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ORIGINAL ARTICLE

Magnetic studies and elemental analysis of river sediments: a case study from the Ponnaiyar River (Southeastern India)

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Abstract The Ponnaiyar River is one of the largest rivers of the Tamil Nadu state (India), flowing a distance of 430 km from its point of origin to the sea. This work contributes with new data of magnetic and elemental composition of river sediments, and improves the knowledge obtained by preliminary and previous studies of rivers from Southeastern India. Magnetic susceptibility, anhysteretic and isothermal remanent magnetization and chemical determinations (major and trace metals) were measured. Magnetic results reveal the predominance of magnetite-like mineral with magnetic grain size variations along the river and in depth. Most of the uppermost samples have the major presence of trace metals and higher values of magnetic concentration. Magnetic and chemical variables were also analysed as potential pollution indicators using multivariate statistical techniques: canonical correlation and fuzzy *c*-means clustering analyses, which confirmed the existence of relationships, but not in a simple way, between magnetic and chemical variables. Furthermore, fuzzy analysis allows classifying the data in different well-differentiated groups regarding the trace metal load, concentration and feature-dependent parameters. The most polluted samples show high concentration of trace elements and magnetic carriers, softer and coarser magnetic minerals; on the contrary, the unpolluted samples (from the deepest sediments) have the opposite characteristics.

Keywords Environmental magnetism · Magnetic susceptibility · Fuzzy *c*-means clustering method · Pollution · River sediments

Introduction

Studies of magnetic parameters and their interpretation on pollution have been conducted in different environments, including soils, sediments and vegetation since the 1980s (Thompson and Oldfield 1986). According to Petrovský and Ellwood (1999), atmospheric pollution is identified as one of the most harmful factors for ecosystems. Often, industrial and urban fly ashes include toxic elements and heavy metals; such airborne pollutants are diffused due to the atmospheric circulation. Land environments undergo a major impact because pollutants are transferred to the Earth's surface, made available and taken up by organisms or incorporated into sediments.

In the last years, rivers from different countries have been studied using environmental magnetism, several authors have focused on the magnetic properties of sediments and their relationship with heavy metals to assess the pollutant load that received (e.g. Jordanova et al. 2004;

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Desenfant et al. 2004; Knab et al. 2006; Chaparro et al. 2008a, 2011; Franke 2009; Augustinus et al. 2010).

Some authors have applied multivariate techniques to validate the link between magnetic and chemical variables and to classify data according to the degree of contamination. Papers involving these techniques include: correlation analysis, principal components analysis, cluster analysis, canonical correlation analysis, fuzzy *c*-means analysis and linear discriminant analysis (Durza 1999; Petrovský et al. 2001; Wang and Qin 2006; Knab et al. 2001; Hanesch et al. 2001; El Baghdadi et al. 2012; Chaparro et al. 2008b, 2011, 2012).

New magnetic and elemental studies of sediments from the Ponnaiyar River located in the Tamil Nadu state are reported in this work. The population of the studied area (about 200 km) takes water for drinking, irrigation, construction and agriculture from this river. The small hydraulic structure, barrages and bridges were constructed for drinking, agriculture and transport purposes, respectively, on the study area. On the both sides of the bank of this river, so many living residents and some industries are situated. None of the industries have non-proper and controlled outlet. The discharge wastes (PVC and others) and toxic metals from such industries and living residents are directly let out into the river. Also along the river, lot of agricultural land is available; chemical fertilizers and pesticides that are overused are washed into the river.

In the Ponnaiyar River basin, there are about 7,100 small-scale and medium industries. The small-scale industries include food, beverage, tobacco, cotton, textile, paper, leather, chemical, metal and machinery products and the large and medium industries belongs to the categories like, fertilizer, pesticides, pharmaceuticals, paper, sugar, distillery, dye and dye intermediate, textiles, automobiles and machinery products. Other categories, such as, thermal power plant, tannery, aluminum smelter, cement, integrated iron and steel are located about 30–90 km from the Ponnaiyar River (Annexure 2006; TNPCB 2010). In addition to these pollution sources, agricultural activities (overuse of chemical fertilizers and pesticides) along the river and contaminants generated by urban activities and vehicular traffic play an important role. Although Villupuram and Cuddalore municipalities have compost yards, other municipalities and towns do not have disposal facilities. There is absolutely no solid waste collection and disposable mechanism at village level in the river basin area (Annexure 2006).

This work contributes to the knowledge obtained by previous studies of river sediments and soils from Southern India (Ramasamy et al. 2006; Chaparro et al. 2008a, 2011; Gudadhe et al. 2012; Sandeep et al. 2011). Preliminary magnetic, mineralogical and chemical data have been published in previous papers (Ramasamy et al. 2009; Suresh et al. 2011a, b), only ten sites were chosen for detailed chemical and magnetic analyses and reported here. Magnetic studies and chemical determinations are discussed to investigate the main magnetic carriers and pollutants concerning the influence of pollution sources. Different magnetic parameters were also analyzed as potential pollution indicators using biplots and statistical techniques.

Materials and methods

The study area (Ponnaiyar River, Fig. 1) covers from Sathanur dam (longitude 78°51′10″ E and latitude 12°04′48″ N) to Cuddalore (longitude 79°47′68″ E and latitude 11°45′35″ N) and goes through three districts namely Thiruvannamalai, Villupuram and Cuddalore districts of Tamil Nadu.

The Ponnaiyar River, an interstate river, is one of the largest rivers of the state of Tamil Nadu, India. Ponnaiyar River originates from the Southeastern slope of Nandidrug hills in Karnataka state and flows for 84.8 km in that state before entering Tamil Nadu at about 4.8 km North-West of Bagalur village, Dharmapuri district. The river flows for a distance of 430 km from its point of origin to the sea, 35 km in the Thiruvannamalai district. The total drainage area of the river is 14,130 km^2 of which 3,608 km^2 lies in Karnataka, 95 km^2 in Pondicherry and the remaining 10,427 km^2 falls in Tamil Nadu. Sathanur dam is 226 km from the origin of the river. The river flows through Villupuram and Cuddalore districts for a distance of about 160 km and finally terminated into Bay of Bengal near Cuddalore.

The river basin (approximately 11,441 km^2) has tropical, semiarid climatic conditions. The ground water level follows the topography, where the groundwater flows toward east with a gentle hydraulic gradient. The average annual rainfall of this basin ranges from 1,000 to 1,100 mm per annum. The average pre-monsoon water level of this basin ranges from 5 to 9 m bgl. The groundwater quality of this basin is generally good to moderate with an average TOS of 500–1,000 mg/l. However, along the alluvial coastal zone the quality of groundwater may be saline at depths due to seawater intrusion (Ruby et al. 2010).

