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SPECIATION OF ZINC IN SURFACE WATERS OF THE RUSHIKULYA ESTUARY (BAY OF BENGAL)

DEEPAK R. DASH, SNEHALATA DASH, SUNIL K. PATRO,
K.S. TRIPATHY AND B. K. SAHU
P.G. Department of Marine Sciences, Berhampur University,
Berhampur -760007, Orissa

ABSTRACT

Speciation study on zinc have been carried out over a period of one year in the Rushikulya Estuary, Bay of Bengal. The percentage of dissolved and particulate fractions of zinc showed significant variations in different seasons because of their involvement in the biogeochemical cycles. The transport processes of these fractions of zinc into the estuary have been explained on the basis of adsorption/desorption mechanisms using theoretical dilution line (TDL).

INTRODUCTION

UNLIKE the major elements, many of the trace elements are not conservative in sea water which can be attributed to their high geochemical and biological activities and also partly due to the adsorption and biological uptake processes. The trace elements help in assessing the effects of inputs from human activities which are further coupled by the erosion of orebearing rocks, volcanic activities and vegetation.

Speciation studies in the estuarine environment involve a greater complexity and hence such studies have not received recognisable attention. Duinker and Kramer (1977) studied the dissolved electroactive concentration on Zn, Cd, Pb and Cu in River Rhine and North Sea waters at natural pH. Hart and Davies (1981) explained the speciation of Cu, Cd, Pb, Zn and Fe in the Yarra river system using a simple speciation scheme and a computer model. Speciation studies were carried out in the Mandovi and Zuari estuaries (George, 1989) covering total dissolved and particulate metal as well as organically bound metal. Paul and Pillai (1983) and Shibu *et al.*, (1990) studied the trace metal speciation in the tropical Cochin estuary. However, no information is available on the speciation of trace metals in the Rushikalya estuary. Therefore, an attempt has been made to study the speciation of Zn in the surface waters of Rushikulya estuary (Bay of Bengal). This estuary situated between 19°22′-19° 24′N lat. and 85° 02′—85° 05′E long., is one of the major estuaries of Orissa, opening into Bay of Bengal, and influenced by semidiurnal tide. The estuary receives a constant inflow of land runoff and industrial effluents. The data were treated season wise *viz.* pre-monsoon (Feb.-May), monsoon (June-Sept.) and post-monsoon (Oct.-Jan.) so as to understand the general conditions of the estuarine environment.

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MATERIAL AND METHODS

Surface water samples were collected monthly between December 1993 to January 1994 at five selected stations, both at fresh water (upper) and saline water (lower) reaches of the Rushikulya estuary (fig. 1). Salinity was determined by the standard titration method of Knudesen as described in Strickland and Parsons (1977). Samples were filtered through millipore filter system before analysis. The sequential speciation scheme was shown in fig. 2. The speciation of dissolved chelex 100 labile metal (CLM) fraction was carried out by taking an aliquot of water sample which was passed through a column packed with chelex-100 resin. It was then washed with deionized water and eluted with 3N HNO_3 and subjected to AAS analysis (Florence, 1977).

Organically bound metal (OBM) fraction was estimated by taking an aliquot of filtered water and treating with 0.5 ml of 30% H_2O_2 in a silica tube and exposing to UV light from a 450 W lamp for six to seven hours and subsequently it was subjected to AAS analysis (Brugmann *et al.,* 1983). The results obtained are the combination of CLM and OBM fractions. The metal in the OBM fraction could be obtained by substracting of the CLM fraction.

