The vehicle braking systems as main source of inhalable airborne magnetite particles in trafficked areas

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ABSTRACT

Magnetite (Fe_3O_4) nano-particles (MNPs) have been found in human tissues and causally linked to serious illnesses. The possible negative role of MNPs has been not still fully ascertained even though MNPs might cause health effects due to their magnetic property, redox activity and surface charge. The origin of MNPs in human tissues still remains to be unambiguously identified since biological processes, natural phenomena and anthropogenic production have been proposed. According to this latter increasingly convincing hypothesis, anthropogenic MNPs might enter mainly in the human body via inhalation, penetrate deeply into the lungs and in the alveoli and also migrate into the blood circulation and gather in the extrapulmonary organs and central nervous system. In order to identify the releasing source of the potentially inhalable MNPs, we pioneered an innovative approach to rapidly investigate elemental profile and morphology of a large number of airborne micron and submicron-sized Fe-bearing particles (FePs). The study was performed by collecting a large amount of micron and sub-micron sized inhalable airborne FePs in trafficked and densely frequented areas of Rome (Italy). Then, we have investigated individually the elemental profile and morphology of the collected particles by means of high-spatial resolution scanning electron microscopy, energy dispersive spectroscopy and an automated software purposely developed for the metal-bearing particles analysis. On the basis of specific elemental tracing features, the investigation reveals that almost the total amount of the airborne FePs is released by the vehicle braking systems mainly in the form of magnetite. Furthermore, we point out that our approach might be more generally used to identify the releasing sources of different inorganic airborne particles and to contribute to establish more accurately the impact of specific natural or anthropogenic particles on the environment and human health.

1. Introduction

In recent years, magnetite (Fe_3O_4) nanoparticles (MNPs) have been found in a variety of human organs and an association between presence of MNPS in the brain and incidence of Alzheimer's and Parkinson's disease has been found. Furthermore, a high concentration of Fe has been also associated to inflammatory reactions. The presence of MNPs has been also causally linked with potential cellular responses to external magnetic fields generated by electronic devices and also with ageing phenomena because the β-amyloid associated with Fe (II) ions contributes to oxidative brain damage. MNPs might induce other deleterious effects on human health as respiratory and cardiovascular diseases being potentially biochemically reactive due to their unique combination of high redox activity, surface charge and strongly magnetic behaviour (Ghio et al., 1998; Dobson, 2002; Hautot, et al., 2003; Oberdörster et al., 2004; Calderón-Garcidueñas et al., 2004; Miller et al., 2017; Ghio et al., 2007; Allsop et al., 2008; Collingwood et al., 2006; Castellani et al., 2007; Pirjola et al., 2009; Tabner et al., 2011; Kumar et al., 2013; Kumar et al., 2016; Power et al. 2016; Plascencia-Villa et al. 2016; Struckmeier et al., 2016; Maher et al., 2016; Gieré, 2016; Chen et al., 2017; Maher, 2019; Gonet and Maher, 2019; Maher et al., 2020; Winkler et al., 2020; Gonet et al., 2021a; Gonet et al., 2021b).

The origin of the MNPs found in human tissues is still subject of ongoing researches; possible investigated sources include biological processes, natural phenomena and anthropogenic activities (Sanders et al., 2003; Majestic et al., 2009; Gieré and Querol, 2010; Kumar et al., 2013; Maher et al., 2016; Gieré, 2016; Maher et al., 2016; Struckmeier et al., 2016; Hofman et al., 2017; Gonet and Maher, 2019). The anthropogenic origin of MNPs is increasingly convincing being supported by many studies some of which have proposed that anthropogenic MNPs can arise as combustion-derived Fe-rich particles as well as can be released by different sources including industrial processes or human activities (Johansson and Johansson, 2003; Majestic et al., 2009; Gieré and Querol, 2010; Hansard et al., 2011; Petrovský et al., 2013; Gieré, 2016; Struckmeier et al., 2016; Funari et al., 2018; Maher, 2019; Gonet and Maher, 2019; Maher et al., 2020; Winkler et al., 2020; Gonet et al., 2021a).

Among these potential sources, the non-exhaust vehicle emissions have been proposed some years ago due to the correlation between NO_x concentration and magnetic moment of the urban atmospheric particulate matter (PM) (Sagnotti et al., 2006; Sagnotti et al., 2009; Saragnese et al., 2011; Sagnotti and Winkler, 2012).

The presence in the human tissues of anthropogenic MNPs is worthy of concern due to their possibility of entering into the human body via the respiratory system by inhalation. Along this way, airborne micron- and sub-micron sized magnetite particles can penetrate deeply into the lungs and in the alveoli. The fine and ultra-fine particle can also migrate and gather into the blood circulation, extrapulmonary organs and central nervous system and can be deposited there for a long time potentially causing adverse health effects (Kirschvink et al., 1992; Englert, 2004; Oberdörster et al., 2004; Riediker et al., 2004a; Riediker et al., 2004b; Brunekreef and Forsberg, 2005; Pankhurst et al., 2008; Brook et al., 2010; Guxens and Sunyer, 2012; Barošová et al., 2015; Plascencia-Villa et al., 2016; Gieré, 2016; Maher et al 2016; Kumar et al., 2016; Calderón-Garcidueñas et al., 2019). At present the role played by the MNPs on human health is still poorly understood, and further, the anthropogenic sources that emit inhalable magnetite micron and sub-micron sized particles have been not still unambiguously identified.

In the light of the above information, we have pioneered a tailored approach aimed to acquire rapidly, individually and thoroughly information on elemental profile and morphology of a large number of inhalable Fe-bearing micro and nano-sized airborne particles (FePs) collected in trafficked and densely frequented areas. More specifically, we felt the need of a detailed elemental and morphological investigation concerning a large amount of potentially inhalable FePs to determine unambiguously their nature and emitting source.

The method we adopted is based on the combined use of high-spatial resolution scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and an automated software purposely developed for the metal-bearing particles analysis.

