Research Article

Magnetic biomonitoring of airborne particles using lichen transplants over controlled exposure periods

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Abstract
Lichens are able to retain airborne pollution-derived particles in their thalli for a long time, and therefore, their use in assessing atmospheric pollution may be suitable and beneficial. In this study, we transplanted species of *Parmotrema pilosum* in bags and exposed them to atmospheric pollutants at different sites over the course of 1 year. The exposed lichen retained anthropogenic ferrimagnetic Fe oxides that were identified and characterized by environmental magnetism methods, X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The ubiquitous magnetite, released by metallurgical factories and vehicular sources, had small grain sizes (< 0.1–1 µm) falling in the range of harmful particulate matter $PM_{2.5}$ and $PM_{1.0}$. According to the anhysteretic ratios (χ_{ARM}/χ, ARM/SIRM), magnetic grain size tends to increase (ratios decrease) over time. Concentration-dependent magnetic parameters evidenced the cumulative presence of anthropogenic magnetite-like particles which reached high values during the study period, increasing from an initial mass-specific magnetic susceptibility χ value (mean ± S.D.) of $24.1 \pm 5.0 \times 10^{-8}$ m^3 kg^{-1} to higher values up to $51.2 \pm 23.0 \times 10^{-8}$ m^3 kg^{-1}. Joint analysis of meteorological data and magnetic susceptibility indicated a magnetic enhancement ($\chi/\chi_{initial}$) during the austral winter season when mean temperatures were lower; moreover, relative decreases in χ values after rainy periods are observed. This simple and low-cost methodology allowed us to study, in controlled exposure periods of 1–11 months, the ability of transplanted lichens to retain fine and ultrafine airborne particles that may have impacts on human health.

Keywords Atmospheric pollution · Biomonitor · FTIR · Magnetic PM · *Parmotrema pilosum* · SEM

1 Introduction

Lichens receive nutrients needed for their life processes from precipitation and dry deposition of airborne particles. Epiphytic species also have a high retention capacity for deposition of potentially toxic elements (PTE) and particulate matter (PM) due to the absence of a cuticle and root system [1]. Lichens are become good biomonitors because the exchange of gases occurs throughout the entire body, unlike leaves that do it through stomatal resistance [2]. Sloof [3] and Herzig et al. [4] assume that, within the thallus, trace element concentrations reach equilibrium with atmospheric levels and reflect environmental levels [5, 6].

The increasing urbanization has produced a higher load of pollutants, which adversely affects vegetation and makes it difficult to find native species for study. In urban areas where the presence of lichens may be reduced, the lichen transplant technique is a viable option to control atmospheric contamination and perform a convenient

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(high density, time controlled, etc.) sampling due to its low cost [1, 7, 8].

The lichen transplant technique consists of a bag, generally made of nylon, containing a couple of individual lichen. The advantages of this technique are the well-defined exposure time [9] and the possibility to assess the initial conditions of exposure: by determining the original elemental concentrations, flexibility both in site of deployment selection and in the number of sampling stations, and uniformity of entrapment surface. On the other hand, the disadvantages consist in the unknown collection efficiency for diverse pollutants in different species and, therefore, the impossibility of standardizing the exposure time for any one particular species or for any kind of source of pollution [10, 11]. The transplanted lichen techniques have been used in a variety of studies for the evaluation of air quality involving analysis of chemical and physiological characteristics, and it has been determined that some urban pollutants affect cell membranes [7, 12–14], produce changes in metabolism and symptoms of oxidative stress in the face of excessive exposure to elements such as Ni, Cu, and Cr [15, 16], and cause changes in photosynthetic pigments [7, 17].

Bakar et al. [18] studied the species *Usneabaileyi* using FTIR to determine the chemical composition of individuals living in natural environments without a pollution load, as well as those in polluted environments. Their results indicate that samples from natural sites have higher absorption intensity than those from polluted sites, and individuals living in polluted sites produced different amount of metabolites (dibenzofurans, xanthomas, and terpenoids) in order to survive and as an adaptation to the environment.

The combination of magnetic techniques and biological material (biomonitors) for the study of air pollution has been developed over the decades as an alternative method due to its low cost, small investment of time, and ability to handle a large volume of samples. Several authors have evaluated air quality in urban and industrial areas using these magnetic techniques and biomonitors. Among other biomonitors, researchers have used lichens [19–22], mosses [23–25], *Tillandsia* spp. [26, 27], tree leaves [28–30], and pine needles [31, 32].

A number of authors [20, 22–24, 33, 34] have used the techniques of environmental magnetism and biomonitoring along with complementary techniques (SEM and chemical analyses) to characterize spatial variations in anthropogenic pollution using different species of lichen. In previous studies in Tandil (Argentina), magnetic biomonitoring was carried out using lichens and methodologies identified as: (1) native species collection [20, 21] and (2) in situ magnetic susceptibility (κ_{is}) measurements or "in situ magnetic biomonitoring" [22], respectively. The first methodology used native lichen species living on tree bark in the study area that were collected and measured in the laboratory. The results allowed us to assess the ability of corticolous foliose and microfoliose species to accumulate PM and their suitability for magnetic biomonitoring, to evaluate the spatial distribution of atmospheric PM, to identify impacted areas through magnetic proxies for pollution (e.g., magnetic susceptibility and anhysteretic ratios), and to discriminate between vehicular traffic and industrial emissions. It is possible to apply this methodology in urban areas if enough individuals are available and well distributed; moreover, studies over time are not possible because of the sampling collection. The loss of species by collection, sample without reposition, was one of the main challenges for the second-mentioned methodology, as well as for the one used in this study (i.e., lichen transplants). In situ magnetic biomonitoring of *Parmotrema pilosum* species [22] is the first historically methodology which allows study of species over time because they are preserved in their habitat (tree bark). Such studies also allow us to determine the magnetic particle (falling into categories $PM_{2.5}$ and $PM_{1.0}$) distribution on the lichen's thallus surface from weekly κ_{is} measurements over 16 months.

As previously mentioned, species preservation is not the only advantage of this novel methodology; more importantly, it is possible to collect measurement data over any time period, from weeks to days to years. This method provides a useful low-cost tool that allows assessment of atmospheric pollution over different periods of time. On the other hand, the species transplantation methodology proposed in this study is another alternative methodology to consider because it can be used when native lichen species are absent, scarce, or unevenly distributed in the study area. The usefulness of this methodology is the ability to control initial exposure conditions, control time periods for sampling, measure magnetic properties (concentration, mineralogy, and grain size) over time, and choose sites of concern for purposes of temporal monitoring or control of airborne magnetic PM emissions.

