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# Contrastive Analysis of Heavy Metals in Lichens in Alpine National Parks in Alaska, Canada and Austria

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With 2 Tables and 2 Figures

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Summary

BIEBER W., BENETKA E. & TÜRK R. 1999. Contrastive analysis of heavy metals in lichens in alpine natural parks in Alaska, Canada and Austria. – Phyton (Horn, Austria) 39 (1): 71–78, 2 figures. – English with German summary.

The concentration of lead, cadmium, zinc and copper in the lichens *Cetraria islandica*, *Letharia vulpina* and *Letharia columbiana*, collected in Alaska, Canada and Austria was investigated. The results show a significant difference in lead and cadmium levels in *Cetraria islandica*. The factor of accumulation is 3 to 4 times higher in Austria than in Alaska and Canada. The levels of cadmium in the specimens from Canada and Alaska (0,04–0,12 ppm) and lead (0,3–1,3 ppm) belong to the lowest ever measured, whereas the values in the specimens from the Alps reach from 0,12 to 0,19 ppm (cadmium) and from 2,1 to 4,2 ppm (lead). The levels in zinc reach from 20 to 53 ppm and in copper from 1,5 to 3,2 ppm.

Zusammenfassung

BIEBER W., BENETKA E. & TÜRK R. 1999. Vergleichende Schwermetallanalyse von Flechten in alpinen Nationalparks in Alaska, Kanada und Österreich. – Phyton (Horn, Austria) 39 (1): 71–78, 2 Figuren. – Englisch mit deutscher Zusammenfassung.

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Untersucht wurde die Konzentration von Blei, Cadmium, Zink und Kupfer in den Flechten *Cetraria islandica, Letharia vulpina* und *Letharia columbiana* aus Alaska, Kanada und Österreich. Die Resultate ergeben einen signifikanten Unterschied für Blei- und Cadmiumwerte in *Cetraria islandica.* In Österreich ist die Anreicherung um den Faktor 3 bis 4 höher als in Alaska und Kanada. Für die Arten aus Kanada und Alaska gehören die Cadmiumwerte (0,04–0,12 ppm) und die Bleiwerte (0,3–1,3 ppm) zu den niedrigsten, die je gemessen wurden, während die Werte der Arten aus den Alpen von 0,12 bis 0,19 ppm (Cadmium) bzw. von 2,1 bis 4,2 ppm (Blei) reichen. Die Werte für Zink liegen zwischen 20 und 53 ppm und für Kupfer zwischen 1,5 und 3,2 ppm.

## Introduction

Due to their capability of covering their mineral balance both through substrate (saxicol, terricol) and through atmospherically (epiphytically) transported ions, lichens function as appropriate indicators of the atmospheric heavy metal loading (cf. PUCKETT & FINEGAN 1980, FRENZEL & al. 1990 and CRETE & al. 1992). Extensive studies have been undertaken on the heavy metal content in lichens in areas highly polluted by waste gas (e.g. SKYE 1968, SAEKI & al. 1975, GARTY & GALUN 1976, HYNINEN & LODENIUS 1986), which showed that the heavy metal content in thalli exactly reflects the degree of loading in the atmosphere and the corresponding immissions into the ecosystems. In addition to that the heavy metal content in lichens far off urban and industrial zones in the alpine tundra of Alaska and Canada was analysed (cf. PUCKETT & FINEGAN 1980, PAKARINEN & al. 1978, PALIOURIS 1998, unpubl.) in order to be able to estimate how highly such ecosystems are loaded. The present investigation aims at analysing the heavy metal content of lichens growing far off industrial and urban agglomerations to reveal the "underlying loading" in the atmosphere in the Mid-European Alps as compared to the alpine tundra of Alaska and Canada. National parks in highly montane to alpine regions are suitable for such a purpose, particularly as they provide important refuges for plants and animals as well as recreation areas for man.

