Metal Desorption from the Lichen *Evernia prunastri* (L.) Ach. Using Simulated Acid Rain pH Solutions

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Abstract: In this study, the content of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in washed and unwashed lichen *Evernia prunastri* (L.) Ach. was determined. Solutions similar to acid rain (H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3) with pH 2.02. 2.55, 3.61, 4.33, and 5.15 were used to investigate the desorption of metals from washed lichen *Evernia prunastri*. The metal analysis was conducted by flame atomic absorption spectrometry (FAAS). Content of Fe and Pb was higher in unwashed lichen, Mn and Ni were similar in washed and unwashed lichen, and Cr, Cu, Cd, and Zn were higher in the washed lichen sample. Using solution with pH 2.02, the percentage of desorbed Cu, Mn, Cd, and Zn was higher than 95%, while for Pb it was ~ 80%. Mn was desorbed in a mass percentage higher than 79% in all simulated acid rain solutions, while the percentage of Cr desorption was less than 1%. Solutions with pH 3.61, 4.33, and 5.15 desorbed all metals except Mn in a percentage lower than 68%. The results indicate that the lichen *Everina prunastri* can become a secondary environment pollutant and that the mass percentage of desorbed metals depends on the strength of the bond between the metal and the components of the lichen tissue or cell wall, as well as on the pH value of the precipitation with which the lichen comes into contact.

INTRODUCTION

Lichen are symbiotic organisms of fungi and algae. They lack roots and a protective cuticula layer and stomata, so they accumulate substances (mineral elements, including heavy metals) from the atmosphere using their complete tallus surface at levels that exceed their metabolic requirements. Concentrations of elements found in lichen thalli can be directly related to those present in the environment, so that is one of the reasons that lichens are used as bioindicators of air pollution. The accumulation of metals in lichens is affected by a variety of factors, including metal availability, lichen properties, and climate conditions. The life of lichens depends on the mineral nutrients obtained by wet atmospheric deposition (precipitation, fog, dew) and dry atmospheric deposition (sedimentation, gaseous absorption). The lichen thallus stores metals in its intracellular spaces by particle capture, ion exchange, adsorption, and active uptake (Bačkor and Loppi, 2009). Lichens can survive high levels of heavy metals by storing them as oxalate crystals or lichen acid complexes. They are slow-growing and long living organisms that can provide long-term data on the amounts of heavy metals and other pollutants in the atmosphere. Lichens use the cation exchange mechanism to rapidly absorb soluble substances over their entire surface. Soil particles and aerosols deposited on the surface also contribute to the thalli overall element concentrations (Tošić et al. 2022). Depending on the pH of the environment and competition between metal ions, the lichen can accumulate and desorb metals. Although the accumulation of metals in different lichen species is extensively reported (Conti et al., 2004 Lopi and Paoli 2015; Ramić et al., 2019; Adžemović et al., 2023; Aničić Urošević et al. 2024; Vannini et al., 2024;), information on metal desorption is limited (Piervittori et al. 1997; Čučulovic et al., 2014; Vannini et al., 2021a; Vannini et al., 2021b. Due to the lack of information on metal desorption from the lichen, the aims of this study were: a) to determine the content of eight heavy metals (Cd, Cr,

Cu, Fe, Mn, Ni, Pb, and Zn) in washed and unwashed lichen *Evernia prunastri* (L.) Ach.; b) to estimate the desorption of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from the thallus of the washed *Evernia prunastri* using five simulated acid rain pH solutions (2.02, 2.51, 3.61, 4.33, and 5.12); c) to determine whether the lichen species *Evernia prunastri* could become a secondary environmental pollution source.

