Technogenic magnetic particles of topsoil from different sources of emission – A case study from upper silesian conurbation, Poland

Maria Magdalena Szuszkiewicz[1,*], *Adam* Łukasik[1], *Tadeusz* Magiera[1], *Marcin* Szuszkiewicz[1]

[1]Institute of Environmental Engineering Polish Academy of Sciences, 34 Sklodowskiej-Curie St., 41-819 Zabrze, Poland

Abstract. Studies on the effects of dust deposition on soils in urban-industrial areas were conducted with application of magnetic (soil magnetometry, thermomagnetic analysis) and geochemical (elements content) methods. The study area covers three different forest sites on Upper Silesian Conurbation. The purpose of the research was an estimation of soil pollution and characteristic of air derived particles. Results show magnetite and maghemite as dominant magnetic components of analyzed soil samples. The highest volume magnetic susceptibility (κ) and no correlation with potentially toxic elements (PTEs) were stated close to metallurgical plant whilst the highest correlation coefficient between κ and PTEs was stated in samples from the urban area and in a vicinity of coking plant.

1 Introduction

Upper Silesian Conurbation (USC) is the largest urban-industrial area in Poland and one of larger in Central Europe. This region since many years, being under strong impact of air pollutants, is significant object of environmental studies including air, water and soils. Forest areas of USC are under strong impact of urban-industrial emission and fulfill environmental function – natural barrier that capture air pollution.

Long-standing process of accumulation of pollutants in forest topsoil (mainly in organic subhorizons) enable their detection. Urban-industrial dusts comprise iron minerals and elements formed during high temperature combustion processes [1]. These minerals can be detected in topsoil horizons as technogenic magnetic particles (TMPs) via magnetic susceptibility measurements [2]. Studies on application of geophysical parameter (magnetic susceptibility) to assess quantity and range of emission and deposition of dusts are conducted by many scientists since decades [e.g. 3-12].

PTEs discharged to atmosphere together with dusts and aerosols, are common substances that contaminate environment [e.g. 13-15]. Magnetic and geochemical analysis (including Energy Dispersive X-Ray Fluorescence – EDXRF) in topsoil, indicate on presence of TMPs. TMPs are emitted to atmosphere and then transported on various

* Corresponding author: maria.mendakiewicz@ipis.zabrze.pl

distance depending on grain size, atmospheric conditions and eventually deposited on soil surface.

Magnetic properties of emmited particles depends on temperature and redox conditions in which they are formed [e.g. 16, 17].

Attribute of industrial dusts and fly ashes is presence of iron oxides with ferri- and antiferromagnetic properties [e.g. 18-20] accompanied with elements (Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) [e.g. 21, 22]. Positive correlation between magnetic susceptibility and elements content in soils of urban-industrial areas were proved by many authors [e.g. 23-29]. Main goal of presented research was to indicate on application of integrated methods (soil magnetometry, mineralogy, geochemical analysis) to assessment of pollution as a result of dry and wet deposition.

2 Materials and Methods

2.1 Site Description

Study area cover three various forest sites located on Upper Silesian Conurbation (Southern Poland) and being in direct impact of different sources of emission.

Site A (urban) – area about 10 km^2 surrounded with highly urbanized area with numerous local emission sources (mainly coal burning). North site of area is covered with pine forests (*Pinus sylvestris* L.) developed on initial sandy soils and podzols. South site of area is covered with mixed deciduous forests comprise common oak (*Quercus robur* L.) and birch (*Betula pendula* Roth.).

Site B (coke plant vicinity) – area about 10 km^2, adjacent to coke plant play the role of buffer zone. North site of this area is covered with pine forests (*Pinus sylvestris* L.) developed on quaternary sands whilst South site is covered with mixture forest (pine, oak, beech).

