

EVALUATION OF SOIL CONTAMINATION DEGREE IN THE REGION OF MARITZA-EAST THERMAL POWER PLANTS USING MAGNETIC METHODS

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Abstract

Pilot study on soil contamination degree around the Maritza East thermal power plants, evaluated through applying magnetic methods, is presented. The magnetometry method is based on the well-established fact that anthropogenically contaminated with fly ashes soils display enhanced magnetic susceptibility, as well as other specific magnetic characteristics. Results from the magnetic investigations carried out in our study evidence significant soil contamination near the pollution sources and decreasing degree of anthropogenic load further away. The method applied is economically more efficient compared to classical physical and chemical methods for evaluation of soil contamination.

Key words: magnetic susceptibility, TPP Maritsa East, soil

1. INTRODUCTION

Industrial activities of different type commonly cause significant environmental contamination of soils, air, water and the living organisms. Various geochemical as well as geophysical methods could be applied for evaluation of environmental pollution. During the last decade, in Europe, as well as in Bulgaria, magnetometric method for estimation of soil pollution is applied in different case studies (e.g. Goddu et al., 2004; Jordanova et al., 2006; Jordanova et al., 2013; Dlouha et al., 2013). Magnetometric method for evaluation of soil/sediment pollution is based on the well-known fact that most industrial activities, road traffic, and other production industries discharge/emit jointly with hazardous elements (heavy metals, As, organic compounds) also a strongly magnetic fraction, containing significant amount of Fe (Gomes et al., 1999; McLennan et al., 2000; Abdul-Razzaq & Gautam, 2001; Kukier et al., 2003). A number of studies have shown the presence of anthropogenic fractions magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) as well as weakly magnetic hematite ($\alpha\text{-Fe}_2\text{O}_3$) in different waste products – fly ashes from thermal power plants, metallurgical slag and dump materials, traffic emissions (Veneva et al., 2004; Jordanova et al., 2006; Jordanova et al., 2014). Thus, application of simple magnetic (both field- and laboratory) measurements like these of magnetic susceptibility – provide an efficient and cost effective tool for fast and precise evaluation of anthropogenic load in different environments. Magnetic susceptibility (k) is a measure of the ability of the material measured to become magnetized in a weak magnetic field. By definition magnetic susceptibility $k = M/h$, where M is the induced magnetization and h is the strength of the applied magnetic field. Commonly, magnetic susceptibility depends mostly on the concentration of the strongly magnetic minerals in material measured (Thompson & Oldfield, 1986). As any other analytical method, magnetometric method has some limitations to its applicability. The most serious factor impeding its easy application is the presence of strongly magnetic minerals in soil, inherited from the parent lithology. In such a case, anthropogenic addition of magnetic fraction is masked by naturally occurring Fe-oxides. Typical examples are soils developed on volcanic rocks. Magnetometric evaluation of soil pollution was accomplished in several areas in Bulgaria – in north-east Bulgaria in the Varna-Devnja region (Jordanova et al., 2008), in south-east Bulgaria in Burgas region (Jordanova & Jordanova, 2010), in several smaller areas around Sofia (Jordanova et al., 2003; Daskalova et al., 2008).

The aim of the present study is to further apply and test the method for evaluation of the degree of anthropogenic pollution of soils in the area of the Maritza-East coal mining and power plant complex located in central south Bulgaria.

2. MATERIALS AND METHODS

2.1. Study Area

The study area is situated in the Sazliyka watershed, SE Bulgaria (Fig.1), part of the large Maritsa watershed, and extends between the parallels of latitude N42°00 and N42°20 and meridian of longitude E25°40 and E26°20. Both watersheds extend over part of the Upper Thracian Plain.

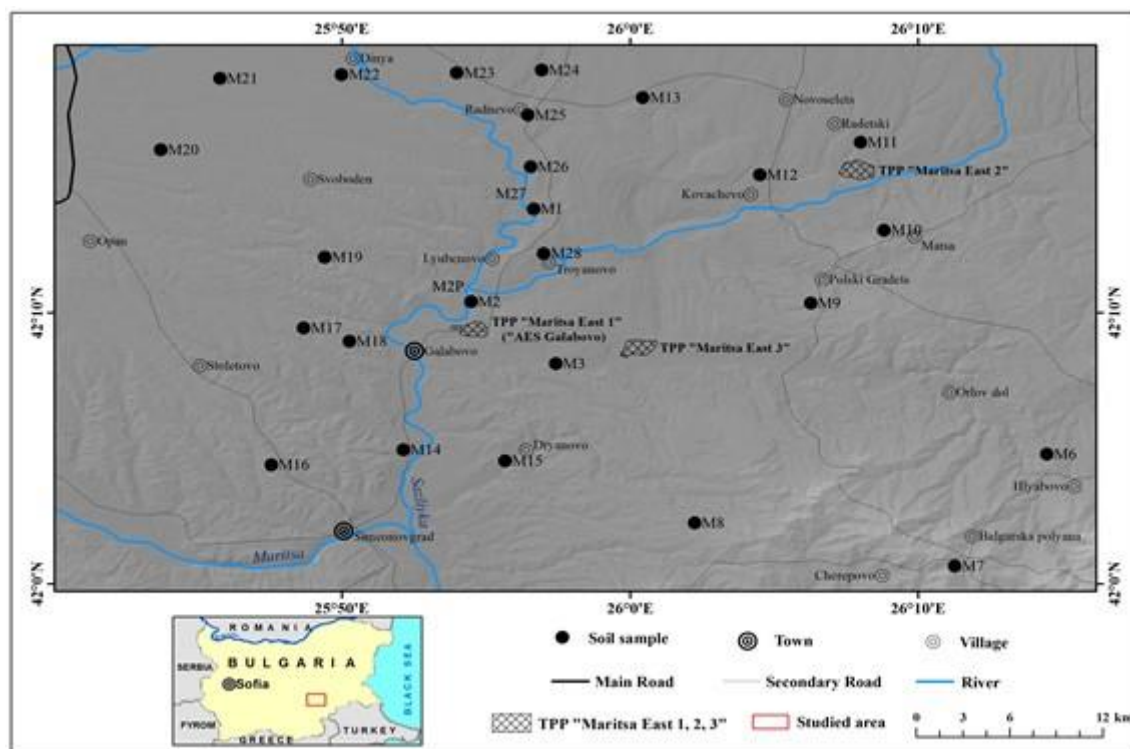


Fig. 1 Study area and sampling points location

Study area is restricted around the thermal power plants “Maritza East” 1, 2 and 3, which are situated near the village of Galabovo and the towns of Radnevo and Stara Zagora. The climate there is transitional-continental, characterized by mild winters and hot summers. Prevailing wind directions are from north-northeast and the typical speed is between 0-2 m/s. Temperature inversions are frequent in the study area which is the reason for the observed strong pollution during such period, due to suppressed vertical movement of all industrial emissions. The major soil types in the region are EutricVertisols, Dystric Planosols, Rendzic Leptosols and Fluvisols/Colluvisols (Ninov, 2002).