EXPERIMENTAL

Sampling and sample preparation

Lichen sampling was carried out under stable weather conditions. Sampling took place at Vuksovići village, about 40 km from Sarajevo the capital of Bosnia and Herzegovina,. The sample location (Figure 1) is 7.1 km

from the major road and at an altitude of about 1100 m a.s.l; there are no production facilities nearby. To avoid contamination of the samples, the lichen was removed from the tree's bark using a plastic knife. Samples were gathered from branches that were 150 cm above ground. Rubber gloves were utilized for sampling. The samples were maintained in paper bags labelled with the sampling date, location, and name of the individual who collected the samples. The samples were kept at room temperature in a dark environment, and after being cleared of physical contaminants, one part of the sample was air dried for seven days, and the other part was washed with demineralized water and air-dried for seven days. The samples were washed in demineralized water since one of the research objectives was to determine whether the metals accumulated inside the lichen are desorbed.
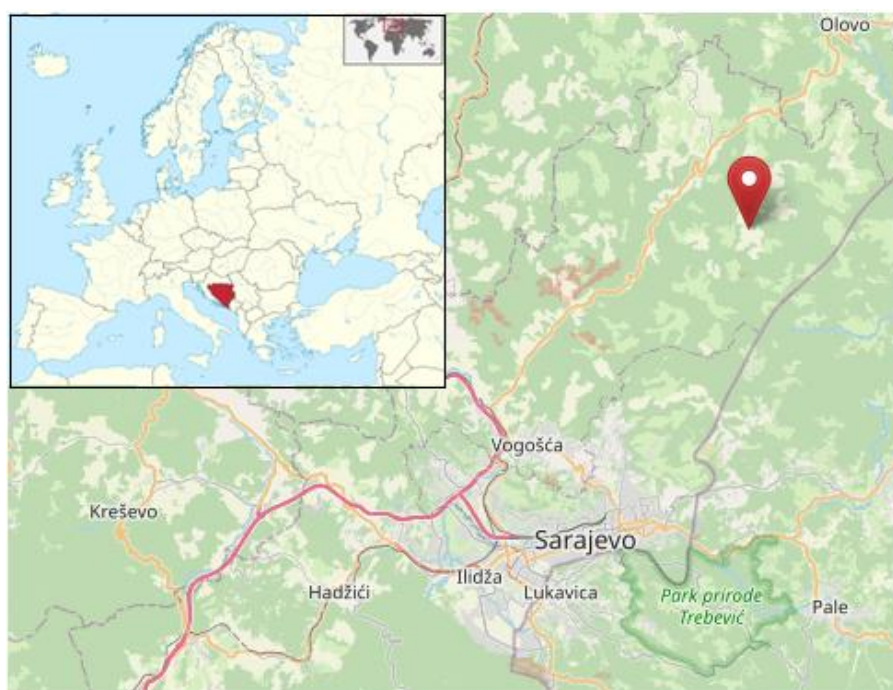

Figure 1 - Vuksovići village, location of sampling lichen *Evernia prunastri*

Metal analysis of the washed and unwashed lichen

Lichen samples from the location of the village of Vukasovići were analyzed for metal content by washing one part of the sample in distilled water, and the other part of the lichen sample did not undergo any cleaning treatment except for the removal of traces of tree bark. The aim of the analysis of the metal content in washed and unwashed lichen was to check how washing the lichen in distilled water affects the metal content in the lichen *Evernia prunastri*. It was ensured that the analysis of washed and unwashed lichen was evenly distributed in the radius of the sampling location. Metal analysis of the washed and unwashed lichen samples was performed as follows: A total of about 1 g (± 0.1 mg) of dry lichens (washed/unwashed) was weighted directly in polytetrafluoroethylene (PTFE) digestion vessels. Both washed and unwashed lichen samples were analyzed in triplicate. After adding 25 mL of concentrated HNO_3 and after the evaporation of nitrogen oxides, the vessel was

sealed and left to react at 60°C for 12 h. Then, 5 mL of H_2O_2 was added and the solutions were heated for 10 min, transferred to 50 mL volumetric flasks and filled to the mark with double-distilled water. The metal analysis was performed using a flame atomic absorption spectrometer, model AA240FS, Varian.