Site C (steelwork vicinity) – area about 12.5 km^2, strongly influenced by metallurgy industry. Forest area is covered with pine and birch stands developed on Triassic dolomites with thin layer of quaternary sands and clays. Topsoils (layer up to 30 cm depth) of this area is marked by mechanical transformation with presence of anthropogenic material (artifacts).

2.2 Materials and Sampling Procedure

The studied material consisted of 130 soil samples derived from 65 soil cores, including 40 soil samples from 20 soil cores collected from complex A („urban complex”); 40 soil samples from 20 soil cores collected from complex B („coke plant complex”) and 50 soil samples from 25 soil cores collected from complex C („steelworks complex”).

The topsoil cores collected in the field were sampled for geochemical analysis. Dependently on vertical distribution of volume magnetic susceptibility (κ), two samples were taken from one core: upper part (U) including organic part of profile where the anthropogenic peak of magnetic susceptibility was observed and lower part (L) including mineral horizon with the natural magnetic susceptibility background. Analyses of the vertical distribution of κ allowed to distinguish between a polluted and unpolluted soil zones and indicated a boundary depth (BD) [30].

2.3 In Situ Magnetic Measurements and Soil Sampling

Measurements of κ on soil surface were conducted in field with application of MS2D Bartington device. On sites A and B, 300 single measurements were done whilst for site C close to 400. The maps of the spatial variability in the magnetic susceptibility were plotted with application of Surfer 8 (Golden Softwear Inc.). For chemical analysis, soil cores (30 cm depth) were sampled with application of Humax SH 300 sampler.

2.4 Laboratory Magnetic and Geochemical Measurements

Sampled material for magnetic and geochemical analysis comprising 65 soil cores (each 20 soil cores in A and B sites and 25 soil cores in C site). In laboratory soil cores were measured on MS2C Bartington device in order to check vertical distribution of (κ) value. After magnetic measurements soil core were sectioned with ceramic knife in two parts; upper part of soil core comprising organic material and lower part of soil core comprising mineral material. In soil samples content of Fe, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Sb, Ba and Pb was determined with application of EDXRF (Epsilon 5, Panalytical).

Analyses of the temperature dependence of magnetic susceptibility of soil samples were performed in the temperature range from 20 to 700°C. Measurements were carried out in the ambient air using AGICO Kappabridge MFK1 equipped with the high temperature furnace CS4 (Advanced Geoscience Instruments Company, Brno, the Czech Republic).

3 Results and Discussion

3.1 Magnetic Susceptibility on Soil Surface

Spatial distribution of κ in forest stand Site A (urban), shows enhanced values in southern and eastern part of site (Fig. 1a). Presented distribution is result of intensive urbanization followed with occurrence of numerous local sources of emissions. Mean value of volume magnetic susceptibility equals to 80.4 $\times 10^{-5}$ SI and is the lowest among studied Sites (Table 1.). In Site B (Fig. 1b), mean 84.1 $\times 10^{-5}$ SI and maximum value 244.8 $\times 10^{-5}$ SI of κ were similar to Site A. Spatial distribution of volume magnetic susceptibility on Site C (Fig. 1c) indicate on strong impact of metallurgical plant on surrounding area.

Table 1. Descriptive statistic for volume magnetic susceptibility (κ) from surface ($\kappa_{surface}$), upper part of soil cores (κ_{core}) and correlation coefficients between $\kappa_{surface}$ and κ_{core} from site A („urban complex"), B („coke plant complex") and C („steelworks complex").

