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Atmospheric pollution assessed by in situ measurement of magnetic susceptibility on lichens

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ABSTRACT

The use of environmental magnetism methods and biomonitors allows us the development of a low-cost tool for assessing atmospheric pollution through trapped magnetic particulate matter. Such particles concentration was monitored in situ, on the lichen's thallus, using magnetic susceptibility as a pollution proxy. We studied the magnetic particle distribution on the thallus surface from weekly measurements of in situ magnetic susceptibility κ_{is} during 16 months for seven sites. A total of ~8300 measurements was carried out; and mean overall κ_{is} values for each lichen varied between 4.1 and 23.9 × 10^{-5}SI revealing the influence of different atmospheric pollution sources on *Parmotrema pilosum*, such as metallurgical factories and vehicular emissions. Weekly measurements of κ_{is} show areas of magnetic accumulation on the thallus over a period of 60 measurement campaigns. Iron rich spherules and irregular particulate matter between $PM_{2.5}$ and $PM_{1.0}$ were observed by SEM-EDS. A joint analysis of meteorological variables and magnetic susceptibility shows an inverse relation between this magnetic parameter and temperature, i.e., a trend of decreasing κ_{is} values during seasons of higher temperatures which tend toward higher values of atmospheric mixing height. Precipitation also affects the magnetic signal over time, producing decreases in mean values of κ_{is} after rainy periods.

1. Introduction

The terms bioindicator and biomonitor have different meanings, the first one refers to the use of organisms through which any current (or past) phenomenon or event related to the study of the environment can be decoded. The second term is the quantitative measurement of particulate matter, elements and compounds (e.g., polycyclic aromatic hydrocarbons PAHs, polychlorinated biphenyls PCBs, etc.) deposited and/or accumulated in organisms or their parts. Among epiphytic species, lichens, *Tillandsia* spp. and mosses in their natural state have been used as bioindicators and/or biomonitors (Shacklette, 1973; Grodzinska, 1978; Schrimpff, 1984; Rhoades, 1999; Ares et al., 2012; Chaparro et al., 2013; Kováčik et al., 2014). Lichens are recognized as air pollution bioindicators and biomonitors, as due to the absence of a root system, a protective cuticle, and of stomata, their exchange of nutrients with the atmosphere occurs over the entire surface of their thalli; moreover, they grow slowly and are long-lived (Zschau et al., 2003; Lodenius, 2013). Lichens accumulate metals and others pollutants (NO_2, SO_2, HF, ozone compounds and particulate matter) from the atmosphere by dry and wet deposition (Sett and Kundu, 2016, Boamponsem and de Freitas, 2017). Particulate matter (PM) and potentially toxic elements (PTE) can be incorporated by these natural collectors in different ways and times.

According to Chaparro de Valencia and Aguirre Ceballos (2002), the accumulation of contaminants in the lichen's thallus over time may be determined because of their longevity. The growth of lichens depends on the presence of PM and/or PTE and may even stop in highly contaminated environments (Bardelás, 2012); since the lichen's sensitivity is greater (and resistance is lesser) when the stems are young. In particular, the growth can be interrupted by high values of SO_2; although some species such as *Lecanora conizaeoides* have shown in experiments to be resistant to this compound. Kováčik et al. (2011) studied the physiological responses of lichens *Hypogymnia physodes and Xanthoria parietina*, as well as the Bromeliaceae *Tillandsia albida,* exposed to

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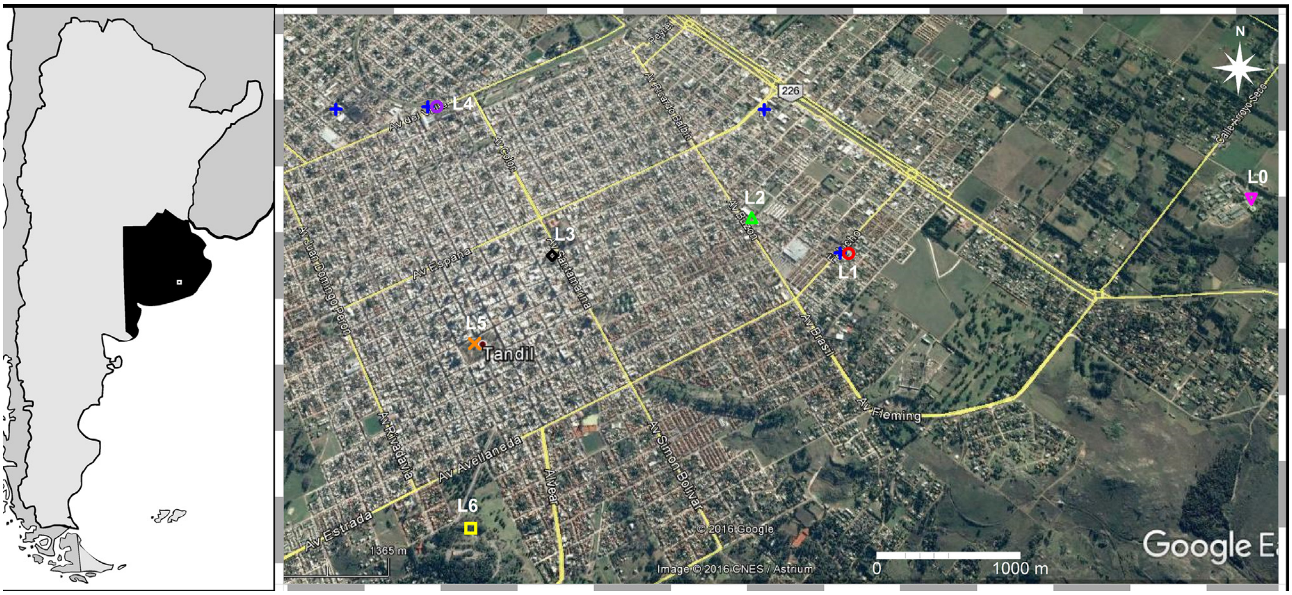

