

## DESORPTION OF METALS FROM *CETRARIA ISLANDICA* (L.) ACH. LICHEN USING SOLUTIONS SIMULATING ACID RAIN

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**Abstract** - Desorption of metals K, Al, Ca, Mg, Fe, Ba, Zn, Mn, Cu and Sr from *Cetraria islandica* (L.) with solutions whose composition was similar to that of acid rain, was investigated. Desorption of metals from the lichen was performed by five successive desorption processes. Solution mixtures containing H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> were used for desorption. Each solution had three different pH values: 4.61, 5.15 and 5.75, so that the desorptions were performed with nine different solutions successively five times, always using the same solution volume. The investigated metals can be divided into two groups. One group was comprised of K, Ca and Mg, which were desorbed in each of the five desorption processes at all pH values used. The second group included Al, Fe, Zn, Ba, Mn and Sr; these were not desorbed in each individual desorption and not at all pH values, whereas Cu was not desorbed at all under any circumstances. Using the logarithmic dependence of the metal content as a function of the desorption number, it was found that potassium builds two types of links and is connected with weaker links in lichen. Potassium is completely desorbed, 80% in the first desorption, and then gradually in the following desorptions. Other metals are linked with one weaker link (desorption 1-38%) and with one very strong link (desorption below the metal detection limit).

**Key words:** Desorption of metals, *Cetraria islandica* (L.) Ach. lichen, acid rain

### INTRODUCTION

Lichens are organisms representing a symbiosis of two or more organisms (fungi, algae and more rarely nitrogen fixing bacteria) genetically fit and based on the metabolic needs of one of them. They do not have roots or a protective cuticle layer, but sorb substances from the environment using their complete talus surface from the substrate or the atmosphere. Lichens are good indicators of air pollution as they are not capable of exuding absorbed matter, so that it is stored in tissue or on the surface in amounts that depend on the lichen's adaptability to chemical changes in

the environment (Veselinović et al., 1995; Jeran et al., 1996, Branquinho and Cataino, 2000, Garty, 2000; Jeran et al., 2002, Pawlik-Skowronska et al., 2002). Lichen tissue reflects the elementary composition of the environment and the talus can be considered a physical surface coming into contact with different material from the ground, air and atmospheric fall-out. Sorption of polluting substances in the lichen talus is the consequence of internal and external factors. For accumulation of polluting substances, lichen must have a suitable bonding point, while for particle accumulation size is of significance in order to build into the talus. If these conditions are not met, the

polluting substance slides down the talus and is not sorbed (Luna et al., 1994; Sarret et al., 1998).

Different lichen react differently to the unfavorable action of polluting substances (Franke et al., 1994). Lichen differently sorb and desorb metals depending on the pH of the environment and competition between metal ions (Salemaa et al., 2004; Aslan et al., 2004; Aloway, 1995; Goyal and Seaward, 1982; Garty et al., 1996; Schmull and Hauck, 2003; Hauck et al., 2002; Hauck and Spribille, 2002; Mangelson et al., 2002; Hauck et al., 2002; Cuny et al., 2004; Glen et al., 1995; Lepp, 1981; Bačkor et al., 2004). Sorption of polluting substances from the environment contaminates the lichen. Substance sorption by lichen can be passive and active. Passive sorption predominates over active sorption. Passive accumulation by ionic exchange or building of complexes results in the distribution of ions on the talus surface's outside cells, while active accumulation leads to ion distribution inside the cell. Lichen sorb available ions and molecules from the environment using complex mechanisms that are not completely selective. Research has shown that at the beginning, cation sorption by lichen is fast and passive (Brown, 1978).

Accumulation of polluting substances in a lichen body depends on its age, reproduction, location and on parameters such as the temperature, moisture and characteristics of the substrate, such as the chemical composition and acidity (Rossbach et al., 1999; Bargagli, 1989). Lichen sorb polluting substances, but also show great tolerance. According to their relation towards polluting substances from the environment, Gorškov divided lichen into four groups: a) stable or resistant; b) susceptible; c) very susceptible, and d) lichen that do not tolerate pollution (Nash, 1989; Gorškov, 1990).