Site	Variable	r	Unit	Min	Median	Mean	Max	SD	V	CV
A	$\kappa_{surface\ (n=20)}$	0.89**	10^{-5} SI	34	77	80	242	42	1763	0.52
	$\kappa_{core\ (n=20)}$		10^{-5} SI	100	227	249	901	179	32031	0.72
B	$\kappa_{surface\ (n=20)}$	0.59*	10^{-5} SI	18	66	84	245	53	2762	0.62
	$\kappa_{core\ (n=20)}$		10^{-5} SI	63	118	163	573	119	14182	0.73
C	$\kappa_{surface\ (n=25)}$	0.29	10^{-5} SI	53	126	183	553	133	17559	0.72
	$\kappa_{core\ (n=25)}$		10^{-5} SI	120	346	692	6336	1215	1475460	1.76

**and ** Significance below 0.05 and above 0.01 levels, respectively*

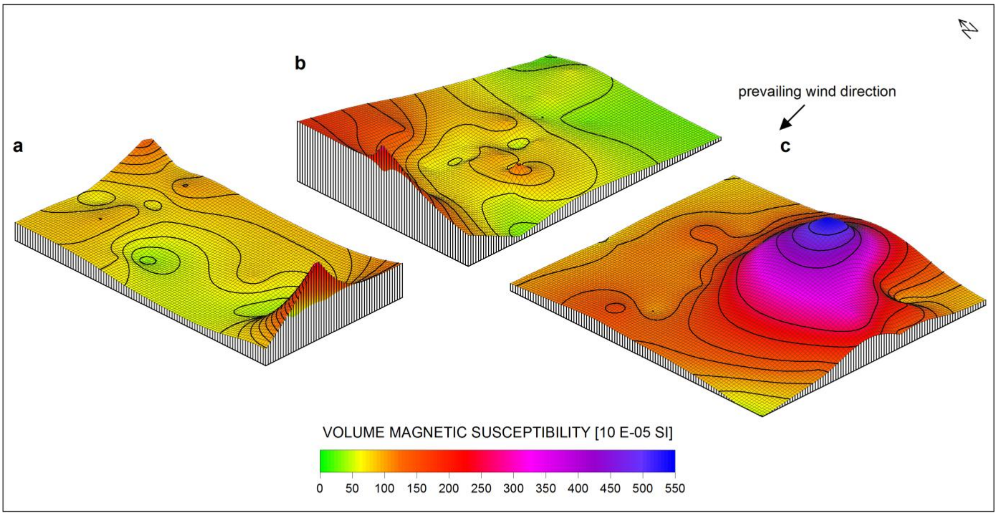

Fig. 1. Spatial distribution of volume magnetic susceptibility (κ) from site A – „urban complex" (a), B – „coke plant complex" (b) and C – „steelworks complex" (c).

3.2 Magnetic Properties of Soil Cores

Vertical distribution of volume magnetic susceptibility in soil cores in all studied areas (Sites A, B and C) present characteristic anthropogenic pattern related with strong urban-industrial emission (Fig. 2a, 3a and 4a). Difference are observed regarding boundary depth (BD) which indicating transition from polluted (uppermost layer) to unpolluted (deeper) layer in contaminated natural soil [30]. Magnetic susceptibility enhancement in uppermost layer of soil cores is result of presence and concentration of TMPs. High positive correlation coefficients between κ value measured on soil surface and in soil cores were stated in Site A and B. (Table 1).

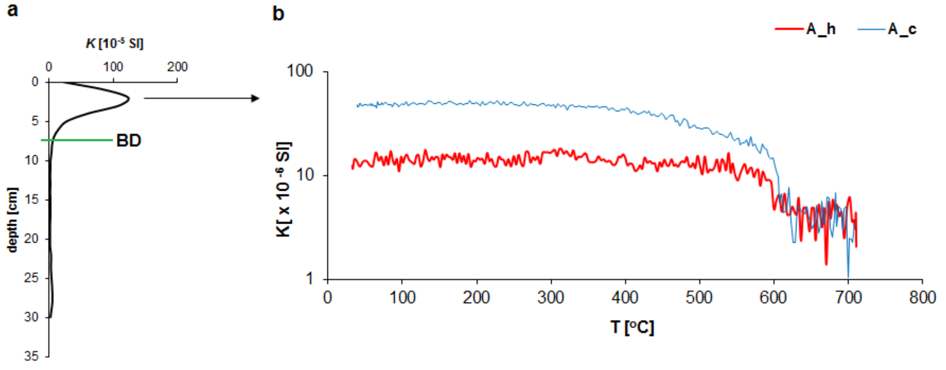

Fig. 2. Vertical distribution of volume magnetic susceptibility (a) and thermomagnetic curves (b) for upper part of soil core in representative soil cores from site A – „urban complex" (κ – volume magnetic susceptibility, BD – boundary depth (green full line), T – temperature, A_h – heating curve, A_c – cooling curve).

