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RESEARCH PAPER

Environmental Magnetism and Heavy Metal Assemblages in Lake Bottom Sediments, Anchar Lake, Srinagar, NW Himalaya, India

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Abstract

Lake sedimentation represents a collective record of atmospheric and surface processes operating over the catchment areas. Magnetic minerals along with heavy metal assemblages can selectively represent the ongoing impact of dominant environmental processes over the catchment regions. Lake bottom sediments collected from Anchar Lake were investigated to trace the magnetic and heavy metal signatures in context to quantify the environmental conditions from one of the ideal setup of lake catchment in the Srinagar valley of Kashmir Himalaya. Magnetic parameters such as χ_{ARM}, SIRM and $Soft_{IRM}$ revealed predominant soft ferrimagnetic mineralogy. The S-ratio showing a mean value of − 0.69 within a range of − 0.77 to − 0.57 depicted majority of PSD-SD ferrimagnetic grains. The χ_{lf} versus χ_{fd} % biplot suggest the presence of mixture of SP and coarser magnetic grains controlling the magnetic susceptibility signals in the lake bottom sediments. The magnetic parameters and heavy metal constituents in particular S-ratio, SIRM/χ_{lf}, χ_{ARM}/χ_{lf} and χ_{ARM} exhibit significant correlation with Cr, Cu, Ni and Zn. Furthermore, spatial variability of these parameters depicts a complex of detritus influx, anthropogenic inputs, and the domain size of minerals reflecting oxidizing and reducing conditions with sharp changes in the peripheral part and gradual mixing towards the central and deeper parts of the lake basin. Multivariate statistical analyses (Pearson correlation, cluster and factor analyses) attest direct relation of the heavy metals with mineral magnetic assemblages. Overall, the results reflect heterogeneity in the record within the lake basin at the scales of 10’s of meters attributed to basin lacustrine conditions.

Keywords Anchar Lake · Environmental assessment · Mineral magnetics · Heavy metals · Spatial distribution · Multivariate analysis

Introduction

Freshwater lakes are one of the most important natural sedimentary archives that preserve proxy signatures of the changing catchment environment. Mineral magnetic and heavy metal assemblages in lake sediments provide a good combination of tools to estimate changes in catchment source, erosional and depositional processes as well as the anthropogenic inputs (Oldfield et al. 1983; Yang et al. 2009; Khan et al. 2012). Such studies on surficial sediments provide useful information on modern lake and catchment processes and thus help researchers to interpret magnetic proxies for paleoenvironment reconstruction in different environmental settings (Thompson et al. 1975; Bali et al. 2011; Hayashida et al. 2015). As a result, several significant inferences are drawn from mineral magnetic assemblages and their signatures in lake sediments to

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decipher the changing environmental conditions (Anderson and Rippey 1988; Foster et al. 1998; Shankar et al. 2006; Warrier and Shankar 2009). The magnetic contents in lake sediments are derived predominantly from the catchment (weathering and anthropogenic sources), with minor amounts contributed from atmospheric sources. Fluctuations in the climate and environmental conditions initiate changes in chemical weathering processes of catchment bedrock and soils, leading to changes in the mineral magnetic and heavy metal concentration, magnetic mineralogy, diagenetic changes and magnetic grain size depositing in lake basins (Sandeep et al. 2017).

The production and dissolution of authigenic magnetite although occurring in much smaller grain sizes (10–100 nm) than detritus magnetic minerals, controls the magnetic properties of lake sediments deposited by a variety of environmental and anthropogenic processes (Thompson et al. 1980; Thompson and Oldfield 1986). Furthermore, the sources of magnetic minerals in lake sediments are quite distinct, for example, detritus input is controlled by hydrological processes occurring in the catchment, while authigenic mineral formation is related to the in situ/aquatic productivity of the lake (Hayashida et al. 2015). Many of these processes are seasonally dependent; however, the anthropogenic processes operate throughout the seasons heavily impacting the catchment environments and its input into the lake basin.

Environmental magnetic studies have proved the existence of a relationship between mineral magnetic properties and heavy metal contents in soils (Lu et al. 2007). This relationship in soils allow magnetic techniques to be used as an indicator for contaminants and their spatial distribution. The use of magnetic mineral and heavy metal assemblages in lake sediments to evaluate recent catchment changes is now well established (Anderson and Rippey 1988; Dekkers et al. 2000; Evans and Heller 2003; Liu et al. 2012). Recent investigations have also established an apparent link between magnetic mineral and heavy metal concentrations in a variety of environmental contexts such as identification of source of industrial pollutants, mapping of soils and sediment pollution, and a proxy parameter for quantifying contents of heavy metals in certain environments (Hunt et al. 1984; Lu et al. 2007).

Anchar Lake is one of the important freshwater urban lakes in Kashmir Valley and serves as a major resource for drinking water purposes, irrigation, fisheries, recreation, tourism, etc. for the local population. However, in the recent past, the lake has reduced significantly in its size as a result of natural and anthropogenic influences, particularly high siltation rates from the catchment areas in the form of weathering of bedrock, domestic and agricultural wastes and unplanned urbanization along the catchments. This has led to the significant portion of the lake undergoing the process of eutrophication. A substantial work has been carried out on the sediment geochemistry, water chemistry and changing physical setup of Kashmir Himalayan lakes by various investigators (Kaul 1977; Vass 1978; Kaul et al. 1980; Kango et al. 1987; Jeelani and Shah 2006; Badar et al. 2013; Sheikh et al. 2013; Lone et al. 2017; Shah et al. 2017). However, a comprehensive study regarding the distribution and source of mineral magnetic parameters and heavy metal assemblages and their relation with sediment texture and organic matter (OM) is still awaited.

In the present study, environmental magnetism and heavy metal investigations of lake bottom sediment samples collected from the Anchar Lake were studied. The objectives of the present study were to: (1) investigate the distribution of magnetic mineral parameters and heavy metal assemblages and (2) explore the statistical correlations between magnetic parameters and heavy metal contents in the lake bottom sediments of Anchar Lake. This is the first such investigation carried out on the magnetic minerals and heavy metal characteristics of the lake bottom sediments from Kashmir Valley. The study was aimed at enhancing the understanding of the relationship between magnetic properties and heavy metal contents in the lake bottom sediments.

Study Area

The Kashmir Valley forms a longitudinal depression and constitutes an important relief feature of geographic significance in the Northwest Himalayan region. The valley abounds with several deep, freshwater lakes of fluvial and glacio-fluvial origin. The present study was carried out on the Anchar Lake situated in the Srinagar City (Fig. 1). The lake lies between 34° 20′–34° 26′N latitude and 74°82′–74° 85′E longitude with an average elevation of $\sim$ 1583 m amsl and with a mean depth of about 4 meters. The lake is a single-basin, with an open drainage-type water body fed by a network of catchment channels and covers a surface area of about 5.8 km^2. Furthermore, a number of small channels from agricultural fields, effluents from settlements and surface runoff from the catchment area directly drain into the lake. The topography of the lake catchment is varied exhibiting altitudinal extremes from 1568 m (near Anchar) to 5236 m amsl towards the Greater Himalayan ranges.

