

# Heavy-Metal Horizontal Distribution in Surface Sediments from Kurusadai Island, Rameswaram, Gulf of Mannar. Tamil Nadu India.

S.Munusamy<sup>1</sup>, Inigovalan<sup>2</sup>, S.Maniyarasan<sup>3</sup>, L.Vijayalakshmi<sup>4</sup>, A. Stephen<sup>2\*</sup>,  
S.G.D. Sridhar<sup>3\*</sup> and V.Narayanan<sup>1\*</sup>

<sup>1</sup>Department of Inorganic Chemistry, Guindy Campus, University of Madras, Chennai – 600025, India

<sup>2</sup>Department of Nuclear Physics, Guindy Campus, University of Madras, Chennai – 600025, India

<sup>3</sup>Department of Applied Geology<sup>3</sup> University of Madras, Guindy campus, Chennai- 600 025, India

<sup>4</sup>TMG College of Arts and Science<sup>4</sup>, Manimangalam, Chennai-601301, India

Corresponding author – vnnara@yahoo.co.in

**Abstract-** 20 surface sample were collected in the summer season very near to the Mangroves area in the Kurusadai Island, Gulf of Mannar, Rameshwaram Tamil nadu. Horizontal distribution of heavy metals of Fe, Mn, Cr, Cu, Ni, Co, Pd and Cd were studied after a spatially intensive sampling campaign. Fe, Mn, Cr, Cu, Ni, Co, Pd, and Cd were determined by the Atomic Absorption Spectroscopy analysis. The presence of iron is determined by Cyclic Voltammetry.

**Keywords-** Heavy metal, Sediment; Mangroves, Kurusadai Island-Gulf of Mannar.

## I. INTRODUCTION

The solid or soil sample from Kurusadai Island contain many risk toxic or heavy elements in the various chemical (Fe, Cr, Co, Mn, Ni, Cu, Cd and Pd) forms. The chemical properties of these soil samples depends on the waves of sea at Kurusadai Island for variation season environments (summer). The Mangrove Kurusadai Island – Gulf Mannar – Rameshwaram. Found along the coastal zone act as a barrier against cyclones, protect coastal erosion and provide good nursery ground for a number of commercially important aquatic organisms. The Mangroves ecosystems are diverse communities growing in the inter-tidal zones of tropical to subtropical coastal sea [1]. The sediments in such area have large capacity to retain heavy metals from tidal waters, fresh waters and storm water runoff and they often act as sink for heavy metals [2]. Mangrove sediments are anaerobic and reduced, rich in sulphide and organic matters content, favouring the retention of water borne heavy metals [3]. Down core variation in sediment cores reflect the geochemical history of a given region, including any anthropogenic impact [4]. The sediments in mangroves are water logged and anoxic due to good supply of both sulphide ions and decomposing organic matter, iron sulphide are enriched within the sediments are enriched within the sediments within the sediments [5]. Metals other than iron can also form insoluble sulphide or can substitute some of the iron in them. Enrichment of metals in bottom sediments represented a critical measure of health for any mangrove ecosystem. Previous studies in Kurusadai Island – Gulf of Mannar mangroves water and sediments were made by R. Ramesh [6]. Studies in Kurusadai Island- Gulf of Mannar – Rameshwaram have been related to mangroves sediments, managements and nature mangrove species of degradation [7]. But little is known about how mangroves or the in fauna in mangrove ecosystems, affect the distribution of heavy metal. Hence as part of a larger investigation the present study focuses on present initial base data on the line data on the level of heavy metal and whether current management measured by AAS, cyclic voltammetry (CV). Heavy metal pollution has become a serious threat to mangroves and ecological systems. Thus different sensitive methods have been developed to the determination of heavy metals. Hence, the electrochemical method is one of the most favourable techniques for the determination of environmental pollutants because of its high sensitivity and easy operation. Among different electrochemical methods, cyclic voltammetry has been proved to be a simple and effective method for the determination of heavy metal ions. The present study deals with the estimation of heavy elements and toxic elements deposited on sediment or sample (soil) in Mangroves ecosystem by AAS, cyclic voltammetry at Kurusadai island- Gulf of Mannar- Rameshwaram.