Solutions used to simulate acid rain were prepared as follows:
- Five (A) solutions were prepared: pH 2.02 (A1), 2.55 (A2), 3.61 (A3), 4.33 (A4), and 5.12 (A5) by adding concentrated H_2SO_4 to 500 mL of demineralized water until the desired pH value was reached. Then, 2.5 g of $(NH_4)_2SO_4$ and 2.5 g of NH_4NO_3 were added to each of these solutions.
- Solutions (B1, B2, B3, B4, B5) were made in the same way as solutions A, only nitric acid was used instead of sulfuric acid.
- Solutions A1 and B1, A2 and B2, A3 and B3, A4 and

B4, and A5 and B5 were mixed in a ratio of 1:1, and the following solutions were obtained 2.02 (C1), 2.55. (C2), 3.61 (C3), 4.33 (C4) and 5.12 (C5). The pH value of each of the five final solutions (C1-C5) was adjusted, if necessary, by adding concentrated H_2SO_4. Solutions C1-C5 were used as acid rain solutions to perform metal desorption experiments from the lichen.

Buffer solutions with pH 4.00 and 7.00 (Reagecon) were used to calibrate the pH meter (MP200, METTLER TOLEDO, Swiss).

The washed lichen *Evernia prunastri* was used to analyze the desorption of metals by simulated acid rain solutions. About 2.5 g ($\pm$ 0.1 mg) of the washed lichen sample was weighed, and the analysis was done in triplicate. The washed lichen samples were transferred into fifteen 250 mL laboratory beakers and 50 mL of the corresponding solution C1, C2, C3, C4 and C5. The extraction was carried out at room temperature for 24 h with occasional mixing of the solution. After extraction, the lichen solution was filtered, and the lichen was dried to a constant mass at room temperature. Then 50 mL of a new portion of the solution (C1-C5) with the same pH was used for successive desorption of the metal from the same replicate of the lichen sample, and the procedure of filtering and drying was repeated. The desorption process was repeated three times on the same replicate of the lichen with a solution of the same pH (C1-C5) (three replicates of lichen were treated three times with the same solution e.g. C1). The contents of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined in the solutions after each

repeated extraction by FAAS.

Analytical quality control

All substances used were of analytical grade and supplied from Merck (Darmstadt, Germany). To ensure accurate heavy metal assessment in lichens, a certified reference material (CRM-IAEA-336-ichen) was analyzed. All samples, blanks, and CRMs were prepared in triplicate. The recovery was calculated and ranged from 95% to 102% for all metals. The value of the detection limit (LOD) (calculated as three times the standard deviation of the blank signal) were: Cd (0.002 mg/L), Cr (0.007 mg/L), Cu (0.06 mg/L), Fe (6.22 mg/L), Mn (0.20 mg/L), Ni (0.01 mg/L), Pb (1.00 mg/L), and Zn (0.75 mg/L).

RESULTS AND DISCUSSION

One of the aims of this study was to determine the content of eight metals: Cr, Cu, Fe, Mn, Ni, Cd, Pb, and Zn in washed and unwashed lichen samples. Table 1 presents the results of determined metals in washed and unwashed lichen samples and the results for the percent relative standard deviation (%RSD). %RSD was used to evaluate homogeneity in the samples between the unwashed and washed procedures. Table 2 presents the results of the mass percentage of desorbed metals after each extraction and the mass percentage of total metals extracted by solutions simulating acid rain.

Table 1 - Average metal content (mg/kg $\pm$ SD) and %RSD in washed and unwashed lichen *Evernia prunsatri*

Metals	Mean $\pm$ SD (mg/kg)		The difference between unwashed and washed samples		%RSD		
	Unwashed	Washed	Amount (mg/kg)	Percent (%)	Unwashed	Washed	Unwashed/ washed ratio
Cr	5.29 $\pm$ 0.896	5.81 $\pm$ 0.36	- 0.52	↑ 10	16.94	6.1	2.8
Cu	3.94 $\pm$ 0.283	5.78 $\pm$ 0.07	- 1.84	↑ 47	7.18	1.19	6
Mn	11.52 $\pm$ 0.114	11.49 $\pm$ 0.004	0.03	↓ 0.3	0.99	0.035	28.3
Fe	401 $\pm$ 21.37	284 $\pm$ 10.20	117	↓ 29	5.33	3.59	1.5
Ni	10.61 $\pm$ 0.35	10.71 $\pm$ 0.22	- 0.1	↑ 1	3.30	2.1	1.6
Cd	0.132 $\pm$ 0.008	0.222 $\pm$ 0.003	- 0.09	↑ 68	6.06	1.35	4.5
Pb	6.53 $\pm$ 0.018	6.21 $\pm$ 0.06	0,32	↓ 5	0.28	1	0.28
Zn	29.94 $\pm$ 0,66	36.45 $\pm$ 2.20	- 6.51	↑ 22	2.20	6.04	0.36

