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MAGNETOMETRIC METHOD AS A TOOL OF MEASURING POLLUTION OF FOREST SOILS BY HEAVY METALS – EXAMPLE OF THE ORLICKÉ HORY MTS.

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This paper introduces the magnetometric method and its application in measuring fly-ash contamination of the forest soils in the Orlické hory Mts. region, Eastern Bohemia. The magnetometric method is highly sensitive; therefore we can measure even small changes in the magnetic characteristics of soils. Under certain conditions the method is useful also in locations with low level of contamination such as national parks and other environmentally unique localities. Topsoil magnetic susceptibility was measured directly in the field by Bartington MS2 instrument. From forest floor and mineral soil samples detailed laboratory magnetic analyses were carried out to understand origin and translocation history of magnetic particles in soil horizon. Dominant ferromagnetic fraction in forest floor (magnetite) was identified by thermomagnetic measurements on Kappa Bridge KLY-3S. IRM acquisition curves discriminate two populations of magnetic contributions; topsoil magnetic particles, derived from atmospheric deposition, and subsoil ones, derived from lithology. We compared our measurements of magnetic susceptibility with concentrations of chosen heavy metals (Fe, Mn, Zn, Cu, Cr, Co, Pb, Cd) and their correlations were statistically evaluated. Results confirmed that magnetometry is suitable and effective proxy method for evaluation of soil contamination in location of Orlické hory Mts.

Key words: *atmospheric deposition, forest soils, heavy metals, magnetic susceptibility, Orlické hory Mts., Czech Republic*

V roce 2006 byla v oblasti Orlických hor zkoumána vhodnost využití magnetometrické metody pro zjišťování znečištění lesních půd pevným atmosférickým spadem deponovaným do povrchových horizontů půd. Vysoká citlivost magnetické metody umožňuje detekovat i malé změny magnetických vlastností půd. Jeví se jako vhodná i pro oblasti, s předpokládaným malým znečištěním. Aparaturou Bartington MS2 byla vyšetřována povrchová půdní susceptibilita a odebrány vertikální profily pro laboratorní měření magnetické susceptibility. Tato měření sloužila k vyloučení lokalit, u kterých hodnota magnetické susceptibility svrchních půdních horizontů byla ovlivněna horninovým podložím. Z měřeného souboru byly z tohoto důvodu vyloučeny tři lokality. Laboratorní magnetická měření byla využita ke stanovení magnetomineralogie a magnetické stability dominantních antropogenních ferimagnetik v půdách. Naměřené hodnoty půdních susceptibilit byly porovnány s koncentracemi některých těžkých kovů a zjišťovala se jejich vzájemná korelace. Plošné rozložení hodnot povrchových půdních susceptibilit indikuje nerovnoměrnou úroveň pevného spadu v Orlických horách.

Výsledky potvrdily vhodnost využití magnetometrické metody při sledování kontaminace půd, jako předběžné monitorovací metody, která ve srovnávaní s klasickými chemickými analýzami je relativně rychlejší a finančně méně náročná.

Klíčová slova: *atmosférická depozice, magnetická susceptibilita, lesní půdy, těžké kovy, Orlické hory.*

1. Introduction

In general, intoxication of environment trough anthropogenic influence is a worldwide problem. Therefore fast and effective new approaches are needed for monitoring and evaluation of source of contamination. In addition to the traditional chemical methods, which are slow and expensive, we present a method based on measurement of magnetic properties of soils. Advantage of this magnetometric method is high sensitivity and possibility to measure large area in relatively short time (Kapička *et al.* 2001, Fialová *et al.* 2006).

We used magnetometric method for detecting contamination by air pollutants. Principal idea of magnetometry is based on the fact that magnetic enrichment in forest floor layers is due to industrial fly ash deposition. Fly ashes are rich in ferromagnetic minerals (magnetite, maghemite) but we can find these minerals also in soils as natural minerals resulting from weathering processes (Maher 1986, Dearing 1994). Another source of magnetic enrichment can be ultra-fine, super paramagnetic particles, due to pedogenetic processes in soils (Fassbinder *et al.* 1990, Maher *et al.* 1988, 1995, 2003). Low-field magnetic susceptibility (MS) is the most useful, concentration-dependent parameter for magnetic mapping of soil pollution. We are able to measure topsoil MS with high precision directly in the field. Many studies confirmed also good correlations between MS and heavy metal concentration in contaminated soils (e.g. Jordanová *et al.* 2003, Spassov *et al.* 2004, Spiteri *et al.* 2005). Practically all, industrial fly ashes contain a significant fraction of ferromagnetic iron oxides; the most important sources are fly ashes being produced during combustion of fossil fuel. Other sources, such as steel works, cement works and road traffic also contribute to contamination by anthropogenic ferromagnetic particles (Prospero 1968, Hunt 1986, Chester *et al.* 1984, Thompson and Oldfield 1986). Magnetic particles and heavy metals have similar sources and similar storing mechanism (Adriano 1986, Uhlířová *et al.* 2002).

