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ORIGINAL ARTICLE

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Magnetic properties of urban topsoils and correlation with heavy metals: a case study from the city of Xuzhou, China

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Abstract Heavy metals in urban topsoils have been shown to be very useful tracers of environmental pollution. Thus, their detailed studies are of great importance. Apart from expensive and time-consuming chemical methods, several simple, rapid and cheap proxy methods have been developed recently, one of them being based on rock-magnetic parameters. This examines the use of rock-magnetic methods designed to assess the degree of heavy-metal pollution of urban topsoils from the city of Xuzhou (China). The aim was to identify the magnetic properties and to link the "magnetic pollution" to the concentrations of the heavy metals. Since a strong correlation has been found between saturation isothermal remanent magnetization (SIRM) and the heavy metals, namely, Fe, Se, Ti, Sc, Ba, Bi, Pb, Cu, Zn, Cr and Mo, an anthropogenic contamination origin is thought to be the cause. The present study shows that SIRM is a fast, inexpensive and non-destructive method for the detection and mapping of heavy-metal-contaminated urban topsoils.

Keywords Urban topsoils · Heavy metals · Environmental magnetism · Pollution · SIRM · Xuzhou · China

Introduction

Starting with the investigation of sediments in the 1980s (Thompson and Oldfield 1986), research of environmental magnetism grew steadily in the last decades. Magnetic measurements were used to reconstruct the paleoclimate (Banerjee 1994), to gain insight into soil-forming processes (Maher 1986), to identify sediment sources (Walling et al. 1979) and to investigate erosion (Dearing et al. 1981). One recent main topic was the use of magnetic measurements as a proxy in pollution studies (Flanders 1994; Hanesch et al. 2003).

Heavy metals in urban soils have been shown to be very useful tracers of environmental pollution (Bacon et al. 1992; Kelly et al. 1996; Manta et al. 2002). Urban soils are the "recipients" of large amounts of heavy metals from a variety of sources including industrial waste, vehicle emissions, coal burning and other activities. Practically, all industrial fly ashes contain a significant fraction of ferromagnetic particles, the most important sources being fly ashes produced during combustion of fossil fuel (Flanders 1994; Kapička et al. 2000). Other sources, such as iron and steel works, cement works, public boilers and road traffic also contribute to contamination by anthropogenic ferromagnetic minerals (Heller et al. 1998; Hoffmann et al. 1999), Magnetics and heavy metals concentrations can be correlated although several factors may dilute links between them (Chaparro et al. 2004).

The connection may be due to either the incorporation of heavy metals into the lattice structure of Fe-rich fly-ash particles (ferri (antiferro)magnetic materials generated from iron-bearing minerals present in fossil fuel during combustion) or a subsequent incorporation of heavy metals onto the surface of ferri (antiferro)magnetic carriers present in the soils (Chaparro et al. 2004). The relationship between heavy metals and magnetic parameters has been exhaustively studied by a large number of authors (Heller et al. 1998; Petrovsky et al. 1998; Bityukova et al. 1999; Durza 1999; Kapicka et al. 1999; Chaparro et al. 2002; Hanesch and Scholger 2002; Chaparro et al. 2003). From the above studies, it is obvious that magnetic properties can be beneficially used as a ‘‘proxy’’ tool in estimating the contamination in various systems.

The aim of this study was to examine in detail urban topsoils from the city of Xuzhou (China) in terms of their magnetic mineralogy, and to establish links between enhanced concentrations of anthropogenic magnetic particles and concentrations of Se, Sc, Bi, Pb, Cu, Zn, Mo, Ag, Co, Cd, Ni, Cr, Sb, Fe, Be, Ti and Ba. The final goal was to document that simple and fast in situ magnetic measurements can reflect, under certain circumstances, the anthropogenic input of certain heavy metals.

The study area

Xuzhou is located northwestern part of Jiangsu, one of the provinces of China, the geographical position being 33°43′–34°58′N, 116°22′–118°40′E. The main wind direction is from the northwest, although in general, wind velocities are low, even approaching zero at times. This enhances the deposition of particulates within the city. Xuzhou has very convenient transportation facilities and current urban population exceeds 1,200,000 inhabitants.

For several centuries, Xuzhou has been a center of mining and heavy industry. Steel production and processing still play an important role in the economic life of the city, nowadays together chemical industries and other activities. Therefore, urban topsoil may have elevated heavy metals and magnetic materials accumulated over a long time span, and a mixture of several sources has to be expected.

Materials and methods

A total of 21 topsoil samples (depth = 0–10 cm) were collected within the city of Xuzhou (Fig. 1).