The objectives of this work are: (a) to study the temporal accumulation of airborne pollution particles in transplanted species of *P. pilosum*, (b) to study the influence of meteorological conditions on lichen transplants during the year, and (c) to validate the use of this methodology (magnetic biomonitoring) for assessing the anthropogenic pollution in urban areas over controlled periods. For this purpose, the lichen transplant technique was used in selected sites in the urban area of Tandil city in Argentina. Magnetic properties were complemented with other independent data, such as FTIR, XRD, and meteorological data (monthly rainfall and temperature).

2 Methods

2.1 Study area

The study area (Fig. 1) is located in an urban zone of Tandil city (37° 19.5′ S 59° 08.3′ W), which is located in the southeast of Buenos Aires, Argentina. Tandil is a medium-sized city (2360 inhabitants per km^2 [35]) and has approximately 60,000 vehicles, including cars, trucks, and heavy transport [36]. Currently, some metallurgical factories are located inside the urban area, and therefore, vehicle and industrial emissions, which are identified as the main sources of air pollutants, are transported, dispersed, and deposited in this urban environment [21, 37].

Tandil city is located in the Pampean region and is characterized by a sub-humid to humid climate, with distinctive summer (hot and rainy) and winter (cold and dry) seasons. Meteorological analysis by Picone and Campo [38, 39] and Sosa [36] in 2001–2010 indicates an annual precipitation of 845.2 mm and an annual mean temperature of 13.4 °C.

The analysis of meteorological data for the study period (October 2013–October 2014) gives an annual precipitation of 1174 mm and maximum and minimum mean temperatures of 38.7 °C and −5 °C, respectively [40].

2.2 Lichen sampling and bag preparation

Parmotrema pilosum species was selected in previous studies [20, 21] because of its availability in the study area and its ability to adsorb and accumulate PM present in the air.

Lichen samples were collected in October 2013 from a natural area that has a high tree density (site S0, Fig. 1). This area is located far away from the study area, and therefore, minimal pollution influence from industrial and vehicular emissions is expected.

In the laboratory, each collected lichen (and its tree bark substratum) sample was cleaned by immersion using distillate water. Seventy-two lichen bag samples were prepared including their substrata to avoid stress during transplantation. Each lichen bag was prepared with five lichens of similar size (approximately 3 g in total) and put in nylon nets (mesh of 2 mm^2) of 10 cm × 15 cm. At each site, 12 lichen bags were transplanted simultaneously during November 2013. The bags were located at a height of 2.5 m to avoid contamination by soil particles. The sampling collection of transplanted lichens was carried out monthly at six sites (S1, S2, S3, S4, S5, and S6, Fig. 1) during 1 year. All sites are influenced by industrial and vehicular PM emissions, which are dispersed throughout the area.

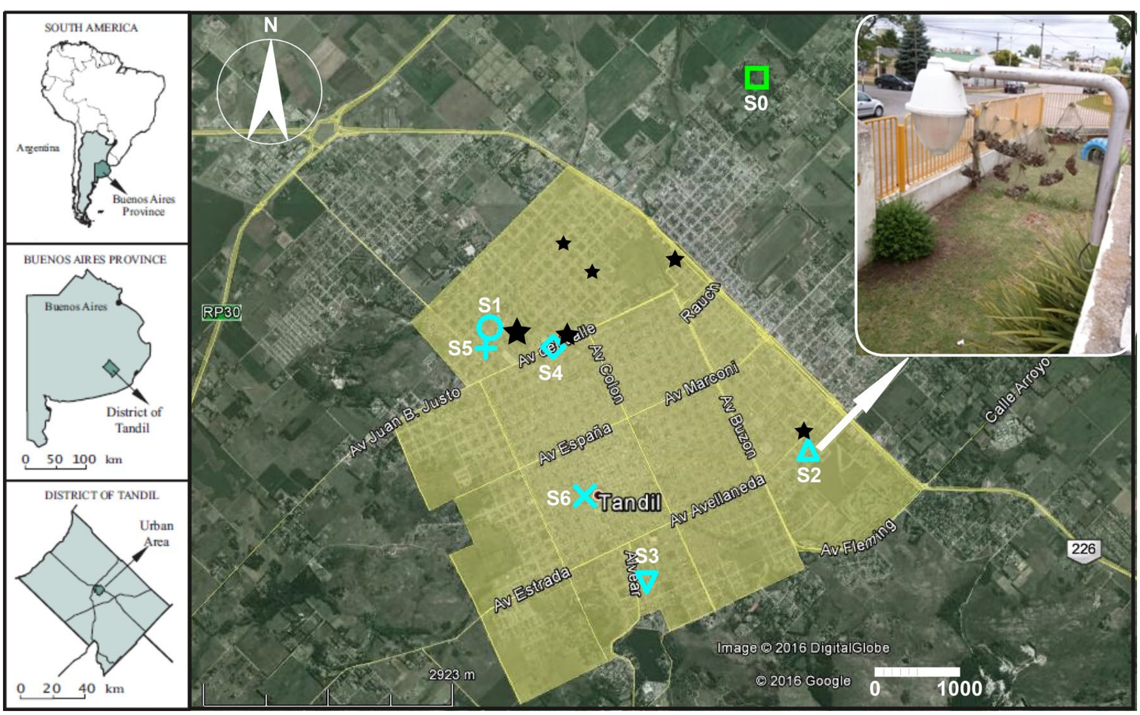

Fig. 1 Study area of Tandil city. Collection site of species *Parmotrema pilosum* (green square, S0), sites with transplanted lichens (S1–S6) and metallurgical factories (black stars); the largest star corresponds to the most important one

For mobile pollution sources, a different influence on lichen bags is expected with respect to their proximity to main avenues, as well as if the bags faced the streets (sites S1, S2, and S4). Sites S3 and S6 were located in a backyard. Sites S1, S2, S4, and S5 were located near metallurgical factories (Table 1) where a higher contribution of coarser particles was expected.

