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Long-term monitoring of atmospheric pollution in Maritime Antarctic with lichen *Usnea aurantiaco-atra* (Jacq.) Bory: a magnetic and elemental study.

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Abstract

Antarctica is a natural research laboratory thanks to its unique climate, geography, flora, and fauna. The conservation of Antarctica's environment is monitored through the Madrid Protocol; however, there are local pollution problems associated to human activities like research and tourism; in particular, there are negative impacts on air quality from the use of fossil fuels. In this work, we studied for the first time magnetic and elemental characteristics of lichen *Usnea aurantiaco-atra* (Jacq.) Bory collected in different years and from various sites in King George Island, Antarctic Peninsula, as well as some samples of its supporting substrate, for long-term monitoring of the atmospheric pollution. Several anthropogenic elements (Ni, Pb, Mo, Cd, and Zn) have been identified on sites close to human activities but also on sites far from it. We found that magnetic proxies from *U. aurantiaco-atra* samples show a spatial correlation with human influence (scientific bases or airstrips). We observed a correlation between magnetic parameters and Ni, and to a lesser extent with Cr, Co, V, and Ag. Results suggest that using these magnetic and elemental techniques, it is possible to implement monitoring with lichen *U. aurantiaco-atra* as a bioindicator for some elements of anthropogenic origin.

Key words: environmental magnetism, biomonitoring, anthropogenic particulate matter, elemental composition, Fildes Peninsula, King George Island.

Introduction

The Antarctica continent covers an area of 14062500 km^2 of which only 0.32% of its total area is free of ice. Vegetation grows on a constrained basis in coastal sectors free from ice and snow during the summer and in some rock outcrops located inland. Despite its remote situation and extreme conditions, human presence has existed in Antarctica for more than 200 years associated to whaling activity (Tin et al. 2009) and for more than 70 years associated to science and tourism. Nowadays, the human presence is represented by 112 research bases throughout the continent, which accommodate over 5000 people during the summer. In winter, 40 stations are in operation, which could accommodate 3916 people, who need water, fossil fuel consumption and management of wastes. Moreover, tourism has been continuously increasing; this caused the visit of over 50000 people during the season 2017-2018, with obvious environmental implications.

King George Island, Antarctic Peninsula, Maritime Antarctica stands out as “hot spot” receiving increasing pressure from human activities. Fildes Peninsula with about 29 km^2 of surface has a high biodiversity and is a major logistic centre for the northern Antarctic Peninsula; it supports the largest number of scientific bases (5 permanent from Chile, China, Russia, Uruguay) and shelters and an airfield for aircrafts arriving from the city of Punta Arenas, Chile.

There is no monitoring of air quality and certainly no inventory of sources in the Fildes Peninsula (Tin et al. 2009). Studies by Mishra et al. (2004) on total atmospheric aerosols (TSP, suspended particles smaller than 45-50 µm) from King Sejong base (Barton Peninsula) indicate that presence of the elements Bi, Cd, Co, Cr, Cu, Ni, V and Zn is

caused by anthropogenic activities associated with local sources. For Fildes peninsula, information is available on fractionated aerosols smaller than 3 µm. The elements Na, Mg, Sr, Mn, Fe, Cr, Co and Ca have a natural origin and Pb, Ni, Zn, Cu and Cd, on the contrary, have an anthropogenic origin. The elements Pb, Cr, Sb, Cu and Mn are partially of extra continental origin. Ca, Ba, Ni and partially Zn and Cu are generated by the human activities in the island (Préndez et al. 2009, Carrasco & Préndez, 1991). Mosses and lichens constitute the main biotic components of terrestrial ecosystems in Antarctica. Exposed biological surfaces, e.g., lichens, mosses and leaves, accumulate atmospheric particles, and are able to provide a record of location-specific and time-integrated information on local air quality (Bajpai et al., 2018). The relatively high humidity and mild temperatures found in maritime Antarctica, together with the absence of competition from higher plants, create the perfect place for stress-tolerant organisms such as lichens (Sancho & Pintado 2011). Lichens are good bio-accumulators of chemical elements transported by air (Préndez et al. 2006, Sancho et al. 2007) and can be used as bio-monitors of the atmospheric deposition of inorganic pollutant also in Antarctica (Poblet et al.1997). Nutrients and/or material derived from the humid and dry atmospheric precipitation deposit can accumulate on or around the thallus. The incorporation of elements through the thallus surface depends on many factors such as the nature of the element, morphologic characteristics of the surface, and environmental parameters (Wolterbeek 2002). When using lichens as bioindicators, it is necessary also to evaluate the contribution of the substrate in which they grow in order to determine only the atmospheric contribution in nutrition and accumulation of contaminants in the thallus. Poblet et al. (1997) have shown that *Usnea aurantiaco-atra* (Jacq.) Bory

(currently *Neuropogon aurantiaco-ater*) is a convenient organism for developing a bio-monitoring of metals in atmospheric aerosols in the area of the South Shetland Islands. The United States Forest Service (2010) provides an extensive database of air quality in relation to biomonitoring through lichens with tables including threshold levels of chemical elements present in Oregon, Washington and in Alaska's national forests. In our knowledge, there is no similar database for Antarctica.

Atmospheric pollution, in particular urban particulate matter (PM), often contains levels of magnetic minerals, e.g., iron oxides like magnetite, hematite and maghemite (e.g., Matzka & Maher, 1999) that are easily measurable magnetically. This PM can accumulate on exposed biological surfaces and deliver accumulated information on local air quality. A group of trace metals, such as Zn, Cd, Pb, Ni, Cu and Cr, are often directly associated with magnetic PM, due to their incorporation in the mineral structure during combustion processes (Cao et al. 2015). Therefore, the magnetic signal may act not only as a PM proxy but be of direct, often health-related, interest in itself.

Only a few magnetic measurements have been carried out on lichens, in situ or as transplants (see Hofman et al. 2017 for a review). These studies show that magnetic properties are good proxies for anthropogenic atmospheric pollution, though they are species-dependent.

The aim of this study was to evaluate the use of *U. aurantiaco-atra* lichen as bioindicator of air quality in the Fildes Peninsula over a period of 13 years (1997-2010) using magnetic and elemental techniques.

Sampling

Substrates and Lichens

Five-g samples of *U. aurantiaco-atra* were carefully collected in some summer/fall seasons between 1997 and 2010. Samples were taken from 1*1 m^2 demarcated and protected sites (Table I), then air-dried in Antarctica, stored in clean paper bags, transported to the laboratory for analyses, and kept isolated from external influences. Lichen thalli, when dried, do not decompose. In the laboratory, duplicates of all lichen samples were sorted, using only the thinnest thalli, and dead and senescent tissue, superficial dust, soil particles, and small stones were manually removed using a Teflon clamp. Samples were dried at 90ºC for 24 h, mashed in an agate mortar, and stored in sterile Petri dishes to provide samples to the different analysis.

