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INTEGRATED MINERALOGICAL AND MAGNETIC STUDY OF MAGNETIC AIRBORNE PARTICLES FROM POTENTIAL POLLUTION SOURCES IN INDUSTRIAL-URBAN ENVIRONMENT

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Abstract: Steel works, combustion of fossil fuel, and vehicles are the most important sources of magnetic particulate matter in the industrial-urban environment. These particles are easily detectable by magnetic measurements on the field. In this paper we present a multidisciplinary mineralogical and magnetic study on some samples directly or closely associated with their pollution sources. Detailed mineralogical investigations (XRD, SEM-EDX, WDX, ATEM) and special magnetic measurements (mass susceptibility, Curie-point, decay rate of the isothermal remanent magnetization in time, frequency dependence of the magnetic susceptibility) were carried out on representative samples. Magnetite was identified as the most important inorganic pollutant using magnetic and mineralogical methods. We found that it had no distinct chemical composition or morphological difference for the different sources, but the extremely small grains are primarily characteristic of traffic. The grain size of magnetite spherules showed decrease among the different sources with the following order: steel factories, combustion plants, traffic. The presence of magnetite as pollutant in the environment can be monitored more easily and cost-effectively by magnetic than mineralogical methods. Nevertheless, the magnetic methods should be combined with detailed mineralogical investigations on representative samples selected by their magnetic properties, in order to obtain full information about the pollutants, including non-magnetic constituents. Additionally, the role of different pollution sources have to be estimated by the complex analyses of the different grain sizes of the dust collected regularly for a long time.

Keywords. air pollution; total and mass susceptibility; magnetite spherules; different pollution sources; mineralogy of airborne particles

1. INTRODUCTION

Airborne particulate matter has been widely associated with health disorders as presented by numerous studies (Selinus, 2005). In urban environment, and especially in those areas where population, industrial activity and traffic density are relatively high, human exposure to such hazardous substances is expected to be significantly increased. In these environments, significant quantities of anthropogenic particulates may be released from fossil fuel combustion in domestic heating systems, smelting industries and vehicles (Shilton et al., 2005). Particles with sizes below 10 μm, and primarily those with submicrometer sizes, may cause the most intense health damage due to their easy penetration to the innermost regions of the lung system. Moreover, these particulates are often associated with potentially toxic trace transition metals such as Pb, Zn, Cu, Cr, Ni, Mo or Cd (Charlesworth & Lees, 1999).

Iron impurities are often found in combustibles and can convert to iron oxides, such as magnetite or hematite, depending of the burning conditions (Muxworthy et al., 2003) but they can be also related to the presence of ferrocene as fuel additive (Braun et al., 2006). Owing to this fact several studies have revealed large concentrations of iron in anthropogenic particulate matter (generally between 5 and 15%) and magnetite was identified as the dominant magnetic phase of Fe-rich particles (e.g., Chen et al., 2006).

Steel metallurgy, coal and biomass combustion are well known sources of such magnetite spherules (e.g. Biswas & Wu, 2005; Buseck & Adachi, 2008; Gieré & Querol, 2010; Maher, 2009; Nowack & Bucheli 2007). It is also well known that coal and biomass combustion plants create magnetite particles (Grobéty et al., 2010; Maher, 2009; Raask, 1985). Traffic pollution can be the most important source of combustion derived (magnetic) nanoparticles in urban areas (Cass et al., 2000; Harrison et al., 2000; Shi et al., 1999). So it is not unexpected that numerous studies found strong correlation between the degree of particulate matter pollution and their magnetic susceptibility (Halsall et al., 2008; Mitchell & Maher, 2009; Muxworthy et al., 2002; Szönyi et al., 2008), and the Fe oxides, because of their sensitivity for ambient conditions, can be used as a proxy for environmental pollution

The properties of magnetic particles, such as chemical composition, grain size and shape, identified in a given sample depend on the characteristics of fossil fuel used and the combustion conditions (Matzka & Maher, 1999). Variation in such characteristics of magnetic particles can be inferred through the use of specific magnetic and mineralogical analyses (Robertson et al., 2003). These kinds of information may help to understand the sources of contaminants to urban particulates, and to predict the pathway, mobility and impact of these contaminants in urban environment.

