

Iron ore pollution in Mandovi and Zuari estuarine sediments and its fate after mining ban

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Abstract

Iron ore was mined from the banded iron formations of Goa, India and transported through the Mandovi and Zuari Estuaries for 6 decades until the ban on mining from September 2012. Here we focus on the environmental magnetic properties of sediments from the catchment area, upstream and downstream of these estuaries and adjacent shelf during peak mining time. Magnetic susceptibility (χ_{if}) and Saturation Isothermal Remnant Magnetization (SIRM) values of sediments were highest in upstream (catchment area and estuaries), decreased gradually towards downstream (catchment area and estuaries) and were lowest on the adjacent shelf. The χ_{if} values of the Mandovi estuary were 2 to 4 fold higher than in Zuari. The sediments of these two estuaries after the mining ban showed enrichment of older magnetite and sharp decrease in the SIRM values. Although the input of ore material has been reduced after mining ban, more flushing of estuarine sediments is required for healthier environment.

Keywords: Iron mining, anthropogenic input, magnetic properties, seasonal variations, mining ban

Introduction

The Mandovi and Zuari (Ma-Zu) estuaries, located on the west coast of India, have been used for transportation of iron ore for the past 6 decades. Open cast iron ore mining takes place in the catchment area of these two rivers with 1:3 of ore: overburden ratios with reject tailings stored as large dumps. High rainfall (3000 mm) during monsoon season (June to August) transports these tailings into the river systems. With the increase in mining activity, high concentrations of Fe and Mn have been observed in sediments close to the mining area (Girap and Nayak 1997). During transportation of ore materials by truck from mine site to the loading points (that are located near river) lot of ore dust pollution occurs that gets accumulated on the roadside during active mining. Ore stored for transportation at different points on the shores of the estuary also gets flushed into the estuaries during heavy monsoon rains. Part of the ore and/or dust ultimately gets accumulated in bottom sediments of the estuaries (Alagarsamy 2006; Dessai et al. 2009a; Mesquita and Kaisary 2007; Shynu et al. 2012; Kessarkar et al. 2013) during ore handling at shore loading points, transportation of ore through estuaries and reloading offshore by trans-shippers or at port.

Iron ore pollution can be effectively studied using environmental magnetic properties. This method has been successfully used in the suspended particulate matter of rivers of Karnataka, India, to trace the anthropogenic input of iron ore (Sandeep et al. 2011). This technique is nondestructive and cost effective and has been extensively used to study heavy metal pollution (Oldfield and Scoullos 1984; Chan et al. 2001; Hanesch and Scholger 2005; Venkatachalapathy et al. 2011; Yang et al. 2012; Chaparro et al. 2013), anthropogenic input in the city that gets transferred from one place to another after the rains (Gudadhe et al. 2012) and, near iron and steel plants (Yang et al. 2007) and shipyards (Choi et al. 2014). Magnetic properties of sediments have been successfully used to study the provenance and transport pathways of sediments in the rivers and oceans (Walden et al. 1997; Joseph et al. 1998; Duck et al. 2001; Kumar et al. 2005; Wang et al. 2010). Studies on the environmental magnetic properties of Goa's estuaries and adjacent shelf are limited while heavy metal concentrations on continental shelves (Alagarsamy 2009) and anthropogenic activity on the central west coast of India have been reported (Singh et al. 2014). Whereas the only report on magnetic properties is by Dessai et al. (2009a) from Zuari estuarine sediments that have been effectively used to trace the sources of iron ore material. The iron ore mining takes place in the catchment of Ma-Zu estuaries and are transported via these estuaries to offshore areas via trans-shippers and/or port for export. But there have been no systematic studies to compare magnetic properties of

sediments from the catchment area to their estuaries and to the adjacent shelf. Here we report for the first time variations in the magnetic properties of sediments from the catchment area, estuaries and continental shelf off the Ma-Zu estuaries during peak mining and the fate of these magnetic minerals after mining ban to comprehend the changes in anthropogenic input.

Study Area

The catchment area of the Mandovi (~1550 km²) is twice that of Zuari (973 km²) estuary. The surface runoff of Mandovi is 3580.4 MCM, while that of Zuari is 2247.4 MCM. Seasonal variations in the concentrations of suspended particulate matter (SPM) have indicated that the SPM content varies from 3 to 158 mg/l and from 2 to 90 mg/l in the Mandovi and Zuari estuaries respectively (Kessarkar et al. 2010 ; Rao et al. 2011). Although the data on sediment discharge by these rivers are not available, Mandovi discharges more sediments leading to the formation of shoals and sand bars at the river mouth during the monsoon, hindering river navigation which has to be closed during June - September (Qasim and Sen Gupta 1981). As a consequence, barges carrying iron ore to the port are diverted into the Zuari estuary through the Cumbarjua canal (Fig. 1b).

The Ma-Zu Rivers drain through a variety of bed rocks (Fig. 1), belonging to the Dharwar supergroup, with similar lithology and weathering conditions. The Mandovi River flows through metagraywacke and argillite in the upper reaches and then passes through a Quartz-sericite schist and phyllite with banded iron formations (BIF) and Quartz-chlorite-biotite schists in the lower reaches. The Zuari River mostly drains through Quartz-sericite schist and phyllite with banded iron formations, Granite gneiss, metabasalts, metasediments and Quartz-clorite-biotite schists (Dessai et al. 2009b). Most of these formations have been lateritized, with original unweathered rocks exposed only in coastal headlands, along steep slopes of high hills or in man-made cuttings like quarries, road cuts and railway tunnels (Fernandes 2009). Two thirds of the area in Goa is covered by laterite (Nayak 2002), that has been formed after extensive leaching of other elements and due to the concentration of iron and aluminum. Further, the catchment area of the two rivers is covered by lateritic soils. River flow dominates in both estuaries during monsoon, but in the remaining period tidal flow dominates and lower estuaries of both rivers become an extension of the sea (Shetye et al. 2007)

Iron ore occurs as banded-iron formations (BIF) that are formed due to supergene alteration resulting in enrichment of iron (Rao et al. 1985). BIF horizons are formed with upper Quartz/Chert magnetite and hematite (magnetite being dominant) and lower with Quartz/Chert hematite (hematite being dominant). Hematite is the predominant mineral with ore reserves of

927171x10³ tonnes and with magnetite reserves of 222673 x10³ tonnes in the year 2010 (IMYB 2010). The state of Goa covers an area of only 0.11% of India (Bhushan and Hazra 2008), but 18% of iron ore comes from this state (IMYB 2010) accounting for 5 million tonnes/month (USGS 2013). Here, the iron ore is found under laterite overburden with ore occurring below the ground level continuing even below the water table (Nayak 2002) and extracted, using open cast mining. Iron ores (with high magnetite content) are also transported from the neighboring states via railways and roads, these ores in turn are loaded onto the barges that are transferred to the port or, using trans-shippers, onto the larger ships. Mining activity, particularly surface excavations, is affecting soils, surface and ground water, fauna and flora (Rath and Venkataraman 1997; Nayak 2002). Mining in Goa has resulted in an environmental threat that was first felt in the year 1978 and as a consequence 287 mining concessions/leases were terminated (Nayak 2002) and again in the year 2012, that led to a complete ban on mining.

Materials and methods

Sediment samples (143 number) were collected from five different areas: (a) the catchment area of Ma-Zu estuaries; (b) upstream of both estuaries (M10-M6 samples, Mandovi; Z9-Z6 samples, Zuari) (referred to here as upstream estuarine samples, Fig. 1b); (c) downstream of Mandovi (M5 – M1) and Zuari (Z5- Z1) estuaries (referred to here as downstream estuarine samples); (d) the adjacent shelf off the estuaries (Fig. 1a) and (e) River mouth of Terekhol, Chapora, Sal and Galgibag Rivers of Goa that are without any iron ore mining activity in the catchment area (Fig. 1a). The sediment samples from the upstream and downstream estuary were collected during the peak mining period (Fig. 1c-d), 4 months and 1 year after mining ban (Fig. 1e-f). Additional Ma-Zu downstream estuarine sediment samples were collected during the pre-monsoon, monsoon and post-monsoon (Fig. 1a-b) through peak mining period to see seasonal variations within the downstream estuary.

