

The Nature and distribution of particulate matter in the Mandovi estuary, central west coast of India

PRATIMA M. KESSARKAR, V. PURNACHANDRA RAO*, R. SHYNU, PRAKASH MEHRA AND BLOSSOM E. VIEGAS

National Institute of Oceanography, Dona Paula – 403 004, Goa, India

Abstract: Systematic seasonal variations of suspended particulate matter (SPM) along a 44 km transect of the Mandovi estuary reveal that the concentrations of SPM are low at river-end stations, increase generally seaward, and are highest at sea-end stations of the estuary. An estuarine turbidity maximum (ETM) occurs at sea-end stations during June–September when river discharge is high and also in February-May when river discharge is low. These are the two windiest times of year, the former associated with the southwest monsoon, and the latter characterized by a persistent sea breeze. The salinity vs. SPM plot shows that high SPM is a seaward deposit and skewed landward. Suspended matter comprised of floccules, faecal pellets and aggregates that consist of clay and biogenic particles occur everywhere in the estuary. Diatoms are the most common and are of marine type at the sea-end and freshwater-dominated at river-end stations of the estuary. SPM is characterized by kaolinite-rich and smectite-rich clay mineral suites at the river-end and sea-end stations, respectively. Smectite concentrations increase seawards with the increase in SPM content and are not influenced by salinity. Wind-driven waves and currents, and bio-geochemical processes at the mouth of estuary likely play an important role in the formation of ETM, in resuspension and transformation of SPM into floccules and aggregates, and in their upkeep / removal.

Key words: suspended particulate matter, turbidity maximum, estuarine sedimentation, bio-geochemical processes, clay minerals

*Corresponding author; tele: 091-832-2450505; fax: 091-832-2450609; e-mail: vprao@nio.org

Introduction

The erosion, transport and deposition of fine-grained sediments in estuaries are complex processes and are largely controlled by three influencing factors: estuarine mixing, aggregation (flocculation), and primary particle properties (Edzwald and O'Melia 1975). Estuarine-type circulation and river flow are traditionally considered to be the most important transport processes as they can advect particles out onto the continental shelf, retain sediment within, and/or transport sediments from the continental shelf into estuaries (Postma 1967; Allen et al. 1980; Castaing and Allen 1981; Kennedy 1984; Verlaan et al. 1997; Hossain et al. 2001). Tidal currents can also be effective at moving sediment via tidal asymmetry and/or from areas of higher wave or current energy towards areas of lower energy via settling/scour lag (Brydsten 1992; Sanford 1994; Schoelhamer 2001; Chen et al. 2006; Scully and Friedrich 2007). The effect of wind-induced circulation has received less attention but may also play a role in suspending and advecting sediment in estuaries (Weir and McManus 1987; Pattiaratchi et al. 1997). The efficiency of trapping within the estuary depends on the capacity of an estuary in relation to the rate of sedimentation and energy available for transport. Winterwerp (2002) reported the influence of turbulence on the flocculation process of cohesive sediment and, concentrations of suspended matter on the settling velocity of sediment. The presence of colloids, organic matter and stability of certain minerals with reference to the salinity affects flocculation and rapid settling of minerals (Eisma 1986).

Tropical estuaries of the west coast of India experience seasonal changes in climate and physical oceanographic processes. Rainfall is maximum and rivers carry abundant fine-grained material into the estuaries and coastal regions during the southwest (SW) monsoon (June-September). The intense river flow during this season is counteracted by the strong westerly winds, wind-induced waves and currents, and tides. On the other hand, rainfall between October and May is negligible, and therefore terrigenous sediment discharge is the least. Winds are moderate at this time and are dominated by the sea-breeze cycle. Weak easterly winds prevail during the northeast (NE) monsoon (November to February). The currents in the estuary however are tidally-dominated, and saline waters occur several km upstream from the river mouth during the dry season (Shetye et al. 1995). Thus the channels of the estuary turn from mainly riverine during the SW monsoon to highly saline for several km from the mouth during the remaining eight months. Although the Mandovi has been well characterized in terms of physical oceanography, ecology and contaminants (Shetye et al. 2007), less research has been reported regarding

its suspended particles. The aim of the paper is to report for the first time systematic seasonal variations on the concentrations, constituents and mineralogy of the suspended matter in the Mandovi estuary, Goa, India, and provide insight into the processes that control them.

Study Area and background data

The Mandovi and Zuari rivers (and interconnecting canal) form an important estuarine system on the central west coast of India, in the state of Goa. It is classified as a coastal plain, monsoonal estuary (Shetye et al. 2007). The Mandovi River is ~75 km long with a drainage basin of ~1895 km² (Qasim and Sengupta 1981). The width of the river at the mouth (in the Bay) is ~ 4 km and the average depth is 5 m. The width of the main channel at its mouth is 3.2 km and gets progressively narrower (to 0.25 km) and shallower upstream. The annual rainfall along the course of the river varies considerably from 660 cm at the upstream end of the river in the Western Ghats to 290 cm at Panaji, ~6 km from the mouth of the river (Shetye et al. 2007). Virtually all of the freshwater discharge occurs only during the SW monsoon (see Fig. 2a). The wind speed of ~4-7 ms⁻¹ and tidal range of 2 to 2.5 m were reported (Shetye et al. 1995; Sundar and Shetye 2005). The runoff of the River in the remaining 8 months is almost negligible and the Mandovi estuary increasingly becomes an extension of sea (Shetye et al. 2007). During these 8 months, the wind field is dominated by sea breeze (Neetu et al. 2006) with strongest sea breezes from February–May (see Fig. 2b). The currents in the estuarine channel are primarily tidal and continue to be so until the onset of the next SW monsoon. Moreover, industrial and mining activities are at a peak during October-May at several points along the estuary and discharge nutrients, heavy metals and other pollutants in the form of organic and inorganic industrial waste into the estuary (Alagarsamy 2006; Ramaiah et al. 2007). The daily to-and-fro traffic of numerous mechanized fishing boats and barges carrying Fe-Mn ores may induce some additional turbidity within the estuarine system. The human-induced activities may therefore affect the energy conditions and fauna of the estuary and play an important role in perturbing the health of the estuary.

The Mandovi River drains through the Western Ghats, which is part of The Western Dharwar Craton (WDC) of Meso-archaeon age. The WDC is predominantly made up of greenstone belts and tonalite-trondhjemite gneisses and is characterized by high-Mg basalts and komatites with metavolcanics and meta-sedimentary rocks. The main constituents are mafic and ultramafic volcanic rocks, arenites, phylites, polymictic and oligomictic conglomerates, greywackes, banded iron formations

and carbonates (Naqvi 2005). The rocks weather under humid tropical conditions and are extensively ferruginized with thick lateritic cappings.

Materials and Methods

Two types of data were collected in the Mandovi estuary under the framework of the ‘Mandovi Monsoon Experiment 2007’, conducted during June 2007–May 2008. (i) Salinity data and surface waters were collected every day at one station in the mid-channel of the Mandovi estuary from June to September, 2007. This station is referred to here as the “regular” station, which is located ~6.3 km away from the mouth of the Mandovi River (Fig. 1). (ii) Salinity data, surface water and bottom sediments were also collected fortnightly at 5 stations along the main channel of the Mandovi estuary (hereafter referred to as “transect” stations) during June-September 2007, using a mechanized boat. From October 2007 to May 2008, stations towards the river-end of the estuary were added in such a way that the last station sampled on the day of collection would be where the salinity of the surface waters was ≤ 5 ‰. Surface waters and their salinity were also collected at 6 sea-end stations along the main channel during January – May 2009 in order to verify the repeatability of SPM at these stations.

Five liters of surface water collected at each station were filtered through 0.4 μm Millipore filter paper. Three filter papers were used for each station and the SPM retained on filter papers was dried and weighted. SPM is expressed as mg/l. Of the 3 filter papers, the SPM on one filter paper was used for identifying constituents and the second for mineralogy. The SPM on filter paper was examined under a binocular microscope and scanning electron microscope (SEM) in order to identify the constituents. The SPM collected on filter paper was transferred carefully to a 50 ml beaker and rendered free of organic matter and carbonate by using acetic acid and H_2O_2 , respectively. They were thoroughly washed to remove excess acid and concentrate the SPM. Oriented clay slides were prepared by pipetting concentrated solution onto glass slides and allowed to dry in air. These slides were glycolated at 100 °C for 1 h, and X-ray diffraction studies were carried out on a Philips X-ray diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation. The instrumental settings, mineral identification and semi-quantitative clay mineralogy are same as that detailed in Biscaye (1965) and Rao and Rao (1995).

Results

VARIATIONS IN THE CONCENTRATIONS OF SPM AND SALINITY

The distribution patterns of SPM collected along transect stations of the estuary (Fig. 3a-b) reveal a gradual increase in the concentrations of SPM from river-end to sea-end stations of the estuary both during the monsoon and non-monsoon months. Higher concentrations of SPM generally occur at sea-end stations of the estuary in June-September (SW monsoon months) when river discharge is the highest (Fig. 2a; Fig. 3a). The salinity gradient between sea-end and river-end stations is high in June, decreases gradually, and is the least during September (Fig. 3b). Highest concentrations of SPM coincide with salinities of 10- 20‰ at sea-end stations during this period. SPM is significantly lower at all stations during October –January and the lowest concentrations of SPM occur in November. The salinity of the waters at sea-end stations quickly return to ~30‰ immediately after the monsoon (see October) and increase gradually within the estuary from October to May (Fig. 3a). Low concentrations of SPM at sea-end stations along with high salinities occur during October-November. The concentrations of SPM at sea-end stations again increase during February – May (non-monsoon months) when river discharge is the least. The SPM concentrations at sea-end stations are often two to four times greater than those at the river-end during this period (Fig. 3a-b). Changes in salinity at different stations are much sharper than that of SPM concentrations during most of the year. The salinity gradient between the sea-end and river-end stations is relatively steeper during February / March and gentler during April / May. Highest concentrations of SPM, however, coincide with high salinity (32 to 34‰) during February- May at the sea-end stations.