## II. EXPERIMENTAL

### A. STUDY AREA

The Government of India has established 18 Biosphere reserves of India. Nine of these biospheres reserves are a part of the world network of Biospheres reserves, based on the UNESCO and Biospheres. In these case includes the Gulf of Mannar Biospheres Reserve that covers an area of 4,054 square miles (10,500 sq km) on the south east coastal of India in the Gulf of Mannar-Kurusadai Islands- Tamil Nadu. Mandapam area

Islands- Kurusadai Island, 65.80 ha 9.24690oN 79.20945 oE near to Pullivasal Islands. These mangrove forests belong to one of India's most extended mangrove area. The dominant species in the Kurusadai Island - Cylindrica, Cerioplastagal, Aegicerias, Corniculatum- mangroves. The present study focused on the transition zone and various locations of the study area (20 sediment samples) with GPRS (value, East, North), the formation of heavy metals deposited soil in these mangroves regions.

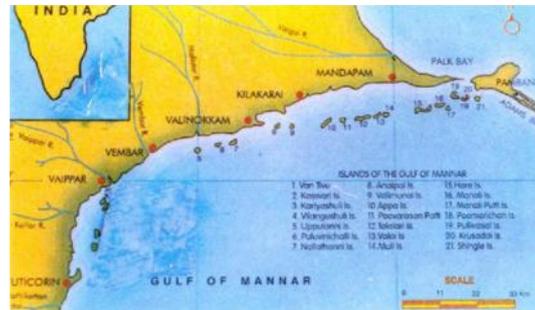


Fig.1 Location Map Gulf of Mannar Island of the study Area kurusadai Island

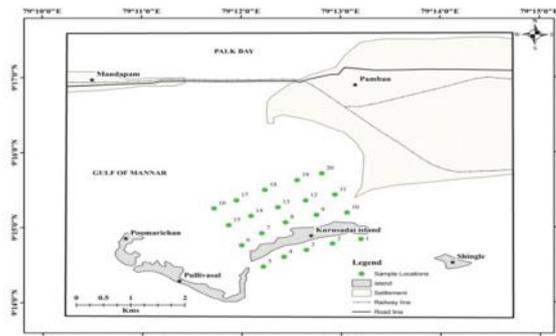


Fig.2 Location Map of the study Area kurusadai Island

## B. METHODS AND ANALYSIS

Bottom sediments samples were collected from 20 stations, at depths ranging from 1m to 5 m, during summer season (May 2013). The sample collection was made in five transects around and off Kurusadai Island with the help of the motor launch. Petersen grab sampler was used for collecting bottom sediment samples. Prior to the analyses, the sample was air dried, oven dried at 50°C and powdered by using agate mortar and heavy elements (Fe, Mn, Cr, Cu, Ni, Co, Pb and Cd) were determined by the trace element analysis. The solid was digested with a mixture of hydrofluoric and Perchloric acids. For a 1 gram of powdered sediments sample following the procedure of Tessier et al (1979) [8]. Heavy Trace element concentration was determined by Atomic Absorption Spectrophotometry (AAS). For heavy metal analysis a known quantity of sediment was digested with an acid mixture of HClO<sub>4</sub> and HF and the final residue was leached with HCl and made up to the required quantity (Tessier et al.1979). Heavy metals concentration (Fe, Mn, Cr, Cu, Co, Pb and Cd) were measured using atomic absorption spectrophotometer (perkin-Elmer AA700) equipped with a deuterium background corrector. The flame was employed except in the instance of Cd, which required the use of a graphite furnace because of its much lower concentration. Suitable internal chemical standards (Merck chemical, Germany) were used to calibrate the instrument. Sample preparation the soil or sample was estimated gravimetrically by digesting 1 g of powdered sample with aqua regia (nitric acid; HCl 1:3 ratio) for 2 h filtering the supernatant and precipitating it as barium sulphate using 5% solution of barium chloride. For acid leachable trace metals plastic bottles of 100 ml capacity were used for the extraction of acid leachable metals in 1 g of raw sediment sample at each interval. The bottles were placed in a mechanical shaker for 24 h after addition of 100ml of 0.5M HCl and the final solution was filtered through Whatman no 40 filters. The filtered sample was measured in AAS equipped with deuterium background correction for analysis of acid leachable heavy metals (Fe, Mn, Cr, Cu, Co, Pb and Cd). Cyclic voltammetry was used to measure the potential with a three electrode system. For Cyclic voltammetry measurements, to determine the potential, 10 ml of the digested sample and supporting electrolyte 0.1M KCl (50ml) were employed.

A. RESULTS AND DISCUSSION

Total Heavy metals the individual result obtained for each metal is shown in Table-1. Table 1 shows descriptive data contents of the metals in the soil and also contains of the metals in Earth Crust, High levels of some elements are observed in the mangroves regions[ 9-10].

