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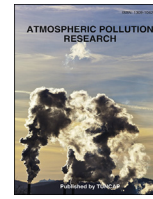

Original article

Magnetic mapping of air pollution in Tandil city (Argentina) using the lichen *Parmotrema pilosum* as biomonitor

Débora C. Marié [a], Marcos A.E. Chaparro [a,*], María A. Irurzun [a], Juan M. Lavornia [b], Claudia Marinelli [c], Rosana Cepeda [c], Harald N. Böhnel [d], Ana G. Castañeda Miranda [d], Ana M. Sinito [a]

[a] *Centro de Investigaciones en Física e Ingeniería del Centro de la Provincia de Buenos Aires (CIFICEN, CONICET-UNCPBA), Pinto 399, 7000 Tandil, Argentina*
[b] *CINEA Centro de Investigaciones y Estudios Ambientales, FCH, UNCPBA, Pinto 399, 7000 Tandil, Argentina*
[c] *Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Pinto 399, 7000 Tandil, Argentina*
[d] *Centro de Geociencias-UNAM, Boulevard Juriquilla No. 3001, 76230 Querétaro, Mexico*

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The lichen *Parmotrema pilosum* is sensitive to pollution and it can live accumulating airborne pollutants for long time, such characteristic allows its use as biomonitor for environmental mapping in urban areas when this epiphytic specie is available. In this work, we investigated the use of such passive collector and magnetic techniques to monitor the air pollution in Tandil, a city located in Buenos Aires province with approximately 125,000 inhabitants, 60,000 vehicles and various metallurgical factories inside the urban area. The sampling strategy was carried out following a random stratified design and measuring magnetic susceptibility, magnetic hysteresis loops, anhysteretic and isothermal remanent magnetization and thermomagnetic studies to determine the magnetic properties of airborne particles accumulated on lichen samples. Scanning electron microscopy observations show particles with different morphologies (individual particles, spherules and aggregates) and composition (Fe, Al, Ni, Cr, Ti, Cu, K and Br) produced by metallurgical factories and by gaseous/solid vehicle emissions. The magnetic mineralogy shows the predominance of pseudo-single domain magnetite-like mineral and the magnetic grain size estimations indicate the presence of fine particles (<0.1 μm) in sites with low vehicular traffic or less polluted, while sites more affected by pollution (high vehicular traffic and metallurgical industries) are characterized by coarser magnetic grain size particles, between 0.1 and 5 μm. Mass-specific magnetic susceptibility was represented in a 2-D contour map to observe in detail the distribution of magnetic particles in this urban area, giving high values (up to 1161.2×10^{-8} m^3 kg^{-1}) that are indicative of areas with high pollution loading.

1. Introduction

An organism is considered a biomonitor when provides quantitative information on the quality of the environment around it, for example air pollution. Some species are unable to adapt ecology or genetically to the altered environmental condition, so its absence is indicative of problems (Nimis et al., 2002; Lijteroff et al., 2009). Biomonitors have several advantages concerning the detection of pollution emission sources such as low costs, the possibility to register the effects of pollution for long periods of time and the possibility of monitoring many sites simultaneously (Wannaz et al., 2006). Some biomonitors can respond to pollution by altering their physiology or their ability to accumulate elements or substances (Lijteroff et al., 2009).

Lichens can be considered as biological indicators of environmental changes, they are sensitive to different pollutants and hence its utilization for environmental monitoring is increasingly common. There are recent studies presented by Jordanova et al. (2010), Salo et al. (2012) and Chaparro et al. (2013) that use magnetic

* Corresponding author. CIFICEN (CONICET-UNCPBA), Pinto 399, 7000 Tandil, Argentina. Tel.: +54 249 4385661; fax: +54 249 4385669.
E-mail address: chapator@exa.unicen.edu.ar (M.A.E. Chaparro).

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techniques and biomonitors for anthropogenic pollution monitoring in Europe and South America. The lichen capacity to accumulate large amounts of trace elements and the sensitivity to them depends on the lichen specie and they are given by the morphological and structural characteristics thereof (Getty et al., 1999; Carreras et al., 2005).

Several studies have used the magnetic properties of deposited particles as a proxy for particulate pollution levels. Natural surfaces as passive collectors of particulate pollution require no power source or protection of vandalism (Mitchell et al., 2010). Magnetic techniques are sensitive, rapid and relatively cheap to identify differences in concentration, magnetic grain size or magnetic mineralogy between areas under study (Fabian et al., 2011).

In environmental magnetism, magnetic measurements have been accepted for mapping anthropogenic heavy metal pollution (Thompson and Olfield, 1986; Petrovský and Ellwood, 1999; Evans and Heller, 2003). For about 30 years, authors have conducted several studies using samples of plants to study their magnetic properties (Flanders, 1994; Matzka and Maher, 1999; Jordanova et al., 2003; Maher et al., 2008).

Preliminary studies show that the magnetic susceptibility parameter seems to be a suitable indicator of traffic-related pollution. The particles emitted from vehicles are soot exhaust and solid particles from tyres, brake-lining, engine corrosion and abrasion of vehicles surfaces (Marié et al., 2010). Observations made by scanning electron microscopy (SEM) on samples coming from vehicular emissions showed small individual particles or spherulites and, small aggregates in form of chains or clusters. Additionally, elements as: Na, Mg, Al, Si, S, K, Ca, Ti, Ba, Mn, Zn, Cr and Pb, were detected by X-ray energy dispersive spectroscopy (EDS, Chaparro et al., 2010).

