ECOLOGIA BALKANICA
2022, Vol. 14, Issue 1 June 2022 pp. 103-111

Soil Magnetic Susceptibility Properties as Indicators of Heavy Metals Pollution in "Bobov Dol" TPP Area (Bulgaria)

Miroslav A. Ivanov*, Konstantin A. Tyufekchiev

South-West University "Neofit Rilski", Faculty of Nature and Mathematics, Department of Geography, Ecology and Natural Protection, 66 Ivan Mihailov Str., Blagoevgrad, BULGARIA
*Corresponding author: m_ivanov@swu.bg

Abstract. All the coal used in the power plants in Bulgaria are mainly high ash coals, which consequently leads to the release of big quantities of ash during their combustion. This cause a significant pressure on ecological status of the soil cover in the plants areas. Recently it has been proved that the magnetic susceptibility of polluted soils increases due to their enrichment with different metal oxides. The main goal of this research is to be analyzed the magnetic susceptibility values in the soils around "Bobov dol" thermal power plant (TPP) as an indicators of heavy metals pollution. More than 60 field measurements of the soil magnetic susceptibility were conducted around "Bobov dol" TPP. This measurements were evenly distributed around the power plan in accordance with the established grid network. The measured field value of the magnetic susceptibility range between 1.9358×10^{-6} SI and 475.233×10^{-6} SI. The higher values of the magnetic susceptibility are observed around the "Bobov Dol" TPP and along the transport line that transport the waste from the burning process to the nearby dump site. In addition frequency-dependent susceptibility - χFD% of the same samples have been measured and very good positive correlation between higher magnetic susceptibility values and lower frequency-dependent susceptibility have been found which proved that the high MS values are due to the presence of coarse spherical particles with anthropogenic origin.

Key words: magnetic susceptibility, heavy metals, contaminated soils.

Introduction

In recent years, soil has been under increasing environmental pressure, driven or exacerbated by human activity. One of the most common soil pollutants that are extremely harmful for the human health are the trace elements/heavy metals. Some of these elements are essential for plants and animals in small amounts but in the recent years there has been an increasing ecological and global public health concern associated with environmental contamination by these metals (Tchounwou, 2012).

Solid fuel (coal) thermal power plants are one of the major industrial pollutants and emitters of heavy metals. Modern thermal power plants are usually equipped with sophisticated filters, however, some of the ash inevitably passes through the filters and is discharged into the atmosphere and accumulated in the surrounding soils. These are predominantly fine ash particles which are the most dangerous, since they usually contain elevated concentrations of some heavy metals and toxic elements (Helble & Sarofim, 1993; Helble, 1994; Ratafia-Brown, 1994, Mokreva et al., 2017; El Bagdadi et al., 2011).

The traditional detection methods of heavy metals in soil have strong specificity and high sensitivity, but they also are expensive and unsuitable for rapid or filed determination. Because of that during recent years, the measurements of magnetic susceptibility have become a broadly applied method to research the spatial distribution of pollution and to identify polluted sources. Measurements of magnetic susceptibility (MS) provide a fast and cheap alternative to conventional chemical analysis and it was proved to be extremely useful in disclosing industrial pollutants, traffic emission and other atmospheric pollutants (Morris et al., 1995; Dearing et al., 2006; Bityukova et al., 1999; Durza, 1999; Hoffmann et al., 1999; Kapicka et al., 1999; Matzka & Maher, 1999; Shu et al., 2000; Lecoanet et al., 2001; Hanesch et al., 2003; Goddu et al., 2004, Mokreva et al., 2017, El Bagdadi et al., 2011).

The main goals of this research is to present the results of the field measurements of the soil magnetic susceptibility (MS) conducted in the proximity of the "Bobov dol" TPP and to compare these data with the data acquired by the laboratory measurements of Frequency-dependent susceptibility which can be used as indicator for the relative contribution of the anthropogenic and pedogenic ferromagnetic minerals to the total magnetic fraction in the soil.