There are only a few studies dealing with mineralogical-geochemical characteristics of such particles and comparative studies between different sources of pollution are virtually absent. In this study, our aim was to characterize the mineralogical and chemical composition of combustion derived magnetic particles which may potentially occur in industrial urban environments. Particulate matter samples from steel metallurgy, coal combustion and vehicle exhaust were studied in details to find the mineralogical, chemical and magnetic similarities and differences of magnetic particulates deriving from these sources.

2. MATERIALS AND METHODS

The magnetite-producing pollution sources studied were the following (Fig. 1).

Figure 1. Location map of the investigated samples.

Settled dust samples were collected on monthly basis at the court of the Diósgyőr Steel Factory (Miskolc, Hungary) in the period of February 2005 – December 2008. An electric-arc-furnace (EAF) dust was investigated from the dump of the Ózd steel factory, Hungary, and another sample from the sludge reservoir of the Linz-Donawitz basic oxygen furnaces of the Dunaferr Ltd., Dunaújváros, Hungary in July 2008. Data of a mineralogical study of 39 surface samples from Bálvány Hill, Bükk Mts., Hungary, were also integrated into this paper. Magnetite spherules were found and were identified as products of the nearby steel factory at Ózd. Soil samples were also studied from the vicinity of the Orava Ferro-alloy Inc., Orava, Slovakia. Six coal combustion fly ash samples were collected from Kazincbarcika Power Plant, Hungary (July 2009), three from the electrostatic precipitator (ESP) and other three from Economizer zone (ECO ash). Two drill cores were also investigated from the fly ash dump of the coal combustion plant at Ajka, Hungary (June 2005, see in detail Bokányi et al., 2010). An exhaust gas filter (from a garage in Budapest, 2009) from a monitor instrument used for petrol fuelled car engines was also studied.

X-ray powder diffraction (XRD) analyses were made on a Bruker D8 Advance diffractometer (40 kV, 40 mA, CuKα radiation, parallel beam geometry) at the Institute of Mineralogy and Geology, University of Miskolc, Hungary and, for the Bálvány samples, on a Nonius Kappa CCD single crystal X-ray diffractometer (MoKα radiation, 300 mm capillary optic collimator, 2–3° rotation at 26–30 mm detector distance) at the Department of Mineralogy and

Crystallography, University of Vienna, Austria. Scanning electron microscopy (SEM) and microanalysis (both energy and wavelength dispersive; SEM-EDX, WDX) were performed on: JEOL JXA-8600 Superprobe (15 kV, 20nA) at the Institute of Mineralogy and Geology, University of Miskolc, Hungary, Cameca SX-100 (20 kV, 20 nA) at the Department for Lithospheric Research, University of Vienna, Austria, JEOL JSM-6400 (10–15 kV, 1–2 nA) at the Institute of Mineralogy and Crystallography, University of Vienna, Austria, AMRAY-1860T6 (25 kV, 1–2 nA) at the Department of Physical Metallurgy and Metalforming, University of Miskolc, Hungary, Hitachi S4800 SEM (20 kV, 10 μA) at the Institute for Nanotechnology, Bay Zoltán Foundation for Applied Research (BAY NANO), Miskolc, Hungary. Laser ablation inductive coupled plasma mass spectroscopy (LA-ICPMS) measurements on 19 magnetite spherules at the National Oceanography Centre, Southampton, UK was performed on a VG Elemental Plasma Quad 2+ mass spectrometer equipped with a 4D Engineering (Hannover, Germany) ablation system (30 μm diameter focused laser). Analytical transmission electron microscopy (ATEM) and selected area electron diffraction (SAED) were carried out in two laboratories. In the Institute of Technical Physics and Materials Sciences, HAS a Philips CM 20 TEM (LaB6 filament) equipped with a Noran EDX system (20 nm spot size, 100 s counting time) was used. For the ATEM and SAED analyses the samples were suspended in ethanol, and dropped onto holey carbon coated Cu grids for the analyses. Chemical composition was calculated estimating 20 nm sample thickness and an average density of 3 g/cm^3. The relative standard deviations of the EDX analyses are below 2.5%, 10% and 50% for element concentrations >10%, 1–10%, and <1%, respectively. We aimed to analyse only one discrete particle in each case, which could be confirmed from the corresponding diffraction pattern. The identification of the individual mineral phases was based on their diffraction pattern and chemical composition.