In this contribution, the urban area of Tandil city was studied in detail using the lichen *Parmotrema pilosum* to monitor the air quality. Taking into account results obtained by Chaparro et al. (2013), where a pilot study was presented in order to evaluate the usefulness of different lichen species for studying anthropogenic pollution in urban areas, the aim of this work focuses on: 1) a detailed sampling strategy based on a random stratified design that included about 660 blocks in the city; 2) the choice and use of magnetic parameters as tools for environmental monitoring; 3) the determination of more impacted areas through concentration dependent magnetic parameters; and 4) the identification of the pollution sources from magnetic grain size dependent parameters. The use of available bioindicators in the area gives the possibility of spatial and temporal monitoring.

2. Sampling and methods

2.1. Study area

Tandil city (37° 19.5′S; 59° 08.3′W) is located in the southeast of the Buenos Aires province, in Argentina, on Tandilia belt (Fig. 1). It is a medium-size city which has an area of 22.1 Km^2, a population approximately of 125,000 inhabitants (Censo, 2010) and a number of 60,168 vehicles (Sosa, 2015), including cars, trucks and heavy transport.

Inside the urban area, few factories, such as metallurgical industries are located (0.2 per Km^2). The pollution problem is recent and seems not to be of long-range (Chaparro et al., 2002, 2013). The vehicular emissions and metallurgical factories seem to be the main sources of air pollution in this area of study.

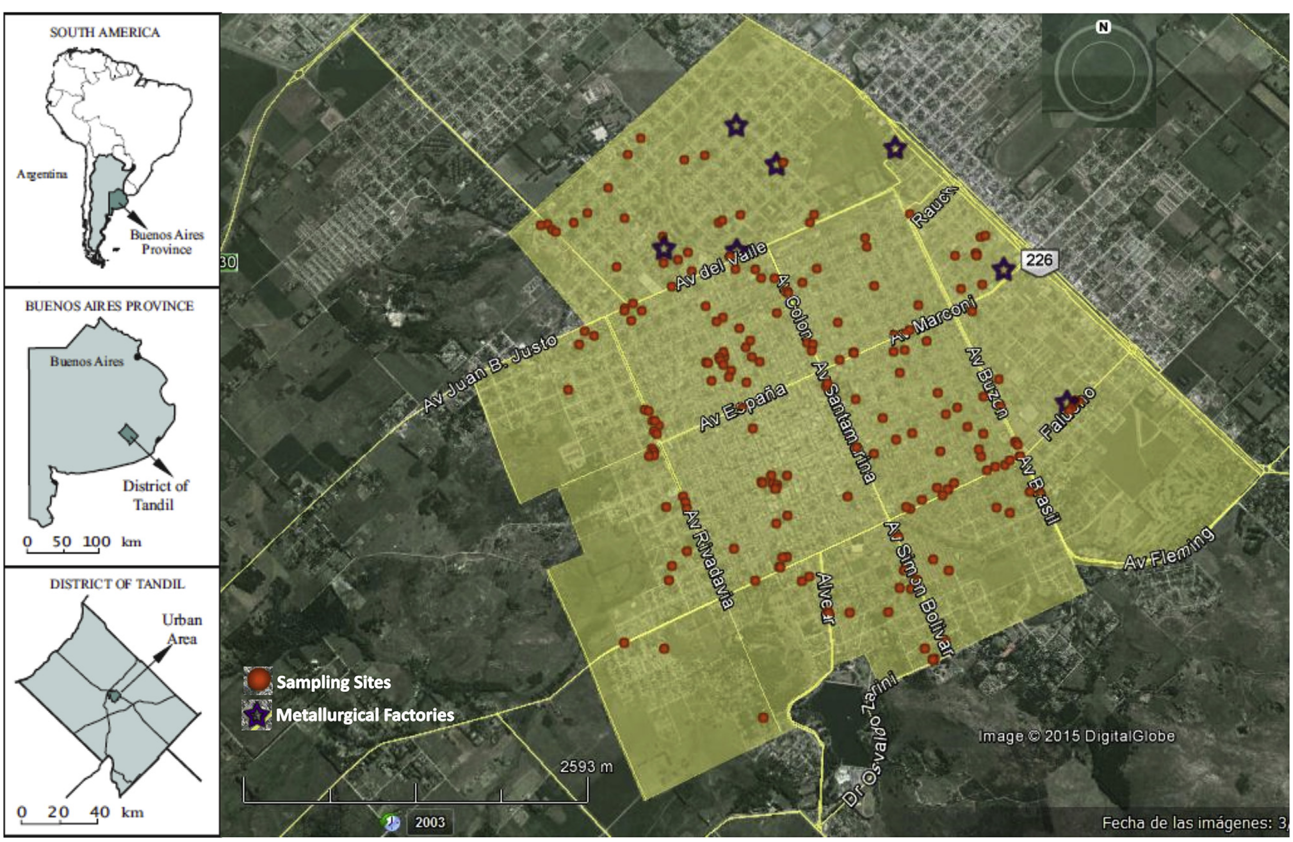

Fig. 1. Study area (Tandil City, Buenos Aires Province, Argentina), sampling points (circles), metallurgical factories (stars) and main avenues (lines in yellow) are shown. A total of 658 blocks were considered for the sampling design.

2.2. Sampling

Sampling campaigns were carried out in a period of about one year; the studied area is shown in yellow in Fig. 1. This area is composed of a total 658 blocks, separated into two main zones, the central area enclosed by main avenues and the peripheral zone that comprises two large areas located at the north of the centre zone. Inside the central area, most of the green spaces, squares and parks are located. While in the peripheral area, but within the urban area, the factories are located.