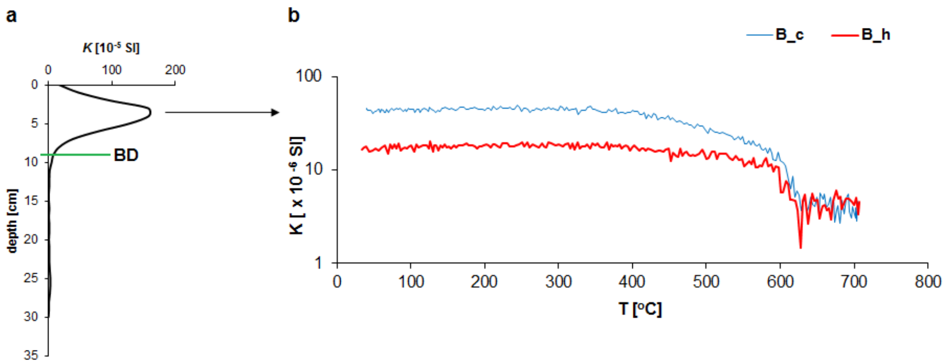

Fig. 3. Vertical distribution of volume magnetic susceptibility (a) and thermomagnetic curves (b) for upper part of soil core in representative soil cores from site B – „coke plant complex" (κ – volume magnetic susceptibility, BD – boundary depth (green full line), T – temperature, B_h – heating curve, B_c – cooling curve).

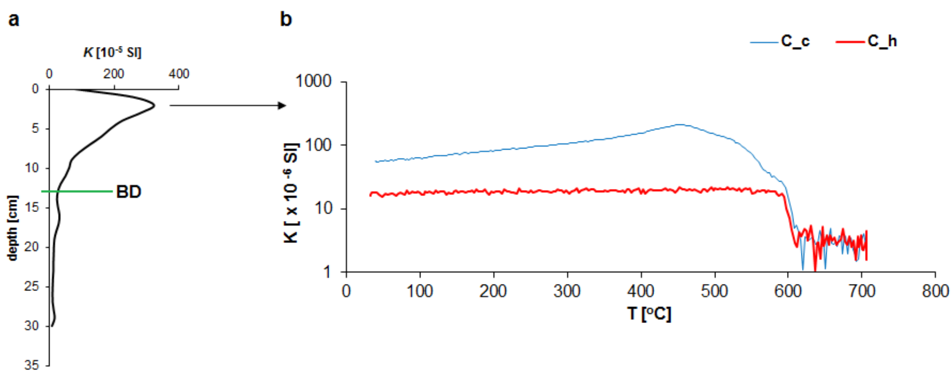

Fig. 4. Vertical distribution of volume magnetic susceptibility (a) and thermomagnetic curves (b) for upper part of soil core in representative soil cores from site C – „steelworks complex" (κ – volume magnetic susceptibility, BD – boundary depth (green full line), T – temperature, C_h – heating curve, C_c – cooling curve).