Material and Methods

Test site

"Bobov dol" TPP is located in the southwestern part of Bulgaria, near the town with the same name. The area of interest in this research represent a square with a side of 6 km. and enclose an area of 36 sq. km.. The "Bobov dol" TPP is situated in the centre of the square. (Fig. 1). "Bobov dol" TPP was commissioned in 1973 - 1975 with three 210 MW units. Since then, mainly lignite coal from the Chukurov, Beloberezh and Stanyantzi basins is burned there, as well as a small amount of brown coal from the Bobov Dol Town and Pernik Town basins as well (Kortensky & Zdravkov, 2008).

The soil cover around "Bobov dol" TTP is diverse (according to WRBSR, 2006): Leached and Typical Cinemon Forest Soils, Endocalcic Luvisols and Haplic Luvisols, Vertic Luvisols, with some steep terrain poorly developed, shallow eroded soils (Cambisols and Leptosols) have been detected, Alluvial meadow soils (Mollic Fluvisols) are located in the lowest parts of the area near the river beds. The foothills of the valley slopes, the dry valley bottoms and the floodplains are occupied of deluvial materials. Alluvial deposits are deposited along the Razmetitsa River. The rest of the basin is composed of Paleogene soft sediments that are easily erodible (Nikova et al., 2013).

In the lands of Bobov Dol Town, close to Palatovo Village, a reclaimed tailing pond was built. All the coal used in the power plant are mainly high ash coals, which consequently leads to the release of significant quantities of ash during their combustion. According to Donchev et al. (2001) the plant generates about 900,000 tonnes of ash annually. Therefore, the degraded ecological status of the soil cover in the plant area could be due to the continued use of solid fuel for the production of electricity in the "Bobov dol" TPP. According to Kortensky & Zdravkov (2008), the ash of the coal used as a fuel in "Bobov dol" TPP is characterized by the relatively high concentration of SiO_2, Al_2O_3, TiO_2 and other metal oxides.

