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Elemental composition of the lichen Umbilicaria decussata

ROBERTO BARGAGLI
FRANCESCA BORGHINI
CARLO CELESTI
Dipartimento di Scienze Ambientali, Università di Siena, via delle Cerchia 3, I-53100 Siena (Italy)

ABSTRACT

Total concentrations of major and trace elements were determined in thalli of the epilithic lichen *Umbilicaria decussata* from 37 habitats in Victoria Land (continental Antarctica). Average concentrations of Pb, Cu, Zn, Cr, Mn and Fe were among the lowest ever reported for lichens of genus *Umbilicaria*. On the contrary, Cd and Hg concentrations fell within the same range or were higher than those usually measured in samples from remote areas of the southern and northern hemispheres. No impact of local or remote human activities was detected. Comparison between average metal concentrations in *U. decussata* samples collected in 1989 and 1999 did not show significant variations, and this result was assumed to be indicative of negligible changes in the environmental biogeochemistry of Antarctic terrestrial ecosystems. The ad/absorption of soil and rock dust particles, atmospheric depositions, marine aerosols, guano of seabirds, and the uptake of soluble elements from widespread salt encrustations and/or rock minerals are the main sources of major and trace elements for epilithic lichens in continental Antarctica. Although the present results can be taken as baseline levels, further research is necessary in view of the expected effects of climatic changes on element bioavailability in ice-free areas of Antarctica.

KEY WORDS: Continental Antarctica - Macrolichens - Elemental composition - Environmental biogeochemistry.

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INTRODUCTION

Models of changes in climate predict that global warming effects will occur mostly in high latitude regions. Although it is not yet clear whether increased temperature in the Antarctic Peninsula (Stark, 1994) and in some coastal areas of the continent (Adamson & Adamson, 1992) are a consequence of global or regional processes, there is little doubt that some changes are already tangibile in Antarctica (Convey, 1997). Furthermore, the recent break-up of Antarctic Peninsula ice shelves is a matter of general concern (Vaughan & Doake, 1996). Retraction of sea ice, penetration of moisture-rich air masses and clouds into the continent and significant changes in precipitation are likely to be the greatest consequences of global warming in continental Antarctica. Schlesinger & Mitchell (1987) predicted a 5-20% increase in atmospheric precipitation for every 1° C increase.

In Antarctic coastal ice-free areas, the availability of free water is the main limiting factor for biotic communities (Smith, 1984; Kennedy, 1993; Bargagli *et al.*, 1999a). Therefore, the expected increase in water availability may be crucial to environmental biogeochemistry of major and trace elements and patterns of microbial and cryptogamic community development. Biological responses to increased chemical weathering and to changes in element bioavailability (both essential or toxic to metabolic processes) are not easily predictable. Antarctic terrestrial organisms, well-adapted to extreme environmental conditions, may be highly sensitive to or intolerant of any changes exceeding pre-existing thresholds. Species-specific differences in response to changes of environmental parameters can affect the competitive ability, leading to great modification of community structure. Moreover, immigrant plant propagules have been found in Antarctic terrestrial habitats (Linskens *et al.*, 1993), and environmental changes may favour the establishment of new pre-adapted and invasive species in areas where they did not occur before (Watson, 1999). For instance, despite the altitude and the limited extent of recently exposed fumarolic ground or Mt. Melbourne (2733 m) and Mt. Rittmann (2370 m), alien bryophyte species have colonized microenvironments because of suitable temperature, shelter (under ice and snow hummocks), and water availability (both from the condensation of steam and melting of snow; Broady *et al.*, 1987; Bargagli *et al.*, 1996a).

Because of the reduced number of species, interactions among organisms, and pristine conditions, terrestrial ecosystems of Antarctica offer a unique opportunity for research on colonization processes of old and/or newly exposed substrata. Fluxes of major and trace elements between biotic and abiotic components of ecosystems can be investigated. Insights into the functioning of ecosystems and effects of climate change can be yielded and used to understand more complex ecosystems elsewhere (Block, 1994). For instance, the increased availability of water and nutrients will affect the growth rate and the elemental composition of lichens and mosses. Therefore, defining current baseline concentrations will be useful in detecting local environmental changes, assessing increased human impact in Antarctica and establishing global biomonitoring networks.

