

**Studies on the Chemistry of Lichens, XX.
The Element Concentration of the Lichen
Species *Alectoria fremontii* and Its Associated
Bark Substrate of *Pinus silvestris* ***

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The element concentration of the lichen species *Alectoria fremontii* and its substrate (bark of *Pinus silvestris*) were studied. It appeared that the content of all the investigated elements, except for vanadium, was higher in the lichen samples than that in the corresponding bark samples. Analysis-of-variance procedure has demonstrated that the concentration of N, P, S, Se, V, Hg and U in lichen samples appeared to change significantly in samples gathered from two different height-zones on the stems above ground level. However, this was not the case with the bark samples. The elements Se, V, Hg, U, Co and Mo determinations of the samples were performed by neutron activation methods.

Introduction

Much of the reviewed current literature [1] dealing with the element content of lichens indicated that they were important accumulators of specific elements from their surroundings. It is known that lichens are eminently different from all other plants in regard to their ability to accumulate trace elements in concentrations several times greater than those found in their associated substrates, and in greater concentrations than those detected in other plants [2–4]. In their behaviour with certain cations lichens appear to be unique, often accumulating concentrations of these which would prove lethal to most other plants [4]. They absorb elements from dust especially adhering to the thallus surface, and from rain (which is a known source of nutrients). Macro- and microelements of the barks of different trees and the lichen growing on these barks have earlier been studied. It is mentioned that the chemical composition of the ash of the lichens *Ramalina farinacea*, *Usnea hirta* and *Evernia prunastri*, differed considerably from that of the bark of *Quercus* on which they grew. Phosphorus among other elements,

accumulates in the lichens [4–6]. Although use of lichens as a food source is limited, unusual accumulations of elements present potentially hazardous situations, for example the level of radioactive isotopes, due to the lichen-to-caribou-to-man food chain [7].

A recent report from our institute [8] concerning the extremely high content of mercury in black-coloured *Alectoria*-species, led us to further investigations of the total content of several elements in the lichen species *Alectoria fremontii*. The main intent of the present investigation was to reveal how some element concentrations of this species, growing on *Pinus silvestris*, vary with change of height above ground level. To our knowledge, this is the first report that attempts to quantify the degree of variability in the concentration of elements.

Materials and Methods

Plant material

The lichen species *Alectoria fremontii* Tuck. growing on *Pinus silvestris* was taken from Alvdal municipality, Østerdalen, at a remote distance from industries, roads or built-up areas. All samples were collected during the months of July and August 1978–79. The samples which were collected from each of the five to six sites located at a distance of more than 60 m from each other, typically consisted of sub-samples taken from several pines not more than 5 m apart, growing within an area of 100 m² or less. The material was gathered at two heights above the ground, zone 1.5–2.5 m, and zone > 4 m, and from all sides of the trees. Associated substrate samples of bark were simultaneously collected. The lichen material was taken by hand and the bark samples were collected from the outermost, loose layers of the bark, in the lichen-free area, using a knife. The lichen and bark samples remained unwashed, but were cleaned, oven-dried at 35–40 °C, and then pulverised. Element analyses were performed after additional mixing of each sample.

Analytical procedures

The nitrogen, phosphorus, sulphur and potassium analyses were carried out by standard micro procedures at The Analytical Laboratories of Engelskirchen, BRD. The other elements were performed by our Institute of Atomic Energy by neutron activation

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Table I. Element content of *Alectoria fremontii* collected from *Pinus silvestris* in two different heights above level. Mean concentrations of the same elements in the associated bark samples are given in the third column. The values are calculated as mg/100 g for N, P and S, and as $\mu\text{g}/100\text{ g}$ dry weight for the other elements.

