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Soil magnetic properties in Bulgaria at a national scale—Challenges and benefits

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Establishing topsoil magnetic database at a national scale provides important information for soil classification, evaluation of soil drainage, indirect estimation of the total soil carbon and initial planning in precision agriculture. The Bulgarian database consists of 511 topsoil samples from the upper 20 cm of natural unpolluted soils. Samples have been characterized by detailed magnetic measurements, including mass-specific magnetic susceptibility, frequency dependent magnetic susceptibility, anhysteretic remanence, isothermal remanence and their ratios, hysteresis parameters and ratios, as well as soil reaction (pH). Histograms of the measured parameters per soil type and for the whole database show specific peculiarities and dependence from various parameters. Statistical factor analysis revealed that 87% from the total variance can be explained by four factors. The main factor is dominated by the contribution from concentration-dependent magnetic parameters, second one reflects the role of fine-grained pedogenic magnetic fraction, the third one is determined by the properties of the parent material, fourth one is governed by the internal structural peculiarities of the magnetic particles. The results from cluster analysis reveal the role of soil type and geology for the observed magnetic characteristics. The results emphasize the major role of geology (parent material) for the magnetic signature of topsoil samples on a national scale using sampling density of 1 sample/200 km^2. Spatial interpolation of different magnetic parameters using modelled experimental variograms and kriging algorithm highlight lateral peculiarities in the concentration and grain size of the strongly magnetic iron oxides in the topsoils. Additional geochemical data for selected set of samples and meteorological information reveal the role of climate characteristics (mean annual temperature and precipitation) on the formation and development of the strongly magnetic pedogenic fraction in soils developed on the same parent material.

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1. Introduction

Knowledge on the spatial distribution of different soil characteristics has important implications both in applied and theoretical soil science. Establishment of soil databases and soil maps allow better constrains on the soil sampling designs at various scales and site-specific purposes in precision agriculture as well as digital soil mapping. On the other hand, soil data are important for modeling different soil functions and revealing the role of soil forming factors (Jenny, 1941) at different spatial and temporal scales.

Several extensive studies of magnetic susceptibility and frequency-dependent magnetic susceptibility of national soil data sets from England, Wales, Austria, Bosnia-Herzegovina, France and others with partial coverage have been published up to now (Hanesch et al., 2007; Hannam and Dearing, 2008; Blundell et al., 2009; Thiesson et al., 2012). However, no published research has presented data on other important magnetic characteristics, for example, hysteresis parameters (coercive force, coercivity of remanence, saturation magnetization, saturation remanence). Although acquisition of such data is much more time-consuming, the information that could be gained concerning the amount, distribution and peculiarities of stable remanence-carrying minerals, is worth doing it. This gap in the present knowledge is overcome by the present research. A comprehensive set of 12 magnetic parameters and ratios are included in the soil magnetic database for Bulgaria, and used for statistical analyses and construction of maps.

Detailed small-scale investigations of soil magnetic properties are widely reported during recent decades in relation to soil pollution studies (Wang, 2013; Sarris et al., 2009; Kapicka et al., 2008; Chaparro et al., 2007; Magiera et al., 2007; Hanesch and Scholger, 2002), which depict spatial changes in magnetic characteristics, linked to the degree of anthropogenic contamination with heavy metals or organic compounds. However, depending on the spatial scale, sampling density and design, different processes and factors govern lateral changes in soil magnetic properties and characteristics (Hannam and Dearing, 2008). Studying scale-dependent importance of various factors on soil properties is an important topic in digital soil mapping, soil classification and precision agriculture.

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In this study, through the established magnetic database and maps for Bulgarian soils, new approach is presented for effective use of quantitative analytical methods for improvement of soil classification and field identification, as well as for revealing the effect of different soil forming factors on soil magnetic properties and iron mineralogy and transformations. Basic knowledge on the role of climate characteristics, sites altitude and weathering of primary parent minerals is obtained.

2. Materials and methods

2.1. Regional settings and sampling

Soil sampling was carried out during the summer periods of 2009–2012, following the general requirements applicable in geochemical analyses of soils and standard soil sampling protocol for studies of soil properties at EU level (Darnley et al., 1995; Toth et al., 2013). The uppermost 20 cm of the soils were sampled at five points (square ends and the center) of the 2×2 m square surface sampling plot. The material was mixed and assigned to a single point with geo- referenced coordinates, taken with a portable GPS (Garmin Vista). As a result, a bulk composite sample of about 1.5 kg was gathered from each location. Sampling was planned to avoid anthropogenically polluted locations (near roads, villages, industrial areas, agricultural lands), those with visible erosion at terrains with high slopes or re-deposition in local depressions. For each sampling location, a soil type was verified and assigned, using the 1:200 000 Soil Map of Bulgaria (Tanov et al., 1956) and the Soil Atlas of Bulgaria (Kojnov et al., 1998). Information on geological background (parent rock lithology) was obtained from the 1:100 000 geological map of Bulgaria for each sampling location. Irregular sampling grid with mean size of 12 km was used and 511 single locations were sampled. Scale factor SN, defined by Hengl (2006) as $SN = (A/N)^{1/2} \times 10^2$ where A is the surface of the study area and N—the number of sampling points. In our study A was 146.7 km^2. This factor determines the map resolution of the magnetic parameters.