Subsamples were oven dried at <40° C and were analyzed for environmental magnetic parameters. Magnetic measurements for different parameters were made using a Barrington MS-2 magnetic susceptibility meter linked to a MS2B dual frequency sensor (470 and 4700 Hz). Low-frequency (0.47 kHz) magnetic susceptibility (χ_{lf}) and high frequency (4.7kHz) magnetic susceptibility (χ_{hf}) were measured three times on each sample and presented as mass specific values in 10⁻⁸ m³/kg SI units. Frequency dependent susceptibility (χ_{fd}) was calculated from the expression $\chi_{fd} (\%) = [(\chi_{lf} - \chi_{hf}) / \chi_{lf}] * 100$. Anhysteretic Remnant magnetization (ARM) was imparted on the samples by superposing a DC biasing field of 0.05 mT on a smoothly decreasing alternating field with a peak of 100 mT. ARM is given as an anhysteretic

susceptibility χ_{ARM} (mass specific ARM / strength of the biasing field). Isothermal Remnant Magnetization (IRM) was acquired at the forward value of up to 1000 mT using the Molspin Pulse magnetizer; remanences were measured by Molspin spinner magnetometer. Saturation Isothermal Remnant Magnetization (SIRM) was acquired at 1000 mT (1T) and later samples were subjected to reverse field. Further calculations were performed following Walden et al (1999) and Bloemendal et al (1988), S-ratio= $((1-IRM_{-300mT}/IRM_{1000mT})/2) * 100$, $\chi_{ARM}/SIRM$ and χ_{ARM}/χ_{if} .

The samples from catchment area were smeared on to the stub and examined under JEOL JSM 5800LV scanning electron microscope (SEM). Chemical analyses were conducted on these samples using the OXFORD- INCA energy dispersive spectrometer detector (EDS, ISIS-300) system attached to SEM. Pure platinum group element was used as standard. The magnetic minerals were separated by using simple magnet, and >63 μm fraction was separated by wet sieving and examined under binocular microscope.

Results

Catchment area of Ma-Zu estuaries: The χ_{if} values of sediments from the flood plains, basic formations (exposed rocks) and accumulated dust on the road side (where transportation of ore takes place) varied distinctly from 8 to $3822.1 \times 10^{-8} m^3 kg^{-1}$. High χ_{if} values were observed in the catchment area associated with upstream of estuaries (avg. $1100.8 \times 10^{-8} m^3 kg^{-1}$), including the flood plains and dust, but the exposed rocks of this region showed low values (avg. $255.5 \times 10^{-8} m^3 kg^{-1}$; Fig. 2a-b, Table 1). High χ_{if} values were however observed in the exposed rocks downstream and low values in the flood plains. Botryoidal maghemite was seen in some surface samples in the mining area. The SIRM values ranged from 121.4 to $53503 \times 10^{-6} Am^2 kg^{-1}$, with relatively high values (avg. $15107 \times 10^{-6} Am^2 kg^{-1}$) in the mining areas/upstream and low values (avg. $2759 \times 10^{-6} Am^2 kg^{-1}$) in the lower reaches/downstream (Table 1). S-ratios ranged from 74.8% to 98.5%, in the catchment area with high ratios (avg. 92.8%) associated with upper reaches of the estuaries and low ratios (avg. 88.2%) associated with the lower reaches. S-ratios >95% are restricted to the mining areas, except at two stations in the flood plains of the Zuari River. High S-ratios are associated with magnetite (Fig. 3 a) and low S-ratios with hematite (Fig. 3 b) and exhibit high Fe content in the spectrum. The χ_{fd} (%) ranges between 0.2 and 14.8 and is relatively higher for the upstream area (Table 1; Fig. 4)

Upstream sediments of Ma-Zu estuaries: The average χ_{if} values of sediments for the Mandovi (M6-M10 stations) and Zuari (Z6-Z9 stations) upstream during peak mining were 467.5

$\times 10^{-8} \text{m}^3 \text{kg}^{-1}$ and $445.7 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$, respectively (Fig. 5a, Table 2). After 4 months of the mining ban these value increased to avg. $698 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Mandovi and decreased to avg. $297.5 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Zuari upstream whereas after one year they increased to avg. $826.6 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ and avg. $745.4 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ respectively (Fig. 5 a, Table 2). Higher averages observed after the mining ban was associated with exceptionally high values at some stations upstream. The SIRM values of sediments for Mandovi are higher (avg. $8912.7 \times 10^{-6} \text{Am}^2 \text{kg}^{-1}$) compared to Zuari (avg. $7285.6 \times 10^{-6} \text{Am}^2 \text{kg}^{-1}$) during active mining period.

Downstream sediments of Ma-Zu estuaries: The χ_{lf} values of sediments in the Mandovi estuary were at least 2 times higher than in the Zuari estuary (Fig. 5b). Looking at the seasonal variations, χ_{lf} values are found to be lowest during monsoon (avg: $410.9 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in the Mandovi and $212.3 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Zuari - Table 3) and highest during the post-monsoon (avg: $521.8 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in the Mandovi and $248.6 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Zuari estuary). After 4 months of the mining ban the χ_{lf} values of sediment samples decreased in both estuaries (avg. $376.1 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ and $203.9 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Mandovi and Zuari estuaries, respectively), whereas after 1 year these values marginally decreased in Mandovi (avg. $343.6 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) and increased in Zuari (avg. $264 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) with exceptionally high values at stations M4 and Z5 (Fig. 1b). The SIRM values of sediments in the Mandovi estuary were much higher than in Zuari in all seasons and in sediments collected after mining ban (Fig. 5b). The frequency-dependent susceptibility χ_{fd} (%) of sediments in the Mandovi (avg. 1.6%) is invariably lower than in Zuari (avg. 3.5%) for all seasons and also for samples collected after mining ban (Table 3; Fig. 4). The $\chi_{\text{ARM}}/\chi_{\text{lf}}$ and $\chi_{\text{ARM}}/\text{SIRM}$ ratios were lower for the Mandovi than in Zuari estuary in all the seasons (Fig. 5b; Table 3). The S-ratio exhibits similar trends for Ma-Zu with relatively lower values observed in Mandovi estuary sediments during the monsoon time (Fig. 5b; Table 3). The χ_{lf} of sediments from other rivers of Goa showed higher values for the rivers in the north ($393.1 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ – Terekhol; $258.2 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ - Chapora Rivers; Fig. 1a) than in the south ($59 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ - Sal, $90.7 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ - Galgibag Rivers - Table 1) of the Ma-Zu estuaries. The SIRM and χ_{ARM} values (Table 1-3) of the sediments were lower for Terekhol and Chapora Rivers than those of Ma-Zu estuaries. S-ratios were high (93.7% to 97.7%) for all these rivers (Tables 1-3).

Shelf sediments off the Ma-Zu estuaries: The χ_{lf} values ranged between 4.6 and $350.8 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ (avg. $79.3 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$), with highest values near the coast and decreased values offshore (Fig. 2b). The χ_{ARM} and SIRM values are also higher near the coast and decreased offshore. The high $\chi_{\text{ARM}}/\chi_{\text{lf}}$ and $\chi_{\text{ARM}}/\text{SIRM}$ ratios of sediments correspond with low χ_{lf} . S-ratios ranged from 90.8% to 98.3% (avg. 94.2% - Table 1).

Discussions

The Ma-Zu Rivers drain through the Banded iron formations (Fig. 1a). Ore extracted from these formations was transported to the shore points of the estuaries and then to the port through these estuaries until September 2012 when a complete halt in mining was announced.

Sources of Magnetic minerals

Magnetic properties of sediments in catchment area of Ma-Zu estuaries

The iron ore mining areas and loading points are located in the upstream catchment area of Ma-Zu estuaries. The magnetic susceptibility of sediments within the catchment area of these two estuaries exhibits a wide range of values (8 to $3822.1 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) with relatively lower values observed in the downstream (non mining area) and high values in the upstream (mining area) see Fig. 1a and 2a, Table 1. High values in the upstream are also seen in the accumulated dust on the roadsides (L25, L26, L28; Fig. 2a) and flood plains (L32, L40, L41, L43) with χ_{if} values of $> 1500 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$. Background values are considered to be very important while studying the anthropogenic input (Hanesch and Scholger 2002) and here we consider exposed rocks as background values. In the upstream catchment area low χ_{if} values are observed in the exposed rocks (L21, L22, L24, L29; Fig. 2a) compared to sediments from the flood plains and roadside dust, this indicates anthropogenic input. The downstream sediments in the catchment area show higher χ_{if} in the exposed rocks (L1, L2, L3, L4, L8, L9, L10, L38) that are mostly lateritized compared to the flood plains (L5, L6, L11, L13, L14, L15, L17, L18, L34, L37, L39) except L35 that was collected in the vicinity of the shipbuilding. This relatively high χ_{if} in the lateritized exposed rocks could be due to hematite weathering into more magnetic soils containing maghemite (Allen et al. 1988). Another possibility could be formation of ferritized iron crust (Mathe et al. 1997) during lateritic weathering.

