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Magnetic susceptibility and the spatial variability of heavy metals in soils developed on basalt

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ABSTRACT

Topsoil magnetic susceptibility (κ) is a fast and convenient method used to detect potentially polluted areas by heavy metals. Topsoil measurements are carried out in situ with Bartington MS2D loop sensor, designed to measure the magnetic susceptibility of top 10 cm of soil and detect 90% of the total signal from a depth of 6 cm. However, soils developed on basalt are difficult to assess due to their large amounts of ferrimagnetic minerals. The aim of this study was evaluate the applicability of κ to discriminate anthropogenic/lithogenic environments characterized by different parent materials in the city of Maringá/Brazil. In this paper, topsoil susceptibility (κ) was measured in 66 urban soils using a Bartington MS2D loop sensor. To investigate the magnetic background levels, samples of a Rhodic Ferralsol profile were measured using a laboratory MS2B sensor. X-ray diffractometry (XRD) analysis was carried out to verify the mineralogical composition of the different lithology. Cu, Fe, Ni, Mn, Pb and Zn concentrations were measured in 29 topsoil samples. The κ values ranged from 316×10^{-5} SI in a sandstone region to $6{,}945 \times 10^{-5}$ SI in soils developed on basalt. The χ_{fd} values of urban topsoil varied from 2% to 11.3%. Lower values of κ and χ_{fd} in the sandstone region indicated that the lithogenic contribution is of primary significance. Significant positive correlations between κ and Cu, Fe and Mn are related to the parent material, enriched in iron oxides, as verified by XRD. The background values (mean of $4{,}235 \times 10^{-8}$ m^3 kg^{-1}) were higher in subsoil, suggesting the inexistence of anthropogenic pollution. The topsoil susceptibility was efficient for distinguish different lithogenic environments. Although anthropogenic pollution in soils developed on basalt is difficult to assess due to the high natural background, our results suggest that heavy metal contents are not related to the human activity.

Capsule Abstract: Topsoil susceptibility distinguished different lithogenic environments such as sandstone and basalt. Anthropogenic pollution in soils developed on basalt is difficult to assess due to their high natural background.

1. Introduction

Measurements of topsoil magnetic susceptibility (κ) have been used by many authors as a fast and inexpensive method for detecting and precise delineating polluted areas (Chianese et al., 2006; Zawadzki et al., 2012). The most efficient environmental interpretation of these areas requires the integration of field measurements performed on the soil surface, frequently using an MS2D loop sensor (Lecoanet et al., 1999) and measurements of the vertical distribution of magnetic susceptibility within a topsoil profile, usually to a depth of about 20 cm (Hanesch and Scholger, 2005; Magiera et al., 2006). Most of the heavy metals from anthropogenic origin are accumulated in Of, Oh and Ah sub-horizons (Magiera, 2004; Magiera et al., 2006), where also the highest values of magnetic susceptibility are observed. On the plots of magnetic susceptibility versus depth in the soil profile, it is visible a large peak between 3 and 7 cm beneath the soil surface (Zawadzki et al., 2010).

However, one of the natural limitations of this method is the magnetic enhancement of soils caused by weathering of magnetically rich parent rock material (Fialová et al., 2006). In soils with low magnetic background values, environmental magnetic screening has been shown to be a suitable method for outlining anthropogenic contamination (Lecoanet et al., 1999; Schimdt et al., 2005; Zawadzki et al., 2012). Soils with highly variable magnetic background values, such as those developed on basalts, require more specific technological approaches for detection of the anthropogenically enhanced magnetic signal (Basavaiah et al., 2012). Basic rocks contain large amounts of iron-rich mineral phases, e.g., magnetite and titanomagnetite, and thus have high natural magnetic values (Maher, 1986). High background values may suppress lower levels of anthropogenic input, preventing an accurate assessment of the degree of contamination (Magiera et al., 2006).

Therefore, in situ and vertical measurements of magnetic susceptibility and the spatial distribution analysis can be very helpful in precise

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delineating areas where the heightened magnetic susceptibility is an influence of anthropogenic pollution from those resultant from lithogenic origin (Zawadzki et al., 2012). This paper aimed to examine the applicability of soil magnetic measurements to discriminate anthropogenic/lithogenic contributions in areas characterized by different geological parent materials in the city of Maringá/Brazil.

2. Materials and methods

2.1. Site selection and soil sampling

The study area is located between the coordinates (UTM SAD69, zone 22) 387673 E–7394096 N and 418554 E–7428039 N in the municipality of Maringá, northwest region of the state of Paraná/Brazil. The regional climate is classified as subtropical Cfa (Köppen, 1936), with hot summers and cold winters, mean temperature of 17.7 °C, precipitation of 1,276 mm year^{-1} and mean altitude of 549 meters.

The topsoil magnetic susceptibility measurements (κ) were performed in 66 sites (Fig. 1) within the urban perimeter of the city, covering roadside of highways, agricultural, residential/commercial, industrial and park/recreation areas. From the geological point of view, this region is characterized by a mixture of sedimentary rocks of the Late Cretaceous sediments deposited on the Paraná Flood, and basalts of the Serra Geral Formation, with large amounts of iron-rich minerals (Maack, 2002), therefore providing great conditions to assess the magnetic measurements to distinguish different lithogenic environments.

From the 66 selected sites, 29 topsoil samples (0–10 cm depth)—represented as square markers on the map—were collected to examine the correlation between in situ vs. laboratory susceptibility measurements and also the heavy metal concentrations. The sampling were carried out in the roadside of the Colombo Avenue—the main road of the city—at intervals of 1 km and in residential and agricultural areas, around the South and North Contour of the city (at intervals of 2–5 km).

