Magnetic response of heavy metals pollution in urban soils: magnetic proxy parameters as an indicator of heavy metals pollution

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Abstract

Magnetic and chemical analyses were performed on urban soils collected from Lishui city, China, to evaluate the potential of magnetic measurements as an indicator of heavy metals pollution in urban soils. Magnetic susceptibility (χlf), saturation isothermal remanent magnetization (SIRM) and concentration of metals (Cd, Cu, Pb and Zn) were measured on samples of urban soils. Concentration-dependent magnetic parameters (χlf and SIRM) are significantly positively correlated to the concentration of heavy metals (Cr, Ni, Cu, Zn, Cd and Pb), but not correlated with V, Co and As. The χlf and SIRM also have strong linear correlation with integrated pollution index (IPI), indicating that χ and SIRM can be used as effective proxy indicators for the pollution degree of heavy metals in urban soils. Magnetite was identified as the possible dominant magnetic carrier using temperature-dependent measurements of saturation magnetization (Ms-T curve). The results proved the applicability of magnetic method in detecting heavy metals pollution in urban soils.

Key Words

Urban soil, heavy metal, magnetic susceptibility, saturation isothermal remanent magnetization.

Introduction

Soil contamination is considered as one of the main threats to the environmental quality and the health of people. Accelerated industrialization and urbanization has resulted in an increased pollution of soil, water and a growing risk for heavy metal uptake by human. Urban soils are the “recipients” of various pollutants and the heavy metal concentration in soils is frequently reported as an indicator of urban environmental quality (Wong *et al*. 2006). Therefore, it is important to understand the content, distribution, mobility and possible sources of heavy metals in urban soils. Recently, the rapid, non-destructive and inexpensive magnetic measurements have increasingly been used as complementary methods to help characterise urban soil pollution. It has been accepted as a rapid mapping tool and proxy indicator of heavy metal pollution in soils and sediments. The concept of magnetic measurement is based on the assumption that magnetic particles and pollutants are produced together during anthropogenic activities, such as industrial and traffic processes. For example, many studies have indicated that there is a good relationship between heavy metals and magnetic parameters in soils (Blaha *et al*. 2008; Chaparro *et al*. 2008; El-hasan 2008; Lu *et al*. 2006, 2007; Spiteri *et al*. 2005; Yang *et al*. 2007). Their close relationship has been proven by combined analyses of chemical composition and magnetic parameters of soils. The strong positive correlation between magnetic parameters and heavy metal contents has been observed in urban soils (e.g. Lu *et al*. 2006, 2007; Yang *et al*. 2007). Although many studies on magnetic proxy of heavy metal concentrations have been carried out in developed countries and big industrial cities in China, only limited data is available on magnetic monitoring of heavy metals in middle and small cities of rapidly developing regions. Therefore, this work aims to apply the environmental magnetism approach to examine the magnetic properties of urban soils, to help assess heavy metal pollution, and to establish links between the enhanced concentrations of magnetic particles and heavy metals.

Methods

Soils

The studied area Lishui city (the geographical position being N28°25-28′ and E119°53′-58′), situated in Zhejiang Province, China, is a small but rapidly growing green city without significant industrial activity. Traffic emissions and anthropogenic activities may be the main source of urban pollution governing the accumulation of heavy metal in soils. Soil parent materials in this urban area are mainly Quaternary alluvial deposits with low magnetic mineral content. A total of 126 topsoil samples were collected from the city planning area of Lishui, which includes all high density inhabited and commercial centre of city, but also extends to new developing industrial parks and un-urbanized areas around the city. The top 10 cm layer of the soil was taken with a stainless steel spade and stored in a plastic bag. At each sampling site, 5-6 subsamples of topsoil were taken and then mixed thoroughly to obtain a bulk sample to get a representative sample. Samples were air-dried, ground, passed through a nylon sieve of a 100 mesh, and stored. Additionally, the outcropping rock and parent material samples were collected in order to estimate the geological background on the magnetic parameters in urban soils.

Methods

Magnetic susceptibility of urban soils was measured using a Bartington MS2 magnetic susceptibility meter linked to a MS2B dual frequency sensor (470 and 4700 Hz). Frequency dependent susceptibility (χfd) was calculated as a percentage of [(χlf-χhf)/χlf×100]. Isothermal remanent magnetization (IRM) was performed using a Molspin pulse magnetizer and measured on a Molspin spinner magnetometer (Molspin Ltd.). The IRM acquired at 1T was referred to as the saturation IRM (SIRM). Using an IRM acquired with a back field of 100mT, the S_{-100mT} ratio was calculated as follows: S_{-100mT} =IRM_{-100mT}/SIRM. High-temperature saturation magnetization (Ms-T) curves for representative soil samples were undertaken in air on a Vibrating Field Transition Balance (VFTB, N. Petersen, Munich). Approximately 1.0 g of each sample was digested by the *aqua regia* in a microwave oven (Mars-5, CEM Company, USA). After digestion, the solution was filtered and diluted with deionised water to get 50 ml of solution. Concentrations of Cr, V, Co, Ni, Cu, Zn, As, Cd, and Pb were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Accuracy of analyses was checked using standard and duplicate samples. Data statistical analysis was made with the EXCEL software.