Analytical transmission electron microscopy (ATEM) measurements (TEM images, HRTEM – high resolution TEM images, SAED – selected area electron diffraction and EDX) of steel works dust trap samples from Ózd and Dunaújváros, Hungary were performed in the BAY NANO, on a FEI Tecnai G^2 transmission electron microscope (200 kV). The samples were prepared on lacey carbon coated 300 mesh copper grid.

Magnetic susceptibility measurements were carried out with a KLY-2 Kappabridge instrument. Each sample 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 or volume) and mass susceptibilities (total susceptibility divided by sample mass) were calculated for each filter. Samples 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 (Dearing, 1999).

3. RESULTS AND DISCUSSION

3.1. Potential sources of pollutants

3.1.1. Iron smelter / Steel works

In Miskolc (Fig. 1) we collected settled dust in the yard of the Diósgyőr Steel Factory. Both magnetic (Fig. 2) and mineralogical methods showed that the samples contained magnetite. The relatively large grain size (SEM) magnetite was present in high concentration (>10 wt%), estimated from the magnetic susceptibility (Márton et al., 2008).

We also found similarly large amount of magnetite spherules in soil samples collected in the neighbourhood of another steel works, Orava, Slovakia (Fig. 3), where the magnetite spherules were in the 10–100 μm size range (Kluciarova et al., 2008).

Dust from collection traps of steel works from Ózd and Dunaújváros (Fig. 1) were also investigated. The size distribution of these dust samples is strongly bimodal: 80 wt% of the dust is in the fine fraction (Dunaújváros: <2 μm, Ózd: <5 μm), where grains down to the 100 nm range are present. In the large size fraction the ca. 100 μm magnetite spherules are dominating. Some agglutinated grains, with size of 400–800 μm, built up of smaller spherules can also be found. The surface of the grains and their structure show strong similarities to the ones observed on the magnetite spherules in the dust from Miskolc. Based on XRD, EDX and ATEM measurements of the submicrometer size particles, the dominant phase is magnetite.

Sometimes the analysed spherules are pure magnetites, but often contain minor amounts of Zn, Mn, Ca, Cr, Mg, Al or Si. Zn and Mn are the far most common. It is only Zn which can be incorporated as continuous solid solution into magnetite (pure Fe-oxide) up to the other end member franklinite ($ZnFe_2O_4$). In the electric arc furnace (EAF) dust the spinel structure Fe and Zn oxides (sometimes with minor amount of Mn) are the far most common;

different chlorides and sulphates are present in minor amount only (Donald & Pickles 1996; Huber et al., 2000; Li & Tsai, 1993; Rocabois et al., 2000; Sofilic et al., 2005; Stegemann et al., 2000).

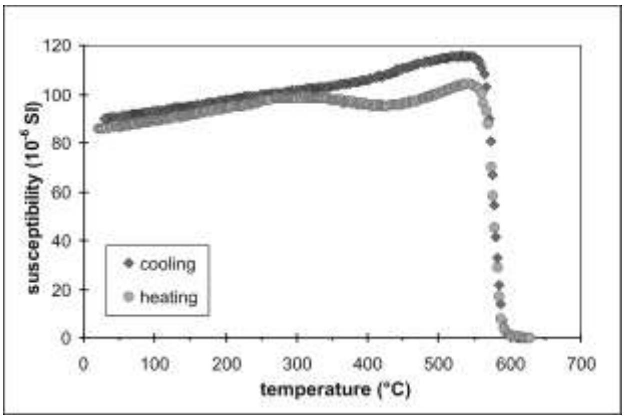

Figure 2. Susceptibility versus temperature curves, identifying the magnetic mineral from the Miskolc steel works as magnetite, since the susceptibility drops to zero at the Curie-point of the magnetite (580°C).

