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ORIGINAL PAPER

Environmental magnetic studies on surface sediments: a proxy for metal and hydrocarbon contamination

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Abstract Visakhapatnam is one of the major port cities, and it is developed into a hub of many large- and medium-scale industries. Due to growing industrialization and urbanization, coast is vulnerable to both organic and inorganic micro-pollutants. Twenty-five surface sediments were collected along the Visakhapatnam coast for the measurement of texture size, petroleum hydrocarbons, trace metals and environmental magnetic parameters. The percentage of coarser particles was more in the northern region, whereas the percentage of fine particles was increased toward south. Elevated levels of petroleum hydrocarbons and trace metals were attributed due to marine and land-based sources, in particular, those were due to shipping activities, treated and partially treated sewage and industrial wastes. The concentrations of trace metals, petroleum hydrocarbons and magnetic minerals were decreased from nearshore to seaward. Our results revealed that the magnetic mineralogy is dominated by magnetite with a small proportion of hematite, and the grain size of magnetic minerals was in the range of pseudo-single domain to multidomain nature with detrital origin. From the principal component analysis, the magnetic concentration and mineralogy-dependent parameters co-vary with the heavy metal and PHC concentrations, suggesting that the inputs of magnetic minerals, petroleum hydrocarbons and heavy metals in the Visakhapatnam shelf sediments were derived from the same anthropogenic sources. Thus, the large magnetic dataset can be used to reduce the number of chemical analysis; hence, environmental magnetic parameters were used as a proxy for both organic and inorganic micro-pollutants.

Keywords Environmental magnetism · Sediment texture · Petroleum hydrocarbon · Trace metals · Multivariate statistics

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Introduction

Environmental magnetism involves the measurement of magnetic properties in environmental materials, including soils, sediments and dusts. The sensitivity of magnetic measurements formulates the possible detection of minute quantities of magnetic material. Magnetic methods are well-known multipurpose technique in the area of geosciences. These magnetic properties frequently give extremely susceptible indicators of environment. With the development of environmental magnetism, magnetic measurement is becoming an important way to delineate pollution sources. Anthropogenic pollution usually has a strong magnetic signature, and magnetic methods have proven to be capable of discriminating between different sources of pollution and to outline polluted areas (Panaiotu et al. 2005). Mineral magnetic measurements are fast, cost-effective, non-destructive, sensitive and informative. Magnetic measurements are proxy for industrial contamination (Goddu et al. 2004; Sangode et al. 2010), heavy metal (Alagarsamy 2009; Venkatachalapathy et al. 2011b) and petroleum hydrocarbons in coastal environment (Venkatachalapathy et al. 2010; Karbassi et al.

2011). Mineral magnetic measurements are also used as a tool for determining the sediment provenance (Oldfield and Yu 1994), transport pathways (Lepland and Stevens 1996) and particle size data (Booth et al. 2005).

Coastal sediments represent natural sinks of petroleum hydrocarbons, heavy metals and magnetic minerals of different origin, from lithogenic as well as pedogenic and anthropogenic sources. Magnetic particles in coastal sediments are usually derived primarily from terrestrial sources via fluvial and eolian transportation. Since industrialization, however, iron oxides are originating from anthropogenic fly ashes from factories, and vehicles may also significantly contribute to the magnetic properties of marine sediments. This is especially common in coastal settings and marginal seas adjacent to heavily populated and industrialized areas (Horng et al. 2009; Venkatachalapathy et al. 2011b; Aguilar et al. 2012).

Magnetic measurements have been employed recently by number of authors in examining the anthropogenic inputs into lakes, as well as stream and marine sediments (Scholger 1998; Chan et al. 2001; Chaparro et al. 2011; Venkatachalapathy et al. 2010, 2011a, b). By measuring magnetic susceptibility, Kapicka et al. (1999) outlined pollution spatial distribution and pollution load near the coal-burning power plant. The magnetic technique is an effective tool for the research of heavy metals contamination. In particular, large amount of heavy metals is improperly emitted during some high-temperature processes such as coal and oil combustion in thermoelectric power stations and industrial plants, automobile exhaust, refuse incineration and kiln operations in cement plants (Lu and Bai 2006). The magnetic susceptibility of surface sediments is a marker of sediment sources and transport trends (Ellwood et al. 2006), if those magnetic materials are derived from weathered continental rocks, both detrital and eolian are transported to a long distance into the deeper areas.

The aims of the present study are as follows: (1) to establish the spatial distribution of sediment texture, magnetic concentration, grain size, mineralogy, petroleum hydrocarbons and trace metals in surface sediments of Visakhapatnam coast collected during December 2009 (Northeast monsoon), Bay of Bengal, India and (2) to examine the applicability of magnetic measurements of sediments to discriminate the anthropogenic and lithogenic contributions in marine environment.

Materials and methods

Study area

Visakhapatnam coast (17°41′34″ N and 83°17′45″ E) is situated along the east coast of India and northeastern coast of Andhra Pradesh with topography like a spoon-shaped basin surrounded by hill ranges on three sides and sea on the other side and is often called as bowl area for assessment of environmental-related issues. The geology of the region is presented by the khondalite suite of rocks (garnetiferrous sillimanite gneisses, quartzo-feldsphatic garnet gneisses) of Archean age in the Eastern Ghats mobile belt. Quaternary deposits consist of red-bed sediments, laterites, pediment fans, colluvium, alluvium and coastal sands (Goddu et al. 2004). The coastline is occupied by a major port, fishing harbors, naval dockyard, shipyard, marinas and recreational beaches, and it is oriented along SW–NE direction. Visakhapatnam has a major and wonderful natural and land-locked harbor as it is connected to the Bay of Bengal by a channel cut through solid rock and sand, and it is the ideal gateway contributing to the development of petroleum, steel and fertilizer industries.

Visakhapatnam experiences typical tropical weather. The wave climate of this region varies from the southwest monsoon (June to September) to the northeast monsoon (October to December). Significant wave height has a range of 1–3 m during May–September, 0.5–2 m during October to December (except during the cyclone periods) and generally less than 1.5 m in the remaining period. The average wave period varies from 9 to 12 s for the greater part of the year. The waves predominantly approach the coast from the south during March–September and from the east during December–February. The wave direction is transitional, shifting from south to east during October to November. The tides in this region are semi-diurnal. As reported in the Indian Tide Table for Visakhapatnam, the mean spring tidal range is 1.43 m and neap tidal range is 0.54 m (Sanilkumar et al. 2004). The East Indian Coastal Current flows northward during April–December due to wind-induced interior Ekman pumping and southward during October to January (McCreary et al. 1996).

Visakhapatnam city is one of the major commercial cities in South India, and it has developed into a hub for many heavy industries such as, Paper mills, Power plant, Tanneries, Polymers, Steel Plant, Lead and Zinc mining, Zinc smelter, Fertilizers, Shipyard, Metal alloy, Shipping industries and Oil refineries.

