Magnetic properties as indicators of heavy metals pollution in urban topsoils: a case study from the city of Luoyang, China

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SUMMARY
This paper deals with the magnetic properties [magnetic susceptibility, saturation isothermal remanent magnetization (SIRM), magnetomineralogical parameters], the contents of heavy metals (Fe, Mn, Cd, Cr, Cu, Pb and Zn) and their mutual relationship in the urban topsoils of Luoyang, China. Magnetic susceptibility measured on 215 urban topsoil samples ranged from $31 \times 10^{-8}$ to $1128 \times 10^{-8}$ m$^3$ kg$^{-1}$ (average $215 \times 10^{-8}$ m$^3$ kg$^{-1}$) and showed that high magnetic susceptibility values were obtained on topsoil samples from industrial areas (average $313 \times 10^{-8}$ m$^3$ kg$^{-1}$) and roadside ($236 \times 10^{-8}$ m$^3$ kg$^{-1}$), whereas lower susceptibility values were observed in parks and green areas ($123 \times 10^{-8}$ m$^3$ kg$^{-1}$). The urban topsoils were enriched with Cd, Cr, Cu, Pb and Zn, with average contents of $1.71, 30.51, 85.40, 65.92$ and $215.75$ mg kg$^{-1}$, respectively. The heavy metals Cr, Cu, Pb and Zn show a statistically significant correlation with magnetic susceptibility and SIRM. The Tomlinson Pollution Load Index (PLI) also shows significant correlation with magnetic susceptibility and SIRM, indicating that the magnetic parameters can provide a proxy method for identifying the heavy metal pollution in urban topsoils. Rock magnetism and X-ray diffraction analyses revealed that the dominant magnetic mineral in the urban topsoils is anthropogenic pseudo-single domain (PSD)-multidomain (MD) magnetite. These magnetic particles are associated with the industrial activities, traffic exhaust and deposition of atmospheric particulate.

Key words: environmental magnetism, heavy metals, magnetite, urban soils.

1 INTRODUCTION
During recent years, magnetic measurements (in particular magnetic susceptibility) have become a generally accepted method to map spatial distribution of pollution, identify polluted sources, provide a alternative to conventional chemical analysis, because its measurements are fast, cost-effective, non-destructive, sensitive and informative. Magnetic susceptibility was shown to be highly useful in investigating industrial pollutants, traffic emission and other atmospheric pollutants (Morris et al. 1995; Hay et al. 1997; Bityukova et al. 1999; Durza 1999; Hoffmann et al. 1999; Kapicka et al. 1999; Matzka & Maher 1999; Shu et al. 2000; Lecoanet et al. 2001; Hanesch et al. 2003; Goddu et al. 2004). Magnetic susceptibility mapping of soils and sediments is becoming one of the most important tools for estimating anthropogenic pollution (Hanesch & Scholger 2002; Hanesch et al. 2003; Boyko et al. 2004; Pozza et al. 2004). It has been used successfully in numerous cases in soils (Heller et al. 1998; Strzyszcz & Magiera 1998; Bityukova et al. 1999; Jordanova et al. 2003; Spiteri et al. 2005; Lu & Bai 2006), leaves (Flanders 1994; Hanesch et al. 2003), road dust (Xie et al. 1999; Hoffmann et al. 1999; Shilton & Austin 2005), airborne particles (Hunt et al. 1984; Oldfield et al. 1985), sediments from sea (Chan et al. 1997, 2001), rivers (Scholger 1998; Chaparro et al. 2004; Desenfant et al. 2004; Jordanova et al. 2004; Pozza et al. 2004) and lakes (Hu et al. 2003). For example, magnetic susceptibility measurements have been used to map the spatial distribution of pollution and degree of anthropogenic pollution around power plants, cement and metallurgical industries (Durza 1999; Kapicka et al. 1999; Petrovsky et al. 2000; Lecoanet et al. 2001). In some European and southern Asian cities, magnetic parameters can be used as a proxy for heavy metals pollution in urban topsoils and sediments (Charlesworth & Lees 1997; Scholger 1998; Hanesch et al. 2003; Goddu et al. 2004; Gautam et al. 2005; Spiteri et al. 2005). Magnetic susceptibility-based bio-monitoring technique has used as proxy of atmospheric pollution in Norwich (UK) (Matzka & Maher 1999), Leoben (Austrian) (Hanesch et al. 2003) and Kathmandu (Nepal) (Gautam et al. 2005). Magnetic measurements have also proved useful to assess transport of pollutants by air or water (Scholger 1998; Petrovsky et al. 2000). Hanesch & Scholger (2002) demonstrated that two powerful applications of susceptibility measurement of soils are the identification of polluted areas and the detailed mapping of these areas to reveal the extent of pollution.

The use of magnetic measurements as proxy of heavy metal pollution is based on the fact that origins of heavy metals and magnetic particles are genetically related. Environmental magnetism studies have demonstrated the relationship between heavy metal contents...
and magnetic properties in soils (Hanesch et al. 2001; Jordanova et al. 2004; Schmidt et al. 2005; Spiteri et al. 2005), respirable airborne particulates (Hay et al. 1997) and street dust (Beckwith et al. 1986; Ng et al. 2003), various types of sediments (Chan et al. 1997; Chaparro et al. 2004; Desenfant et al. 2004), power station fly ash and vehicle emissions (Hunt et al. 1984; Lu et al. 2005; Shan & Lu 2005). Initial work by Beckwith et al. (1986) identified elevated levels of magnetic oxides in soils and linked them to magnetic particles in airborne pollution. Several studies also confirmed a direct correlation between the magnetic susceptibility of contaminated soils and the presence of hydrocarbons and other combustion-related pollutants (Morris et al. 1995). Morris et al. (1994) and Versteeg et al. (1995) showed that concentrations of hydrocarbons and certain heavy metals (Pb, Zn and Fe) are closely tied to magnetic oxide content in core samples from Hamilton Harbour in western Lake Ontario.