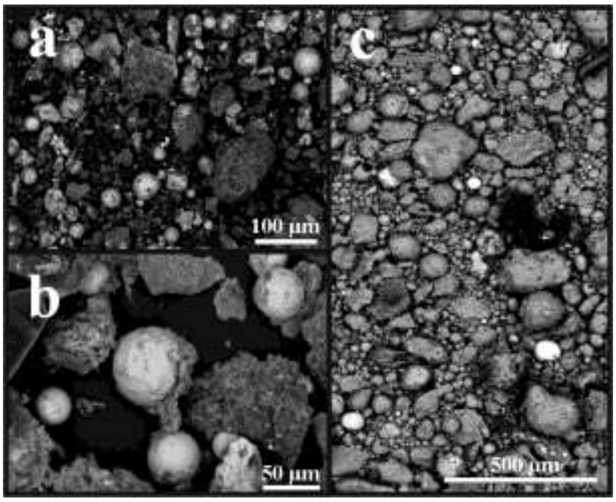

Figure 3. Magnetite spherules (bright grains) from different pollution sources: a) steel works, Orava; b) steel factory, Miskolc; c) coal combustion plant, Ajka. (Backscattered electron images.)

A common feature of the samples from the above industrial sources is the relatively high mass susceptibility and the practical absence of superparamagnetic grains, as indicated by susceptibility measurements at two frequencies. (The decrease of susceptibility at higher frequency was invariably less than 2% for all fractions from Ózd, while slightly exceeded 2 % for the finest grain size fraction in case of Dunaújváros).

Magnetite spherules were found as contaminants in geological samples from the Bálvány (Bükk Mts.) rural outcrop, located SE from the steel works Ózd, Hungary in a distance of about 15 km. They form solid balls or hollow spheres, completely round or droplet shape (Fig. 4). The grain size varies between 60–100 μm. (The <63 μm fraction was not studied.) Both completely smooth and skeletal crystal texture (built up of micrometer size octahedra) can be characteristic for the surface of the spherules. Any intermediate pattern can also be present.

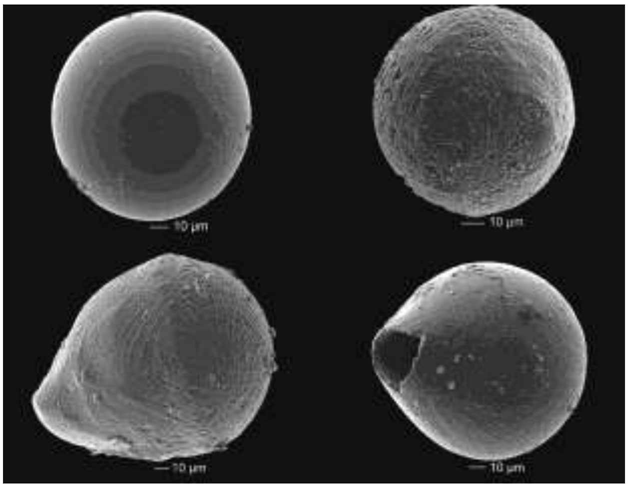

Figure 4. Round and droplet shape, solid or hollow magnetite spherules. Bálvány, Bükk Mts. Hungary. (Secondary electron images.)

According to 50 WDX analyses on polished surfaces of 39 Bálvány grains (Table 1), these iron oxide spherules are of 0.3-0.6 wt% MnO content. Their Fe content is characteristic of magnetite (falls between 89–91 wt%, expressed as FeO). Single crystal XRD measurement on individual spherules also identified them as polycrystalline magnetite. The WDX analyses show a continuous iron content decrease (from 91 wt% to 72 wt%, expressed in FeO), which means that the oxidation state of the iron increases. This further oxidation, compared to magnetite, is probably secondary, and took place during weathering in the outcrop, as the Si content increases together with Ca, Na, Mg and Ti. The PGE content of the Bálvány samples was below the detection limit of the LA-ICPMS used (ca. 1 ppm). Mineralogical similarities of the Bálvány grains indicate a common source for all of them, most probably the steel works nearby, at Ózd.