Sampling and analysis

Twenty-five surface sediment samples were collected along the Visakhapatnam coast from Lawson's Bay to Appikonda beach at 10 transects at three different water depths viz., 10, 15 and 20 m during December 2009 (Northeast monsoon) using a Peterson grab sampler (Fig. 1). The geographical co-ordinates of the sampling locations were recorded by hand-held GPS (Garmin 12). The water depth at each sampling point was determined using single-beam echo-sounder (Odom hydrotrac). Samples were taken from the

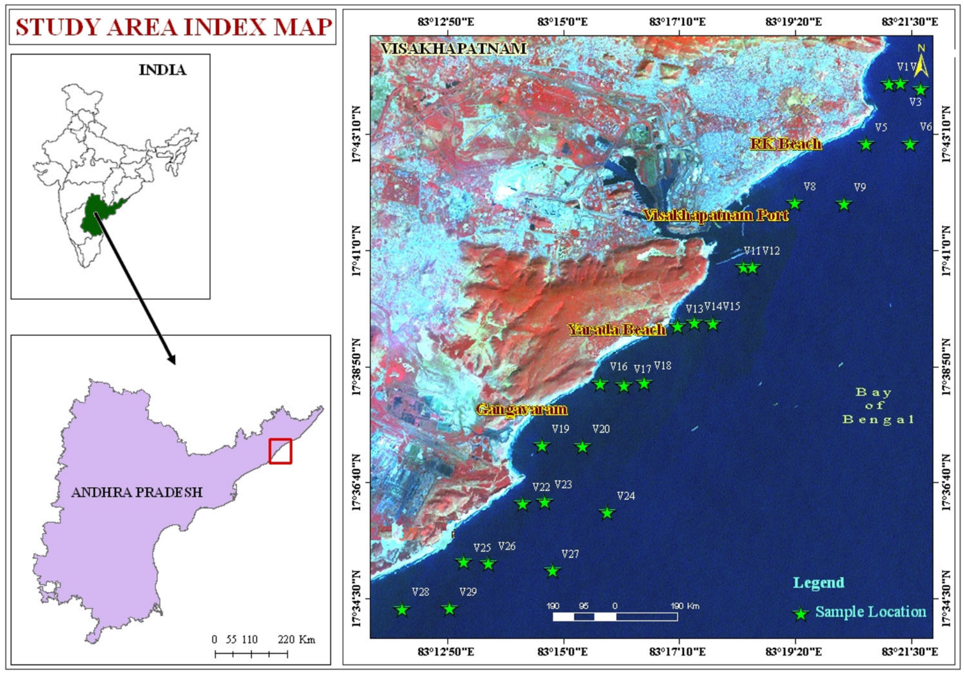


Fig. 1 Study area map with sampling locations along Visakhapatnam coast, Bay of Bengal, India

central part of the grab sampler to avoid any metallic contamination from the metallic sampler. The samples were packed by self-packing polythene bags and were frozen at −4 °C immediately until further analysis.

Analytical methods

Textural and geochemical analysis

Grain-size separation was carried out through the dry-sieving method using ASTM mesh sieves (Retsch AS 200 digital sieve shaker available at Department of Earth Sciences, Annamalai University). Sieving technique is applied to separate the grains of various size classes. Hundred gram of sediment samples was transferred into clean polythene bags. In the laboratory, samples were air-dried at room temperature. After air drying, the samples were dry-sieved with the help of mechanical shaker (Buchanan 1984). The sand fraction was determined as the amount of sediment retained by sieve of 0.125 mm size. The fraction of samples which passed through a sieve of 0.125 mm but retained by sieve of 0.063 mm was silt, and the fraction of sample which passed through a sieve of 0.063 mm was clay (Ingram 1970).

The acid leachable fraction extracts almost the whole degree of elements as it is absorbed by sediments depicting the contamination of an area (Janakiraman et al. 2007). The extraction of acid leachable metals was done by weighing 1 g of dry sediment sample in a 20 ml plastic bottle in which 15 ml of 0.5 N HCl was added, and after mechanically shaking for 16 h, it was filtered with Whatman "A" filter paper. The final filtered solution was analyzed for acid leachable Fe, Cr, Cu, Ni, Pb, Cd and Zn using Inductively Coupled Plasma Optical Emission Spectroscopy (Perkin Elmer, Optima 2100 DV). Suitable internal chemical standards (Merck, Germany) are used to calibrate the instrument. Precision and accuracy of the metal analysis are checked against the 2702 marine sediment Standard Reference material from National Institute of Standards and Technology (NIST), USA, and the results are shown in Table 1.

Petroleum hydrocarbon analysis

The collected sediment was thawed, saponified using a KOH methyl alcohol mixture followed by extraction with n-hexane. The concentrated extract, after drying, was separated into alkane and aromatic fractions in an alumina column, and the intensity of fluorescence of the aromatic fraction was measured (IOC-UNESCO 1982). Petroleum hydrocarbon concentrations in sediment samples were determined using UV-Fluorescence (UVF) Spectroscopy (Varian make Cary Eclipse). The fluorescence of the samples was measured at an emission wavelength of 364 nm (excitation wavelength 310 nm). All blanks, standards and samples were measured in Teflon—capped 1 cm silica fluorescence cell under identical instrumental settings and conditions. All blanks, standards and samples were measured in a Teflon—capped 1 cm silica fluorescence cell under identical instrumental settings and conditions. Duplicates, spikes and blanks were treated identically using chrysene as a standard reference to test precision, accuracy and solvent purity in the analytical procedure, and the data were expressed in terms of chrysene equivalents as ppm.

Table 1 The recovery analysis of trace metals content in 2,702 standard reference material

Metal	Certified values	Measured values	Recovery (%)
Fe (%)	7.91 ± 0.21	7.05	89
Cd (ppm)	0.82 ± 0.04	0.64	78
Cr (ppm)	352 ± 24	192	55
Cu (ppm)	177.7 ± 5.2	113	64
Ni (ppm)	75.4 ± 3.3	51	68
Pb (ppm)	132.8 ± 4.1	100.5	76
Zn (ppm)	485.3 ± 28	423	87

Percentage recovery for spiked samples ranged from 96 to 99 %, whereas precision agreed within 5 %. Blank values were almost negligible. All experiments were conducted in 5 replicates, and the averages of the values were reported along with standard deviations.

Environmental magnetic analysis

Magnetic susceptibility measurements were carried out on subsamples, which were dried at 40 °C and disaggregated. Samples were packed into 10-ml plastic containers, using cling-film to immobilize the sediments. Magnetic susceptibility measurements were conducted using a magnetic susceptibility meter MS2B with dual frequency sensor (0.47 and 4.7 kHz) (Dearing 1999). The percentage of frequency dependence of susceptibility χ_{fd} % is calculated using the formula,

$$\chi_{fd}\,\% = \left(\frac{(\chi_{lf} - \chi_{hf})}{\chi_{lf}}\right) \times 100$$

Anhysteretic remanent magnetization (ARM) was measured after demagnetization in an AF field of 100 mT inducing a DC biasing field of 0.05 mT using a Molspin AF demagnetizer, and its remanence was measured using Molspin Minispin spinner magnetometer. Isothermal remanent magnetization (IRM) was acquired by a sample after exposure to, and removal from, a steady (DC) magnetic field (Walden et al. 1997). IRM depends on the strength of applied field, which is often denoted by a subscript. IRM was measured for forward fields 20 mT, 1 T and reverse field of 20, 30, 40, 60, 80, 100, 200 and 300 mT. IRM_{1T} is hereafter referred to as the saturation isothermal remanent magnetization (SIRM), and IRM is often used as an indicator of the presence of ferrimagnetic minerals, but anti-ferromagnetic minerals such as hematite and goethite also contribute with the excess applied magnetic field of 100 mT. χ_{ARM}/SIRM, SIRM/χ, χ_{ARM}/χ, Soft IRM and Hard IRM were calculated using forward and backward DC fields. S-ratio (=$-IRM_{-300mT}$/SIRM) was also calculated from IRM measurements.

Statistical analysis

The whole set of data in the present study was analyzed by multivariate statistical method, including Pearson's correlation and principal component analyses. Pearson correlation analysis was used to determine the correlations among the mineral magnetic, textural and geochemical parameters. PCA can incorporate the data standardized from all the geochemical and geophysical in one unified comparison, and use the optimized minimum components to explain the original datasets. Then, through defining principal components, the geochemical and geophysical characteristics of sediments were determined. All statistical analyses were done using the statistical software SPSS for Windows Ver. 11. The results of the present study were analyzed to establish the natural processes and to identify the sources of pollution (Bridgman 1992; Ratha and Sahu 1993). Principal component analysis was done to identify the relations among the variables, and the PC scores were computed from correlation matrix rearranged data, so that it explains the sources of magnetic minerals, petroleum hydrocarbons and trace metals. The PC scores were based on the eigenvalues, and the PC scores were computed.

