0 | 0.44 | 8.84 | 67.23 |
| | 2 | 7.23 | 10.01 | 0.1 | 1.0 | 7.3 | 8.0 | 24.4 | 0.1 | 11.71 | 74.27 |
| | 3 | 7.18 | 11.09 | 0.4 | 1.3 | 6.7 | 6.8 | 22.8 | 0.33 | 13.05 | 78.49 |
| | 4 | 7.26 | 13.62 | 0.2 | 1.4 | 6.9 | 8.3 | 23.0 | 0.44 | 14.38 | 80.79 |
| | 5 | 7.14 | 12.34 | 0.3 | 1.7 | 7.2 | 9.0 | 23.0 | 0.33 | 15.49 | 71.97 |
| | 6 | 7.24 | 11.06 | 0.4 | 1.0 | 6.3 | 7.2 | 20.34 | 0.46 | 18.15 | 70.72 |
| | 7 | 7.22 | 12.30 | 0.2 | 1.5 | 7.8 | 8.9 | 23.66 | 0.26 | 19.26 | 82.04 |
| | 8 | 7.20 | 11.20 | 0.3 | 1.4 | 7.0 | 7.3 | 24.14 | 0.34 | 20.59 | 68.27 |
| | 9 | 7.17 | 13.16 | 0.4 | 1.4 | 6.0 | 7.6 | 25.83 | 0.24 | 21.93 | 84.49 |
| | 10 | 7.20 | 10.64 | 0.1 | 1.6 | 8.0 | 8.4 | 25.27 | 0.36 | 24.80 | 85.53 |
| | **Average** | **7.21** | **11.67** | **0.28** | **1.38** | **7.02** | **7.9** | **23.84** | **0.33** | **16.82** | **76.38** |
| V | 1 | 7.48 | 10.62 | 0.3 | 1.7 | 7.4 | 6.6 | 19.8 | 0.21 | 23.79 | 84.32 |
| | 2 | 7.42 | 16.26 | 0.2 | 1.4 | 7.4 | 6.4 | 20.9 | 0.33 | 24.92 | 85.57 |
| | 3 | 7.39 | 9.68 | 0.4 | 1.2 | 6.9 | 8.3 | 18.0 | 0.33 | 27.11 | 86.91 |
| | 4 | 7.34 | 10.36 | 0.3 | 1.3 | 7.2 | 7.7 | 20.2 | 0.1 | 28.38 | 89.26 |
| | 5 | 7.41 | 11.42 | 0.3 | 1.5 | 7.6 | 6.4 | 20.4 | 0.21 | 30.47 | 76.26 |
| | 6 | 7.30 | 10.24 | 0.3 | 1.5 | 6.7 | 7.2 | 20.18 | 0.22 | 14.10 | 78.69 |
| | 7 | 7.46 | 12.66 | 0.3 | 1.4 | 7.7 | 7.4 | 19.56 | 0.18 | 15.37 | 80.03 |
| | 8 | 7.49 | 9.28 | 0.2 | 1.0 | 7.9 | 6.1 | 18.66 | 0.35 | 17.56 | 81.28 |
| | 9 | 7.38 | 14.12 | 0.5 | 1.7 | 7.0 | 8.1 | 20.61 | 0.22 | 18.69 | 91.12 |
| | 10 | 7.43 | 12.08 | 0.2 | 1.5 | 7.2 | 6.6 | 20.30 | 0.26 | 12.01 | 74.48 |
| | **Average** | **7.41** | **11.67** | **0.3** | **1.42** | **7.3** | **7.08** | **19.86** | **0.24** | **21.24** | **82.80** |

The water pH ranged between 7.21 - 7.96 with maximum at station III and minimum at station IV. The slightly basic pH and fairly high amount of DO in various parts of the study indicate the better environment for biological activities. Dissolved oxygen is one of the most important parameters, that plays a vital role in the oxidation of organic and inorganic compounds and there by the release of the metals from suspended matter. DO is positively correlated with nutrients such as nitrite and total phosphorous and also trace metals such as Cu, Zn, Pb and Cd indicate less biological utilization particularly by planktons. The low dissolved oxygen at station III (3.37 mg/l) (Fig 1) reflects the association of thick mangrove vegetation that enhanced more biological activities their by depletion of dissolved oxygen. The pH and DO were positively correlated at station I (0.891), II (0.633), IV (0.934), V (0.756) and negatively correlated at station III (-0.831). Salinity has been viewed as one of the most important variables influencing the utilization of organisms in estuaries (Marshall and Elliot, 1998). The increased salinity will change the habitat pattern of every ecosystem. The present investigation showed a narrow range of salinity just like pH from 5.15 ppm to 7.48 ppm (Table 1). The maximum value of salinity recorded at station III (7.48 ppm) is attributed to the shallowness of water, and the salt pan activities nearby though this station has rich assemblage of mangrove vegetation.