In our previous work, and in this paper, *Cetraria islandica* lichen sampled in 1994 on the Sinjajevina Mountain was used for our research. The same sample was used in all experiments to avoid the influence of lichen type, changes formed due to different vegetation periods, and different sample age. *C. islandica* lichen, according to Gorškov, is a member of the first

lichen group (stable, i.e. resistant). In our previous work we reported on the *C. islandica* lichen, its usability, application and the reason why it was used in our experiments (Čučulović et al., 2006; Čučulović et al., 2007; Čučulović et al., 2009; Čučulović et al., 2009; Čučulović and Veselinović, 2012; Čučulović et al., 2012).

Lichen specificity, longevity, physiological activity in favorable conditions and independently of the season, retaining of old parts and accumulation of many substances in the talus make them extremely suitable as bioindicators and biomonitors of polluting substances (Garty et al., 2003; Hovenden and Seppelt, 1995; Slof et al., 1988; Grozdinski and Yorks, 1981; Seaward, 1995; Market et al., 1997; Szczepaniak and Biziuk, 2003).

Atmospheric fallout reaches lichen by moist fallout (rain, snow, dew) or dry fallout (sedimentation, aerosols soot). Salts and other solid substances and different gases dissolve in atmospheric water. Acid rain is fallout polluted by acids formed from SO<sub>2</sub>, NO<sub>x</sub> and other chemical compositions. In a polluted atmosphere, the pH values of the fallout can be significantly changed.

At the end of the 1950s the first increase in acidity in fallout in Europe and the USA was registered (Mahaney et al., 1995; Railsback, 1997). Ordinary rain usually contains on average 2.0 ppm Na<sup>+</sup>; 0.3 ppm K<sup>+</sup>; 0.1 ppm Ca<sup>2+</sup>; 3.8 ppm Cl<sup>-</sup>; 0.6 ppm SO<sub>4</sub><sup>2-</sup> and about 0.12 ppm HCO<sub>3</sub><sup>-</sup>, and has an acidity (pH) of about 5.7. The pH value of rain can be additionally changed by changing the CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> content in the atmosphere (Veselinović et al., 1995; Wellburn, 1997; Baek, 2004). More recently, the acidity of rainfall due to the presence of SO<sub>2</sub> or NO<sub>x</sub> can even be up to pH 2.00, which represents significantly aggressive solutions (Scott and Hutchinson, 1987; Gauslaa et al., 1996; Piervittori et al., 1997; Fritz-Sheridan, 1985; Gauslaa, 1995; Gilbert, 1986; Denison et al., 1977; Garty et al., 1992; Carreras and Pignata, 2007).

In our previous work, we showed that metals (K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn, Sr and <sup>137</sup>Cs) can

be desorbed from *C. islandica* (L.) Ach. by solutions simulating acid rain. The following solutions were used:  $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-(NH}_4\text{)}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-(NH}_4\text{)}_2\text{SO}_4\text{-NH}_4\text{NO}_3$  with pH values in the interval 2.00-3.75 (Čučulović et al., 2006; Čučulović et al., 2007; Čučulović et al., 2009; Čučulović et al., 2009; Čučulović et al., 2012). The obtained results showed that under the action of these solutions lichen can become a secondary source of pollution of the environment with metals. In our previous work, the sorption and desorption process of  $^{137}\text{Cs}$  from lichen with pH values higher than 4 was explained (Čučulović et al., 2012). The results obtained for the desorption of metal from *C. islandica* could not be compared with literature data as there was none.

Since acid rainfall is a fallout with pH values lower than 5.60 and that there are no data on metal desorption from *C. islandica* with solutions with pH values higher than 3.75, in this work metal (K, Al, Ca, Mg, Fe, Ba, Zn, Mn, Sr and Cu) desorption was investigated using solutions with pH values between 4 and 6 that correspond to acid rain compositions. Solutions with three different pH values were used: 4.61; 5.15 and 5.75, in order to provide better insight into the desorption process of these metals under the influence of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  that are the basic acid-component in acid rain.

## MATERIALS AND METHODS

Samples of the bushy *Cetraria islandica* lichen, collected for commercial purposes, were cleaned of impurities that could be seen visually, mechanically broken in a mortar to about 1 mm and dried in air (protected from dust) to a constant weight. Test samples were measured from this prepared sample for determining the total metal concentration and for desorption using suitable solutions.