The results presented in Table 1 showed that the metal content in unwashed and washed lichen was arranged as the following diminishing series: Fe > Zn > Mn > Ni > Pb > Cr > Cu > Cd. The highest %RSD in washed and unwashed lichen was for Mn (28.3), Cu (6), Cd (4.5) and Cr (2.8) while for the other analyzed metals, the %RSD was below 2%. Paoli et al. (2012) point out that high amounts of lithogenic elements in lichen, including Fe, Cd, Cr, and Ni, originate from airborne soil dust. The content of Fe and Pb was higher in the unwashed lichen sample. One of the reasons for this could be that lichen had particles on the surface that were rich in these two metals. Celik et al. (2005) mentioned that Pb pollution on a local scale is caused by industrial emissions, and on a

larger scale it is caused by emissions from motor vehicles using leaded gasoline. Leaded gasoline has stopped being used in the European Union since 2000, and in Bosnia and Herzegovina since 2010. It is possible that lead has accumulated in lichen from the years when leaded gasoline was still used, or it originates from some other anthropogenic atmospheric sources. Parzych et al. (2016) reported that 73% to 95% of the Pb content in plants is of atmospheric origin (atmospheric particles, combustion of solid fuels used for heating households and residential buildings). The content of Mn and Ni was similar in washed and unwashed lichen, while the content of Cr, Cu, Cd, and Zn was higher in the washed samples. Some authors (Boonpeng et al. 2020; Garty and Garty-Spitz

2015; Kularatne and de Freitas 2013) mentioned that these variations in results may mainly depend upon the contamination level of the sampling location, the chemical composition of the pollution accumulated in the lichen thallus, as well as the accumulation sites of elements (for this study, samples of *Evernia prunastri* were taken in the radius of 200 m). Garty (2001) and St. Clair et al. (2002), in their studies, mentioned that areas with humidity and clean air accumulate metals in minimal amounts and that most metals are intracellular. One of the reasons why the content of some metals is higher in the washed lichen could be that elements accumulated intracellularly are not or are less affected by distilled water washing. Soil particles in clean-air areas with a dry climate can have a significant impact on the amounts of elements in lichen thalli. As a result, big soil particles can collect on thallus surfaces or outside the cell. The elements that accumulate in these places are washed away by water with less difficulty compared to those in the intracellular site, particularly water-soluble elements (Boonpeng et al. 2020; Tošić et al. 2022). The results for metal content in this study were compared with other studies in Europe and the world that used *Evernia prunastri* as a lichen sample, and the results were in the same range as in the studies of: Paoli et al., 2012; Loppi and Paoli, 2015; Vannini et al., 2017. Tošić et al., 2022; Studzińska-Sroka et al., 2023;

Table 2 - Mass percentage of desorbed metals from lichen after successive extractions (I, II, III) with solutions simulating acid rain (C1-C5) and percentage of total extracted metals from lichen

