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CONCENTRATION OF BIOLOGICAL RELEVANT ELEMENTS OF FOLIOSE AND FRUTICOSE LICHENS FROM NAHUEL HUAPI NATIONAL PARK (PATAGONIA), ANALYZED BY INAA

INAA-Untersuchungen zur Konzentration biologisch bedeutsamer Elemente von Laub- und Blattflechten des Nationalparks Nahuel Huapi (Patagonien)

by

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Key words: Lichens, biomonitors, elemental composition, pristine areas, Patagonia, Argentina.

Schlagwörter: Flechten, Biomonitoring, Elementzusammensetzung, unberührte Gebiete, Patagonien, Argentinien.

Summary: Seventy-eight foliose and fruticose epiphytic lichen thalli were collected from urban, periurban and pristine areas of Nahuel Huapi National Park, N-W Patagonia. The lichens correspond to 4 species: *Candelariella vitellina* (EHRH.) MÜLL. ARG., *Hypotrachyna brevirhiza* (KUROK.) HALE, *Physcia adscendens* (FR.) OLIVER and *Parmelia cunninghamii* CROMBIE and 2 fruticose: *Protousnea magellanica* (MONT.) KROG and *Usnea fastigiata* MOT. The elemental composition of each specimen was analyzed using Instrumental Neutron Activation Analysis (INAA).

In total, forty two elements were determined. The lithophile element concentrations were already treated separately (RIBEIRO GUEVARA et al., 1995). In the present study the biological relevant elements (Br, Ca, Cl, Co, Cu, Fe, I, K, Mg, Mn, Na, Ni, V and Zn) were investigated as well as the non-biological Rb (MARKERT, 1992) because of its affinity with K.

The elemental concentrations obtained for different areas are compared among them and with bibliographic data.

Zusammenfassung: Achtundsiebzig Thalli epiphytischer Laub- und Blattflechten wurden in Stadt-, Stadtrand- und unbelasteten Gebieten des Nationalparks Nahuel Huapi (N-W Patagonien) gesammelt. Es handelt sich dabei um die 4 Flechtenarten *Candelariella vitellina* (EHRH.) MÜLL. ARG., *Hypotrachyna brevirhiza* (KUROK.) HALE, *Physcia adscendens* (FR.) OLIVER und *Parmelia cunninghamii* CROMBIE sowie um die Strauchflechten *Protousnea magellanica* (MONT.) KROG und *Usnea fastigiata* MOT. Für jede Art wurde die Zusammensetzung der Elemente mit Hilfe der "Instrumentalen Neutronen-Aktivierungs-analyse" (INAA) untersucht.

Insgesamt wurden zweiundvierzig Elemente bestimmt. Die Konzentrationen der lithophilen Elemente wurden schon separat abgehandelt (RIBEIRO GUEVARA et al., 1995). In der jetzt vorliegenden Studie sind sowohl die biologisch relevanten Elemente (Br, Ca, Cl, Co, Cu, Fe, I, K, Mg, Mn, Na, Ni, V und Zn) als auch das nicht-biologische Rb wegen seiner Affinität zu K (MARKERT, 1992) untersucht worden.

Die für die verschiedenen Gebiete erhaltenen Konzentrationen der Elemente werden untereinander und mit Literaturangaben verglichen.

Introduction

The significance of the use of the elemental composition of biotic and abiotic components of the ecosystem to understand the environment has been discussed during the past fifteen years (MARKERT, 1991; 1992). The elemental composition of lichens has proved to be an useful tool to assess trace-element air pollution (BROWN, 1991; DE BRUIN, 1990; GARTY, 1993; KANSANEN & VENETVAARA, 1991). However, baseline data from remote and/or pristine habitats are scarce (WIERSMA et al., 1992), even when this information could be useful not only for present research but also in future times, for comparison purposes.

The data analyzed in this paper are part of the study of the elemental composition of lichens from pristine areas of Nahuel Huapi National Park, from urban and periurban areas of a small, non-industrial city (Bariloche), iniciated two years ago (ARRIBÉRE et al., 1994). The litophile element concentrations were treated separately (RIBEIRO GUEVARA et al., 1995). In the present work the biological related elements (Br, Ca, Cl, Co, Cu, Fe, I, K, Mg, Mn, Na, Ni, V and Zn) are investigated as well as the non biological Rb because of its affinity with K (MARKERT, 1992), aiming to find out whether the small city of Bariloche might have influenced on the elemental composition of lichens and to obtain baseline data to be used as reference in future studies.

Materials and Methods

Study area: This study was performed at Nahuel Huapi National Park, North-Western Patagonia, an area covered mainly by *Nothofagus* forests. Within the National Park lies Bariloche, a tourist, non-industrial city, with ca.