Results and discussion

Textural and geochemical characteristics of sediments

The textural characteristics of Visakhapatnam coastal sediments were shown in Fig. 2. The sediments collected in the present study ranged from sand to sandy silt (Table 1), and silty sand was dominated in the study area. Sand, silt and clay ranges were 3.32–99.17, 0.63–93.57 and 0.07–5.45 %, respectively. Maximum sand percentage was recorded at V9 near Ramakrishna beach, and minimum was recorded at V28 near Appikonda beach. The maximum silt percentage was recorded at V28 near AK beach, and minimum was recorded at V9 near RK beach. The maximum clay percentage was recorded at V5 near Lawson's bay, and minimum was recorded at V9 near RK beach. Percentage of coarser particles was dominated in the northern region, due to occurrence of shoreline erosion at northern part of Visakhapatnam port by the construction of breakwaters at the port (Sanilkumar et al. 2006) and also formation of rip currents at RK beach (Prasad et al. 2009). Fine particles were dominated in southern region, due to freshwater influx into the harbor through a monsoon-fed stream known as "Mehadrigedda" (Raman 1995) with fine particles that settled to the bottom when current and wind speeds reduce (Muthuraj and Jayaprakash 2008). Low wave action inside the Gangavaram bay and protection from the southerly waves encourages the deposition of sediment

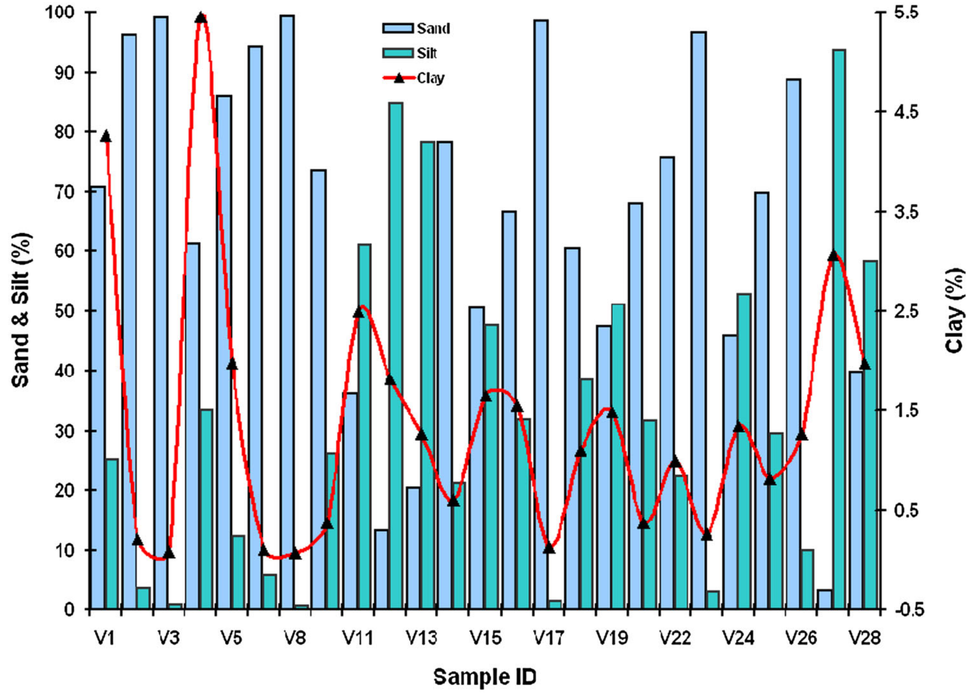


Fig. 2 Sediment texture of surface sediments along Visakhapatnam coast

(Chandramohan et al. 2001). Deposition of sediment leads to domination of fine particles in southern region.

The spatial distribution of petroleum hydrocarbons in surface sediments from Visakhapatnam coast is shown in Fig. 3. Petroleum hydrocarbons concentrations in Visakhapatnam coastal sediments varied from 0.34 to 19.70 µg/g. Figure 3 shows a clear tendency of hydrocarbon concentrations to decrease from the coast toward sea. Concentrations of PHCs were decreased with increasing distance from the shore. The maximum concentration was recorded at V28, near AK beach, and the minimum concentration was recorded at V8, near RK beach. This result suggested the association of PHC with the grain size of sediment. According to Kucuksezgin et al. (2006), concentrations of PHCs in unpolluted marine sediments were ranged from sub µg/g to 10 µg/g. The higher concentrations were found from harbor to Appikonda beach, due to anthropogenic sources. Elevated levels of petroleum hydrocarbons were attributed to marine and land-based sources, in particular, those due to transportation of petroleum-related products to the oil terminal in the harbor (petrogenic), shipping activities and untreated sewage and industrial wastes. In the Bay of Bengal region, no natural oil seeps have been reported, and spills from ships were infrequent. These were primarily derived from incomplete combustion of fossil fuels from the thermal power plant (pyrolytic) (Unlu and Alpar 2006), atmospheric runoff, direct release of oil and its products and its association with fine sediment particles. The enhancement of PHC in Visakhapatnam coastal sediments is contributed by biogenic, petrogenic, pyrolytic and anthropogenic sources.

The spatial distribution of major (Fe) and some trace metals is shown in Fig. 4a, b. In Visakhapatnam coastal sediments, the concentrations of major and some trace metals were in the range of Fe (1,782–1,1392 µg/g), Cd (0.04–0.76 µg/g), Cr (27.26–58.50 µg/g), Cu (8.40–47.32 µg/g), Ni (17.76–34.04 µg/g), Pb (16.20–36.08 µg/g) and Zn (39.60–154.00 µg/g), respectively. The average concentrations of trace metals were higher than that of earth crust (Wedepohl 1995). The higher concentrations of trace metals were randomly distributed throughout the study area. The mean concentrations of Cd, Cu, Fe, Ni, Pb and Zn were lower than the values reported by Satyanarayana et al. (1994) in this region.

The concentrations of trace metals were decreased with increasing of distance from the shoreline. Maximum concentrations of Cd, Cr, Cu, Fe, Ni and Pb were found at V1 (Lawson's Bay—10 m), whereas the maximum zinc concentration was found at V5 sediment samples due to wastewater from lead and zinc mining industries, outlet from sewage treatment plant and low wave energy (Prasad et al. 2009). The elevated levels of trace metals were indicated that the trace metal pollution due to anthropogenic inputs such as industrial effluents and domestic sewage was discharged into the Visakhapatnam harbor (Satyanarayana et al. 1985), Gangavaram port and fishing activities. The point sources of pollution were mainly from Thermal Power plant, Visakhapatnam Steel Plant, Petrochemical industries, Fertilizer industries, Paper mills, Tanneries, Polymers, Lead and Zinc mining, Zinc smelter, Fertilizers, Shipyard, Metal alloy, Shipping industries and Oil refineries.

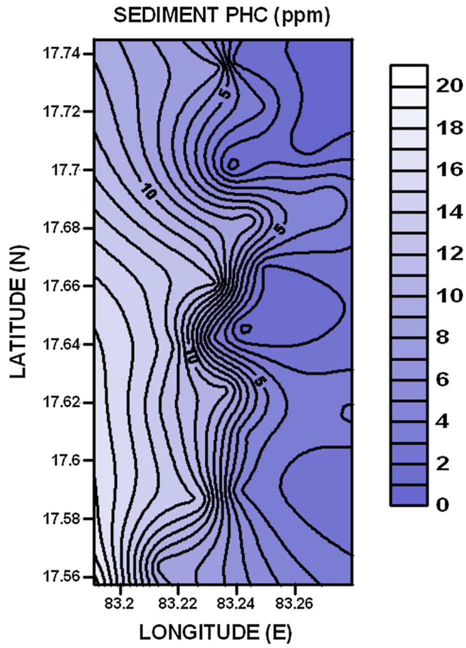


Fig. 3 Spatial distribution of petroleum hydrocarbons in surface sediments along Visakhapatnam coast

To assess the soil environmental quality, an integrated pollution load index (PLI) of the six metals (Cd, Cr, Cu, Ni, Pb and Zn) was calculated according to (Angulo 1996). The PLI is defined as the nth root of the multiplication of the concentrations,

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF}_1 \times \mathrm{CF}_2 \times \cdots \mathrm{CF}_n}$$

where CFmetal is the concentration factor and it is the ratio between the concentrations of each heavy metal and the background values, CFmetal = CHmetal/CHbackground.