Solutions containing basic components of acid rain, i.e. simulating acid rain, were used, with pH values of 4.61 (1); 5.15 (2) and 5.75 (3). They were solutions I –  $\text{H}_2\text{SO}_4$ ; solutions II –  $\text{HNO}_3$  and solutions III –  $\text{H}_2\text{SO}_4\text{-HNO}_3$  mixture. Solutions I and II were made by adding concentrated  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$

to 200 mL distilled until the desired pH value was obtained (solutions  $\text{H}_2\text{SO}_4$ : I<sub>1</sub>, I<sub>2</sub> I<sub>3</sub>;  $\text{HNO}_3$ : II<sub>1</sub>, II<sub>2</sub>, II<sub>3</sub>). Solutions III were obtained by mixing equal volumes of solutions I and II with identical pH values (III<sub>1</sub>, III<sub>2</sub> and III<sub>3</sub>).

Concentrated  $\text{H}_2\text{SO}_4$ , p.a. (Merck), concentrated  $\text{HNO}_3$ , p.a. (Alkaloid) were used for the preparation of solutions for desorption, while puffer solutions with pH 4.00 and 7.00 (Carlo Erba) were used for calibration of the pH meter.

Ten grams of dry lichen mass was measured for desorption adding 200 mL of a suitable solution. The sample was treated for 24 h at room temperature (22°C) with occasional mixing. After filtration, lichen samples were dried at room temperature in an open vessel until a constant mass was obtained. Then, 200 mL of new solution was used for successive desorptions of the same sample, repeating filtering and drying procedures. Five successive desorptions with each of the nine solutions were performed. All series were repeated twice. The content of investigated metals was determined in filtrates after each successive desorption.

Two methods of optical emission spectrometry were used for measuring the metal content: inductively coupled plasma (ICP) and stabilized arch plasma with DC current (DCP). The ICP spectrometer (Spectro Analytical Instruments), model Spectro-flame with a RF generator at 27.12 MHz, strength 2.5 kW, has options for sequential and simultaneous measurement of a larger number of elements in the spectral region from 190 to 450 nm. The Quick Quant procedure was used for scanning the spectral lines of the investigated elements, blind probes and standard solutions. The Smart Analyzer 2.00 program was used to analyze the investigated data: correction of the background radiation next to each measured line was performed, the calibration line was constructed and concentrations of measured elements were calculated. The ICP spectrometer was used to measure all investigated metals except potassium whose most sensitive spectral lines are outside the spectral range of this device. DCP, with an arch chamber laboratory

construction where the sample is introduced as an aerosol, was used as an excitation source for measuring potassium concentrations. A PGS-2 (Carl Zeiss) spectrograph modified for photoelectric signal detection was used as a monochromator. The photodetector is connected to a computer so that analysis of the obtained signals was performed using a suitable data-processing program. Calibration standards were prepared in the corresponding range for each element by diluting commercial standard solutions with a concentration of  $1000 \mu\text{g ml}^{-1}$  from J. T. Baker. Lichen solution and determination of the total metal content in a non-treated sample was described in detail in previous work (Sloof, 1993; Čučulović et al., 2007; Čučulović et al., 2008; Kuzmanović et al., 1996).

The detection limits (in  $\text{ng mL}^{-1}$ ) of the investigated metals in a solution for the analytical methods used were as follows: 15 for Al, 0.9 for Ba, 0.13 for Ca, 3.0 for Fe, 0.3 for K, 0.1 for Mg, 0.9 for Mn, 0.3 for Sr, 1.2 for Zn and 6.0 for Cu (Kuzmanović et al., 1996). The measurement error was between 10% and 30% depending on the concentration measuring range.

## RESULTS AND DISCUSSION

Tables 1-3 show the values obtained for the content of investigated metals in the sample before desorption (average value from two measurements) and also the average value of the percentage of the element desorbed by each individual desorption, for each of the three desorption solutions and every pH value. Of all investigated metals present, Ca and K are present the most, while Sr, Cu, Mn, Ba and Zn are present in traces, in the range between 6 and  $30 \mu\text{g/g}$ .