Objective of our research was to find out whether magnetometry is convenient method for detecting soils contamination in relatively unpolluted region of Orlické hory Mts., where evolution of forest ecosystem exhibit constant degradation (MZE CR VULHM 2004). The forests of Orlické hory Mts. show forest decline along with the change of soil chemistry (Vacek *et al.* 1994a, b; Vacek and Podrázský 1996a, b; Vacek *et al.* 1997).

2. Materials and Methods

In the June and October 2006 measurements of topsoil magnetic susceptibility, including soil core sampling, were carried out in area of Orlické hory Mts., Eastern Bohemia. Eleven locations, of the total area about 120 km^2 were chosen to describe uniformly windward and leeward side (Tab. 1). Altitude of sampling sites varied from 500 to 1,070 m. From point of view of nature protection, majority of chosen locations belong to the most important areas in the region of interest; in addition to protected preserves (NPR Trčkov, PR Pod Vrchmezím, PR Sedloňovský vrch, PR Jelení lázeň, PR Kunštátská kaple, PR Komáří vrch), five localities were chosen (Nad Zdarovem Hlodný, Polom, Neratov I, Neratov II) under conditions of managed forest.

Topsoil magnetic susceptibility (κ_{LF}) was measured directly in the field by Bartington MS2-D probe according to the recommendations for selecting and measuring the sites (Schibler *et al.* 2002). For information about vertical distribution of MS in whole soil profile we used two instruments, Bartington stratigraphic probe MS2F and Susceptibility Meter SM400 [ZH Instruments co.) (Petrovský *et al.* 2004)]. The depth of individual soil pits or soil cores varied from 30 to 40 cm. Furthermore, laboratory measurements of MS were completed on Bartington MS2C probe, where core samples taken from vertical soil profile were measured. From soil cores we separated forest floor (L, F, H) and subsoil (A, B/C) layers. Samples were dried, sieved with 2 mm mash, put into the plastic containers of volume

Table 1. Localities in the area of interest, the Orlické hory Mts.

Locality	Altitude (m)	Aspect	Slope (%)	Site	Stand age (years)	Dominating tree species	Bedrock	Soil
Trčkov	790	NE	< 10	6 S	180	SM, BK	Mica schist, quartzite	Cambisol
Pod Vrchmezím	930	NNW	35	6 S, 7 S	180	SM, BK, JVK	Mica schist	Cambisol, podzol
Sedloňovský vrch	1 010	WSW	35	7 S	180	SM, BK		
Jelení lázeň	1 075	—	< 1	8 T	—	SM	Mica schist + quartzite	Gleysol
Nad Zdarovem	560	NW	50	5 B, 5 A	120	BK, JVK	Permian breccia	Cambisol
Kunštátská kaple	1 040	—	< 1	8 T	—	—	Gneiss + mica schist	Gleysol
Komáří vrch	970	SSW	25	7 K, 7 Z	140	SM, BK	Gneiss	Cambisol, podzol
Hlodný	600	W	50	5 J	120	BK, JL, JVK	Phyllite	Cambisol
Polom	680	ESE	5	5 S	50	SM	Phyllite + amphibolites	
Neratov I	740	NNE	18	6 S	50	SM	Glauconitic sandstone	
Neratov II	740	NNE	18	6 S	50	MD		

Explanation notes: *Site: 5 – beech with fir; 6 – beech with spruce; 7 – spruce with beech; 8 – spruce potential forest vegetation zones. Tree species abbreviations used: SM – Norway spruce; MD – European larch; BK – European beech; JVK – sycamore maple; JL – Scotch elm.*

