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## THE EFFECT OF SIMULATED ACID RAIN ON METAL DESORPTION FROM *CETRARIA ISLANDICA*

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### Abstract

In this paper the possibility of extracting metals: K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn and Sr, from *Cetraria islandica* lichen with solutions simulating acid rain ( $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$ - $(\text{NH}_4)_2\text{SO}_4$ ), pH 2.00 (1) and 3.28 (2) has been investigated. The results obtained suggest that the investigated elements can be classified into ones where the highest percentage was extracted with the first extraction (K, Al, Mg, Ba, Zn and Mn) and others where the extraction percentage is relatively uniform (Ca and Fe). This indicated different bonding methods in lichen that is in accordance with literature data where two cation bonding methods in lichen were shown.

### Introduction

Lichen is sensitive to pollutants in the air such as: ozone,  $\text{SO}_2$  and ammonia. Acid rain, formed from  $\text{SO}_2$  and  $\text{NO}_2$  building  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  during atmospheric transfer and transformation, can cause extinction of lichen<sup>1</sup>. The purpose of this paper is to investigate extraction of K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn and Sr from *Cetraria islandica* lichen with acid solutions corresponding through acid rain and thus possible transfer of these elements into the environment.

### Materials and Methods

*C. islandica* lichen (from the Sinjajevina Mountain, Montenegro, collected in 1994) was cleaned from impurities and mechanically chopped. After drying in air until a constant mass was reached, 0.500 grams was measured out for experiments. The K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn and Sr content was measured in untreated samples before extraction and in solutions after each of the five consecutive extractions for the same sample. In order to determine the element content in lichen before extraction the sample was treated with liquid nitrogen, chopped up and completely homogenized and then it was dissolved in Teflon cups in a mixture of concentrated  $\text{HNO}_3/\text{HClO}_4/\text{HF}$  (10:1:1) acid<sup>2</sup>. Cooled solutions were filtrated and diluted with distilled water until the volume of 100 mL was attained. The K content was measured with a stabilized d.c. arc. All other elements were measured using a Spectro-Flame ICP spectrometer. The extraction solution was made of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , by separately adding them to distilled water until the desired pH of 2.00 (1) or 3.28 (2) was reached. Then 100 cm<sup>3</sup> of each acid solution was mixed, 1 g of  $(\text{NH}_4)_2\text{SO}_4$  per 100 cm<sup>3</sup> of the mixture was added and the pH was adjusted with concentrated sulfuric acid. Extractions were performed at room temperature (ca 22°C) for 24 hours with occasional mixing. All

extractions were repeated twice. The lichen samples were dried at room temperature after each extraction until a constant mass was reached and then they were extracted again using corresponding solutions.

## Results and Discussion

The K, Al, Ca, Mg, Fe, Ba, Zn, Mn, Cu and Sr content in lichen before extraction and the extracted percentage of these elements in extracted solutions after each extraction with solutions (1) and (2) is shown in Table 1. Most probably,  $H^+$  participated in the cation-exchange process, thus leading to even higher  $H^+$  ion exchange with cations accumulated in the lichen. All extractions performed with solution (1) were more efficient than extractions performed with solution (2).

**Table 1.** K, Al, Ca, Mg, Fe, Ba, Zn, Mn, Cu and Sr content in untreated lichen and their extraction percentage with solutions (1) and (2) after every extraction

Elements	K	Al	Ca	Mg	Fe	Ba	Zn	Mn	Cu	Sr	
Starting content ( $\mu\text{g/g}$ )	1475	450	6880	260	265	13	30	10	6	10	
Ex-trac-tion	Solu-tion	Percentage of extracted elements in solutions in relation to the starting content (%)									
I	(1)	60	6,8	19	43	8,5	4,6	40	48	*	16
	(2)	52	4,8	7,7	35	1,6	1,5	13	24	*	8,0
II	(1)	2,1	1,2	12	2,2	2,9	*	*	*	*	2,0
	(2)	2,3	1,5	4,4	3,0	1,2	*	*	*	*	*
III	(1)	0,3	0,7	15	1,7	2,3	*	*	*	*	2,0
	(2)	0,1	0,6	5,0	1,4	1,2	*	*	*	*	*
IV	(1)	0,08	0,6	16	1,5	1,7	*	*	*	*	2,0
	(2)	0,07	0,5	5,6	1,8	1,4	*	*	*	*	*
V	(1)	0,19	0,8	24	3,1	2,1	*	13	*	67	6,0
	(2)	0,08	0,6	8,5	2,5	2,1	*	*	*	*	*
Percentage of total extracted elements from lichen (%)											
(1)	63	10	94	52	18	5	40	48	67*	288	
(2)	55	8	31	44	8	2	13	24			

\* Concentration of elements in these extracts is below the detection limit

Analysis of the results obtained enables the conclusion that K, Mg and Mn desorbed the most in solutions obtained after the first extraction. Earlier research has shown that passive pollutant adoption is dominant over active and hyper accumulation of metals is the consequence of a reactive mechanism with organic acids formed by the lichen and the sensitivity to metals becomes higher due to the formation of different complex

compounds<sup>3,4</sup>. Some cations are actively and passively adopted that is reflected in where they are found. Passive ion adoption by ionic exchange or complexation results in ion distribution outside the cell. It was established that passive cation adoption by lichen represents a universal cation-exchange process modified by the formation of metal complexes where oxygen or oxygen-nitrogen donors represent the adsorption points<sup>5</sup>. Analysis of our results enables the conclusion that they are in accordance with the two described cation bonding methods in lichen<sup>5</sup>. The elements in Table 1 can be grouped into ones where the highest percentage was extracted by the first extraction (K, Al, Mg, Ba, Zn and Mn) and ones where the extraction percentage is relatively uniform (Ca and Fe). This clearly indicates that two types of sorption (bonding) can be clearly differentiated for the first group of elements as described in literature. Compared to that, Ca<sup>++</sup> is extracted evenly and two types of sorption cannot be clearly differentiated. Copper starts to be extracted significantly during the fourth extraction and we assumed that it is most probably dominantly bonded deep inside the cell. Special behaviour is also noted for Sr where the amount of extracted element varies from extraction to extraction.

## Conclusion

Extraction of K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn and Sr elements from *C. islandica* lichen with solutions corresponding to acid rain (H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), pH 2,00 (1) and 3,28 (2) can lead to transfer of these elements into the environment. All sorption performed with solution (1) were more efficient than desorption performed with solution (2).

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## References

- [1] J. E. Sloof, Environmental Lichenology: biomonitoring Trace-Element Air pollution, doctoral thesis, Tehnical Univ., Delft, The Netherlands, 1993.
- [2] M. Kuzmanović, M.S. Pavlović, M. Marinković, Spectrosc. Lett., 1996, **29**(2), 205-215.
- [3] R.P. Beckett, The Lichenologist, 1996, **28**(3), 257.
- [4] M. Hyvärinen et al., Environ. Exp. Botany, 2000, **43**, 211-218.
- [5] A. Čučulović et al., 44. Savetovanje SHD, 2006, 193-196, Beograd.