Sampling sites were selected where chemicals (such as fertilizers, pesticides) and sewage sludge have not been used. At each sampling point, three sub-samples with a 20×20 cm surface were taken and then mixed to obtain a bulk sample. Such a sampling strategy was adopted to reduce the possibility of random influence of urban waste. All the samples were collected with a stainless steel spatula and kept in PVC packages. The soil samples were air-dried and sieved through a 2-mm sieve.

The specific low magnetic susceptibility (χ) was measured using a low-frequency susceptibility bridge KLY-2. Several other magnetic parameters were measured for all 21 topsoil samples:

χ_{fd} = frequency dependence of low-field magnetic susceptibility measured at two frequencies (difference between χ_{lf} at 0.47 kHz and χ_{hf} at 4.7 kHz, expressed as percentage of χ_{lf}) using a MS2B Bartington susceptibility bridge;

SIRM = saturation isothermal remanent magnetization which was acquired at room temperature in a 1-T field, using a Digico fluxgate spinner magnetometer;

IRM = isothermal remanent magnetization measured as a function of the applied field in order to determine the IRM/SIRM ratios at variable fields;

$(Bo)_{CR}$ = coercivity of saturation remanent magnetization;

S_{-100} = defined as the ratios of IRM at a backfield of 0.1 T vs SIRM (Chaparro et al. 2004).

Morphology of particles was observed using SEM on magnetically enhanced samples obtained by extraction from suspended material using a hand magnet.

The element concentrations for Fe, Cr, Ti and Pb were determined by X-ray fluorescence spectrometry (XRF, Philips PW1400 apparatus), on bulk-sample pressed, boric-acid backed pellets. The accuracy of determinations was checked by using certified reference materials. Analytical errors were below 3% for Fe and Ti and below 10% for Pb and Cr.

Samples (approximately 0.2 g) were dissolved in a hot $HF–HNO_3–HCl$ acid mixture (approximately 15 mL), and refluxed with the acid mixture if the sample was only partly dissolved. Sc, Ba, Cd, Co, Cu, Ni, Zn and Mo concentrations were measured by inductively coupled plasma mass spectrometry (ICP–MS). The elements Sb, Se, Bi, Ag and Be were determined by inductively coupled plasma atom emission spectrometry (ICP–AES). All calibration standards were prepared in the acid matrix used for the soil samples. Caution was used in preparing and analyzing the samples to minimize contamination from air, glassware and reagents, which were all of suprapure quality. Replicated measures of standard reference materials (ESS-1 and ESS-2 were provided by the China Environmental Monitoring General Station), reagent blanks and duplicated soil samples (approximately, 20 of the total number of soil samples was used for this purpose) randomly selected from the set of available samples were used to assess contamination and precision. The relative standard deviation from analytical precision was routinely between 5 and 6%, and never higher than 10%.