From December 2013 to October 2014, one exposed lichen bag per site was collected each month. After collection, lichens were dried in paper bags for a period of 7 days and stored in the Laboratory of Environmental Magnetism at the CIFICEN-IFAS-UNCPBA (Argentina). After this period, these lichens were dried in an oven at 25 °C for 2 days and then ground using a hand grinder with a plastic blade. The pulverized material (0.9–1.3 g) was placed in plastic containers 2.3 cm^3 and firmly pressed to prevent physical movement in the sample holder. During the period of study, there was a loss of 26 samples, which cannot be replaced: 7 samples were lost from S1 by vandalism; 1 sample each from S2, S3, and S4 was lost due to stress during the month 12; 5 samples for S5 and 11 samples for S6 were directly affected by human activities such as construction emissions and cleaning products.

2.3 Magnetic measurements

Magnetic properties were determined in the Laboratory of Environmental Magnetism at the CIFICEN-IFAS-UNCPBA (Tandil, Argentina). Magnetic susceptibility measurements were taken using the susceptibility meter MS2 (Bartington Instruments Ltd.) connected to the MS2B dual-frequency sensor (470 and 4700 Hz). Mass-specific magnetic susceptibility χ was calculated using the volume magnetic susceptibility (κ) measurement and the sample weight. Readings of κ were done for each sample in the higher sensitivity range (0.1×10^{-5} SI). The anhysteretic remanent magnetization (ARM) was imparted by superimposing a DC field of 90 µT to an AF peak of 100 mT using a partial ARM device attached to a shielded demagnetizer (Molspin Ltd.); isothermal remanent magnetization (IRM) was imparted with a pulse magnetizer model IM-10-30 (ASC Scientific Ltd.). The remanent magnetization after each step was measured using a Minispin fluxgate spinner magnetometer by Molspin Ltd., which has a noise level $< 2.5 \times 10^{-5}$ A/m and a sensitivity of 10^{-4} A/m. Specific anhysteretic susceptibility (χ_{ARM}) was estimated using linear regression for the acquired ARM at different DC bias fields (7.96, 47.75 and 71.58 A/m). The saturation of IRM (SIRM), the anhysteretic ratios χ_{ARM}/χ and ARM/SIRM, the King's plot (χ_{ARM} vs χ), the remanent coercivity (H_{cr}), the S ratio (-IRM_{-300mT}/SIRM), and the ratio SIRM/χ were also determined.

2.4 Microscopy, element determinations, FTIR, and XRD

Selected lichens' thalli without any magnetic extraction were examined by SEM at the CIFICEN-UNCPBA (Olavarría, Argentina) using a microscope model MA10 by Carl Zeiss SMT Ltd. Before SEM observations, each specimen was prepared with a thin coating of Au/Pd by a metalizer

Table 1 Sites and description of collection sites of *P. pilosum* (S0) and transplanting sites for the magnetic biomonitoring sites (S1–S6) in Tandil city (Argentina)

Site	Latitude (UTM m E); longitude (UTM m S)	Site information, lichen's bag location, and pollution sources	Weight of transplanted lichens (g)	Weight of recovered lichens (g)
S0	312410.00; 5871525.00	Control site, semi-urban area (~5.5 km from the town)		
S1	309311.78; 5868470.88	Site close to an important metallurgical factory. Bags located close to the sidewalk in an open area that faces to the street, at 2.5 m above ground. Vehicular emissions (street low traffic)	3.00–3.50	0.93–1.17
S2	313180.34; 5867124.73	Site close to two metallurgical factories (one of them out of service). Bags located close to the sidewalk, in an open area that faces to the street. Located at 3 m above ground. Vehicular emissions (street low traffic)	3.00–3.50	1.02–1.19
S3	311293.79; 5865554.25	Site far from industrial sources (~3 km). Bags placed in a backyard, at 2.0 m above ground. Vehicular emissions (street moderate traffic)	3.00–3.50	0.92–1.16
S4	310105.69; 5868277.57	Site close to two important metallurgical factory. Bags located close to the sidewalk, in an open area that faces to the avenue, at 3.0 m above ground. Vehicular emissions (avenue high traffic)	3.00–3.50	1.10–1.17
S5	309288.53; 5868237.21	Site close to an important metallurgical factory. Bags placed in a backyard. Located at 2.0 m above ground. Vehicular emissions (street low traffic)	3.00–3.50	0.76–1.14
S6	310531.59; 5866521.55	Site far from industrial sources (~2 km). On a public building at downtown. Bags located close to the sidewalk, in an open area that faces to the street, at 6.0 m above ground. Vehicular emissions (street moderate traffic)	3.00–3.50	1.14

EMITECH module SC7720 sputter coater. The elemental composition was analyzed by X-ray energy-dispersive spectroscopy (EDS). The system used was an EDS Oxford Model INCA Energy, equipped with a laser particle size analyzer (or analyzer particle size distribution by laser diffraction) Malvern Mastersizer 2000E with dry dispersion module Sirocco 2000 M.

The FTIR and XRD studies were carried out in the Laboratory of Chemistry at the UNCPBA (Olavarría, Argentina). The FTIR behavior was analyzed to get information about the mineralogical composition of accumulated PM on lichens. A magnetic extract of about 1 mg was used to carry out this study; this extract was obtained by using a hand magnet. Infrared spectra were recorded on a Nicolet-Magna 550 FTIR instrument with CsI optics, using the KBr pellet technique. The source was a Mid-Far IR and a detector DTGS CsI (6400–200 cm^{-1}). The XRD analysis was performed on a Philips PW 3710 diffractometer, with a Cu anode and graphite monochromator, using radiation of $\lambda = 1.5405$ Å. A diffraction sweep was performed in the range of angles 2θ between 5° and 70° with a sweep speed of 0.5° min^{-1}.

3 Results and discussion

3.1 Properties of particles on unexposed lichens

Prior to transplant, magnetic measurements were taken on three ($n = 3$) prepared (cleaned and pulverized material) samples collected from site S0 located about 5.5 km from downtown. Such measurements allow determination of the initial conditions for this magnetic biomonitoring period, that is, the magnetic properties of natural particles deposited on the lichens' thallus which could not be removed by water immersion.