Lichens are among the first colonizers of exposed rocks in cold, dry and poor nutrient habitats of continental Antarctica. The symbiotic association of fungi and algae has cation exchange properties and takes up rapidly soluble elements over the entire thallus surface. Cations may also enter and accumulate in mycobiont and photobiont cells through slower and more selective uptake mechanisms (Brown & Brown, 1991). Soil particles and aerosols adsorbed to the surface and/or trapped in the loose hyphal weft of the medulla also contribute to total element concentrations in the thalli. Lichens are perennial, have a slow growth rate and are largely dependent on atmospheric deposition for their metabolism. Thus, species with wide geographical ranges are widely used as biomonitors of persistent atmospheric pollutants (e.g., trace metals, organochlorines and radionuclides; Bacci *et al.*, 1986; Smith & Clark, 1986; Bargagli, 1989; Nash & Gries, 1995).

Lichens of the genus *Umbilicaria* are widely distributed in Arctic-Alpine habitats in both hemispheres and have been extensively used as biomonitors of trace element deposition in Canada and northern European countries (Lounamaa, 1965; Puckett *et al.*, 1973; Seaward *et al.*, 1981; Chiarenzelli *et al.*, 1997). Previous surveys on trace metal concentrations in the species *Umbilicaria decussata* (Vill.) Zahlbr. from coastal ice-free areas of Victoria Land (Bargagli *et al.*, 1993; Bargagli *et al.*, 1999b) showed that concentrations of lead and other metals were among the lowest ever reported for related species of lichens. On the contrary, mercury and cadmium concentrations fell within the same range or were higher than in *Umbilicaria* species from the northern hemisphere. This was a rather unexpected result due to the fact that anthropogenic emissions of metals in Antarctica are negligible and there is no evidence of long-range transport from other continents, except for lead (Flegal *et al.*, 1993). Marine aerosols, entrapment of soil rock dust particles, regional volcanic activity, and uptake of soluble elements from the substrate were assumed to be sources of mercury and cadmium in Antarctic lichens.

By analysing samples of *U. decussata* collected in January-February 1999 at the same sites as in austral summer 1989/90, and in several new sites, this paper aims at: (1) assessing current baseline concentrations of major and trace elements in lichens from Victoria Land; (2) understanding further how environmental factors affect the elemental composition of foliose lichens; (3) verifying whether element concentrations in *U. decussata* have changed significantly during the last decade.

MATERIALS AND METHODS

Umbilicaria decussata is one of the most common species in lichen communities of continental Antarctica. It usually occurs on siliceous rocks, sheltered from desiccating winds and where some moisture is available during summer. In ice-free areas of Victoria Land, patchy communities of *U. decussata* generally occur in coastal habitats, like most of the Antarctic cryptogamic flora. However, they can also be found in niches and fissures of north-facing rocks, up to an altitude of 700-800 m and 30-50 km from the coastline.

Samples of *U. decussata* were collected in January and February 1999 from rock outcrops in 37 habitats in Victoria Land, from Football Saddle (72°31°'S) to Granite Harbour (76°49'; Fig. 1). At each site, a composite sample of several thalli was collected by using disposable plastic gloves and clean stainless steel tools. Directly after returning to the laboratory of Baia Terra Nova Station, the samples were air dried at 40° C for 36 h, sorted to remove as much extraneous material as possible (i.e., soil and rock particles, dead and senescent parts) and stored in paper bags to be shipped to Italy.

In the laboratory, samples were dried at 40 °C to a constant weight, unsealed in a chamber under N_2 flow, and the outermost portion (2-3 mm) of each thallus was excised for analytical determinations. About 150 mg of homogenized thalli were mineralized in clean Teflon vessels with 3 ml of concentrated HNO_3 (Merck Suprapur) in a pressurized digestion system, at 120° C for 8 h. Na and K were determined by atomic absorption spectrometry using an air-acetylene flame as atomization source (FAAS). Pb, Cd and