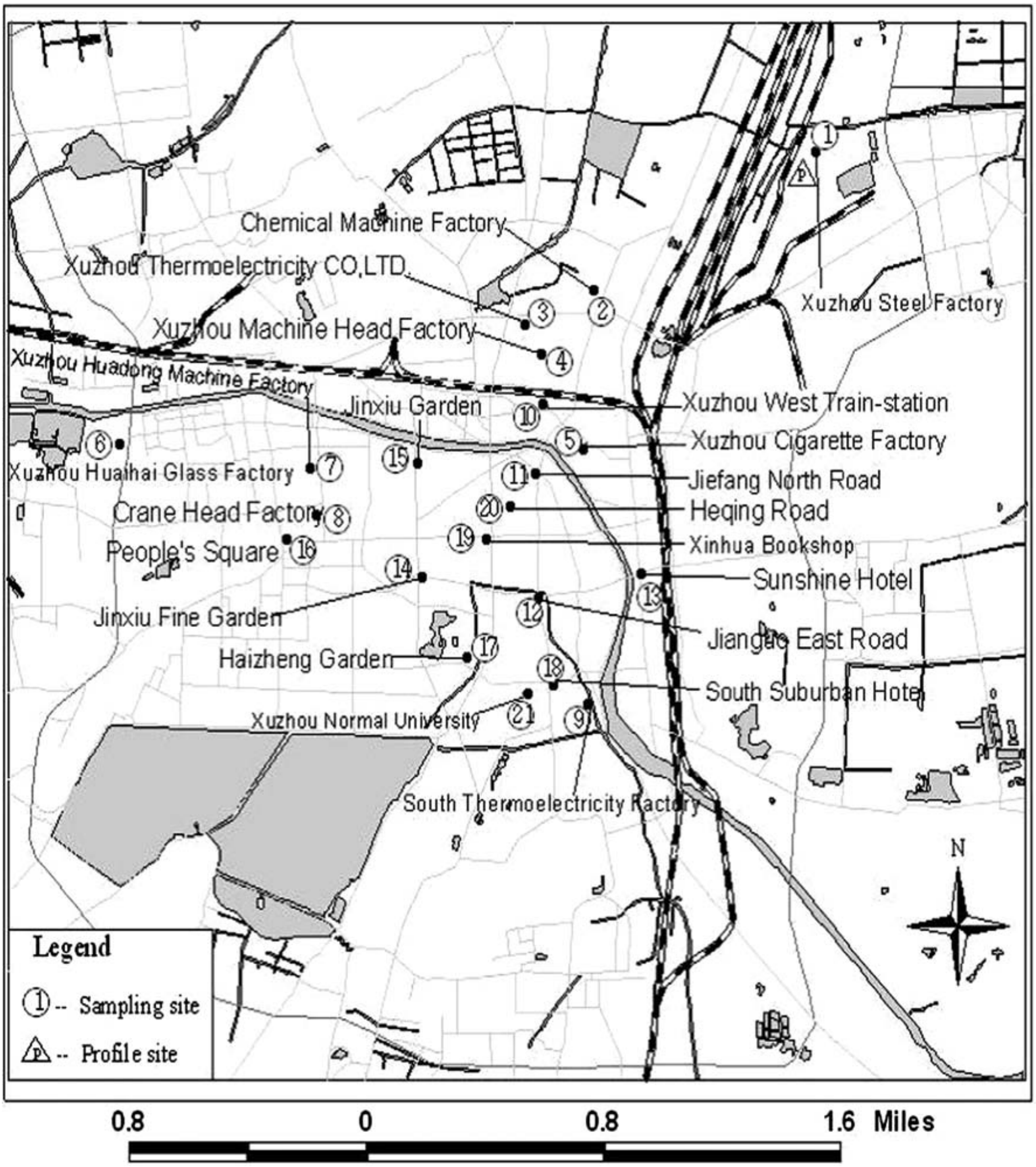


Fig. 1 Map of the Xuzhou city (Jiangsu) with location of sampling sites of topsoil

Results and discussion

Magnetic parameters

The descriptions of the data distributions are given in Table 1. The parameters of χ and SIRM are related to magnetic concentration. The median of specific magnetic susceptibility is $107\times10^{-8}\,m^3\,kg^{-1}$, ranging from 47×10^{-8} to 775×10^{-8}°$m^3\,kg^{-1}$. The median of χ in the topsoil is higher compared to that of the city of Vienna ($80.7\times10^{-8}\,m^3\,kg^{-1}$, Hanesch and Scholger 2002), indicating enhanced magnetic particles in the topsoil of the city of Xuzhou (China). The value of SIRM varies over one order of magnitude, ranging from 582.4×10^{-5} to $7302.2\times10^{-5}\,A\,m^2\,kg^{-1}$. The SIRM/$\chi$ ratios vary in a narrow range, between 8.76 and 26.06 kA m^{-1}. A common feature of all magnetic particles contained in the topsoils is their low χfd values, ranging from 0.97 to 6.78%. Coercivity of remanence ($(Bo)_{CR}$) may be used

Table 1 Magnetic parameters determined for 21 topsoil samples

	χ ($\times10^{-8}$ m^3 kg^{-1})	χ_{fd} (%)	SIRM ($\times10^{-5}$ A m^2 kg^{-1})	SIRM/χ (kA m^{-1})	$(Bo)_{CR}$ (mT)	S_{-100} dimensions
Minimum	47	0.97	582.4	8.76	31	0.519
Percentiles						
25	70.5	2.47	971	12.48	36	0.570
50	107	3.43	1678.2	13.56	37	0.639
75	211	4.45	3022.9	14.96	39.7	0.700
Maximum	775	6.78	7302.2	26.06	45	0.788

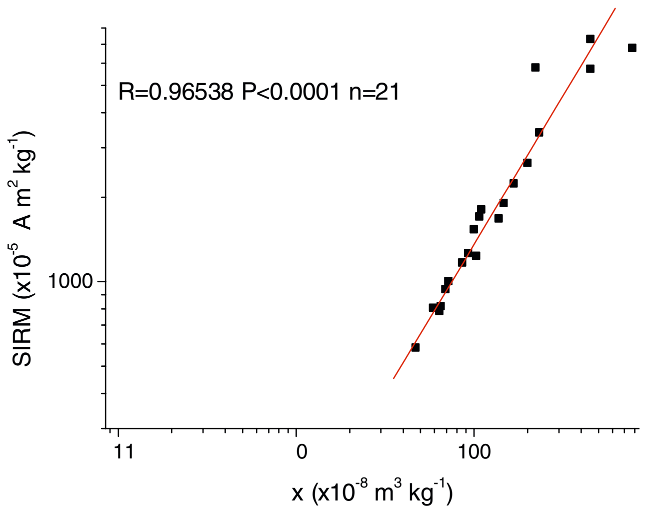


Fig. 2 Bi-logarithmic plot of specific low field susceptibility (χ) vs saturation isothermal remanent magnetization (*SIRM*) in all investigated topsoil samples