The main pollution sources in the region are the thermal power plants (TPP) “Maritza East”1, 2, 3 (TPP AES Galabovo; “TPP Maritza East 2” EAD and ContourGlobal Maritza East 3 TPP). They utilize local lignite coal for power generation. Lignite coal is extracted from the East Maritza coal basin. Waste disposal dumps have a system for active dust suppression at transfer areas but frequent high PM emissions are registered in Galabovo town. The power plants are equipped with Flue Gas Desulphurization installations (FGD) by 95-98% efficiency. The total production of the three TPPs makes up 35-38% of the electric power consumption in Bulgaria.

2.2. Data and methods

During field campaign in 2015, surface soil samples (the uppermost 0-2 cm) were gathered from 30 locations (indicated in Fig. 1 by their names M1-M30). In addition, a depth profile (GL) in location M2 is sampled in 1-cm interval up to 14 cm depth and in 2-cm interval up to 40 cm depth. Soil samples are sealed in plastic bags and transported to laboratory. In laboratory, soil material is air-dried, coarse stone pieces removed and the rest of the material gently crushed and sieved through a 1-mm sieve. This fraction is further used for magnetic measurements performed at the Palaeomagnetic Laboratory in NIGGG-BAS. Magnetic susceptibility of soil samples is measured with kappa-bridge KLY-2 (AGICO Ltd., CzechRep.) using non-magnetic plastic containers of 10cm³ volume. Mass-specific magnetic susceptibility (X) is calculated by dividing the magnetic susceptibility to the sample's weight. Frequency-dependent magnetic susceptibility is also measured for the same samples, using kappa-meter Bartington (Bartington Inc., UK) with 2-frequency sensor MS2C at two frequencies – low ($X_{LF} = 0.46\text{Hz}$) and high ($X_{HF} = 460\text{Hz}$). The parameter “percent frequency dependent magnetic susceptibility” ($X_{fd}\%$) is calculated according to: $X_{fd} \% = (X_{LF} - X_{HF}) / X_{LF} * 100$. Frequency dependent magnetic susceptibility measurements are widely utilized in environmental magnetism for evaluation of the contribution of very fine-grained (nano-meter sized) pedogenic iron oxide particles (Oldfield, 1999). For remanence measurements cubic samples were prepared by mixing 2 g of soil material with gypsum and water and fixing the mixture in plastic containers of 8 cm³ volume. After hardening the container is removed and the cubic sample is used for imparting laboratory remanences – anhysteretic (ARM) and isothermal (IRM) in fields of 300 mT and 2T. Remanent magnetizations are measured using spinner magnetometer Minispin (MolspinLtd., UK). Identification of magnetic mineralogy is done through step-wise thermal demagnetization of composite IRM (Lowrie, 1990) imparted along two orthogonal directions in a sample and using fields of 0.6T and 2T. Thus, the IRM is divided in two fractions – the low-coercivity one acquired between 0 – 0.6T and a high-coercivity component acquired between 0.6 – 2 T. The samples were subjected to stepwise thermal demagnetization in an MMTD shielded furnace (Magnetic Measurements Ltd., UK) from 20 up to 700 °C. For selected samples step-wise acquisition of IRM up to 5T field is performed using the ASC pulse magnetizer IM-10-30. The IRM acquisition curves were analyzed for the coercivity distributions using IRM-CLG 1.0 software by Kruiver et al. (2001).

3. RESULTS AND DISCUSSION

The fossil fuel utilized in power plants is generally non-magnetic (Vassilev and Vassileva, 1996), but the products of combustion of fossil fuels can be rich in magnetic iron oxides. In case of coal ash, magnetite content may reach 160 000 ppm (Flanders, 1999) and thus, fly ashes from such power plants could contain up to 15 weight % magnetic fraction (Petrovsky and Elwood, 1997). Thermal power plants in Bulgaria utilizing coals emit in the atmosphere fly ashes that contain mostly SiO₂ and Al₂O₃ but the main constituent of the fly ashes are Fe-bearing paramagnetic aluminosilicate glasses as well as iron oxide phase (magnetite, hematite) (Silva et al., 2012). According to Vassilev and Vassileva (1996) various trace elements such as (Cr, Co, Ni, Cu, Zn, As and Pb) are also present in the fly ashes from different Bulgarian power plants (including Maritza East TPP). Maritza East TPPs fly ashes contain the highest amount Fe₂O₃ compared to fly ashes from other Bulgarian TPPs (Silva et al., 2012). Thus, additions of fly ashes settled down from the atmosphere in soil will cause significant increase in the concentration of magnetic iron oxide fraction. Magnetic susceptibility obtained for the soil samples gathered in the area of Maritza East TTPs is shown graphically in Figure 2. The highest magnetic susceptibility is measured for the soil sample in point M12 ($X = 249.9 \times 10^{-8} \text{ m}^3/\text{kg}$) located close to a road and 4.57km far away from TTP Maritza East 2 and 3.82 km away from the coal mine (Fig. 2). Such high magnetic enhancement could result from combined influence of fly ash deposition and road traffic emission, since many studies evidence significant iron oxides content in road dusts as well (e.g. Petrovsky and Elwood, 1997; Hoffmann et al., 1999; Jordanova et al., 2014). High values of magnetic susceptibility are observed also in points M2P ($207.44 \times 10^{-8} \text{ m}^3/\text{kg}$), M16 ($172.65 \times 10^{-8} \text{ m}^3/\text{kg}$), M10 ($126.11 \times 10^{-8} \text{ m}^3/\text{kg}$), M24 ($120.55 \times 10^{-8} \text{ m}^3/\text{kg}$), M2M ($111.65 \times 10^{-8} \text{ m}^3/\text{kg}$), M18 ($103.31 \times 10^{-8} \text{ m}^3/\text{kg}$) и M1 ($102.52 \times 10^{-8} \text{ m}^3/\text{kg}$). The lowest magnetic susceptibility is obtained for

location M21 ($11.95 \times 10^{-8} \text{ m}^3/\text{kg}$) (Fig. 2) situated far from the TTPs and from any road. It could be considered that lithogenic contribution to the magnetic susceptibility of soils in the area of Maritza East TTPs is not very high so as to overwhelm the total magnetic signal. Taking into account that the major soil variety is represented by Vertisols and Planosols which are characterized by quite low magnetic susceptibility (Jordanova & Jordanova, 2016, Jordanova, 2016), the extreme magnetic enhancement of surface soils could be related to anthropogenic pollution effects. In addition, a linear relationship has been obtained between the magnetic susceptibility of fly ashes from different Bulgarian TPPs (including Maritza East TPP) and the content of Fe_2O_3 (Veneva et al., 2004). Therefore, magnetic susceptibility of soil in the surroundings of Maritza East TPPs could be used as an efficient tool for fast mapping of anthropogenic pollution.

