

Short Communications

Iron Precipitation in Estuarine Environment

A NSUBRAMANIAN, V RAMADHAS & V K VENUGOPALAN

Centre of Advanced Study in Marine Biology
Annamalai University, Porto Novo 608 502

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Total particulate iron concentration varied from 1336.125 to 350.012 $\mu\text{g/litre}$ and total organic particulate iron concentration from 1099.44 to 290.511 $\mu\text{g/litre}$ in the salinity range 6.8 to 30‰ in the Vellar estuary. Maximum (335.94 $\mu\text{g/litre}$) and minimum (59.501 $\mu\text{g/litre}$) of HCl reactive iron were observed at 0.1 and 30‰ salinities respectively. The relationship between the rate of iron precipitation and salinity was non-linear. The study revealed that (i) inorganic fraction of particulate iron could contribute only lower percentages to total particulate iron (av, 18.8%) and (ii) the role of sedimentary particles could not be neglected while considering precipitation of iron in estuaries.

Studies on the heavy metal iron gathered much interest owing to conflicting findings regarding the non-conservative behaviour of this element in transient zones like estuaries. On the basis of laboratory experiments it was reported that the whole of soluble iron brought by river water gets precipitated completely in the estuary due to sudden increase in salinity of the water^{1,2}. Aston and Chester³ showed that besides salinity, suspended sediments are also essential in enhancing the rate and extent of iron precipitation. Kamat and Sankaranarayanan⁴ observed considerable decrease in particulate iron concentration from the river mouth towards offshore and they related this decrease to flocculation and settling. Holliday and Liss⁵ indicated that under low salinity conditions (< 15‰) soluble iron behaves like a non-conservative element whereas at higher salinities (> 15‰) it behaves like a conservative element. The above mentioned studies were made by analysing either the reactant (soluble iron) or the product (particulate iron) under laboratory conditions.

This paper deals with *in situ* study conducted in the Vellar estuary during December 1977 and presents some information regarding precipitation of iron in estuaries. It is assumed that freshly formed particulate iron through precipitation and flocculation is in the form of either small or intermediate sized particles and would take much time to leave the surface water. Because of this limitation, only an approximate measure of the actual concentration can be given, and this provides better understanding of the pattern of precipitation over a wide range of salinities.

Surface water samples were collected by clean plastic buckets from Vellar estuary, starting from the freshwater zone and ending in the mouth of the estuary, a distance of 5 km. Only surface samples were used, since in shallow waters tidal currents would agitate the bottom (tidal range 70 cm), leading to resuspension of bottom sediments in the water. During the study period the depth of the estuary was comparatively higher (> 5 m). Immediately after the collection the samples for iron determination were preserved in clean polyethylene containers adding few milligrams of mercuric chloride. Samples without mercuric chloride were used for salinity determination⁶. Frequency of sampling for low salinity (< 10‰) sample was 18 and for high salinity (> 10‰) was 8. Particulate matter was collected by filtering a known volume of sample through Whatman glass filters (GF/C) and the filters along with particulate matter were treated with 40% hot hydrochloric acid to leach out ferric iron in the particulate matter⁶. After cooling to room temperature, the contents were filtered through a glass filter and the filter with particulate organic iron was digested with perchloric acid. HCl extractable and organic particulate fractions of iron were estimated separately after removing the residues by centrifugation, adopting the bipyridyl method⁶. Total particulate iron was calculated by adding the HCl extractable and particulate organic fractions. The precision of the method is $\pm 0.67 \mu\text{g/litre}$ on 1 litre sample.

Variations of total particulate and HCl reactive particulate iron with salinity are shown in Fig. 1. During the early mixing process in the estuary heavy precipitation of iron occurred. The extent of precipitation increased steadily from 0 to 6‰ salinity and decreased afterwards. Between 14 and 26‰ there was not much variation in the concentration of total particulate iron. After 26‰ it declined to reach the low value observed for the coastal water.

