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Magnetic response to air pollution recorded by soil and dust-loaded leaves in a changing industrial environment

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HIGHLIGHTS

- Air pollutants are monitored by magnetic and chemical measurements of soil and leaf samples.
- Magnetic signals of soil and leaf samples discriminate between historical and present pollution.
- Vertical distribution of magnetic properties of soil reflects pollutants accumulation.
- Magnetic susceptibility and heavy metals concentrations are well correlated.

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ABSTRACT

Linfen city is one of the World's most polluted cities due to uncontrolled industrial activities of coal combustion releasing huge amounts of heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) into the atmosphere. We used soil and leaves as receptors for atmospheric particulate matter to test the efficiency of magnetic approach for assessing and discriminating past and present pollution. The results indicate that strong magnetic particles in topsoil and leaf samples are mainly low-coercivity magnetite, occurring in a larger grain-size range than in background soil, which is helpful to separate anthropogenic and natural sources. Topsoil magnetic signals reflect pollutants, which accumulated over the last decades. Differences in the vertical distribution of magnetic properties between undisturbed and disturbed (cultivated) soil profiles show that the plowing depth is the most important factor for migration of pollutants in cultivated soils. Magnetic susceptibility (MS) values of leaf samples reflect the present state of pollution and can even trace seasonal changes. Spatial maps of MS identify differences of the past and present environmental conditions caused by the shutdown of industrial sites within the last decade. Correlation coefficients between analyzed HM contents (Fe, Cr, Ni, Cu, Pb) and MS values are significantly positive in leaf samples, and still moderate in topsoil samples. Our results demonstrate the practical and economical value of magnetic techniques for pollution assessment, also for the studied case with a complex pollution history, a relatively high magnetic background and disturbing land use.

1. Introduction

During industrial development, pollution from industry, agriculture, transportation and household became a main environmental threat. Man-made pollutants are released to the environment, transported by air or water, accumulate in soils, sediments, waters and biomass, ultimately destroying the ecosystem and harming human health.

Generally, high-temperature industrial or combustion processes produce both anthropogenic atmospheric pollutants like heavy metals (HMs) as well as magnetic particulates (Hanesch et al., 2003; Machemer, 2004). Because they have a similar discharge and transport path, and also heavy metals are directly absorbed in ferro(i)magnetic phases, these two substances are often closely related and show similar spatial distributions (Gautam et al., 2005; Spiteri et al., 2005; Zhang et al., 2013). Magnetic particulates are not a threat to human health by themselves, however, because of their

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close relationship with hazardous pollutants, they can be used as proxies to assess HM contamination (Jordanova et al., 2003; Robertson et al., 2003) and to target pollution sources (Szönyi et al., 2008; Hansard et al., 2012). A growing body of research (Petrovský et al., 2004; Blaha et al., 2008; Kardel et al., 2012; Hofman et al., 2013) document the benefit of applying magnetic techniques that are fast and easy to use for field measurements, in contrast to traditional chemical analyses which are accurate but more time consuming and costly. Magnetic proxies can well target chemical sampling locations, and allow collecting a smaller number of representative samples for chemical analysis to delineate the spatial distribution of contaminations (Appel et al., 2003).

Different targets are used for magnetic investigation of pollution. Magnetic minerals can be spread through the atmosphere (Gautam et al., 2005; Hansard et al., 2012; Hofman et al., 2013) or through water, e.g. via irrigation (Zhang et al., 2013), and are deposited in soil, partly migrating downward (Sapkota and Cioppa, 2012). Different biotic media were used as natural receptors of atmospheric particulates, such as tree leaves (Hu et al., 2008; Hofman et al., 2013), tree ring cores (Zhang et al., 2008), tree barks (Kletetschka et al., 2003), filters (Muxworthy et al., 2003), lichens and moss bags (Salo et al., 2012), and artificial passive samplers (Cao et al., 2015). Among these, tree leaves are the most common and ubiquitous ones because of their economic advantages. They have a large surface area for dust accumulation, allow a high density of sampling points and good coverage of the area of interest, and the biological magnetic background signal is low. Previous studies have successfully demonstrated that magnetic variation of dusts on leaves can well reflect present air quality (Hanesch et al., 2003; Szönyi et al., 2008) or automobile exhaust (Gautam et al., 2005; Rai, 2013). Topsoils, especially in urban and industrial areas, accumulate anthropogenic dusts over longer periods of years or decades. They have been extensively used to map the spatial distribution of pollution around power plants (Spiteri et al., 2005), steel plants (Duan et al., 2009) cement plants (Goluchowska, 2001), coking plants (Magiera et al., 2007) and metallurgical industries (Durza, 1999). Additionally, using soil magnetic parameters to trace the emission of pollutants is the most reliable fast method so far (Magiera et al., 2007; Hansard et al., 2012). Fly ashes that derive from industrial combustion can cause a significant difference in magnetic signals between topsoil and natural background soil (Petrovský et al., 2004; Blaha et al., 2008). Although the natural background is highly variable in some areas due to complex pedogenesis and land use (Yan et al., 2011), magnetic proxies of topsoil offer a comprehensive technique to reflect a relatively long-term environmental situation.