The lithology around the lake is represented by recent alluvium, Panjal Traps (Permian), carbonates and dolomites (Triassic) and the Karewa deposits (Quaternary age). The nearly 2000-m thick Karewa sediments are glacial-fluvio-lacustrine deposits composed of gravels, silt, marls, lignite and glacial moraines with varved clays (Agrawal et al. 1979; Agrawal et al. 1988; Agrawal et al. 1989; Singh 1982; Agarwal and Agrawal 2005; Agarwal et al.

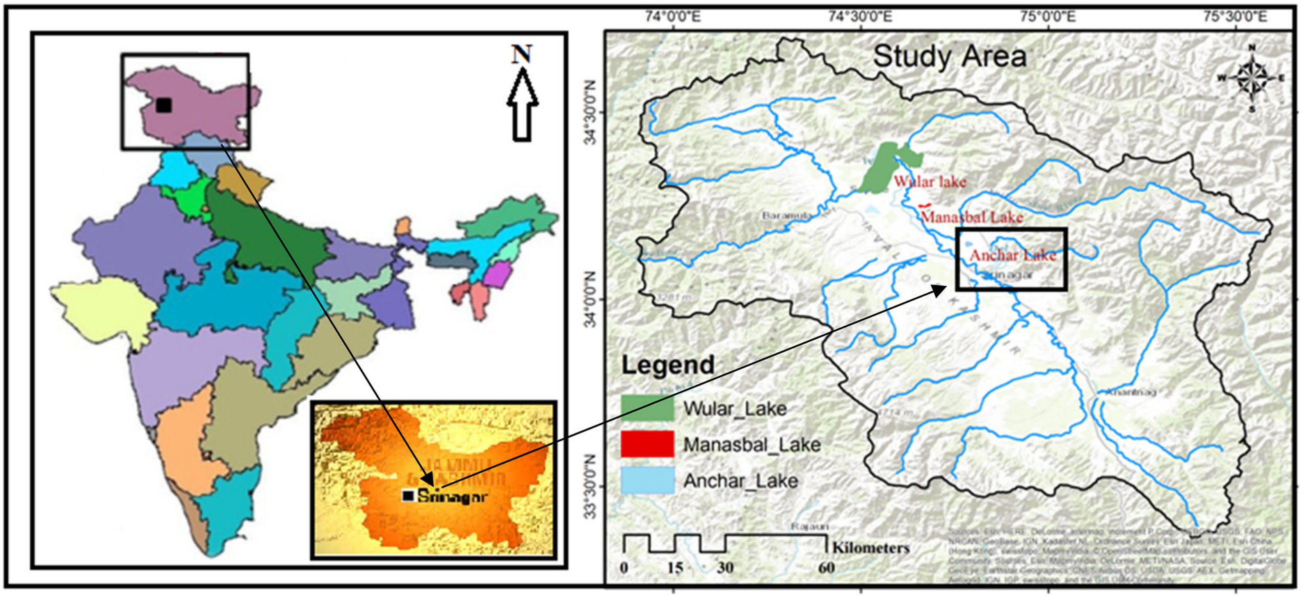

Fig. 1 Location map of the study area showing the Anchar Lake

2018). The lake catchment is also covered by various land-use land cover classes, including built-up (urbanization), parks, roads, open forests, orchards and agricultural fields (Fig. 2). A major portion of the lake, particularly along the margins, is presently dominated by aquatic vegetation and macrophytes due to the anthropogenic influences. The lake lies in the temperate zone, characterized by wet and cold winters driven by westerlies and relatively dry and moderate hot summers (subdued SW monsoon). Most of the precipitation falling in the area is due to the western disturbances (westerlies) mainly during the winter season from November to April. The average annual rainfall is 650–710 mm with an average temperature of 13 °C (Babeesh et al. 2017).

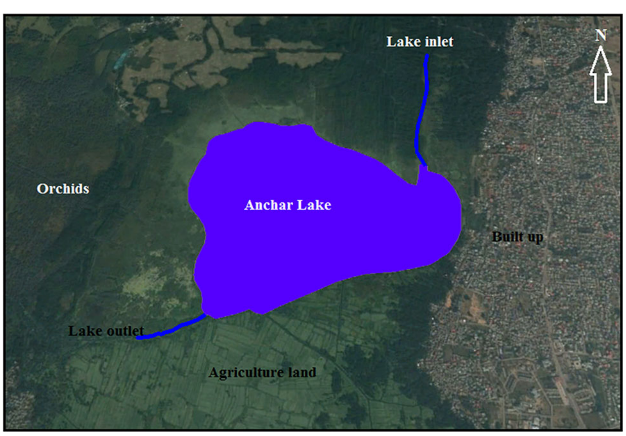

Fig. 2 Google earth imagery of the Anchar Lake and its surrounding catchment area

Materials and Methods

Twenty-four lake bottom sediment samples were collected during July 2015 covering the entire lake basin (Fig. 3). Grab samples were collected at different intervals with varying water depths from margins to the central portions of the lake. The collected grab samples were dried in the oven at 35 °C and later gently disaggregated using a wooden mortar and a pestle. Various magnetic parameters were determined on the sediment samples at the Department of Geology, Savitribai Phule Pune University, Pune. Magnetic susceptibility of the sediments collected were measured at two frequencies (0.465 and 4.65 kHz) using MS2B laboratory sensor (Bartington UK). Anhysteretic remnant magnetization (ARM) was measured by inducing a small bias field of 0.1 mT over an alternating decaying field of 100 mT using AGICO (Czech) alternating field demagnetizer. Isothermal remnant magnetisation (IRM) was induced at different field strengths (20, 60, 100, 300, 500 and 1000 mT) using an ASC impulse magnetiser and the remanence were measured on Minispin spinner magnetometer. Inter-parametric ratios such as S-ratio, χ_{ARM}/χ_{lf}, χ_{ARM}/SIRM and SIRM/χ_{lf} were calculated to determine the magnetic mineralogy and grain size-related parameters (Liu et al. 2012; Walden et al. 1999). The magnetic measurements and correlation are presented in Tables 1 and 2, respectively.

The sediment textural analyses (sand, silt and clay percentage) of the collected sediment samples were analyzed following the method put forward by Carver (1971). Before obtaining the grain size measurement, samples were pre-treated with 30% H_2O_2 and 10% acetic acid to decrease