From the obtained results, the investigated metals could be divided into two groups according to the desorption method. The first group consisted of K, Ca and Mg, which were desorbed in all three solutions, for any pH value and in each individual desorption. For almost all investigated metals, the highest percentage was desorbed in the first desorption. This is most expressed for potassium, where the percentage in the first desorption was about 80% and

it was almost completely desorbed after five successive desorptions.

The other metals behaved in different ways and in most, after a certain number of successive desorptions, the desorbed amount fell below the detection limit. For different metals, insignificant desorption occurred for different desorbent solutions, different pH values and after different numbers of successive desorptions. In some cases such behavior was expressed until the final desorption (Tables 2 and 3). This means that in the sorbent, i.e. the lichen, there were groups whose link to the metal ion was far weaker, i.e. there were at least two types of linking metal ions and lichen as the sorbent. Then for these metals, the metal concentration could be measured for a certain solution and certain pH value in each desorbate, such as, for example, Zn during desorption with solution I and pH of 5.75 and solution II and pH of 4.61. The desorption of Ba with solution I and pH of 4.61 was characteristic, where its content in the desorbate from the first to the last desorption was below the detection limit, i.e. desorption was negligible. Desorption of Ba was the highest for solution II and pH 4.61 and reduced with the increase of the pH value. An explanation for the weaker desorption using solutions I and III could be the presence of the sulfate ion in these solutions forming the highly insoluble barium sulfate with barium, because of which barium cannot be detected in the desorbates.

Cu was an exception, as it was not desorbed in any instance. Similar behavior of copper was observed in a previous work using solutions with lower pH values, which indicates that it is tightly bonded inside the cell itself.

The total desorbed metal amounts, obtained after five successive desorptions (Tables 1-3), are very different. They are the highest for potassium that was almost completely desorbed, while for the other metals the average desorption value was from 3 to 4 %, for Ca and Fe, slightly lower than 10 % for Al, to over 30 % for Mg, Mn and Zn. This indicates that potassium as an alkali metal is exclusively linked with an ionic bond to corresponding chemical groups in

**Table 1.** Starting content ( $\mu\text{g/g}$ ) of K, Ca and Al *C. islandica* lichen, their content (%) in the desorbate in relation to the starting content (100%) depending on the serial number of successive desorption using solutions I, II and III, pH values 4.61, 5.15 and 5.75 and percentage of the total desorbed element from the lichen.

Element		K			Ca			Al		
Starting content ( $\mu\text{g/g}$ )		1475 $\pm$ 75			6880 $\pm$ 345			450 $\pm$ 45		
Percentage of desorbed element in the desorbate in relation to its starting content in the lichen										
Solution										
Desorption, $n_x$	pH	I	II	III	I	II	III	I	II	III
1	4.615.155.75	78	78	78	1.7	1.3	1.2	5.6	3.9	3.6
		73	79	76	1.5	1.4	1.6	4.2	4.8	5.1
		77	77	67	2.0	1.8	1.5	5.1	5.3	5.0
2	4.615.155.75	13	12	13	0.5	0.5	0.5	2.0	2.0	1.1
		12	12	14	0.4	0.4	0.6	1.6	1.6	1.8
		13	13	12	0.6	0.6	0.6	1.2	1.6	1.2
3	4.615.155.75	5.5	6.1	5.5	0.5	0.4	0.4	1.1	0.8	0.5
		5.2	6.1	5.6	0.4	0.4	0.5	0.4	0.4	0.8
		6.1	5.4	5.5	0.6	0.4	0.5	1.1	0.9	0.8
4	4.615.155.75	2.5	2.6	2.6	0.5	0.5	0.5	0.2	0,3	0.2
		2.3	2.2	2.6	0.4	0.4	0.6	0.4	0,7	1.6
		2.5	2.3	2.6	0.6	0.5	0.5	0.6	0,5	*
5	4.615.155.75	1.3	1.3	1.4	0.9	0.8	0.7	0.4	0,7	0.3
		1.0	1.2	1.4	0.7	0.7	0.9	*	0,2	0.7
		1.2	1.1	1.5	0.8	1.0	0.8	0.7	0,4	*
Percentage of the total desorbed elements from lichen (%)										
	4.615.155.75	100	100	100	4.1	3.5	3.2	9.3	7.8	5.6
		94	100	100	3.3	3.3	4.2	6.6	7.6	9.9
		100	99	89	4.6	4.2	3.9	8.7	8.7	7.1

\* The concentration of elements in desorbates is below detection limits

the lichen, while the other metals build either highly insoluble compounds or complex compounds with lower or higher stability constants.