In order to achieve a detailed elemental and morphological knowledge, we have first collected the inhalable airborne PM_{10} at outdoor trafficked areas in Rome (Italy) and neighbouring sites. The sampling sites were selected on the basis of the high density of vehicular traffic and braking events because epidemiological investigations have revealed an association between some forms of cognitive decline and exposure to vehicle-produced PM and also between incidence of dementias and living in proximity to major roads (Thorpe et al., 2007; Gietl et al., 2010; Ranft et al., 2009; Hofman et al., 2017, Chen et al., 2017; Gonet and Maher, 2019; Winkler et al., 2020). Then, we have studied in details the morphology and the elemental profile of a large number of Fe-bearing micron and sub-micron sized particles (FePs) paying a particular attention to distinctive and peculiar elemental tracing features capable of disclosing the FePs origin.

We point out that this approach can be successfully extended also to other metal-bearing or inorganic particles. In this way it could be possible to achieve a wide panorama of information more relevant to human health than other less specific parameters since the particles

elemental profile might be directly associated to the releasing source and to specific health effects (Hofman et al., 2017). Furthermore, the identification of the emitting source could allow to hinder the emission of specific particles into the atmosphere in a targeted way thus avoiding harmful environmental and occupational exposure with a risk for human health.

2. Materials and methods

2.1. Sampling sites

The sampling of the inhalable PM_{10} was carried out at the six outdoors locations listed in Table 1. In the vicinity of these sites, there are not present FePs industrial plants or metalworking factories. Further, iron ore outcrops are not present at a distance of no<250 km. Three sites are located in the city of Rome (Italy, ca 4.3 millions inhabitants): near the entrance of a large city park (villa Ada, ADA) close to a high traffic street and two urban sites characterised by an intense vehicular traffic (corso Francia and Montezemolo square, FRA and MZ, respectively). Furthermore, the intercontinental airport "Leonardo da Vinci" (FIU) and the international Ciampino airport (CIA), located at a distance of about 30 and 20 km from the city centre, respectively, were also included in this study as trafficked areas. The sixth sampling site is the rural context of Montelibretti (ML) located at 30 km North East (NE) from Rome and often impacted by pollutants transported from Rome by the sea-breeze circulation (Brines et al., 2015).

2.2. Sampling methods

The collection of the inhalable PM_{10} has been carried out by using the filtering systems adopted for the air quality monitoring and long-term assessment of pollutant levels in urban areas (see Figure S1).

The airborne particulate matter was collected on 47 mm diameter filters. Both quartz and Teflon (polytetrafluoroethylene, PTFE, 2 μm pore size) fiber filters were used, purchased from Whatman (UK) and PALL (USA), respectively (see Figure S1). All filters were kept in a clean room with environmentally controlled temperature and humidity for 24 h prior to weighing. Weighing was carried out with an electronic microbalance (Sartorius M5P 000 V001) with a sensitivity of ± 1 μg and a capacity in the range of 500 mg. The 24-h PM sampling was performed by using an automatic outdoor station for continuous atmospheric PM_{10} monitoring with the sequential substitution system of 16 filtering membranes [Tecora Skypost PM HV purchased by Tecora (France) and certified by TUV in accordance with the EN 12341 Council Directive

Table 1

Number of investigated micron- and sub-micron-sized particles containing a predominant or a significant amount of Fe and estimation of the daily transiting vehicles (Monday-Friday) for each sampling site. The comparison between the total number of airborne Fe-bearing particles and the number of Fe-bearing particles produced by braking systems (FePs-BS), second and third column, respectively, reveals that the brake Fe-bearing particles are widely present in the entire population of the Fe-bearing particles and allows to precisely quantify the presence of the FePs-BS. The sampling procedure was carried out also in other periods and as regards the aim of the work, no significant variation in the elemental chemical profile of the Fe-bearing particles was observed.

Locus of sampling*	Total investigated Fe-bearing particles	Fe-bearing particles identified as produced by brake systems	Estimation of daily transiting vehicles
ADA-W	1173	1084	12,000–20,000
FRA-S	1668	1482	18,000–30,000
MZ-W	2451	2301	10,000–18,000
FIU-W	1311	1204	15,000–25,000
CIA-2-A	1396	1316	12,000–18,000
ML-W	153	143	< 1,000

*W winter, A autumn, S summer.

1999/30/EC (Kosztowniak et al., 2016)]. The flow rate was set at of 2.3 $m^3 h^{-1}$ according to EN 12,341 standard method. Before the field campaign we tested the accuracy of the instrument by a reference calibrator (Flowcal Air, Tecora). A simultaneous sampling was carried out with a multi-stage impactor (DLPI, DEKATI Ltd) at 10 l/min obtaining a series of particle samples on Teflon filters with different equivalent aerodynamic diameters. These samples were analysed by acid-digestion with HNO_3/H_2O_2 and analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Canepari et al., 2006a; Canepari et al. 2006b, Canepari et al., 2008). It is worth noting that X-ray fluorescence spectroscopy (XRF) technique could be used also *in situ* via a portable apparatus to achieve preliminary elemental information (Angelini et al., 2006; Niu et al., 2010).

Automotive brake dust was collected to carry out an elemental and morphological particle comparative study. The particulate matter was sampled in a car multi-brand maintenance and repair workshop from vehicles produced by well-known European manufacturers and the collected samples can be considered representative of a wide range of the vehicles currently circulating in Europe. The sampling of the particulate brake dust was performed using a suitable super smooth, high purity and double faces adhesive carbon tape with a thick conductive adhesive face on both sides able to efficiently collect the PM from the braking systems of light-duty vehicles. These carbon tapes are commonly used for scanning electron microscopy and EDS investigations including the micron- and sub-micron-sized powders characterisation and are indispensable for SEM specimen preparation and mounting (Ingo and Padeletti, 1994; Ingo et al., 2001). The adhesive carbon tape allows quick sample mounting and ensures the conductivity needed for SEM studies as well as the fine powder collection (Ingo et al., 2004). In particular, we have used an adhesive surface of about 4 cm^2 in order to collect efficiently as much as possible every micron and sub-micron-sized particles including also the smallest ones to achieve exhaustive information.

2.3. FESEM-EDS investigation

The elemental profile and the morphology of the collected PM have been investigated by means of high-spatial resolution field emission scanning electron microscopy (FESEM) combined with energy dispersive X-ray spectroscopy (EDS). The measurements were carried out by using a LEO 1530 FESEM microscope, capable of resolution in the 1–5 nm size range, equipped with an INCA 450 energy-dispersive X-ray spectrometer and four-sector back-scattered electron detectors (BSE). Before the analysis, the filter surfaces were coated with a thin carbon film with a uniform thickness of few nanometers in order to avoid charging effects induced on the sample by the electron beam. The C coating was deposited by using a Bal-Tech SCD 500 equipped with turbo pumping for ultra clean preparations at a pressure of 5x10^{-3} mbar.