In parallel, 2 or 3 samples of the substrate (first 5 cm of the substrate) were taken together with the lichens. Composite substrate samples were assembled and were air-dried in Antarctica and packed in paper bags further stored in plastic containers at -18 C°.

We lack samples of substrate or lichens for some years and/or sites, not because the samples were not taken, but because they were used in other analyzes over the years and there was no more left.

Sampling sites

King George Island is located between 61°50’ and 62°15´S and 57°30 and 59°01´W; it belongs to the South Shetlands Islands and is located near the northern part of the Antarctic Peninsula (Fig. 1). The Collins Glacier covers practically the entire island. The rest of the surface, mostly along the coast, is composed of volcanic rocks (basalts and/or

andesites) which form cliffs about 100 m high. The substrate is composed of material with coarse granulometry.

The sampling points are localized in sites close to potential human emission sources, such as the aerodrome and scientific bases, and more isolated sites where there should be less human influence, such as the Ardley peninsula and the Collins Glacier (Fig. 1).

The sites that are close to emission sources are: Site Aerodromo, located near the Aerodrome Teniente Rodolfo Marsh, which is used by many the scientific bases on the island; Site LARC, located next to the Antarctic Laboratory of Cosmic Radiation, University of Chile that is installed on top of a hill of about 40 m above sea level (a.s.l), close to two Chilean bases; Site Base China which is located about 100 m southeast of the Great Wall Chinese base station, under construction/extension all along the sampling period; Site Aerodromo MET, located in the vicinity at east side of the Aerodrome T.R. Marsh.

The sites chosen far away from possible anthropogenic emissions are: Site Ardley, located on a small peninsula located southeast of Fildes and connected by a sand dam, which is a nesting site for a wide variety of birds and one of the most important habitats of penguin, with a rich and extensive vegetation cover; Site Collins, located at the foot of the glacier Collins in an ice-free area about 10-15m from the sea.

Two more sites were chosen as intermediate: Sites Cerro Fosil and Cerro GPS, located on top of a small hill of about 25 m a.s.l., in the vicinity west of the Aerodrome T.R. Marsh, separated from it by no more than 100 m.

Analytical techniques and methods

Magnetic techniques

Magnetic measurements were carried out with two objectives: to quantify the magnetic minerals through measurements of magnetic susceptibility and remanent magnetization (M_r), and to obtain magnetic parameters that might give information about the nature of magnetic minerals and their magnetic grain size.

In order to perform magnetic measurements, each sample of lichen and substrate was crushed into a powder and tightly packed into a gelcap. A lichen gelcap contains 150-200 mg of material, while a substrate gelcap contains between 300 and 400 mg of material. Then, the gelcaps were used for measurements with two different equipment. Firstly, the magnetic susceptibility, which is the ability of a sample to be magnetized in a weak field, was measured using an AGICO Kappabridge KLY-3 at the Institut de Physique du Globe de Paris (IPGP). The same samples were then used for the measurement of hysteresis parameters and First-Order Reversal Curve (FORC) diagrams with a Vibrating Sample Magnetometer (VSM) from Lakeshore, which is part of the Mineral Magnetism Analysis Platform situated of IPGP-IMPMC. More detail on the measurement of these properties can be found in the Supplementary Information.

Scanning Electron Microscopy with X-ray Energy Dispersive Spectrometry

This technique allows visualization of the external morphology of the sample. To obtain the image of the analysed surface, the sample is swept with an electron beam in a raster pattern. In the case of MEB-EDS, the backscattered electrons are used to generate the image. An X-ray detector is coupled to this system to perform an elemental qualitative and quantitative analysis of the sample.

The analysis was carried out in the microscopy laboratory of the ENES Morelia unit of the Universidad Nacional Autónoma de México (UNAM). Substrate and stem fragments from lichen samples were analysed using a JSM IT300 scanning electron microscope, JEOL brand with EDS X-Max detector with 20 mm^2 window. The substrate samples were metalized with a gold coating. The analysis was done under low vacuum conditions (50 Pa) for the lichen samples and high vacuum (10^{-4} Pa) for the substrate samples. Elemental analysis using X-ray fluorescence (EDS) was done on some individual particles.

Instrumental Neutron Activation Analysis

Instrumental Neutron Activation Analysis (INAA) is a multi-elemental and non-destructive technique that uses characteristic nuclear reactions. Neutron flux interacts with the sample, producing a nuclear reaction, mainly of the type (n, γ). The characteristic gamma rays emitted by each radionuclide are captured by a high-resolution detector.

INAA technique have been used widely to study the elemental composition of samples from Antarctica (e.g. Mroz et al. 2018), whether they are sediments, lichens or mosses. In this work, we used the INAA technique to measure the concentrations of the elements Na, Sc, Cr, Fe, Co, As, La, Ce, Sm, Eu, Yb, Hf in the substrate of the sites LARC, Aerodromo and Ardley peninsula sampled at the same time than the lichens in the years 1997 and 2006. Experimental details can be found in the SI.

Elemental quantification by Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

We selected the elements to be quantified by Inductive Coupled Plama-Optical Emission Spectrometry (ICP-OES) according to these 4 criteria: a) Potentially toxic chemical elements; b) Probability of finding them in the study area in concentrations quantifiable by the technique used, based on previous research; c) Bio accumulative chemical elements; d) Elements of known anthropic origin. Therefore, the quantified elements, both for lichens and for the substrate, were Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, V and Zn. However, many of them were found under detection limits (UDL) of the technique. The experimental procedure is detailed in the SI section.

Results

Magnetic measurements

According to the Day-diagrams, hysteresis parameters for the lichen samples (1997 to 2010) all plot in the pseudo-single-domain (PSD) region, between the single-domain (SD)- multidomain (MD) (MD percentage >60%) and the SD-superparamagnetic (SP) mixing lines (SP percentage >30%) (Fig.2a).

More than 3/4 of the M_r/M_s ratios are between 0.1 and 0.2, and 85% for the H_{cr}/H_c ratios are between 3 and 5. Most of the points that are not in this region are from Ardley site, and they are characterized by a smaller magnetic grain size, with points closer to the SD-SP mixing line, with a higher SP percentage. This tends to show that magnetic particles present on all the sites, except Ardley, have a similar origin. On the contrary, the hysteresis parameters from the substrate samples plot slightly closer to the SD-SP mixing line than the lichen samples, but they are still in the PSD region (Fig. 2b).