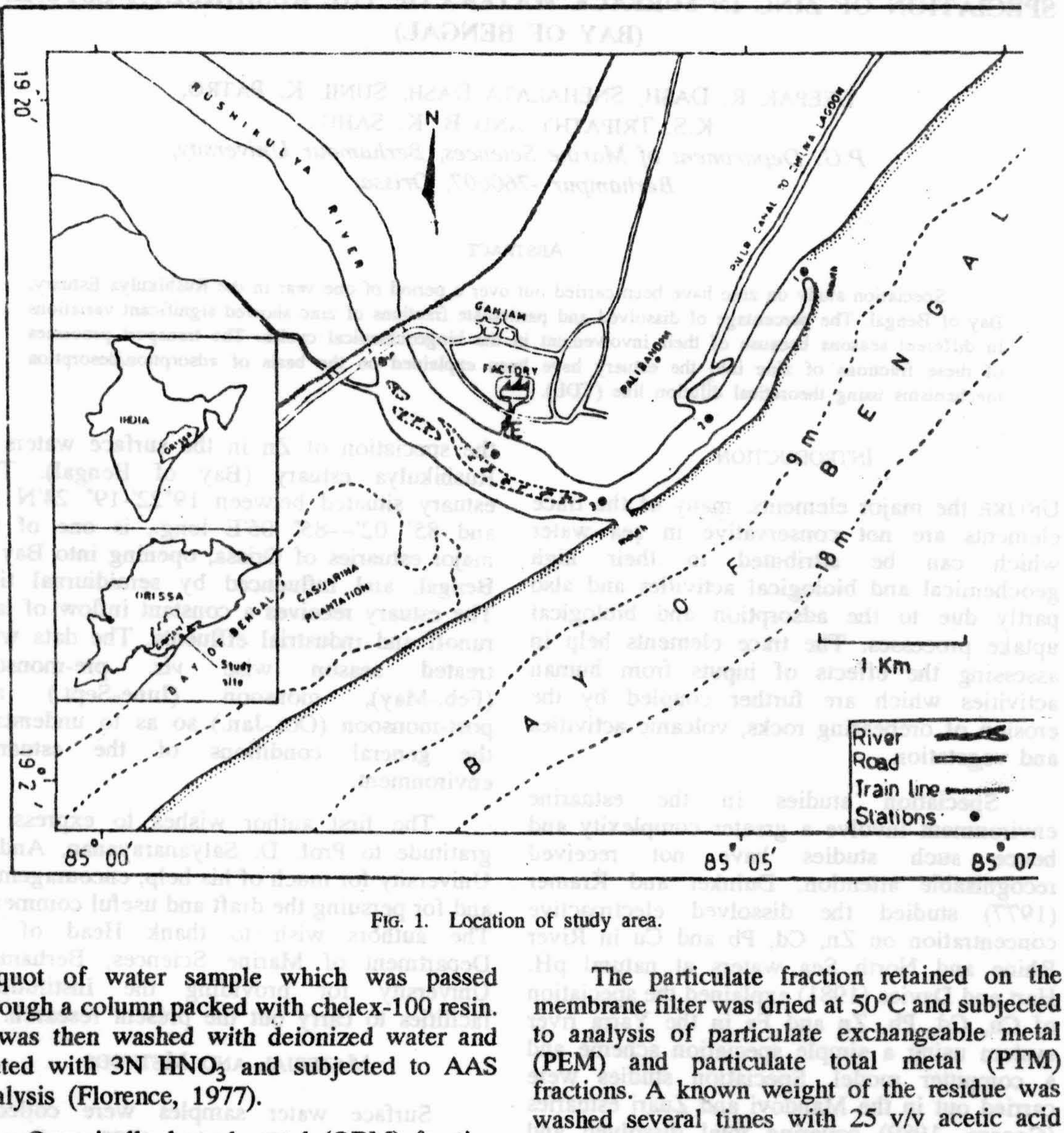

FIG. 1. Location of study area.

The particulate fraction retained on the membrane filter was dried at 50°C and subjected to analysis of particulate exchangeable metal (PEM) and particulate total metal (PTM) fractions. A known weight of the residue was washed several times with 25 v/v acetic acid and the volume was made upto 10 ml and the PEM fraction was determined by AAS (Rantala and Loring, 1985). In order to obtain the PTM fraction, a known weight of the particulate matter retained on the membrane filter was treated with 10 ml of hot (90°C) acid solution

(HCl_4 + HNO_3 + HCl with a ratio of 1:1:3) and equilibrate for six to seven hours (APHA, 1985). The acid leachate after cooling is subjected to AAS analysis. In the present context, the PEM and PTM values were expressed in the μg^{-1} while the CLM + OBM + PTM were considered as the total metal for the studied element.

dissolved zinc gradually decreased towards the lower reaches of the estuary with a significant correlation (r = 0.72 and p = 0.04) which may be due to the salinity induced solubilization of the particulates associated metal (Duinker, 1983; Windom and Smith, 1985 and Windom *et al*, 1991). The decrease of OBM fraction towards the mouth of the estuary can be attributed to