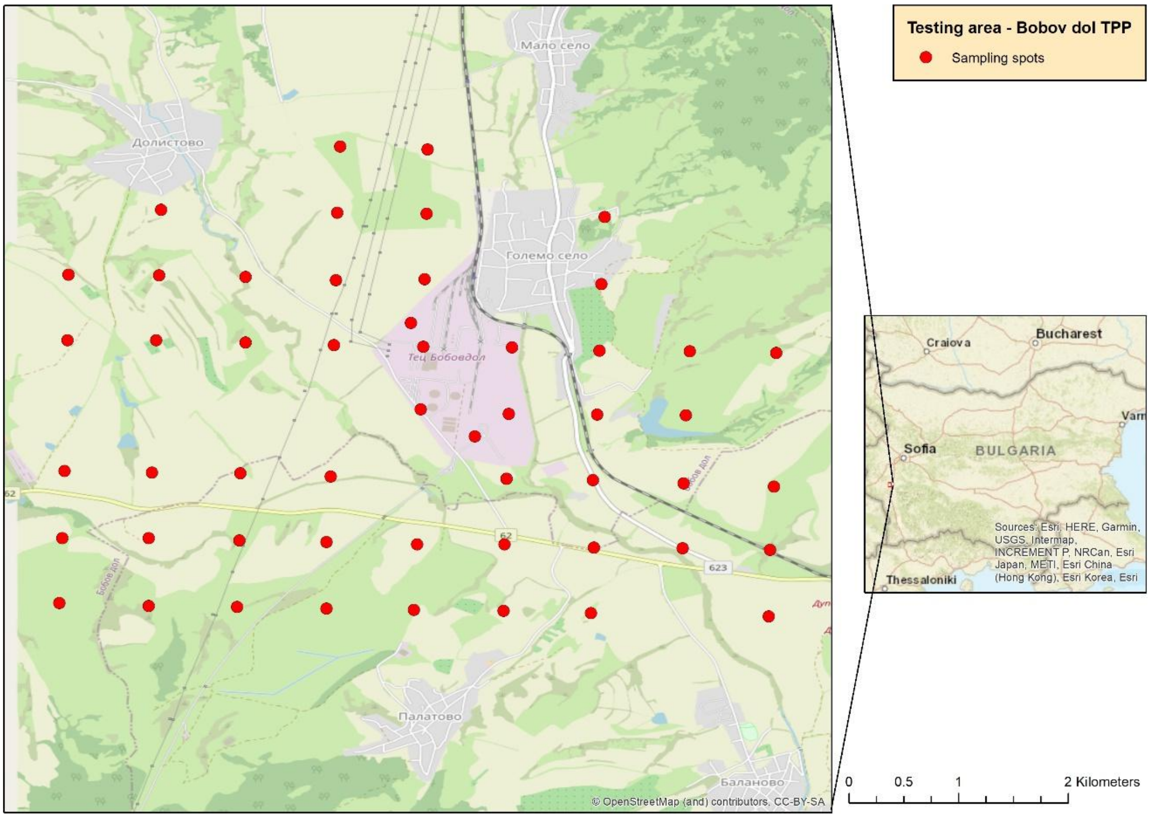

Fig. 1. Map of the "Bobov dol" TPP testing site with the sampling spots.

Field measurements for rapid assessment of the magnetic susceptibility

The assessment is implemented with Bartington MS3 susceptibility system which includes MS3 meter, MS2D surface scanning probe and MS2 probe handle. The MS2D loop is designed for rapid assessment of the magnetic susceptibility (Bartington Manual). In order to receive reliable scientific information the square shaped area of interest is divided by georeferenced grid that forms 700 x 700 m squares each grid cell was examined in a field campaign in order to select suitable spots (Fig.1) for assessment of the concentration of ferromagnetic materials in the top 60 to 80 mm of the land surface. At the suitable locations inside each grid cell, a visibly homogeneous, undisturbed squares with L=1 were selected. The geographical coordinates of each square is measured by portable GPS (WGS 84). Five independent soil magnetic susceptibility measurements were implemented at the vertices and in the center of a square. The mean value are assumed as the magnetic susceptibility of the testing square. For each measurement the grass was removed from the soil for better soil contact. The sensitivity of the Bartington MS3 susceptibility meter is $1x10^{-6}$ SI (Bartington Manual). The depth of penetration when is used with MS2D surface scanning loop is about 8–10 cm when the sensor is in contact with the surface; 50 % at 15 mm and 10 % at 60 mm from the surface (Bartington Manual). All measures were implemented when the sensor is in contact with the surface.

Sample collection for assessment of the frequency depended susceptibility

Sample extraction are implemented according the methodology of Yordanova et al. (2003; 2004; 2008) and Mokreva et al.

(2017). Material of about 50 g was taken from the top-soil at each corner and from the center of the square. It resulted in a pooled sample of roughly 250 g, considered as representative for the point. The material was kept and transported to the laboratory in closed plastic bags.

Measurements of Frequency-dependent susceptibility

Frequency-dependent susceptibility - χFD% was calculated and used as indicator for the relative contribution of the anthropogenic ferromagnetic minerals to the total magnetic fraction in the soil. The formula is $\chi FD\% = 100 \text{ x } (\chi LF - \chi HF) / \chi LF$ (Yordanova, 2008; Mokreva et al., 2017). Following the protocol developed by Yordanova et al. (2008) magnetic susceptibility was measured in the laboratory on homogenized material, sieved through 1 mm-mesh. The material was filled in 10 cm^3 plastic cylindrical containers and magnetic susceptibility is measured by Bartington MS3 meter equipped with dual-frequency sensor (MS2B) at two frequencies − 0.46 (KLF) and 4.6 kHz (KHF). The weight of the samples was measured and used for calculation of the mass-specific magnetic susceptibility (χLF). In order to achieve reliable results the signal and the weight of the empty containers was subtracted from the readings