Aiming to verify differences in mineralogical composition from both lithogenic environments, four of the collected samples (represented as triangles on Fig. 1) were selected and analyzed by X-ray diffractometry (XRD). To distinguish anthropogenic/lithogenic effects in a highly magnetic environment, a Rhodic Ferralsol (FAO/UNESCO, 2006) profile, located at the State University of Maringá–UEM (the circle in Fig. 1), was examined. For this issue, soil cores were collected with a step of 1 cm along the profile (into a depth of 30 cm) and stored in plastic tubes with 10 cm^3 for magnetic measurements in laboratory.

2.2. Soil magnetic measurements

Field topsoil volumetric susceptibility (κ) was determined in 66 sites using a Bartington MS3 Magnetic Susceptibility System (Bartington Instruments LTD), coupled with an MS2D loop sensor and a Trimble® GNSS handheld receiver, model Nomad® 900G series. The MS2D loop sensor is designed to measure the magnetic susceptibility of top 10 cm of soil, with 50% of signal response at 15 mm depth and about 10% at 60 mm (Dearing, 1999). Operating frequency is 0.958 kHz, with diameter, height and weight equal 185, 90 mm and 0.5 kg, respectively (Dearing, 1999). At least 2–5 readings of κ were taken in each selected point, with and without removing the organic litter (Zawadzki et al., 2012). The measured values were averaged and the mean considered the absolute value. The value of κ is recorded in dimensionless SI magnetic units ($SI = \times 10^{-5}$).

The 29 topsoil collected samples and the vertical susceptibility distribution of 30 sample cores were determined in laboratory by mass specific susceptibility (χ_{lf}) and frequency dependent susceptibility (χ_{fd}). Measurements were carried out using an MS2 Magnetic Susceptibility System (Bartington Instruments LTD), coupled with an MS2B sensor, equipped with both low frequency (0.46 kHz) and high-frequency settings (4.65 kHz) for the identification of fine grained superparamagnetic (SP) materials.

2.3. Soil mineralogy and chemical analysis

The 29 collected samples were air-dried and crushed to pass through a 2 mm sieve. Four of them were selected from different lithogenic environments and analyzed by X-ray diffractometry (XRD) (Whitting and Allardice, 1986). The XRD analysis was carried on a Shimadzu XRD-6000 equipment, having a CoKα beam and scanning step of 0.02°2θ, between 3 and 80°2θ, with 1.2 s for the time of pulse accumulation. Chemical analysis by sulfuric digestion (EMBRAPA, 2011) was performed in the 29 topsoil samples using an atomic absorption spectrometry (AAS) model GBC-932 AA, concerning the concentrations of selected heavy metals (Cu, Fe, Ni, Mn, Pb and Zn).

2.4. Statistics and soil spatial variability

Descriptive statistics and Pearson's correlation matrix were calculated using the software Statistica® v8.0. The spatial dependence of soil magnetic susceptibility and heavy metal concentrations were

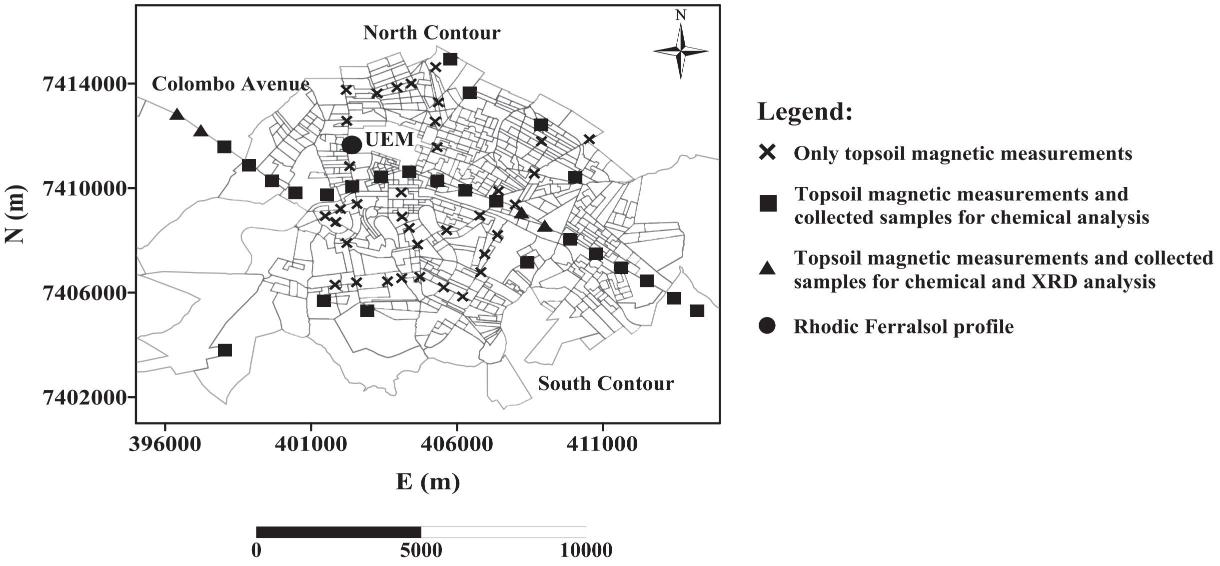

Fig. 1. Location of the vertical soil profile and the 66 topsoil sites where κ measurements, chemical and XRD analysis where carried out.