Magnetic properties of upstream sediments of Ma-Zu estuaries

Sediments from the upstream of Mandovi (M6-M9) and Zuari (Z6-Z9) estuaries during peak mining time exhibit similar average susceptibility values, $467.5 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ and $445.7 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ (Table 2). This area is associated with loading and storing points of iron ore where there could have been spilling (Fig. 1c-d). However susceptibility after 4 months of the mining ban increased to avg. $698.8 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Mandovi whereas it decreased to avg. $297.5 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ in Zuari estuary (Fig. 5a). Surprisingly, increased susceptibility (Fig. 5a) was observed in both the rivers after one year of mining ban with some stations showing exceptionally high values though there is no mining activity or transportation (Fig. 1d). These higher values could be result

of (a) Ma-Zu Rivers during monsoon are fed with a lot of water (precipitation and runoff) and as a result sediment gets flushed out through the estuary; (b) Iron ore that has higher specific gravity may have remained in the system as lower specific gravity and finer material got transferred downstream; (c) Even after the mining ban there are stores of Iron ore on the banks of the rivers, though this ore is protected by cover, there are chances that part of the ore may have entered the river system during the heavy spell of the monsoons, adding to the existing magnetic minerals in the system leading to increased magnetic susceptibility. The mining ban was lifted in April 2014 by the supreme court of India with permission to extract 20 million tonnes of ore per year. It is expected that extraction of ore in Goa will be resumed in 2015.

Magnetic properties of downstream sediments of Ma-Zu estuaries

Downstream of Mandovi (M1 to M5) estuary sediments exhibit higher χ_{if} values compared to Zuari (Z1 to Z5) estuary (Fig. 5b). In the case of the Mandovi estuary a major drainage area comes under Quartz-sericite schist and phyllite with banded iron formations (Fig. 1), that could add more magnetic minerals compared to Zuari estuary. Further 2/3rd of iron ore mining activities come under Manodvi River watershed (Pathak et al. 1988) that results in higher input of magnetic minerals to this area. Industrial activities like shipbuilding are also located on river banks that could add magnetic minerals. Studies by Alagarsamy (2006) ; Shynu et al. (2012); Kessarkar et al. (2013) have shown that high Fe contents in suspended and bottom sediments enters these rivers through river discharge, flushing of ore material into the estuaries and mining and ore handling activities. Further, higher Fe contents of sediments in Mandovi estuary (2.2-49.7 %) compared to Zuari estuary (3-16.8% - Alagarsamy 2006; Dessai et al. 2009a) are consistent with our results.

Seasonal changes in the magnetic properties of sediments in the Mandovi estuary exhibit a distinct trend. χ_{if} values are lower in the Mandovi (avg. $410.9 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) and Zuari (avg. $212.3 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) estuaries during monsoon than in post-monsoon (avg. $521.8 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$ and $248.6 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$, respectively) (Table 3; Fig. 5b). During monsoon there is high precipitation and river runoff that brings detrital material from different sedimentary formations from catchment area, debouching them in the estuaries. Moreover, ore handling activity is relatively low during the monsoon time that could also lead to low input of ore material during this period. Relatively high χ_{if} values in the downstream of Mandovi during post-monsoon (stations M1 and M2, Fig. 5b) could be due to increased ore handling activity immediately after the monsoon. The mining activity in the Zuari estuary has progressively decreased with time

and so have the rejects that are washed into the Zuari (Panchang et al. 2005). Huge bay of Zuari estuary further aids in transporting these sediments offshore.

The low χ_{lf} of the sediment in samples collected after four months of the mining ban (avg. $376.1 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$; Table 2) with seaward decreasing trend may be due to a reduced addition of new magnetic material because of the mining ban and flushing off of the ore material that was deposited previously due to the tidal effect. We cannot rule out the possibility of the reduced susceptibility as a result of dilution in the lower region (close to the sea end) by some non magnetic material being contributed from the sea into the river mouth (Rao et al. 2011). High magnetic minerals are reported to be present in the Ma-Zu estuary (during the active mining period) and are related to the mining activity and other anthropogenic activity along the river banks (Kessarkar et al. 2013; Dessai et al. 2009a). Samples collected after 1 year of the mining ban are expected to flush out more ore-related sediments (mining/anthropogenic accumulated sediment on the river bed) during the monsoon. The χ_{lf} shows overall reduced values (Table 3; Fig. 5b) suggesting that there is reduction in the Fe ore accumulation in the sediments. Surprisingly the χ_{lf} values were high at station M4. Examination of magnetic material separated from this sample showed magnetite crystals, some appear to be fresh and others (Fig. 6c) with weathered red surfaces (Fig. 6d). These magnetites may have been accumulated due to its higher specific gravity. High χ_{lf} at Z5 in the Zuari estuary after mining ban could be from the shipbuilding activity in the river vicinity. If there had to be iron filing from the shipbuilding activity χ_{fd} (%) values would have been higher than 3.9 % (Dearing, 1999). The values of 3.9 % in this sample suggest less contribution from shipbuilding activities.

Comparing the Ma-Zu data with other rivers of Goa, similar χ_{lf} values are observed in sediments at the river mouths of the Chapora and Terekhol Rivers. Whereas relatively low χ_{lf} values are seen in south rivers (Galgibag and Sal Rivers ;Table 1) This may be due to the fact that the former rivers drain through BIF and more influx of iron ore material may also have been introduced into the Terekhol River through iron ore plants in the north (Reddi, Maharashtra, adjoining the above river). The low χ_{lf} values in the southern rivers (Galgibag and Sal) could be due to the influx of more detrital material and absence of mining activity in this region (rivers not passing through BIF; Fig. 1a).

Variations in magnetic properties of the Shelf sediments

The average χ_{lf} value of shelf sediments is lowest ($79.3 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) among the samples investigated in the study. χ_{lf} values decreased in sediments from near shore (close to the river

mouth) to the offshore (Fig. 2b) and compare well with the Fe distribution in the sediments of the inner continental shelf (range: 5 - > 7.5%) and outer shelf (<2.5 % - Paropkari 2009). This suggests more ore material is deposited in near shore sediments and less material is transported to the offshore. These Ma-Zu River estuaries are almost perpendicular to the coast and longitudes (Fig. 1a). Putting all χ_{if} data together along the longitudes, it is observed that the highest values are seen in the upstream catchment area and estuary where most of the mining activity was taking place and the values decrease towards the mouth of the river (Fig. 2b). This further confirms contribution of magnetic material from the mining areas.

Magnetic Grain size

High SIRM indicates the presence of single domain grains (Thomson 1986). The SIRM values of sediments in the upstream catchment are 5 times higher than those in the downstream (Table 1) suggesting more single domain minerals in the mining area. Further, high SIRM in the Mandovi and in Zuari upstream estuary (Table 2) also suggests dominance of single domain minerals that could have been transported from the catchment area covering mining regions and/or by the iron transportation/loading process. We observed substantial decrease in SIRM values of sediments (nearly half the values) from these two estuaries in samples collected after 4 months of mining ban (Fig. 5b) indicating reduction in the anthropogenic contribution by mining activity. We have also compared SIRM data with the other rivers from Goa. Low SIRM values are characteristic of sediments from Galgibag and Sal Rivers, that do not pass through mining area or rock types with BIF (see Fig. 1a). On the other hand, the Chapora and Terekhol Rivers pass through BIF (like the Mandovi-Zuari, Fig. 1a) with no mining activity in their catchment area. The sediments from these rivers also show relatively low SIRM (Table 1). High SIRM in Ma-Zu estuary during active mining period suggests contamination by the single domain magnetic minerals contributed by mining activity. Highest SIRM values are seen in the mining regions in the catchment area of both rivers, followed by Ma-Zu estuaries and lowest in the shelf region (Fig. 2a; Table 1-3).

Magnetic Grain size may be inferred using χ_{ARM}/χ_{if} and $\chi_{ARM}/SIRM$ ratios, with lower values suggesting coarse grains and higher values finer grains (Banerjee et al. 1981; King et al. 1982). The χ_{ARM}/χ_{if} in the upstream catchment area have been relatively lower (avg. 3.8) compared to downstream catchment area (avg. 5.2), suggesting coarser magnetic minerals (Table 1). Similarly $\chi_{ARM}/SIRM$ and χ_{ARM}/χ_{if} in the upstream Ma-Zu estuarine sediments are relatively lower during mining time and after 4 months of mining ban (Table 2), but increases after 1 year of mining ban that could have washed off magnetic minerals during the monsoon.

