

# 9

## Distribution of iron and manganese

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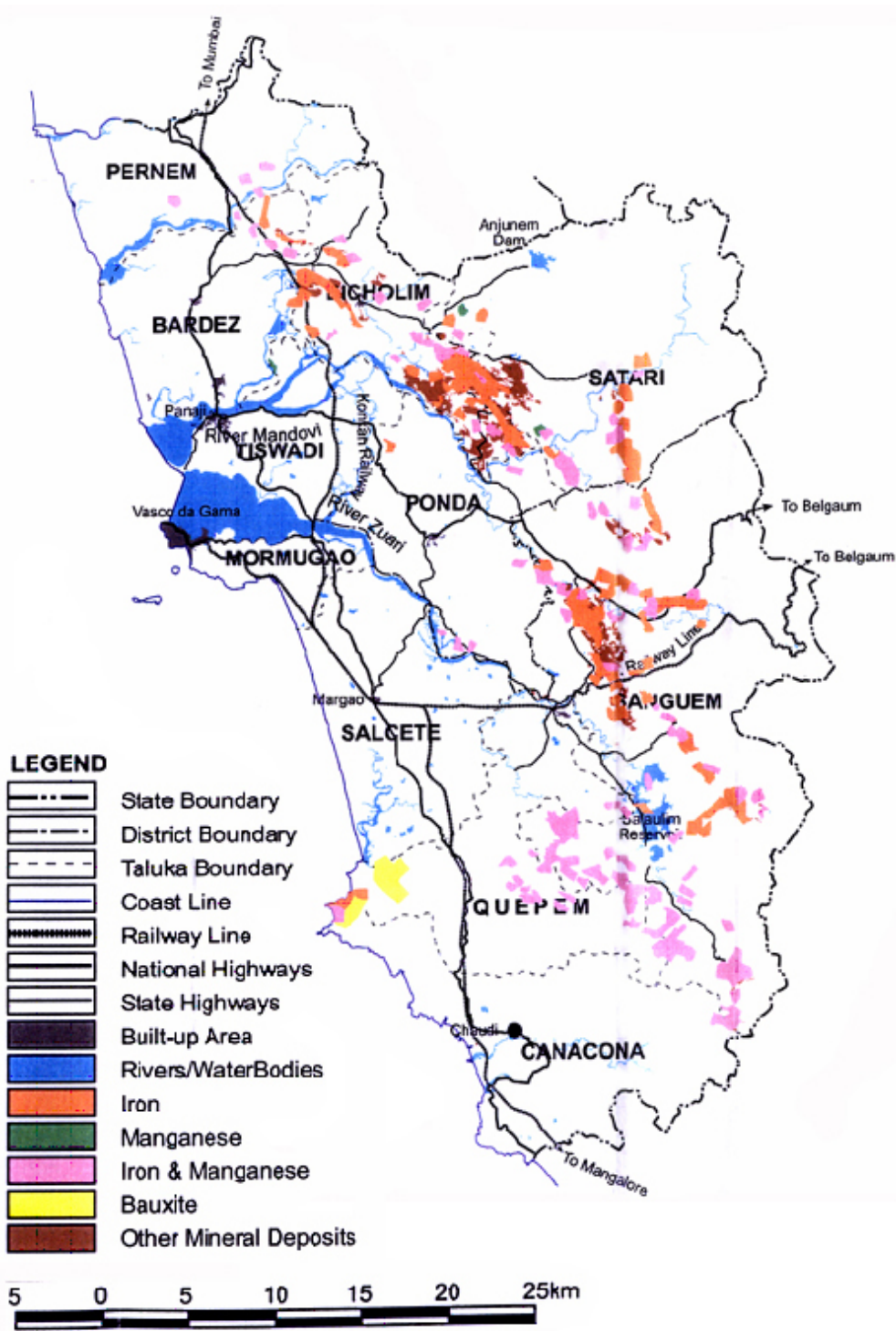
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### 9.1 INTRODUCTION

An important industry in Goa is mining of iron and manganese ore. Active mining goes on at present at a number of locations distributed along a belt that stretches from north to south in the central part of the state. The present mining sites are shown in figure 9.1. The iron ore from these sites is transported in open trucks to a number of nearby convenient locations on the banks of the Mandovi and Zuari estuaries. From these locations the ore is transferred to barges, which take the ore to the Mormugao Port, from where it is shipped to other places.