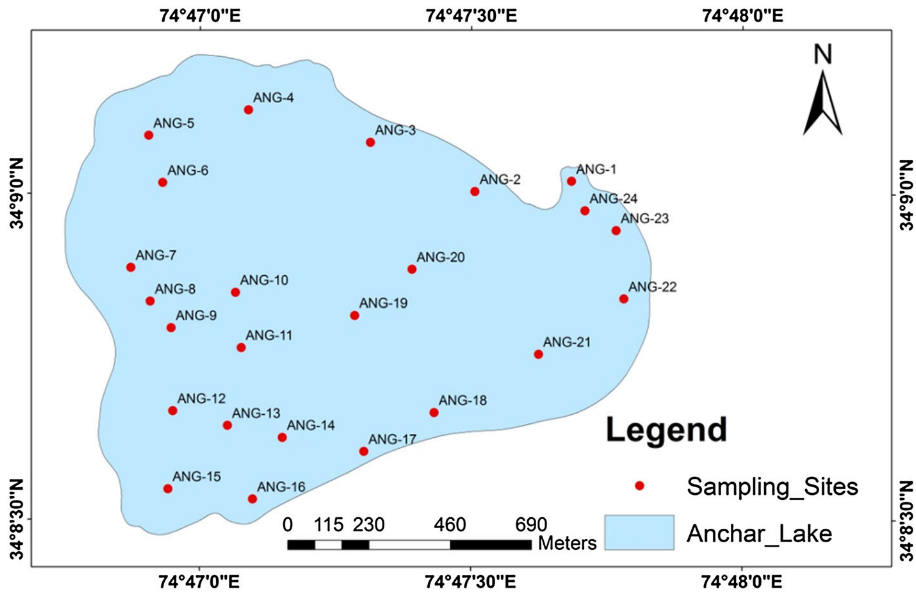

Fig. 3 Map of the Anchar Lake showing sampling stations

the influence of organic matter and carbonates. The sand fraction was separated by wet-sieving through an ASTM test sieve no. 230 (62 µm pore diameter). After removal of sand, the silt + clay fraction was transferred to a 1000-ml measuring cylinder. After making it up to 1000 ml volume, the silt and clay fractions were determined using pipette analysis. The column containing silt and clay was stirred vigorously for about 1 min using a stirring rod. After 20 s, 20 ml of the liquid was pipetted out from 20 cm depth that contains the silt + clay fraction. After 3 h 10 min, 20 ml of the liquid was pipetted out from 5 cm depth that contains only the clay fraction. The total weight of the clay fraction was calculated by multiplying the weight of clay by 50. The collected lake grab samples were also analyzed for heavy metal contents using VP-320 X-ray fluorescence (XRF) spectrometry at the Department of Geology, Savitribai Phule Pune University, Pune. The samples were then powdered and later passed through ASTM-230 mesh sieve. The analytical error for heavy metal concentration is < 1 ppm. The spatial distribution of the studied parameters was interpolated through inverse distance weighted (IDW) algorithm available in the geo-statistical analyst tool of Arc GIS 10.3. The heavy metal (in ppm) concentrations of sediment samples are presented in Table 3.

Multivariate statistical analysis was performed using the IBM Statistical Package of Social Studies (SPSS) software version 21 for windows. Correlation matrix and cluster analyses were applied to find the significant relationship between the mineral magnetic parameters and heavy metal assemblages. Principal Component Analyses (PCA) were then applied for data reduction, to assess the continuity of clusters or similarities in the dataset. Cluster analysis (CA) results were displayed in the form of a dendrogram, to deduce the source of mineral magnetic contents and heavy metals in the lake sediments. Finally, a dendrogram was created based on the level of similarity between the various sampling stations using Ward's method.

Results and Discussion

The lake bottom samples are dominated by clay and silt with minor sand content. A mean clay of $\sim$ 52% and silt content of $\sim$ 45% were estimated. The clay varies from $\sim$ 20 to 75% with a median value of 59%. The silt content also shows similar variability to that of clay with a median value of 40%. The χ_{lf} for these sediments is 1.88 ($\times\ 10^{-8}m^3/Kg$) with a maximum value reaching 2.65. The sediment samples exhibit a fairly good χ_{fd} % with a maximum of $\sim$ 14% indicating an abundance of SP ferrimagnets. The coercivity of remanence ($B_{(0)CR}$) show a mean of $\sim$ 39 mT matching with median and depict low variability within a restricted range of softer SD ferrimagnets. The χ_{ARM}, SIRM and $Soft_{IRM}$ indicate the dominance of soft ferrimagnetic mineralogy. Ferrimagnetic minerals such as magnetite have S-ratio value close to 1 because they acquire most of the remanence at field strengths < 300 mT. Anti-ferromagnetic minerals such as hematite and goethite exhibit lower values because they would not have saturated at 300mT field strength. The S-ratio (at IRM-100) with a mean value of $-$ 0.69 fall within a range from $-$ 0.77 to $-$ 0.57 and depict majority of PSD-SD ferrimagnetic grains. Inter-parametric ratios, χlf *vs.* χ_{fd} %, χ_{ARM}/SIRM and χ_{ARM}/χ_{lf}, were applied to determine the magnetic grain size. High ratio signify finer magnetic domain sizes and vice versa. The biplot of χ_{fd} % versus χ_{lf} was used to decipher the grain size of magnetic minerals and has also been previously used on lacustrine

Table 1 Mineral magnetic parameters and other physico-chemical assemblages for surface sediments of Anchar Lake

Sample Id	Sand %	Silt%	Clay%	OM%	$CaCO_3$%	χ_{lf} 10^{-8} m^3/kg	χ_{fd}%	χ_{ARM} (10^{-5} m^3/kg	BCoR	SIRM 10^{-5} AM^2/kg	Soft IRM	HIRM	S-ratio	SIRM/χ_{lf} 10^3A/m	XARM/χ_{lf}
ANG-1	5.5	45.3	49.2	5.0	11.4	2.6	5.5	0.1	37.0	183.1	52.1	3.1	0.6	69.1	23.7
ANG-2	2.6	48.1	49.3	4.8	10.3	2.6	4.9	0.1	39.0	188.3	49.8	2.6	0.7	71.3	44.4
ANG-3	0.6	30.0	69.4	9.2	9.8	0.8	4.2	0.0	45.0	61.6	13.0	1.6	0.6	74.5	41.5
ANG-4	6.5	34.7	58.8	12.9	6.2	1.8	4.9	0.1	40.0	136.5	31.4	2.3	0.7	76.7	55.2
ANG-5	2.4	38.5	59.2	6.7	8.7	1.9	6.2	0.1	36.0	139.8	37.8	1.7	0.7	71.7	65.6
ANG-6	1.4	19.6	79.1	9.9	7.2	1.0	2.9	0.1	42.0	86.1	18.7	1.6	0.7	87.6	69.8
ANG-7	1.2	48.9	49.9	8.3	10.0	1.4	4.6	0.1	37.0	125.5	31.2	1.7	0.7	92.1	86.1
ANG-8	2.4	28.7	68.9	13.5	8.9	1.8	2.5	0.2	40.0	180.2	40.8	2.2	0.7	99.2	88.1
ANG-9	5.7	45.0	49.3	10.1	9.0	2.5	5.8	0.2	36.0	208.2	53.9	2.1	0.8	83.2	82.3
ANG-10	1.4	39.3	59.3	11.3	8.4	2.6	4.7	0.2	36.0	209.1	55.2	2.6	0.7	80.5	73.1
ANG-11	2.6	28.4	69.0	11.6	9.4	2.5	6.1	0.2	36.0	207.3	53.1	2.2	0.8	84.3	81.1
ANG-12	2.0	19.4	78.6	17.2	9.4	1.5	6.4	0.1	38.0	125.5	30.3	0.4	0.8	83.5	81.8
ANG-13	1.2	39.3	59.5	10.3	9.9	1.3	5.7	0.1	37.0	101.5	25.6	1.2	0.8	79.9	77.1
ANG-14	0.4	40.3	59.3	13.1	6.3	2.4	6.7	0.2	37.0	187.7	47.2	2.6	0.7	79.6	72.9
ANG-15	1.8	38.7	59.5	10.9	12.6	1.3	14.1	0.1	38.0	121.9	28.5	1.4	0.7	92.7	77.3
ANG-16	1.2	69.3	29.5	16.5	7.6	1.6	4.1	0.1	37.0	124.1	30.0	4.8	0.7	76.7	48.4
ANG-17	0.4	60.2	39.4	9.5	8.8	1.8	4.8	0.1	38.0	131.4	33.9	1.8	0.7	73.4	50.2
ANG-18	1.2	59.0	39.8	13.8	8.9	1.0	4.4	0.0	40.0	60.5	14.3	1.9	0.6	62.6	32.5
ANG-19	0.6	40.1	59.3	5.5	12.8	2.3	6.0	0.1	40.0	163.9	42.0	2.3	0.6	71.2	36.5
ANG-20	0.6	69.6	29.8	6.3	13.0	2.2	4.3	0.1	40.0	161.5	41.3	2.6	0.7	73.5	39.7
ANG-21	2.8	77.5	19.8	12.6	8.7	1.5	1.8	0.0	44.0	91.9	21.9	2.7	0.6	60.4	24.0
ANG-22	1.0	39.5	59.5	11.6	11.7	1.6	5.8	0.1	40.0	127.2	30.2	2.0	0.7	78.4	48.0
ANG-23	0.4	79.7	19.9	4.4	10.5	2.6	5.3	0.1	40.0	190.9	50.0	3.2	0.6	73.7	28.1
ANG-24	30.2	40.2	29.6	3.9	15.2	2.4	4.1	0.0	38.0	145.3	39.9	2.2	0.6	60.9	18.9