The FESEM-EDS investigation of the PM on the fiber filters has been planned and carried out by using the INCAGSR software produced by Oxford Instruments (INCAGSR, 2012). We point out that this is the first time that this approach using the INCAGSR software is adopted for the analysis of a large number of environmental particles while is currently used by law enforcement authorities for the detection and elemental analysis of gun shot residues (GSRs) metal-bearing particles. Indeed, the INCAGSR system complies the ASTME1588-Standard Practice for Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectrometry. The INCAGSR software is routinely world-wide adopted by important law enforcement Agencies to reliably identify the author/s of a crime beyond any reasonable doubt via the identification of the elemental profile of the metal-bearing GSRs particles. More in general, this software can be applied to detect metal-containing and inorganic particles due to its a large flexibility to follow specific investigation requirements and to categorise them according to their elemental profile.

The INCAGSR software allows to define the detection criteria and the

analysis parameters as well as the areas to be analysed storing also the position of the micron and sub-micron-sized particles to be traced again for subsequent investigations. The particle detection software uses the minimum possible time by using also some reference standards (Mn-Rh, C, Co, Rh, Au) for optimising the back scattered detector configuration. It is worth noting that the particle elemental profile is identified automatically as commonly performed by the EDS software. Furthermore, it is possible the reprocessing and the reclassification of collected information by automatically relocating the selected particle under the FESEM electron beam.

On the basis of the identification of the elements present in the EDS spectrum the INCAGSR software uses classification schemes already available or other ones previously defined or modified by the user to categorise the particles. This latter is carried out automatically during the analysis on the basis of the elemental profile and the criteria selected by the user.

For what concerns the reliability of the achieved data, certified standards are periodically used to verify if the system is correctly working by also ensuring that the stage and the SEM electron beam are properly calibrated. Different commercially available standards purposely designed for the validation of automated particle analysis can be employed as that we have used, i.e. the synthetic particle specimen SPS 521C produced by Plano W. Plannet GmbH, Wetzlar (Brożek-Mucha, 2007). This standard sample consists of 43 randomly distributed PbSb particles on silicon wafer of known positions and the following approximately sizes: 6 µm, 2.5 µm and 1.2 µm in diameter. The standard also contains additional well defined particles of Pb, Cu and Fe.

From an experimental point of view, the investigation was carried out in two steps in sequence. The first one has allowed to automatically localise the particles on the filter and to achieve preliminary information on their elemental profile. This first step has provided a rapid screening of a very large number of particles and was carried out by selecting an acceleration voltage of 20 kV to minimise the potential misleading effects due to the presence of low atomic number materials. Subsequently, all the particles with a significant content of Fe were retraced and individually examined to precisely identify their elemental profile and morphological features.

In this second step, the elemental profile of the metal-bearing particles was determined by selecting an acceleration voltage of 20 kV while the morphological features were investigated at different acceleration voltages up to 20 kV often also in secondary electron (SE) mode. The metal-bearing particles have been searched by the INCAGSR software by analysing micron by micron a rectangular frame of the filter ranging from about 0.6×0.6 cm to 1.0×1.0 cm. The total analysis time for the first evaluation varied between 8 and 32 h for each sample.

As below described in more detail, the classification of the airborne Fe-bearing PM as particles mainly originated from brake pads abrasion has been proposed on the basis of the elemental profile revealed by the EDS spectra that show a significant amount of Fe generally associated to Ba and S, sometimes also to Sb and more rarely to Cu and Zn even though the presence of the latter element could be originated also from tyre wear and not only from the pads (Garg et al., 2000; Sternbeck et al., 2002; Ingo et al., 2004; von Uexküll et al., 2005; Varrica et al., 2013; Hulskotte et al., 2014; Österle et al., 2014).

2.4. X-ray diffraction

X-ray diffraction patterns were recorded directly on the adhesive carbon tapes with brake dust by a Siemens 5000 X-ray powder diffractometer by operating in the Bragg-Brentano geometry and by using Ni-filtered Cu K$_\alpha$ radiation ($\lambda = 0.154056$ nm) by using the following experimental conditions: angular values between 10° and 90° in additive mode with a step size of 0.05° and a sampling time of 10 s. X-ray diffraction patterns were interpreted by using electronic databases (ICDD PDF-2 of the International Centre for Diffraction Data, ICDD) and compared with literature data.

3. Results and discussion

Table 1 lists the sampling sites and the number of the investigated micron and e sub-micron sized Fe-bearing filter-collected particles, first and second column, respectively. The third column of Table 1 shows the number of the Fe-bearing particles (FEPs) identified as produced by brake systems. In Fig. 1 some representative BSE FESEM images and EDS spectra of the FePs are shown.

The EDS and FESEM findings allow to evaluate in details the chemical and the structural features of the potentially inhalable FePs revealing that they are actually often constituted by complex agglomerates of micron, sub-micron and nano-particles. These latter display a dominant quite rounded morphology, rarely spherical, with diameters ranging from a few tens to several hundreds of nm and a different elemental composition sometimes complex. It is worth mentioning that the spherical particles could indicate a combustion source (Maher et al., 2016, Gonet and Maher, 2019). Other PM_{10} chemical information can be also determined via ICP-MS as the PM_{10} elemental content of metals as a function of the particle size; an example of the achieved results is given in the Figure S2 of the supplementary materials (Canepari et al., 2008). Furthermore, in Table S1 the typical particles size range distribution of some relevant elements and the total mass concentration for PM_{10} sampled in the urban sites is shown. Furthermore, in Figure S3 the total mass concentration of particulate matter by size range is reported. However, it is worth noting that the latter methodological approach is unable to distinguish between different chemical species and does not allow to investigate individually the single particle elemental features and to determine their emitting source as it is possible in some cases via EDS characterisation.