The pollution load index represents the number of times by which the heavy metal concentration in the sediment exceeds the background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The integrated pollution load index (PLI) of the six metals (Cd, Cr, Cu, Ni, Pb and Zn) was calculated and is shown in Fig. 4c. PLI > 1 indicates progressive metal pollution, whereas PLI $= 1$ indicates heavy metals load close to background (Venkatachalapathy et al. 2011b). PLI > 1 was recorded throughout the entire study area. Higher PLI values were recorded at nearshore sediment samples. Maximum PLI was recorded at Lawson's Bay. Clark et al. (2003) also reported that Lawson's Bay had higher pollution index than other regions in Visakhapatnam coast.

Magnetic parameters

Magnetic concentration-dependent parameters

Magnetic susceptibility (χ), susceptibility of anhysteretic remanent magnetization (χ_{ARM}) and SIRM are primarily sensitive to concentration of ferrimagnetic minerals, and they also respond to magnetic grain-size variations and changes in the magnetic mineralogy (Liu et al. 2003). χ and SIRM generally indicate the concentration of magnetic minerals in a sample. The susceptibility of ARM (χ_{ARM}) is roughly proportional to the concentration of ferrimagnetic grains in the fine-grained stable single domain (SSD) state, and higher χ_{ARM} values indicate a great concentration of SSD grains (Maher 1988; Wang et al. 2009). χ, χ_{ARM} and SIRM in Visakhapatnam coastal sediments were shown noticeable variation among the samples, and they were ranged 4.70–213.90 $\times 10^{-8}$, 25.28–286.19 $\times 10^{-8}$ m^3/kg and 30.93–2079.07 $\times 10^{-5}$ Am^2/kg, respectively (Fig. 5), showed the presence of higher concentrations of ferrimagnetic minerals derived from anthropogenic origin (Venkatachalapathy et al. 2010). The average value of χ was 62.91 $\times 10^{-8}$ m^3/kg and it is greater than 50 $\times 10^{-8}$ m^3/kg; they were derived from anthropogenic sources. The maximum values of concentration-dependent parameters were observed at V28, near AK beach, due to enhancement of iron oxides derived from anthropogenic sources such as the combustion of coal from the thermal power plant, emissions from steel plant, untreated and partially treated wastes from industries, abundant of fine-grained sediments. The minimum value was observed at V9, near RK beach, due to abundance of coarse-grained sediments. Concentrations of magnetic minerals were decreased from nearshore to seaward due to prevailing hydrodynamic conditions. The ranges of magnetic susceptibility in coastal sediments are higher when compared with the dust and top soil samples collected from Visakhapatnam city (Goddu et al. 2004), because the concentration of magnetic minerals in the marine sediments was derived from shipping-related activities (Chan et al. 2001), incomplete combustion of fossil fuels from the thermal power plant and treated and untreated effluents from metallurgical industries and smelters present in the study area.

Magnetic mineralogy

S-ratio, Soft IRM and Hard IRM are magnetic mineralogy-dependent parameters. The S-ratio is dimensionless parameter, and it can be used to indicate the relative proportion of ferrimagnetic (e.g., magnetite) and anti-ferromagnetic (e.g., hematite and goethite) minerals in a sample. Soft IRM is a measure of the concentration of low coercivity soft magnetic minerals like magnetite/maghemite, and Hard IRM is a measure of the concentration of high coercivity hard magnetic minerals like hematite/goethite. S-ratio values ranged from 0.80 to 1.00 with an average of 0.93 (Fig. 6b) for the coastal sediments of Visakhapatnam, and they imply predominance of low coercivity and soft ferrimagnetic minerals in this region. Soft IRM values ranged between 27.77 and