CONSTITUENTS OF SPM

The SPM at sea-end stations during the SW monsoon exhibits the least differences in grain size or foreign material. The SPM at sea-end stations shows rounded and irregular floccules and fine fragments of carbonate shell material. Scanning electron microscope (SEM) images show that floccules of 50-60 μm size are abundant at the seaward stations (Fig. 4a-b). Several individual floccules may also become aggregated and become larger and denser (Fig. 4c-e). Floccules adhered to diatom frustules can be seen in Figs. 4f-h. The aggregates consist of clay particles, diatoms, organic and faecal pellet material and occur as irregular to elongated particles (Fig. 4g-h). Diatoms are the most common and

show evidences of dissolution when admixed with clays. Both centric and pennate diatoms are present. When floccules / aggregates are abundant, especially in June and February, the identification of diatoms at sea-end stations is restricted to genera level and includes marine centric (*Thalassiosira* sp., *Coscinodiscus* sp., *Triceratium* sp., *Skeletonema* sp., *Actinoptychus* sp., *Chaetoceros* sp. *Amphora* sp.) and pennate (*Nitzschia* sp.) diatoms. The marine diatoms dominated by *Chaetoceros curvisetus*, *Skeletonema costatum*, *Thalassiosira* sp. *Thalassionema nitzschioides*, and *Fragilariopsis* sp. occur at sea-end stations in November/April.

Floccules and irregular to rounded or elongated fine-sediment aggregates also occur at river-end stations of the estuary (Fig. 5a-d). They are, however, fewer and more loosely structured than those at the sea-end. Freshwater diatoms (*Cyclotella stelligera*, *Diploneis* sp. and *Cymbella* sp.) are dominant together with a few marine (*Coscinodiscus* sp., *Nitzschia* sp. and *Amphiprora* sp.) diatoms at the river-end of the estuary. Abundant faecal pellet materials together with *Coscinodiscus* sp. (Fig. 5e-f) are characteristic of SPM in Cumbarjua canal (station 5), 18 km away from the river mouth. Iron and manganese ores are handled extensively at stations 6 (Sarmanas) and 6a (Ammona), which are about 23 and 27 km, respectively away from the river mouth. The SPM at these points showed aggregation of fine-grained materials together with micro-filaments (Fig. 5g) and floccules adhered to diatoms (Fig. 5h). Marine diatoms (*Coscinodiscus radiates*, *Skeletonema costatum*, *Nitzschia* sp., *Chaetoceros* sp., *Thalassiosira* sp.) dominate along with a few freshwater diatoms (*Cyclotella stelligera*) at these stations.

MINERALOGY OF THE SPM

Regular station

The various SPM samples contain kaolinite, illite, smectite and chlorite as clay minerals and gibbsite, goethite and quartz as non-clay minerals. The proportions of clay minerals, however, change with the concentrations of SPM. Kaolinite is the dominant clay mineral, followed by traces of illite, smectite and chlorite at low SPM concentrations. The proportions of smectite and illite increase from traces to 35% and 20%, respectively, with an increase in SPM from 4 mg/l to 58 mg/l in June during which the salinities range between 11.5 and 34‰ (see Fig. 6a; Table 1). In July and August, the salinities of the surface waters at the regular station vary between 0.05 ‰ and 29‰ on different days. High kaolinite, illite, gibbsite and goethite and traces of smectite and chlorite are present at high SPM concentrations and low salinities (see July and August in Fig. 6a; Table 1). Fig. 6b shows that the

increase in salinity has no effect on the overall concentrations of smectite, illite and chlorite, as long as SPM concentrations remain low (<10 mg/l). Kaolinite followed by illite and traces of smectite are present at low salinities and low SPM (Table 1). Smectite content increases to 30% with an increase in SPM content to >10 mg/l and salinity to >13‰ (Fig. 6b). Although gibbsite and goethite are present in all samples, their reflections become prominent at very high SPM concentrations and low salinities (see July and August in Fig. 6a).

Transect stations

Kaolinite, followed by minor illite, chlorite, gibbsite and goethite along with traces of smectite, are present at the river-end stations of the estuary, where SPM concentrations and salinities are low (Table 2). Smectite content increases gradually seaward, is high at sea-end stations, and corresponds with an increase in SPM and salinities (Fig. 7; Table 2). The salinity of the surface water varies only between 0.04 and 0.42‰ at different stations during the peak monsoon day in August (see Table 2). Despite minor salinity change, smectite content increases from traces at the river-end to 20% at the sea-end and is correlated with the increase in SPM concentrations from 10 to 38 mg/l (see Fig. 7; Table 2). SPM concentrations in November range between 1.5 mg/l to 4.4 mg/l, with higher values at the river-end (Table 2). SPM is dominated by kaolinite and minor illite and chlorite at river-end stations and by trace concentrations of all clay minerals at sea-end stations (Table 2). However, from February to April, high kaolinite, illite and chlorite, with traces of smectite at river-end stations, and increased smectite (upto 35%) and kaolinite and illite are present at sea-end stations (Fig. 7; Table 2).

Discussion

SPM CONCENTRATIONS, TURBIDITY MAXIMUM AND SOURCES OF SEDIMENTS

The SPM concentrations at the sea-end stations are notably greater than those at the river-end during two different periods, namely June – September and February- April (Fig. 3a). This is contrary to the usual distribution of SPM in estuaries, i.e., a decrease of SPM from the river-end to sea-end, and may suggest that the sea-end part of the channel represents an unusual estuarine turbidity maximum (ETM). The ETM is a well known feature in a large number of estuaries through out the world (Schubel 1968; Buller 1975; Festa and Hansen 1978; Allen et al. 1980; Officer 1980; Schubel and Kennedy 1984; Le Bris and Glemarec 1996; Grabemann et al. 1997; Chen et al. 2005; McManus 2005). The magnitude

and location of the ETM has been shown to depend upon the settling velocity of the sediment, the amount of sediment introduced at both the ocean and river source, and the nature of estuarine circulation and tidal resuspension (Festa and Hansen 1978).

The ETM of June-September is present far downstream and is associated with relatively low salinities and high river discharge (Fig. 3a). The average wind speed calculated for 5 h before sampling on that day was used for correlation. The wind speed measured during June-September 2007 ranged between 5.1 and 5.6 ms^{-1} (Fig. 2b). Moreover, the wind speed is strongly correlated ($r=0.98$) with the concentrations of SPM (Fig. 8a). The tidal range varies between 2 to 2.5 m during this period (Shetye et al. 1995). The formation of the sea-end ETM can be explained by resuspension due to the combined effects of strong westerly winds, wind-induced waves and currents, and stirring by tidal currents, with seaward moving river flow concentrated at the surface. A combination of landward advection by estuarine-type circulation and landward directed settling /scour lag away from high energy winds and waves favored movement of sediment up the estuary.

In contrast to the June-September ETM, the SPM concentrations during October-November are low seaward and marginally high at river-end stations (Fig. 3a). River discharge is negligible (Fig. 2a), and weak easterly winds with a speed of 1.8 to 2.6 ms^{-1} prevail during this period. A moderate negative correlation ($r= -0.66$) exists between wind speed and concentrations of SPM (Fig. 8b). The absence of convergent transport processes or strong resuspension at the sea-end (negligible river discharge and weak winds) and rapid intrusion of salt water into the estuary may have suppressed turbulence, as was reported by Hamblin (1989) and Geyer (1993), while estuarine-type circulation continued to favor up-estuary sediment transport. The low SPM concentrations at sea-end stations in October and November (Fig. 3a) further suggest that the fine-grained sediments that remained in suspension may have settled in association with the return of salinity of $\sim 30\%$ immediately after the SW monsoon.

The ETM occurring in February-April 2008 and February – May 2009 at the sea-end stations is conspicuous and coincides with salinities of 25-35‰ and negligible river discharge. Therefore this ETM is not simply related to the one usually reported in the literature at the estuarine freshwater- seawater interface. The occurrence of ETM is an annual phenomenon, as seen in 2008 and 2009 (Fig. 3a-b). The wind during this period is dominated by sea breeze (Neetu et al. 2006) and blows NW and SW directions at a speed of 3.2-3.7 ms^{-1} . A positive correlation ($r = 0.54$ to 0.8) exists once again between

wind speed and concentrations of SPM (Fig. 8c). Several workers have reported the impact of wind (Weir and McManus, 1987), tidal currents (Geyer 1993; Scully and Friedrichs 2007) and sea breeze (Pattiaratchi et al. 2007) causing sediments to resuspend and generate turbidity maxima in other estuaries. As weak tidal currents (2-2.5 m range) prevail in this region, it is likely that this ETM is caused by the impact of a stronger sea breeze and wind-induced waves near the mouth of the estuary, resulting in sediments being resuspended from the bottom and/or transport of wave-suspended oceanic sediments into the estuary.

The river discharge is maximum during the SW monsoon (June-September) but negligible during NE monsoon (October-January) and pre-monsoon (February-May). High SPM is a persistent seaward deposit during February – May (Fig. 3a-b). The salinity vs. SPM plot (Fig. 3c) indicates that SPM is skewed landward. Although both salinity and SPM decrease progressively from sea-end to river-end of the estuary, the decrease in SPM concentrations can be seen at salinities $>15\text{‰}$ and, SPM concentrations are low and consistently uniform at salinities $<15\text{‰}$. Waves and tidal currents contribute to a process of diffusive transport of sediment, which in turn depends on settling velocity of particles and concentrations of SPM in the water. The weak tidal currents (2 to 2.5 m range) prevailing in the estuary may not be sufficient enough to export sediment farther landward from the deposit. The maximum SPM concentration during February-May is up to 35 mg/l (Figs. 3a-b). As high SPM during this period is largely due to resuspension of bottom sediment, particle sizes in resuspended sediments must be larger and could have settled faster. Therefore the impact of sediment by horizontal diffusive transport can only be seen closer to the deposit. Ross and Mehta (1991) suggested that the free settling velocity of cohesive sediment occurs at the low SPM concentrations of <0.4 g/l, the enhanced settling at moderate concentrations $0.4 - 2$ g/l and the hindered settling at the high concentrations >2 g/l.