The statistical design for the sample size, corresponding to the number of trees, was calculated with 95% confidence and 0.02 estimated standard error considering unknown the proportion of lichen living on trees. The sample design was made taking into account a previous work (Tapia, 2007) where each block from Tandil city was classified according to its tree density. Three strata were generated from such classification; that is with low (304 blocks), medium (251 blocks) and high (103 blocks) density of trees. The sampling design was made using a Stratified Sampling in two stages, in the first one, the blocks were proportionally selected in each stratum; and in the second stage, a tree from each street was randomly selected. In addition, there were some special considerations about the squares, avenues and sites near metallurgical industries, which yield a number of 671 trees proposed for sampling. During the sampling collection, the existence of a tree, the ability of the tree bark to provide a good substrate for lichens, and location using one clock scheme at an elevation between 0.5 and 1.8 m was considered.

A census was realized for the different available species inside the study area; twenty epiphytic species were identified and classified by gender and family. From this census, the lichen *P. pilosum* was selected and a total of 180 samples of lichens *P. pilosum* were collected between May 2012 and June 2013. The total of proposed sites was visited, but only 180 out of 671 sites had lichens living of such trees. The site locations were recorded using a Garmin GPS system. The samples were carefully removed using wood tools to avoid magnetic contamination and paper bags to avoid the plant damage, preventing the formation of lichenicolous fungi. The lichen collection was made after 5 days without rain.

The collected lichens were stored in the laboratory and kept dry into their paper bags for a period of 7–10 days. After this period, they were dried in a stove at 25 °C for two days, and then the dried lichens were crushed using a hand grinder with plastic blade. After that, the grinding material was placed in plastic containers, which was firmly pressed to prevent the movement.

2.3. Magnetic measurements

The magnetic measurements were carried out in the laboratory at the IFAS (UNCPBA, Argentina) and the Laboratory of Paleomagnetism at the CGEO (UNAM, México). Rock-magnetic measurements were made using the MS2 susceptibility meter (Bartington Instruments Ltd.) connected to the MS2B dual frequency sensor (470 and 4700 Hz) and the MS2G. The volumetric susceptibility (κ), frequency dependence (κ_{FD}%) and mass-specific magnetic susceptibility (χ) were computed.

The anhysteretic remanent magnetization (ARM) was generated by superimposing a DC field of 90 μT to an AF of 100 mT, using a partial ARM (pARM) device attached to a shielded demagnetizer (Molspin Ltd.). The anhysteretic susceptibility (κ_{ARM}) was estimated using linear regression for ARM acquired at different DC bias fields (7.96, 47.75 and 71.8 A/m). The χ_{ARM}/χ-ratio and the King's plot (χ_{ARM} versus χ, King et al., 1982) were also studied.

A small amount of lichen (<50 mg) was used to measure magnetic hysteresis loops and remanence measurements in fields between −2 and 2 T at room temperature (RT) using a Princeton Measurement Corporation Micromag 2900 AGM system equipped with a 2 T magnet. For remanence measurements, IRM acquisition curves and the saturation of IRM (SIRM) were determined. Saturation remanence (M_{rs}), saturation magnetization (M_s), coercive force (H_c), remanence coercivity (H_{CR}), S-ratio ($-IRM_{-300mT}/SIRM$) and SIRM/χ were also calculated. IRM (acquisition and backfield) studies were also carried out with an ASC Scientific model IM-10-30 pulse magnetizer and its remanent magnetization after each step was measured by a Molspin Ltd. Minispin fluxgate spinner magnetometer.

Thermomagnetic measurements were carried out on samples using a home-made horizontal magnetic translation balance (Escalante and Böhnel, 2011). Measurements were performed in air using a magnetic field of 500 mT. Each sample was heated up to a temperature of about 720 °C and subsequently cooled to RT with a controlled heating/cooling rate of 30 °C min^{-1}.

2.4. Microscopy and elemental studies

Lichen samples (including deposited particles on its surface) were examined by SEM using a Phillips microscope, model XL30. This microscope also allowed to analyse the elemental composition of each specimen by EDS with an EDAX model DX4 (detection limit 0.5%).

2.5. Moran autocorrelation index

Spatial autocorrelation is the correlation among values of a single variable strictly attributable to their geographical positions. Moran's Index measures the deviation of the data of a random pattern. It takes values between −1 and +1 as the classical Pearson's coefficient. Negative values indicate that neighbour sites tend to have different values and a positive index indicates that geographically close sites tend to have similar values. Moran's Index significantly different from zero indicates that the variable follows a spatial pattern. The statistic for this test is the expected Moran's Index, $M = -1/(n-1)$ following an asymptotically normal distribution (Griffith, 1987). In this work, each tree is defined as neighbour of another one, if they are in the same block or if they belong to the opposite sidewalk. Moran's Index is considered significantly different at zero, so the variable has not a random spatial distribution if the p-value is lower than 0.05.

3. Results and discussion

3.1. Lichen species

Different lichen species were found in the study areas, these species live on tree bark and in the sampling campaigns were identified 20 species: 8 foliose (*Punctelia punctilla*, *Punctelia constantimontium*, *Punctelia microsticta*, *Punctelia hipoleucites*, *Canoparmelia carneopriunata*, *Parmotrema eciliatum*, *P. pilosum* and *Flavorparmelia soredians*), 8 microfoliose (*Candelaria concolor*, *Heterodermia diademata*, *Hyperphyscia variabilis*, *Hyperphyscia viridissima*, *Dirinaria picta*, *Phaeophyscia chloantha*, *Physcia aipolia* and *Physcia undulatta*), 3 crustoses (*Caloplaca* sp., *Caloplaca eritrantha* and *Lepraria* sp.) and 1 fruticose (*Teloschistes chrysophthalmus*). Such species are distributed in 13 genus and 6 families, where *Parmeliaceae* and *Physciaceae* are the most represented.