sediments (Sandeep et al. 2017). The χ_{lf} versus χ_{fd} % biplot (Fig. 4) indicates the occurrence of mixtures of SP and coarser magnetic grains. However, two samples (ANGB-21 and ANGB-15) fall in the No SP grains zone and in the virtually all SP grain zone of the biplot, respectively. The χ_{fd} % values greater than 10 indicate fine-grained magnetic minerals with a high proportion of SP magnetic grains (Sandeep et al. 2017). The average χfd% value is 5.23%, suggesting the presence of both; the fine and coarse-grained magnetic minerals in the sediment samples.

Spatial Distribution of Potential Pollution Zones

Heavy Metal and Mineral Magnetic Assemblages

The application of magnetic parameters as a proxy method for the detection of environmental contamination is based

Table 2 Descriptive statistics of the mineral magnetic parameters of the Anchar Lake sediments

	Sand %	Clay%	Silt%	χ_{lf} 10^{-8}	χ_{fd}%	χ_{ARM}	BCoR	SIRM 10^{-5}	Soft IRM	HIRM	S-ratio	SIRM/ χ_{lf}	χ_{ARM}/ χ_{lf}
Mean	3.16	51.87	44.97	1.88	5.23	0.10	38.79	144.12	36.34	2.20	0.69	77.37	56.09
Standard error	1.22	3.47	3.38	0.12	0.46	0.01	0.50	9.10	2.58	0.17	0.01	1.99	4.58
Median	1.38	59.00	40.18	1.80	4.92	0.09	38.00	138.12	35.85	2.20	0.69	76.68	52.66
Standard deviation	6.00	17.00	16.58	0.58	2.25	0.05	2.43	44.58	12.62	0.83	0.05	9.74	22.46
Sample variance	35.98	289.11	274.98	0.34	5.04	0.00	5.91	1987.04	159.27	0.69	0.00	94.95	504.39
Kurtosis	19.84	− 0.58	− 0.12	− 1.21	10.71	− 0.37	0.83	− 0.79	− 0.90	3.32	− 0.79	0.08	− 1.43
Skewness	4.31	− 0.43	0.67	− 0.20	2.60	0.63	1.02	− 0.22	− 0.17	0.92	− 0.35	0.27	− 0.12
Range	29.78	59.29	60.23	1.82	12.26	0.17	9.00	148.59	42.18	4.33	0.20	38.83	69.20

Table 3 Heavy metal concentrations (ppm) in surface sediments of Anchar Lake

Sample Id	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)
ANG-1	50.7	22.4	38.3	38.7	89.7	20.4
ANG-2	67.0	29.0	49.0	51.0	109.0	22.8
ANG-3	83.8	32.7	55.8	66.8	126.7	25.4
ANG-4	96.0	24.0	61.0	71.5	135.4	28.9
ANG-5	110.8	12.4	62.5	75.9	137.6	33.1
ANG-6	104.0	24.0	64.0	135.0	163.7	31.6
ANG-7	100.3	35.1	65.8	166.7	192.0	31.8
ANG-8	97.0	25.0	63.0	112.0	161.0	26.9
ANG-9	92.5	17.7	59.6	65.9	129.2	23.9
ANG-10	86.0	25.0	60.5	61.3	126.0	25.8
ANG-11	77.9	32.1	60.0	55.4	119.8	27.5
ANG-12	87.0	26.0	57.0	47.8	116.4	31.2
ANG-13	93.3	13.8	57.4	42.2	113.0	33.8
ANG-14	82.0	19.0	58.0	55.0	124.0	31.5
ANG-15	68.6	22.0	56.7	66.8	131.1	26.7
ANG-16	76.0	17.0	56.0	76.0	146.0	26.4
ANG-17	80.0	15.7	56.9	90.1	154.1	24.0
ANG-18	76.0	21.0	54.0	85.5	164.0	24.9
ANG-19	77.9	23.9	52.8	82.5	179.4	26.4
ANG-20	75.0	23.0	49.0	58.4	144.0	26.0
ANG-21	71.4	17.9	43.5	33.8	105.8	24.3
ANG-22	71.0	17.0	41.8	37.0	103.4	24.1
ANG-23	73.4	12.0	42.2	37.4	99.6	21.2
ANG-24	48.1	12.0	32.1	22.6	71.4	19.8
Average	81.1	21.7	54.0	68.1	130.9	26.6
Max.	110.8	35.1	65.88	166.7	192.0	33.8
Min.	48.1	12.0	32.1	22.6	71.4	19.8

on the fact that heavy metal pollution in many cases is accompanied by emission of ferrimagnetic particles. Various factors influence the distribution and accumulation of magnetic and heavy metal contents in lakes, in particular the Eh and pH conditions, sediment texture, mineral composition, catchment lithology, weathering intensity, and anthropogenic inputs (Ma et al. 2016). Several workers (Meena et al. 2011; Fialová et al. 2006; Mitchell and Maher 2009) have reported a positive linear correlation between heavy metals and magnetic minerals in anthropogenically