The existence of great differences between total concentrations of determined metals in lichen samples (from 6-30  $\mu\text{g/g}$  for Cu, Sr, Mn, Ba and Zn to 6880  $\mu\text{g/g}$  for Ca, Tables 1-3), points to two possible reasons that do not exclude each other: (i) that the low content of the corresponding metal in the particle or other form in air in relation to the other metal; and/or (ii) a great difference in the strength of chemical bonds of the corresponding sorbent in the lichen.

The amount of sorbed substance for a certain desorption number can be expressed with the equation:

$$\ln C_x = \ln C_0 - a n_x \quad (1)$$

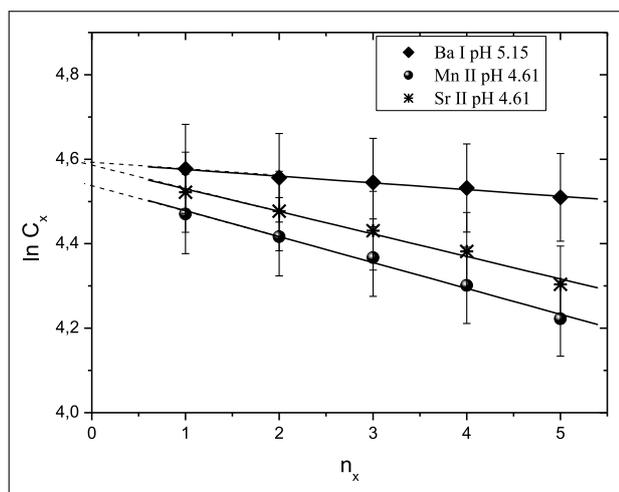
where  $C_0$  = the content of the sorbed substance in the lichen before desorption,  $a$  = a constant,  $n_x$  = the number of successive desorptions with equal volumes of the desorption solution, and  $C_x$  = the amount of sorbed substance (in the lichen) for a certain number of desorptions,  $n_x$ , that approximately follows desorption during uniform rainfall (Čučulović et al., 2006; Čučulović et al., 2007; Čučulović et al., 2009; Čučulović et al., 2009; Čučulović and Veselinović, 2012; Čučulović et al., 2012, Čučulović et al., 2007; Čučulović et al., 2008).

This equation was applied only in cases when the metal content was above the detection limit, as the equation is valid only if one type of metal sorption is present, i.e. if one type of sorption is domi-

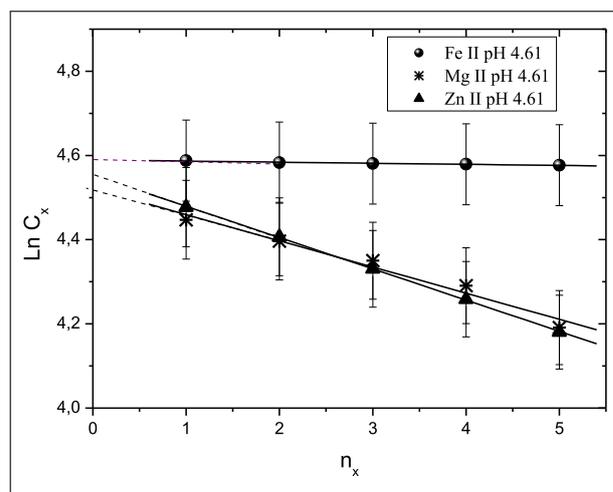
**Table 2.** Starting content ( $\mu\text{g/g}$ ) of Fe, Mg and Zn *C. islandica* lichen, their content (%) in the desorbate in relation to the starting content (100%) depending on the serial number of successive desorption using solutions I, II and III, pH values 4.61, 5.15 and 5.75 and percentage of the total desorbed element from the lichen.