The total of the average lichen coverages (Cob) on the tree bark was assessed in situ and gave low values (mean = 34.19%, s.d. = 7.68%). The 65% of the species show low frequency (f), appearing in at least 30% of the surveyed trees. The three most common species were *Hyperphyscia viridissima* (f = 52.94%;

Cob = 16.84%), *C. concolor* (f = 63.03%; Cob = 6.84%) and *P. pilosum* (f = 75.63%; Cob = 11.77%). The last one, which belongs to a foliose biotype species, presents more advantageous characteristics for collecting and treatment.

In a previous work (Chaparro et al., 2013) was demonstrated that there is not significant differences between species to use for monitoring. The results about lichen coverage and frequency of the lichen species sampling, makes the *P. pilosum* as the most appropriate specie to be used for pollution mapping.

3.2. Magnetic properties

The magnetic hysteresis loops for some samples are shown in Fig. 2. Saturation of the magnetization (M_s) is achieved around a field of 250 mT; the saturation at low field indicates the presence of ferrimagnetic minerals.

Hysteresis parameters H_C, H_{CR}, ratios M_{rs}/M_s, H_{CR}/H_C from hysteresis loops for representative samples (Fig. 2) were calculated. The H_C values are between 9.38 and 11.68 mT, indicating the predominance of magnetite-like minerals in the magnetic signal. H_{CR}/H_C is useful to identify magnetic composition; the results show a minimum of 3.1 and a maximum of 3.8, this indicates the predominant magnetic phase is magnetite (Salo et al., 2012; Jordanova et al., 2010). S-ratio is usually used to indicate the main magnetic carrier in a sample (Thompson and Olfield, 1986; Evans and Heller, 2003). The S-ratio ranges between 0.76 and 1, indicating a predominance of ferrimagnetic minerals for most of the samples. The H_{CR} values (mean = 34.2 mT; s.d. = 2.5 mT) correspond to magnetite-like minerals according to Peters and Dekkers (2003).

Measurements of temperature dependence of magnetization are shown in Fig. 3 for two representative samples, the sample M92b-M1 was collected near a metallurgical industry and the sample M54-M6 on a traffic road (Avenue). The cooling curves

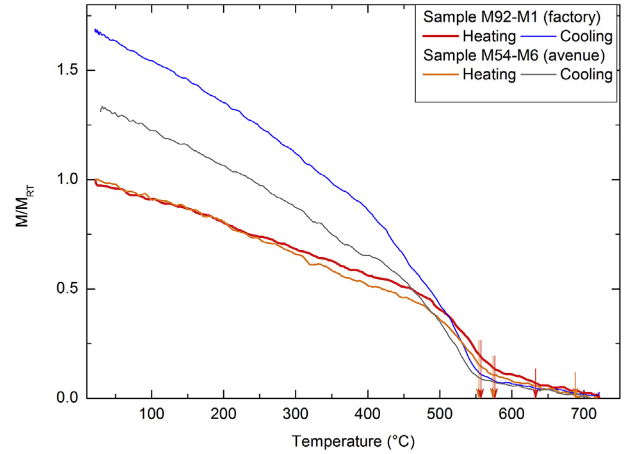

Fig. 3. Thermomagnetic curves for two representative lichen samples from the studied area: sample M92b-M1 corresponds to a site near a metallurgical factory and sample M54-M6 to a site on an Avellaneda Av. The arrows indicate the Curie temperature estimated using the second derivative of M (T).

show higher values than the heating curve, which indicates the formation of magnetite minerals during the heating process.

The analysis of thermomagnetic curves between room temperature and 720 °C shows different slopes along them. The heating runs show M (T) changes starting at about 500 °C, suggesting the presence of other magnetic minerals. The Curie point was estimated using RockMagAnalyzer software (Leonhardt, 2006), using the second derivative of M (T). In sample M92b-M1 (Fig. 3), it is possible to observe three phases, one between room temperature and 600 °C, which Curie temperatures T_{C1} is 555 °C and T_{C2} is 575 °C, and other one between 600 °C and 720 °C, with a T_{C3} = 637 °C. Sample M54-M6 shows Curie temperatures of 553 °C