As shown in Fig. 1 and Table 1, the study of the collected micron and sub-micron sized Fe-bearing particles has revealed that almost the total amount of them (about 90%) is characterised by a chemically complex elemental profile prevalently characterised by the consistent presence of Fe associated with some peculiar elements such as Ba, S and sometimes Sb and more rarely with other metals such as Cu and Zn. The other Fe-bearing particles, about 10 %, contain mostly also variable amounts of crustal elements such as Si, Al, Ca, K Cl. These particles could be likely considered re-suspended particles, i.e. the PM deposited at the roadside, contaminated by soil components and resuspended by the traffic-induced turbulence and the action of the wind. The remaining Fe-bearing particles are a minimal fraction and are constituted by Fe-based alloys with Ni and Cr (likely from the abrasion of stainless steel) thus demonstrating that airborne inhalable micro and sub-micron-sized Fe-bearing particles may result from a variety of sources (Chaparro et al., 2010; Gonet and Maher, 2019). Few rare other metal-bearing particles show a predominant presence of Sn, Cu, Au and Pb with also a low presence of Fe (not shown results).

The contemporaneous presence of Fe, Ba, S and sometimes of Sb, as observed in the inhalable filter-collected PM_{10}, is generally found only in the brake dust being these elements present in the materials which form the brake pads (see Figure S4). Their presence allows to classify these particles as produced by braking events (Garg et al., 2000; Sternbeck et al., 2002; Ingo et al., 2004; von Uexküll et al., 2005; Varrica et al., 2013; Hulskotte et al., 2014; Amato et al., 2014; Flores-Rangel et al., 2015; Grigoratos and Martini, 2015; Beddows et al., 2016; Brines et al., 2015). It is worth noting that the size of the filter-collected particles is in good agreement with the results reported by Garg et al. whose investigations have revealed that 63 % of the airborne PM emitted from brake systems is smaller than 2.5 μm in diameter ($PM_{2.5}$) and a significant fraction is about < 0.1–0.2 μm or smaller (Garg et al., 2000; Gonet et al., 2021a; Gonet et al., 2021b).

These results are also in good agreement with previous characterisations of filter-collected PM carried out in different cities including Rome (Italy) (Canepari et al., 2008, Grigoratos and Martini, 2015; Brines et al., 2015). Indeed, at MZ and ADA sampling sites in Rome (Italy) it has been observed a Fe concentration of 1027 and 394 ng·m^{-3} on a total

PM_{10} mass of 36.1 and 23.3 μg·m^{-3}, respectively with a content of Fe in the airborne PM_{10} of about 3 % in weight. At the same sites, the content of Ba was 24.26 and 10.10 ng·m^{-3} and the amount of Sb was 11.77 and 13.25 ng·m^{-3}, respectively. The content of other possible anthropogenic elements such as Cu was 72.4 ng·m^{-3} and 24.8 ng·m^{-3}, Pb about 13.25 ng·m^{-3} and 9 ng·m^{-3} and Sn 6.64 ng·m^{-3} and 2.74 ng·m^{-3}, at the MZ and ADA sites, respectively (Canepari et al., 2008). The size distribution of the total PM_{10} mass collected at the urban sampling sites is similar to that observed by Brines et al. and Canepari et al. ranging from 14 to 20 μg·m^{-3} for the $PM_{2.5}$, from 12 to 26 μg·m^{-3} for the PM_1 and from 9000 to 11,000 particles·cm^{-3} for the $PM_{(10-360\ nm)}$ (Canepari et al., 2008; Brines et al., 2015).

These findings are also in good agreement with the findings of Paoletti and co-workers who reported that Fe-rich particles can constitute up to 8 % of coarse PM at ground level in the city of Rome, thus unravelling the large amount of the inhalable Fe-bearing particles present in a urban atmosphere (Paoletti et al., 2003; Paoletti et al., 2012).

In general, it can be affirmed that the results achieved adopting our approach combined with the measured amount of Fe in the PM_{10} allows to estimate the effective and consistent emission of Fe-bearing inhalable particles by braking systems and could permit a more accurate evaluation of the role of anthropogenic Fe-bearing particles on human health.

As above mentioned, with regards to the identification of the sources of the airborne inhalable Fe-bearing particles, this subject has been investigated in the last years and it has been ascribed to natural and crustal degradation or to generic anthropogenic Fe-emitting activities such as wood/coal/biomass burning, slag and smelting processes, cement production, steelworks, welding fumes, laser printing, waste incineration and traffic including underground, rail and tram systems (Johansson and Johansson, 2003; Rodriguez-Espinosa et al., 2007; Pratesi et al., 2007; Adamo et al., 2008; Sowards et al., 2008; Kukutschova et al., 2009; Morawska et al., 2009; Lamberg et al., 2011; Kukutschova et al., 2011; Kumar et al., 2013; Moreno et al., 2015; Rovelli et al., 2017; Gonet and Maher, 2019; Winkler et al., 2020; Gonet et al., 2021b).

In a SEM-EDS study of PM collected close to the city of Oporto (Portugal), Slezakova and co-workers reported that, in traffic sampling sites, Fe constituted 70% of $PM_{2.5}$ and 20% of $PM_{(2.5-10)}$ and suggested that Fe-rich particles could be related to vehicle emissions (Slezakova et al., 2008). Also the presence of Sb has been observed close to the major roads thus suggesting that this element derives from brake linings wear (Garg et al., 2000; Sternbeck et al., 2002; Plumlee et al. 2006; Gietl et al., 2010; Harrison et al., 2011; Hulskotte et al., 2014; Grigoratos and Martini, 2015; Gonet et al., 2021b).

Concerning the significant content of S in several airborne Fe-rich particles, this presence was differently attributed to metallurgical industries or to the combustion of low quality carbon or other generic anthropogenic or natural processes (Xie et al., 2005; Malandrino et al., 2016; Mazziotti Tagliani et al., 2017). Pipal and co-workers have proposed that the trace of S in airborne particles might be caused by gas to particles conversion processes during transport (Pipal et al., 2011; Pipal et al., 2014).

Apart from these hypotheses, other authors have suggested that metal-bearing particles could be related to the vehicle non exhaust emissions (Garg et al., 2000; Sternbeck et al., 2002; Sagnotti et al., 2006; Majestic et al. 2009; Sagnotti et al., 2009; Sagnotti et al., 2012; Harrison et al., 2012; Weinbruch et al., 2014; Valotto et al., 2015; Beddows et al., 2016; Gonet and Maher, 2019; Winkler et al. 2020; Gonet et al., 2021b).

