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Combination of geo- pedo- and technogenic magnetic and geochemical signals in soil profiles – Diversification and its interpretation: A new approach☆

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ABSTRACT

Magnetic and geochemical parameters of soils are determined with respect to geology, pedogenesis and anthropopression. Depending on local conditions these factors affect magnetic and geochemical signals simultaneously or in various configurations. We examined four type of soils (*Entic Podzol*, *Eutric Cambisol*, *Humic Cambisol* and *Dystric Cambisol*) developed on various bedrock (the Tumlin Sandstone, basaltoid, amphibolite and serpentinite, respectively). Our primary aim was to characterize the origin and diversification of the magnetic and geochemical signal in soils in order to distinguish the most reliable methods for correct interpretation of measured parameters. Presented data include selected parameters, both magnetic (mass magnetic susceptibility – χ, frequency-dependent magnetic susceptibility – χ_{fd} and thermomagnetic susceptibility measurement – TSM), and geochemical (selected heavy metal contents: Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn). Additionally, the enrichment factor (EF) and index of geo-accumulation (I_{geo}) were calculated. Our results suggest the following: (1) the χ/Fe ratio may be a reliable indicator for determining changes of magnetic signal origin in soil profiles; (2) magnetic and geochemical signals are simultaneously higher (the increment of χ and lead and zinc was noted) in topsoil horizons because of the deposition of technogenic magnetic particles (TMPs); (3) EF and I_{geo} evaluated for lead and zinc unambiguously showed anthropogenic influence in terms of increasing heavy metal contents in topsoil regardless of bedrock or soil type; (4) magnetic susceptibility measurements supported by TSM curves for soil samples of different genetic horizons are a helpful tool for interpreting the origin and nature of the mineral phases responsible for the changes of magnetic susceptibility values.

1. Introduction

Magnetic properties of soil are directly related to the type and concentration of ferrimagnetic iron oxides (Mullins, 1977), in particular, igneous and metamorphic rocks, industrial and urban dust deposition, presence of artefacts and soil formation process. For correct interpretation of soil magnetic properties on a local scale (soil profile or soil sites developed on one type of bedrock) various factors including natural (geo-, pedogenic) and anthropogenic parameters (actual and former land-use, distance from local pollution sources, historical deposition level etc.) which influence magnetic signals have to be considered.

Magnetic susceptibility measurements have been applied in environmental studies of topsoil as a proxy method for determination of atmospheric derived pollution (Flanders, 1994; Petrovský and Elwood, 1999; Hanesch and Scholger, 2002; Lecoanet et al., 2003; Chaparro et al., 2004; Blaha et al., 2008; Jordanova et al., 2008; Fürst et al., 2009; Sapkota and Cioppa, 2012a; Xia et al., 2014) or topsoil transformation (Łukasik et al., 2015) as well as artificial soils (Sapkota and Cioppa, 2012b). Moreover, in soil profile, pedogenic (including biogenic) iron oxides can also influence the magnetic properties of subsoil (Le Borgne, 1955; Fassbinder et al., 1990; Maher et al., 2003; Hanesch and Scholger, 2005; Geiss and Zanner, 2006; Magiera et al., 2008; Jordanova et al., 2013; Quijano et al., 2014; Grison et al., 2016). In addition, mineral soil

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horizons can also be influenced by geological background (Shenggao, 2000; Fialová et al., 2006; Magiera et al., 2006; Hanesch et al., 2007; Grison et al., 2015).

Iron oxides play a significant role in pedogenesis, providing information about distribution, migration and transformation of iron and iron-bearing minerals in soil profiles (Schwertmann, 1988). Diverse forms of iron affect the colour of soil horizons and their structure. Soil magnetic properties may help the characterization of different soil types and individual soil horizons, and even the processes operating within them (Maher, 1986). Changes of magnetic properties observed in soil horizons with domination of redoximorfhic processes can be the result of iron oxidation (Fe^{2+}) or anaerobic transformation of ferrimagnetic minerals (Han and Zhang, 2013). Iron, as a common element in the Earth's crust, is involved in a number of naturally occurring settings, exists in mineral phases and exhibits certain magnetic behaviour. This suggests that magnetic measurement of soils is an independent and reliable method for evaluation of pedo-environmental conditions and processes (Dunlop and Ozdemir, 1997). The presence of magnetic particles in topsoil organic subhorizons (e.g. forest soils) is directly related to anthropogenic impact, but their occurrence downward of soil profiles in mineral horizons can be the result of pedogenic and/or lithogenic and also technogenic combinations.

