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Relationships between magnetic susceptibility and heavy metals in urban topsoils in the arid region of Isfahan, central Iran

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ABSTRACT

Recently methods dealing with magnetometry have been proposed as a proper proxy for assessing the heavy metal pollution of soils. A total of 113 topsoil samples were collected from public parks and green strips along the rim of roads with high-density traffic within the city of Isfahan, central Iran. The magnetic susceptibility (χ) of the collected soil samples was measured at both low and high frequency (χlf and χhf) using the Bartington MS2 dual frequency sensor. As, Cd, Cr, Ba, Cu, Mn, Pb, Zn, Sr and V concentrations were measured in the all collected soil samples. Significant correlations were found between Zn and Cu (0.85) and between Zn and Pb (0.84). The χfd value of urban topsoil varied from 0.45% to 7.7%. Low mean value of χfd indicated that the magnetic properties of the samples are predominately contributed by multi-domain grains, rather than by super-paramagnetic particles. Lead, Cu, Zn, and Ba showed positive significant correlations with magnetic susceptibility, but As, Sr, Cd, Mn, Cr and V, had no significant correlation with the magnetic susceptibility. There was a significant correlation between pollution load index (PLI) and χlf. PLI was computed to evaluate the soil environmental quality of selected heavy metals. Moreover, the results of multiple regression analysis between χlf and heavy metal concentrations indicated the LnPb, V and LnCu could explain approximately 54% of the total variability of χlf in the study area. These results indicate the potential of the magnetometric methods to evaluate the heavy metal pollution of soils.

1. Introduction

Dust that accumulates on soils and roadsides in the urban and industrial areas is indicator of heavy metal contamination from atmospheric deposition (Culbard et al., 1988). Method based on the Magnetometric properties of soils are increasingly applied as proxy methods for evaluating the heavy metal pollution of soils, sediments and dusts, because such methods are rapid, inexpensive and non-destructive and can be used for mapping of the contaminated soils (e.g., Wang and Qin, 2005). In addition, the interest in the use of magnetometric methods is increasing because of their rapidity as a single measurement of soil samples makes it possible to establish dense grids of sampling sites (Hanesch and Scholger, 2002).

There have been numerous studies linking the magnetic properties of soils to the urban contamination in a variety of environments. For example, Lu and Bai (2006) reported that soils near urban and industrial areas had an increased magnetic susceptibility, which they attributed to the deposition of magnetic particles such as dust from the metallurgical industry and fly ash from coal combustion. Strzyszcz and Magiera (1998) reported relatively high correlation coefficients between concentrations of Zn, Pb, and Cd in forest soils of the Upper Silesian industrial regions (Southern Poland) and magnetic susceptibility. Magnetic properties and heavy metal concentration (Cu, Cr, Pb, Ni, and Zn), which were measured on vibracore samples, were found to be potential indicators of the contamination of seabed sediments due to the shipping activities in the Hong Kong Harbor (Chan et al., 2001). The whole-core magnetic susceptibility measurements showed a higher concentration of magnetic particles in the surface layer of the sediment cores, and significant correlations were observed between the magnetic susceptibility and concentrations of Pb, Zn and Cu, as well as the Tomlinson pollution load index (PLI).

Lecoanet et al. (2003) assessed the potential of the magnetic techniques to determine the contaminating emission sources and its effects on the contamination of surface and bottom soil samples. The results showed that the contents of magnetic minerals with higher magnetic coercivity increased with depth from surface to the bottom in the soil profiles.

The scanning electron microscopy (SEM) analysis was used to study the surface soil samples collected from Xuzhou, a large industrial city in China that is a center for mining and heavy industries

Abbreviations: χlf, Low frequency magnetic susceptibility; χhf, High frequency magnetic susceptibility; χfd, Frequency-dependent susceptibility; As, Arsenic; Cd, Cadmium; CU, Copper; Ba, Barium; Sr, Strontium; Cr, Chromium; V, Vanadium; Mn, Manganese; Zn, Zinc; Pb, Lead; MS, Magnetic susceptibility; PLI, Pollution load index; K–S, Kolmogorov–Smirnov; Fe, Iron; EC, Electrical conductivity; pH, Soil acidity; SOM, Soil organic carbon; CCE, Calcium carbonate equivalent; CEC, Cation exchangeable capacity.

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(Wang and Qin, 2005). Magnetic minerals in the topsoil samples were found in the form of spherules and mainly originated from the anthropogenic inputs. In addition, the authors showed that Pb, Cu, Zn, Se, Sc, Mo, Fe, and Bi concentrations were highly correlated with the magnetic susceptibility. The concentrations of Ag, Ba, Cd, Ni, Cr, Sb, and Sn, on the other hand, had weak correlations with magnetic susceptibility. The Tomlinson pollution load index (PLI) was also significantly correlated with the magnetic susceptibility.

A further study of the urban soils in Hangzhou, eastern China revealed a positive correlation between magnetic properties and Cu, Zn, Cd and Pb concentrations (Lu and Bai 2006). Magnetic parameters χ, ARM, $IRM_{20\ mT}$, Hard IRM and SIRM increased in the order of industrial area > roadside > residential ≈ campus > public parks and the trend was nearly in the line with the changes in the concentrations of Pb, Cu, Zn and Cd. The source of the magnetic minerals was attributed to the industrial activity, automobile exhaust and the deposition of atmospheric particulate matter. Contrary to Cu and Cd that had low correlation with studied magnetic properties, Zn showed the highest correlation and Pb showed medium correlation with magnetic properties (Lu and Bai, 2006). The results of the study by Lu et al. (2007) for the soils in Hangzhou confirmed the results reported in the study on the significant relationship between Cr, Cu, Pb and Zn concentrations and the magnetic susceptibility and SIRM.