3.3 Thermomagnetic Measurements

The magneto-mineralogy of the study samples (Figs. 2b, 3b and 4b) was determined by the Curie point estimation from thermomagnetic (heating and cooling) curves. The Curie point (T_C) is the diagnostic temperature above which long-range spontaneous parallel alignment of atomic magnetic moments in ferrimagnetic minerals disappears. In case of antiferromagnetic minerals the relevant temperature is called the Neel temperature (T_N). The Curie point was estimated using the test for paramagnetic Curie-Weiss law at temperatures above T_C according to [31] and [32]. In most cases, the analyses of thermomagnetic curves of investigated soil samples from 3 different forest complex (A – „urban complex", B – „coke plant complex" and C – „steelworks complex") are similar to that displayed on Fig. 2b, 3b and 4b. The behavior of the heating curves is quite similar at all locations. They presumably indicate that the main magnetic mineral in all investigated samples is not a stoichiometric magnetite (T_C ~580-585°C), but probably suggesting the presence of a certain portion of a mineral with higher Curie temperature (approx. 600°C) –

maghemite. These samples may contain a mixture of magnetite and maghemite, but we also cannot exclude a minor amount of haematite (Tc below 700°C). Magnetic susceptibility after cooling was higher than the initial value, which suggests mineralogical changes – weakly magnetic iron minerals turned into more strongly magnetic minerals. Moreover, cooling curves are always upper than the heating.

3.4 Geochemical Analyses of Soil Cores

Assessment of soil pollution was based on calculation of relation PTEs content (Fe, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Ba i Pb) in samples from upper part of soil cores (U) to PTEs content in samples from lower part of soil cores (L). PTEs content in lower part were considered as natural background of studied area (Table 2). Set up of parts (U and L) was based on vertical distribution of magnetic susceptibility and occurrence of boundary depth (BD) (Figs. 2a, 3a and 4a).

Table 2. Mean PTEs contamination in upper (U) and lower (L) parts of soil cores from site A („urban complex") (n=20), B („coke plant complex") (n=20) and C („steelworks complex") (n=25).

Site	Parts of core	Fe	Mn	Co	Ni	Cu	Zn	As	Sr	Cd	Sb	Ba	Pb
		%	mgkg^{-1}										
A	U	2.56	378	7	18	47	563	8	44	6	2	257	245
	L	2.46	321	6	18	29	162	4	41	3	1	246	45
B	U	2.43	504	4	12	43	699	7	33	5	2	156	184
	L	2.08	473	4	10	28	448	4	28	3	1	123	49
C	U	2.89	545	4	12	47	746	8	43	6	1	203	261
	L	2.55	563	4	11	46	849	10	39	8	1	149	288

4 Conclusions

The highest level of pollution and the highest values of magnetic susceptibility as a result of air derived particles were stated in the vicinity of emission sources.

Pattern of vertical distribution of magnetic susceptibility in soil cores is characteristic for regions impacted by urban-industrial emissions.

Thermomagnetic analysis of samples indicate on presence of technogenic magnetite and/or maghemite which are components of air derived particles.

High positive correlation between magnetic susceptibility and PTEs content were stated in Sites A (urban) and B (coke plant).

References

1. L.D. Hullet, A.J. Weinberger, K.J. Northcutt, M. Ferguson. *Chemical species in fly ash from coal-burning power plant*. Science, **210**, 1356-1358, (1980)
2. T. Magiera, M. Jabłońska, Z. Strzyszcz, M. Rachwał. *Morphological and mineralogical forms of technogenic magnetic particles in industrial dusts*. Atmos. Environ., **45**, 281-290, (2011)
3. A. Hunt, J.M. Jones, F. Oldfield. *Magnetic measurements and heavy metals in atmospheric particulates of anthropogenic origin. Sci. Total Environ*., **33**, 129-139, (1984)
4. F. Heller, Z. Strzyszcz, T. Magiera, J. Geophys Res. **103 (B8)**, 17767 (1998)

