Study on Sequential Analysis of Trace Elements in the Sediments of Karaikal Coast, East Coast of India

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Abstract

The present work measures the concentration of different solid species of the trace elements Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in the surface sediments of Arasalar river estuary at different stations & seasons (2011-2012). Analysis of sediments for trace element concentration gives history of accumulation of metals in environments. Estuarine and marine sediments are very important accumulation site of metals in the coastal areas; therefore analyses of these metals are important to assess the degree of pollution in the marine environment. The trace elements were extracted from sediment samples into five chemical phases (I-exchangeable, phase II-bound to carbonate, phase III-bound to Fe-Mn oxides, phase IV-bound to organic matter and phase V-residual). The results obtained from sequential extraction procedure showed that among all the five phases, residual phases (phase-V) was found to have much more metal concentrations for all the eight metals compared to other phases irrespective of seasons. The concentration of the metals at various phases are as follows, Fe – Phase V> III> IV> II> I, Mn – Phase V> III> IV> II> I, Cu – Phase V> III> IV> II> I, Zn - Phase V> III> IV> II> I, Pb- Phase IV> V> III> II> I, Cr - Phase V> III> IV> II> I, Co- Phase V> III> IV> II> I, Ni - Phase V> III> IV> II> I. The high proportion of metals in the residual phase generally related to low levels of extractable metals indicates that the sediments of Arasalar river estuary and adjacent beach environments were relatively unpolluted.

Keywords: Sequential extraction, Trace element concentration, metal origin, mode of occurrence

I. INTRODUCTION

Metals introduced into the water column always finds its settlement with sediments. Sediments are acting as a reservoir site for metal accumulation by its varatious characteristics features. Analysis of sediments for heavy metals concentration gives history of accumulation of metals in environments. Estuarine and marine sediments are very important accumulation site of metals in the coastal areas; therefore, analyses of these metals are important to assess the degree of pollution in the marine environment. Sediment can be considered as a heterogeneous mixture of dissimilar particles. These particles can be considered in turn as a complex assemblage of different organic and inorganic components (Martin et. al., 1987). Sediments receive potentially toxic elements from both natural and a wide range of anthropogenic sources. Investigating the partitioning of metals to sediment fractions provides more information on metal availability, mobility and source, and allows greater understanding of metal behavior than the study of total sediment metal concentrations alone (Marin et. al., 1997, Usero et. al., 1998, Li and Thornton 2001).

Sequential extractions employ a series of successively aggressive reagents to attack specific fractions of the sediment, releasing metals associated with these fractions into solution (Mossop and Davidson 2003, Tuzen 2003) and providing information on operationally defined metal partitioning. There are a range of sequential extraction methods in the literature, and the one of the most widely used protocols is “Tessier” (Tessier et.al.,1979) procedure. The Tessier extraction was designed to study variations in metal release under changing environmental conditions, but has also been used to investigate contaminant source (e.g. Li et. al., 2007), past water quality (e.g. O’Reilly-Wiese et. al., 1997), metal remobilization (e.g. Spencer et. al., 2003) and metal binding behavior (e.g. Yu et. al., 2001). Information concerning the metal origin, mode of occurrence, biological and phsico-chemical availabilities, mobilization and transport of heavy metals can be obtained from sequential extraction procedure when compared to the single extraction.

The present work measures the concentration of different solid species of the heavy metals Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in the surface sediments of Arasalar river estuary environment with respect to different stations & seasons. The heavy metals were extracted from sediment samples into five chemical phases (I-exchangeable, phase II-bound to carbonate, phase III-bound to Fe-Mn oxides, phase IV-bound to organic matter and phase V-residual). Bulk metal concentrations were also determined. The heavy metal concentrations of different phases are presented in Table. I A and B.
The concentration of phase-wise distribution of heavy metals observed at estuary and beach environments during study period is given below. The distributions of different fractions of eight metals (Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni) are shown in Figure 2. The results obtained from sequential extraction procedure showed that among all the five phases, residual phases (phase-V) was found to have much more metal concentrations for all the eight metals compared to other phases irrespective of seasons. The concentration of the metals at various phases are as follows, Fe – Phase V > III > IV > II > I, Mn – Phase V > III > IV > II > I, Cu – Phase V > III > IV > II > I, Zn – Phase V > III > IV > II > I, Pb – Phase IV > V > III > II > I, Cr – Phase V > III > IV > II > I, Co – Phase V > III > IV > II > I, Ni – Phase V > III > IV > II > I.