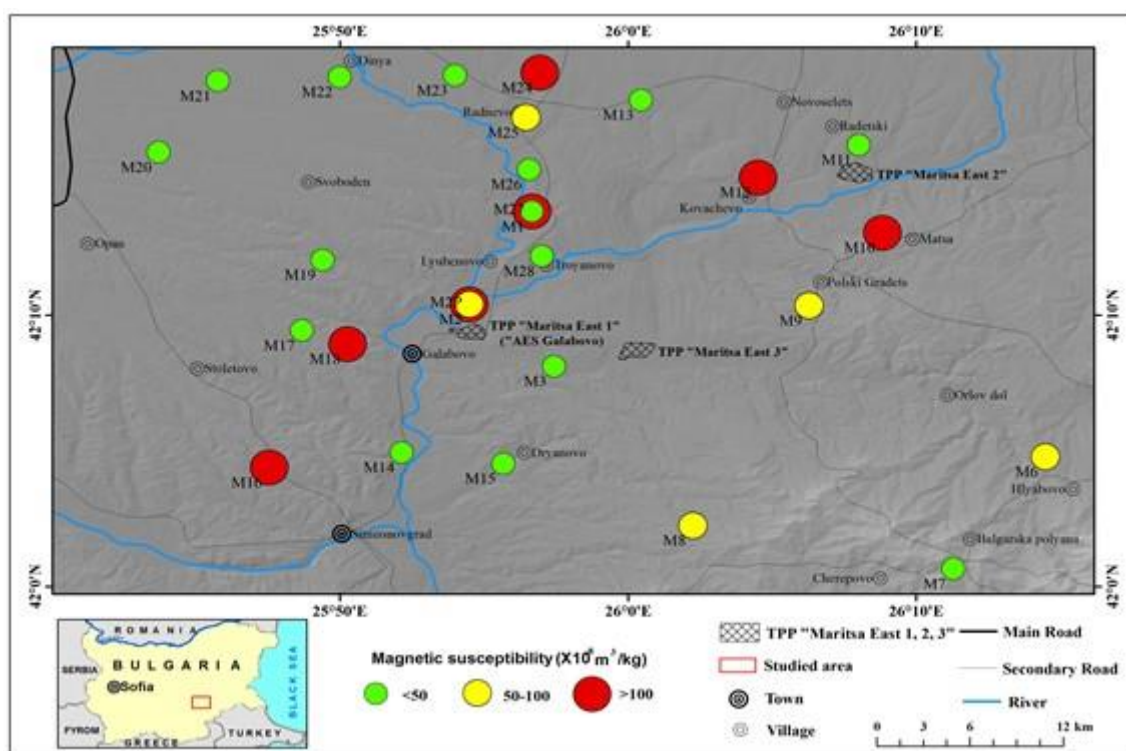


Fig. 2 Magnetic susceptibility (X) for surface soil samples gathered around Maritza East TTPs.

As indicated on Fig.2, magnetic susceptibility of surface soils was divided into three classes: i) $X < 50 \times 10^{-8} \text{ m}^3/\text{kg}$, ii) $50 < X < 100 \times 10^{-8} \text{ m}^3/\text{kg}$ and iii) $X > 100 \times 10^{-8} \text{ m}^3/\text{kg}$. This arbitrary division is used further for consideration of the data related to the frequency dependent magnetic susceptibility and magnetic remanences. Figure 3 shows the relation between magnetic susceptibility (X) and percent frequency dependent magnetic susceptibility ($X_{fd}\%$).

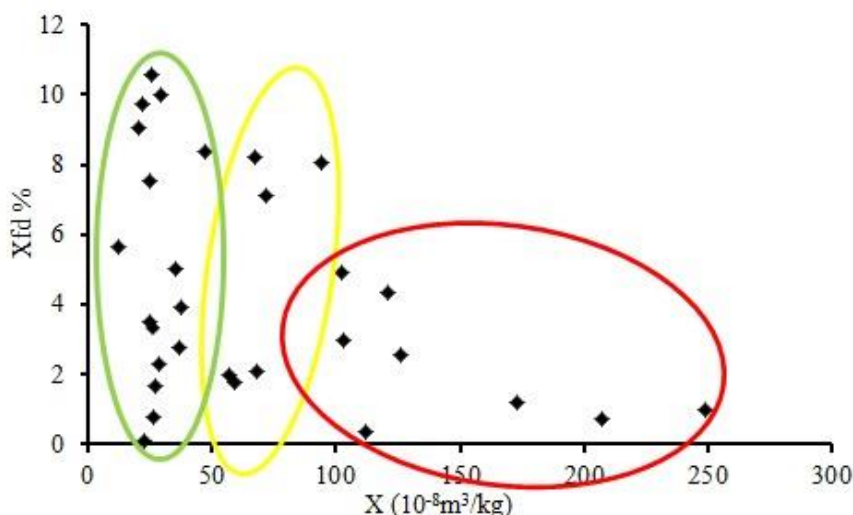


Figure 3. Bi-plot of magnetic susceptibility (X) versus percent frequency dependent magnetic susceptibility ($X_{fd}\%$). The three defined soil groups according to their X are denoted by corresponding colored curves (green – the lowest X ; yellow - medium X ; red - the highest X . For data limits see Fig. 2).

As evident from Figure 3, the highest $X_{fd}\%$ values are typical for soil samples exhibiting the lowest X values. According to the empirical model developed by Dearing et al. (1996), $X_{fd}\%$ could be used for evaluation of the relative contribution of fine superparamagnetic particles (SP) to the total assemblage of the magnetic grains in soils. The following classification is widely applied: $X_{fd}\% < 2\%$ - negligibly low SP fraction; $2 < X_{fd}\% < 10$ – a mixture of SP and coarser stable magnetic grains, $10 < X_{fd}\% < 14\%$ - dominant presence of a SP fraction in the total magnetic fraction of soil (Dearing et al., 1996). Thus, the obtained $X_{fd}\%$ for the first group of samples, spreading up to 13% could be related to the prevailing contribution of the pedogenic iron oxides in Vertisols (Thompson & Oldfield, 1986, Jordanova, 2016). The second group of samples show higher X , but lower $X_{fd}\%$ reaching 9% at maximum (Fig. 3), thus indicating lower proportion of SP grains. Samples showing the highest X -values all have low $X_{fd}\%$, generally below 4%. This indicates that their magnetic mineralogy is dominated by magnetically strong but coarse iron oxide particles. This conclusion perfectly agrees with the established fact that magnetic fly ash grains are generally coarse spherical particles (Veneva et al., 2004; Jordanova et al., 2006).

