Assessment of heavy metal pollution from a Fe-smelting plant in urban river sediments using environmental magnetic and geochemical methods

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ARTICLE INFO
Article history:
Received 10 November 2010
Received in revised form 1 April 2011
Accepted 7 April 2011

Keywords:
Environmental magnetism
Heavy metals
River sediments
Industrial plant
Hunan
China

ABSTRACT
Environmental magnetic proxies provide a rapid means of assessing the degree of industrial heavy metal pollution in soils and sediments. To test the efficiency of magnetic methods for detecting contaminants from a Fe-smelting plant in Loudi City, Hunan Province (China) we investigated river sediments from Lianshui River. Both magnetic and non-magnetic (microscopic, chemical and statistical) methods were used to characterize these sediments. Anthropogenic heavy metals coexist with coarse-grained magnetic spherules. It can be demonstrated that the Pollution Load Index of industrial heavy metals (Fe, V, Cr, Mo, Zn, Pb, Cd, Cu) and the logarithm of saturation isothermal remanent magnetization, a proxy for magnetic concentration, are significantly correlated. The distribution heavy metal pollution in the Lianshui River is controlled by surface water transport and deposition. Our findings demonstrate that magnetic methods have a useful and practical application for detecting and mapping pollution in and around modern industrial cities.

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1. Introduction

Heavy metal pollution of aquatic ecosystems is becoming a growing global problem as population increase, and urbanization and industrialization expand. A consequence of the growth of heavy industry has been the addition of high concentrations of heavy metals originating from anthropogenic inputs including industrial wastewater discharges, sewage wastewater, fossil fuel combustion and atmospheric deposition (Birch et al., 1996; Linnik and Zubenko, 2000; Lwanga et al., 2003; Chaparro et al., 2004; Jordanova et al., 2004; Spiteri et al., 2005; Rijal et al., 2010; Sekabira et al., 2010). Trace amounts of heavy metals are always present in water, and some elements may be immobilized within stream sediments and thus could be involved in adsorption, co-precipitation, complex formation, and co-adsorbed with Fe oxides and hydroxides, or other particulate forms (Awofolu et al., 2005; Okafor and Opueke, 2007; Mohiuddin et al., 2010). The development of sensitive tools and procedures for detecting and monitoring water quality and thus avoiding heavy metal poisoning is a pressing task.

Heavy metal concentrations in soil and stream sediments can be used to reveal the intensity and range of local and regional pollution. However, traditional geochemical methods (e.g. AAS, ICP-MS) are relatively complex, time-consuming and expensive, and are therefore not suitable for performing mapping or monitoring of large-scale pollution. In recent decades, environmental magnetic methods have been widely applied as proxy indicators of environmental pollution because they are simple, rapid, and have low-cost and non-destructive characteristics (Hoffmann et al., 1999; Petrovský et al., 2000; Gautam et al., 2004; Zhang et al., 2008). Measurements of magnetic susceptibility of soil, street dust, sediments etc. have been used to map areas polluted by industrial emissions, such as coal-burning power plants, lead ore smelters, and roadside pollution due to automotive traffic and other atmospheric pollution (Thompson and Oldfield, 1986; Morris et al., 1995; Hay et al., 1997; Strzyszcz and Magiera, 1998; Kapicka et al., 1999, 2001; 2008; Petrovský et al., 2001; Zhang et al., 2006; Blaha et al., 2008a, 2008b). The relationship between magnetic parameters and heavy metals has been investigated on the proxy assumption that sources of magnetic particles and heavy metals are genetically related. High correlation coefficients between certain pollutants and magnetic susceptibility or SIRM (saturation isothermal remanence) have sometimes been reported (Heller et al., 1998; Petrovský et al., 2001; Chaparro et al., 2004; Jordanova et al., 2004) whilst different correlations between certain magnetic parameters and heavy metals like Pb, Zn, Cu have been detected at single emission sites and can be used for identifying potential sources and discriminating between them (Banerjee, 2003; Jordanova et al., 2003; Al-Khashman, 2004; Lu and...
Bai, 2006; Wang and Qin, 2006; Maher et al., 2008; Lu et al., 2009a,b; Bijaksana and Huiliselan, 2010; Bucko et al., 2010; Yang et al., 2010). In recent years the use of magnetic parameters as proxies for quantifying the contents of certain contaminants such as heavy metals in street dust, atmospheric particles or soil have been demonstrated (Shu et al., 2001; Kim et al., 2007, 2009; Duan et al., 2010). Clear correlations were found between PLI and magnetic concentration parameters for topsoil, stream, and marine sediments (Chan et al., 2001; Wang and Qin, 2006; Lu et al., 2007, 2009a,b; Yang et al., 2007; Chaparro et al., 2008; Canbay et al., 2010). These studies prove that quantified relationships between magnetic parameters and heavy metals can be constructed based on appropriate indexes. However, few results have been reported for the detection of heavy metal pollution by surface water transport and deposition in river sediments. This has prompted the present evaluation of whether magnetic parameters can be used as a proxy for such scenarios.