Comparison of the results for surface soil samples collected from urban and agricultural sites in Shanghai using magnetic techniques for monitoring soil pollution showed that compared with the background, magnetic signals of the urban topsoils greatly increased with the magnetic susceptibility, while those of the agricultural surface soil samples were only slightly increased (Hu et al., 2007). Their results suggest that coarse-grained ferromagnetic particles were deposited on the urban topsoils, therefore indicating that the extra magnetic minerals accumulated in the urban topsoils are neither inherited from soil parent materials nor from the pedogenic processes, but originate from anthropogenic activity.

The analytical results of Lu et al. (2008) are in accordance with the accumulation of heavy metals and magnetic minerals in soils along an urban–rural gradient in Hangzhou city, China and indicated that heavy metal concentrations and magnetic susceptibility (χlf) in soils decreased with distance from the urban center of Hangzhou. There were significant statistical correlations between heavy metal concentrations, χlf and distance from the urban center. The soils in the urban areas were enriched with Cd, Cu, Pb and Zn and thus provide evidence for the accumulation of heavy metals through anthropogenic activities (Lu et al., 2008).

However, no study has been reported on the monitoring of metal pollution of soils using the magnetometric methods in Iran. Therefore, the objectives of this study were to (i) to characterize the Zn, Pb, Cu, Ba, Cr, As, Mn, Cd, Sr and V concentrations in topsoils and (ii) to examine the feasibility of using the magnetic susceptibility for the heavy metal pollution assessment of urban topsoils in the arid region of Isfahan, central Iran.

2. Materials and methods

2.1. Study site and sampling

This investigation was conducted in the city of Isfahan, a city in central Iran with a population of 1.6 million inhabitants. The study area extends from 51°31′30″ E to 51°45′29″ E longitude and 32°35′ N to 32°47′47″ N latitude, encompassing an area of approximately 324 km^2 around the Zayandehroud river, which flows from west to southeast (Fig. 1). The parent rock materials are mainly recent river (?) terraces and alluvial deposits, and undifferentiated terraces all of Quaternary age. The soils of this region are Aridisols belonging to different suborders, such as Calciargids, Haplocambids, Haplogypsids and Haplosalids. The average annual rainfall and temperature of the region are 140 mm and 14.5 °C, respectively.

A total of 113 soil samples (0–10 cm depth) were collected from the study area (Fig. 1). Sampling sites were selected from the green vegetated space of roadsides and public parks. Roadside soil samples were collected from the locations along the rim of road, including highways and high-density traffic streets. At each sampling point, three sub-samples were taken over a 5 × 5 m surface, and then mixed to obtain a bulk sample. Such a sampling strategy was adopted to reduce the possibility of random influence of urban waste not clearly visible. All the samples were collected using a stainless steel spatula and were stored in PVC sample bags. Before analyses, the soil samples were air-dried and sieved through a 2-mm sieve.

2.2. Magnetic susceptibility measurement and laboratory analyses

Magnetic susceptibility (χ) was measured at low (0.47 kHz; χlf) and high frequencies (4.7 kHz; χhf), respectively using a Bartington MS2 dual frequency sensor. The χ value is dependent on the concentration of ferrimagnetic minerals within a sample, although it is also sensitive to magnetic grain size (Lu and Bai, 2006). Frequency-dependent susceptibility (χfd), which indicates the presence of superparamagnetic (SP) grain sizes, was calculated using Eq. (1):

$$\chi fd(\%) = [(\chi lf - \chi hf) / \chi lf] \times 100 \quad (1)$$

Soil samples (0.2 g) were dissolved in a hot HF-HNO3-HCl acid mixture (15 ml), and refluxed with the acid mixture if the sample was only partly dissolved. Arsenic, Cd, Cr, Ba, Cu, Mn, Pb, Zn, Sr, and V concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). Soil pH was measured in saturated soil using a glass electrode (McLean, 1982) and electrical conductivity (EC) of the saturated extract was determined using a conductivity meter (Sarkar and Haldar, 2005). Calcium carbonate equivalent (CCE) was measured by Bernard's calcimetric method (USDA, 1996). Soil organic matter (SOM) was determined using the wet combustion method (Nelson and Sommers, 1982) and cation exchange capacity (CEC) by extraction with sodium acetate (Rhoades, 1982). Percentages of clay, sand and silt were measured using the Hydrometer method (Gee and Bauder, 1986).

2.3. Statistical analysis and pollution index calculation

Descriptive statistics including the mean, standard deviation, minimum, maximum, median, range, kurtosis and skewness were determined. Pearson linear correlations among various parameters were calculated using SPSS software (Swan and Sandilands, 1995) and used to interpret the relationships between heavy metals and soil properties.

A stepwise regression procedure was used to regress magnetic susceptibility on the heavy metal concentration. Selection of factors for inclusion in the model was based on probability ≤0.05 (Freund and Littell, 2000). Magnetic susceptibility was the dependent variable and the heavy metal concentrations were the independent variables. The models were of the following form:

$$Y = b_o + b_1F_1 + b_2F_2 + \ldots + b_nF_n + \varepsilon \quad (2)$$

Where Y represents estimated magnetic susceptibility, b_o to b_n are coefficients, F_1 to Fn are the metal concentrations and ε represents residual error. The selection of the best predictive model was performed based on determination coefficient (R^2).

The integrated pollution index for the ten metals was used to assess the soil environmental quality (Tomlinson pollution load index,