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Study of road dust magnetic phases as the main carrier of potentially harmful trace elements

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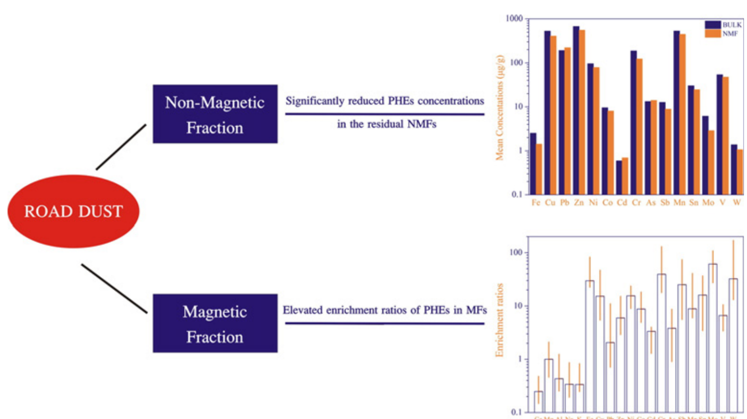
HIGHLIGHTS

- Road dusts presented enhanced magnetizations due to high content of magnetic phases.
- A magnetite-like phase was the main magnetic carrier.
- Elevated concentrations of PHEs indicated seriously contaminated road dusts.
- High enrichments ratios of PHEs in MFs suggested their preferred gather in the MFs.
- Magnetic separation could diminish the pollution of PHEs in urban environments.

GRAPHICAL ABSTRACT



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ABSTRACT

Mineralogical and morphological characteristics and heavy metal content of different fractions (bulk, non-magnetic fraction-NMF and magnetic fraction-MF) of road dusts from the city of Thessaloniki (Northern Greece) were investigated. Main emphasis was given on the magnetic phases extracted from these dusts. High magnetic susceptibility values were presented, whereas the MFs content of road dust samples ranged in 2.2–14.7 wt.%. Thermomagnetic analyses indicated that the dominating magnetic carrier in all road dust samples was magnetite, while the presence of hematite and iron sulphides in the investigated samples cannot be excluded. SEM/EDX analyses identified two groups of ferrimagnetic particles: spherules with various surface morphologies and textures and angular/aggregate particles with elevated heavy metal contents, especially Cr. The road dusts (bulk samples) were dominated by calcium, while the mean concentrations of trace elements decreased in the order Zn > Mn > Cu > Pb > Cr > Ni > V > Sn > As > Sb > Co > Mo > W > Cd. MFs exhibited significantly higher concentrations of trace elements compared to NMFs indicating that these potentially harmful elements (PHEs) are preferentially enriched in the MFs and highly associated with the ferrimagnetic particles. Hazard Index (HI) obtained for both adults and children through exposure to bulk dust samples were lower or close to the safe level (=1). On the contrary, the HIs for the magnetic phases indicated that both children and adults are experiencing potential health risk since HI for Cr was significantly higher than safe level. Cancer risk due to road dust exposure is low.

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1. Introduction

Road dust, an accumulation of solid particles in the form of organic and inorganic pollutants on outdoor ground surfaces, is a valuable medium for characterizing urban environmental quality (Godish, 2005; Liu et al., 2014). Road dust can be re-suspended into the atmosphere by wind, affecting the atmospheric environmental quality and human health (Lu et al., 2009b,c, 2010; Moreno et al., 2013). Road dust emissions are identified as an important source of primary particulate matter (PM) and they became increasingly important as no emission control strategies are taken by authorities (Amato et al., 2014; Kousoulidou et al., 2008). Several studies suggest that road dust emissions contain a significant amount of strongly magnetic, iron-rich particles (Bućko et al., 2010; Magiera et al., 2015; Sagnotti et al., 2006). The presence of ferrimagnetic components in urban road dusts are the cause of enhanced magnetizations, especially in those in the urban areas and sites downwind of industrial centers (Hanesch et al., 2003; Yang et al., 2007). Furthermore, the magnetic particles often have a causal link with heavy metals (such as Cu, Pb, Zn, Cd and Cr) and the existence of positive correlations between magnetic susceptibility and heavy metal content in urban road dusts and/or industrial/urban soils were observed in many cases (Hu et al., 2007; Jordanova et al., 2003; Morton-Bermea et al., 2009; Muxworthy et al., 2002; Xie et al., 2001). Furthermore, there is a growing interest in using magnetic techniques for monitoring environmental pollution (Chan et al., 2001; Gautam et al., 2004; Lecoanet et al., 2003; Lu and Bai, 2006; Wang et al., 2005).

