

TRACKING MAGNETIC POLLUTANTS BY INTEGRATED MINERALOGICAL AND MAGNETIC ANALYSES OF AIRBORNE PARTICLES IN URBAN ENVIRONMENT

Norbert ZAJZON^{1*}, Emő MÁRTON², Péter SIPOS³, Mihály PETHE^{2,4}, Tibor NÉMETH³,
Viktória KOVÁCS-KIS⁵ & János URAM⁶

^{1*}*Institute of Mineralogy and Geology, University of Miskolc, Egyetemváros, Miskolc, H-3515, Hungary (nzajzon@uni-miskolc.hu) tel: +36/46/565-111(1208), fax: +36/46/565-058*

²*Palaeomagnetic Laboratory, Geological and Geophysical Institute of Hungary, Columbus utca 17–23, Budapest H-1145, Hungary (paleo@mfgi.hu)*

³*Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Hungary, Budaörsi út 45, Budapest, H-1112, Hungary (sipos@geochem.hu; ntibi@geochem.hu)*

⁴*Department of Geophysics, Eötvös Loránd University, Pázmány P. sét. 1/C, Budapest, H-1117, Hungary*

⁵*Research Institute of Technical Physics and Materials Sciences, Hungarian Academy of Sciences, Hungary, Konkoly-Thege Miklós út 29–33, Budapest, H-1121, Hungary (kis@mfa.kfki.hu)*

⁶*North Hungarian Environmental, Nature Conservancy and Water Policy Inspectorate, Mindszent tér 4, Miskolc, H-3530, Hungary (ujanos@emikofe.kvvm.hu)*

Abstract: This complex magnetic and mineralogical study, which was carried out on settled dust and PM10 (particulate matter smaller than 10 µm) samples collected for several years in a Hungarian industrial town, Miskolc. The primary aim of the research was to estimate the contribution of different pollution sources which produce magnetic phases to the settled dust and to the PM10 fraction. In both types of the airborne dust, magnetite a spinel type iron oxide was identified as the dominant magnetic mineral with magnetic and mineralogical methods. The latter revealed that the magnetic mineral was either pure magnetite or contained minor amounts, usually few percent in total of other metals like Mn (up to 2.2 at%), Zn (up to 4.6 at%), Co (up to 8.1 at%), Cr (up to 1.3 at%) and Pb (up to 0.5 at%). Comparison between the total magnetic susceptibilities of settled dust samples collected before and after the closing down, respectively of the steel works (DAM) in the town, reveals a significant reduction (50–100%) in magnetic pollution. Such comparison was not possible for PM10 fraction, since systematic PM10 collection in Miskolc started after the closing of DAM. The analysis of the PM10 filters was, however, important from the viewpoint of magnetic pollution originating from other sources, like vehicle traffic, combustion. We found that roughly the half of the magnetic particles are in the superparamagnetic range (< 30 nm), therefore extremely dangerous for the health. The degree of magnetic pollution shows daily and seasonal variations. The former points to vehicle traffic as a general source of magnetic grains, since the total susceptibility is lowest on Sundays ($15 \cdot 10^{-6}$ SI, till on weekdays ca. $20 \cdot 10^{-6}$ SI). The seasonal variation indicates that industrial and household combustion increases the total susceptibility in winter time (from 5 to $8 \cdot 10^{-6}$ SI in PM10). The mass of the PM10, however, increases much more (ca. 3 times) in wintertime than total susceptibility due to emission of large amount of non-magnetic particles, such as carbonaceous phases and sulphates from combustion sources. Thus, we think that restriction of vehicle traffic during wintertime is not an efficient measure to reduce the concentration of PM10 during smog alarm. Comparison between the concentrations of heavy metals (like Pb and Cd) and mass susceptibility lead to the conclusion that the magnetic pollutants and the metals are coming from different sources. The concentration of the latter depends on the direction and intensity of the wind, which may bring them from industrial sources, located North of Miskolc.

Keywords: air pollution; total versus mass susceptibility; magnetite spherules; different pollution sources; PM10; mineralogy of airborne particles

1. INTRODUCTION

Airborne particles have been widely

associated with health disorders as presented by numerous studies (e.g. Selinus, 2005). They often contain potentially toxic metals. Even if the grains

are settled, the associated pollutants can contaminate soil and water.

Magnetite is the most important inorganic dust component from anthropogenic sources. Steel metallurgy, coal and biomass combustion are well known sources of magnetite spherules (e. g. Biswas & Wu, 2005; Bruseck & Adachi, 2008; Gieré & Querol, 2010; Maher, 2009; Nowack & Bucheli, 2007). It is well known that coal and biomass combustion plants also create magnetite particles (Grobéty et al., 2010; Maher, 2009; Raask, 1985). Also traffic pollution can be a significant source of combustion derived nanoparticles (Cass et al., 2000; Harrison et al., 2000; Shi et al., 1999). Numerous studies found strong correlation between urban dust pollution and magnetic susceptibility data of PM10 fractions (Halsall et al., 2008; Mitchell & Maher, 2009; Muxworthy et al., 2002; Szönyi et al., 2008). They are often associated with toxic heavy metals such as Pb, Zn, Cu, Cr, Ni, Mo, Cd. These materials have bad health effects partly because of small grain size, partly because of associated toxic components. The particulate matter which is collected on PM10 filters damages the respiratory system, including the lungs and trigger heart and vein blocks.