3.1.2. Coal combustion plants

Fly ash from two different Hungarian coal combustion plants, Ajka and Kazincbarcika (Fig. 1), were also investigated, where magnetite spherules () were present. The ash mainly consists of perfectly round or droplet shape silicate spherules, and less abundant magnetite spherules, several tens of μm in diameter (Fig. 3c). The compositions of the silicates show large variation, but the most common is a Ca-dominant Ca-Al-silicate.

Table 1. WDX analyses of the iron oxide spherules from Bálvány, Bükk Mts., Hungary*.

Grain ID:	FeO	SiO_2	MnO	Al_2O_3	Summ
4a	78.67	0.32	0.35	0.11	79.62
4b	89.14	0.04	0.43	0.07	89.69
11a	90.98	2.14	0.52	0.10	94.43
11b	88.38	0.02	0.39	1.96	90.83
23a	87.11	0.57	0.42	0.65	88.95
23b	87.24	1.04	0.36	0.62	89.42
29a	87.74	0.00	0.43	0.00	88.24
29b	89.20	0.06	0.40	0.02	89.81
32	87.68	0.96	0.61	0.01	89.33
33	89.39	0.12	0.38	0.14	90.17
35a	88.08	0.84	0.31	0.08	89.45
35b	88.34	0.24	0.31	0.04	88.98
36	72.33	2.80	0.00	0.00	75.82
37a	86.22	2.03	0.52	0.19	89.76
37b	86.66	1.17	0.51	0.16	88.96
69	83.56	2.45	0.28	1.98	89.84
82	88.62	0.34	0.31	0.23	89.64
83a	89.14	0.04	0.37	0.31	90.22
83b	89.10	0.03	0.36	0.31	90.13
88	89.16	0.17	0.39	0.06	89.86
96	89.21	0.23	0.36	0.08	90.00
98	84.04	3.48	0.41	1.60	90.05
99	86.27	2.12	0.40	0.80	90.08
100	87.87	0.27	0.62	0.06	88.94
102	88.71	0.03	0.40	0.08	89.33
107	87.76	1.13	0.41	0.03	89.47
108	89.27	0.01	0.56	0.03	90.01
109	87.93	1.45	0.41	0.10	90.01
110	89.00	0.46	0.54	0.00	90.19
132a	86.07	0.39	0.25	0.02	86.92
132b	88.28	0.32	0.37	0.01	89.10
135	88.69	0.69	0.39	0.05	89.86
136	88.43	0.23	0.44	0.13	89.36
137	89.16	0.08	0.32	0.02	89.65
138	85.51	0.06	0.41	3.38	89.58
139	88.18	0.10	0.37	0.48	89.29
165	89.31	0.07	0.34	0.01	89.82
167a	86.99	0.00	0.31	0.03	87.42
167b	88.61	0.00	0.41	0.04	89.22
168	87.67	0.80	0.34	0.12	89.32
180a	86.59	0.19	0.53	0.01	87.49
180b	87.51	0.20	0.56	0.01	88.43
181	88.01	0.29	0.31	0.35	89.13
182	88.69	0.17	0.34	0.08	89.38
183	88.83	0.13	0.38	0.03	89.48
185	89.34	0.02	0.23	0.03	89.71
186	88.98	0.37	0.46	0.03	89.99
187	87.93	0.23	0.36	0.70	89.36

****Elements measured:*** *Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni. All iron calculated as* Fe^{2+}*. Additional elements detected in grains indicated (wt%):* ***4a*** *Na_2O 0.11;* ***11a*** *Na_2O 0.47, CaO 0.12;* ***36*** *MgO 0.25, CaO 0.28;* ***37a*** *CaO 0.53, TiO_2 0.09;* ***37b*** *CaO 0.33;* ***69*** *MgO 0.23, CaO 1.17;* ***83a*** *TiO_2 0.19;* ***83b*** *TiO_2 0.23;* ***98*** *Na_2O 0.19, CaO 0.22;* ***99*** *CaO 0.30, TiO_2 0.09;* ***107*** *CaO 0.12;* ***108*** *Cr_2O_3 0.13;* ***168*** *MgO 0.14, CaO 0.17;* ***180a*** *Cr_2O_3 0.10;* ***180b*** *Cr_2O_3 0.09;* ***186*** *Cr_2O_3 0.10.*

