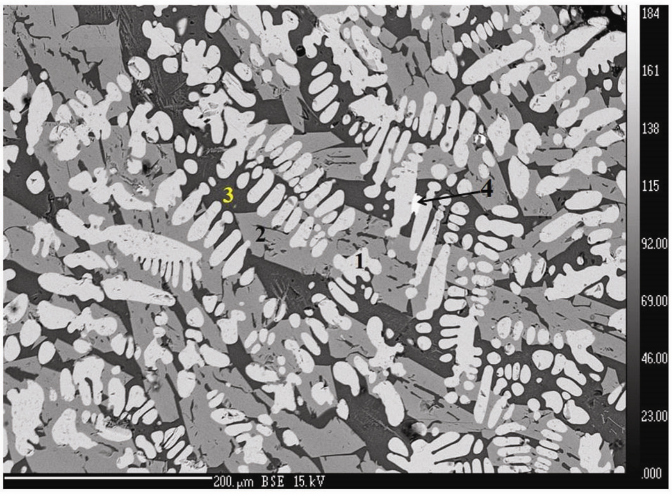


**Figure 4.** BSE image showing magnetite (1), fayalite (2), glassy phase (3) and metallic iron (4) phases in Galla slag.

the furnace, only fayalite (orthosilicate) in liquid form can be the stable phase. The temperature in the furnace may have reached about 1200°C, as the melting point of fayalite is around 1205°C with a FeO–$Fe_2SiO_4$ eutectic point of melting at 1177°C (ref. 3). The fayalite in the slag is formed synthetically from melting of silicate rock and rapid crystallization thereafter. The silicate melt thus formed is richer in Fe, and chills instantaneously forming a high-temperature mineral phase (fayalite) along with a quenched glassy matrix.

Studies on ancient slags worldwide[7–10] have shown that the proportions of phosphorus are in the range 0.05–0.5 wt%, with levels up to 1.0 wt%. The phosphoric content in Galla slag is 0.91 wt%, which is on the higher side. The moderately higher levels of P in Galla slag may be explained due to the presence of fayalite in good amount, which has a lesser dephosphorization efficiency than the common iron-bearing slags. However, moderate to high P may indicate that perhaps flux (limestone) was not used in the charge of ancient Indian bloomer furnaces for producing iron metal[3,11].


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# Spatial distribution of suspended particulate matter in the Mandovi and Zuari estuaries: inferences on the estuarine turbidity maximum

An estuary is a region where a river meets the sea. In these estuarine regions there exists a strong physio-chemical and compositional gradient in the water properties, that varies rapidly from freshwater to sea water[1,2]. Estuaries are important areas as they filter out suspended particulate matter (SPM), sediments and pollutants from the rivers before entering the sea and keep the coastal seas healthy. The concentration of SPM varies from river end to sea end of the estuary, and high SPM concentrations along the transect are controlled by several factors, including the action of tides, gravity circulation, density stratification, resuspension and flocculation, or due to the combined action of one or more of these forces[3–5]. Within the estuary there exists a distinctive zone with high concentrations of SPM compared to the surrounding water in the seaward or landward side, called estuarine turbidity maximum (ETM)[2]. These zones are useful as fish lay eggs and larvae thrive because of abundant food and are protected due to masking[6]. However, excess SPM in ETM with high organic content may give rise to bacterial action reducing dissolved oxygen from water, leading to sub-oxic and anoxic conditions[7] that are unsuitable for other organisms. Therefore, understanding the ETM becomes essential, as it is a feature that extends vertically downwards and is difficult to study based on surface samples or satellite[8,9]. Previous studies on SPM in the Mandovi and Zuari (Ma–Zu) estuaries of Goa, central west coast of India, based on the surface water samples indicate the presence of ETM both during monsoon and pre-monsoon[10,11]. Here we present spatial distribution of SPM in the Ma–Zu estuaries, during post monsoon using laser *in situ* scattering and transmissometry (LISST-25X) to identify the zones of ETM. This instrument can capture continuous *in situ* data by which the particle size and abundance can be simultaneously obtained.