The dust particles in the air are derived from natural (like rocks and soil) and from anthropogenic sources. The natural dust usually contains extremely small amount of iron minerals, therefore its magnetic susceptibility is very low. If a dust contains anthropogenic iron or its oxides, even in low concentration, their presence will considerably enhance the susceptibility. The reason is that while all materials have magnetic properties, the magnetic susceptibilities of iron and certain iron oxides are orders of magnitude higher than that of the other materials. Consequently, magnetic techniques will easily detect magnetic pollutants.

Once the presence of iron or strongly magnetic iron oxides is indicated with magnetic susceptibility measurements, it is reasonable to make on selected samples a complex analysis of the material, with mineralogical and chemical methods and carry out special magnetic measurements (like Curie-points or frequency dependent susceptibility) so that the source(s) of the pollution is identified.

For our study, a mid-size Hungarian town, Miskolc was chosen, because the town is well known for different industrial activities (i.e. iron works, steel processing plant, chemical factories, ore dressing plant, coal combustion plants), and heavy vehicular traffic. In Miskolc and environs, air quality monitoring started from 1978 with collecting monthly the settling dust at 18 locations by the North Hungarian Environmental, Nature

Conservancy and Water Policy Inspectorate (NHENCWPI). The dust filters, after mass measurements, were made available for magnetic (in the Paleomagnetic laboratory of GGIH) and mineralogical (Institute of Mineralogy and Geology, University of Miskolc) investigations from 2005. In the light of the first results (Márton et al., 2008), and due to changing conditions in the pollution sources (e.g. closing down the iron works, opening of a bypass road around the town) on the one hand and to the availability of PM10 filters from a station in central Miskolc on the other, we continued the investigations on settled dust samples only from a reduced number of the official stations, and focused on the PM10 fraction from 2009. Also we established a settled dust station at the official PM10 monitoring station. The systematic PM10 monitoring started at the end of 2007 in the area.

Our aim was to find out how the changing conditions influenced the concentration of magnetic pollutants, to estimate the role of magnetic pollution from different sources in the PM10-fraction, and to see whether the potentially toxic metals and the iron minerals come from the same sources.

2. MATERIALS AND METHODS

2.1. Sample and data collection, preparation

Miskolc is located in NE Hungary (N 48° 06', E 20° 48', the valley floors around 110 m above sea level) and has about 200 000 inhabitants. It lies in the eastern vicinity of the Bükk-Mts. (Fig. 1). The general wind is from NNW-NW along the Sajó-valley. Average yearly wind speed is 0.7 m/s, average temperature 10.8°C (min. -17.8°C on 12th Jan 2003, max. 29.3°C on 19th July 2007), relative humidity is 73.3%, yearly precipitation is 500–1000 mm (24 hour average of the last nine years 2003–2011 at Búza-square). It has continental climate.

The PM10-monitoring-station is located in downtown (Búza-square, Fig. 1). Samples were collected on a 24-hour basis, for two weeks of February, May, August and November. About 720 m³ air was pumped through quartz filters daily. They were collected according to the EN12341-2000 Hungarian and the CEN/TC 264 European Union standards. Mass measurements, toxic metal analysis and magnetic investigations were performed on each filter (Whatmann DHA-80 PAH, 150 mm diameter). Material from the pre-trap of the PM10-collecting instrument was also processed for magnetic and mineralogical investigations. Meteorological (temperature, wind, humidity) and air quality (PAH,

aerosol, NO₂, ect.) data were also recorded at the PM10-station. Sample weights are generally between 0.0106 and 0.0262 g with an average of 0.026 g.



Figure 1. Map of Miskolc and its environs. Relevant sample collection points (settling dust and PM10) and possible pollution sources are indicated as: ●: Búza-square PM10 station; ○: meteorological station for relevant wind data. (Martintelep); “diamonds”: settling dust stations, pollution sources are rectangles or ovals filled with grey (base map is from Google Maps).

Settled dust samples were collected on monthly basis in the period of 2005–2011 (except Búza-square, where it started from May, 2010.), according to the MSZ EN21454/1–83 national standard. After weighing the samples, their magnetic susceptibility was measured. Mineralogical investigations were carried out on filters, or particles partially removed (ca. 95 wt%) from the filters with representative susceptibilities. The number of PM10 and settled dust samples investigated is 168 (2009–2011), and 279, respectively.

2.2. Analytical techniques

2.2.1. Mineralogical and geochemical analyses

X-ray powder diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer. Scanning electron microscopy energy- and wavelength dispersive X-ray spectroscopy (SEM-EDS, WDS) were performed on the following instruments: JEOL JXA-8600 Superprobe, AMRAY-1860T6, Hitachi S4800. Analytical transmission electron microscopy (ATEM) and selected area electron diffraction (SAED) were carried out using Philips CM-20 microscope.

Chemical analyses were done by the NHENCWPI. Pb, Cd concentrations were analyzed by PerkinElmer Optima-4300-DV Inductively-coupled-plasma-excited optical-emission-spectrometry (ICP-OES). Before analysis the dissolution was done in a PTFE bomb by boiling (120–150°C) the sample for 2 hours in a 1:1:1 cc. (concentrated) HNO₃, cc. HCl and cc. HF (extra HF was neutralized with 3% H₃BO₃ solution), following the MSZ13177-1992 (withdrawn) national standard. An UNICAM 939-QZ-AA Inductively-coupled-plasma-excited atomic-absorption-spectrometer (ICP-AAS) was used for As. Before the analyses dissolution was done by boiling the sample in Kjeldahl-lombic for 15–20 minutes in 2:1 cc.HNO₃ and cc. H₂O₂ (MSZ21853-1999 national standard).