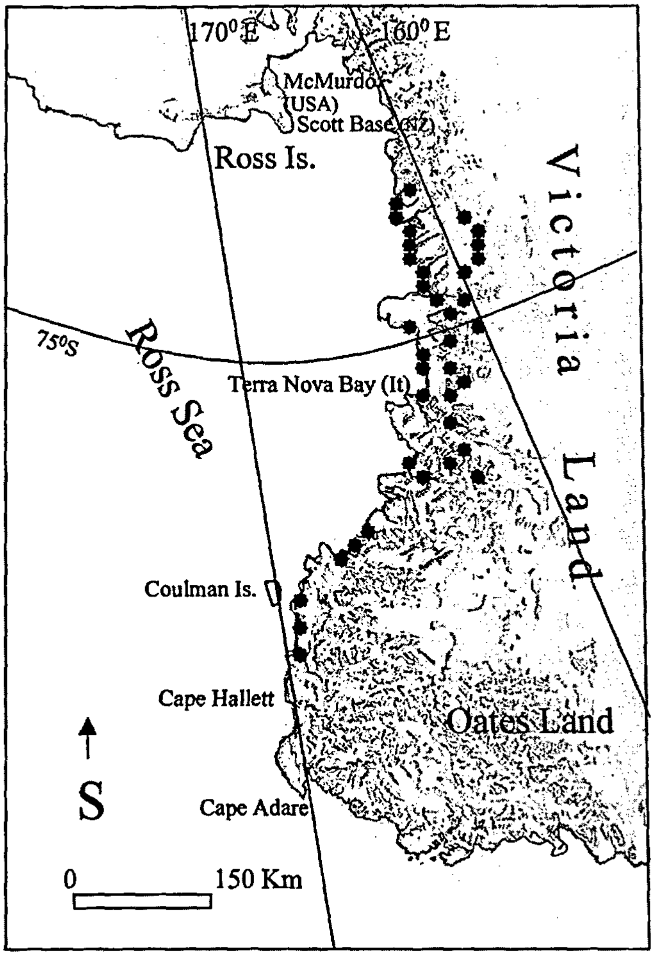

Fig. 1 - Map of the study area and sampling sites.

Cr were analysed by electrothermal AAS equipped with a graphite furnace and background Zeeman corrector (ZETAAS). The analytical determination of Al, Fe, Ca, Mg, Mn, K, Cu, and Zn was performed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Element concentrations (expressed as µg g^{-1} dry wt) were determined by the method of standard additions before mineralization. Standard solutions of inorganic elements (Spectrosil grade, BDH) were prepared by the serial dilution of stock standard solutions containing 1 g l^{-1} of the element to be determined.

Data quality was checked for each batch of samples by analysing blanks and by simultaneous digestion and analysis of the Standard Reference Materials (SRMs) "peach leaves" and "tomato leaves", from the National Institute of Standards and Technology (NIST, Gaithersburg, USA). Sample batches differing by more than one standard deviation from the certified value were repeated. The recovery rate ranged between 92% and 105% and the coefficients of variation calculated through the analysis of five replicates of several samples ranged from 5.5% to 19.4%, depending on the element.

Basic statistics were used to calculate mean and standard deviation; the Mann-Whitney U test was used to determine the statistical significance of differences between groups at probability level < 0.01. Pearson's correlation coefficients (P < 0.01) between elements were also computed by using the software program Statistica (StatSoft Inc., USA).

RESULTS AND DISCUSSION

Table I summarizes the results of *U. decussata* sample analyses from 37 ice-free areas throughout Victoria Land. Concentrations of major and trace elements fell within the same range as those measured in 24 samples from the same region collected in 1989-90, prepared and analysed by the same procedures (Bargagli *et al.*, 1993; Bargagli *et al.*, 1999b). The only statistically significant difference (Mann-Whitney U Test, P < 0.01) between the two surveys is a higher average content of lithophilic elements (i.e., Al, Fe and Mn) in samples collected in January-February 1999. This result is probably due to a greater amount of soil and rock dust particles in lichen thalli rather than to changes in the environmental bioavailability of these elements. Corroborating baseline concentrations of major and trace elements in *U. decussata* established in previous surveys, values summarized in Table I confirm that Hg and Cd concentrations in Antarctic lichens fall within the same range or are higher than those usually reported for *Umbilicaria* species from the northern hemisphere (Chiarenzelli et al., 1997). On the contrary, average concentrations of all the other trace metals in Antarctic lichens are lower than those reported for *Umbilicaria* species from NW Canada (Puckett & Finegan, 1980; Chiarenzelli *et al.*, 1997) and the Canadian high Arctic (France & Coquery, 1996). The most striking result of this comparison is the very low Pb content in Antarctic lichens with respect to those in samples from high latitudes in the northern hemisphere (about one order of magnitude). However, this result is consistent with the lowest ever reported Pb concentrations in mosses from the same Antarctic region (Bargagli *et al.*, 1998a). Much lower Pb levels were also found in snow samples from Adelie Land and Victoria Land (4-5 pg g^{-1}; Görlach & Boutron, 1992; Barbante *et al.*, 1997) than in central Greenland snow (15-18 pg g^{-1} ; Savarino *et al.*, 1994; Candelone *et al.*, 1996).