The highly significant correlation between magnetic susceptibility and heavy metal content in soils allows susceptibility to be used as an indicator for contaminants and their spatial distribution. However, not all case studies show this relationship. Poorer correlation between magnetic susceptibility and heavy metal concentrations was reported in other studies (Charlesworth & Lees 1997, 2001; Chaparro et al. 2004; Schmidt et al. 2005). Schmidt et al. (2005) found that best correlation is obtained for magnetic susceptibility values higher than a site-specific threshold. Therefore, more cases studies are needed in order to understand better and in detail the magnetic proxy method, especially as it works and under which conditions this technique can be applied in different environments, climates and ecosystems.

Urban topsoils are accumulator of toxic pollutants and pose potential threat to urban water bodies, human health and ecosystem. It is therefore important to recognize the level, source, signature and pathway of pollutants in urban soils. There have been a limited number of studies that have tried to resolve these relationships. No systematic magnetic investigation on the spatial distribution of magnetic properties of urban topsoils has been performed in semi-arid environment. The relationship between the magnetic signature of urban topsoil and heavy metals content is still not fully understood. The applicability of magnetic measurements should also be tested in a more complex environment. In this study, the magnetic properties of urban topsoils as well as their associations with heavy metals were examined. Emphases were placed on the characterization of the magnetic carriers in which heavy metals resided and on the comparative ability of magnetic parameters to explain the heavy metal levels. The aims were (i) to determine the magnetic properties of urban topsoils in which the magnetic carrier and heavy metal reside and (ii) to assess the potential of magnetic measurements as indicators of heavy metals pollution at a large scale in arid environment.

2 MATERIALS AND METHODS

2.1 Study area and sampling

The study area Luoyang City, situated in Henan Province of Central China, is a heavy industry city and is known for glass and heavy machine manufacture, petrochemical industry, metallurgical and building industry in China. The express roadway from east to west of China as well as the railway line connecting East Asia to Central Asia passes through the city. The main pollution source is industrial discharge, atmospheric emissions from the various factories and traffic emission. The urban topsoils may have accumulated heavy metals and magnetic materials over a long time span. Therefore, the city is an excellent site for environmental studies of anthropogenic pollution. The climate of the study area is temperate with an average annual rainfall of 546 mm and average annual temperature of 14.2 °C. The prevailing wind direction is westerly. Soils are developed on loess parent materials.

A total of 215 urban topsoils were collected within the city of Luoyang. Sampling sites were chosen to cover different land use zones of city: industrial areas (IA), roadside (RS), residential areas and commercial centres (RC), parks and green recreation areas (PG). Fig. 1 shows the location of the soil sampling sites. Soil samples of industrial areas (50 samples) were collected from bare soils within and surrounding glass, heavy machine manufacture, petrochemical works, coal-burning power plant, cement-making and metallurgical factories. Roadside soil samples (66 samples) were collected from the rim of railway, highway and high-density traffic main streets of city. Soil samples of residential areas and commercial centres (47 samples) were collected within residential areas of high-density population and commercial centres of the city. Soil samples (52 samples) of parks and green areas were obtained from green areas of parks, green areas within campus and within larger, green recreational areas. The sampling depth of urban soils is 0–10 cm, because anthropogenic heavy metals are usually deposited on topsoil. At each sampling site, a composite sample was collected using a stainless steel trowel and stored in a plastic bag. The composite sample was obtained by mixing five to six subsamples collected from the extent of 10–20 m² in the same site. Soil samples were air-dried, passed through a 2 mm sieve and stored in self-locking polythene bags for use. A few loess topsoil samples and some samples from the ‘unpolluted’ area were collected from the surrounding areas, to compare its magnetic properties to those of the urban soils.

Two soil profiles derived from loess parent material were selected from the rural area as the background to define the geological imprint on the soil magnetic susceptibility. Four urban soil profiles were also selected from the representative industrial area, roadside, residential area and commercial centre to define the vertical variation of magnetic susceptibility. Soil profile samples were collected at 2-cm interval from 0 to 20 cm depth and 5-cm interval from 20 to 50 cm depth for the magnetic susceptibility measurement.

Twenty soil samples collected from industrial area and roadside were selected for magnetic fraction separation according to procedure of Walden et al. (1999). The magnetic fraction was separated by placing a parafilm wrapped magnet into a soil solution (1:10 soil:water ratio), stirring vigorously in ultrasound device, separating the parafilm wrap from the magnet and rising collected magnetic particles with water. This procedure was repeated until no more magnetic particles adhered to the magnet. Extracted magnetic and residue non-magnetic fractions were oven-dried at 40 °C and weighed for further chemical analyses.

2.2 Magnetic measurements

Low frequency susceptibility (χlf) and high frequency susceptibility (χhf) were measured using a dual-frequency (0.47 and 4.7 KHz) Bartington MS2 magnetic susceptibility meter. Frequency-dependent magnetic susceptibility was defined as χ(f)% = [(χlf − χhf)/χlf] × 100, here χlf and χhf represent susceptibility values measured at 0.47 and 4.7 KHz, respectively. Saturated isothermal remanent magnetization (SIRM, IRM acquired at 1000 mT field) and isothermal remanent magnetization at different field were produced using a pulse magnetizer. After each forward and
reverse field, the isothermal remanent magnetization (IRM) of the sample was measured using a Molspin Spinner magnetometer. The magnetic parameter HIRM was calculated as \( \text{SIRM} - \text{IRM}_{300\text{mT}} \) and \( S_{100\text{mT}} \) ratio as \( \left( \frac{\text{IRM}_{100\text{mT}}}{\text{SIRM}} \right) \times 100 \). Magnetic susceptibility versus temperature curves of selected samples were obtained by measuring continuously from room temperature to 700 °C and back to room temperature in a KLY-3 Kappabridge with a CS-3 high-temperature furnace (Agico Ltd., Brno, Czech Republic) in an air atmosphere. Hysteresis loop measurements were made by a Princeton Micromag 2900 system (Princeton Measurements Corp., USA). The hysteresis parameters, including saturation remanence (Mrs), saturation magnetization (Ms), coercivity (Hc) and coercivity of remanence (Hcr) of the samples were determined based on the hysteresis loops corrected for SP magnetization.