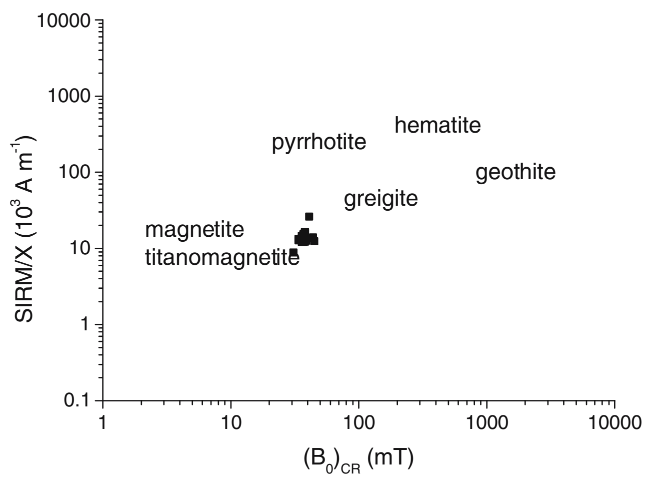


Fig. 3 Magnetic discrimination of minerals according to Peters and Thompson (1998) All the Xuzhou samples form a compact cluster within the magnetite–titanomagnetite range

as a fundamental grain-size parameter. For all topsoil samples, $(Bo)_{CR}$ ranges from 31 to 45 mT, suggestive of the dominance of magnetite. The differences in the proportions of ferromagnetic and antiferromagnetic minerals may be expressed by the S_{-100} parameter. S_{-100} ranges within a narrow limit from 0.519 to 0.788, which indicates the presence of antiferromagnetic minerals but ferrimagnetic minerals are the dominant magnetic minerals (Magiera and Strzyszcz 2000).

To develop a general characterization of magnetic minerals occurring in the topsoils of the city of Xuzhou, all the topsoil data were plotted on a series of diagrams (Figs. 2, 3, 4). This presentation allows visual estimation of which the magnetic particles are of anthropogenic origin. Magiera and Strzyszcz (2000) characterized the soils of Polish national parks in a similar way. They attributed the effect of increase of magnetic susceptibility in the topsoils to the deposition of fly ashes from coal combustion.

Figure 2 presents the relation between specific magnetic susceptibility (χ) and SIRM in a bi-logarithmic plot. The value of the SIRM/χ ratio is used to determine the grain size of the magnetic particles over several microns in diameter (Magiera and Strzyszcz 2000). Most of the data are plotted along the diagonal of the diagram and correspond to a value of approximately 14 kA m^{-1}, which according to Thompson and Oldfield (1986) is characteristic for a magnetite grain size of approximately 5 μm, and according to Magiera and Strzyszcz (2000) for a grain size of about 8 μm. The calculated values indicate the dominance of magnetically soft (probably multi-domain) ferromagnetic particles. Multi-domain grain sizes are common for industrial fly-ash particles (Flanders 1994; Hanesch and Petersen 1999). Maher et al. (1999) give a value of 16 kA $m^{-1}$for soft magnetite particles. The Xuzhou median value of 14 kA m^{-1} is close to the mean value of 12.5 kA m^{-1} determined by Hay et al. (1997) for polluted soils and to the mean values found by Shu et al. (2000) for atmospheric dust samples (12–16 kA m^{-1}). The content of anthropogenic ferromagnetic minerals decreases towards the bottom left corner of the diagram. Data which are displaced in the upper part of the diagram to the right of the group indicate samples with considerable contributions from relatively coarse multi-domain magnetite or from superparamagnetic grains. A higher content of