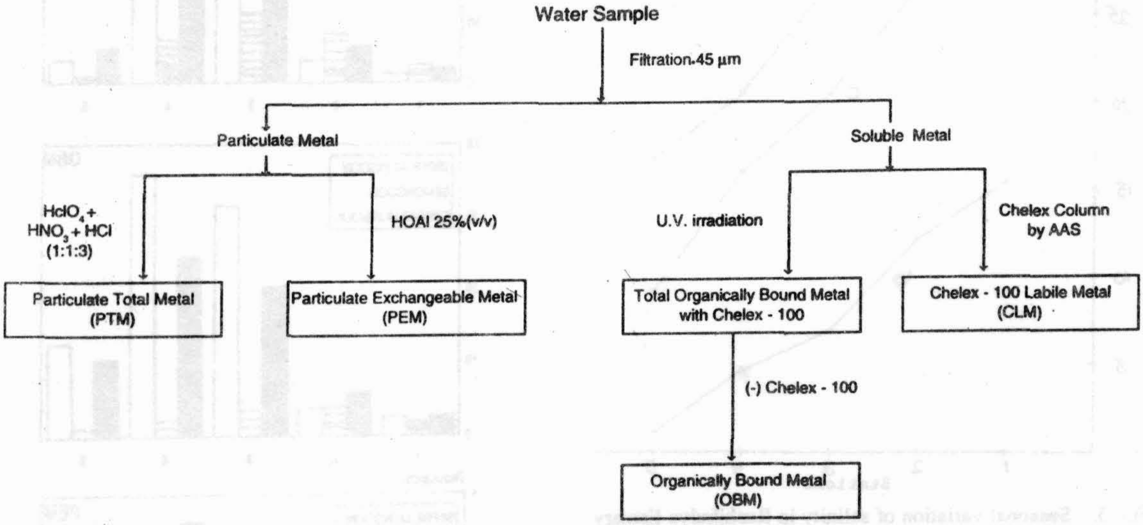

FIG. 2. Speciation scheme of trace metals in estuarine water

RESULTS AND DISCUSSION

Variation in salinity during the period of study in different seasons in Rushikulya Estuary are given in fig. 3. There was a narrow range of variation (26.1 to 33.4 ppt) at the mouth during pre-and post-monsoon while during monsoon, it was between 1.3 to 15.5 ppt. The low salinity values were observed in monsoon due to the influence by the influx of fresh water and intrusion of sea water into the estuary through bar mouth. The high salinity values were observed in Pre - and post-monsoon, because of less influx of fresh water and well mixing with the sea water (Gouda and Panigrahi, 1992). In the present study, salinity is taken as an index of estuarine mixing.

The high concentration of Zn at the upper reach stations of the estuary might be due to coastal inputs (Sen Gupta, *et al.*, 1978). All the fractions of zinc *viz.*, CLM, OBM, PEM and PTM exhibited similar distribution pattern in the estuary (fig. 4). The concentration of

flocculation and to the utilisation of the dissolved organic matter (Florence, 1977; Hart and Davies, 1981; Van der Berg *et al*, 1987; Kuwabara *et al*, 1989; Donat and Bruland, 1990). High concentration of OBM fraction in post-monsoon season may possibly be due to the increased biological activity associated with primary production (Gouda and Panigrahy, 1991). Consequently, the biological uptake of Zn could be low when it undergoes sedimentation during the post-monsoon period (Salomons and Baccini, 1986). The particulate fractions (PEM and PTM) of zinc exhibited similar distribution pattern in Rushikulya Estuary (fig. 4). The concentration of Zn of these fractions were significantly high in upper reaches of the estuary during pre-monsoon indicating a remarkable correlation (r = 0.85 and p = 0.02) which may probably be attributed to the addition of coastal inputs and textural characteristics in the river- transported materials. In general, the concentration of these fractions of Zn gradually decreased towards the mouth of the estuary which might be due to the salinity induced solubilization of the particulate

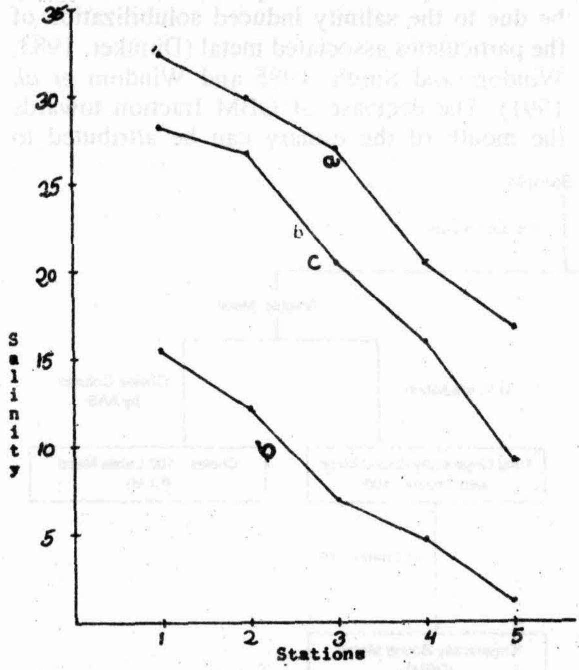

FIG. 3. Seasonal variation of salinity in Rushikulya Estuary a) Pre-monsoon b) monsoon c) Post-monsoon

associated matter (Duinker, 1983; Windom and Smith, 1985 and Windom *et al*, 1991).

