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## FACTORS THAT INFLUENCE SPATIAL VARIABILITY OF SOIL MAGNETIC SUSCEPTIBILITY ACROSS ROMANIA

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#### Introduction

Investigating Magnetic properties of soils became a used method in different environmental sciences like archaeology (Tite and Mullins, 1970), sedimentology (Thompson et al., 1975). paleoclimate reconstruction (Liu et al., 1995; Maher and Thompson, 1995), soil classification (Blundell et al., 2009), as records atmospheric pollution (Retallack et al., 2003), and as a tool for detecting land mines using electromagnetic techniques (Hannam and Dearing, 2008). Le Borgne showed that high values of magnetic susceptibility are recorded in topsoil rather than subsoil. The magnetic enhancement in top soil and the mechanisms of mineral transformations is soils remain even nowadays ambiguous. Several theories have sought to explain the chemistry, physics and formation of the minerals that commonly produce the enhanced magnetic effect (Le Borgne, 1955), and later Mullins (1977), suggests that soil forming processes are responsible for bio-reduction of Fe in anaerobic conditions transforming the iron oxides from goethite and hematite mainly in magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe2O3). Attempts to simulate the process in the laboratory (Maher and Taylor, 1988) showed that fine-grained magnetite could be produced in the absence of Fe-reducers, suggesting that magnetic enhancement in soils involves the competitive abiotic interplay of mineral formation (Maher, 1998). Another observation suggested that magnetic enhancement in soils can be obtained by burnings and deduced that thermal transformation of weakly magnetic Fe-minerals to ferromagnetic magnetite/maghemite took place as the soil shifts from aerobic to anaerobic and back to aerobic as fire diminished in intensity (Le Borgne, 1960). Different studies found evidence that magnetic susceptibility is influenced by bacterial activity in soils especially Magnetotactic bacteria (MTB) through the transformation of different iron oxides (Blakemore, 1975; Fassbinder et al., 1990). A large scale study tested several theories of magnetic enhancement in temperate soils trough analyzing maps of low field magnetic susceptibility and frequency dependent susceptibility of soils across England based on National Soil Inventory (NSI) sampled at 10 km grid intersections (Dearing et al., 1996a). This study showed that the majority of soils had magnetic properties dominated by the presence of nanoscale superparamagnetic particles produced in situ and there are derived from geological sources, the effects of fire, and accumulation of atmospheric pollution particles (Hay et al., 1997). Vertical variability of magnetic susceptibility on soil profiles was assessed on soil types from Romania and concluded that soil forming factors play an important role in soil magnetic properties (Garbacea and Ioane, 2010)

Because soil forming factors are inter-dependent and influence in different amounts magnetic properties of soils, we construct a conceptual model to explain the magnetic enhancement of soils as soil magnetic variations may be viewed in terms of environmental factors or boundary conditions that constrain the dynamic processes of mineral formation and accumulation.

#### Methodology. Spatial Sampling and field data recording

In order to understand complex relationships that influence soil magnetic properties we selected Romania National Forest Inventory (NFI) survey plots that were made according to the following layout: in the south-western corner of each cell measuring 4x4 km (2x2 km) a

square cluster measuring 250x250m was established. A NFI cluster contains four sample plots, located in the four corners of the cluster. At the end of the first NFI cycle, 28.204 sample plots with forest were visited in the field and 15.734 soil samples had been collected. From the total soil database, we selected soil probes with measured soil chemical analyses and we remained with 14470 soil samples to assess magnetic properties. The most important environmental factors associated with soil forming processes taken in consideration in this study were site factors like elevation (Elv), slope, slope aspect (Radiation), annual average temperature (Temp), annual average precipitation (Rain); soil properties like: N. Na, K. Mg. Ca, pH, C, HS (hydrogen saturation), BS (base saturation), soil texture, CEC (cation exchange capacity), BCSR (base-cation saturation ratio), stone content, horizon depth and other climatic factors (17 variables) that influence physical and chemical processes in soils. In the sampling sites were also measured stand biometry parameters and characteristics like forest type, production class, tree height and DBH. Soil samples were collected from an area that represents the general configuration of the site. Soil profiles were carried out with a spade. Vertical soil profiles were cut on the entire morphological thickness, and soil samples were collected from the middle of the diagnostic soil horizons, except O horizon, that had been removed because it is made entirely of organic matter. The slope of the sites was determined using a VERTEX hypsometer.