The relation between anhysteretic susceptibility (X_{arm} , defined as ARM/h , h - the strength of the weak magnetic field applied for ARM induction) and the frequency dependent magnetic susceptibility X_{fd} ($X_{fd} = X_{LF} - X_{HF}$) is shown in Figure 4. Anhysteretic remanence (ARM) and X_{arm} are frequently used for establishing the magnetic grain size of iron oxide particles because it is shown that the most stable single-domain grains of magnetite (with dimensions ~ 0.03 microns) acquire ARM the most effectively, while coarser multidomain grains (MD) have significantly lower ARM (Maher, 1988). Thus, Fig. 4 suggests that soil samples belonging to the third group (with the strongest X values) show also the highest X_{arm} among all the samples. Therefore, highly polluted soils are enriched not only in coarse multidomain grains but also with SD-grains magnetite/maghemite. Soil samples belonging to the first and the second group (low- and medium X values) could be fit with a single regression line on the X_{fd} vs X_{arm} plot (Fig. 4), suggesting that SP and SD grain fractions vary proportionally. The highest concentration of ARM-carrying grains is characteristic for the second group ($50 < X < 100 \times 10^{-8} \text{ m}^3/\text{kg}$).

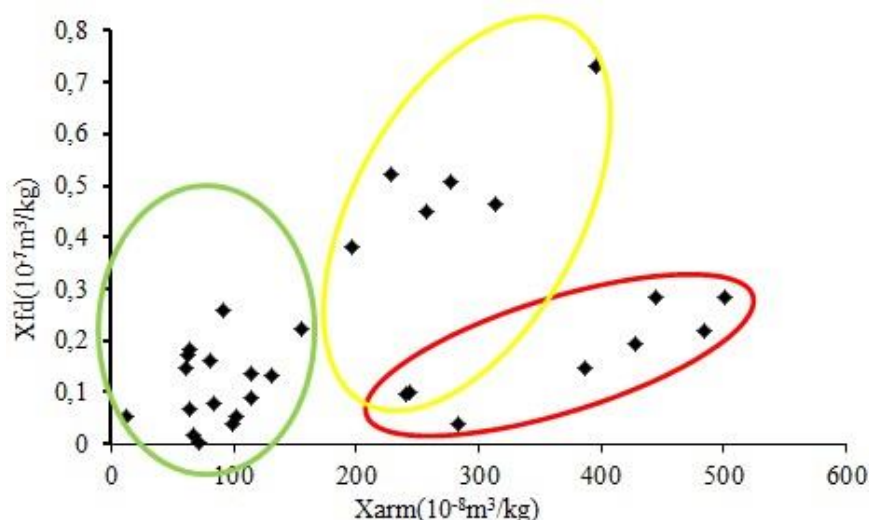


Figure 4. Bi-plot of frequency-dependent magnetic susceptibility (X_{fd}) vs. anhysteretic susceptibility (X_{arm}). Samples belonging to the three groups according to their X are indicated as in Fig. 3.

Among the most important factors for distribution of fly ashes across the area close to the source (the TPP chimney) are the distance from the source and the wind direction. In this way, the coarsest particles will be deposited the closest to the source while finer fly ash particles will be spread out at a longer distance. This regularity is confirmed by the obtained relation X_{fd} - X_{arm} (Fig. 4) showing bigger amount of coarse particles in sampling points located closest to the sources of pollution.

Figure 5 shows the so called “King plot” (King et al., 1982) relating magnetic susceptibility (X) and anhysteretic susceptibility (X_{arm}). It is used in environmental magnetism to distinguish among the grain size of the ARM-carrying grains, the finest ones displaying the steepest slope on the bi-plot, while coarser grains show weaker slope. It is seen from Fig. 5 that samples having low- to medium susceptibilities (1st and 2nd group) lie on one regression line which goes steeper compared to the points linked with the locations of highest magnetic susceptibility. This relation confirms again the conclusion that the most polluted soil samples are dominated by coarse ferrimagnetic grains.

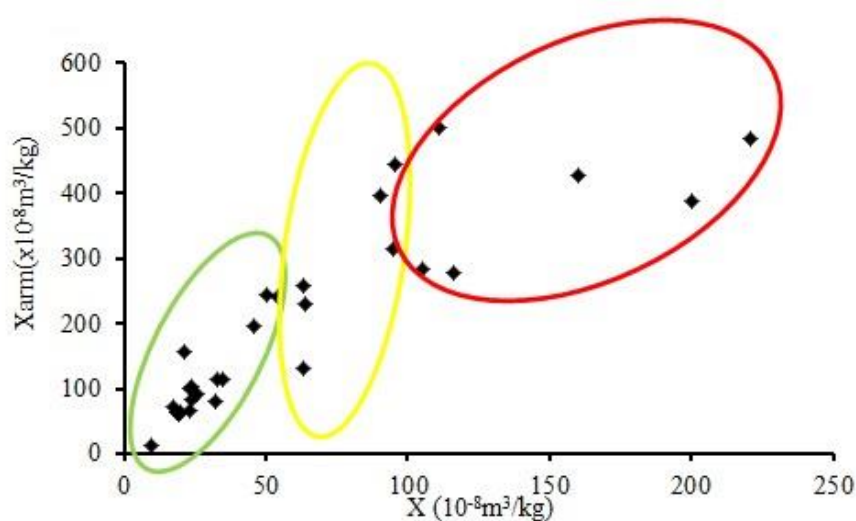
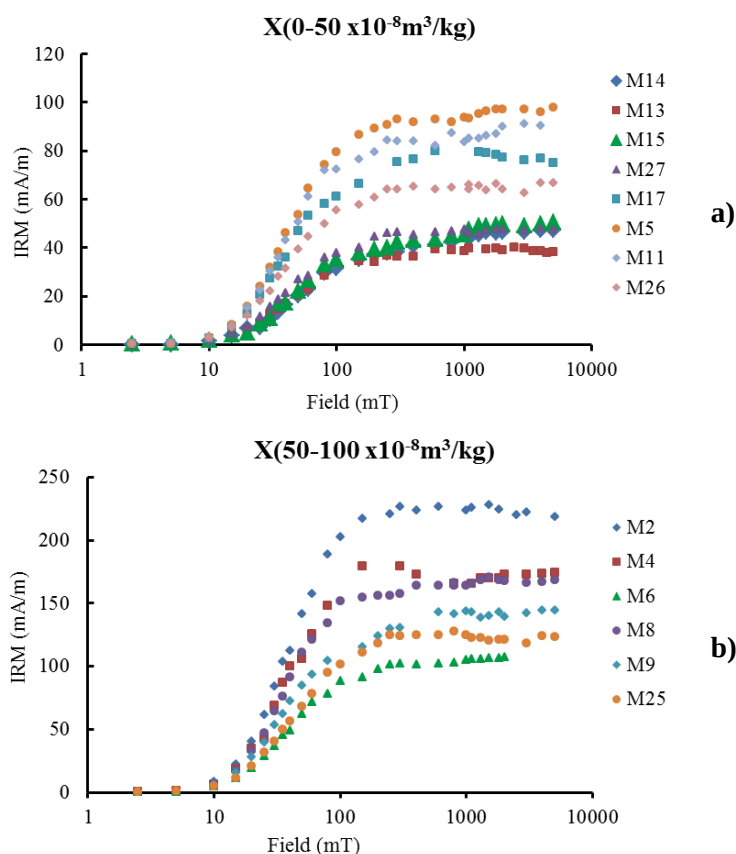