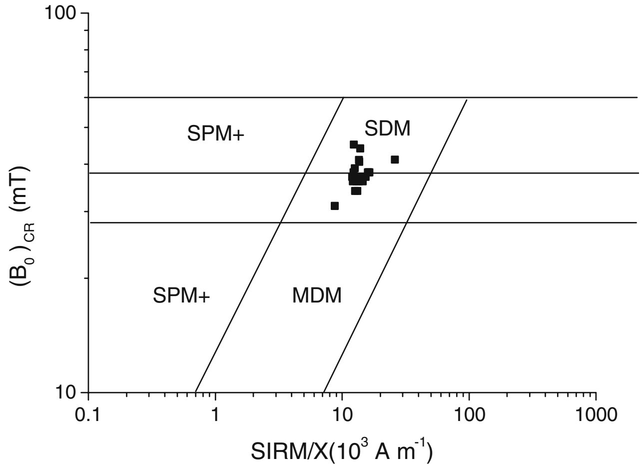


Fig. 4 Bi-logarithmic plot of coercivity of remanence $(Bo)_{CR}$ vs SIRM/χ in all investigated topsoil samples using the Magiera and Strzyszcz (2000) method. *SPM* superparamagnetic magnetite, *MDM* multi-domain magnetitie, *SDM* single-domain magnetite

superparamagnetic grains is excluded here because of the low χ_{fd} values (0.97–6.78%). Therefore, the presence of coarse grained ferromagnetic grains of anthropogenic origin is supported.

Peters and Thompson (1998) have constructed a diagram where $(Bo)_{CR}$ is plotted vs SIRM/χ to identify the carriers of magnetic minerals. All the current data form a close cluster within the (titano) magnetite area, probably slightly shifted toward the magnetically harder greigite area (Fig. 3).

Magiera and Strzyszcz (2000) have constructed a diagram where $(Bo)_{CR}$ is plotted vs SIRM/χ in order to distinguish particular domain structures in magnetic minerals. The corresponding data from the topsoils were plotted in this way (Fig. 4). All the samples are concentrated in the area between single-domain and multi-domain magnetite.

Morphology

Scanning electron microscopy of both magnetic extracts revealed the presence of typical spherules, consisting of a great deal of iron, probably iron oxides (Fig. 5). These spherules are attributed to gas-particle conversion from a high-temperature process (Vazrrica et al. 2003; Desenfant et al. 2004).

Correlation with concentrations of heavy metals

Coefficients of bi- variate correlations, linking all the analyzed elements and SIRM, are listed in Table 2. Table 2 indicates that Fe, Se, Ti, Sc, Ba, Bi, Pb, Cu, Zn, Cr and Mo show strong correlations with SIRM. Ag,

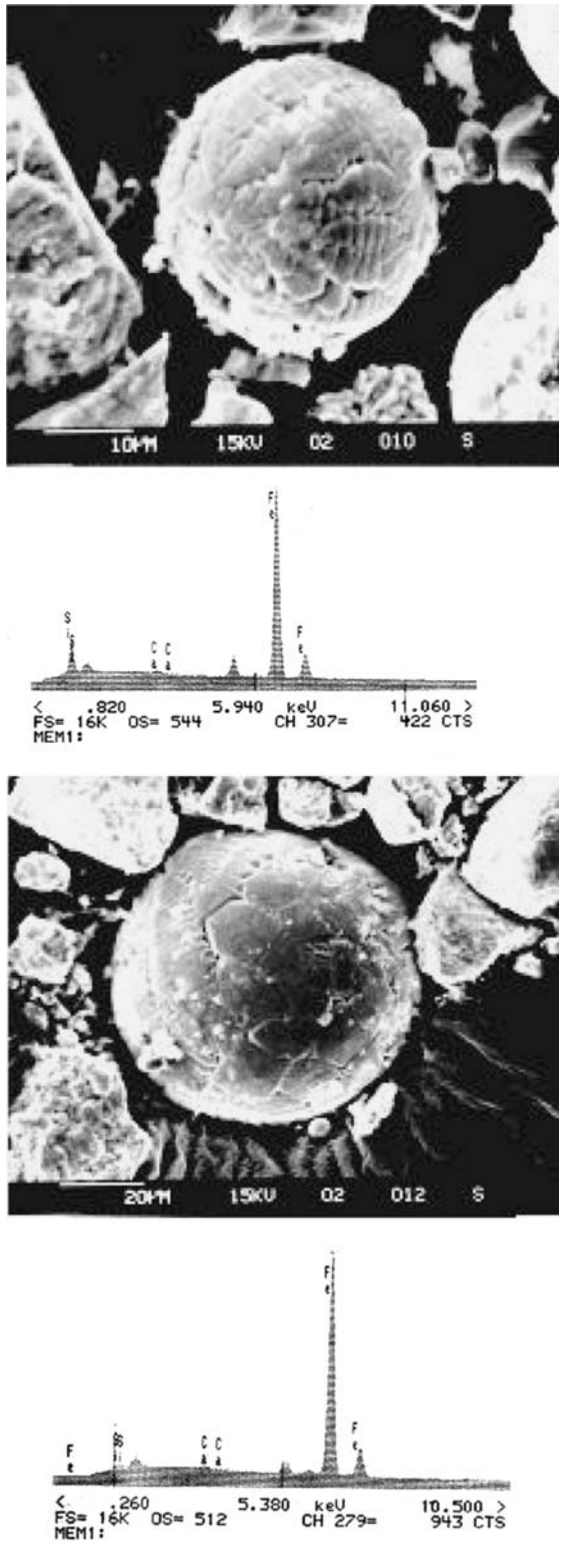


Fig. 5 Fe-rich spherical particles found in the analyzed samples

Table 2 Coefficients of bi-variate correlations between examined metal elements and SIRM (all normalized with respect to Al concentration)