Mass percentage of desorbed metals after extractions with solutions simulating acid rain										
Metals/ No of extraction n_x		**pH**	**Cr**	**Cu**	**Mn**	**Fe**	**Ni**	**Cd**	**Pb**	**Zn**
I	C1	2.02	*ND	60.07	72.60	13.01	8.93	84.19	38.26	65.15
I	C2	2.55	*ND	26.77	74.32	7.82	6.32	72.99	25.41	18.34
I	C3	3.61	*ND	21.28	60.71	6.51	7.20	24.25	9.57	23.18
I	C4	4.33	0.86	14.59	74.37	2.71	5.48	15.27	12.61	7.28
I	C5	5.12	*ND	15.45	72.78	6.65	3.58	24.30	*ND	20.59
II	C1	2.02	*ND	22.71	19.42	8.71	6.73	15.53	26.50	33.68
II	C2	2.55	*ND	58.84	17.56	1.35	2.94	8.04	20.40	9.81
II	C3	3.61	*ND	19.90	12.74	1.11	4.04	*ND	*ND	24.69
II	C4	4.33	0.18	29.68	12.04	0.70	3.92	0.44	13.15	7.79
II	C5	5.12	*ND	49.10	10.44	3.32	3.46	3.82	17.83	39.31
III	C1	2.02	*ND	14.88	7.61	9.89	*ND	*ND	13.13	16.73
III	C2	2.55	0.94	3.67	7.65	1.57	*ND	*ND	0.51	11.24
III	C3	3.61	*ND	4.73	5.65	1.53	*ND	*ND	*ND	12.52
III	C4	4.33	*ND	3.95	6.32	1.35	*ND	*ND	*ND	*ND
III	C5	5.12	*ND	3.57	4.74	1.84	*ND	*ND	*ND	12.19
The mass percentage of total extracted metals										
			Cr	**Cu**	**Mn**	**Fe**	**Ni**	**Cd**	**Pb**	**Zn**
		2.02	ND*	97.7	99.6	31.6	15.7	99.7	77.9	115.6
		2.55	0.94	89.3	99.5	10.7	9.3	81.0	46.3	39.4
		3.61	ND*	45.9	79.1	9.2	11.2	24.3	9.6	60.4
		4.33	1.04	48.2	92.7	4.8	9.4	15.7	25.8	15.1
		5.12	ND*	68.1	88.0	11.8	7.0	28.1	17.8	72.1

*ND- not desorbed

The results presented in Table 2 show that using un acid solution with a pH 2.02, the percentage of desorbed Cu, Mn, Cd, Zn was higher than 95%, while the percentage of desorbed Pb was around 80%. This could indicate that these metals, while accumulating in lichen tissue, build highly insoluble compounds or complexes with higher stability constants. If the pH of the acid solution was 2.55, 81% of Cd and around 90% of Cu were desorbed from *Evernia prunastri*. These results showed that H$^+$ ions have an effect on the desorption of metals from the lichen.

Using solutions with pH 3.61, 4.33, and 5.15, all analyzed metals except Mn were desorbed in percentages less than 68%. There are no literature data for metal desorption from *Evernia prunastri* with acid solutions ranging from 2.02 to 5.15. Čučulović et al. (2007); Čučulović et al. (2008); Čučulović et al. (2014), investigated the desorption of various elements (K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn, Sr, and ^{137}Cs) from the lichen *Cetraria islandica* (L.) Ach with solutions pH 2.00 to 5.75; these solutions were prepared with a variety of components (water, HNO_3; H_2SO_4; H_2SO_4–HNO_3–$(NH_4)_2SO_4$; H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3). The results of this study compared to the results presented in the study of Čučulović et al. (2008) and Čučulović et al. (2014) showed that the mass percentage of desorbed metals (Cu, Mn, Fe, and Zn) from *Evernia prunastri* after three extractions was higher than that presented in *Cetraria islandica* after five extractions. What is similar in this study and other studies investigating metal desorption from the lichen *Cetraria islandica* is that the use of lower pH solutions increased metal desorption. Also, it is very important to know that the metal accumulation in lichens depends on their age, reproduction, location, temperature, moisture, and substrate properties, including chemical composition and acidity.

CONCLUSION

This study showed that the lichen washing procedure did not affect the content of Mn and Ni, while it can increase the content of Cr, Cu, Cd, and Zn in *Evernia prunastri*. In this work, the desorption of metals Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was analyzed using a simulated acid rain solution. Solutions with pH values between 2.02 and 5.15 were used, which corresponds to the composition of acid rain (H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3). There is no previously published data for desorption of metals from *Evernia prunastri* with solutions whose pH values are from 2.02 to 5.15. Based on the presented results, it can be concluded that certain concentrations of the analyzed metals will be desorbed by acid rain; it depends on the pH of acid rain, the stability of chemical bonds and complexes formed between metals and components from lichen tissue or cells, and it also depends on the lichen species. A low mass percentage of metal desorption could indicate that the metal is tightly bound within the lichen cell itself; either they build highly insoluble compounds or complex compounds with lower or higher stability constants. A high mass percentage of metal desorption can indicate that the metals are linked with an ionic bond to the corresponding chemical groups in the lichens. Decreasing the pH value of acid rain will increase the desorbed concentration of metals, except for Cr.