**Fig 1 Dissolved oxygen content in different mangrove sites of Thoothukudi coast**




In coastal water, the interaction between the water column and sediment can have a large influence on nutrition distribution and the overall productivity of the ecosystem (Holland, 1984, Berner and Canifield, 1989). The higher concentration of nutrients above the level of permissible limit indicated the sign of pollution. The nutrients found in sea water such as nitrate, phosphorous, calcium, magnesium, are essential to the survival of plant and marine life. But their extreme level can cause the damage to entire marine viability. The substantial amount of nitrite and phosphorous in the coastal and estuarine environment is due to microbial activity, plant growth and productivity within the ecosystem (Edmond, *et al.,* 1981). The present study revealed that amount of total nitrogen, total phosphorous and their species are substantially high compared to permissible limit in coastal water stated by WHO (World Health Organization) (Table 1). Calcium and

Magnesium are the important constituents of earth's crust also distributed fairly well in all the stations (Table 1). The higher concentration of all the nutrients along with Ca & Mg could be attributed to dumping of garbage waste, letting out of thousands of gallons of sewages, large scale seafood processing along with flourished mangrove vegetation associated in the study area (Plate 2). Elevated level of Ca & Mg at certain location of study area (station II - 34.26 mg/l) reflects rich accumulations of sea shell fragments and other foraminifers. Their positive correlation with organic elements such as nitrogen, phosphorous confirms biogenic origin though they are lithogenic elements.

**Plate 2 : Sewage and waste discharging activities in the study area**

Heavy metals can be introduced into the coastal environment via natural and anthropogenic processes, consequently causing potential danger to the coastal ecosystems (McCready *et al.,* 2006; Chen *et al.,* 2007). Heavy metal levels in water depend on physico chemical parameters of water such as pH, EC and salinity (Wong *et al.,* 2002). The bio – geo chemical processes occurring at the water sediment interface will keep trace metals constantly cycling among the coastal compartments, resulting in comparatively higher concentrations of trace metals in coastal waters as compared to adjacent sea or river waters. The distribution of heavy metals of the study area and comparative account with other mangrove area (world over) are studied and presented in table 2, Fig 2 & Table 3.