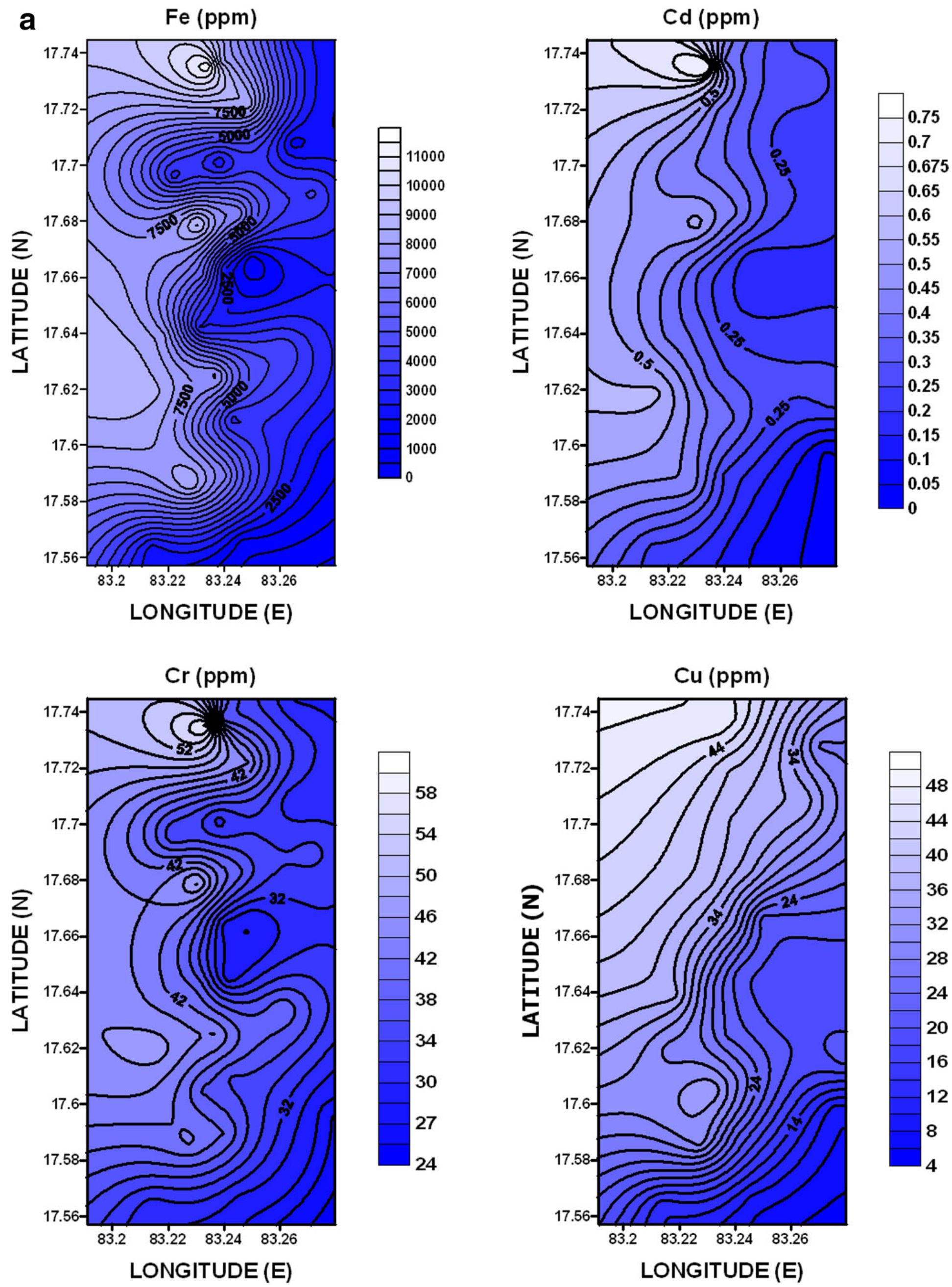


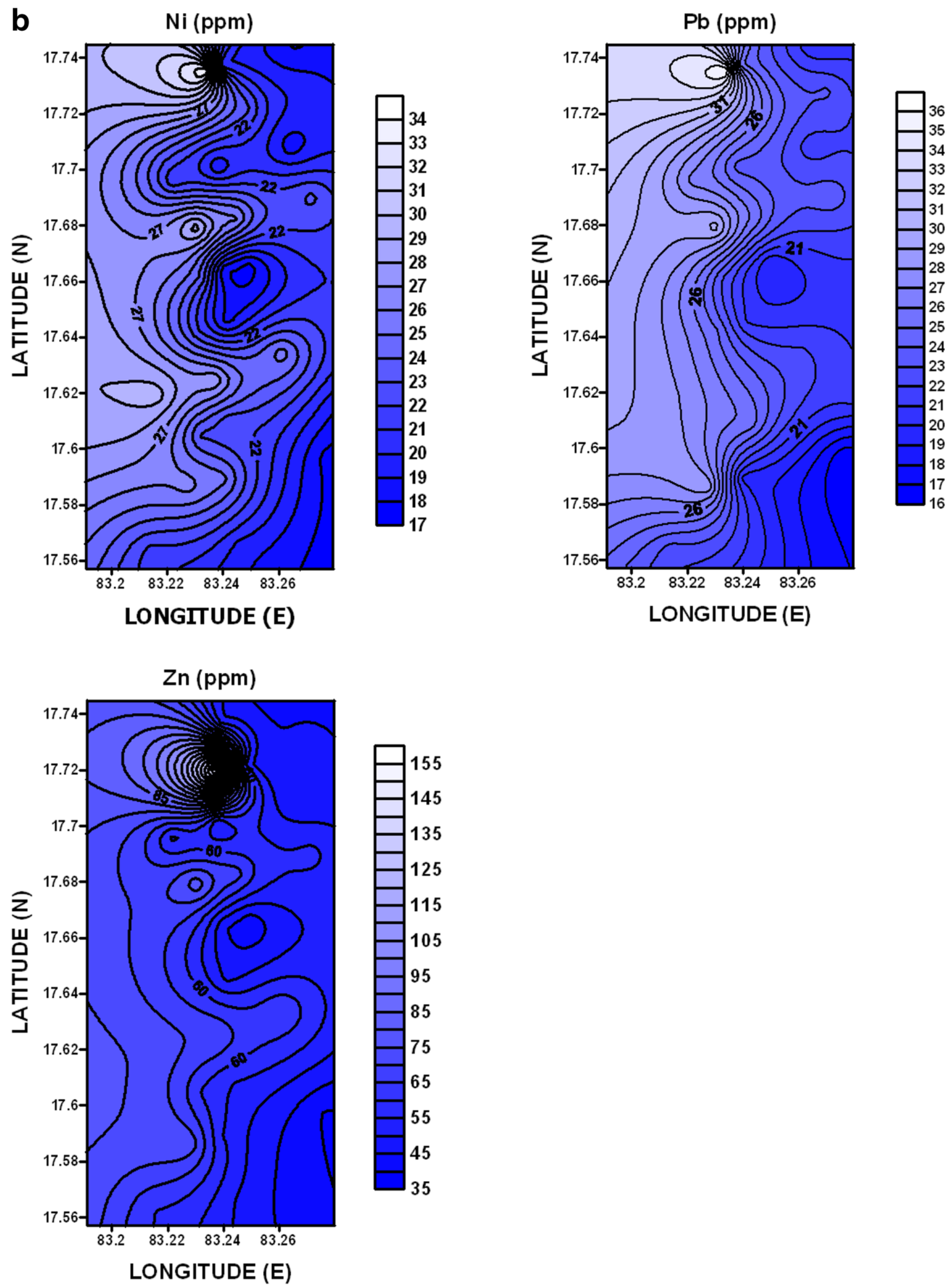
Fig. 4 **a** Spatial distribution of Fe, Cd, Cr and Cu in surface sediments along Visakhapatnam coast. **b** Spatial distribution of Ni, Pb and Zn in surface sediments along Visakhapatnam coast

1706.78 × 10^{-5} Am^2/kg, and Hard IRM values ranged between 1.24 and 79.58 × 10^{-5} Am^2/kg (Fig. 6a). The values of Soft IRM were greater than that of Hard IRM, and it revealed the predominance of soft magnetic minerals. The above results confirmed the presence of higher concentrations of soft magnetic minerals like magnetite.

Grain size of magnetic minerals

χ_{fd} %, SIRM/χ, χ_{ARM}/χ, χ_{ARM}/SIRM are magnetic grain size-dependent parameters (Dunlop and Ozdemir 1997). The ratio of χ_{ARM}/χ is useful to detect the changes in grain sizes of magnetic minerals; the higher ratio represents the higher fraction of fine-grained magnetic minerals (Evans and Heller 2003). Percentage of frequency dependence susceptibility (χ_{fd} %) is an indicator of very fine viscous super paramagnetic grains. χ_{fd} % in Visakhapatnam coastal sediments were ranged between 0.21 and 5.48 % (Fig. 7a) and the average fell below 4 % confirming the dominance of the presence of MD and PSD grains (Hay et al. 1997). Coarse magnetic particles such as MD and PSD grains are frequency independent and show similar susceptibility values at low and high frequencies and they can be characterized by χ_{fd} % < 5–6 % (Maher 1988). SIRM/χ is used

Fig. 4 continued

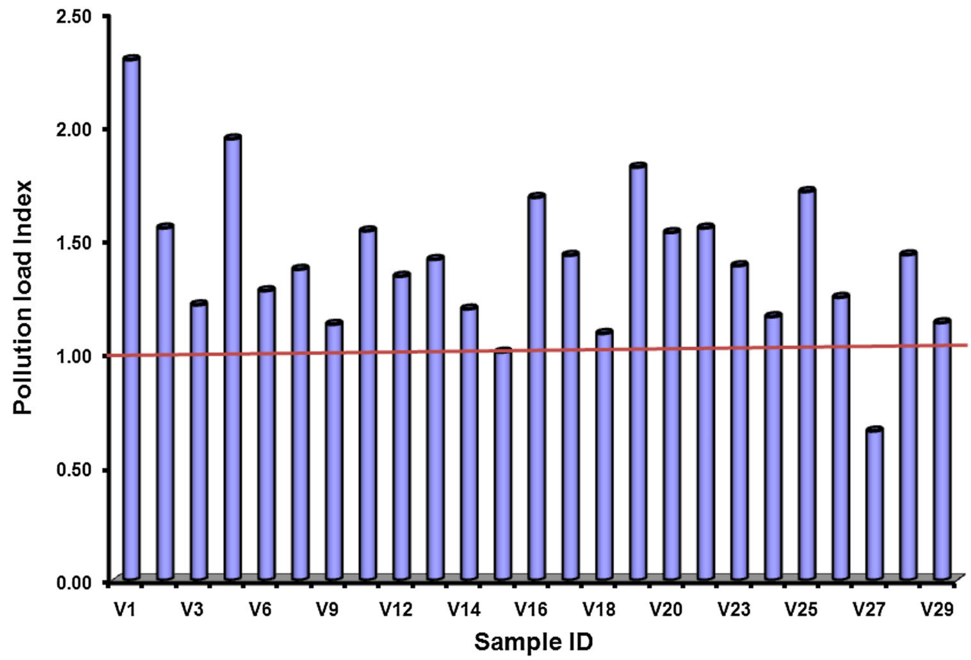


as an indicator of magnetic grain-size variations, and the ratio decreases with increasing magnetic grain size if magnetic grain sizes are larger than the grains at the SP/SD boundary (Oldfield 1994). The χ_{ARM}/χ ratio in Visakhapatnam coastal sediments was ranged from 1.19 to 5.38 with an average of 2.63 (Fig. 7b). The higher values of χ_{ARM}/χ reflect the fine-grained SSD particles and lower values for multidomain (MD) (Zhang and Yu 2003). Peters and Dekkers (2003) have suggested that the values of $\chi_{ARM}/\chi > 5$ are indicative of the presence of very small magnetic grains. The χ_{ARM}/SIRM values were $<0.7 \times 10^{-3}$ m/A, which indicated the dominance of grains coarser than 0.07 mm (Oldfield 1994; Wang et al. 2009). Both χ_{ARM}/SIRM and χ_{ARM}/χ magnetic ratios had shown that the sediment samples from Visakhapatnam coast were lower than the reported values and reflect coarser magnetic grains. This could be seen in magnetically enhanced sediments with coarser grains.