On an average 25% of the total zinc (CLM + OBM + PTM) was found to be transported in particulate phase and 75% in dissolved phase (fig. 5) which were slightly greater than the values reported by de Groot *et al.*, (1976). On the other hand, in the Elliot Bay, ≈ 75% of the total zinc originating from riverine and anthropogenic sources was transported in the dissolved form. The total particulate fraction transport was maximum in monsoon and minimum in post-monsoon period. Of the dissolved phase, zinc was associated with 49% and 39% in the CLM and OBM forms respectively. The CLM percentage was maximum during the post-monsoon period.

In the case of simple mixing of sea and fresh waters and in the absence of any loss due to biological or a biological removal, all the points would lie on TDL. When a chemical

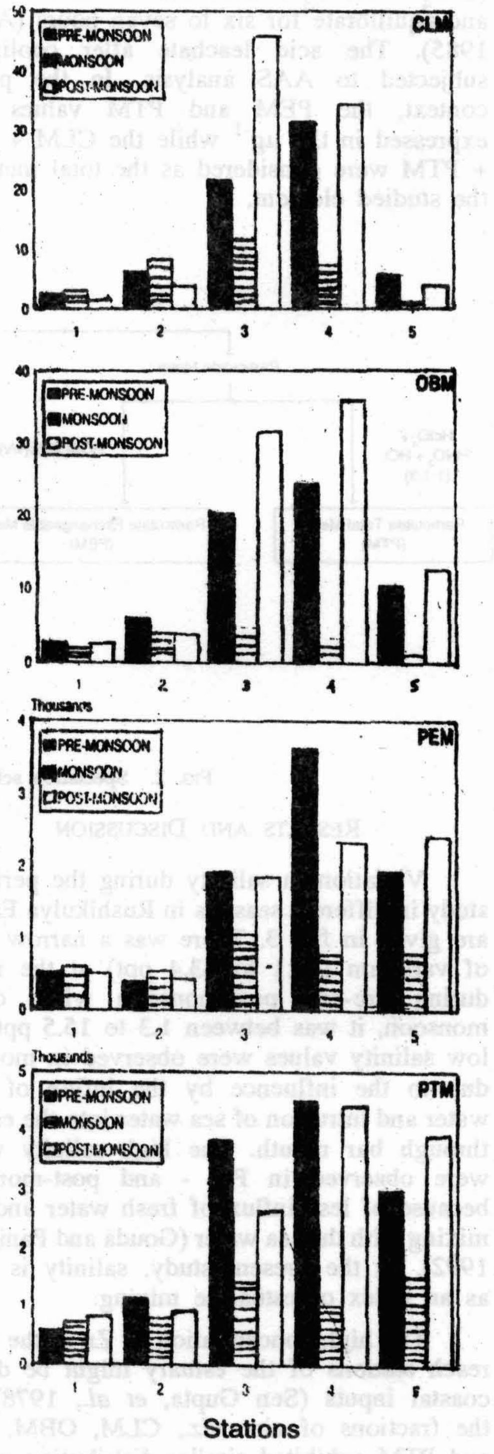

FIG. 4. Seasonal variation of Zinc fractions (CLM & OBM µg/litre) and (PEM & PTM µg/gram)