2.3 Soil chemical analysis

Soils and magnetic fractions were digested in a microwave oven (Mars-5, CEM Company, USA) using a mixture solution of the concentrated acids of \( \text{HNO}_3-\text{HF-HCLO}_4 \). After digestion, the solution was cooled and diluted with 10–15 mL of distilled water and filtered. The filtrate was then made up to 50 mL with distilled water and analysed for Fe, Mn, Cd, Cr, Cu, Pb and Zn using atomic absorption spectrometer (AA6300 Shimadzu Ltd., Japan). Blanks that involved the same treatment but without the soil samples were prepared for quality control. Analytical variability was tested by repeated analysis on every ten samples. The analytical precision, measured as relative standard deviation, was routinely between 5 and 6 per cent, and never higher than 10 per cent.

2.4 X-ray diffraction

Mineralogy of the magnetic extracts was determined by X-ray diffraction. X-ray diffraction analyses of selected samples were performed on a powder X-ray diffractometer (Rigaku D/Max 2550 PC, Rigaku Corporation, Japan) with a CuK\( \alpha \) radiation (40 kV, 40 mA). Scans were conducted from 2 to 75° at a rate of \( 2^\circ \theta \) per min.

Figure 1 Sketch map of the study area and sampling sites (IA = industrial area, RS = roadside, RC = residential and commercial areas, PG = parks and green areas).
2.5 Data analysis

Statistical analyses of the magnetic and chemical data were undertaken using SPSS for Windows 10.0 software. Correlation coefficients and the associated level of significance (p) were employed to establish the relationship between heavy metal levels and magnetic parameters in the soils. Mapping of magnetic susceptibility distribution was created with ArcGIS 8.3 and ArcView 3.2 software.

3 RESULTS

3.1 Magnetic properties and heavy metal contents of urban topsoils

3.1.1 Magnetic properties characterization

The magnetic measurement results of urban topsoil samples are listed in Table 1. Table 1 shows that magnetic susceptibility values for urban topsoils varied by two to three orders of magnitude, ranging from $31 \times 10^{-8}$ to $1128 \times 10^{-8}$ m$^3$ kg$^{-1}$ with an average of $(215 \pm 89) \times 10^{-8}$ m$^3$ kg$^{-1}$. It is decreased in the order of industrial areas $(313 \times 10^{-8}$ m$^3$ kg$^{-1})$ > roadside $(236 \times 10^{-8}$ m$^3$ kg$^{-1})$ > residential and commercial areas $(182 \times 10^{-8}$ m$^3$ kg$^{-1})$ > parks and green areas $(123 \times 10^{-8}$ m$^3$ kg$^{-1})$. In comparison with magnetic susceptibility values ($\sim 30 \times 10^{-8}$ to $120 \times 10^{-8}$ m$^3$ kg$^{-1}$) obtained in Chinese loess (Maher 1998; Guo et al. 2001; Zhu et al. 2001; Wang et al. 2003), the average value in Luoyang urban topsoil is higher. Previous studies demonstrated that magnetic susceptibility variations are caused by differences in geology, soil-forming processes and by anthropogenic input of magnetic material (Thompson & Oldfield 1986; Dearing et al. 1996; Lu 2003). The magnetic susceptibility value of a natural ‘non-polluted’ soil depends on five major soil-forming factors (parent material, climate, geomorphology, vegetation and time). Thus, background susceptibility value should always be determined in an unimpacted soil of similar genesis in order to evaluate the relative enhancement due to anthropogenic influence. The average magnetic susceptibility for the loess parent material is much lower than the signal from urban topsoil samples. The magnetic susceptibility of loess found in the studied area varied, on average, between $20 \times 10^{-8}$ and $100 \times 10^{-8}$ m$^3$ kg$^{-1}$. The relatively high magnetic susceptibility value in urban topsoils cannot be explained by the local geology, as there is little change in this area. Thus, the high magnetic susceptibility in topsoils is mainly attributed to anthropogenic input of various origins.

The vertical variation of magnetic susceptibility in soil profile is shown in Fig. 2. The magnetic susceptibility values of the soils from rural area, representing the background level of soil magnetic susceptibility, ranged from $65 \times 10^{-8}$ to $109 \times 10^{-8}$ m$^3$ kg$^{-1}$ throughout the profile (Fig. 2a). These profiles could be served as a lithogenic background magnetic susceptibility in the investigated area. All soil profiles (Fig. 2b) from urban area show increased magnetic susceptibility in its surface horizons (0–10 cm) and steeply decreased from upper horizon to 20–50 cm horizon, thus suggesting the contribution of ferrimagnetic minerals of anthropogenic origin. The upper 0–10 cm horizon of soil profile from industrial area exhibits the

![Figure 2. Magnetic susceptibility variation along vertical profiles of representative soils from background area (a) and urban area (b) in Luoyang City. IA = industrial areas, RS = roadside, RA = residential areas and CC = commercial centre.](image)

Table 1. Magnetic measurement results of urban topsoils from Luoyang City, China.

