Magnetic- and particle-based techniques to investigate metal deposition on urban green

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Abstract

Urban green works as a recorder of atmospheric PM. This paper reports on the utility of combining magnetic- and particle- based techniques to investigate PM leaf deposition as a bio-indicator of metal pollution. Ivy (*Hedera helix*) leaves were collected from five different land use classes, i.e. forest, rural, roadside, industrial, train. Leaf magnetic measurements were done in terms of saturation isothermal remanent magnetization (leaf SIRM), while ca. 40,000 leaf-deposited particles were analyzed through SEM/EDX to estimate the elemental composition. The influence of the different land use classes was registered both magnetically and in terms of metal content. Leaf area-normalized SIRM values ranged from 19.9 to 444.0 μA, in the following order forest < rural < roadside < industrial < train. Leaf SIRM showed to be significantly correlated ($p<0.01$) with the content in Fe, Zn, and Pb, followed by Mn and Cd ($p<0.05$), while no significant correlation was found with the metals Cr and Cu. Although presenting a similar metal content, roadside and train were magnetically very distinct. By exhibiting a very high content in Pb, and with an Fe content being comparable to the one observed at the forest and rural land uses, the industrial leaf-deposited particles showed to be mainly due to industrial activity. While SEM/EDX is a suitable approach for detailed particle analysis, leaf SIRM of ivy can be used as a rapid discriminatory tool for metal pollution. Their complementary use delivers further knowledge on land use classes reflecting different PM conditions and/or sources.

Keywords

Particulate matter • Metal deposition • Biomonitoring • Environmental magnetism • SEM/EDX • Ivy leaves

1. Introduction

Trace metals of anthropogenic origin are of particular interest within airborne particulate matter (PM), given its non-degradability in the environment (Qian et al., 2014). However, only a small number of air monitoring stations routinely measures metal concentrations (EEA, 2013). As well as polluting the air, metal particulates can get deposited on terrestrial and water surfaces, building up in soils or sediments, and ultimately leading to bioaccumulation in food chains (EEA, 2013). Therefore, the transfer of metals to the biosphere (Kocić et al., 2014) as constituents of PM is one of the most complex issues within the air pollution problem.

In a Flemish study on the chemical composition of PM_{10}, the elements Cr, Mn, Fe, Cu, Zn, and Pb, were identified as traffic-related species (Vercauteren et al., 2011). Several trace metals are emitted through the abrasion of tires (Cu, Zn, Cd) and brake pads (Cu), corrosion (Fe, Cu, Zn, Cd, Cr), lubricating oils (Cu, Zn, Cd) or fuel additives (Zn, Cd, Pb) (Tomašević and Aničić, 2010, and references therein). Pb is strongly associated with historic leaded-fuels usage, while Cu, Cd, and Zn, can also be identified as industrial or incinerator emissions, in addition to traffic (Zhang et al., 2012). Deposition of airborne metals (through wet or dry processes) is a major source of e.g. soil contamination, with urban soils serving as useful indicators of environmental pollution (Wang et al., 2012). The monitoring of soil pollution through geochemical methods (e.g. AAS and ICP-AES) involves the collection and processing of soil samples, which is laborious and time-consuming, making it difficult to perform large scale pollution mapping or monitoring (Dankoub et al., 2012; Xia et al., 2014). In the last decades, magnetic measurements have been increasingly used as a more simple, robust and cost-effective method to investigate soil contamination, allowing the study of extensive areas in short periods. The concept of environmental magnetism as a proxy for air pollution monitoring was first reported based on the analysis of soils, sediments and street or roof dust (e.g. Jordanova et al., 2003; Lu and Bai, 2006; Muxworthy et al., 2003; Petrovský and Ellwood, 1999; Thompson and Oldfield, 1986; Wang et al., 2012). Positive correlations between soil metal content and magnetic susceptibility have been established (Dankoub et al., 2012; Jordanova et al., 2003), and in some countries soil magnetic susceptibility mapping was applied for evaluating anthropogenic soil pollution (Kapička et al., 1999; Lecoanet et al., 2001). Similar correlations were observed by Hunt et al. (1984) between the saturation isothermal remanent magnetization (SIRM), which measures the ferro(i)magnetic fraction, and the metal component of atmospheric particulates, suggesting the use of magnetic parameters as facilitators on the identification and discrimination of PM sources. Because sources of magnetic particles (such as Fe oxides and/or sulfides, derived from e.g. combustion processes (Matzka and Maher, 1999)) and trace metals have shown to be closely related (e.g. Lu et al., 2007; Norouzi et al., 2016), their joint characterization may enable the identification of specific pollution sources.

When studying urban environments, where metal and PM pollution are of critical interest, the accessibility to soil samples can be highly hampered due to soil coverage by roads, pavements and buildings. Nonetheless, urban vegetation is usually widespread in cities, providing natural surfaces for deposition and immobilization of small atmospheric particles (Freer-Smith et al., 2005; Kardel et al., 2012; Litschke and Kutler, 2008; Mitchell et al., 2010; Weber et al., 2014) by leaf deposition or in-wax encapsulation (Kardel et al., 2011; Terzaghi et al., 2013). Therefore, several studies have used vegetation samples (such as plant leaves) as magnetic bio-indicators of air pollution (e.g. Hofman et al., 2013; Kardel et al., 2011; Matzka and Maher, 1999; Mitchell et al., 2010; Moreno et al., 2003; Norouzi et al., 2016; Sagnotti et al., 2009; Vuković et al., 2015; Yin et al., 2013). A review on environmental magnetic studies of PM, with particular focus on magnetic biomonitoring using roadside plant leaves, was also made available (Rai, 2013). The use of e.g. plant leaves as indicators of urban PM, which are then submitted to magnetic techniques, provides a rapid and robust PM monitoring. On the other hand, particle analysis such as in terms of composition and size should not be overlooked, as these factors closely influence the PM impacts on human health. Scanning electron microscopy (SEM) can be used as a particle-based technique for such an investigation on leaf-deposited PM, as it allows the examination of plant surfaces at high resolution (Pathan et al., 2008).