2.2.2. Magnetic measurements

Magnetic susceptibility measurements were performed with a KLY-2 Kappabridge instrument. Each filter was measured 5–10 times, and corrected for sample holder and blank filter (both diamagnetic). Both total (bulk measured susceptibility of the sample, which is not a function of the sample mass) and mass susceptibilities (volume susceptibility divided by density) were calculated for each filter. Filters with representative susceptibilities were selected for special magnetic investigations including Curie-point measurements, measurements of decay rate of the isothermal remanent magnetization (Molspin LTD pulse magnetizer and JR-5A spinner magnetometer) and frequency dependence of magnetic susceptibility (MFK1 Kappabridge, AGICO and Bartington MS2).

3. RESULTS AND DISCUSSION

3.1. Phase composition of the samples

3.1.1. The natural components of the dust

The mineral phase identification by XRD and SEM-EDX showed that the main crystalline mass of the collected samples come from natural sources. The identified components are in order of decreasing concentration: quartz > calcite > albite > muscovite >> dolomite > magnetite > amphibole. Such phases were also observed in the PM10 fraction by ATEM. It is similar to the general composition of a mineral dust (Engelbrecht & Derbyshire, 2010, Márton et al., 2013). All the observed components can be explained with the surrounding geology, except the magnetite which is mostly coming from pollution sources (Zajzon et al., 2013). The pollutants reach only maximum few % in the settled dust, similarly to the worldwide average (Cort & Scot, 2001).

Organic particles (fragments of plants, pollens) were always visible under SEM. Their amounts vary seasonally in the samples. The summer samples always have higher organic fragment compound (up to 50 wt%), than the winter samples (See in detail: Márton et al., 2013).

3.1.2. Magnetic pollutants (Fe-oxides)

The most common magnetic pollutant is magnetite (identified by SEM, XRD and ATEM). It is spherical, perfectly round, or droplet shape. Particle size is usually 1–10 μm , it varies from hundred μm down to sub- μm . The smallest observed magnetite grains are 10–20 nm in diameter. 40–50 nm magnetite particles frequently form grape like aggregates of 1–2 μm size (Fig. 2a). It is sometimes a dense grain (Fig. 2b, c), but more often it is ball / sphere like, thin or thick crust with empty space in the middle (Fig. 2d, e). The surface of the spherules is sometimes perfectly smooth but more often a dendrite like crystal shape can be observed which is built up from minute magnetite octahedra. The extremely big, hundred μm size spherules are restricted to locations, close to industrial pollution sources (e.g. steel works, Zajzon et al., 2013).

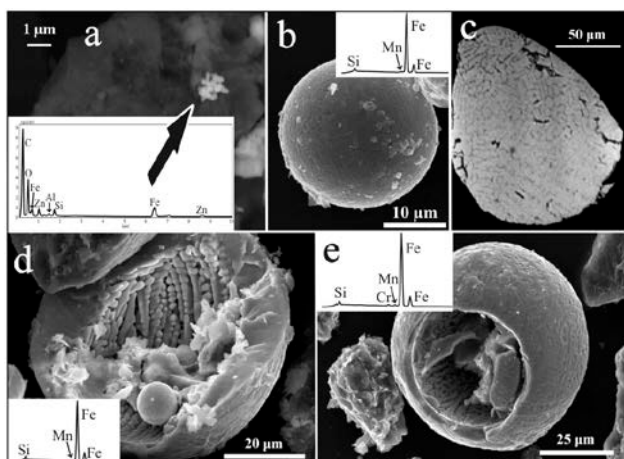


Figure 2. SEM images of magnetite spherules. (a) SEM image and EDX spectrum of a grape like magnetite aggregate from Búza-square (2010 Nov). (b) round spherule from settled dust (2006 Oct., Pesti str., Miskolc) (c) cross section of a dense, droplet shape particle (Nov. 2001, Bálvány-hill, Bükk-Mts., Hungary) (d-e) hollow sphere particles (March 2006, Vargahegy, Miskolc).

Chemical composition of the magnetite grains varies from grain to grain, but no clear location or size specific characteristics can be observed. They are most frequently almost pure Fe-oxides with only few wt% Mn (Fig. 2c). The amount of Zn, when is present, is also only a few wt%, but some grains have franklinite composition (ZnFe_2O_4). Minor amounts of Si, Ca and Cr are also observed in some grains.

Amorphous carbonaceous particles and sulphates commonly serve as a substrate for submicron sized iron oxides. Aggregates of clay and Fe-oxide particles are less typical. Few tens of nm sized iron-oxides may form clusters on the surface of soot aggregates (Fig. 3b), but individual iron-oxide particles up to a few μm of diameter can also found (Fig. 3a). Based on selected area electron diffraction (SAED) patterns the iron-oxide particles are identified as mixture of magnetite and hematite and in some cases pure magnetite (Fig. 3b). The presence of magnetite is in agreement with the results of magnetic analyses, but hematite is very weakly indicated in the isothermal remanent magnetism (IRM) acquisition curves (Fig. 8). ATEM data show that iron oxides often may contain significant amount of Zn (up to 4.6 at%) and Mn (up to 2.2 at%) and in some cases Co (8.1 at%), Cr (1.3 at%) and Pb (0.5 at%).