The Mandovi and Zuari are major rivers of Goa, which originate in the Western Ghats, flow across Goa, and meet the Arabian Sea. They are adjacent to each other (almost parallel) and their estuarine systems are connected by the Cumbarjua canal (Figure 1). These are monsoonal rivers with abundant discharge during the monsoon (June–September) and negligible discharge during the dry period (October–May)[12]. We have used CTD (Sea-Bird Electronics) vertical profiler for measuring conductivity and temperature and LISST-25X (ref. 13) for measuring particle volume concentration (here referred to as SPM) and sauter mean grain size (here referred to as grain size). These instruments were operated onboard a mechanized boat with depth sensors at 12 stations along the 35 km long channel of the Mandovi estuary (M0A to M9), nine stations along the 40 km long channel of the Zuari estuary (Z0 to Z8) and at four stations in the Cumbarjua canal (C0–C3) (Figure 1) during post-monsoon season of 2013. The data collected were processed according to the standard procedures of Sea-Bird Electronics and Sequoia[13], and plotted against distance to obtain the spatial distribution of salinity, temperature, SPM concentration and grain size using Ocean Data View[14] (Figures 2 and 3).

The temperature transects of Mandovi (26.1–29.7°C) and Zuari (24–31°C) estuaries show stratification with colder, deeper waters on the downstream (M0A–M0B in Figure 2 *a*, and Z0–Z1 in Figure 3 *a*) and warmer water upstream. The salinity values range from ~0.04 to 34.15 in the Mandovi estuary and from ~0.03