SEDIMENTARY PROCESSES IN THE ESTUARY

The constituents in the SPM provide insight into the processes operating in the estuary. Broken fragments of carbonate skeletal are most probably derived from resuspension of bottom sediments. Pennate diatoms and diatom frustules (Fig. 4g) and elongated aggregates (Fig. 4f) may also support resuspension. Marine centric planktonic diatoms may indicate biological productivity. Sharp et al. (1984) suggested that the peak production of phytoplankton in the estuary coincides with large dilution of seawater which is often associated with enrichment of nutrients. Diatoms are associated with

aggregates both at the sea-end and river-end stations of the estuary (Fig. 4e-h; Fig. 5b, 5d). Zimmermam-Timms et al. (1998) studied the seasonal dynamics of aggregates and suggested that larger aggregates were found in the presence of diatoms. The aggregates are usually rich in nutrients and enhance colonization and subsequent growth of organisms. Microbial filaments associated with aggregates (Fig. 5h) indicate the role of organic matter associated with bacterial surfaces. Bacterial mediation in sedimentation was noted by Zabawa (1978), who showed that bacteria by attaching to suspended solids secrete a mucus slime of a sticky polysaccharides that not only holds particulates together (see Fig. 5g), but also traps isolated mineral grains as they colloid with agglomerated particles (see Biggs and Howell 1984). Pelletization of fine-grained material into agglomerated faecal pellets (Fig. 5e-f) is a distinct process and suggests the effect of filter-feeding organisms in the packaging or biological mediation in sedimentation of particles. In other words, biological and biogeochemical processes appear active in sedimentation and trapping sediment particulates. Floccules and aggregates enclosing benthic diatoms are found both at the sea-end (Fig. 4h) and river-end (Fig. 5c-d) of the estuary, indicating that resuspension of bottom sediments is an important process everywhere in the estuary.

Diatoms of a marine type at the sea-end and a freshwater-dominated type at river-end of the estuary reflect the dominant water masses in those regions. However, aggregates consisting of dominant marine type diatoms, both benthic (*Coscinodiscus radiates*, *Nitzschia sp.*) and planktonic type (*Skeletonema costatum*, *Chaetoceros sp.*, *Thalassiosira sp.*) with a few freshwater diatoms (*Cyclotella Stelligera*) are present at 23-27 km from the river mouth. The mixed species in SPM may suggest reworking of earlier deposited sediments in the channel. Intrusion of salt water by tidal flows and shallow depths in the upstream of the river probably enabled resuspension, early flocculation and aggregation of particulates. We therefore suggest that the particulate matter is subjected to flocculation and co-aggregation processes everywhere in the estuary, and sediments accumulate largely within the estuary during this period.

COMPOSITION AND SOURCES OF CLAY MINERALS

Two clay mineral suites, kaolinite-dominated at the river-end and smectite-dominated at the sea-end, are evident (Fig. 6-7; Table 1-2). Kaolinite, the major clay mineral, is found along with gibbsite in all samples at the river-end. Kaolinite and gibbsite are considered as proxy indicators of the products of

intense chemical weathering of the hinterland rocks under tropical conditions (Chamley 1989). Relatively high illite and chlorite at river-end stations and their decrease at seaward stations of the estuary (Table 2) point out that these minerals are also transported from the hinterland. The hinterland is a mountainous region (Western Ghats), composed of Western Dharwar Craton with gneissic and schistose rocks and ferruginized lateritic cappings (Naqvi 2005). Therefore, one would expect abundant kaolinite and gibbsite (Chamley 1989) along with residual illite, chlorite and goethite be the weathering products and be transported by the river, as seen at the river-end stations in the present study.

The sources of smectite are less clear. The very high SPM of 158 mg/l and 129 mg/l in July and August, respectively correspond to the active spells of high rainfall and low salinity (0.05‰) of surface waters. This SPM contains largely kaolinite, gibbsite and goethite (see XRD profiles of July and August in Fig. 6a) and implies that the Mandovi River contributed trace quantities of smectite during the monsoon. This statement is augmented by the mineralogy of the SPM of transect stations, which showed trace quantities of smectite at the river-end stations during the peak monsoon (Fig. 7; Table 2).

Smectite proportions are low both at high or low salinities, provided the total SPM is <10 mg/l (Fig. 6b). Smectite reflections increase with the increase in SPM to >10 mg/l or more. Despite the fact that the salinity variations are only minor (0.04 - 0.4‰) at different stations (see August in Table 2), smectite content increases seaward with increase in SPM, which is notably larger at sea-end stations (Fig. 7). This suggests that the concentrations of smectite are more influenced by the amount of SPM and processes operated at sea-end of the estuary, rather than the salinity of the waters.

Smectite proportions increase with the increase in SPM in June, when the surface waters are largely saline (31.5 - 34‰) (Fig. 6a; Table 1). High SPM coinciding with moderate to high salinities at seaward stations in June-September were attributed to the development of an estuarine turbidity maximum (see above). The increase in smectite content may therefore be due to its resuspension from bottom sediments in the estuary or transport of smectite from offshore.

Chemical alteration, flocculation and size segregation of clay minerals have been suggested to influence the along-estuary distribution of clay minerals. Smectite chemically alters to illite and chlorite with time (Whitehouse and McCarter 1958). In other words, chemical alteration decreases smectite content. As SPM reflects the present day conditions and there are no diagenetic changes expected over short period in modern sediments (Grim 1968), chemical alteration does not explain the increased

smectite at sea-end stations (Fig. 7). Differential flocculation, i.e., rapid flocculation of kaolinite and illite at lower salinities and smectite flocculation over a much wider salinity range, is a possible mechanism for along-estuary variations in clay minerals, based on laboratory experiments using kaolinite, illite and smectite (Whitehouse et al. 1960). Our SEM study on suspended matter shows the presence of floccules and aggregates both at the river-end and sea-end stations (Figs. 4-5).

Smectite was found to be low both at low and high salinities (Fig. 6b), suggesting salinity influence is insignificant on smectite content. Evidence for differential flocculation has not been reported in natural environments. Since flocculation is related to the degree of turbulence, it has been suggested that flocculation processes do not differentiate between materials by composition (Manheim and Hathaway 1972). Gibbs (1977) proposed that physical sorting by size is responsible for along-estuary variations in clay minerals. As the grain size of smectite is smaller than that of kaolinite and illite, smectite tends to remain in suspension longer and selectively winnows farther from its source (Gibbs 1977). Moreover, smectites have relatively high surface area and thus bond with organic compounds with greater intensity than the other clay minerals (Hedges 1978; Degens and Ittekkot 1984). As a consequence, optimum aggregation occurs with this mineral. Aggregation or flocculation processes would be effective only when smectite is present in the waters. Since trace quantities of smectite are transported through river discharge (Table 2), smectite resuspended from bottom sediments and/or transported from offshore perhaps could be the primary source of smectite. Bottom sediments indeed showed high smectite content at the sea-end of the estuary, and its concentrations decrease towards the river-end (Bukhari and Nayak 1996; our unpublished data). Resuspension of bottom sediments during the development of the turbidity maximum may have enhanced smectite concentrations. Abundant floccules seen at the sea-end stations indicate bio-geochemical processes (flocculation, coagulation, productivity) are active in the turbidity maximum.

Smectite is the dominant clay mineral in the sediments of the continental shelf north of Goa (Rao and Rao 1995). Although the southerly surface currents and westerly winds prevailing along the margin during the SW monsoon and the sea breeze with wind speeds of 3.2 to 3.8 ms⁻¹ during the pre-monsoon would facilitate transportation of smectite into the estuarine region, available hydrographic data and/or data presented here do not provide sufficient evidence for existence of this process. More work is required to confirm the same.

Conclusions

Knowledge on the concentrations of SPM and their transport and fate in dynamic environments such as estuaries is of vital importance in their management with respect to the maintenance of fairways and harbor development, their turbulence and water quality and the suitability of habitats to numerous species. The concentrations of SPM vary in time and space and are largely affected by river discharge, settling velocities of sediment, flocculation and resuspension of sediments. Turbidity plays an important role in maintaining 'health of the estuary'. If turbidity exceeds 1g/l, oxygen concentrations deplete and correspond to hypoxic conditions and may have deleterious effects on macrofauna. High SPM in the Mandovi estuary is a persistent seaward deposit. The highest concentration of SPM in the turbidity maxima is 35 mg/l. The estuarine turbidity maximum occurs at sea-end stations during the two windiest times of year, June-September and February-May, suggesting the role of winds in its formation. SPM comprising of floccules, aggregates and faecal pellets occurs everywhere in the estuary. The sources of high smectite at sea-end stations are not clear. Resuspension of fine-grained material appears to be an important process in the estuary during the pre-monsoon and monsoon.

ACKNOWLEDGEMENTS

We thank Dr. S. R. Shetye, the Director, National Institute of Oceanography, Goa, for his keen interest on the 'Mandovi Monsoon Experiment', discussions and making us available the manuscript in communication. Dr. Dilepkumar provided funds for Project Assistant from the Project 'SIP 1308'. Dr. Smita Mitbhavkar identified diatoms and helped us in discussions. Shri. D. Sundar and G.S. Michael organized boat cruises fortnightly and provided salinity data. Mr. Girish Prabhu helped us with X-ray diffraction analyses. We thank Prof. Carl Friedrichs, VIMS, USA for the critical and constructive review and two anonymous reviewers for offering several comments on our earlier manuscript. We thank Prof. James Cloern, Editor, Estuaries and Coasts for patience and valuable comments on our paper.