<table>
<thead>
<tr>
<th>Magnetic parameters</th>
<th>Industrial Area ($n =$ 50)</th>
<th>Roadside ($n =$ 66)</th>
<th>Residential and commercial areas (47)</th>
<th>Parks and green areas (52)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi f(10^{-8}$ m$^3$ kg$^{-1})$</td>
<td>Range 111–1128</td>
<td>89–567</td>
<td>106–288</td>
<td>31–186</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>313 ± 149</td>
<td>236 ± 74</td>
<td>182 ± 40</td>
<td>123 ± 23</td>
</tr>
<tr>
<td>Median</td>
<td>256</td>
<td>210</td>
<td>171</td>
<td>125</td>
</tr>
<tr>
<td>$\chi fd (%)$</td>
<td>Range 05–6.9</td>
<td>0.2–8.6</td>
<td>2.1–9.2</td>
<td>0.8–10.9</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>3.3 ± 1.2</td>
<td>3.5 ± 1.6</td>
<td>4.9 ± 1.4</td>
<td>5.8 ± 2.2</td>
</tr>
<tr>
<td>Median</td>
<td>3.2</td>
<td>3.0</td>
<td>4.8</td>
<td>6.3</td>
</tr>
<tr>
<td>IRM$_{20mT}(10^{-6}$Am$^2$ kg$^{-1})$</td>
<td>Range 1378–86 813</td>
<td>1335–10 319</td>
<td>1088–9072</td>
<td>164–8195</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>6956 ± 4943</td>
<td>3693 ± 1200</td>
<td>3031 ± 1127</td>
<td>2074 ± 840</td>
</tr>
<tr>
<td>Median</td>
<td>3989</td>
<td>3337</td>
<td>2558</td>
<td>1998</td>
</tr>
<tr>
<td>SIRM ($10^{-6}$Am$^2$ kg$^{-1}$)</td>
<td>Range 8124–96 977</td>
<td>8393–56 247</td>
<td>8124–41 398</td>
<td>2362–22 504</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>32 801 ± 15 129</td>
<td>24 499 ± 7287</td>
<td>20 748 ± 6085</td>
<td>12 545 ± 3589</td>
</tr>
<tr>
<td>Median</td>
<td>29 314</td>
<td>23 859</td>
<td>19 220</td>
<td>12 460</td>
</tr>
<tr>
<td>HIRM ($10^{-6}$Am$^2$ kg$^{-1}$)</td>
<td>Range 10–18 377</td>
<td>69–18 667</td>
<td>27–6192</td>
<td>11–2093</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>2023 ± 1262</td>
<td>1536 ± 846</td>
<td>1184 ± 566</td>
<td>1080 ± 590</td>
</tr>
<tr>
<td>Median</td>
<td>1386</td>
<td>1244</td>
<td>1022</td>
<td>962</td>
</tr>
<tr>
<td>S$_{100mT}$ ratio (%)</td>
<td>Range 50.7–95.0</td>
<td>46.4–97.7</td>
<td>31.9–76.5</td>
<td>40.1–73.3</td>
</tr>
<tr>
<td>Mean ± SD</td>
<td>68.2 ± 5.8</td>
<td>64.9 ± 4.9</td>
<td>62.4 ± 5.6</td>
<td>58.0 ± 6.0</td>
</tr>
<tr>
<td>Median</td>
<td>68.5</td>
<td>64.3</td>
<td>62.5</td>
<td>58.3</td>
</tr>
</tbody>
</table>

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largest enhancement of magnetic susceptibility, three to four times of those from background area. This indicates that urban topsoils accumulated relatively higher amount of anthropogenic magnetic materials. Due to relatively lower input of anthropogenic magnetic materials in residential area and commercial centre, these soil profiles exhibit lower magnetic enhancement on top horizon (Fig. 2b).

Fig. 3 shows the spatial distribution of magnetic susceptibility of the urban topsoils. Results demonstrate that the susceptibility values differ significantly in different location within the city. The pattern of magnetic susceptibility distribution showed a main anomaly in the region around the suspected emission source in the city. Higher values are concentrated in the northwestern part where a lot of industrial plants (e.g. glass, heavy machine manufacture, petrochemical works, etc.) are located, followed by commercial zone where the magnetic minerals may be derived from the traffic emissions. Soils situated close to the busy road intersection, near the main bus stations and sectors of roads yield elevated magnetic susceptibility. The relatively high magnetic susceptibility values suggested that the soil was enriched with ferrimagnetic grains probably as a consequence of anthropogenic activities compared to other environmental materials. Lower susceptibility values were found in parks and green areas.

Soft parameter (IRM 20mT) is approximately proportional to the concentration of the ferrimagnetic minerals [e.g. magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃)] within a sample, while hard parameter (HIRM) is approximately proportional to the concentration of the canted antiferromagnetic minerals [e.g. hematite (α-Fe₂O₃) and goethite (α-FeOOH)] within a sample. In this study, the relatively low HIRM values indicated a low content of canted antiferromagnetic component in the samples. The IRM 20mT, HIRM and SIRM in soils taken from industrial areas and roadside are much higher (Table 1), indicating a greater accumulation of anthropogenic magnetic minerals. The relationship between magnetic susceptibility and SIRM for all urban topsoil samples is grouped in defined clusters. Clusters of industrial areas and roadside soil show higher ferrimagnetic concentration than their corresponding cluster of residential and green areas.