Correlation co-efficient matrix

The relationships among the textural, geochemical and magnetic parameters were investigated by Pearson correlation analysis, and the correlation matrix is shown in

Fig. 4 continued



Tables 2, 3. Concentration-dependent parameters (χ, χ_{ARM} and SIRM) have high positive correlations among themselves. The high positive correlations observed for χ versus SIRM and SIRM versus Soft IRM indicate that the variation in χ is mainly governed by ferrimagnetic minerals (Zhang and Yu 2003). The positive correlation between S-ratio and Soft IRM had shown the dominance of ferrimagnetic minerals with little amount of anti-ferromagnetic minerals. Magnetic mineralogy parameters had high negative correlation with grain-size (χ_{ARM}/SIRM and χ_{ARM}/χ) parameters, and it had shown the presence of ferrimagnetic minerals (magnetite) with coarser grains. Magnetic susceptibility showed high positive correlation with Ni, Zn, silt and clay, whereas negatively correlated with sand, which implies that fine-grained sediments have higher χ values. χ_{ARM} was positively correlated with clay and silt and could be used to compensate for the particle size effect in sedimentary heavy metal records (Zhang et al. 2001). χ, χ_{ARM} and SIRM showed better linkage with heavy metals like Ni and Zn reflecting the absorption of fine-grained magnetic iron oxides due to their higher surface area to volume ratio. The strong association of Cd, Cr, Cu, Ni, Pb

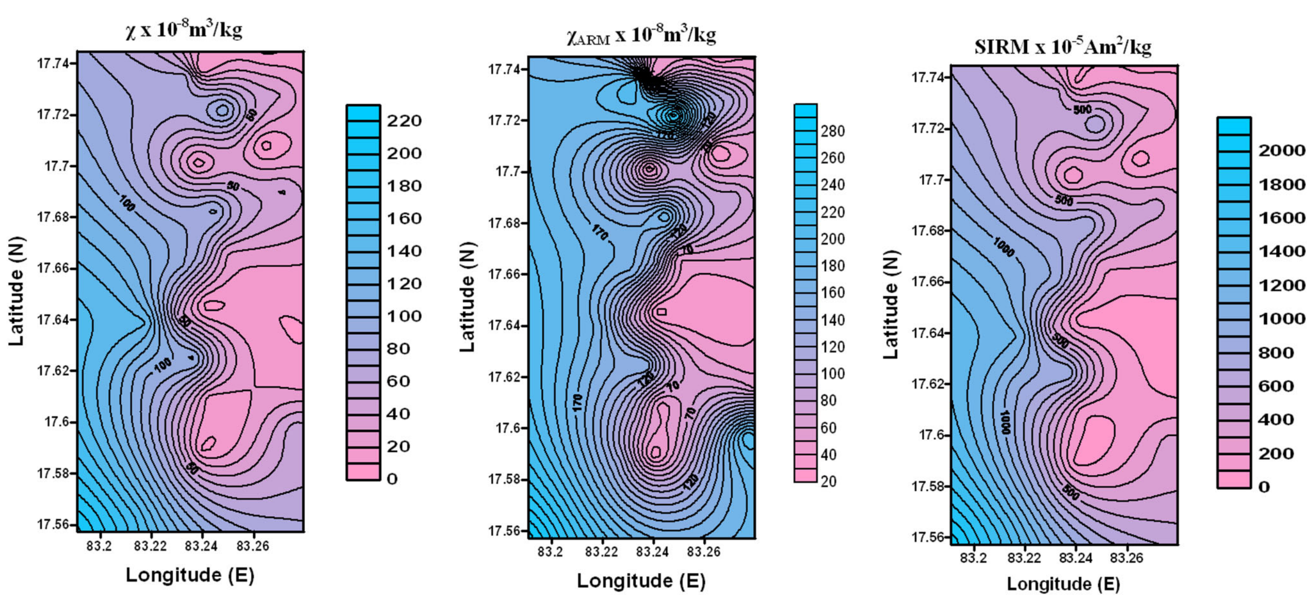


Fig. 5 Spatial distribution of magnetic concentration-dependent parametersχ, χ_{ARM} and SIRM in surface sediments along Visakhapatnam coast