The values (mean ± S.D.) of concentration-dependent magnetic parameters χ, ARM, and SIRM are $24.1 \pm 5.0 \times 10^{-8}$ $m^3\ kg^{-1}$, $182.6 \pm 26.4 \times 10^{-6}$ A $m^3\ kg^{-1}$, and $4.8 \pm 0.8 \times 10^{-3}$ A $m^2\ kg^{-1}$, respectively. Such values are in agreement with ones from control sites reported by Chaparro et al. [20]. Among foliose and microfoliose species, they reported similar values ($\chi = 23.4 \pm 8.0 \times 10^{-8}$ $m^3\ kg^{-1}$, ARM $= 164.4 \pm 51.5 \times 10^{-6}$ A $m^3\ kg^{-1}$; SIRM $= 3.9 \pm 1.2 \times 10^{-3}$ A $m^2\ kg^{-1}$) for *P. pilosum* collected on a rural site located about 5 km from downtown Tandil.

Magnetic mineralogy of these entrapped particles corresponds to ferrimagnetic minerals such as magnetite ($H_{cr} = 37.4 \pm 0.2$ mT) with high values of grain size-dependent magnetic parameters, such as $\chi_{ARM}/\chi = 10.6 \pm 0.7$ and ARM/SIRM $= 0.039 \pm 0.001$, indicating the presence of fine magnetic grains. These results are in agreement with the control values ($\chi_{ARM}/\chi = 10.0 \pm 0.6$ and ARM/SIRM $= 0.042 \pm 0.000$) corresponding to Chaparro et al. [20].

SEM observations of particles trapped on lichen thalli from clean site S0 are shown in Fig. 2a. Such particles comprise semi-spherules and particles with irregular morphology. In a thallus area of 2200 μm^2, 35 particles were classified by size. Six percent were larger than 5 µm, 11% were between 5 and 2.5 µm, 14% were between 2.5 and 1 µm, and the remaining 69% of particles were smaller than 1 µm.

3.2 Exposed lichens: their composition and accumulated particles

The XRD diffraction pattern (Fig. 3a) of a magnetic extract from a lichen sample (site S4 at month 10) shows characteristics of substances of low crystallinity. Registered peaks are at low or medium intensity, and they appear on an intense background, attributable to known fluorescence Fe compounds, which generate the Cu radiation used in this analysis. However, it was possible to identify characteristic peaks of different minerals of interest, that is, Fe oxide minerals such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3). The SiO_2 quartz peaks dominate the diffraction pattern, with intense signals at 3.34 and 4.26 Å. Due to the preferential orientation of the crystallites, quartz is detectable whether it is in very low proportion or a major crystalline phase. It is also possible to find cristobalite, the other structural variety of silica.

In addition, two samples from sites S3 and S4 (collected at month 10) were analyzed by FTIR (Fig. 3b) and both showed strong bands across the spectral range. The broad and intense absorption at high and medium energy is evidence of hydroxylated compounds from organic material, while compounds attributed to inorganic minerals would be located in areas of medium and low energy. The spectroscopic characterization by FTIR is very useful for detection of amorphous components, mainly organic compounds, which do not appear in the XRD pattern.

Iron oxide bands appear with medium resolution, such as on the shoulder, in the low-frequency range (below 600 cm^{-1}), which may partially overlap with quartz vibrations. The presence of quartz, detected by XRD, is confirmed by a poorly resolved doublet located in the lower region of the spectrum, between 800 and 781 cm^{-1}.

According to the analysis of the FTIR spectra (Fig. 3b), functional groups compatible with the chemical composition of main lichen components, including usnic acid and its derivatives, were identified (Supplementary Data, Table I) [41]. Carboxylate groups (–CO (OH)), hydroxyl (–OH), and amine (–NH_2), and other groups containing O-atom electron donors could be identified, which can act as ligands coordinating metal organics (Fe oxides, Fe sulfides, and

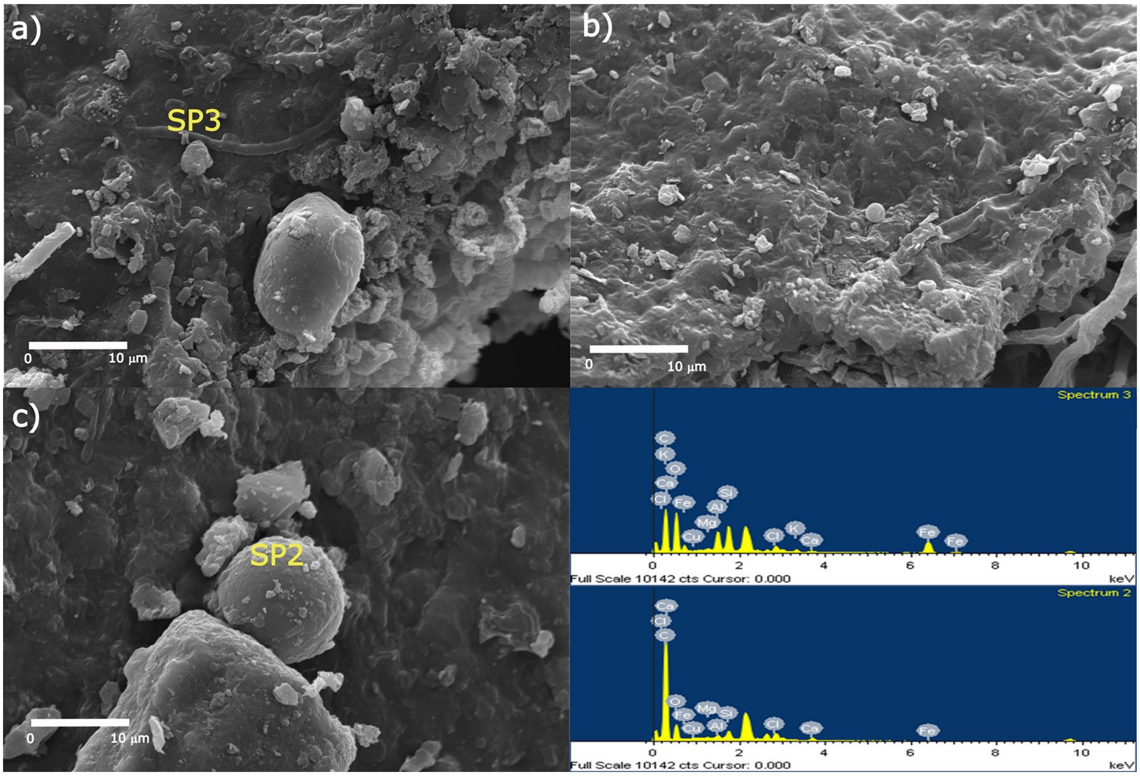

Fig. 2 SEM observations for S0 and exposed lichen's thallus after 9 months corresponding to sites S3 and S4. **a** control site (S0); **b** site with vehicular emissions (S3, located south of the study area); **c** site close to metallurgical factories (S4). The EDS spectra of particles are shown in (**d**)

quartz). The shift of the characteristic bands of these groups suggests the formation of coordination bonds to form a ligand–metal complex. Lichen compounds play an essential role in the adsorption of pollutants (PM and PTE); therefore, they can behave as true biomonitors of the environment.

