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Multiscale correlations of iron phases and heavy metals in technogenic magnetic particles from contaminated soils☆

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ABSTRACT

Technogenic magnetic particles (TMPs) are carriers of heavy metals and organic contaminants, which derived from anthropogenic activities. However, little information on the relationship between heavy metals and TMP carrier phases at the micrometer scale is available. This study determined the distribution and association of heavy metals and magnetic phases in TMPs in three contaminated soils at the micrometer scale using micro-X-ray fluorescence (μ-XRF) and micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy. Multiscale correlations of heavy metals in TMPs were elucidated using wavelet transform analysis. μ-XRF mapping showed that Fe was enriched and closely correlated with Co, Cr, and Pb in TMPs from steel industrial areas. Fluorescence mapping and wavelet analysis showed that ferroalloy was a major magnetic signature and heavy metal carrier in TMPs, because most heavy metals were highly associated with ferroalloy at all size scales. Multiscale analysis revealed that heavy metals in the TMPs were from multiple sources. Iron K-edge μ-XANES spectra revealed that metallic iron, ferroalloy, and magnetite were the main iron magnetic phases in the TMPs. The relative percentage of these magnetic phases depended on their emission sources. Heatmap analysis revealed that Co, Pb, Cu, Cr, and Ni were mainly derived from ferroalloy particles, while As was derived from both ferroalloy and metallic iron phases. Our results indicated the scale-dependent correlations of magnetic phases and heavy metals in TMPs. The combination of synchrotron based X-ray microprobe techniques and multiscale analysis provides a powerful tool for identifying the magnetic phases from different sources and quantifying the association of iron phases and heavy metals at micrometer scale.

1. Introduction

Industrial activities commonly emit a large amount of magnetic particles into the environment. These magnetic particles are characterized by strong magnetic properties and are termed technogenic magnetic particles (TMPs) (Catinon et al., 2014; Lu et al., 2016; Magiera et al., 2011, 2013). TMPs are carriers of various contaminants, including heavy metals and polycyclic aromatic hydrocarbons (Rachwał et al., 2015). The deposition of TMPs on soils, sediments, and leaves commonly leads to elevated concentrations of heavy metals and magnetic enhancement of soils, sediments, and dusts on leaf surfaces (Bourliva et al., 2016; Bućko et al., 2011; Miler and Gosar, 2015; Rachwał et al., 2015). TMPs also contain abundant information on the origin of contaminants (Catinon et al., 2014; Lu et al., 2016; Magiera et al., 2013; Rachwał et al., 2015). Therefore, TMPs can be used to evaluate the degree and spatial distribution of pollution and trace the origin of heavy metals.

Anthropogenic emissions from mining and smelting, coal burning, waste treatment, and other industrial technologies have led to the accumulation of TMPs with higher potentially toxic elements (PTEs) in industrial and urban regions worldwide (Bućko et al., 2011; Goddu et al., 2004; Lu et al., 2007; Zhang et al., 2011a). As magnetic properties are highly correlated with heavy metal contents, rapid, cost-effective, and sensitive magnetic measurements have become a proxy method for investigating and monitoring anthropogenic heavy metal pollution (Blaha et al., 2008; Blundell et al., 2009; Kapička et al., 1999; Lu et al., 2007; Zhang et al., 2011b). In recent years, this method has been widely applied for estimating anthropogenic pollutants, such as industrial pollutants around iron-smelting plants, traffic emissions, and other

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atmospheric pollutants. Moreover, this method is used for mapping the spatial distribution of pollution and revealing the extent of pollution around power plants, and cement and metallurgical industries (Kapička et al., 1999; Lecoanet et al., 2001; Rachwał et al., 2015; Szuszkiewicz et al., 2015; Zhang et al., 2011a; Zhu et al., 2013). However, previous studies are based on the fact that magnetic susceptibility is closely correlated with heavy metal content at the macroscopic scale. Studies of the carriers themselves at the micrometer or even molecular scale are needed to better understand the sources of heavy metal contaminants in TMPs and provide a scientific basis for the magnetic proxy method for its wider application in different environments, climates, and ecosystems.

The capability and versatility of synchrotron-based techniques in performing molecular-scale speciation of heavy metals in soils are well established (Manceau et al., 1996; Sarret et al., 2004). Previous micro-spectroscopic studies have mainly focused on the spatial distribution of Cu, Ni, Pb, and Zn in the soil matrix (Fan and Gerson, 2011; Funasaka et al., 2008; Jacobson et al., 2007; Perez-Lopez et al., 2011; Strawn and Baker, 2008, 2009). In particular, synchrotron X-ray micro-beam techniques can image the distribution of metal elements and solve the metal-bearing phases at the micrometer level (Terzano et al., 2007). Synchrotron-based micro-X-ray fluorescence (μ-XRF), and X-ray absorption fine structure (XAFS) spectroscopy have been extensively utilized in soil systems to perform chemical speciation of Cu and Zn. μ-XRF, coupled with μ-XANES spectroscopy, has been used to investigate the distribution and speciation of soil Cu at the microscale (Strawn and Baker, 2008, 2009). Numerous studies have applied XAFS spectroscopy to determine Pb speciation in a variety of environments, including aerosol particles, soils, and street dusts (Barrett et al., 2010; Funasaka et al., 2008; MacLean et al., 2011; Terzano et al., 2007). Environmental magnetic methods have been widely used to investigate the degree, source, spatial distribution, and temporal evolution of anthropogenic pollution related to industrial and other human activities (Blundell et al., 2009; Bućko et al., 2011). The magnetic measurements are based on the fact that the origins of heavy metals and magnetic particles are generally related (Lu et al., 2007). However, most previous studies have only focused on the macroscale correlation between heavy metals and magnetic particles by investigating large numbers of samples (Blaha et al., 2008; Blundell et al., 2009; Bućko et al., 2011). How the heavy metals associate with magnetic phases at the micrometer scale still remains unknown, and the species of the magnetic phases are not quantified at micrometer scale.