In this paper, we compare the results obtained from magnetic parameters and geochemical analyses of heavy metals by integrating results from a spectrum of methods including environmental magnetic, geochemical, electron microscopy and EDX analyses, and incorporating multivariate statistical analysis including of principal component analysis and cluster analysis. The main objectives have been to discriminate between the contributions of different pollution sources and quantifying relationships between magnetic parameters and heavy metal contamination along the Lianshui River near Loudi City in the Hunan Province of China. The study is thus a contribution to the potential use of magnetic measurements and their application for evaluating the scale of industrial pollution caused by surface water transport and deposition in an urban environment.

2. Sampling and laboratory measurements

Loudi is a fast-developing industrial city located near the middle of Hunan Province and covers about 426 km². The major industry operating for fifty years has been a Fe-smelting plant; this main pollution source is located at the north-western side of the city. The landscape of the region comprises low foothills and the Quaternary cover is represented by red loam, with a parent rock of limestone. The east side of the city is a wide plain with altitudes lower than in the West. Lianshui River enters the city from the north-western side, passes by the outside wall of the industrial plant, and then traverses the city center to leave the city at the north-eastern side (Fig. 1a). At the outside of the Fe-smelting plant (sampling sites LDR6–LDR10) there are three wastewater outlets (Fig. 1; OL1 is the wastewater outlet of the Fe-smelting plant. OL2 is the outlet of the power supply unit of the Fe-smelting plant and includes the sintering net ring water system over water as well as effluent from small blast furnace water and boiler workshops; the remaining outlet OL3 comes from the cleaning ground and road wastewaters. The rate of wastewater flow at OL2 is about 400–500 m³/h.

River sediments were collected along the Lianshui River during July 21–23, 2009, using a gravity sampler. Samples were taken from the upstream section (before entering the city) to the downstream region after leaving the city area; the total sampling distance along the river is about 20 km (Fig. 1a,b). At each sample site, two or three cores were collected and the material was sub-sampled at an interval of 2 cm. In total, 19 sample sites were studied comprising 260 river sediment samples (Fig. 1a).

In the laboratory, all samples were freeze-dried with lyophilizer and mechanically homogenized and sieved through a 1 mm mesh to remove small stones. Plastic boxes 2 × 2 × 2 cm in size were filled with individual samples for magnetic measurements. All sample susceptibility values were measured using a Bartington MS2 susceptibility meter with 470 Hz operating frequency, and mass-specific susceptibility (χ) values were calculated. Anhysteretic remanet magnetizations (ARMs) were imparted in a peak alternating field (AF) of 80 mT with a superimposed direct current (DC) bias field of 0.05 mT parallel to the AF. Isothermal remanent magnetization (IRM) experiments were performed using an impulse magnetizer and the IRM acquired in a field of 1.0 T was regarded as saturation IRM (SIRM). Remanences were measured with a 2G–760 U-channel system. Temperature-dependence of the low-field magnetic susceptibility curves of some samples were conducted using a KLY-3 Kappabridge equipped with a CS-3 high-temperature furnace (sensitivity of 1 × 10⁻⁸ SI, AGICO Ltd., Brno, Czech Republic) in air atmosphere. All measurements were performed from room temperature up to 700 °C with a measurement interval of 2 °C and a heating and cooling rate of about 9 °C per minute.

In addition, hysteresis loops of sediments from four sampling sites (LDR3, LDR11, LDR14 and LDR18) were measured at room temperature using a Model 3900 Micromag vibrating magnetometer. The saturation magnetization at 1 T (M_s), saturation remanence (M_r), which is equal to SIRM, and the coercivity (B_c) were obtained following subtraction of the paramagnetic contribution. Remanence coercivity (B_r) was obtained by back-field demagnetization curve. Low-temperature properties of representative samples were measured using a Quantum Design Model XP-5 Magnetic Properties Measurement System (MPMS XP-5, sensitivity 5.0 × 10⁻¹⁰ Am⁻²). Samples were cooled down from 300 to 5 K in a zero magnetic field (ZFC), and saturation remanance acquired in a 5-T field at 5 K (designated SIRM5 T95 K hereafter) was was measured by warming from 5 to 300 K. To determine the SP contents in these samples, temperature dependence of susceptibility was measured from 300 K to 5 K at frequencies of 1 Hz and 1000 Hz. Frequency dependent χ(T) was calculated from χ(1 Hz) − χ(1000 Hz). All magnetic measurements were carried out in the Paleomagnetism and Geochronology Laboratory in Beijing.

Magnetic extracts were obtained from the middle stream river sediment (LDR1, depth of 8–12 cm) using a strong hand magnet sealed with a plastic bag. Afterward, the magnetic extracts were fixed by gum, and their surfaces were coated with gold for scanning electron microscope (SEM). A LE01450VP was used for SEM observations of the morphology of the particles, and an INCA ENERGY 300 energy dispersive X-ray spectrometer (EDX) was applied to determine elements and composition of the magnetic extracts. The SEM and EDX studies were carried out in the laboratories of the Institute of Geology and Geophysics Beijing.