## Material and Methods

The terricole leaf lichen *Cetraria islandica* (L.) ACH. and the arboricole bush lichens *Letharia vulpina* (L.) HUE and *Letharia columbiana* (NUTT.) were chosen for determining the concentration of lead, cadmium, zinc and copper. The investigated areas are shown in table 1.

Three mountain regions were chosen as areas to be investigated: the Alaska Range, the Canadian Rocky Mountains and the Austrian part of the Alps. In each of the investigated areas the sites selected were subdivided into three altitudinal levels. Five samples per altitude were collected (one in its centre and four more in all directions in a distance of approx. 15 metres). The number of samples n amounts to 15 per species in nearly all investigated areas. Particular care was taken that both the epiphytic as well as the epigeal kind of lichen was found on the sites. Thereby 30 samples per site were available for statistic analysis.

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Table 1

Position of investigated areas and collected data (IA: Investigated Areas)

| | | |
|---|---|---|
| North America, USA, Alaska | Alaska Range | IA 1: Petersville |
| | | 62°32′ N 151°30′ W |
| Date: 31.7.95 | 797–855 msm | *Cetraria islandica* |
| North America, USA, Alaska | Alaska Range | IA 2: Double Mountains |
| | | 63°39′ N 149°30′ W |
| Date: 3.8.95 | 800–825 msm | *Cetraria islandica* |
| North America, USA, Alaska | Alaska Range | IA 3: Talus Mountain |
| | | 63°22′ N 148°30′ W |
| Date: 4.8.95 | 840–895 msm | *Cetraria islandica* |
| North America, Canada | Rocky Mountains | IA 4: Mount Trophy |
| | | 51°47′ N 119°55′ W |
| Date: 8.8.95 | 1950–2065 msm | *Cetraria islandica* |
| | 2015–2065 msm | *Letharia vulpina* |
| | 2035–2040 msm | *Letharia columbiana* |
| North America, Canada | Rocky Mountains | IA 5: Mount Fitzwilliams |
| | | 52°50′ N 118°25′30″ W |
| Date: 9.8.95 | 1945–1955 msm | *Cetraria islandica* |
| | 1880–1885 msm | *Letharia vulpina* |
| | 1400–1890 msm | *Letharia columbiana* |
| North America, Canada | Rocky Mountains | IA 6: Mount Edith Cavell |
| | | 52°41′30″ N 118°2′30″ W |
| Date: 10.8.95 | 1800–2145 msm | *Cetraria islandica* |
| | 1800–2085 msm | *Letharia vulpina* |
| | 2095–2105 msm | *Letharia columbiana* |
| North America, Canada | Rocky Mountains | IA 7: Sentinell Pass |
| | | 51°20′30″ N 116°13′ W |
| Date:10.8.95 | 2115–2355 msm | *Cetraria islandica* |
| | 2155–2285 msm | *Letharia vulpina* |
| | 2145–2285 msm | *Letharia columbiana* |
| Europe, Austria | Alps | IA 8: Hoher Krippenstein |
| | | 47°30′30″ N 13°42′30″ E |
| Date: 24.9.95 | 1925–1950 msm | *Cetraria islandica* |
| Europe, Austria | Alps | IA 9: Überling-Sonnseite |
| | | 47°10′ N 13°54′ E |
| Date: 25.9.95 | 1660–1710 msm | *Cetraria islandica* |
| | 1680–1725 msm | *Letharia vulpina* |
| Europe, Austria | Alps | IA 10: Anlauftal |
| | | 47°3′30″ N 13°12′30″ E |
| Date: 3.10.95 | 1740–2115 msm | *Cetraria islandica* |
| | 1735–1785 msm | *Letharia vulpina* |
| Europe, Austria | Alps | IA 11: Tauerntal |
| | | 47°1′ N 13°8′30″ E |
| Date: 4.10.95 | 1500–1995 msm | *Cetraria islandica* |
| | 1790–1820 msm | *Letharia vulpina* |