Soil profiles were diagnosed in situ and classified, and 500 g of soil were collected from each soil horizon for the physical and chemical analyses to be further done in the laboratory. The collected soil samples were classified in horizons and soil types after the taxonomic Romanian system of soil classification (SRTS-2012), which is consistent with the European classification system (ISO 14688). The methodology of sampling and analysis of soils was conducted according to International Co-operative Program on Assessment and Monitoring of Air Pollution Effects on Forests (Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests - Sampling and Analysis of Soil; ICP Forests Manual; (icp-forests.net). Determination of soil content in organic carbon was made using the wet oxidation method and dosage titration method of changing Doughnut (Walkley and Black, 1934). Soil pH was determined in water electrochemical readings accomplished with a Thermo Orion pH meter. Carbonates were gasvolumetric determined with Scheibler calcimeter. The determination of exchanged hydrogen was carried out by percolating after Cernescu's method (1939). Determination of the CEC and BS was made by extraction with ammonium acetate solution of pH 7. Readings were performed in flame spectrophotometer UNICAM.

The magnetic susceptibility measurements on the soil probes were performed in the laboratory with a SM 30 (GF Instruments) digital portable susceptibility meter. Every soil probe was measured numerous times, because weak contact can influence the measurements, thus the highest obtained value was recorded. This method was applied in view of a fast measuring technique of soil magnetic properties due the large number of samples. The accuracy of apparent magnetic susceptibility ( $K_a$ ) measurements compared with similar observations of mass specific magnetic susceptibility ( $\chi_{LF}$ ) and frequency dependence measures ( $\chi_{FD}$ ) or percentage frequency dependent susceptibility ( $\chi_{FD\%}$ ) on soil samples was previously found satisfactory (Kapick et al., 1997).

A factor that influence magnetic properties of soils derives from the mineralogical component (large number of soil probes we selected statistically from database, a representative number of soil probes for X-ray diffraction (XRD), with a purpose to evaluate the mineralogical variation between soil samples. The selected soil probes were measured using PANalytical aperture with the following settings: scanning interval  $2 - 80 \circ 2\theta$ ; scanning pitch =  $0.01 \circ 2\theta$ ; scanning time = 10 seconds/pitch. The abundance of component minerals in a soil sample has

been calculated by the ratio of peaks intensity of the component minerals. The area of peaks has been measured with High Score program that is a part of PANalytical diffractometer.

## Statistical methodology

For the XRD analyses we used a subsampling algorithm based on the values of magnetic susceptibility of soil probes. Data sampling has been made using classes of magnetic susceptibility and the sampling method was systematic with random start made with XLSTAT statistical software. Sample size was made of 260 soil probes with an addition of 30 extra soil profiles randomly selected from the database, with the purpose to capture vertical mineral transformation in the soil profiles. The best model to explain magnetic susceptibility variation will be constructed using ordinary square regression (OLS) algorithm and geographical weighed regression (GWR). Local regression techniques such as GWR that use spatial scale in ecological data (Da Silva Cassemiro et al., 2007; Hawkins, 2012). Maps generated from these data play an important role in exploring and interpreting spatial non-stationarity. Because of the large numbers of independent variables that have been taken into account we test statistical models using multivariate technique.

# **Results and Discussion**

The magnetic susceptibility of measured soil probes variated from 0.012 to 21.8  $\times 10^{-3}$  SI. The frequency distribution of  $K_a$  (Fig. 1) has a high skewness and revealed that the majority of soil samples recorded low values of magnetic susceptibility.



Fig. 1 – Frequency distribution of Ka ( $10^{-3}$  SI)

The magnetic susceptibility of soil samples shows that in plain areas low values are mainly recorded, while and in mountainous areas high values of *Ka* are generally recorded. From this we can deduce that the geologic factor plays an important role in influencing the magnetic susceptibility of soils. By comparing XRD semi-quantitative estimation of mineral components we can deduce how mineralogy influence the magnetic properties of the soils (Fig. 2)



Fig. 2 - XRD analyses of a soil sample

Because soil particles are drained during time, in the model we included all the environmental factors that influence soil particles dynamics. To test this, we chosed a test area were we evaluated the variability of Ka and measured the mineralogical changes in relation with topographical factors. Multiple regression models may reveal how soil forming factors influence the variance of magnetic parameters. Our assumption is that the main factor that influence is parent material mineralogy and soil forming processes through draining and iron oxidation-reduction processes in soils.

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