3.1.2 Heavy metal contents of urban topsoils

Table 2 shows the results of the chemical analysis of the urban topsoil samples. Results showed that the urban topsoil contained high concentrations of Cd (mean = 1.1 mg kg⁻¹), Cr (mean = 71.42 mg kg⁻¹), Cu (mean = 85.40 mg kg⁻¹), Pb (mean = 65.92 mg kg⁻¹) and Zn (mean = 215.75 mg kg⁻¹). Large standard deviation of these metal concentrations implied a great heterogeneity of heavy metal accumulation. On the other hand, Mn content of urban topsoils does not change much. This element will be mostly of geogenic origin. In comparison with the background values of heavy metals in soils (China Environmental Monitoring Station 1990), high concentrations of heavy metals (especially Cd, Cu, Pb and Zn) in urban topsoil samples are the evidence for the accumulation of heavy metal contaminants from traffic and/or industrial activities. The measured high concentrations of heavy metals and magnetic susceptibility values in industrial areas and roadside soils indicate the presence of a considerable amount of magnetic particles in the material accompanying the heavy metal emission.

Cd, Cu, Pb and Zn concentrations in industrial areas and roadside were significantly higher than those in parks and green areas (Table 2). These metals concentrations in topsoils may be affected by the deposition of dusts emitted from various industrial activities. In addition, Cu is a common element in automobile thrust bearing, brake lining, and other parts of the engine. The corrosion causes metal wear in the automobile engine and release of heavy metals to the environment, and eventually accumulation in the topsoil. Zn compounds are used extensively as anti-oxidants and as detergent/dispersant improving agents for motor oil. Tire wear was also found to contribute a significant loading of Zn to dust, especially in the form of coarse particles. Conventionally, Pb has been the most reliable indicator of traffic-induced pollution. The emission of Pb from automobile exhaust and its deposition near highway and roads has been reported worldwide. However, the utilization of lead petrol as fuel for automobiles had been banned since 1990s. This practice was expected to have reduced greatly the accumulation of this element in the dust. Exhaust particles may no longer be
The highest coefficient between magnetic susceptibility and heavy metal is found for Pb ($r^2 = 0.50$). A correlation between the magnetic susceptibility and the concentration of heavy metals Fe ($r^2 = 0.21$), Cr ($r^2 = 0.37$), Cu ($r^2 = 0.34$) and Zn ($r^2 = 0.31$) exists. Fig. 4 shows the scatter plots of magnetic susceptibility and seven metals. Significant correlations between SIRM and concentrations of Fe, Cr, Cu, Pb and Zn were obtained within a 99 per cent confidence level. As can be seen from Table 3, the highest correlation coefficient is found between SIRM and Pb ($r^2 = 0.31$) and the lowest was obtained between SIRM and Mn ($r^2 = 0.02$). No significant positive correlation between frequency-dependent susceptibility ($\chi_{fd}$) and the amount of different heavy metals is observed. Among the seven metals, Cr, Cu and Pb showed good correlations with the magnetic parameter IRM$_{300\text{mT}}$, followed by Fe and Zn. $\chi_{If}$ and SIRM had the two strongest correlations with heavy metals among various magnetic parameters. On the other hand, parameter $S_{\text{IRM}100\text{mT}}$ ratio generally did not show strong association with heavy metals, indicating that it was not as good indicator of heavy metal content as the magnetic concentration parameters did. In heavily industrialized region of Eastern Germany, Mn, Zn, Pb and Cu showed significant positive linear correlation with $\chi_{If}$, with most $r^2$ values ranging from 0.70 to 0.98. For the other metals, namely Co, Cr and especially Ni, unsatisfactory $r^2$ values were obtained (Spiteri et al. 2005). Results for Cd did not reveal particular trend. Some correlations gave high coefficient, other extremely low or no correlation at all. More details about the specification of this metal would be helpful to explain this outcome.

The Tomlinson Pollution Load Index (PLI) (Angulo 1996) for the urban topsoil samples was calculated to establish its association with magnetic parameters. PLI indicates how much a sample exceeds the heavy metal concentrations for natural environments and give an assessment of the overall toxicity status for a sample (Angulo 1996). The PLI is calculated according to the following equation:

$$\text{PLI} = n\sqrt{(C_{F1} \times C_{F2} \times \cdots \times C_{Fn})}$$

where $C_{F_{metal}}$ is the ratio between the concentrations of each heavy metal ($C_{metal}$) to the background concentrations $C_{background}$. Highly significant correlations between PLI and magnetic susceptibility and SIRM were obtained in soils (Fig. 5). Strong correlations between PLI and $\chi_{If}$ as well as SIRM show that both ferrimagnetic minerals and heavy metals come from the same pollution source, enable them as good indicators of heavy metal pollution in urban soils. Clear correlation was found between the ARM and PLI for the stream and marine sediments (Chan et al. 2001; Chaparro et al. 2004).

Strong correlations between heavy metals and $\chi_{If}$ as well as SIRM, might enable them as simple, rapid and non-destructive proxy indication of heavy metal concentration in urban soils. To find magnetic criteria to identify polluted areas, we suggest that soils with significant concentration of heavy metals can be identified in