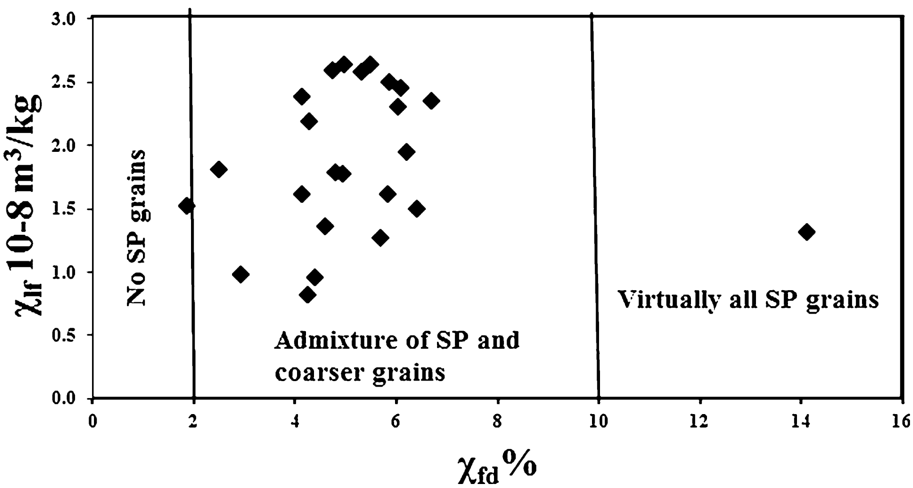

Fig. 4 Biplot of χ_{lf} vs. χ_{fd} % indicating mixture of SP and coarser grains in the Anchar Lake sediment samples

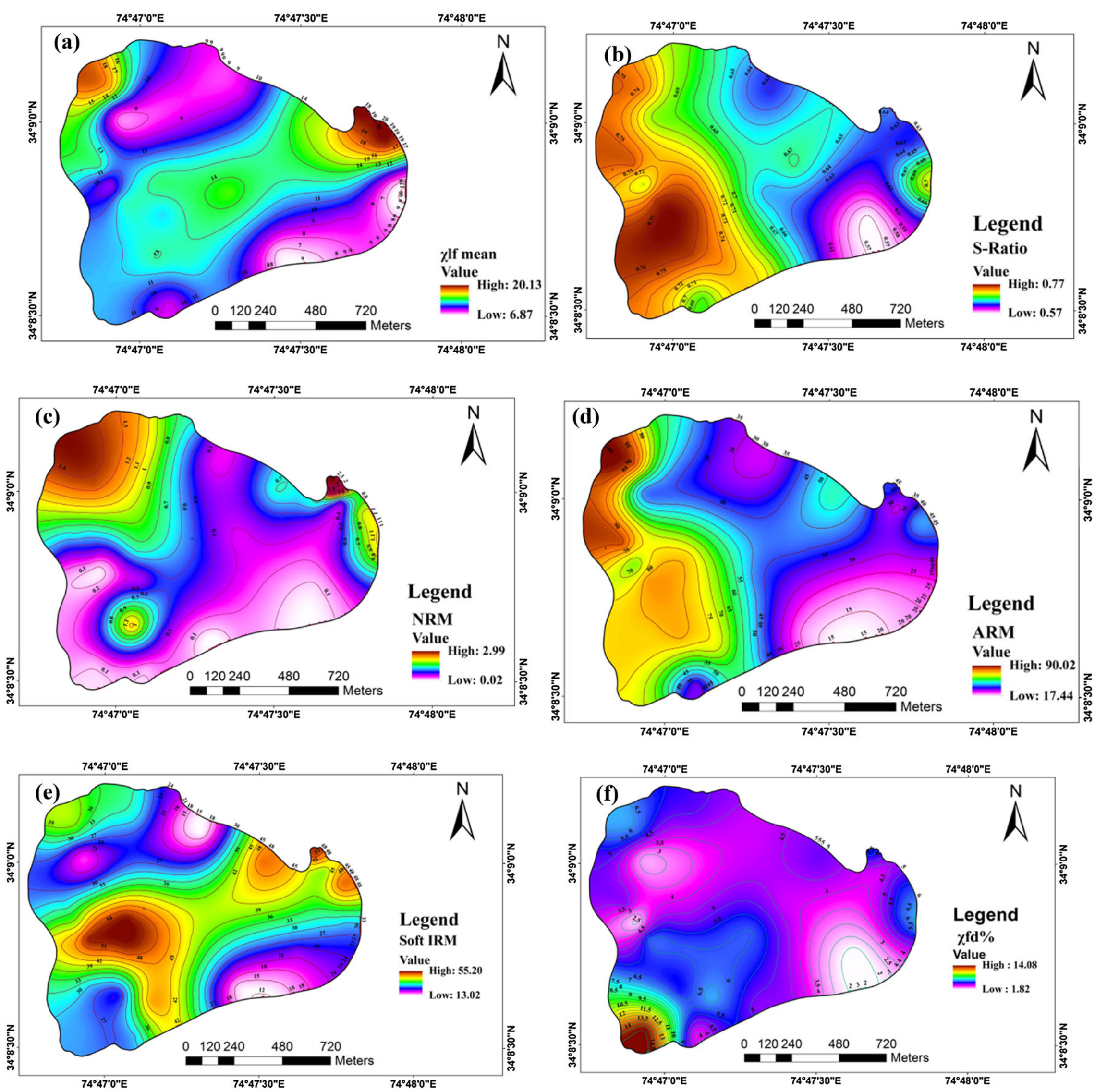

Fig. 5 Spatial distribution of mineral magnetic parameters in the Anchar Lake sediment samples