Element	Number of localities	Mean content of the bark samples	Lichen samples			Mean error	<i>t</i>	<i>P</i>
			Average values from six and five sites respectively		Difference between means of low and high growth-zone			
			1.5 – 2.5 m	4 – 5 m				
Nitrogen	6	162	1062	982	80	19.2	4.2	0.009
Phosphorus	6	10	65.8	56.3	9.5	2.8	3.4	0.019
Sulphur	6	17	116.3	100.7	15.6	4.0	3.9	0.011
Selenium	5	2.1	42.8	37.2	5.6	1.9	2.9	0.043
Vanadium	5	70	69.8	56.8	13.0	3.8	3.4	0.027
Mercury	5	5.3	63.4	58.4	5.0	0.9	5.6	0.005
Uranium	5	0.24	1.60	1.34	0.26	0.08	3.5	0.025
Molybdenum	5	1.4	9.50	10.82	– 1.32	0.49	2.7	0.056

methods. Vanadium was determined via short-lived nuclides, while the other elements were determined via more long-lived nuclides. The molybdenum values in Table I are corrected for the nuclear interference from uranium.

Average dry weight (105 – 110 °C, 4 h) of all the samples was approximately 91.2 and 98.6% of lichens and barks respectively. Average ash content (550 – 600 °C, 4 – 6 h) was 0.8% of the lichen samples. All results presented in the text and in the table are given as arithmetic means of duplicate (sometimes triplicate) determinations made for each site, and expressed on oven-dried weight basis. The statistical evaluation of the analytical results has been performed by our Centre for Experimental Design and Data Processing. Significant tests at the 0.05 probability level.

Results and Discussion

The concentration level of N, P, S, U and Mo detected in this work is almost 6.4 times higher in the lichen than in the corresponding subjacent substrate. For the elements Se and Hg the relationship is even greater with the values of 19 and 11.5 respectively. However, as seen from the table, the vanadium content is as a mean 11% higher in the bark than in the lichen samples. The bark might have some chemical properties that account for the large accumulation rate in bark. In earlier investigation [4] a lower manganese content has been detected in lichens than that in bark substrate. Further investigations are needed in order to understand and solve this problem.

The mean concentration of the elements N, P, S, Se, V, Hg, U and Mo in *Alectoria fremontii* for each of the two growth-zones (1.5 – 2.5 and > 4 m above ground level) on *Pinus silvestris* from 5 – 6 sites are given in Table I. With regard to the bark samples there appeared to be no significant difference in any of the element concentrations in the two zones. Therefore only the mean values of the barks in the two zones are given in the table.

No significant difference in the concentration of K (260 mg/100 g) and Co (9.2 $\mu\text{g}/100\text{ g}$) of the lichen samples in the two investigated growth-zones was found. The lack of distinct difference in the case of these two elements probably indicates that they are more easily leached out from the lichen than the other elements studied. Concentration of the elements N, P, S, Se, V, Hg and U however, was on average 15% greater in the lichen growing in the lower zone than that for the upper one. As seen from the table, the difference between the zones can be considered sufficiently significant. A noteworthy feature of our results is that the content of molybdenum in the lichen in the two zones was found to be in an inverse relationship. It has been intimated [4] that substrate appeared to have little effect on the uptake of molybdenum to the lichens.

Leaching of both organic and inorganic solutes is known to occur by the action of rain, dew, mist and fog [9]. Inorganic substances leached from plant tissue include all the essential elements, and K, Ca, Mg and Mn are usually removed in greatest quantities. Of course, removal of surface particles from plants by such aqueous leaching also occurs. Substrate sur-

face (bark) run-off-water becomes in contact with lichens and provides another rich source of soluble and insoluble components. In all probability this leaching-theory is the cause of the higher concentrations of several elements in *Alectoria fremontii* when the lichen is growing in a lower growth-zone on the stems of *Pinus silvestris*.

The vanadium content of the same lichen species collected from pine stems located alongside a road with traffic, from Kvam to Rondablikk Gudbrands-

dalen, has been found to be 125 µg/100 g (average of 9 samples), an amount which is actually 100% higher than that obtained in the samples collected in Alvdal, Østerdalen. However, the mercury content of the same lichen samples was 66 µg/100 g, or practically the same concentration as that found in the samples in the present investigations. The mean values given in Table I for vanadium can be considered as background concentrations for this element in *Alectoria fremontii* when growing on pine.

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