It is a well-documented fact that most industrial dusts contain anthropogenic iron minerals which are formed during high-temperature technological processes and are accompanied by heavy metals (Hulett et al., 1980). Magnetic susceptibility can be used as an indicator of the accumulation level of heavy metals in topsoil because of their relationship with anthropogenic iron oxides (Strzyszcz and Magiera, 1998; Petrovský et al., 2000; Hanesch and Scholger, 2002). These minerals are detected in topsoils as technogenic magnetic particles (TMPs) and are often significantly different from the minerals produced by natural processes because of morphology, stoichiometry and crystallographic structure (Jabłońska et al., 2010; Magiera et al., 2011). However, correlation with particular heavy metals is dependent on the dust source. Zinc and lead are commonly noted as tracers of anthropogenic impact on topsoils and they usually exhibit high positive correlation with magnetic susceptibility values (Chaparro et al., 2006). Topsoil organic matter acts as a sink for TMPs, and they can be observed both in organic (O) and in mineral (A) horizons depending on soil type and land use (forest, arable land, meadows etc.).

In highly polluted areas, magnetic particles in deeper subsoil mineral horizons (B) can be a mixture of anthropogenic and natural sources. In downward soil profiles in parent rock (C) and bedrock (R) horizons, natural magnetic particles are dominant, although their origin can be related to pedogenesis and/or geological characteristics of rock.

It important to study the vertical variability of geochemical and geophysical parameters in soils and pedogenesis processes strictly attributed to particular soil horizons. Soil sampling from genetic horizons allows for correct interpretation of magnetic signals in the context of pedogenesis instead of sampling based on schematic division of soil profiles (e.g. centimetre-wise).

The main sources of heavy metals in soil are natural processes and human activity and the contribution of metals originating from natural sources is lower than the contribution from anthropogenic ones (Nriagu and Pacyna, 1988). Therefore, to determine the concentration and source of heavy metals in soil as well as to quantify the extent of metal pollution we used enrichment factor (EF) and index of geoaccumulation (I_{geo}).

However, differentiation between geogenic and anthropogenic values of magnetic susceptibility can still be problematic. In this paper we apply a combination of methods to determine sources of magnetic particles in soil profiles. Domination of a single factor is easy to interpret and usually requires only one method, but nonetheless it may mask signals, making it hard to detect the presence of other magnetic signal sources. Detailed analysis of soil material indicates the relations between magnetic particle occurrence, heavy metal contents and pedogenesis. This approach was tested for a chosen group of soil profiles developed on various bedrock types as an initial study of coexisting sources (geo-, pedo- and technogenic) of magnetic particles. A combination of the presented methods appears to be an effective tool for environmental analyses and interpretation of magnetic as well as geochemical signal sources, particularly in complete soil profiles without lithologic discontinuity as well as in soil of diversified geochemical background and magnetic parameters.

Our paper provides an overview of studies of the magnetic and geochemical properties of soil profiles, presents a new approach that focuses on origin, diversification, and interpretation of combinations of geo- pedo- and technogenic magnetic and geochemical signals in soil profiles developed from different bedrocks. The determination of individual factors (geo-, pedo- and technogenic) in soil profiles and their corporate interpretation to find the main causes of magnetic and geochemical enrichment of soils have never been done in this way before. Until now, studies have primarily focused on just one of the aforementioned factors or these factors were analysed separately or in incomplete soil profiles (without consideration of lithologic discontinuity).

The innovation of our paper comprise a methodological aspect. We combine different quantification methods of anthropogenic pollution (enrichment factor and geoaccumulation index) and compare their values with magnetic and geochemical analyses to better understanding how different methods can contribute to interpret magnetic signal in soil profiles.

Presented data are part of a large project (sampling site network involving twenty-eight of soil profiles developed on fourteen various bedrocks occurring in Poland). The aim of the project was to examine the range of variability as well as to compare magnetic and geochemical properties of sedimentary, igneous and metamorphic rocks. Soil profiles considered in this study are developed on bedrocks (the Tumlin Sandstone, basaltoid, amphibolite and serpentinite) characterized by wide range of magnetic susceptibility values (from very low, low, high to very high, respectively) to confirm effectiveness of applied methodology for diversification of the origin of magnetic signal in soils.

2. Geological, soil and environmental settings

The study was conducted in mountain forests and highland forests of south-central and south-west Poland (Fig. 1 and Table 1). Soil and rock samples were taken from hand-dug pits where particular soil horizons were distinguished and measured according to the Polish Soil Classification (2011). Basic soil descriptions were made according to FAO et al. (2006). We distinguished four soil types (*Entic Podzol*, *Eutric Cambisol*, *Humic Cambisol* and *Dystric Cambisol*) – Table 2.

Entic Podzol was developed from the lower Triassic aeolian Tumlin Sandstone (Buntsandstein) of the Holy Cross Mountains. The Tumlin Sandstone is predominantly laminated, medium or fine-grained, moderate to moderately well sorted sandstone (mostly red) with very thin intercalations of mudstones (mostly reddish-brown). The sandstone consists of quartz and sporadic rock fragments (mudstone, quartzitic sandstone and siliceous rocks) as well as feldspars and micas. The cement and matrix (groundmass) consist of quartz and ferruginous binding mass containing iron oxides – i.e. haematite (Gradziński et al., 1979). The soil and rock material comes from a dug pit situated in Tumlin-Podgród, 11 km north-west of the town of Kielce. The soil pit is located a single-