The content of residual phase (phase-V) is refractory organic material and primary as well as secondary weathered minerals which are very stable portions of the element constituents (Brannon et al., 1977, Marcovechio and Ferrer, 2005, Debapriya Mukherjee et al., 2009, Engler et al., 1977, Tessier et al., 1979). Thus the metals associated with this phase are expected to be chemically stable and biologically in active.

II. DESCRIPTION OF THE STUDY AREA

The Arasalar estuary is situated at Karaikal (Lat.79° 52’ E Long.10° 55’ N) of Bay of Bengal. The arasalar is a tributary of the river Cauvery, having a total run of 24 km. It enters Karaikal region, a little east of Akalanganni. It forms the natural boundary line separating Niravi Commune from Tirunallar on the north-west and Karaikal on the north-east. The Nattar, branching off from Arasalar at Sakkotai in Thanjavur District, runs a distance of 11.2 km in a south-easterly direction across Nedungadu and Kottucheri Communes before emptying itself into the sea. The Vanijar fed by the Arasalar, takes its course along the northern boundary of Tirunallar Commune. It drops on a south-easterly curve towards Karaikal Commune and merges with the Arasalar, south-east of Karaikal town after covering a distance of about 9 km. The Nular, also fed by the Arasalar, runs a distance of 13.77 km. before it joins Vanijar northeast of Karaikal town. The study area comprises of estuarine and coastal environment. The estuarine environment from the mouth of the river in downstream to fresh water in upstream direction extends about 9 km. The coastal environment comprises of beach and near shore from the mouth of river. Totally 5 samples were collected along the estuary. The samples were represent as 1, 2, 3, 4 and 5 where Station 1 is situated nearby mouth of the estuary (marine zone), station 2 & 3 in a mixed environment (brackish zone) and 4 & 5 in freshwater zone upstream (figure 1).

Fig. 1: Location and sampling map of the study area

III. RESULT AND DISCUSSION

A. Exchangeable (Phase-I)

The exchangeable phase has been widely accepted that the exchangeable metals in sediments is labile, highly toxic and the most bioavailable fraction. The concentration of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in phase-I (exchangeable) of the sediment samples collected from four seasons at five different stations of Arasalar estuary during the first year of the study period (2011-2012), were found to be ranged from 1.026 to 19.253 ppm, 1.02 to 14.035 ppm, 0.112 to 6.452 ppm, 0.086 to 6.154 ppm, 0.078 to 5.102 ppm, 0.095 to 2.555 ppm, 0.052 to 2.072 ppm and 0.011 to 2.921 ppm respectively (Table 1A and B). The details of the
concentration of heavy metals are shown Figure. 2. The minimum concentrations of all the metals were observed during monsoon season, whereas maximum concentrations of all the metals were observed during summer season. The observed order of concentration of metals in this phase is as follows, Fe>Zn>Mn>Cr>Pb>Cu>Ni>Co. The maximum concentration of Fe was observed at station -3 and it was noticed to decrease either side from this station. This similar trend was maintained for other metals like Mn, Zn, Pb, Cu, Cr, Co and Ni during the study period.

**B. Bound to Carbonate (Phase-II)**

The metals bound to carbonate minerals are bio-available for benthic organisms. During the first year of the study period (2011-2012), the season wise concentration of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in bound to carbonate (phase-II) were found to be ranged from 1.221 to 45.465 ppm, 2.114 to 12.861 ppm, 0.045 to 2.969 ppm, 0.046 to 2.124 ppm, 0.453 to 3.381 ppm, 0.065 to 3.856 ppm, 0.021 to 1.988 ppm and 0.357 to 2.898 ppm respectively. The maximum concentrations for all the metals were observed during summer season throughout the study period. The observed order of concentration of metals in this phase is as follows,

Fe>Mn>Zn> Cu >Cr> Ni >Co> Pb

The maximum concentration for all the heavy metals bound to this phase was observed at stations -2, 3 and 4 (estuary). The minimum level of heavy metals were noticed at station -1 and 5 (mouth and freshwater zone). The heavy metals (Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni) in this phase-II are present at all stations in estuary region but the amount is very low.
Fig. 2.2: Phase-II

Fig. 2.3: Phase-III
Fig. 2: Showing the heavy metal concentration in Phase I-V (Estuary 2011-2012)
The metal concentration in the carbonate bound was minimum during monsoon whereas summer and post monsoon recorded maximum level for all the metals studied except Zn and Ni, where higher levels were observed during monsoon in the year 2011-2012. This may be due to this phase associated with the suspended load derived from continental origin. The reduction of the metals in this phase relates to the rapid digenetic changes after deposition under the influence of saline water or by increasing biological activity. A similar result was obtained by Baruah et. al.., (1996) from Jhanji river sediments. A slightly higher values of Mn observed during premonsoon could be due to terrestrial input of rainfall which could carry the material that contained Mn bound to phosphate and deposited in an estuarine region.