The enrichment of magnetic particles has been associated with trace metals such as Cr, Mn, Fe, Cu, Zn, Cd, and Pb (Lu et al. 2007). However, depending on the local conditions not all metals will be present or occurring in the same proportion, which happens similarly for magnetic particles. Because the fractions of magnetic and metal particles tend to reflect the local conditions in terms of anthropogenic pollution, magnetic analysis as a measure of trace metal content was here applied to ivy leaves sampled from different land use classes. This paper reports thus on the magnetic and metal analyses of ivy leaves collected from different land uses (forest, rural, roadside, industrial, and train) in Antwerp, Belgium. The main objectives here addressed are as follows: (a) to discriminate the influence of different land use classes on PM leaf deposition, according to its magnetic behavior and metal content, (b) to examine the relationship between the magnetic behavior of sampled leaves and the trace metal content from the leaf-deposited PM, and (c) to illustrate the combined use of magnetic analysis with a particle analysis-based technique for a more integrated study of urban leaf-deposited PM.

2. Materials and methods

2.1 Study area

After Brussels, Antwerp is the second largest city in Belgium with ca. 500,000 inhabitants, being also the second most populated city (2,500 inhabitants/km^2). After Rotterdam, Antwerp has the second largest harbor in Europe, presenting a very strong industrial sector, as well as high traffic intensity highways and roads. In Antwerp, leaf samples were collected from five different sites (Figure 1), in an attempt to assess the influence of different land use classes. In principle, different pollution levels and different pollution sources could result in different characteristics within the leaf-deposited PM. The following samples were collected: inside a forested area, in a rural area, in an urban area next to a high trafficked crossroad, near an industrial complex, and close to a train line (Table 1). The forest and rural sites were located in Merksplas, significantly far from Antwerp's city center (ca. 37 km), to limit leaf exposure to traffic, industrial and railway emissions. Combustion processes whether domestic, industrial or vehicle, produce small Fe-bearing spherules, as Fe often occurs as an impurity in fossil fuels (Hofman et al., 2013). Depending on the industrial activity, the variety of metals released to the atmosphere should differ from road-traffic. The targeted industry works with precious and non-ferrous metals, with reported emissions of metals e.g. Pb and Cd. In addition to the motorized vehicles, friction between trains' or trams' wheels and tracks releases high metallic particles (Kardel et al., 2012), which can contribute to the atmospheric PM concentration in the nearby areas.

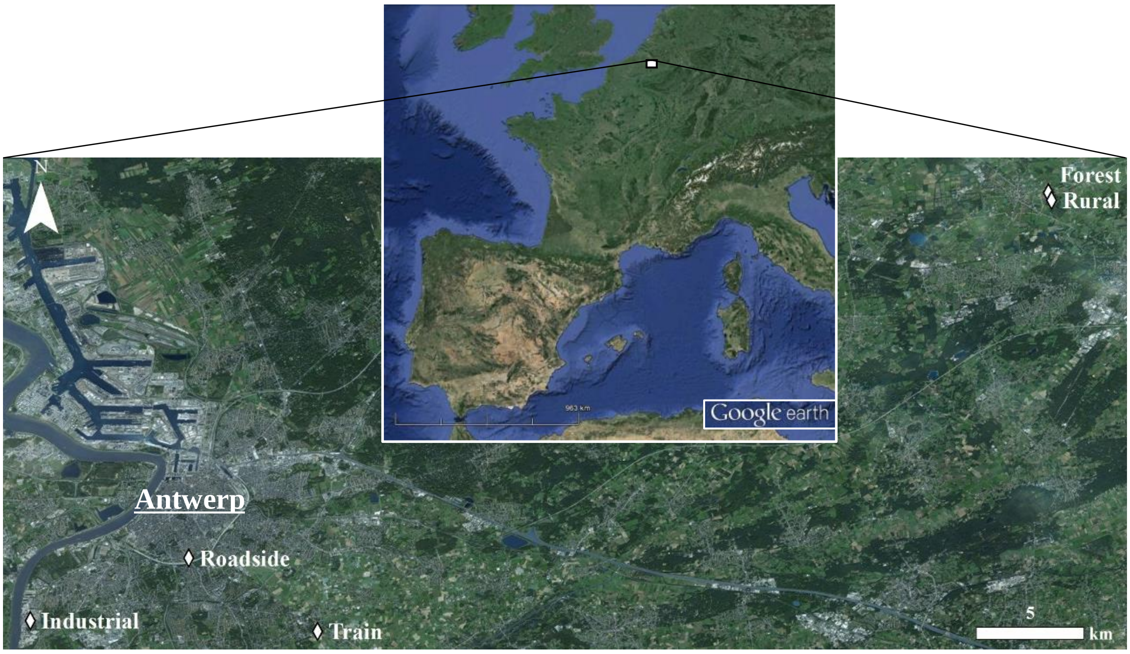

Figure 1 – Location of the different sampling sites within the city region of Antwerp, Belgium (Google Earth; ArcGIS 10.2.2). The forest and rural sites are significantly distant from the city center of Antwerp.

Table 1 – Description and land use class of the studied sampling sites.