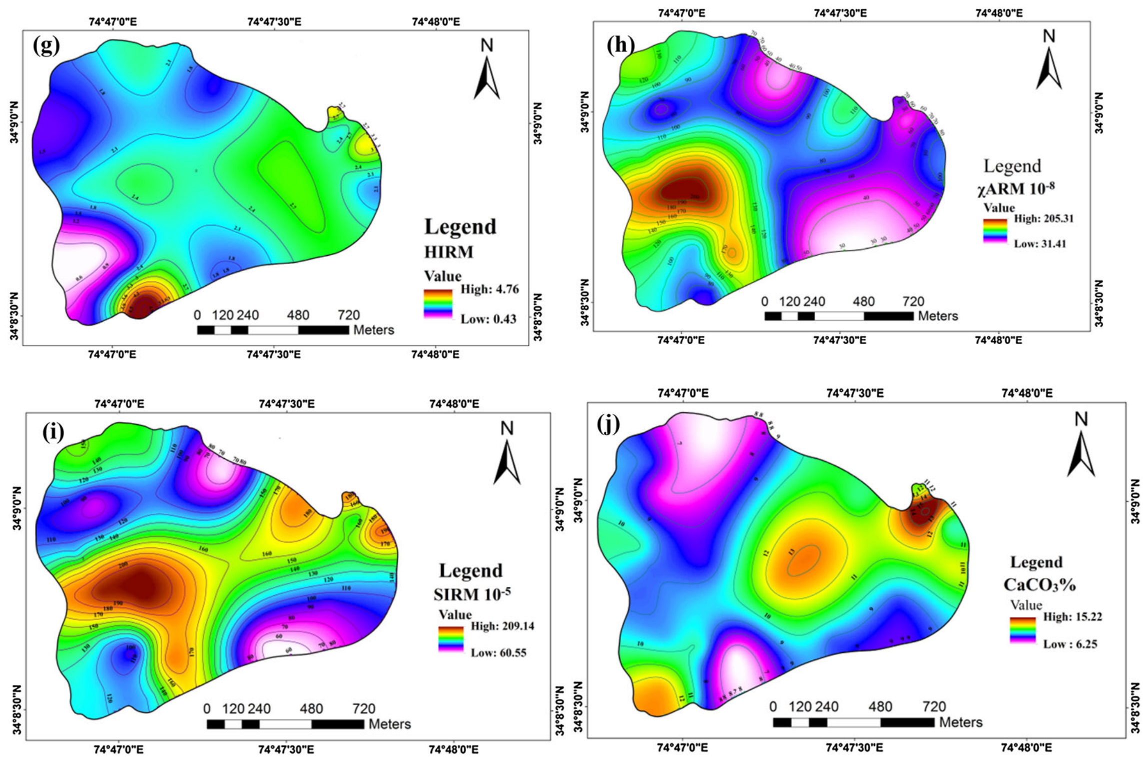

Fig. 5 continued

affected/polluted areas. The spatial distribution pattern for magnetic parameters of Anchar lake sediment is presented in Fig. 5a–j. The χ_{lf} values show a major outlier of high values on the lake inlet site, while another outlier can be observed in NW corner where a low-lying area exists. This indicates that the lake received major input from these two areas, besides depicting the detritus control for χ_{lf}. There is a trend from the inlet towards the outlet of a diffused nature. The NRM shows a major trend from the NW quadrant suggesting the input of remanence carrying minerals (SD-PSD). The ARM pattern coincides with NRM further depicting the SSD dominant zone. The HIRM exhibits a major anomaly in the southern quadrant which is attached to the agricultural field depicting its anthropogenic nature. The SIRM reveals a trend independent of χ_{lf} but coincides with the trend of Soft IRM and χ_{ARM} depicting distribution of hard ferrimagnetic/SD fraction. The χ_{fd} % shows very high values at the southern tip of the outlet again suggesting an anthropogenic input. The $CaCO_3$ content reveals an outlier at the inlet pointing towards its detritus nature. The catchment of the lake is composed dominantly of limestone lithology. Besides, the in situ calcareous matrix also binds the detritus sediments. The OM data revealed two outliers in the southern region independent of any other parameters.

The relative enrichment or depletion of heavy metals in the lake sediments has been widely used to infer source changes in response to weathering of the source rocks and human inputs. When compared with the Upper Continental Crust (UCC) threshold values (Fig. 6), the heavy metals suggest enrichment of all the heavy metals in the lake sediments. The enrichment of Pb, Cr and Cu might have originated from mixed sources (natural and human inputs). The concentration of other heavy metals such as Ni, Co and Zn is attributed to their incorporation by anthropogenic influences mainly from agricultural practices and urban domestic sewage. The margins of the Anchar Lake are governed by complex anthropogenic activities including agricultural land-use, sewage discharges, urban sprawl and human exploitation of lake water for domestic uses. The various points and non-point sources include domestic

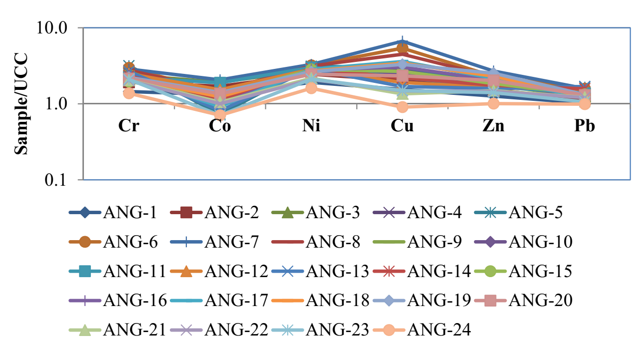

Fig. 6 Sediment normalized diagram for heavy metals of the Anchar lake

wastewaters, and agricultural and catchment runoff, respectively.

The results demonstrate that the heavy metal concentration differ significantly in different sites around and within the lake (Fig. 7). Cr, Ni and Cu show higher concentration towards the NW part of the lake. Co content is higher values towards central and northern corner of the lake. The concentration of Pb shows higher values towards the NW and SW quadrants matching with the magnetic parameter such as χlf although with a different shape. Overall, the concentration of heavy metals show a decreasing trend from the western part tending towards the eastern flanks of the lake. The relatively high concentration in the NE part of the lake suggests that the sediments are enriched with heavy metals probably as a consequence of anthropogenic activities compared to other natural influences. The distribution of heavy metals in the lake bottom sediments can be explained in terms of the proximity to the potential source of contaminants since the western and north western parts of the lake allow settling of heavy metal assemblages through water column without substantial lateral disbursement. Further, the magnetic concentration parameters covary with heavy metal concentrations, in the lake bottom sediments suggesting that the input of magnetic minerals and heavy metals in the lake sediments are derived from the similar anthropogenic sources such as discharge and disposal of treated/untreated sewage from agricultural, horticultural, unplanned expansion of urbanization along catchments and boating activities. In the absence of metallurgical and other industries, magnetic mineral assemblages could have been released along with other heavy metals from a combination of the above sources and introduced into the bottom sediments. Cr and Ni values are almost similar and indicate a mafic or basaltic provenance akin to the Permian Panjal Traps that also explains the presence of highly detritus ferrimagnetic mineralogy in the input/inlet areas of the lake. The higher concentrations of Co, Cu and Zn may be the combined result of Trap weathering in addition to anthropogenic applications from orchard areas where these heavy metals are added as plant micronutrients. The spatial distribution of Pb may be enigmatic. However, anthropogenic additions plus differential adsorption related to clay concentrations can aid its deposition in the lake bottom sediments. Study of the heavy metal distribution patterns suggest that the lake reflects spatial variability of detritus influx, anthropogenic inputs, and the domains of oxidizing and reducing conditions. Overall, the lake shows sharp changes in the peripheral part and a gradual mixing environment in the central part.

Heavy Metal–Magnetic Parameter Relationships

Multivariate Statistical Analysis

Correlation Matrix The relationships between heavy metals and magnetic parameters provided interesting information about their sources and pathways. Correlation matrix was used to analyze the interrelationship and to assess associations amongst the magnetic and heavy metal