10 ml and weighted to determine also mass specific magnetic susceptibility (χ_{LF}). Enrichment of MS due to pedogenic processes was checked by frequency-dependent magnetic susceptibility κ_{FD}, defined as $\kappa_{FD} [\%] = (\kappa_{LF} - \kappa_{HF}) / \kappa_{LF}$), where κ_{LF} and κ_{HF} represent susceptibility values at 0.47 and 4.7 kHz (Dearing *et al.* 1996). To determine hardness of dominant ferromagnetic particles in soils we performed measurement of IRM (isothermal remnant magnetization), acquisition curves and AC demagnetisation curves of SIRM (saturation isothermal remnant magnetization). Measurements were performed by AGICO spinner magnetometer JR-5 (Kapička *et al.* 2003)

Magnetic mineralogy of samples was studied by high temperature measurements of magnetic susceptibility on Kappa Bridge KLY-3S (AGICO co.) with CS-3 furnace. By continuous heating up to 700 °C we defined Curie temperature (Tc) of dominant ferromagnetic minerals.

Concentration of heavy metals (Fe, Mn, Zn, Cu, Cr, Co, Pb, and Cd) was determined with Atomic Absorption Spectrometry (AAS) in certified laboratory. 2M HNO_3 was used as a leaching agent.

On chosen samples, Scanning Electron Microscopy (SEM) with Wavelength Dispersive Spectroscopy (WDS) was done to see morphology and determine the element content. SEM and WDS analyses were carried out in the Institute of Geology, ASCR in Lysolaje by equipment SX 100 CAMECA.

Relations between heavy metals content and MS of forest-floor and mineral soil horizons were visualized by software CANOCO 4.5 (ter Braak and Šmilauer 2002). Data were determined by non--parametric gradient analysis method of Detrended Correspondence Analysis (DCA).

3. Results and Discussion

Magnetic susceptibility in forest floor layers has not reached extremely high values, typical for industrial areas. Some of measured samples were just above the limit of sensitivity of instruments used for measuring of MS.

Frequency-dependent susceptibility (κ_{FD}) of practically all forest floor samples was lower than 4%, what is a proof of negligible or zero content of pedogenic particles. Measurements of κ_{FD} helped us to determine one soil profile (location Hlodný), where magnetic enrichment resulted from pedogenic processes, creating SP magnetite. This soil profile had increased κ_{FD} in deeper horizons.

Magnetic enrichment due to strong lithogenic contribution was detected in 3 locations. Topsoil MS measurements were used for creation of preliminary 2D map expressing surface distribution of contamination. The map can be used only as approximate guide, because better resolution needs much more measuring points of surface MS.

From IRM and SIRM measurements we can conclude, that samples from top- and sub-soil horizons exhibit different magnetic behaviour. Forest floor contain magnetically soft (multidomain) ferromagnetic minerals, which are typical for anthropogenic particles. For saturation of subsoil samples was necessary to applied higher magnetic field, which proof the presence of harder ferromagnetic, of lithogenic and probably also pedogenic origin.

Thermo-magnetic measurements confirmed presence of magnetite in top horizon, with Curie temperature of 580 °C. Shape of heating curves of all forest floor samples was very similar; therefore magnetite has to have one source, most probably of anthropogenic origin.

SEM analyses detected anthropogenic particles only at forest floor samples (Fig. 1b and 1c). In location Sedloňovský vrch titan magnetite of lithogenic origin was