The climate of study area is tropical in nature with little variation in summer and winter temperatures. While April–June is the hottest summer period with the temperature rising up to 40 °C, November–February is the coolest winter period with temperature covering around 20 °C, making the climate quite pleasant. Surprisingly, study area gets all its rains from the Northeast monsoons between October and December. The average annual rainfalls range between 28 and 76 inches (635 and 1,905 mm) per year.

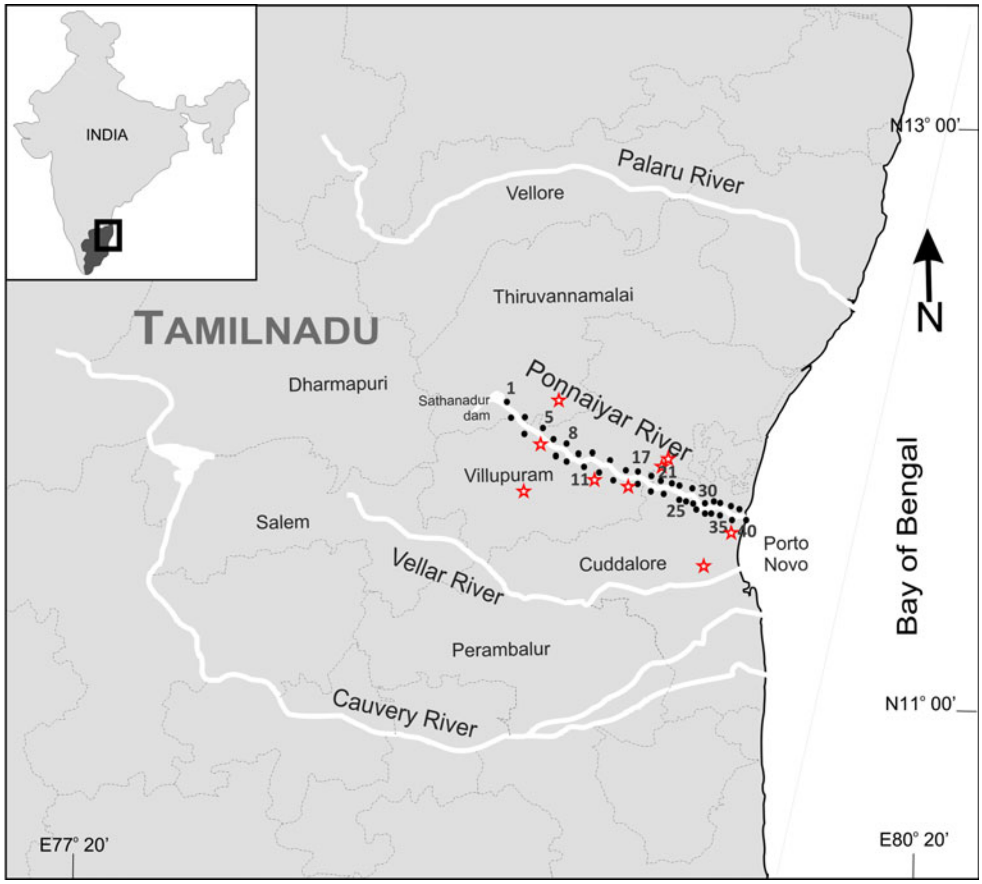

Fig. 1 Map of the study area in Tamil Nadu state. River sediments were collected in ten sites along the Ponnaiyar River. There are about 7,100 small-scale and medium industries in the Ponnaiyar basin. Some "highly polluting industries" (17 categories, TNPCB 2010) located in districts of influence are pinpointed with *red stars*. Sites comprise the following industry categories: distillery and sugar (Villupuram district); pesticides, sugar, pharmaceuticals, dye and dye intermediate, distillery, chemical and thermal power plant (Cuddalore district); sugar (Thiruvannamalai district). Other important contribution comes from urban activities and vehicular traffic (state and national highways are located in sites 2, 6, 12, 19, 21, 23, 35 and 38) (color figure online)

Sampling

The study area (Ponnaiyar River) covers a total length of 200 km and 40 sampling locations that were preliminary studied by Ramasamy et al. (2009). Based on these preliminary results for 40 surface (upper layer) samples, 10 locations were selected for detailed magnetic and chemical analyses. These locations are labeled as sites Po-1, Po-5, Po-8, Po-11, Po-17, Po-21, Po-25, Po-30, Po-35 and Po-40 (Fig. 1). The sample location was recorded (latitudinal and longitudinal position) using Hand-held Global Positioning System (GPS, Model: GARMIN GPS-12) unit. The names of the sampling sites with latitude and longitude are given in Table 1.

The present river fully received water from the Northeast monsoons between October and December; in the remaining months, the river has no water (dry). The recently deposited sediment (freshly deposited samples after the flood) samples were manually collected at the center of the river bed with the help of a non-magnetic stainless steel spade and plastic scoop in separate polyethylene bags during the dry period (March–April 2008) from the upper layer, named 0 (0–5 cm), first feet, named 30 (30 cm) and second feet, named 60 (60 cm) of the river. Due to the gentle hydraulic gradient, grain size distribution in surface samples is uniformly varied (Suresh et al. 2011c). However, in the case of different depth samples, it is not so.

At each site and layer, two samples (one for magnetic studies and another for chemical studies) were collected. One sample of about 3 kg was collected using stainless steel spade in polythene bags. Another one of about 100 g was collected using plastic scoop in Ziploc cover.

In the laboratory, the collected samples were dried at room temperature in open air for a couple of days. After that, the dry samples were sieved (2 mm) to remove gravel fraction, and then they were packed and stored in polyethylene bags. Samples collected by plastic scoop were frozen to minimize loss of volatile elements until experiments were performed. The remainder was stored in vacuumed and marked polyethylene bags.