Figure 5. Bi-plot of anhysteretic susceptibility (X_{arm}) versus magnetic susceptibility (X). Samples are grouped according to their X value, as defined in Fig. 2.

Identification of magnetic minerals present in soil samples is investigated through step-wise IRM acquisition performed for selected samples and data processing utilizing the IRM-CLG1.0 software (Kruiver et al., 2001) for separation of IRM coercivity components. Representative IRM acquisition curves are shown in Figure 8 for samples, grouped according to their magnetic susceptibility (as defined in Fig. 2). The maximum field of 5 Tesla allows to study also the high-coercivity part of IRM, characteristic for goethite (αFeOOH) with coercivities higher than 2 Tesla (Dunlop and Özdemir, 1997). As it is seen from Fig. 8, some samples reach IRM saturation relatively fast up to ~ 200 mT and do not exhibit further increase in IRM upon field increase (e.g. Fig. 8b, sample M2, Fig. 8c, sample M10). For other samples, however, a continuous IRM increase is observed at high applied fields (for example Fig. 8a, samples M11, M15). Thus, magnetic mineralogy is dominated by a magnetically soft mineral which saturates in weak magnetic fields (like magnetite, maghemite) and for some samples a weakly magnetic high-coercivity fraction is the reason for non-saturation of IRM. IRM spectrum can be analyzed using distribution of cumulative Gaussian functions (Robertson and France, 1994; Stockhausen 1998). Each magnetic component is characterized by: its SIRM, the field at which half of the SIRM is reached ($B_{1/2}$), and the width of the distribution, expressed through the dispersion parameter DP (one standard deviation of the logarithmic distribution) (Kruiver et al., 2001). Summarized results are shown in Table 1.

Summary data in Table 1 show that the magnetically soft IRM component (IRM component 1) predominates in the signal, representing 80 – 100% of the total IRM. About half of the samples studied show the presence of a high-coercivity component (IRM component 2) (Table 1) reaching a maximum of 24% of the total IRM in sample M15. The coercivity of IRM component 1, defined by the $B_{1/2}$ parameter, shows consistent narrow distribution generally between 36-55 mT and in only few samples is higher, reaching 60 mT in sample M21. Such coercivity values are characteristic for magnetite-type minerals, possibly with lattice substitutions when high $B_{1/2}$ is observed (Dunlop & Özdemir, 1997). The dispersion parameter of the IRM 1 component is relatively high, indicating wider grain-size distribution of the ferromagnetic particles.



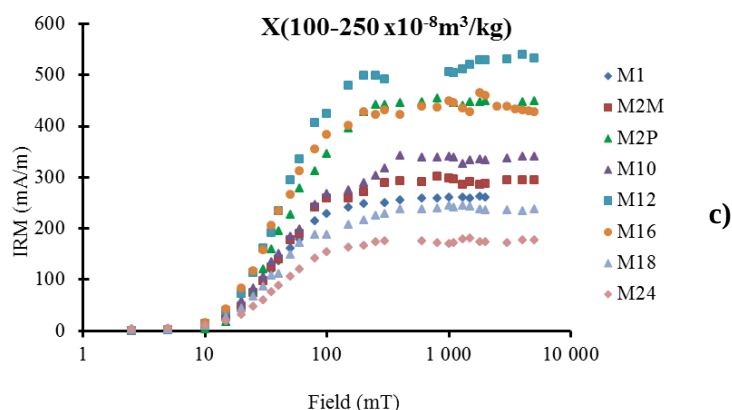


Figure 8. Step-wise IRM acquisition up to 5 Tesla field for selected soil samples. a) Samples with low magnetic susceptibility; b) samples with medium susceptibility, c) samples with most enhanced magnetic susceptibility.

Table 1. Soil samples subjected to step-wise IRM acquisition up to 5 Tesla field. Distance to the biggest TPP- Maritza East 1, magnetic susceptibility (X), and parameters of coercivity components (IRM component 1; IRM component 2) are shown in columns 1-10. Relative contribution (% contr.), absolute intensity (Int.), coercivity ($B_{1/2}$ expressed in mT) and dispersion parameter (DP expressed in $Lg(mT)$) is given for each component.