Heavy metal (Be, V, Cr, Co, Ni, Cu, Zn, Rh, Mo, Cd, Cs, Ba, Nd, Pb and Fe) analysis of river sediments from four sampling sites (LDR3, LDR11, LDR14, LDR18) was performed by inductively-coupled plasma-mass spectrometry (ICP-MS) using the DZ/T0223–2001 method with HR-ICP-MS (Element I) Finningan MAT equipment in the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. Pearson’s correlation coefficient analysis, Principal Component Analysis (PCA) and Cluster Analysis (CA) were performed using the commercial statistics software package SPSS version 13.0 (SPSS Inc.).

3. Results

3.1. Magnetic properties

The mean χ values of surface river silts (0–2 cm) from the 19 sampling sites show low values in the upstream region (typically less than c. 70 × 10⁻⁸ m³ kg⁻¹); strongly enhanced intensities (c. 200–660 × 10⁻⁸ m³ kg⁻¹) in the middle part near the surroundings of the Fe-smelting plant and lower values again
further downstream (c. $150 \times 10^{-8}$ m$^3$ kg$^{-1}$) (Fig. 1b). Lateral and vertical changes of $\chi$ values along Lianshui River are more clearly displayed in Fig. 1c which plots the data as a function of distance and depth. Maximum $\chi$ values are located below 10 cm depth in the middle section.

Vertical profiles of $\chi$, SIRM, $M_s$, and $\chi_{ARM}/\chi$ at four sample sites (LDR3, LDR11, LDR14, LDR18) are selected to identify the differences among upstream, middle and downstream sections (Fig. 2). The sediment profile from LDR11 (middle stream section, polluted river sediments) exhibits the largest enhancement of $\chi$ as its values are four to sixteen times higher than those ($<70 \times 10^{-8}$ m$^3$ kg$^{-1}$) from LDR3 (upstream section, unpolluted river sediments), especially, in the depth of 10–20 cm. Sediment profiles from LDR14 and LDR18 show $\chi$ values higher than those from LDR3 and lower than those from LDR11. In the downstream section LDR18, lower $\chi$ values ($100–300 \times 10^{-8}$ m$^3$ kg$^{-1}$) appear again, however, higher than LDR3. This indicates that these sediments accumulated a high input of anthropogenic material particularly from the Fe-smelting plant and the city. Most maximum values are found below 15–20 cm depth. The variation trends of SIRM and $M_s$ are similar to $\chi$ (Fig. 2a,b,c), and high positive Pearson correlation coefficients ($P > 0.95$) are found between each other, indicating that ferrimagnetic minerals are controlling $\chi$ in these samples (Oldfield, 1991). $\chi_{ARM}/\chi$ values in profile of LDR3 are a little higher than in other profiles suggesting a higher portion of smaller single domain (SD) to small pseudo-single domain (PSD) particles in LDR3 (Oldfield, 1991).

Narrow hysteresis loops that close below $\sim 250$ mT (Fig. 3a) indicate that low coercivity ferrimagnetic minerals are dominant in these river sediments. A Day-plot of hysteresis parameters of all samples from sites LDR3, LDR11, LDR14 and LDR18 shows that all samples locate within the PSD range (Day et al., 1977; Dunlop, 2002) (Fig. 3b). In the Day diagram, it seems that LDR3 (upstream) values plot more to the left than others indicating a more consistent grain size in the less polluted LDR3. The distribution of middle stream samples (LDR11 and LDR14) is closer to the
multidomain (MD) range than in the upstream (LDR3) and downstream (LDR18) samples, suggesting that magnetic particles in the middle-stream sediments have relatively coarse-grained PSD sizes. IRM acquisition and back-field demagnetization curves for the above representative samples are shown in Fig. 3c. IRM acquisition curves rapidly reach saturation below 250 mT and are independent of sampling site whilst back-field demagnetization curves display soft behavior with $B_{cr}$ values of 30–40 mT. All room temperature magnetic measurements indicate that magnetic mineralogy is dominated by low coercivity ferrimagnetic minerals.

Magnetic minerals in river sediments can be identified by temperature-dependent susceptibility ($\chi$-$T$) cycles in air (Fig. 4). The increased susceptibility below 250 °C and the peaks around 250–300 °C may indicate ultrafine particles reaching the SD to superparamagnetic (SP) transition at these temperatures (Oches and Banerjee, 1996; Deng et al., 2004; Liu et al., 2005); the susceptibility increases sharply to just below the Curie temperature of magnetite (585 °C), and shows a $T_c$ of ~580 °C revealing magnetite as the major contributor to $\chi$, in cooling curves $\chi$ is higher than in heating curves for temperatures < 580 °C, which demonstrates new formation of magnetite during heating (Zhang et al., 2010). Magnetic enhancement upon heating of LDR3 is obviously higher than others (Fig. 4).