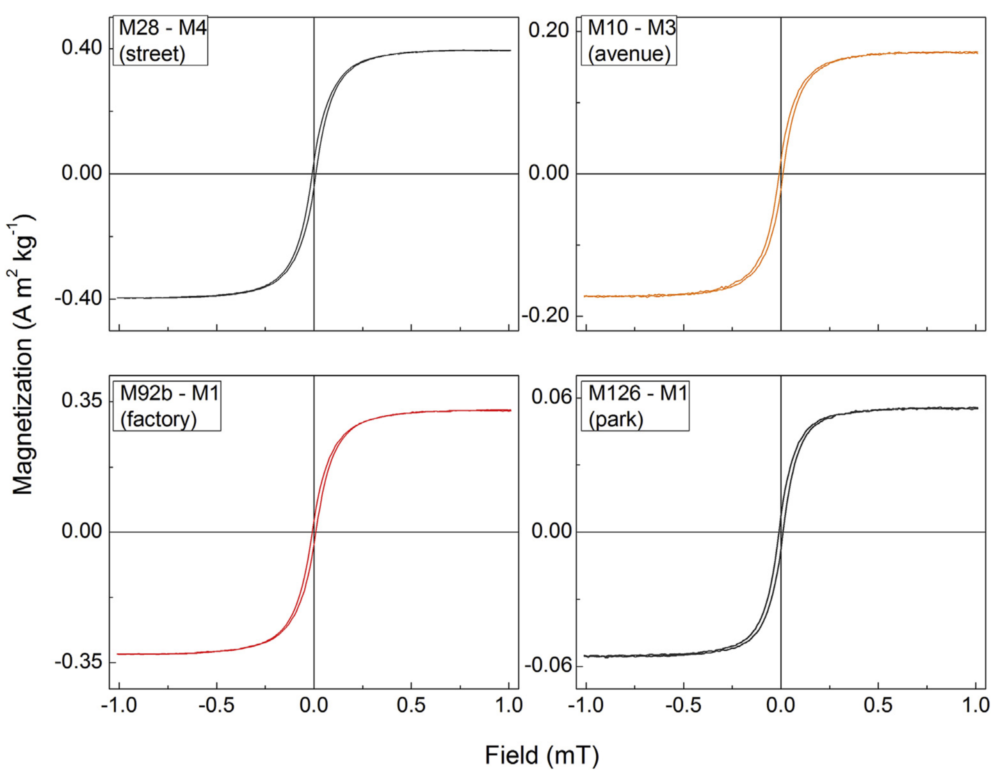

Fig. 2. Magnetic hysteresis loops for representative lichens samples collected from: street centre (M28-M4), avenue (M10-M3), near factory (M92b-M1) and park area (M126-M1).

and 573 °C between RT and 600 °C, and a T_{C3} = 689 °C between 600 °C and 720 °C. These results suggested the dominance of magnetite-like minerals and the additional presence of maghemite and/or hematite (Dankers, 1978). Vehicle emissions are dominated by ferrimagnetic particles whereas the fly ashes coming from industries may be magnetically harder due to the presence of hematite (Lecoanet et al., 2003; Marié et al., 2010; Chaparro et al., 2010; Salo et al., 2012).

Descriptive statistics of magnetic measurements and properties are shown in Table 1 and Figs. 2–6. The χ values varied between 15.7 and 1161.2 × 10^{-8} m^3 kg^{-1}, the lowest value corresponds to a sample situated near the park (the Southern part of the city), while the highest values were observed on samples collected in areas close to the metallurgical factories, avenues and streets with high vehicular traffic. The ARM and SIRM show higher values on samples corresponding to such areas as well.

The Day's plot (Day et al., 1977) was used to evaluate the grain-size trend (Fig. 4), all samples are located in the pseudo single domain (PSD) area, being evident that they correspond to different mixture of single domain (SD) and multi-domain (MD) particles, with a MD contribution of 80–90% (as based on the SD–MD mixing curves of Dunlop, 2002). It is also possible to observe from this representation that samples factories and avenues have a higher MD contribution (90%) than samples streets (between 80 and 85%).

Magnetic grain size estimations were made from the calibration lines based on King's plot (Fig. 5). Most of values are between 0.1 μm and 1 μm, and the grains closer to 0.2 μm correspond to samples collected from avenues or streets with high vehicular traffic. The samples collected from sites with low vehicular influence and vegetation areas show magnetic grain sizes <0.1 μm. In contrast, samples from sites close to metallurgical industries, i.e. samples factories, have coarser magnetic grain size (between 0.2 and 1 μm). Such result was already observed by Chaparro et al. (2013) and it is related to wind spread of the emitted particles. Coarser particles emitted by metallurgical factories and by vehicles seem to be deposited near the source and cannot travel long distance as finer particles.

The representation of two magnetic grain size dependent parameters (ARM/SIRM and χ_{ARM}/χ, Fig. 6) shows the distribution of samples from different sites influenced by the metallurgical industry (factories) and by vehicular traffic (streets and avenues). Although there is an area where some collected samples overlap, all of them are influenced by vehicle emissions. It is possible to observe that most of the samples collected near the factories have coarser magnetic grain sizes than the others (streets and avenues). Comparing avenue and street samples, it is observed that sites on avenues tend to have coarser magnetic grain sizes than streets. Samples with finer magnetic grain size correspond to sites located on streets with low vehicular traffic. In addition, the combination of magnetic concentration and grain size dependent parameters (SIRM and χ_{ARM}/χ, Fig. 6) allows to observe two groupings, one composed by metallurgical samples (factories) and another one by samples avenues and streets. The first group has a higher magnetic concentration and coarser grains; on the contrary, the second one has a lower concentration and finer magnetic grains.

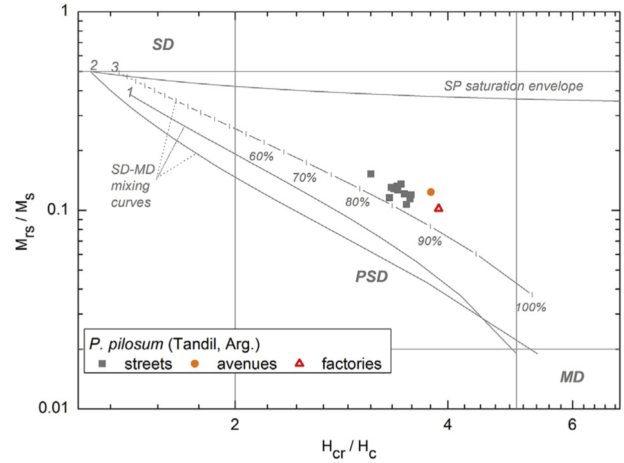

Fig. 4. Day plot for representative samples of lichens from studied area. Boundaries for single-domain, pseudo-single-domain, and multi-domain and mixing lines, indicated by dashed line shown after Dunlop (2002).