Since it was stressed by Sholkovitz² and Holliday and Liss⁵ that precipitation would complete within the salinity range 0 to 20‰, frequency of sampling was increased only for the low salinity samples. The observed decrease in total particulate iron above 6‰ salinity indicated that though precipitation would occur at higher salinities also, the rate of precipitation would generally be low. This might be attributed partly to the decrease in the proportion of freshwater to sea water at higher salinity levels and the consequent

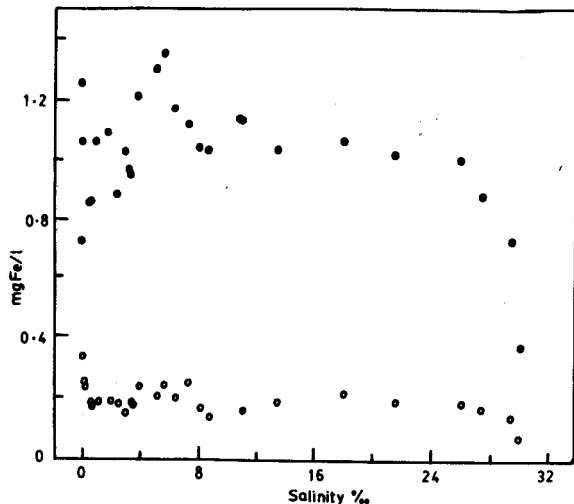


Fig. 1—Variation of HCl reactive (o) and total particulate (●) iron with salinity

decrease in concentration of soluble iron available for precipitation. Holliday and Liss⁵ also indicated that precipitation of iron up to a salinity of 6‰, would be high and thereafter the rate of precipitation would decrease with further increase in salinity thereby altering the pattern of precipitation. From the present observation it can also be assumed that the relationship between the rate of iron precipitation and salinity is non-linear. Similar non-linear relationship between iron and salinity was observed earlier^{2,4}.

Conflicting reports exist regarding the formation of particulate iron in estuarine environments^{1-3,5}. In view of this particulate iron was studied separately as inorganic and organic fraction in the present study. The HCl reactive fraction mostly represented the ferric fraction available as phosphate and anhydrous oxides of iron. It would be interesting to note that such inorganic fraction of particulate iron contributed only a low percentage (13.59- 26.85%; av. 18.81%) to total particulate iron. Because of this fact variations in total particulate iron resembled those of organic fraction. Absence of a well defined pattern in the distribution of HCl reactive fraction throughout the salinity range studied was obvious in the present study. As the concentration of this fraction could be very much affected by phytoplankters through biological utilization^{7,8}, such variations are bound to occur in estuaries. Since the HCl reactive iron contributes only lower percentages of the total particulate iron such variations are not prominent when compared to organic particulate iron. Further, as far as this fraction of particulate iron was concerned, besides salinity the availability of suspended sediments in the water also seemed to be more important. Suspended particles are important in the aqueous geochemistry of iron and this element is known to occur both as oxide coatings on

the surface of minerals such as clays and also as discrete hydrated iron oxide particles. In the present study, differences in the concentration of total particulate iron were observed at times, even between samples of more or less the same salinity, but with varying particulate matter concentrations. The present results suggest that in studies of iron precipitation under laboratory conditions only natural samples should be employed giving importance to both salinity conditions and available suspended sediments.

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Organic Matter in Sediments Off Northeastern Andamans*

M RAMA MURTY, K V VENKATESH &
C V L NARASIMHAM

Geological Survey of India, 4, Chowringhee Lane, Calcutta 700 016

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Organic matter has been determined from 24 surficial sediment samples (from 20 to 500 m depth) collected in the offshore area between Port Cornwallis and Port Blair off Andaman Islands. Wide variation is seen in the organic matter content (0.35 to 3.58 %), and the nearshore sediments are characterised by a low content of organic matter (0.35 to 1.88 %) than the deeper slope sediments (2.64 to 3.58 %). Areal variation of organic matter has been discussed in relation to organic and inorganic materials, prevailing hydrographical conditions, texture of sediments and other factors.

Although organic matter is rarely a major constituent in bottom sediments of the nearshore or offshore areas, it is often a good index of the environment in which the sediments are deposited. Studies of the organic matter of recent marine sediments are of interest especially for their bearing on diagenesis. There is a need to know the composition of organic matter and the conditions under which it accumulates, since the understanding of the connection between the benthos and the amount and composition of organic matter would enhance our

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