Low ratios of χ_{ARM}/χ_{lf} and $\chi_{ARM}/SIRM$ in the Mandovi estuary indicate more of multidomain (MD) or superparamagnetic (SP) grains (Banerjee et al. 1981; King et al. 1982) and higher ratios in the Zuari indicate more of pseudo-single domain (SSD) grains (Fig. 5b; Table 3). These values do not change much after 4 months of the mining ban (Table 3). Highest χ_{ARM}/χ_{lf} and $\chi_{ARM}/SIRM$ values (Table 1) are observed in the shelf sediments suggesting finest magnetic particles. Experiments have shown that the $\chi_{fd}\%$ values decrease after adding multi-domain magnetites (Dearing et al. 1997). The upstream and downstream catchment area show similar $\chi_{fd}\%$ values. Lower $\chi_{fd}\%$ values in the Mandovi estuary than in Zuari (Table 1) may be due to the addition of MD magnetite. The average $\chi_{fd}\%$ value (1.6%) in the Mandovi estuary indicates anthropogenic source material like primary or weathered ore (Sandeep et al. 2011). Changes in this grain size and their proportions can be separated by plotting $\chi_{fd}\%$ vs $\chi_{ARM}/SIRM$ (Maher and Taylor 1988; Dearing et al. 1997). Using this plot the samples of the two estuaries and the shelf can be clearly separated (Fig. 4). Most of the samples from the Mandovi estuary, both during mining activities, and after the mining ban fall under the narrow area where samples are mostly MD+PSD with <10% of SP grains. Whereas the Zuari estuary samples show wide variations in grain size ranging from MD+PSD, Coarse SSD and, to some extent, SSD, and their admixtures fall in the middle area with land samples above it and the shelf samples below it (Fig. 4). The Mandovi estuary, restricted to a narrow range of values (Fig. 4), indicates a large contribution from the mining region and needs detailed monitoring.

Magnetic mineral types

The catchment areas in the upstream region have a higher S-ratio suggesting magnetite to be the dominant mineral compared to the downstream region with lower S-ratios suggesting dominance of hematite. Samples from the catchment area in the lower reaches of both rivers are red in colour and exhibit low S-ratios, confirming the presence of hematite. Further, SEM studies indicate the presence of magnetite (Fig. 3a) in the samples with high S-ratio and hematite (Fig. 3b) in samples with low S-ratio both are with high Fe content. The average S ratio for Mandovi and Zuari estuaries is 91.5% and 91.6% respectively (Table 3) suggesting dominance of magnetite as the major mineral. Further, the IRM acquisition curves (available with authors) of most of the samples from both rivers do not reach saturation at 1T suggesting there may be presence of hematite along with magnetite. Magnetic minerals were separated from the ore samples and some of the river samples using a magnet, and observed under binocular microscope. We found the presence of magnetite in ore samples as well as the river bed samples (Fig. 6). These samples showed distinctive characteristics of holding to each other

or making chains (Fig. 6 a-h). These magnetites on the river bed must have adhered to each other and remained in the system particularly in the low lying areas of the river bed. High χ_{if} observed here in samples collected after the mining ban showed the presence of magnetite, some in oxidized form, some attached together with some cementing material (Fig. 6d) suggesting that these are older and stayed in the present location due to high specific gravity, properties of magnetite to hold together and the bathymetry. Hematite is known to be a predominant ore mineral in Goa (IMYB, 2010), whereas neighboring states have high magnetite in the ore. The upper horizon of BIF consists of Quartzite/Chert magnetite and hematite (Rao et al. 1985) that can also add magnetite into these river systems. High magnetite observed in the present study raises a question whether this magnetite is a result of ore from the neighboring states (spilling during transportation) or has accumulated in the system due to specific gravity. Another possibility is that secondary magnetite in this area may have added to the magnetite content of the samples. S-ratio values are avg. 94.2 in the sediments from the shelf suggesting dominance of magnetite. Though mining has been banned in Goa for over a year, where one cycle of monsoon season is over that flushes out sediment into the sea and removes most of the finer grain size contaminants from the system. As far as the Fe ore mining is concerned one cycle of monsoon has flushed out some of the finer mining pollutants from the estuary but has not been successful in removing completely the mining contamination that has entered these river systems for many years.

Conclusions

Environmental magnetic properties of sediment from the catchment area, estuarine sediments of the Ma-Zu Rivers and adjacent shelf area show distinct variations. High susceptibility values are associated with the upstream catchment area of Ma-Zu estuaries. The upstream catchment sediments of these two rivers have similar χ_{if} values that are higher than the background values (exposed rocks) suggesting input from the mining activity. The χ_{if} of the downstream estuarine sediments of the Mandovi estuary is two times higher compared to that of the Zuari estuary, which is comparable to the mining activity, rock type in the catchment area and morphology of the estuaries. The shelf sediment has higher χ_{if} values close to the river mouths of Ma-Zu estuary. The overall content of magnetic minerals decreased after mining ban but there is increase observed at some stations associated with older ore minerals and related to enrichment due to transportation from the stored ore on the banks during the monsoon time, gravity separation and older ore. The southern river samples (Sal and Galgibag R.) without mining activity show lower χ_{if} values compared to Ma-Zu estuaries. High single domain minerals

are observed in the mining area and the upstream estuary compared to downstream catchment area and estuary and lowest in the shelf region. The decrease in the mining input can be seen by decrease in the SIRM after mining ban. The sediments of the catchment area, Ma-Zu estuaries and shelf sediments can be separated using the environmental parameters. Magnetite is the dominant mineral in the two estuaries showing the characteristic of making chains with enrichment seen at the sites with older magnetite associated with high χ_{lf} . Iron ore mining has been stopped since September 2014, but there has been accumulation of the ore into the Ma-Zu estuarine samples for the past 6 decades, part of it has been moved out of the system, leaving behind the coarser and older ore and would require more cycles of monsoon for healthier systems.

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Figure captions

Fig. 1.(a) Location of samples from the catchment area of Mandovi-Zuari estuaries (L1-L43), offshore samples (S1 to S20), Geology of Goa (Dessai 2011). (b) Mandovi-Zuari estuarine samples. M1 to M5 and Z1 to Z5 are downstream stations; M6 to M9 and Z6 to Z9 are upstream stations (c) Loading of Fe ore onto the barges by trucks (d) Fe ore stored and being transported by trucks (e) Loading points after mining ban without any trucks (f) Iron ore stored on the banks of the river and protected with cover after mining ban.

Fig. 2 (a) Magnetic susceptibility (χ_{lf}) in the catchment area (b) Longitudinal variations of magnetic susceptibility from estuaries, catchment area of Mandovi-Zuari estuary and adjacent shelf.

Fig. 3. Scanning electron microscope photographs from the Mandovi Zuari catchment area (a) Magnetite, (b) Hematite.

Fig. 4. $\chi_{fd}\%$ versus $\chi_{ARM}/SIRM$ for Mandovi (majority of samples inside grey area), Zuari (majority of samples fall inside area marked with dotted line), Sal, Galgibag, Chapora, Terikhol Rivers, catchment area of Mandovi-Zuari Rivers and Sea samples . Note samples above the Zuari River are Mandovi-Zuari catchment samples and below are the sea samples.

Fig. 5b. Magnetic susceptibility (χ_{lf}) of upstream of Mandovi and Zuari Rivers during peak mining time and after 4 months and 1 year of mining ban (b) Seasonal variations in magnetic concentration, magnetic grain size and magnetic mineralogy during mining period and post mining period of 4 months and 1 year from Mandovi and Zuari estuaries (downstream stations).

Fig. 6. Photographs of magnetite from the ore (a-b), from the Mandovi (c-f) and Zuari (g-h) estuaries. Arrow with number 1 shows the oxidized old ore and number 2 shows old magnetite grains that cemented together.