S.No	Fe (ppm)	Mn(ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Co (ppm)	Pb (ppm)	Cd (ppm)
1	3372	166	147.7	6.7	28.5	18.4	39.9	9.1
2	2666	114	244	14.3	11.6	38.7	18.2	7.3
3	1889	125	107.4	13.7	52.8	32.2	32.9	2.5
4	12210	264	249.5	19.9	88.3	30.5	20.3	9.4
5	16010	350	286.5	16.5	96.8	45.7	18.5	15.6
6	3507	167	111.2	5.9	45.2	52.3	37	5.3
7	3282	100	163	7	22.7	87.9	48.2	4.6
8	3282	178	112.6	15.6	2.2	89	64.2	6.6
9	2825	130	188.1	2.9	64	48.3	19.3	4.7
10	2002	133	290.3	0.8	48.7	26.3	82.7	3.7
11	2687	194	211.4	7.3	57.8	27.6	72.1	5.1
12	7873	186	184	7.2	68.3	25.1	90.8	3.1
13	16210	292	298	7.1	37.9	30.2	42.9	0.1
14	16210	194	162.3	5.4	56	25.6	53.3	6
15	3750	134	396.8	3.6	48.2	54.4	49	3.7
16	6332	104	244.8	6.3	23.1	68.4	49	8.5
17	16260	307	346.3	5.3	30.4	28.5	17.4	1.5
18	15890	391	348.3	3.8	36	24.8	41.1	6.7
19	17420	286	189.2	6.4	26.4	29.5	99.6	9.4
20	10640	118	277.9	13.4	34.7	26.3	9.9	3.2
Max	17420	391	396.8	19.9	96.8	89	99.6	15.6
Min	1889	100	107.4	0.8	2.2	18.4	9.9	0.1
Average	8654.1	205.9	236.0	9.0	46.5	42.8	47.9	6.3

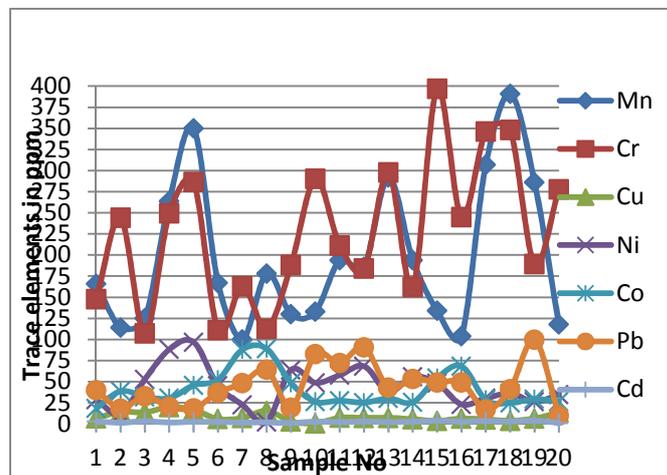


Fig.3 The AAS analysis for heavy elements and heavy metals Mn, Cr, Cu, Ni, Co, Pb and Cd .

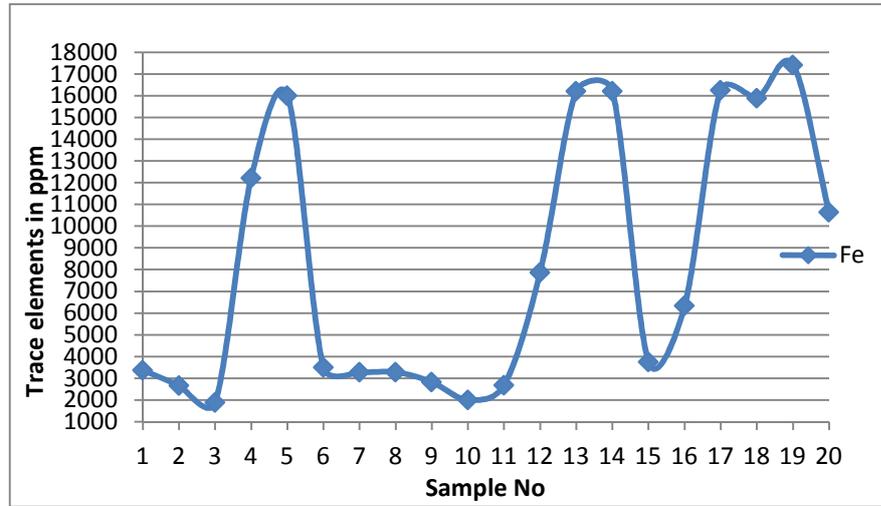


Fig.4 Estimation of Fe by AAS

#### Manganese (Mn)

The amount of manganese present in the samples 1-20 are 166, 114, 125, 264, 350, 167, 100, 178, 130, 133, 194, 186, 292, 164, 134, 104, 307, 391, 286, 118 ppm respectively, in the summer season at kurasadai Island. The highest concentration of manganese, 391 ppm, was found in the location 18. Fig-3 shows the concentration profile of all the heavy metals at different locations. The concentration of manganese was in the range of 100-400 ppm and the average concentration is ~205.9 ppm.