sample No	Distance to the power plant – TPP1 (km)	Magnetic susceptibility X ($\times 10^{-8} m^3/kg$)	IRM component 1				IRM component 2			
			% contr	$B_{1/2}$ (mT)	DP	Int. (mAm^2/kg)	% contr	$B_{1/2}$ (mT)	DP	Int. (mAm^2/kg)
M1	4	102.5	96	36.3	0.32	2500	4	707.9	0.47	110
M2	1.6	67.9	100	36.3	0.32	2200				
M2M	1.6	111.7	100	52.5	0.33	4470				
M2P	1.6	207.4	100	53.7	0.35	4500				
M3	4.51	26.0	94	42.7	0.32	500	6	3162.3	0.4	30
M4	72	59.1	100	38.0	0.27	1730				
M5	64.17	36.8	92	38.9	0.32	900	8	1000.0	0.4	80
M6	28.6	57.2	95	42.7	0.39	1040	5	1949.8	0.18	50
M7	28.22	25.9	100	36.3	0.35	510				
M8	17.13	71.7	95	36.3	0.32	1610	5	1000.0	0.3	80
M9	16.38	94.4	91	41.7	0.40	1350	9	1584.9	0.45	140
M10	20.73	126.1	100	50.1	0.40	3310				
M11	22.16	37.8	91	38.9	0.33	830	9	1584.9	0.3	80
M12	17.37	249.1	93	44.7	0.32	5000	7	1258.9	0.4	400
M13	17.73	26.8	100	47.9	0.40	390				
M14	8.68	26.0	83	51.3	0.39	400	17	1258.9	0.32	80
M15	9.07	28.3	76	42.7	0.21	390	24	691.8	0.44	120
M16	13	172.7	100	39.8	0.34	4350				
M17	8	35.3	100	45.7	0.40	780				
M18	5.93	103.3	100	41.7	0.34	2360				

M19	8.64	23.0	85	38.0	0.33	400	15	631.0	0.39	700
M20	19.4	24.8	90	14.7	0.38	380	10	794.3	0.5	400
M21	21	11.9	100	60.3	0.42	175				
M22	18.52	24.8	78	38.0	0.28	400	22	380.2	0.48	110
M23	17.43	20.8	93	43.7	0.39	240	7	1000.0	0.45	18
M24	17.52	120.6	100	40.7	0.37	1740				
M25	15.06	67.2	100	45.7	0.40	1250				
M26	11.37	47.5	100	42.7	0.40	650				
M27	8.3	29.3	100	46.8	0.40	470				
M28	5.94	21.7	100	42.7	0.37	400				

The high-coercivity component (IRM component 2) shows variable coercivity as expressed by $B_{1/2}$ (Table 1) varying between 380 mT and 3100 mT. Coercivities in the range 300 – 1000 mT are usually related to hematite of different grain size and/or lattice substitutions (Özdemir and Dunlop, 2014), while higher coercivities already indicate the presence of iron oxyhydroxide goethite (Dunlop and Özdemir, 1997). As also evident from Table 1, samples showing high-coercivity component in the IRM acquisition curve belong exclusively to the first group of samples, characterized by lowest X values, and only few fall into the medium-susceptibility group (e.g. M1, M12, M6, etc.).

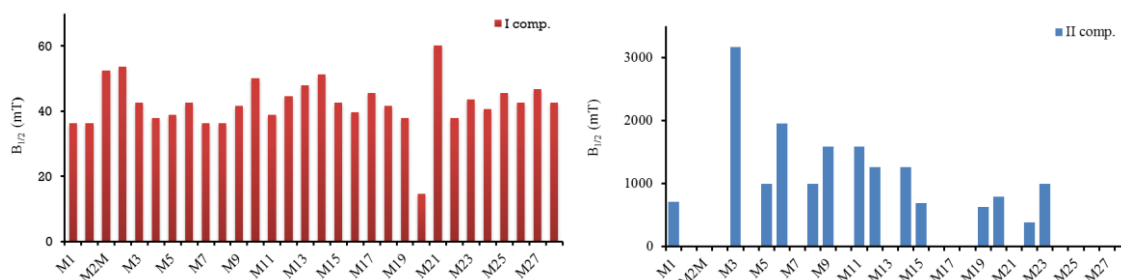


Figure 9. Distribution of coercivity parameter $B_{1/2}$ for the magnetically soft component (a) and magnetically hard component (b). The horizontal axis denotes the sample's number.

Coercivity parameter $B_{1/2}$ for the two IRM components according to samples is depicted in Figure 9a (soft component) and 9b (hard component). As discussed above, magnetically soft component shows relatively uniform coercivity centered around ~40 mT (Fig. 9a). For fourteen out of 28 samples, a second, high-coercivity component is identified, as follows: M3, M5, M11, M14, M15, M19, M20, M22, M23 (56 % of the samples with $X = 0-50 \times 10^{-8} \text{ m}^3/\text{kg}$), M6, M8, M9 (50 % of the samples with $X = 50-100 \times 10^{-8} \text{ m}^3/\text{kg}$), M1, M12 (25 % of the samples with $X = 100-250 \times 10^{-8} \text{ m}^3/\text{kg}$). Thus, increased anthropogenic load (e.g. fly ash content) leads to a predominance of magnetite-type iron oxide mineralogy characteristic of large anthropogenic fly ash spheres (Jordanova et al., 2006). The presence of a high-coercivity mineral in some of the soil samples is evidenced also by exploring the so called S-ratio where $S = \text{IRM}_{300\text{mT}}/\text{IRM}_{2\text{T}}$ (King & Channel, 1991). When high-coercivity fraction is present in a sample, S-ratio is lower than 1 because IRM acquired in 300 mT field is not saturated (e.g. equal to $\text{IRM}_{2\text{T}}$). The relation between $\text{IRM}_{2\text{T}}$ and S-ratio is shown in Figure 10.

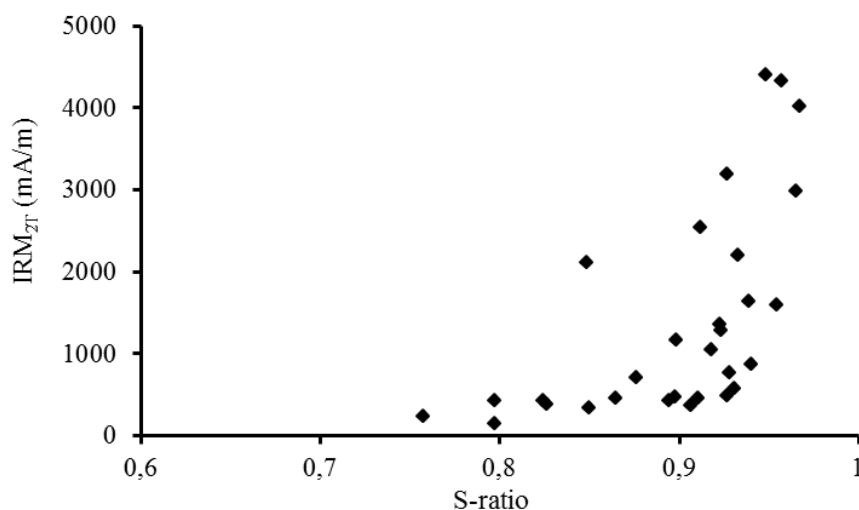
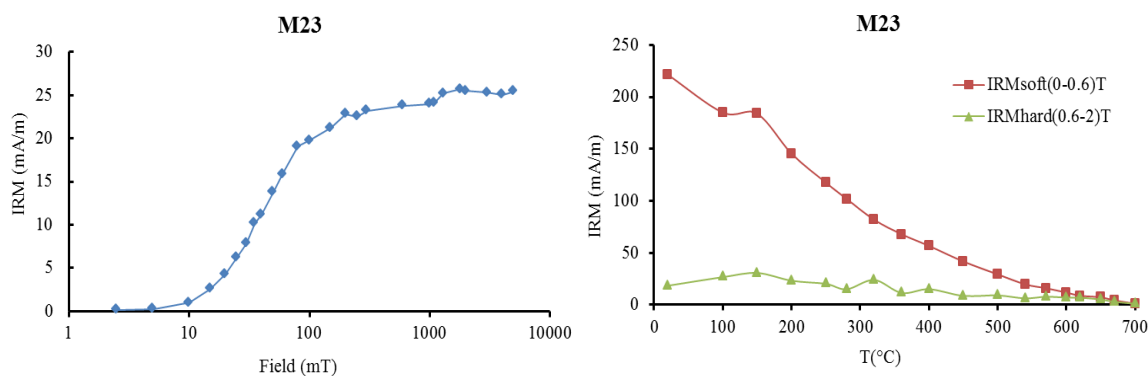