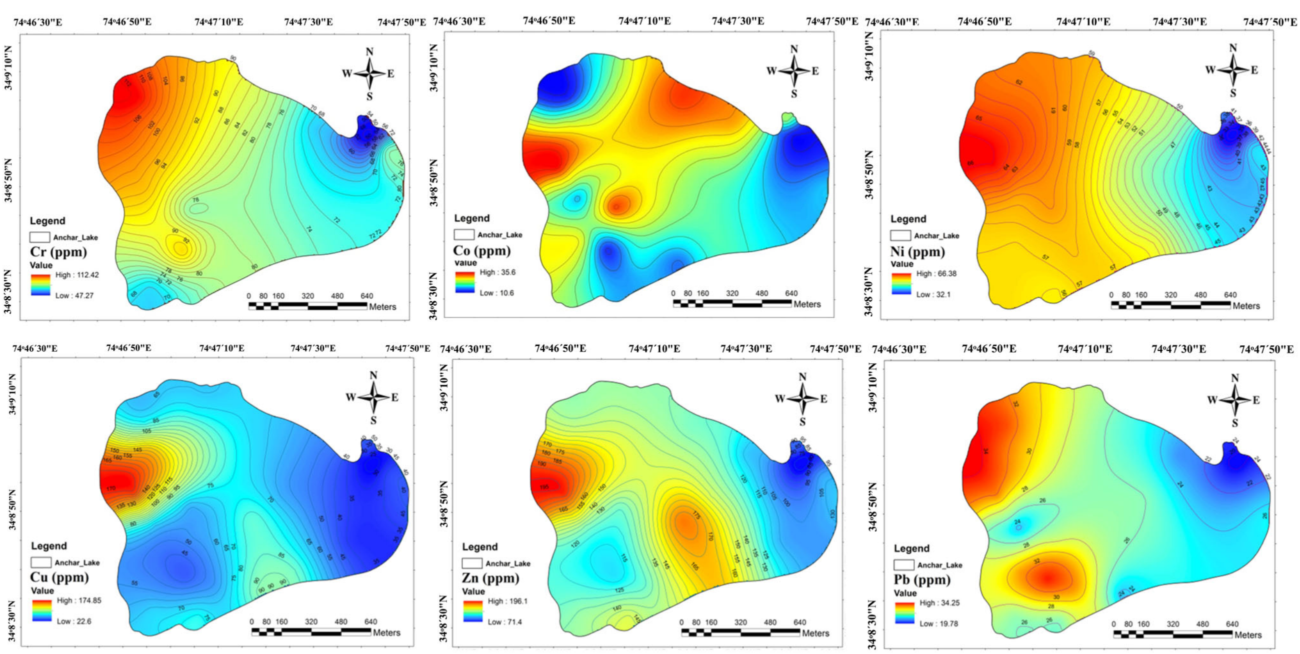

Fig. 7 Spatial distribution of heavy metal assemblages in Anchar Lake sediment samples

Table 4 Correlation matrix of the mineral magnetic, heavy metals and other physico-chemical parameters for the Anchar Lake sediments

	Sand %	Silt%	Clay%	OM%	$CaCO_3$%	χ_{lf} 10^{-8}	χ_{fd}%	χ_{ARM} 10^{-5}	$B_{C(O)R}$	SIRM 10^{-5}	Soft IRM	HIRM	S-ratio	SIRM/χ_{lf}	χ_{ARM}/χ_{lf}	Cr	Co	Ni	Cu	Zn	Pb
Sand %	1																				
Silt%	− 0.11	1																			
Clay%	− 0.25	− 0.94	1																		
OM%	− 0.32	− 0.19	0.3	1																	
$CaCO_3$%	0.46	0.1	− 0.26	− 0.61	1																
χ_{lf} 10−	0.26	0.17	− 0.26	− 0.47	0.22	1															
χ_{fd}%	− 0.1	− 0.2	0.23	− 0.01	0.26	0.03	1														
χ_{ARM} 10^{-5}	− 0.17	− 0.35	0.4	0.21	− 0.31	0.47	0.22	1													
$B_{C(O)R}$	− 0.12	0.11	− 0.07	− 0.01	0.01	− 0.49	− 0.38	− 0.65	1												
SIRM 10^{-5}	0.08	0	− 0.03	− 0.28	0.08	**0.93**	0.12	**0.73**	− 0.57	1											
Soft IRM	0.13	0.05	− 0.1	− 0.37	0.14	**0.96**	0.12	**0.66**	− 0.61	**0.99**	1										
HIRM	0.01	**0.62**	− 0.61	− 0.08	− 0.1	0.45	− 0.28	− 0.07	− 0.06	0.35	0.36	1									
S− ratio	− 0.22	− 0.51	**0.58**	0.36	− 0.27	0	0.43	**0.77**	− 0.71	0.28	0.23	− 0.42	1								
SIRM/χ_{lf}	− 0.35	− 0.5	**0.61**	0.34	− 0.23	− 0.18	0.3	**0.58**	− 0.24	0.19	0.08	− 0.29	**0.72**	1							
χ_{ARM}/χ_{lf}	− 0.32	− 0.57	**0.67**	0.46	− 0.4	− 0.15	0.29	**0.76**	− 0.45	0.19	0.1	− 0.44	**0.91**	**0.87**	1						
Cr	− 0.44	− 0.35	**0.5**	0.32	− 0.62	− 0.37	− 0.14	0.39	− 0.05	− 0.14	− 0.21	− 0.38	**0.54**	**0.53**	**0.69**	1					
Co	− 0.29	− 0.4	**0.49**	0.12	− 0.1	− 0.15	− 0.04	0.21	0.16	0.01	− 0.04	− 0.2	0.14	0.41	0.33	0.17	1				
Ni	− 0.51	− 0.42	**0.59**	0.46	− 0.64	− 0.34	0.08	**0.54**	− 0.21	− 0.05	− 0.14	− 0.32	**0.68**	**0.67**	**0.82**	**0.87**	0.41	1			
Cu	− 0.32	− 0.2	0.31	0.13	− 0.32	− 0.42	− 0.16	0.11	0.02	− 0.22	− 0.27	− 0.18	0.29	**0.55**	0.46	**0.63**	0.46	**0.71**	1		
Zn	− 0.49	− 0.06	0.23	0.21	− 0.29	− 0.4	− 0.09	0.1	0.05	− 0.22	− 0.28	− 0.13	0.24	0.41	0.38	**0.61**	0.39	**0.71**	**0.89**	1	
Pb	− 0.4	− 0.44	**0.57**	0.41	− 0.49	− 0.44	0.11	0.31	− 0.18	− 0.25	− 0.3	− 0.46	**0.63**	**0.49**	**0.7**	**0.79**	0.18	**0.76**	0.46	0.47	1

Bold numbers indicate significant correlation at $p < 0.05$

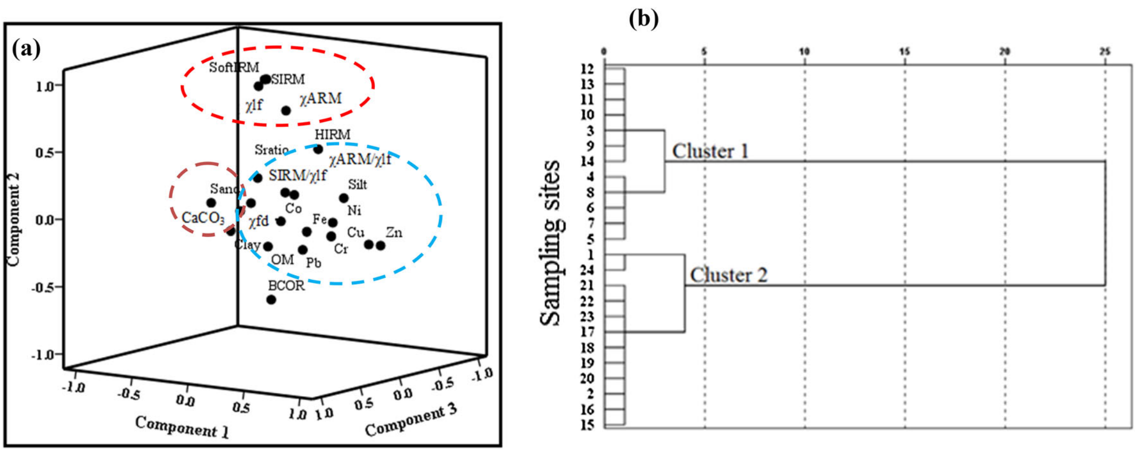

Fig. 8 3D factor plot showing the association between various parameters (**a**) and Hierarchical cluster dendrogram exhibitng the association between sediment sampling stations (**b**) in the study area

Table 5 Factor analysis using the principal component analysis (PCA) method for the mineral magnetic parameters and heavy metal assemblages