TABLE I - *Mean (± SD) and range of major and trace element concentrations (µg g^{-1} dry wt) in* U. decussata *from Victoria Land.*

Year	1999	1989
n	37	24
Ca	456±309 23-1200	578±506 80-1570
K	2296±1387 982-6500	2044±539 1100-3055
Mg	608±500 30-2898	488±420 50-2170
Na	175±88 56-422	226±119 46-586
P	789±507 184-1921	961±515 402-2370
Al	1030±898 101-5254	424±210 62-1075
Fe	1829±1046 224-4972	715±346 205-1269
Mn	25±14 6-80	11±4 6-21
Zn	21±6 7-43	18±5 9-32
Cd	0.19±0.18 0.03-0.79	0.17±0.09 0.04-0.39
Cr	1.86±0.92 0.40-3.94	1.34±0.85 0.23-3.80
Cu	4.9±3.2 1.2-18	6.2±5.3 1.6-23
Hg	0.42±0.28 0.08-1.50	0.36±0.26 0.16-1.06
Pb	0.77±0.48 0.06-1.73	0.66±0.50 0.04-2.14

From the distribution of trace metal concentrations in the study area, local human activities in Baia Terra Nova and Gondwana stations or in field camps do not affect trace element values. Despite the lack of evident anthropogenic impact, concentrations of several elements (e.g., Pb, Hg, Ca, and Mg) fluctuated greatly. Pearson's correlation coefficients between pairs of elements were calculated to investigate the cause of this variability (Table II). The relationship between element concentrations in *U. decussata* thalli and the distance (km) of each sampling site from the seashore was also investigated.

Umbilicaria decussata is a nitrophytic species that avoids rocks near penguin rookeries or other nutrient-rich habitats. However, very large communities of this lichen develop in coastal ice-free areas with nesting petrels *(Pagodroma nivea and Oceanites oceanicus)* and Antarctic skuas *(Catharacta maccormicki)*. There is also evidence of a decrease in *Umbilicaria* thallus size as the distance from nesting sites increases (Ryan &

Watkins, 1989). Owing to the role of seabirds in transferring nutrients and toxic elements accumulated by marine organisms (e.g., Cd and Hg; Bargagli *et al.* 1996b, 1998a, b) to terrestrial ecosystems, possible relationships between trace element concentrations in *U. decussata* and the estimated abundance of nesting seabirds in each sampling sites were also evaluated.

Relationships between lithophilic elements were the most significant ($r > 0.83$) which likely indicate a contamination of lichen thalli by ad/absorbed soil and rock dust particles. On the contrary, P concentrations were inversely related to distance from the sea ($r = 0.44$; $P < 0.01$) and were directly linked to the estimated abundance of nesting seabirds ($r = 0.64$; $P < 0.01$). According to the results of previous surveys using mosses and lichens (Bargagli *et al.*, 1998a, 1999b), Na concentrations were inversely related to distance from the sea ($r = 0.42$; $P < 0.01$). The correlation between P and Na concentrations (Table II) indicates that these elements may have a common source, mainly the marine environment. However, distribution of Na was not affected by the presence of nesting seabirds and the highest values were homogeneously distributed in coastal stations. Probably, this indicates a prevailing Na input through the marine aerosol.

No relationships were found between concentrations of Cd and those of other elements. The highest values in *U. decussata* thalli showed a random distribution in sites with different lithological characteristics and located at different distances from the sea.

Besides a common source and/or association in soil and rock dust particles, relationships between element concentrations in lichens may also reflect common uptake and metabolic pathways. These processes affect the bioaccumulation of more soluble elements (e.g., Ca, Mg, Zn, Cu) which may originate from atmospheric deposition, marine environment, and the solubilization of widespread salt encrustations and/or minerals. A discrimination among these different sources is rather difficult because several interrelated elements such as Ca and Mg are among the major constituents of seawater as well as of salts encrusting Antarctic soils and rocks. The lack of relationships between elements such as Ca, Mg, Mn, Zn, Cu, Fe, and Cr, which are essential to lichen metabolism (Bargagli, 1998) and Na probably indicates that the marine aerosol plays a minor role in supplying macro- and micronutrients to epilithic lichens. Therefore, atmospheric deposition and the solubilization of salts and minerals may be an important source of elements for lichens in Victoria Land.