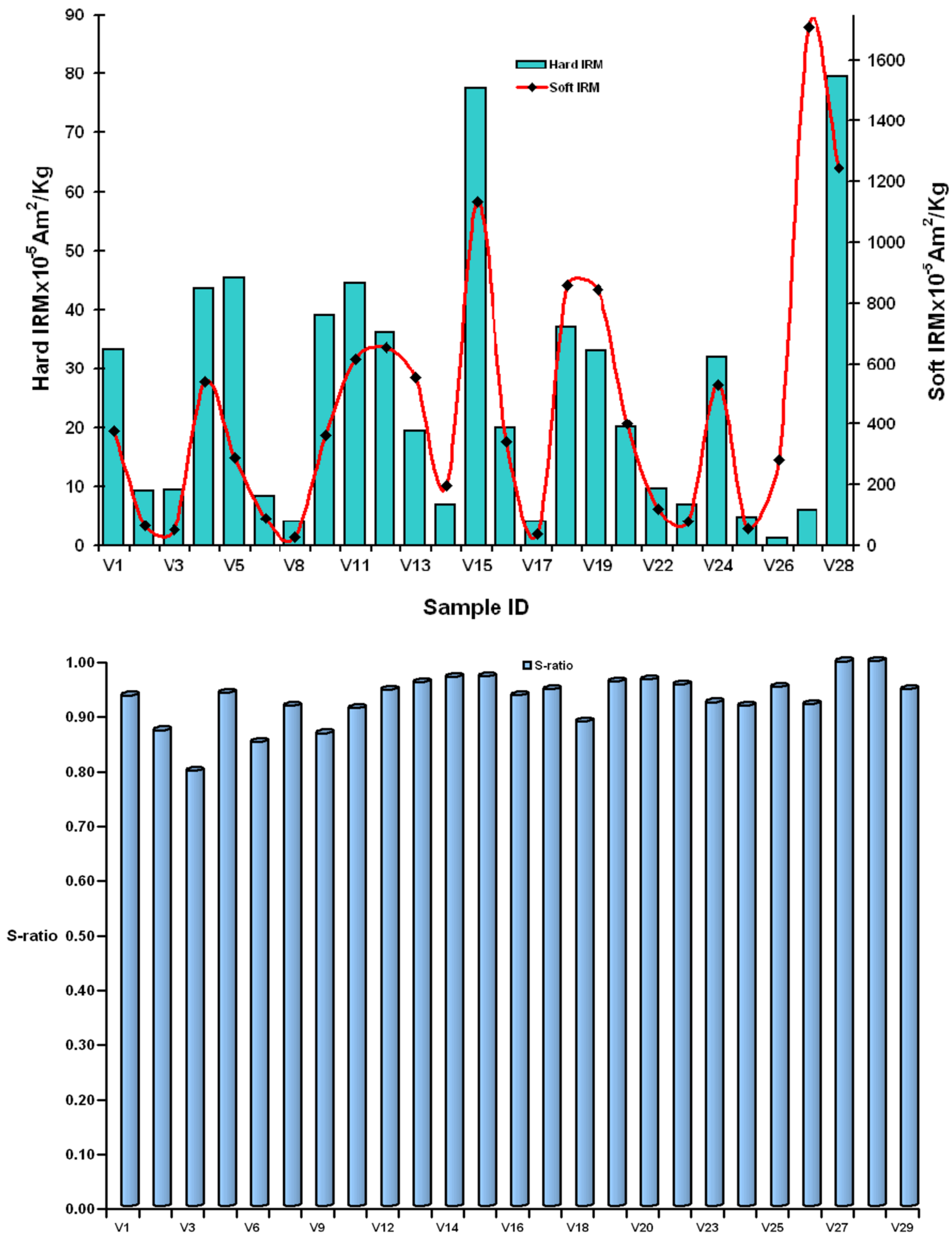


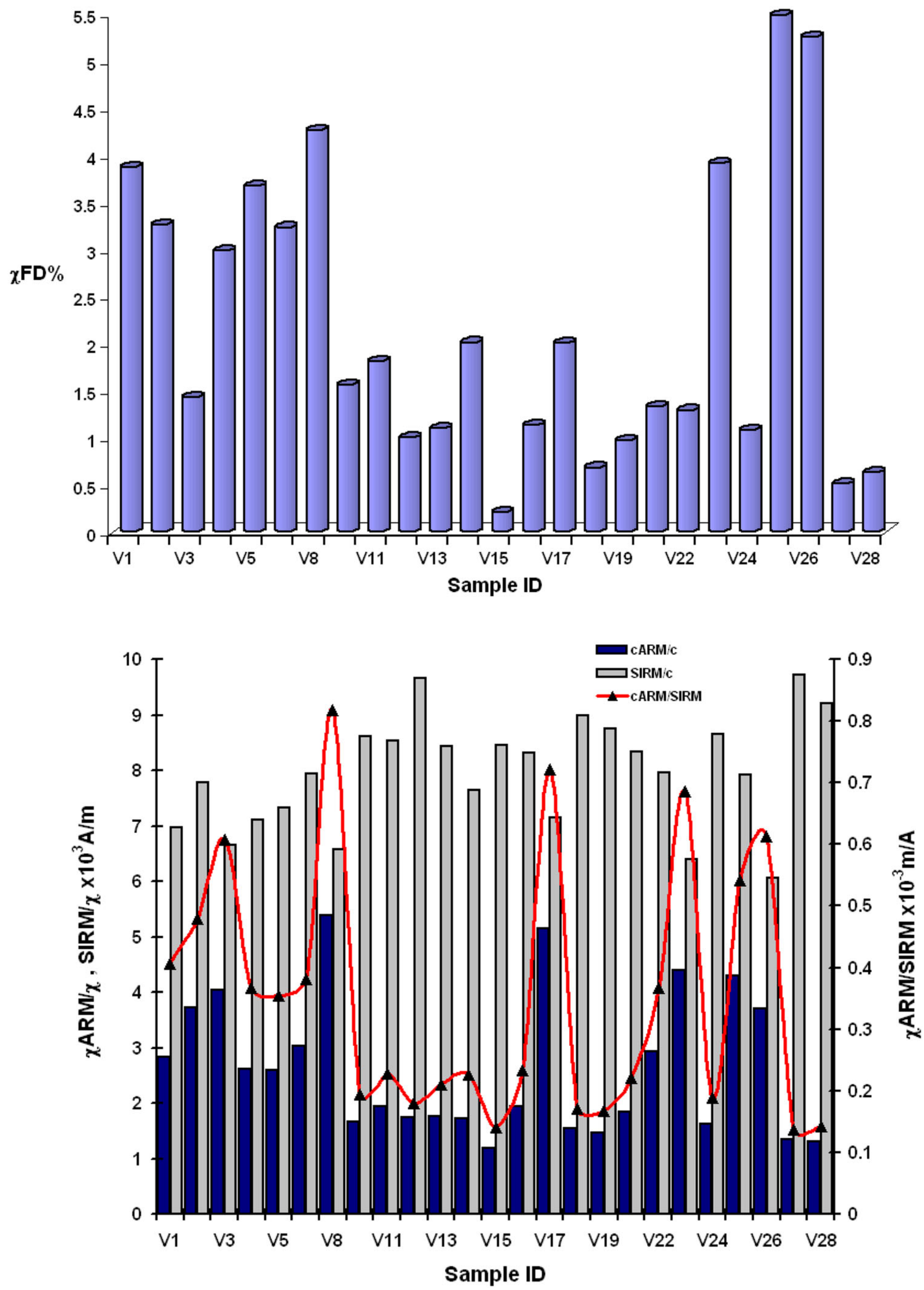
Fig. 6 Magnetic mineralogy-dependent parameters Soft and Hard IRMs and S-ratio in surface sediments along Visakhapatnam coast

and Zn with Fe likely due to their preferential adsorption onto Fe (hydro) oxides appeared to be the most important scavengers of trace metals in sediments. There was significant correlation between Cd, Cr, Cu, Fe, Ni and Pb, suggesting that they had similar geochemical behaviors. Petroleum hydrocarbons had high positive correlations with χ, χ_{ARM}, SIRM, S-ratio and Soft IRM, and SIRM/χ suggested that the sources of petroleum hydrocarbons (e.g., harbor activities, sewage water input, fishing activities and effluent from industries) should be considered as an important source of magnetic minerals (Venkatachalapathy et al. 2010). PHC had high positive correlation with silt and clay, while negatively correlated with sand revealed that concentration of PHC was higher in fine sediments grains.

Principal component analysis

In order to further discern relationships and grouping among the magnetic, textural and geochemical parameters, principal component analysis was performed for sediments from Visakhapatnam coast, and the results are shown in Fig. 8. A varimax rotation was used to better define the principal component 86.99 % of the cumulative variance was explained by first four principle components. PC1 accounts for 51.35 % of total variance with eigenvalue of 11.30. PC1 had high positive loadings on χ, χ_{ARM}, SIRM, S-ratio, Soft IRM, Hard IRM, SIRM/χ, Cd, Cr, Fe, Ni, Pb, Zn, PLI, PHC, Silt and Clay, whereas negative loadings with χ_{fd} %, χ_{ARM}/SIRM, χ_{ARM}/χ and Sand. Based on this

Fig. 7 Magnetic grain size-dependent parameters χ_{fd} %, χ_{ARM}/χ, SIRM/χ and χ_{ARM}/SIRM in surface sediments along Visakhapatnam coast



association, this component described the magnetic minerals, petroleum hydrocarbons and trace metals had the sources of both lithogenic as well as pedogenic and anthropogenic. This also implies that the concentrations of magnetic minerals, trace metals and petroleum hydrocarbons have strong association with fine-grained sediments. As indicated by the PC scores, the magnetic concentration and mineralogy-dependent parameters, co-vary with the heavy metal and PHC concentrations and pollution load index, suggested that the input of magnetic minerals, petroleum hydrocarbons and heavy metals in the Visakhapatnam shelf sediments were derived from the same anthropogenic sources such as discharge and disposal of untreated/treated sewage and industrial wastes, harbor and shipping activities (Venkatachalapathy et al. 2011a), emission of incomplete combustion of fossil fuels from thermal power plant. PC 2 accounts about 22.22 % of total variance with an eigenvalue of 4.889. PC 2 had high positive loadings on Cd, Cr, Cu, Fe, Ni, Pb, Zn and PLI. Based on this association, this component describes the geochemical matrix (Delvalls et al. 1998) composition of the studied sediments. It also revealed that anthropogenic