LITERATURE CITED

- Alagarsamy, R. 2006. Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. *Estuarine, Coastal and Shelf Science* 67: 333-339
- Allen, G. P., J. C. Salmon, P. Bassoullet, Y. Du Penhoat, and C. De Grand, 1980. Effects of tides on mixing and suspended sediment transport in macrotidal estuaries. *Sedimentary Geology* 26: 69-90.
- Biggs, R. B., and A. A. Howell, 1984. The estuary as a sediment trap: alternate approaches to estimating its filtering efficiency. In: *The estuary as a filter*, ed. V.S. Kennedy, 107-130, Academic Press, New York.
- Biscaye, P. E. 1965. Mineralogy and sedimentation of recent deep sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geological Society of America Bulletin* 76: 803-831.
- Brydsten, L. 1992. Wave-induced sediment suspension in the Ore estuary, northern Sweden. *Hydrobiologia* 235/236: 71-83.
- Bukhari, S.S. and G. N. Nayak, 1996. Clay minerals in identification of provenance of sediments of Mandovi estuary, Goa, west coast of India. *Indian Journal of Marine Sciences* 25: 341-345.
- Buller, A. T. 1975. Sediments of the Tay estuary II formation of ephemeral zones of high suspended sediment concentration. *Proceedings of the Royal Society of Edinburgh* 75B: 65-89.
- Castaing, P. G. and P. Allen, 1981. Mechanisms controlling seaward escape of suspended sediment from the Gironde. A macrotidal estuary in France. *Marine Geology* 40: 101-118.
- Chamley, H. 1989. *Clay Sedimentology*, Springer-Verlag, Heidelberg, 623 p.
- Chen, M. S., S. Wartel, B. V. Eck, and D. V. Maldegam, 2005. Suspended matter in the Scheldt estuary. *Hydrobiologia* 540: 79-104.
- Chen, S-L., G-A. Zhang, S-L. Yang and J.Z. Shi. 2006. Temporal variations of fine suspended sediment concentrations in the Changjiang River estuary and adjacent coastal waters, China. *Journal of Hydrology* 331: 132-145.
- Degens, E. T. and V. Ittekkot, 1984. A new look at clay-organic interactions, In Nord-Sud profil, Zentraleuropa-Mittelmeerraum Afrika, Mitteilungen aus dem Geologisch-Paleontologischen, ed. F. G. Knetsch, Heft 56, 229-248, Institute der Universitat Hamburg.
- Edzwald, J. K. and C. R. O'Melia, 1975. Clay distribution in recent estuarine sediments. *Clays and Clay minerals* 23: 39-44.
- Eisma, D. 1986. Flocculation and deflocculation of suspended matter in estuaries. *Netherlands Journal of Sea Research* 20, 183-199.

- Festa, J. A. and D. V. Hansen, 1978. Turbidity maxima in partially mixed estuaries: A two dimensional numerical model. *Estuarine Coastal Marine Science* 7: 347-359.
- Geyer, W. R. 1993. The importance of suppression of turbulence by stratification on the estuarine turbidity maximum. *Estuaries* 16: 113-125.
- Gibbs, R. J. 1977. Clay mineral segregation in the marine environment. *Journal of Sedimentary Petrology* 47: 237-243.
- Grabemann, I., R. J. Uncles, G. Krause and J. A. Stephens, 1997. Behaviour of turbidity maxima in the Tamar (U.K.) and Weser (F.R.G.) estuaries. *Estuarine, Coastal and Shelf Science* 45, 235-246.
- Grim, R. E. 1968, Clay mineralogy, McGraw Hill, New York 468 p.
- Hamblin, P. F. 1989. Observations and model sediment transport near the turbidity maximum of the Upper Saint Lawrence Estuary. *Journal of Geophysical Research* 94, 14419-14428.
- Hedges, J. I. 1978. The formation and clay mineral reactions of melanoidins. *Geochimica et Cosmochimica Acta* 42: 69-76.
- Hossain, S. B. Eyre and D. McConchie. 2001. Suspended sediment transport dynamics in the sub-tropical micro-tidal Richmond River estuary, Australia. *Estuarine, Coastal and Shelf Science* 52: 529-541.
- Kennedy, V. S. 1984. *The estuary as a filter*, Academic Press, New York, 511 p. .
- Kranck, K., 1984. The role of flocculation in the filtering of particulate matter in estuaries, In *The estuary as a filter*, ed. V.S. Kennedy, 159-167. Academic Press, New York.
- Le Bris and M. Glemarec, 1996. Marine and brackish ecosystems of south Brittany (Lorient and Vilaine Bays) with particular reference to the effect of the turbidity maxima. *Estuarine, Coastal and Shelf Science* 42, 737-753.
- Manheim, F. T. and J. C. Hathaway, 1972. Suspended matter in surface water of the northern Gulf of Mexico. *Limnology and Oceanography* 17: 17-27.
- McManus, J., 2005. Salinity and suspended matter variations in the Tay estuary. *Continental Shelf Research* 25: 729-747.
- Naqvi, S. M., 2005. *Geology and evolution of the Indian Plate (from Hadean to Holocene – 4 Ga to 4 Ka)*. Capital publishing company, New Delhi, 450 pp.
- Neetu, S., S. R. Shetye, and P. Chandramohan, 2006. Impact of sea breeze on wind-seas off Goa, west coast of India. *Journal of Earth System Science* 115, 229-234.

- Officer, C. B., 1980. Discussion of the turbidity maximum in partially mixed estuaries. *Estuarine, Coastal Marine Science* 10: 239-246.
- Pattiaratchi, C B., B. Hegge, J. Gould, and I. Eliot, 1997. Impact of sea-breeze activity on nearshore and foreshore processes in southwestern Australia. *Continental Shelf Research* 17, 1539–1560.
- Postma, H. 1967. Sediment transport in the estuarine environment. In: Estuaries, ed. G. H. Lauff, American Association for Advancement of Science, Washington, D.C. Publication 83, 158-179
- Qasim, S. Z., and R. Sengupta, 1981. Environmental characteristics of the Mandovi-Zuari estuarine system in Goa. *Estuarine, Coastal and Shelf Science* 13: 557- 578.
- Ramaiah, N., V. Rodrigues, E. Alvares, C. Rodrigues, R. Baksh, S. Jayan and C. Mohandas. 2007. Sewage pollution indicator bacteria. In; *The Mandovi and Zuari estuaries*, eds. S.R.Shetye, M. Dileep Kumar and D. Shankar, National Institute of Oceanography, Goa, India. 115-120.
- Rao, V. P., and B. R. Rao, 1995. Provenance and distribution of clay minerals in the continental shelf and slope sediments of the west coast of India. *Continental Shelf Research* 15: 1757-1771.
- Ross, M. A., and J. A. Mehta, 1991. Fluidization of Soft Muds by Waves. In: *Microstructure of Fine-Grained Terrigenous Marine Sediments from Mud to Shale*, eds. R. H. Bennett, W. R. Bryant, and M. H. Hulbert, Frontiers in Sedimentary Geology, Springer Verlag,
- Schubel, J. R., 1968. Turbidity maxima of the northern Chesapeake Bay. *Science* 161: 1013-1015.
- Schubel, J. R., and V. S. Kennedy, 1984. The estuary as a filter: an introduction, In: *The estuary as a filter*, ed. V.S. Kennedy, 1-14. Academic Press, New York,.
- Schoelhamer, D.H., 2001. Influence of salinity, bottom topography and tides on locations of estuarine turbidity maximum in northern San Francisco Bay. In: *Coastal and estuarine fine sediment transport processes*, eds. Mc Anally, W.H. Mehta A.H., Elsevier Science B.V. 343-357.
- Sanford, L.P. 1994. Wave-forced resuspension of upper Chesapeake Bay muds. *Estuaries* 17: 148-165.
- Scully, M. E. and C.T. Friedrichs, 2007 Sediment pumping by tidal asymmetry in a partially mixed estuary. *Journal of Geophysical Research* 112: CO7028, doi 10: 1029/2006 JC003784.,
- Sharp, H. H., J. R. Pennock, T. M. Church, J. M. Tramontano, and J.M., Cifuentes, 1984. The estuarine interaction of nutrients, organics, and metals: A case study in the Delaware estuary, In: *The estuary as a filter*, ed. V.S. Kennedy, 241-260. Academic Press, New York. .
- Shetye, S. R., A. D. Gouveia, S. Y. S. Singbal, C. G. Naik, D. Sundar, G. S. Michael, and G. Nampoothiri, 1995. Propagation of tides in the Mandovi – Zuari estuarine network. *Proceedings of Indian Academy of Sciences (Earth and Planetary Sciences)* 104: 667-682.

- Shetye, S. R., M. D. Kumar, and D. Shankar, 2007. *The Mandovi and Zuari estuaries*. National Institute of Oceanography, Goa. 145 p.
- Sundar, D., and S. R. Shetye, 2005. Tides in the Mandovi and Zuari estuaries, Goa, west coast of India. *Journal Earth System Science* 114: 493-503.
- Verlaan, P.A., M. Donze, P. Kuik, 1997. Marine vs. Fluvial suspended matter in the Scheldt estuary. *Estuarine, Coastal and Shelf Science* 46: 873-883.
- Winterwerp, J. C. 2002. On the flocculation and settling velocity of estuarine mud. *Continental Shelf Research* 22, 1339-1360.
- Weir, D. J. and J. McManus, 1987. The role of wind in generating turbidity maxima in the Tay estuary. *Continental Shelf Research* 7, 1315-1318.
- Whitehouse, U. G. and R. S. Mccarter, 1958 Diagenetic modification of clay minerals in artificial seawater. *Clays and Clay minerals National Academy of Sciences, National Reserch Council Publication* 566, 81-119.
- Whitehouse, U. G., L. M. Jeffrey, and J. D. Debrecht, 1960. Differential settling tendencies of clay minerals in saline waters, In *Clays and Clay minerals, 5th National Conference on clay and clay minerals*, 81-119. Pergamon, Oxford.
- Zabawa, C. F., 1978. Microstructure of agglomerated suspended sediments in Northern Chesapeake Bay estuary. *Science* 20: 49-51.
- Zimmermam-Timms, H., H. Holst, and S. Muller, 1998. Seasonal dynamics of aggregates and their typical Biocoenosis in the Elbe estuary. *Estuaries* 21: 613-621.