SEM observations of exposed lichen thalli after 9 months are shown in Fig. 2b, c and correspond to sites with vehicular (S3) and industrial (S4) influences, respectively. Particles from S3 are displayed in Fig. 2b, and the grain size count shows that 4% of particles are 5–2.5 µm, 33% of particles range from 2.5 to 1 µm, and 63% of the smaller irregular particles are ≤ 1 µm, which are consistent with those produced by vehicular emissions. On the other hand, for S4 (Fig. 2c), 32% of particles correspond to coarse particles (> 5 µm), while 24% and 44% of them are 2.5–1 µm and < 1 µm, respectively. These coarser particles are associated with pollutants released by metallurgical factories in this area.

The analysis of accumulated particles on lichen thalli shows gradual changes in concentration and magnetic mineralogy during the exposure period of collection (Supplementary Data, Table II). Accumulated magnetic particles are ferrimagnetic ones according to the IRM curves and to the S ratio values that varied between 0.92 and 1 for all samples during the study period, i.e., 46 samples from sites S1–S6. The H_{cr} values decreased slightly with exposure time (Fig. 4), from 37.9 to 32.4 mT, indicating the anthropogenic contribution of lower coercivity or magnetically softer minerals such as magnetite-like minerals released by traffic-derived (H_{cr} = 17.4–33.1 mT; [42]) and metallurgical factory (H_{cr} = 37.2–37.6 mT; [20]) emissions. Similar results were obtained by Salo et al. [33] for samples of transplanted mosses (H_{cr} = 22.4–38.9 mT) near a Cu–Ni smelter and native lichen species *Hypogymnia physodes* (H_{cr} = 28.2–33.5 mT) collected from Turku city, Finland.

In general, it is observed from parameters χ_{ARM} and χ (the King's plot, Fig. 5a) that these magnetic grains are between < 0.1 and 0.2 µm, corresponding to harmful inhalable PM that belongs to the $PM_{2.5}$ and $PM_{1.0}$ categories. Both PM categories have adverse effects on human health that involve breathing and cardiovascular diseases, asthma, and possibly mental disorders (e.g., [43, 44]). Such particles are able to reach deep portions of the respiratory system such as the pulmonary alveoli and interact directly with the bloodstream quickly reaching vital organs such as the heart and causing cell damage [45]. In addition, Maher et al. [46] proved that anthropogenic ultrafine iron-rich

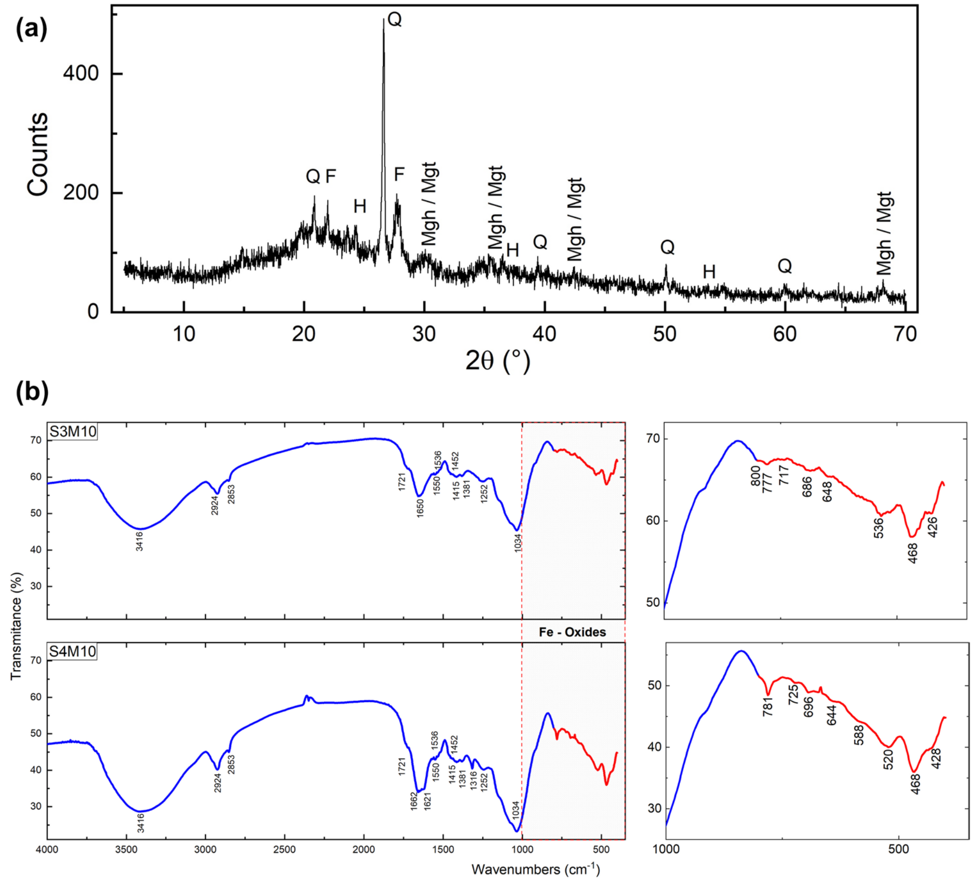

Fig. 3 **a** XRD diffraction pattern on magnetic extract of lichen samples from site S4 at month 10. Nomenclature used for the identified minerals: maghemite/magnetite (Mgh/Mgt), hematite (H), quartz (Q), feldspar (F). **b** FTIR on magnetic extract of two lichen samples from sites S3 and S4 at month 10