Further proof of the presence of magnetite in surface and deep samples is the clear Verwey transition at ~120 K (Fig. 5a,d,g,j). The behavior of frequency-dependence of $\chi''$ between 5 and 300 K (Fig. 5b,c,e,f,h,i,k,l) shows that in-phase $\chi'$ is different for both frequencies above 120 K. This indicates that SP magnetite particles are present in these river sediments (Kosterov, 2003). An obvious $\chi''$ peak between 5 and 80 K (Fig. 5e,f,h,i,l) could be caused by relaxation of domain walls associated with MD magnetite particles (Moskowitz et al., 1993, 1998; Kosterov, 2003; Balanda et al., 2005).

**Fig. 2.** The vertical profiles of (a) $\chi$, (b) SIRM, (c) $M_s$ and (d) $\chi_{ARM}/\chi$ for all samples from LDR3, LDR11, LDR14 and LDR18, different symbols refer to different sampling sites.
and supporting the dominance of MD magnetite particles in the middle (LDR11, LDR14) and downstream (LDR18) sections. The sharp decrease in remanence and $\chi$ during warming from 5 to 50 K (Fig. 5a–c,j,k) may relate to the main presence of SP particles and paramagnetic minerals in the upstream (LDR3) and at the surface of the downstream (LDR18) sediments (Coey, 1988; Dunlop and Özdemir, 1997).

Magnetic results (Figs. 3–5) show that PSD–MD magnetite is the dominant ferrimagnetic phase in the middle stream and downstream sediments, especially at depths >20 cm, whereas, PSD with SP magnetite is predominant in the upstream sediments; this differences of magnetic mineral phases between different sections of Liangshui River shows that enhancements of magnetic concentration values are controlled by coarse magnetic particles in the sediments. One can conclude that anthropogenic magnetite adds a different grain size fraction to the natural magnetite content which leads to a shift of data points toward “right-down” from the range occurring for uniform grain sizes in Day-plot (Fig. 3b).

Fig. 3. (a) Magnetic hysteresis loops for representative river sediments following before (dash line) and after (solid line) subtraction of the paramagnetic contribution; (b) Day-plot of the ratios $M_s/M_0$ and $B_c/B_a$ for all samples in LDR3, LDR11, LDR14 and LDR18, grain size boundaries for SD—PSD—MD are according to Dunlop (2002); (c) IRM acquisition and back-field demagnetization curves of respective samples.

Fig. 4. Temperature-dependence of magnetic susceptibility ($\chi$–$T$) heating (solid line) and cooling (dashed line) curves of representative samples in LDR3, LDR11, LDR14 and LDR18 sampling sites. Each curve was normalized with its corresponding magnetic susceptibility at room temperature $\chi_0$. 
3.2. SEM and EDX

Samples from 8 to 12 cm depths at LDR11 (representing the range of highest anthropogenic input according to maximum $c$) have been observed and analyzed by SEM and EDX. Results are shown in Fig. 6; magnetic spherules with diameters of 9–140 μm (Fig. 6a–c) and irregular-shaped particles (Fig. 6d) are observed and identified as iron-oxides by EDX analysis. The EDX of spherules surfaces show dominant peaks of Fe, along with smaller peaks of Si or Al (Fig. 6a–c, spectrum 1), whereas the EDX of broken sides on spherules show that Si and Al are predominant with small amounts of Fe, Mg, K and Ca etc (Fig. 6b–c, spectrum 2). The irregular-shaped...

Fig. 5. Low-temperature magnetic measurements for representative samples in LDR3, LDR11, LDR14 and LDR18, respectively: (a, d, g and j) accompanying thermal warming of SIRM$_{5\text{T}5\text{K}}$ from 5 to 300 K and after cooling in zero field (ZFC) for surface (heavy solid line) and deep (dashed line) sediments, respectively; (b, c, e, f, h, i, k and l) Low-temperature-dependence of magnetic susceptibility at 1 Hz (light hollow line) and 1000 Hz (heavy solid line) curves ($\chi' - T$) and low-temperature $\chi_{a\text{ld}} - T$ curves (dashed line), respectively.
particles (Fig. 6a, d, spectrum 2) have variable Fe contents (13–70%) with different contents of Si, Al, Mg, Ca, Mn, K etc, and small amounts of Zn are also present in some particles (Fig. 6d). SEM and EDX results from the magnetic spherules are consistent with previous studies of fly ashes and smelting slag (Hoffmann et al., 1999; Xie et al., 2001; Goddu et al., 2004; Jordanova et al., 2004; Gautam et al., 2005; Zhang et al., 2006; Blaha et al., 2008b; Kim et al., 2009; Chaparro et al., 2010; Huliselan et al., 2010; Rosowiecka and Nawrocki, 2010).