In general, the highest concentrations of Ca, Cu, Mg, Mn, and Zn occurred in lichens growing on gabbro and ultramafic rocks such as at Vegetation Island, Teall Nunatak and Fleming Head (Carmignani *et al.*, 1988). Average concentration of Hg and Pb proved significantly higher (Mann-Whitney U Test, $P < 0.009$) in samples ($n = 18$) collected in ice-free areas located at a distance >10 km from the seashore than in those ($n = 19$) from coastal habitats. As suggested by statistically significant relationships with Mg, Zn, Fe, Mn (Table II), the main source of Pb for *U. decussata* thalli seems to be the substratum (i.e., gabbro and ultramafic rocks at Fleming Head, Teall Nunatak, and Vegetation Island) or metamorphic complexes at Cape Sastrugi, Miller Nunatak, and in moraines along the Campbell Glacier (Carmignani *et al.*, 1988).

Although Hg concentrations were positively related with those of Pb, Mg, Cr, Zn, and lithophilic elements, their distribution in the study area showed a distinctive pattern (Fig. 2). Most of the highest values occurred in lichens collected in inland stations with granitic rocks, in the southernmost part of the study area.

TABLE II - *Pearson's correlation coefficients between element concentrations in lichen thalli.*

	Hg	Pb	Ca	Mg	Zn	Al	Mn	Fe	Cd	K	Cu	Cr	Na	P
Hg	1.00													
Pb	0.55*	1.00												
Ca	0.31	0.06	1.00											
Mg	0.46*	0.52*	0.42*	1.00										
Zn	0.48*	0.42*	0.28	0.50*	1.00									
Al	0.45*	0.63*	0.37	0.91*	0.43*	1.00								
Mn	0.59*	0.57*	0.45*	0.88*	0.54*	0.91*	1.00							
Fe	0.63*	0.62*	0.45*	0.84*	0.56*	0.86*	0.97*	1.00						
Cd	-0.03	-0.07	0.05	-0.10	-0.07	-0.19	-0.18	-0.16	1.00					
K	0.15	-0.11	0.19	0.23	0.48*	0.14	0.31	0.29	0.28	1.00				
Cu	0.36	0.30	0.16	0.40*	0.25	0.35	0.41*	0.52*	-0.04	0.09	1.00			
Cr	0.56*	0.39	0.29	0.55*	0.34	0.51*	0.66*	0.75*	-0.05	0.35	0.62*	1.00		
Na	-0.15	-0.31	0.18	0.11	0.08	-0.06	-0.03	-0.02	-0.04	0.21	0.28	0.08	1.00	
P	-0.26	-0.34	0.16	0.05	0.12	-0.20	-0.10	-0.11	0.31	0.41*	-0.03	-0.07	0.53*	1.00