Fe	Ti	Ag	Se	Sc	Ba	Bi	Pb	Be
0.825**	0.459*	0.359	0.718**	0.684**	0.733**	0.466*	0.734**	0.580**
Cu	Zn	Ni	Co	Cr	Cd	Sb	Mo	
0.652**	0.583**	0.226	0.356	0.605**	0.061	0.347	0.581**	

Note: *Correlation is significant at the 0.05 level (two tails), **Correlation is significant at the 0.01 level (two tails)

Ni, Co and Sb, on the other hand, show only a weak correlation with SIRM. The coefficient of bi-variate correlation between Cd and SIRM is 0.061, suggestive of no correlation between them.

Scatter plots and linear regressions of SIRM vs Fe, Se, Sc, Ba, Pb, Be, Cu, Zn, Cr and Mo are shown in Fig. 6.

Conclusions

From the results of the present study, the following conclusions can be drawn:

Magnetite was found as the dominant magnetic phase. Grain-size sensitive parameters indicated grain

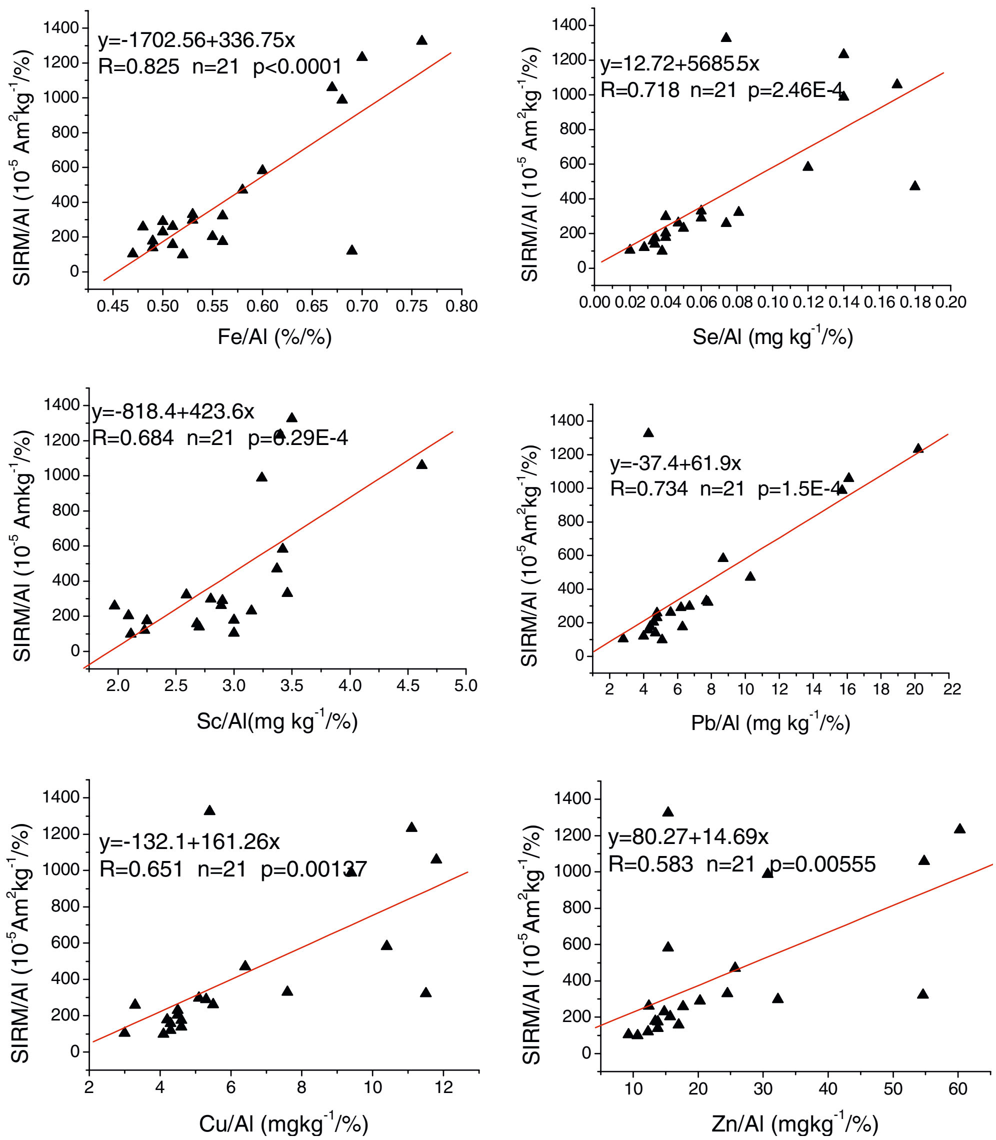
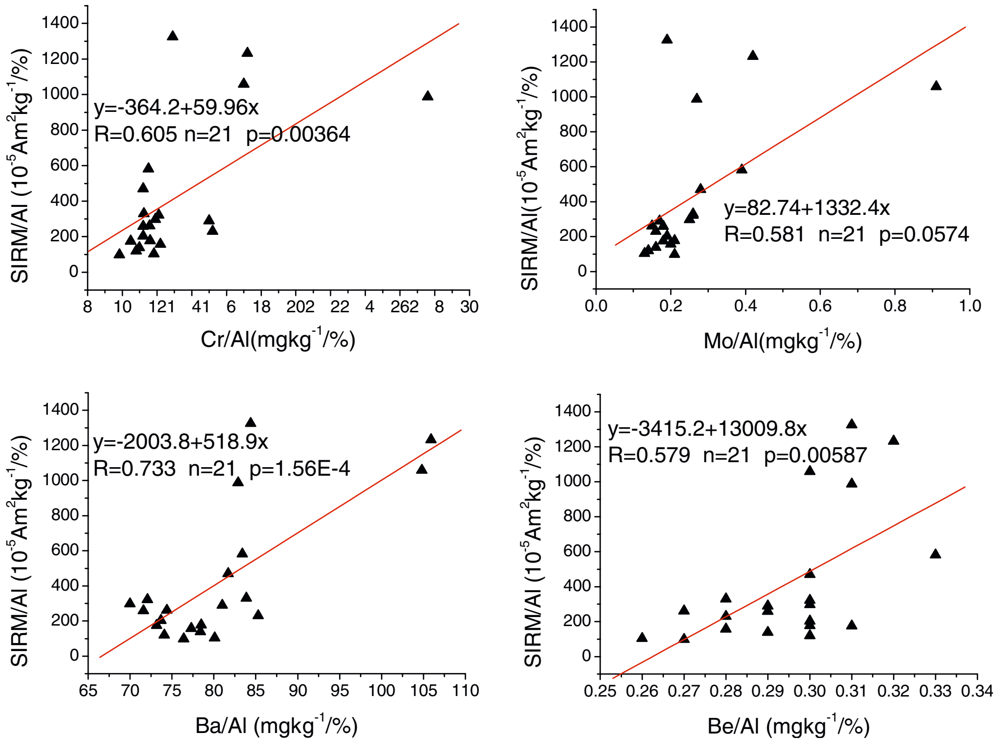


Fig. 6 Scatter plots and linear regressions of metal elements vs SIRM (all normalized with respect to Al concentration)

Fig. 6 (Contd.)



sizes of the magnetic minerals in all topsoil samples are between single-domain and multi-domain range.

Morphology of magnetic particles rich in iron corresponds to particles derived from combustion processes.

In this specific case, high correlation was found between the concentration of magnetite, presumably of anthropogenic origin, and the concentrations of Fe, Se, Ti, Sc, Ba, Bi, Pb, Cu, Zn, Cr and Mo, with weak correlation with Ag, Ni, Co and Sb. These findings suggest a common source and transport mechanism.

The main advantages of magnetic measurements are their simplicity, speed and low costs. Large data sets can be acquired in short times and repeated measurements easily performed. But, the application potential of magnetic methods should not be overestimated. Results obtained in one specific region may not be simply transferable to another region. Instead, detailed analysis should be carried out to establish basic correlations between various magnetic parameters and concentrations of heavy metals. Only if such a relationship is obvious, then can magnetic measurements be used in tracing and observing the future temporal and spatial variations of metal concentration.

