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Vertical and horizontal distribution of magnetic susceptibility and metal contents in an industrial district of central Iran

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ABSTRACT

This study was conducted to determine the vertical and horizontal distribution of selected metals and magnetic susceptibility (χlf) in an industrial site located in Isfahan province, central Iran. For this purpose, we used a grid sampling methodology and excavated 202 profiles. Soil samples were then collected from 0–30, 60–90, and 120–150 cm depths. The mass magnetic susceptibility (χ) of the soil samples was measured at both low and high frequencies (χlf and χhf) using the Bartington MS2 dual frequency sensor; and χfd was also calculated. Soil samples were also analyzed for iron (Fe), manganese (Mn), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), chromium (Cr) and cobalt (Co) concentrations. The results showed that there were positive significant correlations among selected metals including Zn, Pb, Fe and Mn, which were mainly added through coal fly ash from an iron smelting factory at the studied site, while the concentration of Ni, Cr and Co was mainly controlled by the parent material of the soils. The trends in results at the site of study were similar in vertical and horizontal distribution for the industrial originated metals as judged by pollution load index (PLI) using χlf. The results of SEM/EDX also confirmed the presence of spheroid of magnetic particles in the surface soil samples taken in close proximity of the factory. Based on the results using the contamination factors (CF) determined for selected metals, the following order was observed: Pb > Zn > Mn > Fe > Cu > Ni ≥ Co > Cr. The results also suggested that magnetic methods could be used to estimate the metal contamination from anthropogenic sources in industrial soils.

1. Introduction

Soil pollution is a serious environmental issue throughout the world (Gallego et al., 2002; Mico et al., 2006). Among the soil pollutants, heavy metals are especially hazardous due to their toxicological importance in ecosystems and human health (Facchinelli et al., 2001; Mico et al., 2006). It is generally considered that heavy metals accumulated in soils come from two primary sources natural (e.g. parent material weathering) (Nanos and Rodríguez Martín, 2012), and anthropogenic (e.g. metalliferous industries and mining, vehicle exhaust, agronomic practices, etc.) (Zhang, 2006). Various sources have been reported in literature that are involved in the enrichment of metals in soils including vehicle exhaust, metal ore processing and smelting, mining, milling operations (Davies, 1997), as well as the agricultural production practices such as organic and mineral fertilization, the application of pesticides and irrigation water (Romic and Romic, 2003).

Due to increased industrialization, the problem of environmental pollution has been increasing for the past several decades (Karimi et al., 2011). These problems are caused by the disposal of industrial wastes whether solids, liquids or gases, which have the potential to pollute the soil. Several studies have shown that the area in close proximity of the industrial activity leads to the contamination of soil, water and crops (Miro et al., 2004).

Magnetic properties of soils reflect the effects of soil mineral composition, especially the quantity of ferrimagnetic minerals. Magnetic susceptibility measurements can serve a variety of applications including the changes in soil forming processes and ecological services (Singer et al., 1996), study of parent material and lithological effects (e.g., Lu, 2000), understanding sedimentation processes (Caitcheon, 1993), soil drainage (Mathe and Leveque, 2003), and soil redistribution (Ayoubi et al., 2012; Mokhtari Karchegani et al., 2011; Rahimi et al., 2013).

The magnetic measurement is increasingly used as a tool for the detection of heavy metal contamination in soils and sediments caused by industrial emissions (Dankoub et al., 2012; Karimi et al., 2011). Magnetic measurements have been shown to be an effective proxy for investigating pollution by industrial and exhaust emissions, and other atmospheric pollutants (Lu et al., 2007). This method is based on the fact that industrial activities such as the combustion of fossil fuel that produce fly ash contain a significant fraction of magnetic minerals (Flanders, 1994). Thompson and Oldfield (1986) reported that soils near urban and industrial zones have increased χlf, which is attributed to the deposition of magnetic particles such as dust from metallurgical industry and fly ash produced by the combustion of coal.

Using geochemical analysis, additional data can be obtained; and in combination with magnetic data, polluted areas can be characterized to determine the relative contribution by geologic and anthropogenic

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sources (Hanesch and Scholger, 2002). Lecoanet et al. (2003) used magnetic parameters to discriminate individual sources of soil contamination. There have been numerous studies linking the magnetic properties of soils to the industrial contamination in a range of environments, especially in industrial areas. For instance, 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.

Lu and Bai (2006) reported that soils near 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. Karimi et al. (2011) observed significant correlations between the χlf and heavy metals in urban top soils in the arid region of Isfahan, central Iran. They proposed that magnetic parameters can be used as a proxy for the detection of heavy metals (Pb, Zn, Ba and Cu) emitted by vehicles. Dankoub et al. (2012) also reported a significant correlation between magnetic properties and the concentrations of Cu, Zn, Pb, Mn, and Fe in calcareous soils as affected by land use in the Isfahan region, central Iran. Lecoanet et al. (2003) assessed the potential of the magnetic techniques to determine the sources of contamination; and its effects on the contamination of surface and sub-surface soil samples. They showed that the contents of magnetic minerals with higher magnetic coercivity increased with depth from surface to the bottom in the soil profiles.