Figure captions

Fig. 1. Location map of the Mandovi River and sampling stations (numbers 1-10) along the estuary.

Fig. 2. (a) Annual runoff computed over 1981-1998 into the main channel of the river (after Shetye et al. 2007), (b) Wind speed (ms^{-1}) during 1 May 2007 to 31 May 2008. Horizontal axis gives 24 h running average and vertical axis gives wind speed.

Fig. 3. Seasonal distribution of SPM (histograms) and salinity (line) along transect stations during June 2007 – May 2008 (a), and January 2009 – May 2009 (b). Numbers 1 - 10 correspond to stations shown in Figure 1. (c) A plot on Salinity vs. SPM.

Fig. 4. Scanning electron microscope photographs of SPM at sea-end stations 1 and 2 of the estuary. (a) Low magnification photo showing abundant floccules, (b) large floccules together with diatom; (c), (d) and (e) aggregation of floccules in different months; (f) elongated aggregate together with diatoms; (g-h) floccules adhered to diatom frustules.

Fig. 5. Scanning electron microscope photographs of SPM from river-end stations (a-d) and from station 5, 6 and 6a (e-h). (a-d) floccules and aggregates together with centric and pennate diatoms. (e) Faecal pellets and centric diatoms, (f) High magnification photo of faecal pellet, (g) Aggregate with microbial filaments (top right); (h) Floccules adhered to marine diatom.

Fig. 6. X-ray diffractograms of the SPM collected at the regular station in June 2007 (a) and August 2007 (b), arranged with increasing SPM. S-smectite, K-kaolinite, Ch-chlorite, I-illite, Gi-gibbsite and Go-goethite.

Fig. 7. Smectite distribution in suspended matter along the transect stations. Numbers 1 - 5 correspond to stations shown in Figure 1.

Fig. 8. Correlation between wind speed and SPM concentrations during (a) June to September 2007, (b) October 2007 to January 2008 and (c) February –April 2008 and February – May 2009. The average wind speed calculated for 5 h before sampling on that day was used for correlation.

Table 1: Distribution of major clay minerals along with salinity and suspended particulate matter (SPM) concentrations at the 'regular station' on different dates of June-August 2007.

Regular Station	Salinity (‰)	SPM (mg/l)	Clay Minerals			
			S (%)	K (%)	I (%)	Ch (%)
08.06.07	31.8	3.9	8	30	46	14
21.06.07	11.5	7.5	23	33	28	15
15.06.07	33.9	32	27	42	19	13
17.06.07	31.5	58	25	37	22	16
06.08.07	0.05	129	8	67	18	7
09.07.07	0.05	158	5	71	21	3
20.08.07	2.1	5.7	13	44	38	6
18.08.07	5.9	6.7	12	44	31	13
14.08.07	13	13	23	48	20	9
26.08.07	27	5.7	22	42	27	9
28.08.07	29	11	20	37	31	12

S- smectite, K kaolinite, I-illite and Ch-chlorite

Table 2: Distribution of major clay minerals along with salinity and suspended particulate matter (SPM) concentrations at the 'transect stations' from June 2007 to May 2008.

Month	Stations	Salinity	SPM	Clay Minerals			
		(‰)	(mg/l)	S (%)	K(%)	I (%)	Ch(%)
June '07	1	21.6	20.0	16	33	31	20
	2	15.7	19.8	11	35	35	19
	3	13.5	5.3	7	37	35	13
	4	6.1	0.3	4	49	39	8
	5	10.9	0.3	3	45	32	20
July '07	1	19.2	8.3	16	53	23	8
	2	17.9	5.2	19	56	17	8
	3	16.1	--	16	59	19	6
	4	7.4	3.5	8	41	43	8
	5	7.4	0.1	8	45	37	10
August '07	1	38.1	0.4	13	63	17	7
	2	21.4	0.2	11	69	13	7
	3	9.5	0.1	7	41	46	11
	4	6.4	0.1	3	51	40	6
	5	9.6	0.0	6	71	20	3
September '07	1	4.5	8.7	10	39	32	19
	2	1.0	8.9	8	45	29	17
	3	0.1	9.8	4	53	26	17
	4	0.1	5.4	6	58	29	8
	5	0.1	5.4	3	67	16	14

	1	28.8	2.5	6	34	49	11
October '07	2	19.1	2.5	8	33	52	7
	3	13.9	3.9	5	27	54	15
	4	3.6	3.3	4	28	60	8
	5	2.4	3.2	5	32	50	13
	1	31.4	1.5	7	35	41	17
November '07	2	22.3	2.9	7	38	36	19
	3	16.2	2.4	6	31	43	20
	4	5.5	3.8	3	40	33	24
	5	4.1	4.2	7	41	38	14
	1	29.5	8.7	14	43	30	12
December '07	2	27.9	4.5	6	36	36	23
	3	23.2	5.9	6	52	26	15
	4	13.3	4.4	8	33	33	26
	5	14.2	4.6	2	34	56	8
	1	33.1	5.8	11	31	39	19
	2	31.5	9.9	6	38	40	16
January '08	3	27.6	5.1	5	40	40	15
	4	19.4	11.8	2	54	18	26
	5	17.9	5.2	4	39	31	26
	1	33.4	30.7	35	45	15	5
February '08	2	32.0	29.8	20	50	20	10
	3	27.9	6.9	18	33	34	14
	4	21.6	7.8	6	43	29	23
	5	20.1	7.1	12	38	35	16

	1	33.8	10.4	15	49	22	14
	2	33.2	17.0	8	46	24	22
March '08	3	31.0	12.2	7	63	16	15
	4	26.1	13.1	7	68	17	9
	5	24.9	9.8	3	49	35	13
	1	33.8	16.8	28	41	23	8
	2	33.2	12.8	15	41	27	16
April '08	3	29.5	11.9	4	67	21	8
	4	23.8	6.7	9	42	28	21
	5	22.4	7.3	9	56	27	8
	1	34.5	6.7	2	53	27	19
	2	33.9	6.0	3	50	26	21
May '08	3	32.4	13.5	2	64	12	22
	4	25.5	5.6	1	41	43	15
	5	23.9	2.9	1	48	35	16

S- smectite, K kaolinite, I-illite and Ch-chlorite; see Fig. 1 for stations 1-5.

