

International Journal of Green and Herbal Chemistry

An International Peer Review E-3 Journal of Sciences

Available online at www.ijghc.com

Green Chemistry



Research Article

CODEN (USA): IJGHAY

Iron Fractionation in the Sediments of Kerala Coast

Manju P. Nair and Sujatha C. H*.

Department of Chemical Oceanography, School of Marine Sciences,
Cochin University of Science and Technology, Kochi-16, Kerala, India

Received: 20 May 2013; **Revised:** 12 June 2013; **Accepted:** 24 June 2013

Abstract: This study gives the first report on the spatial changes of different iron fractions in the sediments of Kerala Coast. Sediments were collected from four prominent areas of Kerala Coast. A sequential extraction procedure was applied to identify the forms of Fe. This scheme extracts different chemical forms of metals in five sequential steps, namely- exchangeable (EXC), carbonate –bound (CA), Fe-Mn oxide– bound (FMO), organic matter–bound (OM), and residual (RES) fractions of metals. Most content of Fe was found in residual fraction in all designated sites. Comparatively Cochin revealed to be more viable for secondary pollution due to high content of EXC and CA. FMO fraction recorded in the sampling site was rich at Cochin and poor at Trivandrum. This exposes the greater scavenging ability of hydrous iron oxide from the water column. OM fractions are the second largest key scavenger for the heavy metals was high at Cochin and low at Trivandrum. Principal component analysis and correlation analysis were done to understand the interrelationship between the parameters. Principal component analysis showed two components govern the distribution of Fe fraction in the study area. Correlation analysis revealed except residual fraction all the other fraction were directly related to TOC, mud content, total phosphorus, total nitrogen and total hydrogen.

Keywords: Fractionation, Iron, Sediment, Kerala Coast, Cochin.

INTRODUCTION

Heavy metal pollution of coastal environments has been reported throughout the region of the world. Release of heavy metals to the marine environment is increasing as industrial development continues in areas where monitoring and enforcement of environmental regulations is difficult due to a lack of laboratory facilities and enforcement mechanisms. Heavy metals, in contrast with most pollutants, are not biodegradable and undergo a global ecobiological cycle in which natural waters are the main pathways¹. Once heavy metals are discharged into coastal waters, they rapidly become associated with particulates and are incorporated in bottom sediments.

The accumulation of metals from the overlying water then to sediment is dependent on a number of external environmental factors such as pH, Eh, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for adsorption caused by the variation in grain size distribution². Various remobilization mechanisms of bed sediments including physical resuspension³, geochemical remobilization from organic matter, dissolution of hydrous oxides of iron and manganese biomethylation^{4,5}, and other biological processes can cause release of these elements to the water column. Additionally, these categories have different behaviors with respect to remobilization under changing environmental conditions⁶. Studies of the trace metal contamination of sediments often rely on the analysis of total metal content; however, information on total concentration is not sufficient for understanding the environmental behaviour of trace metals, as only a fraction of the total metal is available for biological or diagenetic processes. Assessment of heavy metal contamination of the coastal environment based solely on total metal content also possesses difficult problems to regulators; how to distinguish between background lithogenic trace metal that is relatively unavailable to marine biota and the accessible labile trace metal.

The aqueous chemistry of iron and its role in controlling the release and availability of sediment-associated contaminants is of major concern. Iron can exist in aquatic systems (natural waters and their sediments) in several oxidation states: metallic iron (iron metal), ferrous iron (Fe II), and ferric iron (Fe III). The occurrence of elevated levels of trace metals especially in the sediments can be a good indicator of man-induced pollution and high levels of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering². The objective of the present study was to estimate the amount and variation pattern of Fe in the sediments of Kerala Coast using a sequential extraction procedure.

MATERIALS AND METHODS

Sediment samples were collected in cruise no. 267 in FORV Sagar Sampada on May to June 2009 from Tuticorin to Cochin. Sediments were collected from four identified stations [Cape (1), Trivandrum (2), Kollam (2) and Cochin (2)] of Kerala coast, India. The description of location sites are given in **Table-1**. Surficial sediment samples were collected using a Van veen grab, it was sealed, transported to the lab and stored in deep freezer. Sediments were air dried, finely powdered and used for chemical analysis.

For metal analysis, 0.5g samples were treated with 5:1 mixture of concentrated⁷ HNO₃ and HClO₄. Iron fractionation of sediment portions was performed in replicates by sequential extraction with chelating compounds⁸. Textural characteristics (sand, silt, and clay) were determined using pipette analysis by Lewis⁹. TOC was determined by total organic carbon (TOC) analyzer (Elementar Vario Select, Germany). Elemental compositions - CHN of the samples were determined by using Vario EL 111 CHN Analyser. Total phosphorus was estimated by using the standard method. All the samples,

chemical solutions, and standards were prepared using ultrapure water. Statistical analysis was performed by Statistical Package for Social Sciences (SPSS Version: 11; SPSS Inc. 1995).