Indeed, Winkler and co-workers have studied the particulate matter present on the lichen *Evernia prunastri* (very sensitive bioindicators of air pollution) exposed for 3 months in Milan (Italy) and have revealed that brake abrasion from vehicles is the main source of the airborne metal-bearing particles accumulated by lichens.

Our investigation confirms that the wear of brake pads and iron discs is a relevant source of inhalable micro and nano Fe-bearing particles, highlighting the relevance of the abrasion of brake system components
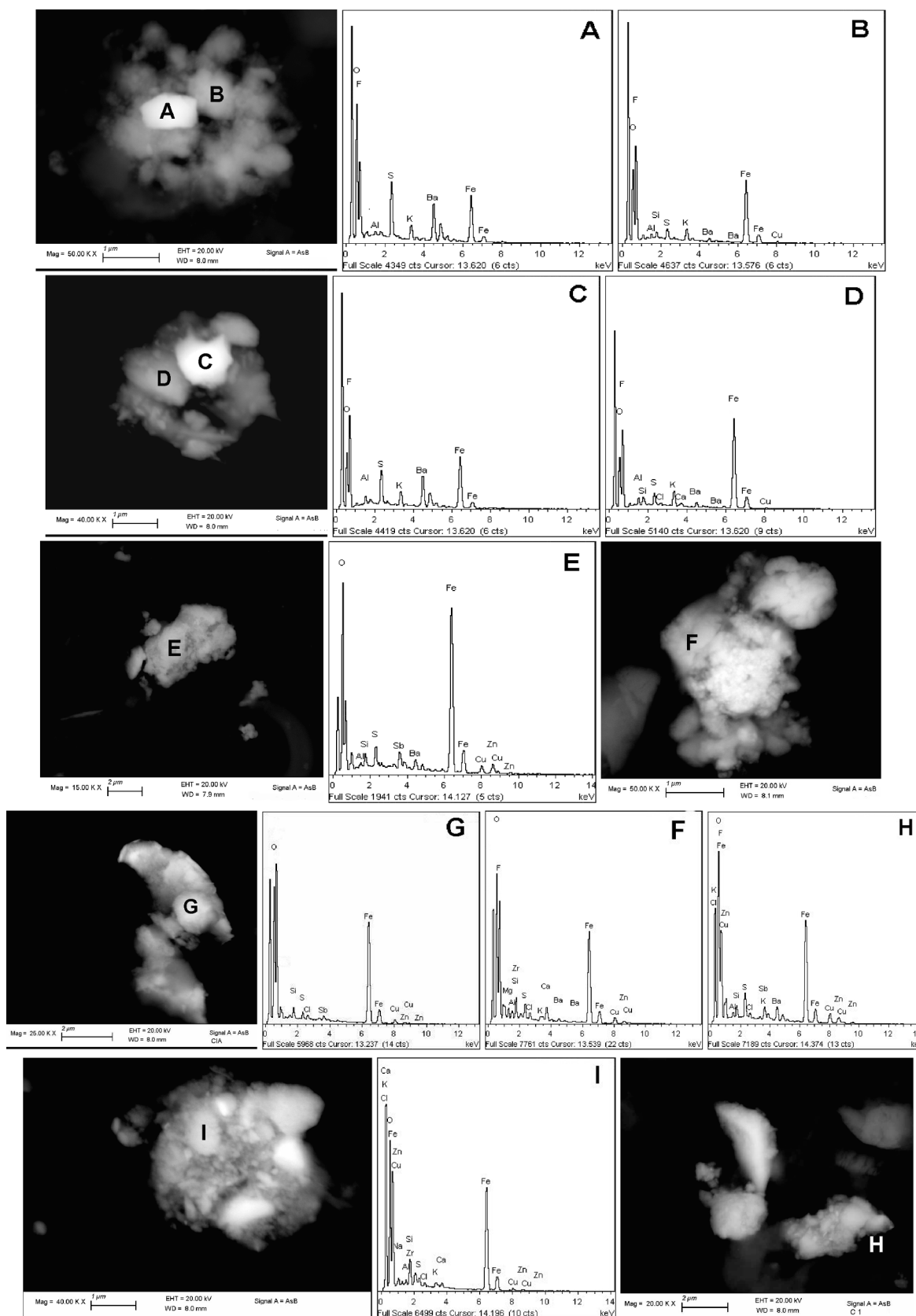
Fig. 1. Representative BSE FESEM images and EDS spectra of the airborne Fe-bearing particles that can be inhaled in trafficked areas. The micrographs reveal that the Fe-bearing particles are mainly constituted by agglomerates of micron and nano-sized particles containing elements typically present in the brake constituents. The EDS fluorine signal is due to the use of the Teflon filters.

as significant process releasing airborne inhalable Fe-bearing PM.