Land use	Site description
Forest	Inside a forested area, 30 m apart from a low traffic road, which is mainly used by the inhabitants of the small residential/rural area
Rural	300 m apart from the forest site and in the same residential/rural area; located 1 m distant from a low traffic road, which is the main local PM source

Roadside	7 m distant from a crossroad with high intensity traffic, close to traffic lights; tram lines are also present (30 m away) in the site, but the main local PM source is assumed to be road traffic
Industrial	4 m distant from a low/medium traffic road within an industrial complex; since that the road is mainly used for loading/unloading of materials and by factory workers, the main PM source here is considered to be the industrial activity; the targeted industry deals with the recovery, processing and recycling of precious and other non-ferrous metals (e.g. Ag, Au, Pt, Se, Bi, Pb, Cu, Ni)
Train	About 5 m apart from a railway track, close (about 700 m distant) to Boechout train station; the closest traffic road is located ca. 300 m apart, and so road traffic can be considered a negligible source

2.2 Leaf sampling

Common ivy (*Hedera helix*) leaves were used as vegetation samples as they are extensively widespread and easy to find within the land use classes under study. From each sampling site, a total of eight fully-developed undamaged leaves were collected (passive monitoring mode) from the outer canopy of an ivy plant, between 1.30 – 1.70 m as this resembles adult human inhalation height. No precipitation was registered during the sampling (which happened on March 27 and April 16, 2014) nor on the three days prior to sampling.

2.3 Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDX)

Of every collected ivy leaf, a circular sample with a diameter of 1 cm was removed from the center of the leaf lamina and between its principal veins, using a metallic puncher. Per sampling site (total of eight leaves), four adaxial samples and four abaxial samples were obtained (Figure 2). Each sample was fixed on a metallic pin stub, using conductive double-sided tape, and left to dry at room temperature for at least three days. This dehydration is required to avoid sample damage, as water would evaporate too fast at low pressure conditions. Before the microscope analysis, samples were vacuum-coated with carbon, using a CED 010 (Balzers Union) apparatus, to make them conductive in order to prevent a charge build-up effect. Finally, samples were examined using a Quanta 250 field emission gun scanning electron microscope (FEI, USA) operated at high-vacuum conditions (10^{-3} Pa), with an accelerating voltage of 20 kV, magnification of 500×, and spot size of 3.6. The backscattered electron detector was used to spot the leaf-deposited particles due to its capability for discrimination based on atomic weight. The particles were then analyzed using an energy-dispersive X-ray detector coupled to the SEM microscope (SEM/EDX) (Figure 3).

The central part of each analyzed sample surface was subdivided into 50 fields, each field with an area of 414 µm × 285 µm. As such a total surface area of ca. 5.9 mm^2 per sample was considered. The automated software mode (INCA provided by Oxford Instruments, UK) was defined to analyze 20 particles per field (the first 20 particles within the x direction), yielding about 1,000 leaf-deposited particles per leaf sample. The minimum size threshold was set on 2 µm, meaning that only particles with equivalent circular diameter (ECD) greater than 2 µm were considered for analysis. This limitation arises from the fact that the SEM/EDX requires a minimum of sample interaction volume so that it can correctly identify individual particles from particle agglomerates and/or from the leaf surface. This threshold implementation is particularly important when the identification of the different particles is computer controlled (CCSEM) and not assisted by a permanent operator, which was the case.

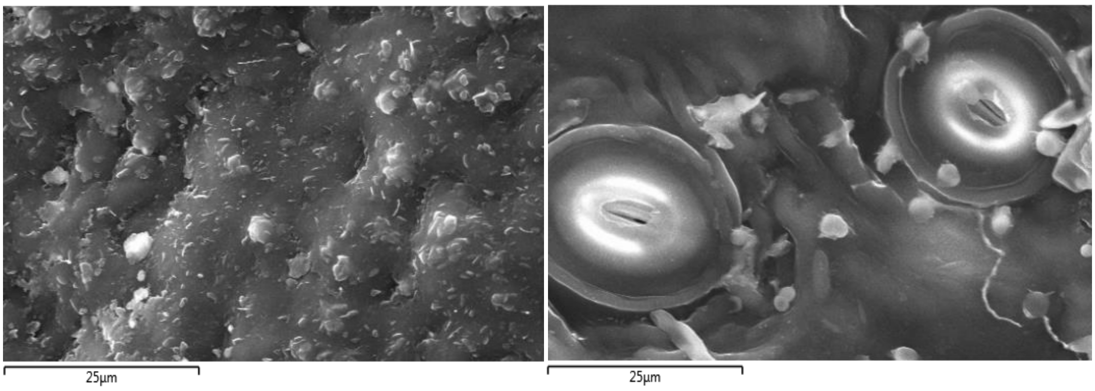

Figure 2 – SEM images showing leaf-deposited PM on ivy: example of adaxial (left) and abaxial (right) samples.

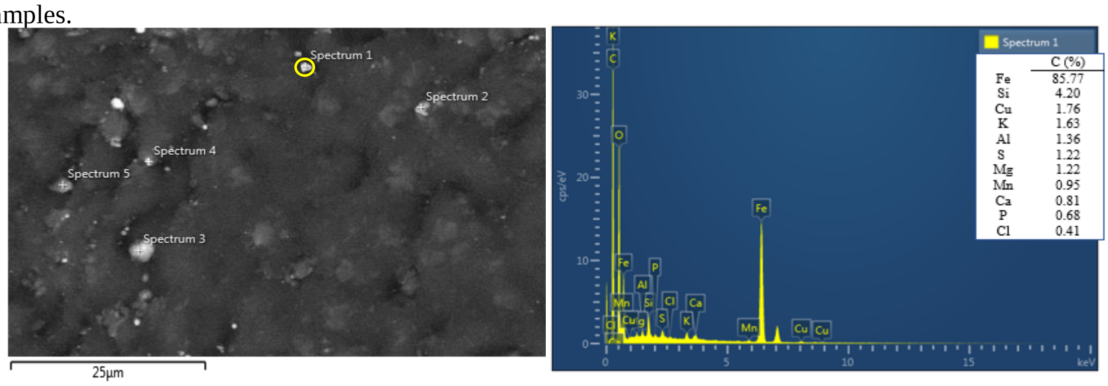

Figure 3 – SEM/EDX analysis of PM deposited on ivy. After the collection of a backscattered electron image (left), the EDX detector acquires the spectra of each selected particle. Spectrum 1 (right) corresponds to a Fe-rich particle. Using the CCSEM mode, the leaf-deposited particles were automatically identified and SEM/EDX analyzed.