5. A. Kapička, N. Jordanova, E. Petrovský S. Ustjak, Phys. Chem. Earth (A) **25**, 431 (2000)
6. E. Petrovský, A. Kapička, N. Jordanova, M. Knab, V. Hoffmann, Environ. Geol. **39**, 312 (2000)
7. C. Spiteri, V. Kalinski, W. Rösler, V. Hoffman E. Appel, Environ. Geol. **49**, 1 (2005)
8. L. Cao, E. Appel, W. Rosler, T. Magiera, Geophys. J. Int. **203**, 767 (2015)
9. M. Rachwał, T. Magiera M. Wawer,Chemosphere **138**, 863 (2015)
10. D.C. Marie, M.A.E. Chaparro, M.A. Irurzun, J.M. Lavornia, C. Marinelli, R. Cepeda, H.N. Bohnel, A.G. Castaneda Miranda, A.M. Sinito, Atmos. Pollut. Res. **7**, 513 (2016)
11. E. Błońska, J. Lasota, M. Szuszkiewicz, A. Łukasik, A. Klamerus-Iwan, Environ. Earth Sci. **75(16)**, 1 (2016)
12. T. Gonet, B. Górka-Kostrubiec, B. Łuczak-Wilamowska, Polar Sci. **15**, 75 (2018)
13. J. Zawadzki, M. Szuszkiewicz, P. Fabijańczyk, T. Magiera, Chemosphere **164**, 668 (2016)
14. T. Magiera, J. Zawadzki, M. Szuszkiewicz, P. Fabijańczyk, E. Steinnes, K. Fabian, E. Miszczak, Chemosphere **195**, 48 (2018)
15. A. Horváth, P. Kalicz, A. Farsang, P. Balázs, I. Berki, A. Bidló, Sci. Total Environ., **637-638**, 1197 (2018)
16. U. Kukier, C.F. Ishak, M.E. Sumner, W.P. Miller, Environ. Pollut. **123 (2)**, 255 (2003)
17. S. Gupta, M. Dubikova, D. French, V. Sahajwall, Energy Fuels. **21**, 303 (2007)
18. P. Flanders, J. Appl. Phys. **75 (10)**, 5931 (1994)
19. E. Petrovský, R. Zbořil, T. Matys, G. Bohumil, K. Novák, A. Kapička, H. Grison, Stud. Geophys. Geod. **57**, 755 (2013)
20. M. Szuszkiewicz, T. Magiera, A. Kapička, E. Petrovský, H. Grison, B. Gołuchowska, J. Appl. Geophys. **116**, 84 (2015)
21. S.G. Lu, X. Yu, Y. Chen, Sci. Total Environ. **543**, 239 (2016)
22. J. Wang, S. Li, H. Li, X. Qian, X. Li, X. Liu. H. Lu, C. Wang, Y. Sun, Sci. Rep. **7**: 9865
23. H. Lecoanet, F. Leveque, J.P. Ambrosi, Environ. Pollut. **122**, 229 (2003)
24. T. Magiera, J. Zawadzki, Environ. Monit. Assess. **125**: 19 (2007)
25. A. Kapička, E. Petrovský, H. Fialová, V. Podrázský, I. Dvořák, Stud. Geophys. Geod. **52**, 271 (2008)
26. C. Fürst, C. Lorz, F. Makeschin, Water Air Soil Pollut. **202**, 33 (2009)
27. Z. Zhu, Z. Li, X. Bi, Z. Han, G. Yu, J. Hazard. Mater. **246-247**, 189 (2013)
28. A. Łukasik, P. Gruba, T. Magiera, Catena, **150**, 246 (2017)
29. A. Bourliva, L. Papadopoulou, E. Aidona, K. Giouri, Environ. Sci. Pollut. Res. **24**, 17041 (2017)
30. U. Blaha, E. Appel, H. Stanjek, Environ.mental Pollut. **156**, 278 (2008)
31. E. Petrovský, A. Kapička, J. Geohys. Res. **111 (B)**, 1 (2006)
32. K. Fabian, V.P. Shcherbakov, S.A. McEnroe, Geochem. Geophys. Geosyst. **14(4)**, 947 (2013)