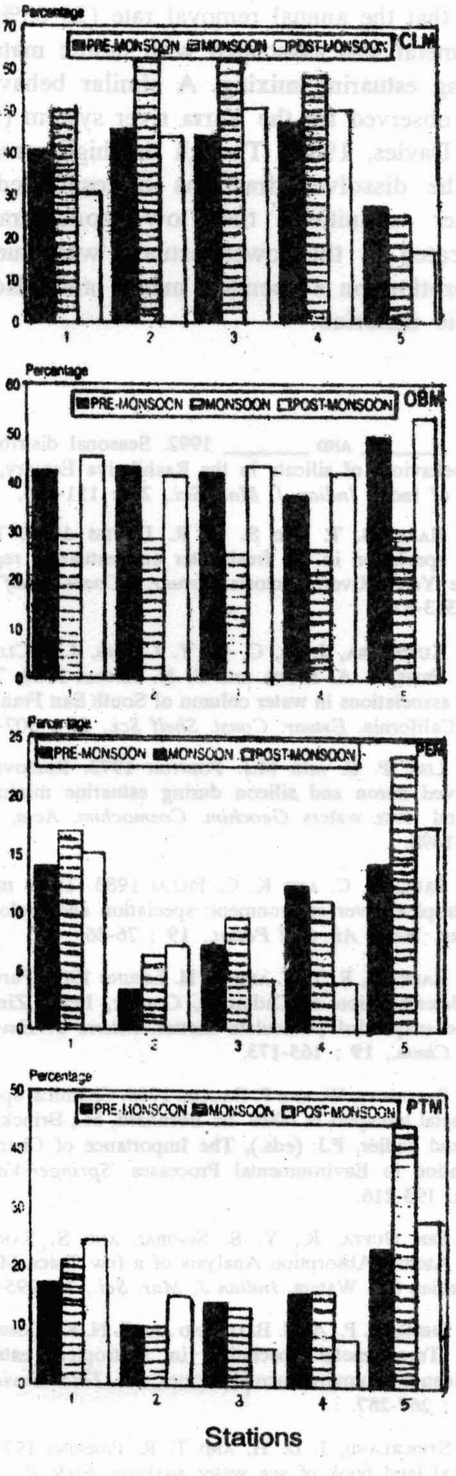

FIG. 5. Seasonal variation of Zinc fraction in percentage

constituent is removed from or added to the water, the point would be either below or above the TDL depending on removal or addition of the constituent under study.

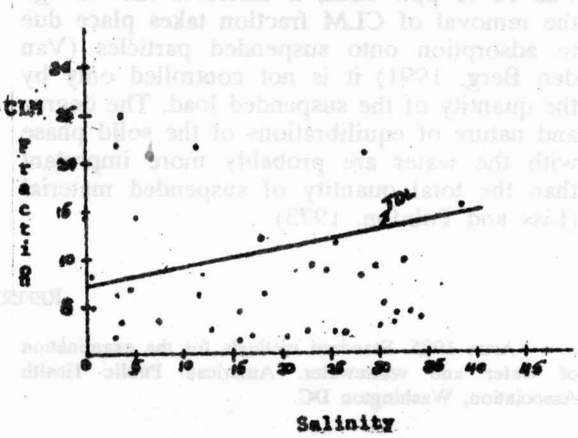

FIG. 6. Variation of CLM fraction with Salinity and their theoretical line (TDL)

The CLM fraction was considerably low and ranged from 0.5 to 2.4 ugl^{-1} at salinity 15-20 ppt whereas the OBM fraction was 0.6 to 2.9 ugl^{-1} at salinity 0-5 ppt (fig. 6 & 7). Salinity showed a strong positive correlation with the dissolved fractions of Zn ($r = 0.52$ (CLM) and 0.42 (OBM). There were variations in the removal of CLM and OBM at different salinity values and it was maximum between 15 and 33 ppt salinity values.

From the least square regression equation

$$CLM = 7.3598 + (0.198)\ salinity\ and$$

$$OBM = 3.459 + (0.208)\ salinity$$

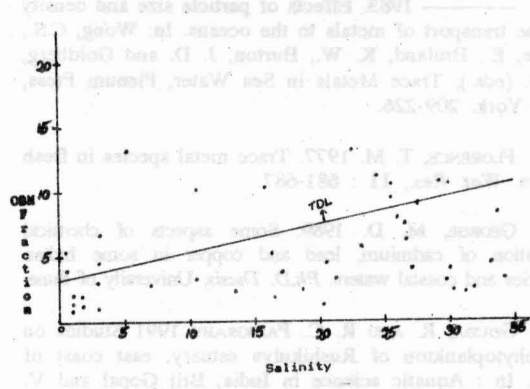

FIG. 7. Variation of OBM fraction with Salinity and their theoretical line (TDL)

It was found that the minimum removal of these fractions of zinc occurred between 0 and 5 ppt salinity values. The average annual removal rate of the CLM values in the estuary was 10-45 ppt. Thus, it indicated that though the removal of CLM fraction takes place due to adsorption onto suspended particles (Van den Berg, 1991) it is not controlled only by the quantity of the suspended load. The degree and nature of equilibrations of the solid phase with the water are probably more important than the total quantity of suspended material (Liss and Pointon, 1973).

In case of the OBM fraction, it might be said that the annual removal rate (25-63%) of the metal was associated with humic material during estuarine mixing. A similar behaviour was observed for the Yarra river system (Hart and Davies, 1981). Though the high removal of the dissolved fractions corresponded to higher salinities, the low concentration indicated at the lower estuary was due to adsorption on suspended matter and also in humic material.

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