Soils were classified in terms of main soil groups (orders), each one including a number of sub-orders. More detailed classification was not attempted in view of the grid density and the resulting map resolution. Soil classification is presented according to the WRB system and the correspondence with Bulgarian soil classification system is given according to Ninov (2000). Sampling sites overlain on the general soil map of Bulgaria (Shishkov and Kolev, 2014) are presented in Fig. 1a. The simplified geological map of Bulgaria is shown on Fig. 1b, highlighting the major rock types.

The simplified soil map of Bulgaria (Fig. 1a) shows the great variability of the soil cover, which includes 20 out of a total 28 FAO soil map units. This diversity is dictated by the environmental conditions established since the Pliocene up to the present day, including also the neotectonic influences. The mosaic of the soil cover is also influenced by the variability of modern climate (Kolchakov et al., 2005). Geology is one of the main factors of soil formation (Jenny, 1941), thus information about the surface geology of the Bulgarian territory is given in Fig. 1b. Bulgaria is divided into three major geological units: Moesian plate; Sredna gora zone (incl. Balkan zone) and Rila-Rhodopes massif. The Moesian plate is covered by Upper Paleozoic and Mesozoic sediments, overlain by Quaternary loess deposits. Balkan mountain range is represented by thick carbonate strata of Malm-Valanginian, Middle Triassic and Upper Devonian age, built up of limestone and dolomite. The western Rila-Rhodopes massif is mainly built of Precambrian metamorphic and granite rocks. Permeable terrigenous-clastic materials in the deep Neogene and Paleogene grabens cover the central part of the Tracian plane.

2.2. Laboratory methods and procedures

Magnetic susceptibility of the main rock and sedimentary formations have been measured in the field (where outcropping) or in the laboratory on small pieces in order to estimate its influence on the soil magnetic enhancement. Vegetation at each sampling point was recorded in the field book but was not included in the analysis. Soil samples were air dried in the laboratory, gently crushed and sieved through 1 mm sieve. Powdered material was used for magnetic susceptibility and hysteresis measurements. Remanence measurements of isothermal and anhysteretic magnetizations are carried out on cubic $2 \times 2 \times 2$ cm samples, prepared in plastic boxes by mixing 2 g of soil material, some gypsum powder and water. After hardening, boxes were removed. A blank gypsum sample was prepared and measured in line with the rest of the samples in order to subtract the effect of gypsum component on the total magnetization of the cubic samples.

Magnetic susceptibility (χ) was measured on Kappabridge MFK-1 (Agico, Brno) at an applied field of 300 A/m and single low frequency. The values were calculated on mass-specific basis using sample's weight, measured on an analytical balance KERN ABJ with precision of 0.0001 g. Frequency-dependent magnetic susceptibility (χ_{fd}) was measured on Bartington dual frequency sensor MS2B (Bartington Ltd., UK) with frequencies of 0.47 kHz and 4.7 kHz. Frequency dependent magnetic susceptibility (χ_{fd}) is calculated as a difference between low and high frequency signal on mass-specific basis. Percent frequency-dependent magnetic susceptibility was calculated as: $\chi_{fd}\% = 100 * (\chi lf - \chi_{hf})/\chi_{lf}$ according to Mullins and Tite (1973). Anhysteretic remanent magnetization (ARM) was acquired by using a Molspin AF-tumbling demagnetizer with 100 mT maximum amplitude of the alternating field and ARM attachment with applied weak dc field of 0.1 mT (Molspin Ltd., UK). Anhysteretic susceptibility (χ_{arm}) was calculated as $\chi_{arm} = ARM/h/\rho$, where h is the intensity of the dc-field. Isothermal remanent magnetization (SIRM) was acquired in ASC pulse magnetizer (ASC Scientific, USA) at 2 T field. After acquisition of ARM and SIRM, they were stepwise-demagnetized by AF field at 10 steps up to 100 mT. From these demagnetization curves, Median Destructive Field (MDF) of ARM and SIRM were calculated. Remanence measurements were carried out using JR6a automatic spinner magnetometer (Agico, Czech Rep.) and Minispin (Molspin Ltd, UK) magnetometer. Measurements done with the two magnetometers were inter-calibrated in advance using standards. Hysteresis measurements were carried out on Micromag 3900 (Princeton Measurements Corporation, USA) with maximum applied field of 1 T using the facilities at the University of Helsinki and ETH—Zurich. After correcting for paramagnetic contribution, a set of magnetic characteristics were obtained: saturation magnetization (Ms); saturation remanence (Mr); coercive force (Bc) and coercivity of remanence (Bcr).

Soil pH was measured with a Hanna 213 pH-meter (HANNA Instruments, USA) in water (1:5 soil:water ratio). A representative group of 82 soil samples, chosen on the basis of their magnetic characteristics was analysed by X-ray fluorescence analysis using energy-dispersive XRF spectrometer (Spectro-X-Lab 2000) at ETH-Soil Chemistry (Zurich). Samples were crushed and pellets for analysis were prepared according to the standard geochemical procedure.

Statistical analyses of the data base (descriptive statistics, Factor analysis, Cluster analysis) were performed by using STATISTICA 8 (StatSoft Inc.) software. Variogram analysis, data gridding and plotting of the maps were carried out within the options of SURFER 11 software package (Golden Software Ltd.).

Meteorological information was provided by the National Institute of Meteorology and Hydrology (Bulgarian Academy of Sciences) covering mean annual precipitation (MAP) and mean annual temperature (MAT) from a 20 years observation period for 102 permanent meteorological stations in Bulgaria.

3. Results

Our study is based on the assumption that soil type (order) and parent material of each sample from the database are properly identified, which allows reliable analysis of the peculiarities and typical magnetic

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