Magnetite was most probably formed from pyrite, widespread in the coal. The iron impurity of a fuel, e.g. pyrite, oxidizes at high temperatures to wuestite (FeO), which becomes unstable during cooling (below 572°C), and further oxidizes to magnetite ($FeFe_2O_4$) or hematite (Fe_2O_3) (Maher, 2009; Raask, 1985). According to our observations, magnetite spherules formed during combustion has smaller maximum grain size, than those coming from iron and steel works.

3.1.3. Traffic

Vehicle engines (both diesel and spark-ignition) are well known sources of nanoparticles (Collings & Graskow 2000; Kittelson 1998; Woo et al., 2001). Magnetic particulate matter is supposed to be emitted primarily by tailpipe exhaust. About 90% of it is carbonaceous material (Cadle et al., 1999). Among the rest, iron oxides are common and they are often associated with potentially toxic metals, such as Cr and Pb (Maher et al., 2008). Additionally, Ca, Cu, Zn, P (and Ni, Ba, Cr) were detected (Sharma et al., 2005), but their host phases were identified only for diesel engines until now (Liati et al., 2012). These latter authors found Zn-Mg-phosphates, hematite, Ca-oxide, Zn-oxide, cordierite, Al-oxide, Ca-sulphate and Ti-oxide in such materials. However, there are still no data on non-carbonaceous phases in exhaust particulate matter of petrol fuelled vehicles. To evaluate the contribution of the traffic to the magnetic and metal pollution, one particulate material sample collected from a vehicle exhaust filter (for petrol fuelled cars only) was analysed by analytical electron microscopy for this study.

Soot aggregates of a few hundreds of nm size are the predominant components of this material, as it was expected. The size distribution of the individual nanospheres inside the aggregates depends on the source engine type, ranging between 10 and 60 nm of diameter (Su et al., 2004). The other components of vehicle exhaust dust are generally attached to the soot aggregates. Their size is also mostly in the few tens of nm range. Electron diffraction and EDX analyses showed that they are primarily various oxides, such as alumina, magnetite, hematite and perovskite-like Ca, Zr and Ce-oxides. Moreover, sulphates of Ba and Ca were also identified. Alumina nanocrystals may have formed during the ageing of the alumina-ceria washcoat of the catalytic converter (Twigg, 2007). In some cases they contain Ni (2 at%) and Zn (0.9 at%), which may also come from the catalyst's washcoat (Shelef & McCabe, 2000) or the engine oil and gasoline (Somayaji & Aswath, 2008). Hematite and magnetite occur mostly in close association to each other, however pure aggregates of both phases were also found (Fig. 5).

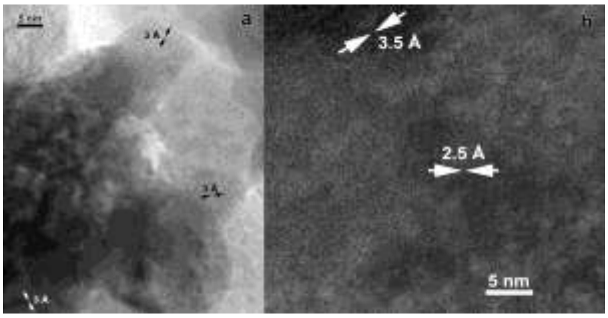

Figure 5. HRTEM images of vehicle exhaust gas aerosol: a) Aggregate of magnetite nanoparticles identified by the 220 fringes. b) An ultra thin iron oxide nanoparticle on the surface of soot. The measured d-value, 2.5 Å can be (110) hematite and (113) magnetite as well. The curved graphitic layers showing the typical 3.5 Å spacing are also seen.