Magnetic measurements

The air-dried samples were sub-sampled for magnetic studies using plastic containers (about 2.3 cm^3). Then they

Table 1 Sampling sites in Ponnaiyar River (Po)

Site	Latitude; longitude	Location	Comment
Po-1	12°10′6.06″ N; 78°50′46.4″ E	Satthanur	Origin of the river—plastics and other waste materials are discharged. Near (Po-2), small state highway (SH-6A) bridge
Po-5	12°06′41.6″ N; 78°55′0.80″ E	Royandapuram	Near (Po-6), small state highway (SH-6) bridge. Sugar factories (6 –17 km)
Po-8	12°00′27.1″ N; 79°05′48.1″ E	Manalurpettai	Small town—residential wastes are derived from this town
Po-11	11°57′8.60″ N; 79°09′8.38″ E	Karadi	Small leather company and national highway (NH-9). Domestic wastes and traffic effluents are discharged. Refractory manufacturing company and sugar factory (5–7 km)
Po-17	11°55′08.2″ N; 79°22′37.7″ E	Saethur	Near (Po-19), very big national highway (NH-69) bridge. Heavy traffic actions. Sugar factory (8 km)
Po-21	11°51′6.88″ N; 79°29′7.31″ E	Korathirur	Traffic effluents are continuously emitted from heavy vehicle. National highway (NH-38). Distillery and sugar factories (9–16 km)
Po-25	11°50′40.6″ N; 79°35′45.1″ E	Meikumercmangalam	Near (Po-23), small national highway (NH-36, Pantruti to Chennai) bridge
Po-30	11°47′8.53″ N; 79°38′7.36″ E	Elangikuppan	Phosphate fertilizers and waste disposal. Intensive agricultural activities in and around the site. Power plant in Neively city (~32 km)
Po-35	11°47′54.9″ N; 79°42′28.7″ E	Alagiyanallur	State highway (SH-68) bridge and small-scale hollow brick manufacturing company
Po-40	11°45′35.0″ N; 79°47′6.85″ E	Thalanoadai	Termination point of the river. Near (Po-38), national highway (NH-32). Huge amount of waste materials disposed and influence of industries from Cuddalore city (~4 km)

There are about 7,100 small-scale and medium industries in the Ponnaiyar basin (Annexure 2006). Other pollution contribution comes from vehicular traffic (state and national highways are listed)

were packed, weighted, and labeled. After that, all samples were fixed using sodium silicate to prevent unwanted movements in studies of remanent magnetisation.

Magnetic susceptibility measurements were made using the magnetic susceptibility meter MS2 (Bartington Instruments Ltd.) linked to the MS2B dual frequency sensor (0.47 and 4.7 kHz). The volumetric susceptibility (κ), κ_{FD}% frequency-dependence ($\kappa_{FD}\% = 100 \times [\kappa_{0.47} - \kappa_{4.7}]/\kappa_{0.47}$) and mass-specific susceptibility (χ) were computed.

The anhysteretic remanent magnetisation (ARM) was imparted using a partial ARM (pARM) device attached to a shielded demagnetizer (Molspin Ltd.). The remanent magnetization was measured with a spinner fluxgate magnetometer (Minispin, Molspin Ltd.). Anhysteretic susceptibility (κ_{ARM}) was estimated using linear regression for ARM acquired at different DC bias fields (7.96, 47.75 and 71.58 A/m). The κ_{ARM}/κ ratio and the King's plot (κ_{ARM} vs. κ, King et al. 1982) were also studied.

The isothermal remanent magnetisation acquisition (IRM) studies were performed using a pulse magnetizer model IM-10-30 (ASC Scientific). Each sample was magnetized by exposing it to growing stepwise DC fields, from 4.3 to 2,470 mT. The remanent magnetization after each step was measured using the above-mentioned magnetometer Minispin. In these measurements, IRM acquisition curves and the saturation of IRM (SIRM) were determined using forward DC fields. Remanent coercivity (H_{cr}) and *S*-ratio (= $-\mathrm{IRM}_{-300\ \mathrm{mT}}$/SIRM) were also calculated using backfield once the SIRM was reached.

Elemental analysis

The frozen samples were used for analysis. About 0.5 g of the sediment sample was accurately weighed into pre-cleaned glass vessel and digested at room temperature with HNO_3/$HClO_4$ (4:1) mixture for 24 h. Following, the suspensions were evaporated at 80 °C until dryness. Then, 10 % HNO_3 was added to residues. The final suspensions were filtered through the Millipore unit (Rocker 400) to eliminate the remaining solids and washed by milliQ water. The digested solutions were analyzed by ICP-OES and Flame Photometer. All chemicals used were of analytical reagent grade. All glasswares and plastic containers were washed with 10 % nitric acid solution and rinsed thoroughly with milliQ water.

The concentration of metal elements (Al, Fe, Mg, Mn, Cu, Cr, Ni, Pb and Zn) was measured by ICP-OES (Perkin Elmer 2100 DV) and Flame Photo (Systronics) meter, respectively. Suitable internal chemical standards (Merk chemicals, Germany) were used to calibrate the instruments. All the reagents used were analytical grade of high purity. The wavelengths (nm) of the measured elements Al, Fe, Mg, Mn, Cu, Cr, Ni, Pb and Zn were 396.153, 238.204, 285.213, 259.372, 324.752, 267.716, 231.604, 220.353 and 213.857, respectively. Detection limits (ppm) of the

measured elements Al, Fe, Mg, Mn, Cu, Cr, Ni, Pb and Zn are 0.023, 0.0046, 0.0016, 0.0016, 0.0097, 0.0071, 0.015, 0.042 and 0.0018, respectively. Detection limit of alkaline metals is 1 ppm.

Statistical methods

Multivariate statistical analyses were performed using the software InfoStat (InfoStat 2009). The descriptive statistics (mean, SD, median, interquartile interval) and correlation Pearson's coefficients for all variables and data were calculated as a first step. Then, among multivariate statistical analyses, canonical correlation analysis (CCA) and the fuzzy *c*-means clustering (FCC) were studied.

There were two aims of the statistical studies: (1) the relationship between groups of magnetic and chemical variables; (2) a description of the magnetic characteristics according to the degree of contamination.

Thirty ($n = 30$) samples were used for this investigation. The dataset included eight magnetic variables (χ, ARM, SIRM, κ_{ARM}/κ, $\kappa_{FD}\%$, SIRM/κ, H_{cr}, *S*-ratio) and nine chemical variables (Al, Fe, Mg, Mn, Ni, Pb, Cr, Cu, Zn).