Results and Discussion

Magnetic susceptibility values around "Bobov dol" TPP

During the field campaign a total of 60 measurements of the magnetic susceptibility were conducted around "Bobov dol" TPP. This measurements were evenly distributed around the power plan in accordance with the established grid network. The value of the magnetic susceptibility range between $1.9358 \text{x} 10^{-6}$ SI and $475.233 \text{x} 10^{-6}$ SI. The higher values of the magnetic susceptibility are observed around the "Bobov Dol" TPP and along the transport line that transport the waste from the burning process to the nearby dump site. Whereas background soils are dominated by thin superparamagnetic and single domain particles, large multi- domain particles prevail in urban soils (Veneva et al., 2004). Field measurements for assessment of the magnetic susceptibility are useful instrument for detecting the presents of ferromagnetic materials in the soils, however field sensors do not provide absolute values of mass-specific susceptibility, but a kind of relative volume-related data instead, because of that additional investigation is needed to obtain the frequency depended susceptibility and to distinguish if the high values of the magnetic susceptibility are due to presence of primary minerals that are connected with the process of pedo-genesis or because of the presents of industrial pollutant. The frequency dependent susceptibility in the research area varies between 1 and 17.78 percent. There is very good connection between the high values of the magnetic susceptibility and low values of the frequency dependent one (Fig.2). This fact confirm the conclusion that the majority of the magnetic minerals are with natural pedogenic origin and only in a small area around "Bobov dol" TPP the source of the magnetic minerals are the anthropogenic activities in the power plant.

Spatial distribution of the magnetic susceptibility values

The measurements of the magnetic susceptibility were evenly distributed around the "Bobov dol" TPP (Fig. 1). The value of the magnetic susceptibility range between $1.9358 \text{x} 10^{-6}$SI and $475.233 \text{x} 10^{-6}$SI. The higher values of the magnetic susceptibility are observed around the "Bobovdol" TPP and along the transport line that transport the waste from the burning process to the nearby dump site (Fig. 3). Because of the local wind patterns and the presents of the transport line the area with high magnetic susceptibility values has an elongated towards the South shape.

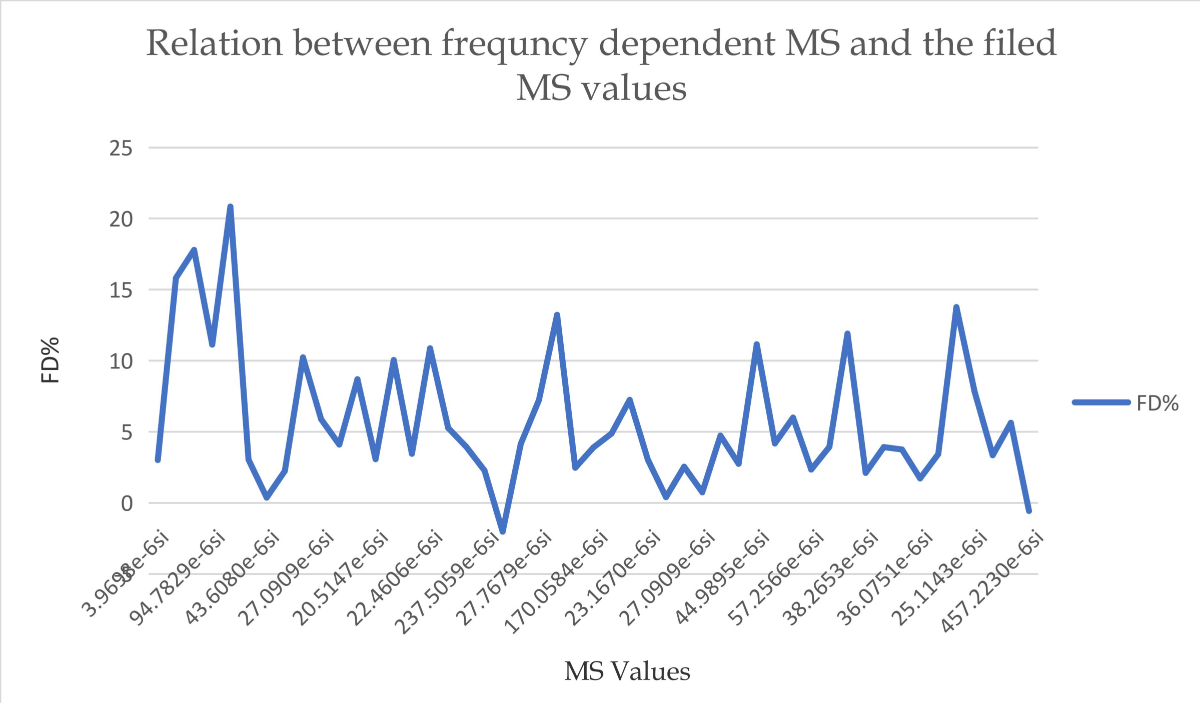

Fig. 2. Relation between frequency dependent MS and the field MS values around "Bobov dol" TPP.

