Science of the Total Environment 485–486 (2014) 83–92

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Combination of magnetic parameters and heavy metals to discriminate soil-contamination sources in Yinchuan — A typical oasis city of Northwestern China

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HIGHLIGHTS

- Relation between magnetic properties and heavy metals of urban soil were examined.
- Magnetic assemblage in Yinchuan topsoil is dominated by PSD and MD magnetite.
- Different pollution sources were discriminated using PCA and FCA analysis.

ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form 12 March 2014
Accepted 16 March 2014
Available online xxxx

Editor: F.M. Tack

Keywords:
Environmental magnetism
Soil pollution
Heavy metals
Yinchuan

ABSTRACT

Various industrial processes and vehicular traffic result in harmful emissions containing both magnetic minerals and heavy metals. In this study, we investigated the levels of magnetic and heavy metal contamination of topsoils from Yinchuan city in northwestern China. The results demonstrate that magnetic mineral assemblages in the topsoil are dominated by pseudo-single domain (PSD) and multi-domain (MD) magnetite. The concentrations of anthropogenic heavy metals (Cr, Cu, Pb and Zn) and the magnetic properties of χ_{lf}, SIRM, χ_{ARM}, and 'SOFT' and 'HARD' remanence are significantly correlated, suggesting that the magnetic minerals and heavy metals have common sources. Combined use of principal components and fuzzy cluster analysis of the magnetic and chemical data set indicates that the magnetic and geochemical properties of the particulates emitted from different sources vary significantly. Samples from university campus and residential areas are mainly affected by crustal material, with low concentrations of magnetic minerals and heavy metals, while industrial pollution sources are characterized by high concentrations of coarse magnetite and Cr, Cu, Pb and Zn. Traffic pollution is characterized by Pb and Zn, and magnetite. Magnetic measurements of soils are capable of differentiating sources of magnetic minerals and heavy metals from industrial processes, vehicle fleets and soil parent material.

1. Introduction

A consequence of the global expansion of industrialization and urbanization is the release into the environment of significant quantities of heavy metals originating from processes such as energy production, mining, metal smelting and refining, manufacturing processes, waste incineration, and fossil fuel combustion (Stroganova, 1998; Siegel, 2002; Manta et al., 2002; Al-Khashman, 2004; Sekabira et al., 2010). Heavy metal pollution of urban surface soil is a significant aspect of this problem and it is a significant source of concern for human health as the fine particles can be dispersed widely by wind and are inhalable, and therefore monitoring heavy metal concentrations in urban soil is an important task. However, traditional geochemical methods (e.g. AAS and ICP-AES) are relatively complex, time-consuming and expensive, and are therefore not suitable for performing large-scale pollution mapping or monitoring.

In the past several decades, magnetic measurements of soils and urban dusts have been widely used to identify pollution sources, and the methodology is regarded as a reliable, efficient and sensitive method for evaluating polluted samples (Kapička et al., 1999; D. Jordanova et al., 2003; N.V. Jordanova et al., 2003; Goddu et al., 2004; Gautam et al., 2004; Xia et al., 2007, 2008; Zhang et al., 2008; Blundell et al., 2009; Bijaksana and Huliselan, 2010; Karimi et al., 2011). Positive correlations between the magnetic and heavy metal concentrations in urban soils and sediments have been demonstrated in several studies (Petrovský et al., 2001; Hanesch and Scholger, 2002; D. Jordanova et al., 2003; N.V. Jordanova et al., 2003; Canbay et al., 2010; Karimi

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http://dx.doi.org/10.1016/j.scitotenv.2014.03.070
0048-9697/

et al., 2011; Wang et al., 2013a). Moreover, in recent years the use of magnetic parameters as proxies for quantifying or semi-quantifying the concentrations of certain contaminants, such as heavy metals in street dusts, and in atmospheric particles and soils, has also been demonstrated (Shu et al., 2001; Kim et al., 2007, 2009; Hu et al., 2008; Canbay et al., 2010; Zhang et al., 2011; Wang et al., 2013b), and the results suggest that the method is a promising alternative to conventional chemical analysis. Recent studies have shown that although the concentrations of certain heavy metals are positively correlated with magnetic properties such as magnetic susceptibility, the sources of the magnetic minerals and associated pollutants may be varied, such as from iron foundries and vehicular traffic (Hoffmann et al., 1999; Zhang et al., 2006, 2011; Wang, 2013b). In addition, soil parent material is another factor source of magnetic mineral in the urban environment and it needs to be carefully considered (Wang et al., 2014). Therefore, it is necessary to effectively distinguish the different sources of samples when using properties such as magnetic susceptibility for monitoring urban heavy metal pollution.

In this paper, we present the results of magnetic and geochemical analyses of urban topsoil samples from Yinchuan city in northwestern China, and analyze them using multivariate statistical analysis, including principal component analysis and fuzzy cluster analysis. Our main objectives are as follows: (a) to examine the relationship between the magnetic properties and heavy metal contamination of soil samples in a typical oasis city; (b) to discriminate among the contributions of different pollution sources; and (c) to characterize the anthropogenic magnetic particles present. The study is thus a contribution to the development of the use of magnetic measurements for characterizing the degree of heavy metal contamination in an urban environment.