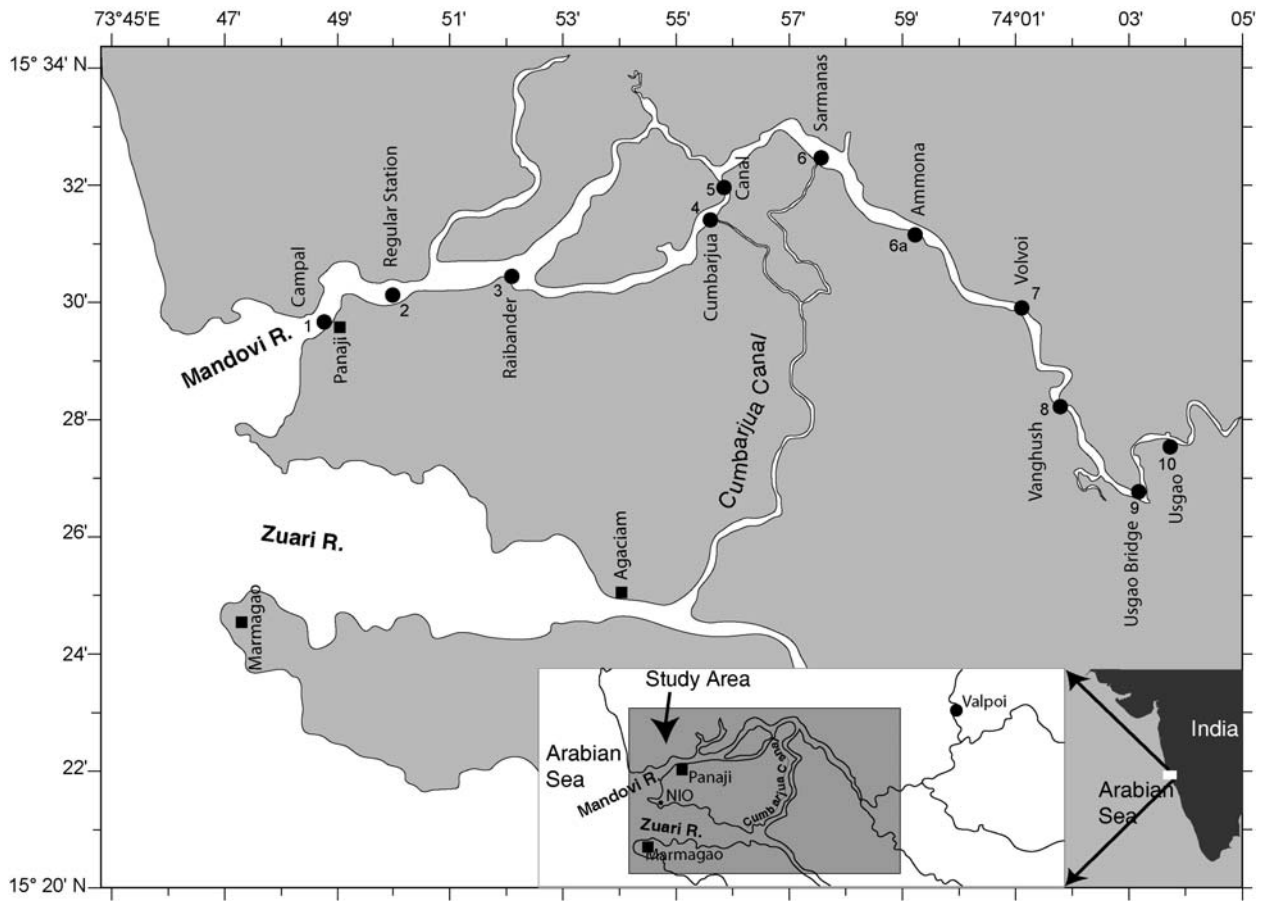


Fig. 1

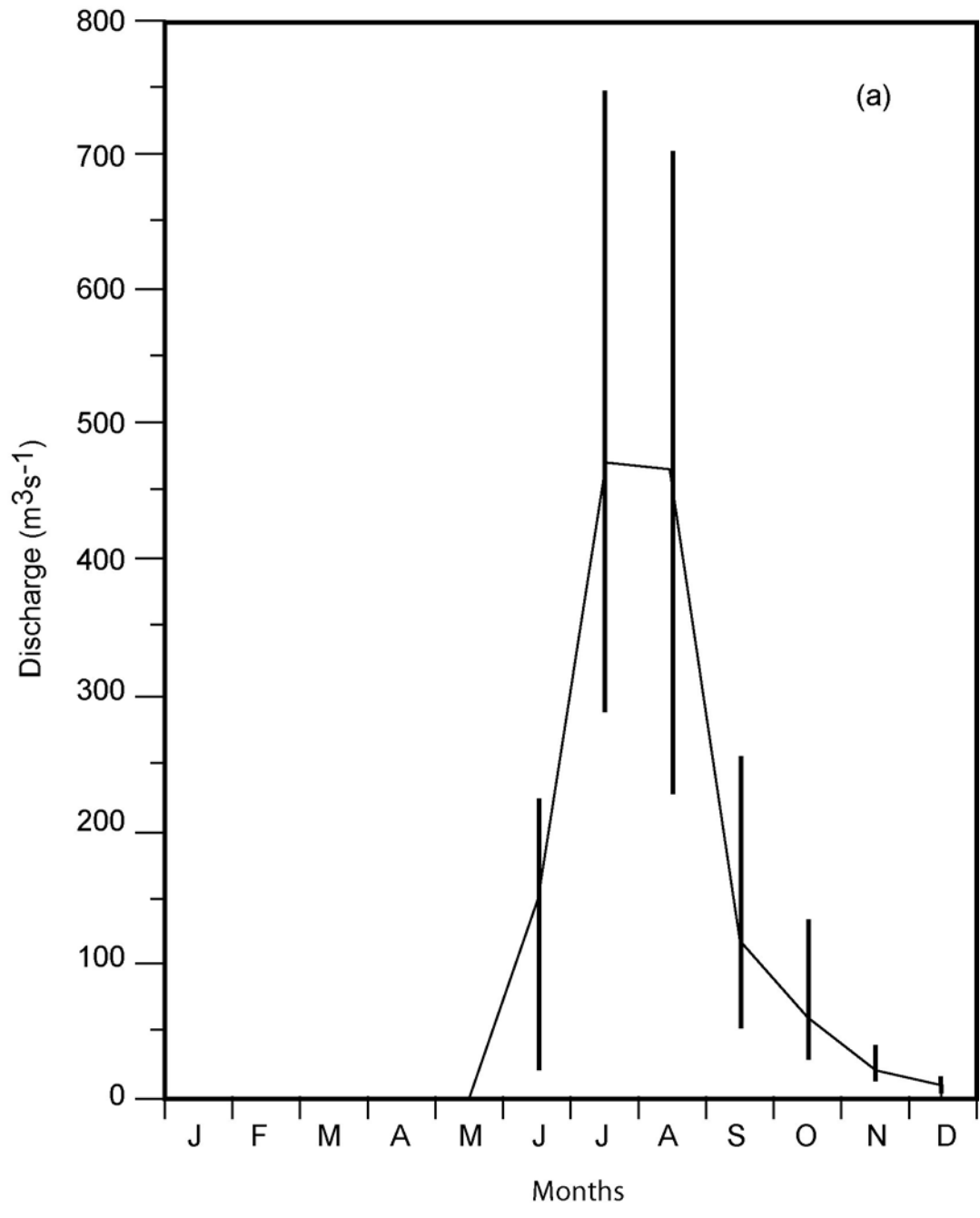


Fig. 2a

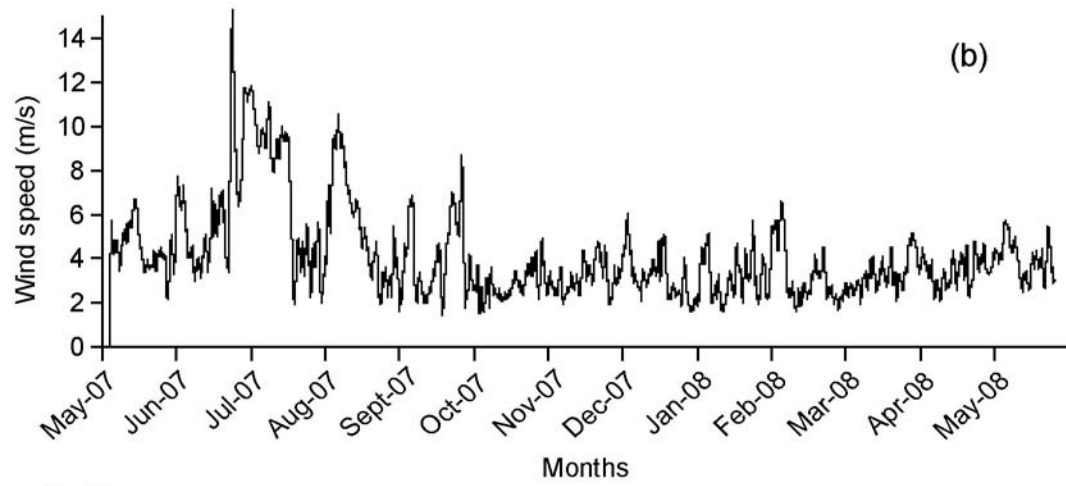


Fig.2b

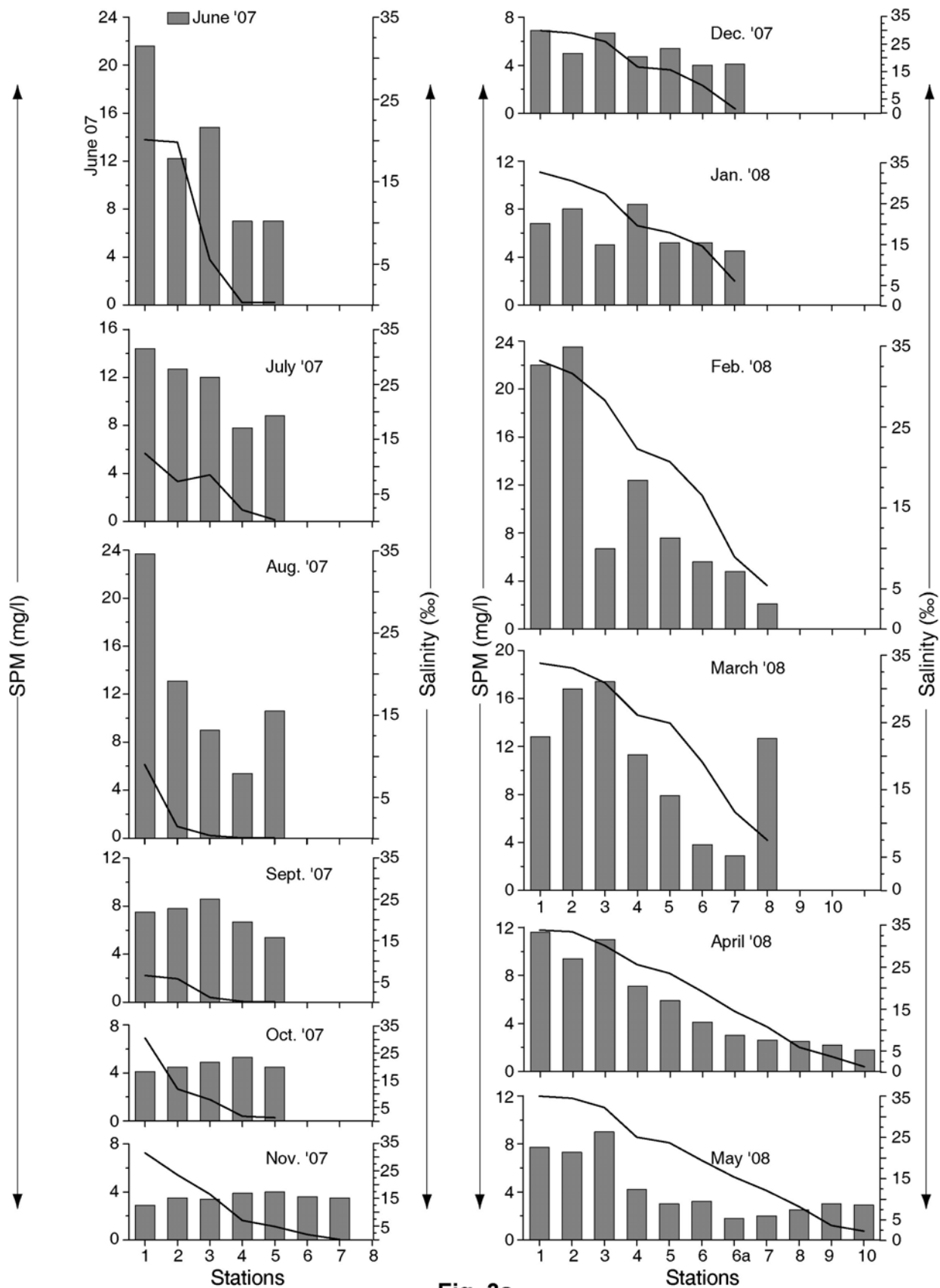