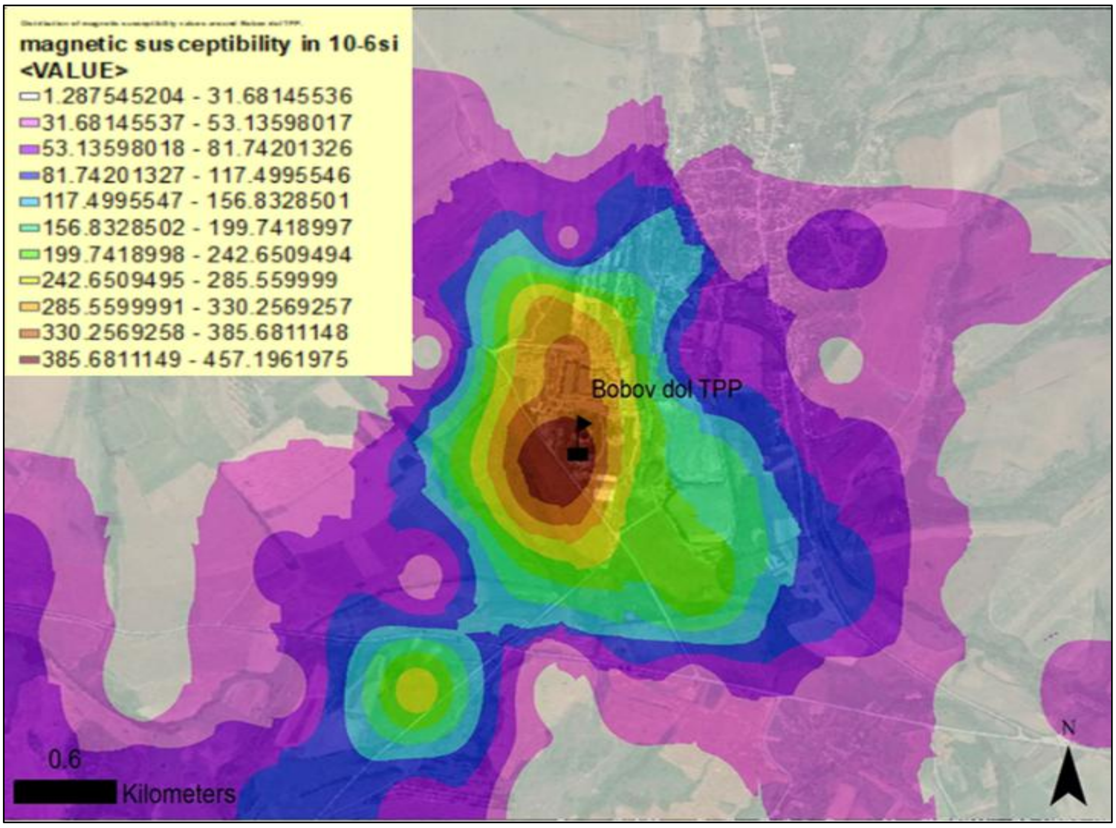

Fig. 3. Distribution of magnetic susceptibility values around "Bobov dol" TPP.

Heavy metal and magnetic susceptibility relation

The magnetic fractions of the urban topsoil are highly enriched in heavy metals. Many previous studies have reported the strong relationships between magnetic susceptibility and heavy metals in polluted soils (Hu et al., 2007; Chaparro et al., 2008; Bijaksana & Huliselan, 2010; El Bagdadi et al., 2011; Mokreva et al., 2017).