TMPs from industrial activities are heterogeneous assemblages of diverse iron particles of sizes that typically range from the millimeter to nanometer scale; all of these iron particles are potential sites for metal sequestration (Lu et al., 2016). The distribution and speciation of heavy metals vary between these iron phases at different spatial scales. Fully characterizing the spatial distribution and speciation of Fe phases in TMPs is challenging, as several Fe phases are often present in a single magnetic particle. Therefore, the microscale distribution and speciation of Fe phases need further characterization. An improved understanding of the microscale magnetic properties of Fe phases will help to explain the relationship between magnetic properties and heavy metals, and trace their sources and response to environmental variations. Furthermore, the multiscale correlations of heavy metals in anthropogenic contaminated soils have not yet been determined. The combination of synchrotron-based microprobe techniques, including μ-XRF, μ-XANES, and advanced data analytical methods (the maximal overlap discrete wavelet transform) (Milne et al., 2011) and heatmap analysis (Eisen et al., 1998) provide a new window for resolving the above issues.

The aims of this study were to: (1) image the spatial distribution of heavy metals in TMPs from different anthropogenic pollution sources at the micrometer scale; (2) identify and quantify the species of magnetic iron particles in studied soils; (3) reveal the multiscale correlations of heavy metals in TMPs; and (4) analyze the association of iron phases and heavy metals.

2. Materials and methods

2.1. Soil samples

Three soil samples with different TMPs content were collected from topsoil (0–10 cm) in Anshan, Liaoning Province, China. Anshan has a total urban area of 174 km^2 and approximately 1.46 million inhabitants. The city, the largest iron and steel industry base in China, has performed iron and steel production for more than 100 years. Between 1949 and 2014, it has produced 5.09, 5.11, and 4.01×10^9 tons of iron, steel, and steel products, respectively. The urban topsoils in the city have been strongly influenced by iron and steel industry (Xiao et al., 2015). Sample A, representing soil severely polluted by the steel industry, was collected from bare land within a steel factory. The soil has much high TMPs content (43.5%) and magnetic susceptibility (7284×10^{-8} m^3/kg, Table S-1). Sample B, representing soil moderately affected by steel production, was collected from the topsoil around the steel factory. The soil has TMPs content of 29.6% and magnetic susceptibility of 3656×10^{-8} m^3/kg. Sample C was collected from the roadside in the residential areas of the city. The soil, affected mainly by traffic-related activities and coal-burning, has TMPs content of 8.27% and magnetic susceptibility of 1132×10^{-8} m^3/kg. At each sampling site, five sub-samples were randomly collected from the surface layer (0–10 cm) using stainless steel shovel, and thoroughly mixed to form a composite sample. Samples were carefully transported to the laboratory, air dried at room temperature, sieved to less than 2 mm, and stored in plastic containers for further analysis. TMPs in the soils were extracted using a magnet bar wrapped with a polythene film as previously described (Lu et al., 2016).

2.2. Chemical analyses

Part of the bulk soils was ground to pass through a 0.25-mm sieve for physical and chemical analyses of soils. Soil physical and chemical properties were determined using standard methods (Bao, 2004). Total metal contents were determined using a three-acid digestion followed by inductively coupled plasma atomic emission spectrometry (ICP-AES; iCAP6300DUO, Thermo Electron Corporation) (Bao, 2004). Briefly, 0.5 g of soils was digested using a mixture of 10 ml HF, 5 ml $HClO_4$, and 5 ml HNO_3 on a hot plate (200 °C). The digested solution was cooled, filtered, and diluted to 25 ml. The concentration of heavy metals was determined using ICP-AES. Quality assurance and control (QA/QC) included the procedure blank, duplicate analysis, and standard reference materials. The physical and chemical properties of the studied soils are shown in Table S-1.

2.3. Synchrotron radiation-based microprobe analysis

The TMPs extracted from the soils were observed using an optical microscope (JIFEI-XL7045TS, Nanjing Optical Instrument, China). Under the optical microscope, ferroalloy pieces and TMP aggregates with completely different morphology were identified. The ferroalloy was characterized by a tiny piece, with some tiny particles adhered on it, whereas TMP aggregates consisted of different sized particles. The typical ferroalloy piece and TMP aggregate (450–550 μm in size) in the TMP samples were carefully picked up using a capillary tube. These ferroalloy and TMPs were