Our study area, Linfen city (Shanxi Province, northern China) (Fig. 1), is located at the heart of China's enormous coal industrial belt, supplying about two-thirds of the nation's energy. The local environmental condition dramatically deteriorated since the beginning of China's economic reform in the 1980s. Countless illegal and uncontrolled coal mines, steel factories and tar refineries made Linfen known as one of the most polluted cities in the world (Blacksmith Institute, 2006). In 2007, the State Environmental Protection Administration branded Linfen for the worst air quality in the country. The extremely high level of pollution took a serious toll on the inhabitants' health. Under such pressure, the local government was forced to undertake strong efforts for improving the air quality, and closed about two thousand polluting enterprises during 2006–2008. As a result, atmospheric pollution significantly reduced in the subsequent years; however, accumulated contaminants in soil and groundwater remain as a great environmental threat.

This study is a part of ongoing magnetic and geochemical investigations using different collectors (soil, tree-leaves, reservoir sediments and passive samplers) that reflect environmental pollution at Linfen city. Here, we report magnetic characteristics of soils and tree leaves as natural pollutant receptors. The main aim is to test the possibility of using magnetic susceptibility results from soil and leaf samples for discriminating between pollution that was accumulated during the period of uncontrolled industrial activity and the present state of pollution, i.e. after the governmental actions. Widespread agricultural activities and a relatively strong magnetic natural background of soil set up high challenges for this study.

2. Materials and methods

2.1. Study area

The larger Linfen area extends on ~20,000 km^2 with a population of about four million. Limestone dominates the geology of the mountains surrounding the basin. The area belongs to the Chinese Loess Plateau, and naturally, Quaternary loess is the parent material of soil in the study area. Linfen has a continental, monsoon-influenced climate with an average annual rainfall of 468.5 mm. The prevailing wind direction is from northwest. Main pollutants are industrial emissions from various factories such as coking plants, power plants and chemical plants. In addition, roads and railways for coal transportation pass through the city area, which exacerbates dust distribution.

2.2. In situ measurements, sampling and laboratory analyses

A total of 105 locations were probed in situ by a Bartington MS2D loop-sensor for soil surface volume-specific magnetic susceptibility (κ) in four campaigns (March 2010, October 2011, April 2012, November 2012), including present and abandoned industrial areas, farmland, and less polluted mountain areas (Fig. 1a). At each location, we performed 40 measurements within a 2 × 2 m area to check spatial homogeneity. For further analyses, we used the median value (κ_{median}) of these 40 readings. At 58 out of 105 locations, we recorded κ values in 5–7 ca. 0.5-m deep vertical sections by in situ measurements using an SM400 (ZH instruments) down-hole device (Petrovský et al., 2004). We created the holes in area of 2 × 2 m using a handheld 'Humax' corer, which allows obtaining cores in plastic liners (35 mm diameter, 50 cm length). Based on the variability seen in the SM400 curves and the visual conditions of the cores (preservation, avoiding stones and roots), we chose one representative core from every site for further measurements. The soil sampling sites were categorized into four categories i.e., farmland area ($n = 35$), industrial area ($n = 9$), abandoned industrial area ($n = 10$) and mountain area ($n = 4$) (Table 1). Naturally, grouping into these categories is only roughly possible because industrial places are ubiquitous in the study area. All sites in farmland area, and some sites in the other areas were cultivated, and thus must be considered as disturbed by human activities. The other sites were regarded as undisturbed soil profiles. At 78 topsoil locations in situ X-ray fluorescence measurements were performed for heavy metal analysis using an Innov-X portable X-ray fluorescence spectroscopy equipment (portable XRF) (Fig. 1a).

For leaf samples, we chose the evergreen *Platycladus orientalis*, a species relative to *Juniperus and Cupressus*, which is widespread in parks and gardens in China. Leaves were sampled from all around the trees at 1.5-m height. Fully developed new twigs with an age of 5–8 months were taken (Lehndorff et al., 2006; Hu et al., 2008). We placed the leaf samples in plastic bags and transported them to the laboratory. In October 2011, we collected 110 samples, and in April 2012 another 80 samples. At 44 sites, we performed sampling during both campaigns (Fig. 1b).