* relationships significant at $P < 0.01$ level

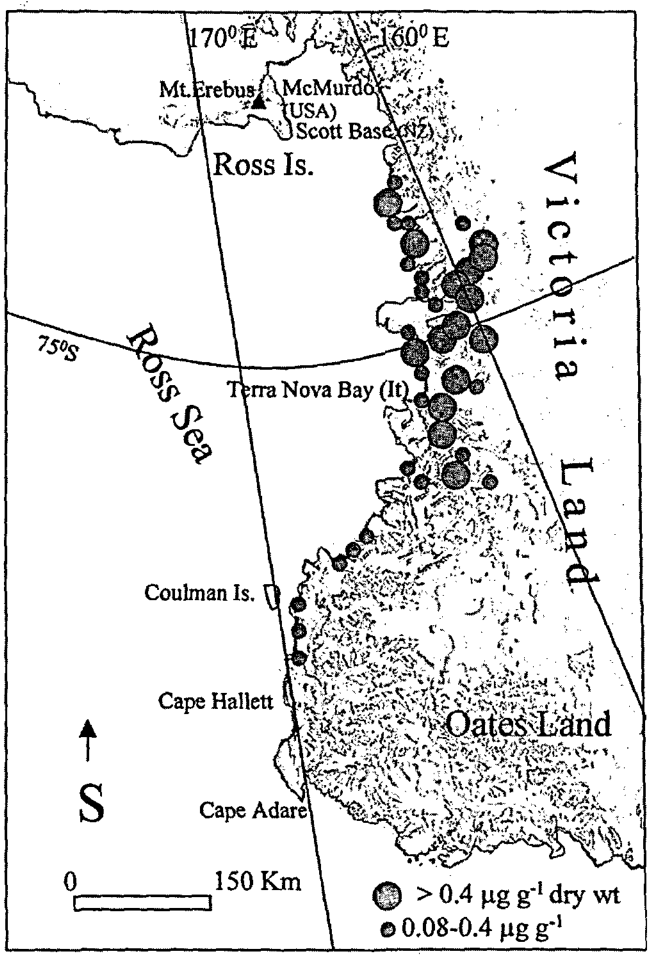

Fig. 2 - Distribution of Hg in lichen samples from Victoria Land.

Since the first Hg biomonitoring in Victoria Land (Bargagli *et al.*, 1993) average concentrations of Hg in epilithic macrolichens (0.034 ± 0.023 µg g^{-1}) were found to be much higher than those in granitic rocks and soils from the same region or in related species of lichens from other remote areas of the northern and the southern hemisphere. As anthropogenic sources of Hg in Victoria Land are negligible and it was well known that volcanic and fumarolic emissions are primary sources of Hg (Varekamp & Buseck, 1986; Bargagli & Barghigiani, 1991), it was hypothesized that at least in part, the bioaccumulation of Hg in lichens was due to emissions from the active volcano on the top of Mount Erebus and fumaroles on Mount Melbourne and Mount Rittmann. The very slow growth rate of lichens in extreme Antarctic environmental conditions was assumed to be another factor enhancing the bioaccumulation of Hg in Victoria Land. Apparently, this hypothesis was in contrast with very low concentrations of Hg measured in snow (Sheppard *et al.*, 1991) and air (de Mora *et al.*, 1993) in southern Victoria Land (just below the volcano). However, considering that Mount Erebus emissions occur at an altitude of 3794 m and are generally blown towards the north, the results of the present survey (i.e., the accumulation of Hg in thalli of *U. decussata* growing in inland nunataks or mountains of the Scott Coast with homogenous granitic substrata; Figure 2 seem to corroborate the previous hypothesis.

CONCLUSIONS

The results of analytical determination in 37 samples of *U. decussata* from boulders and rock outcrops throughout Victoria Land (continental Antarctica) confirmed baseline concentrations of major and trace elements measured in previous preliminary surveys. The only statistically significant difference was an increase of Al, Fe, and Mn concentrations, probably due to the contamination of 1999 samples with soil and rock dust particles. Although the increase of water availability and chemical weathering processes are among the most probable effects of climate change on ice-free areas of continental Antarctica, comparisons between the elemental composition of lichens collected in 1989 and 1999 seem to exclude significant change in the environmental biogeochemistry of major and trace elements in Victoria Land. Because of the negligible input of trace metals from local or remote anthropogenic sources in this region, the *U. decussata* thalli showed one of the lowest concentrations ever recorded of Pb, Cu, Zn, Cr, Mn, and Fe for lichens of the same genus. The most important exceptions were Cd and Hg concentrations, which fell within the same range as, or were higher than, those usually measured in lichens from remote areas of the southern and the northern hemispheres.

The enhanced bioaccumulation of Hg in lichens that grow in granitic rocks (with very low metal content and located in mountains and nunataks very far from the sea) seems to support the general assumption that most elements in lichens come from atmospheric depositions. In particular, this result supports the previous hypothesis of Hg contribution from active volcanoes and fumaroles in Victoria Land. Besides elements in dry deposition and snow, inputs of Na (mainly through the marine aerosol) and P (through the guano of seabirds) were detected in coastal ecosystems. Moreover, there is evidence of soluble element uptake by the lichen thalli from salt encrustations and/or rock minerals. The geochemical nature of the substratum probably, plays a role in determining Pb bioaccumulation in lichens from inland sites. All the environmental factors affecting the elemental composition of Antarctic lichens and their slow growth rate should be taken into account, using values of the present survey as reference concentrations for lichen biomonitoring in other continents.

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