### Table 2. Heavy metal contents of urban topsoils from Luoyang City, China.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Industrial Area ($n = 50$)</th>
<th>Roadside ($n = 66$)</th>
<th>Residential and commercial areas ($n = 47$)</th>
<th>Parks and green areas ($n = 52$)</th>
<th>All urban soils ($n = 215$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Median (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.72–6.07</td>
<td>2.33–7.23</td>
<td>2.03–4.77</td>
<td>2.54–4.37</td>
<td>2.03–7.23</td>
</tr>
<tr>
<td>Mn</td>
<td>Median (mg kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>366.19–785.49</td>
<td>330.26–751.64</td>
<td>400.05–1197.15</td>
<td>331.39–704.20</td>
<td>313.39–1197.15</td>
</tr>
<tr>
<td>Cd</td>
<td>Median (mg kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.66</td>
<td>1.65</td>
<td>1.58</td>
<td>1.57</td>
<td>1.59</td>
</tr>
<tr>
<td>Cr</td>
<td>Median (mg kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>52.57–137.83</td>
<td>45.16–113.43</td>
<td>46.04–215.61</td>
<td>30.51–77.98</td>
<td>30.51–460.10</td>
</tr>
<tr>
<td>Cu</td>
<td>Median (mg kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.58–12.27</td>
<td>68.05–7.56</td>
<td>72.91–14.18</td>
<td>63.84–6.65</td>
<td>71.42–12.22</td>
</tr>
<tr>
<td>Pb</td>
<td>Median (mg kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.76</td>
<td>66.76</td>
<td>67.61</td>
<td>65.33</td>
<td>66.93</td>
</tr>
<tr>
<td>Zn</td>
<td>Median (mg kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>83.72–569.94</td>
<td>100.05–1195.08</td>
<td>112.13–492.62</td>
<td>68.40–590.87</td>
<td>68.40–1195.08</td>
</tr>
</tbody>
</table>

### Table 3. Correlation coefficients ($r^2$) between magnetic parameters and heavy metal contents ($n = 215$).

<table>
<thead>
<tr>
<th>Magnetic parameters</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{If}$</td>
<td>0.21</td>
<td>0.11</td>
<td>0.37</td>
<td>0.08</td>
<td>0.34</td>
<td>0.50</td>
<td>0.31</td>
</tr>
<tr>
<td>$\chi_{fd}$</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>-0.12</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>IRM$_{300\text{mT}}$</td>
<td>0.05</td>
<td>0.02</td>
<td>0.17</td>
<td>0.04</td>
<td>0.20</td>
<td>0.30</td>
<td>0.08</td>
</tr>
<tr>
<td>SIRM</td>
<td>0.27</td>
<td>0.02</td>
<td>0.15</td>
<td>0.04</td>
<td>0.21</td>
<td>0.31</td>
<td>0.06</td>
</tr>
</tbody>
</table>

$^a$After China Environmental Monitoring Station (1990).

$^b$Correlation is significant at the 0.01 level.
Luoyan urban soils combining two magnetic parameters: $\chi_l f > 100 \times 10^{-8}$ m$^3$ kg$^{-1}$ and the $\chi f d < 4$ per cent. A similar result was reported by Hay et al. (1997) for Bucharest soils and topsoils in England.

### 3.3 Magnetic carriers and origin in urban topsoils

For identification of these ferrimagnetic minerals responsible for the enhanced magnetic signals in soils, rock magnetism and X-ray diffraction were conducted on the typical topsoil samples from industrial areas and roadsides.

#### 3.3.1 IRM characterization

IRM acquisition curves of typical samples are shown in Fig. 6. From IRM acquisition curves it is clear that the magnetic minerals in the soil samples are close to saturation in a field of 300 mT, indicating that low coercivity magnetic minerals, for example, magnetite-like phase, are the main magnetic minerals in the soils. Curves of demagnetization of SIRM, shown also in Fig. 6, can be interpreted in the same way as IRM acquisition curves. They confirm a very soft magnetic phase present in the soil samples.

#### 3.3.2 Magnetic hysteresis

Hysteresis loop measurements carried out in our study showed that the samples acquired a saturation magnetization at 0.2–0.3 T field strength. Four magnetic parameters: saturation magnetization (Ms), saturation remanence (Mrs), coercive force (Hc) and coercivity of remanence (Hcr), are obtained from the hysteresis loop. The Mrs/Ms and Hcr/Hc were 0.124–0.180 and 2.601–3.785, respectively. This is
Magnetic properties as indicators of heavy metals pollution in urban topsoils

3.3.3 Susceptibility versus temperature curves

High-temperature behaviour of susceptibility (heating and cooling measurements from 20 to 700 °C), revealing the Curie point (Tc) of the magnetic minerals, was used to identify the ferrimagnetic iron oxides responsible for the increased magnetic susceptibility of soils. The susceptibility versus temperature curves of soil samples taken at industrial area and roadside are shown in Fig. 8. The curves for all samples show nearly similar results. In particular, the cooling curve is significantly more intense than the heating curve. Results demonstrated an increase of susceptibility between 400 and 500 °C, followed by a subsequent decrease and a resulting Curie-point in the range of magnetite at about 580 °C. The susceptibility versus temperature curve confirms that magnetite with Tc 580 °C is the dominant iron oxide in the source material, which contributes to the susceptibility signal in polluted soils. The significant peak around 500–580 °C observed in the curves is likely caused by the neoformation of magnetite through the transformation of iron-containing silicates/clays. The small peak around 250–270 °C in the curves may be due to annealing of defects or internal stresses in magnetic particles (probably maghemite) and conversion of maghemite to hematite.
3.3.4 X-ray diffraction

All urban topsoils had similar X-ray diffraction patterns indicating similarity in their mineralogical compositions. All topsoil contained magnetite and hematite (Fig. 9). The diffraction data also suggest the presence of traces of the Fe-oxyhydroxide, akaganeite, though its origin is not clear. In all samples, the magnetic peak intensity was greater than the hematite peak intensity, indicating that crystalline iron in the magnetic fraction was present mainly as magnetic mixed in various proportion with hematite. In combination with high-temperature behaviour of magnetic susceptibility for the magnetic extract show unambiguously that magnetite is the dominant ferrimagnetic phase in magnetic extracts from the topsoil samples. This result corroborates findings of other workers (Goddu et al. 2004; Gautam et al. 2005). Therefore, the magnetic susceptibility of topsoils in the urban region reflects mainly the concentration of anthropogenic ferrimagnetics. Summarizing, it can be concluded that magnetite is a major ferrimagnetic constituent within the soils.