Using combined SEM/EDX, the elemental composition *C* of each analyzed leaf-deposited particle was obtained, as well as its ECD (equivalent circular diameter: diameter of a circle with an area equivalent to the projected particle area on a plane). Considering that a large fraction of the observed particles were mostly near-spherical, the particle ECD was used to calculate the volume v_i of each particle *i* following Eq. (1). The mass density of the particles was assumed to be constant for all deposited particles in order to obtain the weighted volume percentage *W%* of each chemical element *x* along the analyzed particles. The mean volume percentage (%, v/v) was calculated for the *n* deposited particles per leaf sample as described in Eq. (2). Because the considered approximations might be unrealistic for some cases (as e.g. some particles are rather angular than spherical), and to reduce the associated error, a large number of particles per leaf sample (ca. 1,000 leaf-deposited particles) was analyzed. Because leaf samples are of organic nature and they were carbon-coated, the element C was not considered in the SEM/EDX analysis. The main elements detected in the leaf-deposited particles were N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb. Because of the uncertainty of EDX in measuring O, this element was removed from the obtained SEM/EDX data, and the composition of each element (C_{xi}) was recalculated in order to obtain a total particle composition of 100% (excluding O).

$$v_i = 4\pi/3 \,.\, (ECD_i/2)^3 \qquad (1)$$
$$W\%_x(\%, v/v) = \sum_{i=1}^{n} v_i . C_{xi} \,/\, \sum_{i=1}^{n} v_i \qquad (2)$$

2.4 Determination of saturation isothermal remanent magnetization (SIRM)

After the collection of leaf samples for SEM/EDX analysis, the remaining leaves were submitted to a SIRM-based magnetic analysis while still fresh. Each leaf was tightly packed with cling film and pressed into a 10 cm^3 plastic container. Following the protocol of Hofman et al.

(2014b), the sample containers were magnetized with a pulsed field of 1T using a Molspin pulse magnetizer (Molspin Ltd., UK). After magnetization, their remanent magnetic intensity (SIRM equivalent, in mA m^{-1}) was measured using a calibrated Molspin Minispin magnetometer (Molspin Ltd., UK). Each leaf was measured twice to reduce measurement errors, and the mean of the two values was considered. The magnetometer was calibrated using a magnetically-stable rock specimen after each eight samples. The SIRM signal of empty containers was used as blank signal, therefore subtracted from the measured values. Subsequent to the magnetic analysis, the leaves were removed from the sample containers and from the cling film and submitted to a leaf area meter LI-3100C (Licor Biosciences, USA), in order to determine their surface area. The magnetic intensity values, expressed in mA m^{-1}, were normalized for the sampling container volume (10 cm^3) and for the leaf surface area (in cm^2) to obtain SIRM values normalized for leaf area, expressed in A.

For ferromagnetic materials such as Fe-particles, the (induced) magnetization does not disappear after removal of the applied external field (H), therefore, leaving the sample with magnetic remanence (or SIRM, when H is large enough to lead to saturation). The SIRM parameter corresponds thus to the point where, after a saturation magnetization, H equals zero (external field is removed) within the hysteresis loop (Evans and Heller, 2003).

2.5 Chemical composition and SIRM of leaf-deposited PM

Leaf samples corresponding to the eight collected leaves per sampling site were analyzed with SEM/EDX in the following way: four samples on their adaxial side and four samples on their abaxial side. The chemical composition of each leaf sample was calculated as explained in section 2.3. The particle elemental composition of the four adaxial leaf samples was arithmetically averaged and considered as the mean elemental composition for particles deposited on the adaxial leaf side within a certain site. A similar procedure was followed for the abaxial leaf samples. While the magnetic leaf measurements considered total leaves, the microscope allowed to analyze particles deposited either on the adaxial or abaxial side. Therefore, in order to compare the leaf SIRM with the elemental content observed within the leaf-deposited PM, both leaf sides (i.e. adaxial and abaxial) were considered to estimate the overall composition of leaf-deposited PM. In the context of this paper, the trace metal content (TM) in terms of Cr, Mn, Fe, Cu, Zn, Cd, and Pb, was estimated per land use class.

2.6 Data analysis

The large dataset generated from the SEM/EDX analysis was handled using Microsoft Excel. Because of the replicates at each sampling site, land use effects on leaf SIRM could be distinguished from statistical outliers. Two statistical outliers within leaf SIRM results (n=40) were detected using SPSS 23.0 (IBM Corp, USA) and replaced by the mean leaf SIRM of the considered land use class. Spearman's correlation coefficients between leaf SIRM and the metal content from the analyzed leaf-deposited $PM_{2.5-10}$ were also obtained using SPSS.