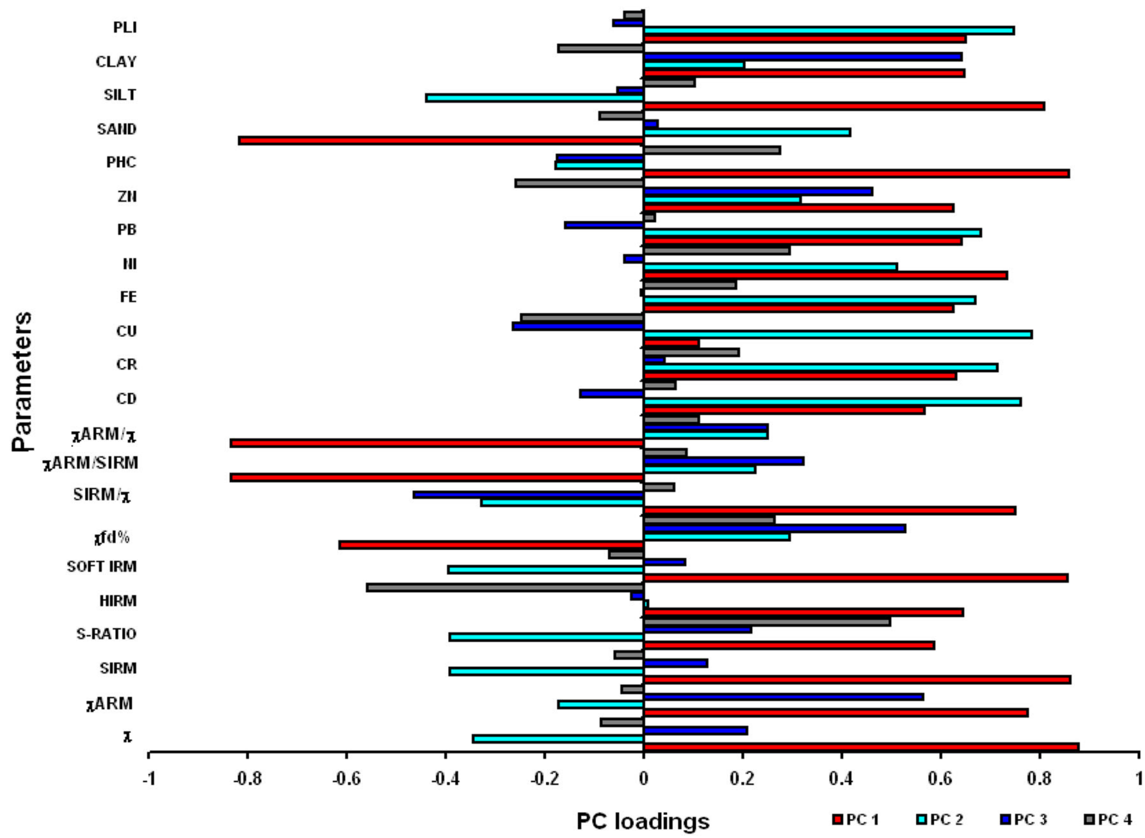


Fig. 8 Principal component loadings of surface sediments from Visakhapatnam coast, India

Table 2 Correlation coefficient matrix of magnetic concentration, minerology and grain size-dependent parameters in surface sediments from Visakhapatnam coast, Bay of Bengal, India

	χ_{lf}	χ_{ARM}	SIRM	S-ratio	HIRM	Soft IRM	χ_{fd} %	SIRM/χ	χ_{ARM}/SIRM	χ_{ARM}/χ
χ_{lf}	1.00									
χ_{ARM}	**0.88**	1.00								
SIRM	**0.99**	**0.82**	1.00							
S-ratio	**0.58**	**0.59**	**0.56**	1.00						
HIRM	**0.59**	**0.49**	**0.55**	0.12	1.00					
Soft IRM	**0.97**	**0.76**	**0.98**	**0.57**	**0.58**	1.00				
χ_{fd} %	**−0.56**	−0.25	**−0.60**	−0.25	**−0.45**	**−0.62**	1.00			
SIRM/χ	**0.65**	0.35	**0.71**	**0.47**	0.44	**0.71**	**−0.73**	1.00		
χ_{ARM}/SIRM	**−0.70**	**−0.51**	**−0.70**	**−0.57**	**−0.60**	**−0.71**	**0.73**	**−0.85**	1.00	
χ_{ARM}/χ	**−0.73**	**−0.58**	**−0.72**	**−0.60**	**−0.62**	**−0.73**	**0.72**	**−0.78**	**0.99**	1.00

Bold values indicate significant correlation at $p < 0.05$

contribution of these heavy metals from Thermal Power plant, Visakhapatnam Steel Plant, Petrochemical industries, Fertilizer industries, Paper mills, Tanneries, Polymers, Lead and Zinc mining, Zinc smelter, Fertilizers, Shipyard, Metal alloy, Shipping industries and Oil refineries. PC 3 accounts about 8.49 % of total variance with an eigenvalue of 1.867. PC 3 had high positive loadings on χ_{ARM}, χ_{fd} %, Zn and Clay, and it had high negative loading on SIRM/χ. As indicated by their respective PC scores, the grain size of the magnetic minerals was coarser. PC 4 accounts for 4.93 % of total variance with an eigenvalue of 1.084. PC 4 had high positive loading on S-ratio, and it has high negative loading on Hard IRM.

Conclusion

The textural, geochemical and mineral magnetic properties of coastal sediments collected from Visakhapatnam coast, Bay of Bengal, India were measured. The sediment texture sizes revealed that the study area was ranged from sand to sandy silt. The high concentration of petroleum hydrocarbons and

Table 3 Correlation coefficient matrix between magnetic and geochemical parameters in surface sediments from Visakhapatnam coast, Bay of Bengal, India

	χ_{lf}	χ_{ARM}	SIRM	S-ratio	HIRM	Soft IRM	χ_{fd} %	SIRM/χ	χ_{ARM}/SIRM	χ_{ARM}/χ
Cd	0.26	0.31	0.23	0.04	0.30	0.20	−0.20	0.22	−0.32	−0.30
Cr	0.31	0.41	0.26	0.19	0.37	0.24	−0.10	0.22	−0.34	−0.33
Cu	−0.17	−0.11	−0.19	−0.41	0.10	−0.22	0.00	−0.06	0.00	0.03
Fe	0.33	0.39	0.29	0.17	0.34	0.26	−0.12	0.28	−0.36	−0.33
Ni	**0.48**	**0.51**	0.45	0.31	0.44	0.42	−0.21	0.40	−**0.46**	−0.44
Pb	0.34	0.38	0.30	0.11	0.43	0.28	−0.27	0.27	−0.40	−0.39
Zn	0.44	**0.59**	0.38	0.22	0.38	0.34	−0.15	0.15	−0.28	−0.29
PLI	0.30	0.33	0.26	0.40	0.26	0.06	−0.24	0.27	−0.39	v0.37
PHC	**0.83**	**0.63**	**0.85**	**0.59**	0.39	**0.83**	**−0.63**	**0.76**	**−0.70**	**−0.70**
Sand	**−0.77**	**−0.61**	**−0.79**	**−0.65**	−0.43	**−0.81**	**0.59**	**−0.81**	**0.76**	**0.74**
Silt	**0.76**	**0.59**	**0.79**	**0.65**	0.42	**0.80**	**−0.60**	**0.82**	**−0.76**	**−0.74**
Clay	**0.55**	**0.74**	**0.48**	0.36	0.44	0.48	−0.05	0.14	-0.34	−0.37

Bold values indicate significant correlation at $p < 0.05$

metals was obtained from Visakhapatnam harbor to south of Gangavaram due to anthropogenic inputs such as industrial effluents, and domestic sewage was discharged into the Visakhapatnam harbor, Gangavaram port, fishing activities, Thermal Power plant, Visakhapatnam Steel Plant, Petrochemical industries, Fertilizer industries, Paper mills, Tanneries, Polymers, Lead and Zinc mining, Zinc smelter, Fertilizers, Shipyard, Metal alloy, Shipping industries and Oil refineries. The magnetic concentration, grain size and mineralogy parameters of marine sediments showed the presence of high proportion of magnetite with a small proportion of hematite and is primarily of a pseudo-single domain to multidomain nature with detrital origin. The geochemical and magnetic concentrations in the study area were generally decreased from nearshore region to deep. The relationship between geochemical and mineral magnetic properties was identified by Pearson's correlation matrix, and principal component analyses indicating the input of magnetic minerals, petroleum hydrocarbons and heavy metals in the Visakhapatnam shelf sediments were derived from the same anthropogenic sources such as discharge and disposal sewage and industrial wastes, harbor and shipping activities, emission of incomplete combustion of fossil fuels from thermal power plant. Thus, the large magnetic dataset could be used to reduce the number of chemical analysis; hence, environmental magnetic parameters were used as a proxy for both organic and inorganic micro-pollutants.

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