**Table 2: Heavy metal distribution in mangrove water ecosystem of Thoothukudi.**

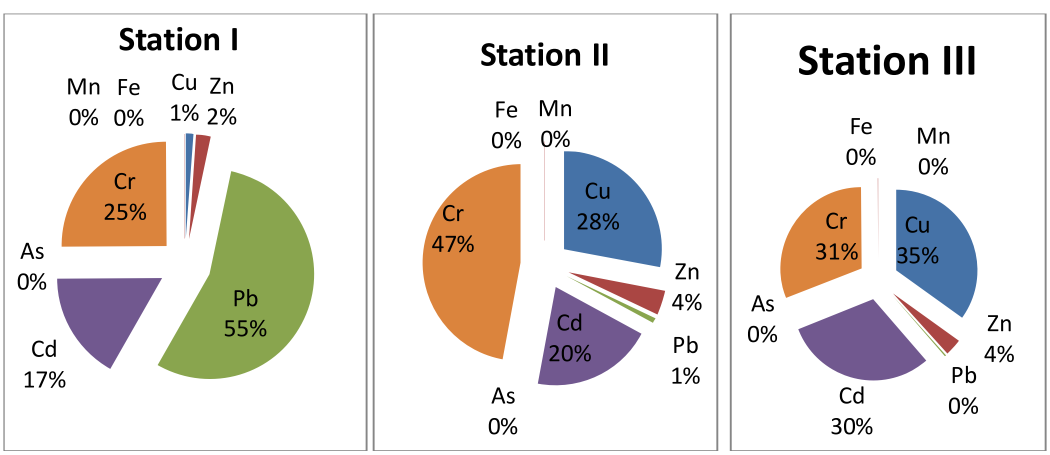
| Station | Sample | Water sample µg/l | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Fe(%) | Mn | Cu | Zn | Pb | Cd | Cr | As |
| I | Site 1 | 0.003 | 0.003 | 0.959 | 3.466 | 69.636 | 11.450 | 17.600 | BDL |
| | Site 2 | 0.104 | 0.018 | 1.279 | 0.746 | 48.308 | 12.500 | 19.200 | BDL |
| | Site 3 | 0.048 | 0.014 | 0.639 | 1.919 | 22.50 | 14.650 | 18.200 | BDL |
| | Site 4 | 0.068 | 0.013 | 0.586 | 1.173 | 43.189 | 12.400 | 17.700 | BDL |
| | Site 5 | 0.003 | 0.002 | 0.906 | 0.853 | 21.435 | 11.500 | 20.800 | BDL |
| | Site 6 | 0.004 | 0.014 | 0.844 | 1.740 | 43.102 | 16.100 | 15.200 | BDL |
| | Site 7 | 0.014 | 0.010 | 0.963 | 1.201 | 54.114 | 10.100 | 19.700 | BDL |
| | Site 8 | 0.008 | 0.013 | 0.838 | 1.617 | 31.027 | 12.000 | 20.100 | BDL |
| | Site 9 | 0.028 | 0.004 | 0.726 | 0.709 | 40.013 | 13.300 | 16.500 | BDL |
| | Site 10 | 0.003 | 0.022 | 0.790 | 3.107 | 36.814 | 11.000 | 22.000 | BDL |
| | Average | **0.028** | **0.011** | **0.853** | **1.653** | **41.014** | **12.500** | **18.700** | **BDL** |
| II | Site 1 | 0.001 | 0.002 | 0.053 | 3.839 | 0.799 | 12.500 | 26.600 | BDL |
| | Site 2 | 0.003 | 0.016 | 69.795 | 2.559 | 0.159 | 14.700 | 30.786 | BDL |
| | Site 3 | 0.009 | 0.012 | 5.225 | 0.853 | 0.426 | 11.500 | 30.820 | BDL |
| | Site 4 | 0.012 | 0.013 | 8.104 | 3.412 | 0.853 | 12.400 | 26.810 | BDL |
| | Site 5 | 0.006 | 0.003 | 4.212 | 2.239 | 0.533 | 11.400 | 31.984 | BDL |
| | Site 6 | 0.020 | 0.012 | 18.614 | 4.038 | 0.764 | 11.100 | 25.570 | BDL |
| | Site 7 | 0.006 | 0.013 | 12.082 | 1.562 | 0.547 | 10.400 | 31.776 | BDL |
| | Site 8 | 0.013 | 0.011 | 14.850 | 1.039 | 0.602 | 15.000 | 31.860 | BDL |
| | Site 9 | 0.046 | 0.003 | 26.703 | 2.628 | 0.122 | 11.000 | 25.800 | BDL |