2. Materials and methods

2.1. Study area

Yinchuan city, the capital of Ningxia Province, is located on the Yellow River, central Ningxia Plains, in the arid region of northwestern China (Fig. 1a). The city area extends from 105°49′E to 106°35′E in longitude and from 38°08′N to 38°53′N in latitude, and covers both mountains and plains. Geographically, it is situated on Helan Mountain alluvial plain, within the warm temperate zone. The average annual temperature is ~8.5 °C and the average annual precipitation is 193–202.7 mm, which is concentrated in summer. The main soil types are sierozem, gray cinnamonic soil, meadow soil and an anthropogenic-alluvial soil (Yinchuan city records: http://dfz.yinchuan.gov.cn/SiteAcl.srv?id=1725930). The soil textural characteristics are typical silt loam, sandy and sandy loam, with soil pH ranging from 6.68 to 8.83 (mean 7.89); the organic matter content is low, ranging from 0.29 to 2.1% (mean 0.94%) (Cao et al., 2009).

In terms of land use, the urban area of Yinchuan city can be divided into four functional regions (Fig. 1b). Urban industrial areas, where there are many factories emitting significant levels of various types of pollution, are mainly concentrated in the southwestern part of the city, whereas the administrative, business, cultural and residential areas are mainly concentrated in the eastern part. The universities and colleges, such as Ningxia University and Beifang University of Nationalities, are located in the northern part of Xixia district. Greenbelt zones are mainly distributed in the northeastern part of Jinfeng and Xingqing districts.

2.2. Sampling methods

The sampling sites were designed to cover the three districts of Yinchuan city (i.e. Xingqing, Jinfeng and Xixia). Surface soil samples were collected during October 2–6, 2012, and the weather was clear and sunny two weeks prior to and during the sampling period. The samples were collected 2–3 m from the edge of the road in the urban areas of the three districts. Industrial, residential, campus and greenbelt areas and areas with a high traffic density were sampled. In order to ensure the representativeness of the soil samples within a small sampling area, the soil within a 10 m radius of each sampling point was measured with a Bartington MS2D surface scanning loop sensor. Sites with anomalously high magnetic susceptibility were avoided. A total of 75 samples were collected from a depth of 2 cm, and samples from each soil sampling point were mixed and combined to produce a single sample. 16 sampling sites were in industrial zones, 28 in areas with high vehicular traffic density, 10 in residential areas, 6 in university campuses and 15 in greenbelt zones. All samples were sealed in plastic bags. In the laboratory, the samples were air-dried at room temperature, and then passed through a 1 mm sieve to remove refuse and coarse lithogenic material.

2.3. Laboratory methods

2.3.1. Magnetic measurements

5.5 g of powdered soil from each sample was packed into plastic boxes for the following sequence of routine magnetic measurements (Thompson and Oldfield, 1986; Evans and Heller, 2003): (i) low frequency (470 Hz) magnetic susceptibility (χ_{lf}); (ii) high frequency (4700 Hz) magnetic susceptibility (χ_{hf}); (iii) anhysteretic remanent magnetization (ARM); (iv) saturation isothermal remanent magnetization (SIRM) at 1 T; and (v) isothermal remanent magnetization at successively increasing reverse fields of −20, −40, −60, −100 and −300 mT.

Low- and high-frequency magnetic susceptibility measurements were carried out using a Bartington Instruments MS2B magnetometer. The difference between the measurements at the two frequencies was used to calculate the frequency-dependent susceptibility, $\chi_{fd} = \chi_{lf} - \chi_{hf}$, which can also be expressed as a percentage of the low frequency susceptibility, $\chi_{fd}\% = [(\chi_{lf} - \chi_{hf}) / \chi_{lf}] \times 100$. Anhysteretic remanence was inparted using a DTECH demagnetizer in a peak alternating field (AF) of 100 mT, with a steady direct (DC) bias field of 0.1 mT superimposed, and is expressed as an anhysteretic susceptibility (χ_{ARM}). Forward and reverse field isothermal remanences were induced using an MMPM10 Pulse Magnetizer. All remanences were measured using a Molspin spinner magnetometer with a noise level of ~0.1×10^{-8} Am^2. From these measurements, a range of additional parameters were calculated in order to obtain information about magnetic grain size and mineralogy. HIRM is calculated as $(SIRM + IRM_{-300\ mT}) / 2$ and is a measure of the concentration of high coercivity magnetic minerals, e.g., hematite and goethite (Liu et al., 2012). 'SOFT' is calculated as $(SIRM\text{-}IRM_{-20\ mT}) / 2$, and is commonly used to reflect magnetite content, particularly the contribution of low coercivity multidomain (MD) magnetic grains and magnetic grains on the superparamagnetic/stable single domain (SP/SSD) border. IRM-100 mT is the magnetization which was acquired after applying a 100 mT anti-direction magnetic field to the SIRM. All of these components (HIRM, $IRM_{-100\ mT}$, and SOFT) can also be expressed as percentages of SIRM, i.e. HARD% = HIRM / SIRM × 100, SOFT% = SOFT / SIRM × 100, and $S_{-100} = -IRM_{-100\ mT} / SIRM$, respectively. In addition, two interparametric ratios were calculated, χ_{ARM}/χ and χ_{ARM}/SIRM, both of which are sensitive to the size of ferrimagnetic grains. The magnetic parameters were measured in the Key Laboratory of Western China's Environmental System, Lanzhou, China.

2.3.2. Soil chemical analysis

Samples (approximately 0.2 g) were dissolved in a hot $HF\text{-}HNO_3\text{-}HCl$ acid mixture (approximately 15 mL), and refluxed with the same acid mixture if the sample was only partially dissolved. Cr, Cu, Pb and Zn concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). All calibration standards were prepared in the acid matrix used for the soil samples. Caution was exercised in preparing and analyzing the samples to minimize contamination from air, glassware and reagents, and the latter were all of ultrapure quality. Replicate measurements of standard reference materials, reagent blanks and