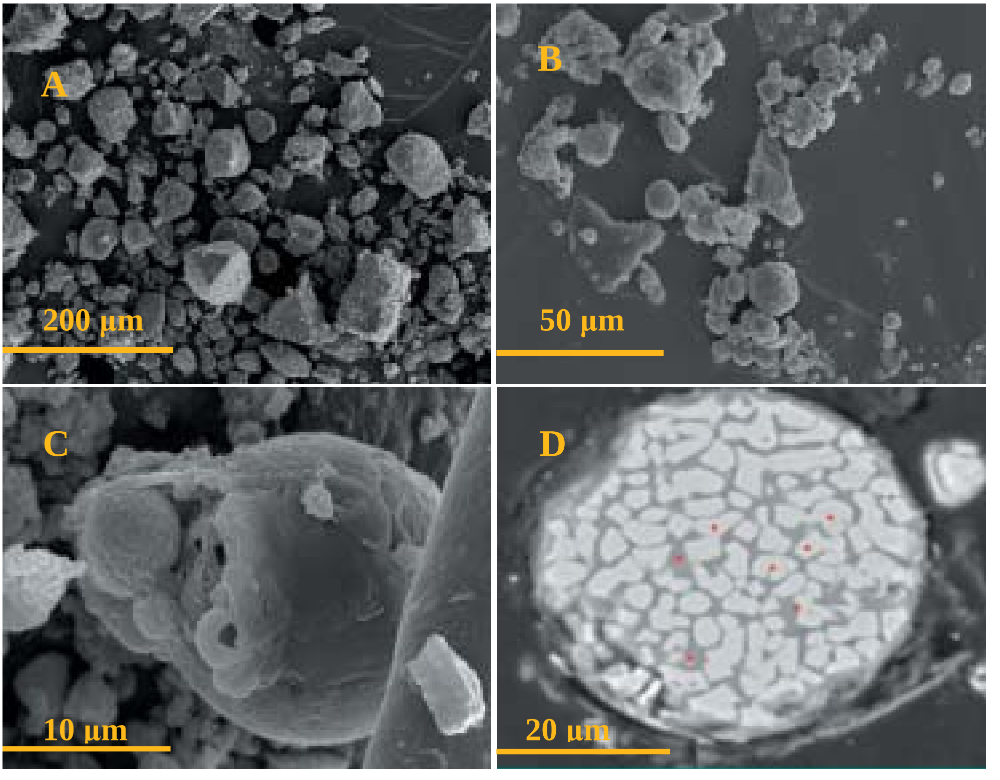

Fig. 1. Examples of SEM: a) mineral soil sample with non-spherical fragments from location Sedloňovský vrch; b) forest-floor sample with spherical fragments from location Sedloňovský vrch; c) spherical fragment from forest-floor layer from location Nad Zdarovem; d) cross section of spherule, where WDS element content was determine. Lighter parts are more enriched by FeO compared with darker parts.

identified (Fig. 1a) in sub soil horizon. Exception at sample in location Trčkov was observed in depth of 16–20 cm, where MS extremely increased. SEM observations discovered atmospheric particles in this part of "B" horizon. Exact explanation of transport mechanism is not known. SEM analyses showed wide variety in the morphology, but clearly confirmed that magnetic enrichment of forest floor is due to presence of anthropogenic "spherules". WDS analyses exactly determined element composition of different particles; one example is present in Figure 1d, where spherical particle is composed of $FeO+Al_2O_3$ (white part) and $FeO+SiO_2$ (dark part).

One of our goals was to determine possible correlations between concentration of heavy metals in forest soils and mass specific magnetic susceptibility (χ_{LF}). For evaluation of pollution level, concentrations of selected heavy metals were set out. Correct interpretation of contamination of forest soils by heavy metals is connected

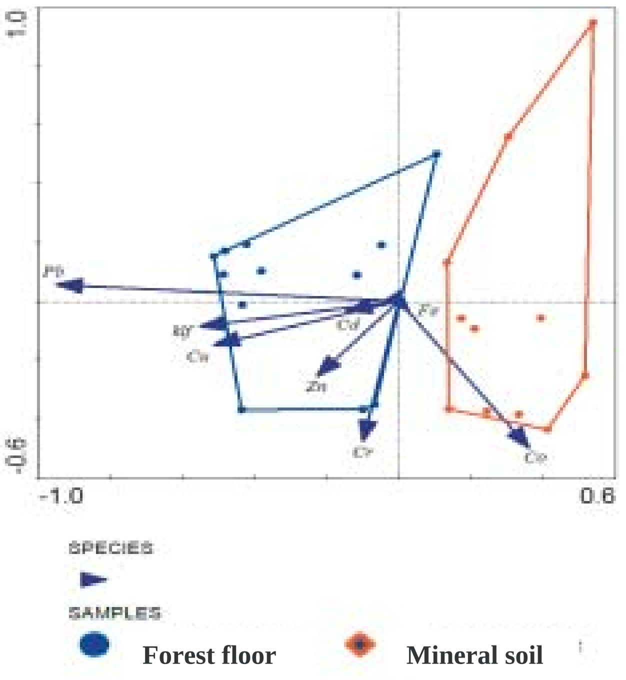

Fig. 2. Ordination diagram describes well relations between concentration of heavy metals Fe, Mn, Zn, Cu, Cr, Co, Pb, Cd and magnetic susceptibility (κ_{LF}) in top layers of forest floor (blue spots) and sub layers of mineral (red spots) soils (red spots).