Samples from Ardley have a behaviour different from the rest of the samples, identically to what we observed in the lichens, and they plot closer to the SP region.

These results are further confirmed with the good correlation between magnetic susceptibility and M_r in the case of the lichen samples (Fig. 3a), where the determination coefficient R^2=0.889 (95% significance level), but for the substrate samples, there is only little correlation between magnetic susceptibility and remanent magnetization (R^2=0.378), showing that the magnetic sources in these samples are diverse (Fig. 3b). The magnetic signal in the substrate is likely caused not only by the anthropogenic signal, but it also takes into account geological sources.

The variation of M_r with time shows an increase in M_r values in 1997 (when there is available data) and another one in 2006-2007(Fig. 4a). Susceptibility values show a large variation, from almost zero to 2.5×10^{-6} SI m^3/kg. The variation of magnetic susceptibility is similar, again with a peak in 1997 and 2006-2007 (Fig. 4b).

In order to study the spatial variation of magnetic parameters, we plotted the remanent magnetization values and the susceptibility values for lichen samples from 2010 on a cartographic representation of the sites (Fig. 5). That year corresponds to a sampling of all the sites and the results do not seem to be affected by the external causes that increased the magnetization and susceptibilities everywhere. The lowest values correspond to samples from the Collins ice sheet and Ardley peninsula, where there is little human activity. On the contrary, the sites with the highest magnetic susceptibility are the sites close to the airport and the site of Cerro Fósil in particular.

Unfortunately, the only sampling years for which we have substrate samples available for this study are 1997, 1998 and 2006, which are the years corresponding to the possible occurrences of external sources of magnetic input. It is therefore difficult to make any interpretation on the variations of magnetic parameters with time (Fig. SI-2).

FORC diagrams- Comparison magnetic signal lichen/substrate

Because they are calculated with a second derivative of magnetization, FORC diagrams are extremely sensitive to noise, and therefore can only be measured on the magnetically strongest samples. We measured FORC diagrams on the strongest lichen samples (most of them from the 1997 sampling) and on corresponding lichen and substrate samples whenever available.

Fig. 6 shows some of the FORC diagrams measured, over three different sampling years. Figs 6a., c., e. and g. are FORC diagrams measured on lichens, and Figs 6b., d., f. and h. show FORC diagrams measured on the substrate samples. The first three pairs were measured on corresponding lichen and substrate samples. Firstly, patterns characteristic of a SD-PSD magnetic grain size are visible on all FORC diagrams. The SD contribution is identified with the high coercivity tail, and the PSD contribution by the peak of FORC distribution close to the origin of the diagram and the fact that most contours do not close but instead they intersect the vertical axis. The spread along the vertical axis is quite limited, except for sample ALL97 (Lichen- LARC 1997), which shows that magnetic interactions are moderate.

Elemental concentrations in the substrate determined by INAA and ICP-OES

Figure 7 shows the elemental concentrations determined by INAA and ICP-OES of substrate from three of the sites sampled in the years 1997 and 2006.

These results are somewhat surprising since the continental terrestrial crust normally presents higher concentrations of Al than Fe. The higher concentrations of Na than Al agree with the marine aerosol contribution on King George Island.

Scandium, Yb and Eu are natural elements, which could explain the low variability of these elements on the different sites. In contrast, Cu, Zn, Co, Ni, Pb and As are anthropogenic elements, and therefore they show a great variability depending on the sites and years.

Elemental concentrations determined by SEM-EDS

Figure 8 shows examples of SEM micrographs and semi-quantitative EDS analysis corresponding to individual particles that contain heavy elements, and therefore could carry the magnetic signal as well as heavy metals, both in lichen and the substrate. SEM micrographs of lichens (Fig. 8a-b) show the presence of particles of a wide range of sizes (from sub-micrometres to several tens of micrometres), dispersed in the sample. EDS analysis in lichens all show the presence of natural elements such as Si, Al, Mg. Among the possible anthropogenic elements, Cr is present on two sites sampled in 1997 (Collins and Base China). Small amounts of K, P and V are also measured in various sites and sampling years. Calcium is also present in small amounts but widely throughout the different sites.

Angular particles between 1-20 µm can be seen on SEM micrographs of substrate samples (year 1997) (Fig.8c-d). EDS measurements also show the presence of the same

natural elements (Si, Al, Mg) that were identified in the lichen samples. Titanium is also present in the soil; the origin of this is probably natural. Other elements present in small amounts are Ca, V and K. These elements were also present in small amounts in the lichens.

Elemental concentrations in lichens determined by ICP-OES

Figure 9 shows the elements Fe, Al, Mn and Zn that are present with an important concentration (10-200 000 mg/kg), but different concentrations in the different sites. The concentrations of Zn in LARC site and Aerodromo site in 2006 are particularly high. Iron and Al concentrations are similar, and have the highest values in 2010, and the lowest in 2006, while Mn and Zn concentrations do not show such large variations.

The Fe concentrations measured here are above the USDA recommended maximum limits for *Usnea spp* (272 mg/kg) for all the years and sites except Collins and Ardley in 1997 and Ardley 2006. Aluminium exceeds the recommended value (499 mg/kg) at LARC and Base China in 1997, Base China, Cerro Fosil and Ardley in 2006 and everywhere except Aerodromo MET in 2010.

Figure 10 shows the presence of 13 elements in concentrations between 0.01 to 5 mg/kg, in lichens of the different sites in 1997. The highest concentrations of Cu and Pb are measured at the sites closer to the airfield and bases (Cerro Fosil, Aerodromo, Base China), while Ardley and Collins sites have much lower values.

The same information for the years 2006 and 2010 is presented in the Supplementary Information (Figs. SI-3 and SI-4). Overall, the concentrations of Cr, Cd and Pb have a tendency to decrease over the years, but the concentration of Cu at the airfield shows a

strong increase in 2006. The lowest values are found at Ardley and Collins sites, the two sites most isolated from human activities.

Vanadium concentration is above the USDA recommended limit (1.5 mg / kg) at Base China, Aerodromo, Aerodromo MET and Cerro Fosil in 1997 and all sites except Ardley in 2006. Regarding Mo, the maximum recommended concentration is 0.40 mg/kg, and this value is exceeded at LARC, Aerodromo and Aerodromo MET in 1997, at LARC in 2006 and everywhere except Aerodromo and Ardley in 2010. Beryllium concentration is 0.06 mg/kg or less.