85000 inhabitants, where atmospheric pollution would not be expected (GRIGERA et al., 1989). Three different Collection Sites were selected for the present study (Fig. 1), representing three different degrees of anthropogenic perturbations.

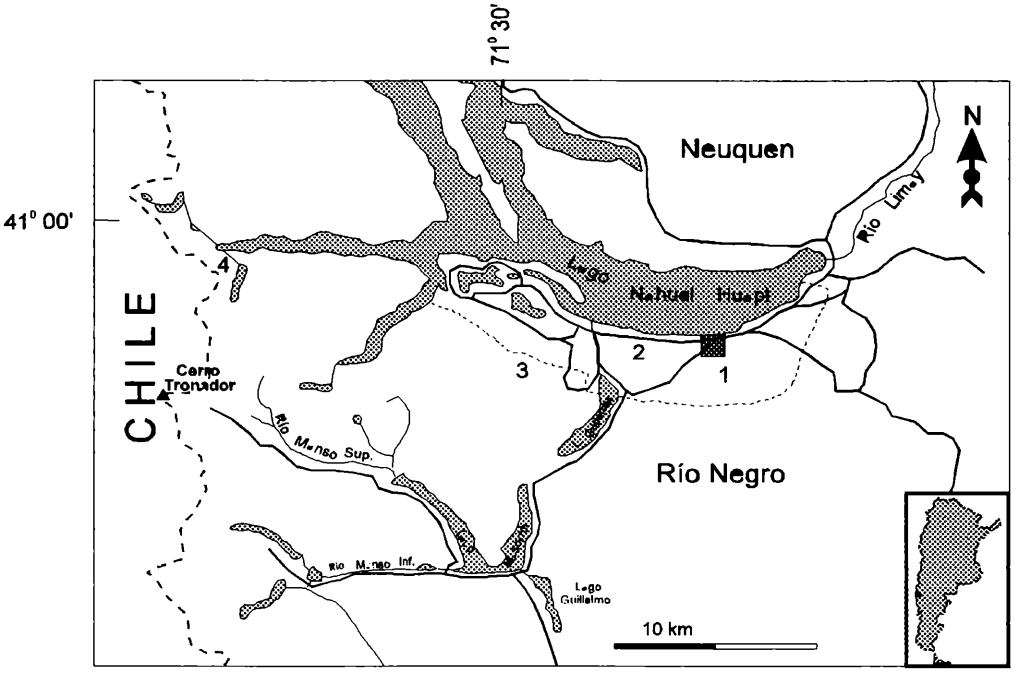

Fig. 1: Study Area.

References:
1 Urban Bariloche (**U**)
2 Av. Bustillo
3 Periurban (**PU**)
4 Puerto Blest (**PT**)

A- **Pristine (PT)**: Puerto Blest, with none or extremely reduced man activities. The collections (eighteen specimens of *Parmelia cunninghamii, Protousnea magellanica* and *Usnea fastigiata)* were made at both margins of Río Frías, in a deep forest habitat, well protected of the dominant West winds, to avoid potential contamination with clastic particulate.

B- **Periurban (PU)** areas near Bariloche, without human settlements, at least 2 km away from roads and human residences, where twenty-six specimens of *Candelariella vitellina, Hypotrachyna brevirhiza, Physcia adscendens* and *Usnea fastigiata* were collected.

C- **Urban (U)**, areas in downtown Bariloche, 1 to 10 m from the heaviest vehicle circulation streets, where thirty two specimens of *Candelariella vitellina, Hypotrachyna brevirhiza* and *Physcia adscendens* were collected.

Specimen preparation: The specimens collected were all corticolous, except for two collections of *Candelariella vitellina* that grew on a cement post (**POST**). Each collection was identified using the usual morphological-, anatomical- and chemotaxonomical- techniques.

The samples were examined and cleaned under dissecting microscope, to eliminate substrate and particulate, washed three times with demineralized water and dried to constant weight at ca. 26° C during 48 to 72 hours. The sample masses ranged from 2 to 150 mg.