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Under the binocular 5,5 grams of air-dried lichen per sample were separated from substrate and remains of other plants. After that parts of the thalli were soaked in glass bowls containing twice distilled water for 3,5 minutes. The *p*H-values of these samples were measured on the surface with a glass membrane electrode. Then the samples were dried at 105 °C for a period of 48 hours until they reached constant weight and pulverised in a titanium rotary mill. The granulate won in this process was the primary product for the granulate *p*H-measurement as well as for the heavy metal analysis. 1 g of *Cetraria islandica* granulate was mixed with 3 ml of twice distilled water, 1 g of *Letharia* sp. granulate with 5 ml. The liquids were mixed into labor test tubes, which were then sealed off and kept at a temperature of 7 °C for 24 hours. Afterwards the *p*H-values were measured with a labor *p*H-meter.

Open digestion was chosen for the analysis of lead and cadmium. 1 g of homogenized sample granulate was weighed into a Kjeldahl bulb made of quartz, mixed with 10 ml $HNO_3$ and 2 ml $HClO_4$ consecutively and boiled for approx. 2–4 hours in a bulb-shaped boiler. After cooling down the samples were put into a 50 ml volumetric flask, which was then filled up with twice distilled water.

Reflux digestion was chosen for the analysis of zinc and copper. 1 g of homogenised lichen granulate was weighed into a 50 ml volumetric flask and mixed with the same acids as above. After that a reflux condenser was mounted on top of it, filled with 7 ml $HNO_3$ and boiled on a cerane plate for 2–4 hours. The nitric acid in the condenser was added to the liquid in the flask and filled up with twice distilled water.

The content of cadmium and lead was analysed with an atomic-absorption-spectrometer (AAS) on a Perkin-Elmer-instrument of the series 5100 ZL with a graphite tube heated at right angles to the light beam and Zeemann-compensation. Zinc and copper were analysed in an inductively coupled plasma-emission-spectrometer (ICP-AES). The results were statistically evaluated with SPSS software.

*Evernia prunastri* (L.) ACH. with the International Atomic Energy Agency code IAEA-336 was used as reference material for the analysis.

## Results

### pH-value

The results of the *p*H-measurement of *Cetraria islandica* and *Letharia* sp. are presented in table 2. It can be seen that the *p*H-values measured on the surface are higher than those measured in the mixture of granulate and water.

Table 2

pH-value in the lichens *Cetraria islandica* and *Letharia* sp.

| | pH-value on the surface | pH in the granulate |
|---|---|---|
| *Cetraria islandica* | 4,6–5,0 | 4,0–4,4 |
| *Letharia* sp. | 4,2–4,5 | 3,6–3,9 |

### Zinc and copper

The mean values for zinc in *Cetraria islandica* range from 20 to 36 ppm ($mg.kg^{-1}$). In IA 4 the value was 53 ppm. Generally, a significant difference

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could not be found, the high value in IA 4 is probably the result of a geologically different subsoil. In *Letharia* sp. values from 24 to 31 ppm were measured. No statistically significant differences could be detected between the individual investigated areas.

The analysis of copper revealed values between 1,5 and 3,2 ppm for *Cetraria islandica* and 1,6 to 2,8 ppm for *Letharia* sp. Again no significant differences in the content of copper could be found in the individual investigated areas.

Cadmium

The results of the analysis of the amount of cadmium in *Cetraria islandica* are presented in figure 1. The number n of samples taken in each of the investigated areas is 15 (standard deviation s = 0,015 to 0,08), with the exception of IA 4 (n = 14; s = 0,016) and IA 5 (n = 5; s = 0,015). A significant difference could be found between the loading of cadmium in Alaska and Canada and the loading of cadmium in Austria (the probability level being $p < 0,05$). The individual values in the samples taken in Alaska and Canada range from 0,04 to 0,12, whereas the samples from Austria reveal higher values ranging from 0,12 to 0,19 ppm. With the exception of IA 3 this amounts to a degree of loading in lichens in Alaska and Canada which is two to four times lower than the amount of cadmium found in the samples in Austria. Within Austria the values measured in the samples collected on the northern side of the Alpine ridge are 20 to 60 % higher than in the samples collected on the southern side.