The significant amount of Fe in the airborne collected particles is mainly related to its presence in the cast iron discs and brake pads, indeed, according to its own formulations, some producers add micrometric magnetite (Fe_3O_4) powder finely ground as a lubricant and filler. The presence of some peculiar elements such as Ba, S and Sb is while related to the use of barite ($BaSO_4$) and stibnite (Sb_2S_3) as highlighted by the FESEM_EDS results shown in Figure S4, where a typical
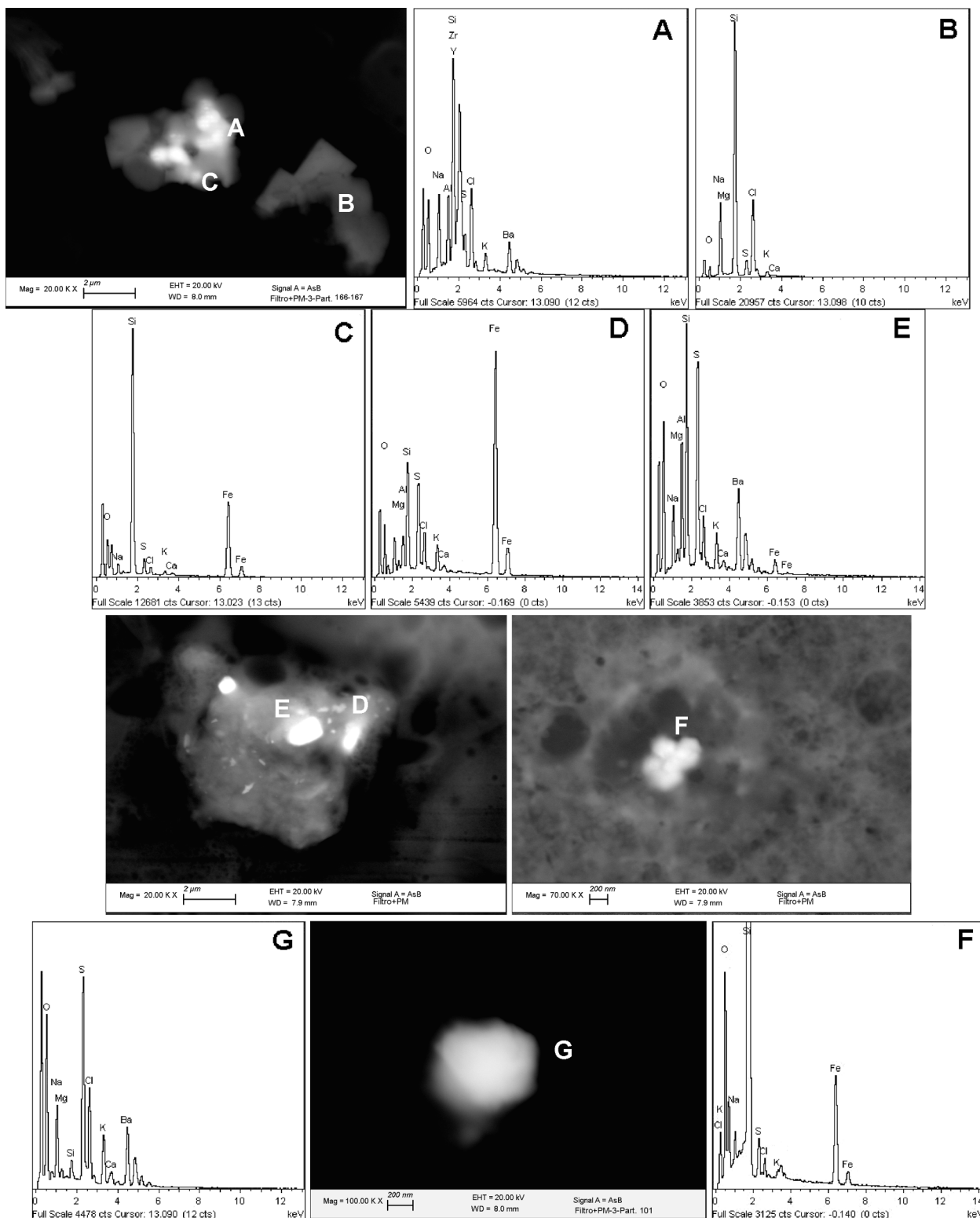

Fig. 2. FESEM images and EDS spectra showing elemental profile and morphology of the micron and nano-sized particles after leaching the filters with the collected airborne inhalable PM_{10} by using a solution mimicking the lung deep interstitial fluid (Mazziotti Tagliani et al., 2017) The EDS signal of Si is related to the substrate, i.e. $Si_{(100)}$, where the drop of solution was placed and dried, the signals of Na, K, Cl, S, Ca could be related also to the solution mimicking the lung deep interstitial fluid, the crystals whose EDS spectrum is labelled B are originated by this latter solution.

micro-chemical structure of a brake pad is shown.

Despite brake pads vary considerably in terms of formulation and amounts of constituting materials and can contain many different and sometimes unknown compounds, barite is largely used as filler and solid lubricant materials (up to about 7% by weight) while stibnite is added less frequently to reduce vibrations and excessive wear in the high-load as well as to improve the friction stability. (Garg et al., 2000; Sternbeck et al., 2002; Chan and Stachowiak, 2004; Ingo et al., 2004; Furuta et al., 2005; von Uexküll et al., 2005; Kukutschová et al., 2011; Varrica et al., 2013; Hulskotte et al., 2014; Österle et al., 2014; Grigoratos and Martini, 2015; Gonet and Maher, 2019).

We have estimated via semi-quantitative EDS that some airborne filter-collected Fe-bearing particles contain up to about 20 % of Ba while the content of Sb can reach about 6 %. The variation of the Ba and Sb amount could depend on the materials used to produce the brake pads and the morphology of the Fe-bearing particle as well as on the parameters of the braking event (Garg et al., 2000; Grigoratos and Martini, 2015).

It is worth mentioning that Gietl et al. have measured that Ba is significantly present in the brake wear PM_{10} as whole and further, that about 35 % of the brake pad mass loss is emitted as airborne PM with an iron content of about 50% and that any braking event produces up to about 10^{11} Fe-bearing nano-particles (Garg et al., 2000; Gietl et al., 2010; Harrison et al., 2011; Harrison et al., 2012; Gonet and Maher, 2019).

As shown by the FESEM and EDS results shown in Fig. 1, we have investigated in details also the morphology of the airborne Fe-bearing particles (FePs). The FESEM images and EDS spectra reveal that the FePs are often constituted by agglomerates of smaller sub-micron or nano-particles commonly containing micron- or nano-sized fragments of brake lining materials as the $BaSO_4$ particles shown in Fig. 1 (see the EDS spectra A and C). These aggregates of particles could be easily separated by human fluids when are inhaled as demonstrated by the results reported in Fig. 2. Indeed, in order to clarify what happens when the airborne Fe-bearing particles come in direct contact with the human fluid of the lungs, we have leached the filters with the collected PM_{10} by using a solution mimicking the lung deep interstitial fluid (Malandrino et al. 2016; Mazziotti Tagliani et al., 2017). The results shown in Fig. 2 reveal the separation of the FePs into sub-micron and nano-moieties constituted by Fe-particles and brake pad compounds.

These results support the hypothesis that the Fe-bearing sub-micron and nano-particles can enter the body through inhalation and may also become blood-borne and migrate as sub-micron-sized or nano-particles towards other organs (Oberdörster et al., 2004; Oberdörster et al., 2005; Geiser and Kreyling, 2010; Calderón-Garcidueñas et al., 2019). Indeed, as the particles size decreases, the fine and ultra-fine particles are more able to access human organs since this process becomes even more efficient with decreasing particle size.

Our results also support the hypothesis formulated by Barošová et al. which have found micro-particles of barite ($BaSO_4$) containing iron, in the amniotic fluid in human fetuses; the authors have proposed that a possible releasing source of these barite particles is the vehicular braking systems (Barošová et al., 2015).