3.3.5 Magnetic quotients

Magnetic quotients are useful for identification of certain magnetic minerals and their domain states. $S_{100mT}$ ratio can be used as approximate indication of relative importance of ferrimagnetic and canted antiferromagnetic components. $S_{100mT}$ ratio values falling between 1.0 and 0.7 characterize coarse (MD) low coercivity magnetic minerals, and values below 0.4 characterize high coercivity minerals of antiferromagnetic minerals. The $S_{100mT}$ ratio values for topsoils from industrial area and roadside were 0.68 and 0.65 (Table 1), respectively, suggesting that the soil samples were dominated by coarse-grained MD ferrimagnetic minerals.

Frequency-dependent susceptibility ($\chi_{fd}$) is used to determine the possible presence of a superparamagnetic (SP) mineral fraction (Dearing 1999). Table 1 shows that $\chi_{fd}$ values (mean = 4.4 per cent) in the urban topsoil samples were low, indicating that the samples did not contain significant amount of superparamagnetic (SP) grains. Many samples in industrial areas and roadside have $\chi_{fd}$ of <2 per cent, which is indicative of frequency-independent coarse multidomain (MD) or PSD grains. Unpolluted soils are usually characterized by the presence of an important superparamagnetic fraction (less than 0.03 $\mu$m) produced by pedogenesis (Maher 1998; Lu 2003). The low $\chi_{fd}$ values indicate that soil does not contribute much magnetic material to the formation of susceptibility in urban topsoils.

The lack of positive correlation between magnetic susceptibility and $\chi_{fd}$ in Chinese loess and paleosols (Guo et al. 2001; Zhu et al. 2001; Wang et al. 2003). Anthropogenic magnetic minerals, mainly magnetite, are usually large magnetic grains in multidomain state. Mean values of $\chi_{fd}$, together with results from other magnetic measurements, suggest a significant MD component in urban topsoils. In summary, magnetic quotient parameters indicate a strong ferrimagnetic mineral component with coarse MD-PSD grains dominating the urban topsoil samples.

3.4 Enrichment effect of heavy metal in magnetic fraction

The application of magnetic parameters as a proxy method for the detection of environmental contamination is based on the fact that
heavy metal pollution in many cases is accompanied by emission of ferrimagnetic particles. The extracted magnetic fraction (MF) content was highly correlated with susceptibility and iron oxide content in the bulk soil samples (Fig. 11). The chemical analysis of magnetic and non-magnetic fractions showed that heavy metals were enriched in the magnetic fraction (Table 4). The highest enrichment factor (element concentration in magnetic fraction/non-magnetic fraction) occurred in the Fe, Cu and Cr. The Zn had the lowest enrichment in the magnetic fraction. Cd and Mn were also concentrated primarily in the magnetic fraction. Kukier et al. (2003) reports that magnetic fraction of fly ashes had about 10 times higher concentration of Fe and two to four times higher concentrations of Co, Ni and Mn.

4 DISCUSSION

4.1 Source of magnetic particles

Magnetic particles, in the form of fine iron oxide dusts, could have been released along with other heavy metals from a combination of different sources and introduced into the urban topsoils. Compared to the background value, the magnetic enhancement of urban topsoil demonstrated the anthropogenic inputs of magnetic minerals. The anthropogenic magnetic particles are likely to have come from three sources: (1) emissions from fossil-fuel combustion processes (fly ash); (2) vehicle emissions (vehicular exhaust, abrasion of tyres, brake linings as well as road construction materials) and (3) waste products and dusts from metallurgical and other industries. All three sources contributed to the increase of the magnetic susceptibility of the urban topsoils.

Many mineralogical and geochemical studies have proven the presence of a significant amount of iron oxides (magnetite and hematite) together with different heavy metals in fly ashes (Kapicka et al. 1999; Klose et al. 2001; Kukier et al. 2003; Shan & Lu 2005). Practically all coal-burning fly ashes contain a significant fraction of ferrimagnetic particles. The Chinese fly ashes had magnetic susceptibility of 494 × 10⁻⁸–1680 × 10⁻⁸ m³ kg⁻¹ and average $\chi_{fd}$ of 2.5 per cent (Shan & Lu 2005). The atmospherically deposition of fly ashes on topsoils, especially in industrial areas and sites downwind of industrial centre, significantly contribute to the ferrimagnetic particles of soils, resulting in enhancement of magnetic susceptibility of topsoils. Vehicle emissions have been suggested to be another significant source of magnetic pollutants (Hunt et al. 1984; Hoffmann et al. 1999). Roadside soils are commonly serves as an archive of particulate matter derived mostly from traffic/motor vehicle emission, abrasion of tyres, brake linings as well as road surface, cycling of dust in suspension due to vehicular movement, dispersion of construction material, etc. Hence, roadside soils have elevated concentrations of magnetic materials and heavy metals. The waste products and dusts from metallurgical industry, machine manufacture, cement works and petrochemical industry in the city also contain magnetic materials. It is obvious that these magnetic materials can significantly influence magnetic properties of soils in the surrounding areas. They are directly responsible for the increase in the magnetic susceptibility of topsoil horizons.