Fig. 3a

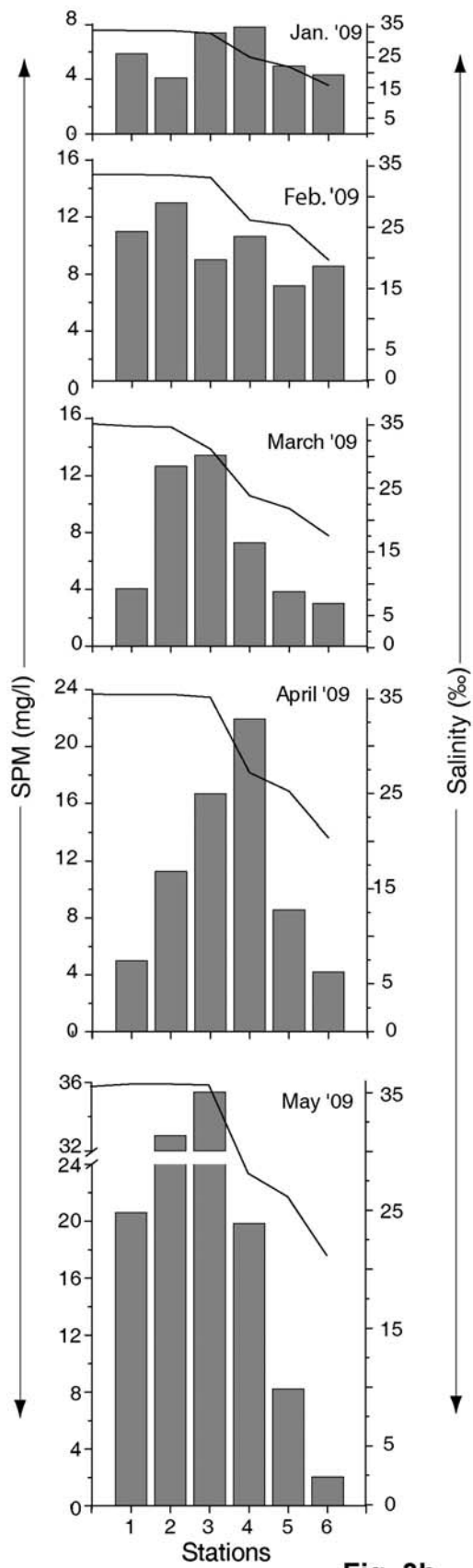


Fig. 3b

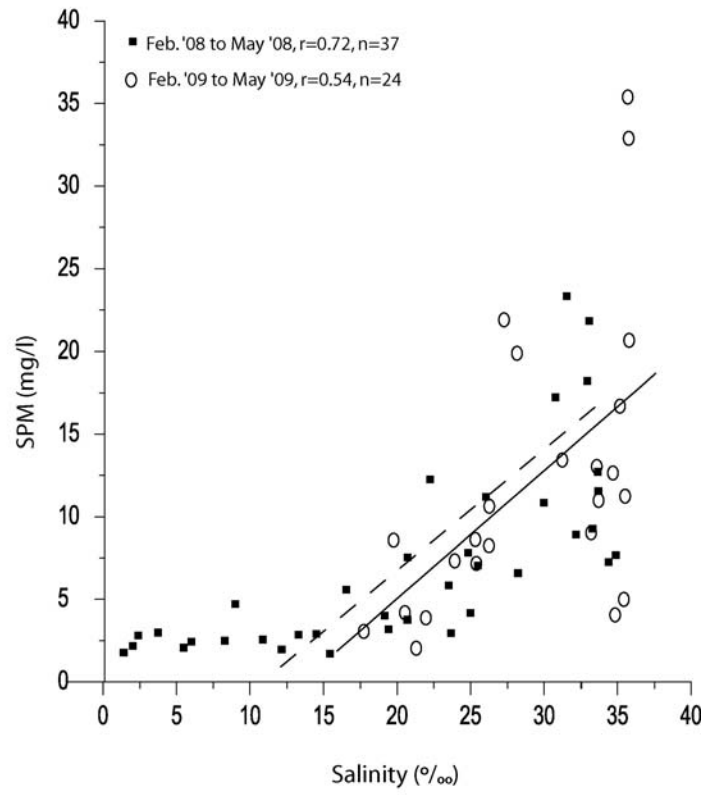


Fig. 3c

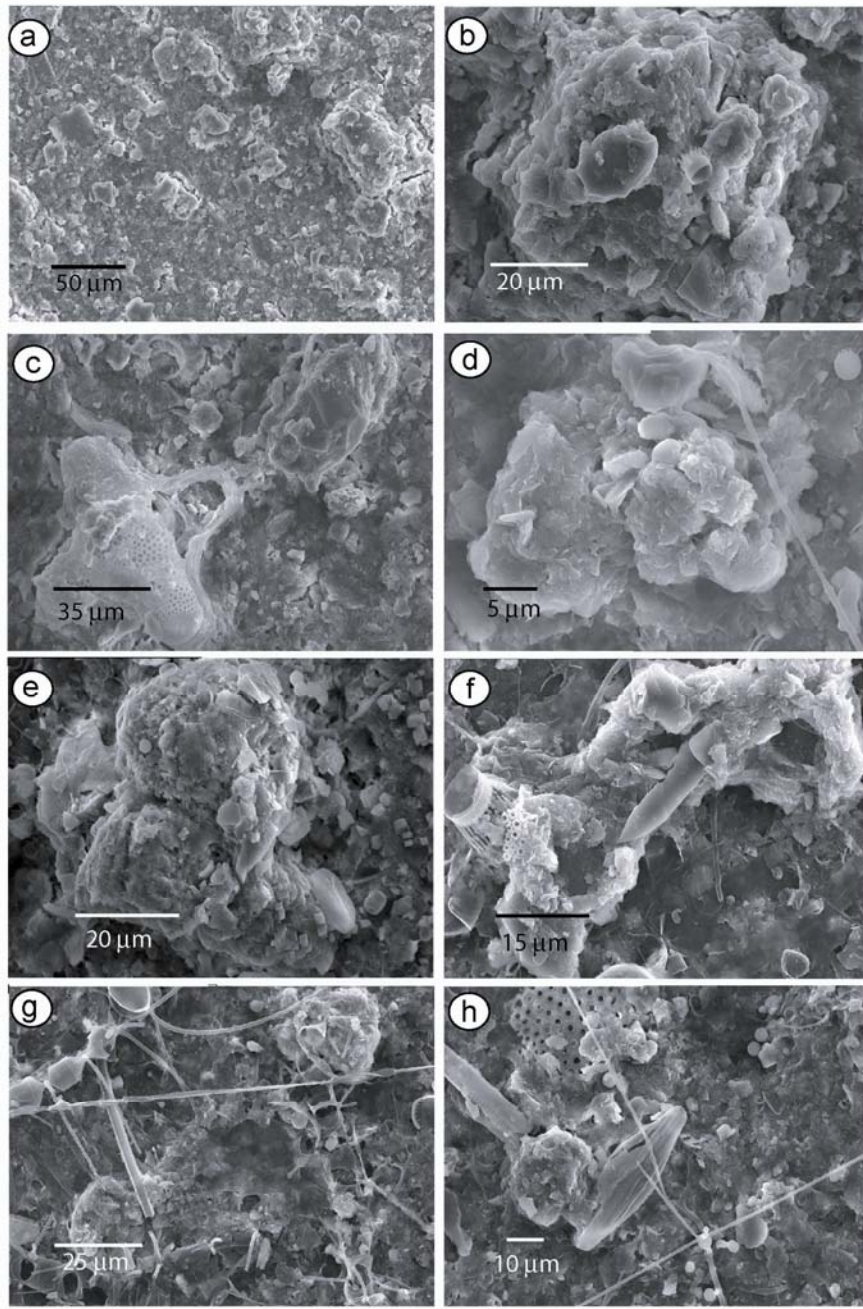


Fig. 4

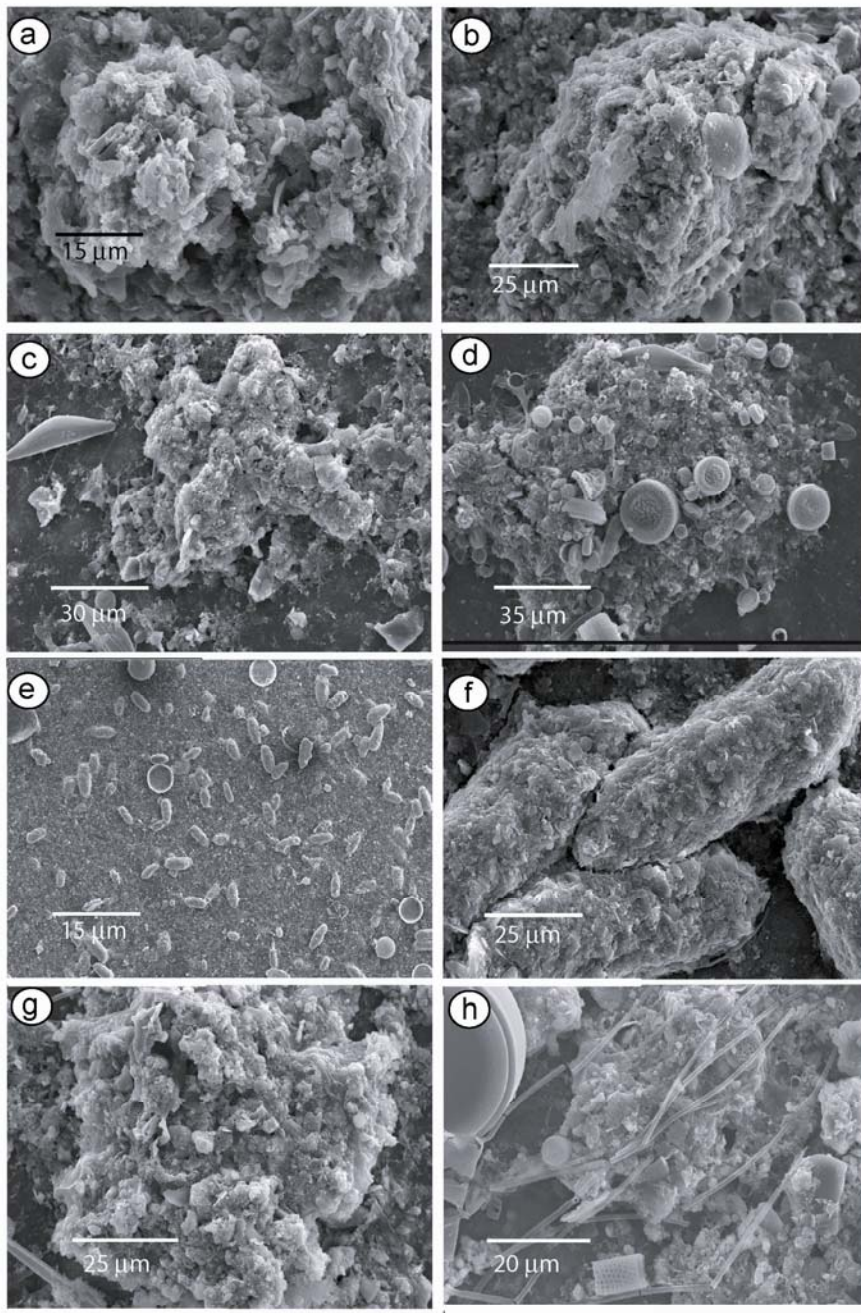