The analysis of cadmium in *Letharia* sp. produced no significant differences between the investigated areas in North America and Europe. The values for this genus range from 0,09 to 0,18 ppm.

Lead

The value of 4,35 ppm found in the analysis of the reference material (*Evernia prunastri*) lies just underneath the tolerance range of 4,4 ppm as defined by the IAEA.

The results of the determination of lead in *Cetraria islandica* are presented in figure 2. The number n of samples of *Cetraria islandica* taken in each of the investigated areas is 15 (standard deviation s = 0,07 to 0,84), with the exception of IA 4 (n = 14; s = 0,21), IA 5 (n = 20; s = 0,027) and IA 10 (n = 10; s = 0,29). There are significant differences in the results for all three mountain ranges (the probability level is $p < 0,05$). The samples collected in Canada show a concentration of lead three times as high as in the samples collected in Alaska. The content of lead in the samples from Austria is again three times as high as in the Canadian samples. Within Austria significant differences can be found, too: The content of lead in the

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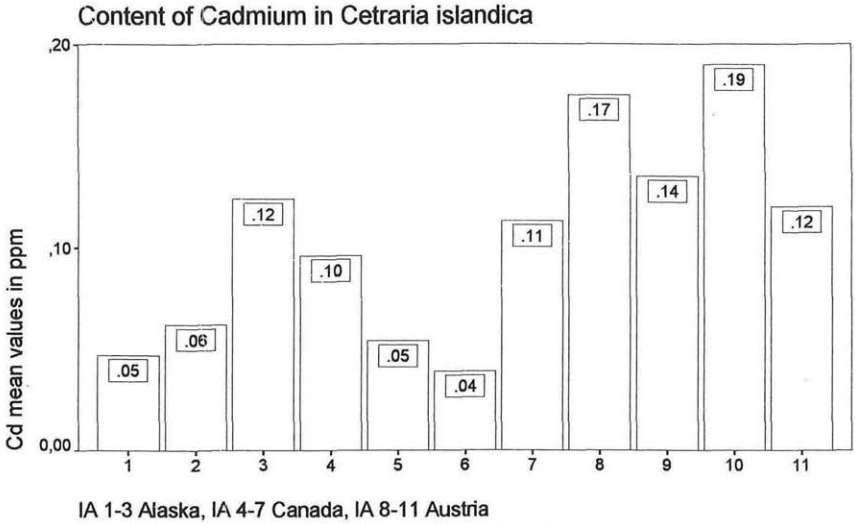


Fig. 1. Mean values for cadmium (in ppm) in the individual investigated areas

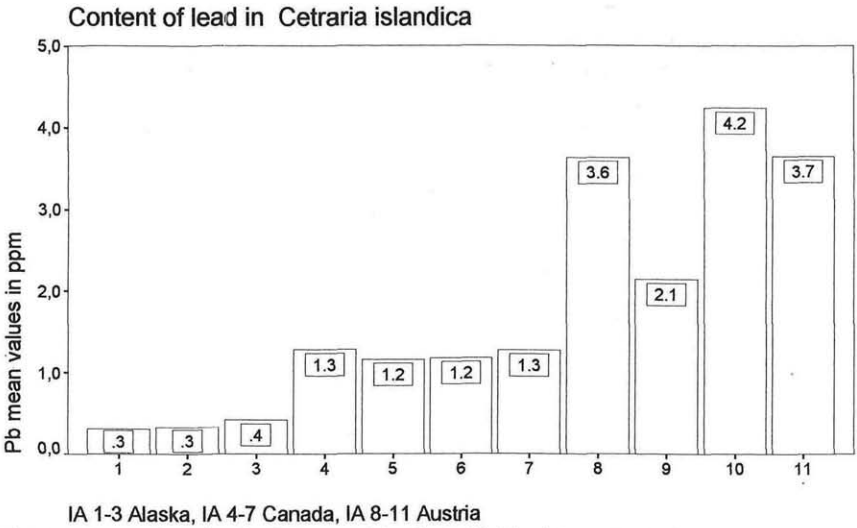


Fig. 2. Mean values for lead (in ppm) in the individual investigated areas.