The mining operations and the process of transporting the ore generate dust that is then carried by winds to nearby areas. The wind-borne transport of dust is particularly strong during the dry season. It is expected that some of the dust would settle in the waters of the two estuaries, leading to significant concentrations of dissolved and particulate iron and manganese. Also contributing to these concentrations is water-borne transport of dust and sediments by streams that flow through the areas around active mining sites. This transport is particularly high during the summer monsoon. While the mining operations are suspended during this season because of rains (hence wind-borne transport is minimal), the runoff over mining areas, which ultimately ends in the Mandovi and Zuari estuaries, becomes a significant source of iron and manganese in the estuaries. In view of this, it is of interest to



**Figure 9.1** Map of Goa showing areas of types of ores and mining activities. (Courtesy: Goa State Pollution Control Board, Goa.)

determine concentrations of dissolved and particulate iron and manganese in the water column in the estuaries and in the sediments. In this chapter, we report on the observed concentrations.

## 9.2 SAMPLING AND ANALYTICAL METHODS

The schedule of sampling of water for data discussed in this chapter is given in table 9.1. During each period of observation, water samples were collected at stations  $M_1$ – $M_7$  in the Mandovi and at  $Z_1$ – $Z_5$  in the Zuari (Map B). Station  $M_Z$ , which represents the regime off the mouths of the two estuaries, was also worked. During each period of simultaneous observations (stations were occupied by separate boats), which lasted 24 hours, a water sample was collected every three hours. Hence, at each station during each period of observation, there were eight samples. The variability during the 24-h period gives a measure of change due to tidal movement of water. Each water sample was collected using a Niskin bottle at a depth of approximately 3 m from the surface. Sediment samples were collected once during a 24-h observation period by using a Van Veen grab of 0.04 m<sup>2</sup> area.

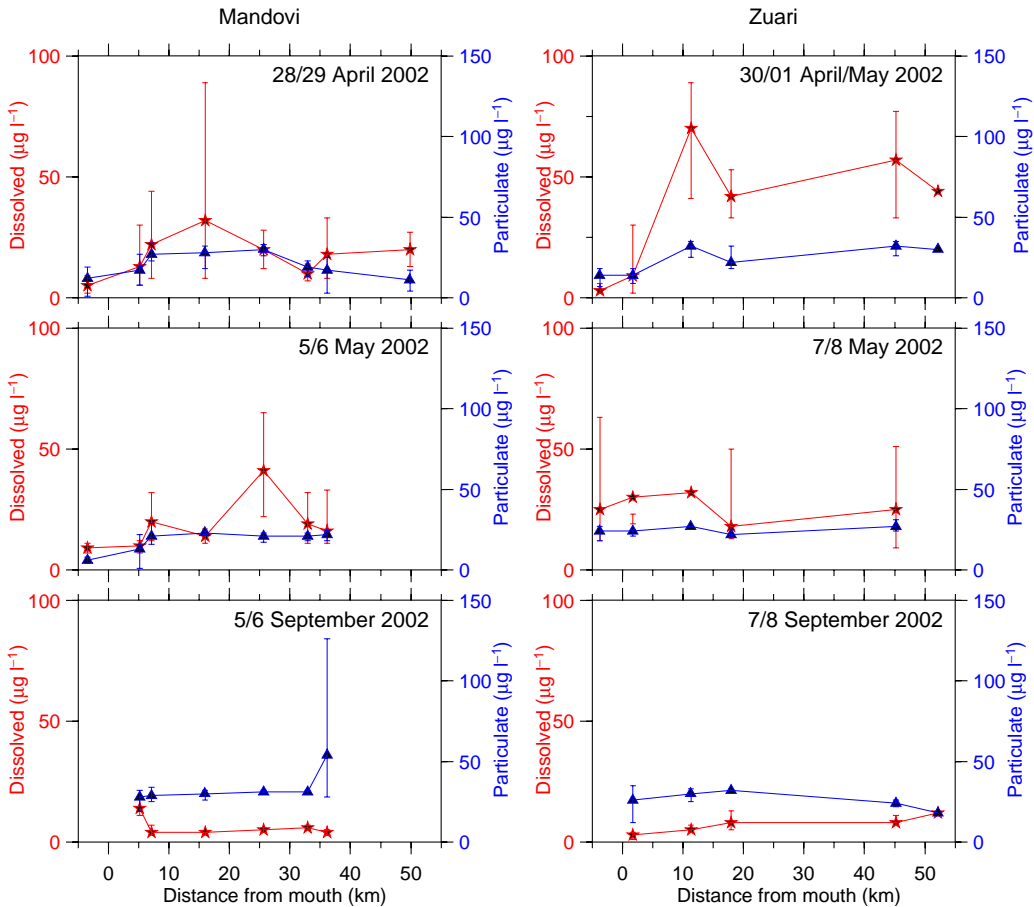
Sample collection, filtration, treatment, and analysis for iron and manganese was carried out according to the protocols of ultra-trace-metal analysis (Bruland *et al.* 1979; Danielson 1980) using atomic absorption spectroscopy (AAS). The accuracy of the dissolved metal analyses was found to be  $\pm 5\%$  using certified reference waters CASS-3 and NASS-4 (supplied by National Research Council of Canada). Extractable metal concentrations in suspended particulate matter (SPM;  $> 0.45 \mu\text{m}$ ) were analyzed after the acid digestion of SPM and drying of the residue to a constant weight on membrane filters. The same digestion procedure was performed on filters without particles to find procedural blanks. Dried bottom sediment samples were digested with a mixture of hydrofluoric-nitric-perchloric acids. The residue was dissolved in dilute hydrochloric acid and metal concentrations were determined by AAS. Analysis of the certified reference materials PACS-1 and BCSS-1, following the same protocol, showed good recoveries ( $\sim 95\%$ ) of the metals.