Discussion

Magnetic measurements

The average magnetic susceptibility in lichen samples for the year 2010 is 7.5×10^{-8} m^3/kg, and the average SIRM for that same year is around 1 to 10 mAm^2/kg. These values are one to two orders of magnitude lower than the values measured on lichens from Argentinian cities by Chaparro et al. (2013), and about the same order of magnitude as values measured on lichens sampled close to a cement factory in Slovakia (Paoli et al. 2016). For the years 1997 and 2006-2007, when both susceptibilities and SIRM values are the highest, the SIRM values are comparable to the lowest values measured in these three studies, and susceptibilities are comparable to the highest values. However, it should be kept in mind that the lichen species are all different in all these studies so direct comparison with these previous results is difficult.

The cartography of magnetic parameters enables us to identify the sites that receive the most magnetic particles. Regardless of the sampling year, the highest values are measured for the sites that are close to the airstrip: either one of the three sites the closest to the airstrip, or the site Aerodromo MET, or either the site of Cerro Fosil or Cerro GPS. These two sites are slightly further from the airstrip but they are higher in altitude and therefore could be impacted by the emissions from planes during take-off or landing.

At the other side of the spectrum, the lichen samples from Collins ice-sheet and Ardley peninsula have a very low magnetic signal. They are almost not impacted by direct human activities because they are far from all the scientific bases. Furthermore, hysteresis parameters for samples from Ardley peninsula are different from other samples: on the Day-plot, they all plot closer to the SP mixing line and SD region. The Peninsula hosts a penguin colony, and this difference in hysteresis parameters could be linked to an incipient formation process of soil by organic matter accumulation and associated phosphatization (Machado et al. 2006). Actually, high levels of SP grains in soils are often due to magnetic enhancement by secondary magnetite/maghemite produced by pedogenic processes (Dearing et al. 1997).

The FORC diagrams measured in this study can be compared with those measured by Salo et al. (2012) on lichens from urban and industrial sites. Despite the low resolution of their measurements, it is easy to see that their FORC diagrams are much more characteristic of multidomain (MD) magnetic grains than ours are. The FORC diagrams measured by Sagnotti & Winkler (2012) on tree leaves from Rome are also MD-like and therefore quite different from the diagrams we measured.

The only published paleomagnetic study from Antarctic Peninsula also includes FORC diagrams (Gao et al. 2018). Measurements on basalt samples from three different formations show patterns that are MD-like, with no high-coercivity component and a large vertical spread. On the other hand, a FORC diagram measured on volcanoclastic rocks from Fildes Peninsula is SD-like. In any case, our FORC diagrams show patterns that are very different from those measured on rocks from the Antarctic Peninsula, which tends to indicate that the magnetic signal we have measured is not mostly caused by geological input.

Comparison of magnetic results between corresponding lichen and substrate samples show a few differences. The substrate samples from sites close to the airstrip still have higher values than the samples from the other sites, but unlike for lichen samples, substrate samples from LARC and Collins have high M_r and susceptibilities. FORC diagrams for lichen and substrate samples also bear some differences. Even though they bear similar SD-PSD patterns, there are two significant differences: the SD tail is more prominent and longer, and the spread along the vertical axis more limited for the substrate than for the lichen samples. This shows that the magnetic particles deposited on the substrate are different from those on the lichen. It is probable that the magnetic signal in the substrate samples contain a geological part as well as anthropogenic part. Another explanation could also be that coarser-grain particles from anthropogenic origin are more efficiently fixed on the lichens, that in the substrate. It also seems that magnetic particles are more dispersed in substrate than in lichens, perhaps because they become more strongly fixed when deposited on lichen than on substrate. These observations are further confirmed by the fact that there is no correlation between M_r or magnetic susceptibility on sister substrate/lichen samples (Fig. 11). This shows that the signal

from the lichen *U. aurantiaco-atra* is likely to be more representative of the anthropogenic contribution than the signal from the substrate.

Comparison magnetic-elemental concentration measurements

The concentrations of Fe determined by INAA in the substrate samples of 1997 from Aerodromo, LARC and Ardley sites are consistent with the saturation magnetization measurements: for both data sets, the highest values are observed for the Aerodromo site, then an intermediate value for LARC and a lower value for Ardley. Similarly, the increase of Fe concentration from 1997 to 2006 also corresponds to an increase of saturation magnetization. However, when looking at the concentrations of the other elements, only the Ni concentrations for the year 1997 show similar variations of concentrations among sites.

In the lichen samples, the concentrations of the various elements measured by ICP-OES can be compared with the magnetic proxies (saturation magnetization and magnetic susceptibility). The element that shows the highest correlation with magnetic parameters is Ni (R^2=0.832 for M_r and 0.6173 for MS).

Some elements show a weak correlation: Cr (R^2=0.334 for M_r and 0.349 for MS); Co (R^2=0.420 for M_r and 0.243 for MS); V (R^2=0.342 for M_r and 0.154 for MS) and Ag (R^2=0.088 for M_r and 0.254 for MS). The correlation for Cu is even weaker (R^2=0.069 for M_s and 0.136 for MS). Nickel and Cr are elements for which an association with magnetic parameters has been described (e.g., Cao et al. 2015, Salo et al. 2016), however it is somewhat surprising that no stronger correlation is observed for the other elements such as Cu, Pb, Cd, Ba, Mo.

Possible sources of the various elements

Possible explanations for the presence of the various elements in sometimes fairly high concentration, both in the lichen and the substrate, are presented in Table II.

Conclusion

We carried out for the first time magnetic and elemental analysis on *Usnea aurantiaco-atra* (Jacq.) Bory lichen and its substrate from various sites on the Antarctic Peninsula with various levels of influence from human activities. The main results are the following:

- Several anthropogenic elements have been identified on sites close to human activities: Ni, Pb, Mo, Cd, and Zn are the most prevalent. Some of the elements were found in sites that should have very little human influence, which shows that elements coming from other continents can travel long distances and contribute to the pollution in Antarctica.
- Magnetic proxies from lichen show a spatial correlation with human influence (scientific bases or airstrips). The temporal variation shows that on average, magnetic parameters started with high values in 1997, then decreased with time until 2007 but increased again in 2006-2007. The most recent measurements indicated nonetheless a general decreasing trend.
- It seems that the magnetic signal from the lichen is likely to be more representative of the anthropogenic contribution than that from the substrate.
- We observed a correlation between magnetic parameters and Ni, and to a lesser extent with Cr, Co, V, Ag.

- All these results suggest that using magnetic and elemental techniques, it is possible to implement monitoring with lichen *Usnea aurantiaco-atra* (Jacq.) Bory as a bioindicator for anthropogenic pollution.

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Author contribution

MP performed the fieldwork and supervised the entire work. RF, CE, NG and CC performed the different analysis of the samples. CC, MP, BA and NG interpreted the obtained results. CC and MP prepared the manuscript and created the figures with input from BA and NG.