#### Chromium (Cr)

The amount of chromium present in the samples 1-20 are 147.7, 244, 107.4, 249.5, 286.5, 111.2, 163, 112.6, 118.1, 290.3, 211.4, 184, 298, 162.3, 396.8, 244.8, 346.3, 348.3, 189.2, 277.9 ppm respectively, in the summer season at kurasadai Island. The highest concentration of chromium, 396 ppm, was found in the location 15. The concentration of chromium was in the range of 100-400 ppm and the average concentration is ~236ppm.

#### Cobalt (Co)

The amount of cobalt present in the samples 1-20 are 18.4, 38.7, 32.2, 30.5, 45.7, 52.3, 87.9, 89.0, 48.3, 26.3, 27.6, 25.1, 30.2, 25.6, 54.4, 68.4, 28.5, 24.8, 29.5, 26.3 ppm respectively, in the summer season at kurasadai Island. The highest concentration of cobalt, 89 ppm, was found in the location 8. The concentration of cobalt was in the range of 18-89 ppm and the average concentration is ~42.8ppm.

#### Nickel (Ni)

The amount of nickel present in the samples 1-20 are 28.5, 11.6, 52.6, 88.3, 96.8, 45.2, 22.7, 2.2, 64, 48.7, 57.8, 68.3, 37.9, 56, 48.2, 23.1, 30.4, 36, 26.4, 34.7 ppm respectively, in the summer season at kurasadai Island. The highest concentration of nickel, 96.8 ppm, was found in the location 5. The concentration of nickel was in the range of 11-97ppm and the average concentration is ~46.5ppm.

#### Copper (Cu)

The amount of copper present in the samples 1-20 are 6.7, 14.3, 13.7, 19.9, 16.5, 5.9, 7, 15.6, 2.9, 0.8, 7.3, 7.2, 7.1, 5.4, 3.6, 6.3, 5.3, 3.8, 6.4, 13.4 ppm respectively, in the summer season at kurasadai Island. The highest concentration of copper, 19.9 ppm, was found in the location 4. The concentration of copper was in the range of 1-20ppm and the average concentration is ~9ppm.

#### Cadmium (cd)

The amount of cadmium present in the samples 1-20 are 9.1, 7.3, 2.5, 9.4, 15.6, 5.3, 4.6, 6.6, 4.7, 3.7, 5.1, 3.1, 0.1, 6, 3.7, 5.1, 3.1, 0.1, 6, 3.7, 8.5, 1.5, 6.7, 9.4, 3.2ppm respectively, in the summer season at kurasadai Island. The highest concentration of cadmium, 15.6 ppm, was found in the location 5. The concentration of cadmium was in the range of 0.1-20ppm and the average concentration is ~6.3ppm.

#### Lead (Pb)

The amount of lead present in the samples 1-20 are 39.9, 18.2, 32.9, 20.3, 18.5, 37, 48.2, 64.2, 19.3, 82.7, 72.1, 90.8, 42.9, 53.3, 49, 49, 17.4, 41.1, 99.6, 9.9, ppm respectively, in the summer season at kurasadai Island.

The highest concentration of lead 99.6 ppm was found in the location 19. The concentration of lead was in the range of 18.2-99.6 ppm and the average concentration is ~47.9 ppm.

#### Ferric (Fe)

The amount of Ferric present in the samples 1-20 are 3372, 2666, 1889, 12210, 16010, 3507, 3282, 2825, 2002, 2687, 7873, 16210, 16210, 3750, 6332, 16260, 15890, 17420 and 10640 ppm respectively, in the summer season at kurusadai Island. The highest concentration of iron, 17420 ppm, was found in the location 19. Fig-4 shows the concentration profile of iron at different locations. The concentration of iron was in the range of 2666-17420 ppm and the average concentration is ~8654.1 ppm.

#### Cyclic Voltammetry to determination of Heavy metal.

The electrochemical response for the determination of the ferric ions is shown in Fig 5. The potential window used is +1.2 to -0.8 V vs SCE. The scan rate is 50 and 75 mV/s. The observed voltammograms are well defined. The cyclic voltammograms of ferric ions shows one reduction peak in the cathodic direction at -0.1 v vs SCE. The anodic response observed is very poor. The electron transfer process in the given condition is observed to be quasi-reversible. The quantification and speciation is under progress.