Three groups of variables according to magnetic characteristics were chosen, the first group was called: "Concentration" (χ, ARM, SIRM) corresponding to the magnetic concentration, the second group, called "Size" (κ_{ARM}/κ, $\kappa_{FD}\%$, SIRM/κ) corresponds to the magnetic grain size and the third group, called "Mineralogy" (H_{cr}, *S*-ratio) corresponds to the magnetic mineralogy. The choice of these three magnetic groups is based on well-known studies of different parameters in environmental magnetism. Commonly used room temperature magnetic parameters for assessing concentration are the χ, ARM and SIRM. Magnetic susceptibility is, perhaps, the best parameter for assessing magnetic concentration in environmental samples, assuming uniform mineralogy and consideration of paramagnetic and diamagnetic components (Peters and Dekkers 2003). Characteristic values of SIRM/κ and H_{cr} are very useful for assessing magnetic mineralogy. The *S*-ratio is a dimensionless parameter that indicates content of ferrimagnetic versus antiferromagnetic materials; values close to 1 correspond to the predominance of ferrimagnetic materials. On the other hand, the κ_{ARM}/κ-ratio is a grain size sensitive parameter (Dunlop and Ozdemir 1997; Peters and Dekkers 2003), for example, values of κ_{ARM}/κ greater than 5 are indicative of the presence of very small magnetite grains. Also, SIRM/κ can be a grain size sensitive parameter for sediments that have similar magnetic mineralogy (Maher 1986; Maher et al. 1999). The $\kappa_{FD}\%$ values can help to discriminate superparamagnetic (SP) from single and multi-domain (SD and MD) grains. There seems to be a maximum observational limit on $\kappa_{FD}\%$ of 15 % (Dearing et al. 1996).

On the other hand, two groups of chemical variables regarding the elemental composition were built. One group, called "Major" comprised Al, Fe, Mg, Mn, and the second group, called "Trace" comprised Ni, Pb, Cr, Cu, Zn.

Detailed information and the usefulness of these multivariate statistical methods for environmental magnetism can be found in Chaparro et al. (2006, 2008a); however, the main concepts of these techniques are briefly introduced. The CCA (Cuadras 1981) allows investigating the correlation between a set of variables Xi and another Yi. Calculations for CCA were made to determine which group of magnetic variables has the highest significant correlation with each chemical group.

The FCC method allows us to get a fuzzy clustering using the classification variables (in this work, all magnetic groups and the trace group were used). The classification obtained by this method allows us to describe the magnetic and chemical relevance of the different group of samples.

Results and discussion

Magnetic carriers

Measurements of IRM acquisition revealed the dominance of ferrimagnetic carriers for Ponnaiyar samples (Fig. 2). This fact is especially concluded from *S*-ratio results, which varied between 0.898 and 0.998. *S*-ratio values clearly show the predominance of ferrimagnetic minerals over antiferromagnetic minerals.

Remanent coercivity values varied between 34.5 and 59.4 mT, corresponding to values of magnetite-like mineral with different characteristics. The H_{cr} correlates at 0.01 level of significance with concentration-dependent parameters, that is, χ ($R = -0.783$ and -0.805, at 0 and

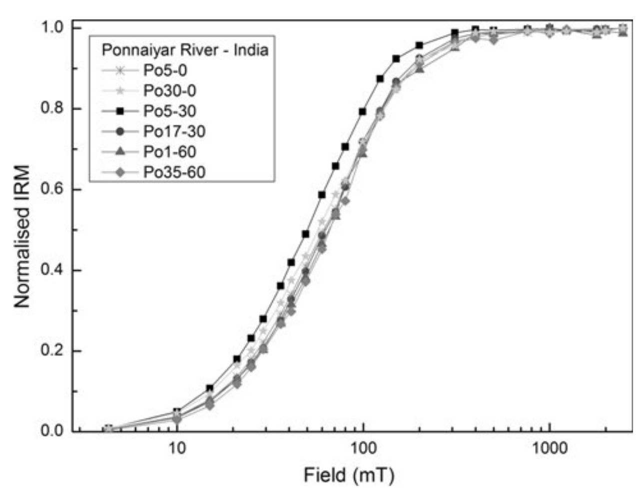

Fig. 2 Curves of acquisition IRM for selected samples

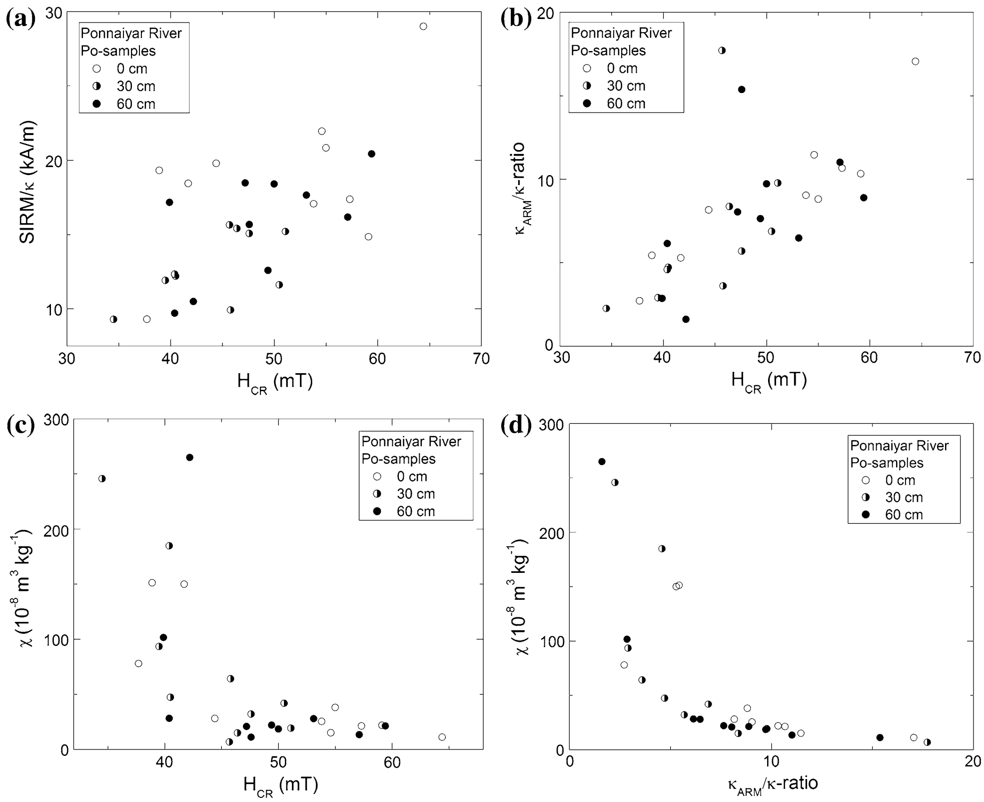

Fig. 3 *Biplots* using features and concentration-dependent parameters. **a** SIRM/κ versus H_{cr}, **b**κ_{ARM}/κ versus H_{cr}, **c**χ versus H_{cr} and **d**χ versus κ_{ARM}/κ

30 cm, respectively) and SIRM ($R = -0.671$ and -0.778, at 0 and 30 cm, respectively). This fact indicates a similar behavior along the river in the uppermost sediments (0–30 cm). Furthermore, it is noted that magnetic concentration is driven by magnetic mineralogy and, higher concentrations seem to be associated to lower-coercivity minerals.