Fig. 5

Regular station

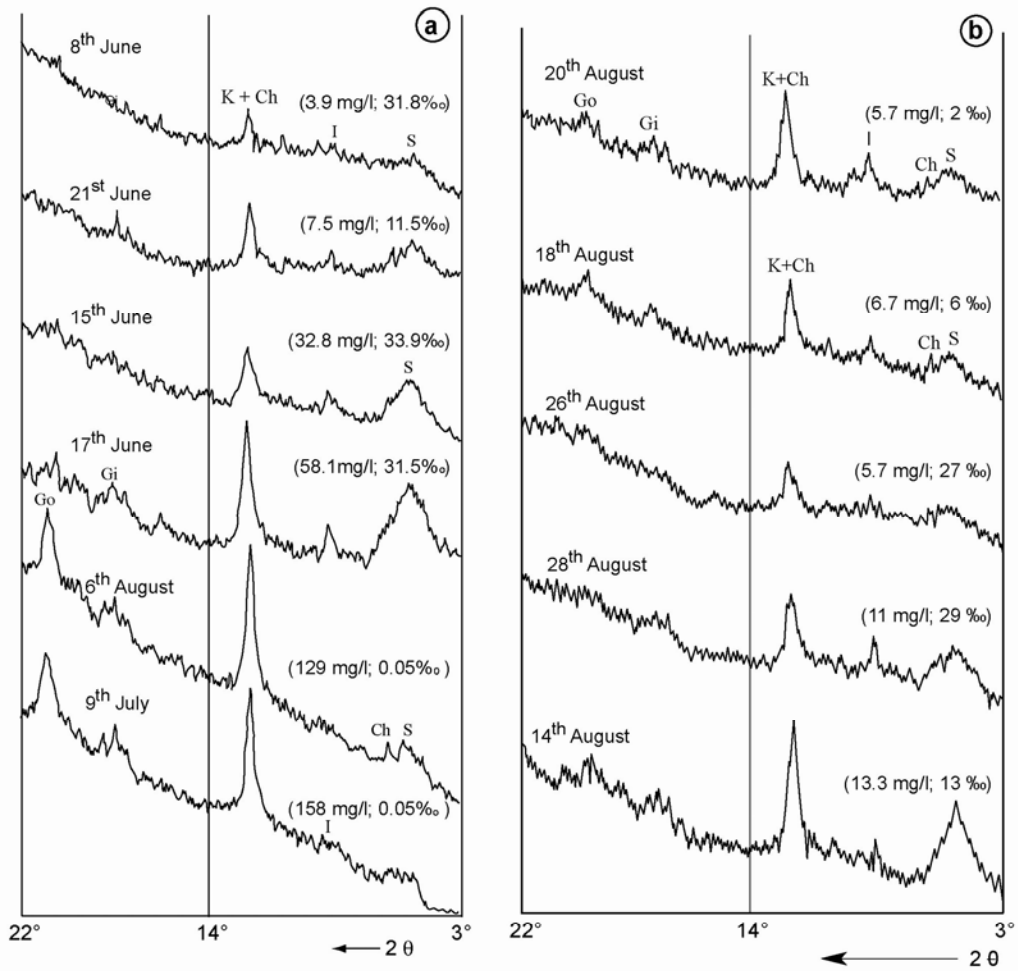


Fig. 6

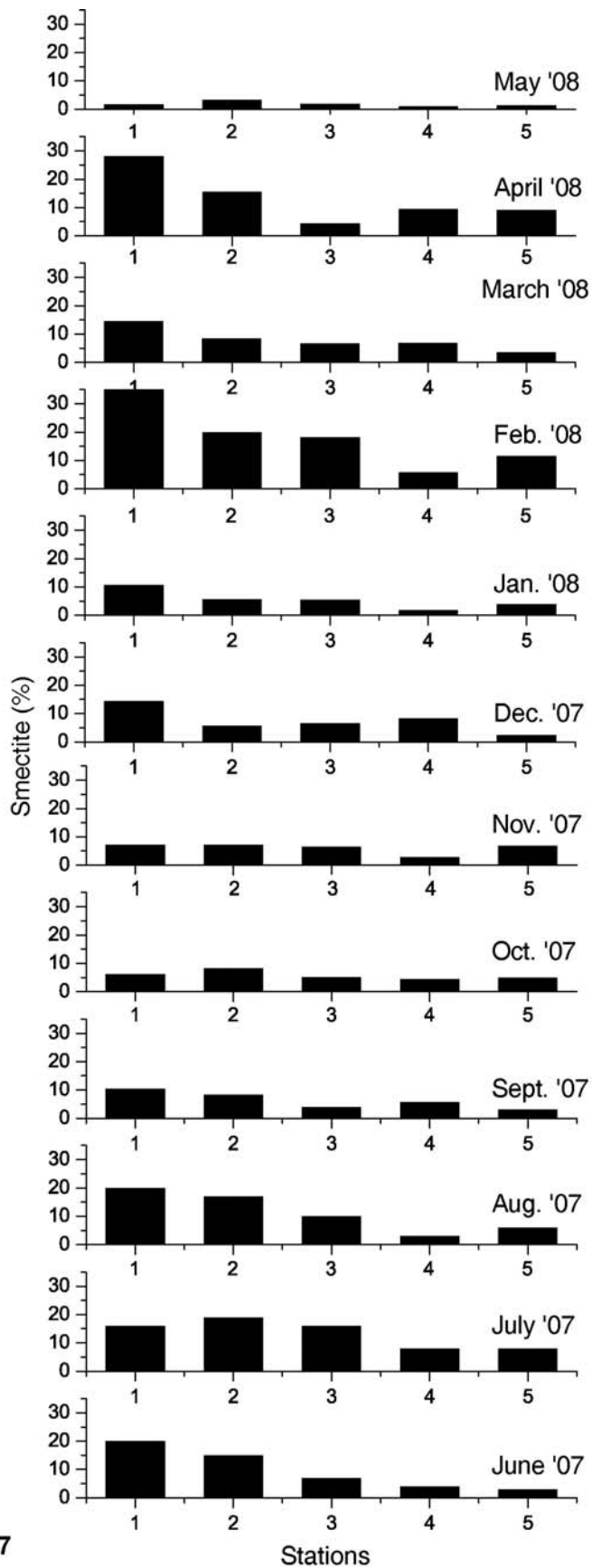


Fig. 7

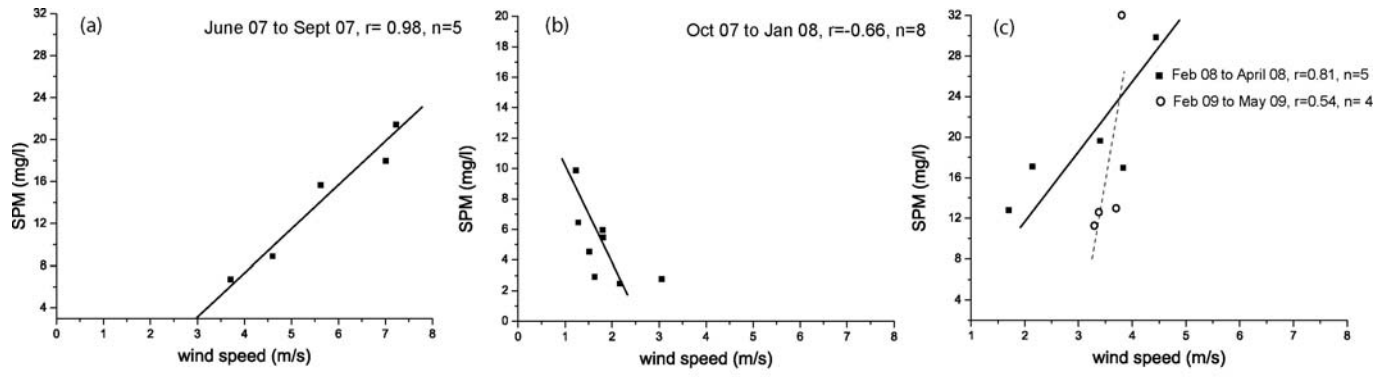


Fig.8