Results

Magnetic parameters and heavy metal contents of urban soils

Magnetic susceptibility (χlf) and saturation isothermal remanent magnetization (SIRM) from urban soils of Lishui city are shown in Table 1. The χlf and SIRM of bedrocks and parent materials (geological background) show low mean values of less than 32×10^{-8} m^3/kg and 26.0×10^{-4} Am^2/kg, respectively, reflecting a rather insignificant geological background effect. Urban soils yield relatively high mean χlf values of 95.5×10^{-8} m^3/kg, ranging from 9.8×10^{-8} to 503×10^{-8} m^3/kg. The elevated χlf and SIRM values in the urban soils indicate that the anthropogenic inputs contain a higher portion of magnetic material than the lithogenic/pedogenic background. SIRM shows a good linear correlation with χlf (r^2=0.94, p<0.01) (Figure 1), suggesting that the two parameters can be assumed as representative of the amount of ferrimagnetic particles in the urban soils and equally suited for the magnetic proxy.

Table 1. Statistical summary of magnetic parameters in urban soil samples in Lishui city, China

	χlf (10^{-8} m^3/kg)	χfd (%)	IRM_{20mT} (10^{-4} A m^2/kg)	SIRM	S_{-100mT} (%)
Min	9.8	0.00	6.1	954.4	15.2
Max	503.9	11.11	3182.0	28517.5	100.0
Mean	95.5	3.42	603.9	7078.4	84.6
SD	64.1	2.49	449.9	4678.8	12.4
Median	67.6	2.70	379.9	4832.3	89.2
Skewness	1.84	0.60	2.04	1.77	-1.93

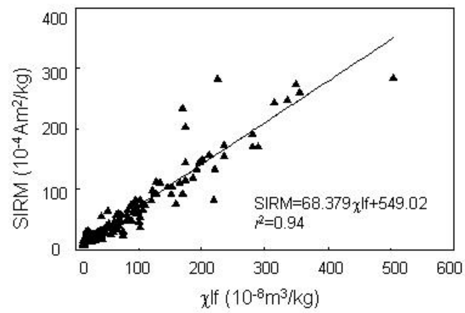

Figure 1. Plot of SIRM versus magnetic susceptibility (χlf) for urban soils

The concentration of heavy metals in urban soils is shown in Table 2. Results show the contents of Cd, Cu, Pb, and Zn are higher than the background concentration (BC) of soils in the Zhejiang Province (ZPSSO 1994), indicating that these urban soils have been strongly polluted with Cd, Cu, Pb, and Zn. This is considered to be the result of a gradual accumulation from automobile exhausts and other anthropogenic pollution sources over time. Compared to average concentrations in urban soils of other larger cities in China, especially large and/or old industrialized cities (e.g. Lu *et al*. 2006, 2007; Yang *et al*. 2007), the Cr,

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Cu and Ni concentrations in urban soils samples of Lishui city are much lower (Table 2). On the other hand, Ni does not present evident enrichment with respect to background values.

To assess the soil pollution level, a pollution index (PI) of each metal and an integrated pollution index (IPI) of the seven metals were calculated. The PI was defined as the ratio of the heavy metal concentration in the study to the background concentration of the corresponding metal in the studied area. The IPI of the seven metals was defined as the mean value of the metal'PI, which is an indicator of the heavy metal contamination. The mean IP of Cd, Cu, Pb, and Zn were 4.3, 2.2, 2.7, and 3.3, respectively, indicating the presence of metal pollution in soils. By contrast, Cr, Ni and As show low contamination with mean PI of 1.06, 0.71, and 1.28, respectively, indicating that there was no obvious pollution of these heavy metals in these urban soils. The IPI of soils varied from 0.76 to 5.51 with an average of 1.92 (Table 2).

Table 2 Statistical summary of heavy metal concentrations (mg/kg) in urban topsoil samples in Lishui city, China (n=126)

	Cr	V	Co	Ni	Cu	Zn	As	Cd	Pb	IPI
Min	9.41	17.95	2.17	3.70	4.72	60.04	0.93	0.05	29.18	0.76
Max	105.10	177.26	34.00	50.21	140.83	873.53	36.45	3.19	166.93	5.51
Mean	34.54	42.55	6.35	14.33	35.80	192.38	8.81	0.53	63.15	1.92
SD	10.64	10.81	1.78	4.92	14.57	86.91	3.53	0.37	15.38	0.93
Median	32.36	39.08	5.99	12.74	30.92	157.00	7.60	0.34	58.73	1.66
Skewness	2.08	3.94	5.02	2.16	2.24	2.89	2.51	2.41	1.89	2.02
BC	36.73	-	-	22.31	17.76	69.00	6.45	0.167	25.61	