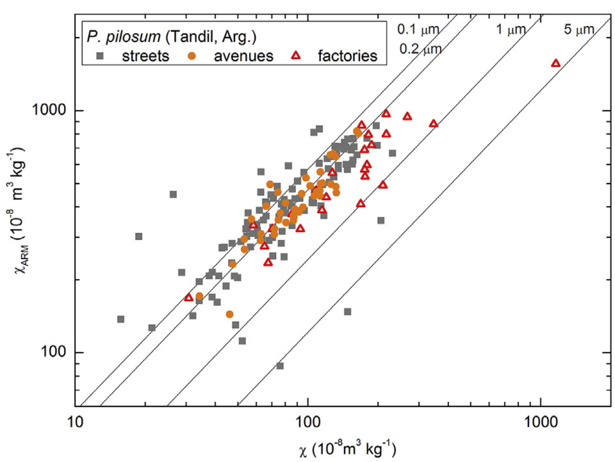

Fig. 5. King's Plot (χ_{ARM} versus χ) for lichen samples from urban area of Tandil City.

The combination of different magnetic parameters was used by different authors, such as Salo et al. (2012) and Szuszkiewicz et al. (2015), to identify pollution sources. In particular, the joint analysis of both biplots (Fig. 6) allows us to determine the most impacted sites (higher SIRM values) and to identify the sources of pollution, i.e. metallurgical factories located in the Northern and Eastern zones and traffic-derived emissions, using the parameters ARM/SIRM and χ_{ARM}/χ.

Table 1
Descriptive statistics of magnetic measurements and properties of lichens samples from urban area of Tandil city.

Parameters	Sample N	Mean	Standard deviation	Minimum	Maximum
χ[10^{-8} m^3/kg]	180	105.1	94.1	15.7	1161.2
ARM [10^{-6} A m^2/kg]	180	323.8	148.9	77.9	1180.8
SIRM [10^{-3} A m^2/kg]	180	13.6	12	2.5	147.6
χ_{ARM}/χ [a.u.]	180	3.1	1.56	6.89	0.05
ARM/SIRM [a.u.]	180	0.026	0.007	0.008	0.087
SIRM/χ [kA/m]	180	13.19	3.38	2.8	49.77
H_{CR} [mT]	180	34.2	2.5	25.4	39.3

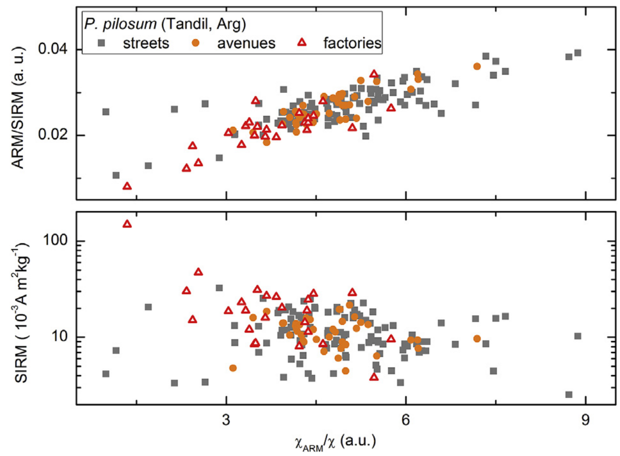

Fig. 6. Biplots of ARM/SIRM versus χ_{ARM}/χ and SIRM versus χ_{ARM}/χ for lichen samples collected in the urban area of Tandil city.

3.3. SEM

SEM observations on lichen samples show spherules and particles of different shapes and sizes (Fig. 7). The sample near metallurgical factories (M92b-M1) is composed of spherules (about 6 μm, Fig. 7a) and particles of varied grain size (e.g.: acicular grains of about 5 μm, Fig. 7b), with different morphologies. The grain size of anthropogenic particles observed by SEM corresponds well with the magnetic grain size estimated from King's plot, spherules of 1–6 μm, larger particles (10–15 μm) and finer particles (<5 μm). Similar particles were previously observed on lichens from 20 sites from Tandil that involved mentioned industrial and traffic-derived sources. In addition, sub and micron-sized particles are expected from the combustion of diesel and gasoline powered engines and wear particles from brake materials. The EDS results show high contents of Fe, Al, Ni, Cr, Ti, Cu and K, in particular, as observed in Fig. 7a–b, the spherule particle has 97.7% of Fe and the acicular particle has 66.8% of Fe, 15.1% of Cr and 10.3% of Ni. These elements and others were reported by Chaparro et al. (2010, 2013) from vehicle and industrial pollution sources.

On the other hand, SEM observations on a sample corresponding to a site with low vehicular influence and faraway of factories (M126-M1, located in the Southern part of the study area, Fig. 1) are displayed in Fig. 7c–d. Such analysis shows particles of lithogenic origin, particles with well-defined edges and of irregular morphology. Most of these coarser particles are predominant in this site; however, finer spherules were seldom found (Fig. 7d). Such particles could be end-product of traffic-related sources, they can also come from metallurgical industry but factories are located faraway of M126-M1. The EDS analysis shows that these particles are made of Fe, Br, Ca, Al and Ti.