Details of data deposit

The article will be deposited with free access in the libraries of the Universidad de Chile, the Sorbonne Université and the Universidad Nacional Autónoma de México.

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Figure captions

Figure 1. Sample sites in Fildes peninsula, King George Island, and lichen *Usnea aurantiaco-ater*(Jacq.) Bory.

Figure 2. Day-plot showing the hysteresis parameters with the mixing lines of Dunlop (2002) for: a: lichen *Usnea aurantiaco-atra* (Jacq.) Bory samples; b: substrate samples.

Figure 3. Susceptibility vs remanent magnetization for: a: lichen *Usnea aurantiaco-atra* (Jacq.) Bory samples; b: substrate samples.

Figure 4. Variation of a: remanent magnetization; b: magnetic susceptibility of lichen *Usnea aurantiaco-atra* (Jacq.) Bory samples with time (1997-2010).

Figure 5. Cartography of: a: remanent magnetization; b: magnetic susceptibility for lichen *Usnea aurantiaco-atra (Jacq.) Bory* samples sampled in 2010.

Figure 6. FORC diagrams. Top row: *Usnea aurantiaco-ater*(Jacq.) Bory samples; bottom row: substrate samples. Horizontal and vertical scales are the same for all samples except AsAr-06.

Figure 7. Elemental concentrations determined by INAA (Fe, Na, Zn, Sc, Cr, Ce, Co, As, La, Hf, Sm, Yb and Eu, labeled with an asterisk) and ICP-OES (Al, Cu, Ba, Ni, Pb and Cd) of substrate from three of the sites sampled in the years 1997 and 2006.

Figure 8. Examples of representative micrographs and EDS semi-quantitative analysis for: a: lichen sampled at Collins site in 1997; b: lichen sampled at Base China site in 1997; c: substrate sampled at Collins site in 1997; d: substrate sampled at Aerodromo MET site in 1997.

Figure 9. Concentrations of major elements determined by ICP-OES of *Usnea aurantiaco-ater*(Jacq.) Bory from the seven sites sampled in the years 1997, 2006 and 2010.

Figure 10. Concentrations of 13 minor elements determined by ICP-OES of *Usnea aurantiaco-ater*(Jacq.) Bory from the seven sites sampled in the year 1997.

Figure. 11. a: M_r of substrate sample vs. M_r of the corresponding *Usnea aurantiaco-ater*(Jacq.) Bory sample (taken at the same location on the same year). b: Magnetic

susceptibility of substrate sample vs. magnetic susceptibility of the corresponding lichen sample.

Tables

Table I. Coordinates of the sampling sites of lichens *Usnea aurantiaco-atra (Jacq.) Bory* and the corresponding substrate

Sampling site	Coordinates	
Aerodromo	-62º11’23.28’’	-58º58’27.12’’
Cerro Fosil	-62º12’18.72’’	-58º58’23.16’’
Cerro GPS	-62º11' 57.74"	-58º58'28.89"
Aerodromo MET	-62º11’20.76’’	-58º58’43.68’’
Base China	-62º12’51.84’’	-58º57’47.52’’
LARC	-62º12’07.56’’	-58º57’39.96’’
Ardley	-62º12’’46.44’’	-58º55’49.8’’
Collins	-62º10’08.76’’	-58º51’06.84’’

Table II – Possible origins of the elements detected in lichen *Usnea aurantiaco-atra (Jacq.) Bory* and the corresponding substrate samples

Element	Possible source
Fe, Al (2010)	Dust from road construction and extension of Chinese scientific base
Ni	Oil and diesel combustion(Pereira et al. 2010); use of lubricating oil (Song et al. 2010); additives in airplane fuel to increase motor efficiency (Marín-Flores et al. 2010); electric batteries
Pb	Airplane fuel burning (Pereira et al. 2010), abrasion of brake pads (Hong et al. 2020) and vehicle tires (Lough et al. 2005), oil lubricants (Song et al. 2010, Altıntaş et al. 2019); electric batteries
Cd	Elimination of wastes from incinerators (Boccaccini and Ondracek, 1995, Sekito et al. 2014); electric batteries
Mo	Elimination of wastes from incinerators (Boccaccini and Ondracek, 1995, Sekito et al. 2014); fossil fuel combustion (Pereira et al. 2010, Celo et al. 2015) and use of lubricating oil with molybdenite (Song et al. 2010) used in Antarctica in airplanes and machines such as snowploughs and construction machines; additives in airplane fuel (Marín-Flores et al. 2010)
Zn	Electric batteries, building construction work.
V	Use of diesel to produce electric energy (Hope 1997)
Be	Used with Cu or Ni alloys (Goddard et al. 2016)
La, Hf, Sm (Ardley)	Increasing use of these elements in catalytic systems of the new motor vehicles used in all other continents and arriving to Antarctica.
P (Ardley)	Presence of the penguin colony: the substrate is formed by organic matter accumulation and associated phosphatization (Machado et al. 2006).
Cr (Collins, 2006)	Extra-Antarctic source*

*The earth crust and rocks contain about 100 mg/kg of Cr. Soils contain normally on the average about 40 ppm of Cr, sometimes up to some hundreds mg/kg. (Merian 1984). In this work we find around 20 mg/kg in substrate. Some plants can take up higher Cr amounts, for instance lichens, mosses, ferns, grasses and others. We find lower concentrations of Cr in the lichen. On the other hand, practically all chromium compounds used by man originate from chromite, of which largest resources are placed in South Africa, Zimbabwe and Russia.