Table-1: Location of sampling sites

Transect	Depth(m)	Location
Cape1 (P ₁)	50	0747.64 ⁰ N,7730.177 ⁰ E
Trivandrum1(P ₂)	30	0830.048 ⁰ N,7650.874 ⁰ E
Trivandrum 2 (P ₃)	100	0828.117 ⁰ N,7629.712 ⁰ E
Kollam1 (P ₄)	50	099.010 ⁰ N,0756.851 ⁰ E
Kollam2 (P ₅)	200	0900.084 ⁰ N,07623.524 ⁰ E
Cochin1 (P ₆)	<200	957.77 ⁰ N,7616.919 ⁰ E
Cochin2 (P ₇)	<100	959.213 ⁰ N,7616.084 ⁰ E

RESULTS AND DISCUSSION

Textural characteristics, pH, Carbon, Nitrogen, Hydrogen, Phosphorus and TOC are given in **Table 2**.

Table- 2: Variation of pH, Carbon, Nitrogen, Hydrogen, Phosphorus, Texture and TOC

Sample code	pH	P(%)	N (%)	C (%)	H (%)	Sand (%)	Clay (%)	Silt (%)	TOC (%)
Cape- P1	7.1	0.96	0.01	4.38	0.34	87.72	6.85	5.43	0.47
Trivandrum- P2	8.2	0.65	0.05	6.5	0.26	94.91	2.34	2.75	0.42
Trivandrum - P3	8.3	1.70	0.01	2.31	0.07	99.05	0.203	0.75	1.3
Kollam- P4	8.5	2.60	0.07	9.29	0.42	97.87	1.998	0.13	1.61
Kollam- P5	8.6	2.50	0.07	9.03	0.53	97.97	1.66	0.37	0.52
Cochin- P6	8.8	3.76	0.23	3.83	2	11.9	31.88	56.22	5.98
Cochin- P7	8.9	5.24	0.2	5.76	2.09	24.35	33.17	42.75	1.51

Textural characteristics revealed high sand content was found in Cape, Trivandrum and Kollam (> 87%). Both clay (>30%) and silt (>40%) content were greater in Cochin. Among the eleven stations the percentage of sand fraction was highest in Trivandrum (99.3%) and lowest in Cochin (11.9%). Clay was highest in Cochin (33.171%) and lowest in Trivandrum (0.203%). Silt was maximum in Cochin (42.748%) and minimum in Kollam (0.132%). Grain size is one of the basic attributes of sediments and its distribution is essential to delineate the sedimentary environments. PH in the sediment varied between 7.1 to 8.9, revealed the alkaline nature of the sediment. TOC in the

sediment varied between 0.47 to 5.98%. TOC value < 5% indicate the unpolluted sites. In present study except one site in Cochin (P6) all others revealed to be having less polluted. Elemental distribution showed the order as $C > P > H > N$ in all the stations.

Total metal content distribution in the study area is given in **Fig.1**. The variation showed as $Fe > Mn > Zn > Cu > Pb > Co > Cd$ at Cape, Trivandrum and Kollam but at Cochin it gives the trend as $Fe > Zn > Mn > Cu > Pb > Co > Cd$. High concentration of all the metals in the present study reported at Cochin due to the heavy industrial, domestic and agricultural discharges. These sediments contains greater mud content also help them to adsorb these metals tightly. Metal distribution showed greater content Fe. So fractionation of this particular metal carried out.