3.3. Heavy metals concentrations

Concentrations of 15 heavy metals and their mean, standard deviation, minimum and maximum values in different sections of the Lianshui River are given in Table 1. The middle stream section LDR11 contains the highest mean concentrations: Fe (74.19 g/kg), Pb (831 mg/kg), Zn (2528 mg/kg), Cu (84 mg/kg), Cd (13 mg/kg), V (178 mg/kg), Mo (3 mg/kg) and Cr (122 mg/kg). The lowest mean concentrations of Fe (40 g/kg), Pb (58 mg/kg),...
Zn (284 mg/kg), Cu (50 mg/kg), V (115 mg/kg), and Cr (73 mg/kg) are found at ~6 cm and ~12 cm in the sediment profile LDR11; when depths >20 cm are considered, concentrations of Pb and Zn are more stable in LDR11 although they are still higher than those in LDR3 (Fig. 8a–c). From the top to 22 cm, concentrations of Cu in LDR11, LDR14 and LDR18 are similar to each other and are all higher than in LDR3, increasing gradually with depth (Fig. 8d). In contrast, concentrations of Ba and Nd in different sampling sites appear to be more stable and are essentially independent of the depth (Fig. 8e).

The pollution load index (PLI) proposed by Tomlinson et al. (1980) has been used obtained from concentration factors $CF = C_{metal}/C_{background}$ value for selected metals. The PLI is then calculated by the n-root from the product of the n CFs of the metals included: $PLI = n/(CF_1 \times CF_2 \times CF_3 \times \ldots CF_n)$ (Angulo, 1996); the lowest concentration value for each element was used as background value $C_{background}$ value. According to Singh et al. (2003) PLI values vary from 0 (unpolluted) to 10 (highly polluted) as follows: $PLI = 0$ background concentration; $0 < PLI \leq 1$ unpolulated; $1 < PLI \leq 2$ moderately to unpolulated; $2 < PLI \leq 3$ moderately polluted; $3 < PLI \leq 4$ moderately to highly polluted; $4 < PLI \leq 5$ highly polluted; $PLI > 5$ very highly polluted. As shown in Table 1, including all 15 heavy metals, the highest mean value is 3.46 in LDR11, followed by LDR14 (3.14), LDR18 (2.84) and LDR3 (2.22). A more detailed discussion of the PLI index is given in section 4.

### 3.4. Correlations of heavy metal concentrations and magnetic parameters

Pearson’s correlation coefficients ($P$) between heavy metal concentrations and magnetic parameters are listed in Table 2. $M_r$ and $x_{ARM}$ have significant positive correlations with V, Cr, Cu, Zn, Mo, Cd, Pb, Fe and PLI (of all 15 metals). They show significant negative correlation with Co, Ni, Pb and Nd. However, no significant correlations between magnetic parameters and Be as well as Cs are found; γ and SIRM correlate negatively with Ba (Table 2). Since the $P$ between SIRM and heavy metals are highest among all the magnetic parameters, we select SIRM to quantify the relationship between magnetic parameters and heavy metals. The scatter plots of SIRM versus Fe, Pb, Zn, Cu, Ba and Nd are given in Fig. 9 including the coefficient of determination $R^2$ values. All heavy metals except Ba ($R^2 = 0.10$) and Nd ($R^2 = 0.09$) show a good correlation with SIRM i.e., Fe ($R^2 = 0.90$), Pb ($R^2 = 0.88$), Zn ($R^2 = 0.86$), Cu

<table>
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<th>Heavy metals</th>
<th>LDR3 (upstream)</th>
<th>LDR11 (middle stream)</th>
<th>LDR14 (middle stream)</th>
<th>LDR18 (downstream)</th>
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<td>Fe (g/kg)</td>
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<td>74.19–17.97</td>
<td>61.42–4.39</td>
<td>50.96–4.15</td>
<td>56.58–14.76</td>
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<td>Zn (mg/kg)</td>
<td>Range 46–73</td>
<td>360–1735</td>
<td>246–821</td>
<td>95–294</td>
<td>46–1736</td>
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<td>Co (mg/kg)</td>
<td>Range 58 ± 8</td>
<td>831 ± 450</td>
<td>546 ± 183</td>
<td>194 ± 59</td>
<td>412 ± 413</td>
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<tr>
<td>Cu (mg/kg)</td>
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<td>958–5349</td>
<td>742–2182</td>
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<td>Ni (mg/kg)</td>
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<td>2528 ± 1461</td>
<td>1613 ± 468</td>
<td>704 ± 147</td>
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<td>Mo (mg/kg)</td>
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<td>Cr (mg/kg)</td>
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### Table 1
Summary of heavy metals in river sediments from four different sections.

The CFs of the heavy metals included in this study are given in Table 3.
$R^2 = 0.71$. The differences in the correlations between magnetic parameters and heavy metals are likely dependent on their sources.