3. Results and discussion

3.1 SIRM variation

The area-normalized leaf SIRM results obtained from the collected ivy leaves ranged from 19.9 to 444.0 µA, which is in agreement with former SIRM values reported by Hofman et al. (2014c) who observed SIRM values between 33.5 and 639.7 µA for ivy leaves collected at 1.5 m height in the same study area (city of Antwerp). Matzka and Maher (1999) observed values between 5.1 to 67.4 µA from birch (*Betula pendula*) trees in the city of Norwich, England, at a sampling height of 1.5 to 2 m. In the Flemish city of Ghent, Hofman et al. (2013) had found SIRM values between 3.5 and 64.1 µA from London plane (*Platanus x acerifolia*) tree leaves sampled at 5, 8 and 12 m height. Still in Ghent, Kardel et al. (2011) reported e.g. mean leaf SIRM values of 86 µA for *Carpinus betulus*, 99 µA for hairy *Tilia sp*, and 46 µA for non-hairy *Tilia sp*, for leaf samples collected at 2 - 4 m height in high polluted sites (urban and industrial areas with high traffic and industrial activity), while the low polluted sites showed mean leaf SIRM values of 15 µA for *Carpinus betulus*, 34 µA for hairy *Tilia sp*, and 11 µA for non-hairy *Tilia sp*. These findings suggested that PM collection on leaf surfaces is species-dependent, which was also corroborated by the studies of Jordanova et al. (2010), Sæbø et al. (2012) and Speak et al. (2012). Due to differences in plant species, but also in study area, sampling height, and sampling time, it is not possible to compare directly our obtained leaf SIRM results against the values from the mentioned studies. Nonetheless, the obtained values appear to be in the same order of magnitude as former published SIRM values.

In this study and in Hofman et al. (2014c), SIRM of ivy leaves showed to be relatively higher than published SIRM values of e.g. plane and birch leaves, possibly due to the fact that as an evergreen species, ivy leaves might have been longer exposed than deciduous leaves. When magnetically comparing leaves of evergreen oak (*Quercus ilex*) with plane tree leaves (*Platanus sp*) collected in Rome, Moreno et al. (2003) observed that the evergreen species presented higher magnetic intensities than the deciduous species. While deciduous species only accumulate pollutants on their leaves during the vegetation season, evergreen species accumulate particles throughout the entire lifespan of their leaves.

3.2 Influence of different land use classes on PM leaf deposition

The influence of different land use classes on PM leaf deposition was investigated in terms of the magnetic behavior of leaves i.e. leaf SIRM, and in terms of the trace metal content within the leaf-deposited particles.

3.2.1 Leaf SIRM

The highest SIRM values were observed at the land use classes defined as train (mean SIRM of 399.0 µA ± 8.0 µA (SE)) and industrial (mean SIRM of 323.1 µA ± 7.5 µA (SE)). The mean SIRM measured near the roadside was 204.6 µA ± 12.9 µA (SE), while the lowest values were obtained at the rural (65.4 µA ± 5.3 µA (SE)) and forest land use classes (24.0 µA ± 1.0 µA (SE)) (Figure 4). As SIRM strongly correlates with atmospheric PM_{10} mass (Hofman et al., 2014b; Matzka and Maher, 1999; Mitchel and Maher, 2009; Muxworthy et al., 2003), the results suggest that the highest PM levels were exhibited in the train and industrial land uses, while forest can be considered a non-polluted site in terms of PM. Several studies (Hansard et al., 2011; Matzka and Maher, 1999; Mitchel and Maher, 2009) have reported a high correlation between leaf or dust magnetic properties such as magnetic remanence, and atmospheric PM concentrations, indicating a coherent co-existence of magnetic and other urban dust particles. McIntosh et al. (2007) compared leaf SIRM values of London plane trees collected in Madrid with the registered atmospheric concentration of NO_x and PM_{10}, and observed that the magnetic signal was specific to traffic-related emissions, not to the total particle mass. This link between SIRM and traffic-related PM was also confirmed by the works of e.g. Kardel et al. (2012), Sant'Ovaia et al. (2012), and Maher et al. (2008). In addition to traffic, industrial activities (Goddu et al., 2004; Hansard et al., 2011; Zhang et al., 2012) and railway lines (Kardel et al., 2012; Lorenzo et al., 2006; Moreno et al., 2003) have been recognized as important sources of magnetic particles. Our results suggest that leaf SIRM of ivy leaves can be used as a bio-indicator of anthropogenic PM, being able to distinguish between land use classes with different urban habitat quality. If one major pollution source such as road- or rail-traffic or industry, dominates the PM emissions, the SIRM signal can be interpreted as proportional to the amount of PM emitted by that particular source.

On the other hand, the presence of multiple pollution sources can result in different relative contributions of the various sources to the magnetic signal, and might thus disturb the source-specific relationships observed between PM and SIRM. Leaf SIRM values should thus be understood as indicators of anthropogenic PM emissions, instead of e.g. total PM mass.

Although only five different sites were considered, our results suggest that leaf-deposited PM, and its composition, is not homogeneously distributed over the city region of Antwerp, but mainly depends on local emission conditions: the highest SIRM values were found near railways, industries and intense traffic roads, in agreement with what was verified in other European cities such as Braga (Sant'Ovaia et al., 2012), Cologne (Urbat et al., 2004) and Rome (Moreno et al., 2003). Magnetic techniques including SIRM are mainly sensitive to ferro(i)magnetic particulates and thus preferentially characterize the fraction of atmospheric PM that derives from combustion processes or metallic wear and abrasion (Lehndorff et al., 2006; McIntosh et al., 2007). During combustion, carbon and organic material is lost by oxidation whereas Fe forms a non-volatile residue, often comprising glassy spherules due to melting (Hofman et al., 2013). The produced spherules contain variable amounts and grain sizes of strongly magnetic (as magnetite, Fe_3O_4) and/or weakly magnetic (as hematite, Fe_2O_3) Fe-particles, depending on the fuel type and temperature of combustion (Matzka and Maher, 1999). In addition to combustion-related particles, non-spherical Fe-rich particles can be generated via exhaust emissions and metallic wear/abrasion (e.g. tire and brake wear, abrasion of vehicle parts and road pavement) (Matzka and Maher, 1999; McIntosh et al., 2007). Similar processes have also a great importance when considering rail traffic. The high magnetic signal coming from the train site is probably due to particles released from the mechanical wear and friction at the rail-wheel-brake interfaces, as Lorenzo et al. (2006) estimated a contribution of 67% of Fe-based particles to the PM_{10} emissions of a very busy railway line studied in Zurich. When studying the exposure to particle emissions in the subway of New York, Chillrud et al. (2004) observed that the sampling packs carried by teenagers when using the subway had, besides higher concentrations of Mn and Cr, significantly higher concentrations of Fe than domestic indoor and ambient samples.