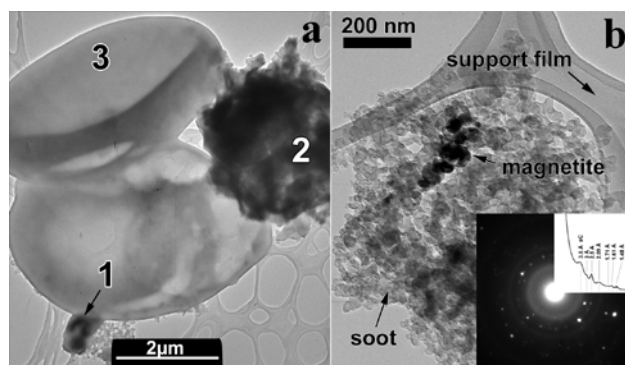


Figure 3. TEM images (a) Iron-oxide particle (1) with high Zn content attached to a thick amorphous carbonaceous particle (3) and an iron (oxide) containing thick sulphate aggregate (2). (Feb. 2009, Búza-square) (b) Pure magnetite particles attached to the surface of a soot aggregate. The inset shows the SAED pattern of some randomly oriented magnetite crystals and the diffraction rings of soot. (Aug. 2009, Búza-square).

3.1.3. Non-magnetic pollutants

Glassy silicate particles are common both in the settling dust, and in the PM10 samples. Their perfectly round (Fig. 4a), droplet, or fibre shapes (Fig. 4b) indicate that they solidified in the air, and very likely have anthropogenic origin. Their surfaces are featureless. The dense round or droplet shape spherules are in the same size range (maximum size 20–40 μm) as the magnetite spherules. The hair-like forms are 10–20 μm in diameter, and up to several hundred μm long.

The composition of the silicate melt particles is constant in one grain, but varies from grain to grain. They always contain Al, up to half of the wt% of Si content. The other cations present in them are: Na, Mg, K, Ca and Fe, in highly variable amounts. A Ca-

dominant phase is the most common one, followed by Na+K dominant phases. A unique Ca-dominant Mg-Al-Ca-silicate spherule (Fig. 4c) was found, which contained square and round shaped Fe dominant Mg-Fe-oxides, with probably spinel structure.

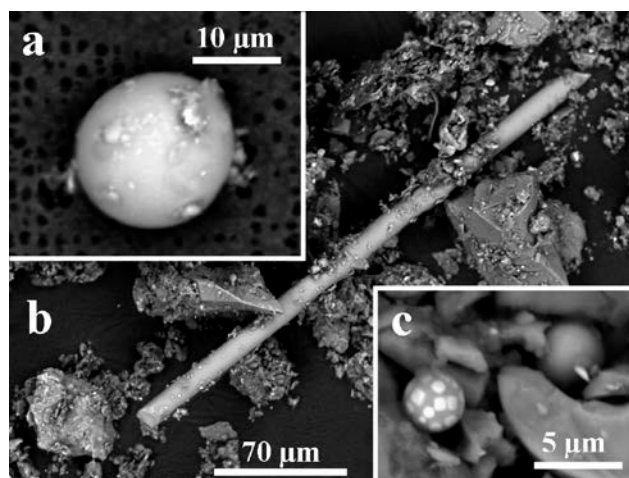


Figure 4. SEM images of sphere shape (a) and hair like (b) forms of silicate-melt pollutants. (c) BSE image of a Ca-dominant Mg-Al-Ca-silicate spherule, with square and round-shaped, Fe dominant Mg-Fe-oxide inclusions (Nov. 2010, Búza-square, Miskolc).

There is a particular group of spherules, which are Ca-Fe-oxides, sometimes with minor amounts of other elements. The Ca-Fe ratio is around 1:1. Spherules with this composition were found mostly around the cement factory (Fig. 1, No. 8), so they were probably formed in the clinker making furnace.

ATEM analyses showed that PM10 samples are mainly composed of amorphous carbonaceous particles and minor amount of silicates like clay particles. Amorphous carbonaceous particles are mostly represented by aggregates of soot nanoparticles which diameters of 10–50 nm (Fig. 3b), occasionally being as large as 250 nm. Soot nanoparticles are formed by curved graphitic layers (similar to Zajzon et al., 2013) of carbon with significant amount of aromatic compounds (Kis et al., 2006). Besides soot, large, plate-like carbonaceous particles can also be found (Fig. 3a). These contain higher amounts of S and P than soot, which implies organic origin. In the winter samples significant amount of K and Ca-sulphates are also present (Fig. 4 a). The sulphate particles have typically isometric shape (rectangular or spherical). Their size shows large variation from a few tens of nm to µm. Potentially toxic metals in non-magnetic particles were not found in the PM10 samples. Only one Pb-O particle appeared in a summer sample.

Sometimes particles with unique compositions can be found in the settled dust. Their sizes are

average, but their compositions are highly variable. They are Cu-oxides, Ba-Al-silicates, Zr-silicates, or in one case a Zr-oxide and Al-oxide with eutectic segregation structure. These compositions prove anthropogenic origin, except for the Zr-silicate, which can also be a small fragment of naturally formed zircon.

3.2. Toxic metal content of the PM10 samples

The toxic metal content of PM10 samples are summarised in Table 1. The official threshold limit values are 0.01 µg/m³ for As, 0.3 µg/m³ for Pb and 0.005 µg/m³ for Cd for a year according to the 2004/107/EK EU directive. These average yearly threshold limit values were never reached, not even temporally for Pb and Cd. Only the daily As content was higher for 6 days during the 01–10th of February, 2010 period.