4.2 Relationship between magnetic parameters and heavy metal contents

The correlation between magnetic parameters and heavy metal contents revealed an obvious link between ferrimagnetic oxides and heavy metals. In various studies, the relationship between magnetic susceptibility and heavy metal concentrations was usually analysed by simple linear regression analysis (Beckwith et al. 1986; Chan et al. 1997; Strzyszcz & Magiera 1998; Hanesch et al. 2001; Knab et al. 2001). Although the correlation between magnetic susceptibility and heavy metals for all samples of this study was already significant at 1 per cent level (Table 3), selecting a subset of topsoil samples for which the magnetic susceptibility proxy measurements would be even more strongly correlated seems desirable. Clearly, our data originate from a collection of different sample sources and demonstrate some evidence of clustering, which should be treated separately for correlation analyses. When the data are separated into site-specific relationships, the significance of the association continues to be evident, especially in industrial areas and roadside soils. Previous studies indicate that the correlation between magnetic susceptibility and heavy metal contamination only exists for the polluted samples, like those that carry magnetic inclusions (Schmidt et al. 2005). Incorporating background samples into the statistical analysis can therefore adversely affect the results.
The relationships between magnetic particles and pollutants are complex and they are different for each industrial process. Upon closer investigation of the recorded values it becomes clear that the correlation is better for higher values. If only samples collected from industrial areas and roadside are considered, higher correlation coefficient would be obtained. Schmidt et al. (2005) reported that a strong correlation between metal concentration and magnetic susceptibility exists if only samples above a threshold value are considered. The threshold is 2 per cent higher than the mean of all samples, 52 per cent higher than their median. Although the threshold will be site-specific, using a value 50 per cent above the median of all samples is suggested for other studies (Schmidt et al. 2005). This may explain why correlation of magnetic susceptibility with heavy metal concentrations in our study did not exceed a correlation coefficient \( r^2 \) of 0.50. Similar observations were also found by Beckwith et al. (1986) who found that the correlation between heavy metals and magnetic susceptibility is lost if sediment samples with low magnetic susceptibility were added to the statistical analysis.

In areas with multiple pollution sources, the link between the magnetic signal and heavy metal concentration was found to be too complex to be describe by simple linear statistics, but could fit log normal distributions, in which the logarithmic values of chemical concentration and magnetic susceptibility were used as input for multivariate statistical analyses (Hanesch et al. 2001). The use of simple linear correlation methods for relating might not be suitable. In the work of Knab et al. (2001), magnetic susceptibility values along a highway were found to be positively correlated with heavy metals, in particular Pb, Cu, Cd and Zn. Fuzzy C-means cluster analysis was employed to discriminate between anthropogenic and pedogenic/geogenic background values in shallow sections along soil profiles. There also is the need for further research that demonstrates both the nature of the linkage and stronger correlations between heavy metals and magnetic properties.

4.3 Enrichment mechanism

Various mechanisms for the correlation of heavy metals with iron oxides in soils have been identified, especially adsorption and incorporation. Where iron-oxide particles are discharged from industrial processes, associated heavy metals can either be incorporated into their atomic lattice or be adsorbed to their surfaces and their concentrations are therefore correlated. For example, Scholger (1998) found that iron producing and manufacturing industries in Styria emitted Zn, Pb, Ni, Cu and Cr together with macroscopic scale magnetic particles, which were easily quantified in river sediments through magnetic measurements. In these studies, airborne pollutants were formed from iron-oxide particles and the measured magnetic susceptibility was hence directly proportional to the level of contamination. In solutions, Zn, Cu, Cd and Cr have similar replacibility and have a tendency to coprecipitate with hydrous Fe oxides. Laboratory studies of soil iron oxides revealed that these particles are highly adsorbent of heavy metals.

The relative order of the correlations between heavy metals and magnetic parameters represents the relative affinity of these metals to the ferrimagnetic minerals. The samples taken around industrial areas showed a significant accumulation of such spherules, hence the main anomaly was produced by deposition of particulate pollutants from the suspected point emission sources. Soil retention strongly depends on the inherent soil properties, which are controlled by the soil-forming processes (Cornell & Schwertmann 1996).

One of the mechanisms proposed is the surface adsorption of metal oxides. The authors also refer to a preferential adsorption of Pb, Zn, Cu, Cd and Cr on the surface of ferric oxyhydroxides as an alternative mechanism to describe the association with heavy metals. Other studies draw attention to the enrichment of first transition group elements (V, Cr, Mn, Fe, C, Ni, Cu and Zn) in the magnetic fraction of coal fly ash (Hunt et al. 1984) in the form of substituted spinels of \( \text{Fe}_2x\text{M}_3\text{O}_4 \). There also is the need for further studies that demonstrates both the nature of the linkage and strong correlations between heavy metals and magnetic properties.

5 CONCLUSION

Magnetic measurement and chemical analysis indicated an enrichment of magnetic particles and heavy metals in urban topsoils, which was characterized by enhanced magnetic signals and high concentrations of Cd, Cu, Pb and Zn. The enrichment of magnetic particles and heavy metals in industrial areas and roadside is considerably obvious. Significant correlation exists between magnetic susceptibility and the concentrations of Cr, Cu, Pb and Zn of urban topsoils in the studied area, as well as the Tomlinson PLL. The highest correlation was found with Pb. The significant correlation indicated a strong affinity of heavy metals to magnetic materials. Chemical analyses revealed that magnetic fractions in soils had about 15 times higher concentration of Fe, and three to six times higher concentrations of heavy metals than those of bulk samples. Rock magnetism and X-ray diffraction confirmed that the dominant ferrimagnetic component is magnetically soft coarse-grained magnetite responsible for the enhancement of magnetic signal of the topsoil, suggesting that the magnetic mineral is attributed to input of anthropogenic origin from industrial activities and traffic emission. These results confirm the applicability of magnetic susceptibility as a simple and rapid proxy method to investigate the heavy metal pollution in urban soils.

ACKNOWLEDGMENTS

This research was supported by National Nature Science Foundation of China (No.40371056), Zhejiang Provincial Natural Science Foundation of China (R305078) and The Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (No. 200149). The authors wish to Mrs C. Zhou, Paleomagnetic Lab, Institute of Geology & Geophysics, Chinese Academy of Sciences, for hysteresis loop and thermomagnetic measurement. We thank Prof Erwin Appel and two anonymous reviewers for their critical reviews and useful comments on this manuscript.

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