El Bagdadi et al. (2011) for example found a very good correlation between higher MS values and the presence of heavy metals in the urban soils close to roads and automobile repair depos in Beni Mellal City (Morocco). El Bagdadi et al. (2011) *in situ* magnetic susceptibility measurements closely to the road ranged from 67.9 to 577x 10^{-5} SI with median value 206 x 10^{-5} SI which is significantly higher than the magnetic susceptibility value of background soils ranging from 15 x 10^{-5} to 114 x 10^{-5} SI. El Bagdadi et al. (2011) also found that the content of Cd, Cu, Zn, Fe and Pb in the studied areas is significantly higher than those of background soils in Beni Mellal region with average concentrations of Cd, Cu, Zn, and Fe up to three times higher than the mean values of rural soils; but these of Pb is six time higher El Bagdadi et al. (2011).

One of the first regional magnetic maps was created in the Czech Republic for the area near the brown coal fired TPP (Kapicka et al., 1999). In the testing area, the *in situ* magnetic susceptibility ranged from 16 × 10^{-5} to 118 × 10^{-5} SI. Within the same area, the total content of cobalt varied from 1.5 to 12.6, that of arsenic from 0.5 to 6.8, and copper from 6 to 62 mg/kg (Kapicka et al., 1999). On the maps, contamination by these heavy elements is found to be consistent with magnetite contamination of soils (through magnetic susceptibility) and depends on the wind rose and distance from TPP (Kapicka et al., 1999).

The same conclusions were made by Mokreva et al. (2017) in a research about 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. In this research Mokreva et al. (2017) used the magnetic susceptibility as proxy method to detect soil pollution with heavy metals and they reaffirm the conclusions made by Veneva et al., (2004) that a linear relationship has been obtained between the high magnetic susceptibility of fly ashes from different Bulgarian TPPs (including "Maritza iztok" TPP) and the content of Fe_2O_3. Furthermore Mokreva et al. (2017) also proved that the samples showing the highest MS values all have low frequency dependent susceptibility (Xfd%), generally below 4%. Which can be used as evidence that their magnetic mineralogy is dominated by magnetically strong, but coarse iron oxide particles (Mokreva et al., 2017). This reaffirm the fact that magnetic fly ash grains are generally coarse spherical particles (Veneva et al., 2004; Jordanova et al., 2006).

Similar results were obtained during the filed measurements of magnetic susceptibility (MS) values around "Bobov dol" TPP. The value of the magnetic susceptibility range between 1.9358x10^{-6} SI and 475.233x10^{-6} SI. The higher values of the magnetic susceptibility are observed around the "Bobov dol" TPP and along the transport line that transport the waste from the burning process to the nearby dump site (Fig. 3). Furthermore the higher MS values are very well correlated with the lower values of the frequency dependent susceptibility (Xfd%) of the same samples. The values of the χFD% of the samples with higher MS values are well below 4 % which according the Mokreva et al. (2017), Veneva et al. (2004) and Jordanova et al. (2006) can be used as evidence that higher MS values of the soil around "Bobov dol" TPP are due to the presence of fly ash grains which are generally coarse spherical particles with anthropogenic origin and are not related to the natural pedogenic processes. However the prevailing soil type in the proximity of the "Bobov dol" TPP and at the sampling spots with higher MS values is Vertic Luvisols. This soil type is in close relation with the Vertisols and according Jordanova (2016) this soil type is characterized by quite low magnetic susceptibility. This fact also confirms the conclusion that the higher MS values around "Bobov dol" TPP are due to the presents of magnetic particles with anthropogenic origin.

Conclusions

Although there are areas around "Bobov dol" TPP where the measured values of the magnetic susceptibility are high, generally the MS values show that the contamination of the soil around the power plant is limited to the very close perimeter of the power plant and one tight strip of land along the transport line that transport the waste products of burning process to the tail pond. As a whole except for the above mention territories the magnetic susceptibility values around the testing area are in line with the mean MS values for the presented in the test site soil types. These conclusions are reaffirm by the data obtain from the laboratory measurements of the frequency dependent susceptibility. Moreover these conclusions are also in line with the findings of the previous researches (Nikova & Tsolova, 2017) that regard the presence of trace elements in the soil cover around "Bobov dol" TPP area which are made by traditional methods. The magnetic susceptibility measurements are proved to be a reliable and cheap alternative of the traditional chemical methods for analyses of the anthropogenic pollution and the presents of heavy metals in the soils. However the reliability of the results and the effectiveness of the methodological approach need additional validation by the traditional chemical analyses for the presence of trace elements/heavy metals in the soils.