We have further consolidated the identification of the braking systems as main releasing source of airborne Fe-bearing particles by investigating elemental profile and morphology of brake dust collected in the braking system of light-duty vehicles.

The FESEM-EDS investigation was aimed to have detailed specific elemental and morphological data considering that limited information are currently available on chemical profile and morphology of brake dust at a micro and nano-scale level (Ingo et al., 2004; Kreider et al., 2010; Grigoratos and Martini, 2015). Our investigation was not carried out to achieve the precise size classification of the brake dust but only to determine possible tracing elemental and morphological similarities between filter-collected airborne particles and brake dust (BD) with the aim to identify the emitting source of the airborne Fe-bearing particles.

Some representative FESEM images and EDS spectra of the BD are shown in Fig. 3. The findings reveal that BD contains particles with a wide dimensional range including the micron- and nano-sized particles and further, that a significant proportion of BD is potentially inhalable and might be transported towards other human organs (see Fig. 4).

Furthermore, the EDS results confirm that the Fe-bearing particles collected inside the brake systems are mainly associated with Ba and S and more rarely also with Sb, Cu and Zn. FESEM images provide also evidence that the frictional contact between brake pads and disc generates mostly semi-rounded or rounded micron- and sub-micron sized particles often composed by agglomerates of smaller particles whose size varies from several tens to a few hundreds of nanometres.

The comparison between the results achieved from the filter-collected particles and brake dust confirms that a large amount of the inhalable airborne Fe-bearing particles and the brake dust are characterised by similar morphological and elemental features. Specifically, we have observed that they have a common and distinctive elemental profile with an often predominant or significant presence of Fe associated with Ba and S sometimes with also Sb, Cu and Zn.

The FESEM and EDS results show striking elemental and structural similarities even though differences in relative elemental abundance and ratios can be observed. These differences are due to the complex particles production mechanism by wear, to the difference of composition of the physical mixture of the brake pad constituents produced by manufacturers and likely also to the multifaceted morphological and chemical features of the particles analysed via EDS.

These results are also in good agreement with the micro-chemical structure of the brake pads (see Figure S4) and with the findings of other authors. These latter have shown that a significant amount of brake wear particles lies in the fine and ultrafine fractions although the brake dust is also emitted as a coarse size fraction via a predominantly mechanical process (Garg et al., 2000; Sanders et al., 2003; Ingo et al., 2004; Kukutschová et al., 2009; Kukutschová et al., 2010; Kukutschová et al., 2011; Winkler et al., 2020).

In order to identify the crystalline structure of brake dust and airborne FePs, we performed a XRD investigation and the results are shown in Figure 4, S5 and S6. The XRD patterns reported in Figure 4 and S5 shows the presence of magnetite (Fe_3O_4) as principal crystalline component even though a small presence of hematite (Fe_2O_3) can be infrequently observed. It is worth pointing out that other authors have analysed PM_{10} collected in urban settings and their results clearly indicate the ferromagnetic nature (*sensu lato*) of the Fe-bearing particles even though magnetite is not always the only one magnetic iron-based compound (Sanders et al., 2003; Chaparro et al., 2010; Saragnese et al., 2011; Sagnotti et al., 2006; Sagnotti et al., 2009; Hansard et al., 2011; Sagnotti and Winkler, 2012; Aránzazu Revuelta et al. 2014; Szuszkiewicz et al., 2015; Paoli et al., 2017; Hofman et al., 2017; Gonet and Maher, 2019; Winkler et al., 2020). Indeed, Kukutschová et al. have observed that magnetite was the predominant specie in both fine and coarse fractions, but, they have found also maghemite (γ-Fe_2O_3) in the nano-particle fraction of airborne nano/micro-sized particles released from automotive brakes (Kukutschová et al., 2011). Furthermore, in Figure S6 we have reported a XRD pattern of a Teflon filter with the airborne particulate matter (sample ADA). Even though the amount of the sampled airborne particulate matter is very small and the resulting pattern noisy, the XRD pattern suggests that magnetite is present in the airborne Fe-bearing particulate matter sampled in trafficked areas. This finding is in good agreement with the above present findings and with the data reported by Winkler and co-workers (Winkler et al., 2020).

The dominant presence of magnetite in the airborne inhalable FePs often mixed with other mineral species such as $BaSO_4$ and Sb_2S_3 is justified also in view of the fact that these particles are produced by abrasion during the braking event. The latter pulverises the brake pad constituents (magnetite, barite and stibnite) into micron and nano-sized particles that are dispersed in the air.