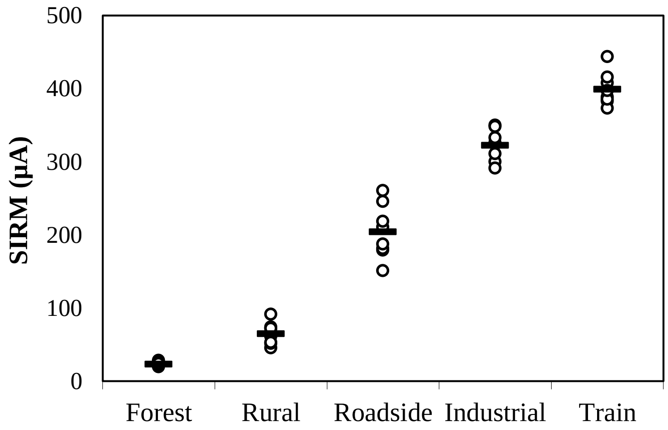

Figure 4 – Area-normalized SIRM values for the considered land use classes. Each leaf SIRM is represented by a circle, while the mean SIRM per land use (n=8) is indicated by a black dash.

Because the forest site was assumed to be representative for a non-polluted environment, a corresponding low SIRM value (mean of 24.0 µA) was expected. Although the rural site was only located 300 m away, mean SIRM was almost three times higher (mean of 65.4 µA) than the value observed for the forest. This difference, which should be explained by the low-intensity traffic road present in the rural site, highlights again the strong contribution of vehicle traffic sources to the SIRM signal. The high-trafficked roadside showed the highest deviation in terms of magnetic signal from all sampling sites, which may be related to the specific local conditions, as leaves were collected near traffic lights. While an intense brake wear can be expected at such site, it may also vary according to fluctuations in traffic volume and behavior.

Moreno et al. (2003) found no correlation between magnetic tree leaf properties and the hourly or daily PM_{10} values as recorded by classical air monitoring stations. Instead of delivering an instantaneous reading of PM pollution, magnetic biomonitoring of leaves provides a time-integrated assessment of local PM exposure. This time integrating nature was also shown by Hofman et al. (2014b) who observed that leaf SIRM was related to the cumulative daily average atmospheric $PM_{2.5}$ and PM_{10} concentrations, while no relation was found for daily or weekly concentrations. This time-integrating character is appropriate for e.g. the study of health effects due to prolonged PM exposure.

3.2.2 Trace metal content

From the almost 40,000 analyzed leaf-deposited particles, the range between 2.5 and 10 µm ($PM_{2.5\text{-}10}$) comprised ca. 26,000 particles. The mean metal content within the leaf-deposited $PM_{2.5\text{-}10}$ was estimated per land use class (Table 2). For all studied sites, the metals Cr, Mn, and Cd, appeared to be very low (< 0.1 %). The metals Cu, Zn, and in particular Pb, registered slightly higher values, particularly for the industrial land use class. In this latter land use class ca. 30% of the total volume of leaf-deposited particles ($PM_{2.5\text{-}10}$) was composed of Pb. This high Pb content suggests high atmospheric Pb concentrations at breathing height, as the leaves were collected between 1.3 and 1.7 m. Pb is a harmful neurotoxin and although its use in leaded-fuels has been internationally banned, Pb contamination is still observed in certain urban areas (Maher et al., 2008). The resuspension of soil material formerly enriched in Pb can thus act as a possible source of particulate Pb. However, the values observed for the studied industrial site are rather expected to be due to current industrial emissions than to be due to historic pollution, as indicators of dust resuspension (e.g. Al, Ca, Si, Fe) (Jancsek-Turóczi et al., 2013) were the lowest detected within the five land use classes. Studies on the topic have confirmed that, in the absence of heavy industry, the main source of magnetic particles on leaves is derived by traffic pollution (Hanesch et al., 2003; Maher et al., 2008; Moreno et al., 2003). While around industrial sites a close relation between the distribution of magnetic particles and the distribution of metals is verified (Hanesch et al., 2003; Hansard et al., 2011; Zhang et al., 2012), which was corroborated by our magnetic and particle analyses.

Table 2 – The mean metal content (%, v/v) obtained with SEM/EDX analysis per land use class. TM corresponds to the sum of trace metals considered (Cr, Mn, Fe, Cu, Zn, Cd, and Pb). The absence or very low content (<0.01 %) is indicated with a black dash.

	(%, v/v)							
Land use	Cr	Mn	Fe	Cu	Zn	Cd	Pb	TM
Forest	0.05	0.08	9.83	0.06	0.07	-	0.77	10.9
Rural	0.02	0.06	8.97	0.02	0.02	-	-	9.1
Roadside	0.03	0.06	24.72	0.17	0.17	-	0.13	25.3
Industrial	0.06	0.02	10.91	5.17	1.43	0.02	29.51	47.1
Train	-	0.02	23.96	0.02	0.27	0.01	0.03	24.3

3.3 Leaf SIRM as a record of metal pollution

Because the SIRM parameter quantifies the ferro(i)magnetic PM fraction (Hofman et al., 2013; Kardel et al., 2012), the obtained leaf SIRM values were compared against the estimated particle Fe content (Figure 5a). While leaf SIRM increased in the following order forest < rural < roadside < industrial < train, the leaf particulate Fe content displayed a somewhat different behavior. The Fe content ranged from 9 to 11% for the forest, rural and industrial sites, but for roadside and train site almost 25% of the total volume of leaf-deposited particles was composed of Fe. Although ferro(i)magnetism is by definition associated with the element Fe, an increasing Fe content does not necessarily corresponds to an increasing magnetic signal or vice-versa, as verified by the non-linear relationship obtained between leaf SIRM and the Fe content.