**Table 9.1** Schedule of sampling.

Estuary	Period of observation
Mandovi	28–29 April 2002 (spring tide)
Mandovi	5–6 May 2002 (neap tide)
Mandovi	5–6 September 2002
Zuari	30 April–1 May 2002 (spring tide)
Zuari	7–8 May 2002 (neap tide)
Zuari	7–8 September 2002

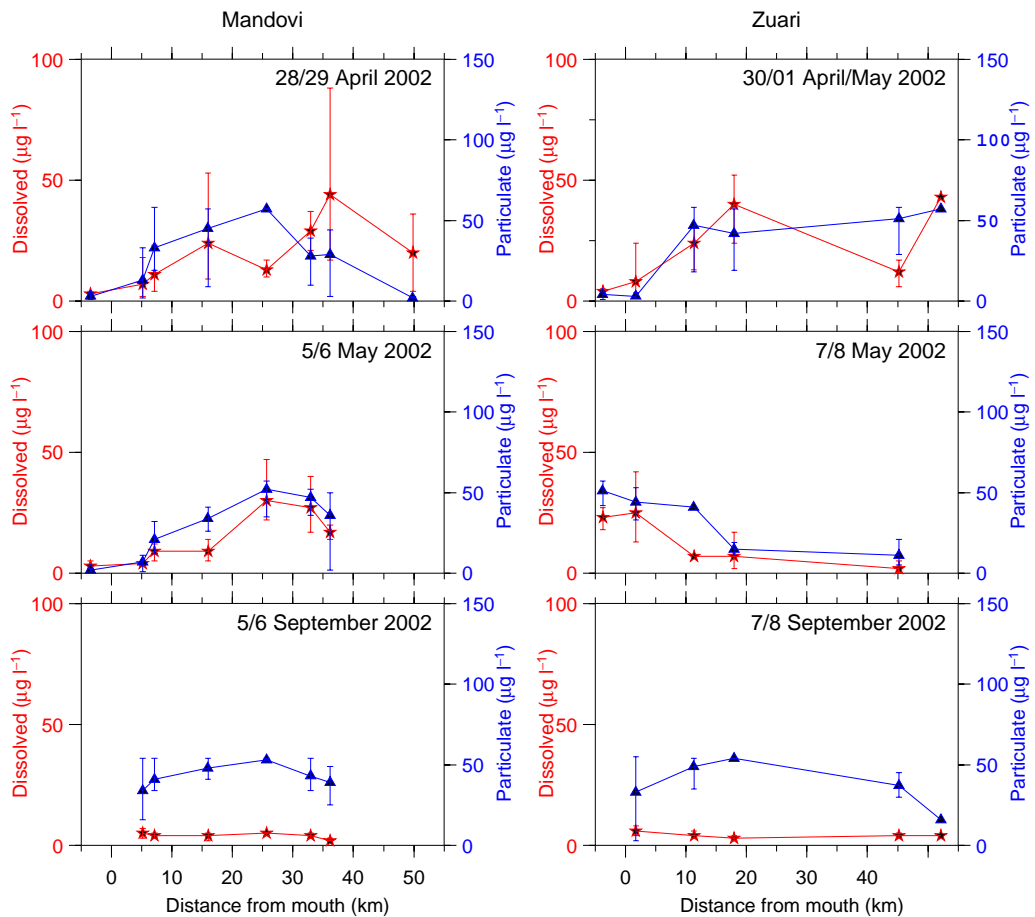
## 9.3 RESULTS AND DISCUSSION

Figures 9.2 and 9.3 summarize the observed spatial and temporal distribution of iron and manganese respectively. From the figures, no clear pattern emerges. On average, concentration of particulate iron in the Mandovi and Zuari vary from negligible concentration to about  $50\mu\text{g l}^{-1}$ . The range for dissolved iron too is similar. Dissolved manganese also varied from negligible concentrations to about  $50\mu\text{g l}^{-1}$ , and concentration of particulate manganese has a similar range. The observed concentrations in sediments are shown in figure 9.4. Again there is no clear temporal or spatial pattern. The range of concentration of iron in the two estuaries is  $0\text{--}20\text{mg g}^{-1}$ , and that for manganese is  $0\text{--}15\text{mg g}^{-1}$ .