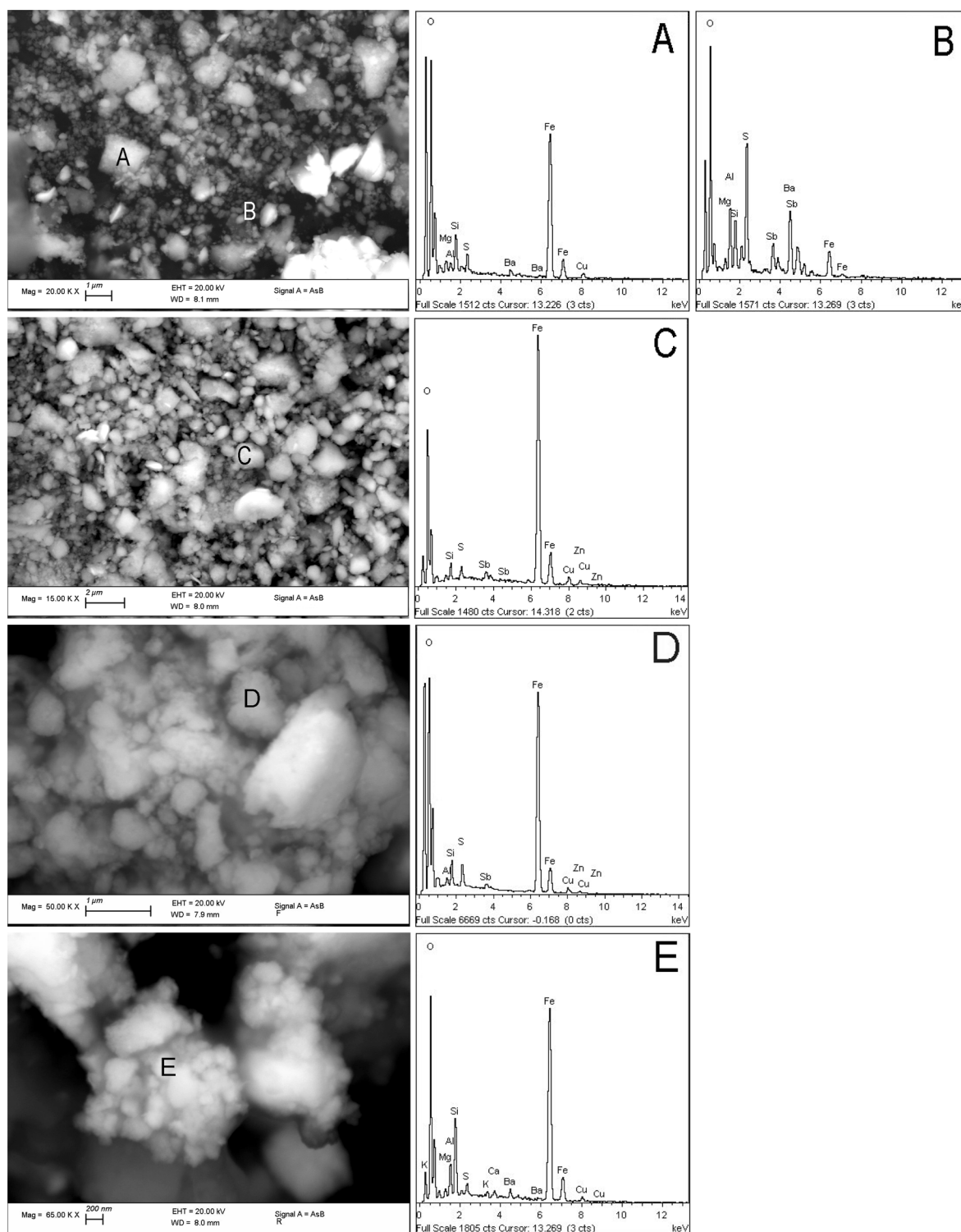The above presented results demonstrate also that alternative

Fig. 3. FESEM images and EDS spectra of automotive brake pad wear residues collected inside the braking system of road light vehicles produced by well-known European manufacturers.

anthropogenic sources or a natural origin are poorly probable also considering the absence of barite along with stibnite and magnetite ores in the Rome's surrounding areas (Tanelli and Lattanzi, 1983a; Tanelli, 1983b; Tanelli et al., 2001; Dini, 2003; Dongarrà et al., 2007; Dongarrà et al., 2009; Chiarantini et al., 2018).

Furthermore, our results highlight that of FePs produced by the brake systems are present also in the rural areas even though in less degree. Indeed, the FESEM-EDS findings reported in Table 1 show the

presence of airborne FePs at the rural site of Montelibretti (Rome, Italy). This result is not surprising if we consider the continuous loss of brake materials by abrasion combined with the action of the wind blowing and the vehicle-generated turbulence (Thorpe et al., 2007; Kukutschová et al., 2010; Kukutschová et al., 2011; Pant and Harrison, 2013; Struckmeier et al., 2016).

Finally, it is worth pointing out that the ubiquitous and widely distributed presence of FePs produced by the brake systems should be
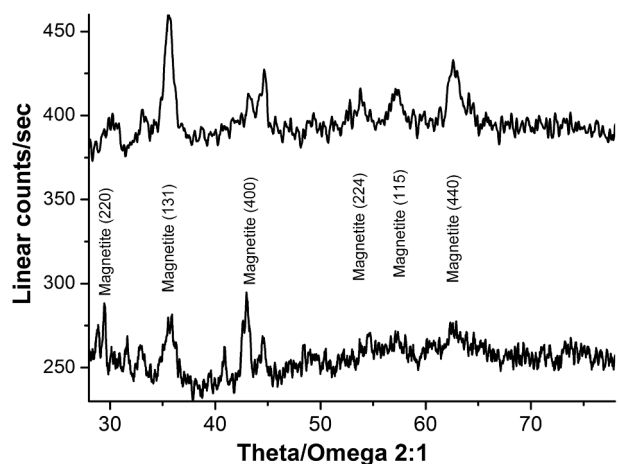
Fig. 4. XRD patterns of the particulate matter sampled inside vehicle brake systems i.e. the brake dust. The position of the main magnetite reflection peaks is also reported.

considered not only for the potential effect on human health but also for environmental consequences: indeed, the airborne aggregates of MNPs along with carbonaceous aerosols have an impact on climate forcing being MNPs a significant anthropogenic contributor to shortwave atmospheric heating (Moteki et al., 2017).

4. Conclusions

In this work we pioneered an innovative approach to determine individually and rapidly elemental profile and morphology of a large number of airborne inhalable Fe-bearing micron and sub-micron particles (FePs) collected in trafficked areas with the aim to locate their releasing source.

The investigation approach combines the high-spatial resolution of the field emission scanning electron microscopy (FESEM), the elemental sensitivity of the energy dispersive spectroscopy (EDS) and an automated tailored software purposely developed for the inorganic particles analysis.

The study of a large number of airborne FePs reveals their ubiquitous and significant presence in trafficked areas and that Fe is very frequently associated to Ba and S and sometimes to Sb, Cu and Zn. These specific elemental tracing features reveal that the airborne FePs are anthropogenic in nature being produced mainly in the form of magnetite by the vehicle braking systems.

Our results suggest to investigate in details the health effects of the prolific environmental release of micro and sub-micron-sized Fe-bearing particles from braking systems. If these effects will be clearly established as adverse, the release in the urban atmosphere of the FePs should be hindered by banning the use of noxious compounds in order to avoid an environmental and occupational exposure with a risk on human health, in particular, for vulnerable people.

From a larger perspective, the approach here described allows a significant breakthrough in the detailed elemental and morphological investigation of the PM and offers a new opportunity to thoroughly and individually study large amounts of airborne particles. Indeed, our findings suggest that specific tracer elements such as Fe associated to Ba, Sb and S, or more in general other peculiar tracer elements, can be successfully used to reveal the complex nature of the environmental micro and sub-micron-sized particles, to identify their releasing source and to evidence similarities with the particles found in the human tissues.

Combined with the state-of-the-art knowledge this innovative approach could provide relevant information allowing to more clearly identify specific effects of the PM thus extending the impact of the environmental studies on the human health.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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