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Detecting the sensitivity of magnetic response on different pollution sources – A case study from typical mining cities in northwestern China



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ABSTRACT

Rapid monitoring and discriminating different anthropogenic pollution is a key scientific issue. To detect the applicability and sensitivity of magnetic measurements for evaluating different industrial pollution in urban environment, characteristics of topsoil from three typical fast developing industrial cities (Jinchang, Baiyin and Jiayuguan in Gansu province, northwestern China) were studied by magnetic and geochemical analyses. The results showed that magnetic susceptibility was enhanced near industrial areas, and PSD-MD magnetite dominated the magnetic properties. Magnetic concentration parameters (χ_{lf} , SIRM, and χ_{ARM}) showed different correlations with heavy metals and PLI in the three cities, indicating significantly different magnetic response to different pollution sources. Principal component analysis showed that ferrimagnetic minerals coexist with heavy metals of Fe, As, Cu, Pb, and Zn in Baiyin and Fe, V, Cu, Mn, Pb, and Cr in Jiayuguan. Fuzzy cluster analysis and regression analysis further indicated that the sensitivity of magnetic monitoring to fuel dust is higher than that to mineral dust near non-ferrous metal smelters, and fossil fuel consumption is an important factor for increasing magnetite content. In all the three cities, the sensitivity of magnetic monitoring to pollutants from steel plants is much higher than that from non-ferrous metal plants. Therefore, magnetic proxies provide a rapid means for detecting heavy metal contamination caused by multi-anthropogenic pollution sources in a large scale area, however, the sensitivity was controlled by pollution sources.

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1. Introduction

A consequence of the global expansion of industrialization and urbanization is the release into the environment of significant amount of heavy metals originating from processes such as energy production, mining, metal smelting and refining, manufacturing processes, waste incineration, and fossil fuel combustion (Al-Khashman, 2004; El Khalil et al., 2008; Rodríguez et al., 2009; Cheng et al., 2011). Therefore heavy metals can accumulate in the soil surrounding industrial areas through atmospheric deposition and sewage sludge percolation, and this has caused serious pollution, as well as soil quality degradation and health threat (Li et al.,

2014; Mackay et al., 2013). Environmental disasters caused by mining and smelting are increasing rapidly, especially in China (Miao et al., 2012; Liu et al., 2013). Thus, monitoring heavy metal concentrations rapidly in urban soil is an important task.

In recent years, magnetic properties of materials such as soil, sediment, dust, and leaves have been investigated in order to monitor the degree of urban pollution, as well as to discriminate different pollution sources. The sensitivity of magnetic techniques allowed its use for rapid measuring very small amount of magnetic particles in bulk samples, which is generally equivalent to the ppb used in chemical analyses. It facilitates many studies that simply cannot be accomplished by any other techniques without costly and time-consuming direct analyses (Hoffmann et al., 1999; Lecoanet et al., 2003; Xia et al., 2008; Hoffman et al., 2013; Warriar et al., 2014; Jones et al., 2015). Numerous previous studies have concentrated on identifying the magnetic contamination in industrial areas (Goddu et al., 2004; Basavaiah et al., 2012;

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Jordanova et al., 2013; Salo and Mäkinen, 2014), traffic areas (Hoffmann et al., 1999; Zhang et al., 2006; Mitchell and Maher, 2009), and larger spatial scale analysis using sub-national data sets (Blundell et al., 2009a, 2009b; Jordanova et al., 2014). Some studies have focused on spatial and temporal distribution in order to detect the pollution situations, trends, regularity, and sources (Maher et al., 2008; Xia et al., 2008; Marx et al., 2010). While some studies have linked the anthropogenic magnetic enhancement with metal contamination, and significant positive correlations have been found (Hu et al., 2008; Karimi et al., 2011; Zhang et al., 2012, 2013; Qiao et al., 2013; Wang et al., 2013a). Moreover, in recent years magnetic parameters have been used as proxies to quantify or semi-quantify the contents of certain contaminants in soil (Canbay et al., 2010; Zhang et al., 2011; Wang et al., 2013b), and show a promising alternative to the chemical analyses.

Although previous studies have indicated the potential use of environmental magnetism to monitor the degree of anthropogenic pollution in different cities which were dominated by industrial and/or traffic-related pollution, until now, there are few studies that have focused on determining whether difference existed in magnetic response for various pollutions (Blaha et al., 2008; Zhang et al., 2011). Our previous studies have demonstrated that magnetic proxies provide a rapid means for distinguishing the local parent materials, industrial and traffic pollution in different cities (Wang et al., 2014). However, how do these different sources affect the sensitivity of magnetic 'fingerprints', and how deeply can different sources impact the relationship between magnetism and pollution degree? To answer these questions, the present study selected three typical cities, i.e. mining cities, as the research target areas, which have entirely different industrial productions. We detected pollution source of topsoil samples and evaluated their sensitivity of magnetic response using magnetism method and geochemical analyses, with the aim of revealing magnetic properties of the contaminants emitted from different industrial processes, and detecting the applicability and sensitivity of magnetic monitoring of heavy metals in different pollution sources.