Correlation between magnetic parameters and heavy metal contents in urban soils

Table 3 lists the linear correlation coefficients between the concentration of heavy metals and magnetic parameters in urban soils. The correlation matrix indicates that the concentration-dependent magnetic parameters (χlf, IRM$_{20mT}$, and SIRM) all have a strong linear correlation with heavy metal concentrations except for V, Co and As (Table 3). The highest coefficients are found for Zn (0.703) and Cd (0.687). Of the three concentration-dependent magnetic parameters, χ is the best indicator of heavy metal pollution. Significant correlations between magnetic parameters (χlf and SIRM) and PLI can be clearly seen from the scatter plots shown in Figure 2. The results indicate the existence of positive relationship between heavy metal contamination and magnetic enhancement in urban soils. The fact that content of heavy metals associated closely with magnetic parameters suggested that magnetic measurements can be used a proxy indicator of heavy metals pollution in urban soils.

Table 3 Correlation coefficients of magnetic parameters and heavy metal concentrations in urban soil samples in Lishui city, China (n=126)

	Cr	V	Co	Ni	Cu	Zn	As	Cd	Pb
χlf	**0.461**	0.014	0.040	**0.493**	**0.542**	**0.703**	0.017	**0.687**	**0.526**
IRM$_{20mT}$	**0.406**	0.014	0.040	**0.422**	**0.455**	**0.586**	0.022	**0.631**	**0.414**
SIRM	**0.417**	0.064	0.082	**0.440**	**0.467**	**0.603**	0.010	**0.691**	**0.431**
χfd	-0.185	0.082	0.052	0.044	0.053	-0.117	0.165	-0.156	0.088
SIRM/χ	-0.095	**0.539**	**0.358**	0.022	-0.124	-0.218	-0.142	**-0.243**	**-0.236**
S$_{-100mT}$	0.165	0.030	0.069	0.124	0.022	0.081	0.010	0.166	0.081

Correlations in bold are significant at p<0.01.

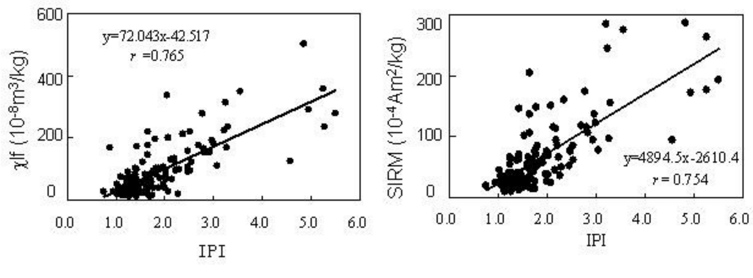

Figure 2. Correlation between the integrated pollution index (IPI) and magnetic parameters (magnetic susceptibility and SIRM). The correlation analysis was carried out after eliminating two outlier samples.

Identification of magnetic particle source in urban soils
High-temperature magnetization (Ms-T) curve showing that magnetization varies with temperature are useful for the identification of magnetic mineralogy. Figure 3 illustrates the temperature-dependent magnetization variations of representative sample. The Ms-T curve show a major decrease in magnetization at about 580°C, the Curie temperature of magnetite, suggesting that magnetite is the dominant magnetic carrier. In addition, the increase of magnetization at 410°C could be due to the presence of a small amount of pyrite, which is transformed into magnetite. However, the transform is much weaker than the phase transition at 580°C (magnetite), revealing that magnetite is the dominant magnetic carrier. Upon cooling, a sharp increase was initiated at around 580°C, indicating the presence of magnetite.

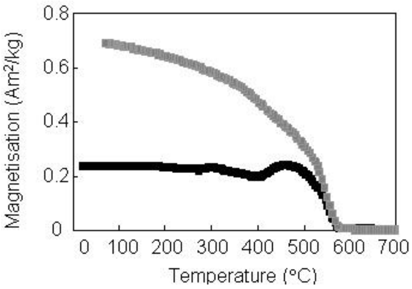

Figure 3. High-temperature magnetization (Ms-T curve) of representative urban soil sample. Solid and dashed lines represent heating and cooling runs, respectively. The applied field is 355 mT.

Conclusion
Magnetic measurements and heavy metal analyses performed on urban soils from a rapidly growing small city showed significantly elevated concentrations of magnetism and heavy metals. Concentration-related magnetic parameters have significant linear correlation with the concentration of Cr, Ni, Cu, Zn, Cd and Pb. The magnetic susceptibility and SIRM of urban soils also significantly correlates with PLI, their correlation coefficients are 0.765 and 0.754, respectively. High-temperature magnetization variation of urban soil indicates that the predominant magnetic carrier in urban topsoils is magnetite. The elevated magnetism and heavy metal concentration of urban soils are attributed to traffic emissions and anthropogenic activities. These results suggested that magnetic parameters can serve as an effective surrogate indicator for heavy metal pollution in these urban soils.

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