Element		Fe			Mg			Zn		
Starting content ( $\mu\text{g/g}$ )		265 $\pm$ 26			260 $\pm$ 26			30 $\pm$ 3		
Percentage of desorbed element in the desorbate in relation to its starting content in the lichen										
Solution										
Desorption, $n_x$	pH	I	II	III	I	II	III	I	II	III
1	4.61	2.6	1.7	0.7	16	15	15	19	12	15
	5.15	2.1	2.1	1.7	14	14	15	6.0	15	17
	5.75	2.1	2.6	2.0	16	167	14	15	17	11
2	4.61	0.8	0.4	0.5	4.5	4.2	4.2	5.3	6.0	4.0
	5.15	0.3	0.6	0.8	3.8	4.3	4.4	*	8.0	4.7
	5.75	0.3	0.6	0.6	4.5	5.4	4.5	6.7	9.3	*
3	4.61	0.2	0.2	0.2	4.0	3.7	3.5	4.0	6.0	3.3
	5.15	0.2	0.3	0.2	3.6	3.5	4.0	*	*	*
	5.75	0.2	*	0.2	4.8	3.8	3.7	8.0	*	2.0
4	4.61	*	0.2	0.1	4.5	4.5	4.0	*	5.3	1.3
	5.15	*	0.2	0.3	4.0	3.9	4.2	*	*	*
	5.75	*	*	*	4.7	3.6	5.2	11	*	4.0
5	4.61	*	0.2	0.1	7.1	6.9	6.3	4.0	5.3	4.0
	5.15	*	0.2	*	5.7	5.8	6.5	*	*	4.0
	5.75	*	*	*	5.1	7.3	6.0	8.0	*	*
Percentage of the total desorbed elements from lichen (%)										
	4.61	3.6	2.8	1.5	37	34	33	33	35	28
	5.15	2.6	3.3	2.9	31	32	34	6.0	23	31
	5.75	2.6	3.2	2.7	35	37	33	49	27	17

\* The concentration of elements in desorbates is below detection limits



**Fig. 1.** Logarithm of the Ba, Mn and Sr contents (%) in *C. islandica* lichen,  $\ln C_x$ , depending on the consecutive desorption number ( $n_x$ ) using solutions: I (pH 5.15) and II (pH 4.61).

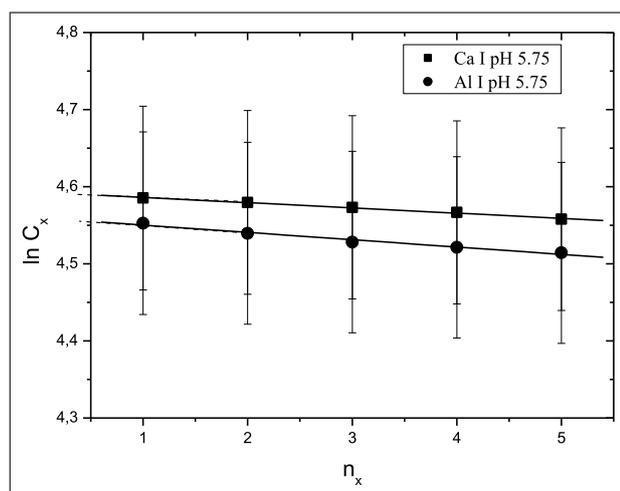


**Fig. 2.** Logarithm of the Fe, Mg and Zn contents (%) in *C. islandica* lichen,  $\ln C_x$ , depending on the consecutive desorption number ( $n_x$ ) using solution II (pH 4.61).

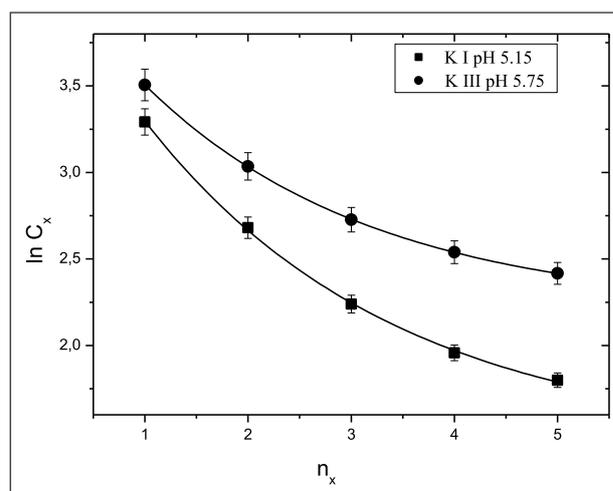
**Table 3.** Starting content ( $\mu\text{g/g}$ ) of Ba, Mn and Sr *C. islandica* lichen, their content (%) in the desorbate in relation to the starting content (100%) depending on the serial number of successive desorption using solutions I, II and III, pH values 4.61, 5.15 and 5.75 and percentage of the total desorbed element from the lichen.