Table 1. Summarized chemistry (As, Pb, Cd) data of the investigated PM10 samples, with the indicated official values (d.l. detection limit; adv. / oyt. average daily value as percentage of the official yearly threshold limit).

daily values in microgram/m ³	As	Pb	Cd
general daily values	0.0007-0.0035	0.0111-0.0333	0.0003-0.0013
average daily value	0.0026	0.0275	0.0009
commonly reached high daily values	0.0056-0.0070	0.0417-0.0556	0.0017-0.0019
highest daily value	0.0303	0.1574	0.0034
lowest daily value	<0.0002 (d.l.)	0.0056	0.0002
official threshold limit for a year	0.01	0.3	0.005
adv. / oyt limit	26%	9%	18%

3.3. Magnetic properties

The total magnetic susceptibilities for the PM10 fraction collected on the filters vary from 3–42 x10⁻⁶ SI (noise level of the measuring instrument is 0.2x10⁻⁶ SI). Thus the susceptibilities, which are calculated from 5–10 repeat measurements, are highly reliable. As the mass of the pollutant varies from filter to filter, mass susceptibilities were also calculated, using the values provided by the NHENCWPI. The mass susceptibilities calculated are 0.9–16.0x10⁻⁶ m³/kg, (similar to the settled dust samples collected at points with heavy traffic in Miskolc, e.g. locations 4 and 5.) the highest values characterizing the filters with the lowest mass. It is remarkable that extremely high values of the mass susceptibilities invariably appear as soon as the mass of the pollutant drops below 0.01 g.

As the total susceptibilities are not influenced by the factors which may handicap the precise mass determination, we suggest relying more on the total than on the mass susceptibilities in the interpretation of the degree of magnetic pollution, especially when the source of the pollution is to be identified. The magnetic pollutant was identified as magnetite by Curie–point measurements in settled dust samples. IRM (isothermal remanent magnetization) acquisition curves (Fig. 5) for a PM10 sample document that the magnetic mineral is dominantly fast saturating, most likely magnetite. Contribution of small grains close to the superparamagnetic range ($0.03 \mu\text{m}$) is identified, since the IRM decays with time (Fig. 5). These characteristics are similar to those found in vehicle exhaust material (Zajzon et al., 2013).

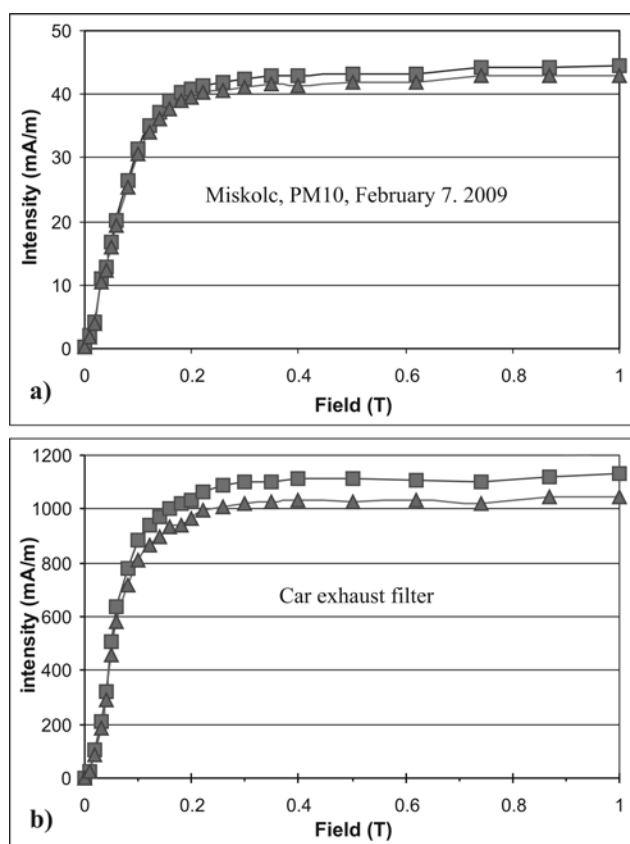


Figure 5. IRM (isothermal remanent magnetism) acquisition curves for a PM10 sample and a car exhaust filter. Squares (upper curve) measured immediately after magnetization and triangles (lower curve) with the elapse of 30 minutes (5b from Zajzon et al., 2013).

Total susceptibilities exhibit considerable daily variation, and the minimum for most of the monitored 16 weeks is observed on Sundays (Fig. 6). Obviously, the minima are related to less traffic, thus a considerable part of the magnetic pollution must be produced by vehicles. This is further supported by susceptibility measurements at different frequencies of the settled dust and of the car exhaust filter (see

details in Zajzon et al., 2013). The susceptibility at higher frequency is 6.6% less than at lower frequency for a car exhaust filter, similar to the settled dust samples from Búza-square in May (5.7 %) and August (5.8 %), 2010, which documents the presence of superparamagnetic magnetite grains in similar proportions in them. According to Dearing (1999) when measurements in different frequencies differ by less than 2%, there are no superparamagnetic grains ($<0.03 \mu\text{m}$), above 10% all grains are superparamagnetic, while in-between the material is a mixture of grains below and above $0.03 \mu\text{m}$.