Although it should be confirmed, an extra contribution of antiferromagnetic materials may be expected in samples with higher H_{cr}. Values of SIRM/κ, from 5.3 to 20.4 kA/m, belong to the range of (titano)magnetite (Peters and Dekkers 2003); and higher values can be interpreted as finer magnetic grain sizes abundance.

Different magnetic feature-dependent parameters are displayed in biplots (Fig. 3). A linear trend is observed between SIRM/κ and H_{cr} ($R = 0.63$ $p < 0.01$; Fig. 3a), and between κ_{ARM}/κ and H_{cr} ($R = 0.68$ $p < 0.01$; Fig. 3b), which may be interpreted as magnetic grain size variation rather than important magnetic mineralogy changes. Higher values of remanent coercivity seem to be associated to finer (higher values of κ_{ARM}/κ) magnetic carriers. This fact is not so evident with the parameter SIRM/κ that also depends on the magnetic mineralogy. On the other hand, the magnetic concentration parameter (χ) shows a decay-like dependence with the magnetic mineralogy (H_{cr}, Fig. 3c) and grain size (κ_{ARM}/κ, Fig. 3d).

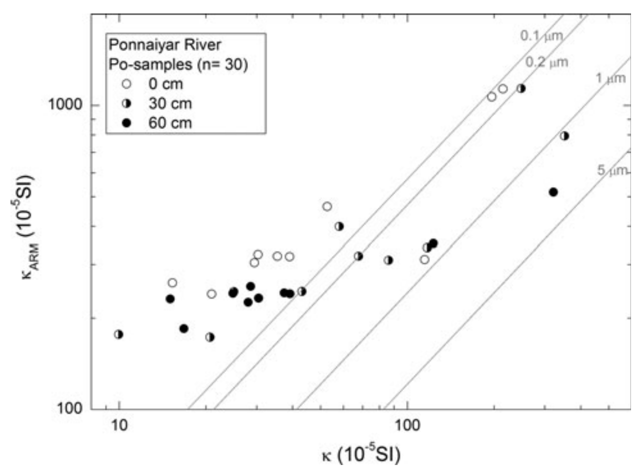

Fig. 4 The King's Plot (κ_{ARM} vs κ) for Po samples. As a general trend, samples with higher magnetic concentration-dependent parameters showed coarser magnetic grain sizes

Magnetic grain size-dependent parameters, i.e. SIRM/κ, $\kappa_{ARM} - \kappa$-ratio and the King's plot show the presence of coarser (0.2–5 µm) magnetic grain size for samples with higher concentration. This trend can be appreciated in Fig. 4, as well as from the parameters $\kappa_{ARM} - \kappa$-ratio and SIRM/κ where higher values correspond to finer magnetic grain sizes.

The κ_{FD}% parameter is sensible to the presence of SP material, from Bartington Instruments Ltd. (1994); values

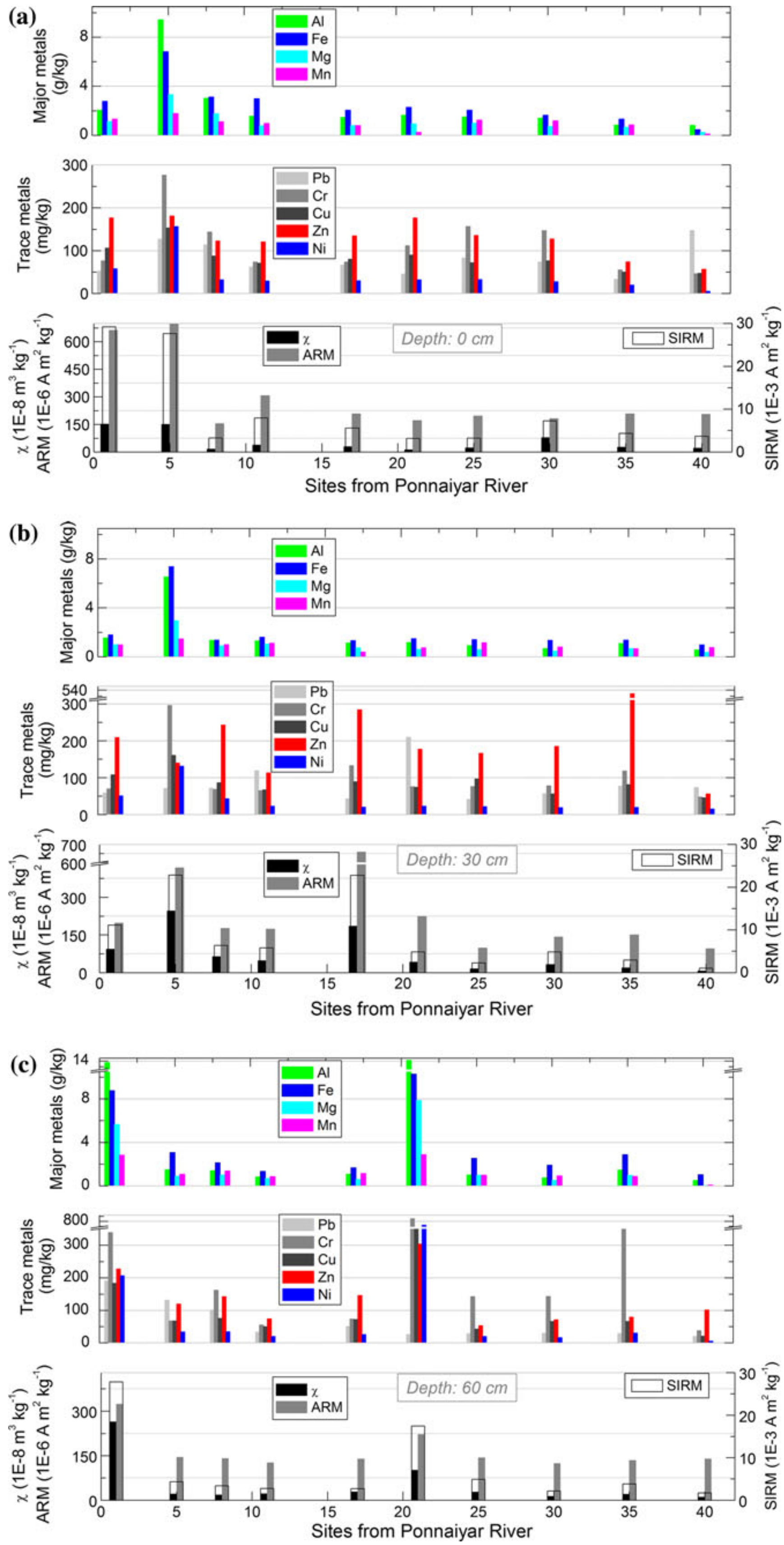

Fig. 5 Results of magnetic concentration-dependent parameters (χ, ARM and SIRM) and contents of trace (Pb, Cu, Cr, Zn and Ni) and major (Al, Fe, Mg and Mn) elements for different depths: **a** 0 cm, **b** 30 cm, **c** 60 cm

of $\kappa_{FD}\%$ <2.0 % indicate virtually no SP grains; between 2.0 and 10.0 % indicates admixture of SP and coarser non-SP grains; between 10.0 and 14.0 % indicates virtually all SP grains. In these river samples, the $\kappa_{FD}\%$ mean value is 0.0 % and the SD is 2.3 %. Only two high values (5.7 and 6.1 %) were obtained for the samples Po-35-0 and Po-11-60, the others were below 2.5 %. The presence of SP grains can be discarded.