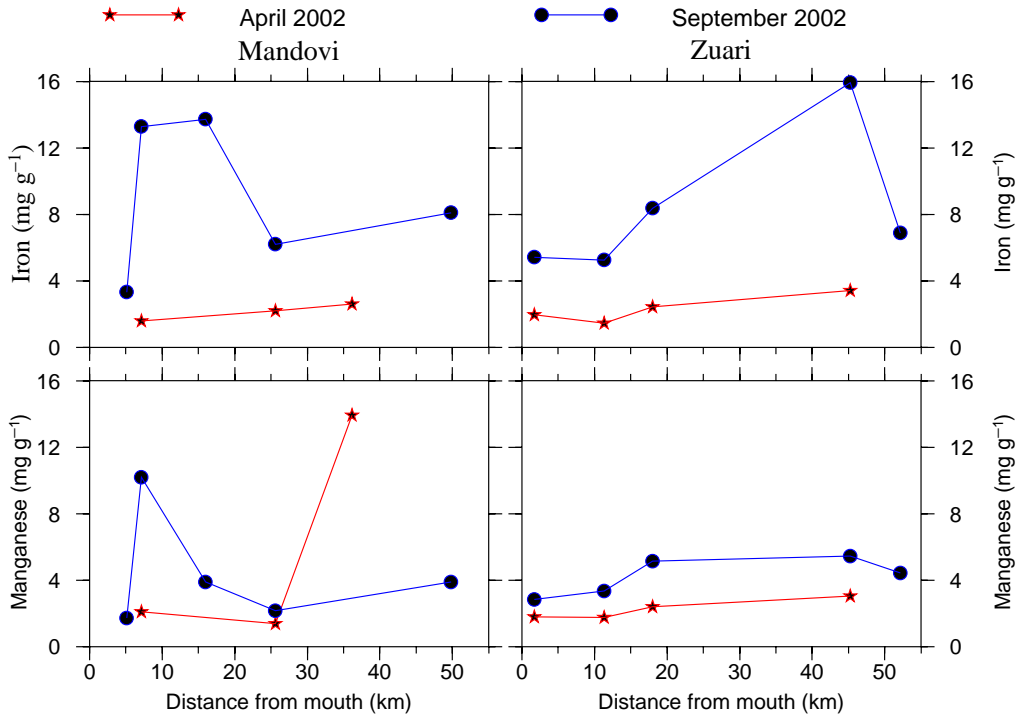


**Figure 9.2** Variation in dissolved (red line) and particulate (blue line) iron ( $\mu\text{g l}^{-1}$ ) in the Mandovi estuary (left panels) and the Zuari estuary (right panels) with distance from the mouth (km) of each estuary. The period of observations is identified at the upper right hand corner of each panel. The vertical bars indicate the range of observed values at the respective stations.

While there is no clear pattern for dissolved and particulate iron or manganese in the two estuaries, there is a weak tendency that is noticeable. The values often tend to be higher in the middle estuary, that is, somewhere mid-way between the head and the mouth of the estuary. This tendency implies that the source of iron and manganese is largest somewhere in the middle estuary, and not in the water that enters the estuary at the upstream end, or in the water on the shelf. This does make sense in view of the known sources: wind-borne dust or water-borne material, both arising from mining operations. The mines are distributed over a wide area (figure 9.1). As the material carrying iron and manganese is expected to reach the estuaries after following a chaotic path, it is not surprising that there is no clear spatial or temporal pattern to the distribution. It is also not surprising that



**Figure 9.3** Variation in dissolved (red line) and particulate (blue line) manganese ( $\mu\text{g l}^{-1}$ ) in the Mandovi estuary (left panels) and the Zuari estuary (right panels) with distance from the mouth (km) of each estuary. The period of observations is identified at the upper right hand corner of each panel. The vertical bars indicate the range of observed values at the respective stations.



**Figure 9.4** Variation in sediment Fe and Mn ( $\text{mg g}^{-1}$ ) in Mandovi and Zuari estuaries as a function of distance from the mouth (km).

the sediments did not show any systematic pattern. After deposition on the surface of the bottom of the estuary, the sediments would have been moved around in the estuary by tidal flows, until somehow they reach subsurface levels, where they would not be vulnerable to further movement. On the other hand, a mid-estuarine increase could also result from the release or re-precipitation of reduced or oxidized forms of iron and manganese from organic rich sediments; the relative importance of these processes is unknown.

It is worth noting that the samples that were analyzed here were derived from surface sediments. It is possible that a core collected in the estuary would exhibit a sharp change in iron and manganese distribution with depth because mining of iron and manganese in Goa started around 1950. If our hypothesis, that the concentration of metals in the estuaries today is primarily due to mining, is correct, then there should be a distinct reduction in concentration in sediments that were deposited prior to the 1950s.

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