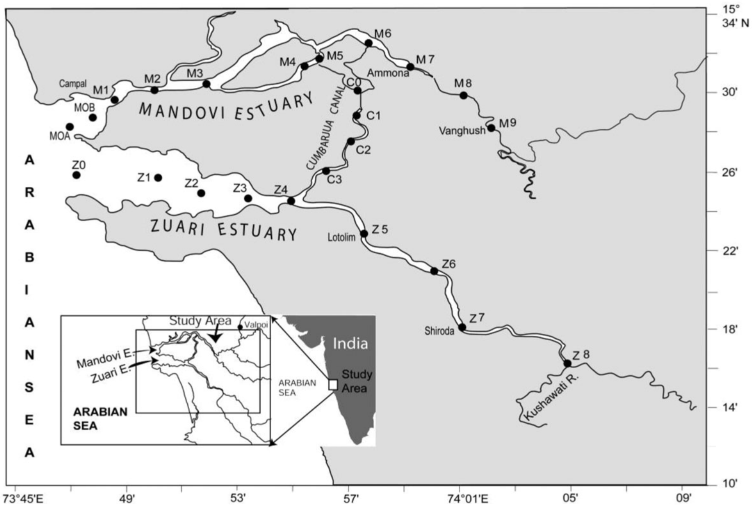


**Figure 1.** Location of samples from the Mandovi (M0A–M9) and Zuari (Z0–Z8) estuaries and Cumbarjua canal (C0–C3).

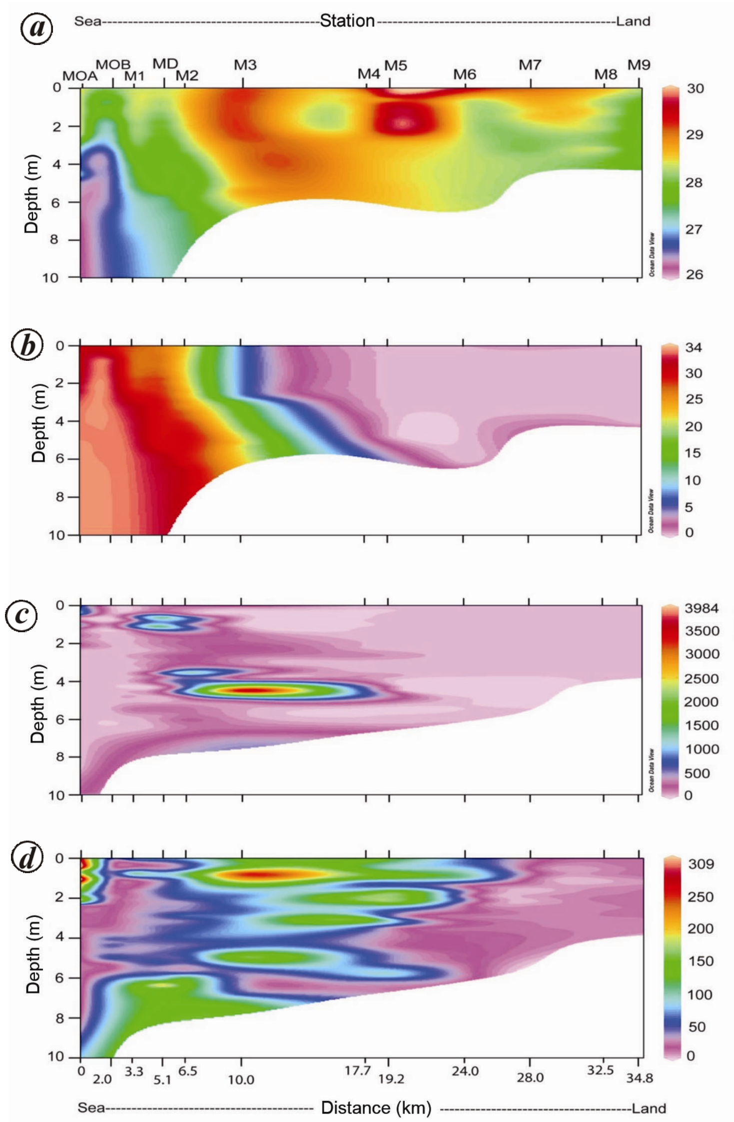


**Figure 2.** Mandovi estuary: along-channel variations of (***a***) temperature (°C), (***b***) salinity, (***c***) concentration of SPM (μl/l) and (***d***) grain size (μm).

to 35 in the Zuari estuary (Figures 2 *b* and 3 *b*), with relatively low values along the Cumbarjua canal (6–22). Salinity shows vertical mixing in both the estuaries, with decreasing values upstream (Figures 2 *b* and 3 *b*). There is a sharp salinity gradient on the seaward side between M1 and M5 stations as well as Z1 and Z5 stations. The SPM concentrations are similar in both Mandovi (2–3984 µl/l) and Zuari (3–3698 µl/l) estuaries (Figures 2 *c* and 3 *c*), and lower in Cumbarjua (21–216 µl/l) canal. Grain size does not show much change in the Mandovi (8–353 µm) and Zuari (7–370 µm) estuaries (Figures 2 *d* and 3 *d*), but shows a lower range in the Cumbarjua canal (13–93 µm). Relatively high SPM prevails at M0A and Z0 stations in the top 2 m of the water column (Figures 2 *c* and 3 *c*). High SPM prevails between M1 and M4 stations (between 3.3 and 17.7 km from the mouth of the estuary) as well as in Z1 and Z6 stations (5.2–25.7 km from the mouth of the estuary), and extends up to about 7 m depth. It is also associated with the highest grain size (Figures 2 *c*, *d* and 3 *c*, *d*). Relatively high SPM concentrations corresponding to low grain size of SPM are also seen in the bottom water at stations between Z3 and Z5 (Figure 3 *d*). The SPM concentrations decrease with decreasing salinity landward and are the lowest for salinity below 4 in both the estuaries.

The high SPM concentration near the mouth of the Ma–Zu estuaries (Figures 2 and 3) may be related to ETM associated with high salinity. The particle grain size in this high SPM zone (8–353 µm) falls within the range of microzooplankton and mesozooplankton, and can contribute to ETM. However, organic carbon content in this area was found to be ~8% during the dry period[15]. In other words, the SPM consisting of more than 90% of inorganic material, probably represents resuspended particles, due to tidal and wind-driven waves and currents. Our results corroborate the findings of Kessarkar *et al.*[10,16] that high ETM is associated with high salinity at the sea end. The vertical profiles of SPM suggest extension of this ETM up to 2 m depth in both the estuaries.

The spatial distribution of SPM profiles shows higher concentration upstream (100–3900 µl/l), prevailing at a distance of ~3.3 km from the mouth at station M1 in Mandovi and about ~5.2 km from the mouth at station Z1 in Zuari estuary (Figures 2 and 3). These concentrations extend vertically down to about 7 m. These high SPM concentrations are associated with the salinity gradient (30–4) that is observed up to ~18 km for Mandovi and ~25 km for Zuari estuary. Beyond this, salinity is <4 and SPM is less than 100 µl/l. These zones of high SPM concentration suggest that ETM is associated with the salinity gradient, with grain size of 50–320 µm in Mandovi and 50–370 µm in Zuari estuary probably representing floc sizes. This second ETM has not been observed so far based on the surface samples[10,16] probably associated with the flocculation and coagulation and settling of SPM that can be seen in the profiles as patches of high SPM concentration and larger grain sizes (Figures 2 *c* and 3 *c*), and may be related to change in salinity[2]. The presence of organic matter and colloidal material helps in the settling of SPM and with changes in salinity, certain minerals which are in suspension tend to flocculate and settle[5]. In the Ma–Zu estuaries SPM is dominated by kaolinite[17], and flocculation of this clay is completed by salinity value more than 4 (ref. 18), that can be noticed in these estuaries where SPM content increases with salinity more than 4. There is also an increase in temperature as we move upstream and flocculation is less effective due to increase