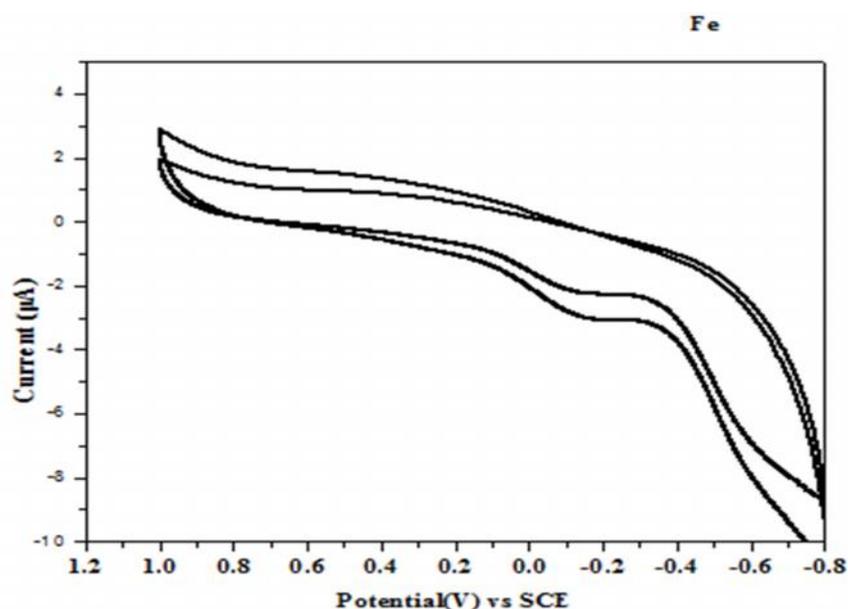


Fig-5 Cyclic voltammetric determination of Fe in 0.1M KCl

#### IV. CONCLUSION

The soil present in the Kurusadai island –Rameshwaram gulf of Mannar. These are all the location present in the concentration of heavy metal was determine by AAS. Its large amount of present in the ironS at summer season. The cyclic voltammetry was determine iron for -0.1 vs SCE at 0.1M KCl. The concentration order of the heavy metals at Kurusadai Island for Fe> Mn> Cr> Pd> Ni > Cu> Co> Cd.

#### ACKNOWLEDGEMENT

The authors gratefully thank full UGC-CPEPA financial supports university of madras and National Center for Nanoscience for extending the TEM image facility.

#### REFERENCES

[1]-Dang, Z. Liu, C. Haigh, M.J, “Mobility of heavy metals associated with the natural weathering of coal mine spoils”, Environ Pollut, No.118,pp. 419-426, 2002

- [2]- Sulochannan, S. Krishnakumar, P.K.. Prema, D, Kaladdharan, P. Valsala. K.K, “Trace metal contamination of the marine environment in palk bay and Gulf”, J. Mar. Biol. Ass. India, No.49, pp. 12-18, 2007
- [3]Amundsun ,CE. Hanssen, JE. Ssemb, A. Steinnes, E. “Long range transport of trace elements to southern Norway”, Atmos Environ, No.26A, pp. 1309-1324,1992
- [4- ]Fent. K., “Ecotoxicological effects at contaminated sites”, Toxicology , No.205,pp. 223-240, 2004
- [5]Sutherland ,RA. “Bed sediment associated trace metal in an urban stream”, Environ Geol, No.39,pp.611-627. 2000.
- [6]Ramesh, R, Purvaja.R. Ramesh.S. Jame.R.A. “Historical pollution trends in coastal environments of india Environ monit and Assess” ,No.79, pp 151-171, 2001
- [7]Dajkumar .S, Chandrasekar. S, Victor .G.) “Distribution of arsenic and mercury in subtropical coastal beachrock , Gulf of mannar india”, J.Earth Syst .Sci.No.119, pp. 129-135, 2010
- [8] Tessier. A, Campbell. P.G.C, Bisson .M, “Sequential extraction procedure for the speciation of particulate trace metals” Anal.Chem.No. 51,pp. 844-851,1979
- [9-]Ravichandran.R, and Shanthy., “Heavy metal distribution in the coastal sediment of Chennai coast”, The IIOAB journal, No. 3, pp. 12-18, 2012
- [10].Balakrishnan .A, Ramu .A, “Assessment of Heavy metal Distribution in Groundwater in and around Gulf of mannar seashore area using GIS Technique”, Res .J. Chem.Sci .No. 4 pp. 9-16, 2014