Sample analysis: All samples were irradiated at Bariloche RA-6 Research Reactor and the trace element concentrations were determined by INAA, using the absolute parametric method as described in a previous work (Ribeiro Guevara et al. 1995). The first irradiation lasted 180 seconds, the isotopes detected were ^{28}Al, ^{48}Ca, ^{38}Cl, ^{165}Dy, ^{152}Eu, ^{128}I, ^{42}K, ^{27}Mg, ^{56}Mn, ^{24}Na, ^{51}Ti and ^{52}V. The second irradiation was done after a minimum of 15 days, it lasted 8 hours, the isotopes detected were ^{76}As, ^{198}Au, ^{131}Ba, ^{82}Br, ^{141}Ce, ^{58}Co, ^{60}Co, ^{51}Cr, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{203}Hg, ^{42}K, ^{140}La, ^{177}Lu, ^{99}Mo, ^{24}Na, ^{147}Nd, ^{239}Np, ^{233}Pa, ^{86}Rb, ^{124}Sb, ^{46}Sc, ^{153}Sm, ^{85}Sr, ^{182}Ta, ^{160}Tb, ^{187}W, ^{169}Yb, ^{175}Yb and ^{65}Zn. Standard Reference Material Citrus Leaves NIST-SRM-1572, IAEA-SOIL-7 and Lichen IAEA-336 samples were processed. Cu was determined by Flame Atomic Absorption Spectrophotometry.

Data handling: The elemental concentrations of macro- and micronutrients were investigated, namely Br, Ca, Cl, Co, Cu, Fe, I, K, Mg, Mn, Na, Ni, V, Zn, as well as the non-biological Rb, because its affinity with K. The elemental concentration mean value was computed for each element, discriminated by lichen species and collection sites. These values were compared with other bibliographic data.

Results and discussion

Elemental concentrations: The minimum, mean (in bold) and maximum elemental concentrations, discriminated by species and collection sites are presented in Table 1. Blank cells indicate elemental concentrations under the detection limits, except for Co, whose concentration could not be evaluated due to an eventual interference of a Co source, stored accidentally close to the counting room, when the analysis were done. Cu, I and Ni were detected only in Pristine areas, for the other specimens, the elemental concentrations were

under the detection limit.

Contrasting the mean elemental concentration values and the minimum-maximum (m-M) intervals obtained it can be remarked that:

	Br	Ca	Cl	Co	Cu	Fe	I
P. adscendens							
PU	6.8- **10.1**- 16.0	2824- **5257**- 10700	622- **941**- 1110			3298- **7946**- 20855	
U	14.2- **41.6**- 79.9	5370- **10127**- 17200	619- **815**- 1120			9468- **16622**- 22579	
H. brevirhiza							
PU	4.6- **8.8**- 15.4	31000- **49720**- 57900	632- **833**- 1270			2204- **9691**- 22421	
U	9.9- **17.6**- 27.4	14400- **26882**- 33600	558- **769**- 949			7957- **11996**- 18182	
C. vitelina							
PU	5.4- **8.0**- 11.0	6740- **9616**- 13700	417- **693**- 806			6360- **12911**- 23869	
U	20.1- **30.0**- 55.7	9050- **12141**- 18000	464- **901**- 1500			15079- **19585**- 26821	
POST	4.8- **7.0**- 9.2	3780- **6290**- 8790	439- **452**- 465			2799- **3840**- 4881	
U. fasciata							
PU	1.4- **2.5**- 4.0	7584- **17296**- 33100	148- **172**- 209	0.65		1084- **1265**- 1393	
PT	0.6- **2.7**- 5.8	1010- **4290**- 11400	39- **78**- 138	0.28- **0.33**- 0.40		394- **614**- 700	
P. cunninghamii							
PT	4.5- **5.4**- 7.0	3800- **4500**- 6800	626- **975**- 1229	0.44- **0.67**- 1.28		476- **1351**- 2810	
P. magellanica							
PT	0.42- **0.57**- 0.78	746- **976**- 1304	55- **78**- 128	0.09- **0.11**- 0.17	1.02- **2.67**- 6.94	40- **69**- 106	0.7- **1.0**- 1.2

PU: Periurban area; U: urban area; PT: pristine area, POST: cement post

Table 1. Minimum, mean, and maximum elemental concentrations (µg/g)