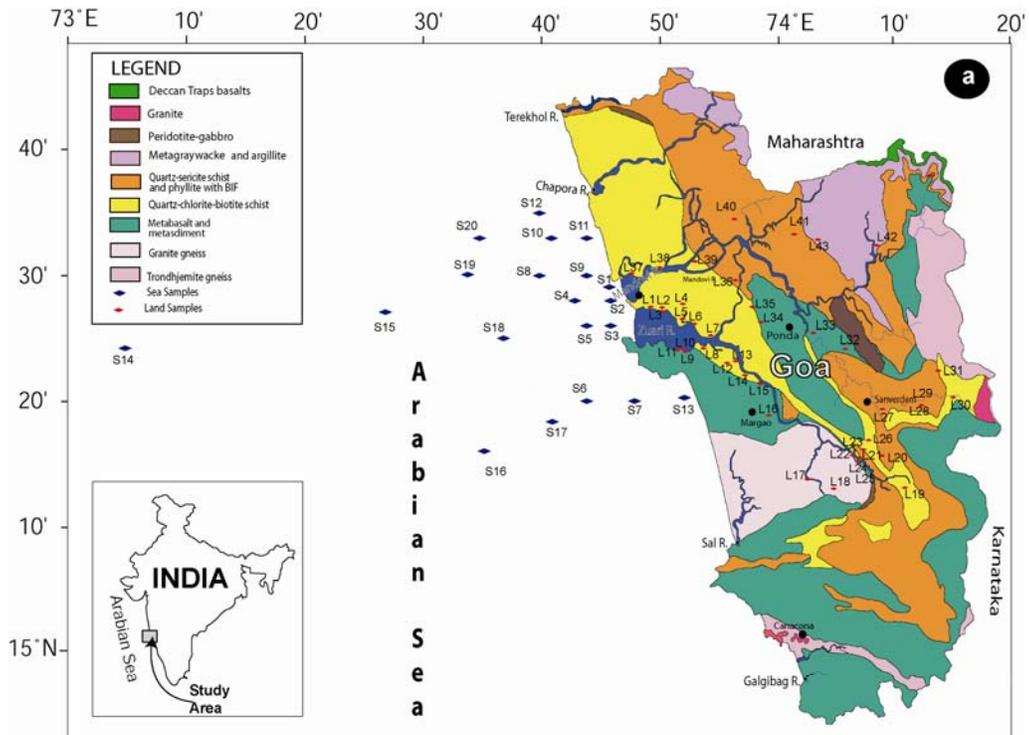


Fig. 1a

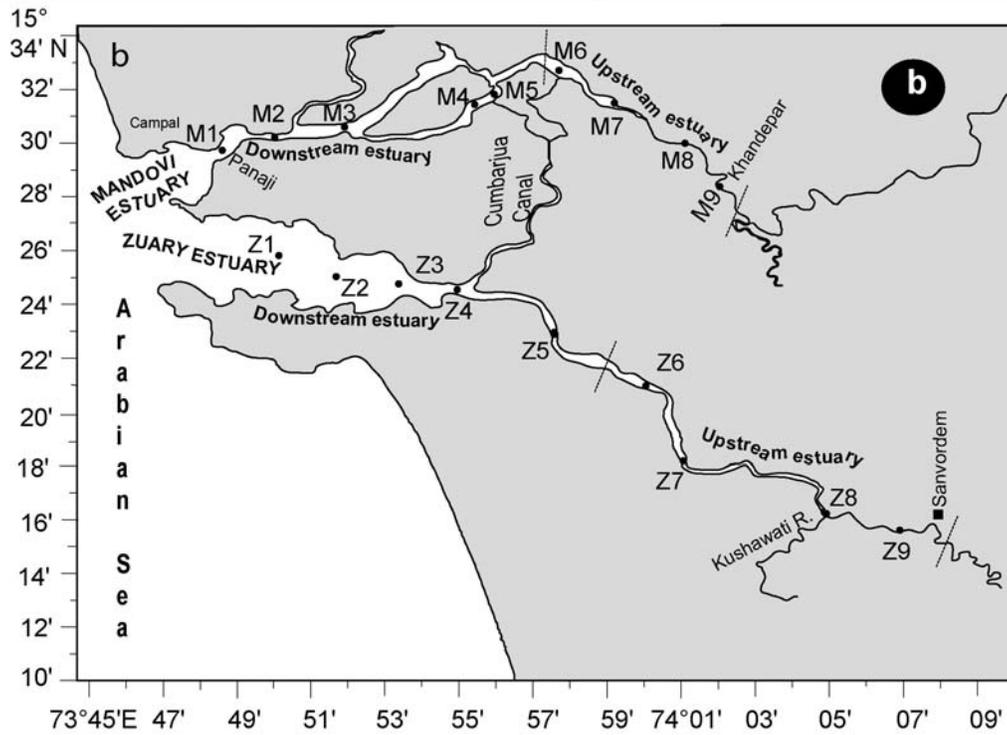


Fig. 1b

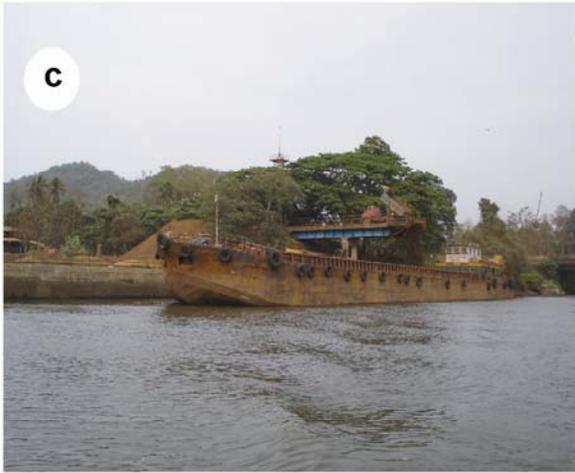


Fig. 1(c-f)