C. Bound To Fe-Mn Oxides (Phase-III)
Fe-Mn oxides are one of the most important geochemical phases impacting the mobility and behaviors of heavy metals. The concentration of heavy metals are shown in Table.1 A and B. During the first year of the study period (2011-2012), the season wise concentration of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni bound to Fe-Mn oxides (phase-III) were ranged from 2.453 to 58.562 ppm, 10.238 to 25.981 ppm, 0.452 to 3.856 ppm, 0.335 to 2.854 ppm, 1.145 to 3.856 ppm, 0.452 to 3.856 ppm, 0.021 to 1.852 ppm, 0.357 to 3.658 ppm. The maximum concentration of Zn, Pb, Cu and Co were observed during post monsoon season of first year of the study period. The observed order of concentration of metals in this phase is as follows,

\[ \text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Co} \]

In general, Fe-Mn oxides to scavenge the heavy metals from solution through processes such as adsorption and co-precipitation. The slightly higher concentration of metals in this phase when compared to the phase I and II indicates the mobility of elements with the environmental changes (Papadopoulos et. al., 1997). The proportion of heavy metals bound to Fe-Mn oxides is highly variable and depends on environmental changes as depth of water and redox reactions taking place in the depositional environment. The maximum concentration of heavy metals in the phase III was observed during summer season when compared to the other seasons. The slightly higher concentration of metals in this phase in an estuarine region during low river discharge indicated a change in the point of mixing zone and supports the elevated values during summer and premonsoon periods.

D. Bound To Organic Matter (Phase-IV)
It is well documented the organic matter is a potential site for accumulation of heavy metals besides controlling the mobility and bioavailability of heavy metals. The concentration of heavy metals are shown in Table. 1 A and B. The concentration of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in the first year of the study period (2011-2012), ranged from 6.246 to 24.354 ppm, 1.054 to 4.545 ppm, 0.715 to 7.589 ppm, 0.813 to 4.061 ppm, 0.009 to 0.035 ppm, 0.009 to 0.225 ppm and 0.008 to 0.032 ppm respectively. In the present study the higher level of heavy metals Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni belong to this phase were observed at stations - 2, 3 and 4 (estuary region). Whereas the lower levels were observed at station-1 (mouth) and station-5 (freshwater zone). The metals bound with this phase reflect the status of the sedimentary processes that influence metal behavior and reveal the natural levels as well as those superimposed by external stresses. The nature of organic coatings on sediments is partly determined by the surface mineralogy and bonding mechanism of organic coating to inorganic substrates (Abbrl et. al., 2002).

E. Residual (Phase-V)
Residual phase of metals are generally much least available to aquatic environment. In general, the metals in this phase have strongest association to the crystalline structure of the minerals and which are therefore the most difficult to separate from the sediments (Kersten and Forstner, 1991). This phase contains primary as well as secondary weathered minerals which are very stable portion of the elemental constituents (Brannon et. al. 1976). The metals associated with this phase were expected to be chemically stable and biologically inactive. The concentrations of heavy metals are shown in Table. 1 A and B. The levels of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in this phase V (residual) in estuary ranged from 456.28 to 1895.25 ppm, 5.258 to 28.568 ppm, 2.254 to 32.258 ppm, 0.114 to 3.954 ppm, 12.547 to 38.874 ppm, 1.025 to 9.025 ppm, 1.145 to 5.254 ppm and 0.854 to 5.225 ppm during the first year of the study period (2011-2012). The concentration of eight different metals observed to the overall concentration of each metals to the phase-V, can be rated as follows,

\[ \text{Fe} > \text{Cu} > \text{Mn} > \text{Zn} > \text{Cr} > \text{Co} > \text{Ni} > \text{Pb} \]