Enviromagnetic parameters reflect the presence of magnetic particles in terms of their composition, concentration and grain size (Evans and Heller, 2003), and so their interpretation might be less straightforward. While magnetic measurements are sensitive to the chemical structure (note the difference between magnetite and hematite), the metal content obtained from the SEM/EDX is provided in terms of elemental composition, making no distinction between e.g. Fe particles with different crystal structures. In terms of particle size, whereas the metal content was estimated for the range 2.5-10 μm, no size fractionation is done along with the leaf SIRM measurement, although it is known that smaller particles generally yield higher magnetic signals as they are more efficient at acquiring remanence (Evans and Heller, 2003). Although additional magnetic parameters would be required to investigate further compositional or grain size effects, leaf SIRM is known to increase monotonically with the amount of magnetic material present (Evans and Heller, 2003).

The magnetic signature of urban polluted sources is mainly due to ferromagnetic minerals such as Fe-oxides, Fe-sulfides, or more rarely native Fe (Lu et al., 2011), and it is also strongly correlated with the occurrence of a variety of trace metals. Based on the recognized association between magnetic and metal particles, leaf SIRM was plotted against trace metal content composed by a wide range of metals (Cr, Mn, Cu, Zn, Cd, Pb, and Fe) (Figure 5b). With exception of the train land use class, leaf SIRM results seemed to reflect better the content of the seven considered metals, instead of the Fe content alone. When the train site is not considered, the relation between leaf SIRM and the particles' metal content follows an approximately linear behavior. However, given the still limited number of samples (i.e. one sampling site per land use class) and land use classes (five), this linear trend should not be extrapolated to other urban locations without further study on the magnetic characterization of the main urban PM sources. Furthermore, the observed behavior is until a certain extent caused by the high Pb content observed on the leaves from the industrial site, while the other metals appeared to be of less influence.

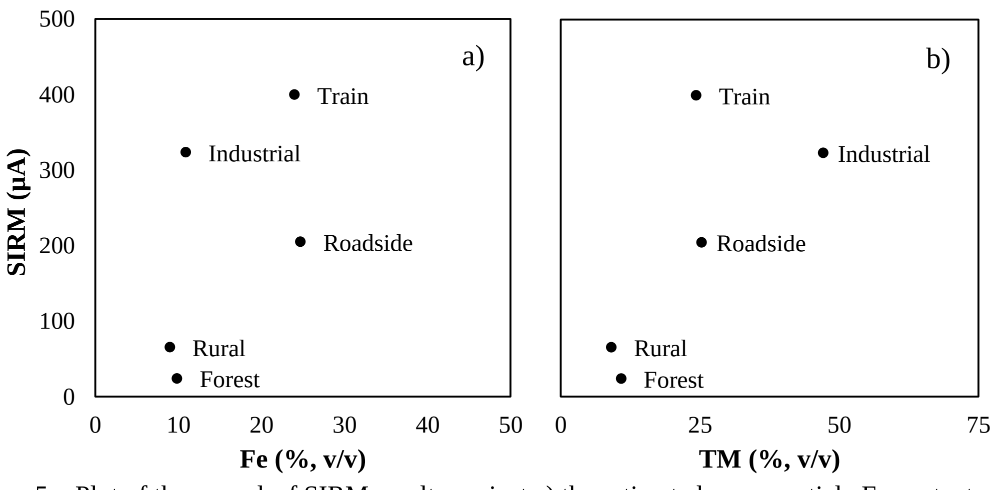

Figure 5 – Plot of the mean leaf SIRM results against a) the estimated mean particle Fe content, and b) the estimated mean particle trace metal content (TM as the sum of Cr, Mn, Fe, Cu, Zn, Cd, and Pb, content), for the different land use classes tested.

Already in the 80s, Hunt et al. (1984) established a link between magnetic minerals and metal concentrations that holds in a variety of environmental contexts. Maher et al. (2008) observed that urban roadside tree leaves exhibit significant enhancement in their values of SIRM, Fe and Pb, when compared with leaves growing at a background site, while metals as Zn and Mn showed limited roadside enhancement. In Cologne, high contents in Pb, Fe and also Zn, identified regions affected preferentially by traffic-derived emissions in the sampled pine needles (Lehndorff and

Schwark, 2010). Although the concentrations of particulate matter and certain metals, which can be captured by vegetation, are positively correlated with magnetic parameters, the sources of the magnetic minerals and associated pollutants may be variable, such as from Fe foundries, vehicle traffic or ship emissions (Jiang et al., 2015; Xia et al., 2014).

Leaf SIRM showed to be significantly correlated with Fe, Zn and Pb ($p<0.01$), followed by the metals Cd and Mn ($p<0.05$) (Table 3). On the other hand, no significant correlations were observed between Cr and Cu, and leaf SIRM. The correlation between leaf SIRM and particulate Mn content appeared to be negative, while it was positive for the other correlated metals (Fe, Zn, Cd, and Pb). Although traffic-related processes constitute the principal source of e.g. Fe, Cr, Cu and Zn, high percentages of these metals can also originate from e.g. industrial metallurgical processes. The investigated industrial site, which is associated with metal handling and processing, revealed the highest content in Zn, Cu, and Pb. Given the high Pb content detected at this site, further investigations must be pursued at soil level to assess the possibility of historic industrial pollution as well. The correlation coefficient was the highest when considering the content of the seven considered metals (TM) in comparison with the Fe content alone (Table 3).