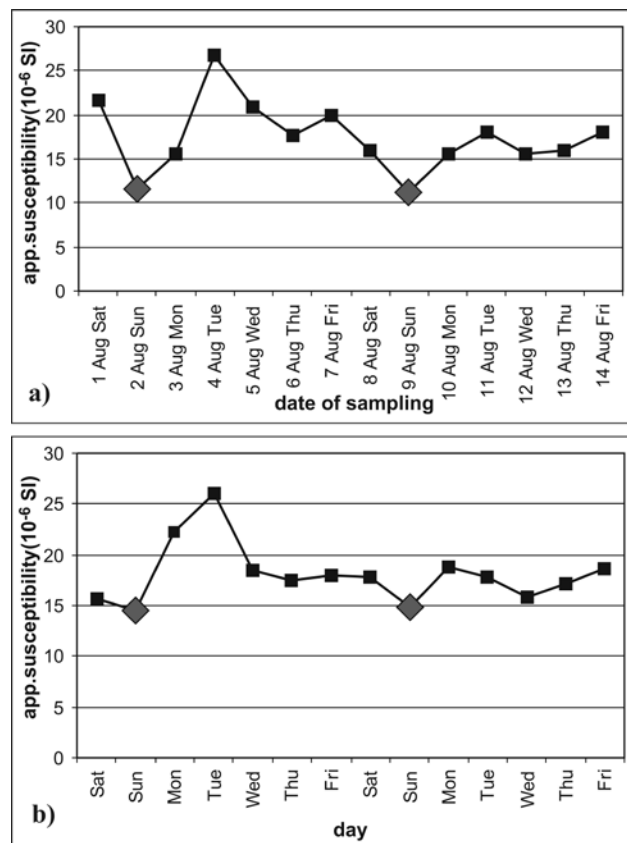


Figure 6. (a) total susceptibility data show minima on Sundays. For the time period of 1–14th of August 2009 (b) and the same calculated from the whole data set for the years of 2009–2010 by combining the values measured for the daily filters for the corresponding days of the weak of the two- week runs.

Another important source of the magnetic pollution must be from domestic coal and wood combustion during winter, since the maximum values of the total susceptibilities are significantly higher in November than in May or August, and reach their maxima in February (Fig 7). It is interesting to emphasize that, even though the total susceptibilities are higher in the wintertime, the mass susceptibilities are lower, because the amounts of non-magnetic pollutants (sulphates and soot, probably also produced by burning coal and wood) is even higher

than that of the magnetic particles. It is a further argument in favour of using the total susceptibility to characterize the degree of magnetic pollution instead of the mass susceptibility.

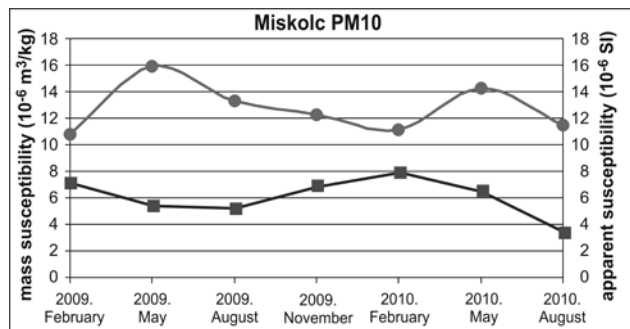


Figure 7. Miskolc, PM10 filters. Maximum total susceptibility (lower curve, squares) and mass susceptibility (upper curve, circles) for each of the two-week runs, the former showing maxima in wintertime, the later in May.

Concerning industrial sources of pollution, magnetic measurements on PM10 filters do not exclude neither support them. However, comparison of the total susceptibilities of settled dust samples from different stations before and after closing down the iron works in Miskolc suggest that this industry significantly contributed to the magnetic pollution before December, 2008 (Fig. 8).

3.4. Integrated interpretation of mineralogical, chemical, magnetic and meteorological data

As presented above, the dominant magnetic mineral in the settled dust and PM10 samples was identified with magnetic and mineralogical methods as a spinel-type iron oxide, basically magnetite without or with additional minor elements in the lattice, like Zn, Mn, Co, Cr and Pb.

Magnetite grains of the car exhaust filter contained Pb and Zn, those from steel factories contained dominantly Mn and Zn (Zajzon et al., 2013). Filipelli et al., (2005) called attention to strong correlation between magnetic signal, Fe and Pb in urban environment. They suggested that these components have the same source, which is most likely the fuel combustion, without having identified Pb in the magnetite itself.

The magnetite grain size in the settled dust samples is usually not larger than 10–20 μm , and it is dominantly below 2 μm . Larger grains were only observed around steel works (Fig. 1, location 6). The magnetite in the PM10 filters and the car exhaust filter are in the sub-micrometer range and the magnetic measurements of the filter plus pollutant

suggest that part of them is superparamagnetic (< 30 nm) (Zajzon et al., 2013). This extremely fine grained magnetite fraction is also present in the settled dust samples, shown by both, mineralogical and magnetic observations.