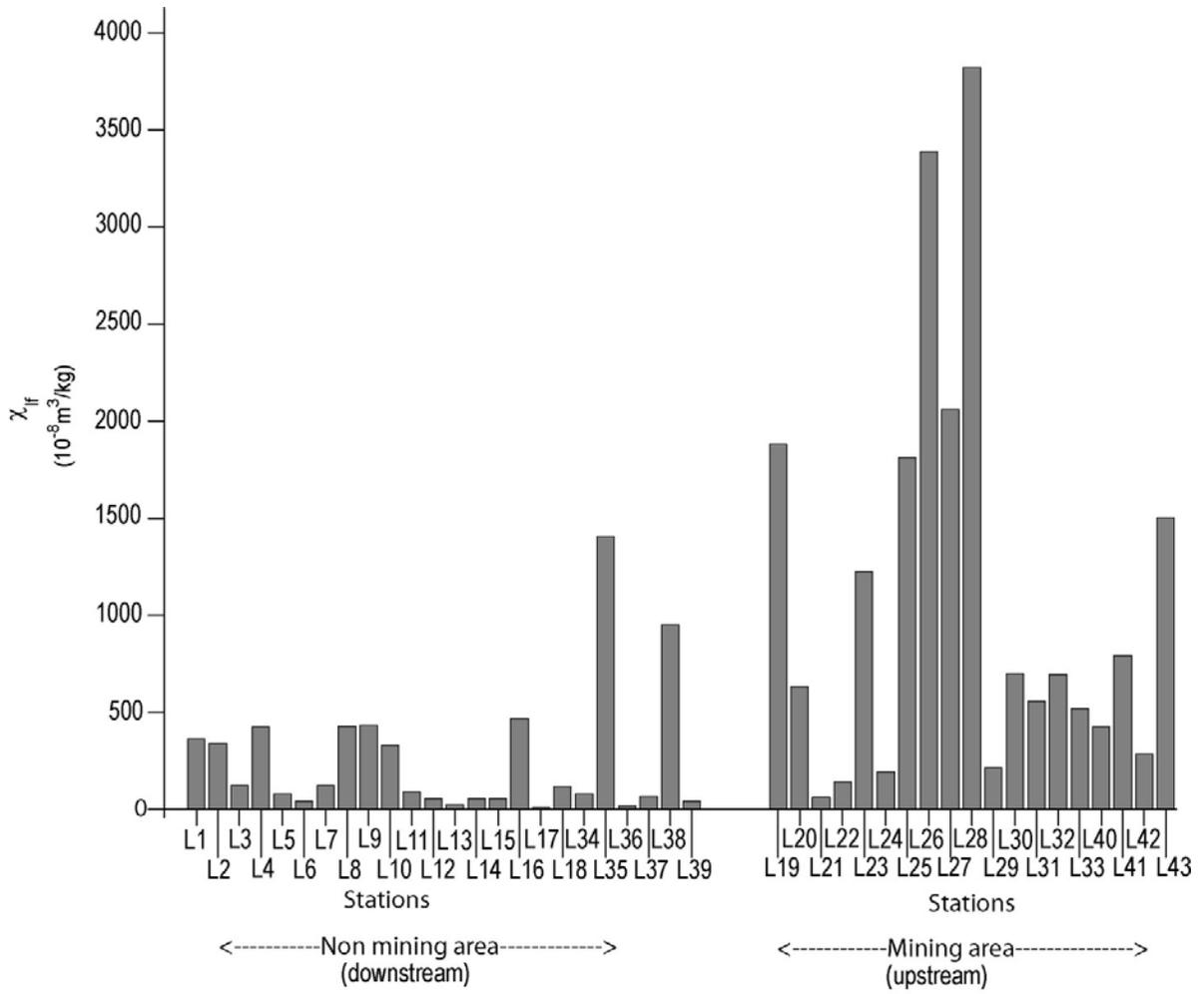


Fig 2a

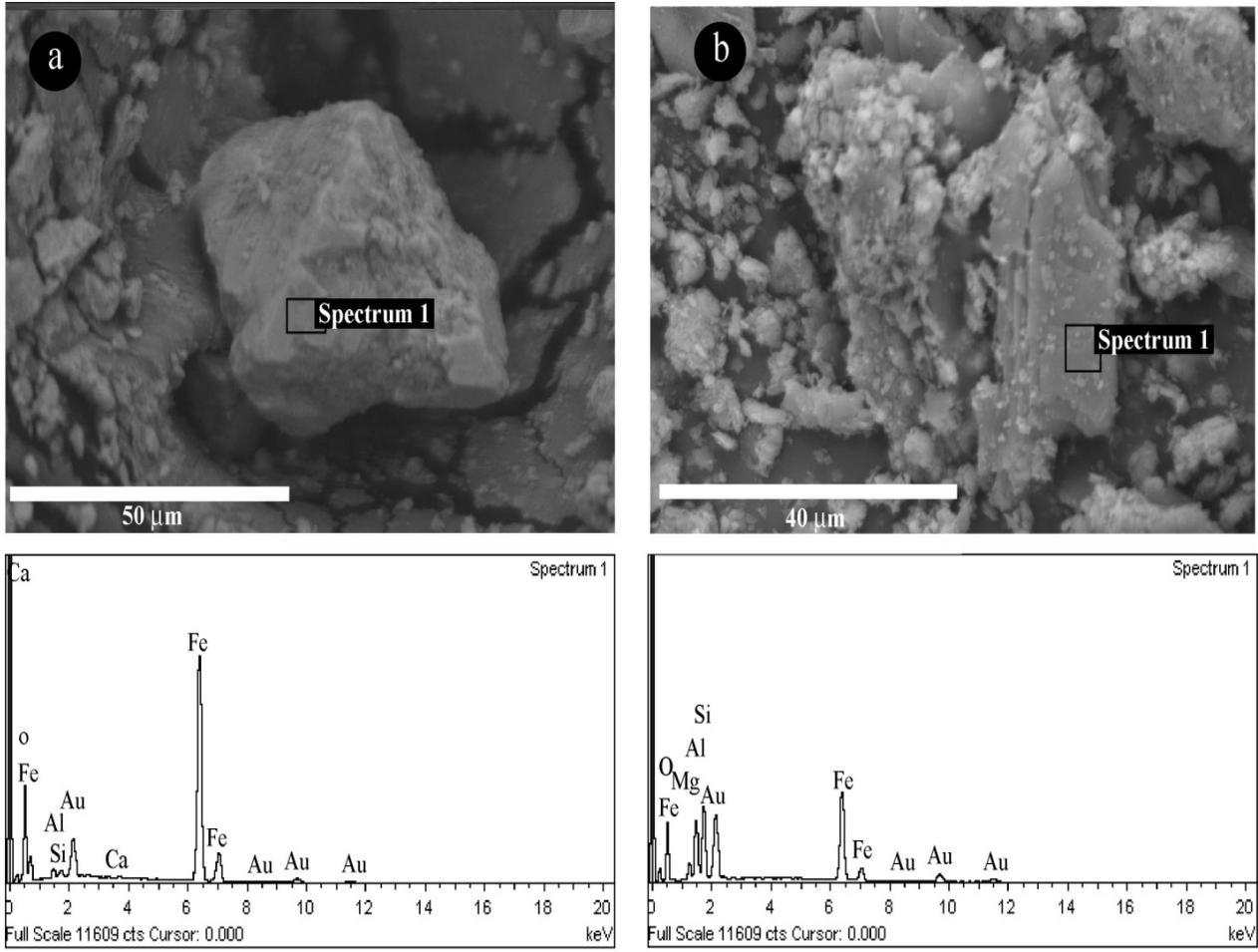


Fig. 3

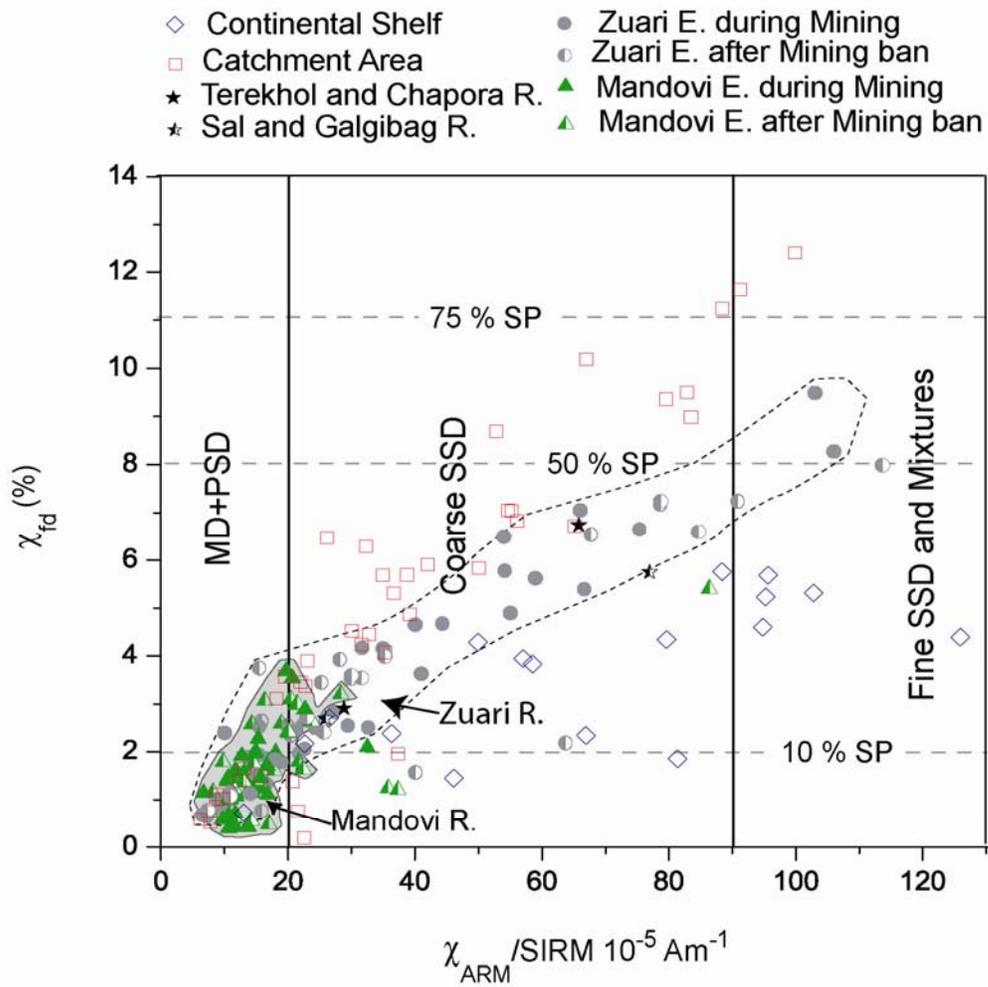


Fig. 4

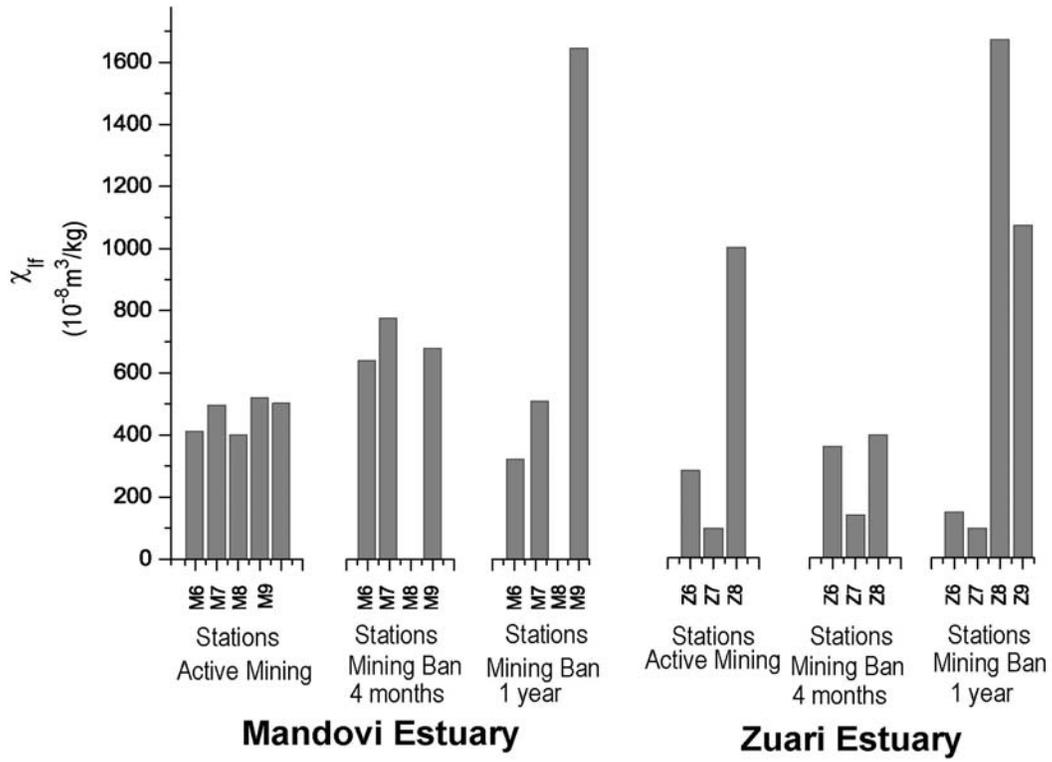


Fig 5a

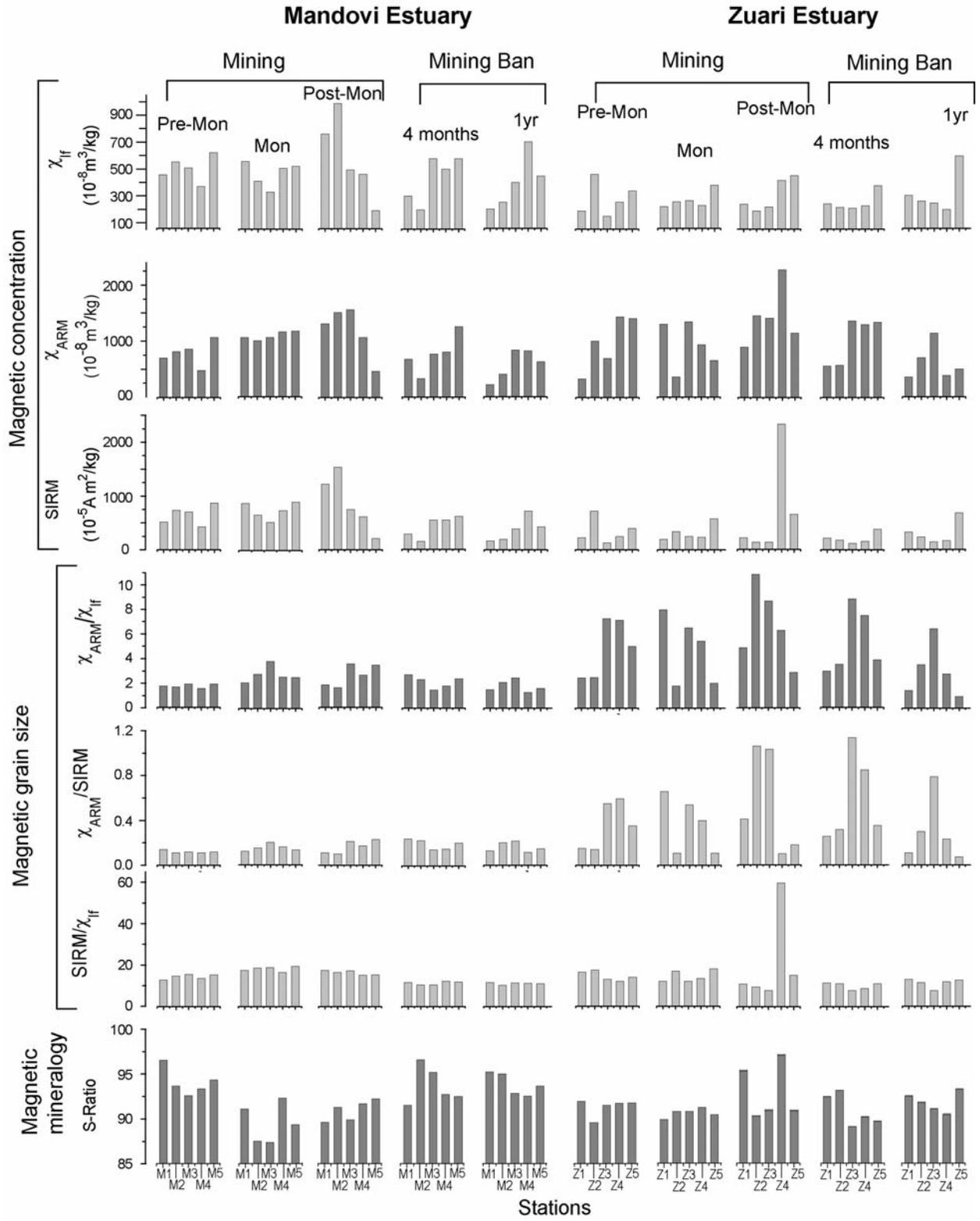


Fig. 5b