Magnetic concentration parameters

Values of χ ranged from 6.8 to 265.0 × 10^{-8} m^3/kg. Mass-specific susceptibility is a magnetic concentration-dependent parameter, and its values vary according to the kind of materials, i.e.: diamagnetic (~−6 × 10^{-9} m^3/kg), paramagnetic (~10^{-6} m^3/kg), antiferromagnetic (~6–7 × 10^{-7} m^3/kg), and ferrimagnetic materials (~0.5–5.6 × 10^{-3} m^3/kg, in detail in Maher et al. 1999).

As noted in Fig. 5, the highest χ values belong to sites Po-1, Po-5 and Po-17. Intermediate peak values were found for samples Po-30-0, Po-8-30 and Po-21-60.

The other concentration-related remanent parameters, such as ARM and SIRM, were also represented in Fig. 5. They varied between 94.5 and 697.9 × 10^{-6} A m^2/kg for ARM; and between 1.1 and 29.2 × 10^{-3} A m^2/kg for SIRM. As observed in Fig. 5, distribution of these remanent parameters along Ponnaiyar River is in agreement with the χ distribution. High and intermediate values in some Ponnaiyar sites, e.g.: Po-1, Po-5, Po-8, Po-17 and Po-30, may be interpreted as magnetic enhancement.

Magnetite concentration was estimated from Thompson's plot (Thompson and Oldfield 1986). Such concentration varied between 0.003 and 0.117 %, showing high contents of this magnetic carrier and magnetic enhancement in various samples. Such magnetic enhancement may arise as pollution consequence—input of magnetic particles and heavy metals—produced by anthropogenic, industrial activities or other process (see Table 1).

Trace and major metals

Values of different metals are shown in Fig. 5. A similar pattern along the river for trace and major metals is noted at different depths (Fig. 5a–c). Furthermore, both groups of metals correlate with the concentration-dependent magnetic parameters.

The values of heavy metal recorded in these sediments are higher in relation to other study areas in Southeastern India (Chaparro et al. 2008a, 2011); e.g. the median values were 28.7 mg/kg (Ni), 64.0 mg/kg (Pb), 77.2 mg/kg (Cr), 74.9 mg/kg (Cu) and 137.8 mg/kg (Zn). In addition, values of these trace metals are several times (between 3 and 12 times) higher than their corresponding minimum values, i.e. 5.2 mg/kg (Ni), 19.8 mg/kg (Pb), 37.4 mg/kg (Cr), 20.6 mg/kg (Cu) and 52.8 mg/kg (Zn). Such a fact is in agreement with the magnetic enhancement observed in different sites along the Ponnaiyar River.

The pollutants—trace metals and magnetic particles—are expected to be the end product of urban and industrial activities. Both kinds of pollution are probable in this area according to the waste discharge, vehicle traffic (on highways and on streets), and to the influence of industries (sugar, distillery, leather and hollow brick manufacturing company, see Table 1).

Analysis of magnetic and chemical variables

As the coefficient of variation (CV) ranges widely, between 60 and 180 %, the mean is not representative in this case; therefore, the median (ME) is used as a relevant index of the descriptive statistics. In order to analyze the behavior of variables, the difference between ME of all data and data at different depths (ΔME = ME all data − ME sub-dataset) was calculated (Table 2) and compared, observing differences between them. Higher differences for each variable are consequence of the samples (sub-dataset) that do not follow the general trend (all data); for example for

Table 2 Median (ME) differences between all data and sub-dataset at three depths are listed

	ΔME = ME all data − ME sub-dataset		
	0 cm	30 cm	60 cm
Concentration			
χ	1.2	−16.7	6.3
ARM	−31.4	0.0	34.4
SIRM	−0.4	−0.8	1.0
Size			
κ_{ARM}/κ	−1.1	2.6	0.0
$\kappa_{FD}\%$	0.0	−0.2	0.1
Mineralogy			
H_{cr}	−6.8	1.7	−1.1
S-ratio	0.0	0.0	−0.2
Major			
Al	−0.2	0.2	0.1
Fe	−0.3	0.4	−0.5
Mg	0.0	0.1	−0.1
Mn	−51.4	78.3	−35.6
Trace			
Ni	−2.5	6.6	0.6
Pb	−5.8	−7.5	32.7
Cr	−16.8	1.6	−65.1
Cu	−3.3	−9.0	8.0
Zn	6.9	−43.0	27.5