Parameters	Factor 1	Factor 2	Factor 3
Sand	− 0.493	0.105	− 0.412
Silt	-0.592	− 0.114	0.630
Clay	0.752	0.073	− 0.469
OM	0.514	− 0.187	0.097
$CaCO_3$	− 0.573	0.074	− 0.498
χlf	− 0.403	0.855	0.163
χfd %	0.123	0.296	− 0.503
χARM	0.494	0.807	0.191
BC(o)R	− 0.173	− 0.752	0.038
SIRM	− 0.098	0.952	0.168
SoftIRM	− 0.192	0.946	0.146
HIRM	− 0.475	0.221	0.686
S-ratio	0.649	0.446	− 0.173
SIRM/χlf	0.781	0.279	− 0.082
χARM/χlf	0.896	0.340	− 0.119
Cr	0.856	− 0.111	0.225
Co	0.449	− 0.055	− 0.038
Ni	0.944	0.012	0.209
Cu	0.661	− 0.253	0.334
Zn	0.617	− 0.278	0.425
Pb	0.824	− 0.119	− 0.048
Eigen values	8.45	4.51	2.32
% of variance	38.44	20.53	10.57
Cumulative %	38.44	58.98	69.56

parameters (Table 4). Positive correlation of SIRM/χ_{lf} and χ_{ARM}/χ_{lf} with the clay percentage and Ni, Pb and Cr indicates the residence of SD fraction within the clays. This suggests diagenetic binding of the heavy metals within clay fraction (Oldfield et al. 1985; Beckwith et al. 1986; Canbay 2010). The χ_{ARM} and χ_{ARM}/χ_{lf}, therefore, are good indicators of the heavy metal concentration at the lake bottom. On the other hand, the silt shows positive correlation with HIRM. This indicates that the silt is derived from the catchment, sensitive to warm-humid conditions. The χ_{lf} shows significant positive correlation with SIRM and Soft-IRM indicating its overall contribution from the ferrimagnetic mineralogy. χ_{ARM} has significant positive correlation with SIRM, Soft-IRM and S-ratio and weakly positive correlation with χ_{lf}. This indicates the bulk nature of χ_{lf} while the χ_{ARM}, SIRM and Soft IRM are controlled by the stable single-domain (SSD) contribution. The χ_{lf}, therefore, is influenced by the overall contributions from the ferrimagnetic material and occasionally by the introduction of antiferromagnets as depicted by the combination of HIRM and silt fractions. This suggests an unique sink mechanism of the lake receiving heavy detritus influx in the form of silt during the monsoon while the heavy metal input throughout the year attempts geochemical bonding with the clay. The clays are deposited in the reducing zones of the lake and the heavy metals prefer to deposit in these zones attached to the clay as marked by their good positive correlations (amongst Cr, Ni, Cu, Pb and χ_{ARM} and clay%). This also indicates the effective scavenge of the heavy metals that occur during the monsoon while rest of the season is functional in the distribution of the heavy metals to the various lake domains, the reducing zones being one of the most favorable as indicated by the χ_{ARM}. However, this needs to be further substantiated with seasonal pH and EC variation over the Anchar Lake.

Factor Analyses

The variance of large set of inter-correlated variables and sampling stations can be explained with factor/cluster analysis. The principal component plot for the various parameters in rotated matrix (Fig. 8a) analysis was followed using varimax normalization and was applied to extract the variables. The relationship between studied parameters considering the first three factors is taken into account. The cumulative percentage of variance is accounted for 69.56% of the total variances. In which, factor 1 contributed 38.44% followed by factor 2 (20.53%) and factor 3 (10.57%) (Table 5). The close affinity of sand and $CaCO_3$ content is probably due to their similar source from the inlet streams that bring in lot of coarser materials rich in calcium from the catchment rocks. Factor 1 shows a close positive affinity of clay, OM, χ_{ARM}, S-ratio, SIRM/χ_{lf}, χ_{ARM}/χ_{lf}, Cr, Co, Ni, Cu, Zn, and Pb. Similarly, Factor 2 indicates a close association of χ_{lf}, χ_{ARM}, SIRM and SoftIRM. Factor 3 reveals a positive correlation of silt content with HIRM. These relations attest the behavior of the magnetic and geochemical parameters as inferred above.

Cluster Analyses

Cluster analyses were applied to find out the homogenous groups with close similarity and mutually correlated stations within the study area (Fig. 8b). The obtained dendrogram indicated two major stable clusters/associations for the studied parameters. Cluster 1 shows a good relationship between sampling locations (14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3), whereas cluster 2 has the following sampling locations (24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 2, 1). The site-wise discrimination of these sediment sampling locations reveals that samples collected from western, central and SW parts of the lake exhibit similar heavy metal and magnetic characteristics compared to the samples collected from the eastern fringe of the lake. Sample number 1 and 24 show close geochemical association as they were collected closer to the lake inlet where the Sindh river joins the lake. The sediment samples collected at different locations of the lake clearly demonstrate some evidence of clustering. The samples taken around the western fringe seem to have deposited from catchment with agricultural, horticultural and open forest areas. Sediment samples collected towards the eastern margins of the lake exhibit another cluster. The mineral magnetic and heavy metal contents in these samples may be added from the urbanization, roads, parks, traffic emissions, which are the prominent land-use classes located along the catchment region. Overall, the results suggest that the lake sediments receive magnetic and heavy metal assemblages from diverse micro-environments along the catchment areas. Further, these results reflect heterogeneity of the record within the lake basin which is attributed to the basin lacustrine conditions.

Conclusions

Magnetic mineral assemblages marked by variation in χ_{ARM}, SIRM and SoftIRM indicate a predominance of soft ferrimagnetic mineralogy with majority of PSD-SD ferrimagnetic grain assemblage in the Anchar lake bottom sediments. The χ_{lf} revealed a high concentration towards the lake inlet sites, while an outlier is observed in NW corner where a low-lying area exists indicating that the lake receives major input from these two areas with dominant detritus control of χ_{lf}. The overall distribution of the mineral magnetic components and heavy metal assemblages show sharp changes in the peripheral part and gradual mixing towards the central parts of the Anchar lake. The integrated environmental magnetism and heavy metal study, therefore, can be used to study paleolimnological changes caused by the changing environmental conditions over the catchment area with considerations of lateral variability at local scales. Positive correlation of SIRM/χ_{lf} and χ_{ARM}/χ_{lf} with clay percentage and heavy metals indicated the residence of SD grains within the clay fractions. The lake receives detritus influx in the form of silt during the monsoon while the heavy metal input is received throughout the year enabling sufficient time for the redistribution and geochemical bonding that demands further detailed investigation. The effective scavenging of the heavy metals occur during monsoon while rest of the season is useful in studying the distribution of heavy metals to various lake domains, the reducing zones being one of the most favorable as indicated by χ_{ARM} and its correlation with other parameters. Further, the relative variation in silt to heavy metal content can be inferred for the monsoonal intensity of the paleo-records of recent past from the lake bottom. These domains identified on the spatial maps demarcate the areas of sink for the heavy metals although a geochemical mechanism needs to be explained by detailed future study. The large lateral heterogeneity of depositional environments further indicate a precautionary prerequisite to be adopted for using the lake sediment cores for high-resolution paleoclimate studies.

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