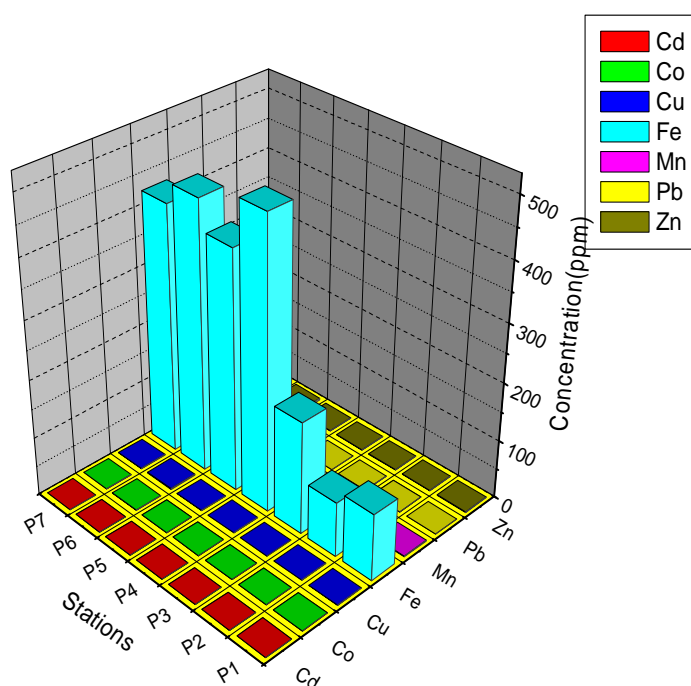


Fig.1: Distribution of total metal in the study area

Iron is associated in various geochemical fractions. In general spatial distribution of iron fractions in the coastal sediments of Kerala (**Fig.2**) were in the following order P1: RES > FMO > OM > EXC > CA ; P2: RES > OM > FMO > CA > EXC; P3: RES > OM > EXC > CA > FMO; P4: RES > FMO > OM > CA > EXC; P5: RES > OM > FMO > EXC > CA ; P6: RES > OM > FMO > EXC > CA ; P7: RES > OM > FMO > CA > EXC.

Spatial variation of Fe fractions is given in **Table 3**. EXC fraction of heavy metals can be easily released back to the water column, which may cause secondary pollution and subsequent health risk to the exposed pollution. Most mobile fraction among the five fraction extracted in the sediment found to be EXC followed by CA creates secondary pollution. Comparatively Cochin is viable for secondary pollution due to high content of EXC and CA. FMO fraction recorded in the sampling site was rich at Cochin and poor at Trivandrum.

This reveals the greater scavenging ability of hydrous iron oxide from the water column. OM fractions are the second largest key scavenger for heavy metals. This fraction was high at Cochin and low at Trivandrum. FMO and OM fractions also support the granulometric adsorption in the sediment.

All the studied fraction abundance of metal was found in the RES. Exchangeable and carbonate bound metals are weakly bound to sediment components and may equilibrate easily with the aqueous phase. In the present study, relatively low concentrations were found in these fractions. These suggest that these metal concentrations would be solubilised and may become available following a slight increase of the pH.

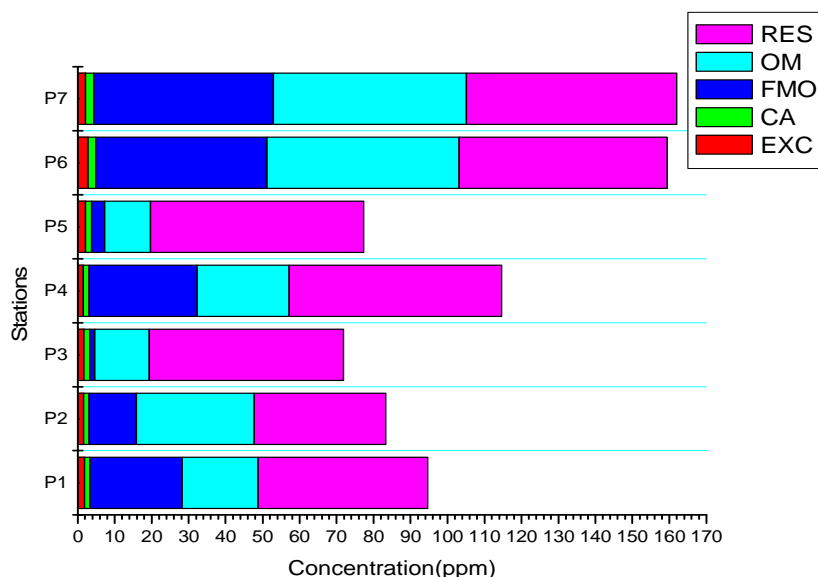


Fig.2: Spatial distribution of iron fractions in the Kerala Coast

Table-3: Spatial variation of Fe fractions

Fe fractions	Spatial Distribution
EXC	Cochin > Kollam > Trivandrum > Cape
CA	Cochin > Kollam > Trivandrum > Cape
FMO	Cochin > Kollam > Cape > Trivandrum
OM	Cochin > Trivandrum > Kollam > Cape
RES	Kollam > Cochin > Trivandrum > Cape

Principal component analysis and correlation analysis were done to understand the interrelationship between the parameters. Principal component analysis showed two components (**Fig.3**) govern the distribution of Fe fraction in the study area. Correlation analysis revealed except residual fraction the other fraction directly related to TOC, mud content, total phosphorus, total nitrogen and total hydrogen. Sand fraction is inversely related to different extract of Fe. Previously organochlorine pesticide residues, sediment organic matter and nutrients have been reported in this study area¹⁰⁻¹² also supported the granulometric dependence.