Table 3 – Spearman's correlation coefficients between leaf SIRM (n=40) and the different trace metals. TM corresponds to the sum of trace metals considered (Cr, Mn, Fe, Cu, Zn, Cd, and Pb).

	Cr	**Mn**	**Fe**	**Cu**	**Zn**	**Cd**	**Pb**	**TM**
SIRM	- 0.17	- 0.39 *	0.54 **	0.23	0.48 **	0.39 *	0.41 **	0.64 **

*Correlation is significant at $p<0.05$. **Correlation is significant at $p<0.01$.

3.4 Complementary use of leaf SIRM and SEM/EDX trace metal content

In this study, two different methodologies were employed for the investigation of leaf-deposited PM: magnetic analysis via leaf SIRM and metal content estimation via SEM/EDX analysis. Leaf SIRM provides a bulk analysis of the leaf in terms of its magnetic content, while the SEM/EDX allows a detailed, micrometer level, examination of the leaf surface and the particles deposited on it. Despite the differences described throughout this paper between both methodologies, their combined use can help on the study of urban leaves as indicators of PM and metal pollution.

An analysis done only on the Fe content retrieved from the SEM/EDX analysis would have displayed two different groups of land use classes: forest, rural and industrial with approximately 10%, and roadside and train in another group with about 25%. While the forest and rural land use classes can be associated with a similar magnetic signal, the industrial site is magnetically very distinct from those. The fact that the Fe content from the industrial site is comparable to the Fe content observed within the forest and rural sites suggests that the targeted industry is not a major Fe emitter, and that the Fe-particles at the industrial site may be as well derived from road traffic, or in a less proportion from crustal soil resuspension, rather than from the industrial activity at the sampling location. This finding is also in accordance with the type of industrial activity present, as the targeted industry has no reported emissions of Fe.

Although the roadside and train samples exhibited leaf-deposited particles with a similar Fe content, magnetically they exhibited different SIRM values as they were exposed to different emission sources of PM, thus reflecting different local urban conditions. The Fe-particles at the train site should occur in a very specific way so that it leads to leaf SIRM values higher than the values measured at the roadside location. The chemical structure of the Fe-particles at the train site might be e.g. pure Fe or Fe-alloy, which are true ferromagnets, therefore yielding very high SIRM values in comparison to the Fe content. Because SEM/EDX only provides an estimate of the amount of Fe and not its chemical structure, further research using e.g. additional magnetic parameters, is required to confirm this hypothesis. Nevertheless, the complementary information produced by leaf SIRM and SEM/EDX already facilitates source discrimination between road- and rail-traffic conditions.

Our results showed that the measurement of leaf SIRM allows a rapid and easy identification of sites with different urban activities i.e. different land use classes. On the other hand, SEM/EDX analysis applied to leaf-deposited PM increases the understanding on which metals and to what extent they are present across the different land uses. While leaf SEM/EDX offers a close look into the composition and size of deposited particulates, which is of particular interest for PM source investigation, a high-spatial city scale resolution is impossible to reach due to time and economic constraints. The combined use of leaf SIRM and SEM/EDX provided complementary knowledge about urban PM and metal pollution registered along different land use classes, offering thus more potential for purposes of source attribution than their individual use.

4. Conclusions

Ivy leaves showed to be a reliable bio-indicator for urban PM and metal pollution. Being an evergreen plant (i.e. leaves can be sampled throughout the entire year) widely available in the study area, as well as in most Europe, ivy offers a great potential for air pollution monitoring with a high spatial- and temporal- resolution. Time-integrative biomonitoring is of particular interest as most PM related- health impacts are also due to long-term exposure. The obtained leaf SIRM results confirmed the validity of using enviromagnetic parameters for the identification and discrimination of different urban activities. The investigation of the magnetic differences between traffic and industrial PM, as well as railway PM, may enable source attribution (Hansard et al., 2011), which can be of great use for e.g. policy implementation of targeted PM mitigation strategies.

The influence of the different land use classes was registered both by the magnetic and metal analysis of leaf-deposited PM, which is a proxy for atmospheric PM concentrations. Given the correlations observed between a range of trace metals (Fe, Zn, Cd, Pb, and Mn) and leaf SIRM, magnetic measurements may work as an overall indicator of metal pollution. The occurrence of trace metals in the air and soil is of concern to the public health and the environment. Thus, magnetic parameters as a discriminatory tool for this specific type of pollution provides a rapid general overview for subsequent detailed monitoring. In addition to leaf SIRM, further research should include parameters such as magnetic susceptibility and anhysteretic remanent magnetization, for the production of magnetic bivariate ratios and plots for source apportionment.

The use of SIRM alongside with a particle analysis-based technique such as SEM/EDX allows the distinction between the different studied land use classes: forest and rural were rather comparable, but roadside, industrial and train presented a different magnetic behavior, as well as a different metal composition. The SEM/EDX offers an estimation of chemical composition, as well as information on particle size and shape, while magnetic measurements provide a cost-effective and efficient tool to identify pollutants. The complementary use of particle- and magnetic- based techniques is thus suggested as an integrated approach to investigate PM deposition on urban green.

5. Acknowledgments

This research was supported by a PhD grant of the Research Foundation Flanders (FWO). The authors thank W. Dorriné for his help and supervision on operating the SEM, and G. Nuyts and K. Wuyts for their valuable comments on data treatment. The authors also acknowledge the three anonymous reviewers for their constructive comments, which helped to improve the manuscript.

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