Figures

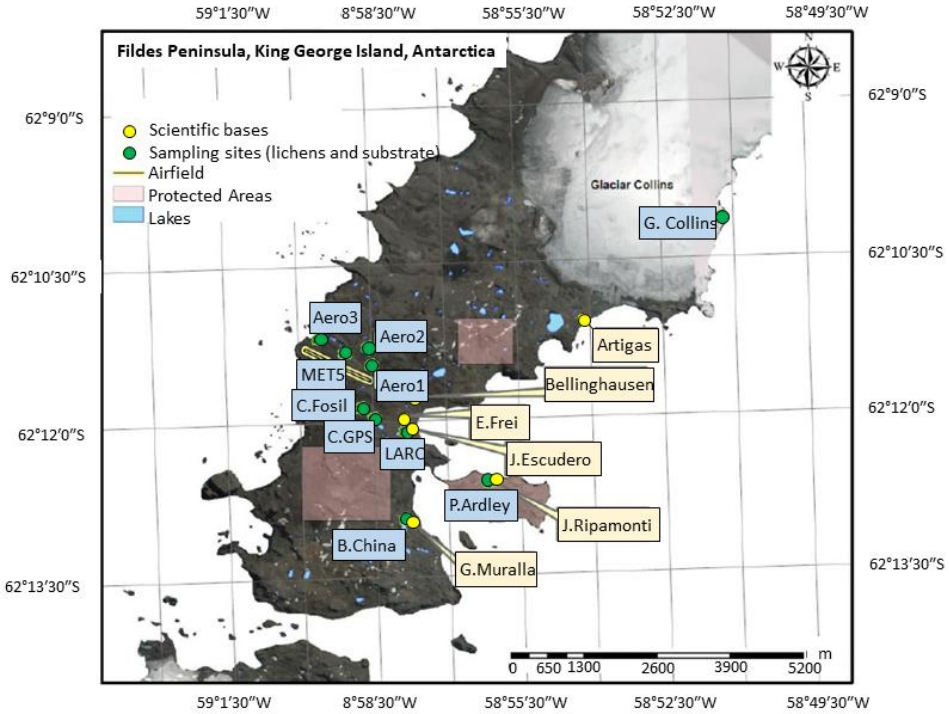


Figure 1

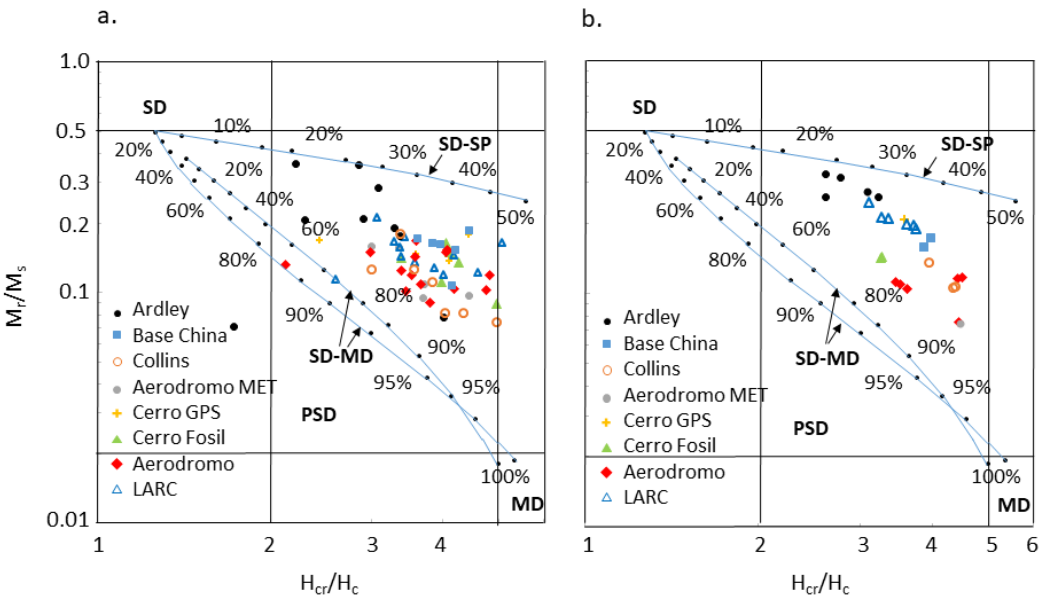
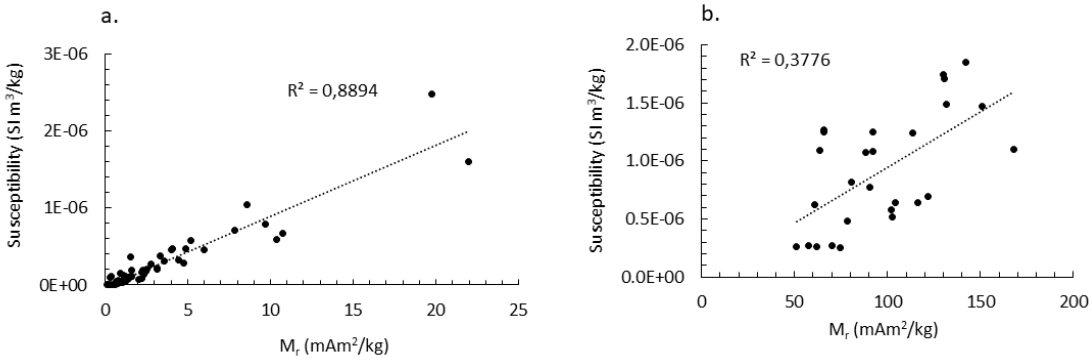


Figure 2



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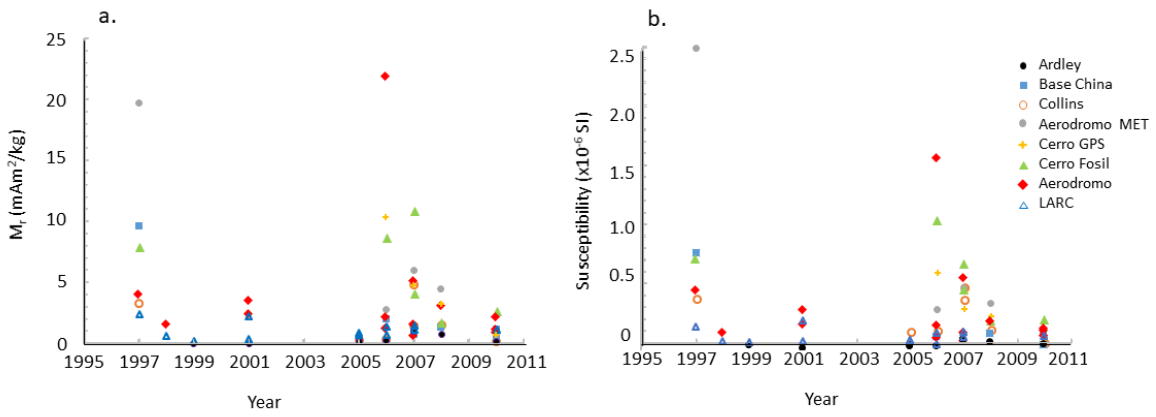