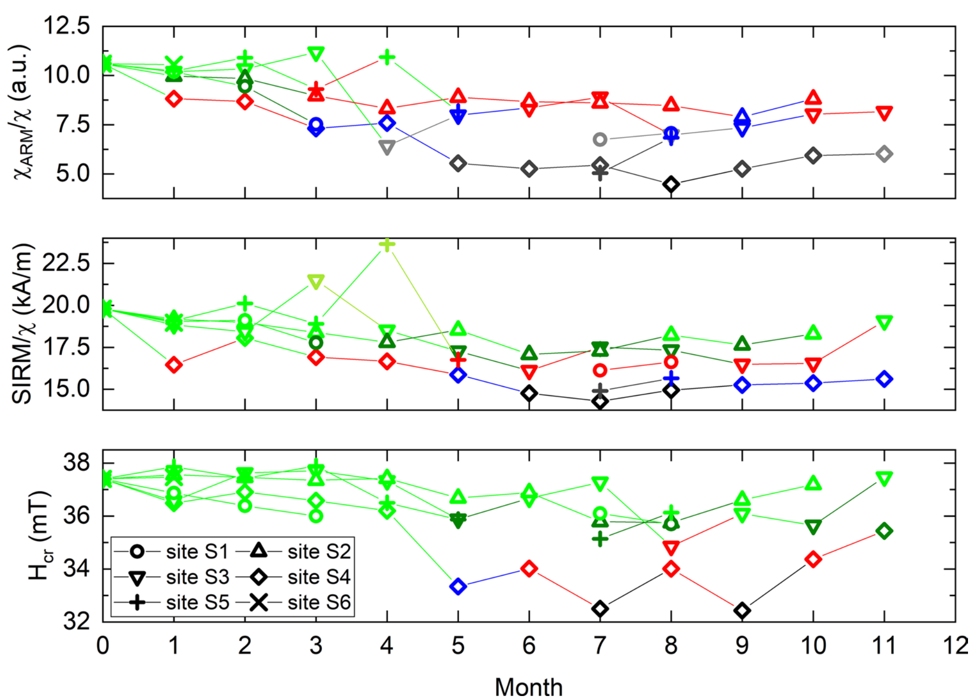

Fig. 4 Monthly χ_{ARM}/χ, SIRM/χ, and H_{cr} values for collected samples from lichen transplants, sites S1–S6. The 1-year period corresponds to November 2013–October 2014

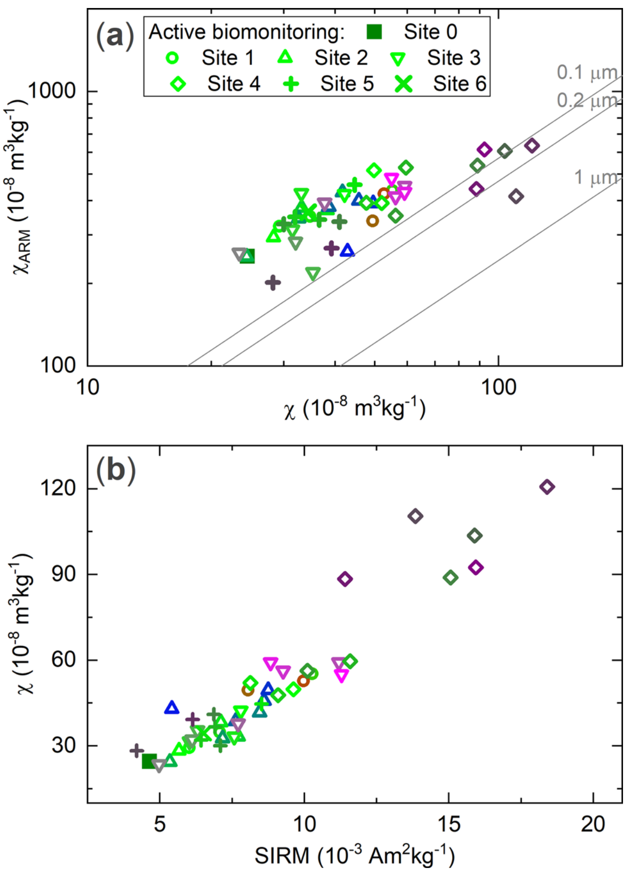

Fig. 5 **a** Magnetic grain size estimation using parameters χ_{ARM} and χ and **b** concentration-dependent magnetic parameters for monthly collected samples of *P. pilosum* transplants (1-year period)

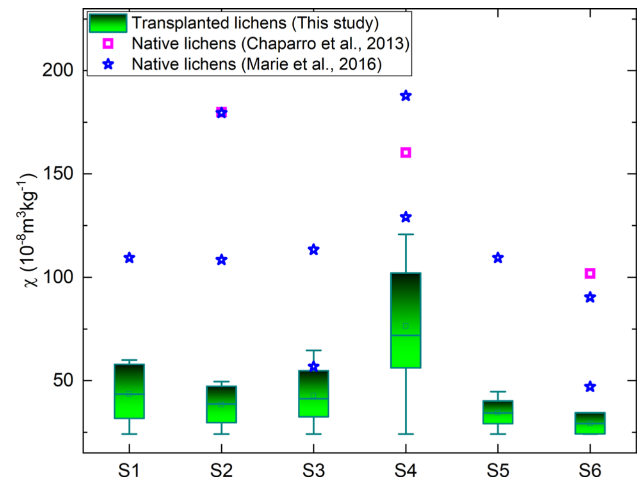

Fig. 6 Measured values of χ for this study using transplanted *P. pilosum*. Reported values are displayed for comparison purposes and correspond to sites located near sites S1–S6 when available. Previous studies using native *P. pilosum* in 2011 [20] and 2012–2013 [21]

particles (< 0.2 µm) can be transported and biologically accumulated in the human brain via the olfactory bulb and may be associated with neurodegenerative diseases such as Alzheimer's disease.

Values of grain size-dependent magnetic parameters are lower ($\chi_{ARM}/\chi = 8.1 \pm 1.8$ and ARM/SIRM = 0.033 ± 0.005, Supplementary Data, Table III) than the corresponding ones from the control site (month 0, see Sect. 3.1), and consist of relatively coarse grains. Both independent ratios are significantly correlated ($R = 0.84$, $p < 0.01$) and show a decay with time (Fig. 4) which indicates the increasing contribution of coarser magnetic particles during the latter months of the study period.

The concentration of magnetic particles was dominated by ferrimagnetic minerals—among diamagnetic, paramagnetic, and antiferromagnetic—as observed from the significant correlation between χ and SIRM ($R = 0.98$, $p < 0.01$; Fig. 5b). These parameters and ARM evidence the cumulative presence of anthropogenic magnetite-like particles reaching ever-increasing values during the period. The mean values of such parameters, i.e., $\chi = 51.2 \pm 23.0 \times 10^{-8}$ m^3 kg^{-1}, ARM = $280.9 \pm 72.2 \times 10^{-6}$ A m^3 kg^{-1}, SIRM = $8.7 \pm 3.1 \times 10^{-3}$ A m^2 kg^{-1} (Supplementary Data, Table III), surpass twofold their initial values.