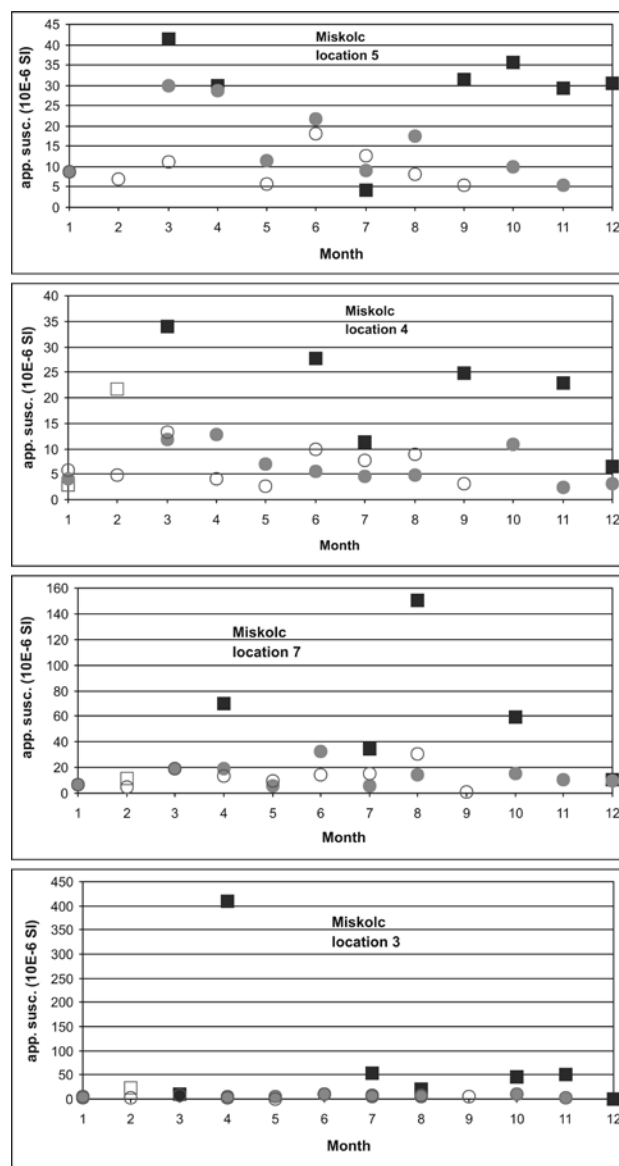


Figure 8. Comparison of the total susceptibilities of settled dust samples at four different locations in Miskolc, before (2005 (filled squares) and 2006(empty squares)) and after (2009 (filled circles) and 2010 (empty circles)) the closing down of DAM RT.

The compositions of magnetite particles from different pollutant sources are quite similar; thus on this basis unambiguous identification of them is not possible (Zajzon et al., 2013). On the other hand, the size of the magnetite particles is more relevant information. According to our observations, the maximum and average sizes of magnetite spherules created in steel works, ore dressing plants, combustion power plants, domestic house heating

systems and car engines decrease with the above listed order (Zajzon et al., 2013). However, daily and seasonal variations in the magnetic pollutants, comparison with meteorological observations and major changes in the urban environment (e.g. closing down steel factories) are the most important factors helping the proper interpretation of the data in terms of sources of the pollution.

Susceptibility minima in PM10 daily filters on Sundays suggest that the main source of magnetite is the traffic. Susceptibility measurements at 2 and 3 frequencies documented that superparamagnetic grains are important contributors to susceptibility in PM10 dust filters, settled dust and car exhaust filters, this fact also confirmed by ATEM data.

The pollution components from traffic and industrial sources are not expected to show seasonal variation; thus, the only difference between the winter and summer samples should be caused by domestic house heating systems and power plants. Susceptibility maxima in February suggest that heating with coal and wood, even gas in winter increases the pollution. This observation is supported by mineralogical data where sulphates and water soluble chlorides were dominant in the winter samples.

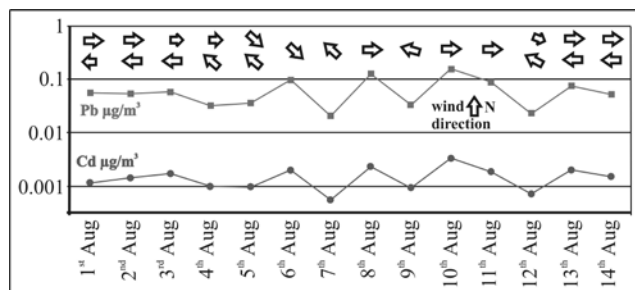


Figure 9. Relationship between Pb and Cd concentrations and wind-direction. The sizes of wind arrows are proportional to the amount of wind in the indicated direction.

Most of the studies dealing with air pollution found correlation between magnetic susceptibility and toxic heavy metals (e.g. Filipelli et al., 2005). In our case, the concentration of the monitored Pb, Cd and As do not show correlation with the magnetic susceptibility despite small amounts of Pb was detected in magnetite. Metal concentrations correlated with the wind direction strongly. Pb and Cd concentrations increase with N–NW wind and decrease with S–SE wind (Fig. 9). Towards NNW there are multiple industrial sources: combustion plant, ore-dressing plant, chemical factories. The most probable source could be the ore-dressing plant or the nearby chemical factory for Pb and Cd pollution (Fig. 1, locations 9 and 10).

Concerning the iron works as one source of

the heavy pollution in Miskolc, somewhat lower values of susceptibilities and also the mass of the settled dust is observed at some stations most likely affected by this source.

4. CONCLUSIONS

Magnetic susceptibility measurement is quick, cheap, non-destructive, powerful tool to monitor environmental pollution from sources which produce ferromagnetic particles. Further advantage of the method is that in most experiments the filter and the pollutants can be measured together, without the need of removing the pollutant. Thus, the filters, selected after the susceptibility measurements can be further processed for mineralogical/chemical measurements.

Long records from settled dust and PM10 stations are needed for interpreting the observations in terms of possible sources. Dependence of the intensity of the magnetic and heavy metal pollution on the time (daily and seasonal basis), the wind direction, changes in the urban environment must be investigated so that the contribution of the different sources to the air pollution could be estimated. In Miskolc, after closing down steel metallurgy (Fig. 1, location 6), the most important source of the magnetic pollution is traffic. However, industrial activity outside of the town also contributes to the pollution. Since the susceptibility is twice as high in winter than in summer, heating is also an important pollution source at wintertime. We think, therefore, that the restriction of the traffic during smog alarm in winter in Miskolc is hardly an efficient method in reducing air pollution.

ACKNOWLEDGEMENTS

This work was supported by the Hungarian Scientific Research Funds (OTKA K75395 and OTKA K76317) and also the TÁMOP-4.2.1.B-10/2/KONV-2010-0001. P. Sipos also thanks for the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. František Hrouda and Martin Chadima are warmly thanked for helping in MFK1 measurements at AGICO and the authors are also thankful for technical assistance from Ádám Domján and Ferenc Kristály.