In the present investigation, the maximum concentration of metals were observed at stations - 2, 3 and 4 in estuarine region. Whereas minimum concentration of metals were observed at stations - 1 and 5 in mouth and fresh water zone respectively. The metal concentrations in this phase were higher than other phase. The major quantity of Fe is found to be associated with residual phase, probably because this is an element basically of natural origin and it is one of the most common element in the earth’s crust. The present results are in good agreement with the data reported by Usero et. al., (1998) and Yuan et. al., (2004). A higher level of Cu in this phase indicates the chemisorbed nature of clay minerals. Pickering (1995) reported, the clay minerals are the important scavenger for the Cu and Zn. The Pb and Cr associated with this phase indicate metals contain mainly primary and secondary minerals such as aluminosilicate minerals, which may hold the metals within their crystal structure.
The present work measures the concentration of different solid species of the trace elements Fe, Mn, Zn, Pb, Cu, Cr, Co, and Ni in the surface sediments of Arasalar river estuary at different stations & seasons (2011-2012). Analysis of sediments for trace element concentration gives history of accumulation of metals in environments. Estuarine and marine sediments are very important accumulation site of metals in the coastal areas; therefore analyses of these metals are important to assess the degree of pollution in the marine environment. The trace elements were extracted from sediment samples into five chemical phases (I-exchangeable, II-carbonate, III-silicates, IV-bound to organic matter and V-residual). The results obtained from sequential extraction procedure showed that among all the five phases, residual phases (phase-V) was found to have much more metal concentrations for all the eight metals compared to other phases irrespective of seasons. The concentration of the metals at various phases are as follows, Fe – Phase V>III>IV>II>I, Mn – Phase V>III>IV>II>I, Cu – Phase V>III>IV>II>I, Zn – Phase V>III>IV>II>I, Pb – Phase IV>V>III>II>I, Cr – Phase V>III>IV>II>I, Co – Phase V>III>IV>II>I, Ni – Phase V>III>IV>II>I. The estuarine environment indicates that the residual phase is the main accumulative phase of most of the studied metals, more importantly for Fe and Cu as the sediments were comprised of detrital silicates. In the present investigation, even though less percentage of metals were found in fractions 1 to 4 of the sediment samples. They have the potential of being released in the environment if there is any change in environmental conditions such as

### Table 1

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<th>Metals (ppm)</th>
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<th>Phase III</th>
<th>Phase IV</th>
<th>Phase V</th>
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### Table 2

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<td>Cr</td>
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### IV. SUMMARY AND CONCLUSION

The present work measures the concentration of different solid species of the trace elements Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in the surface sediments of Arasalar river estuary at different stations & seasons (2011-2012). Analysis of sediments for trace element concentration gives history of accumulation of metals in environments. Estuarine and marine sediments are very important accumulation site of metals in the coastal areas; therefore analyses of these metals are important to assess the degree of pollution in the marine environment. The trace elements were extracted from sediment samples into five chemical phases (I-exchangeable, phase II-bound to carbonate, phase III-bound to Fe-Mn oxides, phase IV-bound to organic matter and phase V-residual). The results obtained from sequential extraction procedure showed that among all the five phases, residual phases (phase-V) was found to have much more metal concentrations for all the eight metals compared to other phases irrespective of seasons. The concentration of the metals at various phases are as follows, Fe – Phase V>III>IV>II>I, Mn – Phase V>III>IV>II>I, Cu – Phase V>III>IV>II>I, Zn - Phase V>III>IV>II>I, Pb- Phase IV>V>III>II>I, Cr - Phase V>III>IV>II>I, Co- Phase V>III>IV>II>I, Ni - Phase V>III>IV>II>I. The estuarine environment indicates that the residual phase is the main accumulative phase of most of the studied metals, more importantly for Fe and Cu as the sediments were comprised of detrital silicates. In the present investigation, even though less percentage of metals were found in fractions 1 to 4 of the sediment samples. They have the potential of being released in the environment if there is any change in environmental conditions such as
pH, redox potential or the presence of natural and synthetic chelators (Lim and Kiu, 1995). Under this circumstance, the sequential extraction results will be useful to distinguish between anthropogenic and geochemical sources of metals in the sediments. The high proportion of metals in the residual phase generally related to low levels of extractable metals indicates that the sediments of Arasalar river estuary and adjacent beach environments were relatively unpolluted.

**REFERENCE**