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638 Figure 4

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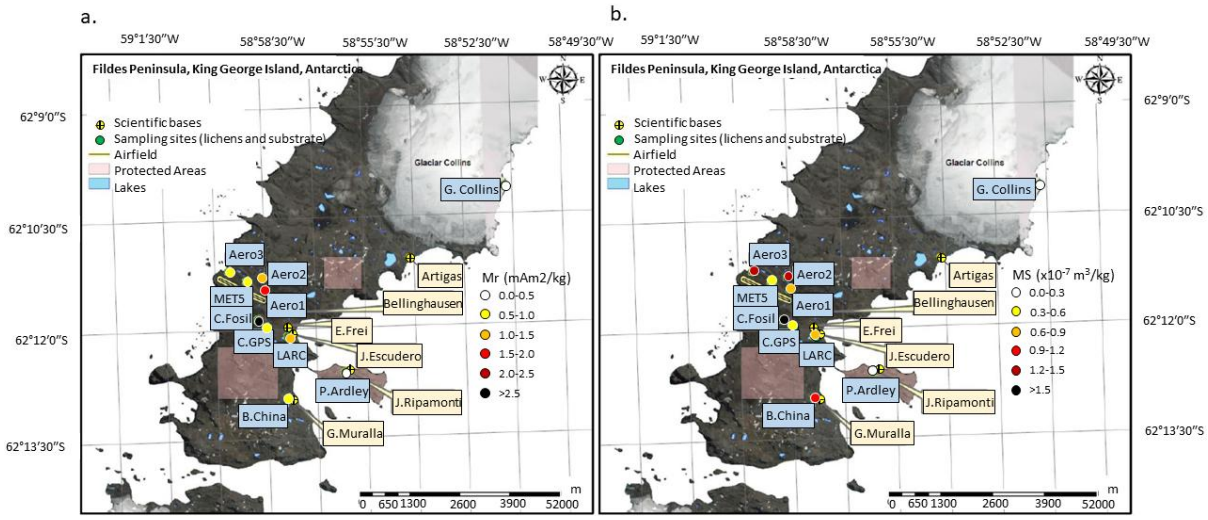

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641 Figure 5

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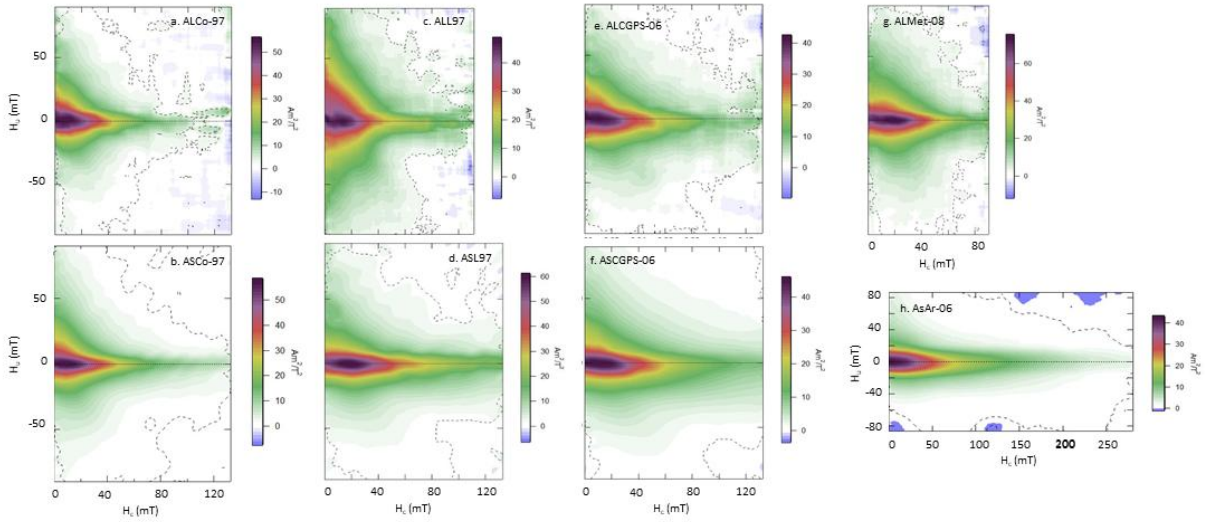