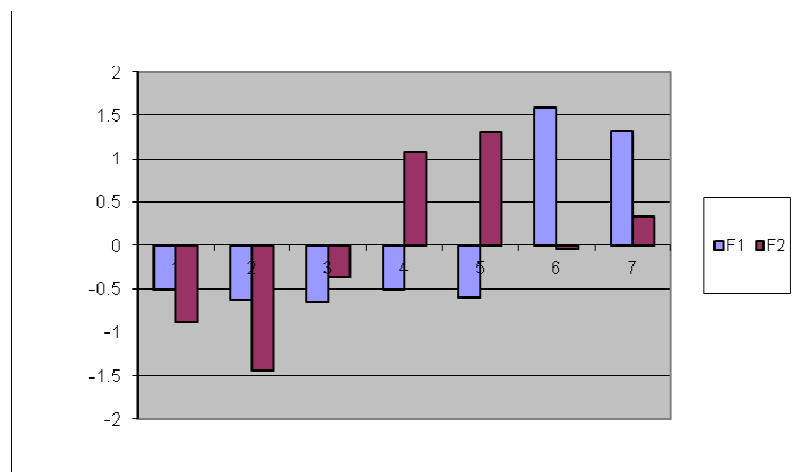


Fig.3: Factors controlling Fe fractions in the sediments of Kerala Coast

CONCLUSION

The study shows that the total metal concentrations generally decrease in the order Fe > Mn > Zn > Cu > Pb > Co > Cd at Cape, Trivandrum and Kollam but at Cochin it gives the trend as Fe > Zn > Mn > Cu > Pb > Co > Cd. Most content of Fe was found in the residual fraction in all the designated sites. Concentrations of Fe in clayey silt sediments are all clearly higher than that of sand ones. Comparatively Cochin is viable for secondary pollution due to high content of EXC and CA. FMO fraction recorded in the sampling site was rich at Cochin and poor at Trivandrum. This reveals the greater scavenging ability of hydrous iron oxide from the water column. OM fractions are the second largest key scavenger for the heavy metals. This fraction was high at Cochin and low at Trivandrum. FMO and OM fractions also support the granulometric adsorption in the sediment

ACKNOWLEDGEMENT

We express our sincere gratitude to Director, CMLRE for providing cruise berth in the cruise no. 267. We thank the crew of the FORV Sagar Sampada. Sincere thanks to MoES for providing financial support. We gratefully acknowledge the facilities and support provided by the Director, School of Marine Sciences and the Head, Department of Chemical Oceanography, CUSAT.

REFERENCES

1. H. W. Nurnberg . *Anal Chim Acta*, 1984, **164**, 1-21.
2. C. A. Davies, K. Tomlinson & T. Stephenson. *Environ. Technol.* 1991, **12**, 961-972.
3. L. Bengtsson, T. Hellstrom and L. Rakoczi. *Hydrobiologia*, 1990, **129**, 167-181.
4. F. M. D'Itri. The biomythylation and cycling of selected Metals and Metalloids in aquatic sediments. In: Baudo R, Giesy JP, and Mantau H (Eds), *Sediment--chemistry and toxicity of in-place pollutants*. Chelsea, Michigan: Lewis Publishers, 1990. P
5. M. R. Winfrey and J. W. Rudd. *Environ Toxic Chem*, 1990, **9**, 853-869.
6. U. Forstner. Chemical forms and reactivities of metals in sediments. In: Leschber R, Davis RD, and L'Hermite P (Eds), *Chemical methods for assessing bioavailable metals in sludges and soils*. London: Elsevier. 1985, 1-30.

7. D. H. Loring and R. T. T. Rantala, *Earth-science reviews*, 1992, **32**, 235-283.
8. A. Tessier, P. G. C. Campbell and M. Bisson. *Anal Chem*, 1979, **51**: 844-851.
9. D. W. Lewis, Hutchinson Ross Publishing Co; Stroudsburg. Pa **22** 1984.
10. M. P. Nair and C. H. Sujatha, *International Journal of Environmental Sciences*, 2012, **3**(1), 707-719.
11. M. P. Nair and C. H. Sujatha, *International Journal of Environmental Sciences*, 2013, **3**(5), 1562 -1568.
12. M. P. Nair and C. H. Sujatha, *Global Journal of Applied Environmental Sciences* (Accepted) 2013.

***Corresponding Author: Sujatha C. H;** Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi-16, Kerala, India