References

Bartington Manual, retrieved from https://bartingtondownloads.com/wp-content/uploads/OM3227.pdf.

Bijaksana, S. & Huliselan, E.K. (2010). Magnetic properties and heavy metal content of sanitary leachate sludge in two landfill sites near Bandung, Indonesia. *Environmental Earth Science, 60*, 409–419. doi: 10.1007/s12665-009-0184-4.

Bityukova, L., Scholger, R. & Birke, M. (1999). Magnetic susceptibility as indicator of environmental pollution of soils in Tallinn. *Physics and Chemistry of the Earth, 24*, 829–835. doi: 10.1016/S1464-1895(99)00122-2.

Chaparro, M.A.E., Sinito, A.M., Ramasamy, V., Marinelli, C., Chaparro, M.A.E., Mullainathan, S., Murugesan, S. (2008). Magnetic measurements and pollutants of sediments from Cauvery and Palaru River, India. *Environmental Geology, 56*, 425–437.

Dearing, J.A., Hay, K., Baban, S., Huddleston, A.S., Wellington, E.M.H., Loveland, P.J. (1996). Magnetic susceptibility of topsoils: a test of conflicting theories using a national database. *Geophysical Journal International, 127*, 728-734.

Donchev, I., A. Lenchev, J. Ninov, L. Gigova. (2001). Study on some mineral and technological properties of fly-ashes from thermoelectric power stations Republika and Bobovdol, Bulgaria. *Comptes rendus de l'Académie bulgare des Sciences, 54*(11), 75-80.

Durza, O. (1999). Heavy metals contamination and magnetic susceptibility in soils around metallurgical plant. *Physics and Chemistry of the Earth*, 24, 541–543. doi: 10.1016/S1464-1895(99)00069-1.

El Baghdadi, M., Barakat, A., Sajieddine, M., Nadem, S. (2011). Heavy metal pollution and soil magnetic susceptibility in urban soil of Beni Mellal City (Morocco). *Environmental Earth Science, 66*, 141–155. doi: 10.1007/s12665-011-1215-5.

Goddu, S.R., Appel, E., Jordanova, D. & Wehland, R. (2004). Magnetic properties of road dust from Visakhapatnam (India) – relationship to industrial pollution and road traffic. *Physics and Chemistry of the Earth*, *29*, 985–995. doi: 10.1016/j.pce.2004.02.002.

Hanesch, M., Scholger, R. & Rey, D. (2003). Mapping dust distribution around an industrial site by measuring magnetic parameters of tree leaves. *Atmospheric Environment, 37*, 5125–5133. doi: 10.1016/j.atmosenv.2003.07.013.

Helble, J. (1994). Trace element behavior during coal combustion: results of a laboratory study. *Fuel Processing Technology, 39*, 159-172. doi: 10.1016/0378-3820(94)90178-3.

Helble, J.J., Sarofim, A.F. (1993). Trace Element Behavior during Coal Combustion. *American Chemical Society Division Fuel Chemistry, 39*(1-3), 159-172. doi: 10.1016/0378-3820(94)90178-3.

Hoffmann, V., Knab, M. & Appel, E. (1999). Magnetic susceptibility mapping of roadside pollution. *Journal of Geochemical Exploration, 66*, 313–326. doi: 10.1016/S0375-6742(99)00014-X.

Hu, X.F., Su, Y., Ye, R., Li, X.Q., Zhang, G.L. (2007). Magnetic properties of the urban soils in Shanghai and their environmental implications. *Catena, 70*, 428–436. doi: 10.1016/j.catena.2006.11.010.

Jordanova, N.V., Jordanova, D.V., Tsacheva, T. (2008). Application of magnetometery for delineation of anthropogenic pollution in areas covered by various soil types. *Geoderma, 144*, 557–571. doi: 10.1016/j.geoderma.2008.01.021.