Principal component analysis (PCA) was applied to identify the source of heavy metals in the river sediments by applying Varimax rotation with Kaiser normalization (Wu, 2004). The results show that there are four factors that explain 85.6% of the total variance in the river sediments (Table 3). As shown in Table 3, the first factor explains 34.9% of the total variance and is dominated by $M_s$, $\chi$, SIRM, $\chi_{ARM}$, V, Cr, Mo and Fe; Factor 2 accounts for 26.4% of the total variance and loads in Cu, Zn, Cd and Pb; Factor 3 is dominated by Be, Rb, Cs and Nd, and accounts for 14.8% of the total variance; Factor 4 is dominated by Co, Ni and Ba and accounts for 9.5% of the total variance. The relationships between the heavy metals and the magnetic parameters based on the first three principle components of the sediments are illustrated in Fig. 10a in 3D space.

Cluster analysis (CA) was performed to evaluate further the similarities of the heavy metal sources by applying Ward’s method (Wu, 2004). The CA results for magnetic parameters and heavy metals are shown in Fig. 10b as a dendrogram. Fig. 10b displays four clusters: (I) $\chi$, SIRM, $M_s$, Fe, $\chi_{ARM}$, V, Cr, Mo; (II) Zn, Pb, Cd; (III) Cu; (IV) Be, Cs, Rb, Nd, Co, Ni, Ba. As shown in this figure the clusters I, II and III join together at a relatively high level, likely implying anthropogenic activities, however, they differ from cluster IV. The CA results are in agreement with the PCA results listed in Table 3 and illustrated in Fig. 10a.

4. Discussion

4.1. Sources of magnetic minerals and heavy metals

Magnetic, SEM and EDX results (Figs. 3–6) reveal that PSD–MD magnetite often occurring as spherules is the dominant ferrimagnetic phase with small amounts of SP magnetic particles in the middle stream and downstream sediments (at depth < 20 cm); large particles input obviously accounts for the high $\chi$ values in these sections. In contrast, PSD and SP magnetite particles are present in the upstream sediments corresponding to lower $\chi$ values. The SP magnetite particles are likely to come from the contribution of pedogenic processes in this subtropical region (Lu, 2000).

The heavy metals can be separated into two groups based on the multivariate statistical analysis results (Tables 2 and 3, Fig. 10). Group I (including Be, Cs, Rb, Nd, Co, Ni, Ba) reveals neither correlation with magnetic parameters nor any obvious differences between upstream, middle stream and downstream sections (Table 2, Figs. 7–10). Noting that the main source of Rb, Cs, Ba, Nd and Be etc is from soil (Pan and Yang, 1988; Wang and Wei, 1995), we infer that the contents of these heavy metals come from pedogenic sources in the catchment region upstream of Loudi city. Group II includes Fe, V, Cr, Mo, Zn, Pb, Cd and Cu which show significant correlations with magnetic concentration parameters $M_s$, $\chi$, SIRM and $\chi_{ARM}$ suggesting that magnetic
particle contents and these heavy metals stem from anthropogenic activities. Zn, Cd and Cu are common in iron ores (Wong and Au, 1984) and Mo, V and Cr are typically used as additives in the Fe-smelting industry (Farmaki and Thomaidis, 2008); Pb and Zn are used in steel wire heat-treatment (Kientzl and Dobránszky, 2007). Each of these heavy metals could enter into the environment with the emission of slag, dust and wastewater by the Fe-smelting activities in Loudi. The magnetic properties (Figs. 3–5) and SEM and EDX (Fig. 6) results reveal that most of magnetic spherules with larger dimension (9–140 μm) at depths of 8–12 cm stem from fly ash of the coal-fired Fe-smelting plant. Maximum values of heavy metals in Group II at depths of 8–14 cm (Fig. 8), suggest that most of the spherical particles and the heavy metals Fe, V, Cr, Mo, Pb, Zn, Cd and Cu are concomitant and may originate from Fe-smelting plant.

4.2. Environmental implications of magnetic parameters in river sediments

As mentioned above Group II heavy metals (Fe, V, Cr, Mo, Zn, Pb, Cd, Cu) show a good positive correlation with $M_s$, $\chi$, SIRM and $\chi_{ARM}$ and suggest that these magnetic concentration parameters are efficient indicators of the anthropogenic heavy metals input into the river sediments. Among all the magnetic concentration parameters, correlation coefficients between SIRM and heavy metals are highest (Table 2), moreover SIRM values exclude the contribution of pedogenic SP particles. Hence SIRM is considered as the optimum proxy parameter for the detection of heavy metal pollution in the river sediments of Loudi.