References

Bacon JR, Berrow ML, Shand CA (1992) Isotopic composition as an indicator of origin of lead accumulations in surface soils. Int J Environ Anal Chem 46:71–76

Banerjee SK (1994) Contribution of fine-particle magnetism to reading the globe paleoclimate record. J Appl Phys 75(10):5925–5930

Bityukova L, Scholger R, Birke M (1999) Magnetic susceptibility as indicator of environmental pollution of soils in Tallin. Phys Chem Earth (A) 24(9):829–835

Chaparro MAE, Gogorza CS, Lavat A, Pazos S, Sinito AM (2002) Preliminary results of magnetic characterization of different soils in Tandil region (Argentina) affected by the pollution of metallurgical factory. Eur J Environ Eng Geophys 7:35–58

Chaparro MAE, Bigegain JC, Sinito AM, Gogorza CS, Jurado S (2003) Preliminary results of magnetic measurements on stream sediments from Buenon Aires Province, Argentina. Stud Geo-Phys Geod 47:53–77

Chaparro MAE, Bigegain JC, Sinito AM (2004) Magnetic studies applied to different environments (soils and stream sediments) from a relatively polluted area in Buenos Aires Province, Argentina. Environ Geol 45:654–664

Dearing JA, Elner JK, Happy-Wood CM (1981) Recent sediment fux and erosional processes in a welsh upland lake-catchment based on magnetic susceptibility measurements. Quatern Res 16:356–372

Desenfant F, Petrovsky E, Rochette P (2004) Magnetic signature of industrial pollution of stream sediments and correlation with heavy metals: case study from South France. Water, Air, Soil Pollut 152:297–312

Durza O (1999) Heavy metals contamination and magnetic susceptibility in soils around metallurgical plant. Phys Chem Earth (A) 24(6):541–543

Flanders P (1994) Collection, measurement, and analysis of airborne magnetic particulates from pollution in the environment. J Appl Phys 75:5931–5936

Hanesch M, Petersen N (1999) Magnetic properties of a recent parabrown-earth from Southern Germany. Earth Planet Sci Lett 169:85–97

Hanesch M, Scholger R (2002) Mapping of heavy metal loadings in soils by means of magnetic susceptibility measurements. Environ Geol 42:857–870

Hanesch M, Scholger R, Rey D (2003) Mapping dust distribution around an industrial site by measuring magnetic parameters of tree leaves. Atmos Environ 37:5125–5133

Hay KL, Dearing JA, Baban SMJ, Loveland P (1997) A preliminary attempt to identify atmospherically-derived pollution particles in English topsoils from magnetic susceptibility measurements. Phys Chem Earth 22(1–2):207–210

Heller F, Strzyszcz Z, Magiera T (1998) Magnetic record of industrial pollution in forest soils of Upper Silesia, Poland. J Geophys Res 103:17767–7774

Hoffmann V, Knab M, Appel E (1999) Magnetic susceptibility mapping of roadside pollution. J Geochem 66 (1–2):313–326

Kapicka A, Petrovsky E, Ustjak S, Machackova K (1999) Proxy mapping of fly-ash pollution of soils around a coal-burning power plant: a case study in Czech Republic. J Geochem Explor 66:291–297

Kapička A, Jordanova N, Petrovsky E, Ustjak (2000) Magnetic stability of power-plant fly ash in different solutions. Phys Chem Earth (A) 25(5):431–436

Kelly J, Thornton I, Simpson PR (1996) Urban geochemistry: a study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain. Appl Geochem 11:363–370

Magiera T, Strzyszcz Z (2000) Ferrimagnetic minerals of anthropogenic origin in soils of some polish national parks. Water, Air, Soil Pollut 124:37–48

Maher BA (1986) Characterisation of soils by mineral magnetic measurements. Phys Earth Planet Interiors 42:76–92

Maher BA, Thompson R, Hounslow MW (1999) Introduction. In: Maher BA, Thompson R (eds) Quaternary climates, environments and magnetism. Cambridge University Press, Cambridge, pp 1–48

Manta DS, Angelone M, Bellanca A, Neri R, Sprovieri M (2002) Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci Total Environ 300:229–243

Peters C, Thompson R (1998) Magnetic identification of selected natural iron oxides and sulphides. J Magn Magn Mater 183:365–374

Petrovsky E, Kapicka A, Zapletal K, Sebestova E, Spanila T, Dekkers MJ (1998) Correlation between magnetic parameters and chemical composition of lake sediments from northern Bohemia—preliminary study. Phys Chem Earth 23(9):1123–1126

Shu J, Dearing JA, More AP, You L, Li C (2000) Magnetic properties of daily sampled total suspended particulates in Shanghai. Environ Sci Technol 34:2392–2400

Thompson R, Oldfield F (1986) Environmental magnetism. Allen & Unwin, London

Vazrrica D, Dongarra G, Sabatina G, Monna F (2003) Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy. Environ Geo 44:222–230

Walling DE, Peart MR, Oldfield F, Thompson R (1979) Suspended sediment sources identified by magnetic measurements. Nature 281:110–113