Figure 6

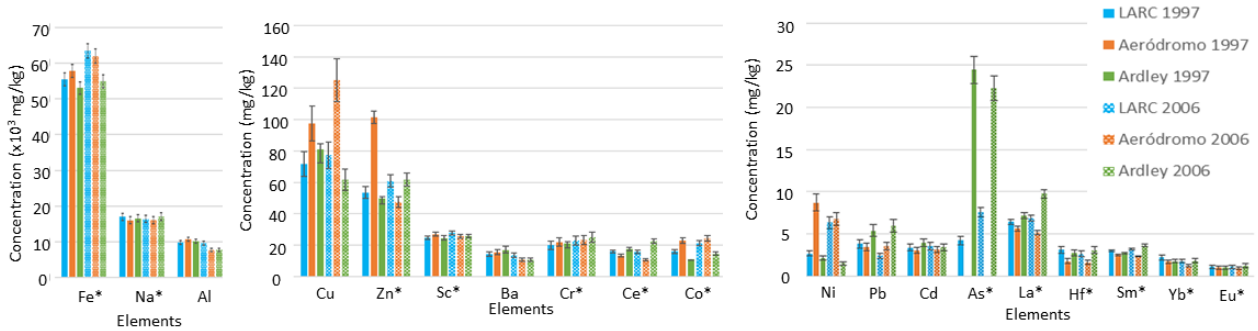

Figure 7

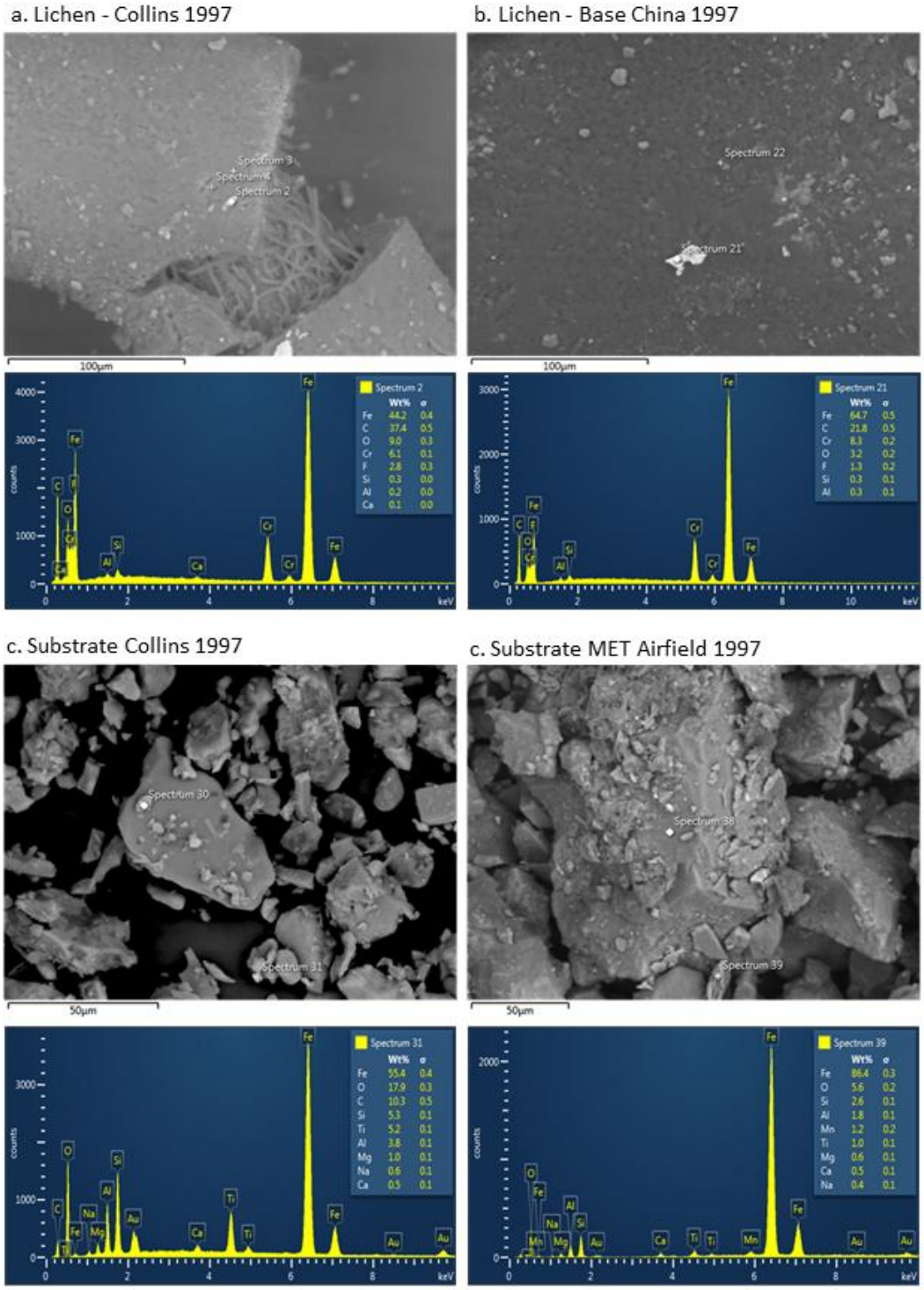
a. Lichen - Collins 1997
b. Lichen - Base China 1997
c. Substrate Collins 1997
c. Substrate MET Airfield 1997
Spectrum 2
Spectrum 21
Spectrum 31
Spectrum 39
counts
keV

Figure 8

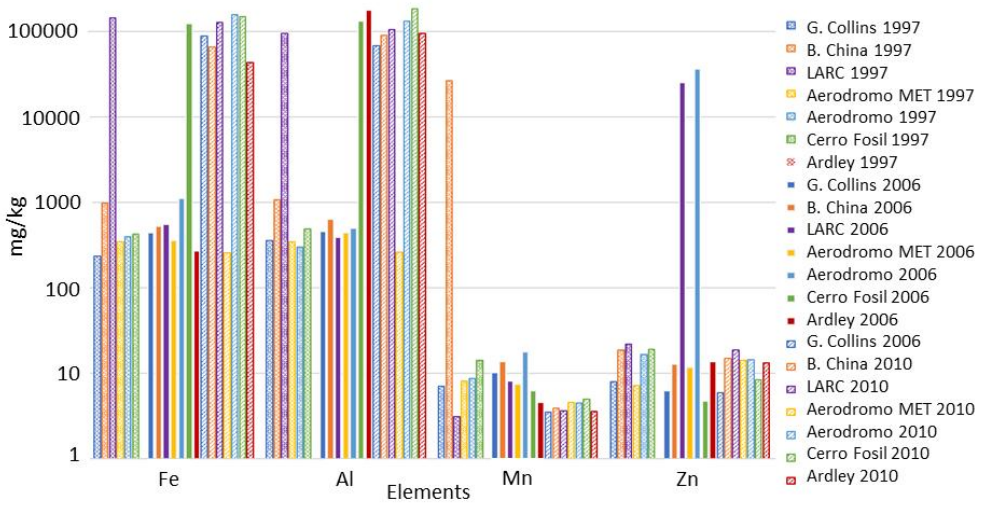

Figure 9

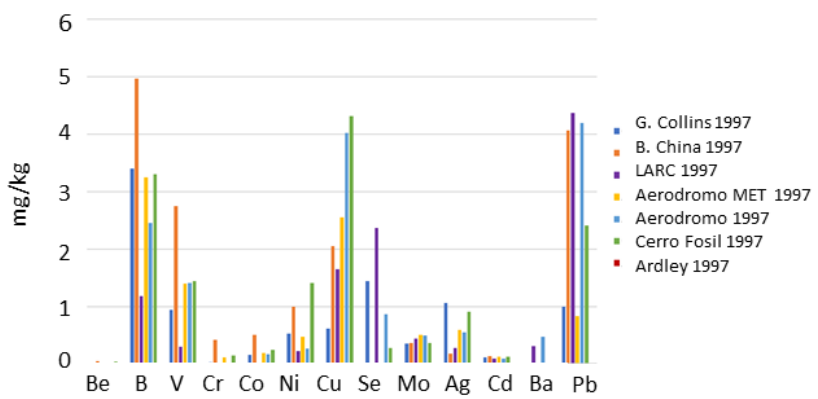

Figure 10

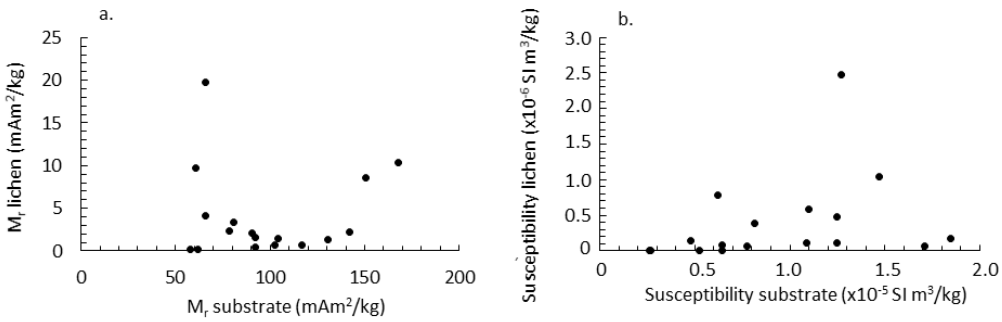
a.
25
20
15
10
5
0
0
50
100
150
200
M_r lichen (mAm^2/kg)
M_r substrate (mAm^2/kg)
b.
3.0
2.5
2.0
1.5
1.0
0.5
0
0
0.5
1.0
1.5
2.0
Susceptibility lichen (x10^{-5} SI m^3/kg)
Susceptibility substrate (x10^{-5} SI m^3/kg)

Figure 11