The results suggest that acid rain with pH values below 2.6 may enhance the desorption of metals from *Evernia prunastri,* indicating that this lichen could serve as a secondary source of environmental pollution with the analyzed metals.

REFERENCES

Adžemović, S., Aliefendić, S., Mehić, E., Ranica, A., Vehab, I., Alagić, N., ... & Huremović, J. (2022). Estimation of atmospheric deposition utilizing lichen *Hypogymnia physodes*, moss *Hypnum cupressiforme* and soil in Bosnia and Herzegovina. *International journal of environmental science and technology,* 20, 1905–1918.

Aničić Urošević, M., Ilić, M., Radnović, D., Vergel, K., Yushin, N., Chaligava, O., & Zinicovscaia, I. (2024). Comparative biomonitoring of airborne potentially toxic elements using mosses (*Hypnum cupressiforme*, *Brachythecium* spp.) and lichen (*Evernia prunastri*) over remote areas. *Environmental Science and Pollution Research,* 1-17.

Bačkor, M., & Loppi, S. (2009). Interactions of lichens with heavy metals. *Biologia plantarum*, *53*, 214-222.

Boonpeng, C., Sangiamdee, D., Noikrad, S., Watthana, S., & Boonprago, K. (2020). Metal Accumulation in Lichens as a Tool for Assessing Atmospheric Contamination in a Natural Park. Environment & Natural Resources Journal, 18(2), 166-176.

Celik, A., Kartal, A. A., Akdoğan, A., Kaska, Y. (2005). Determining the heavy metal pollution in Denizli (Turkey) by using *Robinio pseudo-acacia* L. Environment international, 31(1), 105-112.

Conti, M. E., Tudino, M., Stripeikis, J., & Cecchetti, G. (2004). Heavy metal accumulation in the lichen *Evernia prunastri* transplanted at urban, rural and industrial sites in Central Italy. *Journal of Atmospheric Chemistry*, *49*, 83-94.

Čučulović, A., Veselinović, D., & Miljanić, Š. S. (2007). Extraction of 137Cs from *Cetraria islandica* lichen using acid solutions. *Journal of the Serbian Chemical Society*, 72(7), 673-678.

Čučulović, A. A., Pavlović, M. S., Veselinović, D. S., & Miljanić, Š. S. (2008). Metal extraction from *Cetraria islandica* (L.) Ach. lichen using low pH solutions. *Journal of the Serbian Chemical Society*, *73*(4), 405-413.

Čučulovic, A., Pavlović, M., Savović, J., & Veselinović, D. S. (2014). Desorption of metals from *Cetraria islandica* (L.) Ach. Lichen using solutions simulating acid rain. *Arch. Biol. Sci*, *66*(1).

Garty, J. (2001). Biomonitoring atmospheric heavy metals with lichens: theory and application. *Critical reviews in plant sciences*, *20*(4), 309-371.

Garty, J., & Garty-Spitz, R. L. (2015). Lichens and particulate matter: inter-relations and biomonitoring with lichens. *Recent Advances in Lichenology: Modern Methods and Approaches in Biomonitoring and Bioprospection,* 1, 47-85.

Kularatne, K. I. A., & De Freitas, C. R. (2013). Epiphytic lichens as biomonitors of airborne heavy metal pollution. *Environmental and experimental botany*, 88, 24-32.

Loppi, S., & Paoli, L. (2015). Comparison of the trace element content in transplants of the lichen *Evernia prunastri* and in bulk atmospheric deposition: a case study from a low polluted environment (C Italy). *Biologia*, 70, 460-466.

Paoli, L., Corsini, A., Bigagli, V., Vannini, J., Bruscoli, C., & Loppi, S. (2012). Long-term biological monitoring of environmental quality around a solid waste landfill assessed with lichens. *Environmental Pollution*, 161, 70-75.

Parzych, A., Zdunczyk, A., Astel, A. (2016). Epiphytic lichens as bioindicators of air pollution by heavy metals in an urban area (northern Poland). *Journal of Elementology*, 21(3), 781-785.

Piervittori, R., Usai, L., Alessio, F., & Maffei, M. (1997). The effect of simulated acid rain on surface morphology and n-alkane composition of *Pseudevernia furfuracea*. *The lichenologist*, 29(2), 191-198.