They may be the result of the ageing of the steel and other alloy compounds of the engine followed by a stepwise oxidation on the one hand, and that of fuel combustion on the other (Filipelli et al., 2005). Abdul-Razzaq & Gautam (2001) also observed the common presence of the mixture of strongly magnetic (magnetite-like) and weakly magnetic (hematite-like) iron oxides in exhaust material of diesel engines. Some of the iron oxide particles may contain small amount of Pb (0.5 at%) and Zn (0.4 at%). Barium-sulphate (barite) can be the by-product of the NO_x reduction as sulphates originate from the gasoline or engine oil may react with BaO, the transition product of the NO_x reduction (Twigg, 2003). Oxides composed mostly of Ca, Zr and Ce showing perovskite-like structure may be the result of the abrasion of the washcoat (Ce_2O_3 stabilized by Ca) (Shelef & McCabe, 2000) and the air sensor (ZrO_2 stabilized by Ca) (Lee, 2003). They may contain Ni (3–3.5 at%) and Zn (0.2 at%), too. Calcium-phosphate, often of significant (up to 10–15 at%) Zn content, probably originates from the zinc-dialkyl-dithiophosphate used as antiwear additive in the engine oil (Somayaji & Aswath, 2008).

The magnetite identified in the vehicle exhaust dust (Fig. 5) could be responsible for the magnetic signal of the sample. Low amounts of potentially toxic metals (such as Pb and Zn) may be also incorporated in its structure. Filipelli et al., (2005) found strong correlation between magnetic signal, Fe and Pb in urban environment. They suggested that these components (magnetic particles and Pb) have the same source, which is most likely the fuel combustion. However, our data show that other vehicle dust components (such oxides and phosphates) enrich Zn and Ni in much higher amounts. Moreover, the presence of Zn as major component in several phases (oxides or phosphates) can not be excluded either, by analogy of particulate matter compounds from diesel engines.

In contrast to the above discussed industrial sources, the car exhaust filter contains tiny magnetite grains, close to the superparamagnetic threshold, as suggested by the isothermal remanent magnetization (IRM) acquisition curves (Fig. 6). The IRM acquisition characteristics are indicating the presence of magnetite, and the re-measured remanence values after the acquisition at regular intervals point to sizable contribution of small grains close to the superparamagnetic range (0.03 μm).

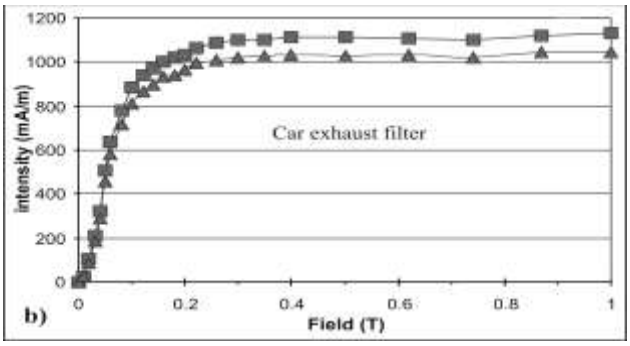

Figure 6. IRM (isothermal remanent magnetism) aquisition curves for a car exhaust filter. Squares (upper curve) measured immediately after magnetization and triangles (lower curve) with the elapse of 30 minutes.

4. CONCLUSION

We investigated different sources emitting magnetic pollutants and found that the dominant iron containing phase was always magnetite. No significant chemical or morphological differences were found among the magnetite spherules produced by different sources. However, the grain size of the magnetite spherules showed a variation depending on the different sources, grain size decreased in the following order: steel factories, combustion plants, traffic.

The presence of magnetite as pollutant in the environment can be monitored more easily and cost-effectively by magnetic than with mineralogical methods. It is also possible to detect and estimate the contribution of tiny magnetic grains, in or close to the superparamagnetic range by measuring the magnetic susceptibility at different frequencies or making isothermal remanent magnetization experiments.

Nevertheless, the magnetic methods should be combined with detailed mineralogical investigations on representative samples selected by their magnetic properties, in order to obtain full information about the pollutants, including non-magnetic constituents.

Anthropogenic dust in urban areas comes usually from different sources. Our study reinforces the need to treat the pollution problem as a complex one. This means that in order to estimate the role of different sources of pollution we have to analyze dust of different grain sizes collected regularly during a long time, possibly on daily basis, during different seasons and weather conditions.

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