REFERENCES

- Biswas, P. & Wu, C. Y., 2005. *Critical review: Nanoparticles and the environment*. Journal of Air and Waste Management Association, 55, 708–746.
- Bruseck, P. R. & Adachi, K., 2008. *Nanoparticles in the Atmosphere*. Elements, 4(6), 389–394.
- Cass, G. R., Hughes, L. A., Bhave, P., Kleeman, M. J., Allen, J. O. & Salomon, L. G., 2000. *The*

- chemical composition of atmospheric ultrafine particles*. Philosophical Transactions of the Royal Society of London: A, 358, 2581–2592.
- Cort, A. & Scot, T. M.**, 2001. *Atmospheric Nanoparticles*. In: J. F. Banfield, A. Navrotsky (Eds.), *Nanoparticles and the Environment*, Reviews in Mineralogy and Geochemistry (44), (pp. 293–349). Washington DC, USA: Mineralogical Society of America, P. H. Ribbe (series ed.), Geochemical Society, J. J. Rosso (series ed.).
- Dearing, J. A.**, 1999. *Environmental magnetic susceptibility using the Bartington MS2 system*. Chi Publishing, Kenilworth, UK. 54 p.
- Engelbrecht, J. P. & Derbyshire, E.**, 2010. *Airborne Mineral Dust*. Elements, 6(4), 241–246.
- Filipelli, G. M., Laidlaw, M. A. S., Altimer, J. C. & Raftis, R.**, 2005. *Urban lead poisoning and medical geology: An unfinished story*. GSA Today, 15, 4–11.
- Gieré, R. & Querol, X.**, 2010. *Solid Particulate Matter in the Atmosphere*. Elements, 6(4), 215–222.
- Grobéty, B., Gieré, R., Dietze, V. & Stille, P.**, 2010. *Airborne particles in the urban environment*. Elements, 6(4), 229–234.
- Halsall, C. J., Maher, B. A., Karloukowsky, V. V., Shah, P. & Watkins, S. J.**, 2008. *A novel approach to investigating indoor/outdoor pollution links: Combined magnetic and PAH measurements*. Atmospheric Environment, 42, 8902–8909.
- Harrison, R. M., Shi, J. P., Xi, S. H., Khan, A., Mark, D., Kinnersley, R. & Yin, J. X.**, 2000. *Measurement of number, mass and size distribution of particles in the atmosphere*. Philosophical Transactions of the Royal Society of London: A, 358, 2567–2579.
- Kis, K. V., Posfai, M. & Labar, J. L.**, 2006. *Nanostructure of atmospheric soot particles*. Atmospheric Environment, 40, 5533–5542.
- Maher, B. A.**, 2009. *Rain and dust: magnetic records of climate and pollution*. Elements, 5, 229–234.
- Márton, E., Márton, P. & Zajzon, N.**, 2008. *Environmental magnetism – role of magnetic particles in the investigation of the state of the environment*. In Hungarian with english summary: (*Környezeti mágnesség – mágneses részecskék szerepe a környezet állapotának kutatásában*). Földtani Közlöny, 138(1), 97–106.
- Márton, E., Sipos, P., Zajzon, N., Szentmarjay, T., Lautner, P. & Pethe, M.**, 2013. *Magnetic monitoring, geochemical and mineralogical analysis of settled dust from North and Central Transdanubia, Hungary*. Central European Geology. Vol. 55/4, DOI:10.1556/CEuGeol.55.20124.3
- Mitchell, R. & Maher, B. A.**, 2009. *Evaluation and application of biomagnetic monitoring of traffic-derived particulate pollution*. Atmospheric Environment, 43, 2095–2103.
- Muxworthy, A. R., Schmidbauer, E. & Petersen, N.**, 2002. *Magnetic properties and Mössbauer spectra of urban atmospheric particulate matter: a case study from Munich, Germany*. Geophysical Journal International, 150, 558–570.
- Nowack, B. & Bucheli, T. D.**, 2007. *Occurrence, behavior and effects of nanoparticles in the environment*. Environmental Pollution, 150, 5–22.
- Raask, E.**, 1985. *Reactions of nonsilicate impurities in coal flames*. In: E. Raask (Ed.) *Mineral Impurities in Coal Combustion (Behavior, Problems and Remedial Measures)*. (pp. 85–102). Washington, New York, London. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo: Hemisphere Publishing Corporation.
- Selinus, O.**, 2005. *Essentials of medical geology*. London: Academic Press. 812 p.
- Shi, J.P., Khan, A. A. & Harrison, R. M.**, 1999. *Measurements of ultrafine particle concentration and size distribution in the urban atmosphere*. Science of the Total Environment, 235, 51–64.
- Szőnyi, M., Sagnotti, L. & Hirt, A. M.**, 2008. *A refined biomonitoring study of airborne particulate matter pollution in Rome, with magnetic measurements of Quercus Ilex tree leaves*. Geophysical Journal International, 173, 127–141.
- Zajzon, N., Márton, E., Sipos, P., Kristály, F., Németh, T., Kis-Kovács, V. & Weiszbürg, T. G.**, 2013. *Integrated mineralogical and magnetic study of magnetic airborne particles from potential pollution sources in industrial-urban environment*. Carpathian Journal of Earth and Environmental Sciences, 8(1), pp. 179–186.

Received at: 07. 05. 2013

Revised at: 12. 10. 2013

Accepted for publication at: 21. 10. 2013

Published online at: 28. 10. 2013