Fig. 1. Study area in Tandil city (Buenos Aires Province, Argentina). Measurement sites (and lichen individuals L0–L6) and metallurgical factories location (plus signed).

simulated acid rain. Pigments were depressed in all species, with *Tillandsia* sp. being the most affected. Macronutrients (K, Ca, and Mg) decreased more pronouncedly in comparison with micronutrients in all species. The comparison between lichen species showed that *X. parietina* has the highest tolerance, suggesting its use as a long-term biomonitor. Recently, studies carried out by Kováčik et al. (2018a,b) showed changes in metabolism and oxidative stress symptoms for two lichen species *Cladonia arbuscula* subsp. *mitis* and *Cladonia furcata* exposed to Ni, Cu, and Cr excess.

Sett and Kundu (2016) found that the lichen's size is a good indicator of air quality. However, the lichen growth rate is species dependent and is influenced by their habitat, that is, specific geographical conditions for each zone, such as height above the sea level, length of sun exposure, etc. Dumont et al. (2013) obtained a growth rate for lichen *Caloplaca cinericola* of 0.2 mm/year that is comparable to those obtained by Lindsay et al. (1973) for the species *Rhizocarpon geographicum* (0.13 mm/year), where their studies were carried out in the Antarctic Peninsula.

The use of biological material for atmospheric pollution monitoring is an alternative method to assess the air quality in urban areas and other sites of interest such as industrial settings (e.g., Salo et al., 2014; Abril et al., 2014; Castañeda Miranda et al., 2016; Gargiulo, 2018). Magnetic biomonitoring combines environmental magnetism techniques and the use of biological collectors (e.g., epiphytic species) for assessing industrial and urban pollution. This kind of magnetic biomonitoring studies has become a methodology of growing interest since last decades. Jordanova et al. (2010), Chaparro et al. (2013), Marié et al. (2016), and Kodnik et al. (2017) have conducted magnetic monitoring studies using different lichen species as biomonitors of atmospheric pollution. Chaparro et al. (2014), Castañeda Miranda et al. (2016) and Mejia-Echeverry et al. (2018) proved the inexpensive use of *Tillandsia* spp. as efficient collectors and sensors of airborne pollutants, which allowed identifying adversely impacted areas in Argentina, México and Colombia. Fabian et al. (2011), Salo et al. (2012), and Vuković et al. (2015) used in situ and transplanted mosses for monitoring air pollution in Norway, Finland and Republic of Serbia.

Marié et al. (2016) determined that among 20 species of corticolous foliose and microfoliose lichens, *Parmotrema pilosum* was the most abundant species living in tree bark and having a good distribution over the urban area of Tandil city (Argentina). The aims of the present work are: a) to study the *P. pilosum* morphological change and its growth rate during 60 measurement campaigns; b) to determine the distribution of magnetic particulate matter on thalli surface for lichens exposed to different pollution sources; c) to evaluate temporal changes of such PM distribution and the influence of meteorological conditions during about one year; d) last but most important, to validate the use of in situ measurements of magnetic susceptibility (κ_{is}) on lichen's thallus as a novel methodology for magnetic assessment of the atmospheric pollution over periods from days to years, which is non-destructive and thus preserves the species.

2. Methods

2.1. Study area, measurement sites and lichens

This study was carried out in Tandil city (37° 19.5′ S; 59° 08.3′ W), which is located in the SE part of Buenos Aires Province, Argentina. The city has a population of 125,000 inhabitants (Censo, 2010) and a number of 60,000 vehicles (Sosa, 2015), including cars, trucks and heavy transport. The study area has a sub-humid to humid climate and is characterized by strongly differing summer and winter seasons that is a distinctive characteristic at this Pampean region. As general characteristics, summer seasons are hot and rainy, and the winters are cold and dry. Meteorological analysis realized in 2001–2010 (Picone et al., 2012) indicates an annual mean temperature of 13.4 °C and annual precipitation of 845.2 mm (Picone, 2014; Sosa, 2015). Meteorological variables for the study period (March 2016–July 2017) indicate an annual precipitation of 1237.6 mm, and maximum and minimum mean temperatures of 19.6 °C and 6.7 °C, respectively (CIM, 2017).

Seven lichen individuals labelled as L0 to L6 were selected in locations with variable pollution sources and intensities within this urban area (Fig. 1- Table 1). The species *Parmotrema pilosum* living on tree bark was studied for these seven sites.

The longest measurement period was carried out on a lichen located close to a car parking at the University Campus (L0, Fig. 1) where the only pollution source is vehicular emission of busses and cars. An individual thallus of about 70 mm of diameter located at 98 cm above the ground was selected. In addition, other six lichens of the same species exposed to other pollution sources were selected (L1–L6, Fig. 1). Lichen L1 is located in the vicinity of two metallurgical factories and on an avenue with high vehicular traffic, being one of the main accesses to the city. L4 is pinpointed in front of an important metallurgical factory and