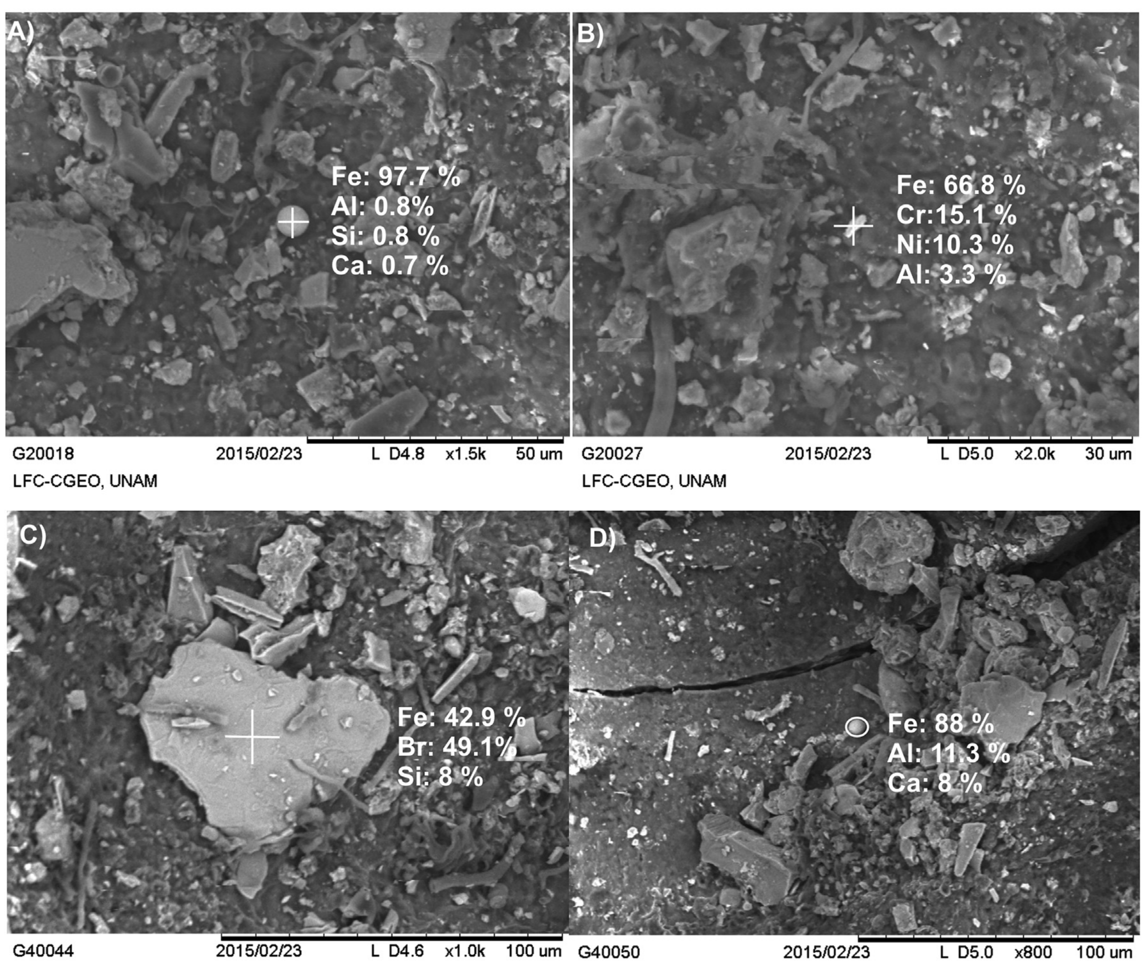

Fig. 7. a–b: SEM observations on samples from sites near the metallurgical factories (M92b-M1), c–d: SEM observations on samples from a site with low vehicular influence (M126-M1, a site located in the Southern part of the study area).

3.4. Moran's autocorrelation index

Most of the studied variables showed a highly significant spatial correlation. A spatial association patterns is observed in the central area (Table 2) for the variables χ, χ_{ARM}, ARM, SIRM and H_{CR}, these parameters show significant Moran's Indexes ($p < 0.05$) varying between 0.511 and 0.619 while the magnetic grain size ratios (SIRM/χ and χ_{ARM}/χ) seem to have a random behaviour without spatial association ($p < 0.06$ and $p < 0.07$, respectively). On the other hand, high significant Moran's Indexes ($p < 0.01$) and values from 0.535 to 0.727 are observed for all variables in the peripheral area (Table 2). In this case, the neighbour places tend to have similar values of every variable. In both areas, magnetic concentration dependent variables show positive spatial autocorrelation, indicating that cannot be considered with a random spatial behaviour; therefore there is a tendency to cluster spatially such variables. These autocorrelation results allow the use of concentration and grain size dependent magnetic parameters (i.e., χ and χ_{ARM}/χ) for the construction of magnetic contour maps in Tandil city.

3.5. Magnetic mapping

Most of the magnetic monitoring studies have focused on χ because measurements are easy, prompt and cost-effective to carry out (Petrovský and Ellwood, 1999). However, additional magnetic parameters (e.g.: Ms, high-field susceptibility χ_{hf}, SIRM, and κ_{ARM}/κ) may have to be considered in different study cases as proposed by Chaparro et al. (2015). Magnetic concentration and grain size are relevant properties for these pollution mapping studies; for this reason and according to the spatial autocorrelation determined by the Moran's Index results, the spatial pattern of magnetic parameters such as χ, ARM, SIRM, H_{CR} and χ_{ARM}/χ were considered for this work (Tables 1 and 2).

The 2-D contour map for magnetic concentration (Fig. 8) was constructed using the mass-specific susceptibility values. Zones of higher χ values (from 128.8×10^{-8} m^3 kg^{-1}) are observed in sites around the metallurgical factories in the Northern (del Valle Av.) and Eastern (near Route 226) part. In addition, higher values are noted in sites with high vehicular traffic, for example, in España Av. (between Rivadavia Av. and Buzon Av.) and in Avellaneda Av. (between Santamarina Av. and Buzon Av.). It is worth mentioning that both avenues (España and Buzon Avs.) are ones of the main traffic accesses to the city. On the other hand, the lowest values correspond to areas with low vehicular traffic or vegetation areas. In general, a decrease of the magnetic concentration with the distance to pollution sources (metallurgical industries or avenues with high traffic) can be appreciated in Fig. 8.