Element		Ba			Mn			Sr		
Starting content ( $\mu\text{g/g}$ )		13 $\pm$ 1			10 $\pm$ 1			10,0 $\pm$ 0,6		
Percentage of desorbed element in the desorbate in relation to its starting content in the lichen										
Solution										
Desorption, $n_x$	pH	I	II	III	I	II	III	I	II	III
1	4.61	*	4.0	1.7	12	12	7,0	2.0	8.0	4.4
	5.15	2.8	2.0	1.5	10	10	12	6.8	6.0	6.0
	5.75	2.2	1.5	1.1	10	13	8.2	6.0	7.0	5.4
2	4.61	*	2.5	0.5	*	6.0	*	*	4.0	1.6
	5.15	2.0	1.2	*	4.0	4.0	*	3.2	*	2.0
	5.75	*	*	*	*	4.6	3.0	*	3.8	2.4
3	4.61	*	1.7	0.2	*	6.0	*	*	4.0	1.6
	5.15	1.1	*	*	*	*	*	3.2	*	2.0
	5.75	*	*	*	*	4.0	1.0	*	3.2	2.4
4	4.61	*	2.2	0.9	*	6.0	*	*	4.0	2.0
	5.15	1.2	*	*	4.0	*	4.0	3.2	*	2.0
	5.75	*	*	*	*	5.0	*	*	3.2	2.4
5	4.61	*	3.4	0.6	*	8,0	*	*	6.0	3.0
	5.15	2.0	1.4	*	4.0	*	4.0	4.0	4.0	4.0
	5.75	*	1.2	*	*	5.6	3.0	*	5.2	3.0
Percentage of the total desorbed elements from lichen (%)										
	4.61	*	14	3.8	12	38	7.0	2.0	26	13
	5.15	9.1	4.6	1.5	22	14	20	20	10	16
	5.75	2.2	2.8	1.1	10	32	15	6.0	22	16

\* The concentration of elements in desorbates is below detection limit



**Fig. 3.** Logarithm of the Ca and Al contents (%) in *C. islandica* lichen,  $\ln C_x$ , depending on the consecutive desorption number ( $n_x$ ) using solution I (pH 5.75).



**Fig. 4.** Logarithm of the K content (%) in *C. islandica* lichen,  $\ln C_x$ , depending on the consecutive desorption number ( $n_x$ ) using solutions: I (pH 5.15) and III (pH 5.75)

**Table 4.**  $C_{0e}$  values (%) determined according to equation (1) for the desorption of metals from lichen using solutions I, II and III, pH 4.61-5.75.

Metal	Solution	pH	$C_{0e}$ (%)	$\Delta C_0=100- C_{0e}$
Calcium	I	4.61	98.5	1.5
	I	5.15	99.0	1.0
	I	5.75	99.0	1.0
	II	4.61	99.0	1.0
	II	5.15	99.2	0.8
	II	5.75	98.5	1.5
	III	4.61	100.5	-0.5
	III	5.15	101.0	-1.0
	III	5.75	99.0	1.0
Aluminium	I	4.61	94.6	5.4
	I	5.75	94.6	5.4
	II	4.61	96.1	3.9
	II	5.15	94.6	5.4
	II	5.75	94.6	5.4
	III	4.61	96.1	3.9
	III	5.15	95.1	4.9
	III	5.75	95.1	4.9
	Iron	II	4.61	98.0
II		5.15	97.5	2.5
III		4.61	99.0	1.0
Magnesium	I	4.61	87.8	12.2
	I	5.15	89.1	10.9
	I	5.75	87.8	12.2
	II	4.61	89.1	10.9
	II	5.15	88.7	11.3
	II	5.75	86.5	13.5
	III	4.61	88.7	11.3
	III	5.15	88.2	11.8
	III	5.75	90.0	10.0
Zink	I	5.75	94.2	5.8
	II	4.61	91.4	8.6
	III	5.15	83.5	16.5
Barium	I	5.15	98.0	2.0
	II	4.61	97.5	2.5
	III	5.75	92.3	7.7
Manganese	II	4.61	93.7	6.3
	II	5.75	90.9	9.1
Strontium	I	5.15	95.6	4.4
	II	4.61	95.1	4.9
	II	5.75	95.1	4.9
	III	4.61	97.0	3.0
	III	5.15	95.1	4.9
	III	5.75	95.1	4.9