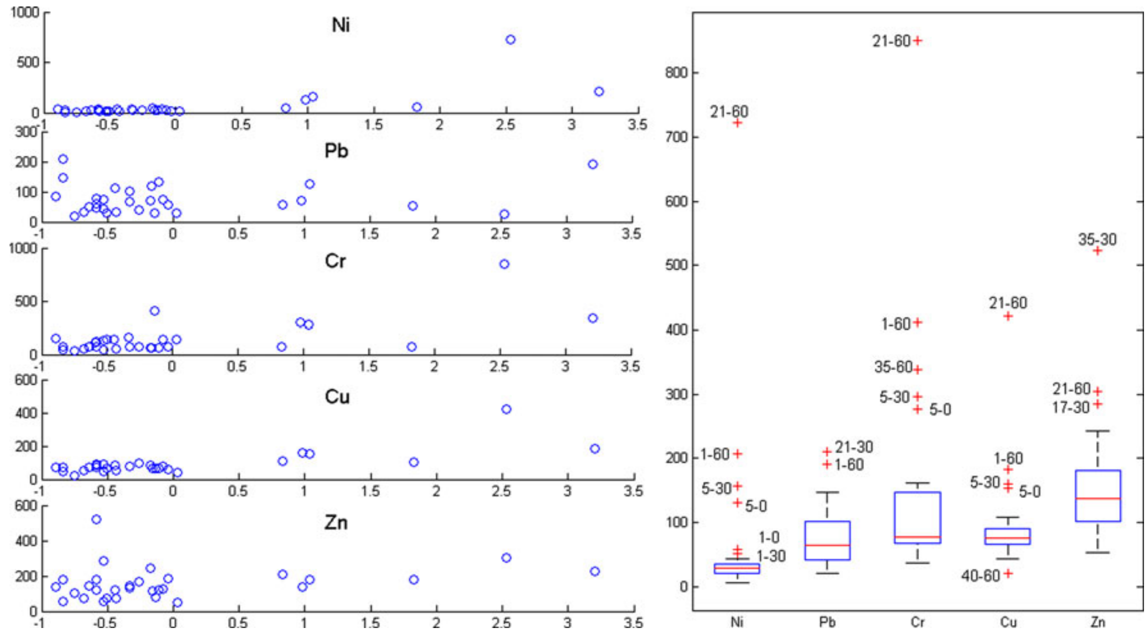

Fig. 6 *Biplot* of concentration values of trace metals and magnetic variables (canonical *x* axis); and *boxplot* of trace elements (in mg/kg for all elements). The *box* delineates interquartile range 25–75 % (q1–q3) and the *horizontal line* in *box* indicates the median. Minimum and maximum values are shown using *whiskers*. Extreme values or "outliers" were selected according to the whisker criteria. Points are identified as outliers if they are larger than q3 + 1.5 × (q3 − q1) or smaller than q1 − 1.5 × (q3 − q1). These samples are showed in the *boxplot* with their corresponding *label*

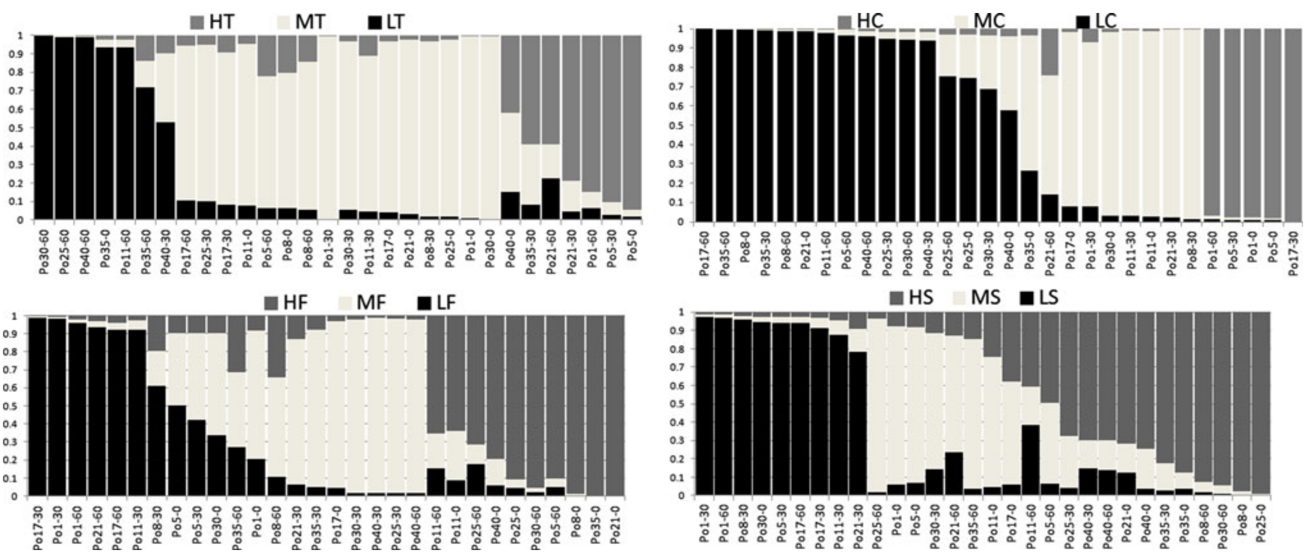

Fig. 7 Membership values from fuzzy *c*-means clustering. Magnetic (C: concentration, S: size, F: mineralogy) and chemical (T: trace) variables are shown. H, M and L correspond to high, moderate and low values, respectively

chemical and concentration variables: positive/negative values of ΔME indicate that this sub-dataset has lower/higher values than the dataset.

In particular, the values close to 0 of the group Major are indicative of a similar behavior with the depth. The negative values (the highest concentration) of the group Trace are noted at 0 (except Zn) and at 30 cm (except Ni and Cr) depth. At 60 cm depth, respectively, the concentration of the group Trace is the lowest one (positive ΔME), except Cr.

The analysis of magnetic data groups shows negative values of ΔME, hence the highest concentration, respectively, at 0 (ARM and SIRM) and at 30 cm (χ and SIRM) depth for the group Concentration (Table 2). The group Size, displays negative ΔME at 0 and 30 cm (higher ME at such depths) indicating the presence of finer magnetic

Table 3 Results from the fuzzy *c*-means clustering analysis

Samples	Classification	T: Trace					C: Concentration			F: Mineralogy		S: Size		Observation
		Ni (ppm)	Pb (ppm)	Cr (ppm)	Cu (ppm)	Zn (ppm)	χ (10^{-8} m^3/kg)	ARM (10^{-6} A m^2/kg)	SIRM (10^{-3} A m^2/kg)	H_{cr} (mT)	*S*-ratio (dimensionless)	κ_{ARM}/κ (dimensionless)	$\kappa_{FD}\%$ (%)	
	Polluted													
	HHLL	247.2	91.5	378.9	201.5	227.3	189.4	463.7	23.7	39.7	0.943	3.3	0.2	Trace and Concentration: H, M → H; mineralogy: L, M → L (lower-coercivity carriers); Size: L, M → L (coarser grains)
Po5-0		H					H			L		M		
Po1-60		H					H			L		L		
Po5-30		H					H			ML?		L		
Po21-60		H					M			L		M		
Po21-30		H					M			M		L		
Po17-30		M					H			L		L		
Po35-30		H					L			M		H		
	Relatively polluted													
	MMLL	38.8	83.0	67.8	87.0	188.3	68.3	181.9	7.8	41.9	0.950	3.7	0.9	
	MLHH	27.3	104.1	105.1	72.8	122.3	18.1	174.0	3.6	59.0	0.950	11.7	−0.9	
Po1-0		M					H			M		M		Trace and concentration: M, M → M; mineralogy: L, M → L (soft-coercivity carriers); size: L, M → L (coarser grain)
Po1-30		M					M			L		L		
Po8-30		M					M			L		L		
Po11-30		M					M			L		L		
Po17-0		M					M			M		MH?		
Po30-0		M					M			M		L		
Po11-0		M					M			H		M		
Po17-60		M					L			L		L		
Po8-60		M					L			M		H		
Po25-30		M					L			M		H		
Po30-30		M					L			M		M		Trace and concentration: M, L → M; mineralogy: M, H → H (higher-coercivity carriers); size: M, H → H (finer grain size)
Po8-0		M					L			H		H		
Po21-0		M					L			H		H		
Po25-0		M					L			H		H		
Po5-60		M					L			H		HM?		
Po40-0		MH?					L			H		H		