Although, a few studies have been conducted in Iran at regional scale to explore the efficacy of magnetic measurements to investigate the heavy metal pollution (Dankoub et al., 2012; Karimi et al., 2011), little attention has been paid to characterize the pollution with metals in and around industrial sites. The main objectives of this study therefore, were to (i) quantify the contamination of soils by selected metals using contamination factor (CF) and pollution load index (PLI), (ii) determine the vertical and horizontal distribution of selected metals and χlf, and (iii) examine the feasibility of employing the magnetic parameters in the assessment of metal pollution of soils at an industrial site in central Iran.

2. Materials and methods

2.1. Study area and soil sampling

The industrial site studied is located at south of Isfahan city, and extends from longitudes of 51 18′ 10″ to 51 18′ 59″ E and latitudes of 32 26′ 39″ to 32 26′ 46″ N, in central Iran (Fig. 1). The study area covers about 2000 ha around an iron melting factory. The Isfahan city is one of the most known industrial sites in Iran, especially known for steel production and processing and chemical industries. In recent years, rapid urbanization and industrialization in Isfahan has caused the accumulation of heavy metals in airborne particles (Hojati et al., 2012) and urban soils (Dankoub et al., 2012; Karimi et al., 2011).

The average annual rainfall and temperature of the study area are 110 mm and 16.2 °C, respectively. Soil moisture and temperature regimes of the study area are Aridic and Thermic, respectively (Soil Survey Staff, 2006). According to the geological map of the Isfahan province, the soil parent materials include mainly recent terraces, recent alluvial deposits and undifferentiated terraces (all of Quaternary age); and in some areas, limestone, sandstone, shale with lower Cretaceous age (Haghipour and Aghanabati, 1985). The texture of the soils in the study area is predominantly sandy loam and sandy clay loam. Furthermore, the soils of the selected site are calcareous and gypsiferous (Fig. 2) classified as Calciargids, Haplocambids and Haplogypsids according to the Soil Survey Staff (2006).

Spatial distribution of 202 points selected for the study is given in Fig. 1. The sampling plan was based on a grid in 300 × 300 m surrounding the factory, and covered 600 × 600 m in the farther distance of factory (Fig. 1). The exact coordination of each point was defined by GPS and then profiles were excavated in all the selected points. Soil samples were taken during June through August 2011, from 202 soil profiles at increasing depths of 0–30, 60–90, and 120–150 cm.

2.2. Laboratory analyses

Mass 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 in a sample, although it is also sensitive to magnetic grain size (Lu and Bai, 2006). Frequency dependent susceptibility (χfd), which indicates the presence of super paramagnetic (SP) grain sizes, was calculated using Eq. (1):

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

A subsample (0.2 g) of each soil was used for heavy metal analysis. The soils were extracted using 5 mol L^{-1} HNO$_3$ (Ajayi and Kamson, 1983). The total concentrations of lead (Pb), zinc (Zn), copper (Cu), manganese (Mn), iron (Fe), nickel (Ni), chromium (Cr), and cobalt (Co) were measured with an atomic absorption spectrophotometer (AAS). The precision of the procedure was checked by analyzing a certified reference material San Joaquin #2709 (National Institute of Standard and Technology, USA). The electrical conductivity (EC) and pH of the soil samples were measured in a 1:2 soil to water ratio suspension. Soil organic matter (SOM) content was determined by the method of Walkley and Black (1934). Gypsum was determined using the weight loss method and the percentage of calcium carbonate equivalent (CCE) was measured by the titrimetric method (Burt, 2004) and cation exchange capacity (CEC) by extraction with sodium acetate (Rhoades, 1982). Soil particle size distribution (clay, sand and silt content) was determined using the Pipet method (Day, 1965).

2.3. Pollution quantification

The concentration factor is the ratio obtained by dividing the concentration of each metal in the soil by the base line or background values. Contamination factor ratio was obtained by using the following equation (Rashed, 2010):

$$CF = \mathrm{C}_{\mathrm{metal}}/\mathrm{C}_{\mathrm{background}} \quad (2)$$

where, C$_{\mathrm{metal}}$ is the concentration of metals in the soil surface and C$_{\mathrm{background}}$ is the concentration of each element at the reference site. As the study was based on the soil profile (150–200 cm depth) for each sample; it was possible to avoid the effect of human activity on the baseline calculation. Therefore, the AMD of metal concentrations in deep layers were considered as the background concentration of the selected metals (Bech et al., 2005). The contamination levels may be classified based on the intensity on a scale of 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) (Muller, 1969). The highest number indicates that the metal concentration is 100 times greater than what would be expected in the crust.

We also computed the Tomlinson pollution load index (PLI) for the surface soil samples to detect the relative metal toxicity and environmental quality of the soils in the study area. The PLI index (Angulo, 1996) is obtained as a concentration factor (CF) of each metal with respect to the background value in the sediment. The following equation was employed to calculate PLI:

$$PLI = \sqrt[n]{\prod_{k=1} CF_{metal}} \quad (3)$$

The PLI index characterizes the number of times by which the metal concentration in the soil exceeds the background concentration, and gives a summative basis of the overall level of metal toxicity in a particular sample.