Ramić, E., Huremović, J., Muhić-Šarac, T., Đug, S., Žero, S., & Olovčić, A. (2019). Biomonitoring of air pollution in Bosnia and Herzegovina using epiphytic lichen *Hypogymnia physodes*. *Bulletin of environmental contamination and toxicology*, 102, 763-769.

St. Clair, S. B., St. Clair, L. L., Weber, D. J., Mangelson, N. F., & Eggett, D. L. (2002). Element accumulation patterns in foliose and fruticose lichens from rock and bark substrates in Arizona. *Bryologist*, 415-421.

Studzińska-Sroka, E., Bulicz, M., Henkel, M., Rosiak, N., Paczkowska-Walendowska, M., Szwajgier, D., ... & Cielecka-Piontek, J. (2023). Pleiotropic Potential of *Evernia prunastri* Extracts and Their Main Compounds Evernic Acid and Atranorin: In Vitro and In Silico Studies. *Molecules*, 29(1), 233.

Tošić, S., Pavlović, A., Dimitrijević, I., Zlatanović, I., Mitić, V., & Stojanović, G. (2022). Elemental composition of selected lichen species growing on the Balkan Peninsula. *Journal of the Serbian Chemical Society*, 87(11), 1313-1325.

Vannini, A., Paoli, L., Nicolardi, V., Di Lella, L. A., & Loppi, S. (2017). Seasonal variations in intracellular trace element content and physiological parameters in the lichen *Evernia prunastri* transplanted to an urban environment. *Acta Botanica Croatica*, 76(2), 171-176.

Vannini, A., Jamal, M. B., Gramigni, M., Fedeli, R., Ancora, S., Monaci, F., & Loppi, S. (2021a). Accumulation and release of mercury in the lichen *Evernia prunastri* (L.) Ach. *Biology*, 10(11), 1198.

Vannini, A., Paoli, L., Fedeli, R., Kangogo, S. K., Guarnieri, M., Ancora, S., ... & Loppi, S. (2021b). Modeling heavy metal release in the epiphytic lichen *Evernia prunastri*. *Environmental Science and Pollution Research*, 28, 27392-27397.

Vannini, A., Pagano, L., Bartoli, M., Fedeli, R., Malcevschi, A., Sidoli, M., ... & Loppi, S. (2024). Accumulation and Release of Cadmium Ions in the Lichen *Evernia prunastri* (L.) Ach. and Wood-Derived Biochar: Implication for the Use of Biochar for Environmental Biomonitoring. *Toxics*, 12(1), 66.

Summary/Sažetak

U ovom istraživanju određen je sadržaj Cd, Cr, Cu, Fe, Mn, Ni, Pb i Zn u opranom i neopranom lišaju *Evernia prunastri*. Rastvori koji simuliraju kiselu kišu (H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3) sa pH 2,02. 2.55, 3.61, 4.33 i 5.15 su korišteni za ispitivanje desorpcije metala iz opranog lišaja *Evernia prunastri*. Analiza metala je provedena plamenom atomsko apsorpcionom spektrometrijom (FAAS). Sadržaj Fe i Pb je bio veći u neopranom lišaju, Mn i Ni je sličan u opranom i neopranom lišaju, a sadržaj Cr, Cu, Cd i Zn je veći u opranom uzorku lišaja. Kod rastvora sa pH 2,02 procenat desorbovanog Cu, Mn, Cd i Zn bio je veći od 95%, dok je za Pb bio oko 80%. Mn se desorbirao u masenom procentu većem od 79% u svim rastvorima koji simuliraju kiselu kišu, dok je procenat desorpcije Cr bio manji od 1%. Rastvori sa pH 3,61, 4,33 i 5,15 desorbirali su sve metale osim Mn u procentu nižem od 68%. Rezultati pokazuju da lišaj *Evernia prunastri* može postati sekundarni zagađivač okoliša i da maseni procenat desorbiranih metala ovisi o jačini veze između metala i komponenti unutar tkiva ili ćelijskog zida lišaja, kao i od pH vrijednosti padavina sa kojima lišaj dolazi u kontakt.