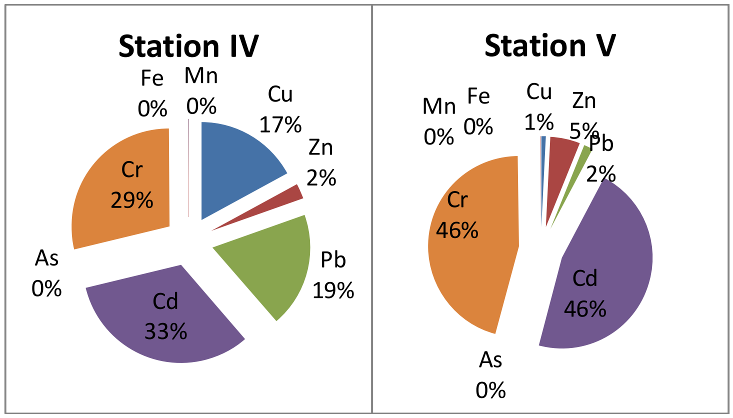
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Site 10 | 0.096 | 0.016 | 15.246 | 3.423 | 0.529 | 15.000 | 32.000 | BDL |
| | Average | **0.021** | **0.010** | **17.488** | **2.559** | **0.533** | **12.500** | **29.400** | **BDL** |
| **III** | Site 1 | 0.014 | 0.063 | 69.849 | 3.839 | 0.426 | 22.600 | 20.510 | BDL |
| | Site 2 | 0.022 | 0.062 | 4.905 | 2.559 | 0.213 | 29.000 | 24.370 | BDL |
| | Site 3 | 0.039 | 0.066 | 4.379 | 2.666 | 0.053 | 26.550 | 28.836 | BDL |
| | Site 4 | 0.048 | 0.081 | 0.479 | 3.626 | 0.319 | 24.350 | 30.384 | BDL |
| | Site 5 | 0.024 | 0.050 | 64.304 | 1.759 | 0.106 | 22.500 | 22.900 | BDL |
| | Site 6 | 0.030 | 0.048 | 60.472 | 2.007 | 0.404 | 26.350 | 18.100 | BDL |
| | Site 7 | 0.043 | 0.041 | 1.644 | 3.821 | 0.116 | 22.000 | 23.180 | BDL |
| | Site 8 | 0.031 | 0.047 | 8.622 | 2.068 | 0.132 | 29.000 | 32.236 | BDL |
| | Site 9 | 0.032 | 0.046 | 68.620 | 3.804 | 0.108 | 25.500 | 28.248 | BDL |
| | Site 10 | 0.038 | 0.058 | 4.118 | 2.642 | 0.257 | 22.150 | 25.240 | BDL |
| | Average | **0.032** | **0.056** | **28.739** | **2.879** | **0.213** | **25.000** | **25.400** | **BDL** |
| IV | Site 1 | 0.026 | 0.046 | 0.213 | 1.919 | 0.799 | 29.402 | 22.500 | BDL |
| | Site 2 | 0.022 | 0.022 | 69.740 | 3.199 | 69.689 | 32.719 | 30.318 | BDL |
| | Site 3 | 0.040 | 0.035 | 7.891 | 2.239 | 9.490 | 26.220 | 38.618 | BDL |
| | Site 4 | 0.049 | 0.048 | 0.906 | 2.666 | 1.919 | 26.110 | 23.944 | BDL |
| | Site 5 | 0.024 | 0.032 | 1.706 | 2.026 | 7.838 | 39.549 | 26.120 | BDL |
| | Site 6 | 0.058 | 0.038 | 25.286 | 1.561 | 21.839 | 33.416 | 22.600 | BDL |
| | Site 7 | 0.043 | 0.045 | 6.121 | 1.226 | 14.566 | 28.583 | 28.218 | BDL |
| | Site 8 | 0.047 | 0.026 | 13.040 | 2.574 | 19.437 | 38.210 | 35.510 | BDL |
| | Site 9 | 0.043 | 0.039 | 14.072 | 2.640 | 17.675 | 27.348 | 25.052 | BDL |
| | Site 10 | 0.042 | 0.030 | 22.057 | 3.943 | 16.352 | 26.446 | 30.120 | BDL |
| | Average | **0.039** | **0.036** | **16.103** | **2.399** | **17.960** | **30.800** | **28.300** | **BDL** |
| V | Site 1 | 0.020 | 0.050 | 0.213 | 5.652 | 0.266 | 26.700 | 25.876 | BDL |
| | Site 2 | 0.016 | 0.048 | 0.053 | 1.493 | 0.107 | 29.494 | 28.702 | BDL |
| | Site 3 | 0.046 | 0.041 | 0.959 | 0.959 | 1.279 | 30.712 | 30.100 | BDL |
| | Site 4 | 0.037 | 0.047 | 0.053 | 0.479 | 0.533 | 26.100 | 24.486 | BDL |
| | Site 5 | 0.023 | 0.046 | 1.279 | 7.144 | 0.959 | 24.396 | 26.340 | BDL |
| | Site 6 | 0.031 | 0.058 | 0.149 | 4.264 | 0.981 | 25.145 | 22.068 | BDL |
| | Site 7 | 0.031 | 0.063 | 0.149 | 3.140 | 0.944 | 30.482 | 30.612 | BDL |
| | Site 8 | 0.042 | 0.062 | 0.273 | 0.736 | 2.608 | 26.716 | 23.514 | BDL |
| | Site 9 | 0.033 | 0.066 | 0.068 | 2.844 | 1.182 | 34.743 | 31.704 | BDL |
| | Site 10 | 0.031 | 0.081 | 0.127 | 4.752 | 0.732 | 20.314 | 27.600 | BDL |
| | Average | **0.031** | **0.056** | **0.479** | **3.146** | **0.959** | **27.480** | **27.100** | **BDL** |