Jordanova, D., Jordanova, N. & Hoffman. V. (2006). Magnetic mineralogy and grain-size dependence of hysteresis parameters of single spherules from industrial waste products. *Physics of the Earth and Planetary Interiors, 154*(3-4), 255-265. doi: 10.1016/j.pepi.2005.06.015 .

Jordanova, D., Hoffmann, V. & Thomas Fehr, K. (2004). Mineral magnetic characterization of anthropogenic magnetic phases in the Danube river sediments (Bulgarian part). *Earth and Planetary Science Letters, 221*, 71–89. doi: 10.1016/S0012-821X(04)00074-3.

Jordanova, N. (2016). *Soil Magnetism. Applications in Pedology, Environmental Science and Agriculture.* (1st Edition), Academic Press (Elsevier).

Jordanova, N.V., Jordanova, D.V., Veneva, L., Yorova, K. & Petrovsky, E. (2003). Magnetic response of soils and vegetation to heavy metal pollution – a case study. *Environmental Science and Technology, 37*, 4417–4424. doi: 10.1021/es0200645.

Kapicka, A., Petrovsky, E., Ustjak, S. & Machackova, K. (1999). Proxy mapping of fly-ash pollution of soils around a coal-burning power plant: a case study in the Czech Republic. *Journal of Geochemical Exploration, 66*, 291–297. doi: 10.1016/S0375-6742(99)00008-4.

Kortenski, J. & A. Zdravkov. (2008). Occurrence and distribution of major elements in coals from Bobov dol basin, Bulgaria, *Annual of the University of mining and geology "St. Ivan Rilski", Geology and Geophysics, 51*(I), 34-40. (In Bulgarian).

Lecoanet, H., Leveque, F. & Ambrosi, J. (2001). Magnetic properties of saltmarsh soils contaminated by iron industry emissions (southeast France). *Journal of Applied Geophysics, 48*, 67–81. doi: 10.1016/S0926-9851(01)00080-5.

Lu, S.G. & Bai, S.Q. (2006). Study on the correlation of magnetic properties and heavy metals content in urban soils of Hangzhou City, China. *Journal of Applied Geophysics*, *60*, 1–12. doi: 10.1016/j.jappgeo.2005.11.002.

Mokreva, A., Jordanova, N., Jordanova, D., Stoyanova, V., Petrov, P. (2017). Evaluation of soil contamination degree in the region of Maritza east thermal power plants using magnetic methods. *Journal of International Scientific Publications, Ecology & Safety, 11*, 70-84.

Nikova, I., Hristov, B., Zdravkov, A., Ruskov, K., Petrov, D., Bakardzhiev, D. (2013). Monitoring of chemical characteristics in soils from "Bobovdol" valley. *Soil Science Agrochemistry and Ecology, XLVII*(3), 55-62. (In Bulgarian).

Nikova, I. & Tsolova, V. (2017). Mobility of trace elements in virgin soils from the Bobov dol valley, Bulgaria. *International Research Journal of Engineering and Technology (IRJET), 4*(10), 743-751.

Ratafia-Brown, J. (1994). Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers. *Fuel Processing Technology, 39*, 139-157. doi: 10.1016/0378-3820(94)90177-5.

Shu, J., Dearing, J.A., Morse, A.P., Yu, L.Z. & Li, C.Y. (2000). Magnetic properties of daily sampled total suspended particulates in Shanghai. *Environmental Science & Technology, 34*, 2393–2400. doi: 10.1021/es9910964.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K. & Sutton, D.J. (2012). Heavy metal toxicity and the environment. *Experientia supplementum*, *101*, 133–164. doi: 10.1007/978-3-7643-8340-4_6.

Veneva, L, Hoffmann, V, Jordanova, D, Jordanova, N & Fehr, T (2004). Rock magnetic, mineralogical and microstructural characterization of fly ashes from Bulgarian power plants and the nearby anthropogenic soils. *Physics and Chemistry of Earth, 29*, 1011-1023.

Received: 03.02.2022
Accepted: 15.05.2022