To evaluate accurately the contamination degree of anthropogenic activities-related heavy metals, the Tomlinson PLI including Fe, V, Cr, Mo, Zn, Pb, Cd and Cu was calculated for all samples and termed as PLI$_{anthro}$. We note that the correlation coefficient between the PLI$_{anthro}$ and magnetic parameters ($P = 0.869$ for $M_s$, $P = 0.900$ for $\chi$, $P = 0.912$ for SIRM and $P = 0.679$ for $\chi_{ARM}$) is higher than for the PLI of all heavy metals. Scatter plots of log(SIRM) versus

![Fig. 8. Vertical profiles of (a) Fe, (b) Pb, (c) Zn, (d) Cu, (e) Ba and (f) Nb for all samples from LDR3, LDR11, LDR14 and LDR18. The different symbols refer to different sampling sites.](image)

<table>
<thead>
<tr>
<th>Pearson Correlation (P)</th>
<th>$M_s$</th>
<th>$\chi$</th>
<th>SIRM</th>
<th>$\chi_{ARM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.155</td>
<td>0.186</td>
<td>0.184</td>
<td>0.174</td>
</tr>
<tr>
<td>V</td>
<td>0.697$^a$</td>
<td>0.679$^a$</td>
<td>0.669$^a$</td>
<td>0.706$^a$</td>
</tr>
<tr>
<td>Cr</td>
<td>0.800$^a$</td>
<td>0.785$^a$</td>
<td>0.789$^a$</td>
<td>0.721$^a$</td>
</tr>
<tr>
<td>Co</td>
<td>-0.728$^a$</td>
<td>-0.763$^a$</td>
<td>-0.767$^a$</td>
<td>-0.564$^a$</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.559$^a$</td>
<td>-0.601$^a$</td>
<td>-0.604$^a$</td>
<td>-0.460$^a$</td>
</tr>
<tr>
<td>Cu</td>
<td>0.652$^a$</td>
<td>0.716$^a$</td>
<td>0.739$^a$</td>
<td>0.557$^a$</td>
</tr>
<tr>
<td>Zn</td>
<td>0.684$^a$</td>
<td>0.708$^a$</td>
<td>0.721$^a$</td>
<td>0.428$^a$</td>
</tr>
<tr>
<td>Rb</td>
<td>-0.568$^a$</td>
<td>-0.588$^a$</td>
<td>-0.570$^a$</td>
<td>-0.470$^a$</td>
</tr>
<tr>
<td>Mo</td>
<td>0.799$^a$</td>
<td>0.776$^a$</td>
<td>0.783$^a$</td>
<td>0.681$^a$</td>
</tr>
<tr>
<td>Cd</td>
<td>0.522$^a$</td>
<td>0.532$^a$</td>
<td>0.543$^a$</td>
<td>0.417$^a$</td>
</tr>
<tr>
<td>Cs</td>
<td>0.144</td>
<td>0.203</td>
<td>0.235</td>
<td>0.063</td>
</tr>
<tr>
<td>Ba</td>
<td>-0.243</td>
<td>-0.262$^b$</td>
<td>-0.254$^b$</td>
<td>-0.110</td>
</tr>
<tr>
<td>Nd</td>
<td>-0.407$^a$</td>
<td>-0.419$^a$</td>
<td>-0.412$^a$</td>
<td>-0.297$^a$</td>
</tr>
<tr>
<td>Pb</td>
<td>0.721$^a$</td>
<td>0.755$^a$</td>
<td>0.770$^a$</td>
<td>0.483$^a$</td>
</tr>
<tr>
<td>Fe</td>
<td>0.924$^a$</td>
<td>0.933$^a$</td>
<td>0.934$^a$</td>
<td>0.748$^a$</td>
</tr>
<tr>
<td>PLI</td>
<td>0.741$^a$</td>
<td>0.782$^a$</td>
<td>0.795$^a$</td>
<td>0.615$^a$</td>
</tr>
</tbody>
</table>

$^a$ Correlation is significant at the 0.01 level (2-tailed).

$^b$ Correlation is significant at the 0.05 level (2-tailed).

Table 2: Pearson’s correlations matrix for the heavy metals concentrations and magnetic parameters ($n = 64$).
**Fig. 9.** Relationship between SIRM and (a) Fe, (b) Pb, (c) Zn, (d) Cu, (e) Ba and (f) Nb for all samples in LDR3, LDR11, LDR14 and LDR18. Equations and coefficient of determination ($R^2$) between SIRM and heavy metals contents are listed on the figures.

$PLI$ and $PLI_{anthro}$ are shown in Fig. 11: the coefficient of determination ($R^2 = 0.83$) with $PLI_{anthro}$ is higher than with $PLI$ ($R^2 = 0.77$) based on a linear equation (Fig. 11); standard errors of linear regression are ±0.09 and ±0.68, respectively. It reinforces the finding that the magnetic concentration parameter log(SIRM) is reasonably proportional to the concentration of the sum of Group II heavy metals.

The degree of heavy metal pollution is clearly outlined as an isoline plot of the $PLI_{anthro}$ values showing the data as a function of distance and depth (Fig. 12). $PLI_{anthro}$ values are in the range of 0–2 before the river reaches the city identifying the upstream section as un polluted to moderately polluted. The $PLI_{anthro}$ values increase gradually from 2 to 5 after entering into the city indicating that the river is moderately to highly polluted by anthropogenic activity here. The $PLI_{anthro}$ reach values vary from 5 to 6 near and beyond the Fe-smelting plant and increase to almost 8 at a distance of ~2.5 km (LDR11) downstream from the plant. It then again decreases gradually to ~5 near to the city boundary (LDR15); this shows that the river is highly polluted in this city region. $PLI_{anthro}$ values of ~5–2.5 are sustained within a distance of ~7 km after the river leaves the city indicating that this downstream section of the river remains moderately to highly polluted.