Site S4, located near important metallurgical factories on an avenue with high vehicular traffic, presented the highest values of $\chi = 76.5 \pm 29.4 \times 10^{-8}$ m^3 kg^{-1}. These results are comparable with those registered in the magnetic biomonitoring of native lichens by Chaparro et al. [20] and Marié et al. [21] whose values for that area were 160.3×10^{-8} m^3 kg^{-1} and $129.0–187.8 \times 10^{-8}$ m^3 kg^{-1}, respectively (Fig. 6). Sites S1 and S5, both close to one important metallurgical factory, had high values of χ, i.e., $45.2 \pm 17.5 \times 10^{-8}$ m^3 kg^{-1} and $34.5 \pm 7.0 \times 10^{-8}$ m^3 kg^{-1}, respectively. These results are lower than those obtained by previously mentioned studies [21], $\chi = 109.5 \times 10^{-8}$ m^3 kg^{-1}. Site S2 is close to two factories and has lower values of χ ($38.4 \pm 9 \times 10^{-8}$ m^3 kg^{-1}) than previously reported data, $\chi = 179.9 \times 10^{-8}$ m^3 kg^{-1} [20] and $108.5–179.4 \times 10^{-8}$ m^3 kg^{-1} [21]. It is worth mentioning that during the transplant period (December 2013 to October 2014), these factories reduced their activity and the most impactful one was out of service.

On the other hand, site S3, located far away from metallurgical factories, showed relatively high values of χ ($42.7 \pm 13.1 \times 10^{-8}$ m^3 kg^{-1}), although the results were lower than previously reported data for this area ($\chi = 56.8–113.3 \times 10^{-8}$ m^3 kg^{-1}). Site S6 was located downtown where the main source of pollutants is vehicle emissions, and values of χ were also lower ($29.3 \pm 7.3 \times 10^{-8}$ m^3 kg^{-1}) than reported ones, i.e., 101.8×10^{-8} m^3 kg^{-1} [20] and $47.0–90.4 \times 10^{-8}$ m^3 kg^{-1} [21].

It is important to mention and clarify that Chaparro et al. [20] and Marié et al. [21] carried out their studies in

2011 and in 2012–2013 using native lichens (they did not use transplanted lichens); therefore, higher χ values are expected in those studies because native lichens accumulate PM throughout their long life time. On the other hand, values reported in this study, using transplanted lichens, are representative of controlled periods up to 1 year. Although all χ values are lower for this magnetic biomonitoring using lichen transplants than both previously cited studies using native lichens [20, 21], the transplanted *P. pilosum* showed a high accumulation of magnetic particles during this relatively short period.

3.3 Biomonitoring of magnetic PM

Increasing temporal changes in magnetic parameters χ, ARM, and SIRM evidenced an important accumulation of magnetic particles during the 1-year period. The amount of such magnetic particles seems to increase from the 3rd and 4th month (February–March) when their relative concentration increased ($\chi/\chi_{initial} \approx 1.5/2.5$, Fig. 7) in relation to natural particles present in native lichens from site S0. The grain size-dependent magnetic parameters χ_{ARM}/χ, SIRM/χ (Fig. 4), and ARM/SIRM showed a decreasing trend when magnetic concentration increased, which indicates that higher magnetic concentrations are associated with relatively coarse magnetic grains. The presence of coarse magnetic particles was apparent after months 4 and 5 (March–April) when the anthropogenic contribution seemed to balance or dominate the natural contribution (on site S0) of magnetic particles trapped on the lichens' thallus. Although the anthropogenic magnetite-like minerals showed differences for parameters, H_{cr}, SIRM/χ, and χ_{ARM}/χ (Fig. 4), between site S4 and the others, magnetic mineralogy changed only slightly with time at each site, indicating the existence of a primary pollution source.

Monthly values of χ, rainfall, and mean temperature data during the study period are shown in Fig. 7 for comparison purposes. Changes in specific magnetic susceptibility in relation to the initial month ($\chi = 24.1 \pm 5.0 \times 10^{-8}$ m^3 kg^{-1}) reached increments more than twofold initial values between the 7th and 9th months at sites S1, S2, and S3 (i.e., $\chi = 52.7 \times 10^{-8}$ m^3 kg^{-1}, 49.6×10^{-8} m^3 kg^{-1}, and 59.2×10^{-8} m^3 kg^{-1}, respectively; Fig. 7). The highest increment of χ ($= 120.7 \times 10^{-8}$ m^3 kg^{-1}), a fivefold initial value, was observed for site S4 between the 8th and 9th months. This significant increase is due to the proximity of two important metallurgical factories plus vehicular influence on transplanted lichen facing an avenue.

Sites S1 and S4 near these important metallurgical factories showed, in general, higher χ values than the other sites up to the 7th month. Lichen bags at S3 were located in an interior backyard, and the atmospheric pollutants came from a street with minor traffic; moreover, its location is far from industrial sources (about 3 km). On the other hand, the lichen bags at site S2 faced a street with minor traffic; they were also influenced by a small metallurgical factory approximately 0.2 km away.

The most significant χ increases were from April 2014 for transplanted samples at S4 (metallurgical and vehicular influence). The most pronounced decline for this site took place between September and October 2014. For S1, S2, and S3, the increases and decreases in χ values were gradual and not simultaneous at these three sites. In particular, samples collected at S2 and S3 showed an important