nant over other possible sorption types. The equation was applied when investigating desorption of  $^{137}\text{Cs}$  and the investigated metals with water and acid solutions (Čučulović et al., 2006; Čučulović et al., 2007; Čučulović et al., 2009; Čučulović et al., 2009; Čučulović et al., 2008).

Straight lines for desorption were obtained for the dependency  $\ln C_x$  on  $n_x$  for all investigated metals (Figs. 1-3), except for potassium (Fig. 4). Extrapolation from the obtained linear dependencies determined the values of  $\ln C_0$ . Table 4 shows that graphical extrapolation gave values of  $C_0$  for all eight metals that were mostly higher than 90%, i.e. very close to the metal content in the lichen before desorption. This indicated that in these metals one type of sorption is dominant. Obtaining a straight line according to equation (1) is the consequence of saturation of those groups in the lichen that build very stable compounds with metal ions with high values of the balance constant. This saturation is the consequence of the presence of a larger number of metal cations building a stable complex or highly insoluble compounds with the sorption group of the lichen tissue and not only the observed cation. Balanced ionic concentrations originating from these stable complexes or highly insoluble compounds are very low and practically do not have an influence on the balance when building compounds with low values of the balance constant.

Differing from all the other investigated cations, a linear dependence of  $\ln C_x$  on  $n_x$  was not obtained for potassium (Fig. 4). This means that the  $\text{K}^+$  ion builds at least two compounds with acid or anion groups in the lichen that have relatively low, but different, dissociation constants. Confirming this analysis is the information that about 80% of potassium is desorbed by the first desorption, and that for successive desorptions the desorbed amount gradually decreases (Table 1). The reason for this is that potassium, as well as other alkali metals, enter compounds with an ionic bond, so they are desorbed by ionic exchange with  $\text{H}^+$  ions or other cations.

A comparison of the total amounts of desorbed metals obtained in this work with data for their total desorption, and also desorption of  $^{137}\text{Cs}$  in previous work (Čučulović et al., 2006; Čučulović et al., 2007; Čučulović et al., 2009; Čučulović et al., 2009; Čučulović et al., 2012; Čučulović et al., 2012; Čučulović et al., 2007; Čučulović et al., 2008) using solutions with lower pH values (2.00-3.75), shows that the percentage of desorbed potassium and  $^{137}\text{Cs}$  is slightly higher, while for other metals this percentage is lower. Desorption solutions used in previous papers contained besides  $\text{H}^+$  ions  $\text{NH}_4^+$  ions, that can have an influence on desorption mechanisms by ionic exchange. Ionic exchange is considered the most significant process in metal accumulation in lichen and can be one of the reasons for the obtained differences in the amounts of desorbed metals.

## CONCLUSION

In this work, the desorption of metals (K, Al, Ca, Mg, Fe, Ba, Zn, Mn, Sr and Cu) using  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  solutions comprising the basic components of acidity in acid rain was investigated. Solutions with pH values between 4.61 and 5.75 corresponding to the composition of acid rain that usually has a pH value lower than 5.60, were used. There are no literature data to date on metal desorption from *Cetraria islandica* lichen with solutions whose pH value is higher than 3.75. The interaction process between the environment and lichen is very complex as parallel to ionic exchange, the process of unstable (physical-chemical) extracellular bonding of cations and irreversible (chemical) inclusion of metals into the internal cellular structure of the lichen take place. Based on the presented data it can be concluded that certain concentrations of the investigated metal will always be desorbed by fallout. With the increase in pH value of the fallout, the desorbed concentration will decrease, except for alkali metals where it was almost complete in both cases. The obtained results indicate that for fallout with pH values higher than 4, lichen can become a secondary source of environment pollution with the stated metals.

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