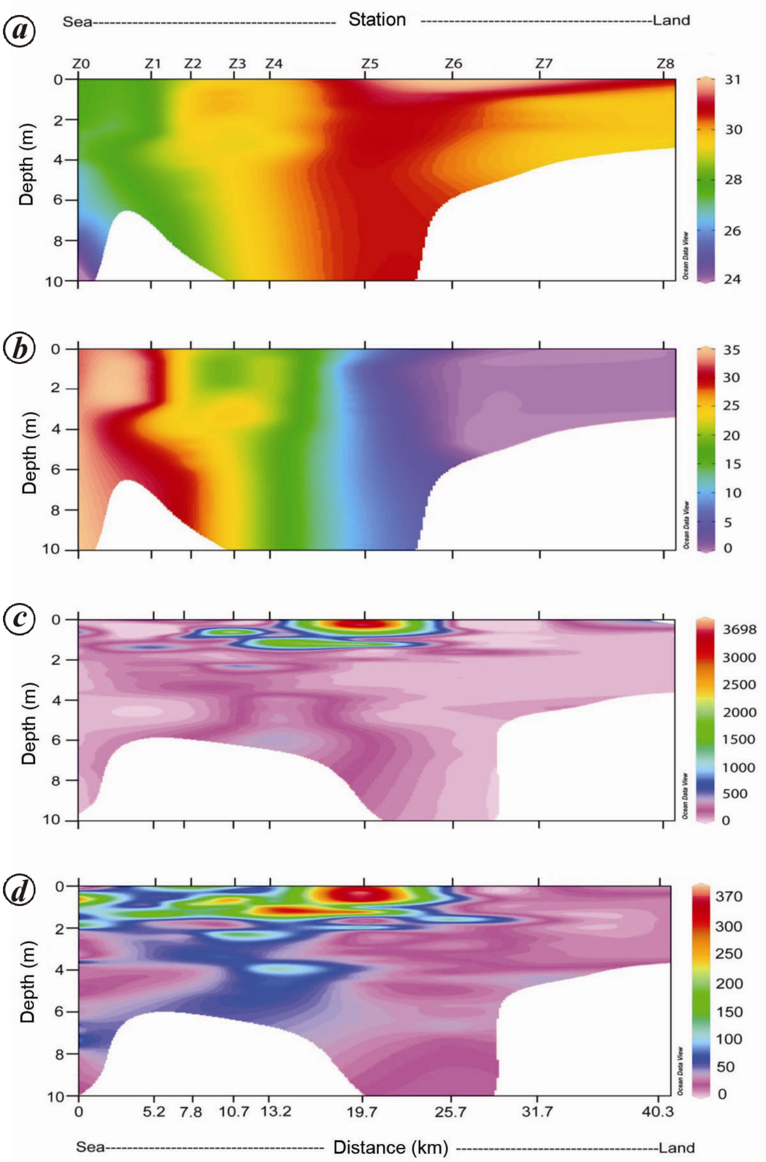


**Figure 3.** Zuari estuary: along-channel variations of (***a***) temperature (°C), (***b***) salinity, (***c***) concentration of SPM (µl/l) and (***d***) grain size (µm).

in the repulsion of ions caused by thermal motion[2], which can be another reason for low SPM in the upstream. In the Ma–Zu estuaries, the area of inland ETM is associated with mud flats with marshy areas[15], with mangroves growing on them. It has been observed that there is a new island formation in the Mandovi estuary which falls within the vicinity of the ETM, but the processes for its formation are yet to be identified.

The ETM was not clear in the Mandovi estuary during post-monsoon, but was observed in Zuari estuary during the neap tide[18]. The present study, based on the spatial distribution of SPM, shows the occurrence of two ETMs at the same time along transects of the estuaries. The first ETM is at the sea end of the estuary, associated with high salinity and is probably due to resuspension of particles caused by wind-induced and tidal currents. The second ETM in the upstream is associated with salinity gradient and is probably due to flocculation and coagulation and settling of SPM. The Indian coastline covers 7517 km (including Andaman and Nicobar Islands and Lakshadweep Islands)[19], with numerous small, medium and large rivers debouching suspended matter into the estuarine environment[20]. Further, the estuaries also receive industrial pollutants. Thus systematic studies are necessary to better understand the ETM and pathways of pollutants.


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