**Table 3.Comparitive account on metal distribution in mangrove water with world over**

| **S.N** | **Place** | **Water sample (µg/l)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **Fe** | **Mn** | **Cu** | **Zn** | **Pb** | **Cd** | **Cr** | **As** |
| 1. | Australia | 4.9 | 3.8 | 2.7 | 67 | 55 | 0.77 | 0.47 | 8.2 |
| 2. | Singapore | 6.2 | 4.9 | 0.17 | 2.37 | 0.006 | 0.015 | 0.067 | 0.312 |
| 3. | Thoothukudi, India (2014) | 0.039 | 0.59 | 28.74 | 3.15 | 41.01 | 30.80 | 29.40 | BDL |

**Fig 2 Pie diagram showing station wise metal distribution**






The station wise highest average values of eight metals reported in the study area include Fe at station IV (0.039), Mn at station III, IV (0.056), Cu at Station III (28.74 µg/l), Zn at Station V (3.15 µg/l) Pb at station I (41.01 µg/l), Cd at station IV (30.80 µg/l) and Cr at station II (29.40 µg/l). However As was not reported at any station. During the study period the Fe showed narrow range of distribution at all the stations (Table 2 & Fig 2). The comparison of the trace element concentrations in this present study with EIA (Environmental Impact Assessment) metal acceptable limit indicating that study area has slightly enriched with Cu, Pd and Cd. This reflects the association of heavy metal producing industries such as thermal power plant, SPIC and other industries that discharge the untreated effluents directly to these stations. The maximum value of Pb reported at station I (41.01 µg/l), could be due to high metal mobilization to the water column due to oxidized environment. The pattern of distribution of the analyzed metals in water, in the study area is in decreasing order of Pb > Cd > Cr > Cu > Zn > As. The metal distribution trend in the study area is reverse to the distribution pattern of metals in the coastal water confirm industrial origin.

The pearson correlation matrix for the water sample of these study area were calculated and presented in Table 4. The relationship between most of the trace elements reveals that, there may be common source for these pollutants. According to Aragon *et al.,* (1986), Mn exhibits its maximum leachability under reduced condition from the sediment to water surface. The significant positive correlation between Fe and Mn (0.632) confirms the behavior of these metals which is similar with respect to their redox sensitivity. Lack of positive correlation of Fe with metals such as Cu, Zn, Pb, Cd and Cr confirmed recent anthropogenic origin of these industrially based heavy metals.

For the assessment of anthropogenic inputs, some of the most often used indicators in the water sample are enrichment factor (EF) and Geo Accumulation Index (Igeo). According to this technique, metal concentrations were normalized to metal concentrations of average crust value. In this study, iron has also been used as a conservative tracer to differentiate natural from anthropogenic components. The metal enrichment factor is defined as follows.

$$EF = \frac{\dfrac{M\ sample}{Fe\ sample}}{\dfrac{M\ average\ shale}{Fe\ average\ shale}}$$

According to Chen *et al.,* (2007), EF < 1indicates no enrichments, Ef < 3 is minor enrichment, EF= 3 – 5 is moderate enrichment, EF = 5 – 10 is moderately severe enrichment, EF = 10 - 25 is severe enrichment, EF = 25 - 50 is very severe enrichment and EF > 50 is extremely severe enrichment. Based on this index the study area manifested minor enrichment with respect to metals such as Cu, Pb, Cd, Cr and the environment is considered as safe in relation to metals such as As, Mn.

**Table 4 : Correlation co- efficient of coastal water**
**Note: Total value at 4% level of significance = 0.22**

The study also quantitatively assessed the degree of pollution by applying the geo accumulation index as proposed by Muller, 1979.