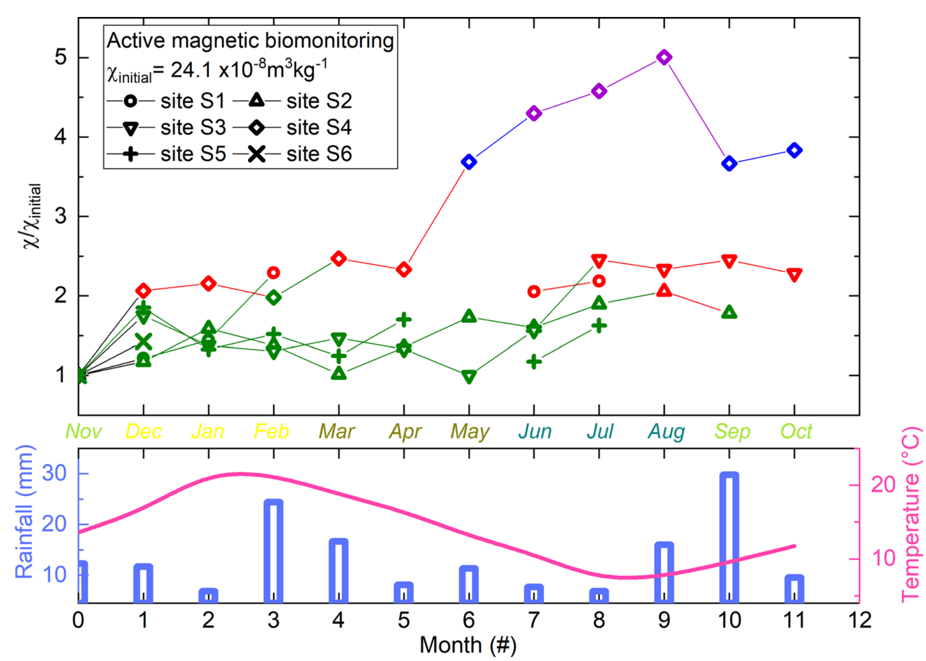

Fig. 7 Monthly specific magnetic susceptibility ($\chi/\chi_{initial}$) values of collected samples from transplant sites (magnetic biomonitoring). Temperature and rainfall data for Tandil city recorded by the National Meteorological Service from November 2013 to October 2014 [40]

increase in χ in March 2014 and May 2014, respectively (Fig. 7).

A magnetic enhancement ($\chi/\chi_{\text{initial}}$) was observed during the austral winter season when mean temperatures were low (7.1–10.7 °C) and rainfall varied between 6.9 and 16.0 mm. Decreases in χ values were observed after intense rainy periods, e.g., February and September 2014, such decreases seem to be caused by the superficial washing of particles deposited on the lichens' thallus and by a reduction of airborne PM in the air due to wet deposition. Marié et al. [22] observed similar changes in PM trapped by the species *P. pilosum* through detailed in situ measurements of magnetic susceptibility. Matzka and Maher [47] and Castañeda-Miranda [48] reported the rainfall effect on reducing the trapped magnetic particles on tree leaf surfaces. The rainwater effect is more important on tree leaves than on lichens. The epiphytic species does not have a root system, a protective cuticle, or stomata and is able to accumulate nutrients, metals, gases, and PM from the atmosphere via both wet and dry deposition [49, 50].

4 Conclusions

Analysis of magnetic parameters indicates that trapped magnetic particles are ferrimagnetic, i.e., magnetite-like minerals. XRD and FTIR studies confirmed the presence of these Fe oxides (magnetite/maghemite and hematite) for transplanted lichen samples exposed to atmospheric pollution. In addition, carboxylate (–CO (OH)), hydroxyl (–OH), and amine ($-NH_2$) groups were identified by FTIR spectra, suggesting the formation of coordination bonds to form a ligand–metal complex. Lichen compounds play an essential role in the adsorption of PM and PTE.

Although values of grain size-dependent magnetic parameters are lower (e.g., $\chi_{ARM}/\chi = 8.1 \pm 1.8$) than in unexposed samples, magnetic grains are < 0.1–1 µm in size and correspond to dangerous PM categories ($PM_{2.5}$ and $PM_{1.0}$) for humans and other living things because they are highly inhalable. These particles are able to reach deep portions of the respiratory system and cause many adverse effects on human health, i.e., cell damage to the heart and cardiovascular diseases, asthma, and neurodegenerative diseases such as Alzheimer's, among others.

The independent ratios χ_{ARM}/χ, SIRM/χ, and ARM/SIRM showed a decay with time that indicates an increasing contribution of coarser magnetic particles in the latter months of the study period. SEM observations of exposed lichen thalli showed that particles ≤ 1 µm were in higher proportion for vehicular sites (S3) than for metallurgical sites (S4), which reflects and confirms the production of fine particles by vehicular traffic and relatively coarser particles by metallurgical factories.

This methodology showed the ability of transplanted *P. pilosum* to retain magnetic particles for short periods of time. In general, higher magnetic concentrations are associated with relatively coarser magnetic grains. Concentration-dependent magnetic parameters demonstrated the cumulative effect of anthropogenic magnetic particles at different sites and in different seasons. For example, sites S4 and S2, located near two metallurgical factories, experienced significant increases in magnetic concentration (twofold and even fivefold initial values of χ, up to $125.0 \times 10^{-8}\ m^3\ kg^{-1}$); moreover, site S3, influenced by vehicular emissions, reached high magnetic concentration values (twofold the initial values of χ). Concentrations of accumulated magnetic particles during exposure periods of months were lower than values reported in previous studies using native lichen species collections [20, 21]. This fact evidences that monthly and annual accumulation of PM by *P. pilosum* is not enough to reach a state of PM saturation, that is, longer periods are required to reach saturation as evidenced by native lichens collected in urban areas who trapped/accumulated magnetic PM throughout their long life history, which may take up to several decades.

The accumulation of airborne particles on the transplanted lichens, determined by parameters χ and SIRM, was influenced by meteorological conditions (temperature and rainfall). Values of concentration-dependent magnetic parameters increased during the winter season (lower temperatures) and decreased after periods of intense rainfall; the latter due to partial washing of particles deposited on the lichen's thallus, as well as an overall reduction of PM in the air. This temporal pattern, observed in 2013–2014 by lichen transplants, is in agreement with a study recorded over 2016–2017 using another methodology—in situ magnetic biomonitoring [22]. Both methodologies, as well as traditional monitoring of PM, record seasonal changes in airborne PM via the lichen's ability to trap and retain particles on its thallus.

Also, magnetic biomonitoring using lichen transplants is an efficient tool for studying the impact of anthropogenic particles over controlled periods of time, on the order of months. Although in situ magnetic biomonitoring is the first historically methodology that allowed study of species over time, it also produced an important collection of measurement data and helped to preserve species in their habitat. The lichen transplant methodology is an alternative strategy that can be used when native lichen species are scarce or unevenly distributed over target areas. This methodology allows scientists to select sites of concern for purposes of temporal monitoring and/or control of airborne magnetic PM emissions.

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Compliance with ethical standards

Conflicts of interest The authors declare no conflict of interest.

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