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K	Mg	Mn	Na	Ni	Rb	V	Zn
4590- **6198**- 6600	2471- **6450**- 12400	95- **210**- 564	1280- 2734- 7020		14.4- **15**- 15.6	12.5- **24.1**- 56.3	92.0- **100.4**- 125.0
4360- **8452**- 10700	5000- **10689**- 15500	152- **340**- 475	3000- **6957**- 9680		13.6- **29.6**- 44	29.7- **64.9**- 94.4	95.1- **166.3**- 198.0
3870- **4287**- 4910	2414- **6334**- 17-300	57- **250**- 591	841- **3410**- 7650		11.1- **17.2**- 22.3	5.8- **29.9**- 61.2	53.1- **62.0**- 72.0
3850- **6317**- 9840	5000- **7682**- 10600	169- **258**- 356	3230- **4576**- 7000		10.1- **18.9**- 26.2	27.5- **37.1**- 50.7	98.7- **118.3**- 143.0
4360- **6616**- 8480	5820- **8165**- 15200	175- **304**- 567	3050- **4551**- 6140		12.7- **22.7**- 32.0	26.5- **41.1**- 78.1	44.6- **60.7**- 113.7
7100- **10330**- 14800	9690- **11965**- 14500	247- **385**- 554	5750- **7801**- 10200		24.0- **31.3**- 39.1	51.1- **66.8**- 98.5	97.2- **158.7**- 228.0
4830- **4940**- 5050	1820- **2485**- 3150	61- **73**- 86	877- **1092**- 1308		4.9- **6.2**- 5.41	8.2- **10.7**- 13.1	75.1- **79.7**- 84.3
3530- **4096**- 4590	2230- **3140**- 3650	47- **48**- 50	348- **439**- 501		9.7- **10.9**- 12.0	2.7- **3.3**- 3.8	41.4- **46.2**- 49.7
859- **1333**- 2420	503- **926**- 1630	34- **41**- 57	229- **306**- 436		1.7- **2.3**- 2.9	1.1- **1.6**- 2.3	20.6- **26.0**- 32.4
1760- **1980**- 2280	1054- **1403**- 2120	93- **113**- 177	216- **464**- 857		4.4- **5.4**- 8.4	2.2- **4.7**- 9.3	33.7- **39.8**- 62.1
1317- **1418**- 1591	717- **919**- 1167	8- **13**- 41	47- **63**- 97	0.26- **0.55**- 0.83	0.9- **1.1**- 1.6	0.2- **0.3**- 0.5	10.8- **12.7**- 13.8

*) All elemental concentration m-M intervals of different corticolous foliose lichens from PU areas overlap, except for Ca, which shows a wide range of values.
*) Among all lichens species collected in PU areas, fruticose lichen *U. fastigiata* has the lowest mean elemental concentrations values.
*) In PU areas, the *C. vitellina* collections from cement Post have mean lower concentrations than the corticolous specimens of the same species and area.
*) For each species the mean concentration values and the intervals m-M of elements are lower in Periurban areas than in Urban areas, except for Ca in *H. brevirhiza* and Cl in *H. brevirhiza* and *P. adscendens.*
*) Elemental composition of *U. fastigiata* specimens from PT areas are lower than those of PU areas, for all elements, except Br, Mn and Ca. For these elements the intervals value overlap.
*) In Pristine (PT) areas, specimens of fruticose lichens have always smaller concentration m-M intervals than the foliose lichen *P. cunninghamii.*
*) *P. magellanica* has the smallest mean concentration values for every element.

As a general rule, the concentrations measured are around the lowest concentration values found in the literature (DE BRUIN 1990; LOONEY et al. 1985; LOPPI et al. 1994; NIMIS et al. 1993; PAKARINEN, 1985; WIERSMA et al. 1992). A few cases deserve some comments:

*) Co concentrations, ranging 0.09-0.65 μg/g, are lower than those reported by Sloof (1993): 1.0-20 μg/g.
*) Cu concentrations, ranging 1.02-6.94 μg/g, measured for *P. magellanica* are:
   - lower than the values reported by Sloof (1993) for *Lecanora conizaeoides* NYL. and *Parmelia sulcata* TAYLOR (12-320 μg/g); by LOPPI et al. (1994) for *Parmelia caperata* (L.) ACH. (5.4-16.2 μg/g) and by PAKARINEN (1985) for *Hypogymnia physodes* (L.) NYL. (4.4-10.2 μg/g).
   - similar to those of *Parmelia sulcata* and *Cladonia stellaris* (OPIZ) POUZAR & VEZDA (2.4-7.2 μg/g) (PAKARINEN, 1985).
   - similar to the concentration values reported by WIERSMA et al. (1992) for *Nephroma antarcticum* (WULF.) NYL. (4.5 μg/g), and also similar or lower than the values reviewed by the same author for different species and sites (2.9-63 μg/g).
*) Ni concentrations, ranging 0.26-0.83 μg/g, are similar to the lower values reported by SLOOF (1993): 1.9-53 μg/g.

Conclusions

All concentration values are similar or lower than the values reported in the literature. Except for Ca, *P. magellanica* concentrations are the lowest values

reported up to now. These could be considered as baseline data for the area.

Fruticose lichens tend to have lower elemental concentrations than foliose lichens of the same collection-site.

Even when Bariloche is a small city, the differences found between elemental composition of lichens of the same species from PU and U areas indicate that there are alterations affecting them.

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