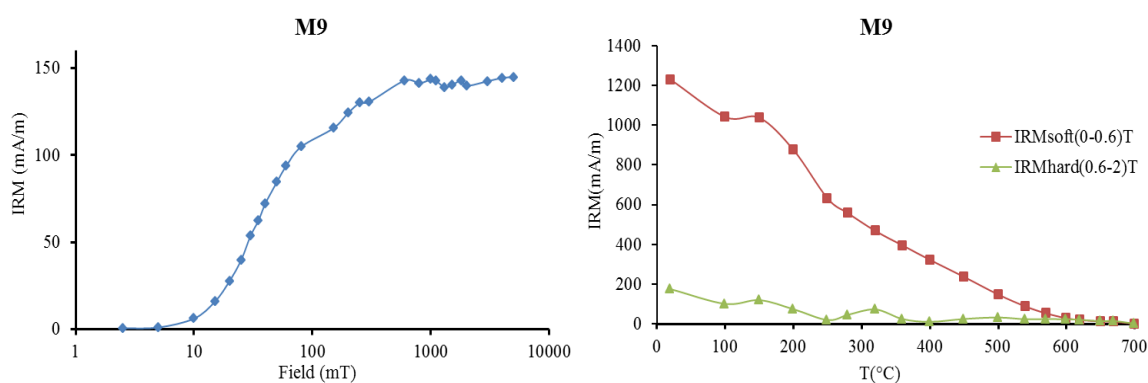
Figure 10. Bi-plot of saturation remanent magnetization acquired in a field of 2 Tesla (IRM_{2T}) and the S-ratio.

It is evident from Fig. 10 that samples with the lowest IRM_{2T} show also lower S-ratio. This implies the presence of high-coercivity mineral phase influencing the remanent magnetization.

a) $X (0 - 50 \times 10^{-8} \text{ m}^3/\text{kg})$



b) $X = 50-100 (\times 10^{-8} \text{ m}^3/\text{kg})$



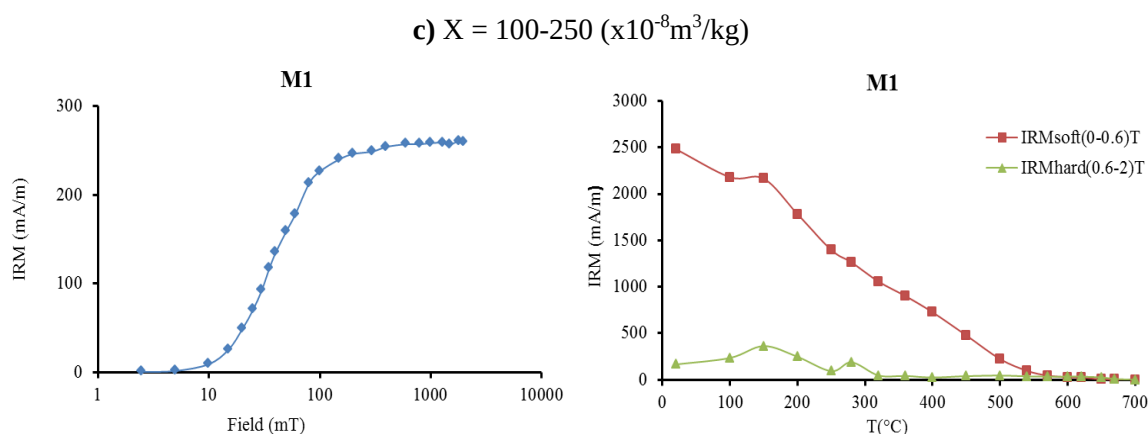


Figure 11. Examples of IRM acquisition curves compared to step-wise thermal demagnetization of composite IRM for identification of magnetic mineralogy.

Step-wise thermal demagnetization of composite IRM gives valuable information about the unblocking temperatures (T_{ub}) of the main magnetic minerals, thus indicating the kind of the magnetic phase present in a sample. Several representative examples showing direct comparison between already discussed IRM-acquisition curves and thermal demagnetization experiment are shown in Figure 11. Sample M23 from the magnetically weak samples (Fig. 11a) shows the presence of a very weak high coercivity component, but thermal unblocking evidences continuous progressive decrease of IRM until 700°C (Fig. 11a, right-hand graph) of both coercivity components. Therefore, the coercivity spectra of hematite identified through its final T_{ub} at 700°C is probably quite wide and involved in both soft and hard IRM components.

Sample M9, belonging to the group of samples with medium strong magnetic susceptibilities is characterized by major IRM unblocking at ~600°C in its soft component (Fig. 11b, right-hand graph). At the same time, magnetically hard component disappears after ~300°C. Thus, the high-coercivity fraction cannot be attributed to hematite, but rather to goethite – the iron oxyhydroxide which at ~300°C dehydrates and transforms to hematite (Dunlop and Özdemir, 1997). This conclusion is supported by the $B_{1/2}$ obtained for the IRM component 2 (Fig. 11b, left-hand graph) – $B_{1/2} \sim 1585$ mT, characteristic for goethite. Finally, the magnetically strong sample M1 from the third group of samples (Fig. 11c) shows the predominance of magnetite-like phase with $T_{ub} \sim 580^\circ\text{C}$, characteristic of magnetite. The identified hematite's component in the coercivity distribution (Fig. 11c left-hand graph) is not visible in the thermal demagnetization probably because of its weak intensity.