2. Materials and methods

2.1. Sample collection

Jinchang (JC), Baiyin (BY) and Jiayuguan (JYG) are all located in the arid and semi-arid regions in Gansu Province of northwestern China (Fig. 1), with dry climate, high temperature and abundant sunshine. Southeast and northwest winds prevail in summer and winter in these cities, respectively. JC is China's largest nickel producer, well known for its non-ferrous metal production, and known as China's 'Nickel Capital'. BY is the base for non-ferrous metal mining in China, and is known as China's 'Copper Capital'. JYG is a rapidly developing artificial oasis industrial city, famous for steel production. Topsoils of the three cities were all dominated by fine sand, with some coarse sand and silt, and a few clay particles (Wang, 2014).

Topsoil samples in the uppermost 2 cm layer were collected 2–3 m from the edge of the road in the three cities. In order to ensure the representativeness of soil samples, magnetic susceptibilities of the soil within 10 m of each sampling point were measured using a Bartington MS2 magnetometer, and areas with relatively homogeneous magnetic susceptibility were selected as sampling site. For each sampling sites, four topsoil samples were collected and mixed together as one sample for further analysis. A total of 52, 87 and 58 samples were collected in JC, BY and JYG, respectively. After air-dried for two week in laboratory, samples were sieved through a 0.9 mm mesh to remove all hair, animal and plant debris before laboratory measurements were conducted.

2.2. Laboratory measurements

5.5 g of powder from each sample was packed into plastic boxes for the following series of magnetic measurements. The low field (470 Hz) and high field (4700 Hz) magnetic susceptibilities were measured using a Bartington Instruments MS2B magnetometer, and mass susceptibilities (χ_{lf} and χ_{hf}) were calculated by mass normalization (Liu et al., 2012). The percentage of the frequency-dependent magnetic susceptibility ($\chi_{fd}\%$) was calculated based on the following formula: $\chi_{fd}\% = (\chi_{lf} - \chi_{hf}) / \chi_{lf} \times 100$. Anhysteretic remanent magnetizations were grown using a DTECH demagnetizer in a peak alternating field of 100 mT and with a steady direct current (d.c.) biasing field of 0.1 mT, and expressed as the susceptibility of ARM (χ_{ARM}) by dividing the ARM by the d.c. biasing field (Lyons et al., 2012). Isothermal remanent magnetizations were imparted via a MMPM10 pulse magnetizer, and the IRM produced at 1000 mT was defined as saturation IRM (SIRM) (Thompson and Oldfield, 1986). At this point, a stepwise backfield remagnetization of the SIRM was performed, and the result was used to calculate HIRM (HIRM = [(SIRM + IRM₋₃₀₀)/2]/mass) and SOFT (SOFT = [(SIRM - IRM₋₂₀)/2]/mass). Magnetic hysteresis loops (content M_s , M_{rs} , B_c , maximum field is 1 T), and thermomagnetic curves (heating and cooling cycles measured from 25 °C to 700 °C by 4 °C/s in a 100 mT magnetic field, performed in atmosphere), were then determined using a variable field translation balance (VFTB). The low-temperature magnetic susceptibility of samples was measured using a KLY-3 Kappabridge equipped with a CS-L in atmosphere. The measurement was performed from -194 °C to 0 °C, and refrigerated using liquid nitrogen. Magnetic parameters were measured in the Key Laboratory of Western China's Environmental System, Lanzhou University.

Samples (approximately 0.2 g) were dissolved in a hot HF-HNO₃-HCl acid mixture (approximately 15 mL), and refluxed with the same acid mixture if the sample was only partially dissolved. Cr, Cu, Fe, Mn, Ni, Pb, V and Zn concentrations were measured by IRIS Advantage 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 duplicate soil samples (approximately 20 of the total number of soil samples were used for this purpose), randomly selected from a set of available samples, were used to assess contamination and precision. The relative standard deviation of the analytical precision was mostly between 5% and 6%, and never higher than 10%. In addition, back-testing was conducted after testing of every five samples to verify the results. The heavy metal of arsenic was measured by using an AFS-9800 Double ways atom fluorescence. Heavy metal content was measured at the Analysis and Test Center, College of Chemistry and Chemical Engineering, Lanzhou University.

2.3. Statistical methods

A single factor index (SI) was calculated by $SI = C_i / C_{back}$, C_i is the content of a particular metal, and C_{back} is the background content. A single gene index reflects the pollution degree for a single heavy metal. Pollution Load Index (PLI) reflects the combined action of many heavy metals. PLI was used to obtain the concentration factors $CF = C_{metal} / C_{background}$ for the selected metals and was calculated using the n-root from the product of the n CFs of the metals included: $PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n}$. PLI in a region is calculated by $PLI_{zone} = \sqrt[m]{PLI_1 \times PLI_2 \times PLI_3 \times \dots \times PLI_m}$, where m represents the number of samples in a zone (Angulo, 1996). The

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