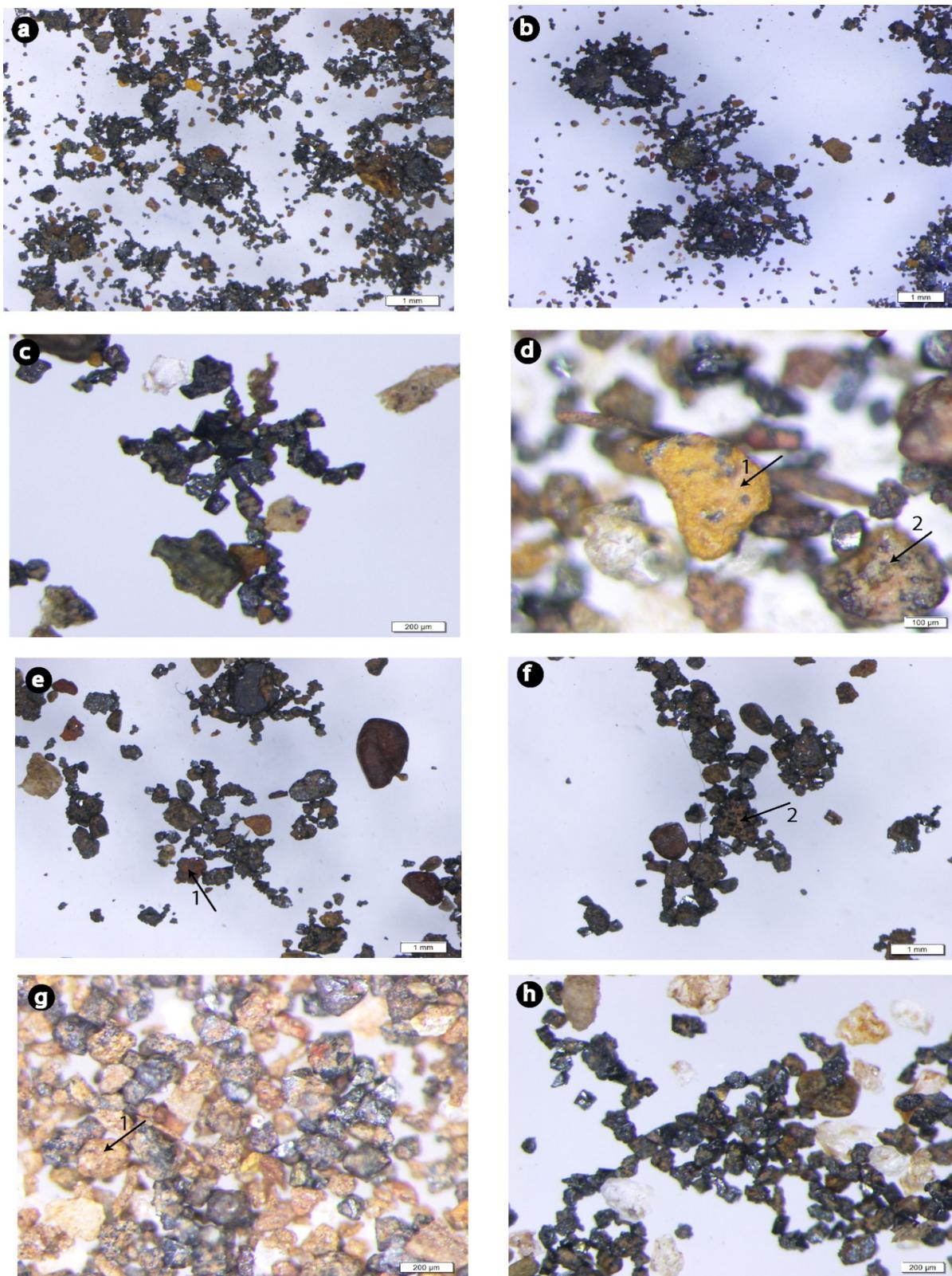


Fig. 6

Table 1. Magnetic parameters of catchment area of Mandovi Zuari (Ma-Zu) estuaries and Sea samples offshore of Ma-Zu estuaries and Galjibag, Sal, Chapora and Terekhol Rivers. *Data based on two samples from the river mouth.