Magnetic properties along soil depth profiles are very useful for identification of pedogenic and/or anthropogenic processes occurring in the soil (e.g. Jordanova, 2016). A number of studies evidence that atmospheric additions of fly ashes and/or other pollutants on the soil surface cause local surface-restricted strong magnetic enhancement which is easy to discriminate from natural pedogenic enhancement in case of relatively weakly magnetic parent rocks (Petrovsky and Elwood, 1997; Magiera et al., 2006). Variations of the main magnetic parameters along the depth profile of polluted soil sampled in location M2 (Fig. 1) are shown in Figure 12.

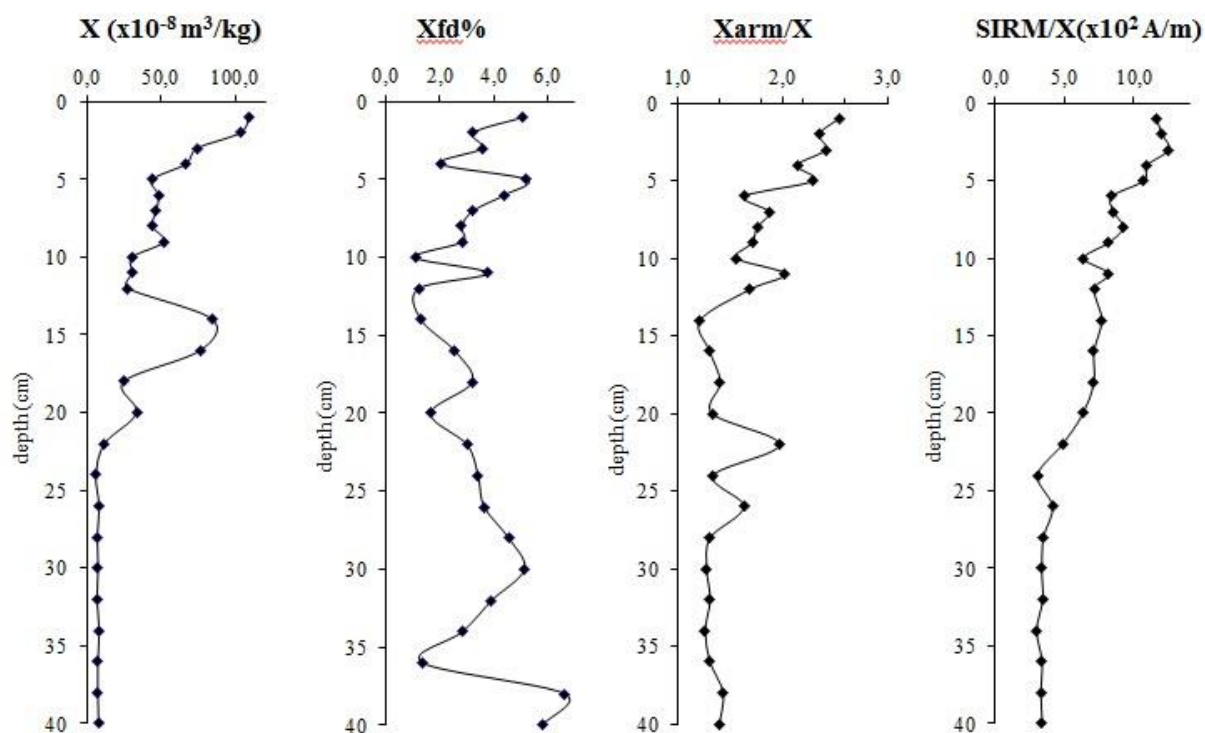


Figure 12. Depth variations of magnetic susceptibility (X), percent frequency-dependent magnetic susceptibility ($X_{fd}\%$, the ratio of anhysteretic susceptibility (X_{arm}) and magnetic susceptibility (X), and the ratio of saturation remanent magnetization ($SIRM$) to magnetic susceptibility (X) along the soil profile GL.

Depth variations in magnetic susceptibility suggest a well-defined magnetic enhancement in the uppermost 5-cm of the profile followed by slower X -decrease interrupted by a local maximum at ~15 cm depth (Fig. 12). This surface related maximum in X is also underlined in the $SIRM/X$ variations. At the same time $X_{fd}\%$ is relatively lower in this upper part of the profile. Magnetic proxy for the content of stable single domain grains X_{arm}/X (Fig. 12) also shows fairly higher values in this part of the profile. Therefore, magnetic characteristics suggest that the upper surface layer of 5-cm thickness is enriched in magnetically strong coarse particles, while deeper part of the profile shows lower magnetic enhancement (Fig. 12). Based on the above observations, it could be supposed that the surface soil layer is strongly polluted with fly ash coarse magnetic particles. It also shows that fly ash grains migrate down-profile up to ~5 cm (Fig. 12). Magnetic susceptibility of polluted soils around Maritza East TPPs from our study compares very well with previous magnetic investigations on few soil samples taken from the same area but some 20 years ago (Veneva et al., 2004) which show $X \sim 100\text{--}200 \times 10^{-8} \text{ m}^3/\text{kg}$. Spatial distribution of soil magnetic susceptibility (Fig. 2) reflects complex picture of fly ash deposition from several sources (three TPPs). This is the reason for non-unique susceptibility pattern in the study area. Nevertheless, it is clearly seen that soils located nearest to the corresponding pollution source display the highest magnetic enhancement. In addition, maximum susceptibility values are found in an elongated area oriented N-NE – S-SW, well corresponding to the prevailing wind direction.

4. CONCLUSIONS

Rock magnetic study on surface soils from an area of strongly polluted by thermal power plants operation and coal mining showed high efficiency of magnetometry as a sensitive indicator for the relative anthropogenic pollution. Magnetic measurements evidence the presence of magnetically strong coarse particles, corresponding with the established mineralogy of Bulgarian fly ashes (Veneva et al., 2004, Jordanova et al., 2006). Three arbitrary groups of samples according to their magnetic susceptibility were defined – i) weakly or non-polluted with $X < 50 \times 10^{-8} \text{m}^3/\text{kg}$; ii) medium pollution level with $50 < X < 100 \times 10^{-8} \text{m}^3/\text{kg}$ and iii) highly polluted soils with $X > 100 \times 10^{-8} \text{m}^3/\text{kg}$. Magnetic minerals identified include magnetite, hematite and goethite. The surface soil horizon enriched in fly ashes is characterized by the presence of coarse multidomain and to lesser extent single domain grains, linked to iron oxides in fly ash spherulites formed during coal combustion.

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