As mentioned, the χ_{ARM}/χ is a magnetic grain size-dependent parameter, low values (Fig. 9) indicate coarser magnetic grain size and vice versa. These results show lower χ_{ARM}/χ values (coarser grains) following higher χ values around the metallurgical sources, in general, a decrease in magnetic grain size with distance is noted from mentioned pollution sources to less impacted areas. On the other hand, the mentioned impacted areas by vehicular traffic, i.e. España Av. and Avellaneda Av. evidence that high χ values are follow by high χ_{ARM}/χ values (finer grains). Thus, both parameters χ and χ_{ARM}/χ are useful for identifying impacted zones and different pollution sources.

Table 2
Observed Moran's Index, standard deviation (s.d.) and p-value for each variable. The expected Moran's Index was −0.007 and −0.025 for the central and peripheral area, respectively.

Variable	Moran's Index	s.d.	p-value
Expected Moran's Index for the central area			
χ	0.592	0.082	<0.01
ARM	0.592	0.082	<0.02
χ_{ARM}	0.511	0.082	<0.03
SIRM	0.575	0.082	<0.04
H_{CR}	0.619	0.082	<0.05
SIRM/χ	0.344	0.058	<0.06
χ_{ARM}/χ	0.604	0.082	<0.07
Expected Moran's Index for the peripheral area			
χ	0.535	0.088	<0.01
ARM	0.629	0.153	<0.01
χ_{ARM}	0.636	0.156	<0.01
SIRM	0.564	0.091	<0.01
H_{CR}	0.697	0.166	<0.01
SIRM/χ	0.727	0.165	<0.01
χ_{ARM}/χ	0.650	0.169	<0.01

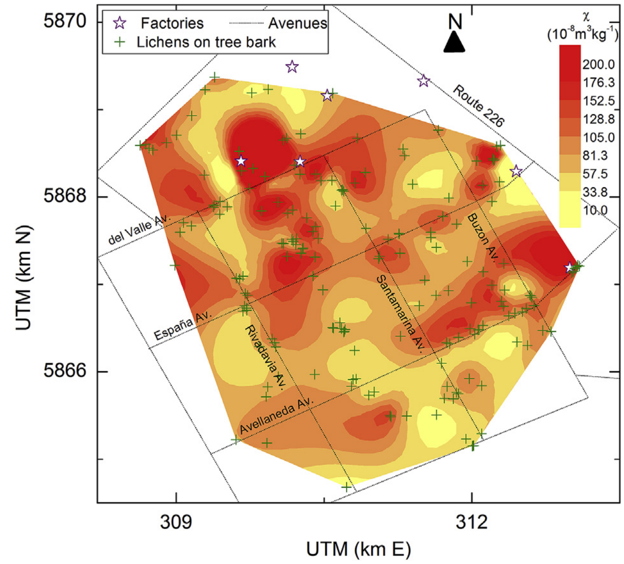

Fig. 8. Contour map of the mass-specific susceptibility of the urban area (Tandil city). High χ values indicate areas with high vehicular traffic and/or industrial influence.

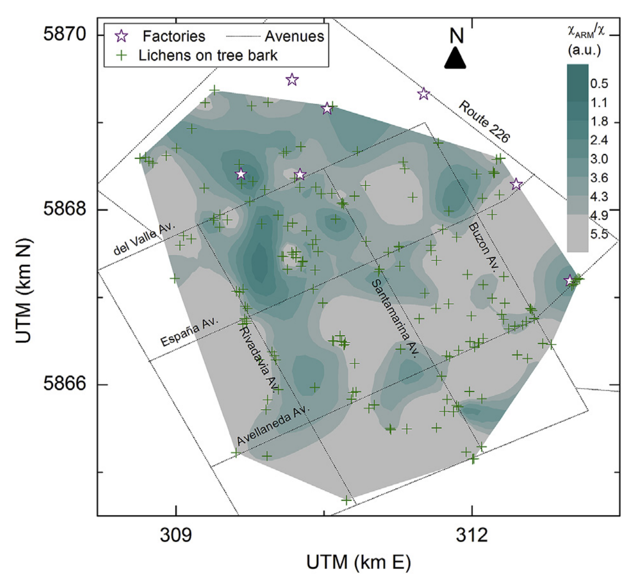

Fig. 9. Contour map of χ_{ARM}/χ of the urban area (Tandil city). Low values (coarser grains) are found in areas with high vehicular traffic and industrial influence.

4. Conclusion

The magnetic measurements revealed the predominance of magnetite-like minerals and the presence of maghemite and/or hematite. Magnetic grain size estimations indicate finer magnetic grains in less impacted areas (<0.1 μm), while lichen samples from the most impacted areas, in general, have coarser magnetic grain sizes (0.2–1 μm). Besides, it is observed coarser magnetic grain sizes for sites close to metallurgical factories than sites with high vehicle traffic on main access to the city. These particles were also observed by SEM, showing the presence of spherules and irregular particles, containing Fe as well as trace metals, with different grain sizes and morphologies. The analysis of biplots, and parameters χ and χ_{ARM}/χ allows us discriminating the most polluted sites and their respective source. Results from this work show that the vehicles and factories emissions are the main pollution sources affecting Northern and Eastern part in the study area and the ones of the main vehicular accesses to the city. This study supports the use of both χ and χ_{ARM}/χ for lichen *P. pilosum* as mapping tools. In addition, these parameters may be used to spatial and temporal pollution assessment in this medium-sized city and other ones with this biomonitor.

Conflict of interest

There is no conflict of interest.

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