It is also interesting to note that the highest $PLI_{anthro}$ values are not found directly at the Fe-smelting plant (sites LDR7–LDR9), but are present in the bend of the river (LDR11) within a distance of ~2.5 km to the plant; at the same time, the highest value appears at a depth of ~10–20 cm and not at the surface (Fig. 12). This is likely to result from the change of the hydraulic flow conditions along this section of the channel: pollutants will be retained in suspension where the width of the river is ~80 m and the course is relatively straight as it is at the plant. After site LDR10 where the river makes a strong bend and the width is expanding to ~150 m (LDR11), the flow velocity decreases and the solid particles precipitate from the suspension and deposit by helical water flow. Due to rapid flow and three wastewater outlets only little sediment is present directly at the plant (with the exception of gravels in the vicinity of LDR7–LDR9). In contrast sediment accumulation is high after the strong river bend and long sediment cores (such as LDR11) can be recovered here. High flow velocity leads to strong fluvial abrasion at the boundary between the water and the riverbed which can remove and transport coarser materials like the large anthropogenic 9–140 μm spherules. This coarser...
Fig. 10. (a) PCA results of LDR3, LDR11, LDR14 and LDR18 samples in the three-dimensional space: plots of loading of the first three principal components (different symbols mean different cluster-groups); (b) Dendrogram results of all samples from Ward method of hierarchical cluster analysis for 15 elements and 4 magnetic parameters.

Fig. 11. The relationship between (a) SIRM and PLI, (b) SIRM and PLIanthro for all samples in LDR3, LDR11, LDR14 and LDR18. Equations and coefficient of determination ($R^2$) between log(SIRM) and PLI, PLIanthro are listed on the Figure. PLIanthro refers to the Tomlinson PLI of Fe, V, Cr, Mo, Zn, Pb, Cd and Cu in river sediments originating from anthropogenic activities.

Fig. 12. Isoline plot of PLIanthro values as a function of distance and depth. PLIanthro = 0: background concentration; 0 < PLIanthro ≤ 1: unpolluted; 1 < PLIanthro ≤ 2: moderately to unpolluted; 2 < PLIanthro ≤ 3: moderately polluted; 3 < PLIanthro ≤ 4: moderately to highly polluted; 4 < PLIanthro ≤ 5: highly polluted; PLIanthro > 5: very highly polluted (Singh et al., 2003).
fraction then precipitates after the river bend where the flow velocity becomes lower, whilst the fine particles are transported further downstream.

5. Conclusions

We have shown that the coexistence of magnetic particles and heavy metals with significant correlations between them, make it possible to use magnetic methods as a tool for assessment of heavy metal pollution in industrial regions by surface water runoff. Specifically we find that the enrichment of coarse PSD—MD magnetic particles is the main reason for enhancement of magnetic concentration parameters \((M_s, \gamma, SIRM, \chi_{ARM})\) in the river section downstream of a Fe-smelting plant. Anthropogenic spherical particles from suspension. Most of earlier works on magnetic by surface water transport and deposition by precipitation of solid at Loudi, it can be concluded that log(SIRM) mapping is best suit-

SIRM) can be established. Therefore, for the studied river sediments further downstream.

of elevated \(\gamma\) and SIRM values with heavy metal (Fe, V, Cr, Mo, Zn, Pb, Cd, Cu) concentrations from industrial activities (mainly the Fe-smelting plant) prove that magnetic concentration parameters can be used as proxies for the anthropogenic contribution of pollutants to the river sediments. In contrast, very weak correlations with Be, Cs, Rh, Nd, Co, Ni and Ba, indicate that these metals stem from soil in the catchment region. The Tomlinson pollution load index (PLI) shows significant correlations with magnetic concentration parameters; most notably PLIanthro (including Fe, V, Cr, Mo, Zn, Pb, Cd, Cu) shows a strong positive correlation with SIRM values and a linear relationship with log(SIRM) can be established. Therefore, for the studied river sediments at Loudi, it can be concluded that log(SIRM) mapping is best suitable for quantitative assessment of heavy metal pollution. The degree and range of Lianshui River sediment pollution is controlled by surface water transport and deposition by precipitation of solid particles from suspension. Most of earlier works on magnetic proxies have considered pollution of soil and sediments by atmospheric input of fly ash. Our results demonstrate that also for transport by surface water the use of environmental magnetic methods in conjunction with auxiliary geochemical analysis can provide a fast and non-destructive tool for assessment of heavy metals pollution.

Acknowledgments

Qingsong Liu and two reviewers (Erwin Appel and Eduard Petrovsky) are gratefully acknowledged for their constructive suggestions. This work was financially supported by the National Science Foundation of China (Grants 40804014, 20677059, 40525013 and 40821091).

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