with fact that there does not exist any limit for concentration of heavy metals in forest soils in the legislation of the Czech Republic. This gap can be partly solved by using recommended maximal values for four elements (Cd > 3,5; Cu > 20; Pb > 150; Zn > 300 (mg/kg)) set by international programme IPC Forests (Uhlířová *et al.* 2002). In their methodology concentration of heavy metal is set by leaching in aqua regia, therefore we can not compare correctly our measurements, where leaching in 2M HNO_3 was used. Data analyses were performed using non-parametric Detrended Correspondence Analysis (DCA) in the CANOCO software v. 4.5 (ter Braak and Šmilauer 2002). We tested 1st and 2nd ordination axis ($p < 0.05$). Results are presented as ordination diagram (Fig. 2). Samples are presented as points surrounded by "envelopes"; forest-floor and mineral soil horizons and elements are visualized as arrows pointing towards growing concentration.

Statistical analyses determine good correlation between Pb, Cu, Cd, Zn, Cr and mass specific magnetic susceptibility (χ_{LF}) in forest-floor humus. Pb reached the highest concentration in forest-floor humus, what results from anthropogenic origin. Furthermore, elements as Cu, Cd and Zn (Fig. 2) showed also high concentration in organic layers. Cobalt (Co) had the highest concentration in mineral layer and it was

Table 2. Results of correlation analyses of elements concentrations and magnetic susceptibility in the forest floor and mineral soil

Indep. var.	Depen. variable	r	F	P value
Horizon	κ_{LF}	0,739	25,199	<0.001
	Fe	0,542	8,725	0.008
	Zn	0,455	5,473	0.029
	Cu	0,700	20,143	<0.001
	Cr	0,038	0,030	0.865
	Co	0,649	15,309	<0.001
	Pb	0,685	18,557	0.001
	Cd	0,588	11,098	0.003

Abbreviations: indep. var. – independent variable – horizon (forest floor and mineral horizon), dependent variable – soil concentration of selected elements, κ_{LF} *– magnetic susceptibility.*

not correlated with MS (χ_{LF}). This is likely to indicate its lithogenic origin. According to DCA, the effect of horizon was significant and explained 60.2% variability of all collected data (P = 0.022)

Variability in concentration of the element was tested between forest floor and mineral soils horizons using one-way ANOVA in STATISTICA 8.0 software (StatSoft 2007). It was used to evaluate the effect of horizon (forest floor and mineral soil) on soil chemical properties and magnetic susceptibility (χ_{LF}). In the case of significant ANOVA result, Tukey's post-hoc comparison test was applied to identify significant differences between horizons.

To demonstrate that the ordination diagram shows correctly the relation between all analysed data, the results of the most important correlation analyses are given in Table 2.

4. Conclusions

The main goal of this study was to test suitability of magnetomeric method for the evaluation of contamination of forest soils in the region of Orlické hory Mts. by air pollutants. Investigated area belongs to the category of relatively clean forest ecosystems. There are no local heavy-contamination sources situated nearby, therefore we assume that contamination is mostly due to long-range transboundary atmospheric pollution. Magnetic measurement carried out directly in the field and detailed laboratory measurements as well identified anthropogenic particles and discriminate lithogenic and pedogenic minerals. Three locations (Hlodný, Polom, and Komáří vrch) were evaluated as areas with strong lithogenic influence; therefore they were excluded from the evaluated data set used for magnetic mapping. Magnetic measurements based on low values of MS confirmed relatively low level of contamination by air pollutants nevertheless whole area shows increased concentration of anthropogenic particles in forest-floor horizons (O_L, O_F, O_H). Statistical analyses showed that concentration of Pb, Cu, Cd, Zn, and Cr correlate well with magnetic susceptibility of forest-floor layers. Anthropogenic influence of the surface conditions confirms that as well.

We can conclude that magnetometric method is fast and relatively inexpensive. Our results indicate that this method can be used (as proxy method) for evaluation of forest soil contamination also in areas with relatively lower pollution levels as in region of the Orlické hory Mts.

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