		Catchment Samples of Mandovi-Zuari Estuaries		Shelf Samples off Mandovi-Zuari Estuaries	South Goa Rivers		North Goa Rivers	
		downstream	upstream		Galjibag River*	Sal River*	Chapora River*	Terekhol River*
$\chi_{if}(10^{-8}m^3 kg^{-1})$	Mean	255.5	1100.8	79.3	90.7	59	258.2	393.1
	Min-Max	8.5-1405.9	62.5-3822.1	4.6-350.8				
$\chi_{ARM}(10^{-8}m^3 kg^{-1})$	Mean	1424.9	2950.3	652.2	564.1	147.2	1003.7	2319
	Min-Max	24.1-9024.2	143.2-9568.7	103.0-1090.6				
SIRM($10^{-6} Am^2 kg^{-1}$)	Mean	2759.7	15107.8	1126.2	728.3	569.9	3473.6	3491.6
	Min-Max	121.4-10859.6	682-53503	82.4-4731.9				
χ_{ARM}/χ_{if}	Mean	5.2	3.8	13.8	6.2	2.5	3.9	5.9
	Min-Max	1.9-7.9	1.1-8.4	1.8-72.4				
$\chi_{ARM}/SIRM(10^{-5}mA^{-1})$	Mean	0.4	0.4	0.9±0.7	0.8	0.3	0.3	0.7
	Min-Max	0.1-1.0	0.1-2.0	0.1-3.1				
SIRM / $\chi_{if}(kA m^{-1})$	Mean	13.7	12.9	14.7	8	9.7	13.5	8.9
	Min-Max	6.7-25.8	4.1-22.6	11.4-23.5				
S ratio	Mean	88.2	92.8	94.2	94.3	93.7	96.5	97.7
	Min-Max	74.8-98.5	75.6-97.9	90.8-98.3				
$\chi_{fd}(\%)$	Mean	6.0	4.6	3.9	5.7	2.7	2.9	6.7
	Min-Max	0.2-14.8	0.5-13.4	0.7-10.3				

Table 2. Magnetic parameters of upstream Mandovi and Zuari estuary during peak mining and after mining ban.

		Mandovi estuary , upstream			Zuari estuary, upstream		
		During mining	After 4 months mining ban	After 1 year mining ban	During mining	After 4 months mining ban	After 1 year mining ban
$\chi_{if} (10^{-8} \text{m}^3 \text{kg}^{-1})$	Mean	467.5	698.0	826.6	445.7	297.5	745.4
	Min-Max	399.3-519.58	640.0-775.6	323.0-1645.0	95.4-999.3	138.1-396.1	95.2-1668.6
$\chi_{ARM} (10^{-8} \text{m}^3 \text{kg}^{-1})$	Mean	997.0	953.3	2871.4	620.5	507.4	1955.3
	Min-Max	644.2-1802.16	797.0-1112.2	1235.9-4356.2	207.1-1116.0	175.6-686.4	424.9-3453.1
$SIRM (10^{-6} \text{Am}^2 \text{kg}^{-1})$	Mean	8912.7	9094.7	8727.4	7285.6	3430.5	9386.9
	Min-Max	6147.6-11988.22	6156.3-13043.5	3444.4-17708.5	1344.3-17229.5	1663.9-4450.9	1060.8-21840.7
χ_{ARM}/χ_{if}	Mean	2.1	1.4	4.7	1.6	1.6	4.1
	Min-Max	1.5-3.59	1.2-1.6	1.8-8.5	1.1-2.2	1.3-1.9	2.1-7.1
$\chi_{ARM}/SIRM (10^{-5} \text{m}^3 \text{A}^{-1})$	Mean	0.1	0.1	0.5	0.1	0.1	0.4
	Min-Max	0.1-0.15	0.1-0.1	0.2-0.9	0.1-0.2	0.1-0.2	0.2-0.6
$SIRM /\chi_{if} (\text{kA m}^{-1})$	Mean	18.9	12.6	10.4	15.4	11.7	11.9
	Min-Max	14.6-23.36	11.8-13.5	9.9-10.8	14.1-17.2	10.5-12.4	11.1-13.1
S ratio	Mean	89.5	89.3	92.9	92.7	89.2	92.2
	Min-Max	80.1-96.05	81.3-93.5	91.2-94.8	91.9-94.3	87.3-91.7	91.1-93.2
$\chi_{fd} (\%)$	Mean	1.6	1.9	2.4	1.3	2.5	1.8
	Min-Max	1.2-2.29	1.2-2.6	0.5-5.4	0.7-2.0	0.9-3.8	0.8-2.6

Table 3. Magnetic parameters of downstream Mandovi and Zuari Estuary

		Mandovi Estuary- Mining Time			Mandovi Estuary- After Mining Ban		Zuari Estuary- Mining Time			Zuari Estuary- After Mining Ban	
		Pre-monsoon	Monsoon	Post-monsoon	After 4 months mining ban	After 1 year mining ban	Pre-monsoon	Monsoon	Post-monsoon	After 4 months mining ban	After 1 year mining ban
$\chi_{if}(10^{-8}m^3kg^{-1})$	Mean	443.7	410.9	521.8	376.1	343.6	224.0	212.3	248.6	203.9	264.9
	Min-Max	312.5-563.7	275.8-502.7	134.7-930.6	142.2-523.9	142.5-637	96.4-405.7	162.8-320.1	134.3-398	154.4-343.2	140.9-539.3
$\chi_{ARM}(10^{-8}m^3kg^{-1})$	Mean	789.4	1087.9	1184.6	769.1	581.4	976.3	915.7	1440.8	1026.0	615.4
	Min-Max	482.5-1073.2	998.9-1173.1	466.8-1561.7	331.1-1261.3	218.1-834.3	329.3-1436.4	359.9-1340.6	899.9-2277.6	557.1-1362.3	351.2-1140.8
SIRM($10^{-6}Am^2kg^{-1}$)	Mean	6521.4	7414.1	8656.3	4268.6	3816.6	3408.1	3200.5	6965.2	2106.3	3104.9
	Min-Max	4304.9-8693.7	5213.3-9022.1	2074.4-15382.7	1476.8-6156.3	1683.9-7207.3	1266.8-7145	1962.2-5818.5	1375-23327.9	1199.7-3806.8	1451.1-6823.3
χ_{ARM}/χ_{if}	Mean	1.8	2.8	2.6	2.2	1.8	4.9	4.7	6.7	5.3	3.0
	Min-Max	1.5-1.9	2.1-3.8	1.6-3.6	1.5-2.7	1.3-2.5	2.5-7.3	1.8-8	8.4-64.4	3.0-8.8	0.9-6.4
$\chi_{ARM}/SIRM(10^{-5}mA^{-1})$	Mean	0.1	0.2	0.2	0.2	0.2	0.4	0.4	0.6	0.6	0.3
	Min-Max	0.1-0.1	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.6	0.1-0.7	0.1-1.1	0.3-1.1	0.1-0.8
SIRM / $\chi_{if}(kA m^{-1})$	Mean	14.6	18.1	16.3	11.3	11.1	14.7	14.6	22.3	10.1	11.3
	Min-Max	12.9-15.7	16.4-19.4	15.2-17.3	10.4-12.2	10.3-11.7	12.1-17.6	12.1-18.2	8.4-64.4	7.8-11.6	7.6-13.0
S ratio	Mean	94.1	89.5	90.9	93.7	93.8	91.3	90.6	92.9	91.0	91.9
	Min-Max	92.5-96.5	87.3-92.3	89.6-92.2	91.5-96.6	92.5-95.2	89.6-91.9	89.9-91.3	90.3-97.1	89.1-93.2	90.5-93.3
$\chi_{fd}(\%)$	Mean	0.7	2.1	1.9	1.9	2.0	3.5	4.1	5.1	4.9	3.1±2.6
	Min-Max	0.4-1.4	1.5-3.7	0.6-3.5	0.5-3.1	1.2-3.0	1.1-5.6	1.1-7	1.8-9.5	2.4-8.0	0.8-7.2