Table 3 continued

Samples	Classification	T: Trace					C: Concentration			F: Mineralogy		S: Size		Observation
		Ni (ppm)	Pb (ppm)	Cr (ppm)	Cu (ppm)	Zn (ppm)	χ (10^{-8} m^3/kg)	ARM (10^{-6} A m^2/kg)	SIRM (10^{-3} A m^2/kg)	H_{cr} (mT)	*S*-ratio (dimensionless)	κ_{ARM}/κ (dimensionless)	$\kappa_{FD}\%$ (%)	
	Unpolluted													
	LLHH	15.4	59.3	96.6	51.6	63.8	21.1	149.6	3.4	54.2	0.942	9.0	2.0	Trace and concentration: L, M → L; mineralogy: H, M → H (higher-coercivity carriers); size: H, M → H (finer grains)
Po40-60		L					L			M		H		
Po40-30		LM?					L			M		H		
Po35-60		L					L			MH		M		
Po35-0		L					M			H		H		
Po11-60		L					L			H		HL?		
Po25-60		L					L			H		M		
Po30-60		L					L			H		H		

Three centroids for magnetic and chemical groups (and variables) were determined. Each sample is classified as H (high values), M (moderate values) and L (low values) according to its membership value (see Fig. 7)

The question mark indicates that both classification would be possible

grains in the uppermost samples. On the other hand, the positive ΔMEs (lower ME at 30 cm depth) of the group Mineralogy suggest that this sub-dataset comprises softer magnetic minerals than the sub-datasets at 0 and 60 cm.

As a first approach, the Pearson correlation coefficients between pairs of variables were obtained; the Pearson's coefficients showed high correlation values (and statistically significant) between variables of Concentration group in all depths, as well as H_{cr} with most of variables. Otherwise, the correlation values between the other magnetic variables varied with the depth.

The correlations between chemical and magnetic variables showed positive and negative correlations, there are clear differences between concentration-dependent (positive values) and features-dependent (negative values) parameters. Most of concentration-dependent parameters correspond to significant values; in particular, significant relationships with trace metals. It is worth-mentioning that the effect of extreme values or "outliers" (Fig. 6) on correlation analyses was investigated. Although Pearson's coefficients changed when these extreme values were not considered for calculus, canonical correlations did not vary significantly. Thus, the Pearson's coefficient seems not to be a good indicator of relationships between the magnetic and chemical variables of this dataset, being necessary to use multivariate statistical techniques, among them, CCA and others.

From CCA, the group Concentration has the highest values of canonical correlation with both chemical groups, 0.88 ($p < 0.01$) with the group Major, and 0.78 ($p < 0.01$) with the group Trace. The CCA between groups Concentration and Major showed that the variable SIRM (group 1) and Al and Mn (group 2) are the main contributors to the relationship. And, between groups Concentration and Trace, the main contribution is made by variables SIRM (group 1) and Cu (group 2). CCA confirmed the existence of a relationship between magnetic and chemical variables. Groups of variables are correlated indicating that various magnetic properties contribute to describe metal pollutants.

From FCC, three groups (H: high values, M: moderate values, L: low values) were distinguished taking into account the magnetic and chemical variables (Fig. 7). The centroid values of the group H are the highest one, and the values of group L are the lowest one. In Table 3, data that belong to different groups are showed. In the group of more polluted samples (Polluted), most of these samples are characterized by high concentration (high values of group T and C) of trace elements and magnetic carriers, softer (low values of group F) magnetic minerals and coarser (low values of group S) magnetic grains (group HHLL). Such samples comprise sediments from sites Po-1, Po-5, Po-17 and Po-21 where traffic-derived activity is the main pollution source; other possible pollution sources comprise

waste disposal from towns and villages, and possibly, emissions from refractory manufacturing company, distillery and sugar industries (6–17 km from site Po-5 and 8–16 km from site Po-17/Po-21, see Fig. 1).

On the other hand, the relevant magnetic characteristics of the unpolluted group (Unpolluted, Table 3) indicate low concentration values of trace elements and magnetic carriers, fine and relatively fine magnetic grain sizes and higher-coercivity magnetic mineralogy (group LLHH). Most of these samples correspond to the deepest sediments (60 cm) from sites Po-11, Po-25, Po-30, Po-35 and Po-40. The site Po-30 is an area with important agricultural activity, but there are no important traffic and industrial activity. Although the site Po-35 could be influenced by traffic from a state highway and a small brick manufacturing company, these sediment samples do not seem to record the influence of pollution. A similar behavior is noted for Po-11, Po-25 and Po-40 where the deepest sediments seem not to be affected by industries and the vehicular traffic from national highways.

Conclusions

- Predominance of ferrimagnetic (magnetite-like) minerals over antiferromagnetic minerals; with magnetic grain size variations (<0.1 μm and up to 5 μm) along the river and in depth
- High and intermediate values of magnetic concentration-dependent parameters reveal the characteristic behavior of the Ponnaiyar River regarding sites with different load and input of magnetic particles. The highest values (e.g. χ values varied widely, 6.8–265.0 $\times 10^{-8}$ m^3/kg) are interpreted as magnetic enhancement that may arise as pollution consequence produced by anthropogenic, industrial activities or other process. This is supported from the elemental determinations, which also show important increases
- From the descriptive statistics, different characteristics were observed with depth: the highest values of trace metals and magnetic concentration at 0 and 30 cm (extreme values at 30 cm); coarser magnetic grain sizes and softer magnetic mineralogy at 30 cm; the lowest concentration and low ME values of magnetic concentration and higher-coercivity magnetic mineralogy of trace metals at 60 cm
- Canonical correlations indicate statistically significant positive correlations between magnetic concentration variables and chemical (major and trace metals) variables (canonical correlation of 0.78 with trace metals) and non-significant canonical correlations between magnetic features and chemical variables
- Using FCC was possible to classify samples in different groups: (1) polluted samples with high concentration of trace elements and magnetic carriers, softer magnetic minerals and coarser magnetic grains; (2) unpolluted samples with low concentration, higher-coercivity magnetic mineralogy and finer grains

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