| | pH | Salinity | DO | Total nitrogen | Total phosphorous | Fe | Mn | Cu | Zn | Pb | Cd | Cr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **pH** | 1 | 0.16 | 0.33 | 0.84 | 0.30 | 0.000 | 0.49 | 0.22 | 0.18 | -0.31 | 0.14 | -0.12 |
| **Salinity** | | 1 | 0.38 | 0.38 | -0.04 | -0.03 | 0.58 | 0.18 | 0.46 | -0.28 | 0.53 | 0.43 |
| **DO** | | | 1 | 0.12 | 0.26 | 0.42 | 0.38 | 0.02 | 0.21 | 0.16 | 0.55 | -0.19 |
| **Total nitrogen** | | | | 1 | -0.23 | -0.42 | -0.26 | 0.32 | 0.06 | -0.17 | 0.09 | 0.14 |
| **Total phosphorous** | | | | | 1 | 0.09 | 0.27 | -0.17 | -0.03 | 0.02 | 0.19 | -0.35 |
| **Fe** | | | | | | 1 | 0.67 | -0.09 | -0.10 | 0.01 | 0.23 | 0.03 |
| **Mn** | | | | | | | 1 | 0.02 | 0.28 | -0.47 | 0.67 | 0.17 |
| **Cu** | | | | | | | | 1 | 0.09 | 0.10 | 0.06 | 0.08 |
| **Zn** | | | | | | | | | 1 | -0.10 | 0.14 | 0.13 |
| **Pb** | | | | | | | | | | 1 | -0.09 | -0.26 |
| **Cd** | | | | | | | | | | | 1 | 0.22 |
| **Cr** | | | | | | | | | | | | 1 |

$$\text{Igeo} = \log_2 \frac{\text{Cn}}{1.5\ \text{Bn}}$$

Where Cn is the concentration of the metal observed in the study area and Bn is the concentration of metal in uncontaminated sediments. The classifications of waters depending on the Igeo values are as follows. Igeo ▪ 5 = extremely contaminated, 4 – 5 = strongly to extremely contaminated, 3 – 4 = strongly contaminated, 2 – 3 = moderately to strongly contaminated, 1 -2 = moderately contaminated, 0 – 1 = uncontaminated to moderately contaminated and ▪ 0 = uncontaminated. The calculated Igeo values of the study area are presented in Table 3.

**Table 3 Geo accumulation Index (Igeo) in the study area**

| Study area | Fe | Mn | Cu | Zn | Pb | Cd | Cr | As |
|---|---|---|---|---|---|---|---|---|
| **Station I** | 0.158 | 0.192 | 1.027 | 0.002 | 1.079 | 0.067 | 0.017 | BDL |
| **Station II** | 0.201 | 0.284 | 0.096 | 0.031 | 0.012 | 1.054 | 1.052 | BDL |
| **Station III** | 0.168 | 0.270 | 0.063 | 0.035 | 0.038 | 1.109 | 1.093 | BDL |
| **Station IV** | 0.108 | 0.018 | 1.055 | 0.03 | 1.161 | 1.014 | 1.014 | BDL |
| **Station V** | 0.254 | 0.189 | 1.036 | 0.026 | 0.043 | 1.194 | 1.149 | BDL |

According to Muller's classification the heavy metals like Zn, Mn, As of the study belong into uncontaminated to moderately contaminated category, and Cu, Pb, Cd, and Cr are in moderately contaminated category. Broadly, the results of EF and Igeo strongly suggest that the study area is moderately polluted with heavy metals such as Cu, Pb, Cd and Cr.

## CONCLUSION

This study provides information on some physic – chemical parameters with reference to heavy metal distribution from five different stations along Thoothukudi coast. The nutrient parameters such as nitrogen, phosphorous, calcium and magnesium were sustancially high compared to permissible limit in coastal water as stated by WHO. The low concentration of dissolved oxygen at specific location reflects the association of of thick mangrove vegetation that enhanced more biological activities and there by depletion of dissolved oxygen. The influences of anthropogenic metal pollutions were determined using EF and Igeo. These indices suggest that the study area is moderately polluted with heavy metals such as Cu, Pb, Cd and Cr. However, the result also indicate that the metal concentration level have not exceeded the maximum polluted level. As such, the study has shed a light that this ecosystem is already moderately polluted due to accumulation of nutrients and heavy metals such as Cu, Pb, Cd and Cr. So this situation calls for regular monitoring and implement the strict industrial regulation act to avoid further metal accumulation in this coastal zone.

## ACKNOWLEDGEMENTS

The authors are grateful to **UGC** for providing financial assistance under which the project [**F.No: 40.336/2011(SR)]** was undertaken. We also express our sincere thanks to the principal, **St. Mary's College (Autonomous), Thoothukudi** for the facilities provided to pursue the research project.

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