Although accumulation of trace metals and magnetic enhancement in urban road dust has been well demonstrated in the literature and the magnetic properties of urban dust collected directly from streets have been extensively studied (Bućko et al., 2010; Goddu et al., 2004; Shilton et al., 2005; Xie et al., 2000; Yang et al., 2010), up to now there are no detailed studies considering the magnetic fraction of urban road dust. There is a lack of information on concentration and enrichment of potentially harmful elements (PHEs) in the magnetic phases of road dust. On the contrary, the enrichment and solubility of PHEs associated with magnetic extracts in industrially derived contaminated soils were investigated (Lu et al., 2012), while a number of studies on the magnetic fraction of fly ashes have been conducted (Kukier et al., 2003; Lu et al., 2009a, 2009b, 2009c; Vassilev et al., 2001, 2004; Yang et al., 2014). Furthermore the morphology and composition of vehicle-derived particles have been well determined in previous literature (Bućko et al., 2010, 2011) and detailed microscopic observations on single grains from the anthropogenic magnetic phases of polluted river sediments (Jordanova et al., 2004) and industrial dusts (Magiera et al., 2013) have been carried out. However, reports on internal structure and phase composition of anthropogenic magnetic dust particles are missing.

Thessaloniki which is one of the most densely populated cities in Greece accounting for approximately 16,000 inhabitants km^{-2} (Samara et al., 2003), is characterized by aggravated air quality due to intense source emissions, topography and meteorological/climatic conditions. Eventhough road dust has been estimated as a main contributor on ambient air particulate levels (Manoli et al., 2002; Samara et al., 2003), only sporadic studies have reported the contents of toxic heavy metals contained in it (Bourliva et al., 2011, 2012; Ewen et al., 2009; Misaelides et al., 1989; Samara et al., 2003), while no investigation was focused on the heavy metal content associated with magnetic particles extracted from it. Considering the role of road dust emissions in air quality and their impact on human health, the aim of the present work was a detailed description of mineralogical characteristics, morphology and heavy metal content of urban road dusts from the city of Thessaloniki, with special regard to the magnetic fraction as the main carrier of PHEs.

2. Materials and methods

2.1. Sample collection and magnetic separation

Road dust samples (each weighting almost 100 g) were collected from selected roads in Thessaloniki's city core (3 sampling locations) and in the western region that is in the vicinity of the industrial district (2 sampling locations) (Fig. 1). Specifically, roads in the vicinity of big industrial units (cement and metallurgy industry) which were recognized as significant contributors to ambient PM10 were selected. The road dust samples were collected twice within a gap of 5 months before and almost at the end of the dry season (April and September) in the year 2014. The dust samples were mainly collected by gently sweeping at all sites a comparable area of one square meter (1 m^2) from pavement edges using clean plastic dustpans and brushes for each sampling site. Care was taken to reduce the disturbance of fine particles. This sampling procedure is similar to those used in previous studies reported in the literature (Al-Khashman, 2007; Lu et al., 2009b, 2009c; Tanner et al., 2008). The efficiency of this sample collection has been reported to be equivalent to that of vacuum cleaning (Tanner et al., 2008). Samples were placed in self-sealed polyethylene bags and transported to the laboratory. In a first step, extraneous matter such as small pieces of brick, paving stone, leaves and other debris were removed. Then, the samples (bulk sample) were dried in an oven at 35 °C for 3 days and mechanically sieved. The <250-μm size fraction was used for subsequent analyses because it is the particle size that adheres to children's hands (USEPA, 2002). Because the subject of this study was the magnetic particles of road dusts, magnetic extracts were obtained by using a hand magnet sealed with a propylene bag. The extraction procedure was run continuously until no magnetic particles were attached to the magnet. The extracted magnetic fractions (MFs) and the residue (hereafter called non-magnetic fractions, NMFs) were collected and weighed.

2.2. Magnetic measurements

Different magnetic properties were used to characterize and identify the magnetic minerals in the road dusts. The mass specific magnetic susceptibility (χ) of dust samples was measured at low (0.46 kHz) and high (4.6 kHz) frequency using a Bartington MS2 laboratory magnetic susceptibility meter (Bartington Ltd., UK), equipped with a dual frequency MS2B sensor. Magnetic susceptibility value provides an indication of the concentration within the sample of strongly ferrimagnetic minerals, such as magnetite. Frequency-dependent magnetic susceptibility (χ_{fd}) was defined as $\chi_{fd}(\%) = [(\chi_{lf} - \chi_{hf}) / \chi_{lf}] \times 100$, where χ_{lf} and χ_{hf} represent magnetic susceptibility values at 0.46 and 4.6 kHz, respectively. Thermomagnetic analyses which measures low-field magnetic susceptibility versus temperature (K–T curves) were obtained by measuring continuously from room temperature to 700 °C and back to room temperature using a Bartington furnace in free air at the Department of Geophysics of the Aristotle University of Thessaloniki. Thermomagnetic curves allow the determination of the Curie temperature and the stability of the magnetic carriers upon heating. All magnetic measurements were carried out on bulk samples of road dust. Measurements that were carried out on different size fractions exhibited no significant differences.

2.3. SEM/EDX

A scanning electron microscope (JEOL JSM-840 A) was used to analyze the overall size distribution and morphology of road dust magnetic particles. A representative portion of each magnetic fraction sample was sprinkled onto double-sided aluminum tape mounted on a SEM stub, carbon-coated and observed by randomly selected fields of view. Elemental composition of the magnetic particles was determined using an X-ray energy dispersive spectrometer-EDX (INCA 300). The