samples collected north of the Alpine ridge is 15 to 70 % higher than in the samples taken in the south.

The number n of samples of *Letharia* sp. is 15 again, except in IA 5 (n = 21) and IA 6 (n = 13). The analysis of lead in *Letharia* sp. reveals values between 2,1 and 5,75 ppm. However, there are hardly any differences in the

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content of lead in the samples taken from Canada and the samples from Austria.

## Discussion

Statistically no connection could be found between the *p*H-value and the content of lead and cadmium. Therefore, the *p*H-value need not be taken into consideration as a factor of heavy metal uptake in lichens.

The amount of zinc found in *Cetraria islandica* resembles the results in the data collected by PUCKETT & FINEGAN 1980 in the North West Territories, Canada. The values of copper found by PUCKETT & FINEGAN 1980 are three times as high as the values presented by the present study. Generally, the present results are situated on the lower end of the scale represented in the relevant literature and confirm the assumption that the investigated areas are on the whole anthropogenically unloaded areas.

The Cd-values found in the present study are lower than the values presented by other comparable studies. Only FRENZEL & al. 1990 have found lower concentrations (0,008–0,04 ppm) in montane national parks in the USA (Mount Rainier). CRETE & al. 1992 found similar Cd-contents (around 0,17 ppm) in the bush lichen *Cetraria nivalis* in the north of Quebec. Further studies, e. g. LODENIUS & KUMPULAINEN 1993 and MUKHERJEE & NUORTEVA 1994, found higher Cd-values than the present study. The four times higher Cd-loading in Austria cannot be explained with any of the investigated factors. Therefore, it can be assumed that the higher Cd-loading is caused by anthropogenically influenced atmospheric input. The higher values in the northern Alpine regions can be explained with the higher amount of rainfall, which consequently brings along a higher amount of Cd-immissions as well.

As for lead, our values for *Cetraria islandica*, ranging from 0,3 to 4,3 ppm, and for *Letharia* sp., ranging from 2,1 to 5,7 ppm, are again on the lower end of the scale presented in the relevant literature. The studies of CRETE & al. 1992 and PUCKETT & FINEGAN 1980 reveal a similar concentration of lead. The results of other studies, e.g. PAKARINEN & al. 1978, SLOOF & WOLTERBEEK 1993 reveal a Pb-content 5 to 10 times higher than the lichens analysed in our study. The input of lead in Austria is also three times as high as in North America, which obviously has to be attributed to anthropogenically influenced higher atmospheric loading.

Great differences can be found in the individual investigated areas for the concentration of the metals Cd and Pb in the lichen *Cetraria islandica*. Lichens in the Alps (Austria) are more highly loaded with lead and cadmium than in the Canadian Rocky Mountains and in the Alaska Range (USA). This can only be explained with a higher input in Europe. Within Austria the concentration of lead and cadmium in lichens on the northern side of the Alpine ridge (IA 8; Dachstein-Plateau) is 1,7 times as high as on

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the southern slopes of the Central Alps (IA 9; Überling-Alm). Further it could be shown that the samples of *Letharia* sp. contain higher heavy metal concentrations than the samples of *Cetraria islandica*. The content of zinc and copper does not reveal any significant differences as far as the investigated areas are concerned. Hardly any differences exist in the heavy metal content between *Letharia vulpina* and *Letharia columbiana*.

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